

Diluted magnetic interactions in an oxygen-deficient perovskite cobaltite: magnetoresistance in the series $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ ($0 < x \leq 0.5$)

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Abstract

A series of the oxygen-deficient perovskite $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ has been successfully prepared by using close ampoules for compositions in the range $0.05 \leq x \leq 0.5$. The unit cell expansion with x is ascribed to the larger Sc^{3+} ionic radius than those of the $\text{Co}^{3+}/\text{Co}^{4+}$ cations. At 300 K, resistivity (ρ) values of about $\sim 10^{-2} \Omega \text{cm}$ are measured for both $x = 0.05$ and 0.10 , but for larger x values ρ increases, reaching $\rho_{300\text{K}} = 10^2 \Omega \text{cm}$ for $x = 0.5$. For the former, the lower resistivity values result from their weak ferromagnetic behavior characterized by a Curie temperature T_C of ~ 60 K. Interestingly, these oxides exhibit similar negative magnetoresistance values, reaching 12% in 7 T at 5 K, to those reported for the $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ samples. It is concluded that the simultaneous presence of non-magnetic ($3d^0$) Sc^{3+} species, substituted for cobalt, and of oxygen vacancies induce magnetic disordering, exemplified by the spin-glass like behavior of $\text{SrCo}_{0.5}\text{Sc}_{0.5}\text{O}_{3-\delta}$, which favors the existence of magnetoresistance.

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1. Introduction

Among the materials exhibiting magnetoresistance (MR) properties, several $3d$ metal-transition oxides crystallizing in the perovskite structure have been shown to exhibit negative MR. This is the case of the colossal MR manganites for which the ferromagnetic $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ double-exchange interactions and the strong electron–phonon coupling play a major role (for a review, see Ref. [1]). Another example is given by the perovskite cobaltites [2,3], as for instance $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ with $0 < x \leq 0.5$, the coexistence of Co^{3+} species around a Co^{4+} cation creating a small ferromagnetic-conducting polaron [4] which grows under magnetic field application leading to a negative MR. More recently,

negative MR was also reported for the iron-based metallic perovskite SrFeO_3 , with values reaching about 10% in 9 T [5,6]. In the latter, the MR was proposed to originate from the magnetic structural changes from helical to conical under field application which favors the reduction of e_g -electron scattering [5]. A last example is given by the mixed iron–cobalt perovskite, $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ [7,8], which exhibits ferromagnetic metallic state for $0.2 \leq x \leq 1$ with T_C beyond or close to 300 K [9]. Interestingly, for the compositions such as $x < 1$, a negative MR of about $\sim 10\%$ in 7 T is measured at 10 K [7,8]. The MR magnitude decreases as T increases and it vanishes in the T_C vicinity. Nonetheless, these $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ oxides prepared in normal conditions are oxygen deficient and a large oxygen pressure is required to reach the O_3 stoichiometry (6 GPa in Ref. [10]). The report of MR in oxygen-deficient series obtained by post-annealing the

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air-prepared compounds [8] in only 15 MPa suggests that both oxygen vacancies and disorder on the *B*-site could play a role in the MR generation.

In this respect, a very large oxygen non-stoichiometry can be achieved in $\text{SrCoO}_{3-\delta}$, the compound structure evolving from brownmillerite ($\delta = 0.5$) to perovskite (up to $\delta = 0.00$) [11]. Moreover, the chemical formula of the oxygen-deficient perovskite, post-annealed in oxygen pressure (15 MPa), can be written $\text{SrCoO}_{2.75}$, and for this composition only a positive MR of small magnitude was found (0.5% in 7 T) in contrast with the negative MR ($\sim 10\%$ in 7 T) of the series $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ [7,8].

In order to check if a possible effect of disordering on both *B*- and oxygen-site of the perovskite could contribute for the generation of a negative MR in the $\text{SrCoO}_{3-\delta}$ cobaltite, a series of compounds was prepared, using close ampoules to ensure oxidizing conditions during the chemical reaction, by substituting a non-magnetic and large cation, Sc^{3+} ($3d^0$), for cobalt. We report in the following on the stabilization of an oxygen-deficient perovskite $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ with x in the range $0 < x \leq 0.5$. It is found that these as-prepared compounds exhibit a weak ferromagnetism responsible for MR properties persisting up to $T_C \approx 160$ K. This opens a new route to generate MR properties in cobaltites. It is believed that this dilution by the foreign cation generates competing ferro- and antiferromagnetic interactions.

2. Experimental

The polycrystalline samples of $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ were prepared for x values in the range $0 \leq x \leq 1$ by reacting mixtures of SrO_2 , Co_3O_4 and Sc_2O_3 in stoichiometric proportions. The powder of precursors was pressed in bars ($\sim 10 \times 2 \times 2$ mm³), which were put in alumina crucibles. Silica tubes containing the crucibles were sealed under primary vacuum. The tubes were heated at 1100°C for 12 h and then finally quenched in air. A part of selected samples was subsequently annealed at 600°C for 24 h in high-pressure oxygen (15 MPa).

