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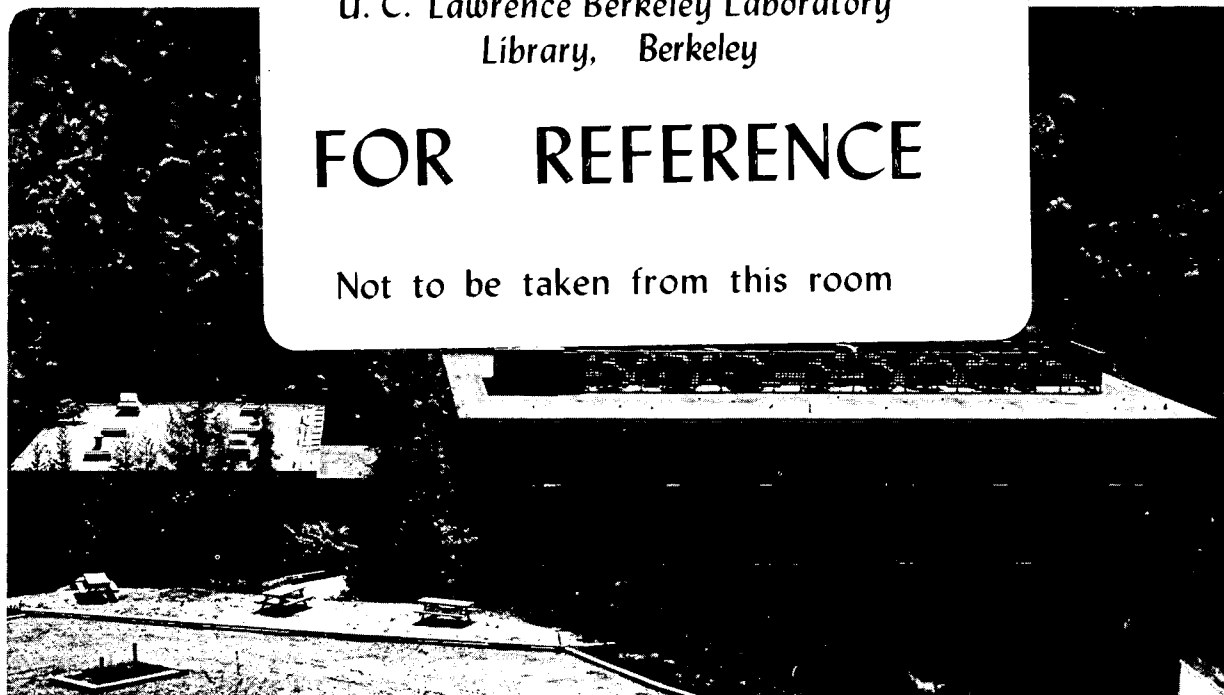
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THE SPECIFIC HEAT OF THALLIUM OXIDE SUPERCONDUCTORS

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CHAPTER XV

THE SPECIFIC HEAT OF THALLIUM OXIDE SUPERCONDUCTORS

By

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I. Introduction

The discovery of superconductivity in the Tl-Ba-Ca-Cu-O (TBCCO) system¹ generated intense interest and led to numerous structural studies and measurements of physical properties on these compounds. Interpretations of the measurements are in most cases complicated by the evident occurrence, or at least the possibility of the occurrence, of more than one phase in the samples. Furthermore, even ignoring that complication, the specific-heat measurements have been neither detailed nor extensive enough to establish the kind of correlations among sample-dependent parameters that have been recognized from the much more extensive data on $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ (YBCO) and which have provided a basis for the current understanding of the specific heat of that material. For these reasons, it is not useful to discuss specific-heat measurements on the Tl-O superconductors except in the context of what is known about other high- T_c superconductors, HTSC's. The measurements on YBCO are more complete and better understood than those for any other high- T_c superconductor, which suggests a discussion of the specific heat of the Tl-O superconductors based on a comparison with measurements on YBCO and their interpretation. Such an approach is not entirely satisfactory, both because the current understanding of the specific heat of YBCO is itself incomplete -- and based to a significant degree on comparisons with the specific heat of conventional superconductors -- and because the complications associated with oxygen stoichiometry ($\delta \neq 0$) which are attendant on the occurrence of CuO chains, as well as the CuO_2 planes, in YBCO may have no counterpart in the case of the Tl-O superconductors. Nevertheless, this seems to be the most satisfactory approach, and it is the one taken here.

This review is organized into six sections: Sec. II is a brief description of the information obtained from specific-heat measurements on conventional superconductors, and Sec. III is a summary of the measurements on YBCO and their interpretation. Since there is a natural division of the specific-heat-derived results into "low-temperature" ($1 \leq T \leq 10\text{K}$) results and results near T_c , which is reflected in the discussion in Sec. III, the low-temperature measurements and the measurements near T_c on the Tl-O superconductors are presented in Sections IV and V, respectively. Section VI includes additional discussion of the parameters derived from specific-heat data for the Tl-O superconductors, and their relation to the corresponding parameters for other high- T_c superconductors, to the electron density of states at the Fermi surface, to the phonon spectrum and to the strength of the coupling.

II. Specific Heat of "Conventional" Superconductors

The two components of the specific heat, C , common to all materials containing conduction electrons are the lattice and the conduction electron contributions, C_l and C_e , respectively.

C_l is generally taken to be independent of applied magnetic field, H , and the same in the normal and superconducting states. (In fact, for HTSC's there are indications, both

theoretical and experimental, that differences in the phonon spectrum, and therefore in C_l , between the normal and superconducting states should be taken into account. However, the effects are small, still not well defined and not relevant to the present state of the data for the TI-O superconductors or their interpretation. This complication will not be considered in the following.) At low temperatures,

$$C_l = B_3 T^3 + B_5 T^5 + B_7 T^7 + \dots, \quad (1)$$

where

$$B_3 = (12/5) \Pi^4 R \theta_0^{-3} \quad (2)$$

and θ_0 is the Debye characteristic temperature in the limit of zero temperature. The higher order terms in Eq. (1) give some information about phonon dispersion, but they are not sensitive to the details of the phonon spectrum. They are frequently replaced by Einstein terms that are interpreted in terms of singularities in the phonon spectrum, but in fact the difference in C_l from that associated with the peaks in the phonon spectrum produced by more or less normal phonon dispersion is usually not meaningful.

In the normal state, i.e., for $H > H_{c2}$, the upper critical field, C_e is

$$C_{en} = \gamma T, \quad (3)$$

with

$$\gamma = (1/3) \pi^2 k_B^2 N(E_F), \quad (4)$$

where $N(E_F)$ is the density of electron states at the Fermi energy, for both spin directions. Band-structure calculations give the band-structure or "bare" density of states $N_{bs}(E_F)$ which is related to $N(E_F)$ by

$$N(E_F) = (1 + \lambda) N_{bs}(E_F), \quad (5)$$

where λ represents the electron-phonon enhancement. For $H=0$, i.e., in the superconducting state, the temperature dependence of C_e is changed dramatically by the development of the gap in the electron density of states at E_F , and becomes

$$C_{es} \approx a \gamma T_c \exp(-b T_c / T). \quad (6)$$

At T_c there is a discontinuity in C_e , $\Delta C(T_c)$, that is directly related to the temperature dependence of the gap at T_c , and, with the assumption of a model for the temperature dependence of the gap over the whole interval to 0K, to the 0-K gap, $2\Delta_0$. The temperature dependencies of C_{en} and C_{es} are illustrated as C_e/T vs T in Fig. 1. The solid curve for C_{es} corresponds to the weak-coupling BCS case in which $2\Delta_0 = 3.53 k_B T_c$. The dashed curve

corresponds to a strong-coupling case here represented by the " α model". In that model², which represents C_{es} for a number of conventional superconductors quite well, the BCS temperature dependence of the gap is preserved but the ratio $\alpha \equiv 2\Delta_0/k_B T_c$ is taken as an adjustable parameter. For the dashed curve $\alpha = 3.0$, and $\Delta C(T_c)/\gamma T_c = 4.13$; to be compared with the weak-coupling values, 1.764 and 1.43, respectively. For conventional superconductors, the highest known values are $\alpha \approx 2.4$ and $\Delta C(T_c)/\gamma T_c \approx 2.8$, but the still higher values represented by the dashed curve may be relevant for YBCO. For very strong coupling, the shape of the specific-heat anomaly at T_c is qualitatively different: the ratio $(dC_{es}/dT)_{T_c}/\gamma$ is greater, and the curvature of C_{es}/T is positive.

For most conventional superconductors it is quite practical to measure C for $H > H_{c2}$, and to analyze the data with Eqs. (1) and (3) to obtain reliable values of the coefficients in those equations. The values of C_2 so determined, can be used to subtract that contribution from the C measured for $H=0$, and thus to obtain C_{es} . In many cases C_2 is small enough relative to C_e , even at T_c , that the features illustrated in Fig. 1, including the sharp (limited only by temperature resolution) discontinuity at T_c , have been well determined. Thus, specific-heat measurements on conventional superconductors have given: for $H > H_{c2}$, the value of $N(E_F)$ which is of fundamental importance in understanding the properties of both the normal and superconducting states, the value of θ_0 which defines the phonon spectrum in the long-wave-length limit and the higher order coefficients in Eq. (1) which give some (limited) information about phonon dispersion; for $H=0$, the temperature dependence of C_{es} and the value of $\Delta C(T_c)$ which give information about the strength of the electron-electron coupling that produces the transition to the superconducting state.

III. General Features of the Specific Heat of HTSC's

In this description of the general features of the specific heat of HTSC's, most features are illustrated by results for YBCO. Only a few references to original work are given; other references, and more detail, can be found in a recent review³.

A. Overview

The total specific heat (including C_2) of a reasonably representative polycrystalline sample of YBCO, for $H=0$, is shown in Fig. 2 as C/T vs T . In this case C_2 is so large relative to C_e that the specific-heat "anomaly" at T_c is only about 3% of the total. This is typical of HTSC's and limits the accuracy with which data near T_c can be analyzed to obtain detailed information about C_{es} . Furthermore, because the values of H_{c2} are so high, of the order of 100T, data for $H > H_{c2}$ and their analysis into C_{en} and C_2 are not available. Thus, the direct determination of $N(E_F)$ that has been made routinely for conventional superconductors has not been made for HTSC's. On the other hand, since C_2 is the dominant contribution above a few K, it has been possible to obtain reasonably accurate estimates of C_2 , and representative results for several HTSC's are shown in Fig. 3 as C_2/T^3 vs $\log T$.

B. The Low-Temperature Specific Heat

There are two contributions to the low-temperature specific heat that set HTSC's apart from conventional superconductors, and that are qualitatively apparent in the low-temperature inset to Fig. 2. One is a low-temperature "upturn" in C/T . As shown by its magnetic field dependence in fields of a few T--it becomes a Schottky anomaly with H and T dependencies expected for Cu^{2+} magnetic moments--it is associated with Cu^{2+} moments that, for $H=0$, order in the vicinity of 0.1K under the influence of internal interactions. For $H=0$ and $T \geq 0.4\text{K}$, as in Fig. 2, it is only the high-temperature tail of the $H=0$ anomaly that is observed. In fields of a few T, the applied field is large enough, relative to the internal fields, that a Schottky anomaly is a good approximation, and the concentration of Cu^{2+} moments associated with this feature, n_2 , is determined by the in-field data (see below). Because the distribution of internal fields broadens the anomaly relative to a Schottky anomaly, the high-temperature "tail" is not well represented by the T^{-2} dependence characteristic of a magnetic Schottky anomaly, and requires additional terms in negative powers of T . Since certain superconducting-state properties are correlated with n_2 , it is clear that these moments are located, at least predominantly, in the YBCO phase. The other is a "linear" term $\gamma^*(H)T$. The field dependence of this term is well represented by

$$\gamma^*(H) = \gamma^*(0) + Hd\gamma^*/dH, \quad (7)$$

with $d\gamma^*/dH$ independent of H to within experimental uncertainty. The $H=0$ component⁴, $\gamma^*(0)$, received a great deal of attention in the first few years of research on HTSC's both because it has no counterpart in conventional superconductors and because it corresponded to a prediction of early versions of the RVB theory. For YBCO, there is no doubt that $\gamma^*(0)$ includes a contribution associated with impurity phases, BaCuO_2 in particular⁵. The total concentration of Cu^{2+} moments in a sample, n , which includes those in impurity phases such as BaCuO_2 , n_1 , as well as those in the YBCO lattice, n_2 , can be determined from the Curie-Weiss term in the high-temperature magnetic susceptibility. Thus, n_1 and n_2 are both determined. To within an accuracy of the order of $\pm 1\text{mJ/mole} \cdot \text{K}^2$, the value of $\gamma^*(0)$ is well represented by a sum of two terms, one proportional to n_1 , and the other proportional to n_2 . This suggests that a part of $\gamma^*(0)$ is associated with impurity phases, and the rest is associated with non-superconducting regions of the samples that are present in an amount proportional to n_2 and associated with the Cu^{2+} moments that produce the upturn⁶. Thus, at least in this case, any intrinsic contribution to $\gamma^*(0)$ associated with the superconducting state is $\leq 1\text{mJ/mole} \cdot \text{K}^2$. The H -dependent part of $\gamma^*(H)$, $Hd\gamma^*/dH$, however, is similar to a contribution that is well known in conventional type II superconductors and is associated with increasing flux penetration for $H_{c1} < H < H_{c2}$.

The analysis of low-temperature data for YBCO into the components C_2 , $\gamma^*(H)T$, and C_m , the contribution associated with Cu^{2+} moments, is illustrated in Fig. 4 for $H=0$ and 7T . In this figure another contribution, not mentioned above, but well known in other materials, is also apparent: for $H=7\text{T}$ there is an upturn in C/T associated with the interaction of nuclear magnetic moments with H . This contribution, C_b , is readily

distinguishable from the $H=0$ upturn associated with Cu^{2+} electronic moments by its magnitude and also by its H and T dependencies--for the temperatures of interest here, it is accurately proportional to $(H/T)^2$.

