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# Variable Hall coefficient in $Bi_2Sr_2CaCu_2O_{8-x}$ across the metal-insulator transition

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Measurements are reported of the Hall coefficient $R_H$ and *ab*-plane resistivity for single-crystal $Bi_2Sr_2CaCu_2O_{8-x}$, with variable oxygen configuration. As the system is driven through the metal-"insulator" transition, $R_H$ increases strongly but continues to obey the empirical expression $1/R_H = \gamma + \beta T$, where $T$ is the temperature. For low oxygen content the Hall mobility $\mu_H$ becomes temperature independent. We examine these results in terms of various normal-state transport models.

In several new classes of Cu-O based superconducting oxides, the normal state is characterized by either hole or electron carriers in low concentration, with moderate to severe structural and electrical anisotropy. The transport properties are often very different from those expected for a simple metal, and are sensitive to chemical doping (in particular oxygen). Recently, it was demonstrated[1] that for $Bi_2Sr_2CaCu_2O_{8-x}$ a metal-"insulator" transition can be induced by changing the oxygen configuration (i.e., the actual oxygen content with possible associated defect structure). The term insulator here refers to a nonmetallic state where the electrical resistivity increases with decreasing temperature, similar to semiconducting behavior. Both the resistivity and thermoelectric power obey simple empirical expressions with application to other high-$T_c$ oxides.[1,2]

In this paper we report on experiments measuring simultaneously the *ab*-plane Hall coefficient $R_H$ and *ab*-plane normal-state resistivity $\rho_{ab}$ of $Bi_2Sr_2CaCu_2O_{8-x}$ single crystals. The temperature dependences of both $R_H$ and $\rho_{ab}$ follow simple functional forms, which remain intact as the sample is driven across the (loosely defined) metal-insulator transition by oxygen depletion. We use these transport coefficients to extract characteristic transport parameters, and compare our results to the predictions of various novel normal-state conduction mechanisms.

High-purity single crystals of $Bi_2Sr_2CaCu_2O_{8-x}$ were grown from a mixture of $Bi_2O_3$, $SrCO_3$, $CaCO_3$, and CuO as described elsewhere.[3] The crystals were cleaved and cut into thin *ab*-plane sheets of typical dimensions 2.0 mm × 1.0 mm × 10 $\mu$m, where the small dimension corresponds to the *c*-axis direction. The samples were optically smooth and shiny and had no major visible defects. The resistivity was measured using a modified linear four-probe contact configuration with fired-on silver paint contact pads, and the Hall voltage was obtained simultaneously using an ac current source and lock-in detection with a five-probe arrangement.[4] The magnetic field was oriented parallel to the *c* axis, and hence the Lorentz force was in the *ab* plane. $R_H$ showed linearity in applied current up to 1.0 mA and applied magnetic field up to 10 kG, the maximum values applied.

Figure 1 shows the *ab*-plane resistivity and Hall coefficient of a particular $Bi_2Sr_2CaCu_2O_{8-x}$ crystal for four different oxygen configurations. The lower half of the figure shows the temperature-dependent resistivity. Curve *A* is for the crystal following an initial high oxygen anneal (5 h at 650 °C, followed by a 12-h ramp to 25 °C, in 1-atm $O_2$ flow). The resistivity is linear and metallic

