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Variable normal-state transport properties of $Bi_2Sr_2CaCu_2O_{8-y}$

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The normal-state thermoelectric power S and resistivity ρ of crystalline $Bi_2Sr_2CaCu_2O_{8-y}$ are strongly influenced by oxygen configuration. In general, the temperature dependences of the coefficients follow simple empirical expressions. For the *ab*-plane and *c*-axis thermopower, $S \sim A+BT$, while for the *ab*-plane resistivity, $\rho \sim T^{\alpha}\exp[\Delta/k_BT]$. Only A and Δ depend on oxygen configuration. These expressions may hold also for other classes of high-T_c superconducting oxides and are suggestive of and place restrictions on normal-state transport models; normal-state transport models should in turn relate to superconductivity mechanisms.

The discovery of a new class of high-temperature superconductors, $(BiTl)_2(Sr,Ba)_2Ca_{n-1}C_nO_y$ $(n=1,2,3)$, with critical temperatures as high as 120 K,[1,2] has generated much effort aimed at finding structural and electronic similarities between these compounds and the rare-earth-based superconductors discovered earlier.[3,4] One possible path leading to an understanding of the mechanism of high-temperature superconductivity in these materials is to begin with an understanding of their normal-state properties.[5] Electrical transport measurements on single crystals are essential in this respect. Striking anisotropies have been seen in the resistivity,[6-8] thermoelectric power (TEP),[7,9-11] and Hall effect[6] of the rare-earth oxides. Recent transport measurements[12,13] show striking anisotropies in the Bi-based superconductors as well. While different groups have used their results to support different theories, no definitive picture has emerged that explains the wide variety of results.

We report here on experiments measuring the normal-state *ab*-plane resistivity and anisotropic TEP of $Bi_2Sr_2CaCu_2O_{8-y}$ single crystals. In contrast to earlier resistance measurements[14] performed on polycrystalline samples of Bi-Sr-Ca-Cu-O, we find that the normal-state properties of crystalline $Bi_2Sr_2CaCu_2O_{8-y}$ are extremely sensitive to the oxygen configuration. The *ab*-plane resistivity, which can be reversibly changed from metalliclike to semiconductorlike, is well described over the entire oxygen configuration range by a simple empirical expression which holds also for $YBa_2Cu_3O_{7-\delta}$ and other high-T_c oxides. The oxygen-configuration-dependent TEP in $Bi_2Sr_2CaCu_2O_{8-y}$ is highly anisotropic, and is described by a related empirical expression which again finds application to other classes of high-T_c oxides. The normal-state transport coefficients in $Bi_2Sr_2CaCu_2O_{8-y}$ can thus be used to make useful empirical models and relate heretofore unexplained differences observed in the in-plane and out-of-plane transport properties of the high-T_c oxides.

Crystals of $Bi_2Sr_2CaCu_2O_{8-y}$ were grown from a mixture of Bi_2O_3, CuO, $SrCO_3$, and $CaCO_3$, as described elsewhere.[15] The crystals were cleaved into thin *ab*-plane sheets of typical dimension $2.0\times1.0\times0.01$ mm^3. The resistivity in the *ab* plane was measured using a standard linear four-probe contact configuration. The TEP data were obtained in a two-probe configuration. One "four-point" TEP measurement was performed to ensure that contact electromotive forces did not influence the TEP measurements. Other checks were made to ensure that contact effects did not affect the resistivity and TEP measurements.

Figure 1 shows the temperature dependence of the *ab*-plane resistance for a particular $Bi_2Sr_2CaCu_2O_{8-y}$ crystal for three different oxygen configurations. The HO1 curve is for the crystal following an initial "high-oxygen" (HO) anneal cycle (1.5 h at 650 °C, followed by a 5-h ramp to 25 °C, all at 1 atm O_2). The resistance is linear and metallic before dropping to zero at T_c. After measurement, the oxygen configuration of the sample was changed by a "low-oxygen" (LO) anneal cycle (1.5 h at 650 °C, followed by a 5-h ramp to 25 °C, all at ~10 mTorr O_2). After the LO cycle, the resistivity of the crystal increased by over an order of magnitude and displayed a semiconductorlike resistive upturn, as shown in the LO curve of Fig. 1. The resulting superconducting transition was severely broadened and depressed by as much as 40 K. This behavior is very similar to that associated with con-

