JOURNAL OF SOLID STATE CHEMISTRY **131,** 144–149 (1997)
ARTICLE NO. SC977369

Magnetic Study of the $Ca_{1-x}Eu_xMnO_3$ ($0 \leq x \leq 1$) Perovskites

I. O. Troyanchuk and N. V. Samsonenko

Institute of Solid and Semiconductor Physics, Academy of Sciences of Belarus, P. Brovki str. 17, Minsk 220072, Belarus

and

H. Szymczak and A. Nabialek

Institute of Physics, Academy of Sciences of Poland, al.Lotnikow 32/46, Warsaw, Poland

Received August 2, 1996; in revised form January 9, 1997; accepted March 3, 1997

The magnetization and crystal structure of $Ca_{1-x}Eu_xMnO_3$ ($0 \leq x \leq 1$) perovskites have been studied. It is shown that these compounds present four concentration regions in which different magnetic phases coexist. The antiferromagnetic phase is associated with a regular arrangement of Mn^{3+} and Mn^{4+} ions in ratios 1:3 and 1:1. The ferromagnetic phase is attributed to the charge disordered states and is found in $0 \leq x \leq 0.2$ and $0.6 < x < 1$ concentration ranges. The samples $0.1 < x < 0.2$ show metamagnetic behavior which might result from the collapse of the charge ordered state (1:3). The $CaMnO_{2.94}$ and $EuMnO_{3.02}$ are weak ferromagnets with $T_N = 122$ and 40 K, respectively. © 1997 Academic Press

INTRODUCTION

Lanthanum and rare-earth orthomanganites exhibit a strong correlation between electric and magnetic properties (1, 2). During the past years these compounds have been of a great interest due to unusual transport properties (2). The $Pr_{1-x}Ca_xMnO_3$ system may achieve the magnetoresistance of 10^6% in a field of 60 kOe (3). The transition to ferromagnetic state is accompanied by a large magnetovolume effect (4). A change in the crystal lattice symmetry induced by the external magnetic field has been also observed in these compounds (5). At present, the compositions formed from $LaMnO_3$ and $PrMnO_3$ by the replacement of $La^{3+}(Pr^{3+})$ with $Ca^{2+}(Sr^{2+})$ up to 50% are among the most studied. This is caused by the magnetoresistance effect being the most pronounced for these compounds in the range of 10–30% Mn^{4+} ion content (or alkaline-earth ion content, respectively). There are few data on the magnetic properties of compositions with a high content of Mn^{4+} ions. The substitution of Ca^{2+} for Bi^{3+} ($x \approx 0.1$) leads to the appearance of rather high spontaneous magnetization (6). This was attributed to the formation of the ferromagnetic clusters in which the Mn^{3+} ion content is more than that in the antiferromagnetic matrix (6). However, this phenomenon is not revealed by the neutron diffraction and magnetic study of $Ca_{1-x}Pr_xMnO_3$ (7). Measurements of transport properties of $Ca_{1-x}La_xMnO_3$ have revealed insulator–metal transitions for $x = 0.1$ and $x = 0.2$ compositions above room temperature (8). To better understand the properties of the orthomanganites with high Mn^{4+} ion content we undertook a detailed investigation of the system $Ca_{1-x}Eu_xMnO_3$ in the range $0 \leq x \leq 1$.

EXPERIMENT

$Ca_{1-x}Eu_xMnO_3$ samples were prepared from high purity oxides and carbonates mixed in stoichiometric ratio. The final synthesis was done at 1670 K in air. The cooling rate was 100 K/h. The powder X-ray diffraction study showed all the samples to be single phase perovskites with a slightly distorted unit cell (Table 1). Pseudotetragonal distortions ($a \approx b \neq c$) change to orthorhombic distortions by substitution of Ca^{2+} for Eu^{3+}. The average manganese oxidative state of end members of the $Ca_{1-x}Eu_xMnO_3$ series was determined by chromatometric titration.

