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Metal–insulator and magnetic transition in Nd$_{1-x}$Sr$_x$MnO$_3$ solid solutions

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In this article we report the results of electrical resistivity, thermopower and ac magnetic susceptibility measurements on Nd$_{1-x}$Sr$_x$MnO$_3$ with $x = 0.40$, 0.33 and 0.30. The room temperature paramagnetic to low temperature ferromagnetic transition temperature T_C and electrical resistivity $\rho(T)$ are observed to depend on the processing conditions. $\rho(T)$ exhibits a shoulder at T_C and a peak below T_C. The latter peak is likely to be of intrinsic origin rather than due to lattice defects/grain boundaries, etc. The resistivity decreases with increasing x as well as upon Ar annealing. Upon Ar annealing the thermopower $[S(T)]$ below T_C shows no appreciable change in magnitude, while above T_C $|S|$ decreases. $S(T)$ exhibits considerable differences between $x = 0.33$ and $x = 0.3$, which we attribute to a dopant induced insulator–metal ($I-M$) transition. Our thermopower data along with the resistivity and magnetic measurements show that the changes in the observed features in the $\rho(T)$ and $S(T)$ cannot be related to magnetic ordering alone but the electronic transitions also have to be taken into consideration. © *1999 American Institute of Physics.* [S0021-8979(99)76308-5]

I. INTRODUCTION

Doped perovskite manganites with the general formula Ln$_{1-x}$A$_x$MnO$_3$ (Ln=La, Nd, Sm, Pr, etc. and A=Ba, Ca, Sr, etc.) which exhibit colossal magnetoresistance (CMR)[1] undergo simultaneous magnetic, electronic and structural transitions in a narrow temperature interval for certain concentration values (e.g., $x = 0.20$ in LaSrMnO and $x = 0.33$ in NdSrMnO). The general understanding is that the magnetic ordering paramagnetic–ferromagnetic (PM–FM) transition induces a structural distortion which in turn changes the electronic band structure leading to an insulator-to-metal ($I-M$) transition and decreased scattering of the charge carriers by the spins during the ordering process resulting in a resistivity anomaly across the PM to FM transition.[2] While there are many reports on the transport properties of these CMR oxides there is considerable scatter in reported values of transition temperatures for the same composition reported by different groups[3-6] possibly due to various factors such as lattice strain, inhomogeneous distribution of the cations, oxygen nonstoichiometry, etc. From the information available in the literature in this specific composition range, it is observed that the effects due to both the transitions (PM–FM, $I-M$) overlap. There are no reports to date showing distinct changes in resistivity features that can clearly separate the effects due to the magnetic transition and the $I-M$ transition.

II. EXPERIMENTAL DETAILS

Polycrystalline Nd$_{1-x}$Sr$_x$MnO$_3$ with $x = 0.4$, 0.33, 0.3 were prepared by conventional solid state method. X-ray diffraction results for the O$_2$ annealed samples showed that the compounds were of single phase with impurity phase below 5 vol%. Wet chemical analysis by inductively coupled plasma technique confirmed the stoichiometry of the compounds to the formulae indicated. The batches that were annealed in O$_2$ and Ar are designated as samples IO2 (0.4),

IIO2 (0.33), IIIO2 (0.3) and IAr (0.4), IIAr (0.33), IIIAr (0.3), respectively. The numbers in parentheses indicate Sr composition. The ac susceptibility measurements were performed at a frequency of 313 Hz in the temperature range 300–12 K. The van der Pauw technique was used for resistivity measurement and for dc thermopower measurement, the absolute temperature and the temperature gradient were measured using a calibrated Au–Fe (0.07%)/chromel thermocouple.

III. RESULTS AND DISCUSSION

The general observations from the magnetic, electrical and thermopower measurements are as follows: The samples IO2, IIO2 and IIIO2 showed low room temperature resistivity ρ_{RT} (30–170 mΩ cm). The resistivity increases with decreasing x and upon Ar annealing due to reduced Mn^{4+} (hole) concentration. ρ_{RT} of sample I increases by 3 orders of magnitude upon Ar annealing but only about five times for samples II and III (Table I). The resistivity, ac susceptibility and thermopower of the O$_2$ and Ar-annealed samples are shown in Figs. 1–3. The Ar-annealed samples have lower magnetic transition temperatures than the O$_2$-annealed ones. The shift in T_C due to change of annealing environment decreases as we move from $x = 0.40$, 0.33, 0.30. In all the samples $\rho(T)$ shows a prominent peak below T_C (which we call as T_p). For $x = 0.40$, T_p nearly coincides with T_C, and both shift to lower temperatures upon Ar annealing. For $x = 0.33$ and 0.30 T_C shows up as a shoulder above T_p which disappears upon Ar annealing with a greatly reduced shift in T_C and T_p.

