

## Spin-Glass Behavior and Giant Magnetoresistance in the (RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> (RE = La, Nd, Sm) System

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(RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> (RE = La, Nd, Sm) oxides with the perovskite structure have been studied. All of these compounds show a spin-glass behavior at low temperatures. Isostructural compounds in which Ni or Co are replaced by a nonmagnetic element do not show spin-glass behavior. Therefore, simultaneous presence of Ni and Co is needed to develop competitive ferro- and antiferromagnetic interactions in the (RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> compounds. Moreover, large negative magnetoresistance below freezing temperature is observed in these samples. We conclude the existence of an electronic transfer between Ni<sup>3+</sup> and Co<sup>3+</sup> ions in these compounds which gives rise to ferromagnetic interactions. [S0031-9007(98)05513-6]

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The (RE)MO<sub>3</sub> oxides with perovskite structure, RE being a trivalent rare-earth ion and *M* being a 3*d* transition metal, have generated a great deal of interest due to the variety of the magnetic and electrical behavior [1,2]. This interest has grown due to the high temperature superconductivity in related copper perovskites and the recent discovery of the colossal magnetoresistance in manganese perovskites [3–5]. The electronic (RE)NiO<sub>3</sub> phase diagram is composed of a paramagnetic insulator, an antiferromagnetic insulator, and paramagnetic metal phases depending on the temperature and the RE ionic radius [6,7]. The perovskite lattice distortions, in particular the Ni–O–Ni angle, are related to the RE<sup>3+</sup> ionic size. Therefore, a systematic change of the transfer integral between Ni-3*d* and O-2*p* orbitals (*p*-*d* mixing) is observed in (RE)NiO<sub>3</sub> perovskites. When the Ni–O–Ni angle is close to 180°, a metallic phase is favored while the insulator phase is stabilized when this angle decreases [8]. Then, LaNiO<sub>3</sub> is a metallic compound while NdNiO<sub>3</sub> and SmNiO<sub>3</sub> show a metal-insulator transition at 220 and at 400 K, respectively. In addition, NdNiO<sub>3</sub> and SmNiO<sub>3</sub> develop an antiferromagnetic ordering at 220 K. On the other hand, (RE)CoO<sub>3</sub> perovskites [9–14] show a semiconductor behavior below room temperature. Their ground state is a nonmagnetic Co<sup>3+</sup> (*S* = 0, *t*<sub>2g</sub><sup>6</sup>). This low spin state changes to a higher spin configuration with increasing temperature but the exact transformation is still an open question; some authors [10] claim a change from the low spin to the high spin state (*S* = 2, *t*<sub>2g</sub><sup>4</sup>*e*<sub>g</sub><sup>2</sup>) while other authors [13] suggest the formation of the intermediate spin configuration (*S* = 1, *t*<sub>2g</sub><sup>5</sup>*e*<sub>g</sub><sup>1</sup>).

The magnetic and electrical behavior of (RE)Ni<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> mixed perovskites have been studied by several authors [14–18]. LaNi<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> shows metallic behavior below room temperature up to *x* = 0.6 and semiconductor behavior for higher Co content. In the Nd and Sm compounds, the main effect of Ni replacement by Co is the

suppression of the temperature-driven metal-insulator transition, stabilizing the metallic phase for *x* ≤ 0.2. Higher Co content leads to semiconducting samples as occurs in the La compounds. Earlier magnetic measurements have shown the presence of ferromagnetic interactions in the semiconducting LaNi<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> samples near the metal-insulator boundary [16]. Recently, we have performed a thorough study of NdNi<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> obtaining both semiconducting behavior and a spin-glass state for 0.3 ≤ *x* ≤ 0.8. Nevertheless, an explanation of the origin of ferromagnetic interactions which are needed for the formation of a spin glass is still lacking [18]. In this Letter, we present a detailed study of the magnetic and transport properties of the (RE)Ni<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> series. Our results show how the simultaneous presence of Ni and Co is needed to develop the ferromagnetic interactions and the spin-glass state in these systems. Moreover, we observe a giant magnetoresistance coupled to the spin-glass state which suggests a ferromagnetic interaction with electronic transfer as occurs in mixed valence manganites or in mixed valence Co<sup>3+</sup>/Co<sup>4+</sup> perovskites [19–23].

(RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> samples were prepared by using high oxygen pressure *P*<sub>O<sub>2</sub></sub> = 200 atm, and *T* = 900 °C for RE = La, 950 °C for RE = Nd, and *T* = 1000 °C for RE = Sm. The precursors were obtained by means of a sol-gel method in order to get an intimate mixture of the reactants. The isomorphous compounds LaGa<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> and LaNi<sub>0.3</sub>Ga<sub>0.7</sub>O<sub>3</sub> were also prepared in order to separate the magnetic contribution of Ni and Co. NdGaO<sub>3</sub> and SmScO<sub>3</sub> were prepared by standard ceramic procedures in order to obtain the magnetic contribution of the rare-earth ions. The oxygen content was determined by thermogravimetric analysis in reducing atmosphere. (RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3-δ</sub> samples can be considered as stoichiometric with δ < 0.03. All samples were characterized as single phases by means of x-ray powder diffraction. Profile analysis was performed in the Pbnm

TABLE I. Spatial groups (SG), lattice parameters,  $M$ - $O$ - $M$  angles, and  $M$ - $O$  interatomic distances for the studied compounds ( $M$  = transition metal).

(RE) $M_{0.3}M'_{0.7}O_3$ ( $M/M'$ )	La Ni/Co	Nd Ni/Co	Sm Ni/Co	La Ni/Ga	La Ga/Co
SG	$R-3c$	Pbnm	Pbnm	$R-3c$	$R-3c$
$a$ (Å)	5.456	5.364	5.304	5.503	5.455
$b$ (Å)	...	5.367	5.397	...	...
$c$ (Å)	13.108	7.567	7.525	13.429	13.133
Vol/ $z$ (Å <sup>3</sup> )	56.3	54.6	53.8	58.7	56.4
$\langle M-O-M \rangle$	164.5	156.8	154.1	163.8	160.8
$d_{M-O}$ (Å)	1.935	1.936	1.938	1.963	1.945

spatial group for RE = Nd, Sm and in the  $R-3c$  for RE = La, in agreement with the reported structures. The main structural parameters of these samples and of the Ga compounds are collected in Table I. The structural distortion of the perovskite unit cell increases with decreasing the RE<sup>3+</sup> ionic size as is expected.

Magnetic susceptibility has been measured as a function of temperature in a SQUID magnetometer. Figure 1 shows  $\chi(T)$  curves for the three studied samples. We observe a peak in the susceptibility curves at 50, 26, and 13 K for La, Nd, and Sm, respectively. These peaks are hallmarks of a spin-glass phase at low temperatures as was studied for the NdNi<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> series [18]. The features of a spin-glass state, such as the frequency dependence of the susceptibility near the freezing temperature and thermomagnetic effects, have also been measured for both LaNi<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> and SmNi<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> samples. As an example, Fig. 2 shows the frequency dependence of the susceptibility and the zero field cooled (ZFC) and field cooled (FC) magnetization curves for the SmNi<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> sample. In order to study the origin of the spin-glass behavior, one must keep in mind that the transition-metal sublattice, a primitive cubic cell, is nonfrustrated being impossible to develop a spin-glass state with only the com-

petitive superexchange antiferromagnetic interactions shown by Ni<sup>3+</sup>-O-Ni<sup>3+</sup> and Co<sup>3+</sup>-O-Co<sup>3+</sup> in nickelates [7] and cobaltates [13]. Therefore, the formation of a spin-glass state can only be understood if a ferromagnetic interaction competing with the antiferromagnetic superexchange interactions is present. Long-range ferromagnetism is not developed due to the competitive interactions and the randomness of the transition-metal sublattice.

Magnetic properties of the isomorphous LaGa<sub>0.7</sub>Ni<sub>0.3</sub>O<sub>3</sub> and LaGa<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> compounds have also been studied. In each case, one of the magnetic ions (Ni<sup>3+</sup> or Co<sup>3+</sup>) has been substituted with a nonmagnetic ion (Ga<sup>3+</sup>). This substitution changes neither crystallographic structure (see Table I) nor formal valence of transition metals (Ni or Co). Susceptibility measurements for these samples are shown in the inset of Fig. 1 together with those obtained for the LaNi<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> sample. No anomaly was observed in the gallium compounds, demonstrating that the formation of the spin-glass state and, consequently, the presence of ferromagnetic interaction is due to the simultaneous presence of Ni and Co. Moreover, LaNi<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> shows the highest paramagnetic signal, indicating that the electronic state for Co<sup>3+</sup> or Ni<sup>3+</sup> is different for this sample.

