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Enhanced magnetoresistance in the Ruddlesden–Popper compound $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$

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Abstract

We report the synthesis of the Ruddlesden–Popper material $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$ (a compound usually obtained under high-pressure conditions) by a simpler normal pressure liquid-mix method and its structural characterization by means of X-ray powder diffraction. In this material—which is semiconducting and shows a glassy magnetic behavior—the combination of the reduced dimensionality of the structure compared to 3D perovskites, the small grain size obtained by our synthesis method and the selected stoichiometry, results in a record magnetoresistance in these kind of compounds, -47% at $T = 5\text{ K}$ and $H = 50\text{ kOe}$, that is explained on the basis of intragranular and intergranular effects.

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1. Introduction

Materials exhibiting colossal magnetoresistance (a very large change in the electrical resistance in response to an applied magnetic field) are a very hot topic in materials science, not only because of the interest they have generated in basic research but also for their potential application as magnetic sensors.

In the search for materials exhibiting such remarkable behavior, besides the well-known

manganese perovskites (commonly called “manganites”), other systems containing isoelectronic $3d^3$ and/or $3d^4$ ions have been investigated. Among them, a “new” family of compounds, the Fe(IV) ($3d^4$) mixed oxides, is starting to receive attention even if traditionally its availability has been rather reduced and constrained by the fact that high oxygen pressures are needed to stabilize iron in this rather high oxidation state and achieve the right oxygen stoichiometry.

Similar to the case of manganese, Fe(IV) mixed-oxides form 3D perovskites, for example, the well-known CaFeO_3 and SrFeO_3 compounds [1,2] as well as other perovskite-related phases of lower dimensionality such as Ruddlesden–Popper series

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of intergrowth oxides. These latter compounds, which have the general formula $(\text{AO})(\text{ABO}_3)_n$ $\text{B} = \text{Fe}$, $1 \leq n \leq \infty$, consist of perovskite blocks, n octahedra thick, separated by rock-salt SrO layers. Included in this category are the K_2NiF_4 -type structures, with $n = 1$, A_2FeO_4 (A^{2+} : Sr, Ba) [3]; and the Ruddlesden–Popper-type phase with $n = 2$ $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ [4], which exhibits a wide range of oxygen non-stoichiometry $0 \leq \delta \leq 1$ maintaining the same average structure, that is shown in Fig. 1. As it can be seen, the perovskite-like double layers of corner-sharing $[\text{FeO}_6]$ octahedral are separated by SrO layers, resulting in a decrease in the dimensionality of the structure and a reduction from six to five of the number of nearest-neighbor Fe ions around sites at the edge of the $(\text{SrFeO}_3)_2$ slabs.

The electronic properties of these ferrates, in which the Fe(IV) is in the high spin state ($\text{Fe(IV)}: t_{2g}^3 e_g^1$), are rather complex and due, as in the case of manganites, to a very fine balance between localizing and delocalizing effects and a competition between ferromagnetic and antiferromagnetic exchange interactions [5].

For example, while SrFeO_3 is a metallic antiferromagnet ($T_N \approx 130 \text{ K}$) with a helical spin structure [2,6], CaFeO_3 also orders antiferromagnetically below $\approx 120 \text{ K}$, but is semiconductor due to the occurrence of a charge disproportionation of the type $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$ [1,7]. And as the

dimensionality decreases from 3D to 2D in Sr_2FeO_4 this compound becomes a Mott-type antiferromagnetic semiconductor with a much lower Néel temperature ($T_N \approx 60 \text{ K}$) [8]. Meanwhile $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ is a semiconductor that orders antiferromagnetically at low temperatures for the whole range of oxygen non-stoichiometry and that also suffers charge disproportionation [9].

Apart from these compounds, other ferrates in which the B site has been partially occupied by other transition metal ions are known. In this context the partial substitution of Fe by Co is particularly interesting, as it is known to increase the conductivity of these materials and enhance the ferromagnetic interactions, as it has been demonstrated in $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ compounds [10,11] and in $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_{7-\delta}$ [12].

