Evidence of charge-carrier compensation effects in $La_{0.67}Ca_{0.33}MnO_3$

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We report on detailed Hall-effect measurements of thin films of $La_{0.67}Ca_{0.33}MnO_3$ above and below the metal-insulator transition. In the metallic ferromagnetic regime, we find a temperature-independent holelike nominal charge-carrier density $n_h^* = 1.3$ per unit cell, consistent with a partly compensated Fermi surface. The mobility is only 92 $mm^2/V\,s$ at 4 K, and decreases with increasing temperature. Huge negative magnetoresistivity results from an increase in mobility. In low magnetic fields or at high temperatures, an anomalous electronlike contribution dominates the Hall voltage. For possible side jumps, we estimate an average jump length of the electron wave packet of 10^{-13} m.
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Up to now, published transport measurements on the perovskite compounds $A_{1-x}B_xMnO_3$ $(0 \leqslant x \leqslant 1)$ concentrated on the colossal negative magnetoresistive effects of the longitudinal resistivity $\rho_{xx}(B,T)$. We present a detailed study of the nondiagonal transverse resistivity ρ_{xy} of $La_{0.67}Ca_{0.33}MnO_3$ films, since this quantity contains valuable information on the number and mobility of charge carriers. Furthermore, one can determine the average length of the side jumps introduced by spin-orbit coupling in scattering events of charge carriers from the anomalous Hall effect. Nevertheless comparably few results have been published on ρ_{xy},[1–4] due to experimental difficulties determining ρ_{xy}.

The films were prepared by high-pressure dc-magnetron sputtering on (100) MgO substrates, and annealed in oxygen for a full loading of the oxygen sublattice. X-ray-diffraction measurements showed a distorted cubic cell of dimension $(2a_0, 2a_0, 2a_0)$, with $a_0 = 0.385$ nm and epitaxial c-axis-oriented growth. The angular spread of the c and a,b axes are 0.6° and 1°, respectively. By scanning electron and scanning force microscopy, we found an average grain size of 300 nm and a homogeneous surface and composition. Therefore we do not expect a noticeable influence of grain-boundary resistance on our transport measurements.

We patterned the samples photolithographically to a 3-mm-wide and 8-mm-long Hall bar structure. The measurements were performed in an Ohmic regime with a current $I = 1$mA. During a magnetic-field sweep the temperature was stabilized to better than 0.02 K and the field was increased from zero to maximum, decreased to the negative maximum, and again increased to zero. Before starting, we ensured the position of opposite Hall contacts to be on an equipotential line in zero field by a bridge circuit and current injection along three terminals.[5] A nonperfect adjustment was compensated for by taking data at reversed current and field directions. In order to avoid hysteresis effects in the ferromagnetic state, we evaluated only the reproducible field sweeps from the positive and negative maxima down to zero.

In Fig. 1, we show $\rho_{xx}(T)$ in zero field and in 8 T for one sample with thickness $t = 211$ nm. The thermally activated part is mathematically best described by $\rho(T,B) \propto T \exp(E_A/k_BT)$, with an activation energy $E_A = 81.5$ meV. Such a behavior results from a polaron hopping model,[6] where the mobility rather than the number of charge carriers is thermally activated. With decreasing temperature, ρ_{xx} reaches a maximum at 244 K and drops sharply. This maximum is strongly suppressed $[(\rho(0\ \mathrm{T}) - (\rho(8\ \mathrm{T})/\rho(8\ \mathrm{T}) = 600\%]$ by field-induced increasing spin order. Spin disorder also dominates the metallic low temperature resistivity $[\rho(4\ \mathrm{K}) = 3.16 \times 10^{-6}\ \Omega\,\mathrm{m}]$. This is obvious from the inset of Fig. 1, where $\rho_{xx}(T) - \rho_{xx}(10\ \mathrm{K})$ is plotted together with the decrease of the spontaneous magnetization $M(10\ \mathrm{K}) - M(T)$ of this sample. The data have been taken on a (3×10)-mm^2 piece of the same sample at a field of $B = 20$ mT in a falling temperature run with a superconducting quantum interference device magnetometer. From these results, we conclude that we investigate a representative high-quality sample with a stoichiometry close to the nominal composition.

