Resistivity and Hall effect at high temperatures in $La_{0.67}Ca_{0.33}MnO_3$

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The resistivity tensors of $La_{0.67}Ca_{0.33}MnO_3$ films were investigated at temperatures from the Curie temperature up to 600 K in magnetic fields up to 20 T. The diagonal transport is described by hopping of a small spin polaron cluster of 4 ions to nearest-neighbor spins. A spin-dependent activation energy and a mean field approximation for the magnetization of clustered polaron spins and unclustered Mn ion spins allowed the description of $\rho(B,T)$ with a minimum of free parameters. The electron-like low field Hall coefficient showed a thermally activated behavior with an activation energy higher than that extracted from diagonal data. © *1999 American Institute of Physics.* [S0021-8979(99)19408-8]

The double-exchange magnetism provides the basic mechanism favoring charge transport in the ferromagnetic regime of doped manganites of type $A_xB_{1-x}MnO_3$. The colossal negative magnetoresistivity found close to the Curie temperature T_C is attributed to an improved spin order in the presence of magnetic field. Above T_C short-range magnetic correlations in form of magnetic polarons are expected to exist and charge transport by magnetic polaron hopping has been proposed.[1] A temperature dependence of the resistivity $\rho(T)=\rho_0 T^{\alpha}\exp(E_A/k_BT)$ was found in accordance with the Emin–Holstein theory.[2] The influence of magnetic fields on polaronic transport is difficult to investigate in manganites due to the necessity of applying high fields at high temperatures. Using conventional cryostats one can decrease the T_C by doping in order to access this regime in the temperature magnetic field phase diagram.[3] Here we present experiments on pure $La_{0.67}Ca_{0.33}MnO_3$ films with $T_C \approx 236$ K, close to that of the bulk material.

Microscopic models for activated transport in the presence of strong electron phonon coupling and polaron formation have been solved in mean field approximation by Millis *et al.*[4] and Sheng *et al.*[5] However, closed analytical expressions for temperature and magnetic field dependence of electrical transport are not available. Therefore, we correlate our data to the mean field magnetization of small magnetic clusters in a phenomenological model. This gives a quantitative description of $\rho(B,T)$ over a wide range of the phase diagram and allows an estimation of the cluster size.

Preparation and characterization of the sputtered epitaxial films are described elsewhere.[6] Measurements on a photolithographically patterned Hall bar have been made from 4 K up to 300 K in a standard superconducting magnet cryostat.[7] Above 300 K an 8 T superconducting coil and a 20 T Bitter type magnet system, which both allowed room temperature access to the magnetic field, have been used. For measurements up to 600 K, we placed a small tube furnace into the respective room temperature bores.

A compilation of high temperature resistivity data is shown in Fig. 1. The zero field data show the transition from a metallic, positive temperature coefficient of the resistivity to a thermally activated behavior at high temperatures with a maximum located at $T_{\max}=240$ K. In small field magnetization measurements ($B=20$ mT), the onset of spontaneous magnetization is detected slightly below this temperature. Magnetic fields broaden the resistivity cusp and shift $T_{\max}$ as shown in Fig. 2. In the high temperature regime, the curves in magnetic fields are asymptotic to the zero field curve.

Analyzing $\rho(B=0\ \mathrm{T})$ in the framework of polaron hopping yields an exponent of the temperature dependent prefactor of $\alpha=1.6$. In Fig. 1 all lines are calculated with the value theoretically expected for nonadiabatic polaron hopping ($\alpha=1.5$). In the nonadiabatic case, there is only a small probability for the polaron to hop during the existence of the excited state. Trial fits with other models such as variable range hopping and nearest neighbor hopping yielded worse fits with strong systematical deviations. However, an acceptable fit was also possible in terms of adiabatic polaron hopping ($\alpha=1$).[6] From the value of ρ_0 we cross checked that the adiabatic limit is not fulfilled.[3] The localized carriers are assumed to distort the surrounding lattice and magnetically polarize the manganese atoms in the neighborhood, thereby gaining exchange energy and forming a bound magnetic

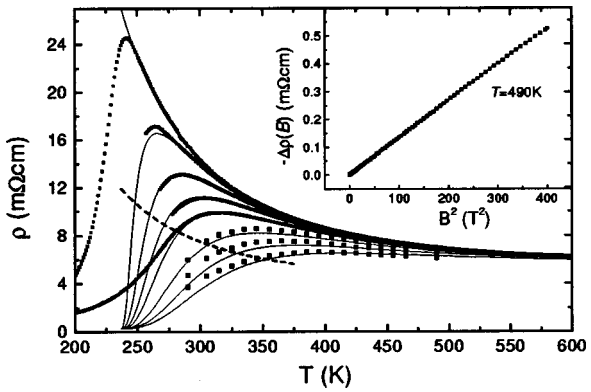

FIG. 1. Temperature dependence of the resistivity in magnetic fields of $B=0,2,4,6,8,12,16,20$ T between 200 and 600 K (symbols). The data for $B=1,3,5,7,10,14,18$ T are omitted for clarity. The inset shows the B^2 dependence of the magnetoresistivity for $T=490$ K.

