CONFERENCE ICESS 2012 SAINT-MALO

12th international conference

Electronic spectroscopy and structure

September 16-21, 2012

Palais des Congrès « Le Grand Large »

SAINT-MALO, FRANCE

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CONFERENCE ICESS 2012 SAINT-MALO

12th International Conference on Electron Spectroscopy and Structure
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Palais du Grand Large, Saint Malo, France

September 16-21, 2012

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Electronic spectroscopy and structure
12th international conference
CONFERENCE ICESS 2012 SAINT-MALO
September 16-21, 2012 - Palais des Congrès - Saint-Malo, France

Welcome Message

Welcome to the twelfth International Conference on Electron Spectroscopy and Structure: ICESS-12, a major scientific event where about 350 participants are gathered from all over the world.

Electronic structure is one of the fundamental properties of matter, and there have been important discoveries recently, in AMO (e.g. fundamental problems of electron scattering or localization), materials science (Nobel Prize awarded for pioneering research on graphene properties) or nanoscience at the frontiers of gas phase and surface science, with significant input from theoretical modeling.

In this context, state-of-the-art instrumentation and scientific support available at large-scale facilities worldwide have played a major role. These laboratories also act as incubators for emerging scientific and technological advances (ultrafast, ultrasmall, XFEL technology, diffractive imaging etc.).

This series of conferences started in 1971 in Asilomar (USA) as the International Conference on Electron Spectroscopy (ICES), and since 2000 the scope has been widened to include electronic structures. After Berkeley, Uppsala, Iguaçu Falls and Nara, the newly opened Synchrotron SOLEIL is honored to host the twelfth edition of the conference in Saint-Malo, with the support of other French research institutions and universities and the Brittany District. During the last few years completely new scientific opportunities have emerged and have given rise to amazing discoveries, which we are convinced will be highlighted at this conference. Few commercial exhibitors and staff from the facilities who have accompanied our research over the years are present.

The conference is held in Saint-Malo on the North coast of Brittany, France. Saint Malo is the city from where one of its sons, Jacques Cartier, left to navigate round the world and discovered Canada. Saint-Malo, with its imposing gray granite walls and historic streets, is one of the most charming tourist spots in France.

The conference venue is the “Grand Large” convention center overlooking the coast and the walls of Saint-Malo built in the 17th century by the famous architect Vauban. Meals are served in the dining area offering panoramic views of the ramparts and the sea.

We hope that our guests from all over the world will enjoy discussion on the most advanced science of today.

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PROGRAM

Monday, Sept. 17th, 2012

Monday, September 17th, 2012

08:30 - 08:40 **Opening – Paul Morin**

08:40 - 09:25 **Ab initio spectroscopy: A quantum puzzle**
C. Draxl **(Plenary)**

09:25 - 10:10 **XUV/X-ray light for structural determination and ultrafast electronic control in gas-phase chemistry**
F. Martín **(Plenary)**

10:10 - 10:30 **Coffee Break**
Jacques Cartier Rotunda & Grand Large Room

	Imaging Spectroscopy 1 **&** **Ultra Fast Dynamics** Maupertuis Auditorium	**Atomic and Molecular Science 1** ***Fundamental processes (theory)*** Chateaubriand Auditorium	
10:30 - 11:00	Magnetization dynamics in nanostructures probed with time-resolved photoemission electron microscopy *J. Vogel* (Invited)	Insight to hydrogen bonding from X-ray photoelectron spectroscopy and modeling *K.J. Borve* (Invited)	**10:30 - 11:00**
11:00 - 11:30	The spin interface at organic-ferromagnetic contact in organic spintronics *Y.J. Hsu* (Invited)	Theoretical study on Auger decay of molecular double core-hole state *M. Tashiro* (Invited)	**11:00 - 11:30**
11:30 – 12:00	Photoemission electron microscopy,a tool for plasmonics *L. Douillard* (Invited)	Experimental and theoretical investigation of the parabanic acid molecule following VUV excitation and photodissociation *A. Lago* (Contributed)	**11:30 - 11:50**
12:00 - 12:15	Charge density wave and mott gap dynamics by ultrafast Tr-ARPES in TaS2 *C. Cacho* (Hot Topic)	Effect of screening by external charges on the atomic orbitals and photoinduced processes within the Hartree-Fock-Slater atom *R. Thiele* (Contributed)	**11:50 - 12:10**
12:15 – 12:30	Probing ultrafast dynamics in electronic structure of epitaxial Gd(0001) On W(110) *N. Beaulieu* (Hot Topic)	Valence state of transition metal atoms in single-crystal and ceramic multiferroics by XPS *A. Kochur* (Hot Topic)	**12:10 - 12:25**

12:30 - 13:45 **Lunch**
Lammenais Area

Condensed phase	Gas phase

13:45 - 15:30

Posters Session I

- Atomic & Molecular Science 1
- Imaging Spectroscopies
- Surface & Material Science 1

Jacques Cartier Rotunda & Grand Large Room

15:30 - 16:00

Coffee Break

Jacques Cartier Rotunda & Grand Large Room

	Novel Electronic States 1 ***Highly correlated systems, Superconductivity*** Chateaubriand Auditorium	**Photo-chemistry and Reactivity 1** ***Ambient pressure, Nano / complex systems*** Maupertuis Auditorium	
16:00 - 16:30	Many-body physics versus band theory in alkali/Si(111):B semiconducting interfaces : A combined photoemission, STM/STS and DFT study *Y. Fagot-Revurat* (Invited)	Operand observation of catalytic surface reactions with synchrotron-based core-level spectroscopy H. *Kondoh* (Invited)	**16:00 - 16:30**
16:30 - 17:00	Iron based superconductors by ARPES *V. Brouet* (Invited)	Ambient pressure photoelectron spectroscopy using soft X-ray and hard X-ray *Z. Liu* (Invited)	**16:30 - 17:00**
17:00 - 17:20	Low doping superconducting state anomalies in the high-T_c cuprates as a signature of spin fluctuation mediated superconductivity *F. Onufrieva* (Contributed)	Theoretical spectroscopy of TiO_2*A.* *L. Hung* (Contributed)	**17:00 - 17:20**
17:20 - 17:40	Coexistence of different electronic phases in the $K_{0.8}Fe_{1.6}Se_2$ Fe-based superconductor: a bulk-sensitive hard x-rays spectroscopy study. *L. Simonelli* (Contributed)	Excitons in molecular solids: picene vs pentacene P.L. Cudazzo (Contributed)	**17:20 - 17:40**
17:40 - 18:00	Dispersive-high-energy spin excitations in iron pnictide superconductors investigated with resonant inelastic X-ray scattering *T. Schmitt (*Contributed)	Inner shell spectra and linear dichroism of single chirality carbon nanotubes by X-ray absorption and electron energy loss spectromicroscopy *A. Hitchcock.* (Contributed)	**17:40 - 18:00**

Free Evening

Condensed phase

Ab Initio Spectroscopy: A Quantum Puzzle

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ABSTRACT

The beauty of the Hohenberg-Kohn theorem of density-functional theory (DFT) lies in the proof of universality, *i.e.*, the applicability of the same formalism to all kinds of materials. This comes, however, with two drawbacks, which are (i) the fact that the exact functional is not known, and (ii) that this theory is only valid for the ground state. The interaction between radiation and matter, on the other hand, is key to characterizing a vast array of materials, ranging from elemental solids to complex surfaces and interfaces up to nanoscale systems.

Ab initio spectroscopy thereby is a powerful combination of quantum-based theories and computer simulations, covering a wide range of theoretical and computational methods which go beyond DFT by incorporating many-body effects and interactions showing up in the excited state. They not only allow for analyzing data obtained by experimental probes like photoemission, optical absorption and ellipsometry, Raman, infrared, X-ray, and electron-loss spectroscopy, and other techniques, but also gaining deep insight into the underlying processes.

With the availability and wide usage of electronic-structure codes for molecules, bulk crystals, and surfaces, such calculations have become more and more routine, and the progress of recent years is impressive. However, for many important and timely materials and/or excitations, current state-of-the-art methods and approaches are not sufficient: Some aspects are hardly treated so far, as for example, the electron-vibrational coupling in opto-electronic excitations or the dynamics of excited states in extended systems.

What needs to be done to reach predictive power and to tailor excitations of materials on the computer?

In this talk, I will confront different kinds of spectroscopies with different kinds of materials. With a variety of examples [1-13], ranging from the electron loss of elemental metals via photoemission spectra of organic molecular crystals to electron-hole pairs in hybrid materials, I will highlight where we are in putting together the puzzle stones on the way towards a universal description and quantitative understanding of condensed matter in the excited state.

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XUV/X-ray Light for Structural Determination and Ultrafast Electronic Control in Gas-phase Chemistry

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ABSTRACT

The development of 3rd generation synchrotron radiation sources and femto- and attosecond laser pulses allows one to probe the structure and inner working of atoms and molecules on the timescale of the electronic and nuclear response. For example, in molecules, attosecond pump-probe spectroscopy enables investigations of the prompt charge redistribution and localization that accompany photo-excitation processes, where a molecule is lifted from the ground Born-Oppenheimer potential energy surface to one or more excited surfaces, and where subsequent photochemistry evolves on femtosecond timescales. Also, the use of synchrotron radiation in combination with high energy-resolution photoelectron detection allows one to infer the structure of single molecules in gas phase. In this talk I will present a few theoretical examples on H_2, N_2, CO [1], CH_4 and C_2H_2 of how the escaping photoelectron carries all the necessary information, through diffraction and coherence, about the structure of the molecule. I will also present numerical attosecond pump-probe experiments in which H_2 is ionized with a single attosecond pulse [2] (or a train of attosecond pulses [3]) and is subsequently probed by one or several infrared or xuv few-cycle pulses. The localization of the electronic charge distribution within the remaining molecular ion is calculated with attosecond time-resolution and is visualized by varying the delay between the pump and probe pulses. The results of these calculations are compared with recent experimental measurements and provide the different mechanisms that are responsible for the observations. Recent advances for more complicated systems will also be reported.

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SESSION:

Imaging Spectroscopy 1
&
Ultra Fast Dynamics

Magnetization Dynamics in Nanostructures Probed with Time-resolved Photoemission Electron Microscopy

J. Vogel[1], M. Bonfim[1], N. Rougemaille[1], V. Uhlíř[1], O. Boulle[2],
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ABSTRACT

The combination of magnetic circular dichroism in x-ray absorption (XMCD) and photoemission electron microscopy (PEEM) provides a powerful for the detailed study of magnetic nanostructures. Making use of the temporal structure of the x-ray bunches, magnetization dynamics induced by excitation with magnetic or current pulses can be studied with a temporal resolution of better than 100 picoseconds. In this talk, I will show results that we have obtained the last few years at the ESRF and SOLEIL, where we have used this technique to investigate the dynamics of magnetic domain walls in nanostripes, induced by current pulses.

Upon passing through a homogeneously magnetized material, an electric current can become spin-polarized. The interaction between this spin-polarized current and a magnetic domain wall can lead to domain wall oscillations or domain wall motion. Most microscopic studies of current-induced domain wall dynamics have been performed using quasi-static measurements, where the domain wall position and structure are images before and after a current pulse. In order to better understand the interaction between domain walls and spin-polarized currents, direct imaging of the magnetization during the current pulses is needed. This can be achieved using time-resolved XMCD-PEEM, as will be shown in this talk. In the case of FeNi/Cu/Co nanostripes with in-plane magnetization, our measurements show that the FeNi magnetization direction during the current pulses is strongly modified by the Oersted field[1]. The action of the Oersted field may explain why the efficiency of current-induced domain wall motion is higher in these trilayers[2] than in single FeNi layers where the Oersted field is negligible. Our dynamic measurements also reveal that domain walls in Pt/Co/AlO$_x$ nanostripes with perpendicular magnetic anisotropy show very little inertia, i.e. they start moving at a constant velocity as soon as the current pulse starts and stop immediately at the end of the pulse. This behavior makes these 'massless' domain walls very interesting for applications in domain wall devices.

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The Spin Interface at Organic-ferromagnetic Contact in Organic Spintronics

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ABSTRACT

Organic spintronics with organic tailored functionality and enduring spin coherence offers a new and tantalizing approach toward multifunctional devices. Recently, the interface of ferromagnetic-organic hybrid structures is found to critically affect the efficiency of spin injection and transport in devices. A fundamental understanding of how interfacial properties engineer the surface spin polarization is important to facilitate the spin injection and transport and the design of the local spin polarization in organic spintronics.

We emulate the interfacial regimes of organic-ferromagnetic heterostructure (FM/Org/FM) in a spin-valve structure to investigate how the interfacial hybrid state affects the spin injection/detection. The ultrathin films in a reversed deposition order of Org/FM and FM/Org bilayers were fabricated. Through measurements of synchrotron x-ray spectroscopy and microscopy, the chemistry and magnetic configurations at interfaces were studied for exploring the spin scattering at interface. The origin of interfacial electronic and magnetic degradation for ferromagnets atop organics is also addressed.

To design efficient spin injection at organic-ferromagnetic contact for organic spintronics, we have implemented donor-acceptor pair via a strong organic acceptor in contact with ferromagnetic metal to tailor the FM/Org interface. The electronic structures and magnetic couplings are examined by utilizing various spectroscopy and microscopy techniques. The tailored interface not only is capable of tuning energy levels with a surface dipole layer but also expresses an efficient spin injection.

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Photoemission Electron Microscopy, a Tool for Plasmonics

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ABSTRACT

A key challenge to plasmonics is the development of experimental tools allowing access to the spatial distribution of the optical near field at the nanometre scale. To date this issue is commonly addressed using scanning near field optical microscopy *SNOM* and related methods. While offering a lateral resolution down to tens of nanometres (50 - 100 nm) the measurement proceeds by the insertion of a probe in the immediate vicinity of the object under study making its intrinsic optical characterization complex due to possible strong tip/object coupling.

A recent approach for mapping the near optical field is the use of the photoemission electron microscopy *PEEM*. Indeed, photoemission can be strongly enhanced upon excitation of surface plasmons. By collecting the photoemitted electrons, two-dimensional intensity maps reflecting the actual distribution of the optical near-field are obtained. The imaging technique makes use of well established electron optics, i.e. involves no physical probe altering the measure. This approach provides full field spectroscopic images with a routine spatial resolution of 20 nanometers.

This presentation will give a brief overview of the possibilities of the photoemission electron microscopy as a tool for plasmonics. The focus will be set on experimental results regarding the mapping of the near optical field at nanometer scale [1], the investigation of the spatio-temporal dynamics of plasmons-polaritons on surfaces [2] and the manipulation of the near field through polarisation, interference, pulse shaping [3]….

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Charge Density Wave and Mott Gap Dynamics by Ultrafast Tr-ARPES in TaS_2

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ABSTRACT

Charge density waves (CDWs) underpin the electronic properties of many complex materials [1]. In layered dichalcogenide 1*T*–TaS_2, the Mott gap opens as the CDW become commensurate to the lattice [2] and yields to an insulating ground state. The CDW gap instead opens between occupied sub-bands at finite binding energy and momentum [3]. Here, we perform time-resolved ARPES with XUV pulses to observe the evolution of momentum-dependent electronic structure throughout the reconstructed Brillouin zone [4]. A new laser-driven HHG XUV beamline at Artemis offers a unique combination optimised for ultrafast time-resolved ARPES. The pump laser wavelength is tunable from mid-IR to near-UV (15µm - 200nm), to drive a wide variety of excitations.

A prompt collapse of the Mott gap is observed followed by a rigid oscillation at the CDW amplitude mode frequency, agreeing with earlier results [5-6] for states near E_f at Γ. The CDW order, observed as a splitting between occupied sub-bands at the edge of the Brillouin zone, melts well before the lattice responds, synchronously with Mott-gap collapse at E_f. The lattice then responds on its own time scale. The different processes take place on distinct electronic and structural timescales giving new information about both the static band structure of 2D CDW materials, and the process by which they melt after ultrafast excitation. These measurements highlight the importance of electron-electron correlations in localizing the charge on each site, challenging the view of the CDW as caused by Fermi surface nesting alone.

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Probing Ultrafast Dynamics in Electronic Structure of Epitaxial Gd(0001) On W(110)

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ABSTRACT

Experiments on fast demagnetization on transition metals (TM), rare earths (RE) and their alloys are opening new perspectives to the future of information storage because of the possibility to reverse the magnetization with femtosecond laser pulses [1]. After the pioneering experiments of Vaterlaus in 1991 on Gd [2] and the firsts measurements performed with femtosecond lasers in 1996 [3] on Co it is now well established that Gd, present a slower demagnetization process characterized by two decay times.[4]

The description of the observed demagnetization are usually related to the energy transfer between the electrons, the spins and the phonons in a two steps models [4]. The different time scale observed for TM and Gd is also supposed to be at the origin of the magnetization reversal observed in TM/Gd alloys where the antiferromagnetic coupling between the magnetic moment of the 3d electrons in the transition metal and the one of the 4f electron in Gd is done through the 5d electrons of Gd.

We have studied magnetic and electronic properties of epitaxial Gd(0001) on W(110) under fs laser excitation. Results obtained as a function of the sample temperature are compared to time resolved properties measured with 50 ps time resolution. Magnetic properties are extracted from X-ray Magnetic Circular Dichroism at the $M_{4,5}$ absorption edge and in photoemission of 4d and 4f core levels. They are directly related to the ARPES 5d band structure where the exchange splitting and the Lorentzian width of minority and majority bands [5] can be extracted precisely at the gamma point of the Gd Brillouin zone.

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SESSION:

Atomic and Molecular Science 1

Fundamental processes (theory)

Insight to Hydrogen Bonding from X-ray Photoelectron Spectroscopy and Modeling

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ABSTRACT

X-ray photoelectron spectroscopy is arguably the simplest member of the family of short-wavelength electron spectroscopies and yet most useful to chemistry. Chemical information is abundant in core spectra -- in the (chemical!) energy shifts between non-equivalent atoms of the same element, in relative peak areas (intensities), and in the width, shape or fine structure of the main peaks. However, translating the spectroscopic information into chemical terms may be less than straight forward, and computational chemistry has proven invaluable in the process.[1,2]

Hydrogen bonding is a powerful construct that permeates and reinforces our understanding of chemistry. For any kind of spectroscopy, including that of X-ray photoelectron spectroscopy, it is therefore important to establish how hydrogen bonding is expressed in the spectrum, and conversely, what can been learnt about hydrogen bonding in a specific system from the spectral expression.

In this talk, we present recent advances in the combined use of XPS and computational chemistry to explore how hydrogen bonding contributes to structure in isolated molecules [3] and in unary and binary molecular clusters. [4,5] Moreover, the interplay between hydrogen bonding and protonation/deprotonation is explored through examples from solution [6] and cluster chemistry.

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Theoretical Study on Auger Decay of Molecular Double Core-hole State

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ABSTRACT

Recently, molecular double core-hole (DCH) state, i.e., a state with two core-hole vacancies in its K-shell orbital, has been successfully detected in several experiments using X-ray free electron laser (XFEL) or synchrotron radiation (SR) with multi-electron coincidence technique. Only single-site (ss-) DCH state, in which two core electrons are ionized from the same atomic site, has been found in the earlier experiments.[1,2] Later, two-site (ts-) DCH state, whose two core electrons are ionized from different atomic sites, has also been detected in both XFEL and SR experiments.[3,4] The motivation of these experiments is partly related to the theoretical observation[5] that so-called inter-atomic relaxation energy can be extracted from ionization energy of ts-DCH state, which contains information not available by single core-hole ionization energy.

Molecular DCH state decays by Auger electron emission or X-ray emission, as single core-hole state does. Auger electrons emitted by DCH state have been observed in some experiments. For example, the Auger spectrum of ss-DCH decay was measured for NH_3 using triple electron coincidence in SR experiment,[2] while two-dimensional Auger spectra of N_2 and C_2H_2 ss-DCH states, showing energy correlation between two Auger electrons, were obtained by four-electron coincidence experiment.[3] In the XFEL experiments, Auger spectra of N_2 and CO have also been obtained.[1,4] These Auger electron spectra are expected to contain valuable information on how molecular DCH state decays.

In this presentation, I will show our recent theoretical work[6] on Auger decay of molecular DCH state, using several small molecules as representative examples. In the calculated Auger spectrum of ss-DCH state, two well separated components are recognized. One is originated from the 1st Auger transition from the DCH state to the triply ionized states with one core hole and two valence holes (CVV states) and the other is originated from the 2nd Auger transition from the CVV states to quadruply valence ionized (VVVV) states. In case of the ts-DCH Auger decay, these two Auger electron distributions overlap each other, which makes isolation of individual Auger component difficult in experiment. I will describe how peaks in the Auger spectrum can be assigned in terms of molecular orbitals or electronic configurations. In addition to the normal Auger decay of the DCH main state, Auger spectra of a shake-up satellite state and two-hole one-particle resonance ($K^{-2}V^{+1}$) state will be explained. I will also briefly discuss the effect of nuclear motion on DCH Auger spectrum.

I would like to thank M.Ehara, K.Ueda, P.Lablanquie and many other collaborators.

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Experimental and Theoretical Investigation of the Parabanic Acid Molecule Following VUV Excitation and Photodissociation

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ABSTRACT

Time-of-flight mass spectrometry in coincidence mode (PEPICO) and synchrotron radiation have been employed to the investigation of the parabanic acid ($C_3H_2N_2O_3$) molecule. PEPICO mass spectra have been recorded in the 11.2–21 eV valence region of the vapor phase parabanic acid. The relatively high photo-stability of this molecule has been confirmed from our results and is mainly due to strong bonding resulted from its closed molecular structure.

We have performed high level DFT calculations for the neutral and ionic species at the B3LYP/augcc- pVTZ level of theory where electronic and molecular structure data were determined.

From the analysis of PEPICO spectra and calculations we have been able to identify the dissociation products and propose the main dissociation mechanisms for this molecule.

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Effect of Screening by External Charges on the Atomic Orbitals and Photoinduced Processes within the Hartree-Fock-Slater Atom

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ABSTRACT

X-ray free electron lasers (XFELs) are a promising tool for structural determination of macro- and biomolecules, using coherent diffractive imaging. During imaging the intense XFEL pulses also ionize the molecules efficiently, creating core-hole states within deep atomic shells. The contribution of photoinduced processes such as X-ray absorption and subsequent relaxation through Auger decay or fluorescence emission have to be analyzed in detail. In particular, it is important to estimate how the charged environment within the molecule modifies the ionization thresholds and rates for these processes, in comparison to the case of an isolated atom.

Here, we apply the XATOM toolkit [1] to obtain predictions on the modified ionization thresholds and rates of some photoinduced processes in carbon. The Hartree-Fock-Slater model [2] is extended so as to include the electron screening and ion correlation effects, induced by the charged environment of an atom or ion. Two models are considered: (i) Debye model, accounting for screening by free thermalized electrons, and (ii) ion-sphere model, accounting for screening by non-thermal net-neutral electrons and ions [3]. Ion correlations are treated with the radial distribution function, estimated for liquid carbon [4]. With these approaches we obtain predictions on modifications of orbital energies, photoabsorption cross sections, Auger decay rates, fluorescence emission rates, and atomic scattering factors, as a function of the density and temperature of the surrounding charges. Our results have implications for the studies of dynamics within XFEL irradiated samples, in particular for those dedicated to coherent diffraction imaging.

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Valence State of Transition Metal Atoms in Single-crystal and Ceramic Multiferroics by XPS

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ABSTRACT

Multiferroics are the materials that can demonstrate ferroelectric and ferro/ antiferromagnetic properties simultaneously. Valence state of 3d-metal ions in those compounds is of great interest. We study valence state of Fe and Mn in single-crystal and ceramic multiferroics using 2p- and 3s XPS. The spectra are taken with an X-ray photoelectron microprobe ESCALAB 250; they are calculated in one-electron isolated-ion intermediate coupling approximation.

Up to now, numerous attempts have been made to estimate relative abundances of different ions of the same transition metal using decomposition of 2p-XPS into symmetric components of which each was supposed to reflect a specific ionic state. In contrast to this approach we calculate the actual profiles of the 2p spectra of different ions and find them to be not only shifted in energy but also to have specific characteristic shapes due to the multiplet effects. We determine relative Fe^{2+}/Fe^{3+} and Mn^{3+}/Mn^{4+} abundances by fitting the profiles of $2p_{3/2}$ peaks with weighted superpositions of calculated spectra of ions.

The peculiarity of Mn2p-spectra is that they are temperature dependent. Ground state terms of bi-, tri- and quadrivalent Mn are ^6S ($3d^5$), ^5D ($3d^4$), and ^4F ($3d^3$). Only in the Mn^{2+} case the ground state term ^6S is well separated from other higher-lying terms, and then all the atoms can be considered to be in that state before photoionization. In the case of tri- and quadrivalent Mn, the initial state terms ^5D_J and ^4F_J are J-split, and since this splitting is very small, thermal excitations in the initial state are possible. Theory was able to reproduce experiment only after the temperature effect was included.

3s XPS have very simple two-peak structure and they are very tempting to be used for identification of the ionic states since energy separation of the peaks and their relative intensity are directly connected with the number of the unpaired 3d-electrons in one-electron approximation. However, complex interplay between delocalization of 3d electrons and strong many-electron effects often makes the 3s-spectrum-based results unreliable.

Principal results

- In single-crystal $BiFeO_3$ and $PbFe_{0.5}Nb_{0.5}O_3$ all the Fe atoms are in a trivalent state [1];
- In ceramic samples $BaFe_{0.5}Nb_{0.5}O_3$ both Fe^{2+} and Fe^{3+} ions are present; relative Fe^{2+}/Fe^{3+} content depends on the technology of the synthesis [1];
- In single-crystal RMn_2O_5 (R = Y, Bi, Eu, Gd) both Mn^{3+} and Mn^{4+} ions are present in approximately equal quantities; R are trivalent [2];
- In $La_{1-\alpha}Bi_{\beta}Mn_{1+\delta}O_{3\pm\gamma}$ ceramic samples both Mn^{3+} and Mn^{4+} ions are present. Relative Mn^{3+}/Mn^{4+} ions abundances are determined. Amount of the Mn^{4+} ions correlates with the deviation δ in $La_{1-\alpha}Bi_{\beta}Mn_{1+\delta}O_{3\pm\gamma}$ from stoichiometry, $La_{1-x}Bi_xMnO_3$.

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SESSION:

Novel Electronic States 1

Highly correlated systems, Superconductivity

Many-body Physics versus Band Theory in Alkali/Si(111):B Semiconducting Interfaces : A Combined Photoemission, STM/STS and DFT study

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ABSTRACT

Semiconducting surfaces being √3x√3 reconstructed exhibit sp surface dangling bonds bands narrow enough to obtain 2D Half-filled Mott insulators as early proposed for alkali/Si(111)[1], SiC(0001)[2] or more recently for Sn/Ge(111)[3] and Sn/Si(111)[4]. The triangular topology common to all these materials, has been predicted to exhibit magnetic properties originating in the frustrated triangular lattice and even superconductivity upon doping[5]. Nevertheless, surface reconstructions are also known to play a role on the ground state properties of semiconducting interfaces. Recently, we have evidenced by LEED and STM a novel 2√3x2√3 surface reconstruction for K, Rb and Cs thin films deposited on Si(111):B implying a quadrupling of the surface unit cell[6]. The 2√3 charge ordering occurring mainly in Si dangling bonds has been evidenced by high resolution photoemission measurements on core levels whereas ARPES spectra agrees with the 2√3 symmetry establishing a full gap higher than 1.2 eV[6,7]. A bipolaronic insulating phase expected in the Holstein-Hubbard model when the e-ph coupling g is large enough to over-compensate the on-site repulsion U has been proposed to be reached in these materials[6-8]. Recent ab initio LAPW-DFT calculations give evidences for a giant atomic distortion associated with a charge ordering in dangling bonds in connection to the large energy gap. Calculated core levels shifts and voltage dependent STM images are in very good agreement with our experimental results solving the controversy of the origin of the insulating ground state of alkali/Si:B materials[9,10]. Moreover, the √3x√3, 3x3 and 2√3x2√3 surface reconstructions competing as function of coverage could reveal a transition from a half-filled correlated magnetic material to a strongly distorded band insulator at saturation.

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ARPES investigation of the new Fe superconductors

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ABSTRACT

In 2008, a new family of superconductors was discovered, based on square Fe planes. This was a great surprise for the community, as the superconducting transition temperatures are relatively high (up to 56K), even though Fe was not thought to be a good candidate for high temperature superconductivity. Indeed, it is heavy, reducing the electron-phonon coupling traditionally responsible for superconductivity, and strongly magnetic, which is usually antagonist to superconductivity. A lot of efforts has been devoted in the past years to understand the properties of these compounds and explore different possible mechanisms for superconductivity.

There is a consensus that the multiband nature of iron pnictides is essential for defining their electronic properties. Many models for the superconducting and antiferromagnetic orders heavily rely on the interaction between different electron and hole Fermi Surface (FS) sheets. ARPES experiments are then very appealing in these materials, as they can in principle resolve the properties of each hole and electron bands independently. By combining ARPES measurements in different experimental configurations, we have clearly resolved the 2 bands forming one elliptical electron pocket. We identified a deep electron band along one ellipse axis with the dxy orbital and a shallow electron band along the perpendicular axis with the dxz/dyz orbitals, in good agreement with band structure calculations. We find that the mean free paths and Fermi velocities associated with dxy are longer than those for dxz/dyz. This suggests that the two types of orbitals play different roles in the electronic properties. We further study how the electronic structure evolves with Fe/Co and Fe/Ru substitutions, which are two different ways to turn a magnetic compound into a superconductor.

NE1-CT-ONU

Low Doping Superconducting State Anomalies in the High-Tc Cuprates as a Signature of Spin Fluctuation Mediated Superconductivity

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ABSTRACT

Spin fluctuation (SF) are considered as a good candidate for the mediator of high T_c superconductivity in the cuprates. This scenario explains naturally the d-symmetry of pairing, the low energy electronic properties such as the nodal kink, peak-dip-hump form of spectral functions etc., and moreover, the characteristic energies extracted from different experimental data (ARPES, STM, optical conductivity) are close to the observed SF energies.

Here we show that the glaring anomalies observed in the low doping superconducting (SC) state and non understood until now, also found a natural explanation within the SF scenario. The results are obtained within a microscopic strong coupling dynamical theory [1]. The key point is that SFs become soft and strong at low doping in approaching the AF instability and that such SFs turn out to be a destroyer of the electron coherence and therefore rather a destroyer than a glue for superconductivity contrary to the case of phonon induced superconductivity. Namely we show that (i) at low doping electronic quasiparticles remain coherent only within a limited area of the Brillouin zone near the node, (ii) this area shrinks with SF softening, (iii) there are two characteristic gaps, the nodal and antinodal ones, which can behave in a divergent way, the nodal gap being obligatory proportional to the SF characteristic energy and therefore decreasing with underdoping, (iv) the SC order parameter (OP) scales with the nodal gap and not at all with the maximum gap which can behave in a way opposite to the OP, the properties that explain well the remarkable and still non understood electronic anomalies observed in the low doped cuprates.

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Coexistence of Different Electronic Phases in the $K_{0.8}Fe_{1.6}Se_2$ Fe-based Superconductor: a Bulk-sensitive Hard X-rays Spectroscopy Study.

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ABSTRACT

The discovery of superconductivity in FeSe (11)-type chalcogenides has been an important finding to progress in the understanding of Fe-based superconductors (pnictides and chalcogenides) since it has emphasized the central role played by the ubiquitous Fe-Fe planes and interacting anion (pnictogen or chalcogen) atoms. Although FeSe (11)-type chalcogenides have been widely regarded as model systems to explore the electronic structure [1], they lack the spacer layers present in the most common RFeAsO (1111) and AFe_2As_2 (122)-type of pnictides. Very recently, FeSe layers have been successfully intercalated by alkaline atoms (K, Rb, Cs), with intercalated chalcogenides showing superconductivity at 30 K [2-6], unlike the (11)-type of chalcogenides (maximum T_c: 15 K). Several experiments indicate the importance of Fe vacancies in $A_xFe_{2-y}Se_2$ (11)-type chalcogenides to play a crucial role in determining their electronic and magnetic properties. Superconductivity appears to occur only in Fe-deficient samples, where the alkali metals are intercalated between the FeSe layers [7-9]. Here we report on the electronic and magnetic structure of the new $K_xFe_2Se_2$ superconductor by x-ray emission (XES) and high resolution absorption spectroscopy (XAS). We report a temperature dependent study where the electronic and magnetic properties are investigated at the same time as a function of temperature in several consistent thermal cycles in the temperature range 10-600 K. In particular, we discuss the effect of ordered and disordered Fe vacancies [10-12] on the electronic and magnetic structure, the existence of memory effects on thermal cycles, and the relation between electronic and magnetic properties and superconductivity. The results on the $K_xFe_2Se_2$ are compared with the electronic and magnetic properties of (11)-type chalcogenides [1] to distinctly identify the effect of the intercalation on the electronic properties of Fe-based superconductors.

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Dispersive High-energy Spin Excitations in Iron Pnictide Superconductors Investigated with Resonant Inelastic X-ray Scattering

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ABSTRACT

The discovery of iron-based high temperature superconductivity has triggered tremendous research efforts in searching for novel high-Tc superconductors. Unlike the cuprates whose parent compounds are long-range ordered antiferromagnetic Mott insulators, the iron-based parent compounds are 'spin-density wave' metals with delocalized electronic structure and more itinerant magnetism. ARPES studies suggest that superconductivity in iron-based materials may be connected with interband scattering between the quasi-nested electron-hole Fermi surfaces. On the other hand, the observation of spin fluctuations by Inelastic Neutron Scattering (INS) in these materials, similar to those seen in cuprates, suggests that cuprate and iron-based high-Tc superconductors may share a common pairing mechanism.

Recent developments of the high-resolution resonant inelastic X-ray scattering (RIXS) technique [1] have enabled investigations of magnetic excitations in cuprates [2,3], which show excellent agreement with results from INS. In this presentation we demonstrate that RIXS can be used to measure collective magnetic excitations in iron-based superconductors and their parent compounds despite their much stronger itinerancy compared to cuprates. The persistence of high-energy spin excitations even in optimally doped pnictide superconductors of the '122' and '1111' families in a wide range of temperatures strongly suggests a spin-mediated Cooper pairing mechanism as proposed in cuprate superconductors [4].

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SESSION:

Photo-chemistry and Reactivity 1

Ambient pressure, Nano / Complex systems

Operand Observation of Catalytic Surface Reactions with Synchrotron-based Core-level Spectroscopy

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ABSTRACT

The synchrotron-based core-level spectroscopies such as XPS and NEXAFS are promising to conduct operand monitoring of the surface reaction. We have developed a fast-NEXAFS technique to study surface dynamic processes [1], whose data acquisition time is recently reduced to a few tens milliseconds per spectrum [2], though it takes more than several hundred seconds by the conventional method. Quantitative analyses for the fast-NEXAFS spectra continuously taken under reaction conditions provide information on the reaction order, activation energy and reaction intermediates and so on. This technique has been applied to mechanistic studies on prototypical surface catalytic reactions such as water formation reaction on Pt(111) [3,4], CO oxidation on Pt(111) [5], NO reduction [6] and ammonia formation on Rh(111) [7] and revealed that it is essentially important to observe the progress of the reaction directly for the understanding of surface catalytic reaction.

We have been working on interactions of molecules with metal surfaces under ambient-pressure conditions by means of XPS with a differentially-pumping electron-energy analyzer (ambient-pressure XPS). The direct observation of adsorbed molecules under ambient-pressure conditions indicated that the ambient-pressure atmosphere induces formation of unexpected metastable phases and opens new reaction pathways [8]. Very recently we have constructed an ambient pressure (AP) XPS station at the Photon Factory, Tsukuba, Japan and applied to operand monitoring of CO oxidation over Pt-group metal surfaces [9]. This monitoring revealed that surface oxide phases contribute to the high reactivity in case of Pd surfaces while on Ir surfaces a chemisorbed oxygen species is highly reactive. The origin of the CO oxidation reactivity will be discussed based on the monitoring results.

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Ambient Pressure Photoelectron Spectroscopy using Soft X-ray and Hard X-ray

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ABSTRACT

The ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations[1] pioneered at ALS based on differentially pumped electron energy analyzers have been recognized by scientific communities as an important in-situ tool to study water, environmental science, catalysis and many other important fields. There is perhaps no better evidence than the fact that eight new AP-XPS endstations are currently under planning or development at US and international synchrotron light sources.

I will give an overview of science projects at BL9.3.2 in heterogeneous catalysis and electrochemical cell. I will mainly present results from the new AP-XPS station[2]. This new instrument, Scienta HiPP4000, is a result of collaboration between ALS and its industrial partner VG-Scienta. Beside an improved performance of electron transmission, this instrument can be operated in spectro-microscopy mode with a spatial resolution of ~ 20 μm in one dimension, or angle-resolved mode.

Currently, we are installing a new a new hard x-ray APXPS endstation at ALS to increase the probing depth limit to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. It will be a powerful in-situ tool for studying the electrolyte/electrode interface and electrochemical devices.

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Theoretical Spectroscopy of TiO_2

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ABSTRACT

TiO_2 has been shown to be an efficient photocatalyst in the UV range, but despite widespread interest, even the bulk structure of TiO_2 has not been fully characterized. Here, we study the electronic structure and spectra of single-crystal TiO_2 using *ab initio* techniques, comparing properties of the three most common polymorphs (rutile, anatase, and brookite).

Recent theoretical calculations on the absorption spectra of these polymorphs have already been shown to reproduce experimental results well.[1-3] But beyond reproducing experiments, first principles simulations can also provide additional ways of characterizing TiO_2 and interpreting experimental data. In particular, the electronic structure of the material is much more easily examined. We present first-principles absorption and electron energy loss spectra for the valence states of TiO_2, with comparison to experiment and the electronic structure of each polymorph. We briefly review the accuracy and computational cost of theoretical techniques employed. In our work, ground state properties are modeled with Kohn-Sham density-functional theory (DFT), and optical properties are modeled with time-dependent DFT and many-body perturbation theory techniques (GW approximation and Bethe-Salpeter).

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Excitons in Molecular Solids: Picene vs Pentacene

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ABSTRACT

We report first-principles GW-Bethe-Salpeter equation calculations of the optical and electronic properties of organic molecular crystals (Picene and Pentacene). Many-body effects dominate the optical spectrum and quasiparticle gap of these systems. Although very similar for the electronic and structural properties Picene and Pentacene present remarkable differences in the optical spectra. While in the latter the onset of the absorption is set by a charge transfer exciton in the former it is related to a strong localized Frankel like exciton. We find that the interplay between exchange electron-hole interaction and electronic band dispersion play a fundamental role in setting the character of the exciton.

Inner Shell Spectra and Linear Dichroism of Single Chirality Carbon Nanotubes by X-ray and Electron Spectromicroscopy

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ABSTRACT

Electron energy loss spectroscopy in transmission electron microscopes (TEM-EELS) [1] and scanning transmission X-ray microscopes (STXM) [2] are two types of imaging spectroscopies that use inner shell electronic excitation for materials analysis. Both techniques have been applied to carbon nanotubes (CNT). While chemical identification is a key goal of these studies, structural characterization beyond imaging and spectroscopy is also important. Typically, species like CNT which have large geometric anisotropy, also have a strong electronic anisotropy which can be probed using the linear dichroism (polarization dependence) of specific inner shell electronic transitions. Over the past 5 years we have developed X-ray linear dichroism (XLD) measured in STXM as a tool to characterize the quality of the local sp^2 geometry [3] which can be correlated to defects [4] or chemical functionalization [5].

Since the spatial resolution of TEM is much better than that of STXM, measuring the corresponding electron linear dichroism (ELD) of CNTs by **q**-dependent TEM-EELS offers the potential to map defects in CNTs at higher spatial resolution. This is relatively challenging since control of the direction of **q** relative to an anisotropic structure in a TEM is not straightforward. However it is possible [6], and demonstration maps of structural quality at a few nm spatial resolution have been achieved [7].

Recently single chirality single-walled carbon nanotubes (SWCNT) of high purity have become commercially available. Here we report the C 1s spectra and XLD of semi-conducting and metallic carbon nanotubes measured on small bundles of SWCNT using STXM. We also report the C 1s spectra of individual chiral-SWCNT using TEM-EELS. These imaging spectroscopies allow correlation of real space structure and electronic spectra and reduces the influence of impurities on the spectra. Differences in the shapes of the C 1s $\rightarrow \pi^*$ band (284-286 eV) are observed and compared to literature calculations [8].

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8. Research is supported by NSERC and Canada Research Chairs; performed at the Advanced Light Source (ALS) BL11.02, BL5.3.2.2 and at the Canadian Light source (CLS) BL 10ID1. ALS supported by DoE BES. CLS supported by CFI, NSERC, CIHR and U. Saskatchewan.

POSTERS SESSION I:

Monday, Sept. 17th, 2012

Electronic spectroscopy and structure

12th international conference

CONFERENCE ICESS 2012 SAINT-MALO

September 16-21, 2012 - Palais des Congrès - Saint-Malo, France

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Atomic & Molecular Science (1)

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Study of Fano Resonances with the Rabitt Technique

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ABSTRACT

We present a detailed theoretical study of the photoionization of the helium atom subject to a train of XUV attosecond pulses in conjunction with a strong near-IR probe pulse in the energy region of the first excitation threshold of the He+ parent ion. This pump-probe scheme extends the Rabitt technique (Reconstruction of Attosecond Beating by Interference of Two photon Transitions) **[1]** to the energy domain where resonances and inelastic thresholds appear. In the usual application of the Rabitt method, one assumes slowly varying atomic transition matrix elements to reconstruct, from the phaseshifts between consecutive sidebands in the photoelectron spectrum, the profile of an XUV train **[2]**. Conversely, if the phase relation between the harmonics in the XUV train is known, one can extract information on the intrinsic phases of the atomic transition amplitudes. This latter approach has already been employed to highlight the role of discrete intermediate states in the two-photon single ionization of helium **[3]**. Here, we apply the same scheme at higher energies to illustrate the effect of autoionizing states and threshold openings on continuum-continuum transitions.

To do so, we solve the time-dependent Schrödinger equation in a close-coupling B-spline basis with the Arnoldi propagator in a quantization box with a radius of 1200 Bohr radii. At the end of each simulation, the wave packet is projected on a complete set of multi-channel scattering states of the atom in order to extract channel-resolved, fully differential photoelectron distributions **[4]**. In the photoelectron spectrum we observe characteristic sideband phaseshifts associated to resonant and non-resonant multi-photon transitions as a function of the time delay between the XUV and the IR pulses, and a corresponding modulation of the Fano profiles (Fig. 1). In addition, we observe shifts on resonance positions when the XUV pulse train is close to the maximum of the IR probe pulse. This effect is a signature of the dressing of the atom due to the interaction with the comparatively strong IR probe pulse.

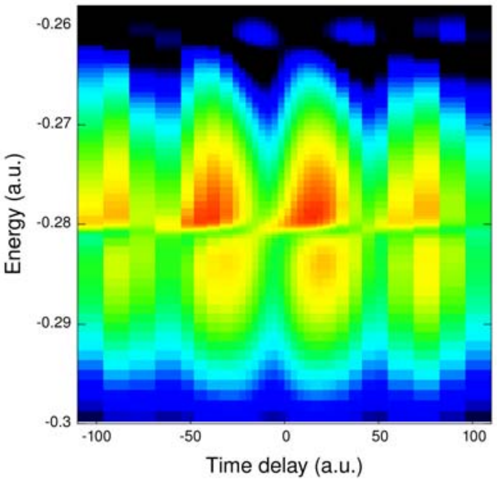

Fig. 1: *Detail of a sideband in the 2sEs photoelectron spectrum of helium close to the (3,2)$_4$ ^{1}S doubly excited state* ***[5]****.*

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Diffractive Franck-Condon Breakdown Mechanism in K-shell Photoionization of BF_3

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ABSTRACT

We report experimental and theoretical evidence of intramolecular photoelectron scattering in the collective vibrational excitation that accompanies high-energy B*1s* photoionization of the BF_3 molecule. We measured the boron *1s* vibrationally resolved photoelectron spectrum of BF_3 in the photon energy range of 200 eV – 600 eV at the PLEIADES beamline **[1]** at SOLEIL (France). The vibrational envelope deviates from Franck-Condon prediction; it exhibits strong oscillations with periodicity $\Delta k_e \sim \pi / R$ as a function of the photon energy, the hallmark of the intramolecular photoelectron scattering mechanism **[2]**.

This interpetation is confirmed by quantitative agreement with *ab-initio* DFT calculations **[3,4]** and by qualitative agreement at high energies with a first-Born approximation model **[2,5]**, in which intramolecular scattering is the only mechanism responsible for the change with energy of the relative intensity of symmetric-stretching vibrational photoelectron peaks.

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Ab-initio Computation of Excited States of Molecular Hydrogen: Halfium Model

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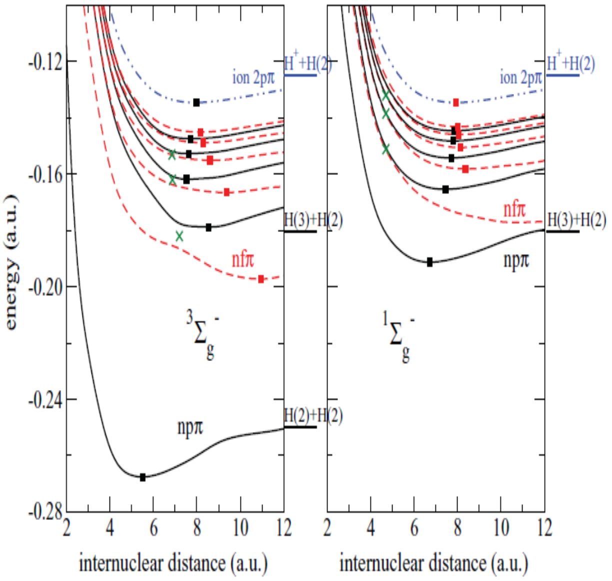
ABSTRACT

The "*Halfium Model*" combines the variational eigenchannel R-matrix method with the generalized multichannel quantum defect theory (GMQDT), implemented using prolate spheroidal electron coordinates [1] . Our previous results concerning $^{1,3}\Sigma^{+}_{g,u}$, $^{1,3}\Pi_{g,u}$, $^{1,3}\Delta_{g,u}$ symmetries of H_2 are in good agreement with quantum chemistry data which are available only for the lowest states [2].
In order to study $^{1,3}\Sigma^{-}_{g,u}$ symmetries, one has to take account explicitly of σ_v symmetry (reflection of all electron coordinates at any plane containing the two nuclei). To achieve this, we have reformulated the *Halfium* formalism and implemented it in our computer code. Numerous Born-Oppenheimer potential energy curves of Σ^{-} states [3] have been calculated.
In collaboration with Laboratoire Onde et Milieux Complexes (Le Havre, France), we begin to use these structure calculations as input data to compute the cross-sections and the rate coefficients for a variety of molecular processes based on ion electron scattering.



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Decoherence of Coherent Superpositions of Spatially Separated Electron Emission Sites

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ABSTRACT

Decoherence of coherent superpositions of spatially separated electron emission sites in inversion symmetric systems occurs if the gerade and ungerade parity eigenstates of these systems are coherently superimposed. This can occur either in the decay or excitation process. We have chosen the excitation of the core electron of O_2 to energetically degenerate gerade and ungerade states, which are hence supposed to be coherently superimposed. This coherent superposition shows up by the Fano profile of the corresponding partial cross section. The coherent superposition of the gerade and ungerade parity eigenstates causes decoherence of the position states and hence localization of the electron emitter site. By choosing two very different decay time scales for the so-called first [1] and second step Auger emission [2] we were able to demonstrate the electron tunneling effect by Doppler shifted electron-fragment ion coincidence experiments as introduced by Kugeler *et al*. as a tool for studying the behavior of dissociating molecular systems in such a decoherence situation [3]. This complex but enlightening relationship will be explained in more detail in the talk or poster.

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The Transition from Randomness to Order in Photoionduced Processes

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ABSTRACT

The electronic states of inversion symmetric systems such as homonuclear diatomic molecules are eigenstates of the Parity operator, the so-called delocalized gerade and ungerade eigenstates. These states are coherent superpositions of both atomic sites of the molecule giving rise to double slit like oscillations in the photoabsorption cross section of these molecules. These are the well-known Cohen-Fano oscillations [1,2]. A less well-known fact is the characteristic behavior of these oscillations depending whether the electrons are emitted from a randomly distributed or an oriented target. This should give rise to a phase shift of π/2 between both situations regarding their corresponding Cohen-Fano oscillations because the random target results from an integration over all orientation directions in space or turning the other way around the behavior of the oriented target can be derived by differentiating the random axis distributions along all spatial directions.

We show this phase shift effect unambiguously for the first time for the photoionization of molecular hydrogen. More surprising is, however, the unexpected phenomenon, that even for the randomly oriented target the oscillatory behavior converts into the one of an oriented target for high photoelectron kinetic energies. This transition between the two behaviors is brought about by the recoil momentum of the photoelectron, which reveals the molecular axis orientation at the moment of its emission. This unexpected transition phenomenon between randomness and order has been observed for the first time for the case of molecular hydrogen.

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Coherent Oscillations in the Angular Distributions of Photoelectrons

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ABSTRACT

Coherent oscillations appear in both the cross section and the angular distribution asymmetry parameter. There is the assumption that these oscillations are closely related to each other. In fact, the β-oscillation should be the inverse of the σ-oscillation on the basis of Cooper and Zare's formulation of the photoionization process in form of partial photoelectron waves [1].

This relation is due to the fact that in the formula for the angular distribution asymmetry parameter β the interference term between the two partial photoelectron waves appears in the numerator whereas in the denominator only the squares of these partial waves appear. Assuming that the k-dependent cross-section oscillations are offset by a phase shift of π between each other two different partial waves, this gives rise to a β behavior approximately inverse to the partial cross section behavior. We could prove this intriguing relationship for the N_2 valence ionization over a wide photon energy range for the first time. Experiments on further molecules are required to prove the generality of the statement.

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Variational Approach to Electron Impact Ionization of Helium Atom

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ABSTRACT

Electron impact ionization is a fundamental process in atomic physics. The single ionization (*e,* 2*e*) process plays a key role in many natural and technological processes. The (*e,* 2*e*) technique can be used to probe the structure of ionized target and to understand the collision dynamics through a choice of desired kinematics.

Schwinger Variational Principle of (*e,* 2*e*) calculations are presented for electron-impact ionization of He atom in its ground state. The first Born term [1] is calculated in the whole analytical way and the second Born term [2] is performed in the closure approximation using semi-analytical calculations. The theoretical results are corrected by the so-called Gamow factor to take account of Post Collision Interaction (PCI) effects between the outgoing scattered and ejected electrons.

Experimental and theoretical Triple Differential Cross Sections (TDCS) results of electron-impact ionization of He(1s^2) are presented and compared with those of Milne-Brownlie et al. [3], where experiments are performed in coplanar asymmetric geometry with the incident electron energy $E_i = 250\ eV$ and a scattered angle $\theta_s = 15°$ and where theoretical calculations are implemented using the Three Distorted Wave approach (3DW) [4, 5].

Good agreement is found with both theoretical results and experiments.
Variational calculations improve the results mainly in the binary pick region.

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Resonant Inelastic X-ray Scattering in Gas-phase CF2Cl2, CH2Cl2, and CHFCl2 following Cl 1s Excitation

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ABSTRACT

We present an experimental analysis of polarization-dependent resonant inelastic x-ray scattering (RIXS) measurements following Cl 1s excitation of a series of dichloromethanes. Using the angular properties of the measured emission we were able to derive the β parameter value for each resolved component of the KV emission spectra, and the electronic state populations of the KL angle-dependent spin-orbit ratios.

Combined Photoelectron and Photoion Spectroscopic Studies of Valine

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ABSTRACT

Here we present an experimental and theoretical investigation based on ion and electron spectroscopy in the valence region of DL-Valine. In order to check the quality of our experimental findings a careful study of the thermal degradation effects in the mass spectrum of DL-Valine is carried out. We present Partial Ion Yield curves (PIY) of DL-Valine fragments when irradiated by photons in the range 11.20 - 21.55 eV Eight appearance energies (AE) above 11.2 eV are identified. Most of these channels are defined by an initially weak production of ions, which are strongly affected by high order light. A gas filter used provides five order of magnitude harmonic rejections thus removing any source of ambiguity in the AE identification. The PIY curves allow asserting different assignments from previous results for some of the ions detected. A photoelectron He I spectrum (PES) (hν = 21.22eV) of DL-Valine is presented along with theoretical calculations based upon high-order electron propagator. Based on the PES spectrum and the calculated spectrum the presence of conformers at the experimental conditions is discussed.

Dissociation and Recapture Dynamics of Tri-atomic Molecules Following O 1s Inner-shell Excitation

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ABSTRACT

The emission of low–energy and Auger electrons from H_2O, N_2O and CO_2 has been investigated following photo-excitation/ionization at photon excitation energies just below and just above the O 1s ionization threshold. It is found that neutral oxygen atoms in high Rydberg states are formed in H_2O and CO_2, but not in N_2O. Direct evidence of post-collision interaction (PCI) between the Auger electron and the photo-electron is observed in H_2O. The initially-excited electron is captured into a Rydberg orbital of H_2O^+, and remains associated with the oxygen fragment even after the cleavage of both O-H bonds. This implies that the Rydberg states are stable, with the electron behaving as a spectator during the dissociation of H_2O^+.

Phase Dependence in the Molecular Double Slit Experiment

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ABSTRACT

Oscillations of the partial photoionization cross sections of homonuclear diatomic molecules have been described by Cohen and Fano more than 40 years ago[1] as an photoelectron interference phenomenon analogous to a Young type double slit experiment. Such cross section oscillations have been verified by several experiments in the meantime although they are mostly dedicated to inner shell electrons[2,3]. With respect to the original prediction of Cohen and Fano it is nevertheless of high interest to study related interference pattern for electrons emitted from valence states. In addition to the cross section also the angular distribution asymmetry parameter β is described to show oscillations[4]. It is interesting to study the physical reason of these oscillations as such effects could be caused by the phase shifts and not only by the amplitude of the outgoing partial waves as it is the case for the partial cross sections. We show oscillation patterns for all outer valence electrons of N_2 both in the partial cross section ratios as well as in the electron angular distribution parameter β. These results indicate additional aspects of a double slit experiment and call for further theoretical effort on this very fundamental phenomenon.

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Photoelectron Spectroscopy of Pyrene and Fluorene in the Extreme UV Range

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are fused aromatic rings without any heteroatom or any functional group. Their signatures are present in the interstellar medium, comets and meteorites. They have been also proposed as precursors of the earliest forms of life [1]. Considering the fact that nearly 10% carbon in a typical galaxy is locked in the form of PAHs, the understanding of their structure and photoinduced dynamics has attracted several investigations worldwide [2,3]. The typical photoabsorption spectrum of a PAH molecule is dominated by two main features namely, the π-π^* resonance at about 6 eV and a very broad and strong σ -σ^* at approximately 20 eV. The effects of these features in the photoionization cross section are well studied [4] in the case of fullerene and similar effects can be expected in PAHs due to the similar structure.

We performed photoelectron (PES) and photoelectron-photoion coincidence (PEPICO) experiments on Fluorene and Pyrene in the photon energy region 15-40 eV at the Gas Phase Photoemission beamline of the Elettra synchrotron radiation source in Trieste. Both molecules show a PES spectrum starting with peaks due to the HOMO, HOMO-1 and so on orbitals, followed by series of broad peaks with complex structure, which are expected to be the result of shake up processes and *e-e* correlations. These peaks show a rapid variation in the relative cross sections as a function of photon energy, different in the Pyrene and Fluorene molecules. Comparison with theoretical calculations is in progress, and is expected to shine some light on the nature of these states.

In the PEPICO experiments we attempted to study the branching ratios of the fragmentation products with respect to ionisation.

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Radiative X-ray Processes in Chlorinated Molecular Systems: Features and Dynamics

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ABSTRACT

Inner-shell radiative spectroscopies constitute a powerful probe of the molecular electronic structure [1]. An X-ray photon interacting with a molecular target leads to the promotion of a tightly bound core electron from its orbital to higher unoccupied virtual orbitals. The core-hole excited system eventually decays following two paths: resonant Auger emission or resonant X-ray photon emission. In a first part, this work deals theoretically and experimentally with the X-ray absorption spectrum (NEXAFS) at the L shell of Chlorine in Vinyl Chloride. The theoretical calculations shed light on the nature of the electronic and vibrational states involved in the resonant transitions. In a second part, we present a combined theoretical and experimental analysis of the Resonant Inelastic X-ray Scattering (RIXS) spectra of two isomers of dichloroethylene following the core-level excitation of an electron from the K shell of Chlorine. The K_α emission lines, resulting from the transition of an L shell electron filling in the hole, were examined. It is proven with the help of *ab-initio* calculations that the nuclear motion induced following the absorption plays a crucial role in the RIXS spectral profiles [2]. The detuning from the resonance frequency of the first transition monitors the time of excursion of the nuclear wave packet in the core-excited state [3]. The dependence of RIXS spectra on frequency detuning manifests itself by a nonlinear dispersion of the K_α emission lines. Around the resonance, a narrow width of the K_α lines is observed. On the contrary, away from the resonance, the same lines present a broader width.

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Advanced Studies of N_2^+ Based on Resonant Photoelectron Spectroscopy and *Ab Initio* Calculations

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ABSTRACT

The paper is devoted to advanced study of the excited ionic states of N_2 in the framework of resonant photoelectron (RPE) spectroscopy. The RPE process used here consists in Auger decay of the intermediate $1s^{-1}\pi^*$ core-excited state resulting from resonant absorption of an x-ray photon. The absence of strict dipole selection rules in Auger decay enables access to a larger number of final states, which are dark in the direct photoelectron or fluorescence spectroscopies. We utilize a powerful combination of the ultra-high resolution experimental measurements performed at the PLEIADES beamline [1] (SOLEIL Synchrotron) with the state-of-the-art configuration interaction *ab initio* calculations [2] for analyzing of more than twelve excited ionic states in the region of high spectral overlap at 22-34 eV binding energy. Thanks to the high brilliance narrow band synchrotron radiation, one can transfer the molecule to an excited vibrational sublevel of the intermediate electronic state controlling spatial distribution of the vibrational wave packet in the core-excited state. That results in a broad vibrational excitation of the final states and allows for the accurate imaging of the molecular potential energy curves of hardly observable $1^2\Pi_g$ and $1^2\Delta_g$ states of N_2^+ [3]. The RPE spectra are recorded for nine photon energies within the x-ray absorption resonance, and its dependence on excitation energy is analyzed. Mapping of the correspondent vibrational wave functions of the core-excited state is observed for the first time using the bound final states. The effect of avoided crossings between the final states on the RPE profile is discussed making use of the theoretical simulations accounting for the vibronic coupling [4]. The time-dependent analysis of the wave packet reveals the nuclear dynamics and spectra formation in the molecular states with sufficiently elongated equilibrium bond-length and dissociation-like character at the Franck-Condon region. Using an example of the nitrogen molecule we suggest that the method described here is general and can be applied for an advanced study of the excited ionic states of a large class of small molecules.

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Valence Photoionization of the N_2 Molecule in the Region of the N 1s → Rydberg Excitations

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ABSTRACT

The valence photoelectron spectrum of the N_2 molecule has been measured with vibrational resolution at the photon energies corresponding to the N 1s → 3sσ and 3pπ Rydberg excitations, where it is affected by participator decay from the core-excited states. The vibrational structure of the photoelectron bands has been simulated numerically by taking into account the contributions from lifetime vibrational interference, direct photoionization and interference between direct and resonant photoionization channels. The relative partial ionization cross sections to the X, A and B states of N_2^+ have been extracted from lower-resolution photoelectron spectra, recorded at small photon energy steps across the N 1s → Rydberg excitations. The intensities to the X and A states of the N_2^+ ion appear to resonate at all Rydberg excitations, while that of the B state is essentially affected only by the first Rydberg excitation, N 1s → 3sσ. The intensities of the A and X states display Fano line shapes as a function of photon energy, which is due to interference between direct and resonant photoionization channels. The simulated photoionization cross section of the A state, taken from the total intensity of the calculated photoelectron vibrational structure as a function of photon energy, reproduces the experimental results fairly well, but fails in some details. The effects of participator decay from core-to-Rydberg excited states also manifest themselves in the partial ion yield of the N_2^+ ion measured in the N 1s threshold region. The experiments were performed at the Gas Phase Photoemission beamline of the Elettra synhcrotron radiation laboratory at Trieste, Italy.

Cascade De-excitation Processes in Gaseous Boron Initiated by Photons with Energies Scanned Through L and K-Ionization Thresholds

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ABSTRACT

In [1] we simulated the cascade decay processes in gaseous boron within an infinitely long cylindrical interaction zone by 20 Ryd photons at various atomic densities of the medium. It was shown that the secondary processes start to manifest themselves at densities of about 10^{20} m^{-3}.

In this work, Monte Carlo technique is applied to simulate the processes of the cascade relaxation of gaseous boron at atomic density of 2.5×10^{22} m^{-3} ionized by 0.7 to 25 Ryd photons passing through a limited-in-space cylindrical interaction zone along its axis

Cascade decays of inner-shell vacancies are considered with inclusion of all energetically allowed radiative and non-radiative branches using the methods of [2]. The following interaction processes in the medium are included in the simulations:

- single photoionization,
- photoionization accompanied by additional shake up excitations,
- photoionization accompanied by additional shake off ionizations,
- electron-impact excitation,
- electron-impact ionization,
- electron-impact ionization accompanied by additional shake up excitations,
- electron-impact ionization accompanied by additional shake off ionizations,
- elastic electron scattering.

Numbers of electrons and photons leaving the interaction zone per one initial photoionization, their energy spectra, the energy transferred to the medium, and the probabilities of final ions formations are shown to change noticeably as the incident photon energy is scanned through boron atom ionization thresholds. These variations can be explained only if secondary electron-impact-produced processes are thoroughly considered.

Full-track simulations similar to this one may give a base for developing the strategies of optimization of the regimes in numerous problems having to do with the effect of the ionizing radiation on matter, say in a beam cancer therapy.

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Analysis of Evolution of the Electron Density in Si Crystal Illuminated by the XFEL Femtosecond Pulses

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ABSTRACT

The X-ray Free Electron Laser (XFEL) is a unique and promising facility that makes possible to study crystal matter with angstrom resolution at timescales corresponding to atomic electron motion. However, description of interaction of the XFEL femtosecond pulses with a crystal is still an open question. Due to the extremely intense XFEL radiation the illuminated sample undergoes severe damage up to its complete destruction. In this case conventional diffraction theory can not be applied anymore because of the very fast evolution of the electron density in crystal.

Our approach based on the coupling of the Boltzmann kinetic equation for unbound electrons to the total system of rate equations [1]. This inclusion gives birth to new channels in the system of rate equations such as electron-impact ionization, electron-ion recombination and induced photo recombination. Specific feature of this analysis is defined by the essential role of the free electron density in a crystal in comparison with the case of isolated molecules and clusters.

In order to consider all channels involved into analysis effectively the corresponding differential cross sections are calculated within the framework of the effective charge approximation for the electron configurations in atoms and ions [2]. This method is applied for calculation of the atomic form factors as well [3]. The evolution of different parts of the electron density is numerically analyzed for the example of a Silicon crystal.

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Relationship between Molecular Geometry and Vibrationally Resolved Molecular-frame Photoelectron Angular Distributions

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ABSTRACT

Vibrationally resolved molecular-frame photoelectron angular distributions (MFPADs) from randomly oriented and fixed-in-space molecules have been evaluated for diatomic and polyatomic molecules, such as N_2, CO, CH_4 and SF_6. We have used the static-exchange density functional theory[1], which has been recently extended to include the nuclear motion[2]. Both K-shell and valence-shell photoionization have been considered. The excellent agreement with the available experimental data, for both randomly oriented diatomic molecules[3] and fixed-in-space CH_4 at low photoelectron energies, supports the validity of this treatment.

Our predictions for molecular-frame photoelectron angular distributions of N_2 (see figure 1) show the signature of electron confinement and coherent two-centre interferences as those previously found in H_2. For CO, they exhibit diffraction patterns associated with the scattering of the ejected electron by the neighboring atomic centre.

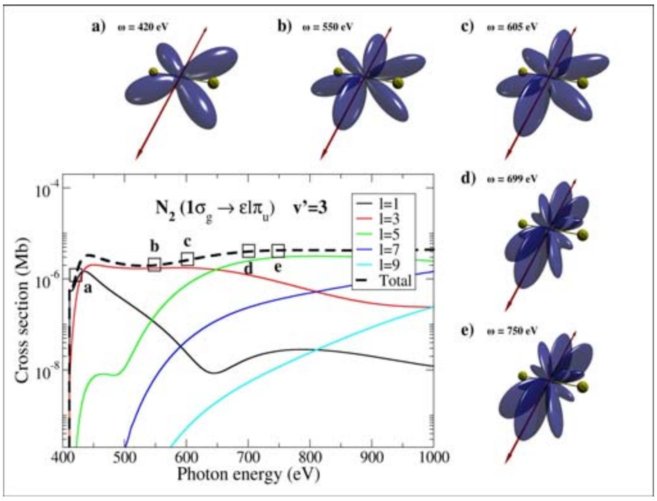

Fig. 1 MFPADs for the $1\sigma_g^{-1} \rightarrow \varepsilon l\pi_u$ photoionization of N_2 for v'=3

A systematic study of the vibrationally resolved MFPADs for different molecular systems suggests that geometry information could be retrieved from such quantities.

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Resonances in Photoemission from Caged Molecules

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ABSTRACT

Molecular electronics is the subject of intriguing changes taking place when a molecule happens to be confined in a cage. What kind of changes are they? Answering the question we advance in understanding of many elementary processes that occur in biological, pores and complex composite systems.

Special emphasis is put on unoccupied valence states of a quasifree molecule that is confined in a nanosize cage. X-ray absorption and inner-shell photoionization spectra are regarded as a basic probe of the cage effects. Their origin is being attributed mainly to (i) changes in molecular dynamics [1, 2], (ii) electron scattering at the cage [3, 4] and (iii) intermolecular interaction and dynamic polarization of the cage [5]. These phenomena as well as the influence from electro-optical properties of the cages, their size and shape on spectral distribution of oscillator strength for core-to-valence transitions in the caged molecules are discussed.

Inner-shell excitations in small caged molecular species such as CO, N_2 and SF_6 incorporated in molecular (van-der-Waals) clusters and confined in fullerene shells C_{60}, C_{240} and C_{540} or carbon nanotubes are investigated in more detail. Core excitations in solids that contain quasi-isolated chemically stable molecular units are also examined. Two limiting cases of weak and strong cage effects on the encapsulated molecular units are revealed. The shape resonances, confinement resonances and window-like resonances in the single-hole creation and single-hole ionization cross sections of the caged molecules are computed. As an illustration the *figure* presents the effect of C_{240} on the S $2p_{3/2} \rightarrow 2t_{2g}$ shape resonance in the encapsulated. For comparison the shape resonance in free SF_6 is also shown. The cage effects on core-to-valence transitions are discussed within the quasiatomic approach.

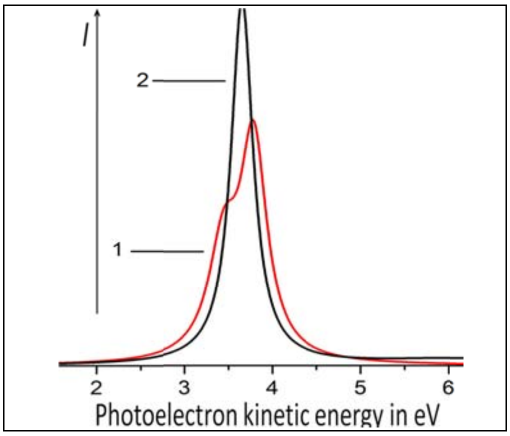

Figure The computed intensity of the S $2p_{3/2} \rightarrow 2t_{2g}$ shape resonance in free SF_6 (*2*) and SF_6@C_{240} (*1*).

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Photoelectron Recoil as a Probe of Monolayer-substrate Interaction

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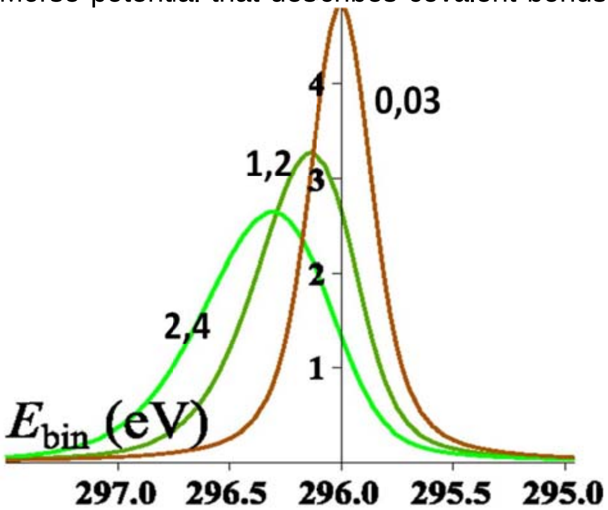
ABSTRACT

Structure and properties of atomically sharp interfaces between sp^2-bonded materials (such as graphene and monolayer hexagonal boron nitride) and *nd*-metal surfaces are intensively studied nowadays in an effort to utilize their peculiar characteristics in electronics and nano- technology. To specify the interfaces and chemical bounding of B, C and N with metal surfaces the perspectives of inner-shell-high-kinetic-energy-photoelectron spectroscopy are examined. Relationships between spectral changes in the B, C, N $1s^{-1}$ photoelectron lines and chemical bonds are investigated within the strong dynamic core-hole localization concept [1,2]. Our main attention is focused on the $1s^{-1}$-line shapes regarded as functions of the photon energy and the photoemission angles. The quasi-molecular model is introduced to describe the recoiled dynamics of the core-ionized interfaces. The clearest situation is realized when the electric vector of incident light is nearly perpendicular to the surface *xy*-plane and the $1s^{-1}$-photoelectron kinetic energy is so high that the contribution of the back-scattered photoelectrons is negligible. The flux of the primary photoelectrons ejected from the core-ionized atom altering within a monolayer, controls the photoelectron current. In this case the main spectral changes are originated by the photoelectron pulse transferred to the core-ionized adatoms and directed towards the substrates. Photon energy variations provide a sensitive probe of the monolayer-substrate interaction. The calculations are performed by using harmonic approximation to the Morse potential that describes covalent bonds formed by the $2p_z$ and nd_{z^2} atomic orbitals. The resulting $1s^{-1}$-photoelectron line is an envelope of the photoelectron-induced vibrational transitions within the adatom-substrate quasi-molecule. In the low temperature regime the envelope is approximated by the Poison distribution P_a(v') of the non-Franck-Condon v=0→v' transitions with the energy-dependent parameter $\boldsymbol{a}$:

$$a = \frac{mK}{\hbar\omega\mu}$$

Figure exhibits the C 1s photoelectron lines computed for different a =0.03, 1.2 and 2.4. *m* and *K* is mass and kinetic energy of the photoelectron, ω and μ are the frequency of the local bending mode in the monolayer and the reduced mass of the quasi-molecular oscillator. Relationships between the line shape and the monolayer-substrate potential are discussed.



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Resonance Enhancement of Rotational Excitation of the B $^2\Sigma^+_u$ State in N_2^+ at the $1\sigma_u \rightarrow 1\pi_g$ Resonance in Photoelectron and Fluorescence Spectra

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ABSTRACT

Rotational heating of the molecular ion increases with kinetic energy of the ejected photoelectron. This is evidenced by recent photoelectron and fluorescent decay studies of the $B\,^2\Sigma_u^+$state in N_2^+ [1]. Special emphasis is put on photoelectron-recoil-induced rotational excitation of the $B\,^2\Sigma_u^+$state in N_2^+ in the vicinity of the intense $1\sigma_u \rightarrow 1\pi_g$ excitation, which is observed in N_2 400.84 eV photon energy. Changes in rotational energy δE as a function of excitation energy are examined and computed within the vibration-dependent-fixed-nuclei model [2] in order to take the zero-point vibrational motion into account. The calculations evidence a linear spectral dependence of δE below the intense $1\sigma_u \rightarrow 1\pi_g$ transition and an increase of the rotational excitation of the $B\,^2\Sigma_u^+$ state in N_2^+ at 400.84 eV. The computed sharp increase $\delta E \approx$ 5,93 meV agrees reasonably with the photoelectron measurements [1]. The increase is associated with the interplay of ro-vibrational interaction and population of highly-excited vibrational levels in the intermediate N_2^* $(1\sigma_u^{-1}\pi_g^1)$ state. In the fluorescence spectra the computed increase is expected to be more substantial $\delta E\approx$10,88 meV because of intermolecular interaction in gas phase.

Rotationally resolved measurements of the fluorescence decay of the $B\,^2\Sigma_u^+$ state in N_2^+ are carried out in the π_g*-resonance regime. These results confirm the resonance behavior of the rotational excitation of the $B\,^2\Sigma_u^+$ state in N_2^+ and highlight the different enhancement of the rotational excitations at the $1\sigma_u^{-1}1\pi_g$ resonance in the photoelectron and fluorescence spectra. The difference in the enhancement of the N_2^+ rotations at 400.84 eV is discussed.

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New Generation Photoelectron-Auger Electron Coincidence Experiments

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ABSTRACT

Although Auger spectroscopy has developed into one of the most important analytical methods, our understanding of the underlying processes is hampered by the conventional Auger electron energy spectrum containing many transitions between different intermediate (singly cationic) and final (dicationic) states. A powerful method to overcome this problem is to simultaneously record both electrons emerging from the same autoionization process. As the technique has already proven to be a viable experimental tool in previous experiments [1,2,3], we have further improved the experimental set-up by combining two very high resolution spectrometers, a conventional hemispherical electron energy analyzer and a novel linear time-of-flight electron spectrometer. In this way it has been possible to increase the energy resolution such that the vibrational levels of simple molecules can be separated. At the same time, our experimental configuration allows a reasonable solid angle of acceptance to be maintained for both spectrometers, so that acquisition times with good statistics are possible. We present recent results for the O_2 [4], $C_2H_2F_2$ and CO molecules.

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Final-state Diffraction Effects in Angle-resolved Photoemission at an Organic-metal Interface

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ABSTRACT

DISENTANGLING MOLECULAR ORBITALS FROM SUSBTRATE STATES

The growth of organic thin films on metallic substrates has become a field of growing interest for organic electronics as well as for fundamental surface science [1]. Indeed, molecules on surfaces reveal a wealth of interesting properties such as electronic correlations, magnetism, self- assembly...

We show that angle-resolved photoemission performed using low-energy photons on an organic-metal interface allows to clearly distinguish genuine interface states from features of substrate photoelectrons diffracted by the molecular lattice [2].

As a model system, an ordered monolayer of Zn-phthalocyanine is used as a diffraction lattice to probe the electronic band structure of a Ag(110) substrate. Photoemission close to normal emission geometry reveals strongly dispersive features absent in the pristine substrate spectra. Density functional theory modeling helped identifying these as bulk *sp* direct transitions undergoing surface-umklapp processes. The present results establish the important role of final-state diffraction effects in photoemission experiments at organic-inorganic interfaces.

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Development and Progress of Three-dimensional Scanning Photoelectron Microscope (3D Nano-ESCA) at SPring-8 BL07LSU

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ABSTRACT

In order to achieve nondestructive observation of the three-dimensional spatially resolved electronic structure of nanostructure species such as stacking structures in semiconductor devices and the surface/interface reactions of catalytic materials, we have developed a scanning photoelectron microscope system with the capability of depth profiling in electron spectroscopy for chemical analysis (ESCA). We call this system “3D nano-ESCA.” [1]

Figure 1 shows a photograph of the 3D nano-ESCA system. For focusing the X-ray, a Fresnel zone plate with an outermost zone width of 35 nm is used. In order to obtain the angular dependence of the photoelectron spectra for the depth-profile analysis without rotating the sample, we adopted a modified VG-Scienta R3000 analyzer with an acceptance angle of 60 degrees as a high-resolution angle-resolved electron spectrometer. The system has been installed at the University-of-Tokyo Materials Science Outstation beamline, BL07LSU, [2] at SPring-8. From the results of the line-scan profiles of the poly-Si/high-k gate patterns, we achieved a total spatial resolution better than 70 nm. From the angular dependence of the photoelectron spectra, we have succeeded in obtaining precise depth profiles for HfO2/SiO2/Si stacking structures using a maximum entropy method analysis. Recent research activities for exfoliated graphene FET devices, [3] nanowire ReRAM devices, semiconductor FET devices, etc., using the 3D nano-ESCA system will be presented.

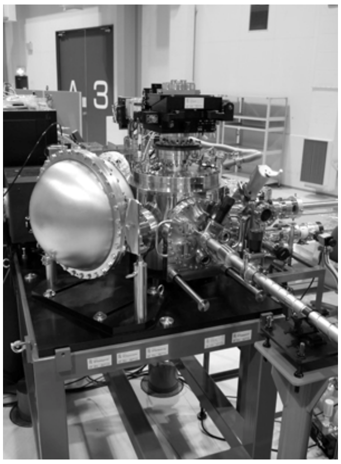

Fig. 1 A photograph of 3D nano-ESCA

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Local Structural Disorder in REFeAsO Oxypnictides by XANES Spectroscopy

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ABSTRACT

The local geometry of the REFeAsO (RE= La, Pr, Nd and Sm) oxypnictides has been investigated by x-ray absorption near edge structure spectroscopy (XANES). Combination of RE L_3-edge and As K-edge XANES has permitted to explore the correlation between the REO spacers and the electronically active FeAs slabs. The As K-edge XANES of the LaFeAsO is found to be significantly different from the other oxypnictides, while the site projected density of states appears similar for all systems. Full multiple scattering calculations have showed that this difference can be ascribed to the oxygen order in the REO spacer, that is more prominent in the La-content system [1]. Also the near edge feature just above the RE L_3 white line is found to be sensitive to the ordering/disordering of oxygen atoms in the REO layers. In addition, the shape resonance peaks evolve systematically with the RE size, indicating local structural changes in the FeAs slabs and the REO spacers due to RE size [2,3]. These results suggest that both the misfit strain between the REO and the FeAs slabs and the oxigen order/disorder in the REO play an important role in the superconductivity and itinerant magnetism of the oxypnictides.

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Electronic Structural Studies of Fe-Chalcogenide Superconductors by X-ray Absorption Spectroscopy

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ABSTRACT

The electronic structure of $FeSe_{1-x}Te_x$ chalcogenide has been investigated by x-ray absorption spectrosopy at Fe and Se K-edge (XANES) [1] and Fe $L_{2,3}$-edge (XAS) [2].
An intense Fe K-edge pre-edge peak due to Fe 1s →3d (and admixed Se/Te p states) is observed, showing substantial change with Te substitution and x-ray polarization. The pre-peak features reveal that Fe 3d unoccupied states close to Fermi level mainly have d_z character and are suppressed by increasing the Te content. The Fe $L_{2,3}$ spectra are apparently similar to those observed for Fe metal without any multiplet peak structures in characteristic Fe-based materials with strong correlations such as iron oxides. A combined analysis of experimental and theoretical spectra underlines a substantial change in the hybridization between the Fe 3d and chalcogen p states, which is redistributed substantially with the Te substitution. On the other hand, the white line peak in the Se K-edge XANES due to Se 1s→ 4p transition appears similar to the one expected for Se^{2-} systems and changes with Te substitution. Moreover, polarization dependence show that unoccupied Se orbitals near the Fermi level have predominant $p_{x,y}$ character. These results highlight that the hybridization of Fe 3d and chalcogen p states play a key role on the superconducting properties of the Fe-chalcogenide materials.

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X-ray Photoelectron Spectra and Magnetic Properties of Heterometallic Complexes Transition 3d Metals

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ABSTRACT

For the first time the X-Ray Photoelectron Spectroscopy (XPS) method has been used to study the electronic structure and the spin magnetic state of the heterometallic molecular complexes with common formula $Fe_2M(\mu_3\text{-}O)(Piv)_6(HPiv)_3$ (M = Co, Ni, Piv is anion of pivalic acid). The XPS spectra were recorded on the Kratos Axis Ultra DLD spectrometer using a monocromator (AlKα).

Heterometallic complexes with the high-spin transition 3d metal atoms are convenient objects to study the possibility of varying the magnetic properties as a function of molecular complex structure. The presence of different metal atoms in these molecules provides the additional possibilities to control the magnetic properties of molecular systems.

