

Electronic States of Colossal Magnetoresistive Manganites $\text{La}_{0.67}\text{Pb}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ from Photoemission Spectroscopy

M. KOWALIK^{a,b,*}, R. ZALECKI^a AND A. KOŁODZIEJCZYK^a

^aFaculty of Physics and Applied Computer Science, AGH University of Science and Technology
al. Mickiewicza 30, 30-059 Kraków, Poland

^bDepartment of Physics, Rzeszów University of Technology
Powstańców Warszawy 6, 35-959 Rzeszów, Poland

The electron photoemission spectra of valence bands and core-level states of manganese perovskite $\text{La}_{0.67}\text{Pb}_{0.33}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ with $x = 0, 0.01, 0.03, 0.06, 0.10$ and 0.15 were measured by the X-ray and Ultraviolet Photoemission Spectroscopy (XPS and UPS) below and above the metal-insulator transition. From analysis of the Mn $2p$ core-level spectra the ratio $\text{Mn}^{3+}/\text{Mn}^{4+}$ was calculated as a function of the iron content. Comparison of the valence band spectrum with band structure calculations and with the high-resolution spectra measured at synchrotron radiation for Ca-, Ba- and Ce- substituted manganites revealed the strong hybridisation of Mn $3d$ and of O $2p$ states between -3 eV and -7 eV, and no estimated oxygen states between 0 eV and -2 eV where the Mn- $3d$ states play a predominant role. The composition dependent insulating energy gaps were measured at room temperature. Reasons for the behaviour were discussed taking into account previous analysis of XPS/UPS spectra of other manganese perovskites.

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1. Introduction

Substitution of Pb^{2+} for La^{3+} in the antiferromagnetic insulator LaMnO_3 gives rise to an equivalent amount of Mn^{4+} which induces ferromagnetism (FM) and metallicity in $(\text{La}_{1-y}\text{Pb}_y)(\text{Mn}_{1-y}^{3+}\text{Mn}_y^{4+})\text{O}_3$ compounds [1] due to the so-called double exchange interaction (DE). This interaction is associated with the hopping of the e_g electron between Mn^{3+} and Mn^{4+} ions.

In this work we have focused our effort on the study of the effect caused by the substitution of Mn by Fe ions on photoemission from electronic states in $\text{La}_{0.67}\text{Pb}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ compounds with $x = 0, 0.01, 0.03, 0.06, 0.10$ and 0.15 . We found only two papers on photoemission spectroscopy of $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$ [2, 3] and no papers with the iron substitution. Some controversies and an inconsistent interpretation of the data still exist, especially as far as the role of Pb in valence band and the mixed valence of Mn ions are concerned.

2. Samples and experiments

Polycrystalline compounds $(\text{La}_{0.67}\text{Pb}_{0.33})(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ ($x = 0, 0.01, 0.03, 0.06$ and 0.1) were prepared by the sol-gel low-temperature method

followed by the heat treatment at 1273 K in air [1]. Powder X-ray diffraction (XRD) patterns were collected with a D5000 Siemens diffractometer using Cu K_α radiation and a graphite secondary monochromator. The XRD showed the single-phase rhombohedrally distorted perovskite structure (space group $R\bar{3}c$) for all compounds, with the lattice parameters ranging from $a = 5.4904$ Å to $a = 5.4928$ Å for $x = 0$ to $x = 0.1$, respectively [1]. Iron doping up to $x = 0.1$ does not change the crystal structure of the parent compound [1].

The field cooled-zero field cooled (FC-ZFC) dc magnetization in magnetic fields of 50 Oe, 1 kOe and 10 kOe, and hysteresis loops up to 89 kOe, as well as, four-probe magnetoresistance measurements have been performed from 4 K up to 400 K at the fields up to 80 kOe using the Quantum Design physical property measuring system [4]. Iron doping up to $x = 0.1$ suppresses locally double exchange interactions and decreases the Curie temperatures T_C and the metal-insulator transitions T_{M-I} [4]. The doping reduces also the magnetization and increases the magnetoresistance. The magnetic transition temperatures T_C and saturation magnetic moments show an almost linear decrease with increasing iron content x [4].

