Hall-Effect Sign Anomaly and Small-Polaron Conduction in $(La_{1-x}Gd_x)_{0.67}Ca_{0.33}MnO_3$

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The Hall coefficient of Gd-doped $La_{2/3}Ca_{1/3}MnO_3$ exhibits Arrhenius behavior over a temperature range from $2T_c$ to $4T_c$, with an activation energy very close to $\frac{2}{3}$ that of the electrical conductivity. Although both the doping level and thermoelectric coefficient indicate holelike conduction, the Hall coefficient is electronlike. This unusual result provides strong evidence in favor of small-polaronic conduction in the paramagnetic regime of the manganites. [S0031-9007(96)02285-5]

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A recent resurgence of interest in the transport properties of doped lanthanum manganites has resulted in the realization that electron-lattice interactions play a significant role. Studies of the archetypal system $(La_{1-x}R_x)_{1-c}Ca_cMnO_3$ have demonstrated that the ferromagnetic transition temperature T_c (and with it, the metal-semiconductor transition) are suppressed by the addition of rare-earth ions R whose smaller size further closes the Mn-O-Mn bond angle [1,2]. The temperature dependence of the resistivity above T_c is remarkably unaffected by rare-earth substitutions, following a universal semiconductorlike curve. This supports the view that replacement of a trivalent rare-earth ion by Ca introduces a hole that is presumably associated with the Mn e_g state. Theoretical attempts [3,4] to describe the large changes in resistivity and their sensitivity to magnetic fields in the vicinity of T_c in the context of the double exchange model have led to the conclusion that strong electron-lattice effects are essential, and that the transition shares aspects of "polaron collapse" such as occurs in EuO [5]. The conductivity in the high temperature regime should be dominated by the hopping motion of self-trapped, small polarons. Indeed, quite recent experiments have shown the importance of electron-phonon interactions in CMR via the oxygen isotope effect [6].

A stable polaron in an ionic solid may be either a large (multisite) polaron that moves itinerantly, or a small (singlesite) polaron that moves with a low ($\ll 1$ cm^2/Vs) thermally assisted mobility [7]. In the singlesite limit, the self-trapped carrier's energy is taken to depend only linearly on the displacement of atoms from their carrier-free positions. Consequently, the characteristic energy of the Seebeck coefficient E_s is significantly smaller than the activation energy of the electrical conductivity E_σ; that $E_s \ll E_\sigma$ was demonstrated in earlier work [8], and taken as evidence of small-polaronic motion. E_s measures the chemical potential of the self-trapped polaron.

Perhaps the most distinctive property of steady-state small-polaronic transport is its Hall mobility μ_H. The activation energy of the Hall mobility is calculated to be always less than that for drift mobility E_d. The simplest model predicts $\approx E_d/3$, and this has been observed in, for example, oxygen-deficient $LiNbO_3$ [9]. The sign of the Hall effect for small polaron hopping can be "anomalous." A small polaron based on an electron can be deflected in a magnetic field as if it were positively charged and, conversely, a hole-based polaron can be deflected in the sense of a free electron. As first pointed out by Friedman and Holstein [10], the Hall effect in hopping conduction arises from interference effects of nearest-neighbor hops along paths that define an Aharonov-Bohm loop. Sign anomalies arise when the loops involve an odd number of sites [11]. In this Letter we report the first measurement of the high-temperature Hall coefficient of manganite samples, finding that it exhibits Arrhenius behavior and a sign anomaly relative to both the nominal doping and the thermoelectric power. The results are discussed in terms of an extension of the Emin-Holstein (EH) theory [7] of the Hall mobility in the adiabatic limit.