Powder X-ray and electron diffractions (ED) and thermogravimetric analysis (TGA) were employed to characterize the structure and the oxygen content, respectively. Especially, transmission electron microscopy (TEM) was used to check for the occurrence of superstructures and determine the space group. This work has been carried out with a JEOL 200 Cx microscope equipped with a Kevex analyzer to determine the cation content from Energy Dispersive Spectroscopy (EDS) data. In parallel, powder X-ray diffraction data have been collected with an Xpert Philips diffractometer working with $\text{CuK}\alpha$ radiation and treated with Winplotr Package [12]. The oxygen content was determined by the thermogravimetric hydrogen

reduction method (At/ H_2 10%) on a Setaram TAG92 microbalance.

Magnetic properties were studied by means of a SQUID magnetometer and an ac susceptometer. Resistivity values were measured by the four-probe technique (indium contacts) for temperatures in the $5 \text{ K} \leq T \leq 400 \text{ K}$ range and for magnetic field up to 7 T.

3. Results

In such synthesis conditions, it was not possible to prepare a pure cobalt $\text{SrCoO}_{3-\delta}$ ($x = 0.00$) sample but instead the $\text{Sr}_6\text{Co}_5\text{O}_{15}$ phase was systematically obtained [13]. On the contrary, for the Sc^{3+} rich composition corresponding to $x > 0.5$ in $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$, the Sc^{3+} solubility was found to be limited and a systematic presence of a large amount of Sc_2O_3 was detected by XRD. Interestingly, for all compositions in the nominal $0.05 \leq x \leq 0.5$ range, the XRD patterns were all found to be characteristic of a perovskite type structure. An example is given in Fig. 1 for the as-prepared $\text{SrCo}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$ sample. At first, these X-ray diffraction patterns were refined by using a *Pm3m* space group similar to that previously used for the perovskite $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ [8]. The obtained cell parameters (Table 1) clearly show a cell expansion with increase of the Sc^{3+} content. From the EDS analysis, it is found that the analyzed cation content is very close to the nominal one (Table 1) up to $x = 0.25$. In contrast, for $x = 0.5$, the cationic composition deduced from EDS data “ $\text{SrCo}_{0.61}\text{Sc}_{0.39}$ ” shows that in the present preparation conditions, the Sc^{3+} solubility limit is close to 40%. In the following, the samples are named from their

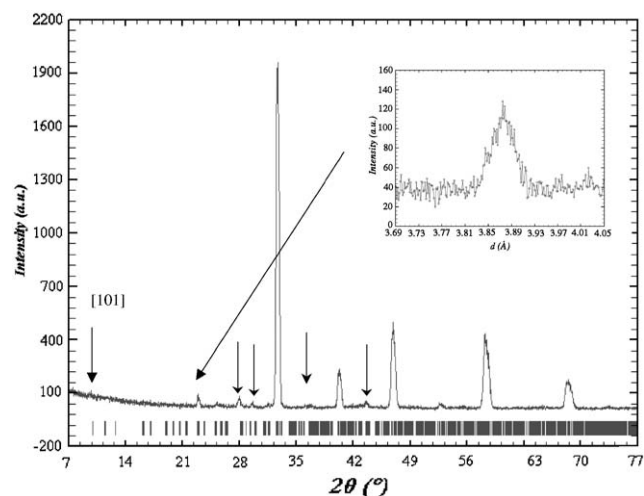


Fig. 1. X-ray diffraction pattern of the $\text{SrCo}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$ as-prepared sample indexed in the $(2a_p\sqrt{2} \times 2a_p\sqrt{2} \times 4a_p)$ supercell. The orthorhombic distortion is illustrated by the splitting of the (100) a_p peak (inset) setting at 3.8 Å of the perovskite subcell.

Table 1
Nominal and final (from EDS) cationic compositions for the $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ samples

Nominal composition	Cations contents from EDS	<i>Pm3m</i>	<i>Pbnn</i>			Oxygen content ($3-\delta$)
		<i>a</i> (Å)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	
$\text{SrCo}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$ as-prepared	$\text{SrCo}_{0.85}\text{Sc}_{0.10}$	3.8754 (6)	10.8918 (1)	10.9924 (1)	15.548 (1)	
$\text{SrCo}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$ PO_2 -annealed	$\text{SrCo}_{0.85}\text{Sc}_{0.10}$	3.873 (5)	10.895 (1)	10.987 (1)	15.539 (1)	
$\text{SrCo}_{0.75}\text{Sc}_{0.25}\text{O}_{3-\delta}$	$\text{SrCo}_{0.78}\text{Sc}_{0.22}$	3.9170 (5)				2.70
$\text{SrCo}_{0.5}\text{Sc}_{0.5}\text{O}_{3-\delta}$	$\text{SrCo}_{0.61}\text{Sc}_{0.39}$	3.9712 (4)				2.71

The *a* subcell parameters are obtained from refinement of the powder X-ray diffraction data. The cell parameters in the orthorhombic supercell are also given for the as-prepared and PO_2 -annealed samples. The oxygen deviation (δ) from the stoichiometric formula (O_3) determined by TGA is also given.

