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The thermopower of $YBa_2Cu_3O_{7-\delta}$ single crystals

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Abstract. We present results for the measured thermopower of a number of $YBa_2Cu_3O_{7-\delta}$ single crystals. One of the crystals was untwinned and allowed us to measure the thermopower in the a and b crystallographic directions and discuss the contributions to the thermopower from the chains and planes of Cu–O. The thermopower near T_c is fitted to recent models of superconducting fluctuation effects in the thermopower and it is found that the a axis coherence length is almost five times the b axis coherence length. A sharp peak near T_c is nearly always observed and we argue that while this may be a superconducting fluctuation effect it may also be the result of a combination of the a axis and b axis thermopowers which are of *opposite* sign. The thermopower in the b direction is nearly temperature independent well above T_c, which is consistent with conduction in a narrow band. The a axis thermopower, due essentially to the $Cu–O_2$ planes, is metallic-like and similar to results on other high-T_c systems.

1. Introduction

There have been many studies of the thermopower in polycrystalline $YBa_2Cu_3O_{7-\delta}$ and a few in single-crystal samples of $YBa_2Cu_3O_{7-\delta}$ [1–8]. The results indicate a strong dependence of the thermopower on the oxygen stoichiometry, with $\delta = 0$ having a small negative thermopower while there is a crossover to positive thermopowers at around $\delta = 0.1$. Of course, nearly all studies have been on twinned samples. Recently we presented the first measurements [2] of the thermopower of an untwinned crystal and were able to show that the a axis and b axis thermopowers have different signs, with the b axis thermopower being larger and negative, in a sample with δ close to zero. Cohn *et al* [8] have also recently measured the thermopower of an untwinned crystal obtaining similar results to ours. Results on the resistivity of untwinned crystals also show that the resistivity in the b direction is about half that in the a direction [9]. Here we present data on a number of twinned crystals along with an untwinned crystal measured between T_c and 200 K using an AC optical heating technique. This allows us to make measurements close to T_c with a temperature precision of better than 50 mK. We believe the behaviour close to T_c shows evidence of fluctuation effects and we discuss how, at higher temperatures, the data for both twinned and untwinned samples are consistent with other measurements using more conventional DC techniques.

2. Experimental details

The $YBa_2Cu_3O_{7-\delta}$ crystals were grown using a self-flux technique as outlined by Rice *et al* [10]. The crystals typically measured 1 mm × 1 mm × 50 μm, along the a, b

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and c axes respectively, and had gold strips evaporated on to each end. In order to provide a good ohmic contact between the gold and the crystal, and to oxygenate the sample, the crystals were annealed at 600 °C for 1 hour followed by an anneal at between 400 °C and 500 °C in flowing dry oxygen for several days. As shown in figure 1 the samples were then mounted on a thin mylar strip. The mylar was coated with about 200 nm of Pb with a narrow gap in the middle across which the crystal was placed. The Pb acted as the thermopower reference voltage leads using the Roberts scale [11]. On one side a 3 mm thick Pb lead was also added. This provided a good thermal link to the copper heat sink on one side of the sample and helped to establish the temperature gradient. A chromel versus constantan thermocouple was used to measure the temperature across the sample. Two arrangements were used: either the thermocouple measured the temperature of one end of the sample with reference to the heat sink or a differential thermocouple was placed across the sample. Both methods produced similar results. The thermocouple was made from 25 μm diameter chromel and constantan wire, spot welded to form the junctions. The sample was heated using light from a diode laser operating at 780 nm and producing between 1 and 18 mW. The light was passed from outside the cryostat to the sample using a 200 μm fibre pigtailed to the diode package. The end of the fibre was about 1 mm from the crystal; the light was 'flashed' at an adjustable frequency of between 5 and 30 Hz and there was no appreciable difference between measurements made at different frequencies; the reported measurements were carried out at 29 Hz. During the experiment the crystal was kept in about half an atmosphere of helium exchange gas.

