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### The Specific Heat of High- $T_c$ Superconductors

N.E. Phillips, R.A. Fisher, and J.E. Gordon

April 1990



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# THE SPECIFIC HEAT OF HIGH-T<sub>c</sub> SUPERCONDUCTORS

BY

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## 1. Introduction

### 1.1. HIGH $T_c$ SUPERCONDUCTORS

The intense interest in high- $T_c$  superconductors (HTSC) stems from the confirmation, late in 1986, of the existence of superconductivity with  $T_c \approx 30\text{K}$  in the Ba-La-Cu-O system. That discovery followed the report by Bednorz and Müller (1986) of a drop in the electrical resistivity, and their suggestion that it might be indicative of a transition to the superconducting state. The earlier discovery of superconductivity at  $T_c \approx 13\text{K}$  in  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  by Sleight et al. (1975) had provided the first indication that these perovskite oxides might be of interest in connection with the search for high  $T_c$ 's, but superconductivity, below 1K, had been predicted (Cohen 1964) and discovered (Schooley et al. 1964) even earlier in one compound of this class,  $\text{SrTiO}_3$ . The work on the Ba-La-Cu-O system was quickly followed by the discovery of superconductivity in other alkaline earth-doped  $\text{La}_2\text{CuO}_4$  samples (Chu et al. 1987, Kishio et al. 1987, Cava et al. 1987) and, in March 1987, by the discovery of superconductivity above liquid nitrogen temperatures, with  $T_c \approx 90\text{K}$ , by Wu et al. (1987). Within another year superconductivity had been discovered in the Bi-Sr-Ca-Cu-O (Michel et al. 1988, Maeda et al. 1988) and Tl-Ba-Ca-Cu-O (Sheng et al. 1988a, 1988b) systems with  $T_c$ 's ranging from 80 to 125K. Superconductivity has also been discovered in alkali metal-doped  $\text{La}_2\text{CuO}_4$ ,  $\text{La}_{2-x}\text{A}_x\text{CuO}_4$  with  $\text{A}=\text{Na}$  or  $\text{K}$  (Subramanian et al. 1988a); and in  $(\text{Ba},\text{K})\text{BiO}_x$  and  $(\text{Ba},\text{Rb})\text{BiO}_x$ , the first non-Cu-containing oxide superconductors since  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  (Mattheiss et al. 1988).

$\text{YBa}_2\text{Cu}_3\text{O}_{7.6}$  was the first HTSC discovered in the Y-Ba-Cu-O system, and it has been investigated more intensively than any other HTSC. It is of particular interest because the occurrence of two Cu sites --in Cu-O chains and in Cu-O planes -- and the variability of the oxygen content both provide opportunities for probing structure-property relationships. However, there are other compounds in this series that are superconducting. The most important is  $\text{Y}_2\text{Ba}_4\text{Cu}_8\text{O}_{16}$  (or  $\text{YBa}_2\text{Cu}_4\text{O}_8$ ) in which there is an additional Cu-O layer and a doubling of the unit cell. It was discovered first as an intergrowth at grain boundaries in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Viegers et al. 1987, Narayan et al. 1987, Zandbergen et al. 1988, Kogure et al. 1988); and then as a distinct phase in thin films (Marshall et al. 1988, Kwo et al. 1988, Char et al. 1988, Mandich et al. 1988); and more recently it has been synthesized in bulk (Karpinski et al. 1988, Morris et al. 1989a). There have been only a few measurements on this material to date, but it is of interest because of its relation to  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and because achieving the optimum oxygen stoichiometry is less difficult than in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

In all of the HTSC mentioned above, the conduction is by holes. Compounds represented by  $\text{R}_{2-x}\text{M}_x\text{CuO}_{4.6}$  with  $\text{R}=\text{rare earth}$  and  $\text{M}=\text{Ce}$  or  $\text{Th}$  include HTSC in which the conduction is by electrons. The first to be discovered were the  $\text{R}=\text{Pr}$ ,  $\text{Nd}$  and  $\text{Sm}$ ;  $\text{M}=\text{Ce}$ ;  $x=0.15$  compounds (Tokura et al. 1989) and they were followed by the  $\text{R}=\text{Eu}$ ;  $\text{M}=\text{Ce}$  and  $\text{R}=\text{Pr}$ ,  $\text{Nd}$  and  $\text{Sm}$ ;  $\text{M}=\text{Th}$  (Markert et al. 1989a, Markert and

Maple 1989, Early et al. 1989).  $\text{Nd}_2\text{CuO}_{4-y}\text{F}_y$  is another electron-carrier superconductor (James et al. 1989).

Abbreviations that will be used for some of the most frequently mentioned HTSC are listed in table 1.

## 1.2. SCOPE OF THE REVIEW

In the three years since their discovery, there has been an enormous amount of research on HTSC and this is reflected in the existence of a considerable number of review articles, including a number on the specific heat (C). There have been several fairly general reviews devoted to specific heat measurements, including an earlier one by the present authors (Fisher et al. 1988a) and others by Srinivasan and Sankaranarayanan (1988), Salamon (1989), Atake (1990) and Junod (1990). Fischer et al. (1988), von Molnár et al. (1988) and Gmelin (1989) reviewed specific heat and other thermal properties. Stupp and Ginsberg (1989) and Stupp (1990) focused on the "linear term" in the specific heat of YBCO and (L,M)CO, respectively. However, the pace of the research justifies frequent updating of the reviews.

A considerable amount of new information has appeared since our earlier review, but it must be recognized that there are still uncertainties in interpretation of the data and that a final picture is not yet available. Sample quality and inadequate characterization have been major problems, and have led to contradictory results for measurements on samples that otherwise appear to be similar. The situation is improving steadily but further improvement is needed.

At this time, the recognition of the properties characteristic of the ideal superconducting and normal states, and their separation from effects associated with chemical and structural imperfections has to be a major goal of any review. Although there is reason to think that HTSC may differ fundamentally from conventional superconductors, there is little in the way of quantitative predictions suitable for comparison with experiment that are based on microscopic theory directed specifically to HTSC. Comparisons of experiment with theory must therefore be based largely on the theory, both microscopic and phenomenological, of conventional superconductors, but must take into account certain obvious differences such as the anisotropy and the short coherence length ( $\xi$ ) that characterize HTSC. In addition, the emphasis of this review is on material that has come to light since our earlier review and on certain topics judged to be either of most interest or most clearly understood. It is certainly not intended to be comprehensive in the sense of including references to all specific heat or associated measurements.



### 1.3. ORGANIZATION OF THE REVIEW

Because it is convenient to discuss the specific heat of HTSC in relation to that of conventional superconductors, a brief summary of the information that has been obtained from specific-heat measurements on conventional superconductors is given in sec. 2. An example of the zero-field specific heat of a YBCO sample is given in sec. 3.1. The principal features are compared with those of conventional superconductors, and the experimental problems and complications in the analysis of the data are summarized. Section 3.2 is a summary of the contributions to the specific heat of HTSC and their temperature and magnetic field dependences. Most analyses of the specific heat into its component contributions have been made at low temperatures or in the vicinity of  $T_c$ , and the general methods employed in those analyses are outlined in secs. 3.3 and 3.4, respectively. The general features of the lattice heat capacity and the nature of analyses of the data at intermediate and high temperatures are summarized in sec. 3.5. Perhaps the feature of the specific heat of HTSC that has received the most attention is the "linear" term (actually a term proportional to temperature) that occurs in the zero-field specific heat. This term was recognized very soon after the discovery of HTSC; the first published reports of its existence were by Reeves et al. (1987), Wenger et al. (1987) and Dunlap et al. (1987a). Such a term does not occur in conventional superconductors (except as a consequence of imperfections of one kind or another) but it was predicted, as an intrinsic property of HTSC, by the resonant valence bond (RVB) theory (Anderson 1987). Most of the attention to this term has been focused on its interpretation: is it an intrinsic property of the ideal superconducting state or not? However, its empirical validity as a component of the specific heat has also been questioned, and that issue is addressed in sec. 3.3.3. Discussion of its interpretation is reserved to later sections, primarily sec. 4.2. Throughout section 3 measurements on various HTSC are used as examples, and that section 3, supplemented by section 2, constitutes an overview of some of the major features of the specific heat of HTSC, and particularly of the analysis of specific heat data.

More detailed descriptions and discussions of the specific heats of individual HTSC are given in secs. 4-9. Most of the measurements have been made on YBCO, and they are covered in sec. 4. Measurements on the other HTSC are discussed in secs. 5-9, often by comparison or contrast with the corresponding results for YBCO. The hyperfine contribution to the specific heat is most conveniently discussed as a separate topic, and it is treated in sec. 10. Trends in the properties from one HTSC to another are noted, and conclusions stated, throughout the review, but some major conclusions are summarized in sec. 11.

## 2. The Specific Heat of Conventional Superconductors

Figure 1 shows the electronic specific heat ( $C_e$ ) normalized to its normal-state value ( $C_{en} = \gamma T$ ), and plotted against  $T/T_c$  ( $T_c$  is the critical temperature) for a BCS,

weak-coupling superconductor. In most cases the critical fields are small enough that the normal state can be retained to arbitrarily low temperatures and  $\gamma$  can be determined without ambiguity. The lattice specific heat is often only a small part of the total, and in most cases it can be determined by analysis of the normal-state data and subtracted from the total superconducting-state specific heat to obtain the electronic superconducting-state specific heat ( $C_{es}$ ).

In zero field there is a discontinuity in  $C$  at  $T_c$ ,  $[\Delta C(T_c)]$ . In the best high-quality samples the transition is sharp, limited primarily by resolution in the temperature measurement. At  $T_c$  a gap ( $2\Delta$ ) opens in the electronic density of states at the Fermi energy, and increases with decreasing temperature reaching  $2\Delta_0 = 3.53k_B T_c$  at 0K. At low temperatures  $C_{es}$  varies approximately exponentially with  $T/T_c$ . In particular,  $C_{es}/T=0$  in the limit  $T=0$ , i.e., there is no linear term. In the weak-coupling limit  $\Delta C(T_c)/\gamma T_c = 1.43$  and  $C_{es} = C_{en}$  at  $T/T_c = 0.51$ . These relations are changed by strong-coupling effects, which increase  $\Delta C(T_c)/\gamma T_c$ , e.g., to 2.7 for Pb, and shift the point of equality of  $C_{es}$  and  $C_{en}$  to higher values of  $T/T_c$ , as required for entropy balance. These effects are associated with an increase in the ratio  $2\Delta_0/k_B T_c$  to a value greater than 3.53. Blezius and Carbotte (1987) have predicted a maximum value of  $\Delta C(T_c)/\gamma T_c$  of approximately 3.7, depending on the phonon spectrum and coulomb repulsion, and a decrease in  $\Delta C(T_c)/\gamma T_c$  from the maximum value with further increase of the coupling strength.

The specific heat is a true measure of bulk properties, and can play an important role in determining the volume fraction of superconductivity, which is not determined by, e.g., resistivity measurements, and not determined unequivocally even by magnetic-susceptibility measurements. For a conventional superconductor an incomplete transition to the superconducting state would be indicated by the appearance of a linear term in the zero-field specific heat and a reduction in  $\Delta C(T_c)$ .

### 3. General Features of the Specific Heat of HTSC

#### 3.1. SPECIFIC HEAT OF A YBCO SAMPLE: COMPARISON WITH CONVENTIONAL SUPERCONDUCTORS

The total specific heat of a YBCO sample that is reasonably typical of the better polycrystalline samples currently available is shown in fig. 2. At  $T_c$  the lattice specific heat is large compared with the electronic contribution, and the feature associated with the transition to the superconducting state is only 3% of the total. Furthermore, there is no obvious discontinuity in specific heat. Comparison of data for different samples shows that a major part of the apparent breadth of the transition is associated with sample-to-sample differences, presumably inhomogeneities and other imperfections, but the nature of the specific heat anomaly at  $T_c$  for an ideal sample has not yet been unambiguously established. For YBCO there can be inhomogeneities associated with oxygen stoichiometry and with the ordering of the O atoms. Other

HTSC, e.g., (L,M)CO, are solid solutions. The inclusion of impurity phases is probably also a contributor to the breadth. The effect of small-scale defects of all kinds can be expected to be enhanced in HTSC relative to that in conventional superconductors because  $\xi$  is smaller by a factor of  $10^{-1}$  to  $10^{-2}$  and is comparable to the lattice parameters. Furthermore, there is the expectation, also based on the small value of  $\xi$ , that fluctuation effects should be important in determining the shape of the specific-heat anomaly at  $T_c$ . Thus, there are a number of factors bearing on the shape of the anomaly in specific heat at  $T_c$ .

Figure 2 also shows the low-temperature "upturn" in  $C/T$  that is characteristic of virtually all samples of HTSC, at least those that have been studied below 1K. It is associated with electronic magnetic moments that order below 1K as shown by its magnetic-field dependence (see sec. 3.3.2). After appropriate correction for the upturn there is still a non-zero intercept of  $C/T$  at  $T=0$ . This is  $\gamma(0)$ , the coefficient of the linear term that has attracted so much attention.

Perhaps the most serious problem associated with specific-heat measurements on HTSC is the impossibility of quenching superconductivity (except very close to  $T_c$ ) with the magnetic fields available in the laboratory. Thus, the relatively simple methods for obtaining  $\gamma$  and the lattice specific heat, which are so important for the interpretation of data for conventional superconductors, do not work for HTSC.

### 3.2. NOTATION AND TEMPERATURE AND MAGNETIC FIELD DEPENDENCES FOR THE COMPONENT CONTRIBUTIONS TO THE SPECIFIC HEAT OF HTSC

Because there are a number of different contributions to  $C$ , some of which take different forms in the normal, mixed and superconducting states, it is convenient to adopt, and to summarize here, a notation that reflects these complications. The lattice ( $C_l$ ), electronic ( $C_e$ ) and hyperfine ( $C_h$ ) contributions are the ones generally expected in a metallic system at low temperatures. The hyperfine contribution arises from an interaction of nuclear magnetic moments with a magnetic field -- either an applied field, or, in the case of an ordered magnetic material, an internal field produced by the ordered electronic moments -- or an interaction of nuclear quadrupole moments with an internal electric-field gradient. The quadrupole contribution is usually small compared with the magnetic contribution associated with a magnetic field of a few T or more, and in most cases  $C_n$  is only a small fraction of  $C$  for  $T \geq 1K$ .

For almost all samples of the oxide superconductors there is an additional, magnetic-moment contribution ( $C_m$ ) evidently associated with localized electronic magnetic moments. In zero-field, this contribution usually manifests itself as an upturn in  $C/T$  that starts at a temperature of a few K and increases with decreasing  $T$ , taking the form of a Schottky-like anomaly at temperatures well below 1K. However, in extreme cases in which the concentration of moments is sufficiently high, the maximum in  $C/T$  may occur above 1K. For magnetic fields of a few T or more, the maximum

always occurs above 1K.

In addition to the subscripts  $\ell$ ,  $e$ ,  $h$  and  $m$ , a second set of subscripts,  $n$ ,  $m$  and  $s$  will be used, when necessary, to distinguish the normal, mixed and superconducting states. (There should be no confusion associated with the use of the subscript  $m$  for both mixed-state and magnetic contributions.) For specific-heat contributions that vary with magnetic field ( $H$ ), and for parameters derived from them, the value of the magnetic field will be indicated in parentheses following the symbol when that is useful.

The lattice specific heat is independent of magnetic field and usually assumed to be the same in the normal and superconducting states. In the low-temperature limit,

$$C_{\ell} = B_3 T^3 + B_5 T^5 + B_7 T^7 + \dots \quad (1)$$

The Debye characteristic temperature at  $T=0$  ( $\theta_0$ ) is

$$\theta_0 = (12\pi^4 R / 5B_3)^{1/3}. \quad (2)$$

The most common convention for HTSC has been to use the value of  $B_3$  per g-atom in eq. 2, e.g., for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  one thirteenth of the value per mole, and that convention is followed in this review. In the high-temperature limit the harmonic contribution to  $C_{\ell}$  can be approximated by an expansion in powers of  $T^{-2}$  (Thirring 1913, 1914a, 1914b) but other forms converge more rapidly, e.g., (Sack 1961, Gordon et al. 1989a),

$$C_{\ell, \text{harmonic}} / 3R = 1 + \sum_{n=1}^{\infty} B_n u^n, \quad (3)$$

where  $u = (T/T_b + 1)^{-1}$  and  $T_b$  is a parameter that depends on the material. In addition, a term that is approximately proportional to temperature must be included at high temperatures for the anharmonic contribution.

The temperature dependence of  $C_{\ell}$  can be characterized over broad intervals of temperature by the harmonic lattice expressions, eqs. (1) and (3). A sum of Debye and Einstein specific-heat functions is often used for the same purpose. The Einstein function represents the contribution of vibrational modes at a single frequency that corresponds to the Einstein temperature ( $\theta_E$ ). Deviations from the Debye specific heat are frequently represented by a temperature-dependent Debye temperature ( $\theta_T$ ) defined by equating  $C_{\ell}$  to the Debye function of  $T/\theta_T$ .  $\theta_{\infty}$  is the high-temperature limiting value of  $\theta_T$ .

The normal-state electronic specific heat is

$$C_{en} = \gamma T \quad (4)$$

where  $\gamma$  measures the electronic density of states  $[N(E_F)]$ , for both spin directions, at the Fermi energy ( $E_F$ ),

$$\gamma = (1/3)\pi^2 k_B^2 N(E_F). \quad (5)$$

$N(E_F)$  and  $\gamma$  are composed of bare, or band-structure contributions,  $N_{bs}(E_F)$  and  $\gamma_{bs}$ , and a phonon enhancement part that is determined by the electron-phonon interaction parameter ( $\lambda$ ). For example,

$$\gamma = (1 + \lambda)\gamma_{bs}. \quad (6)$$

In fact,  $\lambda$ , and therefore  $\gamma$  and  $N(E_F)$ , are temperature dependent. When this is important  $\lambda$  and  $\gamma$  will be written as  $\lambda_T$  and  $\gamma_T$ , with  $\gamma_T = (1 + \lambda_T)\gamma_{bs}$ . The temperature dependence involves the phonon spectrum which, in the simplest models, may be represented by a single parameter,  $\theta$ . In the high-temperature limit,  $\lambda_T$  vanishes; as  $T \rightarrow 0$   $\lambda_T$  approaches a constant limiting value,  $\lambda$ . The symbols  $\gamma$  and  $\lambda$  without subscripts refer to the 0-K values.

For most conventional superconductors  $T_c$  is sufficiently low that  $\lambda$  is essentially constant below  $T_c$ . For HTSC, however, the high value of  $T_c$  means that, at least in principle, variations of  $\lambda_T$  and of  $\gamma_T$  with temperature should be taken into account in analyzing specific-heat data. In practice this complication has generally been ignored in the analysis of experimental data. Figure 3 shows an example of the predicted temperature dependence of  $\gamma_T$  for parameters appropriate to (L,M)CO (Kresin 1990).

Another possible difference between the HTSC and conventional superconductors may lie in the temperature dependence of  $C_{es}$ . For the latter, for  $T < 0.6T_c$ ,

$$C_{es} \approx a\gamma T_c \exp(-bT_c/T), \quad (7)$$

where  $a$  and  $b$  are weakly temperature dependent. However, it is not clear, either on theoretical or on experimental grounds, that a similar exponential expression is applicable to the case of the HTSC. The notation  $\gamma(0)T$  is used for the zero-field linear term, with no implication that it is electronic in origin.

For conventional type-II superconductors,  $C_{em}$  includes an approximately linear-in-temperature, linear-in-field contribution associated with normal-state-like excitations in the vortex cores, and a contribution from interactions between the vortices. Both contributions are observed experimentally and are consistent with theory. Since the leading term in the latter contribution is proportional to  $T^3$  (Maki 1965),

$$C_{em} = \gamma(H)T + \delta(H)T^3 + \dots \quad (8)$$

for conventional superconductors, and it seems reasonable to look for this behavior in HTSC.

For the temperatures of interest here,  $C_h$  is well represented by the lowest-order term in the high-temperature expansion of a Schottky anomaly:

$$C_h = D(H)T^2. \quad (9)$$

In the case of a nuclear magnetic moment interacting with the applied field  $D(H) \propto H^2$ , but this relation would not apply if electric quadrupole interactions or internal magnetic hyperfine fields associated with electronic moments were important.

In zero applied field  $C_m$  is not a simple Schottky anomaly. No doubt this reflects the existence of a distribution of effective magnetic fields associated with disorder in the spatial distribution of the moments and their interactions. Several different approximations to the high-temperature "tail" of the anomaly by expansions in inverse powers of temperature have been used, and they can be represented by the general expression

$$C_m = \sum A_n T^{-n}. \quad (10)$$

In the presence of a magnetic field of a few T or more the anomaly is shifted to temperatures above 1K. The field dependence is consistent with  $\text{Cu}^{2+}$  moments. If the concentration of moments is sufficiently low the anomaly may take the form of the Schottky anomaly expected for  $\text{Cu}^{2+}$  moments in the applied field (to within the accuracy of the data) but for higher concentrations, and depending on the field, the anomaly is broadened by the internal fields.

### 3.3. ANALYSIS OF LOW-TEMPERATURE DATA

#### 3.3.1. *Measurements in Zero Field*

The upturn in  $C/T$  at low temperature and in zero field, i.e.,  $C_m(0)$ , complicates the analysis of the low-temperature data, as illustrated in fig. 4 for data for YBCO. Following a common convention the data are plotted as  $C/T$  vs  $T^2$ . The dashed line is a possible graphical fit to  $C/T = \gamma(0) + B_3 T^2$ . However, an analytical fit by  $C/T = A_3 T^{-4} + A_2 T^{-3} + \gamma(0) + B_3 T^2 + B_5 T^4$  leads to the substantially different values of  $\gamma(0)$  and  $B_3$  that are represented by the solid line. No doubt some of the variation in reported values of  $\gamma(0)$  and  $B_3$  (and of  $\theta_0$ ) arise from such differences in the fitting procedure. Nevertheless, it is possible to derive reliable values of  $\gamma(0)$  and  $B_3$ , and with somewhat lower precision of  $B_5$ , if the fitting expression includes the number of terms appropriate to the temperature interval of the fit (see sec. 3.3.3).

### 3.3.2. Measurements in Magnetic Fields

The application of a magnetic field modifies  $C_m$ , changing it from an upturn in the vicinity of 1K to a Schottky or Schottky-like anomaly at a temperature appropriate to the field and  $\text{Cu}^{2+}$  moments. It also produces an approximately linear-in-field increase in the linear term,  $\gamma(H)T$ , and a hyperfine term  $D(H)T^2$ , and, in some cases, an observable  $T^3$  term in  $C_{em}$ . Some of these features are illustrated in fig. 5 with data for an (L,C)CO sample for which the concentration of magnetic moments is particularly low. The zero-field upturn is small; the Schottky anomalies are not conspicuous; and the field dependence expected for the mixed state,  $\gamma(H)T$  linear in field, is clearly displayed. Similar data for an (L,S)CO sample with a higher concentration of magnetic moments are shown in fig. 6. In that case,  $C_m(0) = A_2 T^2$ , and the approximately constant shifts in  $C/T$  with increasing field for  $T > 5\text{K}$ , which are apparent in fig. 5, are modified by Schottky anomalies that shift to higher temperatures in higher fields. The solid curves in fig. 6 represent the sums of the  $C_h$ ,  $C_m$ ,  $C_e$  and  $C_l$  contributions that are shown separately in fig. 7. The latter figure also illustrates another feature: the deviations from constant  $C_e/T$  at  $T > 5\text{K}$  are approximately proportional to  $T^3$ , as expected for the mixed state (see eq. 8).

Most YBCO samples have higher concentrations of magnetic moments than the samples represented in figs. 5-7, and correspondingly larger values of  $C_m$ . An example of an analysis of the specific heat into its components similar to that of fig. 7, but for a reasonably typical YBCO sample, is shown in fig. 8. In that case, the 3.5- and 7-T  $C_m$  are well represented by Schottky anomalies, but for still higher concentrations of magnetic moments, as occur in some samples, the anomalies would be broadened.

### 3.3.3. Empirical Validity of the Linear Term

In secs. 3.3.1 and 3.3.2, the sum of a linear term,  $\gamma(H)T$ ,  $C_h$  and  $C_m$  was used to fit the low-temperature specific heat in excess of  $C_l$ . This is consistent with the most common interpretation of specific-heat data for HTSC. However, other expressions for the excess specific heat have been proposed, the empirical validity of the linear term has been questioned on various other grounds and impurity phases are known to contribute to  $\gamma(0)$ . In this section these issues are addressed, drawing on a few examples from various HTSC that are the most relevant. Other closely related results are discussed in the later sections devoted to the individual HTSC.

First, it must be recognized that the linear term that has been identified in analyses of experimental data is a significant part of the total specific heat only in a limited interval of temperature. This is apparent in figs. 7 and 8. On the high-temperature side,  $C_l$  is comparable to  $\gamma(H)T$  in the vicinity of 5K, but the ratio  $C_l/\gamma(H)T$  increases approximately as  $T^2$ , and the contribution of the linear term drops to 10% of the total somewhere near 10K. On the low-temperature side,  $C_h$ , or in zero field  $C_m$ , dominates below about 0.5K, but the data from figs. 5, 6 and 8 do

show a significant linear term to the lowest temperatures, 0.4 or 0.5K, in all fields. For example, the low-temperature 7-T data from fig. 8, replotted for  $T \leq 1\text{K}$ , as  $CT^2$  vs  $T^3$  in fig. 9, are well represented by  $D(7T)T^2 + \gamma(7T)T$  to the lowest temperature, 0.4K, where the  $\gamma(7T)T$  term is still 50% of the total.

Baak et al. (1989a, 1989b) showed that the specific heat of YBCO could be approximated without using a linear term. They used a different expression, corresponding to a particular model (Bulaevskii et al. 1975), for the specific heat in excess of  $C_2$ . The zero-field data between 0.4 and 30K were fitted by a three-parameter expression of the form  $aT^{1-\alpha} + bT^3$ . It is impressive that the data can be represented even approximately with only three adjustable parameters, but the fit was displayed on a log C-log T plot that did not make clear its quality, and only 10% accuracy was claimed for the data. When the same relation was fitted to data that are accurate to a few tenths of a percent, in the same temperature interval, the non-linear fitting procedure used did not converge; when the fitting interval was reduced to 0.4 to 12K, there was a 4% rms deviation, and systematic deviations of as much as 6%. A fit to the same data by the more usual expressions gave an rms deviation of 0.4%. Thus, the fit to zero-field data does not persuasively support the model. On the other hand, the prediction of the field dependence of C from the zero-field parameters is also impressive, the accuracy of the data notwithstanding. It seems possible that the Bulaevskii expression would be useful for  $C_m(H)$  alone, i.e., with the inclusion of  $\gamma(H)T$  and the higher order terms in  $C_2$  appropriate to the temperature interval (but note that it can not be correct in the 0-K limit).

Lasjaunias et al. (1988) reported zero-field single-crystal data on YBCO between 0.09 and 5K. This work is one of a very small number that extend to such a low temperature, and one interesting feature is the clear evidence of the expected maximum in  $C_m(0)$ . The data were represented by the sum of  $T^2$ ,  $T^{1/2}$ , Schottky and  $T^3$  terms. The fit is "generally better than 5% below 3.5K", but only limited consideration was given to other possible representations. [In connection with the temperature interval and the observation of a maximum in  $C_m(0)$  below 1K, the measurements by Gutsmedl et al. (1988), reproduced in the article by Fischer et al. (1988), should also be mentioned.]

Several authors have suggested that reliable values of  $\gamma(0)$  cannot be obtained for samples that show a significant upturn in  $C/T$  because the required number of adjustable parameters is too high. It is certainly true that an upturn can set a lower limit to the temperature interval in which a linear term has empirical significance, just as  $C_2$  inevitably sets an upper limit. However, analyses of the data over temperature intervals that are different, but are chosen to include that in which the linear term makes a major contribution, do give consistent values of  $\gamma(0)$  if the expressions used to fit the data are appropriate to the temperature intervals of the fits. An example is represented in table 2 where the coefficients of the various terms in C obtained by fitting over different temperature intervals are listed. For each interval, the number



of terms in eq. 1 for  $C_2$  and the number of terms of the form  $A_n T^n$  for  $C_m$  were chosen to give an rms deviation of 0.4%. The consistency of the values of  $\gamma(0)$  and  $B_3$  is apparent, as is the variability of some of the other parameters. The fits represented in table 2 were among 25 in which the upper- and lower-cutoff temperatures were varied independently, and for which  $\gamma(0) = 7.10 \pm 0.16$  mJ/mole  $\cdot K^2$ ;  $B_3 = 0.261 \pm 0.012$  mJ/mole  $\cdot K^4$ ; and  $B_5 = 1.03 \pm 0.06 \times 10^{-3}$  mJ/mole  $\cdot K^6$ . Other tests of the reliability of  $\gamma(0)$  values derived from BSCCO data are reported by Fisher et al. (1988c).

It has been noted (Fischer et al. 1988, Junod 1990) that logC-logT plots of zero-field YBCO data show that there is no temperature region in which there is a clearly established straight line with a slope of one, and (Junod 1990) that there is a regular progression of shapes for samples of different quality (as measured by the upturn). These features prove that there is no extended region of temperature in which the linear term dominates, which is also made evident by other displays of the data, e.g., those in figs. 7 and 8. They do not prove that there is no linear term: similar logC-logT plots can be constructed from superpositions of  $C_m$ ,  $C_2$  and  $\gamma(0)T$  of the types used to fit data in sec. 3.3.1.

For YBCO the concentrations of magnetic moments and the values of  $C_m$  are generally rather high, and the determination of the linear term below a few K must be based heavily on measurements in magnetic fields (see fig. 8) of which there are very few. In-field data for two samples that have essentially identical zero-field specific heats, including the values of  $\gamma(0)$ , but different field dependences of the specific heat, are compared in fig. 9 in a plot that should give a straight line with intercept  $D(H)$  and slope  $\gamma(H)$ . Sample 1 was studied by Caspary et al. (1989), from 0.06 to 1K in fields of 0 and 8T and by Ahrends et al. (1988) above 1.5K in zero field; sample 2 was studied by Fisher et al. (1990) from 0.4 to above 100K in fields of 0 and 7T. The measurements on sample 1 were directed to a determination of the hyperfine specific heat,  $C_h = D(H)T^2$ , i.e., to the 0-K limit of  $CT^2$ . For that reason a heat-link, thermal-relaxation technique, designed to give good accuracy at the lowest temperatures, was used. For the lowest temperature points, shown in the inset to fig. 9, the estimated error in  $C/T$  was 1 mJ/mole  $\cdot K^2$ . However, above 0.6K the decreasing value of the measured heat capacity itself, and also the associated decreasing sample-bath relaxation times, produced errors in  $C/T$  that increased with increasing temperature and reached  $\pm 2.5$  mJ/mole  $\cdot K^2$  near 1K [see the error bars in fig. 3a, Caspary et al. (1989)]. The discrepancy in the values of  $D$  for the two samples is probably not significant because the data for sample 1 were taken on a longer time scale and  $C_h$  for sample 2 is believed to be limited by nuclear relaxation times which are different on the two Cu sites, and also vary from sample to sample (see sec. 10). For sample 1 the expected field-dependent part of the linear term,  $\gamma(8) - \gamma(0)$ , is within the stated uncertainty. However, it is evident that above 0.6K the field dependence of  $C_m$  and/or that of the linear term determined at higher temperatures differ for the two samples, and the behavior of sample 1 has been cited by Junod (1990) as

contributing to the conclusion that the linear term is "fortuitous", an artifact of the fitting procedure. The difference between sample 1 and sample 2 certainly deserves further investigation (it may possibly reflect differences in sample preparation) but we take the behavior of sample 2, which is typical of those of a number of samples prepared by different techniques, as more representative. [In any case, the interpretation of the linear term is unaffected -- the conclusion reached by Caspary et al. (1989) is similar to that proposed in sec. 4.]

A major complication in the interpretation of the linear term is the possibility of a contribution arising from impurity phases. For YBCO there is no doubt that impurity phases, most notably  $\text{BaCuO}_2$ , make significant contributions to  $C$  and in particular to  $\gamma(0)$  for most, if not all, samples. Examples of the specific heat for several possible impurity phases are compared with that of YBCO in fig. 10 (Kuentzler et al. 1988a). Similar data have been obtained by others (Ramirez et al. 1987a, Eckert et al. 1988a). In the window of temperature in which the linear term is an appreciable part of the total,  $\text{BaCuO}_2$  can have a large approximately constant value of  $C/T$ , that is presumably associated with  $\text{Cu}^{2+}$  moments that order near 10K. To the extent that there is a contribution to  $\gamma(0)$  of such an origin, there must be deviations from the  $\gamma(0)T$  form at  $T > 10\text{K}$  where  $C/T$  for  $\text{BaCuO}_2$  deviates significantly from a constant (but where those deviations would be a negligible part of the total specific heat of the YBCO sample). It is reasonable to assume that at least all Cu-containing HTSC, may contain impurity phases that make contributions to the apparent value of  $\gamma(0)$  that do not reflect the presence of a linear term in an arbitrarily broad temperature interval. It should be noted that the specific heat of an impurity phase may depend on the conditions of preparation (see the data for two  $\text{BaCuO}_2$  samples in fig. 10) and also that the contribution to  $C$  of small inclusions of an impurity phase may differ significantly from that of the pure phase. For these and other reasons it is difficult to predict or even identify in detail impurity phase contributions to the specific heat.

The validity of the  $\gamma(H)T$  term, with  $\gamma(H)$  roughly linear in field, as an empirical representation of the specific-heat data, is demonstrated most convincingly by the (L,M)CO results. For YBCO the contribution of  $C_m$  is generally larger and the uncertainty in  $\gamma(H)$  correspondingly greater. However, for the data represented in fig. 8, as well as for data on a number of other samples, this representation provides a much more accurate fit than any proposed alternative. Furthermore, although it takes us somewhat beyond the strict issue of empirical validity, it is reasonable to expect similarities in behavior of (L,M)CO and YBCO, and at least the field dependence of  $\gamma(H)$  is physically very plausible. The difference between samples 1 and 2 in fig. 9 deserves further attention, but sample 2 displays the more typical behavior. With the qualifications that the existence of the linear term has not been established to arbitrarily high or arbitrarily low temperatures, and that any contribution from impurity phases is not expected to be strictly linear, it can be said that the linear term is an empirically valid component of the specific heat.

### 3.4. ANALYSIS OF DATA IN THE VICINITY OF $T_c$

Most specific heat data for HTSC have been analyzed on the assumption that an ideal sample would exhibit a discontinuity,  $\Delta C(T_c)$ , at  $T_c$ . There are different methods of estimating  $\Delta C(T_c)$  from the data, several of which are illustrated in fig. 11, with data obtained on a polycrystalline sample of YBCO (Fisher et al. 1990). The dot-dash curve is an estimate of  $(C_l + C_{en})$  based on a harmonic lattice approximation with the addition of a term proportional to temperature which is fitted to the data from 50 to 280K with the region between 70 and 110K excluded from the fit and the data below 70K corrected for a small contribution from  $C_{es}$ . The dashed lines in the figure represent simple linear extrapolations of the  $C/T$  data just above and just below  $T_c$ .  $T_c$  and  $\Delta C(T_c)$  are determined by an entropy-conserving construction that equalizes the two areas between the dashed lines and the data. The height of the vertical dashed line,  $\Delta C(T_c)/T_c$ , is 66 mJ/mole  $\cdot$  K<sup>2</sup> and  $T_c = 90.3$ K. An entropy-conserving construction that uses the dot-dash curve corresponding to the harmonic lattice background rather than the straight line extrapolation above  $T_c$  gives  $\Delta C(T_c)/T_c = 69$  mJ/mole  $\cdot$  K<sup>2</sup> and essentially the same value of  $T_c$ . The smooth curve through the data is the sum of the estimated lattice contribution and a term representing  $C_{es}$  calculated for a BCS superconductor with a Gaussian spread of  $T_c$ 's. The fit was obtained by adjusting the value of  $\gamma$  for  $C_{es}$  and the width of the Gaussian distribution. The mean  $T_c$  is 91K,  $\gamma = 45$  mJ/mole  $\cdot$  K<sup>2</sup> and  $\Delta C(T_c)/T_c = 64$  mJ/mole  $\cdot$  K<sup>2</sup>, in reasonable agreement with the other two estimates of  $\Delta C(T_c)/T_c$ . [ $\gamma$  is here used as a scaling factor to fit the observed specific-heat anomaly. Its high value relative to that determined for the normal state is an indication of strong-coupling effects (see sec. 4.5).]

