Anomalous peak in the thermopower of $YBa_2Cu_3O_{7-\delta}$ single crystals: A possible fluctuation effect

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We present results for the thermopower of five crystals of $YBa_2Cu_3O_{7-\delta}$ from the transition temperature T_c to 250 K and in magnetic fields to 2 T. The thermopower is approximately -4 μV/K at 250 K for all samples, with a broad phonon drag peak around 150 K. Sharp peaks in the thermopower are observed in the vicinity of T_c. The thermopower is qualitatively the same for all crystals except one that was annealed at 650 °C in oxygen That crystal had a positive thermopower and exhibited no peak at T_c. After a reanneal in oxygen at 400 °C, the negative thermopower and peak at T_c appeared. We discuss the possibility that the anomalous peak at T_c is a fluctuation effect and suggest a simple kinetic argument for the presence of a divergent fluctuation contribution.

INTRODUCTION

In a previous paper[1] we presented results for the thermoelectric power (TEP) of a single crystal of $YBa_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O) at temperatures close to the transition temperature T_c. A sharp peak was observed at T_c, which we argued could be due to fluctuations. In this paper we present more detailed measurements of the TEP up to 250 K, and in fields up to 2 T, for a number of crystals, and investigate the effect of heat treatments. We discuss the magnitude and temperature dependence of the TEP and look more closely at the possible effects of fluctuations near T_c.

The thermopowers of both polycrystalline and single-crystal samples of $Y_1Ba_2Cu_3O_{7-\delta}$ have been measured by a number of groups.[1-4] A wide variety of different temperature dependences and magnitudes, both positive and negative, have been reported. Most of the single-crystal measurements have used a dc differential method with very poor temperature resolution and poor signal-to-noise ratios. Our previous paper was an exception, having employed a novel ac technique that gives very precise results at a temperature resolution of about 50 mK and a signal-to-noise ratio > 100. The technique was developed to search for fluctuation effects in the thermopower. Although predicted to occur, such TEP fluctuation effects have never been seen in the "classical" superconductors. This is because they typically have a zero-temperature coherence length $\xi_0 \geq 1000$ Å so that the temperature range over which one might expect to see such effects would be extremely small. In Y-Ba-Cu-O, however, ξ_0 is thought to be ~ 1 nm and the range over which one might observe three-dimensional (3D) fluctuation effects could be several Kelvins.

EXPERIMENTAL DETAILS

The crystals, grown using a flux method outlined elsewhere,[5] were typically 1 mm $\times$ 1 mm $\times$ 50 μm in size. The resistivity was measured using a four-probe ac technique. The crystals typically had T_c's between 92 and 93 K, with widths ranging from 0.6 down to 0.3 K, measured from the 90% to 10% points in the resistive transition. The sample on which we concentrate for the analysis of fluctuation effects had a midpoint T_c of 92.6 K.

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 from a tungsten lamp, through quartz windows in the cryostat, while the other half was masked and thermally anchored. This results in an oscillating temperature gradient of ≈ 50 mK rms at 6 Hz in the *a-b* plane. The crystal was mounted on a strip of Mylar 75 μm thick, one half of which was covered with 2000 Å of evaporated 99.999% Pb. The other Pb contact was made to a 1.5-mm thick strip of Pb supported by the Mylar. Electrical contact to the Pb was made with Ag painted to Au pads, evaporated on opposite ends of the crystal (in order to get good contact the crystal was annealed at 400 °C in oxygen after the Au pads were evaporated). The temperature gradient across the sample was measured using a chromel versus constantan thermocouple made with 25-μm diameter wire, which was thermally anchored to the sample with a small quantity of GE varnish towards the end of the crystal. The absolute temperature of the sample was measured using a Pt thermometer placed in the Cu block which acted as a heat sink. One side of the crystal was thermally anchored through the strip of 1.5-mm thick Pb to this block. The other end of the sample was only in

