4-1999

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Published in *Journal of Applied Physics*, Vol. 85 No. 8 (1999) at doi: 10.1063/1.369987

Recommended Citation

Gebhardt, J. R., Roy, S. and Ali, N.. "Colossal Magnetoresistance in Ce Doped Manganese Oxides." (Apr 1999).

JOURNAL OF APPLIED PHYSICS VOLUME 85, NUMBER 8 15 APRIL 1999

Colossal magnetoresistance in Ce doped manganese oxides

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In this study we investigate the effects of Ce doping in $R_{1-x}A_xMnO_3$ (R = La, Ce, and A = Sr, Ce) on the magnetic and transport properties of this system. For $La_{1-x}Ce_xMnO_3$ (LCMO), an increase in Ce concentration is accompanied by an increase in T_C from 225 to 236 K, as well as an increase in the electrical resistivity. An extremely high resistivity is observed in the new system $Ce_{1-x}Sr_xMnO_3$ (CSMO) which becomes insulating below its Curie temperature of 43 K. A maximum magnetoresistance (MR) ratio of 40% for CSMO and 53% for LCMO is observed. A larger change in resistivity is seen to correspond to an increase in the Ce concentration, however this is offset by an overall resistivity increase which keeps the MR ratio low. The high resistivity may be due to unreacted oxides in the samples. If true, the amount of impurity appears to be proportional to the Ce doping. If this impurity level can be reduced, a significant colossal magnetoresistance effect could be exhibited by these systems. © *1999 American Institute of Physics.*
[S0021-8979(99)35908-9]

Rare-earth doped manganites of the form $R_{1-x}A_xMnO_3$ (R = rare earth, A = divalent cation), have been widely investigated due to their remarkable magnetic and transport properties as well as their potential for device applications.[1] There have been a variety of compounds investigated, with the $La_{1-x}Sr_xMnO_3$ $0.2 \leqslant x \leqslant 0.5$ class of perovskites receiving extensive attention.[2–4] The parent compound, $LaMnO_3$ is an insulator whose crystal and magnetic structure is greatly effected by its stoichiometry in respect to oxygen.[5,6] Stoichiometric $LaMnO_3$ has been shown by Elemans *et al.*[7] to be orthorhombic and antiferromagnetic. When this system is doped with a divalent element such as Sr, a proportionate amount of Mn^{3+}, with electronic configuration $t_{2g}^3 e_g^1$, is substituted with Mn^{4+} (t_{2g}^3) creating holes in the e_g band. The holes permit charge transfer in the e_g state which is highly hybridized with the oxygen $2p$ state.[8] Due to the intra-atomic Hund's rule, this charge transfer induces a ferromagnetic coupling between Mn^{3+} and Mn^{4+} ions which in turn has a dramatic effect on the electrical conductivity.[9] The reduction in disorder of the manganese spins causes a large decrease in the resistivity and the system exhibits a metal–insulator transition near T_C. This process is known as double exchange,[10,11] and was initially thought to be the only significant mechanism involved in colossal magnetoresistance until Millis *et al.*[12] demonstrated that double exchange alone could not account for the large resistivity values at temperatures above T_C. The authors suggested that a strong electron–phonon coupling due to a Jahn–Teller distortion was a necessary component for explaining the transition from a paramagnetic insulator to a ferromagnetic metal occurring at temperatures just below T_C. Colossal magnetoresistance (CMR) arises at temperatures near T_C by inducing a transition into the ferromagnetic state through the application of a magnetic field. The CMR effect in the $La_{1-x}Sr_xMnO_3$ system has been shown to be at a maximum when $x \sim 1/3$.[13]

Recently, a study by Das and Mandal[14–16] has investigated the effect of replacing the divalent cation with tetravalent Ce for a doping of $x = 0.3$. This study raises the possibility of CMR occurring in a system with a mixed manganese valence state of Mn^{2+}–Mn^{3+}. In this work we investigate the role of cerium doping, $0.2 \leqslant x \leqslant 0.4$, on the magnetic and transport properties of $La_{1-x}Ce_xMnO_3$. We then continue with a study of the effects of substituting the trivalent lanthanum with cerium to form the compound $Ce_{1-x}Sr_xMnO_3$. This new system possibly possesses yet another mixed valence state of manganese.

