An anomalous peak in the thermopower of $Y_1Ba_2Cu_3O_{7\delta}$ crystals

1989 J. Phys.: Condens. Matter 1 465

(http://iopscience.iop.org/0953-8984/1/2/015)

J. Phys.: Condens. Matter 1 (1989) 465–471. Printed in the UK

LETTER TO THE EDITOR

An anomalous peak in the thermopower of $Y_1Ba_2Cu_3O_{7-\delta}$ crystals

M A Howson†, M B Salamon‡, T A Freidmann‡, S E Inderhees‡, J P Rice‡, D M Ginsberg‡ and K M Ghiron‡

† Department of Physics, University of Leeds, Leeds LS2 9JT, UK

‡ Department of Physics and Material Research Laboratory, University of Illinois, 1110 West Green Street, Urbana, Illinois 61801, USA

Received 4 November 1988

Abstract. We have measured the thermopower of five $Y_1Ba_2Cu_3O_{7-\delta}$ crystals, from 300 K to T_c with high resolution, in the *a–b* plane. The value of the thermopower at 100 K is $-3.90\ \mu V\ K^{-1}$ for one that has a resistive transition at 92.6 K. An anomalous peak was observed just above T_c. The peak rapidly diminishes in the presence of a magnetic field and is completely removed by a field of 1 T. We consider a fluctuation contribution suggested by Maki, but find that a divergent contribution obtained from a simple kinetic argument is in better agreement with the data.

The thermopower of polycrystalline $Y_1Ba_2Cu_3O_{7-\delta}$ has been measured by a number of groups (Uher and Kaiser 1987, Lee *et al* 1988, Goncalves *et al* 1988), while Yu *et al* (1988) and Crommie *et al* (1988) have reported results on single crystals. However a wide variety of different temperature dependences and magnitudes have been observed; indeed, both positive and negative thermopowers have been reported. Single crystal measurements to date have had a temperature resolution of a few kelvins and a signal-to-noise ratio of about 10. In an attempt to settle some of these differences and to investigate possible fluctuation effects in the thermopower we have made very precise measurements on single crystals of $Y_1Ba_2Cu_3O_{7-\delta}$. Here we consider an anomaly at T_c only; the full details of the magnitude and temperature dependence will be discussed elsewhere (Howson *et al* 1989).

The crystals, grown using a flux method outlined elsewhere (Rice *et al* 1988), were typically 1 mm × 1 mm × 50 μm in size. The resistivity was measured using a four-probe AC technique; the observed paraconductivity is discussed elsewhere (Freidmann *et al* 1989). The crystal we concentrate on here had a resistive transition with a width of 0.6 K, measured from the 90% to 10% points, and a midpoint at 92.6 K (shown in the inset of figure 1).

The thermopower was measured relative to Pb reference leads using a novel AC method. One half of the (001) surface was exposed to chopped light heating while the other half was masked and thermally anchored. This results in an oscillating temperature gradient of $\simeq$50 mK RMS in the *a–b* plane. With this method it was possible to measure the absolute magnitude of the thermopower to an accuracy of 10% and to measure changes to a precision of 0.3%. Since only a 50 mK temperature difference is required,

0953-8984/89/020465 + 07 $02.50

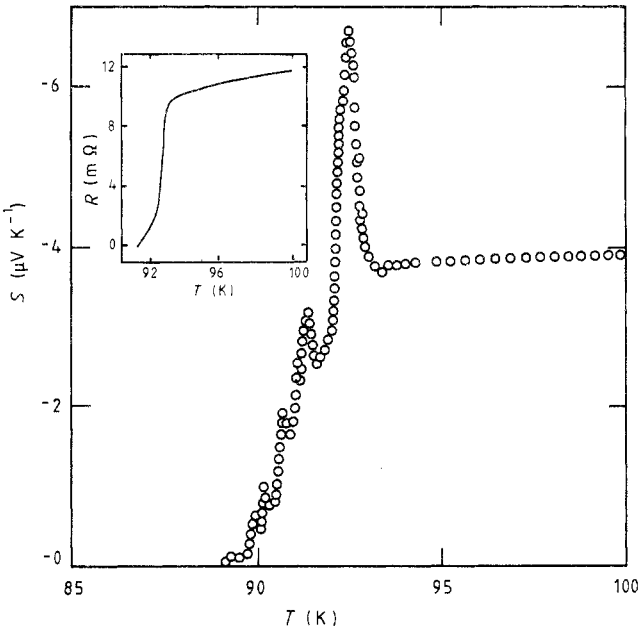

Figure 1. The thermopower of sample A versus temperature over a temperature range 85 to 100 K. The inset shows the resistance versus temperature at the transition.