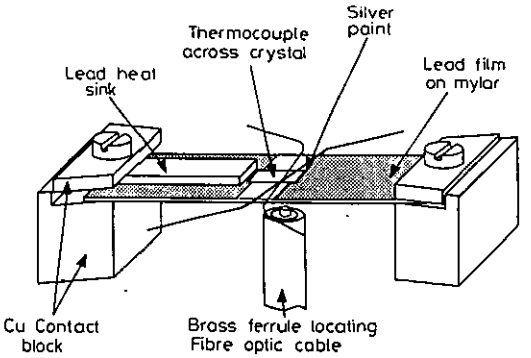

Figure 1. A schematic diagram of the sample holder.

Lock-in amplifiers were used to detect the thermopower signal and the thermocouple signal at the frequency of the 'flashing' light. Since we are measuring the thermopower very close to the superconducting transition at which the thermopower drops rapidly to zero, we have to be sure that the derivative of the thermopower does not appear in the signal. This is especially important since one of the interesting features we measure is a sharp peak in the thermopower at T_c which at first sight may be mistaken for the appearance of the derivative in the signal. In fact it is only the second harmonic of the signal which is proportional to $\partial S/\partial T$. At the fundamental frequency the signal is simply proportional to the thermopower. This is easy to show if we consider the following and calculate the signal as

$$V(t) = \int_{T(t)}^{T'(t)} S(T)\,\mathrm{d}T \tag{1}$$

where $T'(t)$ refers to the temperature of the 'hot' end of the crystal and $T(t)$ refers to the temperature of the 'cold' end. Both may depend on time, t, so

$$T(t) = T_0 + \delta T \sin(\omega t) \qquad T'(t) = T_0' + \delta T' \sin(\omega t). \tag{2}$$

If we simply write the indefinite integral as

$$v(T) = \int S(T)\,\mathrm{d}T \tag{3}$$

then equation (1) becomes

$$V(t) = v[T'(t)] - v[T(t)] \tag{4}$$

and equation (4) can be Taylor expanded using equation (2) to give

$$V(t) = [v(T_0') - v(T_0)] + \left[\left(\frac{\mathrm{d}v(T)}{\mathrm{d}T}\right)_{T=T_0'} \delta T' \sin(\omega t) - \left(\frac{\mathrm{d}v(T)}{\mathrm{d}T}\right)_{T=T_0} \delta T \sin(\omega t)\right] \tag{5}$$

which reduces to

$$V(t) = \int_{T_0}^{T_0'} S(T)\,\mathrm{d}T + [S(T_0')\delta T' \sin(\omega t) - S(T_0)\delta T \sin(\omega t)]. \tag{6}$$

Here the first term is the DC component and the other two terms are the AC components. The second term arises because of the oscillating 'hot' end while the third term arises if the temperature of the 'cold' end is not held at a fixed temperature. The terms which depend on $\partial S/\partial T$ appear in the second term of the Taylor expansion with twice the driving frequency and so are not detected by the lock-in. It is possible to pick up $\partial^2 S/\partial T^2$ from the $\sin^3(\omega t)$ term in the Taylor expansion which when factorized gives a $\sin(\omega t)$ contribution but this third-order term is likely to be too small to be important.

As regards the temperature of the cold end of the sample, it will be oscillating but at a very much smaller amplitude than the hot end. There are two reasons for this. The first point is that the sample is surrounded by half an atmosphere of helium exchange gas and thus the temperature decays exponentially along the crystal because the greater fraction of the heat absorbed by the crystal is transmitted to the helium exchange gas by conduction and convection. Only a very small fraction is conducted along the crystal to the cold end. If the thermal conductivity of the crystal is 5 W mK^{-1} and if we estimate the heat transfer coefficient from the crystal to the surrounding helium gas to be about 10^2 W K^{-1} m^{-2} then the exponential decay length is about 300 μm, that is about a third of the length of the crystal. The second point is that the ratio of the thermal resistance of the crystal to the thermal resistance of the thick Pb lead is about 500. Both these points help to ensure that the temperature of the cold end of the crystal is as near constant as possible. We confirmed this by placing a thermocouple junction at the cold end of the sample and found the temperature oscillations were at least 100 times less than at the hot end. This is extremely important if we want the last term in equation (6) to be negligible so that we are accurately measuring $S(T)$.

