

Magnetic and transport properties of $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$ (Ln = La, Eu or Lu)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 10627

(<http://iopscience.iop.org/0953-8984/8/49/047>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 05:51

Please note that [terms and conditions apply](#).

Magnetic and transport properties of $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$ (Ln = La, Eu or Lu)

I O Troyanchuk[†], N V Kasper[†], N V Samsonenko[†], H Szymczak[‡] and A Nabialek[‡]

[†] Institute of Solid and Semiconductor Physics, Academy of Sciences of Belarus, P Brovki 17, 220072 Minsk, Belarus

[‡] Institute of Physics, Polish Academy of Sciences, al. Lotnikow 32/46, 02-668 Warsaw, Poland

Received 10 July 1996, in final form 19 September 1996

Abstract. The magnetization and transport properties of $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$ (Ln = La, Eu or Lu; $0 \leq x \leq 0.3$) perovskites have been studied. It is shown that the substitution of Ca^{2+} by La, Eu or Lu up to $x = 0.1$ leads to a sharp increase in the magnetization and conductivity. Further replacement of Ca results in a decrease in the magnetization due to the regular arrangement of Mn^{3+} and Mn^{4+} ions in the ratio 1:3. The samples with $0 \leq x \leq 0.2$ show metamagnetic behaviour which might result from a collapse of the charge-ordered (1:3) state. The samples with $x = 0.1$ and $x = 0.15$ exhibit a resistance variation up to 500% with $H = 12$ T.

1. Introduction

Recently, there has been a surge of interest in the properties of LaMnO_3 and related rare-earth orthomanganites doped by alkaline-earth ions. The magnetic ordering in these materials is accompanied by a sharp drop in the resistivity [1, 2]. The magnetic and transport properties have traditionally been explained within the framework of the ‘double-exchange’ model considering the magnetic coupling between Mn^{3+} and Mn^{4+} as result of the motion of an electron between two partially filled d shells [3]. At present, compositions based on the LaMnO_3 and PrMnO_3 with the substitution of La^{3+} (Pr^{3+}) by Ca^{2+} (Sr^{2+}) up to 50% appears to be the most studied. There are few data on the magnetic properties of the composition with a high content of Mn^{4+} ions. It was shown that CaMnO_3 is a weak ferromagnet or antiferromagnet with a G-type magnetic structure [4, 5]. The substitution of Ca^{2+} by Pr^{3+} by up to 20% leads to the formation of a C-type antiferromagnetic structure due to the regular arrangement of Mn^{3+} and Mn^{4+} ions in a 1:3 ratio [6]. To obtain a better understanding of the properties of the orthomanganites with a high content of Mn^{4+} ions we undertook a detailed investigation of the magnetic and transport properties of $\text{Ca}_{1-x}\text{Ln}_x\text{MnO}_3$ (Ln = La, Eu or Lu).

2. Experimental details

Samples were synthesized by a solid state reaction technique from the high-purity reagents CaCO_3 , Ln_2O_3 and MnO_2 . The starting materials were mixed in stoichiometric proportions, ground and sintered at 900°C for 2 h. The resulting powders were reground, sintered at 1370°C for 2 h in air and cooled to room temperature in the furnace. Powder x-ray

diffraction showed clean single-phase patterns. The unit-cell parameters of some samples are listed in table 1.

Table 1. Unit-cell parameters and primitive unit-cell volume of manganites at room temperature.

Compound	a (Å)	b (Å)	c (Å)	V (Å ³)
Ca _{0.85} Lu _{0.15} MnO ₃	5.251	5.261	7.448	51.439
Ca _{0.85} La _{0.15} MnO ₃	5.297	5.316	7.499	52.791
Ca _{0.9} Eu _{0.1} MnO ₃	5.263	5.272	7.470	51.817
Ca _{0.85} Eu _{0.15} MnO ₃	5.274	5.284	7.479	52.106
Ca _{0.8} Eu _{0.2} MnO ₃	5.286	5.298	7.508	52.566
Ca _{0.7} Eu _{0.3} MnO ₃	5.297	5.311	7.519	52.882

The resistivity ρ was measured by a standard four-probe method, and the magnetization M was measured using a commercial vibrating sample magnetometer.

