



# ELETTRA HIGHLIGHTS 2005-2006 EDITORIAL COMMITTEE

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*Cover Picture:* View of Experimental Hall from the bridge to the machine

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*Print:* Graphart s.n.c. Publication of Elettra's Highlights coincides this year with the 20th anniversary of the foundation of Sincrotrone Trieste S.C.p.A., the managing company of the Elettra Laboratory. Elettra was one of the first two medium-energy third-generation synchrotron radiation sources in the world. Many of our employees and of our Partners will recall the heady feeling of seeing a world-class laboratory emerge from a green field. Today, there are 22 beamlines in operation and four under construction, most of them built and operated together with our Partners. We have attracted and collaborate with Partners such as CNR-INFM, several major Universities, the Academies of Sciences of Austria and the Czech Republic and several international organizations, including EU and UN Agencies. We are hosting over 100 staff and some important central facilities and laboratories of such Partners, and welcoming approximately 1,000 users a year to perform experiments.

Growth of our facility does not occur in a vacuum, however. The economic, political, and demographic trends facing Italy and Europe must be taken into account, as well as trends in research policy. Such an environment produces threats as well as opportunities. In particular, 2003 and 2004 were especially difficult years for the national research community in general, and for our Laboratory, but the recent financial crisis is fortunately behind us. Continued success will depend upon how well our organization will adapt to the environment. Elettra's successful growth will require our laboratory to expand its role as a multidisciplinary laboratory and provide services and training for the national and international community. We must promote social and economic growth through basic and applied research in relevant fields and technology transfer. The scientific and technical community collected around Elettra must assist Italian and European leaders in defining and implementing scientific policy.

Our Laboratory is again at a beginning. A new 5-year plan has been developed and the structure of our organization has been reconfigured. We have evaluated critically the mission, vision and core values of our organization, defined our strategic objectives and developed a project-oriented operational structure to better pursue such objectives. Major investments are being directed at the Elettra synchrotron source, that is being upgraded with a new full-energy injector and top-up operation scheduled for 2008, and at FERMI, one of the first free electron lasers (FEL) of its kind in the world, that is being built through extensive international collaborations and will provide femtosecond pulses of unparalleled brilliance at nanometer wavelengths. Such facilities and resources are to support an expanded and strengthened network of researchers worldwide. The knowledge developed from these initiatives will be transferred to the community through education and strategic partnerships with the private sector. To successfully implement our plans we will need the direct involvement of all of our stakeholders.

We take this opportunity to thank our employees, our Partners and external Users for their enthusiasm and dedication over the years. We trust that with their help we will be able to meet the major challenge of implementing and fully exploiting an upgraded Elettra together with the new FEL source FERMI.

#### **Alfonso Franciosi**

Director, Elettra Laboratory Chief Executive Officer, Sincrotrone Trieste S.C.p.

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# RESEARCH HIGHLIGHTS

# ATOMIC AND MOLECULAR SCIENCE

In this year's highlights the first contribution in the field of molecular science is a photoemission study of a compound consisting of a magnesium atom, sandwiched between two hydrocarbon rings [Decleva et al.] Photoemission (in which electrons are kicked out by photons) is a technique widely used at synchrotrons, and usually cross-sections of molecules are fairly well-known and smoothly varying functions. However in this study, the cross-section is found to oscillate strongly over a wide energy range. This kind of behaviour has been seen before for bucky balls, but was thought to be limited to molecules in that class. The new results show the effect is much more general and may be expected to occur often in sandwich and cage type compounds. Thus the measurement of cross-section, which is relatively simple, provides a new way of probing the electronic structure of molecules.

The second contribution deals with an atom, namely helium [Rubensson+Prince]. Although it has been studied intensively for many years, this deceptively simple atom still yields surprises in the realm of fundamental physics. One such area is the response of an atom to an applied electric field. Since helium has tightly bound electrons, they are expected to react very weakly to fields. Calculations some years ago indicated that fields up to 100,000 volts per cm were necessary to induce observable effects. Now however, effects at a few hundred or a few thousand volts per cm have been observed in two independent studies at Elettra. This helps to refine our understanding of quantum mechanics, which is fundamental to modern science.

The last study (M. Gisselbrecht et al) is of the simplest molecule, hydrogen, but even in this well-studied system, new science is found. In the experiment, photons from Elettra smash a hydrogen molecule into its four basic components, two protons and two electrons, which are all detected simultaneously. The electrons fly apart quickly as they are very light and fast, and then the slower protons separate. By looking at the directions in which the particles move, and how the energy put into the molecule is divided up, it is possible to understand in detail this complicated event.

Kevin Prince

# STRONG OSCILLATIONS IN MOLECULAR VALENCE PHOTOEMISSION: A NEW PROBE INTO MOLECULAR STRUCTURE

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**Figure 1.** Photoemission spectra of MgCp<sub>2</sub> recorded at photon energy hv = 42 and 58 eV, that is, respectively near the minimum and the maximum of the HOM0-1/HOM0 curve. Strong oscillations in molecular photoemission cross sections, which persist up to hundreds of eV above threshold, have been first detected in  $C_{60}$ , both in the solid state and gas phase [1], and deemed unique to the almost spherical cage of carbon atoms. In the course of a theoretical investigation into photoemission from transition metal sandwiches, the same phenomenon has been uncovered in Magnesium Cyclopentadienyl (MgCp<sub>2</sub>, Figure 1) [2]. Since the simulation approach, based on an accurate solution of the scattering problem in a Density Functional frame-



work, provides excellent reproduction of the  $C_{60}$  features, an experimental study of this problem was planned at Elettra.

MgCp<sub>2</sub> was synthesized according to the literature procedure and sublimed prior to use. The photoelectron spectral measurements were carried out on the undulator based Gas Phase Photoemission beamline at the Elettra synchrotron light source (Trieste, Italy), using a 50 mm mean radius electron energy analyzer (VSW Ltd.) mounted at the magic angle. The overall resolution was better than 300 meV at all photon energies used. MgCp<sub>2</sub> is an air sensitive solid and therefore particular care was taken in handling it to minimize exposure to air or moisture. Samples of MgCp<sub>2</sub> were warmed in a resistively heated oven just a few degrees above room temperature.

The two outermost valence ionizations of MgCp<sub>2</sub>, HOMO and HOMO-1, corresponding to the in-phase and out-of-phase combinations of the highest p orbitals of the Cyclopentadienyl rings, have been studied. Two spectra at 48 and 58 eV are reported in Figure 1. The strong intensity change, with reversal of the strongest band, is clearly seen. To check the influence of electron correlation at the level of first order response theory, in addition to the DFT (KS; Kohn-Sham) results new calculations were per-

formed with a TDDFT (Time Dependent Density Functional Theory) algorithm recently developed.

The results obtained are presented in Figure 2 as the cross section ratio between HOMO-1 and HOMO, as compared to the analogous results for  $C_{60}$ . Calculated results are reported as solid lines. Several aspects are readily apparent.

1. It is clear that, while qualitatively similar, the oscillations in MgCp<sub>2</sub> are very different from those observed in  $C_{60}$ . First of all the period in MgCp<sub>2</sub> is much larger, which can be attributed to the smaller size of the  $Cp_2$ cage: the Mg – C distance is 2.339 Å compared to the radius of 3.562 Å of  $C_{60}$ . While the inverse relationship is obvious from box quantization, or Fourier Transform [23], a precise quantitative relationship, which is very interesting, is still to be determined. Also the difference in shape may be important. The second quantitative aspect is the size of the oscillations. If we quantify it as the deviation of the first oscillations (excluding the threshold region) from the statistical ratio, which is 1.0 for MgCp<sub>2</sub>, but 0.6 for  $C_{60}$ , we obtain a value around 0.4 for MgCp<sub>2</sub>, and 0.3 for  $C_{60}$  (0.6 for the first peak). So, perhaps surprisingly, oscillations in MgCp<sub>2</sub> are as strong as in C<sub>60</sub>. The third aspect is a quicker damping of the oscillations at higher energy. Unfortunately we have not been able to follow the spectra beyond 140 eV but the calculation clearly predicts a flattening out towards the statistical ratio at 200 eV. On the contrary oscillations in  $C_{60}$  apparently persist up to at least 300 eV, without any clear sign of damping.  $C_{70}$ , where oscillations are rather similar to those in  $C_{60}$ , shows however a significant damping, although not as sharp as in MgCp<sub>2</sub>. Here the most obvious candidate is the different shape. It appears that deviations from the spherical symmetry are principally apparent in the damping of the oscillations. Already the reduced symmetry in C<sub>70</sub> gives rise to significant damping, and it becomes rather abrupt in the MgCp<sub>2</sub> case, probably also because of its open cage in comparison with  $C_{60}$  and  $C_{70}$ .

2. The quality of the agreement between the experimental and calculated values is very



satisfactory, showing that the KS Hamiltonian, when accurately solved, is capable of an excellent reproduction of the experimental pattern. This gives, therefore, a handle for the interpretation of such data, and the extraction of structural information, by least squares adjustment between the experimental and computed spectra, in a similar way to which structural information is extracted from NEXAFS data.

3. Concerning the theoretical approach, it is clear that the agreement between KS and TDDFT results employing the same exchange-correlation potential is rather close, so that response effects have a rather limited influence on the ratio, which therefore reflects accurately the single particle potential. This is an important simplifying feature for the purpose of interpretation, and possible correlation with the geometrical structure of the cluster. Even adoption of a different potential has a negligible effect, apart from close to threshold, where the calculated values are somewhat larger, but do not change the qualitative picture. Again this is a good sign indicating that the cross section oscillations are in a sense robust, that is, not very sensitive to fine details of the potential, and therefore a potential source of structural information.

A comparison with other sandwich molecules is reported in Figure 3. It is apparent Figure 2. Upper: Experimental HOMO-1/HOMO cross section ratio in MgCp2 and computed value at KS and TDDFT levels. Calculated values are shifted by 6 eV to higher energy. Lower: HOMO/HOMO-1 cross sections ratio of  $C_{60}$  evaluated at the KS level, and experimental results [1].



Figure 3. H0M0-1/H0M0 cross section ratio for metallocenes evaluated at the KS level. Upper: MgCp<sub>2</sub>. Central: FeCp<sub>2</sub>. Lower:  $Cr(C_6H_6)_2$ .

that significant oscillations are quite widespread at least in such compounds, although not as pronounced as in MgCp<sub>2</sub>. These differences are a clear reflection of the different electronic structure. The most interesting signature is the lack of convergence of the ratio to the statistical value. We interpret it as a neat indication of the metal d orbital participation of the Fe and Cr compounds in one of the two p ring orbitals, the symmetric combination  $e_1$ " in FeCp<sub>2</sub> and  $e_{1g}$ in  $Cr(C_6H_6)_2$ , which are strongly  $d \rightarrow p$ bonding  $(3d_{xz}, d_{vz} \text{ components})$ . Since at higher energies the metal 3d cross section is significantly larger than the C 2p one, and is probably non oscillating, its contribution causes both a decrease of the ratio with increasing energy and a smoothing of the oscillations. Conversely, when properly interpreted, such features give a clear cut indication of the amount of metal d orbital participation, and in general of orbital composition.

In conclusion it appears that long range oscillations in molecular photoemission cross sections are a general phenomenon, which can convey important information on the geometric and electronic structure of the target. Elucidation of the detailed mechanism will require a more extensive survey, but an excellent reproduction is obtained by accurate scattering solutions at the DFT level.

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# DOUBLY EXCITED He STATES IN STATIC ELECTRIC FIELDS

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Helium is the simplest quantum mechanical three body system in atomic physics, and consequently has been extensively studied. While the Schrödinger equation can be solved exactly for the hydrogen atom, this is not possible for helium because there is correlation and exchange interaction between the two electrons. All descriptions of the wave function are therefore necessarily an approximation, and experimentalists and theoreticians interact to measure and describe the physics of helium as exactly as possible.

One clear manifestation of electron correlation is the existence of doubly excited states of helium, excited by synchrotron radiation of about 60 to 80 eV. In these states, a single photon promotes both 1s electrons to higher orbitals; in an independent electron picture, only one of the electrons would be excited by a photon. The doubly excited states of helium have been extensively studied to understand the dynamics of this prototypical system, and recently attention has turned to their behav-



iour in electric fields [1]. Harries et al showed that a wealth of spectral information could be obtained by applying strong fields (up to 84 kV/cm) to the helium atom while doubly exciting it with synchrotron radia-

Figure 1. Experimental and theoretical fluorescence yield spectra close to the N=2field-modified ionization thresholds (indicated by the arrows), excited at various **E** fields. Just below 65.32 eV the 13+ state appears, the peaks in this series having almost constant intensity. Less intense and with decreasing intensity we find the unresolved  $[n - 1]^{-1}$  and  $n^0$  peaks in between the  $n^+$  and  $(n+1)^-$  states, with the unresolved 14<sup>-</sup>/13<sup>0</sup> just above 65.32 eV.



**Figure 2.** Partial fluorescence yield spectra of helium with **E** perpendicular to the polarization of the incident light. New features induced by the field are labeled 1 and 2. These correspond to <sup>1</sup>P<sup>e</sup> and <sup>1</sup>D<sup>e</sup> states. tion. From previous theoretical calculations, it had been expected that strong fields were necessary to observe effects.

Now however two independent studies at the Gas Phase Beamline have shown that this is not so: even at weak to moderate fields, many phenomena can be observed [2,3]. Experimentally, the electric field can be aligned parallel to the polarization vector or perpendicular: the first study used the parallel geometry and concentrated on lower fields and higher Rydberg states [2]. Both studies used Vacuum Ultraviolet Fluorescence yield spectroscopy as the primary investigation method. Säthe et al found that near threshold, fields of a few tens of V/cm changed the intensity of the peaks, and caused the disappearance of a well known spectral dip at 65.39 eV. For a few hundred to a thousand V/cm, the spectral intensities were very different, and at several kV/cm, they were completely different from the zero field intensities.

In the work of Prince et al [3], the spectra were mostly taken with the electric field perpendicular to the electric vector of the light. The geometry has consequences for the selection rules which dictate which states may be excited. In this geometry new states, labeled <sup>1</sup>P<sup>e</sup>, were observed, as well as shoulders assigned to <sup>1</sup>D<sup>e</sup> states. These cannot be observed in normal photoabsorption because they are forbidden by selection rules, which require a parity change from the even ground state to the odd excited state. The electric field mixes the symmetry of states in a well-known phenomenon called Stark mixing, and so that "dark" or forbidden states become visible.

Both of these studies were supported by theoretical calculations which guided the interpretation and supported it. They also arrived at an important conclusion in common. The doubly excited states can decay by autoionization, in which an electron is emitted, or by fluorescence, in which a photon is emitted. The electric field mixes the states not only in terms of symmetry, but also in terms of their decay mode. Thus a state that decays mostly by fluorescence may mix with a state that decays mostly by autoionization, and so its fluorescence yield decreases. Vice versa, a state that decays mostly by electron emission may mix with a state that decays by fluorescence, and its intensity in the fluorescence yield spectrum will increase.

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# COMPLETE DYNAMICAL STUDY OF THE BREAK-UP OF H<sub>2</sub>

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If a molecule absorbs enough energy, bonds can be broken and ions can form, allowing neutral and charged constituents to react with neighbouring molecules. These processes occur everywhere from car engines to industrial chemical plants, and, of course, in the atmosphere driven by the Sun's energy. The removal of two electrons, i.e photodouble ionisation (PDI), in the simplest two-electron molecule,  $H_2$ 

$$hv + H_2 \rightarrow H^+ + H^+ + e_1 + e_2 (1)$$

is an example of such processes. It is more complex than the well-studied atomic case and introduces new physical effects. Firstly, the PDI threshold is not unique, because it depends on internuclear separation as the upper potential curve is purely repulsive. Secondly, the ground state electronic configuration is inevitably more complex due to the two-center nuclear potential. Thirdly, PDI in  $H_2$  is followed by a 'Coulomb explosion' as the two protons rapidly separate in opposite directions. Since the process is rapid compared to molecular rotation, the relative momentum of the two escaping protons defines the molecular alignment at the instant of double ionisation. Energy and angle-resolved detection of all four particles completely defines the PDI dynamics and allows one to study fully differential cross sections (FDCS) within the molecular frame using such 'fixed-in space' molecules. These measurements provide the most stringent tests for theory and the greatest possible physical insight into this 4-body process. In this study we report on such measurements

performed at the Gas Phase Beamline at Elettra, when Elettra was operated in the four bunch mode. They made use of the CIEL momentum imaging apparatus [1], which allows the detection of the two electrons and two protons from the Coulomb explosion with 4p sr detection efficiency (Figure 1). Approximately 1.1 million fourparticle coincidence events were obtained, resulting in significantly improved data quality and a clearer understanding of this fundamental process.

In the experiments  $H_2$  molecules are ionised by 100% linearly polarised radiation and the resulting charged particles are extracted by a static electric field applied across the interaction region. An axial magnetic field is applied to the system to confine electrons having an initial large orthogonal velocity component.

The photon energy was 76.09 eV, 25 eV above the nominal threshold at the equilibrium internuclear separation and near the peak of the PDI total cross section.

We present here a subset of the data in the equal electron energy sharing case,  $E_1 = E_2 =$ 



**Figure 1.** Diagram showing the TOF system used in the experiment.

**Figure 2.** Absolute H<sub>2</sub> FDCS's in the 'coplanar' geometry for four molecular orientations with  $\theta_1 = 90^\circ$  and  $E_1 = E_2 = 12.5 \pm 2.5$  eV. The radii of the circles give the absolute scales in millibarns/eV<sup>2</sup>/sr<sup>3</sup>: 120 (a); 120 (b); 60 (c); 30 (d). The full lines give the fit from Eq. (1) folded with experimental bandwidths.

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 $12.5 \pm 2.5$  eV. Firstly, we focus on the 'coplanar' geometry, where the electron momenta,  $k_{1,2}$ , and polarization vector,  $\hat{\varepsilon}$ , all lie in the same plane. In the dipole approximation the FDCS have axial symmetry around  $\hat{\varepsilon}$ and reflection symmetry with respect to the plane perpendicular to it. These properties can be used to sum equivalent events together, thus improving the statistics, and allow us to write the FDCS as:  $d\sigma^7/d\theta_1 d\theta_2 d\Delta \phi_{12}$  $d\theta_N d\Delta \phi_{eN} dE_1 dE_2$ , where  $\theta_{1,2,N}$  are the angles of electrons 1 and 2 and the molecular axis, N, with respect to  $\hat{\varepsilon}$ , and where  $\Delta \phi_{12} = \phi_1 - \phi_2$  and  $\Delta \phi_{eN} = \phi_e - \phi_N$  (with e = 1 or 2) are the relative azimuthal angles. FDCSs for  $\theta_1 = 90^\circ$  are shown in Figure 2 for a series of 'in-plane' molecular axis orientations. An inspection of Figure 2 reveals these features: (i) In Figure 2(a) and (d), corresponding to the P and S orientations respectively, the FDCSs have a symmetrical two-lobe structure very similar to that observed in He with  $E_1 = E_2$  at the same  $\theta_1$ . Coulomb repulsion between the electrons is responsible for the ejection of the electrons in opposite hemispheres, with a strict node for 'back-to- back' emission. The two lobes slightly closer together in Figure 2(a) than in 2(d) indicate a greater degree of electron correlation.

(ii) The electron-electron angular distribution *does* depend on the molecular alignment, as the two lobe patterns become strongly asymmetric for all  $\theta_N$  between the  $\Pi$  and  $\Sigma$  orientations. Within the constraints of electron-electron repulsion, there is a *reduction* in the yield orthogonal to the bond direction.

(iii) The absolute cross section value decreases by about a factor of five from  $\Pi$  to  $\Sigma$  ori-



entation. The improved statistics in the present results allows us to even obtain the FDCS in the pure  $\Sigma$  case.

To rationalize the observed phenomena we have utilized Feagin and Reddish's model for H<sub>2</sub> PDI [3]. This model, which uses a single center approach, represents the lowest order approximation in the electron pair angular momentum consistent with homonuclear H<sub>2</sub>. The form of the FDCS simplifies in the equal energy sharing and is given by:

$$\sigma^{(7)} = \begin{vmatrix} (a_{\Sigma} \cos^2 \theta_N + a_{\Pi} \sin^2 \theta_N) \cos \theta_1 + \cos \theta_2 ) \\ + (a_{\Sigma} - a_{\Pi}) \sin \theta_N \cos \theta_N \\ (\sin \theta_1 \cos (\phi_1 - \phi_N) + \sin \theta_2 \cos (\phi_2 - \phi_N)) \end{vmatrix}^2$$

where,  $a_{\Sigma}$ ,  $a_{\Pi}$  are transition amplitudes which depend on  $E_1$ ,  $E_2$  and the mutual angle  $\theta_{12}$  of the two electrons. They account for the process when the molecule is oriented parallel/perpendicular to  $\hat{\varepsilon}$ . For  $\theta_N = 0^\circ$ ,  $90^\circ$ Equation (2) reduces to  $|a_{\Sigma}(\cos\theta_1 + \cos\theta_2)|^2$ and, respectively, corresponding to pure S and P transitions. In general s<sup>(7)</sup> depends on the molecular alignment and it is sensitive to the ratio and relative phase of the amplitudes.

The differential cross section for He at equal sharing is given by, with a single amplitude,  $|a_g|^2(\cos\theta_1 + \cos\theta_2)|^2$ , that is often approximated by the Gaussian function:

$$a_g \Big|^2 \propto \exp \Big[ -4 \ln(2) (180 - \theta_{12})^2 / \theta_{1/2}^2 \Big]$$
 (3)

with the correlation half-width,  $\theta_{1/2}$ , depending solely on  $E = E_1 + E_2$ . This form gives accurate shapes for a wide range of E. The Gaussian ansatz has also been used in the analysis of previous studies in  $H_2/D_2$ , but with restrictive hypotheses (see [2]). In this work we extracted all four parameters as independent variables using a least squares fitting procedure. The whole 3-dimensional  $E_1 = E_2$  coplanar data set has been considered. Our best values are:  $|a_{\Pi}/a_{\Sigma}| = 2.25 \pm$ 0.35,  $\theta_{1/2}^{\Pi} = 73 \pm 2^{\circ}$ ,  $\theta_{1/2}^{\Sigma} = 93^{\circ} \pm 4^{\circ}$ , and  $\delta_{\Pi}$  $\Sigma = 70 \pm 10^{\circ}$ . Firstly, we find that it is impossible to obtain the observed shapes in the coplanar FDCS with  $\delta_{\Pi-\Sigma}=180^{\circ}$ , the value used in all the previous studies. Secondly, we find that  $\theta_{1/2}^{\Sigma} > \theta_{1/2}^{\Pi}$  which is consistent with the variation of angular correlation between



**Figure 3.** Absolute FDCSs for H<sub>2</sub> (**b**, **c**, **d**) and He (**a**) - for E<sub>1</sub> = E<sub>2</sub> = 12.5  $\pm 2.5$  eV (**a**, **b**, **c**) and  $\pm 4$  eV (**d**), in the 'orthogonal' geometry ( $\theta_1 = 90^\circ$ ,  $|\varphi_{12}| = 90^\circ$  or 270°). Molecular orientation:  $|\varphi_{1N}| = 0^\circ$  or 180° (**b**) and  $|\varphi_{1N}| =$  90°or 270° (c, d). The full lines are: (a)  $(\cos\theta_2)^2$ ; (b, c, d) fits with partial waves up to  $\ell = 2$ . Absolute scale given by the maxima : 5.8 barns/eV/sr<sup>2</sup> (a) and 22 (b), 13.9 (c), 6.9 (d) millibarns/eV<sup>2</sup>/sr<sup>3</sup>.

Σ and Π orientations. The width  $\theta_{l/2}^{\Pi} = 73 \pm 2^{\circ}$  for the dominant Π component is significantly smaller than the width for He at the same excess energy. Thirdly, the ion asymmetry parameter  $\beta_N \approx -0.73 \pm 0.1$ , calculated from our value  $|a_{\Pi}/a_{\Sigma}| \approx 2.25 \pm 0.35$ , is fully compatible with previous ion measurements yielding  $\beta_N \approx -0.68 \pm 0.04$  for E = 25 eV [2].

In Figure 3 a second subset of data, where  $\hat{k}_i$  is perpendicular to the plane containing  $\hat{k}_2$ ,  $\hat{\epsilon}$  is reported. The FDCSs for three different molecular orientations and the corresponding results for He (a) are shown. In this geometry, the electron-electron mutual angle is constant and the electron correlation aspect is "frozen". In He the shape of the FDCS is given exactly by  $\cos^2(\theta_2)$  as verified in Figure 3a. For H<sub>2</sub> the shapes of FDCSs differ from  $\cos^2(\theta_2)$  and are all different from each other, contradicting Feagin's model.

This is not so surprising as in the coplanar geometry the dominant physical effect, the angular correlation, is accounted for in the model through the two amplitudes. The orthogonal geometry probes the so-called "kinematical factors" which reduce to the exact  $(\cos\theta_1 + \cos\theta_2)^2$  dependence in He at equal energy sharing. The latter originates in angular momentum conservation in the atomic case, and in the *P* character of the outgoing electron pair. In the molecular case only the projection of angular momentum onto the nuclear axis is conserved, and the outgoing pair may have higher angular momentum and may not have axial symmetry around the  $\hat{\varepsilon}_{\Pi}$  component, as assumed in the theory. Therefore only an approach which uses generalized shape coordinates for the H<sub>2</sub> system [2] may shed some light on the present observations.

In summary the reported analysis of the  $H_2$  break-up has been focused on the effect of molecular orientation on the electron angular distributions. Further investigation, including unequal energy sharing and other dynamical effects – such as the role of the internuclear separation – is in progress.

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# **BIOSCIENCE AND POLYMERS**

Synchrotron radiation has been used for years in the various disciplines relating to soft matter physics and the life sciences. The request of synchrotron beamtime for such applications has been rapidly increasing in recent years. The increase in demand has been paralleled by a diversification of techniques and thematic applications. Established techniques in structural biology, based on X-ray scattering and diffraction, have been extended to the study of systems of increasing complexity, for example composites of synthetic and biological molecules characterized by structuring on the nanometer scale. Novel or upgraded infrastructure, including the introduction of synchrotron FTIR and X-ray microscopy, has augmented the park of techniques available for such applications, extending the range of disciplines that can advantage themselves from the use of synchrotron radiation.

In one application, Binder *et al.* have used SAXS measurements to characterize the formation of pseudo block copolymers via non covalent interactions. The use of hydrogen bonding as a driving force for blockblock interaction allows the authors to tune the assembly and structuring of the system by temperature control. The resulting copolymers display nanophase structuring on the scale of 10 nm. Performing SAXS measurements with synchrotron light allows them to follow temperature induced phase transitions that result in phase formation.

In another experiment, Caracciolo *et al.* have described the phase transitions of DNA/liposome complexes. The systems are of interest as potential vectors for gene delivery in gene therapy. The authors have used SAXS measurements to characterize structuring and phase transitions for complexes with variable lipid composition. The results provide a basis for engineering the properties of the systems in view of an optimized performance for therapy applications.

De Giacomo *et al.* present an application of the new beamline for FTIR spectromicroscopy involving the study of polypeptide polysaccharide mixtures. The mixtures are of considerable technological interest because of their recurrence in food products. The authors show as proof of principle that the technique is applicable to the spectroscopic characterization and imaging of phase separation on the micron scale. In addition they demonstrate the unexpected existence of residual water droplets in the mixtures, even under conditions when evaporation of bulk water was expected.

Massaro *et al.* take advantage of the brightness of synchrotron IR light to perform spectromicroscopy and imaging of retinal rod cells. The measurements confirmed the presence of millimolar concentrations of rhodopsin in the outer segment. Orientation of the rhodopsin polypeptide chain was demonstrated by using measurements with polarized light. Most previous mapping measurements with subcellular resolution were aimed at identifying the location of generic cellular components, such as proteins, lipids, DNA. This experiment proves the viability of synchrotron FTIR to obtain detailed spectroscopic measurements on specific subcellular compartments in proteins and specific molecular components.

Overall the reported activity testifies to an intensification and diversification of applications requiring synchrotron light in soft matter physics and testifies to the ability of Elettra to adapt to developments in its scientific user community.

# POLYMERIC MATERIALS BUILT VIA SUPRA-MOLECULAR ASSEMBLY: STUDIES BY IN-SITU SAXS, REVEALING MODULATIVE BEHAVIOR

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The combination between extremely soft polymers (i.e.: low T<sub>g</sub> polymers exhibiting high chain flexibility) and stiff polymers (i.e.: those characterized by inflexible, rodtype chains with a usually high glass transition temperature) is a technically important task offering the possibility to generate processable materials with high mechanical flexibility. The concept of supramolecular polymer chemistry offers an interesting approach to combine strongly different polymers by use of intermolecular bonds instead of covalent linkages [1,2]. The generation of tunable supramolecular materials made from two strongly phase separating polymeric fragments has become possible by affixing hydrogen bonding elements (showing an A-B type structure) with a vari-

able association strength (i.e.: displaying an association constant of either 800 M-1 or ~3.10<sup>4</sup> M<sup>-1</sup>) onto strongly phase separating poly(isobutylene) (PIB)- and poly(etherketone) (PEK)-polymers respectively in order to combine these two strongly different polymers by use of a directed supramolecular interaction. As depicted in Figure 1, an unusual temperature behaviour, changing between micro- and macrophase separated states can be expected, due to the competing micro/macrophase separation and the attractive hydrogen bonding interactions between the telechelic PIB- and PEK fragments. The complex interplay between microphase- and macrophase separation of the resulting materials (featuring pseudo*block copolymers*, **BCP's**) is demonstrated by

Figure 1. Self assembly of telechelic polymers (PEK and PIB respectively) into pseudo-block copolymers (**BCP1** and **BCP2, BCP3**) by use of two heterodimeric hydrogen bonding systems (thymine/ triazine with an association constant of ~800 M<sup>1</sup> and the Hamilton-receptor/ barbituric acid interactions with ~3.10<sup>4</sup> M<sup>1</sup>).



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Figure 2. SAXS and TEM pictures of the pseudoblock copolymers BCP1, BCP2 and BCP3. (a) TEM-picture of BCP1. The domain spacing is seen as dark stripes of the PEK polymer, separated by stripes of the PIB polymer. The spacing is approx. 14 nm. (b) TEMpicture of BCP2. The microdomains are seen as dark stripes with spacing of approx. 14 nm. (c) SAXS-curves of the pseudo-block copolymers **BCP1, BCP2** and **BCP3**. The scattering curves show the first scattering peak calculating distances of 14 nm (**BCP1**), 14 nm (**BCP2**) and 17 nm (**BCP3**).

use of temperature dependent SAXS-measurements [2].

A solution blending approach of PEKand PIB-polymers was used by simply mixing two PEK and PIB components [3] respectively in a good solvent for the PIBand the PEK-telechelics, followed by evaporation of the solvent and subsequent pressing of the materials (~10 bar) at elevated temperature thus generating the pseudoblock copolymers BPC1 – BPC3. The existence of microphase separated domains consisting of pure PIB- and PEK domains was proven by the presence of two separate glass transition temperatures (BCP1: Tg = (-59 °C; +154 °C); **BCP2**:  $T_g = (-54 \text{ °C}; +151)$ °C). In order to check for the distribution and size of the domains, additional information on the microphase separation was collected from SAXS- and TEM measurements (see Figure 2). Both methods demonstrate the presence of separated PIB- and PEK-microphases with sizes of 14 nm for BCP1 and BCP2, with the PEK-phases appearing dark in the TEM. As expected from the molecular design sheet-like structures consisting of alternating layers of PEK and PIB are observed.

Both polymers (**BCP1** and **BCP2**) were investigated by temperature-dependent SAXS-measurements in order to reveal their phase behaviour as a function of temperature. Additionally, a polymer similar to BCP2, but with higher molecular weights of the PEK-block (**BCP3**;  $M_n$  (PEK) = 5450  $g \text{ mol}^{-1}$ ,  $M_n$  (PIB) = 9600 g mol^{-1}) was investigated. As expected, there is a strong interplay between micro/macrophase separation and the strength of the hydrogen bonding systems between the PIB and PEKtelechelics. Temperature-dependent SAXSmeasurements clearly show the dynamic feature of the hydrogen bonds within the supramolecular polymer BCP1, BCP2 and BCP3. The scattering curves show an increase of the repeating distance with increasing temperature, starting on from about ~100°C. However, materials with different hydrogen bonding systems display very different behaviour when plotting the repeating distance as a function of temperature (see Figure 3). The scattering angle in BCP1 is constant up to temperatures of about 110 °C. At temperatures between 110 °C to 145 °C the scattering angle is reduced, indicating an increase in spacing length. Up to 145 °C this process is reversible, showing the dynamic reversibility of the breaking of the hydrogen bonds versus the phase separation process. Above ~145 °C the scattering angle irreversibly changes to zero, indicative of an infinite d-spacing. At this point (corresponding approximately to the glass transition temperature of the pure PEK-polymer **2b**) the polymer is melting and macrophase separation is observed. From this temperature



Figure 3. Graph relating the spacing <d> of the microdomains against the temperature T. The end of the graphs denotes the point were irreversible macrophase separation is observed. on no reversibility under rebuilding of the previous microphase-separated material **BCP1** is observed.

In contrast, the thermal behavior of the polymer **BCP2 and BCP3** (held together by the more stronger multiple hydrogen bonding system with  $K_{Ass} = 3.10^4 \text{ M}^{-1}$ ) is different as shown in Figure 3. The domain-spacing (observed: 14 nm for BCP2; ~17 nm for BCP3) is stable up to temperatures of ~150 °C, only changing with a slight widening of the microphases, presumable due to reversible opening of the hydrogen bonding systems and subsequent thermal dilatation. At temperatures above 150 °C the distance is increasing more strongly, but is still present up to 230 °C. Up to this temperature the process is still reversible, leading to the initial spacing of 14.5 nm after cooling to temperatures below 150 °C). The moderate widening of the phases above 150 °C may be due to thermal expansion as well as the successive breaking of hydrogen bonds. Only above a heating temperature of 230 °C the dissociation is irreversible, leading again to the formation of a macroscopic two-phase system consisting of isolated PIB and PEK phases. The reversible breaking of the hydrogen bonds at lower temperatures can be demonstrated via temperature sensitive ATR-IR measurements of BCP2. Again, there is a reversible, steady shift of the N-H from 3306 cm<sup>-1</sup> (at 30 °C) to 3330 cm<sup>-1</sup> (at 180 °C), indicative of the breaking of the H-bond (strengthening of the N-H bond). Only above a heating temperature of 230 °C is the dissociation irreversible, leading again to the formation of a macroscopic two-phase system consisting of isolated PIB and PEK phases. Thus this material is entirely fixed together by hydrogen bonds up to temperatures exceeding the glass transition temperature of PEK by ~80 °C (i.e.: 150 °C plus 80 °C = 230 °C), also resisting the macrophase separation process.

In conclusion we have demonstrated a new type of polymeric material, where strong hydrogen bonds simply stick two components together, furnishing materials with a tunable micro- or macrophase separated structure, as proven via SAXS-measurements. The weaker hydrogen bond (thymine/triazine, with an association constant of ~800 M<sup>-1</sup>) can stabilize the microphase-separated material up to temperatures corresponding to the Tg of the PEK component. A stronger association between the components is achieved with a stronger bond (i.e.: Hamilton receptor/barbiturate;  $-10^4 - 10^6 \,\mathrm{M}^{-1}$ ), leading to a stabilization of the material up to 80 °C above the glass transition temperature of the PEK-component within the pseudo-block copolymer. It turns out, that SAXS-measurements are the best method to follow the dynamic behavior of the supramolecular material in real time. Moreover, this example demonstrates a new dynamic feature of these pseudo-block copolymers leading to materials with a variety of tunable properties useful as switchable coatings and processable polymers combining a multitude of different material features. It can be envisioned, that the presented method allows the combination of nearly all different kinds of polymeric materials, thus opening a strong method for the formation of (nano-)composite materials, where microphases can be tuned and reversible arranged.

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# MULTI-COMPONENT CATIONIC LIPOSOME/DNA COMPLEXES: NEW EFFICIENT VECTORS FOR GENE DELIVERY

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Medical research continues to illuminate the origins of many human diseases. Gene delivery has been widely proposed as a novel strategy by which this knowledge can be used to deliver new and improved therapies. The recent conclusion of the working draft of the human genome mapping has strongly reinforced the hope of using gene medicines to combat genetic diseases. At present, the most common method of gene delivery uses viral-based carriers of DNA. But viral vectors have their shortcomings not the least of which is the potential for disease transmission. Recently, tragic setbacks in clinical trials with viral vectors occurred: the death of a patient due to a severe immune response induced by engineered adenovirus vectors and the insertional mutagenesis caused by retroviral vectors. As a result, urgency for developing efficient nonviral vectors has immediately arisen as shown by the persevering research activity involving nonviral strategies that is currently unprecedented. Therefore, the development of an efficient non viral vector remains a highly desirable goal. Among non viral strategies, cationic liposomes (CLs) -binary mixtures of cationic and neutral "helper" lipids- are currently the most promising gene delivery vectors both in vitro and in vivo. By using a plethora of experimental techniques, a variety of structures was observed with topology controlled by the choice of the helper lipid. In the so-called multilamellar  $L^{C}_{\alpha}$  phase DNA chains are condensed between opposing cationic lipid membranes in the liquid-crystalline phase while the inverted hexagonal phase  $H_{II}^{C}$  is comprised of lipid-coated DNA

strands arranged on a hexagonal lattice. As with most synthetic transfection systems, the use of CL-DNA complexes, referred to as lipoplexes, is limited by our poor understanding of the mechanism of formation, of the structure-activity relationship. This lack of knowledge is essentially due to the high



Figure 1. At the top: schematics of the inner structure of lamellar  $L_{a}^{C}$ phase, with alternative lipid bilayers and DNA monolayers, the repeat spacing is given by  $d = d_{B} + d_{W}$ Representative SAXD patterns of A-B-DNA complexes as a function of increasing molar percentage of B liposomes in the lipid dispersions  $R_{AB} = A/(A+B)$ from the bottom to the top: **(a)** *R*=0; **(b)** *R*=0.4; (c) *R*=0.6; and (d) *R*=1. Intermediate SAXD patterns (b) and (c) do not arise from the linear combination of (a) and (d) patterns. DNA-DNA peak is marked by a black arrow.

