Electronic and magnetic phase diagram of $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$

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Magnetic and electrical transport properties of $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ perovskites, with $0 \leq x \leq 1$, have been studied in the temperature range $5 \leq T \leq 700$ K. This series shows paramagnetic metal, paramagnetic insulator, antiferromagnetic insulator, and spin-glass-like insulator regions. Ferromagnetic interactions between different $3d$ ions show up at intermediate x concentrations, $0.3 \leq x \leq 0.8$. We found a large negative magnetoresistance in the same region. A dynamic mechanism with spin memory, a type of double exchange interaction, can give rise to the observed magnetoresistance and spin-glass behavior. The role played by both electron-electron interactions and structural disorder in electrical transport properties of these systems is discussed.

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I. INTRODUCTION

Perovskite-type RMO_3 oxides, where R^{3+} is a trivalent rare-earth ion and M^{3+} is a trivalent $3d$ transition-metal ion, show a huge variety of different physical properties. Nowadays, because of their potential technological applications, there is a renewed interest in the study of mixed-valence manganese oxides. Other RMO_3 also display new and unusual behavior open to study, such as orbital and charge ordering phenomena as well as large changes in the electrical, magnetic, and structural properties, driven by small variations of temperature, composition, or magnetic field.¹ Many of these properties are still not understood.

Here, we present a study of $\text{RNi}_{1-x}\text{Co}_x\text{O}_3$ series with $R = \text{Sm}^{3+}$. Previous research has been focused on undoped RCO_3 and RNiO_3 compounds, as well as on $\text{RNi}_{1-x}\text{Co}_x\text{O}_3$ series with large rare-earth ions ($R = \text{La}^{3+}, \text{Nd}^{3+}$).¹⁻¹⁰ RCO_3 oxides show temperature-dependent electronic and spin-state transitions. The ground state of LaCoO_3 is a non-magnetic insulator whose Co^{3+} configuration is of low spin (LS), $t_{2g}^6 e_g^0$ ($S=0$). The competition between Co^{3+} crystal-field splitting and intra-atomic Hund coupling leads to a temperature-driven transition from LS to either thermally excited high spin (HS), $t_{2g}^4 e_g^2$ ($S=2$), or intermediate spin (IS), $t_{2g}^5 e_g^1$ ($S=1$), configuration.² In addition, RCO_3 oxides show a crossover from a semiconducting to a metallic regime above 500 K. The reported metal-insulator transition temperature (T_{MI}) for SmCoO_3 is² 600 K. On the other hand, LaNiO_3 is one of the few RMO_3 oxides which shows metallic conduction in the whole temperature range studied. In the other members of this series ($R = \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}$), either strong electronic correlations or antiferromagnetic polaronic effects bring about a temperature-driven metal-insulator (MI) transition.³ RNiO_3 shows a complex phase diagram which consists of paramagnetic metal, paramagnetic insulator and antiferromagnetic insulator regions whose boundaries change with the rare-earth size. Moreover, several kinds of orbital ordering have been proposed to explain the complex low-temperature antiferromagnetic (AF) arrangement in the series.⁴ The magnetic ordering of the Ni^{3+}

ions can be described by a propagation vector $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$ relative to the orthorhombic unit cell. The proposed magnetic ground state implies the symmetrical coexistence of ferro- and antiferromagnetic couplings along the three pseudocubic axes.⁴ In SmNiO_3 , the MI transition takes place at 400 K and an AF ordering³ at 220 K.

$\text{RNi}_{1-x}\text{Co}_x\text{O}_3$ mixed oxides show ferromagnetic interactions in the Ni/Co sublattice for the intermediate x range,^{5,6} $0.3 \leq x \leq 0.8$. Some of these compounds exhibit giant magnetoresistive effects in the low-temperature spin-glass-like regime.^{7,8} In addition, different temperature-driven and composition-driven MI transitions have been found in the transport properties.

We report the electrical and magnetic $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ phase diagram. X-ray powder diffraction, ac initial magnetic susceptibility, dc magnetization, electrical resistivity, and magnetoresistance measurements have been performed in a wide temperature range and in fields of up to 12 T. We discuss diverse conduction behavior found in $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$, compare it with results obtained for series with large rare-earth ions ($R^{3+} = \text{La}^{3+}, \text{Nd}^{3+}$) and, finally, look for possible relations between structural, transport, and magnetic properties in these compounds.

The complex phase diagram obtained experimentally for $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series suggests two mechanisms of electronic localization. Electronic and magnetic correlations localize the current carriers for $x \leq 0.2$ as it occurs in the undoped^{3,4} SmNiO_3 . The semiconducting behavior found for $x \geq 0.3$ can be likely explained by disorder effects, i.e., the Anderson localization.

