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Critical behavior in the perovskite-like system Y(Ni,Mn)O_3

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Abstract

The electrical and magnetic properties of the perovskite-type solid solution $YNi_xMn_{1-x}O_3$ have been studied at different temperatures and magnetic fields. Electrical conductivity measurements have shown a semiconductor behavior throughout the solid solution. The room temperature conductivity increases with the Ni concentration until $x = 1/3$, and then decreases for higher Ni contents. The effective moment in the paramagnetic state shows a clear break at $x = x_{\mathrm{crit}} = 1/3$, presenting a constant value at $x \leq x_{\mathrm{crit}}$ and decreasing at higher nickel concentration. In the ordered state, other magnetic parameters show similar discontinuities versus the nickel content, such as a sudden increase of the magnetization at high field or a maximum in the coercive strength of the ferromagnetic-like $M(H)$ loop. By charge-conservation arguments we can readily identify such critical value as an optimum conversion of Mn^{3+} into Mn^{4+}, leading to the charge-balance formula $Y^{3+}[Ni^{2+}_{1/3}(Mn^{3+}_{0.5}Mn^{4+}_{0.5})_{2/3}]O^{2-}_3$, that is, equal amounts of Mn^{3+} and Mn^{4+} in the sample. Magnetic data shows that, at $x \leq x_{\mathrm{crit}}$, the solid solution behaves as a spin-glass and/or antiferromagnetic system, while at $x > x_{crit}$, full ferromagnetic characteristics are observed. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Giant magneto-resistance systems based on the manganese-oxide perovskite structure $REMnO_3$ (RE = rare earth) has attracted a great deal of interest since their rediscovery a few years ago [1–3]. Indeed, these systems, first studied in the 1950s, show an interesting magnetic and electronic features, such as ordering and insulating–conducting phase transitions [4–6]. The electron configuration [7] and the basic exchange-interaction mechanisms (e.g. double exchange [8]) well described in the past, still constitute the fondamental points for any experimental or theoretical description of these systems.

The key mechanism for such striking properties is connected to the charge transfer induced by either stoichiometric defects (cation vacancies or varying oxygen content in, for instance, $RE_{1-\alpha}MnO_{3\pm\delta}$) or hole doping (thanks to the partial substitution of trivalent cations by divalent elements, as in $RE_{1-x}M_xMnO_3$). This mechanism induces, by electrical-charge equilibrium arguments, the transformation of Mn^{3+} ions into Mn^{4+}. An enormous amount of reports has dealt with cation-substituted systems, in which large-sized rare-earth elements (mainly La) have been partially replaced by large-sized alkaline-earth atoms (e.g. Ba, Sr). Less studied are the cases of small-sized atoms (for instance, RE = Gd, Er; M = Ca) in which, in addition to the steric effects, the intrinsic magnetism of the lanthanide atom may provoke interesting situations thanks to the competition of two magnetic sublattices [9].

On the other hand, very little is known about heavy rare-earth- or yttrium-based manganites in which a partial substitution at the B sublattice, that is, on the Mn site, has been carried out. It can be expected, for instance, that elements of lower valence than Mn^{3+} may also induce the formation of Mn^{4+} cations. The case of the Mn → Co substitution has been commonly reported [10,11], but almost no work (to our knowledge) has dealt with the Ni substitution [12]. The advantage of this latter ion over the former is its simplicity (Co^{3+} can adopt several spin states, t^6_{2g}, $t^5_{2g}e^1_g$, $t^4_{2g}e^2_g$, depending on its environment and/or temperature [13], while nickel usually adopts only one spin state, Ni^{2+}:d^8, $S = 1$). We herein report the effect of substitution of Mn^{3+} by Ni^{2+}

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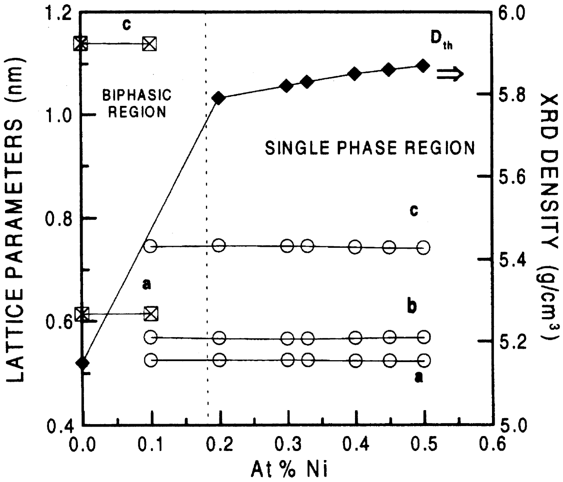

Fig. 1. Lattice parameters and weight density of the $YNi_xMn_{1-x}O_3$ solid solution as a function of the Ni concentration.

ions on the structure and on the electrical and magnetic properties of the Y-based manganite perovskite $YMnO_3$.