MULTI-COMPONENT CATIONIC LIPOSOME/DNA COMPLEXES: NEW EFFICIENT VECTORS FOR GENE DELIVERY

Figure 2. Mechanism of formation of mixed multi-component lipoplexes. When adding DNA to one mixed dispersion containing DOTAP/DOPC (A) and DC-Chol/DOPE (B) binary cationic liposomes (top, on the right) or to a dispersion containing DOTAP/DOPE (C) and DC-Chol/DOPC (D) binary cationic liposomes (top, on the right), DNA induces aggregation and fusion of liposomes and a large lipid mixing occurs. As a result, only multi-component lipoplexes exist. Identical lipoplexes can be formed by adding DNA to a mixed dispersion containing A, B, C and D binary liposomes or, alternatively, to one dispersion of quaternary DOTAP/DOPE/DC-Chol/DOPC CLs. The formation of multicomponent lipoplex does not depend therefore on which liposomes the lipid dispersion is composed of, the only relevant condition being the equimolar composition of lipid species. For clarity, each color refers to a specific lipid species.



complexity of the self-assembly process. Nevertheless, it is well accepted that decoding the underlying molecular mechanisms may yield new therapeutic means for a large quantity of disorder. Within this frame, we have recently prepared multi-component lipoplexes and we have also investigated the mechanism of formation of lipoplexes by performing synchrotron small angle x-ray diffraction (SAXD) experiments at the Austrian SAXS station of the synchrotron light source ELETTRA. Cationic lipids 1,2-Dioleoyl-3-Trimethylammonium-Propane (DOTAP) and  $(3\beta_{N-(N_N-dimethy$ laminoethane)-carbamoyl]-cholesterol (DC-Chol) and neutral lipids dioleoylphosphatidylethanolamine (DOPE), and dioleoylphosphocholine (DOPC) were purchased from Avanti Polar Lipids (Alabaster, AL, USA) and used without further purification. Multilamellar DOTAP/DOPC (A), DC-Chol/DOPE (B), DOTAP/DOPE (C)

and DC-Chol/DOPC (D) binary CLs were routinely prepared at a molar ratio of neutral lipid in the bilayer  $\Phi$ =(neutral lipid/total lipid) (mol/mol)=0.5. First, mixed lipid dispersions were prepared by mixing different populations of binary cationic liposomes. Preliminary SAXD measurements on mixed lipid dispersions with no DNA added revealed that, upon mixing of distinct CLs, no fusion occurs. Indeed electrostatic charges localized on the surface of liposomes create a repulsive barrier which dominate over short-range attractive van der Waals forces and prevent membranes aggregation and fusion. Then we injected DNA into mixed lipid dispersions containing A and B CLs at seven relative molar ratios  $R_{AB} = A/(A+B) = (mol/mol) = 0, 0.2, 0.4, 0.5,$ 0.6, 0.8, 1. SAXD patterns of Figure 1 show that, for each R<sub>AB</sub> value, only mixed A-B lipoplexes do exist. In principle, the presence of A-DNA and B-DNA rich domains can

not be excluded at all. Nevertheless, several reasons arise that a complete lipid mixing at the molecular level occurs. First and foremost, the SAXS patterns of Figure 1 did not arise from the superposition of the patterns of A-DNA and B-DNA lipoplexes (d and a panels of Figure 1). In addition, the lamellar spacing d varied monotonously as a function of RAB whereas the full width at half maximum (FWHM) of all the Bragg peaks was the same within experimental errors. Further support to this interpretation was also provided by DNA packing density within mixed lipoplexes. Indeed, lamellar lipoplexes adjust the interaxial spacing  $d_{DNA}$ in order to minimize the total free energy by separating the DNA strands. If lipid mixing was not almost complete and different DNA packing density regimes existed, there distinct DNA peaks would be certainly detected. In contrast, we noted that all the SAXS patterns of Figure 1 exhibited a single DNA peak (marked by arrow). Undoubtedly, A–B-DNA lipoplexes can exist only if A and B liposomes break up during complex formation. As liposomes fusion was not observed merely by mixing A and B, it was therefore the DNA which allowed the liposomes to come into contact, aggregate and fuse by reducing the intermembrane repulsive barrier due to electrostatic, steric and hydration forces. DNA acted therefore as a molecular glue enforcing close apposition of vesicles. Upon fusion of A and B liposomes, the lipid bilayer, being a fluid mixture, allowed for lateral diffusion of lipid molecules leading to a spatial distribution of the four lipid species, on average, uniform. The same experiment was replicated by adding DNA to a mixed dispersion containing C and D CLs as a function of  $R_{CD}=C/(C+D)$ . Significantly, we observed that the inner structure of C-DNA lipoplexes (coexisting

 $L_{q}^{C}$  and  $H_{\parallel}^{C}$  phases) closely resembled that of pure C membranes (coexisting  $L_{\alpha}$  and  $H_{//}$ phases) with the water space inside the inverse micelle of the hexagonal phase and the interbilayer water region of the lamellar phase both filled by DNA. It means that, upon complexation, DNA let C liposomes break up and penetrate the accessible water regions. Conversely, we observed that C-D-DNA lipoplexes were only assembled in the lamellar phase. Thus, some molecular events occurring during C-D-DNA lipoplexes formation were able to induce the  $H_{II} \rightarrow L_{\alpha}$ phase transition of C membranes firstly assembled in the  $H_{//}$  phase. Although we identified DNA-induced liposomes fusion as the first step in the lipoplex formation, it could not be the DNA to induce the observed  $H_{II} \rightarrow L_{\alpha}$  phase transition. By comparing the different phase behavior of C and C-D lipid dispersions upon lipoplex formation we argued that lipid mixing was the driving force that induced the observed phase transition. While no detectable structural change can be observed if lipid dispersion is only composed of C vesicles, lipid mixing occurring during C and D liposomes fusion can produce evident structural changes. Indeed, cationic DOTAP and neutral DOPC have a cylindrical shape with the cross section area of headgroups approximately equal to the hydrophobic chain area. Thus they tend to self-assemble into lamellar structures with a spontaneous curvature  $C_0=1/R_0=0$ . DOPE, due to its cone-like molecular arrangement, gives rise to a negative natural curvature and forms inverted hexagonal phases. Thus, lipid mixing gradually reduced the relative molar percentage of DOPE in the emerging lipid bilayer with respect to pure C membranes and the lamellar phase becomes more and more favored with respect to the inverted hexagonal one as

Table 1. Structuralparameters of multi-component lipoplexes.Within experimentalerrors, structure wasfound to be unique anddid not depend on thekind of cationicliposomes the lipiddispersion is composedof but it only dependedon the number andmolar ratios of the lipidspecies.

	d (Å)	d <sub>B</sub> (Å)	d <sub>w</sub> (Å)	d exp (Å)	s <sub>м</sub> (10 <sup>-3</sup> e/Ų)	
AB-DNA	65.9	38.2	27.7	33.7	7.8	
CD-DNA	66.2	38.4	27.8	33.1	7.9	
ABCD-DNA	66	38.2	27.8	33.7	8.0	
E-DNA	66.2	38.4	27.8	33.5	7.8	

a function of increasing content of DOPE. Lipid mixing therefore induced the hexagonal  $\rightarrow$  lamellar phase transition by controlling the spontaneous curvature of the emerging membranes [2]. With the aim of providing all the relevant structural parameters of A-B and C-D lipoplexes, electron density profiles (EDPs) along the normal to lipid bilayers were calculated from the SAXD patterns of both A-B/DNA and C-D/DNA lipoplexes. EDPs allowed us to calculate the lipid bilayer thickness,  $d_B$ , the thickness of the water region occupied by DNA molecules,  $d_W$ , and by applying a recently developed model, to estimate the surface charge density of mixed membranes,  $\sigma_M$ . Interestingly, EDPs showed that A-D and B-C lipid bilayers exhibit identical physical properties, such as bilayer thickness, thickness of the water gaps, and surface charge density (Table 1). Our finding was of central importance since it opened the door to the rational designing of multi-component lipoplexes to be performed just by varying the composition of lipid dispersions. It was a significant result. Indeed, the engineering of multi-component lipoplexes, incorporating the specific properties of very different lipid species, may represent the starting point for rationally designing highly specific gene vectors. Lastly, we showed that the equilibrium structure of multi-component lipoplexes was found to be unique and did not depend on the number and kind of populations the lipid dispersion is composed of but only on the lipid species involved and on their relative molar ratio (Figure 2). By using a functional of free energy calculated for lamellar lipoplexes by Harries et al., we also could demonstrate that spontaneous formation of multi-component lipoplexes is a thermodynamic process driven by two-dimensional (2D) lipid mixing entropy. With the aim of investigating the structure/activity relationship of lipoplexes and their ability to transfer DNA into cells, we performed transient transfection assay of mouse fibroblast cell lines (NIH 3T3) and A17, which is a tumoral myofibroblast-like cell line, established from a mouse mammary carcinoma model established from a mouse mammary carcinoma model (FVB/neuT transgeneic mice). To this end, we chose two binary systems, DOTAP-DOPC/DNA and DC-

Chol-DOPE/DNA and the four-component lipid system incorporating all the lipid species simultaneously. TE experiments have shown that multi-component lipoplexes are extremely efficient and promising vectors for gene delivery applications.

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### INTRODUCTION

Natural polymers are widely used in many applications ranging from medicine to food engineering, being their main advantages abundance, biocompatibility and biodegradability. Growing interest in several technology areas has promoted many investigations for the understanding, characterisation and design of biopolymer matrices, based on mixtures of polysaccharides and proteins, with a suitable texture for every specific function required. Most of the examples of biopolymer matrices and films are in the food field, whereas high-value non-food applications come from the biomedical field, such as drug-delivery, tissue engineering, cell scaffold and enhancement of transplants performance and biocompatibility.

The fundamental idea in texture tailoring lies on the possibility of modulating the thermodynamics of biopolymer phase separation with the kinetics of biopolymer aggregation and gelation. While the thermodynamics of phase-separated aqueous mixtures of biopolymers has already been studied in some detail, there is little or no information at all for the low-moisture state, like films or blends. As a consequence, also the kinetics governing mixed gelation is almost unexplored. The importance of filling this gap is that physical and chemo-biological properties are functionally dependent on the microscopic structure of materials.

The major obstacle for the morpho-structural characterisation of biopolymer composites resides in the absence of detectable contrast, often by-passed by labelling specific groups with fluorescent probes, as in confocal laser microscopy, staining, etc, introducing however other substances to the system or altering the original components by chemical reactions. Unlike most instrumental techniques, FTIR spectroscopy probes the very chemical nature of the components and samples needs neither staining nor labelling, which makes it suitable and attractive for a vast range of applications and materials.

In this work, the results of a FTIR microspectroscopy analysis performed on a mixed gelling system of a protein (gelatine) and a polysaccharide (maltodextrin) are presented.

# MATERIALS AND METHODS

Gelatine sample is the first extract of alkaline-processed lime hide, kindly provided by Systems Bio-Industries (SBI), purified by dialysis at 38 °C, with molecular weight 1.2 10<sup>4</sup>. Maltodextrin (Paselli SA-2) is a commercial product obtained by enzymatic hydrolysis of potato starch and was kindly provided by Unilever Research, UK. The polysaccharide is characterised by a bimodal distribution of molecular weight, namely 8 10<sup>5</sup> and 7 10<sup>3</sup>, and by its low rate of crystallisation. Both biopolymer samples have been amply characterised in the framework of a EC project (FAIR CT 96-1015).

Solutions with 2% w/w gelatine or maltodextrin were prepared by swelling the biopolymers in deionised water. Dispersions were kept under stirring at 60°C, until clear and transparent. Equal volumes of gelatine and maltodextrin solutions were mixed to obtain a 2% final concentration solution. A small volume of this mixed solution was poured on the golden surface of a CFR (corner frosted) 1 x 3 inch MirrIR slide (Kevley Technologies, Chesterland, OH), as meas-



Figure 1. Spectral features of Gelatine, Maltodextrin and their mixture. The spectrum of the blend maintains the characteristic frequencies of the single biopolymers.

Figure 2. Sample RT (Room Temperature). Chemical mapping of: (a) Gelatine, (b) Maltodextrin, (c) Gelatine over Maltodextrin Ratio, and (d) water. The ratio corrects the effects of topography, giving a more realistic view of the distribution of polymers. urements were performed in reflexion configuration (transmission). Samples were prepared according to different procedures and water evaporated at low (C), room (RT) and high (H) temperatures (at 10°C, 25°C and 50°C respectively).

Films were studied at the SISSI (Source for Imaging and Spectroscopic Studies in the Infrared) beamline, Elettra Synchrotron Radiation Facility in Trieste, Italy. Beamline Instrumentation includes a Bruker VER-TEX 70 digital FT-IR spectrometer, connected to a Bruker Hyperion 3000 Microscope. The interferometer-microscope pair was operated in the mid-IR configuration, using a KBr beamsplitter and a single element MCT detector. Spectra were recorded in transmission with 4 cm<sup>-1</sup> resolution, in the 600 - 4000 cm<sup>-1</sup> range. The number of scans per sample and the aperture settings were changed depending on the signal to noise ratio. Data were analysed using OPUS software (Bruker). Interferograms were



apodized with a Blackman-Harris 3 term function and extended using a 2 zero filling factor before performing the Fourier transform.

Spectra were integrated taking the area under the curve between two frequency limits and a baseline properly selected. The region chosen for gelatine includes Amide I and II absorption bands at 1630 cm<sup>-1</sup> and 1540 cm<sup>-1</sup> while for maltodextrin, the glycosidic linkage absorption in the 1170-980 cm<sup>-1</sup> region. (see Figure 1) In addition, for RT sample, water absorption bands at the 2100-2700 cm<sup>-1</sup> interval have been integrated.

#### **RESULTS AND DISCUSSION**

A series of spectra were acquired consecutively by raster scanning of a surface over a region of interest, and reassembled by the software to represent the spatial (and topological) distribution of the different chemical species in the original area. Having known the main spectral features of each component, the "chemical fingerprint", it was possible to create a map representing the intensity of the absorption of IR radiation due to the selected chemical groups. In other words, this integration procedure provided the chemical mapping of the sample. The extension of the map is established as a compromise between the time of measurement and the minimum representative surface, and the lateral resolution is determined by the size of the apertures, which is generally around 10-15 m with a conventional globar source. The higher the signal to noise ratio, the smaller the apertures -- and so the resolution- can be. While working with a synchrotron source, because of its high brightness (photons flux per source area and solid angle) and coherence, the signal to noise ratio is remarkably improved and spatial resolution is determined by radiation's diffraction limit. Although this phenomenon determines the physical limit where intensity starts to fall drastically, there are plenty of examples in literature where apertures are set well beyond the diffraction limit [1] as in our case, where apertures are 4x4 µm (RTsamples)  $5x5 \ \mu m$  (C-samples) and  $6x6 \ \mu m$ (H-samples).

In the following results, three samples prepared in different ways, at low (C), room

IR MICROSCOPY OF BIOPOLYMERS UNDERGOING PHASE SEPARATION AT THE SISSI BEAMLINE



Figure 3. Gelatine/Maltodextrin ratio for samples: C

(RT) and high (H) temperatures (at 10°C, 25°C and 50°C respectively) are shown to discriminate the effect of kinetics and thermodynamics on the texture of the final product.

The first important information arises from the spectrum of the mixture. It can be seen in Figure 1 that the spectrum of the blend can be obtained by adding the spectra of the single polymers. This is possible only if there is no chemical reaction or strong physical interaction between components, otherwise peaks would shift in frequency or change shape. Another important feature is water vibrations, which are present in the 2000-2400 cm<sup>-1</sup> region. They are quite unexpected, since water should evaporate almost completely, but still occur in the sample RT, shown in Figure 2. The maps in the Figure correspond to the intensity distributions for gelatine (a), maltodextrin (b), gelatine/maltodextrin ratio (c), and water (d). Phase separation is evident, and there are some complementarities in the intensity distributions. The water bubbles are clear in d, where the top of the intensity of water seems to be associated to a polysaccharide rich zone, surrounded by a protein ring.

Figure 3 shows the maps reporting the intensity of gelatine/maltodextrin ratio for the three samples. This kind of representation compensates the thickness variation in the sample and therefore gives an interpretation of the biopolymer(s) distribution more realistic than the absolute value of intensity. Thus, the different curing temperature in sample preparation clearly show that at high temperature (HT) the phase separation involve a massive biphasic system, given the absence of gel formation of both gelatine and maltodextrin. The point of higher ratio (in pink) has three times more

gelatine than a point of low ratio (blue). Conversely, at low temperatures (C) the gelation process arising for gelatine is almost completed before the phase separation can be extended over droplets of a few microns; therefore, although separation is present, the spots are of a minor size than in sample HT. This is confirmed also by the fact that the extremes in the scale of the ratio changes slightly, so from a maximum to a minimum there is a difference of about 20%. Samples stored at room temperature (RT) lie between these two structures.

The relevant result on the gelatine-maltodextrin system taken as a model for more complex and naturally occurring samples concern the possibility to follow the microstructure formation of a solid phase composite without any chemical perturbation and to get information about the interaction between biopolymers with a single and simple technique.

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# INVESTIGATION OF INDIVIDUAL PHOTORECEPTOR ROD CELLS BY FT-IR SPECTROMICROSCOPY

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Rod cells are involved in the detection of weak light by the retina and are responsible for achromatic night vision. The cells possess a highly specialized extension denominated the outer segment (ROS) that contains the molecular components of the phototransduction cascade. ROS are filled with a stack of about 1000 flattened membrane disks and incorporate photosensitive rhodopsin molecules and other proteins involved in signal amplification and transduction. The outer segment is connected to the rod inner segment (RIS) where metabolic processes occur. Absorption of light by rhodopsin in the outer segment triggers a cascade of intracellular events which eventually results in a cellular response. Key events in this transduction cascade have been identified by extensive studies using various techniques [1]. Numerous in vitro studies have already been carried out on the

Figure 1. Absorption spectra of outer segment (blue) and inner segment (green) of a rod cell.



infrared spectroscopic characterization of changes occurring during excitation of rhodopsin in rod cells [2].

#### SINGLE CELL MEASUREMENTS

We applied Fourier Transform Infrared (FT-IR) microspectroscopy with synchrotron radiation to study individual retinal rod cells. Our work aims to repeat in vivo some of the experiments performed for in vitro systems and to gain new insight into different aspects of the transduction cascade initiated by photoexcitation. We recorded IR absorption spectra of rod cells from Bufo regularis in transmission mode using the synchrotron IR emission from the beamline SISSI. Rod cells from amphibians are about 5-10 µm wide and spectromicroscopy measurements require the use of an IR microscope with the confocal apertures closed down to 4-6 microns in size. For wavelengths in the mid-IR range this corresponds to the diffraction limit and requires the use of a synchrotron light source.

We characterized the absorbance due to the Amide I band in the range 1600-1700 cm<sup>-1</sup>. The band is of interest because of its sensitivity to the secondary structure of proteins. It is often used with pure protein samples to estimate their composition in terms of secondary structure. Spectra recorded from the outer segment show an Amide I absorption band peaking at 1656 cm<sup>-1</sup>, characteristic of large concentrations of  $\alpha$ -helical protein (Figure 1). This is consistent with the presence of rhodopsin, estimated to be about 5 mM in concentration. In contrast, spectra recorded from the inner segment display Amide I peaks, centred between 1645 and 1650 cm<sup>-1</sup>. The shape and position of the band are due to the absorption of the complex mixture of proteins that is present in the inner segment, comprising both  $\alpha$ -helix rich and  $\beta$ -sheet rich proteins. The latter have Amide I maxima closer to 1630 cm<sup>-1</sup> and their contribution is likely responsible for the downshift of the apparent Amide I peak position.

We tested the conclusion that the Amide I absorption band for the outer segment is dominated by rhodopsin absorption by performing spectromicroscopy measurements with polarized IR light. Rhodopsin is a transmembrane protein constituted by seven transmembrane  $\alpha$ -helical segments oriented nearly perpendicular to the membrane plane. Within a rod cell, rhodopsin molecules are therefore expected to be on average oriented along the rod cell axis. Such an anisotropic system is expected to display polarization effects, with preferential absorption of IR light with a specific polarization. Figure 2 shows the spectra of rod outer segments in D2O-Ringer's solution recorded with light polarized parallel and perpendicular to the rod longitudinal axis. The spectra display a clear difference in absorption in the Amide I region, with maximum difference at 1660 cm<sup>-1</sup>, corresponding to the  $\alpha$ -helix contribution being polarized along the rod axis. Other contributions to the Amide I band on the lower frequency side appear also polarized but in the opposite direction, indicating that some degree of orientation is observed also for  $\beta$ -sheet containing proteins.

We performed IR mapping of rod cells. Cells were submerged in  $D_2O$ -based Ringer's solution to prevent dehydration and the solution was sandwiched between two



 $CaF_2$  optical windows. We studied the region of the Amide I band by plotting the ratio of absorbance at frequencies characteristic of  $\alpha$ -helix and  $\beta$ -sheet absorption. This provides us with a representation of the relative abundance of the two types of secondary structure throughout the cell. Maps of the ROS (Figure 3) show the presence of abundant  $\alpha$ -helical proteins throughout the outer segment, as expected from single spot measurements. In most maps the shape of



Figure 2. (a) Polarized absorption spectra of rod outer segments recorded with light polarized parallel (blue) and perpendicular (red) to the rod longitudinal axis. (b) Dichroism spectrum (parallel minus perpendicular).



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the distribution of  $\alpha$ -helical protein displays a narrowing in the region between the outer and inner segment. This corresponds to the location of the cilium, where the disks start to form from folding of the cytoplasmic membrane and are still reduced in diameter. In contrast, the inner segment is characterized by the presence of contributions from proteins of more varied conformation.

## **CONCLUSIONS AND FUTURE PERSPECTIVES**

Single cell spectroscopy and mapping have been a successful application of infrared spectromicroscopy with synchrotron light, because of the inadequacy of conventional light sources for a task requiring such high resolution and signal-to-noise. The technique has already been used to characterize changes occurring in individual cells during regular life cycle evolution or as a consequence of chemical stimuli [3]. In all such cases, the complexity of the system and of the changes under study prevented a detailed interpretation at the molecular level. In contrast to other cellular systems studied so far, ROS possess a relatively simple composition, with few abundant proteins, and provide an interesting case where spectroscopic information can be translated into specific structural information and molecular events can be observed. In our experiments we have shown that it is possible to detect the secondary structure of the major protein components of ROS. In addition we have been able to perform polarized IR spectromicroscopy measurements on a portion of a cell for the first time. Overall this work has been a proof of principle for the feasibility of more advanced and potentially more informative IR spectroscopic studies at the subcellular level. For example, it paves the way for functional studies where the effect of stimulation by light is followed by IR spectromicroscopy.

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# **CONDENSED MATTER PHYSICS**

Nanoscience is considered a cutting-edge research area, uniting the fields of physics, chemistry, biology and molecular medicine. New generation of researchers, attracted by the inter-disciplinarity and exciting new phenomena, are contributing to revolutionizing technology by gaining precise control over the matter.

Synchrotron radiation has provided tools to the scientist in exploring and solving a wide variety of open questions in nanoscale physics. They include: dimensions of phase separation domains in strongly correlated systems, magnetic domain structure, magnetic multilayers, quantum dots, nanocrystal and macromolecules, as well as inhomogeneities leading to static and dynamic anomalous behaviour at wavelengths typical of the soft X-ray region.

Enormous effort, made in the last years at ELETTRA, have demonstrated that the capability of the laboratory and its staff to tackle new insights in the condensed matter physics on the nanometre and atomic length scales.

This section illustrates how different spectroscopic techniques like X-ray magnetic circular dichroism, photoemission, inelastic ultraviolet scattering and electron microscopy have provided results at the forefront of nano-science research.

P. Schattschneider and collaborators took advantage of the combined use of synchrotron radiation and a transmission electron microscope to provide a new method for the analysis and characterization of magnetic materials down to the nanoscale. The authors have measured the magnetic circular dichroism of Fe/GaAs both with electrons and X-Rays showing that the spectra obtained contain comparable spectroscopic features. This opens up the possibility for studies of magnetic properties down to nanometre scales.

Circular magnetic dichroism has been used also by L. Sangaletti et al to detect for the first time, the ferromagnetic ordering af a Mn:Ge metallic thin film used as a seed layer for the growth of Mn<sub>5</sub>Ge<sub>3</sub>: a possible candidate for spintronic devices.

The third contribution to this section (M. Kläui et al) reports on the study of the interplay between spin polarized currents and domain walls in NiFe wires. The authors observed the effect of electrical currents on the propagation and spin structure of vortex walls in the sample discovering that magnetic vortices are nucleated and annihilated due to the spin torque effect.

Measurements of the dynamic structure factor of vitreous silica by  $\mu$ eV resolution inelastic UV scattering (C. Masciovecchio et al) have demonstrated the existence of a cross-over in the sound attenuation coefficient. This is interpreted as the existence of a critical length scale (of the order of 40 nm) below which classical continuum elasticity breaks down. This result calls for a revision of old ideas on the thermal conductivity of glasses.

Claudio Maschiovecchio

# FIRST EVIDENCE OF CIRCULAR MAGNETIC DICHROISM IN THE TRANSMISSION ELECTRON MICROSCOPE

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Figure 1. Simplified TEM scattering geometry: Bragg diffraction creates a coherent superposition of two incident plane waves ( and ) in the Fe crystal. A phase shift of  $\Pi/2$  is set between the two wave fronts by tilting the incoming beam. The detector (or a contrast aperture) selects and. The dotted circle represents the points for which is perpendicular to. The full circles show the two positions for which also the condition is true and indicate the actual experimental setup. As the two positions "+" and "-" have opposite chirality, EMCD can be detected by acquiring spectra at the two positions and taking their difference.

Dichroism is the property of certain materials that their photon absorption spectrum depends on the polarisation of the incident radiation. In the case of X-Ray Magnetic Circular Dichroism (XMCD) the absorption cross-section of a ferromagnet or a paramagnet in a magnetic field changes when the helicity of a circularly polarised probing photon is reversed relative to the magnetisation. Although the similarities between Xray absorption (XAS) and electron energy loss spectra (EELS) in the transmission electron microscope (TEM) have long been recognised, it was presumed that extending such equivalence to circular dichroism would require a beam of spin polarised electrons. In 2003 it was argued on theoretical grounds that this is wrong [1]. This finding has been recently proved experimentally by comparing Electron Energy Loss Magnetic Chiral Dichroism (EMCD) results achieved in a TEM with XMCD spectra from the same specimen, under particular scattering conditions [2]. A first step in studying linear magnetic dichroism in a TEM was taken in 1997 [3]. This discovery was made possible by the earlier consideration that the polarisation vector  $\vec{\epsilon}$  in XAS is formally equivalent to the momentum transfer  $\hbar \vec{q}$  in electron scattering. A further step can be taken if we extend such equivalence to circularly polarised photons considered as a superposition of two linearly polarised waves de-phased by 90° (formally represented by the imaginary unit i). We consider therefore  $\vec{q} \pm i\vec{q}'$  with  $\vec{q}$  perpendicular to  $\vec{q}'$  and  $|\vec{q}| \pm |\vec{q}'|$ , where  $\hbar \vec{q}$ ,  $\hbar \vec{q}'$  are momentum transfers in electron impact ionisation. The inelastic electron scattering cross-section is proportional to a sum over squared matrix elements of the form  $|\langle f | \vec{q} \cdot \vec{r} | i \rangle|^2$  for dipole allowed transitions from initial atomic states  $|i\rangle$  to final empty states  $|f\rangle$ . Expanding  $|\langle f|(\vec{q}+i\vec{q}') \bullet \vec{r} |i\rangle|^2$  we obtain



two direct and one interference term. The situation is similar to the double slit experiment where a coupling term between plane waves with wave vectors  $\vec{q}$  and  $\vec{q}'$  gives rise to interference fringes. In this case the double differential inelastic scattering cross section  $\sigma$  with respect to the energy loss E and solid angle  $\Omega$  for fast electrons reads:

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} \propto \frac{1}{q^4} \{ S(\vec{q}, E) + S(\vec{q}', E) + 2 \text{Im}[S(\vec{q}, \vec{q}', E)] \}$$

The first two terms in brackets are Dynamic Form Factors (DFFs). They describe inelastic scattering of an incident plane wave into an outgoing plane wave with wave vector transfer  $\vec{q}$  and energy loss E. They appear in angle resolved EELS and produce directional dependence of spectra in anisotropic materials. The last term in brackets is the Mixed Dynamic Form Factor (MDFF [2-3]). The interference term is ultimately responsible for the dichroism: The two incident plane electron waves are de-phased by a quarter of a wavelength causing the appearance of the imaginary part in the equation. This can be achieved by the experimental setup shown in Figure 1. The energy loss spectra are measured in the diffraction plane with simultaneous wave vector transfer of  $\vec{q}$  and  $\vec{q}'$  from the coherent plane wave sources (000) and (110). The necessary phase shift of

$$\frac{2\pi\delta z}{\lambda} = \frac{\pi}{2}$$

(where  $\lambda$  is the electron wavelength and  $\delta z$ the difference in the optical path) between the transfer vectors is realised by an excitation error of w = 0, i.e. in the exact twobeam case of a systematic row of Bragg spots. Shifting the detector from position "+" to "-" is equivalent to the exchange of  $\vec{q}$ and  $\vec{q}'$  thus reversing the sign of the phase shift. We chose Fe for the experiment since the Fe L<sub>2,3</sub> ionisation edge shows a strong dichroic effect. In XAS it shows up as a variation of the intensity ratio of the L<sub>3</sub> and the  $L_2$  edges when the helicity of the photon is changed. The magnitude of the dichroism is represented by the difference between the two spectra. A (10±2) nm thick Fe single crystal film was epitaxially grown in UHV



on top of a GaAs [001] self-supporting substrate previously thinned and ion milled to electron transparency and protected by 2.5 nm of Cu. Remanent in-plane magnetisation was determined by measurements of transverse and longitudinal Magneto Optic Kerr Effect (MOKE): the MOKE hysteresis loops indicated a coercive field of 80 Oersted and full remanence in the (100) inplane easy magnetisation direction. The substrates suitable for both XAS and TEM experiments, were prepared at the centre for electron microscopy at TASC-INFM-CNR laboratory, then the magnetic film was deposited and transferred in UHV to the APE-HE (High Energy) endstation for XMCD measures. Circularly polarised X-Rays were focussed to a 50 µm spot on the sample surface, at 45° incidence. The dichroic signal was obtained by scanning in energy over the Fe  $L_{2,3}$  edge and by reversing the photon helicity, as well as, for a given Xray helicity, by rotating the sample by 180° around an axis perpendicular to its surface. Representative data are plotted in Figure 2. A further capping layer of 2 nm of Cu was deposited to prevent Fe layer oxidation. EELS spectra were taken in Vienna on a FEI Tecnai F20-FEGTEM S-Twin equipped with a Gatan Image Filter. A flat region of 100 nm radius and uniform thickness was selected in a single grain of Fe. Chemical microanalysis revealed negligible traces of contaminants (C, O and Mo). The sample is immersed in the magnetic field of the TEM objective lens pole piece, which is

**Figure 2.** XMCD at Fe L<sub>2,3</sub> edge of epitaxial iron on GaAs(001). The full and dashed curves are obtained by reversing the handedness of circular polarization at each energy. The magnitude of the dichroism is represented by the difference (dotted) spectrum.



**Figure 3.** EMCD. Measured **(a)** and simulated **(b)** Fe L<sub>2,3</sub> edges for 10 nm Fe on GaAs (001) in the two configurations "+" and "-" as in Figure 1. The difference (magnified by a factor of 5) is 0.07 for the measured spectra and 0.32 for the simulations. The *r.m.s* of the noise is

 $\pm$  8% of the difference.

approximately 2 Tesla and oriented perpendicular to the surface. The magnetisation of the iron film in the TEM experiment is therefore saturated in the out-of-plane direction by a field large with respect to the inplane coercitivity. This is crystallographically equivalent to the in-plane magnetisation used in the XMCD experiment. The measured spectra are shown in Figure 3. The dichroic signal is given by the difference between the two spectra taken at the position "+" and "-". For the simulations of the EMCD spectra we used the electronic structure calculated with the WIEN2k code - a full-potential, fully- relativistic Augmented Plane Wave code. EMCD spectra require evaluation of the MDFF. For this purpose we extended a program for the calculation of inelastic interference terms to the case of two perpendicular momentum transfers  $\hbar \vec{q}$  and  $\hbar \vec{q}$  [2]. A comparison (Figure 3) with the TEM experiment shows that the observed dichroic signal is smaller than predicted. This can be qualitatively understood by considering the effects of the simplifications we used: as the  $\vec{q}$  selecting aperture is placed on the (200) spot of the GaAs substrate, a large part of the collected signal is non-dichroic Bragg and thermal diffuse scattering. The (200) GaAs spot contributes more than 50% of non-dichroic intensity by coupling of quasi-elastic (Bragg) to inelastic scattering. Moreover, the integration of the signal over the finite Spectrometer Entrance Aperture and the non-zero convergence angle reduces the dichroic effect [2]. Both EMCD and XMCD of Fe/GaAs sample show comparable spectroscopic features, referred to either remanent or forced magnetisation. Our results provide a new method for the analysis and characterisation of magnetic materials at the nanometer scale, capable of addressing key problems in modern magnetic materials. In combination with the analytical and crystallographic tools available in a TEM, EMCD may become a key microscopic method in nanomagnetism.

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# FERROMAGNETIC THIN LAYERS IN THE Mn:Ge(111) SYSTEM PROBED BY DICHROIC SOFT X-RAY SPECTROSCOPY

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The discovery of ferromagnetism in Mn<sub>x</sub>Ge<sub>1-x</sub> dilute alloys has triggered a large number of studies of the electronic and magnetic properties of these compounds, in the form of bulk alloys, thin films or Mn:Ge interfaces [1]. Among Mn:Ge interfaces, considerable attention has been paid to the Mn:Ge(111) system, which is usually grown by evaporating Mn atoms onto a c(2x8)reconstructed Ge(111) surface. Subsequent annealing at about 300°C of the unreacted interface yields a  $(\sqrt{3}x\sqrt{3})R30^\circ$  reconstructed surface which is known to act as a seed layer for the growth of the metallic, ferromagnetic, Mn<sub>5</sub>Ge<sub>3</sub> phase. Due to the relatively high Curie temperature, the Ge-Mn<sub>5</sub>Ge<sub>3</sub> interface is currently under investigation as a possible candidate to develop spintronics devices. However, in spite of a large number of theoretical studies on the electronic properties, the experimental investigation of the electronic structure is still in the early stages, and few photoemission studies have been reported so far [2,3]. The major findings of these studies are the metallic nature of the interfaces down to a coverage of about 4 ML, and the presence of Mn-derived states at the Fermi edge, as shown by resonant photoemission experiments [2]. These features make the Mn:Ge(111) annealed interface different from the bulk Mn<sub>x</sub>Ge<sub>1-x</sub> alloys, which in turn should be regarded as a dilute magnetic semiconductor, with physical properties similar to those of Ga1-xMnxAs and

Zn<sub>1-x</sub>Mn<sub>x</sub>O dilute alloys. Ordered Mn:Ge(111) alloy films, with a  $(\sqrt{3}x\sqrt{3})R30^\circ$  unit cell relative to the unreconstructed Ge(111) surface, can be formed for very thick layers down to a few monolayers (ML).

Sangaletti and coworkers have reported on the magnetic properties of a rather thick (190 ML) Mn:Ge(111) ordered film produced by annealing Mn multilayers evaporated onto a Ge(111) single crystal [2]. As in the case of Mn<sub>5</sub>Ge<sub>3</sub> single crystals, ferromagnetic ordering with a  $T_c$  of about 260 K was detected in this thick film, but evidence of ferromagnetism in thinner Mn:Ge(111) films has not yet been reported. Very thin layers (down to a few ML) are inaccessible to conventional bulk magnetometric techniques, therefore evidence of ferromagnetic ordering should be sought by using surface specific techniques, such as dichroic photoemission or X-ray magnetic circular dichroism (XMCD).

In this study we provide evidence of surface magnetization of a metallic ordered  $Mn_xGe_{1-x}$  thin film obtained after the annealing of about 12 Å of Mn deposited on Ge(111) and displaying a ( $\sqrt{3}x\sqrt{3}$ )R30° low energy electron diffraction (LEED) pattern. Absorption measurements at the Mn L<sub>2,3</sub> edge show XMCD effects below the Curie temperature, and dichroism is observed in valence band (VB) photoemission spectra indicating the presence of spin polarized states close to the Fermi level. The experiment has been carried out at the BACH beamline at ELETTRA. XMCD and dichroic photoemission measurements were performed using a 150-mm VSW hemispherical analyzer in remanent magnetization after a 0.30 T field was applied at an angle of 30° to the surface at low temperature. A  $12 \pm 2$  Å thick Mn layer was deposited in-situ at room temperature on a clean Ge(111) c(2x8) reconstructed surface. Postgrowth annealing was carried out at 300°C for 120 seconds to induce the formation of a single phase surface alloy with a  $(\sqrt{3x}\sqrt{3})$ R30° LEED pattern, as also reported for Mn<sub>5</sub>Ge<sub>3</sub> layers [3].

In the formation of the Mn:Ge(111) ordered alloy, the evolution of Ge 3d core lines is rather interesting, Figure 1. The Ge 3d photoemission spectrum of the clean substrate is that expected for a Ge(111)-c(2x8) reconstructed surface. The Ge 3d line of the unreacted Mn:Ge(111) interface can be deconvoluted using a pair of doublets separated by about 0.4 eV and shifted by 0.42 eV (A1) and 0.86 eV (A2) to lower BE relative to the bulk Ge emission (B). After annealing the intensity of the Ge 3d emission increases and the A1 component is found to contribute mainly to the spectral weight. The A1 component corresponds to

Ge atoms surrounded by Mn atoms in the alloy-like environment (reacted) and we tentatively assign the A2 component to the (unreacted) surface and sub-surface Ge atoms at the Ge(111)/Mn interface affected by band-bending. It is worth noting that for the reacted component A1 it is necessary to introduce a finite asymmetry parameter ascribed to the metallic character of the layer (Figure 1-d), also determined by VB photoemission (not reported here).

In Figure 2-a the Mn 2p-3d XAS ( $\sigma^{\dagger}$  and  $\sigma^{-}$ ) spectra of the reacted thin layer are shown, along with the XMCD spectrum ( $\sigma^2$  $-\sigma^{\dagger}$ ). Here  $\sigma^{\dagger}$  and  $\sigma^{-}$  represent the absorption intensity for the two photon helicities. For the Mn  $2p_{3/2}$  component a peak at about 642 eV with a tail towards higher photon energies is observed, while the Mn  $2p_{1/2}$ component shows a peak at about 652 eV. The lineshape of these peaks is similar to that of Mn in metallic systems, such as Heusler alloys, whereas the absence of fine structure due to Mn 2p<sup>3</sup>d<sup>o</sup> final state multiplets is interpreted as evidence of the lack of strongly localized magnetic moments on Mn lattice sites. The XMCD spectrum is very similar to that found in Mn<sub>5</sub>Ge<sub>3</sub> single crystals where the lineshape of XMCD was tentatively ascribed to a prevalent 3d° con-

Figure 1. (a) Ge 3d photoemission spectrum collected from clean Ge(111)-c(2x8) reconstructed substrate (thin line), from the unreacted Mn:Ge(111) interface (thick line). and from the reconstructed Mn:Ge(111) interface (dashed line). (b-d) Deconvolution of the shallow core level spectra of the clean Ge surface in terms of bulk, surface, adatoms and rest-atoms components (b), of the unreacted Mn film on Ge (c) and of the reacted

Mn layer (d). Spectra (b) to (d) have been normalized by setting a common value for the maximum intensity, in order to clearly display the data deconvolution, whereas the spectra shown in (a) are normalized to the photon flux and are therefore directly comparable. The label B indicates the contribution from bulk Ge atoms, while A1 and A2 denote the contributions from Ge atoms after Mn deposition and prior to annealing.



figuration of the initial state Mn atoms. This finding can be regarded as an indication that the metallic character induces a redistribution of electrons within the M-shell, with a possible transfer of charge from the 4s to 3d band. Further evidence that our film is magnetic comes from the observation of magnetic circular dichroism in the VB photoemission spectra as shown in Figure 2-b. A clear dichroic effect is observed, but only for states within 1 eV of the Fermi level. By assuming for our ordered thin layer the structural properties of Mn<sub>5</sub>Ge<sub>3</sub> epitaxial films [3], we note that this compound presents two inequivalent Mn sites having different magnetic moments (i.e. MnI and MnII with 1.96  $\mu_B$  and 3.23  $\mu_B$ , respectively). Band structure calculations of the Mn<sub>5</sub>Ge<sub>3</sub> phase indicate that magnetic circular dichroism should extend over a range of the VB as large as 6 eV due to the strong contribution of MnII atoms to the DOS far from E<sub>F</sub>. It is interesting to note in comparison to the calculation for the Mn<sub>5</sub>Ge<sub>3</sub> phase is that MnI states mainly contribute to the dichroism in the narrow energy range (up to 1.0 eV) below the Fermi edge, which is where we observe a strong spin polarization in our film. The fact that we observe a clear dichroic effect in VB photoemission only for states within 1 eV from the Fermi level, which is reminiscent of the behavior of MnI atoms in Mn<sub>5</sub>Ge<sub>3</sub>, suggests that only the MnI-like atoms contribute to the magnetic signal, while the intercalated Mn atoms do not. This is supported by the fact that, while dichroism effects have been observed in Mnrelated levels, there is no evidence of surface dichroism for Ge 3d shallow core levels measured in photoemission experiments (not reported here), indicating that the Gerelated electronic states we are probing are not involved in magnetic ordering. Furthermore, it has also been shown that the Mn<sub>5</sub>Ge<sub>3</sub> layers are MnI terminated [3], which indicates that with our surface sensitive soft X-ray probe we are mainly detecting magnetization effects from MnI-like atoms. The present itinerant surface alloy is, therefore, different from the bulk dilute systems, which are expected to show a strong Mn-Ge hybridization resulting in spin polarized orbitals for Ge atoms surrounding the Mn impurity [1].



In conclusion, XMCD allowed us to detect ferromagnetic ordering of the metallic Mn:Ge(111) ( $\sqrt{3}x\sqrt{3}$ )R30° thin film alloy that cannot be explored with conventional magnetic tools due to the reduced layer thickness. In addition, dichroic photoemission allowed us to detect spin polarization effects near the Fermi edge. The present data have been interpreted by comparison with theoretical calculations on the Mn<sub>5</sub>Ge<sub>3</sub> bulk phase by assuming that we are mainly probing the Mn atomic layer at the alloy surface.

