Journal of Alloys and Compounds, 195 (1993) 547–550
JALCOM 7524

Specific heat of the 90-K superconductor $Tl_2Ba_2CuO_6$ ("2201") prepared in high pressure Ar or He gas.

A. Junod[a], K.Q. Wang[a], G. Triscone[a], C. Opagiste[b], M. Couach[b], A.F. Khoder[b] and J. Muller[a]

[a]DPMC, Université de Genève, CH-1211 Genève 4 (Switzerland)

[b]Centre d'Etudes Nucléaires de Grenoble, SPSMS/LCP, BP85X, F-38041 Grenoble Cedex (France)

Abstract

We present high resolution heat capacity data in the temperature range 30-300 K for several homogeneous samples of the superconductor $Tl_2Ba_2CuO_6$ ("2201") with transition temperatures in the vicinity of 90 K. The specific heat peaks that appear close to the superconducting transition in some samples are identified as being due to gases trapped in the pores of the ceramics. The very small intrinsic anomaly at T_c, of the order of 1% of the total specific heat, is best observed in samples prepared under He atmosphere. The data are analysed using a model that includes a parametrized phonon spectrum, a mean-field jump at T_c, and a fluctuation contribution of the Lawrence-Doniach type. The fit yields an average coherence length of 7.5 Å (sample with T_c=92 K) and 8.2 Å (sample with T_c=87 K), and a vanishingly small mean-field jump. The homogeneity of the electronic subsystem is questioned. The data are compared with new results for $Bi_2Sr_2CaCu_2O_8$ ("2212", T_c=93 K) and $YBa_2Cu_3O_7$ ("123", T_c=91 K). The fluctuation component is similar for all three, but $YBa_2Cu_3O_7$ stands out with its relatively large mean-field jump.

1. Introduction

The critical temperature of the tetragonal phase of $Tl_2Ba_2CuO_6$ ("2201") exceeds 90 K when prepared under appropriate reducing conditions. Samples obtained by a new process [1] show a high level of phase purity. A systematic survey of their physical properties was undertaken [1-3]. We focus here on the specific heat between 30 and 300 K, using high resolution calorimetry, with special emphasis on the superconducting transition.

2. Experimental

Samples 12EA11 and TA2-850 were sintered in an argon atmosphere at 100 bar to prevent thallium losses. Argon was replaced by helium at the same pressure for samples THE-850 and TH3-850. The critical temperature of these samples ranges from 84 to 92 K. The fraction of full Meissner effect is 40 to 60% in 20 G. The porosity is typically 25%. Details on sample preparation, characterization and assessment of purity are given elsewhere [1-3].

The specific heat was measured in an adiabatic calorimeter using a continuous heating method. The accuracy, using 0.5 g samples, is 0.5 to 1%, whereas the scatter is of the order of 0.04 to 0.15% rms, depending on the voltmeters used at the time of the experiment.

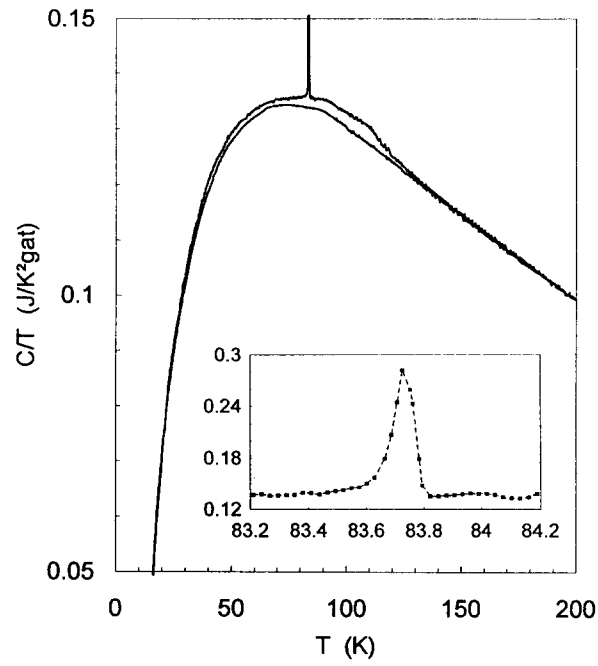

Figure 1. Specific heat C/T of samples TA2-850 (upper curve) and THE-850 (lower curve). Inset: enlargement of the argon peak at 83.7 K in the former sample, using 0.05 K averaging.