Magnetization measurements were carried out with a vibrating sample magnetometer in a steady magnetic field up to 120 kOe.

RESULTS AND DISCUSSION

Magnetization of $Ca_{1-x}Eu_xMnO_3$ samples at low temperature depends on the magnetic history. Figure 1 shows the magnetization vs temperature measured in the course of heating after cooling in either a zero field (ZFC) or a field of measurement (FC) for $CaMnO_{2.94}$. ZFC and FC curves for $CaMnO_{2.94}$ samples differ below 122 K (Fig. 1). The sharp magnetization anomaly at this temperature indicates the

0022-4596/97 $25.00

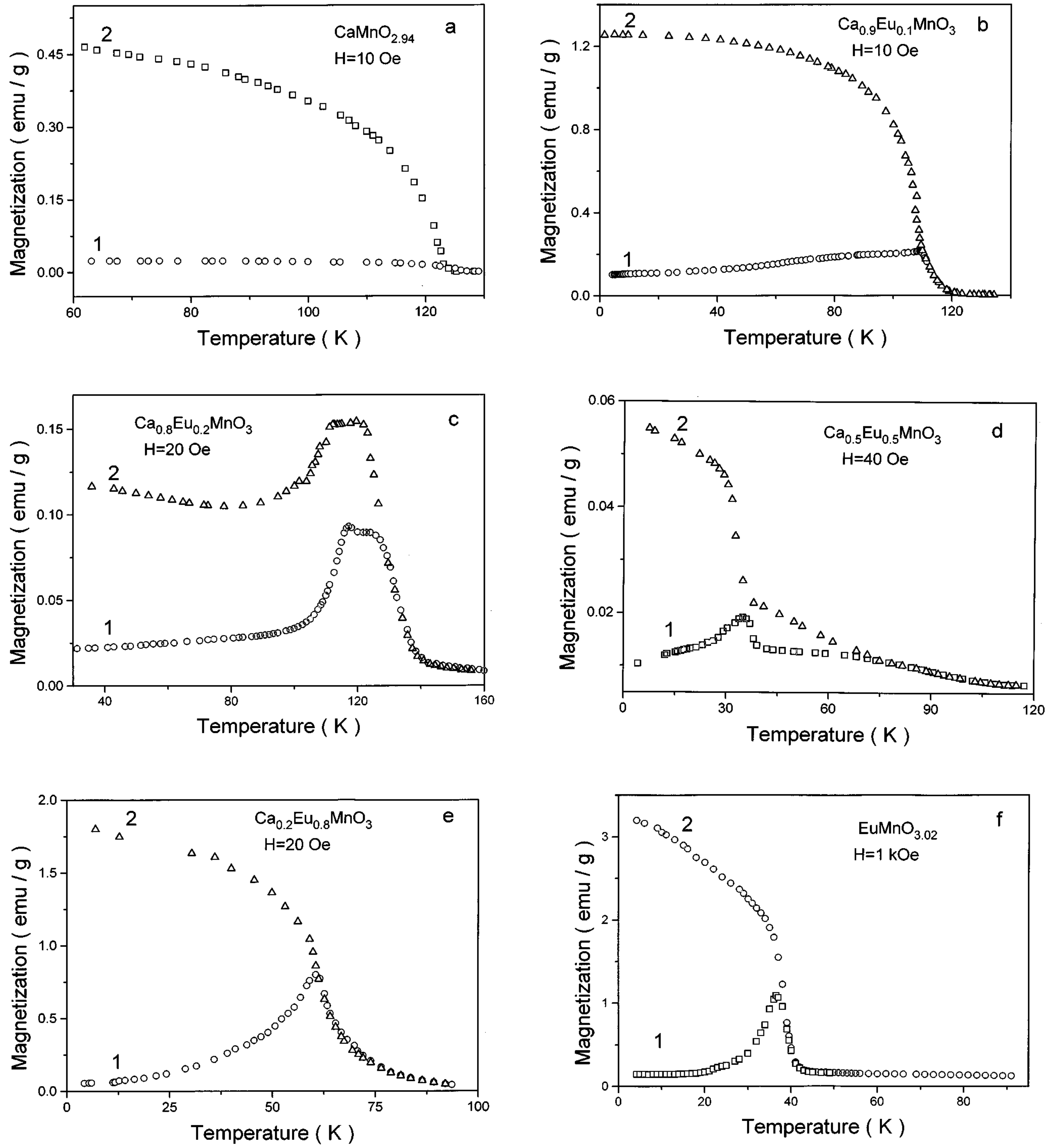

FIG. 1. Temperature dependence of ZFC (1) and FC (2) magnetizations for $Ca_{1-x}Eu_xMnO_3$: (a) $x = 0$ at $H = 10$ Oe; (b) $x = 0.1$ at $H = 10$ Oe; (c) $x = 0.2$ at $H = 20$ Oe; (d) $x = 0.5$ at $H = 40$ Oe; (e) $x = 0.8$ at $H = 20$ Oe; (f) $x = 1$ at $H = 1$ kOe.

existence of a disorder–order phase transition. $Ca_{0.9}Eu_{0.1}MnO_3$ shows a small decrease in the magnetic ordering temperature down to 110 K at which a sharp magnetization increase is observed (Fig. 1b). For both samples the ZFC magnetization is smaller than FC magnetization by one order of magnitude at 4.2 K in the field $H =$ 10 Oe. ZFC and FC magnetization measurements for $Ca_{0.8}Eu_{0.2}MnO_3$ are characterized by a broad peak near

TABLE 1
Unit Cell Parameters of the Compounds $Ca_{1-x}Eu_xMnO_3$

Compounds	a (Å)	b (Å)	c (Å)	$V/4$ (Å^3)