C. The Specific-Heat Anomaly at T_c

The normal/superconducting transition is substantially broadened in HTSC's relative to that in many conventional superconductors. There are no doubt two contributions to the breadth of the transition as observed in the specific heat, both related to the short value of the coherence length, ξ , although otherwise quite different in origin. One is simply sample inhomogeneity -- fluctuations in concentration in the case of solid solutions or in oxygen stoichiometry in YBCO or other atomic-scale defects which are typical of oxides such as the HTSC's. In HTSC's with ξ of the order of the lattice parameter these defects can produce regions differing in the superconducting properties whereas the greater values of ξ in conventional superconductors have an averaging effect. The small values of ξ also produce an intrinsic broadening of the transition by fluctuation effects that is orders of magnitude larger than in conventional superconductors. In the latter case fluctuation broadening is too small to be observed, but in HTSC's, although the magnitude of the effect is sample dependent (at least in YBCO), there is good evidence for its existence. The example in the second inset in Fig. 2 shows a reasonably sharp transition for a polycrystalline YBCO sample; sharper transitions have been observed in a few polycrystalline samples; but generally the sharpest transitions have been observed in single crystals, for which the analysis of the data for fluctuation effects is most convincing⁷. An example of fluctuations in a polycrystalline sample is shown in Fig. 5.

For YBCO it is clear that the shape of the specific-heat anomaly at T_c is influenced by sample inhomogeneities, by strong-coupling effects and by fluctuations. Furthermore, analysis of the shape of the anomaly is always complicated by uncertainty in the subtraction of the "background" or lattice specific heat. In principle all of these effects can be represented by analytical expressions, but there are different possibilities, among which somewhat arbitrary choices have to be made, and the results of the analysis are not uniquely determined by the data. For example, positive curvature in C/T below T_c may be associated with strong-coupling effects or fluctuations; positive curvature just above T_c with fluctuations or sample inhomogeneities. Nevertheless, for a particular sample, quite consistent values of the mean-field contribution to the anomaly, the discontinuity $\Delta C(T_c)$, are obtained by different reasonable approaches. Figure 6 provides an example: The dashed straight-line representation is a simple entropy-conserving construction that gives one value of $\Delta C(T_c)$; the dash-dot curve is a different extrapolation of the high-temperature data based on a harmonic-lattice fit to the data extending to 280K that gives a value of $\Delta C(T_c)$ that is only slightly different; the solid curve is a fit with an expression that takes strong-coupling effects into account, allows for a Gaussian distribution of T_c 's and it also gives essentially the same value for $\Delta C(T_c)$. Similar results have been obtained when fluctuation effects have been included.

Measurements on series of different YBCO samples in two different laboratories^{6,8} have shown, however, that the values of $\Delta C(T_c)$ do show a strong sample-to-sample dependence -- varying by factors of more than two. In both cases, this variation was shown to be correlated with sample-to-sample variations in the low-temperature specific heat, specifically the low-temperature upturn in C/T and $\gamma^*(0)$ (although the actual parameters on which the correlations were based were different in the two cases).

D. Interpretation of Sample-to-Sample Variations of the Specific Heat of YBCO as Reflecting Varying Volume Fractions of Superconductivity

$\Delta C(T_c)$ is one of three sample-dependent parameters derived from specific-heat data that might be expected to reflect sample-to-sample variations in the volume fraction of superconductivity, f_s , in fact to be proportional to f_s . The other two are $d\gamma^*/dH$ (see Eq. 7) and ΔS , an entropy change associated with the effect of magnetic field on the specific-heat anomaly at T_c that is defined in detail in Ref. 9. In fact, all three of these parameters are mutually proportional with respect to sample dependence, and they can be used to assign relative values of f_s ⁹. The f_s scale has been made absolute on the basis of the observation that the same three parameters decrease approximately linearly with increasing n_2 , the concentration of Cu^{2+} magnetic moments. This was taken as an indication that the Cu^{2+} moments are themselves, or are associated with, defects that suppress the superconducting transition and produce non-superconducting regions. The limit $n_2=0$ was taken as determining $f_s=1$ and the values of $\Delta C(T_c)$, $d\gamma^*/dH$ and ΔS characteristic of the ideal, fully superconducting state. For example⁶, for $f_s=1$, $\Delta C(T_c)/T_c=77\text{mJ/mole}\cdot\text{K}^2$. [Similar conclusions, in that case for $\Delta C(T_c)/T_c$ alone, was reached on the basis of a related criterion and reported in Ref. 8.]

IV. The Low-Temperature Specific Heat of TBCCO

Specific heats at low temperatures have been measured in the TBCCO system for the compositions Tl-2201, Tl-2212 and Tl-2223. (This notation is used to distinguish the Tl-O superconductors from the corresponding phases of the Bi-O superconductors, and to specify the mole numbers of Tl, Ba, Ca and Cu, by the four digits, in that order.) Table I summarizes parameters characterizing these samples and their low-temperature specific heat, and gives references to the original work. The Tl-2201 and Tl-2212 materials were probably predominantly single phase. However, the Tl-2223 phases are best synthesized by starting with an off-stoichiometric mixture, and consequently, the Tl-2223 polycrystalline samples contained some or all of the possible additional phases Tl_2O_3 , BaO, BaCuO₂, CuO, CaO and other TBCCO compounds, e.g., Tl-1212, Tl-1223, Tl-2201 and Tl-2212.

Figure 7 is a plot of C/T vs T^2 for sample 7, a polycrystalline, mixed-phase sample (Tl-2212 + Tl-2223) for $H=0$ and $7T$. These were possibly the first low-temperature specific-heat measurement on TBCCO. (Samples 5, 6 and 7 seem to be the only samples that have been measured in magnetic fields.) In Fig. 8 C/T vs T^2 is compared for a single crystal and

a polycrystalline aggregate of Tl-2223, samples 1 and 2, respectively, while Fig. 9 is a similar plot for Tl-2212 and Tl-2201, samples 8 and 9, respectively.

The specific heat displayed in Fig. 7 is similar to that observed for YBCO: a low-temperature upturn in C/T at $H=0$, that becomes a Schottky anomaly in $7T$, and a finite $\gamma^*(0)$. All of the low-temperature specific-heat measurements on TBCCO show a low-temperature upturn in C/T , but the upturn for the single crystal (see Fig. 3) is much smaller than that for the polycrystalline samples. These results are similar to those observed for single crystal¹⁰ and polycrystalline¹³ BSCCO samples, which have the same structure. In the TBCCO system $\gamma^*(0)$ ranges from 0 to $63\text{mJ}/\text{mole} \cdot \text{K}^2$.

Since Cu is the only potentially magnetic element present in TBCCO, the C/T upturn can be assumed to be associated with localized Cu^{2+} electronic magnetic moments, as it is in YBCO. Furthermore, as in YBCO, in a magnetic field of $7T$ (see Fig. 7) this upturn becomes a Schottky anomaly which can be fitted with $g=2$ and $S=1/2$ (characteristic of Cu^{2+} at low temperatures). The amplitude of that anomaly gives a reliable estimate of the amount of Cu^{2+} present (see n_2 of Table I). For that sample¹³, the amount of Cu^{2+} was about an order of magnitude larger than that found for a typical YBCO sample, but comparable to that of BSCCO polycrystalline samples¹³. Junod et al.¹² have measured the magnetic susceptibility above T_c for TBCCO (samples 4, 8 and 9) and from fitting the data to a Curie-Weiss Law they have derived the total Cu^{2+} concentration of magnetic moments (see Table I). These concentrations are comparable to the value of n_2 for sample 7. The Cu^{2+} magnetic moments in TBCCO samples could be associated either with localized Cu^{2+} moments located in the CuO_2 planes of the TBCCO structure or with impurity phases.

For samples 3, 8 and 9, the $H=0$ upturns in C/T were fitted with T^{-2} terms; for sample 7, additional terms were required because the data extended to lower temperatures. Urbach et al.¹⁰ interpreted the upturn as being due to spin-glass ordering of Cu^{2+} . They used a term proportional to T^{-1} , which corresponds to the high-temperature limit for spin-glass ordering, to fit the upturn, and calculated n_2 from the coefficient of that term using a spin-glass model and an estimate of the exchange energy based on the antiferromagnetic interactions of La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_6$. However, neither the validity of the T^{-1} representation of the upturn nor the applicability of the spin-glass model is clear. The fitting expression was apparently not really adequate to represent the data; it was used only above 3.5K, where the T^{-1} term contributes only 14% of the total C ; and the T^{-1} term drops to 4% of the total at 5K. It is clear from the magnitude of the upturn that n_2 is small, but the assumptions underlying the estimate leave room for doubt as to its quantitative significance.

The fact that to within experimental error $\gamma^*(0)=0$ for nearly all BSCCO samples (single crystal or polycrystalline) while $\gamma^*(0)$ is finite for YBCO, LMCO ($M=\text{Ca}, \text{Sr}, \text{Ba}$) and for some, but not all, TBCCO samples is interesting and deserves further study. For YBCO it has been shown⁶ that $\gamma^*(0)$ can be interpreted as arising from a combination of

the "linear term" associated⁵ with some forms of BaCuO_2 , present as impurity phases, and the presence of normal metallic material interspersed with the superconducting material, and present in an amount proportional to n_2 . For LSrCO , $\gamma^*(0)$ is associated entirely with normal material¹⁵. [Too few measurements have been made for LBaCO and LCaCO to allow any conclusions to be drawn about the origin of the observed finite $\gamma^*(0)$.] Structurally, the TBCCO and BSCCO compounds are alike; however, one significant difference may be that the former contain Ba, and hence there is the possibility of BaCuO_2 phases, which could contribute to $\gamma^*(0)$. This view is supported by the fact that for a single crystal of TBCCO (Tl-2223)¹⁰, which might be expected to have relatively small amounts of BaCuO_2 present, $\gamma^*(0) \approx 0$. However, there remains an inconsistency in that for YBCO. A part of $\gamma^*(0)$ seems to be associated with Cu^{2+} moments (n_2), while for many BSCCO samples these moments are present in relatively high concentrations, but $\gamma^*(0)$ is at least small, if not zero. One possibility is that, unlike YBCO, BSCCO and TBCCO have no CuO chains in their structure, and none of the attendant problems with oxygen stoichiometry. Perhaps the Cu^{2+} moments in YBCO that give rise to a finite $\gamma^*(0)$ are associated with these chain sites and not the CuO_2 planes.

For YBCO⁶ and LSrCO ¹⁵ there is a correlation between the size of $\Delta C(T_c)/T_c$ (which has been taken as a measure of the fraction of the sample which is superconducting) and that part of $\gamma^*(0)$ not due to impurity phases. At present there are insufficient data for either BSCCO or TBCCO to make such a comparison. (See Sec. V for a discussion of the specific heat near T_c for TBCCO.)

As shown in Table I, the limiting low-temperature Debye temperature, θ_0 , decreases as the number of CuO_2 planes in the unit cell decreases. (The variation in θ_0 for the Tl-2223 samples is undoubtedly due to the presence of other phases--except possibly for the single crystal sample¹⁰.) For comparable BSCCO and TBCCO structures θ_0 is about the same. Figure 3 is a plot of C_2/T^3 vs $\log T$ for LCO, YBCO, BSCCO (Bi-2212) and TBCCO (Tl-2212 + Tl-2223). For both the YBCO and LCO [similar to LMCO (M = Ca, Sr, Ba)] the T^3 region lies below 5K and there is a pronounced peak near 20K that shows the presence of a peak in the phonon density of states near 50K. For both BSCCO and TBCCO the T^3 region extends about a factor of two higher in temperature with only a small peak in C_2/T^3 that occurs just below the rapid decrease of C_2/T^3 at higher temperatures. The lattices for both BSCCO and TBCCO, with θ_0 in the range 250-290K, are much softer than those of LCO and YBCO, for which θ_0 's range from 450-500K.

A hyperfine specific heat has been observed only in the case of Sample 7. C_h was much smaller than expected for the combined Cu and Tl contributions. The size of the measured C_h suggests that the hyperfine contribution is due to the Tl nuclear moments and, therefore, that the Cu nuclear moments are not relaxing sufficiently rapidly to contribute. These results are similar to those found for the BSCCO compounds¹³.

V. The Specific-Heat Anomaly at T_c for TBCCO

The early specific-heat measurements on YBCO provided evidence of a bulk superconducting transition near 90K, but the observed anomalies were relatively broad with heights considerably lower than those observed in later experiments. As sample quality improved, the YBCO anomalies became higher, narrower and sufficiently well-characterized to provide clear evidence that a simple weak-coupling BCS picture is not adequate for a full understanding of the superconducting phase transition. That such a definitive view is not yet possible in the case of the superconducting Tl-O superconductors (or, for that matter, in the case of other HTSC's) is made clear in Fig. 10 where some of the recent measurements on TBCCO and BSCCO are compared with those on YBCO¹⁶. These specific-heat data, unlike some of the earlier Tl-O and Bi-O HTSC results (see, for example, Refs. 17 and 18) do show departures from the "background" (lattice plus normal electron) specific heat. Nevertheless, the striking difference between the Tl-2212 and Tl-2223 anomalies on the one hand and that of YBCO on the other, strongly suggests that much work on sample preparation remains to be done before interpretations of the Tl specific-heat data near T_c can be made with confidence. To be sure, band-structure calculations (see section VI) suggest that the bare density of states, $N_{bs}(E_F)$, for the two Tl HTSC's are only about half as large as for YBCO. For that reason, it is possible that the specific-heat anomalies in the Tl-2212 and Tl-2223 compounds will never be as large, and therefore not as sharply-defined, as that in YBCO. Nevertheless, the experience with YBCO sample preparation, and the improvement already made in producing single phase Tl superconductors, give hope that the next few years will help to clarify what is presently a confusing picture of superconductivity in these materials. In fact, some very recent results¹⁹ indicate that the anomaly in Tl-2223 may be at least as pronounced as that in YBCO, and that therefore the similarities between this HTSC and YBCO may be greater than Fig. 10 suggests.

The specific heats of $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ for $n=1, 2$ and 3 have been measured¹². Tl-2201 was found to show no calorimetric evidence of a superconducting transition although there was evidence from ac susceptibility data of an incomplete superconducting transition that began just above 12K. Fig. 10 shows that the specific heats of both Tl-2212 and Tl-2223 provide evidence for superconducting transitions at temperatures above 100K. A sample¹³ that contained roughly equal parts of Tl-2212 and Tl-2223 showed a broad anomaly that began at ~ 113 K. These data are shown in Fig. 11, along with data obtained in a 7T magnetic field. The difference between the zero field and the 7T data are also shown as the dotted line in Fig. 12, where they are compared with $\Delta C = C(0) - C(5T)$ as computed from reversible magnetization²⁰ on Tl-2223. Fisher et al.¹³ compare their results with similar data obtained on YBCO and estimate that the observed differences between the zero- and the in-field results are likely to be 2 to 3 times smaller than would be expected for a fully-superconducting sample.

