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Thermal conductivity of $YBa_2Cu_3O_{7-\delta}$ below 1 K: Evidence for normal-carrier transport well below T_c

J. L. Cohn, S. D. Peacor, and C. Uher

Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

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We report measurements of thermal conductivity at temperatures below 1 K on superconducting and insulating (oxygen-deficient) ceramic $YBa_2Cu_3O_{7-\delta}$. For the superconductor, the temperature dependence of the thermal conductivity κ begins to weaken below ~0.5 K, approaching a T-linear behavior. Below 1 K, the insulating material, produced by vacuum-annealing the superconductor, exhibits a $\kappa \propto T^3$ dependence characteristic of phonon boundary scattering. Reannealing samples in flowing oxygen restores superconductivity at 90 K and the T-linear behavior of the thermal conductivity at the lowest temperatures. Scanning electron micrographs reveal an identical grain structure before and after successive heat treatments, indicating that the anomaly in κ for the superconductor is not associated with the specific geometry of the microstructure. The data are consistent with the presence of a small number of normal carriers in the high-T_c material.

It is well established that the superconducting properties of $YBa_2Cu_3O_{7-\delta}$ are very sensitive to oxygen content.[1-5] The orthorhombic structure supports high-T_c (90-K) superconductivity for $0 < \delta < 0.3$ and has metallic properties, whereas the tetragonal phase $(0.8 < \delta < 0.6)$ is a nonsuperconducting insulator. An understanding of the differences in electronic structure between these two phases may provide important insight into the mechanism responsible for high-T_c superconductivity. Here we report measurements of the thermal conductivity κ at sub-Kelvin temperatures on superconducting and insulating (oxygen-deficient) ceramic (1-2-3) material. We find that the temperature dependence of κ for the superconductor weakens below ~0.5 K, approaching a T-linear behavior at 0.2 K. In contrast, the insulator exhibits a T^3 dependence characteristic of phonon boundary scattering below 1 K. We discuss the implications of this surprising difference in heat transport.

The starting material, prepared according to standard methods, exhibited superconductivity at 91 K as determined by dc resistance and susceptibility measurements. Samples were cut from as-prepared disks into parallelepipeds of typical dimensions $0.3\times0.3\times1.5$ cm^3. Two calibrated germanium-resistance thermometers, housed in tiny copper holders, were clamped and affixed with Stycast to opposite ends of the sample. A metal film resistor, serving as a heater, was mounted on the free end of the specimen with the other end thermally anchored to the mixing chamber of a dilution refrigerator. Temperature gradients during the steady-state measurements were typically 5–10% of the average temperature. The accuracy of these measurements is limited by the uncertainty in the geometry of the samples which we estimate as ~5%.

Samples from separate starting disks were measured in both the superconducting and insulating states. The latter was achieved by vacuum annealing the superconducting specimens for 5 h at 600 °C. From microbalance measurements, we calculate $0.7 \leq \delta \leq 0.8$ for the vacuum-annealed material, assuming that the reduced mass is associated with the oxygen loss. The field-cooled magnetization (Meissner effect) for one of the samples is shown before and after heat treatments in Fig. 1. The vacuum-annealed material shows no indication of superconductivity above 2 K. Two samples were annealed at 600 °C and cooled slowly to room temperature in flowing oxygen. This procedure restored superconductivity at 90 K and allowed for a check on the reproducibility of the low-temperature thermal conductivity data of the superconducting material. The as-prepared and reannealed materials had the same measured density of 5.22 g/cm^3, 80% of the theoretical density. The slightly larger flux expulsion exhibited by the reannealed material suggests a reduced pinning apparently resulting from the heat treatment.

