X-ray absorption of the negative charge-transfer material $SrFe_{1-x}Co_xO_3$

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(Received 12 November 2001; revised manuscript received 1 February 2002; published 15 April 2002)

We studied the relation between the electronic structure and the phsyiscal properties of $SrFe_{1-x}Co_xO_3$. The main technique used in the study was Fe $2p$, Co $2p$, and O $1s$ x-ray absorption spectroscopy. The experimental spectra were analyzed in terms of the configuration-interaction cluster model calculation. The analysis of the spectra shows that both $SrFeO_3$ and $SrCoO_3$ are in the negative-charge transfer regime (this means that their ground states are mostly covalent and contain considerable O $2p$ hole character). $SrFeO_3$ is in a high-spin state and $SrCoO_3$ in an intermediate-spin state stabilized by strong hybridization. The local electronic structure and the corresponding spin state are mostly preserved in $SrFe_{1-x}Co_xO_3$. The relatively large O $2p$ hole weight in the ground state explains the absence of Jahn-Teller distortions, as well as the relatively large value of the magnetic moment observed at the O sites in these materials. $SrFe_{1-x}Co_xO_3$ illustrates both ferromagnetism and magneto-resistance in a negative charge-transfer material.

DOI: 10.1103/PhysRevB.65.165120 PACS number(s): 78.70.Dm, 71.30.+h

I. INTRODUCTION

Colossal magnetoresistance (CMR) materials, such as manganites[1] and double perovskites,[2] are attracting considerable attention. The interest in these materials was originally sparked by their potential applications as magnetic sensors in reading heads. Additional interest was provided by the challenges in the elucidation of the microscopic origin of the CMR mechanism. It is generally invoked that the physical properties of manganites, such as $La_{1-x}Ca_xMnO_3$, are dominated by the double-exchange mechanism.[1] Whereas tunneling magnetoresistance between (half-metallic) ferromagnetic phases was proposed in double-perovskites materials, such as Sr_2FeMoO_6.[2]

The $SrFe_{1-x}Co_xO_3$ compound[3–5] also presents a large negative magnetoresistance for a wide concentration range ($0 \leqslant x \leqslant 0.7$).[6] Despite several studies of the physical properties of this system, still very little is known about the electronic structure and the magnetoresistance. The electronic structure of this material is particularly interesting because the transition metal ions are in a relatively high oxidation state. In fact, it is expected that the ground state could be qualitatively different with respect to manganites[1] and double perovskites.[2] This provided the motivation to investigate the electronic structure of the $SrFe_{1-x}Co_xO_3$ series using direct spectroscopic techniques.

The purpose of this work is to study the relation between the electronic structure and the physical properties of $SrFe_{1-x}Co_xO_3$. The main experimental techniques used in this study were Fe $2p$, Co $2p$, and O $1s$ soft x-ray absorption spectroscopy (XAS). The experimental results were analyzed in terms of combined atomic multiplet, crystal field and cluster model calculations. The analysis of the spectra shows that the electronic structure of these materials is dominated by a negative-charge-transfer character. This means that the ionic state of the Fe and Co ions is not really $+4$, but rather that the charge state is compensated by O $2p$ holes.

The structure of the $SrFeO_3$ perovskite is cubic (space group $Pm3m$) with a lattice parameter of $a = 3.845$ Å.[3] $SrFeO_3$ is antiferromagnetic with a screw structure along the $\langle 111 \rangle$ propagation vector. The ordering temperature of stoichiometric $SrFeO_3$ is $T_N = 134$ K and the Fe magnetic moment is $3.1\mu_B$.[3] $SrFeO_3$ is metallic ($\partial\rho/\partial T > 0$) down to 4 K and has a room-temperature resistivity of 10^{-3} Ω cm.[3] $SrCoO_3$ has the cubic perovskite structure (space group $Pm3m$) with a lattice parameter of $a = 3.835$ Å.[4] Stoichiometric $SrCoO_3$ is ferromagnetic with a Curie temperature of $T_C = 280$ K and the Co magnetic moment is $2.1\mu_B$.[4] $SrCoO_3$ is also metallic ($\partial\rho/\partial T > 0$) down to 4 K and has a room temperature resistivity of about 10^{-3} Ω cm.[4]