II. EXPERIMENT

$\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ samples ($x = 0, 0.03, 0.075, 0.1, 0.15, 0.2, 0.3, 0.5, 0.7$, and 0.9) were prepared under high oxygen pressure (200 bar) at 1000 °C, from a precursor obtained by means of a citrate sol-gel route. A stoichiometric mixture of Sm_2O_3 , Co, and $2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ was first dissolved in a nitric acid solution, and then appropriate citric acid and ethylene glycol amounts were added. Such solutions were

TABLE I. Lattice parameters and magnetic constants for $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series. Magnetic constants were obtained by fitting $\chi_{\text{Ni/Co}}, \chi_{\text{Ni/Co}}(T) = \chi(T) - \chi_{\text{Sm}^{3+}}$, to the equation $\chi_{\text{Ni/Co}}(T) = \chi_o + C/(T - \Theta)$. The temperature range was 100–250 K except for $x = 0.15$ (125–250 K) and for $x = 0$ (280–400 K). These limits are imposed by both the MI transition of some of the samples and the spin transition of Co ions. The expected paramagnetic effective moments are: $\mu_{\text{teo}} = [(1-x)(\mu_{\text{LS Ni}^{3+}})^2]^{1/2} \dots (*)$. The data of SmNiO_3 have been fitted to a Curie-Weiss law, the addition of the χ_o parameter does not improve the fit significantly.

Sample	A(Å)	B(Å)	C(Å)	χ_o (emu mol/Oe)	Θ (K)	$\mu_{\text{eff}}(\mu_B)$	$\mu_{\text{teo}}(\mu_B)$
$x = 0.9$	5.294	5.371	7.511	4.1×10^{-4}	−0.4	0.72	0.55
$x = 0.7$	5.304	5.397	7.525	3.9×10^{-4}	32	1.30	0.95
$x = 0.5$	5.312	5.409	7.536	6.9×10^{-4}	49	1.35	1.22
$x = 0.3$	5.320	5.420	7.548	1.0×10^{-3}	21	1.45	1.45
$x = 0.2$	5.331	5.421	7.550	3.0×10^{-4}	−23	1.60	1.55
$x = 0.15$	5.323	5.421	7.552	2.8×10^{-4}	−52	1.71	1.60
(*) $x = 0$	5.328	5.430	7.565	0	−113	1.69	1.73

heated until green-red gels were formed. These gels were dried by heating at 300 °C. The remaining brown powders were calcined in alumina crucibles overnight with a flow of oxygen at 500 °C in order to obtain the precursors. These precursors were pressed to 5 Kbar and sintered in the high-pressure system for 12 h. SmCoO_3 and SmScO_3 oxides were prepared by standard solid-state ceramic procedures at 1200 °C in air, with some intermediate regrindings.

The oxygen content for $\text{SmNi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ samples was determined from thermogravimetric analysis. A Texas-Instrument TGA system was used in a reducing N_2/H_2 (95:5) flow, working at a heating rate of 10 °C/min. A small oxygen deficiency was detected in $\text{SmNiO}_{3-\delta}$ ($\delta = 0.04$), while all other $\text{SmNi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ oxides show a nearly perfect stoichiometric composition, with $\delta = 0.00 \pm 0.02$. Step-scanned x-ray-diffraction (XRD) patterns were collected at room temperature using a D-max Rigaku system with a rotating anode. A graphite monochromator selected the $\text{Cu-K}\alpha_{1,2}$ radiation.

Electrical conductivity and magnetoresistance measurements were performed by a standard six-probe method on $1.5 \times 1.5 \times 10$ mm sintered bar-shaped samples, in $4 \leq T \leq 700$ K temperature range. A superconducting coil was used to produce steady magnetic fields of up to 12 T. Magnetic measurements (ac susceptibility and dc magnetization) were made between 4 and 400 K with a commercial Quantum Design (superconducting quantum interference device) magnetometer, equipped with an ac susceptibility attachment, and with a vibrating sample magnetometer in the $350 \leq T \leq 700$ K temperature range. Magnetization was measured in external magnetic fields of up to 5 T.

III. RESULTS

Profile analysis of x-ray-diffraction patterns indicates single-phase compounds for all $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$, $0 \leq x \leq 1$, samples. The diffractograms were indexed in the orthorhombic $Pbnm$ spatial group, which is one of the most common distorted structures derived from the $Pm\bar{3}m$ cubic perovskite. Both SmNiO_3 and SmCoO_3 structures agree with the ones reported earlier.⁹ When nickel atoms are substituted by cobalt atoms, only slight differences in lattice parameters, distances, and angles between the atoms are found. The average transition-metal–oxygen distance (d_{M-O}) and the superexchange angle ($\langle M-O-M \rangle$) change from 1.955 Å and

152.4° for SmNiO_3 to 1.926 Å and 154.6° for SmCoO_3 , respectively. Lattice parameters are listed in Table I.

