

Magnetic properties of $(\text{Co}, \text{Ni}, \text{Mn})_3\text{O}_4$ spinels

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Magnetic properties of new materials, based on the general formula $\text{Co}_x\text{Ni}_y\text{Mn}_z\text{O}_4$ ($x+y+z=3$), have been investigated as a function of magnetic field and temperature. The behavior observed in the paramagnetic regime ($220 \text{ K} \leq T \leq 400 \text{ K}$) shows a direct correlation with the nominal cation concentration. The paramagnetic-ferrimagnetic transition which takes place at $T = T_c$ depends on the overall composition, going from $T_c = 120 \text{ K}$ (for $\text{Co}_{0.2}\text{NiMn}_{1.8}\text{O}_4$) up to $T_c = 210 \text{ K}$ (for $\text{Co}_{1.2}\text{Ni}_{0.3}\text{Mn}_{1.5}\text{O}_4$). A second transition is observed at lower temperatures, corresponding to a second ordered magnetic sublattice. This second transition takes place at about 60 K (for $\text{Co}_{0.6}\text{NiMn}_{1.4}\text{O}_4$), increasing with the cobalt content up to about 160 K . Under an external magnetic field, both transitions merge into a single one, with a characteristic temperature T_{max} , which rapidly decreases with increasing field. Magnetization loops $M(H)$ obtained at 5 K show a typical behavior of soft magnetic materials, with low coercive fields. Low conductivity values were observed at room-temperature, increasing by a factor of 200-1000 at high temperatures (400 C), which make these compounds to be very interesting materials for potential applications as NTCR thermistors.

Keywords: magnetic oxides, spinels, magnetic exchange, ferrimagnetic properties

Propiedades magnéticas de las espinelas $(\text{Co}, \text{Ni}, \text{Mn})_3\text{O}_4$

Se han investigado las propiedades magnéticas de materiales de fórmula $\text{Co}_x\text{Ni}_y\text{Mn}_z\text{O}_4$ ($x+y+z=3$), en función del campo magnético aplicado y de la temperatura. El comportamiento observado en el régimen paramagnético ($220 \text{ K} \leq T \leq 400 \text{ K}$) está en relación directa con la concentración catiónica nominal. Se observa una transición paramagnética-ferrimagnética a $T = T_c$, cuyo valor depende de la composición global del compuesto, variando entre $T_c = 120 \text{ K}$ ($\text{Co}_{0.2}\text{NiMn}_{1.8}\text{O}_4$) y $T_c = 210 \text{ K}$ ($\text{Co}_{1.2}\text{Ni}_{0.3}\text{Mn}_{1.5}\text{O}_4$). Se ha observado una segunda transición a una temperatura inferior, relacionada con una segunda subred magnéticamente ordenada. Esta segunda transición ocurre a $T = 60 \text{ K}$ ($\text{Co}_{0.6}\text{NiMn}_{1.4}\text{O}_4$), aumentando progresivamente con la concentración del cobalto hasta alcanzar aproximadamente 160 K . En presencia de un campo magnético externo, ambas transiciones se confunden en una sola, cuya temperatura característica T_{max} decrece rápidamente en función de campos magnéticos crecientes. Se realizaron ciclos de magnetización $M(H)$ a $T = 5 \text{ K}$, obteniéndose ciclos típicos de materiales magnéticos blandos, con campos coercitivos pequeños. Con el objeto de estudiar posibles aplicaciones de estos materiales como termistores NTCR, se realizaron igualmente medidas eléctricas por sobre la temperatura ambiente: los valores de conductividad aumentan de un factor 200-1000 entre la temperatura ambiente y 400 C .

Palabras clave: óxidos magnéticos, espinelas, interacciones de intercambio, ferrimagnetismo

1. INTRODUCTION

Spinel materials based on 3-d transition-metal oxides of Mn and Ni or Mn and Co, have been well studied due to their outstanding semiconducting properties. Their fields of application concern mainly temperature sensing devices, as for instance, the negative temperature coefficient (NTC) thermistors [1-3]. Ternary-oxide materials obtained from the above cited cations (Mn, Ni and Co) have also been described in the literature, some of them presenting similar peculiar conduction properties. Most of the previous work have been focused on varying cation composition and on their structural and electrical properties [4-6] but, in contrast to other related compounds based mainly on Fe [7], almost none of these reports have dealt with the magnetic properties, in particular those occurring at low temperatures [8]. It becomes then interesting to study such compounds from the point of view of their electrical and magnetic aspects in order to establish any eventual correlation which may lead to interesting potential applications, such as in the recently investigated giant-magnetoresistance ferromagnetic perovskites.

