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Specific heat and ac susceptibility of $Hg_{0.8}Cu_{0.2}Ba_2CuO_{4+\delta}$ single crystals with $T_C = 95$ K

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We report on the specific heat and magnetic susceptibility of several single crystals of the superconducting compound $Hg_{0.8}Cu_{0.2}Ba_2CuO_{4+\delta}$ with optimum T_C (around 95 K), and a mass varying between 6 and 18 μg. We analyze the heat-capacity data with the purpose of extracting the intrinsic behavior of the compound. The accent is put on the shape of the specific-heat anomaly, its height, its symmetry, and its temperature position with respect to the transition in the ac susceptibility. The specific-heat peak in Hg-1201 is seven times less than in YBCO in correlation with the computed density of state at the Fermi level. We define a parameter β allowing a classification of the sample's quality. The specific-heat anomaly is asymmetric. These considerations allow us to conclude that this compound has a dimensionality intermediate between the three-dimensional $YBa_2Cu_3O_{7-\delta}$ (YBCO) and the two-dimensional $Bi_2Sr_2CaCu_2O_8$ (BSCCO). [S0163-1829(97)00842-4]

I. INTRODUCTION

The high-temperature superconducting (HTSC) compound $HgBa_2CuO_{4+\delta}$ (Hg-1201) is the first member ($n=1$) of the recently discovered mercury-based family $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$. Its optimal T_C is comparable with $YBa_2Cu_3O_{7-\delta}$ (YBCO): about 95 K. This compound is particularly attractive due to its simple structure. Indeed, it grows in a tetragonal lattice with only one superconducting CuO_2 layer per cell avoiding intergrowths induced by the presence of Ca (as in the $n \geqslant 2$ members of the family). This makes it an ideal candidate for fundamental studies of the symmetry of the superconducting order parameter; therefore extensive measurements comparable to those realized on YBCO are necessary. A few measurements have already been performed on Hg-1201: dc magnetization,[1,2] ac susceptibility,[3] and specific heat on polycrystalline[4] and single-crystal samples.[3] Each of them was based on one sample. Hg-1201 being a recently discovered compound, we thought that it could be hazardous to extract the behavior of the material from data concerning only one sample. For this reason, we have measured the specific heat and ac susceptibility of several Hg-1201 single crystals, in order to extract the basic characteristics of this compound. We measured five crystals synthesized by Pelloquin *et al.*[1] following a slightly different method than the Saclay group.[5] Crystals are in the form of black plates with dimensions ranging from $200 \times 200 \times 10\ \mu m^3$ to $1000 \times 750 \times 70\ \mu m^3$. Structural studies on these crystals point out a partial substitution of Hg by Cu in the insulating layers leading to the following formula: $Hg_{0.84}Cu_{0.16}Ba_2CuO_{4.19}$. By combining a transport-type measurement (ac susceptibility) with a thermodynamical measurement (specific heat), we are able to extract qualitatively the main features of the superconducting transition for the Hg-1201 HTSC.

II. EXPERIMENTAL

ac susceptibility is a straightforward measurement to observe the superconducting transition and also obtain an idea about sample inhomogeneity. Here we have not used the classical method consisting of two coils in opposition but a more local and sensitive one, namely Hall probe magnetometry.[6] Hall probe size is $10 \times 10\ \mu m^2$. Figures 1(a) and 1(b) give the real and imaginary parts of the dimensionless ac susceptibility for the five crystals in zero field. Note that except for $C5$ the transition width ΔT_x (defined from 10–90% criterion) is between 0.5 and 1.4 K, as sharp as in Ref. 3 suggesting a sample with a fairly good homogeneity. The paramagnetic peak for $C5$ is due to the proximity of the Hall probe to the sample edges. Note also that the transition temperature varies only by a few tenths of a degree from one sample to another, T_C being around 95.3 K. But the ac susceptibility is a transport measurement and so does not inform one about bulk quality and properties. In this view, specific-heat measurement will be much more powerful. A very sensitive specific-heat setup was recently built in the CRTBT.[7] This microcalorimeter, based upon the ac technique, can measure μg samples. The achieved resolution in $\delta C/C$ is about 10^{-4}, comparable to the best current differential calorimeter. But this is not a differential one so we can measure the absolute heat capacity of the sample (together with the addendum of order 1 μJ/K). Raw C_p data for $C1$ are shown in Fig. 2(a). Note the smallness of the effect of the superconducting transition (quasi-invisible) on the $C_p(T)$ curve: it appears, after background substraction, that the anomaly at T_C represents only 0.2–0.6 % of the total heat capacity. Substraction of the background is crucial and can always be put into question. However, based upon our experience on YBCO,[8] we observed that an optimal degree for a polynomial ''background'' fit gives exactly the same result as the use of more physical functions (such as Einstein functions). For the Hg-1201 samples, the optimum degree was 7 or 8: an