And very interestingly, MR effects have been recently found in these Fe/Co mixed oxides, even if up to now there are relatively few reports on these systems. They were initially discovered in $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ compounds synthesized under high oxygen pressure [13,14] ($\text{MR}_{\text{max}}(\text{SrFe}_{0.9}\text{Co}_{0.1}\text{O}_3) = -12\%$ at $T = 4 \text{ K}$ and $H_{\text{appl}} = 12 \text{ kOe}$ [13]) and more recently in compounds that belong to the $n = 2$ Ruddlesden–Popper series $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_{7-\delta}$ [15,16], where the reduced dimensionality of the structure enhances the MR values, as it occurs in the case of manganites [17] ($\text{MR}(\text{Sr}_3\text{Fe}_{1.6}\text{Co}_{0.4}\text{O}_{7-\delta}) = -45\%$ at $T = 5 \text{ K}$ and $H_{\text{appl}} = 90 \text{ kOe}$ [15], $\text{MR}(\text{Sr}_3\text{FeCoO}_{7-\delta}) = -24\%$ at $T = 10 \text{ K}$ and $H_{\text{appl}} = 70 \text{ kOe}$ [16]).

In this context and aware of the fact that the compounds $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_{7-\delta}$ had been very recently successfully synthesized at ambient pressure for other purposes (even if with a small oxygen deficiency) [12] and in view of the magnetic and electrical properties displayed by the so-obtained samples, we decided to focus in the compound that seemed the best candidate to present very high magnetoresistance: an oxygen-deficient $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ sample. Even if this composition had not been studied before, it could be expected to show a magnetic glassy behavior [12]; a relatively high resistivity, but intermediate between that displayed by higher and lower-doped samples [12]; it would have the majority of the B ions in the formal oxidation state of $4+$, but also a

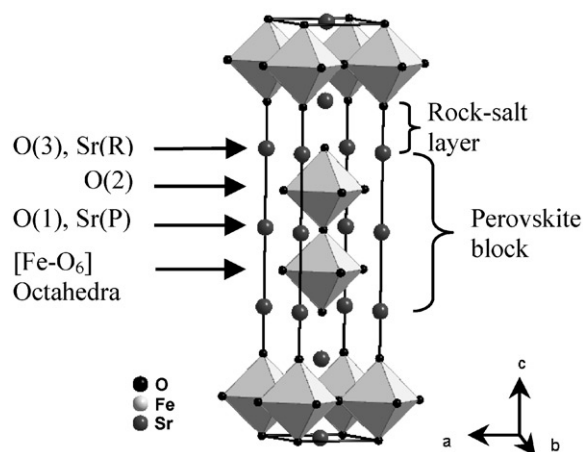


Fig. 1. Schematic representation of the ideal crystal structure of the stoichiometric compound $\text{Sr}_3\text{Fe}_2\text{O}_7$.

number of oxygen vacancies that would help localizing the conduction electrons. Moreover, by similarity with manganites [18], its magnetoresistance would be higher if we could enhance the intergranular MR effects by preparing a polycrystalline sample of relatively small particle size using soft-chemistry routes.

By these means we were able to obtain a material with very high negative magnetoresistance: $MR_{\max}$: -47% at $T = 5\text{ K}$ under $H_{\max} = 50\text{ kOe}$, whose structural and magnetotransport properties we will show and explain below.

During the preparation of this manuscript, other study on the magnetotransport properties of $\text{Sr}_3\text{Fe}_{1-x}\text{Co}_x\text{O}_{7-\delta}$ compounds ($x \leq 1$) has been published [19]. It is mainly focused on materials annealed under high-oxygen pressure, but it does not include the $x = 0.5$ composition and it reports MR values smaller than the ones we show here.

Therefore, our study on the structural and magnetotransport properties of this oxygen-deficient sample with $x = 0.5$ $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{7-\delta}$ supplements the information available in the literature about this interesting system and provides a more detailed interpretation of its magnetotransport properties.

2. Experimental

This sample was prepared by the so-called “liquid-mix” or Pechini Method using analytical grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, SrCO_3 as starting materials. The procedure was as follows: We dissolved stoichiometric amounts of the transition-metal ions and SrCO_3 in dilute ($\approx 5\%$) HNO_3 aqueous solution to which we then added a 1 M citric acid solution. After diluting the so-obtained solution, we carefully added ethyleneglycol in a proportion of 10% v/v. The resulting solution was heated at 200°C until a brown resin formed, whose organic matter subsequently decomposed at 400°C . The obtained ashes were given accumulative heating treatments at $600^\circ\text{C}/24\text{ h}$ and $900^\circ\text{C}/12\text{ h}$, with an intermediate grinding, and the pelletized sample was sintered at $1100^\circ\text{C}/24\text{ h}$. Finally, it was subjected to the following heating treatment under an oxygen flow:

it was heated at $900^\circ\text{C}/1\text{ h}$ and cooled slowly ($1^\circ/\text{min}$) to 500°C , temperature at which it was held for 6 h and then cooled slowly ($1^\circ/\text{min}$) to room temperature.

