

Phase Transformation in the $\text{Eu}_{1-x}\text{Ca}_x\text{MnO}_3$ Perovskites

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Abstract. Magnetization and crystal structure of $\text{Eu}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0 \leq x \leq 1$) perovskite have been studied. It is shown that these compounds can be divided into four concentration regions in which different magnetic phases coexist. The antiferromagnetic phases are associated with the regular arrangement of Mn^{3+} and Mn^{4+} ions in ratios 1:0, 1:1, 1:3 and 0:1 respectively. The ferromagnetic phases are attributed to the charge disordered states and arise in $0 \leq x \leq 0.4$ and $0.8 \leq x \leq 1$ concentration regions. The samples $x=0.8$ and 0.85 show metamagnetic behavior which might result from destruction of the charge ordered (1:3) state.

1. INTRODUCTION

Lanthanum and rare-earth orthomanganites exhibit the strong correlation between electric and magnetic properties [1,2]. Last years these compounds are of a great interest due to unusual transport properties [2,3]. At present the compositions on the base of LaMnO_3 and PrMnO_3 with the substitution of $\text{La}^{3+}(\text{Pr}^{3+})$ by $\text{Ca}^{2+}(\text{Sr}^{2+})$ up to 50% appear to be the most studied. There are few data on the magnetic properties of the compositions with a high content of Mn^{4+} and other rare-earth ions [4,5]. For better understanding the properties of the orthomanganites we undertook the detailed investigation of the system $\text{Eu}_{1-x}\text{Ca}_x\text{MnO}_3$ in the range $0 \leq x \leq 1$.

2. EXPERIMENT

$\text{Eu}_{1-x}\text{Ca}_x\text{MnO}_3$ samples were prepared from high purity oxides and carbonates mixed in stoichiometric ratio. The final synthesis was done at 1620 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 the slightly distorted unit cell. Orthorhombic distortions change to pseudotetragonal ($a \approx b \neq c$) ones by substitution of Eu^{3+} by Ca^{2+} .

3. RESULTS AND DISCUSSION

Compositional dependences of spontaneous magnetization, coercive field and temperatures of magnetic transformations are shown in Fig.1. The $\text{EuMnO}_{3.02}$ is characterized by spontaneous magnetization 2.5 emu/g, the temperature of antiferromagnetic ordering is 40 K, and coercive field at 4.2 K is very large - 25 kOe.

The substitution of europium by calcium, i.e. an increase of x in $\text{Eu}_{1-x}\text{Ca}_x\text{MnO}_3$, causes a rise in the temperature of transition to the paramagnetic state and spontaneous magnetization. For $x=0.3$ the transition appears near 70 K. For compositions in the interval $0.1 < x < 0.3$ ZFC (zero field cooled) and FC (field cooled) magnetizations are equivalent above the temperature of the peak on the ZFC curve. In contrast to the Ca-poor compositions the ZFC and FC magnetizations for $x=0.4$ and $x=0.5$ do not coincide in the wide temperature range above the phase transition near 40 K. For $x=0.4$ ZFC and FC magnetizations are different below 100 K. The spontaneous magnetization reaches maximum value for $x=0.2$. The further increase of Ca content leads to the decrease of magnetization and coercive field (Fig.1).

For $x=0.6$ no sharp anomaly of magnetic properties has been observed at the temperature below 200 K. ZFC and FC curves gradually come apart below 100 K. Further Ca^{2+} content increase leads to the magnetization and Curie temperature increasing (Fig.1). Magnetic susceptibility for $x=0.7$ increases above 150 K with increasing temperature apparently due to the structural phase transition. The spontaneous magnetization increases abruptly up to 35 emu/g by the substitution of Eu^{3+} by Ca^{2+} up to $x=0.9$. For $x=0$ the spontaneous magnetization at 4.2 K falls to 1.4 emu/g. In the field above 40 kOe the magnetic susceptibility of $x=0.8$ enhances and the large field hysteresis arises due to the

metamagnetic first-order phase transformation (Fig.2). Spontaneous magnetization increases from 2 emu/g up to 3.5 emu/g with increasing temperature from 4.2 K up to 100 K. Magnetization vs field dependence at 88 K is similar to that at 4.2 K, although the hysteresis is less pronounced.