The specific heat of Tl-2212 has been measured from low temperatures up to 300K by two groups^{12,21,22}, and in the region 60-140K by several others^{17-19,23}. Atake et al.^{21,22} measured C for 3 different Tl-2212 samples in which the number of Tl atoms was 2.10, 1.94,

and 1.82 (samples a, b and c respectively). They found values for $\Delta C(T_c)$ and T_c of 2.6, 2.8 and 2.2 J/mole \cdot K and 104, 96 and 89K, respectively. In the case of sample a they used the technique described by Sharifi et al.²⁴ for analyzing the specific heat near T_c . This technique, similar to that employed by Gordon et al.²⁵, is based on the assumption that the measured C is the sum of a lattice term and an electronic term that has a Gaussian distribution in T_c . In order to account for the possibility of strong-coupling and for a fluctuation contribution, Atake et al.²¹ approximate their data with an adjustable 8 parameter fit in which the fluctuation term is assumed to be due to three-dimensional Gaussian fluctuations, and in which the mean-field part of the anomaly is assumed to vary as $|1-T/T_c|$. Fig. 13 shows their data after the computed "background" (lattice plus normal electron) specific heat has been subtracted off. The smooth curve in the figure is their fit to the data. From this fit they find that the sample has a spread in T_c of $\sim \pm 7K$, a mean coherence length $\xi \sim 5.4 \text{ \AA}$, and a γ of 21mJ/mole \cdot K². The fit also indicates BCS weak coupling. The authors rightly caution, however, that a sample with a narrower distribution in T_c might yield different results.

The data of Wohlleben et al.²³ and Braun et al.¹⁶ on Tl-2212 near T_c (see Fig. 10) are quite similar to those reported by Atake et al.^{21,22} and by Junod et al.¹². They differ, however, from earlier results^{17,18} that showed no cusp in the specific-heat data but did have discontinuities in the slopes of the C/T vs T data. Seidler et al.¹⁸ suggested that these results could imply the existence of a third-order phase transition in the Tl and Bi oxide superconductors; however, their own later data (as well as the results of the other groups) indicate that no such hypothesis need be entertained. Wohlleben et al.²³ and Braun et al.¹⁶ obtain a fit to the "background" specific heat by fitting the data well above and below T_c , and then subtract the "best" background fit from the data in the vicinity of T_c . The authors represent the remaining ΔC as the sum of a BCS mean-field specific heat plus a fluctuation term. The former authors²³ assume that this term arises solely from critical fluctuations, $C_{fl} \propto \log|1-T/T_c|$, whereas Braun et al.¹⁶ assume the fluctuations to have this form only within $+5K$ of T_c , and to have the $|1-T/T_c|^{-1}$ dependence characteristic of 2-D Gaussian fluctuations for $|T-T_c| > 5$ (as opposed to the $|1-T/T_c|^{-1/2}$ dependence of the 3-D Gaussian fluctuations assumed by Atake et al.²¹). Fig. 14a shows the ΔC data near T_c as well as the fit corresponding to an anomaly made up of mean-field and 2-D Gaussian fluctuation components. These authors¹⁶ obtain a value for γ of 3.7mJ/mole \cdot K², while for the same data Wohlleben et al.²³ obtain 12mJ/mole \cdot K². Both values are considerably lower than the value of 21mJ/mole \cdot K² obtained by Atake et al.²¹, a result that surely reflects the different assumptions regarding the fluctuation term as well as possible differences in the fitting procedures and in sample composition.

Several groups^{12,14,16,19,23,26} have reported observations of an anomaly in the specific heat of Tl-2223. The techniques for making this Tl-O superconductor differ among the various groups (the data reported by Wohlleben et al.²³ and by Braun et al.¹⁶ were taken on the same samples). Junod et al.¹² found x-ray evidence for nonsuperconducting phase impurities. Panova et al.¹⁴ report that their samples were at least 90% Tl-2223, while Braun et al.¹⁶ and Bandyopadhyay¹⁹ report that x-ray analysis indicated a sample with the Tl-2223

structure. The specific-heat measurements of Gavrichev et al.²⁶ showed anomalies at 97 and 125K, and a break in the slope of C/T vs T at 110K. This break indicates the presence of Tl-2122 in the sample, while the two anomalies are evidence for the existence of both Tl-1122 and Tl-2223 phases in this nominal Tl-2223 material.

Wohlleben et al.²³ and Braun et al.¹⁶ analyze the Tl-2223 specific-heat data using the same techniques they had used on Tl-2212. That is, they assume the anomaly to be due to a BCS mean-field term plus a fluctuation term. The former group²³ assumes this fluctuation term to be due solely to critical fluctuations and obtain a value for γ of 15.4mJ/mole \cdot K². The latter group¹⁶ reexamined the Tl-2223 data and concluded that they can be better fitted assuming 2-D fluctuations for $|1-T/T_c| > 5K$, with a crossover to critical fluctuations in the region nearer T_c . This analysis yields $\gamma \sim 8\text{mJ/mole} \cdot \text{K}^2$. These results are shown in Fig. 14b. The data of Bandyopadhyay et al.¹⁹ are shown in Fig. 15. These authors do not attempt to include a fluctuation term in their analysis, although the curvature in the data above T_c (see inset in Fig. 15) probably indicates that mean-field analysis of the type they carry out should be modified. The authors report a value of 50.9mJ/mole \cdot K² for $\Delta C(T_c)/T_c$, a result that gives $\gamma \sim 36\text{mJ/mole} \cdot \text{K}^2$ assuming the BCS weak-coupling relationship, $\Delta C(T_c)/T_c = 1.43\gamma$. The considerable difference between their value for γ and that calculated by either of the other two groups^{12,16} reflects, in part, their failure to include a fluctuation term. However, it also appears that the data of Bandyopadhyay et al.¹⁹ show a surprisingly-pronounced anomaly. In fact, an "entropy-conserving" construction to estimate $\Delta C(T_c)/T_c$ from their data gives a discontinuity of almost 85mJ/mole \cdot K², a value comparable to that characteristic of a fully-superconducting YBCO sample. Panova et al.¹⁴ have made electrical-resistance, thermal-emf, magnetic-susceptibility and specific-heat measurements on two samples of Tl-2223. They measured C in magnetic fields to 16T and estimated that for $H=0$ the samples had a 40-50% Meissner fraction. They also found the samples to have $\Delta C(T_c)/T_c \sim 30\text{mJ/mole} \cdot \text{K}^2$. From the BCS weak-coupling result, $\gamma = \Delta C(T_c)/1.43T_c$, they obtain $\gamma = 21\text{mJ/mole} \cdot \text{K}^2$, a value consistent with that which they calculate from their high-temperature magnetic-susceptibility data.

Braun et al.¹⁶ point out that evidence for fluctuation effects in the Tl-O superconductors can also be found in their own thermal expansion data and in the values for $\Delta C = C(0) - C(H)$ calculated from reversible magnetization measurements²⁰. The authors¹⁶ note that their measured specific-heat anomalies have the same triangular shape as that obtained from the magnetization data²⁰. However, the measured values are considerably larger than $C(0) - C(5T)$, thereby indicating that fields considerably larger than 5T would be necessary to suppress completely the specific-heat anomaly near T_c . This conclusion is consistent with that of Fisher et al.¹³. Figure 12 is a graph of $C(0) - C(5T)$ for Tl-2223 as calculated from the reversible magnetization data²⁰. The dotted curve in the figure shows the $C(0) - C(7T)$ data of Fisher et al.¹³.

The general class of Tl compounds we have discussed thus far can be regarded as the $m=2$ subset of the series $\text{Tl}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2(n+1)+m}$. In the $m=2$ case the CuO_2 planes responsible for superconductivity are separated by two insulating TlO sheets and T_c

increases with $n=1, 2$ and 3 . The $m=1$ series of compounds has a single TlO layer separating the CuO_2 planes and, for a given n , has a T_c 10-15K lower than that for the corresponding $m=2$ compound. Kim et al.²⁷ have suggested that the $m=1$ series should have a higher critical current, J_c , than the $m=2$ series because Josephson tunnelling between CuO_2 layers is greater through a single TlO sheet than through the double TlO layer of the $m=2$ series. This suggestion has been confirmed by Liu et al.²⁸ who have measured both J_c and C for the lead-stabilized Tl-1223 compound, $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$. They find that J_c is greater than for Tl-2223 and is, in fact, comparable to the J_c of YBCO. Their measurements of C show a broad anomaly that begins at $\sim 115\text{K}$ and has $\Delta C(T_c)/T_c \approx 29\text{mJ/mole} \cdot \text{K}^2$. According to the authors, the high temperature "tail" of the anomaly is consistent with a contribution to C from 3-D Gaussian fluctuations. They note that this fluctuation term is more like that present in YBCO⁷ than the 2-D fluctuation observed in Tl-2223¹⁶. They predict that this Tl-1223 HTSC, with a J_c comparable to that of YBCO and a T_c that is $\sim 25\text{K}$ higher, may prove to have considerable technological promise.

One other set of specific-heat measurements on an HTSC thallium-containing compound deserves mention. The system $(\text{Y}_{1-x}\text{Ca}_x)\text{Sr}_2\text{Tl}_{0.5}\text{Pb}_{0.5}\text{O}_7$ shows behavior²⁷ reminiscent of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. Here $\text{Tl}_{0.5}\text{Pb}_{0.5}$ replaces the Cu atom in the CuO chains of YBCO while Sr replaces Ba. The substitution of Ca^{2+} for some of the Y^{3+} permits a variation of hole concentration in the material, and allows the experimenter to achieve a wide variation in both T_c and $\Delta C(T_c)/T_c$. The results are shown in Fig. 16. The authors use a differential calorimeter that permits the electronic contribution to the total specific heat to be determined with high precision. As is evident from the figure, the system has an optimum composition near $x=0.8$, with both T_c and $\Delta C_{el}(T_c)/T_c$ decreasing as x varies on either side of the optimal value.

Table II is a compilation of results on several of the Tl-2212 and Tl-2223 Tl-O superconductors. Included in the table are estimates of f_s , the volume fraction of superconductivity, predicted on the basis of Meissner effect and/or ac susceptibility measurements. Because of the uncertainties that arise in attempting to interpret these magnetic measurements, the listed values of f_s should be regarded as no more than a rough guide to the actual volume fractions. Also included in the table are values for: a) χ_0 , the temperature-independent paramagnetic susceptibility; b) the value of γ_χ inferred from χ_0 by setting it equal to the Pauli susceptibility--assuming that the core diamagnetic contribution to χ_0 is essentially offset by the Van Vleck paramagnetic contribution and that the Landau-Peierls diamagnetic term is small enough to be ignored; c) γ_{bs} , the value of γ calculated from $N_{bs}(E_F)$ without taking into account enhancement effects, i.e., $\gamma_{bs} = \gamma / (1 + \lambda)$ (see Eq. 5).

VI. Further Discussion and Summary

A. Lattice Specific Heat

Kulkarni et al.³⁰ have calculated the phonon spectrum and lattice specific heat of the Tl-O HTSC's. They predict that $\theta_{300} \sim 600\text{K}$, in agreement with the experimental results reported in Ref. 14 on Tl-2223. However, their predictions regarding the range over which $C_l \propto T^3$ and the values of θ_0 are not in accord with the experimental results (see Table I and Fig. 5).

B. Low Temperature Upturn C/T and $\gamma^*(0)$

Within the experimental uncertainty of $\sim 1\text{mJ/mole} \cdot \text{K}^2$, $\gamma^*(0)$ for YBCO can be represented as the sum of a contribution from impurity phase, particularly BaCuO_2 , and a contribution from non-superconducting regions in the YBCO associated with Cu^{2+} moments present in a concentration n_2 ; but with the same uncertainty, $\gamma^*(0) \neq 0$ for all samples. On the other hand, $\gamma^*(0) = 0$ for most BSCCO samples and for some TBCCO samples. The fact that $\gamma^*(0) = 0$ for BSCCO samples, including some for which n_2 is large, suggests that the relation between Cu^{2+} moments and $\gamma^*(0)$ is different from that for YBCO. If there are localized Cu^{2+} moments in the CuO_2 planes of BSCCO and TBCCO, they may produce non-superconducting material that is not metallic, i.e., which does not have a γ associated with it.

C. Fluctuations

The data on Tl-2212^{16,21,23}, Tl-2223^{16,19,23} and on (TlPb)-1223²⁸ provide evidence for a fluctuation contribution to C near T_c . In Ref. 21 it is assumed that this contribution comes from 3-D Gaussian fluctuations, whereas in Refs. 16, 23 and 28 the contribution for $|T - T_c| > 5\text{K}$ is attributed to 2-D fluctuations. The authors in Ref. 16 argue that there is a crossover from 2-D Gaussian fluctuations to 3-D critical fluctuations as $|T - T_c|$ approaches zero. Sokolov³¹ has examined the results from Refs. 16 and 23 and argues that they span the cross-over region but do not adequately penetrate the temperature region close to T_c to be considered as evidence for true 3-D critical behavior.

Because strong-coupling effects can produce upward curvature in the C_{es}/T vs T data below T_c (see Fig.2), the evidence for fluctuations for $T > T_c$ is somewhat clearer than that for $T < T_c$. This is especially true in the data on (TlPb)-1223²⁸. However, even above T_c the apparent evidence for a fluctuation contribution to C will depend upon how the estimate is made for the background specific heat, and also upon whether or not broadening of the anomaly due to sample inhomogeneities is included in the data analysis. Only in Ref. 21 is the possibility of such broadening included in the analysis.

D. Strong Coupling

In most of the results reported here the authors assume BCS weak coupling to be applicable, that is, they assume that (in the absence of a fluctuation term) $\Delta C(T_c)/T_c = 1.43\gamma$. This assumption proves to be consistent with the fitting procedure used in Ref. 21, but, as is noted in Refs 16 and 21, the data do not point unambiguously to such a conclusion. The best-defined specific-heat anomaly for any of the TI superconductors is that reported by Bandyopandhyay¹⁹. In their analysis the authors do not include the effects of fluctuations, strong-coupling or broadening due to inhomogeneities. Nevertheless, the data above T_c indicate the possible presence of a fluctuation contribution. However, data below T_c are like many of the results on YBCO in that there is little evidence of curvature just below T_c , but give a very large value of the ratio $T_c(dC/dT)/\Delta C(T_c)$. A large value for this ratio is characteristic of strong- rather than weak-coupling (see Fig. 1). The results in Ref. 19 give hope that as sample quality improves, specific-heat data on the TI-O compounds may provide clearer evidence of strong coupling (or its absence) and of 2-D versus 3-D character.