The sample was characterized by X-ray powder diffraction with a Siemens D-5000 diffractometer and $\text{Cu K}\alpha = 1.5418\text{ \AA}$ radiation. Rietveld analysis of the powder X-ray diffraction data was carried out using the Rietica software suite [20].

The morphology and size of the particles were studied in a scanning electron microscopy (SEM) Jeol 6400.

Magnetic properties were studied in a Quantum Design MPMS Squid magnetometer. Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility data were obtained in a field of 1000 Oe in the temperature range $4.2\text{ K} \leq T \leq 300\text{ K}$. Hysteresis loops in ZFC conditions were obtained at 5 K cycling the field between -50 and $+50\text{ kOe}$.

The four-probe electrical resistivity of pressed pellets was measured as a function of temperature in the range $4\text{ K} \leq T \leq 300\text{ K}$ in a zero magnetic field ($H = 0$) and with a constant field $0 < H$ (kOe) < 50 using a homemade device. In this device the magnetoresistance of the samples was measured at a constant temperature between 0 and 50 kOe.

3. Results

The so-obtained polycrystalline sample was single phase, according to the powder X-ray diffraction results, and consists of platelets of averaged diameter $1\text{--}2\text{ }\mu\text{m}$ as seen by SEM.

As for its oxygen content, the iodometric titrations indicate that it is oxygen-deficient so that its real composition is $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67 \pm 0.01}$. This gives an average formal oxidation state per transition metal ion B of $3.67+$.

Although the sample deteriorates under prolonged exposure to air, we were able to obtain good enough X-ray powder diffraction data in air so that we could refine the lattice parameters, atomic coordinates, M–O distances and angles by Rietveld analysis using the the Rietica software suite.

As indicated above, this compound belongs to the Ruddlesden-Popper series of compounds, with $n = 2$, and displays an average $\text{Sr}_3\text{Ti}_2\text{O}_7$ -type structure [4], space group $I4/mmm$, with lattice parameters $a = 3.8535(1) \text{ \AA}$ and $c = 20.114(1) \text{ \AA}$.

And a very interesting result was that, even if X-ray are not very sensible to light atoms such as oxygen, the Rietveld refinements significantly improved when changing the degree of occupancy of the different oxygen sites of the structure. In this context we found the best results, and are summarized in Tables 1a and 1b, when assuming that more than half of the oxygen vacancies were concentrated in the O(1) site, in the apical position within the perovskite slab, so that in those oxygen-deficient regions the double layers of corner-sharing MO_6 octahedra change into square-based pyramids. This result is in good agreement with previous neutron diffraction experiments performed on the undoped $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ compound [4].

As for the magnetic properties of this $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$ sample, the obtained results, shown in Fig. 2, provide evidence of the glassy magnetic behavior displayed by this compound. As can be seen, a smooth increase in the magnetic susceptibility χ_m occurs below a T_c (onset) of $\approx 200 \text{ K}$, and a sharp maximum appears in the ZFC χ_m curve at a $T_g \approx 60 \text{ K} < T_c$, while the FC data are nearly temperature independent below T_g . In addition, the M versus H curve of the ZFC sample shows no saturation under the highest field used (50 kOe).

From the electrical point of view, this sample is semiconducting. Its resistance increases as temperature decreases, and the rise is specially pronounced below $T < 30 \text{ K}$ (Fig. 3). In the paramagnetic range, $T > 150 \text{ K}$, the electrical conductivity is thermally activated and we have calculated the activation energy from the linear part of the $\ln \sigma$ versus $1/T$ plots. The estimated E_{act} , i.e. 0.045 eV , is of the some order as that described for the $\text{Sr}_3\text{FeCoO}_{7-\delta}$ compound [16]. Nevertheless, at lower temperature the electrical conductivity data cannot be adequately fitted neither to the above temperature dependence nor to any other $\rho = \rho_0 \exp(-T/T_0)^{1/n}$ expression.

