ELECTRONIC STRUCTURE OF DOPED La–Mn–O PEROVSKITES

M. DEMETER\textsuperscript{a},*, M. NEUMANN\textsuperscript{a}, V.R. GALAKHOV\textsuperscript{b}, N.A. OVECHKINA\textsuperscript{b}, E.Z. KURMAEV\textsuperscript{b} AND N.I. LABACHEVSKAYA\textsuperscript{c}

\textsuperscript{a}University of Osnabrück, Faculty of Physics
Barbarastr. 7, 49069 Osnabrück, Germany

\textsuperscript{b}Institute of Metal Physics, Russian Academy of Sciences – Ural Division
620219 Yekaterinburg GSP-170, Russia

\textsuperscript{c}Institute of Chemistry of Solids, Russian Academy of Sciences – Ural Division
620219 Yekaterinburg GSP -145, Russia

The electronic structure of the doped perovskite manganese oxides La\(_{1-x}\)Sr\(_x\)MnO\(_3\) and La\(_{1-x}\)Ba\(_x\)MnO\(_3\) has been investigated by X-ray photoelectron and X-ray emission spectroscopy. By comparing the O \(K\alpha\) and Mn \(L\alpha\) X-ray emission spectra with the valence band X-ray photoelectron spectra we could localize the Mn 3d and O 2p states into the valence band. Our data are compared with previous band structure calculations. The value of the Mn 3s splitting does not change with Sr-doping in the concentration region from \(x = 0.0\) till \(x = 0.3\). This shows that the doping holes have mainly oxygen \(p\) character. The large value of the splitting indicates that the 3d electrons are in the high-spin state.

PACS numbers: 71.70.Gm, 79.70.+q

1. Introduction

Nowadays great interest exists in manganese perovskite oxides due to the discovery of the colossal magnetoresistance (CMR) effect [1]. The parent compound LaMnO\(_3\) is an A-type antiferromagnetic (AFM) \((T_N = 140\text{ K})\) insulator with a distorted perovskite structure. The manganese ions are Mn\(^{3+}\) (3d\(^4\)) having three electrons in the t\(_{2g}\) band and one in the e\(_g\) band. When this compound is doped with divalent alkaline-earth cations A\(^{2+}\) (Sr, Ba), a charge redistribution from Mn\(^{3+}\) to Mn\(^{4+}\) occurs. In a certain range of doping \((0.2 \pm 0.5)\) these compounds show simultaneously ferromagnetism and metallic behaviour. This effect has been explained by Zenner in the double-exchange model [2]. According to this, the conduction is achieved through the hopping of an electron in the e\(_g\) state of the Mn\(^{3+}\) ions into the unoccupied e\(_g\) band of the Mn\(^{4+}\) ions. Later it has been shown

\*corresponding author; e-mail: mdemeter@uos.de
that the electron–phonon interaction also plays a very important role [3]. The microscopic origin of the strong electron–phonon coupling is the large Jahn–Teller effect which occurs for $d^{4+}$ ions in an octahedral environment [4].

The electronic and magnetic diagram of La$_{1-x}$Sr$_x$MnO$_3$ has been established from electrical and magnetic measurements. Curie temperatures of 145 K, 309 K, and 369 K for $x = 0.1, 0.2, 0.3$ were also determined [5]. For $x < 0.1$ the system is a canted AFM insulator and for $0.1 < x < 0.17$ it is FM insulator. For $x = 0.175$ at room temperature there is also a structural transition from orthorhombic to rhombohedral. For $x > 0.2$ a transition from FM insulator to FM metal takes place. The crystal structure of La$_{1-x}$Ba$_x$MnO$_3$ changes from orthorhombic through rhombohedral to cubic ($x > 0.35$) with increasing concentration. The Curie temperatures of La$_{1-x}$Sr$_x$MnO$_3$, where $x = 0.1, 0.2, 0.3$ are 145 K, 309 K, and 369 K, respectively.

X-ray photoelectron and X-ray emission spectroscopies (XPS, XES) are known as powerful tools to investigate the electronic structure of perovskites and the changes with carriers doping. In this paper we present new results of XPS and XES studies of the single crystals of La$_{1-x}$Sr$_x$MnO$_3$ ($x < 0.3$) and La$_{0.8}$Ba$_{0.2}$MnO$_3$. Our experimental spectra are compared with the previous band structure calculations [6].

