Hall effect of the colossal magnetoresistance manganite $La_{1-x}Ca_xMnO_3$

P. Matl, N. P. Ong, and Y. F. Yan*
Joseph Henry Laboratories of Physics, Princeton University, Princeton, New Jersey 08544

Y. Q. Li,† D. Studebaker, T. Baum, and G. Doubinina
Advanced Technology Materials Inc., 7 Commerce Drive, Danbury, Connecticut 06810
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The Hall resistivity ρ_H and magnetoresistance of $La_{1-x}Ca_xMnO_3$ (T_c=265 K) have been measured at temperatures to 360 K in fields H to 14 T. By comparing ρ_H with the magnetization M, we have extracted the anomalous coefficient R_s. We uncover an interesting relationship: R_s is proportional to the zero-field resistivity from 200 to 360 K. Above T_c, the Hall angle tan $\theta_H \sim M$. Further, the effective Hall mobility is H independent over a wide range of H. We contrast these scaling relations with the Hall effect in typical ferromagnets. [S0163-1829(98)01618-X]

The double exchange manganite $La_{1-x}Ca_xMnO_3$ undergoes a magnetic transition from a high-temperature, insulating state to a metallic, ferromagnetic state at a critical temperature T_c that depends on the dopant concentration x ($T_c \sim 260$ K at $x=1/3$). Strong interest in the transport and magnetic properties has been stimulated by the observation of ''colossal'' magnetoresistance (MR) in the vicinity of T_c.[1–5] A transition from a high-temperature phase that is poorly conducting to a metallic state at low temperatures is unusual. Many aspects of the transition are successfully accounted for by the double exchange model[6] augmented by Jahn-Teller effects.[7] Nonetheless, strong interest remains on the nature of charge transport. Hall measurements on the manganites are especially interesting in this regard. A number of such studies have appeared recently.[8–10]

We report a detailed Hall investigation that reveals a strikingly simple relation with the magnetization in a broad temperature interval around T_c. The measurements were performed on epitaxial films of $La_{1-x}Ca_xMnO_3$ ($x=1/3$) grown on $LaAlO_3$ substrates using metallo-organic chemical vapor deposition (MOCVD). X-ray diffraction showed that the films are expitaxial and single phased.[11] Two samples (1 and 2) of thickness 250 and 150 nm, respectively, were measured as grown (without annealing), with the applied field **H** normal to the substrate.

The field and temperature dependences of the resistivity $\rho(H,T)$ [Fig. 1(a)] are similar to those observed in bulk,[1,4,5] and thin films.[12,8] As in earlier reports, the zero-field resistivity $\rho(0,T)$ attains its maximum value (here 16.1 mΩ cm) near 290 K, and decreases rapidly below T_c (=265 K). The colossal MR shown in Fig. 1(a) is also very similar to published results.

Figure 1(b) displays the Hall resistivity ρ_H versus field at selected temperatures. At temperatures above 250 K, the large values attained by ρ_H in weak fields, and its pronounced variation with field, are quite unusual for a material exhibiting such a high resistivity. At each T above T_c, $|\rho_H|$ shows a rapid initial increase, followed by a broad peak and a slower decrease in high fields. The field profile is closely correlated with the steep field dependence of ρ. The broad maximum in $|\rho_H|$ occurs close to the inflection point of ρ (where its magnitude is only half the zero-field value). The correlation suggests that, in the colossal MR regime, the Hall resistivity should be analyzed together with the large changes occuring in ρ. Our Hall traces are broadly similar to those of Wagner *et al.*[10]

