Field dependence of the specific heat of single-crystal $HgBa_2Ca_2Cu_3O_{8+\delta}$

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Using a sensitive ac technique, we have measured the specific heat (C) of a small single crystal of $HgBa_2Ca_2Cu_3O_{8+\delta}$ in fields up to 7 T. In zero field the superconducting anomaly has the form of a quasilogarithmic peak, which is almost symmetric about T_c. In increasing fields the anomaly is strongly suppressed and is shifted to lower temperatures (with a slope of ~ -0.8 K/T). This unusual behavior is qualitatively different from that of $YBa_2Cu_3O_{6.95}$, and seems to be intrinsic to the quasi-two-dimensional, high-T_c superconductors. We find that the three-dimensional XY model of critical fluctuations best describes our data.
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It is by now well known that a combination of factors, such as short coherence lengths, low dimensionality, and high T_c, mean that fluctuation effects play an important role in determining the properties of high-temperature superconductors near T_c. Many experimental studies have focused on the magnetization and transport properties of high-quality single-crystal samples. Detailed specific heat (C) measurements of single crystals have, however, been mainly limited to $YBa_2Cu_3O_{7-\delta}$ (YBCO) near optimal doping. As for this compound, the anomaly in C at T_c is a relatively large proportion ($\sim$3.5%) of the phonon dominated background, and is easy to detect. In this paper we present specific heat data for the three-layered, Hg-based, high-T_c superconductor, $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223), in fields up to 7 T applied parallel to the c axis. Both the shape of the zero-field anomaly, and its dependence on field, are qualitatively different from that found for YBCO (Refs. 1 and 2) and conventional low-T_c superconductors. It is likely that this originates from the larger anisotropy of Hg-1223 (Ref. 3 estimates that $\gamma\sim52$) compared to that of YBCO, which leads to much stronger fluctuation effects. The close similarity between the behavior of Hg-1223 and recent results for $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212)[4] suggests that these are rather general properties of these quasi-two-dimensional systems.

Single crystals of Hg-1223 were grown by a single step synthesis route as described in Ref. 5. The crystal structure and stoichiometry were verified by x-ray analysis which is reported elsewhere.[5] The sample measured here was a small, platelet crystal with approximate dimensions $0.23\times0.12\times0.032$ mm^3 (the shortest dimension being along the c axis), and a mass of $\sim$5 μg. The transport properties and NMR of crystals with a similar bulk T_c to that here are reported elsewhere.[6,7] Specific heat was measured by a sensitive ac technique[8] similar to that of Salamon *et al.*[9] The sample, and a suitably chosen reference, were attached to thermocouples and heated independently by light. With our configuration it was possible to measure either the total specific heat of one sample, or the difference in $C(T)$ between the sample and the reference. This differential method greatly improved the sensitivity and reproducibility of our measurements, and effectively eliminated the effect of field on the thermocouple calibration. Using impedance-matched electronics, we achieved a very low noise level of $\sim$0.10 nV, which with a typical temperature oscillation of 50 mK, translates to a noise level in the specific heat of $\sim$0.01% of the total at 100 K. To obtain a reference with a phonon specific heat well matched to our sample, we vacuum annealed one of our Hg-1223 crystals for 12 h at 450 °C. With this treatment, the reference sample had no traces of superconductivity (by ac susceptibility) above 60 K. Absolute values of C were estimated by normalizing our data, at 150 K, to that of Calemczuk *et al.*[10] for a large polycrystalline sample of Hg-1223 ($T_c\sim$133 K) [C(150 K)=268 J/K mol].

The homogeneity of our sample was checked by ac susceptibility (acs) measurements. The sample was placed in a small (1.6 mm diameter) balanced detection coil and a drive field of 1.0 Oe at 72 Hz was applied $\parallel$ c. A weakly temperature-dependent background was subtracted and the results normalized so that $\chi'=-1$ in the superconducting state.[11] The results (inset Fig. 1) show that there is a sharp transition (the 10–90 % width equals 1.2 K) at T_c (midpoint) =110.4 K. We remark that this value is somewhat lower than the optimum T_c of 133 K for this compound at ambient pressure.[12] This is probably because of a small oxygen deficiency in our crystals.[13] Indeed the transport properties[6] and NMR (Ref. 7) of crystals grown in the same way show all the usual signs of being slightly underdoped. The close resemblance of our results in zero field to the data of Calemczuk *et al.*[10] means, however, that we expect our conclusions to also hold for the optimally doped material (at least at the qualitative level).

