

Electronic structure of the two-dimensional negative charge-transfer material Sr_3FeMO_7 ($M=\text{Fe}, \text{Co}$)

M. Abbate,^{1,*} L. Mogni,² F. Prado,² and A. Caneiro²¹*Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19091, 81531-990 Curitiba PR, Brazil*²*Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, 8400 San Carlos de Bariloche RN, Argentina*

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We studied the relation between the electronic structure and the physical properties of Sr_3FeMO_7 ($M=\text{Fe}, \text{Co}$). The main technique used in the study was Fe 2*p*, Co 2*p*, and O 1*s* x-ray-absorption spectroscopy. The experimental spectra were analyzed in terms of cluster model and band-structure calculations. The analysis of the spectra shows that both $\text{Sr}_3\text{FeFeO}_7$ and $\text{Sr}_3\text{FeCoO}_7$ are in the negative-charge-transfer regime (this means that their ground states are highly covalent and contain considerable O 2*p* hole character). The Fe ions are in a high-spin state and the Co ions in an intermediate-spin state stabilized by strong hybridization. The electronic structure helps to explain the trends in the electrical conductivity and the observed magnetic moments. Further, the relatively large O 2*p* hole weight in the ground state explains also the absence of Jahn-Teller distortions. $\text{Sr}_3\text{FeCoO}_7$ illustrates ferromagnetism and magnetoresistance in a two-dimensional negative-charge-transfer material.

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I. INTRODUCTION

The Ruddlesden-Popper material $\text{Sr}_3M_2O_7$ ($M=\text{Fe}, \text{Co}$) has transition-metal ions in an M^{4+} tetravalent state.^{1,2} The crystal structure can be viewed as two SrMO_3 perovskite layers stacked between a SrO rock salt layer.³⁻⁶ The structure is tetragonal (space group $I4/mmm$) with a distinct two-dimensional (2D) character due to the insulating SrO layer. The substituted $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_7$ compounds are semiconductors characterized by (thermally) activated carriers.³⁻⁶ The electrical conductivity of the series increases several orders of magnitude as the Co content increases. Further, the mixed compound exhibits a relatively large (up to 45%) negative magnetoresistance.^{7,8}

The electronic structure of the pure $\text{Sr}_3\text{Fe}_2\text{O}_7$ compound was studied using reflectance⁹ and x-ray photoemission spectroscopy (XPS).¹⁰ These studies showed that $\text{Sr}_3\text{Fe}_2\text{O}_7$ is in the negative-charge-transfer regime and the gap is of the *p-p* type. The electronic structure of the mixed $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_7$ series was studied using Mössbauer^{4,5} and x-ray-absorption near-edge structure (XANES).^{5,6} These studies confirmed that the transition-metal ions are in a highly covalent and formally tetravalent ground state. Despite these efforts, the electronic structure of the mixed $\text{Sr}_3\text{FeCoO}_7$ material was not completely elucidated. This information is needed to understand the origin of the interesting physical properties of these compounds.

The purpose of this work is to study the electronic structure of the Sr_3FeMO_7 material ($M=\text{Fe}, \text{Co}$). The technique used in the study was Fe 2*p*, Co 2*p*, and O 1*s* x-ray-absorption spectroscopy (XAS).¹¹ The experimental results were analyzed in terms of combined cluster model and band-structure calculations.¹¹ The analysis of the spectra shows that these materials are in the negative-charge-transfer regime. These results show that the ground state is highly covalent and contains considerable O 2*p* hole character. The band gap involves *p-p* fluctuations and is opened due to a

relatively large value of the O 2*p*-*M* 3*d* hybridization. The electronic structure helps to explain the trends in the electrical conductivity, the observed magnetic moments, and the absence of Jahn-Teller distortions.

II. EXPERIMENTAL DETAILS

The Sr_3FeMO_7 ($M=\text{Fe}, \text{Co}$) samples were prepared using an acetic acid based gel route. The resulting powder was pressed into pellets and fired in air at 1300 °C during 24 h. The pellets were then annealed in flowing O_2 at 700 °C during 12 h, and cooled down to room temperature at a rate of 1 °C/min. The oxygen content after the annealing procedure was determined by iodometric titration (the content was about 6.76 for the pure Fe sample and around 6.67 for the mixed Fe/Co sample). The x-ray diffraction (XRD) analysis confirmed that the samples were a single phase with the correct structure.³ The electrical and magnetic properties of these samples were similar to those reported previously.³

The XAS spectra were measured in the spherical-grating (SGM) beam line at the Laboratório Nacional de Luz Síncrotron (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 collected using the total-electron-yield method with a probing depth of around 50 Å.¹² The energy resolution at the Fe 2*p* and Co 2*p* edges was 0.7 eV and at the O 1*s* edge was about 0.5 eV. The energy scale was calibrated using the corresponding peak positions in SrFeO_3 and SrCoO_3 . The spectra were normalized to the maximum after a constant background subtraction.