Below 200 K, the field dependence of ρ is weak (at 200 K

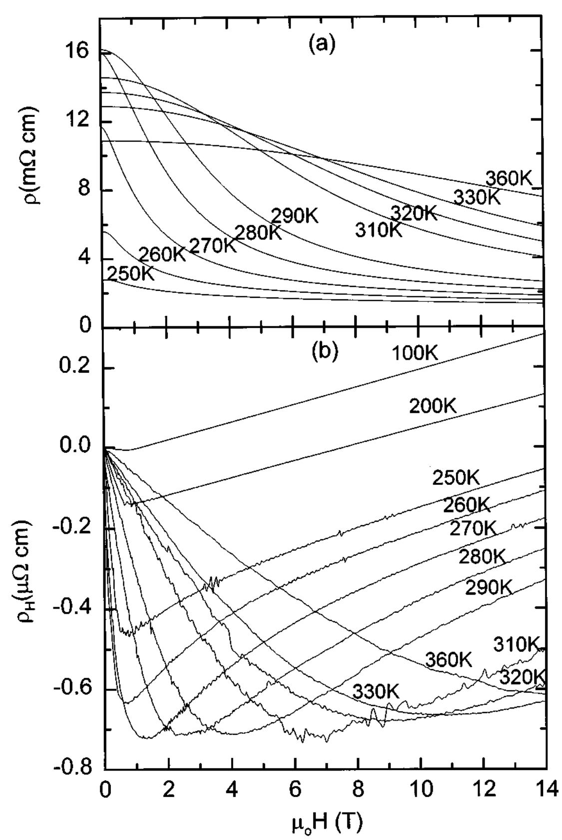

FIG. 1. (Upper panel) The resistivity ρ of $La_{1-x}Ca_xMnO_3$ (T_c =265 K) versus field H at indicated temperatures (sample 1, film thickness 250 nm). The lower panel shows the Hall resistivity ρ_H versus H in sample 1 at temperatures 100 to 360 K. Above T_c, ρ_H is strongly affected by the colossal MR in ρ and by the susceptibility χ. ρ and ρ_H are averaged over four scans from -14 to 14 T and back to -14 T.

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the net decrease is $<10\%$ at 14 T). Unlike the high temperature results, ρ_H deep in the ferromagnetic state (at 100 and 200 K) resembles more the results in magnetic conductors such as Ni, Fe, CoS_2, Dy, and Tb.[13,15–17] The Hall results on sample 2 (mostly below 250 K) are similar to those in Fig. 1(b).

In ferromagnets, ρ_H is the sum of the conventional term R_0B and an anomalous term proportional to the observed magnetization, viz.,[13,14]

$$\rho_H = R_0 B + \mu_0 R_s M. \tag{1}$$

Here R_0 is the ordinary Hall coefficient, R_s the anomalous Hall coefficient, μ_0 the vacuum permeability, and $B = \mu_0[H+(1-N)M]$ is the induction within the sample (as the demagnetization factor $N\sim 1$ in our geometry, we set $B = \mu_0 H$ from here on).

In terms of Eq. (1), the Hall results below T_c may be decomposed into a positive term ($R_0\mu_0 H$) and a negative anomalous term that is strongly T dependent. Below 100 K (where the latter is insignificant), the value of R_0 (2.5×10^{-10} m^3/C) corresponds to an effective ''Hall density'' $n_H(\equiv 1/eR_0)$ of 2.5×10^{22} cm^{-3} (in sample 2, $n_H = 2.0\times 10^{22}$ cm^{-3}). These numbers correspond to 1.5 holes per Mn site. We note, however, that n_H may be considerably larger than the actual carrier concentration n if both hole and electron pockets are present.

As T increases above 100 K, the anomalous Hall term $\rho_H' \equiv \mu_0 R_s M$ becomes dominant. To extract R_s accurately, we have measured M on the *same* sample (sample 1), using a Quantum Design magnetometer. The uncertainty in our measured moment is estimated to be $\pm 3\times 10^{-6}$ emu. To subtract the large diamagnetic contribution of the substrate material ($LaAlO_3$), we also measured a blank substrate of closely similar size at each value of T and H. (In contrast to the present work, Snyder *et al.*[8] and Jaime *et al.*[9] did not attempt to extract R_s. Wagner *et al.*[10] only calculated the weak field M from the susceptibility χ. Our analysis below differs from these earlier studies in several important aspects.)

