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Low-temperature specific heat of single-crystal $Bi_2CaSr_2Cu_2O_8$ and $Tl_2Ca_2Ba_2Cu_3O_{10}$

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We report on specific-heat measurements from 2 to 15 K on single crystals of $Bi_2CaSr_2Cu_2O_8$ and $Tl_2Ca_2Ba_2Cu_3O_{10}$. We find low-temperature deviations from the Debye law that can be attributed to spin-glass behavior of a small concentration of isolated impurity copper moments. At higher temperatures, we observe contributions to the specific heat that can be attributed to a soft-phonon mode, possibly associated with the superstructure in the Bi-O and Tl-O layers. From our single-crystal data, we conclude that the thallium- and bismuth-based copper oxide superconductors show no measurable linear term in the specific heat [$\gamma(0) \leq 1$ mJ/mole K^2].

Extensive measurements of the low-temperature specific heat of both ceramic and single-crystal $YBa_2Cu_3O_{7-\delta}$,[1-3] as well as measurements on the La-Cu oxide superconductors,[4,5] have revealed the existence of a contribution proportional to temperature, $\gamma(0)T$. This has always been accompanied by a low-temperature (< 3 K) upturn attributed to magnetic impurities, which has been ignored or fit with $1/T^2$ and $1/T^3$ terms. Early measurements on ceramic $YBa_2Cu_3O_{7-\delta}$ showed a large $\gamma(0)$, on the order of 20 mJ/mole K^2. In a thorough study of the low-temperature specific heat of a sequence of samples of increasing quality, Eckhart *et al.* showed that the value of $\gamma(0)$ for good $YBa_2Cu_3O_{7-\delta}$ material can be as small as 4 mJ/mole K^2. They also found that $\gamma(0)$ for $BaCuO_{2+x}$, an impurity phase always present in ceramic samples, was about 50 times larger than that measured in the superconductor itself, thus suggesting that impurity phases could account for the observed linear term.

Recently, several laboratories have reported measurement on polycrystalline and single crystal $Bi_2CaSr_2Cu_2O_8$ with analysis that shows no linear term within experimental error (typically ~ 1 mJ/mole K^2).[6-9] It is conceivable that the difference between the bismuth compounds and the yttrium compounds of oxygen doping and charge distribution on the oxygen[10] could lead to a different symmetry of the superconducting wave function, hence a different form of low-temperature specific heat. In this context, the observation of a large $\gamma(0)$ in ceramic $TlCaBaCu_2O_{5.5}$,[6] which is structurally very similar to Bi-Ca-Sr-Cu-O, is surprising.

This paper reports specific-heat measurements in the range 2–15 K on a single crystal of Bi-Ca-Sr-Cu-O as well as single crystal and polycrystalline $Tl_2Ca_2Ba_2Cu_3O_{10}$ (possibly with inclusions of $Tl_2CaBa_2Cu_2O_8$). The data cannot be adequately described in any temperature range solely by a sum of the low temperature form of the Debye law $C_{\text{lattice}} \propto T^3$ and a linear term. We attribute the low-temperature deviations from the Debye law to spin-glass behavior of a small concentration of isolated impurity copper moments, perhaps due to oxygen defects, and the deviations at higher temperatures to a soft-phonon mode, possibly associated with the superstructure in the Bi-O and Tl-O layers. The lack of a reliable model for the background contributions to the heat capacity is the primary source of uncertainty in determining the possible excitations in the superconducting state. Within this uncertainty, the data on Bi-Ca-Sr-Cu-O show no measurable linear term [$\gamma(0) < 1$ mJ/mole K^2], in agreement with previously published results. Although the polycrystalline Tl-Ca-Ba-Cu-O shows a measurable linear term (somewhat reduced from that found by Fisher *et al.*[6]), the single crystal Tl-Ca-Ba-Cu-O gave no linear term [$\gamma(0) < 1$ mJ/mole K^2]. These measurements, when combined with those of Fisher *et al.*,[6] demonstrate that, as with Y-Ba-Cu-O, the measured linear term is strongly dependent on the purity of the material used.

