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Anisotropic thermopower in the *a-b* plane of an untwinned $YBa_2Cu_3O_{7-\delta}$ crystal

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We have measured the thermopower of an untwinned crystal of $YBa_2Cu_3O_{7-\delta}$ in both the *a* and *b* directions. In the *a* direction the thermopower is about +0.7 μV/K just above T_c, while in the *b* direction the thermopower is opposite in sign and −6 μV/K. The sharp peak observed at T_c in twinned crystals is only clearly present in the *a*-axis measurement. At temperatures close to room temperature the *a*-axis thermopower becomes temperature independent and very small. It is argued that the peak is evidence of superconducting fluctuation effects in the thermopower.

Measurements of the thermopower of polycrystalline and single-crystal $YBa_2Cu_3O_{7-\delta}$ are widespread,[1-3] but in all cases the material has been heavily twinned and it has not been possible to measure the thermopower along the *a* and *b* axis separately. Recently the resistivity has been measured in an untwinned crystal and a significant difference between the two directions was observed, with the *b* axis having a lower resistivity.[4] We report here on measurements of the thermopower on an *untwinned* crystal of $YBa_2Cu_3O_{7-\delta}$ for both the *a* and *b* directions.

The crystal was grown by a self-flux method similar to that reported by Rice *et al.*[5] The crystal was approximately 1.2 mm×1.2 mm×50 μm, with a large untwinned region in the center measuring approximately 1×1 mm^2. Much of the residual twinned region was cleaved off, although some small regions on the edges remained. The crystal was oxygenated initially by annealing at 500 °C in flowing oxygen for 4 days. Gold contacts were then evaporated onto the sample so as to pick out the *a* or *b* axis, which had previously been identified by x-ray analysis —here the *b* axis is parallel to the Cu-O chains. Once the gold was evaporated the sample was annealed for 1 h at 500 °C in flowing oxygen. This helped to improve the contact resistance to the sample. After the thermopower had been measured in one direction the gold was removed mechanically and reevaporated to pick out the other crystallographic axis. The gold contacts were also positioned so as to short out as much of the residual twinned regions as possible. The sample was reannealed each time the gold was evaporated.

The thermopower was measured using an ac optical heating technique similar to that described by Howson *et al.*,[6,7] the major modification being that the light was passed into the cryostat down an optical fiber and the light source was an ir laser diode which could produce between 5 and 18 mW of 780 nm monochromatic light. The light was chopped at a frequency of 29 Hz. The frequency dependence of the thermopower signal was investigated between 6 and 60 Hz. 29 Hz was a compromise between a good signal-to-noise ratio and a sufficiently low-enough frequency that the thermal skin depth of the crystal was much larger than the actual thickness of the crystal. The important feature of this technique is the ability to measure the thermopower with great temperature resolution (less than 100 mK) and so obtain precise results close to T_c. The thermoelectric voltage was measured with reference to lead.

The results for the thermopower are shown in Fig. 1. The *a*-axis thermopower is *positive* while the *b*-axis thermopower is much larger and *negative*. In Fig. 2 we show the thermopower for the *a* and *b* directions up to 200 K. The *b*-axis thermopower remains large and relatively temperature independent. In contrast, the *a*-axis thermopower drops to a very small value of approximately 0.1 μV/K at which point it appears to become temperature independent.

The Fermi surface of $YBa_2Cu_3O_{7-\delta}$ will have a sheet associated with the Cu-O planes and a sheet associated with the Cu-O chains. The measurements in the *b* direction will be due to a combination of the planes and chains, while the *a*-axis measurement will be mainly due to the planes. Thus, the results presented here suggest that the

