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Anisotropic specific-heat behavior under a magnetic field of a $YBa_2Cu_3O_7$ single crystal

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Specific-heat experiments have been performed on single-crystal $YBa_2Cu_3O_7$ under magnetic fields up to 6 T applied parallel and normal to the (ab) planes. The curves show a weak influence of the field parallel to (ab) on the C_p anomaly, by comparison with the smearing effect observed when the field is normal to the (ab) planes. These results are consistent with the recently published magnetic data, which allow us to calculate the anisotropy factor of the C_p discontinuity and the entropy changes under a field.

In the abundant theoretical and experimental work devoted to high-temperature superconductivity (HTSC), great interest has been focused on the analysis of the C_p anomaly at the superconducting transition.[1,2] In the case of $YBaCuO_{7-\delta}$ the occurrence of a well-defined anomaly has been confirmed for the highest oxygen stoichiometry, but the amplitude and the shape of the anomaly are very sensitive to the sample preparation.[3]

In the presence of an applied field, a smearing effect of the anomaly is observed.[4] In the case of ceramic samples, this may be explained as a simple broadening of the transition due to the H_{c2} field anisotropy operating on a distribution of randomly oriented crystallites.[5] The depression of the anomaly is more pronounced on a single crystal, for $\mathbf{H}\perp(ab)$, and such an influence of the field has been essentially analyzed in terms of a shrinkage of the fluctuation contribution.[6]

We have recently presented results[7] concerning the heat-capacity jump of highly textured $YBa_2Cu_3O_7$ samples measured under a field applied along two different directions; when the field is parallel to the (ab) planes the anomaly is only slightly broadened by a 6 T field. No investigation has been reported until now, concerning the C_p study of a single crystal with field applied along the two directions. In this paper we present such experiments performed on a single crystal prepared by a "grain-growth" method. The results are analyzed essentially on a thermodynamic basis, by comparison with the recent studies dealing with the anisotropy of the magnetization of grain-aligned samples,[8] and of the single crystal.[9]

EXPERIMENTAL

The crystal was prepared by a grain-growth technique.[10] Its specifications are the following: total volume $\approx 55\ mm^3$, mosaic spread $<0.3°$, porosity $\approx 15\%$, and Y_2BaCuO_5 content ≈ 8 wt. %.

The thermal treatment, under 7 bars oxygen pressure, which was used to achieve the best oxygen content was the following: 8 hr at 440 °C; cooling at 3 °C/h down to 410 °C and at 1 °C/h down to 280 °C; and final cooldown to room temperature in a further 2 h. From the variations of the sample weight, the deduced oxygen content was 6.97. However, as shown in Fig. 1, the SQUID measurements with a field of 2 Oe,applied along the ab plane, indicate a rather sharp transition in zero-field cooling, although a small Meissner effect ($<9\%$). The heat-capacity measurements were performed using a dynamical method in which the sample is warmed up at a constant power. The adiabatic conditions are maintained by means of a controlled heat shield. The sample, 280 mg weight, was closed inside an Al container, two faces of which were preformed to allow a precise crystallographic

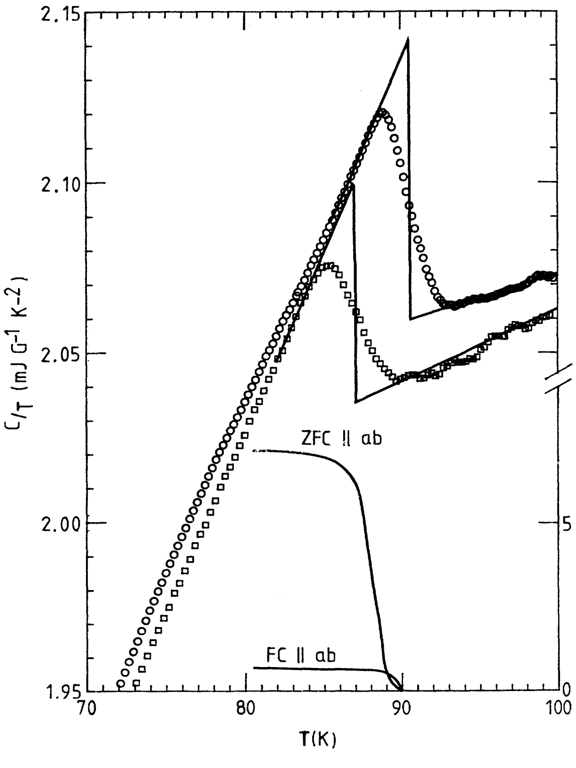

FIG. 1. Compared C/T vs T curves of polycrystalline sample (○) and single crystal sample (□) around T_c (left scale). Solid line: reconstructed mean-field step (see text). $\chi(T)$: Meissner (FC) and shielding (ZFC) (right scale).

orientation with respect to the field (directions [001] and [110] with, respectively, 4 and 2 degrees of possible misorientation).

