

## Anisotropic thermoelectric power and conductivity in single-crystal $\text{YBa}_2\text{Cu}_3\text{O}_y$

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Thermoelectric power (TEP) and electrical conductivity measurements are reported for different crystal directions and for varying oxygen deficiency in single-crystal  $\text{YBa}_2\text{Cu}_3\text{O}_y$ . The dependency of the transport parameters on direction are compared with the predictions of band theory. The  $c$ -axis conductivity and TEP are suggestive of non-band-transport as might be displayed by a localized system.

Since the discoveries of superconductivity in La-Ba-Cu-O (Ref. 1) and Y-Ba-Cu-O,<sup>2</sup> there has been significant interest in the mechanisms responsible for the high-temperature superconductivity in these unusual oxides. Isotope-effect experiments<sup>3,4</sup> have demonstrated highly reduced oxygen, barium, and copper isotope effects in the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  structure, suggesting that the electron pairing mechanism may contain nonphonon contributions in the  $T_c = 90\text{-K}$  structure. A similar conclusion has been suggested for the  $T_c = 37\text{-K}$   $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  structure because of its reduced oxygen isotope effect.<sup>5</sup> These conclusions are based on isotropic-interaction calculations. Interpretations of transport and magnetic measurements on polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_y$  based on free-electron gas expressions suggest that an important role is played by Coulomb interactions.<sup>6</sup> On the other hand, it has been demonstrated that the crystal structure of the high- $T_c$  oxides is highly anisotropic. Resistivity measurements<sup>7</sup> on single-crystal  $\text{YBa}_2\text{Cu}_3\text{O}_y$ , for example, indicate anisotropies greater than 100, and band-structure calculations reveal complex and anisotropic dispersion near the Fermi energy.<sup>8-10</sup>

In this Brief Report, we present the first measurements of the thermoelectric power (TEP) of single-crystal  $\text{YBa}_2\text{Cu}_3\text{O}_y$  in two different crystallographic directions, and compare them to the band predictions of Ref. 11. We have also studied the TEP of polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_y$  and the anisotropic conductivity of single-crystal  $\text{YBa}_2\text{Cu}_3\text{O}_y$ . The TEP and conductivity parallel to the  $c$  axis were measured for different oxygen contents. We find the TEP to be positive both parallel to the  $c$  axis and perpendicular to it, indicating holelike conduction in both directions. In the limit of an energy-independent scattering time, band theory predicts a positive TEP in the  $c$ -axis direction, but it is unable to account for the positive TEP in the  $a$ - $b$  plane.<sup>11</sup> The TEP and conductivity are both sensitive to oxygen concentration ( $y$ ). These anisotropic conductivity and TEP results raise the possibility of a non-band transport mechanism.

Single-crystal specimens of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  were initially grown by slow cooling a nonstoichiometric melt in an  $\text{Al}_2\text{O}_3$  crucible, as described in Ref. 12. Crystal sizes were on the order of  $0.75 \times 0.75 \times 0.15 \text{ mm}^3$ . The crystals were characterized by dc resistivity and dc magnetic susceptibility measurements which demonstrated bulk supercon-

ductivity. Contacts to the crystal faces were made by gold wires silver-painted to fired-on silver pads. The resistivity in the  $a$ - $b$  plane was measured using a 4-probe contact configuration in which current is injected through the edges of the platelets and voltage is measured between two parallel strips placed apart approximately one-third of the crystal length. This direct method does not suffer the complications and analysis problems of the Montgomery method. Comparison of 2- and 4-probe resistivities demonstrated negligible contact resistances. The  $c$ -axis resistivity was determined by a similar method or, more commonly, by the standard two contact method where the current injection leads serve simultaneously as voltage probes. TEP data were obtained with a 2-probe configuration. In-plane measurements make no distinction between the  $a$  and  $b$  axes. Oxygen content in the crystals was controlled by a schedule of annealing in a reduced oxygen environment, and the TEP was measured using a resistive heater and Chromel-Constantan thermocouple (the TEP of the gold leads attached to the sample was taken into account).