Photoemission measurements were carried out by the use of the X-ray and angle resolved ultraviolet (XPS/ARUPS) Omicron photoemission spectrometer equipped with dual Al- and Mg- K_α X-ray sources of Prevac RS40B1 (resolution of 0.85 eV), the high intensity UV

* corresponding author; e-mail: mkowalik@prz.edu.pl

helium source of Omicron HIS 13 and angle-resolved electron kinetic energy analyser AR 65 (resolution of about 50 meV). To avoid surface degradation all the experiments were performed under vacuum better than 10^{-9} mbar. To get the most representative spectra, as compared to our previous ones [5, 6], the sample surfaces were scrapped *ex-situ* with a diamond file. Next, they were heated up to 300°C *in-situ* during pumping, cleaned by Ar ion gun and heated once more. The XPS/UPS electron photoemission spectra of the core level states and the valence bands of the manganese perovskite $\text{La}_{0.67}\text{Pb}_{0.33}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ (with $x = 0, 0.01, 0.03, 0.06, 0.10, 0.15$) were measured below and above the metal-insulator transition.

3. Results and discussion

3.1. X-ray photoemission spectroscopy

The examples of full scan X-ray (Al- K_α) and (Mg- K_α) photoemission spectra are shown in Fig. 1a,b. The low binding energy spectra as well as Mn $2p$ -core-level spectra were separately measured and analysed. They are shown in Figs. 2–3.

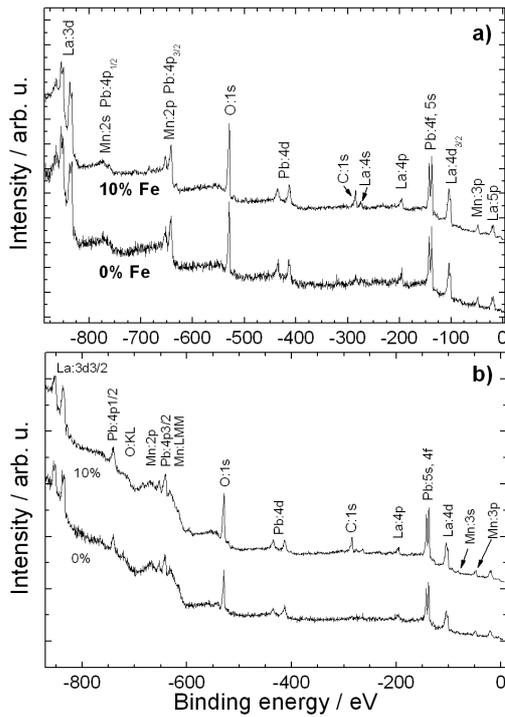


Fig. 1. The full scan of (a) X-ray (Al- K_α) and (b) (Mg- K_α) spectra of $(\text{La}_{0.67}\text{Pb}_{0.33})(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ for $x = 0$ and $x = 0.10$, at room temperature, with the core-level and Auger lines indicated.

From the spectra, at the binding energy about 85 eV (Fig. 2), the exchange splitting energy may be estimated as $\Delta E_{\text{ex}} = 5.0 \pm 0.2$ eV and it is roughly the same for all investigated compounds also as in our previous papers

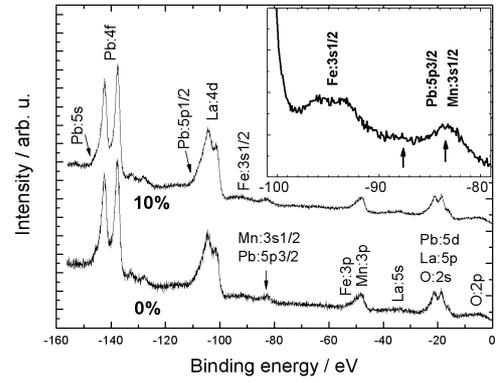


Fig. 2. Low binding energy X-ray Al- K_α spectra of $\text{La}_{0.67}\text{Pb}_{0.33}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ for the given x , with core-level lines indicated. Inset: X-ray Mg- K_α Mn $3s$ and Fe $3s$ core-level spectra of $\text{La}_{0.67}\text{Pb}_{0.33}\text{Mn}_{0.94}\text{Fe}_{0.06}\text{O}_3$.