RESULTS

Figure 1 shows the C_p/T curves around the transition in zero field of the single crystal compared to that of a ceramic (a sample from Junod, Université de Genève) measured in the same calorimeter. The amplitudes of the C_p/T discontinuity determined by the extrapolation method with the balance of the entropy are 47 (corrected value free of second phase) and 55 mJ $\text{mole}^{-1}\,\text{K}^{-2}$ and the transition temperatures T_c, 87 and 90.2 K, respectively. So we observe a shift and a relative broadening of the anomaly of the single crystal compared to that of a good reference of polycrystalline material.[11]

From the "shielding" SQUID measurements (ZFC) of the crystal, the onset temperatures for the χ and C_p curves are very close and the transition widths are almost the same for the two properties.

When the magnetic field is applied, up to 6 T, in a direction normal to the (ab) planes (Fig. 2), we observe a smearing of the C_p anomaly which is roughly similar to that previously reported by Salamon.[6] Deducing the temperature transition by the extrapolation method as mentioned above, we obtain for the slope of the upper critical field dH_{c2}/dT a value of -1.5 ± 0.3 T/K. By contrast, when the field is applied along the (ab) plane (Fig. 3) the depression of the anomaly is very small at equal field. Roughly speaking, the 6 T curve $[\mathbf{H}\|(ab)]$ may be superimposed on the 1.5 T one with $\mathbf{H}\perp(ab)$; the value of $dH_{c2}/dT\|(ab)$ determined as above is -8 ± 2 T/K, and so the mean anisotropy factor, taken as a whole (amplitude and T_c shift of the anomaly), is about 5.

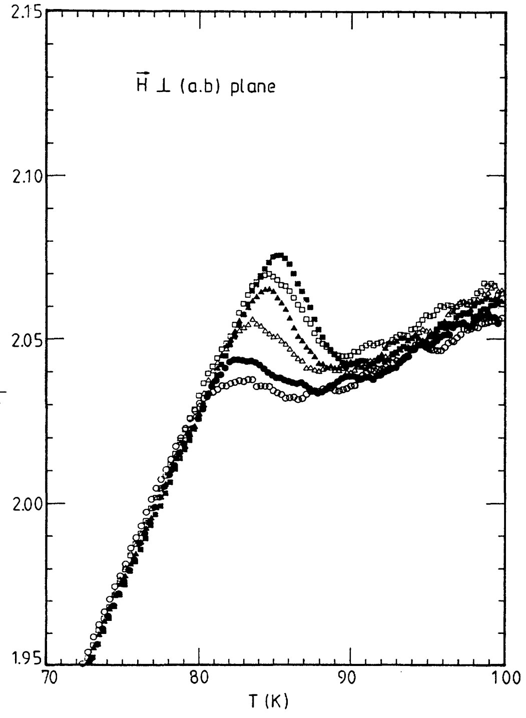

FIG. 2. Single-crystal C/T (T) curves under magnetic field, with orientation $\mathbf{H}\perp(a,b)$ planes: (■, $H=0$ T), (□, $H=1$ T), (▲), $H=1.5$ T), (△, $H=3$ T), (●, $H=4.5$ T), (○, $H=6$ T).