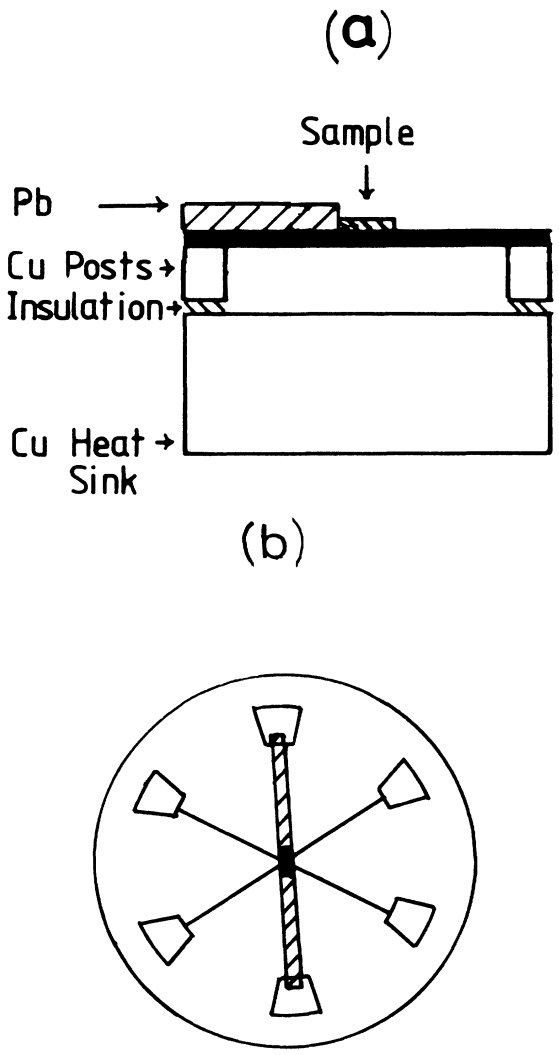

FIG. 1. A schematic diagram showing how the crystals were mounted. (a): cross section; (b): plan view. The positioning of the sample, the Pb reference leads and the cross thermocouple wires may be seen. The Mylar support is marked by the black area in (a) and the shaded area in (b). (Not to scale.)

thermal contact to the block through the 2000 Å film on 75-μm thick Mylar. This difference in thermal conductance helped to maintain the 50 mK ac temperature gradient across the sample. Figure 1 is a schematic diagram showing how the crystal was mounted.

With this method it is possible to measure the absolute magnitude of the thermopower to an accuracy of 10% and to measure changes to a precision of 0.3%. We verified this by observing that the measured thermopower below T_c is precisely that of Pb. Since only a 50 mK temperature difference is required, features in the thermopower down to this temperature resolution can be observed, making this method ideal for investigating fluctuation effects close to T_c.

RESULTS AND DISCUSSION

The results for the absolute thermopower of four of the crystals (A–D) investigated are shown in Fig. 2 over a narrow temperature range about T_c. In Figs. 3 and 4 the thermopower of crystals A and D are shown up to 250 K. It can be seen that there is relatively little change between 100 K and room temperature. The TEP in all the crystals is around $-4.0\ \mu$V/K at 100 K. This is a typical metallic value and we could argue that its negative sign indicates an essentially electronlike Fermi surface. However, the Mott formula for the thermopower of a metal shows that the sign depends not just on the energy derivative of the Fermi surface area but also on that of the scattering rate. Crabtree *et al.*[6] 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 essentially holelike. 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, dominates the sign of the thermopower.

There is evidence of a small, broad phonon drag peak located just above 100 K. The broadness of the peak is consistent with a large effective Debye temperature. There is no evidence of a diffusion (linear in T) contribution to the highest temperatures measured. There has been some debate over the possibility of seeing electron-phonon mass enhancement effects[7] in the diffusion thermopower, but this is possible only if the phonon drag contribution can be subtracted reliably. The phonon drag peak seen here is small enough that the introduction of disorder by neutron irradiation or elemental substitution might remove it, revealing the diffusion thermopower.

In Fig. 5 the thermopower of sample E is shown after successive heat treatments. All five crystals, which were grown in air, were given a 1 h soak in oxygen at 600 °C followed by a 4 day soak at 400 °C in flowing oxygen. However, sample E was subjected to a further 12 h soak at 650 °C in flowing oxygen, followed by two additional 12 h soaks at 400 °C in oxygen. The thermopower of sample E was remeasured after each treatment. The 650 °C treatment had a dramatic effect on the sign of the thermopower—changing it to positive—but did not change T_c appreciably. However, this change of sign was reversed by a further soak at 400 °C; the thermopower was negative but approximately a factor of 2 larger in magnitude than observed initially. Following a further 12 h soak at 400 °C, the TEP returned to its initial state. Thus the thermopower is extremely sensitive to the processing conditions and only samples that are thoroughly equilibrated with O_2 near 400 °C for several days exhibit a negative thermopower. This may explain differences in the sign of the thermopower reported for polycrystalline samples.

