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Magnetothermal conductivity of $Ba_{1-x}K_xBiO_3$ crystals

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We have investigated the thermal conductivity of single-crystal $Ba_{1-x}K_xBiO_3$ (BKBO). The measured temperature and field dependences reveal that both electrons and phonons contribute to the thermal conduction of BKBO in both the normal and the superconducting states, and that the phonon mean free path can be manipulated by potassium doping concentration. The potassium-underdoped samples exhibit a suppression of phonon diffusivity, and consequently a more pronounced electronic contribution, indicating that the statistical fluctuation of potassium concentration may lead to an increase of defect density. The field-dependent thermal conductivity of BKBO in the superconducting state exhibits scaling behavior, which indicates the presence of an unconventional superconducting gap.

The unique physical and structural properties of $Ba_{1-x}K_xBiO_3$ (BKBO) (Refs. 1 and 2) have drawn much attention. The interest is centered around three aspects of the system. First, unlike other high-temperature superconductors, BKBO is copperless and it lacks the layered structure associated with Cu-O planes. The latter is thought to be the essential ingredient for causing high-temperature superconductivity. Second, with a cubic crystal structure and without a magnetic ground state, BKBO should have a relatively simple model Hamiltonian and no complication arising from antiferromagnetic interactions. Third, the presence of a clean gap[3] and of an isotope effect[4] both support electron-phonon coupling as the mechanism for superconductivity in BKBO. Due to the abrupt metal-insulator transition as a function of K concentration and the presence of mixed phases,[5,6] the electrical resistivity of BKBO is high; thus galvanomagnetic transport measurements are very difficult. Thermal transport, on the other hand, avoids these problems, and it probes directly the behavior of carriers and phonons in both normal and superconducting states.[6,7] Thermal conductivity of polycrystalline BKBO has been studied earlier.[8] The reported behavior is consistent with strong scattering by grain boundaries. In this paper we report results on temperature and field dependences of thermal conductivity of BKBO single crystals. We show that in the superconducting state the thermal conduction of BKBO is different from those of both high-temperature and conventional low-temperature superconductors, and that the contributions from phonons and electrons to the transport can be manipulated by the amount of K doping.

The single-crystal samples used in this research were prepared by a top-seeded electrochemical technique with nominal stoichiometric concentrations of potassium.[9] They were typically 1–2 mm long and about 1 mm across. The stoichiometric range, however, is very broad. Thermal gradient was established by a resistive heater mounted at one end of the crystal, with the other end anchored on the copper block of the magnet cryostat, and it was measured by constantan-chromel differential thermocouples. Results from two BKBO crystals with different K doping are discussed in this paper. They correspond to limiting behaviors of thermal transport in BKBO. Sample A with superconducting transition temperature T_c of 18 K has a higher K concentration (~ 0.46) than sample B (~ 0.37), which has a T_c near 30 K; hence sample B is referred to as the "underdoped" sample. Our magnetization measurements show that the transitions are 4–8 K wide with their midpoints defined as T_c.

The different temperature dependences of thermal conductivity $\kappa(T)$ for samples A and B are shown in Fig. 1. They represent various scattering processes that involve different length scales in these samples. The underdoped sample B exhibits a strong suppression of thermal conductivity compared with sample A, more than a factor of 10 at low temperatures [Fig. 1(b)]. This is attributed to a reduction in the phonon mean free path in underdoped samples due to defects. The estimated phonon mean free path for sample B at 25 K is about 10 Å using data from specific-heat measurements,[10] and it is expected to be even shorter at higher temperatures. This length scale corresponds to a defect density of nearly one per unit cell. The apparent high defect density may arise from statistical fluctuations of dopand concentration from one unit cell to another in underdoped samples. The high-temperature behavior of sample B exhibits a slow increase with temperature [Fig. 1(a)]. The behavior is consistent with the short mean free path, and thus a glasslike temperature dependence.[11] It is not that unusual to see glassy behavior in crystalline materials; other examples do exist.[12,13] The behavior for sample A, on the other hand, exhibits a decrease as temperature increases indicating a strong phonon contribution dominated by umklapp

