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Dimensionality of localization in nonsuperconducting $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ crystals

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Transport, magnetoconductivity, and tunneling were measured in nonsuperconducting $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ single crystals ($x,y \lesssim 0.2$), which show two-dimensional localization within the CuO_2 planes. The weakening of disorder in the planes is found to be by itself insufficient for superconductivity. Negative magnetoconductivity, evidence for the onset of superconductive pairing, is observed when transport perpendicular to the planes indicates extended states in three dimensions.

A central concern in understanding the mechanism for the occurrence of high-T_c superconductivity is the nature of the transition from insulating to superconducting phase. Extensive study of La-Sr-Cu-O and Y-Ba-Cu-O systems has invoked the notion of a transition driven primarily by Sr or O doping.[1] Less attention has thus far been given to the issue of dimensionality, i.e., of whether superconductivity can appear in an isolated Cu-O sheet. Early experiments indicated a connection between superconductivity and weak two-dimensional (2D) localization.[2] In view of proposed models for superconductivity emphasizing the necessity of coupling between the CuO_2 planes,[3,4] the present work was undertaken in similarly-prepared crystals of $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$.[5] This is a system of equally-spaced CuO_2 planes encompassing a range of stoichiometric and structural variations.[5-15] Three groups of nonsuperconductors and a superconductor were examined for systematic variations in conductivity components and tunneling curves. Our conclusions are drawn from semiquantitative and tentative classification based on similarities to either semiconducting or metallic behavior, as the interesting intermediate region is not well understood theoretically. We find that a transition from variable-range hopping (VRH) in three dimensions (3D) to extended states within the CuO_2 planes is not by itself sufficient for superconductivity. Negative magnetoconductivity, interpreted as evidence for superconducting fluctuations,[16] is measured only in samples for which transport and tunneling spectra indicate extended states in 3D. These results suggest the importance of interplanar coupling for superconductivity in CuO_2-layered materials.

The nonsuperconducting $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ crystals for this work, presented as groups *A*, *B*, and *C* in Table I, were grown by slowly cooling solutions of composition $Bi_{1+\chi}Si_{1-\chi}CuO_Y$/NaCl in air.[5] Excess Sr with lower O_2 partial pressure yields superconductors ($T_c = 9$ K) while higher pressure produces semiconductors.[5] Crystals in the form of ribbons 1-2 mm×2-5 mm×2-8 μm were readily separated from the solidified flux. The lattice parameters determined from single-crystal x-ray diffraction and precession measurements are referenced to the orthorhombic subcell (2 formula units) of the monoclinic structure.[14] We note strong superlattice periodicities of $2c_0$ and $\tilde{b}$, the latter increasing monotonically from $4.43b_0$ in semiconducting samples to nearly $5b_0$ in superconducting samples. Stoichiometries determined by Rutherford scattering vary much less than in the melt composition. Absence of superconducting transitions in groups *A*-*C* was checked by resistance and ac screening measurements.[17] Magnetoconductivity and tunneling results show that group *A* lies closest to a superconducting phase.

Electrical contacts were made with silver cement cured at ~300 °C. Deconvolution of four-probe resistance measurements for various contact placements[18] was used to find the in-plane conductivity $\sigma_{ab} = (\sigma_a \sigma_b)^{1/2}$ shown in Fig. 1 and the out-of-plane *c*-axis component σ_c shown in Fig. 2. We find $\sigma_a/\sigma_b \approx 1 \pm 0.2$, but the anisotropy σ_{ab}/σ_c exceeds 10^5 at low temperatures. The 2D nature of transport points to particularly weak coupling between the CuO_2 layers across the $BiSrO_2$ layers, as in $Bi_2Sr_2CaCu_2O_8$.[18]

Since it is possible for disorder to depress T_c,[19] we present in Table I the 2D disorder parameter computed from the effective sheet resistance per CuO_2 layer: $k_F l_{(ab)} = (c_0/2)h/e^2\rho_{ab}(0)$, i.e., the product of in-plane Fermi wave vector and elastic scattering length, where $\rho_{ab}(0)$ is the extrapolated residual resistivity and $(c_0/2)$ the interlayer spacing. The result is least 2D disorder in group *B* and most disorder in group *C*. A prediction of the depression in T_c associated with the 2D disorder

TABLE I. Parameters for $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ crystals: stoichiometry $2+x$ and $2-y$ (± 0.03), $\delta \lesssim 0.5$, lattice parameters a_0, b_0, c_0, superlattice periodicity $\tilde{b}$, and 2D disorder parameter $k_F l_{(ab)}$.