The measurement of ρ_{xy} in cubic materials requires a symmetry-breaking field, which is in Hall-effect measurements the external magnetic field B. In ferromagnetic mate-

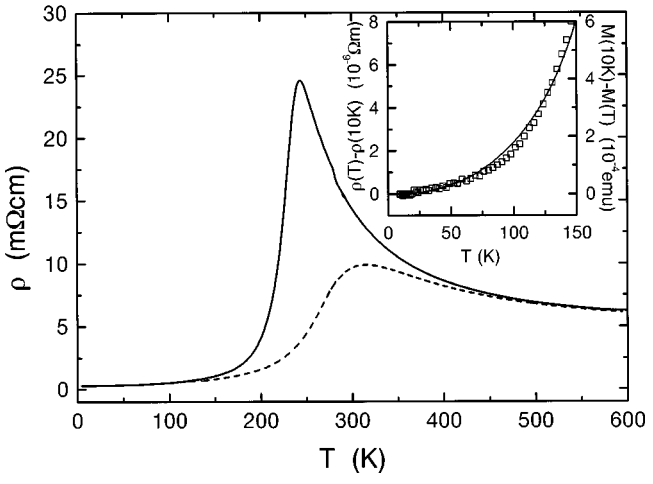

FIG. 1. Resistivity in zero field (solid line) and in an 8-T magnetic field (dashed line) as functions of temperature. The inset shows the increase of the low-temperature resistivity (solid line, left axis) and the decrease of the spontaneous magnetization (open symbols, right axis).

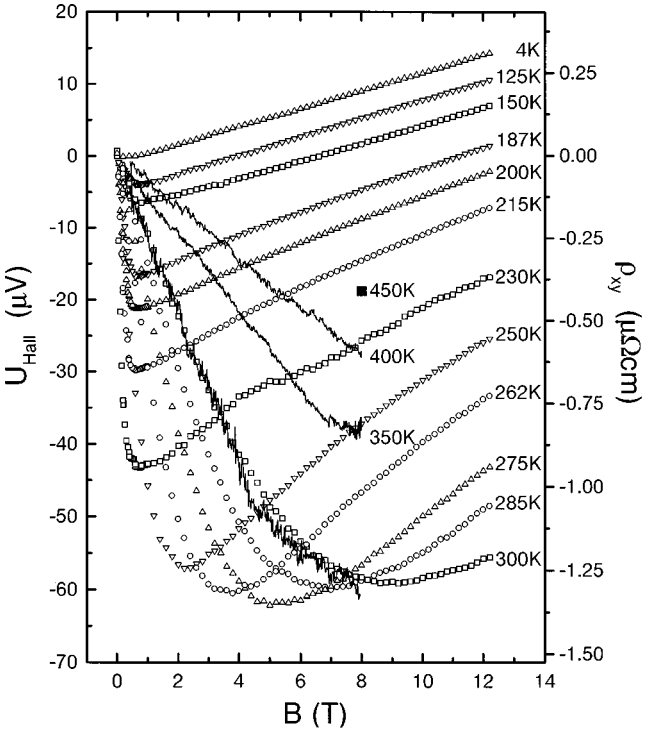

FIG. 2. Measured Hall voltages (left axis) and transverse resistivities ρ_{xy} (right axis) as functions of magnetic field for constant temperatures. Data at low (high) temperatures are shown as open symbols (solid lines). Note the agreement of the 300-K data measured with different experimental setups. In the temperature range between 200 and 4 K, we omitted five measured curves with the same low noise level for clarity. The apparent oscillations on the 230-K isotherm result from the extreme field and temperature dependence of the resistivity close to T_c.

rials it is also well known that the magnetization M of the sample is symmetry breaking. Therefore, the transverse resistivity is generally given by

$$\rho_{xy} = U_H t/I = R_H B + R_A \mu_0 M, \tag{1}$$

with the ordinary and anomalous Hall coefficients R_H and R_A, respectively.[7] A compilation of the Hall voltage data $U_H(B)$ at constant temperatures is shown in Fig. 2. The curves taken below T_c all show the same behavior. At low fields, U_H decreases steeply with increasing field, reaches a minimum around 1 T, and then rises with a linear slope at high fields. At the field value of the minimum, the magnetization, as determined by hysteresis loops, is close to saturation. Therefore the initial part of the U_H curves is dominated by the magnetization of the sample, and not by the external field. This anomalous contribution becomes even more pronounced at higher temperatures. The interplay of holelike ordinary and electronlike anomalous contributions can give rise to a field-dependent sign change of the Hall voltage. Therefore it is necessary to evaluate the data over a wide temperature and field range in order to distinguish clearly both effects.