The M2p, M3s, M3p, O1s, N1s and C1s spectra of discussed complexes have been fitted with the different states in accordance with their structures obtained by XSA. Spectral fitting was accomplished using the Kratos Analytical package. The difference between the states of metal atoms has been determined both from the chemical shift and from the distinction of the satellite structure M2p, M3s, M3p lines. The XPS data allow identifying the heterometallic complexes as the high spin ones with metals in M^{II} and M^{III} state. The influence of replacement the Fe by Co or Ni atoms in the heterometallic complexes on the structure of the XP-spectra and its magnetic state was determined. Comparison of spin-sensitive characteristics of M2p- and M3s-spectra with the corresponding magnetic measurements data demonstrates a strong magnetic interaction within complexes with formation of the intramolecular magnetic structures. It was shown that thermal decomposition of the $Fe_2M(\mu_3\text{-}O)(Piv)_6(HPiv)_3$ complexes (350-440 ^oC) leads to the formation of nano powders - crystallites of cobalt or nickel ferrites Fe_2MO_4.

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Direct Observation of Interfacial Charge Transfer in Graphene Devices by 3D Nano-ESCA

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ABSTRACT

Graphene has attracted growing interest for its fascinating electronic properties such as giant carrier mobility (>10^5 cm^2/Vs) and conical dispersions with massless Dirac fermions. Although graphene-based devices have been actively studied for post-silicon electronics, the present device characteristics are far restrained from the ideal. One of the reasons for the response deterioration in graphene field effect transistors is a charge transfer at the graphene/electrode interface [1,2]. In this study, we have employed nondestructive nano-scale three dimensional spatial distribution analysis using angle-resolved scanning photoelectron microscopy (3D nano-ESCA) [3] for direct observation of the interfacial charge transter region in graphene devices.

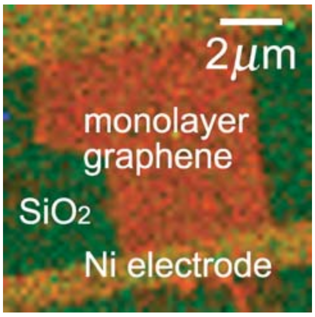

Fig. 1 3D nano-ESCA image of a graphene device structure.

Exfoliated monolayer graphene was transferred to SiO_2/p^+-Si(100) wafer and Ni electrodes were fabricated by vacuum deposition. Experiments were carried out with the 3D nano-ESCA system at BL07LSU of SPring-8.

Figure 1 shows an elemental mapping image of the graphene device structure by the photoelectron spectroscopy intensity. The monolayer graphene sheet is clearly distinguished. A pinpoint analysis of the C *1s* core level spectrum taken on the graphene is presented in Figure 2. The C *1s* peak is decomposed into the graphene sp^2 (I) and surface contaminants (II). We have succeeded in precisely determining the binding energy (BE) and the peak shape of the component purely from the graphene sp^2 by excluding the contaminant component. To investigate the spatial variation of the electronic states, the line-profile for the BE of the graphene is taken across the graphene/electrode contact interface. The energy shift of ~70 meV is clearly detected over the width of 500 nm. This result is the direct observation of the charge transfer region. Moreover, the depth profiling for O *1s* spectra suggests that the bonding state at the graphene/substrate interface can affect the charge transfer region at the graphene/electrode interface.

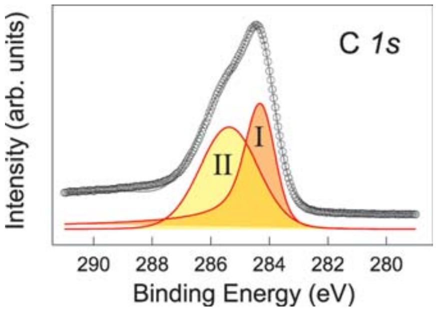

Fig. 2 C *1s* core-level spectrum on the monolayer graphene sheet in Fig.1

In the presentation, we will discuss these 3D nano-ESCA results with a model calculation [4] in detail for fundamental understanding and possible applications.

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Potential Energy Surfaces in Complex Solids: Resonant Inelastic Soft X-ray Scattering with Vibrational Resolution on Natural Clay

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ABSTRACT

Clay is an interesting material in many fields such as geosciences, pharmacy, and biology and widely applied in industrial applications. The structure and physical origin of the gelation of swelling clay have been debated since the 1930s [1] and a qualitative understanding of the macroscopic behavior of swelling clay has been reached in many cases. Direct experimental data on the microscopic origin is, however, largely lacking.

It has been shown that the swelling process can be controlled, giving a layer by layer swelling at small water concentrations. For low concentrations, the structure of the water between the layers is thought to be ordered and even ‘crystalline’ in the vicinity of clay molecules [2]; as the water content grows, it increasingly simulates the structure of normal bulk water. In order to increase understanding, a thorough investigation of the states near the band gap is necessary, as they define the physical and chemical properties of the clay.

Resonant inelastic soft x-ray scattering (RIXS) has unique features which make it an ideal tool for the investigation of complex samples as it yields information about the local electronic structure at specific atomic sites and thus reflects the local chemical environment of the probed atom.

We have studied dry natural swelling clay as well as kaolinite as a model system for wet swelling clay with vibrationally resolved RIXS and we observe for the first time the existence of vibrational progressions in solids at the oxygen K-edge. This will allow us to map the potential energy surfaces of the different oxygen species in the solid as has been proven for oxygen gas [3] and acetone [4].

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Thickness-dependent Polarization of Strained BiFeO$_3$ Films with Constant Tetragonality

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ABSTRACT

We investigated ferroelectric domains written by Piezoresponse Force Microscopy (PFM) in BiFeO$_3$ strained films. Polarization-dependent work functions of oppositely-polarized domains are measured independently by PhotoElectron Emission Microscopy and Low Energy Electron Microscopy [1]. These experiments led to an estimation of remnant polarization in BiFeO$_3$ when decreasing thickness from 70 nm to 3.6 nm. This original combination of electron microscopy gives access to polarization in films too conducting to be probed by classic electrical measurements.

The measured polarization decays strongly below a critical thickness of 5-7 nm predicted by continuous medium theory whereas the experimental tetragonal distortion does not change (in contradiction to PbTiO$_3$ behavior [2]). We resolve this apparent contradiction using first-principles-based effective Hamiltonian calculations. In ultra-thin films the energetics of near open circuit electrical boundary conditions, i.e. unscreened depolarizing field, drive the system through a phase transition from single out-of-plane polarization to a nanoscale stripe domains, giving rise to an average remnant polarization close to zero as measured by the electron microscopy whilst maintaining the relatively large tetragonal distortion imposed by the non-zero polarization state of each individual domain.

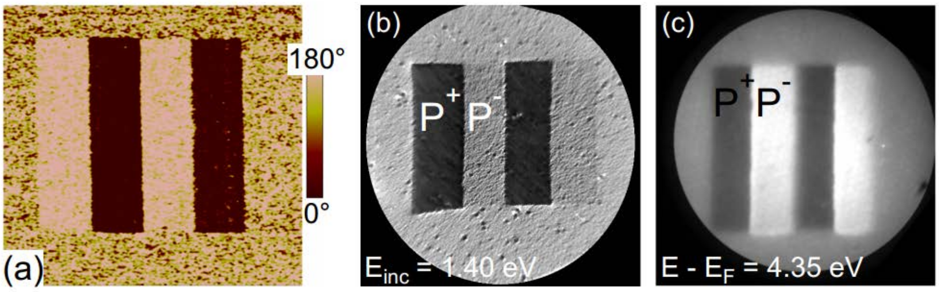

Figure 1: (a) PFM phase image of written P+/P domains, (b) LEEM image for E = 1.40 eV and (c) PEEM threshold image at E - E$_F$ = 4.35 eV with a 33 µm field of view.

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Laser-induced Ultrafast Demagnetization in the Presence ef a Nanoscale Magnetic Domain Network

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ABSTRACT

Ultrafast demagnetization refers to a rapid loss of magnetization (on the order of a few hundreds of femtoseconds) upon non-thermal heating by a femtosecond laser pulse. This phenomenon has been discovered by E. Beaurepaire and co-workers in 1996 [1] and since then studied in a variety of ferro- and ferrimagnetic transition metal and rare earth compounds. Over the past years the initially proposed three temperature model [1] has been further developed to a convincing phenomenological model, see, e.g., Ref. [2]. However, there is no ab-initio explanation for the origin of the ultrafast demagnetization phenomenon. Further experimental data are thus needed. In particular, there are hardly any data available so far revealing how the magnetization evolves on the nanometer length scale.

Experiments using high order harmonics (HHG) of a femtosecond IR laser are well-positioned to provide novel experimental data. Contrary to IR and visible sources, their shorter wavelength allows obtaining information with nanometer spatial resolution. For example, HHG based resonant magnetic scattering or x-ray imaging techniques can yield information on eventual appearance, growth or shrinking of magnetic domains.

A key strength of HHG sources is the very short duration of harmonics pulses and the inherent jitter free relationship between the IR pump and HHG probe pulse. This will allow for reaching unprecedented temporal resolution.

In my presentation, I will report on the first results obtained on ultrafast demagnetization with the HHG source of the Laboratoire d'Optique Appliquée in Palaiseau (France). I will show that ultrafast demagnetization can be observed at the nanometer scale with a time resolution of 40 fs with an HHG based set-up. These results will be compared to those obtained with other sources of ultrashort EUV and X-ray pulses (e.g. free electron laser and femto-slicing). In particular in regard of the significantly faster demagnetization dynamics we observe in comparison to what has been measured so far on magnetically saturated thin films of comparable materials. We attribute this acceleration to the nanoscale magnetic domain structure present in our samples and suggest that angular momentum transport by hot, spin-polarized electrons is the underlying mechanism [3].

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Linewidth of Image State at Metal Surfaces: High Energy-resolved Two Photon Photoemission Spectra

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ABSTRACT

Combining narrowband short pulse laser excitation with energy- and angle-resolved two-photon photoemission (2PPE), we have investigated the electronic properties of the Cu(001) surface. A picosecond Ti:Sapphire laser and UHV-system equipped with a 2D-electron detector offer new insight into electron dynamics in a photoexcited states on solid surfaces with the millielectronvolt level, which cannot be achieved with the ultrafast ($\lesssim$100 fs) laser excitation.

Lifetime of the electrons in the excited states (the intermediate states in the 2PPE process) are governed by Quasielastic and inelastic scattering. The former determines the so-called pure dephasing rate Γ^*, the latter the decay rate Γ. The ultrafast time-resolved 2PPE experiments enable us to determine the decay rate. The linewidth of the 2PPE spectra Γ_{tot} is described by $\Gamma_{tot} = \Gamma + 2\Gamma^*$, and Γ is comparable to the line width of the ultrafast laser pulse. Thus, high energy resolved 2PPE exited by the narrow band laser is highly required for accurately determining the pure dephasing rate.

In this talk, we will show the highest energy resolution (<10 meV) is achieved by the narrowband picosecond pulse laser excitation. Owing to the high energy resolution, the image states were well separated in the spectra up to n=4, and the energy positions of the higher image states (n=5,6, and 7) were determined. Finally, we have succeeded in measuring the pure dephasing rate for the n=1 and 2 image states.

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Electronic Structures in Bimetallic Prussian-blue Analogues during Li-ion Insertion/extraction Studied by Soft X-ray Absorption

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ABSTRACT

Prussian blue analogues (PBAs) are promising candidates of electrode materials for Li-ion batteries because of their porous coordinating and rich physical properties [1-3]. Recently, we found in $K_{0.1}Ni[Fe(CN)_6]_{0.7}$•$4.7H_2O$ (NiFe-PBA) that the average discharge voltage of 3.3 V vs. Li/Li$^+$ is comparable to conventional electrode materials for Li-ion batteries, and the cyclability of the charge/discharge is very high. However, the electronic-structure change of the NiFe-PBA frameworks has not been investigated during the Li-ion insertion/extraction. To obtain a clear strategy to improve the electrode properties, it is highly important to perform element-specific investigation of the electronic structure, in particular for the transition-metal 3*d* orbitals.

We have studied the electronic structure of Li_xNiFe-PBA ($0 \leqq x \leqq 0.63$) by means of soft x-ray absorption spectroscopy (XAS). We fabricated five samples with various Li concentrations by the electrochemical method. The XAS experiments have been performed at the BL-7A of the Photon Factory. The total-electron yield (TEY) detection mode was employed.

The multiplet structure for the Fe $L_{2,3}$-edge XAS changed from Fe^{3+} (3d^5) low-spin (LS) to Fe^{2+} (3d^6) LS states with Li-ion insertion. The configuration-interaction full-multiplet calculation revealed that the metal-to-ligand charge transfer (MLCT) exists in addition the ligand-to-metal CT (LMCT). Compared to the Fe^{3+} LS state, the degree of LMCT for the Fe^{2+} LS state (Li-ion inserted state) was suppressed because of the filled t_{2g} orbital while that of MLCT was enhanced. On the other hand, the Ni $L_{2,3}$-edge XAS showed the multiplet structure of Ni^{2+} (3d^8) high-spin state regardless of the Li concentrations. The calculated results suggested the presence of MLCT from Ni 3*d* to N 2*p*.

In the presentation, we will also compare the electronic structure of NiFe-PBA with that of $K_{0.1}Mn[Fe(CN)_6]_{0.7}$•$4.7H_2O$ (MnFe-PBA) which has similar charge-discharge properties [1,4].

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Soft X-ray Absorption and Emission Studies of Electrode Materials for Li-ion Batteries

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ABSTRACT

To improve the performance of Li-ion batteries, understanding the electronic structure and redox reaction of the electrode materials is highly important. In the field of electrochemistry, hard X-ray absorption spectroscopy which covers 3*d*-transition-metal (TM) *K* edges has been widely used to investigate the valence state of TMs. However, the electronic-structure parameters of the 3*d* orbital, e.g., crystal-field splitting, charge-transfer energy (Δ) and Coulomb interaction, have not been discussed because it is difficult to obtain detailed information of the 3*d* orbital from *K*-edge (1*s* → 4*p* absorption) spectra.

On the other hand, soft X-ray absorption spectroscopy (XAS) covers TM $L_{2,3}$ edges (2*p* → 3*d* absorption) [1]. Thus, the electronic-structure parameters can be determined by XAS in combination with multiplet calculations. Furthermore, soft X-ray emission spectroscopy (XES) provides the information of occupied state including *d*-*d* excitation [1,2]. Combination of XAS and XES should be very useful to reveal the electronic-structure change of the electrode materials with Li-ion insertion/extraction.

We have performed *ex situ* XAS/XES for several cathode materials to fully understand the 3*d* electronic structures. For example, the Mn $L_{2,3}$ XAS for $LiMn_2O_4$ [3] showed a mixed multiplet structure consisting of Mn^{3+} and Mn^{4+} high-spin (HS) states. When Li ions were fully extracted (charged state), only the Mn^{4+} HS state was observed. With proceeding Li-ion insertion (discharge), the volume fraction of the Mn^{3+} HS state increased. Multiplet calculations revealed a small Δ for both Mn^{3+} and Mn^{4+} HS states, suggesting a large orbital overlap between the Mn 3*d* and O 2*p* orbitals. The Mn 2*p*-3*d*-2*p* XES for $Li_xMn_2O_4$ showed clear changes in the *d*-*d* excitation region during Li-ion extraction/insertion. These XES results were consistent with the XAS results.

In the presentation, the XAS/XES results with multiplet calculations for several cathode materials including $LiMn_2O_4$ will be discussed.

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A New Concept in Scanning Photoelectron Microscopy : Nano-ARPES at Synchrotron SOLEIL

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ABSTRACT

A wide range of structural and chemical imaging techniques are now available for research in nano-materials and Low Dimensional Systems. In particular, the synchrotrons offer various spectrometers equipped with micrometric or even nanometric beam sizes. It is clear that the highly improved flux level of the third generation synchrotron sources is being highly beneficial in the area of the X-ray microscopy. In such context, a new scanning photoelectron microscope (SPEM) beamline has been constructed at SOLEIL. Contrary to the PEEM microscopy, the imagery in SPEM is generated by a simple nanometric sweeping of the samples and a focusing of the incident light.

Our innovative project is extending the classical SPEM technique to the domain of low photon energy using angle resolved photoemission (Nano-ARPES), allowing the states of the valence band and their k// dispersion be detected with extremely high energetic and angular resolution. The objective is to be able to determine the electronic band structure and the Fermi surface together with the chemical shift of core level of light elements with nanometer spatial resolution.

In essence, this new beamline of SOLEIL is fitting the existing emptiness between the atomic information provided by the STM microscopy and the low-spatially resolved data supplied by the traditional ARPES and NEXAFS techniques. The beamline delivers photons with energy in the 20-900 eV range, making use of two soft X-ray undulators with circularly and linearly polarized light. It comprises a high-resolution variable line spacing (VLS) and varied groove depth (VGP) plane grating monochromator (PGM) with a spectral resolving power of 25000 at 100 eV. This high brightness source illuminates a set of selected Fresnel zone plates after being focalized by a double Wolter optics passing by a pinhole. The design and the first results of this recently inaugurated station will be presented.

This instrument, with a spatial resolution of several tens of nanometers, has proved being able of carrying out direct imaging of core levels, their chemical shifts and tiny features of the electronic band structures of ordered materials. High precise images with chemical and valence band information have been recorded of nano-objects like nano-wires and micrometric exfoliated samples of graphene and other layered compounds. Moreover, several ordered granular materials have been investigated by imaging Nano-ARPES and core levels of individual grain. Finally, an overview of the utilization limits and complementarity of different x-ray microscopes will be detailed.

Photo-induced Insulator-metal Transition in Magnéli-phase Ti_4O_7 Studied by Time-resolved Photoemission Measurement

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ABSTRACT

Magnéli-phase Ti_4O_7 is well-known as the material exhibiting the thermal metal-insulator transitions called as Verwey transition.[1] Watanabe *et al.* reported a metastable phase induced by the laser irradiation above a threshold value from the low temperature insulator phase by transient reflection spectroscopy.[2] Some candidate of the laser-induced electronic states and the possible mechanism were proposed in the reports but have not been clarified yet. Time-resolved photoemission (TRPES) measurements are powerful technique to investigate the dynamical changes in the electronic states induced by photo-excitation, pulsed heating, and other transient perturbations. Therefore, we have applied the TRPES to the study of the laser-induced phase transition in the Ti_4O_7 crystal.

All the measurements in the present report were conducted at the Saga University Beamline BL13 in SAGA-LS.[3] The fundamental of 1.51eV from a 100kHz Ti:sapphire regenerative amplifier and the 4th harmonics of 6.05 eV was used as pump and probe light, respectively. The Ti_4O_7 single crystals used in the present measurements were about 1.0 mm × 0.5 mm × 5.0 mm, which were grown by chemical transport reaction as same as those used in the optical measurements.[2] These samples were fractured in the analyzing chamber with the base pressure of less than 1.5×10^{-8} Pa. The obtained surfaces were checked by the X-ray photoemission spectroscopy (XPS) using the synchrotron radiation (SR) of 660 eV and the signal from the contamination was not observed in the carbon 1s core level region. Thermal metal-insulator phase transition was observed in the valence band photoemission measurement by both the SR of 110 eV and 6.05 eV laser. It indicates that the present laser-TRPES measurement covered the Brillouin zone related to the metal-insulator transition.

The transient metallic state has been clearly observed in the valence band TRPES measurement in the insulator phase of Ti_4O_7. This state builds up within one picosecond indicating the non-thermal phenomena and survives in about one nanosecond. In addition, this state can be stimulated above the threshold excitation density which strongly suggests the cooperative phenomena. Therefore, we conclude that the laser-induced metallic state is not due to the locally destroyed insulating state but originated from the photo-induced insulator-metal transition.

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Electronic structure of Co_2MnSn studied by Resonant Photoemission Spectroscopy.

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ABSTRACT

The electronic structure of Co_2MnSn has been investigated by using valence-band photoemission at different photon energies ranging from 45 to 72 eV. Resonant photoemission has been observed near the 3p threshold of Mn and Co at 50 eV and 61 eV. [1] In addition to Mn and Co 3p-3d transitions, the constant initial-state spectra shows two more features at 53 eV and 67 eV related to the cubic surface modification as observed for Mn metal [2] and the shake-up excitations similar to Co metal [1] respectively. Constant initial state spectra exhibit Fano-type resonance profile having 3d character [3]. The valence band is found to be dominated with the Co 3d and Mn 3d like states. The features in the valence band and the shape of the resonance profile have been explained with the help of theoretical first principle calculation performed by full potential linearized augmented plane wave method. The conventional $L2_1$ structure in cubic phase has been confirmed by angle dispersive X-ray diffraction measurements and the shape of the valence band spectra and is in good agreement with theory. Detailed theoretical calculations indicate that on-site electron-electron correlation can be of importance in this system.

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Electronic States of Correlated Electron Systems Studied by High Resolution Resonant Photoemission

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ABSTRACT

Electronic structures of correlated electron systems like $EuCu_2Ge_2$ and $CeAg_2Ge_2$ are studied by high resolution resonant photoemission spectroscopy (HRRPES) across the 4d-4f resonances of Eu and Ce respectively. It is well known that the degree of the overlap between 4f states and the conduction bands, or the degree of hybridization, influences the properties in these systems. The motivation behind this work is to understand the origin of correlation and the magnetism in these systems which are mostly dependent on the electronic structure near the Fermi level [1]. Hence it is necessary to probe the 4f electronic states by HRRPES, which is a unique technique able to provide a direct access to both single-particle excitations and many body effects. HRRPES on $CeAg_2Ge_2$ shows clearly two Ce 4f related features at the 4d threshold of Ce at 121eV which were not resolved in our earlier studies [2] and hence unable to experimentally determine the coulomb correlation energy in this system. Coulomb correlation energy can be determined from the position of the 4f states above and below the Fermi level. In $CeAg_2Ge_2$ the unoccupied states above the Fermi level show the effect of correlation which are probed by inverse photoemission spectroscopy. Experimentally determined correlation energy is in very good agreement with the theoretically determined Hubbard U term by the first principles density functional calculations within the generalized gradient approximations. For $EuCu_2Ge_2$, correlation effect has been found to play a major role on the occupied electronic states. HRRPES data on $EuCu_2Ge_2$ shows two resonance features at 141eV and 143eV related to the divalent and trivalent states of Eu [3]. However, $EuCu_2Ge_2$ is reported to exist in a stable divalent state by other bulk measurements and hence the origin of the Eu^{3+} state is not known. Supporting evidence for the existence of Eu in Eu^{2+} (92%) and Eu^{3+} (8%) states are also obtained from the Eu L_3 x-ray absorption edge spectra. The absence of Eu 4f states in the vicinity of Fermi level and the energy separation of the absorption edges of Eu^{2+} and Eu^{3+} gives the evidence that Eu exists in the inhomogeneous mixed valence state in $EuCu_2Ge_2$.

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The Unusual Electronic and Morphological Structures of SiGe alloys Grown on Ge Substrates

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ABSTRACT

We report on the study of the electronic and morphological structures of the SiGe alloys grown by the molecular beam epitaxy on the Ge (001) substrates through the x-ray absorption spectra (XAS) and scanning electron microscopy (SEM). The XAS recorded at the Si $L_{2,3}$-edge were carried out by the surface sensitive total electron detection. To have a clear vision of the electronic structures, the L_3 XAS was obtained by numerically deconvolving the experimental spectra with the known spin-orbital coupling energy interval and intensity contribution of the $L_{2,3}$ electrons. The hydrostatic splitting of the Δ_1 band minimum was found in the thin SiGe alloys, indicating that the alloys are highly strained. The SEM showed that the morphologies of the alloys changes from pyramids to squares and rectangle grids by increasing the alloy thickness. Images from the alloy samples made by the physical vapor deposition method were employed for comparison. The strain was mainly attributed to the usual lattice mismatch, which shows multi-crystal-like morphology of the SiGe alloys as a result of the sample growth.

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X-ray Photoelectron Diffraction Studies of Structure and Surface Termination of $SrTiO_3$(001) Surfaces and Epitaxial $La_{0.7}X_{0.3}MnO_3$ (X=La, Ca, Sr, Ce) Films

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ABSTRACT

Perovskite oxides have been in the focus of research for quite some time because of their interesting magnetic, electric and transport properties. Recently, there have been structural studies using photoelectron diffraction of these types of materials[1,2,3]. We have investigated surface composition, structure and termination of $SrTiO_3$(001) (STO) samples (substrates) and of epitaxial LXMO (X=La, Ca, Sr, Ce) films by perfoming X-ray Photoemission Spectroscopy (XPS) and X-ray Photoelectron Diffraction (XPD) experiments, and multiple scattering cluster (MSC) calculations[4]. STO surfaces have been studied following typical steps of standard ex-situ and in-situ preparation procedures. Well-developed diffraction features have been observed in all XPD polar-angle scans demonstrating the good structural ordering of the investigated surfaces of STO. A fingerprint region has been identified in Sr3d polar-angle scans, which has exhibited both evident dependencies on surface preparation steps in the experiments and clear sensitivity to surface termination in the theoretical modeling. In this manner we have been able to describe as received samples and in situ-treated samples as being TiO_2- and SrO-terminated, respectively, while standard HF-etched samples turned out to be mostly TiO_2-terminated but with a non-negligible admixture of different, likely SrO-type termination. Thus, both TiO_2- and SrO-terminated STO samples have been successfully prepared in this investigation.

Further, epitaxial LXMO (X=La, Ca, Sr, Ce) films have been grown lattice matched on STO by pulsed laser deposition[5] as confirmed by X-ray Diffraction (XRD). Again, well-developed XPD features have been observed, and direct comparisons support that doping atoms occupy La substitutional sites, essentially. Further, from comparison of experimental XPD and MSC calculations we suggest the surface termination of the films to be MnO_2. Structural relaxations in the $LaMnO_3$ and $La_{0.7}Ce_{0.3}MnO_3$ films are discussed.

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Electronic Structure of Al-doped ZnO Transparent Conductive Thin Films Grown in Various Magnetic Fields Ambient Studied by X-ray Absorption and Emission Spectroscopy

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ABSTRACT

Al-doped ZnO (AZO) transparent conductive thin films have been prepared on glass substrates by pulse laser deposition method with an expanding magnetic field along the direction perpendicular to the sample's surface. The AZO thin films were deposited by ablating ZnO targets containing 2 wt% Al_2O_3 without heating the substrates. O *K*-, Zn L_3-, and Al *K*-edge X-ray absorption near-edge structure (XANES) and x-ray emission spectroscopy (XES) measurements were used to investigate the electronic structure of AZO thin films and to determine the influence of the variable magnetic fields. The analysis of the XANES spectra showed increased numbers of O 2*p* states as the resistance of the film decrease, suggesting that the enrichment of O 2*p* dangling bond along ***c***-axis is the main factor affecting the electric performance of AZO thin films. Moreover, the electrons transition from Zn atom to Al site through O 2*p*–Zn 3*d* and Al 3*sp*–O 2*p* hybridizations changes with the magnitude of the magnetic fields and consequently weaken the O 2*p*–Zn 3*d* hybridization with the downsizing of the grain size. XES and XANES spectra of O 2*p* states at the O *K*-edge also revealed that the changes in E_g is related to the shifts in CBM and the VBM almost keeps the same with the changes in the magnitude of the magnetic fields. The preferential orientation of (002) along c-axis of AZO thin films, the changes of magnetic fields accompanied by the thermal/annealing effect, the increase in surface effect, the decrease of the energy bandgap, and the increase in density of unoccupied O 2*p*-derived states are the factors to affect the magnitude of the resistance/electric conductivity of AZO thin films.

Influence of Confinement on Charge Doping Properties of Iodine Doped Carbon Nanotubes

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ABSTRACT

Carbon nanotubes are promising candidates in the development of new electronics devices [1-3]. Their electronic properties, which depend on tube diameter, can be controlled and tuned by inserting atoms or molecules in the hollow core of the tubes. For instance when iodine atoms are inserted inside carbon nanotubes, a p-doping of the nanotubes is induced via the charge transfer from the tubes to the iodine atoms leading to the formation of polyiodides chains [4-5].

Depending on the nanotubes diameter, it has been shown that different kinds of structures are formed in the nanotubes. In nanotubes of small diameter only single chains are found while in thicker nanotubes, double helix and triple helix chains are observed [6-7].

Although structural informations on the long range order is available, less is known on the local order and the nature of the polyiodides formed inside the carbon nanotubes. To go further in the understanding of these confined systems, we have used EXAFS spectroscopy to study of polyiodides chains as function of the nanotube diameter.

We will discuss about the influence of the confinement on the polyiodides chains at the local order and the possible influence on the charge doping of the nanotubes.

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Pd Doped SnO_2 Nanorods

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ABSTRACT

Tin oxide is widely used in commercial processes. It is used in catalysis, solar cells, transparent electrodes and optoelectrical devices or as protective coating. Last years it became predominant material used in gas sensors as in household so in industrial and commercial spaces. Most gas sensors are made of porous SnO_2 thick films with a high surface to volume ratio, doped by catalytically active metals. The exact fundamental mechanisms that cause a gas response is still controversial, but essentially trapping of electrons at adsorbed molecules and band bending induced by these charged molecules are responsible for a change in conductivity.

In our study we examined growth of SnO_2 and SnO_2-Pd thin films. Films were prepared by nonreactive radio-frequency magnetron sputtering on Si(100) substrate from composite target using a glancing angle deposition technique (GLAD). Combination of GLAD with magnetron sputtering allowed us to prepare highly porous thin films in form of nanorods, which are highly suitable for catalytic and sensing reactions. Studies showed that films thickness has an influence on chemical states of SnO_2-Pd nanorods. To examine this influence, samples with thickness of 5, 20 and 80 nm were studied. Chemical state was studied by X-ray photoelectron spectroscopy (XPS). XPS showed increase of Pd^0 and Pd^{4+} states and decrease of Pd^{2+} state with growth of the film thickness. Heating of the substrate was used in order to check the influence of temperature on the nanorods growth. X-ray diffraction (XRD) showed change of crystalline structure in dependence on the substrate temperature. Crystalline structure was inspected by high resolution transmission electron microscopy (HRTEM). Morphology of all samples was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Construction of Hard X-ray Photoemission Spectroscopy Data Base with Photon Energy of around 8keV at BL46XU of SPring-8: 3d Elements

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ABSTRACT

High-energy, high-resolution hard x-ray photoelectron spectroscopy (HAXPES, total energy resolution of ~0.25eV with hv~8keV at room temperature) has attracted great interests for investigating electronic structure of bulk materials, Nano scale buried layers and their interfaces, since the relative contribution of signal from the surface region is reduced[1, 2], due to the large escape depth of photoelectrons with high kinetic energy. The advances in x-ray undulator technology at third generation synchrotron light sources enable the delivery of unprecedented high photon flux[3, 4], which can well compensate the suppression of photoionization cross section (PICS) and analyser transmission, and make HAXPES experiment accessible. Recently, it was widely used in the industrial applications such as high K electronic device, catalyst, batteries, and so on. Usually, the industrial users need some standard spectra as well as the parameters of those core level spectra for comparison. Unfortunately, the standard spectra for lab XPS some time is insufficient, due to the change of PICS against excitation photon energy. Additionally, the Auger spectra move out of the regions where they appear in lab XPS, owing to the change of kinetic energy of photoelectrons. The demands push us to construct spectra data base of HAXPES at the industrial application beam line III -- BL46XU of Spring-8, where the most industrial proposals will be performed for HAXPES, since no such kind of data base can be referred to so far due to the recent development of HAXPES.

This presentation focuses on the spectra of 3d elements (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) with monochromatic photon energy of around 8keV (Si (444) channel cut). Possible core levels (such as 1s core levels up to Co) and valence band are investigated. The background and peaks are fitted by thinking about inelastic mean free path (IMFP) of photoelectrons. The line shapes of 1s core levels show more Lorentzian contributions and asymmetry due to the screening from out levels. In order to evaluate PICS and the surface induced effects at different electron kinetic energies, the intensity of core levels and valence band is used. As a result, valence bands are compared with the calculated ones by considering PICS and total energy resolution.

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Oxygen Vacancy Induced Core Level Shifts in SnO_2: A Combined HAXPES and First-principles Study

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ABSTRACT

The wide-band-gap oxide SnO_2 has attracted great interest for a variety of technical applications including solid state sensors, oxidation catalysts, transparent conductors, and so on. The understanding of the electronic properties is crucial for applications of this oxide. As a direct technique, photoemission spectroscopy (PES) is used to detect the chemical states by electronic structures and core level shifts. Even though a lot of work[1, 2, 3] has been done so far, the core level shifts and their relations to the valence structure still remain to be clarified due to some reasons such as the oxidization, hydration and vacancies on the surface, the limited probing depth of PES technique, the surface charging effect, and the impurity pinning of Fermi level. The newly developed high-energy, high-resolution hard x-ray photoelectron spectroscopy (HAXPES, total energy resolution of ~0.25 eV with $h\nu$~8 keV) at third generation synchrotron light sources, improves greatly the probing depth (~3 nm for lab XPS at $h\nu$~1486 eV, and 10 ~ 20 nm for HAXPES at $h\nu$ ~ 8 keV). It indicates that HAXPES can be used to detect the bulk information, interface or buried phases, even for the samples without surface treatment that usually has to be done for lab XPS or UPS methods.

In this presentation, the core levels and valence band spectra of SnO_2 single crystal was investigated with varying the electron take-off angles (TOA, the angle between the direction of take-off electrons and sample surface) by HAXPES. It was found that the core levels shift to high binding energy side with reducing TOA. The Fermi edge falls around the bottom of conduction band, which means the SnO_2 single crystal is typically an *n*-type semiconductor. However, the trends of core level shifts are opposite to the behaviours of *n*-type semiconductors[4], which indicates nonuniform band bending takes place around surface region, such as more O vacancies around surface than that in bulk. Furthermore, the core level shifts relate to the band tail states at 3.5~4 eV below Fermi level by careful investigation of valence band. These band tail states are confirmed to relate to the O vacancies[2, 5]. To understand these, first-principle calculations were performed for electronic structures and core level shifts. It shows that the band tail states are related to vacancies of oxygen on the surface region. As a result of O vacancies, the core levels shift to higher binding energy side. These results correspond well with our experimental ones. The findings will help us to understand the behavior of O vacancies on SnO_2 and give new explanation of the difficulties to evaluate the core level shifts of Sn in its various oxides.

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Depth of Buried Layers Studied by Background Analysis of Hard X-ray Photoemission Spectra

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ABSTRACT

Recent advances in x-ray undulator technology at third generation synchrotron light sources enable the delivery of unprecedented high photon flux[1], which can well compensate for the suppression of cross section and analyzer transmission, and make high-energy, high-resolution hard x-ray photoelectron spectroscopy (HAXPES) accessible. The larger inelastic electron mean free path (IMFP) of photoelectrons with higher kinetic energy facilitates electronic structure studies of bulk materials, nano scale buried layers and their interfaces since the relative contribution of signal from the surface region is reduced [2,3]. It is well known that by analysis of the background of inelastically scattered electrons one can get information on the depth distribution of atoms up to ~10 IMFP depths[4]. Since the IMFP at these higher energies can be in the 5-10 nm range this opens up for non-destructive analysis of structures at depths up to ~ 50 nm. The background analysis can be used to determine the thickness of overlayers and buried layers. On the other hand, if the thickness is known the method can be used to determine the IMFP of the overlayer.

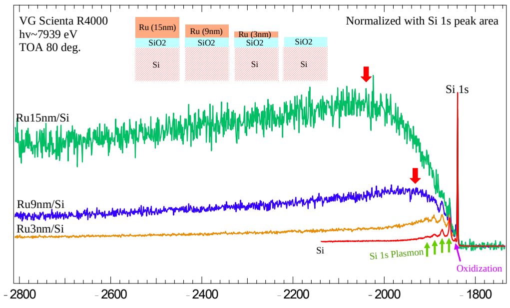

Fig. 1 The Si 1s spectra and background under different thicknesses of Ru overlayer. All the spectra were nomalized by the intensity of Si 1s peaks.

In this presentation, the background coming from buried layers and the substrate with different overlayer thickness is investigated with excitation photon energy around 8KeV at different electron take-off angles (TOA). It is observed (see Fig.1) that with increasing transfer path of photoelectrons, the intensity of the background is enhanced relative to the height of the primary peak. These Si1s spectra as well as Ru spectra from the overlayer were analysed and the thicknesses of overlayers were determined. We use the IMFP calculated by TPP2M[5] at the respective kinetic energies for the Si1s (6100 eV) as well as through analysis of the Ru peaks (in the 4600 – 5200 eV range). The background analysis was done with the QUASES software package which implements the Tougaard background analysis[4]. The analysis shows very good account for the observed changes in peak intensity and shape of the background over an energy range of several hundred eV and the determined thicknesses from analysis of the Si1s and Ru peaks are in good accordance to each other and near to the nominal thickness value when the films were fabricated.

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Study of Lattice Distortion of Porous Si by Li Adsorption using Two-dimensional Photoelectron Diffraction

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ABSTRACT

There is an increasing demand for lithium ion batteries (LIB) with higher energy and power density and cycling stability. Silicon has been widely studied as a promising candidate for the next-generation anode materials, due to its highest theoretical specific capacity ($Li_{22}Si_5$ ≈4200mAhg−1). Much effort has been devoted during the last decade to replace the current graphite anode by silicon; however, lithium insertion/extraction into/from bulk silicon is associated with drastic volume change and structural collapse giving rapid capacity fading. The volume expansion/contraction is better accommodated with nanosized structures, such as nanoparticles, nanofilm and nanowires, but the inherently high surface energy of nanosilicon resulted in the re-agglomeration and deterioration of cycling performance.

Porous silicon is an another candidate of nano-sized Si crystal. Because the nano crystals of porous silicon surface are parts of the original Si substrate the orientation of them is the same as that of the substrate. Hence porous Si is an ideal nano crystals to be studied their structure change during lithiation and delithiation. In this study we studied the structure change atomically using RHEED and photoelectron diffraction.

Nanocrystalline porous silicon layer was prepared by electrochemical etching of p-type silicon (001) wafer in ethanolic solutions containing hydrofluoric acid. Porous silicon (001) surfaces were characterized using Scanning Electron Microscope (SEM), Reflection High Energy Electron Diffraction (RHEED), X-ray Photoelectron Spectroscopy (XPS), and two-dimensional photoelectron diffraction including stereo atom-scope. The morphology of the as-grown porous silicon was studied by SEM to be filled by about 8 nm holes. This porous silicon is optically active with visible photoluminescence. Lithiation and delithiation of porous silicon was studied using RHEED and stereo atom-scope, which is realized by the combination of display-type spherical mirror analyzer (DIANA) [1], Display-type Ellipsoidal Mesh Analyzer (DELMA) [2] and circularly polarized soft X-rays. The result of RHEED and the Si 2p photoelectron pattern (Fig. 1) from porous Si (001) surface revealed the distortion of the lattice. This distortion was restored by delithiation.

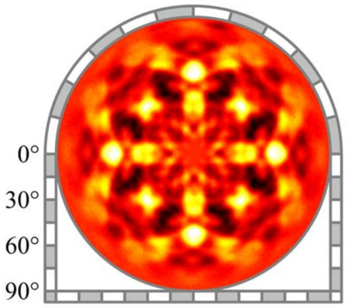

Fig.1 . Photoelectron diffraction pattern of porous silicon

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Resolving Interfacial Mechanisms in Silicon Electrodes of Li-ion Batteries by Soft and Hard X-ray Photoelectron Spectroscopy

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ABSTRACT

Future applications of lithium-ion batteries require better performances, in particular increased capacities. Metals and semimetals that can electrochemically form alloys with lithium are interesting alternative materials to replace the carbonaceous materials commonly used as negative electrodes. Silicon can alloy with 3.75 Li per Si atom and appears to be an ideal candidate for many reasons [1].

The use of silicon nanoparticles to improve the electrochemical performances of such systems gives a great importance to interfacial mechanisms. Lithium insertion/extraction in silicon gives rise to a complex mixture of phases, and the surface of the particles is being covered by a passivation layer formed by decomposition products of the liquid electrolyte. Moreover, considerable volume increase/decrease following lithium insertion/extraction leads to a perpetual reconstruction of the solid/liquid interface. It is therefore of great importance to understand the limitations due to such interface phenomena [2].

In this work a unique combination of soft ($h\nu$ = 100-800 eV) and hard ($h\nu$ = 2000-7000 eV) X-ray Photoelectron Spectroscopy complemented with in-house XPS (1487 eV) has been used to develop a non-destructive depth-resolved analysis of silicon electrodes after electrochemical working (instead of using common argon ion etching, that is very destructive in this kind of study). The variation of the analysis depth allowed us to access the interfacial phase transitions at the surface of silicon particles and the composition and thickness of the passivation film. Several mechanisms were evidenced, especially involving the silicon oxide layer covering the surface of the particles. A participation of the salt used in the electrolyte ($LiPF_6$) in the aging mechanisms of the electrode material by fluorination of the surface was also evidenced.

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XANES and XPS Investigations of Multilayered Nanostructures $(Co_{45}Fe_{45}Zr_{10}/a\text{-}Si)_{40}$ and $(Co_{45}Fe_{45}Zr_{10}/SiO_2)_{32}$

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ABSTRACT

The electronic structure and phase composition of amorphous multilayered nanostructures (MLNS) $(Co_{45}Fe_{45}Zr_{10}/a\text{-}Si)_{40}$ and $(Co_{45}Fe_{45}Zr_{10}/SiO_2)_{32}$ with different layer thicknesses from 0.5 nm to 15 nm were investigated by means of X-ray Absorption Near Edge Structure technique (XANES). The spectra of Fe $L_{2,3}$, Co $L_{2,3}$, Si $L_{2,3}$ and O K-α were obtained. The measurements were performed on the Russian-German beamline of BESSY II synchrotron (Berlin, Germany). The fact of interatomic interactions leading to formation of composite "nanoferrite" like FeO•Fe2O3•ZrO_2(CoO) was established. Also there was shown that in mentioned nanoferrite there is an exchange interaction which involves not only two- and three-charged ions of iron (Fe^{2+} and Fe^{3+}), ions of Zr^{4+} and partially ions of Co^{2+}. The transformation of thin structure of $L_{2,3}$-edges for iron component of multilayered nanostructures in XANES spectra reflects on the change of the relation of two- and trivalent ions in iron oxides as a part of composite "nanoferrite". The experimental results were supplemented with mathematical modeling of O K-α for MLNS which was helpful to determine the metal and oxide phases in MLNS.

The X-ray Photoelectron Spectroscopy technique with photon energy 800 eV has been performed to amplify the information about the chemical composition of MLNS. In the result of XPS investigations there was established the chemical composition before and after ion etching. This technique was useful for detection of appearance pure metals Co, Fe, Zr side by side with the oxides phases CoO, Fe_2O_3/Fe_3O_4 and ZrO_2.

The obtained data could be an evidence of partial atoms mixing of metallic and nonmetallic silicon layers in MLNS. This phenomenon promotes the fall of a percolation threshold and transformation of conductivity to three-dimensional type. Therefore the temperature dependence of conductivity of the MLNS appears similar to dependence for metal - dielectric nanocomposites $(CoFeZr)_x(SiO2)_{1-x}$ [1, 2].

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Pre- Edge Interference of Synchrotron Radiation in SOI Structure

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ABSTRACT

The appearance of interferential frequency-modulated waves has been observed in the SOI structure with an 80 nm silicon layer at small grazing angles of SR ($\theta < 21°$) in the energy range preceding the main absorption edge of silicon $L_{2,3}$ (~100 eV). Phase-frequency characteristics of the wave packages of interferential waves on a sample change to opposite every 2°. The value of grazing angles, at which the substantial reflection effect on the absorption edge shape in SOI begins is the individual structure characteristic and is determined by the thicknesses of layers forming it.

We calculated the total photoelectron yield Y(ω) by the general formula:

$$Y(\omega,\theta) = \int_0^\infty T(z)A(z,\omega,\theta)dz$$

where A(z,ω) is the number of the electrons created at depth z and as T(z) is the function of the electron yield from the depth z.

We have shown that the remarkable features of the quantum yield spectra measured in Pre- edge of Si $L_{2,3}$ absorption at different glancing angles of the radiation are not connected with some specific changes of the XANES spectra but originates from the standing wave $|E(z)|^2$ and the influence of the reflectivity formed by the whole multilayer structure . The special structure of the investigated natural SiO_2/Si/ thermal SiO_2 multilayer allows us to enhance and reveal such influence in the most impressive way due to the formation of the wave-guide modes in the middle Si layer.

ACKNOWLEDGEMENTS

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Electronic Structure and Magnetic Properties of $SmCo_{6.8}M_{0.2}$ Ribbons (M=Ti, Zr and Hf)

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ABSTRACT

The Sm-Co intermetallic compounds with $TbCu_7$ -type structure is of great interest due to their potential application in novel high-temperature permanent magnets. The pure $SmCo_7$ alloy with $TbCu_7$-type structure is not stable. However, doping of a small amount of the third elements such as Ti, Zr, and Hf can stabilize the 1:7 phase. In this study, the $SmCo_{6.8}M_{0.2}$ (M=Ti, Zr, and Hf) ribbons with $TbCu_7$-type structure were prepared by single-roll melt spinner. The structure refinement shows that the doping element M prefers to occupy the 2*e* site of $TbCu_7$-type structure. The electronic structure of $SmCo_{6.8}M_{0.2}$ (M=Ti, Zr, and Hf) ribbons were investigated using Sm $M_{4,5}$-edge and Co $L_{2,3}$-edge x-ray absorption near-edge structure (XANES). The XANES spectra reveal that while the number of Co 3d unoccupied states is increased, the number of Sm 4f unoccupied states is decreased, implying that the charge transfer may occur between Co and Sm. The remanence was found to be reduced by the M substitution. The magnetic properties of both Sm and Co were then investigated by using x-ray magnetic circular dichroism (XMCD). The XMCD results indicates that the substitution of Co by M, not just reduces the magnetic moments at the Co site but also at the Sm sites.

Angle-resolved Photoemission Study of P-induced Surface States on $Ni_2P(10\overline{\ \ },10)$

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ABSTRACT

The surface properties of Ni_2P have attracted much attention because it has been found to have high catalytic performance for hydrodesulfurization (HDS) for petroleum fuels.[1] In order to obtain the microscopic understanding as to the origin of the high catalytic activity, it is necessary to elucidate the electronic structure of Ni_2P single-crystal surfaces. In this work, we investigated the surface electronic structure of $Ni_2P(10\overline{\ \ },1\ 0)$ by angle-resolved photoemission spectroscopy (ARPES) utilizing synchrotron radiation.

The clean surface prepared by Ar^+ ion sputtering (3kV, 15 min) and annealing (400℃) showed a c(2×4) LEED pattern. The PES spectra in the valence band region consist of a Ni 3d – P 3p hybrid band (main band) and a satellite at 0 – 4 eV and 8 eV, respectively. Resonant PES study showed that the satellite is associated with a photoemission process leading to a two-hole bound final state. A surface state is observed around 0.6 eV along the boundary of the surface Brillouin zone (SBZ) of the c(2×4) lattice ($\overline{\ \ }$,H' $\overline{\ \ }$,N' $\overline{\ \ }$,H'). The two-dimensional band structure of the $Ni_2P(10\overline{\ \ },10)$ surface deduced from ARPES spectra measured along the [0001] direction is shown in Fig. 1. The state has a dispersion along the [0001] direction with the width of more than 0.03 eV. Resonant PES study showed that the state mostly consists of P 3p component. These results are compatible with the previously published structural model (missing row + added row model) in which the topmost layer is predicted to be composed of P rows along the [0001] direction.[2]

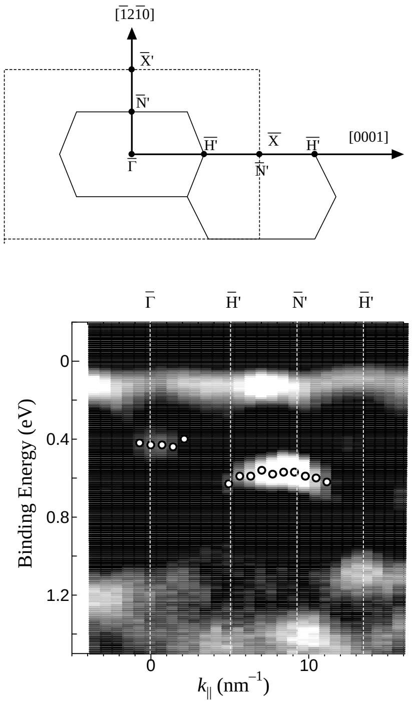

Fig. 1. Two-dimensional band structure of $Ni_2P(10\overline{\ \ },10)$. The SBZ of the c(2×4) lattice is shown in upper portion

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Polarization Dependent ARPES Measurement of the Valence Band Structure of Anatase TiO_2

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ABSTRACT

Anatase TiO_2 has attracted much attention as the most promising photocatalyst[1,2]. However, fundamental properties of anatase TiO_2 are less known than those of rutile TiO_2. In order to understand the mechanism and the superiority of the photocatalytic activity of anatase TiO_2, it is necessary to experimentally examine the band structure of anatase.

In the present study, we fabricated high-quality single-crystal anatase thin films, and elucidated the electronic structures by angle-resolved photoelectron spectroscopy (ARPES).

TiO_2(001) thin films were grown using pulsed laser deposition with a KrF excimer laser (λ = 248 nm) on $LaAlO_3$(100)[3]. The ARPES measurements were performed utilizing synchrotron radiation at Beam Line 3B of the Photon Factory, High Energy Accelerator Research Organization (KEK). The synchrotron radiation was linearly polarized in the incidence plane of the light. The spectra were acquired with incidence angles of 55° and 20° so that the ratio of p- and s-polarized components was varied.

The ARPES spectra show emission structures from the O 2p-dominant valence states between 3 and 9 eV (Fig.1). The shallowest peaks are associated with Pπ non-bonding state, while the contribution from the σ bonding states gives the deepest peaks[4]. In the energy region between the Pπ and σ, π bonding states are identified. From the polarization-dependent measurements, the deeper π bands, which shows high intensity with the s-polarized light, are mainly composed of the O 2p and Ti 3d orbitals in the (001) atomic plane whereas the shallower π bands should be composed mainly of the atomic orbitals out of the (001) plane.

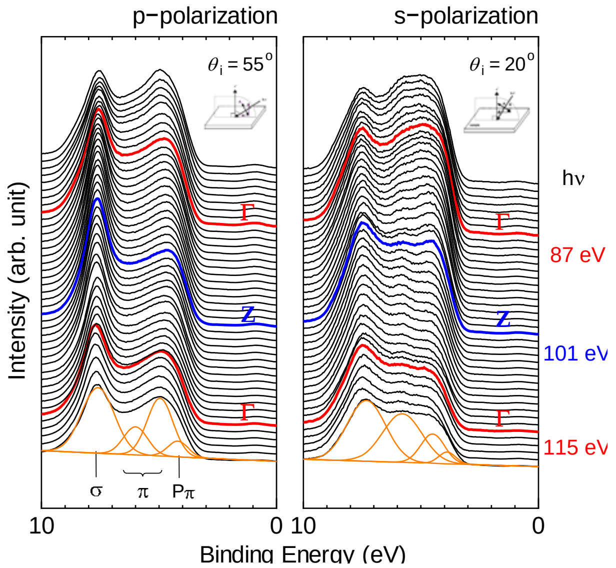

Fig.1 Normal emission spectra of anatase TiO_2(001) surface measured by p-polarized (left) and s-polarized (right) synchrotron light.

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Observation of Boron Diffusion in an Annealed Ta/CoFeB/MgO Magnetic Tunnel Junction with Standing-Wave Hard X-ray Photoemission

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ABSTRACT

Standing-wave photoemission has emerged as a powerful tool to elucidate the composition of buried layers, including buried interfaces[1,2]. Another recent development in photoemission is to use hard x-ray excitation (HXPS or HAXPES)[3] which yields larger probing depths. We have combined standing-wave photoemission with hard x-ray excitation to investigate the elemental distribution, particularly of B, in a Ta/FeCoB/MgO magnetic tunnel junction (MTJ). This system is a promising candidate as a magnetic tunnel junction with perpendicular magnetization and low critical current densities for current-induced magnetization switching[4]. The magnetic tunnel resistance is greatly enhanced on annealing, and this enhancement has been linked to a migration of B out of the FeCoB layer. We have measured the elemental distributions after annealing at 593 K for one hour, using a photon energy of 5950 eV. To obtain depth selectivity, the tunnel junction was grown on top of a multilayer mirror composed of 60 bilayers of Mo(1.58 nm) and Si(2.36 nm). Bragg reflection from this mirror generates a strong standing wave (SW), and varying the incidence angle around the Bragg condition scans the SW through the MTJ, yielding rocking curves (RCs) for each element. By comparing experimental RC data to x-ray optical calculations, we show that ~21% of B has migrated uniformly into MgO, and ~38% into a thin TaB interface layer on the Ta side of the tunnel junction. This study also demonstrates the effectiveness of SW-HXPS for probing composition distributions in a variety of spintronic structures.

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Optical Pumping in Silicon Thin Films Studied by Spin-resolved Photoemission Spectroscopy

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ABSTRACT

Optical orientation of electron spin in semiconductors has been evidenced for the first time in silicon 40 years ago by observing the induced enhancement of ^{29}Si nuclei polarization under circularly polarized light illumination [1]. Since that time, optical pumping and related techniques (such as polarized photoluminescence) have furnished a great number of results on spin dynamics in direct bandgap semi-conductors and on spin injection in semiconductor-based devices [2,3]. In silicon, although the electron spin relaxation time is known to be large, the situation is not so favorable because of the indirect band gap structure, the weak spin-orbit interaction and above all, because of the large value of the carrier lifetime relative to the spin relaxation time. In particular, this makes luminescence techniques hardly usable. Thus, very few experimental results have been obtained [4] and from a theoretical point of view, only recently partial calculations of optical pumping in silicon has been performed [5,6].

Here we report on a study of optical orientation of electron spin in silicon by means of energy- and spin-resolved photoemission. We use a silicon-on-insulator structure with a p-doped top layer of 5 μm thickness which limits the electron escape depth to a value smaller than the expected electron spin diffusion length. The silicon surface is activated to negative electronic affinity by cesium and oxygen adsorption. In this situation [7], electrons excited with near-band-gap circularly polarized light, can be emitted into vacuum where their energy and spin-polarization can be analyzed. We use different excitation energies ranging from 1.16eV, close to the indirect gap value, up to 4eV, above the direct bandgap. This excitation energy range is covered with a tunable Ti:Saphire laser followed by SHG and THG.

For near-UV excitation close to the direct bandgap, hot electron polarization up to about +7% is obtained in reasonable agreement with previous measurements on bulk silicon [8,9] and about a factor of 2 smaller than calculations of optical orientation at the Γ point. The maximum polarization value obtained for 3.30 ± 0.02 eV excitation energy provides an estimate of the direct bandgap value. For IR excitation of indirect transitions close to the absorption threshold, we measure a very weak polarization (which weakly increases in the visible excitation range) although the electrons are expected to escape from the silicon layer before noticeable spin relaxation takes place. These results will be discussed.

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Spectroscopic Characterization of Sr-rich $Sr_xTi_{1-x}O_y$ Films Synthesized by Atomic Layer Deposition Method. Influence of Interfacial Layer Material on Structure of Film

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ABSTRACT

Further scaling of dynamic random access memories with 1 Gbit density or higher requires an equivalent oxide thickness (EOT) in the 0.5–0.7 nm range for metal-insulator-metal capacitors in the memory cell, maintaining low leakage current densities. To achieve such small EOT the dielectrics with high-k values (>50) are required. One of the potential candidates for this application is perovskite $SrTiO_3$ (STO). The dielectric properties of STO are critically dependent on the film thickness and stoichiometric composition of the film. The including an interfacial layer can reduce the leakage current and the thickness dependence of the dielectric constant. Moreover in Sr-rich STO a significant decrease of leakage current compared to stoichiometric compound STO for the same values of the EOT can be achieved.

We present the results of study of the internal structure of $Sr_{0.62}Ti_{0.38}O_x$/ interfacial layer (SiO_2 or HfO_2 or Si_3N_4)/Si – ALD stacks obtained by four independent nondestructive techniques: X-ray photoelectron spectroscopes (XPS and HXPS)), X-ray reflection spectroscopy (XRS) and external X-ray photoeffect quantum yield in current mode (NEXAFS spectra). The STO films of 7nm and 15nm thick were analyzed. A joint analysis of Photoelectron spectra, $TiL_{2,3}$- and OK- NEXAFS spectra and atomic concentration profiles of all the chemical elements composing the samples reconstructed from the reflectivity curves indicates the following regularities:

1. In thin films in varying degrees but clearly there is a tendency to enrich the film with strontium. During the process of film growth (increase in film thickness) the enrichment of the film with Sr as it were suspended and is even in some extent compensated.
2. There is a significant amount of the Sr atoms (unoxidized) in the surface region of the 7nm thick film grown onto Si_3N_4 interfacial layer. The conducted research clearly demonstrated that only Si_3N_4 interfacial layer allows to synthesize the Sr-rich STO films.
3. The surface of the investigated STO films is carbonate-rich surfaces in the form of $SrCO_3$. The use of TiN as a capping surface layer of the film STO prevents the penetration of the carbon into the film and promotes the synthesis of strontium – rich film.

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Influence of Porous SiO_2 substrate on the Internal Structure of Al_2O_3 Nanolayers Synthesized by Atomic Layer Diposition Method

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ABSTRACT

Modern microelectronics industry develops today on the way of transistor density maximization. It is recognized, however, that device physics is not the first limiting factor to the continued performance improvement for systems. It is matter of fact that distance between nearest metallic wires in integrated circuit (IC) decreases dramatically as we move into the nanometer regime so the challenge will be to carry electric power inside IC. Parasitic capacitance caused by these wires creates effects of signal delay which will challenge further progress. Also increasing frequencies and higher transistor density lead to a dramatic increasing in power consumption related with interlayer dielectric polarization and leakage current. It's obvious that dielectric constant has to be strongly decreased. There are plenty of different ways to do this one and pore injection in SiO_2 is one of them. Porosity can decrease dielectric constant below 2 and this is very promising solving of mentioned problems in modern microelectronics [1].

It's well known that substrate material strongly influences on properties of thin film deposited on this substrate. Porous SiO_2 is new material and process of film growth on such substrate is of scientific interest. Therefore we investigated by x-ray reflection spectroscopy thin Al_2O_3 films with different thicknesses deposited by ALD method on porous SiO_2 substrate. Such film material was chosen because it's chemically stable and deposition on traditional substrates is broadly investigated. Also some measurements were carried out for films deposited on crystalline Si and thermal SiO_2.

It was founded that all films are almost amorphous without any crystallization signs and film microstructure does not depend on substrate material for thicknesses more than 13 nm. Also film continuity was founded for films deposited on porous SiO_2 and dependence of their microstructure on thickness was established: film growth starts from excess of tetrahedral coordination of Al atoms. On the contrary thin films deposited on crystalline Si consist generally of octahedral coordinations of Al atoms [2].

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Spectroscopic Characterization of Thin Films Internal Structure. New Approaches to Inter Layer Identification and Analysis

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ABSTRACT

Nowadays, ultra-thin film structures have become increasingly important in various fields. Understanding the processes occurring during deposition of the individual film is crucial for gaining insights into material quality. In many cases the properties of these layers govern the performance of the fabricated device. The thickness of an individual film can be as small as a fraction of a nanometer. Hence, the interlayers generated at the interface between two different substances owing to processes such as interdiffusion, chemical reactions and implantation during synthesis of films play increasingly important roles. The kinetics of the interlayer growth, its thickness and composition depend on large number of factors including the film deposition method, substrate surface preparation and post-deposition processing. A large number of incoming influences make it difficult to predict a priori interlayer properties. As a result, the formation of interlayer at the interface needs to be closely monitored.

The aim of this talk is to review our recent data illustrating significant advances in the characterization of thin films internal structure and interlayer identification (including the extension of interlayers) using two independent techniques (Soft X-Ray Reflectometry and Hard X-Ray Photoelectron Spectroscopy). We are focusing on the developed mathematical analysis methods [1] and their application to the investigation of different nanostacks based on high-k dielectrics. The derived results are compared with the results of High Resolution Transmission Electron Microscopy.

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Electronic Structure of Rhodium Oxide by X-ray Photoelectron Spectroscopy (Core Peaks-Valence Spectra)

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ABSTRACT

The study of electronic structure and the XPS signature of 4d transition metal (Rh) has been the subject of numerous studies but focus mostly on the rhodium-based catalysts. Few detailed XPS data [1, 2, 3, 4] reported the Rh 3d core peaks and valence spectra of rhodium oxides. In this work, we have performed a detailed X-ray photoelectron spectroscopy study on various rhodium oxides in order to study their electronic structure. The materials are oxides in which the rhodium cation is in oxygenated octahedral environment: the delafossite $CuRhO_2$, the perovskite $LaRhO_3$, the corundum Rh_2O_3 and the K_2NiF_4-type oxide Sr_2RhO_4.

The samples have been cleaved inside a glove box directly connected to the XPS spectrometer and the measurements have been performed on the “clean” surface. The spectral features of the Rh 3d core peaks show a dependence of the electronic structures with the crystallographic structure and the oxidation state. We have identified a fine structure satellite peak whose characteristics are related to the oxide structure.

This work also reports on investigations of rhodium oxide by means of valence spectra and theoretical calculations (Density Functional Theory calculations – APW-GGA). The calculations were achieved on four crystallized rhodium oxide phases and valence band spectra (visualization of the occupied electronic density of states) were precisely interpreted through modulated density of states with photoionization cross-section. This work will allow a more precise investigation of valence spectra of $CuRh_{1-x}Mg_xO_2$ thermoelectric materials.

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Molybdenum-based Thin Films: Depth-resolved Analysis of the Bonding States by Hard X-ray Photoelectron Spectroscopy

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ABSTRACT

Sodium (Na) is known to improve the efficiency of Cu(InGa)Se_2 solar cells (CIGS) [1-4]. An efficient and reproducible method for Na doping can be achieved by using MoNa sputtering targets [5], which are manufactured by PLANSEE by a powder-metallurgical process. A part of the molybdenum (Mo) back contact is replaced by a MoNa layer, which acts as a Na reservoir. During the further CIGS manufacturing process at high temperature Na diffuses into the absorber layer, thus improving the efficiency.

Up to now, no investigations of the Na and Mo bonding states in a MoNa layer have been published. Lab-scale X-ray Photoelectron Spectroscopy (XPS) is relatively surface sensitive, and sputter cleaning of the surface can modify the investigated area by ion-induced defects. A MoNa layer is more sensitive to humidity and air compared to a pure Mo film. Therefore, a non-destructive depth resolved analytical technique is required for an accurate understanding of the MoNa film chemistry.

In the present contribution we report on first results of hard x-ray photoelectron spectroscopy performed on MoNa thin films aimed at clarifying the bonding state of Na as well as the formation of oxides at the surface of Mo and MoNa layers. The experiments were carried out at the KMC-1 beamline [6] of BESSY II synchrotron in Berlin using the HIKE end-station [7]. The excitation energy was varied between 2, 4, and 6 keV to access an information depth of up to 20 nm. We find a similar chemical environment for Na at all depths which may be mainly dictated by the sodium compound used in the target production. Therefore we propose a Molybdate Na environment for our films. A Na enrichment at the surface of the films is also found.

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Depth- and Orbital- resolved Electronic Structure of the Buried $GdTiO_3/SrTiO_3$ Interface from Standing-wave ARPES

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ABSTRACT

Angle-resolved photoelectron spectroscopy (ARPES) is a technique widely used for the direct **k**-space mapping of valence-band electronic states. However, such measurements are often very surface sensitive, and probing buried layers and interfaces is difficult. To increase the depth resolution of such measurements, we have used higher-energy soft x-ray radiation at ~1300 eV, together with standing wave (SW) excitation created by Bragg reflection from a multilayer sample consisting of bilayers of $GdTiO_3$ and $SrTiO_3$. By varying the photon beam incidence angle, the maxima of the SW electric field intensity can be scanned through the different depths of the sample [1-3], thus providing for the first time depth-resolved ARPES.

We applied standing wave ARPES to a multi-layered heterostructure composed of the band insulator $SrTiO_3$ and the Mott-Hubbard insulator $GdTiO_3$ that also exhibits ferromagnetic order below 30K [4]. These strongly correlated materials have recently attracted attention due to the existence of emergent properties when they are put in proximity, such as 2D electron gas formation [5]. Therefore special attention was paid to the study of the electronic states near E_F at the $GdTiO_3/SrTiO_3$ interface. Linearly polarized light with two different E-vector orientations provided additional information on the origin of the particular orbitals contributing to the measured valence bands. The experimental results are compared both to the simple model of spatially resolved differential photoelectron cross-sections [5] and KKR single-step photoemission theory simulations [6].

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Depth-resolved Standing-wave Photoemission from a $BiFeO_3/La_{0.7}Sr_{0.3}MnO_3$ Superlattice using Soft and Hard X-ray Excitation

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ABSTRACT

$BiFeO_3$(BFO) is a multiferroic material that has attracted considerable attention due to the ability to electrostatically control its antiferromagnetic domains at room temperature[1], as well as its display of interface ferromagnetism when placed in proximity to $La_{0.7}Sr0_{.3}MnO_3$ (LSMO) or other ferromagnetic materials[2,3]. The combination of BFO and LSMO in superlattices thus holds promise for future applications to devices based on electric field control of magnetism.

To gain a fundamental understanding of the microscopic mechanisms that cause this emergent behavior, we have used standing-wave excited photoemission to obtain depth-resolved information on the electronic structure. We combine hard x-ray- and variable-polarization soft x-ray- excitation, which permits investigation at greater depths and more precise access to band dispersions, respectively. In addition to deep penetration by hard x-rays, this study includes data at incidence angles corresponding to total external reflection of the superlattice, providing a further enhancement of near-surface layers. Both core and valence levels were studied. At lower photon energies, variable linear polarization was used together with standing-wave rocking curves to selectively probe the atomic character of the valence band region at different depths in the superlattice, including ARPES measurements.

The results are discussed within the framework of a full x-ray optical theory[4,5], which is used to model the standing wave data so as to obtain layer-resolved structure, composition, and electronic energy levels. In addition, one-step first-principles SPR-KKR photoemission calculations[6] are used to model the ARPES data in order to gain insight into band identities and dispersions at the BFO/LSMO interface.

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Layer-resolved Densities of States and Valence-band Offsets in Oxide Superlattices from Soft and Hard X-ray Photoemission and Standing-wave Photoemission

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ABSTRACT

During the past decade, oxide heterostructures have attracted a great deal of attention, as they can exhibit functional properties that are dramatically different from those of the bulk constituents. For instance, although the bulk materials comprising a multilayer structure might be non-magnetic insulators, putting them in close proximity with variable layer thicknesses in the nm-range can show metallic, ferromagnetic, or even superconducting behavior [1,2,3] These effects are strongly influenced by buried-interface properties. Standing-wave x-ray photoemission (SW-XPS) of both core and valence levels is a powerful approach for studying such buried layers and interfaces [4]. We have used SW-XPS to study a multilayer of the form ($LaNiO_3$/$SrTiO_3$)x10. A detailed analysis of the valence band region reveals a non-uniform electronic structure inside the $LaNiO_3$ layer, with strong suppression of the Ni e_g and t_{2g} states near the interface between $LaNiO_3$ and $SrTiO_3$ layers [5].

XPS is often used to determine valence-band offsets (VBOs) at such interfaces, important properties for understanding electronic level alignment and charge carrier mobility [6]. Hard x-ray excitation (HXPS, HAXPES) [3] is beneficial for this, in reducing charging. We have used XPS and HXPS to determine the VBOs of ($LaNiO_3$/$SrTiO_3$)x10 and ($GdTiO_3$/$SrTiO_3$)x20 heterostructures, with results in good agreement with local density theory.

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Ab-initio Description of Satellites in Semiconductors

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ABSTRACT

Theory is an essential tool for a full understanding of experimental data. This is particularly true in photoemission spectroscopy of valence electrons, where quasiparticle peaks can be difficult to sort out due to e.g. surface effects and satellites. The GW method from Many-Body Perturbation Theory has been very successful in describing photoemission spectra in a variety of systems. In particular, GW is known to give good quasiparticle properties like band gaps, but it has shown some limitations in the description of complex correlation effects like satellites. Satellite peaks in photoemission come from higher-order excitations and are still poorly studied in the valence bands. In perturbative GW the spectral function can describe additional features beside the quasiparticle peaks, but these satellites are known to be too weak and too low in energy, as it appears from calculations on the Homogeneous Electron Gas and some real materials. We have recently shown that including additional diagrams in the Green's function [1] (similarly to what has been done with the cumulant expansion [2]) we obtain an excellent description of satellites series in the test case of bulk silicon, where GW is unable to cope [3]. We now focus on a more complex system, i.e. graphite, with this same approach. Using our newly measured XPS valence data, we investigate the effects of anisotropies on satellites and give a prediction on the spectral changes following the transition towards a single graphene layer.

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The Electronic Structure of the Fluorinated Self-assemble Monolayer by Photoemission and Absorption Spectroscopy

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ABSTRACT

The study of nanoimprint lithography (NIL) [1-2] has attracted much attention for many industrial field because it is a promising method to fabricate various nanostructures with a low cost and a high throughput. In the process of NIL, the mold is usually coated with an antisticking layer to avoid resist adhesion. As an antisticking layer of nanoimprint mold, the fluorinated self-assemble monolayer (F-SAM) is used, for example. The evaluation of the F-SAM with different chain length is one of the critical issues in NIL [3]. In addition, it is important to investigate the thermal stability of antisticking layers since the temperature of the antisticking layer coated on the mold increases around the glass transition temperature of thermopalstic resin in thermal NIL. In this study, four kinds of F-SAMs with different chain length were evaluated and the thermal effect was investigated as a function of temperature using the photoemission and the absorption spectroscopy.

In the photoemission spectra of the C 1s core-level, three peaks at ~293, ~286, and ~284.5 eV were observed in the FAS-3 although four peaks at ~293, ~291, ~286, and ~284.5 eV were observed in the FAS-9, 13, 17 at room temperature. Here, we denoted FAS-3, 9, 13, and 17 as F-SAM assembled by a precursor [$CF_3(CF_2)_n(CH_2)_2Si(OCH_3)_3$; n=0, 3, 5, and 7], respectively. The intensity of the peak at 291 eV increased with increasing the chain length. On the other hand, the intensity of the peaks at ~293, ~286 eV did not change with increasing the chain length. From the chemical compositions of four kinds of F-SAMs with different chain length, these peaks at ~293, ~291, ~286, and ~284.5 eV were assigned to the CF_3, CF_2, CH, and C-C components, respectively. With increasing the temperature up to 400 °C, the clear change of the chemical components was not observed in the photoemission spectra of the C 1s core-level although the relative intensity of the F 1s peak to the C 1s peak decreased slightly. With increasing the temperature at more than 500 °C, the relative intensity of the F 1s peak to the C 1s peak decreased markedly. These indicate that the F-SAMs degraded thermally at more than 500 °C although they were stable at less than 400 °C. In the presentation, based on these photoemission and absorption spectroscopy results, the effect of the different chain length and the thermal effect on the chemical composition and components are discussed using the curve fitting analysis.

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Full Potential Multiple Scattering Calculation for Photoelectron Diffraction with Self-consistent Potentials

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ABSTRACT

The multiple scattering approach is widely applied to X-ray photo electron spectroscopy. In most cases, non self-consistent potentials of the muffin-tin type are employed, which are generated from overlapping free atom charge densities. The muffin-tin approximation is appropriate for closed-packed, bulk systems, but can lead to large errors in anisotropic and open structures. Especially at low photo-electron energy (<100eV) the spectra are sensitive to small variations of the potential due to directional bonding, charge transfer etc, which requires the use of full-potential and self-consistent potentials. Here we show how highly accurate potentials, generated self-consistently using plane-wave Projector-Augmented-Wave codes, can be adapted to multiple scattering methods. Combining the Ms-Spec-1.0 [1] and FPMS [1,2] codes with potentials from VASP [3], we present applications to photodiffraction from solid surfaces, where the anisotropy of the potential plays an important role.

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An X-ray Fluorescence Holographic Study on a Single Crystal Thin Film of a Phase-change Material GeTe

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ABSTRACT

GeTe is one of the laser-induced crystalline-amorphous phase change materials. Although its phase change speed is much slower than e.g., $Ge_2Sb_2Te_5$ (GST) used as the raw material for the commercially available DVD-RAM disks, GeTe is considered to be a useful material for investigating the fundamental mechanism of the laser-induced phase change.

X-ray fluorescence holography (XFH) is a powerful method that provides three-dimensional (3D) atomic images around a specified element and has a large range of up to a few nm in real space [1]. We utilized this technique to investigate the local structure around the Ge atoms in GST single-crystal thin film [2]. The most important result from this experiment is that distorted rocksalt structure expected from the x-ray diffraction data and amorphous-like tetrahedral environment around the Ge atoms coexist in the GST single-crystal thin film, which may support the umbrella flip model for the phase change mechanism proposed by Kolobov et al. [3].

We have recently measured Ge K˚ XFH on GeTe single-crystal thin film at room temperature at the beamline BL6C of the PF-KEK. Details of the XFH experimental set up are given elsewhere [1]. The sample was manufactured onto a BaF_2 (111) substrate using a MBE apparatus. To compress the twin images intrinsic to the XFH, the measurements were made at seven different incident x-ray energies above the Ga K edge energy, and the data were superimposed by according with Barton's algorism [4].

The first neighboring Te atoms are clearly seen in the obtained 3D image. The Te images are, however, not a normal spherical shape, but ellipsoid with an angular direction. The second neighboring Ge atoms are hardly visible. It can be, thus, concluded that the distortions of the Te images do not originate from the spatial randomness of the Te atoms but that of the central Ge atoms. The fluctuation of positions of the Ge atoms has angular directions of the $Ge\text{-}Te_3$ pyramid, which may support the umbrella flip motion of the Ge atoms in the dynamical sense. In the presentation, we will discuss in detail the experimental result and reasonable model of the movement of the Ge atoms.

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Atomic Resolution Electron Holography with Internal Detector

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ABSTRACT

Atomic resolution holography, such as photoelectron holography and X-ray fluorescence holography, is a new type of the local structure analysis, because they provide 3D atomic arrangements around specific elements within a radius of a few nanometers.[1] Although they are very powerful for characterizing local lattice distortions[2] and fining nano-clusters[3], widespread applications have been limited due to the need of huge synchrotron radiation facilities. Thus, we propose the “internal-detector electron holography” to measure the atomic resolution holograms in laboratories. We successfully demonstrated this method using a scanning electron microscope (SEM) and a solid state detector.[4] The internal-detector electron holography is a time-reversed version of the photoelectron holography. While the normal photoelectron holography measures spatial distributions of photoelectron intensities, the internal-detector electron holography measures characteristic X-ray intensities as functions of the incident electron beam directions.

The measurement way of the internal-detector electron holography is simple. However, we must choose the incident electron energy carefully because the ratio of the signal and background drastically changes by the excitation energy. Using a Monte-Carlo simulation, we estimated adequate electron energies for various samples.[5]

To date, we have measured the holograms of $SrTiO_3$ single crystals[6] and Pt thin films (~10nm) by detecting Ti Kα lines and Pt L lines, respectively. In the both holograms of $SrTiO_3$ and Pt, we have found structures like Kikuchi-lines (We termed these the electron standing wave lines) created by electron diffractions and the forward focusing peaks. These features correspond to those of the conventional photoelectron holography. We reconstructed 3D atomic images from the measured holograms with SPEA-MEM (scattering pattern extraction algorithm using the maximum-entropy method)[7] based on the fitting algorithm. Both perovskite and fcc structures of the $SrTiO_3$ and Pt were successfully reconstructed with very high accuracy.

In conclusion, we can measure holograms at laboratories and can reconstruct 3D images accurately by the internal-detector electron holography. Combining the focusing ability, It has many advantages in the local structure analysis of the various samples such as minerals or device on LSIs.

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Electron Transport Through Single C_{60} Molecule Probed by Superconducting Electrodes

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ABSTRACT

Conductance (*G*) of a single molecular junction, which consists of one molecule and connecting metal electrodes, is generally given by the Landauer formula[1]

$$G = G_0 \sum_{i=1}^{n} \tau_i$$

using the conductance quantum ($G_0 = 2e^2/h$) and transmission coefficient of the *i*-th channel (τ_i). Determination of both the number of channels (*n*) and the transmission coefficient of each channel (τ_i) is prerequisite for the comprehension of the electron transport through the single molecule. I-V measurements with normal conducting electrodes give only the total conductance (*G*) and cannot determine *n* and τ respectively.

Applying superconducting electrodes is one of the solutions to determine *n* and τ. When we construct a nano-junction of superconducting metals, the so-called subharmonic gap structure (SGS) appears in I-V spectra[2,3] due to the multiple Andreev reflections[4] (MAR). Since the current caused by MAR has non-linear dependence on τ, the SGS has characteristic dependence on both *n* and τ, which enables us to determine *n* and τ individually by the analysis of I-V spectra.

We measured the conductance of a C_{60} molecule by scanning tunneling microscope (STM). The C_{60} molecular junction was constructed by contacting the STM tip to the molecule with great controllability. Nb tip and Pb(111) substrate were prepared as superconducting electrodes. The SGS was clearly observed in the I-V spectra taken at 400 mK. From the analysis of the spectra, we evaluated that 3 main conduction channels resided in the C_{60} molecular junction. This result suggests that triplet degenerated LUMO states of the C_{60} molecule are attributable to the main conduction channels. Furthermore, we found that the value of (τ_1, τ_2, τ_3) depended on the molecular orientation.

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Atomic-orbital Analysis of ZrB_2 Valence Band by Linearly-polarized-synchrotron Radiation Two-dimensional Photoelectron Spectroscopy

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ABSTRACT

ZrB_2 is an attractive material for wide applications. It has a high melting point, a high electric conductivity, and a high corrosion resistance. ZrB_2(0001) surface is a promising substrate for the GaN(0001) epitaxial thin film growth too. Additionally, ZrB_2 easily forms a strong oxide film [1]. In our previous study, we focused on this strong oxide film on ZrB_2(0001) and clarified the interface structure at the ZrB_2(0001) substrate and the oxide film by using the method of element-specific two-dimensional photoelectron diffraction at BL25SU of SPring-8 and Refrection High-Energy Electron Diffraction (RHEED). In this study, we focused on the ZrB_2(0001) electronic structure and succeeded in the measurement and atomic-orbital characterization of three-dimensional valence band.

The experiment was done at BL-7 of SR center, Ritsumeikan University [2] using a display-type spherical mirror analyzer (DIANA) [3]. Figure 1 shows a photoelectron angular distribution (PEAD) pattern at the binding energy of 3.1 eV excited by a horizontally linearly polarized synchrotron radiation of 40 eV. A hexagon in Fig. 1 indicates the first Brillouin zone of ZrB_2. We can see the extinction rule in this 2D-PEAD pattern obtained by only our method in the world; 2D-PES with DIANA and synchrotron radiation. This anisotropy in the PEAD also shown by arrows in Figure 2 means that this band consist of p_y or d_{xy} orbitals. In this way the atomic orbitals composing each band can be deduced [5].

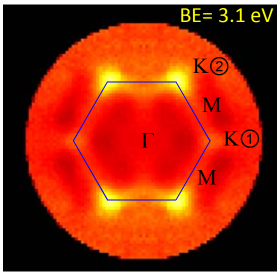

Fig.1 PEAD pattern from ZrB_2 valence band.

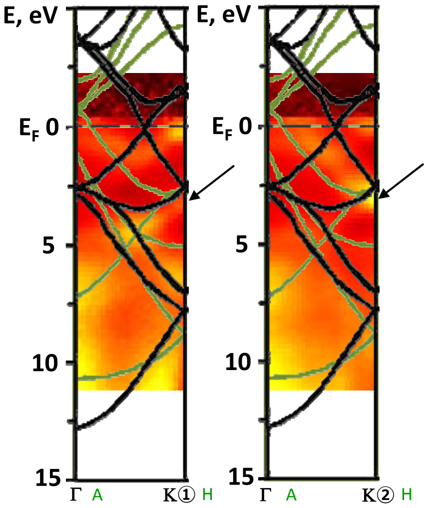

Fig.2 ZrB_2 band structure by the self-consistent full-potential LMTO method [4] and PEAD data of the (a) Γ–K① and (b) Γ–K② direction with the range of binding energy ; from -2.1 to 10.9 eV.