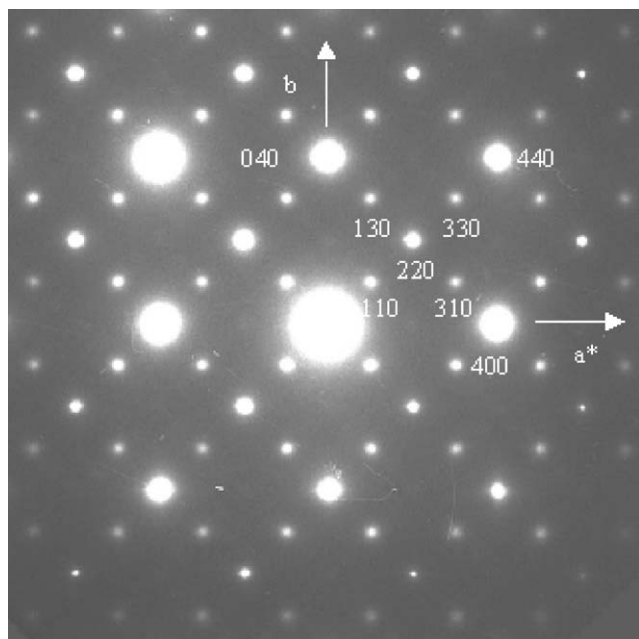


Fig. 2. [001] ED pattern of the as-prepared $\text{SrCo}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$. The spots are indexed in the $2a_p\sqrt{2} \times 2a_p\sqrt{2} \times 4a_p$ supercell.

nominal compositions. In parallel, for all the studied compounds, the corresponding ED patterns revealed a perovskite-type subcell with some extra spots as shown in Fig. 2 for $x = 0.1$. The building of the reciprocal space leads to an actual supercell in $2a_p\sqrt{2} \times 2a_p\sqrt{2} \times 4a_p$ with the reflection conditions, $(0kl) k = 2n$, $(h0l) h + l = 2n$, $(hk0) h + k = 2n$, compatible with the *Pbnn* space group. By considering our synthesis method, involving no such high oxygen pressure as that necessary to obtain stoichiometric $\text{SrCoO}_{3.00}$, it is clear that these perovskites are oxygen deficient. The values of oxygen content from TGA clearly confirm the existence of an oxygen deficiency (Table 1). Note that for $x = 0.1$, traces of the SrCO_3 impurity, detected by XRD, precludes an accurate determination of the oxygen content.

It must also be pointed out that no significant difference has been detected between unit cell parameters (Table 1) coming from the XRD patterns of the

as-prepared (as-prep.) and oxygen pressure-annealed (PO_2) $\text{SrCo}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$ compounds in agreement with the very slight change of oxygen stoichiometry. For both, a clear splitting of the same fundamental peaks (see the enlargement in Fig. 1) and the existence of extra peaks (black arrows in Fig. 1) are evidenced in agreement with TEM observations. These supplementary peaks can thus be indexed in the orthorhombic supercell determined from the ED study (see the cell parameters in the *Pbnn* space group for the $x = 0.1$ sample in Table 1). The lack of difference between the as-prep. and PO_2 -annealed $\text{SrCo}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$ samples is consistent with the fact that an oxygen pressure of 15 MPa is not sufficient to reach the “ O_3 ” stoichiometry in $\text{SrCoO}_{3-\delta}$ [8].

Nevertheless, a fine structural study from neutron diffraction data will be necessary to link the origin of this distortion to the oxygen site positions and occupations in the structure.

