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Thermal transport properties of $YBa_2Cu_3O_7$ superconductors

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We have measured the thermal conductivity, thermopower, Hall constant, and resistivity of a $YBa_2Cu_3O_7$ high-T_c superconductor. The thermal conductivity shows a striking increase below the transition temperature T_c, which we ascribe to an increase in lattice conduction due to a reduction in the scattering of phonons by holes as superconducting pairs form. This property, and the others we have measured, are consistent with ordinary metallic conduction mechanisms with short phonon and carrier free paths, and a strong interaction of phonons with a small density of hole carriers.

Much research activity is currently being focused on the properties of high-T_c superconductors based on the oxygen-deficient perovskite structures. The interest extends far beyond the solid-state community as these materials hold great promise for a variety of futuristic technological applications. The early thrust has centered on the preparation methods, the study of the structural properties and the electromagnetic response of these ceramic materials.[1] As major inroads are being made in these areas, the interest broadens to a wider spectrum of physical and chemical properties in the hope of providing a cohesive picture of the superconducting state responsible for electron pairing at temperatures of the order of 100 K. One research area that is beginning to yield useful information is the thermal properties and the thermopower in particular. Thus, measurements on both a pristine La_2CuO_4 phase,[2] as well as those on dilute and heavily Sr- or Ba-doped samples,[3,4] indicate that the thermopower is far more sensitive to the underlying structural configuration than is the resistivity. Furthermore, a negative sign observed in the high-temperature (above 300 K) thermopower of $La_{1.75}Sr_{0.25}CuO_4$ provided the first demonstration[4] of a multicarrier nature of the carrier spectrum, at least for the heavily doped superconducting compounds.

In this paper we present the results of our thermal and electrical transport measurements on a single-phase $YBa_2Cu_3O_7$ superconductor. We interpret these properties within the framework of the traditional metallic model in order to search for unusual features, or even a breakdown of the model, that might provide a background for understanding the origin of the high-T_c superconducting behavior. The most exciting observation is our discovery of a sharply rising thermal conductivity coinciding with the onset of superconductivity as temperature decreases, which we believe reflects a drastic reduction in the phonon-carrier scattering as the holes begin to form superconducting pairs. We also find that, while the magnitude of the thermopower is significantly reduced in comparison with the $La_{2-x}Sr_xCuO_4$ compounds, the temperature dependence shows an interesting pattern of changes exhibited over a rather narrow temperature range from T_c up to 300 K.

Samples of $12\times2\times1$ mm^3 were cut from a disk of $YBa_2Cu_3O_7$ prepared according to standard recipes, and x-ray measurements confirm its single-phase structure. A sample for the thermal transport studies was fixed with one of its ends in a slotted, close-fitting copper cold tip of a helium cryostat with the aid of Stycast, the other being provided with a metal-film resistor serving as a heater. The temperature gradient was monitored by a combination of a differential Au/Fe-chromel thermocouple and a pair of calibrated glassy-carbon thermometers. Since the thermopower of $YBa_2Cu_3O_7$ is very small, being similar in magnitude to typical pure noble metals, great care must be exercised in selecting thermopower test leads. Due to the rather poor thermal conductivity of this ceramic a direct use of Pb (a universally accepted thermopower standard) is not the best choice, as it is difficult to draw Pb wires sufficiently thin to prevent shunting of heat away from the sample and disturbing its temperature profile. The use of wires of low thermal conductivity alloys such as chromel, manganin, or even cupro-nickel-clad Nb-Ti, usually the most popular choices for routine investigations, is fine in principle but one must be sure of their thermopower calibration. The thermopower of these alloys at ambient temperature is rather high ($\sim$4–20 μV/K) and depends on the manufacturing process and, unless the spool is carefully calibrated, would lead to significant errors in measurements on low thermopower materials. We wish to note further that even the most recent thermopower compilations are often based on the old thermopower scale of Pb assembled by Christian, Jan, Pearson, and Templeton[5] which is known to be in error by as much as 0.3 μV/K above liquid-nitrogen temperature. For a precision work one should refer to the more recent scale of thermoelectricity established by Roberts.[6]

In our measurements we have opted for copper as thermopower leads. Copper can be drawn into very thin wires, effectively eliminating the heat shunting, and it has a small (< 2 μV/K even at 300 K) and reproducible thermopower in the temperature range of interest (77–300 K). We have checked the thermopower of our copper leads against high-purity Pb and found it to agree closely with the data of Crisp, Henry, and Schroeder.[7] Furthermore, the thermopower of copper above 92 K joins smoothly the data below 92 K where $YBa_2Cu_3O_7$ is superconducting and the measurements yield the absolute thermopower of Cu directly. Copper leads were attached to the sample with a minute amount of silver epoxy.

As we have already pointed out, the thermal conductivity of high-T_c superconductors is low which, coupled with their matt and dark finish, i.e., high emissivity coefficient, makes radiation losses a serious error in the thermal conductivity, particularly above 200 K. By suspending the sample by its leads and monitoring the temperature difference for a given heater power we can estimate the radiation loss. While below the liquid-nitrogen temperature it is negligible, at 286 K it amounts to a 25% overestimate of the thermal conductivity. The data were corrected accordingly.