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Polarization Dependent High-resolution ARPES Study of Pb(110) : Fermi Surface and Band Dispersion

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ABSTRACT

Lead (Pb) is a heavy element and a typical strong-coupling superconductor [1-3]. Recent theoretical calculations showed the spin-orbit coupling strongly affects the strength of the electron-phonon coupling in bulk Pb [3]. In addition, surface-derived states under the strong spin-orbit interaction may have unusual spin structures due to the Rashba effect [4]. So far, angle-resolved photoemission spectroscopy (ARPES) has revealed the kink structure due to the electron-phonon interaction in the energy-band dispersion in Pb(110) single crystal [5] and the Fermi surfaces (FSs) of Pb thin films on Si [6]. However, the bulk and surface derived FSs of bulk Pb single crystal were not fully clarified experimentally yet. Therefore, we performed polarization-dependent ARPES measurements on Pb(110) single crystal.

The ARPES measurements on Pb(110) were performed at the linear undulator beamline (BL-1) of Hiroshima Synchrotron Radiation Center (HiSOR). The sample was cleaned by repeated cycles of Ar^+ sputtering (1.5 ~ 4.5 kV) and subsequent annealing at 450 K. A clean Pb(110) surface was confirmed by the Auger electron spectroscopy and low-energy electron diffraction. The present data were mainly measured at 8 K using 43 eV with the energy resolution of 20 meV, except for the photon-energy dependent measurements using 22-64 eV.

By the FS mapping with the *p*- and *s*-polarization geometries, we found that the observed bulk-derived FSs around the Γ, U, and K points agree well with those given by the theoretical calculation [1]. On the other hand, we observed an additional FS around the X point, which is not predicted by the calculation [1]. Because the observed additional structures showed negligible k_z-dependence, it is regarded as the surface derived states. In this presentation, we will discuss the surface derived states around the K point, and the coupling parameter of the electron-phonon interaction for the bulk and surface derived states.

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Effects of Orientational Ordering on Interface Electronic Structures: A Study at Sub-molecular Scale

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ABSTRACT

Enormous efforts have been devoted to expose the impacts of the supramolecular packing structures on the interfacial electronic structures formed at the organic/inorganic and organic/organic heterojunctions. In particullar, the dependence of the ionization energy (IE) and electron affinity (EA) on the molecular orientations relative to the substrates have been widely studied, where the electric dipole formed by the polar end-groud substitution is revealed to be one of the key factors [1-3]. However, a well understanding and modeling of the influence of the packing structure of the organic thin films on the ELA at the interface is still under debating, specially at sub-molecular scale.

In our study, the orientational ordering of the chloroaluminum phthalocyanine (ClAlPc) on Au(111) surface is investigated by scanning tunneling microscopy (STM) with sub-molecular precision. The adoption of the molecular dipole orientations, up or down referring to the substrate, is found to be flexible with the over-all coverage as well as annealing process. The interface electronic properties showing dipole orientation dependence are obtained through high-resolution ultraviolet photoemission spectroscopy (UPS). The vacuum level (VL) decreases continuously as the increase of the film thickness. The doublet HOMO (highest occupied molecular orbital) peaks observed at the as-grown sub-monolayer film are attributed to the coexistence of the up and down orientations. Such orientation-dependent HOMO binding energy at the same environment is very critical for further exploration on how the electric dipole affect the EAL at sub-molecular scale.

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Electronic Structure of Noncharged Unsupported Clusters

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ABSTRACT

The valence and core electron structure of alkali-metal atoms has been investigated in the size range of tens to few hundreds of atoms per cluster. Synchrotron radiation has been used offering a tunable source for photoionization. The cluster-size dependent effects have been monitored offering a tool to study the evolution from the atomic characteristic structures to the solid like features of larger nanostructures. In this - so called quantum-size regime - the electronic structure experiences its most drastic changes.

The alkali-metals are simplest and most evident representatives of metals in general. In order to study the electronic structure of small uncharged metal clusters we have probed the binding energies of valence and core shell orbitals of potassium and rubidium for several size ranges of clusters [1]. The clusters have been produced by the recently developed EXchange MEtal Cluster (EXMEC)-source [2], method essentially based on the pick-up technique. In the EXMEC source a beam of rare-gas clusters is formed by an adiabatic expansion source. This beam is then shot through an oven where the interaction between the metal atoms and cold rare-gas clusters leads to the formation of plain metal clusters.

The observations on the development and variations of the valence band electron spectra have been explained based on a Jellium type of theoretical modelling [3]. The modelling was further used to predict the valence band response as a function of the impact photon energy – effect verified by our further experiments on synchrotron-radiation-excited electron spectra [4]. Presently the research has been extended to the heavier elements such as Au, Pb, Si, Sb, Bi.

In the present contribution an overview of the metal clusters research will be given also providing introduction to the recent progresses in the work on semimetals as possible topological insulator materials.

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Yb Electronic Structure Investigated by Low Energy Photoemission Spectroscopy

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ABSTRACT

The peculiar electronic structure of rare-earth elements and compounds is mostly defined by the partially filled 4*f* band. Of particular interest is the investigation of the valence states, which is linked to the degree of hybridization of *f* electrons with delocalized *s*-*p* bands. In the simple case of atomic Yb, the 4*f* states are fully occupied and in the solid it has been established a Fermi level of 6*s* character and a 2+ valency. However, the occupation of the Yb valence band has been the subject of several investigations over the years, intended in particular to separate the contribution of *d* and *p* states. In order to address this issue we have investigated the Yb electronic structure by using low energy photoemission spectroscopy (LEPES) between 5.5 and 21 eV photon energy, with experiments at the BaDElPh beamline of the Elettra synchrotron radiation facility [1]. For photon energies lower than 11 eV, a prominent peak at the Fermi level is observed. The analysis of its intensity variation versus photon energy and the comparison of the experimental spectra with *ab initio* density of states (DOS) calculations allow to attribute this structure to a *p* band crossing the Fermi level, enhanced at selected photon energies due to the influence of the empty DOS. In this respect LEPES may thus be considered as a probe of the joint DOS [2]. Since in this photon energy regime we observed a moderate increase of the electron attenuation length and, thus, a moderate increase of the information depth when we reach the lowest energies [3] such effect is ascribed as being proper of the bulk electronic structure.

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Electron Mean Free Path of Low Energy Electrons in Metal-oxide Thin Films

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ABSTRACT

The information depth of photoemission spectroscopy (PES) in the most commonly used energy range (from few tens of eV to about 1.5 keV) is limited to few topmost atomic layers [1]. This poses an obvious limitation for the investigation of systems whose electronic structure at surface differs from the bulk one, such as strongly correlated materials, buried interfaces, and capped samples. Among these systems, insulators like many metal oxides are of considerable technological importance, e.g., as insulating barriers in miniaturized electronic circuits, as magnetic tunnel junctions in magnetoelectronics and magnetic data storage, or for the development of a variety of nanodevices based on oxide heterostructures.

Interest for increasing the PES bulk sensitivity has pushed for its applications outside the ordinarily used photon energy range, to take advantage of the expected decrease of the electron scattering probability at low (less than 10eV) and high (several KeV) electron energy. In particular, low energy experiments are experiencing a revival since this latter approach enables an unprecedented energy resolution, thus allowing measurements of the fine electronic structure near the Fermi level that are responsible of the exotic properties of materials [2]. Determination of the bulk sensitivity of such low-energy-PES (LEPES) is however still an open issue, because scattering properties of electrons that determine the mean free path in this energy range are not well known.

In our recent experiments at the BaDElPh beam line of the Elettra storage ring [3], we measured the electron attenuation length (EAL) in thin films of metals and insulators as a function of the photon energy, finding only a moderate increase at low energies, in contrast to the predictive formula commonly used to determine the information depth in PES experiments [4]. The moderate enhancement of the EAL (up to few nm) with respect to PES tuned in conventional energy regime shows in particular that the subsurface sensitivity is relatively more pronounced in the case of MgO, a large energy gap insulator, with respect to CoO, a small gap insulator, for photoelectrons with kinetic energy lower than the gap width. Our results, while giving a warning in the use of LEPES as a bulk-sensitive spectroscopy, also suggest an experimental dependence of the mean free path of slow electrons on the band structure of the material; the full interpretation of this class of experiments claims for a theoretical corroboration that is currently in progress.

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Study of Quantum Well States in Bi Thin Film by Two-photon Photoemission Spectroscopy

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ABSTRACT

The physical properties of quantum well states in Bismuth (Bi) attract much interest since they exhibit unique transport and electronic properties. The quantum well states of Bi thin film in the occupied region have been extensively investigated with photoemission spectroscopy. In contrast to an understanding of the occupied quantum-well-states, the reports of electronic structures in the unoccupied region are very few to date. In addition, to elucidate the quantum confinement phenomena on thin film, it is inevitable to understand the electronic structures of parental bulk bands. In this work, the angle-resolved two-photon photoemission (2PPE) measurements of Bi thin film and bulk Bi have been performed to elucidate the unoccupied electronic dispersion above the Fermi-energy.

The experiments were conducted at Saga University beam line BL13 in Saga Light Source.[1] The electronic dispersions of Bi thin film in the occupied state was characterized by the angle-resolved photoemission spectroscopy with the synchrotron radiation. For the 2PPE measurements, second harmonic generation of the tunable Ti:Sapphire laser with the photon energy of 2.8 – 3.3 eV were used as the excitation source. The detection angles for the 2PPE measurements were along the $\bar{\Gamma} - \bar{M}$ symmetry line in the surface Brillouin zone. The angle-resolved 2PPE spectra contain the information from the occupied electronic structures as well as those from the unoccupied electronic structures, since the detected photoelectrons are emitted with two-photon excitation through the unoccupied electronic structures. The contributions from the occupied and unoccupied electronic states were discriminated with the excitation energy dependence of the angle-resolved 2PPE spectra. By analyzing the details of the excitation energy dependence and in-plane dispersions for d2PPE spectra for bulk Bi, the occupied and unoccupied electronic dispersions were specified. The occupied electronic dispersions of Bi thin film and bulk Bi those obtained from 2PPE measurements were consistent with those obtained from the synchrotron photoemission measurements. The unoccupied energy dispersions were assigned as the electronic dispersions derived from the direct transitions thorough the unoccupied 6p-derived bulk-bands. From angle-resolved 2PPE spectra of Bi thin film and their excitation energy dependence, several unoccupied electronic structures were specified.[2] The comparison of the unoccupied electronic dispersions for bulk Bi and Bi thin-film reveals that the obtained electronic dispersions Bi thin film were derived from the quantizations of the unoccupied *6p*-derived bulk-bands.

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The Effects of P Segregation on the Surface Electronic Structure of Ni_2P Surface

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ABSTRACT

Ni_2P is promising material as catalyst for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) more active than currently used sulfide-based catalysts[1]. It has become important to elucidate the surface electronic structure of single crystal Ni_2P to reveal the origin of its high catalytic performance. In particular, the surface P atoms have been predicted to play important roles in HDS and HDN, and it has become important to elucidate the segregation behavior of P atoms and its effect on the surface structures.

Fig 1 shows the P/Ni intensity ratio of AES peaks for the Ar+ ion sputtered Ni_2P(10-10) surface as a function of annealing temperature. This result indicates that the segregation of P proceeded at 200-300°C. The surface after annealed at ≤ 100°C gave a (1x1) LEED pattern, while the pattern changed to c(2x4) after annealing at ≥ 200°C. These results suggest that the formation of c(2x4) structure is accompanied by the segregation of P atoms, which is consistent with the model proposed by STM investigation[2]. Valence band spectra of Ni_2P(10-10) measured after annealing at various temperatures are shown in Fig 2. As the surface was annealed at 200-300°C, the intensity of the Ni3d-P3p derived band at 0-2 eV is decreased with elevating annealing temperature. This is due to the fact that the 3d levels of the surface Ni atoms are stabilized through the bonding with the segregated P atoms. Therefore, the spectral change shown in Fig 2 can be viewed as a direct evidence for "ligand effect" of P atoms[3].

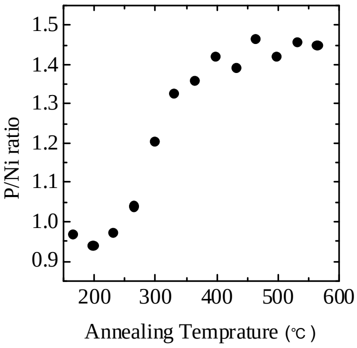

Fig 1. P/Ni intensity ratio of AES as a function of annealing temperature.

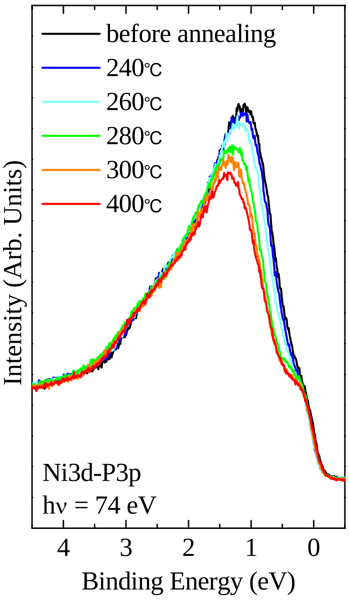

Fig 2. Valence band spectra of Ni_2P(10-10) measured after anneal ing at various temperatures.

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Structure and Electronic States of Defects on Ar$^+$-ion Irradiated MoS$_2$

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ABSTRACT

MoS$_2$ has anomalous electronic states because it consists of two-dimensional layers. Since Radisavljevic *et al*.[1] have demonstrated suitable properties of a single-layer MoS$_2$-based transistor, room-temperature electron mobility and a high on/off ratio, (close to these of graphene nanoribbons), are of great interests. Aimed to the application for electronic devices, study on the surfaces is very important in terms of structure and electronic state at the atomic scale.

We observed defect surfaces of MoS$_2$ after Ar$^+$-ion bombardment at the density of 2.75 x 10^{-3} ions/cm^2 by scanning tunneling microscopy (STM) and measured local electronic state by scanning tunneling spectroscopy (STS). We compared these experimental results with electronic states obtained from density functional calculation using a program STATE-senri.

We see a concave in an STM image near a defect on the surface. Fig. 1 shows STS spectra of the edge and center on a concave defect of MoS$_2$. On the edge site, STS peak appeared at -0.5 V (note that MoS$_2$ is n-type semiconductor). Fig. 2 shows calculated densities of state (DOS) of a single sulfur defect and a clean surface of MoS$_2$. In the defected surface, a defect level appeared in the band gap. We will present a discussion on the defect states on the Ar$^+$-ion irradiated MoS$_2$.

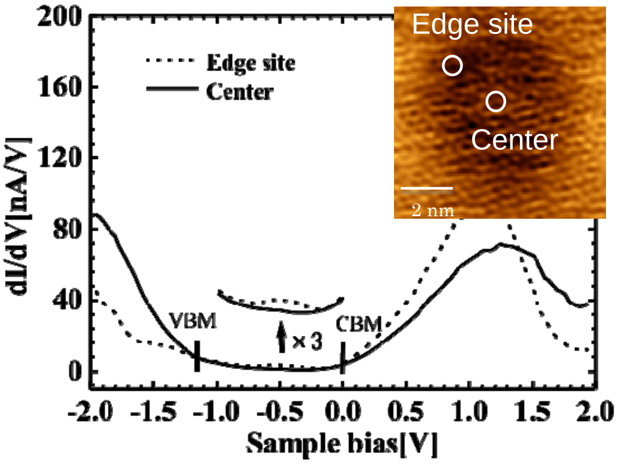

Fig. 1. STS spectra of edge site and center of a concave defect. Inset is an STM image of the concave near a defect on MoS$_2$.

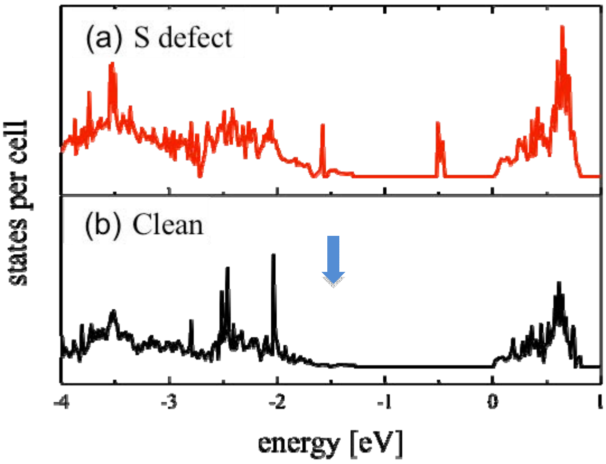

Fig. 2. (a) DOS of a single sulfur defect of MoS$_2$. (b) DOS of clean surface of MoS$_2$. Energy refers to the conduction band minimum (CBM).

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Two Distinct Types of Band Renormalization: High-energy Anomaly vs. Band Narrowing

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ABSTRACT

Understanding of electron correlation is at the heart of the modern condensed-matter physics. In general, electron correlation is responsible for the band renormalization, or “band narrowing” (BN) over a large energy-scale (eV order) [1]. Another well-known band renormalization is originated from the electron-boson interaction at a low energy-scale near the Fermi level (sub-eV order), which results in a “kink” in the energy-band dispersion [1]. Recently, a “high-energy anomaly" (HEA) in the band dispersion has been widely observed in angle-resolved photoemission spectroscopy (ARPES) spectra in high-T_c cuprate superconductors, and triggered a large number of experimental [2] and theoretical studies [3]. This anomaly involves two characteristic features in energy range of ~300-600 meV: a giant kink (“high-energy kink”) and a nearly vertical dispersion (“waterfall”). Despite intense experimental and theoretical efforts [2,3], the nature of the HEA has not been clarified yet.

In this talk, we report two distinct types of the band renormalization, *i.e.*, “HEA-type” and “BN-type” renormalizations, in ruthenate unconventional superconductor Sr_2RuO_4 using high-resolution ARPES with tunable energy/polarization of incident photons. The HEA-type renormalization was observed in the d_{xy} band with the bandwidth of ~ 3 eV, while the BN-type one was observed in the d_{zx} band with the bandwidth of ~ 0.4 eV. These different types of band renormalization can be reasonably explained by using a simple and analytical form of the self-energy within the framework of the Fermi liquid theory [4]. We will also discuss how generic the HEA-type renormalization may be to other systems.

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High Resolution ARPES Study of Many-body Interaction in Cu(110) Surface State

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ABSTRACT

High-resolution angle-resolved photoemission spectroscopy (ARPES) experiments of strongly correlated electron systems have revealed a “kink” structure in the energy-band dispersion, or a sudden reduction of the group velocity, near E_F [1]. In general, the kink structure is derived from the coupling between electrons and bosonic (or elementary) excitations such as phonons or magnons. By clarifying the origin of the kink structure, one may obtain an important clue to understand many-body interactions.

Here we show a detailed study on the kink structure of a typical two-dimensional free-electron-like system, the Shockley state in Cu(110). There have been many high-resolution ARPES studies on photohole lifetime of Cu(111) Shockley state [2,3]. And electron-phonon coupling parameter (l_{ep}) is estimated to be $\lambda_{ep} = 0.16$ for Cu(111) Shockley state [3]. According to the recent theoretical calculation, electron-phonon coupling in Cu(110) Shockley state should be larger than that in Cu(111). However, there is no report on experimental determination of λ_{ep} in Cu(110) Shockley state by kink structure due to electron-phonon interaction near E_F. In order to examine the self-energy and evaluate many-body coupling parameters, we have done high-resolution ARPES with higher momentum resolution using lower photon energy.

The experiments were performed at Hiroshima Synchrotron Radiation Center (HiSOR) BL-1 and BL-9A using high-resolution ARPES spectrometer (R4000, VG-Scienta). Photon energy was set at 31 eV and 8.5 eV. The total energy resolution were estimated to be 10 meV and 5.5 meV at 10 K, respectively. The angular resolutions were θ ~0.6° and 0.2° for the angular acceptance of 30° and 15°, respectively. The sample temperature was set to 10 K. A weak kink structure due to electron-phonon interaction can be observed around 30 meV below E_F. By assuming a parabolic non-interacting band, we can determine real part of self-energy (ReΣ) and $\lambda_{ep} = (\partial \mathrm{Re}\Sigma / \partial\omega)|_{\omega=0}$. By measuring linewidth broadening, imaginary part of self-energy (ImΣ) can be obtained as well. Real and imaginary parts of self-energy agree with Kramers-Kronig transformation.

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A NEXAFS Study of ALD Precursor Effect on Stoichiometry in Ferric Oxide Films

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ABSTRACT

Iron oxide has been combined with other materials, in particular with MgO, in order to modify the properties of the material and, potentially, create magnetic device prototypes. Fe_3O_4 has been described as a ferrite with lattice constant approximately twice as large as that of MgO [1], referring to the possibility to realize substrate-oriented growth and structurally matching interfaces. Fe_3O_4-based spin valve stacks have been fabricated with MgO tunnel dielectrics [2]. In addition, MgO has been used as a base material for nanopatterned surfaces [3], possibly aiming at the further development of patterned magnetic media. It is worth noting, that the useful effects of magnesium (oxide) are not limited to magnetic properties. For instance, Mg-doped Fe_2O_3 can be used in solar energetics [4]. Ternary phase $MgFe_2O_4$, i.e. magnesioferrite, could be applied as humidity sensor [5]. It appears to be quite interesting to study the effect of MgO on the growth of iron oxide phases. Iron oxide films or nanostructures can be fabricated using different methods including atomic layer deposition (ALD).

We report here a O 1s and Fe 2p NEXAFS study of iron oxide and magnesium-doped iron oxide films grown by ALD in the temperature range of 350-500 ^{o}C from ferrocene, (dimethylaminomethyl)ferrocene, magnesium β-diketonate, and ozone. As described by other methods (viz. optical Raman spectroscopy, SEM, XRD), the phase composition depended on the deposition temperature, as magnetite and/or maghemite tended to form instead of hematite upon lowering the temperature. Iron oxide layers were also doped with magnesium oxide by alternate deposition of MgO and Fe_2O_3 layers which also favoured the formation of magnetite or maghemite structure prior to hematite. NEXAFS specroscopy is applied primarily to obtain information of close range order and sample chemistry on a patch of these ALD films of varied growth parameters and dopant content. The NEXAFS experiments were done at beamline I511-3 at the MAX-Lab synchrotron light source in Lund, Sweden.

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Polarisation Sensitive RIXS of Borate NLO Crystals

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ABSTRACT

Search for wide band gap, deep UV grade non-linear optical (NLO) crystals has intensified in recent years significantly [1]. With proper choice of cation, up to 9 eV band gap is estimated to be achievable with borate NLO materials [2] with (partly filled) lone pair orbitals and nonbonding states eliminated (i.e., the electrons bound to filled bonds) at band gap edge. The borates are (quasi-)molecular ionic crystals consisting of planar trigonal BO_3 primary building blocks, which are assembled into $B_3O_6^{3-}$ quasimolecular planar anions in β-BBO crystals, introduced as NLO material back in 1985 by Chen *et al.* [3]. The BBO crystals have large optical nonlinear susceptibilities and anisotropy, but the dangling bonds at the $B_3O_6^{3-}$ out-of-ring oxygens cause the smaller 6.2 eV band gap. In LBO [4], a tetrahedral sp-hybridised BO_4 block is corporated into the anion ring, the nonbonding orbitals are less influential and the band gap widens to nearly 8 eV, but anisotropy and second order optical susceptibilities decrease.

We probe the electronic structure of these prototypical borate NLO materials with B 1s and O 1s polarisation dependent X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) spectroscopy, which give chemical element, atomic site (when excitation resonances relate to different sites) and symmetry specific information of the valence region, and we compare it also to native boron oxide, with the purpose to provide additional detail in describing the electronic structure anisotropy and to test the feasibility to provide information of the presence and occupancy of nonbonding states at band gap edge. The experiments were done at beamline I511-3 at the MAX-Lab synchrotron light source in Lund, Sweden.

We find LBO, as compared to BBO, to relate rather closely to boron oxide with small, but distinct differences in both the X-ray absorption spectra (XAS) with the single B_2O_3 O1s threshold peak split 1.4 eV in LBO) and in X-ray emission excited near XAS resonances, where both boron oxide [5] and LBO, different from BBO, have little resonant behaviour in the oxygen spectra, and an almost rigid shift of the upper valence B 1s emission about an eV above the exciton resonance excitation, and a Raman behaviour of the lower valence emission up to the same excitation energy. The latter is in contrast with observation for BBO, where lower (O 2s - B 2p hybridised) valence B 1s emission is almost stationary on emission energy scale, the upper valence shows Raman dispersion alongside with excitation and orientation dependent spectral changes of the upper valence B 1s and O 1s RIXS.

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Technology for Producing Layered Nanostructures of Noble Metals on the Surface of Single Crystal Si

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ABSTRACT

Using high-vacuum high-resolution scanning tunneling microscopy (STM) investigated the process of formation of metal nanostructures Au, Ag, Cu on the surface of single crystal Si(111). Metal thermally evaporated on the surface of silicon. Surface morphology study was carried out using tunneling microscope JSPM-4610 (Japan). Operating vacuum during the experiment was not lower than 10^{-8} Pa.

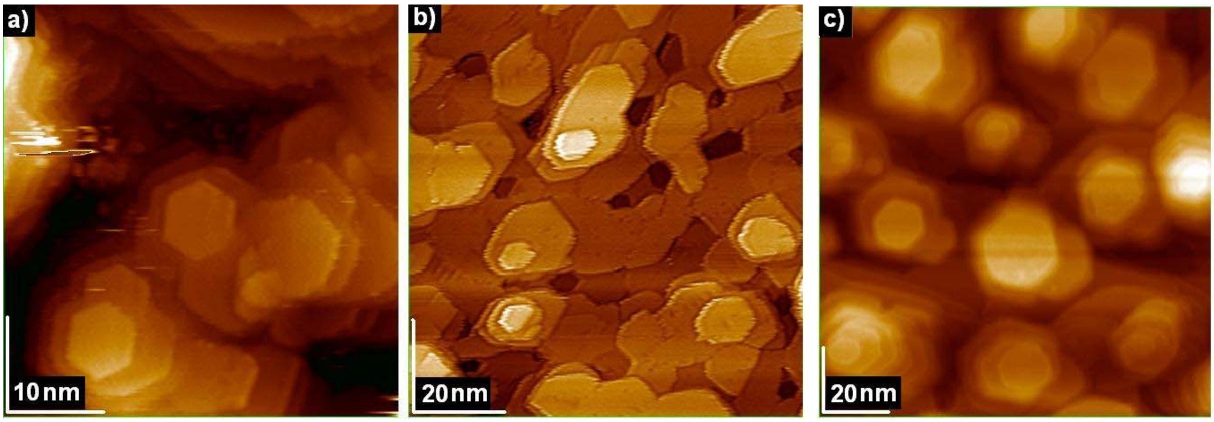

Fig.1. STM image of layered metal nanostructures on the surface of single crystal Si (111): a) Au; b) Ag; c) Cu.

Found that gold, copper and silver on the silicon surface can create layered nanostructures with precise and geometrically correct boundaries. Most nanostructures are of the form of hexagonal pyramids with a flat top. Layered structures create steps. Step height corresponds to the height of one atomic layer. The ordering of hexagonal structures at short distances can be explained by the influence of the matrix substrate. Observed hexagons of different sizes (for both single and for different metals) Fig(1). At the same time, regular hexagons with a long side ~ 5 nm are observed for all studies of metals. For the formation of these nanostructures plays an important role local homogeneity of the flow of matter that is deposited on the surface of the crystal.

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Scanning Tunneling Microscopy of Cu, Ag and Au Nanoformations on Si(111) and Si (110) Surfaces

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ABSTRACT

Using high-vacuum high-resolution scanning tunneling microscopy we have investigated the processes of hexagonal-pyramidal Cu, Ag and Au structures formation after thermal sputtering of metals onto monocrystalline Si (1 1 1) and Si (1 1 0) surfaces. It was found that under homogeneity of melt of deposited metals and vacuum not lower than 10^{-8} Pa there are formed self-ordered hexagonal-pyramidal nanostrucutres consisting of monoatomic layer planes each shifted by a distance of about 3 nm relatively to the growth start of the previous plane (Fig. 1). The mechanism of formation of hexagonal-pyramidal Cu, Ag and Au nanostructures is determined with a character of electron density behaviour at the edge of each monoatomic layer. Extreme atoms of planes have higher energy state and thereby growth of each next monoatomic plane starts not from the edge but at the distance of about 3 nm from it what is caused with relaxation of inhomogeneity of electron density of states at this distance and determines pyramidal shape of formations. In the case of Si(110) plane there are observed only single-layered hexagonal formations.

By other metals deposition modes there was observed formation of conglomerates of nanoparticles with subsequent transformation of them into ellipsoidal particles and further nanocrystal formation.

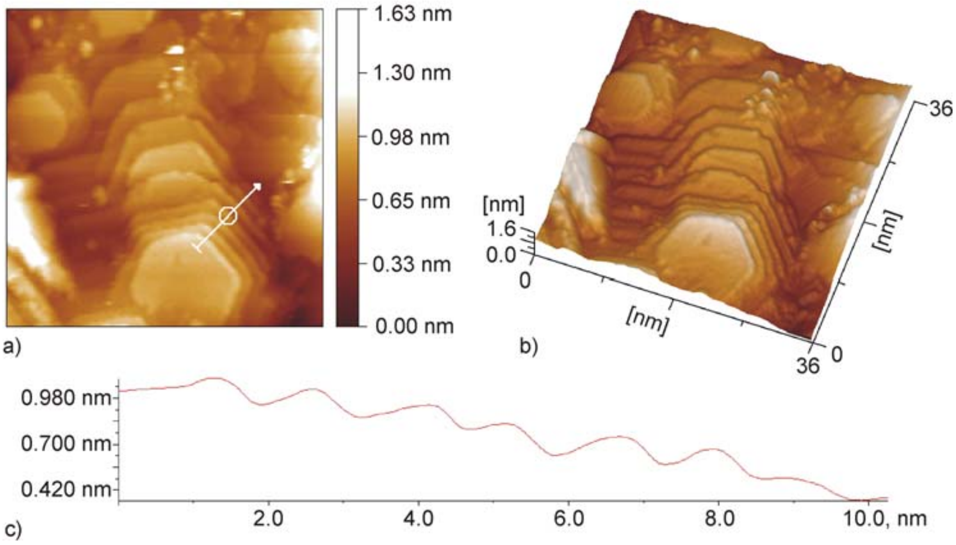

Fig. 1. Nanorelef gold surface on Si (111): a) STM image of the pyramidal formation, b) spatial visualization; c) the profile of the lateral face of the pyramid.

Resonant X-ray Emission Spectroscopy of $SrTiO_3$ under Ultraviolet Laser Irradiation

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ABSTRACT

$SrTiO_3$ (STO) shows several intriguing properties such as ultraviolet (UV) induced ferroelectricity at low temperature [1,2], superconductivity [3] and two-dimensional electron gas [4,5]. Recently a visible luminescence phenomenon is found under ultraviolet (UV) laser irradiation [6]. A phenomenological consideration requires the presence of in-gap states, however, no direct evidence is yet available.

Ti *L*-edge soft x-ray emission spectra of a single crystal STO were measured under UV laser irradiation in order to get direct information of the in-gap states. Regardless of the d^0-ness of Ti^{4+} ions, a weak inelastic peak due to *dd*-excitation (*dd* peak) was observed at low temperature with Ti $2p_{3/2}$-e_g resonance (Fig. 1), which indicates the mixing of UV induced d^1 configuration. At room temperature, however, no trace of the *dd* peak was observed. This *dd* peak observed in an undoped STO under UV irradiation is essentially different from it observed in an electron-doped STO, since no temperature dependence was observed in the latter. In addition, the intensity of the UV-induced *dd* peak grows with a time constant of the order of several tens of minutes. Once the *dd* peak is induced, it retains the intensity even after UV turns off. With the aid of the angle-resolved photoemission and low energy electron-diffraction data, we concluded that this irreversible phenomenon should be caused by the surface reconstruction driven by UV laser irradiation.

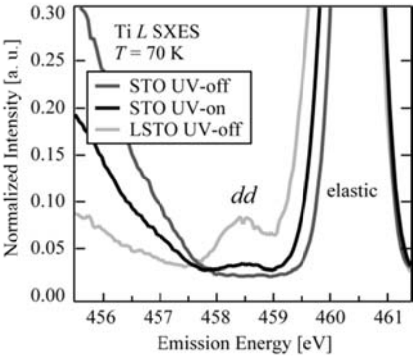

Fig. 1 :The difference of the *dd* peak by UV laser irradiation.

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Plasmon Losses in Core-level Photoemission Studied by Quantum Landau Formula Including Full Multiple Scattering

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ABSTRACT

Plasmon satellites appear in the binding energy region higher than the main peak in XPS spectra for some elements, notably in Na, Al, Mg, and Si. The excitation mechanism of plasmons has been studied since the early days of the photoemission study.

Quantum Landau formula describes overall features in core-level photoemission spectra including plasmon satellite peaks and asymmetry of main peaks due to x-ray singularity [1]. This formula is a powerful tool to study the plasmon losses including higher order satellites. The elastic scatterings before and after the loss are fully taken into account there.

So far elastic scatterings have been neglected in studies of plasmon satellite peaks. Recently we have calculated single bulk and surface plasmon loss features associated with photoemission from Al 2*s* level including single elastic scattering [2]. The single scatterings emphasize the photoemission from deep atomic sites because of *focusing effects*. It has been suggested, however, on the basis of multiple-scattering calculations that if several atoms are linearly arranged along the emission direction, the destructive interference actually reduces the intensity (*defocusing effect*) [3, 4]. It is crucial to take full multiple scatterings into account to calculate plasmon satellite peaks properly.

In this work we calculate plasmon loss features associated with Al 2*s* and Na 2*s* photoemission including full multiple scatterings, which affect the spectral features. The relative importance of the intrinsic and the extrinsic processes, and their interference will be discussed.

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Resonant Soft X-ray Emission at the Oxygen K-edge in Rutile SnO_2

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ABSTRACT

SnO_2 is a wide bandgap transition metal oxide which adopts the tetragonal rutile crystal structure the prototype of which is rutile TiO_2. The electronic structure of an undoped single crystal of SnO_2 is probed using a combination of oxygen *K*-edge x-ray absorption (XAS) and resonant x-ray emission (RXES or RIXS). The polarisation dependence of the O *K*-edge XAS is dominated by the observed natural linear dichroism and likewise the O *K*-edge XES, by this dichroism and the relative orientation of the single crystal and the XES spectrometer. The polarisation dependence, the symmetry selectivity, state selectivity and the *k*-selectivity inherent in RXES (RIXS) can be exploited to obtain a detailed measure of the occupied oxygen partial density of states (PDOS) of SnO_2.

The rutile crystal structure adopted by SnO_2 or TiO_2 gives rise in general to a highly oriented bonding arrangement between the metal *d* and ligand sp^2 orbitals. This is due to each ligand anion coordinated by 3 metal cations forming M_3O trigonal planes. The resulting M-O σ-like bonds are oriented within the M_3O plane with the M-O π-like bonds perpendicular to the plane with all M_3O planes parallel to the rutile *c*-axis. Thus arises a natural linear dichroism, most evident when probing the oxygen environment as in O *K*-edge XAS and XES. O *K* XAS obtained parallel to the *c*-axis compared to XAS obtained perpendicular to the *c*-axis thus probes the O *2p* unoccupied PDOS projections along the rutile crystal *c* and *a* axes, involving the σ*-like and both σ* and π* like M-O bonds respectively,

Electronic structure calculations using density functional theory, specifically the full potential linearized augmented plane wave (FP-LAPW) code as implemented in WIEN2k[1], were used to calculate the SnO_2 electronic structure and to simulate the energy dependent *k*-selective O *K*-edge RXES. The successful comparison of these simulations with the O *K*-edge RXES allows for a further insight into the occupied electronic structure of SnO_2.

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Magnetic Moments and Antiferromagnetic Order in Stable-divalent $EuRh_2Si_2$

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ABSTRACT

$EuRh_2Si_2$ shows a sharp metamagnetic transition at low fields which is highly unexpected given the small anisotropy in Eu systems. To understand this metamagnetism the element specific spin and orbital moments and their magnetic order in the antiferromagnetic ground state need to be known.

EuRh2Si2 single crystals were studied by means of several complementary x-ray techniques. Stable divalence of the Eu ions up to room temperature was verified by both x-ray absorption and resonant x-ray emission spectroscopy. X-ray magnetic dichroism measurements at the Eu M4,5 edges confirmed the expected zero orbital moment and a spin moment MS=7μB at the Eu sites. These moments were found to order antiferromagnetically below TN=24.5 K. Resonant x-ray magnetic scattering revealed that EuRh2Si2 undergoes three different stages of magnetic ordering at low temperatures before it finally becomes paramagnetic at TN, in agreement with our magnetization and specific heat data. All three magnetic structures are incommensurate and the respective magnetic propagation vectors are discussed here. While the two high-temperature phases with critical temperatures of TN,2 = 24.5 and TN,1 = 22.9 K can be described by a single propagation vector Q = (0 0 τ), the magnetic order emerging below Tt = 12.3 K was found to be more complex.

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PROGRAM

Tuesday, Sept. 18th, 2012

Tuesday, September 18th, 2012

08:30 - 9:15 **New avenues to explore ultrafast dynamics at free-electron lasers**
***J. Ullrich* (Plenary)**

09:15 - 10:00 **Surface science studies on graphene by electron spectroscopy**
***E.H. Conrad* (Plenary)**

10:10 - 10:30 **Coffee Break**
Jacques Cartier Rotunda & Grand Large Room

	Photo Chemistry and Reactivity 2 ***Catalysis, Organic molecules*** Chateaubriand Auditorium	**Ultra Fast Dynamics** Maupertuis Auditorium	
10:30 - 11:00	Imaging spectroscopy techniques and applications in surface chemistry *L. Gregoratti* (Invited)	Attosecond delays in XUV photoionization: A theoretical perspective A. *Maquet* (Invited)	**10:30 - 11:00**
11:00 - 11:30	Theoretical spectroscopy of complex systems *O. Pulci* (Invited)	Attoclock reveals new and surprising insight in attosecond ionization dynamics in helium and argon *C. Cirelli* (Invited)	**11:00 - 11:30**
11:30 – 11:50	Properties of NTCDA/metal interface studied by photoemission and NEXAFS *A. Bendounan* (Contributed)	Making the molecular movie”: First frames……Now with REGAE musik *D. Miller* (Invited)	**11:30 - 12:00**
11:50 - 12:05	More than the sum of its parts: Hetero-organic structures on Ag(111) *B. Stadtmüller* (Hot Topic)	Attosecond time delay in atomic photoionization as a probe of many-electron correlation *A. Kheifets* (Hot Topic)	**12:00 - 12:15**
12:05 – 12:20	Electronic interactions at transition metal phthalocyanine - Metal interfaces *T. Chassé* (Hot Topic)	Attosecond transient absorption spectroscopy of doubly excited states in helium *L. Argenti* (Hot Topic)	**12:15 - 12:30**

12:30 - 13:45 **Lunch**
Lamennais Area

Condensed phase	Gas phase

13:45 - 15:30

Posters Session II

- Novel Electronic States
- Photo-chemistry & Reactivity
- Surface & Material Science 2

Jacques Cartier Rotunda & Grand Large Room

15:30 - 16:00

Coffee Break

Jacques Cartier Rotunda & Grand Large Room

	Surface and Material Science 1 Chateaubriand Auditorium	**Atomic and Molecular Science 2** ***Fundamental processes (Synchrotron Radiation)*** Maupertuis Auditorium	
16:00 - 16:30	Adsorption structures of large molecules on single-crystal metal surfaces, from STM, LEED and DFT *M. Van Hove* (Invited)	Experimental proof of resonant Auger decay driven intermolecular Coulombic decay T. *Jahnke* (Invited)	**16:00 - 16:30**
16:30 - 17:00	Spectroscopic study of organic adsorbates on the TiO2(110) surface *J.A. Martin-Gago* (Invited)	Resonant inelastic soft X-ray scattering *J.-E. Rubensson* (Invited)	**16:30 - 17:00**
17:00 - 17:20	Magnetite half-metallicity uncovered by angle- and spin-resolved photoemission *K. Hricovini* (Contributed)	Momentum correlation spectroscopy after deep core-level photoionization *C. Bomme* (Contributed)	**17:00 - 17:20**
17:20 - 17:40	Functionalizing a magnetic oxide/silicon interface for Spintronics by HAXPES *M. Muller* (Contributed)	Core level photoemission studies of tautomerism in free molecules *K.Prince* (Contributed)	**17:20 - 17:40**
17:40 - 18:00	Spin-resolved photoemission and Fe1-xCox/MgO/Fe1-xCox magnetic tunnel junctions *F. Bertran* (Contributed)	Two-slit interference in molecular photoionization *M.N. Piancastelli* (Contributed)	**17:40 - 18:00**

Free Evening

Condensed phase	Gas phase

New Avenues to Explore Ultrafast Dynamics at Free-electron Lasers

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ABSTRACT

Free ***E***lectron ***L***asers (FEL) provide femtosecond, intense and coherent light pulses at eV to keV photon energies that enable, among others, a plethora of novel experiments on ultrafast dynamics in atoms, molecules, clusters or solids. The lecture will highlight pioneering results obtained at the first machines operational worldwide, the FLASH in Hamburg, the LCLS in Stanford and the SACLA in Japan using advanced many-particle imaging and split-mirror techniques.

At FLASH, ultrafast motion in molecules was traced for photon-induced isomerisation or dissociation reactions. First measurements at LCLS capture attosecond multiple ionization dynamics in atoms, the correlated motion of the lattice and electrons in the conduction band of semiconductors, investigate the dynamics in nano-particles, clusters and nano-plasmas and, recently, demonstrated time-dependent structural changes in “photosystem I” light-harvesting nano-crystals upon absorption of optical photons.

Finally, the rich future possibilities are envisioned. Can we record “the molecular movie”, i.e., follow in time the motion of atoms and the rearrangement of electrons during chemical reactions, can we produce single attosecond pulses at keV energies or time-tack the inter-atomic Coulomb decay (ICD) via phase-correlated THz streaking.

Surface Science Studies on Graphene by Electron Spectroscopy

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ABSTRACT

The possibility of graphene-based electronic devices has been and remains the prevalent motivation for graphene research. Progress towards this goal, however, continues to be slow because of a very narrow transport-based approach to fundamental graphene research. While there are many ways of producing graphene, our ability to understand graphene physics is ultimately tied to the interaction of graphene with whatever substrate it is on or environment it is in. With that clearly understood, graphene research is only advanced by being able to controllably and reproducibly place graphene on an interface where it can be studied by a wide variety of surface probes. In other words, flat, well-ordered, characterizable samples are required for any substantive progress towards graphene electronics. Epitaxial graphene meets all these requirements and therefore will be the focus of this talk. The 2D nature of Graphene requires that surface probes be used to study this material. Because surface probes are intrinsically strongly interacting with the material, it is well known that multiple techniques must be employed to fully understand both structure and electronic properties. The ability to prepare atomically flat graphene films, combined with multiple surface analysis techniques, allows impurities and substrate effects to be quantified or separated out from different measurements. This process has subsequently contributed to a substantial body of physics information on graphene and graphene devices. Synchrotron based surface probes have been at the forefront of graphene research. I will show how electron spectroscopies have been able to not only demonstrate many predicted properties of graphene, but more importantly, how they have uncovered significant new discoveries, some of which are at variance to current models. It is these new results that are inspiring new ideas on how graphene electronics can be realized.

SESSION:

Photo-chemistry & Reactivity 2

Catalysis, Organic molecules

Imaging Spectroscopy Techniques and Applications in Surface Chemistry

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ABSTRACT

X-ray photoelectron spectroscopy (XPS), born more than a half century ago, has remained one of the best methods for probing the composition and electronic structure of solid surfaces and interfaces. The severe limitations in the spatial resolution achievable with laboratory or first generation synchrotron facilities XPS machines have been overcome with the construction of the third generation synchrotron laboratories which provide ultra-bright and tunable photon beams, features of fundamental importance to push the XPS lateral resolution into submicrometer length scales.

In the modern XPS microscopes operating at the synchrotron facilities the high spatial resolution is achieved by either, magnifying the image of the irradiated surface area or demagnifying the incident photon beam [1]. They use the power of the surface sensitive photoelectron spectroscopy to obtain chemical characterization of the systems under investigation with spatial resolution down to 30 nm and probing depth up to a few tens A°.

The scientific and technological impact of these microscopes has a positive effect on several important topics including nanostructure and nanodevice characterization, electrochemistry, catalysis and composite materials. The Elettra synchrotron light laboratory hosts 3 photoemission microscopes designed for complementary experiments offering to the scientific community the unique opportunity for a direct comparison of their performances and capabilities. Several users as well as local researchers perform, in fact, their experiments combining results from different microscopic approaches improving the understanding of surface phenomena.

Aim of this presentation is to provide an overview of recent results focused on the chemical characterization of devices for energy applications such as solid oxide fuel cells [2] and chemical characterization of catalytic nanomaterials in model redox reactions [3].

The last part of the presentation will be spent to address one of the near future challenges for the photoemission microscopy community, i.e. the development of machines able to work at near ambient pressure in order to overcome the limits imposed by the so called pressure gap. The recent developments achieved in the photoemission spectroscopy synchrotron based stations in the use a mbar range pressure in situ have stimulated the community to extend these breakthrough application to imaging machines too [4].

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Theoretical Spectroscopy of Complex Systems

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ABSTRACT

Structural, electronic and optical properties of complex systems are nowadays accessible thanks to the impressive development of theoretical approaches and computer power.
Nanostructures, surfaces and even biological systems can be studied within ab-initio methods which fully include exchange and correlation effects. In this talk, we will shortly review the theoretical ab-initio approaches we use, namely Many-Body Perturbation Theory and Time Dependent Density Functional Theory. Then, we will present examples of first principles calculations of electronic and optical excitations for complex systems, ranging from the effect of proton disorder on the excitons in water [1] and ice, to the investigation of the oxidation processes of cellulose causing the yellowing of ancient paper[2].

a)The proton disorder in ice has a role in several properties such as growth condition and thermal properties. We find that, by increasing the proton disorder, a shrinking of the electonic gap appears. Simultaneously, the excitonic binding energy decreases, so that the final optical gaps result to be almost independent on the degree of disorder. We explain this fact with the strong localization of the excitonic wavefunction in the cases studied.

b) The yellowing of paper on aging causes major aesthetic damages of cultural heritage. It is due to cellulose oxidation, a complex process with many possible products still to be clarified. We will show how spectroscopic techniques coupled with ab-initio calculations can provide information on cellulose-based ancient materials such as writing support (paper or papyrus) or textiles. By means of Time-Dependent Density Functional Theory calculation, we assign the UV-Vis spectral features of degradation products of ancient cellulosic materials, opening the possibility of optical measurement of their state of degradation.
Recent studies on the famous Leonardo self-portrait will be also discussed.

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Properties of NTCDA/metal Interface Studied by Photoemission and NEXAFS

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ABSTRACT

In the recent years remarkable interest has been paid in studying properties of organic molecules on metal surfaces. In particular, the planar conjugated molecules with delocalized π-like electron system on noble metals has attracted much attention since they show large scale structures with a high degree of order and a well-defined crystalline orientation. Here, we present systematic investigations on the behavior of NTCDA in contact with (111)-oriented Ag, Au, and Cu surfaces. In the sub-monolayer regime, NTCDA grows flat on Ag(111) and is covalently bound (chemisorbed) to the substrate via the conjugated π-electron system of the naphthalene core. However, on Au(111) the interaction is rather weak and can even be treated as a physisorption process. Core level and valence band data on NTCDA/Cu(111) suggest a significant charge transfer and strong bonding at the interface. More interesting, the coupling between conduction states and localized states within the molecular layer can lead to the formation of Kondo-like resonance feature at the Fermi level, as in the case of NTCDA/Ag(111). This strong coupling is sensitively modified after chemical treatment of the Ag(111) substrate, which permits to define the exact HOMO energy of the NTCDA molecule. In this communication, we demonstrate that the electronic structure of the metal represents the principle key-parameter in the interaction molecule-metal.

More than the Sum of its Parts : Hetero-organic Structures on Ag(111)

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ABSTRACT

One crucial issue for the success of organic materials in electronic devices is the ability to specifically design the interfaces between different active layers according to their functional purpose. For this reason the growth behaviour of the first organic layer on noble metal surfaces was investigated intensively over the last decades[1,2].

This initial growth state is of particular interest not only because the first closed layer acts as a template for the further growth. Also the complex interplay between the intermolecular interaction and the molecule-substrate interaction can be accessed. In cases of a strong chemical bond between the adsorbate and the substrate a charge redistribution occurs at the interface which can affect the intermolecular interaction[3].

While in the last years almost all studies focused on the properties of organic layers containing only one species of molecules we will now present our results for the formation of mixed layers containing two different types of molecules. As a model system we chose hetero-organic layers of copper-II-phthalocyanine (CuPc) and perylen-tetracarboxylicacid dianhydride (PTCDA) in direct contact with the Ag(111) surface since their individual growth behavior has already been studied and understood in detail[4].

Our structural data reveal that depending on the relative coverage of CuPc to PTCDA different long range ordered structures are formed including both types of molecules. The influence of the intermolecular interactions on the electronic valence structure was investigated with angle resolved photoelectron spectroscopy (APRES). Using the orbital tomography approach[5] for the analysis of the ARPES intensity reveals a significant change in the orbital occupation due to the formation of a mixed layer. This modified valance structure will be correlated with the formation of an unoccupied, delocalized interface state expanding over both molecular species in the unit cell. Furthermore the observed changes of the mixed organic layer in contrast to the bare monolayer structure will be discussed.

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Electronic Interactions at Transition Metal Phthalocyanine - Metal Interfaces

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ABSTRACT

Transition metal phthalocyanines (TMPcs) are potential candidates for various applications, most recently they have been considered as promising materials for the development of low dimensional molecular magnets or organic spintronic devices. Although electronic properties of TMPcs have been extensively investigated, both experimental studies and DFT calculations give partly contradictory results. Moreover, at several interfaces the interaction causes a change of the electronic configuration.

We have investigated TMPc films on single crystal Au(100) and Ag(111) surfaces using mainly photoexcited electron spectroscopies (photoemission, resonant photoemission, X-ray absorption). The formation of well-ordered films with very high degree of molecular orientation both at monolayer coverage and in thin films provides a unique opportunity to study and compare the electronic structures of the TM states in spatially fixed orientations. The results of the investigations indicate that the central metal atom of the Pc is of key importance for interface properties – in particular, if the central transition metal atom has an open shell structure. The contribution reports on the interaction of TMPcs (TM: Mn [1,2], Fe[3], Co [1,4,5], Ni, Zn [6]) at metal interfaces (Au, Ag). In all cases, charge transfer processes from metallic substrates to the metal 3d levels of the phthalocyanine molecule occur. However, the detailed electronic situation depends clearly on the system under consideration.

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SESSION:

Ultra Fast Dynamics

Attosecond Delays in XUV Photoionization: A Theoretical Perspective

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ABSTRACT

For the first time, the advent of a new generation of sources of coherent XUV harmonic radiation delivering "attosecond" pulses, makes feasible to investigate the photoionization process in the time domain with unprecedented time resolution. Here, we present a theoretical analysis of recent experiments that have evidenced the existence of attosecond time delays between the emission times of photoelectrons ejected from different sub-shells in noble gas atoms [1], [2]. These experiments were realized via 2-colour schemes involving the presence of an IR field with controlled delay in addition to the attosecond XUV pulse, the IR providing a convenient "reference clock" given by its cycle duration in the femtosecond range.

The theory analysis of this class of phenomena indicates that the measured delays are intimately related to the *phases* of the relevant 2-colour transition amplitudes. This implies that, as compared to standard computations of single-photon ionization transition amplitudes and differential cross sections, the theory must be extended to treat more sophisticated "laser-assisted" photoionization processes. In this presentation, we shall show that the dominant contributions to the observed time delays are the sum of 2 components: i) one is related to the so-called "Wigner time delays" introduced in collision theory, while ii) the other is related to the measurement technique itself, *i.e.* it results from the radiative transitions induced by the IR laser used to determine the timing of ionization at the sub-femtosecond level [2],[3].

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Attoclock Reveals New and Surprising Insight in Attosecond Ionization Dynamics in Helium and Argon

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ABSTRACT

The recent progress of the ultrafast laser technology enables to capture and control electrons dynamics, including electron correlations, which is the key to understand how energy and charge are transported not only in atoms but also in more complex solid-state and molecular systems. Since electron dynamics happen on the attosecond timescale, we need to develop novel measurement techniques with attosecond time resolution. The “attoclock” is a conceptionally simple method, which provides attosecond time resolution without the explicit need of attosecond pulses. We have demonstrated the first attoclock with the goal to measure the tunneling delay time in laser-induced ionization of helium and argon atoms, with surprising results. It was found that the time delay in tunneling is zero for helium and argon atoms within the experimental uncertainties of a few 10’s of attoseconds. Electron correlations are investigated in a double ionization experiment of argon, where the ionization time of both electrons is measured experimentally with attosecond precision. Interestingly the ionization time of the first electron is in good agreement with the predictions, whereas the ionization of the second electron occurs significantly earlier than predicted and clear signatures for an unexpected electron correlation are observed.

“Making the Molecular Movie”: First Frames…… Now with REGAE Musik

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ABSTRACT

One of the great dream experiments in Science is to watch atomic motions as they occur during structural changes. In the fields of chemistry and biology, this prospect provides a direct observation of the very essence of chemistry and the central unifying concept of transition states in structural transitions. From a physics perspective, this capability would enable observation of rarefied states of matter at an atomic level of inspection, with similar important consequences for understanding nonequilibrium dynamics and collective phenomena. This experiment has been referred to as "making the molecular movie". Due to the extraordinary requirements for simultaneous spatial and temporal resolution, it was thought to be an impossible quest and has been previously discussed in the context of the purest form of a gedanken experiment. With the recent development of femtosecond electron pulses with sufficient number density to execute single shot structure determinations, this experiment has been finally realized (Siwick et al. Science 2003). Previously thought intractable problems in attaining sufficient brightness and spatial resolution, with respect to the inherent electron-electron repulsion or space charge broadening, has been solved. With this new level of acuity in observing structural dynamics, there have been many surprises and this will be an underlying theme. Several movies depicting atomic motions during passage through structural transitions relevant to condensed phase dynamics will be shown (Sciaini et al. Nature, 2009, Ernstorfer et al. Science 2009, Eichberger et al Nature 2010). The primitive origin of molecular cooperativity has also been discovered in recent studies of molecular crystals. These new developments will be discussed in the context of developing the necessary technology to directly observe the structure-function correlation in biomolecules — the fundamental molecular basis of biological systems. The future is even brighter with the advent of a new concept in relativistic electron guns that will open up direct observation of atomic motions in solution phase to gas phase systems with femtosecond time resolution to watch even the fastest atomic motions. Some of the important scientific problems to be addressed with ultrabright electron sources will be discussed to give an impression of the potential impact of this emerging field.

Attosecond Time Delay in Atomic Photoionization as a Probe of Many-electron Correlation

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ABSTRACT

We analyze a time delay of one- and two-electron photoemission from an atom or a molecule after absorption of an attosecond XUV pulse. We establish this delay by solving the time dependent Schrödinger equation (TDSE) and by subsequent tracing of the field-free evolution of the photoelectron wave packet. This delay can also be related to the energy derivative of the phase of the complex photoionization amplitude which makes the time delay a sensitive probe of many-electron correlation and the means to perform a complete photoionization experiment.

This technique was first used to analyze the relative time delay between photoemission from the *2s* and *2p* shells in Ne. The experimental time delay difference of τ_{2p}- τ_{2s} = 21±5 as was reported [1] while theoretical modeling could only account for less than a half of this value [2]. This disparity of results opened up a wide discussion but subsequent theoretical papers broadly confirmed our initial prediction [3]. Our next application of the time delay analysis was in a joint experimental and theoretical study of the *3s* photoionization of argon near the Copper's minimum [4] which is affected strongly by correlation with the *3p* shell [5] . Because of this inter-shell correlation, the relative time delay τ_{3p}- τ_{3s} is large and negative in Ar while the corresponding delay τ_{2p}- τ_{2s} is small and positive in Ne, where correlation plays no role.

In theoretical study of single-photon double ionization (DPI) of He [6], we demonstrated that an attosecond time delay measurement can distinguish between the two leading correlational mechanisms of this process. The shake-off mechanism is driven by a fast rearrangement of the atomic core after departure of the primary photoelectron. In contrast, the knockout mechanism involves a slow interaction of the primary photoelectron with the remaining electron bound to the singly charged ion.

In molecules, unlike in atoms, the photoemission time delay becomes sensitive to molecular orientation relative to the polarization axis of light. When the molecular orientation is known, like in the case of DPI of H_2, the time delay can be used as a delicate tool of the phase analysis [7]. The time-delay is shown to have poles at the point corresponding to the kinematic nodes of the reaction. Study of the delay in the vicinity of a pole can provide information about phases of the DPI amplitudes. In single electron photoionization, when the molecule does not break up, the time delay measurement can be used to determine the molecular orientation.

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Attosecond Transient Absorption Spectroscopy of Doubly Excited States in Helium

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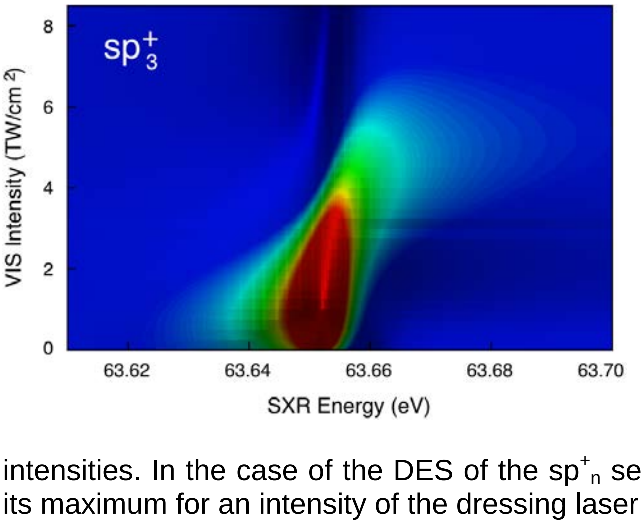
ABSTRACT

New sources of intense femtosecond and attosecond light pulses [1] have opened the way to the study of the coherent ultra-fast dynamics of electronic states in atoms and molecules. Among the various experimental techniques that blossomed in this field, Attosecond Transient Absorption Spectroscopy (ATAS) [2] associates high temporal to high spectral resolution (in two independent variables).

In this work, we use ATAS to investigate theoretically the soft-x-ray (SXR) response of doubly excited states of a helium atom dressed by an intense short visible (730 nm) laser pulse. In the ATAS technique, a weak attosecond SXR pulse is flashed through the sample with a given time delay t_d with respect to the dressing pulse; the effective SXR transient absorption cross section $\sigma(\omega,t_d;I_{VIS})$ — close to what is measured in real experiments — is thereby computed. From the transient absorption cross section, one can derive the off-diagonal electrical susceptibility of the dressed system, $\chi(\omega,\omega')$, which defines the conversion (absorption at ω', stimulated emission at ω) among frequency components of the SXR pulse. These conversions correspond to electronic transitions in the atom, induced by the dressing field, such as multi-photon Rabi oscillations between doubly excited states. In other terms, ATAS provides a systematic way to map non-perturbative transitions in metastable systems.



The transient absorption cross section for helium is obtained by solving the time-dependent Schrödinger equation with the Arnoldi propagator in a close-coupling B-spline basis in a quantization box ~200 Å large, with absorbing boundaries [3]. The SXR response is computed both as a function of the pump-probe time delay and as a function of the dressing-field intensity. Our theoretical results reproduce well recent measurements by Pfeifer and co-workers [4]. In particular, we observe the inversion of the ${}^1P^o$ doubly exicted states Fano profiles, and their fading at large intensities. In the case of the DES of the sp^+_n series, with n>2, the absorption peak reaches its maximum for an intensity of the dressing laser close to 1 TW/cm^2 (see figure).

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SESSION:

Surface and Material Science 1

Adsorption Structures of Large Molecules on Single-crystal Metal Surfaces, from STM, LEED and DFT

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ABSTRACT

We have studied the adsorption and supramolecular assembly of several large molecules on metal surfaces. Starting from experimental data (structure and microscopy), we calculated total energies while optimizing the adsorption configuration, using density functional theory (DFT) calculations, and simulated images obtained by scanning tunneling microscopy (STM). The aim is to enhance our understanding of the bonding of such molecules to metal surfaces.

C_{60} molecules (buckyballs) were studied on both Cu(111)[1] and Pt(111)[2]. It was found that buckyballs can reconstruct both metal surfaces in different ways, by expelling metal atoms, displaying a remarkably strong C_{60}–metal interaction even on Cu.

TCNQ molecules (7,7,8,8-tetracyanoquinodimethane) were mixed with Mn atoms to form a compound two-dimensional monolayer by supramolecular assembly on a Cu(100) surface[3].

BTP-TPE molecules (1,2-bis[4’-(4’-2,2’:6’,2”-terpyridyl)-biphenyl-4-yl]-1,2-diphenylethene) were deposited on Cu(111) and found to exhibit the properties of single-molecule type-I double heterojunctions[4].

BTP-BCO (4',4''''-(bicyclo[2,2,2]octane-1,4-diyldi-4,1-phenylene)–bis-2,2':6',2''-terpyridine) is a rotor molecule whose rotations can be excited stepwise by STM on a Cu(111) surface, through a specific axial vibration mode[5].

We studied an organometallic surface intermediate (formed from 4,4”-dibromo-p-terphenyl) that builds chains along a Cu(111) surface by linking through bridging Cu atoms[6].

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Spectroscopic Study of Organic Adsorbates on the TiO2(110) Surface

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ABSTRACT

The interaction of organic molecules with dielectric surfaces is a relevant research field with significant implications in technological and fundamental physics. Molecular species have revealed as encouraging substitutes of silicon in future electronics. They present donor–acceptor properties, which are fundamental for the development of electronic components such as rectifiers, transistors, etc. However, albeit their importance, and due to the difficulty of applying surface science techniques for characterizing metal oxide surfaces, there is a lack of controlled experiments to determine the role of their interface in the electronic properties. Here we present a comparative study of several organic molecules owing different presumed donor-acceptor character deposited under ultra-high vacuum conditions on the surface of a prototypical high-dielectric constant and wide band gap semiconductor, the rutile TiO2(110) [1].

We have deposited different single-layers of organic molecules (C60 [3], pentacene [1], C60H30 and protoporphyrin IX) and we have made use of a combination of different experimental techniques with theoretical methods. Thus, scanning tunneling microscopy (STM), low energy electron diffraction (LEED), X-ray photoemission spectroscopy (XPS), near edge X-ray absorption fine structure (NEXAFS), X-ray photoelectron diffraction (XPD) and ab-initio DFT calculations, have been used to understand their growth mode and the strength of the molecule-surface and molecule-molecule interaction.

C60 and pentacene show a weak interaction with the substrate at room temperature, forming electronically decoupled layers, whereas porphyrins strongly interact through their N atoms transferring charge from the molecule to the surface, as it can be expected because of their donor character. C60H30 molecules illustrate an opposite example in which there is a small charge transfer from the surface towards the molecule. We have also addressed the issue of the thermal stability of the resulting molecular layers. For this purpose we have performed annealing experiments at different temperatures until molecular desorption or decomposition is observed. Formation of new nanostructures as fullerene-like domes, directly on the surface, has been achieved.

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Magagnetite Half-metallicity Uncovered by Angle and Spin-resolved Photoemission

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ABSTRACT

Magnetite, Fe_3O_4, a ferrimagnet with a Curie temperature of 850 K, has been predicted from band structure calculations [1] to have a half-metallic character. But up to now any clear experimental evidence is lacking. We have performed angle- and spin-resolved photoemission measurements on thin films of Fe_3O_4(001)/MgO(001). Despite the very low spectral weight at the Fermi level due to polaronic effects, a Fe 3d t_{2g} band dispersion is observed. Because at present the calculation of the photoemission process is hardly feasible for complex systems such as Fe_3O_4, we did a simulation of the spectra using a simple model. We used the free-electron approximation for the final states, completely ignoring the matrix elements. In the simulation our GGA+U [2] ground state data were convoluted by Lorentzian and Gaussian functions to account for the lifetime and electron-phonon (polaron) coupling effects, respectively. A good qualitative agreement between the simulation and the experiment is achieved for Fermi surface as well. In spin-resolved photoemission experiments 4.65 and 6.20 eV photons emitted by a laser were used. The spin polarization close to the E_F reaches - 50% and -72% for 6.20 and 4.65 eV photons respectively. Our results demonstrate that Fe_3O_4 can be described by a band model and that it is a half-metal.

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Functionalizing a Magnetic Oxide/Silicon Interface for Spintronics by HAXPES

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ABSTRACT

One major challenge in present-day spintronics research is the efficient electrical injection of spins into semiconductors. Owing to its ability to generate almost fully spin-polarized currents, the magnetic oxide europium oxide (EuO) has been revisited as a material with outstanding potential for silicon-based spintronics applications. Given the high reactivity of both EuO and Silicon, however, this presents a major challenge and requires both to integrate high-quality ultrathin EuO films on Silicon and prepare a structurally and chemically sharp EuO/Si spin transport interface.

Using hard X-ray photoemission spectroscopy (HAXPES), we demonstrated the successful chemical stabilization of stoichiometric EuO ultrathin films grown directly on Silicon [1, 2]. We succeeded in growing single-crystalline EuO/Si(001) heterostructures without any buffer layer via reactive molecular beam epitaxy (MBE). Due to its large probing depth of several nm, HAXPES allows direct access to the bulk electronic structure of the buried EuO films, a throughout depth profiling of the chemical homogeneity and direct insight into the interface chemical state.

HAXPES experiments have been carried out at the beamlines P09 (PETRAIII, Hamburg) and HIKE (BESSY, Berlin) using photon energies of 2-6 keV. We carefully determine the initial state Eu valency via a quantitative analysis of core-level and valence spectra. We performed depth-sensitive measurements and extracted the Eu chemical state in the bulk and interface regions, confirming that nearly ideal, homogeneous and stoichiometric thin films of the metastable compound EuO can be grown on Si(001). Furthermore, our depth-sensitive HAXPES study on the Si 1s and Si 2p levels reveals that we minimized both interfacial silicide ($EuSi_2$) and silicon dioxide (SiO_x) down to one monolayer.

Our study explicitly demonstrates the successful functionalization of EuO ultrathin films directly on Silicon, and points encouragingly towards the future integration of this functional magnetic oxide into silicon-based spintronic devices.

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Spin-resolved Photoemission and $Fe_{1-x}Co_x/MgO/Fe_{1-x}Co_x$ Magnetic Tunnel Junctions

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ABSTRACT

Strong tunneling magnetoresistance (TMR) in MgO-based magnetic tunnel junctions with bcc electrodes is due to their particular electronic structure along the [001] direction and to the symmetry filtering of the MgO barrier. Then, calculations predicted a very strong TMR for bcc-FeCo(001)/MgO/bcc-FeCo(001) magnetic tunnel junctions because of the half-metallicity of Δ_1 states and because of the reduction of the majority Δ_5 density of states when the Co concentration increases. We fabricated such magnetic tunnel junctions and we observed that the TMR actually increases with the Co concentration but only up to 25% of Co. Surprisingly, for higher Co concentrations, the TMR is strongly reduced.

By combining spin-resolved and angle-resolved photoemission measurements on $Fe_{1-x}Co_x$ thin films and band structure calculations, we showed that this transport behavior is due to the appearance of a minority spin surface state with Δ_1 symmetry. This state is present for more than 25% of Co at the surface of the free thin films but also as an interface state when the thin films are covered by MgO. By opening a new conduction channel, this state is responsible for the TMR decrease for more than 25% of Co [1].

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SESSION:

Atomic and Molecular Science 2

Fundamental processes (Synchrotron Radiation)

Experimental Proof of Resonant Auger Decay Driven Intermolecular Coulombic Decay

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ABSTRACT

The efficient interaction of X-rays with high-Z elements is an extensively explored and important topic in biomedical physics [1, 2]. More recently, it has been proposed to use resonant excitation instead of broadband irradiation to locally deposit energy at malignant cells tagged with high-Z elements in an approach termed "X-ray resonant theranostics" [3]. A decay process called intermolecular Coulombic decay (ICD) was found after its prediction in 1997 [4] to create electrons of low energy as a typical decay product. Such electrons are known to effectively cause DNA double strand breakups [5, 6] suggesting ICD as a possible origin for radiation damage of living tissue [7]. The group of L. Cederbaum recently suggested [8] that ICD can be triggered efficiently and site-selectively by resonant excitation of molecules. They realized that this provides a unique tool to create low energy electrons at a specific site inside a biological system. We show experimentally that resonant Auger induced ICD can indeed be observed in model systems of small nitrogen and carbon monoxide clusters and - as expected - produces low energy electrons. Furthermore our simple model systems are able to prove the efficiency of ICD: it occurs before the individual molecule is able to undergo dissociation, i.e on a timescale < 10 fs. Our findings therefore strongly support the idea of resonant Auger-ICD being a promising process to induce radiation damage at a specific site inside a high-Z-tagged cell.

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Resonant Inelastic Soft X-ray Scattering with Vibrational Resolution

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ABSTRACT

Resonant inelastic X-ray scattering (RIXS) reflects fine details in electronic structure and dynamics. The process is site specific on the atomic length scale (sub-nanometer) and time specific on the timescale for nuclear and electronic rearrangements (femto- to attoseconds). Consequently, RIXS spectroscopy has a tremendous potential in atomic and molecular, chemical and condensed matter physics. RIXS techniques have, however, suffered from the lack of adequate radiation sources. In practice this has limited the spectral quality and only a fraction of the inherent advantages have been exploited.

We present RIXS spectra of free molecules [1-3] and liquids [4] excited at the oxygen K edge with an energy resolution ($E/\Delta E \sim 10000$) that allows us to clearly separate vibrational excitations. This opens a wealth of new possibilities, provides detailed information about ultrafast dynamics, and facilitates accurate mapping of ground and excited state potential surfaces.

The measurements were made with the SAXES spectrometer at the ADRESS beamline at the Swiss Light Source of the Paul Scherrer Institut, using a gas/liquid cell with an ultrathin membrane. The data is discussed in terms of *ab-initio* multimode scattering calculations.

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Momentum Correlation Spectroscopy After Deep Core-level Photoionization

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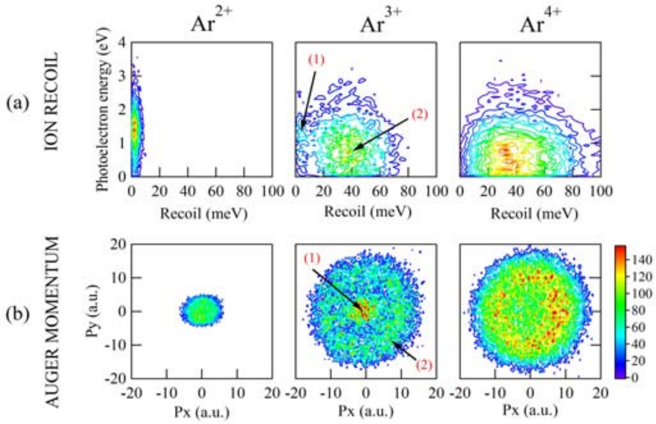
ABSTRACT

We recently developed a new spectrometer, CELIMENE, dedicated to momentum correlation spectroscopy. This apparatus is designed to provide the full momentum vectors of coincident particles emitted after deep core-level photoexcitation in the “tender” x-ray regime (1 to 10 keV). In this regime, excitation, electronic decay, and fragmentation processes are characterized by short lifetimes, the formation of highly charged species and large kinetic energies. After a brief description of the apparatus and experimental scheme, we will present the first results obtained with this setup on the LUCIA beamline at the French synchrotron radiation source SOLEIL. Original results were obtained on Argon after 1s photoionization (~3205 eV) and OCS, after sulfur 1s core ionization (~2475 eV). In the atomic case, we measured the recoil induced on the fragment ions by the emission of fast Auger electrons (up to 3000 eV). This information can be used to disentangle the formation mechanisms of highly charged ions [1]. We also measured the PCI profiles of the photoelectron spectra associated with each ionic channel and derive a method to extract the effective lifetime (or decay rate average lifetime) of all intermediate states involved in the cascade Auger decay of the initial core hole [2]. In the case of OCS, momentum correlations between several fragments give access to molecular frame angular distributions of photoelectrons [3], as well as 3-body fragmentation dynamics.



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Core Level Photoemission Studies of Tautomerism in Free Molecules

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ABSTRACT

In free molecules, prototropic tautomerism is a well-known phenomenon in which a hydrogen atom changes its site within a molecule, often accompanied by an exchange of adjacent single and double bonds. Core level photoemission spectroscopy is a powerful method for studying this effect, which is important in the DNA bases guanine, cytosine and its derivatives for instance [1-4]. An advantage of photoemission is that it is more quantitative than many other spectroscopic techniques, as the signal is directly proportional (within limits) to the population of a particular tautomer. The measurement of populations allows the testing of thermodynamic calculations of tautomeric equilibria, and in particular the relative free energies of tautomers.

In our recent work, we measured the spectra of a series of small heterocyclic molecules, namely 2-mercaptopyridine, 4-hydroxypyrimidine, S-methyl-2-thiouracil and 2-thiouracil [5,6]. The goal of this work was to understand how changes in the functional groups attached to heterocycles change the structural equilibria. 2-mercaptopyridine is an analogue of the much studied compound hydroxypyridine and can exist in mercapto (CSH) or thione (C=S) forms. We applied both S 2p photoelectron and microwave spectroscopy, and found mercapto/thione populations of 95.4%/4.6%. In addition, the microwave spectra determined the ratio of conformers (in which the CSH bond has two different orientations) of the mercapto form. The population of the thione form is lower than the theoretically estimated value, indicating that more refined calculations are required. Substitution of the oxygen in hydroxypyridine by sulfur destabilises the C=X form in favour of the CXH form (X=O,S) and also changes the conformational equilibrium.

In the family of pyrimidine based molecules 4-hydroxypyrimidine, S-methyl-2-thiouracil and 2-thiouracil, we investigated keto-enol tautomerism via C, N, O and S core level photoemission. Attaching additional OH (or SH) groups to the aromatic ring stabilizes the dioxo (or oxo-thione) forms. However, substitution of hydrogen in position 2 by an S-CH3 group (that is, in going from 4-hydroxypyrimidine to S-methyl-2-thiouracil) does not significantly affect the tautomeric equilibrium.

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Two-slit Interference in Molecular Photoionization

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ABSTRACT

We report evidence on two-slit interference phenomena [1-9] in photoionization of polyatomic molecules, which we have observed in the inner valence photoelectron spectra measurement for the series of molecules C_2H_2, C_2H_4 and C_2H_6 over the photon energy range of 70-700eV. The experiments have been performed at SOLEIL on the PLEIADES beamline [10]. Oscillations coming from two orbitals corresponding to in-phase and anti-phase combinations of the same atomic orbitals are predicted exactly out of phase. Theoretical calculations [11] show that similar oscillations are present also in valence molecular orbitals (MOs). Here structures are less regular due to the more complex structure of the relevant MO's, which are generally delocalized over the entire molecule. A notable simple case is for orbitals arising from atomic 2s orbitals. In this case the g/u splitting is much larger, several eV's and can be easily resolved and followed over a large photon energy range. In case of 1s orbitals, the g/u splitting is often very small, although such oscillation have been experimentally and theoretically described in C_2H_2 in a previous work [12]. The experimental results show prominent oscillations in the $2\sigma_g/2\sigma_u$ intensity ratios with photon energy and with a strong dependence on the C-C distance. The theoretical calculations [11] have been done prior to the experiment for $1\sigma_g/1\sigma_u$ as well as $2\sigma_g/2\sigma_u$. The C2s derived orbitals are well defined and can be easily resolved experimentally over a large excitation energy range, and thus the present experiment has been performed to understand the effect of molecular orbital localization/delocalization on photoionization. The observed oscillations are not symmetric, which reflects the different degree of admixture of the H1s orbitals in the two $2\sigma_g/2\sigma_u$ C2s-derived MOs, and thus it is directly informative of the nature of the inner-valence MOs.

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POSTERS SESSION II:

Tuesday, Sept. 18th, 2012

Electronic spectroscopy and structure
12th international conference
CONFERENCE ICESS 2012 SAINT-MALO
September 16-21, 2012 - Palais des Congrès - Saint-Malo, France

Posters list Session II

Tuesday, September 18th, 2012

Novel Electronic States
Photo-chemistry & Reactivity
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Novel Electronic States

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NE-2-PO-CHE-01	***C.M. Cheng*** Polarization dependent X-ray absorption spectroscopy and resonant inelastic X-ray scattering studies at Co K-edge in single crystal $Bi_2Sr_2CoO_{6+\delta}$ compounds
NE-2-PO-CIL-01	***F. Cilento*** Ultrafast electronic dynamics of the Bi_2Se_3 topological insulator, revealed by Tr-ARPES
NE-2-PO-DON-01	***M. Donath*** A "Bird's eye view" of Rashba systems: Spin-resolved bands beyond The Fermi level
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NE-2-PO-NIE-01	***D. Niesner*** Unoccupied surface states of topological insulators
NE-2-PO-NIS-01	***Y. Nishitani*** Bulk-sensitive photoelectron spectroscopy of $TlFe_2Se_2$ ~The parent compound of iron-selenide superconductor~
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NE-2-PO-OKA-02	***M. Okawa*** X-ray absorption spectroscopy of double-perovskite Co oxides with high-spin configuration
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PR-2-PO-RUH-01	***E. Rühl*** The gas-to-cluster and gas-to-solid effects in core excited SF6
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PR-2-PO-TIA-01	***M. Tia*** Valence-shell photoelectron circular dichroism on gas phase alanine
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Surface & Material Science 2

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SM-2-PO-MOU-01	***M. Moustafa*** Spin orbit splitting in the valence bands of ZrS_xSe_{2-x}: ARPES and DFT
SM-2-PO-MOU-02	***M. Moustafa*** Electronic band structure of ZrS_xSe_{2-x} layered semiconductors
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SM-2-PO-STR-01	***V.N. Strocov*** Electronic structure of 3-dimensional systems and multilayer heterostructures by soft-X-ray ARPES

Surface Electronic Structure of Topological Insulator $GeBi_2Te_4$ Observed by Angle Resolved Photoemission Spectroscopy

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ABSTRACT

Topological insulators (TIs) are a new phase of quantum matter. In this material, a quantum spin Hall effect occurs without magnetic field [1]. The nontrivial edge or surface states in a bulk energy gap are caused by strong spin orbit interaction and inversion symmetry. The new phase is classified by a Z_2 topological invariant, which distinguishes it from an normal insulator [2]. The surface of TIs has characteristic electronic structure : spin polarized Dirac corn at time-reversal invariant momenta [3].

The quintuple-layers materials Bi_2Se_3 and Bi_2Te_3 are the most famous and these have been shown to be TIs experimentally [4]. In this work, we studied the electronic structure of the septuple-layers material $GeBi_2Te_4$ predicted to be one of TIs by means of angle resolved photoemission spectroscopy (ARPES) [5].

We have observed a Dirac-corn-like electronic structure around Γ point. From Fermi surface mapping and the photon energy dependence of the ARPES spectra, the Dirac-corn-like electronic state exists at bulk energy gap and consists of the only Fermi surface in whole Brillouin zone. Thus, it is concluded that $GeBi_2Te_4$ is one of TIs.

Although the topological surface state of $GeBi_2Te_4$ is very similar to that of the Bi_2Se_3, the bulk gap is ~ 120 meV and the group velocity around Dirac point is one-third smaller than the case of the Bi_2Se_3. Moreover the circular constant energy contours in the Dirac corn are not found in ARPES mapping image, that is, it is found that the hexagonal warping effect in $GeBi_2Te_4$ is very strong.

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Polarization Dependent X-ray Absorption Spectroscopy and Resonant Inelastic X-ray Scattering Studies at Co K-edge in Single Crystal $Bi_2Sr_2CoO_{6+\delta}$ Compounds

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ABSTRACT

Layered cobalt oxide $Bi_2Sr_2CoO_{6+\delta}$ have attracted much interest because it is isostructural to the high-Tc superconductor $Bi_2Sr_2CuO_{6+\delta}$. Furthermore, $Bi_2Sr_2CoO_{6+\delta}$–exhibit a series of surprising electronic and magnetic properties with various oxygen contents[1-3]. We have carried out polarization dependent X-ray absorption (XAS) and resonant inelastic X-ray scattering (RIXS) measurements to study the orbital symmetry and the energies of ligand to metal charge transfer excitations. The XAS measurement reveals that because the centrosymmetry is broken from D_{4h} symmetry due to strong local distortion, there exists a large mixing among *4p* states or hybridization between *4p* and *3d* states. This distortion of CoO_6 octahedron with $\delta > 0.25$ is more severe than $\delta \sim 0.25$ due to extra oxygen insertion. In the RIXS measurement, spectra of the antiferromagnetic transition temperature T_N~280 K sample exhibit three clear inelastic features around 2.8 eV, 4.6 eV and 7.0 eV. Similarly in the T_N~150 K sample three peaks appear around 3.0 eV, 4.6 eV and 7.7 eV. The lack of dispersion suggests the highly localized characteristics of these excitations. These features may be referred to charge transfer mechanism from a *2p* electron of O to a *3d* hole of Co in the CoO_2 plane. Particularly the energy loss feature at 4.5 eV can be clearly identified as a charge transfer excitation because it resonates at the absorption transition of $1s \rightarrow 4p_{x'}$, $4p_{y'}$ with ligand to metal charge transfer (LMCT) from O $2p \rightarrow$ Co $3d_{x'^2-y'^2}$.