$SrFe_{1-x}Co_xO_3$ remains cubic over the whole composition range with a lattice parameter of $a = 3.835 - 3.845$ Å.[5] The $SrFe_{1-x}Co_xO_3$ material is metallic ($\partial\rho/\partial T > 0$) with a room-temperature resistivity in the range 10^{-3}–10^{-4} Ω cm.[5] The $SrFe_{1-x}Co_xO_3$ compound is antiferromagnetic for $x \leqslant 0.10 - 0.15$ and becomes ferromagnetic for $x \geqslant 0.2$. The Curie temperature T_C increases with x and is maximum around $0.4 \leqslant x \leqslant 0.6$, whereas the saturated magnetic moment μ peaks around $0.2 \leqslant x \leqslant 0.4$.[5] In particular, the $SrFe_{0.5}Co_{0.5}O_3$ compound has a $T_C = 340$ K and a saturated magnetic moment of about $3\mu_B$. Finally, the $SrFe_{1-x}Co_xO_3$ system presents a relatively large negative magnetoresistance for $0 \leqslant x \leqslant 0.7$.[6]

II. EXPERIMENTAL DETAILS

The samples studied here were nearly stoichiometric $SrFeO_3$, $SrFe_{0.5}Co_{0.5}O_3$, and $SrCoO_3$. First, oxygen deficient samples were prepared using the solid-state reaction method. Then, the samples were sealed in gold capsules with the oxygen dispenser $KClO_4$. Finally, the samples were

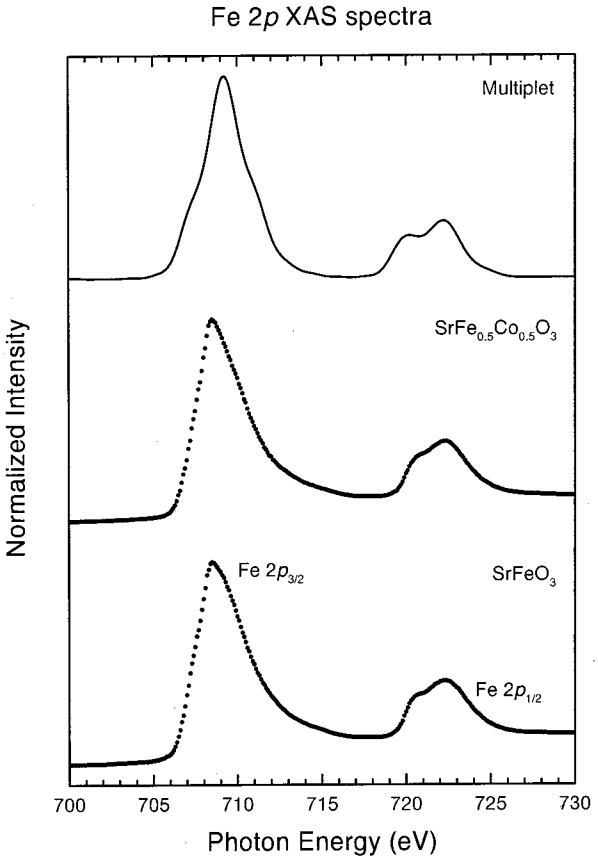

FIG. 1. Fe $2p$ x-ray absorption spectra of $SrFeO_3$ and $SrFe_{0.5}Co_{0.5}O_3$ (dots) compared to an atomic multiplet calculation (solid line).

treated at 6 GPa and 600 °C for 30 min. X-ray diffraction analysis showed that all the samples were single phase.[7] Iodometric tritation showed that the oxygen deficiency was less than 1%.[7] The characterization also included Mössbauer and magnetization measurements.[7]

The XAS measurements were performed at the spherical-grating-monochromator (SGM) beamline in the LNLS. The base pressure in the experimental chamber was in the low 10^{-9} mbar range. The samples were scraped *in situ* with a diamond file to remove surface contamination. The spectra were measured using the total-electron-yield (TEY) method. The mean probing depth of soft x-ray absorption using the TEY method is approximately 5 nm.[8] The energy resolution at the O $1s$ x-ray absorption edge was better than 0.5 eV. The energy scale of the spectra was calibrated using the known peak positions in TiO_2. The spectra were normalized to the maximum after a constant background substraction.