Raw differential specific heat data are shown in Fig. 1. The total variation of the differential signal over the range 70 K to 150 K is around 2% (0.5% between 90 K and 150 K), showing that the phonon specific heats of the samples are fairly well matched. The anomaly in zero field is clearly visible, peaking close to the acs T_c and representing around 0.56% of the total. The measured differential specific heat

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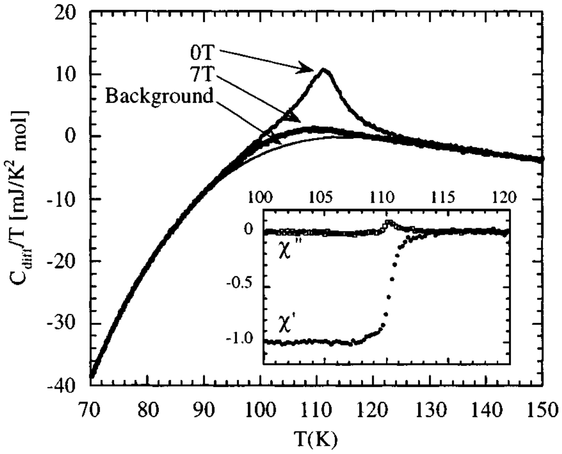

FIG. 1. Raw differential specific heat (C_{diff}/T) of $\mathrm{HgBa_2Ca_2Cu_3O_{8+\delta}}$ in zero field and 7 T ($\| c$) along with the estimated background. Inset: ac susceptibility of the same crystal, in zero dc field ($H_{\mathrm{ac}}=1.0$ Oe $\| c$).

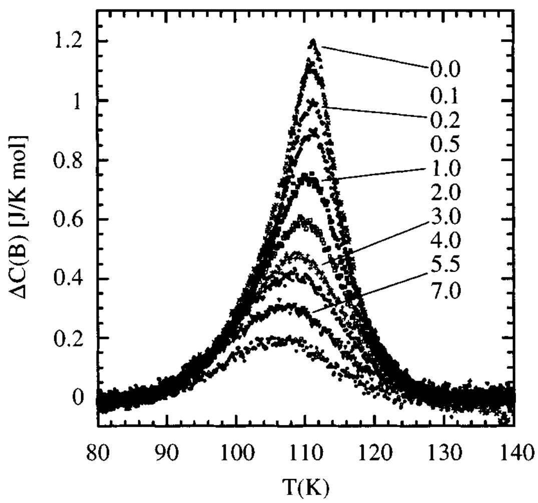

FIG. 2. Field dependence of the specific heat of Hg-1223 after subtraction of the background (see Fig. 1 and text). The field values in T ($\| c$) are indicated in the figure.

(C_{diff}) is the sum of the residual differences in the phonon specific heats, differences in electronic specific heats and differences in the addenda. With this well-matched reference it is clear that a field of 7 T ($\| c$) is not sufficient to completely suppress the anomaly at T_c, and so it is difficult to unambiguously isolate the electronic part of the specific heat of our sample. To proceed with the analysis of the data we have estimated the background by fitting a polynomial (fourth order) to the 7 T data in the temperature intervals 130 K $<T<$150 K and 70 K$<T<$90 K (where C is virtually independent of B) and extrapolating this function across the intermediate temperature region (see Fig. 1). Although there is clearly some uncertainty in this background we have verified that our main conclusions are insensitive to its exact form [any remaining very weakly T-dependent terms, which would not be included in our background, would be absorbed into the constant term in the critical fluctuation fits (see below)].

The raw data with the background subtracted [$\Delta C(B) = C_{\mathrm{diff}}(B) - C_{\mathrm{bg}}$] are shown in Fig. 2. The anomaly in zero field is approximately symmetric about T_c, showing that the mean-field contribution is small, and suggesting that the thermodynamics of this compound are dominated by strong fluctuation effects near T_c. The form of the anomaly is quite different to that of YBCO, but is similar to that reported for ceramic samples of Hg-1223 (Ref. 10) and for several other quasi-two-dimensional cuprate superconductors.[4,14] It is unlikely that inhomogeneity is responsible for this broad anomaly as its peak essentially coincides with the sharp transition observed in the acs. The earlier measurements of Jeandupeux *et al.*[15] also show evidence for strong fluctuation effects far above T_c in Hg-1223. Their choice of background, which leads to the conclusion that there is a sizable mean-field step in Hg-1223, is, however, not supported by the present work.

A striking feature of the data in Fig. 2 is the very strong suppression of the size of the anomaly in increasing magnetic field, accompanied by only a weak decrease of T_c. In a conventional mean-field model the anomaly size is related to $T_{c2}(H)$ by

$$\Delta C(T_{c2}) = \frac{T_{c2}(dB_{c2}/dT)^2}{\mu_0(2\kappa^2-1)\beta}, \qquad (1)$$

where κ is the Ginzburg-Landau parameter and β is the flux-line lattice constant. The fact, suggested by Eq. (1), that a large suppression of the anomaly height is accompanied by a comparable decrease in T_c is a feature of all conventional low-T_c superconductors. The behavior shown here for Hg-1223 is a strong indication of the failure of the mean-field picture to describe, even qualitatively, the thermodynamics of this compound near $T_c(H)$.