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#### Figure 2. (a) XMCD

spectrum measured in remanent magnetization at 245 K at the Mn 2p-3d absorption edge of the Mn:Ge (111) [√3x√3]R30° reconstructed interface. Energy resolution=0.24 eV, circular polarization of light =100% (first harmonic), 15° photon beam incidence angle and 75° emission with respect to the sample surface (b) Magnetic circular dichroism spectrum of the valence band measured in remanent magnetization at 270 K. The dichroism spectra are obtained by calculating the difference between the spectra collected with left and right circular polarized radiation  $(\sigma^{-} \text{ and } \sigma^{+})$ . Circular polarization rate =100% (first harmonic), 30° photon beam incidence angle and 90° emission with respect to the sample surface

# CURRENT-INDUCED DOMAIN WALL PROPAGATION

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Figure 1. (a) Schematic of the experimental setup including the pulse injection equipment. Scanning electron microscopy images of the devices are shown in (b), (c) and XMCDPEEM images of the magnetization configuration after initialization are presented for two different directions of the magnetic contrast indicated by the grey scales (d, taken at SLS), (e, taken at ELETTRA).

The interplay between spin polarized currents and domain walls (DWs) in magnetic nanostructures has been studied intensively in the last decade, driven by fundamental interest in the basic physical mechanisms involved. The fundamental interaction between spin currents and geometrically confined DWs is twofold: strong currents influence the DW spin structure and cause displacement, and conversely DWs influence the currents (domain wall magnetoresistance, DWMR). Intrinsic DWMR and contributions of the DW to other MR effects (e.g. anisotropic magnetoresistance, AMR) have been reported [1]. For applications, MR contributions of DWs can be used to probe their spin structure and in particular their position. We have in the past investigated DWMR [1] and observed surprising and little understood MR effects, which can only be explained if concurrent imaging of the magnetization is available to directly correlate the resistance and the spin structure.

As pointed out before, the reverse action, namely that of electrons on domain walls also exists. Rather than using conventional field-induced DW displacement, this current-induced domain wall propagation (CIDP) is a promising alterative in applications, since no field-generating strip-lines are needed. CIDP has long been known and recently controlled CIDP in magnetic nanostructures has been achieved. DW velocities, critical current densities, and the deformation of the DW spin structure due to current have been determined [2,3]. While CIDP is experimentally well established, the underlying theory of interaction between current and magnetization is still controversial. A discrepancy between room temperature measurements and 0 K calculations of the DW velocity exists, and to reveal possible reasons, a temperature dependent study of the critical current density is key.

Different techniques have been used to measure CIDP such as MFM, spin-SEM,





etc. and XMCDPEEM (X-ray Magnetic Circular Dichroism PhotoEmission Electron Microscopy) was shown to be particularly well suited, since it combines non-intrusive imaging with fast acquisition times. To inject current pulses, a novel sample holder was developed where the contacts that are usually used for heating and a thermo-couple have been modified to connect to the structures. Using a commercial pulse generator and a home-made amplifier, a setup was built that can be inserted into the PEEM rack. To solve the problem of controlling the equipment, which is at 20 kV compared to ground, a fibre-optic connection was made that allows full control via a computer. What is more, switches are included, that allow selection of one of the four contacted structures to inject pulses and measure the resistance. In-situ diagnostics are available to check if any of the equipment has been damaged due to a discharge, etc. A schematic of the setup is presented in Figure 1 (a).

In Figure 1 (b) the layout of our structures is shown in an SEM image. The samples consist of 28 nm thick Permalloy (Ni<sub>80</sub>Fe<sub>20</sub>) zig-zag lines are contacted by Au contacts, which allow us to inject the currents along the wire. To initialize the system we apply a field in the direction indicated in Figure 1 (c) by the arrow. After relaxing the field a magnetization configuration as shown in Figure 1 (d) is present with alternating magnetization directions in adjacent branches of the wires, which corresponds to the black and white contrast in the magnetic image. At each corner a head-to-head or a tail-to-tail domain wall is present. To determine the type of domain, one can mount the sample turned by 90° to obtain the contrast of the domain walls as seen in Figure 1

(e) where vortex walls can be identified by their characteristic black-white contrast.

We then inject current pulses with varying pulse height and length to observe the wall motion and wall transformations as seen in Figure 2 (a). After the first injection the wall has transformed from a single vortex wall to a double vortex wall and after the second injection it transforms back to a single vortex wall and moves. A higher magnification image of the double vortex wall is shown in (b) together with a micromagnetic simulation (c) that reveals the wall spin structure with two vortices and a cross-tie structure in the centre. In Figure 2 (d) we present the evolution of the wall velocity with increasing current density and we observe that different domain wall types move with different velocities and in particular single vortex walls move quickest and more complicated domain wall spin structures move more slowly [3].

Further experiments have revealed the details of the transformation process, which is of paramount importance for the understanding of the underlying spin transfer torque effect. In future experiments we will concentrate on novel materials where stronger spin transfer torque effects are expected resulting in faster and more reproducible wall motion at lower current densities.

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Figure 2. (from [3]) (a) shows a single vortex DW after remagnetization. After the first current injection the wall transforms to a double vortex and after the second injection the wall transforms back to a single vortex and moves in the direction of the electron flow. (b) shows a high resolution image of a double vortex wall and (c) the corresponding micromagnetic simulation. (d) Average wall velocities as a function of current density for walls that move without transformation (black squares). Walls that transform show a smaller velocity depending on the transformation: extended vortex walls (green "down" triangles); double vortex walls (red discs), triple vortex walls (blue "up" triangles).

CURRENT-INDUCED DOMAIN WALL PROPAGATION

# CLASSICAL ELASTIC THEORY FAILURE IN GLASSES

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> The overall sound attenuation in disordered materials, and its frequency and wavelength dependence, is the result of a complicated interplay of two main physical mechanisms: one is due to anharmonicity of the inter-particle interactions and the other to the structural disorder.

The acoustic sound waves, with wavelength  $\lambda$  and frequency  $\omega$  ( $\omega = v 2\pi/\lambda = v$ Q, where v is the sound velocity and Q is the wavevector), have anharmonicity induced attenuation characterized by a specific, temperature dependent, relaxation time  $\tau_1$  and wavevector  $Q_1 = \tau_1/v$ . At low frequencies ( $\omega_1$  $\tau_1 < 1$ ), these acoustic sound waves propagate in disordered materials (glasses) as in any continuum medium. Therefore the sound attenuation is completely dominated by anharmonic processes, like, e.g., the Akhiezer mechanism [1]. Accordingly, the sound attenuation coefficient, as measured for example by the broadening  $\Gamma$  of the Brillouin peak in the dynamic structure factor  $S(Q, \omega)$  is proportional to  $\omega^2$ , or to  $Q^2$ . At high frequencies, such that  $\omega_1 \tau_1 > 1$ , the sound attenuation associated with the anharmonic processes becomes frequency independent. The sound attenuation associated with topological disorder, as described by the Rayleigh scattering of sound waves from point-like defects, gives rise to  $\Gamma \propto Q^4$  for wavelengths larger than the typical defect size  $\xi = 2\pi/Q_2$ . On increasing Q, for Q > Q<sub>2</sub>, when the Rayleigh scattering regime is left, one expects that  $\Gamma(Q)$  is no longer  $\propto Q^4$ . Experimentally, for Q larger than 1 nm<sup>-1</sup>, all studied glasses show  $\Gamma \propto Q^x$ , with x very close to two. This scenario is summarized by a three regime behaviour of  $\Gamma(Q)$ : i) at low Q,  $\Gamma(Q)$  is determined by anharmonic processes, and  $\Gamma(Q) \propto Q^2$  up to a first (temperature dependent) crossover  $Q_1$ ; ii) an intermediate regime where the Q-dependence of  $\Gamma(Q)$  is determined by the interplay and relative strengths of anharmonicity and structural disorder processes. Here  $\Gamma(Q)$  is determined by the specific, system dependent, values of  $\tau_1$  and  $Q_2$ ; iii) a high Q regime where  $\Gamma(Q)$  is determined by the topological disorder and  $\Gamma(Q) \propto Q^2$  with a temperature independent coefficient.

A critical issue, which has been in the last few years a source of debate in the literature, is the location of  $Q_1$  and  $Q_2$  for different glasses. In the most studied case of vitreous silica,  $Q_1$  and  $Q_2$  lie in a region not directly accessed with traditional scattering probes. Clear evidence is reported for the low- and high-Q quadratic types of behaviour of  $\Gamma(Q)$ using Brillouin Light Scattering (BLS) and Inelastic X-ray Scattering (IXS) [,] respectively [2]. Of fundamental importance is the observation that the two kinds of quadratic behaviour do not have the same coefficient, and therefore do not extrapolate from one to the other. This provides a strong indication for the presence of an intermediate regime. The characterization of this intermediate regime is of great importance for the understanding of glass dynamics and so far no clear-cut evidence of the  $\Gamma(Q) \propto Q^4$  dependence has been reported in the literature.

In a recent paper [3], we reported measurements of the dynamic structure factor of vitreous silica using the newly developed Inelastic Ultra-Violet Scattering (IUVS) technique. This probe, using an energy three times larger than that usually employed in normal BLS experiments, allows the study of sound waves up to a momentum transfer region of 0.13 nm<sup>-1</sup>. In Figure 2 we show the IUVS values of the widths  $\Gamma(Q)$  togeth-



Figure 1. Acoustic attenuation, as represented by the peak broadening  $\Gamma(0)$ , as a function of the momentum transfer from different data sets. Circles represent IUVS experimental data [6], triangles and diamonds refer to BLS data [4], and squares to IXS data [5]. The dotted line corresponds to a  $Q^4$ dependence, showing its consistency with the data between  $Q_1$ and  $Q_2$ , also indicated in the Figure.

er with IXS [5] and BLS [4] data. As previously discussed, both the low and the high Q regimes with Q<sup>2</sup> dependence of  $\Gamma(Q)$  are evident but with a coefficient which differs by approximately a factor of two. Therefore, the literature data identify a Q range between  $\approx 0.05$  and 1 nm<sup>-1</sup> where a transition between the two regimes must take place. The new IUVS data partially cover this transition region, and show the departure from the low Q quadratic dependence, and the sharp rise towards the high Q quadratic dependence that, however, is not fully reached in the investigated Q range.

IUVS data allow the cross-over  $Q_2$  value to be estimated as  $0.15 \pm 0.01 \text{ nm}^{-1}$  showing that the validity of the Rayleigh scattering regime is confined to a length-scale larger than  $\approx 40 \text{ nm}$ , and therefore that topological disorder in this glass has an unusually long correlation length. The higher power law, observed between  $Q_1$  and  $Q_2$ , is consistent with a  $Q^4$  behaviour (dotted line in Figure 2).

The derived value of  $\xi$  cannot be associated with density inhomogeneities, as no signature of this kind of effect is found in the static structure factor. However, the propagation of sound waves is controlled not only by density but also by the *local* elastic constants, and therefore the obtained result implies inhomogeneities of the local forces on the scale  $\xi$ . In this respect, it must be pointed out that the existence of such

long range correlation has been recently identified in a computer simulated system. Indeed, in a recent paper, Tanguy and collaborators [4] have shown the existence of a characteristic length in the stress correlation function of a model Lennard-Jones glass in two dimensions. They found inhomogeneous regions on a length scale of about 30 inter-particle distances, a value not too far from our finding, taking into account the differences in the systems' dimensionality (two against three) and interaction potentials (van der Waals against covalent bonding). Therefore a tentative interpretation for the origin of  $\xi$  is to assign this length scale to the scale of force constants fluctuations. The classical continuum elasticity breaks down when the wavelength of the excitation is smaller than the characteristic length  $\xi$ .

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# MATERIAL SCIENCE

Material science is a rapidly growing interdisciplinary field that deals with the properties of matter and their applications to various areas of science and engineering. In particular, one of the most important challenges and opportunities faced by material scientists in recent years is to understand the properties of matter at the nanoscale and to use the improved understanding for designing and manufacturing novel materials with properties tailored to specific needs. Nanoscale materials, which exhibit novel and/or significantly improved physical, chemical and biological properties are in fact dominated by quantum mechanics, material confinement in small structure and by the increasingly dominant role of surfaces and interfaces.

The foreseen applications for this new technology include inorganic and organic (flexible) electronic and optoelectronic devices; more efficient solar cells; biosensors; strong, lightweight materials and novel lubricants. This requires the control of matter at its building blocks, i.e. atoms, molecules or supramolecular assemblies, as well as a detailed knowledge of the interfacial physical and chemical properties of the nanomaterials. A multi-technique approach is therefore required to understand the properties of matter at the nanoscale.

The highlights of the material science section include relevant experiments carried out at different ELET-TRA beamlines, involving a broad spectrum of distinct techniques: spectroscopy, X-ray spectro-microscopy and X-ray imaging.

Valence band and core level photoemission spectroscopy measurements on the atomic deuterium/ silicon carbide (SiC) interface performed at the VUV beamline (H. Enriquez at al) showed that, as for atomic hydrogen, deuterium induces surface metallization of the 3C-SiC(100)3x2 surface, but with a smaller charge transfer to the surface, attributed by the authors to the occurrence of dynamical effects.

Based on X-ray photoemission (XPS) data (S. Sarpa et al) the size-dependent electronic properties of monodispersed PbSe nanocrystals have been studied. They show that larger nanocrystals have a depleted quantum efficiency, which is connected to the formation of trap states provided by a non-stoichiometric  $Pb_{1x}$ Se layer.

The interaction of nitrogen with one of the mostly used solid oxide electrolytes (YSZ) for applications in the field of nitrogen sensors has been investigated at the ESCA Microscopy beamline (I. Valov). The authors have shown that nitrogen can be incorporated into YSZ in different charged states upon electrochemical polarization.

The last two contributions highlighted in the present session exploit the capabilities of the phase-contrast imaging technique offered at the SYRMEP beamline. M. Polacci and co-workers have applied this technique to the study of the 3D geometry of crystals and vesicles in samples of pumice and scoria from active volcanoes. L. Tesei and co-workers have used the method to investigate in real-time the effect of an applied stress to the microstructure of light, high-performance sail fabrics.

Loredana Casalis

# NANOCHEMISTRY AT SIC SURFACES: ISOTOPIC EFFECT IN DEUTERIUM-INDUCED METALLIZATION AND SELECTIVE THIN NITRIDE LAYER GROWTH

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Silicon carbide (SiC) is an advanced semiconductor especially suitable for high power, high temperature, high voltage and high frequency devices and sensors. SiC is also one of the best biocompatible material, and a very promising material for nanotechnology and nanoscience.

Surface metallization and passivation are central issues in semiconductors. Hydrogen (H) and deuterium (D) are very well known to passivate electrically/chemically semiconductor surfaces and interfaces. Recently, the 1<sup>st</sup> example of H-induced semiconductor surface metallization has been discovered for clean but also pre-oxidized 3C-SiC(100)3x2 surfaces [1]. Here, we investigate atomic D interaction with the 3C-SiC(100)3x2 surface by valence band and core level photoemission spectroscopy at the VUV beam line. D is found to also metallize the same surface. However a significant isotopic effect is observed when compared to H with amazingly smaller charge transfer suggesting dynamical effects to be involved [2].

D atoms interaction with the 3C-SiC(100) 3x2 surface could be traced looking at the changes in the valence band (Figure 1). The clean surface displays two spectral features including surface (SS) and bulk (B) electronic states. Atomic D leads to SS

Figure 1. D/3C-SiC(100)3x2 valence band spectra for clean and 100 L D<sub>2</sub> dissociated by a heated tungsten filament. Inset shows the Fermi edge region. hv = 42.2 eV.



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Figure 2. D/3C-SiC(100)3x2 as in Figure 1: Si 2p (a) and C 1s (b) core level spectra with S1, S2 and S3 surface and sub-surface shifted- and R reacted components (Si 2p), and B bulk and A surface chemical shifted components (C 1s). hv = 152.9 eV (Si 2p) and 329.8 eV (C 1s).

quenching which shows D atom terminating top Si surface dangling bonds as observed for H [1]. Metallization is evidenced looking at the Fermi level region displayed as an inset in Figure 1. While the clean 3x2 surface shows no Fermi edge, the 100 L D-exposed one exhibits instead a clear Fermi level build-up indicating surface metallization [2]. This leads to band bending with a 0.6 eV change in the position of the valence band maximum (VBM) (as bulk peak B) from 1.5 eV (clean) to 2.1 eV (D-exposed) surfaces.

Using the Si 2p core level for clean and D-covered 3C-SiC(100)3x2 surfaces (Figure 2a), we probe charge transfer into the Si atomic planes. S1 surface component is related to the top-most asymmetric dimer Si up atom located in the 1st Si plane, S2 to the long dimer located in the 2<sup>nd</sup> atomic plane while S3 is primarily related to the 3<sup>rd</sup> Si plane including Si dimers [2]. Upon D atoms interaction, S1, S2 and S3 shift to lower binding energy by 0.24, 0.26 and 0.18 eV respectively, indicating charge transfers into the three first Si atomic planes. In addition, the deuterated surface exhibits a reactive R component shifted by 0.43 eV from the bulk and assigned primarily to the Si dimer located in the 3<sup>rd</sup> plane broken by D atoms, as proposed for H-induced metallization of the 3C-SiC(100)3x2 surface [1]. Turning to the C 1s core level (Figure 2b), one has to remember that the 1st C plane is located below the 3 topmost surface Si atomic layers [1] and therefore, the C 1s core level for the clean 3x2 surface has a bulk character only, with no surface shifted component. Upon D atom interaction, a new component A, shifted by 0.34 eV to lower binding energy with respect to the bulk peak indicates a charge transfer to the C plane.

The above valence band and core level photoemission study supports a picture of D-induced 3C-SiC(100)3x2 surface metallization, with a clear Fermi edge build-up. Interestingly, upon metallization, the large  $\approx$  0.6 eV band bending is comparable to those taking place with other group I elements at alkali metal/semiconductor interfaces [2]. The strong reacted component developing at the Si 2p core level suggests that D atoms induced bond breaking below the surface, likely on the Si dimers located in the 3<sup>rd</sup> Si plane as depicted [2]. This leads to D atoms terminating one Si dangling bond only, due to steric hindrance (the SiC lattice parameter is 20% smaller compared to Si), the other one remaining empty. It leaves the two Si atoms initially forming a dimer with very different electronic structures as evidenced by the reacted R component (Figure 2a). This

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Figure 3. 1000L NO/Si/3C-SiC(100)3x2 at 25°C and 1000°C: (a) Si 2p core level with S1, S2 and S3 surface shifted- and B bulk components, A1, A2 and A3 related to oxynitrides, and C1 and C2 correspond to Si sub-stoichiometric and stoichiometric  $Si_3N_4$ nitrides respectively, (b) 0 1s core level and (c) N 1s core level. hv = 150 eV (Si 2p), 580 eV (0 1s) and 460 eV (N 1s).



leads to an asymmetric charge transfer into the 1<sup>st</sup> C plane located just underneath, which appears to be significantly involved in the metallization process with a component 0.34 eV shifted to lower binding energy, indicating a larger transfer to the C plane (Figure 2b). Indeed, this view is further supported looking at C and Si electron affinities at 2.55 and 1.9 respectively, C atom being the most electronegative one, and therefore likely to also attract a larger part of the charge. Turning to the top-most layer, such a metallization is mediated by D atoms terminating each Si surface dangling bonds, leading to an effective charge transfer into the three 1<sup>st</sup> Si atomic planes as evidenced by S1, S2 and S3 shifted to lower binding energies (0.24, 0.26 and 0.18 eV respectively) [2].

One should remark that the occurrence of a strong reacted component at Si 2p core level is not consistent with D atoms in bridge bond positions between two Si atoms in the  $3^{rd}$  Si plane as recently favored by first principle calculations for H/3C-SiC(100) 3x2. Indeed, in the latter case, the two Si atoms resulting from dimer breaking would have the same electronic structure which evidently is not the case with R located at 0.44 eV higher binding energy compared to S3 (Figure 2a). One significant difference is that D (H) exposures are performed at 573 K surface temperature with data acquisition at 300 K. The theoretical predictions are based on "frozen 0 K" calculations, not taking into account the entropy. So the two situations cannot really be compared. However, a bridge bond site for D atoms is possible but would require very low temperature experiments not easy to carry out on a wide band semiconductor with likely frozen carriers preventing the use of "electron related techniques".

A final feature of strong interest is the significantly smaller Si 2p surface core level shifts upon interaction with D ( $\Delta E = -0.25$ eV) [2] in comparison to H ( $\Delta E = -0.45$  eV [1]), indicating a smaller D charge transfer to the surface. Since D and H have the same electronic properties, such an isotopic effect is likely to result from the mass difference between the two atoms, suggesting that some dynamics may be at the origin of a smaller charge transfer from heavier D [2]. It also suggests that the induced metallization is likely more stable with deuterium than with hydrogen.

Another aspect of importance is the SiC surface passivation with the effect of a pre-

deposited Si overlayer on oxynitridation process. The Si 2p core level for the Si/3C-SiC(100)3x2 surface exhibit the surface shifted components S1, S2 and S3 (Figure 3a) [3]. Also, this Si overlayer keeps a 3x2 array as evidenced by LEED. NO interaction at 25°C leads to oxynitride products (Si<sub>2</sub>N<sub>2</sub>O, SiO<sub>x</sub>N<sub>y</sub>) formation with either Si <sup>2+</sup> oxidation state or low Si nitridation state or both (Figure 3a) [3]. After annealing at 1000°C, the oxynitrides are removed leaving two peaks only. Peak C1 is related to a low nitridation state while peak C2, shifted by 1.7 eV to higher binding energy, indicates stoichiometric Si<sub>3</sub>N<sub>4</sub> nitride formation [3].

The behavior of the three surface shifted components S1, S2 and S3 is of special interest. Indeed, they are not affected by NO interaction after annealing at 1000°C, with no binding energy change compared to the clean Si-covered surfaces (Figure 3a). This very interesting feature clearly indicates that the surface and immediate subsurface regions are unaffected by nitrogen and that the nitrides grow below [3]. This indicates that the very thin nitride layer has been selectively grown at the Si/SiC interface, as further evidenced by small energy shifts observed at the C 1s indicating nitrogen interaction occurring close from the C plane [3].

Additional insights about the oxynitridation process could be found looking in Figure 3b-c at the O 1s and N1s core levels for the same sequence. At 25°C, the O 1s core level is related to oxy-nitride products. Most interestingly, after a 1000°C annealing, no more oxygen is present on the Si-modified 3C-SiC(100)3x2 surface (Figure 3b) [3]. Together with binding energies of C1 and C2 components at Si 2p (Figure 3a), these features further stress that only the nitrides are present after annealing, as also evidenced by the N 1s core level (Figure 3c), as a result of the total removal of oxygenrelated species [3].

To summarize, we investigated the oxynitridation of 3C-SiC. The results show the very interesting properties of a Si thin overlayer grown on the 3C-SiC(100)3x2 surface. Initial NO exposures at 25°C results in oxynitride formation, primarily below the surface. After annealing at 1000°C, a thin nitride layer including stoichiometric Si<sub>3</sub>N<sub>4</sub>

and sub-stoichiometric nitrides grows at the Si-3x2/3C-SiC(100) interface. This finding is especially interesting since it opens-up post-oxidation of a pre-nitridized Si-3x2/3C-SiC(100) system, a very useful feature to limit dopant diffusion and to passivate electronic defects that are so critical at SiO<sub>2</sub>/SiC interfaces. We have also studied D atoms interaction with the same 3C-SiC(100)3x2 surface. D is found to induce surface metallization with a charge transfer occurring into the three topmost Si atomic planes and in the first C plane. However, an amazing isotopic effect is observed when compared to hydrogen, with a smaller charge transfer to the surface suggesting dynamical effects.

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# PHOTOEMISSION USING VARIABLE ENERGY SYNCHROTRON RADIATION REVEALS THE INTERNAL STRUCTURE OF HIGHLY LUMINESCENT PbSe NANOCRYSTALS

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> Semiconducting nanocrystals (NC) show size dependent optical and electronic properties that make them an interesting class of materials for practical applications. However, at such length scales the observed properties are often dictated by the nature of their surfaces and interfaces. The changes in the structure of NCs as a function of size have been elucidated earlier in the case of CdS [1] and ZnS [2]. PbSe is a narrow band gap semiconductor and thus an important one for applications in the infra-red regime. Tuning of the band gap with size implies that PbSe NCs can be used for detection in the telecommunication window, IR-lasers and waveguides. The quantum efficiency (QE) of emission in such cases needs to be maximized in order to have superior materials for such applications. One would nor-



mally expect the QE to increase with size since the density of surface states decreases with increasing size. However, the variations in QE of PbSe NCs as a function of size are pronounced and counter-intuitive, since the QE of smaller NCs are close to 70%, dropping drastically as the NC size increases, reaching values as low as 4%. In the present work [3] we find that a non-trivial role of the trap states may make important contributions in determining the emission QE for PbSe NCs.

Three sizes of PbSe NCs, with average diameters of 3, 9 and 11 nm were used for the present study, and the 9 nm diameter monodispersed NCs are shown in Figure 1. Monodispersion in size of the NCs is necessary for an accurate study of the variations of the properties of NCs with size. Various core level spectra of these NCs were recorded using the technique of soft x-ray photoemission. Using the tunability of the photon energies at ELETTRA, we varied the surface sensitivity of this technique allowing us to probe the spatial variations and inhomogenities of atomic compositions in terms of their chemical bonding and coordination, as we move from the core to the surface of the NCs. The photoelectron signal originating from a particular atom is sensitive to its chemical environment, which is reflected as a shift in the binding energy. Thus, within resolution limits, spectral decomposition of the photoelectron core-level signal can yield valuable chemical information pertaining to the NCs. We investigated different sizes of

**Figure 1.** TEM of 9 nm PbSe NCs. The scale bar is 10 nm.

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**Figure 2.** Photoemission spectra of the Pb 4f, P 2p and Se 3d core levels for the 3 nm PbSe nanocrystals.

PbSe NCs to monitor the relative variation of surface to bulk photoelectron signals directly, giving us a semi-quantitative idea of their surface composition and stability without the need for any detailed analysis.

Representative photoemission spectra for the smallest (3 nm) PbSe NCs are shown in Figure 2 as open circles. The PES spectra for all three sizes are given in ref. [3]. The panels on the left show the PES spectral range for Pb 4f and P 2p (from TOP) core levels, while on the right are the Se 3d core levels. Detailed spectral decompositions reveal two chemically distinct sites for Pb, corresponding to the Pb atoms in the core of the NCs and another chemically distinct species of Pb residing at the surface. Interestingly, we resolved three distinct chemical sites for Se; these could be attributed to Se in the core, Se at the surface of the NCs and Se which is a part of the capping material, namely TOPSe. An extraneous feature from Pb  $4p_{3/2}$ arising due to the second order radiation transmitted by the monochromator is also marked in the figure. We also noticed an additional Se component (total of four Se species) in the case of the larger, 11 nm diameter NCs arising from oxide islands [3]; our experiments suggest that these exist as separate entities presumably from oxidation

of some free Se and not part of NCs internal structure. Based on a detailed analysis of various PES signal intensities originating from each individual species of the NCs, we reconstructed the internal structure of the NCs in great detail, obtaining the individual thicknesses of various layers defining the NC. This leads to a model of the PbSe NC as shown in Figure 3. The inner region shown in red is defined by the radius  $R_1$  and is the crystalline core composed of stoichiometric PbSe. The thin blue region with thickness  $R_2$ - $R_1$  is the non-stoichiometric





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	small	intermediate	large	
Cap thickness, R-R <sub>3</sub>	1.2	1.0	1.0	
Nanocrystal radius, R <sub>3</sub>	1.7 (3.4)	4.2 (8.4)	5.6 (11.2)	
Radius including the				
non-stoichiometric layer, R <sub>2</sub>	1.3 (2.6)	4.1 (8.2)	5.5 (11.1)	
PbSe core radius, R <sub>1</sub>	1.1 (2.2)	3.6 (7.1)	5.0 (9.9)	

Table 1: Sizes ofdifferent layers (in nm)from the analysisof the photoemissionintensities.The correspondingdiameters of the shellsare given in thebrackets.

 $Pb_{1-x}$ Se shell. The outermost green shell (R<sub>3</sub>-R<sub>2</sub>) consists mainly of Se atoms attached to the capping ligand TOP. This shell provides the structural and electronic stability to the nanocrystals, due to the presence of long chain organic TOP molecules on the surface. The changes in the thickness of the different layers are given in Table 1. The best fit for the organic chain length in each case comes to about 1 nm, very close to 1.3 nm, the value for the unfolded TOP chain length. The crystalline core radius,  $R_1$ , increases as the size of the particle increases. The non-stoichiometric layer is very thin (less than a monolayer) in the smallest NCs and is probably a layer that provides trap states that cause a decrease in the quantum efficiency of emission in the larger NCs. Furthermore, the outermost layer that provides electronic stability is the largest for the smallest NCs, again pointing to the fact that these NCs are well passivated and result in higher emission efficiency. We show that such detailed understanding, only possible using a tunable synchrotron source, not only elucidates the detailed and complex structure of the PbSe nanocrystals, but also provides us with a possible explanation for the surprisingly poor PL yield of larger PbSe NCs.

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# ELECTROCHEMICALLY CONTROLLED REDUCTION OF MOLECULAR NITROGEN AT IRIDIUM MICRO-ELECTRODES ON ZIRCONIA SOLID ELECTROLYTE

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# INTRODUCTION

Nitrogen is often present as a virtually inert component of gas phases in solid state studies of electrode and reaction kinetics, e.g. in solid oxide fuel cells (SOFC), sensors and membranes. However, chemical and electrochemical reactions related to or with molecular nitrogen were ignored for a long time, and thus, the question arises whether nitrogen is in fact sufficiently inert towards oxidation or reduction under all experimental conditions. Additionally, studies of the nitrogen (anion) doping of oxide materials became of significant interest in the context of oxynitrides and their possible applications as materials for the development of nitrogen ion conducting electrolytes, nitrogen sensors or as an alternative/addition to the cation doping of oxides.

Analysing the reactions of molecular nitrogen with YSZ (yttria stabilised zirconia) as an important material and model substance, we know that nitrogen can be chemically reduced and incorporated into YSZ according to the following equation:

## $N_2(gas) + 2V_0^{\bullet\bullet}(YSZ) + 6e^-(electrode) = 2N_0'(YSZ)$ (1)

The Kröger-Vink notation is used here, where  $V_0^{\bullet \bullet}$  denotes a vacancy double positively charged relative to the oxygen sublattice. The incorporated nitrogen (N<sup>3–</sup>) ions are negatively charged with respect to substituted oxygen (O<sup>2–</sup>) anions. Therefore, the symbol N'<sub>O</sub> is used to indicate the single negative charge relative to the oxygen sublattice. In principle the incorporation of nitrogen according to eq. (1) can occur independently, representing the oxidation of an oxide by molecular nitrogen. However, from the thermodynamic point of view such a reaction is highly endothermic, and it will only occur if there is a very low oxygen activity. i.e., we have to consider the reduction of the oxide by the removal of oxygen:

### $2O_{O}^{X}(YSZ) = O_{2}(gas) + 2V_{O}^{\bullet\bullet}(YSZ) + 4e^{-}(YSZ)$ (2)

Here,  $O_O^X$  indicates a regular O lattice site with zero charge relative to the oxygen sublattice. Combining equation (1) and (2), we obtain the following net reaction which represents the substitution of oxygen by nitrogen – without forming electronic defects:

## $N_2(gas) + 3O_0^X(YSZ) = 2N_0'(YSZ) + 2V_0^{\bullet \bullet} + 3/2O_2(gas)$ (3)

A shift of this substitution reaction to the right side requires extreme chemical conditions, i. e. very low oxygen activities and high temperatures. An alternative route is based on the electrochemical nitrogen incorporation from a pure nitrogen atmosphere, as we recently reported [1]. In this case, the electrons are supplied by a cathodically polarised electrode, leading to very large driving forces for reaction (1). We have shown that considerable amounts of nitrogen can be incorporated electrochemically, and based on the results of steady state polarization experiments, a multi-step charge transfer mechanism of the nitrogen



Figure 1. Schematic experimental setup for electrochemical polarization measurements at the ESCA microscopy beamline at Elettra. reduction with the rate limiting step  $N_2^- + e^-$ = $N_2^{2-}$  was suggested [2]. However, only indirect electrochemical information and ex situ SIMS data were obtained, and therefore, no direct evidence of nitrogen surface species under cathodic polarization exists.

At the ESCA microscopy beamline, we have demonstrated by *in-situ* x-ray-photoelectron spectroscopy (XPS) and scanning photoelectron microscopy (SPEM) that molecular nitrogen is in fact electrochemically active at the interface between a micro electrode and one of the mostly used solid oxide electrolytes (YSZ) at voltages between -1.5 V and -3 V. We were also able to show that nitrogen neither adsorbs nor reacts chemically – i. e. without an applied electric field – with the electrode and/or the electrolyte materials.

The current results are the first steps towards the electrochemistry of nitrogen in the solid state and may be very useful for the development of nitrogen sensors or nitrogen ion conducting solid electrolytes. Irrespective of any specific application the heterogeneous electrochemical nitrogen kinetics is of fundamental relevance in the field of the reactivity of solids.

## **EXPERIMENTAL**

For the electrochemical experiments at the ESCA microscopy beamline an experimental setup schematically shown in Figure 1 was used. As working electrode we used an iridium tip with a diameter of approximately 100 µm at the contact point. As solid electrolyte a 9.5YSZ single crystal with (111) orientation was used. The counter electrode was painted on the back side of the YSZ crystal with platinum paste and sintered at 250 °C for 2 hours. The applied overvoltage was varied in the range of  $\pm$  3 V. The working temperature was adjusted in the range between 300 °C and 500 °C as measured at the upper side of the ceramic heating element. The pressure of the nitrogen gas could be increased up to  $p(N_2) = 10^{-5}$  Pa.

# **RESULTS AND DISCUSSIONS**

No nitrogen signal could be detected in the N1s XPS spectrum up to cathodic potentials of U = -1.5 V. When U = -1.5 V was exceeded a signal at a binding energy of  $E_{\rm b}$  = 397.2 eV appeared. The intensity of the signal increased and the peak area became larger with time. The appearance of the N 1s peak is reversible, and after switching off the voltage the peak disappeared completely with time. The binding energy of about  $E_{\rm b} = 397.2$ eV is usually attributed to the N<sup>3-</sup> ion. Thus, we have clearly detected reduced nitrogen species on the surface of the solid electrolyte. However, there is no unequivocal proof for the incorporation of nitrogen into the YSZ. The signal may also be caused by a modification of the top layer of the solid electrolyte.

Applying a more negative voltage to the micro electrode, the intensity of the nitrogen peak increased further as shown in Figure 2.

The process remained reversible applying voltages smaller -2.5 V.

Above this voltage the nitrogen peak remained constant in position and intensity, i.e. we conclude that the nitrogen has now been incorporated into the oxide. In Figure 2 we identify three peak components at binding energies of  $E_{b1}$  = 397.2 eV,  $E_{b2}$  = 397.5 eV and  $E_{b3}$  = 398.4 eV, respectively. The component at  $E_{b3}$  is especially pronounced for a voltage of U = -3.0 V, but it is also found at U = -2.5 V. Clearly, more reducing conditions (higher cathodic potentials) lead to the creation of a nitrogen species with higher binding energy, i. e. smaller formal charge. A microscopic interpretation is beyond the scope of this report at this point. But it is well known from solid state chemistry that stable species exist in certain alkaline earth compounds, e. g. SrN<sub>2</sub> [11,12]. Perhaps YSZ might be capable of accommodating molecular species under extremely reducing conditions at or close to the surface.

In summary, we have shown that nitrogen can be incorporated into YSZ in different charged states upon electrochemical (cathodic) polarization. These states are different from those which are found without an applied electric field (N 1s peak at a binding energy of 396.8 eV). Thus, we can distinguish nitrogen ions being already incorporated in YSZ from those being reduced but still not incorporated at the moment of the scan, i.e. we assume that the experiments display the chemical shift of nitrogen proceeding through intermediate statesupon electrochemical reduction. No nitrogen was detected at the iridium micro electrode during the polarization process. We also confirmed that no chemical reaction between reduced YSZ and molecular nitrogen takes place without an applied electric potential. Also after exposing a nitrogen free, partially reduced YSZ crystal at elevated temperatures to a nitrogen atmosphere, no nitrogen peak was detected. This proves the existence of electrochemical activity of molecular nitrogen, and we found more than one nitrogen species on the YSZ surface.

Using the microspectroscopy mode of the SPEM, we have finally imaged the intensity of the N 1s signal on the surface near to the micro electrode. In the SPEM image shown in Figure 3, each point depicts the intensity of the N 1s peak scaled to the background intensity to remove topographic contrast. Thus, the grey level of Figure 3 is propor-

**Figure 2.** N 1s spectra of a YSZ surface at an iridium micro electrode at different polarization voltages,  $p(N2) = 10^{-5}$ Pa, T = 500 °C



Figure 3. SPEM image of the N 1s signal near to the iridium micro electrode (dark spot at the left side of the image) after nitrogen incorporation.  $U = -3 V, p(N_2) = 10^{-5}$ Pa, T = 500 °C.



tional to the nitrogen concentration in/on the sample. The dark spot in the middle of the left axis represents the position of the iridium electrode, on which no nitrogen signal was detected. The most intensive signal is recorded near to the micro electrode. The intensity of the N 1s signal decreases with increasing distance from the electrode, and it disappears completely approximately 2.7 mm away from the electrode edge. This observation is a second independent proof of the electrochemical incorporation, as the highest nitrogen concentration is found in the vicinity of the triple phase boundary between electrode metal, gas phase and electrolyte.

### CONCLUSIONS

We confirmed the electrochemical activity of nitrogen at  $Ir(N_2)/YSZ$  electrodes by *insitu SPEM* experiments. At least two different nitrogen species were detected during strong cathodic polarization. No chemical reaction between reduced YSZ and nitrogen gas took place in the absence of an applied electric potential. During all experiments nitrogen species were never detected on the iridium micro electrode, whereas our SPEM measurements could confirm an inhomogeneous distribution of nitrogen at the surface after electrochemical polarization, with the strongest N 1s signal being found in the vicinity of the micro-electrode – clearly showing that nitrogen is reduced and incorporated primarily at the electrode.

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# 3D-STRUCTURE OF VOLCANIC PUMICE AND SCORIA BY X-RAY MICROTOMOGRAPHY: IMPLICATIONS FOR CONDUIT PROCESSES

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Characterization of volcanic clasts from explosive and effusive eruptions has proven to be an important approach and complements field, theoretical and experimental studies in understanding magmatic processes through quantification of crystal and vesicle textures. Investigation of volcanic morphologies and textures has allowed us to assess conditions related to magma vesiculation, fragmentation, and ascent to the Earth's surface in explosive volcanic eruptions as well as to recognize the roles of degassing-induced crystallization, development of magmatic permeability and viscous dissipation in eruption dynamics.

Several techniques are available for imaging morphology and measuring the physical properties of volcanic rocks. These include optical and scanning electron microscopy of thin sections, as well as direct measurement of properties in the laboratory based on Archimede's principle, or via helium picnometry and porosimetry. Not only are these methods destructive and extremely timeconsuming, but they do not easily allow reconstruction of the true 3D shape and texture of the sample. Developments in the application of stereological techniques to natural rocks makes some volumetric measurements from 2D data possible, but the methodology is limited only to convex objects, resulting in the introduction of some error when investigating objects with nonconvex shapes or with some degree of interconnection.

In comparison, high-resolution  $\mu CT$  (micro computerised tomography) provides

the ability to obtain 3D data with micronscale resolution in short times. The method requires no sample preparation, is non destructive, leaving the sample intact and unaltered, and allows for reproducible results as well as further complementary studies. This technique has already proven to be a powerful tool in the investigation of fossils and meteorites, and in describing and quantifying porosity and permeability in rocks and soils [1]. Here we report the first study where synchrotron X-ray µCT was applied to investigate the 3D structure of pumice and scoria from active volcanoes characterized by a range of explosive eruptive styles and compositions (basaltic to trachytic), with the goal of linking differences in the textures of tephras to changes in the style of the eruptive activity. Using this technique we were able to visualize in 3D changes in the vesicle content, geometry and distribution within different sub-volumes of each clast under investigation.