$CaMnO_{2.94}$	5.265	5.265	7.446	51.60
$Ca_{0.9}Eu_{0.1}MnO_3$	5.268	5.268	7.470	51.84
$Ca_{0.8}Eu_{0.2}MnO_3$	5.290	5.290	7.508	52.52
$Ca_{0.7}Eu_{0.3}MnO_3$	5.301	5.301	7.519	53.54
$Ca_{0.6}Eu_{0.4}MnO_3$	5.347	5.347	7.536	53.86
$Ca_{0.5}Eu_{0.5}MnO_3$	5.350	5.427	7.560	54.88
$Ca_{0.4}Eu_{0.6}MnO_3$	5.361	5.467	7.563	55.42
$Ca_{0.3}Eu_{0.7}MnO_3$	5.375	5.530	7.540	56.03
$Ca_{0.2}Eu_{0.8}MnO_3$	5.337	5.634	7.517	56.51
$Ca_{0.1}Eu_{0.9}MnO_3$	5.345	5.710	7.468	56.96
$EuMnO_{3.02}$	5.331	5.819	7.494	58.12

the magnetic ordering temperature. The magnetic transition takes place in the temperature range 125–140 K (Fig. 1c). The transition to the state with spontaneous magnetization is still broader for $x = 0.3$. Although the onset temperature of the transition remains the same as for $x = 0.2$, the magnetization abruptly decreases. For $x = 0.4$ no anomaly in the thermal dependence of the magnetization has been observed below 200 K. ZFC and FC curves come gradually apart below 70 K. Magnetization measurements for $x = 0.5$, 0.8, and 1.0 have revealed anomalies at 40, 60, and 40 K, respectively (see Figs. 1d, 1e, 1f). The increasing Eu^{3+} content above $x = 0.5$ leads to a magnetization enhancement. The magnetic behavior of $x = 0.2$ and $x = 0.3$ composition in the temperature interval 50–230 K is shown in Fig. 2. Magnetization for $x = 0.3$ increases above 150 K with increasing temperature apparently due to the structural phase transition.