Single crystals of $Tl_2Ca_2Ba_2Cu_3O_{10+\delta}$ were grown by a melt method similar to Ref. 11. Powders of Tl_2O_3, CaO, BaO, and CuO (all 99.9% pure or better) in cation ratio of 2:1:1:2 were mixed and ground by mortar and pestle. The mixture was sealed in gold tubing (0.2 mm thick, 11 mm diam) with the ends cold-welded in air. The firing profile was 950 °C for 30 min, quick cooling to 900 °C, soaking at 900 °C for 1 h, slow cooling (15 °C/h) to 700 °C, followed by furnace cooling. The crystal used for the measurement was picked out from the crystalline melt. It is a shiny platelet with sharp edges weighing 570 μg, with dimensions $0.75 \times 0.75 \times 0.1$ mm^3. The polycrystalline sample was broken from the melt and weighed 17 mg. Magnetometer data for the single crystal are shown in Fig. 1. The presence of a small fraction of secondary superconducting phase with T_c consistent with it being $Tl_2CaBa_2Cu_2O_8$ is observed.

Single crystals of $Bi_2CaSr_2Cu_2O_8$ were grown from a mix of oxide and carbonate powders (all 99.95% or better) melted at 950° C in air, and then slow cooled at 0.7 °C/h to below 800 °C. X-ray diffraction indicates that the samples are purely single phase, with the sharpness of the (00*n*) peaks being limited by the instrumental resolution of the diffractometer. We report measurements of an 11-mg crystal. Magnetometer data is shown in Fig. 1.

The samples were measured using the relaxation tech-

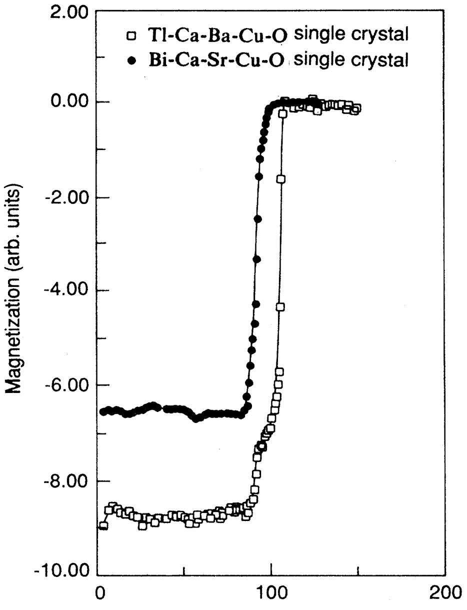

FIG. 1. Magnetization of Tl-Ca-Ba-Cu-O and Bi-Ca-Sr-Cu-O single crystals cooled in ≈ 1 G.

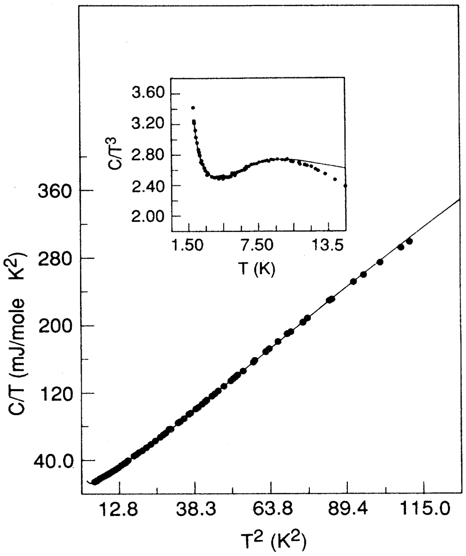

FIG. 2. C/T vs T^2 for Bi-Ca-Sr-Cu-O single crystal. The line represents the best fit to Eq. (1) in the range 2–11 K showing a linear term of 0.6 mJ/mole K^2. Inset: C/T^3 vs T with the same fit.