Synchrotron X-ray  $\mu$ CT was applied to trachytic pumice clasts from the fall deposit of the Campanian Ignimbrite (CI), a large silicic explosive eruption from Phlegrean Fields (Southern Italy) [2], to HK-basaltic scoria and pumice clasts from the 2003-2004 activity of the Stromboli volcano (Aeolian Islands, Italy), and to basaltic andesitic scoria from the November 2004 activity of Villarrica volcano (Chile). The experiments were conducted at the SYRMEP beamline of ELETTRA. Because of the spatial coherence of X-ray beams delivered by third generation synchrotron sources, it was possible to utilize the potential of phase-contrast imaging. The volume rendering procedure allowed us to visualize the internal structure of the analyzed volcanic products and was used for qualitative inspection of the 3D geometry of crystals and vesicles in the samples. Vesicles in the stacked volume images were segmented based upon simple greyscale thresholding, separated after being eroded and dilated, and counted.

The positive correlation between vesicle number density and eruption intensity allowed us to investigate conduit processes in basaltic explosions. Scoria from 'typical' mild Strombolian explosions has the lowest vesicle number density. This observation, combined with evidence of protracted vesicle coalescence highlighted by the large radii of the apertures connecting the small vesicles that form the dominant large vesicle population, and higher porphyricity, testifies to a magma that had time to cool, crystallize and partially degas (lose volatiles) via a network of interconnected vesicles before being erupted. By contrast, the higher vesicle number density of the crystal-poor pumice from paroxysmal activity, together with the occurrence of a population of tube-shaped vesicles, and the small radii of the apertures connecting vesicles, suggest syn-eruptive vesicle nucleation and growth followed by moderate coalescence in a rapidly ascending, volatile-rich magma. Analysis of 3D vesicle geometry also provides constraints on the interpretation of previously measured permeability data. Despite overlapping values of bulk vesicularities and similar volume fractions of connected vesicles, scoria from

typical Strombolian eruptions and pumice from the paroxysmal eruption of Stromboli display permeability values of 10<sup>-13</sup> m<sup>2</sup> and 10<sup>-11</sup> m<sup>2</sup>, respectively. This suggests that magma permeability is affected by the geometry and distribution of vesicles generating the connected flow pathways rather than only by the bulk vesicle content. We propose that the network between the evenly distributed mm-sized alignments of tubeshaped vesicles and the larger, scattered ellipsoidal vesicles produce a higher permeability in the pumice, in comparison to the crystallized, degassed texture of the scoria with large, independent and randomly distributed vesicle blobs. Combining this observation with the two distinct modes of magma degassing, i.e. syn-eruptive degassing and permeable loss of volatiles, allows us to provide some insights into mechanisms triggering paroxysmal eruptions at Stromboli.

Our data on the Stromboli pumice from the 5 April 2003 paroxysmal eruption suggest that rapid ascent of a syn-eruptive vesiculating magma may have developed a network of finely connecting tube vesicles through which gas easily flowed. In turn, the increase in permeability may have affected the fragmentation behaviour of this magma by reducing the gas pressure in the vesicles. This may have inhibited fragmentation and delayed it until a shallower level in the conduit allowing the pumice-generating magma to rise and mingle with the highly porphyritic degassed scoria-like magma. This hypothesis agrees with previous work in which the 5 April event has been interpreted to have been driven by deep, volatile-rich



Figure 1. 2D image

slices of Stromboli (a)

scoria and (b) pumice,

(c) Villarrica scoria, and

(d) CI pumice. Vesicles

phenocrysts are dark

grey and white laths.

Scale bar 1 mm for all

images, and 50  $\mu$ m for

inset in 1d.

are black features,

magma blobs of HK-basaltic composition that have risen through and mingled with the denser, degassed magma that resides in the upper part of the Stromboli volcanic system and that generates the persistent Strombolian activity.

Our measurements of the CI pumice clasts provide insights into magma vesiculation and degassing in evolved, silicic alkaline systems. The vesicle size, shape and, mostly the extremely high vesicle number density values measured in these products suggest instantaneous vesiculation and acceleration of a volatile-rich trachytic magma under conditions of large volatile supersaturation at the onset of bubble nucleation. High temperature and pressure decompression experiments, where similar high vesicles number densities have been generated, indicate that delayed, non-equilibrium degassing was the primary mechanism of nucleation and growth of vesicles in rhyolitic melts. This latter observation, together with that of the overall high water solubility and low to moderate viscosity of trachytes, suggests that these magmas may also experience a delayed, non-equilibrium vesiculation in the conduit compared to mafic magmas. In addition, the CI pumice results corroborate theoretical findings on the dynamics of alkaline magmas feeding large silicic explosive eruptions, which state that in such magmas significant vesicle growth, expansion and eventual disruption occur at shallow conduit levels. Some implications of broad interest for the geological and volcanological community arise from this study. First, µCT represents to date the only non-destructive, high-resolution technique that provides a comprehensive 3D picture of the internal structure of volcanic specimens. Combined with conventional 2D investigations this technique has the potential to open new perspectives in the understanding of the mechanisms of explosive eruptions. Here we have demonstrated that coupled 3D visualization and measurement of vesicle textures in tephras provide better insights of how degassing occurs in volcanic conduits. This information can be used, for example, to interpret variations of gas flux measurements at persistently degassing volcanoes. Second, the positive correlation between vesicle number density and eruption intensity strongly sug-



gests the potential for this relationship to be used as a basis for interpretation of past eruptions whose intensity is unknown. Additionally, the link relating the vesicle geometry of connected, permeable gas flow pathways to known permeability in clasts of Strombolian tephra may be applied to test theoretically and experimentally derived permeabilityporosity relationships of volcanic rocks. This may allow us to better constrain models of magma degassing, ascent and fragmentation that make use of such relationships [3].

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[3] Polacci M., Baker D. R., Mancini L., Tromba G., and Zanini, F., *Geophysical Research Letters* **33**, L13312 (2006) Figure 2. 3D volume renderings of Stromboli (a) scoria and (b) pumice, (c) Villarrica scoria, and (d) Cl pumice. Sample height in (a) 8.2 mm, (b) 6.6 mm, (c) 4.3 mm and (d) 1.2 mm.

# REAL-TIME SIMULATION OF HIGH-PERFORMANCE SAIL FABRICS WITH PHASE-CONTRAST X-RAY IMAGING: THE EFFECT OF REPEATED FLEXING

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The standard type of sail construction until the 1980s has been the crosscut kind, which utilizes panels oriented from luff to leech. The standard material for this kind of sails is woven polyester (Dacron®). Woven clothes are relatively cheap, simple and manageable, very slow to breakdown, but do not hold the original sail shape particularly well under load. The ultimate strength of these materials is a limiting factor, and stretch is high by comparison to composite materials. Today's "oriented" fabrics, where some attempt is made to align the load bearing fibers in a given material with the primary load paths, demand composite laminate materials. Laminates are sailcloths in which some cloth or yarns are glued to one or more layers of films and can be made with a wide range of yarns. These are responsible of the

Figure 1. Wide area (13.5 x 5.6 mm<sup>2</sup>) of microradiography of a high-performance fiber laminate sailcloth. (a) Absorption-contrast and (b) phase-contrast (b).



final behavior of the cloth in terms of initial modulus (ability to resist stretch), tenacity (initial breaking strength), flex life (a measure for the ability to resist flexing and folding), elongation (elongation at break is a measure of the ability to resist shock loads), and UV-resistance. To shield these materials from harmful light, cloth manufacturers often protect the yarns with dyed Mylar® [1]. In order to fully understand the performance of a sail, three approaches are necessary. In the pursuit of better aerodynamics sails with sophisticated fabric/panel layouts that perform over a broader range of conditions and have a longer life, sail designers usually turn to computer model sail simulations for solutions and answers. At the other extreme, manufacturers can observe the microstructure of single fibers at micron- or submicron-resolution, in order to understand fiber failure under different conditions with electron microscopes. However, it is instructive to understand the behavior of sail fabrics on a scale of several millimeters with micrometer resolution in order to understand and predict properties such as uniaxial strength, fracture toughness, impact resistance and hygrothermal effect, not to mention the effect of UV on the ultimate behavior of the fabric.

Scanning electron microscopy (SEM) has been extensively used to study the structure of laminate materials but with several drawbacks. The sample preparation for SEM examinations strongly influences the structure of a soft material and induces the presence of different artifacts, the electron beam



may damage the laminate film, and the vacuum in the SEM chamber can cause delamination of the cloth. Optical microscopy is very useful for transparent cloth, but is not able to detect defects below opaque fibers or when UV-resistant films or dyes protect the sailcloth. Ultrasonic techniques cannot detect with high precision typical defects, such as foreign inclusions, air bubbles and delamination due to inconsistent and erratic test responses. Size and distribution of defects can be seen with X-ray techniques but, because of the light materials used for sail fabric, the contrast obtained with conventional radiography is too poor to resolve details. An alternative approach to visualize low-absorption material defects with a lateral resolution of 20 to 100 microns and a field of view of 5 to 25 millimeters is to use the phase information accessed if the X-ray source has a high spatial coherence. Such a source is provided by 3rd generation synchrotrons like Elettra.

The first phase-contrast imaging for characterization of high-performance sailcloth was performed at the SYRMEP beamline at Elettra. Figure 1 illustrates the potential of phase imaging [2]. The different ribbons (1: high modulus Twaron® fill; 2: high modulus Twaron® warp; 3: Spectra® ripstop fill; 4: Spectra® diagonal axis) can be clearly seen as well as groups of air bubbles between the Mylar® films only in Figure 1(b), whereas all details and even some of the ribbons are not visible because of the low absorption of the sample in simple x-ray absorption (Figure 1(a)).

Almost all high performance sail membranes made today rely on fibers of high modulus materials for their primary strength. The fibers consist of individual filaments twisted together into bundles. All fibers exhibit a certain amount of initial movement because of the twist and crimp that is built into this process; the larger the fiber bundle, the greater the movement.

In most sophisticated composite structures, twist and crimp are reduced by tensioning the yarns prior to lamination. An alternative approach utilizes tiny, untwisted filaments of carbon or Spectra® instead of using fiber bundles. Nearly microscopic filaments are laid down on a paper carrier under tension to form a continuous sheet of fiber. The resulting composite reduces initial movement, as well as creep and crimp, to levels undetectable with standard testing equipment. As a consequence, carbon fiber (CF) sails are much lighter and have many times the life and the damage tolerance of the best, similarly performing substitutes, are much thinner than other laminates and retain strength during repeated flexing. CF sails manufacturers claim that competing Aramid and Carbon laminates lose nearly 80% of their strength after being folded 250 times, while CF retains nearly 100% of its original properties [3].

#### Figure 2.

Microradiography of a 45-degree diagonal scrim high-modulus laminate before and after a a 60-flexing cycle. REAL-TIME SIMULATION OF HIGH-PERFORMANCE SAIL FABRICS WITH PHASE-CONTRAST X-RAY IMAGING: THE EFFECT OF REPEATED FLEXING

### Figure 3. Microradiography

of a Carbon Fiber laminate before and after a a 60-flexing cycle.



We present here a preliminary study based on phase-contrast microradiography of two different types of sailcloth during a standard industrial 60-cycle flexing test. The first sample was a 252 gsm film-on-film high-modulus racing laminate with a 45degree diagonal scrim. In this kind of sailcloth component fibers are combined in scrims that benefit from the strengths of all the fibers used. High modulus Twaron® warp ribbons provide high strength in the primary load bearing axis and are used to resist fill loads, while alternate Spectra® fibers add tear strength to the finished laminate. Finally a double Spectra® diagonal axis scrim adds bias stability to lock in the sail shape. The second sample was a 132 gsm carbon fiber sailcloth. Figure 2 shows the results of the test on the first sample, where permanent deformations on both the scrims and the external films are evident. Figure 3 shows how the effect of the test on the second sample is less evident even when evaluated at higher spatial resolution. The whole sequence of images taken during the test (to be published elsewhere) show in addition that the deformation of the laminate occurs already during the first few applications of the flexing cycle.

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# STRUCTURAL BIOLOGY

The ELETTRA Council and management have realized that Structural Biology is becoming one of the highly requested activities. The close collaboration with the International School for Advanced Studies and the International Centre for Genetic Engineering and Biotechnology in Trieste plays an important role for providing an excellent biological infrastructure and partnership.

The XRD-1 beam line has been available to the User Community with approximately 40 experimental sessions dedicated to protein crystallography, involving more than 100 visiting scientists using 24-48 hours of beam time per visit.

The external scientific Programme continues to provide research highlights resulting in publications in Journals of the highest quality and impact. A survey of the website (http://biosync.rcsb.org, last update 19 October 2006) of the Structural Biology Synchrotron Users Organization (BioSync), for 2005-2006 has revealed well over 45 structural papers where the use of the ELETTRA XRD-1 beam line has been instrumental in undertaking a structural analysis.

This Highlights 2005-2006 includes three selected contributions.

• Matrix metalloproteinases are enzymes involved in extracellular matrix degradation, which is a fundamental step in many physiological processes like tissue remodelling and repair. Bertini *et al.*, summarise the investigations of ligand-adduct conformational changes, discovered by X-ray crystallography and NMR spectroscopy, in the structure of the catalytic domain of matrix metalloproteinase 12 in the presence of Nisobutyl-N-[4-methoxyphenylsulfonyl] glycyl hydroxamic acid.

• The formation of disulfide bonds between cysteine residues is a rate-limiting step in protein folding. To control this oxidative process, different organisms have developed different systems. In thermophilic organisms, a potential key role in disulfide bond formation has recently been ascribed to a new cytosolic Protein Disulphide Oxidoreductase family. *D'Ambrosio et al.*, , report on the functional and structural characterization a new member of this family, which was isolated from the archaeon *Aeropyrum pernix* K1.

• Cobalamin (Cbl, vitamin  $B_{12}$ ) serves for two essential cofactors in mammals. The pathway for its intestinal absorption, plasma transport, and cellular uptake uses cell surface receptors and three Cbl-transporting proteins, haptocorrin, intrinsic factor, and transcobalamin. Wuerges *et al* report the structure determination of a member of the mammalian Cbl-transporter family.

Overall the future for Structural Biology at ELETTRA is very promising and there will be continued efforts to ensure that the XRD-1 beamline is equipped with latest technology, both hardware and software, for efficient and "user friendly" data acquisition (see section facility, beamlines).

We expect that the Structural Biology community will be able to perform more and more challenging experiments whilst still focusing on their underlying biological goals.

Doriano Lamba

# CONFORMATIONAL VARIABILITY OF MATRIX METALLOPROTEINASES: BEYOND A SINGLE 3D STRUCTURE

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### **INTRODUCTION**

Matrix metalloproteinases (MMPs) are enzymes involved in extracellular matrix degradation, which is a fundamental step in many physiological processes like tissue remodeling and repair. Most MMPs are constituted by a prodomain that is removed upon activation, a catalytic domain responsible for hydrolytic activity, and a hemopexin-like domain that probably plays a role in substrate recognition. In several pathologies overexpression of MMPs, or the misregulation of their activity, is related to disease progression. MMPs thus are validated pharmaceutical targets. Many efforts have been devoted to develop inhibitors against these metalloenzymes through rational drug design approaches, which require a detailed knowledge of the structural features of the active sites (1,2). Up to now, drug candidates have failed the clinical trials, often because of side effects probably caused by their low selectivity.

Over the years, it has become evident that, besides their intrinsic similarity, MMPs exhibit some capability of adapting the binding pocket to the inhibitor shape (3), thus suggesting another rationale for the lack of inhibitor selectivity. A more detailed picture of mobility of MMPs, its origin, and its implications for substrate and inhibitor binding would be extremely helpful at this point. With this in mind, we have used an integrated approach conjugating high-resolution x-ray structures and NMR structures to analyze the mobility of a macrophage metalloelastase (MMP12) and performed a systematic comparison with several other MMPs. The major finding is that there are certain loop regions that are subject to mobility and/or conformational heterogeneity in several MMPs. Some of these regions are known to be implicated in substrate and inhibitor binding, substrate recognition, and selectivity toward physiological and nonphysiological inhibitors. It is also apparent that a number of structural models are necessary to characterize a single MMP.



# **RESULTS AND DISCUSSION**

The structures of the catalytic domain of matrix metalloproteinase 12 in the presence of acetohydroxamic acid and N-isobutyl-N-[4-methoxyphenylsulfonyl]glycyl hydroxamic acid have been solved by x-ray diffraction in the crystalline state at 1.0 Å (Figure 1) and 1.3 Å resolution (Figure 1), respectively, and compared with the previously published x-ray structure at 1.2-Å resolution of the adduct with batimastat.

The structure of the N-isobutyl-N-[4methoxyphenylsulfonyl]glycyl hydroxamic acid adduct has been also solved by NMR in solution. The three x-ray structures and the solution structure are similar but not identical to one another, the differences being sizably higher in the loops. We propose that many of the loops show a dynamical behavior in solution on a variety of time scales. Different conformations of some flexible regions of the protein can be observed as "frozen" in different crystalline environments. The mobility in solution studied by NMR reveals conformational equilibria in accessible time scales, i.e., from 10-5 s to ms and more. Averaging of some residual dipolar couplings is consistent with further motions down to 10-9 s. Finally, local thermal motions of each frozen conformation in the crystalline state at 100 K correlate well with local motions on the picosecond time scale.

Flexibility/conformational heterogeneity in crucial parts of the catalytic domain is a rule rather than an exception in matrix metalloproteinases, and its extent may be underestimated by inspection of one x-ray structure. Backbone flexibility may play a role in the difficulties encountered in the design of selective inhibitors, whereas it may be a requisite for substrate binding and broad substrate specificity.





# CRYSTALLIZATION, DATA COLLECTION, AND RESOLUTION OF THE CRYSTAL STRUCTURES

For MMP12–AHA adduct an aliquot of 2  $\mu$ l of protein solution (10 mM Tris, 5 mM CaCl2, 0.1 mM ZnCl2, 300 mM NaCl, 200 mM AHA, pH 8) was mixed with 2  $\mu$ l of reservoir buffer (0.1 M Tris-HCl, 25% PEG 6000, 200 mM AHA, pH 8).

The final protein concentration was 8mg/ml. Crystallization was carried out with the hanging drop vapor diffusion method at 20°C. For MMP12–NNGH adduct, 3 mM of NNGH was added to protein solution before mixing with a reservoir buffer containing 0.1 M Tris\_HCl, 20% PEG 6000, 200 mM AHA, and 1.0 M LiCl2 at pH 8.0. Figure 1. Stereoview of the overall fold of the MMP12–NNGH adduct (a) and enlargements of the active site-bound inhibitors AHA (b) and NNGH (c). In b and c the ligand electron densities are also shown.

The data were measured for both data sets at the ELETTRA XRD-1 beamline (Trieste, Italy) at 100 K, and the crystals used for data collection were cryo-cooled without any cryo-protectant treatment. The MMP12-NNGH crystal had a mosaicity of about 0.6° and diffracted to a maximum resolution of 1.3 Å, whereas the MMP12-AHA crystal, with mosaicity 0.3°, diffracted to 1.0 Å resolution. The crystal space group for the NNGH adduct is P21212 with a= 37.30, b= 62.63, c= 69.24 Å, , α=  $\beta$ =  $\gamma$ = 90° with one molecule in the asymmetric unit. The AHA complex crystallizes in the C2 space group, with a= 50.92, b= 59.59, c= 53.49 Å, ,  $\alpha = \gamma = 90^\circ$ , and  $\beta = 115.14^\circ$  with one molecule in the asymmetric unit.

## CONCLUSIONS

In this work, the solution structure of an adduct of MMP12 has been analyzed in terms of conformational exchange of loops in time scales not directly available through NMR experiments (microseconds to nanoseconds). However, the exchange is supported by the different "frozen" conformations displayed by three x-ray structures, two of them being solved during this research, and also by the reduction of several RDC values in solution. The different frozen conformations provide an estimate of the amplitude of the conformational motions. It appears that this property is characteristic of many, if not all, MMPs. This research shows the power of coupling x-ray structures (possibly more than one) and the solution structure, the latter with an analysis of NOE intensities, RDC values, and relaxation properties, to obtain a structural model that is beyond a single structural datum. The adaptability of loops (and cavities whose walls are constituted by loops) to ligands and other external perturbations are a further challenge to drug discovery bioinformatic procedures, as these slow-exchanging conformations should be sampled before the interaction with the ligand is studied.

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# CRYSTAL STRUCTURE OF THE HUMAN AND BOVINE VITAMIN B<sub>12</sub>-TRANSPORT PROTEIN TRANSCOBALAMIN

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The transport of the essential micronutrient cobalamin (Cbl, vitamin B12) from food to cells employs three successive proteins in mammals, haptocorrin (HC), gastric intrinsic factor (IF) and transcobalamin (TC) [1]. Cbl is used by cells as the basis for two enzyme cofactors, methyl-Cbl for methionine synthase and 5'-deoxyadenosyl-Cbl for methyl-malonyl-CoA mutase. Upon uptake of Cbl from food, Cbl becomes initially bound in the stomach to salivary HC. After proteolysis of HC in the duodenum, Cbl passes on to IF. Mucosal cells in the ileum absorb the IF-Cbl complex via endocytosis mediated by a specific receptor. In the enterocyte, the IF-Cbl complex is degraded and Cbl is transferred to TC which delivers Cbl to cells via the blood. Only the fraction of Cbl bound to TC is taken up via endocytosis by a specific receptor on most cell types.

TC-Cbl is degraded in lysozomes to release Cbl for further conversion into the important cofactors. Cbl-deficiency as a result of impaired intestinal absorption is more common among the elderly population and may lead to defects in the nervous system and the metabolism or to hematologic abnormalities.

We determined the crystal structure of TC which reveals in detail the Cbl-binding mode and represents the prototype for the family of mammalian Cbl-transporters since no structures have been reported yet for IF or HC. Two applications arise from the knowledge of the TC structure. The first is the production of homology models for the unknown structures of IF and HC which can then be exploited to rationalize the divers specificity of the three transporters for Cbl-analogues. Such analogues are produced



Figure 1. Overall structure of transcobalamin. (a) **Ribbon representation** of the protein in complex with cobalamin (in orange sticks).  $\alpha$ -helices of the larger  $\alpha$ -domain are coloured red and pink, the linker in green and the  $\beta$ —domain in blue. (b) Bottom view of the  $\alpha$ 6- $\alpha$ 6 barrel of the  $\alpha$ -domain with disulphide bridges shown as yellow sticks.





Figure 2. The cobalaminbinding site of bovine TC. (A) Close-up view to Cbl in the domain interface (orientation as in Figure 1A). (B) Fo-Fc omit electron density map at  $3\sigma$  with the His residue as upper axial ligand and dimethylbenzimidazole as lower axial ligand of the Co ion (in magenta). by many microorganisms and may harmfully block the active site of Cbl-dependent enzymes. The second application is the rational design of Cbl-based bioconjugates. Such bioconjugates show potential as cytotoxic drugs or imaging agents in cancer treatment or may be used as Cbl-competitors to selectively block cell growth in the treatment of AIDS-related lymphoma or cancer. This application is based on the observation that proliferating cells express more surface receptors for holo-TC, and thus take up proportionally more Cbl, than cells in the stationary phase.

Human TC was expressed in Pichia pastoris and subjected to extensive screening of crystallization conditions. The best crystal form obtained consisted of plate-like crystals that diffracted to 3.2 Å resolution at the ELETTRA XRD beam line. The two molecules in the asymmetric unit of the orthorhombic cell were related by purely translational non-crystallographic symmetry (NCS) [2]. This feature and the weak diffraction hampered the solution of the phase problem by the multiple- or single-wavelength anomalous dispersion (MAD or SAD) method. The problem was solved by switching to the bovine form of transcobalamin which possesses 73% sequence identity with the human form [3]. Two well-diffracting crystal forms were obtained; monoclinic needle-shaped crystals diffracted to

2.0 Å resolution and trigonal crystals to 2.4 Å. As also the first mentioned crystal form showed purely translational NCS, we used the second crystal form with only one molecule per asymmetric unit for successful phase calculation. Highly redundant SAD data were collected with the X-ray wavelength tuned to the Co K-edge. The elevated solvent content of the trigonal crystals (68%) facilitated the calculation of starting phases of sufficient quality with the program SHARP. Solvent flattened electron density maps at 2.8 Å resolution were used with ARP/WARP and on the graphics to build a partial model of bovine holo-TC, comprising 80% of all amino acids and the Cbl ligand. Molecular replacement calculations using this model together with data of the better diffracting monoclinic form allowed completion of the bovine TC model. This could then be exploited as molecular replacement template for human TC. All structures were refined with REFMAC5 using NCS restraints where possible and TLS refinement.

Human and bovine transcobalamin adopt a very similar molecular architecture (1.2 Å root mean square deviation in backbone atoms) which consists of two domains, an N-terminal " $\alpha$ -domain" that is made up of an  $\alpha$ 6- $\alpha$ 6 barrel, and a C-terminal " $\beta$ domain" showing mainly  $\beta$ -strand elements (Figure 1) [3]. Three disulphide bridges are observed in the  $\alpha$ -domain of which two were previously found to be crucial for the stability of this domain. The Cbl ligand, with its 5,6-dimethylbenzimidazole moiety coordinated to the Co ion ("base-on" conformation), is tightly enclosed in the domain interface (Figure 2). Interestingly, the water molecule at the upper axial position of the Co ion in the Cbl ligand originally used for the preparation of holo-TC was displaced upon binding to the protein by the side chain of a histidine residue. A physiological role of this displacement is not yet established. Stronger axial ligand groups than H2O, such as CN or N3, are not displaced as has been concluded by the fact that UV/visible spectral changes upon Cbl-binding to TC occur only for H2O-Cbl. Coordination of a histidine residue to the Co ion has been observed before for some Cbldependent enzymes. This occurs, however, from the lower axial side of Cbl's corrin ring, i.e. the displaced group is the dimethylbenzimidazole rather than the upper axial group. The mode of axial His-Co coordination found in TC is thus unique among Cblbinding proteins.

The amino acid sequences of IF and HC show about 25% identity to the human TC sequence. An alignment suggests that most secondary structure elements of TC are present also in IF and HC and that the disulphide bridges in the  $\alpha$ -domain are conserved. The histidine residue which coordinates to the Co ion in TC, however, is not present in the other two transport proteins.

A rational approach to the design of successful Cbl-based bioconjugates is now possible with the help of the TC structure. Inspection of the Cbl environment in human TC (Figure 3) shows that only the 5'-hydroxyl group on the ribose of Cbl's nucleotide moiety can accommodate the attachment of a larger ligand molecule without disturbing the interactions between TC and Cbl. The upper axial ligand position of the Co ion can be used successfully as well, despite the absence of the His coordination. Attachment at the corrin side chains or the phosphate group will inevitably lead to impaired interactions. Beside steric problems, electrostatic repulsion between the attached ligand and residues of TC should be considered. For instance, the surface of

human TC around the Cbl-containing cavity is in part negatively charged (Figure 3).

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# INSIGHTS INTO A NEW Pdi-LIKE FAMILY: STRUCTURAL AND FUNCTIONAL ANALYSIS OF A PROTEIN DISULFIDE OXIDOREDUCTASE FROM AEROPYRUM PERNIX K1

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# INTRODUCTION

Disulfide bond formation between cysteine residues is a key step in the stabilization of the tertiary structure of a protein. Organisms ranging from bacteria to humans have developed different systems to control this oxidative process. In bacteria, disulfide bond formation is assisted by proteins of the Dsb family, while in eukaryotic cells, disulfide bond formation and rearrangement are catalyzed both by PDI and by its homologues. PDI is a protein localized in the endoplasmatic reticulum (ER) organized into four domains (a, b, b' and a') followed by a C-terminal extension referred to as c. The a and a' domains contain one catalytically active CGHC motif each, while b and b' are redox inactive domains. Recently, the threedimensional structure of yeast PDI has been solved, revealing that the shape of the enzyme structure is a twisted "U" with the a and a' domains at the ends of the "U" and the b and b' domains forming the base. Each domain adopts the thioredoxin (Trx) fold with minor variations and the two active sites face each other on the inside of the "U".

In thermophilic organisms, a potential key role in disulfide bond formation has recently been ascribed to a new Protein Disulphide Oxidoreductase (PDO) family [1-3].

Two members of this family have been characterized from both the structural and functional points of view so far. One was isolated from the archaeon Pyrococcus furious (PfPDO) [1,2], the other from the bacterium Aquifex aeolicus (AaPDO) [3]. Both these enzymes were found to have a molecular mass of about 26 kDa and to be organized into two structural units each of which characterized by a Trx fold and a CXXC active site motif. Although these two structural units can be functionally related to the active domains of the eukaryotic enzyme PDI, unlike those of PDI, they pack tightly together and are thus structurally un-separated.

We have recently identified another member of this new PDO family, named ApPDO, which was isolated from the archaeon Aeropyrum pernix K1. During a general research project aimed to provide insight into the functions and evolution of PDOs we conducted a structural and functional study on ApPDO and correlated it with a computational analysis.

# **RESULTS AND DISCUSSION**

## Functional and structural analysis

The functional characterization of ApPDO demonstrated that this enzyme is able to catalyze the reduction, oxidation and isomerization of disulfide bonds. The enzyme was crystallized in the space group I222 with 2 molecules per asymmetric unit. X-ray diffraction data were collected on XRD1 beamline at the Synchrotron source Elettra in Trieste, using a Mar CCD detector. The structure was solved by molecular replacement using the AaPDO PDB coordinates [3] as starting model. The structure was refined using the CNS program to a crystallographINSIGHTS INTO A NEW Pdi-LIKE FAMILY: STRUCTURAL AND FUNCTIONAL ANALYSIS OF A PROTEIN DISULFIDE OXIDOREDUCTASE FROM AEROPYRUM PERNIX K1



Figure 1 (a) ApPD0 overall fold. (b) Schematic representation of the ApPD0 fold.  $\beta$ -strands are shown as arrows and  $\alpha$ -helices as cylinders.

ic R-factor of 18.7% and an R-free of 20.9% in the 20.0-1.93 Å resolution range. The refined structure presented a good geometry with r.m.s.d. from ideal bond lengths and angles of 0.005 Å and 1.20°, respectively.

ApPDO folds into eight  $\alpha$ -helices ( $\alpha$ 1- $\alpha$ 8) and eight  $\beta$ -strands ( $\beta$ 1– $\beta$ 8) (Figure 1a, 1b). The strand succession in the  $\beta$ -sheet is  $\beta 2\beta 1\beta 3\beta 4\beta 6\beta 5\beta 7\beta 8$ , with  $\beta 3$  and  $\beta 7$  running antiparallel to the others. The eight  $\alpha$ helices are distributed asymmetrically on either sides of the central B-sheet, with helices  $\alpha 3$  and  $\alpha 7$  on one side and helices  $\alpha 1, \alpha 2, \alpha 4, \alpha 5, \alpha 6$  and a 8 on the other (Figure 1b). The ApPDO structure can be divided into two structural units, that pack closely together and thus are not structurally separated. Each unit contains a Trx fold comprising a four-stranded  $\beta$ -sheet and four flanking  $\alpha$ -helices (Figure 1). Despite rather low sequence identity (about 18 %), the two structural units are fairly overlapping and the r.m.s.d. calculated for the superimposition of 93 corresponding C $\alpha$  atoms is 1.5 Å. ApPDO presents two CXXC active site motifs located on the protein surface. The first of these (CETC) is located in the N-terminal unit at the amino end of the second helix, while the second one (CPYC) is positioned in the C-terminal part of the molecule at the beginning of the sixth helix (Figure 1).

The electron density corresponding to these regions is well defined and shows that

the two active sites exist in the oxidized state, by forming two intra-chain disulphide bonds in a right-handed hook conformation. A careful comparison between the two active sites shows a remarkable degree of structural similarity, revealing that dihedral angle values of the two disulfides are similar to each other with values typical of stable disulfide bonds.

### **Pka calculations**

To shed light on the catalytic properties of each ApPDO CXXC motif we determined the theoretical pKa values of the cysteines. In the literature, it had been widely reported that the pKa values of the two cysteines were related to the redox potential of the active-site, thus playing a critical role in the determination of the physiological functions of the members of the Trx superfamily. Our results showed that the pKa values of the Nterminal cysteines (Cys1) of both the active sites were lower than those observed for the C-terminal cysteines (Cys2), thus suggesting that both ApPDO active sites were able to perform catalytic functions (Table 1). In fact, previous experimental and computational pKa studies on members of the Trx family indicated that a low pKa of the first cysteine and a high pKa of the second one were suggestive of catalytic activity. At this point, we also determined the theoretical values of the cysteine pKas in AaPDO and

INSIGHTS INTO A NEW Pdi-LIKE FAMILY: STRUCTURAL AND FUNCTIONAL ANALYSIS OF A PROTEIN DISULFIDE OXIDOREDUCTASE FROM AEROPYRUM PERNIX K1

		ApPD0	Aa PDO	<i>Pf</i> PD0	PDI*	
N-terminal site	Cys1	9.2	9.5	12.0	7.7	
	Cys2	25.4	23.0	26.5	25.7	
C-terminal site	Cys1	7.3	6.0	8.0	6.1	
	Cys2	>30	26.9	25.3	24.3	

\*For PDI N-terminal site refers to the a domain while C-terminal site to the a' domain

Table 1. Estimated pKasfor the active sitecysteines of ApPDO,AaPDO, PfPDO and PDI(a and a' domain).

PfPDO. Similar results to those of ApPDO were obtained for AaPDO; the low pKa values observed for the N-terminal cysteines of the two active sites are in agreement with the experimental observation that both of them perform catalytic functions [3]. Different results were obtained for PfPDO: the pKa value of the first cysteine of the N-terminal CXXC motif was particularly high, thus suggesting the inability of this site to perform the catalytic function. These data are in agreement with mutagenesis and kinetic studies, indicating that this site does not perform any reductive or oxidative activity [2].

Our results suggest that despite similar functional and structural characteristics the members of the PDO family greatly differ in terms of the contribution of each active site to total catalytic activity. Based on its apparent cellular function and the presence of two structural units with an active site each, a link can be drawn between this PDO family and the eukaryotic PDI. It is possible to speculate that the enzyme used by eukaryotes to form protein disulfide bonds in the endoplasmic reticulum might have originated from a similar enzyme contained in thermophilic organisms. Based on these considerations, the members of the PDO family can be considered as the simplest PDI forms found in thermophiles. To test this hypothesis, the theoretical values of the catalytic cysteine pKas of the a and a' domain of yeast PDI have been calculated and compared with those of ApPDO, AaPDO and PfPDO (Table 1). The pKa values obtained for the N-terminal cysteines of both PDI active sites were found to be lower than those determined for the C-terminal cysteines. Moreover, as already observed for the members of the PDO family, the pKa value of the N-terminal cysteine of the a domain was found to be slightly different from that of the a' domain. This difference is in agreement with experimental data, which indicate a higher redox potential for the a' domain (-152 mV) than for the a domain (-188 mV). These findings are further evidence of the functional similarity between these two enzyme families. However, the different three-dimensional organization of the Nand C-terminal units of the PDO family compared to the a and a' domains of PDI strongly point to different mechanisms of action for these two biological systems. Hence the need for further experimental studies to clarify how different three-dimensional structures can give rise to similar functional behaviour.

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# SURFACES AND INTERFACES

Surfaces and interfaces are the boundaries between bulk material and gas or liquids. They have utmost importance because their special physical and chemical properties can explain an amazing number of processes in the 'real world', many of which find relevant technological applications. For this reason, surface and interfacial phenomena have a topical role in a number of disciplines ranging from heterogeneous catalusis to corrosion, from epitaxial growth to semiconductor fabrication, from material science to magnetism.

This section illustrates how X-ray photoemission spectroscopy and related techniques provide powerful and versatile investigation methods in the study of surfaces and interfaces. The well established methods made once available by surface science have now developed tremendous potential at the third generation synchrotron facilities like ELETTRA and allow the exploration of complex systems like organic molecules and thin films, biopolymers and nanoparticle catalysts on oxide supports.

Since long, researchers at ELETTRA are interested in fundamental research in catalysis. The study of carbon monoxide dissociation on Rh nano-pyramids (Buatier de Mongeot and coworkers) is a fine demonstration on how the catalyst morphology and structure can influence reactivity. By controlled exposure of a Rh(110) model catalyst to a beam of noble gas ions, researchers tune the step distribution of a substrate, and show that this directly affects the rate of CO dissociation.

Very active research has been focused on metallic/organic interfaces, motivated by the technological importance of organic based electronic devices. The study of Aristov and co-workers explores the deposition of different metals onto an organic semiconductor film, CuPc. In contrast to K, Sn and Ag lead to formation of metallic films without interdiffusion, intermixing and chemical reaction with the organic layer. These results are expected to impact the technology for elaboration of organic-based electronic devices.

Cavalleri et al reached unprecedented understanding about the molecule-substrate and molecule-molecule interactions in L-Cysteine self-assembled monolayers on Au(110). X-ray methods such as high resolution XPS, polarization-dependent NEXAFS and X-ray diffraction allowed characterising the structural, morphological and electronic properties of a self-organised intermediate phase consisting of paired molecular rows.

With the synchrotron-based study of the physical properties of synthetic eumelanin thin films, L. Sangaletti and collaborators have opened a new trend in the study of biopolymers. Eumelanin has an important role in many biological phenomena, such as protection of UV light and neural activity, besides being an ideal candidate for fabrication of active devices in organic electronics. With the use combined use of XPS and resonant photoemission spectroscopy it was possible unveil the electronic structure of eumelanin thin films, which is still largely unexplored. This study allowed gaining deeper insight in the ultrafast timescale of charge-transfer processes occurring in such polymer films.

Finally, Locatelli et al propose a novel approach to control the growth of Au on titania. By using photon or electron stimulated desorption and subsequent annealing at intermediate temperatures, an ordered array of vacancies are created, providing a one dimensional template for the subsequent Au deposition. The growth of one –dimensional Au is demonstrated by the use of state of the art spectro-microscopy and further corroborated by ab-initio calculations.

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# CARBON MONOXIDE DISSOCIATION ON Rh NANOPYRAMIDS

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The control of the atomic step distribution of clusters and nanostructures is of utmost importance in determining, among others, their magnetic, electrical and catalytic properties. Recent experiments and theoretical models have tried to elucidate the atomistic details underlying the enhanced surface chemical reactivity of transition metals (TM). In particular Density Functional Theory (DFT) suggested that the *d*-band center shift and the relative change in the molecule-substrate interaction strength on low-coordinated atoms is the main reason for the barrier reduction in molecular dissociation.

In this respect, CO dissociation on TM stepped surfaces and supported clusters is particularly important in heterogeneous catalysis being one of the fundamental steps in the Fisher-Tropsch catalytic reaction, where carbon monoxide and hydrogen are converted into hydrocarbons. On Rh, previous results have shown that CO dissociation is negligible on close packed (111), (110) and (100) surfaces, and that it increases on stepped Rh substrates. Experiments on Rh clusters supported on alumina surfaces have shown a strong size dependence of the reactivity towards CO dissociation, but the nature of the active sites was not explained.

Recently, it has been found that it is possible to tune the morphology and step distribution of a crystalline Rh(110) substrate by controlled exposure to a beam of noble gas ions: Xe ion irradiation at few hundreds eV leads to the formation of non-equilibrium periodic nanostructures such as nanoscale ripples, mounds and unexpected Rhomboidal Pyramids (RP) [1]. The latter nanostructures are particularly interesting as candidate model systems for testing catalytic reactivity, since they are endowed with steep facets running along non equilibrium directions, exposing a high density of undercoordinated atoms.

In order to probe the reactivity of artificially prepared Rh nanostructures we used high-energy resolution X-ray Photoelectron Spectroscopy at the SuperESCA beamline [2] of ELETTRA to monitor the CO adsorption sites, the dissociation process and the formation of C and O atomic species [3]. The growth of the RP nanostructures was characterised in-situ by Low Energy Electron Diffraction (LEED). A cartoon model of the RP nanocrystals showing the geometry and the undercoordinated step sites is presented in Figure 1, where the number of exposed layers (and the lateral dimensions) have been scaled down by a factor 2.5. The morphology of the RP nanostructures is metastable, and tends to relax towards the flat fcc(110) morphology upon annealing. We verify that the morphology of the RP surface is preserved in the temperature range below 560 K where CO dissociation and desorption take place.

Once prepared, the RP were exposed to CO at T=200 K up to saturation. C1s and O1s core-level spectra were measured at the photon energies 400 eV and 650 eV, respectively. Figure 2(a) (left) shows the evolution of C1s spectra measured at 250 K after annealing of the saturated layer at different



Figure 1. Model for the RP and for the High Temperature Ripples (HTR) and Low Temperature Ripples (LTR) phases.

temperatures. The presence of two components at 286 and 285.55 eV reflects the occupation of two different adsorption sites. This result is confirmed by the O1s spectra which show also two peaks at 531.7 and 530.9 eV. Thanks to the high sensitivity of XPS to the molecular adsorption site we can assign the higher C1s binding energy component to CO adsorbed in on-top sites, while the lower binding energy peak is related to the CO chemisorbed in bridge sites. Upon a temperature increase, the C1s spectra drastically change: the two components at 286 and 285.55 eV lose intensity due to CO desorption and slightly shift towards lower binding energies at higher temperatures.

