Electronic structure of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Cu$_x$O$_3$ (0.0$\leq$$x$$\leq$0.30)
Electronic structure of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Cu$_x$O$_3$ ($0.0 \leq x \leq 0.30$)

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Abstract

We have investigated the electronic structure of Cu-substituted La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) by x-ray photoelectron spectroscopy and using density functional theory within local spin-density approximations (LSDA) and LSDA + $U$. We find that there is a coexistence of mixed-valent Cu ions, Cu$^{3+}$ with Cu$^{2+}$ dominant, in all Cu-substituted LSMO samples. From a deconvolution of the XPS spectra of Cu-2p$^{3/2}$, we determined the ratios of Cu$^{2+}$/Cu$^{3+}$ and Mn$^{3+}$/Mn$^{4+}$, and in turn calculated the change in the tolerance factors of Cu-substituted LSMO. Valence-band photoelectron spectra show that the density of states at the Fermi level is made up mainly of the O-2p and Mn-3d states with a small contribution near $E_F$ from the Cu-3d states. We find that LSDA + $U$ calculations for La$_{1/2}$Sr$_{1/2}$Mn$_{1-x}$Cu$_x$O$_3$ describe the half-metallicity and ground state ferromagnetic ordering with no evidence of antiferromagnetism for all systems consistent with experimental neutron diffraction data. Two electron transport channels of the major Mn–O–Mn and the minor Cu–O–Cu chains are found. This suggests that the electronic transport behavior of Cu-substituted LSMO systems may be explained by a combination of two different transport mechanisms: (i) a $\sigma$pd hybridization between the eg states in a majority spin-up Mn-d channel with O-2p orbitals in the Mn–O–Mn chain and (ii) a $\sigma$pd hybridization between the eg states in a dominant minority spin-down Cu-d channel with O-2p orbitals in the Cu–O–Cu chain. We also find that the half-metallicity of the compounds is lost upon Cu-substitution with a resulting anisotropic electronic transport of the Cu-pair electrons in the basal plane and along the c axis.

1. Introduction

The ABO$_3$ (A = trivalent rare earth atom, B = 3d transitional metal) perovskites have attracted considerable attention because of their anomalous magnetic and transport properties such as colossal magnetoresistance (CMR) and metal–insulator transitions (MIT). The La$_{1-x}$Sr$_x$MnO$_3$ perovskites are canonical ABO$_3$-type CMR materials. It has been reported that double-exchange (DE) interactions together with Jahn–Teller (JT) distortions in the MnO$_6$ octahedron may be responsible for the large MR effects [1–4]. Because the mixed-valent Mn ion is the center of the DE interaction, the role of the Mn atom and its local environment have become the focus of much of the research on manganese perovskites. To investigate the CMR associated with the lattice deformation and charge ordering of the crucial Mn–O–Mn network, many early studies were carried out by substitution of the A-site with divalent atoms (Ca, Sr, Ba, etc) [5–7]. It has also been shown that substitution of the Mn (B-site) by other atoms dramatically affects the magnetic and transport properties of manganese perovskites. The B-site modification directly affects the Mn$^{3+}$/Mn$^{4+}$ ratio and the electron carrier density [8–11].

Previously, we have studied the structural, magnetic and transport properties of La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Cu$_x$O$_3$ ($0 \leq x \leq 0.20$) using x-ray diffraction, neutron diffraction, magnetization and resistivity measurements. The changes in the lattice...
parameters obtained from neutron diffraction studies indicated the existence of mixed-valent Cu ions, Cu$^{2+}$ and Cu$^{3+}$ in this system [11]. In this paper, we present the results of an x-ray photoelectron spectroscopy (XPS) study on the core-level and valence-band photoelectron spectroscopy (PES) of La$_{0.7}$Sr$_{0.3}$Mn$_{1−x}$Cu$_x$O$_3$ ($0 \leq x \leq 0.30$). To investigate the origin of the XPS peaks and the detailed band structure of p–d hybridization between Mn–O–Mn and Cu–O–Cu channels, ab initio electronic band-structure calculations were performed for La$_{1/2}$Sr$_{1/2}$MnO$_3$ and a hypothetical La$_{1/2}$Sr$_{1/2}$Mn$_{1−x}$Cu$_x$O$_3$ ($x = 1/6, 1/3$) system. These studies provide further evidence for the existence of mixed-valent Cu ions and the effect of Cu–O–Cu percolation channels on the electronic transport properties.