A. Magnetic properties

In Fig. 1 temperature dependence of dc magnetic susceptibility χ_{dc} , measured under an external magnetic field of 1 T, is shown for $x \leq 0.20$ samples. The main magnetic contribution to χ_{dc} arises from paramagnetic Sm^{3+} ions. SmNiO_3 susceptibility exhibits a small kink at 220 K that corresponds to the onset of the antiferromagnetic (AF) arrangement of the low spin Ni^{3+} ions, in agreement with neutron-diffraction data⁴ and heat-capacity measurements.¹⁰ When nickel sublattice is doped with cobalt, a similar feature is observed at 205, 190, and 170 K for $x = 0.03, 0.075$, and 0.1, respectively. It has been interpreted as a signature of AF ordering. Therefore the Néel temperature T_N decreases with increasing Co content at a rate of about 500 K/x in this region. For $x = 0.15$ and $x = 0.2$, the susceptibility curves peak at 95 and 48 K, respectively, which coincide with the MI transition reported below. The T_N values obtained for $x = 0.15$ and $x = 0.20$ samples are far away from the expected values for T_N predicted by the $T_N(x)$ dependence found for $x < 0.10$. The inset of Fig. 1

FIG. 1. Temperature dependence of the dc susceptibility, $\chi_{\text{dc}} = M/H$ ($\mu_0 H = 1$ T), for $0 \leq x \leq 0.2$ $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ samples. The inset shows M/H vs temperature ($\mu_0 H = 0.1$ T) for SmScO_3 , SmNiO_3 , and SmCoO_3 . The arrows indicate the magnetic transitions shown by both SmNiO_3 and SmCoO_3 .

FIG. 2. ac magnetic susceptibility versus temperature for $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$, $0.2 \leq x \leq 0.9$, samples. The inset shows M/H vs temperature ($\mu_0 H = 0.1$ T) for $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$, $0.3 \leq x \leq 0.9$, samples.

shows χ_{dc} vs T for SmScO_3 , SmCoO_3 , and SmNiO_3 . The perovskite oxide SmScO_3 is isomorphous to SmNiO_3 and the Sc^{3+} is nonmagnetic ion ($3d^0$). Consequently, only paramagnetic Sm^{3+} ions contribute to its susceptibility. A comparison of SmCoO_3 and SmScO_3 magnetic data shows clearly that a majority of cobalt ions in SmCoO_3 is in the $S = 0$ Co^{3+} electronic configuration, for $4 \leq T \leq 275$ K. Above 275 K, the susceptibility of SmCoO_3 is larger than that of SmScO_3 (see inset of Fig. 1). It may be explained by an excitation of Co^{3+} ions to states with $S \neq 0$ as has been reported elsewhere.¹¹

The most striking feature of magnetic properties of the $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series is the appearance of short-range ferromagnetic interactions for $0.3 \leq x \leq 0.8$. These are evidenced by a spin-glass-like region observed at low temperature for these compounds. Figure 2 shows how ac susceptibility of $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$, $0.2 \leq x \leq 1.0$, samples varies with temperature in the $4 \leq T \leq 80$ K temperature range. $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ ac susceptibility curves peak sharply at 16, 19, 18, 14, and 6 K for $x = 0.3, 0.5, 0.6, 0.7$, and 0.8 , respectively. Zero-field cooling dc magnetic-susceptibility data, measured with external fields of 1 T, are plotted in the inset of Fig. 2 for the $0.3 \leq x \leq 0.9$ samples. Cobalt doping in SmNiO_3 and nickel doping in SmCoO_3 give rise to ferromagnetic interactions between the $3d$ ions and induce a spin-glass-like magnetic regime. A similar behavior was found earlier⁶ for intermediate x values in $\text{RNi}_{1-x}\text{Co}_x\text{O}_3$ ($R = \text{La}^{3+}, \text{Nd}^{3+}$).

Figure 3 shows how ac susceptibility varies with temperature for different oscillating field frequencies ω in $\text{SmNi}_{0.3}\text{Co}_{0.7}\text{O}_3$. The peak at 14 K decreases in magnitude and shifts to higher temperatures as frequency increases. This dependence is found only at temperatures below the freezing temperature T_f (T_f corresponds to the temperature of the susceptibility cusp). A measure of the frequency shift is obtained from $\Delta T_f/T_f(\log \omega)$, which equals 0.023. This value is close to the reported ones for other spin-glass systems.¹² In Fig. 3, dc susceptibility curves, measured under external magnetic fields of 0.1 and 1 T, are also plotted. The ac susceptibility cusps are smeared out to broad maxima and T_f shifts to lower temperatures as the magnetic-field strength increases. Magnetization versus external magnetic field