We exploit the sensitivity of these materials to rare-earth substitutions to lower the transition temperature from $\sim$260 K at $x = 0$ to $\sim$130 K, thereby extending the accessible temperature range to $\simeq 4T_c$. The samples used in this study were laser ablated from ceramic targets and deposited on $LaAlO_3$ substrates as described previously [8,12]. The ceramic target material (R = Gd and $x = 0.25$) has a resistivity maximum near 100 K, while the thermoelectric power drops abruptly to metallic values below 90 K [12]. The effective rare-earth site radius is $\langle r_A \rangle = 0.113$ nm and, indeed, the properties of this sample are very similar to Y-substitute samples with the same $\langle r_A \rangle$ value [1]. The laser deposited films show somewhat higher transition temperatures: The resistivity maximum is at 140 K and the thermoelectric power becomes metal-like below 130 K. X-ray data indicate that the in-plane lattice parameter of the laser ablated film is larger than that of the ceramic, presumably due to stress induced by the substrate. Figure 1 shows resistivity and thermopower data for the 130 K sample along with

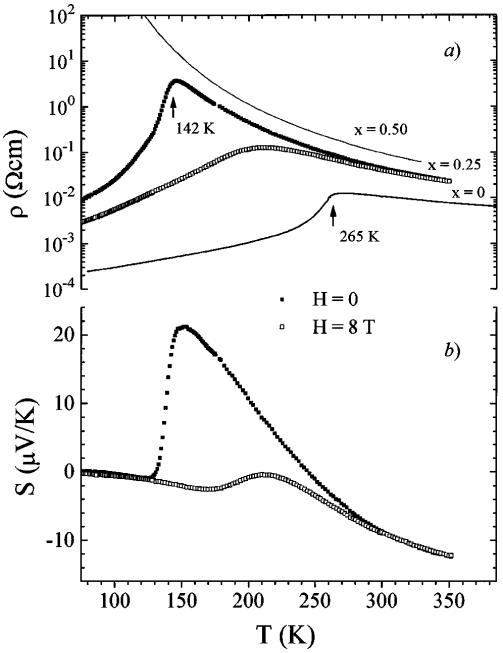

FIG. 1. (a) The resistivity vs temperature for the $x = 0.25$ sample, for magnetic fields (■) $H = 0$, and (□) $H = 8$ T. Data for $x = 0$ and $x = 0.5$ are shown for comparison. (b) The thermoelectric power for $x = 0.25$ in the same range of temperatures and fields showing a saturated $S(H)$ at temperatures $T < T_c$.

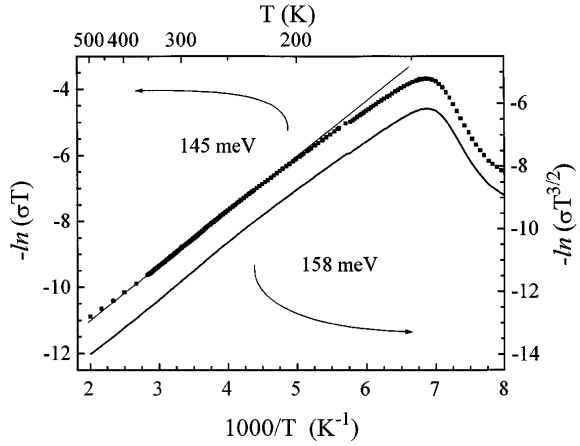

FIG. 2. The resistivity of the $x = 0.25$ sample plotted in the adiabatic (squares) and nonadiabatic (thick line) limits. The fine line is a linear fit indicating an activation energy of 145 meV in the high temperature adiabatic regime.

resistivity data for similar samples with $x = 0$ and $x = 0.5$. We focus here on the 130 K sample, for which ρ drops by a factor 160 between 0 and 8 T at 142 K at which field the peak in the thermopower is almost completely suppressed.

