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Magnetic ordering in perovskites containing manganese and cobalt

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Abstract. The magnetization measurement of systems with the nominal formula $R(Mn_{1-x}Co_x)O_3$ (R = Eu, Gd, Tb, Y) has been made. It has been found that $EuMnO_3$ and $GdMnO_3$ are weak ferromagnets of Dzialoshinsky–Moriya type whereas $TbMnO_3$ is an antiferromagnet. The substitution of manganese ions by cobalt ones leads to the appearance of different magnetic states: cluster-spin-glass-like ($0.1 \leqslant x \leqslant 0.3$), inhomogeneous ferromagnets with well defined Curie temperatures ($0.4 \leqslant x \leqslant 0.8$) and again a spin glass state ($x \geqslant 0.9$). Spontaneous magnetizations and Curie temperatures reach maxima for compounds with $x = 0.5$. External magnetic field induces a metamagnetic transition in $R(Mn_{0.5}Co_{0.5})O_3$ (R = Gd, Tb, Y). The transition becomes irreversible at low temperature in the Tb- and Y-based compounds. The annealing in vacuum of $R(Mn_{0.5}Co_{0.5})O_3$ leads to the increase of the Curie temperature and to the appearance of a metamagnetic transition for the $Eu(Mn_{0.5}Co_{0.5})O_3$ compound. The metamagnetic behaviour is interpreted taking into account the ionic ordering of Co^{2+} and Mn^{4+} ions and possible 3d-orbital ordering in the Co^{2+} sublattice.

1. Introduction

Goodenough *et al* have reported that ternary oxides $La(Mn_{0.5}Me_{0.5})O_3$ (Me = Ni, Co) with a cubic perovskite structure are ferromagnets [1]. Blasse has suggested the ferromagnetism to be governed by the positive superexchange interaction between Co^{2+} and Mn^{4+} ions via oxygen [2]. The Ni^{2+} (Co^{2+}) and Mn^{4+} ions in samples prepared at low temperature are crystallographically ordered to a considerable extent, making up the rock-salt type lattice [2]. This model was supported by the results of NMR measurements [3, 4]. Recently the $R(Mn_{0.5}Co_{0.5})O_3$ (R = Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho) compounds have been obtained using a conventional ceramic method [5]. These compounds were found to be ferromagnets with relatively high Curie temperature and spontaneous magnetization. The $R(Mn_{0.5}Co_{0.5})O_3$ (R = Tb, Y) exhibit metamagnetic behaviour at around T_C [5]. The origin of metamagnetism was not established in these studies.

For better understanding of the magnetic properties of the perovskites containing manganese and cobalt ions we have prepared $R(Mn_{1-x}Co_x)O_3$ (R = Eu, Gd, Tb) solid solutions and investigated their magnetic properties in a wide range of magnetic fields and temperatures. The results are reported here.

2. Experimental details

Ceramic samples $R(Mn_{1-x}Co_x)O_3$ were prepared by a solid state reaction of precursor oxides. A final sintering process step was carried out at 1620 ($0.7 \leqslant x \leqslant 0.9$) or 1690 K ($0 \leqslant x \leqslant 0.6$) in air. All the samples were cooled slowly (100 K h^{-1}) with a furnace. The $EuMnO_{3+\gamma}$ and $GdMnO_{3+\gamma}$ were reduced in a quartz tube at 1070 K using metallic tantalum as a getter. The decreasing weight of samples after reducing corresponds to the loss of oxygen content (approximately 0.4%). The as-prepared materials were characterized by x-ray diffraction using Co Kα radiation and found to be single phase. The x-ray diffraction lines were indexed on the base of an orthorhombic perovskite pseudocell. For $GdMnO_{3+\gamma}$ and $EuMnO_{3+\gamma}$ the oxygen content was determined by chromatometric titration. The chemical analysis of the Co-containing samples was not performed; therefore the denoted compositions are the nominal ones.

Magnetization measurement was performed with a vibrating sample magnetometer in steady magnetic field up to 120 kOe.

