Unusual field dependence of the resistivity and magnetoresistance in $Nd_{0.5}Ca_{0.5}MnO_3$



1996 J. Phys.: Condens. Matter 8 L455

(http://iopscience.iop.org/0953-8984/8/33/003)

J. Phys.: Condens. Matter **8** (1996) L455–L459. Printed in the UK

**LETTER TO THE EDITOR**

# Unusual field dependence of the resistivity and magnetoresistance in $Nd_{0.5}Ca_{0.5}MnO_3$

R Mahendiran†, R Mahesh‡, R Gundakaram‡, A K Raychaudhuri† and C N R Rao‡

† Department of Physics, Indian Institute of Science, Bangalore – 560 012, India
‡ Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore – 560 012, India

Received 11 June 1996

**Abstract.** An unusually large positive magnetoresistance (MR) is found in the compound $Nd_{0.5}Ca_{0.5}MnO_3$ at low temperatures ($T < 50$ K). The positive MR is seen when the magnetic field is first applied and it collapses at higher fields leading to a large negative MR as observed recently in other manganates showing charge-ordering transition. These magnetic field induced effects (negative MR) show large hysteresis even up to temperatures as high as 200 K. We explain the positive MR as originating from antiferromagnetic ordering in the presence of a ferromagnetic interaction.

The recent observation [1, 2] of a magnetic field induced electronic phase transition in the insulating state of $Ln_{0.5}Sr_{0.5}MnO_3$ (Ln = Pr, Nd) has attracted widespread attention. These materials, belonging to the $ABO_3$ class of perovskite oxides, undergo a transition from a ferromagnetic metallic state to an antiferromagnetic insulating state with decreasing temperature. At the onset of antiferromagnetic (AFM) ordering, these materials show an abrupt increase in resistivity which is attributed to the real space (charge) ordering of the doped holes (i.e. $Mn^{4+}$) [3]. The charge-ordered state is unstable under an applied magnetic field. Typically, the charge-ordered state shows a large negative magnetoresistance (MR) on the application of a magnetic field which destroys the AFM ordering as well as the charge-ordering. This magnetic field-induced transition is believed to be of first order and shows a distinct hysteresis accompanying the increase and decrease of the externally applied field. The magnitude of the hysteresis increases with decreasing temperature. Such a first-order field-induced transition and a large negative MR (with associated hysteresis on field cycling) is also found in polycrystalline samples of $La_{0.5}Ca_{0.5}MnO_3$ [4], $Pr_{0.7}Sr_{0.25}Ca_{0.05}MnO_3$ [5] and in polycrystalline as well as single-crystal samples of $Pr_{0.7}Ca_{0.3}MnO_3$ [6]. These samples are however, insulating down to 4.2 K and the resistivity ($\rho$) in zero field does not show a transition from a metallic state to a charge ordered insulating state.

The charge ordering phenomenon is associated with the presence of AFM interaction which generally becomes more prominent as the $Mn^{4+}$ content increases beyond 50%. In this composition range, the long-range ferromagnetic order found in the compositions with lower $Mn^{4+}$ content no longer exists. Importantly, interesting phenomena such as charge ordering and the field-induced first-order transition can be found in materials which have a low average $A$-site cation radius $\langle r_A \rangle$, where $A$ refers to the $A$-site of the $ABO_3$ structure. This site is occupied by cations like La, Nd or Pr or alkaline earth ions like Ca or Sr. The replacement of La by Pr decreases the $\langle r_A \rangle$ markedly and affects the electrical and

0953-8984/96/330455+05$19.50  

magnetic properties by narrowing the band width of $e_g$ electron [7–9]. The strong Coulomb interaction can localize the carriers in such a narrow band system.

In this letter we report the preliminary results of an interesting field-induced transition in $Nd_{0.5}Ca_{0.5}MnO_3$ which has a much smaller $\langle r_A \rangle$ compared to systems studied hitherto. In addition to the magnetic field-induced electronic phase transition we find several other interesting features some of which we report briefly within the limited scope of this letter.

$Nd_{0.5}Ca_{0.5}MnO_3$ was prepared by the solid state reaction of $Nd_2O_3$, $CaCO_3$ and $MnO_2$ at 1273 K for 24 h followed by sintering at 1373 K for 24 h in flowing oxygen. The sample as characterized by powder x-ray diffraction at room temperature was found to be orthorhombic and had an $Mn^{4+}$ content of 52% as determined by redox titration. Magnetoresistance was measured by the four probe method in the temperature range 4.2–350 K and in magnetic fields up to 6 T using a superconducting solenoid. The low field dc susceptibility (at 40 G) was measured using a Faraday balance.

