

Articles

Magnetotransport in $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 < x \leq 0.30$) Perovskites

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We introduce the magnetotransport properties of $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 < x \leq 0.30$) materials. These compounds are semiconducting and show a magnetic transition at $T_c \approx 160$ K associated with the onset of magnetic order of cobalt ions within superparamagnetic clusters, which have a freezing point $T_B < T_c$. Very remarkably, the more resistive samples showed rather large magnetoresistance at the lowest available temperature: $\text{MR}_{\text{max}}(x = 0.10) \approx -16\%$ at $T = 4.2$ K under $H_{\text{max}} = 40$ kOe. We relate these results to the inhomogeneous electronic structure of these cobaltates and to the presence of the paramagnetic Gd^{3+} sublattice, which at low temperatures influences the cobalt ions of the superparamagnetic clusters, provoking an increase in the size of the hole-rich regions and in the hopping probability of the charge carriers, and gives rise to the negative magnetoresistance observed.

Introduction

The interplay between magnetism and electrical conductivity in perovskite-type oxides has been studied in the last few decades¹ and with renewed interest since the discovery of colossal magnetoresistance (CMR) in doped manganese-based compounds.^{2,3}

Among perovskites, cobaltates constitute an especially interesting family of compounds and have been studied since the 1950s, in particular the lanthanum materials.^{4–8}

In this context, LaCoO_3 has been found to exhibit remarkable transport and magnetic properties as a result of thermally induced transitions from low-spin (LS: t^6e^0) to higher-spin states of the trivalent cobalt ions (intermediate spin IS: t^5e^1 , high spin HS: t^4e^2).^{5,9}

Those early studies also showed that while LaCoO_3 shows high resistivity and antiferromagnetic exchange interactions, the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ materials evolve toward a ferromagnetic metallic behavior when doped.¹⁰ Since then, the magnetic and electrical properties of the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ system have been repeatedly investigated, revealing that the evolution takes place smoothly and that a number of different magnetic and electrical behaviors are present for different degrees of doping: superparamagnetism, spin-glass/cluster-glass behaviors and so forth, semiconducting/metallic behaviors, and even metal–insulator transitions as a function of temperature.^{8,11} Those studies have also been extended to the Ca- and Ba-doped materials $\text{La}_{1-x}\text{M}_x\text{CoO}_3$ ($\text{M} = \text{Ca}, \text{Ba}$).^{12–14}

Recently, large magnetoresistance has been observed in the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ systems.^{13,15–17} In both of them the highest negative MR effects were found in low-doped samples and at temperatures where the compounds experience a spin-glass transi-

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(1) Goodenough, J. B.; Longo, J. M. *Crystallographic and magnetic properties of perovskite and perovskite-related compounds*; Landolt-Börnstein Tables, group III/ vol. 4a; Springer-Verlag: Berlin, 1970.

(2) Von Helmut, R.; Wecker, J.; Holzapfel, B.; Schulz, L.; Samwer, K. *Phys. Rev. Lett.* **1993**, *71*, 2332.

(3) Jin, S.; Tiefel, T. H.; McCormack, M.; Fastnacht, R. R.; Ramesh, R.; Chen, L. H. *Science* **1994**, *264*, 413.

(4) Goodenough, J. B. *J. Phys. Chem. Solids* **1958**, *6*, 287.

(5) Raccach, P. M.; Goodenough, J. B. *Phys. Rev.* **1967**, *155*, 932.

(6) Thornton, G.; Morrison, F. C.; Partington, S.; Tofield, B. C.; Williams, D. E. *J. Phys. C: Solid State Phys.* **1988**, *21*, 2871.

(7) Rajoria, D. S.; Bhide, V. G.; Rama Rao, G.; Rao, C. N. R. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 512.

(8) Señaris-Rodríguez, M. A.; Goodenough, J. B. *J. Solid State Chem.* **1995**, *118*, 323.

(9) Señaris-Rodríguez, M. A.; Goodenough, J. B. *J. Solid State Chem.* **1995**, *116*, 224.

(10) Raccach, P. M.; Goodenough, J. B. *J. Appl. Phys.* **1968**, *39*, 1209.

(11) Itoh, M.; Natori, I.; Kubota, S.; Matoya, K. *J. Phys. Soc. Jpn.* **1994**, *63*, 1486.