However the most important feature is the growth of a lower binding energy component at 283.55 eV, which is assigned to atomic carbon originating from dissociated CO. The evolution of the O1s spectra follows the same behaviour indicating an increase of surface atomic oxygen (O1s peak at 528 eV). By fitting the C1s spectra, we obtained the plot for the three different species (Figure 2(a)-right). Up to about 350 K the CO coverage decrease is due only to desorption while at higher temperature even CO dissociation takes place. In agreement with experiments performed on flat Rh surfaces, on-top CO is the only species present on the surface above 450 K. With increasing the surface temperature the CO desorption/decomposition process is completed:  $9.4\pm0.5\%$  of the initial CO has converted into atomic carbon.

When a lower initial coverage is used the surface is mostly occupied by CO in on-top configuration. As shown in Figure 2(b), we observe a similar temperature behaviour of the surface population, with the population of bridge-bonded CO disappearing before the on-top species and the atomic carbon coverage increasing at temperatures above 370 K. Our data thus unambiguously show that when bridge-bonded CO is absent, atomic C still grows, as a product of dissociation of on-top CO. Now the fraction of dissociated CO at 560 K is much larger, 22±3%. The tendency to a higher dissociation probability for a lower initial coverage has been confirmed by the results obtained when a very low initial on-top coverage  $(\theta=0.03 \text{ ML} - \text{Figure } 2(c))$  is present on the surface. In this case 80±14% of the CO molecules undergoes dissociation.

The broad choice of artificial configurations of atomic steps that can be obtained by varying preparation conditions, allowed us to probe the CO reactivity for different nanostructures. In particular we prepared ripples running along [1-10] (High Temperature Ripples-HTR) and along [001]



Figure 2. (a) Left: Sequence of C1s spectra for a saturated CO layer after annealing at increasing temperature. Right: Fitted area of the C1s peaks due to CO in on-top (orange dots) and bridge (green squares) sites, due to total CO signal (full line) and to dissociated atomic carbon (blue dots). (b) Same as above for a lower initial CO dose ( $\theta$ =0.21 ML). (c) C1s core level spectra for a very low CO initial dose  $\theta$  =0.03 ML (orange trace) and after annealing to 570 K (blue trace).

(Low Temperature Ripples-LTR), both structures endowed with a high density of steps. The local structure of these two phases is reported in Figure 1. Photoemission results indicate that for HTR and LTR ~4% of the saturated CO layer undergoes dissociation.

At variance with the (111), (100) and (110) flat Rh surfaces which present first layer atoms with 9, 8 and 7 coordination, respectively, the RP, are composed by a large number of 5- and 6-fold coordinated atoms. We associate the high reactivity of Rh nanopyramids towards CO dissociation with the presence of these undercoordinated Rh atoms, with CO molecules occupying preferentially on-top configurations. The lower is the metal coordination number n of the surface atoms, the smaller the Rh d-band width that results in a shift of the *d*-band center towards lower binding energy. The higher reactivity of these low coordinated TM atoms towards molecular dissociation has been proven for a large number of systems

What appears peculiar to the RP, with respect to the LTR and HTR morphology, is the very high density of kinked microfacets, produced by the steps running along [1-12], which provide a high density of low coordinated atoms labeled K in Figure 1. The local atomic configuration of the RP microfacets, represents an *open* morphology. Indeed, with decreasing the initial CO coverage the availability of 6 Rh atoms, with CO sitting in on-top sites, increases, thus resulting in a higher fraction of dissociated CO. CO preferentially dissociates on RP when placed in on-top configuration. The on-top site has been proven to be the favourite adsorption configuration at low coverage on a large number of flat and stepped Rh surfaces.

In conclusion we have shown that artificially prepared Rh nano-pyramids can induce the dissociation of CO, which would otherwise desorb intact on the (110) terraces. A comparison of different nanostructures allows to indicate that the most probable reaction site for CO dissociation is an on-top configuration at the kinked step edges where Rh atoms have the lowest coordination. Core level photoelectron spectroscopy data indicate that at high CO coverage the dissociation is almost 10% and increases with decreasing the initial CO coverage up to 80%. The possibility to form nanostructured surfaces with high density of low coordinated atoms opens up the possibility to artificially increase the surface reactivity in a controlled way.

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# SHARP, MAINLY NONREACTIVE METAL-ORGANIC SEMICONDUCTOR INTERFACES: Ag AND Sn ON COPPER PHALOCYANINE THIN FILM

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State-of-the-art nanotechnology based on organic semiconductors brought amazing innovations in the area of nanoelectronics with spectacular performances as huge memories, fast optoelectronic response and together with a relatively low cost of fabrication promises to offer the next technological breakthrough in mobile and foldable displays [1]. Moreover, latest research activities reveal that peculiar optical and electronic properties of organic semiconductors give rise to a new generation of light-emitted devices: organic semiconductor lasers offering much stable performance in respect to usual inorganic laser diodes and opening wide perspectives for optical communications and sensor applications. In these regards, prospective commerce opportunities as well as basic scientific interest inspire and motivate studies in the filed of molecular organic semiconductors.

The key elements in architecture of micoand nano-electronic devices are organicorganic or organic-metal interfaces. Therefore to make further progress in development of these organic semiconductor lasers and other similar kinds of devices one requires both the understanding and the tailoring of the physical, chemical and transport properties of the metal-organic molecular thin films (OMTF) interfaces fabricated in UHV conditions. The later becomes a principal base for organic nano- and molecular- device technologies. Moreover, the development and technology of production of different organic based electronic devices require creation of different types of me/organic thin film interfaces and contacts with numerous electronic properties. The case of deposition of organic semiconductors onto metals has got recently considerable research activity and now some progress has been achieved as regards basic interfacial

Figure 1. Top of valence band as a function of Ag deposition on CuPc film at RT.



properties of such organic on metal contacts. In spite of numerous times greater technological importance the other case, metal deposition onto organic films is comparatively much less studied.

Since about a couple years, we have focused on the investigation of evolution of the electronic structure of copper phthalocyanine (CuPc) films at metal deposition and on interface formation during this process. CuPc belongs to the family of the phthalocyanines (archetypal organic molecular semiconductors), which play an important role among other OMTF's. Their potential technological applications are the good reason for researchers to devolve remarkable attention to these materials. Moreover, Pc's demonstrate good compatibility with UHV and can be successfully grown as thin, ultra-clean, well ordered films on various substrates in standard ultra high vacuum (UHV) spectrometers. These films then possess excellent and well defined electronic properties and can be studied in situ in UHV conditions by means of modern surface science techniques.

Here we report an observation of sharp, almost non-reactive interfaces for Ag/CuPc and Sn/CuPc systems. The preparation of the CuPc single crystal films, the Ag and Sn deposition and the soft x-ray photoemission spectroscopy measurements were performed in the ultra high vacuum electron spectrometer on high energy resolution dipole beam

**Figure 2.** Ag 3*d* core level as a function of Ag deposition on CuPc film at RT.



line - BEAR of synchrotron ELETTRA (Trieste). This beam line of dipole type was chosen because it is especially suitable for studies of fragile organic materials which could be damaged under irradiation. The CuPc single crystal thin (of about 70 Å) film was grown on the (100) surface of a gold single crystal by molecular evaporation from CuPc powder. Ag and Sn were deposited onto the CuPc films from the resistively heated tungsten baskets without detectable pressure increase during deposition. Other experimental details, concerning Au(100) substrate preparation etc can be found elsewhere (see e.g. [<sup>2</sup>]).

In order to evaluate degree of Ag and Sn chemical reactivity with CuPc thin film we compare our present results with those for K and In, which were studied in our previous investigations [2, 3]. Among other properties in this publications we have reported a detailed study of the valence band of K(In)/CuPc systems formation by means of photoemission spectroscopy using synchrotron radiation. In particular very fast degradation of HOMO with K and In deposition onto CuPc film was found. Moreover HOMO completely disappears at about 5-7 angstrom of nominal coverage. In addition in [2, 3] the formation of strong electron gap states with metal deposition was observed, which could be considered as reaction-induced ones. Thus K and In atoms being deposited onto CuPc show strong diffusion into this OMTF and strong chemical reaction with organic substrate.

Ag show significantly less chemical reactivity with CuPc thin film than for example K and In. Figure 1 shows the top of valence bands of pristine CuPc (bottom curves) and evolution of the spectra with silver deposition. One can really see that shape of HOMO peak practically does not change. Furthermore, unlike for reactive K and In, the HOMO peak persists till max coverage of Ag studied in the present investigation. One of the most amazing observation, which we would like to stress here - no creation of any gap states during formation of Ag/CuPc interface (see region between E<sub>F</sub> and HOMO onset) was observed. Thus from this type of measurements we can conclude, that Ag/CuPc interfaces are unreactive and abrupt.

Now we discuss the results of investigation of the core level behavior with metal deposition. In [3] studying K/CuPc interface formation we have found appearance and rapid growth of only one narrow reactive K 2p component. No metallic component was observed. The energy position of the doublet and absence of metallic component has given us a ground for assumption that K atoms: (i) intercalate into the molecular solid, (ii) form no metallic film on the top of the OMTF and (iii) strong react with organic film giving over the valence s-electrons to CuPc molecules. As far to In/CuPc system [2], spectra measured at the very early stage of In deposition show two components in the In 4d doublet. The (small) component at lower binding energy is assigned to metallic indium (cluster formation), while the component at higher binding energy to In reacted with CuPc. On the first stage of deposition, the amplitude of the metallic component was relative small and constant, while the other one shows rapid growth. This stage of deposition corresponds to strong indium diffusion into organic film, accompanied by the chemical reaction of In atoms with CuPc. After saturation of the CuPc film by In, the growth of the metallic component is prevalently observed. Finally, the reacted In component is completely screened by the metallic film formed on the top of CuPc film. In summary, In atoms being deposited onto CuPc film diffuse into organic film up to saturation, have a strong chemical interaction with it and finally form a metallic film on the top of OMTF.

As shown in Figure 2, since the first stage of Ag deposition onto CuPc film Ag 3d core level emission, which exhibits a narrow doublet of spin-orbit splitting, indicates that silver is metallic. The tiny peak seen in Ag 3dspectrum at coverage of 32 Å is likely ascribed to the metallic film plasmon of energy  $\approx$  4 eV. No other Ag 3*d* core-level components were observed. This investigation thus confirms the previous conclusion, that the Ag/CuPc interface is really unreactive and abrupt. Additionally we present the C 1s core-level behavior as a function of Ag deposition (Figure 3). Unlike for reactive K and In, one observes only decreasing of the C1s core-level, which basically keeps shape with Ag deposition. The later confirms the



suggestion that Ag atoms do not diffuse into the CuPc film and do not react chemically with substrate atoms.

The Sn/CuPc interface formation shows basically the same behavior as Ag. Therefore we can conclude that room temperate deposition of Ag and Sn on organic semiconductor thin film – CuPc leads to formation of metallic film on the top of organic one, without any interdiffusion, intermixing and without remarkable chemical reaction. We envisage that this observation will have large significance for elaboration of organic based nanoelectronic devices.

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**Figure 3.** C 1*s* core level as a function of Ag deposition on CuPc film at RT.

# ELECTRONIC AND GEOMETRIC CHARACTERIZATION OF THE L-CYSTEINE PAIRED ROWS PHASE ON Au(110)

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> Self Assembled Monolayers (SAMs) of small bio-molecules are extensively investigated aiming at introducing sophisticated functionalities at solid surfaces. These kinds of studies are expected to shed light on the conceivable role of surfaces in the early formation of macromolecules. Cysteine (HSCH2CH(NH2)COOH) is a fundamental amino acid, involved in the regulation of important metabolic processes. The thiol side-chain forms strong bonds with metals. This property is exploited in the modification of electrodes for molecular recognition and to develop sensors for metal ions. Cysteine plays an important role in the anchoring of peptides and proteins, e.g. metallo-proteins, at gold surfaces. The chirality properties are exploited in studies on

**Figure 1.** S2p (left panel) and C1s (right panel) HR-XPS spectra as a function of coverage, photon energy 710 eV, **(a)** 0.14, **(b)** 0.33, **(c)** 0.62, **(d)** 0.8, **(e)** 1 ML. [1].



enantiospecific adsorption. After previous studies on self-assembly from solution, more recently our investigations moved to study deposition from the gas phase on Au(110), under ultra high vacuum conditions. Thanks to a home-designed, differentially pumped source for precise molecular beam deposition, we performed an electronic and structural characterization of the adsorbed phase at the ALOISA beamline. In particular, from High Resolution XPS (HRXPS) we obtained information about the moleculesurface bond and the molecular charge state (e.g. zwitterionic vs. neutral apolar state), from early stages of adsorption up to nucleation of the second layer.[1] Then, we focused on the structural properties of an intermediate phase consisting of paired molecular rows, extending along the direction of the clean surface missing rows [2,3], of which the formation process is still under debate. Figure 1 illustrates the evolution of HRXPS S2p and C1s spectra in the submonolayer regime. The S2p region is characterized by a well defined doublet, S1. Its binding energy  $(161.95 \pm 0.05 \text{ eV})$  lies close to the value (161.9  $\pm$  0.1 eV) measured for SAMs deposited from solution and for alkanethiols chemisorbed on gold surfaces. S1 is assigned to a thiolate compound. In spectrum (e), a second doublet S2, fully developing at higher coverage [1], was required to fit the spectra at the high binding energy side. Together with definite variations of the C1s spectrum, S2 concurred to identify the population of the second layer.[1] The large chemical shift between the first and second

layer components indicates that a strong molecule-surface bond, involving the S atom, occurs. In the C1s region, two peaks (C1 and C2) were identified at 284.7 and 286.2 eV BE, assigned to  $C_{\beta}$  and  $C_{\alpha}$ , respectively (HSC<sub> $\beta$ </sub>H<sub>2</sub>C<sub> $\alpha$ </sub>H(NH<sub>2</sub>)COOH). A broad peak with evident sub-structure occurs with center of mass at 288.7 eV BE, in the energy region typical of carboxyl. The fit confirmed the decomposition into two peaks, C3 (284.8 eV) and C4 (286.3 eV). The  $C_{\beta}$ - $C_{\alpha}$  energy splitting, measured for first layer molecules (1.5 eV), turned out to be much larger than the one measured for molecules belonging to the second layer (0.9 eV), that is close to the value calculated for the free molecule (0.7 eV). The  $C_{\beta}$  energy in the ML regime appears strongly influenced by the molecule-substrate interaction.

In order to look at adsorbate-induced morphological and structural changes of the substrate we performed in-plane Grazing Incidence X-Ray Diffraction (GIXRD) measurements [3]. Radial scans taken as a function of exposure along the [001] direction, enlightened the lifting of the (1x2)reconstruction (Figure 2, upper panel). Fourth-integer diffraction peaks were detected already in the early stages of deposition, confirming the presence of a fourfold reconstruction of the substrate already pointed out by RHEED [1]. While the intensity of the fourth-integer peaks increases with coverage, the intensity of the half integer peaks related to the Au(110) reconstruction decreases. Half-integer peaks display two sub-components (Figure 2B). The narrow component preserves the same width of the bare surface peak up to disappearance. The corresponding correlation length, 500 Å along the [001] direction, is attributed to uncovered parts of the substrate, displaying the intact missing row structure. The broad component is associated with the fourfold L-Cysteine phase. The corresponding periodicity fits the spacing of the paired row phase observed by STM for D-Cysteine [2]. The average correlation length of the fourfold domains in the [001] direction amounts to 32-35 Å, and corresponds very well to the lateral width of two pairs of Cysteine rows. From the width of the azimuthal scans of the fourth-integer peaks (Figure 2C) a correlation length of 200 Å is found along the



[1-10] direction. The fourfold diffraction pattern corresponds to an intermediate deposition stage where the domains formed by two chains of coupled Cysteine rows coexist with bare surface domains. The Au(1x2)rows apparently act to laterally constrain the Cysteine chains. As the coverage approaches 1 ML, the half-integer peaks tend to vanish, while the fourth-integer peaks shift towards the closest integer peak and weaken, suggesting a partial release of compressive strain of the Cysteine domains. For exposures exceeding the monolayer, all the surfacerelated diffraction peaks rapidly vanish. Our findings suggest the tendency toward a poorly ordered overlayer structure, most likely incommensurate, as soon as the whole substrate surface gets completely covered. We also performed some *out-of-plane* x-ray diffraction measurements on the fourfold phase in order to have information about the vertical rearrangement of Au atoms. The data are compatible with a vertically de-constructed (i.e. without missing rows) unit cell with four-fold symmetry, due to lateral displacement of Au atoms, which follows the

Figure 2. (a) Radial GIXRD scans along the [001] direction for increasing exposure of cysteine. (b) deconvolution into two components of the (0,-3/2) peak profile taken at 3/4 ML along the [001] direction. (c) (0,-7/4) peak profile along the [1-10] direction. [3]



Figure 3 Comparison between the NEXAFS spectra taken in p and s polarization. The deconvolution of the spectra into individual components is also shown; the energy position of the deconvoluted peaks is reported in the inset table. [3] chirality of the Cysteine overlayer. The crosscorrelation between HRXPS and GIXRD results led to assign a zwitterionic character to the molecules belonging to the paired row phase. In order to understand the orientation of the backbone of Cysteine molecules in this phase, we measured Near Edge X-ray Absorption Spectra (NEXAFS) at the Carbon K-edge as a function of the surface orientation, with respect to the linearly polarized x-ray beam. The comparison between the spectra taken in p- (upper panel) and spolarization is reported in Figure 3. The deconvolution of the spectra into different sub-components is also indicated. A complete s-polarization azimuthal scan, obtained rotating the surface around the normal, has been measured as well.[3] The comparison with the literature on gas phase and on Cysteine powders indicates that the narrow resonance C4 and the broad structure C8 are the  $\Pi^*$  and  $\Pi^*$  transitions related to the carboxylate group, respectively. The polar dependence of their intensities indicate that the plane of the carboxylate group is preferentially parallel to the surface. The assignment of the other spectral features is less straightforward. It is known from gas phase calculations that two transitions related to methyl carbon (C<sub> $\beta$ </sub>) are located below  $\pi^*$ . These findings, together with the observation that C1 and C3 display the same spatial orientation, support their assignment to  $C_{\beta}$  -  $\sigma^*$  transitions. From azimuthal and polar dependence of C1 and C3, the S-C bond is found to be parallel to the surface, with a preferential azimuthal orientation (30° from [001] direction). [1,3]

To summarize, we have shown that, by applying several structural and spectroscopic techniques based on synchrotron radiation, we have reached an unprecedented understanding of a complex molecular network. In particular, the nature of the molecule-substrate and molecule-molecule interaction was enlightened by the HRXPS measurements. The orientation of the main molecular axis with respect to the main lattice direction of the substrate was provided by polarization-dependent NEXAFS measurements. Further we gained insight in the molecule-induced substrate rearrangement by GIXRD. The cross-correlation between information coming from these techniques, obtained in situ under the same experimental conditions, led us to draw a full 3D model of the paired row phase, taking into account both the chiral properties and the zwitterionic character of L-Cysteine molecules.

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Melanins are "rigid-backbone" conductive polymers composed of polyacetylene, polypyrrole, polyaniline "blacks" and their mixed copolymers. It is a class of naturally occurring pigments, found in all living kingdoms in many different structures and forms. The simplest melanin is polyacetylene, from which all others derive. The exact chemical structure and the physical properties of these polymers are largely unknown and their role in several natural functions and diseases appears conflicting and is subject to debate [1].

Melanin is most prominently known as the pigment that colours the human skin and provides protection from UV light. It also plays a crucial role to vision and its absence may cause blindness. On the other hand, the human brain has highly pigmented non-illuminated areas, such as the substantia nigra and the locus coeruleus, in which melanin is present and must fulfil some other function, e.g. as a sink for free radicals, a redox buffer or a biological device for dissipating excitational energy. Indeed, melanin is envisaged as an energy transducer with the properties of an amorphous semiconductor. It can absorb many different types of energy, (including vibrations, sound and electromagnetic waves and heat), then dissipated under some form of reusable energy (mainly heat).

Being a good electron acceptor melanin forms charge-transfer complexes with compounds which have electron-transfer properties. Already in 1974 it has been demonstrated that melanin can act as a semiconductor "bistable switch", i.e. as an "active device" whose electrical conductivity can be modulated between high and low states by an applying an external electric field. This was the first organic transistor, which also emitted light (electroluminescence) when switched. Later on another kind of melanin, the polyacetylene black, was reported to become highly conductive if chemically modified by adding iodine. The Nobel Prize in Chemistry was awarded in 2000 for this discovery. Melanin is also the best soundabsorbing material known, probably due to the strong electron-phonon coupling it is expected to have, justifying its presence in the inner ear as a noise-protector.

However, the only proven natural functions are that of dye pigment and sunlight filter. A thorough examination of the physical and chemical properties of melanin is required in order to gain a deeper under**Figure 1.** Tapping mode AFM image of a melanin film on gold. The underlying gold terrace structure is well visible. The (dark) holes in the film reveal a film thickness of 3.5nm. Side panel: Calculated Raman modes for IQ, SQ and HQ monomers and the experimental spectrum of eumelanin.



standing of all other functions and properties mentioned above.

Among the several types of melanin, eumelanin is the predominant type present in humans. It is generally accepted that eumelanin protomolecules are formed of three to four stacked planar oligomers which in turn consist of three to seven units of the various redox forms of 5,6-dihydroxyindolequinone: hydroquinone (HQ), indolequinone (IQ) and semiquinone (SQ). In this work we investigate the electronic and charge transfer properties of synthetic eumelanin (Sigma Aldrich) films deposited on polycrystalline metal surface (Au and Cu) by drop casting from a sonicated water solution. Their structure and electronic properties were characterised by AFM, x-ray absorption and emission spectroscopies at the SuperESCA beamline.

As illustrated in Figure 1 eumelanin on gold forms a continuous, smooth film that exhibits very few disruptions. XAS spectra at the C 1s edge (Figure 2a) and N 1s edge (not shown) show an angular dependence of the  $\Pi^*$  absorption peaks and thus clearly



indicate that the melanin layers have a preferred orientation ( $\Pi^*$  states are perpendicular to the molecular plane). Hence the eumelanin polymer dispersed in water and dropped to yield a thin overlayer shows a strong tendency to assemble in ordered structures in spite of the polycrystalline texture of the substrate.

Figure 2-bottom shows the occupied DOS measured via photoemission spectroscopy. The fact that the photoemission spectral weight is null at the Fermi level (0 eV of BE) clearly indicates that the film has a semiconducting character. Due to molecular character of the electronic states, several spectral features can be distinguished. The emission from the highest occupied molecular orbital (HOMO) is expected on the low-BE side of peak A where a deviation from a single peak tail is detectable (indicated by arrows). This can be ascribed either to vibronic effects, affecting the peak A emission, or to additional electronic states. It is worth noting that the valence band lineshape strongly depends on the photon energy (see the spectrum taken at hv=281 eV). Particularly the changes observed near  $E_{F}$ suggest the presence of electronic states close to the chemical potential.

A comparison of the measured spectra with the results of electronic structure calculations for the isolated monomers of which the *protomolecules* consist, provides further insights. The most likely description of solid melanin aggregates involves polymerization of elementary monomers with possible defects and substitution of the side groups as well as a mixing in the same sample of all elementary monomers. Deviations in both energy and intensity from the calculated DOS of the single monomer must be expected in particular for the low-lying electronic orbitals which are the ones primarily involved in the chemical bonding. Moreover, the states close to the HOMO can be modified by charge transfer to and from the metallic substrate and solid-state effects, including disorder, polymerisation and polarization screening. For these reasons the comparison with single monomers has to be considered with caution.

We performed *ab-initio* density-functional calculations of the structural and electronic properties of isolated monomers using the

Figure 2. Top: XAS spectrum at the C 1s edge. The inset shows the angular dependence. Bottom: Valence band photoemission spectra measured at hv=91 eV (red) and hv=281 eV (blue) together with the calculated DOS for IQ, SQ and HQ monomers.

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Quantum-ESPRESSO package [2]. As can be observed in Figure 2-bottom, the calculations show that the DOS heavily depends on the relative presence of either OH- (HQ monomer), oxygen (IQ monomer) or both (SQ monomer). By aligning the calculated HOMO to the Fermi level of the photoemission data (arbitrary choice), the HQ monomer DOS exhibits an overall agreement with the measured spectra, whilst less agreement was found with the IQ and SQ calculations. The comparison of calculated Raman spectra of the three monomers with the measured Raman spectrum of eumelanin (Figure 1 side panel) points into the same direction: in this case the measured spectrum can be mainly viewed as a linear combination of the HQ (dominant) and IQ monomer contributions, with only a small contribution from SQ.

The ultrafast timescale of charge-transfer processes has a crucial relevance to the biological activities of melanin, but little information exists concerning the time scales for the photophysical and photochemical processes that follow electron excitations in melanin. What is known is that eumelanin is a weak emitter and hence radiative processes play a minor role in the photodynamics of the pigment. One way to access both the electronic properties and the timescale of charge transfer processes is provided by resonant photoemission spectroscopy (RESPES). Figure 3 presents the valence band RESPES obtained by scanning the photon energy across the C 1s absorption threshold, from 281 eV to 305 eV. The first resonance is detected at about hv=285.6 eV. At this photon energy all valence band features show an intensity enhancement, which corresponds to an electron excitation into the first unoccupied  $\pi^*$  state. Beyond this enhancement an Auger emission with a clear dispersive behaviour on the BE scale (i.e. a normal Auger emission) appears. A careful analysis of the spectra reveals that pure resonant behaviour is observed only for feature A and for photon energies exciting the first  $\Pi^*$  transition. This suggests that when an electron is excited from the C 1s core level to the first  $\Pi^*$  state, it remains localized for a time long enough to allow interference between the autoionization decay channel and the direct pho-



toemission channel. In turn, when the electron is excited into higher empty states no resonance is detected, suggesting a prompt delocalization of the excited electron compared to the core-hole lifetime [3]. In order to estimate the characteristic timescale of the intermediate excited state, the resonant constant initial state profile of the A feature has been fitted to a Fano lineshape (Figure 3 inset). A lifetime of about 1.6 fs can be estimated by using the energy-time uncertainty principle. However, one has to be aware that several molecular orbitals contribute to the experimentally observed feature A, as suggested by the calculations of the basic monomers DOS. Thus, the Fano asymmetry parameter and the estimated lifetime can be regarded as an effective value accounting for possible contributions from a manifold of orbitals.

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[3] Schnadt J., *et al.*, *Nature* **418**, (2002) 620; Brühwiler P. A., Karis O., and Martensson O., *Rev. Mod. Phys.* **74**, (2002) 703 Figure 3. Valence band RESPES across the C 1s absorption threshold. The inset shows the CIS spectrum obtained by integrating the pure resonant spectrum between 0 eV and 6 eV of BE.

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> The ability to grow one-dimensional Au on the TiO<sub>2</sub> is highly desirable, as this system can significantly contribute to understanding the high catalytic activity of finely dispersed Au on oxide supports in a variety of reactions [1]. The high activity of Au, which is inert in bulk form, is generally attributed to the strongly modified electronic properties of nano-clusters [2], In addition, recent work indicates that also atomically distributed ionic Au has similar catalytic properties [3]. In practice the effect of dimensionality on reactivity is far from being completely understood.

> Here we report an experimental and theoretical study of Au on TiO<sub>2</sub>, indicating a novel pathway to creation of one-dimensional structures by Au deposition on oxy

gen vacancy rows. Photon stimulated desorption (PSD) was used to produce ordered vacancies, by removing the most weakly bound oxygen atoms (i.e. the bridge-bonded atoms). Temperature was kept sufficiently low so that no significant Ti and O exchange between surface and volume occurs, but repulsive interactions between vacancies could lead to long range ordering resulting in a missing row structure. This structure is metastable and is distinctly different from the (1x2) structure obtained by heating to high temperatures, for which the so-called added Ti<sub>2</sub>O<sub>3</sub> row model is generally accepted.

The experiments were performed at the Nanospectroscopy beamline using microspot x-ray photoelectron spectroscopy (u-





**Figure 2.** Intensity of Au 4f<sub>7/2</sub> core level emission as a function of the local irradiation dose for experiments with different Au coverage. Each data point was obtained by fitting the Au 4f spectrum.

XPS) for local chemical characterization, and low energy electron microscopy (LEEM) and LEED for structural characterization. The focused x-ray beam (hv = 170eV) was used to produce regions with different oxygen vacancy densities by irradiation with a flux density (about  $3 \cdot 10^{18}$  photons s<sup>-1</sup> cm<sup>-2</sup>) for different times at about 750 K. With increasing irradiation doses, the initial TiO<sub>2</sub> (1x1) LEED pattern evolves into a (1x2) pattern, indicating vacancy ordering, until an optimum (1x2) pattern is obtained (Figure 1). At higher doses the (1x2) pattern deteriorates. Following the preparation of regions with different vacancy densities, Au is deposited at the same temperature. The Au distribution in the non-irradiated and in the irradiated regions was determined by µ-XPS of the Au 4f core level emission. Minimization of the inelastic mean free path of photoelectrons in Au (about 3Å at 90 eV) ensured optimum discrimination between three-dimensional (3D) clusters and 2D distribution, because of the strong photoelectron screening in 3D clusters.

Figure 1 shows typical Au  $4f_{7/2}$  spectra of a 0.5 ML thick Au film from regions with different irradiation doses, i.e. with different vacancy densities. It is apparent that the Au 4f signal increases with irradiation dose. At Au coverage > 0.3 ML, the Au 4f signal increases in a Au coverage-dependent man-

ner, rapidly for low irradiation doses and then more slowly, as shown in Figure 2. The signal at zero dose is from 3D clusters which very likely nucleate at randomly distributed oxygen vacancies. The rise of the Au signal corresponds to the increasing filling of the vacancy rows. When all rows are filled, the Au 4f signal saturates. The (1x2) LEED of the Au covered surface and its strong increase in Au 4f core level emission indicates that Au atoms form rows with an interrow spacing of 13 Å. The dependence of the Au 4f signal upon Au coverage suggests that not only a single Au row but up to three rows can be adsorbed in the oxygen vacancy rows.

In order to better understand the structure and bonding of the Au, first principle calculations were made, both for the missing row and the added row model, considering single and triple Au rows. Details of the calculations are provided elsewhere. Both the (1x2) missing row (MR) and the added row (AR) models were considered.

Figure 3 displays iso-surfaces of the electron density difference due to different Au bonding configuration in a single row (a) and in a triple row. In the latter case Au can bond in bridging manner or above 5-fold coordinated Ti (b and c respectively). They are calculated as the difference in electron charge densities of the complete adsorption Figure 3. Electron density changes upon Au adsorption on the MR (1x2) surface. Isocharge contours in all graphs correspond to  $\pm 0.03$  electron/Å<sup>3</sup>. (a) single Au row, (b) and (c) triple Au row.



system and that of the missing row (1x2)  $TiO_2$  (110) slab, and the free Au atoms at the positions of the relaxed Au/TiO<sub>2</sub>. In the case of single Au rows (a) Judging by the electron charge gain for single bridging oxygen replaced by Au, the bonding of Au is mainly to the Ti atoms below, and to the neighboring Au atoms.

Summarizing the experimental and theoretical results, Au forms on the reduced  $TiO_2$ (110)(1x2) surface strongly adsorbed onedimensional chains consisting of one to three rows of Au atoms, depending on Au coverage. Intra-chain and inter-chain spacing is determined by the substrate periodicity. The LEED observations and the much stronger bonding of the single Au row of the MR structure suggest that the missing row structure is the preferred one. The calculations indicate that the bonding to the substrate is predominantly covalent with little charge transfer to the Au atoms. The large inter-chain distance (13 Å) on the more or less insulating substrate makes this system ideal for studies of one-dimensional phenomena.

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# THEORY@ELETTRA

Understanding physical and chemical properties of matter examining the processes occurring at nanometric and atomic scale is at the forefront of materials science research. Nanoscale is admittedly the common playground for theory and experiment since the control and description of relevant length and time scales have been achieved by both approaches in recent times. The increasing number of investigations combining quantum mechanical ab initio simulations with spectroscopy or microscopy experiments proves that this combination can greatly enhance our insight into materials properties, providing a scientific output which is way superior to the sum of the individual, experimental and theoretical, inputs. Large-scale facilities are the ideal multi-disciplinary environment for the nucleation of these collaborations, where quantummechanical simulations are stimulated by state-of-the-art experiments and provide, in return, reliable interpretations of their results, as well as complementary insight into properties and processes not easily accessible in the laboratory. first principles calculations

In 2005, a theory group was established at ELETTRA in agreement with *DEMOCRITOS* National Simulation Center of INFM-CNR. The mission is to provide direct support to the scientists at the laboratory, to foster the collaboration between local experimentalists and external theorists, as well as to promote the access of external users to the laboratory. The selected contributions in this section are the best illustration of this mission.

The highlights presented in this section show how numerical simulations based on density functional theory can provide the decisive insight into measurements lacking immediate interpretation. The success of these (and many other) interactions between local theoreticians and experimentalists fostered the quest for an ELETTRA theory group, initially supported by the INFM-CNR DEMOCRITOS National Simulation Center. The establishment of the theory group offers a reference point for the simulation of material properties in within the experimental facility, providing theoretical support to the ELETTRA internal and external users.

The first contribution focuses on reactive surface sites of Ce oxide, an important material in the context of hydrogen production and gas purification. The efficiency of ceria is controlled by the type, size, and distribution of surface defects. The work shows how electron localization effects determine the type of defects formed. It reveals the importance of subsurface defects for the understanding of surface chemistry, and indicates the approach to enhance the oxygen release by Ce, based on the use of dopants.

The second contribution provides an elegant interpretation of x-ray-photoemission and low-energy-electron microscopy experiments performed at the *Nanospectroscopy* beamline. The dependence of thin-film chemical reactivity as a function of film thickness is shown to be controlled by the decay length in the vacuum of the electronic density of states around the Fermi energy. The results unveil important mechanisms determining the initial stages of metal oxidation and have general implications in our understanding of surface chemical reactivity.

The third contribution reports on the characterization of novel nanostructured materials achieved by combining scanning tunneling microscopy and electronic structure calculations. Self-organized metal-organic networks supported by metallic surfaces are shown to expose ordered arrays of coordinatively unsaturated metal centers. These networks are proposed to be ideal model systems for studying low-dimensional magnetism and catalytic reactions. This finding attracted the scientists to study the reactivity of metallorganic networks in collaboration with the theory group as users at the *superESCA* beamline

# ELECTRON LOCALIZATION DETERMINES DEFECT FORMATION ON CERIA SUBSTRATES

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Ceria (CeO<sub>2</sub>) based materials are used in a wide range of catalytic applications ranging from the production and purification of hydrogen to the purification of exhaust gases in the three-way automotive catalytic converter [1]. In all these applications, highly mobile lattice oxygen is involved in oxidation processes. Over a wide range of working temperatures (from room temperature to 1000°C), ceria plays two key roles, (i) release and storage of oxygen and (ii) promoting noble metal activity and dispersion. Both phenomena are controlled by the type, size, and distribution of oxygen vacancies as the most relevant surface defects [2]. Oxygen vacancies are also crucial for binding of catalytically active species to ceria. The high activity of Au/ceria catalysts in the water gas shift reaction has recently been traced back to highly dispersed, ionic Au species that form only in the presence of defects [2].

The control of the density and the nature of oxygen vacancies could provide a means for tailoring the reactivity of ceria-based catalysts. However, despite extensive spectroscopic, microscopic, and diffraction studies, a detailed insight at the atomic level into local defect structure, defect mobility, and

Figure 1. STM images of the CeO<sub>2</sub>(111) surface obtained after short, 1 min (a) and prolonged, 5 min annealing at 900 °C (b), as well as the corresponding representation of the observed defects. STM imaging conditions: -3.0 V (sample with respect to tip), 0.3 nA, 300 °C.

o Single surface vacancy △ Single subsurface vacancy ● Surf. vacancy in linear cluster (LSVC) ● Surf. vacancy in trimer (SVT) × Other





Figure 2. (a) Filled-state and (b) empty-state STM images of single vacancies and related structural models (left: surface vacancy, right: subsurface vacancy, characteristic 0 rim atoms in blue). (c) Calculated density of states and simulated

filled-state STM images (-3.0 V bias). Ce 4f gap states, displayed as unshaded curves, do not contribute to the STM images due to their strong spatial localization. STM imaging conditions: 6.6 x3.5 nm<sup>2</sup>, -3.0 V (A) / +3.0 V (B), 0.1 nA.

valence of the cerium ions is still missing. Ceria crystallizes in a cubic fluorite structure and exposes the thermodynamically most stable (111) surface.

We report [3] high-resolution scanning tunneling microscopy (STM) results on  $CeO_2(111)$ , which we interpret in light of density functional theory (DFT) calculations. Filled-state images are shown to map the positions of the outermost oxygen atoms. Their local relaxation around the defects discriminates between different defect geometries.

On the slightly reduced surface (Figure 1A), single vacancies prevail and can be distinguished in two types (Figure 2A). One type appears as depressions, surrounded by three paired lobes (magenta triangles), and can be assigned to surface O vacancies by comparison to simulated images (Figure 2C). A second type appears as triple protrusions (cyan triangles), centered around third-layer oxygen sites. By imaging empty states (Figure 2B) it is clear that the three protrusions belong to a single unit and are not independent entities, such as adsorbates. Simulated STM images identify this type as subsurface O vacancy (Figure 2C).

The STM can therefore precisely detect and measure the single-vacancy distribution. On slightly reduced surfaces, where vacancy clusters (VCs) are not dominant, both surface and subsurface vacancies are present with similar coverages (in Figure 1A: 1.5% and 1.3% of the surface atoms, respectively). This result agrees with our calculations, which predict the same formation energy for the two defects (within 10 meV/vacancy).

The DFT results explain the structural features observed in the STM images, as described in the following. The relaxation of the surface structure around the single vacancies is mainly controlled by the positive electrostatic field centered on the vacancy that repels the nearest neighbor (NN) Ce cations and attracts, to a lesser extent, the second NN O anions. The same field attracts the two excess electrons near each vacancy, so that the electron localization occurs always on two Ce ions NN to the defect. The resulting Ce<sup>3+</sup> ions increase in size and push further away the neighboring O atoms.

Almost all vacancy clusters that form upon further reduction are linear surface O vacancy clusters (LSVCs) (92% of the vacancy clusters in Figure 1B). Upon closer inspection (Figure 3A), each LSVC is characterized by a pair of rim O atoms that face each other, one appearing 0.1 Å below (magenta arrow), one 0.1 Å above the unperturbed surface (cyan arrow). Both Figure 3. (a) STM image of a double and a triple LSVC as well as a simulated STM image of a double LSVC (inset). The characteristic unit (arrows) is an indication for the presence of a subsurface vacancy in every LSVC. (b) Corresponding structural model; note the exclusive presence of Ce<sup>3+</sup> ions in the LSVCs (Legend as in Figure 2). STM imaging conditions: -3.0 V, 0.1 nA.



atoms are shifted laterally toward the inside of the defect. They constitute a characteristic unit, which we observe once in every LSVC imaged with high resolution. Thus, the double LSVC (upper part of Figure 3) exhibits mirror symmetry, in contrast to the triple one (lower part).

The simulation of the double LSVC (see inset in Figure 3A) can reproduce the characteristic unit only if an additional subsurface O vacancy is included: The lower O atom has relaxed inward by 0.07 Å, the higher outward by 0.1 Å; both move towards the inside of the defect, in remarkable agreement with the STM results. On the contrary, both atoms relax outward (by 0.03 and 0.07 Å) if a double LSVC without subsurface O vacancies is modeled. A double LSVC consists therefore of three oxygen vacancies with the six excess electrons localized on five Ce ions in the first cerium layer and on one Ce ion in the second, so that there are no Ce<sup>4+</sup> NN to vacancies. Note that this condition cannot be satisfied without the additional subsurface vacancy.

We conclude that the double LSVC is a complex of a dimer of surface vacancies with

one subsurface vacancy, making a trimer of vacancies altogether, where only  $Ce^{3+}$  ions are coordinated to the defect. The exposure of only  $Ce^{3+}$  ions holds also for longer LSVCs, where the characteristic unit appears always once and can thus be regarded as the nucleation site that triggers defect growth. The removal of an additional terminating O atom results in a longer LSVC, again coordinated exclusively by  $Ce^{3+}$  ions.