The most rapid motion of a small polaron occurs when the carrier hops each time the configuration of vibrating atoms in an adjacent site coincides with that in the occupied site. This regime is termed adiabatic with a conductivity given by $\sigma = \sigma_o \exp(-E_\sigma/\mathrm{k}_B T)$, where

$$\sigma_o = g_d e^2 \nu_0 / a k_B T \,. \tag{1}$$

Here ν_0 is a characteristic frequency and a is the jump distance, which we take to be the Mn-Mn spacing, 0.39 nm. The factor g_d depends on hopping geometry and has the value $g_d = \frac{3}{2}$ for the triangular lattice treated by EH and $g_d = 1$ for nearest-neighbor hopping on a square planar lattice. A signature of the adiabatic limit is that the prefactor σ_o approaches $e^2/\hbar a \simeq 7000\ (\Omega\ \mathrm{cm})^{-1}$ when $h\nu_0 \simeq k_B T$. If it is much smaller, the motion is termed nonadiabatic, and the prefactor contains an additional factor of $T^{-1/2}$. In Fig. 2 we plot $-\ln(\sigma T)$ and $-\ln(\sigma T^{3/2})$, the adiabatic and nonadiabatic limits, respectively, vs $1000/T$. Close to T_c there are significant deviations from Arrhenius behavior, as has been noted previously [12,13]. At higher temperatures there is no significant difference between adiabatic and nonadiabatic fits; the fitting parameters are given in Table I along with those for Gd concentration $x = 0$ and $x = 0.5$. The adiabatic prefactor for the $x = 0.25$ sample is $\approx 6000\ \Omega^{-1}\,\mathrm{cm}^{-1}$ at 300 K, confirming that the hopping processes are adiabatic. The characteristic frequency ν_0 in Eq. (1) is of order $10^{14}/g_d$ Hz. Evidence, discussed below, implies that g_d is significantly larger than the value for pure nearest-neighbor hopping ($g_d = 1$). This reduces ν_0 to a value characteristic of optical phonons in transition-metal oxides.

Sections of these specimens were patterned by conventional lithographic methods into a five-terminal Hall geometry. Hall experiments were carried out in a high-temperature insert constructed for use at the 20 T superconducting magnet at the National High Magnetic Field Laboratory (Los Alamos, New Mexico). Figure 3 shows the raw data (transverse and longitudinal voltages) obtained in for $x = 0.25$ at 462 K. Although the sample lithography resulted in negligible zero field transverse voltage in the metallic state, a transverse magnetoresistive signal is apparent above T_c; see Fig. 3. This signal peaks around T_c and then decreases with increasing temperature. Clearly this indicates inhomogeneous current paths in the proximity of the metal-insulator transition, possibly due to local relaxation of epitaxial strain and resulting local variations in T_c. Consequently, we did not attempt to follow the behavior of the Hall constant below $\sim 2T_c$. The transverse voltage data taken while sweeping the field from -16 to $+16$ T, and that taken while sweeping back to -16 T, were each fit to a second-order polynomial with the term linear in field attributed to the Hall effect. We verified in each case that the longitudinal magnetoresistance is completely symmetric in field. Figure 4 shows the Hall coefficient derived from the linear term. Several points for the $x = 0$ film are included. Because of the much higher T_c of that sample, extraction of the Hall contribution leads to greater uncertainty. The data are, however, consistent

TABLE I. Parameters from adiabatic and nonadiabatic fits to the resistivity and Hall data.

$(La_{1-x}Gd_x)_{2/3}Ca_{1/3}MnO_3$	E_σ(meV)	$\sigma_o(\Omega^{-1}\text{cm}^{-1})$	E_H(meV)	$R_H^o(10^{-10}\ \text{m}^3/\text{C})$
Sample A ($x = 0$)				
Nonadiabatic limit	102	$2.5 \times 10^7\ K^{3/2}/T^{3/2}$	~69	
Adiabatic limit	85	$7.7 \times 10^5\ K/T$	~59	
Sample B ($x = 0.25$)				
Nonadiabatic limit	158	$5.1 \times 10^7\ K^{3/2}/T^{3/2}$	112	$(4.8 \times 10^{-4}\ K^{-1})T$
Adiabatic limit	145	$1.8 \times 10^6\ K/T$	91	0.38
Sample C ($x = 0.5$)				
Nonadiabatic limit	157	$2.3 \times 10^7\ K^{3/2}/T^{3/2}$		
Adiabatic limit	146	$8.9 \times 10^5\ K/T$		

with the Gd-substituted film. The line through the data points is an Arrhenius fit, giving the expression $R_H = -(3.8 \times 10^{-11}\ \text{m}^3/\text{C})\ \exp(91\ \text{meV}/k_BT)$. Note that the sign is negative, even though divalent dopants should introduce holes. That the Seebeck coefficient approaches a negative value at high temperatures has been attributed in part to the reduction in spin entropy produced when a hole converts a Mn^{3+} ion to Mn^{4+} [8].