### 3.5. SEPARATION OF THE LATTICE AND ELECTRONIC COMPONENTS BY ANALYSIS OF SPECIFIC HEAT DATA AT INTERMEDIATE AND HIGH TEMPERATURES

#### 3.5.1. *Qualitative Features of the Lattice Specific Heat*

The coefficients of the leading terms in the low-temperature expression for  $C_l$ , eq. 1, are well established by the experimental data below 10K (see sec. 3.3.1 and table 2). They establish both the 0-K value of the Debye temperature ( $\theta_0$ ) and the initial deviations from the Debye expression for  $C_l$ . At higher temperatures the electronic specific heat is only a few percent of  $C_l$ , and the qualitative features of  $C_l$  can be determined by making small corrections to the total specific heat. The temperature dependences of  $C_l$  for YBCO, LCO, TBCCO and BSCCO, derived in that approximation, are shown in fig. 12. A Debye specific heat function for YBCO ( $\theta_0 = 450$ K) is included for comparison. The marked deviations from Debye behavior are not unusual; they are in fact quite typical of the normal effects of the structure in the phonon spectrum or phonon density of states (PDOS) associated with phonon dispersion [see, e.g., Bijl (1957)]; they do not require the special explanations that have frequently been invoked. Any interpretation of Einstein terms that are used to represent these deviations should take into account both the relative insensitivity of

$C_2$  to details in the PDOS, and the broad range of temperature over which the contribution of an Einstein term is significant ( $\sim 0.5R$  at  $T=0.2\theta_E$ , and 90% of the high temperature limit,  $3R$ , near  $T=\theta_E$ ). The structure in the PDOS is also manifest in other physical properties. For example, Pickett (1989) has shown that the linear temperature dependence of the electrical resistivity of (L,S)CO and YBCO can be understood on the basis of the experimentally determined PDOS, but is inconsistent with a Debye spectrum.

For  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  several correlations of  $\theta_0$  with other parameters have been noted. There is a regular decrease of  $\theta_0$  with increasing  $\delta$  (Ramirez et al. 1987a, Ayache et al. 1987a, Nakazawa and Ishikawa 1989) and with decreasing  $\Delta C(T_c)$  (Gordon et al. 1990a, Eckert 1989). Some of these results, and discussion of related effects are presented in secs. 4.1.1 and 4.2.

The lattice specific heat itself is of some interest for the information it can give about the PDOS, even though that information is limited to the values of a relatively small number of parameters that do not characterize the phonon spectrum in the detail that would be desirable or that can be obtained from neutron scattering measurements. The determination of  $C_2$ , either by calculation from the PDOS obtained from other data, or by analysis of the total specific heat into its component contributions, is closely linked to the determination of the electronic contributions to the specific heat. In principle it should be possible to get information about  $\gamma$  and  $C_{es}$  from appropriate analyses of the total specific heat above and below  $T_c$ , respectively, but in practice the obstacles are formidable. The root of the problem is simply the small magnitude of the electronic contributions.

A number of PDOS determinations for HTSC have been made using inelastic neutron scattering and model calculations. For references see Fisher et al. (1988a), Junod (1990) and the Proceedings of the M<sup>2</sup>S-HTSC conferences at Interlaken and Stanford [Müller and Olsen (1988), Shelton et al. (1989)]. An example of the agreement of  $C_2$  calculated from experimental PDOS data with experimental  $C_2$  data is given in a paper by Reichardt et al. (1988). In general, there is reasonable qualitative agreement, but the accuracy is not adequate for the purpose of subtracting a calculated  $C_2$  from the measured total to obtain  $C_e$ . Other approximate methods must be used to obtain  $C_e$  from the total specific heat. They include the use of polynomial fits (or other fits, e.g., Einstein terms) to the total specific heat, differential calorimetry using a non-superconducting reference material and conventional calorimetry using a non-superconducting reference material. Examples are described in the following three sections.

### 3.5.2. Separation of the Lattice and Electronic Specific Heats by Analysis of the Data Over a Broad Range of Temperature

At high temperatures, the harmonic contribution to  $C_{\ell}$  takes the form represented by eq. 3. In addition,  $C_{\ell}$  includes terms for anharmonic contributions that are approximately proportional to temperature at high temperature. The major contribution of anharmonic effects is the dilatation term which can be calculated from the bulk modulus and the coefficient of thermal expansion, but there is a constant-volume term that is more difficult to estimate. For  $T > T_c$  there is the additional electronic term, also proportional to temperature,  $C_{en} = \gamma T$ . Gordon et al. (1989a) analyzed the data of Atake et al. (1988) for DBCO and that of Laegreid et al. (1988a) and Boerio-Goates (1988) for YBCO with four terms of eq. 3 and a term proportional to temperature for the anharmonic and electronic contributions. The data were fitted to below  $T_c$ , but the points in the vicinity of  $T_c$  were omitted from the fit, and an approximation for  $C_{es}$  was used for those points that were included for  $T < T_c$ . The fit for DBCO is represented in fig. 13 by the solid curve. A Debye function, in this case chosen to fit the data at 300K, corresponding to  $\theta_{300} = 547K$ , is shown for comparison and illustrates the deviations from Debye behavior that were displayed for  $T < 100K$ , in a different way, in fig. 12. The value of  $\gamma$  deduced, for both DBCO and YBCO, was  $20 \pm 10$  mJ/mole  $\cdot K^2$  [Gordon et al. (1989a) reported different values, but Junod (1989a) pointed out an error in the dilatation term that led to the revised values (Gordon et al. 1990b).] It must be emphasized that the validity of this analysis is heavily dependent on the accuracy of the specific-heat data, that substantial uncertainty also derives from the estimate of the anharmonic contributions and that the error limits assigned to the value of  $\gamma$  are therefore somewhat arbitrary.

A somewhat similar approach to obtaining  $C_{\ell}$  and  $\gamma$ , subject to similar uncertainties, was taken by Junod et al. (1989b) and Junod (1990). They fit the specific heat of YBCO with that calculated for a 6-parameter model PDOS plus a term proportional to temperature. After applying a correction for anharmonic contributions, they obtained  $\gamma = 9$  mJ/mole  $\cdot K^2$ .

### 3.5.3. Separation of the Lattice and Electronic Specific Heats by Differential Calorimetry on Superconducting and Non-Superconducting Samples

With the use of a suitable non-superconducting reference sample, and the application of suitable corrections, differential calorimetry offers a method for obtaining  $C_{es}$  for HTSC. The advantage of the differential technique is that a large part of the specific heat is compensated by the corresponding contribution in the reference sample. This makes possible very high precision, but realizing the benefits of that precision makes greater demands on the accuracy of the corrections that must be made for incomplete compensation. For  $T < T_c$ , the correction, which must be added to the difference  $C_{\text{sample}} - C_{\text{reference}}$  to obtain  $C_{es}$ , is of the form  $\Delta C_c = \Delta C_{\ell} + \Delta C_m + \gamma T + \Delta \gamma(0)T$ , where  $\Delta$  indicates the excess of the specific heat

component of the sample relative to that of the reference sample, and  $\gamma$  and  $\gamma(0)$  are, respectively, the normal-state and 0-K values of the coefficient of the electronic specific heat. The most difficult correction to evaluate is  $\Delta C_\ell$  which is related to differences in the PDOS.

Loram and Mirza (1988) used this method to obtain  $C_{es}$  for two samples of YBCO, with a precision that corresponds to 0.01% in the total specific heat, in the temperature range 1.5 to 300K. The results for the two samples were essentially identical. The reference sample was quenched, non-superconducting, tetragonal YBCO. (The superconducting samples were orthorhombic.) Conventional specific-heat measurements on the individual samples showed large Schottky-like anomalies at low temperature for all three, and non-zero values of  $\gamma(0)$ , respectively,  $5.5 \pm 2$ ,  $5.2 \pm 2$  and  $16 \pm 3$  mJ/mole  $\cdot K^2$  for the two superconducting samples and the reference sample. These measurements were also used to determine  $\Delta C_m$ . The remaining two correction terms,  $\Delta C_\ell$  and  $\gamma T$  were chosen to give an entropy balance at  $T_c$ . In addition,  $\Delta C_\ell$  was calculated "consistently with the neutron results"; and the normal-state value of  $\gamma$  for the fraction of the sample that was superconducting was equal to  $-\Delta\gamma(0)$ , the value of  $\gamma(0)$  for the non-superconducting sample minus that for the superconducting sample, i.e.,  $\gamma$  was the same for all samples, and equal to  $\gamma(0)$  for the reference sample,  $16 \pm 3$  mJ/mole  $\cdot K^2$ . [Loram and Mirza noted that  $\gamma(0)$  for the superconducting sample could be interpreted as an intrinsic superconducting-state contribution or as a consequence of an incomplete transition to the superconducting state.]

The corrected specific-heat difference, equal to  $C_{es}$  to the degree that the corrections are valid, is shown in Fig. 14. The usual entropy-conserving construction gave  $\Delta C(T_c)/T_c = 39$  mJ/mole  $\cdot K^2$ . The results are clearly different from the BCS weak-coupling expressions -- the anomaly is too sharp. They were compared with the phenomenological " $\alpha$ " model (Padamsee et al. 1973) to obtain  $2\Delta_0/k_B T_c = 6$ ,  $\gamma = 9.5$  mJ/mole  $\cdot K^2$  and  $\Delta C(T_c)/\gamma T_c = 4.1$ . In that comparison, the value of  $2\Delta_0/k_B T_c$  is independent of the volume fraction of superconductivity ( $f_s$ ) and of the value of  $\gamma$ . However,  $\gamma$  itself is essentially a scaling factor that can be taken to be a measure of  $f_s$ , and with this interpretation the value 9.5 mJ/mole  $\cdot K^2$  is reasonably consistent with the 16 mJ/mole  $\cdot K^2$  deduced for completely normal material, and with  $\gamma(0) = 5.2$ - $5.5$  mJ/mole  $\cdot K^2$  for the superconducting samples, taken as a measure of  $1-f_s$ .

The major uncertainty in  $C_{es}$  would seem to be associated with the question of the validity of the correction term  $\Delta C_\ell$ . More specifically, could a different  $C_\ell + \gamma T$  and a different  $C_{es}$  still give the required entropy balance? In addition, no consideration was given to the possibility of impurity phase contributions to  $\gamma(0)$  (but they could have been negligible). Furthermore, it is perhaps surprising that  $\gamma$  is the same for the normal and superconducting samples because there is some evidence that  $N(E_F)$  decreases with increasing  $\delta$  (see sec. 4.1) but there is also evidence that  $\gamma$  can be as high as 12 mJ/mole  $\cdot K^2$  for non-superconducting samples with  $\delta \sim 0.8$  (see fig.

27). However, it seems that the results near  $T_c$  are least subject to these uncertainties, and the conclusions about  $2\Delta_0/k_B T_c$  and  $\Delta C(T_c)/\gamma T_c$ , which is also independent of  $f_s$ , are therefore of considerable interest.

More recently, Loram et al. (1989) have applied this technique to a series of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  samples using LCO as the reference. Their data, reproduced in fig. 15, show that for  $0 \leq x \leq 0.3$ ,  $\gamma/x = 28 \text{ mJ/mole} \cdot \text{K}^2$ , and that  $\Delta C(T_c)/T_c$  is a maximum,  $6 \text{ mJ/mole} \cdot \text{K}^2$ , for  $x=0.15$ . These results will be compared with others in sec. 6.

### 3.5.4. Separation of the Lattice and Electronic Specific Heats by Conventional Calorimetry on Superconducting and Non-Superconducting Samples

The effect of fast-neutron irradiation on the specific heat has been studied by Voronin et al. (1987) for (L,S)CO, and by Davydov et al. (1988) and Aleksashin et al. (1988) for YBCO. The irradiation was usually carried out at 80K to retard chemical reaction and oxygen diffusion.  $\Delta C(T_c)$  was attenuated and finally disappeared with increasing fluence, while the orthorhombic symmetry was preserved. Since the specific heat for  $T > T_c$  was unchanged to within 0.5%, it was concluded that the electronic properties were unchanged. For  $\text{La}_{1.83}\text{Sr}_{0.17}\text{CuO}_4$ , but not for YBCO,  $C_s - C_n$  gave an entropy balance. Consistent with speculation based on other data, it was suggested that the discrepancy for YBCO reflected the effect of a lattice instability that was suppressed by irradiation.

The specific heats before radiation and after the apparent disappearance of  $\Delta C(T_c)$  for YBCO are shown in fig. 16. The shape of the specific-heat anomaly at  $T_c$  suggests the importance of strong-coupling effects. The dashed curve in one of the insets represents an entropy-conserving extrapolation. The values of  $\gamma$  were derived from the linear term in the low-temperature specific heats of the non-superconducting samples. For YBCO, it was concluded that  $\Delta C(T_c)/T_c = 39 \text{ mJ/mole} \cdot \text{K}^2$ ;  $\gamma = 7 \text{ mJ/mole} \cdot \text{K}^2$ ; for  $\text{La}_{1.83}\text{Sr}_{0.17}\text{CuO}_4$ ,  $\Delta C(T_c)/T_c = 14 \text{ mJ/mole} \cdot \text{K}^2$ ;  $\gamma = 5.5 \text{ mJ/mole} \cdot \text{K}^2$ .

Substitution on the Cu sites in YBCO provides another method of quenching superconductivity for the purpose of determining  $C_{es}$  by comparison of superconducting and non-superconducting samples. Junod et al. (1988a) used Fe-doping to obtain relatively high-precision data on the shape of the anomaly at  $T_c$ . Strong-coupling effects are clearly evident. Other examples of results of this approach to determining  $C_{es}$  are included in subsequent sections devoted to particular HTSC.

## 4. $\text{YBa}_2\text{Cu}_3\text{O}_{7.6}$

In the  $\text{YBa}_2\text{Cu}_3\text{O}_{7.6}$  system, both tetragonal and orthorhombic structures occur, with the orthorhombic structure derived from the tetragonal by a slight distortion. Ignoring that distinction for the moment, the structure contains  $\text{CuO}_2$  sheets with the Cu atoms at the corners of squares and the O atoms at edge centers. These are the

"plane" Cu atoms. Pairs of these sheets are separated by intervening Y layers with the Y atoms located above and below the (vacant) centers of the  $\text{CuO}_2$  squares. Above and below this unit there are, first, BaO layers with the O atoms in line with the Cu atoms in the  $\text{CuO}_2$  squares and the Ba atoms in line with the Y; and, second, for  $\delta = 0$ , CuO layers with the Cu atoms in line with those in the  $\text{CuO}_2$  layers, and only half of the O sites corresponding to those in the  $\text{CuO}_2$  layers filled. The O atoms are ordered along chains, and this ordering is associated with the orthorhombic structure. The Cu atoms in these layers are the "chain" Cu atoms. As  $\delta$  increases from zero, O atoms are removed from the chain sites, and the ordering of the O atoms in those planes is disrupted. For  $\delta \geq 0.4$ , the long-range order disappears, and the structure is tetragonal.

#### 4.1. SPECIFIC HEAT "ANOMALY" AT $T_c$

##### 4.1.1. *Sample Dependence*

The value of  $\Delta C(T_c)$  for YBCO is strongly sample-dependent. Not all of the factors that influence  $\Delta C(T_c)$  have been identified, but oxygen stoichiometry, i.e., the value of  $\delta$ , which also influences  $T_c$  and the crystal structure, is one.

The material that is formed in the high-temperature ( $\sim 900^\circ\text{C}$ ) sintering process is oxygen-deficient,  $\delta > 0.6$ , and tetragonal in structure. If it is rapidly quenched, the oxygen deficiency and tetragonal structure are "frozen in", and the quenched material is not superconducting. With slow cooling (annealing) in an oxygen atmosphere the oxygen content increases ( $\delta$  decreases), there is a transition to an orthorhombic structure (with ordered CuO "chains" as well as  $\text{CuO}_2$  "planes"), and the product is superconducting. The dependence of  $T_c$  on  $\delta$  is shown in fig. 17. Junod et al. (1989c) removed oxygen from a sample in steps, and measured the specific heat at each stage. As shown in fig. 18, there is a marked reduction in  $\Delta C(T_c)$  as  $\delta$  increases from 0.03 to 0.20. It is also noteworthy that  $\Delta C(T_c)$  is broadened and reduced by more than a factor of 2 at  $\delta = 0.10$ , with little change in  $T_c$  (see also fig. 17). A similar trend has been reported by Slaski et al. (1989a) and by Nakagawa and Ishikawa (1989). The increase in  $\delta$  is also accompanied by a decrease in  $N(E_F)$ , as shown by photoemission spectroscopy (Veal et al. 1989), a decrease in carrier (hole) concentration, as shown by Hall effect data (Wang et al. 1987) and a decrease in the Pauli susceptibility above  $T_c$  (Farneth et al. 1989).

Phillips et al. (1989, 1990) have also noted a correlation of  $\Delta C(T_c)$  with  $n_2$ , the concentration (moles  $\text{Cu}^{2+}$  per mole  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ) of the  $\text{Cu}^{2+}$  moments that produce the low-temperature upturn in  $C/T$  and which order below 1K. The value of  $n_2$  was determined from the Schottky anomaly in the specific heat in a 7-T magnetic field, an example of which is represented in fig. 8. Some of the data from which  $\Delta C(T_c)$  was estimated are shown in fig. 19, and the correlation of  $\Delta C(T_c)/T_c$  with  $n_2$  in fig. 20. Two of the samples used in this work were "Zn-doped", i.e., some of the Cu was replaced with Zn which probably goes on both plane and chain sites. The properties



of the doped sample for which  $n_2 = 0.0060$  are indistinguishable from those of undoped samples with similar values of  $n_2$ . For the other doped sample, with  $n_2 = 0.0089$ ,  $n_2$  is beyond the range of values defined by the undoped samples ( $n_2 \leq 0.0074$ ) and no such direct comparison could be made, but it was assumed that the doping did not affect the properties except through the value of  $n_2$ . For that sample there was a small,  $\sim 0.05$ , Meissner fraction that suggested that  $\Delta C(T_c)$  was not detectable because it was small and the transition broad, but that it was not really zero. That data point was therefore omitted in determining the straight-line fit to  $\Delta C(T_c)$  as a function of  $n_2$  which is shown in fig. 20. The fact that  $\Delta C(T_c)$  correlates with  $n_2$  at all shows that, at least in substantial measure, the  $\text{Cu}^{2+}$  ions that contribute to  $n_2$  must be located on the YBCO lattice. However, because impurity phases can also show low-temperature upturns in  $C/T$  (see fig. 10), it is probable that some of them are in impurity phases and do not affect  $\Delta C(T_c)$ . This would contribute to the scatter in the plot of  $\Delta C(T_c)$  vs  $n_2$ . That possibility is also suggested by the fact that the correlation of  $\Delta C(T_c)$  with another specific heat-derived measure of the volume fraction of superconductivity,  $d\gamma(H)/dH$ , is better (see fig. 30) than that of either of them with  $n_2$ .

The correlation between  $\Delta C(T_c)$  and  $n_2$  displayed in fig. 20 implies a maximum value for  $\Delta C(T_c)/T_c$  that is, very approximately,  $77 \text{ mJ/mole} \cdot \text{K}^2$ . This was interpreted as the value characteristic of an "ideal", fully superconducting sample. As suggested by the usual interpretation of such data for conventional superconductors, Phillips et al. (1989, 1990) interpreted the sample-to-sample variations in  $\Delta C(T_c)/T_c$  as measures of a corresponding variation in the volume fraction of superconductivity. (However, gapless superconductivity, well known in the case of magnetic impurities in conventional superconductors, is another possibility.) Essentially the same conclusions have been reached by the Geneva group on the basis of a correlation of  $\Delta C(T_c)/T_c$  with the minimum (zero-field) value of  $C/T$ . This correlation suggests a maximum value for  $\Delta C(T_c)/T_c$  that is, also very approximately,  $73 \text{ mJ/mole} \cdot \text{K}^2$  (as read from fig. 4, Junod et al. 1989b). Clearly, these two correlations, reported by the Berkeley and Geneva groups, are very closely related: since  $n_2$  determines the low-temperature upturn in  $C/T$ , and contributes to the value of  $\gamma(0)$  (see sec. 4.2), it is a major factor in determining the minimum value of  $C/T$ . Meissner-effect data from both laboratories are consistent with the interpretation of  $\Delta C(T_c)$  as a measure of the volume fraction of superconductivity.

As a measure of the volume fraction of superconductivity in a sample  $\Delta C(T_c)$  should play an important role in interpreting the values of other parameters derived from experimental data. It is probably also relevant to the "weak-link" effect, the apparent presence of normal or weakly superconducting regions that limit the transport critical currents in bulk samples. In this connection it is worth noting that, although the samples used in the Berkeley study were made by a number of different techniques, and in a number of different laboratories, the annealing procedures were in every case chosen with the intention of optimizing the superconducting properties. (Presumably a similar statement would apply to the Geneva samples.) However, a

detailed understanding of the nature and origin of the  $\text{Cu}^{2+}$  moments is lacking at this time. The fact that  $n_2$  affects the value of  $\gamma(0)$  but oxygen stoichiometry does not (see sec. 4.2) suggests that there is no simple relation between  $n_2$  and  $\delta$ . Evidently the mechanisms by which  $n_2$  and  $\delta$  affect  $\Delta C(T_c)$  are different. In the case of  $\delta$ , it appears to be through an effect on  $N(E_F)$ ; some speculation for the  $n_2$  case is reported in sec. 4.2.

#### 4.1.2. *Magnetic Field Dependence*

The application of increasing magnetic fields to a conventional type-II superconductor shifts the anomaly, the discontinuity in specific heat, to lower temperatures, with relatively slight broadening, and with a gradual reduction in amplitude. The measurements by Klopkin (1986) on  $\text{Nb}_3\text{Sn}$  afford a good example. The behavior of polycrystalline YBCO is quite different (Phillips et al. 1987b, Ayache et al. 1987b, Fisher et al. 1988b, 1990, Bonjour et al. 1990), as shown, e.g., in fig. 21. With increasing field, the onset of the transition to the superconducting state and the maximum in  $\Delta C$  are shifted only slightly, but  $\Delta C$  is sharply suppressed in magnitude.

In part, these differences between conventional superconductors and HTSC can be understood in terms of the very high values and the extreme anisotropy of  $H_{c2}$  and  $dH_{c2}/dT$ . The wide variation in reported values for  $dH_{c2}/dT$  derived from measurements on single crystals, listed in table 3, would itself preclude a quantitative comparison, but the complications in treating polycrystalline samples pose an additional problem. However, it seems clear that the relatively small change in the onset temperature cannot be understood on the basis of anisotropy, and Thompson and Kresin (1988) have shown that it corresponds qualitatively to the effect of fluctuations on the transition.

The anisotropy of  $H_{c2}$ , and its inadequacy as a complete explanation for the field dependence of the anomaly are both illustrated by measurements on grain-oriented polycrystalline samples and on single crystals. Bonjour et al. (1990) prepared a melt-textured polycrystalline YBCO sample in which 90% of the  $\mathbf{ab}$  planes were aligned to within  $5^\circ$ . Specific-heat measurements in fields to 6T with  $\mathbf{H} \parallel \mathbf{c}$  and  $\mathbf{H} \perp \mathbf{c}$  are shown in fig. 22. For  $\mathbf{H} \perp \mathbf{c}$  there is only a slight reduction in the maximum value of  $\Delta C$ ; for  $\mathbf{H} \parallel \mathbf{c}$  the anomaly has virtually disappeared in 6T. However, in neither case is there any perceptible shift in the onset of the transition to the superconducting state, consistent with the prediction based on fluctuation effects. The measurements by Inderhees et al. (1988) on a single crystal with  $\mathbf{H} \parallel \mathbf{c}$ , shown in fig. 23, are very similar to the corresponding measurements on the melt-textured sample.

De Jongh (1989) has suggested that the broadening of the transition in a magnetic field can be understood as a consequence of a weakening of the coupling between the Cu-O planes that limits the superconducting order to two dimensions thereby enhancing fluctuations.

### 4.1.3. Effect of Fluctuations

In a mean-field approximation the transition to the superconducting state should appear as a sharp discontinuity in specific heat, as given by the BCS theory. However, the contribution from critical fluctuations should be sizeable for  $t < (1/32)[k_B/\pi\Delta C(T_c)\xi^3]^2$ , where  $t \equiv |T/T_c - 1|$  and  $\xi$  is the zero-field coherence length (Quader and Abrahams 1988, Salamon 1989). For a conventional superconductor with  $\xi \sim 1000\text{\AA}$ , that value of  $t$  is  $\sim 10^{-12}$ . Even for an HTSC with  $\xi \sim 10\text{\AA}$ , these critical fluctuations would be observable only within 0.1K of  $T_c$ . However, Gaussian fluctuations can contribute to the specific heat over a much broader temperature interval if the number of carriers in a coherence volume,  $\xi^3$ , is small. This is the situation in the case of an HTSC, and Gaussian fluctuations might be observable over an interval of as much as  $T_c \pm 10\text{K}$ . Inderhees et al. (1988) reported the first observation of fluctuation effects, in small single-crystal samples of YBCO, one of which in particular showed a very sharp transition. They analyzed their data with the expressions  $C = C_f + C_e + C_p$ , where  $C_f$  is the fluctuation contribution,  $A^\pm t^{-(2-d/2)}$ ,  $C_e = \alpha + \beta T$ ,  $C_e^+ = \gamma T$  and  $C_e^- = a\gamma(1+bt)$ , + and - refer to temperatures above and below  $T_c$ , and  $d$  is the dimensionality of the system. They concluded that the zero-field data, shown in fig. 23, were consistent with  $d=3$  and not with  $d=2$ . Sharifi et al. (1989) have considered the effect of a distribution of  $T_c$ 's on this analysis and concluded that it is difficult to separate unambiguously the effects of broadening of the specific-heat anomaly by inhomogeneities from the details of the fluctuation contribution. Fluctuation effects have also been seen in single-crystal YBCO by Fossheim et al. (1988).

Salamon et al. (1988, 1990) have studied the effect of a magnetic field on the fluctuation contribution. The results, shown in fig. 23, are similar to those for polycrystalline samples (see sec. 4.1.2) in showing departures from the behavior of conventional type-II superconductors. They were interpreted as showing the broadening of the critical region by the field. It was argued (Salamon et al. 1990) that in a field the specific-heat behavior near  $T_c$  is dominated by critical fluctuation effects and the anomaly cannot be represented by a Gaussian correction to the mean-field transition.

A characteristic signature of fluctuation effects, a positive curvature of  $C/T$  just below  $T_c$ , has also been seen in polycrystalline YBCO samples (Gordon et al. 1989b, Laegreid et al. 1989b, Wohlleben et al. 1990), two examples of which are shown in figs. 24 and 25. The failure to observe this indication of fluctuation effects in the vast majority of polycrystalline samples is probably a consequence of broadening of the transitions by sample inhomogeneities. On the other hand, the values of  $\Delta C(T_c)$  for the best single-crystal samples are only about 50% of those for the best polycrystalline samples. The combination of small  $\Delta C(T_c)$  and sharp transitions in the single crystals is surprising: ordinarily one would expect a reduction in  $\Delta C(T_c)$  to be accompanied by a broadening of the transition. The curves used to fit the data in fig. 25, for

example, have the same temperature dependence but approximately twice the amplitude of curves that represent the single-crystal data of Inderhees et al. (1988).

#### 4.2. ZERO-FIELD LINEAR TERM

It has been generally recognized that non-zero values of  $\gamma(0)$  are to be expected if the transition to the superconducting state is incomplete, and in some cases the approximate quantitative consistency of  $\gamma(0)$  with such a model has been noted [see e.g., Phillips et al. (1987a)]. However, the importance of the theoretical implications of a  $\gamma(0)$  that is an intrinsic property of the superconducting state, and the extreme sample-to-sample variation of  $\gamma(0)$  [see Junod (1990), Table II and Fisher et al. (1988a) for an extensive list of values] have driven an intense effort to produce "better" samples and to search for correlations of  $\gamma(0)$  with processing techniques or with other sample properties in the hope that the intrinsic contribution to  $\gamma(0)$  would be determined. Oxygen stoichiometry, i.e., the value of  $\delta$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is an obvious parameter to investigate and there have been numerous measurements of the effect of  $\delta$  on  $\gamma(0)$ . Collocott et al. (1989) have reviewed a number of these studies and also reported values of  $\gamma(0)$  for three samples for  $\delta = 0$ , and, following, deoxygenation, for  $\delta = 1$ . Data with good precision by Ayache et al. (1987a) for  $\delta = 0.08, 0.34$ , and  $1.00$  are plotted as  $C/T$  vs  $T^2$  in fig. 26. Analysis of the data by the expressions given in sec. 3.2 gave  $\gamma(0)$  values constant to within 10%. The results of a recent, particularly extensive, study (Nakazawa and Ishikawa 1989) are shown in fig. 27. The peak in  $\gamma(0)$  for  $0.6 \leq \delta \leq 0.8$  corresponds to metallic, non-superconducting behavior in the phase diagram; for  $0.8 \leq \delta$  the system is a semiconductor. The interpretation of all  $\gamma(0)$  vs  $\delta$  data is clouded by the possible effects of variations in sample preparation (in the case of different samples) or of deoxygenation techniques (in the case of deoxygenation of a single sample) on impurity-phase contributions to  $\gamma(0)$ . With these reservations in mind, however, it is reasonable to take the results of fig. 27, which suggest  $\gamma(0)$  independent of  $\delta$  in the region of superconductivity, as a basis for further discussion.

The possible importance of impurity-phase contributions to  $\gamma(0)$  was recognized in the early stages of the effort to determine the value, or the existence, of an intrinsic contribution (Kuentzler et al. 1988a, Ramirez et al. 1987a, Eckert et al. 1988a). Systematic attempts to measure quantitatively the impurity-phase contribution have usually been based on the use of the Curie-Weiss term in the high-temperature susceptibility to estimate the concentration of  $\text{Cu}^{2+}$  magnetic moments ( $n$ ) which is then taken as a measure of the concentration of impurity phases,  $\text{BaCuO}_2$  in particular. A correlation of  $\gamma(0)$  with  $n$  is represented by the solid triangles in fig. 28 (Phillips et al. 1990). It is similar to results reported by the Geneva group (Eckert et al. 1988a). In part because the roughly linear correlations of  $\gamma(0)$  with  $n$ , such as that portrayed in fig. 28, extrapolate to non-zero values of  $\gamma(0)$  for  $n=0$ , but perhaps more importantly because values of  $\gamma(0) \leq 4 \text{ mJ/mole} \cdot \text{K}^2$  have been reported only very rarely, it has frequently been concluded that there is an intrinsic contribution to  $\gamma(0)$

of approximately 4-6 mJ/mole  $\cdot$  K<sup>2</sup> (see, e.g., Fisher et al. 1988a, Stupp and Ginsberg 1989).

Recently two groups have concluded that the available experimental data does not prove the existence of an intrinsic contribution to  $\gamma(0)$  (Junod et al., 1989b, Phillips et al. 1989, 1990). In both cases, that conclusion was reached on the basis of correlations of  $\gamma(0)$  with the low-temperature upturn in  $C/T$  or with the associated concentration of  $\text{Cu}^{2+}$  moments,  $n_2$ . The concentration  $n$  includes all  $\text{Cu}^{2+}$  moments, those in impurity phases that order, typically, near 10K ( $n_1$ ), and those that produce the low-temperature upturn in  $C/T$  ( $n_2$ ). Because  $\Delta C(T_c)$  is correlated with  $n_2$  (see fig. 20, sec. 4.1.1), those moments must be "on the YBCO lattice". Phillips et al. (1989, 1990) have shown that  $\gamma(0)$  is better represented by the sum of two terms, one proportional to  $n_1$  and the other proportional to  $n_2$ , than by a constant plus a term proportional to  $n$ . That correlation is also represented in fig. 28, by the open circles and open squares. Their conclusion is that  $\gamma(0)=0$  in the limit  $n_1=0$  and  $n_2=0$  -- i.e., that there is no contribution to  $\gamma(0)$  intrinsic to the ideal superconducting state. (However, that conclusion has been criticized on the grounds that it is based in part on data for two Zn-doped samples.) The Geneva group (Junod et al. 1989b) reached essentially the same conclusion by an evidently related argument: their correlation of the minimum value of  $C/T$  with  $\Delta C(T_c)$ , which led them to infer a maximum value of  $\Delta C(T_c)$  not significantly different from that deduced by Phillips et al. (1989, 1990) on the basis of the correlation of  $\Delta C(T_c)$  with  $n_2$  (see sec. 4.1.1), also led them to the conclusion that "the residual linear term appears to be irrelevant to the superconducting system". At this time, although the role of the magnetic moments (concentration  $n_2$ ) that produce the upturn in  $C/T$  in contributing to  $\gamma(0)$  has yet to be elucidated in detail, it is reasonable to conclude that that contribution plus the impurity-phase (concentration  $n_1$ ) contribution account completely for  $\gamma(0)$ .

Phillips et al. (1989, 1990) noted that the linear decrease in  $\Delta C(T_c)$  with increasing  $n_2$ , and the corresponding linear increase in the  $n_2$ -proportional component of  $\gamma(0)$  are suggestive of the operation of the pair-breaking mechanism that is familiar from conventional superconductivity. For the YBCO samples, however,  $T_c$  is essentially constant whereas for pair breaking (or gapless superconductivity) in conventional superconductors  $T_c$  decreases with increasing  $n_2$  at a rate comparable with that of the decrease in  $\Delta C(T_c)$ . That difference, together with the difference in coherence length ( $\xi$ ), led to a suggestion of a different model for HTSC -- one in which a magnetic moment completely suppresses superconductivity in its immediate vicinity, but has no effect on the superconductivity at distances greater than  $\xi$ . This model is consistent with the observed Meissner effect in the same samples (Phillips et al. 1990). The fact that, as shown in fig. 29, the constant term ( $\chi_0$ ) in the high-temperature susceptibility for these samples is independent of  $n_2$ , showing that regions that are either normal or superconducting for  $T < T_c$  have the same density of electronic states at high temperatures (Gordon et al. 1990a), is also consistent with the model. By extrapolation of the  $n_2$ -proportional term in  $\gamma(0)$  to the value of  $n_2$  at

which  $\Delta C(T_c)=0$ , the model also permits an estimate of the normal-state density of states:  $\gamma = 16 \text{ mJ/mole} \cdot \text{K}^2$ .

#### 4.3. MAGNETIC FIELD DEPENDENCE OF THE LINEAR TERM

The field dependence of the linear term,  $\gamma(H)T$ , is of interest in providing an estimate of the normal-state  $\gamma$  by an extrapolation to  $H_{c2}$ . The value of  $\gamma$  derived in this way is uncertain because it involves a long extrapolation of  $\gamma(H)$ . Furthermore, the assumed linearity of  $\gamma(H)$  with  $H$  on which that extrapolation is based, while it is a reasonable approximation, empirically established for the A15 compounds, is not exact, the value of  $H_{c2}$  is itself uncertain and the necessary averaging over the anisotropy of  $H_{c2}$  is not exact. Nevertheless, because  $\gamma$  is of such fundamental importance, it is reasonable to compare the values obtained by different methods.

Since impurity phases are known to contribute to  $\gamma(0)$ , it is natural to ask whether they might also contribute to  $d\gamma(H)/dH$ . For that reason, Sasaki et al. (1988) measured the specific heat of a  $\text{BaCuO}_2$  sample (similar to sample 2, fig. 10, sec. 3.3.3) in zero field and 6T. They found  $d\gamma/dH \sim 2 \text{ mJ/mole} \cdot \text{K}^2 \cdot \text{T}$ .

With the exception of a Zn-doped sample, in which superconductivity was intentionally suppressed, every YBCO sample investigated at LBL showed an approximately linear increase in  $\gamma(H)$  with increasing field. However, the  $\delta(H)T^3$  term (see eq. 8, sec. 3.2) that is also expected for the mixed state (Maki 1965), and which was observed for (L,S)CO (see fig. 7, sec. 3.3.2) was not observed. There are several probable reasons for this difference: the higher values of  $H_{c2}$  and  $T_c$  would make  $\delta(H)$  smaller for YBCO than (L,S)CO, and the larger lattice specific heat for YBCO would further reduce the fractional contribution of that term.

The values of  $d\gamma(H)/dH$  do show considerable sample-to-sample variation, which is to be expected if the volume fraction of superconductivity varies. As shown in fig. 30,  $d\gamma/dH$  is proportional to  $\Delta C(T_c)$ , suggesting that each can be taken as a measure of the volume fraction of superconductivity. The straight line in that figure gives a value of  $d\gamma/dH$  of  $0.27 \text{ mJ/mole} \cdot \text{K}^2 \cdot \text{T}$  for a fully superconducting sample, i.e., one for which  $\Delta C(T_c)/T_c = 77 \text{ mJ/mole} \cdot \text{K}^2$  (see sec. 4.1.1). Since the number of moles of  $\text{Cu}^{2+}$  present in impurity phases in the samples represented in fig. 30 is at most 0.01/mole YBCO, the maximum contribution of  $\text{BaCuO}_2$  to  $d\gamma/dH$  would be  $0.02 \text{ mJ/mole} \cdot \text{K}^2 \cdot \text{T}$ . In fact other impurity phases might make different contributions to  $d\gamma/dH$ , but the very good correlation of  $d\gamma/dH$  with  $\Delta C(T_c)/T_c$  in fig. 30 suggests that this is probably not an important effect. Although individual determinations of the values of  $d\gamma/dH$  are limited in accuracy by the small size of the effect, the correlation with  $\Delta C(T_c)$  shown in fig. 30 contributes to their credibility, and the effective averaging implicit in the straight-line construction further supports the validity of the estimate made for a fully superconducting sample,  $d\gamma/dH = 0.27 \text{ mJ/mole} \cdot \text{K}^2 \cdot \text{T}$ .

