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Thermoelectric power of $Ba_{1-x}K_xBiO_3$

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We report measurements of thermoelectric power of two superconducting samples of $Ba_{1-x}K_xBiO_3$ with differing resistivity behaviors. The thermopower is negative between 50 and 300 K. We find in both samples an unusual temperature dependence similar to that in high-oxygen-content samples of Y-Ba-Cu-O with negative thermopower, suggesting a common mechanism producing this behavior in $Ba_{1-x}K_xBiO_3$ and the Cu-O-plane superconductors. Our sample with an activated temperature dependence of resistivity shows a change to positive thermopower before becoming superconducting, possibly due to the effect of nonmetallic grain boundaries.

INTRODUCTION

The copperless, cubic oxide superconductors $Ba_{1-x}K_xBiO_3$ with $x \sim 0.3-0.4$ undergo a transition to a superconducting state[1,2] near 30 K and represent an interesting material that is viewed as a link between the traditional superconductors and the Cu-O-plane high-T_c superconducting perovskites. Unlike the Cu-O-plane oxides, $Ba_{1-x}K_xBiO_3$ contains no magnetic ions, has a large isotope effect,[3-5] and shows other features[6,7] that suggest the electron-phonon mechanism of superconductivity may be relevant. Furthermore, due to the presence of wide 6*s*- and 2*p*-electron bands near the Fermi level, instead of *d* electrons, strong correlation effects that are so typical of Cu-O-plane superconductors are here believed to be much less important. Nevertheless, $Ba_{1-x}K_xBiO_3$ is an oxide with a low carrier density in which superconductivity occurs on the metallic side of the metal-insulator transition and a proper understanding of its transport and superconducting properties is essential before a final judgment is passed regarding the origin of its superconductivity.

Early papers[8,9] indicate a material with high electrical resistivity and an activated character of the temperature dependence that could, over a limited temperature range, mimic variable-range hopping.[10] In more recent studies, following improvement of the synthesis techniques,[11,12] the resistivity has been brought down to the 10-mΩ cm level and a positive slope of $d\rho/dT$ has been observed below ~ 170 K. However, a *T*-linear dependence extending over the full temperature range, so typical (and puzzling) of the Cu-O-plane superconductors, has not yet been reported. It is worth pointing out that, in spite of the preponderance of $Ba_{1-x}K_xBiO_3$ samples being single-phase materials, the resistivity of even the best specimens is still some two orders of magnitude higher than those of Cu-O-plane superconductors. Presumably, the carrier transport is impeded by nonconducting precipitates at the grain boundaries.

Although the thermoelectric power is a more complicated transport parameter than is the resistivity, it is often less affected by sample imperfections, as explained below. Its sign is frequently used to assess the polarity of the dominant charge carriers. In addition, a careful analysis of its temperature dependence may help in understanding the scattering mechanism of the carriers and, in certain situations, even provide an estimate of the magnitude of the Fermi energy. Regarding the $Ba_{1-x}K_xBiO_3$ system, there are two reports in the literature[13,14] describing the behavior of the thermoelectric power; unfortunately, there is little agreement between these two sets of data and, over most of the temperature range, even the signs of the thermopower contradict each other. In order to ascertain the behavior of the thermoelectric power in $Ba_{1-x}K_xBiO_3$ and to clarify the effect of synthesis conditions on this transport parameter, we have made careful measurements on two samples of nominally the same composition, but with markedly different electrical resistivities that originate as a consequence of somewhat altered preparation procedures.

EXPERIMENT

Starting materials for the synthesis were BaO, Bi_2O_3, and KO_2 powders mixed in the appropriate ratios to produce a superconducting structure with $x = 0.4$. One sample, designated sample *A*, was cut into a rectangular shape of $12 \times 2.45 \times 1$ mm^3 from a disk made using the procedure of Dabrowski *et al.*,[10] where the N_2 anneal was modified as discussed by Hinks *et al.*[15] This sample had a rather high resistivity, $\rho(273\text{ K}) = 231$ mΩ cm, and a distinctly activated temperature dependence of the resistivity, see Fig. 1. Sample *B* of dimensions $12 \times 2.7 \times 1.9$ mm^3 was prepared following the