features in the thermopower down to this temperature resolution can be observed, making this method ideal for investigating fluctuation effects close to T_c. A more detailed description of the experimental arrangement will be given elsewhere (Howson *et al* 1988).

The results for the absolute thermopower of sample A over a narrow temperature range about T_c are shown in figure 1. There is relatively little change between 100 K and room temperature (Howson *et al* 1988). The thermopower is $-3.90\ \mu V\ K^{-1}$ at 100 K. This is a typical metallic value and we could naively argue that its negative sign indicates an essentially electron-like Fermi surface. This is not necessarily the case. The Mott formula for the thermopower of a metal shows that it depends on the energy derivative of both the Fermi surface area and the scattering rate. Crabtree *et al* (1988) argue that since $Y_1Ba_2Cu_3O_{7-\delta}$ consists of a square lattice of CuO_2 units, the Fermi surface is basically cylindrical and report evidence for three sheets. Two of the sheets are a mixture of hole-like and electron-like regions. The other sheet has a small radius and is hole-like, possibly dominating the thermopower because of its smaller area. If this is the case, since the measured thermopower is negative, it would suggest that the derivative of the relaxation rate, and not the effective mass, determines the sign of the thermopower. Of course, we recognise the possibility that a positive diffusion thermopower may be overwhelmed by a large (negative) phonon drag peak. Crabtree *et al* (1988) also point out that this smaller sheet is extremely sensitive to the oxygen content and is present only for δ close to 0. Indeed, Lee *et al* (1988) have shown that the thermopower changes sign from negative to positive as the oxygen content is reduced in polycrystals; changes in the Fermi surface may explain this sensitivity.

We turn next to the rather remarkable peak in the thermopower at T_c. The thermopower is plotted in figure 1 for sample A; qualitatively similar results have been

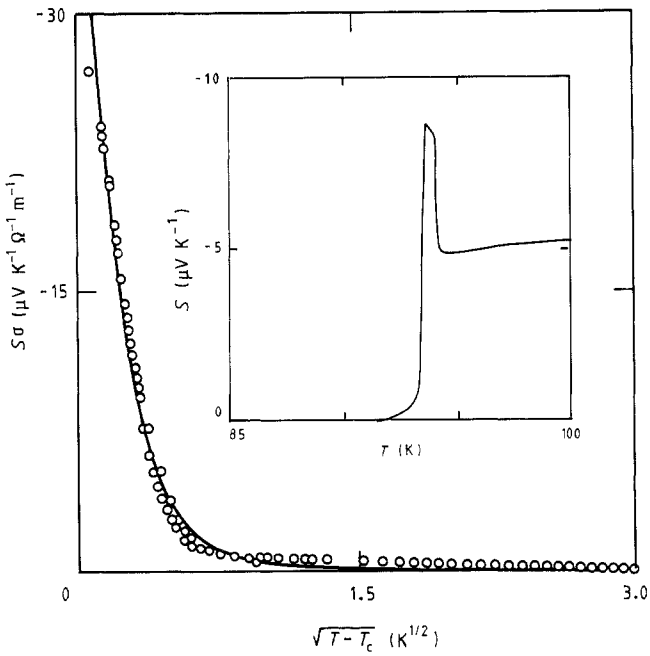

Figure 2. The thermopower of sample A plotted as a function of $(T - T_c)^{1/2}$. The full curve is the 3D fit to the data using equation (1). The inset shows the form of the thermopower transition for sample B.

observed in four other crystals, the form of one is shown as an inset in figure 2 and another as an inset in figure 3. All of the samples show a large, dominant peak at the temperature at which the resistance drops most rapidly, followed by one or more subsidiary peaks in the region of the 'foot' of the resistive transition. We argue that the subsidiary peaks, along with the foot, are indicative of series connection of regions of slightly different, but well defined T_cs. The thermopower at the main peak, on which we focus, increases to almost double its value before dropping rapidly to zero. All of the peaks are quite reproducible for a particular sample but only the main peak is consistently observed in all samples.