A similar effect of field on $C(T)$ has also been reported for Bi-2212 (Ref. 4). An important difference however, is that for Bi-2212 the position of the peak in $C(T)$ varies nonmonotonically with field and shifts by less than 2 K in 14 T, whereas for Hg-1223 the peak shifts monotonically to a lower temperature with increasing field (Fig. 3). The shift is approximately linear with the field having a slope of -1.2 ± 0.1 T/K, although a weak power law [such as $(1-T/T_c)^{4/3}$] is a marginally better fit. This is close to the value of $\partial B_{c2}/\partial T = -1.4$ T/K estimated from recent torque measurements[3] of crystals similar to those measured here. The rapid collapse of the anomaly in increasing field is com-

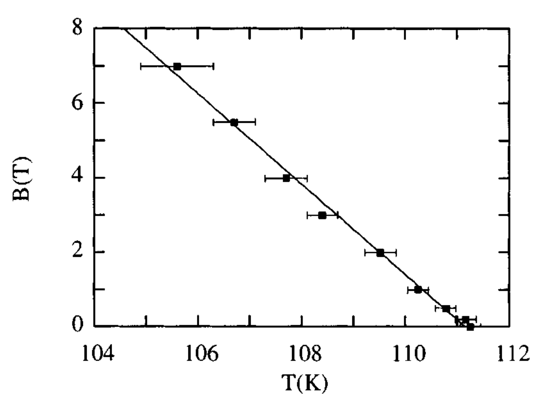

FIG. 3. The evolution of the position of the peak in ΔC with field.

parable to that of Bi-2212, but unlike Bi-2212 the peak temperature decreases with increasing field with a slope which is comparable to that of YBCO. The reason for this difference is not clear but may simply reflect a difference in the inplane coherence lengths.

The correct description of the thermodynamics near T_c of the strongly fluctuating high-T_c materials has been a topic of considerable theoretical interest. Two rather different pictures have been proposed. The first type of model goes beyond the Gaussian approximation by solving the Ginzburg-Landau equation with a finite $\beta\psi^4$ term, but neglecting all but the lowest Landau level (LLL); an approximation which is formally valid near the $B_{c2}(T)$ line. Tešanović *et al.*[16] have recently produced a complete analytical solution for the free-energy in this approximation. The general features of this model are that the size of the mean-field anomaly is roughly preserved in fields $\ll B_{c2}(T=0)$, but is broadened by an increasing field to an extent determined by a fitting parameter, θ_G. This model can only fit our data (even at the qualitative level) if we assume that our background contains a large broad, field insensitive, mean-field-like step, so that our subtracted data (Fig. 2) considerably underestimate the true size of the anomaly. There is, however, independent support for our background determination from other measurements, on polycrystalline samples, where the background is determined by carefully modeling the changes in the phonon contributions to C as a function of chemical doping.[14] Although this analysis has not yet been attempted for Hg-1223, the results for several other quasi-two-dimensional high-T_c superconductors (e.g., Tl-2201, Tl-2223)[14] bear a close resemblance to our data for Hg-1223 (Fig. 2), showing a much reduced mean-field contribution in zero field. We conclude therefore that it is unlikely that the LLL model can explain our results.

Alternative models consider the possibility that the very strong fluctuations in these materials leads to a greatly enlarged critical region. Fisher *et al.*[17] have argued that for a three-dimensional superconductor, with a two-component order parameter, the critical behavior is of the three-dimensional XY type (3DXY), as for ^{4}He, and that the critical region may be several Kelvin wide, especially in a strong field. In this model the most divergent contribution to the fluctuation specific heat (C_f) in zero field has the form

$$C_f = C_0 + \frac{A}{\alpha}|\tau|^{-\alpha} \quad (2)$$

($\tau = T/T_c - 1$). In finite field the divergence of the coherence length is limited by the magnetic length $d_B = (\phi_0/\pi B)^{1/2}$, which introduces a correction that is expected to scale as some function of ξ/d_B (providing B is small compared to B_{c2}). Combining this with Eq. (2) the field dependence of C_f can be written

$$C_f = C_0 - B^{-\alpha/2\nu} f(\tau/B^{1/2\nu}), \quad (3)$$

where ν is the coherence length critical exponent. The experimentally determined critical exponents for ^{4}He are:[18] $A^+/A^- = 1.054$, $\alpha = -0.0129$, and $\nu = (2-\alpha)/3 = 0.671$ (here the + and − refer to the value above and below T_c, respectively). The low value of α means that in zero field the power-law behavior is well approximated by a logarithmic divergence and Eq. (2) may be rewritten

