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Magnetic properties of Er(Co, Mn)O_3 perovskites

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Abstract

The erbium-based manganite $ErMnO_3$ has been partially substituted at the manganese site by Co in the general formula $ErCo_xMn_{1-x}O_3$. The perovskite orthorhombic structure is found from $x(Co) = 0.3$ up to $x(Co) = 0.7$, provided that the synthesis is performed under oxygenation conditions to favour the presence of Co^{3+}. Magnetic properties show unusual phenomena, correlated with the presence of different magnetic entities (i.e., Er^{3+}, Co^{2+}, Co^{3+}, Mn^{3+}, Mn^{4+}): the overall magnetic moment reverses its sign when the sample is cooled under an external magnetic field, while the magnetization loops performed at $T < 4$ K show intersecting branches at low fields and a sudden jump at high fields. A phenomenological model of two interacting sublattices, coupled by an antiferromagnetic exchange interaction, explains the inversion of the overall spin, while the high-field discontinuity is explained in terms of dynamical models.

Keywords: Magnetic properties; Transition-metal oxides; Perovskites; Spin reversal

The discovery of giant magneto-resistance in rare-earth manganese oxides $REMnO_3$ of perovskite structure has resulted in a renewed interest in mixed-valence perovskites over the last decade.[1] Most works deal with the substitution of the rare-earth by an alkaline-earth Æ ($RE_{1-x}Æ_xMnO_3$) and mainly concern light rare-earth elements. Less known are the substitutions at the manganese site $REMe_xMn_{1-x}O_3$, where Me^{2+} is a divalent transition metal. In both kinds of substitutions, a transformation of Mn^{3+} into Mn^{4+} takes place, induced by the charge transfer provoked by hole doping. The electrical and magnetic properties are closely related to the quantity of Mn^{3+} and Mn^{4+} since double-exchange mechanisms will be operated through the oxygen orbital.[2] If, on the other hand, manganese is partially replaced by trivalent elements, no ferromagnetic interactions are expected, since manganese stays always at its 3+ oxidation state.

In this work, we present an interesting case of partial substitution in a rare-earth based perovskite $ErCo_xMn_{1-x}O_3$. Manganese is initially substituted by divalent cobalt, Co^{2+}, up to a maximum limit of 50 at%; at this point, charge equilibrium is $Er^{3+}Co_{0.50}{}^{2+}Mn_{0.50}{}^{4+}O_3{}^{2-}$. At higher contents of cobalt and under special conditions of sintering (i.e., oxygen flow at 1523 K over not very dense samples) presence of Co^{3+} is favoured, and the solid solution may attain higher values of x(Co).[3,4] Structural and magnetic properties are presented herein for the $ErCo_xMn_{1-x}O_3$ solid solution ($0.3 \le x \le 0.7$), paying special attention to the particular case $ErCo_{0.50}Mn_{0.50}O_3$, for which spectacular results on the magnetization loops at low temperatures were observed.

The samples were prepared by solid state synthesis from submicronic powder oxides Er_2O_3, MnO and Co_3O_4. The mixtures were attrition milled using isopropanol as liquid medium, calcined at 1423 K for 6 h and re-milled three times to assure a total reaction. The submicronic resulting powder was uniaxially pressed and sintered for 2 h under O_2 atmosphere at a sintering temperature of 1523 K, for which the shrinkage rate is not so high and ensures a good equilibrium between the ceramic grains and the environmental oxygen atmosphere. Samples were then slowly cooled at −1 K/min. Samples from $x(Co) = 0.30$ up to 0.70 showed a perovskite orthorhombic structure, space group *Pbnm,* while the non-substituted $ErMnO_3$ crystallizes in an hexagonal symmetry and therefore it is not presented in this work. In Table 1, it can be noticed that the c-parameter varies non-monotonically, increasing when x(Co) goes from 0.30 up to 0.50 and decreasing afterwards. These results, which are detailed elsewhere, can be understood in terms of the possible valence states for cobalt: during the first half of the substitution, Co^{2+}, of larger radius, substitutes Mn^{3+}, of smaller radius. When all manganese is converted into Mn^{4+} then Co^{3+}, of lower ionic radius,

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Table 1
Structural and magnetic data for the solid solution $ErCo_xMn_{1-x}O_3$

x(Co)	$a \pm 0.0001$ (nm)	$b \pm 0.0001$ (nm)	$c \pm 0.0001$ (nm)	T_c (K) ± 3	Θ (K)	μ_{eff} (μB) ± 0.15
0.30	0.5216	0.5636	0.7450	55	−4.5 ± 1	10.52
0.40	0.5222	0.5625	0.7456	62	+5 ± 2	10.26
0.50	0.5214	0.5588	0.7461	68	+13 ± 1	10.14
0.60	0.5196	0.5545	0.7441	68	+10 ± 1	10.16
0.70	0.5183	0.5527	0.7424	67	+1.3 ± 0.5	10.19

is incorporated into the structure, producing a decrease of the *c*-parameter. This mechanism is extremely important since it explains most of the magnetic properties discussed in this work.

