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Magnetic 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: Powders-solid state reaction; Electrical properties; Magnetic properties; Spinels; Thermistors

1. 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.

2. 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

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reached values higher than 95% of the theoretical density. Magnetic measurements were performed in a SHE VTS-906 and a Quantum Design MPMS-XL5 SQUID susceptometers. Additional ac characterizations were performed using a home-made mutual-inductance susceptometer. Concerning the transport properties, two temperature regions were investigated separately: above room temperature (i.e., between 25 °C and 400 °C), dc conductivity was measured by a four-points technique, using a constant current dc power supply and 1 μA resolution; at lower temperatures, due to the high resistance values, a low-frequency four-probe ac technique was preferred, fixing the ac voltage and measuring the ac current going through the leads.

3. Results and discussion

All compounds belong to the spinels family, space group (S.G.) *Fd*3*m*, 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. *I*41/*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. *Fd*3*m*), and $a = 5.8537$ Å, $c = 8.5625$ Å (S.G. *I*41/*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.

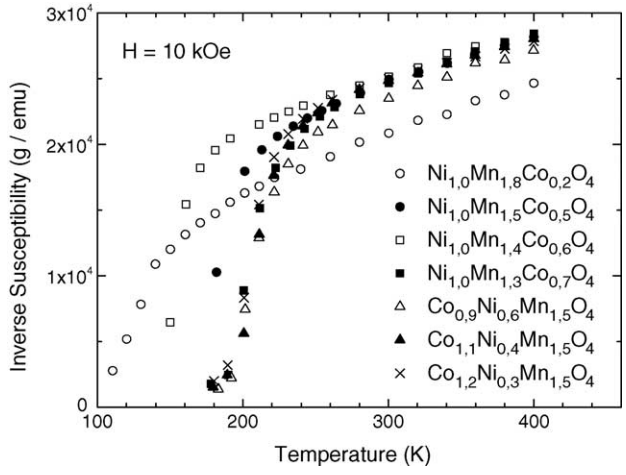

Fig. 1. Inverse susceptibility of $NiMn_{2-x}Co_xO_4$ and $Co_xNi_{1.5-x}Mn_{1.5}O_4$ measured under 10 kOe.

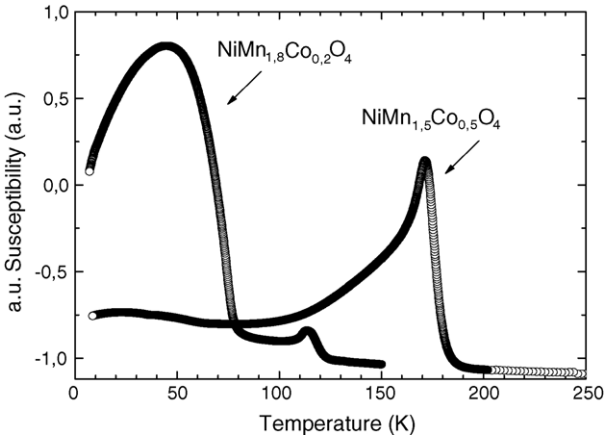

Fig. 2. ac susceptibility of $NiMn_{1.8}Co_{0.2}O_4$ and $NiMn_{1.5}Co_{0.5}O_4$.

Fig. 2 shows the ac 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 ($T_{AF} = T_{max} \sim 115$ 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 Fig. 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 Fig. 2, $T_c \sim 125$ 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 ($0.9 \leq x(\text{Co}) \leq 1.2$).[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. Fig. 3 shows measurements on samples with $x = 0.2$ and 0.5 at low applied fields ($H_{app} = 20$ Oe). It is seen that the ZFC modes undergo similar variations as those observed in the ac susceptibility (compare Figs. 2 and 3). It is also interesting to notice that the magnetization may take negative values below a certain compensation temperature

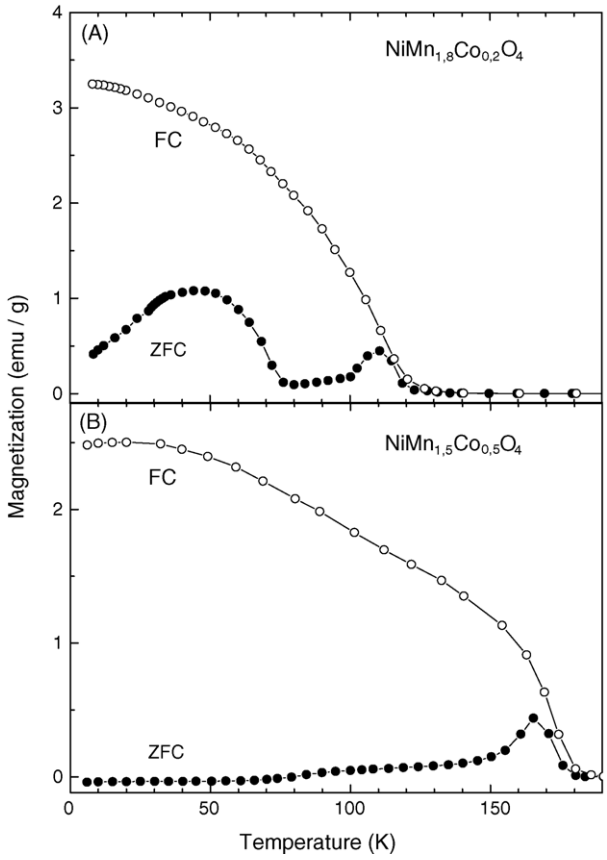

Fig. 3. ZFC/FC cycles measured at 20 Oe for $NiMn_{1.8}Co_{0.2}O_4$ (A) and $NiMn_{1.5}Co_{0.5}O_4$ (B).

