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Photoemission and Hartree-Fock studies of oxygen-hole ordering in charge-disproportionated $La_{1-x}Sr_xFeO_3$

J. Matsuno, T. Mizokawa, and A. Fujimori
Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

K. Mamiya
Photon Factory, High Energy Accelerators Research Organization, Tsukuba, Ibaraki 305-0801, Japan

Y. Takeda
Department of Chemistry, Mie University, Tsu 514-8507, Japan

S. Kawasaki and M. Takano
Institute of Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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We have studied the ''charge disproportionation'' phenomenon in $La_{1-x}Sr_xFeO_3$ by photoemission spectroscopy and unrestricted Hartree-Fock band-structure calculations. We find a systematic decrease of the spectral intensity near Fermi level (E_F) toward $x=0.67$, where the charge disproportion is most stabilized. The spectra for $x=0.67$ show the clearest temperature-dependent changes in the vicinity of E_F across the transition corresponding to the charge ordering of ''Fe^{3+}'':''Fe^{5+}'' = 2:1. The Hartree-Fock calculations indicate that ordering of oxygen holes indeed occurs in the charge disproportionated state. [S0163-1829(99)07831-5]

I. INTRODUCTION

It is well known that carrier doping into a Mott insulator causes various remarkable physical properties. Recently, charge ordering in doped perovskite-type $3d$ transition-metal oxides has been a subject of intensive studies in relation to the colossal magnetoresistance in the manganites[1] and the spin-charge stripes in the high-T_C cuprates.[2] Thus systematic studies on many different systems which show charge ordering of doped carriers are strongly required.

The perovskite-type $CaFeO_3$, where the average formal valence of the iron ion is Fe^{4+}, is known to show a gradual ''charge disproportionation'' $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$ below 290 K with antiferromagnetism below 115 K according to Mössbauer studies.[3] This charge disproportionation has recently been suggested to be a ''triplet pairing'' of oxygen holes rather than a pairing of Fe $3d$ holes.[4] A similar charge disproportionation was reported for $La_{1-x}Sr_xFeO_3$ with $x \simeq 0.7$ below 200 K.[3] This disproportionation is abrupt and is accompanied by both a simultaneous metal-to-insulator transition (MIT) and antiferromagnetic ordering. A neutron diffraction study by Battle *et al.*[5] exhibited that a combination of a charge-density wave (CDW) of threefold periodicity and a spin-density wave (SDW) of sixfold periodicity along the $\langle 111 \rangle$ direction was realized in nonstoichiometric $La_{0.33}Sr_{0.67}FeO_{2.98}$. They could not, however, observe a structural distortion of the same period although such a charge ordering is expected to inevitably couple with freezing of a breathing phonon mode. On the other hand, a local structural distortion along the $\langle 111 \rangle$ direction has recently been suggested by electron diffraction.[6] On the contrary, $SrFeO_3$, where the iron formal valence is also Fe^{4+}, retains metallic conductivity down to 4 K and shows screw antiferromagnetism below the Néel temperature $T_N = 134$ K without any sign of charge ordering.[7] The above phenomenon may be understood in terms of the negative charge-transfer energy Δ of the Fe^{4+} oxides as deduced from configuration-interaction cluster-model analysis of photoemission data, according to which the formal ''Fe^{4+}'' ground state is actually dominated by the $d^5\underline{L}$ configuration, where $\underline{L}$ denotes a hole in the oxygen $2p$ band.[8] Due to the smallness of the charge-transfer energy and hence of the charge-transfer gap in the Fe^{4+} oxides, the band gap may collapse as in $SrFeO_3$ or the ''Fe^{4+}'' state may charge-disproportionate into ''Fe^{3+}'' and ''Fe^{5+}'' as in $CaFeO_3$ and $La_{0.33}Sr_{0.67}FeO_3$. In this paper, we present a high-resolution ultraviolet photoemission spectroscopic study of $La_{1-x}Sr_xFeO_3$ with $x=0.55$, 0.67, 0.80, and 1.00, which cover the metallic and semiconducting regions, in order to see how the charge disproportionation influences the electronic structure near the Fermi level. We have also performed unrestricted Hartree-Fock band-structure calculations on this system to obtain deeper insight into the mechanism of the charge disproportionation.