2. Experimental

Submicronic MnO, NiO and Y_2O_3 powders were used as raw materials to prepare the $YNi_xMn_{1-x}O_3$. The mixtures were homogenized by wet attrition milling before calcination for 2 h at 1000°C. Synthesis was achieved by repeated milling, compaction and heating at various temperatures and times. Optimum apparent density (of the order of 94–96% of the theoretical values) was obtained after 2 h sintering at 1325°C.

Lattice parameters were determined by X-ray diffraction (XRD) techniques using a D-5000 Siemens diffractometer. Samples whose compositions ranged between $YNi_{0.2}Mn_{0.8}O_3$ and $YNi_{0.5}Mn_{0.5}O_3$ were found to be monophased and indexed in an orthorhombic perovskite-like symmetry (space group *Pbmn*). For lower x(Ni) concentration, the orthorhombic phase coexisted with a hexagonal phase, while at larger x (above 50% Ni) the presence of unreacted Y_2O_3 indicated the limits of the solid solution. Fig. 1 shows the evolution of the lattice parameters and of the apparent density with the percentage of the Ni substitution. The single-phase region is thus bracketed by a lower boundary at $x(\mathrm{Ni}) \sim 0.2$ and an upper boundary at $x(\mathrm{Ni}) = 0.5$. Details of the crystallochemical properties of the $YNi_xMn_{1-x}O_3$ system can be found elsewhere [14].

Disk-shaped samples were painted with silver paste. The electrodes were sintered at 800°C, for 1 h. Two-points DC conductivity measurements were carried out at different temperatures, between 300 and 650 K, using a constant current DC power supply, model PS280 from Tektronix, and a Hewlett-Packard multimeter, model 44201A, with 1 μA DC current resolution. Activation energies were calculated from the corresponding Arrhenius plots.

Magnetic properties were measured in a SHE VTS 906 SQUID susceptometer between 5 and 300 K. In order to minimize demagnetizing factors, or at least, to have similar contributions, all pieces were cut in regular shapes from ceramic disks. These pieces were then glued to a thin rod in order to avoid misorientation due to torque forces exerted on the sample. All measurements were performed after cooling the samples in the absence of the magnetic field. Various techniques were then applied, including temperature cycles (ZFC/FC) under 50 and 2500 Oe, susceptibility measurements $\chi(T)$ under a 500 Oe external field, or magnetization loops $M(H)$ at 5 K with the field ranging from −50 up to +50 kOe.

3. Results and discussion

Table 1 gives the room-temperature conductivity values and the activation energies for the electrical conductivity of single-phase samples. Fig. 2 shows the σT versus $1/T$ curves.

According to the results depicted in Fig. 2, two features are noticeable: first, conductivity increase with the nickel concentration, from 20 to 33 at.% Ni and, secondly, its decrease for 40 and 45 at.% Ni. The reason for this behavior could be attributed to the nature of the substituting cations. Indeed, taking into account the XRD results discussed above, the Ni cations seem not to contribute to the controlled-valence conduction mechanism described by Verwey et al. [15], because of the absence of Ni ions with a different valence state (e.g. Ni^{3+}) in the nearest neighbor sites of a Ni^{2+} cation. As a consequence, the only cation pairs which contribute to the conduction mechanism are the Mn^{3+}–Mn^{4+} ones. It is easy to see that the amount of these possible pairs increases up to a concentration of 33 at.% Ni, a subsequent rise in the Ni percentage leading to a decrease in the possibility of forming pairs. Thus, it is possible to form 0.33 pairs per formula unit in the 33/67 composition, whereas it is possible to form only 0.2 pairs in the 40/60

Table 1
Electrical conductivity σ at 293 K and activation energy E_a for the $YNi_xMn_{1-x}O_3$ solid solution

x (Ni)	0.20	0.30	0.33	0.40	0.45	0.50
σ (S m^{-1})	3.05×10^{-2}	1.04×10^{-1}	5.79×10^{-1}	2.01×10^{-3}	1.37×10^{-4}	1.56×10^{-1}
E_a (eV)	0.30	0.24	0.28	0.32	0.50	0.13