And its most outstanding feature is that it displays strong magnetoresistance effects at low

Table 1a

Structural parameters of $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$ at room temperature as obtained from the Rietveld refinement of the X-ray powder diffraction data^a

Atom	Site	X	Y	Z	Occupancy (%)
Fe/Co	4e	0	0	0.0981(2)	100
Sr (P)	2b	0	0	0.5	100
Sr (R)	4e	0	0	0.3174(1)	100
O(1)	2a	0	0	0	82.7
O(2)	8g	0	0.5	0.0918(2)	100
O(3)	4e	0	0	0.8078(6)	100

^aSpace Group: $I4/mmm$, $a = 3.8535(1) \text{ \AA}$, $c = 20.114(1) \text{ \AA}$, $V = 298.68 \text{ \AA}^3$, $R_p = 10.35$, $R_{wp} = 15.28$, $R_{exp} = 12.88$, G.O.F. = 1.41, $R_B = 2.77$.

Table 1b

Important bond-lengths and angles for $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$

	Bond length
Fe/Co–O(1)	$1.9728(1) \times 1$
Fe/Co–O(2)	$1.9309(1) \times 4$
Fe/Co–O(3)	$1.8925(1) \times 1$
Sr(P)–O(1)	$2.7249(1) \times 4$
Sr(P)–O(2)	$2.6691(1) \times 8$
Sr(R)–O(2)	$2.6548(1) \times 4$
Sr(R)–O(3)	$2.7316(1) \times 4$
Sr(R)–O(3)	$2.5185(1) \times 1$

Angles: $\langle \text{Fe/Co–O(1)–Fe/Co} \rangle = 180^\circ$, $\langle \text{Fe/Co–O(2)–Fe/Co} \rangle = 180^\circ$.

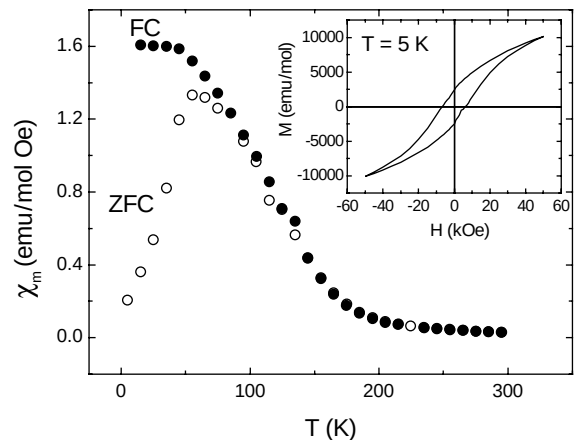


Fig. 2. ZFC and FC molar magnetic susceptibility of $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$ measured under a field $H = 1000 \text{ Oe}$. Inset: ZFC magnetization versus applied field at $T = 5 \text{ K}$.

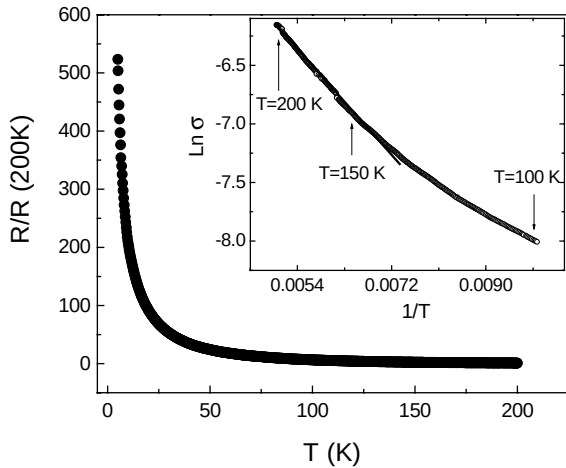


Fig. 3. Normalized electrical resistance $R(T)/R(200\text{ K})$ versus temperature of $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$ for $5 \leq T(\text{K}) \leq 200$. Inset: Plot of $\text{Ln } \sigma$ versus $1/T$ in the temperature interval $100 < T(\text{K}) < 200$.

temperatures (Figs. 4a and b). As already mentioned, the largest effect is seen at $T = 5\text{ K}$, $\text{MR}_{\text{max}}: -47\%$ at $T = 5\text{ K}$ under $H_{\text{max}} = 50\text{ kOe}$ (Fig. 4a), value that is 17% bigger than the highest one reported so far for samples of this system at the same field [19].