Our thermal conductivity data are shown in Fig. 1, in which the most dramatic feature is the sudden increase of the thermal conductivity K in $YBa_2Cu_3O_7$ associated with the onset of superconductivity. We argue that this is an indicator of the strength of the carrier-phonon interaction in these materials. The overall size of the thermal conductivity is small, much smaller than that of typical metals, and more comparable to that for amorphous systems.[8] We can estimate the *electronic* component K_e of thermal conductivity assuming ordinary metallic conduction (for which we discuss the evidence below) from the measured electrical resistivity ρ (Fig. 2). To obtain an upper limit for K_e, we take the value of the Lorenz number $L = K_e \rho T^{-1}$ as the ideal Sommerfeld value $L_0 = 2.45 \times 10^{-8}$ V^2K^{-2}; for inelastic scattering such as by phonons, L may be reduced below L_0, although the discrepancy decreases at high temperature.[9] It is seen immediately from Fig. 1 that close to 90% of the thermal conductivity is due to the phonons.

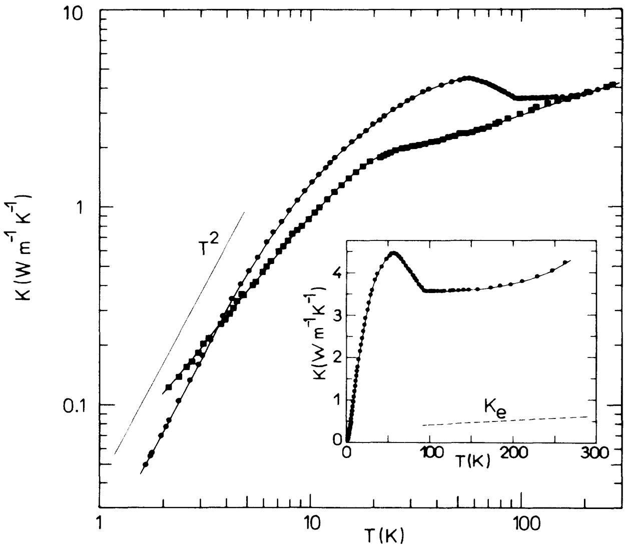

FIG. 1. Thermal conductivity of $YBa_2Cu_3O_7$ (circles) and $La_{1.8}Sr_{0.2}CuO_4$ (squares). The inset shows the data for $YBa_2Cu_3O_7$ using linear scales, with the estimate (dashed line) from the electrical resistivity of the *maximum* contribution of the electronic thermal conductivity K_e (see text).

The electronic component of thermal conductivity normally decays as superconducting pairs form because they do not transport energy.[10] On the other hand, since the paired electrons no longer scatter phonons, the lattice thermal conductivity K_g can increase below T_c. This effect is not usually seen because the electronic thermal conductivity dominates, but in our present case the lattice conductivity represents the dominant contribution to the heat transport. Therefore, we have clear evidence in Fig. 1 of the close coupling of the carrier and phonon systems in $YBa_2Cu_3O_7$. There is also a hint of a small upturn in the curve of K close to T_c($\sim$30 K) in the $La_{1.8}Sr_{0.2}CuO_4$ sample (see Fig. 1) although the effect is much smaller in this case. Presumably, at the much lower transition temperature of this sample ($\sim$30 K) the more rapidly decreasing phonon density effectively compensates for a reduction in the phonon-carrier scattering, washing out the thermal conductivity peak.

We have measured the value of the Hall constant T_H at 106 K as 2.3×10^{-9} m^3/C, corresponding to a carrier density n of 2.7×10^{21} cm^{-3} for a single band of carriers, and we find R_H decreases as temperature increases. We regard this value of n as an approximate upper limit because of the possibility of multicarrier conduction as indicated by the temperature dependence[11] and as demonstrated[4] in the highly doped $La_{2-x}Sr_xCuO_4$ superconductors.

This very small carrier density is one of the major factors causing the very large size of the resistivity in these materials, although it is also clear that the electron mean free path is unusually short. We find that $d\rho/dT \sim 3$ $\mu\Omega$ cm K^{-1}. We compare this value with that expected for phonon-limited metallic resistivity:[12]

$$\frac{d\rho}{dT} \approx \frac{2\pi k_B}{\hbar e^2} \left[\frac{m}{n}\right]_{\text{eff}} \lambda_{\text{tr}} \ , \tag{1}$$

where m is the carrier mass and λ_{tr} the electron-phonon coupling constant for transport. The experimental value is reproduced for $n \sim 3 \times 10^{21}$ cm^{-3} if $\lambda_{\text{tr}}(m_{\text{eff}}/m)$ has the very reasonable value of about 3. As in the case of the $La_{2-x}Sr_xCuO_4$ superconductors,[4] therefore, we find no evidence of the need for alternative inelastic scattering mechanisms such as electron-electron scattering[13] to explain the large size of $d\rho/dT$.

