RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 16 1 DECEMBER 1987

Thermopower of $YBa_2Cu_3O_7$ and related superconducting oxides

H. J. Trodahl and A. Mawdsley
Physics Department, Victoria University of Wellington, Private Bag, Wellington, New Zealand
(Received 31 August 1987)

There is some disagreement in the literature concerning both the measured magnitude and the interpretation of the thermoelectric power of $YBa_2Cu_3O_7$. We report a series of measurements that have guided us to a satisfactory explanation of both our own results and those reported by other groups. Most important is that we have explained the surprising precursor peak just above T_c as resulting from an enhanced phonon mean-free path in the presence of superconducting fluctuations. We develop a model that permits us to separately estimate the values of the diffusion and phonon-drag contributions to the thermopower. At 100 K the diffusion component is estimated to be -14 μV/K, a large negative value that suggests conduction by a narrow electron band. The phonon-drag thermopower is positive with a magnitude that depends on crystallite grain size.

The thermoelectric power of the recently discovered high-T_c superconductor $YBa_2Cu_3O_7$ has been measured by a number of groups.[1-4] The results quoted are qualitatively similar, although there are differences in detail, and the authors have offered contradictory explanations of their results. Gottwick *et al.*[3] infer from the temperature dependence of their results that the conduction is by carriers in more than one band. Uher and Kaiser[2] also suggest multiband conduction, with a negative thermopower from an electron band partially canceling a positive contribution from a hole band. They have also suggested that a broad peak centered near 230 K is due to phonon drag. We interpreted our early results as a diffusion thermopower and suggested that the 230-K peak was due to a possible small concentration of a semiconducting phase.[1] As yet there is no convincing explanation for the surprising enhancement of the thermopower just above the superconducting transition temperature. Srinivasan *et al.*[4] have discussed this feature in terms of a few enhancement models used in normal metals, but without successfully identifying a likely explanation. Uher and Kaiser[2] have suggested that it is a phonon-drag peak that is truncated by the onset of superconductivity, though they admit that the rise is much more rapid than would be expected for a phonon drag peak. In order to form a clearer picture of the thermopower in these materials we have performed measurements on two samples of $YBa_2Cu_3O_7$, which have quite different microstructures, and on one sample of $GdBa_2Cu_3O_7$. Resistivity measurements have also been made as an aid to the interpretation of the thermopower data.

Our samples were prepared by the now familiar solid-state reaction,[5] and x-ray diffraction has established that they consist of at least 95% of the superconducting phase. The thermopower measurements were made against manganin reference leads which had been calibrated using the Pb data of Roberts.[6] Each of the samples was measured more than once, often remounted with different thermal and electrical contacts to ensure reliability. The resulting thermopower data, along with the corresponding resistivities, are displayed in Fig. 1. The results for the three samples are similar in that they are all positive, they show the enhancement just above T_c, and they have a broad peak centered on about 220 K. They do, however, show some variation in magnitude.

The clue to the interpretation of the thermopower is in the enhancement near T_c. Note first that this peak is significantly narrower in the $GdBa_2Cu_3O_7$ sample, which also shows the smallest accompanying drop in the resistivity. Clearly, the thermopower enhancement is a precursor feature related to the existence of superconducting fluctuations. Such a feature is not peculiar to these oxide superconductors, for it is found in Nb_3Sn (Ref. 7) and in an induced intermediate state of type-I superconductors.[8]

An explanation, mentioned in passing by Uher and Kaiser,[2] can be found in the reduced phonon-electron scattering in the superconducting regions, a reduction that is well known in classical superconductors and has already

