Pergamon

Solid State Communications, Vol. 97, No. 7, pp. 599–604, 1996
Elsevier Science Ltd
Printed in Great Britain
0038-1098/96 $12.00+.00

0038-1098(95)00715-6

ANOMALOUS MAGNETOCONDUCTIVITY OF EPITAXIAL $Nd_{0.7}Sr_{0.3}MnO_3$ AND $Pr_{0.7}Sr_{0.3}MnO_3$ FILMS

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(*Received* 20 *September* 1995; *accepted* 17 *October* 1995 *by A. Pinczuk*)

In $Nd_{0.7}Sr_{0.3}MnO_3$ films, ranging in peak resistivity from 1000 Ω·cm to ≤1 Ω·cm, and exhibiting large magnetoresistance effects, the zero-field resistivity above the peak temperature T_p exhibits thermally activated behavior with an activation energy of 0.115±0.005 eV. At T well below T_p, the magnetoconductivity, rather than the magnetoresistance, is linear in B and this linear dependence is observed over a wide B range even when the magnetization is essentially saturated. A cross-over from the linear relation to σ increasing as B^2 is observed near and above T_p. A tentative model is proposed.

Keywords: A. magnetically ordered materials

The phenomenon of negative giant magnetoresistance (GMR) in metallic materials, has drawn considerable attention in recent years. It was first observed in Fe/Cr superlattices,[1] and later found in a large number of ferromagnetic/metal multilayers,[2,3] and alloys.[4,5] Most recently,[6-11] a lot of interest has been focused on the colossal magneto-resistance (CMR) effect in doped manganese oxides (RE,M)MnO_3 thin films, where RE represents a trivalent rare earth element such as La, Nd or Pr, and M is a divalent element such as Sr, Ba, Ca or Pb. In a magnetic field, large resistivity drops have been obtained in these materials. The largest reported value of the resistivity drop in the doped manganese oxide films is over four orders of magnitude at 60 K and 8 T obtained in Nd-Sr-Mn-O films.[10] La-Ba-Mn-O thin films gave a large MR effect at room temperature.[6]

In zero field, a prominent feature of the doped manganese oxides is a large maximum in the $\rho(0,T)$ vs. T curves. Often, though not always, the peak temperature (T_p) is close to the ferromagnetic transition temperature (T_C). At $T > T_p$ the resistivity exhibits activated behavior.[12] The magnetoresistance becomes discernible for T somewhat above T_p, rises to a maximum as T is reduced and eventually becomes small at very low T.

In many ways, the doped manganites parallel the transport properties observed[13] in the ferromagnetic semiconductors (FMS). FMS exhibit activated resistivity, sizable resistivity peaks, GMR and complex magnetic behavior. The activation energies are ~5 meV and some authors,[14,15] invoked magnetic polarons to account for the observations. Alternate explanations[16] involved appeal to temperature dependent shifts in the relevant energy levels. In the FMS, the resistivity peaks and the GMR occur at $T \leq 10$ K. The manganites invite attention because making T_p close to room temperature appears to be quite feasible.

In this letter, we report a systematic study of

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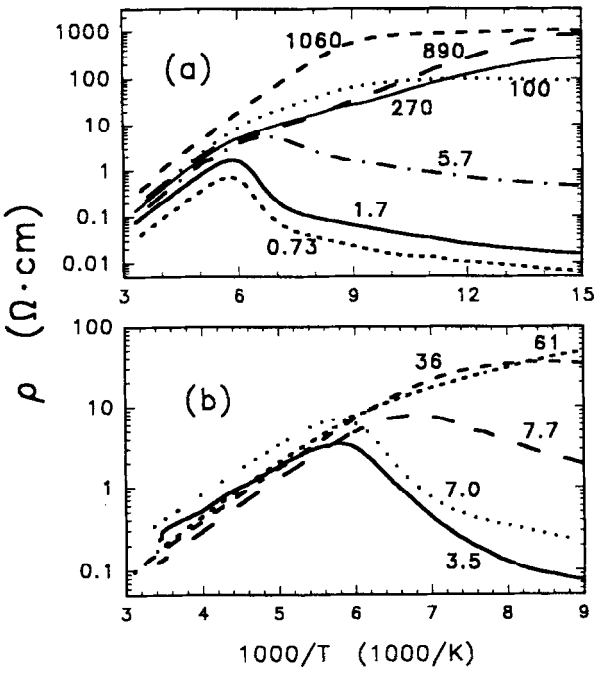
magnetotransport in a variety of manganite films both above and below the zero-field resistivity ($\rho(0,T)$) peak temperature, T_p. Remarkably, we find that, above T_p, the $\rho(0,T)$ data follow activated behavior with a single activation energy value encompassing all the $Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$ films. This in spite of the fact that $\rho(0,T_p)$ ranges over several orders of magnitude (Table I). As before,[6-11] magnetoresistance appears at $T>T_p$, the onset temperature rising with increasing magnetic field. Since the magnetoresistivity in some of these samples is hysteretic,[17] here we present only the virgin curves, that is, $\rho(B,T)$ obtained on first application of field after zero-field cooling to the temperature of interest. The high field resistivity $\rho(B_{max},T_p)$ is nearly the same (0.02-0.1 Ω·cm) in most of the samples (Table I). Below T_p, the magnetoresistivity does not show a strong correlation with the sample magnetization. Instead, it is notable that in epitaxial $Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$ (NSMO) and $Pr_{0.7}Sr_{0.3}MnO_{3-\delta}$ (PSMO) films, the characteristic quantity is the field dependent conductivity, $\sigma(B)$. Surprisingly, $\sigma(B)$ is linear in B for T well below T_p. Near T_p, $\sigma(B)$ shows a quadratic (B^2) variation. These novel results cannot be reconciled with conventional ideas of magnetotransport in the manganites. We propose a model in which one thinks of a paramagnetic matrix paralleled by ferromagnetic filamentary channels to qualitatively account for the observations.

