Specific heat peaks observed up to 16 T on the melting line of vortex matter in $DyBa_2Cu_3O_7$

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The specific heat of a high purity twinned crystal of $DyBa_2Cu_3O_{7.00}$ grown in a $BaZrO_3$ crucible is reported in magnetic field $B\|c$ and $B\perp c$ up to 16 T. First-order-like specific heat peaks are observed on the melting line of vortex matter from ≈6 to 16 T ($B\|c$). The entropy jump is $0.5\pm0.1\ k_B$/vortex/layer. The fields B_m and peak temperatures T_m obey the relation $B_m[T]=139(1-T_m/T_c)^{1.33}$. The anisotropy factor for the effective masses is $(m_c/m_{ab})^{1/2}=5.3\pm0.5$. These characteristics match closely those obtained for nonmagnetic, twinned $YBa_2Cu_3O_{7.00}$. [S0163-1829(98)04442-7]

Recent experiments probing both the dynamics and the equilibrium state of vortex matter in the high-temperature superconductors (HTS's) $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) and $YBa_2Cu_3O_7$ (Y-123) have shown that the true phase transition in a field $B>0$ does not occur on the mean-field upper critical field line $[H_{c2}(T)]$, as was observed generally for classic type-II superconductors, but on the so-called melting line $[H_m(T)]$ where the shear modulus of the vortex solid decreases abruptly. At higher temperatures, vortices remain in a fluid state until they decay in a crossover region about H_{c2}. The electrical resistance vanishes on the melting line, and corresponds to a first- or second-order thermodynamic transition in magnetization and calorimetric experiments, depending on whether the vortex solid is periodic or glassy.[1–12] According to Ehrenfest's classification, the order of the transition is determined by the lowest order of differential coefficient of the Gibbs function which shows a discontinuity on the transition line. If the transition at the melting temperature $T_m(B)$ is of first order, one should observe a discontinuity ΔS in the entropy, i.e., a δ peak in the specific heat $C=T(\partial S/\partial T)$. If the transition is of second order, a specific heat jump ΔC is expected. In real samples, the transition temperature is distributed, so that one expects a more or less Gaussian peak for first order and a rounded step for second order. The distinction is experimentally more subtle for critical transitions.

Up to now, in spite of the anticipated generality of the phenomenon of vortex melting, specific heat anomalies on the melting line could be observed but for one single compound, namely, Y-123.[7–12] We present here the calorimetric observation of the melting line for a second compound $DyBa_2Cu_3O_7$ (Dy-123).

The single crystal used in this work is of high quality grown in a $BaZrO_3$ crucible. This growth method leads to crystals with clean surfaces and purity exceeding 99.995%.[13] Sample AE388G, 18.4 mg in mass, was annealed in high pressure oxygen (100 bar) at low temperature (330 °C) during 230 h. By comparison with p and T values at equilibrium for $YBa_2Cu_3O_x$,[14] the oxygen concentration is estimated to $x\cong7.00$. However, the superconducting transition is located 2.7 K above that of Y-123 annealed in the same conditions. High pressure oxidation suppresses the magnetic ''fishtail'' effect in Dy-123 above 70 K (Fig. 1) as it does for Y-123 (corresponding data are given in Figs. 1 and 2 of Ref. 10). The enhanced reversibility is assigned with the suppression of clusters of oxygen vacancies which act as paramagnetic pinning centers.[13] For the present purpose, the fishtail effect must be avoided because pinning distorts the periodicity of the vortex lattice. A strongly distorted lattice or a glass melts with a continuous transition.[8,15]

The present calorimetric measurements are carried out in a high resolution, continuous heating calorimeter.[16] The field is applied or changed at $T=120$ K to ensure field penetration; the sample is then cooled to 5 K, and data are collected during warming from 15 to 120 K (160 K in $B=0$). Typical heating rates are 0.010 to 0.015 K/s. Gaps in the data at selected temperatures (e.g., 70 and 100 K) are due to measurements of the residual (≈0.1%) nonadiabatic heat losses. The heat capacity of the sample holder (measured separately and subtracted) and that of the crystal are in the ratio ≈4:1 near T_c The resulting random errors of the crystal data amount to 0.03 to 0.05%, whereas the accuracy, which is limited essentially by the evaluation of the heat capacity of the varnish adhesive, is about 2%. Alignment errors between the field and the crystallographic axes are estimated to ±2°.