Any research in these ternary-oxide spinel materials must take into account the relative complexity of the cationic distribution which, partly because of the intrinsic duality among the tetrahedral and octahedral sites, comes from the possibility of the cations to adopt two, or even three, different oxidation states within the same

specimen. As a consequence of this fact, the cationic distribution and the overall composition strongly depend on external parameters, such as the sintering temperature and its heating and cooling rates, or the atmospheric environment associated to it.

We report herein the synthesis, the structural characterization and the electrical and magnetic behavior of mixed-ternary oxides of spinel structure, of general formula $(\text{Co}_x\text{Ni}_y\text{Mn}_z)\text{O}_4$ ($x+y+z=3$). Two main series were studied: one series, keeping constant the nickel content to 1.0 atom per unit-formula (i.e., $\text{Co}_x\text{NiMn}_{2-x}\text{O}_4$), the other series keeping the manganese content to 1.5 (i.e., $\text{Co}_x\text{Ni}_{1.5-x}\text{Mn}_{1.5}\text{O}_4$). In this way, correlations can be established with respect to varying contents of cobalt, nickel or manganese. In this work we will mainly focus on the first series of samples, although some comparisons will be made with samples from the second one.

2. EXPERIMENTAL PROCEDURE

Samples of formulae $\text{Co}_x\text{NiMn}_{2-x}\text{O}_4$ and $\text{Co}_x\text{Ni}_{1.5-x}\text{Mn}_{1.5}\text{O}_4$ were prepared from the corresponding oxides Co_2O_3 , NiO and MnO, of submicronic particle size. Nominal compositions and identification labels are given in Table I. The mixtures were homogenized by wet

attrition milling using isopropanol as liquid medium. The mixtures were calcined at 1050 C for 1h. The materials were milled again, uniaxially pressed and sintered at various temperatures for 2 h, with a heating rate of 5 C/min and cooling in air at a rate of 2 C/min. X-ray diffraction (XRD) patterns were made at each step of sintering. Lattice parameters were determined by X-ray diffraction on a D-5000 Siemens diffractometer using $\text{CuK}\alpha$ radiation and Si as an internal standard. A scanning rate of $1/4^\circ 2\theta/\text{min}$ was used to calculate the lattice parameters. The apparent density measured by water displacement, reached values higher than 95 % of the theoretical density. The sintering temperature at which the higher density is achieved (for equal sintering times) depended on composition, decreasing with increasing content of cobalt, in the same way as observed in $\text{Y}(\text{Co,Mn})\text{O}_3$ perovskites [9].

TABLE I. NOMINAL COMPOSITIONS, IDENTIFICATION (ID) LABELS AND LATTICE PARAMETERS FOR $(\text{Co}_x\text{Ni}_y\text{Mn}_z)\text{O}_4$ SAMPLES

ID label	$\text{Co}_x\text{Ni}_y\text{Mn}_z\text{O}_4$	a (Å) S.G. <i>Fd3m</i>
012	NiMn_2O_4	8.4028
218	$\text{Co}_{0.2}\text{NiMn}_{1.8}\text{O}_4$	8.3956
515	$\text{Co}_{0.5}\text{NiMn}_{1.5}\text{O}_4$	8.3989
614	$\text{Co}_{0.6}\text{NiMn}_{1.4}\text{O}_4$	8.3525
713	$\text{Co}_{0.7}\text{NiMn}_{1.3}\text{O}_4$	8.3818
1235	$\text{Co}_{1.2}\text{Ni}_{0.3}\text{Mn}_{1.5}\text{O}_4$	8.3393
1235 (*)	$\text{Co}_{1.2}\text{Ni}_{0.3}\text{Mn}_{1.5}\text{O}_4$ (*)	a = 5.8537 / c = 8.5625 (*)
210	NiCo_2O_4	8.114

all phases according to formula $\text{Co}_x\text{Ni}_y\text{Mn}_z\text{O}_4$ ($0.0 \leq x \leq 2$), except 1235

