Two-dimensional electron localization in bulk single crystals of $Bi_2Sr_2Y_xCa_{1-x}Cu_2O_8$

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The temperature dependence of the ab-plane electrical transport was investigated on a series of single-crystal $Bi_2Sr_2Y_xCa_{1-x}Cu_2O_8$ samples with a wide range of yttrium content. The observed metal-insulator transition is discussed in terms of two-dimensional localization. The Hall-effect and thermopower results indicate that the driving force of the localization is the random impurity potential.

The presence of Cu-O planes in $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2) strongly suggests the presence of two-dimensional (2D) physical and electronic properties. Experiments have confirmed this. The large anisotropy in the normal-state resistivity,[1] Ginzburg-Landau superconducting effective mass,[2] and upper critical field[3] all indicate a system of weakly coupled superconducting layers. Furthermore, observations of inherently 2D phenomena, such as a Kosterlitz-Thouless phase transition[4] and flux-lattice melting,[5] have been reported on 2:2:1:2. In this paper we argue that the superconductor-to-insulator (SI) transition produced by ion doping 2:2:1:2, if interpreted in terms of 2D localization, is consistent with recent theories[6] of disordered 2D Bose systems. Additionally, we find that the details of the metal-insulator (MI) transition in $Bi_{2.1}Sr_2Y_xCa_{0.9-x}Cu_2O_8$ cannot be explained using current models of transport in disordered systems.

In 2D, the scaling theory of localization[7] predicts that at $T=0$ all single-electron states are localized at the Fermi level no matter how weak the disorder. Recent theoretical work,[6] however, prompted by an interesting series of experiments[8] on disordered granular and amorphous superconducting films, predicts that metallic conductivity is possible in 2D at a sheet resistance $R_{sq} = ch/4e^2$, with c a constant on the order of unity and $h/4e^2 = 6.5$ kΩ. The key point in these theories is that the carriers are treated as bosons ("Cooper pairs") rather than fermions ("single electrons"). The sheet resistance separating superconducting and insulating behavior at zero temperature is predicted to be a universal number, insensitive to the precise mechanism driving the localization.

As stated earlier, the experimental evidence implies that 2:2:1:2 can be pictured as a system of weakly coupled superconducting layers. It is assumed that these layers are Cu-O/Ca/Cu-O "sandwiches" spaced $d = 15$ Å $= c/2$ apart. The coupling between these sandwiches is weak and can be regarded as a perturbation.[1]

With these ideas in mind we performed a dc electronic transport study on a series of single crystals of $Bi_{2.1}Sr_2Y_xCa_{0.9-x}Cu_2O_8$. We measured the resistivity, Hall coefficient, and thermopower for various values of x on both sides of the MI transition. To analyze the resistivity data we calculated the sheet resistance of the Cu-O/Ca(Y)/Cu-O layers. The results indicate that the switchover from a superconducting ground state to an insulating ground state occurs close to the value predicted by theory. Highly resistive samples obey $\rho \propto \exp(T_0/T)^{1/2}$. Two models have been reported which can explain this behavior. The thermopower and Hall results are inconsistent with both explanations.

$Bi_{2.1}Sr_2Y_xCa_{0.9-x}Cu_2O_y$ crystals were grown from a copper-oxide-rich melt, as described in a separate publication.[9] The $x/2 = [Y]/[Sr]$ ratio of the samples has been determined by x-ray fluorescence with an estimated error of $\delta x = \pm 0.01$. For the other elements in the chemical formula the estimated error is ± 0.1. Each crystal was heat treated at 600 °C in air to ensure a reproducible oxygen content, but we did not determine y. The structure has been characterized by x-ray and electron diffraction.

For the resistivity and Hall measurements, very thin, regular platelets were prepared with typical dimensions 1 mm $\times$ 0.5 mm $\times$ 4000 Å for superconducting specimens and 1 mm $\times$ 0.5 mm $\times$ (1–10 μm) for insulators, the smallest dimension in each case being along the crystallographic c axis. For the thermopower measurements the sample dimensions were 2 mm $\times$ 100 μm $\times$ 2 μm, with the smallest dimension again along the c axis. Electrical contacts were made using 12-μm gold wires and silver epoxy fired on at 600 °C. Contact resistances were typically ≤ 1 Ω. The ab-plane resistivity was measured using a conventional four-probe technique. For the Hall measurements a 70-kG field was applied parallel to the c axis. The samples were rotated 180° several times at each temperature to eliminate the misalignment voltage and to ensure reproducibility. For the thermopower measurements thermal gradients of 0.3, 0.6, and 1.0 K were established across the sample, and the voltage was measured at each point. This process was repeated with the gradients applied in the opposite direction. Further experimental details can be found in Ref. 9.