Bulk polycrystalline samples of $Ce_{1-x}Sr_xMnO_3$ (CSMO) and $La_{1-x}Ce_xMnO_3$ (LCMO) for x values between 0.2 and 0.4 were prepared by solid state reaction. Stoichiometric amounts of CeO_2, $SrCO_3$, and MnO_2 powders (CSMO) and La_2O_3, preheated to 900 °C for 12 h, CeO_2 and MnO_2 (LCMO) were thoroughly mixed, then pressed into pellets and sintered in air at 1200 °C (CSMO) and 1100 °C (LCMO) for 96 h with intermediate grindings. The mixed CSMO powders first received a preheating at 900 °C in air for 12 h. Magnetization measurements as a function of temperature from 5 to 375 K and applied magnetic field up to 5.5 T were conducted using a quantum design superconducting quantum interference device (SQUID) magnetometer. Electrical resistance and magnetoresistance was measured, over the same temperature and field range, by the standard four probe method and employed the temperature control and superconducting magnet of the quantum design SQUID. The insulating nature of the CSMO samples did not allow us to take any resistance measurements below 40 K. However, a thermal expansion measurement of the $x = 0.33$ CSMO sample was performed.

In Fig. 1 we present magnetization curves as a function of temperature in an applied field of $H = 0.1$ T for LCMO samples with a Ce doping of $x = 0.2$, 0.3, and 0.4. An impurity phase provides a small contribution to the magnetization of each sample at lower temperatures. The amount of impurity increases with the doping level and is believed to be due to unreacted MnO_2. A magnetization versus temperature scan of MnO_2 powder is shown in the inset Fig. 1(a). The anomaly marked with an arrow occurs at the same tempera-

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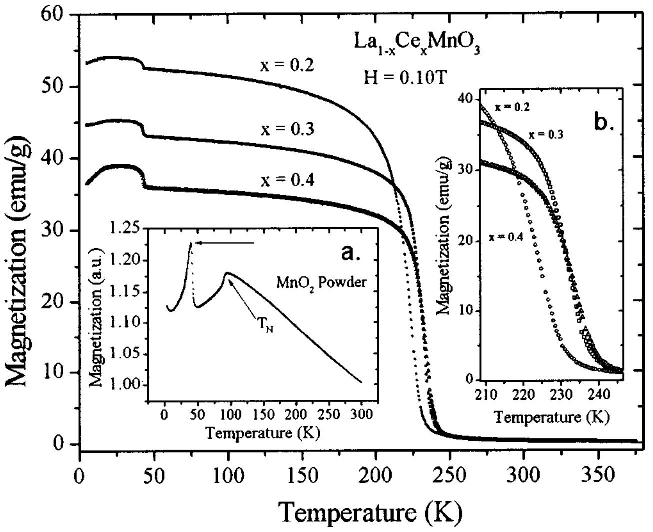

FIG. 1. M vs T curves of LCMO for $x=0.2$, 0.3, and 0.4 in an applied field of 0.10 T. Inset (a); M vs T curve of MnO_2 powder. Arrow points to possible cause of the low field anomaly seen in the LCMO curves. Inset (b); expanded view of the LCMO magnetization curves around T_C.

ture as the impurity phase in the LCMO samples. The Néel temperature of MnO_2 is also indicated in inset Fig. 1(a). At higher temperatures, a sharp drop in the magnetization is observed around T_C. The region around T_C is expanded for clarity in the inset of Fig. 1(b). Three principle effects of the Ce doping level are observed. First, the slope of the magnetization at T_C becomes more pronounced at higher Ce concentrations. Second, as the Ce content increases, there is a drop in the total magnetization at lower temperatures. Third, there is an increase in T_C at higher Ce concentrations. The three samples have a Curie temperature, determined from the peak in the dM/dT vs T curve, of $T_C=225$, 232, and 236 K for $x=0.2$, 0.3, and 0.4, respectively. This is very similar to the 233 K Curie temperature reported by Das *et al.*[15] for an $x=0.3$ doped LCMO sample but is lower than the T_C of 378 K for $La_{1-x}Sr_xMnO_3$.[3]

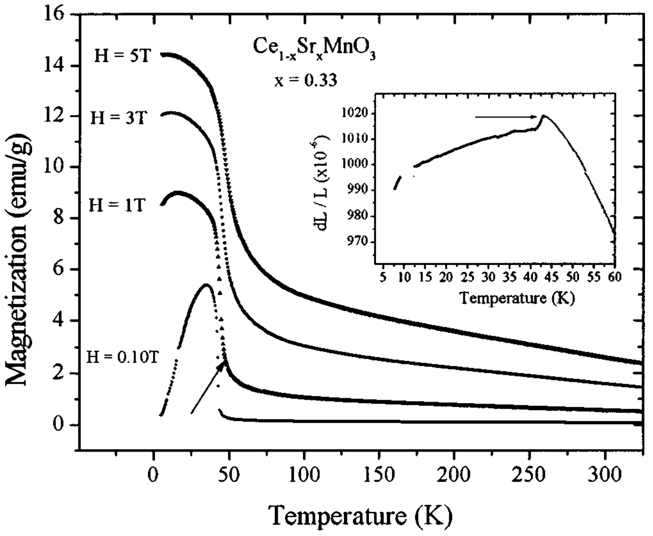

FIG. 2. M vs T curves of the CSMO sample in applied fields of $H=0.1$, 1, 3, and 5 T. Arrow indicates T_C. Inset shows thermal expansion data; the arrow indicates the first order phase transition at T_C.

