# Hall effect of $La_{2/3}(Ca,Pb)_{1/3}MnO_3$ single crystals near the critical temperature

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The Hall resistivity $\rho_{xy}$ of a $La_{2/3}(Ca,Pb)_{1/3}MnO_3$ single crystal has been measured as a function of temperature and field. The overall behavior is similar to that observed previously in thin films. At 5 K, $\rho_{xy}$ is positive and linear in field, indicating that the anomalous contribution $R_S$ is negligible. However, the effective carrier density in a free electron model is $n_{\rm eff}=2.4$ holes/Mn, even larger than the 0.85–1.9 holes/Mn reported for thin films and far larger than the 0.33 holes/Mn expected from the doping level. As temperature increases, a strong, negative contribution to $\rho_{xy}$ appears, that we ascribe to $R_S$. Using detailed magnetization data, we separate the ordinary ($\propto B$) and anomalous ($\propto M$) contributions. Below $T_c$, $|R_S|\propto\rho_{xx}$, indicating that magnetic skew scattering is the dominant mechanism in the metallic ferromagnetic regime. At and above the resistivity-peak temperature, we find that $\rho_{xy}/\rho_{xx}M$ is a constant, independent of temperature and field. This implies that the anomalous Hall coefficient is proportional to the magnetoresistance. A different explanation based on the two-fluid model is also presented. [S0163-1829(99)06517-0]

The paramagnetic insulator to ferromagnetic metal transition of the manganite system $La_{1-x}A_xMnO_3$ (where $A$ is Ca, Sr, or Pb) has long been thought to be roughly described by the double-exchange interaction.[1] After the recent rediscovery of colossal magnetoresistance in this system,[2] a renewed effort was made to understand the physical properties[3]. It now appears that double exchange alone cannot explain the large change in conductivity, and that Jahn-Teller effects should be included.[4] This view is supported by the evidence of strong coupling between lattice effects, magnetic order, and transport behavior.[5]

A consequence of the Jahn-Teller/double-exchange picture is that the charge-carrier characteristics change from a fully spin polarized (half-metallic) band at low temperatures, through a regime of partially polarized bands, before finally becoming localized as polarons well above $T_c$. It is important, therefore, to explore the band properties of the three regimes by means of the Hall effect. The situation is complicated by the presence of the extraordinary Hall coefficient in the ferromagnetic phase. We report here the first complete measurement of both the ordinary and extraordinary Hall coefficients on single-crystal samples spanning the full temperature range, from metallic ferromagnet to polaronic conductor. As in previous measurements on thin films and low-temperature measurements on single crystals, we find the ordinary Hall coefficient to be unexpectedly small at low temperature, corresponding to a hole concentration of 2.4 holes/Mn atom in a simple one-carrier free-electron model. Other researchers have reported values between 0.85 and 1.9 holes/Mn.[6–9] We show that this result can be reconciled with the actual doping level when details of the Fermi surface are taken into account.

In order to extract the extraordinary Hall coefficient, and to treat the data in the presence of ''colossal'' magnetoresistance near $T_c$, we have combined detailed $\rho_{xy}$ measurements with magnetization ($M$) and longitudinal resistivity ($\rho_{xx}$) measurements on the same $La_{2/3}(Ca,Pb)_{1/3}MnO_3$ single crystal. While it is possible to separate ordinary and extraordinary effects at low temperature, only an electronlike transverse resistivity is found in the magnetoresistive regime near $T_c$. In this temperature range, the tangent of the Hall angle, $\rho_{xy}/\rho_{xx}$ is found be remarkably linear in the measured magnetization, despite 300% changes in the longitudinal resistivity. As it seems unlikely that the skew-scattering mechanism continues to operate in the hopping regime, we consider another approach in which the observed conductivity is assumed to be a field- and temperature-dependent admixture of bandlike and polaronic charge carriers, conducting in parallel.[10] This approach also provides a very good representation of the data, but the polaronic Hall constant that emerges increases more rapidly as the temperature approaches $T_c$ than is expected from conventional polaron theory.