Figure 1 shows typical temperature-dependent dc resistivity.

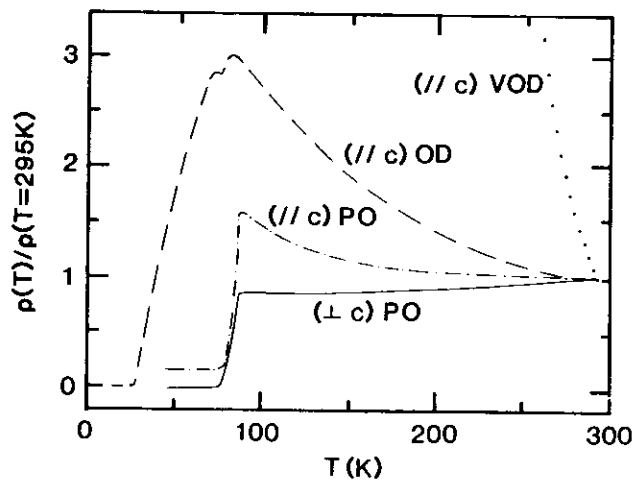


FIG. 1. Normalized resistivity of single-crystal  $\text{YBa}_2\text{Cu}_3\text{O}_y$  for in-plane (perpendicular to  $c$  axis) and out-of-plane (parallel to  $c$  axis) conduction. The resistivity of the  $c$  axis is shown for three different oxygen contents.

tance data for the  $a$ - $b$  plane and  $c$ -axis directions in  $\text{YBa}_2\text{Cu}_3\text{O}_y$ . The fully annealed [or pristine oxygenated (PO)] crystal data are in agreement with previous studies.<sup>7</sup> A sharp transition to the superconducting state occurs for both orientations near  $T_c \cong 81$  K, with transition widths on the order of several degrees K. Figure 1 also shows the  $c$ -axis resistance for two different oxygen contents, which we identify as oxygen deficient (OD) and very oxygen deficient (VOD). The VOD state was achieved by annealing the original crystal in vacuum for 17 h at 625 °C, while the OD state is obtained by re-annealing the same crystal for 5 h at 575 °C under flowing oxygen. The oxygen content in our crystals is not measured directly, but from comparison with the resistivity data of Refs. 13 and 14 we expect the VOD state to correspond approximately to  $y = 6.3$  and the OD state to  $y$  between 6.5 and 6.7.

At room temperature, the  $c$ -axis resistivity  $\rho_c$  increases dramatically with increasing oxygen deficiency:

$$\rho_c(\text{OD})/\rho_c(\text{PO}) = 2.0, \quad \rho_c(\text{VOD})/\rho_c(\text{PO}) = 1.2 \times 10^5,$$

where  $\rho_c(\text{PO}) \approx 0.01$   $\Omega\text{cm}$  (this value was difficult to precisely determine due to geometrical uncertainties); with decreasing temperature, these ratios increase. The superconducting onset temperature for the OD sample was again  $\cong 81$  K, but the transition width was increased to over 50 K. We find no evidence for superconductivity in the VOD samples, as the resistivity rose monotonically with decreasing temperature (Fig. 1). Figure 2 shows the temperature-dependent TEP measured in the  $a$ - $b$  plane and along the  $c$  axis of single-crystal  $\text{YBa}_2\text{Cu}_3\text{O}_y$ . For pristine oxygenated (PO) samples, the TEP along the  $c$  axis is  $\cong +7$   $\mu\text{V/K}$  at room temperature and decreases in a somewhat linear manner with decreasing temperature, falling to zero below  $T_c$  (there is a small positive calibration offset  $\approx 0.2$   $\mu\text{V/K}$ , presumably due to error in the gold TEP calibration). The  $a$ - $b$  plane TEP is again positive and approximately a factor of two larger at room temperature, but shows an opposite temperature dependence, with the TEP increasing slightly with decreasing  $T$ ; below  $T_c$ , the TEP in the  $a$ - $b$  plane again falls to zero as expected for a superconductor. With increasing oxygen deficiency, the TEP in the  $c$ -axis direction still maintains a roughly linear temperature dependence, but decreases with a smaller slope. The increased magnitude of the TEP and the smeared transition at  $T_c$  reflect the changes in the resistivity. For the VOD sample, the very high sample impedance prevented an accurate determination of the  $c$ -axis TEP at low temperature. From 300 to 330 K, however, the TEP increases roughly linearly, from 20 to 22  $\mu\text{V/K}$ .