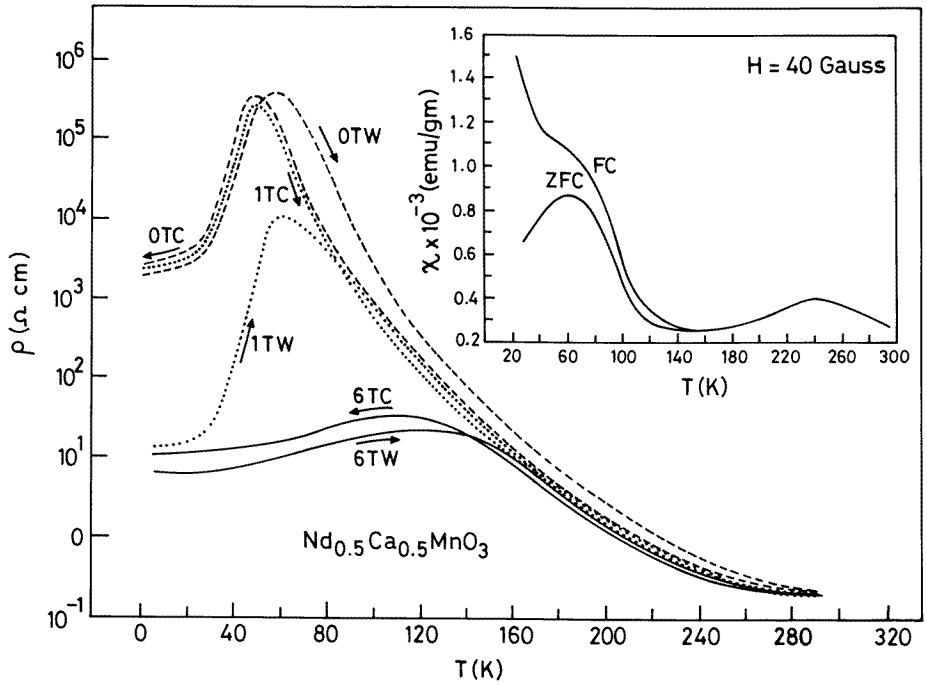


**Figure 1.** Resistivity of $Nd_{0.5}Ca_{0.5}MnO_3$ as a function of temperature for 0 T, 1 T and 6 T (see text for the details). Inset shows zero field cooled (ZFC) and field cooled (FC) susceptibilities ($\chi$) at 40 G as a function of temperature.

Figure 1 shows the temperature variation of resistivity ($\rho$) of $Nd_{0.5}Ca_{0.5}MnO_3$ at zero field. Unlike in the samples discussed in the earlier reports [1, 2, 5, 6], $\rho$ shows a peak at $T_p = 60$ K. The value of the resistivity at the peak ($\rho_p$) is very large and is in excess of $10^5$ Ω cm. For $T < T_p$, $\rho$ falls sharply by two orders of magnitude down to 35 K and stays at a high value as the sample is cooled to 4.2 K. As shown in figure 1, the data were recorded in the following manner. The sample was first cooled to 4.2 K in zero field and data were recorded up to room temperature while warming (marked 0TW). Subsequently the sample was cooled to 4.2 K and the cooling data were recorded (marked 0TC). A strong

difference was found between the data recorded during the warming and the cooling cycles. (This difference is reproducible and it is not due to the sample being in bad thermal contact with the thermometer.) This hysteresis on temperature cycling is probably related to the structural transition observed from the neutron scattering experiments done on the same material [11]. At 4.2 K the field dependence of magnetoresistance was performed for one full cycle of the magnetic field (from 0 T $\rightarrow$ 6 T $\rightarrow$ 0 T $\rightarrow$ $-6$ T $\rightarrow$ 0 T). The field was then ramped up to 6 T and resistivity data were recorded while warming (6TW). The sample was subsequently cooled down and the data recorded (6TC) (see figure 1). In the 6 T field $\rho$ has decreased by orders of magnitude. At 60 K the $\rho$ has been suppressed by more than four orders of magnitude in a field of 6 T. The peak in $\rho$ has become very shallow and shifted to 150 K. The MR is nearly 99.99% at $T_p(= 60$ K). In order to see the effect of a lower field we reduced the field to 1 T and recorded the warming (1TW) and cooling (1TC) curves. As can be seen from figure 1, there is a large difference in $\rho$ measured during the warming and the cooling cycles below 60 K. It appears that when the field is reduced from 6 T to 1 T at 4.2 K, the sample retains the 'memory' of the previously applied field up to 60 K. This large memory effect is also seen for fields other than 1 T. In order to see that such a behaviour arises from a memory effect, we have carried out the following experiment. The sample was first cooled in zero field and at 4.2 K the field was increased to 1 T (i.e. without completing one full field cycle to 6 T as before). The resistivity data were recorded during warming and cooling cycles. In this case we find that $\rho$ closely follows the $\rho$–T curves at zero field. This indicates that the curve 1TW in figure 1 is caused by the memory of the 6 T field which had been applied before the 1 T field was applied.