Below T_c the thermopower of the $YBa_2Cu_3O_{7-\delta}$ is zero and so the measured signal is due to the Pb reference leads alone. This observation was used to check the magnitude and sign of the measured thermopower. The sign was also checked by considering the phase between the 'flashing' light and the signal, and by a DC measurement at a fixed temperature.

3. Results

We present results for the thermopower of four different crystals, the details of which are shown in table 1. The sharpest transitions were observed in samples 1 and 2. Sample 2 had a large untwinned region while sample 1 was untwinned apart from a few small regions near the edge which were cleaved off. Any residual twins in sample 1 were covered over by the gold pads so that sample 1 was essentially an untwinned crystal and we could orient it to measure the thermopower along the a or b axis (here the b axis is in the direction parallel to the Cu–O chains). Results for the thermopowers measured between 80 and 110 K are shown in figure 2. The results for sample 1 (figure 2(a)) show that the thermopower is positive in the a direction and negative along the b direction. The peak, which we have reported before [1, 2] on measurements on many crystals, is only clearly seen in the a axis measurement and the peak is in the direction of positive thermopower. Crystal 2 (figure 2(b)) very much resembles the a axis measurement of the untwinned sample 1 both in sign and magnitude. This is because the sample had a large untwinned region which was aligned with the heat flow along the a axis of the untwinned region. Crystals 3 and 4 (figures 2(c) and 2(d)) are very heavily twinned but the results resemble the b axis measurement on the untwinned sample apart from a sharp peak which this time is in the direction of negative thermopower.

Table 1. Details of the crystals.

Crystal number	Dimensions of a–b plane (mm^2)	T_c onset from AC susceptibility (K)	Transition width (K)	Initial oxygen annealing conditions
1	1.2 x 1.2	93.8 ∓ 0.5	0.25	500 °C/4 days
2	0.6 x 0.4	92.7 ∓ 0.5	0.7	400 °C/16 hours
3	1.2 x 0.4	93.8 ∓ 0.5	2.2	400 °C/4 days
4	1.1 x 0.35	93.6 ∓ 0.5	2.0	400 °C/5 days

The thermopower is shown in figure 3 for samples 1 and 3 between 80 and 200 K. The a axis measurement for sample 1 falls to almost zero at 200 K as though it is about to change sign, while the b axis measurement appears to plateau and become nearly temperature independent. Again sample 3 shows behaviour very similar to the b axis measurement of the untwinned sample 1.

4. Discussion

The most dramatic feature observed in the measured thermopower is the sharp peak at T_c. This is seen in all the twinned samples we have measured and is clearly seen in the a axis measurement of the untwinned crystal. The first point that must be addressed is why this is not seen in other published measurements of the thermopower [3–8]. In a recent comment Logvenov *et al* [12] argued that the peak was an artifact of the AC measuring technique and that the technique picks up a contribution proportional to the derivative of the thermopower which is clearly very large close to T_c. However, in our reply [13] we pointed out the mistake Logvenov *et al* had made in their argument and showed quite clearly that the technique is only