Figure 2 also shows the TEP for a polycrystalline sample of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (PO).<sup>15</sup> At room temperature the TEP is positive and roughly 7  $\mu\text{V/K}$ . The data show a broad maximum near 120 K, with the TEP dropping sharply to zero below  $T_c$ . Similar TEP for polycrystalline samples of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  have been reported by other workers;<sup>6,16,17</sup> the unusual temperature dependence is similar to that observed in polycrystalline La-Sr-Cu-O.<sup>18</sup> There is a striking similarity between the polycrystalline TEP in  $\text{YBa}_2\text{Cu}_3\text{O}_y$  and the  $a$ - $b$  plane TEP in single-crystal  $\text{YBa}_2\text{Cu}_3\text{O}_y$ . This is similar to the resistivity, where the

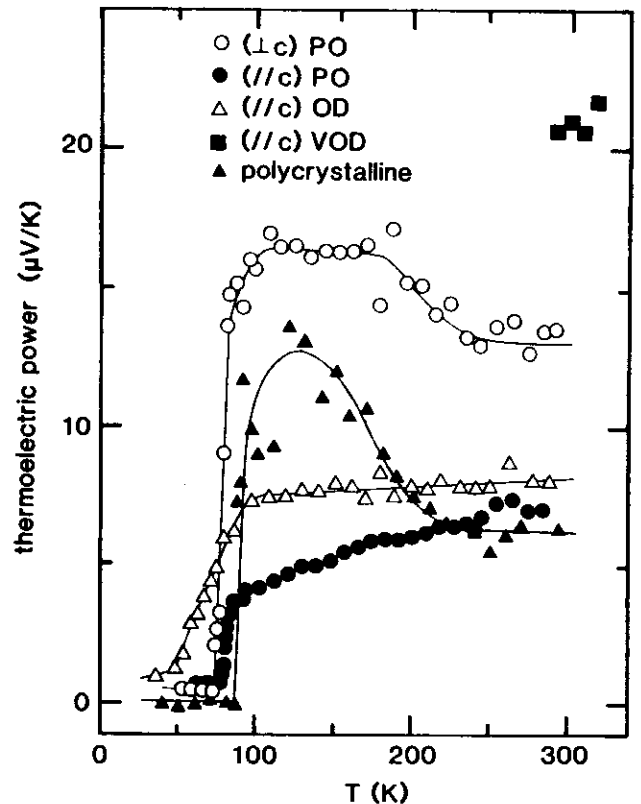


FIG. 2. Thermoelectric power (TEP) of single-crystal and polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_y$ . Single-crystal TEP is shown for temperature gradients both perpendicular and parallel to the  $c$  axis. The  $c$  axis TEP is shown for three different oxygen contents. Solid lines are guides to the eye.

$a$ - $b$  plane resistivity follows a temperature dependence similar to the "bulk" resistance of polycrystalline samples.<sup>19</sup> It thus appears that the  $a$ - $b$  plane transport dominates the polycrystalline samples. For both crystal directions, the TEP is positive, suggesting holes as the charge carriers. We note that our TEP results are in contrast to measurements of the Hall constant<sup>7</sup> which suggest electronlike carriers with  $H$  field oriented parallel to the Cu-O planes. The general increase in TEP magnitude with increasing oxygen deficiency is consistent with the behavior of polycrystalline  $\text{EuBa}_2\text{Cu}_3\text{O}_y$ .<sup>20</sup>

To investigate sample variability we have repeated in part the above resistivity and TEP experiments on  $\text{YBa}_2\text{Cu}_3\text{O}_y$  single crystals from other preparation batches. Samples with slightly higher  $T_c$  (91 vs 81 K) and sharper transitions showed similar resistivity and TEP behavior. In one sample, however, the  $c$ -axis resistivity upturn with decreasing temperature occurred only very close to  $T_c$ .

