RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 1 1 JANUARY 1990

Normal-state transport properties of $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ crystals

S. Martin, A. T. Fiory, R. M. Fleming, L. F. Schneemeyer, and J. V. Waszczak
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 19 September 1989)

Transport anisotropies of $\rho_c/\rho_{ab} \simeq 10^4$ to 10^5 were measured for superconducting and nonsuperconducting $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ crystals. In superconducting samples ρ_{ab} increases linearly with temperature from just above $T_c \simeq 7$ to 700 K. The implication of the ρ_{ab} results is that classical electron-phonon scattering mechanisms are inadequate. The anisotropy and T_c for various layered superconductor systems are compared. In all crystals studied ρ_c is nonmetallic, varying as a power law $T^{-\alpha}$, $\alpha \simeq 0.5$–1.

A characteristic feature of the high-T_c layered superconductors is the extreme two dimensionality of their physical properties. Transport anisotropy studies are hence very significant for establishing the role of the coupling between Cu-O planes on the mechanism of high-T_c superconductivity. Previous measurements in Y-Ba-Cu-O crystals suggested resistivity anisotropies of $\simeq 10^2$ for samples with $T_c = 90$ K,[1,2] and $\simeq 10^3$ for 60-K samples.[2] In Bi-Sr-Ca-Cu-O crystals even larger anisotropies of $\simeq 10^3$ to 10^5 were measured,[3,4] giving rise to two-dimensional (2D) phase fluctuations near the superconducting transition.[3] Similar behavior was recently reported for Tl-Ba-Ca-Cu-O thin films.[5] Presently, the mechanism of charge transport perpendicular to the Cu-O planes is far from being clearly established, owing to the range of anisotropy values and the different types of temperature dependences reported by various groups.[1–3,6–8] The reasons for the lack of a consensus include experimental uncertainties such as nonuniform composition, defect mediated hopping of carriers, inhomogeneous current flow, contributions from ρ_{ab}, improper deconvolution of anisotropic current flow, and contact misalignment. A further issue in understanding high-T_c superconductivity concerns the applicability of conventional electron-phonon scattering mechanisms to the description of normal-state transport properties. However, the problem can be addressed clearly only by normal-state measurements at temperatures well below the typical high T_c's of 80–90 K. In this respect studies of the transport properties in the low-T_c, single-layer Bi-Sr-Cu-O compound are very promising for gaining insight into the behavior of the closely related high-T_c cuprates.

We report here transport anisotropy measurements on $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ crystals which are superconducting with $T_c = 6.5$–8.5 K, or nonsuperconducting, depending upon the Sr/Bi ratio in the melt composition and the oxygen partial pressure (P_{O_2}) during growth.[9] We find $\rho_c/\rho_{ab} = 5\times10^4$ to 2×10^5 at $T \approx T_c$ for both types of samples. The superconducting crystals show a strikingly linear temperature dependence of $\rho_{ab}(T)$ from just above T_c to 700 K, suggesting an extraordinarily small value of the transport Debye temperature of $\Theta_D^* \simeq 35$ K in the context of a classical Bloch-Grüneisen (BG) treatment of electron-phonon scattering. In nonsuperconducting crystals $\rho_{ab}(T)$ shows a logarithmic upturn below $T_{min} = 20$–70 K and a linearity above T_{min}. The resistivity perpendicular to the Cu-O planes is found to be of the nonmetallic form $\rho_c \propto T^{-\alpha}$ with $\alpha \simeq 0.5$–1. Also presented are transport anisotropies in several dichalcogenides and in $YBa_2Cu_3O_{7-\delta}$ crystals where we find $\rho_c/\rho_{ab} \simeq 10^3$ for $T_c \simeq 60$ K and $\simeq 10^2$ for $T_c \simeq 90$ K.

Crystals of $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ ("2:2:0:1") were grown in an alkali-halide flux and crystals of $YBa_2Cu_3O_{7-\delta}$ ("1:2:3") in a $BaCuO_2$-CuO flux, as described previously.[9] The notations 2:2:0:1 and 1:2:3 are used herein generally, rather than for specific compositions. We should emphasize that studies on 2:2:0:1 ceramic samples are revealing a complex phase diagram, implying that the structure of a crystal grown under specific conditions cannot be easily asserted.[10] Typical crystals are platelets 1 mm across and 4 μm (2:2:0:1) or 50 μm (1:2:3) thick. High-quality contacts of low resistance were made by using an Ag paste which was cured in O_2 at 250 °C. The resistivity components were measured using a generalization of the Montgomery method with the contacts placed on the *ab*-plane surfaces.[3]

