The discovery of giant magneto-resistance in manganese oxides has resulted in a renewed interest in mixed-valence manganese perovskites over the last decades because of the many possible technological applications and the very interesting physics coming from the inter-relation between structural, magnetic and transport properties (1-3). Most of these works describe the physico-chemical properties of doped ABO$_3$ perovskites, where the A-site, occupied by a rare-earth element RE, is partially substituted by an alkaline-earth. It is also possible to partially substitute the B site occupied by the mixed-valent manganese, and thus create similar transformations in the Mn oxidation state (from Mn$^{4+}$ to Mn$^{3+}$), triggering the exchange interactions responsible of ferromagnetic order and its associated metal-insulator transition (4).

In recent years we have been studying the magnetic properties of several perovskites of formula RE(Mn,Me)O$_3$ in which the Mn atom has been substituted by a transition-metal element, like Cu, Ni or Co. Interesting results have been obtained, for instance, when the rare-earth element bears a high magnetic moment since it may interact with the ordered Mn-sublattice (5). As such, spectacular behaviours
MAGNETIC BEHAVIOR OF SOLID SOLUTIONS \( \text{REMe}_x\text{Mn}_{1-x}\text{O}_3 \), \( \text{RE} = \text{Y}, \text{La}, \text{Pr}, \text{Nd}, \text{Eu}, \text{Gd}, \text{Er}; \text{Me} = \text{Ni,Co} \)

have been observed by us in the case of \( \text{RE} = \text{Er} \), for which the magnetization loops present two important anomalies: a step-like transition and an intersection of the increasing and decreasing branches of the magnetization loops \( M(H) \) (6,7). These phenomena are especially evident at the particular composition \( \text{Co}:\text{Mn} = 1:1 \) (ErCo\(\text{sub} \)Mn\(\text{sub} \)O\(\text{sub} \)) where ferromagnetic Co\(\text{sup} \)-Mn\(\text{sup} \) interactions are maximized and for which a cation and charge ordering may be expected (8). It becomes then interesting to compare the magnetic behaviour of different rare-earth manganese perovskite at this particular composition since the rare-earth nature (ionic radius and intrinsic magnetic moment) should be a critical factor in setting different types of magnetic interactions. Several authors have examined these series, without going deeply into the magnetic ordering features (9,10).

So, in this work we compare a specific composition, for which the substitution rate was 1:1 between manganese and the transition metal Me. This latter was chosen to be Ni and Co, because different exchange interaction mechanisms were supposed to exist between Mn\(\text{sup} \) or Mn\(\text{sub} \) with respect to Ni\(\text{sup} \), Co\(\text{sup} \) or Co\(\text{sub} \). Results for various rare-earth elements (RE = Y, La, Pr, Nd, Eu, Gd and Er) are reported herein. Our main goal is to look at the influence of the rare-earth nature into the magnetic properties, which we expect to be strongly dependent on the concentration and the oxidation state of the transition metal substitute.

2. EXPERIMENTAL PROCEDURE

Solid solutions were prepared by classical solid state methods (except in the case of LaCo\(\text{sub} \)Mn\(\text{sub} \)O\(\text{sub} \)), for which soft chemistry techniques were applied (11), using submicronic powder oxides RE\(\text{sup} \)O\(\text{sup} \), MnO and Co\(\text{sup} \). The mixtures were mixed and homogenized by attrition milling with zirconia balls, using isopropanol as liquid medium, then calcined and re-milled three times to assure a total reaction. The thermal cycle consisted of a heating rate of 5 °C/min reaching the reaction temperature of 1150 °C, held for 6 h and then cooled at 1 °C/min. Sintering was usually performed under oxygen atmosphere; in this way, Co\(\text{sup} \) and Ni\(\text{sup} \) ions may coexist in the system, together with Mn\(\text{sub} \) (13).

Magnetic measurements were performed in a Quantum Design MPMS-XL5 SQUID susceptometer, between 2 K and 300 K and as a function of the applied field, from -50 kOe up to +50 kOe. All measurements were done in specimens cut from ceramic bulks and glued to calibrated gelatin sample holder, thus avoiding any disorientation due to torque forces exerted on the sample. The ordered regime was investigated by performing magnetization cycles as a function of temperature (ZFC/FC cycles) and applied fields (magnetization loops at 2 K).