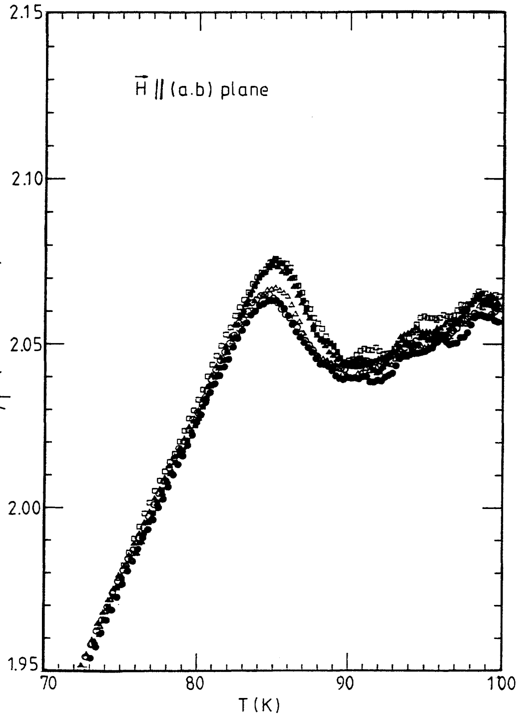

FIG. 3. Single-crystal C/T (T) curves under magnetic field, with orientation $\mathbf{H}\|(a,b)$ planes: (■, $H=0$ T), (□, $H=1$ T), (▲), $H=1.5$ T), (△, $H=3$ T), (●, $H=4.5$ T), (○, $H=6$ T).

Figure 4 shows the evolution of the entropy difference

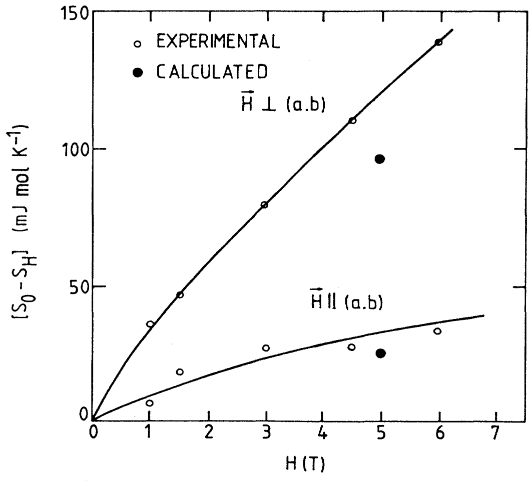

FIG. 4. Entropy differences (S_0-S_H); (○) measured, (●) calculated.

(S_0-S_H) measured between 80 and 90 K, as a function of the applied field, for the two directions; at high field the anisotropy ratio also is close to 5.

DISCUSSION

The C_p/T curves measured in zero field (see Fig. 1) show evidence of a depressive effect of the C_p transition already present for our single-crystal sample, and also a shift of the transition. This could be due to a T_c distribution associated with an inhomogeneity of the oxygen concentration, in domains of relatively large scale as already observed in single crystals;[12] but in the present case the crystal was prepared by a grain-growth method inducing a porosity which eases the oxygen diffusion, and so the depression here is more likely due to a "pair-breaking" effect in the presence of local disorder or point defects (e.g., vacancies, substitution atoms, stacking faults, etc.); this leads to local variations of the order parameter and results in a lowering and a broadening of the calorimetric transition.[13]

On the other hand, the apparently low value of the Meissner effect, around 9%, is not an indication of a low fraction of superconducting material, but is rather evidence of a strong pinning which is known to give a weak apparent Meissner effect in large samples.[14,15]

Concerning the influence of the magnetic field (Figs. 2 and 3), these experiments confirm the previous qualitative results we obtained on highly textured samples: The influence of the field is much less pronounced for $\mathbf{H}\|(ab)$, but this behavior is consistent with a smaller shift of T_c and so with an upper critical field slope that is much higher in this direction; we can add that the appearance of a strong stability of the anomaly for $\mathbf{H}\|ab$ does not imply the absence of a smearing effect in this direction, but only that it would appear for larger fields, with a ratio of about 4 or 5 relative to the $\mathbf{H}\perp(ab)$ case.

However, it is noteworthy that the upper critical field slopes deduced from the reconstruction of the mean-field step are quite realistic, and in good agreement with the values drawn from the magnetization data.[9] In addition the T_c onset temperatures according to our results appear to shift under field; these remarks suggest the idea of a classical behavior with a broadening of the transition under field due to a distributionlike effect, rather than a shrinkage of the anomaly. The C_p curves under field normal to the (ab) planes (Fig. 2) are not much different from that reported on a Chevrel-phase polycrystalline sample,[16] or even, after reconstruction of the mean-field step, from that of some extreme type-II superconductors.[17]