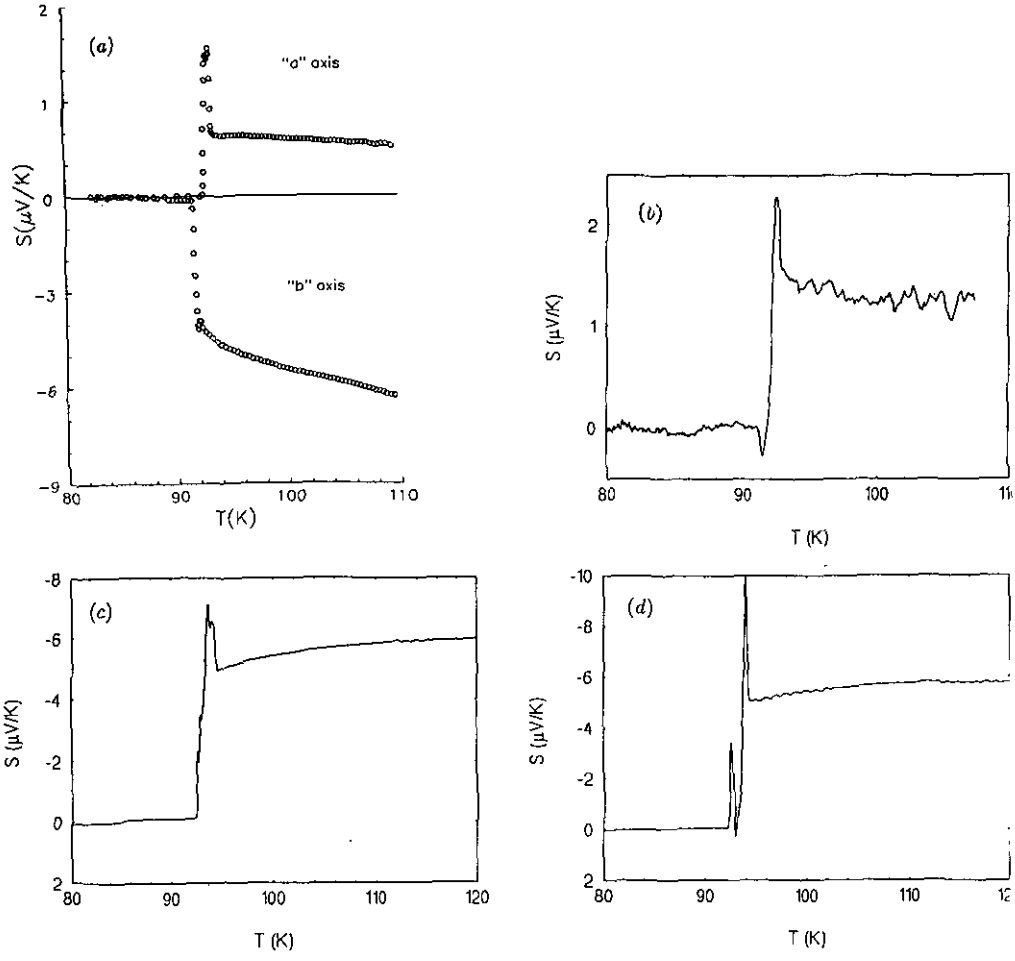

Figure 2. The thermopower of a number of $YBa_2Cu_3O_{7-\delta}$ crystals: (*a*) the untwinned sample 1 showing both the *a* axis and *b* axis thermopowers; (*b*) sample 2; (*c*) sample 3 and (*d*) sample 4.

sensitive to the thermopower and not the derivative of the thermopower. We have also made this point above along with a description of the experiment. The reason why the peak has not been seen in other single-crystal measurements may be due to the difference in temperature precision achievable with an AC method as compared to a DC method. A DC measurement requires a temperature difference across the crystal of at least 500 mK whereas with an AC technique we use a temperature difference of less than 50 mK producing an AC signal of around 50 nV. The peak itself is less than 500 mK wide and so it will be washed out by the temperature gradient in a DC measurement. From our argument below, concerning a 'subtraction' effect between the *a* and *b* axis contributions to the thermopower, the peak may only be present in crystals for which the *a* and *b* axis thermopowers are of different sign. This will only occur in samples with δ close to zero.