The paramagnetic state is well described by a Curie–Weiss law in the temperature range $T > 1.5T_c$, with a magnetic moment which decreases from $x(\text{Co}) = 0.30$ to $x(\text{Co}) = 0.50$, slightly increasing afterwards (Table 1), in agreement with the occurrence of Co^{3+} ions once all Mn is converted into Mn^{4+}. The ordering temperature T_c, defined as the lowest temperature of the reversible paramagnetic state (see below), stays relatively constant (between 55 and 68 K), indicating that the ferromagnetic mechanism is somewhat optimized along the whole series. On the other hand, the Weiss temperature Θ shows a pronounced positive maximum at $x(\text{Co}) = 0.50$, with a tendency toward negative values at both ends of the series. This is the manifestation that antiferromagnetic and ferromagnetic interactions coexist in the system.

The ordered regime was first studied by ZFC/FC cycles at low applied fields. Fig. 1 shows the sample $ErCo_{0.30}Mn_{0.70}O_3$ compared to an yttrium-based sample of equivalent composition reported by us in previous works.[5] It can be noticed that the ZFC process presents similar shapes in both compounds, except for the visible decrease at low temperatures in the erbium-based sample due to a Curie–Weiss dependence ($\chi_{Er}(T) \sim T^{-1}$) of non-correlated erbium moments. The overall behaviour can be described by the usual antiferromagnetic spin-canted mechanism describing the manganites perovskites, that is, antiferromagnetic inter-plane interactions with ferromagnetic in-plane exchange interactions.[6] However, it should be remarked that the peak's amplitude is higher for the yttrium based sample, despite the fact that yttrium is a non-magnetic lanthanide and Ni^{2+} has a lower moment than Co^{2+}. This fact means that other mechanisms, besides a ferromagnetic double-exchange interaction Mn^{3+}–O–Mn^{4+} must to be taken into account. Such a mechanism is well seen in the FC process, as discussed below.

During the FC branch (that is, cooling the sample under the same applied field as before), samples of the erbium-based solid solution follow the reversible paramagnetic state till the ordering temperature T_c ($T_c = T_{rev}$). At $T < T_c$, the magnetization increases abruptly and reaches a maximum at T_{max}; at further cooling, the magnetization decreases until $T = T_{comp}$, where it is equal to zero. Below T_{comp}, the magnetization shows negative values for almost all samples of the $ErCo_xMn_{1-x}O_3$ series (Fig. 2). This procedure has been interpreted by us[7] and other authors[8] as two interacting sublattices, coupled by an antiferromagnetic exchange interaction. In this model, the ferromagnetic transition-metal lattice, which orders at T_c, creates a strong local field at the erbium site, polarizing the Er moments in a direction opposite to the applied field. At low temperatures, when the contribution of the paramagnetic erbium sublattice, which varies as T^{-1}, gets larger than the ferromagnetic contribution, the total magnetic moment changes its sign, leading to an overall ferrimagnetic state. In other words, the resulting magnetization will be the superposition of both

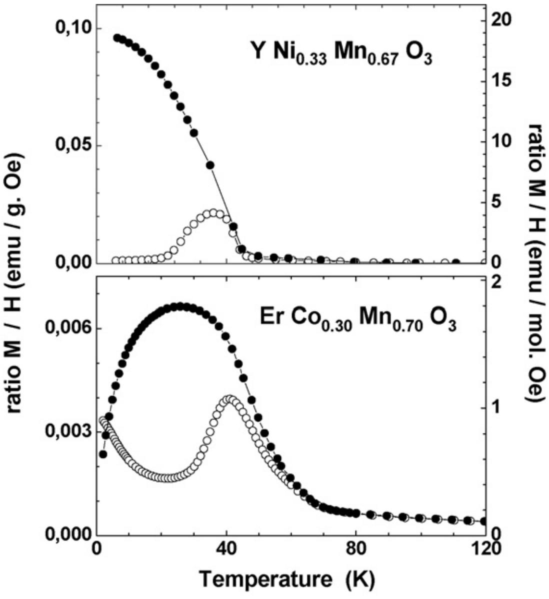

Fig. 1. ZFC (open symbols)/FC (closed symbols) cycles for $YNi_{0.33}Mn_{0.67}O_3$[5] and $ErCo_{0.30}Mn_{0.70}O_3$.