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Ultrafast Electronic Dynamics of the Bi_2Se_3 Topological Insulator, revealed by Tr-ARPES

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ABSTRACT

Topological Insulators (TI) are bulk band insulator supporting metallic surface states in the bulk band gap [1,2,3]. Along the surface, perfect conductance is expected, being the surface state topologically protected from impurity scattering [4]. This is the reason why these newly discovered materials are encountering a growing theoretical and experimental interest, as prominent candidates in new generation electronic devices.

Here, we present the first results of the investigation of the ultrafast dynamics of the bulk and surface electronic states of a Bi2Se3 n-doped TI compound, by Time-Resolved ARPES performed at the T-ReX Laboratory at Elettra, Trieste. Tr-ARPES combines the high energy and momentum resolutions of ARPES with the advantages given by a non-equilibrium approach, allowing to reveal the temporal evolution of the electronic structure after the sample is brought out-of-equilibrium by the absorption of an ultrafast laser pulse.

We studied the transient induced electronic population of both the bulk conduction band (BCB) and the topological surface state (TSS), evidencing the peculiar relaxation dynamics, developing on the picoseconds timescale, in the relevant regions of the (E_k,$k_{||}$) space.

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A “Bird's Eye View” of Rashba Systems: Spin-resolved Bands Beyond the Fermi Level

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ABSTRACT

Rashba-type spin splittings in the surface electronic structure of heavy elements and topological insulators are a hot topic of today’s research in condensed matter physics. The interest is guided by possible applications of these materials in spintronic devices, in which the electron spin is used as an information carrier. While the occupied bands are thoroughly investigated by spin- and angle-resolved photoemission, there is basically a blank area on the $E(k_{\|})$ map beyond the Fermi level. In some cases, however, the understanding of the system hinges on the knowledge about the dispersion and spin character of the unoccupied bands.

In this paper, we present spin- and angle-resolved inverse-photoemission results on selected Rashba systems. Our experimental setup includes spin- and angle-resolved photoemission, which allows us to connect the new data on the unoccupied states to literature results on the occupied states. The proof-of-principle experiment on Au(111) shows the expected Rashba splitting of the surface state beyond the Fermi level and provides insight into Rashba-type spin splittings of *sp*-like bulk transitions.

The Tl/Si(111)-(1x1) surface has outstanding properties. Spin-resolved photoemission experiments reveal an occupied Rashba-split surface state with a peculiar spin structure in reciprocal space [1]. We observe an unoccupied surface state with the same out-of-plane rotation of the spin polarization around K as the occupied state. Here, however, the two spin components are split in energy by more than 0.6 eV. In addition, the lower-lying spin component approaches the Fermi level, which gives rise to nearly complete spin polarization at E_F. We will present a detailed $E(k_{\|})$ map of the surface states and their spin polarization in the unoccupied regime.

Among the surface alloys with heavy elements on noble metals, the √3x√3R30° Bi/Ag(111) ordered surface alloy stands out as the system with largest Rashba parameters, i.e., momentum offset, Rashba energy, and Rashba constant [2]. For these ordered surface alloys with giant spin splittings, there are open questions regarding the spin polarization and the sign of the effective mass of the unoccupied surface bands. Our study on Bi/Ag(111), covering the whole surface Brillouin zone, shows the $E(k_{\|})$ dispersion of several unoccupied surface bands with distinct spin polarization.

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Depth- and Orbital-resolved ARPES of Buried Layers and Interfaces in Oxide Superlattices Via Soft X-ray Standing-wave Excitation

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ABSTRACT

Traditional angle-resolved photoemission spectroscopy (ARPES) in the roughly 50-150 eV regime is a well-established and powerful technique, enabling the direct measurement of the valence electronic structure of materials. However, in many applications, its high surface sensitivity can make it difficult to discern true bulk or buried layer/interface properties. Soft x-ray ARPES in the roughly 400-1500 eV regime has thus been introduced to probe more deeply below the surface [1]. Here we introduce a new depth-selective photoemission technique by combining soft x-ray ARPES with standing-wave (SW) excited photoelectron spectroscopy (SWARPES), wherein the intensity profile of the exciting x-ray radiation is tailored within the sample to be a standing wave that can be scanned through the sample [2,3]. We have applied this SWARPES technique to the investigation of the electronic properties of multilayer oxide samples so as to characterize the buried interface within the magnetic tunnel junction system $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ and an epitaxial $SrTiO_3/LaNiO_3$ superlattice of relevance to low-dimensional heterostructuring and Mott-transition devices. The data include variable-polarization measurements that, together with calculated orbital-specific differential photoelectric cross sections [4], permit identifying orbital components in the spectra. The ARPES data is also compared to state-of-art one-step photoemission theory including matrix element effects [5,6].

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Metal-insulator Transition of $LiRh_2O_4$ Observed by Extremely Low Energy Photoemission and HAXPES

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ABSTRACT

$LiRh_2O_4$ shows the metal-insulator transition (MIT) at 170 K when the temperature is decreased via an intermediate phase, which appears below 230 K and is ascribed to the band Jahn-Teller instability [1]. We have performed combined study of Hard X-ray photoemission (HAXPES) [2] and extremely low energy photoemission (ELEPES) with a Xe discharged lump [3,4]. In both HAXPES and ELEPES spectra, clear spectral changes across the MIT are observed in the valence band near the Fermi level (E_F). Slight spectral changes are also observed across 230 K, induced by the orbital ordering. Temperature dependence accompanied with these phase transitions was also observed in the Rh 3d core level spectra accompanied with these phase transitions. Moreover, the linear polarization dependence of the HAXPES spectra enables us to semiquantitatively evaluate the contribution of the Rh 5*s* state hybridized with the O 2*p* states in the valence band.

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Evidence of Constant U across Metal-insulator Transition and Fermi Surfaces of V_2O_3 Revealed by HAXPES and Micro Soft-X-ray ARPES

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ABSTRACT

$(V_{1-x}Cr_x)_2O_3$ is a paradigmatic example of Mott-Hubbard metal-insulator transition (MH-MIT) materials with a very rich phase diagram as a function of temperature, pressure and Ti- or Cr-doping[1]. To reveal the mechanism of MIT, we have performed high-resolution hard-x-ray photoemission spectroscopy in the paramagnetic metal, paramagnetic insulator, and antiferromagnetic insulator phases. The quality of the spectra enables us to conclude that the essentially degenerate LHB for all three phases yields strong evidence that the on-site Coulomb energy U stays constant through the MIT [2]. Since V *3d* orbital occupation has been reported to change through all phase transitions [3], our finding verifies that the changing Uc/W in an orbital selective Mott transition [4,5] is the only currently viable scenario for the MIT in $(V_{1-x}Cr_x)_2O_3$.

To reveal further the driving force of MIT, it is important to discuss its origin with the direct comparison between the modern theories based on the realistic model and the band structures and Fermi surfaces determined by high accuracy bulk sensitive angle resolved photoemission (ARPES). Nevertheless, only few works [6,7] have so far been reported on the ARPES spectra due to the difficulty to obtain good enough cleaved clean surface for ARPES. To overcome this technical problem, we have utilized the micro soft-X-ray ARPES techniques with well-focused soft X-ray beam (~50 μm) and a long working-distance microscope [8]. In the paramagnetic metal phase, we have revealed Fermi surfaces, one of which is made of a small electron pocket around the Γ point in the metallic phase by sweeping the photon energies.

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ARPES and the Pseudogap Phase of the Cuprate Superconductors

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ABSTRACT

In the under-doped or pseudo-gap phase of the cuprate superconductors, a significant portion of the Fermi surface is still gapped at temperatures above the transition temperature Tc. Further instead of a closed Fermi surface, photoemission studies indicate that the low-energy electronic excitations appear to form Fermi arcs separated by gapped regions. Here we report high-resolution photoemission studies of this underdoped regime [1,2]. A new analysis points to the possibility that the Fermi arcs may in fact be one side of Fermi pockets, consistent with the underlying nature of the spin liquids in these materials. By examining a range of reduced doping levels down into the non-superconducting regime, below 5% doping level, it appears that the areas of the hole pockets scale with the doping level consistent with models such as the YRZ ansatz. A particle-hole asymmetry observed in the nodal region is clear evidence that electron pairing does not originate from the Fermi arcs in the normal state. However in contrast the particle-hole symmetry observed in the anti-nodal region is interpreted as evidence for singlet pairs forming along the copper-oxygen bond directions at temperatures above the superconducting transition temperature Tc.However with the onset of long range phase coherence superconductivity emerges on the hole pockets in the nodal region.

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Ultrafast Quasi-particle Dynamics in the Heavy-fermion Compound $YbRh_2Si_2$

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ABSTRACT

Understanding strongly-correlated rare-earth intermetallic compounds requires knowledge of the nature of the fermionic quasiparticles in states near the Fermi level, E_F. We report on a pump-probe experiment using femtosecond time- and angle-resolved photoemission spectroscopy to determine lifetimes of hot quasiparticles in the heavy-fermion compound $YbRh_2Si_2$. An unoccupied band with electron-like dispersion and a band bottom 0.2 eV above E_F was identified at Γ, in agreement with band structure calculations for the subsurface region. Hot quasiparticle lifetimes from 30 to 80 fs were found for energies between 0.4 and 0.1 eV above E_F. These lifetimes generally follow the typical monotonous increase towards E_F, in agreement with earlier studies on Yb and Rh elemental metals. However, at normal emission the quasiparticle lifetimes at around 0.2 eV exceed this trend by about +20 fs. This difference decreases with increasing photoemission angle and can be assigned to the particular band that is probed in $YbRh_2Si_2$. Potential microscopic scenarios are discussed.

A Tunable Spin-helical Topological Surface State in Ternary Topological Insulator $TlBiSe_2$

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ABSTRACT

Topological insulators (TIs) with a Dirac cone-like surface state forming a helical spin texture are known as a fertile ground to realize new exotic physical phenomena [1]. Up to now, the spin-polarized topological surface states (TSSs) of binary chalcogenides were intensively studied by angle-resolved photoemission spectroscopy (ARPES) [1-3] and spin-resolved ARPES (spin-ARPES) [4-6]. However, the experimentally observed spin polarization was obscured below the crossing point, so called Dirac point (DP). This result can be caused by their characteristic band structure buried in the bulk valence band below DP. The lack of topological nature near the DP could be a serious problem for spintronic applications. Therefore, the search for more ideal TI possessing an energetically isolated TSS from bulk band around DP is strongly required.

Recently, ternary chaldogenide $TlBiSe_2$ was discovered to be one of the most promising TIs with a single TSS [7-9]. Especially, in our previous ARPES study [7], the TSS was found to be energetically isolated well from the bulk state near the DP in contrast to the binary compounds.

Here, we report, for the first time, a Fermi level tuning of spin-helical TSS of $TlBiSe_2$ by means of ARPES and spin-ARPES techniques. The experiment was performed with synchrotron radiation at Efficient Spin Resolved Spectroscopy Observation (ESPRESSO) system of Hiroshima Synchrotron Radiation Center. Our spin-ARPES measurement with variable light polarizations has revealed clear spin polarizations with helicity reversal with respect to the DP in the TSS. Importantly, the Fermi level has been successfully tuned into the topological transport regime across to the DP for this compound. This result paves a pathway to realizing an ambipolar gate control for future spitronic devices.

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Atom-specific Spin Mapping and Buried Topological States in the Topological Insulator $PbBi_4Te_7$

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ABSTRACT

A topological insulator is a state of quantum matter that, while being an insulator in the bulk, hosts topologically protected electronic states at the surface. These states open the opportunity to realize a number of new applications in spintronics and quantum computing. To take advantage of their peculiar properties, topological insulators should be tuned in such a way that ideal and isolated Dirac cones are located within the topological transport regime without any scattering channels.

Here we report ab-initio calculations, spin-resolved photoemission and scanning tunneling microscopy experiments that demonstrate that the conducting states can effectively tuned within the concept of a homologous series that is formed by the binary chalcogenides (Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3), with the addition of a third element of the group IV.

On the example of $PbBi_4Te_7$ we show peculiar properties which arise with the additional lead atom. The crystal structure is built up of alternating quintuple (Bi_2Te_3) and septuple ($PbBi_2Te_4$) layers, leading to two possible surface terminations, which is confirmed by our STM measurements. Strikingly, our ab-initio calculations predict that the topological surface state is mainly localized in the top-most septuple layer independently of the surface termination, but showing termination-characteristic dispersion. Our angle-resolve photoemission (ARPES) data, however, show only the characteristic features of a quintuple-layer-terminated surface, indicating that the surface state is deeply buried under the surface and thus gains additional protection from external perturbation.

In addition we show by spin-resolved ARPES measurements that the strong hexagonal warping of the topological surface state is accompanied by an altering of its spin structure. The observed three-fold oscillatory out-of-plane spin polarization is in agreement with previous theoretical predictions [2].

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Disentanglement of Surface and Bulk Rashba Splittings in Non-centrosymmetric BiTeI

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ABSTRACT

BiTeI has a layered and non-centrosymmetric structure where strong spin-orbit interaction leads to a giant spin splitting in all bands of the bulk band structure, as was predicted by ab-initio calculations [1].

Even though BiTeI has a non-centrosymmetric crystal structure, time-reversal symmetry ensures the bulk band structure to be inversion symmetric around the time-reversal invariant momenta, when neglecting spin. However due to the missing inversion symmetry of the crystal, there are two opposite, non-equivalent surface terminations.

Here we show that the recently reported two-dimensional state at Fermi level [1] is not a quantum well state but a surface state. In fact, both surfaces host an electron- and a hole-like surface state, respectively. The surface state character is proven by spin-resolved UV-ARPES measurements and is supported by ab-initio calculations. More recent publication corroborate this interpretation [2].

Due to photoemission matrix element effects in the UV regime the hole-like surface state overshadows the bulk conduction band. Here we present the first ARPES data on BiTeI in the soft x-ray regime where the spectral intensity of the surface state is very low. The data clearly show the three-dimensional dispersion of the Rashba-type spin-split bulk conduction band, revealing the complex shape of the bulk Fermi surface induced by spin-orbit interaction. It takes the shape of a torus or a spindle-torus, depeding on the position of the Fermi level. Comparison of these soft x-ray data with our UV-ARPES measurements allows to disentangle the surface from the bulk electronic structure.

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Rutile and Anatase TiO_2 – Natural Linear Dichroism at the O *K* Edge – Polarisation and Geometry Dependent X-ray Absorption and X-ray Emission Spectroscopies

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ABSTRACT

The two most frequently occurring polymorphs of titanium dioxide, rutile and anatase, are studied by polarisation and geometry dependent x-ray absorption (XAS) and resonant x-ray emission spectroscopies (RXES or RIXS) at the oxygen *K*-edge. Polarisation dependent XAS applied to single crystal samples reveals a natural linear dichroism arising at the O K-edge due to the sp^2 hybridisation of the oxygen anion and the trigonal coordination of the anion by three titania atoms in Ti_3O planes. Anatase and rutile, both tetragonal crystals, have these Ti_3O planes all parallel to the *c*-axis, although bond-angles within these planes as well as the respective TiO_6 octahedra and their connectivity differ considerably. The highly oriented bonding between the Ti metal *d* (both $e_g^2sp^3$ and t_{2g} orbitals) and ligand sp^2 orbitals gives σ-like and π-like Ti-O chemical bonds[1] giving rise to the natural linear dichroism which exhibits itself differently between the two polymorphs.

Non-resonant O *K*-edge x-ray emission from each polymorph exhibits an emission-like natural linear dichroism which is sensitive to the relative orientation of the single crystal and the x-ray emission spectrometer. Further, resonant x-ray emission spectroscopy (RXES or RIXS) is symmetry and state-selective, i.e. *k*-selective, and thus offers further insight into the occupied electronic structure where the natural linear dichroism in the RIXS intermediate state can be exploited to full effect. Four possible relative orientations of the linear polarisation, crystal axes, and x-ray emission spectrometer give differing energy dependent RXES spectra. Electronic structure calculations using density functional theory, specifically the full potential linearized augmented plane wave (FP-LAPW) code as implemented in WIEN2k[2], were used to calculate both the rutile and anatase electronic structure and to simulate the energy dependent *k*-selective O *K*-edge RXES. The successful comparison of these simulations with the O *K*-edge RXES allows for a further insight into the occupied electronic structure of these polymorphs of TiO_2. These results will inform current and future XAS and RIXS investigations of both TiO_2 nanoparticles and TiO_2 surfaces and interactions.

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Rutile and Anatase TiO_2 – Natural Linear Dichroism at the Ti *L* Edge – X-ray Absorption, Unoccupied States and *2p-3s* X-ray Emission Spectroscopies

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ABSTRACT

The two most frequently occurring polymorphs of titanium dioxide, rutile and anatase, are studied here by polarisation and geometry dependent x-ray absorption (XAS) and resonant x-ray emission spectroscopies (RXES or RIXS) at the titanium *L*-edge. The details of the *2p-3d* XAS spectra have long been described both in rutile and anatase TiO_2 by atomic multiplet theory[1]. In all previous XAS studies no natural linear dichroism had been reported excepting in electron energy loss studies[2]. Polarisation dependent XAS applied to single crystal samples reveals a natural linear dichroism arising at the Ti *L*-edge due to both the D_{2h} point group symmetry of the Ti cation as well as the anisotropic chemical bonding with the ligand anions, this arising from the sp^2 hybridisation of the oxygen anion and the trigonal coordination of the anion by three titania atoms in Ti_3O planes[3]. The differing Ti-O bonds in the TiO_6 octahedra whereby the Ti $e_g^2sp^3$ hybrid orbitals form σ-like bonds with the O sp^2 orbitals result in differing *2p-3d* transition matrix elements when linearly polarized light is either parallel to or perpendicular to the respective *c*-axes in these tetragonal systems. Comparison is made to both atomic multiplet calculations and to the results of density functional theory calculations of the electronic structure of these systems.

It is further instructive to consider the *2p-3s* resonant inelastic x-ray scattering (RIXS) from this system, which similarly to that previously observed in CaF_2, is sensitive to the orbital character of the intermediate state in the *2p-3d* XAS spectrum[4]. A detailed discussion of the differing electronic structure of the intermediate states in rutile and anatase TiO_2 is supported by the calculated bandstructures of the unoccupied *d*-orbitals in both of these systems. Finally, comparisons are made between the *2p-3d* RIXS spectra and more recent higher resolution data which have been recently published.[5]

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Polarisation Dependent XAS and RXES of Rutile Difluoride MgF_2 at the Fluorine *K*-edge

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ABSTRACT

Rutile tetragonal MgF_2 like its transition metal difluoride counterparts, MnF_2, VF_2, FeF_2, CoF_2, NiF_2, and ZnF_2 is a a large band gap insulator. It is widely used in optics research and instrumentation but its' electronic structure has been seldom studied by x-ray spectroscopy, in spite of its abundance and availability. In addition, ab initio calculations of the electronic structure of MgF_2 are not as prevalent as for other rutile fluoride or oxide compounds.

A polarisation dependent x-ray spectroscopic study of the electronic structure of an oriented bulk single crystal of MgF_2, using x-ray absorption spectroscopy (XAS) and resonant x-ray emission spectroscopy (RXES) measured at the fluorine *K*-edge, is presented here. The measurements in each case are compared with original electronic structure calculations made using density functional theory (DFT) and the full potential linearized augmented plane wave (FP-LAPW) approach implemented through WIEN2k.

A natural linear dichroism, or polarisation dependence, of the F *K*-edge XAS spectrum is observed in MgF_2 in line with expectations derived from other rutile metal oxides studied in this manner and from consideration of the chemical bonding in this material. The natural linear dichroism arises due to the sp^2 hybridisation of the fluorine anion and the orientation of all of the trigonally coordinated Mg_3F planes parallel to the rutile *c*-axis. Analysis of both non-resonant XES spectra and the symmetry-selective, geometry dependent and *k*-selective RXES spectra, which are obtained with differing relative orientations of the crystal axes and XES spectrometer, allow for a complete deconstruction of the occupied MgF_2 F *2p* partial density of states (PDOS) from experimental considerations alone, not only into the σ-like and π-like components but into three orthogonal projections. These experimental measures agree closely with the predicted PDOS derived from the DFT calculations. In terms of the details of the chemical bonding, bandstructure and observed RXES, rutile MgF_2 is an effective electronic analogue of rutile SnO_2. This is not the case for the other rutile transition metal difluorides.

Promising Topological Surface States with Persistent High Spin Polarization across Dirac Point in Bi_2Te_2Se and Bi_2Se_2Te

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ABSTRACT

Three-dimensional topological insulators (3D TIs) with massless helical Dirac fermions at the surface in a bulk energy gap have attracted a great attention as key materials to revolutionize current electronic devices. Among the established 3D TIs, Bi_2X_3 (X=Se, Te) has been mostly studied because of their relatively large energy gap and the simplest topological surface state (TSS). The spin-momentum locking feature is experimentally proved at least for the upper-lying TSS by spin- and angle- resolved photoemission spectroscopy with widely spread values of raw spin polarizations (20-80%) [1], but clear spin polarizations are obscured near and below the Dirac point (E_D). The scanning tunneling spectroscopy for Bi_2Se_3 under a perpendicular magnetic field has revealed the peculiar Landau levels (LL) for upper part of TSS. However, such characteristic LLs are missing below E_D [2]. These features obviously tell us that topological nature of the material survives only in the upper part of TSS but is no longer available below E_D in Bi_2Se_3 and Bi_2Te_3. The absence of such a topological nature at TSS below E_D could be a disadvantage for extending its spintronic applications.

Recently, one of the ternary tetradymite compounds, Bi_2Te_2Se, where the central Te layer is replaced with the Se layer in Bi_2Te_3, was shown to be a 3D TI by the ARPES measurement [3]. Importantly, the suppression of the bulk conductivity is anticipated because the well-confined Se atoms in the central layer are expected to suppress the Se vacancy as well as the antisite defects between Bi and Te atoms. Actually, a highly bulk resistive feature in this compound has successfully led to the observation of its surface-derived quantum oscillations in the magnetotransport experiment [4].

We have unambiguously clarified the helical spin texture and the spin polarizations of TSS in Bi_2Te_2Se and Bi_2Se_2Te for the first time by the state-of-the-art spin- and angle- resolved photoemission spectroscopy (SARPES) [5]. The markedly high spin polarization of topological surface states has been found to be •77% and is persistent in the wide energy range across the Dirac point in those compounds. The availability of both upper and lower TSSs promises to extend the variety of spintoronic applications, for instance, to the dual gate TI device and the topological p-n junction.

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Theory of Resonant Inelastic X-ray Scattering for Magnetic Excitations in Cuprates

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ABSTRACT

Recently, resonant inelastic x-ray scattering (RIXS) has been proved to be effective, complementary to inelastic neutron scattering (INS), to probe the magnetic excitation in many fascinating systems [1]. We investigate the magnetic excitation spectra of Cu $L_{2,3}$-edge RIXS in quasi-one-dimensional systems like spin chain and spin ladder. Different from the Cu K-edge event[2,3], the Cu L-edge event is affected by strong spin-orbit coupling of core hole in the intermediate state of the second order dipole process [3,4]. Appling the projection method, we have derived the formulae of the magnetic RIXS spectra, which consist of one- and two-spin correlation functions. Although the former is also found in the conventional theory of INS, it has a characteristic dependence on the transferred momentum since our treatment includes excitations from the neighboring site as well as core-hole site. The latter is specific to RIXS [5].

As examples of the interpretation of the experimental magnetic RIXS spectra, we apply our theory to spin chain (Sr_2CuO_3) and two-leg spin ladder ($Sr_{14}Cu_{24}O_{41}$) systems [6]. The results show that our theory captures semi-quantitatively well the characteristic dispersive behaviors of the observed RIXS spectra of the magnetic excitations [7]. In addition, several possibilities, for instance, the observation of the two-spin correlation function in RIXS experiment and the so-called one-triplon excitation in the spin-ladder system are proposed. It is demonstrated that our theory is relevant whether or not the ground state preserves rotational invariance in spin space [5,7].

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Unoccupied Surface States of Topological Insulators

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ABSTRACT

Topological insulators (TIs) are characterized by a symmetry-induced metallic surface state [1] which has been predicted to give rise to novel spin transport phenomena. Model TIs under discussion at present are bismuth chalcogenides, which are intrinsically p-doped. The occupied part of their band structure is well-studied [2] by spin- and angle-resolved photoemission experiments.

Here we focus on unoccupied topological surface states. By use of pump-probe techniques, namely two-photon photoemission, access to the energetics and the dynamics of those states is granted. It is shown that spin-orbit coupling induced and symmetry-inverted local band gaps above the Fermi level can support a topological surface state. In the experiment a linearly-dispersive feature is found with a Dirac point 1.32 eV (1.12 eV) above the Fermi level in case of Bi_2Se_3 (Bi_2Te_2Se). Calculations and circular dichroism measurements demonstrate the expected helical spin structure. In case of Bi_2Te_3 this topological surface state is absent, indicating that the central Se is essential for the symmetry-inversion for the corresponding band gap.

The new-found states allow for sudies of the dynamics of electrons in excited topological states that are accessible by optical excitation.

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Bulk-sensitive Photoelectron Spectroscopy of $TlFe_2Se_2$
~The Parent Compound of Iron-selenide Superconductor~

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ABSTRACT

Since an Ion-based superconductor (IBSC), $LaFeAsO_{1-x}F_x$ was synthesized in 2008, IBSCs are known to have the 2nd highest transition temperature (T_c) after the cuprates in superconducting materials [1]. $TlFe_2Se_2$ has the $ThCr_2Si_2$-type crystal structure similar to one of the IBSC parent compounds, $BaFe_2As_2$ (so-called 122 system), and shows superconductivity induced by Fe defects ($TlFe_{1.7}Se_2$ with T_c=33K) [2]. Interestingly, most of the IBSC parent compounds are metallic but $TlFe_2Se_2$ is insulating like cuprate superconductors as shown by the *rho*-T experiment [3]. Theoretical studies, however, predict that $TlFe_2Se_2$ is an anti-ferromagnetic(AFM) semimetal whereas Fe-deficient $TlFe_{1.5}Se_2$ is an AFM insulator and point out that the semimetal-insulator transition might be the Mott transition induced by the Fe defect [4]. In order to reveal the detailed bulk electronic structures of $TlFe_2Se_2$ and resolve the discrepancy between the so-far-reported experimental and theoretical results, we have performed soft-x-ray, hard-x-ray, and extremely-low-energy photoemission spectroscopy (SXPES, HAXPES, and ELEPES). The valence band and Fe 2*p* core-level photoemission spectra clearly show the band gap and a strong intensity of the charge-transfer-satellite peak, respectively. We will discuss the electron correlation effects with the help of the band structure calculations and the configuration-interaction cluster model calculations for these spectra.

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Spin Polarized Topological Surface States in Ge Based Ternary Chalcogenides

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ABSTRACT

Topological insulators (TIs) can be distinguished from conventional insulators by having the surface state with a massless Dirac dispersion in the bulk energy gap. The spin orientation of this surface state is locked with its crystal momentum which results in a helical spin texture. By these unique characters, TIs have received great attention both from fundamental physics and application fields [1].

Recently, $GeBi_2Te_4$ (GBT) was predicted to have a single topological surface state (TSS) [2], which was later observed by angle resolved photoemission spectroscopy (ARPES) [3]. However, important features of TI including the size of bulk band gap and the spin polarization feature have not yet been confirmed.

Motivated by this, we have firstly evaluated the bulk band gap by photon energy dependent ARPES measurement ($h\nu$=60-84eV) at the linear-undulator beam line (BL1) of Hiroshima Synchrotron Radiation Center (HiSOR). From this experiment, we demonstrate that the size of bulk band gap is about 170meV. Second, we have studied the spin polarization feature of TSS in GBT by means of spin- and angle-resolved photoemission spectroscopy (spin-ARPES) with newly developed ESPRESSO machine (VLEED spin detector) [4] attached to BL-9B of HiSOR. The measurement has been carried out in $^{-},\tilde{\Gamma}^{-},M$ line of surface Brillouin Zone (SBZ) excited with the He discharged lamp ($h\nu$=21.2eV). In the experiment, the bulk conduction band intensity dominates near the TSS in the 1st SBZ, while it is well suppressed in the 2nd SBZ. In measuring the spin polarization of TSS, it is preferable to avoid the influence of conduction band, which let us perform the spin-ARPES experiment at the 2nd SBZ. As a result, a clear anti-symmetric spin polarization with respect to the $^{-},\Gamma$ point has been successfully observed. The values of polarization are found to be about 60%, which is almost the same as that of Bi_2Te_3 [5].

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X-ray Absorption Spectroscopy of Double-Perovskite Co Oxides with High-spin Configuration

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ABSTRACT

$3d^6$ electrons of Co^{3+} in compounds can realize various spin configurations such as low-spin (LS) and high-spin (HS) states. Among of them, a perovskite Co oxide of $LaCoO_3$ has been known as a spin-crossover material [1]. This crossover is still under controversy whether or not the intermediate-spin (IS) state ($t_{2g}{}^5e_g{}^1$) is realized between low-temperature (T) LS ($t_{2g}{}^6$) and high-T HS ($t_{2g}{}^4e_g{}^2$) phases [2,3]. To investigate 3*d* electron-spin configurations in transition metal (TM) compounds, x-ray absorption spectroscopy (XAS) is a powerful tool because TM *L* and O *K* XAS are very sensitive to them. In $LaCoO_3$, nevertheless, XAS spectra with each spin state have not yet been established owing to its crossover nature. In particular, the XAS determination of spectrum of purely HS Co^{3+} is highly desired for clarifying the spin-crossover in $LaCoO_3$ because the HS state is dominant only at highest *T*'s. Recent XAS studies [4] reported evidences for the HS ground state in Sr_2CoO_3Cl and $BiCoO_3$. However, the ligand coordination in these compounds was not CoO_6-octahedral (O_h) but CoO_5-pyramidal (C_{4v}), thus the results cannot be directly compared with the $LaCoO_3$ case. In this paper, we report XAS of double-perovskite Sr_2CoMO_6 (M = Sb, Nb, Ta) and its relatives, which are all possible HS Co^{3+} oxides without the spin-crossover [5]; the observed Co *L* edge spectra agreed with the cluster-model calculation for HS Co^{3+} under the O_h symmetry well, demonstrating that we have established the XAS spectra of HS perovskite Co oxides for the first time. In addition, the O *K* edge spectra exhibited a double peak reflecting the ligand field splitting of the Co 3*d* orbital, namely 10*Dq*. We found that estimated 10*Dq* values systematically scaled to the Co-O length of each compound. This result experimentally confirms that the simple ligand field theory picture is valid, i.e., a longer Co-O length causes a smaller 10*Dq* and hence the HS ground state.

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Observation of Spin-orbital Separation in Sr_2CuO_3 Spin Chains with Resonant Inelastic X-ray Scattering

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ABSTRACT

Resonant Inelastic X-ray Scattering (RIXS) is a powerful probe of excitations from the electronic ground state in transition-metal oxides. In this talk we present high-resolution RIXS studies of magnetic and electronic excitations in the low dimensional spin chain system Sr_2CuO_3 performed at the ADvanced RESonant Spectroscopies (ADRESS) beamline of the Swiss Light Source with the SAXES spectrometer [1].

In general, quantum effects become important when the space symmetry is lowered. In the extreme case of one-dimensional-materials the electron can break up into separate quasi-particles, i.e., spinons, holons and orbitons that carry their respective spin, charge and orbital degrees of freedom [2]. Sr_2CuO_3 is an ideal realization of the one-dimensional Heisenberg spin-1/2 chain. When an electron is removed from this spin-chain one can for instance observe how spin and charge degrees of freedom are splitting in the so called spin-charge separation mechanism [3].

Our Cu L_3-RIXS measurements on Sr_2CuO_3 reveal the fractionalization of magnons into two-spinons and higher order excitations as previously reported from neutron scattering [4]. Furthermore, we observe the splitting of an orbital excitation into the independently propagating spinon and orbiton quasi-particles [5]. This newly observed spin-orbital separation phenomenon gives thereby rise to strongly dispersive orbital excitations (orbitons) [5,6].

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Unusual Temperature Dependent Spectral Weight near the Fermi Level of NdNiO3

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ABSTRACT

We investigat the behavior of the spectral weight near the Fermi level of NdNiO3 thin films as a function of temperature across the metal-to-insulator transition (MIT) by means of ultraviolet photoelectron spectroscopy. The coexistence of metallic and insulating domains during the transition is demonstrated by a thermal hysteresis in the spectral weight at the Fermi level. A progressive analysis of the temperature dependence further reveals two distinct regimes of spectral loss close to the Fermi level. One regime is directly connected to the MIT, while the other is found to be independent from the MIT and probably correlated to changes in the magnetic state.

Excited Electronic States on Epitaxial Graphene Studied by Two-photon Photoemission Spectroscopy

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ABSTRACT

Recently, extensive studies have been performed for electronic state of graphene due to its fascinating electronic structure or transport property. However, many concerns to date have been paid mainly for occupied electronic state close to the Fermi level which locates at K-bar point of surface Brillouin zone (SBZ) [1, 2]. In addition to the knowledge about the occupied electronic state at thermal equilibrium, transient electron dynamics in unoccupied electronic states are also of great importance, since electrons excited to unoccupied states play important roles in electrical and optical properties. Up to now, while excited electron dynamics on epitaxial graphene has been studied by optical pump-probe methods, direct measurement of transient population in unoccupied electronic state has not been performed. In this work, occupied and unoccupied electronic states have been studied by angle-resolved one-photon and two-photon emission (2PPE) spectroscopy, respectively.

Experiments were performed on the beamline BL13 at the SAGA Light Source. The epitaxial graphene samples that were grown in a separate vacuum chamber were cleaned by heating at 400°C for 14 h in the preparation chamber at about 2×10^{-8} Pa. The surface cleanliness and the thickness of graphene layers were checked by the high resolution core-level and valence band photoemission measurements with synchrotron radiation. We used photon energies of 680 and 40 eV, for core-level and valence band photoemission measurements, respectively. The work function of 4.24 eV obtained for a monolayer graphene is slightly smaller than the value of 4.47eV for thicker graphene layers and 4.49eV for HOPG [3]. Time- and angle-resolved 2PPE spectra were measured using frequency doubled and tripled light of from the Ti:sapphire regenerative amplifier.

From the angle-resolved 2PPE measurement at polar emission angles between -20° and 20°, it was found that this state shows the parabolic band dispersion with an effective mass of unity and ascribed as the first even-symmetry image-potential state (IPS). The binding energy of this IPS with $n^+=1$ is in accordance with recent theoretical report [4]. The binding energy of IPS shifts to vacuum level with increasing the layer thickness and converges to the IPS on graphite [3]. The transient population in the unoccupied π^*-band was elucidated from the time-resolved 2PPE spectra. The lifetime of the excited electrons the unoccupied states depend on their binding energy and number of graphene layers.

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Observation of Raman Components in Resonant X-ray Emission Spectra of Fe cyanide

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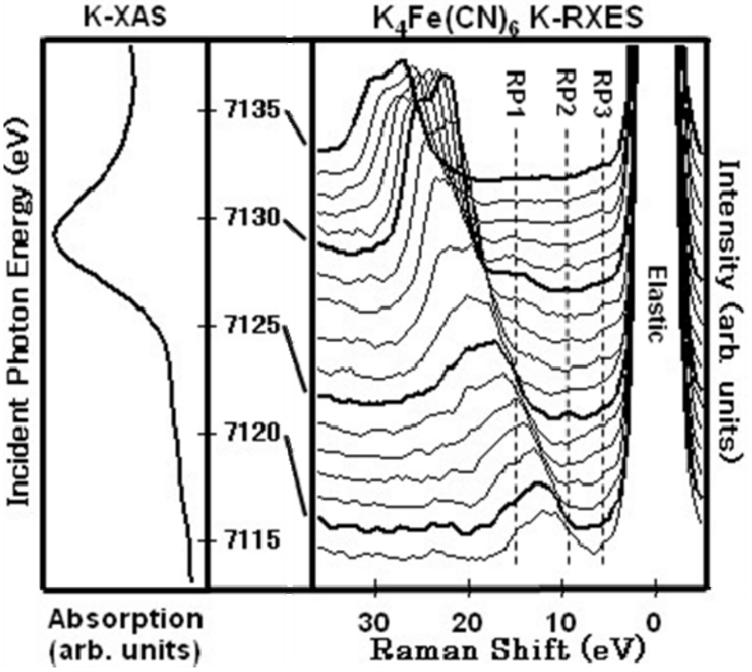
ABSTRACT

In recent years, development of a functional material is progressing. One of the strong candidates is Prussian blue analogues, which are composed of a 3-D network structure in which the transition-metal ions are strongly bridged by cyano groups [1,2]. The characteristics of the electronic states of cyanides are competition of ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT). The importance of MLCT was confirmed both experimentally and theoretically in transition-metal 2p X-ray absorption spectra (XAS) [3-5]. However, the theoretical parameters, Fe 3d-3d Coulomb interaction, for reproducing the experiments are quite different in these two papers [4,5]. In order to verify the theoretical predictions, we have carried out resonant X-ray emission spectra (RXES) measurements around Fe K absorption-edge for Fe cyanide, $K_4Fe(CN)_6$ as standard sample of Prussian blue analogues. Left figure indicates Fe K-XAS and Fe K-RXES results. Three Raman peaks were observed as shown by broken lines in the right panel. These peaks are close to those of MLCT and LMCT predicted by Nanba and Okada [5].



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Photoemission Studies of Kondo Lattice Compounds YbNi$_3$(Ga$_{1-x}$Al$_x$)$_9$ (x= 0, 0.05, 0.1, 0.15, 1)

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ABSTRACT

Recently, new isostructural Kondo lattice compounds YbNi$_3X_9$ (X=Al, Ga) were discovered [1, 2]. YbNi$_3X_9$ possesses ErNi$_3$Al$_9$-type crystal structure [3], and Al and Ga ions are isovalent with nominal valence electron configurations of ($3s^23p^1$) and ($4s^24p^1$), respectively. In spite of the same crystal structure and similar valence electrons, YbNi$_3$Al$_9$ is an antiferromagnetic heavy-fermion system with T_N=3.4 K, while YbNi$_3$Ga$_9$ is a valence fluctuating system [1, 2]. Therefore, YbNi$_3X_9$ is considered to be one of the most ideal systems to investigate the difference in the electronic structures between an antiferromagnetic heavy-fermion system and a valence fluctuation system. In this study, we carried out hard x-ray and vacuum ultraviolet photoemission spectroscopies (HAXPES and VUVPES) on YbNi$_3$(Ga$_{1-x}$Al$_x$)$_9$ (x= 0, 0.05, 0.1, 0.15, 1) to investigate the Yb valence and Kondo resonance behavior.

Single crystalline YbNi$_3$(Ga$_{1-x}$Al$_x$)$_9$ was grown by self-flux method [1,2]. The HAXPES and VUVPES measurements with hν= 5.95 keV and 7-24 eV were performed at the undulator beamlines BL15XU of SPring-8 and BL9A at Hiroshima Synchrotron Radiation Center, respectively.

The Yb 3*d* HAXPES spectra showed that the Yb valence of YbNi$_3$Al$_9$ was almost trivalent, while that of YbNi$_3$Ga$_9$ strongly fluctuated with the averaged Yb valence of 2.5 [4]. The Al substitution for YbNi$_3$Ga$_9$ changed the Yb ions toward trivalent states, which suggests the decrease of the conduction-band electrons and 4*f* electrons (*c-f*) hybridization. The VUVPES spectra of YbNi$_3$Ga$_9$ clearly exhibited Kondo resonance peak near the Fermi level (E$_F$), and the peak was shifted toward E$_F$ and the intensity increased with lowering temperature. The extrapolated peak energy at zero temperature provides T_K~ 600 K for YbNi$_3$Ga$_9$. With increasing Al concentration on YbNi$_3$Ga$_9$, the Kondo resonance peak was shifted toward E$_F$, indicating decrease in T_K. In addition to the change of Yb valence and Kondo resonance energy, we also observed the chemical shifts of Ni 2*p* and Ni 3*d* states toward the deeper binding-energy side with increase in Al concentration. These energy shifts suggest that E$_F$ of the Ni-derived conduction-band density of states is shifted toward the deeper energy side by Al substitution.

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Extreme Ultraviolet Time Resolved ARPES of a Doped Topological Insulator

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ABSTRACT

Topological insulator (TI) is a new class of materials which has spin polarized metallic surface states due to reasons of the topology of the band structure [1]. This new materials system is therefore a promising platform for novel spintronic device functions. There are various attempts to control the surface spin currents through field effect, light, etc. to function the surface of TIs. To this end, it is very important to elucidate the detailed mechanism of interaction between the external stimuli and the surface of TIs.

We performed extreme ultraviolet time-resolved ARPES on a doped TI, $Cu_{0.17}Bi_2Se_3$, and investigated the microscopic interaction of lasers and TI surface from a non-equilibrium standpoint. We observed photo-induced change of the spectral intensity not only around Fermi level, but also throughout the valence-band region. Particularly, the surface states exhibited strong spectral-intensity modulation. The results can be understood through a new mechanism of photo-electric effect from surface involving surface polarization [2]. We also recorded time-resolved ARPES of graphite and find that the photoinduced modulation of spectral intensity is considerably small compared to the of $Cu_{0.17}Bi_2Se_3$.

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Bulk-sensitive Photoemission Study on Sr_2IrO_4

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ABSTRACT

Novel physics induced by strong spin-orbit coupling has attracted a lot of attention from both theoretical and experimental aspects in recent years. A strontium iridate Sr_2IrO_4 has a canted antiferromagnetic (or weakly ferromagnetic) insulating state which seems to be driven by three effects, that is, the strong spin-orbit coupling, lattice distortion, and relatively weak Coulomb interaction.[1,2] The electronic structures near the Fermi level in Sr_2IrO_4 are characterized by the j_{eff}=1/2 states which have a partially quenched, but still a finite angular momentum derived from the strong spin-orbit coupling. In contrast, a strontium rhodate Sr_2RhO_4 has a correlated metallic state due to the weaker spin-orbit coupling.

In order to provide a deeper insight into the spin-orbit-coupling induced states, we have carried out high-energy-resolution photoemission spectroscopy with hv=8.4-8000 eV photons for Sr_2IrO_4 and Sr_2RhO_4. The photoemission spectroscopy in a wide range of excitation photon energies enables us to identify the bulk and surface electronic structures including their origins in the valence band. Both the hard-x-ray photoemission and the extremely-low-energy photoemission spectroscopy (HAXPES and ELEPES) measurements demonstrate the zero-gap semiconducting feature in the occupied state, suggesting an asymmetric band gap in Sr_2IrO_4. This result is consistent with recent theoretical calculations.[3,4]

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Topological Surface of Bi_2Se_3 with Magnetic Impurities Probed by STM, ARPES and XMCD

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ABSTRACT

Topological insulators (TIs), possessing a gapless surface electronic state with spin helical texture, have invoked intensive interests in both experimental and theoretical research fields [1-3]. Most interesting properties appear when the surfaces of TIs are interfaced with ferromagnetic layers. In such system, due to a broken time-reversal symmetry, novel physical phenomena are expected to emerge [4].

In this work, we studied the surface electronic states of topological insulator Bi_2Se_3 in the presence of magnetic atoms (Co, Fe) on the surface by means of scanning tunelling microscopy (STM), angle-resovled photoemssion spectroscopy (ARPES) and X-ray magnetic circular dichroism (XMCD). We have observed a quasiparticle interference of Dirac electrons induced by Co adatoms, and the formation of Fe island on Bi_2Se_3 surface. It was found from the ARPES measurement that the topological surface state is persistently gapless against the Co- and Fe- depositions. The XMCD measurment revealed the absence of long-range magnetic orders of magnetic atoms on the surface of Bi_2Se_3, which is consistent with the gapless feature of topological surface state [5]. Furthermore, we have discoved a giant orbital magnetic moment of Fe on Bi_2Se_3, which may give rise to the magnetic anisotropy of Fe interfaced with topological insulator.

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Ultrahigh-resolution Three-dimensional ARPES Study on the Hidden-order Transition in URu_2Si_2

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ABSTRACT

This work investigates the nature of so-called “hidden-order” transition in URu_2Si_2, one of the long-standing unresolved mysteries in solids, by means of ultrahigh-resolution angle-resolved photoemission spectroscopy (ARPES). Although thermodynamic properties clearly indicate the existence of some second-order phase transition in URu_2Si_2 at T_{HO} ⍰ 17.5 K [1-3], microscopic characters of the transition, such as the order parameter, the ordering vector, and the type of spontaneous symmetry breaking, have not been fully understood for more than a quarter century.

To understand the mysterious order in URu_2Si_2, it is imperative to know the evolution of electronic states upon the transition. Although recent works reveal various important aspects of the electronic states [4-8], the importance of k_z-dependent electronic states has not been fully addressed in a direct way. The motivation of our work is to uncover the k_z-dependent electronic states in URu_2Si_2 from the temperature-dependent investigations of the single-particle spectral functions by means of ARPES.

In this study, the electronic states of URu_2Si_2 were studied by ultrahigh-resolution three-dimensional angle-resolved photoemission spectroscopy employing photons from a third-generation synchrotron source. In the paramagnetic state, we observed a renormalized electron pocket, which shows clear k_z dependence. Temperature-dependent measurements revealed that this electron pocket becomes gapped and evolves into a narrow dispersive band upon the hidden-order transition. In addition, on the basis of the discussion of ‘saturation’ momentum, the gap is suggested to be particle-hole asymmetric. At a k_z location where the electron pocket was not observed in the paramagnetic state, the narrow dispersive band emerges only in the ordered state. These k_z-dependent data of spectral functions directly evidence Fermi-surface gapping and spontaneous breaking of translational symmetry along k_z.

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Electron and Photon Impact on Condensed Alcohols: Relevance to Solid State Astrochemistry

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ABSTRACT

Methanol and ethanol are important precursors of more complex prebiotic species. Both were found on icy mantles of interstellar grains in several astrophysical environments, such as star formation regions, Sgr B2[1], RAFGL 7009[2] and astrophysical bodies such as the Hale-Bopp comet[3]. In all these astronomical environments, molecules in the gas phase and frozen on dust grain surfaces are subjected to ionizing agents like UV and X-ray photons, charged particles such as protons, alpha particles and electrons, leading to ionization, dissociation and desorption processes. Some mechanisms were proposed for the formation of interstellar methanol and ethanol in the gas phase. However, as pointed by Millar and co-workers[4], chemical reactions occurring in the gas phase are not enough to explain the relatively high abundances of these alcohols, therefore reaction pathways on grain surfaces are required.

The interaction of stellar radiation and charged particles with icy alcohols on grain surfaces produces neutral or ionic fragments such as H_2CO, CH_3O, HCO, CH_3, CO and H, C and O free atoms. At surface temperatures around 50 K these radicals can readily diffuse to form more complex molecules like acetic acid (CH_3COOH) and methyl formate ($HCOOCH_3$)[5]. Those chemicals enrich the astrophysical ice composition and can sublimate from the ice surface to the gas phase. To understand the chemical evolution and to quantify the role of methanol, ethanol and more complex organic molecules in the gas phase and in the icy mantles of interstellar grains, it is necessary to establish the main formation routes, which require the study of the ionization, dissociation and desorption of these molecules caused by interaction with ionizing agents.

In the present work we employed soft X-ray photons at the oxygen 1s-edge and variable energy electrons to simulate the effects of stellar radiation field on the astrophysics ices. These results were also compared with effects produced by charged particles from the solar wind. They show that fragments released due to 850-1400 eV electrons are mainly caused by C-O bond rupture, since CH_n and C_2H_n ($1<n<4$) fragments have the highest yields at these energies. Fragments like CH_3O^+ and $CH_3CH_2O^+$ were observed for energies higher than 1400 eV, suggesting that electrons with energy near the O 1s ESID threshold can promote O-H bond breakage more easily. Fragments released due to 537 eV photons tends to provide fragments due to C-O and O-H bonds rupture, since CH_2^+, CO^+, HCO^+ and H^+ were the most intense fragments.

Acknowledgments: CNPq, FAPERJ, LNLS.

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Hydrogen Bonding of Water in 3-methylpyridine Studied by O 1s X-ray Emission and Absorption Spectroscopy

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ABSTRACT

Recently, high resolution X-ray emission spectroscopy (XES) studies of liquid water revealed that XES has sensitivity to chemical environments including hydrogen bond and exhibits two sharp peaks corresponding to the tetrahedrally-coordinated and distorted species [1, 2]. From the viewpoint of an application study using XES, we focused on D_2O/3-methylpyridine (3MP) binary mixture. Water/3MP binary mixture is well known because of the clear isotope effect of water [3] and a salt effect [4] in terms of the phase separation. We investigated the electronic structure of D_2O water in 3MP in the wide range of D_2O concentrations (X_{D2O} = 0.02–1.0) using both O 1s XES and X-ray absorption spectroscopy (XAS). Since 3MP has no oxygen, O 1s XES and XAS enables us to selectively observe the electronic structure of the water in the mixture owing to element selectivity of these methods. All experiments were performed at BL 17SU at SPring-8 with a soft X-ray emission spectrometer [5].

Although O 1s XES and XAS spectra show gradual changes in terms of spectral shape by the addition of 3MP, we identified the three concentration regions which show different tendency for concentration [6]. At the high water concentration region ($X_{D2O} \geq 0.8$), XES spectra are similar to those of liquid D_2O and the pre-edge peak in XAS spectra has no significant peak shift. These results indicate that the water–water hydrogen bond dominates in this region. For the intermediate concentration region ($0.1 \leq X_{D2O} \leq 0.8$), XES spectra show continuous intensity changes of the two peaks and the pre-edge peak in XAS also shifts toward lower energy continuously with X_{D2O} decreases. These results indicate that the average coordination number of hydrogen bonds reduces continuously. At the low water concentration region ($X_{D2O} \leq 0.1$), the energy shift in XAS is noticeably small. Since the peak corresponding to the tetrahedral hydrogen bond is almost disappeared in the XES spectra, we conclude that water molecules are solvated by 3MP molecules with water–3MP hydrogen bond formation in this region.

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EXAFS and XANES Structural Characterization of Bimetallic AuPd Vapor Derived Catalysts.

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ABSTRACT

Using an innovative procedure known as metal vapor synthesis (MVS) to prepare bimetallic catalysts, starting from Au and Pd vapors, [AuPd] co-evaporated and [Au][Pd] separately evaporated bimetallic catalysts were achieved [1]. Since the catalytic activity and selectivity of the [AuPd] catalyst turned out to be quite higher than the [Au][Pd] one, a structural characterization was quite important.

Using EXAFS it was shown that, in the [AuPd] samples, small bimetallic AuPd nanoparticles were present, having an Au rich core surrounded by an AuPd alloyed shell while in the [Au][Pd] sample there was the presence of monometallic Au and Pd nanoparticles showing some alloying only in the boundary regions.

The EXAFS results were also qualitatively confirmed by the XANES spectra looking at the white line intensity in Au L_3 edge spectra and to the shifts of the XANES features in the Pd K edge spectra.

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Probing the Electronic Structure of Methanol using Resonant Inelastic Soft X-ray Scattering

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ABSTRACT

Using specialized experimental setup in our SALSA endstation [1] at Beamline 8.0.1 at the Advanced Light Source in Berkeley/California, we have investigated methanol as a liquid and in gas-phase at atmospheric pressure using resonant inelastic soft x-ray scattering. Together with our high transmission soft x-ray spectrometer [2] our setup allows to measure resonantly excited x-ray emission spectra of methanol with a significantly higher signal-to-noise ratio and resolution than was previously possible. These can even be collected in complete RIXS maps which show the emission intensity as a function of both emission and excitation energy.

We will present RIXS maps both at the O K and at the C K edges which give a local picture of the electronic structure of the molecular orbitals of methanol around the respective atoms. In addition we will show strong similarities between the x-ray emission spectra of liquid and gas-phase methanol indicating a rather small influence of the interaction between neighboring molecules in the liquid on the spectra. The observed emission lines can thus be attributed to different molecular orbitals in accordance to DFT-based spectra calculations of isolated methanol molecules.

For excitation into different absorption resonances we find strong spectator shifts of up to 0.9 eV at the O K edge for the gas-phase. Furthermore we find evidence for nuclear dynamics on the time scale of the x-ray emission process leading to a splitting-off of the hydrogen atom of the hydroxyl group. This effect is very similar to the behavior of water [3,4] and is observed for all excitation energies in the liquid phase but only for excitation into the lowest absorption resonance in gas phase.

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Modification of Porous Silicon Surface with Organic Acids

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ABSTRACT

Porous silicon (PS) is a perspective material for various sensor devices, optoelectronics and biological applications, but it is not durable and stable in air. There are several techniques to overcome this limitation. One of the most reasonable methods is chemical modification of PS layer with different organic compounds.

Samples were obtained from n-type c-Si wafers in a solution of hydrofluoric acid and isopropyl alcohol. Then some of them were treated in polyacrylic acid (PAA) solution, some in tetraethyl orthosilicate (TEOS) solution, some were thermally oxidized and the rest ones were left untreated. All samples were stored in air for half a year. Morphology was explored by scanning electron microscopy. IR-spectra of untreated PS samples involve traces of electrochemical reaction products and atmosphere gases after half a year atmosphere exposure and these PS samples have visible photoluminescence (PL) spectra. PAA treatment changes chemical composition of the surface and increases PL intensity with the main peak arranged at 650-700 nm. TEOS treatment protects the surface from the atmosphere influence and decreases PL intensity without changing its peak position. Thermally oxidized samples also have the same composition after half a year but PL intensity decreases greatly and shows a peak shift to shortwave range .

Thus organic acids modification of porous silicon is a possible way to protect PS from atmosphere impact and also to change its qualities. This could be interesting for the further PS application in optoelectronic and other devices.

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X-ray Absorption Near Edge Structure of ATP Thin Film Irradiated with Soft X-rays

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ABSTRACT

To reveal non-DNA target effects induced by ionizing radiation, we focused on ATP (adenosine tri-phosphate) molecule, which is one of ribonucleic acids. ATP acts as an intercellular transfer, and also used as a substrate to synthesized messenger RNA [1] and as a ligand of inter-cellular signaling [2]. The purpose of this study is to analyze the correlation between molecular alteration of ATP induced by ionizing radiation and biological effect of damaged ATP. To analyze the molecular alteration of ATP, we measured the spectral change of X-ray absorption near edge structure of ATP thin films irradiated with soft X-rays. Experiments were performed at soft X-ray beamline BL23SU in SPring-8 [3]. XANES spectra of ATP thin film were measured before and after irradiation of soft X-rays. We observed the increment of the resonant peak at 399.5 eV by the 560 eV irradiation. Kelly et al. observed the 0.4 eV high energy peak shift of XANES by protonation of nucleobase in ATP [4]. The new peak production is expected to be originated from the protonation of nucleobase in ATP molecule.

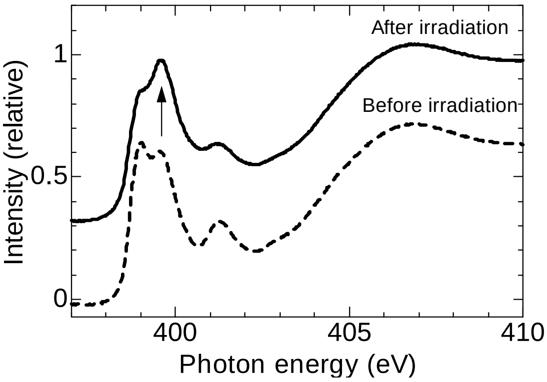

Fig. 1 Typical XANES spectra of ATP thin films before (dashed line) and after (solid line) irradiation of 560 eV monochromatic soft X-rays.

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Properties of Nanoparticles Obtained by Laser Ablation in Liquid Studied by X-ray Absorption Spectroscopy

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ABSTRACT

Inorganic nanoparticles (NP's) have shown very interesting physical effects related to size confinement, which in turn opened the way for new applications. For instance, gold NP's have important applications in nanobiotechnology and medicine due to their high tolerability in living organisms and the easiness of their functionalization [1, 2]. Most part of the methods to synthesize NP's are based on chemical [3] and biosynthetic [4] routes. Physical routes though, especially laser-based synthesis in liquid, are also suitable for the production of NP's with the advantage that it can be made in clean, biologically friendly, aqueous environment not having the toxicity problem usually related to chemical pathways [5, 6]. This is a novel and promising technique for the fabrication of narrow size distribution NP's in environments that enable the production of uncontaminated (and non-toxic) particles. It consists basically of doing the laser ablation of a solid target placed in a liquid solution [7].

In this work we present results of X-ray absorption spectroscopy (XAS) measurements of vanadium-based NP's produced through laser ablation of vanadium-metal in different liquids; deionized water, isopropanol, tetrahydrofuran (THF), and acetone. The interest of vanadium-based NP's stems from a previous and pioneer result obtained by our group for NP's produced in water [8]. A strong interaction of such NP's with cysteine, an amino acid which is a precursor for antioxidant glutathione formation, was observed. It was suggested that it could be used in biosensING applications. XAS measurements of the NP's in solutions were made in fluorescence mode and revealed huge differences, especially in the near-edge region (XANES), depending on the liquid used during ablation. For water, the XANES spectrum of the NP's is very similar to V_2O_5. After the addition of a small quantity of cysteine the color of the solution changes, this is also reflected on a significant change in the XANES spectrum. When the liquid is acetone the XANES spectrum of the NP's turns out very different. Combining XANES and other techniques (TEM, NMR) we concluded that for acetone the structure of the NP's is most likely $V(CO)_6$. It is the first time, to the best of the authors' knowledge, which such NP's are obtained by laser ablation. The effect of the remaining solutions on the NP's formation will also be presented and discussed on the basis of the XAS measurements.

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X-ray Absorption Spectra of UV-pumped Excited Triplet State of Anthraquinone

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ABSTRACT

For X-ray probe experiment from valence excited states of organic molecules prepared by UV pump, we focused the excited triplet state. Excited triplet states have 10^5~10^8 times longer lifetime than singlet states. The difference between triplet and singlet is only spin multiplicity. A triplet state has the same electron configuration. This long lifetime of triplet states make it possible to effectively excite core electrons from valence excited states of molecules. Formation and concentration of triplet states can be examined by measuring phosphorescence from triplet states. Prior to the UV pump and X-ray probe measurement suitable molecular system, kind of molecule and its phase such as solid-solution or pure crystal, has been investigated by measuring phosphorescence spectra. Among molecules species and phases examined, anthraquinone (9,10-dioxoanthracene) in micro crystal phase deposited on Au coated Si substrate shows strongest phosphorescence with long lifetime of 73 msec. An UV LED at 380 nm (0.37 W) was used as the UV source with continuous mode.

Total electron yield spectra of UV pumped anthraquinone in the C K-edge region and the O K-edge region have been measured. In the C K-edge region, no difference in TEY spectra with and without UV irradiation was observed. Contrary to the C K-edge region, an appreciable enhancement was observed at 532eV peak in the O K-edge region when UV was irradiated. Though the lowest resonant transition from the ground state of anthraquinone is located at the same energy, this UV-dependent feature is assigned as a new transition from the excited triplet state of anthraquinone. Since the lowest excited triplet state of anthraquinone is known to be $n\pi^*$ where an electron in the non-bonding orbital (n) localized at oxygen atoms is excited to the lowest π^* orbital, transitions from the O1s to a hole at the n orbital become possible in addition to the transition to the half-filled π^* orbital. The O 1s $\rightarrow n$ transition is a new type transition caused by UV irradiations because this transition is forbidden in the ground electronic state where the n orbital is fully occupied. In principle two low-lying transitions are expected from the electronic configuration $n^1\pi^{*1}$ of the triplet states, however, only one transition was enhanced by UV irradiation. We tentatively assigned that this peak was caused by the transition from the O1s to the non-bonding orbital of anthraquinone. This assignment is based on the fact that appearance of a new peak is observed at the O 1s but not at the C 1s region. Appearance of the new peak only at the O 1s region can be explained by that the n orbital is localized around oxygen atom(s) and has large overlap with O 1s orbital. Although our assignment for this new feature appeared by UV irradiation is tentative, our observation is the first examples of the x-ray absorption spectrum of valence excited organic molecules.

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Solvation Effects on Exotic Molecular Systems: Electron Spectroscopy and Electronic Structure Calculations

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ABSTRACT

Using first-principle methods and electron spectroscopy, we characterized the interaction between some exotic molecular systems and Ar in gas phase. Two examples will be treated: the Ar_mBeO^{q+} ($0\leq m\leq 3$, $0\leq q\leq 2$) multi charged ions (MCIs) and the electronically excited Ar_m-DABCO (1,4-diazabicyclo[2.2.2]octane) ($0\leq m\leq 3$) clusters. We focused on the perturbations of the BeO^{q+} MCIs and of the DABCO molecule upon complexation by Ar atoms.

Theoretically, we used the GAUSSIAN09 [1] program to determine the structure of the DABCO or the BeO^{q+} molecular systems either isolated or complexed with one to three-four argon atoms by *ab initio* calculations. For electronic excited state energy calculations, we used the complete active space self-consistent field (CASSCF) method followed by the internally contracted multireference configutation interaction (MRCI) approach, both of them implemented in the MOLPRO program [2]. These calculations include all possible configuration state functions that can be formed by distributing a set of active electrons among a set of active orbitals.

For Ar_mBeO^{q+} molecular complexes, we characterised their structural parameters, relative stabilities and vibrational wavenumbers [3]. Our calculations confirm the existence of the ArBeO complex. In addition, we predict several new (meta-)stable neutral and ionic complexes such as $ArBeO^+$, $ArBeO^{2+}$, Ar_2BeO, Ar_2BeO^+, Ar_2BeO^{2+}, Ar_3BeO, Ar_3BeO^+ and Ar_3BeO^{2+}. The analysis of the structural parameters and of the electron density differences shows that a strong perturbation in the electronic structure of the BeO^{q+} (q=1,2) moiety occurs upon complexation, resulting in a major increase of covalency in these MCI's. The consequences of solvation of MCI's in argon matrices will be discussed. These theoretical findings can be proved by valence or inner shell multiple ionisation on the neutral species in gas phase.

For Ar_m-DABCO complexes [4], the DABCO is put in the presence of argon atoms placed in various positions. These calculations show three possible equilibrium positions between the DABCO and argons. A distortion of the neutral DABCO is observed through the cage deformation mode (~ 100 cm^{-1}). This is due to non-adiabatic effects (electronic and nuclear motion couplings). However, the $DABCO^+$ cation is not perturbed and remains of D_{3h} symmetry. In addition, we treated the electronic excited states of DABCO-argon complex along the intermonomer distance. We obtained potentials which show the presence of two equilibrium distances between argon and DABCO in the excited states hyper potential energy surfaces, whereas a unique equilibrium distance is found for the ground state potential. This may explain the quite different fast dynamics of electronically excited DABCO embedded in an argon cluster when compared to isolated DABCO dynamics as experimentally observed by Poisson et al [5,6]. These authors used time-resolved response of the Ar_m-DABCO complexes to 266.3 nm electronic excitation of the S1 state with a femtosecond laser [4].

More generally, the effects on the spectroscopy of MCI's and of electronically excited medium-sized molecules either trapped in cold matrices or embedded in rare gas clusters will be discussed.

This work is done with the contribution of K. Mathivon and R. Linguerri (MSME, U. Paris-Est, France), N. Komiha (U. Mohamed V, Rabat, Morocco), and L. Poisson, J.-M. Mestdagh and B. Soep (LFP, CEA-CNRS, France).

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Resonant Soft X-ray Emission at the Oxygen K-edge in liquid Methanol

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ABSTRACT

Methanol (CH_3OH) is one of the primary alcohols. Simple primary and secondary alcohols offer prototypical hydrogen bonded liquids whose electronic structure and scattering dynamics can be uniquely probed using RIXS. In hydrogen bonded liquids the phenomenon of proton transfer is the key underlying mechanism and is also a fundamentally important process throughout nature, for instance in cellular energy management.

This study aims to begin to address the basic mechanism of hydrogen bonding and proton transfer in simple alchohols, and to establish a spectroscopic reference which will allow investigations to extend towards more complicated organic molecular liquid complexes.

To address the nature of proton transfer in hydrogen bonded liquids, it is desirable to study their electronic structure in the element-specific bulk-sensitive fashion afforded by RIXS [1]. The access that the photon-in photon-out RIXS process gives to the bulk properties of samples allows the real-world liquid environment to be probed which is preferable to single molecule adsorbates or crystalline solids. RIXS gives particular insight into the influence of the chemical environment of the proton donating hydroxyl (OH) group on the proton separation dynamics as the size of the alcohol molecule is varied. The dynamic properties of the probed system can also be accessed via RIXS due to the intrinsic link between the lifetime of the core hole and the scattering duration time [2,3].

The methanol samples in this study have been confined within both a liquid-flow cell behind a SiN window, and a liquid jet in front of a Nordgren-type grazing incidence X-ray emission spectrometer.

In this report RIXS results from flow-cell confined methanol at the O *K*-edge are presented and discussed in terms of a molecular bonding model.The results of the RIXS at the O *K*-edge from both the flow cell and the liquid jet are also compared to assess the possible spectroscopic effects of each confinement method.

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Size Selective Spectroscopy of Se Microclusters

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ABSTRACT

In order to explore the electronic structure of the Se_n ($n \leq 8$) microclusters as a function of their size, in this study a mass-selective photoelectron-photoion coincidence (PEPICO)setup has been used [1]. The results of the experimental study of the ionization and fragmentation of Se_n clusters after valence photoionization are presented. The measurements were performed at the FinEst branchline at normal incidence monochromator beamline I3 of MAX-III synchrotron storage ring (Lund, Sweden) [2]. In this work the experimental PEPICO setup [3] consisting of a modified Scienta SES-100 electron analyser and a homemade Wiley-McLaren type ion TOF detector was used.

The experimental ionization potentials of these clusters were extracted from the partial ion yield measurements. The calculations for the possible geometrical structures of the Se_n microclusters have been executed. The ionization energies of the clusters have been calculated and compared with the experimental results.

In addition, theoretical fragment ion appearance energies were estimated. The dissociation energies of Se_n clusters were derived from the recurrent relation between the gas phase enthalpies of the formation of corresponding cationic clusters and experimental ionization energies.

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Electron Angular Distributions in SiO2 Nanoparticles Following Soft X-ray Irradiation

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J.B.A. Mitchell[3], E. Antonsson[4], C. Graff[4], E. Rühl[4], and C. Miron[1*]

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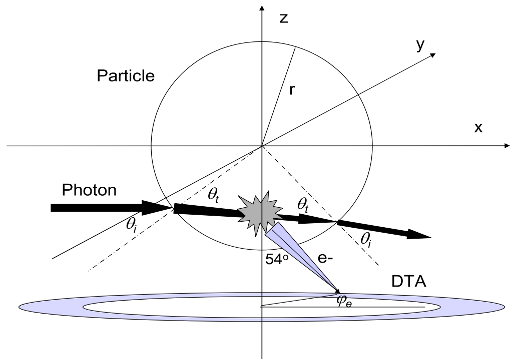
ABSTRACT

Nanoparticles bridge the macro-world described by Newton mechanics and the micro-world described by quantum mechanics. Owing to their specific properties, during the last decades the interest in nano-materials was dramatically increasing all over the world. Angular resolved electron spectroscopy is one of the methods of choice to investigate the electronic structure and the excitation and decay processes in both isolated atoms/molecules as well as in solid-surfaces [1,2].

Recently, Wilson and coworkers observed asymmetries in the photoelectron angular distributions from NaCl nanoparticles irradiated by VUV photons very close to the valence ionization threshold [3]. Thanks to the double toroidal analyzer (DTA) installed at PLEIADES beamline [4], we were able to analyze electrons with kinetic energies from several tens to several hundreds eV. The electrons with polar emission angles between 51° and 57° with respect to the axis are detected by a position sensitive detector. As a result, we could detect electrons emitted forwad/backward with respect to the photo propagation direction, as shown in Fig.1.

Both photoelectrons and Auger electrons were recorded for selected photon energies from 20 eV to 140 eV above Si 2p threshold. 185 nm. The measurements show that whe photon energy is higher, or the nanopartic smaller, the electron angular distribution is isotropic, while the asymmetry does not sh strong dependence on the electron kinetic ene

By comparing the observations with num simulations based on Mie scattering theory could explain qualitatively that the asymme likely to be due to the attenuation of photons i nanoparticle and the electron escape prob from the particles"



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Structural Analysis of Saccharides by Synchrotron-radiation Electronic Circular Dichroism Spectroscopy

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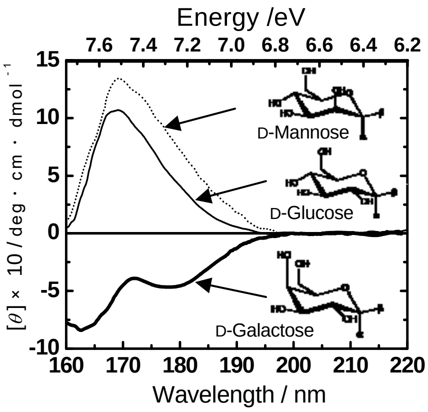
ABSTRACT

ELECTRONIC CIRCULAR DICHROISM, SACCHARIDE, SOLUTION STRUCTURE, SYNCHROTRON RADIATION, VACUUM-ULTRAVIOLET REGION

An electronic circular dichroism (ECD) spectroscopy using a synchrotron radiation (SR) is useful for analyzing the structures of saccharides in aqueous solution because this method allows us to detect the higher-energy chromophores such as hydroxyl group and acetal bond in the vacuum-ultraviolet (VUV) region below 190 nm. In this study, we report the ECD spectra of various saccharides down to 160 nm and discuss the pairwise relationships between the configurations and the ECD spectra of saccharides in aqueous solution. The ECD spectra of various types of monosaccharides showed a positive peak with some shoulders around 170 nm mainly due to the n-σ* transition of ring oxygen atom (See Figure) [1]. These spectra sensitively reflected the structural characteristics such as α- and β-anomers, axial and equatorial hydroxyl groups, and trans (T) and gauche (G) configurations of hydroxymethyl group. The contributions of these configurations were estimated by the deconvolution analysis of these ECD spectra, showing that the spectra of GG and GT configurations exhibit positive and negative ECD signs around 165 nm, respectively. These component spectra were confirmed by the theoretical calculation[2] (time-dependent density functional theory) of the spectra of methyl α-D-glucopyranoside with hydrated water molecules. The ECD spectra of most disaccharides showed a positive peak around 170 nm and were affected by the positions (1→6, 1→4, 1→3, and 1→2) and types (α and β) of glycoside linkages[1]. The comparisons of the ECD spectra between polysaccharides (glycosaminoglycan : GAG) and their component sugars showed that the functional groups (sulfate, carboxyl, hydroxyl, hydroxymethyl, and acetamide) strongly contribute to the higher-energy ECD by affecting the lone-pair electrons of ring oxygen[3]. These results demonstrate that the extension of ECD spectra to the VUV region should open the new field in the structural analysis of saccharides in aqueous solution.



ECD spectra of monosaccharides in aqueous solution

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“Building Block” Principle for Analyzing the Electronic Structure of Amino Acids by Resonant Inelastic X-ray Scattering

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ABSTRACT

At our SALSA (Solid And Liquid Spectroscopic Analysis) endstation[1] at the Advanced Light Source, we have used the element-specific character of resonant inelastic x-ray scattering (RIXS) to investigate the local electronic structure of selected functional groups of molecules in liquid and gas-phase. Using SALSA’s in-situ analysis capabilities[1] together with our high-transmission spectrometer [2], we are able to record “ambient pressure” x-ray emission spectra at each energy step in a regular absorption spectrum. These data can be presented in a two dimensional RIXS-map[3] containing the most complete electronic structure information available with soft x-ray spectroscopy.

We have investigated cysteine in its natural (i.e., aqueous) environment at different pH values by measuring RIXS maps of the O K, N K, and S $L_{2,3}$ absorption edges. The measurements show the strong local character of the electronic structure allowing its analysis by comparing with corresponding reference spectra of simple molecules representing the involved functional groups. We will show that this local “building block” approach works very well for cysteine and is expected to also be very valuable when investigating larger organic molecules. In detail, , we find a strong influence of the pH value on the electronic structure of the functional groups and a prominent signature of ultrafast proton dynamics occurring on the timescale of the x-ray emission process (i.e., a few fs).

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Design and Performance of Experimental Chamber to Study Biological Molecules in Aqueous Solutions

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ABSTRACT

Synchrotron radiation based electron and ionic spectroscopy is a group of very powerful experimental techniques, which have been very successfully used in the study of free atoms and molecules, surfaces and solid-state samples. The main point with this work is extends the possible targets for these techniques to liquids with high vapor pressure, including systems and phenomena of fundamental interest to physics, chemistry and biology. To achieve this we are developing a source for ionic and electron spectroscopy studies of liquid samples. As spectroscopy techniques require vacuum, they have been very difficult to apply to liquid systems. Recent developments of micro-jet techniques, however, have made such studies feasible [1, 2].

The main experimental chamber consist in a time-of-flight spectrometer positioned in 54.7^0 or a Scienta electron spectrometer positioned perpendicular to the plane formed by the micro-jet system, an ultraviolet excitation source, and an efficient high vacuum system allowing to keep a work pressure of 10^{-6} mbar in the spectrometer chamber. A secondary chamber is used to store and freeze the liquid jet, it is called trap chamber and it is in fact a differential pumping chamber.

We will present our experimental set up and the first results. The project is been developed in the Electronic Spectroscopy Laboratory – LEE at the University of Brasília/DF-UnB, and at Brazilian Synchrotron Light Laboratory - LNLS – Campinas/SP. The preliminary results were obtained in sulfur-containing amino acids, methionine and cysteine, in the S2p edge in different concentrations. The XPS spectra of cationic, zwitterionic and ionic structure of methionine and cysteine in aqueous solution were recorded to investigate the electronic and geometric structural effects as a function of pH and the hydrogen bonding pattern.

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Hybrid Organic-inorganic Systems: Metal Nanoparticles Embedded into an Organic Matrix

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ABSTRACT

Materials with a high on-off resistance ratio could become the basis for resistive random-access memory (RRAM) [1]. It is assumed that one of RRAM types can be based on hybrid organic-inorganic systems, while particular attention is focused on hybrid systems consisting of metal nanoparticles (NP) embedded in organic matrix (OM).

By deposition of a metal on organic semiconductor thin film a number of phenomena, such as diffusion of metal species, chemical reactions and distribution of different elements in the surrounded substance, can lead to significantly different morphology and properties. For example, it has been shown [2, 3] that Au may form small clusters/nanoparticles when deposited on top of an organic thin film. In this investigation we created and studied the hybrid organic-inorganic systems made of metal (Al, Au and Ag) nanoparticles embedded in organic semiconductor material CuPc. The CuPc thin films were grown by thermal deposition on atomically clean Au(001) surface in UHV condition. The LEED patterns and NEXAFS data demonstrate that the CuPc films are highly ordered and molecular planes lie parallel to the gold substrate. The metal atoms were deposited on the outer surface of the organic molecular film and assembled into nanoparticles due to surface and bulk diffusion arranging three-dimensional nanoparticle distribution in the bulk of the organic semiconductor film. The properties of nano-composite thin-film materials composed of metal particles embedded in an insulating matrix seem to be significantly dependent on the microstructure, i.e. the size, concentration, bulk- and size-distribution of nanoparticles; therefore we have studied by high resolution transmission electron microscopy (JEOL JEM 100 CX) the evolution of morphology of nano-composite films as a function of nominal metal deposition.

The filled and empty electronic states of the hybrid organic-inorganic systems, energy level alignment at interfaces formed between metal nanoparticles and the organic semiconductor CuPc as well as the chemical interaction at the NP/OM interface were studied by UPS, XPS and NEXAFS methods. All photoemission and NEXAFS measurements were performed at BESSY Berlin and MAX-lab Lund.

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Simulation of the Cluster Structure Cu, Au, Ni In Liquid and Supercooled States

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ABSTRACT

In the present paper a systematic comparative study of the evolution of a cluster structure of single-component d-metals (copper, nickel and gold) has been conducted at supercooling of melt.

With the use of the LMTO-ASA and APW+LO first-principle methods the density of the electronic states has been theoretically calculated. The series of computing experiments has been conducted by classical molecular dynamics for the simulation of the melt supercooling. Semi-empirical many-body embedded atom potentials have been used. The coordinates of atoms are used as input data for the analysis of the cluster structure based on the computations of metrics quantitatively describing the nearest surrounding of atoms and permitting to identify the shape of nanoclusters.

The structure of the melt at the melting temperatures has been experimentally studied by the XPS method on an x-ray electron magnetic spectrometer which has certain advantages over electrostatic spectrometers. It is established that in the liquid state the hybridization of d-electrons with p-electrons takes place depending on the localization of d-electrons in the studied metals. As a result, clusters with strong interatomic bonds can form. The presence of the icosahedral ordering in the melt at melting temperatures and its insignificant increase at supercooling are observed.

In Situ Soft X-ray Emission Spectroscopy of Metal Phthalocyanine-based Oxygen Reduction Catalysts under Ambient Pressure

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ABSTRACT

Carbon-based catalysts such as pyrolyzed Fe phthalocyanine (FePc) show high oxygen reduction reaction (ORR) activities and are expected to be cathode catalyst alternative to Pt for polymer electrolyte fuel cells[1-3]. To clarify the origin of the ORR activity, we have studied the electronic structure of the catalysts under vacuum condition[4]. However, *in situ* observation of the electronic structure during exposure to ambient oxygen is required since the actual catalytic process occurs at such condition.

X-ray emission spectroscopy (XES) is powerful to investigate the electronic states of materials under ambient pressure. In this study, we have fabricated an *in situ* sample cell for XES of carbon-based catalysts. Electronic structure of the catalysts before and after O_2 adsorption to the catalysts, which is the first step of ORR, has been investigated using ultrahigh resolution soft x-ray emission spectrometer installed at BL07LSU in SPring-8 [5]. The XES spectra were recorded at room temperature.

Several O_2 adsorption sites as the first step of ORR have been investigated by *in situ* XES. Comparing the Fe 2*p* XES spectra of the precursor FePc obtained under 1 atm Ar and O_2 atmosphere, it is found that the intensity of the *dd* excitation decreased after exposure to oxygen. This directly indicates the presence of charge transfer from *d*-electron of Fe to π^* orbital of adsorbed oxygen, so-called back donation process. Although it is reported that the oxygen adsorption occurs at the Fe-N_4 site in the center of the FePc molecule, XES spectra of pyrolyzed FePc samples reveal that the adsorption site of the pyrolyzed catalysts is different from that of the precursor FePc. The details of ORR active sites will be discussed.

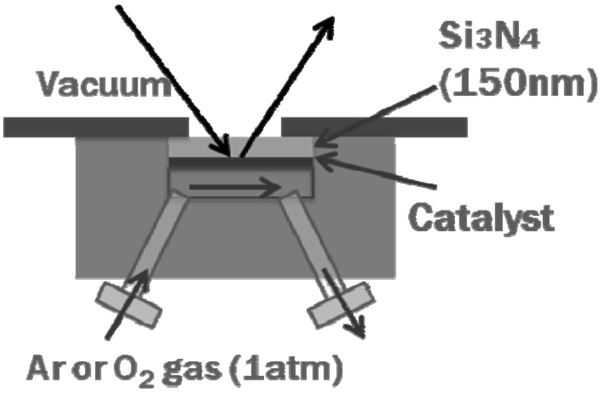

Figure 1. Schematic of *in situ* cell for XES.

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Inelastic Electron Tunneling Through Iron(II) Phthalocyanine Molecules on Ag(111)

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ABSTRACT

Inelastic electron tunneling spectroscopy with STM (STM-IETS) enables us to probe the vibration[1-5] and spin[6,7] excitation of individual adsorbed molecules through the conductance change. In the IET process, the vibration excitation occurs via resonant tunneling mechanism where the tunneling electron is temporally trapped in a molecular orbital and then leads to the vibrationally-excited state upon the relaxation of the temporal state[1-5]. This suggests that IETS spectrum can drastically change if we modify the energy alignment of the molecular orbital relative to the Fermi level and/or the coupling strength between the molecular orbital and the substrate electronic structures by tuning the local environment of the adsorbed molecule. In this presentation, we demonstrate the correlation between IETS spectra, electronic structures and local environment of adsorbed molecules. We deposited iron(II) phthalocyanine molecules onto Ag(111) single crystal surface, and investigated 1st-layer molecules and 2nd-layer molecules by STM, IETS and STS (Scanning tunneling spectroscopy).