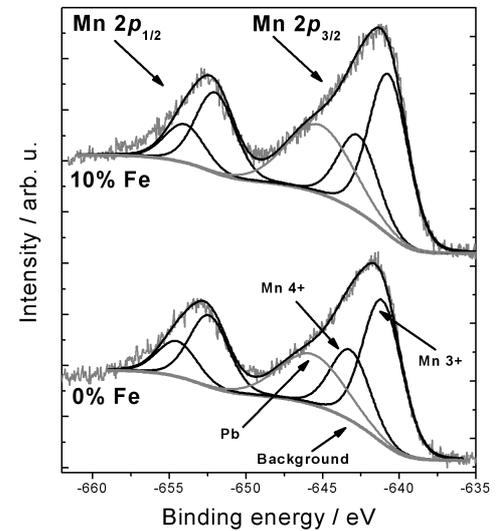


Fig. 3. The Mn $2p$ core-level X-ray Al- K_α spectra together with fitting lines. Each of the spectra consists of $2p_{1/2}$ and $2p_{3/2}$ of Mn^{3+} and Mn^{4+} , as well as of the Pb $4p_{3/2}$ overlapping the $2p_{3/2}$ of Mn^{4+} .

[5, 6]. It may only be taken as an estimate because of the overlap of Mn $3s$ line with Pb $5p_{3/2}$ line. ΔE_{ex} comes from the exchange interaction between the $3s$ core hole produced in a photoemission process and $3d$ electrons, and depends on the valence state of Mn ions. The exchange splitting of MnO is 6 eV, of Mn_2O_3 is 5.5 eV and of MnO_2 is 4.7 eV [7], that is for Mn^{2+} , Mn^{3+} and Mn^{4+} ions, respectively. It proves the mixture of $3+$ and $4+$ manganese valence states in these compounds.

In this paper we have focused our attention on proper analysis of Mn $2p$ core-level spectra taken with X-ray (Al- K_α) and not with (Mg- K_α) because for the latest there is an overlap with Mn:LMM Auger lines (see Fig. 1b). Each the main line of Mn $2p_{1/2}$ and $2p_{3/2}$,

was assigned to the two-component $2p^53d^4$ and $2p^53d^3$ final state configurations, except $2p^63d^4$ and $2p^63d^3$ initial state configurations for Mn^{4+} and Mn^{3+} ionic states, respectively. Thus, the main lines are fairly asymmetric due to dual contributions from Mn^{4+} and Mn^{3+} ionic states to their total intensities. Unfortunately, one has to take into account also a contribution from the Pb $4p_{3/2}$ line overlapping the $2p_{3/2}$ of Mn^{4+} line, which in turn fortunately is the same for all compounds. Two examples of such fitting procedure with two 90% Gaussian and 10% Lorentzian lines of $2p_{1/2}$ and $2p_{3/2}$ of Mn^{3+} and Mn^{4+} , as well as, the Pb $4p_{3/2}$ line overlapping the $2p_{3/2}$ of Mn^{4+} are shown in Fig. 3. The most popular XPS Peak fitting program version 4.1 [9] was used. This program allows

to keep constant the intensity ratio of both spin-orbit split components as theoretically predicted 2:1 for Mn: $2p_{3/2}$ and $2p_{1/2}$ line, respectively. The spin-orbit splitting energy ΔE_{SOS} was 11.3 eV, and it was the same for all compounds during fitting procedure. The full width at half maximum (FWHM) of each manganese line was about 3 eV. The specimen with $x = 0.03$ was not cleaned by argon gun and exhibited a bit larger FWHM. From comparison of fitted areas below relevant peaks, the ratio of amount of trivalent to four-valence manganese ions $\text{Mn}^{3+}/\text{Mn}^{4+}$ was about 2.0 ± 0.1 for all measured compounds, as compared to calculated value 2.0 for $x = 0.0$. The binding energies, $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratios and other fitting parameters are listed in Table.