Figure 1(a) shows the temperature dependence of the in-plane resistivity ρ_{ab} for two 2:2:0:1 crystals grown under conditions indicated. In the nonsuperconducting sample ρ_{ab} has a minimum at $T_{min} = 70$ K, with a slope of $\Delta\rho_{ab}/\Delta T = 1.88$ $\mu\Omega$ cm/K above T_{min}. The extrapolated residual resistivity of $\rho_0 = 800$ $\mu\Omega$ cm can be used to estimate a disorder parameter of $(k_F l)_{ab} = 3.7$. We found that by increasing the Sr/Bi melt ratio T_{min} decreases. By choosing a reduced P_{O_2} of 4% (of 1 atm) during growth, we obtained superconducting crystals with $T_c = 6.5$–8.5 K. In Fig. 1(a) the superconducting sample shows a remarkable linearity of ρ_{ab} from above T_c to 700 K. The $\rho_{ab} = 0$ transition is at $T_c = 6.5$ K. We obtain a slope of $\Delta\rho_{ab}/\Delta T = 0.74$ $\mu\Omega$ cm/K and a residual resistivity of $\rho_0 = 70$ $\mu\Omega$ cm, which yields $(k_F l)_{ab} = 43$. For a superconducting sample with $T_c = 8.5$ K the corresponding values are $\Delta\rho_{ab}/\Delta T = 1.06$ $\mu\Omega$ cm/K, $\rho_0 = 100$ $\mu\Omega$ cm and $(k_F l)_{ab} = 30$. In both cases the values of the disorder parameter indicate clean-limit superconductivity. Xiao *et al.*[11] reported measurements on ceramic samples of 2:2:0:1, where a linear temperature-dependent resistivity was observed from 10 to 300 K with $T_c = 7$ K; however, the data reflect a polycrystalline average of ρ_{ab} and ρ_c.

The linear temperature dependence of the in-plane

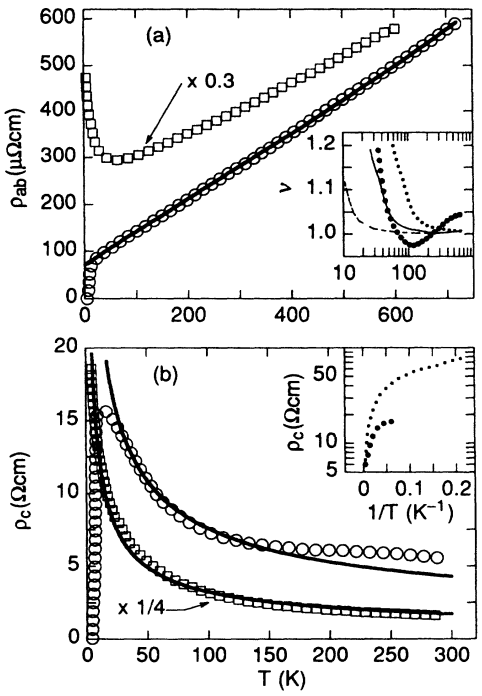

FIG. 1. In-plane (a) and out-of-plane (b) resistivities measured in 2:2:0:1 crystals: a nonsuperconductor (□) grown with Sr/Bi = 1.22 and P_{O_2} = 20%, and a superconductor (○), with Sr/Bi = 1.0 and P_{O_2} = 4%. Curve in (a) is a fit assuming BG; curves in (b) are power-law fits. Inset (a) shows $\nu = d[\ln(\rho_{ab} - \rho_0)]/d[\ln T]$ vs T for the superconducting sample (●) as compared with BG fits with $\Theta_D^* = 10$ K (dashed), 35 K (solid), and 80 K (dotted). Inset (b) illustrates ρ_c is non-Arrhenius.

resistivity is one of the characteristic features of normal-state transport in high-T_c superconductors. Novel models of the mechanism of high-T_c superconductivity predicting $\rho_{ab} \propto T$ include the resonating-valence-bond (RVB) model by Anderson and Zhou,[12] the quantum percolation model by Phillips,[13] and the marginal Fermi-liquid model by Varma *et al.*[14] Until recently, measurements of the normal-state properties in high-T_c materials have not provided especially strong support for novel types of charge transport. It was possible to argue that classical electron-phonon scattering as described by the BG model is valid if $T_c \approx 90$ K.[15] The BG model predicts in 3D an initial T^5 increase of the resistivity for $T < \Theta_D^*$ and a linear temperature dependence for $T > \Theta_D^*$, where the transport Debye temperature Θ_D^* can be typically a factor of 2–4 smaller than the thermodynamic Debye temperature Θ_D for materials with a small k_F. For 1:2:3 Θ_D^* was found to be as low as ≈ 200 K.[15] Thus down to $T_c \approx 90$ K the deviation would not be substantial enough to be apparent.