High-quality single crystals of $La_{2/3}(Ca,Pb)_{1/3}MnO_3$ were grown from 50/50 $PbF_2/PbO$ flux. The actual composition was determined to be $La_{0.66}(Pb_{0.67}Ca_{0.33})_{0.34}MnO_3$ from chemical analysis of crystals from the same batch. Specimens were cut along crystalline axes from larger preoriented crystals. Contact pads for Hall resistivity measurements were made by Au evaporation and standard photolithographic patterning, followed by ion milling. Au wires and silver paint were used for electrical connections. The contact resistances after annealing were less than 1 $\Omega$ at room temperature. We adopted a low-frequency ac method for the measurements. First, the transverse voltage signal was nulled at zero field by a potentiometer at each temperature. The change in the transverse resistance as a function of field was amplified by SR552 low noise preamplifier, and recorded by a phase-sensitive detector. Magnetization was measured by a 7 T superconducting quantum interference device magnetometer.

The crystal has a fairly small residual resistivity ($\rho_{xx}^0 \approx 51\mu\Omega$ cm) and large magnetoresistance (326% at 293 K under 7 T). The metal-insulator transition temperature, determined by the maximum change in resistivity $d\rho_{xx}/dT$ under zero magnetic field, is 287.5 K. Figure 1 shows the field dependence of $\rho_{xy}$ at several temperatures. The overall behavior is the same as that of thin-film samples.[7,8] Far below

 

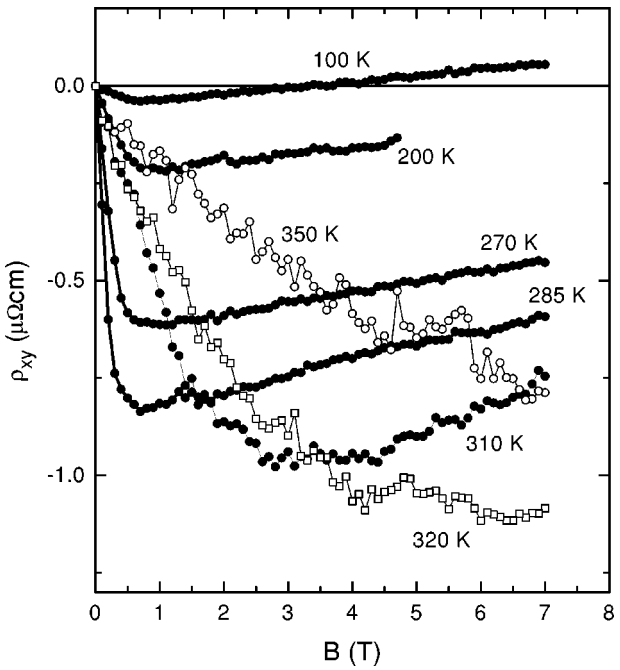


FIG. 1. Hall resistivity $\rho_{xy}$ of a $La_{2/3}(Ca,Pb)_{1/3}MnO_3$ single crystal as a function of field at indicated temperatures.