While the IETS spectra of the 1st-layer molecules show no noticeable structures, several conductance steps associated with spin and vibration excitations appear in the spectra of the 2nd-layer molecules. Furthermore, some of the 2nd-layer molecules show anomalously large conductance changes (~30%) due to the vibration excitations. As for the STS spectra, the line shapes of 1st- and 2nd- layer molecules indicate that 1st-layer molecules are more strongly hybridized with the substrate than 2nd-layer molecules. These STS results indicate longer lifetime of the temporal state of the 2nd-layer molecules, which enhances the cross-section of inelastic tunneling through the 2nd-layer molecules.

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Photofragmentation of Perfluorocyclobutane at the C and F K-edges

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ABSTRACT

Perflurocyclobutane (c-C_4F_8) is used extensively as a plasma feed gas to achieve high selectivity in the etching of silicon dioxide, which is important in the manufacture of semiconductor microelectronics. In order to meet more advanced technical needs such as further microfabrication of large-scale integrated (LSI) circuits, it is necessary to understand the physicochemical behavior in etching processes. This report is a continuation of our previous study on the photofragmentation of c-C_4F_8 [1].

The experiments were performed on the beamline BL27SU in the SPring-8 facility, Japan. A Wiley–McLaren type time-of-flight spectrometer and a multi-stop time-to-digital converter (FAST ComTec, P7886) were used to obtain coincidence spectra. Commercial sample of c-C_4F_8 was used without further purification.

A variety of photofragment ions are found, such as C^+, F^+, CF^+, CF_2^+, CF_3^+, and $C_3F_3^+$. The most abundant fragment ion is CF^+ at the both K-edges. Also, asymmetric shapes can be seen in some peaks: The shapes change as the ion extraction field decreases. This is a clear indication of the formation of metastable ions.

Fragmentation mechanisms of the molecular dications are deduced from the photoelectron–photoion–photoion coincidence (PEPIPICO) maps on the basis of a charge separation model [2,3]. Significantly abundant fragment ion pairs detected are CF_2^+/CF^+, CF^+/F^+, and CF^+/C^+ at the both K-edges, judging from the number of the coincidence events. Their coincidence islands have roundish shape with two vertices. Because such small ion pairs can be formed by various decomposition processes, we focus here on the dissociation into the ion pairs with masses heavier than 40.

The observed slope of –1.00 for the island corresponding to the $C_3F_5^+/CF_2^+$ ion pair can be explained by a two-body fragmentation of $C_4F_7^{2+}$. The measured slope for the $C_2F_4^+/CF_2^+$ coincidence is –1.67, which is well described by the following three-body mechanism:

$C_4F_7^{2+} \rightarrow C_2F_4^+ + C_2F_3^+$,
$C_2F_3^+ \rightarrow CF_2^+ + CF$.

The fragmentation pathways can be classified into two series; i.e., fission of F atom(s) and elimination of CF_2 or CF_3, both followed by charge separation.

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Metastable Atom Electron and Ultraviolet Photoelectron Spectroscopy of Large Cycloalkane on Graphite (0001)

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ABSTRACT

An extraordinarily thin (0.4 nm) monolayer comprising long alkyl chains laid flat on a graphite (0001) surface is a promising “raw aggregate” to create peculiar subnanomaterials [1-4]. In such an attempt it is of fundamental importance to collect typical data of surface characterization techniques for various aggregations (including unfavorable ones) of the chains [5,6]. In this study, a large cycloalkane $C_{48}H_{96}$ (cyclooctatetracontane; COTC) is chosen as the monolayer constituent in expectation of the “edge-on” orientation of the chain (the chain direction is parallel whereas the carbon zigzag plane is perpendicular to the substrate) owing to some peculiar conformation of COTC on the surface. Changes in the He* (2^3S) metasatable atom electron spectra (MAES) and He I ultraviolet photoelectron spectra (UPS) are examined in the course of warming a COTC monolayer prepared on a cooled graphite substrate. Though intense bands due to graphite are detected in the UPS, they are scarcely seen in the MAES, indicating that COTC molecules almost cover the substrate surface to be selectively probed by helium metastable atoms. Since both MAES and UPS bands due to COTC have features corresponding to those of long *n*-alkane on graphite [6,7], there exist all-trans methylene sequences $(CH_2)_k$ with carbon number k larger than 10, which is consistent with a rectangular conformation of COTC. The relative intensities of the MAES bands dependent on the substrate temperature denote that the orientation of $(CH_2)_k$ is close to edge-on at low temperature but to flat-on above room temperature. This means that the orientation of the rectangle is changed from flat-on to edge-on with rising temperature. Not only the rectangular shape of the molecule but the edge-on and flat-on orientation of the long sides and the whole molecule, respectively, are in line with STM topographs obtained for an annealed monolayer, which provides MAES characteristic of the low-temperature monolayer.

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Origin of Strong Rubber-to-brass Adhesion
- Photoelectron Spectroscopy Investigation of the Embedded Interface between Polymer and Metal -

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ABSTRACT

In automotive tires, steel cords are embedded to give rubber tires a structural strength along with flexibility. Strong adhesion between rubber and the steel cords is crucial for a good performance of tires. The tire manufacturers have employed brass-plated steel cords to realize stiff rubber-cord adhesion. It has already been recognized in the early 1970's that copper sulfides are formed at the rubber-brass interface and speculated that these sulfides should be responsible for the interface adhesion [1,2]. However, details of chemical composition of copper sulfides and its formation process have not been obviously understood. One of the reason is that, because of strong adhesion between rubber and brass, it is difficult to expose the interface undestructively for chemical analysis by means of electron spectroscopy.

In the present study [4], high resolution photoelectron spectroscopy (PES) is utilized to investigate the chemical composition at the rubber-brass interface to elucidate the origin of strong adhesion and the degradation between robber and brass. In order to expose the rubber-brass interface, we employed a so-called "filter paper method" [3], in which brass samples were sandwiched by filter papers, embedded in uncured pads of rubber and subjected to vulcanization. The advantage of this method is that, although a direct contact of rubber molecules with the brass surface can be avoided, small molecules such as sulfur and fragments of rubber pass through the papers to reach the brass surface and initiate chemical reactions equivalent to those at the interface. Several brass plates were prepared with different vulcanization time ranging from 2 to 50 min, and the chemical compositions of these surfaces are compared. The PES measurements were done at beamlines 3B and 13A of the Photon Factory (KEK, Tuskuba).

By analyzing the S 2p core-level spectra, at least five sulfur-containing species are resolved at the interface. Among them, crystalline CuS and amorphous Cu_2S are identified as copper sulfide species. These species are not uniformly distributed within the layer, but there exists the concentration gradation; the concentration of Cu_2S is high in the region on the rubber side and is diminished in the deeper region, while vice versa for that of CuS. Degradation of the interface adhesive strength by prolonged vulcanization arises from the decrease in the Cu_2S/CuS ratio accompanying desulfidatoin of the adhesive layer. Therefore, Cu2S in direct contact with rubber is responsible for the strong rubber-brass adhesion.

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State-selective Dissociation of Ammonia Clusters Studied by Electron – Ion – Coincidences

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ABSTRACT

Fragmentation of NH_3 clusters is studied by energy selected electron – ion (ion) – coincidence measurements, triggered either by photoelectron or resonant Auger electron detection. Experiments were carried out at the PLEIADES beamline[1] at SOLEIL synchrotron, using EPICEA coincidence set-up[2]. Clusters were produced by adiabatic expansion of NH_3 gas with 0.4 bar backing pressure through a 100 μm conical nozzle, which was cooled to ~ 268 K. These conditions created large clusters (several hundred molecules in a cluster).

N 1s photoabsorption spectrum of NH_3 clusters is very similar to molecular NH_3 spectrum. The first resonance (excitation to $4a_1$ orbital in NH_3 molecule) appears to have the same excitation energy as the molecular one, and second resonance (excitation to 2e orbital NH_3 molecule) is slightly red-shifted.

N 1s photoelectron – photoion coincidence (PEPICO) measurement reveals that large clusters dissociate producing predominantly $(NH_3)_nNH_4^+$, n = 0,1,2,… fragments, whereas this fragmentation pattern can be modified significantly by exciting the N 1s electron to empty valence orbital ($4a_1$ or 2e in NH_3 molecule). At these resonances the small fragments, N^+, NH^+, and NH_2^+ are much more abundant compared to the excitation to a Rydberg state ($6a_1$ in NH_3 molecule), where the fragmentation pattern resembles the core-ionized one. An especially interesting example is the excitation to the $4a_1$ orbital, which is known to exhibit ultra-fast dissociation in NH_3 molecules[3].

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Adsorption of Cytosine and Some Derivatives on Gold

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ABSTRACT

The adsorption of cytosine on Au(111) and Au(110) has been studied by soft x-ray photoemission and photoabsorption, and the results compared with similar measurements of some derivatives adsorbed on Au(111). The latter are the pharmaceutically relevant compounds 6-azacytosine, 6-azacytidine and 5-azacytidine. All samples were deposited from aqueous solution and in addition cytosine was deposited by evaporation in vacuum. Cytosine/Au(111) has been the subject of a recent STM study [1], and our electron spectroscopy results provide complementary chemical information.

A single tautomer of cytosine, the amino-keto form, is found to be the dominant species on the surface after deposition from vacuum, in contrast to the gas phase where three dominant tautomers have been identified [2]. The molecule lies essentially flat on the surface, in agreement with STM observations. However we find evidence for a second, minority species on the surface, tentatively identified as a deprotonated form of cytosine. After deposition from solution this species constitutes the major part of the population of the molecule on the surface, and there is a minority of the amino-keto form. This second species is oriented at a much larger angle to the surface, and these results are partly consistent with previous electrochemical studies of cytosine adsorbed from solution on gold. The molecule is bound to the surface through one of the nitrogen atoms.

6-azacytosine, 6-azacytidine and 5-azacytidine bind to gold analogously, through the azacytosine ring, and the ribose moiety has little influence on the adsorption. Although 6- and 5-azacytidine are isomers, the change in position of the nitrogen atom from the 6 to the 5 position influences the coordination of the ring to the surface, with 5-azacytidine lying more parallel to the surface.

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The Gas-to-cluster and Gas-to-solid Effects in Core Excited SF_6

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ABSTRACT

Resonances in S 2p and F 1s excited SF_6 either bound in free variable size van der Waals clusters or in the solid are examined. The high-resolution X-ray absorption measurements evidence that intense molecular-like resonances dominate the regimes near the S 2p and F 1s edges in SF_6-clusters and solid SF_6. There are, however, distinct differences associated mainly with red-shifts of the core-to-valence transitions embedded into the core ionization continua and distinct changes in their line shapes. No visible spectral shifts relative to the isolated molecule are revealed for the lowest S $2p^{-1}6a_{1g}$ resonance. The double-barrier-optical-potential model [1, 2] is applied to rationalize and compute the gas-to-cluster and gas-to-solid shifts. They are due to:

1) interference of the primary photoelectron wave and multiply scattered waves in the core-ionized molecular unit with singly backscattered ones at the neighboring SF_6;
2) dynamic F 1s hole localization, inversion symmetry breaking, and geometry changes in the core-ionized molecule;
3) intermolecular repulsion reducing the splitting of the degenerate F 1s excitations,
4) the molecular ion dynamics depending on the photoelectron trapping time *t*.

Analytical relationships between the gas-to-cluster and gas-to-solid effects and the intra- and inter-molecular potentials and molecular dynamics are derived. The triple convolution L_a*L*G of asymmetry and symmetry Lorentz (L_a and L, respectively) and Gauss (G) distributions [3] is successfully applied to (i) reproduce the experimental bands, (ii) separate the S $2p_{3/2}$ and $2p_{1/2}$ spin-orbit doublets, (iii) extract with the highest accuracy the spectroscopic parameters of the both spin-orbit and dynamically split components, (iv) derive the trapping time *t* for the different core-excited states, and (v) check the derived relationships.

Spectral red-shifts of the $2t_{2g}$ and $4e_g$ shape resonances are found to be 35±5 meV and 150±10 meV in clusters and 90±10 meV and 320±10 meV in solid SF_6. The derived trapping times are $t \approx$ 1.1 and 0.2 fs for the $2t_{2g}$ and $4e_g$ quasi-bound states. These are considerably shorter than the S 2p core-hole lifetime. It is shown that the difference in *t* controls the gas-to-cluster and gas-to-solid effects. Substantial spectral shifts in the F $1s^{-1}t_{1u}$ line shape are attributed to the intermolecular repulsion forces reducing the splitting of the triply degenerate excitation from 1.8 eV to 1.1 eV in clusters and reach up to 0.45 eV in the solid.

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Chemical Reactivity of Alkenes and Alkynes from Carbon 1s Ionization Energies, Enthalpies of Protonation and Theory

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ABSTRACT

Electrophilic addition to carbon-carbon multiple bonds is one of the most common and useful reaction types in organic chemistry. Of particular interest has been the question of relative chemical reactivity of carbon-carbon double and triple bonds in proton addition reactions.[1,2] In this work electrophilic addition has been investigated for a series of twelve aliphatic and aromatic alkenes and the corresponding alkynes. For all molecules high resolution carbon 1s photoelectron spectra have been measured in the gas phase and the contribution from carbons of the unsaturated bonds identified. The results are accompanied by calculated enthalpies of protonation and activation energies for HCl addition across the multiple bonds. In each of these processes a positive charge is added to a specific site of the unsaturated bond and provides information of chemical effects, even if the energies involved are quite different.[3-5]

Considering the protonation process as a highly ionic limiting case of electrophilic addition, the sets of protonation enthalpies and gas-phase activation energies represent double and triple bond reactivities in both ionic and dipolar electrophilic reactions. The results from these model reactions show that the alkenes have similar or slightly lower enthalpies of protonation, but have consistently lower activation energies than the alkynes. The same trend is found for relative values of carbon 1s energies when only terminal unsaturated bonds are considered.

Linear correlations are found for protonation and activation energies with carbon 1s energies. However, there are deviations that reflect differences between the three processes. For enthalpies of protonation, the alkyl compounds are correlated with slopes of about 1, indicating that energies involved for protonation and core ionization are similarly affected by the substituents. For activiation energies, the slopes are significantly lower than 1, indicating that the transition-state energy is less sensitive to substituent effects than is the ionization energy. Finally, substituent effects for alkenes and alkynes are compared using both carbon 1s and activation energies. These are found to be largest for the triple bonds, in agreement with experimental results obtained from acid-catalyzed hydration reactions.[6]

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Local Electronic Properties at Organic-metal Interface: Thiophene Derivatives on Pt(111)

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ABSTRACT

The electronic properties at organic–metal interface have received much attention for the basic understanding and the potential application to molecule-based devices.[1-5] In the present study, we examined the valence electronic states of thiophene (TP), 2-thiophenethiol (TT), 2,2'-bithiophene (BTP), and 2,2'-bithiophene-5-thiol (BTT) on Pt(111) by ultraviolet photoemission spectroscopy (UPS), metastable atom electron spectroscopy (MAES) [6], and first-principles calculations based on density functional theory. A special emphasis is placed on how the local electronic states at the organic–metal interface are changed by the size of π-conjugation and the substituent effect. The UPS and MAES spectra of the condensed phases were measured to clarify the native electronic structures, and then the MAES spectra of the chemisorbed species were compared with the calculated local density of states. Our data show that TP and BTP chemisorbs weakly on Pt(111), whereas TT and BTT chemisorb strongly on Pt(111) by forming thiolates. In all cases, chemisorption-induced gap states (CIGS) emerge at just below the Fermi level (E_F), resulting in a metallic structure at the organic–metal interfaces. BTP also chemisorbs weakly on Pt(111) with an inclined configuration, yielding CIGS just below E_F. The relative intensites of CIGS are in the order of TP (flat-lying geometry) > TT > TP (inclined geometry), indicating that the spatial distribution of CIGSs are drastically altered by the strength of organic–metal bond and adsorption geometry. In other words, TP (flat-lying geometry) and TT serve as a good mediator of the extension of metal wave function at E_F. These characteristics are closely related to transport phenomena in molecular junctions linked by metal electrodes.

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Study of the Interatomic Interaction of Organic Zinc Inhibitors with the Surface of Carbon Steel

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ABSTRACT

At present it has been proved that the most effective steel corrosion inhibitors in neutral and alkalescent media are metal-containing organophosphorous compounds, particularly, the complexes of organophosphonic acids with zinc. The absence of reliable data on the molecular structure of metal-containing organophosphorous inhibitors does not allow understanding the mechanism of their inhibiting effect.

The objective of the present paper is the study of the interatomic interaction of organophosphate zinc complexes with the surface of carbon steel by the x-ray photoelectron spectroscopy method.

The chemical bond between of the steel substrate atoms and the inhibitor film atoms has been studied. The covalence bond between the Fe, Zn, O and P atoms is found in the Zn-O-P-Fe surface complex.

The thermal stability of the chemical bond between the atoms of the substrate and coating has been studied. The decomposition of the inhibitor starts at the temperature about 400 K leading to the formation of a zinc-iron-phosphate film that is stable up to 525 K. At the temperature above 525 K, the protective film decomposes, and the Fe atoms from the high-spin state pass into the state characteristic of pure iron. The significantly higher stability of the Fe-Zn-P-O protective film is explained by the formation of direct covalent couplings Me-P and Me-O.

Valence-shell Photoelectron Circular Dichroism (PECD) on Gas Phase Alanine

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ABSTRACT

Photoelectron Circular Dichroism (PECD) is observed as a forward/backward asymmetry, with respect to the photon axis, of the photoelectron angular distributions resulting from the CPL-induced photoionization of gas phase pure enantiomers of a chiral species. This spectacular orbital-dependent chiroptical effect with intensities reaching up to the few tens of %, shows a rich photon energy dependence, and appears as a very sensitive probe of molecular conformation and of the chemical environment.[1] After the study of numerous organic compounds we present here the first PECD study on biomolecules, more precisely amino-acids, the building blocks of proteins with the showcase of alanine, the simplest chiral proteic amino-acid in the first few eVs above the IP located at 8.82 eV.

Experiments were conducted using the new electron/ion coincidence imaging spectrometer DELICIOUS 3, which records Angle-Resolved photoelectron spectroscopy on mass-selected samples to extract the PECD. Fragment-free neutral alanine molecules were produced by thermodesorption of the corresponding homochiral aerosol, according to a method that we recently developed on DESIRS in order to bring in the gas phase fragile species.[2] By alternating right- and left-handed circularly polarized radiation, the photoelectron circular dichroism (PECD) in the angular distribution was extracted from the electron images obtained by coincidence with the ions corresponding to alanine: parent (m/z = 89) and fragment (m/z = 44 and 45), rejecting the spurious contribution from N_2 and NO.

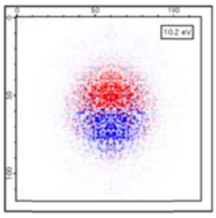

Figure: raw difference (lcp-rcp) photoelectron images of D-alanine.

Analysis of the corresponding images allowed us to observe a clear "mirroring" between the two enantiomers at different photon energies and to quantify the forward/backward asymmetry of photoelectrons, reaching up to 6 % at the lyman α wavelength (See Figure).

Recent Continuum Multiple Scattering (CMS-Xα) calculations compared to data at several photon energies and for several orbitals should allow us to provide a conformational analysis of the produced gas phase molecules. Finally, these data will be discussed within the context of exobiology since it is a candidate to explain a possible enantiomeric enrichment of amino-acids delivered on the primitive Earth, leading to life's homochirality, i.e. the fact that only L-amino acids are found in the biosphere.[3]

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Weak Intermolecular Interaction of Organic Crystalline Films Revealed by High-precision Valence-band Dispersion Measurement

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ABSTRACT

In development of organic electronics, charge transport is an important and fundamental property. In general, the charge transport mechanism in molecular solids is dominated by weak intermolecular interaction. However, it is quite difficult to observe such a weak intermolecular interaction precisely due to the presence of various extrinsic phenomena, which easily overwhelm the intrinsic phenomena.

In the present work, we discuss the weak intermolecular interaction in organic crystalline films of metal phthalocyanine [MPc; M = metal (Zn, in this work)], one of the archetypal organic semiconductor molecules in the field of organic electronics, by means of high-resolution angle-resolved photoemission spectroscopy (ARPES) with synchrotron radiation. The ARPES experiments were performed at a VUV/SX in-vacuum undulator beamline BL6U of the UVSOR-II facility, Institute for Molecular Science.

In order to reveal the weak intermolecular interaction in detail, a flat-lying well-crystallized ZnPc film was prepared on Au(111), wherein the crystallinity could be confirmed by the X-ray absorption spectroscopy and the specular X-ray diffraction. From the photon energy dependence of the normal-emission ARPES spectra, we have succeeded in observation of small valence-band dispersions. The dispersion width for the highest occupied molecular orbital (HOMO) of π character is only ~100 meV at the specimen temperature of 15 K. The periodicity of the HOMO dispersion corresponds to the Brillouin zone of the ZnPc crystal, which is estimated from the intermolecular distance of 3.32 Å. This means that the observed small HOMO-band dispersion is mainly dominated by the van der Waals interaction. Furthermore, we found a temperature dependence of the HOMO-band dispersion, which originates from the change in the intermolecular interaction.

From these results, it is clearly revealed that the band-like transport is realized even in the evaporated MPc films. Furthermore, this result can be regarded as a benchmark for the systematic study on intermolecular valence-band dispersion as a function of the central metal atom and the terminal group in the MPc molecule, which enables us to discuss the intermolecular interaction in terms of the molecular orbital symmetry, the intermolecular distance, and the conformational (stacking) geometry.

Accessing Surface Brillouin Zone and Band Structure of Insulating Picene Single Crystals

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ABSTRACT

Organic single crystals (SCs) have recently attracted considerable attention both for fundamental research and device applications because of some properties not found in inorganics and outstanding functionalities in optoelectronic devices. Recently picene ($C_{22}H_{14}$) has attracted much attention because the solid picene was found to be the first aromatic superconductor upon potassium-doping with a T_c =18 K that is very high as an organic superconductor [1], and also because high-hole mobilities (~5 cm^2/Vs) [2]. We have experimentally revealed the valence-band structure and the surface Brillouin zone of insulating picene SCs with angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) and low-energy electron diffraction with a laser for photoconduction. A hole effective mass of $2.24m_0$ and the hole mobility $\mu > 9{:}0$ cm^2/Vs (298 K) were deduced in the Γ-Υ direction. We have further shown that some picene SCs did not show charging during UPS even without the laser, which indicates that pristine UPS works for high-quality organic SCs [3].

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Atomic and Magnetic Structure Analysis of Sr_2FeMoO_6 by Photoelectron Diffraction and X-ray Magnetic Circular Dichroism

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ABSTRACT

Double perovskite Sr_2FeMoO_6 (SFMO) has been known as high Curie Temperature and giant magneto-resistance material. Therefore it has been expected to be magnetic head. Arrangement of Fe and Mo often are disturb and their valence seem to variable. The mismatch and the mixed valence are regarded to disturb this magnetization.

The sample was grown by Floating zone method. Its height is 10mm and diameter is 3.2mm. The sample was cleaved perpendicular to grow direction using knife in the atmosphere. Then it was inserted chamber immediately. Its new surface was investigated by two Dimensional Photoelectron Diffraction(2DPED). It can analyze elements specific crystal structure.

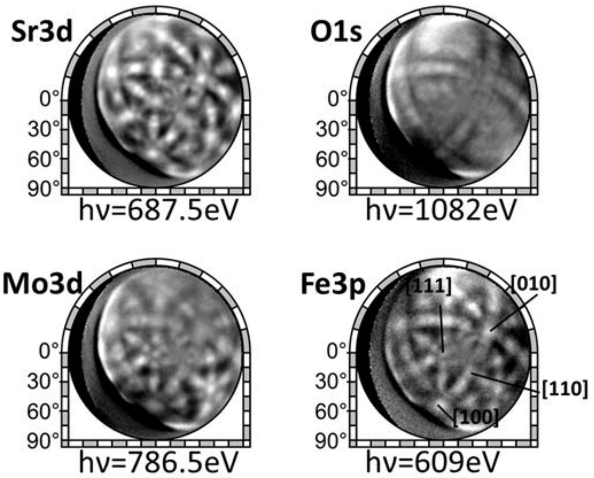

Fig.1 Each element of Sr_2FeMoO_6 was measured using E_K=550 eV

Photoelectron Diffraction patterns are showed at Fig.1. Its patterns called Photoelectron Intensity Angular Distribution(PIAD) pattern. Exciting Sr3d, O1s, Mo3d and Fe3p core level, these patterns were obtained. Then each kinetic energy of photoelectron was 550eV. Each PIAD patterns has a three-fold symmetry. Its crystal growth orientation was determined to be [111].

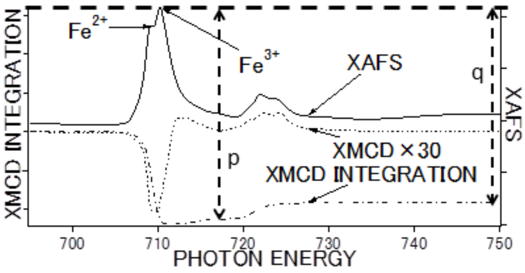

Fig.2 Fe L-edge XMCD and XMCD integration

XAFS and XMCD spectrum are measured at Fe L-edge. Integrating these spectrum, we can get the value p, q, and r. Applying these values, we got orbital and spin magnetic moment quantitatively. Ratio of spin and orbital is bigger than [3]. Since this sample made from mixed crystal. Therefore these domains occur magnetic interaction and its magnetization might be decreased.

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Surface Degeneration of Magnesium Oxide Studied by Near-edge X-ray Absorption Fine Structure Spectroscopy and X-ray Photoelectron Spectroscopy

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ABSTRACT

Magnesium oxide (MgO) is an important material from a fundamental physical point of view. MgO plays a prototype of metal oxides and is also a wide-gap insulator [1]. In addition, MgO is widely used in the field of catalytic, optical and electrical applications [2, 3]. MgO thin films and their surfaces have been extensively investigated because of their importance as surface protective layers for dielectric materials in ac-plasma display panels (PDPs) [4]. The MgO thin film plays the role of protection of the degenerations induced by ion bombardment. It is important to reveal the mechanism of surface degeneration on MgO thin films.

In this study, we have measured the O *K*-edge NEXAFS spectra and the O 1s and Mg 1s XPS spectra of MgO thin films on Si (100) wafer (MgO/Si) before and after Ar^+ bombardment. The MgO/Si samples were purchased by NTT-AT Nanofabrication Corporation, Japan. MgO thin films with about 10 nm in thickness were grown on the Si substrates by RF magnetron sputtering using MgO target. The O *K*-edge NEXAFS spectra were obtained using the total electron yield mode at BL12 of SAGA-LS. The O 1s and Mg 1s XPS spectra were also obtained by using Al *K*α radiation. At first, the MgO thin film was heated at 500 degrees in a vacuum. Subsequently, the surface degeneration was induced by Ar^+ bombardment with 1 keV using ion gun. The sample temperature during the bombardment was set as room temperature.

Figure 1 shows O *K*-edge NEXAFS spectra of the MgO/Si thin films as a function of Ar^+ bombardment time. Three strong peaks are observed at around 539 eV, 547 eV and 557 eV, respectively. The strongest peak at around 539 eV before bombardment is consisted of at least two peaks. After the bombardment, these peaks become broad peak. As a result, the strongest peak becomes also broad. In addition, the results of XPS spectra measurements showed the decrease of the atomic ratio of oxygen to magnesium related to the increase of the Ar^+ bombardment time. These results indicate that the oxygen vacancies were induced by Ar^+ bombardment on MgO surfaces.

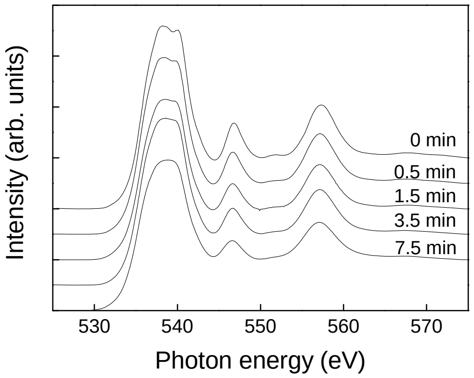

Fig.1 O *K*-edge NEXAFS spectra of the MgO/Si thin films as a function of bombardment time.

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XPS Study of the Mn Ions Valence State in $La_{1-\alpha}Bi_{\beta}Mn_{1+\delta}O_{3\pm\gamma}$ Ceramics

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ABSTRACT

Three ceramic samples with various elemental composition are synthesized: $La_{0.41}Bi_{0.39}Mn_{1.30}O_{2.90}$, $La_{0.30}Bi_{0.43}Mn_{1.20}O_{3.07}$, and $La_{0.26}Bi_{0.50}Mn_{1.33}O_{2.91}$. Also synthesized are the reference compounds containing bivalent ($Mn_2V_2O_7$), trivalent (Mn_2O_3), and quadrivalent ($SrMnO_3$) manganese. Mn2p- and Mn3s-spectra are measured with an X-ray photoelectron microprobe ESCALAB 250.

The spectra are calculated in an isolated-ion one-electron intermediate-coupling approximation using Pauli-Fock wavefunctions. Thermal excitations in the ground state are included in the calculations. Theoretical spectra of Mn^{2+}, Mn^{3+} and Mn^{4+} ions compare very well with the spectra of fixed-valence reference compounds.

Analysis of the Mn2p-spectra showed that both Mn^{3+} and Mn^{4+} ions are present in the $La_{1-\alpha}Bi_{\beta}Mn_{1+\delta}O_{3\pm\gamma}$ ceramics. Relative Mn^{3+}/Mn^{4+} ions contents are determined by fitting experimental Mn2p-spectra with weighted superpositions of theoretical spectra of Mn^{3+} and Mn^{4+} ions. Content of the Mn^{4+} ions correlates with the deviation δ in $La_{1-\alpha}Bi_{\beta}Mn_{1+\delta}O_{3\pm\gamma}$ from stoichiometry, $La_{1-x}Bi_xMnO_3$.

Separation of low-spin and high-spin components of Mn3s-spectrum can be sensible to the relative content of Mn^{3+} and Mn^{4+} ions. Mn^{3+}/Mn^{4+} ratios derived from Mn2p- and from Mn3s-spectra compared well in the case of the RMn_2O_5 manganates [1], however, in the case of the $La_{1-\alpha}Bi_{\beta}Mn_{1+\delta}O_{3\pm\gamma}$ ceramics the results obtained from the Mn3s spectra turned out to be physically meaningless. Due to a complex interplay between delocalization of valence electrons and strong many-electron effects, the 3s spectra of 3d-elements may be misleading.

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VUV Light Induced Valence Degeneration in Sm Over-layer on HOPG

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ABSTRACT

Samarium may be of particular interest from a fundamental point of view in physics of electronic structure since two different isoenergetic states may coexist: the free atomic Sm is divalent $4f^6(sd)^2$, but due to the gain in cohesive energy the bulk of metallic Sm is in a trivalent $4f^5(sd)^3$. However, for the less coordinated Sm atoms in the surface layer the gain in the cohesive energy is smaller, and therefore the Sm atoms in the surface layer turn out to be divalent. Thus, the Sm coverage dependence of valence state has been one of the active subjects in the photoemission spectroscopy (PES) for the various systems consisting of the Sm over-layer over the past two decades. Nevertheless, the valence degeneration feature of Sm has been not completely understood [1]. On the other hands, we found clear time dependence of the degeneration of the Sm divalent state on VUV light-irradiation at $h\nu$ =134 eV with low coverage Sm over-layer on HOPG (highly oriented pyrolytic graphite) in the previous work [2]. In this paper, we report the photon energy dependence of the photo-induced valence degeneration in detail by utilizing photoemission spectroscopy (ARPES, XPS) for the Sm and the other rear-earth element. The interaction between Sm layer and surface of HOPG has been carefully investigated by the ARPES. We suggest that the effect of the VUV irradiation on the Sm valence state variation must be considered for a quantitative evaluation of valence state based on the UPS. The experiment was carried out using the BL7 of a compact electron-storage ring (HiSOR) at the Synchrotron Radiation Center, Hiroshima University.

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ARTOF Electron Spectroscopy on Mn-doped Iron Pnictides

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ABSTRACT

Iron pnictides represent a second class of high-T_c superconductors which probably exhibit unconventional superconductivity. This makes the understanding of the electronic structure and the mechanism of superconductivity a very hot topic. Similar to the cuprate high-T_c superconductors, superconductivity appears close to an antiferromagnetic phase. One of the prototype high-T_c pnictide superconductors is related to the system $Ba(Fe_{1-x}Co_x)_2As_2$[1]. The undoped parent compound (x=0) is an antiferromagnetic metal. With increasing x antiferromagnetism disappears and a superconducting phase evolves showing a maximum T_c= 23 K for x= 0.06. An intriguing issue is the back doping of the system by substitution of Fe by Mn. Various transport measurements indicate not a reappearing of a metallic antiferromagnetic phase but the emergence of a Mott-Hubbard transition into an antiferromagnetic insulating state. Angle-resolved photoemission spectroscopy (ARPES) has become an indispensable tool to study the electronic structure of correlated unconventional superconductors and topological insulators [1,2].

Here we report first ARPES experiments on the system $Ba(Fe_{1-y}Co_{0.06}Mn_y)_2As_2$. The Fermi surface and the renormalized band dispersion, in particular of the hole pocket in the centre of the Brillouin zone has been studied at T = 5K as a function of Mn substitution for y up to 0.028. The band mapping was carried out by a state-of-the-art ultra high resolution Angular Resolved Time Of Flight spectrometer (Scienta ARTOF 10k) [3]. Using this spectrometer a very fast determination of two-dimensional band structures is possible, since it allows the simultaneous recording of data along two momentum directions (k_x and k_y) and binding energy. Data along the third momentum direction (k_z) can be derived from photon dependent measurements.

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Electronic Structure Analysis of Oxynitride Thin Film on SiC(0001) by Depth-resolved XPS and XANES

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ABSTRACT

SiC is a promising material for power device owing to its wide band-gap and high electron mobility. However, defect states at the SiO_2/SiC interface is a barrier for application.The most common technique which passivate defect state of interface is the post annealing the interface in NO or N_2O atmosphere[1].

Display type spherical mirror analyzer (DIANA) is able to get the series of various emission angle spectra at once. By using this analyzer, we can measure the depth-resolved x-ray photoelectron spectrum (XPS) and x-ray absorption near edge structure (XANES).

The experiments were performed at the circularly-polarized soft-X-ray beamline BL25SU of SPring-8, Japan. The SiC substrate was heated at 700 ºC to remove contamination keeping oxide film. 5000 L (Langmuir) of NO molecules (1×10^{-4} Pa) was exposed to the sample.

Fig.1 is the schematic image of the SiO_x/SiC sample. From depth-resolved XPS measurements, we determine that oxide film thickness was 1.0 nm. Fig.2 is the N K-edge XANES spectrum. Black solid line is the spectrum obtained in the experiment. Two compornents at 400(defect state) and 405 eV($1s \rightarrow \sigma^*$) can be seen in the spectrum. We could extract three spectrum by depth resolved analysis for these region. Region 1 and 2 is the oxide film components of surface and bulk, respectively. Both their spectra have sharp peak at 400 eV which are originated from the defect states. On the other hand, region 3 which is the SiO_2/SiC interface spectrum showed no defect state. This indicate NO passivated the defect state completely on the interface between SiC and SiOx film.

By using this method, we can confirmthe passivation of defect at the interface.

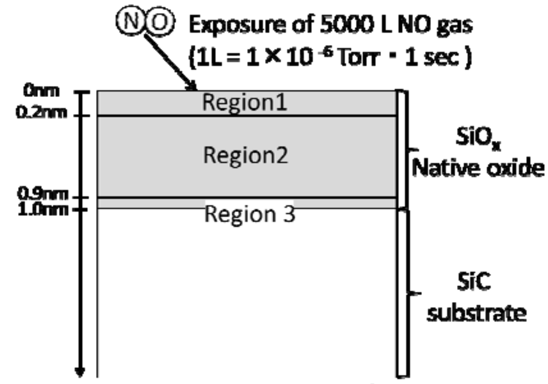

Fig.1 The schematic picture of the SiOx/SiCsample.

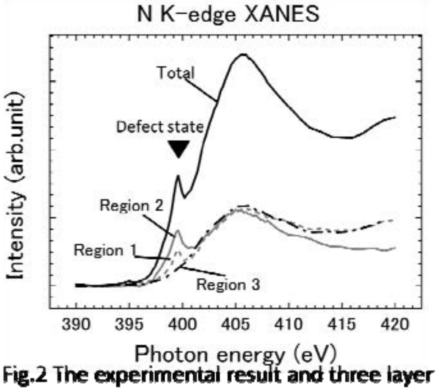

Fig.2 The experimental result and three layer resolved N K-edge XANES.

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Quantum Well States in Ag Thin Films on MoS_2 (0001) Surface

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ABSTRACT

The in-plane dispersions of the quantum well states (QWS's) originated from the electron confinement of Ag *sp* electrons within the MoS_2 band gap region are investigated by the angle-resolved photoemission spectroscopy (ARPES). A number of quantum well resonances (QWR's) have been observed in the ARPES spectra in a binding energy range lying outside the MoS_2 energy gap that is required for the full confinement of the Ag *sp* electrons. In spite of getting the expected free electron-like behavior, these QWS's show a significant increase of the in-plane effective mass with increasing the binding energy which is related to the hybridization of Ag *sp* electrons with the MoS_2 valence bands. The binding energy position dependence of the QWS's bottom as a function of the Ag film thickness has been analyzed. The standard method of phase accumulation model has been applied for calculating the electron phase shifts at the boundaries. It has been seen that the total phase shift behaves very differently for the energies above the MoS_2 valence band maxima, and can be explained by introducing a phase term related to the partial scattering of Ag *sp* electrons from the substrate bands outside the gap energy region, in the framework of extended phase accumulation model.

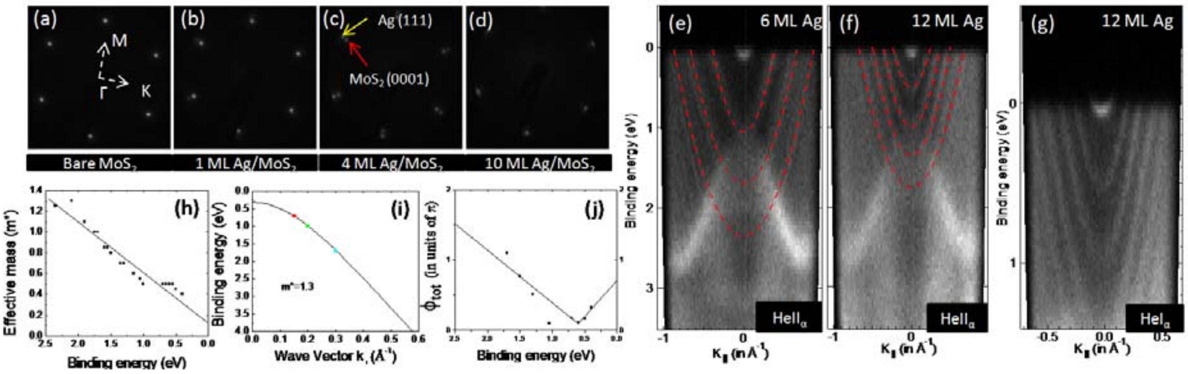

Fig.1: LEED pattern of (a) cleaved MoS_2(0001) surface with the symmetry directions shown, (b) 1 ML of Ag, (c) 4 ML of Ag grown on MoS_2, with the red arrow indicating the spots resulting from the MoS_2 surface and yellow arrow for the Ag(111) surface, (d) 10 ML of Ag grown on MoS_2. ARPES spectra of (e) 6 ML Ag, (f) 12 ML Ag on MoS_2 using HeII*α* and (g) HeI*α* resonance line. (h) In-plane effective mass (*m**) as a function of the QWS binding energy fitted with a linear function, (i) The *sp*-band dispersion of Ag bulk along the Γ-*L* with the solid curve corresponds to the least-square fit based on the two-band nearly free electron model, (j) The change in total phase shift with the binding energy.

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Exploring Unoccupied Electronic Structure of Graphite Probed by ARPES

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ABSTRACT

In the angle-resolved photoemission spectroscopy (ARPES) spectra of graphite, we observe the σ and π bands at the same energy position and with consistent dispersions with the previous ARPES measurements. However, along with these familiar graphite valence bands, we also observe another set of weak dispersive anomalous bands which are not predicted by the bulk band structure calculations. In order to study the origin of these anomalous bands, we have performed ARPES measurements at different photon energies using MAX-Lab synchrotron source. Apart from the anomalous bands observed at 41 eV ARPES spectra, we observe more anomalous features visible at 70 eV photon energy. There is a non-dispersive band near 33 eV and an upper dispersing band ranging from 34.5 eV to about 44.5 eV in [E-E_F] scale. These weak anomalous bands were not visible or partly visible in lower photon energies as those were masked by the valence bands of the graphite. At 70 eV photon energy, the anomalous bands are in a region free of valence band structures of graphite, and can be distinguished rather clearly. The energy positions of all these anomalous bands show a constant kinetic energy (constant energy in [E-E_F] scale) nature for different photon energies. From the observation of constant energy nature of these anomalous bands at different photon energies, we propose that these bands are originated from the unoccupied states or photoelectron final-state bands of graphite due to secondary electron emission (SEE) process. The photoelectrons excited from the valence bands undergo a series of inelastic-scattering and produce cascaded secondary electrons. These secondary electrons make transitions to the high lying conduction bands or unoccupied bands from which they escape into the vacuum without any memory of the initial occupied states of the photoelectrons. Since very low energy electron diffraction (VLEED) experiment maps the unoccupied valence band structures in the solid, we compare our ARPES experimental results with the reported VLEED data on graphite single crystals by Strocov *et al.,*. which show near one-to-one correspondence of the SEE features in the ARPES spectra and the VLEED data of single crystal graphite samples. In particular, the experimental ARPES spectra on graphite support the idea of mapping the unoccupied bands or photoelectron final-states by performing ARPES up to the low kinetic energy (secondary electron energy) region.

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SM-2-PO-MAT-01

Soft X-ray Two-dimensional Photoelectron Structure Factor Analysis of Graphite Valence Band by Newly Developed Display-type Analyzer

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ABSTRACT

Valence band photoelectron intensity from different Brillouin zones (BZs) varies due to the interference effect of photoelectrons coherently excited from several atomic orbitals within the same unit cell which is known as “photoelectron structure factor (PSF)” [1-3]. Coefficients for the linear combination of atomic orbitals (LCAO) composing valence bands can be deduced by analyzing PSF patterns. PSF patterns in a wide k-space range are measured by using soft x-ray as an excitation source and a display-type analyzer as a detector. Recently, we have developed a new display-type analyzer (DELMA: display-type ellipsoidal mesh analyzer) for diffraction angular distribution measurement and microscopic real space imaging with high energy resolution [4-6]. Here we report a PSF analysis of single crystal graphite for each valence band dispersion.

Experiments were carried out at BL07LSU, SPring-8. Figure 1 shows a series of valence band photoelectron angular distributions with kinetic energy of about 500 eV. BZ boundaries are indicated by dashed lines. Photoelectron intensity from σ band appears at the even BZs at binding energy (BE) of 10 eV while that of 2s band appears at the odd BZs at BE of 17 eV. This difference comes from the fact that the sign of coefficient for σ and 2s band are opposite. Photoelectron intensity appearing at the odd BZs at BE of 6 eV is attributed to π band dispersion which has the same LCAO coefficient as 2s band dispersion.

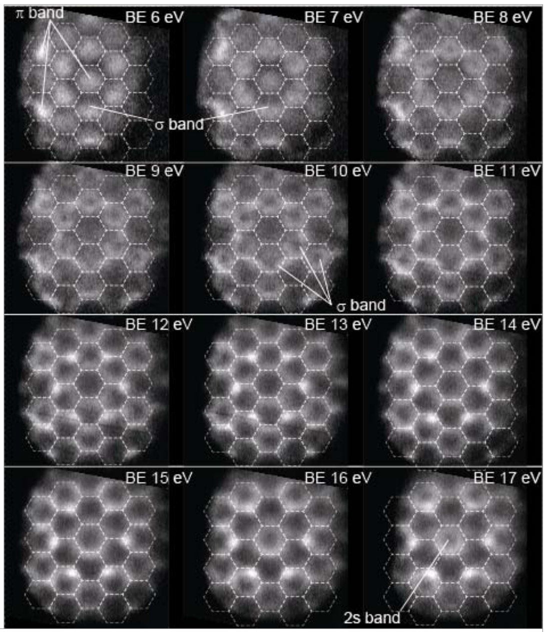

Fig.1 Photoelectron angular distribution patterns from graphite valence band.

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Atomic and Electronic Structure Analysis of Catalytic Ni_2P by Photoelectron Diffraction Spectroscopy

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ABSTRACT

Ni_2P is a promising material for the next generation petroleum processing catalyst with high activity in hydrodesulfurization and hydrodenitrogenation reaction [S. T. Oyama. *et al*., J. Catal. **216**, 343 (2007)]. Photoelectron diffraction spectroscopy is an effective analysis method for investigating the surface and buried interface atomic and electronic structure with surface-sensitivity and site- and element-selectivity. We measured the photoelectron diffraction patterns from single crystalline Ni_2P(10-10) surface using display-type spherical mirror analyzer (DIANA) installed at the circularly-polarized soft x-ray beamline BL25SU, SPring-8. Ni_3P_2 and Ni_3P layers stack alternatively along [0001] direction in Ni_2P bulk. Ni atoms occupy tetrahedral sites in Ni_3P_2 layer and pyramidal sites in Ni_3P layer. Figure 1 (a) and (b) are the 2π steradian Ni 3p and P 2p photoelectron diffraction patterns, respectively, with the kinetic energy of 600 eV. The center of pattern corresponds to the surface normal [10-10] direction. The vertical bright band appeared in each pattern is Kikuchi band originated from the bulk (0001) plane. Both patterns have mirror symmetry at the (0001) plane. Figure 2 shows Ni L-edge X-ray absorption spectrum measured by integrating Ni LMM Auger electron intensity. Typical Ni LMM Auger electron diffraction (AED) patterns are shown in Figure 3. They were normalized by the averaged AED pattern for various photon energy excitations in order to analyze the difference. The pattern contrast at 853.5 eV is the reversed one of 855.5 eV. L_3 peak top (854.4 eV) was found to be isosbetic point, which strongly suggests the existence of two major Ni sites, *i.e.*, pyramidal site in Ni_3P layer and tetrahedral site in Ni_3P_2 layer, and the contribution of pyramidal site electronic state is more dominant at the conduction band near the Fermi level. We succeeded in detecting the site-selective information by diffraction spectroscopy which has been difficult so far.

Fig.1

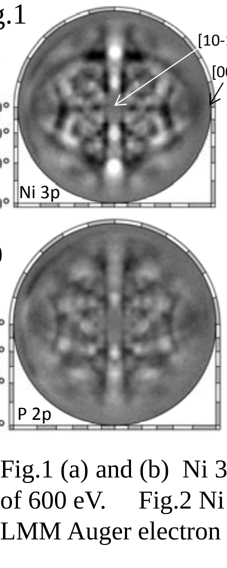

Fig.2

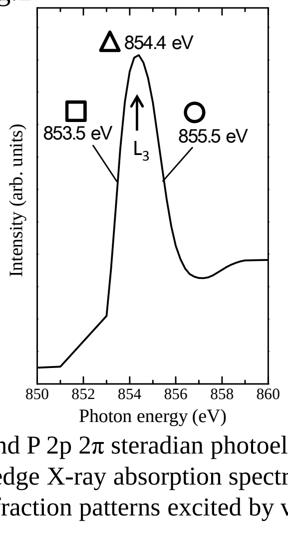

Fig.3

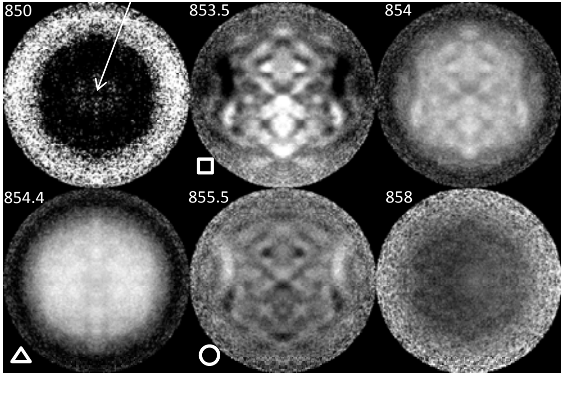

Fig.1 (a) and (b) Ni 3p and P 2p 2π steradian photoelectron diffraction patterns with the kinetic energy of 600 eV. Fig.2 Ni L-edge X-ray absorption spectrum of Ni_2P. Fig.3 The series of 2π steradian Ni-LMM Auger electron diffraction patterns excited by various photon energies.

Core-loss Spectra Fine Structures: A Local Order Probe for Ion-irradiation Induced Modifications.

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ABSTRACT

MAX phases are hexagonal nanolaminated ternary carbides or nitrides built on the stacking of M_6X octahedra layers (M = transition metal, X = C or N) interleaved between pure A element layers (A= Al, Si, Ge, Sn …). Due to their crystallographic structure, MAX phases combine the best properties of metals and ceramics and, as such, are very promising for a wide range of applications. Especially they are expected to sustain extreme environment and their behavior under ion irradiation has recently been studied by Transmission Electron Microscopy (TEM) or X-Ray Diffraction (XRD): Ti-based compounds (Ti_2AlC, Ti_3AlC_2 and Ti_3SiC_2) undergo a phase transformation but hardly amorphize up to high doses (~ 25 displacement per atom – dpa) whereas Cr-based ones (Cr_2AlC or Cr_2GeC) amorphize from very low doses (~ 0.5-1 dpa). [1,2,3] A very interesting point is that most of these materials recover their original structure upon annealing between 500 and 800°C. The influence of chemical composition is thus a key parameter to be understood and the above-mentioned techniques cannot comprehend it.

In this context we focus on a Ti_3AlC_2 thin film irradiated with 340 keV Xe^{2+} or 240 keV Ar^{2+}. We combine Electron Energy-Loss Spectroscopy at the C-K edge to X-Ray Absorption Spectroscopy at the Al-K edge to obtain local order, chemical sensitive information about irradiation induced damages. Fine structures are interpreted using real space multiple scattering calculations performed with FEFF9.1.[4] Special care was taken for the description of final state effects: a screened core-hole together with self-energy effects were taken into account. On the basis of the very good agreement between the calculations and the experiments at the C K-edge, it is shown that the fine structures are not sensitive to the aluminum layer and give thus direct information on the Ti_6C octahedra layers. Comparison between the C-K edge recorded on the virgin and irradiated samples clearly shows that Ti_6C layers are weakly affected by the irradiation. Concerning the Al-K edge, linearly polarized XAS experiments were performed at the LUCIA beamline in the synchrotron SOLEIL. The anisotropy of the charge distribution resulting from the layered structure is evidenced, but because of the muffin tin approximation used in our calculations, simulations are only qualitative. The experimental spectra however clearly show that the Al layers are highly disturbed by the irradiation. The different behavior observed on Ti-based and Cr-based compounds is understood from this preferential perturbation of the Al layer.

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Helium Pressure in Individual Helium Nanobubbles Probed by Spatially-resolved EELS

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ABSTRACT

Defects can modify the physical and mechanical properties of materials. Cavities are a major type of extended defects usually resulting from the incorporation of inert gas or H in solids by high fluence implantation or transmutation reactions in nuclear reactors. Cavities are of major interest in several areas of research, from materials for microelectronics and energy (nuclear and photovoltaic), to more fundamental fields (plasmonic, nanofuidics).

In Si, bubbles (filled cavities) of about 2 nm in diameter are created by He implantation at high fluence. During subsequent annealing, the average size of the bubbles increases, release of He occurs and ultimately bubbles evolve into voids. Despite numerous studies, there are still serious gaps in the understanding of the mechanisms of formation and evolution of the bubbles, which is however a prerequisite to the use of cavities in real practical applications. Helium density and associated pressure in the bubbles is one of the most important quantities to be determined in order to investigate the physical mechanisms of growth of the cavities. In metals and alloys, spatially-resolved EELS experiments have been shown to be a powerful tool to determine He density in individual bubbles, through the measurement of the He 1s->2p transition integrated intensity [1 and references therein]. Another approach, based on the determination of the blue shift of the He K-edge as compared to its position for the free atom could in principle provide an easier way to determine the He density in the bubbles.

In this study, bubbles with diameter in the range 5 – 20 nm have been created in Si by implantation at high fluence followed by an annealing. These bubbles have been investigated by spatially-resolved EELS using in particular a monochromated and probe-corrected microscope. The aim of this study is threefold. First, we show that it is also possible to fully characterize individual He bubbles in Si using spatially-resolved EELS. Second, we report on the *in-situ* mapping of He desorption from individual nanobubbles under the electron beam [2]. Finally, we show that these experiments open new perspectives for the determination of He density and associated pressure in bubbles through the blue shift of the He K-edge.

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Correlation Strength in Iron Pnictide Superconductors

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ABSTRACT

Iron pnictide superconductors represent an entirely new class of superconducting compounds, and have been the subject of intense research since their discovery in 2006. One of the immediate questions regarding the physics of superconductivity in these compounds was related to electron correlation strength; especially in relation to that of high-temperature cuprate superconductors. Using resonant and non-resonant X-ray emission spectroscopy of the iron (or cobalt, nickel, and copper) $L_{2,3}$ edges we provide direct, experimental evidence that the metal *3d* states provide the dominant contribution to the valence band but do not exhibit any of the spectral features inherent in strongly correlated systems. Using the ratio of the non-resonantly excited L_2 and L_3 emission lines we are able to qualitatively classify the correlation strength in these pnictides as closer to a pure metal than a metal oxide.

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Correlation between Structure and Magnetic Properties of $Zn_{1-x}Co_xO$ Oxides

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ABSTRACT

The theoretical prediction of room temperature ferromagnetism (RTFM) in transition metal (TM) doped large band gap semiconductors promoted the research on such kind of systems as one of the most active and attractive topic in materials science and condensed-matter physics. In this direction, a huge effort has been concentrated on TM-doped oxide semiconductors as ZnO, TiO_2 and SnO_2. In spite of the extensive investigations, the origin of the observed RTFM remains inconclusive and controversial. In the present work we report a study of the structural and the magnetic properties of $Zn_{1-x}Co_xO$ bulk samples with Co molar concentrations up to 15%. Polycrystalline $Zn_{1-x}Co_xO$ ($x = 0.15$, 0.20, 0.25 and 0.30) bulk samples were prepared by standard solid state reaction method and sintered in oxygen atmosphere at 1400 °C for 4 h. The as-prepared samples were then annealed in an atmosphere of Ar (95%) and H_2 (5%) for 3 h at 600 °C, the hydrogenation process. The local structure of $Zn_{1-x}Co_xO$ samples was probed by X-ray absorption spectroscopy at Co K-edge. X-ray absorption near edge structure (XANES) spectra shoed that the valence of the dopant ions can be analyzed by comparing their resulting edge structure to those obtained from reference samples (metallic Co, CoO and Co_2O_3). The XANES results undoubtedly indicate that Co on our samples assumes predominantly the 2+ oxidation state. Extended x-ray absorption fine structure (EXAFS) measurements at Co K-edge showed that the first shell (Co-O) coordination number is 4, consistent with a substitution for tetrahedral Zn 2+ ions in the ZnO structure; besides the shell Co-Zn coordination number decreases as Co concentration increases. The structural analysis, including X-ray diffraction measurements, confirms that Co ions are diluted occupying Zn-sites of the ZnO wurtzite structure in hydrogenated $Zn_{1-x}Co_xO$. Clearly, this result excluded the presence of magnetic extrinsic sources as Co-rich nanocrystals and segregated secondary magnetic phases. Thus, the conjugated different techniques confirmed the Zn replacement by Co ions in the wurtzite ZnO structure, which retains a high crystalline quality. No segregated secondary phases neither Co-rich nanocrystals were detected. Magnetic characterizations were performed using a superconducting quantum interference device (SQUID) magnetometer. SQUID magnetometry demonstrates a paramagnetic Curie-Weiss behavior with antiferromagnetic interactions for the as-prepared samples and a coexistence of paramagnetic and ferromagnetic phases at room temperature for the hydrogenated samples. We discuss the observed room temperature paramagnetism of our samples considering the current models for the magnetic properties of diluted magnetic semiconductors.

Hard X-ray Photoemission Study of the Two Valence Transitions in EuPtP

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ABSTRACT

Some Eu compounds show valence transition between Eu^{2+} state (J = 7/2, 7μ_B) and Eu^{3+} state (J = 0). Atomic size of the Eu^{2+} ion is about 10% larger than that of the Eu^{3+} ion. It is well known, therefore, that the Eu mean valence is sensitive to temperature, pressure and magnetic field. Among them, EuPtP undergoes two first-order valence transitions at T_1 = 235 K and T_2 = 190 K [1,2]. The Eu mean valence at $T > T_1$, $T_1 > T > T_2$ and $T_2 > T$ are estimated to be 2.15 (α phase), 2.30 (β phase) and 2.40 (γ phase), respectively [1]. In this study we have investigated the bulk electronic structures of EuPtP by hard X-ray photoemission spectroscopy (HAXPES), in order to understand the mechanism of the valence transitions.

Single crystalline EuPtP was grown by a Pb-flux method. From the susceptibility measurement, T_1 and T_2 of the sample we used were estimated to be 246 K and 200 K, respectively [3]. The temperature-dependent HAXPES measurements with $h\nu$ = 5.95 keV were performed at the undulator beamline BL15XU of SPring-8.

The temperature-dependent HAXPES spectra distinctly showed two valence transitions with stepwise change in the intensities of the Eu^{2+} and Eu^{3+} 3d components. The evaluated Eu mean valences of 2.16±0.03, 2.34±0.03 and 2.50±0.03 in the α, β and γ phases, respectively, are in good agreement with those evaluated from the Eu L_{III} X-ray absorption and Mössbauer experiments [1] and the resonant X-ray diffraction experiments [4].

Furthermore, the Eu^{3+} 3d spectral shape, especially the drastic change in Eu^{3+} 3d feature through the two valence transitions, was hardly reproduced by the atomic calculation. Therefore, we have done calculations based on the impurity Anderson model in which the hybridization of the Eu^{3+} 4f electrons with the conduction electrons and the f-f hybridization between Eu^{2+} and Eu^{3+} with anisotropic symmetry are taken into account. The experimental Eu 3d spectrum of each phase was well reproduced by the calculated Eu 3d spectrum. According to the model calculation, the change in the Eu^{3+} 3d spectral shape through the valence transition is closely related to the degree of admixture of the excitation states (J = 1, 2) and the ground state (J = 0) of Eu^{3+}.

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Spin-orbit Dichroism in SX-ARPES of Pt(111)

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ABSTRACT

Pt shows the largest spin Hall conductivity known to date [1–3]. Its origin has been theoretically studied and the nature of the spin Hall effect (SHE) in Pt was expected to be intrinsic. It is derived from the Berry's phase arising from spin-orbit coupling (SOC) in a multi-orbital system [4–6]. To establish the role of SOC in the electronic structure and investigate the mechanism of the SHE, we study the bulk band dispersions and Fermi surfaces (FSs) of Pt(111) using circular dichroism (CD) in soft x-ray (SX-)ARPES.

The band dispersions and FSs show clear CD and evidence for SOC. The CD shows mirror symmetry with respect to k_y=0 [Fig. 1(b) and (e)] in symmetric experimental configuration of (1) [Fig. 1(f)]. The CD of the L-centered FSs in configuration (2) [Fig. 1(f)] shows the same symmetry as configuration (1) with a rotation of 30deg (not shown here). In contrast, the CD of the Γ-centered FSs show a complex behavior [Fig. 1(c)], possibly superposed on a 3-fold symmetry. Since The FS maps show a clear CD, we believe the CD is directly related to spin Hall effect in Pt.

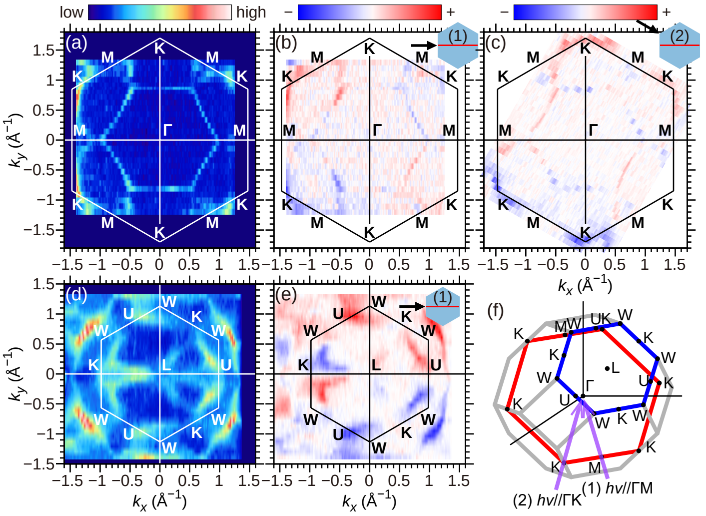

Fig. 1. (a,d) FSs on ΓKK and LWW planes measured at *hv*=463 and 587eV. (b,c,e) CD in the FSs for the experimental configuration (1) and (2) defined in (h). Blue hexagons represent the Brillouin zones of Pt(111), red lines are the mirror planes of the crystal and the arrows denote the incident photon direction. (h) Volume Brillouin zone of fcc Pt. The k_x-k_y planes probed in the present study are indicated by red and blue hexagons. Purple arrows denote the incident photon directions.

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Spin Orbit Splitting in the Valence Bands of ZrS_xSe_{2-x}: ARPES and DFT

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ABSTRACT

Angle-resolved photoemission spectroscopy using synchrotron radiation was performed for ternary layered transition metal dichalcogenide ZrS_xSe_{2-x}, where $0 \leq x \leq 2$. A characteristic splitting of the chalcogen p-derived valence bands along high symmetry directions was observed. The splitting size at the A point of the Brillouin zone is found to increase from 0.06 eV to 0.31 eV with increasing the atomic number of the chalcogenide as moving from ZrS_2 towards $ZrSe_2$, respectively. An almost linear behaviour of the splitting size upon the composition parameter x is observed. Our electronic structure calculations based on the density functional theory prove that this splitting is due to spin-orbit (SO) coupling [1]. When considering spin-orbit coupling, the degeneracy of the valance bands is lifted.

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Electronic Band Structure of ZrS_xSe_{2-x} Layered Semiconductors

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ABSTRACT

The electronic structure of the layered transition metal dichalcogenide ZrS_xSe_{2-x} semiconductors has been studied by means of high resolution angle–resolved photoemission spectroscopy (ARPES) using synchrotron radiation. The chalcogen p–derived valence bands of the complete series of ZrS_xSe_{2-x} are reported along the normal direction and along the major symmetry directions of the hexagonal Brillouin zone parallel to the layers. The results show that the binding energies of the topmost valence band shift almost linearly with the composition parameter x An emission from the conduction band minimum is observed just below the Fermi edge. This emission verifies the indirect nature of the band gap and enabled us to determine the band gap values directly by ARPES. The obtained band gap values are compared to our previous values determined by optical measurements [1].

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Chemical Bonding and Surface Electronic Structures of $Pt_3Co(111)$, $Pt_3Ni(111)$ Single Crystals

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ABSTRACT

With angle resolved photoemission spectroscopy (ARPES), the surface electronic band structures of $Pt_3Co(111)$ and $Pt_3Ni(111)$ single crystals are investigated, which allow to study the bonding interaction between chemically absorbed atomic oxygen and its surfaces. The d-band electrons of subsurface TM are separated from the direct chemical bonding with atomic oxygen. That is, the TM does not contribute to direct chemical bonding with oxygen. From the density functional theory (DFT) calculations, it is identified that the main origin of improved oxygen absorption property, i.e. softening of Pt-O bonding, is due to the suppression of Pt surface-states which is generated from change of interlayer potential, i.e. charge polarization, between Pt-top and TM-subsurface. Our results point out the critical roles of subsurface TM in modifying surface electronic structures, which in turn can be utilized to tune surface chemical properties.

Electronic Structure of 3-Dimensional Systems and Multilayer Heterostructures by Soft-X-ray ARPES

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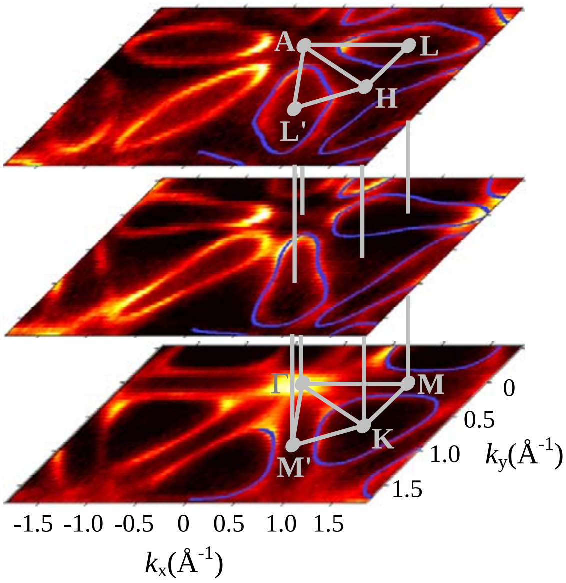
ABSTRACT

A fundamental advantage of ARPES experiments in the soft-X-ray energy range is an increase of the photoelectron escape depth λ. This gives a boost to bulk sensitivity of ARPES as well as enables access to buried heterostructures. Furthermore, by the Heisenberg uncertainty principle, the increase of λ improves intrinsic resolution in surface-perpendicular momentum $\Delta k_z = \lambda^{-1}$. With free-electron final states and simplified matrix elements achieved in the soft-X-ray energy range, the improved k_z definition enables investigations of electronic structure of 3-dimensional (3D) systems under full control of 3D momentum **k**.

The soft-X-ray ARPES facility at SLS is in operation since early 2011. It is installed at the ADRESS beamline[1] which delivers soft-X-ray radiation with variable polarizations in a photon energy range from 300 to 1600 eV. High photon flux topping up 10^{13} photons/s/0.01%BW at 1 keV has allowed us to break through the notorious problem of small valence band crossection in the soft-X-ray range. At an energy around 900 eV, ARPES images of publication quality are routinely delivered within 5 min of data acquisition with a combined energy resolution of 110 meV, and within 30 min with resolution of 60 meV.

Apart from crucial technical issues, we give an overview of pilot in-house and user experiments. These include determination of 3D Fermi surface (FS) of VSe_2 (figure), with out-of-plane warping of the FS giving rise to exotic 3D charge density waves; polarization dependence and alternating FS shapes in pnictide HTSCs, revealing their 3D character and intra-cell interference effects; 3D hybridization between *sp*- and *f*-states in heavy-fermion systems; topological surface state embedded in 3D valence band of $PbBi_4Te_7$, with spatial oscillations of its wavefunction reflected in photon energy dependence of ARPES intensity; electronic structure of Mn magnetic impurities in 3D host lattice of diluted magnetic semiconductor GaMnAs; FS of buried layers in $LaNiO_3/LaAlO_3$ and $SrTiO_3/LaAlO_3$ hererostructures, etc. These unfolding results demonstrate an immense potential of soft-X-ray ARPES to deliver a clear view of the electronic structure of 3D systems and multilayer heterostructures.



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PROGRAM

Wednesday, Sept. 19th, 2012

Wednesday, September 19th, 2012

08:30 - 9:15 **Interface Induced High Tc Superconductivity in Single Unit Cell FeSe on STO**
Q.-K. Xue **(Plenary)**

09:15 - 10:00 **Electronic properties of ultimate nanowires**
F.J. Himpsel **(Plenary)**

	Novel Electronic States 2 ***Topological insulators*** Chateaubriand Auditorium	**Imaging Spectroscopy 2** Maupertuis Auditorium	
10:30 - 11:00	Quantum confinement at topological insulator surfaces *F. Baumberger* (Invited)	Attosecond electronic and nuclear dynamics in high-harmonic generation from aligned molecules B. *Carré* (Invited)	**10:30 - 11:00**
11:00 - 11:30	Engineering Fermi surface topologies in low-dimensional systems *I. Matsuda* (Invited)	Attosecond time-resolved molecular dynamics *M. Vrakking* (Invited)	**11:00 - 11:30**
11:30 – 11:50	Comprehensive observations of Rashba spin-splitting of Bi(111) by means of high-resolution spin-resolved photoelectron spectroscopy *T. Okuda* (Contributed)	Imaging nuclear dynamics in molecules: ultrafast isomerization and proton migration *S. Sorensen* (Contributed)	**11:30 - 11:50**
11:50 - 12:10	Spin polarized photoemission from Bi2Te3 and Sb2Te3 topological insulator thin films *L. Plucinski* (Contributed)	Measuring the mean kinetic energy of atoms in molecules and solids using electron scattering *M. Vos* (Contributed)	**11:50 - 12:10**
12:10 – 12h30	Influence Of The Large Unit Cell On The Electronic Structure Of Topological Insulators *H. Dil* (Contributed)	To be announced (Contributed)	**12:10 - 12h30**

12:30 - 13:45 **Lunch**
Lamennais Area

12:45 - 19:45 **Sight Seeing Tours:**
14h30-18h00: Saint Malo
12h45-19h00: Cap Frehel-Fort Lalatte
12h45-19h45: Mont St Michel-Cancale

20:30 - 24:00 **Banquet**
Jacques Cartier Rotunda & Grand Large Room

Condensed phase	Gas phase

Interface Induced High Tc Superconductivity in Single Unit Cell FeSe on STO

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ABSTRACT

High Tc superconductivity in cuprates has been discovered for 26 years. However, its mechanism remains mysterious. By growing stoichiometric single crystalline FeSe ultrathin films on $SrTiO_3$(001) substrate with molecular beam epitaxy, we show evidence for the occurrence of superconductivity transition at around 77 K by *in situ* low temperature scanning tunneling microscopy. Combined with ARPES and transport measurements, I would like to discuss the possible mechanism for this special case and the implications on all unconventional superconductors including cuprates and the newly discovered Fe-based superconductors in general.

The work was done in collaboration with Xucun Ma, Xi Chen, Lili Wang, Ke He, Jinfeng Jia, Yayu Wang and Xingjiang Zhou.

Electronic Properties of Ultimate Nanowires

Franz J. Himpsel

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ABSTRACT

Stepped semiconductor surfaces decorated with metal atoms make it possible to engineer the ultimate nanowire, a string of atoms connected by a single wave function. Such atomic wires form spontaneously for many metal-semiconductor combinations and thereby provide a playground for low-dimensional electron physics [1]. Angle-resolved photoelectron spectroscopy combined with scanning tunneling microscopy/spectroscopy reveals a variety of unexpected phenomena, such as atomically-precise ribbons of graphitic silicon and spin-polarized Fermi surfaces caused by the Rashba effect.

The broken bond orbitals are so localized at the step edges that they become fully spin-polarized, similar to isolated broken bonds (Pb centers). Density functional theory predicts a spin-polarized ground state which is closely coupled to the formation of a superlattice (neither can exist without the other) [2]. This resembles the situation in complex oxides (HiTc superconductors, multiferroics), where the spin, charge, and lattice degrees of freedom are strongly coupled and make it difficult to find a simple approximation of their electronic structure.

Two-photon photoemission spectroscopy [3] and scanning tunneling spectroscopy [4] provide support for spin-polarized silicon atoms by probing their characteristic minority spin state.

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SESSION:

Novel Electronic States 2

Topological insulators

Quantum Confinement at Topological Insulator Surfaces

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ABSTRACT

Bismuth-chalchogenides are model examples of three-dimensional topological insulators. Their ideal bulk-truncated surface hosts a single spin-helical surface state, which is the simplest possible surface electronic structure allowed by their non-trivial Z_2 topology. However, real surfaces of such compounds, even if kept in ultra-high vacuum, rapidly develop a much more complex electronic structure with ladders of Rashba split conduction and valence subbands [1,2]. Here, we demonstrate that a conceptually simple model, based on a semiconductor-like band bending, can quantitatively explain the entire measured hierarchy of electronic states on such surfaces including their complex spin-texture [3]. We will further discuss how the surface-bulk connectivity in topological insulators is modified by quantum confinement.

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Engineering Fermi Surface Topologies in Low-dimensional Systems

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ABSTRACT

Low-dimensional electronic system, formed in a monatomic layer or in a thin film on a surface, has attracted academic and technological intersts. Since a solid surface is structurally exposed to vacuum and it is also inevitably connected to the substrate, the system can be electronically regulated by various procedures such as surface adsorption or imputity-doping in bulk. Recently, we have found, on a $SrTiO_3$ surface, the surface insulator-to-metal transition by hydrogen adsorption [1]. Edge-states have shown distincitve spin-polarized band structures through the Z_2 topological transition by Sb-doping in a $Bi_{1-x}Sb_x$ crystal[2].

Here, we show another example. We present regulation of the Fermi surface topology, namely the electronic topological transition, for metal thin films on semiconductor substrates [3]. As the thickness of a bulk metal crystal is scaled down to the order of its Fermi wavelength, the electronic system changes from three-dimensional (3-D) to 2-D by the quantum size effect. Moreover, the ultrathin metal film in the quantum regime further changes its topology through the interface atomic layer. We observed the electronic topological transition, opening of the Fermi surfaces, by introducing a 1-D array of indium (In) atomic chains with a 1 nm period into the interface between a 2-D silver (Ag) film with a thickness of 1 nm and a semiconducting silicon (Si) substrate. The demonstration has been carried out on metal films with a thickness of several atomic layers at room temperature. Thus, the results of the present research develop both the topological physics and quantum devices in atomic-scale systems.

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NE2-CT-OKU

Comprehensive Observations of Rashba Spin-splitting of Bi(111) by Means of High-resolution Spin-resolved Photoelectron Spectroscopy

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ABSTRACT

Using the newly developed high-resolution spin resolved photoelectron spectroscopy (SARPES) endstation ESPRESSO [1], at Hiroshima Synchrotron Radiation Center (HSRC), we have precisely measured the spin electronic structure of Bi(111) film fabricated on Si(111) substrate. The high energy and angular resolutions (ΔE~10 meV, $\Delta\theta$~0.37°) realized by the highly efficient VLEED spin polarimeter unveil a peculiar spin texture of the surface states of Bi(111) film caused by the strong spin-orbit interaction with C_{3v} crystal symmetry.

Along the $\bar{\Gamma}-\bar{\mathrm{M}}$ direction, almost fully polarized in-plane spin photocurrent have been observed in two characteristic surface states forming the electron pocket (S1) and hole pocket (S2) at the Fermi level. The higher spin polarization than those in the previous reports with the conventional SARPES set-up [2,3] owes to the much improved energy and angular resolutions of the EPSRESSO machine. On the other hand, significant out-of-plane spin component has been observed in the S2 state at the *k* points away from the $\bar{\Gamma}-\bar{\mathrm{M}}$ line. The out-of-plane spin polarization is anti-symmetric with respect to $\bar{\Gamma}-\bar{\mathrm{M}}$ line being in agreement with the previous paper[4]. We demonstrate that the observed out-of-plane spin polarization can be well reproduced with the k•p model considering the C_{3v} crystal symmetry similarly to the out-of-plane spin polarization emerged in the warped topological surface state of Bi_2Te_3[5]. The oscillative polarization feature of in-plane spin component which is proposed in the previous paper[4], however, has not been observed and the difference of the spin polarization at different position in ***k*** space is probably due to the photoemission final state effect.

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Spin Polarized Photoemission from Bi_2Te_3 and Sb_2Te_3 Topological Insulator Thin Films

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ABSTRACT

The surface electronic properties of important topological insulators Bi_2Te_3 and Sb_2Te_3 [1] are shown to be robust under an extended surface preparation procedure which includes exposure to atmosphere and subsequent cleaning and recrystallization by an optimized *in-situ* procedure under ultra-high vacuum conditions. Clear Dirac-cone features are displayed in high-resolution angle-resolved photoemission spectra from the resulting samples, indicating insensitivity of the topological surface state to cleaning-induced surface roughness and stoichiometry [2]. However, the Fermi velocities in the Dirac cones of Bi_2Te_3 are smaller than in freshly cleaved crystals, and similar to the ones found in films cleaved in vacuum and then exposed to air [3], possibly due to the intercalation of the van-der-Waals region with the foreign atoms [4].

Spin polarized photoemission spectra from these surfaces show up to 45% *in-plane* spin polarization in the Dirac cone near the Fermi level, which is consistent with our dedicated *ab initio* theoretical results which find spin polarization in the order of 40-50% when averaged over the surface quintuple layer with the exponential depth profile related to the scattering mean free path of the VUV photoelectrons. We also find a non-zero *out-of-plane* spin polarization component in Bi_2Te_3 hexagram Fermi surface.

We will discuss the spin-orbit entanglement mechanism [5] behind the non-100% spin polarization in topologically protected surface states, and propose possible surface engineering solutions to increase the spin polarization of the Dirac cone [6] in films grown by the MBE [7]. Furthermore we will compare analytical band structure models [8] with the DFT-based slab calculations [5,6].

Thanks are due to NRW Research School "Research with Synchrotron Radiation" funded by the Northrhine-Westphalia Ministry for Innovation, Science, Research, and Technology (grant No. 321.2-8.03.06-58782).

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Influence of the Large Unit Cell on the Electronic Structure of Topological Insulators

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ABSTRACT

In a simple picture topological insulators can be viewed as bulk band insulators with metallic surface states. The unique properties of this novel class of materials arises from the fact that the spin-orbit interaction causes an odd number of parity inversions of the bulk bands around the Fermi level. The change from such a topological non-trivial to a topologically trivial system forces the existence of spin-polarized metallic states at the interface [1]. In recent years the spin and electronic structure of a variety of topological insulators in the direction parallel to the surface have been studied. It has been found that along this direction the band structure matches nicely the one predicted by ab-initio calculations when a rigid band shift is applied in order to account for defect induced doping.

The electronic structure along the direction of the surface normal has not been extensively studied and here we utilize the simplified photoemission matrix elements in soft X-ray ARPES to measure this dispersion independent of final state effects. For systems with a small unit cell such as for example BiTeI the measured and calculated k_z dispersion correspond very well [2]. In this case a Fourier transform analysis of the data reveals the out-of-plane lattice constant and provides an efficient way of determining the inner potential.

The crystal structure of most topological insulators currently under investigation consists of building blocks connected by van der Waals type binding. For $PbBi_4Te_7$ and $GeBi_4Te_7$ these building blocks are alternating 5 and 7 atomic layer units, resulting in a out-of-plane lattice constant of about 2.4 nm. In the measured band structure along this direction clear free electron-like features can be distinguished. However, the periodicity of these features is different as what would be expected for this crystal structure and would correspond to a much smaller unit cell. It will be explained how this apparent contradiction can be resolved by considering the limited coherence length of the electrons in the direction perpendicular to the layers. This interpretation is supported by a novel Fourier type analysis taking the coherence length into account. The consequences of this finding for both the bulk and surface properties of topological insulators along the directions perpendicular to the surface currently mainly under investigation will be discussed.

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SESSION:

Imaging Spectroscopy 2

Attosecond Electronic and Nuclear Dynamics in High-harmonic Generation from Aligned Molecules

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ABSTRACT

Tracking in real time the ultrafast electronic and nuclear motions in molecules can be performed in pump-probe studies using ultra-short light pulses, i.e., ultra-steep light field temporal gradient [1]. A weak probe field may interact with the system (weak field regime γ_{Keldysh} parameter >1), producing either photoionization or transient absorption [2,3]. A strong probe field can drive nonlinear response in the tunnel ionization regime (γ_{Keldysh} <1), i.e., recollision and scattering of the freed electronic wavepacket, which leads to either electron diffraction [4] or attosecond emission through radiative recombination [5-10]. Attosecond emission in high harmonic generation (HHG) encodes a wealth of information on the system in the spectral amplitude and phase of the polarization components. In small aligned molecules it gives access to the recombination dipole in the molecular frame, from which the radiating valence orbital can be reconstructed using a tomographic procedure [5,9,10], with Angström space and sub-cycle (few 100 as) to few–cycle (few fs) resolution.