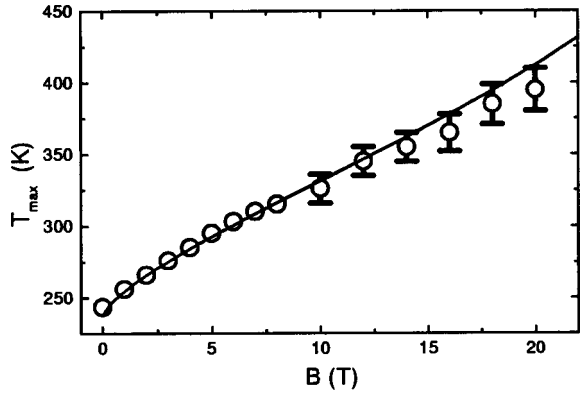

FIG. 2. Measured (symbols) and calculated (line) field dependence of the resistivity maximum.

polaron.[8] Evidence for the existence of magnetic polarons well above T_C has been reported from neutron scattering,[9] low field magnetization,[10,11] and electron spin resonance.[12]

For a hopping transport of magnetic polarons, an exchange contribution to the activation energy E_A was taken into account by Dionne.[13] He expressed E_A by a field-independent term, arising from electrostatic distortions, and a field-dependent exchange contribution. This model gives a linear dependence between E_A and the Brillouin function, i.e., the magnetic field. However, Snyder *et al.* showed the existence of a B^2 dependence of the magnetoresistivty $\Delta\rho(B)=\rho(B)-\rho(B=0)$.[14] We show that the measured behavior can be described by a simple polaron hopping model based on the following considerations: Since Dionne found an almost purely magnetic polaron with only minor corrections from electrostatic energy,[13] we consider only the interaction between the spin of an unclustered single ion ($N_I=1$) and the total spin of a ferromagnetic polaron consisting of a cluster of N_P ions. The spin alignment due to an applied magnetic field minimizes polaron trapping. In the simplest approximation, the activation energy changes to $E_A=E_A^0(1-\langle\cos\Theta_{IP}\rangle)$. The angle between the single ion spin and the cluster spin, Θ_{IP}, is for uncorrelated spins related to the normalized local magnetizations by $\langle\cos\Theta_{IP}\rangle=\langle\cos\Theta_I\rangle\times\langle\cos\Theta_P\rangle=(\langle M_I\rangle/M_I^S)(\langle M_P\rangle/M_P^S)$. We simply calculate in a mean field approximation the magnetizations with the Brillouin functions $B_J(N_I=1,T-T_C,B)$ and $B_J(N_P,T-T_C,B)$. As parameters we used a g factor of 2 and the average value of the angular momentum $J=2.28$ per Mn ion. Within this model we can give a closed expression for the resistivity

$$\rho(T,B)=\rho_0 T^\alpha \exp\left(\frac{E_A^0}{k_B T}[1-B_J(N_I)B_J(N_P)]\right). \qquad (1)$$

The fit of the nonadiabatic polaron hopping transport ($\alpha=1.5$) to the zero field data fixes the parameters ρ_0 and E_A^0. In Fig. 1 we fitted the data for $B=4$ T in order to determine the two free parameters $N_P=3.8$ and $T_C=236$ K. The smallness of the cluster size N_P limits the spin polarization to the nearest neighborhood. Within our model the above equation describes all other field curves without further free parameters. The field and temperature dependence is implicit in the Brillouin functions. The result of the analysis is shown by lines in Fig. 1, and shows good correspondence between the experimental data (symbols) and the respective calculated curves (lines). Fits with fixed cluster sizes, $N_P=1$ and $N_P=7$, respectively, yielded significantly less good correspondence. Here, the first value represents a model of pure electron hopping with spin-dependent barrier energies. The numerical value for N_P should not be considered as exact, however, it demonstrates that a small finite cluster size is necessary to describe the experimental data.

At temperatures well above the Curie temperature ($T>2T_C$) the Brillouin functions in Eq. (1) reduce to effective susceptibilities and the small correction of the activation energy due to the magnetic field will be quadratic in B. Therefore, a Taylor expansion of the exponential will also be quadratic in the leading field-dependent term and one expects: $\Delta\rho(B)=\rho(B)-\rho(B=0)\propto B^2$ as it is visible in the inset of Fig. 1.

In Fig. 2 we show the nonlinear shift of $T_{\max}$ with applied magnetic field. In the superconducting magnet system ($B\leqslant 8$ T), the data were taken densely in temperature and the error of $T_{\max}$ is smaller than symbol size. In the Bitter magnet system, data spacing is less dense resulting in larger errors. With the parameters fixed from above we can solve Eq. (1) numerically for $T_{\max}(B)$. The result of this inversion is shown as solid line in Fig. 2.