We turn next to the rather remarkable peak in the thermopower at T_c. All annealed 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 suggest that the subsidiary peaks, along with the foot, indicate a series connection of regions with slightly different, but well-defined T_c's. The thermopower at the main peak, on which we focus, increases to almost double its magnitude before dropping rapidly to

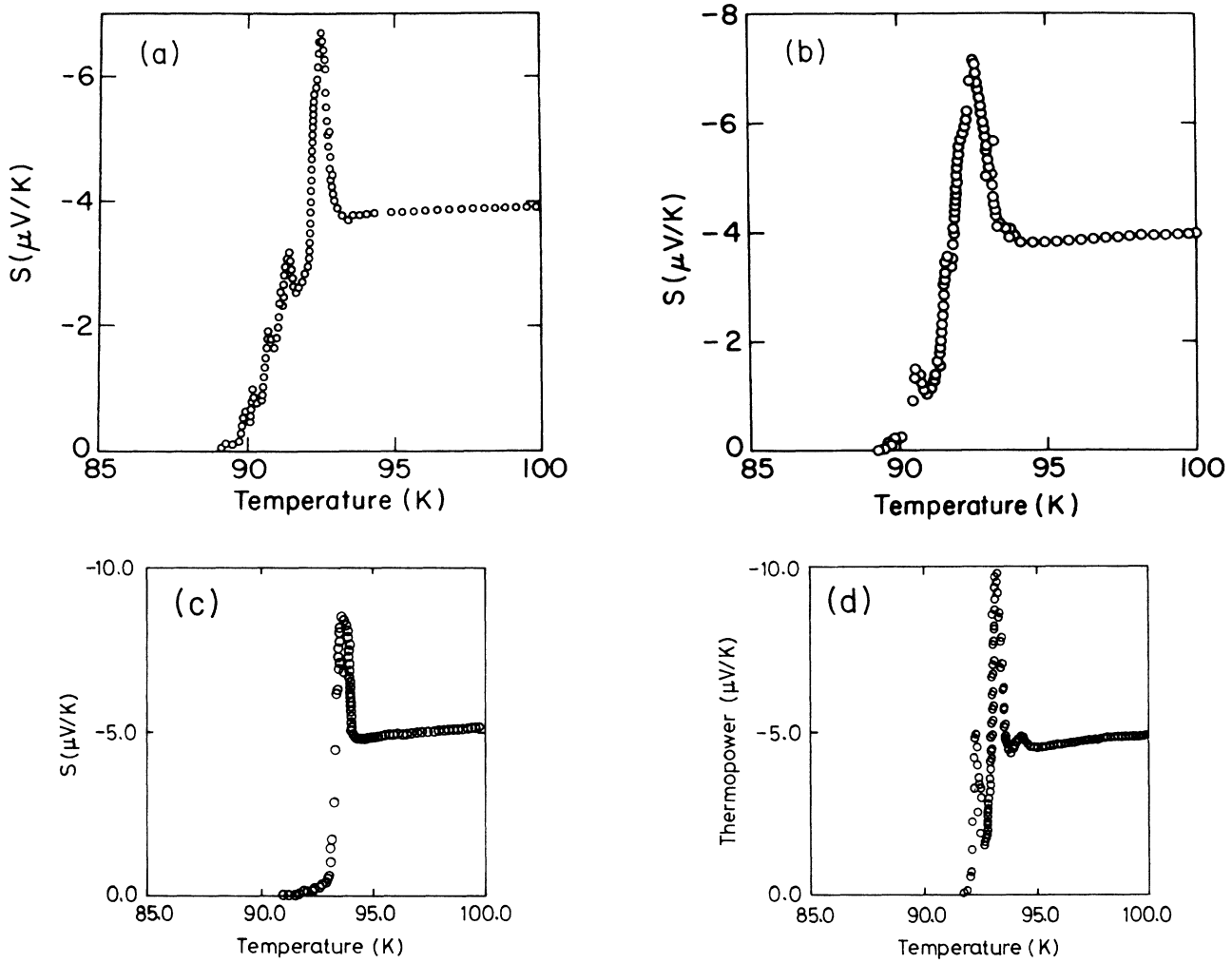

FIG. 2. The thermopower vs temperature over the temperature range 85–100 K for samples $A-D$.