E. The Electron Density of States Near the Fermi Energy and γ .

Table II lists values of $N_{bs}(E_F)$ obtained from band-structure calculations and the values of the γ_{bs} , the value of γ calculated from $N_{bs}(E_F)$ without any allowance for enhancement effects, i.e., $\gamma_{bs} = \gamma/(1+\lambda)$; $\gamma_{bs}(\text{mJ/mole} \cdot \text{K}^2) = 0.424N_{bs}(E_F)$ (states/ev/unit cell). Also listed are the values of χ_0 , the temperature-independent part of the magnetic susceptibility, and the associated gamma, γ_χ ; $\gamma_\chi(\text{mJ/mole} \cdot \text{K}^2) = 7.3 \times 10^4 \chi_0(\text{emu/mole})$. Values for $\gamma_{mf} = \Delta C(T_c)/1.43T_c$, the value for γ to be expected for a weak-coupled BCS superconductor, and γ_{fl} , the mean-field weak-coupled BCS value of γ when fluctuations were used in the data analysis, are also tabulated. In Table II the relatively small values of γ_{fl} obtained from Refs. 16 and 23 reflect the fact that the authors subtract a sizeable fluctuation contribution from the measured $\Delta C(T_c)$ before using the BCS relationship to calculate γ_{fl} . Except for these cases, γ_{mf} and γ_χ are greater than γ_{bs} , a result that might be taken to indicate substantial values of λ , and that strong coupling is present in the TI-O superconductors. However, such a conclusion is clearly inconsistent with the weak-coupling assumption that $\Delta C(T_c)/\gamma_{mf}T_c = 1.43$ (however, see Ref. 32). The fact that the most of the values for γ_{mf} and γ_χ for a given compound are comparable may be significant, but one should be wary of leaping too readily to this conclusion. The values of $N(E_F)$, and therefore of γ_χ , obtained from the susceptibility data, will depend upon whether or not corrections for the core diamagnetism and Van Vleck paramagnetism are included, and also upon the assumptions made concerning the possibility of a Stoner enhancement of χ_0 .

The variation in the values of γ listed in Table II makes it evident that as yet little can be said with confidence about the size of γ in the TI-O HTSC's, or about the possible renormalization of γ by phonon or other enhancement effects. In what is generally a confusing set of results there does exist one bit of clarity: χ_0 , expressed in units of emu/(g-at Cu), is essentially the same for the TI-O HTSC's as for YBCO. However, the calculated $N_{bs}(E_F)$ (in states/ev/Cu atom) for these materials³³⁻³⁵ is substantially lower than

that calculated for YBCO³⁶. This situation for $N_{bs}(E_F)$ mirrors that for the observed $\Delta C(T_c)/T_c$ values, thus indicating some measure of agreement between the specific-heat results and the band-structure calculations. The data reported in Ref. 19 are an exception to this generalization. Should subsequent measurements on Tl-2223 confirm these results, further band-structure calculations will be in order.

In summary, it is evident that better specific-heat measurements on better samples, especially single crystals, should help to remove some of the ambiguities in the data discussed in this review. It is to be hoped that such measurements, in combination with other work on the Tl-O superconductors will clarify the role played by fluctuations, by possible strong-coupling effects, and by dimensionality in determining the characteristics of the only materials yet found to be superconducting at temperatures greater than 115K.

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TABLE I CAPTION

Table I. Parameters characterizing the low-temperature properties of TBCCO. Blanks in the table signify that either those parameters were not measured or were not available. n and n_2 are the ratio of the Cu^{2+} localized magnetic moments to the total Cu content of the starting composition except for sample 1 where the ratio is with respect to the Cu content of Tl-2223. n was derived from Curie-Weiss Law fits to magnetic-susceptibility data above T_c , and n_2 was derived from an analysis of the low-temperature specific-heat measurements (see text). $\gamma^*(0)$ has the units of $\text{mJ}/\text{mole} \cdot \text{K}^2$, where the molecular weight and the number of atoms was calculated from the stoichiometry of the starting composition for samples 4 and 7, and for the superconducting phase stoichiometry for the others. Values of θ_0 and $\gamma^*(0)$ in parentheses were scaled from a graph of C/T vs T^2 for sample 3. Since there may be flux pinning, and because of the possible presence of non-superconducting phases, the Meissner fraction ($-4\pi\chi_v$) is a lower limit on f_s .

TABLE I

#	Starting Composition	Superconducting Phase	T_c (K)	$-4\pi\chi_v$	n	n_2	$\gamma^*(0)$	θ_0	Ref.
1	Tl-2112 ^a	Tl-2223	105	—	—	0.0004	<1	270	10
2	Tl-2112 ^a	Tl-2223	—	—	—	—	5	280	10
3	— ^b	Tl-2223	114	—	—	—	63	(290)	11
4	Tl-1133 ^c	Tl-2223	122	0.24	0.03	—	—	290	12
5	Tl-3223 ^d	Tl-2223	120	0.50	—	0.01	28	270	14
6	Tl-3223 ^d	Tl-2223	112	0.40	—	0.01	~ 0	260	14
7	Tl-1112 ^e	Tl-2223 + Tl-2212	113	0.30	—	0.025	16	268	13
8	Tl-2212 ^f	Tl-2212	99	0.51	0.05	—	<6.8	254	12
9	Tl-2201 ^f	Tl-2201	<12	0.08	0.03	—	0	238	12

TABLE I FOOTNOTES

- a) The starting composition of the melt was Tl-2112. For sample 1, a single crystal of Tl-2223 was separated from the solidified melt, and a polycrystalline mass of Tl-2223, sample 2, was broken from it. The authors state that a small amount of Tl-2212 was probably present in sample 2.
- b) Preparation details were not stated and no indication was given for the presence or absence of other phases.
- c) Since the starting composition was Tl-1113, the Tl-2223 sample was multiphase. The other phases could not be identified with certainty but were consistent with CuO, BaCuO₂, CaO and Tl₂O₃. The phases Tl-1212, Tl-1223, Tl-2201 and Tl-2212 were not detected. All analysis was by x-ray.
- d) Since the starting composition was Tl-3223, the Tl-2223 samples were multiphase. The Tl-2223 phase concentration was given as 90% from x-ray analysis. The authors state that sample 6 was "structurally more perfect" than sample 5, and they speculate that the structural imperfection may be related to a finite $\gamma^*(0)$. Specific-heat measurements were made in the magnetic field range $0 \leq H \leq 16T$.
- e) The starting composition of Tl-1112 resulted in a multiphase sample of approximately equal amounts of Tl-2223 and Tl-2212. CuO was also detected. The analysis was by x-ray.
- f) This sample was stated to be single phase on the basis of an x-ray analysis.

TABLE II CAPTION

Table II. γ and other parameters characteristic of TBCCO near and above T_c . Units are: $\Delta C/T$ and γ in $\text{mJ}/\text{mole} \cdot \text{K}^2$; χ_o in emu/mole ; $N_{bs}(E_F)$ in $\text{states}/\text{ev}/\text{unit cell}$. A mole is the gram-formula-weight of the compound listed. $\Delta C(T_c)/T_c$ is the mean-field height of the anomaly; $\gamma_{mf} = \Delta C(T_c)/1.43T_c$; γ_{fl} is the mean-field weak-coupled BCS value of γ when fluctuation components are used in the data analysis; γ_χ is calculated from χ_o , the temperature-independent part of the magnetic susceptibility above T_c , by assuming that it is equal to the Pauli susceptibility; γ_{bs} is calculated from $N_{bs}(E_F)$, the band-structure density of states at the Fermi energy; f_s is the fraction of superconducting material present in the sample (see Sec. V).

TABLE II

Compound	$T_c(K)$	$\Delta C(T_c)/T_c$	γ_{mf}	γ_n	f_s	$\chi_o \times 10^4$	γ_x	$N_{bs}(E_F)$	γ_{bs}	Ref.
Tl-2201	12<	—	—	—	0.08	0.425	3.1			12
				—				1.24	2.92	33
Tl-2212	104	25 ^a	17 ^b	21	—	—	—			21,22
	100	35±10 ^a	24±8	—	0.51	2.9	21			12
	109	32 ^c	22 ^b	3.7, 12	0.20	—	—			16,23
								2.82	6.7	34
Tl-2223	117	34 ^c	24 ^b	8, 15.4	0.25	—	—			16,23
	122	20±10 ^a	14±7	—	0.24	4.0	29			12
	115	50.9 ^a	36	—	0.90	—	—			19
	120	35 ^a	24	—	0.50	3.0	22			14
	112	27 ^a	19	—	0.40	3.0	22			14
	—	—	—	—	—	2.19	16			35
								3.8	9.0	34
(TlPb)-1223	115	29 ^a	20	—	—	—	—			28
YBCO ^d	91	66 ^e	46	—	0.86 ^f	2.8	20			3
								6.78 ^g	16	36

TABLE II FOOTNOTES

- a) $\Delta C(T_c)/T_c$ as given by the authors (see Refs. for details).
- b) These authors also fit their data near T_c using a fluctuation contribution plus a mean-field BCS contribution. γ_{fl} is calculated from this mean-field contribution and is different from $\gamma_{\text{mf}} = \Delta C(T_c)/1.43T_c$. (See Sec. V and Refs. for details.)
- c) $\Delta C(T_c)/T_c$ was read from Fig. 14.
- d) Values of parameters listed for YBCO are given for the purpose of comparison with the TBCCO parameters.
- e) $\Delta C(T_c)/T_c$ is an average of the values obtained from the various methods used on the data shown in Fig. 6 (see Sec. III C).
- f) f_s for YBCO was obtained using the correlations described in Sec. III D.
- g) This value of $N_{\text{bs}}(E_F)$ is a corrected value of that listed in Ref. 36 (A. J. Freeman, private communication).

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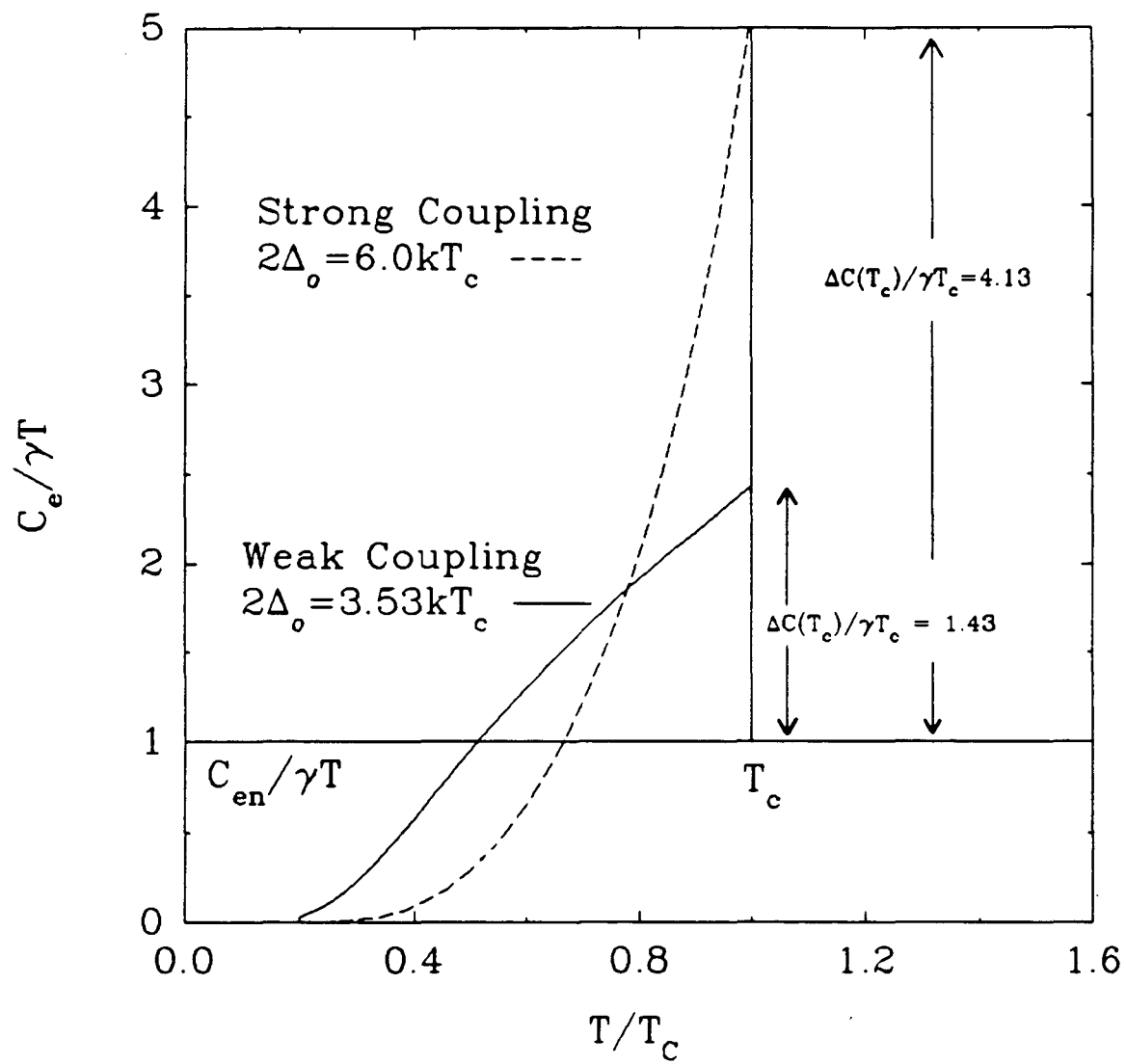
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FIGURE CAPTIONS

- Fig. 1. The electron contribution to the normal and superconducting-state specific heats for conventional superconductors. See text for details.
- Fig. 2. The total specific heat of a typical YBCO sample. The insets are expanded representations of the data at low temperatures and in the vicinity of T_c .
- Fig. 3. Lattice specific heats of YBCO, LCO, TBCCO AND BSCCO. The dashed curve represents the Debye specific heat function for $\theta_0=450K$, the value for a particular YBCO sample.
- Fig. 4. Analysis of the low-temperature specific heat of a YBCO sample into four contributions, for $H=0$ and $7T$. The points represent experimental data from which three of the contributions have been subtracted to illustrate the accuracy of the determination of the fourth contribution--that associated with Cu^{2+} magnetic moments.
- Fig. 5. Specific heat of polycrystalline YBCO near T_c . $\Delta C=C(obs)-C(fit)$ where $C(fit)$ is the sum of a term proportional to temperature and a harmonic lattice contribution. The curves represent the sum of BCS and 3-D Gaussian fluctuation contributions.
- Fig. 6. Specific-heat data for YBCO near T_c , with several constructions used to determine $\Delta C(T_c)$ as described in the text.
- Fig. 7. C/T vs T^2 for a polycrystalline sample of a mixture of Tl-2212+Tl-2223 phases for $T \leq 10K$ and $H=0$ and $7T$. The straight line represents the T and T^3 terms of the least-squares fit to the zero-field data. (Fisher et al.¹³)
- Fig. 8. C/T vs T^2 for Tl-2223 single crystal and polycrystalline samples. The curve represents the best fit of the single crystal data in the range $3.5 \leq T \leq 11K$ --see text for details. The inset shows C/T^3 vs T for the single crystal with the same fit. (Urbach et al.¹⁰).
- Fig. 9. C/T vs T^2 for Tl-2201 and Tl-2212 polycrystalline samples for $T \leq 10K$. The inset shows the same data for the Tl-2212 sample for $T \leq 25K$. (Junod et al.¹²)
- Fig. 10. C/T vs T in the vicinity of T_c for polycrystalline samples of YBCO, Bi-2212, Bi-2223, Tl-2212 and Tl-2223. The data for the Bi-2223 and Y-123 are shifted by $0.005 J/g-at K^2$ upwards and downwards, respectively.