3. Results and discussion

Compositional dependences of the spontaneous magnetization and temperatures of magnetic transformations of Ca_{1-x}Eu_xMnO₃ samples are shown in figure 1. CaMnO₃ is characterized by a spontaneous magnetization of 1.4 emu g⁻¹ at 4.2 K and the temperature of antiferromagnetic ordering is 122 K. The substitution of calcium by europium causes a rise in the spontaneous magnetization, reaching a maximum value for $x = 0.1$. The further increase in the Eu content leads to a decrease in the magnetization (figure 1). In contrast with Ca_{1-x}Eu_xMnO₃ ($x \leq 0.15$) compositions the spontaneous magnetization of Ca_{0.8}Eu_{0.2}MnO₃ increases with increasing temperature. Magnetic ordering in Ca_{0.7}Eu_{0.3}MnO₃ occurs in the wide temperature range 125–140 K. For $x = 0.4$ no sharp anomaly of magnetization has

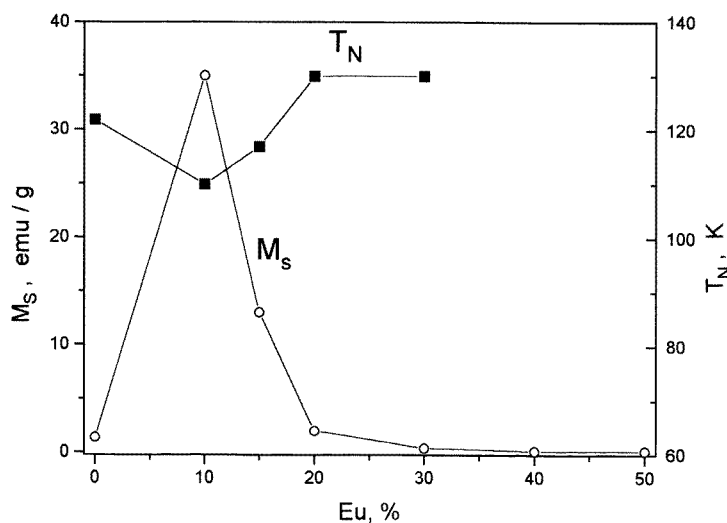


Figure 1. Compositional dependences of the spontaneous magnetization M_S and magnetic ordering temperatures T_N for Ca_{1-x}Eu_xMnO₃.

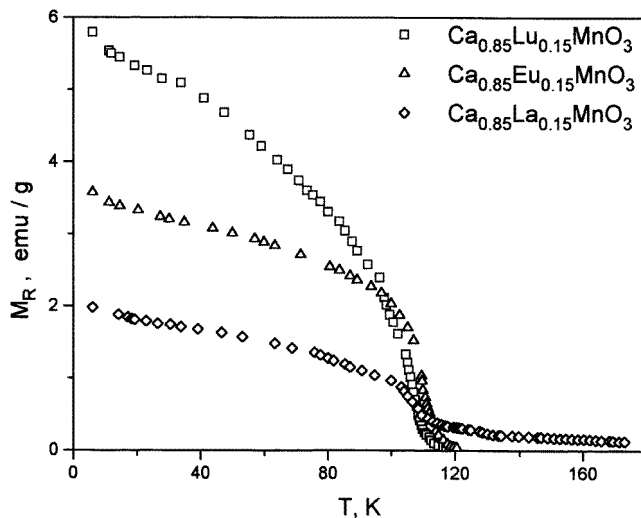


Figure 2. Temperature dependences of the residual magnetization for $\text{Ca}_{0.85}\text{Ln}_{0.15}\text{MnO}_3$ (Ln = La, Eu or Lu).

been observed at temperatures below 200 K. Zero-field-cooled (ZFC) and field-cooled (FC) magnetizations gradually separate below 100 K. It is worth noting that the paramagnetic susceptibility for $x = 0.3$ increases above 150 K with increasing temperature, apparently owing to the structural phase transition.