III. RESULTS AND DISCUSSION

A. Fe 2*p* XAS spectra

Figure 1 shows the Fe 2*p* XAS spectrum of the pure $\text{Sr}_3\text{FeFeO}_7$ compound. This result is similar to the spectrum

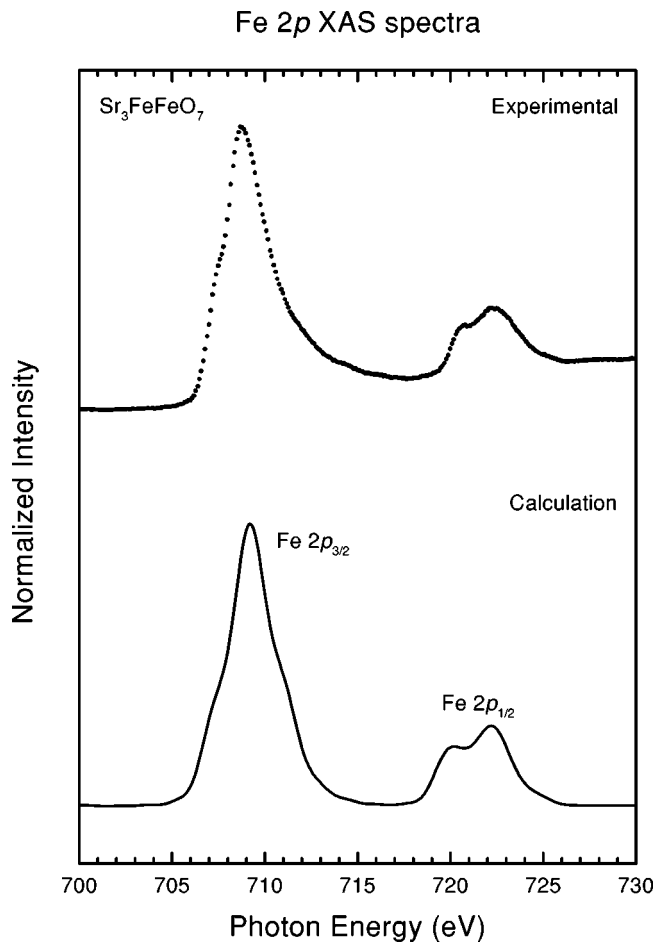


FIG. 1. Fe $2p$ x-ray-absorption spectra of $\text{Sr}_3\text{FeFeO}_7$ (dots) compared to the cluster model calculation (solid line).

of the closely related 3D material SrFeO_3 , which has also Fe^{4+} ions.¹³ The spectrum corresponds to $\text{Fe } 2p \rightarrow \text{Fe } 3d$ transitions and is dominated by multiplet effects.¹¹ The spectrum is split by the Fe $2p$ spin-orbit interaction into the $2p_{3/2}$ and $2p_{1/2}$ regions. These regions are further split by $2p$ - $3d$ and $3d$ - $3d$ electrostatic interactions as well as crystal-field effects. The shape of the multiplet in the spectrum is 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.

The Fe $2p$ XAS spectrum of $\text{Sr}_3\text{FeFeO}_7$ corresponds to Fe^{4+} ($3d^4$) ions in a high-spin (5E) state. The calculation based on the single ionic configuration $t_{2g}^3e_g^1$ (5E) does not account for the spectrum, because the ground state contains also considerable $3d^5\bar{L}$ character (where \bar{L} denotes a ligand O $2p$ hole). Thus, the calculation must include also the contributions of the charge-transfer configurations $3d^5\bar{L}$ [the main $3d^5$ component of the $3d^5\bar{L}$ configuration is given by the high-spin $t_{2g}^3e_g^2$ (6A_1) state].