Since amorphous metals[14] with a resistivity an order of magnitude less (but a carrier density more than an order of magnitude more) have an electronic mean free path of the order of only 10 Å, the mean free path in the $YBa_2Cu_3O_7$ compounds could also be rather small. For sintered compounds with poor intergrain connectivity, however, the effective cross-sectional area of the sample for conductivity may be significantly less than its geometrical cross section. This, together with the fact that the carrier density estimate is an upper limit, and the normal metallic behavior of the resistivity, suggests that the actual mean free path is significantly larger than in amorphous metals. Although the occurrence of the superconductivity prevents an accurate estimate of the "residual" resistivity ρ_0 at low temperatures, the ratio ρ_0/ρ_{RT} (where ρ_{RT} is the room-temperature resistivity) is only of order 0.25 to 0.4 in our sample, much less than the values in Chevrel compounds in which phonon drag thermopower is suppressed.[15] Our conclusion is that although the short phonon and carrier mean free paths in $YBa_2Cu_3O_7$ will reduce the size of phonon drag thermopower, it may not be entirely eliminated as in amorphous metals.[16] From the simple expressions for the low-temperature phonon drag thermopower[17]

$$S_g = c_g/(3nq) \ , \tag{2}$$

where c_g is the lattice specific-heat per unit volume and q is the carrier charge, we note further that the *small* carrier density favors a *large* drag thermopower, as of course does a strong carrier-phonon interaction.

Regarding the temperature dependence of thermopower, we note that the usual T^{-1} decay of S_g at high temperatures[17] arises from phonons interacting more and more with other phonons rather than with carriers. The presence of significant structural scattering of phonons and carriers, besides reducing the size of S_g, would also reduce its rate of decay with temperature. Further, the root-mean-square energy of the phonon spectrum[18] corresponds to a temperature of order 600 K. For these reasons, we would expect any phonon drag thermopower contribution to extend to above room temperature in high-T_c superconductors, as we deduced[4] in $La_{2-x}Sr_xCuO_4$.

Turning now to the thermopower data in Fig. 2, we see that the size of S is very small, i.e., clearly metallic, and furthermore any phonon drag peak is of only modest size, consistent with our discussion above. In view of our comments, the decrease in S above 240 K could possibly be a phonon drag effect, but the main drag effect would appear to be a peak below 100 K truncated by the occurrence of the superconductivity. The sharpness of the decay with temperature of this peak is rather surprising, and could possibly indicate a strong interaction with lower-energy phonons.[19] The diffusion thermopower is difficult to deduce from the data (in the presence of the carrier-phonon interaction it is no longer simply linear in temperature[15,20]), but in contrast to the case of heavily doped $La_{2-x}Sr_xCuO_4$, there is no clear evidence for the presence of negative carriers in addition to holes in the present system. The small size of S, in spite of the low carrier density, would, however, be consistent with some cancellation of hole and electron contributions.

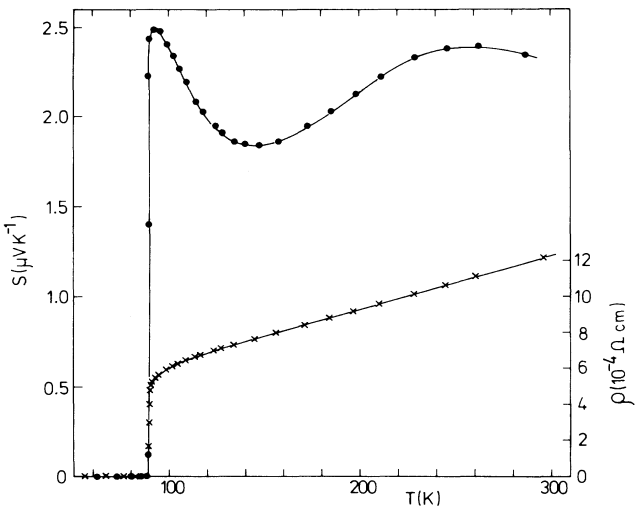

FIG. 2. Thermopower (circles) and resistivity (crosses) for our sample of $YBa_2Cu_3O_7$.

We note that a decrease in carrier density n and increase in phonon current due to superconducting fluctuations above T_c would tend to *enhance* the phonon drag thermopower, see Eq. (2). However, this is difficult to understand as a mechanism contributing to the sharpness of the peak near 100 K, since superconducting pairs will tend to short out the thermoelectric voltage arising from phonon drag as well as from diffusion. Thus the expected precursor effect in S (as in ρ) is a tendency towards the zero value in the superconducting state. Only if the mutual interaction of pairs of holes reduced their interaction with phonons (above the temperature at which they begin to superconduct) would the phonon drag be increased as a precursor effect. Such behavior, although not inconsistent with preexisting pairs,[21] is only speculative.

In conclusion, we have not found any striking evidence of exotic behavior in the thermal and electrical transport properties of $YBa_2Cu_3O_7$; indeed, we are able to form a consistent picture of these properties in terms of ordinary metallic conduction with a strong carrier-phonon interaction.[22]

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