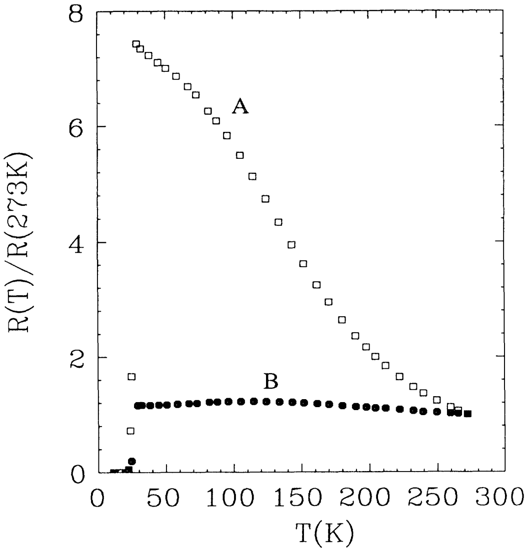

FIG. 1. Temperature dependence of the electrical resistivity of $Ba_{0.6}K_{0.4}BiO_3$ normalized to its value at 273 K. Sample *A* is designated by open squares; sample *B*, by solid circles.

modifications of the above procedure by Folkerts *et al.*[12] and showed a much lower resistivity, $\rho(273\ \mathrm{K}) = 19.1\ \mathrm{m}\Omega\,\mathrm{cm}$. It displayed a small negative temperature coefficient of resistivity which, below about 150 K, changed into a weakly metallic dependence. We note that smaller samples prepared in this way had room-temperature resistivities as low as 6 mΩ cm and displayed an approximately linear temperature dependence of resistivity from 300 down to 33 K. Samples *A* and *B* had a similar onset of the superconducting transition near 26.5 K and the resistance transition was completed at about 24.5 K. The average grain size of both samples estimated from scanning electron microscope (SEM) data is about 10 μm.

We employed a traditional steady-state technique for the determination of the thermoelectric power. Although this technique is well known and time tested, great care must be used when applying it to the determination of the absolute thermopower of high-T_c materials. This is because the leads attached to the sample that measure the thermoelectric voltage also have their ends subjected to a temperature difference and, so, one does not measure just the absolute thermopower of the sample but also a contribution arising from the leads. Obviously, one has to correct for the thermopower of the leads. The difficulty with high-T_c materials stems from the fact that their absolute thermopower is frequently smaller than the thermopower of the leads. The measured thermoelectric voltage is then dominated by the leads and, unless their absolute thermopower is well known, an improper correction or no correction for the leads may not only affect the magnitude of the investigated thermopower but can also result in a wrong sign of the effect. In order to carry out meaningful thermopower investigations, it is essential that the absolute thermopower of the reference leads is on hand. How one can readily obtain this information is described elsewhere.[16,17] Here it suffices to note that we have used a 44 S.W.G. copper wire, the absolute thermopower of which we established to better than 1% accuracy ($\leq 0.01\ \mu$V/K) from measurements against $Tl_2Ca_2Ba_2Cu_3O_{10}$ superconductor up to 120 K. At higher temperatures the copper wire was calibrated against a Pb reference wire using the tables of Roberts.[18] Reliable electrical contacts to the sample are made with indium using an ultrasonic soldering iron. The corresponding temperature difference is determined with the aid of a Chromel-Constantan differential thermocouple backed by a pair of calibrated Pt sensors.

RESULTS

The absolute thermopower of samples *A* and *B* is displayed in Fig. 2. We point out the small magnitude of the thermopower and a negative sign over most of the temperature range. Sample *A* shows a small positive thermopower below 40 K, which is truncated by the onset of superconductivity. It is possible that sample *B* would also display a crossover to a positive thermopower at very low temperatures had not superconductivity set in. There is surprisingly little difference between the thermopower of samples *A* and *B* given the vastly different behavior of their resistivities. Comparing our thermopower data with the existing two reports in the literature, we note the following: Judging by the room-temperature resistivity of $\rho(300\ \mathrm{K}) \sim 90\ \mathrm{m}\Omega\,\mathrm{cm}$ and $\rho(30\ \mathrm{K})/\rho(272\ \mathrm{K}) \sim 8$, the sample of Sera *et al.*[13] is of similar quality to our high-resistivity sample *A*. Yet these authors report that their thermopower is positive