It is also worth mentioning that the variation of resistance upon application of the field shows no sign of saturation up to the highest field used. And that the shape of this curve that is highly hysteretic, reminds of those displayed by polycrystalline manganites in which the small decrease seen for low fields is followed by a larger effect at higher fields, and that has been ascribed to intergranular magnetoresistive effects [18].

As temperature increases, the MR response of this sample decreases, even if rather large magnetoresistance values are still found at $T = 40\text{ K}$ ($\text{MR}_{\text{max}}: -26.5\%$ under $H_{\text{max}} = 50\text{ kOe}$) and at $T = 70\text{ K}$ ($\text{MR}_{\text{max}}: -15\%$ under $H_{\text{max}} = 50\text{ kOe}$) (Fig. 4b). But at difference with the behavior found at $T = 5\text{ K}$, the MR displayed by the sample at these two temperatures shows no hysteresis. It is also worth mentioning the almost linear dependence of MR on the magnetic field at $T = 70\text{ K}$. And at $T = 100\text{ K}$ the maximum magnetoresistance has decreased to -9.5% under $H_{\text{max}} = 50\text{ kOe}$.

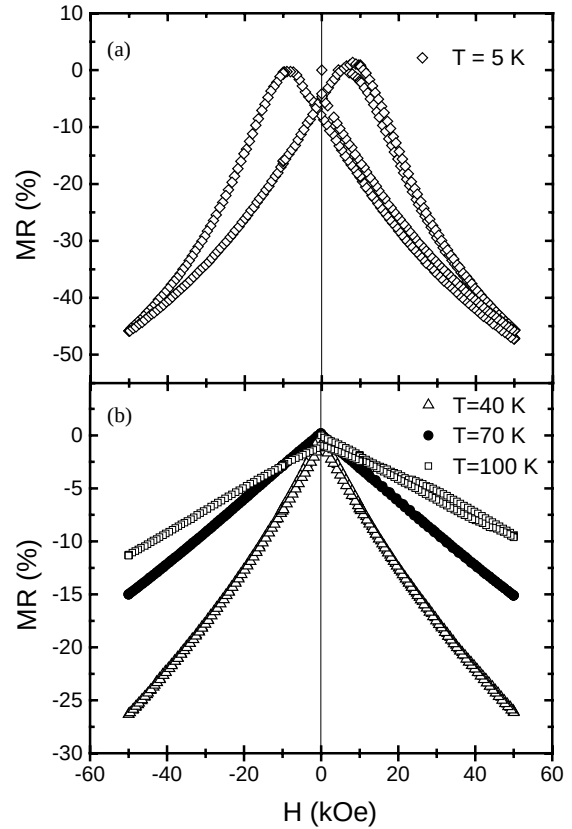


Fig. 4. Field dependence of the electrical resistivity of the sample $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$ measured at: (a) 5 K, (b) 40, 70 and 100 K.

4. Discussion

To try to understand the properties displayed by this $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$ sample it is worth referring first to the electronic structure and characteristics of the undoped compound $\text{Sr}_3\text{Fe}_2\text{O}_7$. In this context, this lamellar compound is a semiconductor in which the three electrons in the π^* iron-oxygen antibonding states are localized, whereas the σ^* iron-oxygen antibonding orbitals form a narrow band [9], that can even be split due to correlation effects [12]. The intermediate bandwidth of this σ^* band, that results in a w (bandwidth) $\approx U$ (intraatomic electron–electron coulomb energy) makes the compound prone to experience charge disproportionation [5,9].

As for their magnetic properties (antiferromagnetic ordering below a $T_N \sim 100$ K, even if ferromagnetic correlations are present above that temperature), they are determined by a competition between ferromagnetic and antiferromagnetic exchange interactions [9]: the antiferromagnetic coupling that dominates below T_N , arises from the superexchange interactions between the localized half-filled π^* orbitals; meanwhile, the ferromagnetic exchange may be attributed to the tendency to delocalize the σ^* electrons in the solid, and that is more favorable if the alignment of the spin on adjacent sites is ferromagnetic, similar to what occurs in the double exchange mechanism.