Using targets with nominal compositions of $Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$ and $Pr_{0.7}Sr_{0.3}MnO_{3-\delta}$, doped manganese oxide films with thicknesses of 200-300 nm were grown on (100) $LaAlO_3$ single crystal substrates by pulsed laser deposition. The sample preparation and structural analysis have been described in ref. 10. In the NSMO case, a wide variety of films were prepared by changing the oxygen pressure during the deposition. It seems most reasonable to designate them by the peak values, T_p and $\rho(0,T_p)$ listed in Table I (that is, 7NSMO denotes a film with $\rho(0,T_p)$= 7 Ω·cm). X-ray diffraction, Rutherford backscattering and ion channeling analyses indicate that, under our deposition conditions, the as-grown films have nearly perfect epitaxial crystalline structure. A standard four-probe method was used to measure the dc resistivity of the samples. The magnetoresistance versus temperature measurements were performed in a superconducting magnet, with the applied magnetic field parallel to the film surface and to the current direction. A Quantum Design SQUID magnetometer was used to measure the magnetization of the samples, with the

Table I. $Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$ films characteristics.

Sample No.	$\rho(0,T_p)$ (Ω·cm)	T_p (K)	$\rho(8T,T_p)$ (Ω·cm)
1	0.7	175	
2	1.7	171	≤ 0.1
3	3.5	173	
4	5.7	150	
5	7.0	173	0.2
6	7.7	148	
7	36	118	< 1.0
8	61	93	
9	100	86	
10	270	69	0.03
11	890	65	0.2
12	1060	70	



Figs. 1a,b. Zero-field resistivity as a function of temperature for the films listed in Table I. Each curve is identified by the peak value $\rho(0,T_p)$ listed in Table I. Note that for $T > T_p$, all the data are consistent with an activation energy of 0.115±0.005 eV.

field in the film plane.

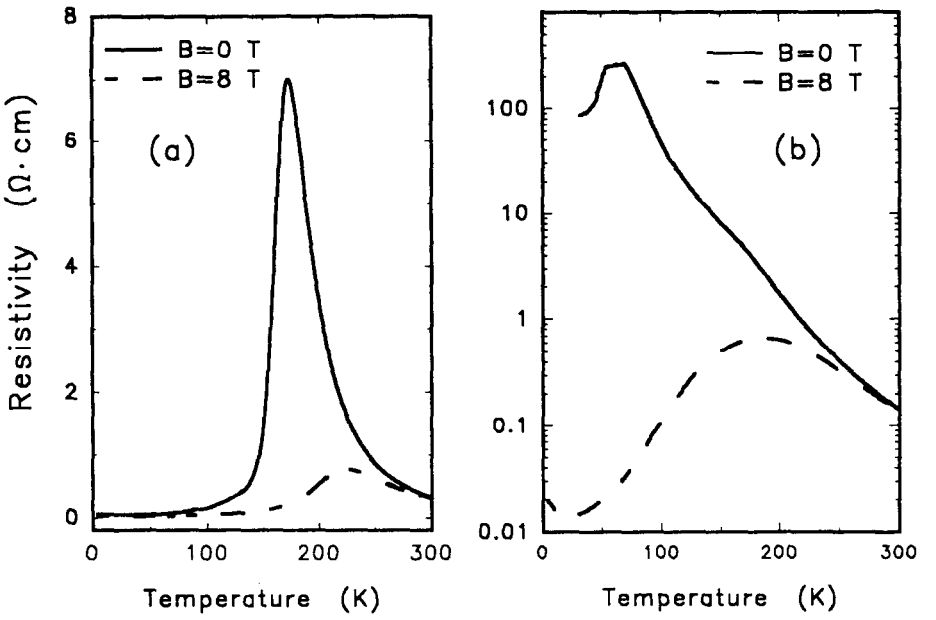
A variety of films of NSMO identified by $\rho(0,T_p)$ and listed in Table I, were chosen and their $\rho(0,T)$ plotted as a function of temperature (Figs. 1a,b). For $T>T_p$, all the samples show activated behavior with a single activation energy of about 0.115±0.005 eV. It is indeed most surprising that the different films can be described by just one activation energy and suggests that the same semiconductor-like mechanism is responsible for the transport above T_p in every case. The energy gap compares well with the value of 0.10-0.14 eV observed in $La_{1-x}Ca_xMnO_3$ with $0.2<x<0.4$.[12] In other words, oxygen stoichiometry variation in the present films leads to the same transport effects as the divalent metal concentration variation, though higher resistivity values are possible with the former. The straightforward implication is that in all these films there is one basic conducting matrix (with an Arrhenius energy of about 0.115 eV), which is left unaltered by the processing conditions.