An important case is provided when the same strong field excites and simultaneously probes wavepacket dynamics. For example, recent studies revealed that some molecules can be tunnel ionized simultaneously from several orbitals [11,12]. The multiple ionization channels lead to coherent wavepacket dynamics in the ionic state, as well as interfering contributions to attosecond emission. Unraveling the multiple channels is difficult in the general case. In N_2 molecule, we show that X and A channel contributions (corresponding to ionization from the HOMO and HOMO-1 orbitals) can be disentangled, allowing tomographic reconstruction of the two orbitals, and giving time-resolved images of the “hole” wavepacket in the ion [8]. Furthermore, we show that variation with the driving laser intensity of the spectral amplitude and *phase* of attosecond emission gives deep insight into the multiple orbital dynamics in the strong field [13].

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Attosecond Time-resolved Molecular Dynamics

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ABSTRACT

Using attosecond light sources based on high-harmonic generation (HHG), pump-probe experiments can be performed where electron dynamics is studied on its natural timescale, providing insight into the fundamental role that electrons play in photo-induced processes. In my talk I will present some of the first applications of these techniques in molecular science, focusing on two-color experiments where several small molecules were exposed to a sequence of one or more attosecond pulses and an infrared field.

Among other things, I will present experiments where attosecond pulses probe the electronic re-arrangement that occurs in neutral molecules and their single-ionized counterparts, under the influence of a moderately strong IR field. These experiments pave the way to the observation of time-resolved electron dynamics in more complex molecules.

Imaging Nuclear Dynamics in Molecules: Ultrafast Isomerization and Proton Migration

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ABSTRACT

Photoionization in molecules is a fundamental process driving nuclear dynamics on the time scale of femtoseconds. Obtaining temporal information on dynamical processes in neutral or ionized molecules is possible in pump-probe experiments, but even in single-photo ionization the temporal signature is embedded in the ion momentum if a sufficient number of particles can be measured. In the present study multiple ion coincidence measurements provide the full three-dimensional momentum of all charged fragments produced in dissociation of dication species of small molecules [1]. Multiple ion coincidences allow energy or angular correlations between particles to be evaluated, and we find evidence correlating the kinetic energy released in the dissociation to the geometry of the dication. The angular anisotropy of fragment emission depends principally upon the alignment of the molecule in the core excitation process, but subsequent geometrical changes on the time scale of the core hole life time affect the angular anisotropy in a distinct way. Several examples of rapid nuclear motion illustrate this principle in triatomic molecules such as carbonyl sulphide, water and carbon dioxide.

A study on core-excited water molecules is presented where the kinetic-energy released in the fragmentation process is correlated to the geometry of the molecule [2]. In addition several examples of ultrafast nuclear motion leading to particular fragmentation channels are studied in water, carbon dioxide [3] and in carbonyl sulfide [4]. The study reveals a time scale for nuclear motion on the order of a few femtoseconds.

In carbon dioxide we find that the Renner-Teller split states populated in core-valence excitation can be treated separately using angular correlations between fragments. The bent component preferentially populates dication states with a bent geometry and an extreme case of complete deformation of the linear carbon dioxide molecules is identified at both the carbon and oxygen core edges resulting in very similar angular distribution and kinetic energy release to the $C^+ + O_2^+$ fragment pair [3].

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Measuring the Mean Kinetic Energy of Atoms in Molecules and Solids using Electron Scattering

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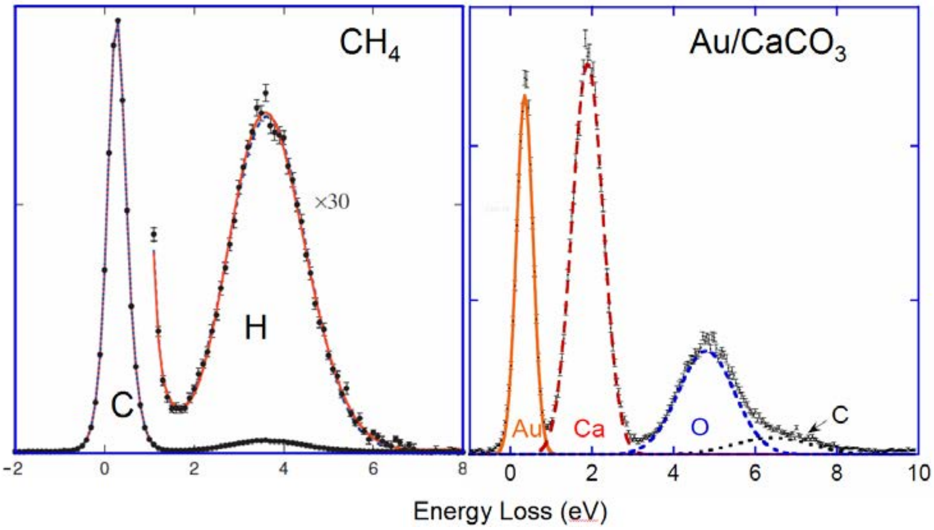
ABSTRACT

The recoil effect does not only influence line shapes in high energy photo-emission[1] but it also leaves a clear imprint on the shape of the elastic peak in electron scattering experiments at high energies [2]. For electrons, scattering from a target with atoms of different mass, the elastic peak splits up into different components (depending on the mass of the scattering atom) and broadens [3,4]. Compared to photoemission these "elastic" electron scattering experiments allows us to study the recoil effect at much larger momentum transfers (up to 192 Å^{-1}), as well as elements without core levels (hydrogen!). In the high-momentum transfer limit the broadening of the elastic peak can be interpreted as Doppler broadening due to the velocity of the scattering atom. Broadening is thus a direct measure of the kinetic energy of that atom. We present surface and gas-phase measurements showing how the mean kinetic energy of atoms can be determined, and compare the results with calculations, based on the rotational and vibrational levels of molecules [5] (for H_2, CH_4, H_20) and lattice dynamics code for solids[6] (graphite, $CaCO_3$, Al, Au).



Spectra of 2 keV electrons backscattered from methane and 40 keV electrons scattered from CaCO3 covered by a 1Å thick layer of Au. Note the large variations in peak width.

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PROGRAM

Thursday, Sept. 20th, 2012

Thursday, September 20th, 2012

08:30 - 9:15 **Spin-polarized electrons on non-magnetic surfaces: From the Rashba effect to topological insulators**
J. Osterwalder **(Plenary)**

09:15 - 10:00 **Small molecule photoelectron spectroscopy: Recoil effects, stoichiometric surprises, and double-core-hole ionization**
T.D. Thomas **(Plenary)**

	Novel Electronic States 3 ***Complex oxides*** Maupertuis Auditorium	**Atomic and Molecular Science 3** ***Fundamental processes (FEL, HHG)*** Chateaubriand Auditorium	
10:30 - 11:00	Inelastic and elastic resonant X-ray scattering investigation of high temperature superconductors *M. Le Tacon* (Invited)	Multiple ionization and Auger decay processes in isolated atoms and molecules during interaction with intense X-FEL radiation *B. Krässig* (Invited)	**10:30 - 11:00**
11:00 - 11:30	Novel two-dimensional electron gases at the surface of transition-metal oxides: from orbital ordering to orbital symmetry reconstruction *A.F. Santander-Syro* (Invited)	Photoelectron spectroscopy of atoms and molecules by using FEL and laser high-order harmonics *M. Fushitani* (Invited)	**11:00 - 11:30**
11:30 – 11:50	Revealing the Fermi surface of the buried LaAlO3/SrTiO3 interface by angle resolved soft X-ray photoelectron spectroscopy *M. Sing* (Contributed)	To be announced (Contributed)	**11:30 - 11:50**
11:50 - 12:10	Electronic structure of magnetic semiconducting Cr0.20Al0.80 and the anti-ferromagnetic-to-ferromagnetic transition in FeRh from hard X-ray photoemission *C. Fadley* (Contributed)	Extracting electron-ion differential scattering cross sections for partially aligned molecules by laser-induced rescattering photoelectron spectroscopy *K. Ueda* (Contributed)	**11:50 - 12:10**
12:10 - 12:25	Magnetic and ligand field properties of copper at the interfaces of (CaCuO2)m/(SrTiO3)n superlattices *M. Minola* (Hot Topic)	Spectral dynamics of amplified X-ray emission from core-ionized diatomic molecules *V. Kimberg* (Hot Topic)	**12:10 - 12:25**

12:30 - 13:45 **Lunch**
Lamennais Area

Condensed phase	Gas phase

13:45 - 15:30

Posters Session III

- Atomic & Molecular Science 2
- Novel Opportunities / Instrumentation
- Surface & Material Science 3

Jacques Cartier Rotunda & Grand Large Room

15:30 - 16:00

Coffee Break

Jacques Cartier Rotunda & Grand Large Room

	Novel Electronic States 4 ***Graphene, Dirac matter*** Chateaubriand Auditorium	**Photo Chemistry and Reactivity 3** ***Nanoparticles, liquids*** Maupertuis Auditorium	
16:00 - 16:30	Pi-Bands, p/n-Junctions and mini cones in intercalated epitaxial graphene on SiC *U. Starke* (Invited)	Photoexcitation, photoionization, and relaxation of isolated and deposited particles *E. Rühl* (Invited)	**16:00 - 16:30**
16:30 - 17:00	Angle resolved Spectroscopy applied to grapheme *A. Bostwick* (Invited)	Aqueous-solution photoelectron spectroscopy: ultrafast charge and energy transfers *B. Winter* (Invited)	**16:30 - 17:00**
17:00 - 17:20	Hole doping of graphene by metal halides adsorption and intercalation *N. Vinogradov* (Contributed)	Surface oxidation states of aged free silicon nanoparticles probed with soft X-ray *C. Nicolas* (Contributed)	**17:00 - 17:20**
17:20 - 17:40	Is charge carrier really Dirac Fermion in silicene on Ag(111) ? *C. Lin* (Contributed)	Resonant inelastic soft X-ray scattering map of gas-phase water and what it tells about liquid water *L. Weinhardt* (Contributed)	**17:20 - 17:40**
17:40 - 18:00	From silicene discovery to graphene-like epitaxial germanium sheets *A. Resta* (Contributed)	Local structures of methanol-water binary liquid studied by soft X-ray absorption spectroscopy *N. Nagasaka* (Contributed)	**17:40 - 18:00**
18:00 - 18:20	Towards graphene-based electronics: graphene on cubic-SiC(001)/Si wafers *V. Aristov* (Contributed)	From molecules to rain: surface propensity and speciation of atmospherically relevant aqueous surfaces studied by photoelectron spectroscopy *O. Björneholm* (Contributed)	**18:00 - 18:20**

Free Evening

Condensed phase	Gas phase

Spin-Polarized Electrons on Non-magnetic Surfaces: From the Rashba Effect to Topological Insulators

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ABSTRACT

The spin-orbit interaction in combination with the breaking of spatial inversion symmetry at surfaces can lead to spin-splitting of electronic surface states on nonmagnetic metals. For partially filled bands, this so-called Rashba effect leads to pairs of non-degenerate Fermi surfaces with different Fermi wave vectors for opposite spins. It is this effect that is exploited in the concept of the spin field-effect transistor. In topological insulators, the non-trivial topology of the bulk electronic states forces the appearance of surface states, where one of the pair of spin-split electronic bands crosses the Fermi level and the other not. While the non-magnetic character of the surface is still maintained due to time-reversal symmetry, the directions of spin polarization and electron momentum are strictly locked in these non-degenerate surface states, which is at the origin of a plethora of unusual properties and physical phenomena.

Being confined to the outermost atomic layers, these surface states can be studied in detail by angle-resolved photoemission spectroscopy (ARPES) and its spinresolved version. They can also be manipulated by the means provided by surface science. Our group has built an angle-resolved photoemission apparatus equipped with a three-dimensional spin polarimeter [1], and introduced a powerful two-step fitting procedure for deriving three-dimensional spin polarization vectors [2] for individual electronic states. In combination with high-resolution ARPES data, precise momentum-space spin structures could be obtained for a number of surface Rasba systems [3] and topological insulators [4-6] over the last few years. A survey will be given on recent results from our studies, as well as a critical reflection on whether the spin-polarization values measured with ARPES truly reflect the spin textures in the condensed matter systems [7,8].

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Small Molecule Photoelectron Spectroscopy: Recoil Effects, Stoichiometric Surprises, and Double-core-hole Ionization

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ABSTRACT

Three features of small-molecule photoelectron spectroscopy will be discussed. (1) Conservation of momentum requires that the atom from which a photoelectron is emitted have a momentum equal to that of the emitted electron. This recoil momentum is shared among the various modes of motion of the molecule – translational, vibrational, and rotational – and can lead to rotational and vibrational excitation of the residual ion. Furthermore, any initial velocity of the atom (due to either translational, rotational, or vibrational motion) will lead to Doppler broadening. Several examples show that these effects are observable and can be accounted for by simple models.[1] In other cases, however, the simple models break down and show that a deeper insight is necessary. (2) Inner-shell photoionization is essentially an atomic process, and it is, therefore, expected that the intensity for emission of a photoelectron from the core of an atom in a molecule will be independent of the chemical environment of the atom. Recent measurements on the carbon 1s photoelectron spectra of CH_3CCl_3 (and related molecules) show that this is not the case.[2] At energies not far above the ionization threshold there are strong oscillations of the intensity ratio (CCl_3/CH_3) with increasing photon energy. These are similar to (and related to) those seen in EXAFS, and can be accounted for by considering backscattering of the outgoing photoelectrons from the chlorine atoms. Moreover, even at high energies the cross section for ionization has been found to depend on the chemical environment of the atom. For CH_3CCl_3, for instance, the intensity ratio (CCl_3/CH_3) is only 0.8 at a photon energy that is nearly 600 eV above threshold. These results have important consequences for the use of inner-shell electron spectroscopy for quantitative analysis. (3) Single-core-hole ionization energies have long been used as a tool for investigating chemical phenomena. Double-core-hole ionization energies provide additional chemical information. By combining the single-hole and double-hole ionization energies it is possible to determine the effects of the initial-state charge distribution and final-state charge rearrangement on the chemical shifts and on other chemical properties. Until recently, however, double core-hole ionization energies have not been experimentally accessible for first row elements. New experimental techniques have, however, made it possible to measure these for not only single sites in a molecule, but also for two different sites in the molecules. The chemical information that can be obtained from such measurements will be discussed.[3]

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SESSION:

Novel Electronic States 3

Complex oxides

Inelastic and Elastic Resonant X-ray Scattering Investigation of High Temperature Superconductors

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ABSTRACT

Motivated by the search for the mechanism of high-temperature superconductivity, an intense research effort has been focused on the evolution of the spin excitation spectrum upon doping from the antiferromagnetic (AF) to the superconducting states of the cuprates. Because of technical limitations, however, the experimental investigation of doped cuprates has been largely focused on low energy excitations (<100 meV) in a small range of momentum space[1]. We have used Resonant Inelastic X-ray Scattering (RIXS)[2] to show that a large family of superconductors, encompassing the model compound $YBa_2Cu_3O_7$, exhibits damped spin excitations - paramagnons - with dispersions and spectral weights similar to those of magnons in undoped AF cuprates over much of the Brillouin zone[3]. This is in excellent agreement with the spin excitations obtained by exact diagonalization of the t-J Hamiltonian on finite-sized clusters. A numerical solution of the Eliashberg equations based on our experimental findings for $YBa_2Cu_3O_7$ reproduces its T_C within a factor of two. The discovery of a well-defined, surprisingly simple spin excitation branch over a wide range of doping levels thus strongly supports magnetic Cooper pairing models for the cuprates.

In parallel to the observation of magnetic excitations, we found, in underdoped compounds, a clear enhancement of elastic scattering around incommensurate wave vectors (0.31,0,L) and (0,0.31,L) indicative of the coexistence of charge ordering and superconducting state[4]. Further investigation revealed that the charge order survives in the pseudogap state of these underdoped compounds, and indicates a competition between the superconducting instability and charge ordering.

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Novel Two-dimensional Electron Gases at the Surface of Transition-metal Oxides: From Orbital Ordering to Orbital Symmetry Reconstruction

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ABSTRACT

The two-dimensional electron gases (2DEGs) at interfaces between $SrTiO_3$ (STO) and other insulating transition-metal oxides display stunning properties, such as superconductivity or magnetoresistance [1], and are at the core of the emerging field of oxide electronics. However, they are difficult to produce, and their electric properties depend strongly on the fabrication details. This has hampered the understanding of the physical origin of such 2DEGs and their generalization to other multifunctional oxides.

In this talk, I will first present our recent discovery that a 2DEG can be simply realized at the vacuum-cleaved surface of STO (STO) [2]. We probed this state using light-polarized angle-resolved photoemission spectroscopy, a technique that gives the band structure and symmetries at the surface of materials. Our data unveil a remarkable electronic structure consisting on multiple subbands of heavy and light electrons, confined within a region of ~5 unit cells beneath the surface, and ordered by their bulk orbital symmetries. The similarity of this 2DEG with those reported in other STO-based interfaces suggests that different forms of electron confinement at the surface of $SrTiO_3$ lead to essentially the same 2DEG. Thus, this discovery provides a model system for the study of the electronic structure of 2DEGs in STO-based devices, and a novel route to generate 2DEGs at surfaces of other functional oxides.

I will then show that a 2DEG can also be created at the surface of $KTaO_3$, a wide-gap insulator with a strong spin-orbit coupling (SOC), more than one order of magnitude larger than in STO. Our data and analysis establish that the 2DEG at the surface of KTO is, in contrast to the previous cases of STO-based 2DEGs, a genuinely new physical system with respect to the bulk: the orbital symmetries of its subbands are entirely reconstructed and their masses are significantly renormalized. This stems from the strong spin-orbit interaction inherited from the bulk, which is comparable to the Fermi energy and subband splittings of the 2DEG. These results demonstrate that in transition-metal oxides the strong couplings between the active electronic degrees of freedom, combined with the electron confinement, can lead to novel electronic states at the surface that are not simple extensions of the bulk bands.

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Revealing the Fermi Surface of the Buried $LaAlO_3/SrTiO_3$ Interface by Angle Resolved Soft X-ray Photoelectron Spectroscopy

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ABSTRACT

The origin of a high-mobility two-dimensional electron system (2DES) at the interface of $LaAlO_3/SrTiO_3$ (LAO/STO) heterostructures is still subject of intense research activities in both theory and experiment[1,2,3]. Its sudden appearance above a critical LAO thickness suggests an electronic reconstruction as the driving mechanism, in which electronic charge is transferred from the surface to the interface to avoid excessive build-up of an electric potential gradient across the polar LAO overlayer. Additionally, extrinsic interface doping by cation intermixing or oxygen vacancies may also play a role. The 2DES is expected to be formed by Ti 3d electrons, as Ti is the only multivalent ion in LAO/STO to accommodate the extra interface charge, as indeed evidenced by recent hard x-ray photoelectron spectroscopy (HAXPES) of the Ti 2p core levels[3]. Unfortunately, a direct observation of the conducting Ti 3d states by HAXPES is hindered by unfavorable photoexcitation cross sections.

Much better spectroscopic access to the interface states can be achieved by resonant photoemission using soft x-rays at the Ti 2p-3d absorption edge, which strongly enhances Ti 3d sensitivity at still moderately high probing depth. With additional angular resolution it should thus become possible to probe the momentum-dependent band structure of the interface. We have applied the method to a conducting LAO/STO heterostructure and report here the direct observation of the metallic Ti 3d- derived 2DES. In particular, we have been able to map out the conduction band dispersion and the Fermi surface topology, representing the first such measurement for a buried interface. The obtained band structure and Fermi surface is consistent with density functional theory calculations.

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Electronic Structure of Magnetic Semiconducting $Cr_{0.20}Al_{0.80}$ and the Anti-ferromagnetic-to-ferromagnetic Transition in FeRh from Hard X-ray Photoemission

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ABSTRACT

We have used hard x-ray photoemission spectroscopy at a photon energy of 5.95 keV, together with density functional theory and Anderson-impurity model (AIM) calculations, to further understand the electronic structure of two interesting magnetic materials. An epitaxial semiconducting $Cr_{0.80}$ $Al_{0.20}$ thin film shows several features in the valence band region, including a gap at the Fermi energy (E_F), with the valence band edge 95±14 meV below E_F. Theory agrees well with the valence band measurements, and shows an incomplete gap at E_F due to the hole band at M shifting almost below E_F.

Stoichiometric FeRh undergoes a temperature-induced antiferromagnetic (AFM) to ferromagnetic (FM) transition at ~350 K, and is of interest for thermally-induced switching. Clear differences between the AFM and FM states are observed across the entire valence-band spectrum and these are well reproduced using density functional theory. Changes in the 2p core-levels of Fe are also observed and interpreted using AIM calculations. These results indicate that significant electronic structure changes over the entire valence-band region are involved in this AFM-FM transition.

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Supported by the U.S. Dept. of Energy under Contract No. DE-AC02-05CH11231.

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Magnetic and Ligand Field Properties of Copper at the Interfaces of $(CaCuO_2)_m/(SrTiO_3)_n$ Superlattices

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ABSTRACT

Cuprate-based superlattices (SLs) can be considered as new, artificial materials belonging to the family of high-T_c superconductors (HTS), offering the opportunity of freely choosing the two building blocks of HTS i.e., the superconducting CuO_2 plane and the charge reservoir layer that provides the extra charge needed to dope the planes and make them superconduct[1-3].

High resolution resonant inelastic x-ray scattering (RIXS) at Cu-L_3 edge is a powerful tool to measure both ligand field (dd)[4] and magnetic excitations in cuprates, as we have recently demonstrated both theoretically[5] and experimentally[6-10]. In particular, after measuring magnon dispersions in undoped insulating cuprates (La_2CuO_4, $CaCuO_2$, $Sr_2CuO_2Cl_2$)[6-8], we have recently shown that also superconducting samples ($La_{1-x}Sr_xCuO_4$, $YBa_2Cu_3O_{6+x}$, $NdBa_2Cu_3O_7$)[9,10] exhibit damped spin excitations – or paramagnons - with dispersions and spectral weights closely comparable to those of the insulating compounds. These paramagnons represent a strong candidate as glue for the Cooper's pairs in the HTS, in analogy to the phonon-mediated pairing mechanism of conventional superconductors.

Here we present Cu-L_3 RIXS measurements on both insulating and superconducting $(CaCuO_2)_m/(SrTiO_3)_n$ superlattices, compared with those on a 14 nm thick $CaCuO_2$ film.

The *dd* excitation spectrum reveals a pyramidal coordination of Cu ions at the $CaCuO_2/SrTiO_3$ interfaces. In all insulating samples spin excitations are in the form of dispersing magnons. In particular in the SLs magnons have similar spectral intensity but reduced dynamics with respect to pure $CaCuO_2$. By fitting the dispersions within linear spin wave theory we have obtained the leading term of the in-plane superexchange parameters: J = 127 meV, 138 meV and 157 meV for m = n = 2, m = n = 3 SLs and $CaCuO_2$ respectively. These results demonstrate that the antiferromagnetic order is preserved in the insulating SLs down to very small cuprate layer thickness and despite the chemical and structural alterations at the interface. On the other hand the superconducting SLs exhibit dispersing paramagnons, similarly to the case of superconducting $YBa_2Cu_3O_{6+x}$.

These findings open the way to the production of new, artificial HTSs based on cuprate/noncuprate SLs where the charge reservoir layer is constituted by the interface itself.

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SESSION:

Atomic and Molecular Science 3

Fundamental processes (FEL, HHG)

Multiple Ionization and Auger Decay Processes in Isolated Atoms and Molecules During Interaction with Intense X-FEL Radiation

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ABSTRACT

Ultraintense, tunable x-ray beams from x-ray free-electron lasers (XFELs) [1] increase the intensity and fluence within each x-ray pulse up to a billion-fold over that typically available at synchrotron facilities. This talk will present results obtained at the SLAC National Accelerator Laboratory’s Linac Coherent Light Source (LCLS) demonstrating how the electronic structure of the neon atom exposed to such bursts of x-rays is continually altered due to the successive absorption of photons and removal of electrons [2]. If the photoabsorption rate in the *K*-shell is higher than the decay rate of a *K*-shell vacancy, transient hollow atomic states with an empty *K*-shell are created more abundantly by sequential *K*-shell ionization than by electron correlation [3]. Similarly, at the x-ray energy of a bound K-shell resonance one can expect Rabi-cycling of resonant excitation and stimulated emission to occur at high x-ray intensities preempting autoionization [4]. In a molecule and at high enough x-ray energies, two or more core vacancies can be distributed at different sites within the molecule. The measurement of the binding energy of molecular double core hole states has been predicted to be a sensitive probe for the molecular environment at the location of these core holes [5-7].

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Photoelectron Spectroscopy of Atoms and Molecules by using FEL and Laser High-order Harmonics

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ABSTRACT

Ultrashort pulses in the EUV region are of great interest as a probe for photoelectron spectroscopy since the photon energy is sufficiently high to ionize most atoms and molecules, and therefore both fragments and parent molecules during chemical reactions can be monitored with changes in the electronic states. In this contribution, we review our recent work on photoelectron spectroscopy using EUV laser pulses obtained from SASE FEL as well as laser high-order harmonics generation.

In the first part, we discuss the generation and application of ultrashort EUV laser pulses at 80 nm [1]. The EUV laser pulses are obtained as the 5th order harmonics of the fundamental pulse at 400 nm by means of selective transmission of an indium foil. The single EUV laser pulses are applied to time-resolved photoelectron spectroscopy of dissociating I_2 molecules in the B and B" electronically excited states pumped by visible laser pulses at 490 nm. A rapid increase (~400 fs) in the yield of atomic iodine in the dissociation process is well reproduced by the wave packet simulation including the B and B" states, showing the simultaneous probing of the nuclear wave packet dynamics in the two different excited states.

In the second part, we report on shot-by-shot photoelectron spectroscopy using EUV-FEL pulses from the SCSS Test Accelerator at RIKEN. In our previous studies [2,3], we have shown that photoelectron spectroscopy provides detailed information on the multi-photon processes of simple atoms in intense EUV-FEL fields, because (i) electronic states involved in the ionization process can be identified directly from the photoelectron energy and (ii) the spectral properties of the FEL pulses can be evaluated on the shot-by-shot basis. The shot-by-shot photoelectron spectroscopy is powerful in unveiling wavelength-sensitive nonlinear processes such as resonance effects, which are otherwise smeared out by the fluctuation of FEL operated in the SASE mode. Here, we apply the single shot photoelectron spectroscopy to double excitation of He by nonlinear multiphoton absorption of intense EUV-FEL at 51 nm. It is revealed from the single shot analysis that there are resonances to the doubly excited states converging to He^+ $N = 3$ level. Theoretical calculations show that the three-photon double excitation is enhanced by intermediate Rydberg states below the first ionization threshold, giving a greater contribution than the two-photon process by more than one order of magnitude.

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Extracting Electron-ion Differential Scattering Cross Sections for Partially Aligned Molecules by Laser-induced Rescattering Photoelectron Spectroscopy

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ABSTRACT

Rescattering of electrons produced by intense ultrafast laser pulses is of current interest due to the possibility of using the returning electrons for self-imaging the target. Recently, it has been demonstrated that elastic differential cross sections (DCSs) for scattering of free electrons from atomic ions can be accurately extracted from the momentum distributions of high-energy rescattering photoelectrons [1] by using the factorization formula for rescattering processes [2]. In this report, we demonstrate the extraction of DCSs of partially aligned molecules with a wide range of electron momentum.

We recorded angle-resolved electron momentum spectra for randomly oriented O_2, CO_2 and C_2H_4 molecules. Field ionization by the intense laser pulse will predominantly occur for the molecules when the lobes of their HOMOs are aligned in the direction of the laser polarization direction. Then without specific alignment technique, we can observe rescattering electron spectra of partially aligned molecules. From these electron spectra we extracted large-angle DCSs of electron-ion field free scattering for these molecules. The experimentally extracted DCSs are compared with theoretical calculations of the DCSs using ab initio electron-ion potentials. We found fairly good agreement between the experimental and theoretical DCSs, and it confirms the validity of the present extraction procedure of the DCSs based on the factorization formula for rescattering processes [3, 4].

We would like to thank all collaborators including Hiromichi Niikura, O. I. Tolstikhin, L. B. Madsen, Kozo Shimada, Chuncheng Wang, and D. Ding. This work was supported in part by Grants-in-Aid for Scientific Research from JSPS, the Budget for ”Promotion of X-ray Free Electron Laser Research" from MEXT, by the Cooperative Research Program of “Network Joint Research Center for Materials and Devices", IMRAM research program, and Matsuo Foundation.

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Spectral Dynamics of Amplified X-ray Emission from Core-ionized Diatomic Molecules

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ABSTRACT

Photoionization of core-electrons creates highly excited states with typical lifetimes of a few femtoseconds. In the case of light elements (Z<20) these core-hole states decay dominantly in non-radiative processes, releasing the excess energy by a fast Auger electron. In spite of the rather low probability of spontaneous x-ray emission, self-stimulated emission can be sufficient for realization of single-pass cavityless x-ray lasing schemes. Recently, the first successful demonstration of an inner-shell photo-ionization based atomic x-ray laser [1] pumped by an x-ray free-electron laser (XFEL) was reported [2]. In contrast to the XFEL source, the atomic x-ray laser is longitudinally coherent, i.e. transform limited x-ray pulses are created. Here we extend that technique from atoms to small molecules and present first theoretical predictions on x-ray lasing in nitrogen molecules pumped with an XFEL source.

Theoretical calculations based on the solution of the Maxwell-Bloch equations in an open quantum system are presented. The emitted x-ray spectrum shows a strong dependence on the propagation length, due to the interplay of various spectral components from different vibrational states of the molecule. In the saturated regime, the amplified x-ray emission spectrum transforms into a narrow line. The spectral width and the duration of the emitted x-ray pulse are determined by the lifetime of the core-ionized state. The numerical simulations based on typical XFEL parameters predict about 10^9 x-ray photons in the molecular x-ray line per pulse, with a conversion efficiency of 0.2%. The amplified x-ray emission frequency can be tuned within the x-ray fluorescence band by manipulating the vibrational wave packet in the ground electronic state with the help of additional strong infrared radiation. The induced nuclear dynamics in the intermediate and final electronic states are strongly dependent on the intensity of the x-ray laser field.

Although this case study is focusing on the nitrogen molecule, the scheme can be applied to other homo- and heteronuclear diatomic systems, thereby extending the spectral range of this coherent x-ray radiation. Fine tunability of the molecular laser line together with the tunable XFEL radiation results in a universal two-colour x-ray radiation source, enabling advanced all x-ray pump-probe experiments.

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SESSION:

Novel Electronic States 4

Graphene, Dirac matter

π-Bands, p/n-junctions and Mini Cones in Intercalated Epitaxial Graphene on SiC

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ABSTRACT

Epitaxial graphene layers grown on SiC(0001) are n-doped due to the influence of a covalently bonded carbon interface layer. This influence can be completely eliminated by atomic intercalation. Hydrogen for example migrates under the interface layer, passivates the underlying SiC layer and decouples the graphene from the substrate [1]. The interface layer alone transforms into a quasi-free standing monolayer while monolayers and bilayers turn into decoupled bilayers and trilayers [2,3,4]. As a result, charge neutral quasi-free standing graphene layers can be obtained. By intercalation of Germanium the graphene layers can also be decoupled. In this process both p- and n-doping can be produced, depending on the amount of Ge material intercalated. Both phases can be prepared in coexistence on the surface. In this way, lateral p-n junctions can be obtained on a mesoscopic scale [5]. Intercalation of Cu induces a coincidence superstructure on top of the SiC surface, which originates from periodic regions of different bond configuration for the carbon atoms in the graphene layer. As a result, a long range periodic potential is imposed onto the graphene layer, which leads to a profound modification of its electronic spectrum. A surprisingly strong doping and the development of mini-Dirac cones are observed [6]. Detailed investigations of the π-band structure, the spatial arrangement, chemical bonding and local surface order are shown based on angle-resolved photoemission spectroscopy (ARPES), low-energy electron microscopy (LEEM), x-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) experiments.

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Angle Resolved Spectroscopy Applied to Graphene

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ABSTRACT

Graphene is a remarkable new electronic material with many unique properties. To realise its promise, it is essential to understand its the electronic structure. By measuring the spectral function of charge carriers using angle resolved photoemission from various type of graphene grown on SiC, we show that it is possible to develop a broad understanding of the electronic structure and many body interactions in graphene. We also show that the structure of the graphene and substrate on which it is placed play a key role in determining both the basic band structure and the strength and type of many body interactions.

Hole Doping of Graphene by Metal Halides Adsorption and Intercalation

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ABSTRACT

The pronounced hole doping of graphene was observed upon *in situ* deposition of metal halides ($FeCl_3$ and $AlBr_3$) on graphene supported on Ir(111) substrate. The impact of metal halides adsorption on graphene/Ir(111) was studied by a combination of core-level and angle-resolved photoelectron techniques (CL PES and ARPES), near-edge x-ray adsorption fine structure (NEXAFS) spectroscopy and low-energy electron diffraction (LEED).

Followed by its thermal decomposition into $FeCl_2$ and Cl upon post-annealing, deposition of $FeCl_3$ results in temperature-assisted intercalation of Cl onto graphene/Ir(111) interface. This chlorination of graphene results in strong hole doping, with the π-band shifted by ~0.6 eV to lower binding energy. Further annealing promotes desorption of Cl from the graphene/Ir(111) interface and allows high degree of control over the doping level.[1]

Upon *in situ* deposition of $AlBr_3$ on graphene/Ir(111), both intercalation of $AlBr_3$ molecular species and hole doping of graphene occurs already at room or slightly elevated temperature. Post-annealing of graphene/$AlBr_3$/Ir(111) system facilitates a thermal decomposition of $AlBr_3$ into $AlBr_x$ and Br/Br_2 species on the Ir(111) surface, which results in gradual desorption of bromine from the system and decrease in the amount of hole doping of graphene. The highest level of the π-band shift induced by doping with $AlBr_3$ has amounted to ~0.35 eV. This fact is in agreement with the suggested mechanism of doping which implies charge transfer from carbon atoms to electronegative halide atoms: since Br is less electronegative than Cl, smaller level of doping is expected if $AlBr_3$ is used.

The ease of preparation, the remarkable reproducibility of the doping level and the reversibility of the doping upon annealing are the key factors making the intercalation of halogens and metal halides a promising route for tuning electronic properties in graphene.

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Is Charge Carrier Really Dirac Fermion in Silicene on Ag(111) ?

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ABSTRACT

Silicene, a two-dimensional single-layer honeycomb structure of silicon, has attracted much attention as an exotic new material. Several groups have successfully synthesized silicene on Ag(111) [1-3]. The theoretical calculation of free-standing silicene has shown the Dirac fermion feature even when the Si-Si bond is lightly buckled [4]. The photoelectron spectroscopy work has shown an excessive linear dispersion till -3eV for the silicene on Ag(111) [2]. However, it is still an open challenge that the charge carrier in silicene on Ag(111) behaves as massless Dirac fermion or not.

In this work, silicene on Ag(111) was investigated by low-temperature scanning tunneling microscopy and spectroscopy (STM and STS) combined with the density functional theory (DFT) calculations. The STS spectrum shows a pseudo-Dirac-cone feature around the Fermi level for the 4x4 silicene. However, it is found by the DFT calculations that this comes from the coincident contributions of the several bands, not from the nature of Dirac fermion. The DFT calculations also show that there are no linear band dispersions across the K-point. Furthermore, even in high magnetic fields up to 9 Tesla, Landau levels are not observed while they are clearly observed for HOPG. Therefore, it turns out that the hybridization of Si with Ag substrate breaks the symmetry of silicene and impedes the Dirac fermion behavior of the charge carriers inside the 4x4 silicene on Ag(111).

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From Silicene Discovery to Graphene-like Epitaxial Germanium Sheets

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ABSTRACT

THE DEMONSTRATION THAT SILICON CAN FORM SHEETS OF SILICENE, A TWO DIMENSIONAL HONEYCOMB LOW BUCKLED STRUCTURE, WHICH DOES NOT EXIST IN NATURE, IS TANTALIZING FOR NEW PHYSICS AND POTENTIAL APPLICATIONS, BUT ALSO SUGGEST THE ROUTE FOR THE SYNTHESIS OF GERMANENE, THE ANALOGUE OF GRAPHENE FOR GERMANIUM.

We provide compelling evidences for the first synthesis of silicene sheets [1], the silicon equivalent of graphene, upon in-situ epitaxial growth on silver (111) surfaces. The honeycomb atomic structure with a Si-Si in-plane distance of 0.23 nm is revealed in scanning tunneling microscopy, while the long-range commensurate order is confirmed by sharp low energy electron diffraction patterns. Conical band dispersions at the corners of the silicene Brillouin zone (K and K' points), evidenced in high-resolution synchrotron radiation angle-resolved photoelectron spectroscopy measurements, point to Dirac fermions, i.e., massless relativistic carriers, with a Fermi velocity of ~1.3E6 ms^{-1}, as theoretically predicted [2], quite the same as graphene. Density functional theory calculations in the general gradient approximation -including the Ag(111) substrate- confirm that silicene is very stable on silver, as indicated by the significant adhesion energy of 0.48 eV per Si atom; they also demonstrate the sp^2/sp^3-like hybridization, as for free standing silicene. The demonstration that silicon can form sheets of silicene, a two dimensional honeycomb low buckled structure, which does not exist in Nature, is tantalizing for new physics and potential applications.

Since, silicon can be considered the workhorse of electronic industry; this synthesis should have a major impact for novel electronic devices –possibly for more than Moore- because of the compatibility with existing Si technologies. Indeed, a key issue in this direction will be the transfer or growth on an insulating substrate, like, possibly AlN [2].

Finally, the epitaxial growth of silicene opens up the route to the synthesis of germanene, the analogue of graphene for germanium, also with nontrivial band topology and a gap induced by effective spin orbit coupling for the π orbitals at the K point in low-buckled geometry corresponding nearly to room temperature; preliminary results in this endeavor will be also presented [3].

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Towards Graphene-based Electronics: Graphene on Cubic-SiC(001)/Si Wafers

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ABSTRACT

Graphene possess astonishing electronic properties, like the exceedingly high charge carrier mobility and the occurrence of Dirac fermions, which make it the most promising candidate for replacing silicon in future electronic devices. Current graphene synthesis requires conditions typically achieved in specialized laboratories. The production resulting in high quality graphene layers, does not meet the requirements of industrial mass-production because it involves hand-made processes like mechanical exfoliation or results in strong graphene-substrate interaction, altering the film properties or/and uses very expensive alpha SiC substrate of relative small diameter (typical < 100 mm in diameter). The development of graphene-based technologies requires an economical fabrication method compatible with mass-production. Here we demonstrate the graphene synthesis on commercially available cubic SiC(001) substrates of > 300 mm in diameter, which result in graphene flakes electronically decoupled from the substrate [1]. The quality of graphene overlayers was characterized by a number of experimental techniques, indicating very weak interaction with the substrate, crucial for preservation of the astonishing intrinsic properties of graphene. The ability to grow large single-crystal-domains is a major target of graphene growth. Despite lattice mismatching, the graphene growth is shown to be guided along the [110] crystallographic direction of the SiC(100) substrate, which might also encourage the formation of reasonable large domains of single-crystal graphene. After optimization of preparation procedure the proposed synthesis method can represent a further big step towards graphene-based electronic technologies.

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SESSION:

Photo-chemistry and Reactivity 3

Nanoparticles, liquids

Photoexcitation, Photoionization, and Relaxation of Isolated and Deposited Particles

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ABSTRACT

Experimental results on the photoexcitation, photoionization, and relaxation of isolated and deposited nanoparticles of variable size, shape, and composition are reported. These serve to probe the structure and dynamics of variable size matter, which is probed by synchrotron radiation as well as short pulse laser radiation.

Isolated particles of variable size and composition in the solid or liquid state are studied in order to probe their intrinsic properties by absorption, elastic light scattering, photoemission, and cation formation. Different experimental approaches, including preparation of nanoparticles in a beam as well as trapping of single microparticles are employed. These studies yield specific information on the structural and optical properties of variable size matter, photoionization dynamics reaching into in the sub-femtosecond time scale, phase transitions, as well as the relaxation dynamics.

Deposited nanoparticles of variable size and shape are prepared in ordered arrays, which are intended to serve as laser driven short pulse XUV-sources. The emission of harmonics, two-photon fluorescence, and white-light supercontinuum generation are observed, where contributions from plasmonic field enhancement in these arrays are optimized.

Aqueous-solution Photoelectron Spectroscopy: Ultrafast Charge and Energy Transfers

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ABSTRACT

The ultrafast electronic relaxation of core-excited liquid water and of aqueous transition-metal ions is explored using liquid microjet photoelectron spectroscopy in conjunction with soft X-ray synchrotron radiation. Relaxation dynamics and the underlying mechanisms are revealed from resonant photoelectron spectroscopy measurements. For neat liquid water we find a unique de-excitation channel, involving core-hole delocalization, which is a signature of an energy transfer to a neighbor water molecule. The origin of the observed large isotope effect, light versus heavy water, will be discussed.

A different ultrafast relaxation mechanism is observed for core-excited transition metal ions in water, involving transient hybridization connected with charge transfers. This is identified through large enhancement of valence signal for photon energy at the respective 2p-level absorption edge. From such measurements we also obtain partial electron-yield X-ray absorption spectra (similar to the ones obtained by photon detection). In some cases we can simultaneously probe valence and deeper lying electronic-state de-excitation (3d to 2p and 3p to 2p), which helps to better understand the details of electronic dynamical coupling between solute and solvent.

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Surface Oxidation States of Aged Free Silicon Nanoparticles Probed with Soft X-ray

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ABSTRACT

Novel experimental investigations are currently carried out to explore fundamental processes involved in the interaction between isolated nano-objects and soft X-ray radiation [1, 2, 3]. This kind of experiment has become possible namely owing to the advanced instrumentation that is now available, as for instance at the PLEIADES beamline [4] - SOLEIL synchrotron facility. In this study, we were able to produce a focused beam of silicon nanocrystals in vacuum from a stable suspension in ethanol. The synchrotron radiation crossed the nanoparticle beam at 90° at the focal point of an aerodynamic lens. In the interaction region, the particle beam diameter and the local particle density are estimated to be 300 µm and 10^7 cm^{-3}, respectively. These conditions allowed us to perform X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) of isolated surface-oxidized silicon nanoparticles of different sizes and different natural oxidation times.

All the oxidation states of silicon from Si^0 to Si^{4+} are present in our XPS spectra, denoting a shallow transition between the Si-core and the oxide shell of the particle. Moreover clear shifts of the whole XPS spectrum are observed towards higher bending energies as oxidation time increases, which could reveal strong interfacial Si/SiO_2 interaction and compressive stress arising upon oxidation. Complementary studies on the same samples using High-Resolution Transmission Electron Microscopy, Fourier-Transform Infrared spectroscopy and tabletop XPS measurements of deposited samples will also be discussed. Finally, the special features in the XPS and NEXAFS of isolated nano sized SiO_2 particles will be highlighted.

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Resonant Inelastic Soft X-ray Scattering Map of Gas-phase Water and what it Tells about Liquid Water

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ABSTRACT

In spite of appearing to be a very simple molecule, its enormous relevance, and the fact that it has been studied intensively, water still has not revealed all of its secrets. In particular the hydrogen bonding environment in the liquid phase has been vividly debated based on soft x-ray spectroscopic experiments (e.g., [1-4]). In the case of x-ray emission spectroscopy, a disagreement about the origin of the observed splitting of the $1b1^{-1}$ emission line exists [3,4]. Due to the fact that the spectra can be influenced by a variety of factors, including proton dynamics on the time scale of the x-ray emission process, as well as the hydrogen bonding environment, an interpretation is difficult. To separate these effects, we have investigated a somewhat simpler system, e.g., water molecules in the gas-phase using resonant inelastic x-ray scattering (RIXS) [5]. Using a newly developed gas cell, we were able to study gas-phase water at atmospheric pressure. Together with our high-transmission soft x-ray spectrometer [6], it was possible to measure resonant data (i.e., complete RIXS maps) of significantly higher signal-to-noise ratio and resolution than was previously possible.

We observe spectator shifts, intensity variations that can be related to the angular anisotropy of the RIXS process, and, in particular, strong nuclear dynamics leading to dissociation for excitation into the $4a_1$ absorption resonance. These experimental results on gas-phase water will be discussed with special focus on their relevance to the interpretation of the liquid phase spectra and show that the origin of the peak splitting in liquid water are nuclear dynamics taking place on the time scale of the x-ray emission process.

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Local Structures of Methanol-water Binary Liquid Studied by Soft X-ray Absorption Spectroscopy

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ABSTRACT

A water molecule has two hydrogen-accepting and two hydrogen-donating sites, and forms three-dimensional (3D) hydrogen bonding networks. On the other hand, a methanol molecule has one donor and one or two acceptor sites due to a hydrophobic methyl group, and forms one- or two-dimensional (1D, 2D) hydrogen bonding networks, such as chains and rings [1]. It is known that the methanol-water binary liquid shows 3D cluster formation by the interaction between water and methanol molecules [2]. But the local structures of the methanol-water mixtures are still unknown. X-ray absorption spectroscopy (XAS) is a promising method to investigate the local structure of liquid. Recently, we have developed a liquid cell for the measurements of XAS in the transmission mode [3]. In this work, we have investigated the local structure of the methanol-water binary liquid at different concentrations by oxygen and carbon K-edge XAS and molecular dynamics (MD) simulation.

The experiments were performed at the soft X-ray undulator beam line BL3U at the UVSOR-II facility. The liquid cell consists of four regions I, II, III, and IV, separated by 100 nm-thick Si_3N_4 membranes (NTT AT Co.). The region I is connected to the beam line in a vacuum condition. The regions II and IV are in an atmospheric condition of helium gas. The liquid thin layer (region III) was sandwiched between two Si_3N_4 membranes. Soft X-rays in the region I pass through the region II and the liquid thin layer III, and reach a photodiode detector in the region IV. The thickness of the liquid layer can be optimized from 20 to 1000 nm by changing the He backpressure in the regions II and IV [3].

In the oxygen K-edge XAS spectra, the pre-edge peak (535 eV) is distributed at the oxygen atom in water. The pre-edge peak is linearly changing with different concentrations by showing the isosbestic point. We could not find any evidence of the CH_3OH-H_2O interaction in the oxygen K-edge. On the other hand, in the carbon K-edge XAS spectra, the peak around 290 eV arises from the methyl group in methanol. This peak is blue-shifted by increasing the water concentration but the blue shift or spectral change is not linearly dependent on the water concentration. Some 3D local structures of methanol molecules are found under dense water condition in the MD simulation. It might indicate that the hydrophobic methyl groups can approach to each other in the 3D local structure under the water-rich atmosphere. More detailed experimental and theoretical results and discussion of the local structure of the methyl group in the methanol-water binary liquid will be presented.

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PR3-CT-BJO

From Molecules to Rain: Surface Propensity and Speciation of Atmospherically Relevant Aqueous Surfaces Studied by Photoelectron Spectroscopy

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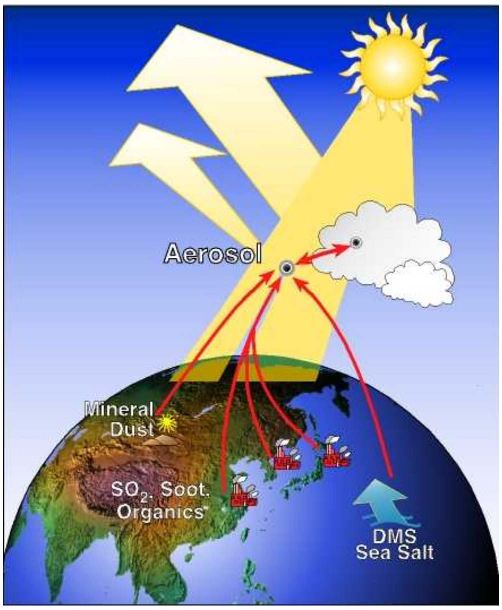
ABSTRACT

Aerosol effects still constitute the greatest uncertainties in assessing anthropogenic contributions to global climate change [1]. Both direct and indirect climate effects of atmospheric aerosol particles are governed by their numbers, sizes, and chemical properties. Particles in the atmosphere are typically mixtures of both organic and inorganic species together with water, and it has become evident that the description using the average bulk composition of an aerosol particle is not enough to describe its climatically relevant properties; a more detailed picture of the surface vs. bulk composition of the aerosols is needed. We will present results obtained by photoelectron spectroscopy on a liquid micro-jet, showing for example how the concentration influences on the molecular surface structure of simple and mixed aqueous electrolytes, and how this may explain why bromine is more important in atmospheric chemistry over the oceans than what would be expected from its relative abundance in sea water [2], how the surface composition of aqueous solutions of small carboxylic acids differ from that of the bulk as function of pH [3], as well as surface-specific reactions between surface-active organic molecules and inorganic ions of atmospheric relevance [4].



Origin of atmospheric aerosols, and their effects upon Earth's radiative balance. The direct effect is scattering of sunlight, promoting cloud formation is the indirect effect.

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POSTERS SESSION III:

Thursday, Sept. 20th, 2012

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Thursday, September 20th, 2012

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SM-3-PO-YUK-01	***R. Yukawa*** Polarization-dependent angle-resolved photoemission studies of hydrogen-adsorbed SrTiO$_3$(001)

Intramolecular Photoelectron Scattering as a Probe of Molecular Geometry

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ABSTRACT

We have studied the influence of core-level photoelectron scattering on neighboring atoms within single gas-phase molecules. We present here a case study of a heteronuclear diatomic molecule, carbon monoxide. Experiment-wise, C 1s photoelectron spectra were recorded in several experiments, performed at SPring-8 (beamline 27SU[1]) and at SOLEIL synchrotrons (PLEIADES beamline[2]). The high-resolution spectra were recorded over a broad ionizing photon energy range and the vibrational structure of the single vibrational mode was analysed, in particular the branching ratios within the vibrational envelope of the C 1s photopeak. Beyond the effects of the near-threshold shape resonance, the vibrational branching ratios exhibit a long range oscillatory behavior. As in our other studied cases, these oscillations can be attributed to the modulation of the cross-sections induced by photoelectron scattering on adjacent atoms, in the present case on oxygen.

As expected from a scattering phenomenon, the period of the modulation is directly determined by the interatomic distance. We applied different levels of theory to reproduce the observed effects and to test the applicability of the method for investigating the molecular geometry. Qualitative agreement is obtained already using a first Born approximation[3], particularly regarding the period of the modulation as a function of the photoelectron momentum k_e. *Ab initio* DFT calculations[4] provide better agreement at a quantitative level.

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Fragmentation Dynamics of Doubly Charged Methionine in a Gas Phase

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ABSTRACT

In this study we report an electronic state selective fragmentation research on methionine using Auger electron Photo-ion Photo-ion Coincidence (AEPIPICO) technique and first-principles molecular dynamics (MD) methods. Methionine ($C_5H_{11}NO_2S$) is an essential amino acid as it is a building block of proteins.

The AEPIPICO technique was used to record the S LMM Auger electron spectra in coincidence with time-of-flight (TOF) mass spectra of cations dissociated from doubly charged methionine (M^{2+}) molecules induced by synchrotron radiation. The dicationic states of the parent molecules were created as the result of initial inner-shell (S 2p) ionization followed by normal Auger decay of the shell vacancy. The measurement instrument consists of a modified Scienta SES-100 hemispherical electron analyzer and a Wiley-McLaren type ion TOF spectrometer [1]. The experiments were carried out at the undulator beamline I411 at the MAX-II storage ring.

To complement the experiments we performed *ab initio* MD calculations. Time-dependent density functional theory (TDDFT) MD within the mean-field Ehrenfest approximation [2] were applied to propagate the electronic degrees of freedom of a non-equilibrium M^{2+} where two electrons are ejected from an inner valence molecular orbital. The time-consuming TDDFT MD calculations were switched to Born-Oppenheimer MD when adiabatic conditions were met. In addition, Car-Parrinello MD was used for a thermal equilibration process as the TDDFT MD would have been overly expensive. The abovementioned calculations were executed with the help of the Gaussian 03 code and the CPMD code [3] where plane wave basis was used and Kleinman-Bylander pseudopotentials were exploited for describing core-electrons.

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Properties of Double Core Holes Formed by Single Photon Double Ionization

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ABSTRACT

Although the interest of molecular double core hole states (DCHs) for a renewal of ESCA (Electron Spectroscopy for Chemical Analysis) was established 25 years ago [1], their experimental observation has been possible only very recently, thanks to the development of two different approaches: multi-photon core ionization using XFEL sources [2] or single photon double core ionization using synchrotron sources [3-5]. We have demonstrated that the latter method provides detailed information on the spectroscopy and decay dynamics of DCHs, even if the associated double photoionization cross section is extremely weak. We have observed not only single-site DCHs, (ss-DCHs, noted K^{-2}), where the two core holes are created on the same atom of the molecule [3], but also two-site DCHs, (ts-DCHs noted $K^{-1}K^{-1}$), where the two core holes are located on different atoms [4,5].

The experiments were performed on BL-16A beam line at Photon Factory (Japan) and on TEMPO beam line at SOLEIL (France) using a magnetic bottle time-of-flight spectrometer. We studied simple molecules including N_2, O_2, CO, CO_2 and C_2H_{2n} (n= 1, 2, 3) compounds. For K^{-2}, the formation and decay process is :

$$h\nu + M \rightarrow M^{2+} (K^{-2}) + 2\, e^-_{\text{Photoelectron}}$$
$$\rightarrow M^{3+} (K^{-1}v^{-2}) + e\text{-}_{\text{Auger Hypersatellite}}$$
$$\rightarrow M^{4+} (v^{-4}) + e^-_{\text{Auger Satellite}}$$

where v designates a valence shell, and the emitted Auger electrons are called 'hyper satellite' or simply satellite, depending on whether the K-shell is filled in the presence of a second K hole or of valence holes.

By detecting in coincidence two photoelectrons with one or two released Auger electrons, we have been able to characterize experimentally K^{-2} and $K^{-1}K^{-1}$ states: their binding energies, their respective Auger decay paths and the relative probability for their formation with respect to single K shell ionization. We also developed theoretical models for both the spectroscopy and the Auger decays.

Single photon double ionization leading to K^{-2} states was found to represent a small fraction of single K shell ionization, of the order of ~10^{-3}. In C_2H_2, this figure drops to ~2. 10^{-5} for $K^{-1}K^{-1}$ formation. A simple collisional model where an initially ionized K-shell electron hits and ejects a second K-shell electron from the neighboring C atom is found to reproduce reasonably well this value.

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Atomic and Molecular Science at the Canadian Light Source

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ABSTRACT

XUV BEAMLINE AND EXPERIMENTAL CHAMBERS

The VLS-PGM (Varied Line Spacing – Plane Grating Monochromator) beamline at the CLS (Canadian Light Source) covers the photon energy range from 5eV to 240eV with a resolving power in excess of 10,000 throughout this range [1].

There are two experimental chambers suitable for gas-phase atomic and molecular spectroscopy available for general use as well as the ability to attach custom equipment to the beamline. The first contains two toroidal electrostatic particle energy analysers that can be operated in co-incidence [2] and has recently been used for angle resolved photoion and angle resolved photoelectron spectroscopy [3,4]. It is also suitable as a sensitive threshold electron spectrometer [5], which matches well the achievable electron resolution with the photon resolution available at the beamline. The other is a Wiley-McLaren type time-of-flight mass spectrometer [6] equipped with multi-hit electronics to allow photoelectron-photoion-photion coincidences to be recorded [7-9]. Both gases and the vapour from volatile liquids and solids may be introduced into these chambers.

Recent experimental results from the beamline will be presented.

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Photo-double Ionization on the Attosecond Time Scale

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ABSTRACT

Double ionization by absorption of a single photon represents one of the most fundamental processes that can only be understood by considering Coulomb interaction between the electrons. This has stimulated experimental development to characterize the electron pair as well as theoretical work to understand the underlying physical processes [1]. Recently, attosecond pump-probe experiments have gained access to single ionization dynamics at its natural time scale [2]. Here we present the first attosecond dynamics experiment on double ionization of xenon with the electrons detected in coincidence.

Access to electron pair dynamics is important for the advance of nonlinear theories based on the time dependent Schrödinger equation. Previous studies on double ionization of xenon have focused on the complex one-photon double ionization dynamics [3] and the exploration of two-color two-photon double ionization with a single harmonic [4]. The latter revealed that the sequential absorption process dominates, suggesting that non-sequential absorption requires shorter light pulses.

In our experiment, we photo-double ionize xenon with attosecond pulse trains (APTs) and detect the correlated electron pair. An IR pulse is used as a dressing field in the perturbative regime to manipulate the ionization dynamics. Fig. 1 shows the sharing of excess energy between the electrons, which allows us to identify the electronic states involved. As we vary the delay between the APT and the IR pulse, several regions in the electron pair-spectrum show intensity oscillations on the attosecond time scale, which can be attributed to non-sequential two-photon absorption. This opens up exciting possibilities to investigate time-delays between different energy sharings and ionization processes, as an extension of what was done for single ionization [2].

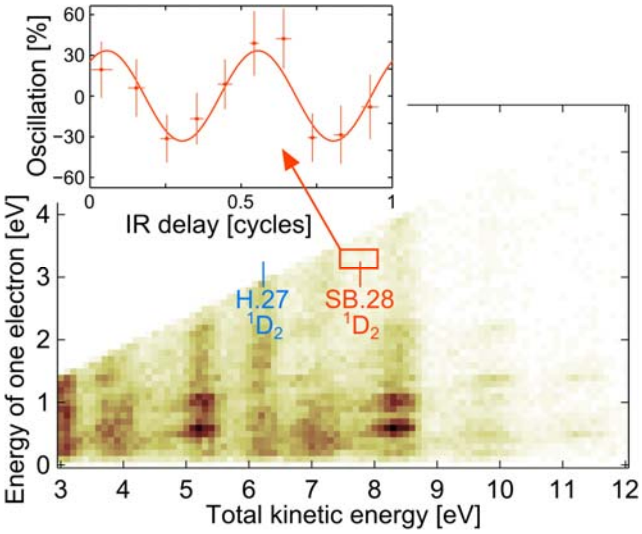

Figure 1: Electron pair spectrum and the oscillation of sideband 28 producing Xe^{2+} $^1D_2$.

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Ab-Initio Analysis of Cluster Structures Sputtered from Icy Surfaces

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ABSTRACT

Oxygen ice at 25 K was bombarded by fission fragments (~65 MeV at target surface); the emitted positive and negative secondary ions were analyzed by time-of-flight mass spectrometry (TOF–SIMS). Observation of cluster ion desorption based on oxygen is very similar to that of other frozen gases but its yields shows an oscillating distribution with a 3- or 6-atom periodicity, suggesting O_3 or O_2 ($3O_2$) units in the cluster structure, respectively [1].

The presence of these oscillations is the motivation for the present work: to verify if the structures proposed in [1] are supported theoretically. In this sense, structures of neutral and charged oxygen clusters have been analyzed theoretically using the Density Functional Theory (DFT) and the Unrestricted Hartree-Fock Method (UHF).

DFT is generally used as a successful research tool due to the inclusion of electron correlation effects. Cluster geometries were optimized at the B3LYP level, with the 6-311G basis set. Calculations shown well defined $(O_2)_n$ structures, as well as the $(O_2)_n^+$ and $(O_2)_n^-$ with n = 1-5 . Vibrational frequencies were investigated to identify minimum energy structures without negative frequencies. As is well known, ozone molecules have a biradical resonance structure, this requires two singly occupied MOs. UHF were utilized for the $(O_3)_n$ with n = 1-5 cluster geometry optimization, allowing the α and β orbitals to be spatially different, thus this method can incorporate both resonance structures.

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Secondary Ion Emission Dynamics of Solid Ammonia Bombarded by Heavy Ions

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ABSTRACT

Theoretically relevant phenomena occurring in the projectile-solid interaction and the emission of secondary ions from the sample surface will be treated in this work. The goal is to determine velocity and energy distributions of secondary ions emitted from a target of solid ammonia, through the description of secondary electron emission by the nuclear track and the establishment of secondary ions trajectories. Calculations were made with the computer code SEID. Theoretical distributions, valid for secondary ions that no longer interact with the solid, were compared with those obtained experimentally for ammonia ice bombarded by fission fragments.

It was observed that ionic species of mass ~86 u, located within 10 Å from de projectile impact point, are desorbed without being neutralized, unlike lighter ions (~18 u) that leave the surface from larger regions. Considering the ionization energy I = 35 eV for the NH_4, experimental value obtained of 6 km/s was reproduced. These comparisons also showed that the model describes partially the behavior observed in the energy distribution of the emitted ions and new processes are proposed to be included in the model.

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Structural Determination of CF_4 Obtained by Core-electron Spectroscopy

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ABSTRACT

In this study the oscillatory structure of the differential photoionization cross section ratio $\nu=1/\nu=0$ of the symmetric stretching mode of C 1s photoionization in CF_4 is investigated. Far from threshold, the observed oscillations are due to the diffraction of the photoelectrons by the neighboring atoms and the observed oscillatory structure has been demonstrated to allow recovery of the molecular geometry for a gas-phase polyatomic molecule[1]. Besides seeing oscillations that can be explained by a simple analytical model based on Born approximation, we now observed extra features, which might be interpreted by the presence of continuum resonances, in particular close to threshold and which can be reproduced by *ab initio* calculations at the DFT level of theory[2,3].

The measurements took place at the PLEIADES beamline[4] at SOLEIL synchrotron, France. C 1s photoelectron spectra were measured using a VG-Scienta R4000 electron energy analyzer at excitation energies ranging between 330 and 650 eV. The $\nu=1/\nu=0$ ratio of the symmetric stretching mode was extracted from the spectra by a fitting procedure taking into account the asymmetric vibrational modes excited by the recoil effect[5].

The experimental results are in good agreement with theoretical predictions, thus indicating the larger scale feasibility of structural information extraction from single-molecule electron diffraction experiments using synchrotron radiation and standard photoelectron spectroscopy.

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Studies of the $2p_{3/2}^{-1}4x^{-1}$-$4x^{-1}4d^{-1}$ X-ray Satellites Spectra in the Lβ_2 Region

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ABSTRACT

The X-ray satellite spectra arising due to $2p_{3/2}^{-1}4x^{-1}$-$4x^{-1}4d^{-1}$ (x ≡ s, p, d) transition array, in elements with Z = 40 to 92, have been calculated. The energies of various transitions of the array have been determined by using available Hartree-Fock-Slater data on $1s^{-1}$-$2p^{-1}4x^{-1}$ and $2p_{3/2}^{-1}$-$4x^{-1}$,$4x'^{-1}$ Auger transition energies, their relative intensities have been estimated by considering cross sections of singly ionized $2x^{-1}$ (x ≡ s, p) states and then of subsequent Coster-Kronig and shake off processes. The calculated spectra have been compared with the measured satellite energies in Lβ_2 spectra have been shown in Fig. 1. Their intense peaks have been identified as the observed satellite lines. The one to one correspondence between the peaks in calculated spectra and the satellites in measured spectra has been established on the basis of the agreement between the separations in the peak energies and those in the measured satellite energies. It has been established that various $2p_{3/2}^{-1}4d^{-1}$-$4d^{-2}$ transitions combine to give rise to a high-energy satellite near the Lβ_2 line. The most intense transition $^3F_4$-$^3F_4$ one, and seven others of this array is the main source of the emission of the satellite $\beta_2^{(a)}$, reported in the spectra of elements with Z < 60. In the range Z > 70, the second most intense transition, namely the $^1D_2$-$^1D_2$, and a comparatively weaker transition of the array $2p_{3/2}^{-1}4f^{-1}$-$4d^{-1}4f^{-1}$, namely the $^3D_3$-$^3P_2$ one assigned to the satellite β_2^0. Unfortunately, no experimental data are available on the intensities of these satellites. This suggests a need of detailed investigation, both theoretical and experimental, of these spectra.

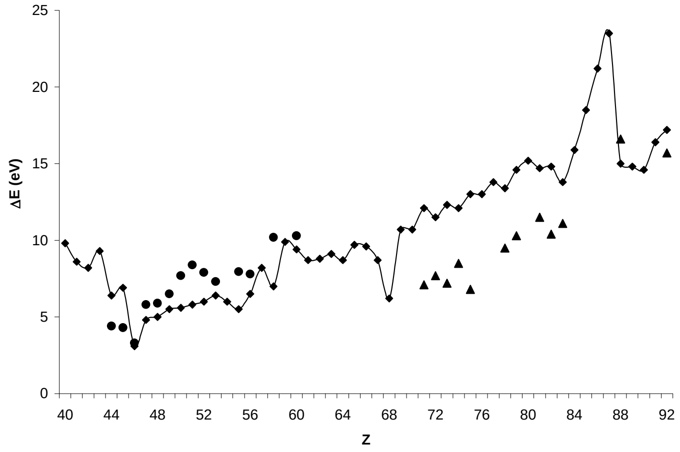

Figure 1. Calculated ΔE values of $2p_{3/2}^{-1}4d^{-1}$-$4d^{-2}$ transitions and of measured $\beta_2^{(a)}$ and β_2^0 satellite energies, relative to respective β_2 line. ■ denote the calculated energies, ● denote the $\beta_2^{(a)}$ line and ▲ denote the β_2^0 line.

Coster-Kronig and Shake Process of X-ray Satellites Spectra in the $L\alpha_1$, $L\alpha_2$, $L\beta_1$, $L\beta_2$ and $L\gamma$ Region of 3d, 4d and 5d Transition Elements

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ABSTRACT

The X-ray satellites $L\alpha'$, $L\alpha''$, $L\alpha'''$, $L\alpha''''$, $L\alpha_3$, $L\alpha_4$, $L\alpha_5$, $L\alpha^{ix}$, $L\alpha^{x}$, $L\alpha_s$, $L\beta_1^{I}$, $L\beta_1^{II}$, $L\beta_1^{III}$, $L\beta_1^{IV}$, $L\beta_2^{I}$, $L\beta_2^{(b)}$, $L\beta_2^{II}$ $L\beta_2^{(c)}$, $L\gamma_1'$, $L\gamma_2'$, $L\gamma_2''$ and $L\gamma'_{2,3}$ observed in the L-emission spectra in elements with Z = 26 to 92, have been calculated. The energies of various transitions have been calculated by available Hartree-Fock-Slater using the semi-empirical Auger transition energies in the doubly ionized atoms and their relative intensities have been estimated by considering cross - sections of singly ionized $2x^{-1}$ ($x \equiv s, p$) states and then of subsequent Coster-Kronig (CK) and shake off processes. In both these processes initial single hole creation is the prime phenomenon and electron bombardment has been the primary source of energy. The calculated spectra have been compared with the measured satellite energies in L emission spectra. Their intense peaks have been identified as the observed satellite lines. The one to one correspondence between the peaks in calculated spectra and the satellites in measured spectra has been established on the basis of the agreement between the separations in the peak energies and those in the measured satellite energies. Group of transitions under the transition schemes L_3M_x-$M_xM_{4,5}$, L_2M_x-$M_xM_{4,5}$, L_3M_x-$M_xN_{4,5}$ and L_2M_x-$M_xN_{4,5}$ ($x \equiv$ 1-5), which give rise to these satellites have been identified. It is observed that the satellite $L\beta_2^{(b)}$ in all these spectra can be assigned to superposition of $^3F_4$-$^3G_5$ and $^3F_4$-$^3D_3$ transitions and that this must be the most intense of all these satellites, contributing in order of decreasing intensity. Each of the remaining satellites is found to have different origin in different elements. The possible contributions of suitable transitions to all these lines have also been discussed.

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Disentanglement of Different Excitation and Decay Pathways in the O 1s Shape-resonance Region of CO

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ABSTRACT

Auger spectra of CO subsequent to O 1s ionization with 549.85 eV-photons, i.e. on the top of the shape resonance, are presented. These spectra, recorded at SPring8 BL27 [1] and at SOLEIL on PLEIADES beamline [2], are compared with the normal Auger spectrum recorded at a photon-energy well above the shape resonance [3] revealing distinct differences. In particular, in the energy region of the O $1s^{-1} \rightarrow b^1\Pi$ and O $1s^{-1} \rightarrow a^1\Sigma^+$ Auger transitions which are well-known to consist of vibrational progressions [3], additional narrow lines are found in the present spectra.

In a detailed fit analysis of the Auger spectra based on the approach presented in Ref. [1] it was found that distortions caused by post-collision interaction are absent. This identifies the additional lines as caused by resonant Auger decay processes. In addition, the angular-distribution of these lines was investigated. From this analysis the resonant Auger decays are assigned to transitions from the doubly excited state O $1s^{-1}\ 4\sigma^{-1}\ 2\pi\ 3l\sigma$ to the excited state $4\sigma^{-2}\ 3l\sigma$ of CO^+ with l = s or p. Two additional spectral features in the 549.85 eV spectrum are tentatively assigned to O $1s^{-1}\ 4\sigma^{-1}\ 2\pi\ 3l\sigma \rightarrow 4\sigma^{-2}nl\sigma$ with n = 4, 5. In summary, the present data analysis allows to clearly single out spectral contributions caused by resonant Auger decay from those caused by normal Auger decay.

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S2p Photoabsorption and ES-AEPICO Spectroscopy of DMDS, a Prototype Molecule for the Study of the Disulfide Chemical Bonds

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ABSTRACT

As a starting point to study the interaction of ionizing radiation with biomolecules containing sulfur-sulfur chemical bonds, we performed a detailed analysis of the electronic excitation and ionic fragmentation of the CH_3SSCH_3 (DMDS) molecule, following excitation and ionization around the S2p edge.

First experiments[1] were conducted at the Brazilian National Synchrotron Radiation Source (LNLS). We here describe here recent experiments performed at the3rd generation French synchrotron, SOLEIL, on the undulator beamline PLEIADES[2] using the coincidence experimental setup (EPICEA) [3-5]. In parallel, total electron yield (TEY) and high-resolution photoelectron and resonant Auger spectra were obtained using a VG-Scienta R4000 hemispherical electron energy analyzer.

High-resolution electron and mass spectra were obtained below and above the S2p edge (161.5 eV and 181.5 eV) and at photon energies corresponding to 5 below-threshold resonances (164.6 eV, 165.9 eV, 167.0 eV, 168.1 eV, and 169.1 eV).

Bands associated with the ionization of the outermost and inner-valence states are observed in the DMDS photoelectron spectra. Bands related to satellite states (excited singly charged species) and Auger decay were also observed. The results of the ionic fragmentation show an increasing degree of fragmentation as we move on from below resonances to the second and third resonances. Above the ionization edge, normal Auger processes lead to a strong degree of fragmentation. CH_nS^+ fragments, which are the signature of the S-S bond breaking, become the dominant species above threshold. Formation of the S_2^+ cation is maximized on the second and third resonances.

Mass-selected photoelectron spectra (MS-PES) demonstrate for instance that while formation of the molecular ions is basically associated with the outermost valence states, the observation of S^+ fragment is mainly related to the ionization of inner-valence states.

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Photon Energy Dependent Crossections in the Photoionization of Gaseous Molecular Oxygen

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ABSTRACT

Many molecules in the gas phase exhibit so-called shape resonances, where the photoionization crossection varies significantly near the ionization threshold. Recently it has been shown that the shape resonances are a part of a larger intra-molecular scattering phenomenon [1], which probably will lead to a greater understanding of this phenomenon in the coming years.

In gaseous molecular oxygen it has generally been believed that the photoionization crossection exhibits no shape resonance, that it is "pushed below" the ionization potential by the sigma resonance. We have investigated both the photoemission as well as the (normal) Auger decay as a function of the photon energy in the photon energy range 550 – 600 eV. In these experiments the polarization vector of the ionizing photons were both horizontal (LH) and vertical (LV) with respect to the axis of detection of the emitted electrons, this allows us to not only draw conclusions about the ionization crossection, but also the angular distribution of photoelectrons.

A striking effect in the measured spectra is that the intensity ratios in the (normal) Auger spectra are not constant as a function of photon energy, see Fig. 1. Furthermore the Auger spectra measured with LH and LV polarization are not identical indicating that the Auger transition is not only a monopole transition, as expected, but partly also a dipole transition, see Fig. 2. A detailed analysis of the photoemission spectra will also be presented together with these findings.

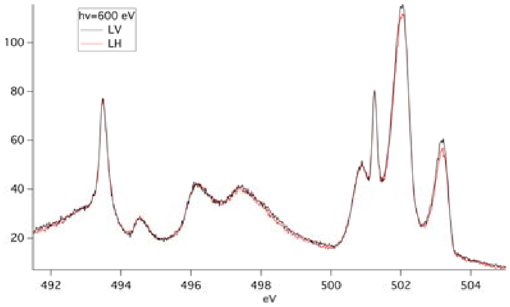

Figure 1. The normal Auger spectra of gaseous O_2 measured in both LV and LH polarization. The energy scale is not calibrated and the relative intensity is normalized on the peak at 493.5 eV. The differences for high kinetic energies could be a sign of a shape resonance in gaseous O_2.

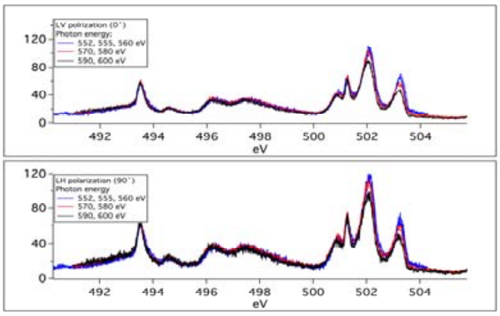

Figure 2. The normal Auger spectra of gaseous O_2 measured at a photon energy of 600 eV for both LH and LV polarization. The energy scale is not calibrated and the relative intensity is normalized on the peak at 493.5 eV. Small differences for high kinetic energies are seen indicating that the Auger transition is not necessarily strictly a monopole transition.

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The ESCA Molecule
Historical Remarks and New Results

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ABSTRACT

The C1s photoelectron spectrum of ethyl trifluoroacetate (CF3-CO-O-CH2-CH3), also known as the `ESCA molecule', is the most illustrative showcase of chemical shifts in photoelectron spectroscopy /1-3/. The binding energies of the four carbon atoms of this molecule spread over more than 8 eV with energy separations ranging from 1.7 to 3.1 eV owing to different chemical environments and hence different charge states of these chemically identical atoms. In this contribution we discuss the history and importance of this spectrum in the field of photoelectron spectroscopy starting from the time of invention of the ESCA technique.

We present a new very highly resolved version of this spectrum, obtained at the PLEIADES beamline at SOLEIL. The result shows that we have to use the most modern experimental and computational tools to observe the important details and to describe the spectrum theoretically. Large geometrical changes, different for each ionization site, and the presence of two conformers of ethyl trifluoroacetate influencing the spectral lineshapes of all four C1s lines can be observed. Also we show that dissociation occurs for C1s ionization of one of the carbon atoms. All these effects have been carefully modeled by theory and investigated in the experimental spectrum.

Finally the relative cross sections for the different C1s levels has been measured as a function of photon energy. Large oscillations have been observed which will be discussed.

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Extracting Chemical Information of Free Molecules from *K*-shell Double Core-hole Spectroscopy

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ABSTRACT

Double core hole (DCH) spectroscopy from the *K*-shell is one of hot topics recently. DCH spectroscopy from other shells have been investigated extensively from 70's to 80's. For the *K*-shell DCH study, theoretical poineering works have been performed by Cederbaum *et al* [1], and followed by Ågren *et al* [2]. Although experimental detections of DCH states were very difficult due to small cross sections, several experimental results were reported recently with experimental improvements of syncrotron radiation [3,4] and emergence of X-ray free electron laser [5,6]. Stimulating such experimental progress, theoretical studies have been revived again [7-12].

In the present study, we have calculated ionization potential (IP) for *K*-Shell single core hole (SCH) creation and double ionization potential (DIP) for *K*-Shell double core hole creation of XH_m-YH_n (X, Y = C, N, O, F, m,n=0-3), NX_2CXO (X=H or F), and C_{60} within the framework of density functional theory (DFT). For these molecules, we estimated the relaxation energies (a measure of the electron density flow to the core-hole site) and the interatomic relaxation energies (a measure of the electron density flow to the two core-hole sites) from the calculated IPs and DIPs. For XH_m-YH_n, we find that the interatomic relaxation energy for the DCH states having two holes at X and Y atoms decreases with increasing in the bond order between X and Y. For NX_2CXO (X=H or F), we find that the substitution of the hydrogen atoms by the fluorine atoms affects the initial-state-bonding shifts but less influences the relaxation energy. For DCH states having two holes at two carbon atoms in C_{60}, we find that the interatomic relaxation energy decreases with increasing in the hole-hole distance.

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Competition between Resonant and Non-resonant Paths in Two-photon Ionization by Extreme Ultraviolet Free Electron Laser Pulses

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ABSTRACT

Phase-shift differences and amplitude ratios of the outgoing *s* and *d* continuum wave packets generated by two-photon ionization of helium atoms are determined from the photoelectron angular distributions obtained using velocity map imaging. Helium atoms are ionized with extreme-ultraviolet free-electron laser pulses with a photon energy of 20.3, 21.3, 23.0, and 24.3 eV, produced by the SPring-8 Compact SASE Source test accelerator. The measured values of the phase-shift differences are distinct from scattering phase-shift differences when the photon energy is tuned to an excited level or Rydberg manifold [1], in accordance with a recent theoretical prediction [2]. The present results unambiguously demonstrate the existence of a competition between resonant and non-resonant paths in two-photon ionization by ultrashort pulses, and will open a way for coherent control of multiphoton ionization.

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Asymmetry in the Molecular Frame Photoelectron Angular Distribution for Oxygen 1*s* Photoemission from CO_2

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ABSTRACT

The photoelectrons emitted in O 1*s* photoemission from CO_2 have been detected in coincidence with the O^+ and CO^+ fragments produced in the subsequent Auger decay of the core hole state.[1] The resulting measured molecular frame photoelectron angular distributions (MFPADs) were not symmetric with respect to the reflection plane of symmetry found in the CO_2 molecule in its ground state. Similar asymmetries have been seen[2] in the MFPADs in C 1*s* ionization of CO_2. In that case, the experimental data could be explained[3] by assuming that when the Auger decay occurs to a directly dissociative double ion state of CO_2^{2+} the longer CO bond is the bond that breaks. In the case of O 1*s* ionization there are two hole states which can best be described as two diabatic states with the hole localized on the left in one state and on the right in the other state.[4,5] Computed fixed-nuclei MFPADs from these two hole states show significant left-right asymmetries. Using the same assumption as in the C 1*s* case leads to much stronger asymmetry than is observed in the experiment. To understand the observed asymmetries, we have considered a one-dimensional vibrational model of the CO_2 system where we have only included the anti-symmetric stretch. Using a modified version of the lifetime-vibrational interference equation[6,7] and the diabatic vibrational states, we then computed the dependence of the MFPAD on the lifetime of the core holes. We could model the experimental MFPADs using computed Auger decay rates for decay to a number of CO_2^{2+} states and by assuming that decay to a directly dissociating state leads to dissociation of the longer CO bond and that decay to a double-ion state which is stable at the equilibrium geometry leads to predissociation with equal probability of breaking each CO bond.

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Linear Magnetic Dichroism in Inner Shell Ionization of Alkali-metal Atoms

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ABSTRACT

Combination of optical-pumping lasers to angle-resolved photoelectron spectroscopy is a powerful method for studying the photoionization dynamics of atoms [1]. In the recent years this method has been applied to various targets, including alkali-metal atoms (see e.g. [2-7] and references therein). In atomic targets magnetic dichroism in photoionization is observed, when the statistical population of magnetic substates is altered by pumping specific states with circularly polarized laser irradiation. Linear magnetic dichroism in the angular distribution (LMDAD) is a phenomenon highly sensitive to the mutual interactions between the electrons and their photoionization dynamics. It can be shown that LMDAD is a pure interference effect between partial continuum waves and the information contained in LMDAD is similar to the angular anisotropy parameter β of photoelectrons. Indeed, in the case of weak transitions – such as photoionization satellites, that carry a lot of information about the electron correlations [7] - measuring the LMDAD can be less prone to experimental error.

In this contribution we present a review of our recent works on LMDAD in the 4p photoionization of Rb atoms [2,3] and combine them together with some preliminary new experimental results. The LMDAD was experimentally recorded for the Rb 4p main and satellite photoelectron lines following both, the 5s-5p$_{1/2}$ and 5s-5p$_{3/2}$ excitations. The ionizing linearly polarized synchrotron radiation covered a wide photon energy region from 24 eV up to 100 eV. The experimental results are in good agreement with theoretical multiconfiguration Dirac-Fock calculations. The results show that the Cooper minimum of the cross section coincides with the zero-point of LMDAD as one of the two partial wave amplitudes diminishes – killing also the interference necessary for LMDAD. This opens a convenient and accurate method for measuring the position of the Cooper minimum [6]. In addition it is shown that LMDAD is a very sensitive probe of electron correlations and continuum interactions [7].