Our experimental results may be examined within the context of the theoretical model recently presented by Allen, Pickett, and Krakauer (APK).<sup>11</sup> These authors predict values of the phonon-induced resistivity  $\rho_{ab}$ , Hall coefficient  $R_{ab}^H$ , and the thermopower  $S_{ab}$  for  $\text{YBa}_2\text{Cu}_3\text{O}_y$  based on band-structure calculations using a variational solution of the Boltzmann transport equations. They consider three models for the energy dependence of the scattering time,  $\tau(\epsilon)$ :  $\tau(\epsilon) = \text{const}$ ,  $\tau(\epsilon) \propto N(\epsilon)$ , where

$N(\epsilon)$  is the density of states, and  $\tau(\epsilon) \propto \lambda_{tr}(\epsilon)$ , where  $\lambda_{tr}$  is the electron-phonon coupling found in transport theory, evaluated at the energy  $\epsilon$ .

Since  $\text{YBa}_2\text{Cu}_3\text{O}_y$  is orthorhombic,  $\sigma_{\alpha\beta}$  and  $S_{\alpha\beta}$  have three independent components and are diagonal. They are given by

$$S_{\alpha\alpha}(T) = -\frac{k_B}{e} \int d\epsilon \left( \frac{\epsilon - \eta}{k_B T} \right) \sigma_{\alpha\alpha}(\epsilon) \left( -\frac{\partial f}{\partial \epsilon} \right) / \int d\epsilon \sigma_{\alpha\alpha}(\epsilon) \left( -\frac{\partial f}{\partial \epsilon} \right),$$

where

$$\sigma_{\alpha\alpha}(\epsilon) = e^2 \int \frac{d\mathbf{k}}{4\pi^3} v_\alpha^2(\mathbf{k}) \tau(\mathbf{k}) \delta(\epsilon(\mathbf{k}) - \epsilon).$$

Some of our data are consistent with the predictions of APK, but discrepancies exist. For example, the measured TEP is positive (holelike) both in the  $a$ - $b$  plane as well as along the  $c$  axis, whereas APK predict that  $S_{xx}$  and  $S_{yy}$  will be negative, and the sign of  $S_{zz}$  is dependent on the choice of  $\tau(\epsilon)$  ( $x$  and  $y$  are in the  $a$ - $b$  plane,  $z$  is parallel to the  $c$  axis). There is qualitative agreement between our measurement of  $S_{zz}$  and the shape of the predicted  $S_{zz}$  for the model using  $\tau(\epsilon) = \text{const}$ . We also find that the resistivity in the  $a$ - $b$  plane agrees in shape but not in magnitude with the predictions of APK, while the temperature dependence of the  $c$ -axis resistivity differs from that predicted.

There are several possible sources for the discrepancies between our data and the predictions noted above. First, phonon drag may play a role well below the Debye temperature of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (400 K); however, it is not clear whether it could account for the sign change in  $S_{xx}$  or  $S_{yy}$  because the magnitude and sign of its contribution to the TEP depend sensitively on the anisotropy of the Fermi surface and the scattering times. The phonon-drag effects would also have to be much stronger in the basal ( $a$ - $b$ ) plane than along the  $c$  axis to explain our data.

Changing the oxygen deficiency will change the band structure and can cause a large residual resistivity,<sup>21</sup> as seen in Fig. 1. These changes will also affect the phonon drag contribution to the TEP. Hence, the variation of TEP along the  $c$  axis in the PO and OD samples could be explained by changes in the band structure and phonon drag, but further calculations are necessary to test this possibility. It is interesting to note, however, that the relative insensitivity of the TEP to changes in the resistivity is reminiscent of weak localization (near the metallic limit) where the entropy transported per carrier is  $k_B T$ ,<sup>22</sup> independent of the resistivity.