FIG. 3. Temperature dependence of both ac magnetic susceptibility at different frequencies (0.12, 1.2, 12, and 120 Hz) and dc magnetic susceptibility at different external magnetic field (0.1 and 1 T) for $\text{SmNi}_{0.3}\text{Co}_{0.7}\text{O}_3$. The inset shows magnetization versus external magnetic field for $\text{SmNi}_{0.3}\text{Co}_{0.7}\text{O}_3$ at 50 K and at 5 K in zero-field cooled (ZFC) and field cooled (FC) processes.

curves $M(H)$ are presented in the inset of Fig. 3 for $x = 0.7$. At $T = 50$ K, the typical paramagnetic linear behavior, far from a saturation, is found. On the contrary, at temperatures below T_f , e.g., $T = 5$ K, magnetization drifts upwards, suggesting ferromagnetic interactions. The curve at $T = 5$ K is also far from saturation. Extrapolating high-field magnetization values to $\mu_0 H = 0$, we obtain an effective ferromagnetic moment of $S_{\text{eff}} = 0.04$. The inset of Fig. 3 shows both zero-field cooled (ZFC) and field cooled (FC) magnetization curves at 5 K. In the low-field region, FC values are larger than the ZFC ones, showing an irreversibility in the magnetization measurements related to the freezing procedure. All of these magnetic properties are consistent with the proposed spin-glass-like behavior at low temperatures for $0.3 \leq x \leq 0.8$ $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ oxides.

SmScO_3 susceptibility data give us Sm^{3+} contribution ($\chi_{\text{Sm}^{3+}}$) to the total susceptibility; therefore the signal associated with the transition-metal sublattice ($\chi_{\text{Ni/Co}}$), can be obtained: $\chi_{\text{Ni/Co}}(T) = \chi(T) - \chi_{\text{Sm}^{3+}}(T)$, where $\chi(T)$ is the experimental $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ susceptibility. All $\chi_{\text{Ni/Co}}(T)$ data were fitted to the relation¹³ $\chi_{\text{Ni/Co}}(T) = \chi_0 + C/(T - \Theta)$. Here, C is the Curie constant, μ_{eff} the effective magnetic moment, Θ the Curie-Weiss temperature, and χ_0 the temperature-independent term of susceptibility. The best-fit parameters obtained from our measurements are listed in Table I. These parameters allow us to construct a magnetic phase diagram of $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$. For $x \leq 0.2$, Θ is negative and μ_{eff} is close to the expected effective moment for the LS Ni^{3+} and LS Co^{3+} paramagnetic Ni/Co sublattice. This suggests the existence of AF interactions and a low-temperature AF ordering. For $0.3 < x \leq 0.8$, crossovers of both Θ and μ_{eff} are observed; Θ changes from negative to positive and μ_{eff} shows larger values than the predicted ones for $\text{LS Ni}^{3+}/\text{LS Co}^{3+}$. It seems that ferromagnetic interactions show up, in agreement with the low-temperature spin-glass-like regime. In the third region, for $x = 0.9$, the Curie-Weiss temperature is nearly zero. This corresponds to a paramagnetic behavior of magnetically isolated Ni and Co ions.

FIG. 4. Temperature dependence of the resistivity $\rho(T)$ for the $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series, $0 \leq x \leq 0.2$. The inset shows $\ln \rho$ vs $100/T$ curves.

The temperature independent term χ_0 in $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series is large ($\chi_0 > 10^{-4}$ emu/mol Oe); the maximum value of χ_0 coincides with a composition-driven MI transition ($x = 0.3$). The large values of χ_0 are usually related to strong electronic correlations, and a χ_0 maximum could be a signature of a composition-driven Mott transition.¹⁴

B. Transport properties

Electrical resistivity of $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ changes drastically with both the relative nickel/cobalt composition and the temperature. Figure 4 shows the temperature dependence of the electrical resistivity for $x = 0, 0.03, 0.075, 0.1, 0.15$, and 0.2 . Undoped SmNiO_3 shows a temperature-driven MI transition. As was reported earlier,^{10,15} the resistivity $\rho(T)$ jumps by more than one order of magnitude in a temperature interval of 20 K. It shows a hysteretic behavior around T_{MI} . Above T_{MI} , SmNiO_3 exhibits a metallic behavior; resistivity varies linearly with temperature: $\rho(T) = \rho_0 + A_{\text{e-ph}}T$. The linear $\rho(T)$ dependence indicates a conduction dominated by electron-phonon scattering. Here, ρ_0 is residual resistivity and $A_{\text{e-ph}}$ gives the strength of electron-phonon interaction. Below T_{MI} , there is a change to a semiconductinglike resistivity behavior, but resistivity does not follow a simple energy activation model.