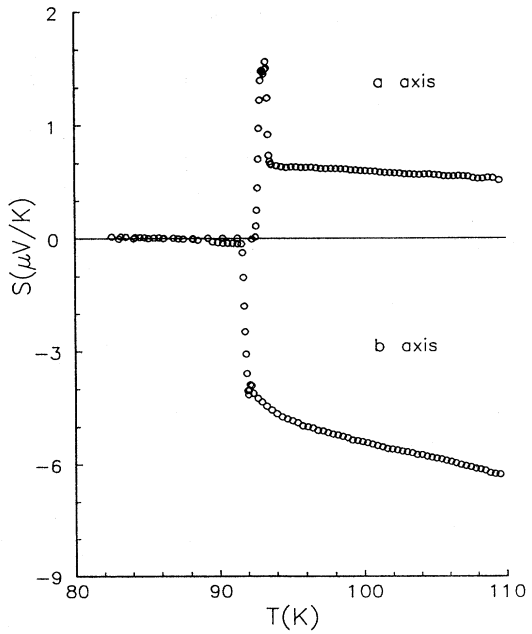

FIG. 1. The thermopower of an untwinned crystal of $YBa_2Cu_3O_{7-\delta}$ close to the transition temperature measured with the thermal gradient along the *a* axis or along the *b* axis.

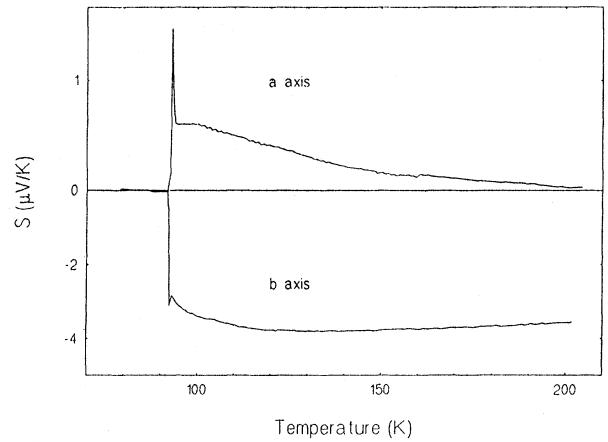

FIG. 2. The thermopower of an untwinned crystal of $YBa_2Cu_3O_{7-\delta}$ from the transition temperature up to 200 K.

thermopower due to the carriers associated with the planes is positive and the thermopower due to the carriers associated with the chains is negative. The negative sign of the thermopower on the chains may well be related to the one-dimensional nature of the Fermi surface. The sign of the thermopower in $YBa_2Cu_3O_{7-\delta}$ has long been a source of confusion. More recent results show, however, that for x less than about 0.1 the thermopower is negative, but as the oxygen content is reduced, the magnitude of the thermopower decreases to zero and then changes sign to positive.[1] It seems that the oxygen is mainly being extracted from the chain sites for small x and so this change in sign may well be related to changes in the Fermi-surface sheet associated with the chains.

The thermopower of a highly correlated electron gas is described by the Heikes formula[8] and is predicted to be temperature independent and zero for a half full band. This is strictly the case only at high temperatures. At low temperatures compared with the Fermi temperature, the thermopower will be metallic, approaching zero at $T=0$. Thus, we might argue that at high temperatures the a-axis thermopower (planes of Cu-O) is consistent with a correlated electron gas at approximately half band filling.

The other remarkable feature of these data is the presence of a very sharp peak at T_c. This has been reported before in twinned crystals.[6,7,9] Other authors also have reported peaks near T_c[3], but these have been very much broader ($\Delta T > 10$ K) and are not related to the very sharp feature seen here. The peak is clearly observable in the a-axis measurement for this untwinned crystal. The b-axis measurement shows signs of a peak, but is a very much smaller feature. Previous measurements of the peak have been on poorer quality twinned samples with obvious oxygen inhomogeneities and instead of one sharp peak, a cluster of peaks were observed.[6,7,9] Here we can see just one peak, for the a-axis measurement, with a width of about 500 mK.