3.1. Transport properties

The *T* dependence of the resistivity (ρ) for the as-prepared $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ samples clearly show that they become less conducting as the Sc^{3+} increases (Fig. 3). The $\rho_{300\text{K}}$ values increases from $\sim 10^{-2}$ to $10^2 \Omega \text{cm}$ as x increases from $x = 0.05$ to 0.50 , respectively, i.e. as the conducting Co–O array is diluted by the non-conducting (empty *3d* orbitals) Sc^{3+} species. Furthermore, it must be pointed out that the values of the resistivity are sensitive to oxygen pressure as shown in Fig. 4 in which it is observed that the resistivity values are slightly shifted down after PO_2 -annealing. This result can be understood as one considers that a part of the oxygen vacancies on the Co(Sc)–O array has been refilled. Although the $\rho_{300\text{K}}$ values for the smallest x values ($x = 0.05$ and 0.10) are similar to those reported for the stoichiometric SrCoO_3 ($\rho_{300\text{K}} \sim 310^{-2} \Omega \text{cm}$ in Ref. [14]), the negative values $d\rho/dT$ values found for all the samples, as-prepared or oxygen annealed, they contrast with the metallic behavior $d\rho/dT > 0$ of SrCoO_3 [14]. This difference, already reported for

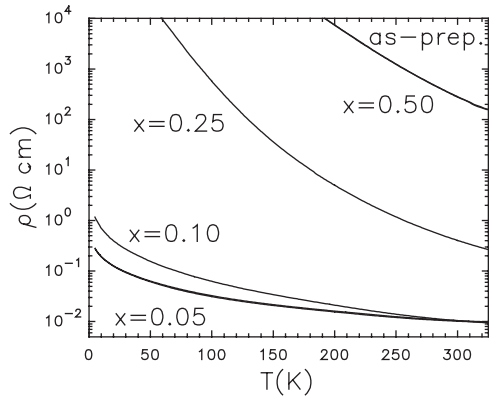


Fig. 3. Temperature (T) dependence of the resistivity (ρ) for the as-prepared $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ samples. The x values are labeled on the graph.

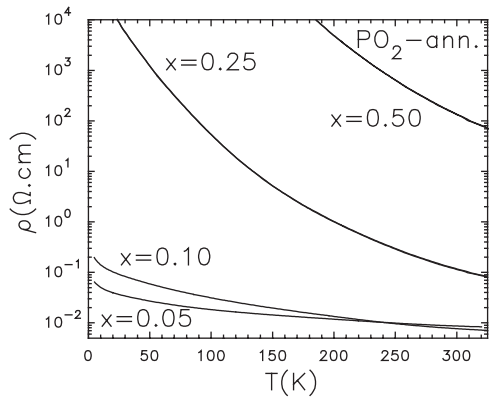


Fig. 4. $\rho(T)$ curves of the PO_2 -annealed samples.

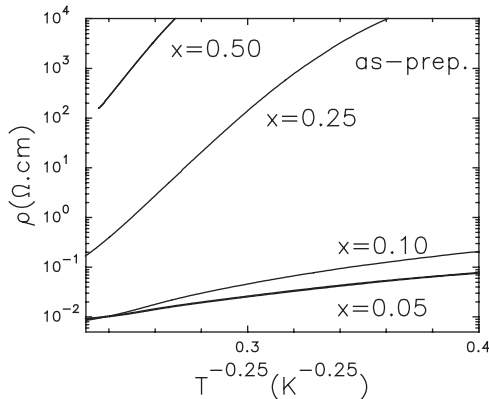


Fig. 5. $\rho(T^{-1/4})$ curves for the as-prepared $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ samples.

$\text{SrCoO}_{2.75}$ compared to SrCoO_3 [8], can be ascribed to both the presence of an oxygen deficiency and scattering by the Sc^{3+} impurity. Attempts to fit the $\rho(T)$ data by using an Arrhenius law [$\log \rho = f(T^{-1})$] or small-polaron hopping [$\log(\rho/T) = f(T^{-1})$] lead to a clear lack of linear regime. The most linear behavior is obtained by plotting $\log \rho = f(T^{-1/4})$ as shown in Fig. 5,

which corresponds to variable range hopping on a 3D conducting network. This result is expected in a disordered system to which the $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ series belongs, with the presence of Sc^{3+} and oxygen vacancies on the conducting array.

3.2. Magnetic properties

One attractive physical property of SrCoO_3 is the existence of ferromagnetism with a Curie temperature $T_C \sim 280$ K and saturation magnetization $M_S \sim 2 \mu_B/\text{Co}$ [14]. As previously reported, this ferromagnetism is very sensitive to oxygen stoichiometry, since only traces of ferromagnetism are detected [8,9] for $\text{SrCoO}_{2.75}$. The $\chi'(T)$ curves in Fig. 6 show that the existence of ferromagnetism is limited to compositions such as $0.05 \leq x \leq 0.25$. For all these compositions, one obtains $T_C \sim 160$ K, a value which does not depend too much on the composition as it is clearly deduced from the dissipation appearance ($\chi'' \neq 0$) on the $\chi''(T)$ curves (Fig. 7). The main difference is obtained for the absolute values of χ' which is maximum for $x = 0.05-0.10$

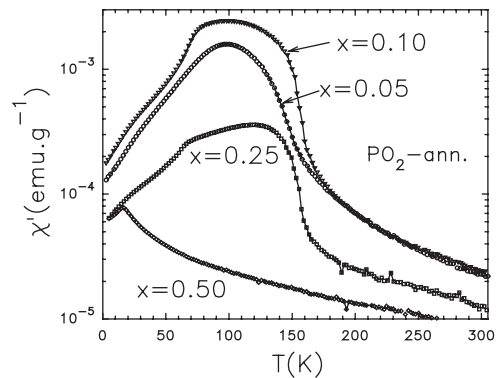


Fig. 6. T dependence of the magnetic ac-susceptibility (real part, χ') for the PO_2 -annealed $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ samples.