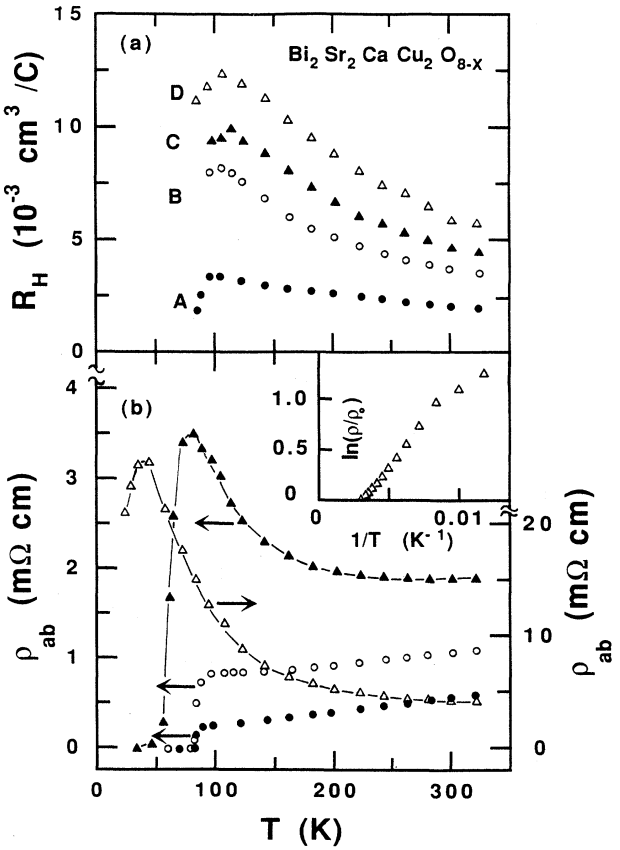


FIG. 1. Hall coefficient and resistivity for the *ab* plane of a $Bi_2Sr_2CaCu_2O_{8-x}$ single crystal for different oxygen configurations. Sample *A* has the highest oxygen content, while sample *D* has the lowest (see text). The inset shows the resistivity data of sample *D* replotted in a form where a straight line would indicate activated conduction (not observed).

before dropping to zero at $T_c \approx 83$ K. Curves *B*–*D* are for the same crystal with successively lower oxygen concentration. Consistent with previous work,[1] oxygen depletion changes $\rho_{ab}$ from metalliclike to insulatorlike (or semiconductorlike), with a concomitant depression of $T_c$. The oxygen configuration of sample "*B*" was established through a low oxygen anneal cycle (5 h at 325 °C, followed by a 12-h ramp to 25 °C, all at ~10 mTorr $O_2$). This treatment increased the resistivity by a factor of 2, still showing metallic behavior (curve *B*) down to ~130 K, where it shows a small upturn before dropping to zero at $T_c \approx 81$ K. The same sample was subjected to another low oxygen anneal cycle (5 h at 345 °C, followed by a 12-h ramp to 25 °C, all at ~10 mTorr $O_2$), after which the resistivity (curve *C*) increased by a factor of 3 from the original high oxygen concentration state at room temperature. Here the semiconductive upturn begins at ~250 K and continues down to $T_c \approx 62$ K. Once again, the sample was subjected to another low oxygen anneal cycle (5 h at 375 °C, followed by a 12-h ramp to 25 °C, all at ~10 mTorr $O_2$), after which the resistivity (curve *D*) showed a total increase by an order of magnitude, with semiconductorlike behavior observed between room temperature and $T_c \approx 25$ K. The inset to Fig. 1(b) shows the resistivity data of curve *D* replotted as $\ln\rho/\rho_0$ vs $1/T$, where $\rho_0$ is the room-temperature resistivity. Simply activated behavior is not observed, hence the resistivity differs quantitatively from true semiconducting behavior.

Figure 1(a) shows the Hall coefficient (measured simultaneously with the resistivity), following the successive anneal cycles described above. The symbols correspond to those of the resistivity specimens [Fig. 1(b)]. For all oxygen configurations, the Hall coefficient grows as the temperature is decreased, down to about 100 K, below which superconducting fluctuation effects dominate. At fixed temperature, the general trend is that a decreased oxygen content increases the Hall coefficient. $R_H$ shows an increase by a factor of 2.9 from the high oxygen anneal cycle (curve *A*) to the extreme low oxygen anneal cycle (curve *D*) at room temperature. Using the expression $R_H = 1/nec$, we find at room temperature an effective hole concentration $n = 3.02\times10^{21}$ cm$^{-3}$ for the high oxygen specimen (curve *A*), and $n = 1.05\times10^{21}$ cm$^{-3}$ for the low oxygen specimen (curve *D*). Normalized to the unit-cell volume ($3.813\times3.813\times30.67$ Å$^3$), this corresponds to $n_H = 1.36$ and 0.474 holes per unit cell, for the high and low oxygen specimens, respectively.

The dramatic difference in the *ab*-plane resistivity and Hall coefficient observed in Fig. 1 for the different specimens of $Bi_2Sr_2CaCu_2O_{8-x}$ is directly related to oxygen configuration. Although we are not able to nondestructively determine the actual oxygen content of the different specimens within a resolution greater than $x = 0 \pm 0.1$ (using weight loss and Rutherford backscattering), from previous studies[5] we estimate a value of $x \approx 0.08$ after the extreme low oxygen anneal cycle. Structural single-crystal x-ray studies on similar crystals showed the presence of stacking faults, but no secondary phases (independent of the oxygen configuration).

