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X-RAY SPECTROSCOPY OF LANTHANUM MANGANITES: NATURE OF DOPING HOLES, CORRELATION EFFECTS, AND ORBITAL ORDERING

V. R. Galakhov,[1] M. C. Falub,[2] K. Kuepper,[3] and M. Neumann[4]

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The Mn3*s* X-ray photoelectron spectra of manganites were studied. It was shown that for the formal valence of manganese from 3+ to 3.3+, the doping holes are O2*p* in character; as the valence of manganese increases further, the Mn3*d* states acquire holes. For $La_{0.7}Sr_{0.3}MnO_3$, the Mn3*p*–3*d* resonance spectra provided information about the occupied and unoccupied Mn3*d* states, and the correlation energy $U = 6.7$ eV was determined experimentally. An analysis of X-ray dichroism on the *L* absorption spectra of three-dimensional $La_{7/8}Sr_{1/8}MnO_3$ showed that the cooperative Jahn–Teller distortion of the orthorhombic phase at 240 K was related to $(x^2 - z^2)/(y^2 - z^2)$ type orbital ordering.
Keywords: X-ray photoelectron spectra, dichroism, manganites, orbital ordering, correlation energy, doping holes.

INTRODUCTION

Doped manganese oxides with a perovskite structure (manganites) are characterized by unusual electric and magnetic properties such as giant magnetic resistance and a semimetallic ferromagnetic nature [1-4]. The coexistence of the ferromagnetic and metallic properties in manganites is generally explained based on the double exchange model [5]. This model, however, fails to give a quantitative description of the observed effects. To examine the nature of these phenomena, we should take into account the Jahn–Teller effects, the charge and orbital ordering, and correlation effects.

The double exchange model suggests that Mn^{3+} and Mn^{4+} ions coexist in doped manganites. According to calculations [6], the doping holes in $LaMnO_3$ are O2*p* in nature, whereas in $SrMnO_3$, the holes lie on both the O2*p* and Mn3*d* orbitals. This effect was confirmed by studies of the oxygen X-ray absorption spectra [7-9], which showed an increase in the near-edge part of the spectrum at increasing concentrations of the dopant holes. Because of the small value of the energy gap in manganites, the nature of the holes could not be determined from the O1*s* X-ray absorption spectra; the holes in the Mn3*d* states could also lead to this effect.

The Coulomb energy *U* is an important parameter for systems with strong electron–electron correlations. It is generally determined by calculations or semiempirically using X-ray photoelectron spectra of the core levels.

Manganites $La_{1-x}Sr_xMnO_3$ at hole concentrations $x \sim 0.125$ have Jahn–Teller distortion combined with orbital ordering, and ferromagnetism. At 270 K, the structure of $La_{7/8}Sr_{1/8}MnO_3$ undergoes a transition from the orthorhombic *O* to

[1]Institute of Metal Physics, Ural Division, Russian Academy of Sciences, Ekaterinburg, Russia; galakhov@ifmlrs.uran.ru. [2]P. Scherrer Institute, Willigen, Switzerland. [3]Rossendorf Research Center, Dresden, Germany. [4]Osnabruck University, Germany. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 49, Supplement, pp. S58-S62, 2008. Original article submitted June 26, 2008.

orthorhombic O' structure with Jahn–Teller distortions; at 183 K, a transition from paramagnetic to ferromagnetic phase takes place; and at 150 K, a transition from the orthorhombic O' to orthorhombic O'' structure with suppression of Jahn–Teller distortions takes place [10, 11]. The type of orbital ordering is difficult to establish because of considerable problems encountered in experiment.

To determine the nature of dopant holes in doped manganites in this work, we used Mn3*s* X-ray photoelectron spectra. To evaluate *U* in $La_{0.7}Sr_{0.3}MnO_3$, we used photoelectron resonance spectra. The type of orbital ordering in $La_{7/8}Sr_{1/8}MnO_3$ was determined from X-ray dichroism spectra at the Mn*L* absorption edge.