We can analyze our results on a purely thermodynamic basis using the magnetic data, obtained in the reversibility temperature range of the magnetization. On the transition line $H_{c2}(T)$ there is continuity of the entropy S_m(mixed state)$=S_n$(normal state). Therefore, the specific-heat discontinuity at the mixed to normal phase transition can be deduced from coupling the Ehrenfest equation[18]

$$\left[\frac{\partial(S_m-S_n)}{\partial T}\right]_H+\left[\frac{\partial(S_m-S_n)}{\partial H}\right]_T\frac{dH_{c2}}{dT}=0\ , \tag{1}$$

with Maxwell relation

$$\left[\frac{\partial S}{\partial H}\right]_T=\left[\frac{\partial M}{\partial T}\right]_H\ , \tag{2}$$

which finally gives

$$\frac{\Delta C(H_{c2})}{T_{c2}}=-\frac{dH_{c2}}{dT}\frac{\partial M}{\partial T}\ , \tag{3}$$

where $\partial M/\partial T$ of the normal phase has been neglected.

We use, for the following calculations, the recent magnetic data of Welp *et al.* obtained on a single crystal;[9] it may be noted that T_c for this crystal was 3 K higher than for our sample.

From these data, the anisotropy ratio of the C_p discontinuity at the transition, calculated from relation (3), for a field of 5 T parallel to (ab) relative to that for a field of 1 T perpendicular to (ab), is about 0.8; this is close to 1, the value that we deduce from our results through the occurrence of a good fit on superimposition of the C_p curve for a field of 6 T parallel to (ab) over that for a field of 1.5 T perpendicular to (ab).

In the same way, the entropy curves $(S_0-S_H)_{T_i}^{T_0}$ (Fig. 4) may be related to the magnetic data; here $T_i=80$ K, temperature where all the C_p curves are still superimposed below the transition, and T_0 is the onset temperature. The field dependence of the entropy in the mixed phase may be written to a first approximation:[19]

$$S_m(T,H)=S_n(T)+\alpha(T)(H_{c2}-H)\frac{dH_{c2}}{dT}\ , \tag{4}$$

where $\alpha=\partial M/\partial H$ and S_n the normal state entropy and

$$\begin{aligned} S_0(T)&=S_n(T)+\alpha(T)H_{c2}\frac{dH_{c2}}{dT}\ ,\\ (S_0-S_H)_{T_i}^{T_0}&=S_0(T_i)-S_m(T_i,H)\\ &=\alpha(T_i)H\frac{dH_{c2}}{dT}\ . \end{aligned} \tag{5}$$

This relation yields a linear dependence on the field changes and the field direction dependence through $\alpha(T)$ and the upper critical field slope. The values for $H=5$ T (Fig. 4), calculated from the relation (5) using the data of Welp *et al.*,[9] agree well with our measured ones. The difference can be explained by the different quality single crystals used in the two experiments.

This latter evaluation of the anisotropic behavior of the C_p transition in the mixed phase is also in good agreement with the results previously inferred by Athreya,[8] where the magnetic field dependence of C_{p_0}-C_{p_H} is deduced from the Gibbs free energy surfaces, derived from the magnetization experiments.

So the level of anisotropy of the measured C_p transition is quite consistent with that inferred from the magnetic data; this is not surprising indeed, while that does not involve any microscopic theory, but this agreement confirms the anisotropic behavior of Y-Ba-Cu-O on the basis of thermodynamic experiments.

One knows as well that the C_p behavior around T_c has been essentially analyzed in terms of fluctuations (critical as well as Gaussian ones),[6] but this kind of analysis is particularly questionable for two reasons: first, because of the experimental difficulties encountered in achieving the necessary level of precision, for such analysis to be made; and second, owing to the effective distribution of T_c, due to inhomogeneities or defects, and which results in an averaging of the different contributions to the C_p anomaly around T_c; so the possibility of extracting standard power laws for the C_p anomaly from experimental data is doubtful as it has been recently reported.[20]

In conclusion, we have presented specific-heat measurements made under magnetic field applied in two directions to a Y-Ba-Cu-O single crystal which show evidence of a weak effect on the C_p anomaly when H is parallel to the (ab) planes, in comparison with the strong effect, already reported, in the normal direction to the planes; these results may be accounted for by anisotropy consideration, and are consistent with the magnetization data. Moreover, one could consider the behavior under field (shift and amplitude of the C_p discontinuity after correction for broadening) as being comparable to the classically expected field influence, without having to invoke the contributions of fluctuations.

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