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Abstract

The electronic structure of La$_{2/3}$Sr$_{1/6}$Pb$_{1/6}$MnO$_3$ has been studied by x-ray photoemission spectroscopy (XPS). The valence band spectrum is compared with *ab initio* electronic structure calculations using a linearized muffin-tin orbital (LMTO) method. The XPS measurements and the theoretical band structure calculations for La$_{1/2}$Sr$_{1/4}$Pb$_{1/4}$MnO$_3$ show that the electronic structure consists mainly of Mn(3d) and O(2p) states. In addition, the Mn(3d) and O(2p) states are hybridized over the whole valence band. States of 3d character localized on Mn sites predominate near the top of the valence band. It was found that the doping, both with the Pb and the Sr ions, increases the spin polarization by up to 48%.

1. Introduction

The (R$_{1-x}$A$_x$)MnO$_3$ mixed-valence manganites, where R is a rare-earth ion and A represents a divalent alkaline-earth ion such as Ca, Sr, Pb and Ba, have attracted considerable attention to the colossal magnetoresistance (CMR) effect as well as to the underlying physics [1]. The manganese ions are Mn^{3+}(3d^4) having three electrons in the t$_{2g}$ band and one in the e$_g$ band. When the LaMnO$_3$ compound is doped with divalent alkaline-earth cations A^{2+}(Sr, Pb) charge redistribution from Mn^{3+} to Mn^{4+} occurs. In a certain range of doping (0.2 $\leqslant x \leqslant$ 0.5) these compounds show, simultaneously, ferromagnetism and metallic behaviour below T_C. The parent RMnO$_3$ compound is an antiferromagnetic insulator. Zener explained this effect in a 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 was shown that the electron–phonon interaction also plays a very important role [3].

Previously, we have studied the tunnelling magnetoresistance effect (TMR) and electronic properties of La$_{1-x}$Sr$_x$MnO$_3$ using the break junction technique [4] and x-ray photoemission spectroscopy [5, 6]. Further improvement of TMR ratio requires manganites characterized

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by a larger spin polarization. The strong Hund coupling and the exchange energy result in a nearly 100% spin polarization of the electrons. The high value of the spin polarization P leads to a large value of the TMR described by the formula $TMR = 2P_1P_2/(1 - P_1P_2)$, where P_1 and P_2 are the spin polarizations of the two electrodes. The value of P is determined by $P = (N\uparrow - N\downarrow)/(N\uparrow + N\downarrow) \times 100\%$, where N is a density of states at the Fermi level for the spin direction marked by the arrow. The *ab initio* LMTO calculations gave polarization P of the order of 5.5% for $La_{0.75}Sr_{0.25}MnO_3$ [5] and 1.2% for $La_{0.75}Pb_{0.25}MnO_3$ [7]. Based on these results it seems interesting to study a mixed compound, i.e., the $La_{2/3}Sr_{1/6}Pb_{1/6}MnO_3$ ceramic.

In this paper, we present results of x-ray photoemission spectroscopy studies on $La_{2/3}Sr_{1/6}Pb_{1/6}MnO_3$. For a comparison, we also show the *ab initio* calculations for the hypothetical $La_{1/2}Sr_{1/4}Pb_{1/4}MnO_3$ perovskite. The results will be compared with earlier experimental and theoretical results for Sr- and Pb-doped manganites [5–7].

2. Experimental details and the method of calculation

The sample with nominal composition $La_{2/3}Sr_{1/6}Pb_{1/6}MnO_3$ has been prepared by the standard ceramic method using stoichiometric quantities of La_2O_3, $PbCO_3$, $SrCO_3$ and $MnCO_3$ at 1350 K for 6 h and annealing at 1000 K for 24 h in flowing oxygen. The room temperature x-ray diffraction patterns with Cu Kα radiation revealed a single-phase perovskite with the lattice parameters $a = 5.523$ Å and $c = 7.786$ Å.

The XPS spectra were obtained with monochromatic Al Kα radiation using a Perkin Elmer PHI 5600 ci ESCA spectrometer. The energy spectra were analysed with a hemispherical mirror analyser with an energy resolution 0.7 eV. The spectra were measured in vacuum below 6×10^{-10} Torr. A calibration of the spectra was performed according to the method of Baer *et al* [8]. Binding energies were referenced to the Fermi level ($E_F = 0$); the 4f levels of gold were found at 84 eV.

