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Thermal conductivity of Ba-K-Bi-O: A contrast to copper oxide superconductors

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We report measurements of the thermal conductivity, $\kappa(T)$, of $Ba_{1-x}K_xBiO_3$ between temperatures of 70 mK and 300 K. We find that, below the superconducting transition temperature, the behavior of $\kappa(T)$ is in sharp contrast to that observed in copper-oxide-based superconductors. Measurements in a 6-T magnetic field indicate that, in this material, the thermal conductivity is *lower* in the superconducting state than it is in the normal state at the same temperature. The information this provides about the strength of the electron-phonon coupling is discussed. Our data show no evidence of the T-linear term in the thermal conductivity below 0.5 K observed in sintered Y- and La-based superconductors.

After three years of intensive research, an understanding of the mechanism of high-temperature superconductivity remains elusive, and there is still a clear need to widen the base of experimental data to help discriminate between different models. Considerable interest was aroused by the discovery[1] of superconductivity (with $T_c \sim 30$ K) in $Ba_{1-x}K_xBiO_3$, since this copperless material without a planar structure, yet with T_c significantly higher than any superconductors known before the discovery of Bednorz and Müller,[2] could serve as a link between high-temperature and conventional superconductivity. The fact that Ba-K-Bi-O is an oxide material with a low density of carriers means that it has important similarities to the Cu-O plane high-T_c superconductors. It is, therefore, worthwhile to compare and contrast the properties of Ba-K-Bi-O with Cu-O perovskites and conventional superconductors, with a view to acquiring clues to the mechanism of superconductivity. In this paper, we report measurements of the thermal conductivity, $\kappa(T)$, of sintered $Ba_{1-x}K_xBiO_3$ and identify a dramatic difference from the Cu-O plane high-T_c superconductors regarding the effect of superconductivity on $\kappa(T)$.

Samples were prepared using the procedure of Dabrowski *et al.*[3] where the N_2 anneal was modified as discussed by Hinks *et al.*[4] Measurements of three samples are presented in this paper. Two superconducting samples, *A* and *B*, were prepared from a mixture of BaO, Bi_2O_3, and KO_2 powders of atomic ratio Ba:K:Bi =0.6:0.4:1. An insulating specimen, sample *C*, was prepared with the atomic ratio Ba:K:Bi=0.8:0.2:1. X-ray-diffraction patterns indicate that all three samples are single phase. Scanning electron micrographs (SEM) reveal samples of high density, with crystallites ~ 30 μm across. The electrical resistivity was measured using the four-probe dc technique. Indium contacts were attached to the samples with an ultrasonic soldering iron. Field-cooled magnetization was carried out in a Quantum Design magnetometer at a field of 30 Oe. Resistivity and magnetization data are displayed in Fig. 1. Measurements indicate an onset superconducting transition temperature of 25.5 and 27.5 K for samples *A* and *B*, respectively.

Measurements of the thermal conductivity were made with the standard steady-state technique. Both the two heater–one thermometer and two thermometer–one heater methods were employed. As temperature sensors we used calibrated germanium and platinum resistance thermometers. For the measurements performed in a magnetic field, we used calibrated carbon-glass resistance thermometers. The heat flow in this case was perpendicular to the field. Our heaters were small metal film resistors attached to the sample with Stycast epoxy. The uncertainty in the thermal conductivity data is estimated as 1.5%.

The resistivity $\rho(T)$ of our superconducting samples is very large and decreases with increasing temperature above T_c (see inset in Fig. 1). This behavior is similar to that seen by other authors,[3-6] although there is consider-