Detailed expressions for the Hall effect in the adiabatic limit have been calculated by EH [7] for the hopping of electrons with positive transfer integral J on a triangular lattice, and results in a normal (electronlike) Hall coefficient. However, the sign of both the carrier and the transfer integral changes for hole conduction, leaving the sign of the Hall coefficient electronlike, and therefore anomalous [10,11]. However, no anomaly would arise if the hopping involves four-sided loops with vertices on nearest-neighbor Mn atoms. A sign anomaly, then, implies that hopping involves odd-membered Aharonov-Bohm loops. Such processes arise when next-nearest-neighbor (*nnn*) transfer processes across cell face diagonals are permitted. If the Mn-O-Mn bonds were strictly colinear, the former processes would be disallowed by symmetry. However, the bond angles are substantially less than 180°, implying the presence of π-bond admixture and opening a channel for diagonal hops. We have extended the triangular-lattice calculation of EH to the situation in which a hole on a Mn ion can hop to any of its four nearest neighbors in the plane normal to the applied field with transfer matrix element $J < 0$ *and* to its four next nearest neighbors (*nnn*) with a reduced transfer energy γJ. We must also consider the effect of these diagonal hops (plus those in the plane containing both electric and magnetic fields) on the conductivity prefactor, Eq. (1). The Hall coefficient can be written as $R_H = R_H^o(T)\exp(2E_\sigma/3k_BT)$, with

$$R_H^o = -\frac{g_H}{g_d}\frac{F(|J|/k_BT)}{ne} \times \exp\{-[\epsilon_0 + (4|J| - E_s)/3]/k_BT\}; \quad (2)$$

EH found that the factor $g_H = \frac{1}{2}$ for three-site hopping on a triangular lattice. In Eq. (2) we have expressed the carrier density as $n\exp(-E_s/k_BT)$, where E_s is estimated to be 8 meV from the thermopower data. The quantity ϵ_0

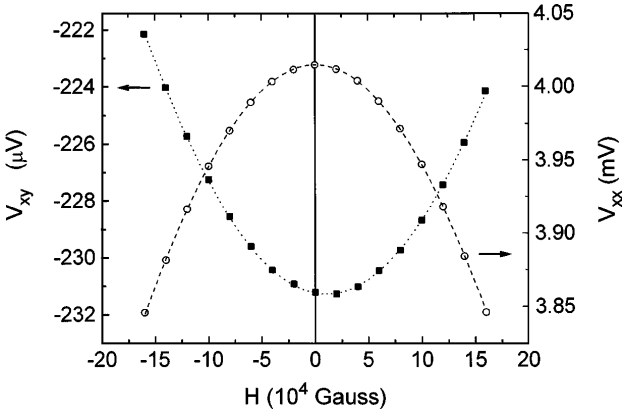

FIG. 3. Raw Hall data in $x = 0.25$ sample at $T = 462$ K, showing an odd contribution in the transverse voltage V_{xy} not present in the longitudinal voltage V_{xx}.

