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Influence of the dimensionality of the structure and the nature of the rare earth on the magneto-transport properties of $Nd_{1-x}Sr_{1+x}CoO_4$ (0 < x < 0.30)

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Abstract

We report the magneto-transport properties of the layered mixed oxides $Nd_{1-x}Sr_{1+x}CoO_4$ ($0 \le x \le 0.3$) compounds. These materials are found to evolve towards an anomalous "cluster-glass" like behavior as *x* increases. The onset of the ferromagnetic order in the bidimensional phase is seen to occur in the x = 0.30 sample at $T_c(2D) \approx 125$ K, followed by a blocking process around T_B (2D) ≈ 55 K. In addition, present in the magnetic response of these materials is the paramagnetic contribution coming from the Nd³⁺ ions $\mu_{eff-Nd^{3+}} = 3.62\mu_B$ together with the signal coming from a minority perovskite phase, that is nevertheless not detected by powder X-ray diffraction.

From the electrical point of view these materials are semiconducting and their resistivity decreases upon doping. In addition, at low temperatures T < 25 K, these compounds show magnetoresistance. The highest effect is found for the sample x = 0.3 that shows a magnetoresistance MR = -17% at T = 10 K under a field $H_{\text{max}} = 50$ kOe.

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1. Introduction

Cobalt mixed oxides with perovskite structure constitute an especially interesting family of compounds which have been studied since the 1950s, in particular the perovskites $La_{1-x}Sr_xCoO_3$ [1–4]. In this context, LaCoO_3 exhibits remarkable transport and magnetic properties as a result of thermally induced transitions from low-spin state to higher-spin configuration in the trivalent cobalt ions [2,4]. Whereas LaCoO_3 shows high resistivity and antiferromagnetic exchange interactions, the $La_{1-x}Sr_xCoO_3$ materials evolve towards a ferromagnetic metallic behavior as doping increases [3]. That evolution takes place smoothly and a number of different magnetic and electrical behaviors have been characterized as a function of *x* and temperature [5–7]: superparamagnetism, spin-glass/cluster

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glass behavior and so forth, semiconducting/metallic behaviors, etc. Also, large MR has been found in the lowest-doped samples $x \le 0.15$ [8]. Other Ln_{1-x}M_xCoO₃ systems (Ln:La, rare earths; M:Sr, Ca, Ba) [9–12] also show interesting electrical and magnetic properties.

Contrary to the case of the 3D Co-perovskites, the study of the magnetic and transport properties of other Co-Ruddlesden–Popper phases of lower dimensionality is a relatively much less explored area, although also very interesting as shown by the recent discovery of superconductivity in layered cobalt oxides [13] and magnetoresistance (MR) in the $La_{1-x}Sr_{1+x}CoO_4$ compounds [14].

In this work we focus in the properties of the bidimensional Nd series $Nd_{1-x}Sr_{1+x}CoO_4$, for which to our knowledge, the only information available in the literature refers to its synthesis and structural characterization [15,16].

We have carried out this study in the compositional range in which a solid solution $Nd_{1-x}Sr_{1+x}CoO_4$ is known to form, namely $0 \le x \le 0.30$ [15].

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Fig. 1. Schematic representation of the K_2NiF_4 structure displayed by the $Nd_{1-x}Sr_{1+x}CoO_4$ compounds.

The structure of these $0 \le x \le 0.30$ compounds shows tetragonal symmetry (space group: *I*4/*mmm*) and can be described as a sequence of CoO₂ layers in between Nd/Sr–O rock-salt planes, in which the Co ions are in a tetragonally elongated octahedral environment while the Nd/Sr ions are randomly distributed in nine-coordinated sites (Fig. 1) [15]. It is worth noting that in this rather rigid structure the Co–O–Co angles are in all cases 180° and that the Co–O distances do not change significantly upon doping [15].