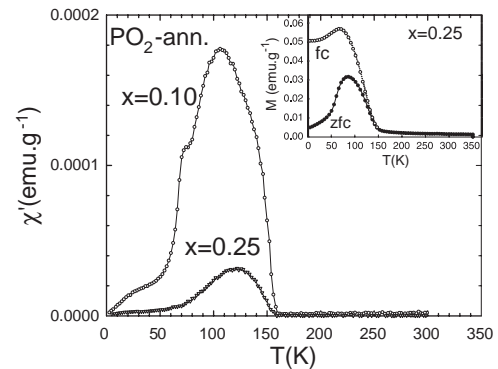


Fig. 7. T dependence of the χ imaginary part (χ'') for two PO_2 -annealed $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ samples corresponding to $x = 0.10$ and 0.25 . Inset. T -dependent magnetization (M) of $\text{SrCo}_{0.75}\text{Sc}_{0.25}\text{O}_{3-\delta}$ ($x = 0.25$) collected in zero-field-cooling and field-cooling modes (100 Oe).

(Fig. 6), i.e. the ferromagnetism is the strongest when the Sc^{3+} content is the lowest. This is in perfect agreement with the fact that the non-magnetic Sc^{3+} cations dilute the Co–O array. One must also point out that after PO_2 -annealing, the χ' absolute values increase as shown for $\text{SrCo}_{0.9}\text{Sc}_{0.1}\text{O}_{3-\delta}$ in Fig. 8 but the T_C is left almost unchanged ($\chi''(T)$ curves in the inset of Fig. 8).

The weakness of the ferromagnetism for these compounds is also illustrated by the magnetic field (H) dependence of the magnetization (M) collected for the PO_2 -annealed $\text{SrCo}_{0.95}\text{Sc}_{0.05}\text{O}_{3-\delta}$ sample (Fig. 9). Although the $M(H)$ curves exhibit a clear hysteresis indicative of ferromagnetism, magnetization is still not saturated in 5 T, reaching only $0.3 \mu_B/\text{Co}$, a value to be compared to $\sim 2 \mu_B/\text{Co}$ for $\text{SrCoO}_{3.00}$. This anomalous ferromagnetism is also exemplified by the $M(T)$ curves (inset of Fig. 7) of the $\text{SrCo}_{0.75}\text{Sc}_{0.25}\text{O}_{3-\delta}$ compound, collected in zero-field-cooling and field-cooling modes. These curves merge only beyond 150 K ($\sim T_C$) which is not expected in the case of a pure ferromagnet. Furthermore, below 70 K, M_{fc} starts to decrease as T decreases. The occurrence of an anomaly at the same

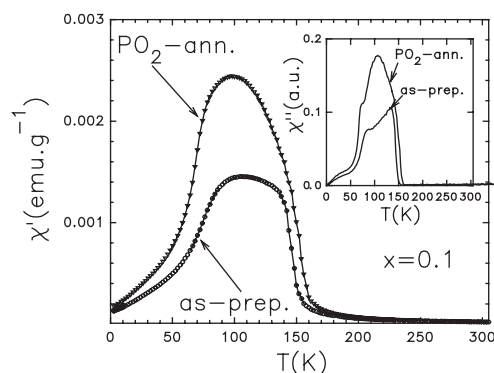


Fig. 8. Comparison of the $\chi'(T)$ curves for the as-prepared and PO_2 -annealed $\text{SrCo}_{0.90}\text{Sc}_{0.10}\text{O}_{3-\delta}$ samples. Inset: corresponding $\chi''(T)$ curves.

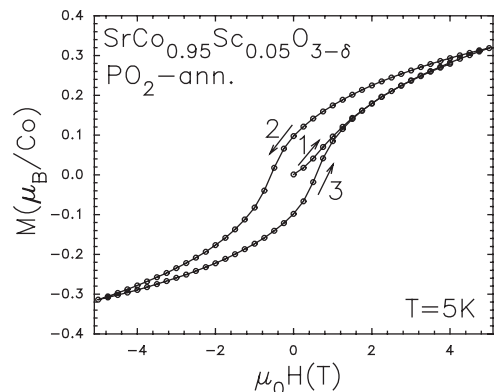


Fig. 9. Isothermal ($T = 5 \text{ K}$) magnetic field (H) dependence of magnetization (M) for the PO_2 -annealed $\text{SrCo}_{0.95}\text{Sc}_{0.05}\text{O}_{3-\delta}$ sample. The arrows indicate the increasing and decreasing branches of the loops.