III. RESULTS AND DISCUSSION

A. Fe 2*p* XAS spectra

Figure 1 shows the Fe $2p$ x-ray absorption (XAS) spectra of $SrFeO_3$ and $SrFe_{0.5}Co_{0.5}O_3$. The spectra corresponds to Fe $2p \rightarrow$ Fe $3d$ transitions and are dominated by multiplet effects. The spectra are split by the Fe $2p$ spin-orbit interaction into the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ regions. In turn, these regions are further split by Fe $2p$-$3d$ electrostatic interactions and crystal field effects. The shape of the multiples in the spectra are directly related to the ground state of the Fe ions. These spectra can be analyzed in terms of combined atomic multiplet plus crystal field calculations.[9]

The Fe $2p$ XAS spectrum of $SrFeO_3$ corresponds formally to Fe^{4+} ($3d^4$) ions in a high-spin state. The calculation based on the single ionic configuration $t_{2g}^3 e_g^1$ (^5E) does not account for the spectrum.[10] The problem is that the ground state contains not only $3d^4$ but also considerable $3d^5\underline{L}$ character (where $\underline{L}$ denotes a ligand hole). Therefore, the calculation must include the contributions of the charge-transfer configurations $3d^5\underline{L}$ [the main $3d^5$ component of the $3d^5\underline{L}$ configuration is given by the high-spin $t_{2g}^3 e_g^2$ ($^6A_1$) state].

The charge-transfer configurations were included using the configuration interaction (CI) method. The ground state of $SrFeO_3$ was expanded in terms of the $3d^4$, $3d^5\underline{L}$, and $3d^6\underline{L}^2$ configurations. The main parameters were the charge-transfer energy Δ, the Mott-Hubbard repulsion U, and the transfer integral T_σ. The value of the parameters were obtained from Ref. 11 ($\Delta = 0$ eV, $U = 7.5$ eV, and $T_\sigma = 2.2$ eV). The occupations of the configurations in the ground state are 36% $3d^4$, 58% $3d^5\underline{L}$, and 6% $3d^6\underline{L}^2$. Figure 1 shows that the CI calculation reproduces reasonably well the features in the $SrFeO_3$ spectrum [the agreement is better than that obtained using a single ionic configuration $t_{2g}^3 e_g^1$ (^5E) calculation, see Ref. 10].

The occupation of the $3d^5\underline{L}$ configuration in $SrFeO_3$ is larger than that of the $3d^4$ configuration. This means that $SrFeO_3$ is in the negative charge-transfer regime with holes in the O $2p$ levels[12] (the effective charge-transfer parameter Δ_{eff} of $SrFeO_3$ is actually negative due to multiplet splitting). This regime is characteristic of compounds with transition metal ions in relatively high oxidation states. The calculated $3d$ count for $SrFeO_3$, approximately 4.7, is larger than the purely ionic value 4.0. This indicates that the covalent contribution to the bonding in the $SrFeO_3$ compound is relatively large.

The Fe $2p$ XAS spectrum of $SrFe_{0.5}Co_{0.5}O_3$ presents only minor changes with respect to $SrFeO_3$. The absence of changes indicates that the Fe ions remains relatively unaffected in $SrFe_{0.5}Co_{0.5}O_3$. This means that the formally tetravalent Fe^{4+} ions in the mixed compound are in a high-spin state, that the material is in the negative-charge-transfer regime with a considerable amount of O $2p$ holes, and finally that the covalent contribution to the bonding in $SrFe_{0.5}Co_{0.5}O_3$ is relatively large. Further support for these conclusions is provided by the analysis of the O $1s$ XAS spectra below.

B. Co 2*p* XAS spectra

Figure 2 shows the Co $2p$ x-ray absorption spectra of $SrCoO_3$ and $SrFe_{0.5}Co_{0.5}O_3$. The analysis of the Co $2p$ XAS spectra follow closely that of the Fe $2p$ XAS spectra above. The spectrum of $SrCoO_3$ corresponds formally to Co^{4+}