The magnetization versus H in the ferromagnetic and paramagnetic states are plotted as discrete symbols in Figs. 2(a) and 2(b), respectively. In the ferromagnetic state, M initially increases linearly with H with a *finite* slope that is T independent (in contrast with the abrupt jump observed[2,4] in bulk crystals). The difference reflects the stronger pinning in films, which prevents the spontaneous alignment of individual magnetic domains. In agreement with Eq. (1) the field profiles of M at 100 and 200 K are well matched by that of the anomalous part of the Hall resistivity ρ_H'. Hence, by matching the vertical scales, we may determine R_s.

In the paramagnetic state (and at 250 K as well), the field profiles of M and ρ_H may be scaled into each other at weak fields, but not at higher fields (the solid line is the ρ_H at 280 K). The disagreement at high fields in fact reflects the colossal MR, which induces very large changes in ρ. We should not expect Eq. (1) to apply in such a situation. However, in the limit $H\rightarrow 0$, Eq. (1) remains valid, with M now the induced magnetization. In the paramagnetic state, we may define operationally the anomalous Hall coefficient as the ratio of initial slopes, viz., $R_s = (d\rho_H/dH)/(\mu_0 dM/dH)$ ($H\rightarrow 0$). We have neglected correcting for R_0 above T_c as it is quite small compared with R_s. The weak-field values of the susceptibility χ are shown in Fig. 3(a) as open symbols.

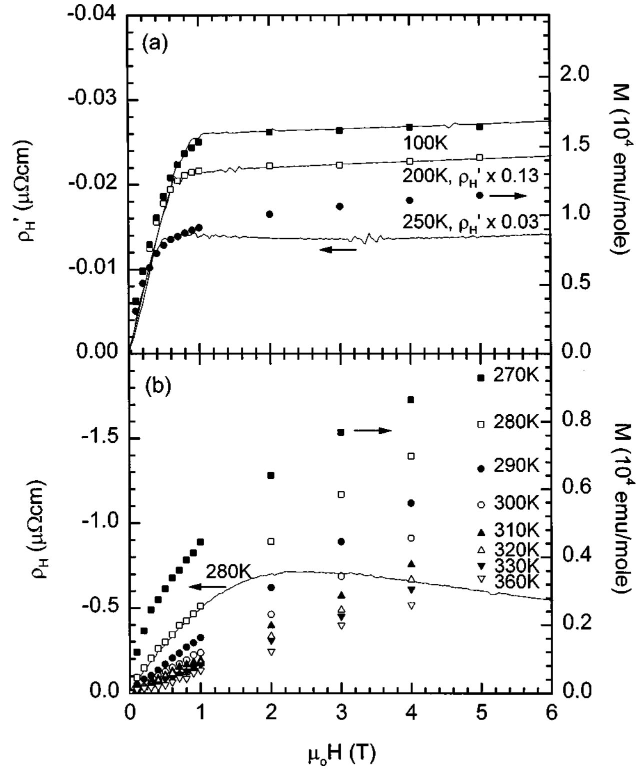

FIG. 2. (Upper panel) The field dependence of the magnetization M in sample 1 at 100 K (solid squares), 200 K (open squares), and 250 K (solid circles). The diamagnetism of the substrate has been subtracted. The anomalous Hall coefficient R_s is the scale factor needed to bring the anomalous Hall resistivity $\rho_H' \equiv \rho_H - R_0 B$ (solid lines) into agreement with M. At 250 K, the agreement is restricted to below 1 T (1 emu/mole=28.2 per volume in SI units). The lower panel shows $M=\chi H$ in sample 1 versus H in the paramagnetic state. The solid line is ρ_H at 280 K scaled to agree with M below 1 T.