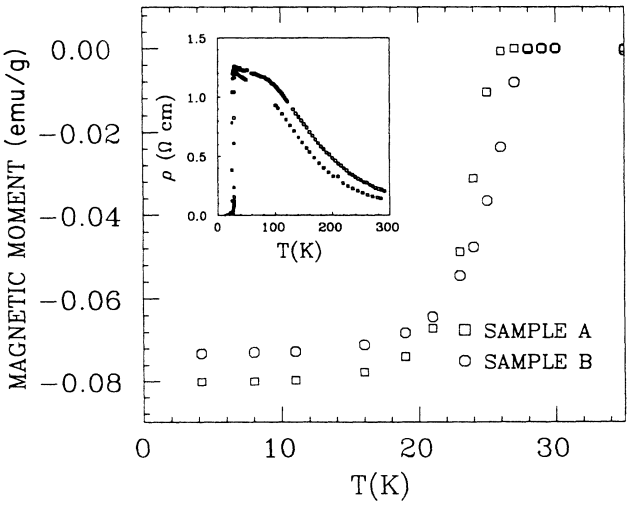

FIG. 1. Field-cooled magnetization for samples *A* and *B*. The inset is the resistivity of the same samples.

able variation, some samples having a smaller resistivity with less temperature dependence. Above about 190 K, the resistivity of our samples is consistent with the $\exp(T_0/T)^{1/4}$ behavior expected for variable-range hopping in disordered semiconductors, as previously seen by Dabrowski *et al.*[3] We obtain a value of $T_0=2.7\times10^6$ K, slightly larger than that calculated in Ref. 3. The temperature dependence below 190 K is weaker than the hopping conduction model implies.

Overall, the thermal conductivity of Ba-K-Bi-O (Fig. 2) is somewhat smaller than that in sintered Y- and La-based superconductors, but it is huge compared to the thermal conductivity expected from applying the Wiedemann-Franz law to the electrical resistivity. The value of the ratio $L=\kappa/\sigma T$, where σ is electrical conductivity, is extraordinarily large, about 3.0×10^{-4} V^2K^{-2} at a temperature of 30 K, i.e., more than 4 orders of magnitude larger than the Sommerfeld value $L_0=2.44\times10^{-8}$ V^2K^{-2} for electronic conduction with the same relaxation time for electrical and thermal resistivity.

In previous high-T_c materials investigated, a value of L an order of magnitude larger than L_0 has been interpreted[7] as demonstrating a dominance of the heat current due to phonons over that due to electrons, which then provides a natural explanation for the peak in $\kappa(T)$ seen below T_c. Perhaps a bit surprisingly, in Ba-K-Bi-O, with an even greater value of L, no sign of a peak in $\kappa(T)$ below T_c is seen. Indeed, the data suggest a decrease in $\kappa(T)$ below T_c rather than an increase. We have confirmed this by remeasuring the thermal conductivity in a field of 6 T that suppresses the superconducting phase boundary to about 18 K. The thermal conductivity above T_c ($\sim$27 K) is unaffected, but it increases upon application of the field below this temperature (Fig. 3), showing that the effect of the superconductivity is to decrease $\kappa(T)$ in Ba-K-Bi-O. Such behavior is expected in conventional superconductors in which charge carriers carry the heat current.[8] We, therefore, suggest that the thermal conductivity in Ba-K-Bi-O is dominated by the charge carriers (holes), and that the huge values of the ratio L arise from the granular nature of the material, as follows. In the simplest case, we model the system by metallic and semiconducting regions

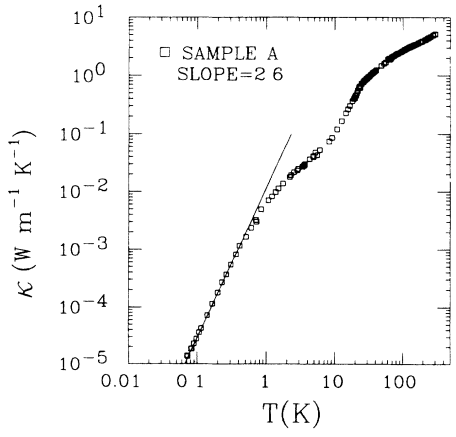

FIG. 2. Thermal conductivity for sample A from 70 mK to 300 K.

