

Electron Spectroscopy of the $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ (Ln = La, Ce, Pr, Eu) compounds

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Photoelectron spectroscopy techniques were used to study the electronic structure of rare earth manganite perovskites, namely $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{Eu}_{0.95}\text{MnO}_3$ single crystals and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, EuMnO_3 , CeMnO_3 , PrMnO_3 ceramics. To investigate the valency of rare earth ions in these compounds, a wide range of incident photon energies (40–1486.6 eV) were employed. Photoemission spectroscopy data demonstrate essentially trivalent character of La, Eu, and Pr ions and mixed valency state of Ce ions in the series of $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ compounds. For single crystalline samples the valence band photoemission spectra taken at different temperatures and photon energies (to achieve on- and off-resonance conditions) were compared.

1. Introduction

Rare earth manganite perovskites $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (A = Ca, Sr) have attracted considerable interest due to their unique electronic and magnetic properties: colossal magneto-resistance phenomena, metal-insulator transition and magnetic phase transitions. These effects make the $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ compounds promising candidates for possible technological applications. Besides, manganite compounds are very interesting from the fundamental point of view. For understanding of the transport and magnetic properties of these compounds, information on the electronic structure is essential.

When doping LnMnO_3 compounds (here Ln is a trivalent rare-earth element) by any divalent element, one has Mn^{3+} and Mn^{4+} ions. This is the reason for double exchange interaction between electrons situated at these ions that determines transport properties of manganites in the ferromagnetic state.

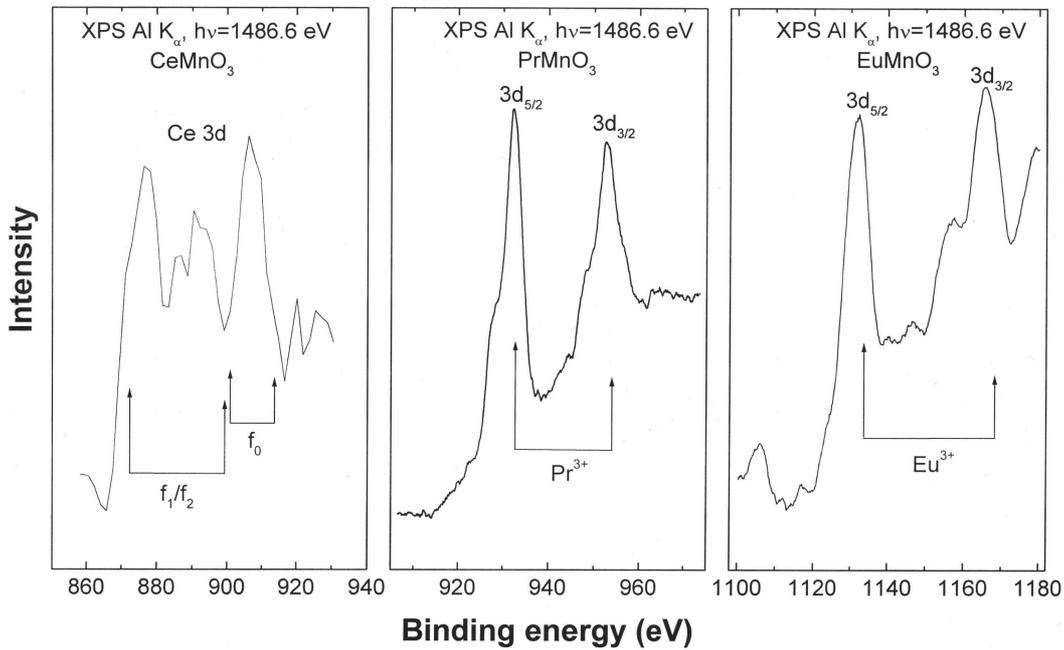


Figure 1. Ce 3d, Pr 3d, and Eu 3d core level XPS (AlK_{α}) spectra of $LnMnO_3$ ceramics.