nique. The basic measurement system has been described in detail elsewhere,[12] although the computer control and data acquisition have been modernized to allow for easier operation. The sample platform is a sapphire on silicon chip where the silicon has been doped with phosphorus to produce elements with strongly temperature-dependent resistivities in the measurement region for thermometry, as well as elements with temperature-independent resistivities for use as heaters. The samples were attached to the sample platform with a small quantity of Wakefield thermal grease. The addenda constituted about 55% of the total heat capacity for the Tl-Ca-Ba-Cu-O single crystal and less than 20% for the polycrystalline Tl-Ca-Ba-Cu-O and the Bi-Ca-Sr-Cu-O single crystal. The uncertainty of the measurements is estimated to be less than 4% for the Tl-Ca-Ba-Cu-O single crystal and less than 1% for the larger samples.

Specific-heat data for the Bi-Ca-Sr-Cu-O crystal are plotted as C/T vs T^2 in Fig. 2. Although the data roughly follow a straight line, characteristic of the Debye law, significant deviations exist. In order to see the deviations more clearly, the inset shows C/T^3 vs T. Two features can be clearly identified, the low-temperature upturn mentioned previously, and a broad peak at about 9 K. At low temperatures (<3.5 K), we found that a plot of C/T^3 vs $1/T^4$ produced a straight line, indicating a term proportional to $1/T$, characteristic of spin glasses well above the freezing temperature.[13] At higher temperatures, fitting the data with an odd power polynomial requires at least a T^7 term. Alternatively, the data can be fit to a low-temperature Einstein mode. We subtracted the Debye contribution estimated as the minimum in the C/T^3 plot at 4.5 K, and plotted T^2C_{excess} vs $1/T$ on a semilog plot. The resulting plot was linear from about 5–11 K, indicating the presence of an Einstein mode or other excitation with a gap (see below). Hence we fit the data from 2 to 11 K by the function

$$C(T)=\frac{g}{T}+\gamma(0)T+\beta T^3+mR(T_E/T)^2\frac{\exp(T_E/T)}{[1-\exp(T_E/T)]^2}\,, \qquad (1)$$

where m represents the number of oscillators per unit cell, R is the gas constant, and T_E is the temperature of the Einstein mode. The fit produces $\beta=2.5$, resulting in $\Theta_D=230$ K, and $\gamma=0.6$ mJ/mole K^2, in good agreement with previously published results, despite the different analysis. The temperature of the Einstein mode is found to be 47 K, and the oscillator strength corresponds to $m=0.2$, or $\frac{1}{5}$ of an oscillator per unit cell [for a one-dimensional (1D) oscillator], in close agreement with the values obtained by hand from the straight-line plot described above. Note that the value of the oscillator strength is exactly that expected from a mode associated with the 1D superstructure, which in the bismuth materials has a periodicity of approximately 27 Å, or about 5 unit cells.[14]

The coefficient of the $1/T$ term is $g=13$ mJ/mole. The magnetic moment concentration can be estimated by using a spin-glass model where the interaction strength is proportional to the concentration of magnetic moments. This gives $g=c^2n_ck_BT_J$, where c is the ratio of the number of impurity moments to copper atoms, and n_c is the number of copper atoms per mole. Assuming an undiluted interaction strength equal to that of the copper oxide parent compounds La_2CuO_4 and $YBa_2Cu_3O_6$ ($T_J\sim1000$ K),[15] we find an impurity concentration of 0.07%. As a consistency check, the value obtained for the $1/T$ term can be compared to a possible $1/T^2$ Schottky term from moments in the average field of their neighbors, assuming the impurity concentration derived above. The Schottky term is estimated as $C_{\mathrm{Schottky}}=(cn_c)k_B(cT_J)^2/T^2$, which is less than $\frac{1}{2}$ the measured $1/T$ term at the lowest temperatures. This procedure probably overestimates the value of the $1/T^2$ term, due to the large disorder expected in the moment distribution, so the result is indeed self-consistent. The upturn at low temperatures has been studied down to 80 mK and in magnetic field by Caspary *et al.* using crystals grown by a similar method. They found spin-glass behavior due to an impurity moment concentration of 0.1%, in good agreement with our results.

