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In-plane thermoelectric power of untwinned $YBa_2Cu_3O_{7-\delta}$

J. L. Cohn, E. F. Skelton, and S. A. Wolf
Materials Physics Branch, Naval Research Laboratory, Washington, D.C. 20375

J. Z. Liu
Physics Department, University of California, Davis, California 95616

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We present the first measurements of the temperature and oxygen-doping dependences of thermoelectric power in the *ab* plane of untwinned $YBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.10$) for $T \leq 330$ K. Employing a two-band model and measured electrical resistivities, we derive the chain and plane components of the thermopower, S_{ch} and S_{pl}. The behavior of S_{ch} indicates that some of the chain conduction occurs via carriers in a narrow band. $S_{pl}(T)$ is similar to the in-plane thermopower of the other cuprates, suggesting a "universal" behavior for the CuO_2 planes. The results are discussed with reference to the known Fermi surface.

Recent observations of Fermi surfaces (FS) in the cuprates which agree quantitatively with band-structure calculations constrain theoretical models of their normal and superconducting states.[1] The availability of high-quality, untwinned single crystals of $YBa_2Cu_3O_{7-\delta}$ (YBCO) now allows for detailed experimental investigations of the low-energy excitations with reference to the FS. The importance of phonons, Coulomb correlations, and magnetic excitations in determining the dynamical character of the carriers remains the focus of much debate.

It is particularly interesting that the electronic structure of YBCO is highly sensitive to oxygen deficiency (δ) in the range $0 \leq \delta \leq 0.2$, whereas the superconducting transition temperature remains essentially unchanged near 92 K. These observations are consistent with a model[2] in which electronic states associated with the Cu-O chains contribute a substantial weight to the density of states at the Fermi level, but do not play a central role in superconductivity. Recent measurements of electrical conductivity[3] and positron annihilation,[4] in untwinned crystals confirm the conducting nature of the chains and the necessity of a multiband picture for YBCO. It has become clear that achieving a deeper understanding of both the normal and superconducting properties of YBCO will entail a careful distinction between chain and plane contributions in the interpretation of many experimental results.

One of the most sensitive probes of small oxygen deficiency in YBCO is the in-plane thermoelectric power (S_{ab}). Measurements of S_{ab} in twinned crystals[5] and polycrystals[6] have shown that, for $T < 310$ K, S_{ab} is negative for $\delta \approx 0$ and becomes increasingly positive with increasing δ, changing sign for $\delta \approx 0.1$. Lowe, Regan, and Howson[7] have recently reported measurements of thermopower on an untwinned YBCO crystal, finding $S < 0$ for transport along the chains and $S > 0$ transverse to the chains.

In this paper we report measurements of in-plane thermopower and electrical resistivity on untwinned YBCO which allow the plane and chain components of the thermopower to be separated. Measurements with heat flow along both the *a* and *b* axes are presented for two oxygen configurations of the same crystal. Two observations offer new insight into the nature of charge transport in this material. The chain thermopower, S_{ch}, is very sensitive to oxygen content and is nearly *T* independent at high temperatures, implying that some of the chain transport involves carriers in a very narrow band. In addition, we find that $S_a(T)$ is quite similar to the in-plane thermopower of the other cuprates. This resolves the heretofore unexplained difference between the thermopower of YBCO and the other materials, and indicates a common behavior associated with the CuO_2 planes.

The crystal used in this study had dimensions $1.20 \times 0.65 \times 0.04\ mm^3$ and was grown in a gold crucible by a self-flux method[8] and detwinned by annealing under uniaxial stress.[9] From measured relative x-ray intensities of $(h,0,0)$ and $(0,k,0)$ peaks before and after the oxygen anneal (100 h at 460 °C in flowing oxygen), it is estimated that any residual twinning occurs in less than several percent of the sample. The *change* in oxygen content after the anneal is directly reflected as a change in the *c*-axis lattice parameter. Before and after the anneal the values were $c = 11.724$ and 11.714 Å, respectively (with uncertainty ±0.002 Å). This change corresponds to a decrease in oxygen deficiency of $\Delta\delta \approx 0.06 \pm 0.02$ according to x-ray-diffraction (XRD) and iodometric titration studies[10] for ($T_c = 92$ K) superconducting polycrystals having oxygen deficiencies $\delta \leq 0.2$.