3. Results and discussion

3.1. Magnetic properties of $Eu(Mn_{1-x}Co_x)O_3$

The $EuMnO_{2.99}$ composition is characterized by a spontaneous magnetization of 1.5 emu g^{-1} at 4.2 K and a well defined Néel temperature of 49 K (figure 1). Enhancement of the oxygen content leads to decreasing Néel temperature and negligibly increasing spontaneous magnetization. After field cooling down to 4.2 K magnetic moments start to reorient in an external magnetic field of 30 kOe (figure 2). The field 60 kOe is too low to complete the full reorientation of magnetic moments. It is apparently due to a large magnetic anisotropy.

The spontaneous magnetization of $Eu(Mn_{0.9}Co_{0.1})O_3$ and $Eu(Mn_{0.75}Co_{0.25})O_3$ is very small and transition into the paramagnetic state occurs in a wide temperature range, indicating the cluster spin glass behaviour (figure 3). This feature is in contrast to the case of $x = 0.5$ and $x = 0.7$ compounds for which well defined Curie temperatures exist at 123 K (figure 3). Further decreasing the Mn content leads to the fall of spontaneous magnetization and of the temperature of transition into the paramagnetic state. For $x = 0.9$ composition the long-range magnetic order seems to be destroyed. The spontaneous magnetization reaches a maximum for $x = 0.5$ composition. The magnetization of the $x = 0.5$ sample is not saturated completely in a magnetic field of 120 kOe at 4.2 K, which is much lower than the Curie temperature, 123 K (figures 2 and 3).

Decreasing oxygen content in the $Eu(Mn_{0.5}Co_{0.5})O_3$ nominal composition leads to increasing Curie temperature, to decreasing residual magnetization and to the appearance of the peak of the field-cooled magnetization at around T_c in the magnetic field above 0.5 kOe (figures 3 and 4).

3.2. Magnetic properties of $Gd(Mn_{1-x}Co_x)O_3$

The temperature dependence of the magnetization of $GdMnO_{2.99}$ in an applied magnetic field of $H = 1$ kOe and the field dependence of the magnetization at 2 K are shown in figures 1 and 5 respectively. The magnetization of the sample with $x = 0$ exhibits a sharp peak at around 6 K on cooling. The spontaneous magnetization appears at 25 K, which is slightly lower than the Néel temperature $T_N = 40$ K of the $YMnO_3$ antiferromagnet [7]. As one can see from figure 5 the $GdMnO_{2.99}$ exhibits a metamagnetic transition at around 5 kOe at 2 K.

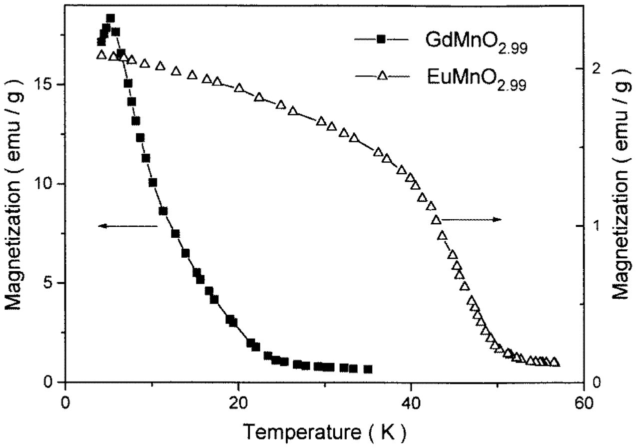

Figure 1. Magnetization against temperature for $EuMnO_{2.99}$ and $GdMnO_{2.99}$ measured at $H = 1$ kOe on cooling.

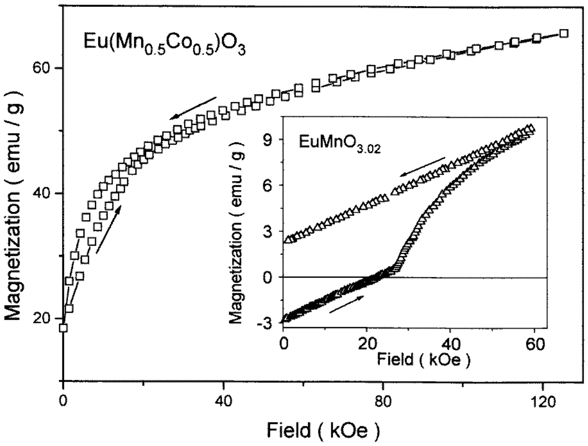

Figure 2. Field dependences of the magnetization of $Eu(Mn_{0.5}Co_{0.5})O_3$ and $EuMnO_{3.02}$ (inset) at 4.2 K measured after field cooling in $H = 1$ kOe.

