Magnetic and transport properties of $NiMn_{2-x}Co_xO_4$ spinel oxides

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ABSTRACT

Magnetic properties of $NiMn_{2-x}Co_xO_4$ spinel oxides have been investigated. The paramagnetic moment shows a direct correlation with the nominal cation concentration. A first transition, from paramagnetism to ferrimagnetism, occurs at high temperature, going from T_c = 125 K ($NiMn_{1.8}Co_{0.2}O_4$) up to 210 K. A second transition is observed at lower temperature. It takes place at about 60 K and increases with Co content up to 160 K. Under an external field, both transitions merge into a single one, with a characteristic temperature T_{max} rapidly decreasing with increasing fields. Magnetization loops show the presence of both antiferromagnetic-type field dependence and irreversible behaviors typical of soft-ferromagnets. Preliminary investigations of R(T,H) point towards novel magneto-transport phenomena.

Keywords : A: Powders-solid state reaction C: Electrical properties C: Magnetic properties.
D: Spinels E: Thermistors

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Introduction

Spinel oxides based on two 3-d transition-metals (e.g., Mn and Ni, Mn and Co, or Ni and Co), have been well studied due to their outstanding semiconducting properties. Pseudo-ternary oxides based on these same three metals (e.g., Mn, Ni and Co) have also been reported, mainly from the point of view of their structural and electrical properties [1,2] ; however, few works deal with magnetic studies, although these materials should be extremely rich on interesting phenomena. It is well known, for instance, that the cation distribution in the tetrahedral and octahedral sites of the spinel structure is intimately related to the possibility of the cations to adopt two, or even three, different oxidation states. These, in turn, will influence the magnetic properties, leading eventually to specific magnetic interactions depending on the location, size and oxidation states on the different cations.

We have undertaken systematic studies in mixed-ternary spinel oxides of formula $Co_xNi_yMn_zO_4$ (x+y+z = 3). In the search for new properties, it looked indeed very interesting to deal with these three magnetic elements at the same time. In this way, the physical properties, in particular magnetism, can be described with respect to varying contents of Co, Ni or Mn. Two main series were studied : one, keeping constant the Ni content to 1.0, another, keeping the Mn content to 1.5. In this work we will mainly present our results obtained for the first series, $NiMn_{2-x}Co_xO_4$ ($0.2 \leq x \leq 0.7$), emphasizing its electrical and magnetic aspects in order to establish any correlation which may lead to technological applications, such as in the widely investigated giant-magnetoresistance perovskites.

Experimental

Samples were prepared from Co_3O_4, NiO, CuO and MnO, of submicronic size, homogenized by wet attrition milling and calcined at 1050 °C for 1 h. Materials were milled

again, uniaxially pressed and sintered for 2 h, with a heating rate of 5 °C/min and cooling in air at 2 °C/min. The apparent density reached values higher than 95 % of the theoretical density. Four-points d.c. conductivity was measured between 25 °C and 400 °C, using a constant current d.c. power supply and 1 μA resolution. Magnetic measurements were performed in a SHE VTS-906 and Quantum Design MPMS-XL5 SQUID susceptometers. Additional a.c. characterizations were performed using a home-made mutual-inductance susceptometer. R(T,H) experiments have been performed at Porto Alegre. Resistance was measured between 5 K and 300 K by conventional four-probe methods, the current being applied parallel to the magnetic field. At some selected temperatures, R(H) data were recorded by sweeping the magnetic field from + 60 kOe to – 60 kOe.

Results and discussion

All compounds belong to the spinels family, space group S.G. *Fd3m*, with cubic symmetry. The series $NiMn_{2-x}Co_xO_4$ presents a small decrease of the lattice parameter when increasing the cobalt content. Samples with high x(Co) could also be indexed in a tetragonal symmetry (S.G. *I41/amd*), suggesting a phase transition during cobalt substitution for Mn and/or Ni. As an example, sample $Co_{1.2}Ni_{0.3}Mn_{1.5}O_4$ has a = 8.3393 Å (S.G. *Fd3m*), and a = 5.8537 Å, c = 8.5625 Å (S.G. *I41/amd*).

The magnetic susceptibility was measured in the paramagnetic state (Fig. 1). Data show the expected behavior for ferrimagnetic materials, that is, large negative values of Θ (strong antiferromagnetic interactions) and a pronounced curvature of $\chi^{-1}(T)$ in the paramagnetic regime (ferromagnetic correlations). The high temperature data almost superpose for all samples, suggesting that any transformation from Mn^{3+} to Mn^{4+}, during the

substitution Co → Mn (at constant Ni content), is accompanied by a similar transformation from Co^{3+} to Co^{2+}, since their ionic moments are the same.