0925-8388/93/$06.00

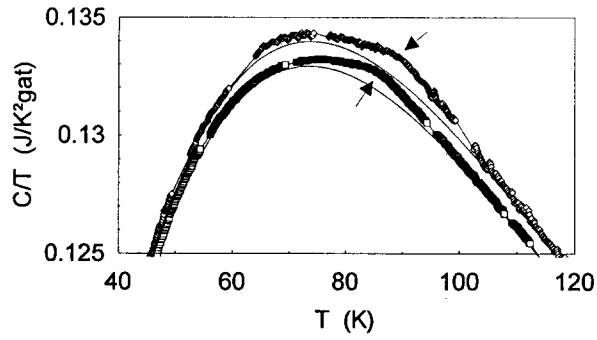

Figure 2 Total specific heat of sample THE-850 and TH3-850 near T_c (shown by arrows). Smooth curves: lattice background.

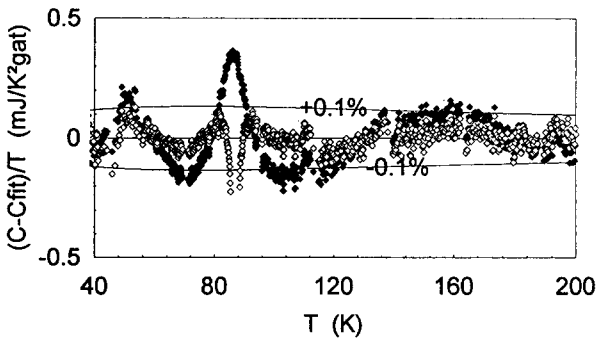

Figure 3 Filled symbols: residue of a fit including only phonons, showing the location of the superconducting anomaly. Open symbols: residue of a full fit including fluctuations. Sample: TH3-850.

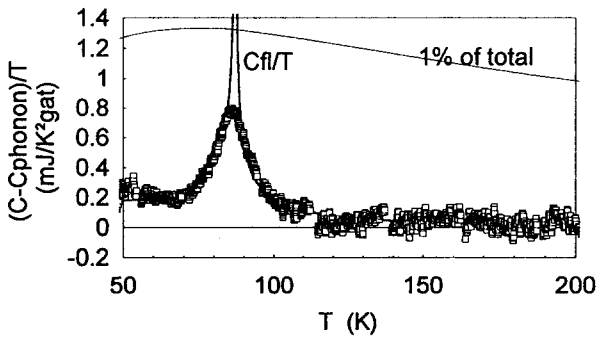

Figure 4. Upper curve: 1% of the total specific heat. Squares: measured points minus fitted lattice contribution. Full line: fitted fluctuation specific heat. Sample: TH3-850.

3. Results

Raw data that are representative of the two categories of samples (Ar or He) are given in Fig. 1. A peak with a width of 0.1 K or less was observed at the triple point of Ar in the samples prepared in an argon atmosphere, indicating that an appreciable amount of gas (0.03% by weight) was sealed in the closed pores. The distribution of the latent heat of evaporation up to ≈120 K gives an estimate of the pressure inside the pores, ≈20 bar at room temperature. The specific heat anomaly at T_c can hardly be separated out from the background in these "Ar" samples.

The samples prepared under helium atmosphere are free from such extrinsic features. The superconducting transition gives rise to a smeared break in the slope of the specific heat (Fig. 2). This anomaly appears more clearly as a ≈1% wiggle at T_c in the residue of a global fit of the data (40-220 K) when only phonon contributions are turned on (Fig. 3, filled symbols). The phonon spectrum is represented by three Einstein modes with adjustable positions and weights. Adding a fourth mode does not improve the fit.