The band structure was calculated for the assumed supercell $La_2SrPbMn_4O_{12}$, which consisted of four $LaMnO_3$ formula units, where the Pb and Sr atoms replaced two of the La atoms. This approach allows differentiation of the ions but the effect of disorder due to the Pb and Sr substitutions is neglected. In the calculations we used the tight-binding linear muffin-tin orbital method in the atomic-sphere approximation (TB-LMTO ASA) [9, 10]. To compensate for errors due to the ASA, the standard [9] combined correction terms were included. The spin–orbit interactions were taken into account in the form proposed by Min and Jang [11]. The Perdew–Wang [12] potential with gradient corrections was used. The spin-polarized calculations were performed for the experimental values of the lattice constants. Computations were done for 1008 k-points in the irreducible wedge of the first Brillouin zone and the tetrahedron method [13] was used during integration over k-space. The iterations were repeated until the energy eigenvalues of the consecutive iteration steps were the same within an error of 0.01 mRyd.

3. Results and discussion

The photoemission spectrum in the valence band region at room temperature is shown in figure 1. The most prominent peaks are at about 3.3 and 6.3 eV.

To investigate the origin of the peaks we performed *ab initio* calculations. The total density of states (DOS) for the assumed $La_{1/2}Sr_{1/4}Pb_{1/4}MnO_3$ system is presented in figure 2. The following situations were considered: (figure 2(a)) Sr and Pb impurities are located in
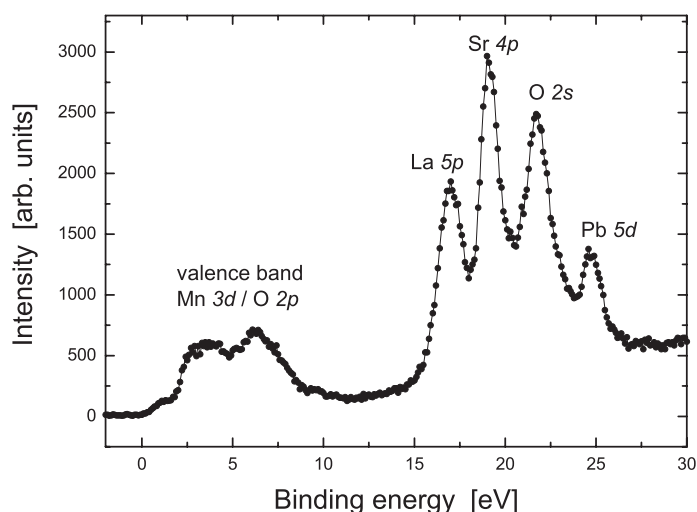
Figure 1. The experimental XPS valence band spectrum for the $La_{2/3}Sr_{1/6}Pb_{1/6}MnO_3$ perovskite system.

the same layer and (figure 2(b)) the impurities are located in different layers. Reconstruction of the electronic structure near the Fermi level changes the width of the gaps in DOS and the volume of the minority carriers' pocket. The Fermi level lies close to a gap in the spectrum of the minority DOS. Recently similar results were obtained for the manganite LaMnO₃ doped by Sr and Pb atoms [4–6]. In contrast to the Sr atom, the Pb atom introduced one additional electron to the valence band. An additional peak appears between 8 and 9 eV below the Fermi level due to the 6s electrons from the Pb atom. The widths of the energy gaps are equal to 0.224 and 0.571 eV and the spin polarizations are equal to 42.5 and 47.6% for the case of figure 2(a) and figure 2(b), respectively. For the Pb system, the gap is about 0.673 eV [7] and, for the Sr system, 1.088 eV [5]. A typical spectrum of the manganite doped by divalent ions has half or almost half metallic character, no matter if the doping ion is a donor of electrons or not [5, 7].

The XPS spectra were calculated from the partial electronic densities of states weighted with atomic photoemission cross sections for the photon energy equal to 1486.6 eV (Al Kα source). The finite experimental resolution was taken into account in the calculations by convoluting the weighted DOS with an energy-dependent Lorentzian function with a half-width $\delta = 0.7$ eV. The calculated XPS spectra are collected in figure 3. We can see that the Mn(3d) and O(2p) states provide a major contribution to the density of states in appropriate subbands of the valence band. Furthermore, there is a strong hybridization of the Mn(3d) and O(2p) states throughout the valence band.