For Ce-doped manganites, it was proposed [1–3] that Ce has the valency +4, so that the Mn valency has to be +3 and +2, and the double exchange will take place between Mn^{3+} and Mn^{2+} ions. In Ref. [4] the Ce-induced Mn valency decrease in the $Ca_{0.8}Ce_{0.2}MnO_3$ compound was demonstrated by X-ray absorption spectroscopy while it was shown in some papers [5,6] that $LaCeMnO_3$ films were not single-phased and considerable amount of CeO_2 was observed. Authors of Ref. [7] explained all magnetic and transport properties of the $Pr_{0.1}Ce_{0.4}Sr_{0.5}MnO_3$ compound suggesting the existence of Ce ions only in +3 states. Similar questions can also arise concerning Eu ions in manganites: they can be in Eu^{3+} and Eu^{2+} states thus changing the Mn valence, as it was proposed in Ref. [8].

This work is devoted to electron spectroscopy studies of the ceramic and single crystalline samples of $Ln_{1-x}Sr_xMnO_3$ compounds.

2. Experimental details and sample preparation

Ceramic samples of $Ln_{1-x}Sr_xMnO_3$ compounds were synthesized from rare earth oxides, MnO_2 , and carbonates of high purity at temperatures 900–1300°C

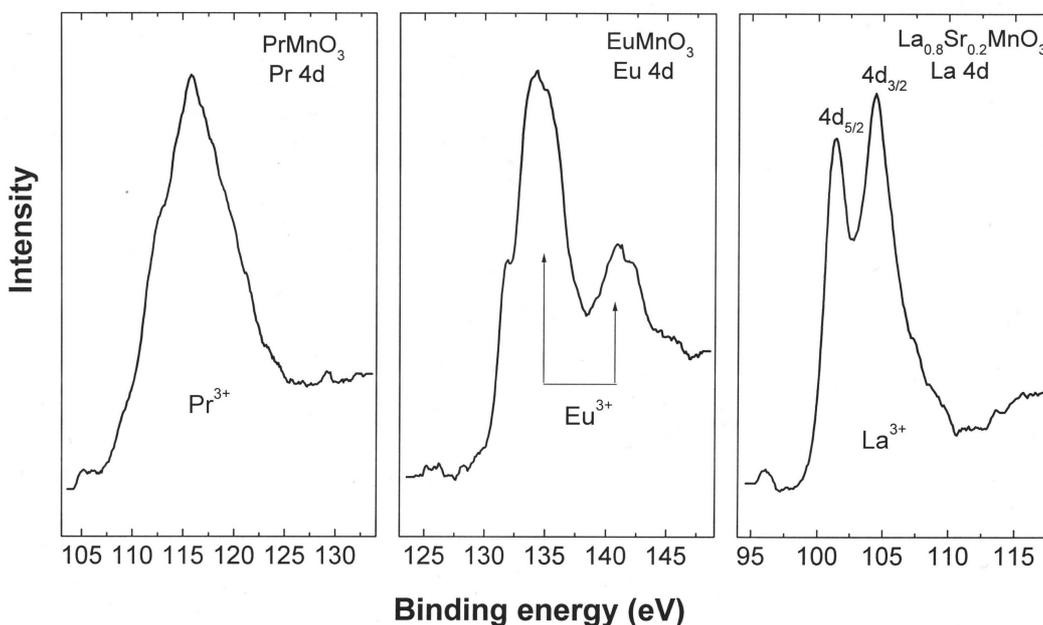


Figure 2. Pr 4d, Eu 4d, and La 4d core level XPS spectra for $PrMnO_3$, $EuMnO_3$ ceramics, and $La_{0.8}Sr_{0.2}MnO_3$ single crystal.

for 24 hours. Then, the samples were annealed in air at 1300°C for 12 hours. Single crystals of $La_{0.8}Sr_{0.2}MnO_3$ and $Eu_{0.95}MnO_3$ were prepared by floating zone melting with radiation heating. The methods of polycrystalline ceramic sample preparation and single crystal growth were described earlier in Refs. [9,10].