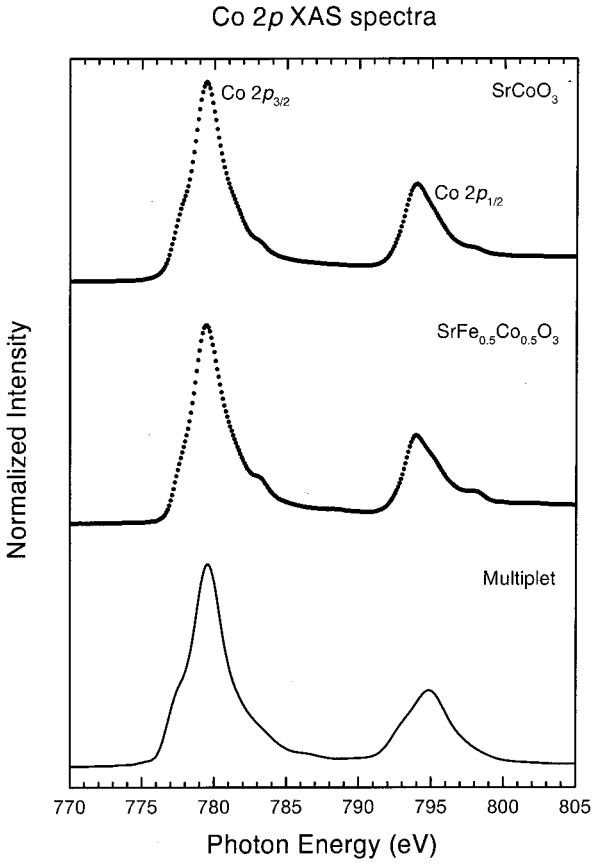

FIG. 2. Co $2p$ x-ray absorption spectra of $SrFe_{0.5}Co_{0.5}O_3$ and $SrCoO_3$ (dots) compared to an atomic multiplet calculation (solid line).

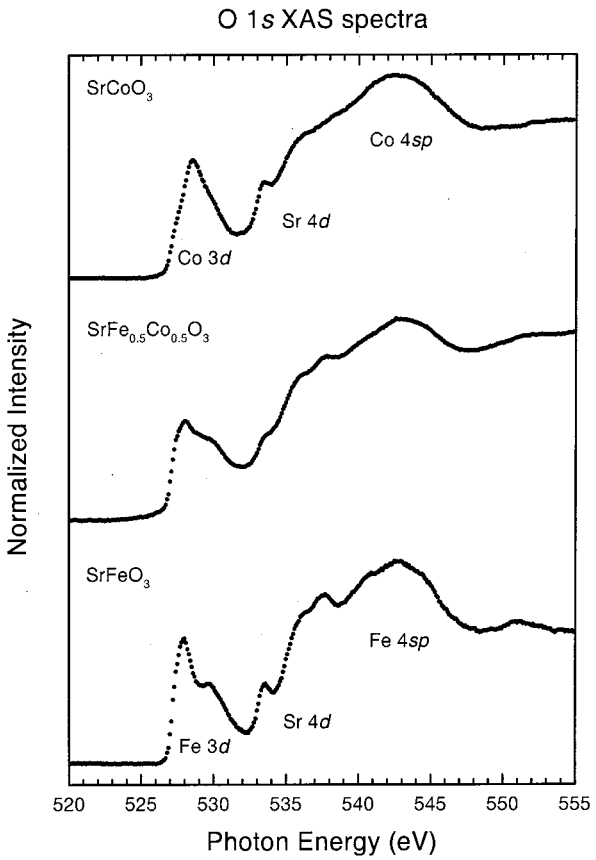

FIG. 3. O $1s$ x-ray absorption spectra of $SrFeO_3$, $SrFe_{0.5}Co_{0.5}O_3$, and $SrCoO_3$ (dots).

($3d^5$) ions in an intermediate-spin state. In a purely ionic picture, the ground state of the Co^{4+} should be either high spin or low spin. The $t_{2g}^4 e_g^1$ ($^4T_1$) intermediate-spin state is stabilized by the hybridization with the $3d^6\underline{L}$ configuration[13] [the main $3d^6$ component of the $3d^6\underline{L}$ configuration is given by the high-spin $t_{2g}^4 e_g^2$ ($^5T_2$) state].

The calculation based on the single ionic configuration does not account for the spectrum of $SrCoO_3$. Again, the calculation must include the contributions of the charge-transfer configurations $3d^6\underline{L}$. The ground state of $SrCoO_3$ was expanded in terms of the $3d^5$, $3d^6\underline{L}$, and $3d^7\underline{L}^2$ configurations. The value of the parameters were obtained from Ref. 13 ($\Delta=-2$ eV, $U=7.5$ eV, and $T_\sigma=2.0$ eV). The occupations of the configurations in the ground state are 22% $3d^5$, 67% $3d^6\underline{L}$, and 11% $3d^7\underline{L}^2$. Figure 2 shows that the CI calculation reproduces reasonably well the features in the $SrCoO_3$ spectrum (the agreement is better than that obtained using either high-spin or low-spin states calculations, see Ref. 13).

The occupation of the $3d^6\underline{L}$ configuration in $SrCoO_3$ is much larger than that of the $3d^5$ configuration. This means that $SrCoO_3$ also is in the negative charge-transfer regime with holes in the O $2p$ levels[12] (which is in agreement with the already negative value of the charge-transfer parameter Δ for this compound). The calculated $3d$ count for $SrCoO_3$, approximately 5.9, is much larger than the purely ionic value 5.0. This indicates that the covalent contribution to the bonding in $SrCoO_3$ is even larger than in $SrFeO_3$.