In the following, we concentrate first on the high-field regime, where the magnetization is field independent. Here the slope $d\rho_{xy}/dB$ is given only by the ordinary Hall contribution induced by Lorentz forces on charge carriers. The

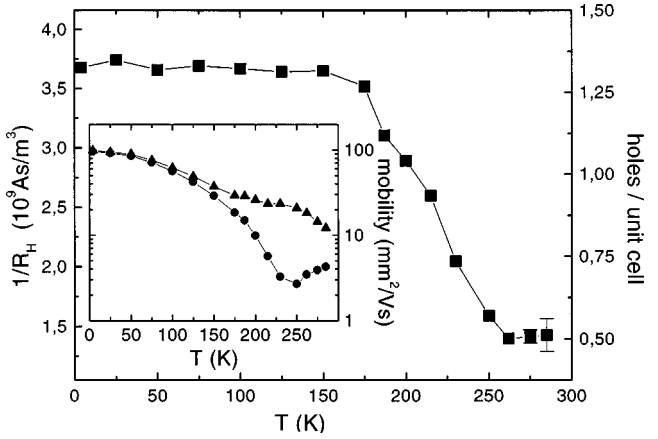

FIG. 3. Inverse of the normal Hall coefficient (left axis) corresponding to the number of holes (right axis) plotted as a function of temperature. Error bars are indicated if larger than symbol size. The inset shows the mobility determined in zero field (circles) and in high field $B=8$ T (triangles).

linear positive slope corresponds to a field-independent number of holelike charge carriers. Since the slope is linear even close to T_c, where huge negative magnetoresistive effects occur, we conclude that the increase in conductivity is due to a magnetic-field-induced increase in charge-carrier mobility, analogous to the charge-ordered compound $Nd_{0.5}Sr_{0.5}MnO_3$.[8]

The inverse of the Hall coefficient $R_H=(dU_H/dB)t/I$, evaluated from the linear high-field slopes, is plotted in Fig. 3, and shows the main result. The nominal charge-carrier density calculated in a single-band model is 1.3 holes per unit cell ($n_h^*=1.3$/uc) at low temperatures, and does *not* correspond to the doping level. The error of R_H in the metallic phase is determined by the sample thickness t, which was evaluated by a Mireau interferometer to 211 ± 15 nm. At 175 K, a sudden decrease of the charge carrier density starts. Well above the zero field T_c it is again nearly temperature independent at a value of 0.5/uc. Since in the high fields used for the Hall-effect measurements the temperature coefficient of the resistivity stays positive up to room temperature, the decrease is not due to the metal-insulator transition, but rather from a structural type.[9] In the inset of Fig. 3, the strong temperature dependence of the mobility is shown. At low temperature, we observe 92 $mm^2/V\,s$, and at T_c a minimum value of 2.5 $mm^2/V\,s$. The nearly field-independent low mobility in the magnetically ordered low-temperature regime shows that the electrons strongly interact with their environment even in the metallic state. With increasing temperature spin disorder scattering seems to be most relevant, since close to T_c a strong enhancement of the mobility with magnetic field is observed, which causes the giant negative magnetoresistance. Measurements on three more samples showed the same qualitative behavior, but with $n_h^*=1.1$/uc, $n_h^*=1.4$/uc, and $n_h^*=1.9$/uc.

In $La_{0.67}Ca_{0.33}MnO_3$ values of n_h^* different from the nominal doping value were observed before. Núñez-Regueiro, Gupta, and Kadin found only $n_h^*=0.07$/uc, but measurements were performed at a fixed field value of $B=\pm1.5$ T, and anomalous effects not taken into account.[2] Snyder *et al.*, however, measured at high magnetic fields,

and found a value of $n_h^* = 0.85$/uc at low temperatures and at $0.9T_c$.[1] The reasons for the deviation between nominal doping value and nominal charge-carrier density have not yet been discussed.