The absolute value of δ cannot be determined directly from the XRD because the substitution[11] (up to 10%) of gold atoms for chain-site Cu atoms is known to result in an expansion of the unit cell along *c* for crystals grown in gold crucibles.[12] Recent magnetization and XRD studies of twinned crystals grown in zirconia crucibles[13] demonstrate a correlation between anomalies in magnetization hysteresis loops and oxygen content. By comparison, the magnetization data on our untwinned crystal implies $\delta \approx 0.12$ and 0.07 before and after the anneal, respectively. We also infer the oxygen content from the measured thermopower in the *b*-axis direction (Fig. 2), which is quite similar to the measured thermopower of polycrystalline specimens.[6] From Ref. 6 we estimate $\delta \approx 0.11$ and 0.08 before and after the anneal, respectively. The consistency of these various estimates gives us confidence that the gold impurities, at this level of substitution, do not substantially alter the thermopower.

The thermopower was measured by a steady-state method employing a differential Chromel-Constantan thermocouple and a small heater, glued to the specimen with varnish. Seebeck probes were calibrated Cu wires, silver painted to fired-on silver-paint pads. The temperature gradient during measurement was typically 0.5–2.0 K/mm. Linearity in the $V(\Delta T)$ response was confirmed by varying the heater power. The uncertainty in the measurements is ± 0.1 μV/K. Four-probe, isothermal dc electrical resistivities (ρ) were measured in separate experiments, yielding $\rho(300\text{ K}) \approx 250$ and 140–180 $\mu\Omega$ cm along the a and b axes, respectively, with ΔT_c (10%–90%) ≤ 0.3 K.

In Figs. 1 and 2 we plot S_a and S_b versus temperature, for both oxygen configurations. The prominent features of the data for S_a are the negative values for $T \geq 130$ K, the apparent inflection point near 160 K marking a sharp upturn to positive values for $T < 130$ K, and the relatively small change with oxygen doping. For S_b the temperature dependence, as mentioned above, is similar to results on polycrystals. The remarkable observation is a nearly constant, negative shift by ≈ 1 μV/K which describes the change with oxygen doping. This behavior clearly reflects a change in the Cu-O chain contribution to S_b.

To gain insight into the chain thermopower we employ a simplified two-band model of independent conduction by planes and chains for transport in the b-axis direction:

$$\begin{gathered} S_a = S_{pl},\quad \sigma_a = \sigma_{pl}, \\ S_b = \frac{\sigma_{ch} S_{ch} + \sigma_{pl} S_{pl}}{\sigma_{ch} + \sigma_{pl}},\quad \sigma_b = \sigma_{ch} + \sigma_{pl}. \end{gathered} \tag{1}$$

Using the measured electrical resistivity ratios [Fig. 3(b)] we derive S_{ch} from these equations [Fig. 3(a)]. We have used the fact that the Hall angle is quite small in YBCO,[14] such that $\rho_a/\rho_b \approx \sigma_b/\sigma_a$.

It is instructive, in attempting to interpret the thermopower data, to consider what is known about the Fermi surface in YBCO. Projections in the (k_x, k_y) plane of four major sections of FS have been identified by photoemission,[15] positron-annihilation,[4] and de Haas–van Alphen[16] experiments, in good agreement with band-structure calculations:[17] large rounded "squares" [centered at $S(R)$ in the Brillouin zone], a quasi-one-dimensional "ridge" (along Γ-X), and a small "pocket" [$S(R)$ centered]. According to the calculations, the squares and the ridge are, respectively, derived from nearly empty, wide (bandwidth $\gg k_BT$) CuO_2 plane and Cu-O chain bands. The pocket arises from rather flat (i.e., narrow), nearly full bands that have chain and bridging-oxygen [O(4) atom] character. Agreement between the calculated (assuming $\delta = 0$ and equilibrium atomic sites) and measured[4,15] (using crystals with $\delta \approx 0.1$) FS suggest that the main features are relatively robust with respect to small oxygen deficiency.