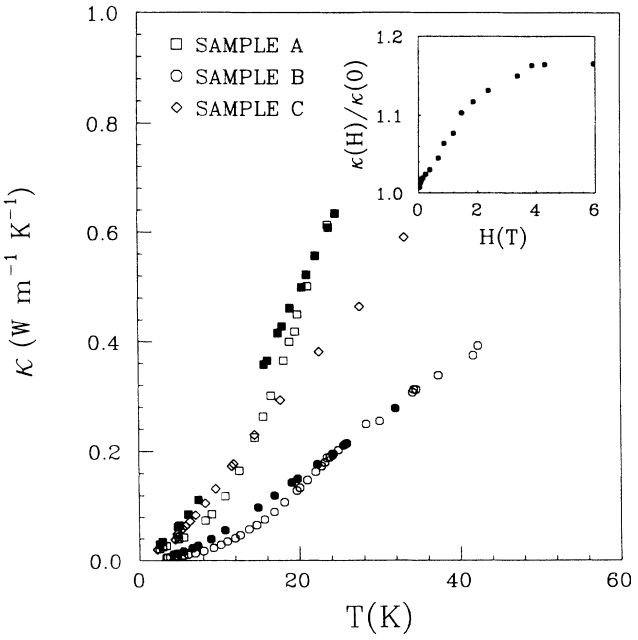

FIG. 3. Thermal conductivity of samples A, B, and C in the region near T_c. The solid squares and circles are for the measurements performed in a 6-T field. The inset shows the ratio $\kappa(H)/\kappa(0)$ of the thermal conductivity for sample B in a magnetic field to the thermal conductivity in zero field, as a function of field strength at constant temperature (20 K).

with the same cross-sectional area in series, so the electrical resistivity is

$$\rho=(1-y)\rho_1+y\rho_2 \tag{1}$$

and the thermal conductivity is given by

$$\kappa^{-1}=(1-y)(\kappa_{e1}+\kappa_{p1})^{-1}+y(\kappa_{e2}+\kappa_{p2})^{-1}, \tag{2}$$

where y is the nonmetallic fraction of the path, κ_{e1} and κ_{p1} are the electronic and phonon thermal conductivities, respectively, in the metallic regions, and ρ_1 is the resistivity of the metallic region. Similar quantities with subscript 2 refer to the barrier regions. We expect $\rho_2\gg\rho_1$, so, even for thin barriers, the resistivity can be dominated by the semiconducting regions. The electronic components κ_{ei} of the thermal conductivity are related to the corresponding components of the resistivity by the appropriate Lorenz numbers L_i, with $L_i\sim L_0$ for elastic scattering (and smaller values for inelastic scattering by phonons). Thus $\rho_2\gg\rho_1$ implies $\kappa_{e2}\ll\kappa_{e1}$, but because we can have $\kappa_{e2}\ll\kappa_{p2}$ (i.e., the phonons can propagate heat with reasonable efficiency across the barriers), the thermal resistance is not necessarily dominated by the barrier regions in the same way as the electrical resistance.

Clearly, in our case we must have κ_{e1} at least of a similar size to κ_{p1} in the metallic regions for the change in electronic thermal conductivity κ_{e1} due to superconductivity to have a large effect on the total thermal conductivity; we also require y to be very small, i.e., the barriers very thin so they do not dominate the thermal resistance. This thinness is, of course, consistent with the achievement of the zero resistance state seen in many samples.

In this way we can resolve the apparent contradiction between the electronic behavior of the thermal resistivity and the nonmetallic behavior of the electrical resistivity. Since, very roughly, $\rho \sim y\rho_2 \gg \rho_1$ and κ is comparable in magnitude to κ_{e1}, the value of $L = \kappa\rho/T$ can be very large, as observed. A similar barrier picture has been used[9] to resolve the discrepancy between metallic thermopower and nonmetallic resistivity in highly conducting polymers, since the thermopower of conductors in series is weighted in favor of those sections with the largest temperature gradient across them. This picture of Ba-K-Bi-O is supported by the observation[6] that the thermopower above 100 K shows linear metallic behavior in a sample with a similar nonmetallic resistivity to ours.

We estimate the intrinsic resistivity of the metallic grains in sample B to be on the order of 120 $\mu\Omega$ cm by taking $\kappa \sim \kappa_{e1}$ [since the term κ_{p1} in Eq. (2) increases κ above κ_{e1} while κ_{p2} decreases it] and applying the Wiedemann-Franz law, with L_1 taken to be equal to L_0. This is orders of magnitude smaller than the observed resistivity. It is still 100 times smaller than the smallest resistivity observed thus far (sample of Hinks *et al.*[4]), suggesting that a similar granular picture could be applicable for such samples as well.

