

High pressure synthesis, crystal, magnetic structure and magnetotransport of $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$

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Abstract

A polycrystalline sample with $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ stoichiometry has been prepared under moderate pressures of 2 GPa in the presence of KClO_4 as oxidizing agent. The crystallographic and magnetic structures have been studied from neutron powder diffraction (NPD), complemented with magnetotransport and magnetic susceptibility data. The study of the crystallographic structure confirms that this compound, with the actual stoichiometry $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{2.88(3)}$, is a simple cubic perovskite at 2 and 295 K, defined in the $Pm\bar{3}m$ space group, where Fe and Co atoms are distributed at random over the B positions. The magnetic measurements show that $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{2.88}$ is a ferromagnet with $T_C \approx 330$ K, which is also confirmed by neutron diffraction: the magnetic structure is collinear, characterized by a propagation vector $\mathbf{k} = 0$; the ordered magnetic moment values for the $(\text{Fe}^{4+}, \text{Co}^{4+})$ cations are 1.54(9) and 0.65(15) μ_B at $T = 2$ and 295 K, respectively. Transport measurements show a semiconducting behaviour, and a negative magnetoresistance (MR) of -6.5% is observed at $T = 5$ K for $H = 9$ T.

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1. Introduction

The discovery of colossal magnetoresistance (MR) effects in perovskite manganites [1] originated the search of new magnetoresistive compounds in various ferromagnetic (FM) transition-metal oxides families, among which $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ oxides have been relatively less studied [2]. The $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ family is interesting because, whereas the end-member SrFeO_3 is antiferromagnetic (AFM), for intermediate compositions ($0.2 \leq x \leq 1.0$) FM properties have been described. SrFeO_3 presents a cubic perovskite structure ($Pm\bar{3}m$ space group) and becomes magnetically long-range ordered below $T_N = 134$ K with an antiferromagnetic helical magnetic structure defined by the propagation vector $k = 0.135a^*$, directed along the $\langle 111 \rangle$

direction [3]. SrCoO_3 has also a cubic perovskite crystallographic structure ($Pm\bar{3}m$) which adopts a long-range FM structure ($\mathbf{k} = 0$) below $T_c = 280$ K [4]. Both SrFeO_3 and SrCoO_3 are metallic down to 4 K. The study of the electronic structure [5,6] of both perovskites has indicated that both Fe and Co cations are tetravalent, Fe^{4+} and Co^{4+} . In a simple picture, Fe^{4+} cations (d^4) are in a high spin ground state, $t_{2g}^3 e_g^1$, whereas Co^{4+} (d^5) are in low spin state, $t_{2g}^5 e_g^0$. The chemical bonds between the $\text{O}(2p)$ – $\text{Fe}(3d)$ and $\text{O}(2p)$ – $\text{Co}(3d)$ orbitals are strongly covalent, leading to the formation of a large conduction band and accounting for the metallic properties of both compounds. This fact also seems to justify the absence of the Jahn–Teller distortion for the Fe compound, in such a way that both crystallographic structures remain cubic.

In the solid solution system $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$, the Fe-rich compounds become ordered with an AFM screw structure and the magnetic transition temperature T_N decreases with

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the Fe content. Interestingly, in the vicinity of $x = 0.2$ an AFM–FM transition takes place, and the compounds with $x > 0.2$ present a FM structure [7,8]. The ordering temperature T_C of the FM phases increases from 230 K for $x = 0.2$ up to 350 K for $x = 0.6$, but for $x > 0.6$ the ordering temperature starts to decrease down to 280 K for $x = 1$ [9]. All the compounds of the system are metallic and their crystal structure is cubic.

The physical properties of the nonstoichiometric compounds $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ have also been investigated [2,9,10]. The oxygen deficiency provokes important changes in the transport properties; the samples synthesized in air present the higher oxygen deficiency and they are semiconducting and weakly FM. However, the samples annealed under a relatively high oxygen pressure show a conductivity nearly independent on the temperature and exhibit a noticeable negative MR at low temperature. MR effects up to -65% at 4 K and 5 T have been achieved in the system $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ [2,11]. The percentage of MR increases from the compound corresponding to $x = 0$, reaching a maximum for $x = 0.4$; above this Co contents the MR effect decreases and vanishes for $\text{SrCoO}_{3-\delta}$. The compounds are FM for $x > 0.2$, but the transition temperatures are lesser than those corresponding to the stoichiometric compounds.