2. Experimental details

Samples of La$_{0.7}$Sr$_{0.3}$Mn$_{1−x}$Cu$_x$O$_3$, $0 \leq x \leq 0.30$, were prepared using the conventional solid state reaction method. Detailed sample preparation and physical property measurements, such as x-ray diffraction, neutron diffraction (ND), saturation magnetization and resistivity measurements, are described in a previous study [11].

The spectra of core-level x-ray photoelectron spectroscopy (XPS) and valence-band photoelectron spectroscopy (PES) of the samples were obtained with monochromatic Al Kα radiation ($hν = 1496.6$ eV) using an AXIS 165 spectrometer. The energy spectra were analyzed with a hemispherical mirror analyzer having an energy resolution of 0.5 eV. The spectra were measured at an accelerating voltage of 15 kV and an output power of 225 W below $7 \times 10^{-10}$ Torr.

The LSDA + U calculations were performed for La$_{1/2}$Sr$_{1/2}$MnO$_3$ and a hypothetical supercell of La$_{1/2}$Sr$_{1/2}$Mn$_{1−x}$Cu$_x$O$_3$ ($x = 1/6, 1/3$) in the framework of the tight-binding linearized muffin-tin orbital method in the atomic-sphere approximation (TB–LMTO–ASA) [12–14]. The crystal parameters of the parent compound, La$_{1/2}$Sr$_{1/2}$MnO$_3$, were taken from previous studies by Spooren et al [15]. In the case of La$_{1/2}$Sr$_{1/2}$Mn$_{1−x}$Cu$_x$O$_3$ ($x = 1/6, 1/3$), the same lattice parameters and atomic positions for La$_{1/2}$Sr$_{1/2}$MnO$_3$ were used. Based on a previous study [11] of Cu-substituted LSMO, it was assumed that the structural parameters were nearly equal and do not produce any significant change in the band structure of the hypothetical structure. For the LSDA + U calculations, values of the Coulomb and exchange parameters $U = 7$ eV and $J = 0.79$ eV were taken from the studies of Medvedeva et al [16]. The von Barth–Heidin–Janak local exchange–correlation potential was used [17]. The self-consistent convergence criterion of total energy is $10^{-4}$ eV and the charge density is $1.0 \times 10^{-6}$/unit cell.

3. Results and discussion

Table 1 presents the structural information of Cu-substituted LSMO, with $0 \leq x \leq 0.30$, obtained from ND measurements at RT and 10 K and Rietveld refinements [11]. The $R3c$ rhombohedral space-group was used to fit the crystal structure and the $P1$ group was used to fit the magnetic structure. The lattice parameters $a$ and $c$ decrease only slightly with increasing Cu content at RT, but at $T = 10$ K the lattice parameters remain almost constant with increasing Cu content.

Tolerance factors were calculated to examine the stability and strains of these systems. The tolerance factor $τ$ is given by the formula: $τ = (r_{(La, Sr)} + r_0)/[(r_{(Mn, Cu)} + r_0)\sqrt{2}]$, where $r_{(La, Sr)}$, $r_{(Mn, Cu)}$ and $r_0$ are the average radii of the A-sites, B-sites and oxygen, respectively. The B-site (six-coordinated) ionic radius of Cu$^{2+}$ (0.73 Å) is larger than Mn$^{3+}$ (Mn$^{4+}$) and the ionic radius of Cu$^{2+}$ (0.54 Å) is close to that of Mn$^{3+}$ (0.53 Å) and smaller than the radius of the high spin state of Mn$^{3+}$ (0.645 Å) [18]. If Cu$^{3+}$ only exists and replaces Mn$^{3+}$, the tolerance factor increases from 0.979 ($x = 0.0$) to 0.989 ($x = 0.30$), $Δτ > 1\%$, which means that the lattice parameters decrease linearly. If Cu$^{2+}$ ions replace Mn$^{3+}$ (or Mn$^{4+}$), the tolerance factor decreases and the lattice parameters increase. Therefore, if the value of $τ$ is between the above two ranges, the change of lattice parameters depends on which ionic state of Cu is dominant and to what extent it changes the Mn$^{3+}$/Mn$^{4+}$ ratio under the constraint of charge balance. Considering the coexistence of Cu$^{2+}$ and