The Co $2p$ XAS spectrum of $SrFe_{0.5}Co_{0.5}O_3$ presents only minor changes with respect to $SrCoO_3$. The absence of changes indicates that the Co ions are not drastically affected in $SrFe_{0.5}Co_{0.5}O_3$. This means that the formally tetravalent Co^{4+} ions remains mostly in the intermediate-spin state. The mixed material is in the negative-charge-transfer regime with a considerable amount of O $2p$ holes, and finally the covalent contribution to the bonding in $SrFe_{0.5}Co_{0.5}O_3$ is considerably large. Further support for these conclusions is provided by the analysis of the O $1s$ XAS spectra below.

C. O 1*s* XAS spectra

Figure 3 shows the O $1s$ x-ray absorption spectra of $SrFeO_3$, $SrFe_{0.5}Co_{0.5}O_3$, and $SrCoO_3$. The spectra correspond to transitions from the O $1s$ to unoccupied O $2p$ states in the conduction band. These empty O $2p$ states reflect, through the oxygen-metal hybridization, bands of mostly metal character.[9] The first peaks at threshold corresponds to the Fe-Co $3d$ band region, the rising structure around 535 eV corresponds to the Sr $4d$ band region, and the bumps around 540–545 eV correspond to the Fe-Co $4sp$

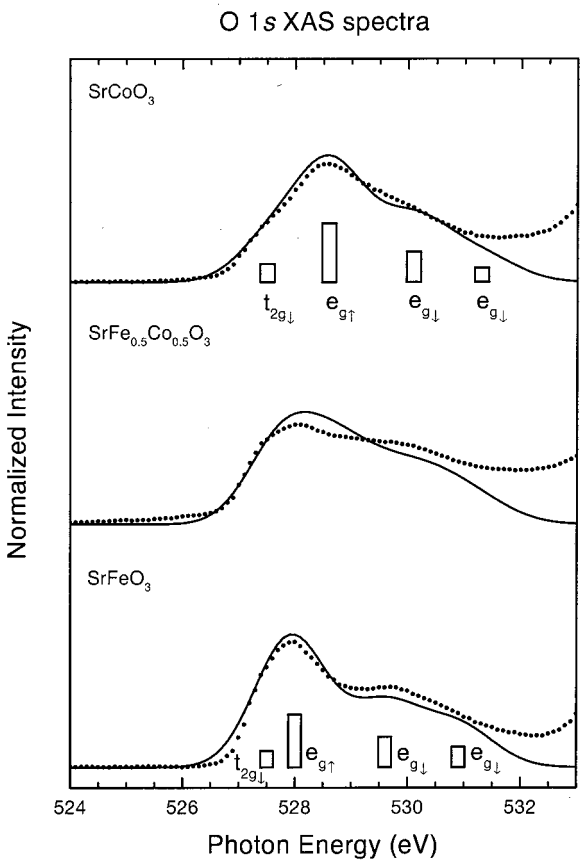

FIG. 4. Metal $3d$ region of the O $1s$ XAS spectra of $SrFeO_3$, $SrFe_{0.5}Co_{0.5}O_3$, and $SrCoO_3$ (dots) compared to cluster model calculations (solid lines).

band region. These assignments are consistent with previous analysis of the $SrMnO_3$ and $SrFeO_3$ spectra.[10]

Figure 4 shows in more detail the metal $3d$ band region of $SrFeO_3$, $SrFe_{0.5}Co_{0.5}O_3$, and $SrCoO_3$. These regions can be analyzed using cluster model calculations including charge-transfer configurations. The method of calculation follows that used in the closely related $SrMnO_3$ and $CaMnO_3$ compounds.[14,15] The metal $3d$ band region spectra corresponds to $3d^{n+1}\underline{L}\rightarrow\underline{c}3d^{n+1}$ transitions, where $\underline{c}$ denotes an O $1s$ core hole. The energies of the final state configurations are related to the value of the Δ, U, and T_σ parameters. The model parameters used here were the same used in the previous analysis of the metal $2p$ XAS spectra.