All spectroscopic measurements were carried out in ultra high vacuum (UHV) chamber (base pressure 10^{-10} mbar). Clean surfaces of ceramic samples were obtained by scrapping *in situ* in the spectrometer chamber. The chemical composition of scrapped ceramic samples was controlled by Auger electron spectroscopy to check for possible contamination of the surfaces after scrapping. Only samples with no carbon contamination were investigated by X-ray (XPS) and Ultra-Violet Photoemission spectroscopy (UPS). Clean surfaces of $La_{0.8}Sr_{0.2}MnO_3$ and $Eu_{0.95}MnO_3$ single crystals were prepared by cleaving in UHV at room temperature.

Photoemission experiments with the synchrotron radiation source were performed at the Berliner Speicherring-Gesellschaft für Synchrotronstrahlung (BESSY-I). Monochromatized radiation in the photon energy range of 40 to 200 eV was obtained from toroidal grating monochromator (TGM3). Photoelectrons from the valence band region were analyzed by hemispherical analyzer AR-65. The

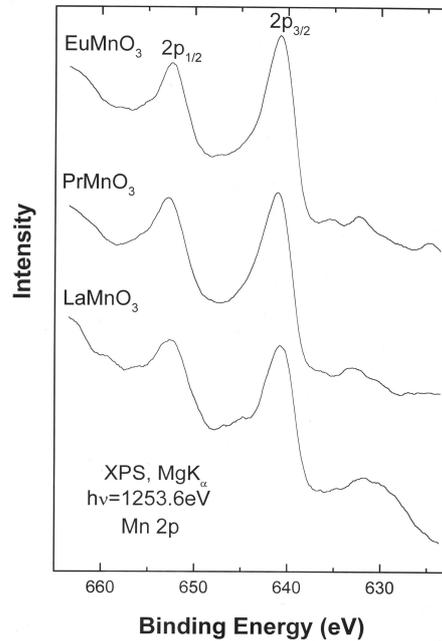


Figure 3. XPS MgK_α spectrum of Mn $2p$ level in LaMnO_3 , PrMnO_3 , and EuMnO_3 ceramic samples.

overall resolution (electrons plus photons) of UPS experiments was approximately 200 meV.

XPS experiments were carried out using twin X-ray source (Al K_α and Mg K_α). XPS spectra were recorded using the electron spectrometers with a spherical sector analyzer ESCALAB-5 and CLAM. The energy resolution for XPS experiments was 1.1 eV (full width at half maximum for Ag $3d$ level).

3. Results

XPS and UPS experiments demonstrate that rare earth ions in all perovskite manganites except, possibly, CeMnO_3 are in trivalent state. Figures 1 and 2 show rare earth $3d$ and $4d$ core level XPS spectra taken from CeMnO_3 , PrMnO_3 , EuMnO_3 ceramic samples and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ single crystal. Rare-earth core level ($3d$ and $4d$) XPS spectra of La, Eu, and Pr manganites shown in Figs. 1 and 2 demonstrate the features corresponding to trivalent rare earth ions ($\text{AlK}_{\alpha_{3,4}}$ satellites are responsible for the shoulders on the lower binding energy side of the main peaks). One can compare energy positions of the measured rare earth core levels with the ones reported earlier for compounds with divalent,