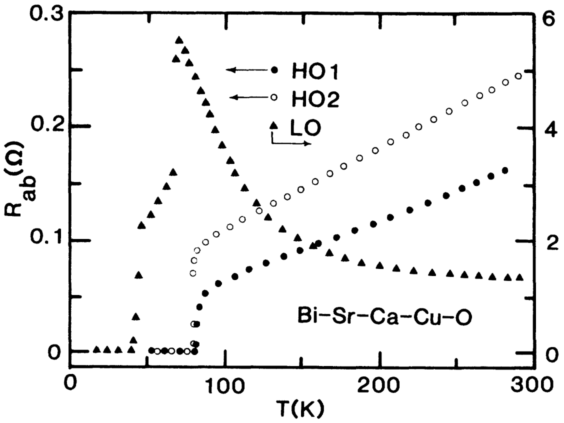

FIG. 1. *ab*-plane R vs T of a single $Bi_2Sr_2CaCu_2O_{8-y}$ crystal with different oxygen configurations (see text). Resistance data can be approximately converted to resistivity by multiplying by 4×10^{-3} cm.

ductivity along the *c* axis in single-crystal $YBa_2Cu_3O_{7-\delta}$,[7,16] and in oxygen-deficient polycrystalline $YBa_2Cu_3O_{7-\delta}$.[17] The sample was then restored to metallic behavior by putting it through a second HO cycle, as shown in the HO2 curve. Subsequent anneals of this sample in flowing oxygen (not represented in this figure) further reduced the slope and offset of the resistivity. Hence the dramatic resitivity changes shown in Fig. 1 are fully reversible.

We attribute the dramatic differences in the *ab*-plane resistivity of $Bi_2Sr_2CaCu_2O_{8-y}$ in Fig. 1 to differences in oxygen configuration. The oxygen content of the crystals was not measured directly, but can be inferred from previous thermograviometric studies[14] on polycrystalline $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8-y}$. From those results, we assume that crystals put through the HO cycle have approximately 0.08 more oxygen atoms per unit formula than those put through the LO cycle.[18] We attempted to measure directly but nondestructively the change in oxygen content of our crystals through weight loss and Rutherford backscattering with H^+ ions. The resolution, however, was limited to approximately 0.1 oxygen atoms per unit formula and no change was seen, consistent with a maximum loss of 0.08 oxygens. We also performed single-crystal x-ray studies on HO and LO samples, and found no evidence for secondary phase intergrowth in either case.

Figure 2 shows the *ab*-plane resistance and anisotropic TEP of $Bi_2Sr_2CaCu_2O_{8-y}$ crystals having different oxygen configurations. Figure 2(a) shows both the resistance and *ab*-plane TEP of a freshly prepared (FP) crystal taken directly from the crucible with no additional anneals. The resistance shows a semiconductorlike upturn before T_c, similar to that seen in the crystal that underwent a LO cycle (Fig. 1). Thus, we identify the freshly prepared crystals as slightly oxygen deficient. The *ab*-plane TEP of this sample is positive and linear with a negative slope $\approx -0.05\ \mu V/K^2$ down to ~ 150 K, where it begins to flatten out before dropping to zero at $T_c \approx 80$ K. The magnitude and linearity of the TEP are indicative of a metal, but there is an unusual temperature-independent offset.

Figure 2(b) shows the resistance and *ab*-plane TEP of a single crystal that has undergone a HO cycle. The resistance shows metallic behavior, similar to that seen in the HO sample of Fig. 1. The TEP, however, has a substantial shift of 14 μV/K, compared to the freshly prepared sample, and now gives a negative value at room temperature. The temperature dependence of the TEP, however, remains linear, and has a slope $\approx -0.04\ \mu V/K^2$ that is almost identical to the slope of the freshly prepared sample. Hence annealing crystals in oxygen at atmospheric pressure causes the TEP to simply shift downwards while preserving the slope. Similar behavior was observed for other crystals with room-temperature TEP, which could reversibly become either positive or negative, depending on whether they were processed with a LO cycle or a HO cycle, respectively. This same behavior of the *ab*-plane TEP can be inferred for $YBa_2Cu_3O_{7-\delta}$ from previous (seemingly contradictory) measurements.[7,9,10]