(12) Rao, C. N. R.; Parkash, O. M.; Bahadur, D.; Ganguly, P.; Nagabhu Share, A. *J. Solid State Chem.* **1977**, *22*, 353.

(13) Barman, A.; Ghosh, M.; De, S. K.; Chatterjee, S. *Phys. Lett. A* **1997**, *234*, 384.

(14) Breijo, M. P.; Castro-García, S.; Señaris-Rodríguez, M. A.; Mira, J.; Fondado, A.; Rivas, J. *Ionics* **1999**, *5*, 213.

(15) Brinceño, G.; Chang, H.; Sun, X.; Schulz, P. G.; Xiang, X.-D. *Science* **1995**, *270*, 273.

(16) Golovanov, V.; Mihaly, L.; Moodenbaugh, A. R. *Phys. Rev. B* **1996**, *53*, 8207.

(17) Mahendiram, R.; Raychaudhuri, K. *Phys. Rev. B* **1996**, *54*, 16044.

tion: MR_{\max} ($M = \text{Sr}$, $x = 0.07$) $\approx -40\%$ at $T = 40$ K under $H_{\max} = 60$ kOe¹⁷ and MR_{\max} ($M = \text{Ba}$, $x = 0.1$) $\approx -9\%$ at $T = 25$ K under $H_{\max} = 60$ kOe.¹³

Other important cobalt perovskites are the rare-earth $\text{Ln}_{1-x}\text{M}_x\text{CoO}_3$ systems ($\text{Ln}^{3+} = \text{Pr}^{3+}$, Nd^{3+} , Gd^{3+} , etc.), which also show complex electrical and magnetic properties,^{12,18–21} although they have been much less investigated than the corresponding lanthanum compounds. This is the case for the sparsely studied series of gadolinium cobaltates which, in fact, are particularly interesting: they contain the Gd^{3+} ion, which has a high magnetic moment with no L–S anisotropy ($L = 0$, $S = 7/2$) (unlike $\text{La}_{1-x}\text{M}_x\text{CoO}_3$, in which the La^{3+} cation is nonmagnetic ($L = S = 0$)), and the magnetism associated with this rare-earth ion could play a role in and add new features to the magnetotransport properties of these materials.

To explore these aspects, we have focused on the $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ system, finding among other interesting features that the lower-doped samples show rather large magnetoresistance at low temperature.

To our knowledge it is the first time such effects have been described for $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_3$ (Ln : rare earth, $\text{Ln} \neq \text{La}$) materials.

Experimental Section

The $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ compounds ($0 < x \leq 0.30$) were prepared by the “liquid-mix” method using Gd_2O_3 , SrCO_3 , and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as starting materials. The procedure was as follows: Gd_2O_3 was first converted into the corresponding nitrate by dissolution in 30% HNO_3 . This product was then added to a 1 M citric acid aqueous solution, in which stoichiometric amounts of SrCO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were also dissolved. 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 we obtained a brown resin, whose organic matter subsequently decomposed at 400 °C.

The obtained ashes were given accumulative heating treatments at 600, 700, and 800 °C followed by intermediate grindings. The pelletized samples were finally annealed at 900–950 °C and cooled slowly to room temperature (at 0.7 °C/min).

The samples were characterized by X-ray powder diffraction with a Siemens D-5000 diffractometer and $\text{Cu K}\alpha = 1.5418$ Å radiation. The unit cell parameters were obtained by Rietveld analysis of the XRD data. The morphology and size of the particles were studied in a scanning electron microscope (SEM) JEOL 6400, where their compositional homogeneity was also studied by EDS analysis.

The thermal stability of the samples was checked by differential thermal analysis (DTA) and thermogravimetric analyses (TGA).

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 $4.2 \leq T \leq 300$ K. Hysteresis loops in ZFC conditions were obtained at 4.2 K varying the field up to ± 50 kOe.

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

Table 1. Orthorhombic Unit Cell Parameters and Pseudocubic Lattice Constant of $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 < x \leq 0.30$)

x	a_{orth}	b_{orth}	c_{orth}	a'
0	5.223(5)	5.397(1)	7.451(4)	3.744(8)
0.1	5.250(1)	5.388(6)	7.470(6)	3.752(4)
0.2	5.268(1)	5.381(1)	7.487(5)	3.757(7)
0.3	5.295(1)	5.383(2)	7.504(7)	3.767(6)

this device the magnetoresistance of the samples was measured at a constant temperature between 0 and 50 kOe.