There are two possible explanations for the peak we observe. First it is possible that the peak is due to a 'subtraction' effect from a combination of the *a* and *b* axis

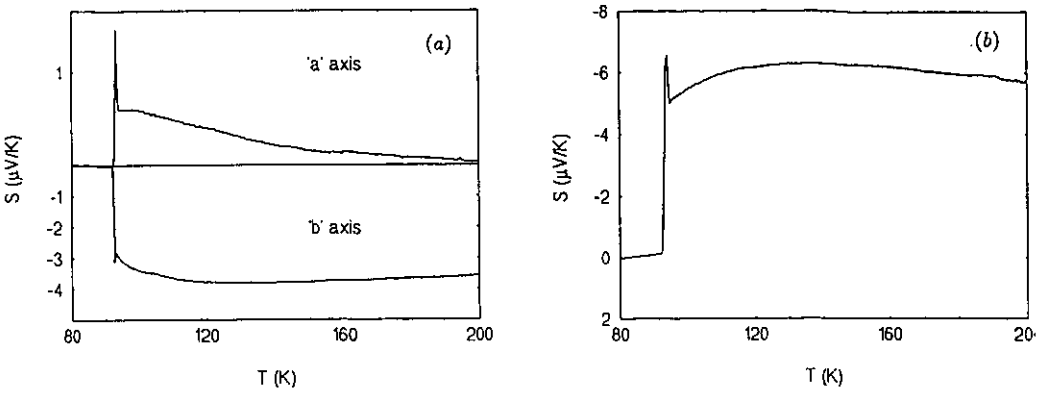

Figure 3. The thermopower of (*a*) sample 1 and (*b*) sample 3 between T_c and 200 K.

thermopowers. In recent publications [1, 2] we have also considered the possibility that the peak is a fluctuation effect. In what follows we will see that we cannot rule out either possibility and indeed both effects may be present.

Let us consider the 'subtraction' effect first. In twinned crystals we are obviously measuring a combination of the a and b contributions to the thermopower. If the positive thermopower in the a direction has a different slope near T_c to the negative thermopower in the b direction then a peak may result. In an untwinned crystal it is possible to estimate how much misalignment of the crystal—so that a combination of the a and b axis thermopower is measured—is required to produce a peak. A feature of the peak is that for the twinned crystals the thermopower is negative and the peak is negative. For the untwinned crystal however the a axis thermopower is positive and so the peak is positive. To model all these features and to see if we can account for the observed results we can write the measured thermopowers along the a and b axes as

$$S'_a = \beta S_a + (1-\beta)S_b \qquad S'_b = \beta S_b + (1-\beta)S_a$$

where S' refers to the measured thermopower and S to the actual thermopower. β is a misalignment parameter which runs from 0 to 1. A twinned crystal would be represented by $\beta = 0.5$. To model the transitions the thermopower was written in the form

$$S = A\tan^{-1}[(T - T_c)/W]$$

which was modified to extrapolate linearly to zero from the point of symmetry ($T = T_c$). The width parameter W was used to make the b axis transition less steep than the a axis transition as suggested by the data in figure 2(*a*). Figure 4(*a*) shows the moduli of the two functions (which are of opposite sign) modelling the a and b axis transitions, which best fit the behaviour of the peak. Other models for the transitions have been tried—for example a power law divergence—and they produce qualitatively similar results. The first point to note is that the two transitions are slightly shifted. Without this shift a peak cannot be produced. It is interesting to note that the data in figure 2(*a*) also show the point at which the thermopower is zero for the b axis measurement to be about 0.6 K lower than for the a axis measurement.