At very low temperatures (below 0.5 K), the thermal conductivity varies as a power law T^n with $n = 2.6$ (Fig. 2). This is close to the behavior expected for phonon transport limited by boundary scattering. Extending the specific-heat data of Stupp *et al.*[10] down to 0.1 K and using the sound velocity of Lang *et al.*[11] we estimate the phonon mean free path at 0.1 K of about 6 μm. Although this is smaller than the average grain size in our samples and it might suggest the presence of some intragrain phonon-scattering mechanism, it is not an unreasonable estimate. We infer that the electronic thermal conductivity has been strongly suppressed by the superconductivity at these temperatures which allows the phonons to dominate. There is no evidence, even down to 70 mK, of a linear-T law as found[7,12–14] in some sintered Cu-O superconductors (except those based on Bi) in spite of the fact that, in Ba-K-Bi-O, the electronic term in $\kappa(T)$ dominates near T_c. We conclude that all free charge carriers in the metallic regions have condensed (charge carriers in the barrier regions appear to be localized).

We plot in Fig. 4 the ratio of the total thermal conductivities in the superconducting and normal states κ_s/κ_n versus the reduced temperature T/T_c. The normal-state values were obtained by the application of a 6-T magnetic field, which shifts the superconducting boundary to lower temperatures ($\sim$18 K). The values of T_c used, found by extrapolating $\kappa(H=0)/\kappa(H=6\text{ T})$ to unity, are 25.3 and 23.5 K for samples A and B, respectively. These values are, in each case, 8% smaller than those deduced from the onset of the Meissner effect in our magnetometer measurements. The appropriate T_c for thermal conductivity is lower than that for magnetization because the thermal conductivity is strongly dependent upon the volume of the superconducting regions, while the Meissner signal appears as soon as a small fraction of the inhomogeneous sample is superconducting.

On viewing these curves, one is immediately struck by

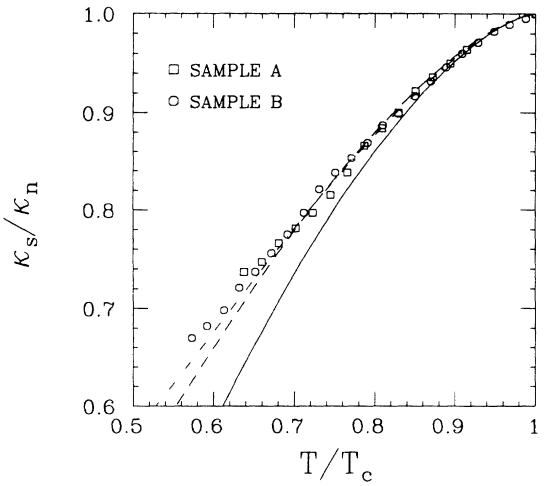

FIG. 4. The ratio $\kappa(H=0)/\kappa(H=6\text{ T})$ of thermal conductivity in zero field to that in a 6-T field for both superconducting samples, with the temperature scale normalized by effective transition temperatures 23.5 K for sample A and 25.3 K for sample B (see text). As discussed in the text, the 6-T field only drives the sample normal above $T/T_c \gtrsim 0.7$. The expected behavior of κ_{es}/κ_{en} for the weak-coupling (solid curve), and strong-coupling (dotted curve) cases are shown. Also shown are two curves representing the predictions of the strong-coupling model with the addition of a phonon contribution: $r_1 = 0.45$, $r_2 = 0$ (dash-dotted curve) and $r_1 = 0.25$, $r_2 = 0.25$ (dashed curve). See text for definitions of r_1 and r_2.

the significant size of the fractional decrease in $\kappa(T)$, in spite of the likelihood of substantial phonon contributions in the metallic regions as well as in the barriers. The fact that the data of Fig. 4 for two samples of different thermal conductivity agree rather well suggests that the effect is reproducible. This implies that phonons must make a similar *relative* contribution to the conduction in each case. Such behavior is expected if disorder scattering is different in the two samples but has a similar effect on the electron and phonon currents. Note that below $T/T_c \sim 0.7$ an upward divergence in the curve with decreasing T/T_c will occur because, in this region, the 6-T magnetic field does not exceed the upper critical field.