(*) all phases indexed in S.G. *Fd3m*, except 1235 also indexed in *I41/amd*

Four-points d.c. conductivity was measured between 25 C and 400 C, using a constant current d.c. power supply (Tektronix PS280), a multimeter (Hewlett Packard 44201A) and 1 μA d.c. current resolution. Magnetic measurements were performed in a SHE VTS-906 SQUID susceptometer, between 5 K and 300 K, on ceramic specimens glued to a thin rod in order to avoid disorientation due to torque forces exerted on the sample. Additional characterization by a.c. techniques was performed using a home-made mutual-inductance susceptometer.

3. RESULTS AND DISCUSSION

3.1. Crystallochemical characterization

Figure 1 shows XRD patterns for three characteristic samples. Compounds containing low cobalt concentrations can be indexed in the classical spinels space group *Fd3m*, with cubic symmetry. Lattice parameters are given in Table I. Samples with high content of cobalt present broader peaks (fig. 1, bottom panel for sample 1235), perhaps due to a bad crystallization of the material. Indeed, XRD spectra of sample 1235 ($\text{Co}_{1.2}\text{Ni}_{0.3}\text{Mn}_{1.5}\text{O}_4$), can be also indexed in a tetragonal symmetry (S.G. *I41/amd*), with lattice parameters given in table I. A small decrease of the lattice parameter is observed at the beginning of the series $\text{Co}_x\text{NiMn}_{2-x}\text{O}_4$ ($0 \leq x \leq 0.7$) but at higher cobalt content, a phase transition might occur, as indicated above.

3.2. Physical characterization

3.2.1. ELECTRICAL PROPERTIES.

Preliminary measurements of the electrical transport properties of some samples of this series were performed between room temperature and 400°C. Results are shown at the Figure 2 for samples 218 and 614. Results obtained on sample 1235 are not clear and, therefore, are

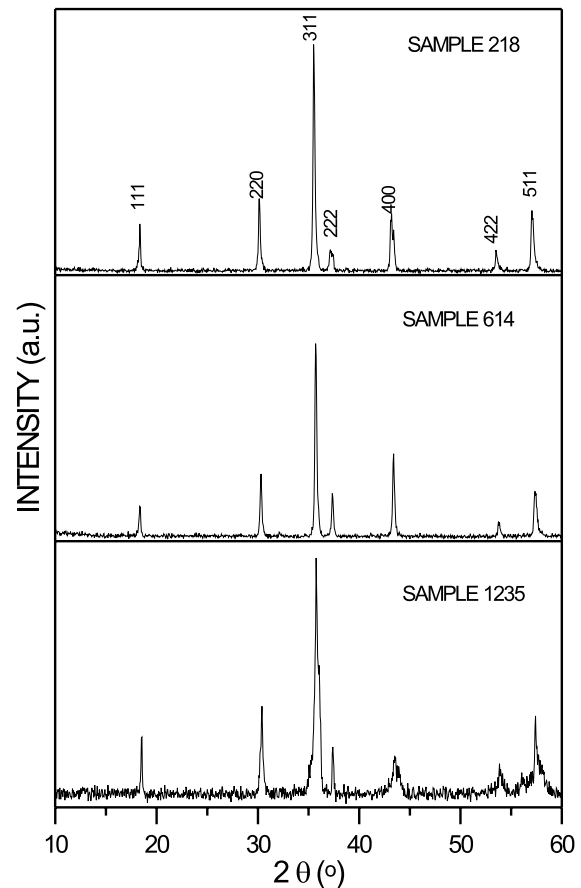


Fig. 1. XRD patterns of three samples of the $(\text{Co}_x\text{Ni}_y\text{Mn}_z)\text{O}_4$ system (see table I for identification labels)