	Sr/Bi (melt)	$2+x$ (Bi)	$2-y$ (Sr)	a_0 (Å)	b_0 (Å)	c_0 (Å)	$\tilde{b}/b_0$	$k_F l$ (ab)
A	1.2	2.00	1.85	5.383(1)	5.384(1)	24.58(1)	4.83(5)	4.3
B	1.0	2.10	1.75	5.385(1)	5.385(1)	24.58(1)	4.81(9)	5.2
C	0.8	2.12	1.75	5.389(2)	5.393(2)	24.56(2)	4.68(3)	2.9

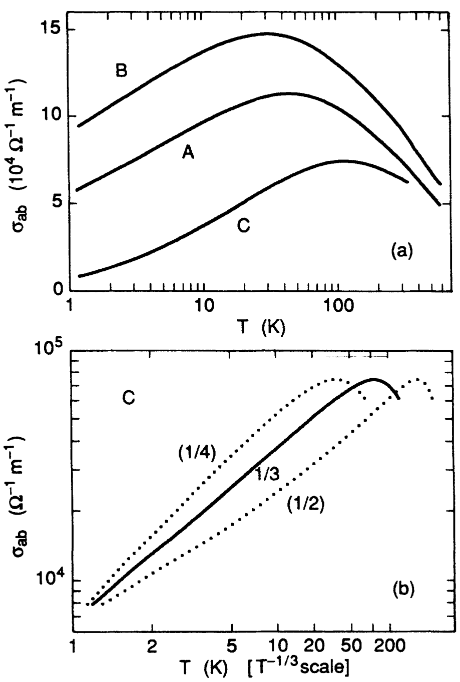

FIG. 1. (a) Temperature dependence of in-plane conductivities for three crystals. (b) Curve C replotted as $T^{-\eta}$, for $\eta=\frac{1}{4}$, $\frac{1}{3}$, and $\frac{1}{2}$, with fixed abscissa range $(1\text{ K})^{-\eta}\leq T^{-\eta}\leq 0$.

is $\Delta T_c/T_c=\delta$,[20] where $\delta=\pi\hbar/8k_BT\tau_{in}$ is the Maki-Thompson pair-breaking parameter,[21] and τ_{in}^{-1} the inelastic scattering rate. Estimating $\tau_{in}^{-1}=(k_BT/\hbar k_Fl)\times\ln(k_Fl)$, from 2D theory for electron-electron interactions,[22] gives $\tau_{in}^{-1}=4\times10^{10}\text{ s}^{-1}$ for $k_Fl=5$ and $T=1$ K. Thus a weak depression $\Delta T_c\approx1$ K is predicted, which is insufficient to explain the absence of superconducting transitions in groups A and B. Further, similar consideration of the resistivity of epitaxial films of $YBa_2Cu_3O_7$ disordered by ion irradiation[19] shows that the transition $T_c\rightarrow0$ occurs at significantly smaller k_Fl of 1 to 2.

The $\ln T$ dependence observed at low temperatures for curves A and B in Fig. 1(a) appears to be a signature of a regime of weak disorder in 2D. A similar $\ln T$ dependence was observed in the normal state of thin (50 Å) films of InO_x, a disordered superconducting system with comparable conductivity and carrier density.[23] To consider this behavior, in the framework of weak localization perturbation theory in 2D, we treat the CuO_2 sheets as isolated conductors and use the expression $\sigma_{ab}=(\alpha+g)(2e^2/\pi h^2c_0)\ln(T/T_0)$, where $-\frac{1}{2}\leq\alpha\leq1$ is the predicted range for the form of τ_{in}^{-1} given above[24] and g is determined by e-e interactions and superconducting fluctuations.[25] Fits to curves A and B in Fig. 1(a) give $(\alpha+g)=1.8$ and 2.1, respectively. While the observed variations in $\sigma_{ab}(T)$ may not be sufficiently small for rigorous interpretation by perturbation theory, values of α and g near unity in the region $T\gg T_c$ are plausible for extended states in 2D for groups A and B.