The formation of LSVCs as the dominant oxygen vacancies demonstrates the tendency to form VCs that expose exclusively Ce<sup>3+</sup> ions. This condition can be fulfilled only for VCs with more than two vacancies; the question arises whether it can be generalized for other VC shapes. The next most abundant case after LSVCs are triangular, surface O vacancy trimers (SVTs). All of the observed SVTs have the same orientation, are centered on a subsurface O atom and exposes exclusively Ce<sup>3+</sup> ions. This result confirms therefore that VCs expose only reduced cerium ions.

Our observations show that electron localization determines which defects are formed on a ceria surface. The structural requirement of one subsurface vacancy per LSVC reveals the high propensity of Ce toward reduction upon O loss: only Ce<sup>3+</sup> ions are coordinated to the vacancy cluster. Whereas this propensity favors further O release once double LSVCs have been formed, it may hamper their nucleation; the two electrons liberated by each of the first two missing O atoms are insufficient to reduce all of the coordinated Ce ions.

In real catalytic applications, one way to increase the oxygen release from ceria is by doping with  $Zr^{4+}$  ions, which are not reduced upon O loss. These two effects, increased oxygen release and thermal stability, seem irreconcilable, but can be rationalized in the light of our results: Preliminary calculations show that, with respect to the pure ceria (111) surface, the single vacancy formation around single  $Zr^{4+}$  dopants is facilitated by 0.9 eV. Once formed, these vacancies can grow into vacancy clusters without requiring anymore the presence of subsurface vacancies and the related major structural rearrangement.

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# INTRODUCTION

Tailoring the chemical reactivity of surfaces, a crucial factor in many technologically important phenomena such as oxidation and catalysis, is a longstanding target of surface science. A recent exciting development in this area is the observation of a correlation between electron quantum-confinement effects, in metal films a few atomic layers thick, and surface reactivity [1]. Combined x-ray-photoemission and low-energy-electron microscopy experiments at the Elettra "Nanospectroscopy" beamline have demonstrated the existence of systematic oscillations, with film thickness, in the oxidation rate of ultrathin Mg films grown on a W(110) substrate, with the largest oxidation rate occurring when a quantum-well state was found to cross the Fermi energy,  $E_{P}$ , in photoemission (PE) spectra taken near normal incidence [1]. In particular, dramatic variations with the number of atomic layers were observed in the *initial* oxidation rate when most of the film was still metallic. The precise mechanism behind such changes is an open issue. Although the effect was initially suggested to be due to a change in the density of states at the Fermi energy, the actual variations in the total density of states of the films at  $E_F$  cannot simply account for the dramatic oscillations in the reactivity.

Here we propose a theoretical interpretation [2] of the experimental observations, in which the decay length in the vacuum of the electronic local density of states around  $E_F$ is identified as the key parameter responsible for the changes in reactivity. Based on first-principles calculations and model predictions, we show that the decay length in vacuum,  $\lambda$ , of the local density of states at  $E_F$  exhibits an oscillatory behavior with film thickness, with local maxima present when the highest occupied quantum-well state with wavevector  $k_{//}=0$  (probed by normalincidence PE) is closest to  $E_{f^*}$ . The predicted changes in  $\lambda$  are significant and are expected to have a direct, exponential impact on the electron transfer rate by tunneling, which is believed to control the initial sticking of O<sub>2</sub> on the metal surface [3].

# **COMPUTATIONAL ASPECTS**

The first-principles calculations were performed within density-functional theory using the pseudopotential plane-wave approach. The Mg(0001) films on W(110) were modeled using slab geometries in a supercell. The details of the calculations are presented in Ref. [2]. Experimentally, above 3 monolayers (ML), the Mg films grow epitaxially on W(110), with lattice parameters corresponding to their bulk values [1]. The in-plane lattice mismatches between Mg(0001) and W(110) are 1.6 % and ~20 % along the W [001] and  $[1\overline{1}0]$  axis, respectively. To model the corresponding epitaxial structures, a commensurate interface atomic structure is needed in our calculations. The inclusion of dislocations would require prohibitively large lateral dimensions of the supercell, and the details of the atomic structure at the interface are unknown in any case. In order to simulate an unstrained Mg film on W(110), we thus elected to laterally strain the W(110) slab to the in-plane lattice parameters of Mg(0001), positioning the atoms of the W(110) layer adjacent to the Mg in the continuation of the Mg (0001) hcp lattice. To assess the effect of the substrate, we also investigated the same Mg films isolated in vacuum. The decay length was derived from a fit, considering an exponential decay of the local density of states at distances beyond 2.15 Å from the outermost atomic plane.

# **RESULTS AND DISCUSSION**

The decay length  $\lambda$  of the Mg(0001) films is displayed as a function of film thickness in Figure 1(a), both for the Mg films on tungsten and for the unsupported films. The behaviors are very similar in the two cases. The decay length exhibits a pronounced oscillation, with a maximum at 9 layers and a minimum at 6-7 layers. The presence of the tungsten substrate tends to reduce the variation of  $\lambda$  from 17 % to 10 %, but has no significant impact on the position of the extrema. In Figure 2(b), we show the partial densities of states (DOS) at  $k_{l/}=0$  of the Mg (0001) films on tungsten and the corresponding electronic levels at  $k_{II}=0$  of the unsupported films. There is a close correspondence between the DOS peak positions for the films on W(110) and the level positions of the unsupported films. With increasing film thickness, an unoccupied quantum-well state is found to cross  $E_F$  in both cases at ~9 layers, which exactly coincides with the maximal decay length in Figure 1(a).

The states indicated by "SS" in Figure 1(b) originate from the Shockley surface state of Mg(0001). In the unsupported films, the Shockley states of the two surfaces strongly interact, giving rise to a pair of split even and odd states-with respect to the center-ofthe-film reflection plane. In the presence of the substrate, such states persist as strong surface/interface resonances. The peak positions in the partial DOS in Figure 1(b) compare well with the near-normal-incidence PE measurements [1], except for a systematic shift, by about +2 Mg ML, of the theoretical spectra with respect to the measured spectra. The same shift exists between the calculated maximum/minima of  $\lambda$  and the measured maximum/minima of the reactivity. We attribute this shift to the presence of partially strained Mg layers close to the interface. Indeed, from separate calculations we find that a pseudomorphic contraction of the Mg layers along the W  $[1\overline{1}0]$  axis induces the entrance of a quantum-well state in the valence spectrum at a lower number of Mg layers, as seen experimentally.



The first-principles results indicate that  $\lambda$  has an oscillatory behavior with the number of Mg layers and is maximal when a quantum-well state at  $k_{I/}=0$  crosses  $E_{F}$ . Such a behavior can be explained based on a model description for  $\lambda$ , considering independent electrons in a square-well potential [2]. The corresponding electronic states read:

$$\psi_{n,k_x,k_y}^E(x,y,z) \propto \chi_n(z) \cdot e^{i(k_x \cdot x + k_y \cdot y)},$$

and have energy,  $E = E_n + \hbar^2 (k_x^2 + k_y^2)/2m^*$ , where  $m^*$  stands for the electron effective mass; the *z*-axis is normal to the film. In the vacuum,  $\chi_n(z)$  behaves as:

$$\chi_n(z) \propto e^{-\alpha_n}$$

with

$$\alpha_n = (\sqrt{2m^*} / \hbar) \cdot \sqrt{-E_n},$$

where the zero of energy is taken at the vacuum level;  $E_n$  corresponds to the energy of the subband state *n* at  $k_{1/2}=0$ , measured rela-

Figure 1. [a] Decay length in the vacuum of the local density of states at the Fermi energy for Mg(0001) films on W(110) (disks) and for the corresponding unsupported films (diamonds). [b] Partial density of states at  $k_{\mu}=0$ of the Mg(0001) films on W(110) (solid lines) and electronic levels at  $k_{\prime\prime}=0$  of the unsupported films (diamonds). The film thickness increases from 5 to 12 atomic layers (bottom to top). The states "SS" originate from the Shockley surface state of Mg(0001) (see text). The zero of energy corresponds to the Fermi level.

tive to the vacuum level. For a given film thickness *L*, all states belonging to subband *n* with energies  $E \ge E_n$  have thus the same decay length  $1/\alpha_n$ . Hence, if  $E_F$  is located between  $E_n$  and  $E_{n+I}$ , the dominant decay length of the local density of states at  $E_F$  is  $1/2\alpha_n$ . With increasing width *L* of the well, the energies of the quantum-well states decrease with respect to  $E_F$ ;  $\lambda$  first decreases thus as

$$1/2\alpha_n \propto 1/\sqrt{-E_n}$$

until the next quantum-well state at  $k_{I/}=0$ crosses  $E_{I2}$  at which point  $\lambda$  increases to the new value

$$1/2\alpha_{n+1} \propto 1/\sqrt{-E_{n+1}}$$
,

 $\lambda$  then decreases again with increasing *L*, displaying systematic oscillations with *L*. For a discrete number of atomic layers, the periodicity of the crossing of  $E_F$  can be obtained from the Bohr-Sommerfeld rule, which for Mg(0001) yields a periodicity of 7.7 ML [1]. The particle-in-a-box model predicts thus oscillations in  $\lambda$ , with local maxima occurring when the highest occupied quantum-well states at  $k_{II}=0$  is closest to  $E_F$ , which exactly accounts for the trends observed in Figure 1.

The changes in the decay length we report here are expected to have a direct, exponential impact on the electron transfer rate by tunneling—from the metal to the  $O_2$ molecule-which has been proposed to control the initial sticking of the oxygen molecules impinging on the surface, via the attractive image charge potential on the ionized  $O_2^-$  molecule [3]. Assuming a transfer rate by tunneling proportional to  $e^{-d/\lambda}$ , with *d* the distance between the metal surface and the molecule, and considering a distance d≈3.5 Å—within the expected physisorption range of the  $O_2$  molecules, a 10 % variation in  $\lambda$  produces a 100 % change in the transfer rate. Such a change is of the order of magnitude of the experimental change in the oxidation rate at low  $O_2$  exposure [1], and provides thus a possible explanation for the observed reactivity changes.

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# TEMPLATED GROWTH OF METAL-ORGANIC COORDINATION CHAINS AT SURFACES

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Metal-organic coordination networks (MO-CNs) formed by coordination bonding between metallic centers and organic ligands can be efficiently engineered to exhibit specific magnetic, electronic, or catalytic properties [1]. Instead of depositing prefabricated MOCNs onto surfaces, it has been recently shown that two-dimensional (2D) MOCNs can be directly grown at metal surfaces under ultrahigh vacuum (UHV), thus creating highly regular 2D networks of metal atoms [2]. We show here [3] that this approach allows to predefine the geometry of the MOCN by using the substrate as a template to direct the formation of novel 1D metal-organic coordination chains (MOCCs).

The templating role of substrates is well known in the field of surface epitaxial growth. Among the highly anisotropic substrates, the Cu(110) surface is one of the most commonly used. To demonstrate its strong 1D templating effect on organic molecules, a ligand with a triangular symmetry was selected, namely 1,3,5-benzenetri-carboxylic acid (trimesic acid, TMA). The three-fold rotation symmetry of TMA supports the formation of hexagonal 2D and 3D architectures, therefore strongly disfavoring the linear geometry.

The deposition of TMA on Cu(110) under UHV at 300 K results in the formation of 1D chains along the <1bar10> direction, as observed by scanning tunneling microscopy (STM). This deposition temperature is high enough to provide mobile Cu adatoms through evaporation from kinks and steps onto the terraces. Analysis of similar systems by X-ray photoelectron spectroscopy showed that these adatoms catalyze the deprotonation of molecular carboxylate groups and are necessary for the formation of copper carboxylate complexes. The chains formed at 300 K typically show irregular kinks and poor long-range order. These inhomogeneities are removed by postannealing to 380-410 K to yield straight and highly periodic chains, referred to as MOCC-I hereafter.



Figure 1. STM images of [-Cu-TMA-Cu-]n chains on Cu(110) for TMA coverages of (a) 0.36 and (b) 0.13 monolayers (ML), respectively. Comparison of (c) the high-resolution STM image, (d) the atomistic model, and e) the corresponding simulated STM image TEMPLATED GROWTH OF METAL-ORGANIC COORDINATION CHAINS AT SURFACES



Figure 2. [-TMA-Fe-]n chains: (a) Overview image of the coordination chains formed upon deposition of 0.04 ML Fe and 0.40 ML TMA. Comparison of (b) the high-resolution STM image, (c) the atomistic model, and (d) the corresponding simulated STM image.

The chains consist of triangles alternating with round protrusions (Figure 1). The apparent height of the two units is significantly different,  $140\pm30$  pm and  $75\pm20$  pm, respectively, when scanning at 1 V and 1 nA. Following previous analysis, the triangles are identified as flat-lying TMA molecules. The round protrusions can be attributed to Cu adatoms, coordinated by two of the carboxylate groups of the TMA molecule. The third functional group of TMA is pointing out of the chain with no preferential up or down orientation (Figure 2 b).

The periodicity of MOCC-I along <1bar10> is five Cu lattice spacings  $(12.70\pm0.15\text{Å})$ . High-resolution STM images indicate that the distance between the Cu protrusions and the oxygen atom of the molecular carboxylate groups is approximately 2.8Å, a rather large value when com-



pared to the typical Cu-O bond length of 1.9–2.2Å. The simplest [-TMA-Cu-]n chain model for the adsorption geometry of MOCC-I seems therefore to be outruled by these observations.

Indeed, the lowest energy structure of MOCC-I as predicted by density functional theory (DFT) calculations is a [-Cu-TMA-Cu-]n chain in which a dimer of Cu metal adatoms forms unidentate Cu-carboxylate bonds with adjacent TMA molecules (Figure 1d). The dimer binds to the surface by 6.3eV with respect to isolated Cu atoms, and each adatom is fivefold coordinated to the substrate. This structure has the correct 5x periodicity. Its simulated STM image (Figure 1e) closely agrees with that found experimentally, with the Cu-Cu dimer imaged as a single spot centered between the adatoms. The resulting Cu-O distance is 2.02Å, which lies in the range of typical Cu O bond lengths. Also the calculated apparent heights, 170 pm for the TMA unit and 90 pm for the Cu adatom unit, are in good agreement with those determined experimentally.

The theoretical analysis provides an unprecedented level of insight into the adsorption geometry of surface MOCNs. The phenyl ring of TMA and the Cu adatoms are located on the short-bridge and hollow sites, respectively (Figure 1d). The molecule stands 1.14Å above the outermost Cu layer, with the carboxylate groups bending towards the surface by as much as 0.69Å.

[-Cu-TMA-Cu-]n chains are the intrinsic nanostructures on Cu(110), but functional

Figure 3. (a) Total density of electronic states (DOS, in [eV] with respect to the Fermi energy EF) of the [-TMA-Fe-]n chain. Projected DOS (PDOS) on the atomic d states of (b) the Fe center in MOCC-II and (c) an Fe atom isolated on the Cu[110) surface. MOCCs also require different elements than Cu as metallic centers. Extrinsic [-TMA-Fe-]n chains (MOCC-II) were created by depositing first TMA and then Fe at coverages higher than 0.04 ML.

The 4x in-chain periodicity of these chains (Figure 2) leaves space for just one Fe metal center between TMA molecules. According to DFT calculations the geometry of the adsorbed TMA molecule is weakly dependent on the metal center, with the phenyl ring lying 0.09 higher in the case of Fe. The metal-carboxylate bond is still unidentate and the Fe–O distance is 1.95Å, thus 0.07Å shorter than the Cu–O distance in MOCC-I. Single metal centers lead to very weak features in the simulated STM image (Figure 2d), in agreement with experiment (Figure 2b).

The projected density of electronic states (DOS) displays a large splitting between the majority spin-up and minority spin-down electronic d states. The former are completely filled and well hybridized with the substrate Cu d states, extending from 5 to 1 eV in the total DOS of the [-TMA-Fe-]n chain (Figure 3a). The latter spin-down states are only partially filled and extend in the energy region dominated by the substrate s states. As a consequence, the Fe atoms are strongly magnetized with a spin polarization of  $3.3\mu_{\rm B}$  per Fe atom. The polarization of a Fe adatom isolated on the Cu(110) surface is very similar,  $3.2\mu_{\rm B}$ . The comparison shows that the coordination with the carboxylate group does not affect the electron localization at the Fe adatoms and thus does not produce any relevant quenching of the spin magnetic moment.

In conclusion, metal–organic coordination chains were created in situ by selforganized growth at a metal surface under UHV. The 1D anisotropy of the substrate was effectively transferred to the resulting metal–organic coordination chains. This strategy was shown to work for intrinsic as well as for extrinsic metal–carboxylate systems. The precise atomic configuration of the structures was revealed by a combined use of STM and DFT. Spin-polarized DFT suggests that Fe centers within the 1D chains have magnetic properties similar to those of isolated Fe adatoms. This renders such regular and unidirectional arrangement of magnetic centers attractive candidates for the investigation of low-dimensional magnetism in thermally stable structures.

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# FACILITY HIGHLIGHTS

# ELETTRA STATUS, ACCELERATOR PHYSICS ACTIVITIES AND PROSPECTS

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During 2005 Elettra operated for 5 runs of 6 to 9 weeks each for a total of 6168 hours, of which 4832 (78%) dedicated to user experiments with a user uptime (Figure 1) of 94.3% (95.4% excluding beam losses due to storms). In addition to storms the other major causes of downtime were due to radio frequency system faults, to delays during the refill phase and to magnet power supplies faults. The storage ring operated at 2 GeV for 72.7% of its user time whereas the 27.3% was at 2.4 GeV. The prevailing user operation's mode was multi bunch (97% of the time), consisting in filling 415 of the 432 available rf-buckets with 330 mA at 2 GeV and 48 hours between refills or 140 mA at 2.4 GeV with 24 hours between refills. The remaining 3% was dedicated to 4 bunch mode; with 4 equidistant bunches of 32 mA total current at 2 GeV and 8 hours between refills.

Each of the 5 runs started with a few days dedicated to accelerator physics whereas the

total accelerator physics and machine time for developments and projects was 1336 hours that is the 21.7% of the total. The percentage of time distribution can be seen in Figure 2. Thus the free electron laser had the 20% of the accelerator physics time, feedback systems 9%, optics tuning 6%, other accelerator physics issues 10% whereas an 11% was sacrificed in repairs.

The beam quality is the measure of the "goodness" of a light source. This depends not only upon the beam up time but also from the beam lifetime, stability and optics amongst other. After the big success of the third harmonic cavity the beam lifetime at 330 mA almost tripled and this allowed for 48 hours continuous operations between refills when at 2 GeV. The elimination also of the longitudinal multi bunch instabilities due to the third harmonic cavity and those transverse due to the transverse multi bunch feedback systems helped in the continuous quest of improving the beam quality, which





is monitored and registered with specially developed software.

For higher operational efficiency and transparency the *elog* server (Figure 2), developed by the operations team was set in function. In this server accessible from any computer of the lab, the machine efficiency in real time, the logbook, the shifting program, the operating communications and procedures, the maintenance programs, the trouble shooting and other useful documentation are available.

The accelerator physics activities have as objective to improve the functioning of the accelerator complex and its beam quality; to find new modes for beam use and to optimize the new projects and developments ensuring thus the high performance. With the exception of accelerator time dedicated to projects such as storage ring free electron laser, orbit feed back, optics tuning; the 10% (other accelerator physics in Figure 3) was dedicated to frequency map analysis for the dynamic acceptance studies with the presence of insertions, optical asymmetries studies to understand the status of the machine after the general realignment of 2004, preliminary studies for the top-up, collaborations with ESRF concerning the machine impedance, controlling the head tail instabilities with the feedback system



and investigating the THz range of coherent radiation in collaboration with the SISSI infrared beam line.

6072 hours of operations are foreseen in 2006, of which 4824 (78.4%) dedicated to the user experiments with 73.1% at 2 GeV and 26.9% at 2.4 GeV, all of them in multi bunch mode. The user uptime for the first half of 2006 is 95.1% (95.9% excluding beam losses due to storms). In parallel to improved operations the Elettra team effort for beam quality is based for the present time on three main projects; namely the global orbit feedback, the rf-upgrade and the booster and its top up mode of operation.





# THE BOOSTER PROJECT

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# INTRODUCTION

ELETTRA delivers photons to users for 5,000 hours a year, at two energies, 2.0 GeV for 75% of the user's time, and 2.4 GeV for the remaining 25%. Since the injection energy is 0.9 GeV, the energy of the electrons is ramped in the storage ring to the operation value. Refilling not at full energy limits the performance of the photon source in terms of available beam time and beam position stability.

A full energy injector is therefore needed to maintain the source attractive for users. Full funding for a new booster injector has been released in April 2005 [1]. The 1.2 GeV linac, no more needed as Elettra injector, will become the core of the new single pass X-ray FEL FERMI *@elettra*. A new 100 MeV linac will be the pre-injector for the 2.5 GeV full energy booster synchrotron, a two-fold symmetry structure composed of eighteen cells. Equilibrium emittance at 2.5 GeV is 226 nm.rad for the nominal optics and 166 nm.rad for the low emittance optics, for top-up operation [2]. Repetition rate is 3 Hz. The booster and the extraction transfer line are designed to operate in topup, which means the beam current intensity in the storage ring will be kept constant to better than +/-1.0 mA by injecting on top of the accumulated electron beam with the insertion devices closed and the beam lines front end stoppers open [3].

## **BUILDING AND TECHNICAL PLANTS**

The new injector complex will be hosted inside the existing storage ring building, using the empty space available in the internal courtyard (Figure 1). This choice allows to optimize the use of available space and to minimize any disruption to the operation of the facility. Given the complex logistic situation and the need to minimize costs, the solution for the building is as simple as possible. A common technical gallery will host both the accelerator and the auxiliary equipment, e.g. the power converters, RF transmitter, control and diagnostic racks. Construction of the building started in September 2005. There were some weeks of delay during winter, given the quite severe weath-



Figure 1. The booster building yard in Summer 2006.

er conditions; the deadline is to complete the construction within December 2006. The activities for the upgrade of all technical plants have also been started. New fridges, water pumps, transformers, are needed to supply the new accelerator and will be installed in the existing technical facility buildings. Accelerator cooling systems and electrical plants will be installed in the new building starting as soon as it is allowed by its construction activities.



# **ACCELERATOR COMPONENTS**

All components of the booster have been designed in house, following a cost saving strategy and pursuing possible integrations between storage ring upgrades and booster construction. For instance, this allows to install on the booster the beam position monitor (BPM) electronics and the radiofrequency (RF) power transmitter which will be available after completion of the upgrade of the storage ring BPM and RF system, respectively. Some components, as the high voltage modulator for the preinjector klystron, the pulsed magnets power supplies and the kicker magnets are constructed at Elettra. The accelerating sections of the pre-injector have been donated by CERN. For the other components tenders based on Elettra specifications have been placed. Magnets. Dipole, quadrupole and sextupole magnets of the booster are presently in construction by Danfysik. The dipole magnet is designed for a maximum field of 1 T over a magnetic length of 2 m and a curvature angle of 12.86°, with a 22 mm gap. The thickness of the lamination is 0.5 mm, as for all other magnets. Magnetic measurements on the prototype started in October 2006 at Danfysik. Quadrupole and sextupole prototypes will be measured within November 2006; delivery of the first batch is expected before Christmas 2006. Another contract was placed with Tesla Engineering Ltd for the supply of the corrector magnets. The bending magnet for the 100 MeV transfer line has been already delivered by SigmaPhi (Figure 2) Magnet girder. The booster beam axis is located 1.6 m above a basement of concrete. A steel frame of 1.3 m will support each dipole magnet, which weight is less then 1.5 tons. The design has been validated by the computation of the natural vibration frequency of the structure. Each group of steerer, quadrupole and sextupole magnets will be assembled on a common girder (Figure 3). The absolute position of sextupole and steerer will be defined by the mechanical tolerance of the girder, which position will be defined by the alignment of the quadrupole. Power Converters. For all magnets, but in particular for dipoles and quadrupoles, the magnetic design was carried out taking into account the resulting inductance in order to decrease as much as possible the total power requested to the power converters for ramping at 3 Hz. In order to operate with a voltage below 1 kV, the booster dipole magnets will be powered by 2 power converters, one dedicated to the upper coils and the other for the lower coils. The magnets of each quadrupole family (focusing: QF, defocusing: QD) and of each sextupole family (focusing: SF, defocusing: SD) will instead be connected in series and powered by only one power supply per family. The power converters for dipoles and quadrupoles are of the Switch Mode Power Supply type and are built by Kempower OY, which has proposed a highly modular and redundant solution for both converters. First test on a prototype is foreseen in November 2006, delivery will follow in January 2007. Vacuum vessels. The vacuum vessels for the booster are basically of two types: the dipole magnet vessel and the vessel of the quadrupole magnet, with the pumping chamber. The dipole vessel cross section is elliptical, internal dimension is 18 mm x 48 mm. Two elliptical bellows are welded at each end of the 2.0 m long vessel, in order to compensate for thermal expansion. The thickness of the vessel, built in stainless steel, is 1 mm.

**Figure 2.** The bending magnet of the 100 MeV Transfer Line.



**Figure 3.** Drawing of the quadrupole section with the girder.

The magnetic permeability of the stainless steel shall be lower than 1.02. The vacuum vessels delivery is scheduled by December 2006.

### **ASSEMBLY AND COMMISSIONING**

The assembly of the accelerator will start from the pre-injector and the low energy transfer line and will continue with the supports of the booster magnets. The installation sequence of the booster magnets will be studied in order to minimize the installation time for both the technical plants and the accelerator components. This phase is expected to start in February 2007 and to last about 4 months. It includes only a part of the booster to storage ring transfer line, namely the part on the booster building side. In summer 2007, after setting to work all systems, the pre-injector and the booster will be commissioned until the beam is extracted at 2.5 GeV to the high energy transfer line. During the Elettra long shutdown in autumn 2007 the booster to storage ring transfer line will be completed and the beam will be transported along it until the injection at full energy into Elettra, for the first time.

# **OPERATION FOR USERS AND TOP-UP**

In the first months of 2008 Elettra will operate for users with the booster. For the first period the benefit will be a much faster refill time than it is now (less than 15 minutes can be estimated, i.e. one third of the time needed today); it will also be possible to refill on the stored beam, as already done in other facilities, which will help in improving the thermal stability. But of course the final goal is top-up mode operation. After a commissioning period, it is expected to establish top-up operation during the first semester of 2008. Assuming the present beam lifetime values, to maintain the current to 330 ± 1mA at 2 GeV, one has to top up every 9 minutes. At 2.4 GeV, the current kept to  $150 \pm 0.5$  mA requires a top up each 15 minutes. Top-up at a fixed time interval is a good solution for the natural decay of the beam; the time interval and beam current decrease values depend upon the users' requests. Since top-up is performed while users are performing their experiments, in order to minimize any disturbance the beam will be injected on top of a "golden" closed orbit and with an optimized injection bump in the storage ring. Along with that, a "golden" trajectory along the booster to storage ring transfer line will be always provided with a feedback, before switching to the top up injection mode. If still needed, users can gate their measurements during the top-up injection process. In top-up mode, beam lifetime is no more an issue, being in fact infinite. This will for instance allow installation of smaller gap, in vacuum insertion devices. The integrated brilliance of the beam, over 24 hours at 2.0 GeV, will be increased by 50% with respect to the present situation. And finally, the excellent thermal stability, which will be achieved by keeping constant the beam current intensity in the storage ring, and the operation of the global orbit feedback will allow to keep the light source point stable to better than 1 micron.

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### INTRODUCTION

Recently, it has been demonstrated that synchrotron radiation storage rings can provide a huge amount of brilliant and broadband radiation in the THz region [1]. At present, bursts of Coherent Synchrotron Radiation (CSR) have been detected at several storage rings, (MAX-I, NSLS VUV ring, ALS, MIT South Hall Ring, ANKA, while steady state CSR has been obtained only at BESSY, when the optics is tuned to obtained the socalled "low-alpha" mode. In this case, however, the steady state is preserved only for bunch currents smaller than 50 µA/bunch (maximum stored current of 20 mA).

In general coherent emission (CE) is observed when the electron bunch (or density modulation inside it) is comparable or shorter than the CE critical length  $\sigma \leq \sigma_{c}$ , where  $\sigma_c$  is given by:

$$\sigma_c = \frac{1}{2\pi} \sqrt{\frac{6h^3}{\pi\rho}}$$

For Elettra  $\sigma_c = 1.24$  mm and in order to have coherent emission the electron bunch length should be therefore 1.24 mm or less. There are 3 main ways in producing CE in a storage ring:

Modify the optics to get the electron bunch length (via the momentum compaction  $\alpha$ ) <u>smaller</u> than the critical length since  $\sigma \approx \sqrt{\alpha}$ .

Set the accelerator to lower energies (since  $\sigma \approx E^{2/3}$ , e,g, for Elettra at 0.7 GeV the bunch length  $\sigma$ =1.15mm)

Create instabilities or perturbations that modulate the bunch density (e.g. multibunch, head-tail, microwave, or coherent synchrotron radiation instability)

Since the summer of 2005 the Accelerator group at Elettra has started a rigorous program to establish operation conditions providing stable and controllable THz radiation. The properties of the coherent THz emission have been measured at the large acceptance angle infrared beamline, SISSI, at the bending magnet section B 9.1 [2], equipped with appropriate instrumentation and detection systems for future expansion into rapidly evolving research fields enabled by the high power THz radiation.

## **RESULTS AND DISCUSSION**

All measurements reported here were performed using a far infrared DTGS pyroelectric detector and a Bruker IFS66v interferometer equipped with a 50-microns Mylar beam splitter. The emission spectra in Figure 1, acquired at an electron energy of 900 MeV with a beam filling of about 13% show how by increasing the ring current above 30 mA, a broad feature grows fast below 20 cm<sup>-1</sup> (0.6 THz or  $\lambda$ =0.5 mm). The increase in intensity of this feature with the ring current is accompanied by a continuous blue shift of its cut-off frequency. At 158 mA the signal intensity at 16 cm<sup>-1</sup> (0.5)THz) is higher by more than three order of magnitude than that measured at 30 mA. The strongly non-linear dependence of the intensity gain on the beam current provides

Machine status and accelerator physics FACILITY HIGHLIGHTS 111 Figure 1. Emission spectra in the THz range measured at 900 MeV and 13% filling for different ring currents. The dips at about 25, 60, and 70 cm<sup>-1</sup> are instrumental. All spectra were measured at a scanning mirror velocity of 5 kHz summing 50 scans and normalized to the thermal background signal (beam stopper closed).

## FIGURE 1





Figure 2. Integrated spectral intensity of the THz emission at 900 MeV for different filling conditions. The integrated spectra and the current intensity are normalized to the bunch number. The arrows are an estimate for the current threshold per bunch required for generating coherent emission. The purple dashed line is an estimate for the incoherent emission.

evidence for coherent emission in the THz range.

The spectral emission at several bunch fillings (95% and 13% of the total 432 available buckets) and in the 4-bunch mode was further characterized in order to get better understanding of the mechanism creating the observed coherent emission. Figure 2 shows the dependence of integrated intensity between 5 and 25 cm<sup>-1</sup> (from about 0.2 to 0.8 THz) on the single bunch current. In all cases a strong non-linear enhancement of the THz spectral weight is observed above a certain current threshold value. Both at 13% filling and in the 4-bunch mode the current threshold (see arrows in Figure 2) is found around 1.2 mA/bunch. The fact that THz signals were observed around 1.2 mA/bunch at 0.9 GeV (the threshold of the instability at 0.9 is 1.1 mA for  $Z/n=0.15\Omega$ ) is a clear evidence of the role of the microwave instabilities in the generation of the coherent emission in our case. At 0.9 GeV the electron bunch length is 1.7 mm  $(\sigma)$  and no coherent emission should occur. However, instabilities seem to create electron density modulations of about 0.5 mm inside the bunch, which emit coherently for currents above thresholds. When working with 95% filling (i.e. < 1 mA/bunch) in order to obtain CE it is necessary to excite

the electron beam either by switching off the transverse feedback, thus rendering the beam unstable, or by activating the kickers resulting in bunch deformations and density modulations inside the bunch.

In the 4-bunch mode, huge coherent signals were again measured for currents >1 mA/bunch. Attempts to combine this with the normal Elettra SR-FEL operations have shown that, as expected, the lasing suppresses the CE signal due to FEL induced Landau damping. On the other hand, since the laser is pulsed, CE bursts seem to occur at complimentary time intervals i.e. when the laser is in relaxation. Further experiments are scheduled and many interesting measurements are planned, provided the proposed femto-slicing FEL experiments get funded.

The results reported here demonstrate that by creating intra-beam density modulations, a powerful THz emission can be generated with intensity gains of more than two orders of magnitude compared to the usual incoherent synchrotron radiation emission in this frequency range. This occurs even if the bunch length is longer than the one defined by the CE critical length. Thus CE is observed for energies up to 1.25 GeV; as mentioned before the driving mechanism is not always the microwave instability; longitudinal and transverse instabilities in gener-
al can generate CE whereas any damping mechanism can suppress it.

Next step was to investigate the steady state CE. Since Elettra can easily change its operating energy, it was set to energies where the bunch lengths are comparable or less to the necessary for CE emission. However, in both 700 and 750 MeV no steady state CE was observed but very strong signals of pulsed CE were measured. At 700 MeV with a bunch length of 1.15 mm ( $\sigma$ ) a steady state CE should be possible. The pulsed CE was observed instead for currents < 0.3 mA/bunch (the microwave limit there is 0.36 mA/bunch) when rendering the beam unstable. It is interesting to note that stabilizing the beam resulted in strong reduction of the CE signal.

Test measurements on L-Arginine monohydrochloride pellets have shown CSR spectra identical with the ones taken using a conventional Hg source.

Future efforts will be focused on detailed characterization of the THz coherent emission at 750 MeV, since still the steady state emission mechanism is not well understood. Setting the optics of Elettra in the "low-alpha" mode is also a possible option, although it is not easy because it requires significant modifications of the operation parameters.

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Figure 3: THz spectra at 700 MeV, at 88 and 76 mA, with 95% filling [≈ 0.2 mA/bunch]. Stabilizing the electron beam by switching 0N the transverse feedback system results in a complete loss of the CE (see text). A spectrum at 900 MeV, 97 mA is also shown for reference.

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# PROGRESS OF THE RF UPGRADE PROJECT

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The upgrade project of the Elettra storage ring radiofrequency (RF) system aims to restore the necessary operating margins when all IDs are operational and to increase the available RF power in view of possible raise of beam current or energy [1]. The RF system had no major upgrades since its installation in 1993 and it is composed of four single cell Elettra type cavities, each one powered by a 60 kW klystron. The design strategy has taken into consideration the boundary condition of upgrading the system avoiding disruption of users' operation and it is based on the technical developments in high power RF systems of the last years. A multi-stage approach has been chosen to minimize the impact on machine operation. For the same reason it was decided to keep unchanged the space in the machine for RF components and therefore the number of the cavities. In the first phase, one RF plant (section 9) is being upgraded from 60 to 150 kW. This means the replacement of the complete power plant (amplifier, circulator, transmission components) [2], while the cavity was already replaced in

Figure 1. The 150 kW amplifier.



2003. The old 60 kW plant will be used to form the core of the new booster injector RF system. The 150 kW amplifier is derived from technology used in broadcast communications and it has been acquired as a turnkey system from an Italian industry. It is made combining two 80 kW transmitters, each one using for the final amplifying stage an inductive output tube (IOT). Each transmitter can work standalone, thus increasing operational flexibility. In this way the fault or maintenance of one transmitter does not imply the interruption of the whole plant. The use of an IOT is a solution only recently adopted for a synchrotron light source, although widely used in TV transmission. An IOT combines aspects of gridded tube and klystron technology. The main difference compared to klystrons is that the electron beam is density modulated, while in a klystron it is velocity modulated. IOTs are widely used in UHF TV applications where they have almost completely replaced klystrons as the preferred tube for the final amplifying stage, mainly due to their basic higher efficiency and moderate loss of efficiency at reduced power levels. Efficiency is typically in the range from 65 to 70 % and for drive modulation it does not drop significantly in the power range of interest for Elettra (generally 2 to 3 dB). Compared to klystrons, IOTs also offer other advantages in terms of electrical and cooling requirements, of physical dimensions and of maintenance and replacement time. The main disadvantage is related to the lower gain, which requires a higher power solid-state preamplifier. The high voltage power supply for each tube (typical requirements around 35 kV, 3, 5 A) is a switched mode power supply. This results in a much compact structure with low residual ripple and higher stabilization of beam voltage versus output power and mains input



Figure 2. View of the switchless combiner.

variations. An other advantage of the solution adopted for the power supply is that the use of oil filled components (such as transformers or capacitors) and of crowbar protecting devices is avoided. The combining system is realized by means of a switchless combiner. This device is made of two hybrids and a variable phase shifter. It gives the advantage of only 3 dB loss in case of one tube is out of service and allows four modes of operation, giving the possibility of the so called hot adjustment of the system. For example, this means that the maintenance of one tube could be done while the other is in operation, unaffected.

The high power amplifier is isolated from the cavity by means of a 200 kW circulator, capable of sustaining both forward and full reflected power at the same time. Due to the power level, the RF power is transmitted by means of a waveguide system. The power which could be reflected by the cavity is eventually absorbed by a 200 kW ferrite load. The combiner, circulator and all power transmission components are mounted suspended on a specially designed structure fixed to the pillars of the storage ring building. This allows to minimize the impact of the installation in the service area of such bulky components. The major part of the installations has taken place during the planned shutdowns in year 2006 and

involved different resources of the laboratory. In fact the installation of a high power component in an operating machine has required considerable upgrades in the cooling and electrical plants as well as civil engineering works, which had to be carefully planned in order to fit in the planned shutdowns. In addition a great effort has been necessary to prevent interference with existing equipment and to study the layout of the waveguide run. The 150 kW amplifier was installed during summer 2006 (Figure 1 and 2) and it was first set into operation on a dummy load. The component has reached the design specifications. In addition to the measurements of parameters as output power, bandwidth, efficiency and gain, the amplifier was tested for 24 hours at full power without failures. Figure 3 shows the transfer curve of the complete amplifier (blue line) and of each of the two transmitters (TXA and TXB). The graph shows the almost equal behavior of the two transmitters. The loss in the combining system is below 0.1 dB. The circulator and the remaining power components have been also tested at low and high power to assure their performances. Nevertheless, before being connected to the cavity the power plant will be tested 24 hours/day continuously till the end of 2006 in order to discover and clear defects, if any. Since wave-





guide components are used for the transmission of the RF power, a transition from waveguide to coaxial is necessary to interface to the cavity input power coupler. This coaxial to waveguide transition has been studied, together with the coaxial input power coupler and the adapter element to the standard coaxial size, and it is now under construction. It is based on a doorknob design and it will allow to cool the inner conductor of the coaxial part. In addition it will be less sensitive to the higher order modes (HOMs) field that could be excited by the beam in the cavity. For further protection, diagnostic devices will be installed in the outer conductor of the coaxial part, such as an arc detector and pick-ups particularly designed to detect the HOMs field, but with a low coupling to the fundamental frequency component. They will provide samples of the HOMs field that, after being detected by a custom designed electronics, will provide interlock signals to stop the plant, minimizing the risk of damages to the coupler in case of excessive HOM excitation. The tests on the power plant will continue till the end of 2006. In January 2007 the new plant will be connected to the cavity and the commissioning will take place during the first run of 2007. The old plant will then be moved to the new booster. The completion of the first

phase of the upgrade will provide a certain amount of margin to the RF system. Based on the results and on the development activities of the facility, the timing for the upgrade of the three remaining RF plants will be taken.

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# THE ELETTRA GLOBAL ORBIT FEEDBACK PROJECT

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# INTRODUCTION

The necessity of active feedback systems to control the closed orbit in third generation light sources, characterized by low emittance electron beams, is driven by the demanding need of position stability and reproducibility of the high brightness photon beams delivered to the beam lines. At frequencies below 0.1 Hz, the main source of disturbance at Elettra is the drift due to the thermal load induced by synchrotron radiation, with its maximum effect after the end of the injection procedure. Faster orbit disturbances are mainly generated by Insertion Device (ID) gap changes, by mechanical vibrations of the quadrupole magnets (spectrum component at 23 Hz) and by ripple of the magnet power supplies (50 Hz and harmonics). In order to stabilize the closed orbit in this range of frequencies a fast global orbit feedback system is being developed. It will take advantage of all of the Beam Position Monitors (BPM) and corrector magnets of the Elettra storage ring.