Our data are in a good agreement with the previous electronic structure [14, 15] results. According to Sarma *et al* [15], the band structure calculations using the local spin density approximation (LSDA) well reproduce the XPS spectrum of LaMnO₃. However, the calculations in the LSDA for LaMnO₃ predict that the unoccupied Mn(3d) components make a strong peak centred at ∼1 eV. On the other hand (a band calculation using the LDA + U method, where an additional Coulomb interaction between the 3d electrons is taken into account, compared with the LSDA method) shows that unoccupied e_g up (majority spin) and t_{2g} down (minority spin) states are distributed from ∼1 to ∼3 eV and above 4 eV, respectively [16]. The peaks at 6.3 eV and 3.3 eV correspond to O(2p) states hybridized with Mn t_{2g} states.
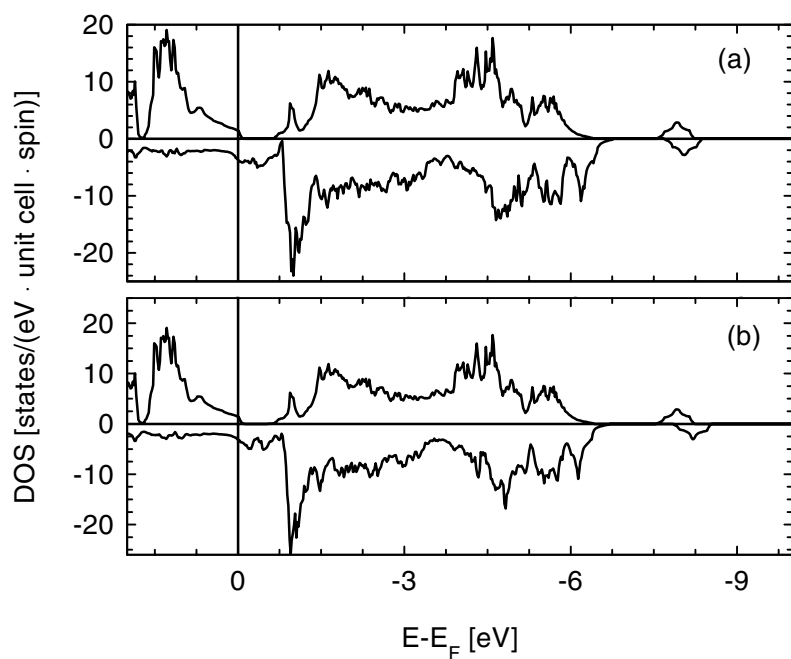
Figure 2. The total density of states (DOS) for $La_{1/2}Sr_{1/4}Pb_{1/4}MnO_3$ with (a) Sr and Pb impurities located in the same layer and (b) the impurities located in different layers.
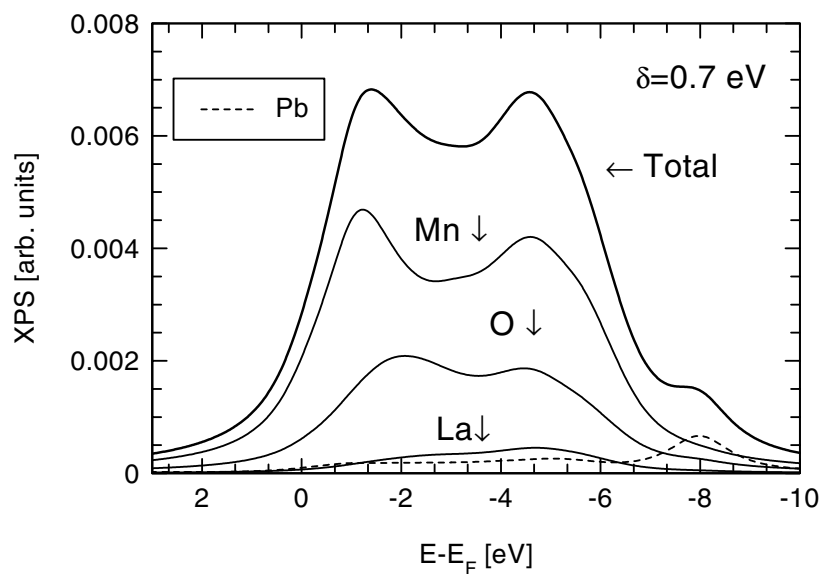

Figure 3. The calculated XPS spectra for the $La_{1/2}Sr_{1/4}Pb_{1/4}MnO_3$ perovskite system where the Pb and Sr impurities are located in the same layer in the unit cell. The differences for the cases (a) and (b) visible in figure 2 are negligible in the XPS spectrum.