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<th>$c$ (Å)</th>
<th>Volume (Å$^3$)</th>
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$T = 10$ K

Table 1. Refined lattice parameters, $a$, $c$ and unit cell volume of La$_{0.7}$Sr$_{0.3}$Mn$_{1−x}$Cu$_x$O$_3$ ($0 \leq x \leq 0.30$) at room temperature (RT). Numbers in parentheses are statistical errors. $O_{occ}$ is the site occupation number, $m$ is the magnetic moment of the Mn site. $d_{Mn–O}$ is the Mn–O bond length, $θ_{Mn–O–Mn}$ is the Mn–O–Mn bond angle.
Table 2. Fitting parameters of the Mn 2p\(3/2\) XPS spectrum of La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1-x}\)Cu\(_x\)O\(_3\) (0 \(\leq x \leq 0.30\)). \(\Delta E\) is the separation of binding energies between two neighboring fitting components. \(I_i\) denotes the fractional intensity of the \(i\)th component as calculated by integrating the fitting areas.

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Figure 1. Mn-2p XPS of La\(_{0.7}\)Sr\(_{0.3}\)Mn\(_{1-x}\)Cu\(_x\)O\(_3\) (0 \(\leq x \leq 0.30\)) at room temperature.

Cu\(^{3+}\), the tolerance factor increases only slightly (\(\Delta \tau < 0.6\%\)) and the lattice parameters decrease slightly with increasing Cu content. These results agree well with the experimental results and suggest that Cu\(^{2+}\) and Cu\(^{3+}\) coexist with the dominant Cu\(^{2+}\) state [11]. Thus, the changes in the lattice parameters, (Mn,Cu)–O bond length and (Mn,Cu)–O–(Mn,Cu) bond angle at RT and low temperature may be ascribed to a mixed state of Cu\(^{2+}/Cu^{3+}\).

X-ray photoelectron spectrometer (XPS) measurements were then initiated to investigate the core-level and valence band of the Mn and Cu ions. The Mn-2p spectra, figure 1, consist of three peaks located at \(~641, 653\) and 647 eV for the spin–orbit doublet Mn 2p\(3/2\), Mn 2p\(1/2\) and a satellite structure, respectively. The intensity of the two main peaks decreases and becomes broad with increasing Cu content. The satellite peak, which arises from the mixed state of Mn\(^{3+}\) and Mn\(^{4+}\), shifts to the high binding-energy (BE) region with increasing Cu content likely due to the increase of Mn\(^{4+}\). To deconvolute the spectra so as to calculate the Mn 2p\(3/2\) spectrum, two main components were used with one extra component whose BEs were 640.5, 641.6 and 643.0 eV, respectively, table 2. In fitting the Mn 2p\(3/2\) spectra, the existence of two different initial states of Mn\(^{3+}\) and Mn\(^{4+}\) was unlikely to be the origin of the two main components because the Mn-2p core levels of Mn\(^{3+}\) and Mn\(^{4+}\) ions have very similar band structures. The energy separation between them is \(\Delta_{\text{ex}} \sim 1.1\) eV and is not changed with increasing Cu content. This is about the same order of magnitude as the exchange interaction between core holes and the valence electrons, about 1.3 eV [19]. The relative intensity \(I_1/I\), the ratio of the first component area to the total area of the 2p\(3/2\) spectrum, increases up to \(x = 0.15\) and decreases with further Cu substitution. In contrast, the relative intensity \(I_2/I\), the ratio of the second component area to the total area of the 2p\(3/2\) spectrum, decreases up to \(x = 0.15\) and then increases with further Cu substitution.