Previous Hall-effect measurements in $YBa_2Cu_3O_{7-\delta}$ (Refs. 6 and 7) suggest a Hall number ($\sim 1/R_H$) proportional to temperature $T$. A similar relation has been suggested for Bi-Sr-Ca-Cu-O and $Tl_2Ca_2Ba_2Cu_3O_x$ ceramics.[8] Figure 2 shows the inverse Hall coefficient $1/R_H$ plotted versus $T$ for the four different oxygen configurations. The plot indicates, for all four specimens, good agreement with the expression

$$1/R_H = \gamma + \beta T , \qquad (1)$$

where $\gamma$ and $\beta$ are constants. As the oxygen deficiency is increased, the zero-temperature offset $\gamma$ is reduced from $0.2\times10^3$ C/cm$^3$ toward zero, and the slope $\beta$ decreases from 0.920 to 0.480 C/cm$^3$K.

Figure 3 shows the Hall mobility $\mu_H$ extracted from the Hall coefficient and *ab*-plane resistivity measurement for

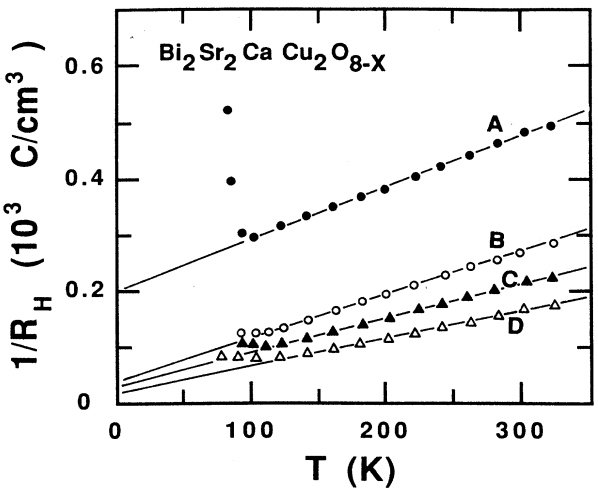


FIG. 2. $1/R_H$ for the *ab* plane of $Bi_2Sr_2CaCu_2O_{8-x}$ showing good agreement with Eq. (1) above $T_c$ for different oxygen configurations (*A* has the highest oxygen content, while *D* has the lowest; see text). The $1/R_H$ data can be converted to Hall number $n_H$ (holes per unit cell) by multiplying by $2.78\times10^{-3}$ cm$^3$/C.

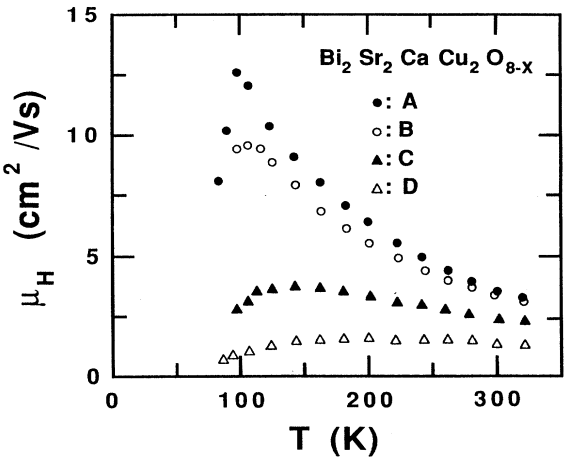


FIG. 3. Hall mobility for the *ab* plane of $Bi_2Sr_2CaCu_2O_{8-x}$ crystals for different oxygen configurations (*A* has highest oxygen content, while *D* has lowest; see text).

the four different oxygen configurations. We see that the Hall mobility decreases as oxygen is depleted from the sample and the specimen becomes more insulating. For high oxygen (metallic) samples (curves $A$ and $B$) the mobility is very temperature dependent (behaving roughly as $1/T$), while for low oxygen content (curve $D$) $\mu_H$ appears to saturate and becomes roughly temperature independent.