When we plot the T dependence of R_s determined by these procedures [solid symbols in Fig. 3(a)], an unexpected correlation with the zero-field resistivity $\rho(0,T)$ emerges. Above 200 K, the anomalous Hall coefficient R_s displays a T dependence closely similar to that of the resistivity, matching equally well its steep increase near 260 K, as well as the slow decrease above 290 K. [Below 200 K, the portion of $\rho(0,T)$ caused by scattering from impurities and defects is substantial. The value of R_s at 100 K falls significantly lower than ρ.] This remarkably simple relationship may be written as

$$R_s(T) = \alpha\rho(0,T) \quad (T \geqslant 200\ \text{K}), \tag{2}$$

where $\alpha = 3.3\times 10^{-4}$ m^2/V s is a T-independent parameter with dimensions of mobility.

The relation between R_s and $\rho(0,T)$ may also be expressed in terms of the Hall angle θ_H. From the relation $\rho_H = \rho \tan\theta_H$, we find the equation

$$\tan\theta_H = \mu_0 \alpha \chi H \quad (H\rightarrow 0), \tag{3}$$

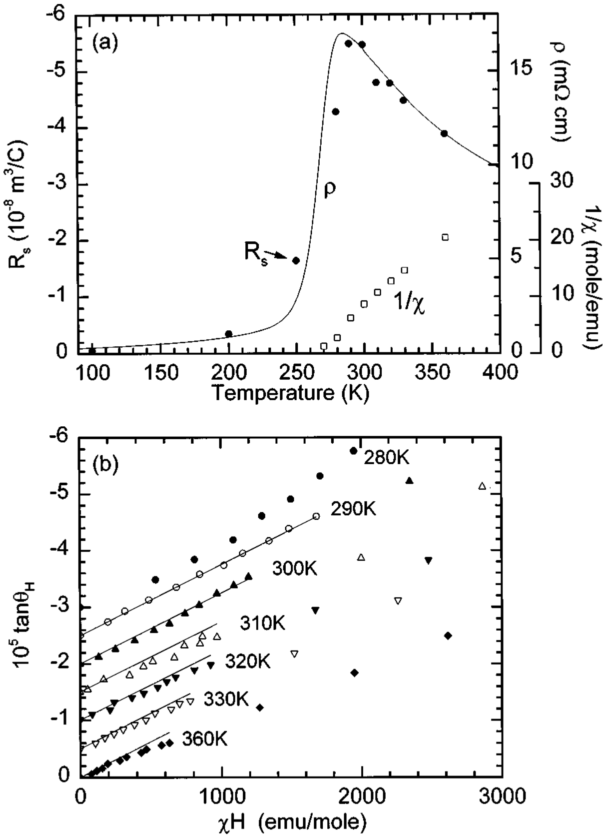

FIG. 3. (Upper panel) The temperature dependence of R_s (solid circles) compared with the zero-field resistivity $\rho(0,T)$ (solid line) in sample 1. R_s at 270 K could not be determined reliably (see text). The inverse susceptibility versus T is shown by the open squares. The lower panel shows tan θ_H (Hall angle) versus M above T_c (curves displaced vertically for clarity). The slope as $H\rightarrow 0$ is T independent, consistent with Eq. (3) (the solid lines are drawn with equal slopes).