In weak-coupling theory, the decrease in thermal conductivity of the electrons (limited by scattering off impurities and defects) as the electrons form superconducting pairs is described[8] by a universal function of $\Delta(T)/T$, where $\Delta(T)$ is the temperature-dependent gap in the energy spectrum, and, therefore, of the reduced temperature T/T_c. The expected decrease in κ_{es}/κ_{en}, the ratio of the electronic thermal conductivity in the superconducting and normal states, for the strong-coupling case is larger than that for weak coupling. For example, the initial decrease for a strong-coupling superconductor like Pb for the defect scattering case is predicted, following Geilikman and Kresin,[8] to be nearly double that found in weak-coupling superconductors. The ratio κ_{es}/κ_{en} for the two coupling cases is plotted in Fig. 4 for comparison with the measured reduction in $\kappa(T)$. We have assumed in the construction of these curves that defect scattering is dominant.

From inspection of Fig. 4, we note that the weak-coupling model for κ_{es}/κ_{en} better approximates our data for κ_s/κ_n. Both theoretical curves, however, lie below the experimental results. The presence of a phonon contribution to the thermal conductivity can account for this discrepancy; if phonons contribute to the thermal transport, $\kappa(H=0)/\kappa(H=6\ \mathrm{T})$ will be an overestimate of κ_{es}/κ_{en}. We have calculated the phonon contribution required for a theoretical fit to the experimental data for the weak- and strong-coupling cases. κ_{p1} and κ_{p2} are assumed to vary as $T^{1.2}$ as in the insulating sample. The weak-coupling model requires the introduction of only a small phonon contribution to match the experimental results. Good agreement is obtained by taking the fractional phonon contribution to the conductivity in region 1 at T_c, $r_1=\kappa_{p1}/(\kappa_e+\kappa_{p1})$, to be 0.15 and neglecting the fraction of the thermal resistance due to region 2 phonons in series with the electronic thermal resistance in region 1 at T_c, $r_2=W_{p2}/(W_e+W_{p2})$. Here W_{p2} is the phonon thermal resistance of region 2 and W_e is the electronic thermal resistance of region 1. Another successful combination of parameters is $r_1=0.08$ and $r_2=0.08$. For the strong-coupling case two-parameter combinations are presented and plotted in Fig. 4: $r_1=0.45$, $r_2=0$ (dash-dotted curve) and $r_1=0.25$, $r_2=0.25$ (dashed curve).

One can see that a critical factor in determining which of the two coupling models is suggested by our data is the fractional phonon conductivity in region 1. The above examples demonstrate that, if a significant phonon contribution in this region exists, our data are consistent with a strong-coupling model. The possibility that there is such a contribution is supported by the following:

(i) The thermal conductivity of sample C, which is entirely due to phonons, is comparable to the total thermal conductivity measured for samples A and B. It should be noted, however, that the phonon thermal conductivity in sample C is, perhaps, somewhat exaggerated by the absence of electron-phonon scattering.

(ii) The electron thermal conductivity, if limited only by scattering from imperfections and impurities, decreases linearly with decreasing T in the region above T_c. Yet, the measured temperature dependence of $\kappa(T)$ for the superconducting samples in this region is equal to that of the insulating sample (~ 1.2). This suggests the presence of a phonon component, which is expected to have a faster T variation.

Although these effects are difficult to quantify in this complex material, we conclude that the size of the reduction we observe in the thermal conductivity below T_c is consistent with a *strong-coupling* mechanism for the superconductivity. Further investigations on single-crystal or high-quality polycrystalline specimens for which the Wiedemann-Franz law applies would allow a more precise quantification of the phonon contribution to the thermal conductivity and, hence, a more definitive estimate of the coupling strength in this material.

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