All the thermopower peaks are extremely sensitive to magnetic field. For fields below 0.25 T the main peak shifts to lower temperature, by $\simeq$0.5 K, and diminishes in magnitude. From 0.25 T up to 2 T (the highest field used) the peak remains at the same temperature, to within 0.1 K, but is strongly reduced in magnitude; it is barely discernible above the noise at 1 T. A similar reduction in the specific heat peak has been noted by Salamon *et al* (1988a) and has been interpreted in terms of fluctuation effects.

We consider the possibility that this peak is due to conventional superconducting fluctuation effects and have attempted to fit a result due to Maki (1974) and separately a kinetic theory argument to our data. Because of the long coherence lengths of classical superconductors, the effects are usually much too small to be observed. In contrast, the coherence length of the $YBa_2Cu_3O_{7-\delta}$ is extremely short: $\leqslant$2 nm in the *a–b* plane and $\simeq$0.5 nm in the *c* direction (Quadar and Salamon 1988). Indeed 3D fluctuation effects have now been reported in the resistivity (Hagen *et al* 1988 (see also Goldenfeld *et al* 1988)), specific heat and susceptibility (Salamon *et al* 1988b). Some

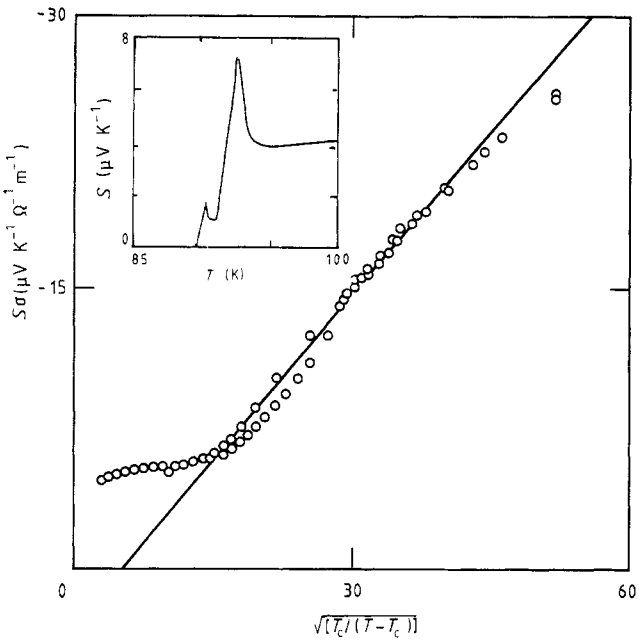

Figure 3. The thermopower of sample A plotted as a function of $(T_c/(T - T_c))^{1/2}$. The full curve is the 3D fit to the data using equation (2). The inset shows the form of the thermopower transition for sample C.

workers report a crossover from 2D to 3D fluctuations in the resistivity above T_c (Oh *et al* 1988), when the c axis coherence length becomes comparable with the lattice spacing.

As we shall see below, we have found a number of problems in obtaining a good quantitative fit to Maki's microscopic theory and we believe a simple kinetic argument suggests that the microscopic theory has neglected the most divergent contribution. Since the peak's width corresponds to $\delta T/T_c \simeq 5 \times 10^{-3}$, we should be in the 3D regime, where the coherence length spans several CuO_2 layers in the c direction and we consider only 3D fits. We have found it impossible to fit to the logarithmic divergence predicted by Maki (1974) for $d = 2$.

Maki (1974) has calculated the Gaussian fluctuation contribution to the thermopower in various dimensionalities. He expresses the thermopower as the ratio of the thermal current to the electrical conductivity. In 3D, a $(T - T_c)^{1/2}$ cusp is predicted for the thermal current, while a logarithmic divergence should occur in 2D.