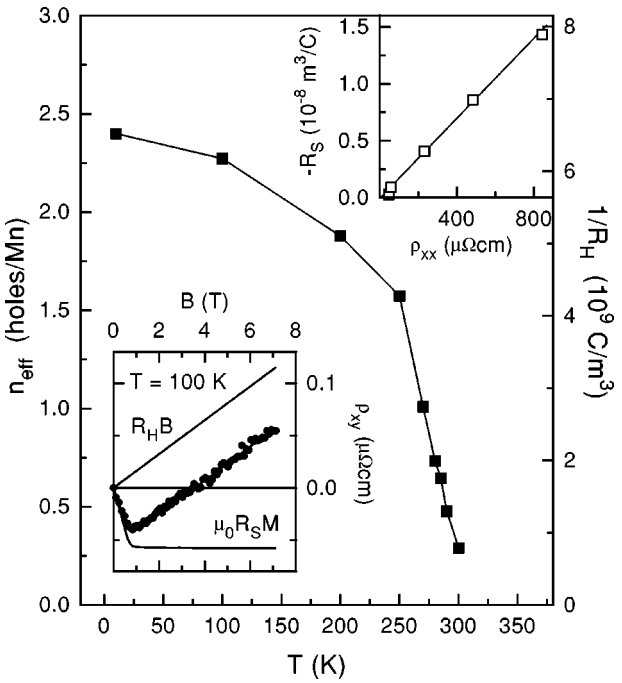


FIG. 2. Effective number of holes/Mn as a function of temperature. The lower inset shows the decomposition of $\rho_{xy}$ into ordinary and anomalous Hall effects below $T_c$. The upper inset shows the linear relation between the anomalous Hall coefficient $R_S$ and the longitudinal resistivity $\rho_{xx}$.

$T_c$, $\rho_{xy}$ decreases at first and then increases, showing a hole-like high-field Hall coefficient. The initial drop becomes larger as $T$ approaches $T_c$. Around $T_c$, $\rho_{xy}$ is strongly curved making a simple interpretation impossible. Far above $T_c$, $\rho_{xy}$ shows a negative Hall coefficient, characteristic of electronlike charge carriers.

In ferromagnetic metals, the embedded magnetic moments cause asymmetric scattering of current-carrying electrons, which in turn produce an additional transverse voltage, called anomalous (or extraordinary) Hall effects. The anomalous Hall field is proportional to the current density and the sample magnetization, so $\rho_{xy}$ is generally written as[11]

$$\rho_{xy}(B,T)=R_H(T)B+\mu_0 R_S(T)M(B,T), \qquad (1)$$

where $R_S(T)$ is the temperature-dependent anomalous Hall coefficient. From separate magnetization measurements corrected for demagnetizing fields, we could extract $R_H$ and $R_S$ from $\rho_{xy}$ for temperatures below $T_c$, as shown in the lower inset of Fig. 2. If we assume the free-electron model for the Hall coefficient, the effective charge-carrier density, $n_{\rm eff}=1/eR_H$, turns out to be $4.1\times10^{22}$ cm$^{-3}$ or 2.4 holes/Mn below 100 K, a value much larger than the nominal doping level (0.33 holes/Mn), so the naive interpretation is not valid here. Others report similar results and some authors interpreted this as an effect of charge carrier compensation.[7,8] We will do the same, as follows. Pickett and Singh calculated the $T=0$ band structure of 1/3-doped manganites, and concluded that the alloy is nearly half-metallic, and that the majority-spin band consists of a spherical Fermi surface containing 0.05 electrons and a nearly cubic Fermi surface containing 0.55 holes, larger than the nominal doping level of 0.33.[12] Since our Hall experiment as well as others is in the weak-field limit even at the lowest temperature and at the highest field ($\omega_c\tau\sim0.01\ll1$, where $\omega_c$ is the cyclotron frequency and $\tau$ the Drude relaxation time), the Hall coefficient $R_H$ of a nonspherical Fermi surface is given not by the high-field limit $R_\infty=1/ne$, but rather by $R_H=r/ne$, where $r$ is a dimensionless factor depending on the details of the Fermi surface. For example, $r$ is known to equal 1/2 for a cubic Fermi surface.[13] In a two-band model, the Hall coefficient is given by $R_H=(r_h n_h\mu_h^2-r_e n_e\mu_e^2)/e(n_h\mu_h+n_e\mu_e)^2$. If we assume equal mobilities for holes and electrons, we obtain $n_{\rm eff}V_c=V_c/eR_H=1.6$ holes/Mn, where $V_c$ is the volume per formula unit. This explains why the observed $R_H$ is much smaller than expected from the doping level. Jacob *et al.* assumed $\mu_e/\mu_h=2.1$ to have a quantitative agreement to their results without considering the shape-dependent factor $r$.[8] They justified their assumption based on the density of states at the Fermi level. Using the electron and hole densities from Pickett and Singh, we can reproduce the low-temperature value of $R_H$ by assuming a mobility ratio $\mu_e/\mu_h=1.5$.