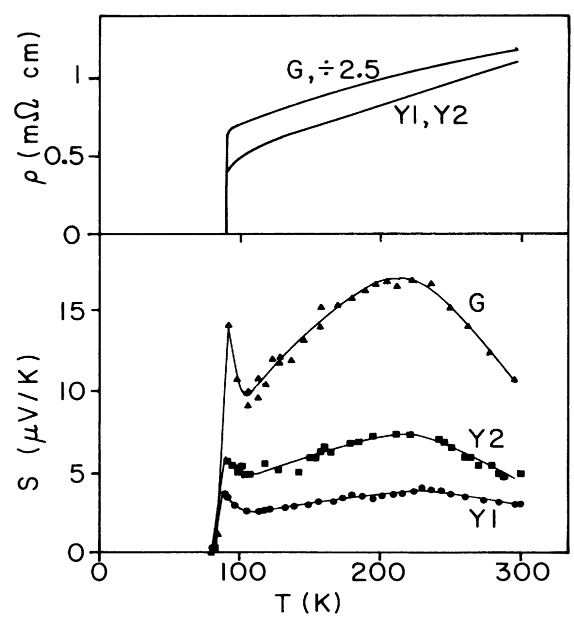

FIG. 1. Resistivity ρ and thermopower S of the samples of $YBa_2Cu_3O_7$ (Y1, Y2) and of $GdBa_2Cu_3O_7$ (G).

been observed in $YBa_2Cu_3O_7$.[2,3] It leads to an enhanced phonon flux in the normal regions of the mixed state near a superconducting boundary, which in turn enhances phonon drag. The diffusion thermopower is, of course, not enhanced. The net thermopower as T_c is approached from higher temperatures is then a weighted average of the normal and superconducting thermopowers. Since the superconducting regions contribute no thermopower, the mixed state will show simply a reduced normal-state thermopower, but the enhancement described above causes the drag thermopower to fall significantly more slowly than the diffusion thermopower. Within this picture the precursor peak can be interpreted as no more than a falling negative diffusion thermopower lying under a broad positive phonon-drag feature.

We now present a simple model which identifies the important parameters in the phonon-drag enhancement. The phonon-drag thermopower is proportional to the net phonon momentum set up by a temperature gradient,[9] and is, therefore, proportional to the temperature difference at a point distant by one phonon mean-free-path Λ. In the normal-phase region near a superconducting fluctuation, about one half of the phonons have passed through the superconducting region, altering their contribution to the momentum. On the average, a phonon scattered in the normal region will have traveled through superconducting regions for a portion of its path equal to the volume fraction f filled by the superconducting fluctuations. The effective mean-free-path Λ_e then becomes

$$\frac{1}{\Lambda_e}=\frac{f}{\Lambda_s}+\frac{1-f}{\Lambda_n} , \tag{1}$$

or

$$\Lambda_e=\Lambda_n/[1-(1-\beta)f] , \tag{2}$$

where

$$\beta=\Lambda_n/\Lambda_s<1 , \tag{3}$$

and Λ_n,Λ_s are the phonon mean-free paths in the normal and superconducting regions. The average momentum of phonons scattered in the normal-phase region, and thus also the phonon-drag thermopower, is enhanced by the same factor as the mean-free path.

The net thermopower is, as stated above, a weighted average, but the form of weighting is not clear. The contributions of the two phases should be weighted by their thermal resistances if they are regarded as connected in series, but by their electrical conductances if in parallel.[10] The correct weighting in the geometry of the intermediate state must await a proper effective-medium treatment, and we here assume weighting by volume fraction alone.

$$S=(1-f)S_n=(1-f)S_d+(1-f)[1-(1-\beta)f]^{-1}S_g \tag{4}$$

where S_d,S_g are the diffusion and drag components of the homogeneous normal-phase material. This equation is suitable only well below the percolation threshold, i.e., it is restricted to small f, and in this limit

$$S\approx(1-f)S_d+(1-\beta f)S_g . \tag{5}$$

Before we interpret our data in terms of this result it is important to point out that it cannot be applied if the typical diameter x_s of a superconducting fluctuation exceeds the value of Λ_s. The breakdown occurs as a result of the fact that only the outer shell, of thickness Λ_s, of a superconducting region contributes to the enhancement of the mean free path of phonons entering the normal regions. The fraction f that appears in Eqs. (1)–(3) and in the enhancement factor of Eq. (4) should be replaced by γf, where

$$\gamma\approx\Lambda_s/x_s . \tag{6}$$

The superconducting fluctuations will extend over distances approximately equal to the coherence length,[11] limited in these materials by the electron mean free path l_e. Transport measurements[2,3] suggest that l_e will be at least as small as Λ_s, and we thus persist with the use of Eq. (5).

