PHYSICAL REVIEW B, VOLUME 65, 113102

Mn 3*s* exchange splitting in mixed-valence manganites

V. R. Galakhov
Institute of Metal Physics, Russian Academy of Sciences, Ural Division, 620219 Yekaterinburg GSP-170, Russia

M. Demeter, S. Bartkowski, and M. Neumann
University of Osnabrück - Fachbereich Physik, D-49069 Osnabrück, Germany

N. A. Ovechkina and E. Z. Kurmaev
Institute of Metal Physics, Russian Academy of Sciences, Ural Division, 620219 Yekaterinburg GSP-170, Russia

N. I. Lobachevskaya
Institute of Chemistry of Solids, Russian Academy of Sciences, Ural Division, 620219 Yekaterinburg GSP-145, Russia

Ya. M. Mukovskii
Moscow State Steel and Alloys Institute, 117936 Moscow, Russia

J. Mitchell
Argonne National Laboratory, 9700 South Gas Avenue, Argonne, Illinois 60439

D. L. Ederer
Department of Physics, Tulane University, New Orleans, Louisiana 70118

(Received 27 July 2001; published 12 February 2002)

We present Mn 3*s* x-ray photoelectron spectra of manganese oxides with the Mn formal valency from 2+ to 4+. We found that the Sr^{2+} doping or cation deficiency in manganites do not change the Mn 3*s* splitting in manganites with the Mn formal valency from 3.0+ to 3.3+. We suggest that doping holes are localized in O 2*p* states.

DOI: 10.1103/PhysRevB.65.113102 PACS number(s): 75.30.Mb, 71.70.Gm, 79.60.−i

I. INTRODUCTION

Mixed-valence manganites have been studied for almost 50 years.[1] An interest in the manganese perovskite oxides of $R_{1-x}A_xMnO_3$ (where *R* is a rare earth element and *A* is Ca, Sr, Ba, etc.) has increased since the discovery of the phenomena of colossal magnetoresistance.[2] They exhibit a great variety of magnetic and transport properties that strongly depend on the stoichiometry and the structure of the materials.

The coexistence of ferromagnetism and metallic behavior in manganites $R_{1-x}A_xMnO_3$ is explained within the framework of the double-exchange model.[3] This mechanism implicitly assumes Mott-Hubbard-type insulators requiring Mn^{3+}/Mn^{4+} mixtures. It contradicts the fact that $RMnO_3$ is a charge-transfer insulator.[4]

According to the calculations of Saitoh *et al.*,[4] the doping holes in $LaMnO_3$ have mainly oxygen 2*p* character, and the doping electrons in $SrMnO_3$ are of Mn 3*d* as well as of O 2*p* character. Therefore, doping of $LaMnO_3$ with Sr^{2+} ions should lead to the appearance of holes in the O 2*p* band. The O 2*p* character of the doping holes in doped manganites was demonstrated by a direct method, the O 1*s* x-ray absorption. It was observed that the peak at the Fermi level corresponding to nonoccupied states at the oxygen sublattice grows with the concentration of the doping element, or along with the oxygen nonstoichiometry.[5]

One can probe the valence state of manganese ions in manganites by studying the Mn 3*s* x-ray photoelectron spectra. The spectral splitting of the 3*s* core-level x-ray photoemission spectra in transition metals and their compounds originates from the exchange coupling between the 3*s* hole and the 3*d* electrons. The magnitude of the splitting is proportional to $(2S+1)$, where *S* is the local spin of the 3*d* electrons in the ground state.

For 3*d* metal compounds, the calculated 3*s* splitting is more than two times larger than the observed one. It indicates that the observed 3*s* splitting is not likely to be due to the spin exchange only. This fact was explained by the intrashell correlation effects between $3s^13p^63d^n$ and $3s^23p^43d^{n+1}$ configurations.[6,7]

In addition to the exchange interaction between the 3*d* and 3*s* states, a charge-transfer process must be taken into account. For Cu and Ni oxides, the charge-transfer effect dominates the multiplet effect in the 3*s* spectra. As the number of the *d* electrons decreases, the role of charge-transfer processes becomes less important.[8]

The Mn 3*s* spectra of manganites $La_{1-x}Sr_xMnO_3$ with $x=0.0$, 0.1, 0.3, and 0.9 were measured by Saitoh *et al.*[4] According to these results, the magnitude of the Mn 3*s* splitting increases with decreasing *x*. However, the spectra in this work were measured with low energy resolution and poor statistics.