In this work, we have prepared under moderate-pressure conditions a slightly oxygen defective perovskite with $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{2.88(3)}$ stoichiometry, exhibiting a FM T_C above RT; we report on a study from neutron diffraction measurements, analysing the crystallographic and magnetic structure in complement with magnetization and transport measurements.

2. Experimental section

The elaboration of $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ required the previous preparation of very reactive precursors, obtained by wet-chemistry techniques. A mixture of $\text{Sr}(\text{NO}_3)_2$, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in citric acid with addition of some droplets of HNO_3 to oxidize Fe to the trivalent state; the solution was slowly evaporated, leading to an organic resin which was dried at 120°C and slowly decomposed at temperatures up to 600°C . The sample was then heated at 800°C for 2 h in order to eliminate all the organic materials and nitrates. This precursor was thoroughly ground with KClO_4 (30% in weight), put into a gold capsule (8 mm diameter, 10 mm length), sealed and placed in a cylindrical graphite heater. The reaction was carried out in a piston-cylinder press (Rockland Research Co.), at a pressure of 2 GPa at 1000°C for 25 min. Then the material was quenched to room temperature and the pressure was subsequently released. The raw product was obtained as irregular-shaped pellets, some of which were kept for the transport measurements. A fraction of the raw material was ground and washed with water in order to dissolve KCl coming from the decomposition of KClO_4 ; then the powder sample was dried in air at 150°C for 1 h.

The magnetic measurements were performed in a commercial SQUID magnetometer from Quantum Design. The dc magnetic susceptibility was measured in the temperature interval $1.9 < T < 395$ K under a 1 kOe magnetic field; the measurements were carried out under both zero-field cooling (ZFC) and field cooling (FC) conditions. Isothermal magnetization curves were obtained at $T = 1.9$, 65 and 200 K, for a magnetic field ranging from -50 to 50 kOe. The resistivity measurements were performed by the conventional four-probe technique on an as-grown pellet, under a zero and a 9 T magnetic field and in the 5–300 K temperature range.

Neutron powder diffraction (NPD) data were collected at the Institut Laue-Langevin, Grenoble (France). Two neutron diffraction patterns were acquired at the high-resolution D2B diffractometer with $\lambda = 1.59 \text{ \AA}$, at room temperature (295 K) and at 2 K; the patterns were obtained in the angular range $-4.95 < 2\theta < 162^\circ$ with a 0.05° step. The NPD patterns were analysed by the Rietveld method [12] by using the Fullprof programme [13]. A pseudo-Voigt function was considered to generate the profile shape; the background was fitted to a fifth-degree polynomial function. The coherent scattering lengths for Sr, Fe, Co and O were, 7.02, 9.45, 2.49 and 5.803 fm, respectively.

3. Results

3.1. Magnetic and transport measurements

Fig. 1 shows the thermal variation of the dc susceptibility. The ZFC and FC curves, that are coincident at high temperatures, start to diverge below 330 K, exhibiting a thermal dependence characteristic of a FM order, in good agreement with previously reported data for $x = 0.5$. The ordering temperature, $T_C \approx 330$ K, is slightly smaller than the transition temperature corresponding to the fully

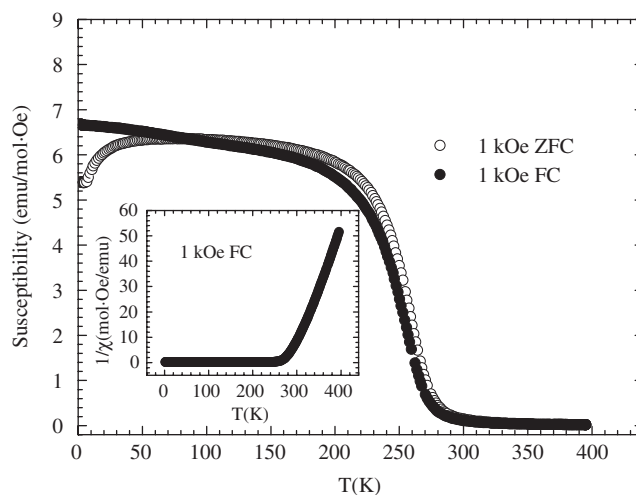


Fig. 1. Thermal variation of the dc susceptibility measured in field cooling (FC) and zero-field cooling (ZFC) conditions under a 1 kOe magnetic field. Inset: thermal evolution of the inverse of the susceptibility (FC curve).

oxygen-stoichiometric compound $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_3$, $T_C \approx 340$ K [9]. This fact possibly indicates the existence of a slight oxygen deficiency in the sample. Below the ordering temperature, the ZFC susceptibility increases and reaches a plateau and then decreases on cooling below 30 K. In contrast, the FC susceptibility, after undergoing a sharp increase below T_C , exhibits a plateau characteristic of a ferromagnet.