# imation scheme. An internal Single Board Computer (SBC) running the GNU/Linux operating system supervises the detector functionalities and performs the external connection for slow data acquisition through a 100 Mbit/s Ethernet port, while a dedicated Gigabit Ethernet link is used to provide low latency closed orbit data at 10 kHz for fast feedback purposes. The Tango control system software [1] has been ported to the SBC in the frame of a collaboration between laboratories of the Tango community.

The upgrade of the 96 storage ring BPM detectors is carried out gradually. During dedicated machine shifts a number of new detectors are installed, tested and added to the closed orbit acquisition system. Particular attention is given in order to provide a perfectly working BPM system after each installation and assure a smooth operation of the accelerator in the following shifts dedicated to the users. A new interlock sys-





#### **UPGRADE OF THE BPM DETECTORS**

As the original multiplexed RF electronics operating at Elettra cannot provide the resolution and the acquisition data rate required by the feedback system, the rhomboidal button-type BPMs of the storage ring are being equipped with new detector electronics. The commercial product selected for the upgrade is called Libera Electron, manufactured by Instrumentation Technologies. Each BPM is equipped with one Libera detector. The electron beam position is determined by sampling at 125 Msample/s the signals from the four BPM buttons and by processing the digital samples with a FPGA in a multiple-stage filtering and dec-



Figure 2. Libera BPM detectors installed in one machine section of the Elettra storage-ring.

> tem that operates independently from the Libera detectors will protect the vacuum chamber from being hit by synchrotron radiation in the event of a strongly distorted orbit inside the IDs. The new orbit interlock system, which is made of a number of distributed local units each dedicated to one ID, is based on a novel design of diode detector.

#### FAST FEEDBACK SYSTEM

The feedback system will correct the closed orbit at 10 kHz repetition rate using 96 BPM and 82 corrector magnets. The system consists of twelve VME-based stations each handling the BPM and correctors of one machine section. The stations are equipped with Motorola PowerPC CPU boards (model MVME6100) running the GNU/Linux operating system with the RTAI real-time extension [2] and the Tango control system software. A reflective memory fibre optic network connects together the twelve stations to share BPM position data in real-time. The layout of one station is depicted in Figure 1. Clock and trigger signals to synchronize all Libera detectors will be distributed from a single point using a fibre optic timing system. The closed loop attenuation bandwidth using a Proportional Integral Derivative (PID) regulator is expected to be about 150 Hz, which is sufficient to attenuate orbit drifts and disturbances due to mechanical vibrations and ID gap changes. Higher-frequency periodic noise components, like the harmonics of the 50 Hz derived from the mains, will be suppressed up to the frequency of 300 Hz by the use of digital selective filters placed in the loop [3]. The fast feedback will correct closed orbit errors with respect to a reference orbit determined by a correction program on the basis of the required beam positions and angles at the ID and bending magnet source points. The orbit correction algorithm of the fast feedback system adopts a global approach based on an opportunely inverted response matrix. Studies have been carried out using a machine simulator to evaluate the correction efficiency of different variants of the Singular Value Decomposition (SVD), including singular values reduction and weighting algorithms. Further global orbit correction experiments have been performed on the Elettra storage ring to verify the correction efficiency of the SVD algorithm and to measure the strength required to the corrector magnets in the presence of real orbit distortions.

## **CURRENT STATUS AND OUTLOOK**

The upgrade of the BPM detectors is currently underway and will continue till the beginning of 2007. Figure 2 is a picture of the Libera detectors installed in one machine section. During the October 2006 shutdown the fast feedback infrastructure (VME stations, fibre optics, connection to the corrector power supplies, etc.) will be installed. The commissioning of the feedback system is planned to start in the first quarter of 2007.

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# MAMMOGRAPHY WITH SYNCHROTRON RADIATION: THE CLINICAL PROGRAM AT SYRMEP

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For the first time Synchrotron Radiation (SR) has been used to carry out mammographic examinations on patients at the SYRMEP (SYnchrotron Radiation for MEdical Physics) beamline. For this purpose, the original beamline has been deeply modified with the realization of a radiological unit. A joint venture among the University of Trieste, the INFN and Elettra makes possible this upgrading, thanks to a substantial financial support of the Fondazione CRTrieste. In conjunction with the Public Hospital of Trieste, the clinical trial on a limited number of patients has been initiated in March 2006. The selection of patients follows a recruitment protocol approved by the concerned authorities and concentrates on those cases in which conventional techniques failed to yield explicit diagnoses. The use of SR in mammography is especially encouraging since its characteristics, such as the monochromaticity and the high degree of spatial coherence, allow the application of low dose phase contrast techniques which result in improved image quality at reduced radiation doses, when compared to conventional radiographs. The gain in image quality has been demonstrated in pre-clinical research, carried out on test objects and biological tissues specimens [1, 2], and will be now validated within the clinical trial. So far the clinical program, which will span over the next two years, has yielded encouraging

preliminary results and will be applied to an overall of 70-100 patients.

## THE BEAMLINE AND THE PATIENT ROOM

In the frame of the clinical program, the SYRMEP beamline has been deeply modified and was extended by a two floor building downstream the existing experimental hutch: the ground floor accommodates the radiological unit and the radiologist room. The upper level houses control room comprising beam line control and instrumentation for the patient safety.

As depicted in Figure 1, to date the beamline is divided into three sections featuring beam preparation (corresponding to the existing optics hutch), beam monitoring and patient safety (in the experimental hutch that has been enlarged) and the patient room. Some new components, located upstream the exposure room, have been implemented for patient safety and dose control: the safety and fast shutters, the radiation monitors and a new slit system. Due to their importance, the radiation monitors have been realized under compliance with the Italian metrology Institute for ionising radiation (ENEA) and their response has been calibrated against the national standard for ionising radiation (provided by ENEA). They are based on two identical custom-made Ionization

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Figure 1. Schematic layout of the medical beamline.

Chambers (ICs) especially optimised for the laminar SR beam geometry and equipped with the readout electronics. The ICs provide a continuous monitoring of the radiation dose during the patient examination. Since the cross section of the X-ray beam in the patient room, shaped by the slits, is about 210x4 mm<sup>2</sup>, planar mammograms are obtained by scanning the patient through the beam itself.

For this a suitable speed controlled movement table was constructed on which the patient is positioned prone (Figure 2). The table features an appropriate opening in which the breast is placed. A mild compression system is used for stretching and equalizing the tissues thickness. The patient support is equipped also with a rotational stage that allows to produce different breast projections and to open the way to future implementation of digital tomosynthesis and tomography.

According to the protocol in the first phase of the clinical trails a conventional screen-film system is used as an image receptor and digital detectors, custom and commercial, are foreseen for the future. The detection system, accommodated in a holder, is mounted on a 2 meters long rail to allow the optimisation of the distance for Phase Contrast imaging. Plain radiographs are obtained by a vertical scan of the film synchronized with the motion of the patient.

The detector holder contains also the exposure system that consists in 4 solid state

photodiodes read by the same electronics of the ICs. The photodiodes are positioned behind the film cassette and are placed in front of the beam during the pre-scan procedure. In fact, due to the scan modality, the exposure time should be determined in advance.

The safety system, based on PLC conforming to the requirements of EN954-1 Category 4, follows two main criteria: redundancy with differentiation in the implementation and fail safe philosophy. The safety system distinguishes two operation modalities for the beamline: the experiment mode, which runs during the experimental research activity, and the patient mode. In the latter mode, the dose control system is active and prevents unwanted radiation exposures. It also verifies the correct working conditions of all the systems involved in the patient examination.

# THE EXAMINATION PROTOCOLS: PRE-EXPOSURE AND SCAN

The exams procedures are controlled by a "Supervision and Human Machine Interface" (SHMI), the exam supervisor that oversees all the phases of the examination, from the system initialization to the patient scan.

The examinations parameters, determining the image quality and the delivered doses, are the X-ray energy and the scanning speed. The beam energy is selected as a function of the breast thickness and glandularity. Once the patient is accommodated, the breast thickness is automatically measured by the exam supervisor and an estimate of glandularity class is given by the radiologist. Moreover, the X-ray energy is automatically selected in the range between 17 keV and 22 keV by the exam supervisor according to a pre-defined table. The adopted energy selection criteria takes into account an estimate of the Mean Glandular Dose (MGD) deliverable by the hospital mammographic unit at the same patient: our goal is to maintain the MGD with SR slightly lower.

The scanning speed depends on the absorption properties of the breast at the selected X-ray energy and varies with the electron current. The measure of average breast attenuation coefficient is performed using the exposure system during the pre-exposure procedure which consists in a scan with a reduced dose and reduced range (2 cm) in a breast region selected by the radiologist. The exam supervisor correlates the signals from the photodiodes with the readings of ICs, positioned upstream the patient, and evaluates the scan speed needed to produce an adequate optical density on the film at the given X-ray energy.

Taking into account the reciprocity law failure and the sensitivity of screen-film an exhaustive study on the film response as a function of the X-ray energy, flux and exposure time has been performed to extract analytical formulation with simple fit parameters for the characteristic curves. At the end of the pre-exposure the scan can start, without further operator intervention.

# THE CLINICAL TRIAL

The patients chosen for SR examinations are selected by radiologists after their routine exams performed at the Hospital unit. The recruitment criteria, included in the clinical research protocol approved by local ethical committee, are based on the BI-RADS classes of the Americal College of Radiology [3] recognized by the European Guidelines for screening. A patient is suited to SR mammography only in the following three cases:

1) if conventional mammography, for a symptomatic patient, shows a dense disomogeneus breast and Ultra-Sound (US) does not solve the problem (class R1);

2) if mammography shows an asymmetry of the two breasts not understood by US (class R3);



**Figure 2.** Patient and detector supports.

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Figure 3a, 3b. MLO projections of patient n.8: (a) conventional image, (b) SR radiograph.



3) if both mammography and US detect doubtful lesions (class R3 and R4).

The new technique will be evaluated on the basis of two important markers: the capability to detect mammary lesions not visible with conventional techniques and the improved accuracy and sensitivity in characterizing lesions.

To date, at the end of Sept 2006, eleven patients have been recruited and examined with SR. All of them underwent to SR imaging at two projections: cranio caudal (CC) and medio-lateral oblique (MLO).

The Figure 3a and 3b show the images obtained at the hospital unit and at Elettra respectively, for the MLO projections of patient n. 8. The patient has been recruited for the presence of a rounded opacity (class R3), indicated by the arrow, that is not understood in the conventional exam. The SR image, taken at 17 keV, shows an improved contrast as well as an enhanced visibility of the lesion borders due to the Phase Contrast effects. The improved visibility of the lesion halo sign allows favouring the benign nature of the opacity. The estimated MGDs for the two images are comparable.

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Infrared spectroscopy and micro-spectroscopy techniques are of great interest since infrared radiation couples directly with the vibrational modes which represent the chemical "fingerprints" of the molecules. Infrared spectroscopy has proven extremely valuable for determining the chemical composition of new materials and biological systems. It permits to identify the components at the surface of materials, or inside the fluid inclusions of minerals, and to detect macromolecules as proteins, DNA and lipids which constitutes the basic components of living cells. In solid state physics, infrared spectroscopy probes the low-energy excitations of solids like phonons, superconducting gaps, and polarons.

In most cases, the structures formed by organic and inorganic molecules are of micrometric size. Their spectroscopic study therefore implies the necessity of using infrared microscopes coupled with high brightness sources with beam dimensions on the order of the infrared wavelengths (in the mid-infrared, 2000 cm<sup>-1</sup> corresponds to a wavelength of 5 microns). Such a high brightness demand is realized at SISSI [1], where mid infrared spectra can be obtained over a few micron dimensions. In order to quantify the advantage of infrared synchrotron radiation for microscopy, we use a Figure of merit I/RMS, defined as the intensity collected by the detector divided by its root mean square noise, between 1100 and 1200 cm<sup>-1</sup>. This quantity allows us to compare the brightness of the two sources, weighted by their noise level and stability. I/RMS is plotted in Figure 1 for each source and aperture settings, after being normalized to the value for the globar source at the

smallest aperture. The advantage of synchrotron radiation for apertures smaller than 10 micron is of about 4 orders of magnitude.

The lateral resolution of the SISSI set-up in chemical imaging has been tested with a piece of synthetic quartz containing an inclusion (Figure 2), which simulates a situation often encountered in geological samples. The chemical identification of such inclusions in rocks is of basic importance for understanding their formation and also in quest for mineral resources. Infrared spectroscopy is the most rapid and efficient tool for such analysis, but the spatial resolution required is often well beyond the limits of devices using conventional sources. The inclusion has a triangular shape with an elongated tail on its left (Figure 2a). The infrared maps (Figure 2b-c) reveals the presence of a bubble of gaseous CO<sub>2</sub>, while liquid water is mainly located at the edges of the inclusion, and in the tail.



Figure 1. Ratio between the detected intensity, l, and the root mean square (RMS) noise between 1100 and 1200 cm<sup>-1</sup> for both the infrared synchrotron radiation d the globar source and for different microscope apertures. The reported values are normalized to the I/RMS of the globar radiation through the smallest aperture. The lines are a guide to the eye.

Figure 2. (a) Visibile image of the inclusion as recorded by the microscope camera. (b) Infrared map of liquid water obtained by integrating the absorbance between 3000 and 3600 cm<sup>-1</sup>. (c) Infrared map of CO2 obtaine dby integrating the absorbance between 2250 and 2500 cm<sup>-1</sup>. The maps in b and c are made up of 20x16 pixel obtained by mapping with a 2 micron step.



These results [2] show the capabilities of the IR beamline SISSI at Elettra to be successfully exploited in microspectroscopy achieving the diffraction-limited spatial resolution both in the far-IR and the mid-IR region. The beamline offers two independent measurement stations, optimized considering diverse multidisciplinary applications. The first branch is dedicated to Solid-State Physics, High-Pressure studies, Chemistry and Geology. The second branch is intended to be focused on IR spectromicroscopy and chemical imaging for bioanalytical, biomedical, biological and environmental research.

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# THE XRD1 UPGRADE

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Starting on July 1<sup>st</sup>, the 1.6T wiggler XRD1 beam line is under reconstruction aiming at substantial upgrade. The improvements concern both the optics and the experimental end-station and related facilities.

The upgrade is mainly dedicated to improving the energy resolution of the beamline and the flux density at the sample, considered to be the most critical parameters for single-crystal protein crystallography Multiwavelength Anomalous Diffraction (MAD) experiments.

In order to meet the scientific community requirements, a 1200 mm vertical collimating mirror will be placed before the existing double silicon (111) monochromator in order to improve the beam line energy resolution and reach the term of 1-2 eV ( $\Delta E/E \sim 10^{-4}$ ) required for MAD measurements.

A single (1200 mm) bendable cylindrical mirror with a tangential radius of 9.31 Km (varying between 3 Km and infinity) and a sagittal radius of 5.53 cm will replace the existing three-segmented focusing mirror. It will simplify the beam line operation and reduce the final spot size from the present 1.5x1.5 mm<sup>2</sup> to 0.7x 0.2 mm<sup>2</sup> (FWHM) allowing a substantial increase of the flux at the sample. A further flux increase will come from the reduction of the heat-induced losses at the monochromator using a water-based direct-cooling of the silicon (111) crystal.

The experimental end-station is being upgraded in order to host a new experimental table, based on a K-geometry diffractometer, provided by the CNR partner, the Institute of Crystallography.

The new set-up will match the needs for fully automated macromolecular crystallography experiments. Furthermore, the beamline components and operations as table movements, detectors and beam stoppers positions, ionisation chambers readout, sample automatic mounting, alignment and manipulation, fluorescence scan measurements will be controlled by a new software via an user-friendly GUI. Most operations on the samples will be managed via remote and a FedEx data collection service is planned.

It is expected that the upgraded beam line will be available for the users in the first semester of 2007.

Figure 1. The new XRD1 beam line optical layout. From left to right, the first (vertical collimating) mirror, the two flat crystals of the monochromator and the second (focusing) mirror.

Figure 2. XRD1 upgrade in progress (July 2006).





# MATERIALS CHARACTERIZATION BY X-RAY DIFFRACTION (MCX) - POWDER DIFFRACTION BEAMLINE AT ELETTRA

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> A new bending magnet beamline for Material Characterization by X-rays (MCX) is under construction at port 7.1 of ELET-TRA. The beamline, a joint effort of Sincrotrone Trieste and of the Department of Materials Engineering and Industrial Technologies of the University of Trento, has been designed to work in the range 3-12 keV, exploiting the high brilliance of ELET-TRA bending magnets in this spectral region. For specific experiments sufficient photon flux will be also available in the ranges 2.3-3 keV and 12-23 keV (Figure 1). The beamline optics is shown in Figure 2.

The first (vertically collimating) mirror is positioned face-up on a bending mechanism which allows changing the tangential radius between 6 and 15 km. The surface of the mirror is polished to a rms roughness less than 3 Å and the rms residual tangential slope error for the mirror mounted on the bending mechanism is of 0.5  $\mu$ rad. The sagittally focusing Double Crystal Monochromator (ELETTRA DCM design and patent) will provide a fixed-exit operation over the wide energy range of operation of MCX. This is achieved by mounting the two crystals on independent rotation stages,

Figure 1. Calculated source brilliance integrated over the beamline acceptance (continuous line, left scale) and photon flux expected at the sample on 1x1 mm<sup>2</sup> spot (dashed line, right scale) as a function of the energy, for the ELETTRA ring operated at 2.4 GeV, 150 mA.



MATERIALS CHARACTERIZATION BY X-RAY DIFFRACTION (MCX) - POWDER DIFFRACTION BEAMLINE AT ELETTRA



Figure 2. Schematic of the MCX optical system, showing, from left to right, the first (vertical collimating) mirror, the first (flat) crystal, the second (horizontal focusing) crystal and the second (vertical focusing) mirror.

thus allowing for the long travel of crystal 2 along the beam direction. The second (focusing) mirror shares the same figures for dimensions, pitch, surface roughness and slope errors as the collimator, but is positioned with the optical surface facing down, so that the beam returns horizontal at the end of the optical system. To avoid the vertical divergence introduced by focusing, which is undesirable, for example, in highresolution powder diffraction, the radius of curvature can be set to infinity. In this way the vertical spot dimension can be varied from 0.3 mm (fully focused) to 4 mm (fully unfocused, parallel beam). The intrinsic flexibility of the geometry makes MCX an ideal tool for diffraction measurements from polycrystalline materials in general (thin films, powder and bulk materials). The spectrum of possible applications is very broad and covers all the characteristics of X-ray diffraction applied to the study of materials (e.g. phase identification, structural solution and refinement, reticular defects and domains, texture analysis). In addition to the scientific heritage, a valuable activity will be the support to technology and industrial production, for specific tasks of non-destructive control as well as for the development of new products. Special attachments will include mechanical testing machines (4-point bending and tensile testing) as well as a high temperature stage. The whole system will be handled by means of the Portable INstrument Control interpretER (PINCER) program and associated macro sets, for which we gratefully acknowledge M.C. Miller, and the support from the CLRC Daresbury Laboratory.

# TWINMIC BEAMLINE FOR THE EU-TWIN X-RAY MICROSCOPE

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Figure 1. Double

hexagonal bio-silicate network features in the skeleton of planktonic diatoms visualized by the first time with TwinMlc in transmission scanning mode with 720 eV photon energy. The novel configured detector system allows simultaneous acquisition and online analysis of the phasegradient information (the image to the right) [2]. Pilot experiment in collaboration with A. Beran of the former LBM, Trieste, Italy.

Scanning, full-field and projection imaging modes have been integrating in a single transmission X-ray microscope, called TwinMic, thanks to the concerted effort of eight European institutions including the large scale facilities ESRF and SLS. The TwinMic EU project started in 2001 in frame of the EC FP5 RT&D program. The developed x-ray microscope station is in operation since 2005 [1]. It is temporarily hosted by the BACH beamline at ELET-TRA. A distinct novelty of the TwinMic scanning part is the implementation of a fast read-out, electron multiplied CCD camera with a phosphor screen based light converting system that allows simultaneously recording images of X-ray signals of the first order diffraction cone for each pixel, and online-display of images in different contrast modes as demonstrated in Figure 1 [2]. The configured detector has been developed by King's College London. Major part of electronic engineering and software support for the microscope has been provided by the Institute Jozef Stefan, Slovenia.

Focusing diffractive X-ray optics are provided by the SLS, TASC/INFM, Zoneplates .com and the BIOX institute at the KTH Stockholm. The novel approach solving the 'coherent' problem of the full-field imaging mode is described U. Vogt et al in this volume. Advanced techniques to control and modulate amplitude and phase of 3rd and 4th generation X-ray sources is in good progress.

To respond the high request by users from various domains of biology, material, environmental, earth sciences etc short undulator beamline is currently under construction, expected to be operational in spring 2007. The TwinMic beamline (Figure 2) is designed to fulfill the requests of full-field and scanning X-ray microscopy capabilities, bridging the gap between infrared, visible light and charged-particle microscopy. The two important beamline components are the 1 m short undulator Xray source and the energy monochromator with adjustable bandwidth: The undulator installed in the straight section 1.1 of the



TWINMIC BEAMLINE FOR THE EU-TWIN X-RAY MICROSCOPE 18m 19m 20m 22m 24m 27m 0m 16m UND CFM PH ΤМ SM END-STATION PGM

Elettra storage ring provides hybrid source characteristics well adapted to the coherence requirements of scanning, full-field and projection imaging. The SX700 Follathtype monochromator is equipped with two diffractive plane blazed gratings, one optimized for the soft X-ray regime, and the other covering the energy range from 600 -3500 eV [3]. Additionally two multilayer mirrors are implemented for high flux, large bandwidth applications as required for dynamic studies, fast imaging and X-ray micro-tomography. X-ray source quality is preserved by a cylindrical focusing mirror collimating the beam into the monochromator and a toroidal mirror behind focusing the X-ray beam stigmatically in a pinhole used as a secondary source for the twin microscope.

The optimized TwinMic beamline should allow the ultimate goal of the project to be met: broad-band instrument with a lateral resolution better than 100 nm depending on the imaging configuration over an energy range from 250 to 3500 eV. Future planned improvements of the twin microscope include cryo-techniques to freeze rapidly biomedical specimen or staining the specimen combined with X-ray microtomography, X-ray microfluorescence in reflection to improve the chemical sensitivity of the instrument allowing simultaneous mapping different chemical elements by multiple photon energy acquisition. The coherence of the beam is sufficient to extend applications to diffraction-based imaging and pilot imaging experiments for the Fermi@Elettra FEL microscopy.

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Figure 2. Outline of the dedicated TwinMic beamline consisting of a short undulator source (UND), sagittally focusing cylindrical mirror (SAM), plane grating monochromator (PGM), steering mirror (SM), toroidal focusing mirror (TFM) and pinhole array (PH). Sideview.

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> The TWINMIC x-ray microscope at ELETTRA is a unique development that combines two operation modes in the same instrument: a scanning x-ray microscope and a full-field x-ray microscope (TXM). Currently the instrument is hosted at the BACH beamline but will move to the dedicated TWINMIC beamline next year (see these Highlights for more information about the TWINMIC project). At both beamlines radiation from undulators is used for the microscope, which in general is preferable over bending magnet radiation because of the increased x-ray flux leading to shorter image acquisition times. Moreover, the scanning mode also takes advantage of the high brilliance since the zone plate used to form a nanoprobe must be illuminated coherently for diffraction limited focusing.

> However, for the full-field mode the high spatial coherence of an undulator beam poses problems for the condenser system. In a conventional TXM arrangement, a large diameter zone plate condenser forms a strongly demagnified image of the source and this intensity profile is used to illuminate the sample (critical illumination). Accordingly, if the condenser is illuminated with a high degree of spatial coherence, the source image formed by the condenser will be very small resulting in a too small illuminated object area. Moreover, the coherence will induce strong diffraction patterns from the sample or the zone plate objective which

will be superimposed on the microscopic image. Therefore a possible operation of the microscope without any condenser is also not feasible. Generally speaking, the condenser needs to influence the spatial coherence in the beam so that TXM with diffraction-limited resolution is possible. This question is of major interest not only for undulator sources but also for next generation free electron lasers, which promise the possibility to obtain a TXM image within a single shot.

We developed a novel condenser based on diffractive optics which tackles the problem from a purely geometrical point of view [1]. A principle sketch of the element is shown in Figure 1. It consists of a number of linear gratings that approximately have the same size. The orientation of the grating lines of each grating is perpendicular to a connection line between the center of the individual grating and the center of the whole optic. Gratings that have the same distance from the center have the same grating constant, resulting in concentric rings of gratings with equal period. Each grating will diffract impinging x-rays towards the optical axis, and the grating constants are calculated in a way that the 1st diffraction orders overlap on the axis at a certain distance from the optic. Therefore the grating constant decreases with increasing distance from the center. The position where the diffracted light from all gratings overlaps defines the position of the sample plane and



Figure 1. Left: Design principle of the condenser consisting of many small diffraction gratings. Right: Scanning electron microscope image of the fabricated condenser.

the size of the illuminated area is roughly given by the area of a single grating. The condenser delivers a Koehler-like homogeneous sample illumination since at each point in the object field a large number of light rays originating from different parts of the undulator beam coincide, while the number of different rays is simply given by the number of gratings. At the same time, the overlapping of the light from different gratings will lead to a strongly decreased degree of spatial coherence in the sample plane. Therefore no diffraction pattern of the sample or the zone plate objective should disturb the image. It has to be noted that an external beamline monochromator delivering a moderate monochromaticity is needed for the condenser operation.

We designed and fabricated (zoneplates.com) a special grating condenser for the TWINMIC full-field mode with an outer diameter of 1 mm and a total number of 256 grating elements in five rings. Each grating of the optic has a size of approx.  $50x50 \mu m$  resulting in a field of view of approx.  $50 \mu m$ . The grating constants are in the range of 218 nm for the innermost ring and 126 nm for the outermost one. The condenser is made of 115 nm tungsten on a 50 nm thick Si<sub>3</sub>N<sub>4</sub>-membrane.

The condenser is now routinely used with the TWINMIC microscope operating

in full-field transmission mode. An imaging example showing the importance of the condenser is shown in Figure 2. Three different images of a tungsten Siemens-star test object can be seen (exposure time 10 s, imaging wavelength 1.72 nm). The thickness of the star is 100 nm and the period of the inner structures is 400 nm. The microscope was operated with a magnification of 680, resulting in a detector-limited resolution of 50 nm. The left image shows the situation without using the condenser. The image of the Siemens star can be seen in the background. However, strong diffraction artifacts from the zone plate as well as from the sample are visible with intensity much higher than the microscopic image itself. The large white area in the image is an overexposed area because of the direct x-ray beam hitting the detector. The center image is made with the condenser. The image quality is significantly improved, but inhomogeneities in the illumination can be seen. These are the result of interference effects of radiation coming from neighboring gratings in the condenser. The interference can easily be canceled out by introducing a vibration either of the condenser or of the x-ray beam. Note that the amplitude of these vibrations has only to be in the order of the largest interference period visible in the image, which is as small as approx. 2 µm.



#### Figure 2. X-ray

microscope images of a Siemens-star test pattern (smallest feature size 400~nm period). Left: Image obtained without condenser, strong diffraction artifacts visible. Center: Image with condenser, but with interference artifacts present. Right: Image with condenser and interference artifacts removed by source vibration. No other image processing than dark image subtraction was performed on the data [1].

For practical reasons an x-ray beam movement was implemented by mechanically vibrating a premirror steering the beam into the microscope vacuum chamber. The result can be seen in the right part of Figure 3. The interference pattern is smeared out giving a nearly homogeneous illumination.

In conclusion, we developed a novel grating condenser for the TWINMIC x-ray microscope that can deliver a homogeneous Koehler-like object illumination. The work shows the importance of an appropriate coherence control if a TXM should employ radiation from a beam with high spatial coherence.

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# FABRICATION OF DIFFRACTIVE OPTICAL ELEMENTS FOR X-RAY MICROSCOPY

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The beam characteristics of the third generation synchrotron radiation sources have allowed a significant progress in X-ray microscopy. The increasing demand for the improvement of the imaging capabilities and spatial resolution can be met only by a design of diffractive optical elements (DOEs), such as zone plates (ZP) able to focus the beam to dimensions less than 50 nm, elements for differential interference contrast (DIC) to improve the visualization of phase (non absorbing) objects, and beam shaping optical elements (for example vortices, doughnut, etc.) for physical micro manipulation of particles via momentum transfer and improved DIC microscopy.

DOEs for X-ray energies ranging from 0.5 to 15 KeV were designed and fabricated at the TASC- LILIT laboratory by means of electron beam and x-ray lithography. Lately the cooperation with the TwinMic partners in the frame of a RTD-EU project pushed the development of DOEs specifically designed for the 0.7 KeV photon energy. Here we present the design, fabrication and measurements of a device family aimed at achieving x-ray vortices with a high topological charge for momentum transfer to micro and nanoparticles. Vortices are characterized by a true zero in the intensity distribution that is stable under propagation; the phase at these points is therefore undefined. A surface of constant phase about the singularity can describe a helix that contains l turns for each wavelength traveling along the propagation axis, where l is an integer and is termed the topological charge (TC) of the optical vortex. These structures have a "doughnut"-like transversal intensity distribution and carry an orbital angular momentum, proportional to the topological

charge. Vortices can be obtained using proper designed diffractive optical elements (DOEs) converting the Gaussian beam generated by a normal laser source. These beams can be used in the range of visible light to trap and manipulate microparticles. They are particularly interesting for setting trapped micro and sub micron particles into rotation by transferring the orbital angular momentum of light to the particles [1,2]. The same techniques used to design DOEs for visible light can be generalized to design DOEs that shape X-ray beams, with interesting applications in X-ray microscopy [2].

The mathematical function of a vortex beam, in a plane orthogonal to the optical axis, can be characterized by the exponential term:

# $\exp\left[-j\Phi(\theta)\right]$ (1)

where  $\Phi(\theta)$  is the phase distribution as a function of angle and l is an integer constant which is known as the TC. The phase of the vortex beam changes by  $2l\Pi$  for one revolution around the optical axis (on the axis the phase is indeterminate), therefore it is known also as helical beam. The TC l also determines the annular intensity distribution ("doughnut" like) characteristic of an optical vortex: the radius of the doughnut is proportional with the root square of the charge, l. Such beams can be generated using properly calculated DOEs, illuminated by a standard Gaussian laser beam, either with plane or spherical wavefront. DOEs with a more complex optical function can be obtained by adding the function of a zone plate (ZP) to the exponential term in Eq. 1. With such elements, the doughnut of the vortex can be focused in the first order

#### FIGURE 1



FIGURE 2



Figure 1. SEM image of the fabricated optical vortex element, topological charge I= 32.

Figure 2. Intensity distribution obtained with the DOE shown in Figure 1. of the ZP. The function of the ZP is expressed by a spherical wave term with a convergence defined by the distance to the ZP's first order. For our experiments we designed two DOEs to generate vortices having TC l=32 and 64 respectively at 8 mm from the DOE, considering an illuminating plane wave with energy 700eV. The DOE structures were fabricated in our facility using e-beam lithography on silicon nitride membrane, 100 nm thick, followed by Au electroplating. The structure of the fabricated DOE, having l=32 as TC parameter, is shown in Figure 2. The lateral resolution is 150 nm and the thickness of the gold layer is about 215 nm which guarantees an absorption higher than 95 % at 700 eV.

The test of the DOEs was performed with the scanning mode of the TwinMic microscope at the BACH beamline at the Elettra [3]. Figure 3 shows the doughnut intensity distribution characteristic to the vortex beams is obtained n the first orders at a distance of about 10 mm from the DOE. Since in this case the DOE also focuses the beam like a ZP does, the doughnut surrounds the zero order but is well separated since the TC is high. Advantages of the combined ZP/Vortex design are the high efficiency and focusing at a desired distance. Future work will be dedicated to design and fabricate phase elements in order to increase the efficiency in the vortex. This implies better control of the metal thickness and the use of alternative materials (e.g. Ni). We believe that these elements will become an useful instrument for micro and nano particle manipulation with x-ray beams in a similar way as it is done with visible light, thus opening new research opportunities for soft x-ray microscopy.

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# X-RAY BEAM POSITION MONITOR WITH $\mu$ M-RANGE ACCURACY

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The high resolution beam position monitor (XBPM-DR1) described hereafter is specifically designed for high flux synchrotron radiation experiments such as X-ray diffraction (protein crystallography, powder and small molecule diffractions, SAX, WAXS), EXAFS, fluorescence and X-ray imaging using X-ray energies from 5 KeV to 40 KeV. These classes of experiments require precise and simultaneous I<sub>0</sub> calibrations in the order of some percent down to some ppm for quantitative measurements. The availability of high intensity micro beams enables time resolved experiments on samples with spatial extensions as small as some tenth of microns; however results may suffer from significant artifacts when fast intensity variations of the beam intensity and/or beam vibration in vertical and horizontal direction occurs. Thus a high-resolution beam position monitor is also essential for these classes of experiments.

The XBPM-DR1 is based on a high-performance segmented longitudinal ionization chamber featuring full integration of a fast 20 bits readout electronics with a direct digital output via ETHERNET. Contrarily to traditional transversal ionization chambers, the X-rays incident on the XBPM-DR1 are parallel to the collecting field and cross 3 electrodes (two high voltage cathodes and the segmented read out anode) and two windows. In order to minimize absorption and scatter effects all high voltage electrodes as well as the entrance/exit windows are made out of thin metallized Kapton foils (25 µm



Figure 1. The XBPM-DR1 high speed X-ray beam position monitor developed at Elettra.



Figure 2. Resolution plotted as function of the photon flux with photon energy as a free parameter for 1 kHz sampling rate. The photon energy varies from 4 KeV (black line) up to 40 KeV (violet line) in steps of 4 KeV. Please note the calculated resolution reported hereafter is related to a single shot experiment with a very high frame rate of 1 KHz. For longer integration times e.g. one second measurements, the stated resolution values decrease by more than a factor of thirty.

foil and 400 Å metallization). Utilizing this configuration, the integrated readout current is decoupled from the beam position. Moreover, the active conversion volume is known with high precision and therefore absolute numbers for the incoming flux in photons/s can be accurately determined. Finally the active conversion volume can be kept small, which greatly reduces recombination effects. Thus, the XBPM-DR1 can be operated with low drift fields and needs only relatively low biasing voltage.

An integrated state machine handles the communication of the readout electronics with the outer world and comprises an integrated time frame generator. Integration times can be arbitrarily selected in the range from 1ms to a few seconds. Moreover, seven different gains can be set (ranging from 50 pC - 350 pC full scale range) in order to adjust the optimum working conditions to different experiments. An embedded micro controller generates all necessary timing signals and handles the communication to the outer world. The measured noise has been characterized to be 10 ppm s<sub>rms</sub> at the highest gain for a typical input capacity of 200 pF of a quarter segment anode.

The XBPM-DR1 is an ionization chamber in the classical sense since it measures ionization released in the conversion gas after photoelectrical absorption or by Compton Effect. Position encoding here is based on the localization of the center of mass of this ionization and is not based on the centroid of scattered radiation as in other systems. Typically the XBPM-DR1 is operated with light gases such as N<sub>2</sub> in order to keep absorption low for low energy Xrays. The choice of N<sub>2</sub> features another advantage since it can quench avalanche processes due to the emission of UV photons. Moreover this gas is in ballistic equilibrium with knock-on electrons emerging from the electrodes. The XBPM-DR1 was calibrated against a national standard and absolute intensities  $(I_0)$  can be measured with a precision better than 0.3 %. At the same time, the X-ray beam position can be measured with extreme accuracy in both vertical and horizontal direction at sampling rates as high as 1 kHz. The precision of position encoding has been experimentally verified to be below 5 µm at 1 kHz sampling rate even with a very moderate flux of 10<sup>8</sup> photons /sec at 9 KeV. With higher photon flux or longer integration times the XBPM-DR1 can achieve micron and submicron resolution. Of note is that the XBPM-DR1 is a fully integrated stand-

X-RAY BEAM POSITION MONITOR WITH  $\mu$ M-RANGE ACCURACY



**Figure 3.** The AH401 high resolution ultra-low current picoammeter developed at Elettra.

alone instrument which does not require additional signal amplifier, converter or scaler units.

#### **AH401 PICOAMMETER**

In parallel with the XBPM-DR1 development, a new instrument for the measurement of extremely weak currents has been designed. The AH401 is a high resolution picoammeter based on the principle of the charge integration and allows high precision measurements with very low noise. The charge-digitizing converter AH401 allows current measurements ranging from 50pA (resolution 50aA) up to 350nA (resolution 350fA) with integration times arbitrarily selectable in the range from 1 ms to 1 s. The nominal dynamic can be quoted with 20 bit. The AH401 is light, extremely compact and allows simultaneous 4 channels operations: it is thus ideally suited for four quadrant diode BPMs, single I0 photodiodes, segmented Ion Chambers and wherever parallel multichannel currents acquisition is a concern. The AH401 is equipped with a Ethernet High-Speed link that allows very fast data acquisition (currently up to 1 kHz) without significant dead time data transfer. Optionally a standard serial (or USB2.0)

communication for longer distance data transmission is available. A new version with extended current range capabilities (up to  $20\mu$ A) and higher data sampling (up to 2 kHz) is currently under development.

# TANGO CONTROL SYSTEM COLLABORATION

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> Triggered by the new challenging projects underway at Sincrotrone Trieste and by the need of providing state-of-art technologies for the Elettra storage ring, different options were considered for the upcoming control system framework. The requirements have been checked against several existing solutions and the effort required by an in-house development has been estimated. As a result of this process, the Tango control system has been adopted and Elettra is now a member of the international collaboration developing Tango.

#### **TANGO INSIGHTS**

Tango [1] is a multi-platform object-oriented distributed control system framework completely based on open source tools. Tango uses CORBA [2], a language independent standard for implementing distributed objects on the network. A number of operating systems are supported: UNIX, GNU/ Linux and Windows. Software applications can be written in C++, Java and Python programming languages.

One of the goals of Tango is to provide users with an object-oriented control system. The basic component of Tango is a software object called "Device", which can



correspond to a physical device, e.g. a vacuum gauge or a power supply, or to a logical device made up of many physical devices, for example an entire accelerator.

A Device defines a set of attributes, properties and commands. Attributes of a Device correspond to quantities or values that can be read from the field or set by the user. Attributes typically correspond to physical values like a current or a temperature. Properties are quantities or values used by the Device for configuration purposes. Properties are saved and read back from a dedicated database in order to ease the maintenance of the Device configuration. Commands are used to carry out tasks: for example a power supply can have the "switch on" command. A client application can read a Device attribute explicitly or can subscribe to it. In this case, the Device sends to the subscriber a notification, also known as an event, whenever the subscribed attribute changes. The Tango event system is a powerful mechanism that allows reducing the network traffic and improves the responsiveness of the whole system. Tango offers several tools for managing a control system: a configuration database, for storing and retrieving Device properties and names, a logging system to collect all warnings and error messages from Devices and an archiving system for storing attribute values in a historical database for off line analysis. Two toolkits allow writing graphical control panels in a very simple way by just laying down the needed widgets and "connecting" them to the chosen Device property or attribute. They are ATK (based on Java/Swing) and Qtango (based on the Qt graphical toolkit), which has been developed at Elettra [3].

## THE TANGO COLLABORATION

The development of Tango started at ESRF in 1999. In 2002 Soleil selected Tango as

Figure 1. Tango Meeting held at ESRF, Grenoble, on 5/6 September 2006

the control system for the new French light source. The two institutes signed a collaboration agreement to share development effort and take strategic decisions together. Elettra joined the Tango collaboration in January 2004, followed by the new Spanish synchrotron ALBA in December 2004. The four institutes have equal ranking in the collaboration. Each institute nominates a technical coordinator whose duties are mainly to keep the other institutes up-to-date about the local developments of Tango and to be the official liaison for Tango related issues. Two or three collaboration meetings are organized every year. The meetings are hosted by each institute in a round-robin manner. The main goal of the meetings is to develop and follow up a task list, which assigns new developments, improvements, tests of new technologies and ideas to the various institutes. On the other hand, each institute is free and encouraged to start up new autonomous developments based on Tango and later share results with the rest of the collaboration. This collaboration scheme has proven to work very well. The success of the formula is due to commonality of interests and similarity of the four institutes: they all host third generation light sources and therefore share most of controls problems and the view about how to solve them. This close collaboration is made possible by the use of Internet based tools (Web, CVS through SourceForge) that allow us to share the code and grant different access rights to different people depending on the role they have in the development. The other fundamental workhorse of the collaboration is the Tango mailing list, on which all sort of news, questions and comments are circulated.