Maki (1974) writes the thermopower in the form

$$S = (e/T)(K_n + K_{fl})/\sigma$$

where K_n is the normal metallic thermal current. For $d = 3$, the fluctuation heat current (K_{fl}) *close* to T_c is given by

$$K_{fl} = \frac{3\pi k_B^2 T^2}{8E_F\hbar} \ln\left(\frac{T_0}{T_c}\right) \frac{d \ln N(E)}{d \ln E} L(\rho)\left[q_0 - \frac{3\pi}{4}\left(\frac{8k_B(T - T_c)}{\pi\hbar D}\right)^{1/2}\right] \tag{1}$$

where $L(\rho)$ is a function of the pair breaking parameter $\rho = \delta/k_B T$, and is typically of order unity. D is the electron diffusion constant; E_F the Fermi energy; and q_0 a wavevector cut-off which is of order $1/\xi_0$. $N(E)$ is the quasiparticle density of states and T_0 is

the characteristic temperature for the pairing interaction, for BCS it is the Debye temperature. However, if the pair mechanism is related to the electron–electron interaction we may expect T_0 to be of the order of the Fermi temperature.

In order to analyse our results we have multiplied our thermopower data by the measured conductivity, subtracted a constant background and plotted $S\sigma$ versus $(T - T_c)^{1/2}$ in figure 2. Since the normal state $S\sigma$ is only weakly temperature dependent over the temperature range of interest we have taken the value at 100 K as a constant background. This then should reveal the experimentally determined behaviour of the function eK_{fl}/T (refer to equation (1)). In figure 2 the full curve is a fit to the data using Maki's *full* 3D expression (Maki 1974); note that equation (1) is valid close to T_c only. We can see that the fit is qualitatively quite reasonable, but quantitatively as we shall see below, this fit is not so good.

In performing the fit shown in figure 2 we have taken E_F to be 0.1 eV (Quadar and Salamon 1988), T_0 to be 450 K (the Debye temperature) (Quadar and Salamon 1988) and T_c to be 92.6 K (the mid-point of the resistive transition and also the position of the maximum in the thermopower peak). The cut-off wavevector q_0 will be of order $1/\xi_0$ (Tinkham 1975). Although the fit looks reasonable, it requires the diffusion constant D, and the logarithmic derivative of the density of states $\mathrm{d}\ln N(E)/\mathrm{d}\ln E$ to have unrealistic values. The value of D obtained from the fit is $3.3 \times 10^{-7}\ \mathrm{m^2\ s^{-1}}$ which is considerably smaller than the $10^{-4}\ \mathrm{m^2\ s^{-1}}$ typical of a metal. The value $\mathrm{d}\ln N(E)/\mathrm{d}\ln E = 26$ required is much larger than is likely from any band model. It is possible to reduce our value for $\mathrm{d}\ln N(E)/\mathrm{d}\ln E$ by increasing T_0. For $T_0 \simeq 10^4$ K (comparable with the Fermi temperature) we find $\mathrm{d}\ln N(E)/\mathrm{d}\ln E$ to be $\simeq 6$ which is still rather large. The value of E_F chosen corresponds to a free-electron density of states of 0.8 states $\mathrm{eV^{-1}}$ Cu (Quadar and Salamon 1988). Choosing a smaller density of states, such as suggested by photoemission measurements will also reduce our value for $\mathrm{d}\ln N(E)/\mathrm{d}\ln E$. However, large values of $\mathrm{d}\ln N(E)/\mathrm{d}\ln E$ are not unreasonable if there is an anomaly in the density of states at the Fermi energy, and band structure calculations do suggest a sharp feature at E_F in both $Y_1Ba_2Cu_3O_7$ and $La_3Sr_1Cu_2O_8$ (Temmermann *et al* 1987, Stocks *et al* 1988).