The Cu-2p spectra, figure 2, consist of two peaks located at 933 and 953 eV for Cu 2p\(3/2\) and 2p\(1/2\), respectively. A broad satellite peak is located around 946 eV. The Cu-2p peaks
presents the fitting parameters of the Cu 2p 3 of Cu content. The BEs of all the core levels shift to the binding energies between two neighboring fitting components. La-3d5/2, La0, sites indicate the Mn atom to be in mixed valence states, compound LSMO, the cation distributions at the A- and B- sites indicate the Mn atom to be in mixed valence states, Cu2+/3+ state decreases linearly with increasing Cu content, while Cu2+/3+ state increases with increasing Cu content. The BEs of both Cu2+/3+ states shift to the lower BE region which suggests that the Cu-2p state may be strongly hybridized with the O-1s state.

Figure 3 presents the BE shift of core levels as a function of Cu concentration (x). The Cu 2p3/2 spectrum was deconvoluted with two components corresponding to the Cu2+/3+ states [19, 20]. Table 3 presents the fitting parameters of the Cu 2p3/2 spectrum of La0.7Sr0.3Mn1−xCu0.3+xCu0.7O3 (0 ≤ x ≤ 0.30). The dominant Cu2+ state decreases linearly with increasing Cu content, while the minority Cu3+ state increases with increasing Cu content. The separation of BE between Cu2+ and Cu3+, ΔE ~ 1.0 eV, is not changed with increasing Cu content. The BEs of both Cu2+/3+ states shift to the lower BE region which suggests that the Cu-2p state may be strongly hybridized with the O-1s state.

Figure 3 presents the BE shift of core levels as a function of Cu content. The BEs of all the core levels shift to the lower BE region, which suggests that the E_F is lowered by introducing holes with Cu substitution. This is very similar to the hole doping effects on the A-site in La1−xSr_xMnO3 [21].

From the results of a deconvolution of the Cu-2p peak we can estimate the ratio of Cu2+/3+ and in turn the fractional ratio of Mn3+/4+Mn4+. Considering the parent compound LSMO, the cation distributions at the A- and B- sites indicate the Mn atom to be in mixed valence states, (La0.7Sr0.3)La(3/2)Mn3+(3/2)4 ortho-MnO2−y. From the ND analysis, we confirmed that the Cu goes to the Mn site. In addition, we assume that the La, Sr and O starting stoichiometry holds and does not induce any charge valence fluctuations at the Mn site. Then, it is necessary that the ratio of Cu2+/Cu3+ and Mn3+/4+ satisfy charge balance and charge neutrality in these compounds. Accordingly, the full ionic configuration of x moles of Cu-substituted LSMO can be represented by

\[
(La_{0.7}Sr_{0.3})_{\text{La-site}} \left( \begin{array}{c} \text{Cu}_{2+(\alpha-x)}^2 \text{Cu}_{3+}^{3+} \\ \text{Mn}_{(1-\alpha)}^{3+} \text{Mn}_{\alpha}^{4+} \end{array} \right)_{\text{B-site}} \text{O}_{2-\gamma}^{-y}
\]