3. RESULTS AND DISCUSSION

3.1. Light rare-earth elements

Typical examples of ZFC/FC cycles for \( \text{REMe}_x\text{Mn}_{1-x}\text{O}_3 \), (Me = Ni and Co) are shown on figure 1, in the case of light rare-earth elements, like yttrium or neodymium. Several features can be remarked. Firstly, there is an obvious dependence of the ordering temperature \( T_O \) with the RE\(\text{sup} \) ionic radii, varying from approximately 85 K up to 170 K when \( r_\text{y} \) = 1.019 Å and \( r_\text{Nd} \) = 1.109 Å, respectively (14). This behavior is well known in the series (RE,Ca)MnO\(\text{sub} \), as it is directly related with the deformation of the perovskite lattice by varying-size lanthanide elements situated at the A site of the ABO\(\text{sub} \) structure (15).

The second feature to be remarked is the qualitatively different behavior for cobalt-substituted or nickel-substituted solid solutions. In the first case, the ZFC procedure (that is, when warming the sample under a low applied field, after being cooled under zero field) leads to a rather sharp peak, characteristic of canted-type antiferromagnetism (16). In the second case, the ZFC section is characterized by a broad plateau collapsing at the transition temperature \( T_O \); this different behavior was also observed in a.c. susceptibility measurements in the case of Y(Me,Mn)O\(\text{sub} \) (Me=Ni,Co) (17) and seems to be a characteristic feature closely connected to the different nature of the ferromagnetic interactions between Co\(\text{sup} \) and Mn\(\text{sub} \), from one side, and Ni\(\text{sup} \) and Mn\(\text{sub} \), on the other side.

A third feature which should be remarked in figure 1, since it appears systematically in other examples of these two families, is the fact that nickel-based compounds show an abrupt variation of both ZFC and FC modes at low temperatures, while the cobalt-based compounds have their FC magnetization continuously increasing (or reaching a constant value) when decreasing the temperature. This abrupt change at low temperature should not be associated to any antiferromagnetic exchange interaction between sublattices, as we shall discuss below for heavy rare-earth elements, since it also occurs for non magnetic yttrium (fig. 1, left-hand panel).

Such a break may be associated to antiferromagnetic interactions within the Mn/Ni lattice, as observed by neutron diffraction measurements performed in YNi\(\text{sub} \)Mn\(\text{sub} \)O\(\text{sub} \) (8). On the other hand, the general behavior observed in the cobalt-based systems, as shown in figure 1 for the case of Y and...
Nd, is confirmed in figure 2 for RE = La and Pr. Here again, large T values are due to the fact that ionic radii for these elements are rather high (1.160 and 1.126 Å, respectively). The ZFC magnetization shows a well defined peak, while the FC magnetization keeps increasing when decreasing the temperature, suggesting strong ferromagnetic Co\textsuperscript{2+}-Mn\textsuperscript{4+} interactions.

In the case of nickel, a strong antiferromagnetic component (fig. 3), differs quite significantly from its cobalt counterpart. The ZFC magnetization shows a well defined peak, while the FC magnetization keeps increasing when decreasing the temperature, suggesting strong ferromagnetic Co\textsuperscript{2+}-Mn\textsuperscript{4+} interactions.

The ferromagnetic nature of the RECo\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} compounds is confirmed by the magnetization loops performed at 2 K, for varying applied fields between -50 kOe and +50 kOe. Figure 3 shows the cases of NdCo\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} (right-hand panel), while inserts of figure 2 show the cases of LaCo\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3} and PrCo\textsubscript{0.5}Mn\textsubscript{0.5}O\textsubscript{3}. High coercive fields are observed in all these cases, typical of hard ferromagnets close to an ideal squared-shape hysteresis. On the contrary, large T\textsubscript{c} values are due to the fact that ionic radii for these elements are rather high (1.160 and 1.126 Å, respectively).

