Thermoelectric Power of $YBa_2Cu_3O_{7-\delta}$: Phonon Drag and Multiband Conduction

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We report measurements of the a-b-plane thermopower (S) on crystalline $YBa_2Cu_3O_{7-\delta}$ ($\delta \leq 0.16$) for temperatures below 310 K. Much sharper features in the T dependence of S are observed than have been previously reported. Both the temperature and oxygen-doping dependences of S, which have caused confusion, are consistently accounted for by conventional metallic theory for the first time. Strong phonon drag and two carrier species are indicated, with holes on the planes and electrons on the chains. An anomalous, positive component to S, observed for $T < 160$ K, is attributed to a freeze-out of carrier-phonon umklapp processes involving holes in the CuO_2 planes and optical-mode phonons.

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The normal-state and superconducting properties of the high-T_c cuprate superconductors offer a great challenge for theoretical explanation. Because many of the normal-state properties (electrical resistivity, optical conductivity, Hall coefficient) are unlike those observed in typical metals, i.e., anomalous for a Fermi liquid, some theories have stressed the non-Fermi-liquid[1] or marginal-Fermi-liquid[2] nature of these materials. Others[3] have emphasized a conventional Fermi-liquid picture, taking into account a small value of the Fermi energy and anisotropic crystal structure.

A particularly interesting transport property is the thermoelectric power S. In typical metals it is a sensitive probe of the carrier balance, of the relative roles of phonon-phonon and carrier-phonon interactions, and of the topology of the Fermi surface. A recent review article[4] demonstrates that, despite considerable experimental effort, the thermopower remains poorly understood in the cuprates. A major difficulty in interpreting the existing thermopower data has been a lack of consensus regarding intrinsic behavior. In $YBa_2Cu_3O_{7-\delta}$, the most frequently studied and well-characterized material, a good deal of confusion has arisen concerning the sign as well as the temperature dependence of the a-b-plane thermopower. In view of several studies, which have correlated the sign of S in polycrystals with variations in oxygen content,[5,6] a multicarrier picture appears necessary for $YBa_2Cu_3O_{7-\delta}$. The temperature dependence of S, and specifically the occurrence of a peak (or minimum for $S < 0$) in the range $T_c < T < 150$ K, has been attributed to a variety of different mechanisms appropriate for metals.[6] A consistent correlation between the oxygen-doping and temperature dependences of S is a crucial, but missing, ingredient to a complete description of the cuprate normal state.

In this Letter we present results of a systematic study of the a-b-plane thermopower on crystalline $YBa_2Cu_3O_{7-\delta}$ which offer new insight into the mechanisms of charge transport and scattering in this material. Our general finding is that the sign and temperature dependence of the thermopower for $T \lesssim 275$ K can be completely accounted for by conventional metallic theory, which incorporates strong phonon-drag effects and two carrier species: holes on the planes and electrons on the chains. The most striking observation is the appearance of a sharply temperature dependent, positive contribution to S for $T \lesssim 160$ K, which is observed irrespective of the sign of S (i.e., independent of δ). We demonstrate that this feature can be explained by a freeze-out of carrier-phonon umklapp processes involving holes in the CuO_2 planes. The results are consistent with the calculated[7] and measured[8] Fermi surfaces for $YBa_2Cu_3O_{7-\delta}$, and support a picture of strong coupling between the planar holes and optical-mode phonons.