However, most other measurements of the field dependence of the specific heat have led to higher values of  $d\gamma/dH$ . Reeves et al. (1989) investigated a polycrystalline sample for which 8 to 12% of the Cu was present in unknown impurity phases ( $n=0.24$  to 0.36), in fields of 0, 1, 2 and 3T, from 2 to 10K. For each field they fit their data with  $C(H)=\gamma(H)T+[B_3+\delta(H)]T^3$ , and from the coefficients derived  $d\gamma/dH=0.85$  mJ/mole  $\cdot K^2 \cdot T$ , and an anomalous negative field dependence of the  $T^3$  term,  $d\delta/dH=-0.019$  mJ/mole  $\cdot K^2 \cdot T$ . Their data are equally well represented by the sum of a Schottky anomaly for  $Cu^{2+}$ ,  $\gamma(0)T$ ,  $H(d\gamma/dH)T$  and  $B_3T^3$ . A simultaneous fit to the data for all four fields gives  $d\gamma/dH=0.47$  mJ/mole  $\cdot K^2 \cdot T$ , and the concentration of  $Cu^{2+}$  moments,  $n_2=9.5 \times 10^{-4}$ , consistent with the absence of an upturn. The apparent negative field dependence of the  $T^3$  term deduced by Reeves et al. (1989) is evidently a consequence of the presence of a low concentration of  $Cu^{2+}$  moments. Forgan et al. (1988) fit data for fields to 4.5T, and  $1.5 \leq T \leq 10K$  with Schottky anomalies and terms in  $T$ ,  $T^3$  and  $T^5$  to obtain  $d\gamma/dH=0.9$  mJ/mole  $\cdot K^2 \cdot T$ , but their plot of  $C/T$  vs  $T^2$  shows that their higher temperature data are more consistent with  $d\gamma/dH \sim 0.2-0.3$  mJ/mole  $\cdot K^2 \cdot T$ . The higher value may be a consequence of forcing the data to fit a Schottky anomaly for a concentration of magnetic moments for which it is not a good approximation. Panova et al. (1987) derived  $d\gamma/dH=0.65$  mJ/mole  $\cdot K^2 \cdot T$  from data with good precision, no upturn in  $C/T$  and taken in fields to 8T. Sasaki et al. (1988) estimated  $d\gamma/dH \sim 0.6$  from data with relatively large scatter, taken in fields to 3T. Caspary et al. (1989) found that below 1K the linear term, which they attributed to spin-glass ordering, disappeared in a field of 8T; in effect  $d\gamma/dH$  was negative (but see sec. 3.3 for further discussion). Some of the high values of  $d\gamma/dH$  are probably associated with inadequate precision of the data, limitation of the measurements to low fields and failure to correct for the effect of field on the specific-heat contribution associated with magnetic moments. Other values are not amenable to such obvious explanations. Nevertheless, for the reasons cited above, the value  $d\gamma/dH=0.27$  mJ/mole  $\cdot K^2 \cdot T$  is taken as the best basis for further discussion.

For conventional type-II superconductors, both single crystals and polycrystalline samples of isotropic materials,  $d\gamma/dH$  is approximately constant for  $H \leq H_{c2}$ , suggesting a comparison of  $d\gamma/dH$  with experimental values of  $H_{c2}$ . Oda et al. (1988) have demonstrated the applicability of the "effective-mass model"

$$H_{c2}(\theta) = H_{c2}(0) \left[ \cos^2\theta + \left\{ H_{c2}(0)/H_{c2}(\pi/2) \right\}^2 \sin^2\theta \right]^{-1/2}, \quad (11)$$

where  $H_{c2}(\theta)$  is the upper critical field for  $H$  at an angle  $\theta$  with the  $c$ -axis, to the anisotropy of  $H_{c2}$  in single-crystal YBCO. For  $H < H_{c2}(\theta)$ , and for a grain with  $H$  at an angle  $\theta$  with its  $c$ -axis,  $\gamma H/H_{c2}(\theta)$ , where  $\gamma$  is the normal-state value, is then a reasonable approximation to  $\gamma(H, \theta)$  for that grain. There are a number of different published values for  $H_{c2}$ , but taking, for  $T=0$ ,  $H_{c2}(0)=40 \pm 5T$  and  $H_{c2}(\pi/2)=110 \pm 10T$

(Nakao et al. 1989), and averaging over angles (assumed random),  $\overline{H_{c2}}=65 \pm 7T$ . With

the experimental  $d\gamma/dH$ , this gives  $\gamma = (d\gamma/dH)\overline{H}_{c2} = 18 \pm 2 \text{ mJ/mole} \cdot \text{K}^2$ . This value for  $\gamma$  is compared with other estimates in sec. 4.4.

#### 4.4. ELECTRON DENSITY OF STATES FROM EXPERIMENTAL DATA

The value of the normal-state  $\gamma$ , or its equivalent, the electron density of states,  $N(E_F)$ , is of central importance in interpreting both the normal- and superconducting-state properties of HTSC. The very high critical fields that are characteristic of these materials preclude the application of the usual method for determining  $\gamma$ , the measurement of the low-temperature, normal-state specific heat. Although the approximate methods that have been used to estimate  $\gamma$  are all subject to reservations, the interest in that quantity justifies consideration of the values that have been obtained. The methods that are discussed in this section include those based on the analysis of high-temperature specific-heat data; differential calorimetry; the interpretation of  $\gamma(0)$ ; the field dependence of the linear term,  $\gamma(H)$ ; analysis of the specific-heat anomaly at  $T_c$  with strong-coupling models in which  $\gamma$  is a parameter; the Pauli susceptibility; and the temperature dependence of the critical field.

Several values of  $\gamma$  have been obtained by analysis of specific-heat data at moderate and high temperatures, as described in sec. 3.5.2. Gordon et al. (1989a, 1990b) obtained  $\gamma = 20 \pm 10 \text{ mJ/mole} \cdot \text{K}^2$ ; Panova et al. (1988) (cited by Junod 1990) obtained  $\gamma = 13 \pm 5 \text{ mJ/mole} \cdot \text{K}^2$ , by the same method; and, by a slightly different approach, Junod et al. (1989b) and Junod (1990) obtained  $\gamma = 9 \text{ mJ/mole} \cdot \text{K}^2$ . In each case, the correction for anharmonicity has been taken as  $15 \text{ mJ/mole} \cdot \text{K}^2$ .

Loram and Mirza (1988) used differential calorimetry to compare the specific heats of two YBCO samples with that of a quenched, non-superconducting sample (see sec. 3.5.3). The two superconducting samples had very similar specific heats, and the average values of the relevant parameters correspond to  $\gamma = 16 \pm 3 \text{ mJ/mole} \cdot \text{K}^2$ . There is substantial uncertainty in this value of  $\gamma$  for reasons that were mentioned in sec. 3.5.3.

The interpretation of  $\gamma(0)$  as including a contribution proportional to the concentration,  $n_2$ , of  $\text{Cu}^{2+}$  moments suggests another estimate of  $\gamma$ . It is based on an extrapolation of the  $\gamma_2 n_2$  contribution to  $\gamma(0)$  to the value of  $n_2$  at which superconductivity disappears, i.e., at which  $\Delta C(T_c) = 0$  (see fig. 20, sec. 4.2) and gives  $\gamma = 16 \text{ mJ/mole} \cdot \text{K}^2$ . This result depends on both the validity of the extrapolation, and on the accuracy of the determination of  $\gamma_2$ . However, the estimate of  $\gamma$  is given some support by more extensive measurements of  $\gamma(0)$  as a function of Zn-doping: With increasing levels of Zn-substitution for Cu,  $\gamma(0)$  first increases approximately linearly, then exhibits a plateau near  $20 \text{ mJ/mole} \cdot \text{K}^2$ , and finally a further sharp increase (Roth et al. 1989). The plateau could correspond to the normal-state value plus a  $4 \text{ mJ/mole} \cdot \text{K}^2$  contribution from  $\text{BaCuO}_2$ ; the subsequent sharp increase probably reflects the



known tendency for the BaCuO<sub>2</sub> content to increase at higher Zn-doping levels (Affronte et al. 1989, Mehbod et al. 1988).

The assumption that  $\gamma(H)$  is linear in  $H$  in the mixed state, empirically valid as a rough approximation for conventional type-II superconductors, permits an estimate of  $\gamma$  by extrapolating  $\gamma(H)$  to  $H_{c2}$ . Such an estimate, described in sec. 4.3, gives  $\gamma = 18 \pm 2$  mJ/mole  $\cdot$  K<sup>2</sup> where the cited error limits reflect only the uncertainty in  $H_{c2}$ . Additional uncertainties in this estimate were noted in sec. 4.3.

Strong-coupling effects modify the temperature dependence of  $C_{es}$  generally and the value of  $\Delta C(T_c)$  in particular. These effects have been represented by the phenomenological  $\alpha$  model (Padamsee et al. 1973) in which  $2\Delta_0/k_B T_c$  is taken as an adjustable parameter. By fitting experimental data in the vicinity of  $T_c$ , in particular the temperature derivative of  $C_{es}$  at  $T_c$  and  $\Delta C(T_c)$ , with this model, the values of both  $2\Delta_0/k_B T_c$  and  $\gamma$  can be obtained, but the apparent value of  $\gamma$  must be corrected for the volume fraction of superconductivity,  $f_s$ . A preliminary analysis of data by Fisher et al. (1990) gave  $2\Delta_0/k_B T_c = 7$  and  $\gamma = 14$  mJ/mole  $\cdot$  K<sup>2</sup>; the differential-calorimetry data of Loram and Mirza (1988) gave  $2\Delta_0/k_B T_c = 6$ , and, when corrected for  $f_s$  using the ratio of their value of  $\Delta C(T_c)$  to that deduced for completely superconducting material in sec. 4.1.1,  $\gamma = 19$  mJ/mole  $\cdot$  K<sup>2</sup>.

The Pauli paramagnetism,  $\chi_p$ , is related to the bare or band-structure density of states,  $N_{bs}(E_F)$ , as  $\chi_p = \mu_B^2 N_{bs}(E_F) S$ , where  $S$  is the Stoner enhancement factor. The relation between  $\gamma$ , or  $N(E_F)$ , and  $N_{bs}(E_F)$  also involves the electron-phonon interaction parameter,  $\lambda$ , through the expression  $N(E_F) = (1 + \lambda) N_{bs}(E_F)$ . In comparing values of  $\gamma$  and  $\chi_p$ , the uncertainties in the enhancement factors,  $S$  and  $\lambda$ , are major problems, and in fact the comparison is of more use as a means of estimating  $S$  than of estimating  $\gamma$ . Furthermore, extracting the value of  $\chi_p$  from  $\chi$ -data is not trivial. The  $\chi$ -data must be analyzed to separate temperature-dependent Curie-Weiss terms from the temperature-independent susceptibility,  $\chi_0$ , and even that analysis is rendered uncertain by the possible occurrence of temperature-dependent fluctuation terms (Lee et al. 1989, Johnston 1989). It is then necessary to correct  $\chi_0$  for the core diamagnetism,  $\chi_c$ , the Van Vleck or orbital paramagnetism  $\chi_{vv}$ , and the Landau-Peierls diamagnetism  $\chi_{LP} = -(1/3)(m/m^*)^2 \chi_p$ . The latter is believed to be small compared with  $\chi_p$  and estimates of  $\chi_c$  and  $\chi_{vv}$  suggest that they approximately cancel (Lee and Johnston 1990). Using these approximations,  $\chi_p = \chi_0$ , and taking  $\chi_0 = (2.8 \pm 0.4) \times 10^{-4}$  emu/mole,  $S = 1$  and  $\lambda = 0$ , gives  $\gamma = 20 \pm 3$  mJ/mole  $\cdot$  K<sup>2</sup>. Estimates of  $S$  are discussed in relation to values of  $\gamma$ ,  $\gamma_{bs}$  and  $\lambda$  in sec. 4.5.

For type-II superconductors in the "dirty" limit,  $\gamma$  is related to the temperature dependence of the critical field at  $T_c$ ,  $dH_{c2}/dT|_{T_c}$  by  $\gamma = -22.3 \rho^{-1} dH_{c2}/dT|_{T_c}$  with  $\rho$  in  $\mu\Omega$  cm,  $H_{c2}$  in T and  $\gamma$  in mJ/cm<sup>3</sup> K<sup>2</sup> (Orlando et al. 1979). Values of  $\gamma$  determined in this way are subject to several major uncertainties: there are wide variations in the values reported for  $dH_{c2}/dT|_{T_c}$  and  $\rho$ ; and there is doubt that HTSC are in the "dirty"

limit (Salamon 1989, Yeszhurun and Malozemoff 1988). However, the most reasonable estimates (for polycrystalline YBCO) of  $\rho = 200 \Omega \text{cm}$  and  $dH_{c2}/dT|_{T_c} = -2 \text{T/K}$  (Salamon and Bardeen 1987) yield  $\gamma = 0.2 \text{ mJ/cm}^3 \cdot \text{K}^2 = 20 \text{ mJ/mole} \cdot \text{K}^2$ .

The value  $\gamma = 16 \text{ mJ/mole} \cdot \text{K}^2$  is taken as a basis for comparison with band-structure calculations and for the evaluation of strong-coupling effects in sec. 4.5.

#### 4.5. ELECTRON DENSITY OF STATES FROM BAND-STRUCTURE CALCULATIONS; COMPARISON WITH EXPERIMENT; STRONG-COUPLING EFFECTS

Pickett (1989) has recently reviewed calculations of the electronic structure of HTSC, including the electron density of states and the electron-phonon interaction. Using the Linearized-Augmented-Plane-Wave (LAPW) method Massidda et al. (1987) and Krakauer et al. (1988) have obtained, respectively, the values 16.0 and 13.1  $\text{mJ/mole} \cdot \text{K}^2$  for  $\gamma_{bs}$  for YBCO. Taking  $\gamma = 16 \text{ mJ/mole} \cdot \text{K}^2$ , the corresponding values of  $\lambda$  are 0 and 0.2. Yu et al. (1987a) derived values of  $\lambda$  from the calculated McMillan-Hopfield parameters using the approximation of a Debye phonon spectrum and the McMillan strong-coupling formula, in which  $\lambda \propto \theta^{-2}$ , to obtain, e.g.,  $\lambda = 0.8$  for  $\theta = 400 \text{K}$ . The value 0.32, obtained by Krakauer et al. (1988), and based on more information about the phonon spectrum than was available to the authors of the earlier work, is in reasonable agreement with the "experimental" values. Because the calculated  $\gamma_{bs}$  is generally expected to be reasonably accurate, but there is considerably more uncertainty associated with the estimate of  $\lambda$ . It is reasonable, based on the assumption that  $\gamma \sim 16 \text{ mJ/mole} \cdot \text{K}^2$  and on the calculated values of  $\gamma_{bs} \sim 13\text{-}16 \text{ mJ/mole} \cdot \text{K}^2$ , to conclude that  $\lambda \sim 0\text{-}0.3$ .

With  $\lambda = 0\text{-}0.3$ ,  $\gamma = 16 \text{ mJ/mole} \cdot \text{K}^2$  and  $\chi_p = 2.8 \times 10^{-4} \text{ emu/mole}$  (sec. 4.4), the Stoner enhancement factor is  $S = 1.3\text{-}1.6$ . The values calculated by Massidda et al. (1987) are so sensitive to  $\delta$  as to make comparisons meaningless.

Although  $\lambda \geq 0.3$  does not correspond to strong phonon coupling, there is conspicuous evidence of strong-coupling effects from a number of measurements including specific-heat data. The discontinuity in  $C$  at  $T_c$  is perhaps the most obvious example: with  $\gamma = 16 \text{ mJ/mole} \cdot \text{K}^2$  and  $\Delta C(T_c)/T_c = 77 \text{ mJ/mole} \cdot \text{K}^2$  (sec. 4.1.1),  $\Delta C(T_c)/\gamma T_c = 4.8$ , which is to be compared with the BCS weak-coupling value, 1.43. The value of this ratio indicates extreme strong coupling. [It exceeds the maximum value predicted theoretically, 3.7 (Blezus and Carbotte, 1987) but there is some uncertainty in the "experimental" value, and the theoretical estimate is based on several approximations.] From differential calorimetry, Loram and Mirza (1988) obtained the value 4.1 for the same ratio. (The effect of an incomplete transition to the superconducting state was not taken into account, but the resulting errors in  $\Delta C(T_c)$  and  $\gamma$  should cancel in the ratio.)

The temperature dependence of  $C_{es}$  in general, and particularly in the vicinity of  $T_c$ , gives additional evidence of strong-coupling effects. In the weak-coupling limit,  $C_{es} = C_{en}$  at  $T/T_c = 0.51$ ; typical YBCO data show this intersection at higher values of  $T/T_c$ , see, e.g., fig. 14, and measurements on Fe-doped YBCO by Junod et al. (1988a). The ratio of the temperature derivative of  $C_{es}$  at  $T_c$  to the magnitude of  $\Delta C(T_c)$  can be analyzed with the phenomenological  $\alpha$  model (Padamsee et al. 1973) to obtain both  $2\Delta_0/k_B T_c$  and  $\gamma$ . Differential-calorimetry data (Loram and Mirza 1988) gave  $2\Delta_0/k_B T_c = 6$ , and an analysis of other data by Fisher et al. (1990) gave  $2\Delta_0/k_B T_c = 7$ , both values substantially greater than the weak-coupling value, 3.53. These values can be compared with those from tunneling data, 4-6 (Tsai et al. 1989) and 7 (Kapitulnik and Char 1989); from Raman spectroscopy, 7.5 (Slakey et al. 1989); and from infrared spectroscopy, 8 (Collins et al. 1989).

Although the specific-heat data consistently show evidence of strong-coupling effects, the value of  $\lambda$  is inconsistent with strong electron-phonon coupling. A possible interpretation of this apparent inconsistency, which is also suggested by other lines of reasoning, is that the coupling is strong, but that the electron-phonon interaction is at least supplemented by another attractive interaction in producing the electron pairing.

#### 4.6. $\text{RBa}_2\text{Cu}_3\text{O}_7$ AND $(\text{Y}_{1-x}\text{R}_x)\text{Ba}_2\text{Cu}_3\text{O}_7$

The perovskite structures in general, and YBCO and (L,M)CO in particular, can tolerate a variety of elemental substitutions. The effects of these substitutions on the superconductivity -- sometimes dramatic, sometimes negligible -- provide an avenue of investigation that has led to important information relevant to the nature of the superconducting state. The effect of replacement of Y in YBCO by other rare-earth elements is considered in this section, the replacement of Cu by other elements mainly 3d elements, in the following section and some examples of the effects of substitutions in (L,M)CO in sec. 6, with, in all cases, an emphasis on specific-heat measurements. Markert et al. (1989b) have given a very useful and more general review of the effects of substitutions in both YBCO and (L,M)CO.

Lanthanum and all of the rare earths except Ce and Tb (and Pm which is radioactive with a half-life of 19 hours, and has not been investigated) can replace Y in the orthorhombic YBCO structure, although special synthetic procedures are necessary in some cases [e.g., the La substituted compound, Maeda et al. (1987)]. Presumably a valence of +3 is important, and under the highly oxidizing conditions required for the synthesis, Ce and Tb assume their +4 valence states. (For Eu and Yb, which can in general be +2 or +3 valent, it is reasonable to expect the +3 state for the same reason.)  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  which is not superconducting and  $(\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_7$  exhibit complicated behavior that will be discussed separately, but with these exceptions all of the rare-earth substituted YBCO's are superconducting with  $T_c$  near 90K, and with values of  $\Delta C(T_c)$  typical of YBCO samples. Examples of the anomalies at  $T_c$  are shown in figs. 31 and 32.

The rare-earth ions in the substituted YBCO's exhibit their typical magnetic moments, crystal-electric-field (CEF) splittings and cooperative magnetic ordering. The observed ordering temperatures range from 0.17K (Dunlap et al. 1987b) for the Ho compound, which is known to have a CEF singlet ground state, to 2.25K for the Gd compound. The Eu compound, which could have a singlet ground state and therefore a particularly low ordering temperature, has been investigated to 0.45K, but there was no evidence of magnetic order. [See Markert et al. (1989b), and references therein.] The Nd, Gd, Dy and Er moments have been shown by neutron diffraction to order antiferromagnetically with the Er moments ordered along the **b**-axis and the others along the **c**-axis (Yang et al. 1989, Paul et al. 1988, Fischer et al. 1988, Goldman et al. 1987, Lynn et al. 1987). Examples of CEF contributions to the specific heat of RBCO compounds for which there is no magnetic ordering above 0.45K are shown in fig. 33, and examples of magnetic ordering in fig. 34. The specific heat associated with the cooperative magnetic ordering is well fitted by an anisotropic two-dimensional Ising model. [For further discussion and additional references see Markert et al. (1989b).]

Since magnetic moments usually suppress the transition to the superconducting state, the lack of effect of the substitution (Pr excepted) on  $T_c$  and  $\Delta C(T_c)$  was unexpected. Nevertheless, there is still some question as to whether the magnetic ordering is completely independent of the superconducting electron system on the adjacent  $\text{CuO}_2$  planes. The Néel temperatures ( $T_N$ ) are of an order of magnitude associated with dipole-dipole coupling, but the effects of oxygen stoichiometry on the magnetic ordering of Dy (Lee et al. 1990), Nd and Sm (Maple et al. 1988), and Gd (Dunlap et al. 1988a, Paul et al. 1988, Chattopadhyay et al. 1988) suggest a coupling that involves the  $\text{CuO}_2$  electron system. [For further discussion and additional references see Markert et al. (1989b).]

Although  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  has the YBCO structure, it is not superconducting (Soderholm et al. 1987, Liang et al. 1987, Dalichaouch et al. 1988). With the proper preparation techniques it is possible to prepare the complete range of solid solutions  $(\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_7$ ,  $0 \leq x \leq 1$ , with stable oxygen content and the orthorhombic structure (Kebede et al. 1989). For  $x \leq 0.6$ , the materials are superconducting and  $T_c(x)$  corresponds to the AG theory for pair breaking by magnetic moments (Abrikosov and Gorkov, 1960). Hall effect (Matsuda et al. 1988) and Cu Knight-Shift (Reyes et al. 1989) data show that the carrier concentration decreases with increasing  $x$  in this region. On the high- $x$  side of the phase diagram,  $\mu\text{SR}$  measurements (Cooke et al. 1989) show antiferromagnetic ordering of the Cu moments in the  $\text{CuO}_2$  planes ( $T_{N1} = 270\text{K}$  for  $x=1$ ), and a second magnetic ordering ( $T_{N2} \approx 17\text{K}$  for  $x=1$ ), probably of the Pr moments, but ordering of the Cu moments in the CuO chains is not completely ruled out, is observed in  $\mu\text{SR}$  (Cooke et al. 1989), magnetic susceptibility and specific heat (Kebede et al. 1989), and neutron diffraction (Li et al. 1989) measurements. From the specific-heat data, the entropy change associated with the second ordering, for  $x=1$ , is approximately,  $0.9R \ln 2$ . If indeed the second ordering

is of the Pr moments, the high value of  $T_{N2}$ , 17K for  $x=1$ , also sets the Pr compound apart from the other rare-earth substituted YBCO's: in comparison with the others, and taking the deGennes factor into account, one would have expected  $T_{N2} < 1K$ . The  $x$  dependences of these transitions are shown in fig. 35.

Two explanations of the unusual behavior of the Pr-substituted compounds are current. One explanation, suggested by the  $x$ -dependence of the carrier concentration, is that Pr has a valence intermediate between +3 and +4 and the extra electrons fill holes in the  $CuO_2$  planes (Soderholm et al. 1987, Liang et al. 1987, Dalichaouch et al. 1988). The resulting Cu magnetic moments suppress the superconductivity. Tang et al. (1989) and Guo and Temmerman (1989) showed that the Fermi energy for the conduction band in the  $CuO_2$  planes was close to the energy of the  $Pr^{3+} - 4f^2$  electrons, leading to hybridization and a reduction in carrier concentration. The latter explanation is supported by experiments by Tang et al. (1989) in which they showed that substitution of Pr on the La sites in  $La_{1.85}Sr_{0.15}CuO_4$ , and on the Ca sites in BSCCO -- both systems in which the energy match required for hybridization does not occur -- does not suppress the superconducting transition.

Specific-heat measurements on  $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$  (Sankar et al. 1988, Kebede et al. 1989, Felner et al. 1989a, Ghamaty et al. 1990) have been made in the range  $1.5 \leq T \leq 70K$  and for  $0 \leq x \leq 1$ . Large values of  $\gamma(0)$  were reported, up to  $750 \text{ mJ/mole Pr} \cdot K^2$ . More recent measurements (Amato et al. 1990a) to lower temperatures, and in magnetic fields, have shown that magnetic ordering contributed to the apparent  $\gamma(0)$  values: the  $x=0.3$ , zero-field data in fig. 36 show an anomaly near 1K that is shifted to 5K by the application of a 7-T field. Similar results, but with the anomalies at lower temperatures, were obtained for  $x=0.1$  and 0.2. An analysis of the data on the low-temperature sides of the anomalies into hyperfine  $C_h = D(H)T^2$ , and electronic,  $C_e = \gamma(H)T$ , contributions is shown in fig. 37. (Small corrections were made for the low-temperature side of a Schottky anomaly.) There is a small field dependence of  $\gamma(H)$ , comparable to that found for YBCO. The  $x$ -dependence of  $\gamma(H)$  is well represented by the linear relation,  $\gamma(7T) = 9 + 200x \text{ mJ/mole} \cdot K^2$ , suggesting a roughly constant contribution from impurity phases and other normal material plus an  $x$ -proportional contribution.

The hyperfine specific heat itself conveys information that should be useful in testing models for the electronic structure of the Pr ions. It shows complex behavior, corresponding to an internal effective hyperfine field associated with ordered Pr moments in zero applied field, and a strongly enhanced increment in the hyperfine field associated with the applied field. The effective hyperfine fields ( $H_h$ ) are independent of  $x$ , and their dependence on applied field is shown in fig. 38.

#### 4.7. $\text{YBa}_2(\text{Cu}_{3-x}\text{M}_x)\text{O}_7$

There have been numerous studies of the effects of the substitution of other elements, mainly 3d elements, for Cu in the YBCO lattice. Substitutions of  $M = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Zn}, \text{Ga}$  and Al for Cu have been shown generally to produce a decrease in the Meissner fraction and in  $T_c$  (Xiao et al. 1987a, 1987b, Chien et al. 1988, Xiao et al. 1988). The same authors suggested, as possible mechanisms for the observed effects: induced localization, and pair breaking by the resulting  $\text{Cu}^{2+}$  magnetic moments; direct pair breaking by the magnetic moment on a substituent ion; change in crystal structure, from orthorhombic to tetragonal, caused by changes in oxygen content, caused in turn by substitution in the chain sites; and a change in carrier concentration and  $N(E_F)$ .

It is generally believed that +3 ions, e.g., Ga and Al, substitute on the chain sites. Howland et al. (1989) have used differential anomalous x-ray scattering to show that Ni and Zn are nearly randomly distributed over chain and plane sites, and that Fe and Co substitute preferentially on the chains for low- $x$ , but for higher- $x$  there is some substitution on plane sites. Tarascon et al. (1988) have shown that for  $M = \text{Ni}, \text{Zn}, \text{Fe}, \text{Co}$  and Al, the orthorhombic distortion decreases with increasing  $x$ ; the oxygen content changed very little for small- $x$ , but exceeded 7 for large- $x$ ; and also noted the decrease of  $T_c$  with increasing  $x$ . Jee et al. (1988a) reported the formation of  $\text{Cu}^{2+}$  moments on the YBCO lattice accompanying Zn substitution, but Affronte et al. (1989) showed that for  $x > 0.15$  there is incomplete incorporation of the Zn on the YBCO lattice; that ZnO is produced; and that increased amounts of the impurity phases  $\text{Y}_2\text{BaCuO}_5$  and  $\text{BaCuO}_2$  are also produced. Mehbod et al. (1988) have also shown the incomplete incorporation of Zn into the YBCO lattice for  $x > 0.15$ .

Loram (1990) has used high-sensitivity differential calorimetry to follow the anomaly in specific heat at  $T_c$  to 30K for Zn-substituted YBCO. Roth et al. (1989) have also measured the specific heat of Zn-substituted YBCO as a function of  $x$ . They found an initial linear increase in  $\gamma(0)$  with increasing  $x$ ; a plateau in  $\gamma(0)$  near  $x = 0.1$ ,  $\gamma(0) \sim 20 \text{ mJ/mole} \cdot \text{K}^2$ ; and a further increase in  $\gamma(0)$  at higher values of  $x$ , where increased contributions from impurity phases are to be expected (Affronte et al. 1989). This behavior is consistent with the interpretation of the dependence of  $\gamma(0)$  for YBCO on the concentrations of the two types of  $\text{Cu}^{2+}$  moments given in sec. 4.2.

Other specific-heat measurements have been reported, at low temperatures, for  $M = \text{Cr}$  (Kim et al. 1989), Fe (Felner et al. 1989b, Kuentzler et al. 1988b, Dunlap et al. 1988b, Junod et al. 1988a), Ni (Jee et al. 1988b), and Zn (Jee et al. 1988a, Kim et al. 1989, Kuentzler et al. 1988b, Remschnig et al. 1988); and near  $T_c$ , for Cr (Kim et al. 1989), Fe (Junod et al. 1988a), Co (Loram 1990), Ni (Jee et al. 1988a), and Zn (Jee et al. 1988b, Kim et al. 1989).

The effects of 3d-element substitution are illustrated by Meissner effect and

specific-heat measurements on the same samples, with  $x=0$ , 0.015, and 0.04 for  $M=Cr$ , in figs. 39-42. The Meissner fraction is shown in fig. 39; the increases in the zero-field low-temperature upturn in  $C/T$  and in  $\gamma(0)$  are apparent in fig. 40; the 7-T Schottky anomalies associated with magnetic moments that produce the zero-field upturns are shown in fig. 41; and the effect on the anomaly at  $T_c$  in fig. 42.

#### 4.8. STRUCTURE IN THE SPECIFIC HEAT ANOMALY AT $T_c$ AND SECONDARY ANOMALIES IN THE VICINITY OF $T_c$

The vast majority of specific heat measurements on YBCO show no indication of structure in the anomaly at  $T_c$ . For example, of the approximately 36 samples studied at Geneva, none showed structure (Junod 1990) and of the 15 samples studied at Berkeley (Fisher et al. 1990) only one showed any sign of structure, and that was a relatively minor asymmetry in the anomaly (see fig. 19, third sample). However, there are a few measurements in which a variety of types of more complicated behavior -- either structure in the anomaly at  $T_c$  itself or a second distinct anomaly in the vicinity of  $T_c$ , but at either a higher or a lower temperature -- have been observed. There are substantial theoretical reasons for expecting structure, or even distinct transitions, in "unconventional" superconductors (e.g., Joynt 1988, Volovik 1988) and a double transition was observed in the heavy-fermion superconductor  $UPt_3$  when samples with sufficiently sharp transitions became available (Fisher et al. 1989a). Choy et al. (1989) have reviewed evidence for exotic behavior in the specific heat near  $T_c$ , and in some cases compared the data with theoretical models.

Butera (1988) reported measurements on a polycrystalline sample (sealed in a calorimeter with  $^4He$  exchange gas) that showed a first-order transition at 90K and a lambda-like anomaly at 87K, both of which were very sharp. Ishikawa et al. (1988) observed a double transition with two well-resolved maxima in some, but not all, of their ceramic samples, and more recently, Nakazawa and Ishikawa (1989) have suggested that the double transition is critically dependent on oxygen stoichiometry. Li et al. (1987) observed two rounded and separated anomalies with maxima at 91 and 94K. One of the first samples investigated by the Geneva group (Junod et al. 1987) which showed a discontinuity in specific heat at 94K, also showed a secondary anomaly at 86K. The specific heat of a single crystal measured by Inderhees et al. (1988) exhibited a small secondary anomaly at 93K, which was well removed from the discontinuity at 89K. Inderhees (1989) suggested that the secondary anomaly could be attributed to experimental noise, and this was borne out by later measurements on other samples, but in the meantime it had been the subject of theoretical analysis (Choy et al. 1989). For an HBCO ceramic sample, Lazarev et al. (1988) reported a double transition at  $T_c$ , as well as a large lambda-like anomaly in the 50-70K region. Keqin et al. (1989) used a differential calorimeter to study a polycrystalline sample of GBCO (the reference material was unspecified) and reported two well-resolved anomalies with maxima at 82 and 85K.

Undoubtedly some of these experimental results are spurious -- associated with, e.g., trapped gases (such as  $N_2$ ,  $O_2$  or  $CO_2$ ) sealed in a calorimeter, or (Junod 1990) trapped in pores in the sample;  $YBa_2Cu_4O_8$ , a possible contaminant, for which  $T_c \approx 80K$ ; sample inhomogeneities corresponding to regions of different oxygen stoichiometry or impurity concentrations -- but some are difficult to explain. There is certainly room for doubt about the origins of the anomalous effects that have been reported to date, and perhaps particularly about detailed theoretical interpretations, but the importance of implications for theory of structure in the superconducting transition suggests further work on better, and better-characterized, samples.

#### 4.9. SPECIFIC HEAT ANOMALY AT 220K

Following the discovery of 90-K superconductivity in YBCO there was a series of reports of irreproducible phenomena that were suggestive of superconducting transitions at much higher temperatures, frequently in the range 200-240K. Perhaps in part for that reason, the discovery (Laegreid et al. 1987) of a broad specific heat anomaly at 220K that seemed to be correlated with that at the superconducting transition near 90K attracted considerable interest. It was suggested that the 220-K anomaly might be associated with oxygen ordering (Laegreid et al. 1987). It was also noted that CuO orders antiferromagnetically at 230K but the possibility that the 220-K anomaly might be associated with CuO impurity was ruled out (Fisher et al. 1987), incorrectly it would now appear, on the basis of the relative magnitudes of the specific heats of CuO and YBCO. Subsequently, anomalies in properties other than the specific heat have been observed in the vicinity of 220K. At this time, there is still uncertainty about the origin of the 220-K anomaly.

Junod et al. (1988b) suggested that the 220-K anomaly might arise from a transition in silicone grease used for thermal contact to the sample, but silicone grease had not been used in the experiments in which the anomaly was observed (Fossheim 1988). Later measurements on a YBCO single crystal (Fossheim et al. 1988) showed two sharp peaks in the specific heat near 210 and 230K, but more recent measurements of the specific heat of CuO (Slaski et al. 1989b, Junod et al. 1989d) have shown essentially the same structure. The variability of the peaks renders estimates of the amount of CuO in the YBCO crystal uncertain, but that amount could correspond to some tens of percent of the total Cu. It has been suggested (Slaski et al. 1989b) that the much broader anomaly in polycrystalline YBCO cannot arise from CuO impurity, but, because sharp features in the specific heat are often "smeared out" when the substance is present as an impurity phase, that possibility cannot be ruled out. The specific heats of CuO and of single-crystal and polycrystalline samples of YBCO that show the anomaly are compared in fig. 43.

Laegreid et al. (1988b) observed hysteretic and anomalous behavior in the sound velocity near and below 200K, and have noted that the specific-heat anomaly is observed only if the sample is cooled into that region and the specific heat is



measured, subsequently, on warming through the region near 220K -- no anomaly is observed while cooling through that region. Calemczuk et al. (1988) observed the 220-K specific-heat anomaly, and, in the same temperature region, hysteretic and anomalous behavior in the electrical resistivity, Young's modulus and internal friction. They associated the effects with a first-order structural transition. On the other hand, no anomaly has been observed, apparently after cooling to a low temperature, in other measurements on YBCO (Junod et al. 1988b, Ishikawa et al. 1988, Gordon et al. 1989b) and on RBCO (Atake et al. 1988, Saito and Atake 1988, Atake et al. 1989b). One of the negative results is shown in fig. 44 where the solid curves represent a fit to the data by eq. (3).

### 5. $\text{Y}_2\text{Ba}_4\text{Cu}_8\text{O}_{16}$

The YBCO (248) structure is related to that of YBCO by the insertion of a second CuO plane (containing the chain Cu sites) adjacent to that in YBCO. The second CuO plane and the layers beyond it in a YBCO unit cell are displaced by half a lattice parameter along the CuO chain.

YBCO (248) is more stable with respect to oxygen stoichiometry than YBCO, simplifying the annealing procedure that is needed to optimize the superconducting properties (Morris et al. 1989b) and leading to the expectation that high-quality samples and high critical currents might be easier to obtain. Junod et al. (1989b) measured the specific heat of a YBCO (248) sample ( $1.3 \leq T \leq 120\text{K}$ ;  $H=0$ ; Meissner fraction  $\approx 0.12$ ; onset  $T_c \approx 81\text{K}$ ). They found (on a per atom basis) a specific heat larger than that of YBCO, e.g., by a factor of 2.5 at 10K; a value of  $\gamma(0)$  greater than that of the "best" YBCO samples by a factor of about 3.5; a much smaller value of  $\Delta C(T_c)$  than for YBCO, but no low-temperature upturn in  $C/T$ . The small value of  $\Delta C(T_c)$  suggest more substantial sample preparation problems than had been anticipated.

### 6. $\text{La}_2\text{CuO}_4$ and $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ )

In the  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  structures there are  $\text{CuO}_2$  sheets, similar to those in the YBCO structure, with the Cu atoms at the corners of squares and the O atoms at edge centers. These sheets are separated by two (La,M)O sheets in which the O atoms are situated above and below the Cu atoms in the  $\text{CuO}_2$  sheets, to give octahedral coordination at the Cu sites. At high temperatures the structure is tetragonal with one formula unit per primitive unit cell. At low temperatures and small-x ( $x \leq 0.20$  for  $M = \text{Sr}$ ) the  $\text{CuO}_6$  octahedra are slightly tilted, to give an orthorhombic cell with two formula units per primitive cell.