Figure 2 shows the total specific heat of Dy-123, together with literature data,[17–19] compared to that of Y-123 over a wide temperature range. Low-temperature measurements have been shown to be consistent with magnetic ordering in a Kramer's doublet ground state at 0.90 K (the sample-dependent anomalies near 11 K are attributed to an

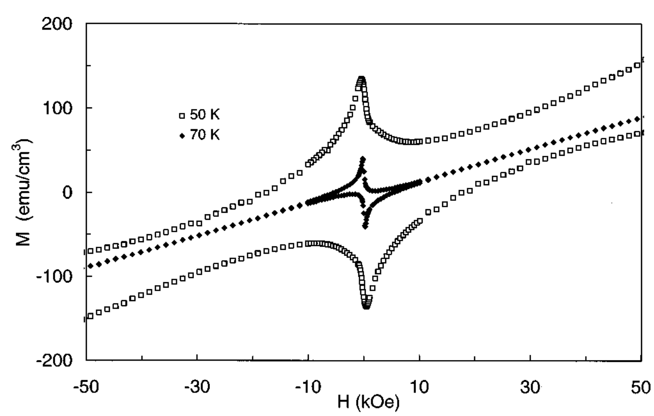

FIG. 1. Hysteresis of the magnetization of $DyBa_2Cu_3O_{7.00}$ at 50 and 70 K, $B\|c$.

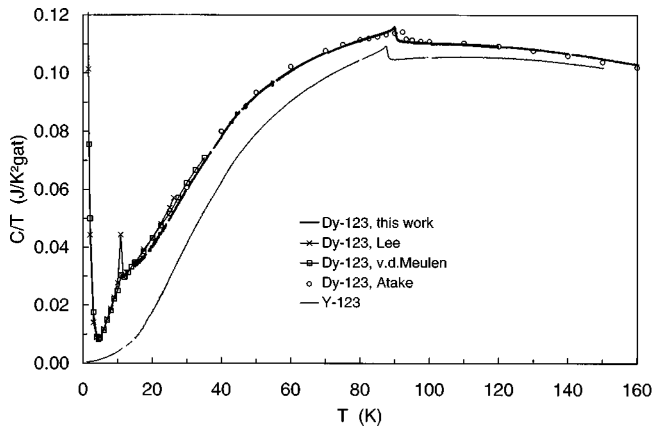

FIG. 2. Total specific heat of $DyBa_2Cu_3O_{7.00}$ (1 gat=1/13 mol =56.90 g) compared to that of $YBa_2Cu_3O_{7.00}$ (1 gat=51.25 g (Ref. 10) and to sampled literature data (Refs. 17–19). The peak at 11 K in the low-temperature data of Ref. 17 is attributed to an impurity phase. The higher T_c of the 26-g sample used in Ref. 19 is due to a lower oxygen content.