where x is the mole percent of Cu on the B-site and α is the ratio of Cu3+ to total Cu content. The value of 1.3 varies with the hole substitution ratio and charge valence of the substituted ion. Table 4 presents the evolution of the Mn-site ionic content and the calculated tolerance factors based on the determined ionic content. For instance, for x = 0.15, the Cu3+ content as determined from XPS measurements is 1.8 mol% at the Mn site and the Mn3+/4+ ratio is calculated to be 0.967. For x = 0.25, the Cu3+ content increases to 5.4 mol% at the Mn site and the Mn3+/4+ ratio is calculated to be 0.5113. The per cent ratio of Cu3+ to total Cu content gradually increases, while the per cent ratio of Mn3+ to total Mn content dramatically decreases. The change of the tolerance factor, from LSMO (x = 0–0.30), is Δτ ∼ 0.82%, which means that the lattice parameters increase slightly. This agrees well with the ND data.
Figure 5. Calculated (solid line) and experimental (dots) x-ray photoelectron spectra for the valence band of La_{0.7}Sr_{0.3}Mn_{0.85}Cu_{0.15}O_3.

Figure 6. Total density of states (DOS) of the Mn-d states of ferromagnetic La_{0.5}Sr_{0.5}Mn_{1−x}Cu_{x}O_3 ground state from LSDA (solid line) and LSDA + U with $U = 7$ eV (thick solid line) calculations. The minority-spin contributions are shown as negative values. The Fermi level is set to 0 eV.

Figure 7. Partial density of states (PDOS) of the Cu-d states of the ferromagnetic La_{0.5}Sr_{0.5}Mn_{1/3}Cu_{1/3}O_3 ground state from LSDA (solid line) and LSDA + U with $U = 7$ eV (thick solid line) calculations. The minority-spin contributions are shown as negative values. The Fermi level is set to 0 eV.

Figure 8. Partial density of states (PDOS) of the Mn-d states of the ferromagnetic La_{0.5}Sr_{0.5}Mn_{1/3}Cu_{1/3}O_3 ground state from LSDA (solid line) and LSDA + U with $U = 7$ eV (thick solid line) calculations. The minority-spin contributions are shown as negative values. The Fermi level is set to 0 eV.

Photoionization cross section for La_{1−x}Sr_{x}MnO_3, the emission intensity is mostly due to the O-2p, and the Mn-3d state accounts for about 30% of the total valence-band intensity [24]. From the area integration of calculated curves, the ratio of the contribution to the total valence-band intensity, O-2p:Mn-3d:Cu-3d, is 64.3:32.7:3.1.

To see the Cu effect on the properties of LSMO compounds, the electronic structures of a supercell of La_{1/2}Sr_{1/2}MnO_3 and the hypothetical Cu-substituted La_{1/2}Sr_{1/2}Mn_{1−x}Cu_{x}O_3, $x = 1/6, 1/3$, were calculated using the LSDA + U method. Each supercell La_{3}Sr_{3}Mn_{6}O_{18} has six LaMnO_3 formula units. Initially, the total energy was calculated for different atomic arrangements to determine the most energetically favorable configuration. Then, band-structure calculations were done both for the ferromagnetic (FM) and for the A-type antiferromagnetic (AFM) phases of the above compounds.

The LSDA + U results give a strong FM interaction without any sign of antiferromagnetism for all three systems, which is consistent with experimental ND data [15]. When compared with previous work [16], no significant changes are observed for the Mn-d states with increasing Cu content and only $e_g$ states in the majority-spin channel contribute to the DOS at $E_F$, figure 6. (LSDA calculations are shown for comparative purposes.)

Figures 7 and 8 show the partial DOS of Cu-d states for $x = 1/6, 1/3$, respectively. As seen from the figures, only the $e_g$ states ($x^2−y^2$ and $3z^2−r^2$ orbitals) in the d-band contribute to the DOS at $E_F$. The $t_{2g}$ bands ($xy$ and the degenerate $xz$ and $yz$) are located about 6.3 eV below $E_F$ and the DOS become weaker and more delocalized with increasing Cu content. When Cu is introduced, the half-metallicity disappears. This
is mainly due to the strong hybridization between the spin-down Cu-d state and neighboring O-2p orbitals, which induces a redistribution of the charge density of Mn atoms. Only the d-states of the Cu eg orbitals and the p-states of the neighboring oxygen contribute to the minority DOS at the Fermi level.