$\text{La}_2\text{CuO}_4$  is an antiferromagnetic insulator. For a number of samples  $\gamma(0) < 0.5$  mJ/mole  $\cdot \text{K}^2$  (Kato et al. 1988, Kobayashi et al. 1988, Kumagai et al. 1988a, 1988b, Wada et al. 1989a, Fisher et al. 1990). Doping with Ca, Sr or Ba produces holes and,

with increasing carrier concentration, a transition first to a semiconducting and then to a metallic state. For

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , which has the highest  $T_c$ 's and is the most intensively studied, antiferromagnetism persists to  $x \approx 0.02$ , and there is evidence of the existence of magnetic moments and spin-glass ordering to somewhat higher values of  $x$  (see e.g., Birgeneau and Shirane 1989 and references therein). Superconductivity, as detected by resistivity and magnetic-susceptibility measurements, occurs for  $0.06 \leq x \leq 0.32$  with a maximum  $T_c$  of approximately 35K, at  $x \approx 0.15$  (see e.g., Torrance et al. 1988, and references therein).

Possibly because they are solid solutions, the (L,M)CO superconductors generally exhibit broader superconducting transitions in specific-heat measurements than YBCO. The values of  $\Delta C(T_c)$  are consequently more difficult to determine and less accurately known. In this respect, (L,B)CO is the extreme example: Loram et al. (1987) observed only a very small anomaly at  $T_c$ ,  $\Delta C(T_c)/T_c \sim 0.07$  mJ/mole  $\cdot$  K<sup>2</sup>, using a differential technique. With a single exception (Gabovich et al. 1987) no anomaly has been observed with conventional methods, and even in that one case its appearance depended on the cooling cycle. There have been only a few specific-heat measurements on (L,C)CO, which has the lowest  $T_c$  (Kitazawa et al. 1987a, Phillips et al. 1987a). For (L,S)CO, for which there have been a substantial number of specific-heat measurements near  $T_c$ , as well as at lower temperatures, a wide range of values of  $\Delta C(T_c)$  has been reported. In this respect, the behavior is very much like that of YBCO. Variation in the volume fraction of superconductivity no doubt contributes to the variation in  $\Delta C(T_c)$  values, but inadequate precision is probably an even more important factor than for YBCO.

Several methods, similar to those used for YBCO, have been used to determine  $\Delta C(T_c)$  for (L,M)CO samples. Phillips et al. (1987a), Amato et al. (1990b) and Goshitskii et al. (1987) subtracted the specific heat measured in a magnetic field from the zero-field specific heat. Results obtained in this way are illustrated in fig. 45 for both (L,C)CO and (L,S)CO, and for another (L,S)CO sample in the inset to fig. 46. The latter figure illustrates the difficulty in determining  $\Delta C(T_c)$  particularly clearly: the observed anomaly is only 0.2% of the specific heat, and is barely discernable in the main figure. Loram et al. (1989) used a differential technique to measure the specific heats of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  as a function of  $x$ , with  $\text{La}_2\text{CuO}_4$  as the reference. A maximum in  $\Delta C(T_c)$  occurred at  $x \approx 0.15$  (see fig. 15, sec. 3.5.3). Wada et al. (1989a) measured the specific heats of superconducting  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  and non-superconducting  $\text{La}_{1.90}\text{Sr}_{0.10}\text{CuO}_4$ , and obtained  $\Delta C(T)$  by subtraction. Fast neutron irradiation has been used to suppress superconductivity in  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  to provide a non-superconducting reference material and obtain  $\Delta C(T)$  by difference (Voronin et al. 1987).  $\Delta C(T_c)$  has been estimated by a number of authors by extrapolating specific-heat data in zero field from above and below  $T_c$  (Junod et al. 1987, Ramirez et al. 1987b, Kitazawa et al. 1987b, Nieva et al. 1987, Rosenberg et al. 1987, Feng et al. 1988).

The values of  $\gamma(0)$  for (L,M)CO samples are smaller than for YBCO. Given the sample-to-sample variations in both cases, generalizations are necessarily very rough, but they are typically an order of magnitude smaller. The low-temperature upturns in  $C/T$  are also smaller, by a similar factor. These differences may arise from differences in the impurity phases in the two cases. For YBCO it is clear that impurity phases, particularly  $\text{BaCuO}_2$ , can make substantial contributions to  $\gamma(0)$ .  $\text{BaCuO}_2$  cannot be present in (L,C)CO or (L,S)CO, and may well be less important as an impurity even in (L,B)CO than in YBCO. Since the properties, and even the identities, of the impurity phases in (L,M)CO are not well established, no definite statement can be made. However, given the differences in the observed values of  $\gamma(0)$  and the known role of impurity phases in determining  $\gamma(0)$  for YBCO, it is reasonable to suppose that impurity-phase contributions to  $\gamma(0)$  are substantially less important in (L,M)CO than in YBCO.

Values of  $\gamma(0)$  for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ , for  $x$  in the range 0 to 0.45, have been reported by a number of authors (Kato et al. 1988, Kobayashi et al. 1988, Kumagai et al. 1988a, 1988b, Wada et al. 1989a, Loram et al. 1989, Fisher et al. 1990). The results for the two systems are qualitatively similar. The data of Wada et al. (1989a) for Sr-doped samples are reproduced in fig. 47. Superconductivity occurs for  $0.06 \leq x \leq 0.32$ , and the carrier concentration ( $p$ ) increases approximately linearly with  $x$  (Torrance et al. 1988). With the assumption that impurity-phase contributions can be neglected, the variation in  $\gamma(0)$  for non-superconducting samples can be interpreted as reflecting changes in the normal-state  $\gamma$ ; for superconducting samples, and invoking the interpretation of  $\gamma(0)$  for YBCO (Phillips et al. 1989, 1990) described in sec. 4.2,  $\gamma(0)$  is a measure of the volume fraction of normal material: For  $x \leq 0.06$ , the increase in  $\gamma(0)$  corresponds to the increase of  $\gamma$  with increasing  $p$ ; the dip in  $\gamma(0)$  for  $0.1 \leq x \leq 0.2$  reflects the occurrence of relatively complete transitions to the superconducting state; and the maximum for  $x \approx 0.3$  [ $\gamma(0)$  decreases with further increase in  $x$  (Loram et al. 1989)] corresponds to a leveling off, or possibly a maximum, in the value of  $p$  -- for larger values of  $x$ , oxygen vacancies become more important and decreases in  $p$  are possible. A different interpretation of the maximum in  $\gamma(0)$  near  $x=0.05$  has been given by Loram et al. (1989). They find that the values of  $\gamma(0)$  in that vicinity are higher than those of  $\gamma$ , and suggest that the difference is associated with spin-glass ordering.

For YBCO,  $\gamma(0)$  and  $\Delta C(T_c)$  show correlations with the concentration of  $\text{Cu}^{2+}$  moments on the YBCO lattice that imply a direct correlation of  $\gamma(0)$  with  $\Delta C(T_c)$  of the form that would be expected if the sample-to-sample variations in both quantities were manifestations of incomplete transitions to the superconducting state. For (L,S)CO, the concentrations of  $\text{Cu}^{2+}$  moments have not been determined as systematically as for YBCO, but, again with the assumption that impurity-phase contributions to  $\gamma(0)$  can be neglected, they are not necessary -- the correlation can be tested directly. Data for six samples of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ , for which both quantities have been measured, are represented by the solid circles in fig. 48 and listed in table

4. In addition, three values of  $\gamma$  for non-superconducting  $\text{La}_{1.7}\text{Sr}_{0.3}\text{CuO}_4$  have been scaled to the values appropriate to  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  by using an empirically derived linear relation (Loram et al. 1989). They are also listed in table 4, and represented by open circles, at  $\Delta C(T_c)=0$ , in the figure. Within the fairly substantial uncertainties, the data are represented by the straight line shown, and are consistent with a model in which both quantities measure the volume fraction of superconductivity, which varies considerably from sample to sample. The maximum value of  $\Delta C(T_c)/T_c$  for a fully superconducting sample, is  $14 \text{ mJ/mole} \cdot \text{K}^2$ ; the normal-state value of  $\gamma$  is  $4.4 \text{ mJ/mole} \cdot \text{K}^2$ ; and  $\Delta C(T_c)/\gamma T_c=3.2$ . The sample-dependent values of the volume fraction of superconductivity,  $f_s$ , are given in table 4.

The field dependence of the linear term,  $\gamma(H)$ , has been measured for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  by Phillips et al. (1987a) and Goshitskii et al. (1987) who found, respectively,  $d\gamma/dH=0.11 \text{ mJ/mole} \cdot \text{K}^2 \cdot \text{T}$  for  $x=0.15$ , and  $d\gamma/dH=0.11 \text{ mJ/mole} \cdot \text{K}^2 \cdot \text{T}$  for  $x=0.17$ . These values become  $0.17$  and  $0.16 \text{ mJ/mole} \cdot \text{K}^2 \cdot \text{T}$  when corrected for the volume fraction of superconductivity calculated from the values of  $\gamma(0)$  and the correlation displayed in fig. 48. At this time the values of  $d\gamma/dH$  cannot be used to calculate the normal-state  $\gamma$  because the critical field data corresponding to those used for YBCO (sec. 4.2.) are not available. However, the calculation can be turned around, and, using  $\gamma=4.4 \text{ mJ/mole} \cdot \text{K}^2$ ,  $\bar{H}_{c2}=26\text{T}$  for  $x=0.15$ .

For  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  there is only one estimate of  $\gamma$  from experimental data,  $\gamma=4.4 \text{ mJ/mole} \cdot \text{K}^2$ , and only one parameter that can be compared with predictions for strong-coupling effects,  $\Delta C(T_c)/\gamma T_c=3.2$ , in both cases for  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ , and noted above. Band-structure calculations give  $\gamma_{\text{bs}}=4.9 \text{ mJ/mole} \cdot \text{K}^2$  (Allen et al. 1987) and  $4.5 \text{ mJ/mole} \cdot \text{K}^2$  (Yu et al. 1987b), corresponding to  $\lambda \sim 0$ . The comparison of these quantities is very similar to that for YBCO (sec. 4.5):  $\Delta C(T_c)/\gamma T_c$  shows evidence for strong coupling, but the value of  $\lambda$  is too small for strong electron-phonon coupling.

There appear to have been no reports of structure in the anomaly at  $T_c$  for (L,M)CO of the kind reported for YBCO, possibly because the number of measurements is so much smaller. However, several other anomalies, probably associated with structural transitions, have been observed. Loram et al. (1987) reported an anomaly near 58K in  $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$  that appears to be associated with a second orthorhombic-to-tetragonal transition that was identified in x-ray diffraction by Axe et al. (1989). Another anomaly, in  $\text{La}_{1.70}\text{Sr}_{0.3}\text{CuO}_4$  near 45K is apparent in fig. 46. It is conceivably associated with a similar, but as yet otherwise unidentified, structural transition.

A few experiments on the effect of elemental substitution on the Cu sites have been carried out, with results similar to those of the corresponding experiments on YBCO. In the case of (L,M)CO, the interpretation of the results is simplified by the occurrence of only a single Cu site. Hilscher et al. (1988) studied

$\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$ , and using x-ray analysis showed that the substitution was random. With increasing  $x$  they found an increase in  $\gamma(0)$ ; a decrease in  $T_c$ ; and a decrease in  $\Delta C(T_c)$ , to 0 at  $x=0.025$ . Strong depressions of  $T_c$  with increasing  $x$  were also reported by Xiao et al. (1989) for  $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Zn}_x)\text{O}_4$  and Cieplak et al. (1989) for  $\text{La}_{1.85}\text{Sr}_{0.15}(\text{Cu}_{1-x}\text{Ga}_x)\text{O}_4$ . For Ga-substitution the carrier concentration decreases and the Curie-Weiss term in the susceptibility increases with increasing  $x$ ; for Zn-substitution the carrier concentration remains constant and the Curie-Weiss term increases [cited by Cieplak et al. (1989)] with increasing  $x$ . It was concluded (Cieplak et al. 1989) that in both cases the substitution produces localization and magnetic moments on the adjacent Cu sites that act as pair-breaking centers.

## 7. Bi- and Tl-Cu Oxides

There are many compounds in these series that differ in the numbers and stacking sequences of the various metal-oxide layers. One series of structures can be represented by the formulae  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  and  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , with structures corresponding to  $n=1, 2$  and  $3$  known in both cases. For  $n=1$ , the stacking sequence is, for one unit cell in the Tl-Ba compound,  $\text{CuO}_2$ , BaO, TlO, TlO, BaO; for  $n=2$ , the  $\text{CuO}_2$  layers are replaced by two  $\text{CuO}_2$  layers separated by a Ca layer; for  $n=3$ , three  $\text{CuO}_2$  layers separated by Ca layers. For the Tl compounds there is an additional series  $\text{TlM}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ , for which the members with  $M=\text{Ba}$ ,  $n=1, 2, 3$  and  $4$ ; and  $M=\text{Sr}$ ,  $n=2$  and  $3$  are known. For small values of  $n$  there is a trend to higher values of  $T_c$  with increasing  $n$ . The large numbers of component elements and possible compounds make the preparation of single-phase samples difficult, but in some cases a single phase can be favored by partial substitution of Pb and/or Sb for Bi or Tl (Takano et al. 1989). Subramanian et al. (1988b) and Chahoumakos et al. (1989) have reviewed the general background, the chemistry, preparation and structure of these compounds.

The most interesting result of the earliest specific-heat measurements on the Bi HTSC was the absence of a linear term --  $\gamma(0)=0$  (Kumagai and Nakamura 1988, Fisher et al. 1988c, Sera et al. 1988). The five samples studied at LBL were multiphase and showed large low-temperature upturns in  $C/T$ , substantially larger than for the better YBCO samples, but analysis of the data by the procedures discussed in sec. 3.3 gave  $\gamma(0)=0\pm 0.5$  mJ/mole  $\cdot \text{K}^2$ . The conclusion was questioned on the grounds that a full Schottky function should have been used in fitting the data rather than  $T^{-2}$  and  $T^{-3}$  terms (Collocott et al. 1988), but it is the Schottky function that is inappropriate because it does not allow for the distribution of internal fields expected for such a system. The large upturns and the large lattice specific heat (nine times greater than for YBCO) do limit the accuracy with which  $\gamma(0)$  is determined, but, as argued in sec. 3.3, data of good accuracy and precision can still give a useful measure of  $\gamma(0)$ . The zero values of  $\gamma(0)$  reported by Kumagai and Nakamura (1988) and Sera et al. (1988) are not subject to the uncertainty associated with large upturns because their samples (which, given the understanding of synthetic procedures at the time, were

probably also multiphase) showed, respectively, no upturn at 2K, and only a small upturn at 1.5K. The preponderance of more recent measurements also gives  $\gamma(0)=0$  (Caspary et al. 1989, Sasaki et al. 1989, Urbach et al. 1989, Muto et al. 1989, Fisher et al. 1989b, von Molnár et al. 1988, Chakraborty et al. 1989, Gang et al. 1989, Yu et al. 1989, Bombik et al. 1989, Mori et al. 1989, Gao et al. 1990), but some non-zero values have been reported (Sasaki et al. 1989, Muto et al. 1989, von Molnár et al. 1988, Collocott et al. 1988, Eckert 1989, Coey et al. 1989). The specific heat of a Pb-single-phase BSCCO sample, which shows a low-temperature upturn in  $C/T$ , but for which  $\gamma(0)=0$ , is shown in fig. 49. Given the probable presence, in amounts that reflect the details of sample preparation, of impurity phases with unknown properties, it is reasonable to assume that  $\gamma(0)=0$  for the "pure" material, and that non-zero values are associated with impurity phases or with other internal "defects" that produce normal regions, as seems to be the case for YBCO. However, it is clear that the relation between the upturns in  $C/T$  and the values of  $\gamma(0)$  are not the same for BSCCO and YBCO or (L,M)CO: the correlation of large values of  $\gamma(0)$  with large upturns in  $C/T$  (Junod et al. 198b) or the associated large values of the concentration of  $\text{Cu}^{2+}$  moments,  $n_2$  (Phillips et al. 1989, 1990) found for YBCO is not observed for BSCCO. Furthermore,  $\text{BaCuO}_2$ , with its recognized role in contributing to  $\gamma(0)$  in YBCO, is not present in BSCCO.

Fewer specific-heat measurements have been made on the Tl HTSC. Both zero values of  $\gamma(0)$  (Urbach et al. 1989, Junod et al. 1989e) and non-zero values (Urbach et al. 1989, Muto et al. 1989, Junod et al. 1989e, Fisher et al. 1988b) have been reported. In this case  $\text{BaCuO}_2$  is a probable impurity. On the basis of the few studies that have been made, and comparison with other HTSC, it is also reasonable in this case to assume that  $\gamma(0)=0$  for the pure materials.

Determination of the form of the anomaly in specific heat at  $T_c$  has proven to be even more difficult for BSCCO and TBCCO than for YBCO, presumably because intergrowths and other impurity phases are difficult to eliminate. Early specific-heat measurements showed no anomaly at  $T_c$  (Fisher et al. 1988b, Seidler et al. 1989), multiple anomalies (Fisher et al. 1988b, Yu et al. 1989, Junod et al. 1989f, Yuan et al. 1988, Junod et al. 1989g), and very broad anomalies (Fisher et al. 1988b, Junod et al. 1989g, Rosenberg et al. 1989). Experimental observations such as these led to the suggestion (Seidler et al. 1989) that the transition might be third order, with no discontinuity  $\Delta C(T_c)$  at  $T_c$ . This suggestion is given plausibility also by the possibility that the two-dimensional character of the groups of  $\text{CuO}_2$  planes is more important in these materials than in YBCO (weaker coupling in the  $c$ -direction) and has received some attention. However, with improvements in sample preparation, the anomalies have become better defined and there is no longer a conspicuous difference between the results for BSCCO or TBCCO and YBCO.

Some examples of more recent specific-heat measurements near  $T_c$  on BSCCO are shown in figs. 50-54. Figure 50 displays data for a Pb-stabilized, single-phase

sample (the sample for which the low-temperature data are shown in fig. 49). The data were analyzed on the assumption that there is a discontinuity in specific heat at  $T_c$ , and the value derived by the construction shown in the figure,  $\Delta C(T_c)/T_c = 37$  mJ/mole  $\cdot$  K<sup>2</sup>, is the largest that has been reported for BSCCO. Figures 51 and 53 show similar data for two other samples with smaller values of  $\Delta C(T_c)/T_c$ , and figs. 52 and 54, respectively, show analysis of the data in terms of fluctuation effects. In both cases there is the usual uncertainty associated with the subtraction of the background to obtain the fluctuation contribution. Okazaki et al. (1990) have emphasized that their data, fig. 54, are consistent with two-dimensional fluctuations, but not with three-dimensional fluctuations as deduced for YBCO (see sec. 4.1.3.).

Transitions for TBCCO samples are shown in figs. 55-57. Atake et al. (1989c) studied the effect of Tl content on the specific heat by starting with excess Tl, removing Tl in steps, and measuring the specific heat at each step. The effect on the transition is shown in fig. 55, and the specific heat is compared with the magnetic and resistive transitions in fig. 56. The sample represented in fig. 57, does not show a particularly sharp transition, but it is apparently the only one for which the effect of a magnetic field on the specific-heat anomaly has been observed.

Measurements on other good-quality Pb- or Sb-stabilized BSCCO samples have been reported by Slaski et al. (1989c), Jin et al. (1988) and Gao et al. (1990).

## 8. Electron-Carrier HTSC

The electron-carrier HTSC have the same chemical formula as the hole-carrier HTSC,  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ , and a closely related crystal structure. In the electron-carrier materials the Cu-O units are square-planar; in the hole-carrier materials they are octahedral.

Ghamaty et al. (1989) and Maple et al. (1989) measured the specific heats of  $\text{Nd}_{1.85}\text{Th}_{0.15}\text{CuO}_{4.6}$ ,  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4.6}$  and  $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4.6}$  and of the parent compounds  $\text{Nd}_2\text{CuO}_{4.6}$  and  $\text{Sm}_2\text{CuO}_{4.6}$  ( $0.5 \leq T \leq 30\text{K}$ ;  $H=0$ ). Magnetic moments, on the  $\text{Nd}^{3+}$  and  $\text{Sm}^{3+}$  ions, and superconductivity coexist, as in the RBCO HTSC. In the substituted compounds the  $\text{Nd}^{3+}$  moments order at 1.2K, and the  $\text{Sm}^{3+}$  moments at 4.58K; in the parent compounds the ordering temperatures are 1.7 and 5.95K, respectively. Data for the Nd-Ce and Nd-Th substituted compound and for the parent compounds are shown in fig. 58, and for the difference,  $\Delta C \equiv C(\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{3.98}) - C(\text{Nd}_2\text{CuO}_4)$ , in fig. 59. The increase in  $\Delta C$  from 15 to 23K is taken as evidence of a broad superconducting transition, and the linear region above 23K as  $\gamma T$  for the normal state, with  $\gamma \approx 53$  mJ/mole  $\cdot$  K<sup>2</sup>.

## 9. $(\text{Bi}_{1-x}\text{K}_x)\text{BiO}_3$

Specific-heat measurements on polycrystalline  $(\text{Bi}_{0.6}\text{K}_{0.4})\text{BiO}_3$  have been reported by two groups: Hundley et al. (1989) ( $1.6 \leq T \leq 40\text{K}$ ;  $H=0, 5, 10\text{T}$ ; Meissner fraction = 0.22; onset  $T_c=27\text{K}$ ) found  $\gamma(0)=0 \pm 0.2 \text{ mJ/mole} \cdot \text{K}^2$  and  $B_3=1.05 \text{ mJ/mole} \cdot \text{K}^4$ . Some of their data are shown in fig. 60. Stupp et al. (1989) ( $1.7 \leq T \leq 91\text{K}$ ;  $H=0$ ; Meissner fraction=0.50; onset  $T_c=27.3\text{K}$ ) found  $\gamma(0)=0.30 \text{ mJ/mole} \cdot \text{K}^2$  from a fit to the data for  $T \leq 3.3\text{K}$ , but there was a noticeable change in the slope of  $C/T$  vs  $T^2$  at that temperature and fits to wider intervals of temperature gave values of  $\gamma(0)$  as low as  $0.20 \text{ mJ/mole} \cdot \text{K}^2$ . Quite apart from the different values reported for the parameters, there is a discrepancy of a factor of 5 in the measured specific heats at 4.5K! There was no observable anomaly in the specific heat at  $T_c$  in either case.

Graebner et al. (1989) developed a modification of the ac technique to obtain a precision of 2-3 in  $10^4$  in specific-heat measurements on a composite sample consisting of 20 single crystals (total mass =  $2.9 \mu\text{g}$ ) of the same material. Only  $\Delta C(T_c)$  and its dependence on magnetic field were measured. As shown in fig. 61, and in sharp contrast with results for other HTSC, the transition remained sharp and moved to lower temperature with increasing field. By using a value of  $N_{bs}(E_F)$  from a band-structure calculation, and an estimate of the volume fraction of superconductivity from a comparison with critical-field measurements, they show that their results are consistent with  $\Delta C(T_c)/\gamma T_c = 1.43$ ,  $\gamma = 1.5 \pm 0.3 \text{ mJ/mole} \cdot \text{K}^2$  and  $\lambda = 0.35 \pm 0.2$ , and cite the result as evidence for weak coupling. [The estimate of  $\Delta C(T_c)$  is somewhat uncertain, because it is only  $\sim 0.1\%$  of the total measured heat capacity, as is the estimate of the volume fraction of superconductivity. Taking them at face value, however, gives a maximum value of  $\Delta C(T_c)/\gamma T_c$ , for  $\lambda = 0$ , of  $\sim 1.9$ .

## 10. Hyperfine Specific Heat

The YBCO samples studied at LBL (Fisher et al. 1988c, 1990) were measured to 0.4K, and in all cases showed a low-temperature upturn in  $C/T$  in zero field. The field dependence of the specific heat shows that these upturns are primarily associated with electronic magnetic moments, but small hyperfine contributions, arising, e.g., from internal fields associated with  $\text{Cu}^{2+}$  localized moments, cannot be ruled out. Measurements were made in 3.5 and 7T, for which fields the hyperfine contribution,  $C_h = D(H)T^2$ , for the Cu nuclei in the applied field can be calculated (contributions from other nuclei are negligible). For every sample, the values of  $D(7\text{T})$  and  $D(3.5\text{T})$  were consistent with an  $H^2$  dependence, showing that internal effective magnetic fields and quadrupole splittings make no large contribution. The values of, e.g.,  $D(7\text{T})$  were never greater than the calculated values, but were in most cases smaller, sometimes by a factor of two. It was assumed that the discrepancies reflected the existence of nuclei for which the relaxation was long compared with the time of measurement. It is known that the nuclei on the two Cu sites have different relaxation times, and extrapolation of the measured relaxation rates (see, e.g., Kitaoka et al. 1988) to low



temperature, ignoring the zero-field contribution of localized electronic moments, which would be effective in 7T, gives values that are of the order of magnitude required by this assumption. The relaxation times should also differ between normal and superconducting regions, and there is a tendency for the larger values of  $C_h$  to be associated with samples with small  $\Delta C(T_c)$  (Fisher et al. 1990).

In zero-field measurements to 0.08K, in a temperature region below that in which the ordering of the electronic moments makes an important contribution, Caspary et al. (1989) observed a  $T^2$  hyperfine contribution. The value of  $D(0)$  was approximately three times greater than their estimate of the quadrupole contribution, and they suggested that  $D(0)$  included a contribution from localized  $\text{Cu}^{2+}$  moments. In 8T, the measured  $C_h$  exceeded that calculated for Cu nuclei in 8T, by approximately 30%. This experiment was designed to accommodate long relaxation times, which could explain the difference between this result and the LBL results mentioned above, but the value of  $D(8T)$  would have to include a contribution from internal effective magnetic fields or quadrupole splitting that was, coincidentally, never observed in the LBL measurements.

In measurements otherwise similar to the zero-field measurements by Caspary et al. (1989), but on YBCO single crystals, and in which relaxation times up to one hour were observed, Lasjaunias et al. (1988) obtained a value of  $D(0)$  that was greater by a factor of two.

For LCO, Gutmiedl et al. (1987) reported a hyperfine contribution to zero-field specific-heat data that corresponded to a hyperfine field of 7.8T on the Cu nuclei, which they cited as evidence for an anti-ferromagnetic state. Wada et al. (1989b) found  $\sim 8.2\text{T}$  in similar measurements. In both cases,  $D(H)$  was evaluated at temperatures below those at which paramagnetic impurities contribute. For four samples studied at LBL (Fisher et al. 1990) the hyperfine fields were 6.6, 7.2, 8.3 and 10.9T, but in these cases the measured specific heat could have included contributions from paramagnetic impurities. In an applied field of 7T, in which there should be no contribution from paramagnetic impurities, the same four samples showed total hyperfine fields of 7T, to within 3%, suggesting that there is no significant internal effective field, and that  $D(0)$  was associated with electronic moments. Wada et al. (1989b) also measured, in zero field, the Cu hyperfine field in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  for  $0 \leq x \leq 0.17$ , and found a gradual decrease with increasing  $x$  in the vicinity of the antiferromagnetic-superconductor transition, and a constant value,  $\sim 1\text{T}$ , in the superconducting samples. For a number of  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  samples measured at LBL (Phillips et al. 1987a), with  $x=0.15$  and  $M=\text{Ca}, \text{Sr}$  or  $\text{Ba}$ , measured in magnetic fields of 3.5 and 7T, the values of  $D(H)$  were equal to the values calculated for the applied field in a few cases, but in many cases they were substantially lower, similar to the behavior noted for YBCO.

Caspary et al. (1989) measured the hyperfine specific heat of BSCCO (2212) in

applied fields to 8T. They interpreted their results in terms of the applied field and an electric-quadrupole contribution of the Bi nuclei. The hyperfine specific heat for a  $(\text{Bi}_{1.66}\text{Pb}_{0.34})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  sample measured in 7T was 25% greater than that calculated for the applied field, but the discrepancy corresponded to the effect of the quadrupole splitting calculated by Caspary et al. (1989) (Fisher et al. 1989b). For five BSCCO samples and one TBCCO sample measured at LBL in 7T (Fisher et al. 1988c) the hyperfine specific heats agreed in every case with the values calculated for the applied field acting on the Bi or Tl nuclei alone -- with no contribution from the Cu nuclei. The discrepancy with the total calculated hyperfine specific heat would be increased if there is a quadrupole interaction. Apart from the sample-to-sample consistency this result is similar to those for YBCO and (L,M)CO.

The hyperfine specific heats of  $(\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_3\text{O}_7$  are described in sec. 4.6.

## 11. Conclusions

For HTSC in general it is clear that fluctuations make significant contributions to the specific-heat anomaly at  $T_c$ . While in principle the fluctuation effects complicate the determination of the discontinuity  $\Delta C(T_c)$ , in practice the ideal value of  $\Delta C(T_c)$ , for fully superconducting samples, seems to be well established for YBCO, and with a lower level of certainty for  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ . The sample-to-sample variation  $\Delta C(T_c)$  can be understood in terms of incomplete transitions to the superconducting state, or possibly gapless superconductivity.

There is no compelling evidence for a low-temperature, zero-field linear term that is intrinsic to the superconducting state in any HTSC. The observed linear terms can be attributed to impurity phases and incomplete transitions to the superconducting state or gapless superconductivity.

There is some indication of strong-coupling effects in the general temperature dependence of the superconducting-state specific heat, but these effects are most clearly evident in the specific heat near  $T_c$  where they suggest extreme strong coupling. However, comparison of band-structure calculations with estimates of the normal-state electronic specific heat give small values of the electron-phonon interaction parameter, that are not compatible with strong phonon coupling. Consistently with other considerations, for example the small isotope effects and high  $T_c$ 's, this suggests the importance of a non-phonon mechanism.

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**Table 1.**  
Abbreviations for HTSC.

Abbreviation	Formula
YBCO	$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$
RBCO	$\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ; R = rare-earth
(Y,R)BCO	$(\text{Y}_{1-x}\text{R}_x)\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ; R = rare-earth
YB(C,M)O	$\text{YBa}_2(\text{Cu}_{3-x}\text{M}_x)\text{O}_{7-\delta}$ ; M = Al, Ga, 3d-element
YBCO (248) <sup>+</sup>	$\text{Y}_2\text{Ba}_4\text{Cu}_8\text{O}_{16}$
LCO	$\text{La}_2\text{CuO}_{4-\delta}$
(L,M)CO	$(\text{La}_{2-x}\text{M}_x)\text{CuO}_{4-\delta}$ ; M = Ca, Sr, Ba
BSCCO (2212)*	$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$
TBCCO (2212)*	$\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$
(R,M)CO; M = C, T	$(\text{R}_{2-x}\text{M}_x)\text{CuO}_4$ ; R = rare-earth; M = Ce, Th

<sup>+</sup> Numbers in parentheses denote cation numbers, for different members of the class, but the 123 is omitted for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

\* Numbers in parentheses denote cation numbers for different members of the class; without numbers in parentheses the abbreviation refers to the class of compounds.

**Table 2.**

Parameters derived by fitting YBCO data over different temperature intervals.  $A_n$  is the coefficient of the  $T^n$  term in eq. 10 for  $C_m$ ;  $\gamma(0)$  is the coefficient of the linear term;  $B_n$  is the coefficient of the  $T^n$  term in eq. 1. See sec. 3.2 for further explanation. Units are in terms of mJ/mole and K.

Temperature Interval	$A_6$	$A_5$	$A_4$	$A_3$	$A_2$	$\gamma(0)$	$B_3$	$B_5$ $\times 10^3$	$B_7$ $\times 10^7$	$B_9$ $\times 10^{10}$	$B_{11}$ $\times 10^{12}$
0.4-30	1.06	-9.7	34.6	-58.7	42.0	7.16	0.254	1.03	1.82	-26.7	1.89
0.6-20		3.9	23.1	-48.7	38.6	7.24	0.249	1.12	-4.39	-8.3	
0.8-15			17.3	-50.2	42.3	6.93	0.266	0.92	0.22		
1.2-10				24.4	32.1	7.19	0.254	1.03			
2.2-5					22.6	7.03	0.284				

**Table 3.**

Initial slopes of  $H_{c2}$ , as measured on single crystals of YBCO.  $\theta$  is the angle between H and the c-axis, i.e., for  $\theta = 0$ ,  $H \parallel c$ ; for  $\theta = \pi/2$ ,  $H \perp c$ . Units are T/K.

Reference	$dH_{c2}(0)/dT$	$dH_{c2}(\pi/2)/dT$
Oda et al. (1988)	-0.56	-3.3
Welp et al. (1989)	-1.9	-10.5
Nakao et al. (1989)	-1.0	-4.0
Bauhofer et al. (1989)	-0.5	-3.5

**Table 4.**

Values of  $\gamma(0)$ ,  $\Delta C(T_c)/T_c$  and  $f_s$  for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . Units are  $\text{mJ}/\text{mole} \cdot \text{K}^2$ .

$\gamma(0)$	$\Delta C(T_c)/T_c$	$f_s$	Reference
$x=0.15$			
0.6	$13 \pm 1^*$	0.9	Wada et al. 1989a
1.54	$9.9 \pm 0.5$	0.65	Phillips et al. 1987a
1.8	$6 \pm 2$	0.59	Feng et al. 1988
1.9	$7 \pm 0.5^*$	0.57	Loram et al. 1989
2	$10 \pm 2$	0.55	Ramirez et al. 1987b
3.8	$3.1 \pm 0.5$	0.14	Amato et al. 1990b
$x=0.30$			
8.4 (4.5) <sup>+</sup>	-	0	Loram et al. 1989
8.7 (4.35) <sup>+</sup>	-	0	Amato et al. 1990b
9.0 (4.2) <sup>+</sup>	-	0	Wada et al. 1989a

\* Errors estimated from the scatter of the data.

+ Values of  $\gamma(0)$  in parentheses have been scaled to  $x=0.15$  from those observed at  $x=0.30$  by using the empirical relation  $\gamma/x=28$   $\text{mJ}/\text{mole} \cdot \text{K}^2$  (Loram et al. 1989).

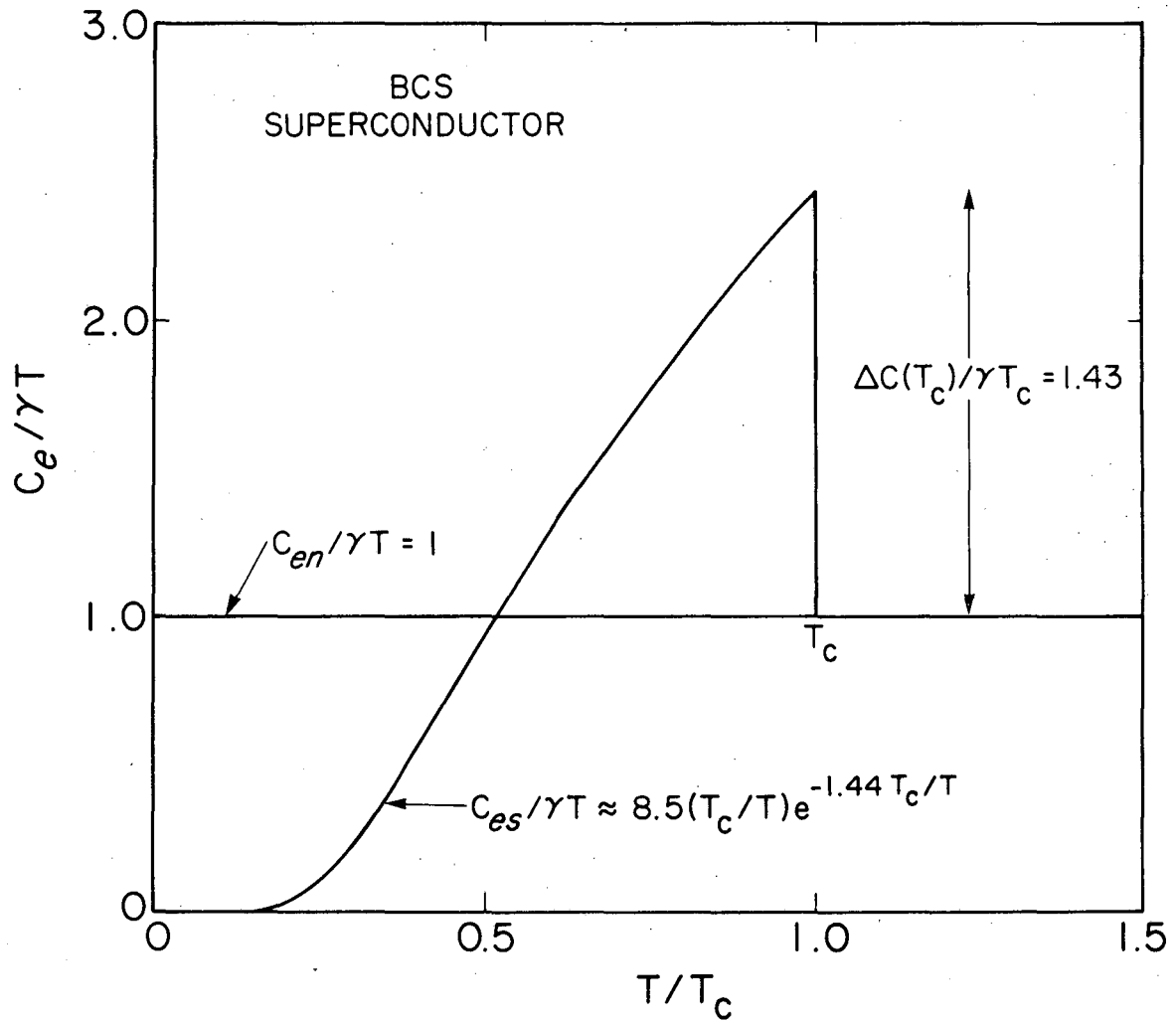


Figure 1. The electronic specific heat of a BCS superconductor in the weak-coupling limit.