Seebeck coefficients of pressed pellets were measured in the temperature interval $77 \leq T \leq 450$ K with a homemade device similar to the one described in ref 22.

Finally, aware of the controversy regarding the compositional homogeneity of samples processed at relatively low temperature and considering that magnetic measurements are a powerful tool for revealing the presence of inhomogeneities in samples of this type,^{23,24} we annealed a few of the samples at higher temperature, 1000 °C (the as-obtained samples melted at $1050 \leq T \leq 1100$ °C), and we compared their magnetic behavior with that displayed by samples annealed at lower temperature (900–950 °C).

Results

1. Sample Characterization. According to the room-temperature X-ray diffraction results, the obtained $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ compounds ($0 < x \leq 0.30$) were all single-phase materials and showed an O-type ($a \leq (c/\sqrt{2}) \leq b$) orthorhombic GdFeO_3 -like perovskite structure ($\approx \sqrt{2}a_c \times \sqrt{2}a_c \times \approx 2a_c$) ($a_c = 3.8$ Å).

The lattice parameters changed with x (see Table 1), but while a and c increased with doping, b decreased slightly. Also included in Table 1 is the pseudocubic lattice constant of these compounds a' , which represents the lattice parameter of a cubic unit cell containing one ABO_3 unit and can be defined as $a' = (V/z)^{1/3}$ (where V is the volume of the unit cell and z is the number of ABO_3 formulas per unit cell of the crystal). As can be seen, a' increased continuously with doping. This means that the incorporation of the larger Sr^{2+} ion ($r_{\text{Sr}^{2+}}^{\text{XII}} = 1.44$ Å)²⁵ in place of the considerably smaller Gd^{3+} ion ($r_{\text{Gd}^{3+}}^{\text{XII}} = 1.36$ Å, $r_{\text{Gd}^{3+}}^{\text{XII}} = 1.22$ Å)²⁵ predominated over the fact that upon doping Co^{3+} ($r_{\text{Co}^{3+}}^{\text{VI}} \text{ l.s.} = 0.55$ Å, $r_{\text{Co}^{3+}}^{\text{VI}} \text{ h.s.} = 0.61$ Å)²⁵ oxidized to the smaller Co^{4+} ions ($r_{\text{Co}^{4+}}^{\text{VI}} = 0.53$ Å),²⁵ resulting in an increase in the unit cell size.

On the other hand, the thermogravimetric results show that although these samples lost some oxygen when heated above ≈ 923 K, they regained it when slowly cooled in air.

As for the morphology and particle size of the obtained $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ materials, SEM micrographs show that they consisted of homogeneous platelets 1–2 μm long.

Finally, the results of EDS analysis showed the compositional homogeneity of the samples.

2. Magnetic Properties. While GdCoO_3 was paramagnetic down to the lowest available temperature, the doped compounds displayed a clearly different magnetic

(22) Goodenough, J. B.; Zhou, J.-S.; Chan, J. *Phys. Rev. B* **1993**, *47*, 5275.

(23) Anil, K. P. S.; Alias, J. P.; Date, S. K. *J. Mater. Chem.* **1998**, *8*, 1219.

(24) Baio, G.; Barucca, G.; Caciuffo, R.; Rinaldi, D.; Mira, J.; Rivas, J.; Señaris-Rodríguez, M. A.; Fiorani, D. *J. Phys.: Condens. Matter* **2000**, *12*, 1.

(25) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *25*, 925.

(18) Rao, C. N. R.; Parkash, O. M. *Philos. Mag.* **1977**, *35*, 1111.

(19) Cassalot, A.; Dougier, P.; Hagenmuller, P. *J. Phys. Chem. Solids* **1971**, *32*, 407.

(20) Brinks, H. W.; Fjellvag, H.; Kjekshus, A.; Hauback, B. C. *J. Solid State Chem.* **1999**, *147*, 464.

(21) Yoshii, K.; Nakamura, A. *Physica B* **2000**, *281&282*, 514.