The relative energy of the transitions is mostly given by the energies of the various $3d^{n+1}$ final state configurations. The relative intensities of the transitions is mainly given by the occupations of the $3d^{n+1}\underline{L}$ terms in the ground state. The Racah parameters (B and C) were reduced to 60–70 % of their initial Hartree-Fock value (this reduction takes into account the extra screening of the O $2p$ ligand holes in the ground state). The crystal field splitting was estimated from LSDA calculations of pure $SrFeO_3$ and $SrCoO_3$.[16] The absolute energy and intensity of the calculations were adjusted so as to match the experimental peaks.

Figure 4 shows the calculations for the metal $3d$ band region of the $SrFeO_3$ and $SrCoO_3$ compounds. The calculation for the $SrFeO_3$ compound corresponds to $3d^4\underline{L}\rightarrow\underline{c}3d^4$ transitions in O_h symmetry. The relative energy and intensity of the calculated spectrum is in reasonably agreement with the experiment. In addition, the calculated spectral weight for $SrFeO_3$ is also in agreement with previous LSDA calculations.[16] The calculated DOS exhibited a sharp minority t_{2g} band at the Fermi level, a broad majority e_g band across E_F, and a broad minority e_g band above E_F.

The calculation for the $SrCoO_3$ compound corresponds to $3d^5\underline{L}\rightarrow\underline{c}3d^5$ transitions in O_h symmetry. The calculated spectrum is in reasonably agreement with the experiment and previous LSDA calculations.[16] This provides further support for the intermediate-spin interpretation of the Co $2p$ XAS spectrum above. The calculated DOS exhibited a sharp minority t_{2g} band at the Fermi level, a broad majority e_g across E_F, and a broad minority e_g band above E_F. The main difference with respect to $SrFeO_3$ is that the majority e_g band in $SrCoO_3$ is further apart from E_F (in fact, $SrCoO_3$ is close to be a half-metallic ferromagnet with a minimum in the majority e_g band at E_F).

The calculation for the $SrFe_{0.5}Co_{0.5}O_3$ compound is a linear combination of $SrFeO_3$ and $SrCoO_3$. The relative energy and intensity of the calculated spectrum is in fair agreement with the experiment. We note that the intensity of the $e_{g\uparrow}$ peak is overestimated and that of the $e_{g\downarrow}$ peaks is underestimated. At first sight, these could be attributed to a partial transformation of some Co ions into a high-spin $t_{2g}^3e_g^2$ ($^6A_1$) state. However, this is unlikely because the Co $2p$ XAS spectrum shows that most of the Co ions remains in the intermediate-spin $t_{2g}^4e_g^1$ ($^4T_1$) state. On other hand, changes in the Fe ions can be ruled out because the high-spin $t_{2g}^3e_g^1$ (^5E) state is rather stable. The differences are attributed to changes in the ground state of O ions located between Fe and Co ions.

D. Physical properties

1. Tendency to ferromagnetism in $SrFeO_3$

The $SrFeO_3$ compound is antiferromagnetic with a screw structure along the propagation wave vector $\mathbf{k}\|\langle 111\rangle$. The Heisemberg-like exchange interactions estimated from the analysis of paramagnetic neutron scattering are $J_1=1.2$ meV, $J_2=-0.2$ meV, and $J_4=-0.3$ meV.[5] The screw structure is due to the competition between the ferromagnetic nearest-neighbor interaction J_1, and the antiferromagnetic second- and fourth-nearest-neighbor interactions J_2 and J_4, respectively. We note that the magnitude of the propagation wave vector in $SrFeO_3$ ($|\mathbf{k}|\cong 0.135a^*$) is relatively small.[5] In turn, this implies that the corresponding wavelength of the magnetic screw structure is relatively large. In fact, the relative phase angle between two adjacent spins along the $\langle 111\rangle$ direction (40°) is rather small. This fact can be understood taking into account that the FM interaction is much larger than the AFM interactions. All this suggests that the magnetic structure of $SrFeO_3$ is on the verge of becoming ferromagnetic, see below.

2. (Half-metallic) ferromagnetism in $SrCoO_3$*?*

The microscopic origin of the ferromagnetism in the $SrCoO_3$ compound is not completely clear at the moment. The results shows that the electronic structure of this material derives from the intermediate-spin $t_{2g}^4 e_g^1$ ($^4T_1$) state. The ground state is not only given by the $3d^5$ configuration, but it contains also a considerable $3d^6\underline{L}$ weight. Potze *et al.* proposed that the ferromagnetism in $SrCoO_3$ was due to a double-exchange-like mechanism,[13] which involves Co-O-Co interactions between partially filled e_g states mediated by the corresponding O $2p$ holes. Band structure calculations of $SrCoO_3$, however, shows a minimum in the majority e_g band at the Fermi level[16] (this is also supported by the above cluster model calculations which show a majority e_g peak far away from E_F). So, in fact, $SrCoO_3$ might be a half-metallic ferromagnet such as the double-perovskite system Sr_2FeMoO_6.