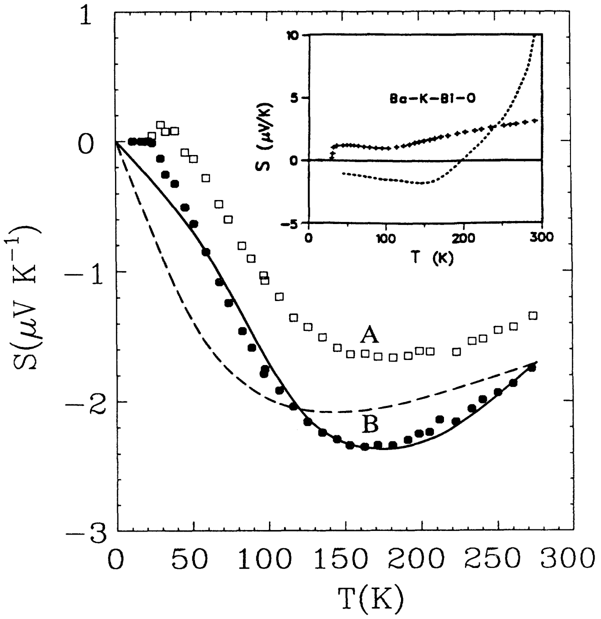

FIG. 2. Thermoelectric power of $Ba_{0.6}K_{0.4}BiO_3$. Samples *A* and *B* are designated by the same symbols as in Fig. 1. The data are compared to theoretical curves showing the effect of the electron-phonon interaction (see text). The inset, adapted from Ref. 17, shows the thermopower data of Sera *et al.* (Ref. 13) (crosses) and Pekala *et al.* (Ref. 14) (dashed line).

throughout the temperature range (see the inset in Fig. 2). They use gold as reference leads and they mention[5] possible errors arising from its contribution to the thermopower. They also find a conflict between the sign of their thermopower and the Hall effect that they report as having a negative sign. It is unusual, though by no means impossible, that the Hall effect and the thermopower signs differ. Preliminary data on our samples indicate that the Hall effect is negative. Our thermopower results are in better accord with the measurements of Pekala *et al.*,[14] although a direct comparison is somewhat skewed by the very high resistivity of their sample quoted at 30 Ω cm. Their thermopower starts at a rather large positive value of $\sim 10\ \mu V/K$ at 300 K but rapidly decreases and becomes negative below 200 K. It shows a minimum near 150 K similar to that seen in our data and the thermopower then gradually decreases in magnitude as T_c is approached. Noting from Fig. 2 that the thermopower of a higher-resistivity sample A is less negative than that of the sample B, it may be possible that a sample with the resistivity some two to three orders of magnitude larger than those of our samples would in fact have a positive thermopower at ambient temperatures. Pekala *et al.* do not provide any information on the sign of the Hall effect and so it is difficult to speculate whether a pocket of positive carriers is responsible for the positive thermopower that they see near 300 K. In any case, the origin of the sharply rising thermopower that they observe at ambient temperatures is unclear.

DISCUSSION

The previous measurements of Sera *et al.*,[13] and of Pekala *et al.*[14] at low temperatures, suggested that the thermopower of $Ba_{1-x}K_xBiO_3$, rather than following the same pattern as the Cu-O-plane superconductors, might be more like the traditional behavior of metallic diffusion thermopower, i.e., being proportional to the temperature (in fact, as mentioned below, the presence of the electron-phonon interaction introduces nonlinearities to a greater or lesser degree). Our data, however, show a distinct similarity between the thermopowers of $Ba_{1-x}K_xBiO_3$ and the Cu-O-plane superconductors. In particular, the thermopower above 100 K shows only a small temperature dependence with a decrease in magnitude above 150 K rather than an increase, similar to the general behavior usually seen in single-crystal samples of $YBa_2Cu_3O_{7-\delta}$ (with negative or positive thermopowers) and reviewed in Ref. 17.

We have already found[7] a decrease in the thermal conductivity of $Ba_{1-x}K_xBiO_3$ samples below T_c as seen in typical conventional superconductors. Thus a major part of the heat current was carried by electrons in $Ba_{1-x}K_xBiO_3$, which was surprising in view of the nonmetallic behavior of the resistivity. We ascribed this apparently conflicting behavior to thin nonmetallic grain boundaries that affected electrical conductivity far more than thermal conductivity, because phonons can carry heat through the thin barriers. Then if electrons dominate transport within the grains, the electronic behavior can dominate the overall thermal conductivity.