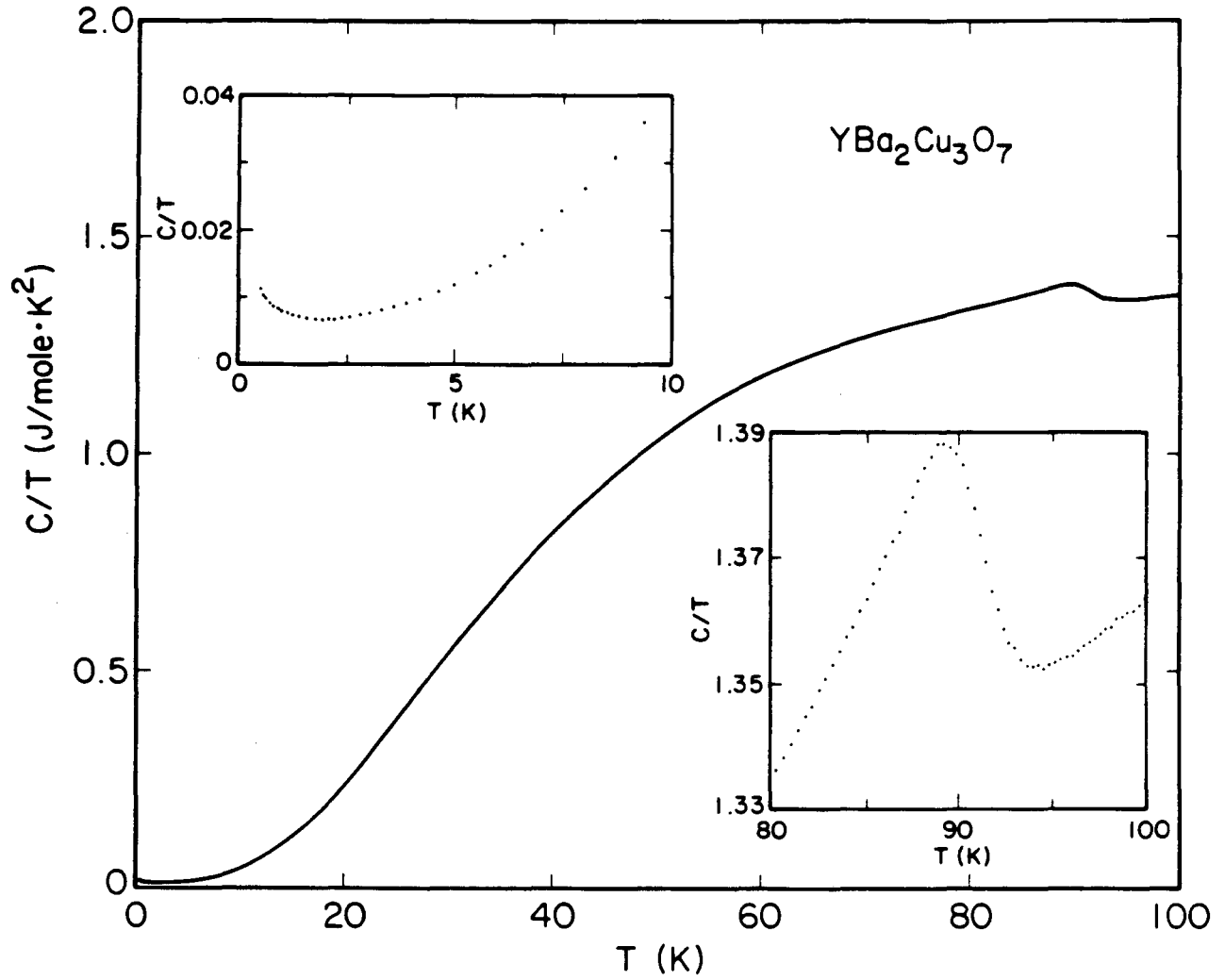
The higher T_c for the Bi-2212 sample resulted after it was heat treated in an argon atmosphere. (Wohleben et al.²³)

- Fig. 11. C/T vs T for a polycrystalline sample of a mixture of Tl-2212+Tl-2223 phases in the region of T_c for $H=0$ and $7T$. (Fisher et al.¹³)
- Fig. 12. Comparison of the effects of magnetic field on the specific heat derived from magnetization measurements for polycrystalline Tl-2223 (solid circles), and from direct measurements¹³ for a mixed phase polycrystalline sample of Tl-2212+Tl-2223 (dashed curve). (Gohng and Finnemore²⁰)
- Fig. 13. The electronic specific heat of Tl-2122 ($Tl=2.1$). The solid curve is a result of a least-squares fit--see text for details. (Atake et al.²¹)
- Fig. 14. a: Specific-heat anomaly for Tl-2212 after subtraction of a background polynomial. The curved line represents a fit made up of a mean-field BCS contribution and 2-D Gaussian fluctuations (the triangular ramp is the mean-field contribution). b: A similar analysis was made for Tl-2223, however, with a crossover to critical fluctuations in a region near to T_c . (E. Braun et al.¹⁶ and Wohleben et al.²³)
- Fig. 15. C vs T data for Tl-2223. The inset shows C/T vs T near T_c . (Bandyopadhyay et al.¹⁹)
- Fig. 16. $\Delta C/T$ for $(Y_{1-x}Ca_x)Sr_2Cu_2(Tl_{0.5}Pb_{0.5})O_7$ where ΔC , the value of C relative to that for a reference sample, was measured using a differential calorimeter. The labels show $100x$. (Loram et al.²⁶)



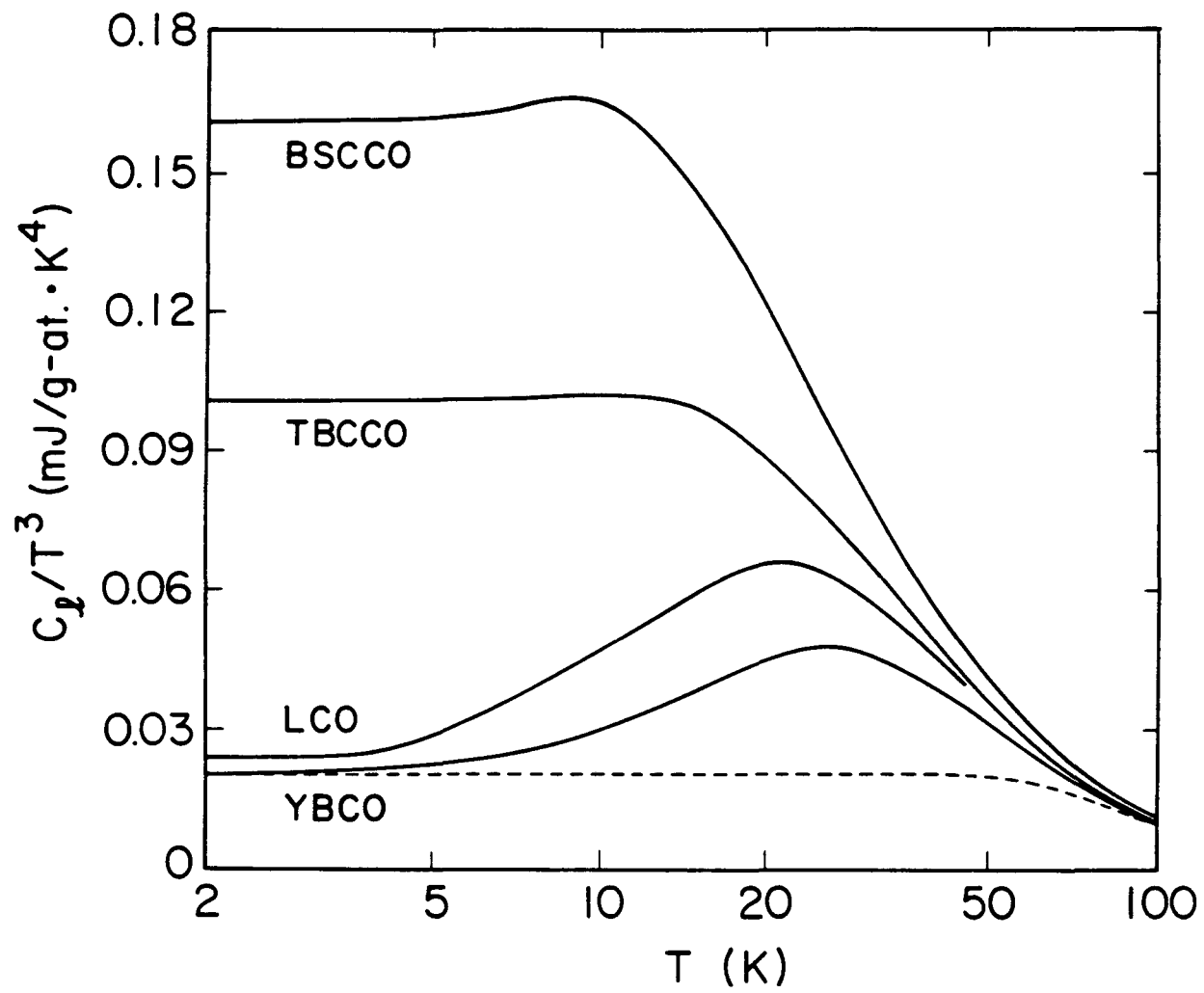
XBL 923-285

FIG. 1



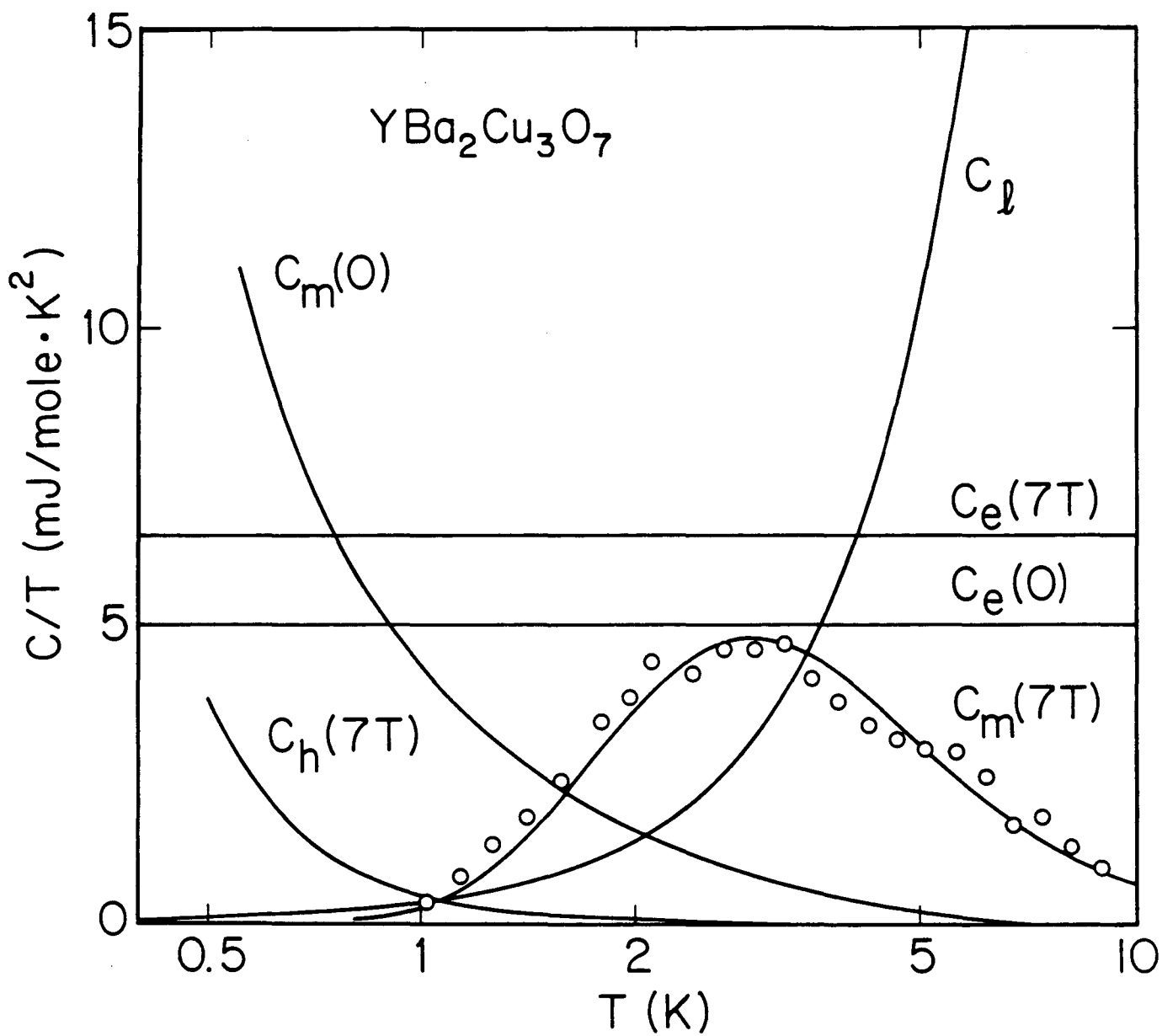
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FIG. 2