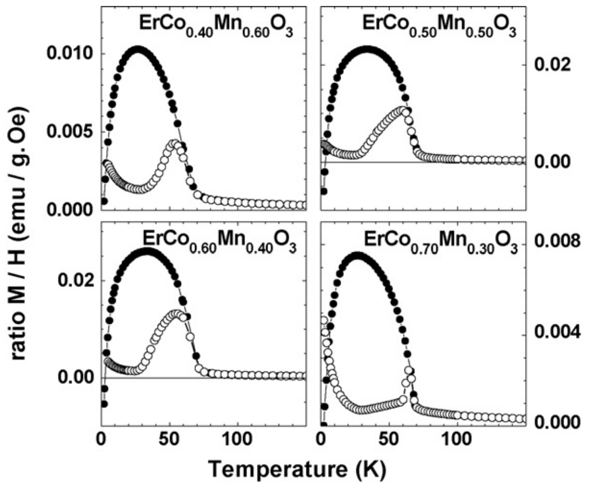

Fig. 2. ZFC/FC cycles for given samples of $ErCo_{1-x}Mn_xO_3$, measured under 50 Oe.

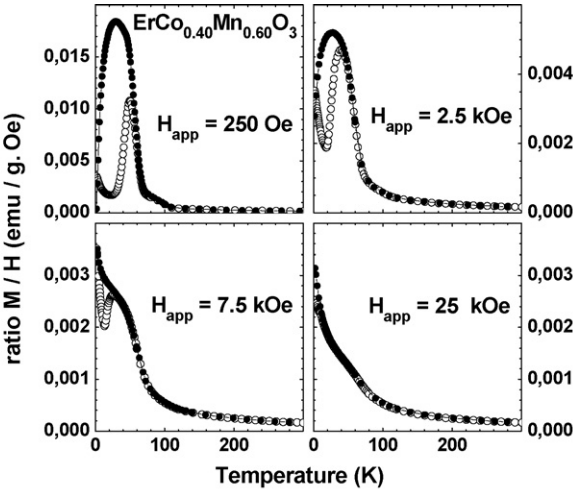

Fig. 3. ZFC/FC cycles for $ErCo_{0.40}Mn_{0.60}O_3$, measured under different applied fields.

sublattices' magnetization, and their relative weight will depend on their thermal behaviour and on their field dependence. Fig. 3 shows, for instance, the spin reversal phenomenon and its evolution with the applied magnetic field. It is immediately seen that the erbium contribution becomes progressively predominant over the magnetization of the transition-metal sublattice due to a re-orientation of the erbium moments under the influence of the increasing applied field.

The magnetic-field dependence of the overall magnetization shows quite interesting features, related to the spin reversal phenomenon and to a sudden re-orientation of ferromagnetic domains. Fig. 4 shows the magnetization loop performed at 2 K for a sample of composition $ErCo_{0.50}Mn_{0.50}O_3$. Two anomalies were identified: at low fields, the increasing and decreasing branches of the magnetization loop intersect (upper inset) while a sudden jump of the magnetization is observed at high fields (lower inset). The low-field anomaly is clearly related to the inversion of the magnetic moment with temperature since it disappears above the compensation temperature of 3.9 K, when both branches approach to each other but do not intersect.[9,10]

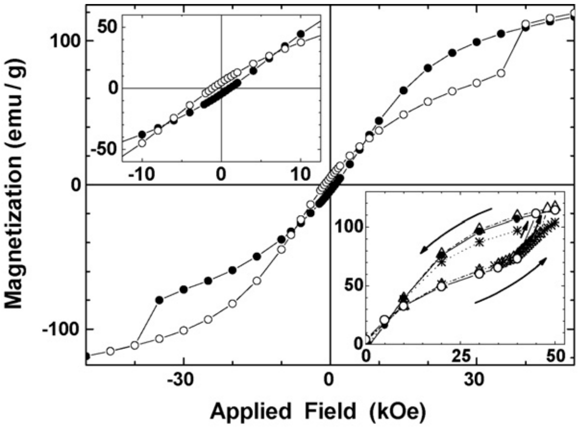

Fig. 4. Magnetization loop performed at 2 K for $ErCo_{0.50}Mn_{0.50}O_3$. Upper left inset: low field data. Lower right inset: high field data showing the magnetization at different field-sweep rates (see text).