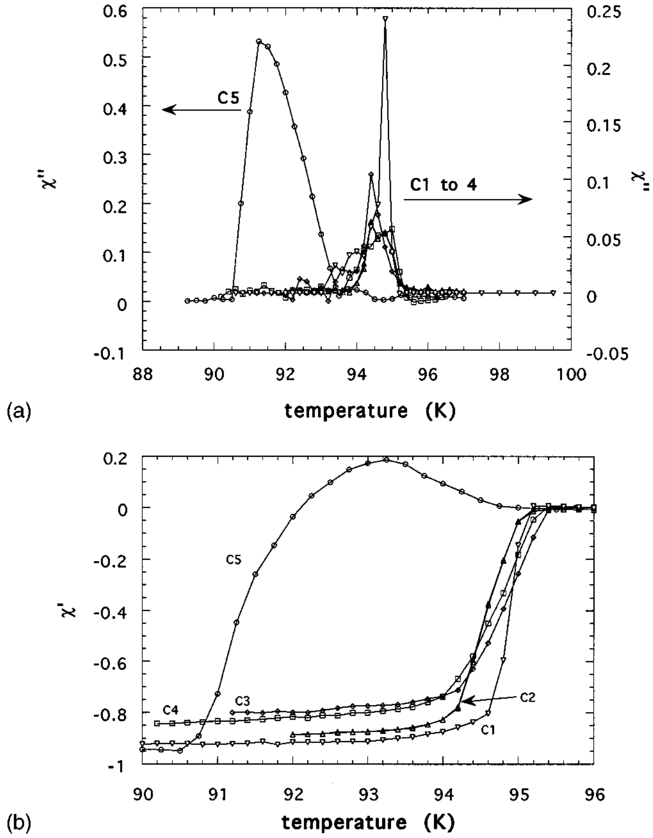

FIG. 1. Imaginary (a) and real (b) part of the dimensionless ac susceptibility for five Hg-1201 single crystals in zero field $(H_{\mathrm{ac}}=0.5\ \mathrm{G},\ f=3\ \mathrm{Hz})$. Left-hand axes on (a) refer to sample $C5$. All other samples refer to right-hand axes. Sharpest χ'' and χ' transition is obviously for $C1$.