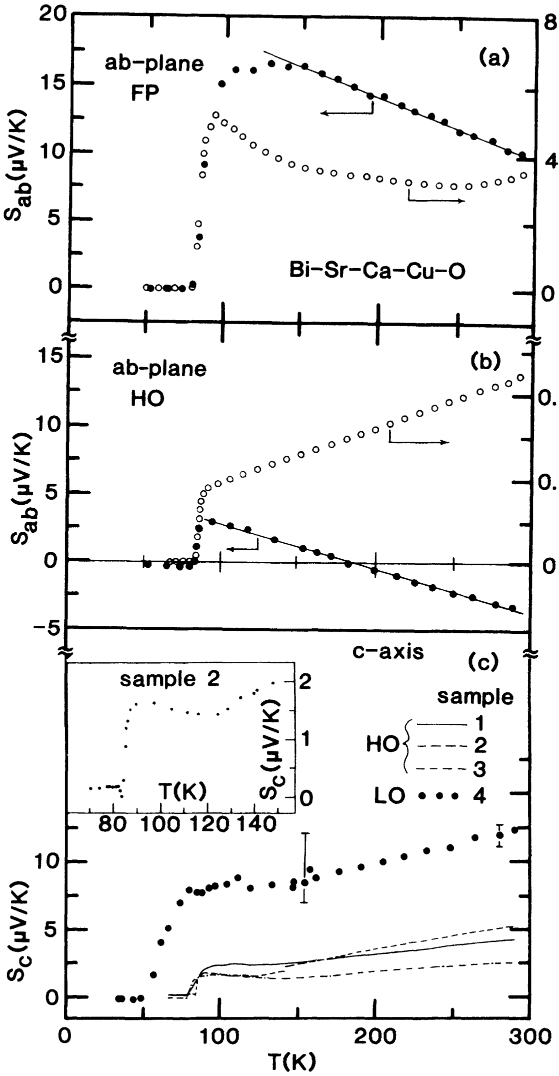

FIG. 2. *ab*-plane *R* and *ab*-plane TEP vs *T* for (a) a single freshly prepared $Bi_2Sr_2CaCu_2O_{8-y}$ crystal and (b) a single crystal having undergone a HO treatment (see text). In (b), the resistance can be converted to resistivity through multiplication by 10^{-3} cm. (c) *c*-axis TEP for different oxygen configurations (see text). The inset shows data for sample 2 in more detail.

Figure 2(c) shows the temperature dependence of the *c*-axis TEP for four $Bi_2Sr_2CaCu_2O_{8-y}$ crystals. Samples 1, 2, and 3 were processed with the HO cycle, while sample 4 underwent the LO cycle. All three of the HO crystals have a *c*-axis TEP that is positive from room temperature to T_c and are fairly linear with a positive slope down to about 130 K. At this point the curves all begin to turn up in a manner reminiscent of phonon drag. This is shown in detail for sample 2 in the inset. The HO curves all extrapolate almost to zero at $T=0$ and look very similar to recent TEP measurements performed on Ba-K-Bi-O.[19] For the $Bi_2Sr_2CaCu_2O_{8-y}$ crystals, not only is the sign of the slope different for the *c*-axis TEP compared to the *ab*-plane TEP in HO samples, but the *c*-axis TEP also never becomes negative. Similar crystal direction dependence of the sign of the TEP slope has been seen in single-crystal $YBa_2Cu_3O_{7-\delta}$ and La_2CuO_4, although the temperature dependence of the TEP is severely influenced by the oxygen content in both materials.[7,11,20] Figure 2(c) also shows the c-axis TEP of a $Bi_2Sr_2CaCu_2O_{8-y}$ crystal that has undergone a LO cycle. As with the ab-plane TEP on LO samples, the c-axis TEP is shifted upward. The TEP appears linear down to ≈ 160 K, at which point it became very noisy. In this sample, as in the LO sample shown in Fig. 1, the superconducting transition region is broadened and severely depressed by approximately 30 K. We point out that while we are able to obtain reproducible, nonhysteretic results on different crystals for the ab-plane TEP, the c-axis TEP is slightly sample dependent [Fig. 2(c)], and is occasionally found to be hysteretic with temperature cycling (especially around 100 K) even when the two-point resistance of the sample remains nonhysteretic.