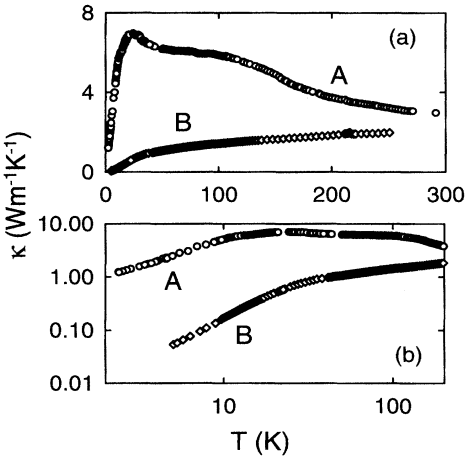

FIG. 1. Temperature dependence of the thermal conductivity for samples A (open circles) and B (open diamonds): (a) linear plot, and (b) log-log plot.

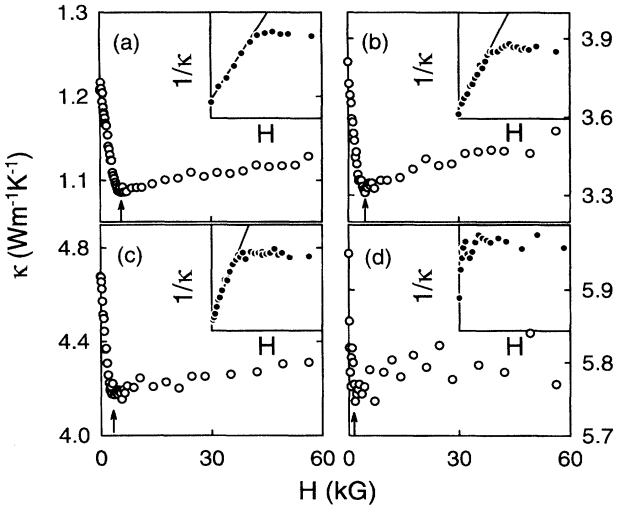

FIG. 2. Field-dependent thermal conductivity for sample A at four different temperatures: (a) 2.5 K, (b) 7.4 K, (c) 9.2 K, and (d) 13.8 K; insets: the corresponding thermal resistivity. The arrows indicate H_d, and the solid lines indicate linear behavior.

processes.[11] This is consistent with a low defect density and the crystalline nature of the sample.

As temperature decreases, the rise in heat conduction of sample A slows down; then it rises to a distinct peak around 23 K, before it drops at lower temperatures (Fig. 1). Sample B exhibits no such peak, but also exhibits a similar decrease at low temperatures (Fig. 1). The peak observed in sample A evidently arises from the transition between the high-temperature rise and the low-temperature drop due to phonon scattering by imperfections.[11] We believe that it is not directly related to the onset of superconductivity, because it occurs well above T_c. The observed low-temperature behavior above 2 K appears to be within a transitional regime, consistent with a continuous shift to longer-wavelength phonons. The ultimate low-temperature dependence will require extending measurements to temperatures below 2 K. As mentioned above, the grain boundaries and scattering centers in these samples arise from the inevitable statistical fluctuations of K doping concentration. We have ruled out the electronic thermal conduction at this temperature because most electrons are condensed into Cooper pairs. A strong suppression of quasiparticle scattering[14] is also not consistent with the field-dependent results discussed below.