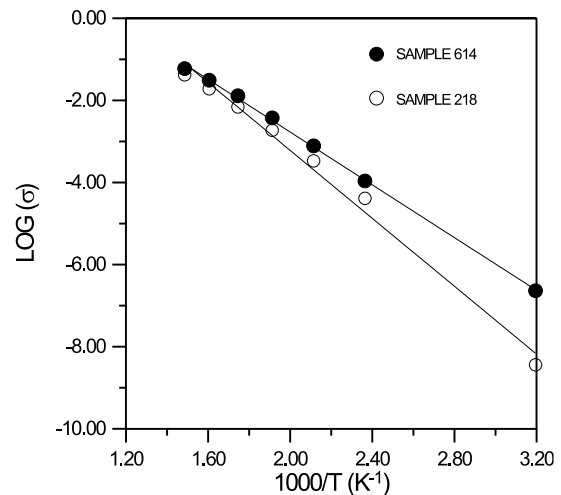


Fig. 2. Arrhenius plots corresponding to the conductivity behaviour between 40° and 400°C of ceramic samples 218 and 614.

not represented. Table 2 resumes some values of conductivity and activation energy for samples 218 and 614. The conductivity values are one order of magnitude lower than those obtained in $\text{Y}(\text{Co,Mn})\text{O}_3$ perovskites. These values are consistent with the possible use as NTC thermistors, particularly sample 218 [9].

TABLE 2. SOME ELECTRICAL PARAMETERS OF CERAMIC SAMPLES 218 AND 614

Sample	E_a (eV)	$\sigma_{20^\circ\text{C}}$ S^*cm^{-1}	$\sigma_{400^\circ\text{C}}$ S^*cm^{-1}
218	0.37	2.16×10^{-4}	0.25
614	0.28	1.31×10^{-3}	0.29

3.2.2. MAGNETIC PROPERTIES.

3.2.2.1. Paramagnetic state

Figure 3 shows the inverse susceptibility of several samples of the series $\text{Co}_x\text{NiMn}_{2-x}\text{O}_4$ ($0.2 \leq x \leq 0.7$) measured between the ordering transition temperature T_c and 400 K, under an applied field of 10 kOe. The strong curvature of $\chi^{-1}(T)$ in the paramagnetic regime may be due to either a temperature-independent paramagnetic contribution χ_{TP} or to the appearance of strong magnetic correlations as one approaches T_c . In both cases, any fit of χ^{-1} versus T , by a Curie-Weiss law $\chi = C/(T-\Theta)$ or by a modified relation $\chi = C/(T-\Theta) + \chi_{\text{TP}}$ may be subjected to caution, and the present results will still be improved by complementary measurements to be performed at higher temperatures in the nearest future. Nevertheless, three major information can be got from figure 3 : firstly, all samples show an almost superposed behavior in the paramagnetic state ; this experimental fact may indicate that, since the Ni content is constant and assuming that it will always be in the 2+ oxidation state (the most favorable state for the Ni cation, [10]), then any transformation from Mn^{3+} to Mn^{4+} , may be accompanied by a similar transformation from Co^{3+} to Co^{2+} , keeping exactly the same overall moment *per* unit formula. The second important information from figure 3 concerns the ordering temperature T_c , from a high-temperature paramagnetic to an intermediate-temperature ordered state ; it is seen that T_c strongly depends on the nominal composition of the sample, as we shall discuss below. Finally, the fact that the Weiss parameter Θ is highly negative (a few hundreds of degrees K) indicates the presence of strong antiferromagnetic correlations, in addition to the ferromagnetic-like interactions which take place at $T = T_c$. From these facts we may conclude that the order must be of ferrimagnetic character, as it usually occurs in spinels.

3.2.2.2. Zero-Field-Cooled/Field-Cooled (ZFC/FC) cycles at $H = H_{\text{rem}} \sim 0$

In order to investigate the low-field properties and, in particular, the transition(s) which may occur at almost zero field, we performed zero-field-cooled/field-cooled ZFC/FC cycles under the remnant