While other groups have observed such two peak features in the $\rho(T)$ curve, this behavior has been explained as occurring due to magnetic inhomogeneity/grain boundary effects, etc.[7] However this two peak feature is also observed in 1500 °C fired samples of Nd$_{0.67}$Sr$_{0.33}$MnO$_3$, where the prominence of the peak around T_p and T_C can be reversibly varied by mere high temperature annealing under varying

TABLE I. Lattice parameters, room and low temperature resistivity and typical thermopower values of $Nd_{1-x}Sr_xMnO_3$ along with the magnetic and insulator–metal transition temperatures.

Sample	Lattice parameters (Å)	ρ (mΩ cm) 300 K	ρ (mΩ cm)	T_C (K)	T_p (K)	$S(T)$ μV/K
IO2	Orthorhombic 5.468, 10.87, 5.003	32	10 (30 K)	262	254	−27 (255 K)
IAr	⋯	14 876	1121 (30 K)	228	224	−30 (256 K)
IIO2	Cubic 3.85	126	103 (35 K)	230	203	−16 (260 K)
IIAr	⋯	673	566 (35 K)	216	210	−13 (260 K)
IIIO2	Cubic 3.86	137	561 (30 K)	207	160	−6 (260 K)
IIIAr	⋯	647	2762 (30 K)	181	151	−1 (259 K)

partial pressures.[8] Hence the two peak feature may not arise only from magnetic inhomogeneity/grain boundary effects etc. but may be intrinsic to the compound.

The room temperature thermopower for all samples is found to be negative, $|S|$ decreasing with x. The rapid rise observed in $S(T)$ for $x=0.30$ as the temperature decreases is suggestive of carrier trapping.[9] The sudden drop of the thermopower at T_C may arise from condensation of trapped carriers into extended states according to a mechanism proposed recently,[10] leading to a corresponding decrease in resistivity. $S(T)$ below 280 K for IIIO2 and IIIAr is predominantly positive while that of IIO2 and IIAr is negative. The sudden change in the temperature dependence of S as x changes from 0.30 to 0.33 may be an indication of a dopant induced insulator–metal transition in the paramagnetic state similar to that observed for $La_{1-x}Sr_xMnO_3$.[11] Higher metallicity due to excess doping can make the effect of polaron condensation less dramatic, thereby resulting in only a slope change across T_C in $S(T)$ for samples II and III.

Although there is a large difference in the low temperature resistivity between the O_2-annealed and Ar-annealed samples (see Table I) the thermopower values are essentially the same at these temperatures. Thus the thermopower is found to be less sensitive to the annealing environment at low temperatures. We have studied the thermopower behavior of $Nd_{0.67}Sr_{0.33}MnO_3$ samples sintered at 1500 °C (designated as IV, see Fig. 2), which have lower resistivity (80

mΩ cm) as compared to that of 1400 °C processed samples (126 mΩ cm). We found little difference between 1500 and 1400 °C processed samples in the $S(T)$.

While it is not possible to ascribe the change in slope of $S(T)$ to either the $I-M$ transition or to the magnetic transition unequivocally, when both of them occur in a narrow temperature range such as for $x=0.4$ or 0.33 the effect of polaron condensation is clearly seen for $x=0.3$ where the two transitions are about 40 K apart (as compared to 25 K for $x=0.33$). The literature on NdSrMnO systems indicates that the composition range which shows a maximum magnetoresistance (MR) effect is around $x\sim0.33$–0.30. The thermopower features change drastically within this narrow composition range.

There have been other reports on the thermopower of the manganites.[9,10,12–14] Out of these Fisher *et al.*[14] have measured $S(T)$ of $Nd_{1-x}Sr_xMnO_{3-(x/2)}$ and our results agree well with their data. They suggest that the nearly temperature independent high temperature values of $S(T)$ are suggestive of transport of a fixed population of charge carriers in a narrow band. They attribute the negative sign of $S(T)$ to a population of uncorrelated electrons in a less than half filled band, the zero crossing to band splitting and the decrease in $|S|$ as x decreases to an increase of the bandwidth.