$$C_f \simeq \left(C_0 + \frac{A}{\alpha} \right) + A \ln(|\tau|). \quad (4)$$

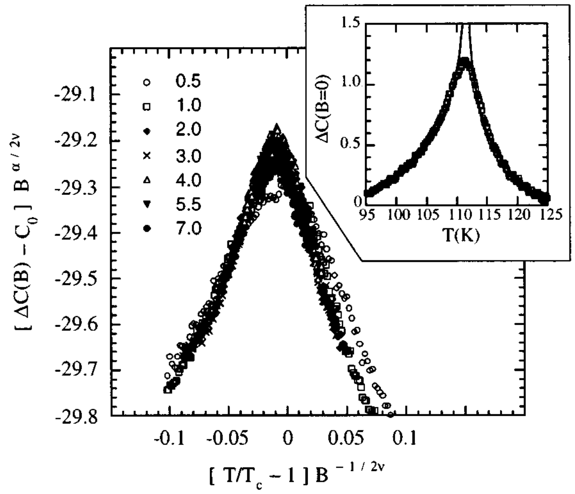

FIG. 4. Critical scaling of $\Delta C(B)$. The field values in T are indicated in the figure. Inset: Fit to the zero field data using the same parameters (given in the text).

It has been claimed that the specific heat of YBCO can be fitted by Eq. (2) with parameters which compare well to the values for ^{4}He (Refs. 2 and 19). In these fits C_0 and A/α are an order of magnitude larger than the actual anomaly, and so a slight asymmetry in either of these parameters produces a marked asymmetry in the resulting fit. This fact alone, however, cannot be used to determine the important amplitude ratio A^+/A^- as both A and C_0 can take different values above and below T_c.[18] Proper determination of this ratio requires data over several decades of reduced temperature, an experimental regime which is unrealizable even with the best YBCO samples.

In Fig. 4 we show a fit to our data for Hg-1223 with Eq. (2), with the critical exponents set to the values for ^{4}He. As for YBCO, the data do not show a true divergence at T_c because of rounding of the transition by inhomogeneities, and so a window of $\pm$ 1 K was excluded from the fit in zero field. Outside this window the fit is good over around one decade of reduced temperature. As the anomaly is approximately symmetric, we need to include an asymmetry in C_0^+/C_0^- of $\sim$4% to compensate for the asymmetry in A^+/A^- (the actual asymmetry in the measured ΔC corresponds to around $\sim$15% of its total height). If we set $C_0^+ = C_0^-$ we find that A^+/A^- is within 0.5% of unity. Leaving the critical exponents as free parameters results in a rather poor estimation of their values. For instance, we find that all values of $|\alpha| < 0.1$ produce comparable fits to the one shown in Fig. 4. The main part of Fig. 4 shows the data replotted with the reduced variables $x = (T/T_c - 1)/B^{1/2\nu}, y = [\Delta C(B) - C_0] B^{\alpha/2\nu}$, given by Eq. (3). The collapse of the data is fairly good in all fields $\gtrsim$0.5 T, using the same parameters as the zero-field fit and the additional critical exponent $\nu = 0.67$ (this scaling plot is fairly insensitive to small changes in $C_0 \lesssim$ 15% and so the same value is used above and below T_c). The reason for the nonscaling of the lower field data is probably because of intrinsic disorder and in fact these data do scale onto the common curve if the actual field is replaced by a higher effective one (i.e., by replacing B in the scaling variables with $B+B_{\rm int}$, where $B_{\rm int}$ represents an effective disorder field).

A possible objection to the above 3DXY analysis is that it might be expected that, in this strongly anisotropic material, the region where the fluctuations are effectively three-dimensional is limited to a temperature interval very close to T_c. However, the experimental fact that the 3DXY model fits the data well over a wide temperature range could conversely be taken as evidence that the three-dimensional region is much larger than might be expected from, for instance, a simple Lawrence-Doniach model.

In conclusion, we have shown that Hg-1223 has a quasi-logarithmic divergence of the specific heat at T_c in zero field, which unlike YBCO is approximately symmetric about T_c. The effect of a magnetic field is to strongly suppress the size of the anomaly and to shift its peak position to a lower temperature at a rate of ~ -1.2 T/K. The rapid suppression of the anomaly height with the field is also seen in Bi-2212, which suggests that this is an intrinsic feature of these low-dimensional high-T_c superconductors. This is further supported by our own recent data for the one- and four-layer members of the Hg-based series, which have similar behavior to the three-layer member reported here.[20] We have argued that the data in finite field are incompatible with the LLL model, but are consistent with a finite size scaling of the zero-field logarithmic anomaly using the critical exponents of the 3DXY model. The fact that the data for YBCO and Hg-1223 can be fitted by the same critical exponents is surprising given the marked difference in the shape of the two anomalies. This suggests that the nonuniversal corrections to the 3DXY scaling form are important in the temperature range of our data.

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