The situation for thermopower is somewhat similar to that for thermal conductivity. The weighting for the thermopower contributions from different segments of material in series for inhomogeneous samples is proportional to the temperature drop T_i across each segment, e.g.,

$$S=\frac{W_1}{W}S_1+\frac{W_2}{W}S_2\ , \tag{1}$$

where W is the thermal resistance across the sample, and W_i and S_i are the thermal resistances and intrinsic thermopowers, respectively, of two types of material. Thus if phonons conduct heat across thin grain boundaries, the weighting factor W_2/W for the thin barriers is small, and the thermopower (unlike the resistivity) can be dominated by the metallic grain interiors. This, we suggest, is the reason why the thermopower has metallic size. A similar effect is thought to account for the strikingly metallic thermopower of highly conducting polymers in spite of the fact that their conductivity increases strongly with temperature.[19]

It is likely that the minor difference in thermopower between samples A and B arises from larger grain-boundary barriers (corresponding to larger resistivity) in sample A. A larger value of the barrier weighting factor W_2/W with a positive value of the barrier thermopower S_2 would account for an upward shift as observed. Semiconductorlike thermopowers typically remain larger than metallic thermopowers as the temperature decreases towards zero, so a grain boundary term such as that proposed can account for the change to positive thermopower in sample A below about 50 K (and also for the apparent trend towards positive values for sample B as the temperature is lowered towards T_c, if a smaller barrier term is also present in this sample).

Given the similarity of our measured thermopower in $Ba_{1-x}K_xBiO_3$ to that in $YBa_2Cu_3O_{7-\delta}$, it is natural to seek a common mechanism for the pronounced nonlinearities seen in each case. This similarity suggests that spin does not play a key role for thermopower in the Cu-O-plane superconductors, given that the susceptibility of $Ba_{1-x}K_xBiO_3$ is diamagnetic. An explanation of thermopower behavior in high-temperature superconductors is controversial and presents a major challenge for the various models proposed for the superconducting mechanism (a discussion of suggested theoretical explanations of the thermopower behavior has been included in our review[17]). Unfortunately, few predictions for thermopower behavior have been made for the most recent models.

One interesting suggestion[20] is an analogy between high-temperature superconductors and heavy-fermion metals, the thermopower peak for the cuprate superconductors being associated with a partially coherent Fermi liquid with a much larger coherence temperature (100–200 K) than for the heavy fermions. However, $Ba_{1-x}K_xBiO_3$ would need to have a coherent state (below a temperature similar to that in the Cu-O-plane superconductors to give a peak at similar temperatures), which would be surprising.

Phonon drag plays a major role in causing low-temperature peaks in the thermopower of crystalline metals, which disappear as the phonon and electron mean free paths are reduced by increasing the scattering (e.g., by increasing disorder). There does appear to be some evidence that phonon drag may also play a role in causing peaks above T_c in high-temperature superconductors,[17] but clear evidence for a decrease with increasing disorder of the broad peaks often seen appears to be lacking.

Thermopower nonlinearities can also arise in diffusion thermopower if there is strong structure in the density of states in the immediate vicinity of the Fermi surface, although these are usually more significant at higher temperatures. Rather special models are required to give large nonlinearities around 100 K, as reviewed previously.[17]

Very recently, it has been pointed out[21] that a thermopower temperature dependence similar to that in high-temperature superconductors has already been seen as a special case in ordinary metals with a tiny thermopower and explained in terms of the electron-phonon interaction.[22] In fact, metallic diffusion thermopower as observed in systems in which phonon drag is suppressed by disorder is virtually always nonlinear due to renormalization of the electron energy by the electron-phonon interaction. Usually this effect is seen in amorphous metallic alloys as a change in slope of thermopower around 50 K, or equivalently an approximately linear thermopower that does not extrapolate to zero at zero temperature. This behavior is expected very generally for metals, but in crystalline samples it is difficult to see it, owing to the problem of separating the phonon drag and diffusion terms. A thermopower nonlinearity in excellent agreement with that calculated for electron-phonon enhancement has, however, been seen in crystalline Chevrel-phase superconductors such as $Cu_{1.8}Mo_6S_{8-y}X_y$ (X=Te,Se) with random substitutions and short mean free paths.[23] Interestingly, the out-of-plane thermopower in several single crystals of the Cu-O superconductors follows this same pattern.[21]

If the electron-phonon interaction is greatly enhanced as calculated[24] for highly anharmonic phonons, the predicted thermopower nonlinearity at low temperatures is very large. The thermopower then deviates strongly from proportionality to T, and can yield behavior consistent with that observed for the in-plane direction of single crystals of the Cu-O-plane superconductors.[21] We point out here that this is also true for our measured thermopower in $Ba_{1-x}K_xBiO_3$. Metallic diffusion thermopower can be written

$$S = S_b + c\lambda_s(T)T \ , \tag{2}$$

where S_b is the unenhanced thermopower, c is a constant that may be of opposite sign to S_b (for example, if the total thermopower is a sum of components of different sign[21]), and $\lambda_s(T)$ is the electron-phonon enhancement of thermopower (which is equal to the usual electron-phonon coupling constant at zero temperature).