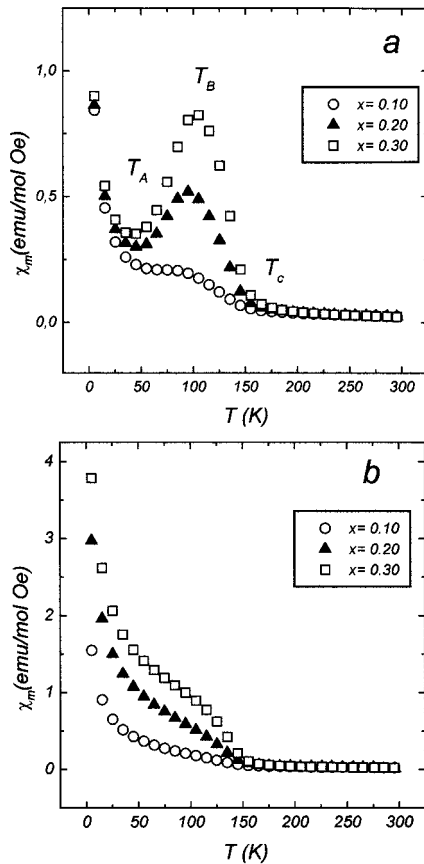


Figure 1. (a) ZFC and (b) FC molar magnetic susceptibility of $Gd_{1-x}Sr_xCoO_3$ ($0 < x \leq 0.30$) ($H = 1000$ Oe).

behavior that, according to our results, was independent of the annealing temperature of the samples.

Figure 1 shows the temperature dependence of the ZFC and FC molar magnetic susceptibility. As can be seen in these curves, a marked increase in χ_m occurred below $T_c \approx 160$ K, and the rise was more pronounced in the more heavily doped samples. Nevertheless, T_c increases only slowly with x .

As the temperature decreased, a maximum appeared in the ZFC $\chi_m(T)$ curves at $T_B < T_c$. This T_B increased with x from ≈ 80 K in the sample with $x = 0.10$ to ≈ 105 K in the $x = 0.30$ sample.

At even lower temperatures, below $T_A < T_B$, χ_m increased again and very rapidly.

The $M(H)$ curves at $T = 5$ K of these samples are shown in Figure 2. As can be seen, the magnetization of these samples did not saturate under the highest field used. Also, the shape of these curves seems to reflect the contribution both from a magnetically ordered phase—that gives rise to a small hysteresis loop—and from a paramagnetic species of high magnetic moment.

These results suggest the following interpretation:

T_c signals the onset of magnetic order of cobalt ions within superparamagnetic clusters, whose number and/or size increases with the doping level. Meanwhile, the local T_c of such superparamagnetic clusters does not change significantly with x , indicating that their nature is very similar in all the samples, despite their different nominal compositions, different Co^{3+}/Co^{4+} ratios, and so forth; a T_c independent of x would have indicated disproportionation into two phases.⁸

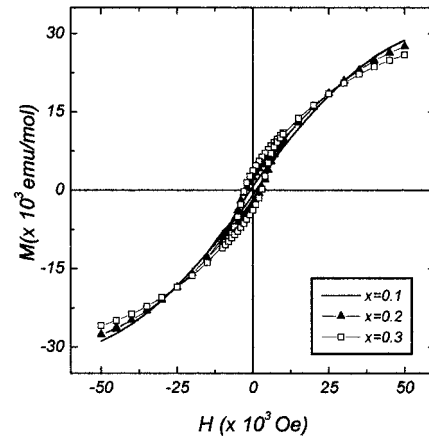


Figure 2. ZFC magnetization versus applied field H of $Gd_{1-x}Sr_xCoO_3$ ($0 < x \leq 0.30$) measured at $T = 4.2$ K.

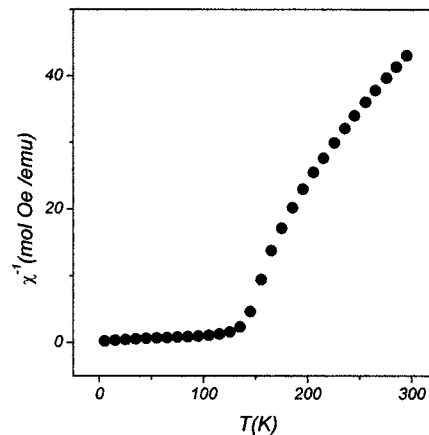


Figure 3. Temperature dependence of the inverse of the molar magnetic susceptibility of $Gd_{0.70}Sr_{0.30}CoO_3$.