II. EXPERIMENT

Polycrystalline samples of $La_{1-x}Sr_xFeO_3$ were prepared by a solid state reaction and a subsequent treatment under high-pressure oxygen.[4] Electrical resistivities of these samples are shown in Fig. 1(a). Figure 1(b) shows the phase diagram of the $La_{1-x}Sr_xFeO_3$ system with the magnetic phase transition temperatures (T_m) denoted by the filled circles. Except for $x=1.00$, magnetic moments appear discontinuously at these temperatures, indicating that these transitions are of the first-order, and at the same time the Mössbauer spectra show signs of charge disproportionation. For

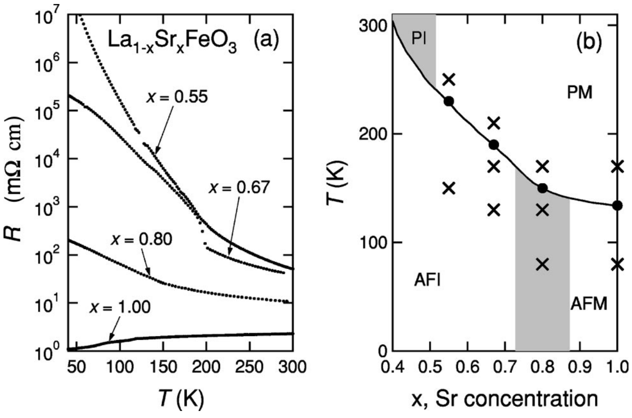

FIG. 1. (a) Electrical resistivity of $La_{1-x}Sr_xFeO_3$. (b) Phase diagram of $La_{1-x}Sr_xFeO_3$. The filled circles represent the Néel temperature for $x = 1.00$ and magnetic phase transition temperatures T_m for the other compositions. The crosses represent the temperatures at which the measurements were done (a, b, and c in decreasing order). The shaded zones represent the metal-insulator transition regions.

$x = 1.00$, T_m corresponds to the Néel temperature at which a second-order phase transition from the paramagnetic to antiferromagnetic phases occurs.

Ultraviolet photoemission (UPS) measurements were made using the He I resonance line ($h\nu = 21.2$ eV) and synchrotron radiation ($h\nu = 100$ eV). The latter measurements were done at beamline BL-3B of Photon Factory, High Energy Accelerators Research Organization. The He I measurements were performed at two or three temperatures in order to study spectral changes above and below the T_m. The He I spectra have been corrected for the He I* satellite. In order to calibrate binding energies and to estimate the instrumental resolution, gold was evaporated on the sample surface after each series of measurements. The energy resolution was 26 meV for He I and 80 meV for $h\nu = 100$ eV, respectively. The samples were repeatedly scraped *in situ* with a diamond file. We have adopted the spectra taken within 40 min after scraping and the reproducibility of the spectra was confirmed by repeated measurements.

III. RESULTS AND DISCUSSION

A. Photoemission spectroscopy

The temperature dependence of the spectra for the $x = 0.67$ sample is shown in Fig. 2. The spectra have been normalized to the integrated intensity of the total valence band. The inset shows that there is no detectable spectral change in the wide energy range above and below $T_m = 190$ K. We also note that there is no feature at ~6 and 9 eV, which is characteristic of surface degradation in transition-metal oxides. On the contrary, a clear change of the intensity from the Fermi level to 0.4 eV below it has been found across T_m for both photon energies. Because the difference between the 170 K and 210 K spectra is large and that between the 130 K and 170 K spectra is small, the change between 170 K and 210 K would be attributed to the phase transition at 190 K. Obviously, the energy scale of ~0.4 eV (~4000 K) is much larger than the transition temperature. This feature is common with Mn perovskite oxides, which also show metal-insulator transitions due to charge ordering such as $La_{1-x}Ca_xMnO_3$,[9] $Nd_{1-x}Sr_xMnO_3$,[10] and $Pr_{1-x}Sr_xMnO_3$.[11] The lower panel of Fig. 2 shows the difference between the 210 K and 170 K spectra. The difference spectrum shows a broad peak at ~0.15 eV below E_F. The comparison of the difference spectrum and the Fermi-Dirac distribution function (solid curve) indicates that the Fermi cutoff is not so clearly identified and that the spectral density of states (DOS) is somewhat pseudogaplike within ~0.05 eV of E_F in the "metallic" phase. The absence of a clear Fermi cutoff may be related with the electrical resistivity showing $d\rho/dT < 0$ just above the transition. In the 130 K spectrum there is no intensity at E_F, indicating that the material is semiconductive. However, one cannot estimate the magnitude of the semiconducting gap because the spectrum shows a soft gaplike behavior near E_F probably due to disorder at the La/Sr site.[12,13] In the spectra taken at $h\nu = 100$ eV, we expect stronger contributions from the Fe $3d$ orbitals than from the O $2p$ orbitals because the Fe $3d$–to–O $2p$ cross-section ratio increases at this photon energy. Our result that the temperature-dependent spectral change is similar for both photon energies indicates that the contribution from the O $2p$ orbitals is remarkable near E_F.