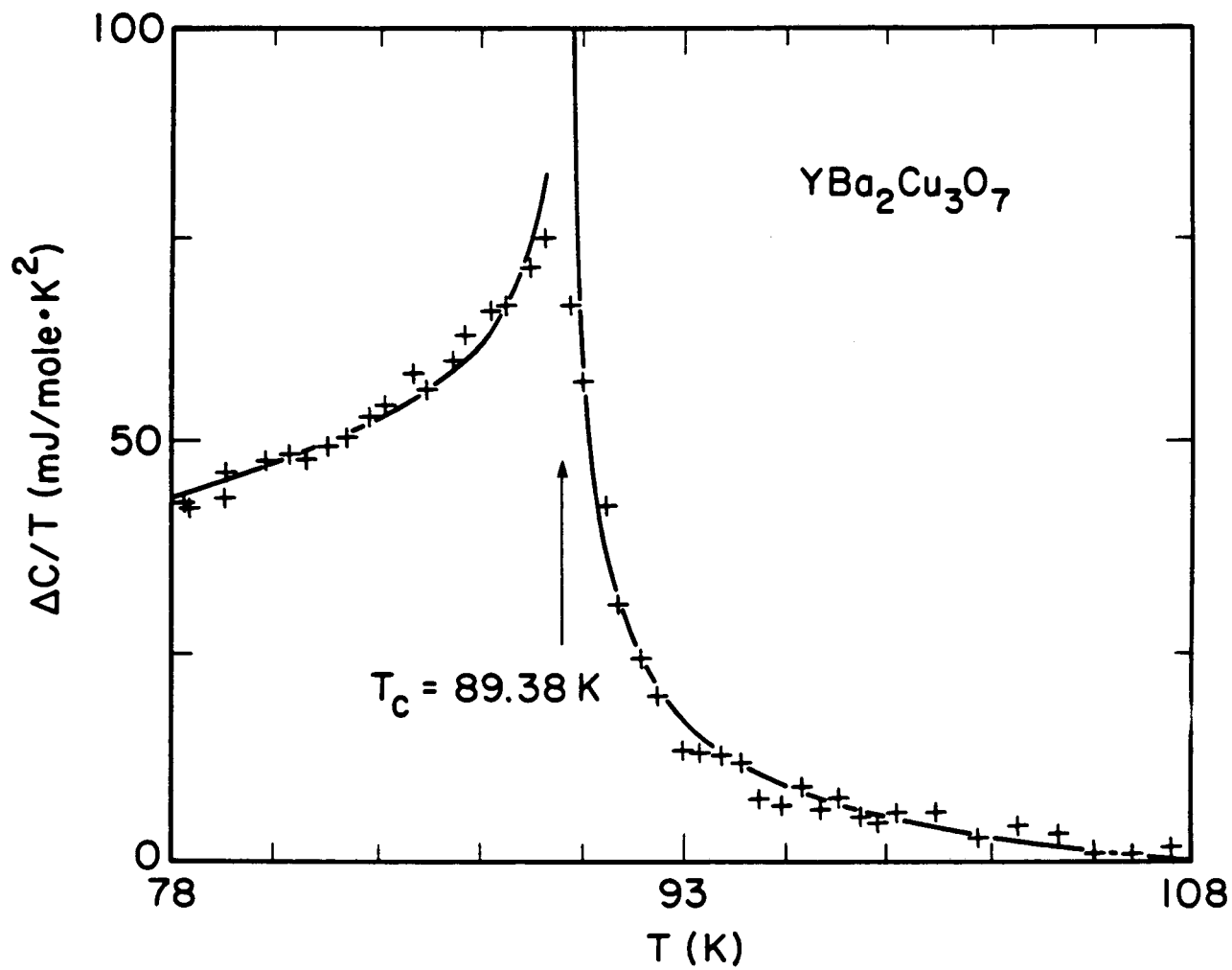
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FIG. 3



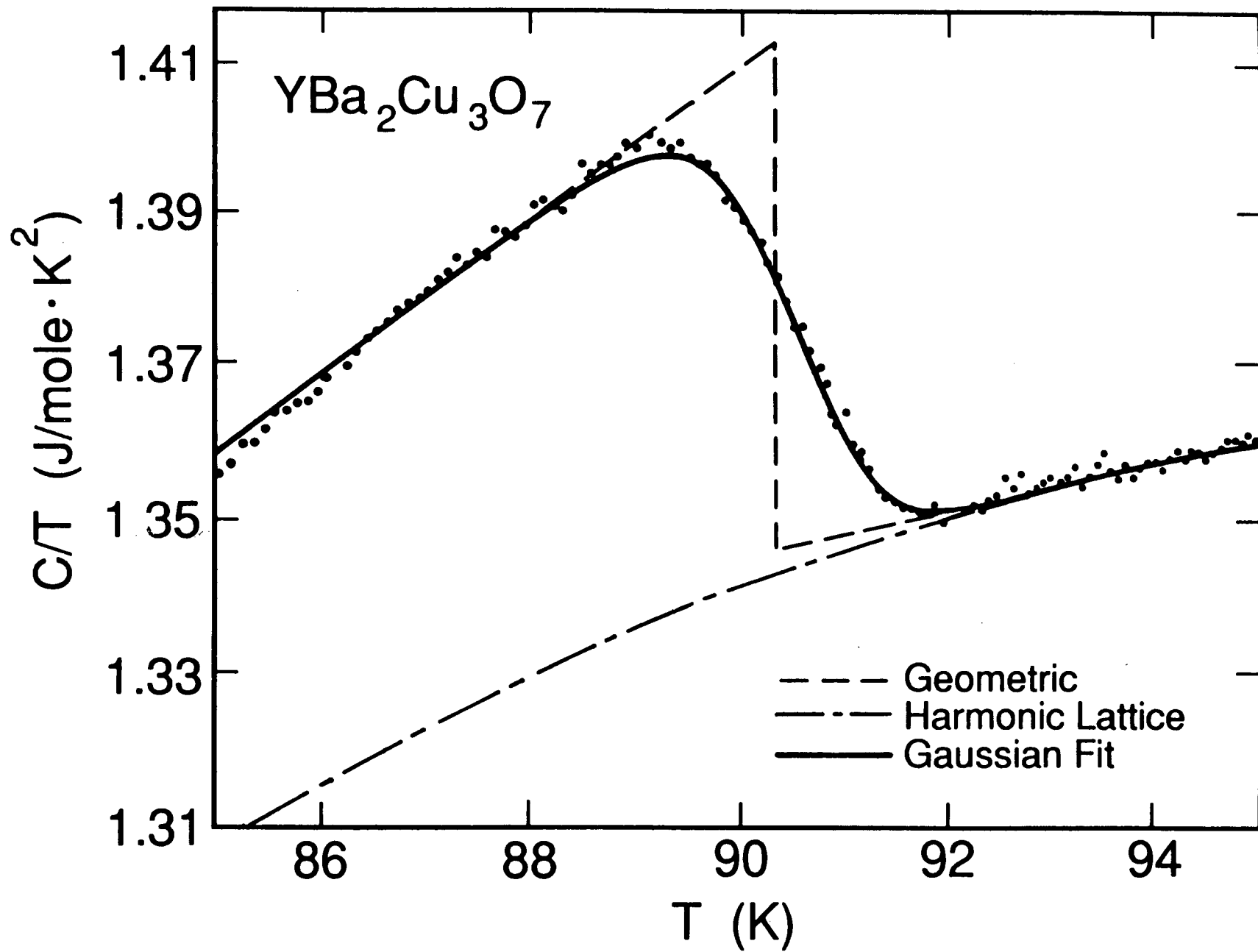
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FIG. 4



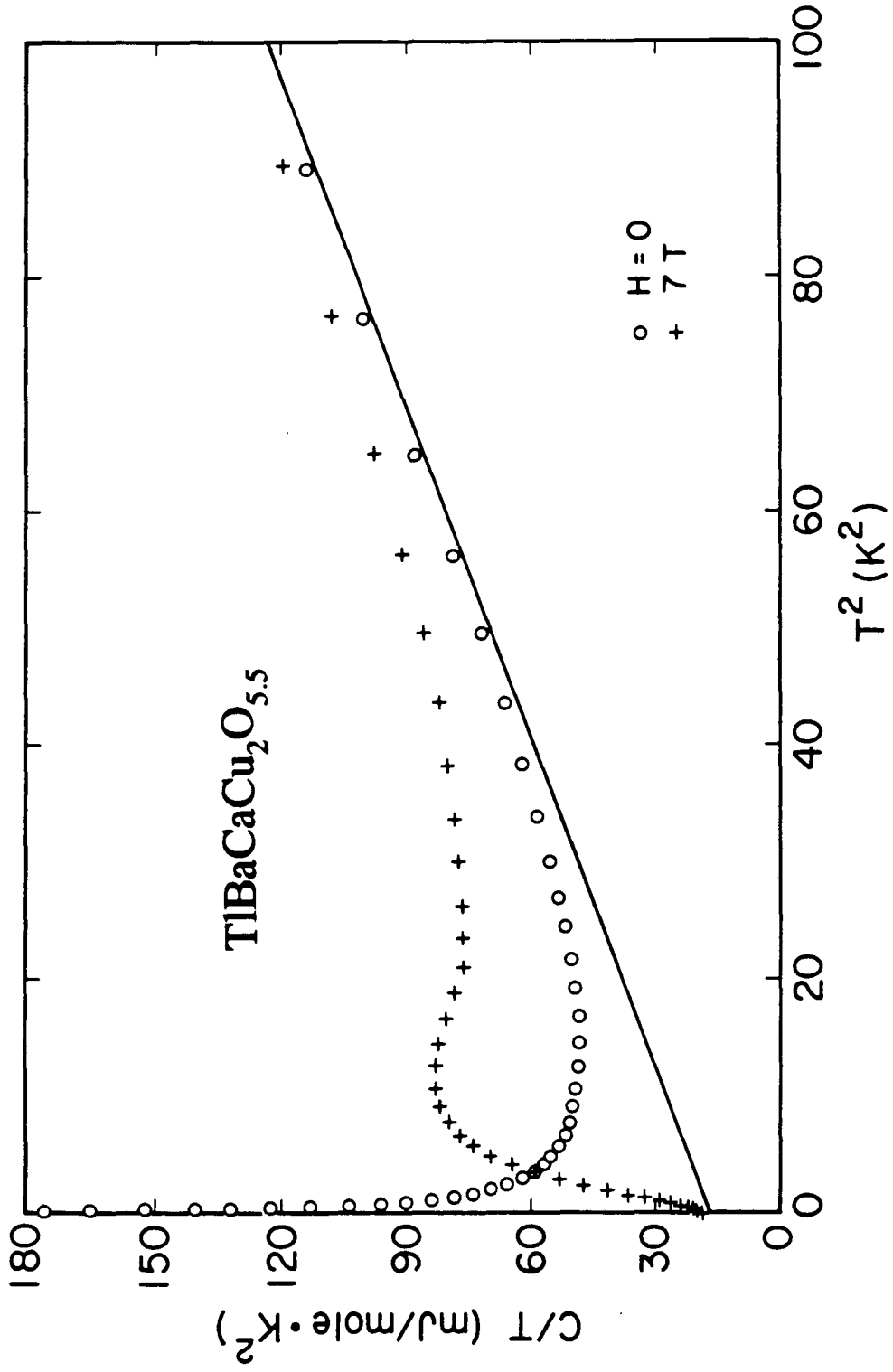
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FIG. 5