The inverse of the susceptibility is displayed in the inset of Fig. 1; a linear fit to the Curie–Weiss law in the temperature interval $370 < T < 395$ K yields a paramagnetic temperature $\theta_P = 295(2)$ K, indicating FM interactions, and an effective magnetic moment value $p_{\text{eff}} = 3.96(1) \mu_B$ per formula. The theoretical effective magnetic moment can be estimated through the expression $\mu_{\text{eff}} = (0.5(\mu_{\text{Fe}^{4+}})^2 + 0.5(\mu_{\text{Co}^{4+}})^2)^{1/2}$. In case that the high-spin configuration is considered for the Fe^{4+} cations (5D_0) and the low-spin for Co^{4+} ($^6S_{5/2}$), the effective spin-only magnetic moments are 4.90 and $1.73 \mu_B$, respectively; so a theoretical effective magnetic moment of $3.67 \mu_B$ would be obtained for stoichiometric $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_3$. However, an oxygen deficiency implies the presence of some Fe^{3+} and Co^{3+} cations. In this case, for a high- and low-spin configurations in Fe^{3+} and Co^{3+} the magnetic moments are $5.92 \mu_B$ and 0, respectively; for the defective composition $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{2.5}$ the expected theoretical magnetic moment would be $4.19 \mu_B$. Therefore, the effective paramagnetic moment determined from the Curie–Weiss law is between the two extreme values.

The isothermal magnetization curves measured at $T = 1.9$, 65 and 200 K are displayed in Fig. 2. At $T = 1.9$ and 65 K an hysteresis cycle is clearly observed with a remnant magnetization of 1.36 and $0.30 \mu_B$ per formula, respectively. Although at $T = 200$ K there is no hysteresis cycle, the dependence of the magnetization with the magnetic field is characteristic of a FM order. At $T = 1.9$ K the magnetization does not reach saturation even for

a 50 kOe magnetic field; the maximum magnetization is around $2.3 \mu_B$ per formula.

The thermal evolution of the resistivity under a 0 and 9 T magnetic field is shown in Fig. 3. In both curves the resistivity increases on cooling, exhibiting a semiconductor-like behaviour in all the temperature range. As it can be observed in the inset of Fig. 3, the application of a magnetic field gives rise to the appearance of a small negative MR. A maximum MR of around 6.5% is observed at $T = 5$ K which gradually drops to $MR \approx -2\%$ and remains nearly constant above 70 K; The important fluctuations observed in the MR curves immediately below RT are ascribable to electronic noise in the experimental data.

3.2. Crystallographic and magnetic structure from NPD data

The refinement of the crystallographic structure and the determination of the magnetic structure were carried out from two NPD patterns collected at RT and at $T = 2$ K with $\lambda = 1.59 \text{ \AA}$. All the Bragg peaks observed in the NPD pattern obtained at RT can be indexed within a cubic perovskite structural model, defined in the $Pm\bar{3}m$ space group. In a first trial refinement, Sr atoms were placed at $1b$ ($1/2, 1/2, 1/2$), positions, Fe and Co were distributed at random over $1a$ (0,0,0) sites and the oxygen atoms at the $3d$ ($1/2, 0, 0$) positions. In a subsequent step, a better fit was obtained if the occupancy factor of the oxygen at the $3d$ site was also refined. After the refinement, 96(1)% of the oxygen positions resulted to be occupied, that corresponds to the stoichiometry $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{2.88(3)}$. The magnetic measurements indicate that $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ is already ordered at RT, however no magnetic peaks appear in the NPD pattern outside the Bragg positions although some magnetic contribution is present on the low-angle reflections. In other words, the magnetic order is defined by the