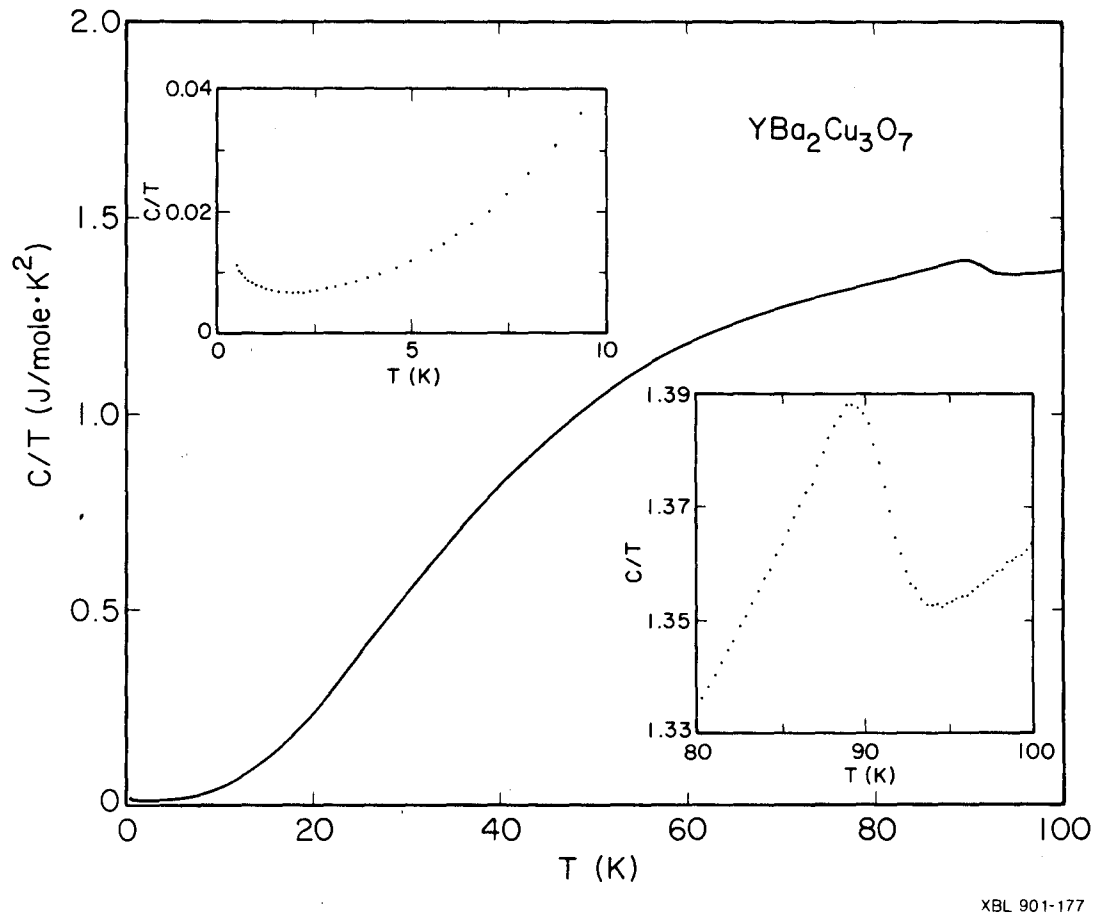
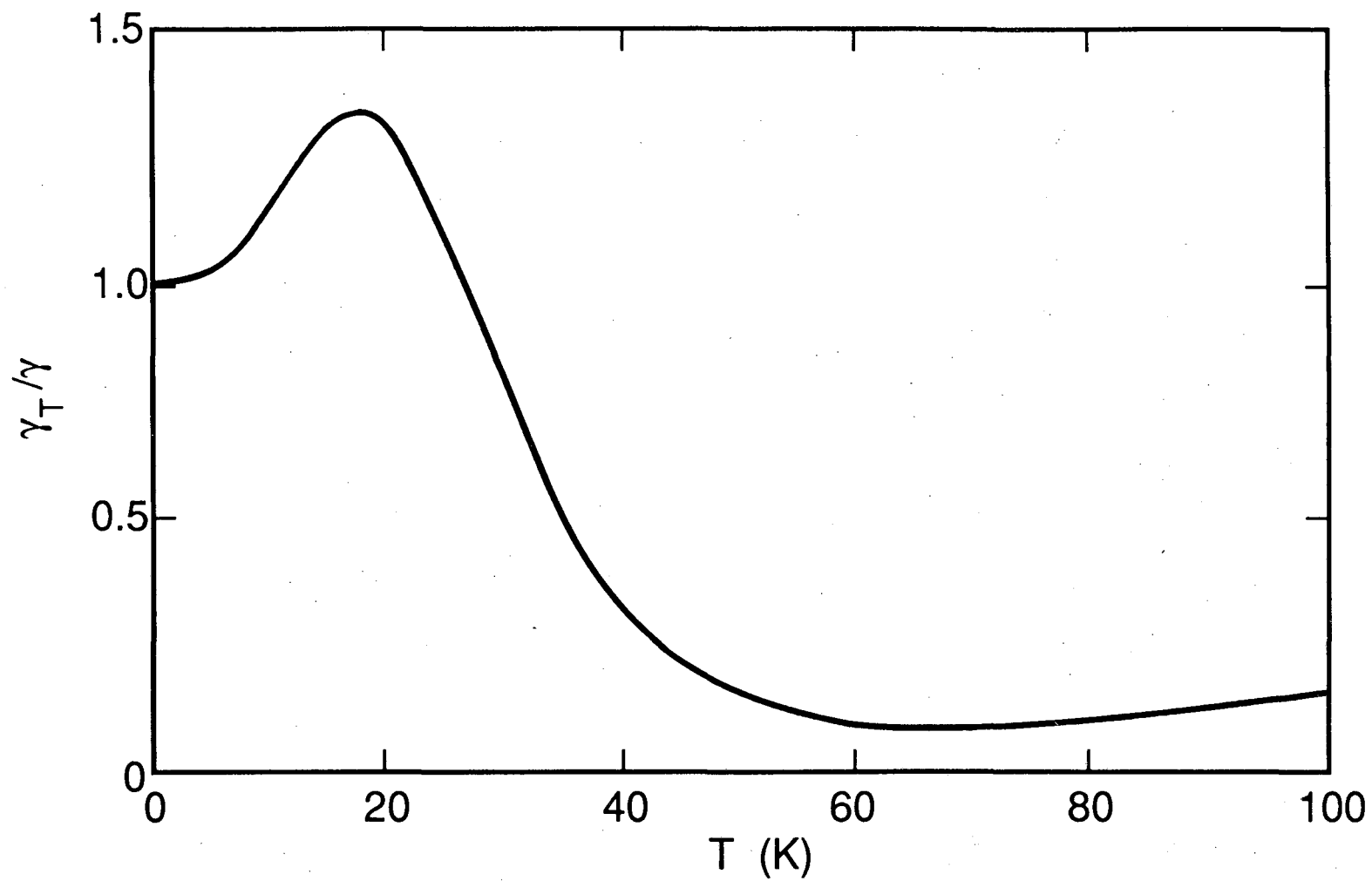
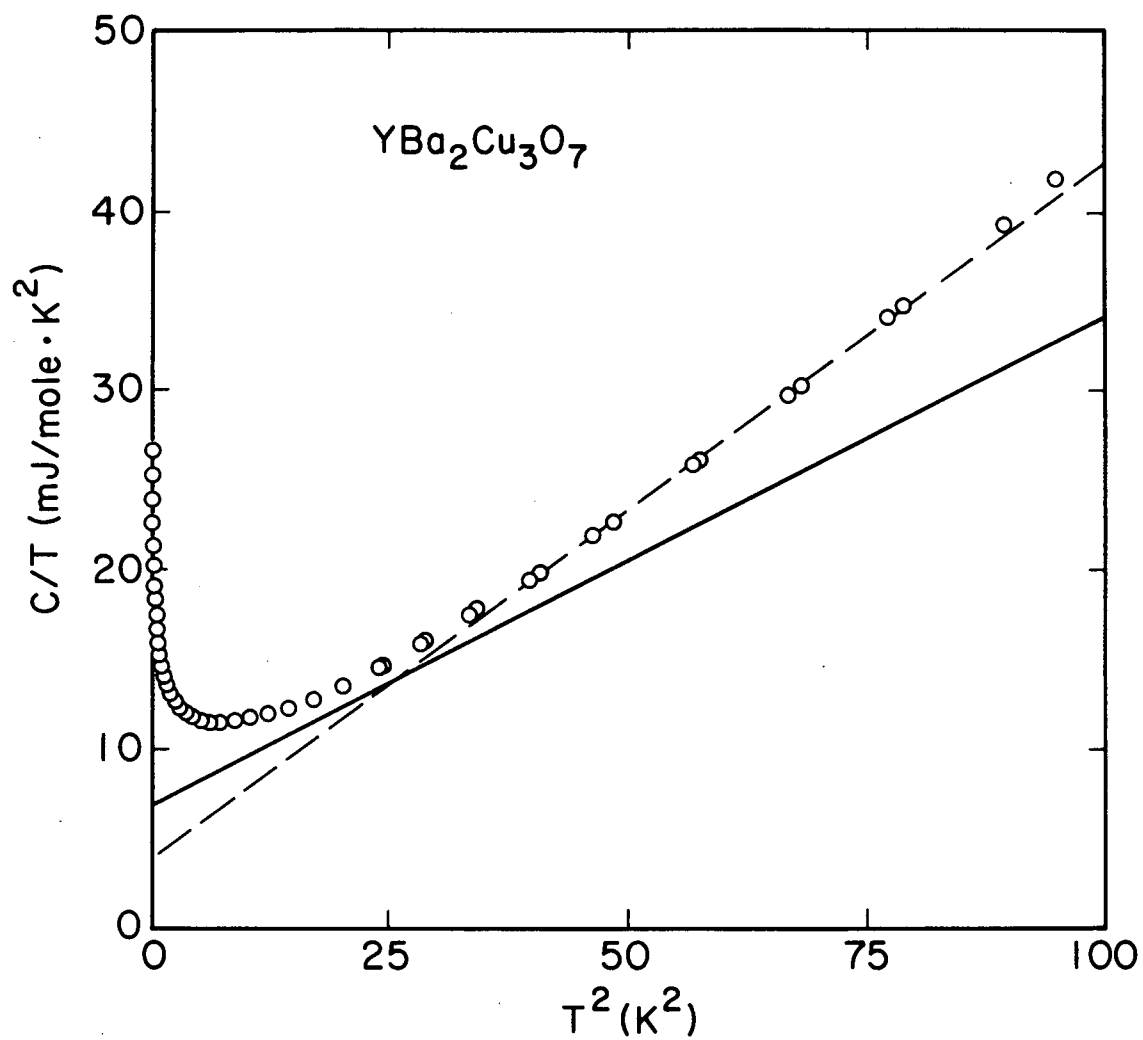


Figure 2. The total specific heat of a typical YBCO sample. The insets show actual data at low temperatures and in the vicinity of  $T_c$  (Fisher et al. 1990).



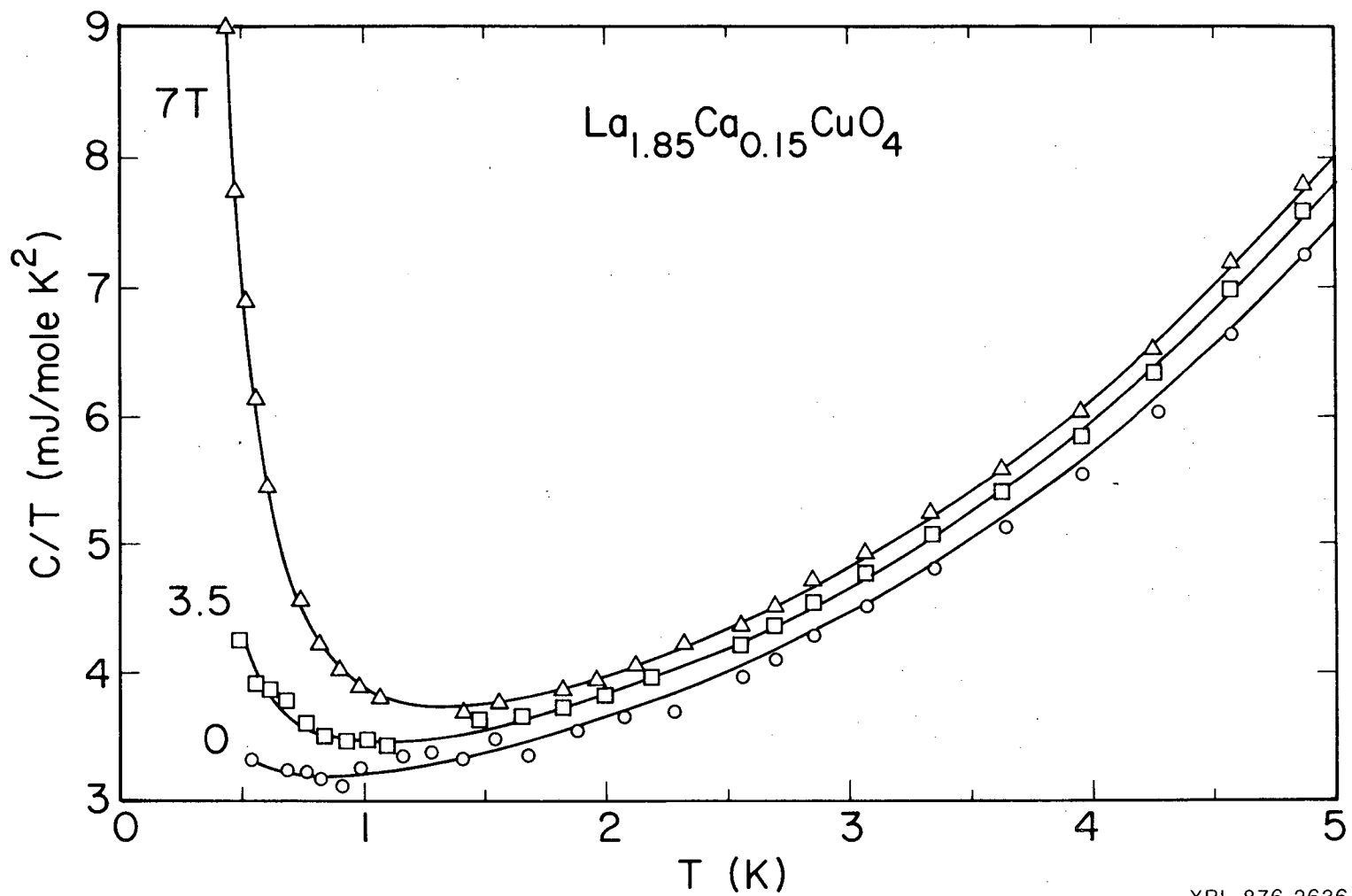
XBL 901-327

Figure 3. An example of the predicted temperature dependence of  $\gamma_T$ . The temperature scale is appropriate to (L,M)CO (Kresin 1990).



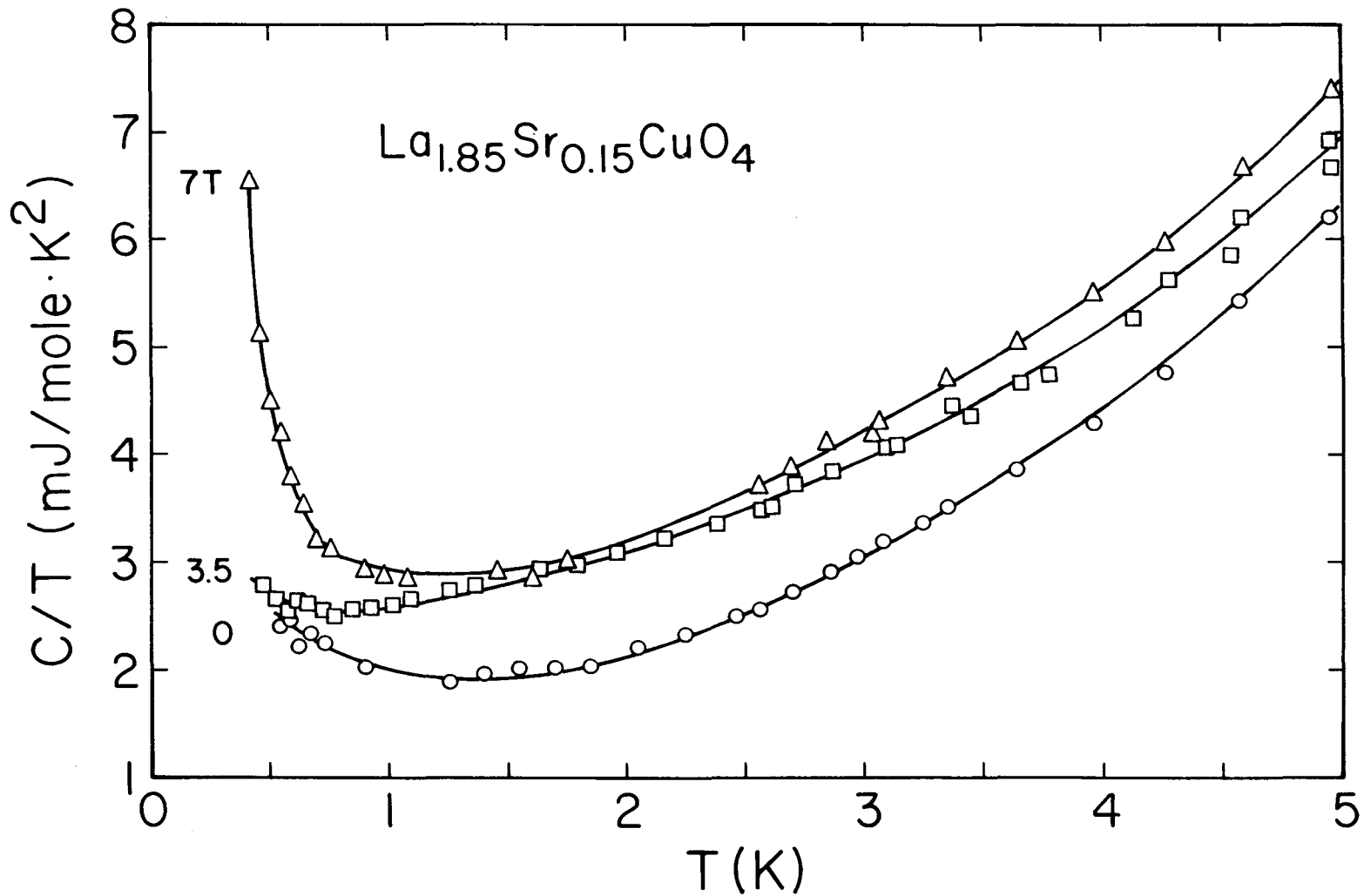
XBL 886-2091

Figure 4. The dashed and solid lines represent the values of  $\gamma(0)$  and  $B_3$  for a YBCO sample derived by different methods, as described in the text (Fisher et al. 1988a).



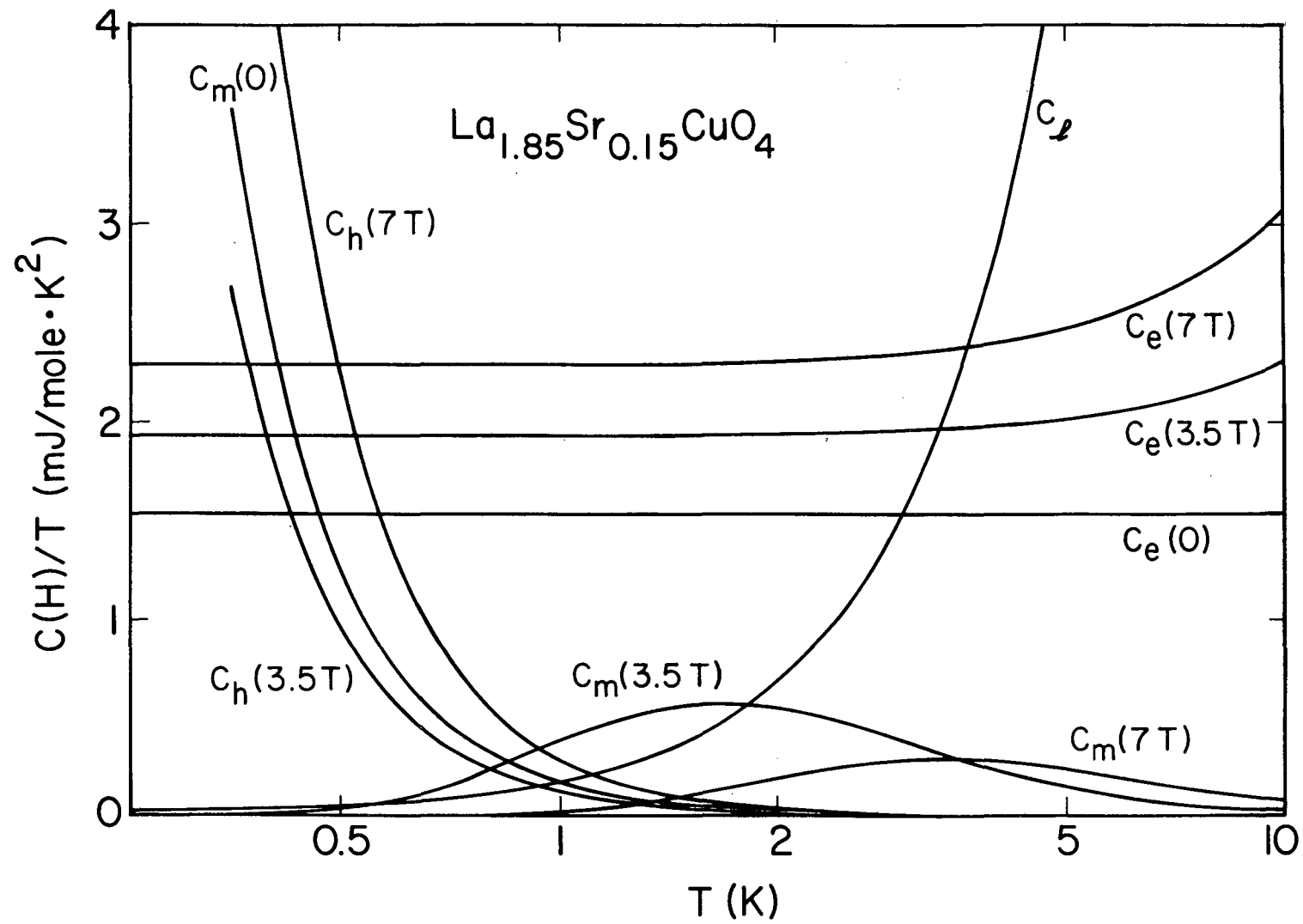
XBL 876-2636

Figure 5. Data for an (L,C)CO sample with a low concentration of magnetic moments in 0, 3.5 and 7T (Fisher et al. 1988a).



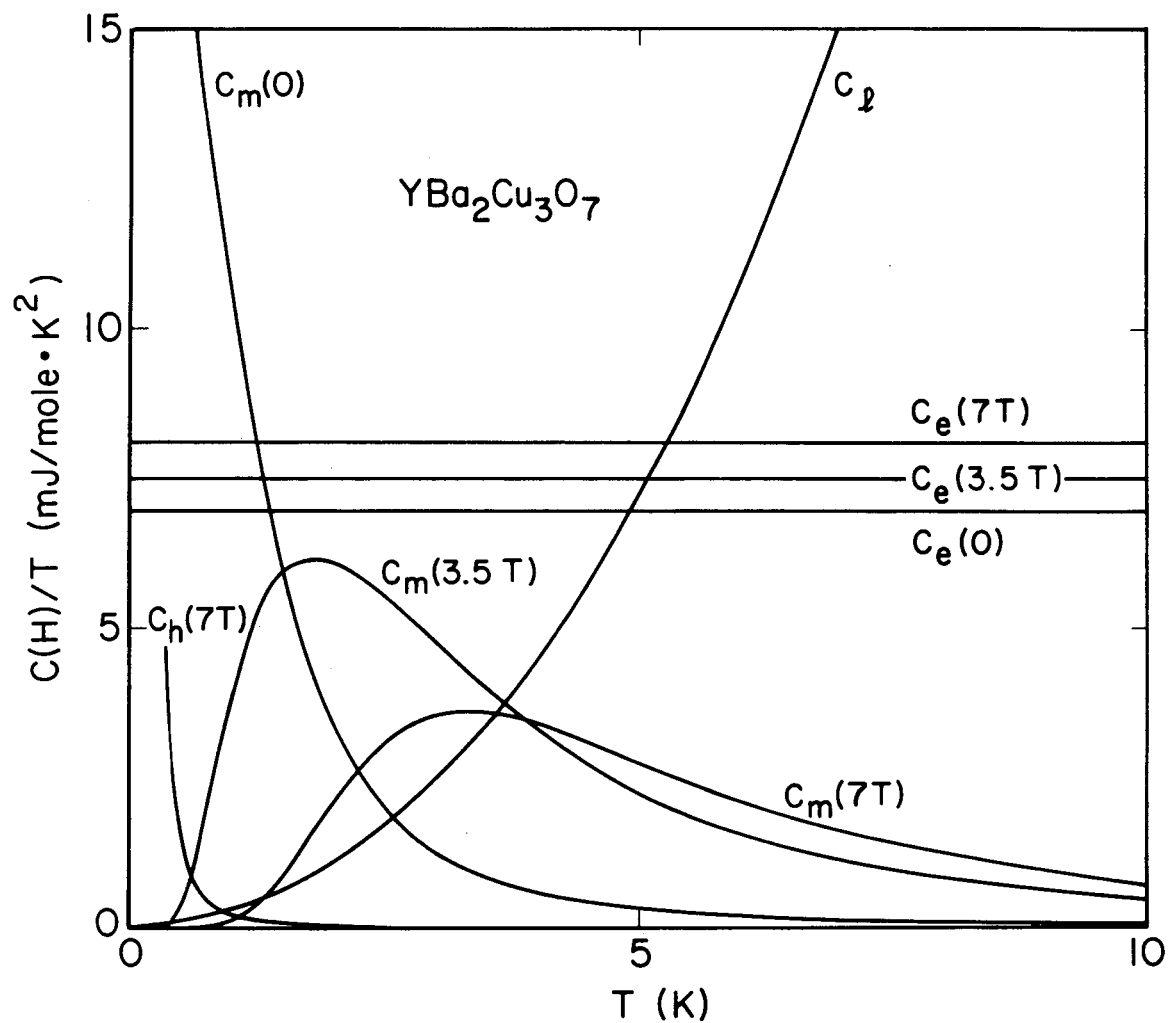
XBL 876-2634

Figure 6. Data for an (L,S)CO sample with a higher concentration of magnetic moments than the sample represented in fig. 5 (Fisher et al. 1988a). The curves correspond to analytical fits to the component contributions to the specific heat.



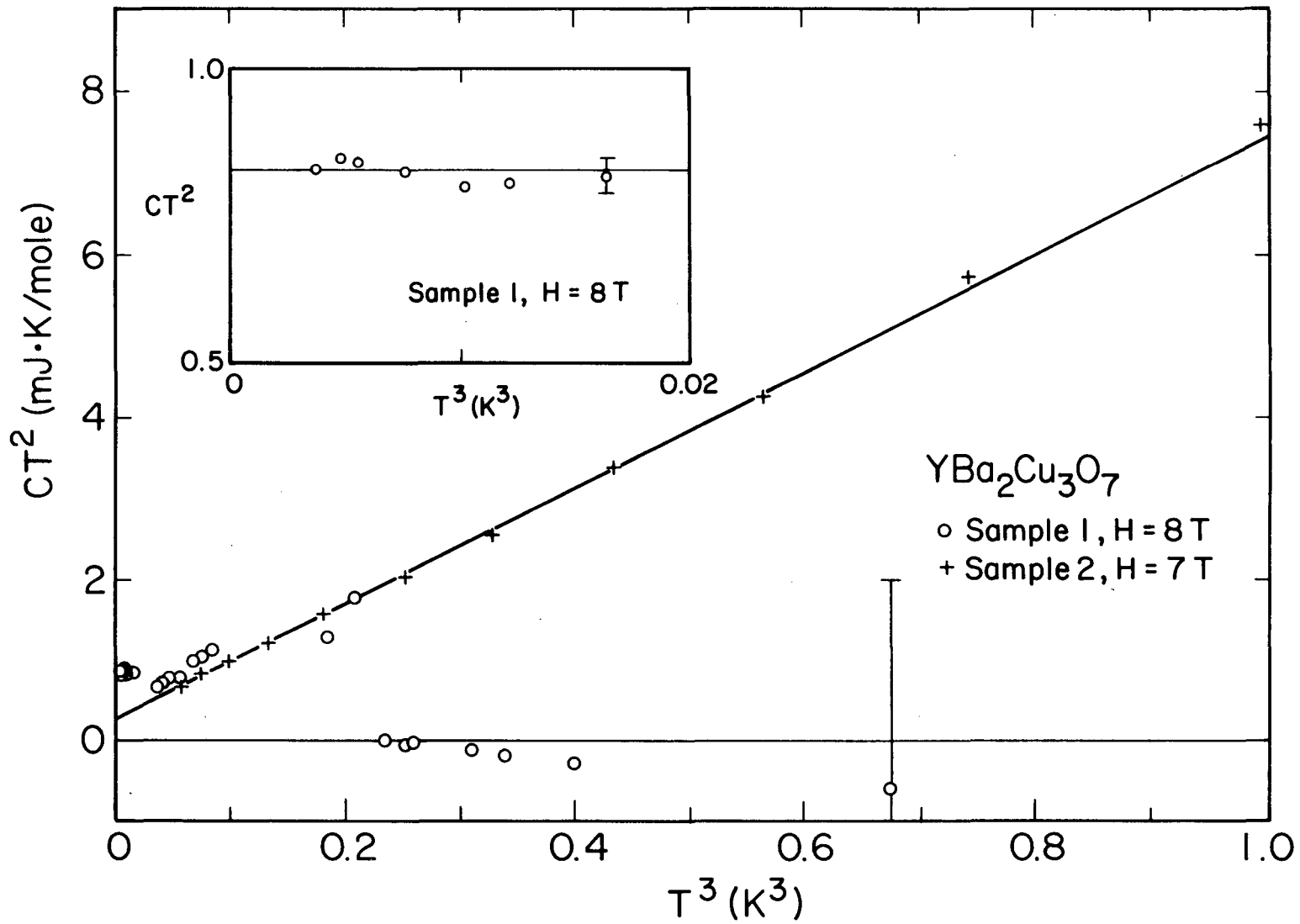
XBL 879-3963

Figure 7. The component contributions to the total specific heat curves in fig. 6 (Phillips et al. 1987a).



XBL 882-491

Figure 8. Components of the specific heat of a YBCO sample in 0, 3.5 and 7T (Fisher et al. 1988b).



XBL 902-347

Figure 9. Low temperature data for two YBCO samples, sample 2 (Fisher et al. 1990) and sample 1 (Caspary et al. 1989).



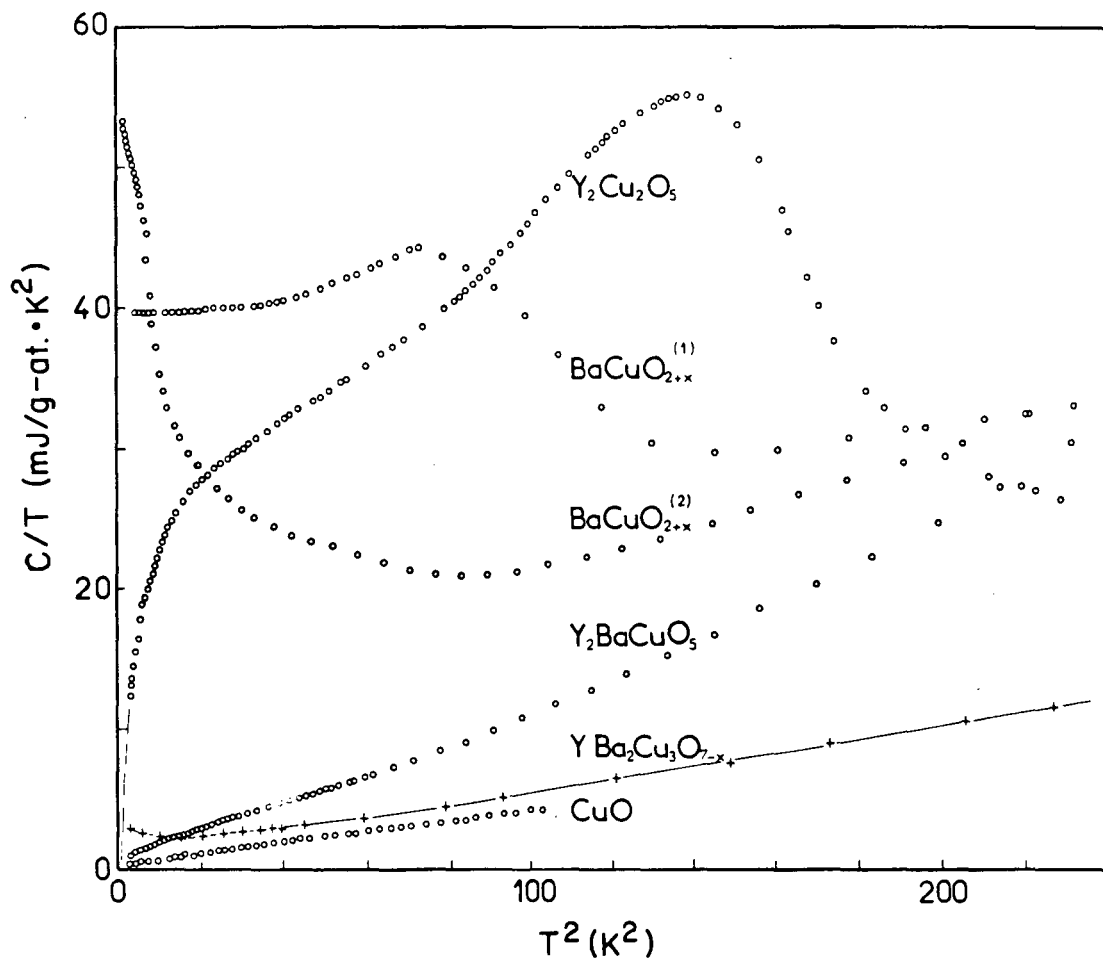
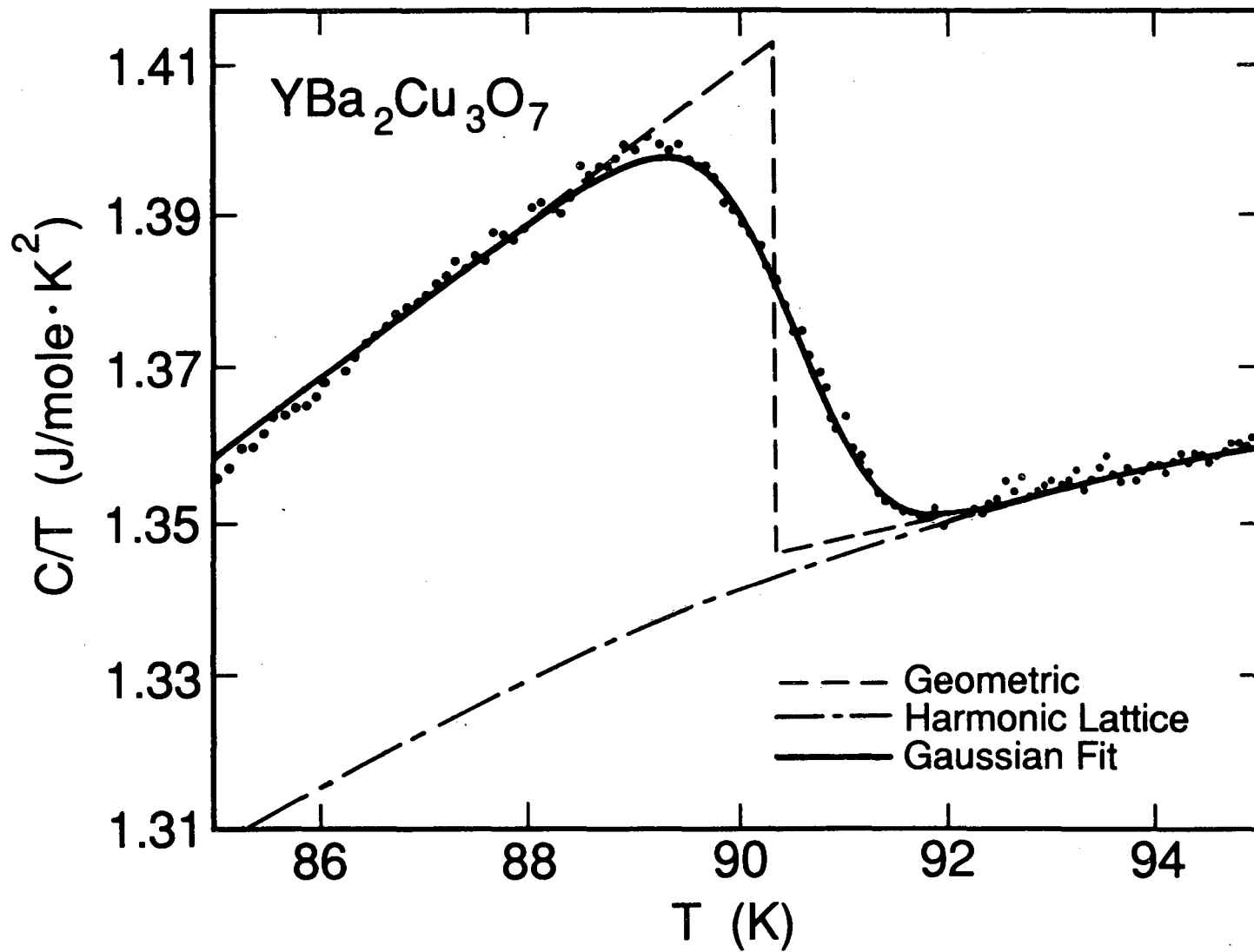
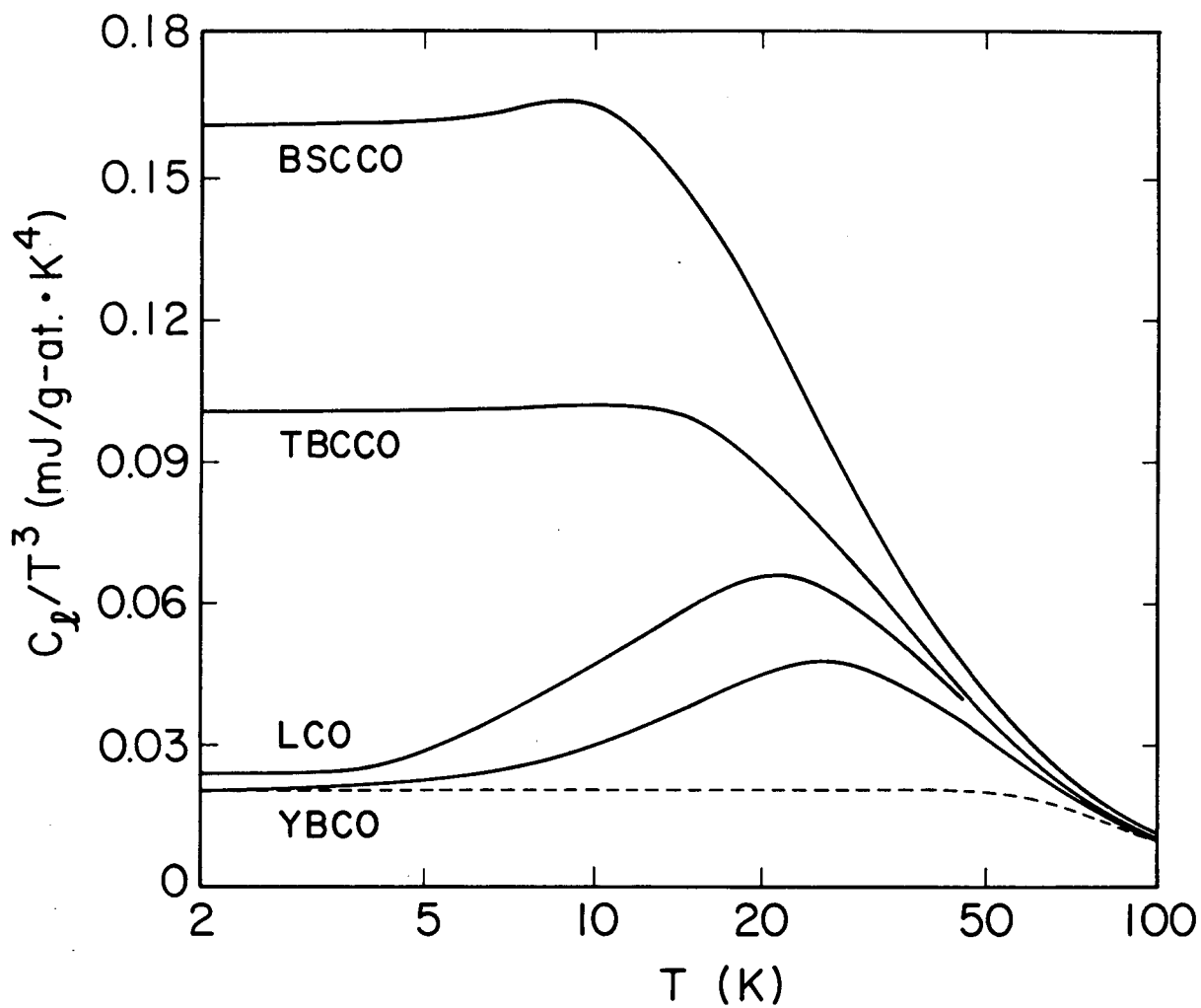


Figure 10. Specific heats of several compounds that might be present as impurities in YBCO compared with that of YBCO (Kuentzler et al. 1988a). The two samples of  $\text{BaCuO}_2$  were prepared under different conditions.