Preparation of the liquid-phase-processed (LPP) specimens is described elsewhere.[9] This material is composed of large, twinned crystalline grains (up to 4 mm dimensions in the a-b plane and 10–20 μm thick) which are highly oriented along the c axis during growth. X-ray analysis indicates that the misorientation of the c axes is less than 5°. Small amounts of Y_2BaCuO_5 are present as distinct entities between the grains. The high degree of crystalline integrity of this material is evidenced by low a-b-plane electrical resistivities [$\rho(300\text{ K}) = 250$–$500\ \mu\Omega$ cm] and transport critical current densities[10] comparable to those measured in single crystals. The two LPP specimens studied ($8\times2\times1$ mm^3) had sharp resistive transitions ($\Delta T_c \leq 0.5$ K), with $R = 0$ at 92.5 K. The LPP material is especially useful in this study because full oxygenation ($\delta \approx 0$) is more readily achieved by oxygen anneal than it is in crystals. The oxygen content of the LPP specimens is inferred by comparing the measured thermopower curves with the data of Ouseph and Ray O'Bryan,[5] as discussed below. The $YBa_2Cu_3O_{7-\delta}$ crystal ($3\times1.5\times0.3$ mm^3) was grown by a flux method[11] and had $\Delta T_c \approx 1$ K, with $R = 0$ at 90 K.

X-ray and magnetization studies[12] of similarly prepared crystals indicate an oxygen deficiency of $\delta \approx 0.16$.

The thermopower was measured using a steady-state technique, employing a differential Chromel-Constantan thermocouple, glued to the specimen with varnish, and Cu Seebeck probes silver painted onto fired-on silver pads. Temperature gradients were typically 0.4–1.0 K. Linearity in the $V(\Delta T)$ response was confirmed throughout the temperature range by varying the heater power. The precision of the measurements is ± 0.1 μV/K.

Figure 1 shows the thermopower versus temperature for each of the three samples. Also shown are data for specimen LPP1 following an oxygen anneal (150 h at 450 °C in 1 atm of flowing oxygen), and designated LPP1A. The change in sign and magnitude of the thermopower supports a picture of multiband conduction,[5] with the dominant carrier species changing from electronlike to holelike with increasing δ. We will return to the issue of the sign change below. Comparing the curves in Fig. 1 with those of Ref. 5 we estimate δ values for our specimens as 0.15 (crystal), 0.12 (LPP1), 0.02 (LPP1A), and 0.01 (LPP2).

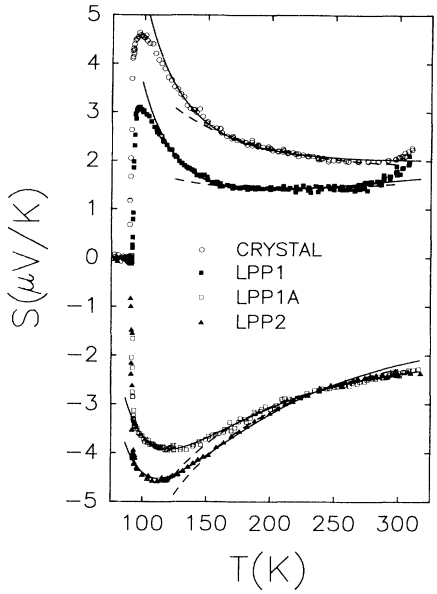

FIG. 1. a-b-plane thermoelectric power (S) vs temperature for $YBa_2Cu_3O_{7-\delta}$ specimens. The dashed lines are fits by the high-temperature metallic form $S = AT + B/T$, and the solid lines include an additional umklapp term, described by Eq. (2).

We begin our analysis of the temperature dependence of the thermopower within the context of a conventional metallic picture, in which contributions to S are due to carrier diffusion and phonon drag. The diffusion thermopower S_d can be described by the Mott expression[13]

$$S_d = \frac{\pi^2}{3}\frac{k_B}{e}\left.\frac{\partial \ln\sigma(E)}{\partial E}\right|_{\mu}, \tag{1}$$

where $\sigma(E)$ is the energy-dependent conductivity and the derivative is evaluated at the value of the chemical potential μ. For a gas of free electrons this reduces to $S_d \sim (\pi^2/3)(k_B/e)(k_BT/\mu)$, yielding the familiar linear temperature dependence.[14] The phonon-drag thermopower for a single band of carriers with isotropic scattering rate is given by Bailyn[15] as

$$S_g = \frac{k_B}{|e|}\frac{\sum_{\mathbf{q}j}[\partial N_0(j\mathbf{q})/\partial k_BT]\sum^{(j\mathbf{q})}\alpha(j\mathbf{q};\mathbf{k},\mathbf{k}')[\mathbf{v}(\mathbf{k})-\mathbf{v}(\mathbf{k}')]\cdot\mathbf{v}(j\mathbf{q})}{\sum V^2(\mathbf{k})[-\partial f_0/\partial E]}. \tag{2}$$