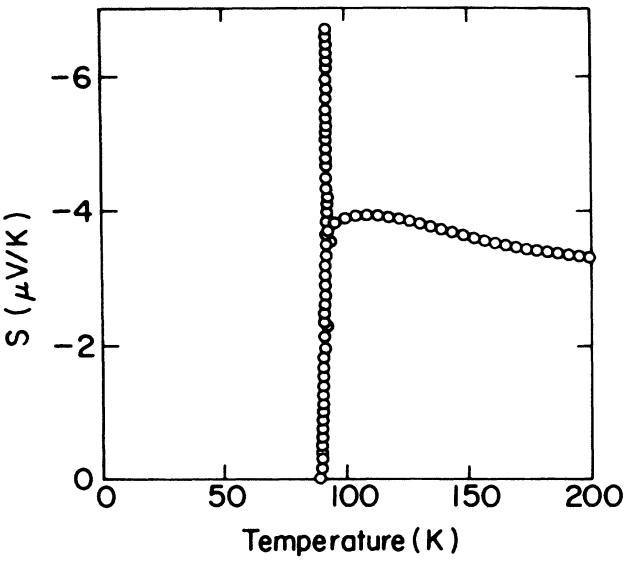

FIG. 3. Thermopower of sample A for temperatures up to 200 K.

zero. All of the peaks are quite reproducible for a particular sample but only the main peak is consistently observed in all samples. In Fig. 5 we showed that the peak disappears when the thermopower of the crystal changes sign. If, as we argue later, the source of the peak is due to fluctuation effects, it remains negative while the

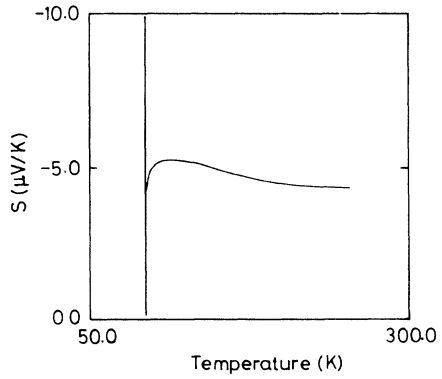

FIG. 4. Thermopower of sample D for temperatures up to 250 K.

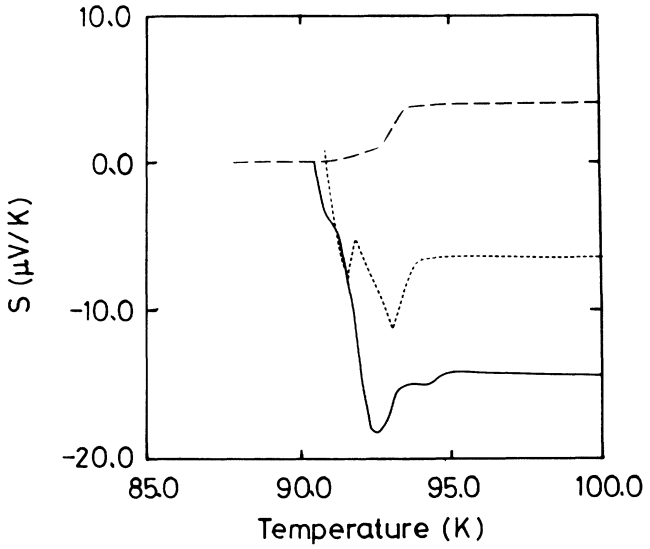

FIG. 5. The thermopower of sample E after various heat treatments in O_2. The sample was annealed initially for 4 days at 400 °C then 12 h at 650 °C (— — —), followed by 12 h at 400 °C (——), and a further 12 h at 400 °C (– – –). (Because of the large number of points the data are shown as lines.)

normal-state contribution changes sign, masking the effect. We did investigate the dependence of the peak on the temperature gradient used, which sets the temperature resolution of the measurement. A temperature gradient of 50 mK was normally used but gradients down to 10 mK were also investigated, with no significant sharpening of the peak, before the signal-to-noise ratio became unacceptably small.