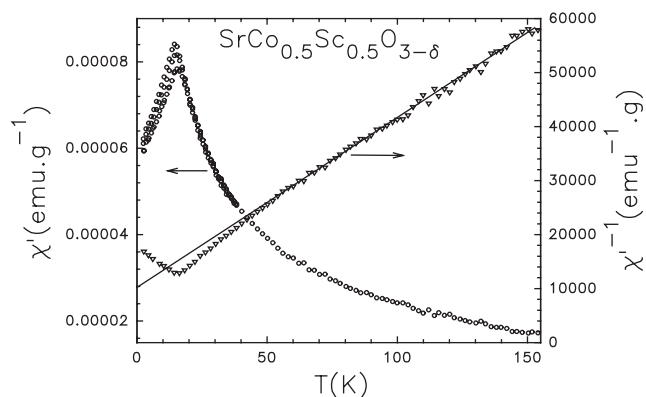


Fig. 10. $\chi'(T)$ and $\chi^{-1}(T)$ curves for $\text{SrCo}_{0.5}\text{Sc}_{0.5}\text{O}_{3-\delta}$.

temperature, $\sim 70 \text{ K}$, on the $\chi'(T)$ curves (for $x = 0.10$ and 0.25 in Fig. 6) could indicate a re-entrant spin-glass transition, associated to a cluster-glass state.

Finally for the largest Sc^{3+} content, $x = 0.5$, the $\chi'(T)$ curve shows a cusp-like curve more typical of spin-glasses (Fig. 10). The inspection of the three curves recorded for different frequencies of the ac magnetic field shows that the temperature of the χ' maximum increases as f increases, as expected for the frequency dependence of the freezing temperature in a spin-glass. The weakening of the ferromagnetic interactions in $\text{SrCo}_{0.5}\text{Sc}_{0.5}\text{O}_{3-\delta}$ can also be deduced from the negative temperature of the extrapolation of the χ^{-1} curve to $\chi^{-1} = 0$ leading to $\theta_p \sim -32 \text{ K}$. In comparison, for $\text{SrCo}_{0.90}\text{Sc}_{0.10}\text{O}_{3-\delta}$, one obtains $\theta_p = +130 \text{ K}$ (not shown), a value close to $T_C \sim 160 \text{ K}$, which demonstrates that ferromagnetic interactions dominate for the small contents of Sc^{3+} .

To summarize, it is found that the dilution by Sc^{3+} progressively reduces the amount of the ferromagnetism in the $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ series but does not reduce T_C for $x \leq 0.25$ too much. For a large enough amount of Sc^{3+} , the sample is ferromagnetic no more but exhibits a spin-glass like behavior with dominating antiferromagnetic interactions.

3.3. Magnetotransport properties

In these oxides, the presence of a weak ferromagnetism together with semi-conducting-like resistivity curves are good components to obtain magnetoresistance (MR) properties. According to the results previously obtained for $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ [7,8], showing the existence of an MR starting around T_C and increasing below T_C as T decreases, one may expect to obtain MR below about $\sim 160 \text{ K}$ in these $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ samples for $0.05 \leq x < 0.50$. This is exactly what is experimentally observed as shown in Fig. 11, where the negative MR is found to be maximum for the lowest temperatures, reaching $\sim 12\%$ in 7 T for the as-prepared $x = 0.05$ (Fig. 11a) and $x = 0.10$ (Fig. 11c) samples. It must be