2. Experimental

Single crystals of La$_{0.8}$Ba$_{0.2}$MnO$_3$, (La$_{0.9}$Sr$_{0.1}$)$_{0.9}$MnO$_3$, La$_{0.8}$Sr$_{0.2}$MnO$_3$, and La$_{0.7}$Sr$_{0.3}$MnO$_3$ were grown by the floating-zone method using the radiation heating of the zone by a xenon lamp at the Moscow Institute of Steel and Alloys by Ya.M. Mukovskii.

The X-ray photoelectron spectra were recorded with an ESCA spectrometer from Physical Electronics (PHI-5600-ci) using monochromatic Al $K_{\alpha}$ radiation. All samples were measured after breaking in a high vacuum ($10^{-9}$ torr). All spectra were recorded at room temperature. They were calibrated using an Au-foil ($E_B$ (4f$_{7/2}$) = 84.0 eV). The energy resolution as determined at the Fermi level of the Au-foil was $\sim 0.4$ eV.

The Mn $L_\alpha$ ($3d4s \rightarrow 2p_{3/2}$ transitions) and O $K_{\alpha}$ ($2p \rightarrow 1s$ transitions) X-ray emission spectra were measured on the RSM-500-type X-ray vacuum spectrometer with a diffraction grating ($N = 600$ lines/mm, $R = 6$ m) and electron excitation. The spectra were recorded in the first order of reflection by a secondary electron multiplier with a CsI photocathode. The energy resolution was 0.4 eV. The X-ray tube was operated at $V = 4.0$ keV and 0.25 mA.

3. Results and discussions

In Fig. 1a the valence band spectra of La$_{0.7}$Sr$_{0.3}$MnO$_3$, La$_{0.8}$Sr$_{0.2}$MnO$_3$, and (La$_{0.9}$Sr$_{0.1}$)$_{0.9}$MnO$_3$ are presented. They exhibit a structured wide band followed by a lower binding energy tail close to the Fermi level. The peaks at 6 eV and 2.5–4 eV correspond to the O 2p states hybridized with Mn $t_{2g}$ states. The low
Electronic Structure of Doped La–Mn–O Perovskites

589

intensity feature close to the Fermi level that is centred at ~ 0.7 eV is due to the emission from the \( e_g \) states. The most prominent peak at 6 eV below the Fermi level does not change with \( x \). The intensity of the La \( 5p \) peak, located at ~ 17 eV decreases with Sr doping, whereas Sr \( 4p_{3/2} \) peak at ~ 19 eV is increasing with \( x \). The peak due to O 2s states is located at 21.5 eV. Similar studies on La\(_{0.84}\)Sr\(_{0.16}\)MnO\(_3\) single crystal [7] and polycrystalline samples (\( x = 0.0 \div 0.9 \)) [8] were reported.

![Fig. 1. (a) XPS valence band spectra of the single crystals La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) — a, La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\) — b and (La\(_{0.9}\)Sr\(_{0.1}\))\(_{0.9}\)MnO\(_3\) — c; the inset shows a comparison between a — up triangle and c — line from -2 to 10 eV. (b) Comparison of the XPS valence band spectra of La\(_{0.8}\)A\(_{0.2}\)MnO\(_3\) (A=Sr, Ba).](image)

In Fig. 1b we present a comparison of the XPS valence band spectra of the single crystals La\(_{0.8}\)(Sr,Ba)\(_{0.2}\)MnO\(_3\). They exhibit similar features, a wide band and a low structure close to the Fermi level. There is a difference in the feature located at about 5 eV where O 2p contribution dominates. For Ba doped compound (\( x = 0.35 \)) it was found that the feature corresponding to this energetic value is not enhanced at a photon energy of 52 eV (the Mn 3p resonance edge) indicating that it has a very little Mn 3d character [9]. We assign the structure close to the Fermi level to \( e_g \) states, whereas the states at 2.9 eV are assigned to \( t_{2g} \) states [6, 9]. The next feature at ~ 4 eV is due to O 2p states hybridised with Mn \( t_{2g} \) states. The highest peak at ~ 6 eV is the same as in the similar Sr-doped compound. Linear muffin-tin orbital (LMTO) band structure calculations performed on the La\(_{1-x}\)Ba\(_x\)MnO system [10] have shown that for \( x = 0.2 \) the contribution to the total density of states (DOS) at the Fermi level comes mainly from \( e_g \) states, whereas for \( x = 0.4 \), in the half-metallic regime (\( x > 0.33 \)) the density of states at \( E_F \) is due solely to \( e_g \) electrons. In the Ba-doped sample, the peak located at 13.4 eV is due to Ba 5p states. The feature at binding energies higher than 25 eV in the Ba-doped sample is given by the Ba 5s peak contribution (not shown here).