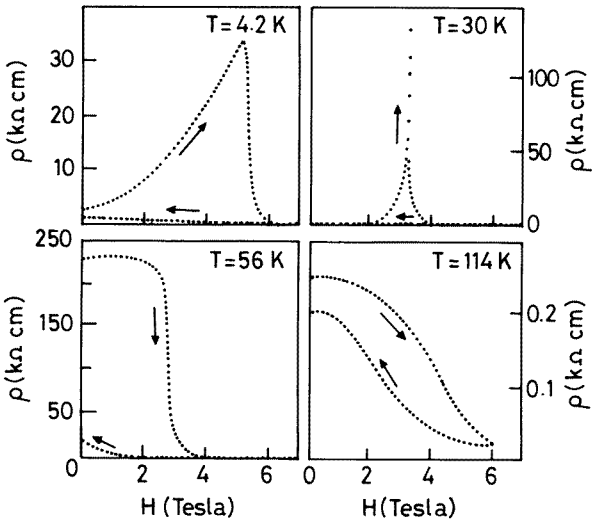


**Figure 2.** Resistivity of $Nd_{0.5}Ca_{0.5}MnO_3$ as a function of applied magnetic field at different temperatures. The temperatures are marked in the figure and the arrow indicates the direction of the field sweep.

In the inset of figure 1 we show the low field magnetic susceptibility data measured using the Faraday balance. The most prominent feature of the susceptibility data is the transition around 60 K where the zero field cooled (ZFC) curve differs significantly from the field cooled (FC) curve. This temperature also coincides with the peak in resistivity. We are currently investigating the nature and origin of this magnetic transition.

In figure 2, we show the resistivity data as a function of applied magnetic field at some temperatures. For recording these data we had to warm the sample to $T > 200$ K for every temperature point and cool the sample in zero field to the desired temperature. This was done to clear any memory of the previously applied field. When $T < T_p$, $\rho$ rises sharply to a rather high value on the first application of magnetic field. With further increase in $H$, $\rho$ collapses rather sharply to a value less than the zero field value. We denote the field at which the sharp decrease in $\rho$ occurs as $H^*$. The value of $H^*$ is maximum at 4.2 K and decreases as $T$ is increased and eventually becomes very small at $T \approx 60$ K. The large giant positive MR observed for $H < H^*$ occurs at $T < 50$ K. However, the sharp reduction in $\rho$ at $H \approx H^*$ (i.e., the large negative MR) persists even for $T > 40$ K. While the large negative MR for $H > H^*$ with the accompanying hysteresis has been observed earlier [1–6], the giant positive MR on the first application of the field at low temperature for $H < H^*$ is a new observation. We see the large positive MR only when the sample is heated above 200 K before data are taken at each temperature so that no field memory is retained in the system. If this is not done one sees only the large negative MR similar to that observed in other charge ordered systems.