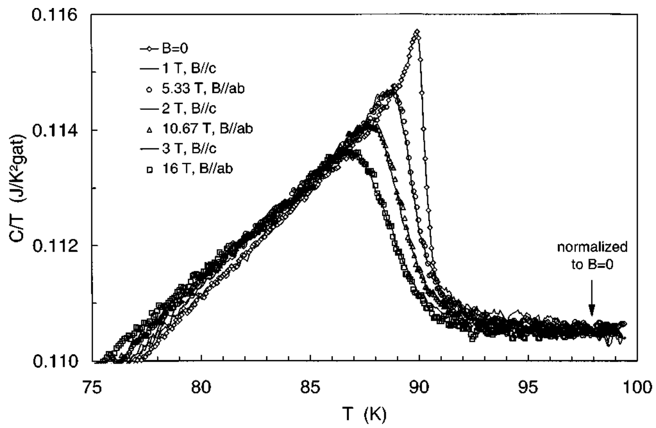

FIG. 4. Total specific heat C/T of $DyBa_2Cu_3O_{7.00}$ versus temperature for $B_{\|ab}$=0, 5.33, 10.67, and 16 T (symbols). The lines under the symbols are separate measurements at the corresponding fields $B_{\|c}$=0, 1, 2, and 3 T. All curves with $B>0$ are shifted vertically so that they match near 100 K, in order to compensate for the nearly isotropic Schottky contribution of the magnetic Dy^{3+} ions.

impurity[17]) with additional entropy appearing from the admixture of higher-lying crystal field levels in the range of a few meV.[18] The excess entropy of Dy-123 with respect to Y-123 is $4.3R\ln 2 \pm 10\%$ at 150 K, taking into account the low-temperature measurements of Lee *et al.* below 5 K and those of van der Meulen *et al.* from 5 to 15 K. This is consistent with full lifting of the degeneracy of the $J=\frac{15}{2}$ Gd^{3+} ion, $4R\ln 2$, together with a contribution from phonon shifts due to the heavier Dy mass, and possibly to the ordering of an impurity phase near 11 K in the literature data. In a field of 16 T, we observe a transfer of entropy from the region below 20 K (where the specific heat becomes smaller) to the 20–85 K range (where it grows).

Figure 3 shows the total C/T in fields from $B=0$ to 16 T by 1 T increments, $B\|c$. Figure 4 shows the same quantity for $B\|ab$, using 5.33 T increments. In the latter case, we have normalized the total specific heat near 98 K to its zero-field value, in order to compare it with data measured in $B\|c$ at lower fields. The fact that the symbols for $B_{\|ab}=5.33$ T coincide with the line $B_{\|c}=1$ T gives a robust determination of the anisotropy ratio $\Gamma=(m_c/m_{ab})^{1/2}=5.3\pm 0.5$ (m_c and m_{ab} are the effective electron masses in the directions parallel and perpendicular to the c axis, respectively). This is confirmed by other couples of curves $\{B_{\|ab}=10.67$ T, $B_{\|c}=2$ T$\}$ and $\{B_{\|ab}=16$ T, $B_{\|c}=3$ T$\}$ (Fig. 4). The underlying assumption is that the variation of the specific heat is a function of $B\xi^2(\theta)$, where ξ is the coherence length and θ the angle $(\vec{B},\hat{c})$.[15] In the effective-mass approximation $\xi^2(\theta) =\xi^2(0)(\Gamma^{-2}\sin^2\theta+\cos^2\theta)^{1/2}$. Therefore the requirement that $C(T,B_1,\theta=0)=C(T,B_2\theta=\pi/2)$ implies $B_1\xi^2(0) =B_2\xi^2(\pi/2)$ and finally $B_2/B_1=\Gamma$. The anisotropy ratio is identical to that found for fully oxidized Y-123.[10]

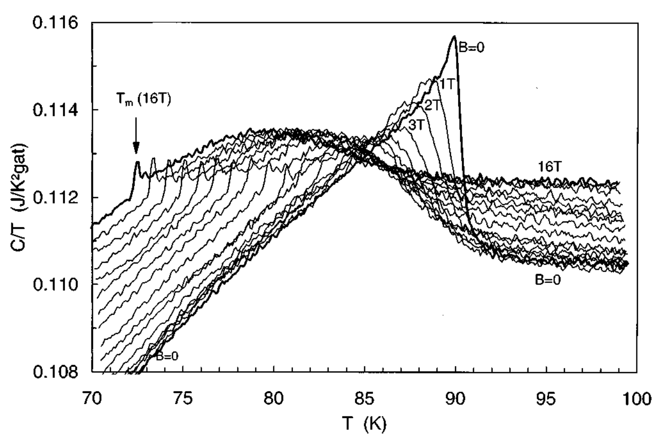

FIG. 3. Total specific heat C/T of $DyBa_2Cu_3O_{7.00}$ versus temperature in fields $B\|c$ from 0 to 16 T.