## CONCLUSION

Since the end of 2004 some fundamental subsystems of the Elettra storage ring are controlled by Tango. Some ad-hoc libraries have been written in order to integrate Tango within the existing control system, which it will gradually substitute. The control system of the booster injector now under construction is entirely based on Tango. Tango has also been adopted for developing the FERMI@elettra control system.



The recent commissioning of the Soleil synchrotron, as well as the positive results at ESRF and Elettra, demonstrated that Tango is perfectly fit to handle the control system of a complex plant. Tango is attracting more and more interest from other research institutes. The last Tango meeting (Figure 1) was attended by a record number of 35 people and 8 of them were observers from institutes not belonging to the Tango collaboration. We expect that the use of Tango will grow further with more institutes joining the collaboration as full partners or as simple users.

The participation of Elettra to the Tango collaboration enabled us to share the effort of developing a modern and effective control system. More resources can therefore be dedicated to face the ever increasing new requests and speed up the integration of specific equipment. The Tango open source distribution model together with the adoption of standard tolls guarantee that we will able to develop and maintain our control system for many years to come.

#### References

[1] A. Goetz et al., "TANGO a CORBA Based Control System", ICALEPCS2003, Gyeongju, October 2003

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# ELETTRA E-SCIENCE PLATFORM

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Imagine FERMI@Elettra is up and running a huge quantities of photons reach the experimental chambers. Suddenly there is a problem with the beam and unfortunately all the experts are at a meeting somewhere around the world. The problem still needs to be fixed immediately. Difficult? Not when the Multipurpose Virtual Lab (MVL) in available. High-speed, high-resolution cameras would allow experts from any place in the world to check the fault: a web-based portal would let them access the controls and tools of the system with a simple "singlesign-on" procedure. This sounds overly futuristic? Consider that the first prototype has already been tested few months ago when an operator in DESY-Hamburg injected an electron beam into the ELETTRA storage ring and brought it to working energy; the second prototype test happened during the last week of August when the remote expert from a hotel room in Berkeley, California performed remotely all the operations that may normally be executed only from the HERA control room (Figure 1).

The current prototype of the MVL is stable, efficient and easy to configure and it is suitable for installation in the working conditions. Thus the obvious following step is to make it available to the entire communi-



ty for testing and use – the next guinea pig for the virtual lab is the Calice collaboration. They are running a test of their calorimeter at CERN in October and will try to control it remotely. By the end of 2006 the toll will be installed in the control rooms of ELETTRA, DESY and GSI.

However, the virtual lab is not just about remote operations. In principle it is already possible to run a control room remotely. This system is radically different in that it takes into account the human aspect of teamwork around the world. How do you get a virtual team to be as efficient as a real one? Why do we have problems working together over distances when it seems so easy when we're all together? For these questions, the physicists and computer scientists sought the help of two psychologists who specialize in "human-computer interfaces".

The implications of a working virtual control room are enormous especially if applied to a project that is the result of an international collaboration in the large experimental installations such as the FER-MI, the LHC or the ILC. For example, it would make possible to run the ILC night shift-free for 24 hours with control rooms in the three regions handing over duty when the next region wakes up.

Another distinct aspect of MVL is its mobility. While other systems allow only access to electronic controls, MVL lets the experts operate and fix real hardware. Technical equipment can be handled and repaired, while the expert does not have to get into a car – or worse, a plane – to fix the bug.

The MVL and Virtual Collaborative System (VCS) are only some of the tools for e-Science developed by the ELETTRA software team in the past few years inside the framework of the different European proj-

Figure 1. The remote expert at work.



# Figure 2. Using GridCC for remote operation.

ects in which it is involved. Particularly interesting is the Multipurpose Collaborative Environment, developed for the GRID-CC project, which is for the first time combining the more "traditional" computational Grid, virtualizing access to computing and storage resources, with the more advanced instrument Grid which is virtualizing access to remote instruments. With this system in the last week of September it was possible to demonstrate an orbit correction feedback via Grid: beam positions were sent via Grid to a remote computing center where orbit correction code was running and the corrections were feedback to the corrector elements thus improving the orbit of the storage ring (Figure 2).

The Elettra e-Science platform will combine all these technologies into a single tool that shall provide scientists and engineers with a unified access to all these disruptive technologies.

#### References

[1] http://www.gridcc.org/, "Grid Enabled Remote Instrumentation with Distributed Control and Computation" EU funded project site.

[2] http://www.eurotev.org/, "European Design Study Towards a Global TeV Linear Collider" project site.

[3] http://www.linearcollider.org/cms/, "International linear collider" site.

# **OPEN VIRTUAL UNIFIED OFFICE**

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The generic nature of experiments performed on beamlines means that the users often have to apply to different sites for their projects. This occurs for a variety of reasons, like availability of the site, logistic issues or research-specific requests. Providing a common application platform for all sites would enhance the efficiency of the application proposal procedure and, if correctly implemented, might lead to a Europe-wide clearing-house for user applications in the midterm future.

The Open Virtual Unified Office is a facility management system based on the VUO application which contains more than 50k lines of mostly PL/SQL code. VUO is a mature product that has been now operating for more than 8 years at Elettra. The VUO application has been transformed in a pure open source project allowing easier adoption by facilities not equipped by such kind of software yet. Facilities with an already operating VUO-like application can be integrated adopting a web services interface.

To enable the exchange of data via VUO and other similar systems we have defined a minimal set of information required by an application form and designed a suitable XML schema. The user can save the application form locally in XML format and then submit the proposal to any of the facilities in the virtual organization (e.g. the IA-SFS).

The final goal is to implement an Europewide clearing-house for application proposal submission. With a database of facilities and beamlines the user is free to submit a beamtime application to the most suitable experimental station.

An important component of the Open-VUO is the VUO runtime library which is going to be published on sourceforge.org as an open source project. This library allows for automatic composition of the html forms and tables from a simple SQL statement. List of values, javascripts checks and comments are defined in a separate support that can be a database table or a XML file.

The main goal of the OpenVUO is management of the beamtime applications and associated workflow: submission, validation, technical and scientific evaluation, scheduling, execution, completion, publication of results, etc.

Since its beginning additional functionalities have been added to the system, such as management of access requests, visits, projects and rooms. Users can now submit access requests on-line, avoiding all the associate paper work and at the same time filling automatically the database required by the EC to support access under the IA-SFS contract. The OpenVUO keeps track of what is going on in the laboratory and can generate real time reports and statistics for strategic management.

New functionalities are constantly being added, so make sure to keep updated on the latest developments! The future of the OpenVUO looks very bright.

# References

http://vuo.elettra.trieste.it
 http://www.elettra.trieste.it/i3/

Figure 1. The OpenVUO at work

# **CONCEPTUAL DESIGN OF FERMI@ELETTRA**

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The single-pass seeded FEL project FER-MI@Elettra will be a User facility providing quality photons in the EUV to soft X-ray range. Photon production will be based on harmonic generation. The concept design has been studied and optimised towards a detailed engineering phase. All major parameters and systems have been studied [1] and an overview is presented here. Comprehensive studies including collective effects from space charge, coherent synchrotron radiation and wakefields as well as nonlinear dynamics from RF waveforms and bunch compressors have been performed to determine the optimum electron beam parameters for the facility. The studies have included error tolerances and beam jitter sensitivities in start-to-end computations.

The project covers the lower energy region of the XUV-X ray spectrum. With a peak brightness of more than ten orders of magnitude greater than 3rd generation sources, full transverse coherence, transform limited bandwidth, choice of pulse lengths of the order of a ps or less, variable polarization and energy tuneability, the FERMI source represents a powerful tool of scientific exploration in a large field of research. The coherence properties will provide single-shot imaging, allowing the study of chemical reactions as they happen. Figure 1 shows the layout of the facility. The accelerator and FEL complex is housed below ground and is composed of the following

parts: (a) A photo-injector and two short linac sections, where a bright electron beam is generated and accelerated to ~100 MeV. (b) The main linear accelerator, where the electron beam is time-compressed and accelerated to a final energy of ~1.2 GeV. (c) A beam transport system to the undulators. (d) The undulator chains where the FEL radiation is generated. (e) The undulator to experimental area transport lines. (f) The experimental area. The new constructions include pushing back by ~ 80 m the linac tunnel and surface klystron gallery to make room for the photo-injector, accelerating sections and the first bunch compressor. At the downstream end, the klystron gallery is extended by ~30 m to power more accelerating sections. A FEL hall will be constructed below ground at the exit of the linac with transverse dimensions for the installation of up to four undulators side-by-side. Finally, an experimental hall, also below ground, will be constructed to house the FEL radiation transport optics and the experimental hutches.

The photo-injector is based on the proven 1.6 cell electron gun developed at BNL/SLAC/UCLA and adopted by the Linac Coherent Light Source (LCLS). The RF gun will provide a peak-accelerating gradient of 110 MV/m and an exit beam energy of around 5 MeV from a 10 MW peak input pulse. The injector will produce a 10ps long pulse with 0.8-1 nC charge and a

Figure 1. Schematic FERMI layout beside the ELETTRA storage ring building (g). See text for details.



rms normalized transverse emittance of 1.2 mm-mrad at 100 MeV. The initial repetition rate of 10 Hz will later be increased to 50 Hz following a modified gun design. A laser pulse provides temporal and spatial shaping of the electron bunch. The photoinjector laser system includes two amplifier stages, a regenerative one followed by a multipass, and reaches pulse energy of 20 mJ in the IR. Beam dynamics in the injector system have been extensively modelled from photocathode emission to the exit of the booster accelerator modules using 2D and 3D space-charge tracking codes (GPT and ASTRA). Simulations confirm that electron beam performance objectives for injection into the main linac at ~ 100 MeV are reachable. The timing and charge stability are both challenging, 0.5 ps and 1% respectively, but have been shown to be within present state of the art techniques.

Figure 2. Schematic layout of the accelerator. The star indicates the position of the laser heater, while the red section the X-band accelerator.

The accelerator is shown schematically in Figure 2. It consists of four linacs, two bunch compressors, a laser heater and a beam transport system (spreader) to the



undulators. The function of this system is to accelerate the electron beam to the FEL energy of ~1.2 GeV and to compress the ~10 ps long pulse from the photo-injector to the final lengths and peak current. Two FEL layouts are envisaged. FEL-1 will provide photons with wavelengths in the range 100-40 nm. Depending on the experiments, electron bunch lengths of 200 fs and a peak current of 800 A or higher can be provided (in this case with shorter bunch lengths). For those experiment where small time jitter is important, and to account for a predicted jitter of up to 400 fs, an electron bunch of 600 fs ("medium bunch") has been designed. Including the inevitable inefficiency of the compression system, the obtainable peak current is ~800 A with 0.8 nC of charge from the photo-injector. FEL-2 will cover the wavelength range 40-10 nm and will make use of a ~1 ps long pulse to provide close to Fourier-transform-limited radiation and or a ~200 fs high brightness FEL radiation using the fresh-bunch technique. In both cases a "long bunch" of 1.5 ps is required from the accelerator. With 1 nC charge from the injector, the attainable peak current is ~ 500 A.

For both FELs the final energy and charge distributions correlated with the distance along the electron bunch should be as flat as possible in order not to broaden the FEL bandwidth. The aim is to produce an energy variation no greater than  $1-2 \times 10^{-4}$  along the useable part of the bunch and a peak current variation no greater than -100

**Table 1:** Principal FELoutput parameters

A. In transverse space, the horizontal and vertical normalized emittances at the end of the linac, 1.2 GeV, will not be greater than 1.5 mm-mrad in order to meet the desired photon throughput. This represents a ~30% increase from the photo-injector simulation results and includes a safety margin against emittance dilution effects.

At the exit of the photo-injector the electrons enter the L1 linac where they are accelerated to ~250 MeV. Acceleration occurs off-crest to provide correlated energy spread along the bunch that will compress it in the first compressor BC1. An RF structure tuned at the 4th harmonic of the main s-band sections, ie at X-band frequency, is placed half-way in L1.

The linac structures L2 and L3 between the first and second bunch compressors accelerate the beam from ~ 250 MeV to ~650 MeV. They also provide the residual momentum chirp for the second compressor, BC2. After BC2 the beam is further accelerated to its final energy in the L4 structure. Exhuastive computations with codes LiTRACK and "elegant" were performed to optimise beam parameters and to simulate expected jitter and parameter sensitivities.

FEL configurations are based on harmonic generation schemes seeded by an external laser. FEL-1 will utilise one stage (modulator, dispersion section and radiator) while for FEL-2 two stages will be used in a fresh part of the bunch seeding scheme. FEL-1 and FEL-2 are required to have continuously tuneable output polarizations at all wavelengths, ranging from linear-horizontal to circular to linear-vertical. For this reason, the FEL-1 radiator and the final radiator in FEL-2 have been chosen to have APPLE-II configurations with pure permanent magnets. For the modulator a simple, linearly-polarized configuration, is optimal both due to its simplicity and because the input radiation seed can be linearly polarized. The tuning of the wavelength will be done by changing the gap of the undulator while keeping the electron beam energy constant. The magnetic lengths of the undulators segments are 2.34 m (containing 36 periods) for the FEL-1 and 1st FEL-2 radiators and 2.40 m (48 periods) for the 2nd FEL-2 radiator. FEL-1 and 2 consist of

Parameter	FEL-1	FEL-2
Wavelength range [nm]	100 to 40	40 to 10
Output pulse length (rms) [fs]	< 100	> 200
Bandwidth (rms) [meV]	17 (at 40 nm)	5 (at 10 nm)
Polarization	variable	Variable
Repetition rate [Hz]	50	50
Peak power [GW]	1 to >5	0.5 to 1
Harmonic peak power (% of fundamental)	~2	~0.2 (at 10 nm)
Photons per pulse	10 <sup>14</sup> (at 40 nm)	10 <sup>12</sup> (at 10 nm)
Pulse-to-pulse stability	≤ 30 %	~50 %
Pointing stability [ $\mu$ rad]	< 20	< 20
Virtual waist size [ $\mu$ m]	250 (at 40 nm)	120
Divergence (rms, intensity) [ $\mu$ rad]	50 (at 40 nm)	15 (at 10 nm)

6 and 10 segments respectively. The intrasegment spools contain electromagnetic quadrupoles, high quality beam position monitors and quadrupole movers to steer the electron trajectory. An exhaustive study through start-to-end simulations, that included the use of FEL codes GENESIS and GINGER, was performed. The simulations took into account perturbations in the accelerator and FEL parameters. In particular parameter sensitivity and time dependent jitter studies were carried out for both FELs. Methods, such as undulator tapering, to reduce the sensitivity to variations, were also examined. Table 1 gives the expected performance parameters for the two FELs.

Timing and synchronization [8] of RF, laser and diagnostic systems will be guaranteed to sub 50 fs levels by an integrated system handling both CW and pulsed transmission schemes.

#### References

[1] FERMI@Elettra Conceptual Design Report, 2006, to be published. See also Proceedings of the FEL Conference 2006 (Berlin, Genrmany).

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> Chemical, physical and biological processes are intrinsically dynamic in nature since they are related to electronic and atomic structures that evolve with time. The characteristic time scales span from a few femtoseconds, in the case of electronic processes, to a few tens or hundreds of femtoseconds, as in the case of atomic and molecular processes. Furthermore other phenomena, which control the behavior of critical systems, may happen at relatively longer time scales, ranging from a few picoseconds to a few hundreds of picosecond or more. These include phenomena produced by phase transitions, such as the processes related to magnetic order or to superconductivity. The capability of measuring these processes at the relevant time scales will open completely new perspectives and analyses. In particular, the direct observation of electronic processes, of structural dynamics and of dynamical critical phenomena (such as phase transitions) represents an unexplored landscape in the study of condensed matter physics. These possibilities were already evident to the inventors of the first coherent sources of femtosecond optical pulses. Ultra-sort pulses of coherent light have generated remarkable scientific progress that was recognized in the 1999 the Nobel Prize for Chemistry awarded to Ahmed Zewail for his pioneering work on the application of ultra-short laser infrared spectroscopy to the study of the dynamics of chemical bonds.

> Currently available, coherent light sources emit radiation only in a limited wavelength range. Their use is limited to optical and spectroscopic techniques in the infrared, visible and near-ultraviolet range, excluding all

the measurements needing photons of energy higher that a few eV. There is therefore a strong scientific need for a tunable light source with an energy range from the vacuum ultraviolet (VUV) to the X-ray with a stable and well-characterized temporal structure in the femtosecond and picosecond time domain. To this end, international research is moving in three main directions: 1) laser-driven light sources which use nonlinear processes to create very high harmonics, 2) interaction between an ultra-short laser pulse and an electron bunch in an storage ring (laser "bunch-slicing technique"), 3) free electron lasers (FEL). The first two techniques are able to produce radiation pulses in the femtosecond time domain and in the soft X-ray region with low brilliance (i.e. a low useful photon flux on the material under investigation). In contrast FELs can produce light pulses with peak brilliance as much as ten orders of magnitude higher than the pulses generated in present third generation synchrotron light sources and with photon energies ranging from the VUV to the hard X-ray, i.e. from about 10 eV (120 nm) to 10 keV (0.12 nm).

FEL sources can operate in several ways. The most studied operational modes in the range of wavelengths that under consideration are SASE operation (Self Amplification of Spontaneous Emission) and amplification of an input coherent signal generated by a traditional laser harmonic (Seeding). SASE operation can produce extremely high brilliance but with a pulse temporal structure which is the envelope of a series of micro-pulses with completely random intensity and duration. In contrast, the FEL sources based on seeding techniques can produce pulses with a controlled, coherent temporal shape and intensity stability. In seeded systems, one can also tune the polarization of the radiation from linear to circular by utilizing helical field undulators. To fulfill user requirements of performing reproducible measurements under controlled conditions, seeded FELs represent a superior choice. SASE sources are restricted to the cases in which the information that one wants to deduce does not depend on the temporal structure of the FEL or where the wavelength is beyond the range thought practical with seeded systems.

A common way to characterize the performance of synchrotron radiation sources has been in graphs of the time-averaged flux (photons/s/mrad/0.1%BW) and brightness (photons/mm<sup>2</sup>/mrad<sup>2</sup>/0.1%BW) available for experiments as a function of X-ray energy. More recently other metrics have been proposed such as flux density on a small sample. Another metric is useful flux within the phase space acceptance of a small sample such as a 50-100 micron protein crystal with a mosaicity of several milliradians [1]. With increasing scientific interest in short pulses, the peak (or instantaneous) values of these metrics during the pulse also become important. Some experiments require as many as 10<sup>12</sup> X-ray photons in a single ultra-fast pulse; others cannot tolerate pulse intensities exceeding 10<sup>8</sup> photons and prefer less intense pulses spaced by the relaxation time of the process under investigation. Some experiments demand lasers synchronized<sup>1</sup> to within-20 fs of the X-ray pulse; some require a high degree (~1%) of pulseto-pulse reproducibility and stability; some require no synchronization signal. Some experiment need tunable polarization of the



Figure 1. Brightness and pulse duration ranges of next generation light sources. The time average brightness is the peak brightness times the duty factor [2].

radiation; others require multiple color X-rays on the sample.

We compare the performance of several types of X-ray sources from the point of view of peak brightness and pulse duration. We believe that these performance metrics will increasingly be used, to complement the flux and brightness spectral curves that are already in general use, to assess source performance for experiments that depend on the peak or instantaneous values.

The prospects for the blossoming of a new field of ultra-fast X-ray science in physics, chemistry and biology are indeed exciting. Nonetheless, such research is likely to remain a small minority of the experiments that rely on synchrotron radiation sources. Storage rings are and are likely to remain the workhorses of synchrotron radiation science for many years to come. By providing X-ray beams with high flux and

	Maximum Duty Factor	Laser synchronization	Pulse repetition rate
Storage rings	~10-3	No	10 - 100 MHz
Slicing Sources	~10-9	Limited	1 - 10 kHz
ERLs	~10 <sup>-3</sup>	No	10 - 100 MHz
ERLs w. XRC	~10-8	Yes	10 kHz
SPPS	~10 <sup>-11</sup>	No	100 Hz
X-ray FELs	~10 <sup>.10</sup>	Some	100 - 1000 Hz
aser Accel. Sources	~10 <sup>.12</sup>	Yes	1 - 10 kHz

 Table 1. Additional

 characteristics of X-ray

 sources

ELEMENTS OF THE FERMI@ELETTRA FREE ELECTRON LASER SCIENCE CASE

**Figure 2.** Accessible experiments by increasing the FEL performances.



brightness and outstanding stability, reproducibility and reliability, they will continue to serve the needs of a vast scientific community even as linac-based sources open up new scientific frontiers with their subpicosecond pulse duration and extremely high peak brightness and coherence.

The FERMI-FEL at Sincrotrone Trieste will be realized in two principal phases. FEL-1 is designed to operate in the time domain and with two complementary operating modes: a) high stability and b) high intensity. FEL-2 is designed to operate in the frequency domain (high energy resolution) and with relatively long photon pulses (~ 1 ps). These design choices will yield a FEL source unique among the other FELs under construction or proposed for construction in Europe, USA and Japan.

The initial FERMI science program is structured to allow experiments with different, and increasingly more demanding photon parameters. This plan will allow performing high quality experiments from the very beginning of the FEL-1 and FEL-2 commissioning.

For these reason we plan the following order of experiments.

• Single Shot Experiments (High Peak Brilliance Experiments)

Pump-Probe Experiments (Experiments in both the time and frequency domains)
High Energy Resolution Experiments (Experiments in the Frequency and Time Domain, non-linear spectroscopy experiments).

This idea is illustrated in the schema of Figure 2.

We have defined three different regimes for the FEL operations during the commissioning. The first regime is identified as "acceptance parameters", the second as the "standard parameters" regime and the third as the "advanced parameters" regime. These parameters are the fundamental physics requirements that drove the design of FEL-1 and FEL-2.

The FERMI FEL source in the ELETTRA laboratory will cover the lower energy segment in the VUV- to soft X-ray region. Therefore, we require that for all the studies requiring spectral brilliance that FERMI is much brighter than the existing third generation synchrotron sources and has a temporal structure that is indispensable for structural studies requiring ultra-short pulses with variable polarization. FERMI will offer a very large variety of operational choices to the experimentalist due to the presence of the adjacent Elettra synchrotron radiation
source. The available range of scientific applications covers several fields in the study of hard and soft matter:

- chemical reaction dynamics;
- study of the electronic structure of
- atoms, molecules and clusters;
- biological systems;
- inhomogeneous materials on a microscopic scale;
- geophysics and study of extra-terrestrial materials;
- material properties under extreme
- conditions (pressure, temperature, etc.);
- surfaces and interfaces;
- nano-structures and semiconductors;
- polymers and organic materials;
- magnetism and magnetic materials;
- superconductors and highly correlated electronic materials.

The FERMI FEL unlocks the gates to new scientific frontiers because the laser-like properties of the output radiation- allow new classes of experiments not possible with incoherent synchrotron radiation sources.

**The coherence properties** will open up a new era for imaging where samples can be probed in time resolved single shot experiments. The coherent imaging technique has a great potential in life sciences as well as in environmental, materials and chemical sciences.

The high peak power at soft X-ray photon energies triggers *non-linear*, *multi-photon* processes in a regime never explored before, unperturbed by any ponderomotive effects that scale with the square of the inverse frequency and, thus, tremendously complicate the understanding of such reactions using optical lasers. **The high average power** enables to study, for the first time, *dilute samples* of paramount importance in atmospheric, astrophysical, environmental physics as well as in the characterization of nano-size materials. Moreover, it allows to access fundamental reactions governed by *small cross sections*.

**The short time properties** will open the door to visualize *ultra-short nuclear and electronic dynamics* such as in electronic relaxation, bond formation and breaking reactions or in conformational molecular changes.

The first and second calls for the first round of experiments at FERMI have attracted proposals from world-class teams of scientists, leaders in their respective fields of study.

#### References

[1] "Synchronization of X-ray Pulses to the Pump Laser in an Ultrafast X-ray Facility", J. N. Corlett, W. Barry, J. M. Byrd, R. Schoenlein, and A. Zholents, *Proceedings of EPAC 2002*, Paris, France.

[2] "Introduction to special section on future light sources," W. A. Barletta and H. Winick, Nuc. Inst. and Meth., A500, pp. 1 – 10, (March 2003).



## **ORGANIZATION CHART**

**ELETTRA** has been built and is managed by "Sincrotrone Trieste": a non-profit Share Company (Società Consortile per Azioni), recognised of national interest by a State Law.

Shareholders are local Authorities and national Research Institutions and Industrial partners. The main local shareholder is the Research Area (AREA Science Park). The two main national Research Institutions are the National Institute for the Physics of Matter (INFM) and the National Research Council (CNR).

Partners are Institutions contributing to the development of the Laboratory, like the Austrian and the Czech Academies of Sciences.

The Company is managed by a **Board of Administration**, which oversees the general policy and approves the budgets, as well as the main projects. This Council is chaired by a scientist who reports to the shareholders, to the national and regional governments and to the Council of Partners.



# **RESOURCES ALLOCATED AT ELETTRA**

#### **BUDGET ALLOCATION FOR 2006**

Ordinary operation	
Societal costs	3.555.000
Personnel	12.000.000
Power, gas, water consumption and telephone bill	4.000.000
Administration	1.278.422
Beamlines	1.275.000
Storage ring	1.900.000
Technical services	1.800.000
Industrial Liason Office operation	450.000
Scientific partnerships	330.000

#### Development projects

6.404.000

#### Special projects

Booster	6.866.570
Fermi	10.748.500

TOTAL

50.607.492

# ELETTRA BEAMLINE STATUS

EXIT	BEAMLINE	ACRONYM	PARTNER INSTITUTION
1.1L	TWINMIC	TWINMIC	ESRF, PSI, SLS, CNR-INFM, Kings College London, RheinAhrCampus Remagen, Göttingen University, ITPO Ljubljana
1.2L	Nanospectroscopy		
1.2R	Free Electron Laser	FEL	
2.2L	ESCA Microscopy		
2.2R	SuperESCA		
3.2L	Spectromicroscopy		
3.2R	VUV Photoemission		CNR
4.2	Circular Polarized Light	POLAR	CNR
5.2L	Small Angle X-ray Scattering	SAXS	Austrian Academy of Science
5.2R	X-ray Diffraction	XRD1	CNR
6.1L	Materials Science Beamline	MSB	Czech Academy of Science, Charles University, Prague
6.1R	SYnchrotron Radiation for MEdical Physics	SYRMEP	University of Trieste
6.2R	Gas Phase		CNR, CNR-INFM, INSTM
7.1	Powder Diffraction Beamline	МСХ	University of Trento, INSTM
7.2	Advanced Lights for Overlayer, Interface, and Surface Analysis	ALOISA	CNR-INFM
8.1L	Bending magnet for Emission, Absorption, and Reflectivity	BEAR	CNR-INFM
8.1R	Laboratory for Interdisciplinary LIThography	LILIT	CNR, CNR-INFM
8.2	Beamline for Advanced diCHroism	BACH	CNR-INFM
9.1	Source for Imaging and Spectroscopic Studies in the Infrared	SISSI	CNR-INFM, University of Rome "La Sapienza"
9.2	Advanced Photoelectric effect Experiments	APE	CNR-INFM
10.1L	X-ray Microfluorescence		
10.1R	Deep-etch Lithography	DXRL	
10.2L	Inelastic Ultra Violet Scattering	IUVS	
10.2R	Beamline for BAnd Dispertion and Electro-Photon investigation	BAD Elph	Wuerzburg University
11.1	X-ray Absorption Fine Structure	XAFS	ICTP
11.2	X-ray Diffraction	XRD2	

CNR - National Research Council

CNR-INFM - National Institute for the Physics of Matter of the CNR

INSTM - Consortium of Italian Universities for the Science and Technology of Materials

## ELETTRA LAYOUT



## ELETTRA STAFF

Sectors	Scientists and Researchers	Technical Personnel	Administrative and Clerical Personnel	TOTAL
Accelerators	5	24	0	29
Electromagnetism	8	25	0	33
П	5	23	0	28
Light Sources	26	16	0	42
Mechanics & Optics	4	22	0	26
Infrastructure	0	26	0	26
Administration	1	4	18	23
Coordination	4	10	33	47
TOTAL	53	150	51	254

Staff Distribution per Sector



## USERS AND MEASUREMENTS PERFORMED AT ELETTRA

(July 2005 - June 200

Research Area	Measurements performed	Shifts used
TOTAL	401	5596
Atom Molecules and Plasmas	45	788
Catalytic Materials / Surface Sciences	89	1554
Environmental and Earth Science	9	87
Hard Condensed Matter - Electronic and Magnetic Structure	86	1424
Instrumentation and Technological Materials	29	430
Life and Medical Sciences (excluding Crystallography)	19	204
Protein and Macromolecular Crystallography	49	246
Polymers and Soft Matter	18	225
Hard Condensed Matter - Structure	57	638



Shifts Used



#### N. USERS

Total	1060
ltaly	346
European Union	593
Other Countries	121



## NATIONAL AND INTERNATIONAL PROJECTS

Elettra has recently undergone a company reorganization (see the organization chart). The major novelty is that each specific activity is assigned as a project with well defined objectives, duration and milestones which permit monitoring of the status and progress of the project. An important category are the research contracts, which include the projects which are (co)funded by an external agency. At present these are: European Commission, Italian Ministry of Research, Region Friuli-Venezia Giulia, International Centre for Theoretical Physics, Italian Ministry of Foreign Affairs, Indian Department of Science and Technology.

Elettra is involved in 26 running research contracts (the highest number since 1994), which are listed in the table below. The important impact of these research contracts is that Elettra gets more than 30 million Euro (out of total funding in excess of 170 million Euro), for expanding the international and national collaborations and development activities.

More detailed information about the various research contracts, including their web site (when available) and the names of the people in charge is available on the Elettra web site.

Michele Bertolo

#### EUROPEAN/INTERNATIONAL RESEARCH CONTRACTS

REGIONAL RESEARCH CONTRACTS

Name	Short name	Coordinator
Exploring new limits to Moore's law	More Moore	ASML, Netherlands
Oxidation of nanomaterials	NAN02	Max Planck Institut, Germany
Biocrystallography on a Highly Integrated Technology Platform		
for European Structural Genomics	BIOXHIT	EMBL, Germany
Integrating Activity on Synchrotron and Free Electron Laser Science	IA-SFS	Elettra, Italy
Grid Enabled Remote Instrumentation with Distributed Control and Computation	GRIDCC	INFM, Italy
European FEL Design Study	EUROFEL	DESY, Germany
European Design Study Towards a Global TeV Linear Collider	EUROTeV	DESY, Germany
Enabling Grids for E-sciencE - II	EGEE-II	CERN, Switzerland
Light Source Theory Network	LighTnet	CCLRC, United Kingdom
ICTP-Elettra Users Programme		Elettra, Italy
Transnational access of the Indian scientists to the Elettra beamlines		Elettra, Italy

Name	Short name	Coordinato
Study and realization of microsystems for the controlled		
in-situ drugs release	Drugs release microsystems	TASC-INFM
A new technique for the study of new materials: construction of an equipment		
for the analysis of high temperature superconductors and colossal		
magnetoresistance materials by the combination of angle resolved		
photoemission spectroscopy with microscopy based on synchrotron radiation	MicroARUPS	Elettra
Micro- and nano- carbon structures laboratory		TASC-INFM
Nano- and micro-spectroscopy by synchrotron radiation integrated with		
advanced STM/AFM systems to study manmade atomic scale functional materials	Integrated nanospectroscopies	Elettra
BOOSTER-Elettra		Elettra
Post-Genomic Structural Biologu: Developing Infrastructures		

for Protein Crystallography	Structural biology	Elettra
FERMI@Elettra - Phase I		Elettra
Pulsed autoamplified source of coherent radiation	SPARC	ENEA

Name	Short name	Coordinator
Characterization and optimization of martensitic steel		
for antiwear applications	Optimization of steel for antiwear application	ns Elettra
Microelectronics devices for spintronics based on nanostructured oxides	Microelectronics devices for spintronics	TASC-INFM
New antitumor therapies and drugs: Inorganic antimetastatic agents,		
genic therapy and nanobiotechnologies	New antitumor therapies and drugs	University of Trieste
Development of a 3D detector with micrometer space resolution		
and picosecond time resolution	3D detector	Elettra
Desorption measurements from photoresists for the Extreme		
UltraViolet Lithography	EUVL photoresists	Elettra
X ray diffraction from polycrystalline materials in controlled environment	XRD from polycrystalline materials	Elettra
Monitoring station for PM10 particles	PM10	Elettra

# **INDUSTRIAL LIAISON OFFICE**

#### **ORDERS 2005 BY CUSTOMER COUNTRY**

Country	Number of Orders	Volume (1000 Euro)
FR	7	612
IT	8	125
UK	4	62
USA	4	50
DE	5	62
СН	1	18
AU	1	1
NL	1	12
DK	1	6
TOTAL	34	948



#### **ORDERS 2005 BY TYPE OF COMMERCIAL ACTIVITY**

Number	Volume
of Orders	(1000 Euro)
4	570
13	262
12	88
6	28
35	948
	of Orders           4           13           12           6           35



Instrumentation

Analytical Services & Beamline Consulting

#### TREND IN TURNOVER OF COMMERCIAL ACTIVITIES (Thousands of Euro)

	2000	2001	2002	2003	2004	2005
Accelerator's parts	61	231	236	260	259	570
Instrumentation			72	50	134	262
Analytical services & beamtime	17		3	3	98	88
Consulting		41			8	28
TOTAL	78	272	311	313	499	948
<ul> <li>Accelerator's parts</li> <li>Instrumentation</li> </ul>			🗖 An	alytical Ser nsulting	vices & Bea	amline





EVENTS

# WORKSHOPS AND INTERNATIONAL SCHOOLS / VISITS

EVENT: TYPE/NAME/VENUE	DATE	ORGANISERS
Workshop 2-colour experiments at synchrotron		
radiation sources: present and future	Nov 10-11, 2005	Elettra
Workshop Research Infrastructures		
on Cultural Heritage (RICH)	Dec 12-13, 2005	Elettra, ISIS
Workshop 4 <sup>th</sup> Generation Light Sources		
and Ultrafast Phenomena	Dec 14-15, 2005	Elettra
Workshop Computer Simulation of Surface		
and Interface Phenomena	Dec 15-16, 2005	Elettra, DEMOCRITOS
School of Syncrotron Radiation HERCULES 2006:		
- Physics and Chemistry of Condensed Matter		
- Biomolecular Structure and Dynamics	Mar 20-24, 2006	ESRF - Elettra
ICTP School on Synchrotron Radiation and Applications	May 8-26, 2006	Elettra
3rd National Conference on		
Nanoscience and Nanotechnology (Nanoltaly) - SISSA	May 21-23, 2006	Elettra, SISSA, TASC
International Workshop on X-ray spectromicroscopy		
and imaging for improving life conditions and human		
health, 1 <sup>st</sup> meeting of the CCDX Consortium and Round		
table on diffractive X-ray optics.	May 20-22, 2006	ICTP, Elettra

#### **VISITS @ ELETTRA**

Totale visite	181
Schools	92
University	31
Other labs	11
Various Institutions	13
Private companies	14
Others	20



# **PHOTO GALLERY**

1

2

#### **RICH – RESEARCH INFRASTRUCTURE FOR CULTURAL HERITAGE** (December, 12<sup>th</sup> 2005) Press conference held in Elettra experimental Hall

**Picture 1.** Carlo Rizzuto introducing the press conference for the presentation of European Network "Ancient Charm" **Picture 2.** Another moment of the press conference held in the experimental hall.





#### **MEETING DECEMBER, 2005 AND SATELLITE WORKSHOPS**

Picture 1. Alfonso Franciosi presenting Elettra status at the Users Meeting, December 15, 2005

- Picture 2. Dr. Jan-Ingo Flege, winner of the Fonda-Fasella Award, User meeting December 15, 2005
- Picture 3. Prof. Fulvio Parmigiani, workshop "4<sup>th</sup> Generation Light Sources and Ultrafast Phenomena", December 14-15, 2005

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4

Picture 4. Prof. Stefano Baroni, workshop "Computer Simulation of Surface and Interface Phenomena", December 15-16, 2005

## Sincrotrone Trieste S.C.p.A. financial data:

- 2004 dowry: €12.911.422
- 101AL short term debt (2003+2004) on 31/12/2004: €12.900.000
- 2005 dowry: €26.911.422
- · Short term debt reduced by
- -> FVG regional grant: €10.400.0 -> FERMI FIRB cost recovery: €1.800.000x0.7 1.3 M€
- -> Booster FIRB cost recovery:
- € 1.300.000x0.7=0.9 M€



## Highly ordered self-a colloidal nanoparti studied by grazingsmall-angle x-ray s

Jan Ingo Flege stitute of Solid State Physics, Univ





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#### INTERNATIONAL WORKSHOP ON X-RAY SPECTROMICROSCOPY AND IMAGING FOR IMPROVING LIFE CONDITIONS AND HUMAN HEALTH, 1ST MEETING OF THE I<CCDX>I CONSORTIUM AND ROUND TABLE ON DIFFRACTIVE X-RAY OPTICS, (May 20<sup>th</sup> -22<sup>nd</sup>, ICTP, Trieste, Italy)

Picture 1. Lecture hall at ICTP Picture 2. Prof. Graeme Morrison (King's College, UK) Picture 3. Dr. Luigi Rigon (ICTP) Picture 4. Prof. Janos Kirz (Stony Brook & ALS, USA) Picture 5. All participants







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## **3<sup>RD</sup> NATIONAL CONFERENCE ON NANOSCIENCE AND NANOTECHNOLOGY (NANOITALY)** (Trieste, May 22-24, 2006)

Picture 1. Conference social dinner

Picture 2. Valeria Garbin, best student prize winner

Picture 3. Celebration of Giacinto Scoles, B. Franklin medal 2006, at the conference dinner



## CEI: SCIENCE AND TECHNOLOGY NETWORK CEREMONY (December, 13th 2005)

**Picture 1.** Carlo Rizzuto and Harald Kreid, Director of CEI-ES (Central European Initiative – Executive Secretariat) during presentation ceremony

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Picture 2. Unveiling of the plate by Carlo Rizzuto and Harald Kreid. The plate identify in Elettra a CEI member

Picture 3. CEI plate has been positioned near IAEA plate

Picture 4. Carlo Rizzuto and Harald Kreid









## ITALIAN AIR FORCE – NATIONAL ACROBATIC TEAM OF RIVOLTO (May, 16<sup>th</sup> 2006)

Picture 1. National Air Force Team visiting Elettra

Picture 2. Gerardo D'Auria showing the Linac

Picture 3. The National Air ForceTeam in LINAC hall

Picture 4. Alfonso Franciosi receiving from Maggiore Andrea Rossi a picture of in action



## **OPEN DAY 2006** (May, 27<sup>th</sup> 2006)

Picture 1. Open Day 2006: visits beginning Picture 2. Looking at the introduction video Picture 3. At Spectromicroscopy Beamline Picture 4. Nanomondi



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2



#### PARTICIPATION OF ELETTRA AT NANOFORUM EXIBITION (Milan, September 27-28, 2006)

- Picture 1. Stand Elettra at NanoForum
- Picture 2. OLEDs fabricated at CRP in Amaro and characterized at ESCA microscopy beamline
- Picture 3. Dr. Sandra Gardonio at the Elettra stand
- Picture 4. Denis Scaini at the Elettra Stand
- Picture 5. Dr. Patrizia Melpignano (CRP-Amaro), Dr. Marco Peloi and Dr. Sandra Gardonio (Elettra)







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#### INNOVACTION, INTERNATIONAL FAIR FOR ENTERPRISES, UNIVERSITIES, TECHNOLOGY PARKS AND RESEARCH (Udine, february 9-11 2006)

Picture 1. Elettra plastic model at the InoovAction stand

Picture 2. Multichannel electron analyzers fabricated at Elettra

Picture 3. Elettra stand at InnovAction

Picture 4. Adriana Pertosi (Elettra), Cristiana Fiandra (Office), Dr. Bibi Palatini (Sissa) and Dr. Giuseppe Cautero (Elettra) at InnovAction



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3







#### VISIT OF THE ITALIAN RESEARCH MINISTER FABIO MUSSI AT ELETTRA (September, 20th 2006)

Picture 1. Carlo Rizzuto welcoming Fabio Mussi (Italian Research Minister) at Elettra

Picture 2. Carlo Rizzuto presenting Fabio Mussi and Maria Cristina Pedicchio Elettra current projects

**Picture 3.** Fabio Mussi and Giuliana Tromba (responsible scientist of SYRMEP beamline), at SYRMEP - SYnchrotron Radiation for MEdical Physics – station



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