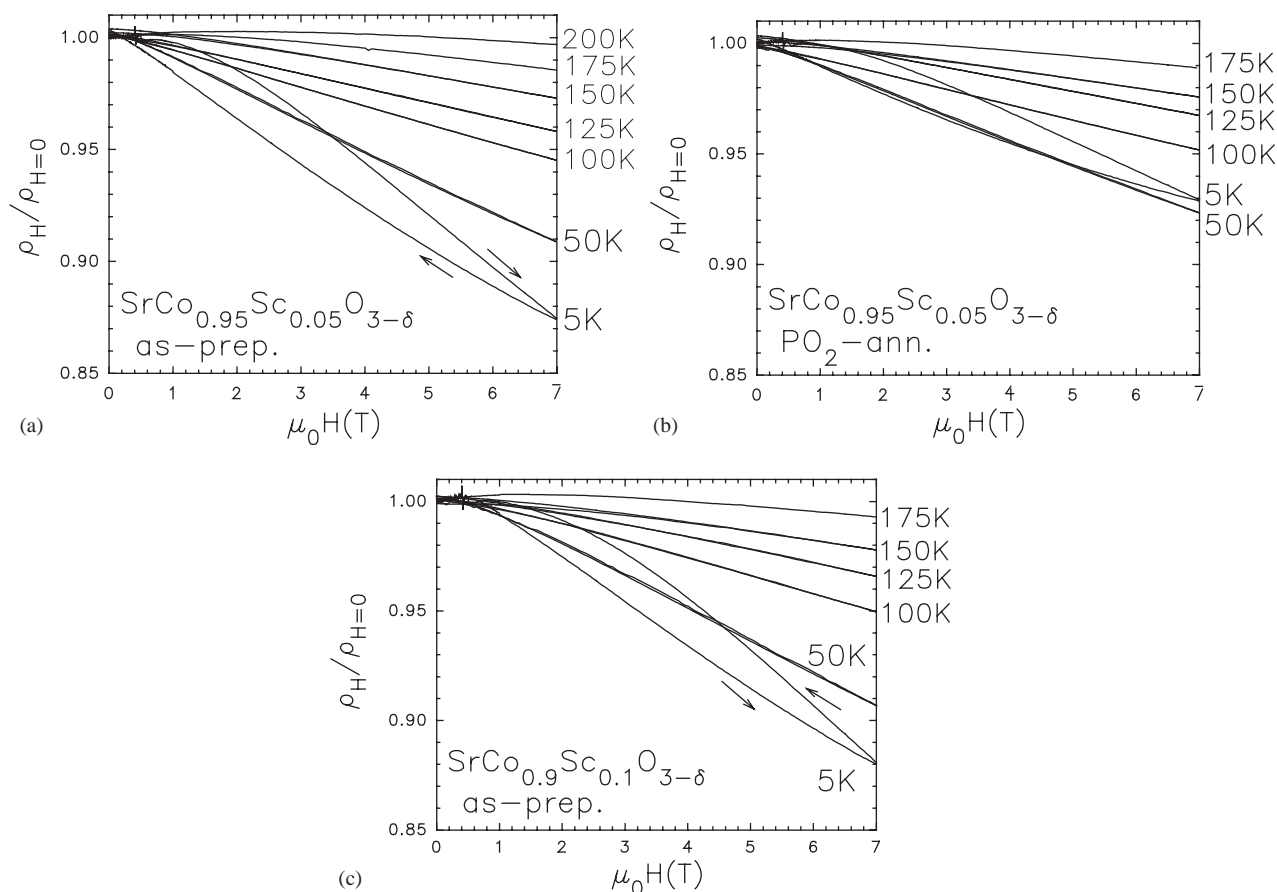


Fig. 11. Magnetic field (H) dependence of reduced magnetoresistance, $\rho(H)/\rho(H=0)$, for $\text{SrCo}_{0.95}\text{Sc}_{0.05}\text{O}_{3-\delta}$ as-prepared (a) and PO_2 -annealed (b) and for $\text{SrCo}_{0.90}\text{Sc}_{0.10}\text{O}_{3-\delta}$ ($x = 0.10$) (c).

also emphasized that the as-prepared samples exhibit higher MR values than the PO_2 -annealed ones (Figs. 11a and b) showing that the oxygen vacancies play an important role on the MR magnitude. The different shapes of the $\rho(H)/\rho(H=0)$ curves at 5 and 50 K, with a clear irreversibility at the former temperature, reflect the existence of a larger hysteresis in the $M(H)$ loop at 5 K. It must also be pointed out that the MR magnitude is as high as that reported for $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ [7,8]. It is thus remarkable that the substitutions of Sc^{3+} , a non-magnetic cation, leads to similar MR properties, the major difference being the lowest T_C (~ 160 K) for $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ than for $\text{SrFe}_{1-x}\text{Co}_x\text{O}_3$ ($T_C \geq 300$ K).

4. Concluding remarks

The present study of the structural and physical properties for $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ series shows that MR properties can be obtained in an oxygen-deficient perovskite cobaltite prepared without extreme conditions. From the obtained values of the cell parameters, calculated by using a cubic space group for sake of comparison, it is found that the cell volume increases

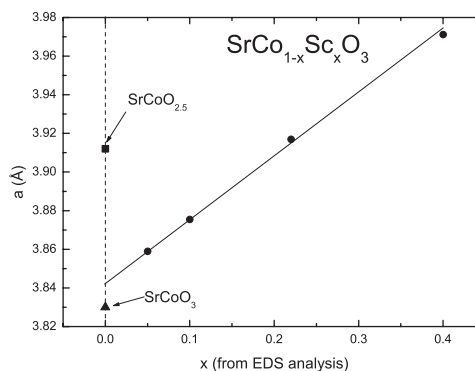


Fig. 12. x dependence of the a cell parameter ($Pm\bar{3}m$) for the $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ series. The values reported for $\text{SrCo}_{2.5}$ (■) and $\text{SrCo}_{3.0}$ (▲) from Ref. [14] are also reported.