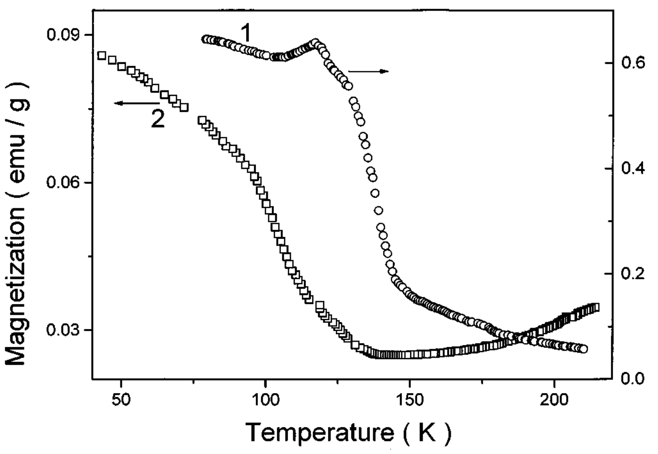

FIG. 2. Temperature dependence of magnetization in the field $H = 300$ Oe for $Ca_{1-x}Eu_xMnO_3$: $x = 0.2$ (1); $x = 0.3$ (2).

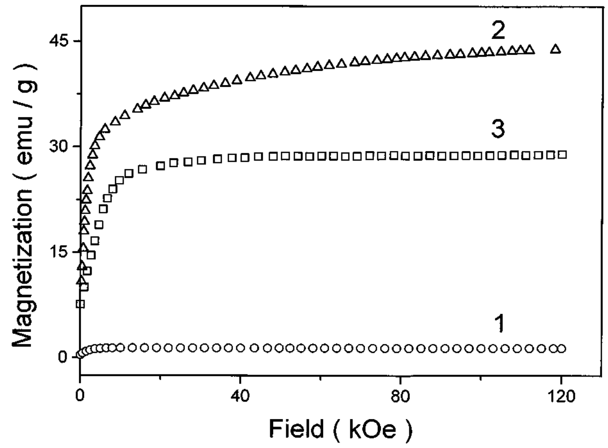

FIG. 3. Magnetization vs field for $Ca_{1-x}Eu_xMnO_3$: $1 - x = 0$ at $T = 4.2$ K; $2 - x = 0.1$ at $T = 4.2$ K; $3 - x = 0.1$ at $T = 89$ K.

The compound $CaMnO_{2.94}$ at 4.2 K is characterized by a low spontaneous magnetization ~1.4 emu/g and low magnetic susceptibility in the high field region (Fig. 3). The spontaneous magnetization increases abruptly up to 35 emu/g by the substitution of Ca^{2+} for Eu^{3+} up to $x = 0.1$ (Fig. 3). For $x = 0.2$ the spontaneous magnetization at 4.2 K falls to 1.5 emu/g (Fig. 4). In the field above 40 kOe, magnetic susceptibility enhances and a large field hysteresis arises due to a metamagnetic first-order phase transformation. Spontaneous magnetization increases up to 3.5 emu/g with increasing temperature up to 88 K. Magnetization vs field dependence at 88 K is similar to that at 4.2 K, although the hysteresis is less pronounced. Field dependencies of magnetization for $x = 0.6$, 0.8, and 1.0 are shown in Fig. 5. For $Ca_{0.2}Eu_{0.8}MnO_3$, spontaneous magnetization reaches a maximum value in the whole $Ca_{1-x}Eu_xMnO_3$ system,