The effect of yttrium doping is expected to be twofold. First, the substitution of trivalent Y for divalent Ca in the immediate neighborhood of the Cu-O planes will lead to a random potential felt by the charge carriers. Second, the addition of Y^{3+} is expected to raise the chemical potential and thereby remove holes from the conduction band. Accordingly, the Hall number ($n_H = 1/R_He$) is found to decrease rapidly with doping, in agreement with the results of Clayhold et al.[10] on thulium-doped material.

In Fig. 1, we show the resistivity versus temperature for several samples of various yttrium content. The superconducting transition temperature is observed to decrease with increasing x. Above $x = 0.45$ the samples are insula-
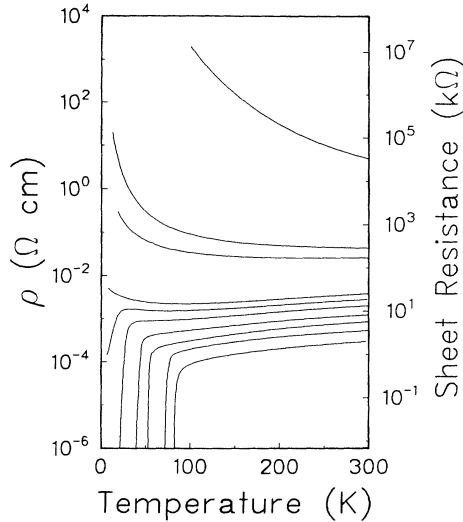
FIG. 1. Temperature dependence of the resistivity (left-hand scale) of $Bi_{2.1}Sr_2Ca_{0.9-x}Y_xCu_2O_y$ samples. The right-hand scale refers to the sheet resistance of the copper oxide double layers. The Y contents x of the samples are (in the order of increasing resistivity) 0, 0.20, 0.34, 0.38, 0.42, 0.44, 0.47, 0.51, 0.55, and 0.80.

tors at low temperature. The sheet resistance of the Cu-O double layers was calculated by dividing the measured resistivity by the distance between the layers $d = 15$ Å. The separatrion between the superconducting and insulating sets of curves extrapolates to zero at $\rho = 1200$ $\mu\Omega$ cm or $R_{sq} = 8$ kΩ. The resemblance to the results of Haviland, Liu, and Goldman[8] on vapor-deposited amorphous bismuth films is striking, supporting the notion that the ab-plane transport in $Bi_{2.1}Sr_2Y_xCa_{0.9-x}Cu_2O_8$ is indeed two dimensional.

The samples with a superconducting ground state but close to 8 kΩ sheet resistance exhibit a slight increase in resistance before the superconducting transition. This may be attributable to weak localization, as discussed by Fiory et al.[11]

The overall behavior of the resistivity of the insulating samples closely resembles that found in granular and quench-condensed metal films.[12−14] Essentially two types of behavior can be observed. Samples with a sheet resistance slightly greater than 8 kΩ ($x = 0.47$ in Fig. 1) have a resistive "tail" with $R_{sq} \propto T^{-1/2}$. Samples with a higher sheet resistance have $R_{sq} \propto \exp(T_0/T)^{1/2}$ over a temperature range which increases rapidly with increasing yttrium content.

A temperature-dependent resistivity of the form $\rho(T) = \rho_0\exp(T_0/T)^\alpha$ is generally analyzed within the context of variable range hopping (VRH).[15] In VRH models, the value of α depends on both the dimensionality of the system and the behavior of the density of states at the Fermi level. For a MI transition driven by disorder (an Anderson[16] transition) the density of states remains nonzero at all temperatures and VRH models predict $\alpha = \frac{1}{4}$ in three dimensions and $\alpha = \frac{1}{3}$ in two dimensions. Electron-electron interactions invariably cause the density of states to vanish at the Fermi energy.[17] VRH models predict

that for a density of states which vanishes as $g(\varepsilon) \propto (|\varepsilon - \mu|)^n$, $\alpha = (n+1)/(n+d+1)$, where d is the dimensionality of the system.