EXPERIMENTAL

Single crystal manganites were obtained by the drifting zone method in the group of Prof. Ya. M. Mukovskii (Moscow State Institute of Steel and Alloys). The Mn3*s* X-ray photoelectron spectra were measured on a PHI 5600 ci photoelectron spectrometer using monochromated AlK_α radiation. To obtain a clean surface, the samples were cut in vacuum. The photoelectron resonance spectra of the $La_{0.7}Sr_{0.3}MnO_3$ single crystal were recorded on a Swiss Light Source ring at 40 K. The spectra were measured at normal emission. To determine the type of orbital ordering, the Mn*L* X-ray absorption spectra were measured for $La_{7/8}Sr_{1/8}MnO_3$ at different orientations of the vector of the electric component of polarized X-radiation relative to the *c* axis of the crystal; the spectra were recorded with an ELETTRA source of synchrotron radiation (Triest, Italy).

DETERMINATION OF THE NATURE OF DOPING HOLES FROM Mn3*s* X-RAY PHOTOELECTRON SPECTRA

According to the van Vleck theorem, the splitting of the spectra of the 3*s* levels is proportional to $(2S + 1)$, where *S* is the local spin of the 3*d* electrons in the ground state. Although the energy splitting of the spectrum is also affected by the charge transfer effect, this is significant for nickel and copper oxides but is not for manganese oxides.

The splitting of the Mn3*s* level for $LiMnO_2$, which is a trivalent manganese reference, is 5.4±0.1 eV. For $SrMnO_3$ (Mn^{4+} ions), the splitting is 4.3±0.15 eV. The presence of two types of ions, Mn^{3+} and Mn^{4+}, should lead either to two doublets from manganese ions with different valences or to a spectrum with a splitting intermediate between the values for tri- and tetravalent ions. However, as follows from the data for a wide class of manganites [12] (Fig. 1), in the region of formal valence from 3.0+ to 3.3+, the splitting of the Mn3*s* level did not change. This can be attributed to the preservation of the electronic configuration of 3*d* ions and the formation of holes in the O2*p* states. Further increase in the formal valence to Mn^{4+}, however, is accompanied by a decrease in the splitting and hence by the formation of holes in the Mn3*d* states. Thus, the spectra of doped manganites for the region from 3.0+ to 3.3+ of the formal valence of manganese are determined by the sum of the d^4 and d^4L^{-1} electronic configurations (here, L^{-1} are the holes in the O2*p* states).

DETERMINATION OF THE CORRELATION PARAMETER *U* FOR $La_{0.7}Sr_{0.3}MnO_3$ FROM PHOTOELECTRON RESONANCE SPECTRA

Figure 2 shows the valence band spectra of the $La_{0.7}Sr_{0.3}MnO_3$ single crystal in the ferromagnetic metallic phase at 40 K measured at excitation energies from 45 eV to 70 eV [13]. The insert shows the X-ray photoelectron spectrum of the same sample measured at room temperature. In manganites, the valence band spectra are determined by hybridization of the Mn3*d* and O2*p* states. The relative Mn3*d*/O2*p* ionization cross sections increase with *h*ν; the Mn3*d* states dominate in the photoelectron spectrum, while the O2*p* states become more pronounced at low photon energies. Peak *A* is associated with the Mn3*d*(e_g) states and is also observed in the X-ray photoelectron spectrum. The spectral intensity of peak *B* is 2.1 eV below the Fermi level and changes strongly with the excitation energy; the shoulder in the spectrum excited with the photon energy

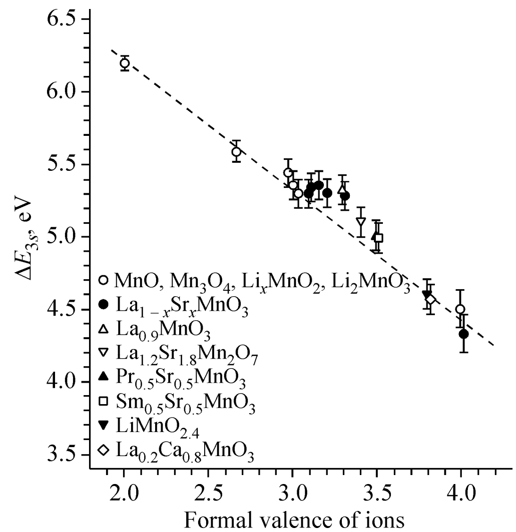

Fig. 1. Mn3s splitting as a function of the formal valence of manganese ions in manganites.