Below the peak temperature, the temperature variation of $\rho(0,T)$ is by no means simple (Fig. 2). If $\rho(0,T_p)$ is small (≤ 10 Ω·cm), the resistivity drops sharply for $T<T_p$, eventually attaining a value of less than $0.1\times\rho(0,T_p)$. For large $\rho(0,T_p)$, however, the drop is less marked; $\rho(0,4K)$ being only about $0.3\times\rho(0,T_p)$. In manganites, it has become customary[18] to attribute the drop in $\rho(0,T)$ to the onset of magnetic ordering. If so, the present results suggest that as $\rho(0,T_p)$ increases, a smaller fraction of the material participates in this transition. We shall return to this idea in the following discussion.

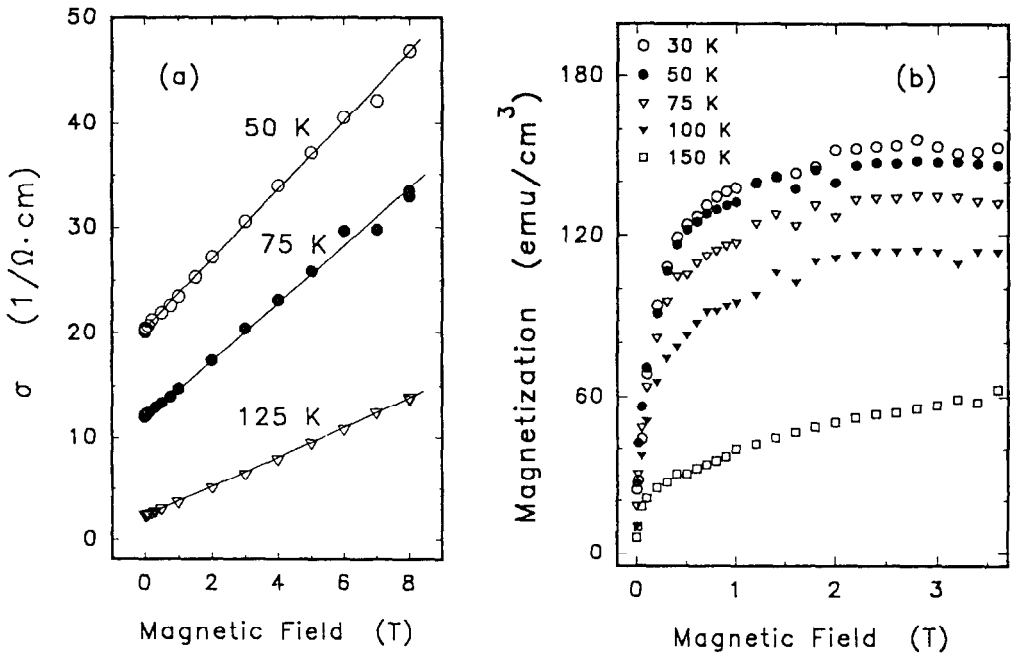
In considering the effects of a magnetic field, the first result of note (Table I) is that at high fields (≅ 8 T, say), $\rho(B_{max},T_p)$ is about the same (within an order of magnitude) for most of the samples although, as we have seen, $\rho(0,T_p)$ values span 3 decades. Next, the 8 T data in Fig. 2b clearly show again the well-documented fact[6-11] that the magnetoresistance is significant at T well above T_p, where it was shown above that the zero-field resistivity is thermally activated (see also Fig. 5b).