Looking more closely to Fig. 1 deviations are obvious. First, the zero-field fit curve exhibits no maximum but diverges in the low temperature limit. This is because fluctuations are not taken into account and therefore the calculated magnetization is exactly zero above T_C. Second the calculated resistivity for all magnetic fields approaches a constant value near T_C. This is an artefact of the model which calculates thermally activated hopping even close to T_C, where the activation energy vanishes. Our model assumes clusters of Mn ions surrounded by a paramagnetic background of single Mn ions. However, close to T_C the clusters are all well aligned and also spin ordering of the not clustered Mn ions is considerably. Thus there is a high probability of having a cluster of N_P Mn ions spin aligned with a neighboring Mn ion. In our model, this is indistinguishable from a cluster of N_P+1 Mn ions. A growing cluster size near T_C was experimentally observed by neutron scattering and magnetization measurements[9,11] and should be implemented in Eq. (1). A cluster growth would lead to a faster decrease of the resistivity when approaching T_C from above than that sketched in Fig. 1. On the other hand, the neglected lattice energy of the polaron will act in the opposite direction. Incorporating these

TABLE I. Fitting parameters according to Eq. (1) for three samples. The values without (with) parenthesis correspond to the nonadiabatic (adiabatic) case.

Sample	A	B	C
ρ_0 ($10^{-10}\,\Omega$ m/K$^\alpha$)	6.44 (209.7)	6.53 (211.4)	4.89 (157.2)
E_A^0 (meV)	120 (103)	96 (80)	133 (117)
T_C (K)	213.3 (203.6)	236.4 (235.9)	202.0 (195.6)
N_P	3.9 (5.9)	3.8 (5.0)	5.5 (7.8)

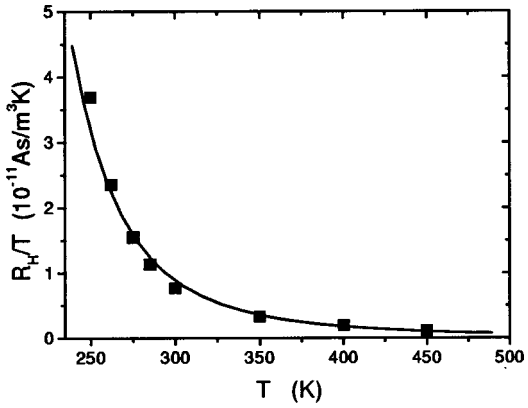

FIG. 3. Hall coefficient R_H/T as function of temperature (symbols) and temperature dependence calculated for an activation energy of 165 meV (line).

effects would require a model for cluster growth and additional fitting parameters. Instead we give an estimate of the region where we think Eq. (1), which deals with independent, not aligned clusters and ions, is applicable. As a criterion we choose $\langle \Theta_{IP}(B,T) \rangle - \langle \Theta_{IP}(B=0,T) \rangle < 10°$. The dashed curve in Fig. 1 marks this criterion. Data values above this crossover line correspond to a spin alignment between clusters and single spins deviating less than 10° from the equilibrium value of 90° expected for random spin orientations.

In Table I we list the resulting fitting parameters for three investigated samples for the adiabatic ($\alpha=1$) and nonadiabatic ($\alpha=1.5$) case, respectively. Regardless of the type of polaron hopping only a finite, small cluster size could successfully describe the experiment.

For the motion of a polaron on a triangular lattice, Friedman and Holstein[15] found a thermally activated electron-like Hall effect $R_H \propto T \exp(2E_A/8k_BT)$ from quantum interference between direct and indirect jumps. We find an electron-like linear slope of the Hall voltage in the polaronic regime which changes to a positive slope in the ferromagnetic metallic regime. The evaluation of the Hall effect in the ferromagnetic state is published elsewhere.[7] In Fig. 3 we show the Hall coefficient R_H/T as function of temperature. From the thermally activated behavior, we can extract an activation energy for the Hall mobility of (165 meV). This value is higher than the activation energy of the drift mobility (96 meV), in contradiction to Friedman–Holstein theory and the experimental results found by Jaime *et al.*[3] However, a more general theory of Schnakenberg[16] found the same activation energy for longitudinal resistivity and Hall mobility.

In summary, we performed detailed high field transport measurements covering a wide temperature and magnetic field range on the colossal magnetoresistive compound $La_{0.67}Ca_{0.33}MnO_3$. With a small polaron hopping model we could quantitatively describe $\rho(B,T)$ with a minimum of free parameters. The cluster sizes determined from the fits were in all cases small, containing 4–6 ions only. Also a thermally activated polaronic Hall effect was found, but it did not agree quantitatively with theoretical considerations.

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