Howson *et al.*[6,7] argued that this peak was evidence of the fluctuation contribution to the thermopower. The thermopower is in fact a ratio of two transport coefficients L_{eT} and the electrical conductivity σ: $S=L_{eT}/\sigma$. Here L_{eT} is related to the current driven by a temperature gradient. Maki[10,11] predicted a contribution to L_{eT} which was not divergent enough to lead to the sharp peak seen. In order to explain the peak Howson *et al.*[7] argued that Maki had missed the most divergent contribution to L_{eT} and showed, using a kinetic-theory argument, that a contribution which diverges as $[T_c/(T-T_c)]^{1/2}$ may be present.

Recently Lu and Patton,[12] and separately Varlamov and Livanov,[13] have also argued, using a more rigorous theoretical calculation, that there is a more divergent contribution to L_{eT} so that a peak in S is possible. Close to T_c Lu and Patton find a thermopower of the form

$$\frac{S_n+S_{fl}}{S_n}=\frac{1+\alpha(\sigma_{fl}/\sigma_n)}{1+(\sigma_{fl}/\sigma_n)}=\frac{1+\alpha(\epsilon/\epsilon_G)^{-1/2}}{1+(\epsilon/\epsilon_G)^{-1/2}}, \quad (1)$$

with $\alpha=3\hbar^2/(2\pi k_B T_c \tau)^2$, while Varlamov and Livanov find a thermopower, in the clean limit, of the same form but with $\alpha=4\ln(\Theta_0/T_c)$. Here S_{fl} (σ_{fl}) is the fluctuation contribution to the thermopower (conductivity), S_n (σ_n) is the normal thermopower (conductivity), τ is the quasiparticle lifetime, ϵ is the reduced temperature $(T-T_c)/T_c$, and finally ϵ_G is a reduced-temperature Ginzburg criterion indicating the crossover temperature to critical fluctuations. In Eq. (1) the denominator comes from the divergence in the electrical conductivity σ and the numerator from the divergence in L_{eT}. For three-dimensional fluctuations, which are expected within 10 K of the transition,[14] both terms diverge as $(T_c/T-T_c)^{1/2}$. In Varlamov and Livanov's model the $\ln(\Theta_0/T_c)$ factor, along with an implicit derivative of the quasiparticle density of states, arises from particle-hole asymmetry which is necessary if a current is to flow in response to a thermal gradient. Curiously, Lu and Patton's model does not include this particle-hole asymmetry.

Both models predict a peak in S if $\alpha > 1$. For Varlamov and Livanov's model this is when Θ_0/T_c is greater than 8.5. Here Θ_0 is the characteristic temperature for the attractive electron-electron coupling. This is usually the Debye temperature, but for high-T_c superconductors it may well be closer to the Fermi temperature. For Lu and Patton's model the peak depends on the quasiparticle lifetime and occurs when $3\hbar^2/(2\pi k_B T_c \tau)^2 > 1$.

In Fig. 3 we show the thermopower plotted against $(T-T_c)/T_c$ for both the a- and b-axis data. The solid lines in Fig. 3 show the fit to the data using Eq. (1). In performing this fit S_n was taken to be a constant over the temperature range. The fits are not perfect but they do indicate that the general temperature dependence of the thermopower can be described by Eq. (1). In the a-axis direction the peak is very sharply peaked, while a square-root divergence is usually quite broad. The sharp peak results because of the similar divergence in σ and L_{eT} leading to a cancellation effect away from T_c. The fits in Fig. 3 give us an a axis value of α of 15.2 and a b axis value of 0.13. The fits also give estimates of the Ginzburg criterion temperature. In the a direction ϵ_G is 1.4×10^{-5} and in the b direction it is 1.2×10^{-2}. If this difference in ϵ_G, for the two directions, is attributed to the coherence lengths only then the ratio $(\xi_0)_a/(\xi_0)_b$ would be approximately 5. However, anisotropy in the Fermi surface may