The high-field slope of $\rho_{xy}$ changes with temperature, becoming steeper as $T$ approaches $T_c$ from below, and changing sign above $T_c$ to show an electronlike Hall coefficient. Because the anomalous Hall effect, which tends to saturate at high fields, cannot explain this slope change, we have to assume a temperature dependent $n_{\rm eff}$. The main panel of Fig. 2 shows the temperature dependence of $n_{\rm eff}$ in the free-electron approximation with $r=1$. As $T$ increases, $n_{\rm eff}$ decreases slowly until 250 K and then drops rapidly. At and above $T_c$, Eq. (1) cannot decompose $\rho_{xy}(B)$ because of the polaronic contribution and large magnetoresistance which will be discussed later. A qualitatively similar change was reported by Jacob *et al.*[8] Although the physical origin is not certain, the participation of the minority-spin band in the charge transport, which is evidenced by decreasing polariza-

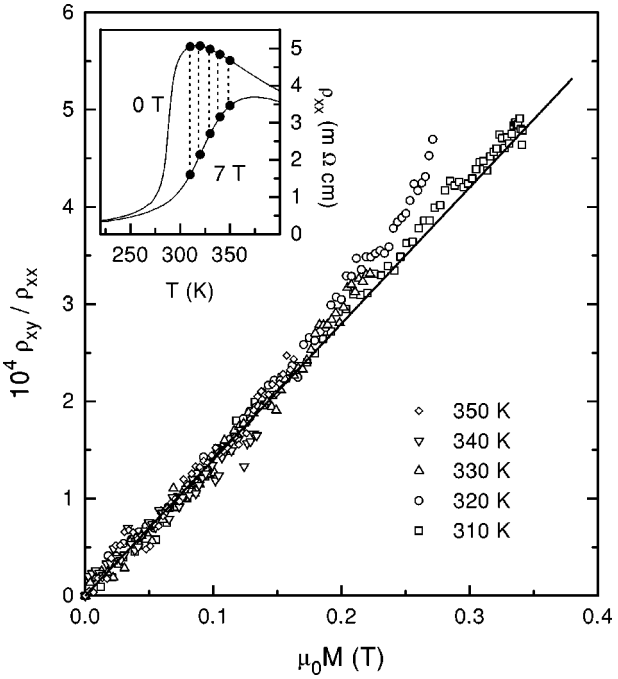


FIG. 3. Scaling behavior of the Hall angle, $\tan\theta_H=\rho_{xy}/\rho_{xx}$ and the sample magnetization $M$ at temperatures from 310 to 350 K. The inset shows the colossal magnetoresistance of this material. Solid circles indicate the region of scaling.

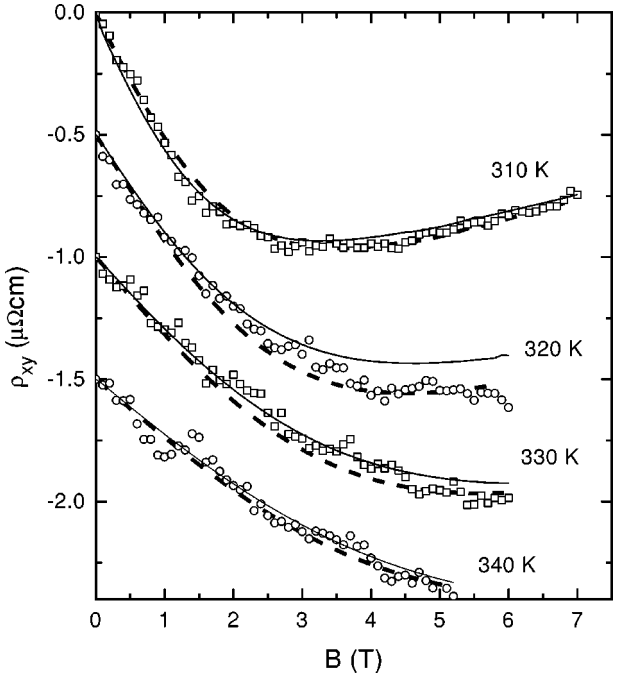


FIG. 4. Hall resistivity data as a function of field at selected temperatures above $T_c$. Thin solid lines come from the assumption of field and temperature dependent $R_S$. Thick dashed lines are from the two-fluid model. See text for details.

