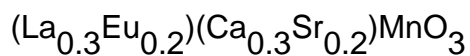


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Sharp step-like metamagnetic transition in the charge-ordered manganite compound $(\text{La}_{0.3}\text{Eu}_{0.2})(\text{Ca}_{0.3}\text{Sr}_{0.2})\text{MnO}_3$

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Received 9 June 2004, in final form 8 December 2004

Published 28 January 2005

Online at stacks.iop.org/JPhysCM/17/989

Abstract

We have performed transport, magnetization and specific heat measurements on the ABO_3 -type half-doped $(\text{La}_{0.3}\text{Eu}_{0.2})(\text{Ca}_{0.3}\text{Sr}_{0.2})\text{MnO}_3$ (LECSMO) manganite. At $T = 2$ K, a sharp step-like metamagnetic transition in the magnetization with a critical field of 3.3 T is observed. The transition is much sharper than that seen at higher temperatures ($T \geq 3$ K). Such step-like transitions have previously been reported only in Pr-based manganites, but the present data show that the step-like metamagnetism can also be found in other manganite compounds.

Charge ordering of the Mn^{3+} and Mn^{4+} ions at specific sites accompanied by antiferromagnetic (AFM) magnetic order has been observed to coexist with a metallic ferromagnetic (FM) state in half-doped manganites of the type $\text{R}_{0.5}\text{A}_{0.5}\text{MnO}_3$ ($\text{R} = \text{La, Pr, Nd}$; $\text{A} = \text{Ca, Sr}$) [1–3]. The resulting phase-separated state in systems such as $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ transforms to a fully FM state upon the application of large magnetic fields [1, 3]. Since Pr-based compounds present very stable charge-ordered (CO) and orbital-ordered (OO) states [4], the reduction of the robustness of these states by a magnetic field has been facilitated by diluting the Mn sublattice through doping with both magnetic and non-magnetic ions [5–13]. The transformation of the CO AFM to a FM metallic state can manifest itself in a series of extremely sharp metamagnetic steps at low temperatures [5–11]. The origin of such sharp steps has been suggested to lie in martensitic-like avalanches [14] and the Barkhausen effect [15] as reported for other metallic hard magnetic compounds.

Apart from the Pr-based systems, the above-mentioned sharp steps have not been demonstrated in other hole-doped manganites without Pr. This leaves open the possibility that there is some factor intrinsic to the magnetic Pr ions which is responsible for the existence of the sharp steps. We report sharp metamagnetic behaviour in a Eu-doped manganite sample, $(\text{La}_{0.3}\text{Eu}_{0.2})(\text{Ca}_{0.3}\text{Sr}_{0.2})\text{MnO}_3$ (LECSMO). To our knowledge this is the first non-Pr-doped

manganite material demonstrated to exhibit sharp metamagnetic behaviour typically associated with the Pr-doped manganites.

LECSMO possesses a large size disorder in the A site: both Eu (ionic radius 1.118 Å) and Sr (1.31 Å) have been substituted simultaneously in the parent ABO_3 compound to induce a size disorder of approximately 0.0039 \AA^2 and to keep the average A-site ionic radius ($r_A \sim 1.204 \text{ \AA}$) close to that of the $La_{0.5}Ca_{0.5}MnO_3$ (LCMO) ($r_A \sim 1.198 \text{ \AA}$) standard composition. Note that these values are somewhat larger than that of the Pr-based compounds ($r_A = 1.18 \text{ \AA}$). This observation demonstrates that the sharp metamagnetic transitions in the low temperature manganites are not associated with some particular characteristic of Pr ions, but more likely associated with strain effects between the different phases as has been suggested previously [8].

The $(La_{0.3}Eu_{0.2})(Ca_{0.3}Sr_{0.2})MnO_3$ sample was synthesized by a conventional solid state reaction route. The constituent oxides and carbonates were mixed in stoichiometric proportions and calcinated at $950 \text{ }^\circ\text{C}$. Subsequent sinterings were done in the temperature range of $1100\text{--}1400 \text{ }^\circ\text{C}$ with several intermediate grindings. The sample was characterized by x-ray diffraction (XRD) studies. Electrical resistance and magnetoresistance measurements were performed using a standard dc four-probe method in the temperature range of $5\text{--}320 \text{ K}$. Magnetization measurements were performed as a function of field and temperature using a commercial SQUID magnetometer. Specific heat measurements as a function of magnetic field and temperature were performed using the relaxation method in a commercial measurement system. The magnetization measurements and the specific heat measurements were performed on the same piece of sample material. In addition, the data for the magnetization and specific heat isotherms were acquired after heating the sample to 300 K (well above T_C or any ordering temperature) during the course of the isothermal measurement to eradicate any hysteretic effects. Also, heating the sample to a high temperature of 300 K makes sure that we completely remove the history of charge ordering.

