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Anomalous Nernst effect in $La_{0.88}MnO_3$

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Nernst coefficient measurements of $La_{0.88}MnO_3$ ($T_c \sim 265$ K) are reported as a function of temperature (100–320 K) in moderate applied magnetic fields ($0.38 < H < 1.8$ T). For $T > T_c$, our data can be accounted for by the transport behavior of small polarons. We find the semiconductor to metal transition is dominated by an increase in the hole density. For $T \leqslant T_c$, an anomalous suppression of the Nernst coefficient was observed when the field increased from 0.38 to 1.8 T. The giant magnetoresistance effect is attributed to a field increased mobility of the charge carriers. [S0163-1829(99)50214-2]

The observation[1] of giant magnetoresistance (GMR) in $La_{1-x}Pb_xMnO_3$ followed by similar and more pronounced effects in other perovskites such as $R_{1-x}D_x{}^{2+}MnO_3$ (R=La,Nd, . . . ; D=Sr,Ca, . . .) has led to an extensive investigation of several other physical properties.[2–5] Partial substitution of La by a divalent ion in the antiferromagnetic parent insulator $LaMnO_3$ leads to the presence of a mixed valency of Mn^{3+} ($t_{2g}^3 e_g^1$) and Mn^{4+} ($t_{2g}^3 e_g^0$). The e_g electron (hole) can then hop to the neighboring Mn^{4+} ion via a ''double exchange'' mechanism[6] which mediates ferromagnetism and metallic conduction. In addition to the ''double exchange'' model, several other models[7–11] including the role played by a Jahn-Teller type electron-phonon coupling, have been proposed to further account for the appearance of a giant negative magnetoresistance occurring close to the paraferromagnetic transition temperature (T_c) and the associated semiconductor to metal transition (SMT). However, a complete theoretical understanding of these properties seems to be still lacking. Some of the crucial experimental quantities that would be interesting to determine in these materials are thermal variation of hole density and mobility and their relation to the GMR, which would improve our comprehension of the fundamental mechanisms involved.

Recently several attempts[12–19] have indeed been made to determine these quantities by means of Hall measurements. However, the interpretation of Hall data is rather involved especially in the case of magnetic materials such as these due to the presence of a rather large anomalous term. In this respect it would be interesting to measure also the Nernst coefficient Q, which is the ratio of the transverse electric-field component to the thermal gradient and magnetic field. At appropriate experimental conditions,

$$Q = ud/Hl\Delta T, \tag{1}$$

where U is the Nernst voltage measured, H is the magnetic field applied perpendicular to the surface, l is the distance between the Nernst leads, ΔT is the temperature difference across the sample, and d is the sample thickness in the direction of ΔT. The most simple theory in the case of metallic conduction with a single type of carrier is given by[20]

$$Q = (\pi^2 k^2/3m) T [d\tau(\varepsilon)/d\varepsilon] \varepsilon = \varepsilon_F, \tag{2}$$

where k is the Boltzmann constant, m is the effective mass and τ is the energy dependent relaxation time of the carrier near the Fermi energy ε_F. Q is normally expressed in units of nV/K T. To our knowledge, no attempt has been made to measure Q in the manganites, the main reasons being the smallness of this effect and the difficulty of theoretically modeling the energy dependent relaxation time. In fact even in the case of the well studied high-T_c cuprates, very few data[21–24] are available. However, we undertook such measurements on the manganite $La_{0.88}MnO_3$ which is known[25–28] to be a ferromagnet below $T_c \sim 265$ K and found an anomalous suppression of the Nernst coefficient in moderate fields for $T \leqslant T_c$. Our data indicate that in this compound the carriers are localized for $T > T_c$ and the SMT is controlled predominantly by a change in the delocalized carrier density. Furthermore, the GMR effect is dominated by a rapid increase in mobility of the carriers in the presence of the magnetic field.