In what follows we will show the most outstanding results about the evolution of the magnetic and transport properties of the $Nd_{1-x}Sr_{1+x}CoO_4$ compounds upon doping and the magnetoresistance they show at low temperature. We will also refer to the influence of the dimensionality of the structure and the nature of the rare earth ion on the observed behavior.

2. Experimental

The samples with nominal composition $Nd_{1-x}Sr_{1+x}CoO_4$ (x=0, 0.10, 0.20 and 0.30) used for this study were prepared by the decomposition of the corresponding mixture of nitrates in the presence of KNO₃, as reported in Ref. [15], where their structural and microstructural characterization is also described and discussed.

It is worth noting that according to the powder X-ray diffraction results, these samples are single-phase crystalline materials, in which the presence of perovskite-related phases (that often appear as impurities of the Ruddlesden–Popper phase with n = 1) is not detected [15].

Meanwhile, we did not consider for this study samples with nominally higher Strontium content as in fact they consisted in a mixture of phases, as revealed by powder X-ray diffraction [15].

Attempts to measure the oxygen content of these materials by iodometric titrations were unsuccessful, as the samples were too oxidizing and decomposed the aqueous media. For this reason this parameter could not be quantified in this work.

Taking into account that in closely related cobalt systems the asprepared x=0 samples are oxygen stoichiometric, while for $x \le 0.30$ a very small but increasing oxygen deficiency can be present (for example, in 2D La_{1-x}Sr_{1+x}CoO_{4- δ} ($0 \le x \le 0.30$), δ_{max} (x=0.30)=0.05 ± 0.01 [15], or in 3D La_{1-x}Sr_xCoO_{3- δ} δ_{max} (x=0.30)=0.01 ± 0.01 [5]), we expect similar features

here. Therefore, in view of those rather small δ values and for simplicity in what follows we will refer to these samples as $Nd_{1-x}Sr_{1+x}CoO_4$.

In any case, the possible presence of a small oxygen deficiency should not substantially alter the magneto-transport behavior of this system and the validity of the discussion we will make.

dc 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 K \leq T \leq 300 K. Hysteresis loops in ZFC conditions were obtained at 5 K varying the field up to \pm 50 kOe.

In addition, ac magnetic susceptibility studies were carried out, as this technique is specially useful to reveal magnetic transitions in complex systems. For this purpose, the ac magnetic susceptibility was measured as a function of temperature with a Lake Shore 7000 system using the mutual-inductance technique. Data were collected on warming from 13 to 300 K after zero-field cooling of the sample. The calibration was performed with a $Gd_2(SO_4)_3$ ·8H₂O paramagnetic standard having the same shape and size as the investigated samples.

The four-probe electrical resistivity of bars $\sim (10 \text{ mm} \times 4 \text{ mm} \times 1 \text{ mm})$ was measured as a function of temperature in the range $4 \le T$ (K) ≤ 300 in a zero magnetic field (H=0) and with a constant field between 0 < H (kOe) < 50 using a homemade device. In this device the magnetoresistance of the samples was measured at a constant temperature using a magnetic field ranging from 0 to 50 kOe.

Seebeck coefficients of bars $\sim (10 \text{ mm} \times 4 \text{ mm} \times 1 \text{ mm})$ were measured in the temperature interval $77 \leq T(K) \leq 450$ with a homemade device.

3. Results

3.1. Magnetic properties

First of all we will refer to the magnetic properties of the x=0 compound with nominal composition NdSrCoO₄. Fig. 2 shows the dc magnetic susceptibility data $\chi_{\rm m}(T)$ for this sample. As it can be seen in this figure, the susceptibility changes markedly below some critical temperatures, marked by arrows, namely ≈ 200 and 50 K.

The dc $\chi_m(T)$ data of this x=0 sample follow a Curie–Weiss law for 200 < T(K) < 300 and from the corresponding fitting we have calculated the effective magnetic moment per cobalt ion (μ_{eff-Co}) from the total μ_{eff} ($\mu_{eff} = \sqrt{8C}$) after appropriate substration of the Nd³⁺ contribution (where L=3 and



Fig. 2. dc ZFC (open circles) and FC (closed circles) molar magnetic susceptibility data for NdSrCoO₄ (x = 0) measured under a field H = 1000 Oe. The solid line corresponds to a simulation of the paramagnetic behavior of the Nd³⁺ cations.