A similar magnetic behaviour was observed for CaMnO_3 doped by La^{3+} or Lu^{3+} ions. The temperature dependences of the residual magnetization of $\text{Ca}_{0.85}\text{Ln}_{0.15}\text{MnO}_3$ (Ln = La, Eu or Lu) are shown in figure 2. The temperature of magnetic ordering increases slightly with increasing ionic radii of Ln. A large magnetic hysteresis has been revealed for the $x = 0.15$ and $x = 0.2$ compositions in high magnetic fields (figure 3). This behaviour might result from a first-order metamagnetic phase transition.

The resistance measurements carried out on cooling in zero field and in a field of 12 T (figure 4) show a semiconducting behaviour in the whole temperature range from 293 to 4.2 K for $\text{Ca}_{0.9}\text{Eu}_{0.1}\text{MnO}_3$. The conductivity is relatively high in comparison with those of the CaMnO_3 and EuMnO_3 parent compounds and has a low sensitivity to the temperature. The application of a magnetic field strongly reduces the resistivity below the temperature of magnetic ordering. The magnetoresistance ratio (MR) defined as $R(H)/R(H = 12 \text{ T})$ where $R(H)$ is the resistivity in the applied field depends strongly on temperature and reaches a maximum at temperatures well below T_N , the temperature of magnetic ordering (figures 1 and 4). The resistivity decreases irreversibly after the first measurement cycle (figure 5). An appreciable hysteresis of resistivity arises in the applied field. The effect of the magnetic field on the resistivity is more pronounced for $\text{Ca}_{0.85}\text{Lu}_{0.15}\text{MnO}_3$ (figure 6). In this case the MR reaches a value of 4.2 at 30 K in a field of 12 T. The decreasing temperature down to 7 K almost does not affect the MR. In the case of cooling in a field of 12 T the resistivity even decreases with decreasing temperature below 50 K. For both $\text{Ca}_{0.9}\text{Eu}_{0.1}\text{MnO}_3$ and $\text{Ca}_{0.85}\text{Lu}_{0.15}\text{MnO}_3$ the MR is negative and does not saturate with increasing magnetic field up to 12 T. It should also be noted that the irreversible drop in the resistivity after first applying a field and the magnetic field hysteresis of the resistivity were observed for both $\text{Ca}_{0.9}\text{Eu}_{0.1}\text{MnO}_3$ and $\text{Ca}_{0.85}\text{Lu}_{0.15}\text{MnO}_3$ at low temperatures.

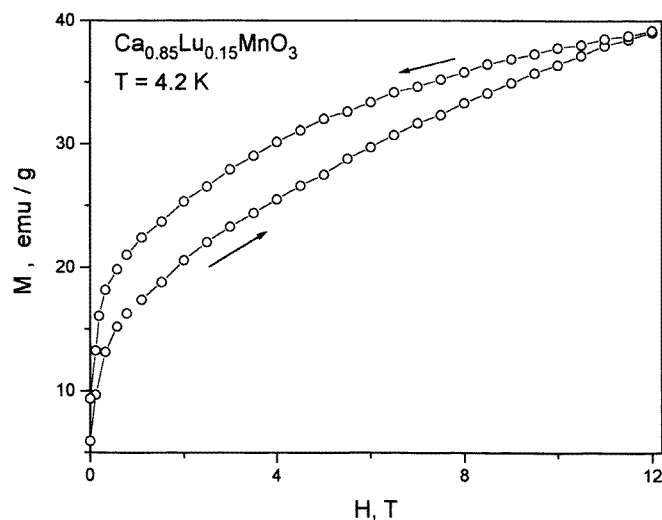


Figure 3. Magnetization versus field at 4.2 K for $\text{Ca}_{0.85}\text{Lu}_{0.15}\text{MnO}_3$.