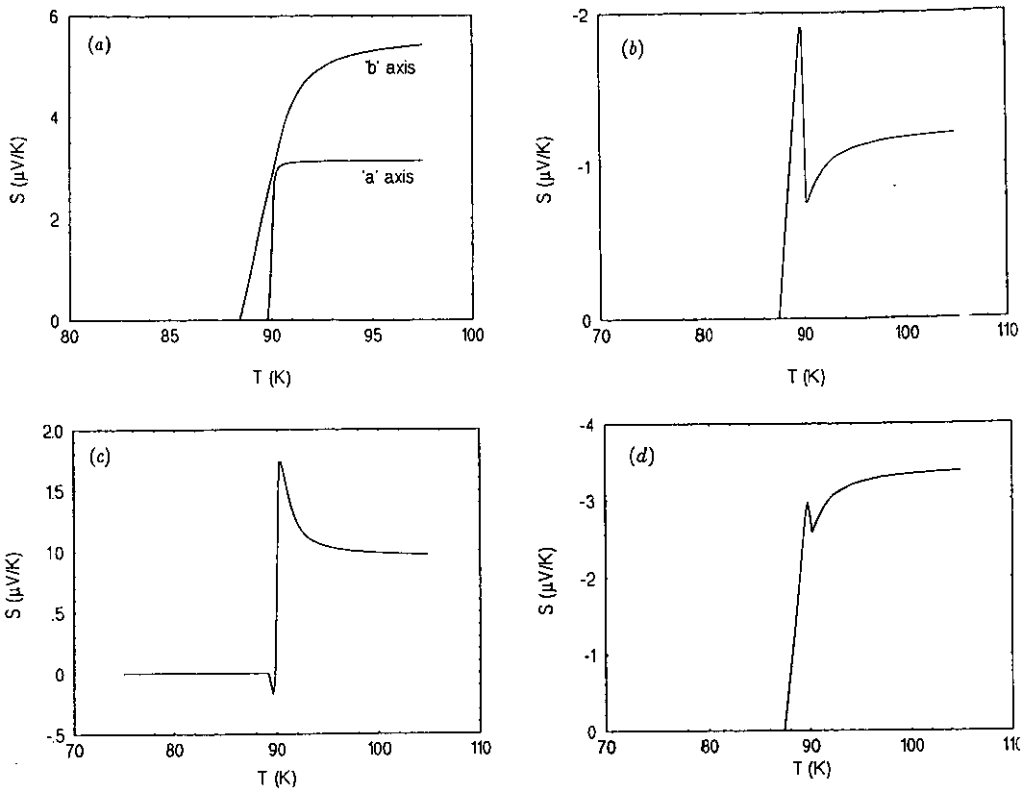

Figure 4. (*a*) The model transitions for the *a* and *b* axes, showing the modulus of the thermopowers; (*b*) the thermopower for the 'twinned' model with $\beta = 0.5$; (*c*) the thermopower for the *a* axis with $\beta = 0.75$; the thermopower for the *b* axis with $\beta = 0.75$.

This shift cannot be accounted for by errors in the temperature measurement. Indeed the crystal was remounted several times in the two different orientations and a similar 0.6 K difference was always observed. We have no explanation for this difference.

Figure 4(*b*) shows the thermopower for a simulated 'twinned' crystal using the transitions in figure 4(*a*) with the alignment factor β of 0.5. It appears to represent the results in figures 2(*c*) and 2(*d*) quite well. Figure 4(*c*) shows S'_a and figure 4(*d*) shows S'_b calculated using the model transitions in figure 4(*a*) for a misaligned untwinned crystal. Again they appear to represent the actual measurements in figure 2(*a*) very well even to the extent of reproducing the small negative peak at the foot of the *a* axis transition. In order to get this result a misalignment factor β of 0.75 was necessary. This is quite large and since β is likely to vary as $\sin^2\theta$ means the crystal would have to be misaligned by about 30° to produce the peak. This is a large misalignment. In fact the crystal and the heat flow are estimated to have been aligned to within about 5°. However, the exact misalignment factor may be model dependent. Figures 4(*a*)–(*d*) simply illustrate the 'subtraction' model; we have not been able to fit to the data exactly.

Let us now turn to consider fluctuation effects. In recent publications we argued that this peak in YBCO could be due to fluctuation effects [1, 2]. It is also interesting to note that in the BiSCCO and thallium systems a cusp is often observed at T_c [6].