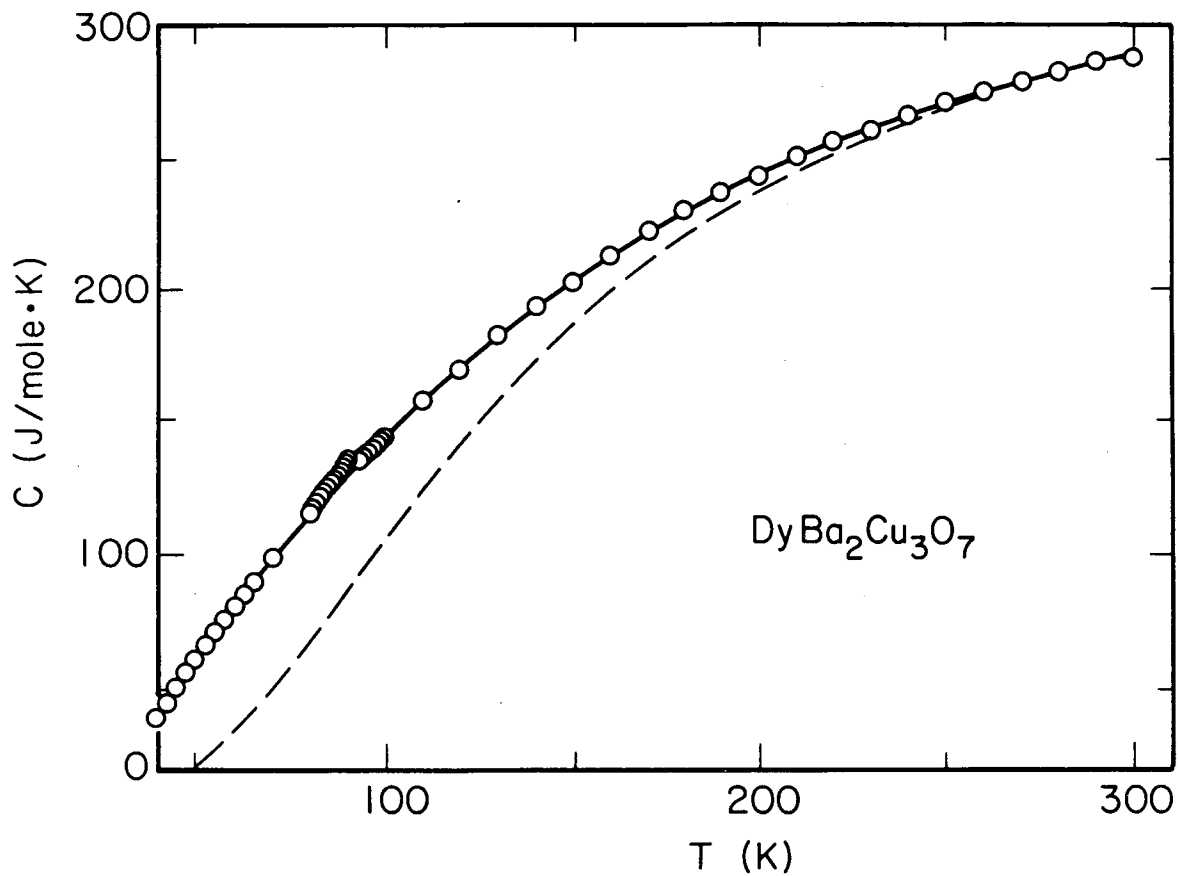
XBL 901-63

Figure 11. Specific heat data for YBCO near  $T_c$  with several constructions used to determine  $\Delta C(T_c)$  as described in the text (Fisher et al. 1990).



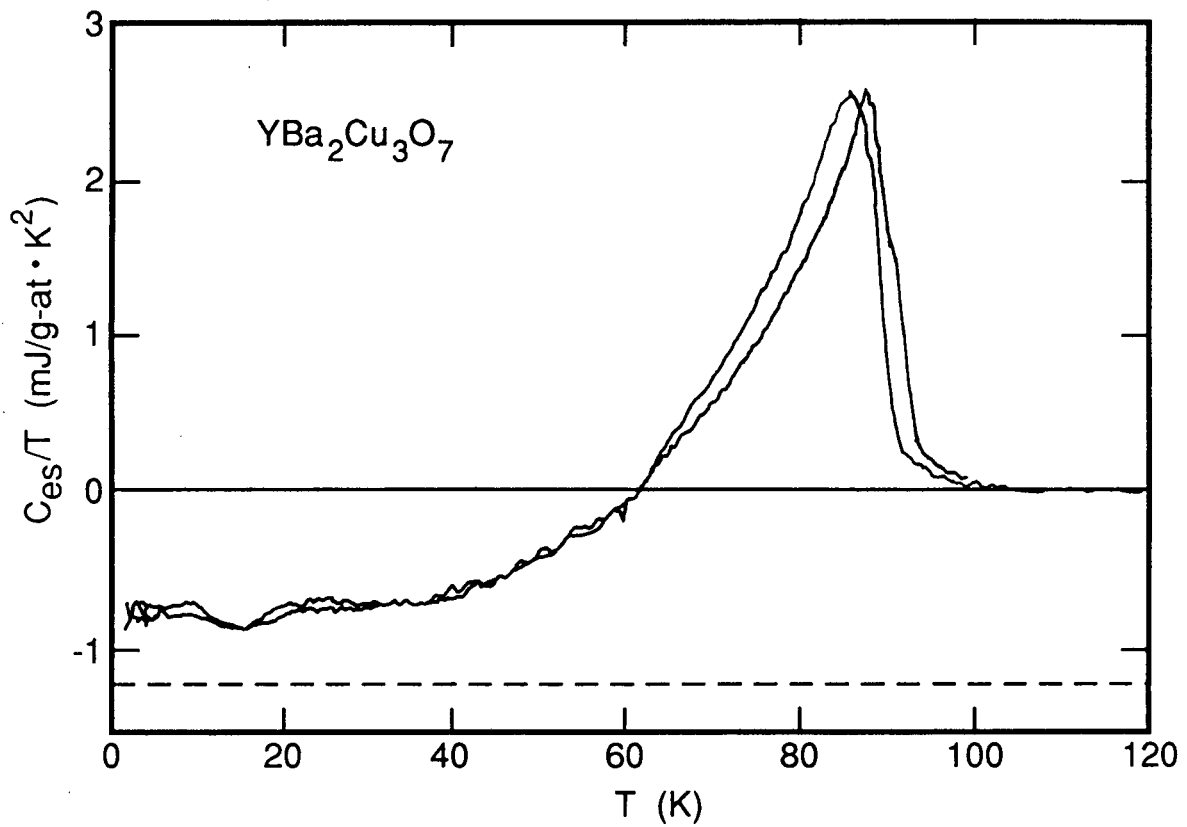
XBL 885-1818B

Figure 12. Lattice specific heats of YBCO, LCO, TBCCO and BSCCO (Fisher et al. 1988c). The dashed curve represents the Debye specific heat function for  $\theta_0 = 450\text{K}$ , the value for YBCO.



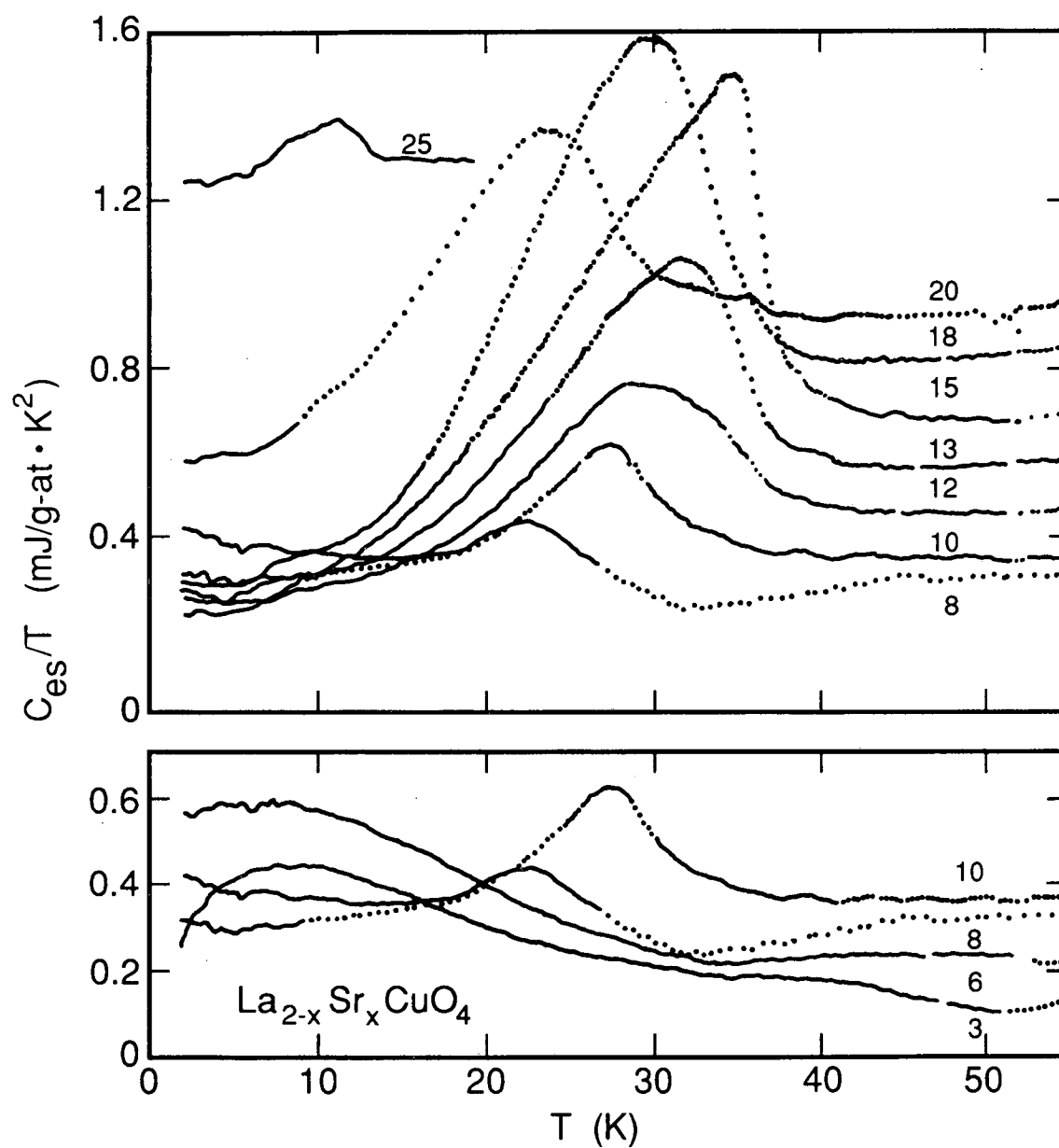
XBL 888-2997 A

Figure 13. Specific heat of  $\text{DyBa}_2\text{Cu}_3\text{O}_7$ . The solid curve represents a fit by the high-temperature harmonic lattice expression plus appropriate terms for anharmonic and electronic contributions. (Points in the vicinity of  $T_c$  were omitted from the fit.) The dashed curve is a Debye function based on  $\theta_{300}=547\text{K}$ . (Gordon et al. 1989a; data from Atake et al. 1988).



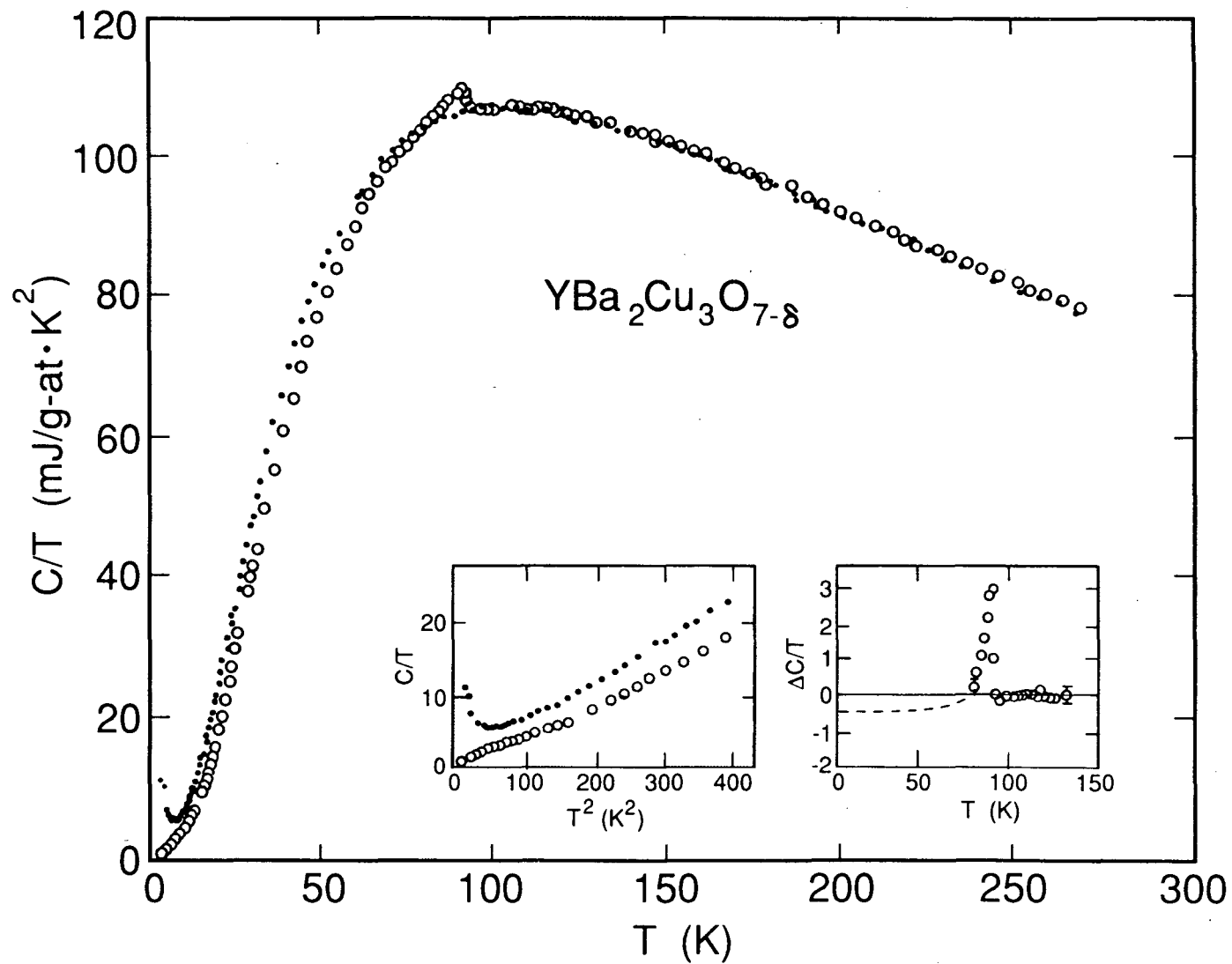
XBL 901-162

Figure 14.  $C_{es}$  for two YBCO samples (Loram and Mirza 1988).



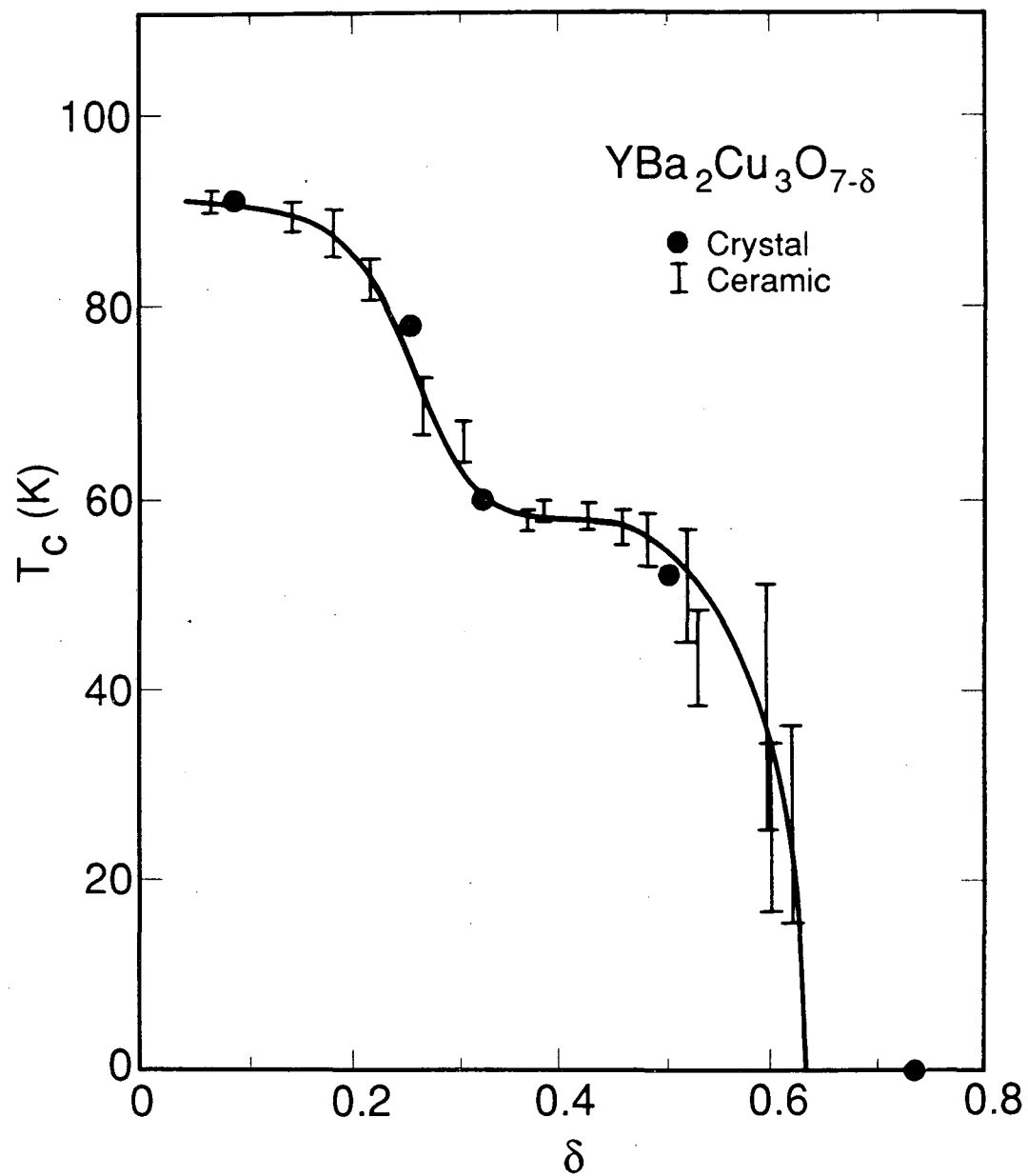
XBL 901-161

Figure 15.  $C_{es}$  for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  samples (Loram et al. 1989). The numbers labelling the data are  $100x$ .



XBL 901-171

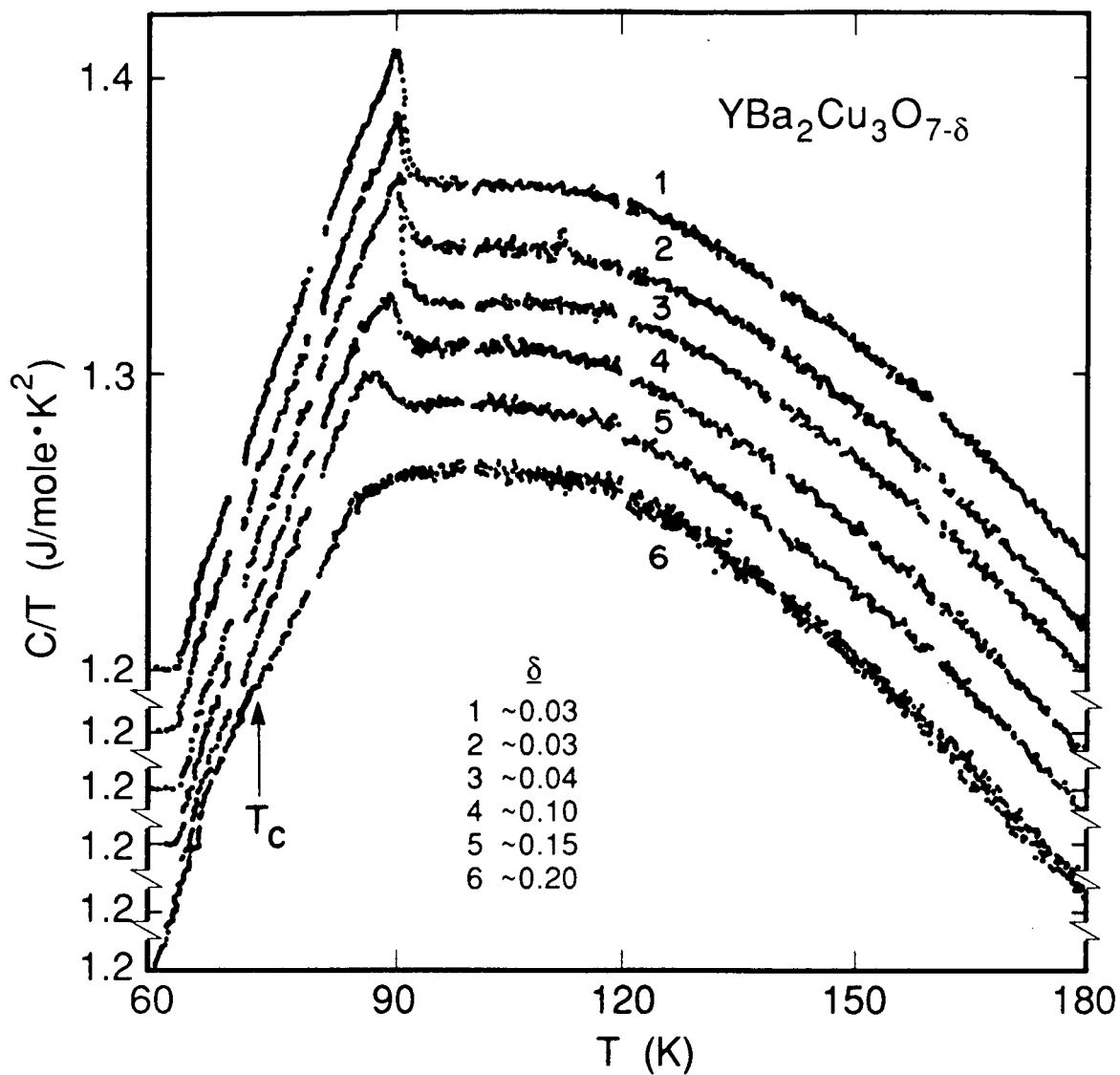
Figure 16. Specific heats of a YBCO sample before (o) and after (•) fast-neutron irradiation (Davydov et al. 1988).



XBL 901-68

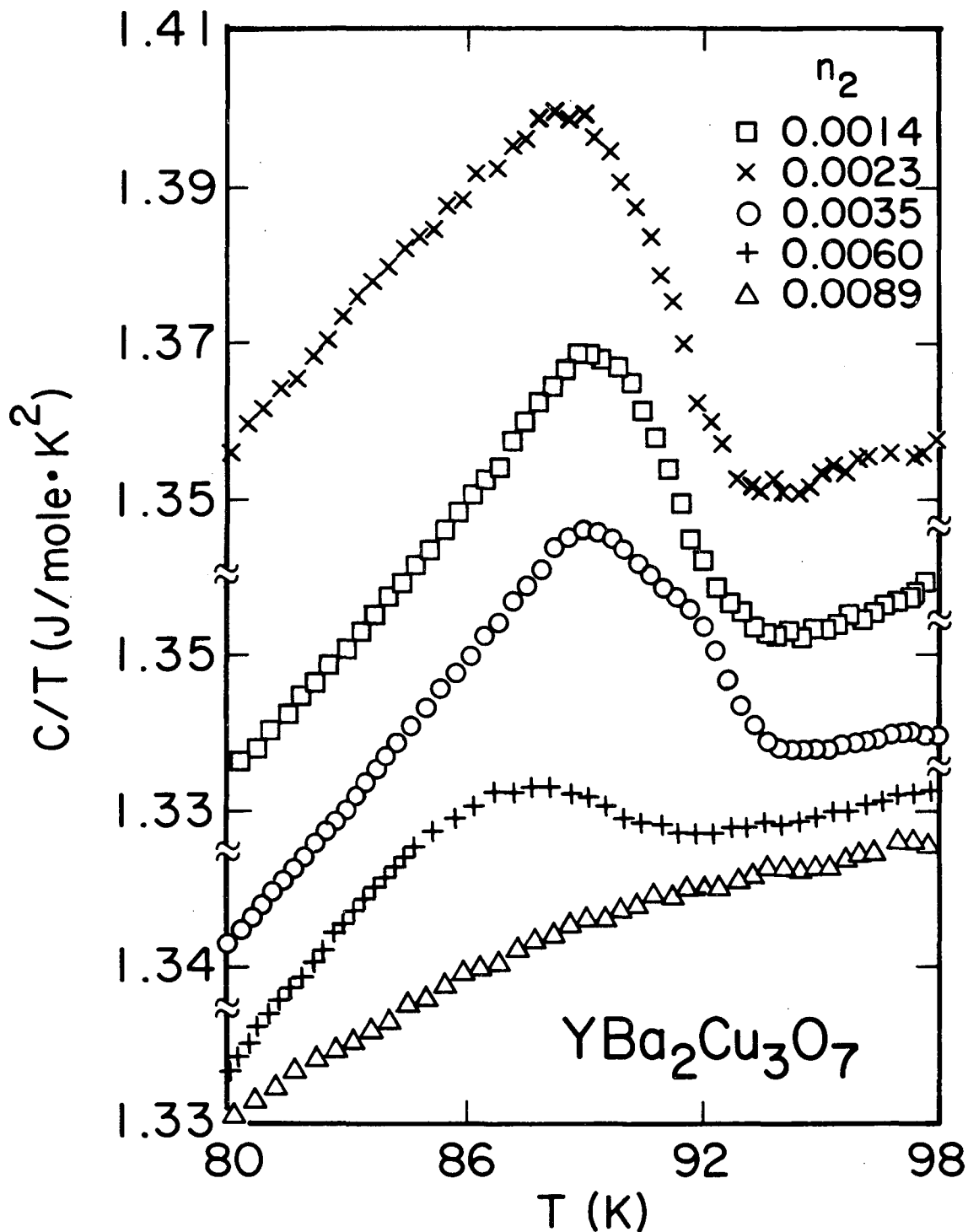
Figure 17.  $T_c$  for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , both single-crystal and polycrystalline samples, as a function of  $\delta$  (Veal et al. 1989).





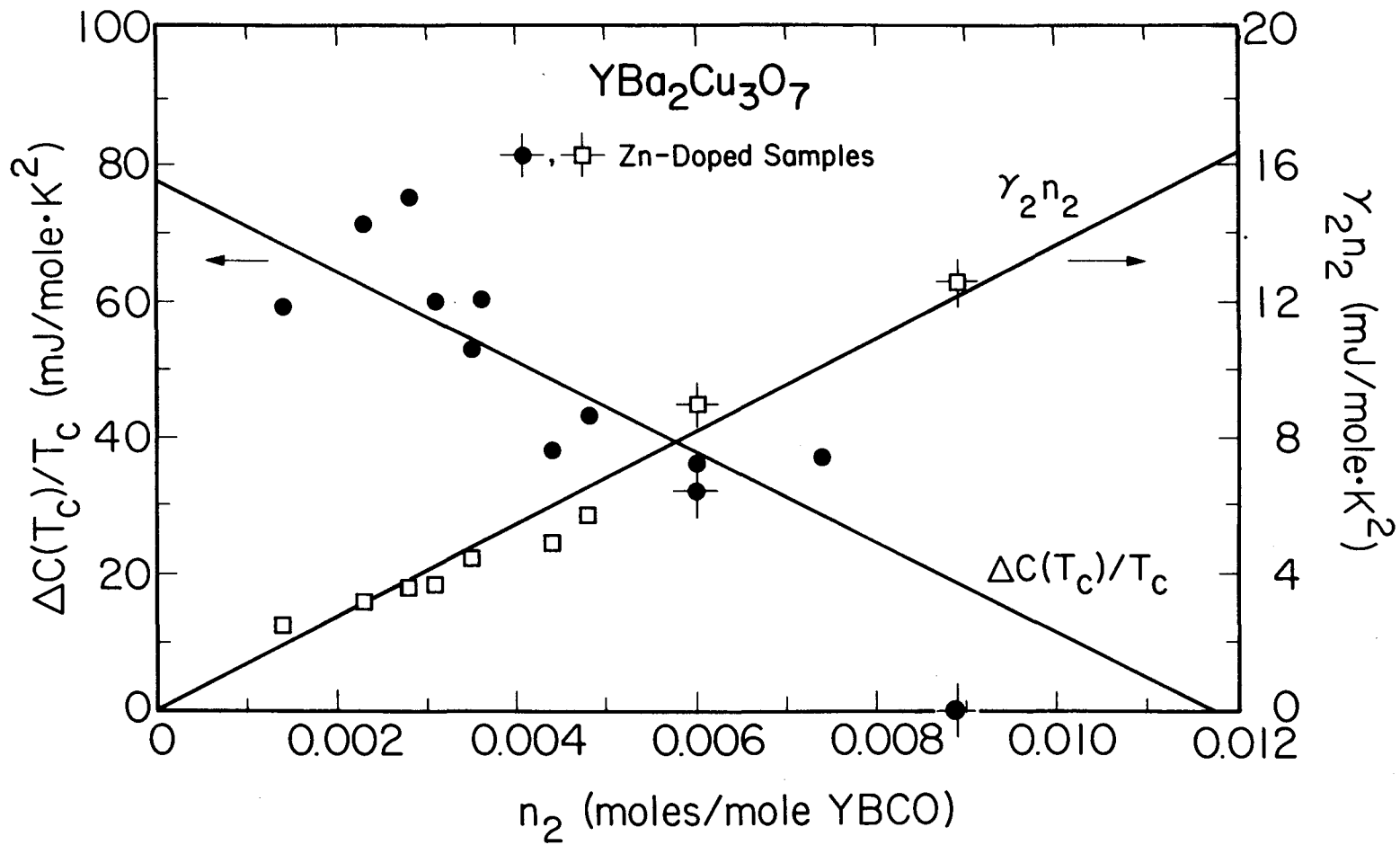
XBL 901-160

Figure 18. Specific heats of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples with different oxygen contents (Junod et al. 1989c).



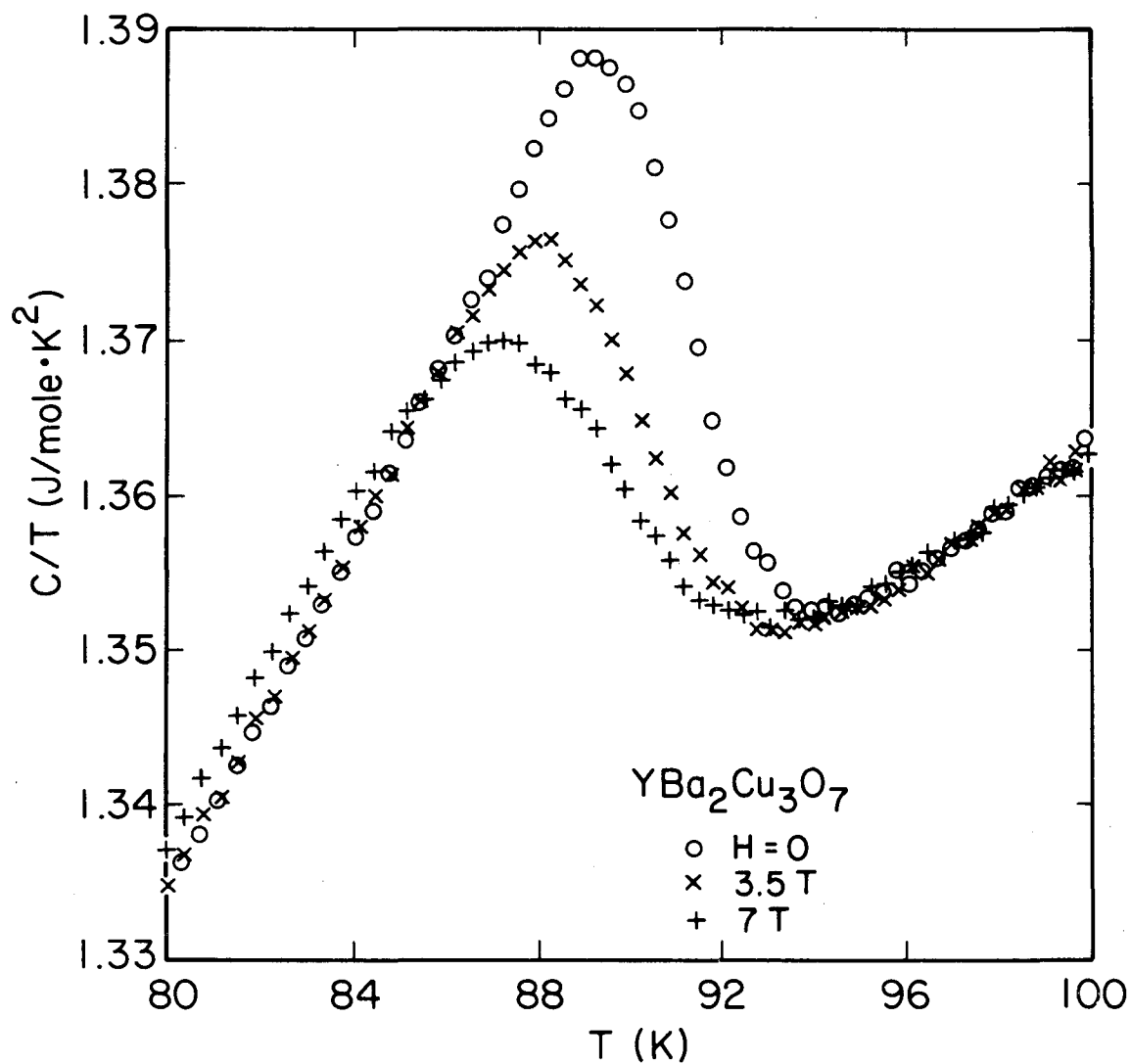
XBL 8911-4190 A

Figure 19. Specific heats in the vicinity of  $T_c$  for YBCO samples with different concentrations of  $\text{Cu}^{2+}$  moments on the YBCO lattice (Phillips et al. 1990).