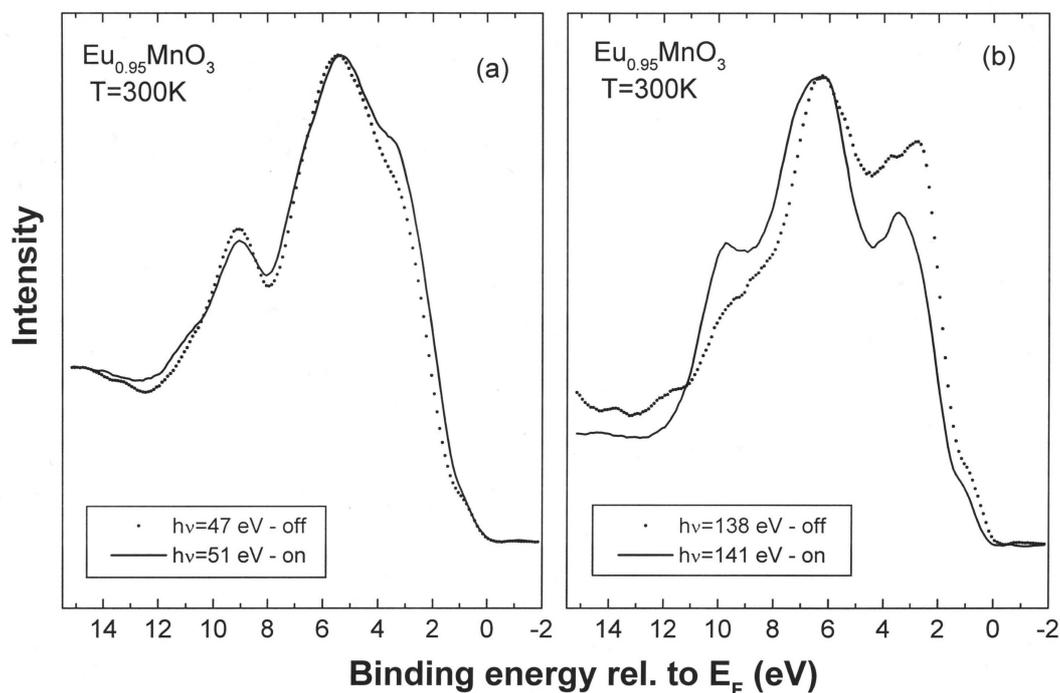


Figure 4. Mn $3p-3d$ (a) and Eu $4d-4f$ (b) resonant photoemission spectra of $Eu_{0.95}MnO_3$ single crystal. Valence band spectra were normalized to equal maximum height.

trivalent, or tetravalent rare earth ions (see, for instance, spectra in Refs. [11–13] presented for different rare earth oxides). For example, as demonstrated in Ref. [13], divalent Eu emission is responsible for the 129 eV peak in $4d$ spectra that is not observed in our case. Binding energy of the most intensive line in Eu $4d$ spectra of $EuMnO_3$ is 134.3 eV that is characteristic of trivalent europium. The shift of Eu^{2+} and Eu^{3+} features is approximately 5.5 eV. In the core level photoemission spectra of $LaMnO_3$ and $PrMnO_3$ presented in Fig. 2 the following positions of $4d$ lines could be found: 115.8 eV for the Pr $4d$ peak, and 101.4 and 104.5 eV for the La $4d_{5/2}$, $4d_{3/2}$ doublet. All these values are typical of trivalent rare earth ion states.

Note that comparison of $3d$ and $4d$ core level spectra taken from ceramic and single crystalline Eu and La manganite perovskites showed similar results for both types of the samples: trivalent rare earth ion configuration can be assumed from the core level structures.

For the $CeMnO_3$ compound, the structure of the core level and valence band XPS spectra was more complicated. We could not conclude the exact state of Ce