The temperature dependences of the residual magnetization of $Gd(Mn_{1-x}Co_x)O_3$ measured at $H = 0$ after cooling in the field $H = 1$ kOe are presented in figure 6. There are no sharp transitions into the paramagnetic state for $Gd(Mn_{0.9}Co_{0.1})O_3$ and $Gd(Mn_{0.75}Co_{0.25})O_3$ compositions. This is apparently due to the formation of clusters with a different magnetic state in these compounds. The residual magnetization of $Gd(Mn_{0.75}Co_{0.25})O_3$ and $Gd(Mn_{0.5}Co_{0.5})O_3$ increases strongly with increasing temperature. This feature may be ascribed to the Gd-sublattice contribution. Apparently the f–d exchange interaction modifies the magnetic state of the 3d sublattice. The negative value of residual magnetization at low temperature arises from Gd magnetic moment ordering. Such a behaviour indicates the negative total f–d superexchange and large magnetic anisotropy. The magnetic moment of Gd ions is opposite to the total magnetic moment of the 3d sublattice. The compositions with $0.4 \leqslant x \leqslant 0.7$ exhibit sharp transitions into the paramagnetic state.

The magnetic field 120 kOe at 4.2 K is too low to saturate the magnetization of $Gd(Mn_{0.5}Co_{0.5})O_3$ (figure 7(a)). It is important to note that the hysteresis in the high-

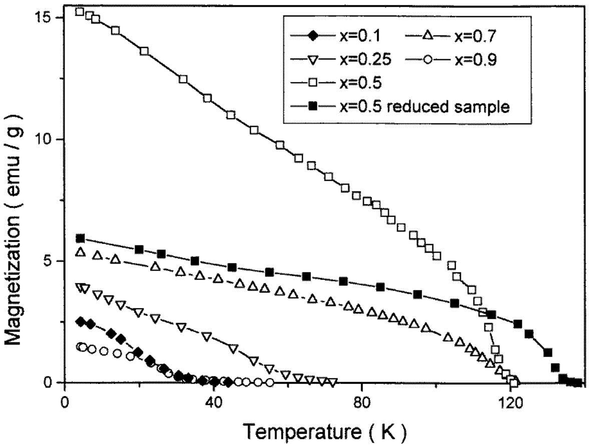

Figure 3. Temperature dependences of the residual magnetization of Eu($Mn_{1-x}Co_x$)O_3 measured at $H = 0$ after cooling in the field $H = 1$ kOe.

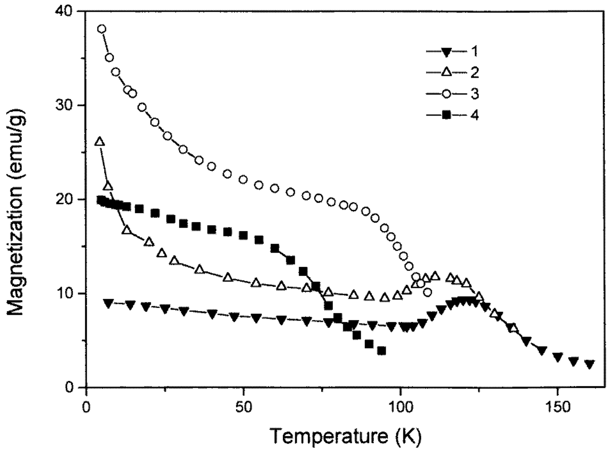

Figure 4. Field-cooled magnetization at $H = 10.9$ kOe of Eu($Mn_{0.5}Co_{0.5}$)O_3 (reduced samples—1), Gd($Mn_{0.5}Co_{0.5}$)O_3 (reduced samples—2); Tb($Mn_{0.5}Co_{0.5}$)O_3 (3) and Y($Mn_{0.5}Co_{0.5}$)O_3 (4).

field regime is much larger than that at low fields. With increasing temperature the critical fields decrease and metamagnetic behaviour becomes more pronounced (figure 7). We did not observe metamagnetism for Gd($Mn_{1-x}Co_x$)O_3 with $x = 0.4$, 0.6 and 0.7 in the whole 4.2–130 K range (figure 6). The annealing of Gd($Mn_{0.5}Co_{0.5}$)O_3 nominal composition in the vacuum leads to the increase of Curie temperature from 115 to 130 K (figure 6).