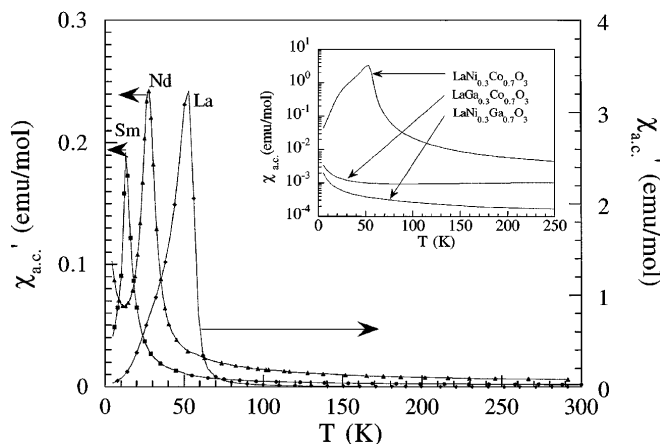


FIG. 1. ac magnetic susceptibility as a function of temperature for the (RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> (RE = La, Nd, Sr) compounds. The inset shows the  $\chi_{ac}(T)$  curves for LaNi<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub>, LaGa<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub>, and LaNi<sub>0.3</sub>Ga<sub>0.7</sub>O<sub>3</sub> samples. Solid lines are guides to the eye.

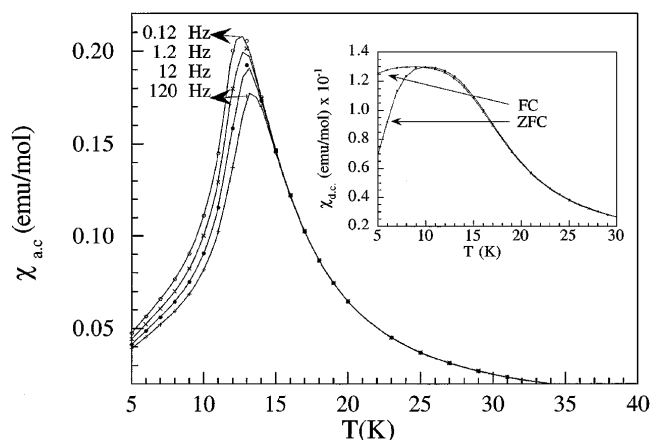


FIG. 2. ac magnetic susceptibility  $\chi_{ac}$  versus temperature at different frequencies for the SmNi<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> compound. The inset shows the FC and ZFC magnetization curves under an external magnetic field of 1000 Oe. Solid lines are guides to the eye.

TABLE II. Magnetic constants obtained by fitting  $\chi(T)$ ,  $\chi(T) = \chi_{\text{exp}}(T) - \chi_{\text{RE}}(T)$  (see text), to the equation  $\chi = \chi_0 + C/(T - \Theta)$  for the (RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> (RE = La, Nd, Sm), LaGa<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub>, and LaNi<sub>0.3</sub>Ga<sub>0.7</sub>O<sub>3</sub> samples.

Composition	$T_f$ (K)	$\chi_0$ ( $\times 10^{-4}$ emu mol <sup>-1</sup> )	$\mu_{\text{eff}}^2$ ( $\mu_B^2$ )	$\Theta$ (K)
LaNi <sub>0.3</sub> Co <sub>0.7</sub> O <sub>3</sub>	50	8.5	4.9	70
NdNi <sub>0.3</sub> Co <sub>0.7</sub> O <sub>3</sub>	26	7.0	1.3	51
SmNi <sub>0.3</sub> Co <sub>0.7</sub> O <sub>3</sub>	13	4.3	1.4	35
LaNi <sub>0.3</sub> Ga <sub>0.7</sub> O <sub>3</sub>	...	1.2	0.10	-1.9
LaGa <sub>0.3</sub> Co <sub>0.7</sub> O <sub>3</sub>	...	6.0	0.15	1.8