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Frontiers of Photoelectron Spectroscopy

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ABSTRACT

Photoelectron spectroscopy (PES) is an excellent tool for investigations of matter due to the possibility to probe both electronic and geometric structure. In this contribution we discuss recent trends in photoemission and present pioneering work within the different applications.

Photoelectron spectroscopy went through a revolution in the 1990's, with the development of parallel angular detection using 2D detectors, a development that VG Scienta is proud to have contributed to. The possibility of simultaneous recording of Angular Resolved PES (ARPES) spectra enables not only band structure measurements, but also X-ray photoelectron diffraction (XPD), depth profiling and standing wave spectroscopy. However, using a hemispherical energy analyser, electron emission angle information may be recorded in one direction. In contrast, the slit-less design of the novel angle resolved time of flight spectrometer Scienta ARTOF accepts electrons in a full cone, thereby allowing for simultaneous measurements of the whole band structure. Recent examples will be given.

Traditionally, PES has been limited to the soft X-ray regime, forming a surface sensitive technique. In recent years there has been considerable interest in PES using higher ionization energies, forming the field of Hard X-ray Photoelectron Spectroscopy (HAXPES). With the high kinetic energies available in HAXPES, studies of bulk materials, including buried interfaces, becomes available. Here we present results obtained in the HAXPES regime, with emphasis on the use of 2-D detectors to obtain angularly resolved or spatially resolved spectra.

Experiments done under normal surface science conditions (Ultra High Vacuum) are of limited use in some applications, e.g. catalysis, due to the pressure gap problem. This motivates the study of systems at ambient pressures. Here we present a High Pressure Photoemission (HiPP) instrument developed in collaboration with Advanced Light Source (ALS). This instrument allows standard PES measurements as well as spatial and angle resolved spectra at HiPP conditions. Some recent results include spatially resolved investigations of solid oxide electrochemical cells (SOC:s) and electrochemical properties of junctions.

Finally, we report on recent advances in constructing a new generation of instrumentation combining HiPP and HAXPES. A novel electron analyser, designed for optimal transmission in combination with very efficient differential pumping, will be presented together with preliminary results.

Novel Applications in Surface Science *In-situ* Sample Analysis in Extreme Environments

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ABSTRACT

Ultra-high vacuum (UHV) is the standard operating environment for all surface science techniques, but the novel materials and processes that are the key to the functioning of many modern devices, e.g., fuel cells, advanced catalysts, are often incompatible with such conditions. At the same time, material surfaces play an increasingly important role in device operations due to miniaturization down to the nanoscale. Transferring the methods and knowledge of traditional UHV surface science studies to advanced material analysis will mean using photoelectron spectroscopy (PES), scanning probe microscopy (SPM), and other relevant techniques in the generic or near generic device environment. Therefore, it will be necessary to conduct experiments in high, elevated, or near ambient pressures of defined working gas mixtures and liquid media, as well as in extreme temperatures, potentials, or magnetic fields.

Our contribution describes state-of-the-art solutions and future development routes toward new instruments and material analysis methods functioning under these working conditions. Opportunities and limitations of new instrumentation will be discussed from the perspective of a supplier of scientific instruments. Finally, applications, examples, and results from existing in-situ measurement solutions will be shown, including complete high pressure or near ambient pressure photoelectron spectroscopy (NAP-PES) or scanning probe microscopy (NAP-SPM) systems, high pressure treatment cells, liquid and electrochemical cells, liquid sample "manipulators", and the concepts and status of equipment designed for operating in the highest and lowest temperatures, high magnetic fields, and static or dynamic potentials.

Hard X-ray Photoelectron Spectroscopy on the GALAXIES Beamline at SOLEIL synchrotron.

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ABSTRACT

The new experimental endstation dedicated to hard x-ray photoemission spectroscopy (HAXPES) is now operational on the GALAXIES beamline of the French synchrotron facility SOLEIL. The incident photon energy covers the 2.4-12keV range and the kinetic energy of the electrons can be analyzed up to 12keV. The HAXPES setup comprises a motorized manipulator hosting a cryostat for solid samples and a gas cell. First results will be presented along with future improvements toward high resolution measurements.

High Harmonics Time-of-flight ARPES at 4 MHz using a Compact Ti-Sapphire Oscillator

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ABSTRACT

High-order harmonic generation (HHG) allows to produce attosecond pulses of coherent vacuum-ultraviolet light and x-ray using a laboratory setup. The applications of HHG-based light sources in electron spectroscopy and microscopy have great potential for studies of ultrafast electron dynamics in atoms, molecules as well as condensed matters. Although HHG has been studied for more than two decades, it is still at the frontier of research to develop HHG setups with a high repetition rate beyond megahertz frequency.

Conventional HHG experiments are driven by amplified laser systems at a repetition rate of several kilohertz. As a consequence, the statistics of experiments are limited to a few thousand events per second and a long acquisition time is required for applications in electron-based spectroscopy and microscopy. To significantly increase the repetition rate of HHG, three different approaches were demonstrated very recently. By using complicated high power fiber-based lasers and amplifiers, Vernaleken *et al*. generate harmonics up to the 17th order at a repetition rate of 20.8 MHz [1]. In order to reduce the complexity of the setup, Kim *et al*. take advantage of the plasmonic nanostructures to induce strong near-field for driving HHG at 80 MHz [2]. However, due to the damages caused by the intense electric field, their results and ideas are currently under critical debate [3]. The third approach is to generate harmonics inside the cavity of a resonator [4,5]. With delicate design of the cavity and demanding optimization of the output coupler for harmonics, this method allows generation of high-order harmonics at a repetition rate of more than 150 MHz [6].

In this contribution, we report a more compact and straightforward design for HHG at megahertz repetition rate. In our setup, we use directly the output of a Ti-sapphire laser at 4 MHz and focus it into a gas jet with a high backing pressure. Furthermore, we apply the HHG setup as a light source for time-of-flight photoemission spectroscopy. Our results suggest an efficient setup for HHG at megahertz repetition rate and provide the basis for applications in electron spectroscopy and microscopy.

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Hard X-ray Photoelectron Spectroscopy at BESSY II - Present and Future Opportunities

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ABSTRACT

In the last decade hard x-ray photoelectron spectroscopy (HAXPES) has lead to a break-through in the field of photoemission due to its non destructive way of investigating the bulk electronic properties of materials and in particular buried interfaces in layered systems. Nanolayered systems are the keystones of current and future spintronics devices. The electronic, magnetic and magneto-transport properties of these structures are determined not only by the characteristics of each layer, but also by the structure and bonding situation of the individual constituents at their interfaces.

In the present contribution several experiments performed at the HIKE HAXPES user facility [1] at the BESSY II light source will be presented as well as a comprehensive account of the future upgrades of the HAXPES user end-station at BESSY II. The HIKE facility successfully combines the bending magnet source of the KMC-1 beamline [2] with a new generation electron spectrometer optimized for high kinetic energy electrons. Several topics will be detailed with emphasis on the performance and abilities of the technique.

The future upgrade of the HIKE user end-station concentrates on the development of an experimental combination of spin filtering and hard x-ray photoelectron spectroscopy to study bulk electronic structures additionally providing the spin information. The electron analyzer detection scheme will be upgraded with a highly efficient spin detector [3].

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High Resolution TOF PEEM-electron Spectrometer

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ABSTRACT

The Time-of-Flight approach in photoemission electron spectroscopy implemented in TOF ARPES-Spin [1,2] and TOF ARPES [3] was used in development TOF PEEM-ES with spatial resolution 2-3 nm in PEEM mode and less than 0.2 degree angle resolution in ARPES mode. Calculated energy resolution of analyzer is in submilivolt range and is mapped to spatial or reciprocal space (or a combination) of emitted photoelectrons, depending on the mode of operations. This makes the analysis effectively three dimensional, leaving two dimensions for real or reciprocal space and a third for electrons energy spectrum converted from time of flight.

The electron optical system (EOS) of the analyzer consist of 4 electrostatic lenses, two variable apertures, two deflectors, a stigmator and aberration corrector, consisting of stigmatic non axial symmetrical focusing elements for correction of EOSs third order spherical aberration. Linear magnification of EOS is M = 2000-10000. Delay line detector with timing accuracy better than 130 ps FWHM and spatial resolution better than 50 μm FWHM was incorporated in the system [4]. Detector can operate at ~0.4MHz count rates for a specified range of incoming electron energies. Data processing software and mechanical design was based on modular approach, and EOS of analyzer could be optimally configured accordingly to setup of ongoing experiment.

A new matrix form of temporal aberrations of “thin” lens model is presented. Times to energy conversion is expressed as a series of polynomial approximations in time-energy domain. Criteria for EOS optimization of TOF-EEA with maximum energy resolution and sensitivity and required image quality were formulated.

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EPICEA: A Setup to Investigate High Kinetic Energy Electron Emission in Molecular Frame

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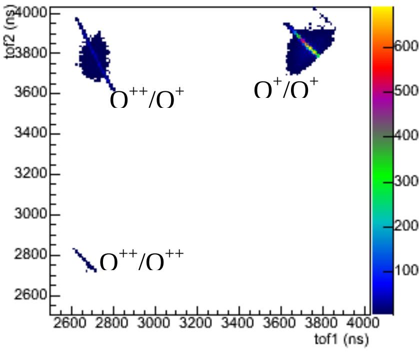
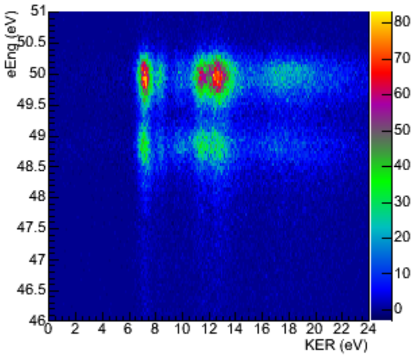
ABSTRACT

Dynamics in many-body systems are a major challenge for theory and experiment. They are the key issue of many fields of physics such as solid state, nuclear as well as atomic molecular physics. The lack of understanding of such dynamics is in troubling contrast to its importance. Coincident experiments, where both electrons and ions are measured and fully analyzed, are always more powerful than pure electron spectroscopy measurements, in providing a direct view of the reaction processes [1-9]. Coincident measurements are always characterized with lower count rate and rather sophisticated techniques.

A high luminosity double toroidal analyzer was developed in our group fifteen years ago [8,9]. Later on, an ion TOF was added to enable electron-ion coincidence measurements [3,4,11]. Most recently, we developed a lens table to drive DTA, which ensures that the electron energy resolution can be routinely better than 0.8% of analyzer pass energy. Furthermore, a new ion VMI-TOF spectrometer was installed, which enables the measurement of ion momenta. All these improvements end up with upgraded EPICEA setup at PLEIADES beamline (SOLEIL).





By using this setup, we investigated the photoionization of O_2 50 eV above the O1s threshold. Different fragmentation channels were identified, and it is found out that the Auger decay processes depends on spin-orbit coupling in the ionized states.

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PLEIADES – an Ultra High Resolution Soft X-ray Beamline for Advanced Spectroscopic Studies of Diluted Species from Atoms to Nanoparticles

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ABSTRACT

PLEIADES is an ultra high-resolution soft X-ray beamline (7 eV to 1 keV) at SOLEIL in France [1]. The beamline is dedicated to spectroscopic studies of dilute samples (atoms, molecules, ions, biological molecules, free Van der Waals and metal clusters, isolated nanoparticles). All types of light polarizations are available from an Apple II (80 mm period) and an electromagnetic (256 mm period) undulator. The optics has been designed to reach an ultimate resolving power of about 100000@50 eV thanks to a novel PGM design employing varied line spacing **VLS** and varied grove depth **VGD** gratings [2].

A high-resolution electron spectrometer (VGScienta-R4000), an energy and angle resolved Auger electron - ion coincidence setup (EPICEA), as well as a dedicated station (MAIA) for positive and negative ion photoionization studies (ECR source) are permanently installed on the beamline. A laser facility (c.w. and pulsed) can be used in addition to the synchrotron beam, for pump-probe experiments.

Open to users since April 2010, PLEIADES beamline has allowed already to obtain numerous results in relation with the decay dynamics of core-excited atoms and molecules, atomic and molecular clusters or isolated nanoparticles, probed by electron-spectroscopy or Auger electron – ion coincidence measurements. Examples illustrating the main performances will be presented, as well as the latest experimental and optical updates.

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NO-3-PO-OUR-01

Time-Resolved Soft X-ray Emission Spectrometer to Study Transient Electronic Structure Induced by an External Field

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ABSTRACT

In order to open up a new field of time-resolved spcetroscopy in the soft x-ray region, we have developed a time-resolved soft x-ray emission spectrometer (TR-SXES). It is well known that the soft x-ray emission (SXE) spectroscopy is a powerful tool to investigate the electronic structure of various materials and the relaxation processes of excited states with a localized core-hole. The SXE spectroscopy also allows us to distinguish the angular momentum components of valence states because of a clear selection rule due to the dipole nature of x-ray transitions. Furthermore, the SXE spectroscopy can provide us bulk sensitivity giving rise to an opportunity to study the intrinsic electronic structure of various materials as well as the buried structure, *e.g.* multi-quantum well, since the mean free path of soft x rays is much longer than that of electron. Thus the present TR-SXES is developed to be aimed at studying transient electronic structure of condensed matter induced by an external field, such as electric field, magnetic field and strong laser field.

The TR-SXES consists of a flat field spectrometer [1] equipped with an MCP-based two-dimensional position sensitive detector (PSD) [2,3]. The present spectrometer employs a slit-less configuration, thus the energy-resolution of the spectrometer is governed by both the beam spot size on the target and the spatial resolution of the PSD. The system is installed at the focus point of a new refocusing mirrors system installed at the b-branch of BL17SU, SPring-8. At the moment, the energy-resolution of the spectrometer does not reach the expected value (E/dE over 1,000), the time-resolution of the system including the electronics (about 700 ps) is short enough than the time interval of the successive bunches of the SPring-8 storage ring. Although the ultimate time-resolution for the time-resolved spectroscopy at SPring-8 storage ring is 40 ps, *i.e.* pulse width of an electron-bunch, if the system is installed at the free electron laser facility it can be applicable to the investigation of ultrafast dynamics in condensed matter.

As a first demonstration of the TR-SXES, the system is being applied for the pump-probe experiment at BL17SU of SPring-8 by combining with a femto-second laser (λ – 800 nm). In the conference, the design concept of the TR-SXES, the diagnostic results of its performance test, and some preliminary results of the pump-probe experiment will be presented.

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Two Concepts of RIXS Instrumentation: From Spherical VLS Grating to One-shot hv^2 Spectrometer

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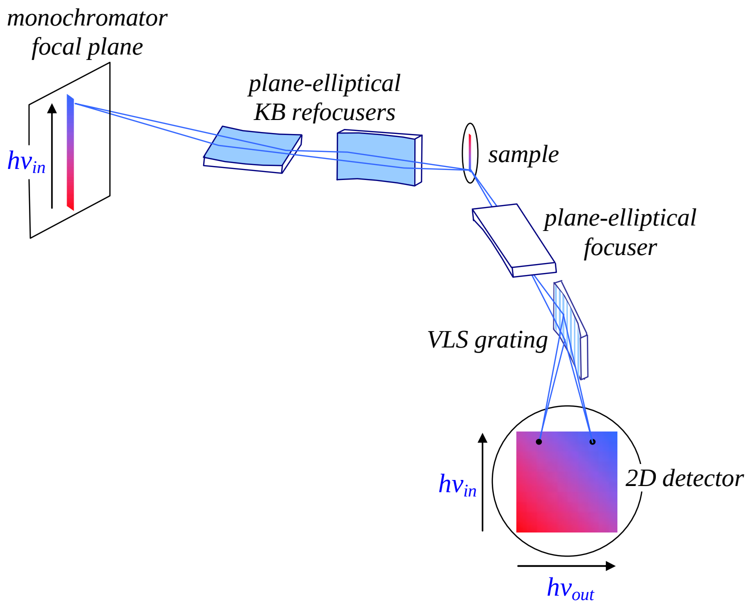
ABSTRACT

The spherical VLS grating spectrometer is a basic but still highly efficient concept of the modern RIXS instrumentation. A novel algorithm for optical design of these spectrometers is developed to enable their operation at negligible aberrations and maximal angular acceptance over extended energy range. First, the VLS coefficients are optimized at a reference energy E_ref to fully cancel the lineshape asymmetry (mostly from the coma aberrations) as well as minimize symmetric aberration at large grating illuminations to dramatically increase the aberration-limited spectrometer acceptance. For any energy away from E_ref, corrections to the entrance arm and light incidence angle are evaluated to maintain the symmetric lineshape and, depending on operational mode, either energy independent focal curve inclination or maximal aberration-limited acceptance.

In view of low quantum efficiency of the RIXS process, increase of the detection efficiency is one of the primary goals of new generations of the RIXS instrumentation. A perspective concept based on the spherical VLS grating is so-called hv^2 spectrometer[2] which combines imaging and dispersion actions, in two orthogonal planes, to deliver full 2D map of RIXS intensity in one shot of parallel detection in incoming hv_in and outgoing hv_out photon energies (figure). Making full use of a broad hv_in bandwidth, this concept brings a detection efficiency increase of the order of 50 without any compromise on resolution. Preliminary ray-tracing simulations with a typical undulator beamline demonstrate a resolving power well above 11K in both hv_in and hv_out near 1 keV, with a vast potential for further improvement. Combining the hv^2 spectrometer with an XFEL source, delivering a round spot profile, simplifies its technical implementation and enables efficient time-resolved RIXS experiments.



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High Resolution Real and Reciprocal Space Photoelectron Emission Microscocopy on Heterogeneous Graphene/SiC(000-1)

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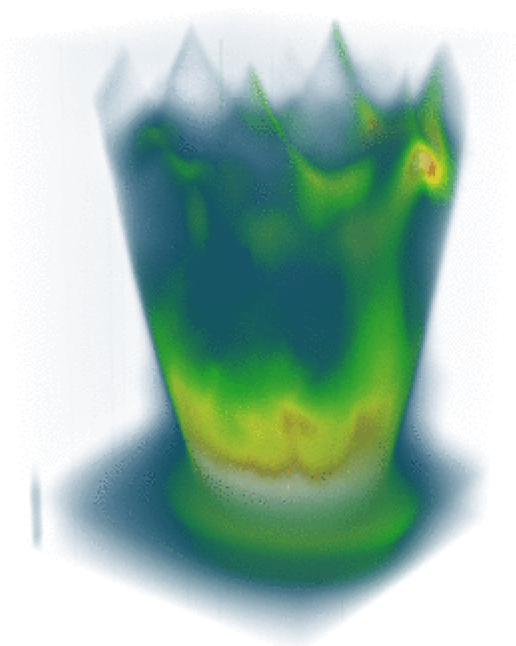
ABSTRACT

We present energy filtered electron emission spectromicroscopy with high spatial and wave-vector resolution on few-layer epitaxial graphene on SiC(000-1) grown by furnace annealing.

Conventional electron spectroscopy methods are limited in providing simultaneous real and reciprocal or k-space information from small areas under laboratory conditions. Therefore, the characterization of materials with only micron scale sample homogeneity such as epitaxially grown graphene requires new instrumentation. Recent improvements in aberration compensated energy-filtered photoelectron emission microscopy (PEEM) can overcome the known limitations in both synchrotron and laboratory environments.

Here we report 2D maps of the k-parallel π-π band dispersion in micron-scale regions and correlate them with spatially resolved chemical information on the same regions. Only the combination of high lateral, high energy, high k-resolution and controlled switching between real space and k-space allows detailed understanding of micron size sample sites with 1–3 layers graphene.

The experiments underline the importance of simultaneous lateral, wave vector and spectroscopic resolution on the scale of future electronic devices in order to precisely characterize the transport properties and band alignments.



Semi-transparent 3D plot of the band structure of Graphene (0-10 eV binding energy) from a 5.7 µm area.

Bias Dependent Electronic States in Gate Stack Structures: HXPES under Device Operation

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ABSTRACT

Although gate stack structures with high-k materials have been extensively investigated, there are some issues to be solved for the formation of high quality gate stack structures. One of the most serious issues in the high-k gate stack structures is the difficulty in evaluating the potential in the gate stack structures, which determines the important device parameter, i.e., the threshold voltage. Especially the potential measurements of two interfaces, which are gate metal/high-k insulator and high-k insulator/substrate Si interfaces, are difficult with electric measurements. Thus a new method is required to measure the potential in the gate stack structures. X-ray photoelectron spectroscopy is a powerful method to investigate the electronic structures in materials and is used to examine band diagrams. Recently hard x-ray photoelectron spectroscopy (HXPES), which exhibits large escape depth, allows us to investigate the electronic states of materials while keeping device structures intact. Here, HXPES is employed to measure electronic states in gate stack structures under device operation [1-4]. Using this method, bias dependent electronic structures are detectable, which enables us to obtain the bias-dependent band diagram and potential distribution in gate structures. In the present study, we investigated electronic states for metal/HfO_2/SiO_2/Si gate structures by means of bias application in hard x-ray photoelectron spectroscopy to obtain the bias-dependent band diagram and potential distribution in the structures.

By analyzing core levels of gate stack structures, the bias dependent potential distribution was obtained. For metal/HfO_2 interface, a potential gradient was formed at the Pt/HfO_2 interface in a Pt-based gate stack structure while a potential gradient was not formed at the Pd/HfO_2 interface in a Pd-based gate structure. Angle resolved photoelectron spectroscopy revealed that a SiO_2 layer was formed at the both interfaces. However the Pt-based gate structure exhibits thicker SiO_2 layer than the Pd-based gate structure. The formation and the thickness of the SiO_2 layer at the interface might concern the Fermi level pinning, which is observed in metal-based high-k gate stack structures.

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High-resolution ARPES Study of La/W(110) Thin Film

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ABSTRACT

In the rare earth metals, the interaction between highly localized 4*f*-electrons and itinerant conduction electrons is the origin of the variety of physical properties.[1] Lanthanum (La) is the lightest element in lanthanide, and is a superconductor [2]. The valence band mainly consists of the 5*d* states, and most of the 4*f* states are located in the unoccupied states. In this study, we have performed high-resolution angle-resolved photoemission spectroscopy (ARPES) measurements using synchrotron radiation on La/W(110) thin film, to evaluate the many-body interactions on the conduction electrons.

ARPES experiments were performed at the linear undulator beamline (BL-1) of Hiroshima Synchrotron Radiation Center. A clean surface of W(110) substrate was prepared by repeated cycles of heating in an oxygen atmosphere (5×10^{-9} Torr) at 1200 K and subsequent flash to 2000 K. La thin film (30 ML) was deposited on the W(110) substrate by the electron-beam evaporation and characterized by using Auger electron spectroscopy and low-energy electron diffraction. Sample temperature was set at 8 K using a liquid He cryostat.

We observed a parabolic band dispersion with the band bottom energy at -0.19 eV along the Γ-K line. A kink in the energy-band dispersion was found close to E_F (~10 meV), and its energy-scale coincides well with the Debye energy of La (Θ_D = 152 K, $k_B\Theta_D$ = 12.9 meV) [3]. In addition, the experimentally determined self-energy respectively exhibits a peak structure and a rapid decrease in its real and imaginary parts both at ~10 meV, indicating that these are arising from the electron-phonon interaction. In this presentation, we will discuss the correlated nature of the electrons in La/W(110) thin film by evaluating the coupling parameters for the electron-electron interaction and electron-phonon interaction.

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Orientation-controlled Surface Immobilization of Alkyl Molecules

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ABSTRACT

Self-assembled monolayer (SAM) of organic molecules which is formed by strong interaction between the organic molecules and a surface has widely been studied because of its wide application such as bio-sensors and transistors. Concerning the formation of SAMs using alkyl chain molecules, which is one of the simplest organic molecules, it is important to control the direction of alkyl chains because the alkyl SAM can be used as a “mold” to immobilize the other organic functional molecules. In this study, we report on the results for the immobilization of alkyl chain molecules on metal and oxide surfaces through functional groups, and present the results for controlling the direction of the alkyl chain.

Experiments were performed at the BL-27A station of the Photon Factory (Tsukuba, Japan). We used mercaptopropyltrimetoxisilane (MPTS) molecules ($HS(CH_2)_3Si(OCH_3)_3$) which have thiol group (SH) and silicon alkoxide group ($Si(OCH_3)_3$) at the terminal sites of the alkyl backbone. MPTS molecules were adsorbed on polycrystalline Au and sapphire R-plane surface by two methods. One is to immerse the substrate in 100% MPTS liquid and rinse by supersonic wave in ethanol. The other is to evaporate in vacuum. The chemical states of the MPTS molecules on the surface were measured by X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) using soft X-rays from synchrotron light source.

Figure 1 shows S K-edge NEXAFS spectra of MPTS on Au and sapphire surface at 90 degree incidence. Peak A observed in both spectra is the resonance from S 1s to σ^* orbital localized in the S-C bond. Peak B, only observed in the spectrum of the MPTS on the sapphire surface, is that localized in the S-H bond. This result indicates that SH groups in MPTS molecules on sapphire do not form the chemical bond with the surface, and keep molecular states. On the other hand, for the Au surface, the peak C appeared at high energy side, which suggests the formation of Au-S bonds. For XPS spectra, the results showed that thiol groups in MPTS form covalent bonds with Au, while alkoxide groups are bound with sapphire. As a result, MPTS molecules are adsorbed on Au with thiol groups and alkoxide groups are located at the upper side, while the direction of MPTS molecules on sapphire surface is opposite. It is concluded that MPTS molecules can be used as a mold to immobilize the other organic molecules through thiol or alkoxide groups.

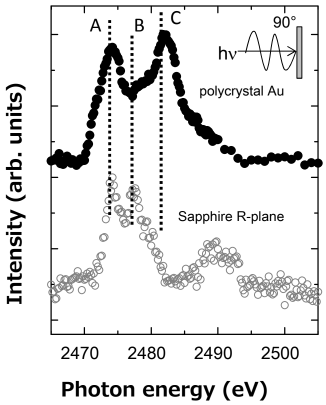

Figure 1. S K-edge NEXAFS spectra of MPTS molecule on polycrystal Au and sapphire surface, respectively.

High-Density Carrier Dynamics at a Semiconductor Surface Studied by Time-resolved Photoemission Spectroscopy

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ABSTRACT

Nowadays, dynamics of photo-induced phenomena in semiconductors have been intensively investigated. In contrast to treatments by thermal heating, excitation by light has advantages to regulate systems with high spatial resolution, down to nanometeters, and in ultrafast time-scale. Moreover, generations of the transient states, especially by high-intense lasers, often lead to unusual properties of matters. Despite the scientific interests, the proper understandings of such dynamical phenomena have been difficult since they are intrinsically fast and complicated. Development of the *real-time* measurement system has, thus, been required to trace the non-equilibrium electronic states with appropriate time and energy resolutions.

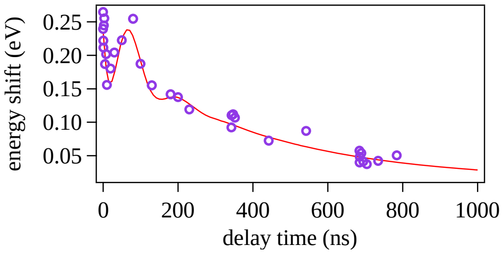

Fig Peak shift of Si 2p due to laser radiation and relaxation with laser power density 100μW/cm^{2}. Time 0 means the time when the laser pulse hits the sample.Dots indicate experimental data points and solid line indicates result of fitting.

Recently, we have constructed at SPring-8 BL07LSU the soft X-ray time-resolved photoemission spectroscopy system, equipped with a high-power femtosecond-pulse laser [1]. In the present research, we have investigated the relaxation of the surface photo-voltage (SPV) effect, which is the well-known photo-induced phenomenon at a semiconductor surface. The SPV effect is induced by spatial separation of photo-excited electrons and holes by electric field near a surface (the surface band bending). The relaxation has been understood as recombination of these two-types of carriers but the detailed mechanism has not been understood yet. Using a model surface of Si(111)7×7, we traced relaxation after the SPV effect by measuring time-evolution of the core-level (Si 2p) spectra. In contrary to the expected monotonous decay, it was composed of the two steps [1] and damping oscillations at a higher power density of the pumping laser, as shown in the figure. The origin of this unexpected oscillatory dynamic behavior was analyzed with oscillator models, such as the Lotka-Voltera scheme, possibly realized at the semiconductor surface. In the presentation, we show the time-resolved photoemission data and analyses, taken at various laser conditions. We would also like to discuss an appropriate kinetic model for carriers of high-density excited states.

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Transport and Escape Processes of Photoelectron from SiO_2(350 nm)/Si Interfaces with 7.2-eV UV Irradiation

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ABSTRACT

Recently, we have developed a new plasma enhanced CVD method for growth of carbonaceous materials [1-4], in which DC plasma is assisted with photoelectrons emitted from a substrate surface irradiated with UV light from Xe excimer lamp ($h\nu$ = 7.2 eV). In this CVD method, Ar glow discharge plasma was successfully generated for Si substrates with SiO_2 layers as thick as 350 nm. In addition, it has been confirmed that photocurrent from the SiO_2(350 nm)/Si surfaces is almost same as that from Si surfaces, while photon energy of 7.2 eV is smaller than band gap of SiO_2 (~9 eV). This implies that photoelectrons can be emitted from the SiO_2(350 nm)/Si interface. In this study, we measured the kinetic energy distributions of photoelectrons from Si surfaces with and without 350-nm SiO_2 to clarify the transport and escape processes of photoelectrons from the SiO_2(350 nm)/Si interface.

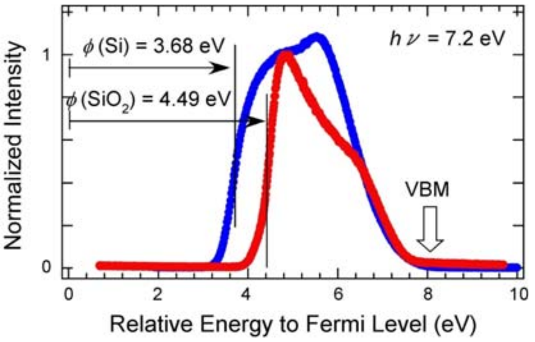

Fig. 1. Photoelectron spectra of SiO_2(350 nm)/Si substrates excited by 7.2-eV UV light compared with that of Si(001) surface.

Figure 1 shows the photoelectron spectra of the SiO_2(350 nm)/Si substrate compared with a Si substrate. The horizontal axis is relative energy to Fermi level obtained from a sample holder made by a Ta foil. The maximum energies of emitted photoelectron from both substrates show a good agreement with each other, so that it is found that the valence electrons of Si substrate is emitted from the SiO_2 surface. This result indicates that photoelectron can be transported through the thick SiO_2 film with 350 nm of thickness. The photoemission mechanism from SiO_2 surface can be considered as below. The UV with 7.2 eV can reach the interface between SiO_2 and Si, because band gap of SiO_2 (~9 eV) is larger than the energy of UV. The valence electrons are excited and injected into conduction band of SiO_2, and these electrons travel into the SiO_2 films without inelastic scattering because low energy electrons cannot excite the atoms and plasmon. As the result, the photoelectron can be emitted from SiO_2(350 nm) surfaces. This research is supported by the Japan Society for the Promotion of Science through its Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program).

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Photoelectron Holography of a 1*T*-TiSe$_2$ Surface

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ABSTRACT

X-ray photoelectron diffraction (XPD) attracts attention as an efficient method for studying the structure of the surface layers of solids. An interesting field of XPD is photoelectron holography (XPH), where experimental 2π diffraction patterns of emitted photoelectrons are considered as holograms. This method can visualize a three-dimensional (3D) local atomic structure around a target atomic site.

The experiments on X-ray photoelectron diffraction on the 1*T*-TiSe$_2$ surface were performed at ESCALAB MK II spectrometer. In the electron spectrum of this dichalcogenide the lines of greatest intensity are attributed to Ti2*p*-electronic core-level states of titanium and the band of Auger transition on the selenium atoms Se($L_3M_{45}M_{45}$). These lines were selected for recording the XPD patterns of titanium and selenium.

We undertook a 3D image reconstruction from X-ray photoelectron and Auger electron diffraction data. Being processed with the scattering pattern extraction algorithm using the maximum entropy method (SPEA-MEM[1]), they provided individual 3D images of the nearest environment of selenium and titanium atoms in the TiSe$_2$ lattice.

The atoms which equivalent in a bulk become inequivalent near the surface such as: *i*) Se atomic sites in the top and bottom layers of a slab; *ii*) entire layers of atoms shifted relative to the bulk positions (both Se and Ti). The diffraction pattern contains contributions from all inequivalent emitters. Hence, the atomic image reconstructed from this diffraction pattern is a superposition of atomic surroundings of each emitter .

The problem of interpretation of 3D-images was solved in the following way. First, we performed simulation of XPD patterns for the 1*T*-TiSe$_2$ surface with the approach of electron multiple scattering within the EDAC code[2]. Second, we reconstructed 3D images in real space for theoretical diffraction patterns and compared them with the previous ones. This approach makes it possible to thoroughly analyze deviations of the real surface structure from the ideal bulk structure.

Using 3D images of local atomic structure around Se and Ti atoms, we reconstructed the positions of 128 atoms in the 2×2×1.5 nm region of the surface layer of TiSe$_2$. The structure was determined as 1*T*-polytype. Both surface lattice parameters increased comparing to the bulk ones: $\boldsymbol{a_0}$ by 0.3 Å and $\boldsymbol{c_0}$ by 1.2 Å. Besides, the holography reconstruction proved the shift of Ti-layer from the middle of the slab.

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Possible Non-trivial Surface-band Dispersion on Bi(111)

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ABSTRACT

The topological order is one of the most attracting subject in the recent years, which characterizes new class of order on the band structure of condensed matter [1, 2]. The low-dimensional states localized at the edge of the material are spin-degenerate on the Kramers-degenerate points of the surface Brillouin zone (SBZ) but spin-polarized in the other region on SBZ due to the spin-orbit interaction (SOI). The spin-polarized branches at the edge of the material with the non-trivial topological order change the partner of spin degeneracy at each Kramers-degenerate points, and hence the edge-state band should disperse in the projected bulk band gap and connect the bulk valence and conduction bands. This partner-switching behaviour [3] of the edge states is regarded to be robust against the non-magnetic perturbation and determined from the parity of the bulk bands at the Kramers-degenerate points. Therefore, the topology of the edge-state dispersion reflects the topological order of the bulk band structure.

We have studied the surface electronic structure of the Bi(111) surface using synchrotron-radiation angle-resolved photoelectron spectroscopy (ARPES). Bi is one of the most important material as the constituent of topologically-non-trivial materials due to its strong SOI [2, 3]. Despite such an importance, the topological behaviour of the surface state on the Bi single crystal has gathered less attention because the topological order of the Bi single crystal is regarded as trivial due to the too strong SOI [4]. However, in contrast to the common understanding, we have demonstrated that the dispersion of the surface-state bands on Bi(111) shows non-trivial partner-switching behaviour: one branch of the surface-state band merged into the projected bulk valence bands but the other into the projected bulk conduction bands at the Kramers-degenerate point on SBZ. Our results suggest the non-trivial order of the band structure of the Bi single crystal, in contrast to the widely-accepted trivial picture.

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Growth Kinetics of Multilayer Graphene on SiO_2 Studied by Hard X-ray Photoelectron Spectroscopy and Infrared Spectroscopy

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ABSTRACT

Multilayer graphene (MLG) has been successfully grown on a large-size SiO_2 substrate at temperatures as low as 400°C without any catalysts by means of photoemission-assisted plasma enhanced CVD (PA-PECVD) [1]. It is noted that there is no structural transition layer between MLG and SiO_2. In this study, the growth kinetics of MLG on SiO_2(90 nm)/Si substrates by PA-PECVD was investigated using hard X-ray photoelectron spectroscopy, and infrared spectroscopy at BL47XU and BL43IR of SPring-8, respectively.

The CVD growth experiments and Raman spectroscopy observations were performed at Tohoku University. The growth temperature and Ar-diluted CH_4 concentration were 650°C and 17%, respectively. The growth period t_{gp} was changed from 1 min to 30 min.

From Raman spectra, it is found that MLG grows laterally up to t_{gp} = 5 min. (Region 1) and then MLG changes its orientation to random directions (Region 2). In Region 1, the MLG grain size increases with t_{gp} and saturates at 10 nm in Region 2, where graphene sheets start to be curved, leading to the formation of randomly oriented networked nanographite (NNG). The transition time of the growth mode from MLG to NNG is determined as 4 min. From XPS spectra of MLG and NNG as shown in Fig. 1, it is indicated the ratio of sp^3-amorphous to sp^2 in NNG is smaller than that in MLG, suggesting the amorphous component growing at the same time of MLG on SiO_2 substrates makes the graphene sheet curved. Corresponding to the growth mode change to Region 2, the peaks derived from C-H vibration appears significantly. Based on these results, we propose a growth kinetics model of MLG on SiO_2 substrates, in which the amorphous component and H-termination of graphene sheet make the lateral growth of graphene sheet difficult. This research is supported by the Japan Society for the Promotion of Science through its Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program).

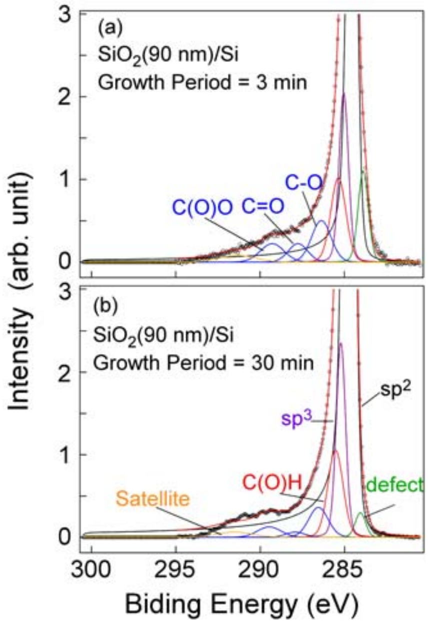

Fig. 1. C 1s photoelectron spectra of (a) MLG and (b) NNG films grown on SiO_2 surface.

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Electronic Structure of Multi-walled Carbon Nanotubes Irradiated by Multiply Charged Ar Ions

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ABSTRACT

Nanostructured carbon materials, such as carbon nanotubes (CNTs)[1] and graphenes[2], have been promising nanomaterials for various nanodevice applications because of their intriguing properties. Modification of the electronic structure of nanostructured carbon materials has been essential to improve the nanodevice performance. For example, singly charged Ar ion irradiation enhanced the field emission properties of CNTs[3]. Singly charged H ion irradiation improve the response time of the electrochemical sensors using CNTs[4]. Thus, singly charged ion irradiation has been commonly used technique to modify the electronic structure of nanostructured carbon materials. On the other hand, multiply charged ion (MCI) irradiation induced unique modification with solid surface, not observed with singly charged ions[5,6]. However, the effect of MCI irradiation on the electronic structure of nanostructured carbon materials has not been fully understood.

In this study, singly and multiply charged Ar ions (Ar^+, Ar^{2+}, Ar^{4+}) were irradiated to multi-walled CNT (MWCNT) films. The electronic structure of irradiated MWCNT films were characterized by soft X-ray photoelectron spectroscopy (XPS) and soft X-ray emission spectroscopy (XES) at BL17SU of SPring-8. The C 1s photoelectron spectra of the as-grown and irradiated MWCNT films were analyzed by means of a least-squares fitting procedure using Doniach-Šunjić functions convoluted with a Gaussian function. The spectra were basically decomposed into five components (bulk sp^2 C, surface sp^2 C, surface sp^3 C, C-O bonds, and C=O bonds). It was found that intensity ratio of sp^2 C to sp^3 C was decreased after Ar^+ ion irradiation, and Γ_G (FWHMs of the Gaussian function) was increased. Moreover, the spectra for Ar^{4+} ion irradiation showed different profiles from Ar^+ ion irradiation. The C Kα X-ray emission spectra were also changed after the ion irradiation. These results were attributed to decrease of sp^2 C region, and increase of disordered region in the irradiated MWCNT films. Differences of XPS spectra between charge states of Ar ions will be discussed, and detailed results of analysis of XES spectra will be also presented.

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Many-Electron Effects in X-Ray Emission and Absorption of Some Wide Band Materials

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ABSTRACT

It is well known emission band and absorption edges of simple metals contain features which can’t be described by one-electron approximation. In emission bands two many-electron effects may significantly distort a shape of the emission spectra: so-called dynamical screening of core hole in the initial state of emission and auger decay of valence band hole in the final state. The first theoretical model for dynamical screening effects was proposed by Mahan [1] and generalized by Nozieres and De Dominicis (Mahan-Nozieres-De Dominicis (MND) theory [2]). Their theory describes correctly only narrow part of X-Ray spectra just before and just above Fermi level. In this work we propose significantly improved real multiband calculation scheme described the spectral distribution in whole energy scale including MND effect. This scheme may be consider as generalized and improved formalism proposed in [3,4] papers. Moreover we include auger correction procedure [5] to describe low-energy ‘’tail’’ in the emission band and estimate lifetime of the hole in valence band of simple metals.

Described calculation schemes were applied to Mg and Al crystal metals K and $L_{2,3}$ emission bands. It was got an excellent agreement with experimental high resolution $L_{2,3}$ spectra by including both MND singularities and auger tail effects. In contrast, not MND, nor the auger effect do not influence on the Mg and Al K emission bands shape. The reasons of this difference are discussed in the report.

Of considerable interest is a discovered effect of asymmetry in MND singularity manifestation in the carbon K X-Ray emission band and K absorption edge of graphene. In the range of K absorption edge MND contribution is very prominent [4], but in the emission band is rather weak. A reason of this effect may be a high electron mobility at Fermi level (Dirac point) as discussed in the report.

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Charge Transfer Transition Contribution in X-ray Emission Bands of Mg and Al Metals and their Oxides

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ABSTRACT

In this work we present the density functional method using the pseudopotential approximation (CASTEP software package [1]) to calculate a form of X-ray Emission Spectra (XES) of metallic Mg, Al and their oxides. It is well known crystal pseudo-wave functions significant differ from exact all-electron orbitals in the region of atomic cores; therefore, to calculate the probabilities of X-ray transitions, ones need to reconstruct all-electron wave-function. For this purpose we used two methodics of reconstruction. The first procedure is based on the transformation that was proposed in [2, 3]. We term this method “PAW-reconstruction” (PAWR) according to the Projector Augmented Wave (PAW) approximation [2]. The second reconstruction procedure is based on projecting the crystal pseudo-orbitals (PSO) onto the space of atomic PSO and replacing the atomic PSO with atomic all-electron wave-function. This method was called “projected Bloch functions reconstruction” (PBFR). RFBR approach makes possible to separate XES into individual partial and local contributions. This separation enables us to single out the contributions of direct (intra-atomic) transitions and of so-called cross-over (charge-transfer) transitions into emission band.

In this way we tracked the redistribution of the intra-atomic and charge-transfer contributions to the K and $L_{2,3}$ emission band of Mg and Al in the crystals: metallic Mg and magnesium oxide MgO, metallic Al and aluminum oxide Al_2O_3. It was found charge-transfer transitions makes significant contribution into $L_{2,3}$ emission band of oxides and small contribution into XES of metallic systems. We have shown an unexpectedly large partial d- intensity of the $L_{2,3}$ XES of MgO is caused by cross-over transition of electrons, centered at oxygen sites.

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L_3/L_2 X-ray Emission Bands Branching Ratio Anomaly in Mg and Al Metals

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ABSTRACT

We have examined well known since 1930-th Mg and Al metals $L_{2,3}$ ultra soft X-Ray emission bands (USXEB) [1]. In 1960-th a discussion on origin of the sharp peaks near Fermi edges in metal $L_{2,3}$ absorption spectra and USXEB has started [2-4]. It leaded to a declaration that the dynamical screening of 2p holes by metal valence electrons is responsible for an appearance of the so called MND singularities both in absorption and emission edges. In [2] deviation of the intensity ratio of L_3/L_2 spin-doublet in absorption from the expected 2:1 was treated by introducing electron-hole exchange scattering, or spin-flip scattering in MND model. In $L_{2,3}$ USXEB L_3/L_2 branching ratios were not discussed because of a large destroyed influence of the selfabsorption effect on them. In our work we try to overcome this trouble. Electron beam excited Mg and Al metal $L_{2,3}$ USXEB were registered with resolution about 0.05 eV for the beam energy E_0 varied in the range 0.8…4.5 KeV. The dependencies of measured $L_{2,3}/L_2$ intensity ratios on E_0 were extrapolated to $E_0 = 0$ (absence of selfabsorption). With about 10% accuracy L_3/L_2 intensity ratios were found to be 3,8:1 for Mg and 2,8:1 for Al, much larger than in absorption spectra and in the simple $L_{2,3}$ spin-orbit splitting model. In Al, there are known an absolute values of $L_{2,3}$ absorption [5], we have successfully checked our extrapolation using Borovsky-Rydnik model of X-ray emission generation in solids under electron bombardment [6].

Possible reasons of the so strong effect are discussed in the report.

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Geometric and Electronic Structures of Hydrogen-bonded Networks Comprising Planar Molecules on Graphite (0001)

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ABSTRACT

Planar organic molecules capable of hydrogen bond formation in two or three directions are useful as building blocks of an extraordinarily thin (0.4 nm) network structure under ultrahigh vacuum. One can prepare such an extrathin network utilizing the self-assembly of the planar molecules in a physisorbed monolayer on a graphite (0001) surface [1-3]. If the networked monolayers are piled up layer by layer, new nanomaterials with thickness and composition controllable at the atomic lever will be obtained. The situation is in a striking contrast to the case of introducing new covalent bonds among chainlike molecules laid flat and arranged to form columnar structures on graphite: meticulous attention must be paid to polymerization, isomerization, and superposition conditions [4-7].

Unlike studies focused on molecular arrangement [2,3], we have tried to observe changes in the electronic structures upon the formation of H-bonded networks. It is not easy because the building block has complicated (electronic) structure although changes in the molecular orientation can be readily detected by metastable atom electron spectroscopy (MAES) [1]. We have constructed in this study a peculiar network of triamide with three-fold symmetry by annealing an amorphous monolayer prepared on a cooled graphite substrate. Using MAES, UPS, STM, and the first-principles calculations, we have revealed the molecular aggregation and succeeded in observing the modification of the electronic structures. Our network does not have the known packing patterns of similar molecules: one side of each trimer triangle (the fundamental unit of the network) is linearly connected to that of the neighbor sharing the apex to constitute a racklike structure. Two parallel racks with facing dents form a double rack structure; they are partially overlapped with each other and slightly tilted to the substrate surface. The double racks are arranged parallel to cover the surface. The STM topographs display the trimer triangle and the rack structure, the MAE spectra indicate the slightly tilted orientation of the rack as well as a complete coverage of the surface, and the difference UP spectra exhibit features corresponding to the difference between calculated density of states for an infinite rack and that for an isolated molecule.

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Possible Semiconductor-metal Transition at the Interface between ZnO and Organic Thin Film

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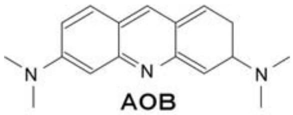
ABSTRACT



ZnO is a wide-band-gap n-type semiconductor with the Fermi level (E_F) lying just below the conduction band minimum (CBM). Electron-doping of the surface by chemical modification by hydrogen (H) adsorption induces significant downward band bending so that the CBM is lowered below E_F and induces surface metallization by forming two-dimensional electron gas [1,2]. Metallization of the ZnO surfaces is also achieved by adsorption of water and methanol, both of which adsorb on the surfaces dissociatively to form adsorbed H acting as an electron donor [1]. Actually, H is a very efficient electron donor on some n-type semiconductors such as SiC [3], $SrTiO_3$ [4], and ZnO. In search of organic molecules that induce metallization of oxide surfaces, we first examined tetrathiafulvalene (TTF) [5] because TTF is a prototype of an electron donor molecule in organic charge-transfer salts. It is found, however, that TTF cannot donate electrons to ZnO but withdraws them from ZnO [5].

In the present study, we have investigated the interaction between ZnO and acridine orange base (AOB), which is proved to be an electron donor on the Au surface [6], by photoelectron spectroscopy (PES). The measurements of the valence band spectra reveal that AOB induces downward bending of the ZnO band on both the Zn-terminated (0001) and O-terminated (000-1) surfaces, while the position of the band is almost intact on the (10-10) surface (Fig. 1). This means that AOB acts as an electron donor on the (0001) and (000-1) surfaces, whereas charge transfer between AOB and the (10-10) surface is not operative. From the degree of band bending and the valence band maximum positions, the CBM on ZnO(0001) is found to be shifted from above E_F to below it by AOB adsorption. The CBM is determined at 0.08 eV below E_F after AOB adsorption, implying that the AOB-covered (0001) surface is possibly in a metallic nature. This is the first organic molecule suggested to induce metallization of the oxide surface.

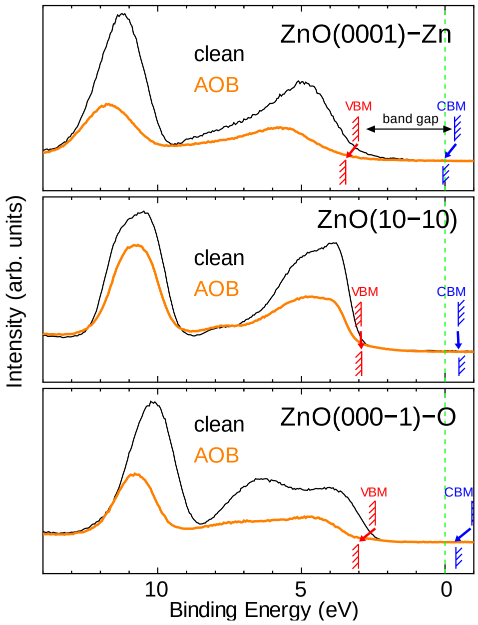


Fig. 1 Normal emission spectra of the valence band region of the clean and AOB-adsorbed ZnO surfaces.

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Investigation of Undoped, Nickel- and Cobalt-doped TiO_2 Thin Films Prepared by the Sol-gel Method

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ABSTRACT

During the last two decades TiO_2 has received great attention due to the many advanced applications in photocatalysis, solar cells, gas sensors, functional coatings etc. For practical applications the sol-gel method is widely used for preparation of TiO_2 films, since it has several advantages over other fabrication techniques [1]. In addition to pure TiO_2 the interest has steadily grown to study metal-ion doped TiO_2 [2,3]. The key idea here is to modify the electronic structure of the material by doping, which would effectively shrink the band gap. This is important for applications using sunlight. Previously it is reported, that nickel and cobalt doping of TiO_2 has improved its catalytic properties and the absorption edge has shifted towards to visible light maximum of the solar radiation [4,5].

In this study thin undoped, nickel- and cobalt-doped TiO_2 films have been prepared on Si(100) and quartz substrate using the sol-gel deposition and annealed in air at 450 to 1050 °C. Several experimental techniques (AFM, XRD, Raman spectroscopy, XRR, EDX, XPS, XAS, UV-VIS spectroscopy) have been used to characterize these films. Furthermore the degree of light-induced hydrophilicity was estimated by measuring the contact angle of a water droplet on the film.

It was found that cobalt (or nickel) addition to TiO_2 led to the formation of a rougher surface as compared to undoped TiO_2. On the basis of XRD it was concluded that cobalt (or nickel) addition promotes an anatase-to-rutile phase transition. $CoTiO_3$ (or $NiTiO_3$) were observed in the Raman spectra of cobalt- (or nickel) doped TiO_2 films. The EDX measurements showed that the annealing of a cobalt- (or nickel) containing TiO_2 films causes a formation of regions with increased Ni and Co concentrations. An analysis of the ratio of Ti 2p and Co 2p (or Ti 2p and Ni 2p) XPS spectral band areas showed that the concentration of cobalt (or nickel) compounds increased on the surface during annealing. Cobalt (or nickel) in films was in 2+ and titanium in 4+ oxidation state, as confirmed by XPS and XAS measurements. Cobalt and nickel addition induced a red shift in UV-Vis absorption spectra. Good light-induced hydrophilicity was effectively achieved in case of undoped and nickel-containing TiO_2 films.

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Surface Photovoltage at Si (001)/SiO$_2$ and Water Saturated Si (001)-2x 1 surface: Laser Pump-Synchrotron Radiation Probe Photoemission Spectroscopy

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ABSTRACT

The photovoltaic effect is of central importance for many semiconductor devices which convert light to electricity, including photodetectors, solar and photoelectrochemical cells. Whereas this effect is theoretically and experimentally well investigated, the related surface photovoltaic effect is less understood. Especially its fast dynamic behaviour which is coupled to the charge carrier recombination rates, often expressed in terms of surface recombination velocity, which is important for the characterization of semiconducting materials and crucial for the design and analysis of semiconductor devices[1,2]. Therefore the understanding of surface effects and their dynamics plays an important role for the comprehension of carriers lifetimes. At semiconductor surface localized states within the band gap pin the Fermi Level[3]. The charge transfer to the surface leads to a band bending within a space charge layer (SCL) typically from 5 to 100 nm thickness depending on the doping level. Illumination with photons of energy higher than the band gap will generate Electron Hole Pairs (EHPs) in both the space charge region and in the substrate. The EHPs generated in the SCL are very quickly separated by the electric field with the minority charge drifting to the surface. Those minority carriers that drift to the surface establish a surface potential or surface photovoltage (SPV) that acts to counter the band bending[,4,5].

In this work we present a combined laser and synchrotron radiation pump–probe study, done at TEMPO beamline (Synchrotron Soleil-France), of the Surface photovoltage (SPV) decay dynamics at thin silicon oxides on Si(001) surfaces (n and p doped) and on water saturated p-doped Si (001)-2 x 1.

At TEMPO beamline we are able to synchronize the laser (fs pulsed RegA9000 laser by Coherent variable High repetition-rate, up to 300 kHz) and the synchrotron radiation pulses in order to have time dependent spectra with the resolution of the synchrotron bunch (50 ps) [6]. We worked in the hybrid mode filling of the machine. This type of operation mode is very useful, because it allows to explore at the same time short time scale (analyzing the isolated bunch) and long time scale (analyzing the full filled part).

We see that for the different doping the SPV acts in order to reduce the band bending, the relaxation time strictly depends on the doping that means on the type of the minority charges involved in the process, but also on the different termination of the surface. The amplitude of the SPV effect depends on the laser intensity[4,7].

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Isolated Silicon Dangling Bonds (IDBs) on Water Saturate Si (001)-2 x 1 Surface

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ABSTRACT

On clean Si (001)-2 x 1, water dissociates into H and OH fragments that decorate the silicon dangling bonds left by surface dimerization. In fact two reaction channels, the intrarow and the on-dimer, are opened with equal probability[1]. The competition between these two channels explains why, at surface saturation, isolated dangling bonds (IDB) in ·Si—SiOH or ·Si—SiH units, are observed by STM as bright features in occupied state images, contrasting with the lower "density-of-state" imprint of the silicon atoms capped with OH or H [2]. An isolated dangling bond is born by a *trivalent Silicon*[3] (similar, but not identical, to the P_b defects at the $Si(111)/SiO_2$ interface), it presents three charge states, denoted D^+, D^0**,** D^- (corresponding to **zero, one or two** electrons in the dangling-bond orbital), depending on the position of the Fermi energy with respect to the charge-transition levels, and a positive Anderson Correlation Energy U (lattice relaxation energy less than electron-electron repulsion)[4,5]. The magnitude and the sign of the charge of the defect are determined by the substrate doping[6,7].

Time-resolved X-ray photoelectron spectroscopy at TEMPO beamline enables the monitoring of the electronic structure (core-level peak position and intensity, measurement of secondary electron cut-offs) while dosing the surface with water.

In this work we examine the role of substrate doping and water vapour pressure on the adsorption kinetics. We also examine in detail the positioning of the surface Fermi level within the gap and the charge state of isolated dangling bonds (IDB_S) left at saturation coverage as a function of doping.

We see that while the initial sticking coefficient S_0 depends on pressure, the different doping types of the substrate do not affect the adsorption. Using Si 2p core-level X-ray photoelectron spectroscopy we have measured the band bending at the surface of water-saturated Si (001)-2 x 1 as a function of silicon doping. We have determined the exact position at the surface of the Fermi level and the range of variation of the charge transition level. We have estimated the maximum value of the Anderson Correlation Energy $U < 0.4$ eV (less than 0.6 eV the value found in the case of P_b defect on $Si(111)/SiO_2$interface[4]). From the band bending we have inferred the macroscopic surface charge density of the surface. These results are in excellent accord with first microscopic view, provided by dual-bias scanning tunneling microscopy (done at the Soleil Surface Laboratory), of water-saturated heavily n-doped Si (001)-2 x 1 surface ($N_D \sim 4\times10^{18}$ cm^{-3}) showing that the isolated silicon dangling bonds ($\sim1.2\times10^{-2}$ defects per Si atom) bear a negative charge[8]. Then we plan other STM/STS measurements in order to localize/determine the charge character of the IDB as a function of doping.

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Nitrogen-functionalized Graphene Nano-flakes (GNFs:N): Tunable Photoluminescence and Electronic Structures

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ABSTRACT

This study investigates the strong photoluminescence (PL) and x-ray excited optical luminescence observed in nitrogen-functionalized two dimensional graphene nano-flakes (GNFs:N), which arise from the significantly enhanced density of states in the region of π states and the gap between π and π^*states. The increase in the number of the sp^2 clusters in the form of pyridine-like N-C, graphite-N-like and the C=O bonding, the resonant energy transfer from the N and C atoms to the sp^2 clusters was found to be responsible for the blue-shift and the enhancement of the main PL emission feature. The enhanced PL is strongly related to the induced changes of the electronic structures and bonding properties, which were revealed by the x-ray absorption near-edge structure, x-ray emission spectroscopy and resonance inelastic x-ray scattering. The study demonstrates that PL emission can be tailored through appropriate tuning of the nitrogen and oxygen contents in GNFs, and pave the way for new optoelectronic devices.

Laser Fields at Flat Interfaces: Plasmon Resonances in PES of Aluminium and Silver Low Index Surfaces

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ABSTRACT

In the long wave length region (LWLR, $\lambda > 12.4$ nm) the UV photoelectron spectrum of plain metals and quantum wells displays plasmon resonances. For a p or transverse magnetic linearlypolarized photon these resonance phenomena are attributed to the surface photoelectric effect.

Results in agreement with the experiment are obtained if a theoretical model explicitly calculates the laser fields function of the penetration coordinate. The vector potential from electron densitycoupled integro-differential equations (VPED-CIDE) model [1] obtain this laser fields as a solution of the Ampere-Maxwell classical and material equations in the real space and the temporal gauge (U=0). These laser fields are used in the calculations of the electron escaping probability from the power density absorption, the photoionization cross section, the reectance, Feybelman's parameter $d^{\perp}$and the induced by the laser electron density

We study low index surfaces (001) and (111) aluminium [2] in the region 10-30 eV and of silver in the region 3-6.5 eV. Our calculations favorably compare with the experimental angle and energy resolved photoelectron yield (AERPY) spectrum of Levinson et al. [3] for Al(001) and of Barman et al. [4] for Al(111) surfaces. For Ag(001) and Ag(111) our theoretical spectra are in agreement with the AERPY spectrum of Barman et al. [5]. Analysis in terms of the induced by the laser electron density and of the Feibelman's parameter $d^{\perp}$permits to identify the nature of the plasmon resonances.

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Defect Exciton Induced Multiple Auger Decay

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ABSTRACT

We study the resonant Photoemission on the O1s and C1s edge of oxides (TiO_2, Fe_2O_3) and thin carbon films (HOPG, Graphene Flakes and Mono Layer Graphene) with resonant photoemission. The X-Ray based measurements were done at the U49/2-PGM2 beam line at BESSYII in Berlin.

We find in both systems a characteristic feature in the Auger decay at resonance. It proceeds with a characteristic slope of 67.5° in terms of a $E_{bind}(\hbar\omega)$ diagram in the vicinity of the first resonance for oxides or in the π*-band of carbon films [1]. This behavior is interpreted as a multiple Auger decay in which the resonant excited electron is trapped in a defect excitonic state that leads to a 3h final state. The trapping of the resonantly excited electron enables a valence (not atomic) electron to fill the primary core hole. The resonantly excited electron decays later and its energy is determined by the screening of the valence holes and no longer of the primary core hole. For this process we present a model where we discuss the individual steps and their lifetime. The number of final state holes (n) causes a change in the resonance profile. We deduce that even more complicated multiple Auger combinations might be identified by this method. Additionally we give evidence about the origin of the characteristic feature at 284eV in Graphene.

We discuss the main requirements of the multiple hole Auger decay, especially the nature of the trap state in detail. For oxides it is related to a (O2p-Metall3d) Charge-Transfer state. For TiO_2 we come up with a detailed band scheme in which the electronic gap is smeared out by the existence of CT-oxides close to the CBM. As a result these states form an optical gap. For carbon based thin films we discuss the formation of bound excitonic defect states but also consider the existence of structural defects (e.g. kinks, pits, steps etc.). Defects states, not visible in the core level spectra, can still be identified in the resPES diagram and show the high sensitivity of our method.

From a combined analysis of the core level and XAS spectra we can give a quantitative estimation about the defect density in carbon thin films. With the appearance of the three-hole process we are able to identify localized states within the π*-band regime either localized in the band gap at the M-point or even at the K-point.

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Ultrafast Charge Transfer in Poly(thiophene) Probed by Resonant Auger Spectroscopy

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ABSTRACT

Charge transfer dynamics is a topic of highly importance in fundamental and in many applied areas like femtochemistry, surface photochemistry, molecular electronics, solar energy, and so on [1,2]. Besides pump-probe optical experiments, Auger decay spectra following core excitation emerges as an alternative with major advantages. Firstly, because the core hole lifetime probed by core level spectroscopy can be used as a fast internal clock and in so far very low timescales can be achieved, the so-called core hole clock (CHC) method [2-6]. Secondly, because of the inherent atomic specificity of core levels. For some applications, the surface sensitivity of low energy electrons adds up.

Ultrafast electron transfer dynamics in the low-femtosecond regime was evaluated for poly(thiophene) by resonant Auger spectroscopy (RAS) using the core-hole clock method. Sulfur $KL_{2,3}L_{2,3}$ Auger decay spectra were measured as a function of the photon energy. Remarkable changes developed by tuning the photon energy along the sulphur 1s edge, depending on the core excited states. It was possible to disentangle transitions to π^*, σ^* [6] and Rydberg states by RAS not resolved by XAS. Competing Raman and Auger channels could be separated and charge transfer times derived.

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Electron Spectroscopy Investigation of Graphene Oxide Thermal Reduction

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ABSTRACT

Graphene oxide (GO)[1] is emerging as a versatile material for applications in nanoscience and nanotechnology because of its easier production and processability as well as simple chemical functionalization respect to graphene. The electrical and the optical properties of GO are easily controlled by reductive processes.[2] The annealing in ultra high vacuum (UHV) is an effective free-contaminant process to obtain the progressive elimination of oxygen from the single GO sheet.[3]

In this paper we present the evolution of the electronic structure of GO single sheets as a function of the temperature in the range 150 – 750 °C in UHV. We studied a GO layer corresponding to a partial coverage of 90% of single sheets spin-coated from aqueous solutions on single crystal silicon substrate covered by a silicon oxide film. The electronic structure of the system under consideration is studied by XPS, UPS and EELS. We observe several spectroscopic changes as a function of the temperature. In particular we observe, after annealing at 750 °C, the presence of typical graphite features in the EELS spectrum and the appearance of electronic state at Fermi level in the UPS spectrum indication of the metallization of the system. The reduction of the GO layer and the formation of graphene-like layer is also testified by intensity variation of the system stretching modes.

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Rashba Spins with Peculiar Scattering Processes

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ABSTRACT

In this paper, we present a Rashba system with spin-polarized metallic surface bands on a semiconducting substrate, in which backscattering of the Rashba spins is considerably suppressed, and even disappears in a special condition. This peculiar scattering process originates from a combination of the Rashba effect [1] and the valley physics [2] of the system. The Rashba effect is a novel exotic low-dimensional solid-state property that produces a spin-polarized two-dimensional electron gas from a combined effect of spin-orbit interaction and structural inversion asymmetry even for nonmagnetic materials, and it is the key factor for operating a spin field-effect transistor [3] that is one of the most prominent semiconductor spintronics devices. In an ordinary Rashba system, however, the Fermi surface shows isotropic vortical spin structures with spin polarization vectors lying in the surface plane, which lead to a high-probability of electron spin backscattering and thus lower the efficiency of the electron spin current. By using direct and inverse spin- and angle-resolved photoelectron spectroscopies, we have measured the Rashba spin bands of an electron-doped Tl/Si(111)-(1x1) surface and a Tl/Si(110)-(1x1) surface. In the former system, spin-polarized electron valleys with peculiar Rashba spins pointing along the surface normal direction were observed at the K and K' points of the surface Brillouin zone. The opposite spin direction at these points indicates that the valleys are polarized and thus the backscattering of electron spin with a non-magnetic impurity is considerably suppressed in this system. Regarding the latter system, we observed an extraordinary quasi-one dimensional Rashba splitting that would also improve the efficiency of the spin current originating from its peculiar spin structure. We will also discuss the origins of these peculiar spin structures based on the symmetries of the surfaces. Furthermore, since the present system is formed on silicon substrates, the present results would provide not only a scientific interest but also a significant step toward the readily realisation of silicon spintronics devices with high-efficiency.

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Electronic Structure of Pb-Absorbed Ge(001) by Angle Resolved Photoelectron Spectroscopy

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ABSTRACT

Pb adsorption on semiconductor surface induces interesting phenomena such as formation of the surface metallic states and induction of band bending. In the case of Pb/Si(111)[1] and Pb/Si(001)[2], it was revealed that valence subband was formed in space charge layer because strong band bending was induced by Pb adsorption. In the case of the Pb/Ge(111), surface resonance band[3] was reported. In Pb-absorbed Ge(001) system, recently, Pb QWS (Quantum Well States)was observed by ARPES because of layer by layer Pb growth on Ge(001) at low temperature[4]. At room temperature or at the higher temperature, it was revealed by STM and LEED study that many superstructures were formed depending on the Pb coverage[5].

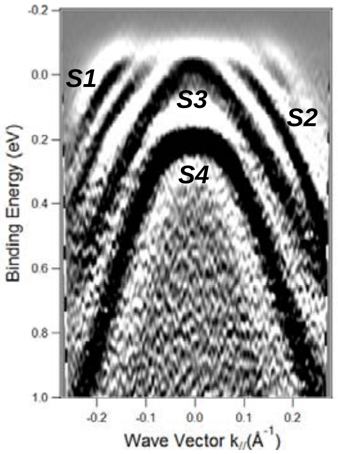

Fig. 1 ARPES data of Pb/Ge(001) near $\bar{\Gamma}$ point ("A stage").

In present study, we studied electronic structure of Pb/Ge(001) by ARPES. Pb coverage was between 1ML and 6ML. In the RHEED pattern, Pb/Ge(001) 6×2 superstructure was observed around 1ML (in "A stage"). Beyond this coverage, additional spots appeared ("B stage"). With further deposition, spots in the RHEED pattern Pb 1×1 appeared ("C stage"). The RHEED patterns indicate that Pb growth on Ge(001) was S-K mode at room temperature. The ARPES result at A stage shows four holelike bands (S1-S4) near $\bar{\Gamma}$ (Fig. 1). Two of them cross Fermi energy. The Fermi number of these metallic bands are ±0.17 [$Å^{-1}$] (S1) and ±0.11 [$Å^{-1}$](S2). These bands were observed in the different Pb coverage (A, B and C stage) despite of the formation of additional surface structures. The energy separation of the bands S3 and S4 did not change with increasing Pb coverage. Therefore, origins of these bands were not Pb QWS but rather Ge band edge. Effective masses of these bands were much heavier than those by *k* *p* method (HH ; $0.38m_0$, LH ; $0.041m_0$, SO ; $0.075m_0$).

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Functionalization of Carbon Copper-containing Nanotubes by Nitrogen Atoms

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ABSTRACT

An effective method for improving the properties of materials is the modification of materials by nanostructures. The nanostructures surface has low reactivity. Therefore, the method of the surface functionalization with sp-elements' groups is used wherein the groups of sp-elements forming the covalent bond with atoms on the nanostructures surface act as binding agents between the nanostructures surface and a base material.

The objective of the present paper is the investigations of the mechanism of the functionalization of the carbon metal-containing nanostructure surfaces, and the obtaining of stable complexes of nanomaterial and polyethylene polyamide.

The functionalization of carbon copper-containing nanotubes by nitrogen atoms using the mechanical activation method in polyethylene polyamide, the influence of the functionalization on the formation of stable complexes and the chemical bond in these complexes have been studied.

The mechanism of the formation of the chemical bond between the atoms of carbon copper-containing nanostructures and nitrogen has been studied by the x-ray photoelectron spectroscopy method. The investigation has been conducted on an x-ray electron magnetic spectrometer which has a number of advantages over electrostatic spectrometers.

The analysis of the C1s and N1s spectra show the presence of the covalent bond C-N(H) between the carbon atoms of carbon copper-containing nanotubes and the amine nitrogen of polyethylene polyamide, which indicates the formation of stable complexes.

It can be concluded that during modification the bond of the atoms of nanostructures with the material atoms is realized due to the nitrogen atoms. The formation of the covalence chemical bond of the atoms of a functional group and nanostructures depends on the following factors: the electronegativity of atoms and the closeness of covalent radii. The bond of metal atoms (Cu) and nitrogen atoms is not formed in the system.

Hard X-ray Photoemission Spectroscopy of Quasi-One-Dimensional $BaVS_3$

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ABSTRACT

Quasi-one-dimensional $BaVS_3$ with a V-chain along the c-axis, exhibits metal ($T > T_{MI}$) - insulator ($T < T_{MI}$) transition (MIT) at T_{MI} = 70 K. Several models for MIT have been proposed, such as the charge density wave (CDW) instability, Mott transition, and orbital ordering. It is considered that both the delocalized a_{1g} and localized e_g^π electrons in the V ion ($3d^1$) contribute to physics of $BaVS_3$. Recently, we have carried out the polarization-dependent angle-resolved photoemission spectroscopy on $BaVS_3$ at $h\nu$=57 eV, and succeeded in the selective observation of the a_{1g} and e_g^π band dispersions [1]. The a_{1g}-derived density of states (DOS) at the Fermi level (E_F) abruptly drops between 150 and 120 K much higher than T_{MI} due to the one-dimensional property, while the e_g^π DOS at E_F monotonically decreases and reaches zero just at T_{MI}. The energy shift associated with an energy-gap open was not observed. In this paper, we report the hard x-ray photoemission spectra (HAXPES spectra) of $BaVS_3$ taken at $h\nu$=5.95 keV, which is sensitive to bulk compared with the spectra at $h\nu$=57 eV.

The HAXPES spectra in the vicinity of E_F clearly exhibited a sharp change across T_{MI}, in contrast to the spectra at $h\nu$=57 eV. The leading edge of the spectra is shifted toward higher-binding energy side below T_{MI}, and the energy gap is estimated to be about 70 meV from the shift, which is roughly consistent with that of 50 meV derived form the electrical resistivity measurements [2]. The Ba $3d_{5/2}$ and S 1s core-level spectra also showed the temperature dependence. With decreasing temperature, the peak position is shifted to the higher-binding energy side and the peak width continuously decreases still across T_{MI}. We analyzed the Ba $3d_{5/2}$ and S 1s spectra based on the Debye model [3], and obtained the Debye temperature of Θ_D~300 K from both spectra. This value is nearly consistent with that derived from the specific heat measurements (Θ_D~200 K) [4] and the spectral changes are interpreted by the thermal effect.

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A Soft X-ray Emission Study on Oxide Glasses

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ABSTRACT

Silica (SiO_2) is a typical oxide glass that has a network structure made of fourfold Si and twofold O atoms. Its structure is well understood even for the partial structure by a combination of high-energy x-ray, neutron diffraction, and reverse Monte Carlo modeling [1]. Another typical oxide glass is borate glass (B_2O_3), in which threefold B atoms and twofold O atoms form a continuous network and the boroxol ring (B_3O_3) is the main building brock [2] like crystalline B_2O_3. The well-known Pyrex glass is a mixture of these glasses.

Investigations on electronic structures of these oxide glasses are very difficult because they are highly insulating and thus usual photoemission studies on the bulk glasses are impossible. On the other hand, knowledge of electronic density of states (DOS), in particular O 2p partials, can confirm the above structural results because the O 2p states may be highly affected by the bond angle distributions around the O atoms. From the above structural work, Si-O-Si bond angle is estimated to be about 150° and B-O-B about 120°.

Soft x-ray emission spectroscopy (SXES) is a powerful tool for obtaining partial DOSs for insulating materials [3-5]. Although some groups already carried out SXES measurements on these oxide glasses [6-8], the data available are mainly partial DOSs of cations, and no systematic results of the O 2p partials were obtained.

We have recently performed O 1s-2p resonant SXES measurement at the beamline BL2C of the KEK-PF on SiO_2, B_2O_3, and Pyrex glasses by varying incident photon energies. In this presentation, we report the obtained O 2p partial DOS in the valence bands, and discuss the relation between the features of these DOSs and the bond angle distributions around the O atoms in these oxide glasses in detail.

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The Electronic Structure of Ga2O3 and In2O3 Transparent Conductive Oxides

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ABSTRACT

We use resonant photoemission spectroscopy to study the valence and conduction band (VB / CB) partial density of states in Ga2O3 and In2O3 single crystals cleaved in UHV. For these transparent conductive oxides (TCO) we distinguish between covalent contributions of O2p and Ga4s4p (In5s5p) states. In addition there are localized states which are attributed to polaronic, oxygen based intrinsic defects and are not related to oxygen vacancies. They form a continuous band which appears throughout the electronic band gap and which is identified by a Fano type anti-resonant behavior of the valence electrons when passing the O1s resonance. In addition we identify O2p-In5s5p as well as O2p-Ga4s4p charge transfer (CT) states. These CT states are identified by a characteristic multiple Auger decay which we find at the O1s edge. They are localized within the electronic gap, appear as a band around the Fermi energy and are attributed to cause the n-type electronic behavior. Also, the CT band defines an optical gap which is smaller than the covalent band gap.

The CT-bands are found in both, the Ga2O3 and In2O3 system. They appear well separated in energy from the empty CB states. We derive a band scheme and define both, the optical and the electronic band gap. Our findings are in excellent agreement with data from optical and cathode-luminescence studies. We propose a model in which the transport properties of these prototype TCO materials are based on the interplay of the polaronic and the CT states.

MsSpec-1.0 : A Multiple-scattering Package for Spectroscopies using Electrons to Probe Materials

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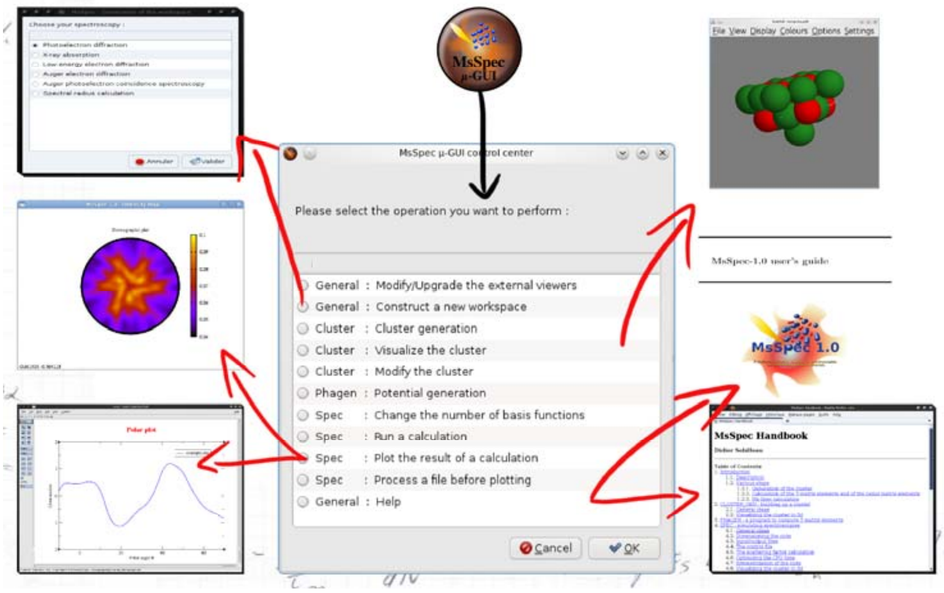
ABSTRACT

We present a package to compute the cross-section of photoelectron diffraction (PED), Auger electron diffraction (AED), X-ray absorption (XAS), low energy electron diffraction (LEED) and Auger photoelectron coincidence spectroscopy (APECS). It is based on multiple scattering theory [1]. This package allows to cover kinetic energies ranging from 0 to 1.5 keV, due to the use of three different algorithms for the evaluation of the multiple scattering. A light Graphical User Interface (GUI) called µ-GUI is also provided. The package makes use of free software to plot and visualise the results [2].



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Determination of an Optimal Modifier of Protein for Improving its Stability using the X-ray Photoelectron Spectroscopy Method

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ABSTRACT

The modification of the functional groups in the composition of a protein macromolecule is one of the trends in the development of biotechnology used in pharmaceutics.

The main investigation tasks are the x-ray photoelectron study of the regularities of the formation of an electron energy spectrum, the determination of the chemical bond between atoms of protein and a modifier, which would allow to determine the direction in the investigation of an increase in the protein stability and to chose an optimal modifier for protein. The study has been conducted by the x-ray photoelectron spectroscopy method on an x-ray electron magnetic spectrometer [1], which has a number of advantages in comparison with electrostatic x-ray electron spectrometers.

The protein native form and the modified protein form have been investigated. The latter was modified by carbon metal-containing nanotubes with the additions of functional sp-groups for increasing the activity of the interaction of nanostructures with the environment, by superdispersed NiO powder and by vinyl pyrrolidone - acrolein diacetal copolymer at the temperature varying from room temperature to 623 K. The method was developed for the determination of the temperature of the protein decomposition and the criteria of the protein decomposition were established. When protein is modified by carbon copper-containing nanotubes, a strong covalent bond of atoms of N-H amides with carbon atoms (C-NH) is formed leading to an increase in thermal stability of modified protein in the temperature range of 523 – 573 K.

In addition to the temperature influence on the oxidation decomposition of protein, the presence of metal catalysts (Ni, NiO) in protein results in oxidation and damage of protein because in contrast to carbon copper-containing nanotubes, the modification of protein by carbon nickel-containing nanotubes leads to the damage of protein.

The dependence of the thermal stability to 473 K of protein modified with vinyl pyrrolidone - acrolein diacetal copolymer on its content in the mixture is found. The growth of the temperature of stabilization with growing content of vinyl pyrrolidone - acrolein diacetal copolymer is shown.

Based on the results obtained, the recommendations are given concerning the modification of proteins for increasing their stability. A model is offered for protein stabilization on the basis of the formation of strong hybridized chemical bond between atoms of protein and a modifier.

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X-ray study of the Functionalizing of Carbon Metal-containing Nanotubes with Phosphorus Atoms

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ABSTRACT

The unique properties of carbon metal-containing nanostructures provide various possibilities for their applications. To improve the material properties, the modification of materials with nanostructures can be used. Since the surface of nanostructures has low reactivity as a binding agent between the nanostructure surface and a material, the functionalization of the nanostructure surface is used, i.e. the addition in the surface of certain chemical groups of sp-elements forming a covalent bond with atoms on the nanostructure surface. In addition, functionalization creates additional conditions for improving nanostructure properties.

In the present paper, the functionalization of carbon metal-containing nanotubes (Me: Cu, Ni, Fe) with phosphorus atoms (ammonium polyphosphate) is studied. The investigation of the influence of the ammonium polyphosphate functionalization on the metal magnetic moment has been conducted by the method of x-ray photoelectron spectroscopy on an x-ray electron magnetic spectrometer [1] which has a number of advantages in comparison with electrostatic x-ray electron spectrometers.

The formation of the covalent (hybridized) bond between atoms of carbon metal-containing nanostructures and sp-elements of functional groups has been investigated by studying X-ray photoelectron Me3s-spectra, in which the parameters of the multiplet splitting correlate with the number of noncompensated d electrons of metal atoms and the metal spin magnetic moment [2]. This model has been used for studying the change of the atomic magnetic moment on the Fe, Ni, Cu atoms of carbon metal-containing nanotubes during the functionalizing with chemical groups containing P at different P concentration.

In the studied functionalized carbon metal-containing nanotubes, the atomic magnetic moment of the Fe, Ni and Cu metals increases in comparison with the atomic magnetic moment in ordinary carbon metal-containing nanotubes, i.e., the number of noncompensated d-electrons increases; consequently, the nearest surrounding of metal atoms and their chemical bond change.