Values of the thermal conductivity reported[6-10] for superconducting $YBa_2Cu_3O_{7-\delta}$ above 2 K vary by as much

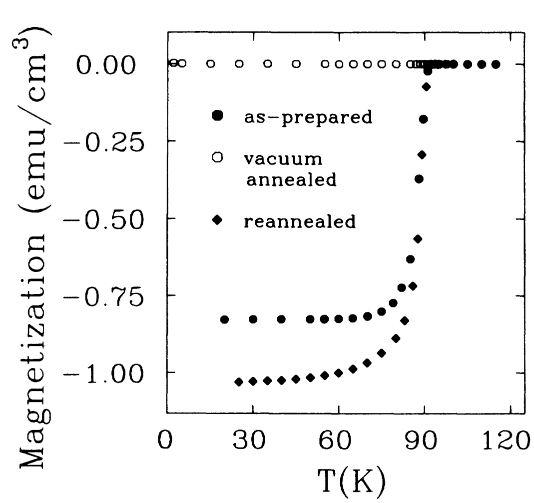

FIG. 1. Field-cooled magnetization (Meissner effect) for $YBa_2Cu_3O_{7-\delta}$ in the as-prepared state and after successive heat treatments. Measurement field was 30 Oe.

as an order of magnitude. This variation can be accounted for, to a large extent, by differences in compactness of the starting material. In the present case, the use of successive heat treatments carried out on individual specimens ensures that no variations associated with different preparation conditions affect the measurements. We have examined the microstructure of each specimen before and after heat treatments for possible changes that could have a bearing on the thermal conductivity data and their interpretation. Scanning electron micrographs (SEM) are shown in Fig. 2 for the as-prepared state, and after successive heat treatments. No changes in the distribution of grain sizes or in porosity are evident. With this result in mind we now address the low-temperature data.

The thermal conductivity for one of the specimens studied is shown in Fig. 3 with heat treatment indicated for each curve. Other specimens show the same qualitative

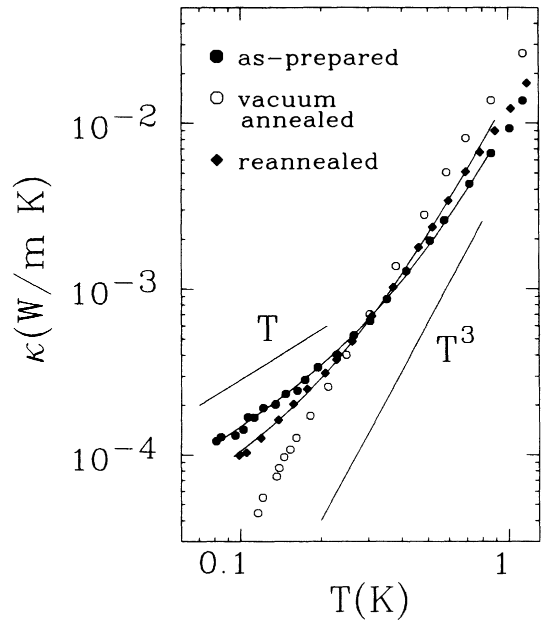

FIG. 3. Thermal conductivity of a specimen in the as-prepared state and after successive heat treatments. The solid lines through the data are fits to the form $\kappa = AT + BT^3$ with parameters listed in Table I. Corresponding Meissner curves are shown in Fig. 1.