Fig. 3. dc ZFC (closed symbols) and FC (open symbols) molar magnetic susceptibility of $Nd_{1-x}Sr_{1+x}CoO_4$ (0.10 $\le x \le 0.30$) measured under a field H = 1000 Oe.

S = 3/2) and $\mu_{\text{eff-Nd}^{3+}} = 3.62\mu_{\text{B}}$ [17]. The obtained results give a $\mu_{\text{eff-Co}} = 2.48\mu_{\text{B}}$ and a negative Weiss constant $\Theta = -78.7$ K.

As the doping degree increases (x > 0), the dc magnetic susceptibility of the samples increases markedly with x below $\sim 200 \text{ K}$ (Fig. 3).

The temperature dependence of the real part of the ac susceptibility, χ' , of these samples is shown in Fig. 4. As it can be seen, the sharp rise of the susceptibility below ~ 200 K is followed by a shoulder at ~ 125 K and a maximum at ~ 55 K. It is also remarkable that as *x* increases the intensity of these last two features increases markedly and their position slightly shifts towards higher temperatures.

Also, the inverse of the dc susceptibility curves follow the Curie–Weiss law for 200 < T(K) < 300 and from the corresponding fitting we have calculated the effective magnetic moment per cobalt ion (μ_{eff-Co}) and the Weiss constant of these compounds. The obtained values are shown in Table 1. As it can be seen, the Weiss constant has negative values for $x \le 0.10$, that evolve towards positive values as *x* increases.



Fig. 4. ac magnetic susceptibility of $Nd_{1-x}Sr_{1+x}CoO_4$ $0 \le x \le 0.30$ compounds measured with a driving field amplitude $H_0 = 2.5$ Oe, oscillating at a frequency of 1 kHz.

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Effective magnetic moment of the Co ions μ_{eff-Co} and Weiss constant (Θ) of Nd_{1-x}Sr_{1+x}CoO₄ ($0 \le x \le 0.30$) compounds

	x = 0.0	x = 0.10	x = 0.20	x = 0.30
$\frac{\mu_{\text{eff-Co}}(\mu_{\text{B}})}{\Theta(\text{K})}$	2.48	2.64	2.62	2.60
	-78.7	-35.6	30.4	91.2

The M(H) curves of these samples are shown in Fig. 5. As it can be observed the magnetization increases with x and none of the curves reach saturation under the highest field used of 50 kOe. Also, the shape of these curves seems to reflect the contribution from a magnetically ordered phase – that gives rise to a small hysteresis loop – and from a paramagnetic species.

3.2. Transport properties

The first general observation is that, for these doping levels $0 \le x \le 0.30$, these samples are semiconducting, with a rather high resistivity (ρ), even if ρ decreases as the Sr content increases (see Fig. 6(a)). In addition, the Seebeck results shown in Fig. 7 reveal that the charge carriers are holes (the Seebeck coefficient (α) is in all cases positive); and that their number increases with *x* (the Seebeck coefficient gets smaller).

It should be noted that in the case of the x=0 sample, where all the cobalt ions are expected to have a formal valence of 3+, the Seebeck coefficient is much lower than expected, as compared with the very high values found in the corresponding 3D perovskite NdCoO₃ [18].

On the other hand, in the temperature range 220 < T(K) < 300, the temperature dependence of both the resistivity and the Seebeck data of all these samples indicate a conduction by non-adiabatic small polaron holes, see Fig. 6 (a), according to the expressions [19,20]:

$$\rho \propto T^{3/2} \exp\left[\frac{E_a}{T}\right]$$
(1)

$$\alpha \propto \ln \left[\frac{1-c}{c}\right] \tag{2}$$



Fig. 5. M(H) curves of the Nd_{1-x}Sr_{1+x}CoO₄ $0 \le x \le 0.30$ compounds measured at 5 K.