In this paper, we present experimental data on the Mn 3*s* splitting in manganites. We have found that for manganites with the Mn formal valency between 3.0+ and 3.3+, the Mn 3*s* splitting remains constant. We conclude that in manganites with such formal valency, the doping holes are localized in the O 2*p* states.

II. EXPERIMENTAL CONDITIONS

Two series of $La_{1-x}Sr_xMnO_3$ were prepared. The samples of the first series were ceramics with $x=0$, 0.1, 0.15, 0.2. The samples of the second series were single crystals with $x=0.1$, 0.2, and 0.3. Polycrystalline and single-crystal samples of $La_{1-x}Sr_xMnO_3$ were prepared by the standard solid-state reaction and the flux method, respectively. The x-ray phase analysis has been done for the specimens.

For MnO, $La_{0.9}MnO_3$, $La_{1.2}Sr_{1.8}Mn_2O_7$, $Pr_{0.5}Sr_{0.5}MnO_3$, single crystals were used.[9] The samples Li_xMnO_2 ($x=0.97$, 1.00, 1.03), Li_2MnO_3, $LiMnO_{2.4}$ were prepared using the ceramic technology.[10,11] The samples of $La_{0.2}Ca_{0.8}MnO_3$ and $Sm_{0.5}Sr_{0.5}MnO_3$ were ceramics as well.

The oxygen-deficient manganite $LaMnO_{3-\delta}$ was produced by reducing of $LaMnO_3$ at an oxygen pressure of about 0.10 Pa at 1300–1350 °C. Whereas $LaMnO_3$ prepared in air or in oxygen has a rhombohedral structure, the sample with the deficiency of oxygen shows the x-ray diffraction peaks typical for the orthorhombic structure.

The experiments were performed using a PHI 5600 ci multitechnique system. The Al $K\alpha$ radiation was monochromatized by a double-focusing monochromator. The energy resolution as determined at the Fermi level of an Au foil was 0.3–0.4 eV. All samples were cleaved in vacuum at a base pressure of 5×10^{-10} Torr.

III. RESULTS AND DISCUSSION

The Mn 3*s* spectra of several manganese oxides are shown in Fig. 1. The spectra are arranged in order of the increasing Mn formal valence. The spectrum of MnO (d^5 ground-state configuration) shows the largest splitting among all manganese oxides. On going from MnO to $LiMnO_2$ (d^4 ground-state configuration), the separation between the two main peaks decreases.

The Mn 3*s* x-ray photoemission spectrum of the oxygen-deficient manganite $LaMnO_{3-\delta}$ shows a splitting larger than in the spectrum of "pure" $LaMnO_3$. The defects in $LaMnO_{3-\delta}$ can be considered as clusters of oxygen vacancies, each bound with two Mn^{2+} ions.[12] The increase of the Mn 3*s* splitting is explained by impurities of Mn^{2+} ions ($3d^5$ configuration).

The doping with Sr should lead to the increase of the Mn^{4+} content such as $La^{3+}_{1-x}Sr^{2+}_{x}Mn^{3+}_{1-x}Mn^{4+}_{x}O_3$. Likewise, the cation vacancies on the La sites are accommodated by the Mn^{4+} ions: $La^{3+}_{1-x}\square_x Mn^{3+}_{1-3x}Mn^{4+}_{3x}O_3$ (where $\square$ is a vacancy). It must be followed by a decrease of the Mn 3*s* splitting. What actually happens is that the splitting does not change with the increase in the formal valency of the manganese ions up to a valency of 3.3–3.4. A mistake in determination of the dopant's concentration can be excluded since measurements done on both single crystals and tablets show the same results. From $La_{1.2}Sr_{1.8}Mn_2O_7$ on (the formal Mn valency is 3.4+), the splitting decreases. The $SrMnO_3$ oxide with Mn^{4+} ions exhibits the minimal splitting among the manganites studied in the present work (about 4.2 eV).