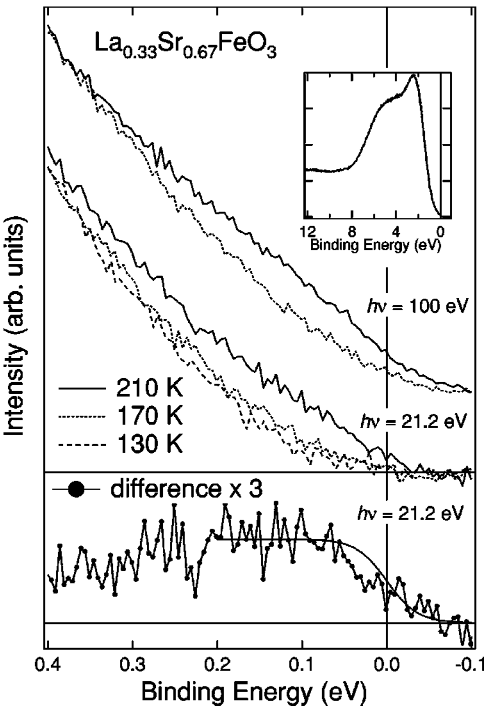

FIG. 2. Photoemission spectra ($h\nu = 21.2$ eV and 100 eV) of $La_{0.33}Sr_{0.67}FeO_3$ in the vicinity of E_F taken at various temperatures. Inset shows the spectra taken at $h\nu = 100$ eV in a wide energy range, where the temperature dependence is barely recognized. The lower panel shows the difference spectrum between 210 K and 170 K taken at $h\nu = 21.2$ eV. The solid curve is the Fermi-Dirac distribution function at 210 K convoluted with the instrumental resolution.

Figure 3(a) shows the temperature dependence of the He I spectra of $La_{1-x}Sr_xFeO_3$ near E_F for various compositions. One can see that the spectra of $x = 0.67$ show the most dramatic temperature dependence and the spectra for $x = 1.00$ do not change with temperature. In order to illustrate this point more clearly, we show the x and temperature dependences of

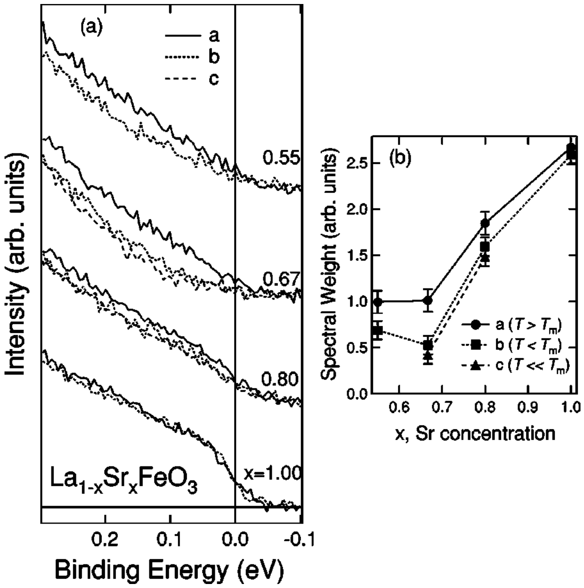

FIG. 3. (a) Photoemission spectra ($h\nu = 21.2$ eV) of $La_{1-x}Sr_xFeO_3$ for $x = 0.55$, 0.67, 0.80, and 1.00 at various temperatures. Intensity normalization between the different samples is arbitrary. (b) Spectral weight integrated from 0.20 to -0.05 eV at temperatures *a*, *b*, and *c*. See Fig. 1(b).