The charge-transfer configurations were included using the configuration-interaction method. The ground state of the Fe ions was expanded in terms of the $3d^4$, $3d^5\bar{L}$, and $3d^6\bar{L}^2$ configurations. The main parameters were the charge-transfer energy Δ , the Mott-Hubbard repulsion U , and the transfer integral T_σ . The values of the model parameters (Δ

$=0$ eV, $U=7.5$ eV, and $T_\sigma=2.2$ eV) were obtained from Ref. 14. The occupations of the different configurations in the ground state are 36% $3d^4$, 58% $3d^5\bar{L}$, and 6% $3d^6\bar{L}^2$. Figure 1 shows that the calculation is in very good agreement with the features in the $\text{Sr}_3\text{FeFeO}_7$ spectrum.

The calculation above shows that the ground state of the Fe ions is dominated by the $3d^5\bar{L}$ configuration. This happens because the $\text{Sr}_3\text{FeFeO}_7$ compound is in the negative-charge-transfer regime (the effective charge-transfer parameter Δ_{ct} is actually negative due to multiplet splitting).¹⁵ This regime is characteristic of compounds with transition-metal ions in a relatively high oxidation state. The occupations show that the ground state of the Fe ions is highly covalent and dominated by O $2p$ holes.

The Fe $2p$ XAS spectrum of $\text{Sr}_3\text{FeCoO}_7$, not shown here for brevity, presents only minor changes. The absence of changes indicates that the Fe ions remain in a high-spin Fe^{4+} state in the mixed material. Further, the Fe ground state is also highly covalent and is dominated by considerable O $2p$ hole weight. The analysis of the Co $2p$ XAS spectrum below shows that the same arguments apply to the Co ions. Therefore, the overall ground state of the mixed $\text{Sr}_3\text{FeCoO}_7$ material is also in the negative-charge-transfer regime.

B. Co $2p$ XAS spectra

Figure 2 shows the Co $2p$ XAS spectrum of the mixed $\text{Sr}_3\text{FeCoO}_7$ compound. The spectrum resembles the result of the closely related 3D material SrCoO_3 , which has also Co^{4+} ions.¹³ The shape of the spectrum corresponds to Co^{4+} ($3d^5$) ions in an intermediate-spin (4T_1) state. In a purely ionic picture, the ground state of the Co^{4+} should be either a high-spin (6A_1) or a low-spin (2T_2) state. The $t_{2g}^4e_g^1$ (4T_1) intermediate-spin state is stabilized by the hybridization with the $3d^6\bar{L}$ configuration [the main $3d^6$ component of the $3d^6\bar{L}$ configuration is given by the high-spin $t_{2g}^4e_g^2$ (5T_2) state].

The calculation must again include the contributions of the charge-transfer configurations. The ground state of the Co ions was expanded in terms of the $3d^5$, $3d^6\bar{L}$, and $3d^7\bar{L}^2$ configurations. The values of the model parameters ($\Delta=-2$ eV, $U=7.5$ eV, and $T_\sigma=2.0$ eV) were obtained from Ref. 16. The occupations of the different configurations in the ground state are 22% $3d^5$, 67% $3d^6\bar{L}$, and 11% $3d^7\bar{L}^2$. Figure 2 shows that the calculation reproduces reasonably well the features in the Co $2p$ XAS spectrum. The extra peaks around 783 and 798 eV are attributed to contributions from higher-order configurations (these contributions are larger than in the Fe $2p$ XAS spectra due to the larger weight of the $3d^{n+2}\bar{L}^2$ configuration).

The calculation shows that the ground state of the Co ions is dominated by the $3d^6\bar{L}$ configuration. This means that the ground state of the Co ions is highly covalent and contains a considerable amount of O $2p$ holes (which is to be expected directly from the negative value of the charge-transfer parameter Δ in this case). The same conclusions for the Fe ions were obtained from the analysis of the Fe $2p$ XAS spectrum above. This shows that the mixed