Finally, it is important to consider the explicit dependence of the conductance on applied field and the sample magnetization. Figs. 3a and 3b show, respectively, the field dependence of the conductivity and the magnetization in 7NSMO. Note that Fig. 3a encompasses temperatures well below T_p. It is clear that the conductivity continues to increase linearly well beyond the field (~0.5 T), required for technical saturation. Therefore, a close connection between $\sigma(B)$ or $\rho(B)$ and the magnetization is not indicated by our data. This is in sharp contrast to previous claims[6,8,11] pertaining to manganite samples with smaller $\rho(0,T_p)$ values. Data showing explicit field dependence of ρ at T well below T_p are rather sparse. However, von Helmolt *et al.*'s results[6] on $La_{0.6}Sr_{0.4}MnO_3$ at 100 K and annealed $La_{2/3}Ba_{1/3}MnO_3$ at 300 K, give σ varying linearly with B upto 4-6 T. An as-grown, PSMO film with $\rho(0,T_p)= 0.263$ Ω·cm at T_p = 170 K shows very similar behavior (Fig. 4).

The field dependence shows a marked change as T gets close to, and above, T_p as is evident from Figs. 5a,b for a 1.7NSMO (T_p = 173 K, Table I) specimen. It appears that the conductivity varies as $\sigma = \sigma_0 + \sigma_1 B^n$, with n increasing from 1 as T rises. The data at 180 K are well represented by $\sigma = (0.63 + 0.17B^2)$ $(\Omega\cdot cm)^{-1}$. In a comparable temperature regime, Tokura *et al.*[11] report that $\rho(B)$ varies as the square of the dc magnetization in single crystal $La_{1-x}Sr_xMnO_3$ with x = 0.15 and 0.175. In previous data on thin films,[6,8] $\sigma(B)$ exhibits a variety of field dependencies for $T>T_p$, some of which are quite close to the present results. However, to our



Figs. 2a,b. Isochamps showing resistivity as a function of temperature in 7NSMO (a) and 270NSMO (b). Note that in the former, $\rho(0,T)$ drops to a very low value at low T while in the latter, the 4 K resistivity is still quite high. Also, the application of field affects ρ at temperatures well above T_p.



Figs. 3a,b. Field dependence of conductivity (a) and magnetization (b) in 7NSMO at temperatures well below T_p = 173 K. The linear rise in σ persists to fields well beyond technical saturation.

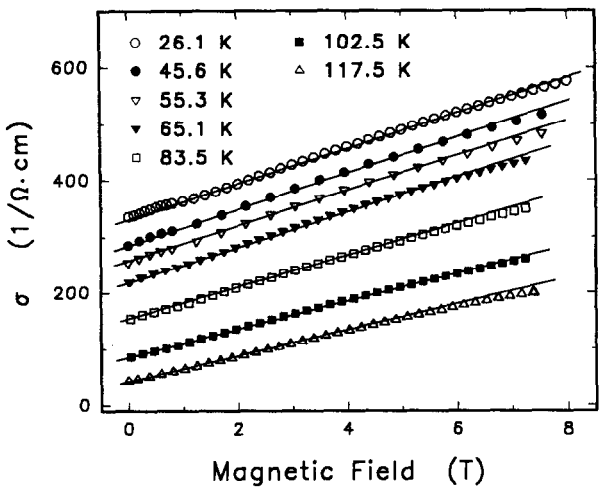


Fig. 4. Linear field dependence of conductivity in PSMO at temperatures well below T_p = 170 K.

knowledge, none of them are understood at this time.

The above results are not easily described by any of the conventional models for transport in magnetic systems. Although there are strong similarities to the behavior of FMS,[13] the temperatures and concomitant energy scales are rather different; being nearly one to two order of magnitude higher in the present study. Also, the peak resistivities are very high and, in view of the relatively large carrier concentrations revealed by Hall data,[19] these materials are far from being ordinary metals. It is fairly clear that the transport is dominated by spin-dependent mechanisms, since any alignment of the spins tends to enhance the conductivity. However, considering the high carrier density and the large (0.115 eV) activation energy involved, a naive appeal to magnetic polaron hopping is not advisable.[16]