Fig. 6. (a) Electrical resistivity vs. temperature curves corresponding to $Nd_{1-x}Sr_{1+x}CoO_4$ $0 \le x \le 0.30$ compounds $(80 \le T(K) \le 300)$ and fits (solid line) to a non-adiabatic small polaron behavior. (b) Fits (solid line) of electrical resistivity vs. temperature curves of $0.10 \le x \le 0.30$ compounds to VRH behavior.

where c = x/N is the ratio of charge carriers (holes/electrons) to the number of sites available.

From the corresponding fits we have calculated an activation energy that decreases from 220 meV for x=0 to 100 meV for x=0.30.



Fig. 7. Temperature dependence of the Seebeck coefficient of $Nd_{1-x}Sr_{1+x}CoO_4$ ($0 \le x \le 0.30$) in the temperature range $100 \le T(K) \le 450$. The solid line fits to VRH behavior while the dash line corresponds to fits to polarons behavior.



Fig. 8. Temperature dependence of the electrical resistance of the x = 0.20 and 0.30 samples in the absence of a magnetic field and under a field of 40 kOe ($5 \le T(K) \le 25$). Inset: MR as a function of temperature measured under a field of 40 kOe in this same interval.

Meanwhile, for 80 < T(K) < 175 the temperature dependence of both the resistivity and the Seebeck coefficient of these compounds is best fitted to the 2D Mott variable-range hopping (VHR) expressions, see Fig. 6(b) [19,21]:

$$\rho \propto \exp\left[\frac{T_0}{T}\right]^{1/3}$$
(3)

$$\alpha \propto T^{1/3} \tag{4}$$

where T_0 is related to the density of states at the Fermi energy and the localization length.

To study the influence of the magnetic field on the electrical resistivity of these materials, we measured $\rho(T)$ under a constant magnetic field of 40 kOe. As it can be seen in Fig. 8, the magnetic field reduces the samples' resistivity at low temperatures T < 25 K and the effect becomes more pronounced as temperature diminishes. Therefore, we performed magnetoresistance versus magnetic field experiments at the lowest possible temperature. Representative results are shown in Fig. 9 including the high values of MR {defined as MR = $(R_H - R_{H=0})/R_{H=0}$ } that are obtained for x = 0.20 MR (x = 0.20) = -15% under $H_{\text{max}} = 50$ kOe and x = 0.30 MR (x = 0.30) = -17% under $H_{\text{max}} = 50$ kOe at 10 K.



Fig. 9. Field dependence of the electrical resistivity of the x = 0.20 and 0.30 samples measured at 10 K.

4. Discussion

As it occurs in the previously studied $La_{1-x}Sr_{1+x}CoO_4$ system, the magnetic and transport properties of the $Nd_{1-x}Sr_{1+x}CoO_4$ compounds are rather complex.

Starting by the sample with nominal composition NdSrCoO₄ (x=0), that in principle should be a Co³⁺ compound (assuming it is stoichiometric, for the reasons explained before), its magnetic and electrical behaviors are rather surprising.

But one has to be careful with the interpretation of the obtained results as some features, of both the dc and ac susceptibility curves, show analogies with those of the 3D $Nd_{1-x}Sr_xCoO_3$ perovskite ([18] and references therein). In this context, the 3D system has a ferromagnetic-paramagnetic transition around 200 < T(K) < 225 [18], that could be well one of the features appearing in Fig. 2 and marked as $T_{\rm c}(3D)$. This would mean that the sample with x = 0 and nominal composition NdSrCoO₄ contains a small impurity of Nd_{1-m}Sr_mCoO₃, as minority phase, and a majority layered phase $Nd_{1-v}Sr_{1+v}CoO_4$ with y > 0 (and therefore 3+ and 4+ mixed-valence in the cobalt ions). And although we did not detect the presence of this perovskite phase by powder X-ray diffraction it is very feasible that it exists as small intergrowths within the major lamellar phase, as it has been revealed to occur in the case of $La_{1-x}Sr_{1+x}CoO_4$ by means of very detailed TEM studies [15].