3. Absence of Jahn-Teller distortion in $SrFeO_3$

The ground state of the Fe^{4+} ions in the cubic perovskite $SrFeO_3$ derives from the high-spin $t_{2g}^3 e_g^1$ (^5E) state. At first sight, it is surprising that this double-degenerate state does not exhibit a (cooperative) Jahn-Teller distortion. This apparent discrepancy can be reconciled taking into account the relatively large occupancy of the $3d^5\underline{L}$ configuration. In fact, the ground state of $SrFeO_3$ is dominated by the $3d^5\underline{L}$ configuration (58%) and not by the $3d^4$ configuration (36%). The main $3d^5$ component of the $3d^5\underline{L}$ configuration is given by the high-spin $t_{2g}^3 e_g^2$ ($^6A_1$) state which inhibits the distortion. The isoelectronic Mn^{3+} ions in $LaMnO_3$ are also in a high-spin $t_{2g}^3 e_g^1$ (^5E) state and present a Jahn-Teller distortion, but in this case, the ground state (given by 55% $3d^4$, 40% $3d^5\underline{L}$, and 5% $3d^6\underline{L}^2$) is more ionic than in $SrFeO_3$. This indicates that a strong covalency could eventually quench Jahn-Teller distortions (and/or charge-ordering phenomena).

4. Magnetic moment at the oxygen sites

The ground state of the $SrFeO_3$ and $SrCoO_3$ compounds contains a considerable amount of O $2p$ hole character. This follows from the relatively large occupancy of the charge-transfer configurations $3d^{n+1}\underline{L}$ in the ground state. In turn, this fact helps to explain the relatively large magnetic moment observed at the O sites in both compounds. The magnetic moment at the O sites derived from neutron measurements is approximately $0.1\mu_B$ in both cases.[17] A magnetic moment at the O sites was also observed in O $1s$ magnetic-circular-dichroism results in $SrCoO_3$.[18] The magnetic moment obtained from LSDA calculations is about $0.14\mu_B$ for $SrFeO_3$ and $0.19\mu_B$ for $SrCoO_3$.[16] The larger moment for $SrCoO_3$ can be understood taking into account that $SrCoO_3$ is more covalent than $SrFeO_3$ (the occupancy of the charge transfer $3d^{n+1}\underline{L}$ configuration in $SrCoO_3$, 67%, is larger than that in $SrFeO_3$, 58%).

5. Origin of the ferromagnetism in $SrFe_{1-x}Co_xO_3$

The microscopic origin of the ferromagnetism in the $SrFe_{1-x}Co_xO_3$ compound is not completely understood yet. As indicated above, the dominating interactions in the starting member of the series, $SrFeO_3$, are ferromagnetic.[3] In fact, a relatively small amount of Co, $x \geqslant 0.2$, is enough to turn the $SrFe_{1-x}Co_xO_3$ material ferromagnetic.[5] The main question left is how the Co presence quench the residual antiferromagnetic interactions in $SrFeO_3$.[3] The most invoked possibilities would be the double-exchange mechanism and half-metallic ferromagnetism. The first is related to a model of fluctuations between (localized) spins, whereas the second derives from (itinerant) band structure calculations.

We argue that a mechanism based on double-exchange is unlikely in the mixed $SrFe_{1-x}Co_xO_3$ compound, simply because the potential felt by the supposedly active e_g electrons at the Fe and Co sites is different (although, we must note here that a double-exchange mechanism remains a valid possibility in pure $SrCoO_3$).[13] The second possibility is that the Co ions induce a minimum at E_F in the majority e_g band of $SrFe_{1-x}Co_xO_3$, eventually turning the material ferromagnetic as in the alternative half-metallic ferromagnetism scenario. In this sense, the ferromagnetism in $SrFe_{1-x}Co_xO_3$ resembles the half-metallic ferromagnetism in Sr_2FeMoO_6,[2] and not the double-exchange ferromagnetism often proposed for manganites, such as $La_{1-x}Ca_xMnO_3$.[1]