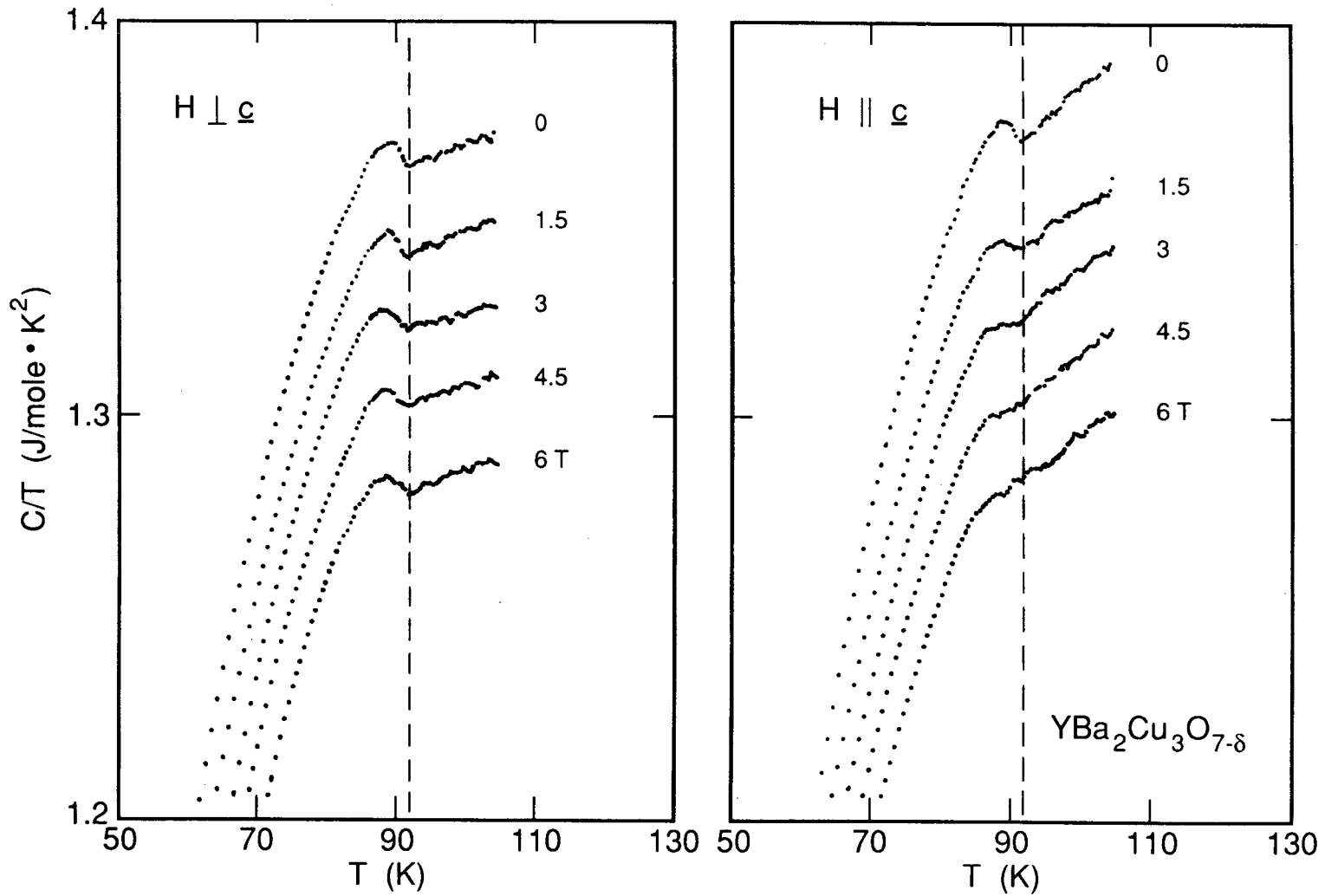
XBL 8911-4187 A

Figure 20. Correlation of  $\Delta C(T_c)/T_c$  with  $n_2$ , the concentration of  $\text{Cu}^{2+}$  moments on the YBCO lattice (Phillips et al. 1990).



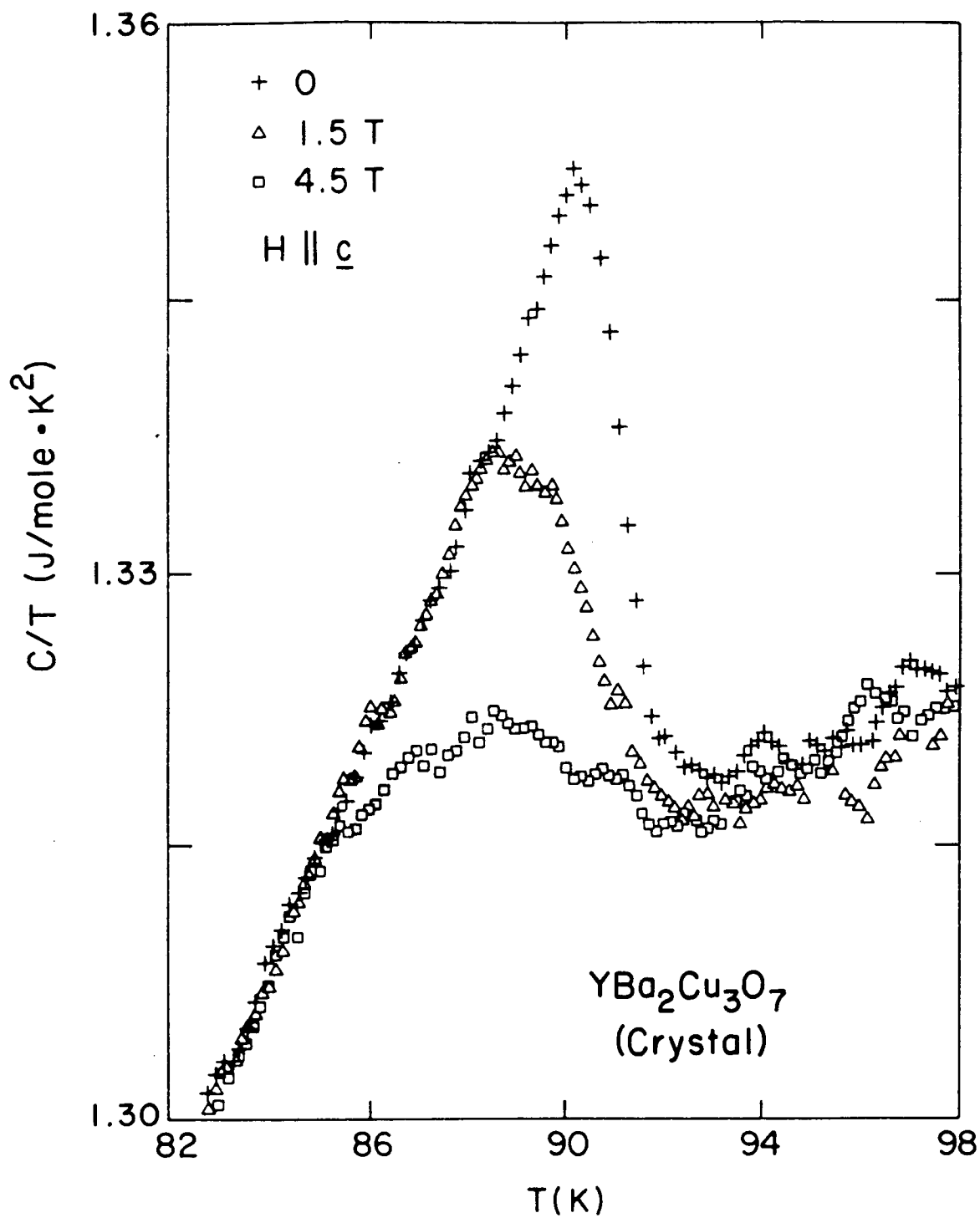
XBL 901-172

Figure 21. The magnetic field dependence of the specific heat anomaly at  $T_c$  for polycrystalline YBCO (Fisher et al. 1990).



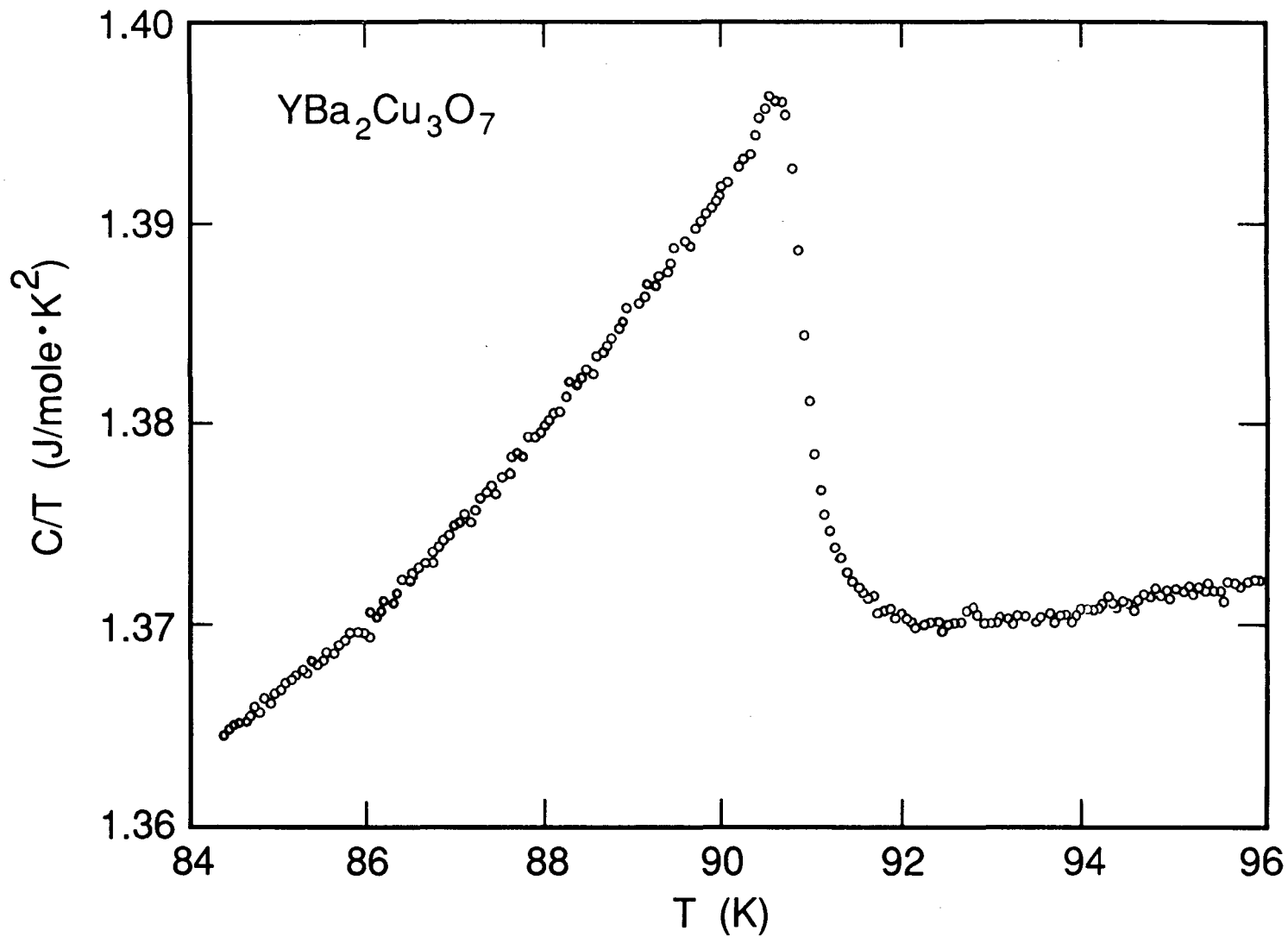
XBL 901-326A

Figure 22. The magnetic field dependence of the specific heat anomaly at  $T_c$  for a melt-textured (90% aligned, see text) polycrystalline YBCO sample (Bonjour et al. 1990).



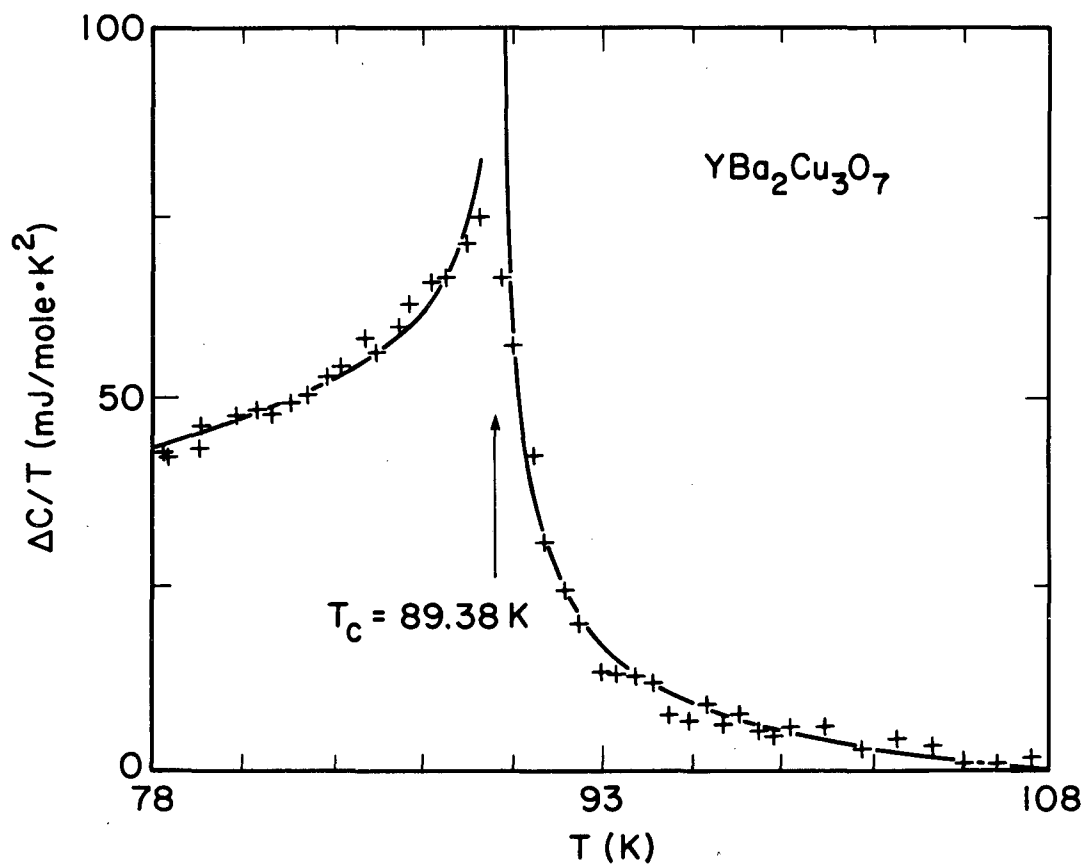
XBL 901-325A

Figure 23. The magnetic field dependence of the specific heat anomaly at  $T_c$  for a single-crystal YBCO sample (Salamon et al. 1988).



XBL 901-74

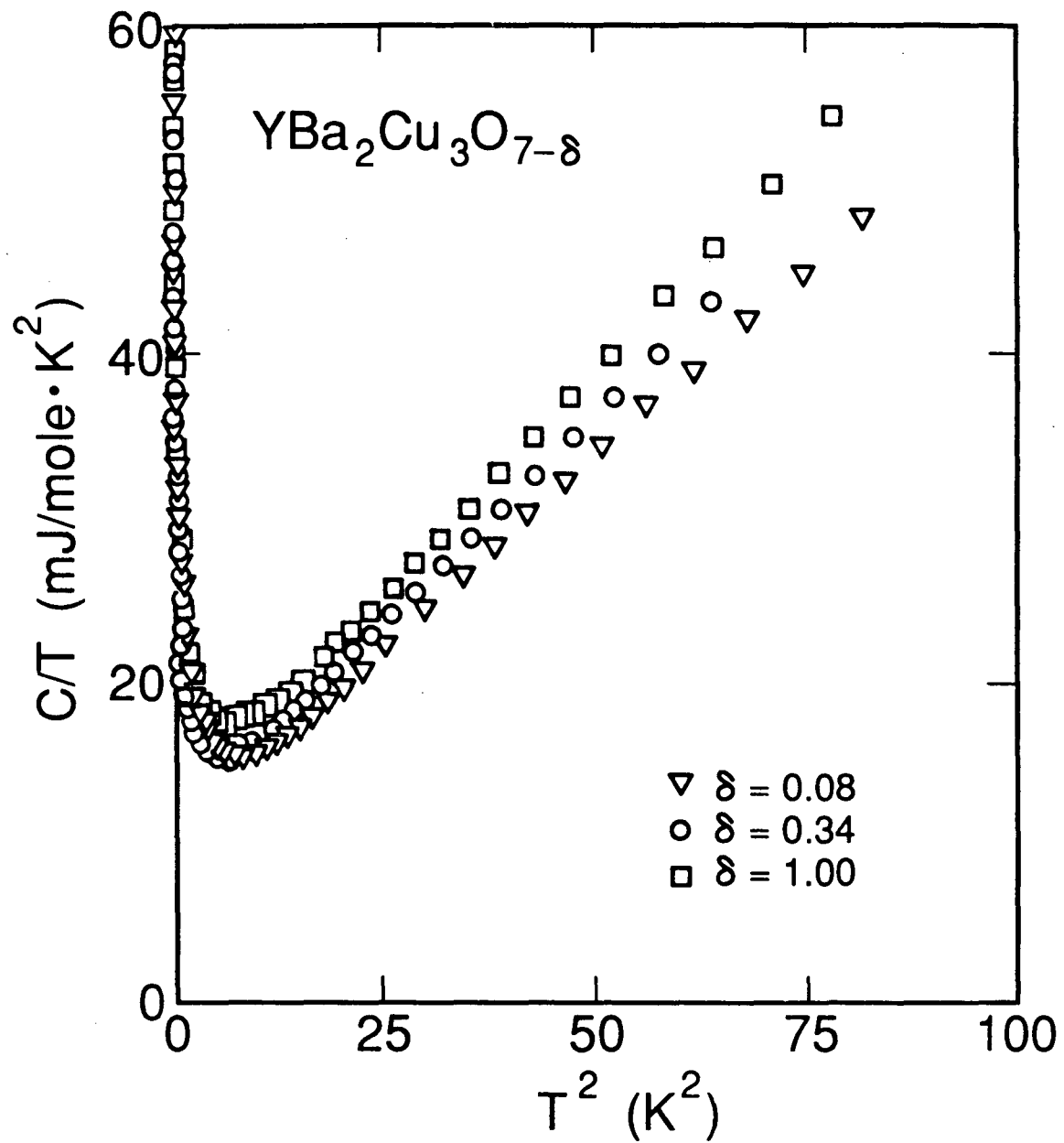
Figure 24. Specific heat of polycrystalline YBCO showing the positive curvature of  $C/T$  just below  $T_c$  that is characteristic of fluctuation effects [Laegreid et al. 1989a (same data as Laegreid et al. 1989b)].



XBL 896-2282

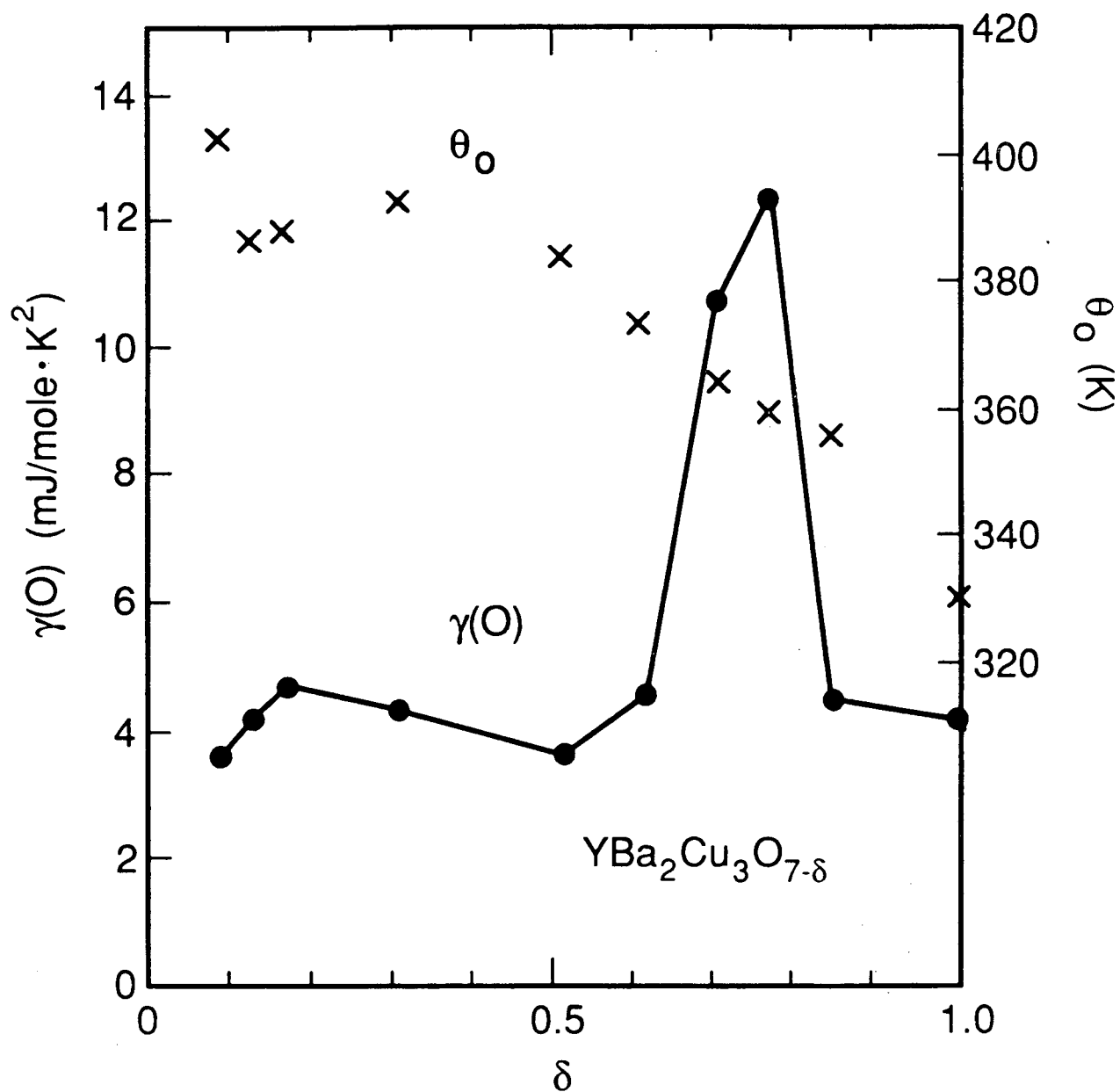
Figure 25. Specific heat of polycrystalline YBCO. The curves represent a fit by the expression for the fluctuation contribution given in the text (Gordon et al. 1989b).





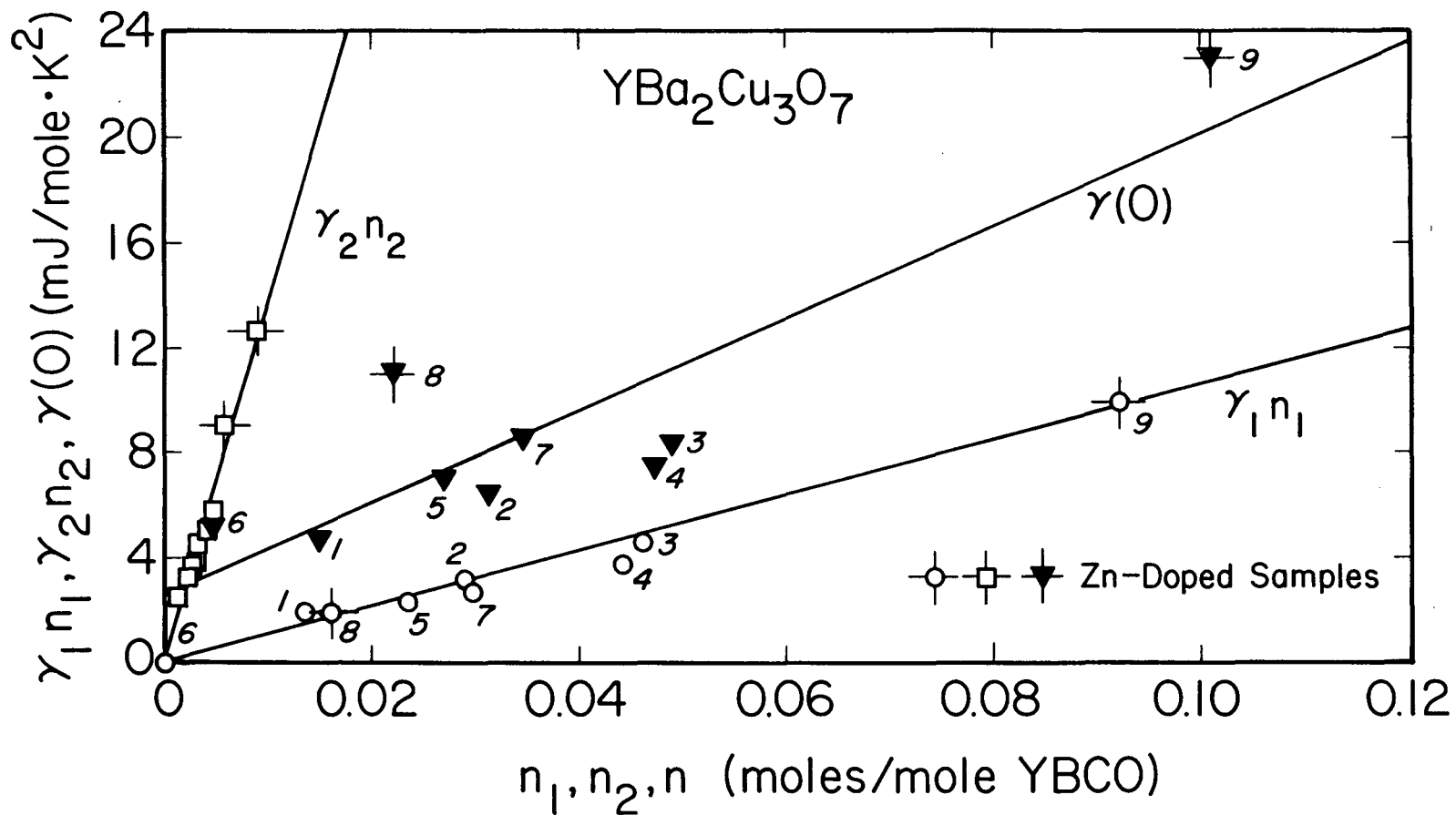
XBL 901-66

Figure 26. Specific heats of YBCO samples with different oxygen contents (Ayache et al. 1987a).



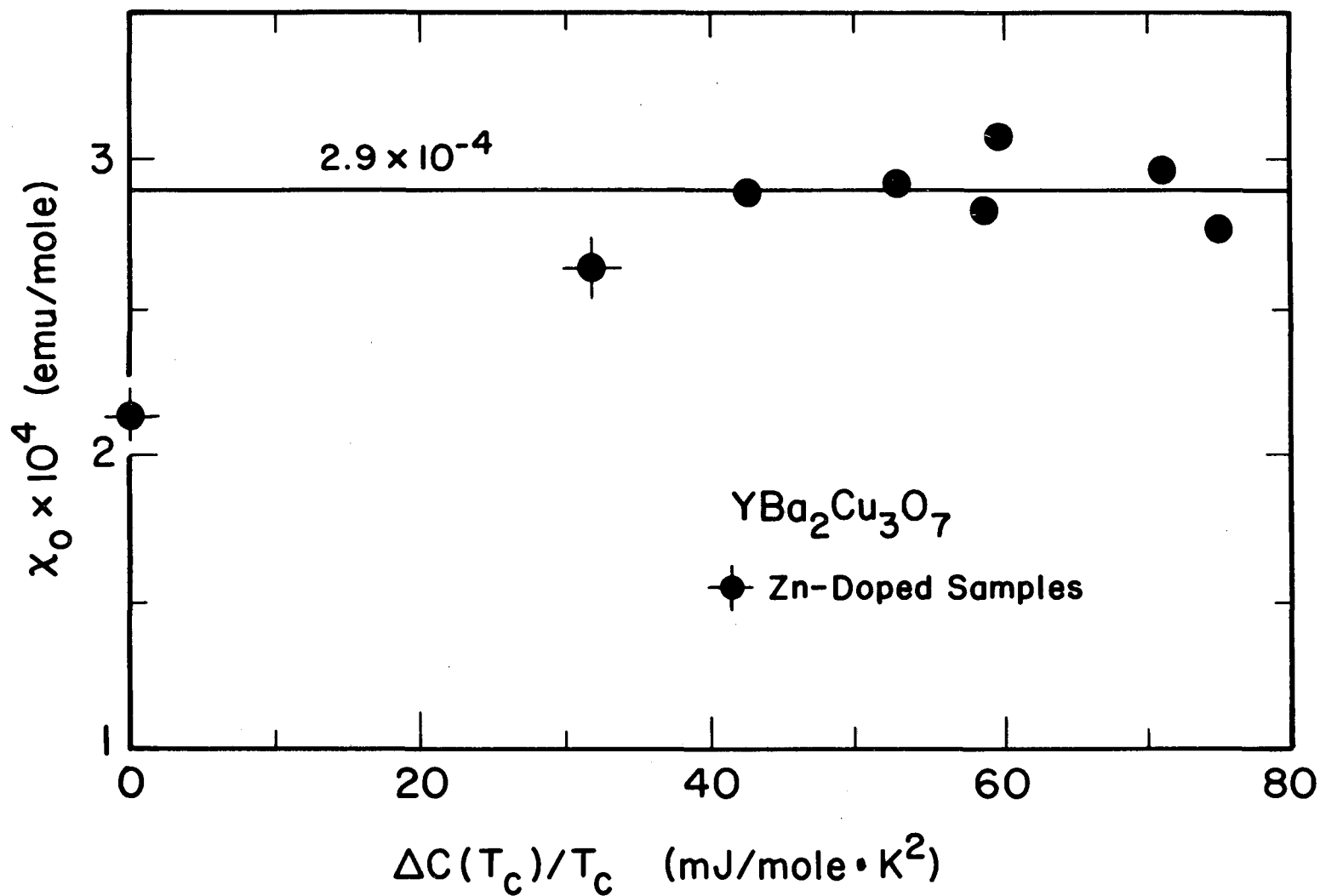
XBL 901-165

Figure 27. Values of  $\gamma(O)$  for YBCO samples with different oxygen contents (Nakazawa and Ishikawa 1989).



XBL 897-2700B

Figure 28. Values of  $\gamma(0)$  for YBCO samples displayed in two different ways: solid triangles represent  $\gamma(0)$  vs  $n$ , the total concentration of  $\text{Cu}^{2+}$  moments; open circles and squares represent  $\gamma(0)$  decomposed into two components, proportional to the concentrations,  $n_1$  and  $n_2$ , of two types of  $\text{Cu}^{2+}$  moments,  $n=n_1+n_2$  (Phillips et al. 1989).



XBL 902-443

Figure 29. The temperature-independent term in the high temperature susceptibility for samples represented in fig. 28 (Gordon et al. 1990a).