The results of the thermoelectric power of this sample of nominal composition x = 0 corroborate this picture: as already mentioned the Seebeck coefficient of this material is much lower than expected for a purely trivalent Co compound, result that reveals that the starting layered compound is in fact already doped with a certain number of holes, so that the nominal composition and the real composition of the compound are different.

As for the sharp increase of the magnetic susceptibility of this sample at lower temperature, T < 50 K, it is due to the paramagnetic contribution of the Nd³⁺ ions with L=3 and S=3/2, as seen in the corresponding fit shown in Fig. 2.

On the other hand, the estimated effective magnetic moment per cobalt ion in this nominally x = 0 sample is $\mu_{eff-Co} = 2.48 \mu_B$ in sharp contrast with the case of the 3D NdCoO₃ sample in which $\mu_{eff-Co} = 0\mu_B$. This means that while in the 3D compound 100% of the trivalent cobalt ions are in the low spin configuration (t⁶e⁰) $\mu_{eff-Co} = 0\mu_B$ in the lamellar compound the axially elongated octahedral environment of the Co ions [15] would be favoring an intermediate spin configuration (t⁵e¹) $\mu_{eff-Co} = 2.8\mu_B$ in 80% of the cobalt ions, as found in related lamellar compounds [22,23].

As the doping degree increases x > 0, so does the susceptibility and the compounds are seen to slowly evolve towards an anomalous ferromagnetic cluster-glass behavior.

Specially interesting are the data corresponding to the x = 0.30 sample, where in addition to the signals coming from the perovskite impurity and the paramagnetic contribution of the Nd³⁺ ion (that is stronger at low temperatures and for low doping degrees), the magnetic behavior of the layered phase is clearly observed in the $\chi(T)$ curves. In this context we assign the shoulder seen in the ac curves around ~125 K to the ferromagnetic ordering in the 2D compound $T_c(2D)$, while we attribute the maximum at ~55 K to a blocking process within the lamellar phase T_B (2D).

In the $x \le 0.2$ compounds, little ferromagnetic clusters are probably also present (see below), but in the $\chi_m(T)$ curves their magnetic signal would be hidden by the stronger ferromagnetic response coming from the 3D perovskite impurity and the paramagnetic behavior of the Nd³⁺ ions.

The evolution of the Weiss constant with *x* corroborates a progressive increase in the strength of the ferromagnetic interactions, as *x* gets higher.

From the electrical point of view, even if the resistivity of these samples decreases upon doping, it remains rather high in the whole compositional range studied and all the materials remain semiconducting.

If we now compare these results with the corresponding 3D $Nd_{1-x}Sr_xCoO_3$ compounds to see the influence of the dimensionality of the structure on the obtained results we observe the following: in the 2D samples T_c and Θ are considerably lower than in the corresponding 3D compounds $T_c(2D) \sim 125$ K versus $T_c(3D) \sim 225$ K [18]; on the other hand, the resistivity of the 2D samples is several orders of magnitude higher that in the 3D analogues [18].

To understand these differences one has to take into account that the K_2NiF_4 and perovskite structure are both based on corner-shared [CoO₆] octahedra, that in the case of the 2D phase are just linked to other four $[CoO_6]$ octahedra within the *a*-*b* plane, while they are linked to six in the three space directions in the case of the 3D perovskites.

As a consequence and as the Curie temperature depends on the number of nearest neighbors [24]:

$$T_{\rm c} \approx \frac{2zS(S+1)J}{3k_{\rm B}} \tag{5}$$

where z is the number of nearest neighbors, S the total spin angular momentum, J the exchange integral and $k_{\rm B}$ is the Boltzmann constant.