The XRD measurements (not shown here) of the $(La_{0.3}Eu_{0.2})(Ca_{0.3}Sr_{0.2})MnO_3$ sample reveal it to be a single-phase compound with a distorted orthorhombic structure (space group $Pnma$, No 62). Refinement of the XRD pattern by Rietveld analysis (FULLPROF code) yields lattice parameters of $a = 5.431(2) \text{ \AA}$, $b = 7.663(2) \text{ \AA}$ and $c = 5.432(4) \text{ \AA}$. The results of electrical resistance versus temperature measurements for the $(La_{0.3}Eu_{0.2})(Ca_{0.3}Sr_{0.2})MnO_3$ sample are shown in figure 1, from which it can be seen that the sample shows a sharply rising resistivity with decreasing temperature, consistent with a predominantly charge-ordered state. Zero-field resistance measurements could not be performed below $T \approx 100 \text{ K}$ because the resistance increased beyond the measurable limit of the instrument. The resistivity measured in applied magnetic fields of 5 and 7 T reveals that the charge-ordered insulating state transforms to metallic state through an insulator–metal transition at $T \approx 110 \text{ K}$ as indicated by the peak in these measurements. A very high residual resistance in the metallic state may be attributed to various factors such as pinning of Mn ion spin at the grain boundaries, defects, phase separation etc. Owing to all these factors, the resistivity in the metallic state is well above the Mott–Ioffe–Regel universal limit of $0.3 \text{ } \Omega \text{ cm}$.

The zero-field-cooled (ZFC) and field-cooled (FC) magnetization versus temperature measurements of $(La_{0.3}Eu_{0.2})(Ca_{0.3}Sr_{0.2})MnO_3$, carried out in a field of 50 Oe , are shown in figure 2. The Curie point (T_C) occurs at $T \approx 75 \text{ K}$ (T_C is taken as the bifurcation temperature of the ZFC and FC magnetization curves). The inset in figure 2 shows the inverse susceptibility (including the identical measurements as the main panel and as measured in a field of 5 kOe) as a function of temperature. The inverse magnetic susceptibility is linear above $T \approx 270 \text{ K}$, with a ferromagnetic Weiss theta of $\sim 150 \text{ K}$. The deviation from Curie–Weiss behaviour occurs at a temperature of around 250 K and signifies the development of short-range order in the system.

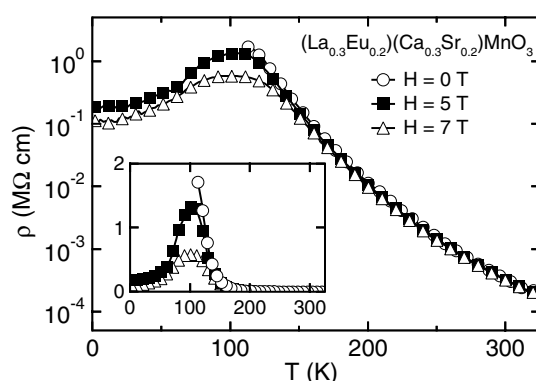


Figure 1. Resistivity as a function of temperature for $(\text{La}_{0.3}\text{Eu}_{0.2})(\text{Ca}_{0.3}\text{Sr}_{0.2})\text{MnO}_3$ at applied magnetic fields of $H = 0, 5$ and 7 T. Data in zero field could not be recorded below 100 K because the resistance was beyond the measurable range of the instrument. The main panel plots data on a logarithmic scale; the inset depicts the results plotted on a linear scale.