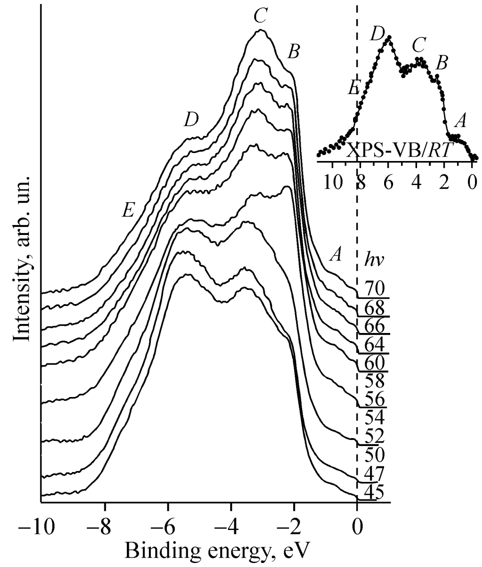

Fig. 2. Valence band spectra of the $La_{0.7}Sr_{0.3}MnO_3$ single crystal measured at 40 K at excitation energies $h\nu$ from 45 to 70 eV. Insert: X-ray photoelectron spectrum (XPS, AlK_α radiation, $h\nu = 1486.6$ eV) of the same sample.

$h\nu = 45$ eV developed into an acute peak with the maximum intensity at $h\nu = 56$ eV. For the B states, there is no dispersion; this is indicative of their highly localized character and hence we can ascribe peak B to the occupied $t_{2g\uparrow}$ states.

The difference spectra obtained by subtracting the spectrum measured at the excitation energy $h\nu = 49.0$ eV from the spectra measured at higher photon energies (Fig. 3) reflect the valence band, which is strongly Mn3d in character. The acute resonance peak B at 2.1 eV increases with energy, reaching maximum at 56 eV; then its intensity decreases slowly, as shown in the insert to Fig. 3. The resonance maximum Mn3p–3d corresponds to the process in which the occupied $t_{2g\uparrow}$ and unoccupied $t_{2g\downarrow}$ states are involved. The energy position of the $t_{2g\downarrow}$ states relative to the Fermi level is recorded as the difference between the energy of photons corresponding to the start of the resonance "window" (51.4 eV) and the resonance energy (56.0 eV); the difference is estimated at 4.6 eV. Given the binding energy of Mn3d($t_{2g\uparrow}$) electrons, we evaluate the correlation energy U from the difference $E_B(t_{2g\uparrow}) - E_B(t_{2g\downarrow}) = 6.7$ eV. Note that for the related $La_{2/3}Ca_{1/3}MnO_3$, the Coulomb interaction was approximately the same, $U = 6.4$ eV [14] when determined from the combination of the Mn2p X-ray photoelectron and Mn$L_{2,3}$–$M_{2,3}M_{4,5}$ Auger electronic spectra.

DETERMINATION OF THE TYPE OF ORBITAL ORDERING IN $La_{7/8}Sr_{1/8}MnO_3$ BY LINEAR DICHROISM AT THE MnL ABSORPTION EDGE

The orbital ordering [15, 16] was studied by resonance X-ray scattering near the MnK edge. A new type of orbital ordering was suggested [15], namely, hybridization of the $(x^2 - z^2)/(y^2 - z^2)$ and $(3x^2 - r^2)/(3y^2 - r^2)$ orbitals at low temperatures (below 145 K) for the ferromagnetic phase; however, the authors did not find any proof of the orbital ordering in the distorted Jahn–Teller phase. On the other hand, it was found [16] that the cooperatively distorted Jahn–Teller phase (27-170 K) showed $(3x^2 - r^2)/(3y^2 - r^2)$ type orbital ordering.