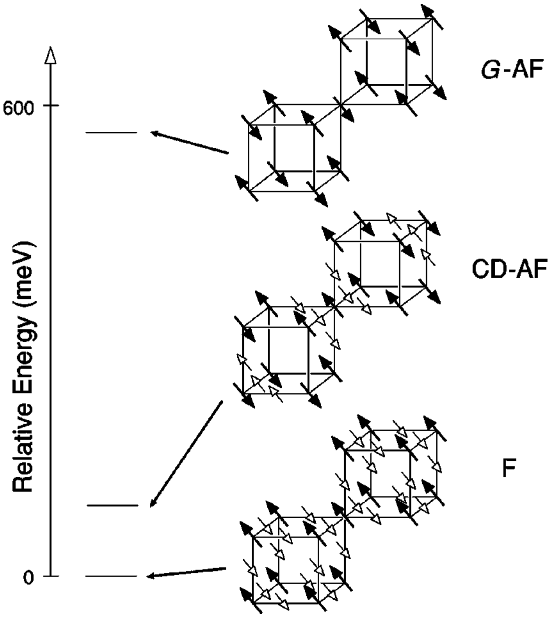

FIG. 4. Various spin- and charge-ordered structures for $LaSr_2Fe_3O_9$ and their relative total energies obtained by the unrestricted Hartree-Fock band-structure calculation. The filled and open arrows represent the spin moment at the iron and oxygen sites, respectively.

the spectral weight integrated from 0.20 to -0.05 eV in Fig. 3(b). This result indicates that the temperature dependence is clearly the strongest for $x = 0.67$ and that the absolute value of the spectral weight rapidly decreases on going from $x = 1.00$ to $x = 0.67$. Figure 3 also indicates weaker but finite changes between temperatures *a* and *b* for $x = 0.80$ and $x = 0.55$. This temperature dependence well corresponds to that of the transport properties shown in Fig. 1(a), which indicates that the spectra reflect bulk properties of this system and hence the possible effect of nonstoichiometric surfaces on the electronic structure near E_F may be neglected. These facts mean that the Fe^{3+}:Fe^{5+} charge ordering realized in $x = 0.67$ influences the phase transition over a certain composition range around $x = 0.67$ and causes incomplete charge disproportionation reminiscent of the complete one for $x = 0.67$, consistent with the influence in the transport properties.

B. Hartree-Fock calculation

In order to further clarify the electronic structure of $La_{1-x}Sr_xFeO_3$ with $x \simeq 2/3$, where the charge disproportionation occurs most clearly, we have carried out unrestricted Hartree-Fock calculations for the multiband *d*-*p* lattice model, in which the full degeneracy of the Fe 3*d* and oxygen 2*p* orbitals is taken into account.[14] Parameters in the model are the charge-transfer energy Δ, the multiplet averaged *d*-*d* Coulomb interaction *U*, and Slater-Koster parameters $(pd\sigma)$, $(pd\pi)$, $(pp\sigma)$, and $(pp\pi)$, which represent transfer integrals between the transition-metal 3*d* and oxygen 2*p* orbitals. From the previous cluster-model analysis of the core-level photoemission spectra of $LaFeO_3$ (Fe^{3+}) and $SrFeO_3$ (Fe^{4+}),[8] the values of Δ, U, and $(pd\sigma)$ were estimated to be 1, 6, and -1.8 eV, respectively, for $LaSr_2Fe_3O_9$ ($x = 2/3$). Here, because we deal with the intermediate-valence $x = 2/3$ material (represented by $LaSr_2Fe_3O_9$ with $Fe^{3.66+}$), we have adopted a linear interpolation between the parameter values for Fe^{3+} and those for Fe^{4+} with respect to *x*. This is especially important for Δ, the change of which between Fe^{3+} (3 eV) and Fe^{4+} (0 eV) is significantly large.[15] The ratio $(pd\sigma)/(pd\pi)$ was fixed at -2.16 and $(pp\sigma)$ and $(pp\pi)$ at -0.60 and 0.15 eV, respectively.[16] Because $LaSr_2Fe_3O_9$ has a rhombohedral distortion with little deviation from the cubic perovskite structure,[3] we have assumed the structure of $LaSr_2Fe_3O_9$ to be cubic. In order to simulate the stability of the magnetic structure $3+(\downarrow)5+(\downarrow)3+(\downarrow)3+(\uparrow)5+(\uparrow)3+(\uparrow)$ along the $\langle 111 \rangle$ direction suggested by Battle *et al.*,[5] we assumed the unit cell to have six lattice spacings along that direction. We studied four magnetic structures as initial conditions, namely, ferromagnetic (F), *G*-type antiferromagnetic (*G*-AF), antiphase antiferromagnetic (AP-AF), and Battle *et al.*'s structure. In the AP-AF structure, the ordering of the moments of the iron sites was assumed to be $\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow$ along the $\langle 111 \rangle$ direction as in Battle *et al.*'s structure but without charge disproportionation. Battle's type will be referred to as the charge-disproportionation-type antiferromagnetic (CD-AF) structure hereafter.