Recent band-structure calculations by Pickett and Singh, based on a virtual-crystal approximation, show that $La_{0.67}Ca_{0.33}MnO_3$ is half metallic.[10] They calculated a spherical Fermi surface centered around the Γ point, containing 0.05 electrons/uc and a nearly cubic Fermi surface with rounded corners centered around the R point, containing 0.55 holes/uc in the majority band. In the spin minority band, a low density of electrons is localized by potential fluctuations due to disordered occupation of the La site, and does not contribute to electrical transport. This motivates us to explain our data in a two-band model. Then the Hall coefficient is related to the number of carriers by $R_H = (n_h\mu_h^2 - n_e\mu_e^2)/[e(n_h\mu_h + n_e\mu_e)^2]$. With equal mobilities $\mu_e = \mu_h$, this corresponds to a number of charge carriers in the single-band model $n_h^* = +0.72$/uc. We have to assume a mobility ratio between holes and electrons $x = \mu_e/\mu_h = 2.1$ to obtain a quantitative agreement. This assumption is justified by the following consideration. Since Pickett and Singh found a nearly constant Fermi velocity $v_F = 7.6 \times 10^5$ m/s even on the cube, we approximate both Fermi surfaces by an independent-electron (hole) sphere. With the values they calculated for the density of states at the Fermi energy, $D(E_F,h) = 0.38/(\text{eV uc})$ and $D(E_F,e) = 0.09/(\text{eV uc})$, and the parabolic approximation, we find an effective-mass ratio $m_h/m_e = 2.0$. Assuming equal scattering times $\tau_h = \tau_e$ for both charge carriers, this value is directly the mobility ratio. In view of the approximations made, the perfect coincidence of the effective-mass ratios is fortuitous, but it demonstrates the necessity to include electron and hole conduction in an interpretation of Hall-effect measurements. The sample-to-sample variations found in the nominal charge-carrier density result from slight differences in stoichiometry. They give rise to opposite effects on electron and hole numbers, which will change the nominal charge-carrier density dramatically in a compensated model.

From the residual resistivity ρ_0 we estimate, with $1/\rho_0 = e^2\tau(n_e/m_e + n_h/m_h)$ and the free electron mass m_e, the mean free path $l = \tau v_F = 1.6$ nm to several lattice constants. This is still in the metallic range, though the assumption of perfect periodicity in the band-structure calculation is violated. Nevertheless, the band-structure description of the electronic properties seems to work well up to 175 K. At this temperature, the mean free path is of the order of one lattice constant only, indicating the formation of localized states at the metal-insulator transition. The observed slight increase of the charge-carrier density above T_c is due to thermal activation.

In the low-field regime, the Hall effect is dominated by anomalous contributions. An anomalous Hall coefficient R_A related to sample magnetization can result from two different elementary processes, as discussed by Berger.[11] A left-right asymmetry of the scattering process (skew scattering) or a nonclassical side jump of the center of weight of an electron wave packet. Both effects scale with the longitudinal resistivity $R_A\mu_0 M = \gamma\rho_{xx}^n$, but with different power laws $n = 1$ and 2 for skew scattering and side jump, respectively. The

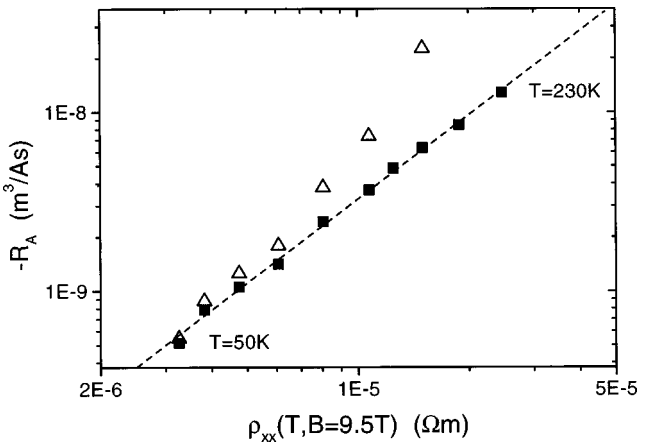

FIG. 4. Anomalous Hall coefficient R_A vs longitudinal high-field resistivity $\rho_{xx}(B=9.5\text{ T})$. The resistivity increases with temperature. Solid symbols assume full saturation, and open symbols are calculated with the measured high-field magnetization. The line has a slope of $R_A \propto \rho_{xx}^{1.56}$.