The low temperature behavior of ρ_{ab} shown in Fig. 1(a) for the nonsuperconducting sample is found to be caused by weak localization effects in 2D which are studied in detail elsewhere.[16] For the superconducting sample a BG fit with $\Theta_D^* = 35$ K is shown as the nearly linear solid line. In the inset of Fig. 1(a) the logarithmic derivative $\nu = d[\ln(\rho_{ab} - \rho_0)]/d(\ln T)$ is plotted versus T. The sensitivity of ν to the choice of Θ_D^* is analyzed in detail by plotting the data (denoted by ●) and, for comparison, BG fits with $\Theta_D^* = 10$ K (dashed curve), 35 K (solid curve), and 80 K (dotted curve). The data show a smooth decrease from $\nu = 1.05$ at 700 K to 0.97 at 120 K followed by a pronounced increase at lower temperatures. Within a deviation of ±5% the linearity of ρ_{ab} with T can be asserted over a range of $T = 50$–700 K. A characteristic test of BG behavior is the onset of the nonlinearity $\nu > 1$ at low temperatures. The BG fit for $\Theta_D^* = 35$ K describes the data best, e.g., $\nu = 1.1$ is attained at $T = 40$ K in both the data and the fit. In contrast, neither $\Theta_D^* = 10$ K nor $\Theta_D^* = 80$ K adequately fit at the onset of nonlinearity. Although it is in best agreement with data, there is no clear understanding for such a small value of $\Theta_D^* = 35$ in terms of electron-phonon scattering. The thermodynamic Debye temperature is expected to be $\Theta_D \simeq 350$ K, as found in the related high-T_c compound $Bi_2Sr_2CaCuO_8$ (2:2:1:2).[17] A reasonable lower limit would therefore be $\Theta_D^* \simeq 80$ K, which deviates from the data significantly. Interestingly, in the nonsuperconducting La-Sr and La-Ba cuprates the resistivities reported for polycrystalline materials resemble classical metals, deviating from linearity near 175–300 K.[18]

The lack of any saturation of $\rho_{ab}(T)$ up to 700 K is another similarity between 2:2:0:1 and the high-T_c materials. It implies a weak scattering mechanism and imposes an upper limit of $\lambda < 0.1$ for the electron-phonon coupling constant.[19] If we assume only phonon scattering, then the resistivity slope provides the following quantitative estimate:[19]

$$\lambda = (0.246\ \mathrm{eV}^{-2}\mu\Omega^{-1}\mathrm{cm}^{-1}/\mathrm{K})(\Delta\rho_{ab}/\Delta T)E_p^2,$$

where

$$E_p = (1.8\times10^3\ \mathrm{eV\,\AA})(1+\lambda)^{1/2}/\lambda_L(0)$$

is the plasma energy and $\lambda_L(0)$ the London penetration depth. Taking $\lambda_L(0) = 3100$ Å (Ref. 20) and an average slope of 0.9 μΩ cm/K, we obtain $\lambda = 0.08$, suggesting particularly weak electron-phonon coupling.

Figure 1(b) shows the temperature dependence of the resistivity perpendicular to the Cu-O planes measured in the same 2:2:0:1 crystals. We find that ρ_c is nonmetallic and typically several orders of magnitude larger than ρ_{ab}, as in other layered cuprates.[3] The nonmetallic behavior and the explicit form of the temperature dependence of ρ_c is an important issue for understanding the normal-state transport mechanism. In high-T_c materials the accessible low-temperature range is limited, thus obscuring the distinction between thermal activation and power-law behavior. In 2:2:0:1, however, measurements down to 4–8 K clearly indicate inconsistency with an Arrhenius law, as shown by the inset of Fig. 1(b), for both superconducting (denoted by ○) and nonsuperconducting (denoted by □) samples. Rather, better fits are obtained for a power law, $\rho_c \propto T^{-\alpha}$ with $\alpha = 0.61$ for the nonsuperconductor and 0.52 for the superconductor, as shown by the solid curves in Fig. 1(b). For comparison, we have previously found that $\alpha \simeq 1$ adequately describes the temperature dependence of ρ_c in 2:2:1:2.[21] In the RVB model of high-T_c superconductivity proposed by Anderson and Zhou,[12] the temperature dependence of ρ_c is expected to be inverse to