TABLE

Binding energies E_B , the full width at half maximum (FWHM) and the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio of $\text{La}_{0.67}\text{Pb}_{0.33}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ for given x .

x	E_B [eV]			FWHM [eV]		$\text{Mn}^{3+}/\text{Mn}^{4+}$
	$2p_{3/2}$ Mn^{3+}	$2p_{3/2}$ Mn^{4+}	$4p_{3/2}$ Pb	$\text{Mn}^{3+,4+}$	Pb	
0	641.1	643.2	645.7	3.0	5.0	2.02
0.03	640.8	643.6	646.1	3.4*	5.5*	2.05
0.10	640.7	642.7	645.2	3.0	5.0	2.09

*The specimen was not cleaned by argon gun.

3.2. Ultraviolet photoemission spectroscopy

The common feature of UPS spectra, shown in Fig. 4, was the two-peak structure at about -4.0 eV and -6.0 eV below the upper edge of the valence band. The same was observed in [3, 5–7] for other manganese perovskites.

This behaviour may be discussed taking into account our previous analysis of UPS spectra of other manganese perovskites [5, 6] as well as the paper [3] on electronic structure examination using the techniques of angle resolved photoemission, resonance photoemission and inverse photoemission with synchrotron radiation. Studies in Ref. [3] were performed only for two Ca- and Ba-substituted films of $\text{La}_{0.65}(\text{Ca}, \text{Ba})_{0.35}\text{MnO}_3$ grown on LaAlO_3 . However, we do not expect a significant difference for an assignment of electronic band states for our Pb-substituted compounds. Comparison of the spectra with band structure calculations and with high-resolution spectra measured at synchrotron radiation for Ca- and Ba-manganites [3] revealed strong hybridisation of Mn $3d$ and O $2p$ states between -3 eV and -7 eV. There is no oxygen states between 0 eV and -2 eV where the Mn- $3d$ states play a predominant role. There is nothing more than a vanishing small spectral weight at Fermi energy, even though the measurements were made in the ferromagnetic metallic state of the compound in lower temperature. The depression of spectral weight was called as

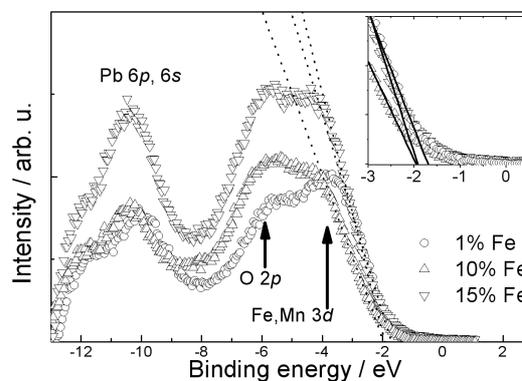


Fig. 4. UPS spectra of $\text{La}_{0.67}\text{Pb}_{0.33}(\text{Mn}_{1-x}\text{Fe}_x)\text{O}_3$ for $x = 0.01, 0.10$ and 0.15 at room temperature. The inset shows an estimation of energy gaps for these compounds.

a pseudo-gap [10]. Insulating energy gaps were estimated at room temperature by linear extrapolation of spectral intensities close to 0 eV of binding energy. They were from about 1.7 eV to 2.0 eV depending on the composition as it is shown in the inset of Fig. 4. The interpretation of the peak at about -10.0 eV is still debatable. We ascribed tentatively this peak to Pb $6p^2$ and/or Pb $6s^2$

atomic states contribution to the valence band. In the future a contribution from lead valence states should be explained from comparison with band structure calculations.

4. Conclusions

We can conclude that: (1) The Mn $2p$ core-level X-ray photoemission spectra can not be fitted with one spin-orbit split spectrum. The spectrum was fitted with two spin-orbit split spectra for Mn^{3+} and Mn^{4+} with some small admixture of Pb $4p_{3/2}$ line overlapping the $2p_{3/2}$ of Mn^{4+} (Fig. 3). From the analysis, the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio is 2.0 ± 0.1 for all compounds. It's the same as calculated value for $x = 0$. (2) UPS spectra of the valence band consist of contributions from $3d$ manganese and $2p$ oxygen states, which are hybridised between -3 eV and -7 eV. Contribution from the $3d$ manganese is predominant in the density of states close to the upper edge of the valence band.

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