Polycrystalline samples of $La_{0.88}MnO_3$ were prepared by solid-state sintering of a mixture containing adequate quantities of La_2O_3 (99.99%) and MnO_2 (99.5%) as described earlier.[28] The mixture pressed into pellets was repeatedly ground and fired at temperatures which were increased progressively from 980–1200 °C. A final sintering was done at 1300 °C in air for a period of 36 h and furnace cooled. The pellets were then annealed in oxygen at 850 °C for a period of 24 h. X-ray diffraction (XRD), resistivity, and magnetization were carried out to check the quality of the sample, The XRD pattern indicated a rhombohedral symmetry with no extra phases.[29] The lattice parameters were found to be $a_R = 5.475 \pm 0.001$ Å and $\alpha = 60.57°$. Comparing our data with those published earlier,[30] we estimate the oxygen content to be ~ 2.98.

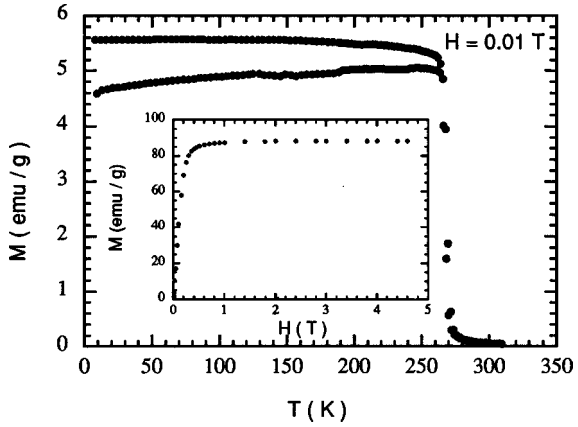

FIG. 1. Magnetization M of $La_{0.88}MnO_3$ as a function of temperature. The upper and lower branches denote, respectively, field cooled and zero-field cooled data points; (inset) M as a function of H at 5 K.

Magnetization M as a function of temperature measured in an applied field of 0.01 T using a MPMS5 Quantum Design superconducting quantum interference device (SQUID) magnetometer is shown in Fig. 1. A sharp increase in M for $T<275$ K was observed indicative of a paramagnetic to a ferromagnetic transition at around $T_c \sim 265$ K. At 5 K, M increased rapidly (Fig. 1 inset) for $H>0.1$ T and saturated for $H>0.5$ T. The magnetic moment at ~ 5 T was 3.57 μ_B/Mn atom.

Resistivity ρ as a function of temperature, measured using a standard ac (20 Hz) four-probe method and in a field of $H=0$ and 1.25 T, is shown in Fig. 2. In $H=0$, a SMT was observed with a maximum value of ρ at ~ 265 K (close to T_c). In an applied field of 1.25 T, ρ reduced considerably especially near T_c and the maximum shifted to a lower temperature. A giant magnetoresistance, $\mathrm{GMR}=-100(\rho_H-\rho_0/\rho_0)$, as noted earlier[25–28] in La deficient manganite, was observed with a maximum value of around 35% at $T \sim 265$ K.

The Nernst coefficient was measured in a constant reversible magnetic field by soldering two thin gold wires placed on the sample surface. The measured voltage was checked at ~ 320 K to be nearly linear in ΔT, H, and distance between

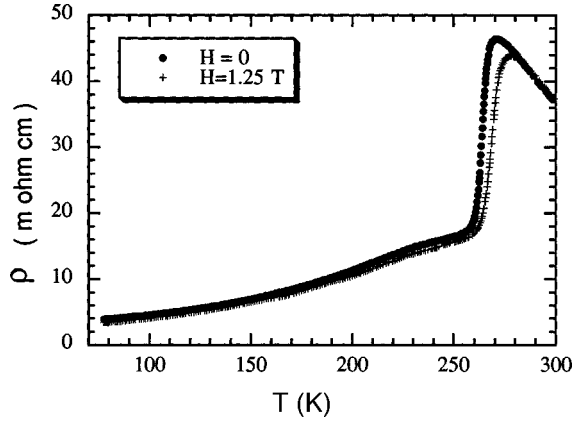

FIG. 2. Resistivity as a function of temperature in $H=0$ and 1.25 T.