Thus, in carbon metal-containing nanotubes, the bond between phosphorus atoms and atoms of the nanostructures is formed via metal atoms and not carbon because the degree of the covalence of Me-P is higher than that of Me-C [3]. The presence of the phosphorus atoms does not let carbon atoms bind with metal, which results in the increasing activity of nanostructure surface and increasing probability of the formation of the chemical bond with the material atoms during the material modification with nanostructures.

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Angle-resolved Photoemission Study of Heusler-type $Fe_{2-x}V_{1+x}Al$

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ABSTRACT

We have investigated the electronic states of Heusler($L2_1$)-type alloys $Fe_{2-x}V_{1+x}Al$ by soft X-ray angle-resolved photoelectron spectroscopy (ARPES) as well as angle-integrated one (AIPES). Thermoelectric powers of Fe_2VAl-based alloys are much enhanced on small off-stoichiometric concentration or doping of the fourth element. The enhancement on doping has been ascribed to a rigid band-like behavior with a sharp pseudogap across the Fermi energy E_F [1], while large thermoelectric power observed in $Fe_{2-x}V_{1+x}Al$ cannot be explained in terms of the rigid band model [2]. Fe_2VAl shows unusual transport properties, reminiscent of the heavy fermion system [3]. Theoretical studies [4,5] suggest that the unusual properties may be caused by magnetic clusters formed around anti-site defects, i.e. the excess Fe or V occupying at the respective V or Fe site in the $L2_1$ structure, their *d* states appearing within the pseudogap. This may also induce the peculiar thermoelectric properties [6]. Thus it is important to clarify their origins not only for scientific interest but for application.

ARPES and AIPES measurements were performed at BL23SU and BL27SU, respectively, of SPring-8 at the temperature of ~20 K with a total energy resolution of ~0.15 eV. Single crystalline specimens were prepared by the Czochralski pulling method in a tetra-arc furnace [2] and polycrystalline specimens for AIPES by arc-melting and annealing [3,6]. Their clean surfaces were obtained by in situ fracturing them at low temperatures.

For Fe-rich and V-rich $Fe_{2-x}V_{1+x}Al$, newly emerging bands are observed around the binding energies E_B of 0.3 and 0.5 eV, respectively, in AIPES spectra. In off-normal and normal ARPES, $Fe_{2.05}V_{0.95}Al$ shows a weakly dispersive band at $E_B \sim 0.3$ eV in the Γ-X direction and an almost dispersion-less one around 0.3 eV in a gap of dispersive bulk bands in the Γ-L direction. We attribute the band observed at ~0.3 eV to the anti-site Fe defect. At the Γ point, the bulk band appears not to cross E_F, consistent with the rigid band model for the excess Fe content bringing about the increase in the valence electrons, but no band crossing E_F down is found at the X point. The anti-site Fe defect states near E_F might push up the band at the X point and cause the p-type thermoelectric properties, unexpected with the rigid band picture.

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Characterization of Nb Hydrides Synthesized in Supercritical Water by Micro-beam Hard X-ray Photoelectron Spectroscopy

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ABSTRACT

Recently it has been found that Nb hydrides may be formed by laser-beam heating in supercritical water with almost no oxides [1]. This is unusual because supercritical water is believed to have great ability of oxidation. According to Yoshimura et al., stable Nb_2O_5 is finally formed through hydrothermal reactions of Nb with water below ~1100 K under a pressure less than 0.1 GPa, while NbH_x is produced as intermediates, depending on a partial pressure of hydrogen [2]. Thus we have tried to characterize the “Nb hydride” synthesized in supercritical water by using micro-beam hard X-ray photoelectron spectroscopy (μ-HAXPES).

“Nb hydride” specimens are prepared by irradiating a laser beam onto Nb foils of 0.1 mm x 0.1 mm x 0.025 mm in size under 2 ~ 11 GPa in a diamond anvil cell. X-ray diffraction (XRD) measurement in transmission geometry shows NbH_x patterns together with metallic Nb ones for the specimens obtained by heating at relatively low temperatures. Almost no change in the XRD patterns is observed on keeping the specimens three days long in vacuum. The specimens are mounted on a Cu pin with commercially available carbon adhesive tape. An X-ray micro-beam of 0.035 mm x 0.040 mm (FWHM) in cross-sectional size and of 7940 eV in photon energy is employed as an excitation source for photoelectron measurement at BL47XU of SPring-8. The inelastic mean free path is estimated to be ~10 nm for 6 ~ 8 keV electrons in Nb [3]. Recently developed angle-resolved photoelectron measurement has been also performed to obtain the depth profile of the chemical states.

The Nb 2p core level spectrum of the “Nb hydride” specimens is found to consist of an intense Nb_2O_5 component with a shoulder structure, which might be attributed to Nb hydrides, at the high binding energy side of a metallic component of a reference Nb foil. The “Nb hydride” specimen also shows a broad band at the binding energy E_B between 5 and 9 eV, which is ascribed to the Nb oxide, while the valence band spectrum of the Nb foil is composed of a triple-peaked feature below E_B ~ 5 eV, which agrees well with the density of states of Nb calculated with a code WIEN2K [4], and of a broad band around E_B = 5 ~ 9 eV, which is attributed to a Nb surface oxide layer. Thus it is found that the surface of the “Nb hydride” specimen is covered with several 10 nm thick Nb oxides.

In summary, we have successfully obtained the depth-profiling of the “Nb hydride” specimens by μ-HAXPES; Nb hydrides observed in XRD may be formed deep inside the specimens, although its formation is not definitely confirmed by the present measurement yet.

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Unraveling Multiplets in NiO $M_{23}M_{45}M_{45}$ by APECS

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ABSTRACT

The experimental $M_{23}M_{45}M_{45}$ Auger spectra of NiO has been measured in coincidence with the photoelectron current excited from the Ni 3p core level. The Auger profiles denoted as AN and NN are APECS[1] spectra taken at different angles, at a low temperature, i.e., with the NiO film in the AF phase. The notation NN means that both electrons are not aligned with the photon polarization whereas AN means that the photoelectron is aligned with the photon polarization while the Auger electron is not. In the case of the antiferromagnetic CoO[2], it has been recently observed that the AN and NN profiles are different, due to the spin selectivity power of the DEAR APECS technique, which is capable to assign different weights to the various spin components. In particular it has been shown[3] that the low- spin two-hole final states are favored in the NN geometry while the AN configuration favors high- spin. We clearly see from the Auger lineshape that the dichroic effect is also visible in the antiferromagnetic NiO film. This observation motivated us to perform a spin-resolved calculation of the Auger lineshape of NiO, in the same spirit of Ref.3.

We have calculated spin-resolved Auger spectra for the S = 2, S = 1 and S = 0 contributions. As in the case of CoO, our calculation of the unrelaxed spectrum is able to explain the experimental pattern in detail, at least in the spectral region closed to the threshold. Indeed all the main features in the AN and NN profiles are unambiguously identified as quintets and triplets respectively. Only one structure is not assigned according to such a naive rule, namely, the one at 46.5 eV (AN), which seems, instead, to belong to a singlet final state. It must be noticed, however, that this structure occurs more than 10 eV below the threshold (which is estimated to lie around 59 eV), and the unrelaxed approximation might not be very accurate in this spectral region.

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Spin-dependent Electron Correlations by Auger Photoelectron Coincidence Spectroscopy

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ABSTRACT

Itinerant electron systems are often characterized by a Coulomb interaction energy (U) that is small compared to the valence band width (W), and are well described within the independent electron approximation using approaches such as density functional theory. On the other hand, for systems where U is large compared to W, the mutual repulsion among the electrons cannot be neglected when describing material's electronic properties. Transition metals and their compounds often are intermediate cases where electron-electron interactions cannot be ignored, but may be adequately described in a perturbative manner. It has to be noted that the Coulomb repulsion among electrons is typically characterized by a single average interaction energy U when its value is important with respect to W. On the other hand, in ferromagnetic systems where the magnetic exchange interaction energy is of a similar magnitude as U and W, this may no longer be the case. In such circumstances, majority and minority spin electrons may exhibit dramatically different degrees of localization. In order to investigate this issue we used a combined experimental and theoretical angle-resolved Auger-photoelectron coincidence spectroscopy (AR-APECS) study of the Fe $M_{2,3}VV$ Auger transition from 3-monolayers of Fe grown epitaxially on the Cu(100) surface. The final state in this core-valence-valence Auger transition consists of two holes in the Fe valence band. By appropriate choice of experimental parameters, sensitivity of the AR-APECS spectra to triplet (primarily parallel spin) configurations of the two-hole final state can be enhanced or suppressed with respect to that of the singlet (antiparallel spin). We find that, while contributions to the spectrum from decay channels that involve minority spin electrons are well described within an independent electron approximation, significant correlation effects must be included to account for the final state with two majority-spin holes. This dramatically different interaction between majority and minority spin holes arises because a hole in the completely filled majority-spin band is significantly more localized than a hole in the half-filled minority-spin band.

Orbital Tomography: Deconvoluting Photoemission Spectra of Organic Molecules

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ABSTRACT

Large π-conjugated organic molecules are attracting considerable interest due to their potential applications; however, their valence bands necessarily consist of closely spaced molecular states, which is often challenging for both theory and spectroscopic experiment. We propose a tomographic method that uses the energy and momentum dependence of photoemission from adsorbed molecules to deconvolute the valence band into individual orbitals beyond the limits of energy resolution. The method allows the purely experimental determination of molecule-projected densities of state (PDOS), to be compared to theoretically calculated PDOS. The method further allows the direct observation of the effects of bonding on individual orbitals, and in so doing, provides stringent tests for the development of ab-initio electronic structure theory.

Photoemission experiments on differently ordered phases of perylene-tetracarboxylic-dianhydride (PTCDA) molecule on Ag(110) were performed at BESSYII using a toroidal electron energy analyzer. The valence band of PTCDA was unambiguously disentangled into contributions from six molecular orbitals with a binding energy below 4 eV, four of them within an energy range of only 0.4 eV [1]. For the PTCDA phase including two differently oriented molecules, the method grants an access to electronic properties of either molecule in the unit cell separately. This enables detailed description of site- and orientation-specific bonding of organic molecules at metals.

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ELEPES of YbB_{12} and SmB_6 Kondo Semiconductor Families by Microwave Excited Xe and Kr Electron Cyclotron Resonance Lamp

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ABSTRACT

Extremely high resolution cw photon sources (FWHM $\Delta h\nu<600$ μeV) are now easily accessible in laboratories at ~8.4, ~10.0 and ~11.6 eV by Xe, Kr and Ar electron cyclotron resonance lamps excited by microwave [1]. Thin sapphire, CaF_2 and LiF filters are used to cut high hν components [2]. LiF window can be used to isolate the UHV analyzer chamber from the low pressure lamp in 10^{-3} mbar range. So photoelectron measurements can be continued on a clean surface over tens of hours. The photon beam can be easily focused down to 2mmϕ by 45° incidence toroidal mirror. At some sacrifice of the high photon flux, one can focus down to 0.5 mmϕ without difficulty by putting an aperture of 0.5mmϕ at the exit of the lamp. In contrast to the hard X-ray photoemission called HAXPES, we call this as extremely low energy photoelectron spectroscopy (ELEPES).

In both YbB_{12} and SmB_6, small gap formation was reported at low temperatures. Owing to the high resolution and high counting rate of ELEPES, we studied the temperature dependence of the ELEPES spectra of $Yb_{1-x}Lu_xB_{12}$ and $Sm_{1-x}Eu_xB_6$ single crystals fractured in UHV. We found clear differences of the gap formation in two systems in regard to the temperature and doping x dependence. The origin of the gap formation is discussed [3].

Bulk sensitivity and surface sensitivity of ELEPES depending upon materials will also be discussed.

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Diversity of Recoil Effects on Photoelectron Emission from Valence and Core Level States in V Compounds

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ABSTRACT

Owing to the recently achieved high resolution (<60 meV) and high precision (<10 meV) measurements in photoelectron spectroscopy in the hard X-ray (~8 keV) and soft X-ray regions (hereafter called HAXPES and SXPES), recoil effects on photoelectron emission became verified in various solids.

In addition to core level photoemission from light elements in various materials, the recoil effects (RE) were observed from valence band photoemission in Al and LiV_2O_4 [1]. We studied RE in various V compounds (V_3Si, VO_2, V_2O_3, V_5O_9) and found that there are three typical cases. 1) All core levels and VB show RE. 2) Neither core level(s) nor VB show RE. 3) Although some core level(s) and VB show RE, no RE is observed for other core level(s) [2]. The origin of such differences is examined and discussed. It is also demonstrated that partial density of states (PDOS) in the VB can be studied from these recoil behaviors.

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Mn 3s-3d Exchange Splitting in Mn 3s-2p X-ray Emission Spectra of Manganese Oxides

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ABSTRACT

Doped manganites exhibit a variety of interesting properties, for example, colossal magnetoresistance, half-metallicity, metal-insulator transition and so on [1]. In order to obtain information about the number of the Mn 3d electron or the spin moment among factors involved in such complex phenomena in the manganites, we have measured Mn 3s-2p x-ray emission spectra in the Mn 2p absorption region for MnO and doped perovskite manganites, $La_{1-x}Sr_xMnO_3$ and $Pr_{1-x}Ca_xMnO_3$, whose formal Mn valency ranges from 2+ to 4+. The Mn 3s photoemission spectra of manganese oxides show two peaks due to the 3s-3d exchange interaction and the 3s splitting energy decreases almost linearly with increasing Mn valency from 2+ to 4+ [2]. Conventional photoemission spectra, however, convey information about the electronic states near the surface, and it is difficult to carry out the measurements for insulating materials. The x-ray emission spectroscopy has much longer probing depth than the photoemission spectroscopy and it is free of the charging effect by irradiation. The x-ray emission associated with an electronic transition from 3s to 2p introduces a 3s hole in the final state just like the 3s photoemission and the multiplet splitting is expected in the Mn 3s-2p emission spectrum. The chemical effect on the Mn 3s-2p emission spectrum has been previously examined for metallic Mn, MnF_2, MnO and $LaMnO_3$ [3]. Clear systematic trend in the splitting energy was not found as a function of the Mn valency among those compounds.

Two-peak structure associated with Mn $3s\text{-}2p_{1/2}$ transitions in the manganites is observed in the x-ray emission spectrum taken with the exciting energy corresponding to the Mn $2p_{1/2}$ absorption peak and it is reminiscent of Mn 3s photoemission spectrum. It is found that the splitting energy of the two peaks in the emission spectra for the manganese oxides also decreases almost linearly with the Mn valency from 2+ to 4+. The splitting energy in the emission spectra is about 0.8 times that in the photoemission spectra. Resonant photoexcitation from 2p to 3d does not only increase the signal intensity but also it does the splitting energy by adding an electron to Mn 3d. Although the corresponding splitting energy of divalent MnO falls on the same line as a function of the Mn valency, the spectral shape of the Mn 3s-2p emission for MnO is strongly dependent on the excitation energy in contrast to those for manganites. This results from highly ionic character or weak hybridization between Mn 3d and O 2p of MnO [3,4]. Numerical simulation based on a cluster model has been carried out to analyze the excitation energy dependence of the spectrum for MnO.

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Molecular Spin at Surface Explored by Single Molecule Spectroscopy

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ABSTRACT

The molecular magnetism at surface attracts much attention not only from the fundamental points of view but also from the potential device applications to utilize both spin and charge degrees of freedom. Recent advance in single molecule spectroscopy with scanning tunneling microscopy (STM) enables us to unveil the magnetism by interogating individual molecules at surface.

The magnetism of iron phthaloccyanine (FePc) adsorbed on noble metal surfaces was investigated mainly by using inelastic electron tunneling spectroscopy (IETS) and scanning tunneling spectrosocpy (STS) with STM working at 400 mK under strong magnet fields. The bulk FePc molecule takes spin triplet (S = 1) in the electronic ground state as a result of ligand field splitting. The degeneracy of S=1 is lifted by the spin orbital interaction, which is known as zero field splitting (ZFS) because the splitting takes place even when an external magnetic field is absent. Depending on the strength and symmertry of the interfacial coupling between the molecule and substrate, we have found interesting phenomena such as the switching in magnetic anisotorpy on Cu(110)(2x1)-O[1], the symmetry-driven novel Kondo effect on Au(111)[2,3], and the formation of two-dimensional Kondo lattice where the Kondo screening and RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction compete[4].

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ARPES Measurement of Valence Band Structure in Strained Silicon

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ABSTRACT

Strained silicon, in which stress is applied to change Si lattice constant, has been attracted much attention recently due to its enhanced charge carrier mobility [1,2]. Because the enhanced charge carrier mobility induces higher device performance speed, strained silicon is now routinely used in MOSFETs for ULSI. The enhancement of the mobility ($\mu = e < \tau > /m^*$) should be a consequence of the strain-induced change of electron life time ($< \tau >$) or effective mass (m^*). However, because the change of the $< \tau >$ and m^* upon strain has not been clarified, the actual contribution of these two factors on the mobility enhancement remains an open question

In this study, we investigated the effect of strain on the valence band structure of strained Silicon using High-resolution Angle Resolved Photoelectron Spectroscopy (HR-ARPES). The sample was Si(001) layers grown on Si_{1-x} Ge_x alloys with different Ge concentrations and conventional silicon as a reference. The Si over-layer has an increased lattice constant depending on the Ge concentration of the underlying Si_{1-x} Ge_x alloys so as to match the lattice constant between the substrate alloy and the over-layer. The biaxial tensile strain in the Si over-layers was confirmed by Raman scattering measurement. ARPES result from conventional silicon showed degeneracy of the heavy hole (HH) and light hole (LH) states at the top of the valence band. In the case of the strained Si, ARPES results indicate an upward lift of the band having lighter in-plane effective mass at the top of the valence band. This lift makes non-degenerated valence band top. This non-degeneracy makes the effective mass of the valence band edge smaller, which is consistent with the mobility enhancement observed in strained Si.

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Peculiarities of the Silicon $L_{2,3}$ X-ray Absorption Edge Behavior In SiO_x:C/Si Film Structures with Silicon Nanocrystals

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ABSTRACT

Investigations of the silicon $L_{2,3}$ X-ray absorption edge behavior peculiarities in SiO_x/Si(100 and 111) film structures with silicon nanocrystals in SiO_x layer were performed with the use of XANES technique. Layers containing nanocrystals at the depth 100-200 nm were modified by carbon implantation to form the SiO_x:C/Si structure.

Si $L_{2,3}$ XANES investigations were performed at Mark V beamline of SRC synchrotron radiation (SR) facility (University of Wisconsin-Madison, Stoughton, USA). Instrumental broadening was ~0.05 eV. Sample current measurement technique was used to detect XANES spectra. Sampling depth in case of Si $L_{2,3}$ XANES spectra is ~ 5 nm. For deeper near surface layers control (sampling depth ~ 60 nm) K absorption edges of silicon were recorded with the use of DCM beamline of the same synchrotron.

It is shown that without C implantation the annealing of the SiO_x/Si structures leads to nanocrystals formation in the SiO_2 matrix and to the intensity inversion of the fine structure of the elementary silicon $L_{2,3}$ absorption edge at SR grazing angles from 90 to 30. This phenomenon was observed as the result of backscattered waves interference at silicon nanocrystals in silicon dioxide matrix with greater refraction coefficient in X-rays [1].

Carbon implantation and following anneal is resulting in noticeable XANES spectra reconstruction at Si $L_{2,3}$ edge. Intensity inversion phenomenon of the elementary silicon $L_{2,3}$ XANES fine structure is disappeared. At the same time the intensity of the Si $L_{2,3}$ XANES spectra in the range of the silicon dioxide is inversed. Moreover this inversed structure peculiarities observed at SR grazing angles from 90 to 2 are dependent on the carbon implantation dose.

Observed reconstruction of the XANES spectra of carbon implanted and annealed samples is connected with changes of the optic characteristic of the scattering centers as the result of the silicon carbide formation at the surface of Si nanocrystals with refraction coefficient greater that one for SiO_2 phase. Silicon carbide formation at nanocrystals surface is confirmed by Si $L_{2,3}$ as well as by Si K XANES spectra.

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X-ray Absorption Spectroscopy Investigation of Multilayer Nanoperiodical Structures Si/Mo/Si…c-Si (100)

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ABSTRACT

Multilayer nanoperiodical structures (MNS) Si/Mo/Si…c-Si (100) are very promising object for integrated electronics and X-ray optics. Quality requirements for the MNS structure is rising with their modern fields of development. It should be noted that applied properties of the MNS are in a strong dependence on its interlayer's boundary perfection.

Since the X-ray absorption near edge structure spectroscopy (XANES) is the characterization technique sensitive to local atomic surrounding sensitive to near surface layers structure MNS were investigated with the use of this method. The thicknesses of Mo nanolayers in MNS were varied from 0.35 to 3 nm while Si interlayer thickness was constant 5.5 nm. Total number of nanolayers periods was 162 with 4 nm silicon capping layer. Si $L_{2,3}$ XANES investigations were performed at the Mark V beamline of the SRC synchrotron radiation facility (University of Wisconsin-Madison, Stoughton, USA). Instrumental broadening was ~0.05 eV. Sample current measurement technique was used to detect XANES spectra. Sampling depth in case of Si $L_{2,3}$ XANES spectra is ~ 5 nm. For deeper near surface layers analysis (sampling depth greater than 60 nm) silicon K and molybdenum $L_{2,3}$ absorption edges were recorded with the use of DCM beamline of the same synchrotron.

Additional X-ray diffraction study demonstrated that lateral sizes of Mo nanocrystals could be greater than thickness of containing Mo nanolayer. With the increase of Mo nanolayer thicknesses (up to 10 nm) nanocrystals gained more equiaxial shape with [100] orientation as well.

Silicide phase formation at the heterophase interlayer boundary Si/Mo/Si as a result of solid-phase interaction between the layers of silicon and molybdenum is shown by Mo L2,3 absorption edges fine structure analysis. TEM confirmed this intermediate nanolayer formation.

Significant distortions of silicon-oxygen tetrahedron bonds' structures of the surface silicon oxide layer covering amorphous Si capping layer are demonstrated by shape and relative intensity of Si $L_{2,3}$ XANES fine structure.

This work is based in part upon research conducted at the Synchrotron Radiation Center, University of Wisconsin-Madison which is supported by the National Science Foundation under award No. DMR-0537588. This work is based upon research supported by the Federal Targeted Programs "Scientific and Scientific-Educational Personnel of the Innovative Russia".

PEEM Characterization of the Submicron Ni Rods Distributed in SiO2 Matrix

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ABSTRACT

Ni particles embedded in a dielectric matrix (SiO_2) attract presently enormous attention because of its recently discovered giant magnetoresistance. This material is a potential candidate for magnetic field sensing devices (e.g. magnetic tomography matrixes). Also known publications show that these materials are candidates for introduction of such structures to metal-oxide semiconductor field-effect transistor like (MOSFET) electronic elements called the TEMPOS (Tunable Electronic Material in Pores in Oxide on Semiconductors) structures. The present work aims at microscopic characterization of the morphology and local electronic structure of the submicron Ni rods distributed in SiO_2 matrix.

Massives of Ni rods with about 500 nm diameters in the SiO_2 matrix on the Si (100) substrate were formed by electrochemical deposition from $NiSO_4$ solution into silicon dioxide layers pores formed with the use of the heavy ions tracking technique (Au ions, 380 MeV). Obtained sample was studied by the photoemission electron microscopy (PEEM) technique using the synchrotron radiation of the Helmholtz Zentrum Berlin BESSY II storage ring.

PEEM measurements were performed at the Ni L2/3 resonance that allowed us identifying the predicted partial oxidation nearby individual Ni rod and investigate their interfaces to the surrounding silicon dioxide matrix. It is shown that rods of the Ni metal are forming mainly in small groups and are connected to each other by the 50 nm bridge. It is shown that the 20-50 nm transitional area nearby each rod contain the metallic Ni as well as its defective residual nickel oxides pollutions. Additionally the microscopic remanent magnetization distribution data were demonstrated.

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XANES and XPS Investigations of the Oxygen Surface Vacancies Influence on SnO_2 Nanowires Electronic Structure

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ABSTRACT

Wire-like crystals of SnO_2 were produced by gas transport synthesis technique with the use of pure tin burden in the high temperature furnace (1050 - 1150 C). Aiming to reveal the influence of the oxygen vacancies the moss-like wires massive were annealed in UHV (10^{-10} Torr) for half an hour at 100, 200, 300 and 400 C consequently in sample preparation camera . After each anneal as well as for the unannealed sample the X-ray absorption near edge structure (XANES) spectra were taken near the M4,5 absorption edge of tin and O K edge of oxygen. Also XPS data were taken for core and subvalnce levels of tin and oxygen. As references we used commercial samples of tin foil, SnO powder and SnO2 lumps. All samples modifications and measurements were performed at the Russian-German Beamline (HiRes end station) of the Helmholtz Zentrum Berlin BESSY II storage ring.

Obtained XPS data demonstrated that binding energies values for the references we used have the tendency to grow up with the increase of the oxidation degree. At the same time the difference between tin oxide and tin dioxide O 1s or Sn 3d core levels was found 0.3 eV. According to X-ray diffraction measured previously the initial wires was SnO_2. Besides the surface sensitive XPS of the initial wires proves the existence of the native oxide nanolayer covering each wire. This native surface tin oxide is similar to the one covering metallic foil.

For the first time the $M_{4,5}$ absorption edge of pure metallic tin is registered the reference sample after in-situ mechanical removing of the native oxide. This allowed to clearly divide (by their shape and energy position) the absorption edge of metallic tin states and the "defect" pre-peak observed before near the absorption edge of SnO_2. This pre-peak is mostly like caused by oxygen vacancies states that exists over the surface layer and is observed for reference samples of SnO_2, SnO and initial wires. In the latter case the relative intensity of this spectral feature is most noticeable.

For wires samples the relative intensity of the "defect" feature observed before the main Sn $M_{4,5}$ absorption edge of SnO_2 is growing up with the increase of the UHV anneal temperature. This is a good demonstration of the oxygen vacancy nature for this prepeak observation at the energies ~ 3.1 eV lower that Sn $M_{4,5}$ main absorption edge for SnO_2 and ~ 1.8 eV higher than the Sn $M_{4,5}$ absorption edge for the metallic tin. At the same time spectral features at energies higher than Sn $M_{4,5}$ absorption edge of the SnO_2 confirm that the bulk of wires is tin dioxide by their shape and energy positions. The same situation is observed for oxygen K edges as well.

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Coherent Metallic Screening in Strongly Correlated Oxides: Experiment and Theory

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ABSTRACT

Strongly correlated transition metal oxides, which show a satellite structure due to a coherent metallic screening process in core-level photoemission, were studied by hard x-ray photoemission spectroscopy (HAXPES) and configuration interaction theory based on a cluster model. In the cluster model calculation, we take the hybridization between transition metal 3d states and metallic coherent states (V*) into account [1]. As reported by Tanaka *et al*., the intensity of the satellite structure (I_s) due to coherent metallic screening in the Mn 2*p* core-level spectra of $La_{1-x}Ba_xMnO_3$ (LBMO) thin films shows strong temperature dependence [2, 3] and is proportional to $(V^*)^2$ [2]. To clarify this linear relationship between, we have carried out a series of cluster model calculations, in which the multiplet states were neglected for simplicity. These calculations give us the spectral weight in the final states for various V* values and I_s as a function of $(V^*)^2$. The linearity between I_s and (V*) was found when the charge transfer energy (Δ and Δ^*), the Coulomb interactions (U_{dc} and U_{dd}) and the Mn 3*d* - O 2*p* hybridization strength (V_{eff}) were treated as fixed parameters.

To further explore the relationship between I_s and $(V^*)^2$, we have performed V 2*p* core-level and valence band HAXPES measurements for $V_{1-x}W_xO_2$ thin films [4] at BL15XU [5] of SPring-8. In this system, the W-doping increases metallic behavior. With increased W-doping, the I_s of the V 2*p* core-level spectra steeply increases. To estimate V*, we used the electronic structure parameter set for VO_2 in Ref.[6], and calculated I_s as a function of V*, where Δ , Δ^*, V_{eff}, U_{dc}, and U_{dd} were again treated as fixed parameters. From these calculations, we found that I_s is neither proportional to V* nor to $(V^*)^2$ for $V_{1-x}W_xO_2$ thin films. On the other hand, $(V^*)^2$ determined from the experimental I_s showed that the intensity observed at the Fermi level was proportional to $(V^*)^2$. This relationship is also expected from the impurity Anderson model [7]. We will present the experimental and theoretical results for both LBMO and $V_{1-x}W_xO_2$ thin films in detail.

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Magnetic Anisotropy in Ni Ultrathin Films on Pd(001) Investigated by X-ray Magnetic Circular Dichroism Spectroscopy

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ABSTRACT

Magnetic anisotropy is one of the most important and interested properties of magnetic ultrathin films. Spin reorientation transition (SRT) is a phenomenon that the magnetization direction reorients with varying film thickness, capping layers, or adsorption of molecules. Magnetic properties of Ni ultrathin films on Pd(001) has not revealed at all in spite of several reports on whose atomic structure [1–4]. Photoelectron diffraction study revealed the structural phase transition from face-centered-tetragonal (fct) to face-centered-cubic (fcc) with increasing film thickness [1]. In addition, anomalously strained interlayer distance in particular thickness region 6.5–10.5 monolayers (ML) is reported [4]. Thus the strong correlation of magnetism with atomic structure is expected in this system. In order to reveal the magnetic anisotropy, we have carried out X-ray magnetic circular dichroism (XMCD) spectroscopy on Ni/Pd(001). XMCD spectroscopy enables one to investigate the magnetic anisotropy and the local magnetic moments in an element specific way.

Experiments were performed at the soft X-ray beamline HiSOR-BL14 of Hiroshima Synchrotron Radiation Center, Hiroshima University, Japan [5,6]. Sample was fabricated by Ni deposition on a Pd(001) surface at room temperature in ultra-high vacuum. Film thickness was calibrated by Auger electron spectroscopy and intensity oscillation of reflection high-energy electron diffraction. Wedge-shaped films were also fabricated for thickness dependent measurements. *In situ* XMCD experiment was performed using an electromagnet with magnetic flux density of 0.3 T. Field dependent magnetization curves were obtained as absorption intensity at Ni L_3 edge. At lower thickness, the easy magnetization axis was in-plane, however, it directs out-of-plane with increasing Ni coverage. So-called Inverse SRT; the magnetization directs from in-plane to out-of-plane with increasing film thickness was observed in Ni/Pd(001). Inverse SRT is also observed in Ni/Cu(001) [7,8]. We also found emergence of the ferromagnetic order between 2 ML and 3 ML at 89 K.

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Atomic Structure of The 1*T*-TiSe$_2$ Surface Layers by Means of STM, XPD and Photoelectron Holography

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ABSTRACT

The atomic structure of the 1*T*-TiSe$_2$ surface layers was investigated by the complex of experimental and calculated methods. Treated are the problems of surface structure identification for layered materials.

The atomic clear TiSe$_2$ (001) surface was obtained by cleaving of a monocrystall in the high-vacuum camera of ESCALAB MK II spectrometer combined with a STM-microscope VT Omicron. So, the STM-experiment and X-ray photoelectron diffraction (XPD) were carried out for the same samples of 1*T*-TiSe$_2$. The XPD experiment was made for both types of emitters: Ti (2*p* core-level, E_k~1030 eV) and Se (Auger line – *LMM,* E_k~1310 eV).

On STM-images of the crystall face (100) there are observed triangular Se-clusters rised on the surface on 0.3 Å. By DFTB-calculations[1] their formation causes by a structural distortion of surface slabs [Se-Ti-Se]. The information about structure of slabs was obtained by XPD method. XPD-patterns were interpreted by two different approaches: *i*) by contrasting with calculated XPD-pattern (used only for 2π-pattern of Se), *ii*) as holograms of real atomic enviroment of emitters (both Ti and Se).

The first manner required searching a model structure of TiSe$_2$ cluster for best agreement XPD patterns calculated by EDAC-code[2] and experimental pattern. The agreement was measured by *R*-factor. Varying of the lattice parameters, different stacking faults and bending of slab showed no planar defects in a 1*T*-TiSe$_2$ surface. There were found two local minima of *R*-factor value for 1*T*-polytype with different lattice parameters: 1) $\boldsymbol{a_0}$ increased by 0.3 Å, and 2) $\boldsymbol{c_0}$ increased by 1.8 Å (from parameters of bulk TiSe$_2$ – $\boldsymbol{a_0}$=3.5 Å and $\boldsymbol{c_0}$=6.0 Å).

The second approach of holographic reconstruction allowed to visualise atomic enviroment of Ti- and Se-emitters directly. By means of SPEA-MEM algorithm[3] XPD-patterns were reconstructed as two 3*D*-images with positions of 128 atoms in two surface slabs[4]. The structure was determined the 1*T*-polytype and both lattice parameters increased ($\boldsymbol{a_0}$ by 0.3 Å and $\boldsymbol{c_0}$ by 1.2 Å) and Ti-layers were shifted from middle of slab.

To summarise, the structure of the surface layers 1*T*-TiSe$_2$ retains the polytype of the bulk crystal, but complex distortions were revealed. They include increase of lattice parameters, shift of Ti-layer in slab, different thickness of the first and second slabs and the width of van der Waals gaps. It is assumed that similar structural distortions of the lattice lead to the formation of an energy gap between the valence band and the conduction band of 1*T*-TiSe$_2$, which is observed by angle-resolved photoemission spectroscopy (ARPES).

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Pt-CeO_2 Thin Films Deposited on Carbon by Means of Magnetron Sputtering: Promising Catalyst for Fuel Cell Applications

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ABSTRACT

Pt-doped CeO_2 thin film catalysts 10 nm thick were prepared by means of magnetron sputtering on carbon coated silicon wafer. It was shown by means of SEM and AFM that the films exhibit rough and porous surface morphology while the uncoated silicon wafer simultaneously covered by the Pt-CeO_2 reference films reveal smooth surface morphology. Hard X-ray Photoelectron Spectroscopy (HAXPES) is very suitable technique for porous thin film chemical state study because of its high information depth. HAXPES studies demonstrated that Pt was dispersed in CeO_2 mostly in form of ionic Pt · $^{+}$. It was also found that at surface parts of the film are partially reduced and contain higher concentration of Ce^{3+} and Pt^{2+} ions. Such morphological and stoichiometric behaviour are explained by the thin film growth process including oxygen plasma etching of carbon substrate.

Element-specific Kikuchi Patterns

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ABSTRACT

After an (incoherent) large-angle scattering event the electron interacts with the crystal lattice along its outgoing trajectory, resulting in an angular variation in the intensity, the so-called Kikuchi pattern. Generally, these patterns are measured using a phosphor screen, and there is very limited information of the energy of the electrons hitting this screen. Recently we measured these patterns using an electrostatic analyzer with sub-eV resolution. This made a more quantitative comparison of measured and calculated of Kikuchi patterns possible [1] and we could determine the depth of the sample that contributes to the pattern [2]. Even more interestingly, when combining these measurements with the recoil effect, it is possible to determine the diffraction patterns of different elements of a crystal separately. For the case of Sapphire we found large differences in Kikuchi patterns for electrons backscattered from Al and O [3]. The observed patterns were well reproduced using the dynamical theory of diffraction.

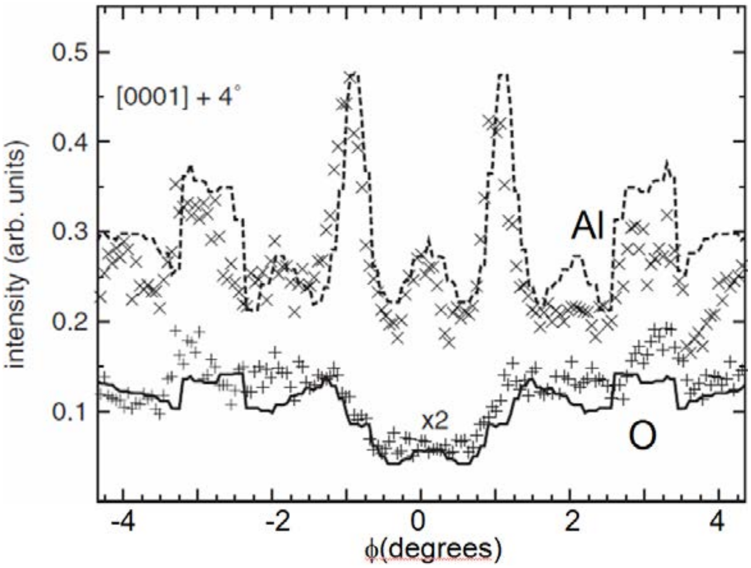

Fig. 1: Measurement (symbols) of the (1,1,-2,0) Kikuchi band for Al (top) and O (bottom) in Sapphire (Al_2O_3) compared to the theory based on the dynamical theory of diffraction (lines).

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Chemical Bonding States and Electronic States of Reduced Graphene Oxides Studied by Real-time Photoelectron Spectroscopy

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ABSTRACT

Graphene has attracted a great deal of attention in recent years because of its superior physical properties. The reduction of graphene oxide (rGO) is the most applicable method to obtain the large-area graphene, which is used for a transparence electrode [1]. However, the electric property of rGO is poorer than that of graphene made by another methods such as CVD and SiC annealing. In order to improve the electric property of rGO, the reduction process of GO must be clarified. In this study, we have investigated the vacuum-annealing induced changes of the chemical bonding states and electronic states of GO, which was treated with and without hydrazine using real-time photoelectron spectroscopy. The experiments were performed at BL23SU, SPring-8.

As shown in Fig. 1(a) and (b), the C 1s spectra were curve-fitted with 8 components. After annealing, all of oxides and sp^3 components decrease while sp^2 and defect components increase. This indicates that carbon vacancies are generated by reduction of GO, implying that these vacancies make rGO poor electric property. As shown in Fig. 1 (c) and (d), the Fermi edge can be clearly observed in rGO. This result also supports the assumption that the atomic vacancies are generated in the graphene sheets [2]. Furthermore, the effect of hydrazine treatment on GO will be also discussed.

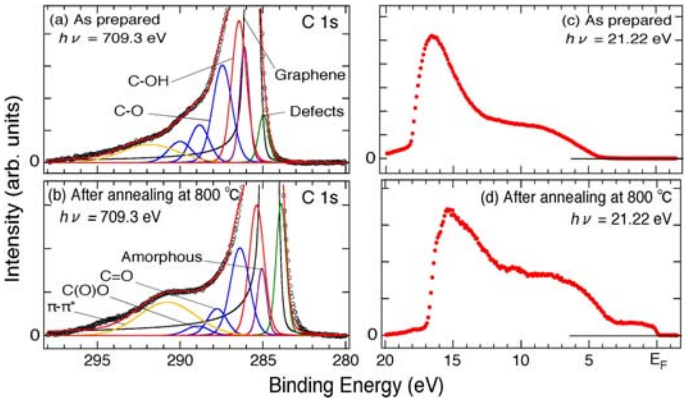

Fig. 1. C 1s photoelectron and valence band spectra of (a) and (c) for pristine GO and (b) and (d) for reduced GO by annealing at 800°C in vacuum, respectively.

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Chiral or Achiral: Electron Pairs in Core-resonant Double Photoemission

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ABSTRACT

The electron-electron interaction allows one photon to eject two electrons into vacuum, a process named double photoemission (DPE). The angular- and energy- distribution of the DPE pairs is usually quantified as triple differential cross section (TDCS), viz., the differential intensity of the DPE pairs with respect to specific solid angles and sum energy. The TDCS of the DPE pairs carries unique information related to the electron correlation, which is not directly accessible with normal single photoemission spectroscopy. For example, the angular distribution of the *spin-unresolved* photoelectrons from *isotropic* targets is independent of the helicity of the incident circularly polarized photons. However, the TDCS of the DPE pair in general is changed with the inversion of the photon's helicity[1], inducing a circular dichroism (CD): the combined system of the DPE pair and the spin of photon may exhibit a definite handedness and be chiral. It reflects the phase difference of the complex optical transition amplitudes, and is crucial to characterize the complete dynamics of the DPE process[2].

CD on DPE was first discovered on free helium atoms, the simplest 2-electron system[3]. Since there remains no electron in the residual ion, the helicity of the photon is transferred to the DPE pairs. However, for heavier atoms, it is questionable whether the DPE pairs always forms a chiral system with the spin of the photon, since the helicity can also be carried away by the electrons in the residual ions. Thus the *spatial symmetry* of the final ionic state decides whether the DPE pairs are involved in the chiral system or not.

This question has not been attacked experimentally before. We approach it by investigating the photo- Auger-electron pairs from photo-induced Auger decay process. Different from the direct DPE process in helium atoms, the photo-induced Auger decay involves at least one core- and two outer-shell electrons, and is a core-resonant DPE process. It also shows CD for DPE pairs from singlet ionic states[4]. However there is no experimental evidence whether CD will become zero if DPE pairs are emitted from triplet ionic states.

We performed a DPE experiment with circular polarized light on a Cu(100) surface. The photon energy was chosen to be 125 eV, leading to comparable kinetic energies of the *3p* photo electron and related Auger electron. We did find that the core-resonant DPE pairs from singlet ^1G ionic state displays circular dichroism, while that from triplet ^3F ionic state does not. Our results clearly demonstrate how the helicity of the incoming photon is transferred to either the DPE pair or the final ionic states.

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Direct Observation of One-dimensional Metallic Bands of Pt-induced Nanowires on Ge(001) by Angle-resolved Photoelectron Spectroscopy

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ABSTRACT

One-dimensional electronic systems are well known as sources of intriguing physical phenomena such as Tomonaga-Luttinger liquid and Peierls type metal-insulator transition. For these peculiar phenomena of one-dimensional electronic states, Pt-induced nanowires formed on Ge(001) surface (Pt/Ge(001)-NW) is remarkable. The defect-less Pt/Ge(001)-NW was firstly observed by Gürlu *et al*. with scanning tunneling microscopy (STM) [1]. After that, Houselt *et al*. reported that the surface periodicity changes from a p(4 × 2) at room temperature to a p(4×4) below 80 K [2]. Recently, we experimentally proposed the atomic configuration of Pt/Ge(001)-NW by means of reflection high-energy positron diffraction [3]. In the present study, we report on the surface and electronic structures of Pt/Ge(001)-NW with single-domain, investigated by low energy electron diffraction (LEED), STM and angle-resolved photoelectron spectroscopy (ARPES).

The single-domain nanowires were prepared on a vicinal Ge(001) surface. From the LEED patterns and the STM images, we have found the nanowires that line up parallel to the step edges. The ARPES measurements were performed at BL19A in KEK-PF and CASSIOPEE in SOLEIL. We have observed three metallic bands associated with Pt/Ge(001)-NW along the nanowire direction. The ARPES measurements also provide the constant energy map at the Fermi level. We found that the Fermi surfaces of the metallic bands consist of straight lines in the surface Brillouin zone. This indicates that the metallic bands exhibit one-dimensional properties. We believe that the one-dimensional metallic bands of Pt/Ge(001)-NW is very suitable for the study of the peculiar physics in one-dimensional metals.

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Surface Metallization of SrTiO3(001) by Adsorption of Hydrogen

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ABSTRACT

Strontium titanate (SrTiO3; STO) has attracted growing attention as next generation oxide electronics because of its unique electronic properties. For example, a 2D metallic layer with high carrier mobility is formed at the interface of the two insulating oxides STO/LaAlO3 [1] or on the vacuum-cleaved STO surface [2, 3]. Recent theoretical study [4] has proposed a novel way to create the 2D metallic layer on STO by chemical doping (hydrogen adsorption), which has not been evidenced by experimental studies. In this study, we report the first experimental demonstration of the 2D metallic layer on the H-adsorbed STO(001) surface using photoelectron spectroscopy (PES) and surface transport measurements [5].

The electronic structures of the clean and H-adsorbed STO(001) surfaces (0.05 wt% Nb, n-type) were investigated by valence band and core-level PES at the TEMPO beamline of SOLEIL and at SPring-8 BL07LSU. For the clean STO surface, no state is observed at the Fermi level in the valence band PES spectra as expected from an insulating nature of STO. Upon H-adsorption, however, a sharp new feature appears at the Fermi level. Angle-resolved PES spectra reveal that this metallic feature has parabolic band dispersion similar to the 2D metallic layer on the vacuum-cleaved STO surface. By H-adsorption, in addition, the core-level PES peaks shift to higher binding energies by a downward band bending. Therefore, surface metallization of H-adsorbed STO originates from electron accumulation at the STO surface induced by electron donation from adsorbed hydrogen to the surface. Surface transport measurements using a four terminal method reveal that the observed change in the electronic structures of STO by H adsorption, the insulator-to-metal transition, is indeed concurrent with the increase in surface conductivity. The high surface conductivity of the H-adsorbed STO surface confirms that the electrical conduction is in the metallic conduction regime.

In summary, by a combined PES and surface transport study, we have demonstrated the formation of the 2D metallic layer on the STO surface using surface chemical doping (hydrogen adsorption). The present study opens up the possibilities of designing the future oxide devices using nano-scale molecular electronics techniques and of extending to much detailed studies on their carrier dynamics.

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Inverse Photoemission Spectroscopy in the Near-ultraviolet Range

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ABSTRACT

Inverse photoemission spectroscopy (IPES) is an ideal experimental method for examining the density of unoccupied states in solid materials [1]. In previous IPES, either X-ray (hv > 1 keV) [2] or vacuum ultraviolet (VUV; hv ≈ 10 eV) [3] photons has been detected following the injection of electrons with energies of 10 - 1000 eV into solid materials. The high energy electrons can damage the organic samples preventing further analysis of the unoccupied states. Also, the energy resolution is limited to about 0.5 eV due to the difficulty of detecting X-ray or VUV photons with high resolution and sensitivity. Surprisingly, such instruments have been used without any fundamental improvement since the late 1970s.

Here, we have demonstrated IPES in the near ultraviolet (NUV) range for the first time [4]. As shown in Fig. 1, varying the kinetic energy of electron from 0 to 4 eV, emitted photons in the NUV range (< 5 eV) are detected using a bandpass filter and photomultiplier. As an example, the NUV-IPES spectra of a typical organic semiconductor, Cu-phthalocyanine, is shown in the upper panel of Fig. 2.

The distinct features of this new method can be summarized as follows:

1. The damage to organic samples is significantly reduced because the electron kinetic energies are below the damage threshold. Fig. 2 compares the sample damage due to the electron irradiation; in the present method, the sample damage is negligible even after 14 hours whereas significant deterioration is observed only after a few ten minutes under the similar condition as the conventional VUV-IPES. This method is, therefore, especially suitable for organic or bio-molecules.
2. The high energy resolution is easily attained without losing the throughput using the bandpass filters (bandwidth is typically 0.1-0.2 eV). The obtained overall energy resolution of 0.3 eV is better than those of commonly used VUV-IPES by a factor of 2-3.
3. Various focusing optics and photon detection methods are available in the NUV range.

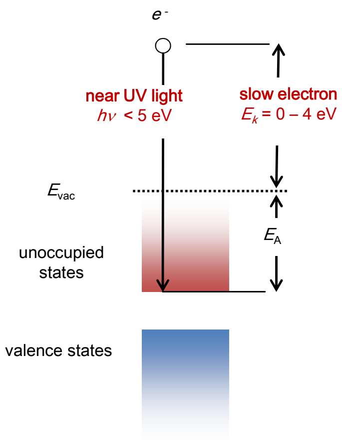

Fig.1: Energy level diagram showing the concept of the present method.

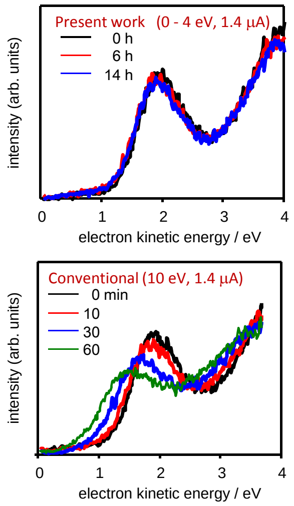

Fig.2: NUV-IPES spectra of Cu-phthalocyanine, comparing the sample damages (see text).

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Polarization-dependent Angle-resolved Photoemission Studies of Hydrogen-adsorbed SrTiO3(001)

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ABSTRACT

Strontium titanate ($SrTiO_3$; STO) is one of the most promising wide-gap semiconductors which show many intriguing properties, like visible-light-driven photo catalytic properties on the noble metal ion doped STO [1] and high-mobility electron gas at the $LaAlO_3/SrTiO_3$ interface [2]. Moreover, two-dimensional (2D) electron gas [3] and liquid [4] were observed on the cleaved- and laser-irradiated STO(001) surfaces. Recently, we have succeeded in the experimental demonstration of the insulator-to-metal transition of the STO(001) surface by adsorption of hydrogen atoms [5]. Various characteristic features such as metallic states and in-gap-states (IGSs) have been observed in the valence band electronic structures. In spite of their importance in understanding the mechanism of surface metallization, the origin of 2D metallic states and IGSs is still under the discussion and the subject of intense research.

We have performed polarization-dependent angle-resolved photoemission studies on the hydrogen-adsorbed STO(001) surface at TEMPO beamline of SOLEIL. The difference in the intensity ratios of photoelectrons by the p- and s- polarized incident light have been observed for the metallic states, IGSs, and the O-H peak. By considering experimental configuration and dipole approximation, insights into the orbital character of the metallic states, IGSs, and non-vanishing intensities observed at the higher binding energy side of the metallic states have been obtained.

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PROGRAM

Friday, Sept. 21st, 2012

Friday, September 19th, 2012

	Surface and Material Science 2 Chateaubriand Auditorium	**New Opportunities / Instrumentation** Maupertuis Auditorium	
08:30 - 09:00	Topological insulators from the view point of chemistry *C. Felser* (Invited)	Design, performance, first results and future opportunities for FERMI@ELETTRA *G. De Ninno* (Invited)	**08:30 - 09:00**
09:00 - 09:30	Depth-resolved electronic structure of complex materials and nanostructures with hard X-ray and standing-wave excited photoemission *A. Gray* (Invited)	Multidimensional electron spectroscopy with ArTOF 10k *R. Ovsyannikov* (Invited)	**09:00 - 09:30**
09:30 – 10:00	Visualization of electrons dynamics in real time *L. Perfetti* (Invited)	XMCD spectroscopy on mass-selected metal clusters using a Penning-like ion trap *M. Neeb* (Contributed)	**09:30 - 09:50**
10:00 - 10:20	X-ray spectroscopic study of charge injection and interfacial structure of CdSe-QDs sensitized TiO2 NPs and NWs *J. Guo* (Contributed)	Ultrahigh resolution soft X-ray emission spectroscopy *Y. Harada* (Contributed)	**09:50 - 10:10**

10:20 - 10:45 **Conclusion**

11:00 - 16:00 **Transfer by bus from St Malo to SOLEIL**

12:00 - 13:30 **Lunch**
Lamennais Area

16:00 - 18:00 **Synchrotron SOLEIL Tour**

From 18:00 **Transfer by bus from SOLEIL to Massy TGV - RER station**

SESSION:

Surface and Material Science 2

Topological Insulators from the View Point of Chemistry

C. Felser, L. Müchler, S. Chadov, B. Yan, J. Kübler,
HJ Zhang, and SC Zhang

ABSTRACT

Topological insulators are a hot topic in condensed matter physics. The excitement in the physics community is comparable with the excitement when a new superconductor is discovered. Recently the Quantum Spin Hall effect was theoretically predicted and experimentally realized in quantum wells based on the binary semiconductor HgTe. Many Heusler compounds with C1b structure are ternary semiconductors that are structurally and electronically related to the binary semiconductors. The diversity of Heusler materials opens wide possibilities for tuning the bandgap and setting the desired band inversion by choosing compounds with appropriate hybridization strength (by the lattice parameter) and magnitude of spin-orbit coupling (SOC, by the atomic charge). Based on first-principle calculations we demonstrate that around 50 Heusler compounds show band inversion similar to that of HgTe. The topological state in these zero-gap semiconductors can be created by applying strain or by designing an appropriate quantumwell structure, similar to the case of HgTe. Many of these ternary zero-gap semiconductors (LnAuPb, LnPdBi, LnPtSb and LnPtBi) contain the rare-earth element Ln, which can realize additional properties ranging from superconductivity (for example LaPtBi) to magnetism (for example GdPtBi) and heavy fermion behaviour (for example YbPtBi). These properties can open new research directions in realizing the quantized anomalous Hall effect and topological superconductors. C1b Heusler compounds have been grown as single crystals and as thin films. The control of the defects, the charge carriers and mobilties will be optimized and quantum well structures will be grown. Recently some of the C1b Heusler compounds were predicted to be excellent piezoelectrics. The combination of a piezoelectric Heusler compounds and compounds at the borderline between trivial and topological insulators offers the possibility of a switchable device.

It is also possible to design new topological insulators with strong correlations. In AmN and PuTe a band gap is opened by correlation effects. In a family of semiconductors with the simple NaCl structure band gaps up to 0.4 eV were found. This is not so surprising since the SOC should be large in Actinides.

Heusler compounds are similar to a stuffed diamond, correspondingly, it should be possible to find the “high Z”' equivalent of graphene in a graphite-like structure or in other related structure types with 18 valence electrons and with inverted bands. Indeed the ternary compounds, such as LiAuSe and KHgSb with a honeycomb structure of their Au-Se and Hg-Sb layers feature band inversion very similar to HgTe which is a strong precondition for existence of the topological surface states. LiAuSe is a strong TI, whereas KHgSb a weak TI.

We will discuss the necessary and sufficient conditions for new TI materials, based in symmetry and bonding arguments.

Depth-resolved Electronic Structure of Complex Materials and Nanostructures with Hard X-ray and Standing-wave Excited Photoemission

A. X. Gray[1,2,3], J. Minar[4], S. Ueda[5], C. Papp[6], L. Plucinski[7], A. Bostwick[8],
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ABSTRACT

In this talk I will describe several new directions in the field of x-ray photoelectron spectroscopy, made possible with the advent of third-generation synchrotron light sources and recent advances in the fields of x-ray optics and photoelectron detection. I will present several case-studies wherein *hard x-ray photoelectron spectroscopy (HAXPES)* in the multi-keV regime is used to probe the bulk properties of complex thin-film materials and heterojunctions, which would be otherwise impossible to investigate using conventional soft x-ray XPS [1]. I will present the first results of *hard x-ray angle-resolved photoemission measurements (HARPES)*, at excitation energies of 3 and 6 keV [2,3]. Compared to the traditional ARPES, carried out in the UPS regime (20-100 eV), this new technique enables one to probe on average 10-40 times deeper into the bulk. Finally, I will introduce a new photoemission technique *(SWARPES)* which combines soft x-ray ARPES with standing-wave (SW) excited photoelectron spectroscopy, wherein the intensity profile of the exciting x-ray radiation is tailored within the sample in order to provide a depth-selective probe of the electronic structure of buried layers and interfaces [4].

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3. A. X. Gray *et al*. Bulk Electronic Structure of the Dilute Near-Ferromagnetic Semiconductor $Ga_{1-x}Mn_xAs$ via Hard X-ray Angle-Resolved Photoemission. Nature Materials, under review.
4. A. X. Gray *et al*. Depth-Resolved ARPES of Buried Layers and Interfaces via Soft X-ray Standing-Wave Excited Photoemission, in preparation.

Visualization of Electrons Dynamics in Real Time

L. Perfetti

Laboratoire des Solides Irradiés, Ecole polytechnique, 91128 Palaiseau cedex, France

ABSTRACT

We will present recent advances of time resolved photoelectron spectroscopy in materials with strong electron-phonon interaction and large spin-orbit coupling. The structure of electronic excitation in such compounds strongly depends on the entanglement of different degrees of freedom. In particularly the spin-orbit interaction generates spin and orbital polarizations, while the electron-phonon coupling results in to insulating phases with speudogapped spectral density. Time resolved photoelectron spectroscopy offers new means to investigate the physics of such complex systems by monitoring the dynamics of excited electronic states out-of-equilibrium conditions. We will treat several problems of high scientific interest as selective coupling of coherent phonons to Bloch states, the giant anisotropy of spin-orbit coupling and the photoinduced quenching of an electronic gap.

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X-ray Spectroscopic Study of Charge Injection and Interfacial Structure of CdSe-QDs Sensitized TiO_2 NPs and NWs

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ABSTRACT

TiO_2 is one of the most intensely studied materials for photovoltaics and photocatalysis. Two critical issues, however, need to be addressed to enable TiO_2 based materials to work effectively. First, the activity in the visible or near IR spectral region must be enhanced. Second, charge carrier separation upon photoexcitation needs to be facilitated so these charges can participate in useful photochemistry instead of simply recombining. Semiconductor quantum dots (QDs), because of their unique and desirable properties, have attracted significant attention as possible sensitizers that can drastically enhance the performance of TiO_2 based photovoltaic cells and photocatalysts. TiO_2 sensitized with CdSe-QDs is a potential promising material for photovoltaic and photochemical cells. The mechanism by which the QDs sensitize the TiO_2 is not fully understood. We will report the X-ray absorption spectroscopy and resonant X-ray emission spectroscopy study of the CdSe-sensitized TiO_2 nanoparticles (NPs) and nanowires (NWs). The interface structure of CdSe-QDs/TiO_2 and electron injection upon illuminated with sunlight have been revealed, which provides the crucial information for understanding the electronic interaction between QDs sensitizers and TiO_2.

SESSION:

New Opportunities / Instrumentation

Design, Performance, First Results and Future Opportunities for FERMI@ELETTRA

G. De Ninno

Sincrotrone Trieste S.C.p.A. S.S. 14 km 163,5 – in AREA Science Park
34149 Basovizza - Trieste, Italy

ABSTRACT

FERMI@Elettra is the first VUV/soft X-ray seeded free-electron laser in the world open to user experiment. Presently, it has unique performance in terms of stability, (longitudinal and transverse) coherence and variable polarization.
During the talk, we will present the concept on which FERMI is based, as well as the first obtained results and future planned developments.

Multidimensional Electron Spectroscopy with ArTOF 10k

R. Ovsyannikov[1], A. Vollmer[1], M. Gorgoi[1], S. Krause[1],
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ABSTRACT

During the last 5 years a new concept for a very high-resolution and very high transmission instrument ArTOF 10k [1] emerged was worked out in collaboration of Uppsala University, VG-Scienta AB and Helmholtz-Zentrum Berlin. ArTOF 10k is a time-of-flight electron spectrometer which combines position-sensitive detection with an advanced focusing electron lens system. The instrument allows the simultaneous recording of kinetic energy and the angular pattern of photoelectrons in a cone of up to 30° opening angle with very high resolution. Additionally, the temporal evolution of the sample electronic structure can be easily extracted from the corresponding data set. The principle is based on a time-of-flight scheme combined with electrostatic focusing precisely preserving the angular information. The instrument detects simultaneously four parameters: two components of the momentum, the kinetic energy and the time of the events. Compared to the best instruments so far the resolution is improved to the theoretical limit of about 100 μeV and the transmission is increased by a factor of more than 250! An interesting consequence of the large increase of transmission at a given resolution compared to a normal electron spectrometer is that it is possible to perform experiments at a much lower intensity of the exciting radiation, thus minimizing radiation damage. This helps to overcome a serious limitation e.g. in connection with band mapping of organic molecules on surfaces. In this contribution we will present an ArTOF approach of performing photoelectron spectroscopy experiments and demonstrate its potential in different application fields on examples of the prototype topological insulator Bi_2Se_3 [2], organics single crystals [3] and gas phase coincidence studies [4].

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XMCD Spectroscopy on Mass-selected Metal Clusters using a Penning-like Ion Trap

M. Neeb[1], S. Peredkov[1], W. Eberhardt[1], J. Meyer[2], M. Tombers[2], G. Niedner-Schatteburg[2]

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ABSTRACT

A Fourier-transform-ion-cyclotron-resonance mass spectrometer (FT-ICR) has been installed at the BESSY II synchrotron storage ring which allows recording of XMCD spectra of free metal clusters [1]. By this unique setup spin and orbital magnetic moments of free, mass-selected cluster ions are provided using circularly-polarized soft X-ray radiation. The photoabsorption signal is obtained by recording the fragmentation pattern of the core excited mother ion produced after X-ray absorption and subsequent Auger decay. Collisional cooling of the trapped ions is applied for temperature-dependent XMCD measurements down to 20 K. The experimental setup and magnetic moments of small transition metal clusters [1] will be presented.

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Ultrahigh Resolution Soft X-ray Emission Spectroscopy

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ABSTRACT

Soft X-ray emission (SXE) spectroscopy has attracted much attention because of its high potential for probing the electronic states of a wide range of materials such as wide gap insulators, superconductors, correlated transition metal oxides and rare earth compounds[1,2]. Recent advances in energy resolution of SXE with the energy resolving power above E/ΔE ~ 5000 enable us to observe extremely low energy excitations below 100 meV, e.g. element- and symmetry-specific electronic, vibrational, magnon, spinon and orbiton excitations that cannot be accessed by other methods. This potential of SXE benefits studies on unexplored electron and spin based materials. The target is also extending to liquids, electrolytes, corrosions and so on. In view of the above potential we have designed and constructed an in situ SXE spectrometer that features experiments in ultrahigh vacuum and ambient condition with an ultrahigh energy resolution ΔE < 100 meV and/or E/ΔE ~ 10000 in the range of 350 eV to 750 eV[3]. The spectrometer was installed at BL07LSU in SPring-8 where SXE with polarization correlation could be performed using more than 99 % linear polarization in both vertical and horizontal directions as well as left- and right-handed circular polarization of the incident beam. We will present the design concepts, numerical optimization of the optical parameters, and recent SXE results on strongly correlated systems, liquids in various conditions as well as gas adsorption of fuel cell catalysts. Future prospects of SXE spectroscopy will also be discussed.

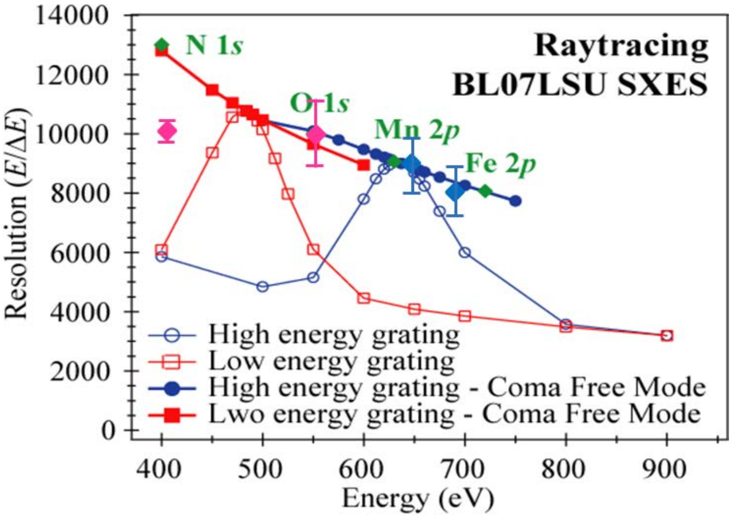

FIG. 1 Numerical estimation of resolving power for an ultrahigh energy resolution soft X-ray emission spectrometer installed at BL07LSU in SPring-8. Experimentally obtained values are also given.

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AUTHOR INDEX

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12th International Conference on Electron Spectroscopy and Structure

Palais du Grand Large, Saint Malo, France

September 16-21, 2012

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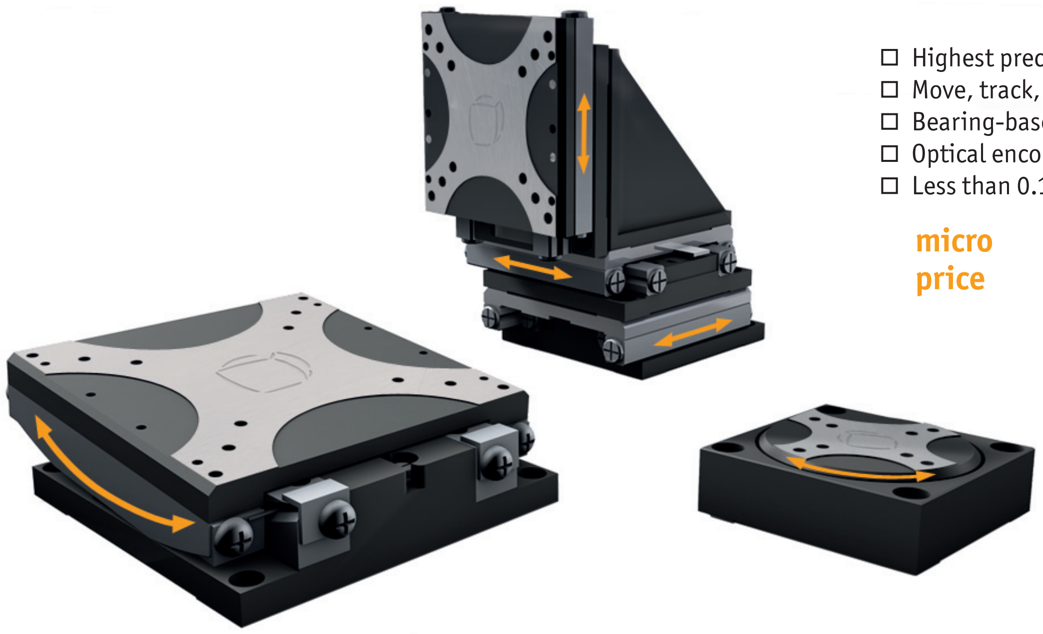


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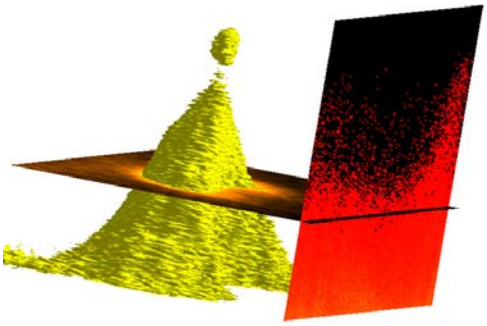

Electronic stucture of graphene recorded with fixed manipulator position using the full k-parallel detection of Scienta ARTOF 10k. Data courtesy: A. Lindblad, R. Ovsyannikov.

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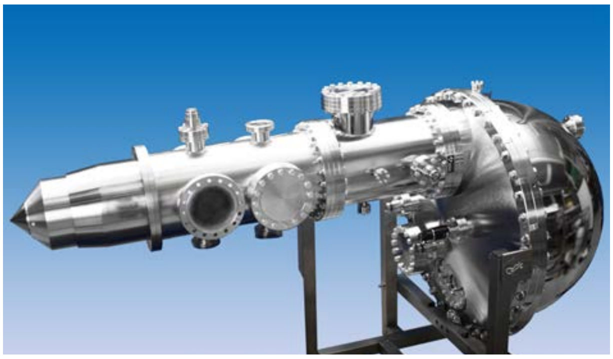

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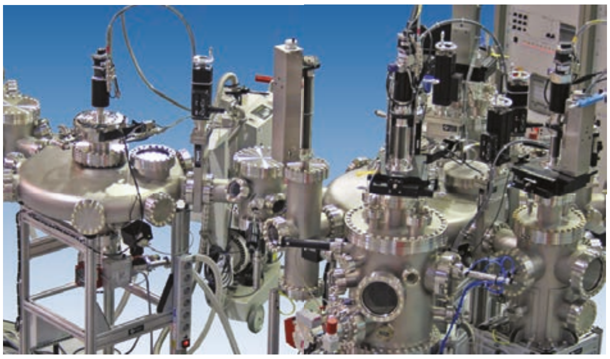

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12th International Conference ICESS-12 Saint Malo, France September 16-21,2012

Tentative Time Schedule

TIME	Sunday 16	Monday 17	
8:00 - 18:00		Registration	
8:30 - 8:40		Opening: P. Morin	
8:40 - 9:25		C. Draxl (Pl.)	
9:25 - 10:10		F. Martin (Pl.)	
10:10 - 10:30		COFFEE BREAK	
10:30 - 12:30		Imaging Spectroscopy 1 & Ultra Fast Dynamics J. Vogel (Inv.) Y.-J. Hsu (Inv.) L. Douillard (Inv.) C. Cacho (HT) N. Beaulieu (HT)	Atomic & Molecular Science 1 K. J. Borve (Inv.) M. Tashiro (Inv.) A. Lago (C.) R. Thiele (C.) A. Kochur (HT)
12:30 - 13:45		LUNCH	
13:45 - 15:30		Posters Session 1	
15:30 - 16:00		COFFEE BREAK	
16:00 - 18:00	Welcome Registration	Novel Electronic States 1 Y.Fagot-Revurat (Inv.) V. Brouet (Inv.) F. Onufrieva (C.) L. Simonelli (C.) T. Schmitt (C.)	Photo-chemistry Reactivity 1 H. Kondoh (Inv.) Z. Liu (Inv.) L. Hung (C.) P.L. Cudazzo (C.) A. Hitchcock (C.)
18:30 - 20:30	COCKTAIL	Free Evening	
20:30 - 24:00	Free Evening		

TIME	Tuesday 18	
	Registration	
8:30 - 9:15	J. Ullrich (Pl.)	
9:15 - 10:00	E. H. Conrad (Pl.)	
10:00 - 10:30	COFFEE BREAK	
10:30 - 12:30	Photo-chemistry Reactivity 2 L. Gregoratti (Inv.) O. Pulci (Inv.) A. Bendounan (C.) B. Stadtmueller (HT) T. Chassé (HT)	Ultra Fast Dynamics A. Maquet (Inv.) C. Cirelli (Inv.) D. Miller (Inv.) A. Kheifets (HT) L. Argenti (HT)
	LUNCH	
13:45 - 15:30	Posters Session 2	
15:30 - 16:00	COFFEE BREAK	
16:00 - 18:00	Surface & Material Science 1 M. Van Hove (Inv.) J.A.Martin-Gago (Inv.) K. Hricovini (C.) M. Muller (C.) F. Bertran (C.)	Atomic & Molecular Science 2 T. Jahnke (Inv.) J.-E. Rubensson (Inv.) C. Bomme (C.) K. Prince (C.) M.N. Piancastelli (C.)
18:30 - 24:00	IAB Meeting Free Evening	

TIME	Wednesday 19	
	Registration	
8:30 - 9:15	Q.-K. Xue (Pl.)	
9:15 - 10:00	F.J. Himpsel (Pl.)	
	COFFEE BREAK	
10:30 - 12:30	Novel Electronic States 2 F. Baumberger (Inv.) I. Matsuda (Inv.) T. Okuda (C.) L. Plucinski (C.) H. Dil (C.)	Imaging Spectroscopy 2 B. Carré (Inv.) M. Vrakking (Inv.) S. Sorensen (C.) M. Vos (C.) To be announced (C.)
	LUNCH	
13:30 - 19:45	**Sight seeing tour** **Saint Malo: 14:30-18:00**  **Cap Frehel-Fort Lalatte: 12:45-19:00**  **Mont Saint Michel-Cancale: 12:45-19:45** 	
20:30 - 24:00	BANQUET	

TIME	Thursday 20	
	Registration	
8:30 - 9:15	J. Osterwalder (Pl.)	
9:15 - 10:00	T.D. Thomas (Pl.)	
	COFFEE BREAK	
10:30 - 12:25	Novel Electronic States 3 M. Le Tacon (Inv.) A.F. Santander (Inv.) M. Sing (C.) C. Fadley (C.) M. Minola (HT)	Atomic & Molecular Science 3 B. Krässig (Inv.) M. Fushitani (Inv.) To be announced (C.) K. Ueda (C.) V. Kimberg (HT)
	LUNCH	
13:45 - 15:30	Posters Session 3	
15:30 - 16:00	COFFEE BREAK	
16:00 - 18:20	Novel Electonic States 4 U. Starke (Inv.) A. Bostwick (Inv.) N. Vinogradov (C.) C. Lin (C.) A. Resta (C.) V. Aristov (C.)	Photo-chemistry Reactivity 3 E. Rühl (Inv.) B. Winter (Inv.) C. Nicolas (C.) L. Weinhardt (C.) M. Nagasaka (C.) O. Björneholm (C.)
18:30 - 24:00	Free Evening	

TIME	Friday 21	
	Registration	
8:30 - 10:20	Surface & Material Science 2 C. Felser (Inv.) A. Gray (Inv.) L. Perfetti (Inv.) J. Guo (C.)	New Opportunities Instrumentation G. De Ninno (Inv.) R. Ovsyannikov (Inv.) M. Neeb (C.) Y. Harada (C.)
10:20 - 10:45	**Conclusion - ICESS13 venue** **10:45: End of conference**	
12:00 - 13:30	LUNCH	
11:00 - 16:00	**11:00: Transfer by bus from St Malo to SOLEIL**	
16:00 - 18:00	**Synchrotron SOLEIL Tour**	
18:00	**Transfer by bus from SOLEIL to Massy TGV - RER station**	

12th International Conference on Electron Spectroscopy and Structure – ICESS2012

Palais du Grand Large, Saint Malo, France

September 16-21, 2012

ADDENDUM

Wednesday 19/09 *Contributed Talk* Imaging Spectroscopy 2	Molecular Imaging by High-order Harmonic Generation *C. Vozzi*
Thursday 20/09 *Contributed Talk* Atomic & Molecular Science 3	The Photoreaction of $Fe(CO)_5$ in Solution Studied by Femtosecond Time Resolved RIXS *A.Föhlisch*
Monday 17/09 *Poster* Surface & Material Science 1	Layer-resolved Densities of States and Valence-band Offsets in Oxide Superlattices from Soft and Hard X-ray Photoemission and Standing-wave Photoemission *A. X. Gray*
Monday 17/09 *Poster* Surface & Material Science 1	A New Concept in Scanning Photoelectron Microscopy : Nano-ARPES at Synchrotron SOLEIL *M.C. Asensio*

DATES MODIFICATIONS

Monday 17/09 Poster Atomic & Molecular Science 1 **AM-1-PO-MAR-01 (instead of AM-3-PO-MAR-01)**	Relationship between Molecular Geometry and Vibrationally Resolved Molecular-frame Photoelectron Angular Distributions *F. Martín*
Tuesday 18/09 Poster Photochemistry & Reactivity 2 **PR-2-PO-OZA-01'** **(instead of SM-3-PO-OZA-01)**	Geometric and electronic structures of hydrogen-bonded networks comprising planar molecules on graphite (0001) *H. Ozaki*

Molecular Imaging by High-order Harmonic Generation

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ABSTRACT

A macroscopic ensemble of molecules exposed to an intense laser pulse emits coherent XUV radiation appearing as high-order harmonics of the laser frequency. The spectral amplitude and phase of the radiation produced by single molecules is encoded in the macroscopic emission.

Molecular imaging by high-order harmonics requires the measurement in amplitude and phase of the harmonic field emitted by a single molecule for different molecular orientations [1]. By modulating the angular distribution of the molecular ensemble and by exploiting a self-referencing approach, we show that both the amplitude and phase of single-molecule XUV emission can be directly retrieved from harmonic intensity spectra as a function of photon energy and angular orientation. This result is based on the exploitation of few-cycle mid-IR laser pulses [2]. The outcomes are exploited for a tomographic reconstruction of the outermost molecular orbital of CO_2 [3].

The approach for molecular orbital tomography presented here provides a route for the solution to major difficulties in contemporary HHG spectroscopy of complex species. These findings redeem the idea of HOMO spectroscopy by high-order harmonic generation and open new perspectives on the imaging of molecular orbitals.

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[2] C. Vozzi et al., Opt. Lett. 32, 2957 (2007).
[3] C. Vozzi et al., Nat. Phys. 7, 822 (2011).

The Photoreaction of $Fe(CO)_5$ in Solution Studied by Femtosecond Time Resolved RIXS

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B. Kennedy,[5] D. Nordlund,[8] M. Odelius,[6] W. Quevedo,[1] I. Rajkovic,[4]
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ABSTRACT

X-ray free electron (FEL) laser lightsources providing high intensity and femtosecond duration x-ray pulses have recently become available for experiments. FELs provide new possibilities to apply x-ray techniques, which are very successfully used to investigate the structure of matter, for studies of dynamics in time-resolved fashion. We present here results of a first liquid phase femtosecond time-resolved resonant inelastic x-ray scattering (RIXS) experiment.

In the UV driven photoreaction of $Fe(CO)_5$ in ethanol solution the chemical state of the $Fe(CO)_4$ intermediate in solution has been under debate for many years [1]. Coordinatively unsaturated $Fe(CO)_4$ moiety is highly reactive and represents important step in the reaction pathway. With femtosecond time resolved RIXS we reveal that photoexcited $Fe(CO)_5$ decays faster then 300 fs to a singlet state of $Fe(CO)_4$. The primary $Fe(CO)_4$ intermediate has a weak interaction to the solvent, that we attribute to the high vibrational state of the intermediate.

The RIXS experiments were performed both at the BESSY II and the Linac Coherent Light Source (LCLS) with a dedicated liquid jet RIXS set-up. These results demonstrate the potential of time-resolved RIXS for studies of chemical dynamics.

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Layer-resolved Densities of States and Valence-band Offsets in Oxide Superlattices from Soft and Hard X-ray Photoemission and Standing-wave Photoemission

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S. Stemmer,[4] S. Ueda,[6] K. Kobayashi,[6] A. Gloskovskii,[7] W. Drube,[7]
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ABSTRACT

During the past decade, oxide heterostructures have attracted a great deal of attention, as they can exhibit functional properties that are dramatically different from those of the bulk constituents. For instance, although the bulk materials comprising a multilayer structure might be non-magnetic insulators, putting them in close proximity with variable layer thicknesses in the nm-range can show metallic, ferromagnetic, or even superconducting behavior [1,2,3] These effects are strongly influenced by buried-interface properties. Standing-wave x-ray photoemission (SW-XPS) of both core and valence levels is a powerful approach for studying such buried layers and interfaces [4]. We have used SW-XPS to study a multilayer of the form ($LaNiO_3$/$SrTiO_3$)x10. A detailed analysis of the valence band region reveals a non-uniform electronic structure inside the $LaNiO_3$ layer, with strong suppression of the Ni e_g and t_{2g} states near the interface between $LaNiO_3$ and $SrTiO_3$ layers [5].

XPS is often used to determine valence-band offsets (VBOs) at such interfaces, important properties for understanding electronic level alignment and charge carrier mobility [6]. Hard x-ray excitation (HXPS, HAXPES) [3] is beneficial for this, in reducing charging. We have used XPS and HXPS to determine the VBOs of ($LaNiO_3$/$SrTiO_3$)x10 and ($GdTiO_3$/$SrTiO_3$)x20 heterostructures, with results in good agreement with local density theory.

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This work was supported by the Army Research Office Multi-University Research Initiative, under Grant W911-NF-09-1-0398, and by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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A New Concept in Scanning Photoelectron Microscopy : Nano-ARPES at Synchrotron SOLEIL

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ABSTRACT

A wide range of structural and chemical imaging techniques are now available for research in nano-materials and Low Dimensional Systems. In particular, the synchrotrons offer various spectrometers equipped with micrometric or even nanometric beam sizes. It is clear that the highly improved flux level of the third generation synchrotron sources is being highly beneficial in the area of the X-ray microscopy. In such context, a new scanning photoelectron microscope (SPEM) beamline has been constructed at SOLEIL. Contrary to the PEEM microscopy, the imagery in SPEM is generated by a simple nanometric sweeping of the samples and a focusing of the incident light.

Our innovative project is extending the classical SPEM technique to the domain of low photon energy using angle resolved photoemission (Nano-ARPES), allowing the states of the valence band and their k// dispersion be detected with extremely high energetic and angular resolution. The objective is to be able to determine the electronic band structure and the Fermi surface together with the chemical shift of core level of light elements with nanometer spatial resolution.

In essence, this new beamline of SOLEIL is fitting the existing emptiness between the atomic information provided by the STM microscopy and the low-spatially resolved data supplied by the traditional ARPES and NEXAFS techniques. The beamline delivers photons with energy in the 20-900 eV range, making use of two soft X-ray undulators with circularly and linearly polarized light. It comprises a high-resolution variable line spacing (VLS) and varied groove depth (VGP) plane grating monochromator (PGM) with a spectral resolving power of 25000 at 100 eV. This high brightness source illuminates a set of selected Fresnel zone plates after being focalized by a double Wolter optics passing by a pinhole. The design and the first results of this recently inaugurated station will be presented.

This instrument, with a spatial resolution of several tens of nanometers, has proved being able of carrying out direct imaging of core levels, their chemical shifts and tiny features of the electronic band structures of ordered materials. High precise images with chemical and valence band information have been recorded of nano-objects like nano-wires and micrometric exfoliated samples of graphene and other layered compounds. Moreover, several ordered granular materials have been investigated by imaging Nano-ARPES and core levels of individual grain. Finally, an overview of the utilization limits and complementarity of different x-ray microscopes will be detailed.