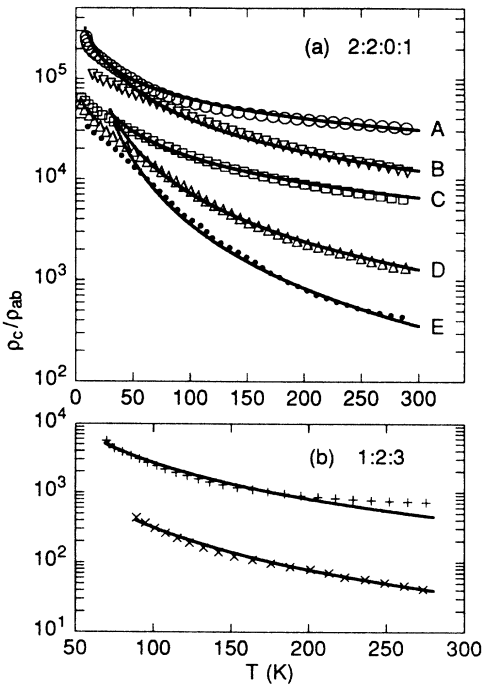

FIG. 2. Temperature dependence of resistivity anisotropies for crystals of (a) 2:2:0:1 and (b) 1:2:3 with $T_c = 90$ K (×) and 60 K (+), grown under different conditions. Curves are power-law fits.

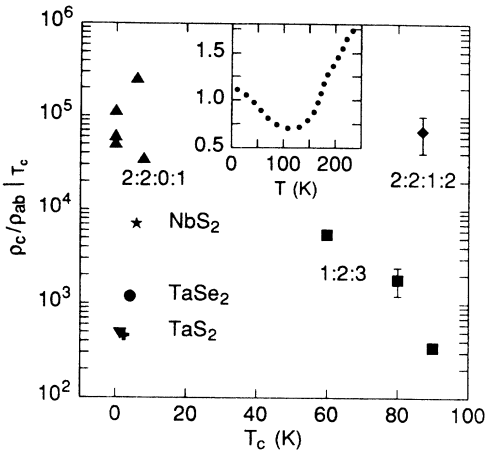

FIG. 3. Anisotropies just above T_c vs T_c for several layered cuprates and layered dichalcogenides (Refs. 22–24). The inset shows the temperature dependence for $2H$-$TaSe_2$.

that of ρ_{ab}. Although it was observed in the high-T_c materials,[1–3,21] our measurements in superconducting 2:2:0:1 crystals suggest a weaker power law for ρ_c than given simply by ρ_{ab}^{-1}.

Figure 2(a) shows the anisotropy ρ_c/ρ_{ab} for 2:2:0:1 samples grown with different Sr/Bi ratios in the melt composition and under different P_{O_2}. Sample A is the open circles and sample C is the open squares of Fig. 1. Samples A and E are superconducting with $T_c = 6.5$ and 8.5 K, respectively. For both samples $P_{O_2} = 4\%$, but Sr/Bi = 1 for A and 1.5 for E. The results imply that the change in Sr/Bi ratio in the melt has led to a decrease of the anisotropy by nearly an order of magnitude at T_c and two orders of magnitude at 300 K. The nonsuperconducting samples were grown under the following conditions: Sr/Bi = 1 (B), 1.22 (C,D) and $P_{O_2} = 20\%$ (B,C), 10% (D). The results in Fig. 2(a) suggest that the anisotropy becomes smaller as the Sr/Bi ratio is increased and P_{O_2} is decreased. The presence or absence of superconductivity, however, appears to be more strongly affected by P_{O_2}. The solid curves are fits to a power law $\rho_c/\rho_{ab} \propto T^{-\beta}$ with $\beta = 0.64$ (A), 1.07 (B), 0.84 (C), 1.57 (D), and 2.1 (E). Subtracting the residual resistivity $\rho_0 = 70$ $\mu\Omega$ cm, we obtain $\beta = 1.40$ for sample A. The results suggest that β tends to increase towards the value 2, as the anisotropy decreases. It is striking that the sample with the highest T_c, E, has a power-law exponent like that observed in high-T_c materials and predicted by the RVB model.

In Fig. 2(b) the resistivity anisotropies are plotted for Y-Ba-Cu-O crystals with $T_c \simeq 90$ K (denoted by ×) and $T_c \simeq 60$ K (denoted by +), where oxygen content was controlled by postannealing. We find that the lower-T_c crystal has an order of magnitude larger anisotropy, as also reported by Brawner, Wang, and Ong.[2] The temperature dependence of the anisotropy can be fit to a power law (solid lines) with $\beta = 1.73$ for the 60-K sample and 2.01 for the 90-K sample. Note again the tendency of β to approach the value 2 as the anisotropy decreases.