One of the most striking features of our data is that the  $c$ -axis conductivity appears to be semiconducting or insulating while the  $c$ -axis TEP exhibits metallic behavior. The  $c$ -axis resistivity is very sensitive to oxygen deficiency, while the TEP is only slightly changed between the PO and OD samples. If the  $c$ -axis conductivity were that of a semiconductor, then one would expect activated conduction,  $\sigma \sim \exp(-E_g/2k_B T)$ , and a TEP inversely proportional to temperature:  $S \approx \Delta E_g/k_B T$  (neglecting temperature-dependent mobility effects). This is in contrast to the observed linear dependence on temperature of the TEP. In Fig. 3 we plot the log of the  $c$ -axis conductivity versus  $1/T$  for the PO, OD, and VOD samples. At

high temperature, the data appear activated, with activation energies  $E_g = 2.4$  meV, 41.0 meV, and 0.45 eV for the PO, OD, and VOD samples, respectively. The activation energy of the conductivity mechanism thus appears to increase with a decrease in the oxygen content of the sample. At low temperatures, however, the data curve away from exponential behavior as shown in Fig. 3. The resistivity temperature dependence is similar to that observed in low-dimensional disordered metals, where carries become localized with decreasing temperature.

We have searched for obvious power-law dependences of (or logarithmic corrections to) the conductivity between room temperature and 80 K. For the OD and VOD samples, no obvious fit is obtained for the  $c$ -axis conductivity. The PO  $c$ -axis data, however, agree qualitatively with the expression for resistivity recently proposed by Anderson and Zou:<sup>23</sup>  $\rho = A/T + BT$ . When the resistivity is plotted as  $\rho_{zz} T$  vs  $T^2$ , a straight line occurs with a sharp break in slope at 170 K ( $A = 124 \Omega \text{ K}$ ,  $B = 4.67 \times 10^{-4} \Omega/\text{K}$ ). Anderson and Zou suggest that  $c$ -axis conductivity is due to the tunneling of quasiparticles between the Cu-O planes. Hagen *et al.*,<sup>24</sup> have studied the resistivity of single-crystal  $\text{YBa}_2\text{Cu}_3\text{O}_y$  and find good agreement with their prediction. Our data, however, agree with the Anderson-Zou expression only over a limited temperature range when the sample has high oxygen content.

In conclusion, we note that our measurements of the TEP and conductivity for single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  show some disagreement with the predictions of band theory. This result raises the possibility of a nonband conduction mechanism in  $\text{YBa}_2\text{Cu}_3\text{O}_y$ , such as weak localiza-

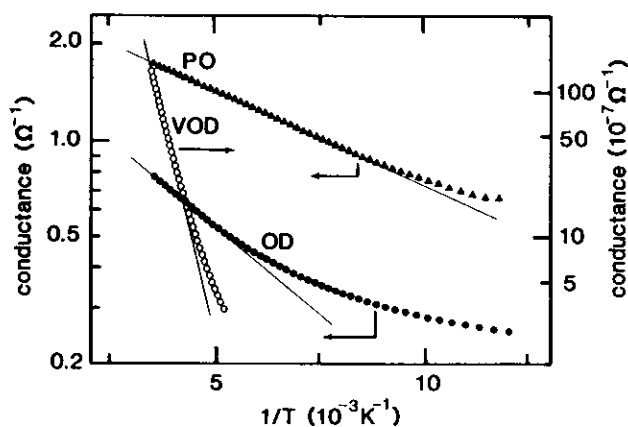


FIG. 3. Logarithm of conductivity vs  $1/T$  shown for a single crystal along the  $c$  axis for three different oxygen contents. Linear regions indicate activated behavior. The activation energy increases with decreasing oxygen content.

tion or the quasiparticle tunneling model proposed by Anderson and Zou.

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