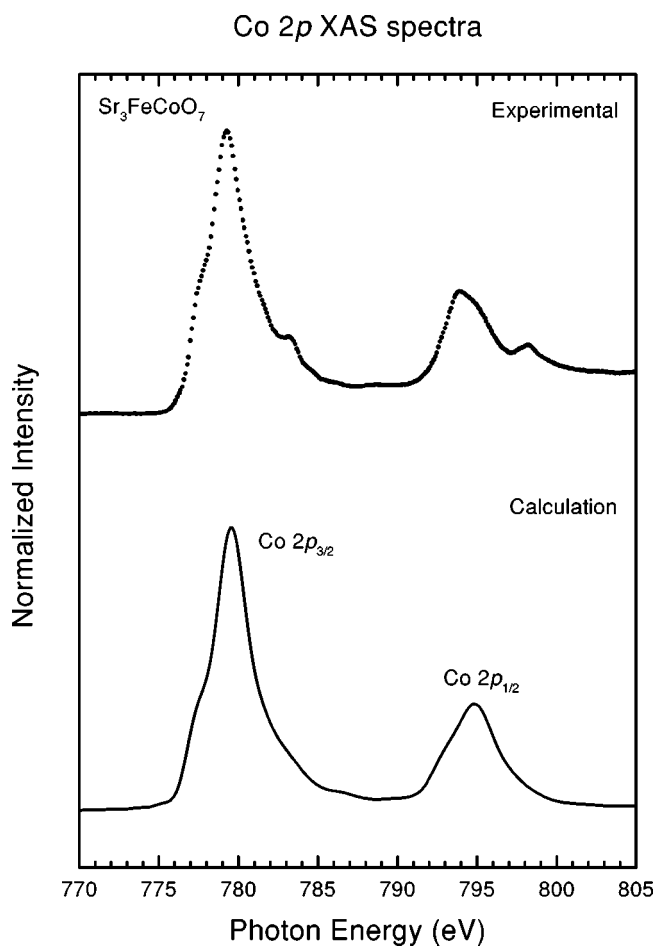


FIG. 2. Co $2p$ x-ray-absorption spectra of $\text{Sr}_3\text{FeCoO}_7$ (dots) compared to the cluster model calculation (solid line).

$\text{Sr}_3\text{FeCoO}_7$ compound, as a whole, is in the negative-charge-transfer regime.

C. O $1s$ XAS spectra

Figure 3 shows the O $1s$ x-ray-absorption spectra of the $\text{Sr}_3\text{FeFeO}_7$ and $\text{Sr}_3\text{FeCoO}_7$ compounds. These results are similar to the spectra of the closely related 3D materials SrFeO_3 and $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_3$.¹³ The spectra correspond to transitions from the O $1s$ level to empty O $2p$ states in the conduction band.¹¹ These O $2p$ states reflect, due to the metal-oxygen hybridization, different bands of mostly metal character. The peaks around 528–532 eV correspond to the Fe/Co $3d$ band, the structure around 533–539 eV corresponds to the Sr $4d$ band, and the bumps around 540–548 eV correspond to the Fe/Co $4sp$ band. These assignments are consistent with previous analysis of the SrMnO_3 , SrFeO_3 , and SrCoO_3 O $1s$ XAS spectra.^{17,18}

Figure 4 shows the Fe/Co $3d$ band region of $\text{Sr}_3\text{FeFeO}_7$ and $\text{Sr}_3\text{FeCoO}_7$ in a more detailed scale. The Fe/Fe $3d$ region of the pure $\text{Sr}_3\text{FeFeO}_7$ material can be analyzed using a band-structure calculation. The LDA calculation was done using the standard linear muffin-tin orbital (LMTO) method.^{19,20} The exchange and correlation part of the potential was obtained using the von Barth–Hedin