The high field anomaly seems to be a dynamical phenomenon, which depends on the sweep rate of the applied field. Other authors have reported similar sweep rate dependence in related systems, which was attributed to a subtle balance between the elastic energy associated with the strains created at the AF/FM interfaces and the magnetic energy due to the development of the ferromagnetic phase.[11] In our case, large changes in the applied field (typically by steps of 5 kOe, which we estimate to a sweep rate of 0.2 T/min) lead to a sudden jump in the magnetization (main frame in Fig. 4 and open and closed circles in the lower inset); when data were taken at a lower rate (ΔH of 0.5 or 1 kOe) the magnetization curve changed smoothly, showing just an inflexion point at high fields (stars symbols). Finally, if the magnetic field was swept at an intermediate rate ($\Delta H \sim 2$ kOe), a clear and definite jump occurred, but at a slightly higher critical field than before (open triangles). Phase separation seems to be at the origin of such dynamical phenomena,[12] so present work is now aimed towards getting reliable data as a function of a well-controlled sweep rate.

The ordered state also depends on the annealing conditions. As stated before, an oxygen flow at 1523 K favours the formation of Co^{3+} ions, which may interact with the other magnetic entities in the lattice Er^{3+}, Mn^{3+}, Mn^{4+} or Co^{2+}. Such a case is seen in Fig. 5, which shows an $ErCo_{0.40}Mn_{0.60}O_3$ sample treated under normal air conditions (upper panel) and under oxygen flow (lower panel). The spin reversal phenomenon occurs in both cases, although it is better seen in the oxygen-treated sample for which no apparent changes in the lattice parameter were observed with respect to the air-annealed sample. However, the magnetization jump at high fields is absent in the air-treated sam-

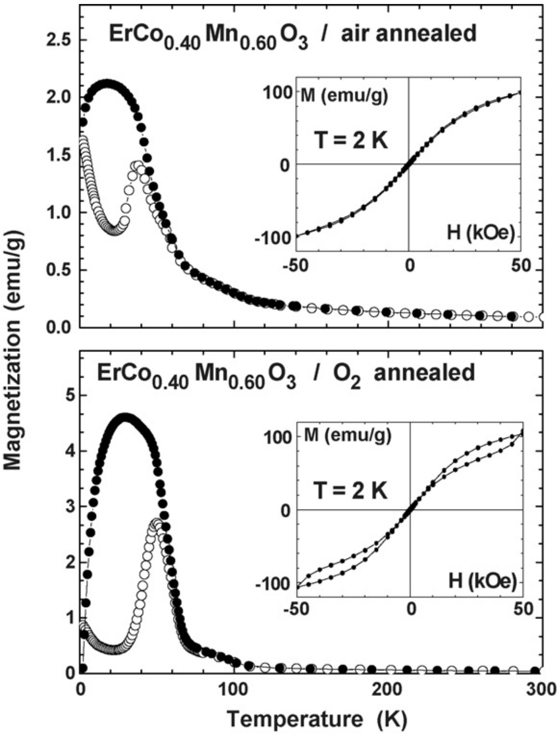

Fig. 5. Effect of annealing on the magnetization of $ErCo_{0.40}Mn_{0.60}O_3$. Insets show the magnetization loops performed at 2 K.

ple, meaning that presence of Co^{3+} is an essential factor in the dynamical interactions between the sublattices. It is quite possible that small quantities of Co^{3+} in the structure play a determinant role in the phase separation observed in these materials.

In conclusion, the phenomenon of spin reversal described in this work results from three basic ingredients: a “frozen” ferromagnetic state due to the transition-metal sublattice, paramagnetic independent Er spins with a magnetization proportional to $1/T$, and finally, a negative exchange interaction between these two networks. The relative importance of both sublattices will evolve with varying temperature, reaching a point where they are fully compensated (crossing the $Y = 0$ axis), and becoming negative if the rare-earth moment is sufficiently large compared to the transition-metal moments. The $ErCo_xMn_{1-x}O_3$ series constitutes a surprisingly rich model system, in which several magnetic entities coexist. The magnetization loops performed at low temperatures showed two important anomalies: at low fields, the intersection of the magnetization branches, which is intimately connected with the spin reversal phenomenon, and at high fields, a dynamic magnetization jump which depends on the sweep rate of the applied external field.

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