In samples from group C, on the other hand, σ_{ab} falls off distinctively more rapidly than $\ln T$. The data for C are replotted in Fig. 1(b) with coordinates scaled according to VRH formulas, $\sigma_{ab}\propto\exp[-(T_0/T)^\eta]$, for various exponents $\eta=\frac{1}{4}$, $\frac{1}{3}$, and $\frac{1}{2}$. The optimum straight line is obtained with $\eta=\frac{1}{3}$, the 2D exponent,[26] and a scaling temperature of $T_0=33$ K. Dotted curves show that $\eta=\frac{1}{2}$ is ruled out by the positive curvature and $\eta=\frac{1}{4}$ is possible though it does not fit as well. Compared to A or B, the disorder in group C is evidently much stronger, albeit in a marginal regime of VRH because of the small T_0.[27]

The variation of σ_c is shown in Fig. 2 on a linear scale since the temperature dependence is close to being linear for $T\lesssim100$ K. The slope for A, $\sigma_c(100\text{ K})/100\text{ K}\approx0.025\,\Omega^{-1}\,\text{m}^{-1}K^{-1}$, is the same order of magnitude as for $Bi_2Sr_2CaCu_2O_8$,[18] showing that the $BiSrO_2$ barriers are essentially equivalent in the two structures. A model of high T_c for two layers in terms of stronger interaction between the two CuO_2 planes[3] is consistent with this result, since the c-axis transport is limited by the $BiSrO_2$ barrier. Using σ_c as a measure of the interplanar coupling, Fig. 2 shows A and B to be more strongly coupled than C.

The most striking difference between groups A and B is the opposite sign of the a-b-plane magnetoconductivity, as shown in Fig. 3. At low temperatures, we find that group A and superconducting crystals show negative magnetoconductivity, whereas groups B and C show positive magnetoconductivity. These data are for H applied along the c axis. Signals are 2 to 3 times smaller for H in-plane and perpendicular to the current, which suggests various orbital mechanisms.[16,28] The positive magnetoconductivity could be a vestige of the behavior seen in the VRH regime of disordered semiconductors, where the magnetic field interferes with coherent backscattering associated with random paths.[28] Negative contributions to the magnetoconductivity are most pronounced between 2 and 3 K in both sets of data in Fig. 3. For group A they are dominant and cause the sign to be negative. For group B they appear as a perturbation in the temperature dependence of the positive magnetoconductivity. We presume these effects are due to superconducting fluctuations in the normal state.[16] However, instead of the usual monotonic increase as $T\rightarrow T_c$, these fluctuations vanish in the limit $T\rightarrow0$, which suggests $T_c\approx0$.

To reveal the nature of transport from a 3D perspective we examine an equivalent isotropic $\sigma_{abc}=(\sigma_a\sigma_b\sigma_c)^{1/3}$, which models the conductivity of an anisotropic medi-

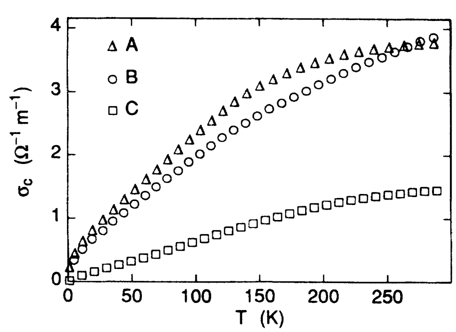

FIG. 2. Temperature dependence of out-of-plane conductivities.

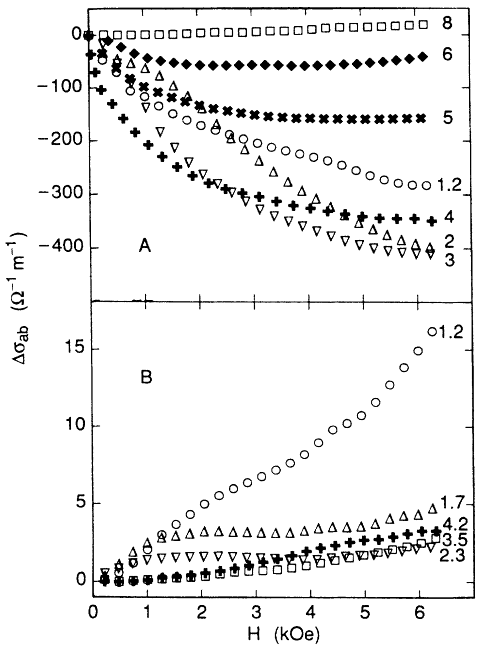

FIG. 3. Magnetoconductivities of crystals A and B at temperatures indicated. Negative sign is evidence for superconducting fluctuations.