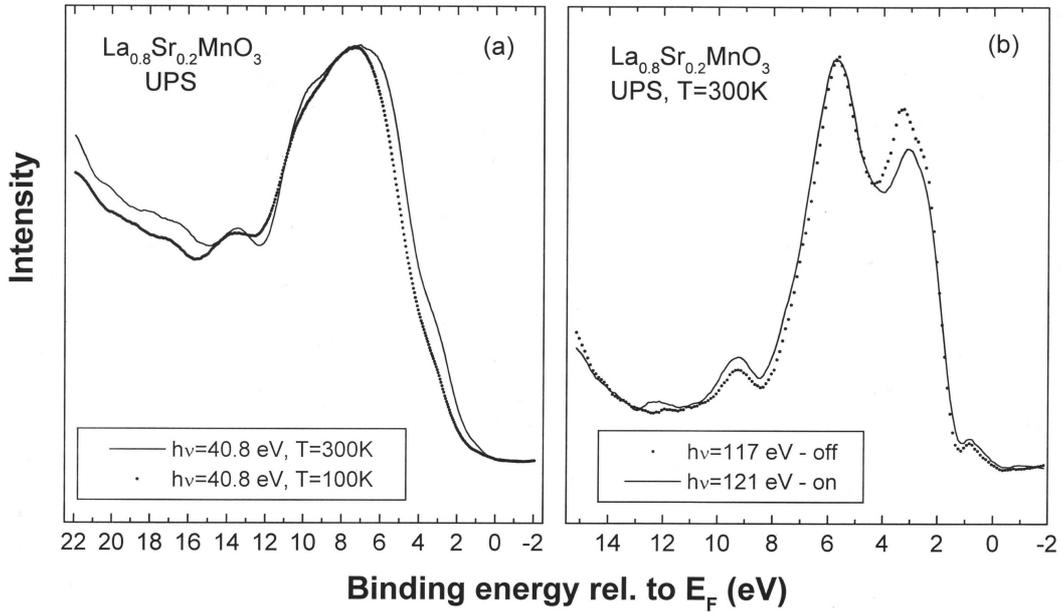


Figure 5. (a) Comparison of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ single crystal valence band spectra taken at $h\nu = 40.8$ eV and different temperatures. (b) Comparison of the valence band spectra at different photon energies (off- and on- the $4d$ - $4f$ resonance). Spectra were normalized to equal maximum height.

ions in this compound but the energy position and wide peaks of $3d$ and $4d$ lines allow us to assume that the valency of Ce ions is between 3 and 4. The energy position of Ce core level lines is not consistent with those observed for Ce^{4+} and Ce^{3+} states. As it is known (see, for example, spectra in Ref. [12]), Ce^{3+} derived photoemission features related to the $3d^{10}4f^1$ initial state located in the binding energy range of 880–905 eV whereas the $3d^{10}4f^1$ initial state of Ce^{4+} ions is responsible for photoemission lines at higher binding energies. The assumption of mixed valency Ce ion states in CeMnO_3 correlates with conclusions of Refs. [2,4,14] where mixed valency character of Ce ions with a valency between 3 and 4 was proposed. The authors assumed that these mixed valency states are arising from the hybridization with O $2p$ band.

Investigations of Mn core level states showed similar results for all rare earth manganite perovskites studied. As an example, Figure 3 presents Mn $2p$ core level XPS spectra taken from EuMnO_3 , PrMnO_3 , and LaMnO_3 ceramic samples. All spectra in Fig. 3 demonstrate similar structure: the same binding energies and line widths of Mn $2p_{3/2}$, $2p_{1/2}$ peaks (at 640.8 and 652.5 eV, respectively).