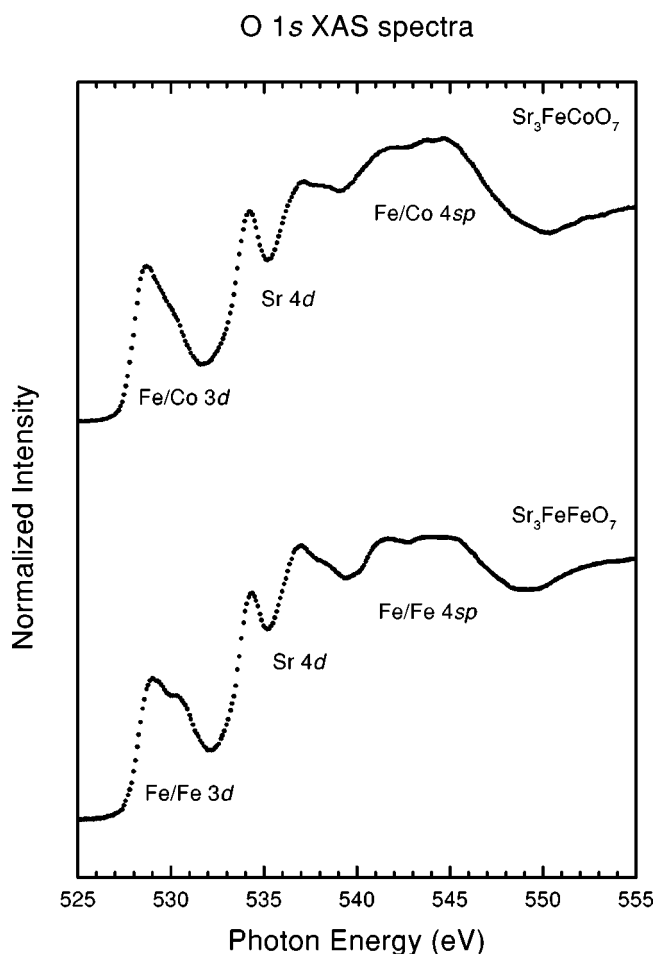


FIG. 3. O $1s$ x-ray-absorption spectra of $\text{Sr}_3\text{FeFeO}_7$ and $\text{Sr}_3\text{FeCoO}_7$ (dots).

approximation. The space group, the lattice parameters, and the nonequivalent atomic positions were taken from Ref. 2. The self-consistent potential and the density of states were obtained using 13 irreducible \mathbf{k} points.

Figure 4 compares the Fe $3d$ region of $\text{Sr}_3\text{FeFeO}_7$ to the calculated O $2p$ partial density of states. The calculated spectrum was broadened with a 0.5 eV Gaussian function to take into account the energy resolution. The energy scale and the intensity of the calculation were adjusted so as to match the experiment. The calculated spectrum reproduces reasonably well the main features in the experimental spectrum. The main peak at threshold, around 529 eV, corresponds to the minority spin Fe t_{2g} band, whereas the shoulder corresponds to the majority/minority e_g bands. The e_g band in the experiment spectrum is enhanced due to the attraction of the O $1s$ core-hole potential; the same argument was used to explain the discrepancy in the e_g band of the SrTiO_3 compound.²¹

D. Physical properties

The ground state of the Fe ions in $\text{Sr}_3\text{FeFeO}_7$ derives from the high-spin $t_{2g}^3 e_g^1 ({}^5E)$ configuration. This double-degenerate state is unstable and should lead to a Jahn-Teller distortion which is not observed. However, the ground state

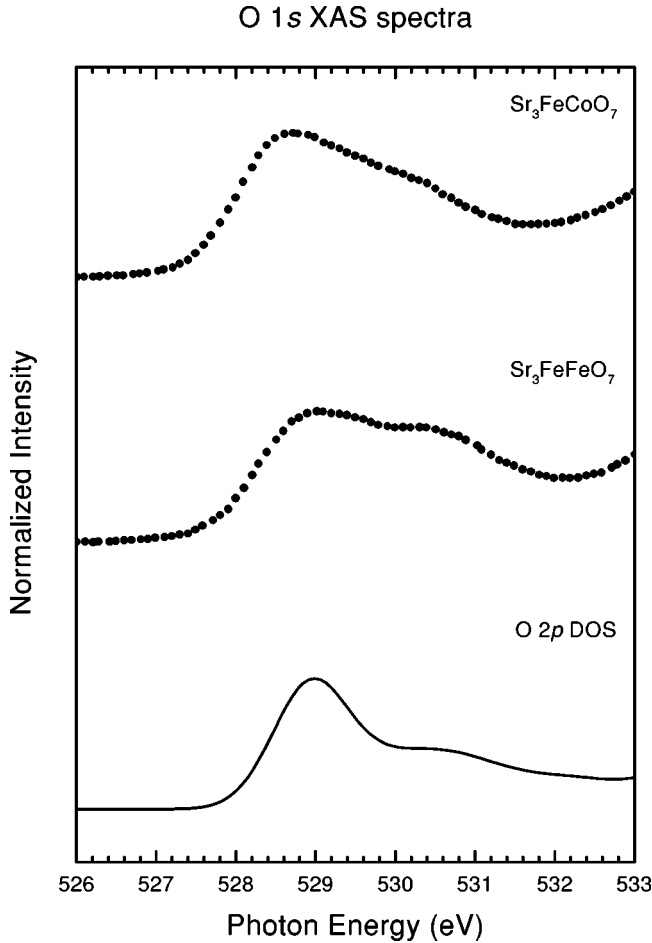


FIG. 4. Fe/Co $3d$ region of the O $1s$ XAS spectra of $\text{Sr}_3\text{FeFeO}_7$ and $\text{Sr}_3\text{FeCoO}_7$ (dots) compared to the O $2p$ partial density of states for $\text{Sr}_3\text{FeFeO}_7$ (solid line).