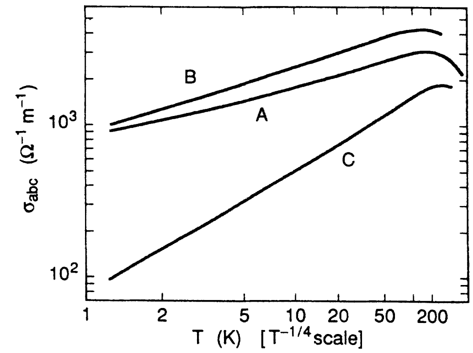

FIG. 4. Effective conductivities σ_{abc} plotted on a 3D variable-range hopping scale.

um.[29] Data for the three groups are plotted on a $T^{-1/4}$ scale in Fig. 4, because the $\eta = \frac{1}{4}$ VRH exponent in 3D provides the best fit for groups B and C.[30] The progressively shallower slopes imply a systematic lengthening of the mean ranges of the localized electron states in 3D across the sequence C, B, and A. The VRH picture just barely applies to group B, because of the shallow slope. The temperature dependence is weakest for group A and generally there is upward curvature, features which place group A nearest to metallic behavior in 3D.

Further evidence that group A is near a superconducting phase can be found in tunneling spectra. Figure 5 shows differential tunneling conductivities $g(V_{\text{bias}})$ for group A and B crystals and for reference a superconducting crystal S. The junctions were prepared by etching the crystals in CH_3OH:Br and vacuum evaporating Pb-film counter electrodes (area 0.01 mm^2), with a native barrier being formed at the interface. Magnetic fields (H = 0.1–0.5 T, field cooled) were applied to quench the Pb superconductivity. Curves taken at $H=0$ for diagnostic purposes show $g(0)=0$, confirming single-step tunneling into superconducting Pb; singularities at the Pb gap and Pb-phonon structure for S (see Fig. 5, inset); broadened Pb gap structure in cases A and B. The curves in a field show low leakage, indicating good junction quality, and smooth cusps at low bias, but otherwise no distinctive gap features because of disorder.[31] An essentially linear $g(V)$ is characteristic of the cuprate superconductors.[32] Qualitatively comparing low-bias regions, curve A strongly resembles the superconducting case S, being V shaped with a rounded cusp, whereas the flatter curve B tends to be more U shaped. The overall sublinear appearance of curve A is reminiscent of the behavior of Pb/InO_x tunnel junctions,[33] and suggests correlations with 3D character associated with disorder.[34] The tunneling data indicate that the e-e correlations associated with superconducting interactions and with disorder are closely related, if not indeed the same, phenomena.

From a materials point of view, the interlayer coupling could be due to defects as proposed by Phillips[4] and one may also question the stacking uniformity among $\sim 10^3$ CuO_2 layers within the crystals. The distinction among groups A, B, and C is fixed by the growth stoichiometry and is not changed by post annealing in O_2 up to 500 °C. Hole carrier concentrations of about 1 per Cu were determined from Hall coefficients R_H at 295 K and are comparable to the high-T_c cuprates. However, since R_H was found to increase by $\sim$50% on cooling to 1.2 K, there are uncertain mobility corrections.

The conclusion from these results is the existence of a relationship between the onset of superconductive pairing, observed as negative fluctuation magnetoconductivity, and comparatively weaker disorder in 3D shown in both the

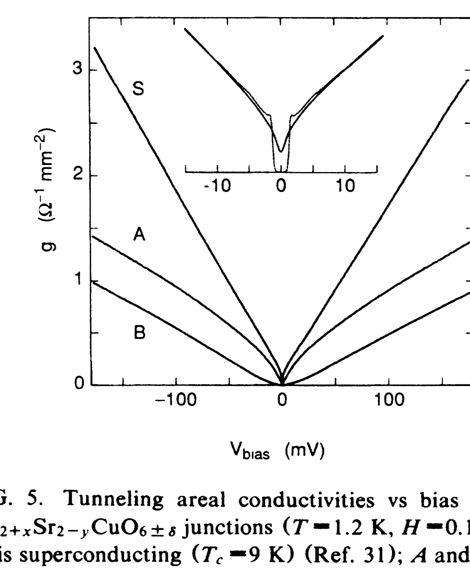

FIG. 5. Tunneling areal conductivities vs bias voltage for Pb/$Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ junctions ($T=1.2$ K, $H=0.1$ T). Crystal S is superconducting ($T_c=9$ K) (Ref. 31); A and B are nonsuperconducting. Inset: expanded scales for S, with dotted curve for $H=0$.

tunneling and transport (group A). This indicates that interplanar coupling is very important in the mechanism of superconductivity[3,4] and in this connection $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ tends toward a continuum of CuO_2 layers, rather than a single layer. Contrasting this is the intermediate regime of extended states primarily in the a-b plane, where the magnetoconductivity is positive (group B), and the limit of strong localization with variable-range hopping both within and between planes (group C). The effect of anisotropic localization on superconductivity in $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ differs from previous experience with thin films of 3D superconductors, where quasi-2D effects associated with disorder are responsible for the depression of T_c.[20]

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