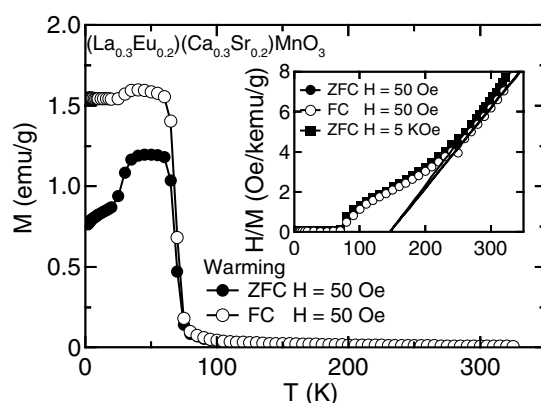


Figure 2. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization versus temperature measured in a field of 50 Oe for $(\text{La}_{0.3}\text{Eu}_{0.2})(\text{Ca}_{0.3}\text{Sr}_{0.2})\text{MnO}_3$. The inset shows the inverse susceptibility (including main panel data and further results measured in a field of 5 kOe) versus temperature. Solid lines in the inset are a simultaneous Curie-Weiss fit to the high temperature ($T \geq 270$ K) data.

Magnetization isotherms of $(\text{La}_{0.3}\text{Eu}_{0.2})(\text{Ca}_{0.3}\text{Sr}_{0.2})\text{MnO}_3$ at various temperatures are shown in figure 3. As shown in figure 3(a), magnetization isotherms at $T = 300, 200$ and 150 K indicate purely paramagnetic behaviour up to the highest measured fields of $H = 50$ kOe. Although at $T = 100$ K (figure 3(a)) there is no significant hysteresis present, there is clear ferromagnetic behaviour observable at lower temperatures in figure 3(b). A metamagnetic transition can be clearly seen in the $M-H$ isotherms at $T = 5, 3$ and 2 K as shown in figures 3(c) and (d), presumably associated with the coexisting FM and AFM states becoming fully ferromagnetic. At 5 K, a clear but broad step in the magnetization appears around a critical magnetic field (H_C) of approximately $H = 25$ kOe with a transition width of 10 – 12.5 kOe. At $T = 3$ K, this magnetic transition shifts to higher fields and the transition region spans the field range of approximately 30 – 40 kOe. This suggests that the AFM phase is stabilized at the expense of the FM phase at lower temperatures in the zero-field-cooled state. The large transition width in the $T = 3$ and 5 K isotherms indicates the inhomogeneous nature

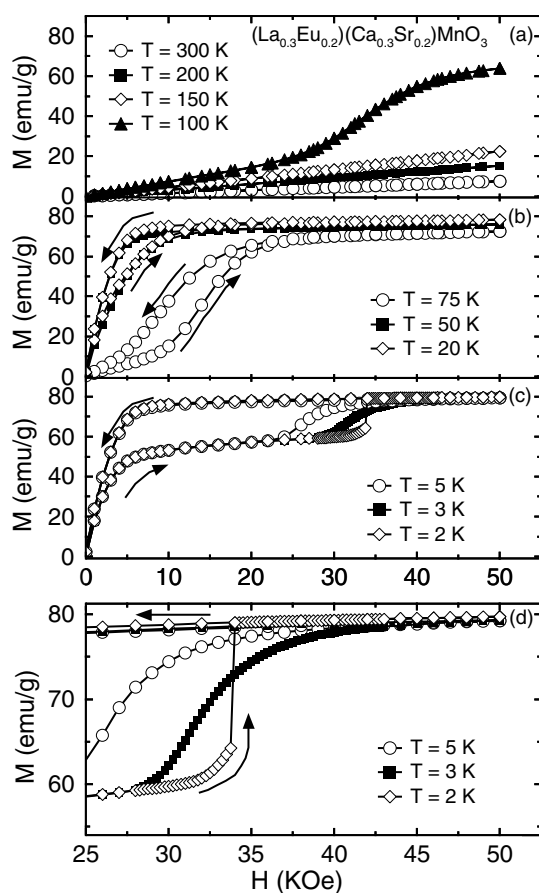


Figure 3. Magnetization versus applied magnetic field isotherms at (a) $T = 300, 200, 150$ and 100 K; (b) $T = 75, 50$ and 20 K; (c) $T = 5, 3$ and 2 K; and (d) magnified for $T = 5, 3$ and 2 K for $(\text{La}_{0.3}\text{Eu}_{0.2})(\text{Ca}_{0.3}\text{Sr}_{0.2})\text{MnO}_3$. Data were acquired after zero-field cooling from $T = 300$ K to the indicated temperature. Measurements were performed by first increasing and then decreasing the magnetic field as indicated by the arrows in the figure. Data in (a)–(c) are plotted using the identical scaling.

of the phase separation. However, there is an appreciable difference in transition width for the $T = 2$ K data, which show a very sharp step. To emphasize the sharpness of the transition, the data in the transition region for the $T = 3$ and 2 K isotherms were recorded in steps of 250 Oe as shown in figure 3(d). The transition width decreases from nearly 10 kOe at $T = 3$ K to a value smaller than the step size of 250 Oe at $T = 2$ K. Such a sharp transition denotes the sudden collapse of charge- and orbital-ordered antiferromagnetic phases, thus resulting in the enhancement of the ferromagnetism.