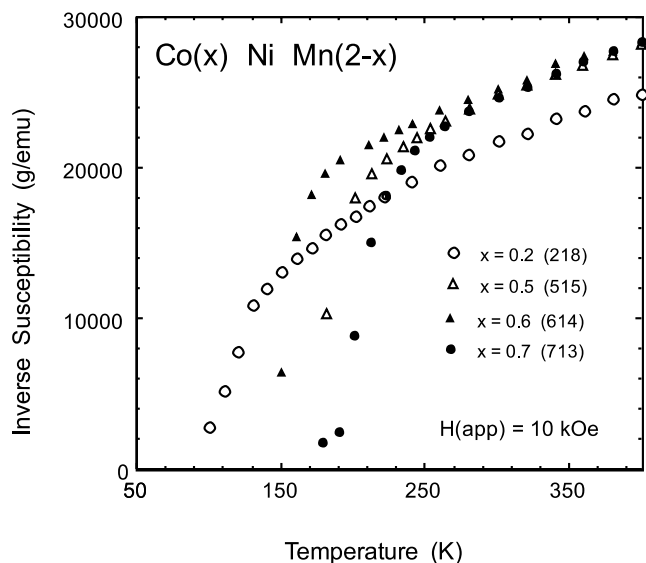


Fig. 3. Inverse magnetic susceptibility of samples belonging to the series $\text{Co}_x\text{NiMn}_{2-x}\text{O}_4$, measured under an applied magnetic field of 10 kOe

field of our superconducting coil (estimated to about 20 Oe). Figure 4 shows the thermal dependence of the magnetization during such cycles, for three samples of the series ($\text{Co}_{0.2}\text{NiMn}_{1.8}\text{O}_4$, $\text{Co}_{0.6}\text{NiMn}_{1.4}\text{O}_4$ and $\text{Co}_{0.7}\text{NiMn}_{1.3}\text{O}_4$). Two magnetic transitions are observed : at high temperatures, the paramagnetic-ferrimagnetic transition at T_c , characterized by a sudden increase of the magnetization when temperature decreases and, at lower temperatures (at $T = T_{\text{low}}$), a transition towards a probably collinear Néel state, as pointed out by C. Boudaya et al. [8]. Both transitions were confirmed by a.c. susceptibility