The resistivity and Hall data of Fig. 1, and Eq. (1) in particular, are not generally consistent with simple metallic (band) behavior. Nevertheless, we briefly examine the consequences of a simple metallic transport model which allows evaluation of characteristic fundamental parameters. The temperature-dependent resistivity $\rho_{e\text{-ph}}(T) = m^*/ne^2\tau_{e\text{-ph}}(T)$ relates the carrier concentration $n$ and scattering time $\tau_{e\text{-ph}}$. At sufficiently high temperature, $\tau_{e\text{-ph}}$ varies inversely with $T$ and is related to the transport electron-phonon coupling parameter $\lambda_{tr}$ by $h/2\pi\tau_{e\text{-ph}} = 2\pi\lambda_{tr}k_BT$. $\lambda_{tr}$ is a good estimate of $\lambda$ which determines $T_c$ in Eliashberg theory. The most metallic sample (curve $A$) in Fig. 1 has a resistivity slope 1.46 $\mu\Omega$ cm/K. Combining this with the room temperature $n = 3.02\times10^{21}$ cm$^{-3}$, we estimate $\tau_{e\text{-ph}} = 0.62\times10^{-12}$ $(m^*/m)T^{-1}$ (sec K) and $\lambda_{tr} = 1.95$ $(m/m^*)$ for the high oxygen specimen. Within conventional BCS electron-phonon superconductor theory, an electron-phonon coupling parameter of this order is not unreasonable for the observed $T_c$ of 85 K.

Numerous other transport models have been suggested for the high-$T_c$ oxides. Two-band models[9,10] are problematical in that the observed temperature dependence of $R_H$ restricts too severely the band parameters,[11] and in a way inconsistent with pressure studies[12] (at least for $YBa_2Cu_3O_7$). Strong electron-electron interaction effects can lead to the opening of a soft Coulomb gap at $E_F$,[13,14] with a resulting resistivity $\rho\sim\exp(T_0/T)^{1/2}$. In two dimensions, additional disorder leads[15] to a scaling between the fractional increase in $\rho$ and the fractional increase in $R_H$: $\delta R_H/R_H = 2\delta\rho/\rho$. At relatively low temperatures, curves $C$ and $D$ in Fig. 1(b) roughly follow such an exponetial temperature dependence, but we fail to find a scaling with $R_H$. Hence, we rule out the Coulomb-gap behavior in this parameter range of $Bi_2Sr_2CaCu_2O_{8-x}$. Another model, used previously[16] to interpret resistivity and Hall data for insulating $La_2CuO_4$, is that of a doped semiconductor. However, the conductivity and Hall coefficient for this process are both simply activated, in contrast to our findings for $Bi_2Sr_2CaCu_2O_{8-x}$ here. We also note that the thermoelectric power of $Bi_2Sr_2CaCu_2O_{8-x}$ was shown previously[1] to obey the expression $S = A + BT$, with $A$ and $B$ constants ($A$ depends on oxygen configuration). This expression is also obtained for small polaron hopping transport, and has been applied to the boron carbides.[17] However, the predicted Hall coefficient for polaron hopping is not consistent with Eq. (1) and the data for Fig. 1(a).

We have previously demonstrated that in $Bi_2Sr_2CaCu_2O_{8-x}$ (Ref. 1) and $YBa_2Cu_3O_{7-\delta}$ (Ref. 18) the resistivity closely follows the empirical expression

$$\rho(T) = \rho_0 T^{\alpha}\exp(\Delta/k_BT)\,, \tag{2}$$

where $\alpha$ is between 0.5 and 1.0. Combining Eqs. (1) and (2) yields a mobility consistent with Fig. 3. The physical justification of Eq. (2) is not clear, but it may arise from a quantum-percolation-type transport as suggested by Phillips.[19]

In conclusion, the resistivity and the Hall constant of $Bi_2Sr_2CaCu_2O_{8-x}$ are extremely sensitive to oxygen configuration. The temperature dependence of these transport coefficients follows simple empirical expressions. The Hall constant for the magnetic field applied perpendicular to the Cu-O planes is $p$ type with a $1/T$ behavior for different oxygen configurations. This unusual behavior has also been observed in other high-$T_c$ oxides suggesting that these expressions may be inherent to the high-$T_c$ superconductors.

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