When the transition-metal sublattice is doped lightly with cobalt, T_{MI} decreases. It shifts to 315, 252, and 163 K for $x = 0.03, 0.075$, and 0.1 , respectively. With increasing x the magnitude of the resistivity jump at MI transition decreases and the transition itself becomes broader. Moreover, the thermal hysteresis found in SmNiO_3 is not observed for $0.03 \leq x \leq 0.1$ for the same measurement conditions (see Fig. 4). MI transitions are also found for $x = 0.15$ and $x = 0.2$. Here, they occur at 73 K for $x = 0.15$ and at 25 K for $x = 0.2$, with a jump of resistivity of two orders of magnitude. In addition, the thermal hysteresis is large for these samples (about 50 K). In samples with $0.15 \leq x \leq 0.2$, the onset of the magnetic arrangement T_N coincides with T_{MI} , while for $x \leq 0.10$ oxides, $T_{\text{MI}} > T_N$. The data for $0.15 \leq x \leq 0.2$ are quite similar to the reported ones¹⁶ for NdNiO_3 and $\text{NdNi}_{1-x}\text{Cu}_x\text{O}_3$ series, where $T_{\text{MI}} = T_N$.

In the inset of Fig. 4, $\ln \rho$ vs $1/T$ plots are presented for $0 \leq x \leq 0.2$ samples. A continuous decrease in the slope of

FIG. 5. Derivative $d(\ln \rho)/dT$ vs temperature curves for various concentrations of the $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series ($x = 0, 0.03, 0.075$, and 0.1). T_{MI} and T_N are denoted by arrows.

$\ln \rho(1/T)$ is observed, denoting a decrease in the activation energy, $E_a = d \ln \rho / d(1/T)$, with the temperature. Resistivity data cannot be fitted either to the Arrhenius law, $\ln(\rho/\rho_0) = E_a/K_B T$, or to other simple activation models of form $\rho(T) = \rho_0 \exp(\Delta/K_B T)^p$ with $p = \frac{1}{2}$ or $p = \frac{1}{4}$. Here, K_B is the Boltzman constant, ρ_0 is the value of resistivity in $T \rightarrow \infty$ limit, while E_a or Δ are activation energies.

In an earlier paper¹⁰ we have pointed out a small anomaly in the SmNiO_3 resistivity data which occurs at 220 K in the semiconducting regime. It coincides with the T_N for this compound. This anomaly is clearly visible in the derivative $d(\ln \rho)/dT$ vs T plots. In Fig. 5 plots of this kind are shown for $x = 0, 0.03, 0.075$, and 0.1 . The doped compounds show similar kinks at 200 and 187 K for $x = 0.03$ and $x = 0.075$, respectively, which coincide with the onset of the long-range AF ordering in Ni/Co sublattice. These small kinks may suggest changes in electronic conduction associated with the magnetic order. However, any reliable interpretation of the origin of these variations require more experimental work, in particular Hall effect measurements.

Temperature dependence of electrical resistivity $\rho(T)$ for $x \geq 0.3$ compounds ($x = 0.3, 0.5, 0.7$, and 0.9) is shown in Fig. 6, for $4 \leq T \leq 300$ K. Resistivity shows a semiconducting behavior, $d\rho/dT < 0$, in the whole temperature and composi-

FIG. 6. Temperature dependence of the resistivity $\rho(T)$ for $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series, $0.3 \leq x \leq 0.9$. The inset shows $\ln \rho$ vs $100/T$ curves.

FIG. 7. Temperature dependence of magnetoresistance and electrical resistivity in zero field and in a magnetic field of 5 T for $\text{SmNi}_{0.5}\text{Co}_{0.5}\text{O}_3$. The inset shows in detail the magnetoresistance curves $[\rho(H)-\rho(0)]/\rho(0)$ vs H at the indicated temperatures. Solid lines are guides to the eyes.

tion range. $\rho(T)$ changes one order of magnitude for $x=0.3$ and more than eight orders of magnitude for $x=0.9$ in the temperature range studied. Several conduction regimes can be seen depending on the temperature. A constant activation energy regime is observed between 100 and 250 K. The resistivity data for $100 \leq T \leq 250$ K can be fitted to the Arrhenius law yielding E_a values of 5, 19, 40, and 67 meV for $x=0.3, 0.5, 0.7$, and 0.9 , respectively. In the inset of Fig. 6, $\ln \rho$ vs $1/T$ plots are shown for $x \geq 0.3$. Below 100 K, E_a decreases with decreasing temperature. For $T \leq 50$ K, resistivity data are fitted to $\rho(T) = \rho_0 \exp[(\Delta/K_B T)^p]$. The best fit yields $p \approx 0.25$ which indicates a variable range hopping (VRH) conduction mechanism. Thus we observe a change from $p=1$ to $p=\frac{1}{4}$ between 100 and 50 K. Such continuous change from thermal carrier activation or nearest-neighbor hopping ($p=1$) at high temperatures to VRH ($p=\frac{1}{4}$) at low temperatures often occurs in disordered systems.¹⁷ Above 250 K, E_a increases with increasing temperature and reaches a maximum at about 500–600 K. E_a decreases with increasing temperature thereafter. This behavior can be related to the changes in the spin state of the Co^{3+} ions (see inset of Fig. 1). Therefore high-temperature resistivity ($300 \leq T \leq 700$ K) for $0.3 \leq x \leq 0.9$ shows a crossover from activated conduction to the so-called degenerated metallic regime¹⁸ at about 600 K. It shows a MI transition quite similar to that reported by Yamaguchi, Okimoto, and Tokura¹⁸ for SmCoO_3 and other $R\text{CoO}_3$ oxides.