tion as $T$ increases, could be one of the reasons. We compared $n_{\rm eff}(T)$ with $\rho_{xx}(T)$ or $M(T)$, but no simple relation was found. In particular, no logarithmic dependence on $M(T)$ was seen.[14]

The decomposition shown in the lower inset of Fig. 2 enables us to extract the temperature dependence of anomalous Hall coefficient $R_S$ also. It is customary in ferromagnetic metals to compare $R_S$ with $\rho_{xx}$ to determine the origin of the anomalous Hall effects. From 10 to 270 K, where $R_S$ is well defined, we find $R_S$ is proportional to $\rho_{xx}$ (Fig. 2, the upper inset). The coefficient $\alpha$ is $-1.7\times10^{-3}\mathrm{T}^{-1}$ and the absolute magnitude of $R_S$ is comparable to that of Ca-doped thin-film samples.[7,8] This linear relation is in agreement with the classical skew scattering theory, where moving charge carriers experience a force due to the magnetic field produced by a localized magnetic moment and are scattered asymmetrically.[15] However, the sign difference relative to the ordinary Hall coefficient and the absence of an $R_S$ peak below $T_c$ disagree with the predictions. We note here that Kim *et al.* presented an interesting explanation for the opposite sign between $R_H$ and $R_S$ from the appearance of topological flux.[16] The presence of $R_S$ and its proportionality to $\rho_{xx}$ supports our earlier argument that the metallic resistivity is dominated by spin-dependent scattering.[17]

Around and above $T_c$, $\rho_{xy}(B)$ is not easy to interpret because of the large magnetoresistance in this region and the electronlike polaronic contribution as verified by Jaime *et al.*[18] A strong curvature in $\rho_{xy}(B)$ was observed at temperatures where the zero field $\rho_{xx}$ shows a peak and the magnetoresistance is the largest (the inset of Fig. 3). Considering the large changes in both $\rho_{xy}$ and $\rho_{xx}$ as a function of field, it is instructive to consider the Hall angle, defined by $\tan\theta_H=\rho_{xy}/\rho_{xx}$. Interestingly, if we plot $\tan\theta_H$ as a function of the sample magnetization, all the data above 310 K fall on a single line crossing zero as shown in Fig. 3. This means that we can describe the Hall resistivity in this temperature regime simply as

$$\rho_{xy}(B,T)=\alpha'\mu_0 M(B,T)\rho_{xx}(B,T)=\mu_0 R_S'(B,T)M(B,T), \tag{2}$$

where the field- and temperature-dependent anomalous Hall coefficient $R_S'(B,T)=\alpha'\rho_{xx}(B,T)$ and $\alpha'=-1.4\times10^{-3}\ \mathrm{T}^{-1}$. The high-temperature coefficient $\alpha'$ is a little smaller than the low-temperature one $\alpha$. The linear relationship between the Hall angle and the magnetization was already noted by Matl *et al.*, but only in the low-field regime.[7] Our results show that the Hall angle scales with the magnetization over the entire field investigated for temperatures at and above the resistivity peak temperature. In Fig. 4, we compare $\rho_{xy}$ data with the calculation from Eq. (2) as a function of field (thin solid lines). The agreement is quite good except for some high-field data at 320 K. The origin of $R_S'$ is not certain at this time. The skew scattering theory, which was applied to low-temperature data, assumes an interaction between band electrons and localized magnetic moments. The current understanding is, however, that the charge carriers are dominantly small polarons and the conduction is by means of hopping processes at temperatures where Eq. (2) holds. Furthermore, the universal relation between the Hall angle and magnetization despite more than 300% change in magnetoresistance requires a more general theory that does not depend on the scattering length of charge carriers.