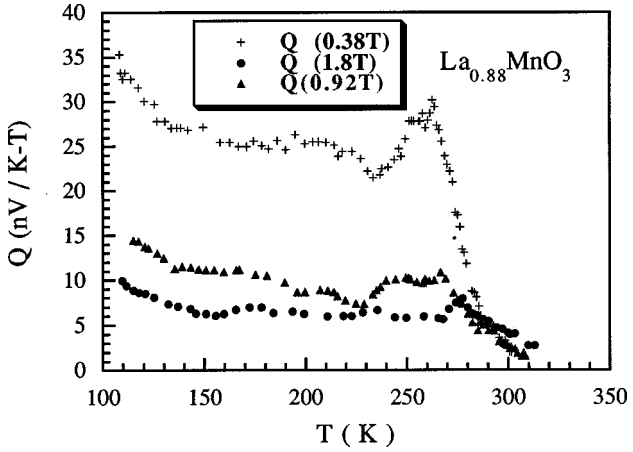

FIG. 3. Nernst coefficient Q as a function of temperature at three different magnetic fields.

leads according to Eq. (1). The error in the determination of Q was estimated to be ± 0.2 nV/K T. The Nernst coefficient of the sample as a function of temperature taken at three different magnetic fields (0.38, 0.92 and 1.8 T) presents several interesting and original features (Fig. 3). The first most striking result is the strong suppression of Q from ~ 280 K to 100 K, when the applied field was increased. Looking at the data taken at the lowest field of 0.38 T, we note that the value of Q increased rapidly from about 2 nV/K T at 310 K to a well defined maximum value of 31 nV/K T at 230 K followed by a slow increase reaching a value of 35 nV/K T at 110 K. Note the remarkable decrease in the value of Q when H was increased from 0.38 to 1.8 T as T approached T_c and decreased further below T_c. For example, at 110 K, Q was reduced from 32.6 nV/K T to 9.95 nV/K T when the field was increased from $H=0.38$ T to $H=1.8$ T. For materials without magnetic ordering, the measured Nernst voltage is linear in applied field so that the value of Q is independent of H according to Eq. (1). One should note that in the case of $YBa_2Cu_3O_7$, at 250 K (far away from the superconducting critical temperature of 92 K and fluctuation effects), such a linear behavior of U was found[22] in fields $0 \leqslant H \leqslant 12$ T. The anomalous behavior of the Nernst coefficient observed here must naturally be related to the para- to ferromagnetic transition and the associated magnetotransport properties. This will be more evident from the following discussion.

We further note that the temperature at which Q was maximum (close to T_c) shifted to higher temperatures as the field strength was increased, a feature observed[2,3] while taking the GMR data. One would think if we could increase further the magnetic field, the maximum in Q around T_c may be completely suppressed and one might be left with a monotonic increase or a fairly constant value of Q as T decreased. Unfortunately the available magnetic field, which was limited to <2 T, did not allow us to demonstrate this.

With the present incomplete understanding of the transport properties of the manganites, the above data are difficult to interpret quantitatively. We will make an attempt here to discuss our findings in the light of recently reported data on magnetoresistance and Hall effect on divalent substituted $LaMnO_3$.

For the sake of clarity, first let us discuss the data taken at

$H=0.38$ T for $T>T_c$. Though our data are available over a narrow temperature range, one could deduce an activation energy of $\Delta E=480$ meV. For $H=1.8$ T, a similar argument gave a reduced value of $\Delta E=206$ meV. To account for these data, we will assume $Q\propto\tau$, the scattering time. In the case of small polarons, the carriers hop from site to site with a low mobility u that is thermally activated. It is given[31] by $u\sim u_0(1/T)\exp(-W/kT)$ where W is the energy barrier that the hopping carrier should overcome. If $u\propto\tau$, then we deduce that Q should increase when T decreased, as was observed. An increase in the applied field from 0.38 to 1.8 T, leads to a decrease in W (we suggest W is the same as ΔE) resulting in an attenuation of Q and in resistivity.