Samples with $x=0.5$ and $x=0.2$ were chosen for magnetoresistance (MR) studies in $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series. Figure 7 shows resistivity versus temperature under external magnetic fields of 0 and 5 T for $x=0.5$. MR ratio, defined as $\text{MR} = 100[\rho(\mu_0 H) - \rho(0)]/\rho(0)$, is also plotted. The two curves $\rho(0)$ and $\rho(\mu_0 H = 5 \text{ T})$ are nearly identical for $T > 25$ K. Negative MR is observed only at low temperatures, below the freezing temperature T_f . Therefore magnetoresistance effects are coupled to the spin-glass-like behavior. Magnetoresistance as a function of the external magnetic field at different temperatures is shown in the inset of Fig. 7. At $T = 15$ K, $\text{SmNi}_{0.5}\text{Co}_{0.5}\text{O}_3$ shows an approximately linear, nonsaturated MR up to 12 T, with a MR ratio⁸ of about 45% at highest applied fields. Similar behavior of MR

FIG. 8. Temperature dependence of the electrical resistivity ρ vs T in zero field and in a magnetic field of 10 T for $\text{SmNi}_{0.8}\text{Co}_{0.2}\text{O}_3$. The inset shows in detail the magnetoresistance curves $[\rho(H)-\rho(0)]/\rho(0)$ vs H , at the indicated temperature. Solid lines are guides to the eyes; c indicates a temperature reached after a cooling process from 100 K; h indicates a temperature reached after a heating process from 15 K.

have been observed in mixed-valence $R\text{MO}_3$ perovskites, such as cobaltates¹⁹ $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, manganites²⁰ $\text{Tb}_{1/3}\text{La}_{1/3}\text{Ca}_{1/3}\text{MnO}_3$ or $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ doped²¹ with Al and In.

Figure 8 shows the temperature dependence of resistivity under magnetic fields of 0 and 10 T for $x=0.2$. Negative MR is found below the onset of the magnetic arrangement at $T_N \approx 48$ K. For this sample, the temperature-driven MI transition and AF ordering take place at the same temperature, $T_{\text{MI}} = T_N$. In the inset of Fig. 8 isotherms of MR, up to 12 T, are presented. The MR behavior at $T = 40$ K is the most striking one. The values of MR at this temperature depend on the thermal history of sample and show temperature and field hysteresis. In spite of the AF arrangement, suggested by the magnetic susceptibility behavior (see Fig. 1 and Table I), the negative MR effect and its hysteresis seem to indicate that magnetic interactions for $x=0.2$ are more complex, likely with ferromagnetic contributions. These data support the idea that cobalt doping induces short-range ferromagnetic correlations in the Ni/Co sublattice. These correlations are progressively enhanced as x increases, and lead to a change from AF to a spin-glass-like behavior at $x \approx 0.3$.

C. Magnetic and transport phase diagram

Figure 9 shows a phase diagram for the $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series which has been constructed using our results of the magnetic and transport measurements. Here, the temperature-driven MI transitions have been represented by solid circles. The ground state ($T \rightarrow 0$) for all of the compositions is semiconducting. However, there is a sharp change at $x \approx 0.2$ which divides the phase diagram in two principal regions with different transport behavior. For $x \leq 0.2$, cobalt doping favors the metallic state. T_{MI} values decrease linearly with x at approximately a constant rate of 2000 K/ x . Resistivity data in semiconducting regime cannot be fitted to a simple activation law. Such features resemble the properties of $R\text{Ni}_{1-x}\text{Cu}_x\text{O}_3$ series.¹⁶ At $x \approx 0.3$, resistivity data suggest

FIG. 9. Schematic phase diagram of $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series. Cobalt concentration (x) is shown along the X axis and temperature along the Y axis. Solid circles correspond to T_{MI} temperatures, crosses to T_N and T_f , and open circles to the kink in the resistivity data (see text). AF represents an antiferromagnetic regime, SG spin-glass-like, P paramagnetism, M metallic, and I the two semiconducting regimes described in the text. Solid lines are the proposed boundary regions.