All the thermopower peaks are extremely sensitive to magnetic field. This is shown in Fig. 6. For fields below

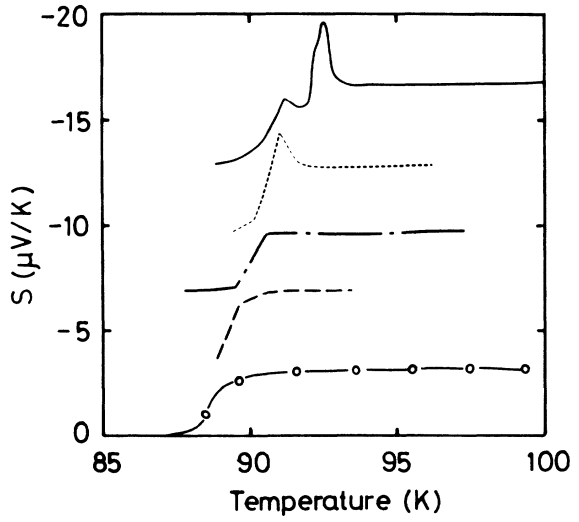

FIG. 6. The thermopower of sample A in various magnetic fields. ——, 0 T; – – –, 0.25 T; —·—·—, 0.5 T; ———, 0.75 T; o —o, 1 T. (Because of the large number of points the data are shown as lines. The data are shifted along the y axis for clarity.)

0.25 T the main peak shifts to lower temperature, by ≈ 0.5 K, and diminishes in magnitude. From 0.25 up to 2 T (the highest field used) that 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.*,[8] and has been interpreted in terms of fluctuation effects.

In our earlier paper[1] we considered the possibility that the TEP peaks are due to conventional superconducting fluctuations and compared the main peak with a result due to Maki.[9] Fluctuations in the thermopower have received little attention; no experimental observation of such effects have been reported even in reduced dimensions. Maki's calculation is the only theoretical consideration of the problem that we know. As for other properties, fluctuation contributions to the TEP depend inversely on a power of the zero-temperature coherence length. In classical superconductors $\xi_0 \geq 100$ nm, while for $Y_1Ba_2Cu_3O_{7-\delta}$ ξ_0 is expected to be small, $\xi_0 \lesssim 2$ nm in the a-b plane and $\xi_0 \approx 0.5$ nm in the c direction.[10] As a result, 3D fluctuations are large and have now been reported in the resistivity, specific heat, and susceptibility.[8,11–13] Similar fluctuation effects should also be observable in the thermopower.

Before discussing Maki's calculation[9] we consider a simple derivation of the fluctuation contribution to $S = L_{eT}/\sigma$, where σ is the *total* electrical conductivity and L_{eT} is an Onsager coefficient. The standard kinetic theory result is[14]

$$(L_{eT})_{\text{fl}} = \frac{e\tau}{3} \frac{\partial \langle nv^2 \rangle}{\partial T} ,$$

where n is the number density, τ is the lifetime, and v is the velocity of the carriers—here taken to be pair fluctuations. Arguments[15] that give conductivity fluctuations, also lead to the expression

$$(L_{eT})_{\text{fl}} = \frac{\hbar^2 e}{3m^2} \sum_k k^2 \tau_k \frac{\partial \langle |\psi_k^2| \rangle}{\partial T} ,$$

where

$$\tau_k \simeq \frac{\pi\hbar}{8k_B(T-T_c)} \frac{1}{(1+k^2\xi^2)}$$

and

$$\langle |\psi_k|^2 \rangle \simeq \frac{k_B T}{(1+k^2\xi^2)} \frac{2m}{\hbar^2} \xi^2 .$$

Taking the temperature derivative and evaluating the 3D integrals, we find, close to T_c,

$$(L_{et})_{\text{fl}} = \frac{\hbar e}{24\pi m \xi_0^2 T_c} \left[\left[q_0 - \frac{3\pi}{4\xi_0} t^{1/2} \right] - \left[\frac{3\pi}{16\xi_0} t^{-1/2} \right] \right] , \quad (1)$$

where $t = (T/T_c - 1)$, ξ_0 is the BCS zero-temperature coherence length and q_0 is a momentum cutoff. A convenient estimate for $q_0 = 2\pi/\xi_0$ (i.e., $q_0 \simeq 6 \times 10^9$ m^{-1} for

$\xi_0 \simeq 1$ nm. The mass in Eq. (1) is the pair mass $m = 2m^*$, where m^* is the effective mass of the quasiparticle involved in the superconductivity.