monotonously with the Sc^{3+} content (Fig. 12). This is understood by considering the larger ionic radius of Sc^{3+} ($r_{\text{Sc}^{3+}}^{\text{VI}} = 0.745$ Å) compared to those of Co^{3+} (0.545 and 0.61 Å for low- and high-spin, respectively) and Co^{4+} (0.53 Å). For instance, with 50% Sc^{3+} substituted for cobalt, the a cell parameter, $a = 3.971$ Å, is much larger than the average value of the cell parameters of the $\text{SrCo}_{2.5}$ brownmillerite, ~ 3.91 Å (Fig. 12). It must

be outlined that for the $x = 0.25$ and 0.50 compounds, an oxygen content close to ~ 2.7 is found. According to a previous study of $\text{SrCoO}_{3-\delta}$, such an oxygen non-stoichiometry is consistent with the stabilization of a perovskite structure [11]. The extrapolation to $x = 0$ of the $a(x)$ curve of Fig. 12, leads to ~ 3.84 Å, a value larger than that reported for SrCoO_3 ($a = 3.83$ Å [14]), in agreement with the existence of an oxygen non-stoichiometry.

This deviation from the “O₃” stoichiometry could partially explain the lack of metallicity observed on the $\rho(T)$ curves in contrast to the metallic behavior of $\text{SrCoO}_{3.00}$. The increase of the absolute value of ρ with x is also the result of the charge carrier scattering by the $3d^0$ Sc^{3+} impurities. Nonetheless, the ρ absolute values, at room temperature, for the $x = 0.05$ and 0.10 samples ($\sim 10^{-2} \Omega \text{cm}$) are comparable to those reported for $\text{SrCoO}_{3.00}$ [14], showing that the oxygen non-stoichiometry is not too detrimental to the charge carrier delocalization. $\text{SrCoO}_{3.00}$ semi-metallicity was explained on the basis of a partial transfer of t_{2g} electrons to e_g levels creating a Co^{4+} fraction in the intermediate spin state [14]. Since the ρ -values for $\text{SrCoO}_{3.00}$ are larger than that of $\text{Co}^{3+}/\text{Co}^{4+}$ oxygen stoichiometric perovskite ($\rho_{300\text{K}} \sim 10^{-3} \Omega \text{cm}$ for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ [4]), one cannot simply ascribe the ρ -values of $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ to a similar mechanism of conduction by $\text{Co}^{3+}/\text{Co}^{4+}$ mixed valency but rather to the strong covalency [15]. From the linear part of the curves of inverse magnetic susceptibility as a function temperature, the effective paramagnetic moments μ_{eff} values are all found to lie in the range $2.5\text{--}3.1 \mu_{\text{B}}/\text{Co}$. These values are similar to that of $\text{SrCoO}_{3.00}$ ($\mu_{\text{eff}} = 3.0 \mu_{\text{B}}$), for a mixture of both Co^{4+} spin-states, low-spin ($1.8 \mu_{\text{B}}$) and intermediate-spin ($3.8 \mu_{\text{B}}$), explaining the experimental values. But, the presence of both non-magnetic Sc^{3+} impurity, which dilutes the magnetic network, and oxygen vacancies responsible for a large amount of Co^{3+} makes that, at low temperature, the magnetization, even in a 5 T magnetic field, exhibits lower values than expected for a mixture of low-spin and intermediate-spin Co^{4+} ($1 \mu_{\text{B}} < M_S < 3 \mu_{\text{B}}$). The strong impact of the B-site dilution together with the oxygen deficiency on the magnetic properties is also demonstrated by the Curie temperature decrease, from ~ 280 K for $\text{SrCoO}_{3.00}$ against a maximum T_C value of ~ 160 K in the $\text{SrCo}_{1-x}\text{Sc}_x\text{O}_{3-\delta}$ series. The spin-glass behavior ob-

tained for the half-doped compound, $\text{SrCo}_{0.5}\text{Sc}_{0.5}\text{O}_{3-\delta}$, together with the negative θ_p value, demonstrates that competing positive and negative magnetic exchange energies exist in those materials. The systematic maximum on the $\chi'(T)$ curves supports the existence of ferromagnetic clusters characterized by a blocking temperature. The disorder at both Co- and O-sites favors such magnetic behavior. The negative magnetoresistance must be related to this disordering. Application of an external magnetic field favors the parallel alignment of the clusters magnetization. Due to their more conducting behavior, the reduced magnetic scattering induced by this alignment is certainly responsible for the observed negative magnetoresistance.

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