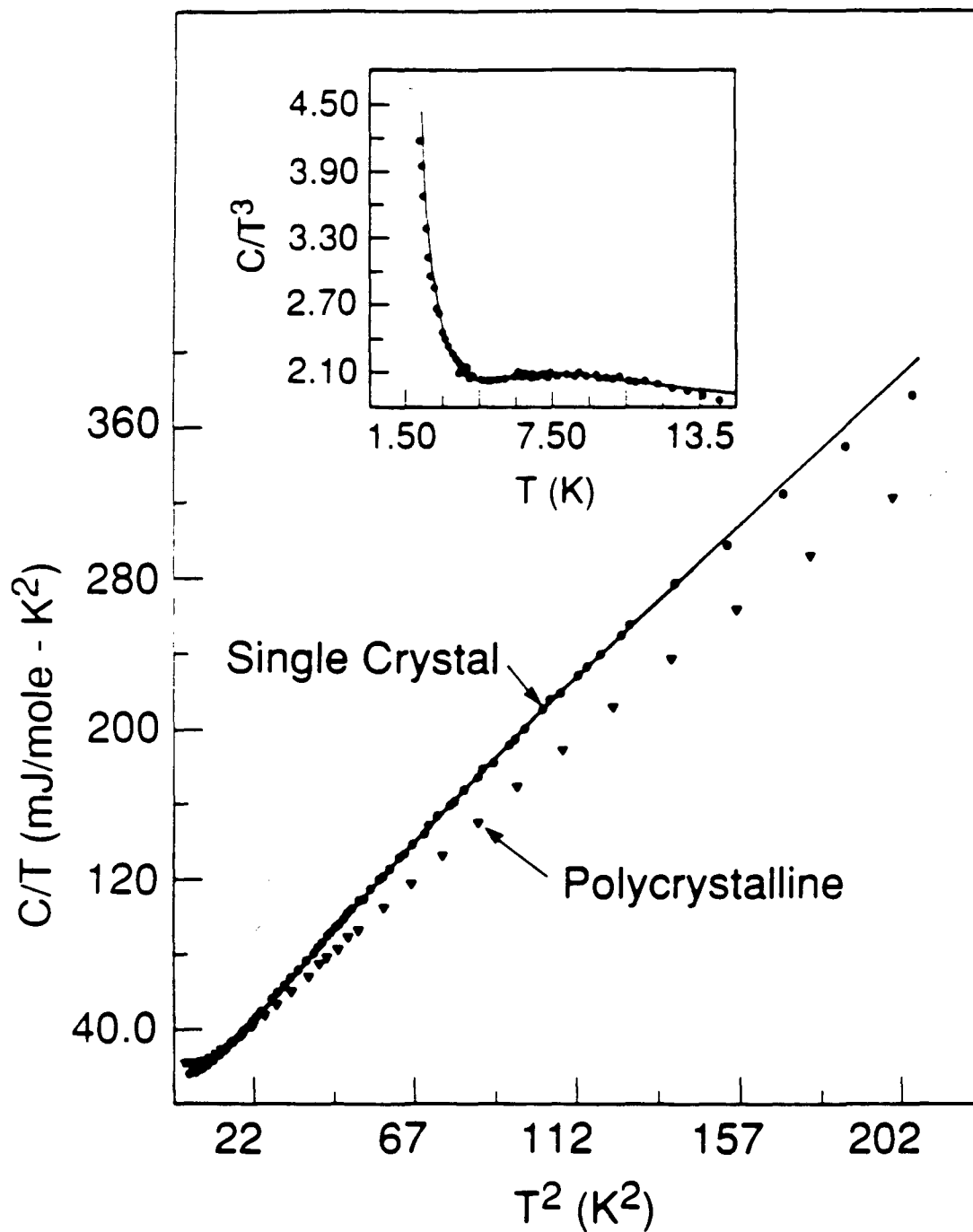
XBL 901-63

FIG. 6



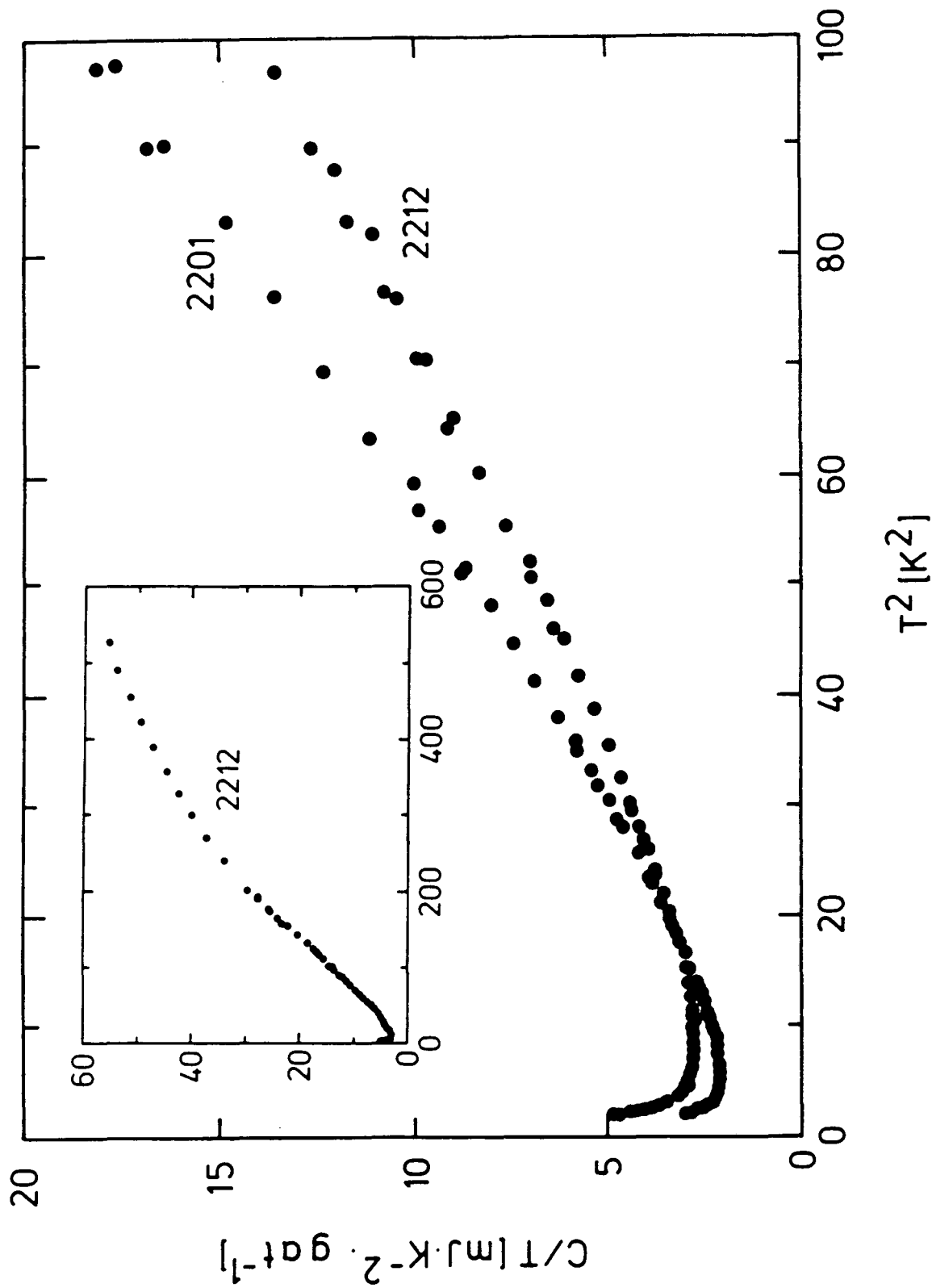
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FIG. 7