Varlamov and Livanov [14], and independently Maki [15], have discussed how the fluctuation contribution to the thermopower diverges near T_c to produce a cusplike peak. They both find an expression for the thermopower (S) which can be written in the form

$$S = S_0\{[1 + \alpha(\sigma_{fl}/\sigma_n)]/[1 + (\sigma_{fl}/\sigma_n)]\} \tag{7}$$

where the subscripts fl and n refer to the fluctuation and normal contributions respectively. The fluctuation electrical conductivity σ_{fl} diverges as $t^{-1/2}$ where t is the reduced temperature $(T - T_c)/T_c$. Both the numerator and the denominator are diverging in the same way so that a cusp is seen in the thermopower. For the thermopower to peak at T_c the parameter α must be greater than one. Varlamov and Livanov [14] and Maki [15] find α proportional to $\ln(\Theta/T_c)$ assuming a free-electron-like density of states. Here Θ is the characteristic pairing temperature—this would conventionally be the Debye temperature. Therefore in order to give rise to a peak the Varlamov–Livanov and Maki models require a large Θ. In Lowe *et al* [2] we investigated the consequences of the peak in this model. We also considered whether the peak marked the onset of critical fluctuations at which point the numerator and denominator in equation (7) might not have the same form of divergence leading to a peak.

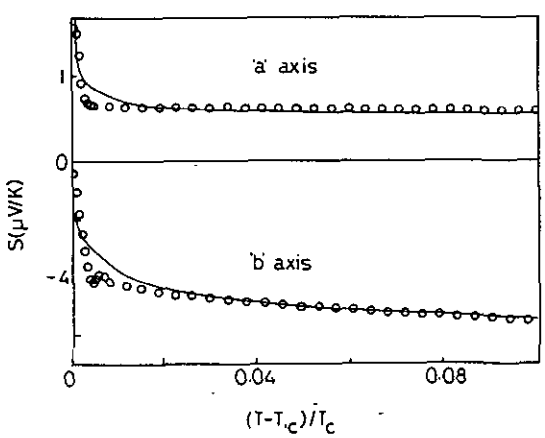

Figure 5. The thermopower of sample 1 close to T_c. The solid lines are fits to the data using equation (7) for the fluctuation contribution to the thermopower.

In figure 5 we show the fit to our data using equation (7). The details of this fitting procedure were discussed by Lowe *et al* [2]. In fitting the data the most important point was that the Ginzburg criterion for the onset of critical fluctuations is different for the two different axes. This could be interpreted as the a axis superconducting coherence length (ξ_a) being about five times the b axis coherence length (ξ_b) or it could be associated with an anisotropic Fermi surface, since the Ginzburg criterion depends on the value of the coherence length and the Fermi wavevector. We also found Θ to be 100 K from the b axis results but 4000 K in order to fit the a axis peak. If we consider that the peak is due to the subtraction effect discussed above and not due to fluctuations the difference in widths of the two transitions still suggest that fluctuations when the thermal current is along the b axis are the stronger.

The temperature dependence of the thermopower is shown up to 200 K in figure 3. There have been a number of recent measurements of the thermopower of

polycrystalline and twinned single-crystal $YBa_2Cu_3O_{7-\delta}$ samples [3–8]. The results on polycrystalline samples will represent some average of the thermopower in all three crystallographic directions weighted by the conductivity in the a, b and c directions. The results on twinned crystals in the a–b plane will represent the same weighted average but for the a and b directions only. There appears to be some sort of consensus of results now for twinned crystals: the thermopower well above T_c is nearly temperature independent up to room temperature while near T_c the fluctuation effects drive the thermopower towards zero. The sign depends critically on the value of δ, with the thermopower being negative when δ is close to zero but changing sign at around $\delta = 0.15$. This behaviour of the temperature dependence is also seen in the b axis measurements of our untwinned crystal. The reason the twinned results are so similar to the untwinned b axis results is that for the twinned crystal the thermopower is an average of the thermopowers along the a and b axes weighted by the corresponding conductivities. The thermopower along the b axis is six times that along the a axis while the electrical conductivity along the b axis is twice that for the a direction, leading to an overall dominance of the b axis contribution in twinned crystals.