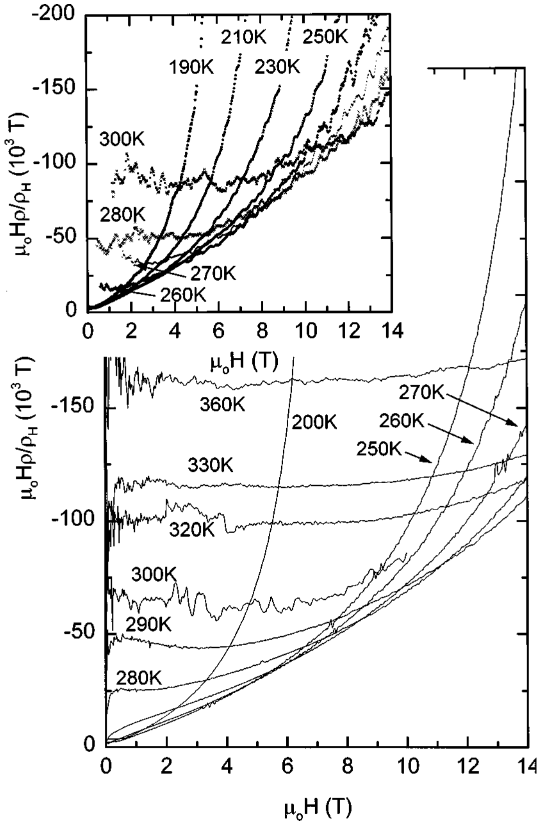

FIG. 4. (Main panel) The field dependence of B cot $\theta_H = \mu_0 H\rho/\rho_H$ in sample 1 at temperatures mostly above T_c (265 K). Above T_c, the plotted quantity ($=1/\mu_H$) is nearly field independent below a characteristic field H_p. Above H_p, $1/\mu_H$ starts to rise steeply. The inset shows similar plots for sample 2.

which states that the weak-field value of θ_H depends only on the susceptibility. Figure 3(b) displays plots of tan θ_H against χH for T above T_c (curves have been staggered for clarity). In the weak-field limit, tan θ_H is proportional to χH with a T independent slope, in agreement with Eq. (3). Close to T_c, however, it is difficult to establish this behavior because our resolution is insufficient to define the H-linear region in both ρ_H and M [as $H\rightarrow 0$, the magnetization data at 270 K in Fig. 2(b) retains significant curvature].

In strong fields, the relations in Eqs. (2) and (3) no longer hold. However, even at moderately high fields where ρ is changing rapidly, there exists a simple pattern involving θ_H. In Fig. 4 we plot against the field the reciprocal of the quantity tan $\theta_H/B=\rho_H/\rho B\equiv\mu_H$, with μ_H the Hall mobility. (We emphasize that the the Hall mobility should be carefully distinguished from the drift mobility $\mu_D=R_0/\rho$. When $|R_s|\gg|R_0|$ it is difficult to determine μ_D.) At each T, the data fall into two distinct regimes separated by a characteristic field H_p. Below H_p, the curve is nominally flat, implying that μ_H is almost field independent. This is especially striking because the resistivity decreases steeply at these field values. For example, H_p is about 8 T at 290 K. The Hall mobility remains within 10% of its zero-field value below H_p (Fig. 4 main panel), but ρ has decreased by a factor of 4 at 8 T [Fig. 1(a)].

In the weak-field limit, $\mu_H\rightarrow\alpha\chi$ [as Eq. (3) requires]. Hence, the decrease of the flat region in Fig. 4 with decreasing T just reflects the decrease in $1/\chi$. The behavior of μ_H in sample 2 is closely similar (inset).

To place our results in perspective, we briefly discuss the anomalous Hall effect in conventional magnetic systems. In ferromagnets, the relation $R_s\sim(\rho_m)^n$, with $n=2$ is well known[13] (ρ_m is the part of the resistivity caused by magnetic scattering). However, the comparisons are confined to low temperatures where the isolation of ρ_m (always uncertain) seems less ambiguous. Closer to, or above T_c, the profiles of R_s in Ni,[15] Tb, Dy,[16] and CoS_2 (Ref. 17) bear no resemblance to their resistivity. Typically (though not always), R_s exhibits a broad peak at 0.7–0.8T_c, and then decreases to a *T independent* value in the paramagnetic state. To our knowledge, there are no previous reports of an R_s that scales as ρ over the wide range shown in Fig. 3(a), at temperatures close to T_c and above.

We discuss the physical picture suggested by these results. From the transport viewpoint, a key feature that distinguishes $La_{1-x}Ca_xMnO_3$ is its large resistivity above T_c. In the paramagnetic state, conduction proceeds by hopping, with a hopping amplitude J that depends on the angle Θ between adjacent core spins.[6] The sensitivity of both T_c and Θ to the external field underlies[7] the colossal MR observed near T_c.