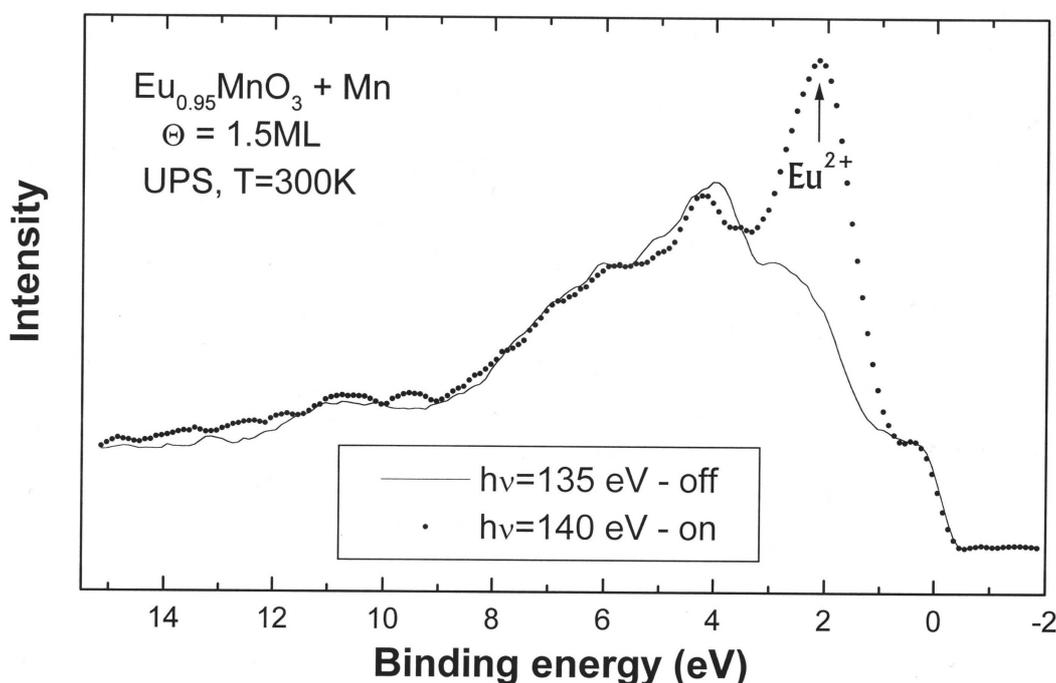


Figure 6. Eu $4d-4f$ resonant photoemission spectra of $\text{Eu}_{0.95}\text{MnO}_3$ single crystal after Mn deposition. Spectra were normalized to equal Fermi level cutoff height.

Features at lower binding energies (approximately 632–633 eV) correspond to Auger excitations in rare earths. One can assume similar state of Mn ions in different LnMnO_3 compounds. However, additional comparative experiments are necessary to find the exact valency of Mn ions in these compounds.

The valence band structure of single crystalline and ceramic samples of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{Eu}_{0.95}\text{MnO}_3$ was also investigated by UPS with the synchrotron radiation source. The valence band structure in these compounds is determined by Mn, rare earth (Eu $4f$ and La $5p$), and strongly hybridized Mn $3d$ – O $2p$ states (wide peak between 3 and 7 eV). Figures 4 and 5 present some UPS spectra taken from clean cleaved surfaces of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{Eu}_{0.95}\text{MnO}_3$ single crystals. The valence band spectra were recorded at different temperatures and photon energies to look for possible modification of the electronic structure and identify the origin of the valence band features. Photon energies in photoemission experiments were chosen to achieve on- and off-resonance conditions for certain electronic states (Mn $3p-3d$ and rare earth $4d-4f$ resonances).

In Fig. 4 we present UPS valence band spectra of $\text{Eu}_{0.95}\text{MnO}_3$ single crystal

taken at room temperature and photon energies above and below energies of Mn $3p-3d$ (a) and Eu $4d-4f$ (b) transitions. As shown in some papers (see, for example, Refs. [15,16]), by varying the photon energy one can obtain both on- and off-resonance conditions to enhance the valence band features corresponding to Eu^{2+} and Eu^{3+} states. One of the resonant energies for enhancement of Eu^{2+} features is 140 eV. However, the spectra from cleaved surfaces of $\text{Eu}_{0.95}\text{MnO}_3$ single crystal do not show any enhancement of the features in the range of binding energies from 1 to 3 eV assigned to divalent Eu. Moreover, normalizing the spectra presented in Fig. 4(b) to the Fermi level cutoff height, one can notice enhancement of the trivalent Eu feature at around 7 eV in the off-resonance spectrum which correlates with the assumption of trivalent Eu ion character for EuMnO_3 compounds made earlier from core level XPS spectra.

Fig. 4(a) presents the valence band spectra of $\text{Eu}_{0.95}\text{MnO}_3$ taken at photon energies of 47 eV and 51 eV (off- and on- Mn $3p-3d$ resonance, respectively). From this figure one can see slight enhancement at approximately 2 eV and attenuation of the valence band peak at 9 eV. However, the valence band spectrum modification is not so large as that observed for Eu states under on- and off-resonance conditions. This fact perhaps reflects a strong hybridization of Mn $3d$ and O $2p$ states. In this paper we do not show the valence band spectra of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ single crystal recorded at the same photon energies (47 and 51 eV) but the difference between the on- and off-resonance spectra for the La compound was smaller compared to the europium manganite.