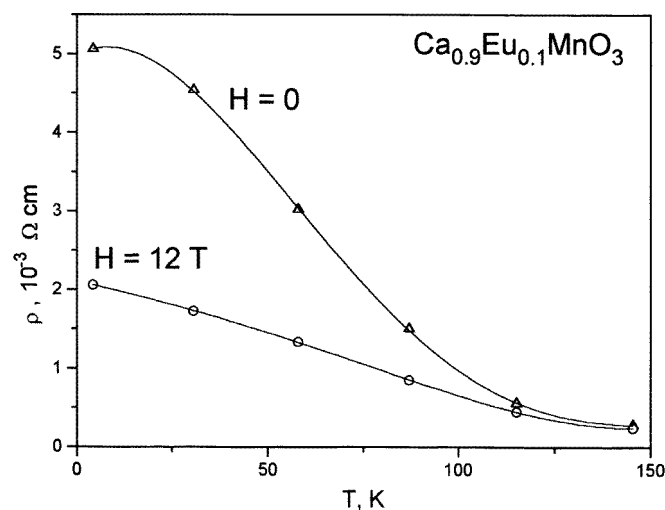


Figure 4. Temperature dependence of the resistivity for $\text{Ca}_{0.9}\text{Eu}_{0.1}\text{MnO}_3$ measured on cooling with $H = 0$ and $H = 12$ T.

It is well known that the superexchange interactions $\text{Mn}^{4+}\text{-O-Mn}^{4+}$ in oxides with a perovskite structure are antiferromagnetic while the superexchange interactions $\text{Mn}^{4+}\text{-O-Mn}^{3+}$ and $\text{Mn}^{3+}\text{-O-Mn}^{3+}$ in orbitally and charge-disordered phases are strongly positive if the Mn-O-Mn angle is close to 180° [7]. The substitution of Ca^{2+} by Eu^{3+} leads to an increase in the ferromagnetic part of the superexchange interaction due to the increase in the Mn^{3+} content; so the magnetization rises drastically (figure 1). The magnetization drop at $x > 0.1$ probably results from the formation of domains with a regular arrangement of Mn^{3+} and Mn^{4+} in the 1:3 ratio. The charge-ordered (1:3) phase was revealed in the $\text{Ca}_{0.8}\text{Pr}_{0.2}\text{MnO}_3$ sample by neutron diffraction [6]. Charge ordering leads to the formation of