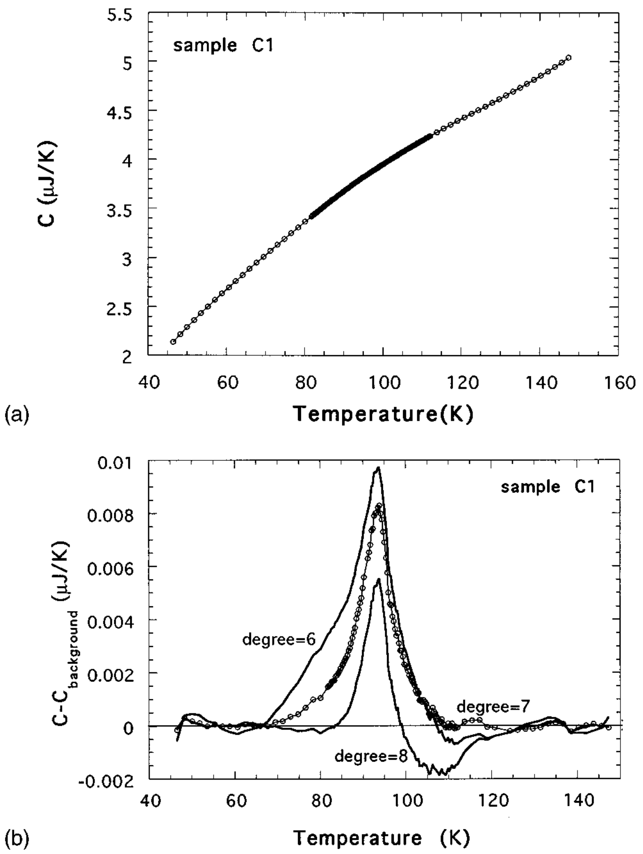

FIG. 2. Heat-capacity raw data for $C1$ (a). The anomaly is indistinguishable. (b) Influence of substraction of polynomial background for the same sample: the excess C_P around T_C appears regular only for a seventh-order polynomial fit.

example for $C1$ is given in Fig. 2(b). The temperature region where the background fit is performed excludes the expected ''transition region'' situated for Hg-1201 between 70 and 120 K.

III. RESULTS AND DISCUSSION

It is interesting to know what parameters model the shape of the specific-heat superconducting anomaly. As noticed by Junod,[9] this shape is essentially linked to the effective dimensionality of the studied compound. In a three-dimensional (3D) material (like YBCO), mean-field theory predicts the existence of a step for C_p at $T_C(H=0)$. This step is possibly hidden by a divergent behavior due to critical fluctuations enhanced by the smallness of the coherence volume in HTSC's. In a strictly 2D compounds, no long-range order is authorized[10] because fluctuations are important at all length scales. However, a superconducting transition is observed in quasi-2D compounds like BSCCO. In the true 2D case, the relevant model for superconductivity (e.g., in thin films) is the 2D-XY model involving the Kosterlitz-Thouless transition at T_{KT}, a temperature where the specific heat is assumed to be regular. For YBCO, the 3D-XY model was successfully applied. The presence or absence of a mean-field step is the main explanation for the apparent asymmetrical (for 3D) or symmetrical (for 2D) shape of the superconducting specific-heat anomaly. Figure 3(a) presents the superconducting anomaly (after background substraction) for the five Hg-1201 single crystals. In Figure 3(b) we define the parameters needed for a close study of the curves. Those parameters are listed in Table I. The anomaly is obviously broad (namely 20 K) above and below $T_{\mathrm{peak}\,C_p}$, but is nevertheless clearly asymmetric. Indeed, for all samples, a slope break point is visible roughly 2 K above $T_{\mathrm{peak}\,C_p}$. The numerical derivative dC/dT gives a better idea about the curve asymmetry (Fig. 4). The absolute value of maximum slope above and below $T_{\mathrm{peak}\,C_p}$ (corresponding to the inflexion points) are clearly different. Moreover, the ratio

$$\alpha=\frac{|\max(dC/dT(T>T_{\mathrm{peak}}))|}{|\max(dC/dT(T<T_{\mathrm{peak}}))|}$$

appears to be constant and close to 2 for all samples (see Table I). In the asymmetrical case (like for BSSCO), α equals 1,[9] while it is about 5 for our best C_p measurements for YBCO.[8] Moreover, slope break and inflexion points occur simultaneously inciting us to think that the slope break is no more than a simple but marked inflexion point. The ratio α is (to our point of view, and for the HTSC's) a good indicator for the symmetry of the C_p superconducting anomaly and so for the system dimensionality suggesting that the dimensionality of Hg-1201 is intermediate between those of BSSCO (2D) and YBCO (3D), which agrees well with the conclusions on the anisotropy of this compound