Figure 5 presents the on- off-resonance spectra ($4d-4f$ resonance) for $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and comparison of valence band spectra taken at room and liquid nitrogen temperatures. The UPS valence band spectra of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and $\text{Eu}_{0.95}\text{MnO}_3$ at low temperature (approximately 100 K) demonstrate changes in the electronic structure upon single crystal cooling. For the La compound these are narrowing and a slight shift of the valence band features [see Fig. 5(a)] while for the Eu compound the measurements at 100 K (not shown here) demonstrated changes of the energy position and broadening of spectra (results at this temperature were not well reproducible in a series of experiments). This result may be caused by the magnetic or metal-insulator transition observed earlier for manganite perovskites in this temperature range [9].

An interesting result was obtained after the deposition of 1.5 monolayers of Mn onto $\text{Eu}_{0.95}\text{MnO}_3$ clean surface at room temperature (Fig. 6). Mn was evaporated *in-situ* in the spectrometer chamber after photoemission experiments on cleaved single crystal surface. The amount of Mn deposited was controlled by a quartz microbalance. UPS spectra from Mn/ $\text{Eu}_{0.95}\text{MnO}_3$ interface were measured at different photon energies including the values in the vicinity of $4d-$

4*f* resonance. As an example, Figure 6 presents UPS spectra taken at $h\nu = 135$ and 140 eV (off- and on-resonance, respectively).

Strong enhancement of the shallow core level photoemission at photon energies close to the 4*d*–4*f* photothreshold and resonant behavior of the photoemission spectra of rare earth compounds originates from the process of photoexcitation (near 4*d*–4*f* absorption region) followed by the decay of the excited configuration via direct and indirect processes. These processes produce the resonant enhancement of photoemission and can be described as shown below for Eu:

direct: $4d^{10}4f^7 + h\nu \rightarrow 4d^{10}4f^6 + e^-$,

indirect: $4d^{10}4f^7 + h\nu \rightarrow 4d^94f^8 \rightarrow 4d^{10}4f^6 + e^-$.

Photoemission spectra of Mn/Eu_{0.95}MnO₃ interface clearly demonstrate (Fig. 6) a remarkable resonance of Eu 4*f* states so that the spectral intensity for Eu compound near 2 eV is strongly enhanced (Fig. 6, on-resonance: 140 eV), an effect which one tends to attribute to emission from Eu 4*f*⁷ states proving the existence of Eu²⁺ (4*f*⁷) at the interface. Apparently, this could mean that the deposition of 1.5 ML Mn even at room temperature could change the electron density distribution on Eu sites and induce Eu³⁺ → Eu²⁺ transition at the interface. It would be interesting to investigate the transport properties as well as the electronic structure of such Mn/LnMnO₃ interfaces in more detail.

4. Conclusions

We have investigated rare earth manganite perovskites $\text{Ln}_{1-x}\text{Sr}_x\text{MnO}_3$ (Ln = La, Ce, Pr, Eu; $x = 0, 0.2$) by photoelectron spectroscopy.

Photoemission experiments demonstrated trivalent rare earth ion states for La, Pr, and Eu compounds. The trivalent La and Eu ion states were observed both for ceramic (polycrystalline) and single crystalline samples. For the CeMnO₃ compound, the mixed valency Ce states with the valency between 3 and 4 were supposed from XPS data. Deposition of 1.5 monolayers of Mn onto Eu_{0.95}MnO₃ single crystal clean surface led to quite intriguing result: strong enhancement of divalent Eu feature in the on-resonance valence band spectra was observed after Mn deposition while the Eu_{0.95}MnO₃ clean surface spectra only revealed the existence of Eu³⁺ states.

Acknowledgements

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