The light rare-earth elements discussed above, producing a strong lattice distortion and a net deviation of the Mn\textsuperscript{4+}-O-Mn\textsuperscript{4+} superexchange angle from the ideal value of 180° expected for non distorted perovskites; as a consequence, the ordering temperature T\textsubscript{o} is much lower, compared to the examples reported in §3.1. Secondly, most of the heavy rare-earth elements (with the exception of non-magnetic lutetium, or mixed-valents Tm or Yb) have strong magnetic moments, much higher than those due to the transition metal network composed of (Ni+Mn) or (Co+Mn). Under such consideration, an exchange interaction may occur between two magnetic networks, the one due to the rare-earth element and the one due to the ferromagnetic Mn\textsuperscript{4+} network.

3.2. Heavy rare-earth elements

When dealing with heavy rare-earth elements, two major modifications occur. Firstly, due to the well-known lanthanide contraction, their ionic radii are small compared to those of the light rare-earth elements discussed above, producing a strong lattice distortion and a net deviation of the Mn\textsuperscript{4+}-O-Mn\textsuperscript{4+} superexchange angle from the ideal value of 180° expected for non distorted perovskites; as a consequence, the ordering temperature T\textsubscript{o} is much lower, compared to the examples reported in §3.1. Secondly, most of the heavy rare-earth elements (with the exception of non-magnetic lutetium, or mixed-valents Tm or Yb) have strong magnetic moments, much higher than those due to the transition metal network composed of (Ni+Mn) or (Co+Mn). Under such consideration, an exchange interaction may occur between two magnetic networks, the one due to the rare-earth element and the one due to the ferromagnetic Mn\textsuperscript{4+} network.
Magnetic behavior of solid solutions $\text{RE}_x\text{Mn}_{3-x}\text{O}_3$, RE = Y, La, Pr, Nd, Eu, Gd, Er; Me = Ni, Co

sublattice. If the temperature is sufficiently low, then the rare-earth contribution (which varies as $T^1$ because of the non-coherent behavior of their spins) will overcome the constant contribution of the ordered $|\text{Mn} + \text{Co}|$ sublattice and, because of the negative exchange (that is, moments pointing in opposite direction), the total moment will start to decrease, reaching a compensation temperature (when $M_{\text{comp}} = -M_{\text{Co+Mn}}$) and becoming negative at still lower temperatures.

In this system (24) lead us to conclude that the high-field jump is deserved to the ErCo$_{0.50}$Mn$_{0.50}$O$_3$ material, for which a step-like transition at high fields due to a reorientation of magnetic domains, and an intersection of the increasing and decreasing branches, were observed.

4. CONCLUSION

As a general conclusion, we might say that nickel-based and cobalt-based systems behave differently with respect to the ZFC/FC and the magnetization cycles. Strong ferromagnetic Ni$^2+$-Mn$^4+$ interactions are observed in all compounds studied in this work, characterized by a flat plateau of large absolute value during the initial warming of the zero-field-cooled process. During the field-cooled process, a sharp decrease of $M^c$ is usually observed due to antiferromagnetic interactions within the transition metal lattice (observed for non-magnetic Y and La and low-magnetic Nd and Eu). The cobalt-based samples show a steady increase of $M^c$ when cooling, if the rare-earth is a light element.

Quite different results were obtained in the case of heavy rare-earths bearing a large magnetic moment, such as Gd and Er. In this case, a significant inter-sublattice interaction exchange interaction of antiferromagnetic nature between two magnetic sublattices (RE and |Co+Mn|) leads to a reversal of the total magnetic moment, as if the system was of ferrimagnetic type.

Magnetization loops also show different behaviors depending if the transition metal substitute is nickel or cobalt. For all nickel-based compounds studied in this work, an antiferromagnetic-like variation predominates over small ferromagnetic loops. On the contrary, cobalt-based samples show much larger coercive fields, as if the Co$^2+$-Mn$^{4+}$ interactions were much stronger than the Ni$^2+$-Mn$^{4+}$ ones. Special mention is deserved to the ErCo$_{0.50}$Mn$_{0.50}$O$_3$ material, for which a step-like transition at high fields due to a reorientation of magnetic domains, and an intersection of the increasing and decreasing branches, were observed.

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