Here, $\alpha(j\mathbf{q};\mathbf{k},\mathbf{k}')$ represents the relative probability that a phonon of wave vector $\mathbf{q}$ and polarization j will induce the electron transition from state $\mathbf{k}$ to $\mathbf{k}'$, compared to all other scattering processes in which it may participate; $\mathbf{v}(\mathbf{k}) = \hbar\mathbf{k}/m^*$ is the electron velocity (m^* is the effective mass); $N_0(j\mathbf{q})$ is the equilibrium phonon distribution in state $j\mathbf{q}$, frequency $\omega(j\mathbf{q})$, and velocity $\mathbf{v}(j\mathbf{q}) = (\mathbf{q}/q)\partial\omega/\partial q$. The second sum $\sum^{(j\mathbf{q})}$ is over all states and transitions that need the $j\mathbf{q}$ phonon. The temperature dependence in this expression arises principally from that of the phonon population factor, $\partial N_0/\partial T$, and of the weighting factor α. A great simplification is achieved by taking α to be independent of $\mathbf{q}$, such that $\alpha = \tau_g/\tau_{pe}$, where τ_g is a mean phonon relaxation time involving all processes, and τ_{pe} is that associated with scattering by carriers alone. At high temperatures (typically $T \geq \Theta_D/4$), anharmonic phonon-phonon interactions (governed by the rate τ_{pp}^{-1}) tend to dominate the lattice scattering such that $\tau_g \approx \tau_{pp}$. In this temperature range $\tau_{pp} \propto 1/T$, $\tau_{pe} \sim$ const, yielding $\alpha \sim 1/T$.[16] Provided $\partial N_0/\partial T$ is weakly T dependent in this regime we have $S_g \propto 1/T$.

Combining this with the expression for S_d we arrive at the simple high-temperature metallic relation,

$$S = S_d + S_g = AT + B/T. \tag{3}$$

This form adequately describes the behavior of the thermopower in, for example, the noble metals for the range $77\ \text{K} \leq T \leq 250$ K. We see that this expression also fits the data in Fig. 1 (dashed curves) for $160\ \text{K} \leq T \leq 275$ K. We find $A, B > 0$ for the crystal and LPP1, and $A, B < 0$ for LPP1A and LPP2. That the $1/T$ contribution to the thermopower is due to the temperature variation of the phonon-phonon scattering rate is supported by measurements of the thermal conductivity (κ) for these same specimens[17] and by those of others,[18] where it is found that κ has a substantial $1/T$ component for $T > T_c$. Recent measurements of thermal diffusivity[19] in $YBa_2Cu_3O_{7-\delta}$ also reveal $\tau_g \propto 1/T$ in the normal state.

A sharp, positive upturn away from the simple metallic expression is observed in all specimens for $T < 160$ K. Interestingly this additional contribution to S is nearly