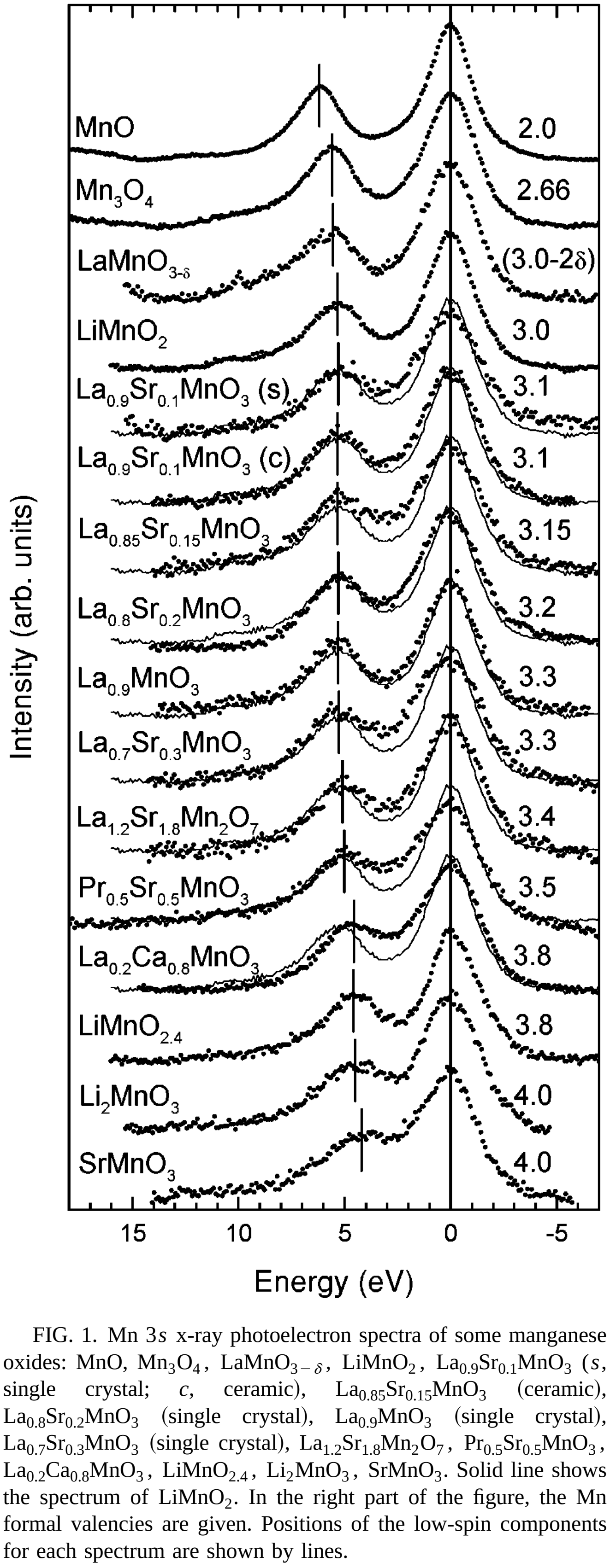

FIG. 1. Mn 3*s* x-ray photoelectron spectra of some manganese oxides: MnO, Mn_3O_4, $LaMnO_{3-\delta}$, $LiMnO_2$, $La_{0.9}Sr_{0.1}MnO_3$ (*s*, single crystal; *c*, ceramic), $La_{0.85}Sr_{0.15}MnO_3$ (ceramic), $La_{0.8}Sr_{0.2}MnO_3$ (single crystal), $La_{0.9}MnO_3$ (single crystal), $La_{0.7}Sr_{0.3}MnO_3$ (single crystal), $La_{1.2}Sr_{1.8}Mn_2O_7$, $Pr_{0.5}Sr_{0.5}MnO_3$, $La_{0.2}Ca_{0.8}MnO_3$, $LiMnO_{2.4}$, Li_2MnO_3, $SrMnO_3$. Solid line shows the spectrum of $LiMnO_2$. In the right part of the figure, the Mn formal valencies are given. Positions of the low-spin components for each spectrum are shown by lines.