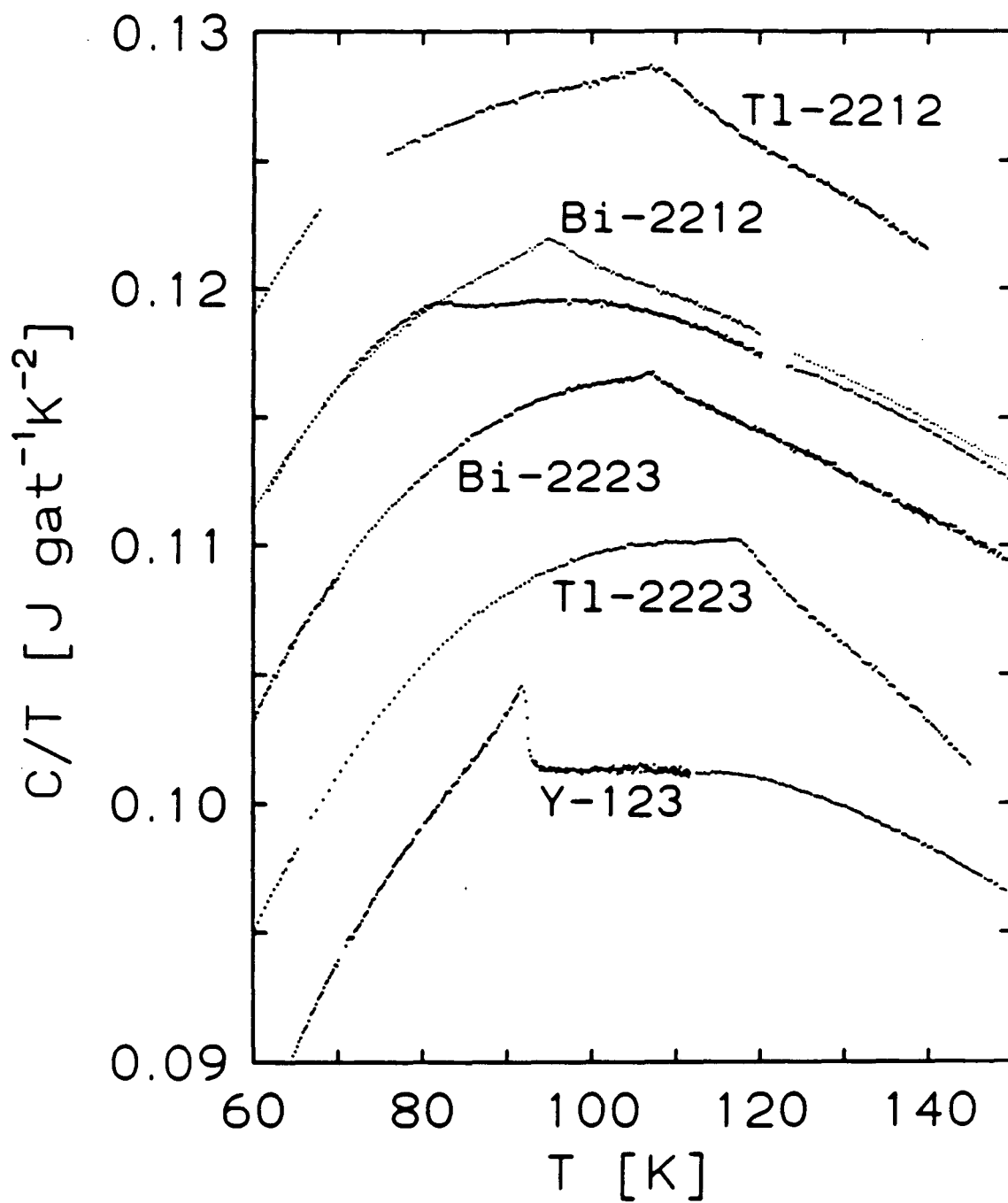
XBL 923-288

FIG. 8



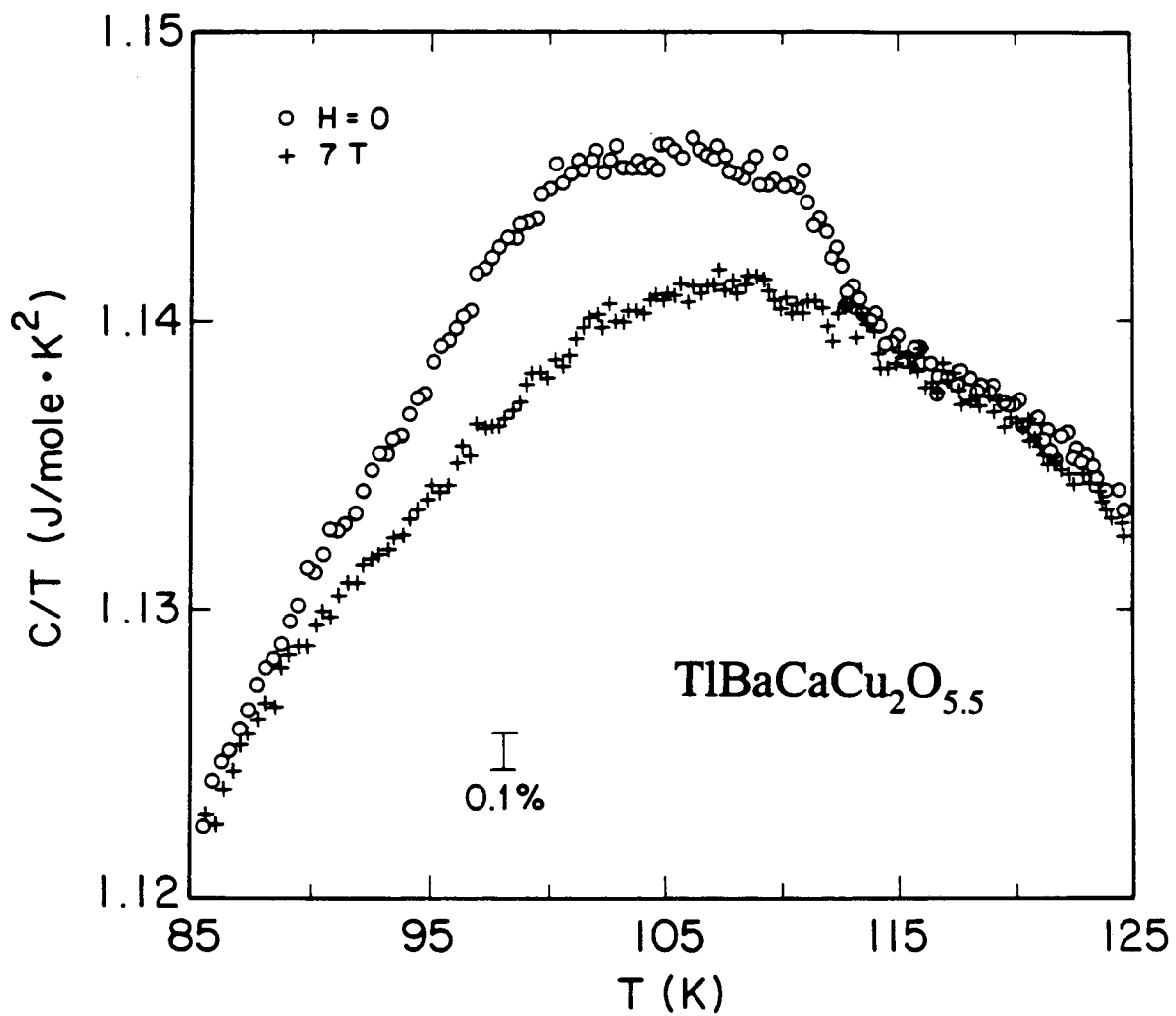
XBL 923-286

FIG. 9



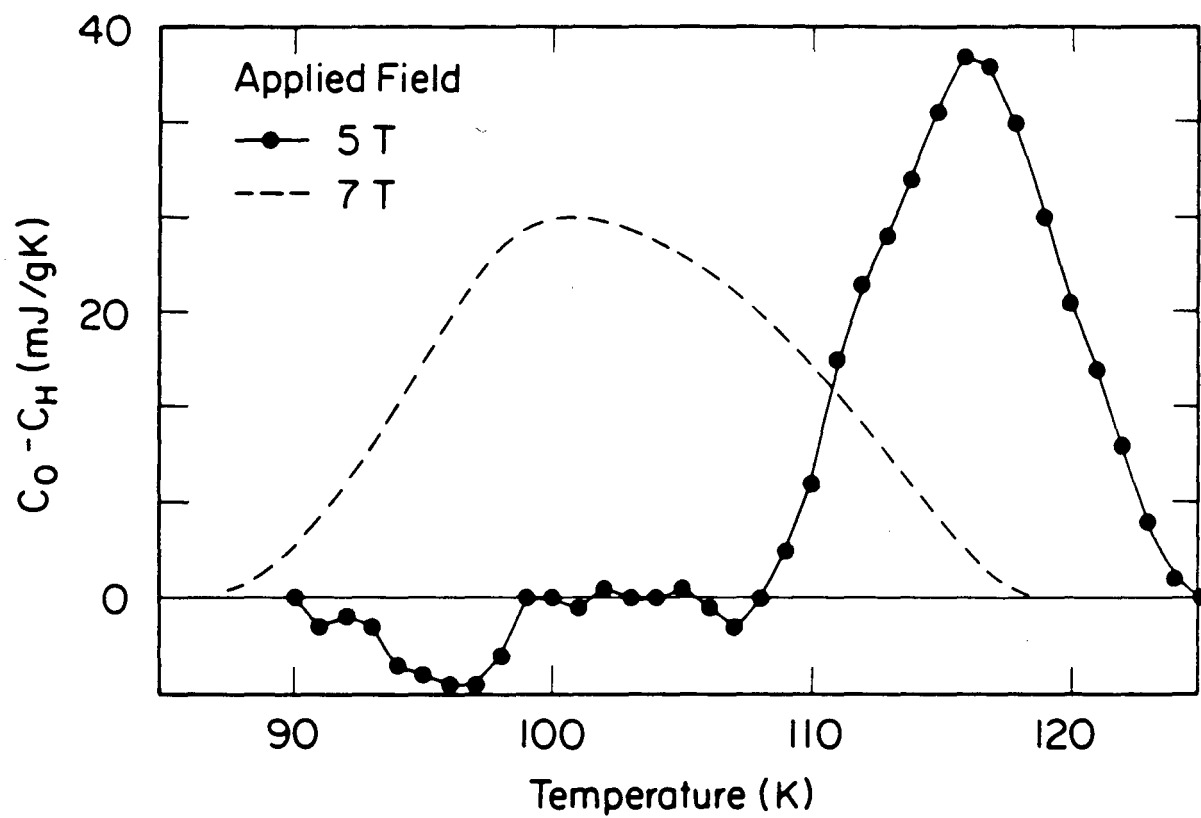
XBL 923-287

FIG. 10



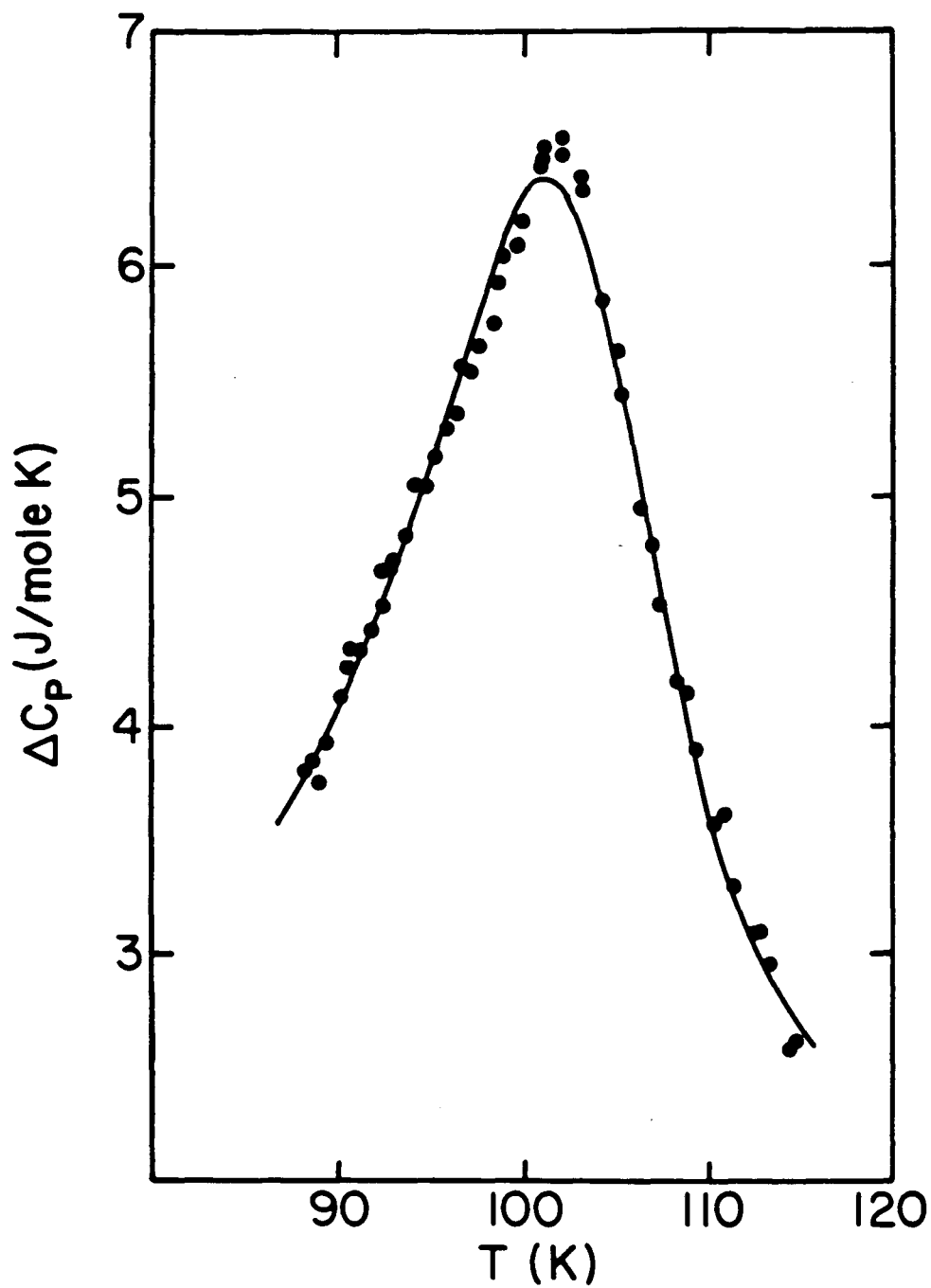
XBL 923-294

FIG. 11



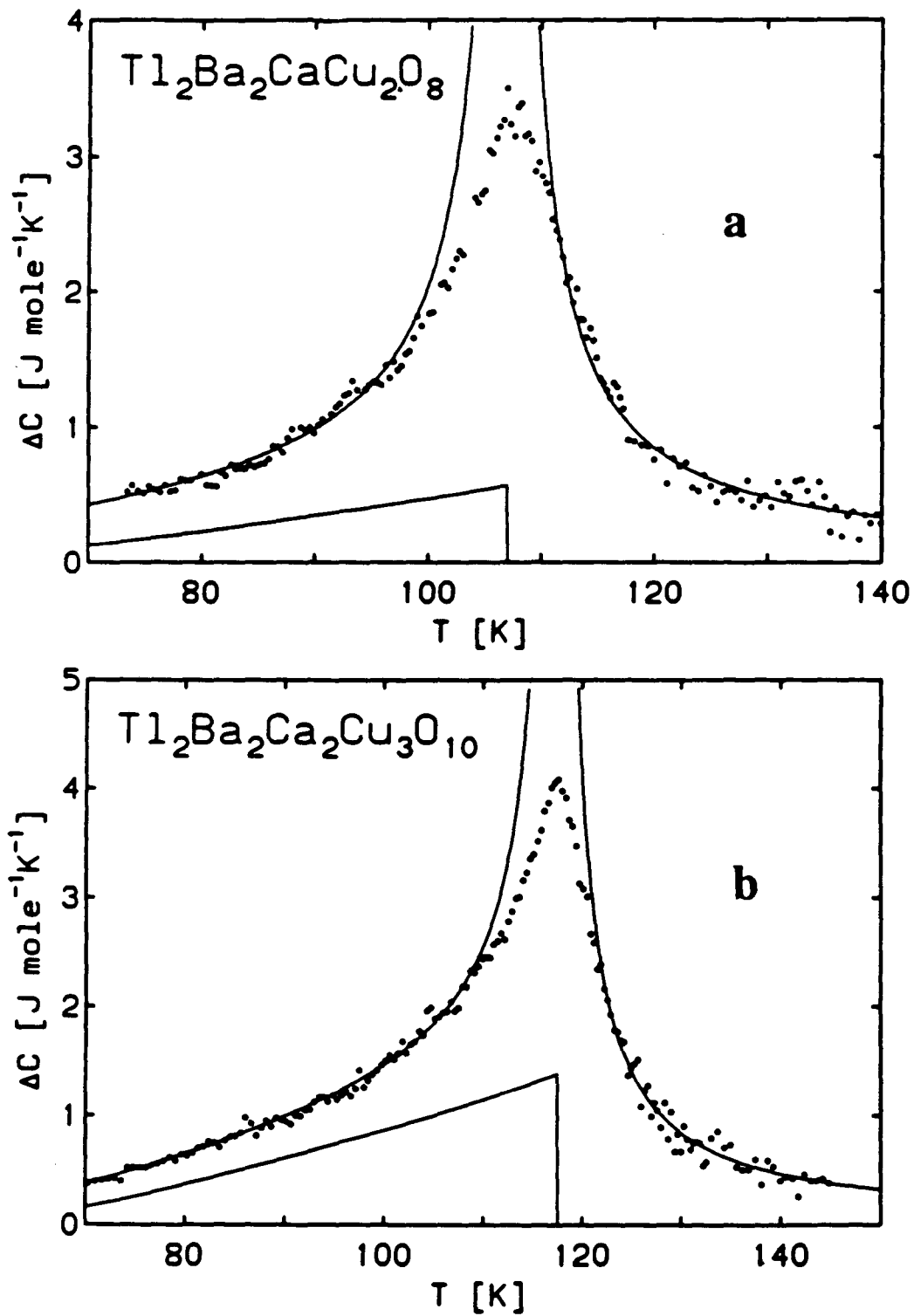
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FIG. 12



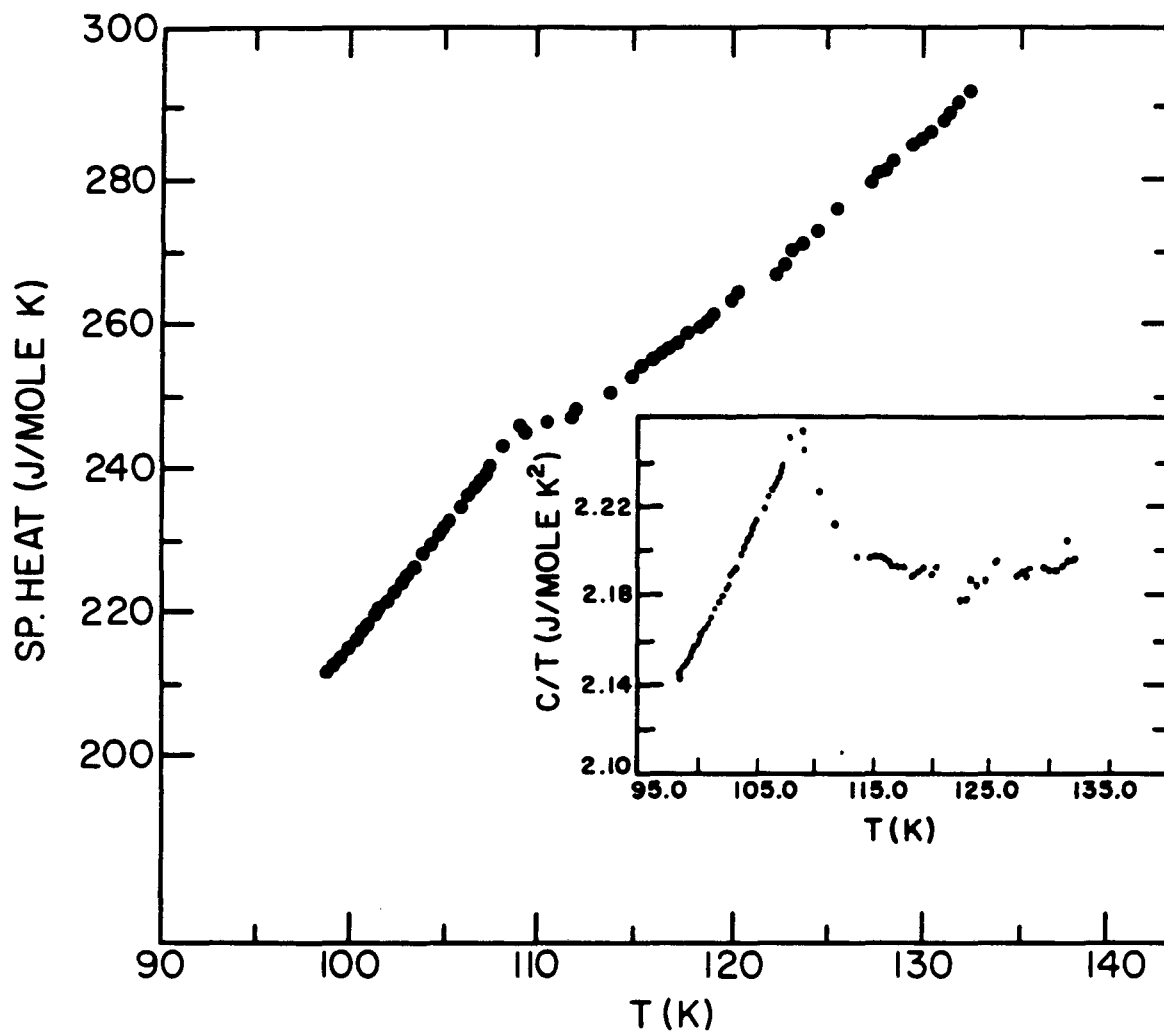
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FIG. 13



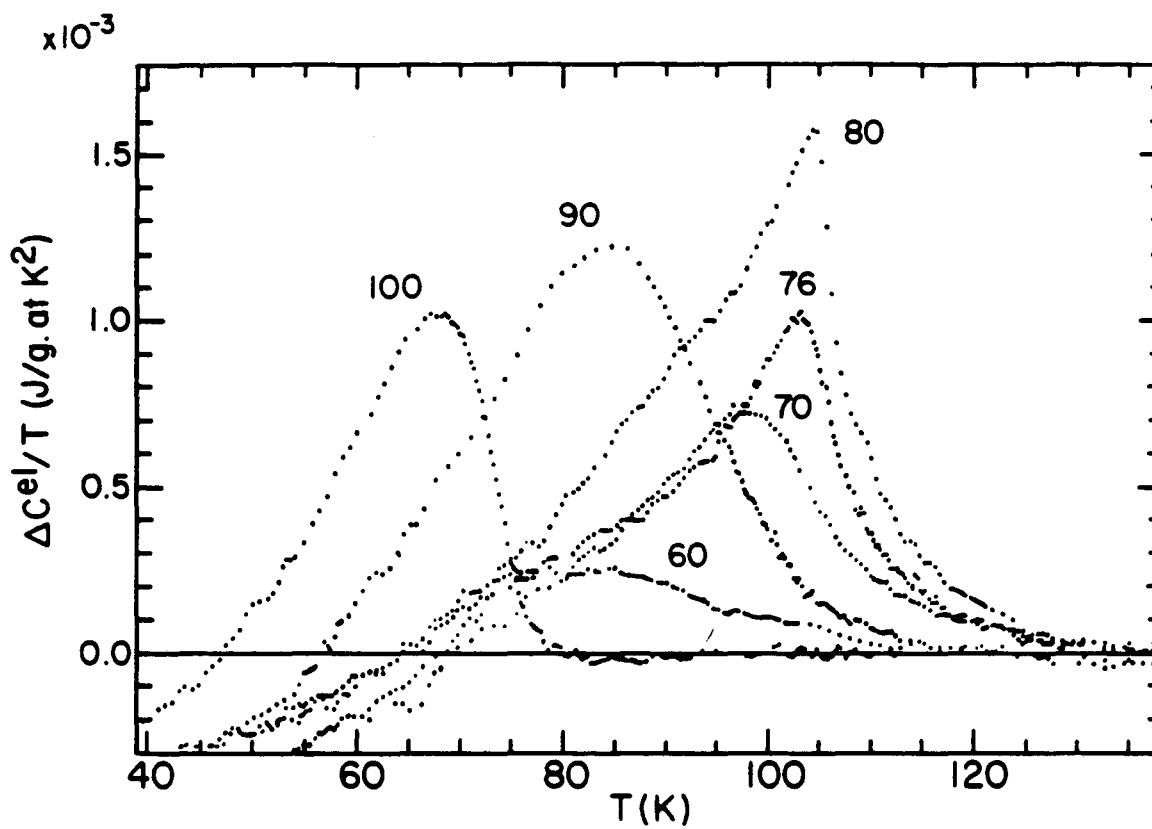
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FIG. 14



XBL 923-291

FIG. 15



XBL 923-292

FIG. 16

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