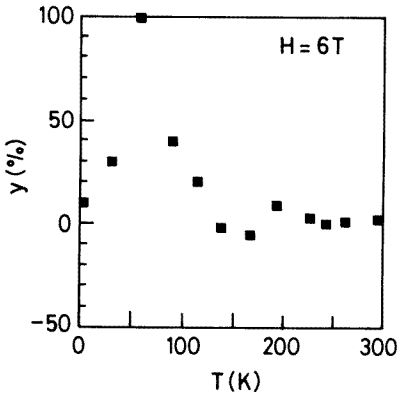


**Figure 3.** The nonclosure $y$ of the hysteresis in magnetoresistance as a function of temperature.

At a given temperature, when the field is reduced to 0 T from 6 T, $\rho$ increases again but does not reach the starting zero field value resulting in hysteresis (see figure 2). Thus the hysteresis loop does not close at $H = 0$ T. The extent of the nonclosure of the hysteresis at 0 T is shown in figure 3 as a function of $T$. The nonclosure is defined by the quantity $y = (\rho_0 - \rho_0^*)/\rho_0$, where $\rho_0$ is the zero field resistivity before the application of the field and $\rho_0^*$ is the same after the field has been increased to 6 T and then reduced to 0 T. The magnitude of $y$ reaches a maximum at $T = T_p$ and decreases as $T$ is increased further. The $y$ becomes significant below 100 K where (as seen in the inset of figure 1) the FC and ZFC susceptibilities start differing and $y$ has finite value even up to 240 K. Interestingly, in the temperature range 140–190 K $y$ even becomes negative. It is noteworthy that in this temperature region the unit cell volume also changes as much as 0.45% as revealed by our recent neutron scattering experiments [11]. It has also been found from the neutron scattering experiments that the structural parameters such as the Mn–O bond distance and the Mn–O–Mn bond angle undergoes substantial change on cooling to 4.2 K. These structural changes are expected to have a marked effect on the magnetic exchange and the resulting magnetic state of the sample.

As pointed out earlier the important observation is the existence of a giant positive MR at low $T$ for $H < H^*$. We explain this as the characteristic of a two-sublattice antiferromagnet proposed by Yamada and Takeda [10]. Based on the molecular field approximation these authors argue that for a two-sublattice antiferromagnetic metal, the resistivity ($\rho$) can be decomposed into two components which are related to the transverse and the longitudinal modes of spin fluctuations. The application of a magnetic field increases the spin fluctuation in one sublattice and decreases in the other. Hence with increasing field, $\rho$ initially increases and for larger field when both the sublattices are aligned in the same direction resistivity starts decreasing as in a ferromagnet. If the ferromagnetic interaction is stronger than the AF interaction (which aligns the spins antiferromagnetically in the two sublattices), one will not see any positive MR. This probably happens at higher temperatures where we observe only negative magnetoresistance. These effects are all related to the coexistence of FM and AFM interactions, the positive MR being determined by the relative strengths of these two interactions.

In conclusion, we have found interesting features in the magnetoresistance studies of $Nd_{0.5}Ca_{0.5}MnO_3$ which include a new observation of the giant positive MR which collapses at higher fields, a large hysteresis in MR as a function of field and a large memory effect. Magnetization studies along with the structural determination in the presence of magnetic field may shed new light on the understanding of these new observations and further studies are in progress.

One of the authors (AKR) thanks Department of Science and Technology, Government of India for financial support.

## References

[1] Tomioka Y, Asamitsu A, Moritomo Y, Kuwahara H and Tokura Y 1995 *Phys. Rev. Lett.* **74** 5108
[2] Kuwahara H, Tomioka Y, Asamitsu A, Moritomo Y and Tokura Y 1995 *Science* **270** 961
[3] Goodenough J B 1955 *Phys. Rev.* **100** 580 and references therein
[4] Xiao G, McNiff E J, Gong G Q, Gupta A, Canedy C L and Sun J Z 1996 preprint
[5] Maignan A, Simon Ch, Caignaert V and Raveau B 1996 *J. Magn. Magn. Mater.* **152** L5–L9
[6] Lees M R, Barrat J, Balakrishnan G, Mck Paul D and Yethiraj M 1995 *Phys. Rev.* B **52** R14303
Barrat J, Lees M R, Balakrishnan G and Mck Paul D 1996 *Appl. Phys. Lett.* **68** 424
[7] Hwang H Y, Cheong S W, Radaelli P G, Merezio M and Batlogg B 1995 *Phys. Rev. Lett.* **75** 914
[8] Mahesh R, Mahendiran R, Raychaudhuri A K and Rao C N R 1995 *J. Solid State Chem.* **120** 204
[9] Coey J M D, Viret M, Rano L and Ounadjela K 1995 *Phys. Rev. Lett.* **75** 3910
[10] Yamada H and Takeda S 1973 *J. Phys. Soc. Japan* **34** 51
[11] Vogt T, Cheetam A K, Mahendiran R, Raychaudhuri A K, Mahesh R and Rao C N R 1996 *Phys. Rev.* B submitted