A number of points make us cautious in applying Maki's result to our data. First, the calculation is valid only in the dirty limit. The quasiparticle mean free path inferred from the Drude expression for the conductivity is of the order of 10 nm. We are therefore not strictly in the dirty limit but, indeed, closer to the clean limit. This *may* explain the low values for D obtained from the fits. Further, Maki has made various simplifying approximations in obtaining his result and of course it is strictly only valid for the case of singlet pairing. There is also a curious problem with the sign of the thermopower. We argued above that the carriers were holes and reason that the measured thermopower is negative because of a dominant negative contribution from the derivative of the relaxation rate. The sign of Maki's fluctuation term depends only on the sign of the carriers and should therefore be positive for holes. However, to fit the data the Maki terms must be negative requiring that the carriers be electrons. We return to this below. Finally, there is considerable ambiguity in choosing values for θ_D and E_F and this may explain the large values of $\mathrm{d}\ln N/\mathrm{d}\ln E$ obtained. However, overall the fit is quantitatively poor.

These difficulties in interpreting our data in terms of Maki's calculation have led us to consider a simple kinetic derivation of K_{fl}. This is in the same spirit as the electrical conductivity where the fluctuation contribution can be estimated (Tinkham 1975)

$$\sigma = \frac{ne^2\tau}{m} \simeq \frac{2e^2}{m} \sum_k \langle |\psi_k|^2 \rangle \tau_k$$

The thermal current is proportional to the Onsager coefficient L_{eT}, and is thus related to the electric current generated by a temperature gradient; the thermopower is given by $S = L_{eT}/\sigma$. For the fluctuations, L_{eT}, in simple kinetic theory, is given by (Ashcroft and Mermin 1976)

$$L_{eT} = (e\tau/3)\partial\langle nv^2\rangle/\partial T$$

where n is the number density, τ is the lifetime and v is the velocity of pair fluctuations. Following the same procedure as with the conductivity calculation and using Maki's notation ($K_{fl} = TL_{eT}/e$) this can be written in the form (Tinkham 1975)

$$K_{fl} = \frac{\hbar^2 T}{3m^2}\sum_k k^2\tau_k \frac{\partial\langle|\psi_k|^2\rangle}{\partial T}$$

where

$$\tau_k \simeq \frac{\pi\hbar}{8k_B(T-T_c)}\frac{1}{(1+k^2\xi^2)} \quad \text{and} \quad \langle|\psi_k|^2\rangle \simeq \frac{k_B T}{(1+k^2\xi^2)}\frac{2m}{\hbar^2}\xi^2.$$

Taking the temperature derivative and evaluating the three dimensional integrals, we find, close to T_c

$$K_{fl} = \frac{\hbar}{24\pi m\xi_0^2}\left[\left(q_0 - \frac{3\pi}{4\xi_0}\sqrt{\frac{(T-T_c)}{T_c}}\right) - \left(\frac{3\pi}{16\xi_0}\sqrt{\frac{T_c}{(T-T_c)}}\right)\right]. \qquad (2)$$

The first part of this expression has the same form as Maki's results; a $(T-T_c)^{1/2}$ cusp. But the second part has a $(T-T_c)^{-1/2}$ divergence which does not appear in Maki's calculation. Further, this divergent term, which will clearly dominate at T_c, is of opposite sign to Maki's cusp term. This is because the divergent term represents a flow of current, against the temperature gradient, driven by the density gradient of the fluctuations themselves, i.e. there is a higher density of fluctuations at lower temperatures. Maki's term, however, arises because the fluctuations each carry $k_B T$ of thermal energy which increases as the fluctuations move up the thermal gradient. We therefore suggest that Maki's original microscopic calculation may not have included the most divergent contribution.

Since the $(T-T_c)^{-1/2}$ divergence will dominate close to T_c we have plotted $S\sigma$ versus $(T_c/(T-T_c))^{1/2}$ in figure 3. The straight line fit to the data only depends on ξ_0. The fit is quite reasonable and gives a smaller sum of residuals than the fit using just Maki's term. The value of ξ_0 obtained is 1.3 nm. This is a reasonable value for ξ_0 so that the fit is also quantitively better than the Maki fit.