A more rigorous calculation by Maki[9] predicted Gaussian fluctuation contributions to the thermopower in various dimensionalities in the dirty limit. Maki's result for $d = 3$ can be written as

$$(L_{eT})_{\rm fl} = \frac{3\pi k_B^2 Te}{8E_F\hbar}\alpha\left[q_0 - \frac{3\pi}{4}\left[\frac{8k_B T_c t}{\pi\hbar D}\right]^{1/2}\right], \quad (2)$$

where

$$\alpha = \ln\left[\frac{T_0}{T_c}\right]\left[\frac{d\ln N(E)}{d\ln E}\right]\Bigg|_{E=E_F} L(\rho) .$$

Here $L(\rho)$ 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; $N(E)$ is the quasiparticle density of states and T_0 is the characteristic temperature for the pairing interaction; for BCS it is the Debye temperature but for an electronic interaction it will be of the same order as the Fermi temperature.

Using the BCS result

$$\xi_0 = 3.17\hbar v_F/\pi^2 k_B T_c$$

and approximating $D \cong \frac{1}{3} v_F l$, where l is the electron mean free path, we can rewrite Eq. 2 as

$$(L_{eT})_{\rm fl} = \frac{28.56}{4\pi^3}\frac{e\hbar}{m^*\xi_0^2 T_c}\alpha\left[q_0 - \frac{3.57\pi}{4}\left[\frac{t}{l\xi_0}\right]^{1/2}\right] . \quad (3)$$

This is quite similar to the nonsingular term in the kinetic theory calculation, Eq. (1).

In order to compare our results with Eq. (2) we multiply the TEP data by the measured conductivity, σ. The data for sample A, after subtraction of a constant normal-state value, defined as $S\sigma$ at 100 K, are plotted versus $(T - T_c)^{1/2}$ in Fig. 7. Note that we are considering here *only* the increase in TEP as we approach the main peak with decreasing temperature. The solid line in Fig. 7 is a fit to the data using Maki's *full* 3D expression;[9] note that Eq. (2) is valid only close to T_c. The peak in the thermopower is quite sharp, with a width of ~ 1 K, and we only fit the data in the region of this peak. The fluctuation contribution itself may extend to very high temperatures, as it does in the resistivity, but unlike the resistivity data it is impossible to subtract the normal contribution correctly to reveal the high-temperature behavior. A similar problem is found in the specific heat analysis.[11]

Although the fit is acceptable, the diffusion constant D takes on an unreasonable value. For $q_0 = 6\times 10^9$ m^{-1} the fit gives $D \cong 10^{-8}$ m^2 s^{-1}, much smaller than the 10^{-4} m^2 s^{-1} typical of a metal. The overall amplitude, however, gives $\alpha \sim 4.5$ for $m^* \sim 6m_e$ and $\xi_0 \sim 1$ nm and is reasonable if $L(\rho) \sim 1$, $(d\ln N/d\ln E)_{E_F} \sim 1$ and $\ln(T_0/T_c) \sim 4.5$; then the value $T_0 \sim 8000$ K and is of the same order of magnitude as other estimates, if we assume an electronic pairing mechanism that has a characteristic temperature of the same order of magnitude as the Fermi energy.[10] We have also attempted to use Maki's $d = 2$ results, but are unable to fit a logarithmic divergence to our data.

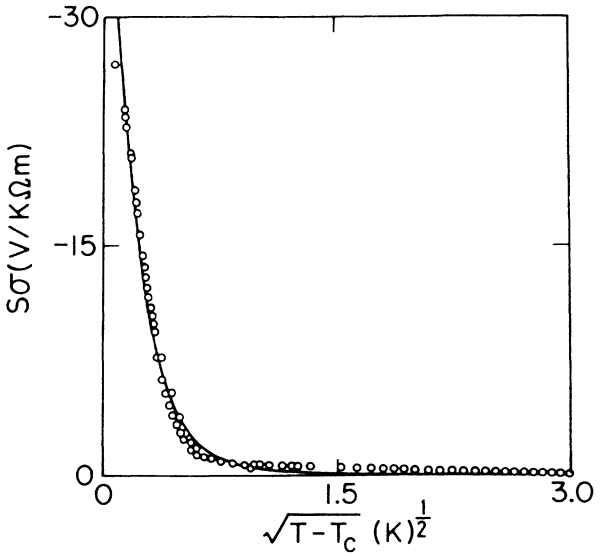

FIG. 7. The thermopower of sample A plotted as a function of $(T - T_c)^{1/2}$. The solid line is the 3D fit to the data using Maki's expression [Eq. (2)].