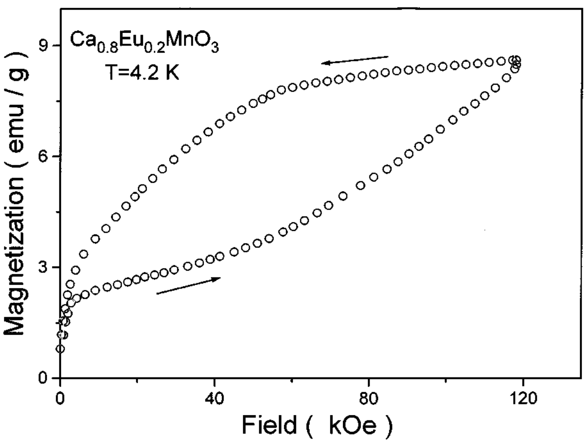

FIG. 4. Magnetization vs field for $Ca_{0.8}Eu_{0.2}MnO_3$ at $T = 4.2$ K.

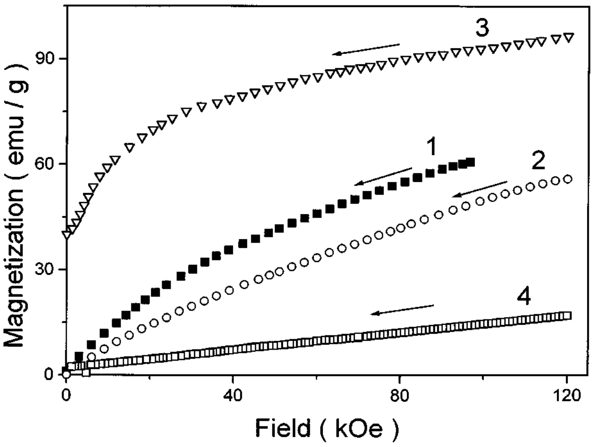

FIG. 5. Field dependences of the magnetization for $x = 0.6$ at 4.2 K (1) and 97 K (2); for $x = 0.8$ at 4.2 K (3); for $x = 1$ at 4.2 K (4).

65 emu/g. It is 1.3 times lower than one could expect in the case of the ferromagnetic alignment of 4 μ_B per Mn^{3+} and 3 μ_B per Mn^{4+}. $EuMnO_{3.02}$ is characterized by the spontaneous magnetization of 2.5 emu/g. The temperature of the magnetic ordering is 40 K (Fig. 1f) and the coercive field at 4.2 K is very large, 25 kOe. Compositional dependences of coercive field, spontaneous magnetization at 4.2 K, and temperatures of magnetic ordering for $Ca_{1-x}Eu_xMnO_3$ compositions are presented in Fig. 6.

The $Ca_{1-x}Eu_xMnO_3$ ($0.1 \leq x \leq 0.2$) samples exibit a correlation between magnetic and electrical properties. The application of a magnetic field reduces strongly the resistivity below the temperature of magnetic ordering (Fig. 7). The resistivity decreases irreversibly after the first measurement cycle. An appreciable hysteresis of resistivity arises under the applied field.

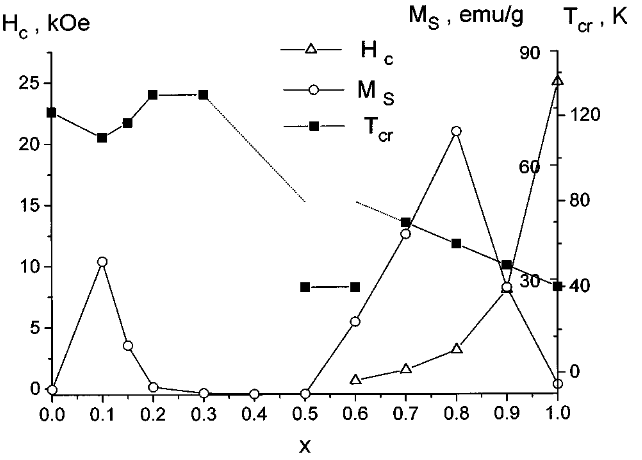

FIG. 6. Concentrational dependences of coercive field (H_c) at 4.2 K, spontaneous magnetization (M_S) at 4.2 K and temperatures of magnetic ordering (T_{cr}) for $Ca_{1-x}Eu_xMnO_3$. Below dashed line magnetization depends from magnetic prehistory.