The specific heat may be accurately fitted only when additional electronic contributions are considered. We first include a mean-field step as given by the two-fluid model. The choice of the latter is irrelevant since the step turns out to be negligibly small. The macroscopic Ginzburg-Landau model with effective-mass tensor and Josephson coupling of the layers is then used to describe the Gaussian fluctuations in the vicinity of T_c [4]. This contribution reads:

$$C_{fl} = \frac{k_B}{8\pi V_c \sqrt{(\tau d/2\xi_c)^2+\tau/2}} \quad , \qquad T<T_c$$

where $V_c = \xi_{ab}^2 \xi_c$ is the coherence volume, $\tau = |1-T/T_c|$ is the reduced temperature, and d is the interlayer distance. The leading power of τ close to T_c is -1/2, and the term containing $d/2\xi_c$ may be omitted with practically unchanged results. The last term $\tau/2$ in the square root is replaced by τ when $T>T_c$. The phonon and electron contributions are refined in a single step. They fit the total specific heat between 40 and 210/230 K down to the experimental scatter, omitting a 3 K window at T_c (Fig 3, 4 and Table I). The Einstein frequencies θ_i lie in the expected range for phonons, with a total weight exceeding slightly the ideal value of 3N modes per gram-atom (Table I). The excess is believed to be due to anharmonicity. The specific heat jump at T_c, and hence the Sommerfeld constant γ (half the jump in the two-fluid model used here), are found to be zero within

Table 1. Parameters derived from the fit of high resolution specific heat data

	composition sample code	$Tl_2Ba_2CuO_6$ THE-850	$Tl_2Ba_2CuO_6$ TH3-850	$Bi_2Sr_2CaCu_2O_8$ BSC-TS	$YBa_2Cu_3O_7$ J466G2
T_c	(K)	91.8	87.3	93.1	91.1
θ_1	(K)	106	110	122	148
θ_2	(K)	296	308	325	333
θ_3	(K)	767	701	640	677
modes/gat	(×3N)	1.04	1.05	1.01	1.05
$\Delta C/T_c$	(mJ/K²mole)	(0.4)	0.0	3.9	42
$<\xi>$	(Å)	7.5	8.2	6.2	6.4
rms dev.		0.15%	0.039%	0.10%	0.037%

experimental uncertainty (Table I). The fluctuation contribution determines the average coherence length $<\xi> = (\xi_{ab}^2\xi_c)^{1/3} = 7.5$ Å for the sample with $T_c = 91.8$ K and 8.2 Å for the sample with $T_c = 87.3$ K.

4. Discussion

A comparison with superconductors having the same critical temperature, i.e. $YBa_2Cu_3O_7$ [5] (Fig. 5, Table I) and optimized $Bi_2Sr_2CaCu_2O_6$, [6] (Fig. 6, Table I), shows that the fluctuation contribution, which is essentially determined by $<\xi>$ and therefore by the average Fermi velocity, tends to be similar for all three. In contrast to this, the mean-field jumps conspicuously differ by at least one order of magnitude (Table I). This surprizing result places a severe constraint on any theory that establishes a relation between the critical temperature and the electronic density of states at the Fermi level ("EDOS"), and suggests the following two lines of thought.

In a first picture, we may consider that the exceptionally high EDOS of YBaCuO is due to the existence of CuO chains, as suggested by band-structure calculations [7], and that the specific heat jump originates from proximity-induced superconductivity in the metallic chains. This picture implies that high-temperature superconductivity primarily occurs in semiconducting CuO_2 planes. Bi- and Tl- compounds do not contain CuO chains.