More evidence on a large phonon thermal conduction of sample A is obtained from the field-dependent behavior shown in Fig. 2 at various temperatures. For increasing field, the thermal conductivity κ drops initially at low field and, after reaching a "dip" at H_d, it exhibits a slow rise to saturation. The initial rise in thermal resistivity $1/\kappa$ (Fig. 2, insets) is due to additional phonon scattering by magnetic vortices as the sample enters a mixed state. It cannot be attributed to electron scattering by vortices because the electron mean free path is less than 10 Å, as indicated by results from our measurements and those of others.[5] For a "dilute" system of vortices, the additional phonon scattering is approximately laH/Φ_0 (Ref. 15) with l the phonon mean free path, a the diameter of the vortex line, Φ_0 the flux quantum, and H the magnetic field. Note that the cross section of the vortex line is approximately equal to the superconducting coherence length. The phonon thermal conductivity $\kappa_{ph}(H)$ in this limit, is therefore, given by[15]

$$\frac{1}{\kappa_{ph}(H)} = \frac{1}{\kappa_{ph}(0)}\left(1+\frac{laH}{\Phi_0}\right). \quad (1)$$

The linear dependence on H fits the observation rather well (see insets in Fig. 2) with a slope that depends on the product of l and a. At higher fields the strong interaction between vortices leads to the formation of a flux lattice, and consequently phonon scattering by vortices diminishes; thus κ_{ph} no longer drops at H_d. This happens when the penetration depth λ is comparable to the separation of flux lines, so while λ increases with increasing temperature one expects H_d to decrease, as shown in Fig. 2.

The slow rise of κ above H_d arises from increasing electronic contribution due to the continuous breakup of Cooper pairs. This enables us to estimate the electronic contribution κ_e from the size of the total increase. At 4.6 K, κ_e is less than $\frac{1}{5}$ of the total κ at normal state. From this we estimate the phonon contribution to κ and the phonon mean free path l using the published specific-heat data;[10] at 4.6 K l is $\sim$4000 Å. The large mean free path makes the initial drop in κ possible because, if l is shorter than the average distance between vortices, κ_{ph} would not be affected by them. Note that the vortex spacing of 4000 Å corresponds to a field strength of $\sim$100 G. The observed large drop at low field further supports the notion that the phonon contribution is dominant at zero field.

In sample B the expected higher defect concentration would lead to a shorter phonon mean free path, hence a smaller phonon contribution to the thermal conduction. This in turn would result in a smaller or no phonon dip in κ at low fields, and consequently a larger electronic rise at high fields. Our measurements support this picture (see Fig. 3). As shown in Fig. 3, the much smaller phonon dip in sample B, which can only be resolved below 4.6 K, indicates a much shorter phonon mean free path ($\sim$100 Å at 4.6 K) compared

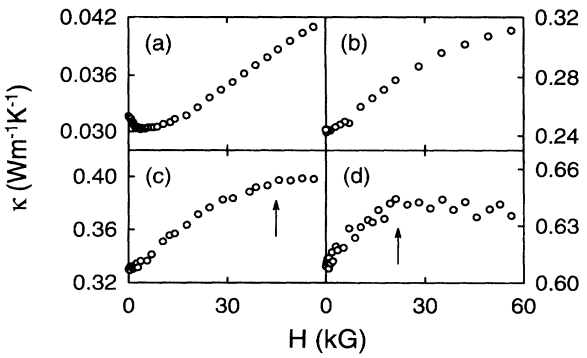

FIG. 3. Field dependence of thermal conductivity for sample B at four different temperatures: (a) 2.6 K, (b) 12.4 K, (c) 15.2 K, and (d) 23.9 K. The low-field phonon dip is suppressed. Arrows in (c) and (d) indicate H_*.

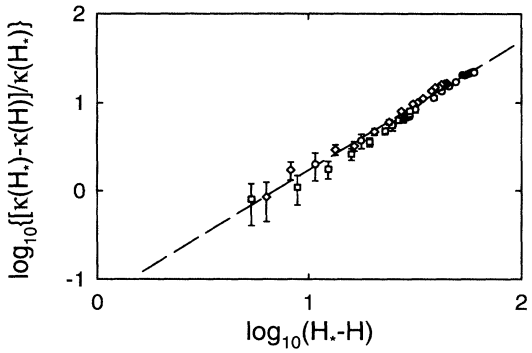

FIG. 4. Scaling behavior of thermal conductivity $\kappa(H)$, $\log_{10}[\kappa(H_*)-\kappa(H)]/\kappa(H_*)$ versus $\log_{10}(H_*-H)$, for sample B at three different temperatures: 12.4 K (circles), 15.2 K (diamonds), and 19.8 K (squares). The respective H_* for the three temperatures are 3, 4.5, and 6 T. The dashed line corresponds to a slope of 1.5.

to that in sample A; the large rise in κ indicates a much larger *fractional* electronic contribution in the normal state, even though the electronic thermal conductivity of sample B is actually comparable to that of sample A.