The fit to Eq. (1) cannot be extended to higher temperatures without corrections to the Debye law for the acoustic phonons. Consequently, the form of the Einstein mode in Eq. (1) could be replaced by any excitation with a gap of 5.2 meV, including a Schottky anamoly or an anomalously small BCS-type gap involving $\sim\frac{1}{5}$ of the charge carriers, assuming 1 carrier per unit cell. (A BCS gap requires $T^{-1.5}$ instead of T^{-2} in the prefactor, but the fit is not highly sensitive to this.) Finally, while this model describes the data quite well (0.5% rms deviation, mostly in the low-temperature portion of the fit), the deviations from T^3 are small and could probably be reasonably well described by other functional forms.

The specific heat of both Tl-Ca-Ba-Cu-O samples is plotted as C/T vs T^2 in Fig. 3. Both samples show the low-temperature anomaly, but the upturn is less pronounced in the single crystal than in the polycrystalline sample, and in both it is significantly less than that measured in ceramic samples by Fisher *et al.*[6] This is presumably due to the presence of fewer impurities. The high-temperature increase above T^3 is evident in the single-crystal sample, but not in the polycrystalline one, due to the presence of significant impurity phases. In the region from 3–9 K, the polycrystalline sample is reasonably well fit (with derived parameters roughly independent of the endpoints of the fit) by $C=\gamma(0)T+\beta T^3$, with $\gamma(0)=5$ mJ/mole K^2 and $\beta=1.7$ mJ/mole K^4, so $\Theta_D=225$ K. The Debye temperature is somewhat lower than that measured in the ceramic TlCaBaCu$_2$O$_{5.5}$ in Ref. 6, but is similar to that found in the Tl$_2$Ca$_2$Ba$_2$Cu$_3$O$_{10}$ single crystal (see below), and to those measured in Bi-Ca-Sr-Cu-O which, as noted above, is structurally very similar.

For the Tl-Ca-Ba-Cu-O single crystal, C/T^3 vs T is the inset of Fig. 3. Unlike the Bi-Ca-Sr-Cu-O fits, the values obtained are sensitive to the lowest temperature included in the fit.[16] This is shown graphically in Fig. 4, where the values for $\gamma(0)$ obtained from the fit, together with the rms deviation of the fit, are plotted as a function of the starting temperature of the fit. This dependence is primarily due to the large contribution of impurities at low temperature (several times larger than that observed in the Bi-Ca-Sr-Cu-O crystal) that is not adequately accounted for by a $1/T$ term, thus illustrating the danger of extracting a linear term from specific-heat data without a complete model for the background heat capacity. The fit from 3.5–11 K produces $g=45$ mJ/mole, yielding an impurity concentration of 0.13%, $\beta=1.8$ and $T_E=40$ K, with $m=0.13$, i.e., about $\frac{1}{7}$ oscillator per unit cell, again on the order of that expected for a mode associated with the superstructure, and $\gamma(0)=1$ mJ/mole K^2. A simple straight-line fit of C/T vs T^2 from 3–9 K gives $\beta=2.1$

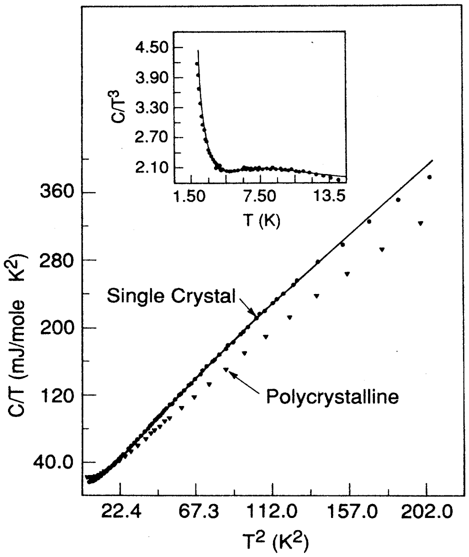

FIG. 3. C/T vs T^2 for the Tl-Ca-Ba-Cu-O single crystal and polycrystalline samples. The line represents the best fit of the single crystal to Eq. (1) in the range 3.5–11 K, showing a linear term of 1 mJ/mole K^2. Inset: C/T^3 vs T for the single crystal with the same fit.