The freezing temperature, T_B , is the magnetic blocking temperature for such superparamagnetic clusters, and its value increases with x , indicating the growth of such clusters. T_A represents the temperature below which the magnetic contribution from the paramagnetic Gd^{3+} ions, which have a high magnetic moment, becomes more important than the relatively small contribution from the cobalt ions, giving rise to a sharp increase in χ_m .

The $M(H)$ curves measured at 5 K (Figure 2) seem to corroborate this picture. In this context, the small hysteresis loop would reflect the blocking of the superparamagnetic clusters at low temperatures; meanwhile, the magnetization data obtained with higher magnetic fields would correspond to the contribution of the paramagnetic Gd^{3+} ions, as those results are very similar to those displayed by a pure Gd^{3+} paramagnetic system except that the magnetization observed here was 10–15% smaller, probably due to the influence of the crystalline environment.

As for their behavior above T_c (Figure 3), the $\chi_m(T)$ data can be fitted to a Curie–Weiss law only in a very narrow temperature interval, $225 < T \leq 300$ K, as a strong positive deviation from that linearity appears below ≈ 225 K. From the corresponding $\chi^{-1}(T)$ fitting, we estimated the effective magnetic moment per cobalt ion (μ_{eff-Co}) from the total μ_{eff} ($\mu_{eff} = \sqrt{8C}$) after appropriate subtraction of the Gd^{3+} contribution ($\mu_{eff}(Gd^{3+})$)

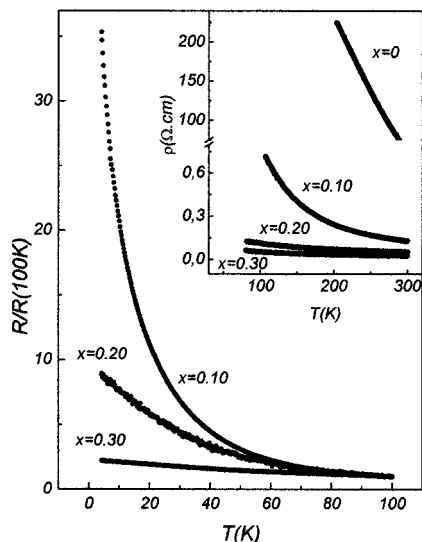


Figure 4. Normalized electrical resistance $R(T)/R(100\text{ K})$ versus temperature of $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 < x \leq 0.30$) for $77 \leq T \leq 330\text{ K}$. Inset: Electrical resistivity data for the temperature interval $4.2 \leq T \leq 100\text{ K}$.

$= 7.8 \mu_B$ ²⁶). The values we obtained range from $1.6 \mu_B$ (for $x = 0.1$) to $1.3 \mu_B$ (for $x = 0.3$). Taking into account the expected effective magnetic moments for trivalent and tetravalent cobalt ions in different spin states ($\mu_{\text{eff-SO}}(\text{Co(III)}_{\text{l.s.}}) = 0 \mu_B$, $\mu_{\text{eff-SO}}(\text{Co}^{3+})_{\text{h.s.}} = 4.91 \mu_B$, $\mu_{\text{eff-SO}}(\text{Co(III)}_{\text{i.s.}}) = 2.83 \mu_B$, $\mu_{\text{eff-SO}}(\text{Co(IV)}_{\text{l.s.}}) = 1.73 \mu_B$, $\mu_{\text{eff-SO}}(\text{Co}^{4+})_{\text{h.s.}} = 5.91 \mu_B$), our results indicate that in these samples most of the cobalt ions were in the low-spin configuration.

In any case, high-temperature susceptibility measurements will be needed to obtain more accurate magnetic moment values.

On the other hand, the Weiss constant θ , that was practically zero in the undoped compound, increased to small positive values with x (from $+5\text{ K}$ for $x = 0.10$ to $+56\text{ K}$ for $x = 0.30$), in full agreement with the results found by other authors.¹²

3. Transport Properties. The first general observation is that, for these doping levels, these samples were semiconducting and their electrical resistivity ρ diminished as x increased (Figure 4).

These $\rho(T)$ data can be fitted to $\ln(1/\rho) \propto T^{-1/4}$ in the temperature range $77 \leq T \leq 307\text{ K}$, but they clearly deviate from it at lower temperatures.