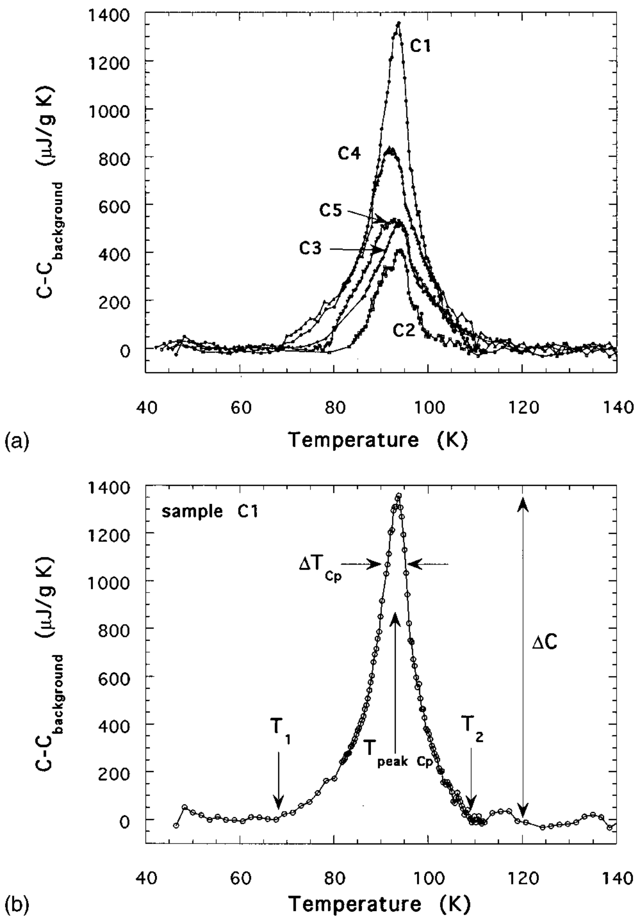

FIG. 3. (a) Specific-heat anomaly normalized to the estimated mass (with 20% precision) after background substraction for the five samples. (b) Definition of the essential parameters that characterize the specific-heat anomaly. Temperature T_1 and T_2 define where the excess C_P falls to zero.

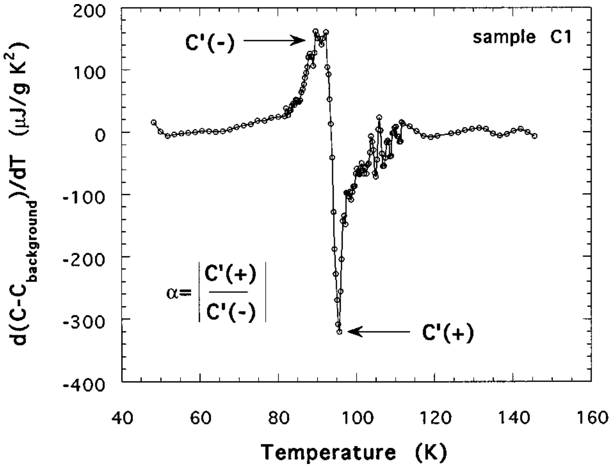

FIG. 4. Numerical derivative of excess C_P for sample $C1$ in order to define the parameter α. This parameter defines the curve asymmetry and therefore the compound dimensionality.

based on magnetization measurements.[1] The magnetization along ab and along c was measured giving an anisotropy ratio of $\xi_{ab}/\xi_c = 30$, to compare with 50 for BSSCO and 7 for YBCO. Two parameters are then essential to define the sample quality and its proximity to the ideal, intrinsic superconducting transition of the considered material: the height ΔC and the width ΔT_{C_p}. They are reported in Table I for all samples. The ΔT_{C_p} definition assumed here is the difference between the two inflexion points temperatures. ΔT_{C_p} decreases with the sample quality, while ΔC increases. Both ΔC and ΔT_{C_p} are related to T_C inhomogeneities or disorder in the samples, since impurities generate pair-breaking effects and also a cutoff length for fluctuations. Finally the real superconducting volume (presence of nonsuperconducting phases, etc. . . .) may influence ΔC. The main problem in the determination of ΔC is the sample mass (20% error at least because of the irregular shape of the crystals). For this reason, $\Delta C/C(T_{\rm peak})$ appears to be a better variable to compare samples' specific-heat height anomaly. We therefore introduce a good parameter to compare the samples quality: the dimensionless ratio $\beta = \Delta C/\Delta T_{C_p} \times T_{{\rm peak}\,C_p}/C(T_{\rm peak})$. They are both reported in Table I. Of course, β depends strongly on system dimensionality: it is therefore very different for different materials. According to Table I, $C1$ is undoubtedly the best sample among our five crystals. Because of the nonregular shape of the samples, we prefer to estimate their mass by using a normalization of the absolute heat capacity with a bulk piece of the same material synthesized by Pissas.[11] This normalization provides for our best crystal ($C1$) a height ΔC comparable with the one obtained by Carrington *et al.*,[3] suggesting an equivalent quality of samples. Normalizing our data to those of Woodfield *et al.*[4] lead to the same results. It is essential to note that $\Delta C/C(T_{\rm peak})$ in Hg-1201 is seven times less than in YBCO (4%) and two times less than in BSCCO (about 1%). This is probably due to a smaller γ in Hg-1201, as deduced from band calculations:[13] $\gamma = 3$ mJ/mol K^2 in Hg-1201 to compare