Nevertheless, LaGa<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> shows a similar behavior that the undoped compound LaCoO<sub>3</sub>, a nearly independent magnetic susceptibility which increases with increasing temperature. In the latter two samples, cobalt cations are in its low spin state ( $S = 0$ ) but, due to the small energy difference with higher and magnetic Co<sup>3+</sup> spin states, the thermal excitation induces the slight increase of the susceptibility. LaGa<sub>0.7</sub>Ni<sub>0.3</sub>O<sub>3</sub> shows weak paramagnetism Curie-Weiss-like in agreement with the spin  $S = 1/2$  shown by the Ni<sup>3+</sup>. In order to obtain the magnetic contribution of the transition metal sublattice, the magnetic susceptibility of isomorphous NdGaO<sub>3</sub> and SmScO<sub>3</sub> compounds were used to extract the rare-earth contribution ( $\chi_{\text{RE}}$ ). The data  $\chi(T) = \chi_{\text{exp}}(T) - \chi_{\text{RE}}(T)$ ,  $\chi_{\text{exp}}(T)$  being the measured susceptibility for (RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> samples, were fitted to the formula  $\chi(T) = \chi_0 + C/(T - \Theta)$ . The best fit values are reported in Table II. The value of the magnetic moment obtained from the Curie constant is near zero for the gallium samples, being quite different for the (RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> samples. The maximum value of the paramagnetic moment is about 2.2 bohr magneton/f.u. (formula unit) in the LaNi<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> sample. This value is higher than expected for the Ni<sup>3+</sup> only spin moment contribution ( $S = 1/2$ ). Therefore, a paramagnetic contribution from the Co<sup>3+</sup> ion can be estimated. The Curie temperatures are positive for (RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> samples, suggesting ferromagnetic interactions. Both, the Curie temperature and the spin-glass freezing temperature  $T_f$  increase with increasing RE<sup>3+</sup> ionic size as can be observed in Table II. This feature can be explained on the basis of structural details. As can be observed in Table I, the  $M$ -O- $M$  angle decreases with increasing RE atomic number. The transfer integral  $t_{pd}$  between  $3d(M)$  and  $2p(O)$  orbitals is, as a first approximation,  $t_{pd} \approx \cos(\omega/2)$ ,  $\omega$  being  $180^\circ$ - $M$ -O- $M$ . It is well known that  $t_{pd}$  controls the double exchange ferromagnetic interaction in manganites [21]. Therefore, the obtained increase in ferromagnetic correlations (higher values of  $\Theta$  and  $T_f$ ) with increasing  $M$ -O- $M$  angle could indicate a double exchange-like ferromagnetic interaction.

Resistivity measurements between 4.2 and 250 K are shown in Fig. 3. We observe a semiconductor behavior in the whole temperature range. If the temperature dependence of resistivity is approximated by an Arrhe-

nius law for  $T > 50$  K, the values of activation energies obtained are 17, 30, and 40 meV for La, Nd, and Sm compounds, respectively. Samples with higher conductivity show higher ferromagnetic correlations, i.e., higher values of  $\Theta$  and  $T_f$ . Figure 4 shows magnetoresistance measurements for SmNi<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub>, NdNi<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub>, and LaNi<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> samples. SmNi<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub> was measured instead of SmNi<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> due to the high resistance shown by the latter sample. Negative giant magnetoresistance is observed at temperatures below the freezing temperature for the three samples studied, while there is no significant change at temperatures above  $T_f$ . Figure 5 shows the magnetoresistance of LaNi<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub>, defined as  $[\rho(10 T) - \rho(0)]/\rho(0)$ , between 5 and 100 K as well as the magnetic susceptibility measurement. This figure clearly shows the relationship between giant magnetoresistance and the spin-glass state.

The occurrence of giant magnetoresistance coupled to a spin-glass state has been observed in related perovskite such as mixed valence cobalt compounds [19,20] La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub>, and manganites [22-24] (Tb<sub>2/3</sub>La<sub>1/3</sub>)Ca<sub>1/3</sub>MnO<sub>3</sub>, or La<sub>2/3</sub>Ca<sub>1/3</sub>MnO<sub>3</sub> doped with Al and In. In these samples, the ferromagnetic interaction is coupled with metallic conduction due to the so-called double-exchange mechanism. It is thought that the application of an external field increases the size of the ferromagnetic domains giving rise to more metallic paths

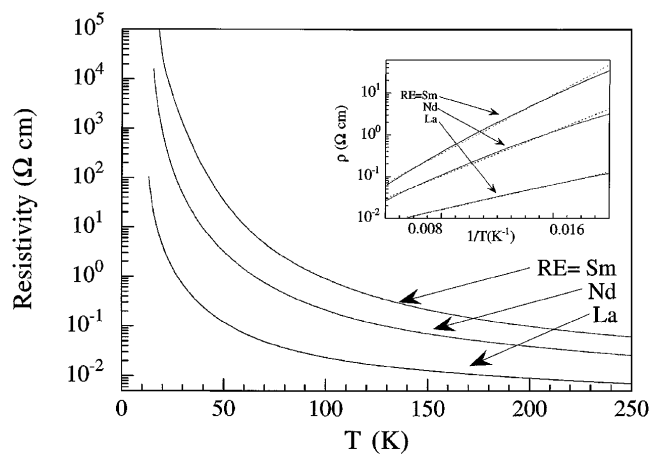


FIG. 3. Resistivity versus temperature curves for the (RE)Ni<sub>0.3</sub>Co<sub>0.7</sub>O<sub>3</sub> compounds. The inset shows the  $\ln \rho$  versus  $1/T$  curves.