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 intermediate between clean and dirty limits. This is probably not enough to 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. Although the kinetic expression Eq. (1) reproduces Maki's $t^{1/2}$ cusp, it contains a $t^{-1/2}$ divergence which does not appear in Maki's calculation. Further, this divergent term, which will clearly dominate at T_c, is of the *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. The cusp, however, arises because the fluctuations each carry $k_B T$ of thermal energy, which results in a flow of energy down the thermal gradient. We therefore suggest that Maki's original microscopic calculation may not have included the most divergent contribution.

Since the $t^{-1/2}$ divergence will dominate close to T_c we have plotted $S\sigma$ versus $t^{-1/2}$ in Fig. 8. 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 quantitatively better than the Maki fit.

Other papers have reported a precursor peak in the thermopower of polycrystalline samples.[3,4,16] This peak is, however, much broader and smaller than the peak we

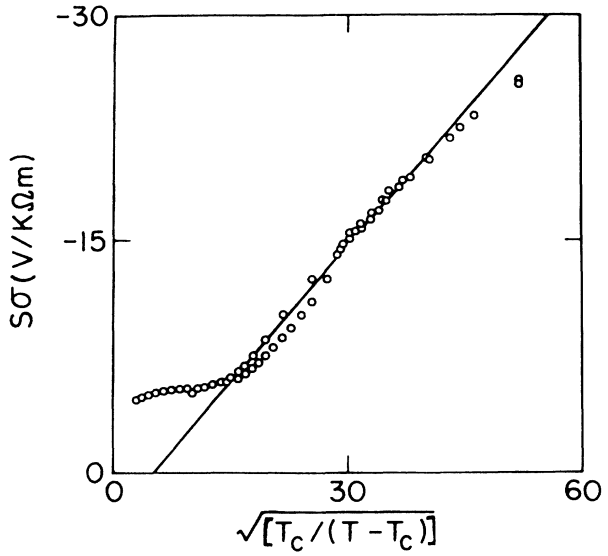

FIG. 8. The thermopower of sample *A* plotted as a function of $[T_c/(T-T_c)]^{1/2}$. The solid line is the 3D fit to the data using Eq. (1).

observe; the width of the peak is between 20 and 30 K. Uher and Kaiser[16] 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 presently under study.

CONCLUSION

In summary, we have made very precise measurements on the thermopower of a number of crystals of $YBa_2Cu_3O_{7-\delta}$. In all equilibrated crystals we have found a sharp peak in the thermopower close to T_c. The peak is very sensitive to a magnetic field and to the oxygen content of the samples. We have argued that the peak may be due to fluctuation effects. A microscopic theory due to Maki[9] exists, which fits the peak qualitatively but with an unreasonable value of the electron diffusion constant. We have suggested that this microscopic theory may 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.

It should be noted that this divergent contribution is of opposite sign to that of the effective mass of the carriers so that in a free electronlike system, the fluctuation contribution is of opposite sign to the normal-state TEP, and may not appear as a peak. It is only when the fluctuation and the normal-state contributions are of the same sign that a peak will be seen. Here we believe that the carriers may be holes but the normal-state contribution is negative because of a dominant contribution from the energy derivative of the scattering rate. The dominant fluctuation contribution, which is opposite in sign to the carriers, therefore has the same sign as the normal-state TEP and a peak is seen.

Finally, in this paper we have considered the possibility that the peak in the thermopower is a fluctuation effect. This is still a matter of some controversy. Indeed recent analysis of the resistivity in single-crystal Bi-Sr-Ca-Cu-O suggests there may be a Kosterlitz-Thouless transition (Ref. 17) T_{KT} approximately 2 K below the superconducting mean-field transition. Since the thermopower is related to a ratio of L_{eT}/σ this could very well lead to a sharp feature between T_c and T_{KT}.

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