Figure 2 shows the a.c. susceptibility measured under an excitation field of about 10 mOe and a measuring frequency of 119 Hz, for two samples of $NiMn_{2-x}Co_xO_4$ (x = 0.2 and 0.5). Since these measurements are performed at almost zero-field, the sharp peaks observed at high temperature correspond to the antiferromagnetic interactions ($T_{AF} = T_{max}$ ~ 115 K and 170 K, for x = 0.2 and 0.5, respectively). At lower temperatures a very broad transition centered at about 45 K, is clearly observed for $NiMn_{1.8}Co_{0.2}O_4$, while a "shoulder-like" bump is observed at about 140 K, for $NiMn_{1.5}Co_{0.5}O_4$. This low-temperature transition may correspond to a specific ordering of a magnetic sublattice [3], but it does not have any incidence on the transport properties, as we will discuss later. As seen in Fig. 2, when x(Co) increases, the low-temperature transition merges into the high-temperature ordered state, becoming almost undetectable. This fact suggests a distribution of cobalt atoms in the tetragonal and octahedral sites leading to an ill-defined magnetic sublattice of the cobalt and/or manganese moments. It becomes also clear from figure 2 that the transition temperature T_c between the paramagnetic state and the ferrimagnetic ordering increases with the cobalt concentration. By defining T_c as the temperature of the sudden increase of the magnetization (from figure 2, T_c ~ 125 K and 190 K, for x = 0.2 and 0.5, respectively), we observed that this transition temperature saturates to about 210-220 K at high Co contents ($0.9 \leq x(Co) \leq 1.2$) [4]. It should be noted that for other transition-metal *Me* substitutions (including *Me* = Ni) in $NiMn_{2-x}Me_xO_4$ compounds, T_c is independent of x(*Me*) [5], indicating that the large increase of T_c should be ascribed to the presence of cobalt.

In order to get a better knowledge of the ferromagnetic interactions existing in the ferrimagnetic state, several zero-field-cooled/field-cooled (ZFC/FC) cycles were performed

under different fields. Figure 3 shows measurements on samples with x = 0.2 and x = 0.5 at low applied fields. It is seen that the ZFC modes undergo similar variations as those observed in the a.c. susceptibility (compare Figs. 2 and 3). It is also interesting to notice that the magnetization may take negative values below a certain compensation temperature (e.g., $NiMn_{1.5}Co_{0.5}O_4$, Fig. 3), confirming the existence of at least two magnetic sublattices oriented anti-parallel. This is not an isolated phenomenon since it is also seen in many other compounds of this family [4,5], and it is just an expected feature for ferrimagnetism.

When increasing the applied field, the ferrimagnetic state is progressively destroyed, favoring a ferromagnetic lattice. This is seen in figure 4, which shows the temperature dependence of the magnetization for samples $NiMn_{1.8}Co_{0.2}O_4$ and $NiMn_{1.5}Co_{0.5}O_4$, under 2.5 kOe and 10 kOe. Although a clear change in the curvature is still seen at about 70 K for x(Co) = 0.2, the presence of two maxima is not observed anymore ; in addition, the large irreversibility which occurred at low fields gradually vanishes at higher fields, becoming completely reversible at H_{app} = 2.5 kOe. Similar features are observed for $NiMn_{1.5}Co_{0.5}O_4$, but this time a much larger field (H_{app} = 10 kOe) is needed to turn the ZFC/FC cycle completely reversible.

The ordered state (ferrimagnetic at low fields, ferromagnetic at high fields) is confirmed by the magnetization loops performed at various temperatures (Fig. 5) : high moments and noticeable hysteresis at low fields, typical of ferromagnetic systems. In addition, the magnetization at high fields does not fully saturate and varies quite linearly with H ; this is an indication that antiferromagnetic correlations should be still considered. The coercive fields H_{coerc} are low, but replacing nickel by copper seems a good option to increase H_{coerc}, as it goes from 600 Oe up to 3000 Oe, in $Co_{0.9}Ni_{0.6}Mn_{1.5}O_4$ and $Co_{0.9}Cu_{0.6}Mn_{1.5}O_4$, respectively.