The LSDA + U model provides a good description of the spin-dependent electronic properties. Table 5 presents the LSDA + U calculations for La_{1/2}Sr_{1/2}Mn_{1- x}Cu_{x}O_{3}, x = 0, 1/6, 1/3. The contribution of the majority-spin channel to the DOS at the Fermi level, N↑(E_F), does not change with increasing Cu content; 2.7, 2.8, 2.7 states for all three samples. However, the contribution of the minority-spin channel to the DOS at the Fermi level, N↓(E_F), changes with increasing Cu content; 0.0, 1.9, 1.6 states eV\(^{-1}\) for x = 0, 1/6, 1/3, respectively.

To investigate the anisotropy of the electronic conduction of Mn and Cu atoms at E_F, the ratios between the eg states of \(x^2 - y^2\) and \(3z^2 - r^2\) contributing to the DOS (E_F) were calculated. For the Mn atom, we have an almost isotropic electronic transport character with a ratio of \(\sim 1\) for all three samples. However for Cu atoms, the contribution from the \(3z^2 - r^2\) orbital is about times larger than that from the \(x^2 - y^2\) orbital and the ratio is not changed with increasing Cu content. The anisotropic character of Cu transport suggests that electron hopping along the c axis is preferable to that in the Cu–O chains in the ab plane.

The effective exchange interaction parameters were calculated to determine the effect of Cu substitution on the exchange coupling of Mn atoms. The exchange interaction parameters \(J_{ab}^{dd}\) between Mn pairs located close to the Cu ion decrease with increasing Cu content, while the parameter \(J_{ad}^{dd}\) between Mn pairs located further away from Cu slightly increase with increasing Cu content. At any rate, there is no antiferromagnetic coupling induced by Cu. These results agree with the ND data and saturation magnetization measurements.

The average magnetic moment on the Mn atoms slightly decreases from 3.614, 3.593, 3.571 \(\mu_B/\text{Mn}\) for \(x = 0, 1/6, 1/3\), respectively. For the Cu ions, small magnetic moments are obtained with 0.225, 0.069 \(\mu_B/\text{Cu}\) for \(x = 1/6, 1/3\), respectively. Using the calculated exchange parameters, we estimate the Curie temperature within the mean-field approximation as

\[
T_C = \frac{2S_i(S_i + 1)}{3k_B} \sum_a z_{ia} J_{ia},
\]

where \(S_i\) is the spin of the ith ion and \(J_{ia}\) is the exchange integral between the ith and ith ions. We also assume that the dilution of Mn moments affects \(z_{ia}\) in a linear fashion, \(z_{ia}(n_p) \propto (1 - n_p)z_{ia}(0)\), where \(z_{ia}(0)\) refers to the undiluted system and \(n_p\) is a relative substitutional concentration. The calculated \(T_C\) is 481 K, 383 K and 265 K for \(x = 0, 1/6, 1/3\), respectively. Again the calculated \(T_C\)s are higher in value than those of the real systems due to the larger magnetic moments.

4. Summary

In summary, we have investigated the electronic structure of Cu-substituted La_{0.7}Sr_{0.3}Mn_{1- x}Cu_{x}O_{3} by XPS, PES and \textit{ab initio} density functional LSDA and LSDA + U calculations. Mixed-valent Cu ions, Cu\(^{3+}\) with dominant Cu\(^{2+}\), are observed in all of the Cu-substituted LSMOs. LSDA + U calculations reveal that the electronic transport behavior is well described by a combination of two different conduction mechanisms resulting from (i) pd hybridization of the \(e_g^1\) states in the majority spin-Mn-3d channel with O-2p orbitals in the Mn–O–Mn chain and (ii) pd hybridization of \(e_g^2\) states in the minority spin-Cu-3d channel with O-2p orbitals in the Cu–O–Cu chain. We also find that the half-metallicity of compounds is lost upon Cu substitution. The contribution from the \(3z^2 - r^2\) orbital is
about three times larger than the $x^2 - y^2$ orbital, which indicates anisotropic electronic transport resulting from the Cu states.

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References

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