usual way to determine this anomalous contribution is to extrapolate the linear high-field data ($7\text{ T} < B < 12$ T) to zero field.[7] According to Eq. (1), the extrapolated value is the anomalous Hall coefficient times the saturated magnetization $\rho_{xy}^\star = R_A\mu_0 M_{\text{Sat}}$. A double logarithmic plot of $\rho_{xy}^\star(T)$ versus $\rho_{xx}(T,B=0)$ shows a strong curvature and an average slope smaller than 1 in disagreement with theory. However, Berger did not take into account the magnetoresistance effects on ρ_{xx}, since in normal metallic alloys this is just a minor correction. But for the manganites this is a dramatic effect. Especially close to T_c, one cannot expect the zero-field semiconductorlike resistivity to scale with the properties of the metallic ferromagnetic high-field phase. Since $\rho_{xy}^\star$ is also not a zero-field property by definition, but a high-field property of the material whose value is just extracted by interpolation to zero field, in Fig. 4 we show a plot of the anomalous Hall coefficient $R_A = \rho_{xy}^\star/(\mu_0 M_{\text{Sat}})$ against the average high-field resistivity $\rho_{xx}(T,B=9.5\text{ T})$. This gives a perfect power law in the ferromagnetic regime, with an exponent $n = 1.56$. Data points at temperatures smaller than 50 K have been omitted, since with increasing magnetic order R_A vanishes[12] and isotropic scattering dominates ρ_{xx}. Subtracting estimated isotropic residual resistivities will also lead to scaling behavior, but with lower slopes $1.1 < n < 1.56$. On the other hand, taking into account the increasing spin disorder with increasing temperature will increase the exponent. This is shown in Fig. 4 by replotting the data values with the measured values of the magnetization determined in a field of 5 T at the respective temperatures instead of the zero-temperature magnetization. Though the linear correlation of the data points is less good, the exponent of this rescaled data is $n = 2.1$, close to the side jump value.

Since for high-resistivity samples such as ours the side jump effect is expected to dominate, we will discuss this process in the following. The proportionality constant $\gamma = \rho_{xy}^\star/\rho_{xx}^2$ is experimentally determined to be in the range of $25 \pm 15\ \Omega^{-1}\,\text{m}^{-1}$, with ρ_{xx} taken at $B = 9.5$ T. It is related to the side jump lengths per scattering event, Δy_e and Δy_h, in a two-band model by

$$\gamma = \frac{e^2}{v_F m_e}\left(n_e \Delta y_e + n_h \frac{\mu_h}{\mu_e} \Delta y_h \right) = \frac{(n_e + n_h) e^2}{v_F m_e} \Delta y_{\text{eff}}. \quad (2)$$

In the above formula, we assumed equal scattering times and Fermi velocities for holes and electrons, but kept a different effective mass, and therefore the mobility ratio enters the equation. Disregarding the accuracy of these details we achieve an order of magnitude estimate of the effective jump width $\Delta y_{\text{eff}} \approx 10^{-13}$ m. Inspecting the data of Wagner *et al.* for $Pr_{0.5}Sr_{0.5}MnO_3$ with respect to this quantity yields a comparable low value.[4] These are two orders of magnitude smaller than theoretically predicted,[11] and even three orders smaller than observed in iron.[13] One possibility might be that the electron and hole contributions by chance compensate. However, in discussing these small values, one must keep in mind that the elementary side jump of a free electron in a scattering event is only 10^{-15} m. It is the spin-orbit interaction in a periodic lattice that is responsible for the necessary enhancement factors in ferromagnetic metals. Due to the low mean free path in the manganites, this periodicity is less pronounced, and therefore smaller side jump values might result.

With increasing temperature a wide field range is dominated by the anomalous Hall contribution, and the normal effect becomes unmeasureable. This temperature-dependent electronlike low-field slope of the Hall voltage was observed in Gd-doped $La_{0.67}Ca_{0.33}MnO_3$ by Jaime *et al.*[3] at high reduced temperatures $T/T_c > 2$. Since the activation energy E_H for the Hall coefficient was found to be two-thirds of the value of the drift mobility E_A, they interpreted this as evidence of a polaron transport mechanism.[6] If we try to fit the slope $\partial \rho_{xy}(T)/\partial B$ with thermal activation, we can also obtain reasonable agreement, but find $E_H \geqslant E_A$.

Concluding we made high-resolution longitudinal ρ_{xx} and transverse ρ_{xy} transport measurements on high-quality epitaxial thin-film samples of $La_{0.67}Ca_{0.33}MnO_3$. We can clearly identify a metallic regime up to 175 K with a temperature-independent charge-carrier density, corresponding to more than one nominal charge carrier in a single band. This high value confirms band-structure calculations, which predict a semimetallic behavior with electron and hole bands. The giant negative magnetoresistance is found to result mainly from an increased mobility of a constant number of charge carriers. We discuss the anomalous low-field Hall effect in terms of a nonclassical side jump model, resulting from spin-orbit coupling in a periodic potential. The estimated jump width is several orders of magnitude smaller than in *d*-band metals.

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