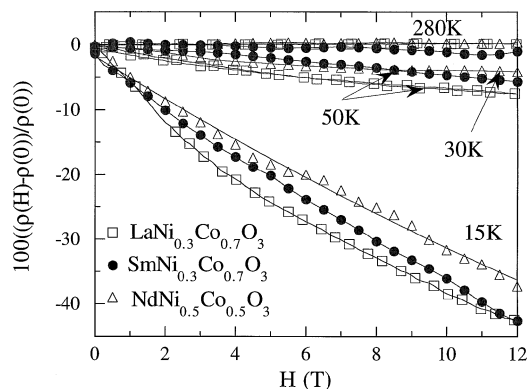


FIG. 4. Magnetoresistance curves for  $\text{SmNi}_{0.5}\text{Co}_{0.5}\text{O}_3$ ,  $\text{NdNi}_{0.3}\text{Co}_{0.7}\text{O}_3$ , and  $\text{LaNi}_{0.3}\text{Co}_{0.7}\text{O}_3$  at the temperatures indicated. Solid lines are guides to the eye.

in the sample. The results obtained for  $(\text{RE})\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$  samples allow one to argue that a similar mechanism should occur in these compounds. Nevertheless, several differences can be noted between  $(\text{RE})\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$  and manganites or cobaltates. First, Ni and Co cations are formally in the 3+ valence state while Mn in manganites or Co in cobaltates are in a mixed valence state. Second, ferromagnetic interaction in the  $(\text{RE})\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$  system when cobalt and nickel are simultaneously present suggests a ferromagnetic double exchange-like interaction between different transition metal elements.

Taking into account these considerations, we think that there are two possibilities to develop the ferromagnetic interaction. On the one hand, Co is forced to the high or intermediate spin state due to the presence of Ni and the ferromagnetic interaction is established between these two ions. On the other hand, the large electronegativity of  $\text{Ni}^{3+}$  can induce a charge transfer as follows:  $\text{Ni}^{3+} + \text{Co}^{3+} \rightleftharpoons \text{Ni}^{2+} + \text{Co}^{4+}$ , and the ferromagnetism arises from the  $\text{Co}^{3+}\text{-Co}^{4+}$  interaction as occurs in cobaltates [19,20]. Both kinds of electronic transfer could explain the increase of the magnetic moment in the paramagnetic

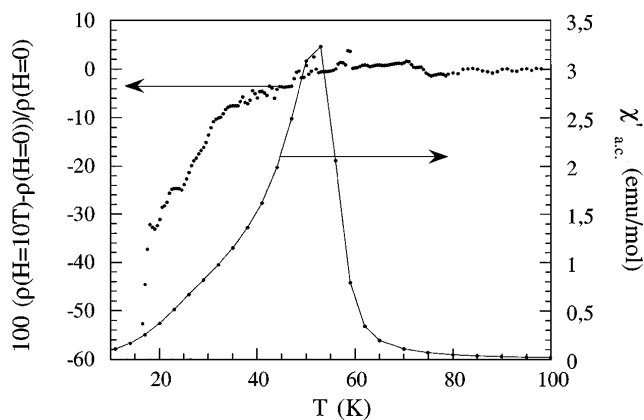


FIG. 5. Comparison of magnetoresistance and magnetic susceptibility for the  $\text{LaNi}_{0.3}\text{Co}_{0.7}\text{O}_3$  sample. Solid lines are guides to the eye.

phase for the  $(\text{RE})\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$  system. The transfer would be dynamic, supplying an exchange mechanism similar to the double exchange but between different transition metal atoms, giving rise to the spin-glass state and the magnetoresistive behavior. Moreover, this exchange through the oxygen atoms is highly dependent on the  $M\text{-O-M}$  angle.

In conclusion, the  $(\text{RE})\text{Ni}_{1-x}\text{Co}_x\text{O}_3$  system shows a similar behavior to the magnetoresistive manganites or cobaltates with a mixed valence state where ferromagnetism and magnetoresistance are coupled. It has been demonstrated that the Ni-Co interaction is needed for this behavior, suggesting the possibility of a type of double exchange interaction between different kinds of atoms, well directly or well by a charge transfer.

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