3.3. Magnetic properties of Tb($Mn_{1-x}Co_x$)O_3 and Y($Mn_{0.5}Co_{0.5}$)O_3

There is no spontaneous magnetization in the temperature range 2–40 K for $TbMnO_3$ nominal composition. Magnetization–temperature curves have maximum at around 6 K apparently due to the Tb-sublattice antiferromagnetic ordering.

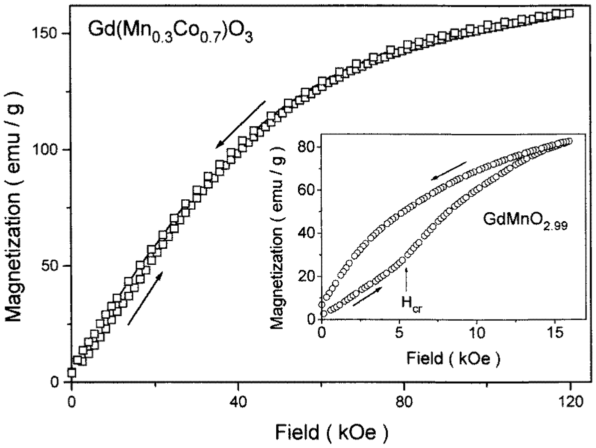

Figure 5. Field dependences of the magnetization of $GdMnO_{2.99}$ at 2 K (inset) and $Gd(Mn_{0.3}Co_{0.7})O_3$ at 4.2 K.

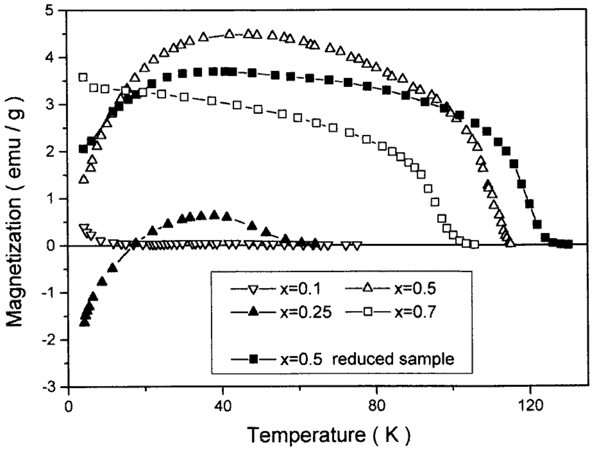

Figure 6. Temperature dependences of the residual magnetization of $Gd(Mn_{1-x}Co_x)O_3$ measured at $H = 0$ after cooling in the field 1 kOe.

The substitution of Mn ions by Co ones leads to the appearance of the spontaneous magnetization. The residual magnetization of $Tb(Mn_{0.75}Co_{0.25})O_3$ increases strongly with increasing temperature whereas that of $Tb(Mn_{0.5}Co_{0.5})O_3$ has a minimum at approximately 7 K (figure 8). Further increasing the Co content leads to decreasing Curie temperature and magnetization.

The field dependences of the magnetization of $Tb(Mn_{0.5}Co_{0.5})O_3$ at 4.2 and 50 K are shown in figure 9. After field cooling in $H = 1$ kOe the $M(H)$ dependences at 4.2 K show large hysteresis associated with metamagnetic behaviour. The second cycle of the measurement coincides with the first part of the cycle obtained by decreasing magnetic field. After the first measurement cycle the field-induced phase becomes stable at $H = 0$ (figure 9). We did not observe any decay of the field-induced magnetic phase during 1 h at 4.2 K. The metamagnetic transition is reversible at temperatures above 20 K as clearly seen