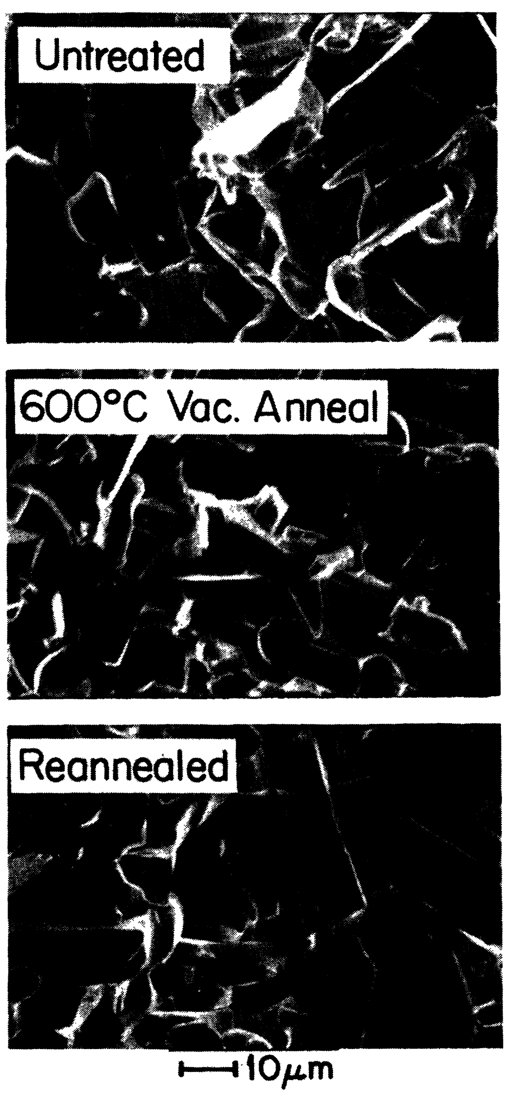

FIG. 2. Scanning electron micrographs for a single specimen of $YBa_2Cu_3O_{7-\delta}$ before and after successive heat treatments. The view is perpendicular to the direction of heat flow on freshly cleaved material.

behavior. While the curves have a similar temperature dependence above ~0.8 K, there is an apparent increase in the magnitude of κ for the vacuum-annealed material by roughly a factor of 2 over that of the superconductors (as-prepared and reannealed). A decrease in the Debye temperature, Θ_D, from 410 K for the orthorhombic phase to 300 K for the tetragonal phase has been observed in low-temperature specific-heat measurements[11] on single-crystal $YBa_2Cu_3O_{7-\delta}$. This lattice softening in the tetragonal structure may account for the enhanced thermal conduction of the vacuum-annealed specimen at temperatures above 0.8 K. Since at low temperatures one expects the lattice conductivity to vary as $\kappa_L \propto \Theta_D^{-3}$, the change in Θ_D would suggest an increase in κ_L by a factor of 2.5 in reasonable agreement with the data. The T^3 variation of κ exhibited by the vacuum-annealed material below 1 K is typical of polycrystalline insulating materials where the phonon mean free path is fixed by scattering at grain boundaries. For phonon transport, the thermal conductivity can be expressed as

$$\kappa_L = \tfrac{1}{3} Cvl = (2\pi^2 k_B^4 l / 15\hbar^3 v^2) T^3 ,$$

where C is the Debye heat capacity, v is the sound velocity, and l is the phonon mean free path. From the data in Fig. 3 and using[12] $v = 7000$ m/sec we estimate $l \approx 25$ μm. This value is consistent with the range of grain sizes (5–40 μm) evident in the micrographs for this sample (Fig. 2).

The most dramatic feature of the data is the behavior below 0.5 K. In this regime, the temperature dependence of κ for all superconducting specimens measured begins to weaken and approaches a T-linear variation, with values at 0.1 K nearly an order of magnitude larger than that of the oxygen-deficient material. This result is quite surprising since, at temperatures far below T_c, one expects heat transport by phonons only and, thus, a thermal conductivity that has the same temperature dependence for both superconducting and insulating materials.