Measurements of electrical properties were performed at high temperatures in order to get the physical parameters in the semiconducting (or semimetal) regime. Results showed low conductivities, consistent with the possible use of these materials as thermistors. The activation energies, evaluated between 300 K and 700 K, are of the order of 0.3 – 0.4 eV.

We are presently working on the magneto-transport properties of these materials. Fig. 3 shows R(T) measured under no magnetic field, for $NiMn_{1.8}Co_{0.2}O_4$ and $NiMn_{1.5}Co_{0.5}O_4$. The electrical properties are compared, in the same figure, to the magnetization behavior discussed before. Three regimes are observed : at high temperatures, the resistance increases with decreasing T, confirming the semiconducting or semimetal character presented above. At intermediate temperatures, corresponding to the temperature range bracketed by both magnetic transitions, a sudden drop of R(T), by more than a factor of 2, is observed. Finally, below the lowest magnetic transition, the resistance stays almost constant, as if the new ordered state had no incidence on the transport properties.

In order to investigate deeper these different regimes, we performed R(H), resistance measurements as a function of magnetic field, at some specific temperatures. Inserts of figure 5 show the resistance variation during a magnetic loop performed between 0 and + 60 kOe, followed by a field decrease down to – 60 kOe, and back up to zero field. These inserts show results obtained at 120 K, that is, in the ordered state bracketed by both magnetic transitions. A steady increase of the resistance, of about 5-10 %, is observed during the full cycle, stabilizing during the final field variation (from - 60 kOe up to 0). This positive magneto resistance will be further investigated under different conditions of field and temperature. Other samples (e.g., $Co_{0.9}Ni_{0.6}Mn_{1.5}O_4$) show no variation with the applied field, suggesting interesting correlations between the magnetic transitions, the electronic conduction and the overall composition in these materials.

Conclusions

The magnetic properties of mixed ternary-oxide spinels $NiMn_{2-x}Co_xO_4$ (in general, $Co_xNi_yMn_zO_4$; x+y+z = 3), were investigated. Two transitions were observed, one related to a ferrimagnetic state at T_c, the other one due to some specific ordering whose nature should be determined, for instance, by neutron diffraction techniques. Both transitions merge into a single one at high cobalt content and/or under high magnetic fields. A continuous increase of T_c is observed with increasing x(Co) and saturates at 210-220 K. This high value for T_c makes these compounds to be very interesting for applications provided some correlations could be found between magnetic and electronic transitions. In this sense, our present work is devoted to a full description of the R(T,H) behavior ; up to now positive magneto resistances of about 10 % in absolute value have been observed.

Acknowledgements

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Figures captions

Fig. 1: Inverse susceptibility of $NiMn_{2-x}Co_xO_4$ and $Co_xNi_{1.5-x}Mn_{1.5}O_4$ measured under 10 kOe

Fig. 2: a.c. susceptibility of $NiMn_{1.8}Co_{0.2}O_4$ and $NiMn_{1.5}Co_{0.5}O_4$

Fig. 3: ZFC/FC cycles measured at 20 Oe, and electrical resistance under zero field for $NiMn_{1.8}Co_{0.2}O_4$ (A) and $NiMn_{1.5}Co_{0.5}O_4$ (B)

Fig. 4: ZFC/FC cycles measured at 2.5 kOe, for $NiMn_{1.8}Co_{0.2}O_4$, and at 2.5 and 10 kOe, for $NiMn_{1.5}Co_{0.5}O_4$

Fig. 5: Magnetization loops measured at 5 K, for $NiMn_{1.8}Co_{0.2}O_4$ and $NiMn_{1.5}Co_{0.5}O_4$. Inserts : resistance change (in arbitrary units), measured at T = 120 K, during a field sequence ($0 \rightarrow + 60$ kOe $\rightarrow - 60$ kOe $\rightarrow 0$)