In Fig. 2 the Mn 3*s* splitting of manganites is plotted as a function of the formal valence of the Mn ions. The magnitude of the Mn 3*s* splitting decreases monotonically with the increase of the formal valency of the manganese ions (except the area from Mn^{3+} to $Mn^{3.3+}$). We did not include in this

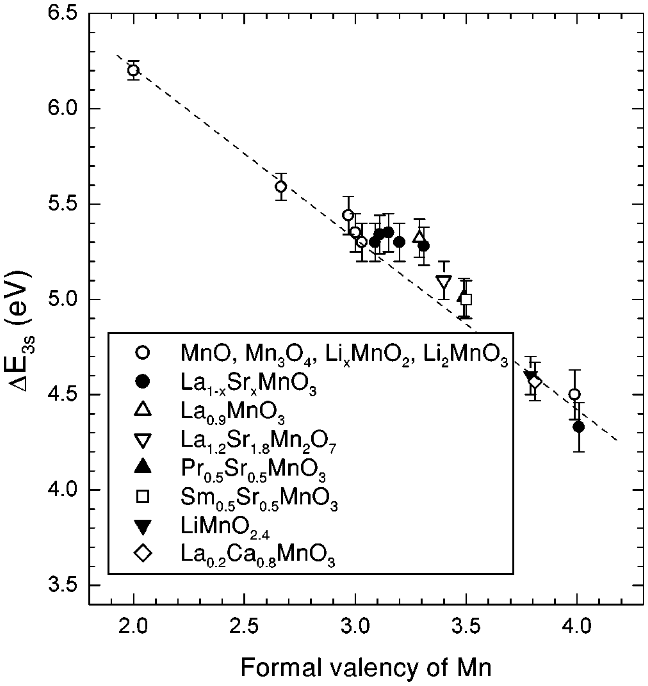

FIG. 2. Mn 3s splitting as function of the formal valence of Mn ions.

graph the magnitude of the splitting for $LaMnO_{3-\delta}$ since the concentration of oxygen in this compound is unknown. We can assume that the magnitude of the oxygen deficiency δ in this oxide is between 0.02 and 0.05. This value is estimated from the comparison of the sample-preparation conditions of our work and that of Kuo *et al.*,[13] where the oxygen content in $LaMnO_{3\pm\delta}$ has been measured.

It is known that for MnF_2 and FeF_2, 3s splittings are determined mainly by the exchange interaction between the 3s hole and the localized 3d electrons in the ground state.[14] For manganese oxides, the charge-transfer satellites become important, and the peaks in the 3s spectra lose their purity as spin-split states. Mn 3s splitting decreases in the row MnF_2-MnO-$MnCl_2$-$MnBr_2$, i.e., with the increase in the degree of covalency.[14] The doping with Sr in $La_{1-x}Sr_x$ MnO_3 leads to an increase of the degree of covalency and thus a decrease in the Mn 3s splitting would be expected.

The increase of the degree of Mn-O covalency as well as the increase of the formal valence of Mn ions should lead to reduced Mn 3s splitting. Actually the Mn 3s splitting is constant for the formal-valency manganese ions in the range from 3.0+ to 3.3+.

The main line of the Mn 3s spectrum of MnO reflects mainly $3s^13d^5$ final-state configuration. The main lines of the Mn 3s spectra of $LiMnO_2$ and Li_2MnO_3 should reveal $3s^13d^4$ and $3s^13d^3$ final-state configurations, respectively. For $LaMnO_3$ the Mn 3s main line has the same nature as for $LiMnO_2$. The constant Mn 3s splitting in the concentration region from $x=0$ to $x\approx0.3$ means that the electronic configuration of doped manganites with $x<0.3$ is not changed. One can suggest that the doping holes are localized in the O 2p states, and the ground-state wave function should be written as the sum of the d^4 and $d^4\underline{L}$ configurations, where $\underline{L}$ denotes holes in the oxygen 2p states.

There are following experimental data showing the oxygen nature of holes in manganites. The first is a direct observation of the O 2p holes in the O 1s x-ray absorption spectroscopy measurements.[5,15] Second, Tyson *et al.*[16] in their studies of the Mn $K\beta$ x-ray emission spectra of $La_{1-x}Ca_xMnO_3$ have found that the Mn $K\beta$ emission results are consistent with a mixed-valence Mn^{3+}/Mn^{4+} mixing except for the $0<x<0.3$ range, where the Mn valence is constant. Our measurements of Mn 3s splitting behavior is a further proof of the O 2p nature of doping holes in manganites.

Next we discuss why the spectra of the doped manganites have large width. For all Mn 3s spectra of $La_{1-x}Sr_xMnO_3$, an increase of the spectral width with doping can be seen. This effect is typical for both ceramics and single crystals. From the above discussion it is clear that the Mn 3s spectra in mixed-valence manganites should be presented as a sum of two configurations. If the doping holes are localized in the manganese ions, each line is a sum of mainly d^4 and d^3 configurations. These configurations have different splittings and different energies. Therefore, it changes the separation between the peaks in Mn 3s spectra.