The superconducting transition gives rise to the main structure in zero field on the right side of Figs. 3 and 4. The peak of C/T occurs at 89.87 K and inflection in the descending part at 90.16 K. A study of the critical behavior and scaling properties is left for a forthcoming publication. We only mention here that except for four points in the interval between the above temperature, where the singularity is most sensitive to the residual inhomogeneity, the data can be described within experimental scatter by a critical cusp $(A^{\pm}/\alpha)(T/T_c-1)^{-\alpha}$. Although the critical exponent α measured for ^{4}He at the λ point fits the data, the amplitude ratio A^+/A^- above and below T_c is significantly different.[20]

The curves shown in Fig. 3 ($B\|c$) differ from the corresponding ones for Y-123 by the monotonous increase of the smooth background as a function of the field. This is due to the tail of the Schottky anomaly caused by the magnetic Dy^{3+} ions. The small peaks at high fields (>6 T) on the leftside of Fig. 3 are assigned with the melting transition of the vortex lattice. They appear more clearly in the difference $\Delta C(B,T)\equiv C(B,T)-C(0,T)$, which is expanded in Fig. 5. These peaks give way to steps for $B<6$ T, and finally merge at very low fields in the overshoot that arises from thermal fluctuations in a three-dimensional (3D) superconductor.[21]

The same sample does not show any specific heat peak up to 16 T in the geometry $B\|ab$ (Fig. 6). The anisotropy of the melting field being given by the effective mass ratio,[15,22] a 16 T field parallel to the (a,b) plane is equivalent to a 3 T field along the c axis. As no peak is observed for $B_{\|c}>6$ T, no peak is expected for $B_{\|ab}<32$ T either. The same anisotropy

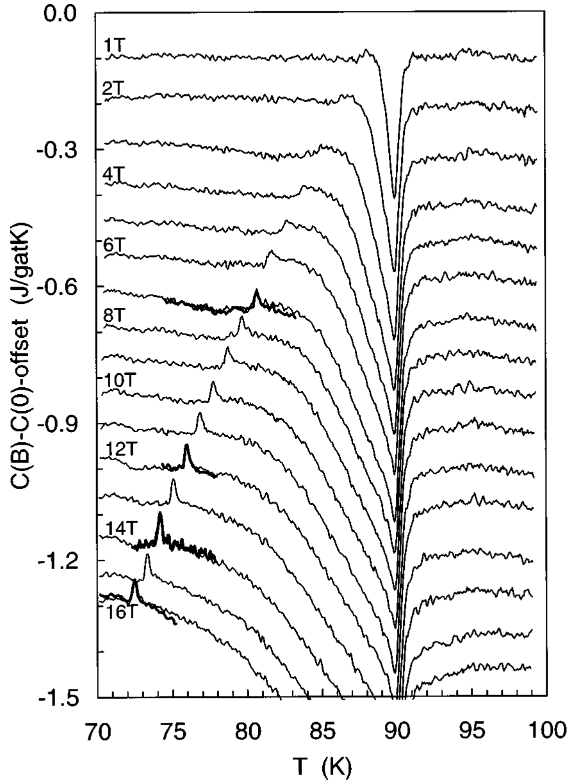

FIG. 5. Difference between the specific heat in a field $B\|c$ and that in zero field, as a function of temperature. Curves are shifted for clarity. Thick lines superposed on thin lines show additional runs.

argument explains the presence of weak structures at the noise limit at the locations marked by arrows in Fig. 6.