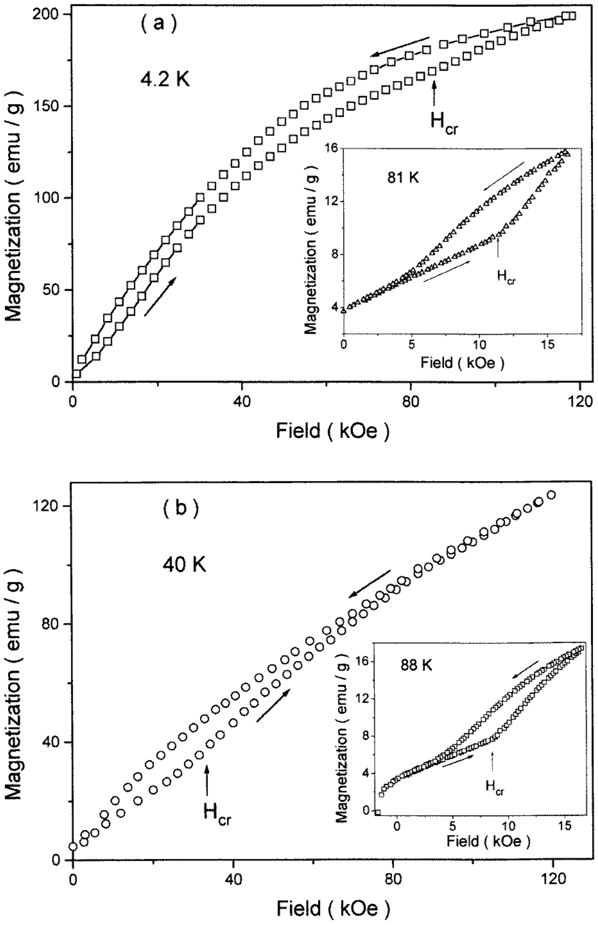

Figure 7. Field dependences of the magnetization of $Gd(Mn_{0.5}Co_{0.5})O_3$ at different temperatures.

from inset to figure 9. The field-induced phase can be stabilized on cooling in magnetic fields above 7 kOe (figures 4 and 10). Fields below 6 kOe are not sufficient to stabilize the field-induced phase at low temperatures (figure 10). The transition between the two phases is accompanied by a large temperature hysteresis indicating a first-order phase transition (figure 10). The field-induced phase transforms gradually into the low-field phase on heating at $H = 0$ (figure 11). The field $H = 10.9$ kOe is too low to stabilize the magnetic-field induced phases in the $Eu(Mn_{0.5}Co_{0.5})O_3$ and $Gd(Mn_{0.5}Co_{0.5})O_3$ reduced samples (figure 4). The $Y(Mn_{0.5}Co_{0.5})O_3$ sample exhibits the same behaviour as $Tb(Mn_{0.5}Co_{0.5})O_3$ (figures 4 and 11).

3.4. Discussion

The magnetic properties of $R(Mn_{1-x}Co_x)O_3$ solid solutions are governed by magnetic interactions between different magnetic ions. The most important interactions are antiferromagnetic Mn^{3+}–O–Mn^{3+}, Co^{2+}–O–Co^{2+} and Mn^{4+}–O–Mn^{4+} and ferromagnetic Co^{2+}–O–Mn^{4+} and Mn^{3+}–O–Mn^{4+}. We suppose that Co^{3+} ions have low-spin diamagnetic

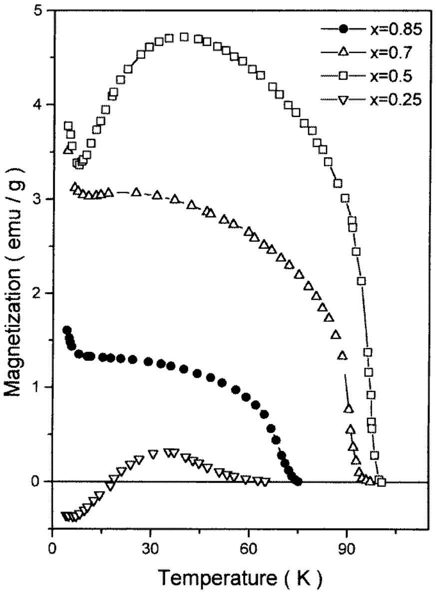

Figure 8. Temperature dependences of the residual magnetization of $Tb(Mn_{1-x}Co_x)O_3$ measured at $H = 0$ after cooling in the field 1 kOe.