For high enough temperature, the adiabatic small-polaron hopping theory predicts the Hall mobility, $\mu_H\equiv\tan\theta_H/B$, is an increasing function of temperature,[19] while the present result is the opposite since $\mu_H\propto M/B=\chi$. In manganite sys-

tem, the high-temperature Hall effect results are in accord with the small-polaron theory.[18] So Eq. (2) might be valid for the limited temperature regime and should change to the activated form as temperature increases. In order to have an explanation with wider application range, we have tried another method motivated by the two fluid model, recently proposed by Jaime *et al.*[10] In the context of the effective-medium approximation, they analyze the resistivity of manganite films and find that strongly elongated conducting regions are required to fit the resistivity data. In this limit, the effective conductivity is close to that for parallel channels. Therefore, we assume that charge carriers in manganites move through two parallel channels: one has metallic conductivity $\sigma_m(T)$, and the other has hopping conductivity $\sigma_h(T)$. The key element of this model is the introduction of the *mixing factor* $c(B,T)$, which is the portion of the total carriers that are band electrons and which absorbs the field dependence of the conductivity. Then, the total conductivity reads as

$$\sigma_{\text{tot}}(B,T)=c\sigma_m(T)+(1-c)\sigma_h(T), \tag{3}$$

and $\sigma_m(T)$ and $\sigma_h(T)$ are assumed to be field independent, and are extracted by fitting the conductivity data far from $T_c$. The mixing factor is calculated from Eq. (3) by assuming that $\sigma_m(T)$ and $\sigma_h(T)$ can be extrapolated to the region nearer $T_c$. This two-fluid model can be applied to the Hall effect in a similar way as in multiband model as following:

$$\frac{\rho_{xy}}{B}=\frac{R_m c^2\sigma_m^2+R_h(1-c)^2\sigma_h^2}{[c\sigma_m+(1-c)\sigma_h]^2}, \tag{4}$$

where $R_m=(R_1+\alpha\mu_0\sigma_m^{-1}M/B)/c$ and $R_h=R_2/(1-c)$ are effective Hall coefficients due to band electrons and polarons, respectively. $R_1$ and $R_2$ are free parameters for fitting. As we can see in Fig. 4, the agreement with the data is excellent (thick dashed lines). The normal Hall coefficient of metallic phase $R_1$ corresponds to about 1 holes/Mn and slightly temperature dependent. The resulting values of $R_2$, the polaron Hall coefficient, are a rapidly decreasing function of temperature, which is more or less proportional to the magnetic susceptibility $\chi$. When Emin and Holstein's theory valid for polarons in a nonmagnetic material is applied to the temperature dependence of $R_2$,[19] we obtain $\Delta=4500$ meV, five times larger than that determined by the conductivity curve. Since Emin and Holstein's theory was derived for high-temperature limits, it may not apply close to the metal-insulator transition. It is quite likely that these polarons have significant magnetic character and that the double-exchange mechanism continues to strongly affect their mobility near $T_c$.

In conclusion, we measured $\rho_{xy}$, $\rho_{xx}$, and $M$ of a $La_{2/3}(Ca,Pb)_{1/3}MnO_3$ single crystal and observed a change from holelike $R_H$ below $T_C$ to electronlike $R_H$ far above $T_c$. We obtained 2.4 holes/Mn at 5 K and interpreted as a result of carrier compensation. We also found a linear relation between the negative anomalous Hall coefficient and zero field $\rho_{xx}$ below $T_C$ in accord with the magnetic skew scattering theory. At and above the resistivity peak temperature, we found that $\rho_{xy}/\rho_{xx}M$ is a constant, independent of temperature and field. This implies that the anomalous Hall coefficient is proportional to the magnetoresistance. Another interpretation based on the recently proposed two-fluid model also produces a good agreement with the data, but the temperature dependence of polaronic contribution to the Hall effect is different from the high-temperature-limit prediction.

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