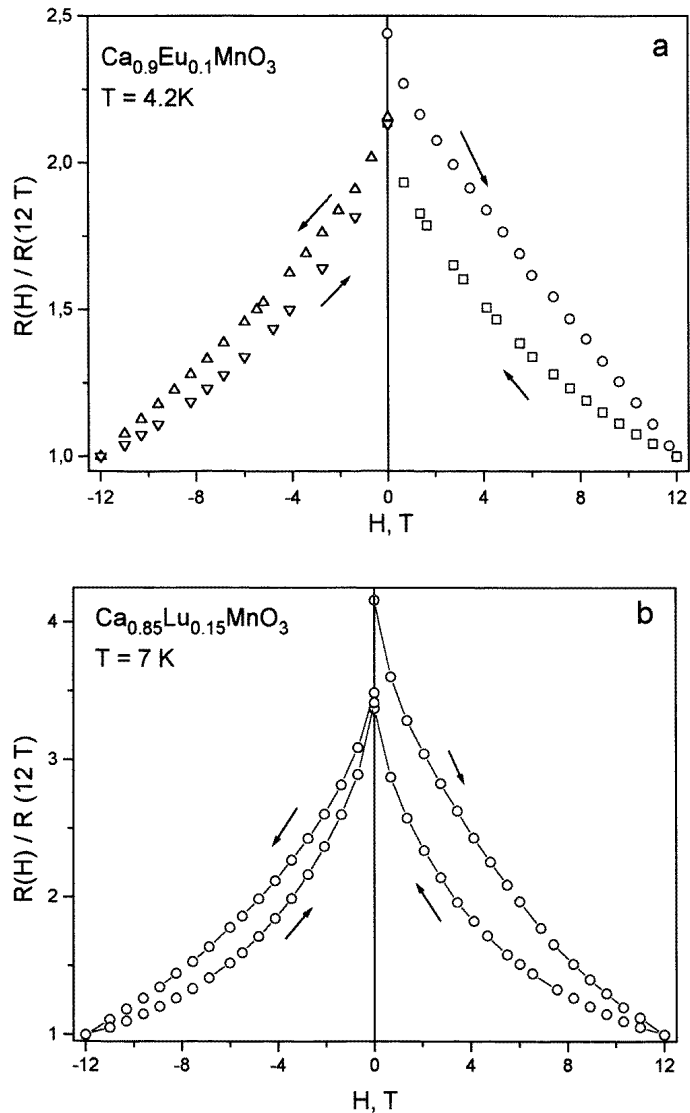


Figure 5. Magnetic field dependence of the MR recorded for (a) $Ca_{0.9}Eu_{0.1}MnO_3$ at 4.2 K and (b) $Ca_{0.85}Lu_{0.15}MnO_3$ at 7 K.

the antiferromagnetic C-type structure [6]. We suppose that the samples with $0.1 \leq x \leq 0.2$ consist of a ferromagnetic charge-disordered phase and the antiferromagnetic charge-ordered (1:3) phase. The metamagnetic behaviour (figure 3) results most probably from some domains of the antiferromagnetic C-type phase transforming to the ferromagnetic phase in the applied field. The transition from the antiferromagnetic state to the ferromagnetic state induced by the magnetic field has been observed for the charge-ordered (1:1) phase in $Pr_{1-x}Ca_xMnO_3$ ($0.3 \leq x \leq 0.5$) perovskites [2]. We think that the peculiarities of the resistivity versus field dependences (irreversibility and field hysteresis; see figure 5) result from the collapse of the charge-ordered state. The charge-ordered (1:3) state is more stable

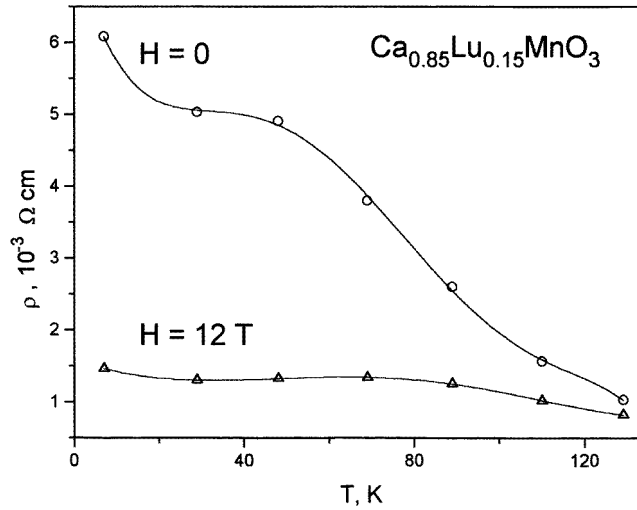


Figure 6. Temperature dependence of the resistivity for $\text{Ca}_{0.85}\text{Lu}_{0.15}\text{MnO}_3$ measured on cooling with $H = 0$ and $H = 12$ T.

than the 1:1 state [2] and the magnetic field of 12 T is not sufficient for full ‘melting’ of the charge-ordered (1:3) phase.

References

- [1] Schiffer P, Ramirez A P, Bao W and Cheong S-W 1995 *Phys. Rev. Lett.* **75** 3336
- [2] Yoshizawa H, Kawano H, Tomioka Y and Tokura Y 1995 *Phys. Rev. B* **52** 145
- [3] Zener C 1951 *Phys. Rev.* **82** 403
- [4] Wollan E O and Koehler W C 1955 *Phys. Rev.* **100** 545
- [5] MacChesney J B, Williams H J, Potter J F and Sherwood R C 1967 *Phys. Rev.* **164** 779
- [6] Jirak Z, Krupicka Z, Simsa Z, Dlouha M and Vratislav A 1985 *J. Magn. Magn. Mater.* **53** 153
- [7] Goodenough G 1963 *Magnetism and the Chemical Bond* (New York: Interscience)