Now let us look at the data for $T\leqslant T_c$ for $H=0.38$ T. The thermal behavior of Q was very different from that above T_c. Initially, Q decreased from 31 to 22 nV/K T with decreasing T and then slowly increased as T decreased further. Note that the small broad maximum at around 220 K was also observed in the ρ-T curve[32] and is not understood at present though it may be attributed to sample inhomogeneities. The reduction in Q may be attributed to (partial) delocalization of carriers resulting from a changeover from a small polaron behavior to a large polaron behavior resulting in an increase in the itinerant character[30] and to a reduction in scattering of carriers due to spin ordering. However, as T decreased further, Q began to increase though ρ continued to decrease. Hence the principal cause for the reduction in ρ (for $T<T_c$, in $H=0$) should be related to a substantial increase in the carrier density. On the other hand, when the applied field was increased to 1.8 T, for $T\leqslant T_c$, the value of Q reduced considerably compared to that in $H=0.38$ T, quite similar to the strong reduction in ρ resulting in a negative magnetoresistance. Hence, the data suggest that the GMR results from an increase in the carrier mobility. At these fields below T_c, the magnetic moment increased rapidly (Fig. 1) indicating an increase in spin ordering. This would considerably reduce the scattering of carriers resulting in a reduction in the relaxation rate as observed. A further increase in Q in $H=1.8$ T for $100<T<200$ K, may be related to the influence of additional scattering in the presence of incomplete alignment of spins since the magnetic moment at these temperatures is still far from the saturation value. It is interesting now to plot [Fig. 4(a)] the thermal variation of $-100(Q_{1.8}-Q_{0.38})/Q_{0.38}$ where $Q_{1.8}$ and $Q_{0.38}$ are the Nernst coefficients measured, respectively, at 1.8 and 0.38 T at a given temperature, and call it a ''giant Nernst effect (GNE)'' in analogy with the giant magnetoresistance. Though our GMR data [Fig. 4(b)] are taken in a smaller field of 1.25 T, the analogy is quite striking. The rapid increase in GMR corresponds well to a similar increase in GNE. To end our discussion, we might note briefly that our findings are not in contradiction with those reported[13,16,17] from Hall data. In the case of divalent substituted $LaMnO_3$ ($T_c\sim240$ K), it was shown that the SMT resulted from a strong increase in the hole density whereas the GMR could be attributed to field increased mobility.

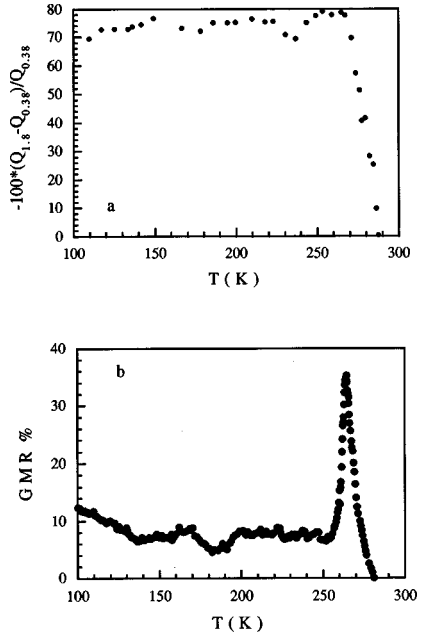

FIG. 4. (a) Giant Nernst effect (GNE)$=-100(Q_{1.8}-Q_{0.38})/Q_{0.38}$ as a function of temperature. (b) Giant magnetoresistance (GMR)$=-100(\rho_{1.25}-\rho_0)/\rho_0$ as a function of temperature.

In summary, we have measured the Nernst coefficient of $La_{0.88}MnO_3$ ($T_c\sim265$ K) in moderate applied magnetic fields. For $T>T_c$, our data can be accounted for by the transport behavior of small polarons.[14,33,34] The SMT is dominated by an increase in the hole density. For $T\leqslant T_c$, our data support the view that the behavior changes from small polarons to large polarons with increased itinerant character. An anomalous suppression of the Nernst coefficient for $T\leqslant T_c$ when the field increased from 0.38 to 1.8 T points out that the GMR effect may be attributed to a field increased mobility of the charge carriers. The present data when extended to other materials in this class, and preferably in higher fields and lower temperatures and along with further theoretical inputs, should contribute to a further understanding of the scattering mechanisms controlling the magnetotransport behavior.

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