We have suggested that the $\text{EuMnO}_{3.02}$ is antiferromagnet with inclusions of ferromagnetic clusters. The increase of Ca^{2+} content leads to the crystal structure distortion decrease and hence rising temperatures of magnetic ordering of both antiferromagnetic and ferromagnetic phases. In the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ for $0.2 < x < 0.3$ the magnetization value approaches that for the case of ferromagnetic alignment of all the Mn^{3+} and Mn^{4+} moments [1]. In contrast compositions $\text{Eu}_{1-x}\text{Ca}_x\text{MnO}_3$ are not homogenous ferromagnetics in this range because the spontaneous magnetization for $x=0.2$ is 1.4 times lower than one could expect in the case of ferromagnetic alignment of 4 μ_B per Mn^{3+} and 3 μ_B per Mn^{4+} .

The drop of magnetization at $x > 0.2$ is apparently due to the charge ordering of Mn^{3+} and Mn^{4+} ions in ratio 1:1. For the $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ system such a phenomenon occurs in the concentration range $0.3 \leq x \leq 0.6$ at temperature below 250 K [3]. In the $\text{Eu}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ the magnetization anomaly is revealed at 40 K (Fig.1). This is probably conditioned by the antiferromagnetic ordering in basic charge ordered matrix. It is worth to notice that the antiferromagnetic ordering in the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ is observed at higher temperature - 170 K [3].

With increasing Ca^{2+} ion content in $\text{Eu}_{1-x}\text{Ca}_x\text{MnO}_3$ system another type of the charge ordering occurs. In sample $x=0.7$ the phase with a regular arrangement of Mn^{3+} and Mn^{4+} ions in 1:3 ratio appears. The ordering takes place above 200 K as it is seen from anomalous behavior of paramagnetic susceptibility. Further increase of Mn^{4+} content leads to the destruction of the charge ordered in 1:3 ratio phase and sharp increase of spontaneous magnetization due to the formation of charge disordered domains.

The metamagnetic behavior results most likely from some domains of the antiferromagnetic charge ordered in 1:3 ratio phase transforming to the ferromagnetic state in magnetic field. It was found in [3] that with application of the external magnetic field the charge ordered state of Mn^{3+} and Mn^{4+} ions in 1:1 ratio in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ undergoes a sort of "melting" transition of the first order.

In the case of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ with rather wide 3d-band the field induced charge order-disorder transition takes place at $0.3 \leq x \leq 0.5$. In the case of $\text{Eu}_{1-x}\text{Ca}_x\text{MnO}_3$ with a narrower 3d-band the charge ordered state 1:1 is more stable than that in Pr-containing perovskites and the magnetic field of 120 kOe is not sufficient for the "melting" charge ordered in 1:1 ratio phase.

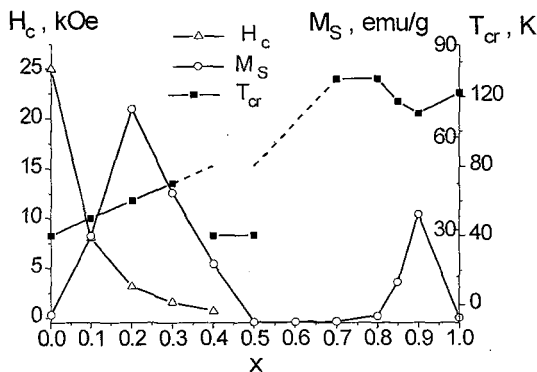


Figure 1: Concentrational dependence of spontaneous magnetization (M_S) at 4.2 K, coercive field (H_c) at 4.2 K and temperatures of magnetic ordering (T_{cr}) for $\text{Eu}_{1-x}\text{Ca}_x\text{MnO}_3$. Below dashed line the magnetization depends on magnetic prehistory.

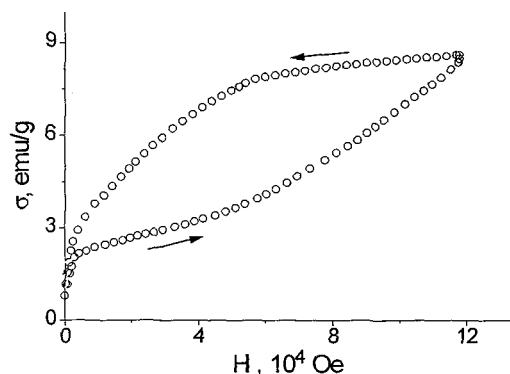


Figure 2: Magnetization vs field dependence for $\text{Eu}_{0.2}\text{Ca}_{0.8}\text{MnO}_3$ at 4.2 K.

References

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