Following the argument of Cohn *et al* [8], the thermopower along the b axis is due to conduction in the Cu–O_2 planes and Cu–O chains, while the thermopower along the a axis is due to conduction in the Cu–O_2 planes only. that is

$$S_b = (\sigma_{ch} S_{ch} + \sigma_{pl} S_{pl})/(\sigma_{pl} + \sigma_{ch}) \qquad S_a = S_{pl} \tag{8}$$

where the subscripts pl and ch refer to the plane and chain contributions respectively. Recent measurements [9] have shown that $\sigma_b = \sigma_{pl} + \sigma_{ch}$ is about twice $\sigma_a = \sigma_{pl}$ which means that $\sigma_{pl} \approx \sigma_{ch}$ and since S_b is much larger than S_a then we can approximately write

$$S_{ch} \approx 2(S_b - S_a) \approx 2S_b \qquad S_{pl} = S_a.$$

So the b axis measurement reflects the thermopower primarily due to the chains while the a axis measurements gives us the thermopower of the Cu–O_2 planes.

Cohn *et al* [8] have also recently measured the a axis and b axis thermopower in an untwinned crystal. They get similar results to ours for the a axis thermopower but rather different results for the b axis. Interestingly their derived chain contribution to the thermopower is very similar to our results for the b direction in both temperature dependence and magnitude but *opposite* in sign. This would tend to confirm Cohn *et al*'s argument that the Beni model for a narrow band thermopower is appropriate for the chain contribution. This predicts the thermopower to be temperature independent at high temperatures but change sign as the band crosses from less than to more than half filling. The band filling parameter depends on the value of δ thus the difference in sign of the b axis contribution between our sample and that of Cohn *et al* may simply reflect a difference in δ.

Apart from the fact that Cohn *et al* observe a change in sign at around 150 K, whereas the thermopower we measure appears to be changing sign around 200 K, the a axis contribution to the thermopower—which is simply the contribution from the planes—is very similar to Cohn *et al*'s data. These results are also very similar to the thermopower measured in the BiSCCO and thallium systems [3] which do not have a chain contribution to the thermopower. In measurements on these systems a cusp is

very often observed at T_c [6] as predicted by the Varlamov–Livanov and Maki models of fluctuation effects in the thermopower. This suggests that the general behaviour of the thermopower of the $Cu–O_2$ planes is much the same in all the cuprates: namely a metallic-like negative diffusion thermopower at high temperatures, a sign change around 150 K and a cusp or peak at T_c.

5. Conclusion

We have presented results for the thermopower of a number of single crystals of $YBa_2Cu_3O_{7-\delta}$ including one which was untwinned. We have found the thermopower along the a axis to be positive and around 1 $\mu V\ K^{-1}$ falling to nearly zero at around 200 K, suggesting a sign change to a negative diffusion thermopower at high temperatures. This seems to be a consistent feature of the $Cu–O_2$ plane contribution to the thermopower. The thermopower along the b axis is negative and roughly temperature independent at about 6 $\mu V\ K^{-1}$. This taken together with the recent results of Cohn *et al* suggests a narrow band contribution to the thermopower from the Cu–O chains. We have argued that fluctuation effects can be observed in the thermopower close to T_c; the rounding of the thermopower transition is consistent with the fluctuations being stronger in the b axis measurement. Recent theoretical models of fluctuation effects in the thermopower predict a cusplike peak at T_c if the characteristic pairing interaction is large. However, the peak seen in the a axis measurement and the twinned crystals may also be due to a 'subtraction' effect because of the opposite signs of the a and b axis thermopowers.

Acknowledgments

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