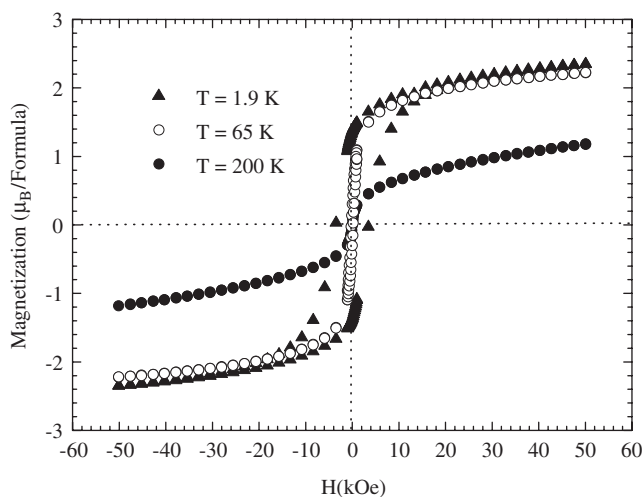


Fig. 2. Isothermal magnetization curves obtained at $T = 1.9$, 65 and 200 K.

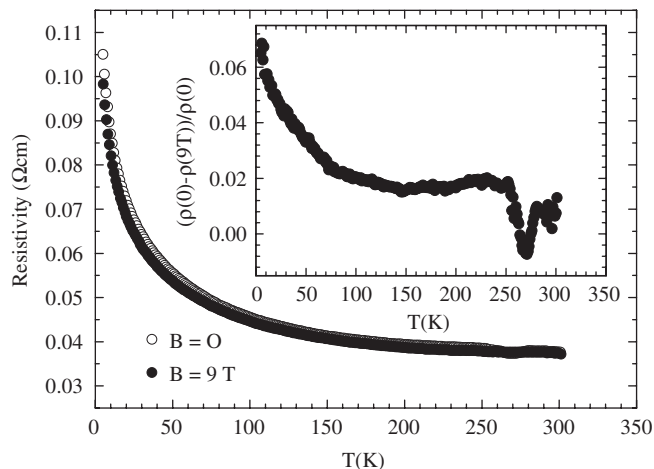


Fig. 3. Thermal variation of the resistivity for $5 < T < 300$ K under a 0 and 9 T magnetic field. Inset: Magnetoresistance vs. temperature plot for $H = 9$ T.

propagation vector $\mathbf{k} = 0$ as it corresponds to a FM structure, where the magnetic unit cell coincides with the chemical one. In the final refinement the magnetic structure was added to the structural model and the overall ordered moment at the (Fe,Co) sites was refined to $0.65(15) \mu_B$. The final parameters after the refinement at RT are included in Table 1; the quality of the fit is shown in Fig. 4a.

A similar fitting was carried out for the NPD pattern collected at $T = 2$ K; the characteristic parameters after the refinement are presented in Table 1. At $T = 2$ K, the occupancy factor for the oxygen positions is very similar, 97(1)%, and the ordered magnetic moment for the cations at the $1a$ site is $1.54(9) \mu_B$. The good agreement between the observed and calculated patterns is shown in Fig. 4b. Let us point out that the small peaks that appear in the NPD pattern collected at $T = 2$ K (see Fig. 4b), are spurious peaks coming from the cryostat. The bond distances in the

Fe/CoO₆ octahedra are 1.91889(3) and 1.91273(4) Å for RT and $T = 2$ K, respectively. For the SrO₁₂ polyhedra the bonding distances are 2.71372(4) and 2.70501(6) Å for 295 and 2 K, respectively.

4. Discussion

Neutron diffraction experiments have confirmed that the crystallographic structure is cubic at 2 and 295 K and that the sample stoichiometry is SrFe_{0.5}Co_{0.5}O_{2.88(3)}. The presence of 0.12(3) oxygen vacancies per formula implies that 0.24(6) Fe⁴⁺/Co⁴⁺ are reduced to Fe³⁺/Co³⁺. Under the moderately oxidizing conditions used to prepare the sample, it is presumable that Fe is predominantly oxidized to Fe⁴⁺, whereas Co requires a higher oxidation potential to fully adopt the tetravalent state. Therefore, it can be expected a certain disorder in the oxidation state of Fe and Co ions at the $1a$ site. In the SrFe_{1-x}Co_xO₃ system, for the rich Fe compounds the AFM interactions prevail over the FM ones, so the disorder over the $1a$ site could yield to competing AFM and FM interactions that can account for the irreversibilities suggested by the divergence of the FC and ZFC magnetic susceptibility curves below 30 K.