The low-intensity feature close to the Fermi level that is centred at ≈ 1 eV (figure 1) is due to the emission from the e$_g$ states [14–16].
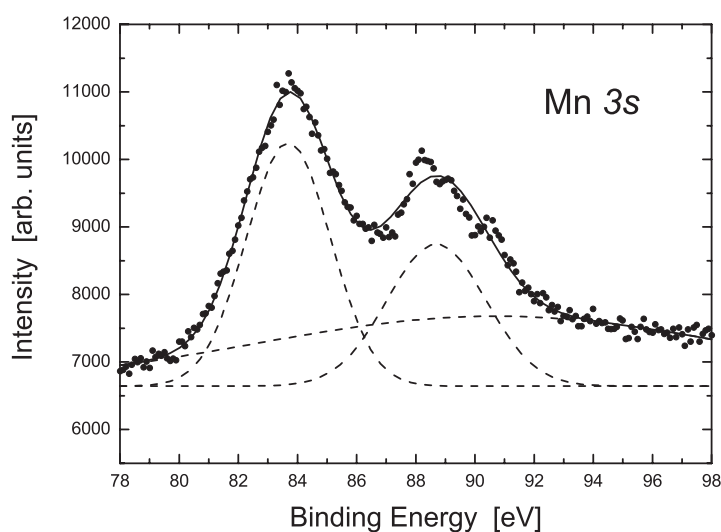

Figure 4. XPS spectra of Mn 3s of the La$_{2/3}$Sr$_{1/6}$Pb$_{1/6}$MnO$_3$ perovskite.

Previously, x-ray bremsstrahlung isochromat spectroscopy (X-BIS) spectra of a series of polycrystalline La$_{1-x}$Sr$_x$MnO$_3$ were reported by Chainani *et al* [17]. In their spectra, the peak derived from Mn 3d states was observed at $\sim$2.4 eV.

In the valence band of LaMnO$_3$ three peaks are found at $E_B = 16.8$, 19.1 and 21.5 eV. According to Park *et al* [18] they can be attributed to La(5p$_{3/2,1/2}$) and O(2s) states. The intensity of the peak located at $E = 19.1$ eV increases with Sr doping as in the spectra of La$_{1-x}$Sr$_x$MnO$_3$, and its energy position coincides with that of SrMnO$_3$. Therefore, we identify the Sr(4p) states which are located at $E = 19.2$ in the XPS VB of La$_{2/3}$Sr$_{1/6}$Pb$_{1/6}$MnO$_3$. We suggest that the energy positions of the peaks at $E = 16.9$ and 24.8 eV in the XPS VB can be attributed to La(5p) and Pb(5d) states, respectively. The O(2s) states have binding energies between 21.2 and 22 eV in all manganites [20]. A similar position of the Pb(5d) state was observed by Park *et al* [20] for La$_{0.7}$Pb$_{0.3}$MnO$_3$ using photoemission spectroscopy (PES).

The 3s exchange splitting in transition metal compounds is due to the exchange interaction between the 3s-core hole created in a XPS process and 3d electrons. The splitting magnitude of the Mn(3s) XPS spectra (ΔE) depends on the valence state of the Mn ions [5]. In figure 4 the Mn(3s) XPS spectrum of La$_{2/3}$Sr$_{1/6}$Pb$_{1/6}$MnO$_3$ is presented. The highest peak is located at 83.7 eV. In [10], it has been reported that the Mn(3s) splitting of polycrystalline La$_{1-x}$Sr$_x$MnO$_3$ monotonically decreases with x. Our spectrum shows that the value of the Mn(3s) splitting $\Delta E = 5$ eV decreases with Pb and Sr doping [5]. The large value of the splitting is consistent with high-spin configurations.

In figure 5(a), the Mn(2p) XPS spectrum of La$_{2/3}$Sr$_{1/6}$Pb$_{1/6}$MnO$_3$ is shown. The spectrum displays 2p$_{3/2}$ and 2p$_{1/2}$ spin–orbit coupling doublet peaks located at $\sim$643 and $\sim$655 eV, respectively. The Mn(2p) spectrum shows the satellite structure at $\sim$667 eV ($\sim$12 eV above the main peak). According to Saitoh *et al* [19], such structure indicates that the Mn(3d) states are strongly hybridized with the O(2p) orbitals in the ground state. The Mn(3p) spectrum also shows satellite structure $\sim$16 eV below the main peak as shown in figure 5(b). Saitoh *et al* [19]