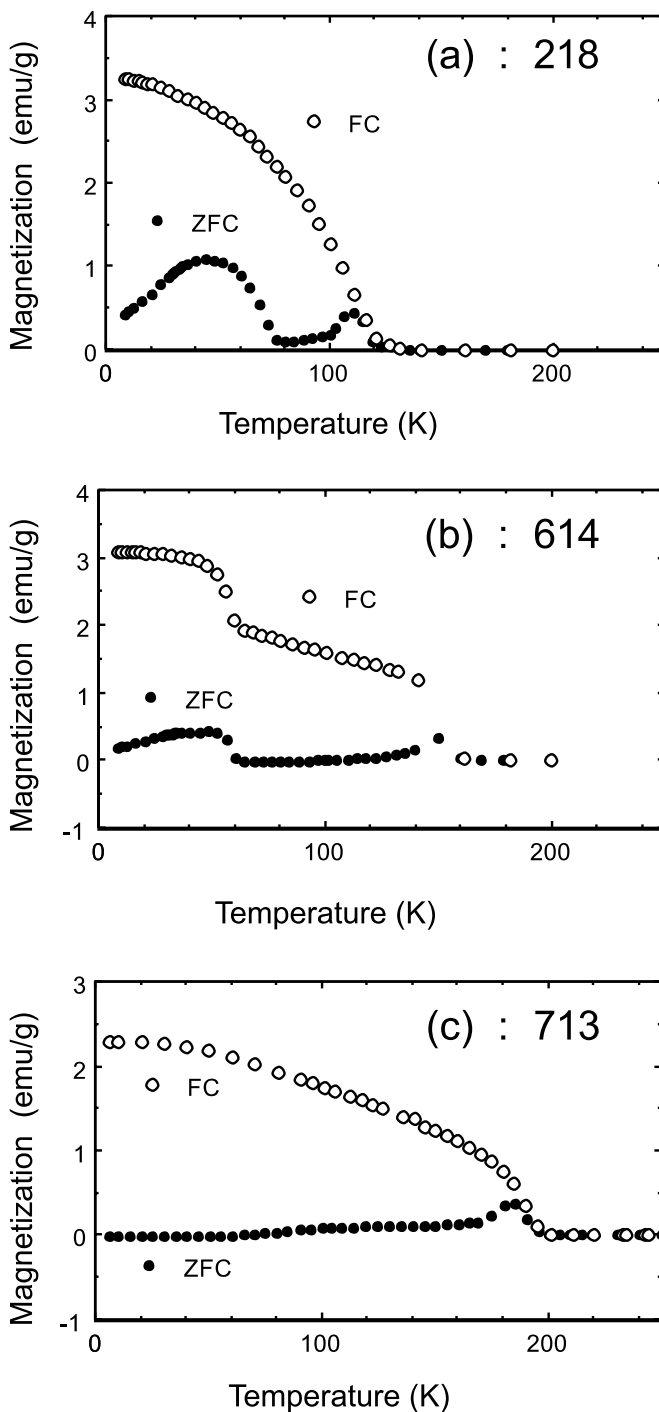


Fig. 4. Thermal variation of the magnetization for samples 218 (a), 614 (b) and 713 (c), measured on a ZFC/FC mode. Notice that the magnetization takes negative values at high cobalt contents

measurements. Neutron diffraction experiments are planned in the near future in order to unambiguously characterize both transitions and the associated magnetic states. The fact that the lowest transition at T_{low} becomes less noticeable with increasing cobalt concentration may suggest a strong dependence with the cobalt distribution in the tetragonal and octahedral sites, leading to an ill-defined magnetic sublattice of the cobalt and/or manganese moments. It is interesting to notice that the magnetization may take negative values below a certain compensation temperature, due to the presence of at least two magnetic sublattices, the higher the cobalt content, the larger is this effect. Figure 5 shows the cobalt dependence of T_c , the temperature at which takes place the paramagnetic-ferrimagnetic transition. The temperature of the lowest transition at T_{low} also increases with increasing Co content, taking place at about 60-70 K (for 218 and 614) up to almost 160 K (for 1235). However, as noticed in fig. 4(c), at high cobalt concentrations, T_{low} merges into the high-temperature ordered state and becomes almost undetectable.

3.2.2.3. Ferromagnetic state at high magnetic fields

Application of high magnetic fields progressively destroys the ferrimagnetic state, yielding a (presumably 100%) ferromagnetic lattice. This is seen in figure 6, which shows the temperature dependence of the magnetization for sample 218 ($\text{Co}_{0.2}\text{NiMn}_{1.8}\text{O}_4$), under various applied fields. Although a clear change in the curvature is still seen at about 75 K, the presence of two well-distinguishable maxima is not observed anymore. In addition, the large thermomagnetic irreversibility which occurs at low fields (fig. 4.a) gradually vanishes at higher fields, becoming completely reversible at $H_{app} = 2.5$ kOe during a ZFC/FC cycle.

The ordered state (ferrimagnetic at low fields, ferromagnetic at high fields) is further confirmed by magnetization loops performed at various temperatures on several samples of this series. Figure 7 shows samples 218 and 614, measured at 5K, which present a typical ferromagnetic behavior: high saturation moments and a noticeable hysteresis at low fields. The coercive fields H_{coerc} are rather low, as in soft ferromagnets. However, a non-monotonic dependence of H_{coerc} was observed with varying temperature, increasing, in the case of sample 614 ($\text{Co}_{0.6}\text{NiMn}_{1.4}\text{O}_4$), by a factor of 2 between 5 and 70 K, and decreasing afterwards. Current work is devoted to low temperature electrical conductivity measurements under applied magnetic fields, in order to correlate the magnetic transitions to eventual changes of the electronic conduction in these materials.

4. CONCLUSIONS

The magnetic properties of two series of mixed ternary-oxide spinels were investigated ($\text{Co}_x\text{NiMn}_{2-x}\text{O}_4$ and $\text{Co}_x\text{Ni}_{1.5-x}\text{Mn}_{1.5}\text{O}_4$). Two magnetic transitions were observed, one due to a paramagnetic-ferrimagnetic state at T_c , the other one which could be due to a specific ordering towards a collinear Néel state [8]. Both transitions merge into a single one at high cobalt content and/or under high applied magnetic fields. A continuous increase of T_c is observed with increasing cobalt content, which tends to saturate at about 210 K at high Co concentrations. This high value for T_c makes these compounds to be very interesting for technological applications provided some eventual correlations could be found between magnetic and electronic transitions. These materials behave as typical soft ferromagnets at low temperatures and high magnetic fields, and as ferrimagnetic materials at intermediate temperatures and low fields.