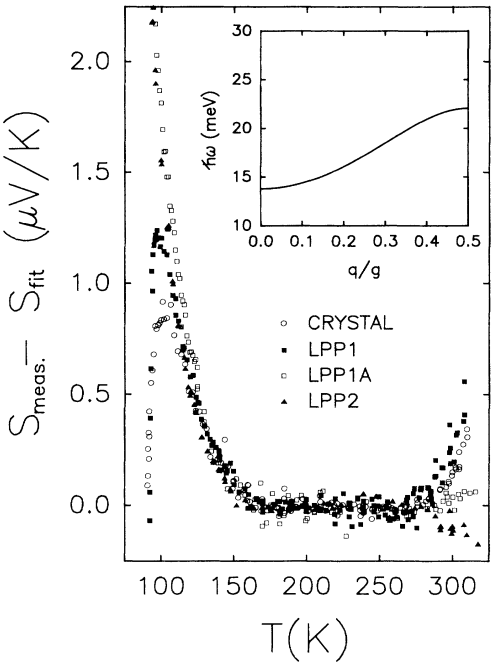

FIG. 2. The difference between the measured thermopower and the fits to the high-temperature metallic expression (dashed lines, Fig. 1). Inset: Phonon branch used in calculating the umklapp term as discussed in the text.

the same in magnitude and temperature dependence for all samples, as shown in Fig. 2 where we plot the difference $S_{\text{meas}} - S_{\text{fit}}$ vs T. It is this component of S which gives rise to the very sharp peak when $S > 0$ and to the broader minimum when $S < 0$. These features appear to arise from a common mechanism. Conventional superconducting fluctuation effects cannot account for the common sign of this component in specimens with thermopowers of opposite sign.

We propose a new explanation of these features which involves carrier-phonon umklapp scattering and phonon drag, the formal description of which is contained within Eq. (2) above. The assumptions leading to the derivation of the result $S_g \propto 1/T$ do not take into account the shape of the Fermi surface (FS) and its effect on the population factor $\partial N_0/\partial T$. For example, when the FS does not touch the Brillouin-zone (BZ) boundary, the phonon wave vectors which may induce umklapp events are restricted to $q \geq q_{\min}$ (see Fig. 3). This condition translates, through the population factor and the dispersion relation, into a temperature criterion for the "freeze-out" of umklapp processes. In the situation depicted in Fig. 3, for $T \ll \Theta = \hbar\omega(q_{\min})/k_B$, we should anticipate an umklapp process phonon-drag thermopower given by $S_g^U \sim \alpha \exp(-\Theta^*/T)$, reflecting the freeze-out of the Bose-Einstein distribution. This picture has been applied successfully in studies of the alkali metals,[13] where FS's are nearly spherical.

Band-structure calculations[7] and photoemission experiments[8] for $YBa_2Cu_3O_{7-\delta}$ support a picture in which quasi-two-dimensional portions of the FS, arising from the CuO_2 planes, do not touch the BZ boundary throughout a substantial portion of the zone. Thus there is precedent for precisely the situation described above. For a simply connected FS (the plane-derived surfaces are "rounded squares"), the scattering vector $\mathbf{K} = \mathbf{k}' - \mathbf{k}$ tends to be directed opposite to $\mathbf{q}$ in an umklapp event. This leads to a phonon drag that is opposite in sign to that of the charge of the carriers. Thus for holes in the CuO_2 planes, S_g^U should be negative. A freeze-out of umklapp processes involving these planar holes might then be expected to yield a rapidly increasing, positive contribution to S that could account for the behavior observed in the experiments. With regard to the phonon spectrum we note that the measured acoustic-phonon branches in $YBa_2Cu_3O_{7-\delta}$ do not extend in energy beyond ~ 10 meV (115 K).[20] Since the thermopower data require $\Theta^* \geq 160$ K, we conclude that if an umklapp process freeze-out is to explain our results, the relevant phonons must be optical modes.

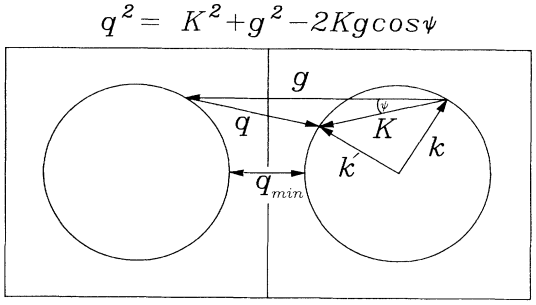

FIG. 3. Schematic diagram of a two-dimensional Fermi surface on a square lattice, demonstrating the geometry of the umklapp process.