TABLE I. Essential parameters characterizing the specific heat and the ac susceptibility superconducting transition for each sample. These parameters are defined in Fig. 1 for the ac susceptibility and in Fig. 3(b) and Fig. 4 for the specific heat. α is related to the curves asymmetry, while β characterizes the sample quality.

Sample	Mass (μg)	$T_{{\rm onset}\chi}$ (K)	$\Delta T\chi$ (K)	$T_{{\rm peak}\,C_p}$ (K)	$T_2 - T_1$ (K)	ΔC (μJ/gK)	$\Delta C/C(T_C)$ (%)	ΔT_{C_p} (K)	α	β
$C1$	6	95.2	0.5	93.8	42	1330	0.6	3.3	1.9	0.17
$C2$	6	95.3	0.9	93.8	30	410	0.2	3	2.1	0.05
$C3$	13	95.4	1.1	94.2	41	500	0.26	4.2	2.2	0.05
$C4$	18	95.4	1.4	92.2	50	830	0.4	5.2	1.9	0.07
$C5$	6			92.8	45	530	0.23	6.8	2	0.03

with 21 mJ/mol K^2 in YBCO (Ref. 14) and 8 mJ/mol K^2 in BSCCO.[13] At last, a comparison between the temperature location of the ac susceptibility transition with respect to the specific-heat anomaly can be instructive about the studied system. Indeed, a transition in ac susceptibility indicates the first percolation paths for a supercurrent to flow around the sample, while the maximum in C_P anomaly accounts for volume superconductivity. Here (cf. Fig. 5), we observe that the transition in susceptibility occurs systematically above $T_{\text{peak}\,C_P}$ and below the upper inflexion point. Comparison with YBCO is not easy because transition of both χ and C_P have the same width (~ 0.1 K). However, as a general rule, screening of a magnetic field starts above the upper inflexion point in YBCO. One should note that critical densities for percolation are smaller in 3D than in 2D systems. In the case of BSCCO, Junod[12] has reported an onset of screening significantly below the specific-heat peak (about 0.5 K), which seems quite surprising.

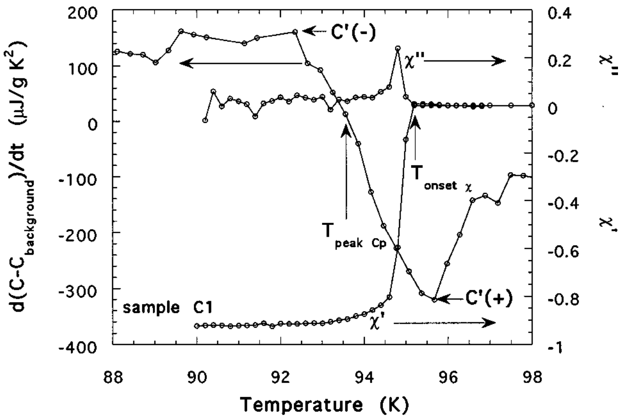

FIG. 5. Juxtaposition of the numerical derivative of excess C_P with the transition in (dimensionless) ac susceptibility for sample $C1$. The χ transition occurs systematically for all samples above the C_P peak temperature and below the upper inflexion point for all samples.

In conclusion, we studied the specific-heat anomaly and the ac susceptibility of the recently discovered HTSC Hg-1201 compound around T_C for five single crystals. Assuming a link between the system dimensionality and the symmetry of the C_P anomaly, we propose a simple way to derive an estimation of the relative dimensionality of this compound with respect to other HTSC's thanks to the parameter α: Hg-1201 dimensionality is found to be intermediate between 2D and 3D. We then introduce a second parameter (β) allowing a classification of the sample quality in order to guide the synthesis of a homogeneous material.

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