As for their thermopower (Figure 5), at room temperature and above, the α coefficient was positive and its magnitude decreased as the degree of doping increased. Also, very interestingly, in these samples $\alpha(T)$ decreased with temperature and tended to zero at low temperatures. This temperature dependence reflects a progressive trapping out of charge carriers and/or diminution in the number of sites over which they could move as the temperature was lowered.²⁷

To study the influence of the magnetic field on the electrical resistivity of these materials, we measured $\rho(T)$ under a field of 40 kOe. As can be seen in a typical example in Figure 6, at low temperatures the magnetic

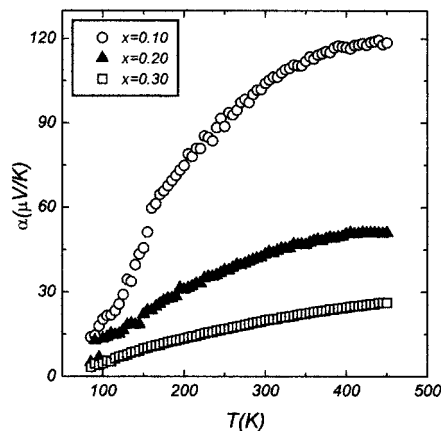


Figure 5. Temperature dependence of the Seebeck coefficient of $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 < x \leq 0.30$) in the temperature interval $77 \leq T \leq 330\text{ K}$.

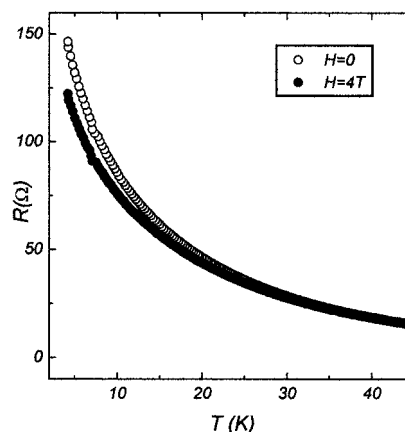


Figure 6. Temperature dependence of the electrical resistance of $\text{Gd}_{0.90}\text{Sr}_{0.10}\text{CoO}_3$ in the absence of a magnetic field and under a magnetic field of 40 kOe ($4.2 \leq T \leq 45\text{ K}$).

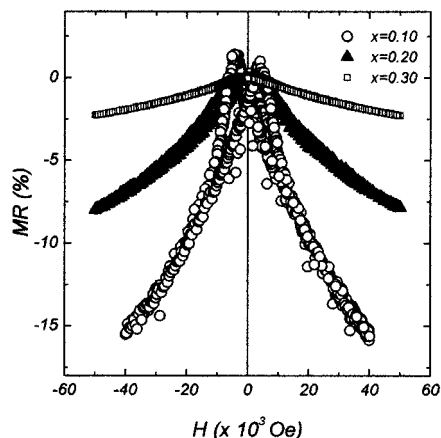


Figure 7. Field dependence of the electrical resistivity of samples of $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 < x \leq 0.30$) measured at 4.2 K.

field reduced the samples' resistivity, and the effect became more pronounced as the temperature diminished. We therefore measured their magnetoresistance at the lowest available temperature (4.2 K), finding that the maximum value of $\text{MR}_{\text{max}} [(\rho(0) - \rho(H))/\rho(0)] \approx -16\%$ was achieved for $x = 0.10$ (Figure 7). Upon further doping, the value of the negative MR decreased to $\text{MR} \approx -8\%$, for $x = 0.20$, and $\text{MR} \approx -2\%$ for $x = 0.30$ (Figure 7).

(26) Madhusudan, W. H.; Jagannathan, K.; Ganguly, P.; Rao, C. N. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1397.

(27) Zhou, J.-S.; Goodenough, J. B. *Phys. Rev. B* **1995**, *51*, 3104.

Discussion

The magnetic and transport properties of these Sr-doped gadolinium cobaltates bear a strong parallelism to those displayed by the $La_{1-x}Sr_xCoO_3$ system,^{8,10} modulated by the presence of the rare earth Gd^{3+} instead of La^{3+} .