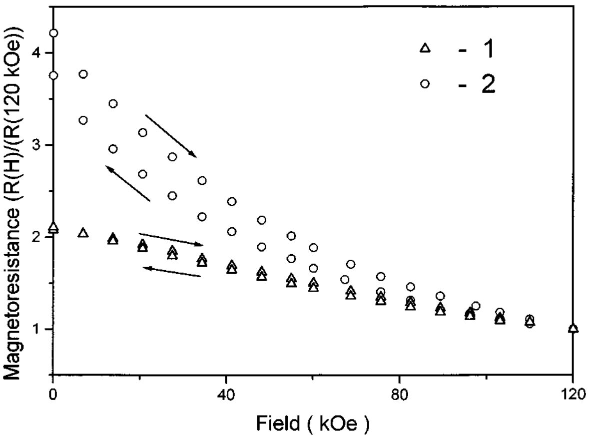

FIG. 7. The magnetoresistance ratio $R(H)/R(H = 120\ kOe)$ for $Ca_{0.85}Eu_{0.2}MnO_3$ at $T = 90$ K (1) and $T = 30$ K (2).

For $Ca_{0.8}Eu_{0.2}MnO_3$ and $Ca_{0.5}Eu_{0.5}MnO_3$ compounds anomalies of elastic modulus have been revealed at 190 and 280 K, respectively (Fig. 8). Below 190 and 280 K resistivity of both samples start to increase rapidly on cooling (Fig. 9).

Magnetic parameters of $CaMnO_{2.94}$ obtained in the present work are in a good accordance with the results of the magnetic measurements of $CaMnO_{2.98}$ obtained by annealing at 670 K for 154 h under high oxygen pressure (9). Néel temperatures of both compositions are 122–123 K. Spontaneous magnetization appears to be closely allied. The appearance of a low spontaneous magnetic moment in $CaMnO_{2.94}$ was related to the existence of weak ferromagnetism (9) by analogy with orthoferrites and orthochromites. Low susceptibility of paraprocess (Fig. 3) is consistent with this assumption. However, in the orthoferrites and orthochromites the substitution of rare earth ions for alkaline earth ions does not lead to an increase in the spontaneous magnetization (10). At substitution of Ca^{2+} for Eu^{3+} magnetization increases sharply (Fig. 3). Two different

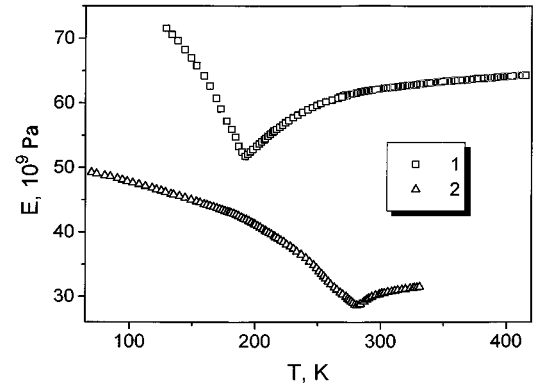

FIG. 8. Modul Young vs temperature dependences for $Ca_{0.8}Eu_{0.2}MnO_3$ (1) and $Ca_{0.5}Eu_{0.5}MnO_3$ (2).