a crossover to another regime with different transport mechanisms. For $0.3 \leq x \leq 1.0$ and below 500 K, the conduction is thermally activated. A constant activation energy is well defined between 100 and 250 K and varies from 5 meV for $x = 0.3$ up to 67 meV for $x = 0.9$. We will propose two simple models for both regions. The insulating states for $x \leq 0.2$ likely come out from strong electronic and antiferromagnetic correlations, as it has been proposed for the RNiO_3 series.¹⁰ Therefore the corresponding MI transition is Mott-like. On the other hand, the structural and magnetic disorder could be responsible for the $x \geq 0.3$ insulator state (Anderson transition).

The onset of the magnetic transitions, either the Néel temperatures T_N or the freezing temperatures T_f , are represented by crosses. Our magnetic data lead to distinguish the following three magnetic regions at low temperatures:

(a) For $x \leq 0.2$, AF interactions between the Ni^{3+} ions are predominant and the SmNiO_3 magnetic structure remains up to $x = 0.2$. Nevertheless, cobalt doping induces progressively an increase in the ferromagnetic correlations. Neutron-diffraction experiments in this region would provide the necessary evidence to support this conclusion.

(b) For $0.3 \leq x \leq 0.8$, the randomness and the competition between the ferromagnetic and AF interactions bring about a spin-glass-like state. It shows spin-blocking characteristic features and a spontaneous magnetization at low temperatures.

(c) For $0.9 \leq x \leq 1$, no sign of magnetic ordering above $T = 4$ K has been observed. The ferromagnetic correlations, which are evident at intermediate x concentrations, have disappeared. A paramagnetic behavior with predominant LS Co^{3+} ions, $t_{2g}^6 e_g^0$, follows.

IV. DISCUSSION

The electronic configurations of the nickel and cobalt ions in RNiO_3 and RCoO_3 compounds are LS Ni^{3+} ($t_{2g}^6 e_g^1$, $S = \frac{1}{2}$)

and LS Co^{3+} ($t_{2g}^6 e_g^0$, $S = 0$), respectively. Nevertheless, a recent study⁸ of the paramagnetic susceptibility of the isostructural $\text{RNi}_{0.3}\text{Co}_{0.7}\text{O}_3$, $\text{LaGa}_{0.3}\text{Co}_{0.7}\text{O}_3$, and $\text{LaNi}_{0.3}\text{Ga}_{0.7}\text{O}_3$ compounds, where Ga^{3+} is a 3d nonmagnetic ($S = 0$) ion, as well as the magnetic properties of the mixed $\text{RNi}_{1-x}\text{Co}_x\text{O}_3$ oxides with intermediate x values point out that new electronic configurations for nickel and cobalt ions are needed to bring about ferromagnetic interactions in the $\text{RNi}_{1-x}\text{Co}_x\text{O}_3$ series.

Electronegativity of Ni^{3+} creates a highly covalent nickel ground state in the RNiO_3 series through $\text{Ni}3d$ and $\text{O}2p$ hybridization.³ New electronic states out of the formally $\text{LS } 3+$ configurations can be put forward in the $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series. Ni^{3+} electronegativity could lead either to a charge transfer $\text{Ni}^{3+} + \text{Co}^{3+} \rightleftharpoons \text{Ni}^{2+} + \text{Co}^{4+}$ or to a stabilization of the high spin Co^{3+} configuration ($S = 1$ or $S = 2$) as a result of a small local lattice distortion.²² These new stabilized Ni^{2+} , Co^{3+} , or Co^{4+} configurations are not a majority in the $M = \text{Ni/Co}$ sublattice but they permit formation of small clusters with magnetic interactions embedded in the paramagnetic matrix. A kind of dynamic mechanism (hopping) with spin memory may bring about ferromagnetic interactions within these clusters. As the spin of the carrier is coupled to the atomic internal magnetic moment following the Hund rule, the maximum hopping probability occurs when the two nearest sites are ferromagnetically aligned. An external magnetic field enhances this alignment and negative magnetoresistance effect appears. A similar carrier hopping mechanism, induced by double exchange (DE) interactions, is commonly used to explain the magnetoresistance in mixed-valence manganites and cobaltates.^{19,23} Therefore these ideas allow us to propose an exchange mechanism similar to DE but taking place between different transition-metal ions as a plausible origin for the spin-glass-like state and the coupled magnetoresistance for intermediate x concentration in the $\text{SmNi}_{1-x}\text{Co}_x\text{O}_3$ series. However, the DE between Co ions with different valence can also contribute to the observed behavior. In both cases, the presence of Ni is necessary to induce changes in the electronic state of the Co ions.