Some Fe⁴⁺ containing compounds, typically CaFeO₃ or Sr_{0.67}La_{0.33}FeO₃, have been described to exhibit a charge disproportionation effect [14–16]: below a characteristic temperature, two Fe⁴⁺ cations disproportionate into Fe³⁺ and Fe⁵⁺, which become ordered at different crystallographic positions of the structure, driving to a reduction of the crystal symmetry. This effect has been followed by diffraction methods, photoemission techniques or Moessbauer spectroscopy. This is not the case for our SrFe_{0.5}Co_{0.5}O_{3-δ} material: a NPD study performed at RT and 2 K shows that this compound keeps the same crystallographic symmetry in the considered temperature range, thus excluding the presence of any charge disproportionation effect. A similar result was obtained for SrFeO₃, which does not present charge disproportionation nor Jahn–Teller effect since the electronic ground state for Fe in this compound should better be described as d^5L instead of d^4 [14], where L denotes a hole in the oxygen $2p$ band.

The magnetization measurements have confirmed that SrFe_{0.5}Co_{0.5}O_{2.88} orders ferromagnetically below $T_C \approx 330$ K; the ordering temperature is slightly below that described for the oxygen-stoichiometric compound, which is around 340 K, due to the existence of some oxygen deficiency. In order to understand the magnetic structure in SrFe_{0.5}Co_{0.5}O₃, it is necessary to consider all the possible superexchange interactions that can play a role in the magnetic order, the Fe–O–Fe, Fe–O–Co and Co–O–Co interactions. The features of the Fe–O–Fe and Co–O–Co interactions can be examined, respectively, in the magnetic order of the two end-compounds of the SrFe_{1-x}Co_xO₃ system, SrFeO₃ and SrCoO₃. As regarding the Fe–O–Co interactions, their features can be obtained from the

Table 1
Structural and magnetic parameters obtained after the Rietveld refinement of the crystallographic and magnetic structure for SrFe_{0.5}Co_{0.5}O_{3-δ}

		$T = 295$ K	$T = 2$ K
Sr	B (Å ²)	0.70(1)	0.43(3)
Fe/Co	B (Å ²)	0.32(2)	0.23(3)
O	B (Å ²)	1.40(6)	1.11(3)
	Occupancy	0.96(1)	0.97(1)
	a (Å)	3.83778(6)	3.82546(8)
Fe/Co	Ordered moment (μ_B)	0.65(15)	1.54(9)
	R_B (nuclear) (%)	6.0	7.5
	R_B (Magnetic) (%)	8.8	11.2
	χ^2	2.1	2.3

The atomic positions are $1b$ (1/2,1/2,1/2), $1a$ (0,0,0) and $3d$ (1/2,0,0) for the Sr, Fe/Co and O atoms, respectively.

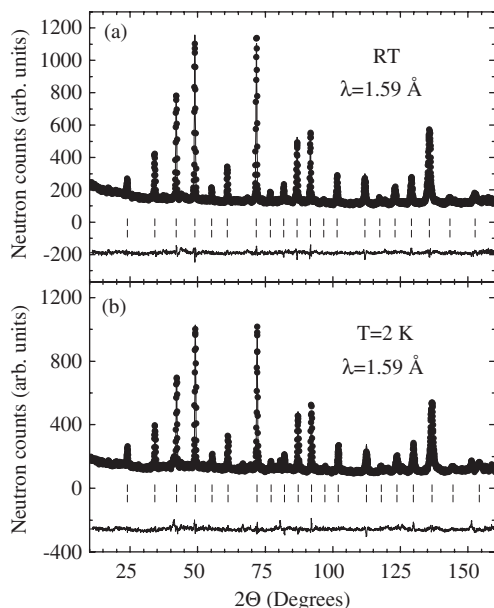


Fig. 4. Observed (●), calculated (solid line) and difference (at the bottom) NPD profiles for: (a) $T = 295$ K and (b) $T = 2$ K. The first series of vertical markers corresponds to the allowed nuclear Bragg reflections and the second to the magnetic peaks.

evolution of the magnetic order in $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ system on increasing the Co content.