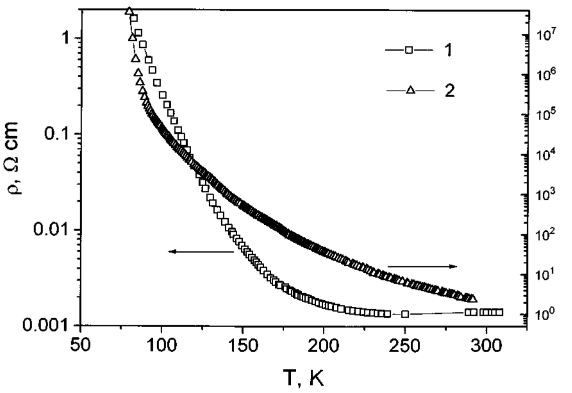

FIG. 9. Resistivity vs temperature dependences for $Ca_{0.8}Eu_{0.2}MnO_3$ (1) and $Ca_{0.5}Eu_{0.5}MnO_3$ (2).

crystallographic phases have been revealed by the neutron diffraction study of $Pr_{0.1}Ca_{0.9}MnO_3$ (7). The first phase is pseudotetragonal; its content is about 2/3 of the sample. The second phase is pseudocubic. The pseudotetragonal phase is associated with regular arrangement of Mn^{3+} and Mn^{4+} ions in 1 : 3 ratio (charge ordering effect). The pseudotetragonal phase is matched by the antiferromagnetic *C*-type ordering (7). We suggest that the magnetic properties of $Ca_{0.9}Eu_{0.1}MnO_3$ can be explained by assuming that this compound consists of the antiferromagnetic *C*-type phase to the extent of 60% and the ferromagnet phase to the extent of 40%. Under this phase ratio the spontaneous magnetization corresponds to $2.6\,\mu_B$ magnetic moment per Mn^{4+} ion in the ferromagnetic phase. (In accordance with (11) $\mu(Mn^{4+}) = 2.6\,\mu_B$ for $CaMnO_3$). Strong dependence of magnetic properties on magnetic history (Fig. 1) is common for mictomagnets (the mixture of the antiferro- and ferromagnetic states). Sample $x = 0.2$ consists mainly of the *C*-type antiferromagnetic charge ordered phase. The most probable charge ordering takes place near 200 K because at 190 K we observed anomaly elastic properties (Fig. 8) and below 200 K resistivity started to increase on cooling. The ferromagnetic phase is present in minor amounts. We believe that the ferromagnetic phase corresponds to the charge disordered state. The metamagnetic behavior results most likely from some domains of the antiferromagnetic *C*-type phase transforming to the ferromagnetic state in a magnetic field. The transition from the antiferromagnetic state to the ferromagnetic state induced by a magnetic field was observed in $Pr_{1-x}Ca_x(Mn^{3+}_{1-x}Mn^{4+}_x)O_3$ $(0.3 \le x \le 0.5)$ (3) and $Pr_{0.5}Sr_{0.5}(Mn^{3+}_{0.5}Mn^{4+}_{0.5})O_3$ perovskites. It was found in (3) that with application of the external magnetic field the charge order in 1 : 1 ratio state of Mn^{3+} and Mn^{4+} ions undergoes a sort of "melting" transition of the first order. The stability of the charge ordered phase decreases with increasing deviation of an ideal 1 : 1 ratio for Mn^{3+} and Mn^{4+} ions (3).

The antiferromagnetic–ferromagnetic transition in the charge ordered phase of the orthomanganites is induced by the field due to the competition of antiferromagnetic and ferromagnetic superexchange interactions between manganese ions. The Mn^{3+}–Mn^{4+} superexchange interactions in orbitally and charge disordered phases of perovskites, as a rule, are ferromagnetic (12). The superexchange interactions between manganese ions (4 +) depends on the Mn–O–Mn angle and changes from antiferromagnetic in the $CaMn^{4+}O_3$ perovskite to ferromagnetic in the $In_2Mn^{4+}_2O_7$ and $Tb_2Mn^{4+}_2O_7$ pyrochlores (13).