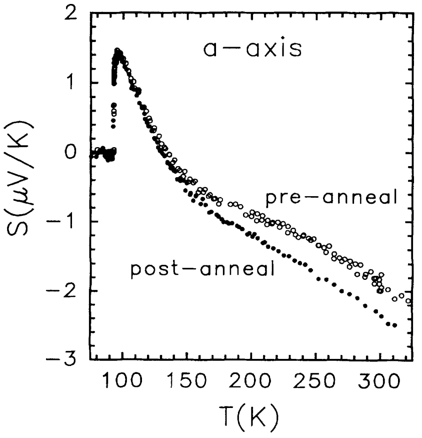

FIG. 1. a-axis thermopower vs temperature before and after oxygen anneal.

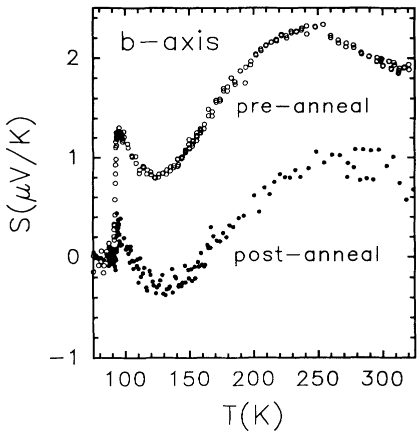

FIG. 2. b-axis thermopower vs temperature before and after oxygen anneal.

Returning to Fig. 3(a), we first discuss the high-temperature behavior of S_{ch}. Generally speaking, any

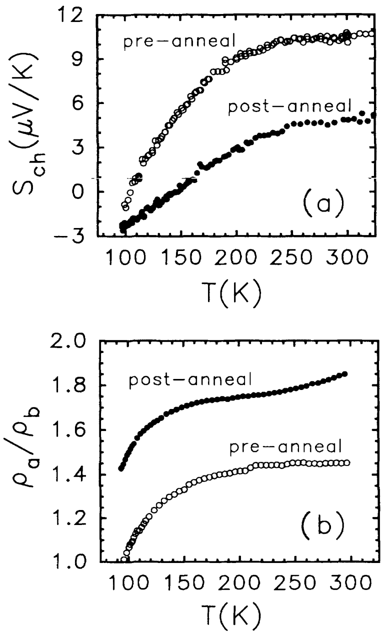

FIG. 3. (a) Chain thermopower vs temperature before and after oxygen anneal, as derived from the two-band model [Eqs. (1)] and using measured resistivity ratios [(b)].

phonon-drag contribution to thermopower[18] decreases with increasing temperature so that the thermopower of a metal at high T can usually be safely interpreted as arising from carrier diffusion. Both the rather large magnitude of S_{ch} (especially before the anneal) and its tendency to saturate at $T \gtrsim 240$–250 K are not characteristic of diffusion thermopower in wide-band metals.

A T-independent thermopower at high temperatures is the canonical narrow-band behavior. For a narrow band[19] of width W and noninteracting electron density n, the thermopower saturates, for $T \gtrsim W/4$, at a value $S_{\mathrm{sat}} = (k_B/|e|)\ln[n/(2-n)]$. S_{sat} is positive when the band is more than half filled (i.e., $n > 1$). Note that in this regime the narrow-band electrical resistivity remains linear in T. The existence of a narrow band has been postulated previously[20] to explain the high-temperature ($300 < T < 800$ K) thermopower and resistivity in polycrystalline, oxygen deficient ($0.1 \leq \delta \leq 0.5$) YBCO. These authors found that experimental values of S_{sat} were consistent with a simple model in which chain-site oxygen atoms each donate a single hole to the narrow band, i.e., $n = 1 + \delta$.