The dashed line in Fig. 2 shows the shape of the electron-phonon term $c\lambda_s(T)T$, calculated[23] assuming an Eliashberg function $\alpha^2F(E)$ proportional to the measured[25] phonon density of states $F(E)$ in $Ba_{1-x}K_xBiO_3$, with a quadratic extrapolation to zero below the limit of measurements. Clearly such a term could contribute to the pronounced nonlinearity observed in thermopower. The peak in $F(E)$ near 60 meV is much more prominent[25] in $Ba_{0.6}K_{0.4}BiO_3$ than in nonsuperconducting $BaBiO_3$. Further, tunneling measurements[6] find that the strength of tunneling structures corresponding to the optical model of the oxygen atoms between 40 and 65 meV indicates that $\alpha^2F(E)$ is weighted toward the high-energy side compared to $F(E)$. We have therefore also made calculations assuming $\alpha^2F(E)$ is dominated by the coupling of electrons to phonon modes above 40 meV, in which case the predicted peak in $c\lambda_s(T)T$ is shifted to higher temperatures. As shown by the solid line in Fig. 2, a good description of the data for sample B is obtained in this case with $c\lambda_s(0) = -19.1$ nV/K^2 and $S_b = 6.4$ T nV/K; an extremely strong coupling to some electrons showing a negative thermopower contribution would be required to produce an effect of this magnitude.[21]

CONCLUSION

We can summarize the main conclusions drawn from our data as follows.

(i) The thermopower of superconducting $Ba_{1-x}K_xBiO_3$ is similar to that seen for the in-plane direction of 1:2:3 superconductors. This new result tends to reinforce the view that $Ba_{1-x}K_xBiO_3$ should be regarded as being in the same category as the cuprate superconductors. This comment is not contradicted by the fact[7] that the effect of superconductivity on thermal conductivity is opposite in $Ba_{1-x}K_xBiO_3$ to that in the Cu-O-plane superconductors, since this difference arises from dominance of electronic heat conduction in $Ba_{1-x}K_xBiO_3$ but dominance by phonon heat conduction in $YBa_2Cu_3O_{7-\delta}$. In both cases the behavior is similar to that observed in conventional BCS superconductors, the large size of the observed effects in each material signifying a large coupling between the electron and phonon systems.

(ii) The sample inhomogeneities that appear to play a dominant role in the resistivity of $Ba_{1-x}K_xBiO_3$ samples prepared so far are much less important for the thermopower and thermal conductivity, since phonons can carry the heat current through nonmetallic intergrain boundaries.

(iii) Although other nonlinearities may, of course, be present, the shape of the large nonlinearity seen in the thermopower of $Ba_{1-x}K_xBiO_3$ is consistent with that expected from the electron-phonon interaction and seen to a lesser extent in diffusion thermopowers of normal metals.[17] If these electron-phonon effects are a major cause of the observed nonlinearities, there would have to be an extremely large coupling of some electrons to phonons. Such an interaction would obviously be consistent with other evidence[4-6,25] for an electron-phonon mechanism for the superconductivity in $Ba_{1-x}K_xBiO_3$. A recent model calculation[26] of the Eliashberg function $\alpha^2F(E)$ in $Ba_{1-x}K_xBiO_3$ indicates that higher-energy phonon modes between 40 and 60 meV couple far more strongly to the electrons than do modes at lower energies, in agreement with the tunneling measurements[6] mentioned above; this result provides further justification for our calculation assuming such dominance by higher-energy modes shown by the solid line in Fig. 2.

(iv) From an experimental point of view, due to generally very small thermopowers encountered in high-T_c superconductors, it is imperative that the absolute thermopower of the measuring leads (often comparable to, or even larger than, the thermopower of the sample itself) is well known and properly accounted for. Only then can one be sure that the data represent the true thermopower of the sample under investigation.

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