With increasing Eu^{3+} ion content in the $Ca_{1-x}Eu_xMnO_3$ system another type of charge ordering occurs. In sample $x = 0.3$ a phase with a regular arrangement of Mn^{3+} and Mn^{4+} ions in 1 : 1 ratio appeared. The ordering takes place above 200 K. It shows up in the anomalous behavior of the paramagnetic susceptibility (Fig. 2) and anomaly Young's modulus (Fig. 8). In the sample $x = 0.5$ the magnetization anomaly is revealed at 40 K (Fig. 1). This is probably conditioned by the transformation of magnetic structure in the basic charge ordered matrix. It is worth noting that the antiferromagnetic ordering in $Pr_{0.5}Ca_{0.5}MnO_3$ is observed at higher temperature, 170 K (3).

The increase in the magnetization for the samples with Eu^{3+} content above 50% is due to disordering of Mn^{3+} and Mn^{4+} ions. However, the spontaneous magnetization of $Ca_{0.2}Eu_{0.8}MnO_3$ is lower than the value expected for the ferromagnetic alignment of magnetic moments of Mn^{3+} and Mn^{4+} ions. In contrast with the $Ca_{1-x}Pr_xMnO_3$ system, the magnetic structure of $Ca_{1-x}Eu_xMnO_3$ does not transform in the external magnetic field for $x = 0.6$ and 0.7 (Fig. 5). The charge ordering phenomena seem to be the generic properties of $Ca_{1-x}Ln_xMnO_3$ (Ln = lanthanoid and $x = 0.25$ and $x = 0.5$). This feature depends strongly on the ionic radii of Ca^{2+} (Sr^{2+}) and rare earth ions or equivalently on the width of the 3*d* bands. In the case of $Ca_{1-x}Pr_xMnO_3$ with rather wide band, the field induced charge order(1 : 1)–disorder transition takes place at $0.5 \le x \le 0.7$. In the case of $Ca_{1-x}Eu_xMnO_3$ with a narrower 3*d* band, the charge ordered state is more stable than that in Pr-containing perovskites and the magnetic field of 120 kOe is not sufficient for the "melting" charge ordered (1 : 1) phase.

The magnetic properties of $EuMnO_3$ (Figs. 1 and 6) are typical for a weak ferromagnet. It seems that the high magnetic anisotropy of this compound results from structure distortions due to d_{z^2} orbital ordering in the manganese sublattice.

REFERENCES

1. J. H. Van Santen and G. H. Jonker, *Physica* **16,** 599 (1950).
2. B. Raveaux, A. Haignan, and V.Caignoert, *J. Solid State Chem.* **117,** 424 (1995).

3. Y. Tomioka, A. Asamitsu, H. Kuwahara, and Y. Tokura, *Phys. Rev.* **53,** R1689 (1996).
4. M. R. Ibarra, P. A. Alagarabel, C. Marquina, J. Blasco, and J. Garsia, *Phys. Rev. Lett.* **75,** 3541 (1995).
5. A. Asamitsu, Y. Moritomo, Y. Tokura, and Y. Tomioka, *Nature* **373,** 407 (1995).
6. A. T. Starovoitov, V. I. Ozhogin, and V. A. Bokov, *Fizika tverdogo tela Interscience* **11,** 2153 (1969). [in Russian]
7. Z. Jirak, S. Krupička, Z. Simsa, M. Dlouha, and S. Vratislav, *J. MMM* **53,** 153 (1985).
8. H. Taguchi and H. Shimada, *J. Solid State Chem.* **63,** 290 (1986).
9. J. B. MacChesney, H. J. Williams, J. F. Potter, and R. C. Sherwood, *Phys. Rev.* **164,** 779 (1967).
10. N. Sakai, H. Fjellvag, and B. Hauback, *J. Solid State Chem.* **121,** 202 (1996).
11. E. O. Wollan and W. C. Koehler, *Phys. Rev.* **100,** 545 (1955).
12. J. Goodenough, "Magnetism and the Chemical Bond," Interscience, New York, 1963.
13. I. O. Troyanchuk, V. N. Derkachenko, and E. F. Shapovalova, *Phys. Stat. Sol. A* **113,** 249 (1989).