Alternatively, we may focus on the difference between YBaCuO on the one hand, and Bi- or Tl-based phases on the other hand, from the point of view of granularity. The AC susceptibility of Bi- and Tl- samples studied here discloses an extreme granular behaviour, with well separated intra- and intergrain transitions [1,2]. In contrast to this, YBaCuO usually shows sharp single-step

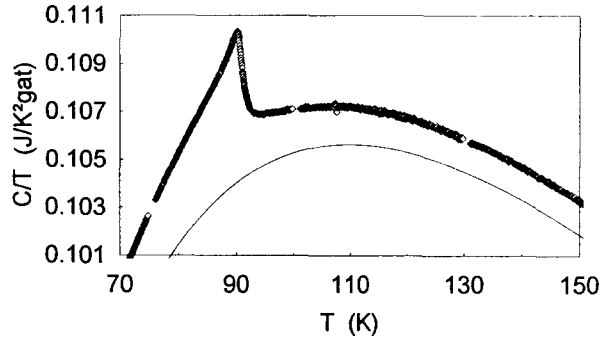

Figure 5. Specific heat of a $YBa_2Cu_3O_7$ ("123") sample (code J466G2) [5]. The continuous line represents the lattice background deduced from a simultaneous fit of the phonon and electron contributions similar to the one described for $Tl_2Ba_2CuO_6$ samples.

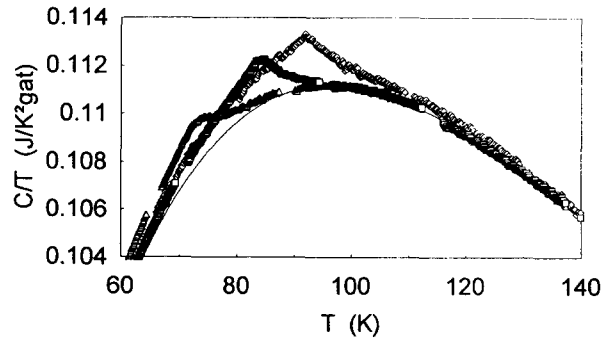

Figure 6. Specific heat of a $Bi_2Sr_2CaCu_2O_8$ sample ("2212", code BSC-TS, BSC-TLQ and BSC-550) measured in three states of oxidation [6]. The continuous line represents the lattice background deduced by a simultaneous fit of the phonon and electron contributions for the highest T_c sample. Note that the lower T_c samples support the estimation of the baseline.

transitions, pointing to high critical currents and well-connected grains. We may then speculate that the loss of phase coherence in highly granular samples leads to the inadequacy of the mean-field approximation and to the absence of jump at T_c.

A careful analysis of the AC and DC susceptibilities [1] suggests that the superconducting fraction for these Tl-based samples is of the order of one half. This may lead to an overestimation of $<\xi>$ in the above analysis by a factor of $2^{-1/3}$. The corrected values would fall in the range 6.0-6.5 Å, close to the value for YBaCuO.

5. Acknowledgements

The authors are grateful to the team of M.Th. Cohen-Adad at the University Claude Bernard Lyon I (France) for their collaboration, and to J.A. Fernandez and M.J. Blanchard for their technical assistance. This work was supported by the Fonds National Suisse de la Recherche Scientifique.

References

1 C. Opagiste, M. Couach, A.F. Khoder, T.K. Jondo, J.L. Jorda, M.Th. Cohen-Adad, A. Junod, G. Triscone and J. Muller, these proceedings.
2 G. Triscone, A. Junod, J. Muller, C. Opagiste, M. Couach, A.F. Khoder, T.K. Jondo, J.-L. Jorda and M.Th. Cohen-Adad, these proceedings.
3 L.A. Bursill, O. Leckel and M.G. Blanchin, these proceedings.
4 L.N. Bulaevskii, V.L. Ginzburg and A.A. Sobyanin, Physica C 152 (1988) 378 and 156 (1988) 652.
5 A. Junod, D. Eckert, T. Graf, G. Triscone and J. Muller, Physica C 162 (1989) 482; new high-resolution data.
6 G. Triscone, J.-Y. Genoud, T. Graf, A. Junod and J. Muller, Physica C 176 (1991) 247; specific heat to be published.
7 S. Massidda, J. Yu and A.J. Freeman, Phys. Lett. A122 (1987) 198.