For that extensively studied $La_{1-x}Sr_xCoO_3$ system, it has recently been proposed⁸ that, upon doping, this material segregates into hole-rich, metallic ferromagnetic regions and a hole-poor matrix similar to $LaCoO_3$. The cobalt ions of the ferromagnetic phase are in the intermediate-spin configuration, and the cobalt ions of the hole-poor matrix experience a thermally induced transition from low to high spin.

According to that model,⁸ corroborated in further investigations,^{24,28,29} for low Sr^{2+} -doping, the hole-rich regions are isolated from one another and show superparamagnetic behavior below a $T_c \approx 240$ K, that changes very little with x . Long-range magnetic order via frustrated intercluster interactions occurs below a superparamagnetic freezing temperature T_B that increases with x . A magnetic percolation threshold is reached at x_m , and for $x_m < x \leq 0.50$, the ferromagnetic hole-rich regions couple ferromagnetically to give bulk ferromagnetism below T_c . Metallic behavior is found for $x_c > x_m$, but the presence of the hole-poor matrix interpenetrating the metallic ferromagnetic regions persists and gives rise to peculiar magnetic behavior.

In this context, and in view of the similarities found between these two cobalt perovskite systems, we propose that the above model can also be extended to the $Gd_{1-x}Sr_xCoO_3$ materials ($0 < x \leq 0.30$).

Of course, to do so, one has to take into account that the presence of Gd^{3+} (instead of La^{3+}) will influence the crystal structure, the spin state of the cobalt ions, and the characteristics of the hole-poor and hole-rich regions as well as the magnetic and electrical connection between them.

In this context, the smaller size of the Gd^{3+} ion compared to the La^{3+} ion²⁵ forces the perovskite structure to distort more than in the case of the $La_{1-x}Sr_xCoO_3$ series, resulting in $GdFeO_3$ -type structures with Co–O–Co bond angles smaller than 180° .¹ This, in turn, reduces the electronic transfer integral between Co sites that controls hole conduction. It also makes the stabilization of ferromagnetic interactions via double-exchange more difficult, resulting in lower T_c ($T_c(Gd_{1-x}Sr_xCoO_3) \approx 150$ K compared with $T_c(La_{1-x}Sr_xCoO_3) \approx 250$ K⁸).

On the other hand, at a given temperature, the presence of Gd^{3+} stabilizes lower spin states in the cobalt ions than in the corresponding lanthanum compounds. For example, in the undoped compounds, while the cobalt ions in $GdCoO_3$ are in a low-spin configuration up to ≈ 270 K, and a ratio of 30% $Co^{3+}_{h.s.}$ to 70% $Co(III)_{l.s.}$ is present for $270 < T < 500$ K,¹⁹ in $LaCoO_3$, a ratio of 50% $Co^{3+}_{h.s.}$ to 50% $Co(III)_{l.s.}$ is already stabilized

for $110 < T < 350$ K, with a further evolution toward higher spin configurations taking place from 350 K.⁹

In the case of the doped compounds ($0 < x \leq 0.30$), the approximate $\mu_{\text{eff-Co}}$ that we estimate for the $Gd_{1-x}Sr_xCoO_3$ samples reveals that the majority of cobalt ions from the matrix are in the low-spin configuration for $225 < T \leq 300$ K (i.e., on the order of 90–95% of $Co(III)_{l.s.}$ if the stable spin states are $Co(III)_{l.s.}$ and $Co^{3+}_{h.s.}$ at those temperatures), while a ratio of almost 50% $Co^{3+}_{h.s.}$ to $Co(III)_{l.s.}$ gets stabilized in the $La_{1-x}Sr_xCoO_3$ compounds.⁸

Such differences in the spin state of the cobalt ions arise from the fact that Gd^{3+} , compared to La^{3+} , competes more strongly with cobalt in covalent bonding to the oxygen atoms because it has a higher acidity (i.e. a higher charge/radius ratio).³⁰ And as the Gd–O bonds get stronger, the Co–O bands get narrower and the $\pi^*(Co-O)$ levels become more stable,³⁰ so the splitting between t_{2g} and e_g becomes larger, resulting in lower spin states in the cobalt ions, as found in the experimental data.

The transition from low-spin to high-spin configurations can be induced thermally (as will occur in the matrix as a function of temperature), or it can be provoked by polarization of the O-2p σ electrons toward the Co(IV) and away from the neighboring Co^{3+} ions (as will occur within the clusters).