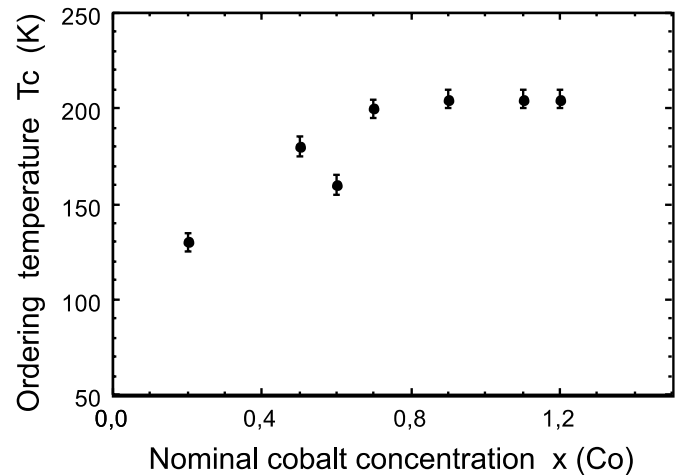


Fig. 5. Paramagnetic-ferrimagnetic transition temperature T_c as a function of the cobalt content, for samples belonging to the series $\text{Co}_x\text{NiMn}_{2-x}\text{O}_4$ ($x = 0.2, 0.5, 0.6, 0.7$) or to the series $\text{Co}_x\text{Ni}_{1.5-x}\text{Mn}_{1.5}\text{O}_4$ ($x = 0.5, 0.9, 1.1, 1.2$)

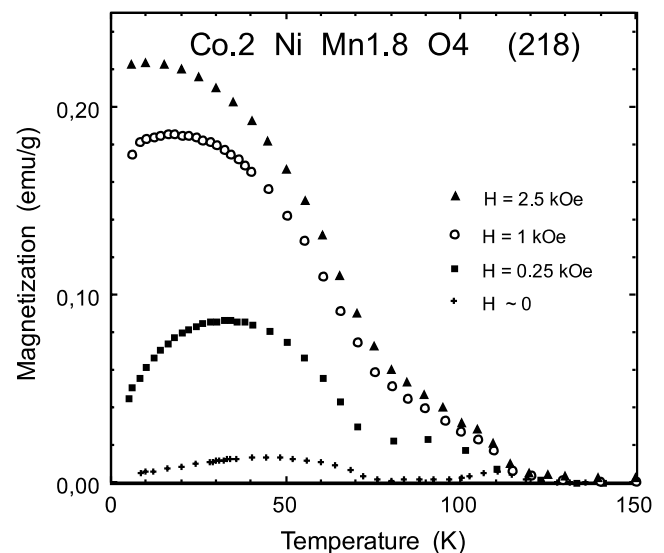


Fig. 6. Thermal variation of the magnetization for sample 218, under given applied fields

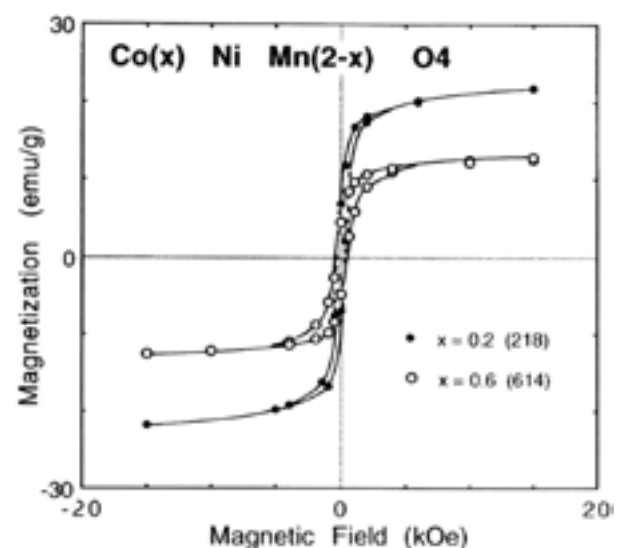


Fig. 7. Magnetization curves measured at 5 K with increasing and decreasing applied magnetic fields, for samples 218 and 614

ACKNOWLEDGEMENTS

This work has been supported by the Project CAM07N/0096/2002, of the Autonomous Community of Madrid

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