In conclusion we have measured resistivity, ac susceptibility and thermopower of $Nd_{1-x}Sr_xMnO_3$ with $x=0.4$, 0.33, 0.3 and found that for all the samples $\rho(T)$, T_C and T_p
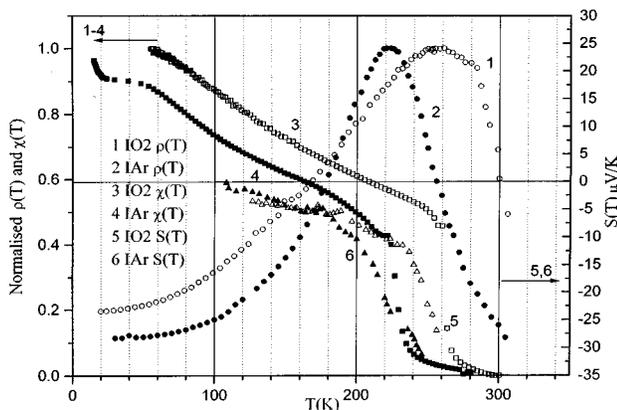

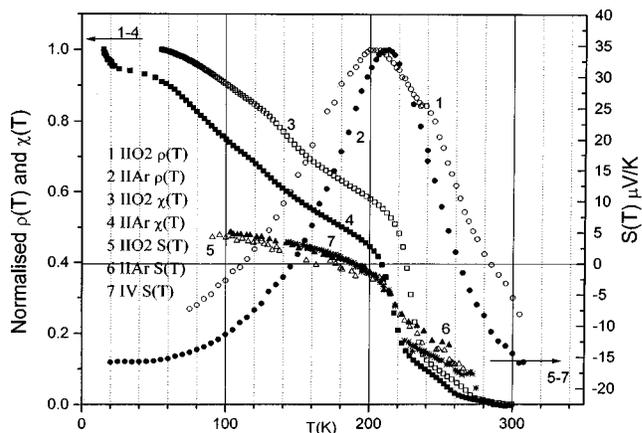FIG. 1. Plot of resistivity, ac susceptibility and thermopower vs temperature for samples IO2 and IAr.

FIG. 2. Plot of resistivity, ac susceptibility, and thermopower vs temperature for samples IIO2 and IIAr. Thermopower on 1500 °C processed samples of the same composition is also shown for comparison.
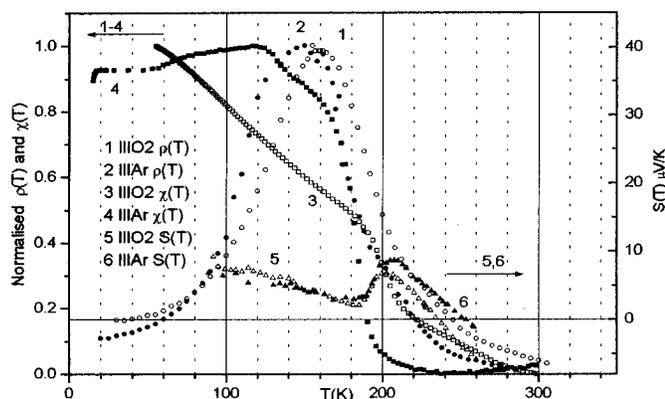
FIG. 3. Plot of resistivity, ac susceptibility and thermopower vs temperature for samples IIIO2 and IIIAr

depend sensitively on composition and annealing environment. The effect of the annealing treatment on resistivity, T_p, T_C, etc. increases with x. We find that the $\rho(T)$ features can be controlled by the annealing environment and hence these features are possibly intrinsic and not due to magnetic inhomogeneity/grain boundary effects etc. The drastic change in the $S(T)$ feature across $x = 0.30 - 0.33$ may be attributed to a dopant induced $I-M$ transition. However, $S(T)$ is not as sensitive as resistivity (which increases with Ar annealing). Further systematic work on this compound with varying x (other than the three compositions studied) and varying process parameters (sintering temperatures, annealing atmospheres, etc.) and other related measurements (thermal conductivity, magnetoresistance, etc.) on polycrystalline bulk and also on thin films is in progress.

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