In Fig. 2(a) we plot $\ln(\rho)$ vs $T^{-\alpha}$ for the $x = 0.55$ sample and $\alpha = \frac{1}{4}$, $\frac{1}{3}$, and $\frac{1}{2}$. Ruling out $\alpha = \frac{1}{4}$ as clearly inferior, we see that both $\alpha = \frac{1}{3}$ and $\frac{1}{2}$ seem reasonable, with $\alpha = \frac{1}{2}$ perhaps a bit better. For an improvement upon this "eyeball" approach, we adopt the method used by Hill.[18] He introduces the quantity $\varepsilon_a = d[\ln(\rho)]/d(1/T)$ as the temperature-dependent activation energy; for VRH conduction, ε_a corresponds to the characteristic hopping energy of the carriers.[19] In Fig. 2(b) we plot ε_a vs T on a log-log scale for the same $x = 0.55$ sample discussed above. The straight line represents a least-squares fit to the low-temperature portion of the data, and the slope m is related to α by $m = 1 - \alpha$. The value of α obtained in this way is $\alpha = 0.50 \pm 0.1$ for all insulating samples with a sheet resistance greater than 100 kΩ (this includes many more samples than appear in Fig. 1). In other studies of the MI transition in high-T_c materials, Valles et al.[20] obtained $\alpha = \frac{1}{2}$ in ion-beam-irradiated YBa_2Cu_3-O_7, Fiory et al.[11] obtained $\alpha = \frac{1}{3}$ in $Bi_2Sr_2Cu_2O_8$, and Briceno and Zettl[21] observed $\alpha = \frac{1}{2}$ in oxygen doped 2:2:1:2.

Two models have been proposed which can account for $\rho \propto \exp(T_0/T)^{1/2}$, but neither is consistent with our Hall effect (Fig. 3) and thermopower (Fig. 4) results. Sheng, Ables, and Arie[12] specifically considering granular films, find that tunneling between the grains can result in $\alpha = \frac{1}{2}$ behavior. It is conceivable that in ion-doped 2:2:1:2 metallic "islands" can form within an insulating matrix, and that transport can proceed via carriers tunneling between these islands. The model predicts an activated carrier density, which is not observed.
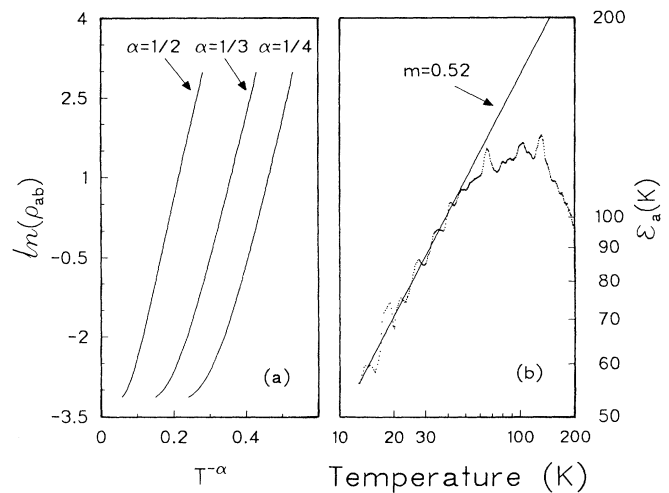
An alternate explanation of the overall resistive behav-

FIG. 2. (a) Variable range hopping, $\rho = \rho_0\exp(T_0/T)^\alpha$, fits to the resistivity of the $x = 0.55$ sample. The $\alpha = \frac{1}{2}$ exponent gives the best straight-line fit with $T_0 = 900$ K. (b) Generalized activation energy $\varepsilon_a = d(\ln\rho)/d(1/T)$ vs T on a log-log scale. The straight line represents a least-squares fit to the low-temperature portion of the data. The slope m of the line is related to α by $m = 1 - \alpha$ (see text).
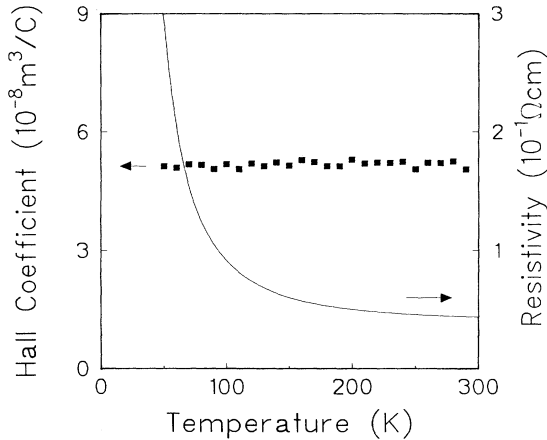
FIG. 3. Hall coefficient (left-hand scale) and resistivity (right-hand scale) vs temperature for the $x = 0.55$ sample.