Guided by these qualitative observations, we proceed to calculate S_g^U using a simple model and emphasizing the temperature dependence predicted by (2) for the crossover regime, $T \sim \Theta^*$. We consider a single Fermi circle as an approximation to the CuO_2-plane-derived surfaces and employ an approximation due to Ziman[21] to calculate the umklapp phonon-drag thermopower from Eq. (2). In this calculation the Brillouin zone is approximated by a Debye circle with radius $g/2 = \pi/a$ (a is the lattice parameter) and we have taken $\alpha \propto 1/T^n$.[16] In accordance with Refs. 7 and 8 we take $k_F/g = 3/8$, i.e., $k_F \sim 6 \times 10^7$ cm^{-1}. For simplicity we consider a single phonon branch, and employ an expression for $\omega(q)$ which is quadratic in q for small q and flattens at the zone boundary, approximating the form of the measured[20] optical branches in the range 10–30 meV. The resulting umklapp term, $S_{g,\text{pl}}^U$, is added to the high-temperature expression (3), and the data in Fig. 1 refitted with the constraint that the magnitude of the umklapp term, represented by an adjustable prefactor, be the same for all specimens. Note that the term B/T

accounts for the normal-process phonon drag from the planes, $S_{g,\mathrm{pl}}^{N}$, as well as $S_{g,\mathrm{ch}}$. Excellent agreement with the data (solid lines in Fig. 1) is found using the phonon mode shown in the inset of Fig. 2 and with $n=1.3$. The values of the other parameters were $A=1.79\times10^{-3}$, 2.53×10^{-3}, -3.40×10^{-3}, and -1.78×10^{-3}, and $B=1669$, 1475, 816, and 725, for the crystal, LPP1, LPP1A, and LPP2, respectively.

Irrespective of the details, e.g., Fermi-surface geometry, etc., our calculations suggest that the umklapp phonons correspond to the optical modes observed in the energy range 10–30 meV. This conclusion is consistent with an analysis of tunneling data,[22] which indicates that the main contribution to the Eliashberg function $\alpha^2F(\omega)$ arises from 20–30-meV phonons. To derive more specific information from these measurements would require a more detailed knowledge of the phonon (anisotropic) coupling strengths to the holes.

Based on our results we arrive at the following picture of transport in $YBa_2Cu_3O_{7-\delta}$. For $\delta\approx0$ we postulate two conduction bands: holes in the planes and electrons on the chains.[23] This supposition regarding the chains is supported by positron-lifetime experiments.[24] Though a sign change in S is possible in a single-band picture, the associated changes in Fermi-surface topology or scattering would, in general, alter Θ^*, in contradiction to our experimental observation that Θ^* is independent of oxygen doping. The overall diffusion component of the thermopower (in a twinned crystal) is negative, presumably reflecting a chain mobility higher than that of the planes.[25] Oxygen vacancies at this level of deficiency ($\delta\leq0.16$) are on the chain site. The removal of oxygen should have two principal effects, both of which will contribute to the observed sign change of S: a decrease in S_{ch} due to a reduction in the average charge on the chains, and a decrease in the effective chain mobility due to oxygen disorder. Measurements of the planar-Cu-bond-valence sums[26] indicate that the hole concentration in the planes is nearly constant for $\delta\leq0.2$. This tends to support our observation that $S_{g,\mathrm{pl}}^{U}$ is the same in the specimens studied.

Finally, we note that an umklapp freeze-out might also explain the negative curvature widely observed in the electrical resistivity for temperatures $T\leq160$ K. Interestingly, this curvature is evident in the plane but not in the chain component of the resistivity according to recent measurements on untwinned crystals.[25] This is consistent with the model presented here.

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