However, X-ray resonance scattering near the MnK edge (Mn1$s \rightarrow 4p$ transition) only indirectly reflects the ordering of d orbitals. To determine the type of orbital ordering, we measured MnL X-ray absorption in $La_{7/8}Sr_{1/8}MnO_3$

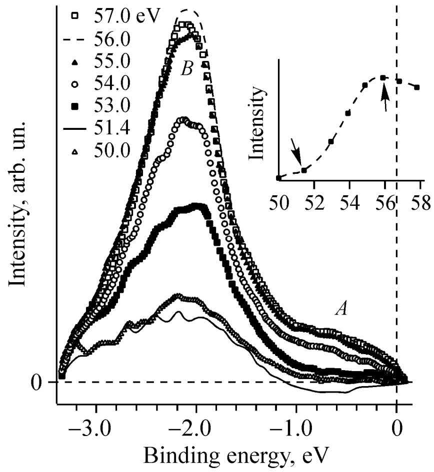

Fig. 3. Difference spectra obtained by subtracting the spectrum ($h\nu = 49.0$ eV) from the spectra measured at higher photon energies. Insert: dependence of the intensity of peak *B* on $h\nu$. The maximum of resonance at $h\nu = 56.0$ eV.

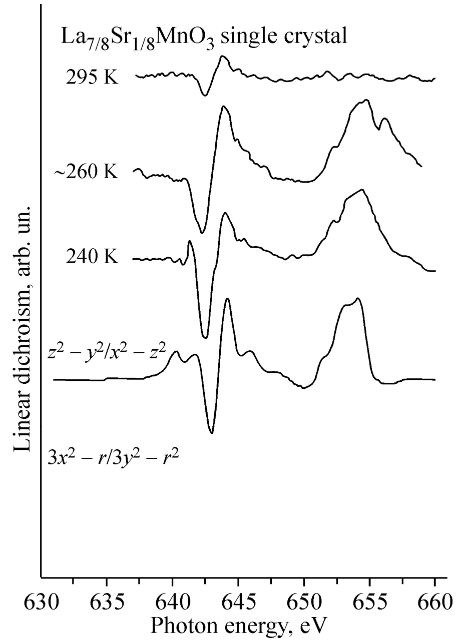

Fig. 4. X-ray dichroic signal obtained from the Mn*L* absorption spectra of the $La_{7/8}Sr_{1/8}MnO_3$ single crystal at different temperatures compared with the calculated data for the MnO_6 cluster [18].

at different orientations of the vector of the electric component of polarized X-radiation relative to the *c* axis of the crystal using an ELETTRA source of synchrotron radiation. Figure 4 shows the Mn*L* X-ray linear dichroism spectra at different temperatures of $La_{7/8}Sr_{1/8}MnO_3$ [17], obtained from the difference of the absorption spectra measured at two crystal orientations. The experimental spectra were compared with the data of cluster calculations [18]. Our data unambiguously show that the cooperative Jahn–Teller distortion of the orthorhombic phase at 240 K is mainly related to orbital ordering of $(x^2 - z^2)/(y^2 - z^2)$ type.

CONCLUSIONS

The Mn3*s* X-ray photoelectron spectra showed that in the range from 3.0+ to 3.3+ of formal valence, the electronic configuration of 3*d* ions was preserved, and the holes were O2*p* in character. As the formal valence increased further, holes formed in the Mn3*d* states.

The correlation energy *U* for $La_{0.7}Sr_{0.3}MnO_3$, obtained with the aid of the resonance photoelectron spectra and the spectra of the constant initial state, is 6.7 eV.

For the three-dimensional single crystal of $La_{7/8}Sr_{1/8}MnO_3$, X-ray dichroism measurements at the Mn*L* absorption edge showed that the orbital ordering for the orthorhombic phase at 240 K occurred according to the $(x^2 - z^2)/(y^2 - z^2)$ type.

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