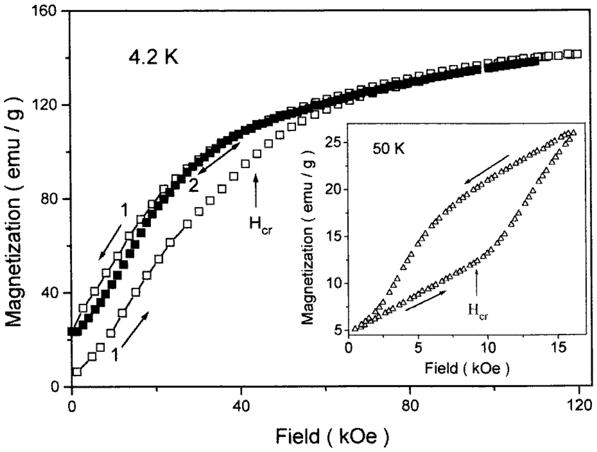

Figure 9. Field dependences of the magnetization of $Tb(Mn_{0.5}Co_{0.5})O_3$: 1, first cycle of the measurement; 2, second cycle of the measurement.

state and play a passive role in the superexchange interaction. It is important to note that Mn^{3+}–O–Mn^{3+} magnetic interaction in a perovskite lattice becomes positive if the Mn–O–Mn angle is close to 180° and there are no static Jahn–Teller distortions [6].

The relatively low spontaneous magnetic moment of $EuMnO_{2.99}$ may be ascribed to a weak ferromagnetic interaction of Dzialoshinsky–Moriya type because there are no Mn^{4+} ions interacting ferromagnetically with Mn^{3+} ones. It is well known that the ABO_3 perovskite (A = rare earth, B = Fe, Cr, V) exhibits weak ferromagnetism of Dzialoshinsky–Moriya type [6]. A large magnetic anisotropy is associated with Mn^{3+} ions occupying highly

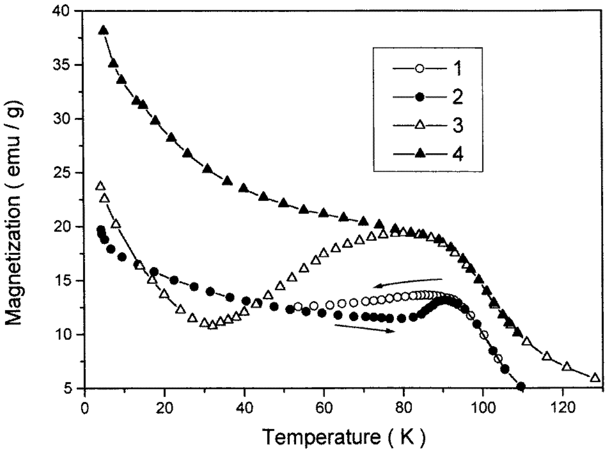

Figure 10. Field-cooled magnetization of Tb($Mn_{0.5}Co_{0.5}$)O_3 at $H = 5.4$ kOe measured on cooling (1) and heating (2); zero-field-cooled magnetization (3) and field-cooled magnetization (4) of Tb($Mn_{0.5}Co_{0.5}$)O_3 at $H = 10.9$ kOe.

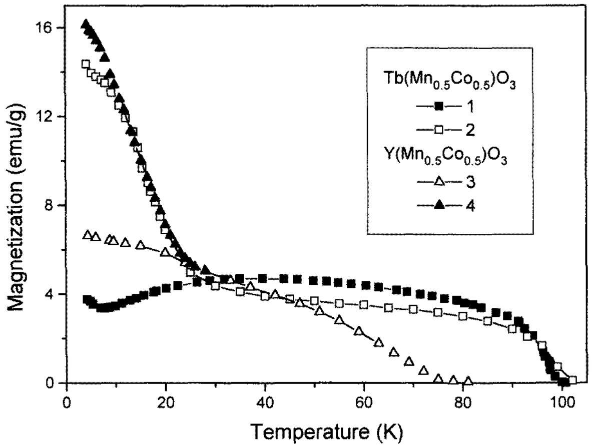

Figure 11. Temperature dependences of the residual magnetization of Tb($Mn_{0.5}Co_{0.5}$)O_3 and Y($Mn_{0.5}Co_{0.5}$)O_3 measured at $H = 0$ after cooling in the field 1 kOe (curves 1 and 3) and 10.9 kOe (curves 2 and 4).