(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 Fig. 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.

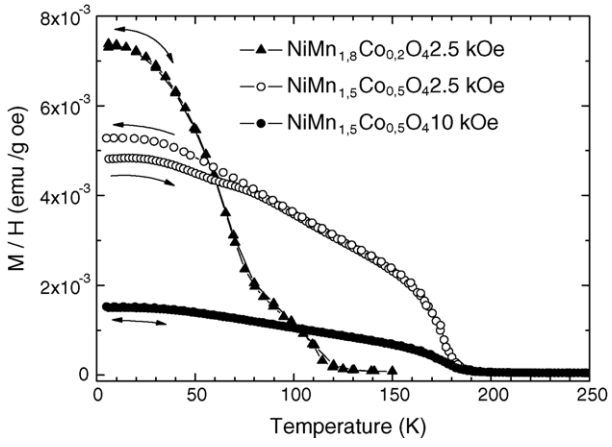

Fig. 4. ZFC/FC cycles measured at 2.5 kOe, for $NiMn_{1.8}Co_{0.2}O_4$, and at 2.5 kOe and 10 kOe, for $NiMn_{1.5}Co_{0.5}O_4$.

The ordered state (ferrimagnetic at low fields, ferromagnetic at high fields) was confirmed by the magnetization loops performed at 5 K (Fig. 5). High moments and a noticeable hysteresis, typical of ferromagnetic systems, are observed at low fields. At high fields, the magnetization does not saturate and varies quite linearly with H, which is an indication that antiferromagnetic correlations should still be considered. The coercive fields H_{coerc} are relatively 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 (Fig. 5). At higher manganese contents, keeping the copper concentration fixed to 0.6, H_{coerc} still increases, as seen for sample $Co_{0.7}Cu_{0.6}Mn_{1.7}O_4$.

The semiconducting (or semimetal) regime was investigated at high temperature by performing electrical measurements by dc techniques. 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.

The low temperature regime, in particular, the influence of the magnetic field on the electrical conductivity is being investigated at present in these materials. Due to their very high resistance at the approach of the ordered regime, the ac measurements were performed keeping a constant ac voltage and monitoring the ac current going through the sample. Three

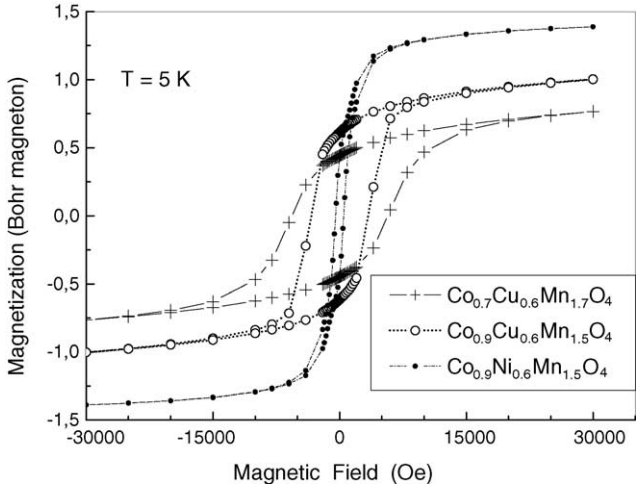

Fig. 5. Magnetization loops measured for copper-substituted samples $Co_{0.7}Cu_{0.6}Mn_{1.7}O_4$ and $Co_{0.9}Cu_{0.6}Mn_{1.5}O_4$ compared to $Co_{0.9}Ni_{0.6}Mn_{1.5}O_4$.

different regimes have been observed: the semiconducting or semimetal character is maintained down to T_c, due to a thermally activated process. At lower temperatures, corresponding to the temperature region bracketed by both magnetic transitions, the increase of resistance slows down and tends to saturate. Below the lowest magnetic transition, the resistance stays constant, as if the new ordered state had no incidence on the transport properties. Since similar effects have been observed in other samples of the same series we think that these are intrinsic phenomena, which should be explained by excitation processes other than a simple activation mechanism or some residual resistance effects. We are presently working on the interpretation of these three regimes, under no applied field but also applying external magnetic fields to determine any eventual magneto-resistivity due to the presence of ferromagnetic domains.

4. 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. Three different regimes were observed in the thermal dependence of the conductivity, which seem to correlate well with the magnetic phenomena observed by magnetization measurements. Our present work is devoted to a full description of the $R(T, H)$ behavior; up to now an interesting dependence of the impedance with respect to the measuring ac phase has been observed, suggesting new excitation mechanisms related to the presence of magnetic domains.

Acknowledgements

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