As shown here, $La_{1-x}Ca_xMnO_3$ provides a rare example of a large, anomalous Hall effect in the *hopping* regime. As such, it stands apart from well-studied ferromagnetic metals where the anomalous Hall effect causes scattering between itinerant Bloch states. To discuss this situation, we first ignore the magnetization. Generally, the hopping-regime Hall effect involves hopping among at least three sites. The magnetic flux Φ in the area enclosed by the three sites introduces an Aharonov-Bohm phase $\varphi = 2\pi\Phi/\Phi_0$ that generates a Hall current[18] $\sigma_H \sim J^3 \sin\varphi$. Imry[19] has estimated that, in the strong localization regime, the Hall hopping conductivity is close to the ''Drude'' value or, equivalently, $\rho_H \sim B/ne$.

In the present system, the spin of the hopping electron is constrained to align with the core spin at each site it visits. Our results show that, as M increases with H, an enhanced Hall current is produced. Moreover, $\tan\theta_H$ remains linear in H up to high fields, even as ρ decreases by a factor of 3 or 4 (Fig. 4). The linearity suggests that the anomalous Hall current is associated entirely with a phase $\varphi(M)$ that is sensitive to the core spin configuration. As the electron hops around the loop, it accumulates an overall phase that reflects the induced alignment of the core spins. The specific scaling relationships in Eqs. (2) and (3), as well as the constancy of μ_H in Fig. 4 suggest that there may be rather simple principles governing both the longitudinal and Hall currents in magnetic systems in this regime. Finally, we remark that Hall measurements should not be used to infer the behavior of μ_D or n in the manganites above 100 K, until the anomalous part R_s has been experimentally isolated and understood.

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*Present address: Lucent Technologies, VLSI Technologies Department, 9333 South John Young Pkwy, Orlando, FL 32819.

†Present address: NZ Applied Technologies, 150 C New Boston Street, Woburn, MA 01801.

[1] S. Jin *et al.*, Science **264**, 413 (1994).

[2] Y. Tokura *et al.*, J. Phys. Soc. Jpn. **63**, 3931 (1994).

[3] H. L. Ju, C. Kwon, Qi Li, R. H. Greene, and T. Venkatesan, Appl. Phys. Lett. **65**, 2108 (1994).

[4] H. Y. Hwang, S-W. Cheong, P. G. Radaeli, M. Marezio, and B. Batlogg, Phys. Rev. Lett. **75**, 914 (1995).

[5] J. J. Neumeier, M. F. Hundley, J. D. Thomson, and R. H. Heffner, Phys. Rev. B **52**, R7006 (1995).

[6] P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).

[7] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).

[8] G. Jeffrey Snyder *et al.*, Appl. Phys. Lett. **69**, 4254 (1996).

[9] M. Jaime *et al.*, Phys. Rev. Lett. **78**, 951 (1997).

[10] P. Wagner *et al.*, Phys. Rev. B **55**, R14 721 (1997).

[11] Y. Q. Li *et al.*, J. Mater. Res. **10**, 2166 (1995).

[12] J. O'Donnell *et al.*, Phys. Rev. B **54**, R6841 (1996).

[13] For a review, see, *The Hall Effect in Metals and Alloys*, edited by Colin Hurd (Plenum, New York, 1972), p. 153.

[14] Jun Kondo, Prog. Theor. Phys. **27**, 772 (1962).

[15] J. P. Jan, Helv. Phys. Acta **25**, 677 (1952).

[16] J. J. Rhyne, Phys. Rev. **172**, 523 (1968).

[17] Kengo Adachi and Katshuhiko Ohkohchi, J. Phys. Soc. Jpn. **49**, 154 (1980).

[18] T. Holstein and Lionel Friedman, Phys. Rev. **165**, 1019 (1968).

[19] Y. Imry, Phys. Rev. Lett. **71**, 1868 (1993).