The insulator ground state and the temperature-driven MI transition for the RNiO_3 have been explained by a competition between two main factors.^{3,10,24} On the one hand, hybridization between the $\text{Ni}3d$ and $\text{O}2p$ orbitals which gives the conduction bandwidth W favors metallic behavior. On the other hand, the strong electronic and antiferromagnetic correlations lead to a carrier localization. The presence of spin polarons with large effective mass and strong local AF correlations has been suggested for these systems.¹⁰ Therefore all these properties place RNiO_3 on the borderline between the models proposed for Mott insulators (in this case, charge-transfer type) and for strong correlated metallic systems.²⁵

When RNiO_3 oxides are doped with transition metals ($\text{RNi}_{1-x}\text{M}_x\text{O}_3$ series with $M^{3+} = \text{Cu}^{3+}$, Co^{3+} , Fe^{3+}), T_{MI} decreases drastically. Qualitatively, the decrease is not related to the M^{3+} ionic configuration and is independent of the nature of the doping element.²⁶ The temperature-driven MI transition is progressively suppressed by either electron (Cu^{3+}) or hole (Co^{3+} , Fe^{3+}) injection in the conduction band. We propose that a weakening of the AF correlations

can explain these results. A similar T_{MI} decrease and the related stabilization of the metallic conduction by doping was extensively studied for the $RNi_{1-x}Cu_xO_3$ series, where metallic phases have been obtained upon doping¹⁶ with Cu. $SmNi_{1-x}Co_xO_3$ oxides with $x \leq 0.2$ show the same behavior. A Mott insulator (charge-transfer type) regime is proposed as the origin for the thermally activated conduction at low temperatures in this concentration range.

The above arguments suggest that metallic ground state should exist for $x \geq 0.3$. On the contrary, a new semiconducting behavior appears. In order to understand the possible origin for these states we propose a simple model based on the Anderson localization. In $SmNi_{1-x}Co_xO_3$ series, the conduction band associated with the e_g electrons is made up of two different overlapping $3d$ -ion orbitals as Co and Ni are located at random. Therefore the tail of conduction band with localized states is formed.²⁷ There exists a critical energy in the conduction band, the mobility edge (E_μ), which separates localized and extended energy levels. In this model, the appearance of metallic or nonmetallic conduction depends on the relative position of the Fermi energy level E_F and the mobility edge E_μ . By changing the concentration of the carriers, for instance by electron doping, E_F can cross the mobility edge and an Anderson transition is expected. An analogous situation would occur for hole doping.

We propose, for highly doped $SmNi_{1-x}Co_xO_3$ oxides, $x \geq 0.3$, the existence of the Anderson localization. First, in these compounds, the electronic and AF correlations, which are responsible for the MI transition in the $RNiO_3$ series, have been practically removed by doping. Then, the disorder effects give rise to a semiconducting ground state. When Co replaces Ni atoms, the carrier concentration is reduced. The Fermi level likely moves below the mobility edge, and a thermally activated hopping conduction occurs. Activation energy is proportional to $E_\mu - E_F$. The activation energy dependence found in the $100 \leq T \leq 250$ K range for the $0.3 \leq x < 0.9$ $SmNi_{1-x}Co_xO_3$ oxides supports this model.

V. CONCLUSION

The $SmNi_{1-x}Co_xO_3$ series have been extensively studied by means of XRD, ac and dc magnetic susceptibility, dc resistance, and magnetoresistance in order to establish the phase diagram from 4 K up to 700 K. Below $x \leq 0.2$, the temperatures of MI transition and of the AF ordering, which have been observed in $SmNiO_3$, decrease with increasing x . This leads to three regions in the phase diagram: paramagnetic metal, paramagnetic insulator, and antiferromagnetic insulator. Between $x = 0.2$ and $x = 0.3$, a sharp change in the magnetic and transport properties occurs. A new semiconducting ground state appears and short-range ferromagnetic interactions are evident. These give rise to new paramagnetic-metal, paramagnetic-insulator, and spin-glass-insulator region for $0.3 \leq x \leq 1$.

The origin of the spin-glass state and of the negative magnetoresistance found for intermediate x values have been discussed in terms of the high Ni^{3+} electronegativity. New electronic configurations for the nickel and cobalt ions, out of the low spin +3 valence states, as well as short-range ferromagnetic interactions induced by a dynamic mechanism with spin memory can account for such features. Finally, different models have been proposed in order to explain the transport behavior along the series. Spin polarons with highly effective local AF correlations, which explain the properties of $SmNi_{1-x}Co_xO_3$ for $0 \leq x \leq 0.2$, are progressively removed by Co doping. The new semiconducting regime for $0.3 \leq x \leq 0.9$ is mainly determined by disorder effects.

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