of $\text{Sr}_3\text{FeFeO}_7$ is dominated by the $3d^5\bar{L}$ configuration with a weight of 58%. The main $3d^5$ component of the $3d^5\bar{L}$ configuration is given by the high-spin $t_{2g}^3e_g^2$ (6A_1) state; the orbital part of this state is fully symmetric (A_1), which inhibits the Jahn-Teller distortion. This example illustrates that a strong covalent character could eventually quench a Jahn-Teller distortion; the same argument was invoked to explain the absence of Jahn-Teller distortion in the related $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ material.¹³

The occupation of the $3d^{n+1}\bar{L}$ configuration in Sr_3FeMO_7 is larger than that of the $3d^n$ configuration. This means that the ground state is dominated by O $2p$ holes in a negative-charge-transfer regime.¹⁵ But the $3d^{n+1}\bar{L}$ configuration is actually a continuum and should lead to a metallic ground state. The band gap in the Sr_3FeMO_7 material appears because the hybridization T_σ is larger than the bandwidth W .¹⁵ The lowest-lying charge excitations in this regime are of the form $3d^{n+1}\bar{L} + 3d^{n+1}\bar{L} \rightarrow 3d^{n+1} + 3d^{n+1}\bar{L}^2$. These charge fluctuations involve O $2p$ holes and the band gap is consequently of the p - p type.¹⁵

The band gap, in this case, depends on the relative magnitude of the hybridization T_σ and the bandwidth W .¹⁵ The value of the T_σ model parameter decreases from 2.2 eV in $\text{Sr}_3\text{FeFeO}_7$ to 2.0 eV in $\text{Sr}_3\text{FeCoO}_7$. Contrarily, the value of

the bandwidth W is not expected to change much because the crystal structure is the same. Thus, the smaller value of the hybridization in $\text{Sr}_3\text{FeCoO}_7$ would effectively decrease the band gap, helping to explain the marked increase in the electrical conductivity of the mixed compound (this effect seems to be more important than the tendency to charge localization due to Fe/Co potential disorder).

The effective magnetic moment μ_{eff} per Fe/Co site can be estimated using the spin-only formula $\mu = g \mu_B [S(S+1)]^{1/2}$. The relative fraction of Fe/Co⁴⁺ and Fe/Co³⁺ ions was obtained from the oxygen content of the samples. The spin state of the Fe/Co ions was obtained from the analysis of the electronic structure above. The calculated moment for $\text{Sr}_3\text{FeFeO}_7$ was $5.14\mu_B$, in good agreement with the experimental $5.24\mu_B$ value. The calculated moment for $\text{Sr}_3\text{FeCoO}_7$ was $4.49\mu_B$, which is reasonably close to the experimental value of $4.19\mu_B$. This shows that the calculated electronic structure is consistent with the observed magnetic moments.

The analysis above shows that the Sr_3FeMO_7 compound is in the negative-charge-transfer regime. The most important degrees of freedom in this regime are O $2p$ holes rather than Fe/Co $3d$ electrons. In this sense, the ground state of Sr_3FeMO_7 is qualitatively different from manganites and double perovskites.¹³ In these other materials, the ground state is less covalent and dominated by the transition-metal $3d$ electrons. The $\text{Sr}_3\text{FeCoO}_7$ compound exhibits ferromagnetism and magnetoresistance in a 2D negative-charge-transfer material. The origin of these properties should be different from those invoked for manganites and double perovskites.

IV. SUMMARY AND CONCLUSIONS

In summary, we studied the electronic structure of the substituted Sr_3FeMO_7 compound ($M=\text{Fe,Co}$). The main technique used in the study was Fe $2p$, Co $2p$, and O $1s$ x-ray-absorption (XAS) spectroscopy. The experimental spectra were analyzed in terms of cluster model and band-structure calculations. The analysis of the spectra shows that these materials are in the negative-charge-transfer regime (this means that their ground states are highly covalent and contain considerable O $2p$ hole character). The Fe ions are in a high-spin state and the Co ions in an intermediate-spin state stabilized by strong hybridization. The relatively large O $2p$ hole weight in the ground state explains the absence of Jahn-Teller distortions. The electronic structure helps to explain the trends in the electrical conductivity and the observed magnetic moments. $\text{Sr}_3\text{FeCoO}_7$ illustrates both ferromagnetism and magnetoresistance in a 2D negative-charge-transfer material. The nature of the ground state is qualitatively different from manganites and double perovskites.

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- *Corresponding author. Email address: miguel@fisica.ufpr.br
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