Figure 4 shows specific heat as a function of applied magnetic field at the isotherms of $T = 2, 3$ and 5 K. The overall shape of the $C(H)$ data can be understood in terms of antiferromagnetic and ferromagnetic spin excitation contributions to the specific heat [16]. An irreversible drop appears in the $T = 3$ and 5 K measurements at nearly the same critical field as the metamagnetic transition in the magnetization isotherms. There is no visible feature in the $T = 2$ K data corresponding to the step, which is consistent with the small step in

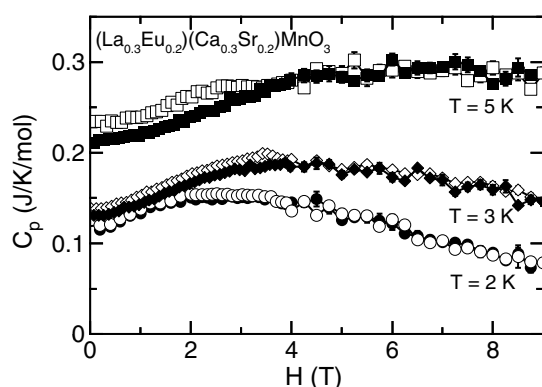


Figure 4. Specific heat (C_p) versus applied magnetic field (H) isotherms at $T = 5, 3$ and 2 K for $(\text{La}_{0.3}\text{Eu}_{0.2})(\text{Ca}_{0.3}\text{Sr}_{0.2})\text{MnO}_3$. The hollow symbols denote the field scan in the forward direction (0–9 T) while the solid symbols denote the field scan in the backward direction (9–0 T).

$C(H)$ recently observed in a similar transition in a Pr-based compound [17]. The absence of a feature at $T = 2$ K also suggests that the relative difference in heat capacity between the two magnetoelectronic phases decreases with decreasing temperature.

It is believed that, in the Mn-site-doped Pr-based manganites, the defects created by doping of other cations such as Ga, Cr, Ni etc at the Mn site results in the formation of FM clusters in the AFM matrix. These FM clusters are formed around the doped ion, thus resulting in a breakdown of long-range AFM order. Therefore, the metamagnetic transition in these compounds has been attributed to the melting of AFM phases to enhance the proportion of the FM phase content. In the present investigation of $(\text{La}_{0.3}\text{Eu}_{0.2})(\text{Ca}_{0.3}\text{Sr}_{0.2})\text{MnO}_3$, we conjecture that the coexistence of FM and AFM phases is enhanced by the large size disorder induced by the combination of cations. In LECSMO, a martensitic-like behaviour (invoked for the Pr manganite compounds) may explain the origin of such sharpness of the step, especially considering the structural distortion and magnetic inhomogeneities in the interfacial regions of the phase-separated state. The presence of a single step in the magnetization of LECSMO, in contrast to multiple steps in many of the Pr-based compounds [5–8, 12, 13], makes a martensitic-like transition an even more plausible cause for such behaviour.

In summary, we have observed sharp metamagnetic steps in the magnetization in the unconventionally Eu-doped CO manganite at low temperatures. This suggests that this class of metamagnetism is not limited to Pr-based compounds and that other means of creating the necessary field-sensitive phase separation via the interplay of tolerance factor and size disorder may also induce sharp magnetic steps as seen in the present Eu-based manganite compound.

Acknowledgments

DGK is grateful to the University Grants Commission (UGC), New Delhi, India, for financial assistance in the form of a Major Research Project. DSR is thankful to CSIR, New Delhi for providing a senior research fellowship (SRF). The PSU authors acknowledge the support of NSF grants DMR-0101318 and DMR-0401486. The authors thank D Buddhikot for help in experiments.

Note added in proof. We have just learned that two other papers, (i) Granja *et al* 2004 *J. Low Temp. Phys.* **135** 111 and (ii) Fonseca *et al* 2004 *J. Appl. Phys.* **95** 7085, have appeared, which confirm the results that Pr is not needed for the effect.

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