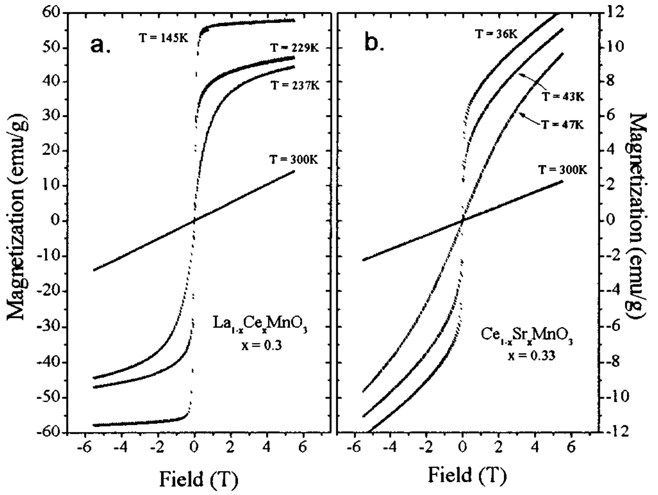

FIG. 3. (a) M vs H curves of the LCMO $x=0.3$ sample at constant temperatures above and below T_C. (b) M vs H curves for the CSMO sample. Below T_C the magnetization shows a near linear response in a field greater than 0.5 T.

Figure 2 shows the magnetization versus temperature data for $Ce_{1-x}Sr_xMnO_3$, $x=0.33$ in applied fields of $H=0.1$, 1, 3, and 5 T. The sample was zero field cooled from room temperature before each M vs T scan. A slight increase in T_C, which is identified with an arrow on the $H=0.1$ T curve, with increasing magnetic field is observed. The inset of Fig. 2 shows thermal expansion data. The step change shown by an arrow in these data occurs at the Curie temperature of $T_C=43$ K and indicates a first order phase transition. The amount of magnetization observed in CSMO is far less than that seen for LCMO in Fig. 1. This may be due to a noncollinear magnetically ordered state. However, this point needs to be further investigated.

Figure 3(a) presents several M vs H curves at temperatures around T_C for LCMO with $x=0.3$. At temperatures below $T_C=232$ K the material is ferromagnetic with saturation occurring at relatively low fields. Above T_C the material

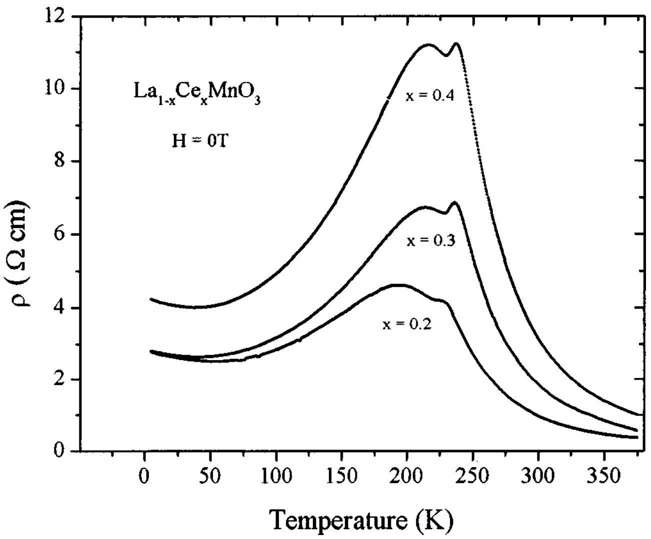

FIG. 4. R vs T data of LCMO for the three Ce dopings showing a large increase in the resistivity with an increase in the Ce concentration.