In Fig. 2 XPS valence band together with XES Mn \( L_\alpha \) and O \( K_\alpha \) spectra are shown for LaMnO\(_3\) and Sr(Ba)-doped samples (\( x = 0.2 \)). Mn \( L_\alpha \) X-ray emission
arises from the $3d4s \rightarrow 2p_{3/2}$ electronic transition and reflects the Mn 3$d$ distribution in the valence band. O $K\alpha$ X-ray emission corresponds to the $2p \rightarrow 1s$ transition and reveals the O $2p$ partial density of states. The XES Mn $L\alpha$ and O $K\alpha$ spectra were brought to the binding energy scale by using the Mn $2p_{3/2}$ and O $1s$ binding energies, respectively. The Mn $L\alpha$ and O $K\alpha$ XES spectra are localized in the same energy area, which indicates a strong Mn 3$d$ – O 2$p$ hybridization. In the O $K\alpha$ spectrum, the maximum at $\sim 3.5$ eV corresponds to the antibonding $pd\pi$ states and the shoulder at 6 eV reflects the bonding $pdc$ states. Our experimental results are in good agreement with local spin-density approximation (LSDA) calculations [6].

![Fig. 2](image)

**Fig. 2.** XPS and XES spectra of LaMnO$_3$, La$_{0.8}$Sr$_{0.2}$MnO$_3$, and La$_{0.8}$Ba$_{0.2}$MnO$_3$.

![Fig. 3](image)

**Fig. 3.** XPS Mn 3$s$ splitting of the single crystals of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (a), La$_{0.8}$Sr$_{0.2}$MnO$_3$ (b), and (La$_{0.9}$Sr$_{0.1}$)$_{0.9}$MnO$_3$ (c).

The 3$s$ exchange splitting in transition metal compounds is due to the exchange interaction between the 3$s$ core hole created in a XPS process and 3$d$ electrons. The magnitude of the Mn 3$s$ splitting ($\Delta E_s$) depends on the valence state of the Mn ions. In Fig. 3 the Mn 3$s$ XPS spectra of (La$_{0.9}$Sr$_{0.1}$)$_{0.9}$MnO$_3$, La$_{0.8}$Sr$_{0.2}$MnO$_3$, and La$_{0.7}$Sr$_{0.3}$MnO$_3$ single crystals are presented. The highest peak is located at $\sim 83.5$ eV. In Ref. [8] it has been reported that the Mn 3$s$ splitting of polycrystalline La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0.0 \div 0.9$) monotonically decreases with $x$. However, our spectra on single crystals samples show that the value of the Mn 3$s$ splitting (5.3 eV) does not change with Sr doping from $x = 0.0$ to $x = 0.3$. This indicates that the doped holes have mainly oxygen $p$ character. The large value of the splitting is consistent with the high-spin configurations.
4. Conclusions

We have presented new XPS and XES results on manganese doped perovskites, single crystals. The same 3s splitting of the Sr-doped samples with \( x < 0.3 \) indicates the oxygen 2p character of the doped holes. The large value of the splitting shows that the Mn 3d electrons are in the high spin state. The Mn \( L_\alpha \) and O \( K_\alpha \) XES spectra are localised in the same energy area indicating strong Mn 3d – O 2p hybridisation. Our data are in good agreement with the previous LSDA results.

Acknowledgments

The financial support from DFG, especially Graduiertenkolleg is gratefully acknowledged. One of the authors (V.R. G.) want to thank for the financial support from the RFBR-99-02-16280 Project. We thank Ya.M. Mukovskii for supplying the single crystals.

References