The effect of variable oxygen configuration on the thermopower of $Bi_2Sr_2CaCu_2O_{8-y}$ is similar to that found for other high-T_c superconductors. In the case of $YBa_2Cu_3O_{7-\delta}$, removing oxygen causes the magnitude of the ab-plane thermopower to increase considerably and changes its temperature dependence.[11] Analogous behavior occurs in $La_{2-x}Sr_xCuO_4$ where the dopant is generally Sr rather than oxygen.[11] As in $Bi_2Sr_2CaCu_2O_{8-y}$, the c-axis thermopower in the rare-earth-based superconductors shows less sensitivity to doping than the ab-plane thermopower.[7,11]

The resistance and TEP data shown in Figs. 1 and 2 indicate dramatic dependences on oxygen configuration and temperature. Despite their apparent complexity, both transport coefficients are well described by simple empirical expressions. For the resistivity, we assume

$$\rho(T) = \rho_0 T^{\alpha} e^{\Delta/kT} . \tag{1}$$

In our previous study[16] it was found that the c-axis resistivity of single-crystal $YBa_2Cu_3O_{7-\delta}$ fits Eq. (1) very well with $\alpha = 0.7$ and $\Delta = 22$ meV. Both the ab-plane and c-axis resistivity in $YBa_2Cu_3O_{7-\delta}$ have been seen to vary from metalliclike ($\Delta \approx 0$) to semiconductinglike ($\Delta > 0$) behavior with changes in the oxygen stoichiometry.[11,21-23] Figure 3 shows the results of plotting the LO, FP, and Ho $Bi_2Sr_2CaCu_2O_{8-y}$ resistivity data of Figs. 1 and 2 as $\ln(R/T^{\alpha})$ vs $1/T$ for $\alpha = 0.7$. Over a large temperature range, Eq. (1) accounts well for the data. As oxygen deficiency increases, Δ increases from 0 to 23 meV. The excellent fit of Eq. (1) to $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_{8-y}$ raises the possibility that similar conduction mechanisms are involved in the different crystal directions for both rare-earth-based and Bi-based superconductors.

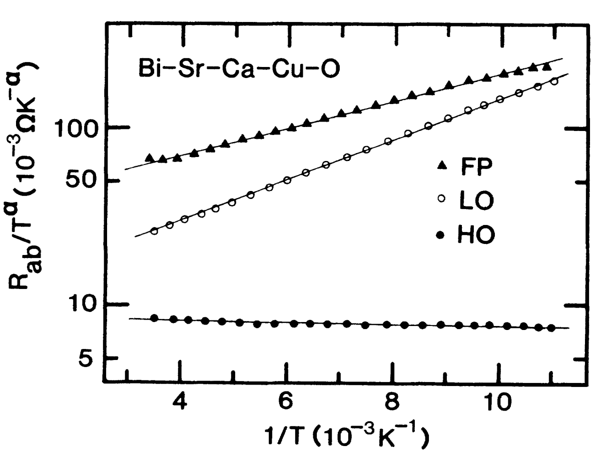

FIG. 3. Ratio of ab-plane R/T^{α} ($\alpha = 0.7$) vs $1/T$ [see Eq. (1)] for three $Bi_2Sr_2CaCu_2O_{8-y}$ crystals with different oxygen configurations (see text).

Neglecting anomalies near T_c, the anisotropic TEP in $Bi_2Sr_2CaCu_2O_{8-y}$ is well described by the empirical expression

$$S(T) = A + BT . \tag{2}$$

Only the parameter A is appreciably changed by changes in oxygen configuration; this is seen dramatically by comparing Figs. 2(a) and 2(b). As mentioned previously, there are striking similarities between the anisotropic TEP of $Bi_2Sr_2CaCu_2O_{8-y}$ and the TEP of other rare-earth (and even non-Cu-containing) high-T_c oxides. Hence, Eq. (2) may find general applicability.

We now investigate possible normal-state transport mechanisms that are consistent with these results. As was pointed out in Ref. 16, the observed temperature dependence of the resistivity is consistent with the percolation model of Phillips,[5] in which the defect structure of the high-T_c materials play an important role in their transport properties. In the present study, the dramatic variation seen in Δ due to small changes in oxygen content also supports a defect-related transport model.

If the current is carried by electrons in extended states near the Fermi level, the thermopower and conductivity are related through the Mott formula[24] $S \sim T(d\ln\sigma/dE)_{E_F}$. Using the empirical expression for the resistivity given in Eq. (1), this formula yields Eq. (2) for the thermopower. Thus the observed resistivity and thermopower are at least qualitatively consistent. Quantitatively, the data for $Bi_2Sr_2CaCu_2O_{8-y}$ samples with different oxygen configuration place restrictions on the form of Δ. In particular, it is found that the simple form $\Delta = |E - E_0|$ does not allow for changes in $S(T=0) = A$ with varying oxygen configuration. Based on the empirical evidence, a possible form for Δ which leads to consistent results within this framework is $\Delta = a|E - E_0|^{\beta} + b|E - E_0|$, with $\beta > 1$.