The position of the C peaks and steps are reported in the phase diagram of Fig. 7. Although we cannot measure the corresponding M jumps and breaks in fields from 6 to 16 T because of the limitations of standard SQUID magnetometers, a comparison with extensive data in the literature[5–10] leaves little doubt that the line defined in this way is the melting line $B_m(T)$ of the vortex solid. A fit with the function $B_m = B_0(1-T/T_c)^n$ yields the parameters $B_0 = 133$ T and $n = 1.29$, using $T_c = 89.87$ K from the peak value of $C(B=0) - C(B=16\text{ T})$; using rather $T_c = 90.16$ K from the inflection point in $B=0$ (which seems to be a better choice, see Ref. 20), we find $B_0 = 139$ T and $n = 1.33$. These values are very close to the corresponding parameters for Y-123, which are $B_0 = 133$ to 140 T and $n = 1.30$ to 1.33.[10] The value of the exponent strongly suggests a relation with criticality, which leads naturally to $n \cong \frac{4}{3}$.[15] The description based on Lindemann's criterion outside of the critical regime rather leads to $n=2$, but adjustments are possible.[22]

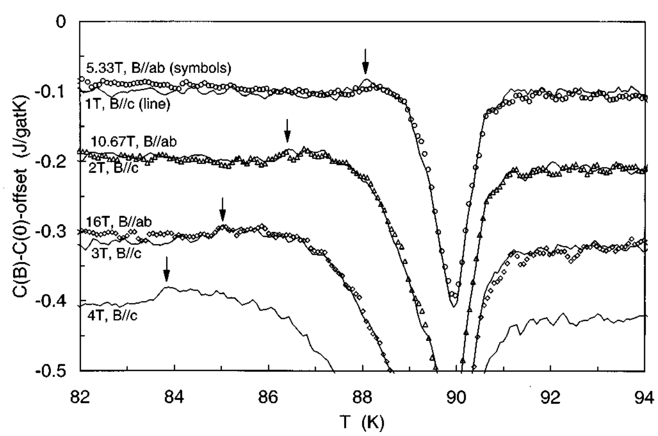

FIG. 6. Symbols: difference between the specific heat in a field $B\|ab$ and that in zero field, as a function of temperature. Lines: corresponding data for $B_{\|c} = B_{\|ab}/\Gamma$. Sets for each field are shifted for clarity. The arrows indicate the temperatures at which melting is expected.

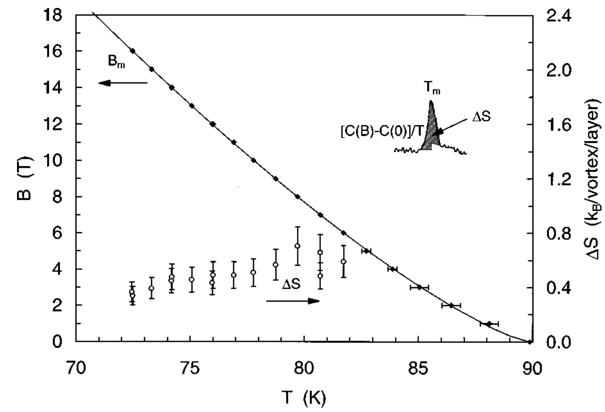

FIG. 7. Filled diamonds: phase diagram in the B-T plane, $B\|c$. Full line: function $B_m = B_0(1-T/T_c)^\alpha$ with $B_0 = 133$ T and $\alpha = 1.29$. Open circles: melting entropy ΔS determined by integration of the C/T peaks as shown in the inset.