As converged self-consistent solutions, we obtained three magnetic structures as shown in Fig. 4 with the F solution having the lowest energy. The F solution is a metallic one and does not agree with the experimental results. The total energies per formula unit of the CD-AF and *G*-AF solutions relative to the F solution are 87 and 567 meV, respectively. The CD-AF solution was obtained as an insulating solution from the CD-AF initial condition as well as from the AP-AF initial condition. Hence this CD-AF state was the most stable insulating ground state within our calculation. Note that the charge disproportionation was realized without any lattice distortion in the CD-AF solution, indicating that the charge ordering can be driven by purely electronic interactions, which is consistent with the smallness of lattice distortion as observed in the neutron diffraction study.[5] In the CD-AF solution, an energy gap of 0.14 eV opened at E_F and the magnetic moments for the ‘‘Fe^{3+}’’ (d^5) and ‘‘Fe^{5+}’’ ($d^5\underline{L}^2$) sites were 4.49 and 4.27 μ_B, respectively. These values do not quantitatively agree with the values 4.6 and 3.8 obtained by neutron diffraction, but qualitatively explain the smallness of the difference of the magnetic moments between the ‘‘Fe^{3+}’’ and ‘‘Fe^{5+}’’ sites. We point out another feature of the CD-AF solution that not only electrons on the iron sites but also holes on the oxygen sites disproportionate into different charge states. The magnetic moment for an oxygen atom between the ‘‘Fe^{3+}’’ and ‘‘Fe^{5+}’’ sites and that between the ‘‘Fe^{3+}’’ and ‘‘Fe^{3+}’’ sites are 0.07 and 0.00 μ_B, respectively.

The origin of the charge disproportionation is thus described as follows. First, holes doped into $\mathrm{LaFeO_3}$ are accommodated primarily at the oxygen sites because of the small charge-transfer energy $\Delta \sim 1$ eV (or $\Delta_{\mathrm{eff}} \sim -2$ eV if Hund’s rule exchange energy at the Fe sites is taken into account). Then the holes prefer oxygen sites between iron sites of the same spin directions thereby gaining the kinetic energy of $\sim t_{pd}^4/|\Delta|^3$.[17] This results in a ferromagnetic coupling between the ‘‘Fe^{3+}’’ (d^5) and ‘‘Fe^{5+}’’ ($d^5\underline{L}^2$) sites, whereas ordinary antiferromagnetic superexchange coupling exists between ‘‘Fe^{3+}’’ and ‘‘Fe^{3+}.’’ In general, conventional charge disproportionation at the transition-metal sites is not favored because of the strong on-site d-d Coulomb repulsion. In the case of $\mathrm{LaSr_2Fe_3O_9}$, ordering of holes at the oxygen sites avoids this strong d-d repulsion and at the same time gains the kinetic exchange energies. This ordering of oxygen holes is expected to be a generic feature of carrier doped Mott insulators like $\mathrm{La}_{2-x}\mathrm{Sr}_x\mathrm{NiO}_4$ and $(\mathrm{La,Nd})_{2-x}\mathrm{Sr}_x\mathrm{CuO}_4$, of which the charge-transfer energy Δ is small.[18]

IV. CONCLUSION

We have studied the electronic structure of $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{FeO}_3$ associated with the charge disproportionation by photoemission spectroscopy and unrestricted Hartree-Fock band-structure calculations. The spectral changes across the transition temperature were most pronounced for $x=0.67$. A charge-disproportionated insulating solution was found for $\mathrm{LaSr_2Fe_3O_9}$, which suggests that the ordering of holes on the oxygen sites plays an essential role in realizing the charge-disproportionated ground state.

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[15] The charge-transfer energy Δ is defined by $\Delta=\epsilon_d^0+nU-\epsilon_p$ for the d^n configuration, where ϵ_d^0 and ϵ_p are the energies of the bare metal $3d$ and oxygen $2p$ orbitals (Ref. 8). As the value of U is estimated to be 6 eV for both Fe^{3+} and Fe^{4+}, we deduce the $\epsilon_d^0-\epsilon_p$ value to be -27 eV for Fe^{3+} and -24 eV for Fe^{4+} using the values of Δ and U. We have interpolated these values to find that U and $\epsilon_d^0-\epsilon_p$ are 6 and -25 eV, respectively, for $\mathrm{Fe}^{3.66+}$($d^{4.33}$). Thus we obtain $\Delta=1$ eV.

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