 $T_{\rm c}$ turns to be lower (and the ferromagnetic interactions weaker) in the layered compounds as compared to the corresponding 3D perosvkites, as found experimentally.

In addition, the bandwidth $w \approx 2zb$ [25], that also depends on the number of neighbors z will be narrower in the case of the 2D compounds and will hinder stabilization of ferromagnetic interactions via double-exchange.

As a result, the 2D compounds show lower T_c , lower magnetization and lower conductivity than the corresponding 3D compounds.

On the other hand, if we now compare the here obtained results with those of the related 2D La compounds $La_{1-x}Sr_{1+x}CoO_4$ to see the influence of the rare earth on their properties we find that in the Nd compounds the $T_c(2D)$ value is slightly lower than that of the La compounds, $T_c(2D, Nd) \sim 125$ K and $T_c(2D, La) \sim 150$ K. Also, the effective magnetic moments of the Co ions are slightly smaller in the case of the Nd-compounds. Meanwhile, the electrical resistivity of the Nd samples is one order of magnitude higher than in the La compounds.

These differences arise from the smaller size and thus the stronger acidity (higher q/r ratio) of the Nd³⁺ cation (^{IX} $r_{Nd^{3+}} = 1.163 \text{ Å}$) compared to the La³⁺ one (^{IX} $r_{La^{3+}} = 1.216 \text{ Å}$). As a consequence Nd³⁺ competes more strongly with the cobalt for bonding to the oxygen atoms, which results in a progressive stabilization of the π^* (Co–O) levels and a larger splitting between the t_{2g} and e_g ones [26]. Therefore, at a given temperature the spin state of the cobalt ions in the Nd compounds are lower than in the corresponding lanthanum ones.

Another important point is that as the Nd–O bonds get stronger, the Co–O bands get narrower, so that the hole conduction will be worse and the ferromagnetic interactions weaker than in the corresponding $La_{1-x}Sr_{1+x}CoO_4$ compounds. These two facts explain why in these Nd-samples the susceptibility values are lower, the resistivity values higher than in the corresponding 2D La compounds.

But this Nd_{1-x}Sr_{1+x}CoO₄ system is probably even more complex than described so far. In this context, an electronic phase segregation has been shown to occurs in very closely related cobalt mixed oxides such as 3D La_{1-x}Sr_xCoO₃ [5,7] or 2D La_{1-x}Sr_{1+x}CoO₄ [14].

For those systems, we have proposed [5,14] that upon doping the material segregates into hole-rich, ferromagnetic and more conducting regions and a hole-poor matrix, insulating and with antiferromagnetic interactions, both coexisting within the same crystallographic phase. According to that model, for lower doping degrees the holerich regions are isolated from one another and show FM ordering below a critical temperature T_c that changes very little with x (for example, $T_c \sim 250$ K in the case of the La_{1-x}Sr_xCoO₃ perovskite [5]). Long-range magnetic order via frustrated intercluster interactions occurs below a blocking process at a lower T_B (for example $T_B \sim 60$ K in the case of the La_{1-x}Sr_xCoO₃ perovskite [5]).

In view of the similarities, the same situation could be present in the $Nd_{1-x}Sr_{1+x}CoO_4$ materials, even if the lower dimensionality of the structure and the presence of the Nd^{3+} cations would induce differences in the spin state of the Co ions, the characteristics of the hole-poor and hole-rich regions, as well as the magnetic and electrical connections between them.

The magnetoresistive effects shown by these polycrystalline Nd-samples could be explained invoking this electronic phase segregation scenario. Within this model, we can explain the high MR exhibited by these samples at low temperatures on the basis of two contributions:

- Intragranular effects: this would consist of a reduction in the scattering of the electrons at the boundaries between the FM regions and the matrix upon application of the magnetic field, due to a better relative alignment of the magnetic clusters. This mechanism would be rather similar to that present in heterogeneous ferromagnetic alloys [27,28], magnetic multi-layers [29] and keeps also an analogy with that acting on the lamellar Mn perovskites.
- 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 [30]. 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.

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