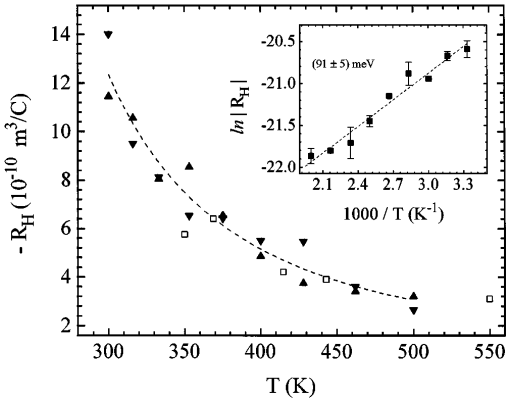

FIG. 4. The magnitude of the Hall coefficient $-R_H$ vs temperature showing the values obtained ramping the magnetic field up (solid triangles) and down (solid nablas) in the $x = 0.25$ sample. Open squares correspond to $x = 0$ and have large error bars. The dashed line is an Arrhenius fit. Inset: The natural logarithm of the Hall coefficient (average of up and down field values) for $x = 0.25$ vs $1000/T$. The solid line is a linear fit giving 91 meV for the activation energy.

is the J-dependent portion of a carrier's energy achieved when the local electronic energies of the three sites involved in an Aharonv-Bohm loop are equal. For the problem considered by EH, an electron hopping within a lattice composed of equilateral triangles, $\epsilon_0 = -2|J|$ and $g_H/g_d = \frac{1}{3}$. Within the domain of validity of EH, the temperature dependence of R_H arises primarily from the factor $\exp(2E_\sigma/3k_BT)$ when $E_\sigma \gg E_s$. For holes hopping within a cubic lattice in which three-legged Aharonov-Bohm loops include face-diagonal transfer, we find $\epsilon_o = -|J|(\sqrt{8 + \gamma^2} - \gamma)/2$. In particular, ϵ_o varies from $-\sqrt{2}|J|$ to $-|J|$ as γ increases from zero to unity [14], and the temperature dependence of R_H remains dominated by the factor $\exp(2E_\sigma/3k_BT)$. Indeed, the energy characterizing the exponential rise of the Hall coefficient that we observe, $E_{\rm Hall} = 91 \pm 5$ meV, is about $\frac{2}{3}$ the measured conductivity activation energy, $E_{\rm Hall}/E_\sigma = 0.64 \pm 0.03$, in excellent agreement with theory.

The geometrical factor g_d depends on the ratio of the probability P_{nnn} of *nnn* hops to P_{nn}, that of *nn* hops, through $g_d = (1 + 4P_{nnn}/P_{nn})$. If these probabilities are comparable ($\gamma \sim 1$)$g_d = 5$, $g_H = \frac{2}{5}$ and the exponential factor in Eq. (2) becomes $\exp[(E_s - |J|)/3k_BT] \simeq 1$. In the regime $|J| \gtrsim k_BT$, the function $F(|J|/k_BT)$ is relatively constant with a value $\approx$0.2, and we find $R_H^o \simeq -0.02/ne = -3.8 \times 10^{-11}$ m^3/C. This yields an estimated carrier density $n = 3.3 \times 10^{27}$ m^{-3}, quite close to the nominal level of 5.6×10^{27} m^{-3}. Diagonal hopping also reduces the value of the attempt frequency ν_0 required to fit the conductivity prefactor to $\approx 2 \times 10^{13}$ Hz, as noted above.

In conclusion, we have measured the high-temperature Hall coefficient in manganite films and found that its temperature dependence is consistent with small-polaron charge carriers that move by hopping. Further, the magnitude of the conductivity prefactor indicates that the carrier motion is adiabatic. Finally, the sign anomaly in the Hall effect implies that small polarons hop not only among near-neighbor sites (making Aharonov-Bohm loops with an even number of legs) but must have a significant probability of traversing Hall-effect loops with odd numbers of legs. As such, the results indicate the occurrence of significant *nnn* transfer across face diagonals, and therefore a crucial role for deviations of the Mn-O-Mn bond angle from 180°. An interesting possibility, that may also relate to unusual high-temperature values observed for the Seebeck coefficient [8], is that transport is a type of impurity conduction in which carriers remain adjacent to divalent cation dopants (i.e., Ca ions). The local distortions associated with the presence of the impurity may also increase the admixture of π bonds and enhance diagonal hopping.

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