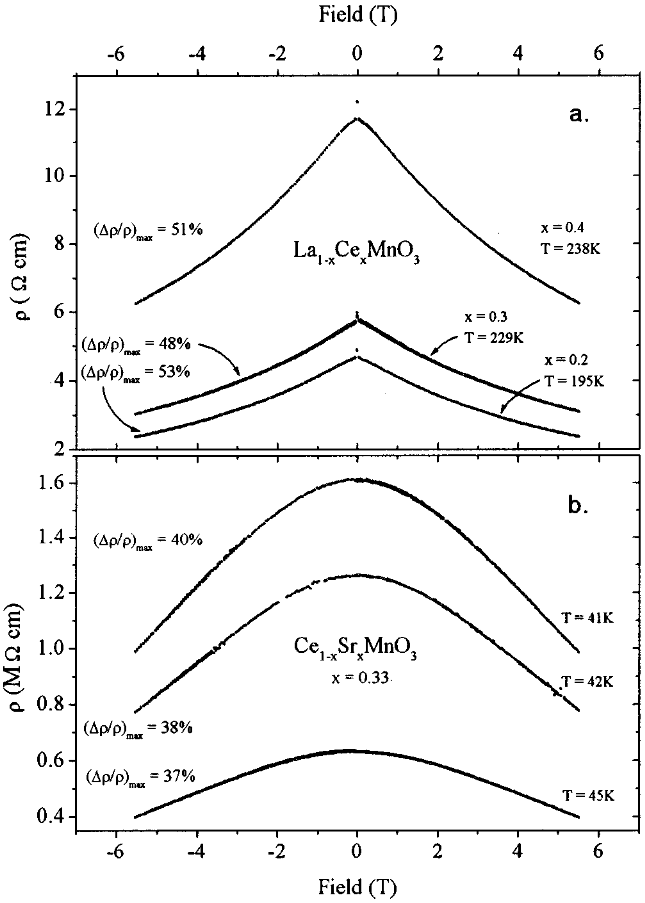

FIG. 5. (a) R vs H curves of the three LCMO samples showing a maximum MR ratio of 53%; (b) R vs H data for the CSMO sample at temperatures just above and below T_C and a maximum MR ratio of 40%.

becomes paramagnetic as demonstrated by the linear M vs H curve at 300 K. Figure 3(b) shows several M vs H curves for the CSMO sample. Below T_C a spontaneous magnetization is observed. Above a field of 0.5 T the magnetization increases almost linearly with field. This may be due to a noncollinear magnetic state as mentioned earlier. Above T_C the material becomes paramagnetic.

Resistance versus temperature in zero applied field are given for the three LCMO samples in Fig. 4. The curves show a sharp peak in the resistivity along with a broad peak at a slightly lower temperature. These peaks shift to lower temperatures with a decrease in cerium doping and is accompanied by a flattening of the sharp resistivity peak. Samples with higher cerium concentration possess a higher resistivity. We believe further investigation over a larger doping range is needed to adequately explain this observation. The sharp peak of the $x=0.3$ sample occurs at a temperature of 237 K and the broad peak 214 K which is in agreement with the results of Das *et al.*[15,16]

In Fig. 5(a) we show magnetoresistance (MR) data as a function of field for the three LCMO samples. The MR curves presented are at the temperature for which $\Delta\rho/\rho$, defined as $[\rho_0-\rho_H]/\rho_0$ where ρ_0 is the zero field resistivity and ρ_H is the resistivity in a 5.5 T applied magnetic field, is a maximum. This temperature at which this maximum occurs is slightly below T_C for $x=0.2$ and 0.3 and very slightly above T_C for the $x=0.4$ sample. Again, the $x=0.4$ sample has a much higher resistivity which accounts for a $\Delta\rho/\rho$ of 51%. A maximum $\Delta\rho/\rho$ of 53% is observed for the $x=0.2$ LCMO sample. The $\Delta\rho/\rho$ of 48% for the $x=0.3$ sample is consistent with Das *et al.*[16] who report a MR ratio of 54% in a 7.7 T field. The MR vs H curves in Fig. 5(b) for the CSMO material were conducted at temperatures slightly above and below T_C. A maximum ratio of 40% at $T=41$ K is observed and decreases with increasing temperature. Resistance measurements below 40 K could not be performed, thus we cannot report on the MR behavior of CSMO at low temperatures.

In conclusion, we investigated the magnetic and transport properties of $La_{1-x}Ce_xMnO_3$ for Ce concentrations of 20%, 30%, and 40% and $Ce_{1-x}Sr_xMnO_3$ for $x=0.33$. For LCMO we found that the Curie temperature and electrical resistivity increase with the Ce concentration, while the low temperature magnetization decreases. MR ratios at all concentrations are comparable, even though a larger change between ρ_0 and ρ_H is observed in samples with a higher Ce concentration. However, this change is offset by the overall large resistivity which makes $\Delta\rho/\rho$ small. Results for the $x=0.3$ sample agree well with the results of Das *et al.*[14–16] Magnetization and thermal expansion data reveal the CSMO sample exhibits a first order phase transition at $T_C=43$ K. The material appears to be a ferromagnetic insulator below T_C and a paramagnetic semiconductor above T_C, however its low temperature phase needs to be confirmed. It shows a maximum MR ratio of 40% at 41 K just below T_C. Further study of these materials including a determination of the cerium and manganese valence states is needed in order to understand the mechanism behind their unique magnetic properties.

This work was supported in part by a grant from the Consortium for Advanced Radiation Source, University of Chicago, Chicago, IL, USA.

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