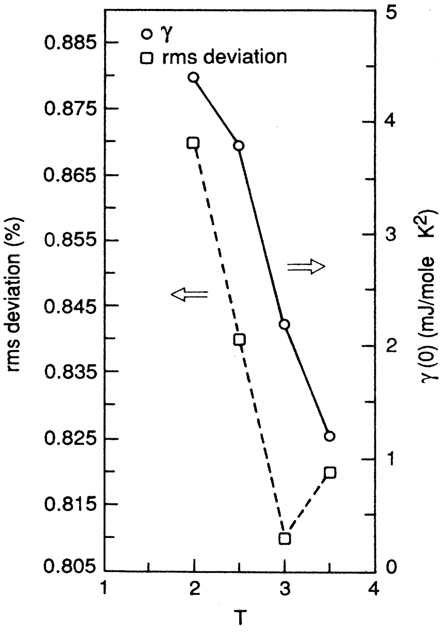

FIG. 4. The coefficient of the linear term derived from a fit of the Tl-Ca-Ba-Cu-O single-crystal data to Eq. (1), and the rms deviation of the data from the fit, are plotted against the lowest temperature included in the fit. All fits include data up to 11 K. The linear term tends to zero when the data below 3.5 K, which cannot be accurately modeled, are excluded.

and $\gamma(0) = -0.2$ mJ/mole K^2. If a term proportional to T^5 is added, the value obtained for the linear term increases to $\gamma(0) = 0.1$ mJ/mole K^2. Therefore, we conclude that, as with the bismuth compound, in the thallium compound $\gamma(0)$ is smaller than 1 mJ/mole K^2. The apparent linear term observed previously in Tl-Ca-Ba-Cu-O ceramic is most likely due to inhomogeneities or impurities, particularly $BaCuO_{2+x}$, as is evidenced by the reduction in the low-temperature anomaly seen in the single crystal from that observed by Fisher *et al.*

The persistence of the linear term in single crystal Y-Ba-Cu-O can be explained in several ways. Y-Ba-Cu-O is a point compound in the phase diagram, so any deviation from perfect stoichiometry will result in impurity phases of $BaCuO_{2+x}$, CuO, and Y_2BaCuO_5. It is also known that $BaCuO_{2+x}$ grows epitaxially with Y-Ba-Cu-O in thin films,[17] so it is possible that Y-Ba-Cu-O crystals contain $BaCuO_{2+x}$ inclusions, whereas Tl-Ca-Ba-Cu-O may not. Alternatively, the high mobility of oxygen in the chains of Y-Ba-Cu-O may result in more oxygen vacancies than in Bi-Ca-Sr-Cu-O or Tl-Ca-Ba-Cu-O. This would allow for a quasilinear term in the specific heat, conceivably by low-energy atomic tunneling or from spin-glass behavior of the isolated copper moments generated by the vacancies. Finally, the symmetry arguments discussed above may explain an intrinsic linear term which is much larger in Y-Ba-Cu-O than in Tl-Ca-Ba-Cu-O or Bi-Ca-Sr-Cu-O. More work on high-quality Y-Ba-Cu-O single crystals will be required to fully resolve this question.

In summary, we have found that the low-temperature specific heat of both Tl-Ca-Ba-Cu-O and Bi-Ca-Sr-Cu-O is reasonably well described by the Debye law for the phonons and a contribution from a low-frequency Einstein phonon mode possibly associated with the superstructure, with no contribution from electronic excitations. The difference between our single crystal results and those on polycrystalline and ceramic Tl-Ca-Ba-Cu-O are probably due to small amounts of impurities in the ceramic that are apparently not present in the single crystal. A unified theoretical description of the copper oxide superconductors must be consistent with an upper limit on the linear contribution to the specific heat of 1 mJ/mole K^2.

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