Now, when in this compound cobalt partially substitutes for iron, the M–O–M ((Fe,Co)–O–(Fe,Co)) covalent interactions get locally strengthened and the bandwidth of the σ^* conduction band (w_{σ^*}) increases [21]. This, in turn, has important implications: (a) charge disproportionation is prevented, once a critical bandwidth is achieved [21], (b) the electronic conductivity of the samples increases, (c) in the surroundings of the cobalt ions, the M–O–M ferromagnetic interactions become stronger as the tendency to delocalize the σ^* electrons increases and as Co (either as Co(IV) or Co(III)) helps in that delocalization by double exchange. This probably results in the formation of Co-containing ferromagnetic clusters (Fig. 5), and that gives rise to an increase in the magnetization of the sample below T_c . Nevertheless, the presence of antiferromagnetic interactions in the Fe–O–Fe matrix gives rise to a glassy behavior below $T_g < T_c$.

In view of the results presented here and those given by other authors in more samples of this system [9,19], we can visualize these samples, on a very simplified model, as layered structures consisting of non-magnetic and insulating Sr–O slabs that separate an antiferromagnetic highly resistive Fe–O matrix in which the presence of Co ions induces the creation of ferromagnetic islands of higher conductivity (Fig. 5). In addition, the presence of oxygen vacancies that seem to concentrate within the perovskite blocks along the apical position, locally reduces the dimensionality of the structure in the defective areas preventing the interaction along the c -axis, in-

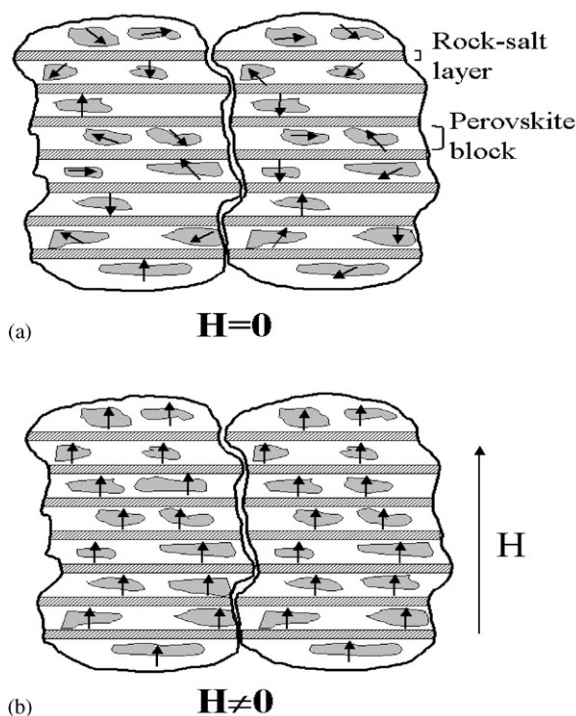


Fig. 5. Schematic and very simplified representation of the most outstanding features of the crystal and magnetic structure of $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$ (a) in the absence of a magnetic field ($H = 0$), (b) under a magnetic field ($H \neq 0$).

creasing the trapping of the charge carriers, lowering their mobility and weakening the magnetic interactions.

Within this model, we can explain the high magnetoresistance exhibited by these samples at low temperatures, particularly $\text{Sr}_3\text{Fe}_{1.5}\text{Co}_{0.5}\text{O}_{6.67}$, on the basis of two contributions:

(a) *Intragranular effects*: This would consist of a reduction in the scattering of the electrons at the boundaries between the ferromagnetic regions and the antiferromagnetic matrix upon application of the field, due to a better relative alignment of the magnetic clusters (Fig. 5a). This would result mainly in an improved in-plane conductivity (within the perovskite-block), even if the out of plane conductivity can also be favored. This mechanism would be rather similar to that present in heterogeneous ferromagnetic alloys [22,23], magnetic multilayers [24] and keeps also an

analogy with that acting on the lamellar Mn-perovskites.

(b) *Intergranular effect*: This would consist of a reduction in the scattering of the electrons at the grain boundaries, as it also occurs in polycrystalline Mn-perovskites [25]. In this context, at zero field the magnetization vectors in each grain are randomly oriented in addition to the intrinsic spin disorder at the grain boundaries. Nevertheless, when a field is applied the spins within the grains reorient and therefore reduce the scattering between the grains, leading to a lower resistance (Fig. 5b). And it is worth noting that the relatively small particle size of these particles will enhance this effect.

Acknowledgements

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