Furthermore, we find an indication of a higher T_c being correlated with a stronger coupling between the Cu-O planes. This feature is illustrated in Fig. 3, where the anisotropy values just above T_c are plotted versus T_c for the layered cuprates 2:2:0:1 ($T_c \simeq 0$, 6, and 8 K), 2:2:1:2 ($T_c \simeq 87$ K), and 1:2:3 ($T_c \simeq 60$, 80, and 90 K). The 80-K 1:2:3 sample was annealed in an oxygen deficient atmosphere. The error bars shown for these data and for 2:2:1:2 indicate typical variations of the anisotropy measured in several samples. For comparison, results on layered dichalcogenides are also plotted. The temperature dependence of ρ_c/ρ_{ab} for $2H$-$TaSe_2$ is drawn in the inset. This material undergoes a charge-density-wave transition at $T = 110$ K, below which we find that the anisotropy also increases with decreasing temperature, as in the layered cuprates. The remaining data are taken from other reports for $4Hb$-TaS_2,[22] $1T$-TaS_2,[23] and $2H$-NbS_2.[24] We see in Fig. 3 that the anisotropies in layered dichalcogenides are of similar magnitudes as in 1:2:3 samples ($\simeq 10^2$ to 10^4). The layered Bi compounds are, however, more strongly anisotropic ($\simeq 10^4$ to 10^5), the 2:2:0:1 samples showing variation with growth conditions.

In conclusion, a linear temperature dependence of the ab-plane resistivity from above $T_c \simeq 7$ to 700 K was measured in superconducting 2:2:0:1 crystals, which cannot be accounted for by classical electron-phonon scattering. Nonmetallic behavior was found for transport perpendicular to the Cu-O planes, which appears to be universal. Anisotropies of $\rho_c/\rho_{ab} \simeq 10^4$ to 10^5 were found near T_c and show tendencies to decrease with higher T_c.

We acknowledge many useful discussions with M. Gurvitch, P. B. Littlewood, J. C. Phillips, S. A. Sunshine, and C. M. Varma.

[1]S. W. Tozer *et al.*, Phys. Rev. Lett. **59**, 1768 (1987).
[2]S. Hagen *et al.*, Phys. Rev. B **37**, 7928 (1988); D. A. Brawner, Z. Z. Wang, and N. P. Ong, Phys. Rev. B **40**, 9329 (1989).
[3]S. Martin *et al.*, Phys. Rev. Lett. **60**, 2194 (1988); *ibid.* **62**, 677 (1989).
[4]D. E. Farrell *et al.*, Phys. Rev. Lett. **63**, 782 (1989).
[5]D. H. Kim *et al.*, Phys. Rev. B **40**, 8834 (1989).
[6]Y. Iye *et al.*, Jpn. J. Appl. Phys. **26**, L1057 (1987); Physica C **153–155**, 26 (1988).
[7]L. I. Buranov *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 43 (1988) [JETP Lett. **47**, 51 (1988)].
[8]Y. Hidaka *et al.*, Rev. Electr. Commun. Lab. **36**, 567 (1988).
[9]L. F. Schneemeyer *et al.* (unpublished); Nature (London) **328**, 601 (1987).
[10]S. A. Sunshine *et al.* (unpublished).
[11]G. Xiao *et al.*, Phys. Rev. B **38**, 11 824 (1988).
[12]P. W. Anderson and Z. Zhou, Phys. Rev. Lett. **60**, 132 (1988); *ibid.* **60**, 2257 (1988).
[13]J. C. Phillips, Phys. Rev. B **40**, 7348 (1989).
[14]C. M. Varma *et al.*, Phys. Rev. Lett. **63**, 1996 (1989).
[15]S. Martin *et al.*, Phys. Rev. B **39**, 9611 (1989).
[16]A. T. Fiory *et al.* (unpublished).
[17]J. E. Graebner (private communication).
[18]B. Raveau and C. Michel, in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 599.
[19]M. Gurvitch and A. T. Fiory, Phys. Rev. Lett. **59**, 1337 (1987).
[20]$\lambda_L(0)$ was obtained from the 2300 Å value for La-Sr-Cu-O and scaling the copper density; D. R. Harshman (private communication).
[21]S. Martin *et al.*, Appl. Phys. Lett. **54**, 72 (1989).
[22]W. J. Wattamaniuk, J. P. Tidman, and R. F. Frindt, Phys. Rev. Lett. **35**, 62 (1975).
[23]P. D. Hambourger and F. J. Di Salvo, Physica B **99**, 173 (1980).
[24]B. W. Pfalzgraf and H. Spreckels, J. Phys. C **27**, 4359 (1987).