Other workers have reported a precursor peak in the thermopower of poly-crystalline samples (Uher and Kaiser 1987, Lee *et al* 1988, Goncalves *et al* 1988). This peak is, however, much broader and smaller than the peak we observe; the width of the peak is between 20 and 30 K. Uher and Kaiser (1987) have argued that this may be an enhanced phonon drag peak as a precursor to the transition. They suggest that fluctuation effects may lead indirectly to a decrease in electron phonon scattering and hence enhance the phonon drag contribution. Of course any phonon drag enhancement is unlikely to appear on the temperature scale of about a kelvin, as seen here. There is also the possibility that the measured thermopower has a small c axis component to it which is of opposite sign. If the c axis component goes to zero at T_c slower than the a–b axis component then a

peak may result. Finally there is a possibility that inhomogeneities, in some subtle way, produce a peak. These possibilities are at present under study.

In summary, we have found a sharp peak in the thermopower close to T_c, and we have considered the possibility that the peak may be due to fluctuation effects. A microscopic theory exists, due to Maki (1974), which fits the peak qualitatively but quantitively predicts a smaller effect, unless there is a large density of states anomaly at E_F. We have suggested that this microscopic theory does not include the most divergent contribution to the thermopower and have presented a simple kinetic argument for the presence of a more divergent term, which is in better agreement with the data.

We are grateful to James Annett, Jorgen Rammer and Alan Kaiser for helpful advice and discussions. One of us (MAH) would like to thank the Physics Department and the Materials Research Laboratory at the University of Illinois for their support and hospitality during his stay. This work was supported through the Illinois Physics Department and Materials Research Laboratory by National Science Foundation grant No DMR-86212860 and DMR 87-14555. MAH would also like to thank the Royal Society for additional financial support.

References

Ashcroft N W and Mermin N D 1976 *Solid State Physics* (Philadelphia: Holt, Rinehart and Winston) p 24

Crabtree G W, Kwok W K and Umezawa A 1988 *Quantum Field Theory as an Interdisciplinary Basis* ed. F C Khanna, H Umezawa, G Kunstatter and H C Lee (Singapore: World Scientific)

Crommie M F, Zettl A, Barbee III T W and Cohen M L 1988 *Phys. Rev.* B **37** 9734

Freidmann T A, Rice J P and Ginsberg D M 1989 *Phys. Rev.* B submitted for publication

Goldenfeld N, Olmsted P D, Freidmann T A and Ginsberg D M 1988 *Solid State Commun.* **65** 465

Goncalves A P, Santos I C, Lopes E B, Henriques R T, Almeida M and Figueiredo M O 1988 *Phys. Rev.* B **37** 7476

Hagen S J, Jing T W, Wang Z Z, Horvath J and Ong N P 1988 *Phys. Rev.* B **37** 7928

Howson M A, Salamon M B and Freidmann T A 1989 *Phys. Rev.* B submitted for publication

Lee S C, Lee J H, Suh B J, Moon S H, Lim C J and Khim Z G 1988 *Phys. Rev.* B **37** 2285

Oh B, Char K, Kent A D, Naito M, Beasley M R, Geballe T H, Hammond R H, Kapitulnik A and Graybeal J M 1988 *Preprint*

Maki K 1974 *J. Low Temp. Phys.* **14** 419

Quadar K and Salamon M B 1988 *Solid State Commun.* **66** 975

Rice J P, Pazol B G, Ginsberg D M, Moran T J and Weissmann W B 1988 *J. Low Temp. Phys.* at press

Salamon M B, Inderhees S E, Rice J P, Pazo B G, Ginsberg D M and Goldenfeld N 1988a *Phys. Rev.* B **38** 885

Salamon M B, Inderhees S E, Goldenfeld N, Rice J P, Pazol B P, Ginsberg D M, Liu J Z and Crabtree G W 1988b *Phys. Rev. Lett.* **60** 1178

Stocks G M, Temmermann W M, Szotek Z and Sterne P A 1988 *Supercond. Sci. Technol.* **1** 57

Temmermann W M, Szotek Z, Durham P J, Stocks G M and Sterne P A 1987 *J. Phys. F: Met. Phys.* **17** L319

Tinkham M 1975 *Introduction to Superconductivity* (New York: McGraw-Hill) p 252

Uher C and Kaiser A B 1987 *Phys. Rev.* B **36** 5680

Yu R C, Naughton M J, Yan Z, Chaikin P M, Holtzberg F, Greene R L, Stuart J and Davies P 1988 *Phys. Rev.* B **37** 7963