Our results provide strong support for the existence of a very narrow band which predominates in transport *along the chains.* A crude estimate based on the thermopower saturation temperature (240–250 K) suggests a bandwidth $W \lesssim 1000$ K. However, the values of $S_{\mathrm{ch}}(325\ \mathrm{K}) \approx 11\ \mu\mathrm{V/K}$ (before anneal) and $\approx 5\ \mu\mathrm{V/K}$ (after anneal) are not in quantitative agreement with $S_{\mathrm{sat}} = 19$ and $13\ \mu\mathrm{V/K}$, as given by the model of Ref. 20 using our estimates for δ. Nevertheless, we believe it is significant that the shift in $S_{\mathrm{ch}}(325\ \mathrm{K})$ implies, within the simple narrow-band framework, a change in band filling ($\Delta n \approx -0.04$) consistent with the change in δ. This supports the view[20] that doping of oxygen atoms onto the chains results in the transfer of holes to a p-type narrow band.

Regarding the possible role of Coulomb correlations we note that $S_{\mathrm{ch}}(T)$ is similar to the thermopower of the quasi-one-dimensional charge-transfer salt N-methylphenazinium-tetracyanoquinodimethane (NMP-TCNQ).[21] An on-site Coulomb repulsion energy $U \approx 300$ K has been estimated for this material from a model for thermopower on a Hubbard chain.[22,23] A more realistic analysis should consider multiple hopping sites per cell and an extension to finite bandwidth.

A further constraint on models for the chain transport can be obtained by estimating S_{ch} at $\delta = 0$. We do so by taking the measured thermopower of $\delta = 0$ polycrystals as representative of S_b and assuming that $S_a(\delta = 0)$ is not substantially different from the data of Fig. 1. Using a fully oxygenated resistivity ratio,[4] $\rho_a/\rho_b = 2.2$, we compute [from Eqs. (1)] an $S_{\mathrm{ch}}(T)$ curve quite similar to those of Fig. 3(a), but shifted downward such that $S_{\mathrm{ch}}(300\ \mathrm{K}) \approx -2.5\ \mu\mathrm{V/K}$. It is difficult to reconcile this latter behavior and the data of Fig. 3(a) with any model for doping in a single narrow band.

A plausible scenario is that the narrow-band, p-type component of S_{ch} is partially compensated (for $\delta \leq 0.1$) by a negative component. This hypothesis is consistent with the FS observations and their assignments according to the band-structure calculations, indicating two chain-derived bands crossing the Fermi energy. We tentatively attribute the p-type component to the pocket states and the n-type component to the quasi-one-dimensional ridge.

We now turn to the a-axis thermopower. The qualitative behavior of S_a, i.e., negative, nearly linear in T near 300 K, changing to positive for $T > T_c$, is quite similar to the in-plane thermopowers of the Bi and Tl materials.[24] Recently the same features have been observed for NdCeCuO crystals.[25] Thus it is now clear that this behavior is common to the cuprates and appears to be intrinsic to the $\mathrm{CuO_2}$ planes, as ubiquitous a characteristic as the temperature-dependent Hall coefficient.[26]

We interpret the negative sign of S_a at high temperatures as indicating a negative diffusion thermopower for the $\mathrm{CuO_2}$ planes. This is consistent with the band-structure transport calculations of Allen, Pickett, and Krakauer,[27] which predict negative S_a for all temperatures, independent of their model for the electron-phonon scattering rate.

The sharp increase in S_a to positive values for $T \leq 160$ K has been inferred previously from the in-plane thermopower of twinned crystals[5] and is also observed in the in-plane thermopower of the other cuprates. We have previously discussed a model[5] for phonon-drag thermopower, which can explain this feature as arising from a freeze-out of electron-phonon umklapp scattering involving holes in the $\mathrm{CuO_2}$ planes and optical-mode phonons. Kaiser[28] emphasized a strong electron-phonon enhancement of diffusion thermopower as an explanation for the sign change. The latter model postulates two bands having thermopowers of opposite sign, a picture which is now constrained in view of our results for S_a: the $\mathrm{CuO_2}$ plane-derived bands would have to contribute thermopowers of opposite sign.