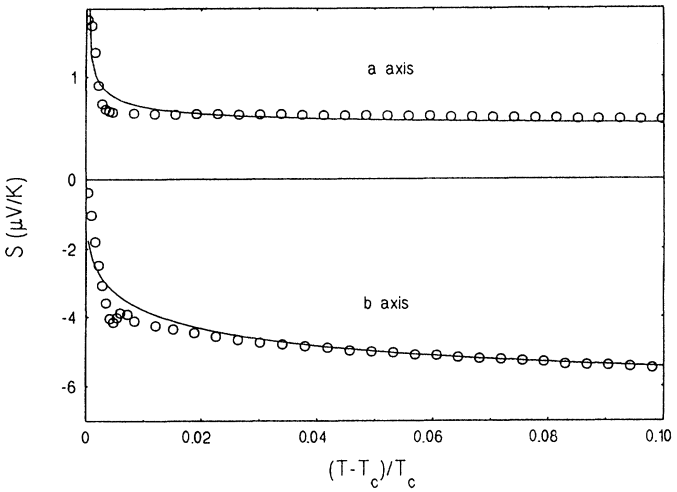

FIG. 3. The thermopower of an untwinned crystal of $YBa_2Cu_3O_{7-\delta}$ plotted against the reduced temperature $(T-T_c)/T_c$. The solid lines are fits to the data using Eq. (1).

also explain the difference in ϵ_G.

The values of α lead to values of Θ_0 of approximately 4000 K from the *a*-direction result and 100 K for the *b*-direction result. These results are certainly unusual, first because of the difference in Θ_0 and second because the value of 100 K is much too small. In the model of Lu and Patton, however, the values of α give us estimates of the quasiparticle lifetime. The values of τ are 5×10^{-15} s in the *a* direction and 5×10^{-14} s in the *b* direction. If we assume an isotropic Fermi velocity of 5×10^5 m/s these correspond to mean free paths of 2.5 and 25 nm, respectively. Since the *average a-b* coherence length is about 1.5 nm this suggests that while the *b* axis is almost certainly in the clean limit, the *a* axis may well be in the dirty limit.

There are other possible explanations of this peak. First, one of the features of the peak is that it is very sharp and this raises the question that it may be associated with a crossover to critical fluctuations. If L_{eT} diverges faster than σ, within the critical region, there will be a rapid divergence of S close to T_c. In this case the peak width of 500 mK suggests a critical region of about 500 mK. Second, if the pairing were not conventional *s*-wave pairing, the possibility that the *a*- and *b*-axis coherence lengths diverge at different temperatures would certainly give rise to a peak. A feature of the data in Fig. 1 is that the temperature at which the measured thermopower is zero is different for the two crystallographic directions, with the *a*-axis thermopower going to zero about 0.8 K higher than the *b*-axis data. This difference is significant and is reproducible on warming to room temperature, remounting, and remeasuring. It is interesting to point out that Bucher *et al.*[15] have also observed T_c approximately 1.5 K higher in the *a* direction for untwinned $YBa_2Cu_4O_8$. We have no explanation for the difference.

The fact that the *a*- and the *b*-axis thermopowers are of opposite sign may also explain the origin of the peak. If there were a small misalignment of the crystal, with respect to the thermal gradient, then the *a*-axis measurement may have a small *b*-axis contribution and vice versa. However, it appears that the small peak seen in the *b*-axis data is far more sensitive than the *a*-axis peak to slight changes in the alignment of the crystal. This would imply that the *a*-axis peak is intrinsic while any small peak seen in the *b* axis may be due to a small misalignment.

In conclusion, we have reported measurements of the thermopower of an untwinned crystal of $YBa_2Cu_3O_{7-\delta}$. We find the thermopower to be positive in the *a* direction and larger but negative in the *b* direction. The peak which is seen at T_c in twinned crystals is only seen in the *a*-direction measurement. We have shown that the thermopower close to T_c is consistent with recent predictions for the fluctuation contribution to the thermopower.

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