also reported strong covalency and suggested that the gap of LaMnO$_3$ should be considered to be of the charge-transfer type.
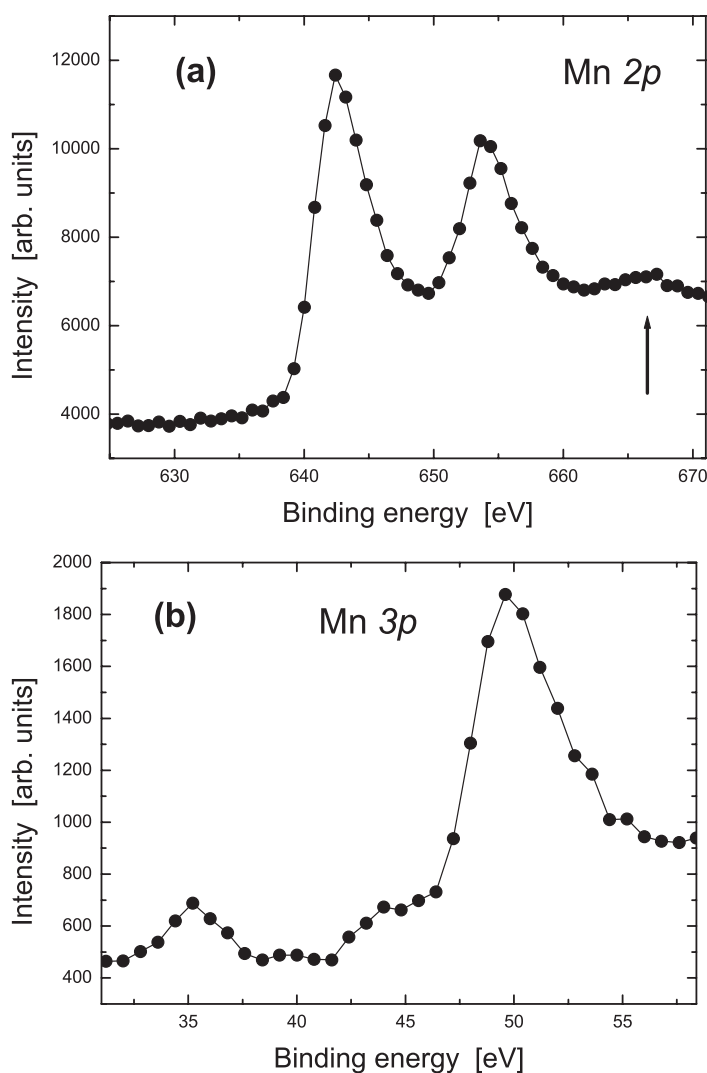

Figure 5. XPS spectra of Mn 2p (a) and Mn 3p (b) La$_{2/3}$Sr$_{1/6}$Pb$_{1/6}$MnO.

In all of the photoemission studies mentioned above, the main valence spectra have a strong increase around 1.7–2.6 eV binding energy, remain large in the region in the 2.6–6.8 eV, and fall off in the range 6–8 eV. In our calculations [5, 7], we find a strong increase at 0–2.6 eV below E_F, O(2p) states occupying the range down to a lower peak around 6 eV below E_F, and then a fall off to zero near 8 eV.

The experimental core-level spectra for La$_{0.65}$Pb$_{0.35}$MnO$_3$ [7], La$_{0.7}$Sr$_{0.3}$MnO$_3$ [5] and La$_{2/3}$Sr$_{1/6}$Pb$_{1/6}$MnO$_3$ are very similar, with the positions of the peaks remaining almost identical in all cases.

4. Conclusions

We have presented new XPS results on manganese-doped perovskites. Comparing XPS and band structure calculations, we conclude that the electronic structure of $La_{2/3}Sr_{1/6}Pb_{1/6}MnO_3$ consists mainly of hybridized Mn(3d) and O(2p) states. States of 3d character localized on Mn sites predominate near the top of the valence band. According to an LSDA analysis [14–16] of the orbital character of Mn 3d electrons, the highest subband of the top of the valence band has e_g symmetry, t_{2g} states prevail in the central part. The e_g and t_{2g} electrons give a similar contribution to the subbands at the bottom of the valence band. A large splitting $\Delta E = 5$ eV of the Mn(3s) states is consistent with high-spin configurations.

The theoretical spectrum of doped LaMnO₃ manganite has half or almost half metallic character. The La, Pb and Sr form bands mainly by s, p and d electrons and their contributions to the total spectrum are relatively small. An additional peak appears between 8 and 9 eV below the Fermi level due to 6s electrons from the Pb atom.

The partial doping of LaMnO₃ with Sr and Pb leads to an increase of the spin polarization from 5.5% for $La_{0.75}Sr_{0.25}MnO_3$ and 1.2% for $La_{0.75}Pb_{0.25}MnO_3$ up to about 48% in the case of the mixed $La_{1/2}Sr_{1/4}Pb_{1/4}MnO_3$. This value should give a large tunnelling magnetoresistance effect in the tunnelling junctions.

Acknowledgments

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