In this porous, ceramic material we must consider the possibility of a strongly frequency-dependent phonon scattering (e.g., Rayleigh) from the microstructure which can result in a weakened temperature dependence of κ or a plateau as is characteristic of amorphous materials.[13] This behavior would be expected at temperatures where the dominant thermal phonon wavelength, $\lambda_{\mathrm{dom}} = hv/2.7k_BT$, exceeds the size of grains or pores. Our scanning electron microscopy (SEM) studies indicate no discernible changes between the as-prepared and heat-treated materials and clearly rule out the specific geometry of the microstructure as a source of such scattering. Another possibility is that the oxygen defect structure is causing the scattering. Neutron-diffraction results[1,2] indicate that the oxygen-deficient tetragonal structure has a highly disordered two-dimensional network of Cu-O in the basal plane as a consequence of the break-up of the Cu-O chains which occur in the high-T_c phase. The corrugated Cu-O planes are apparently the same in both phases. Thus, one would expect a point-defect (Rayleigh) phonon scattering from this atomic-site disorder to be more pronounced in the tetragonal rather than the orthorhombic structure. Furthermore, this disorder occurs on a scale of tens of Å which corresponds to the wavelength of phonons above 10 K, and would seem unlikely to explain the data below 0.5 K. We are thus led to consider the anomalous behavior of the thermal conductivity in the superconducting material as associated with a nonphonon contribution to thermal transport.

At sufficiently low temperatures where the contribution from phonons decreases rapidly, even a small number of free carriers may dominate the heat transport. In this temperature regime, where carriers are scattered from impurities and defects, the thermal conductivity is expected to vary linearly with temperature. From the Wiedemann-Franz law (WFL) the electronic thermal conductivity can be written as

$$\kappa_E = (L_0/\rho T) ,$$

where $L_0 = (\pi^2/3)(k_B/e)^2 = 2.45\times10^{-8}\ \mathrm{V^2K^{-2}}$ and ρ is the electrical resistivity. The data for the as-prepared and reannealed materials have been fitted to the form $\kappa = \kappa_E + \kappa_L = AT + BT^3$ (solid curves in Fig. 3) and the fitting parameters for all of the superconducting samples studied are summarized in Table I. We may attempt to apply the WFL to the leading term, $A = L_0/\rho$, thus postulating that a small density of carriers remain normal well below T_c. Since we cannot directly measure the residual electrical resistivity at low temperatures, we invert this procedure and extract from our thermal conductivity data an "effective residual resistivity" ρ_0^{eff} that would be associated with these normal carriers. This value may be compared to that estimated by making a linear extrapolation of the normal-state resistivity to zero temperature[14] ρ_0^{xtr}. The ratio $(\rho_0^{\mathrm{eff}}/\rho_0^{\mathrm{xtr}})^{-1}$ can be interpreted as the fraction of normal carriers contributing to low-temperature heat transport. The values for the as-prepared material are $\rho_0^{\mathrm{eff}} \approx 1600\ \mu\Omega\,\mathrm{cm}$ and $\rho_0^{\mathrm{xtr}} \approx 75\ \mu\Omega\,\mathrm{cm}$, yielding a normal carrier fraction of $\sim5\%$. Implicit in this estimate is the assumption that the "metallic" linear behavior of the normal-state resistivity would persist down to low temperatures.[15]

TABLE I. Properties of superconducting $YBa_2Cu_3O_{7-\delta}$ samples. A and B are coefficients from fits of the data to the form $\kappa = AT + BT^3$. Sample numbers refer to different starting disks (sample 1 is shown in Fig. 3).

Sample	Treatment	A (mW/m K^2)	B (mW/m K^4)	ρ (300 K) (mΩ cm)
1	As-prepared	1.40	8.74	2.01
1	Reannealed	0.92	13.5	2.53
1b[a]	Reannealed	1.66	12.0	1.40
2	As-prepared	1.95	8.81	1.60

[a]From the same disk as sample 1 and subjected to the same successive heat treatments.