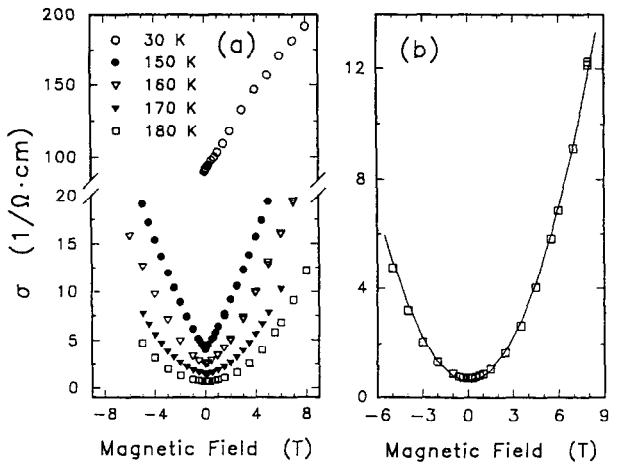


Fig. 5. Field dependence of conductivity in 1.7NSMO at several temperatures. In (a), note the change over from linear to quadratic behavior as T is varied through T_p = 171 K. (b) shows the 180 K data with the full line representing $\sigma = (0.63 + 0.17B^2)$ $(\Omega\cdot\text{cm})^{-1}$.

Although we do not have a complete study of the magnetization for every film listed in Table I, the existing data indicate that the higher the $\rho(0,T_p)$, the lower the high field magnetization. For example, in Fig. 3b it is only about 30% of the saturation value derived[18] from the effective valence of the Mn^{3+}-Mn^{4+} combination with a Sr content of 0.3. This may be suggestive of spin canting. Alternatively, it is likely that only part of the film becomes ferromagnetic (see below). Further studies are essential prior to any definitive conclusion. However, failure to observe a ferromagnetic resonance[20] in any of the present samples, is a clear indication of sizable magnetic inhomogeneity.

At this stage, one can at best offer only a tentative model to qualitatively account for all the observations. We propose that the film consists mainly of a matrix which supports the activated resistivity. Embedded in the matrix and acting in parallel to it (in the transport sense) are ferromagnetic filamentary regions whose conductance is strongly influenced by spin alignment, consequent on magnetic ordering for $T<T_p$. One imagines the filaments to be meandering paths consisting of ferromagnetically aligned segments separated by regions of weakly coupled misoriented spins. Although attempts are being made to observe them by high power microscopic examination, there is no direct evidence as of yet. The large variety of films listed in Table I differ from one another only with regard to the number density of filaments, the lowest density corresponding to the highest $\rho(0,T_p)$. T_p decreases for increasing $\rho(0,T_p)$ because of the lower filamentary component. Lowering of T below T_p promotes spin alignment in the filaments, causing their conductance to rise thereby "shorting" out the matrix. Clearly, with fewer filaments (cf. Fig. 2b), the effect on film conductance is less marked giving rise to the observations described in Figs. 2a,b.

Application of a magnetic field modifies the charge transport. If a filament is made up of ferromagnetic segments interspersed with misaligned spins, one is implicitly talking of an extended spin valve network whose conductance is altered by the degree of alignment induced by B. Although

there is no theory to describe the magnetotransport in such a system, there is no compelling reason to tie it to the total magnetization. Rather, one would expect significant changes in charge transmission as a function of the angle between the magnetization of two neighboring segments and this effect could persist up to high B values. The matrix is also affected by B, giving the magnetoconductivity for $T>T_p$. Hence, the crossover in the $\sigma(B)$ dependence.

In summary, magnetotransport studies on a wide variety of $Nd_{0.7}Sr_{0.3}MnO_{3-\delta}$ epitaxial films, characterized by their zero-field resistivity peaks, reveal several unexpected results:

i) although the peak resistivities span a wide range (10^3-1 Ω·cm), the temperature dependence of the zero field resistivity at high T ($T > T_p$), is consistent with activated behavior and a characteristic energy of 0.115±0.005 eV, in every case,

ii) the virgin magnetoconductivity at T well below T_p is linear in the applied field B, upto field values well beyond those required for technical saturation,

iii) For T close to T_p and above, $\sigma(B)$ has a quadratic dependence on B.

A naive model is proposed, but clearly one needs extensive theoretical and experimental studies to completely understand these results.

Acknowledgments.- The authors would like to thank useful discussions with D. Drew and S.C. Wu, and the help of S. E. Lofland, X.G. Jiang, J. Wu, X.X. Xi, C. Kwon and S.N. Mao. R.L.G. and T.V. acknowledge partial support from NSF contract No. DMR9510475. G.C.X. thanks the IUEP Committee of the University of Maryland. M.D. and J.M.B. thank the DGICYT (Spain) and the NRC, respectively, for a postdoctoral fellowship.

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