In any case, such transitions will be hindered more than in the case of the $La_{1-x}Sr_xCoO_3$ compounds. Therefore, at a given temperature the spin state of the cobalt ions in the matrix will be lower than that in the corresponding lanthanum compounds and the stabilization of high- or intermediate-spin states in the hole-rich regions will occur to a lesser extent than in the $La_{1-x}Sr_xCoO_3$ compounds.

As a result, in the studied temperature range the matrix will be mostly diamagnetic and insulating and will act as a barrier to the magnetic and electrical connection between the hole-rich regions. This, together with the fact that within the clusters the hole conduction is worse and the ferromagnetic interactions weaker than in the corresponding $La_{1-x}Sr_xCoO_3$ compounds, will also explain why in these Gd samples the susceptibility values are lower, why the resistivity values are higher, and why the magnetic and electrical percolation is reached at higher x .

On the other hand, and very interestingly, the Gd^{3+} ions have a high magnetic moment with no L–S anisotropy ($L = 0$, $S = 7/2$), unlike La^{3+} , which has no magnetic moment ($L = S = 0$). Therefore, the Gd^{3+} ions can be easily oriented with small magnetic fields. At low temperature the magnetic contribution of this almost paramagnetic Gd^{3+} system is more important than the tiny cobalt contribution, and the Gd^{3+} sublattice polarizes the cobalt magnetic clusters. In fact, we propose that this effect is one of the causes of the appearance of low-temperature MR: at low temperatures the presence of the paramagnetic Gd^{3+} sublattice influences the cobalt ions of the superparamagnetic clusters and provokes an increase in the size of the hole-rich regions and in the hopping probability of the charge carriers and thus gives rise to a reduction in sample

(28) Caciuffo, R.; Rinaldi, D.; Barucca, G.; Mira, J.; Rivas, J.; Señaris-Rodríguez, M. A.; Radaelli, P. G.; Fiorani, D.; Goodenough, J. B. *Phys. Rev. B* **1999**, *59*, 1068.

(29) Caciuffo, R.; Mira, J.; Rivas, J.; Señaris-Rodríguez, M. A.; Radaelli, P. G.; Casargui, F.; Fiorani, D.; Goodenough, J. B. *Europhys. Lett.* **1999**, *45*, 399.

(30) Goodenough, J. B. *Prog. Solid State Chem.* **1971**, *5*, 145.

resistivity. That reduction is more readily seen in the more resistive samples, which are therefore the ones that exhibit the highest MR values.

Consequently, while, in the low-doped lanthanum compounds ($\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$), the highest MR is achieved around the blocking temperature ($T \approx 40 \text{ K}$ ¹⁷ and 25 K ,¹³ respectively), in the $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ samples the highest MR is observed at the lowest available temperature, 4.2 K .

Conclusions

We prepared $\text{Gd}_{1-x}\text{Sr}_x\text{CoO}_3$ ($0 < x \leq 0.30$) as pure samples by the liquid-mix method and studied their magnetic and transport properties.

Interestingly enough, as x increased, the magnetic susceptibility of these samples increased below a T_c that marked the onset of magnetic order of cobalt ions within superparamagnetic clusters, which become blocked at a freezing temperature, T_B . Below it, the paramagnetic Gd^{3+} sublattice had a more important role from the magnetic point of view.

From the electrical point of view, these samples were semiconducting and their resistivity decreased as x increased. Also, as the temperature decreased, the

charge carriers became trapped out and/or the number of sites over which they could move diminished.

Very remarkably, the more resistive samples showed large negative magnetoresistive effects at very low temperatures: $\text{MR}_{\text{max}}(x = 0.10) \approx -16\%$ at $T = 4.2 \text{ K}$ under $H_{\text{max}} = 40 \text{ kOe}$.

We relate these results to the inhomogeneous electronic structure of these cobaltates and to the presence of the Gd^{3+} ions, which, once their magnetic contribution becomes important, polarize the cobalt ions of the superparamagnetic clusters, provoking an increase in the size of the hole-rich regions and in the hopping probability of the charge carriers, and thus give rise to the large negative magnetoresistivity observed.

More work is in progress to fully characterize these samples and to delve deeper into the magnetic structure of these interesting materials.

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