Firstly, SrFeO_3 presents a screw magnetic structure; the exchange integral for the first, second and fourth nearest neighbouring are $J_1 = 1.2$, $J_2 = -0.2$ and $J_4 = -0.3$ meV, respectively [17]. A positive value for J_1 implies that the superexchange interaction Fe–O–Fe is FM; however, according to the Goodenough–Kanamori rules [18,19], the superexchange interaction between half-filled e_g orbitals would lead to an AFM interaction. It means that the qualitative Goodenough–Kanamori rules are not applicable in this case, because the strong covalency between the d^5 and O $2p$ orbitals induce an itinerant character on the e_g electrons. However, for the localized electrons in the t_{2g} orbitals, the Goodenough–Kanamori rules are valid and the superexchange interactions between the half-filled t_{2g} orbitals are AFM. This could explain the negative character of the J_2 and J_4 superexchange parameters.

Secondly, SrCoO_3 displays a FM structure, so the Co–O–Co superexchange interaction is FM; however, the microscopic origin of this FM interaction is not clear. On the one hand a double exchange mechanism between the intermediate spin state $t_{2g}^4 e_g^1$ and the low spin state $t_{2g}^5 e_g^0$ has been invoked [20]; however, band structure calculations seem to support the fact that SrCoO_3 is a half-metallic ferromagnet [21,22] as the $\text{Sr}_2\text{FeMoO}_6$ double perovskite.

Thirdly, in the $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ system, for the Fe-rich compounds ($x < 0.5$) the evolution of the ordering temperature from SrFeO_3 indicates that the partial replacement of Fe^{4+} by Co^{4+} cations enhances the FM interactions, as initially ($x < 0.2$) the screw magnetic structure appears at smaller T_N 's and from $x = 0.2$ the compounds become FM; therefore the Fe–O–Co interactions are mainly FM. It seems that a double exchange mechanism through the e_g orbitals as responsible of the FM interactions is not possible [5], because the delocalization of the e_g electrons of the Fe^{4+} cations. As regarding the interactions through the t_{2g} orbitals, in the Co ions there are half-filled and filled orbitals, whereas in the Fe ions all the orbitals are half-filled; the interactions between half-filled orbitals are AFM. In contrast, the hopping of an electron from a filled orbital to a half-filled one through an oxygen yields to a FM superexchange interaction. Besides, it must be considered the existence of a certain degree of mixed valence in these compounds due to the oxygen deficiency, with the presence of $\text{Fe}^{4+}/\text{Fe}^{3+}$ and $\text{Co}^{4+}/\text{Co}^{3+}$ cations; the charge transfer via $\text{Fe}^{3+}(t_{2g}^3 e_g^2) - \text{Co}^{4+}(t_{2g}^4 e_g^1)$ and $\text{Co}^{3+}(t_{2g}^5 e_g^0) - \text{Fe}^{4+}(t_{2g}^3 e_g^1)$ also implies a FM coupling between both ions.

At $T = 2$ K the ordered magnetic moment obtained from the refinement of the magnetic structure from NPD data is $1.54(9) \mu_B$. This value is in acceptable agreement with the remnant magnetization observed at $T = 1.9$ K, of $1.36 \mu_B/\text{f.u.}$ (Fig. 2). However, it is much smaller than that expected for high-spin Fe^{4+} ($S = 2$) and low-spin Co^{4+} ($S = 1/2$), of $2.5 \mu_B/\text{f.u.}$ Moreover, X-ray absorption measurements in related compounds [5,23] indicate a