This estimate of 5% uncondensed carriers could account for the large T-linear term (γ) that has been observed in the low-temperature specific heat of this material.[11,16–18] In the free-electron approximation, this term is given by

$$\gamma = \tfrac{1}{3}\pi^2 k_B^2 N(\varepsilon_F) ,$$

where $N(\varepsilon_F)$ is the density of states at the Fermi level. Taking 5% of a total carrier concentration[19] of $n = 5\times10^{21}\ \mathrm{cm^{-3}}$ reproduces the range of experimental values[11,16–18] of γ (5–9 mJ/mol K^2) with a reasonable effective mass ($4m_e$-$8m_e$). Measurements on single crystals[11] indicate that γ does not change appreciably in going from the superconducting to the insulating state. If normal carriers are present in both phases, then we must conclude from our transport data that the electronic states become localized in the insulating material, thus allowing the rapidly decreasing phonon contribution to serve as the principal heat conduction channel. In support of this interpretation are measurements of resistivity at high temperatures[20] in $YBa_2Cu_3O_{7-\delta}$ which indicate that as oxygen content decreases a change from metallic to activated transport occurs for $\delta \approx 0.5$. We emphasize that our measurements, while suggesting an intrinsic origin to the free carriers, do not rule out the possibility that these carriers are associated with regions of normal material[21] that may be present in the sinter. In this regard, we note that measurements of thermal conductivity on a single-crystal specimen[22] of superconducting $YBa_2Cu_3O_{7-\delta}$ indicate an order of magnitude larger value than in the ceramic. These data show a slight weakening in the temperature dependence of κ near ~0.4 K, though a T-linear behavior is not achieved. Finally, we mention that sub-Kelvin measurements of the thermal conductivity in superconducting and oxygen-deficient $La_{1-x}Sr_xCuO_{4-y}$ material show the same qualitative behavior as those presented here for $YBa_2Cu_3O_{7-\delta}$. These results will be reported elsewhere.[23]

In summary, we observe dramatic differences in the thermal conductivity of ceramic $YBa_2Cu_3O_{7-\delta}$ at temperatures $T \leq 0.5$ K depending on whether the material is superconducting or insulating. The consequence of the different limiting power-law behavior is an order of magnitude larger thermal conductivity at 0.1 K in superconducting specimens. In the absence of any discernible changes in the microstructure of the samples arising from heat treatments, the data suggest the presence of a small number of free carriers well below T_c in this material. We estimate that these represent roughly 5% of the total carrier density, and provide a plausible explanation for the large γ term in the specific heat.

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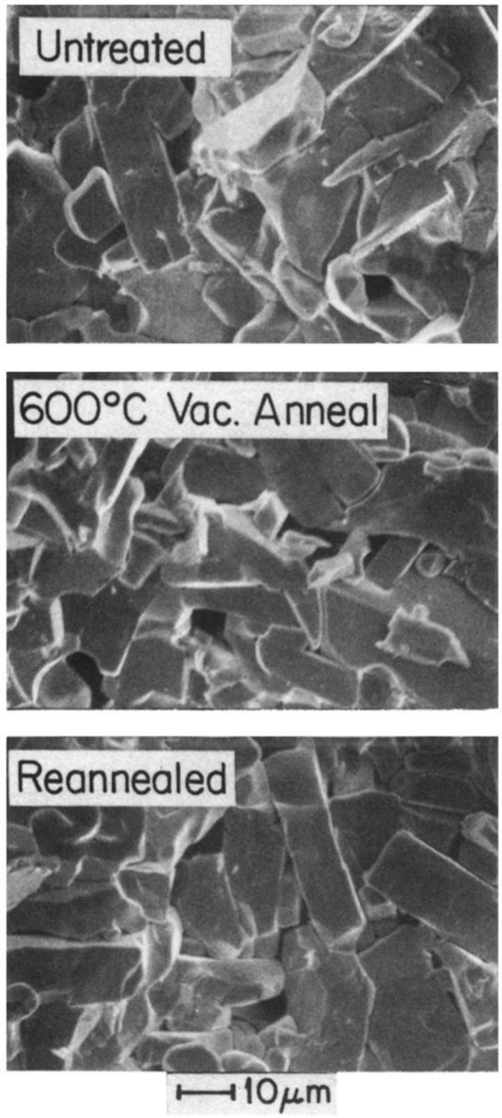

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