The phase diagram shown in Fig. 7 displays two interesting features: first the absence, within the range of available fields, of an upper multicritical point terminating the line of first-order transitions, and second the existence of a lower critical point at 6 ± 1 T separating first-order from continuous transitions. Both features confirm the observations made on twinned $YBa_2Cu_3O_{7.00}$.[10] A crossover to a quasi-2D system is expected when the field is large enough to decouple the CuO_2 layers, and is indeed observed near 10 T in oxygen-deficient Y-123 with a larger anisotropy,[1,9] and in Bi-2212 near 0.04 to 0.1 T.[3,4] Our measurements set a lower limit of 16 T for such a multicritical point. This is more compatible with Josephson coupling of vortices, characterized by a crossover field of $\Phi_0/\Gamma^2 s^2 \approx 50$ T in the present case (s = interplanar distance), than with magnetic coupling, characterized by $\Phi_0/\lambda_{ab}^2 \approx 0.1$ T. Both 123 compounds differ drastically from Bi-2212 in this respect.

On the low field side, the present data show that the first-order-like peak disappears below 6 T. Experiments on $YBa_2Cu_3O_{7.00}$ at 4 T have shown that the peak can be recovered neither by detwinning the sample,[11] nor by tilting the field with respect to the c axis,[10] tending to rule out an explanation in terms of correlated disorder introduced by twin boundary pinning. The presence of a lower critical point near 6 T is now confirmed in three high-quality 123 crystals in the overdoped state;[10] when the oxygen concentration decreases, the point moves to lower fields.[9] The possibility that the 6-T point is an intrinsic property of fully oxidized 123 phases with a low anisotropy cannot be excluded at the present time; however, additional experiments on fully oxidized untwinned and strain-free crystals are still required to ascertain this issue. Different theoretical approaches predict the existence of a lower critical point.[23,24]

The value of the entropy jump ΔS at high fields was evaluated by integrating the excess C/T as shown in the inset of Fig. 7. The average value is $0.5\pm 0.1k_B$ per vortex and per layer, with a tendency to increase with temperature. This is close to the result $0.6\pm 0.1k_B$/vortex/layer obtained for $YBa_2Cu_3O_{7.00}$,[10] and more generally to other magnetic and thermal determinations for $YBa_2Cu_3O_x$ in the literature.[5–7] A jump component can be discerned below the peaks, confirming that the specific heat of the vortex liquid is larger than the specific heat of the vortex solid.[7–10]

Dy-123 is the second compound in which the *thermal* signature of vortex melting is detected, the only other example being Y-123. The specific heat peaks suggest that the vortex lattice melts with a first-order transition, but an unambiguous confirmation requires independent experiments such as the observation of hysteresis.[11] The anisotropy ratio, the melting entropy, the absence of an upper critical point, the presence of a lower critical point and the shape of the melting line are practically identical to those of fully oxidized Y-123.[10] These results, which form a first step towards the generalization of the Y-123 findings, show in particular that the vortex system is insensitive to the presence of magnetic moments on the Dy/Y site.

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[20] A fit from 75 to 100 K with two Einstein specific heat functions and a singular component $C^{\pm}=k[(A^{\pm}/\alpha)(T/T_c-1)^{-\alpha}+A_0]$ yielded the following results: $T_c=90.30$ K, Einstein temperatures 112.4 and 367.6 K with amplitudes 6.10 and 15.74 mJ/K^2 gat), respectively, k=0.146 mol(He)/mol(Dy-123) and $A^+/A^-=1.081$, rms deviation 0.046% (319 data). The parameters α, A^-, and A_0 were taken from the measured values for ^{4}He at the λ point: $\alpha=-0.01285$, $A^-=5.7015$, and A_0=456.28 J/(K mol He) [J. A. Lipa *et al.*, Phys. Rev. Lett. **76**, 944 (1996)]. However note that $A^+/A^-=1.054$ for ^{4}He. The value of the parameter k, which scales the singularities of Dy-123 and ^{4}He, would suggest the condensation of 8.4×10^{20} Bose particles per cm^3 (0.15 per unit cell) at T_c in a scenario of preformed Cooper pairs.
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