To summarize, two new insights into the plane and chain conduction in YBCO have been gained from these measurements. The chain thermopower has a strongly oxygen-dependent component that saturates for $T > 250$ K, suggesting that some of the chain conduction occurs via carriers in a very narrow band ($W \approx 1000$ K). The a-axis thermopower is quite similar to the in-plane thermopower of the other cuprates, being positive and sharply peaked near T_c and becoming negative at high temperatures. These features are clearly a fundamental signature of the $\mathrm{CuO_2}$ plane excitations.

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[1] W. E. Pickett *et al.*, Science **255**, 46 (1992).

[2] V. Z. Kresin and S. A. Wolf, Physica C **169**, 476 (1990); V. Z. Kresin and S. A. Wolf (unpublished).

[3] T. A. Friedmann *et al.*, Phys. Rev. B **42**, 6217 (1990); U. Welp *et al.*, Phys. Rev. B **42**, 10 189 (1990).

[4] H. Haghighi *et al.*, Phys. Rev. Lett. **67**, 382 (1991).

[5] J. L. Cohn *et al.*, Phys. Rev. Lett. **66**, 1098 (1991).

[6] P. J. Ouseph and M. Ray O'Bryan, Phys. Rev. B **41**, 4123 (1990).

[7] A. J. Lowe, S. Regan, and M. A. Howson, Phys. Rev. B **44**, 9757 (1991).

[8] D. L. Kaiser *et al.*, J. Cryst. Growth **85**, 593 (1987).

[9] J. Z. Liu *et al.* Phys. Lett. A **144**, 265 (1990).

[10] M. E. Parks *et al.* J. Solid State Chem. **79**, 53 (1989).

[11] A. F. Hepp *et al.*, in *Superconductivity and Its Applications*, edited by H. W. Kwok and D. T. Shaw (Elsevier, New York, 1988), p. 146; M. Cieplak *et al.*, Phys. Rev. B **42**, 6200 (1990).

[12] W. Wong-Ng *et al.*, Phys. Rev. B **41**, 4220 (1990).

[13] M. S. Osofsky *et al.*, Phys. Rev. B **45**, 4916 (1992).

[14] J. P. Rice *et al.*, Phys. Rev. B **44**, 10 158 (1991).

[15] A. J. Arko *et al.*, Phys. Rev. B **40**, 2268 (1989); J. C. Campuzano *et al.*, Phys. Rev. Lett. **64**, 2308 (1990).

[16] F. M. Mueller *et al.*, Physica B **172**, 253 (1991); G. Kido *et al.*, in *Advances in Superconductivity III*, edited by H. Kajimura and H. Hayakawa (Springer-Verlag, Tokyo, 1991), p. 237.

[17] W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989); W. E. Pickett, R. E. Cohen, and H. Krakauer, Phys. Rev. B **42**, 8764 (1990).

[18] F. J. Blatt *et al.*, *The Thermoelectric Power of Metals* (Plenum, New York, 1976).

[19] B. Fisher and M. Fibich, Phys. Rev. B **37**, 2820 (1988).

[20] B. Fisher *et al.*, J. Supercond. **1**, 53 (1988); J. Genossar *et al.*, Physica C **157**, 320 (1989).

[21] J. F. Kwak, G. Beni, and P. M. Chaikin, Phys. Rev. B **13**, 641 (1976).

[22] G. Beni, Phys. Rev. B **10**, 2184 (1974).

[23] Physically, a small $U \approx 300$ K must correspond to an interatomic interaction since intra-atomic repulsion energies are expected to be 2 orders of magnitude larger.

[24] A. B. Kaiser and C. Uher, in *Studies of High Temperature Superconductors*, edited by A. V. Narlikar (Nova Science, New York, 1990), Vol. 7.

[25] X.-Q. Xu *et al.*, Phys. Rev. B **45**, 7356 (1992).

[26] N. P. Ong, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Teaneck, NJ, 1990), Vol. II, p. 459; T. R. Chien *et al.*, Phys. Rev. Lett. **67**, 2088 (1991).

[27] P. B. Allen, W. E. Pickett, and H. Krakauer, Phys. Rev. B **37**, 7482 (1988).

[28] A. B. Kaiser, Phys. Rev. B **37**, 5924 (1988); A. B. Kaiser and G. Mountjoy, *ibid.* **43**, 6266 (1991).