6. Magnetoresistance mechanism in $SrFe_{1-x}Co_xO_3$

The origin of the magnetoresistance mechanism in the $SrFe_{1-x}Co_xO_3$ compound[6] remains unclear at the moment. The main possibilities would be based on the double-exchange mechanism and on tunneling between ferromagnetic phases. Again, the double-exchange mechanism is not possible due to the potential differences between the Fe and Co sites. Tunneling between ferromagnetic phases, within a phase separation scenario,[19] seems to be a more likely explanation. In fact, this scenario is supported by previous studies of the magnetic properties of the Fe-rich phase of $SrFe_{1-x}Co_xO_3$. These studies suggest that $SrFe_{1-x}Co_xO_3$ ($x \leqslant 0.15$) is composed by ferromagnetic islands coupled antiferromagnetically.[5]

We note that large magnetoresistance in Sr_2FeMoO_6 is observed in polycrystalline samples and not in single crystals.[2] This was interpreted as being due to tunneling between half-metallic ferromagnetic grains in the polycrystalline samples.[2] In this sense, the origin of the magnetoresistance in $SrFe_{1-x}Co_xO_3$ seems to be similar to the origin in Sr_2FeMoO_6,[2] and has less in common with double-exchange based explanations usually proposed for manganites such as $La_{1-x}Ca_xMnO_3$.[1] It remains to be checked if the inhomogeneities in $SrFe_{1-x}Co_xO_3$ are intrinsic or due to the microstructure of the samples, this could be eventually tested by means of magnetotransport measurements in single crystals of $SrFe_{1-x}Co_xO_3$.

7. Negative charge-transfer character of $SrFe_{1-x}Co_xO_3$

The analysis of the spectra above shows that the $SrFe_{1-x}Co_xO_3$ compound is in the negative charge-transfer

regime.[12] This means that the ionic state is not really Fe^{4+} and Co^{4+}, but rather that the charge state is compensated by O $2p$ holes (in terms of the CI cluster model, the occupation of the $3d^{n+1}\underline{L}$ configuration is larger than that of the $3d^n$ configuration). Therefore, $SrFe_{1-x}Co_xO_3$ illustrates both ferromagnetism and magneto-resistance in a negative charge-transfer material, and confirms that the ground state of $SrFe_{1-x}Co_xO_3$ is qualitatively different from manganites[1] and double perovskites.[2] We note that $La_{1-x}Ca_xMnO_3$ is in a mixed charge-transfer/Mott-Hubbard regime and has a dominating $3d^n$ configuration.[14] The situation is less clear in Sr_2FeMoO_6, although recent XAS studies show that the Fe ions are indeed in a Fe^{3+} state, with a mixed pd-metal ground state which is mostly dominated by the first ionic $3d^n$ configuration.[20]

IV. SUMMARY AND CONCLUSIONS

In summary, we studied the relation between the electronic structure and the physical properties of $SrFe_{1-x}Co_xO_3$. The main technique used in the study was Fe $2p$, Co $2p$, and O $1s$ x-ray absorption spectroscopy (XAS). The experimental spectra were analyzed in terms of the configuration-interaction cluster model calculation. The analysis of the spectra shows that both $SrFeO_3$ and $SrCoO_3$ are in the negative-charge transfer regime (this means that their ground states are mostly covalent and contain considerable O $2p$ hole character). $SrFeO_3$ is in a high-spin state and $SrCoO_3$ in an intermediate-spin state stabilized by strong hybridization. The local electronic structure and the corresponding spin state are mostly preserved in $SrFe_{1-x}Co_xO_3$. The relatively large O $2p$ hole weight in the ground state explains the absence of Jahn-Teller distortions, as well as the relatively large value of the magnetic moment observed at the O sites in these materials. The origin of the magnetoresistance in the $SrFe_{1-x}Co_xO_3$ compound remains unclear at the moment. The double-exchange mechanism seems unlikely due to the difference in the Fe and Co on-site energies. Tunneling between ferromagnetic phases, within a phase separation scenario, is a more likely explanation. $SrFe_{1-x}Co_xO_3$ illustrates both ferromagnetism and magnetoresistance in a negative charge-transfer material. The ground state is qualitatively different from manganites, such as $La_{1-x}Ca_xMnO_3$, and double-perovskites, such as Sr_2FeMoO_6.

ACKNOWLEDGMENTS

We would like to thank the technical staff of the LNLS for their helpful assistance during the measurements. We would like to thank D.D. Sarma for useful comments on the manuscript. This work was partially supported by CNPq, PRONEX, LNLS, Fundación Antorchas and Fundação Araucaria.

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