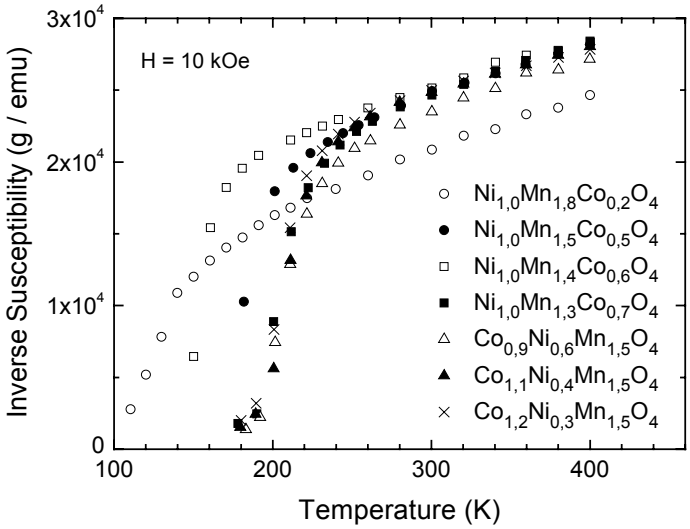
H = 10 kOe
Inverse Susceptibility (g / emu)
Temperature (K)
3x10^4
2x10^4
1x10^4
0
100
200
300
400
Ni1,0Mn1,8Co0,2O4
Ni1,0Mn1,5Co0,5O4
Ni1,0Mn1,4Co0,6O4
Ni1,0Mn1,3Co0,7O4
Co0,9Ni0,6Mn1,5O4
Co1,1Ni0,4Mn1,5O4
Co1,2Ni0,3Mn1,5O4

Figure 1

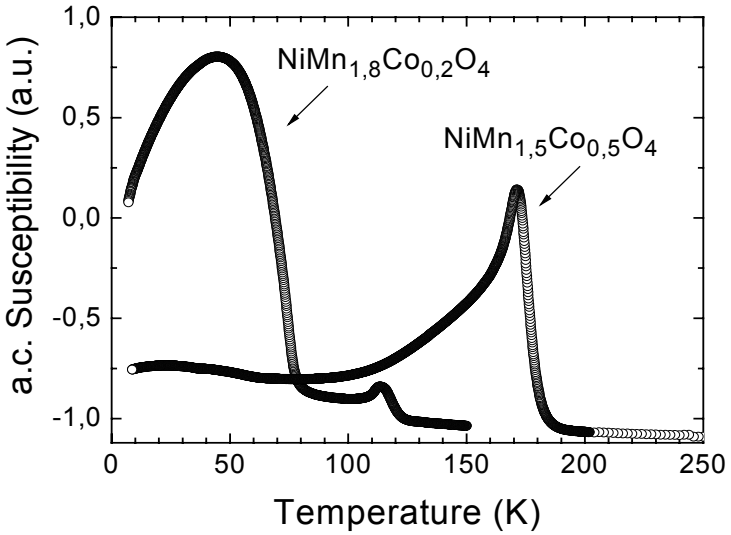
1,0
0,5
0,0
-0,5
-1,0
a.c. Susceptibility (a.u.)
0
50
100
150
200
250
Temperature (K)
NiMn1,8Co0,2O4
NiMn1,5Co0,5O4

Figure 2

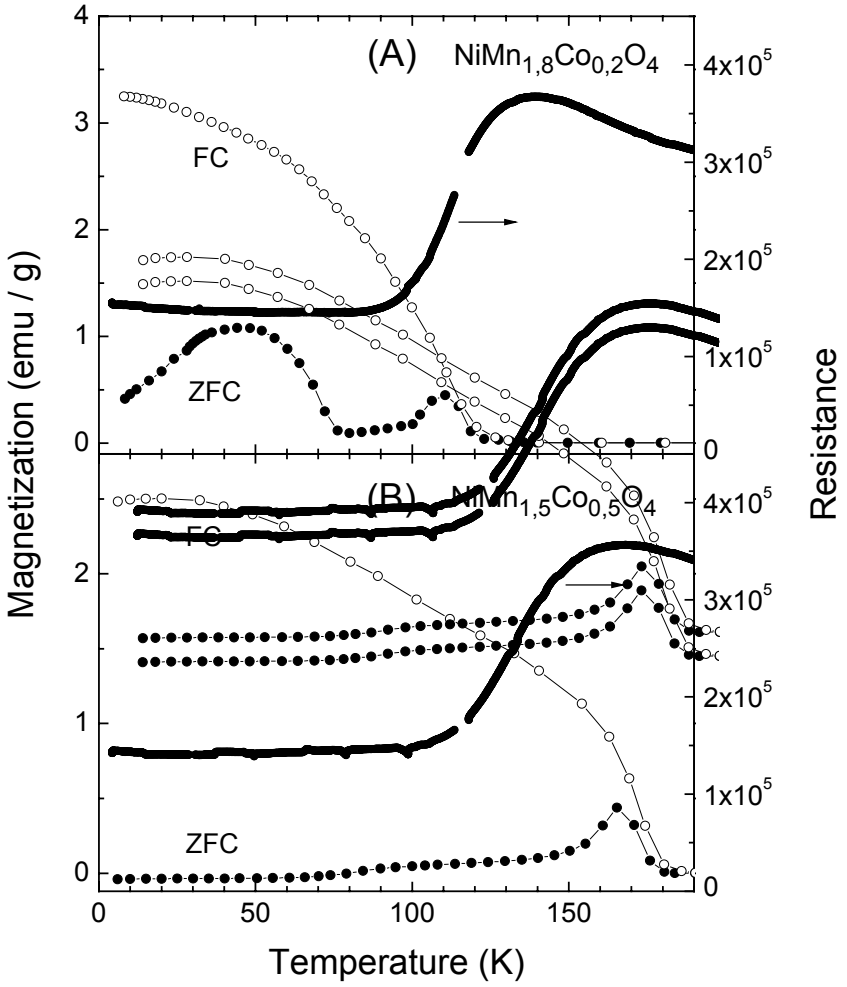
(A) NiMn1,8Co0,2O4
FC
ZFC
(B) NiMn1,5Co0,5O4
FC
ZFC
Magnetization (emu / g)
Resistance
Temperature (K)
0
1
2
3
4
0
50
100
150
0
1x10^5
2x10^5
3x10^5
4x10^5