In the case when the doping holes are localized on the oxygen sites, the spectrum is mainly represented by the sum of the d^4 and $d^4\underline{L}$ configurations. These configurations have different corresponding energies, but the splitting is the same. As a result, the spectral width increases, but the spectral splitting remains unaffected.

IV. CONCLUSION

In conclusion, we have reported Mn 3s x-ray emission spectra in mixed-valence manganites. We have shown that the change in the Mn formal valency from 3+ to 3.3+ is not accompanied by any decrease in the Mn 3s splitting. We propose that this effect can be explained by the appearance of holes in the O 2p states ($d^4\underline{L}$ ground-state configuration).

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (Grants Nos. 99-02-16280, 99-03-32503, and 00-15-96575) and by the National Science Foundation (Grant No. DMR-9801804).

---

[1] J. Volger, Physica (Amsterdam) **20**, 49 (1954).

[2] S. Jin, T.H. Tiffel, M. McCormack, R.A. Fastnacht, R. Ramesh, and L.H. Chen, Science **264**, 413 (1994).

[3] C. Zener, Phys. Rev. **82**, 403 (1951).

[4] T. Saitoh, A.E. Bocquet, T. Mizokawa, H. Namatame, A. Fujimori, M. Abbate, Y. Takeda, and M. Takano, Phys. Rev. B **51**, 13 942 (1995).

[5] H.L. Ju, H.-C. Sohn, and K.M. Krishnan, Phys. Rev. Lett. **79**,

3230 (1997).

[6] P.S. Bagus, A.J. Freeman, and F. Sasaki, Phys. Rev. Lett. **30**, 850 (1973).

[7] E.-K. Viinikka and Y. Öhrn, Phys. Rev. B **11**, 4168 (1975).

[8] K. Okada and A. Kotani, Tech. Rep. ISSP, Ser. A No. 2541 (1992); J. Phys. Soc. Jpn. **61**, 4619 (1992); K. Okada, A. Kotani, and B. Thole, J. Electron Spectrosc. Relat. Phenom. **58**, 325 (1992).

[9] E.Z. Kurmaev, M.A. Korotin, V.R. Galakhov, L.D. Finkelstein, E.I. Zabolotzky, N.N. Efremova, N.I. Lobachevskaya, S. Stadler, D.L. Ederer, T.A. Callcott, L. Zhou, A. Moewes, S. Bartkowski, M. Neumann, J. Matsuno, T. Mizokawa, A. Fujimori, and J. Mitchell, Phys. Rev. B **59**, 12 799 (1999).

[10] D.G. Kellerman, V.S. Gorshkov, V.G. Zubkov, V.A. Perelyaev, V.R. Galakhov, E.Z. Kurmaev, St. Uhlenbrock, and M. Neumann, Russ. J. Inorg. Chem. **42**, 1012 (1997).

[11] V.R. Galakhov, M.A. Korotin, N.A. Ovechkina, E.Z. Kurmaev, V.S. Gorshkov, D.G. Kellerman, S. Bartkowski, and M. Neumann, Eur. Phys. J. B **14**, 281 (2000).

[12] J.A.M. Van Roosmalen and E.H.P. Cordfunke, J. Solid State Chem. **93**, 212 (1991).

[13] J.H. Kuo, H. Andersen, and D. Sparlin, J. Solid State Chem. **83**, 52 (1989).

[14] S.-J. Oh, G.H. Gweon, and J.-G. Park, Phys. Rev. Lett. **68**, 2850 (1992); G.H. Gweon, J.-G. Park, and S.-J. Oh, Phys. Rev. B **48**, 7825 (1993).

[15] J.-H. Park, C.T. Chen, S.-W. Cheong, W. Bao, G. Meigs, V. Chakarian, and Y.U. Idzerda, Phys. Rev. Lett. **76**, 4215 (1996).

[16] T.A. Tyson, Q. Qian, C.-C. Kao, J.-P. Rueff, F.M.F. de Groot, M. Croft, S.-W. Cheong, M. Greenblatt, and M.A. Subramanian, Phys. Rev. B **60**, 4665 (1999).