For transport models in which the Mott formula may not be valid, no complete theory for the thermopower is available. However, in the boron carbides, in which small polaron hopping has been suggested as the transport mechanism, the thermopower has been observed[25] to follow Eq. (2). In the high-T_c materials conduction by hopping may result from localization due to the presence of defects. Measurements of transport properties in the La-based superconductors have been interpreted[26] by some authors in terms of hopping models. With $\alpha = 1$, the expression for the resistivity given in Eq. (1) is consistent with transport by fixed-range hopping.[27]

In conclusion, the temperature dependences of transport coefficients in $Bi_2Sr_2CaCu_2O_{8-y}$ are oxygen content sensitive and follow simple empirical expressions. Experiments on other classes of high-T_c superconductors suggest that these expressions may have extended application among high-T_c oxides.

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[1] H. Maeda, Y. Tanaka, M. Fukutumi, and T. Asano, Jpn. J. Appl. Phys. Pt. 2 **27**, L209 (1988).

[2] Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 138 (1988).

[3] J. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[4] M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987).

[5] J. C. Phillips, *Physics of High-T_c Superconductors* (Academic, Boston, 1989); see also J. C. Phillips, Phys. Rev. Lett. **59**, 1856 (1987); Solid State Commun. **65**, 227 (1988); Phys. Rev. B (to be published).

[6] S. W. Tozer *et al.*, Phys. Rev. Lett. **59**, 1768 (1987).

[7] M. F. Crommie, A. Zettl, T. W. Barbee III, and M. L. Cohen, Phys. Rev. B **37**, 9734 (1988).

[8] S. J. Hagen, T. W. Jing, Z. Z. Wang, J. Horvath, and N. P. Ong, Phys. Rev. B **37**, 7928 (1988).

[9] R. C. Yu *et al.*, Phys. Rev. B **37**, 7963 (1988).

[10] Z. Z. Wang and N. P. Ong, Phys. Rev. B **38**, 7160 (1988).

[11] M. Sera, S. Shamoto, and M. Sato, Solid State Commun. **68**, 649 (1988).

[12] S. Martin *et al.*, Phys. Rev. Lett. **60**, 2194 (1988).

[13] S. Yan, T. Chen, W. Zhang, H. Zhang, K. Wu, and L. Tong (unpublished).

[14] J. M. Tarascon *et al.*, Phys. Rev. B **37**, 9382 (1988); J. M. Tarascon *et al.*, *ibid.* **38**, 8885 (1988); for T_c shifts with different oxygen content see also D. E. Morris *et al.* (unpublished).

[15] F. V. Hillebrecht *et al.*, Phys. Rev. B **39**, 236 (1989).

[16] M. F. Crommie *et al.*, Phys. Rev. B **39**, 4231 (1989).

[17] S. Sugai, Phys. Rev. B **36**, 7133 (1987); K. Kishio *et al.*, Jpn. J. Appl. Phys. Pt. 2 **26**, L1228 (1987); K. R. Krylov *et al.*, Phys. Lett. A **131**, 203 (1988).

[18] One of the studies of Ref. 14 found that with oxygen loss $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8-y}$ samples remained metallic, although their resistivity increased and the transition region broadened. This was attributed not to oxygen loss *per se*, but to the generation of staking faults within the samples. We cannot exclude a concomitant increase in stacking faults together with oxygen loss in our crystals. Hence by "oxygen configuration" we mean the actual oxygen content of the crystal together with possible associated lattice defects.

[19] M. Sera, S. Kondoh, and M. Sato, Solid State Commun. **68**, 647 (1988).

[20] M. F. Hundley, S.-W. Cheong, J. D. Thomson, and Z. Fisk (unpublished).

[21] Y. Iye *et al.*, Physica C **153-155**, 26 (1988).

[22] L. Ya. Vinnikov *et al.*, Physica C **153-155**, 1359 (1988).

[23] A. Behrooz and A. Zettl (unpublished).

[24] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge Univ. Press, New York, 1972), p. 237.

[25] Charles Wood and David Emin, Phys. Rev. B **29**, 4582 (1984).

[26] M. A. Kastner *et al.*, Phys. Rev. B **37**, 111 (1988); E. J. Osquiguil *et al.*, *ibid.* **38**, 2840 (1988); N. W. Preyer *et al.* (unpublished).

[27] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Clarendon, Oxford, 1979).