Figure 3

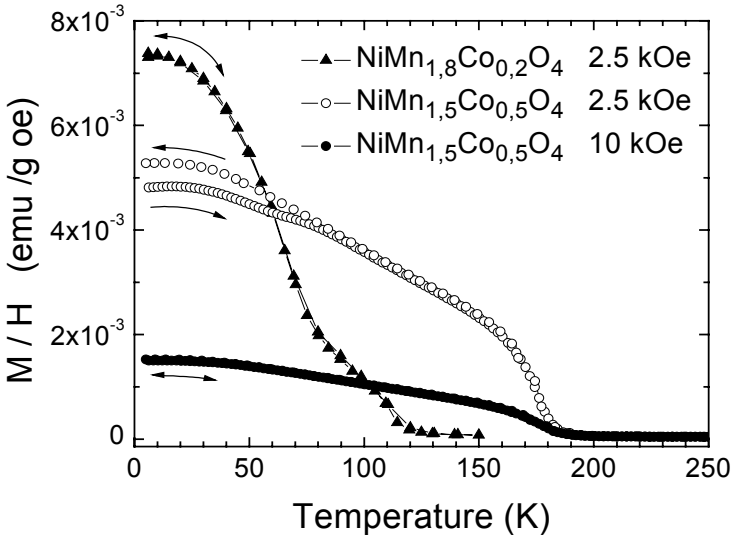
8x10-3
6x10-3
4x10-3
2x10-3
0
M / H (emu /g oe)
0
50
100
150
200
250
Temperature (K)
NiMn1,8Co0,2O4 2.5 kOe
NiMn1,5Co0,5O4 2.5 kOe
NiMn1,5Co0,5O4 10 kOe

Figure 4

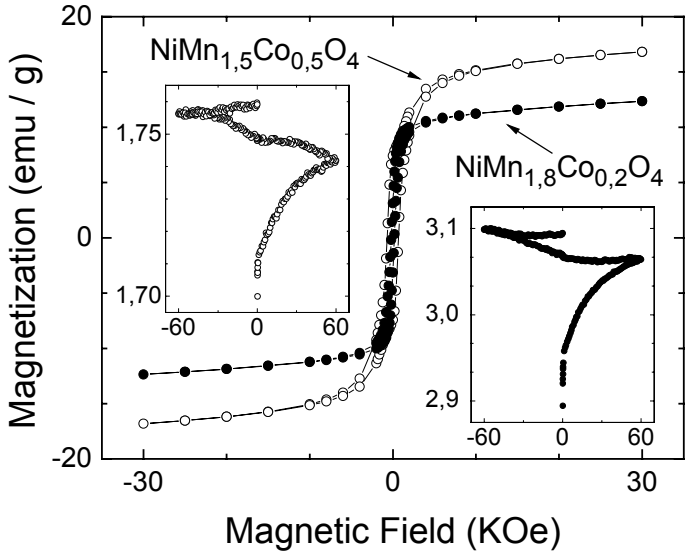
20
0
-20
-30
0
30
Magnetization (emu / g)
Magnetic Field (KOe)
NiMn1,5Co0,5O4
NiMn1,8Co0,2O4
1,75
1,70
-60
0
60
3,1
3,0
2,9
-60
0
60

Figure 5