The existence of a positive thermopower with a positive precursor is explained by the model if S_g is positive and S_d negative, with

$$0<\frac{|S_g|-|S_d|}{|S_g|}<(1-\beta) . \tag{7}$$

As an aid to estimating β we note that the phonon thermal conductivity[2,3] rises by about 30% between T_c and 55 K, a range in which the heat capacity drops by about a factor of 3.[12] The thermal conductivity is given by the product of the heat capacity, the phonon speed, and the mean free path, so we take a value of $\beta=\frac{1}{4}$ in the calculations below.

We can proceed further to an estimate of the diffusion and drag components if we assume that the relative drop in the resistivity precursor is given by $(1-f)$. In our $YBa_2Cu_3O_7$ samples a resistivity drop of 10% is accompanied by a 1-μV/K rise in the thermopower, and we find that at 100 K

$$S_d\approx-14\ \mu\text{V/K}$$

$$S_g\approx\begin{cases}16\ \mu\text{V/K for sample Y1}\\ 19\ \mu\text{V/K for sample Y2.}\end{cases}$$

A similar treatment of the $GdBa_2Cu_3O_7$ data leads to

$$S_d\approx-65\ \mu\text{V/K} ,$$

$$S_g\approx 80\ \mu\text{V/K} .$$

Based on this model we can immediately see that the variations in different samples of $YBa_2Cu_3O_7$ are related to relatively small shifts in the balance between S_d and S_g. This interpretation is consistent with the microstructure shown in electron microscope pictures. Sample Y1 consists of small (0.2–5 μm), loosely packed grains, while sample Y2 has large (up to 50 μm) well-compacted grains. It can be expected that the extra phonon scattering associated with the higher density of defects in Y1 reduces the fraction of the phonon momentum passed on to electrons, and thus also reduces the phonon-drag componant S_g. The negative thermopower in the sample studied by Gottwick *et al.*[3] signals the dominance of the diffusion component, and in accordance with our model no enhancement was seen in that sample. It is worth mentioning that indium in the intermediate state shows a similar effect; when the size of indium crystallities is reduced the thermopower changes from a positive value with an enhancement peak to a negative value without enhancement.[8]

The most important direct result of our interpretation is that it establishes that the diffusion thermopower is negative, suggesting that the dominant carriers in the new oxide superconductors are electrons rather than holes. Caution must be used however; note that the noble metals all show a positive diffusion thermopower.[10] S_d is also large, suggesting conduction in relatively narrow bands[9] with a Fermi energy smaller than 1 eV. The positive phonon-drag thermopower must result from a phonon scattering event that reverses the electron velocity. The larger values in $GdBa_2Cu_3O_7$ of both components of the thermopower result from a lower carrier density,[10] which leads also to its larger resistivity (Fig. 1).

The authors are grateful to J. Tallon and his team at the Physics and Engineering Laboratory of the New Zealand Department of Scientific and Industrial Research for supplying and characterizing the samples used in this work. We are particularly indebted to K. Card and M. Presland for the scanning electron microscopy work.

[1] A. Mawdsley, H. J. Trodahl, J. Tallon, J. Sarfati, and A. B. Kaiser, Nature **328**, 233 (1987).

[2] C. Uher and A. B. Kaiser, Phys. Rev. B **36**, 5680 (1987).

[3] U. Gottwick, R. Held, G. Sparn, F. Steglich, H. Rietschel, D. Ewert, R. Renker, W. Bauhofer, and S. von Molnar (unpublished).

[4] R. Srinivasan, V. Sankaranarayanan, N. P. Raju, S. Natarajan, U. V. Varadaraju, and G. C. Subba Rao (unpublished).

[5] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[6] R. B. Roberts, Philos. Mag **36**, 91 (1977).

[7] P. J. Turner, M.Sc. thesis, University of Western Australia, Perth, 1987 (unpublished).

[8] R. H. Dee and A. M. Guénault, Solid State Commun. **25**, 353 (1978).

[9] F. J. Blatt, *The Physics of Conduction Electrons* (McGraw-Hill, New York, 1968).

[10] D. K. C. MacDonald, *Thermoelectricity* (Wiley, New York, 1962).

[11] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).

[12] B. Bibby and S. Hill (private communication).