complicated electronic configuration. The electronic configuration for the Fe atoms is a mixture of $3d^4$ (Fe^{4+}), $3d^5 L$ (Fe^{3+}) and $3d^6 L^2$ (Fe^{2+}), where we recall that L denotes a ligand hole linked to the O $2p$ level. Since the Fe ions are in a high spin-state, it would correspond to the configurations $t_{2g}^3 e_g^1$, $t_{2g}^3 e_g^2$ and $t_{2g}^4 e_g^2$, respectively. For the Co atoms the mixture is given by the configurations $3d^5$ (Co^{4+}), $3d^6 L$ (Co^{3+}) and $3d^7 L^2$ (Co^{2+}); according to Ref. [5], the Co^{4+} ions are in the intermediate spin state $t_{2g}^4 e_g^1$, whereas the Co^{3+} and Co^{2+} are, respectively, in the intermediate spin states $t_{2g}^4 e_g^2$ and $t_{2g}^5 e_g^2$. On considering the contributions of the different configurations determined in Ref. [5], the theoretical saturation magnetic moment for $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ would be $3.76 \mu_B$. This value is significantly larger than the ordered magnetic moment obtained from the NPD data at 2 K. This can be understood if we take into account that the oxygen vacancies strongly perturb the superexchange paths and hinder the establishment of a full long-range ordering across the solid. This effect accounts for: (i) the relatively low ordered (Fe,Co) magnetic moments; (ii) the low saturation magnetization at low temperatures; and (iii) the divergence between ZFC and FC curves, indicating the existence of inhomogeneities and a poor long-range magnetic ordering.

As regarding the transport properties, the oxygen-stoichiometric $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_3$ compound has been reported to exhibit a metallic behaviour and a certain negative MR [2]; however, for nonstoichiometric $\text{Sr}(\text{Fe}_{1-x}\text{Co}_x)\text{O}_{3-\delta}$ perovskites, it has been shown that on increasing δ , the compounds become semiconducting and the ordering temperature decreases. This is the case of $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{2.88(3)}$, semiconducting and with a small negative MR of 6.5% at 5 K (Fig. 3). The MR mechanisms in this system of oxides is not clear. A double-exchange-like mechanism has been excluded due to the itinerancy of e_g -electrons. Recently, MR effects have been found in single crystals of $\text{SrFeO}_{3-\delta}$ [24], ascribed to different mechanisms depending on the oxygen contents; the MR effects differ from those in manganites as no FM states are involved. In any case, let us point out that the transport mechanism in both ends of the series, $\text{SrFeO}_{3-\delta}$ and $\text{SrCoO}_{3-\delta}$ are different, since on increasing δ , $\text{SrFeO}_{3-\delta}$ becomes semiconductor whereas $\text{SrCoO}_{3-\delta}$ becomes more metallic. In our $\text{Sr}(\text{Fe}_{1-x}\text{Co}_x)\text{O}_{3-\delta}$ compound, the observed semiconducting behaviour seems to exclude a transport mechanism via itinerant e_g electrons, probably because the transport paths are interrupted at random by the presence of oxygen vacancies; a conventional MR mechanism based on the reduction of the charge-carriers magnetic scattering upon application of an external magnetic field on this FM material (intrinsic mechanism) combined with a tunnelling MR across grain boundaries is mostly probable for this system.

5. Conclusions

A polycrystalline sample of actual stoichiometry $\text{Sr}(\text{Fe}_{0.5}\text{Co}_{0.5})\text{O}_{2.88(3)}$ has been prepared under moderate pressure conditions, at 2 GPa, 1000 °C, and characterized

by NPD data, which confirm that it is a simple cubic perovskite at 295 and 2 K, showing no departure from the aristotype, with $Pm\bar{3}m$ space group. Magnetic measurements indicate that this material becomes ferromagnetically ordered below $T_C \approx 330$ K; the microscopic nature of the long-range ordering has been examined by neutron diffraction. The magnetic structure is collinear with an average magnetic moment value for the $\text{Fe}^{4+}/\text{Co}^{4+}$ cations of $1.54(9)\mu_B$ at $T = 2$ K; at RT the ordered magnetic moment is $0.65(15)\mu_B$. The low-temperature magnetic moment is significantly smaller than that expected for an admixture of the $3d^4$ (Fe^{4+}), $3d^5L$ (Fe^{3+}) and $3d^6L^2$ (Fe^{2+}) electron configurations for the Fe ions and a mixture of the configurations $3d^5$ (Co^{4+}), $3d^6L$ (Co^{3+}) and $3d^7L^2$ (Co^{2+}) for the Co ions; this is ascribed to the presence of randomly distributed oxygen vacancies, that break the superexchange paths and hinder the establishment of long-range magnetic ordering. The present study confirms that a mixed $\text{Fe}^{4+}/\text{Co}^{4+}$ composition enhances the FM coupling in the $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ system, in a matrix where the $\text{Fe}^{4+}\text{--O--Co}^{4+}$ interactions, via 180° superexchange paths, are namely FM.

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