At higher fields, the measured thermal conductivity saturates at a critical field H_* which unexpectedly is far below the upper critical field $H_{c2}(>5.5$ Telsa just below $0.8T_c)$ obtained from magnetization measurements.[16] The behavior below H_* exhibits scaling in the form

$$\kappa(H_*)-\kappa(H)\sim(H_*-H)^{3/2}, \tag{2}$$

as shown in Fig. 4 for sample B. Equation (2) corresponds approximately to the electronic contribution to the thermal conduction in the superconducting state, κ_{es}. The $\frac{3}{2}$-power law differs from the linear behavior of the conventional dirty type-II superconductors[17] given by

$$\kappa(H_{c2})-\kappa(H)\sim(H_{c2}-H). \tag{3}$$

The observed functional dependence on field suggests the presence of a novel gap structure in BKBO. In what follows we derive self-consistently the effective gap from the observed field dependence [Eq. (2)].

According to the single-vortex model,[18] the effective gap ε for systems without a magnetic ground state is given by $\varepsilon=[\Delta^2/E_F-\mu_B H/2\alpha]$. The first term here corresponds to zero-field behavior which depends on the order parameter Δ and Fermi energy E_F; the second term is the Zeeman energy with μ_B the Bohr magneton and α the ratio between the effective mass and free-electron mass. For conventional superconductors, a relatively small field suppresses the effective gap due to the small ratio of Δ/E_F $(<\frac{1}{1000})$. This is not the case for high-temperature superconductors, where the Δ/E_F ratios is between $\frac{1}{10}$ and $\frac{1}{100}$.[19] With $\Delta\sim3.5T_c$ and $\alpha>1$, the effective gap in BKBO, therefore, should persist to fields as high as 6 T.

The dependence of thermal conductivity on energy gap for a BCS-like superconductor is described by the theory of Bardeen, Rickayzen, and Tewordt.[20] For temperature much greater than the effective gap, $\varepsilon\sim2$ K in the case discussed here, the theory predicts that $\kappa_{es}(H)\sim\varepsilon^3$. When compared with Eq. (2) this leads to a field-dependent energy gap given by

$$\varepsilon(H)\sim(H_*-H)^{1/2}, \tag{4}$$

with H_* the field at which the effective gap vanishes. The measured H_* coincides with magnetic irreversibility field obtained from magnetization measurements.[16] The latter field signals the onset of supercurrent. It is reasonable to conclude that both fields are the same, and that they also determine the onset of the unconventional superconducting gap given by Eq. (4).

The mean-field-like superconducting gap, indicated by the exponent of $\frac{1}{2}$, appears to exist in all BKBO crystals we have studied. However, its effects on thermal conductivity are more pronounced in potassium-underdoped samples with higher T_c, because the phonon contribution is suppressed by the higher defect concentration, as discussed above. The presence of a robust gap with a relatively high critical field H_* suggests that the electron-phonon interactions in BKBO are quite strong. While potassium concentration affects directly the thermal conductivity of BKBO through phonon diffusion length, it does not appear to influence the form and strength of the gap.

In summary we have studied the thermal conductivity of BKBO crystals in a wide range of temperatures and fields. The different roles of electrons and phonons on thermal conduction are identified. Our results reveal that both thermal conductivity and superconducting transition can be tuned by K doping concentration, and that the statistical fluctuation of the K concentration determines the phonon diffusion length. The observed scaling behavior for the high-field thermal conductivity indicates the presence of an unconventional and mean-field-like gap structure in BKBO. The gap and the related phenomena reveal insight into the fundamental processes that cause the superconductivity in BKBO, and they warrant further investigations.

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