FIG. 4. Thermopower vs temperature for several samples. The Y contents are (in the order of increasing thermopower) $x = 0, 0.20, 0.38, 0.44, 0.47, 0.55$, and 0.70.

ior takes into account Coulomb correlations between the electrons. Altshuler et al.[22] have shown that in disordered metals the density of states has a minimum at the Fermi level, its depth increasing with disorder, and this minimum leads to $R \propto T^{-1/2}$. If the disorder grows sufficiently large that the states at the Fermi level become localized, Efros and Shklovskii[23] have shown that this minimum becomes a gap (known as a "soft Coulomb gap") and leads to VRH conductivity with $\alpha = \frac{1}{2}$ in two and three dimensions. Although these ideas have received experimental confirmation in thermopower[19,24] (and other) measurements on granular metal films, the results of the thermopower measurements on $Bi_{2.1}Sr_2Y_xCa_{0.9-x}Cu_2O_y$ show unambiguously that no gap develops in the density of states at the Fermi level.

The thermopower of several metallic and nonmetallic samples is shown in Fig. 4. For small x the thermopower is small, as expected for a metal, but it does not exhibit a linear metallic temperature dependence. For the large resistance samples at high temperatures the thermopower is of the order of $2k_B/e = 170$ μV/K. As the temperature is lowered, the thermopower drops to zero; close to $T = 0$ the temperature dependence can be represented by $S \sim T^\beta$, with $\beta \leq \frac{1}{2}$. A logarithmic temperature dependence is also compatible with the data.

For the evaluation of the thermopower results we adopt an approach originally by Burns and Chaikin.[19] The thermopower is related to the Peltier coefficient by $S = \Pi/T$, where $\Pi = $ (heat current)/(electric current). It is assumed that whenever an electric charge is displaced, it carries an appropriate amount of "heat," or energy, the same distance. For a semiconductor of gap Δ, one obtains $\Pi = \Delta/e$ and $S = (k_B/e)(\Delta/k_BT)$. Large, temperature-independent thermopower of the order of $S = (k_B/e)$ occurs when
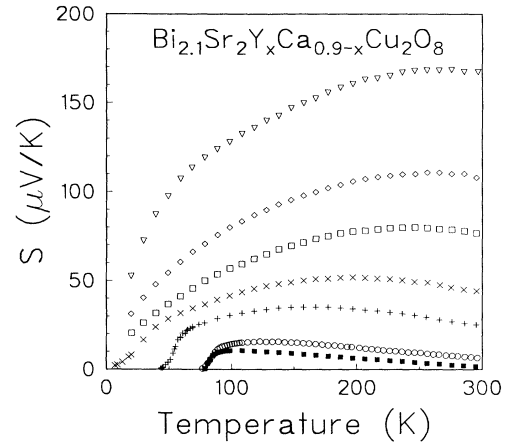
the electronic system has an internal degree of freedom (like spin) carrying a temperature-independent configuration entropy of the order of k_B. In the case of variable range hopping, with no electron-electron interactions, the charge carriers can tunnel without significant investment of energy, and the thermopower approaches zero at low temperature; $S \sim T^\beta$ with $\beta = (d-1)/(d+1)$. If the interactions result in a gap or a soft gap in the density of states, then the thermopower is divergent or, at least, nonzero at low temperatures. According to Burns and Chaikin this dramatic difference in the thermopower is better evidence for Coulomb correlations than the subtle change in the resistivity exponent α.

Following this line of argument, we have to conclude that there is no gap or pseudogap at the Fermi energy. The thermopower of our high-resistance samples is compatible with an Anderson transition to a Fermi glass, with the density of states remaining nonzero as $T \to 0$.

In conclusion, we have shown that $Bi_{2.1}Sr_2Ca_{0.9-x}$-$Y_xCu_2O_y$ exhibits a SI transition upon increasing x. We argue that the transition is two dimensional and that the sheet resistance separating insulating from superconducting ground states is close to $R_{sq} = h/4e^2$, in agreement with current theories. The overall resistive behavior of the insulating samples suggests either tunneling between grains or strong Coulomb correlations, but the Hall and thermopower measurements do not support either interpretation.

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