distorted MnO_6 octahedra. A large distortion of the crystal lattice results from d_{z^2}-orbital ordering in the manganese sublattice which takes place in $EuMnO_3$ at around 1370 K [8]. In accordance with neutron diffraction data [9]. $TbMnO_3$ is a spiral antiferromagnet below 40 K. It is possible that $GdMnO_3$ shows the temperature-induced transition from collinear to spiral magnetic structure. In the collinear magnetic phase ($T < 25$ K) $GdMnO_3$ exhibits spontaneous magnetization due to weak ferromagnetic interaction as observed for $EuMnO_3$ (figure 1). It is necessary to carry out the neutron diffraction experiment to justify this hypothesis. We think that the peak of magnetization at around 6 K for $GdMnO_3$ (figure 1) is associated with antiferromagnetic ordering in the Gd sublattice. External magnetic field induces the antiferromagnet–ferromagnet transition for the Gd subsystem. Such a transition has been observed for $GdFeO_3$ perovskite in the Gd-ordered phase [10].

In the range $x < 0.3$ cobalt ions probably have a low-spin 3+ valence state because there is no well defined Curie temperature and the temperature of the transition into paramagnetic state for $x = 0.1$ is lower than that for $x = 0$. For $x \geqslant 0.3$ the configuration $\mathrm{Co}^{2+} + \mathrm{Mn}^{4+}$ seems to be more stable than the $\mathrm{Mn}^{3+} + \mathrm{Co}^{3+}$ one and magnetic properties are governed by a positive Mn^{4+}–Co^{2+} magnetic interaction in accordance with the consideration of Blasse [2]. The ionic ordering of Mn^{4+} and Co^{2+} ions leads to a decrease of antiferromagnetically coupled Mn^{4+}–Mn^{4+} and Co^{2+}–Co^{2+} pairs, which gives rise to increasing magnetic moment of the 3d sublattice. The Curie temperature of the compounds in the range $0.5 \leqslant x \leqslant 0.8$ does not depend on composition. Therefore one can assume the materials in this range behave like a mixture of two materials, i.e. a material with low content of manganese ions and a material which resembles the $\mathrm{Eu(Mn_{0.5}Co_{0.5})O_3}$ oxidized sample.

The metamagnetism of $\mathrm{R(Mn_{0.5}Co_{0.5})O_3}$ compounds is associated with a transformation of the magnetic order in the 3d sublattice because this phenomenon is observed at relatively high temperatures. The ordering of Co^{2+} and Mn^{4+} ions apparently plays an important role because only the $x = 0.5$ composition exhibits the metamagnetic behaviour. In the reduced samples the oxygen content seems to be close to an ideal value—3. The temperature and field dependences of the metamagnetic transition in the $\mathrm{R(Mn_{0.5}Co_{0.5})O_3}$ compounds resemble the metamagnetic behaviour of $\mathrm{R_{0.5}Sr_{0.5}(Mn^{3+}_{0.5}Mn^{4+}_{0.5})O_3}$ charge-ordered perovskites. In these materials both orbital and charge ordering occurs simultaneously. These orderings can be removed by applying an external magnetic field [11, 12]. The transition is irreversible at low temperature. We think that the $\mathrm{R(Mn_{0.5}Co_{0.5})O_3}$ perovskites exhibit orbital ordering in the Co^{2+} sublattice of the ionic ordered phases. In the orbital-ordered phase magnetic moments form the noncollinear magnetic structure whereas in the orbital-disordered phase the magnetic structure is collinear. An external magnetic field apparently induces the order–disorder transition in the orbital subsystem of Co^{2+} ions leading to the appearance of the collinear magnetic structure. Most probably the orbital ordering takes place at around T_C because the critical field in the vicinity T_C falls below 1 kOe. Further experiments such as x-ray analysis of magnetically ordered phases and magnetostriction measurement are under way to clarify this hypothesis.

Acknowledgments

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