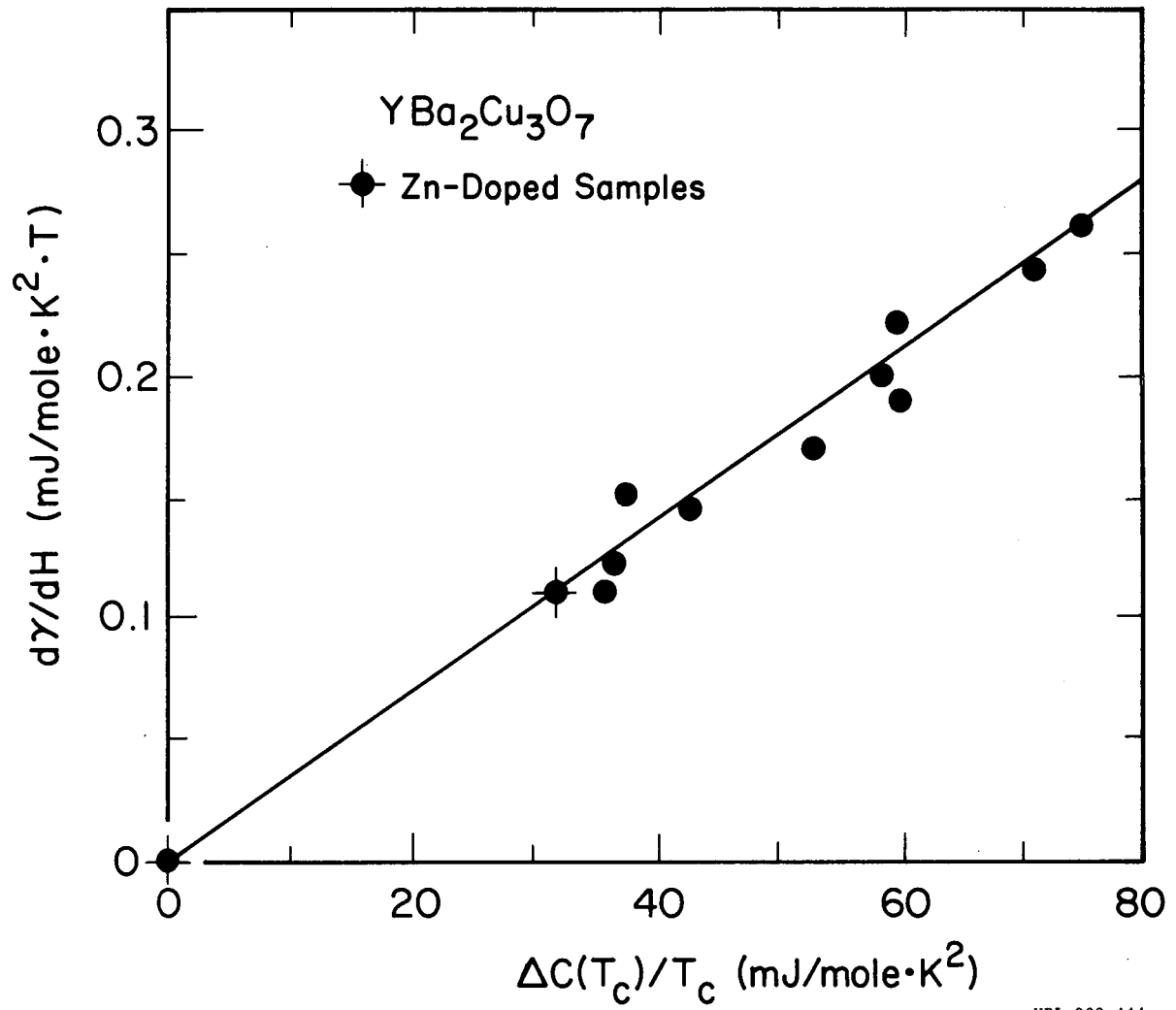
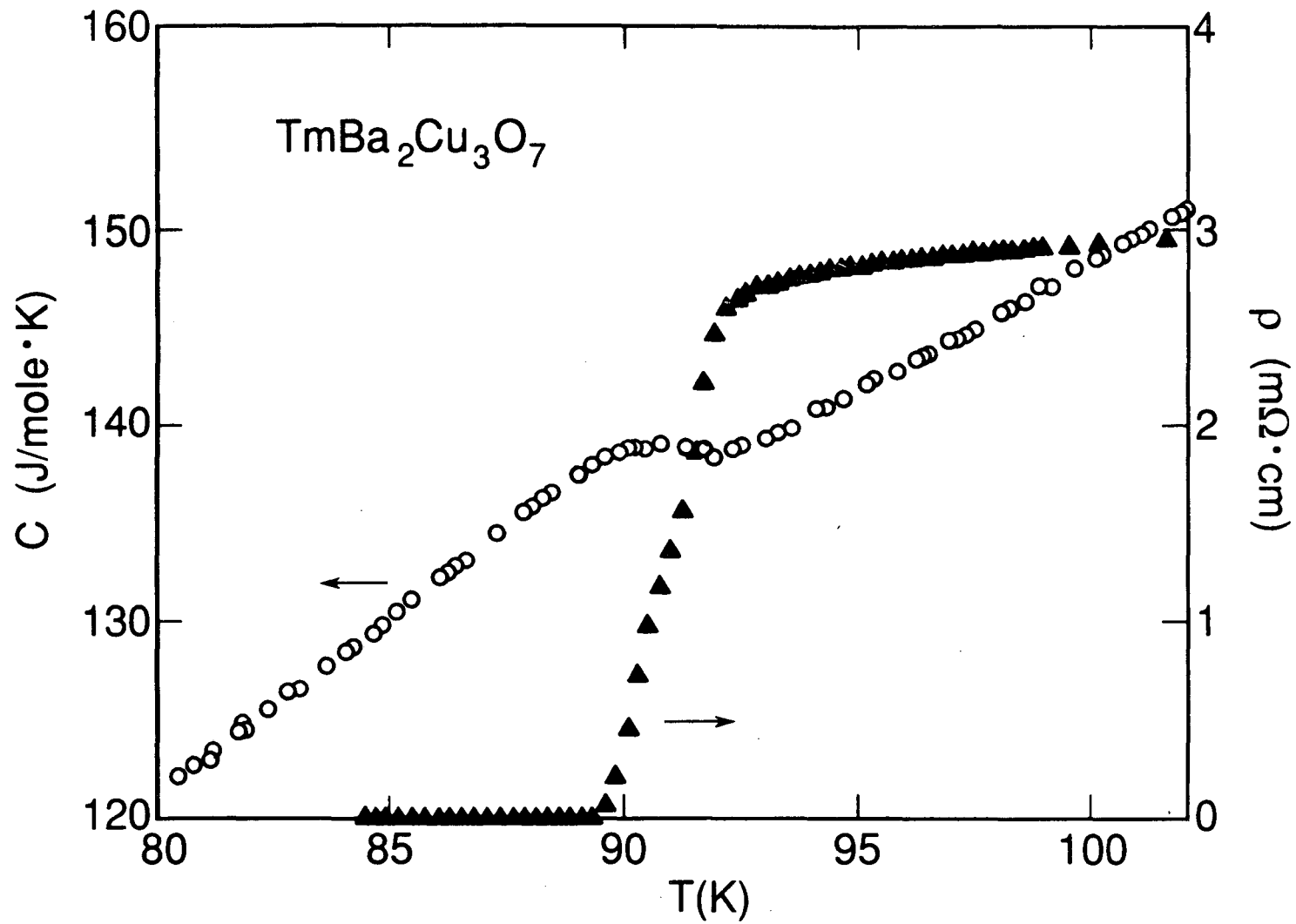
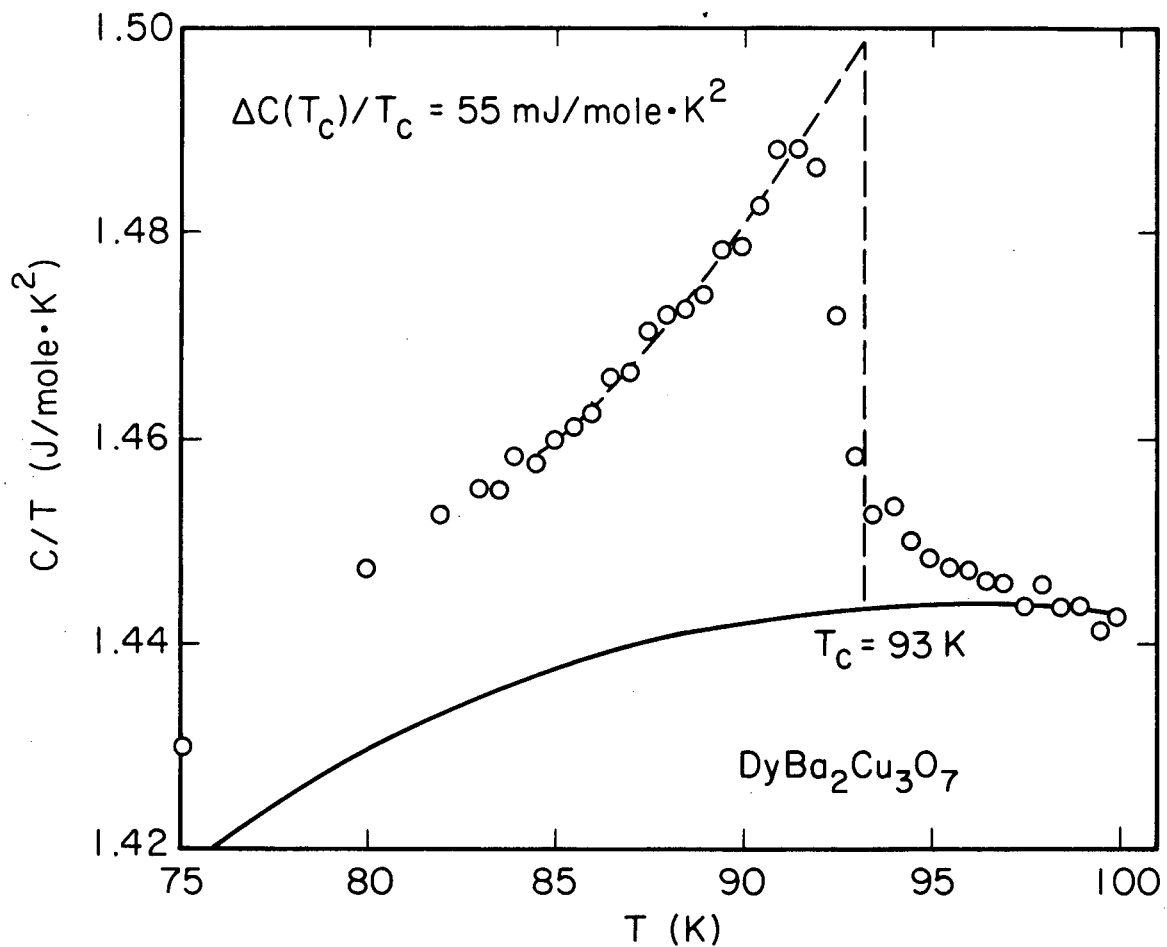


Figure 30.  $d\gamma/dH$  vs  $\Delta C(T_c)/T_c$  for YBCO (Gordon et al. 1990a).



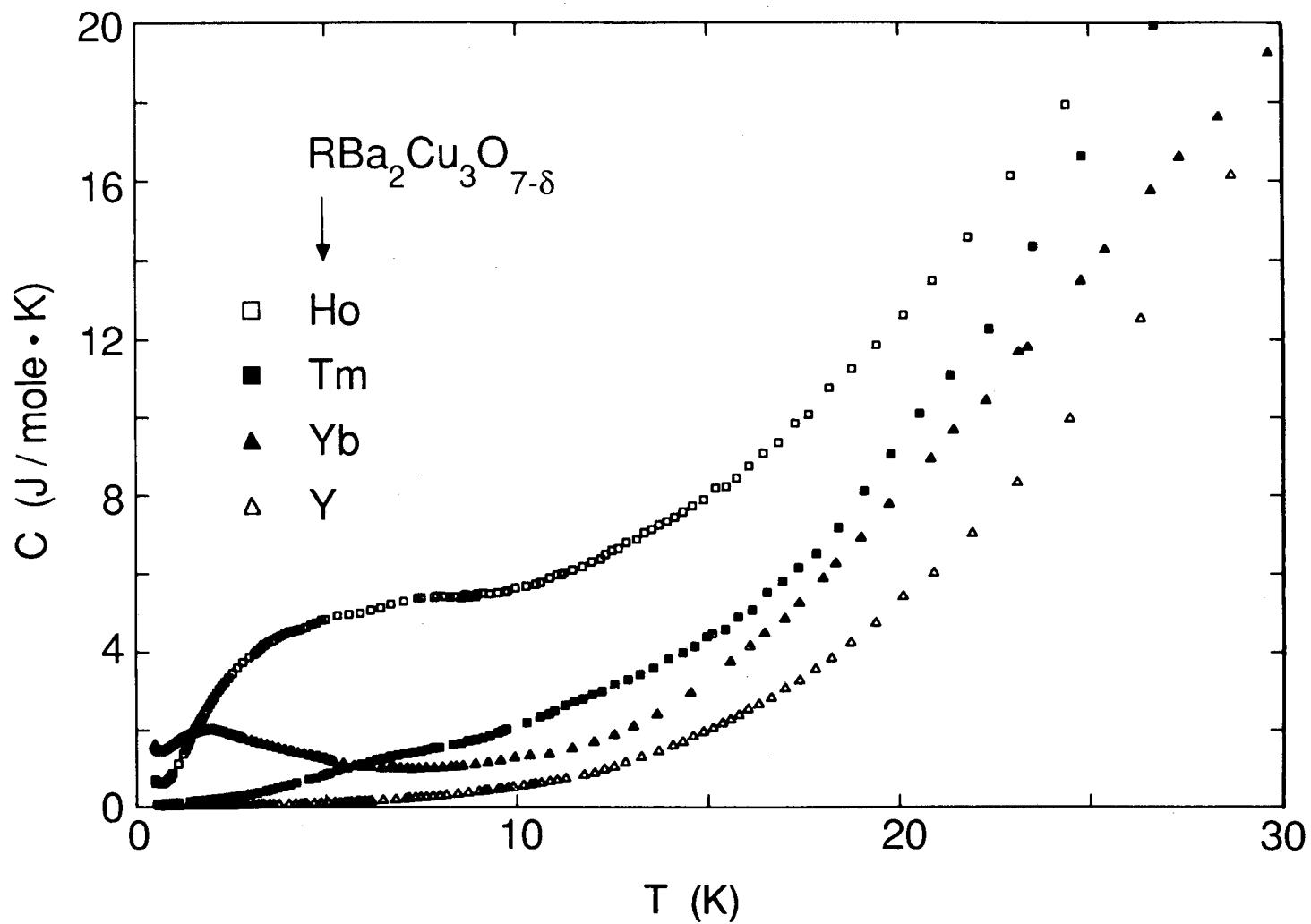
XBL 901-61

Figure 31. Specific heat and electrical resistivity of  $\text{TmBa}_2\text{Cu}_3\text{O}_7$  in the vicinity of  $T_c$  (Atake et al. 1989a).



XBL 888-2998A

Figure 32. Specific heat of  $\text{DyBa}_2\text{Cu}_3\text{O}_7$  in the vicinity of  $T_c$  (Atake et al. 1988). The solid curve is a high-temperature harmonic-lattice fit to high-temperature data (Gordon et al. 1989a).



XBL 885-1772

Figure 33. Specific heats of rare-earth substituted YBCO's that show no cooperative magnetic ordering above 0.45K (Maple et al. 1987).



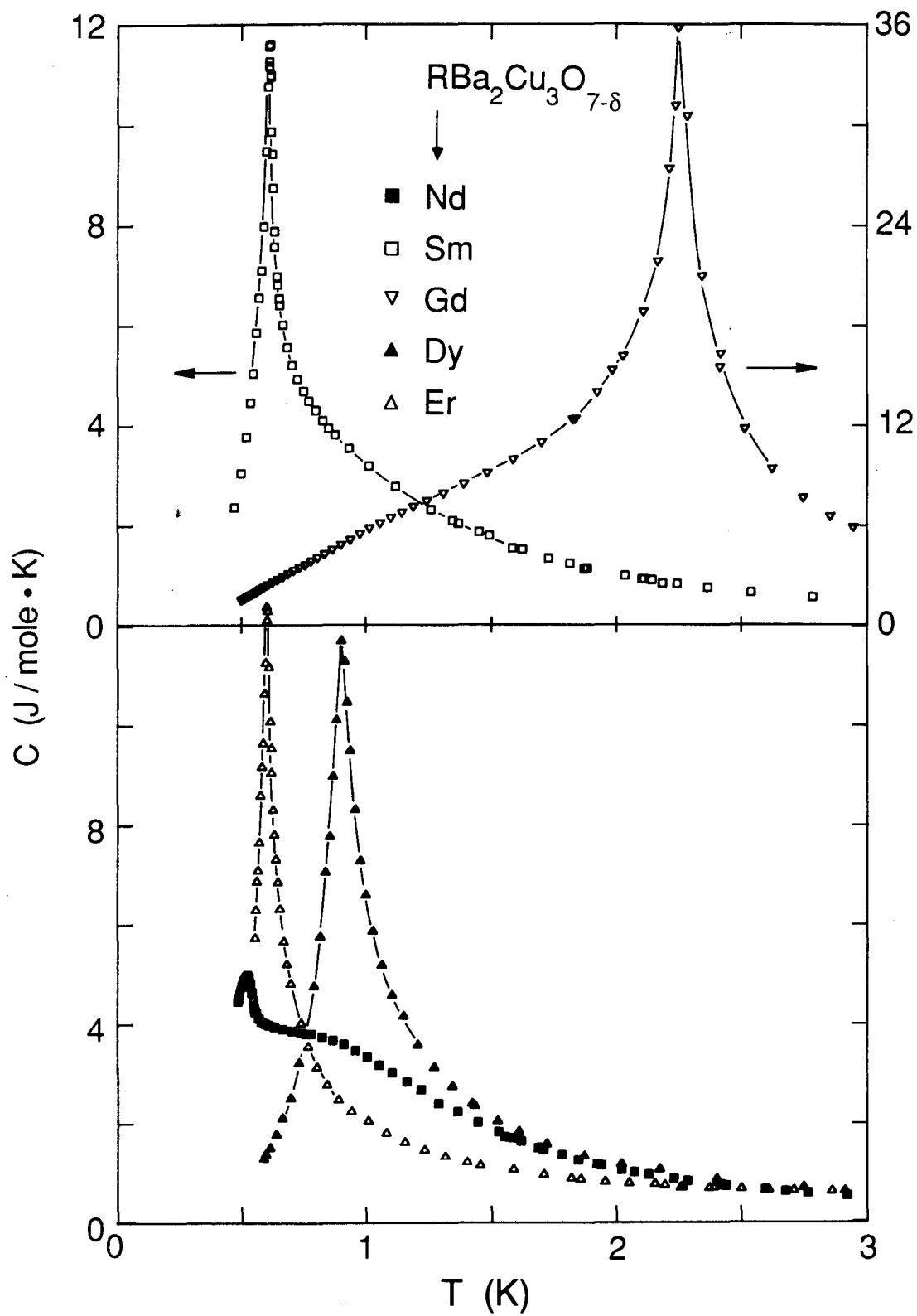
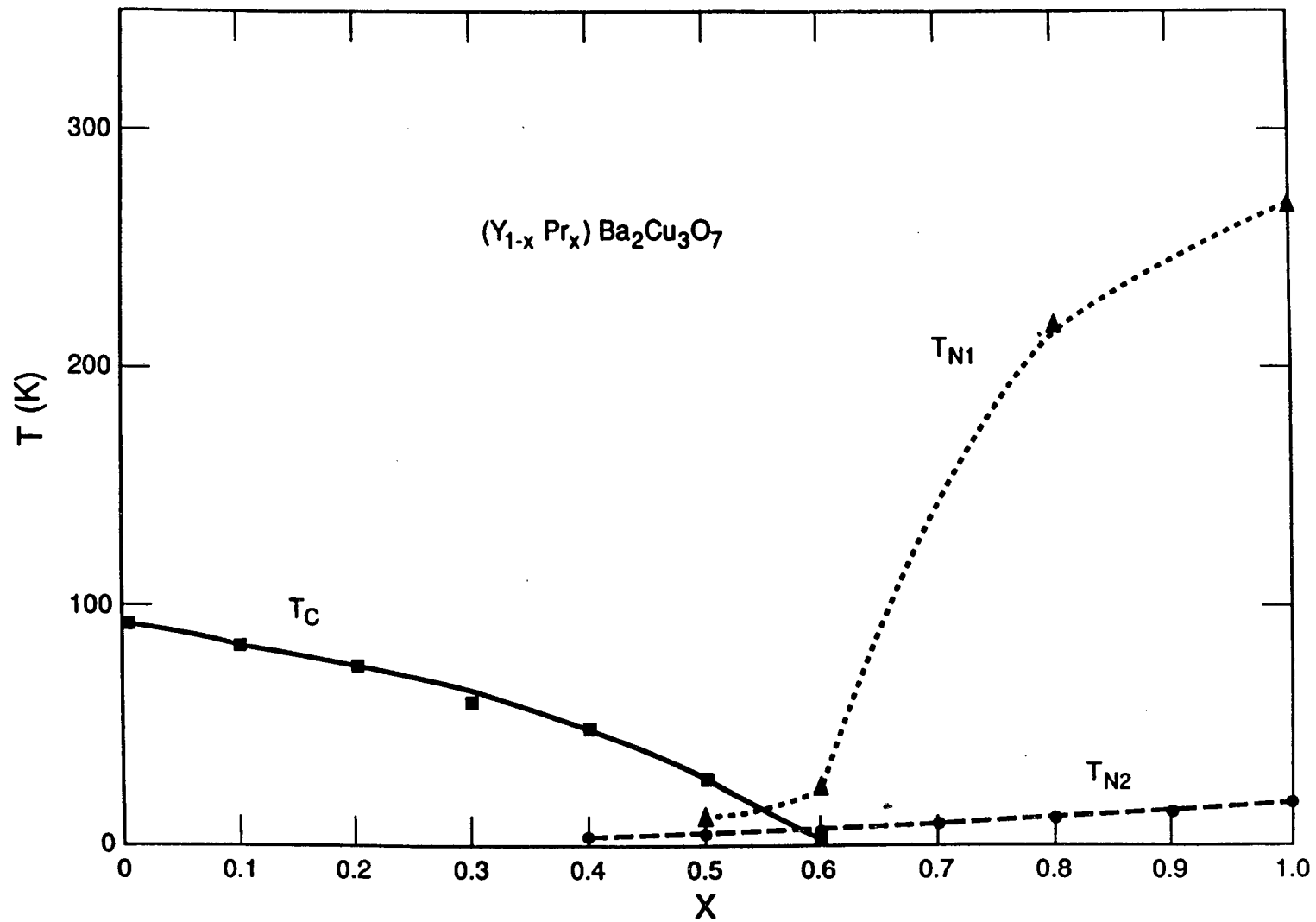
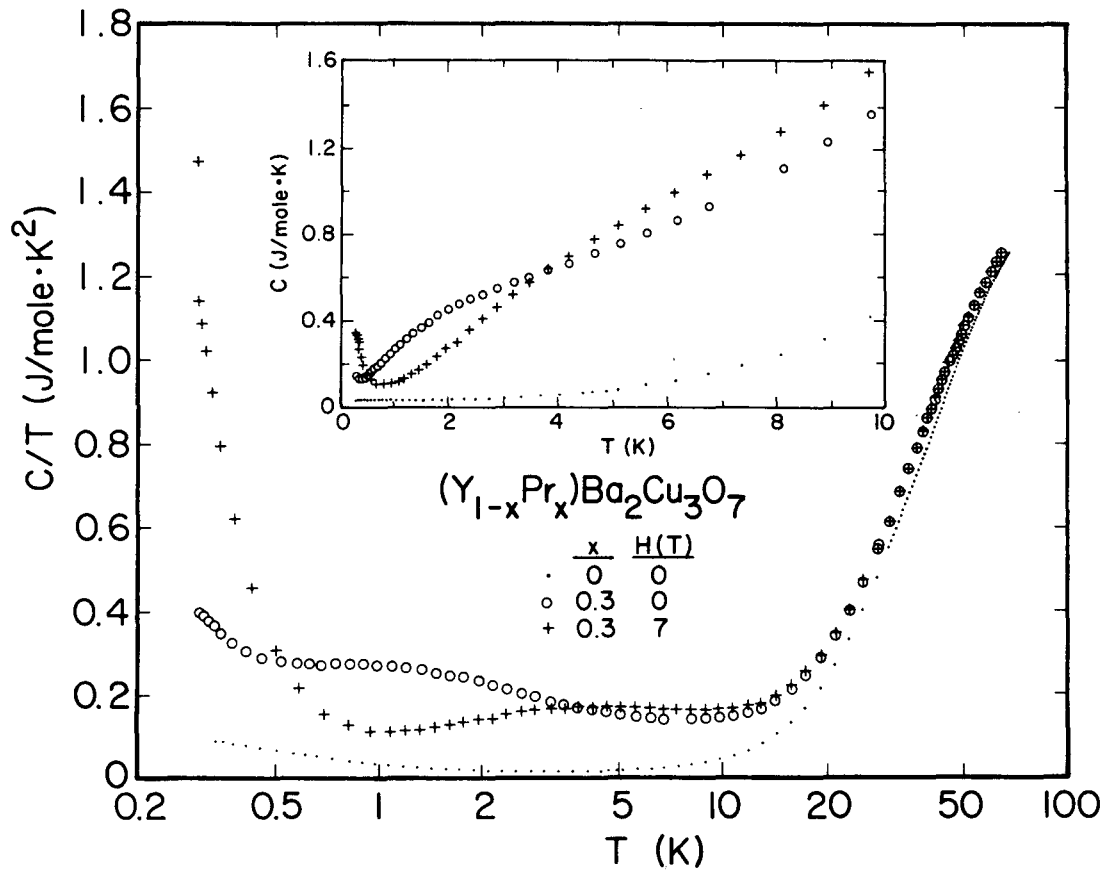


Figure 34. Examples of cooperative magnetic ordering in rare-earth substituted YBCO's (Maple et al. 1987).



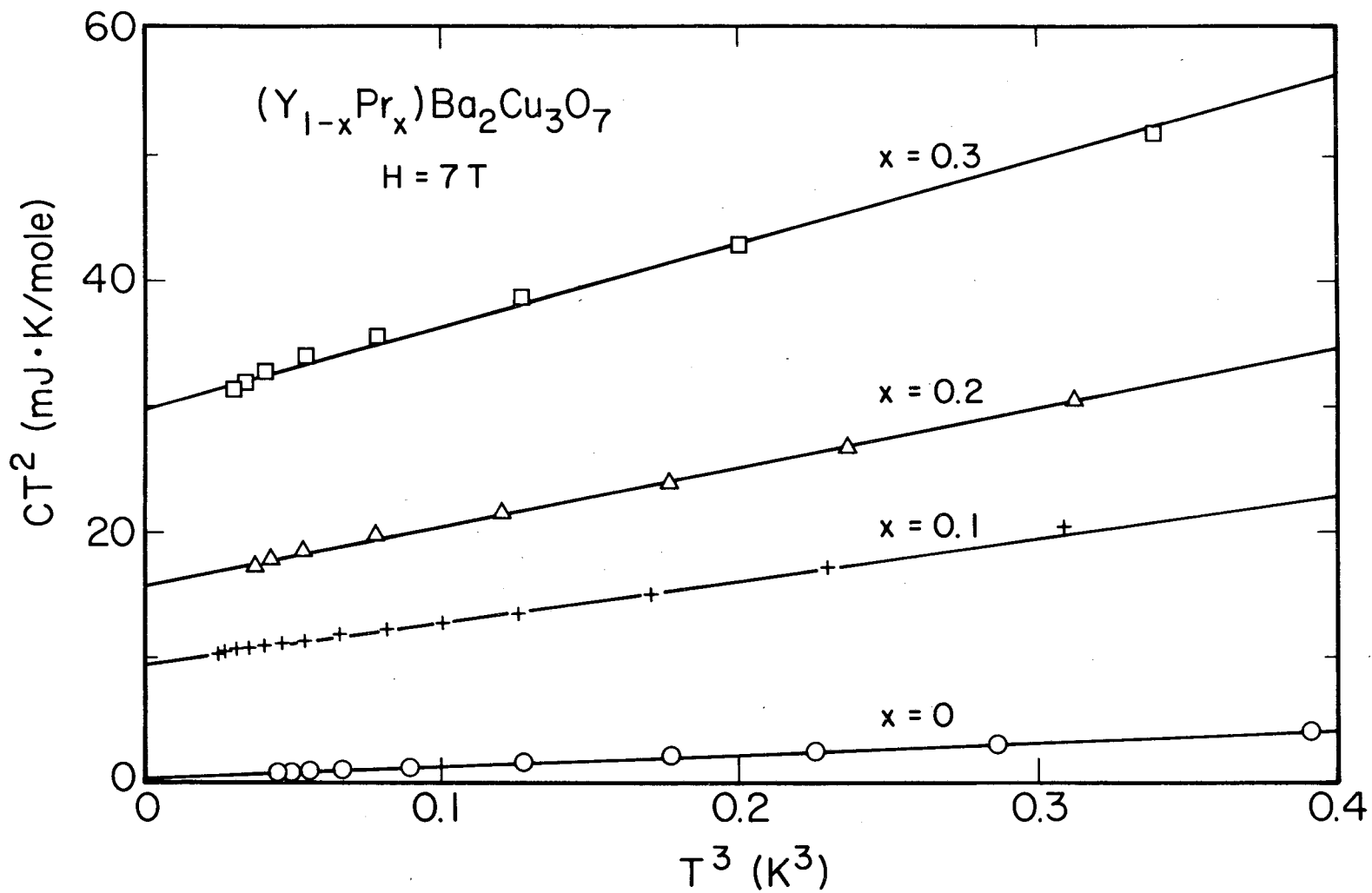
XBL 903-880

Figure 35. Superconductivity and antiferromagnetism in the phase diagram for  $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$  (Cooke et al. 1989).



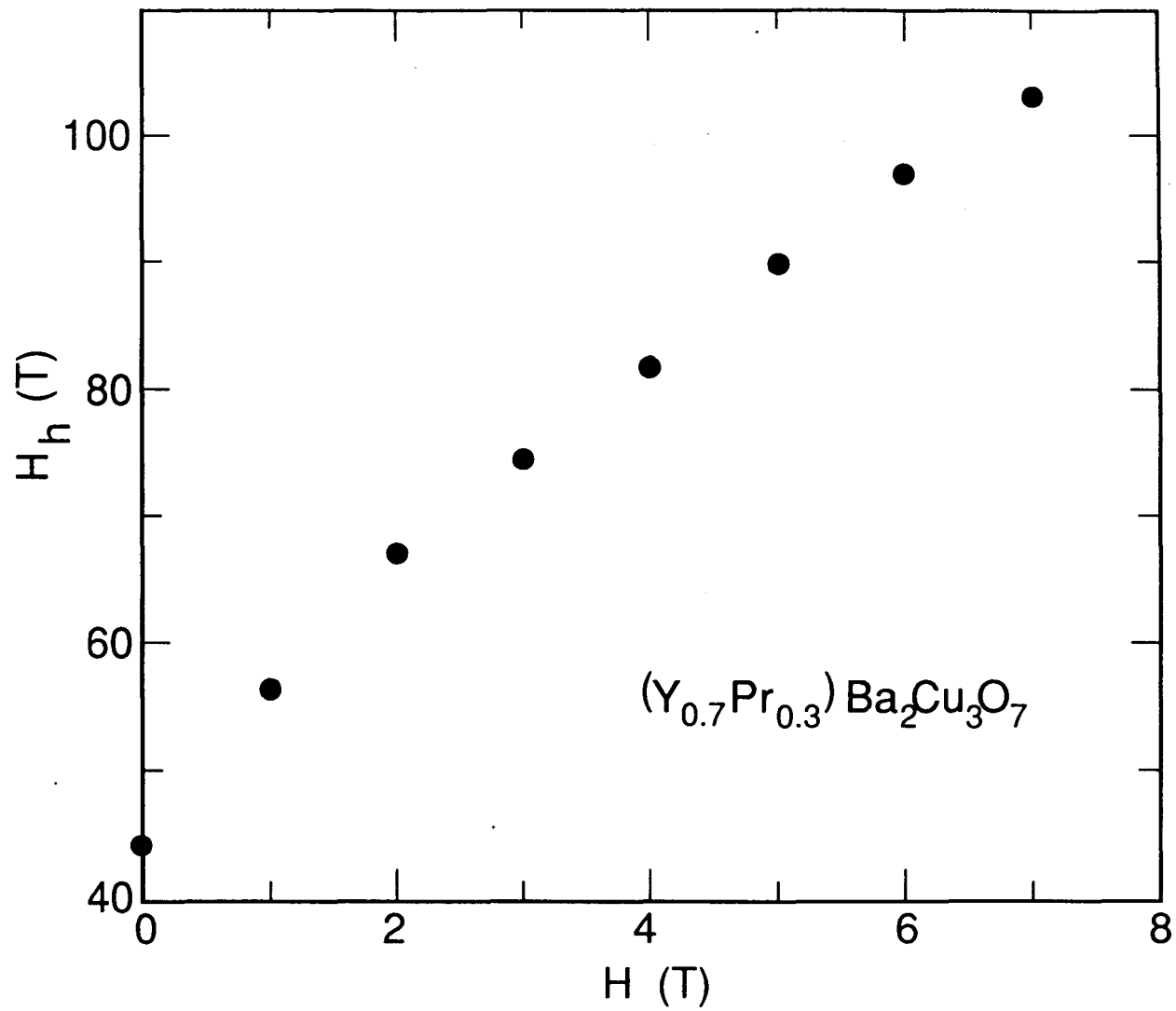
XBL 901-175

Figure 36. Specific heat of  $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$  (Amato et al. 1990a).



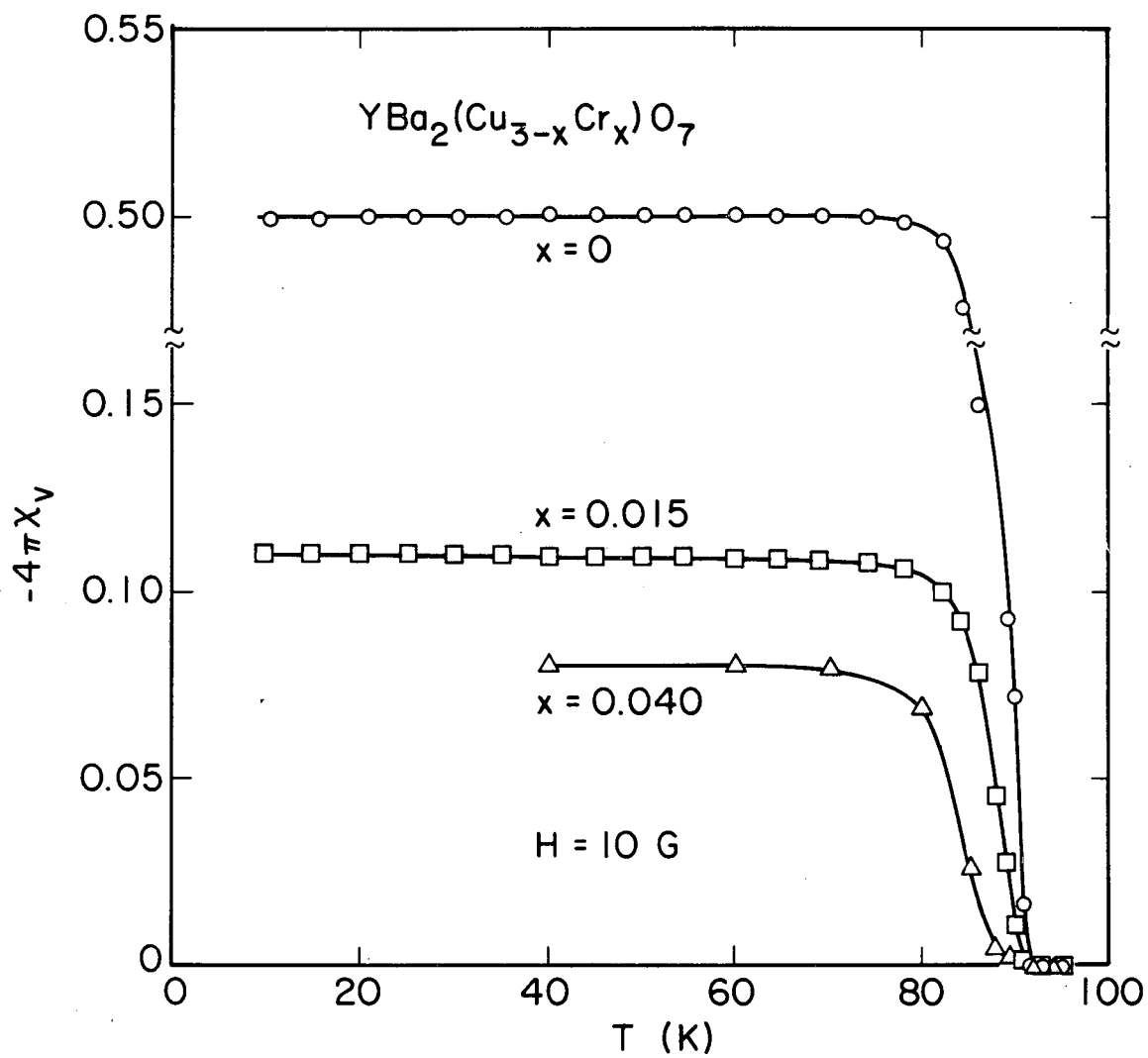
XBL 902-543

Figure 37. Hyperfine and linear-term contributions to the specific heat of  $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$  (Amato et al. 1990a).



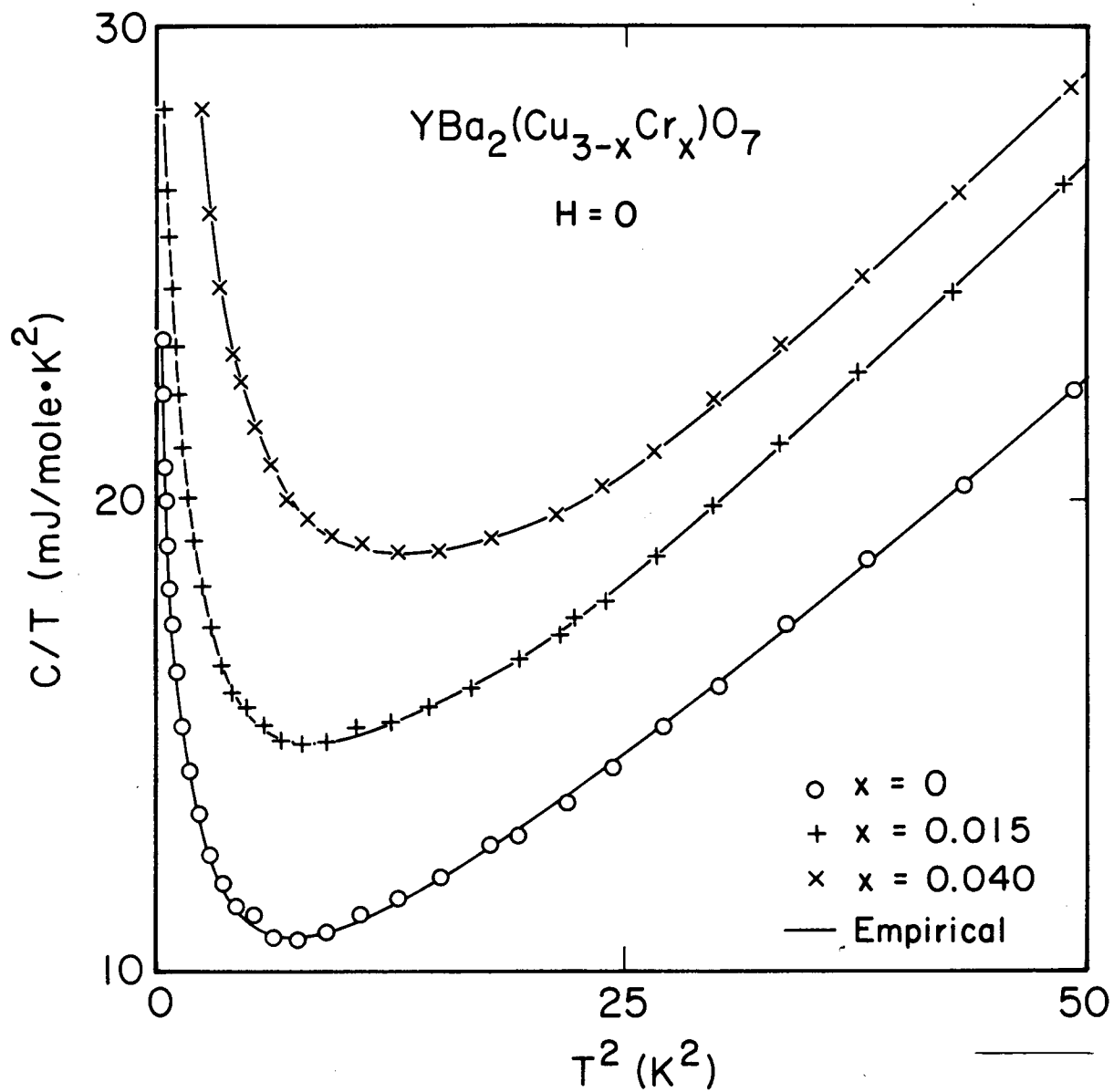
XBL 903-836

Figure 38. Effective hyperfine fields in  $(Y_{0.7}Pr_{0.3})Ba_2Cu_3O_7$  as a function of applied field (Amato et al. 1990a).



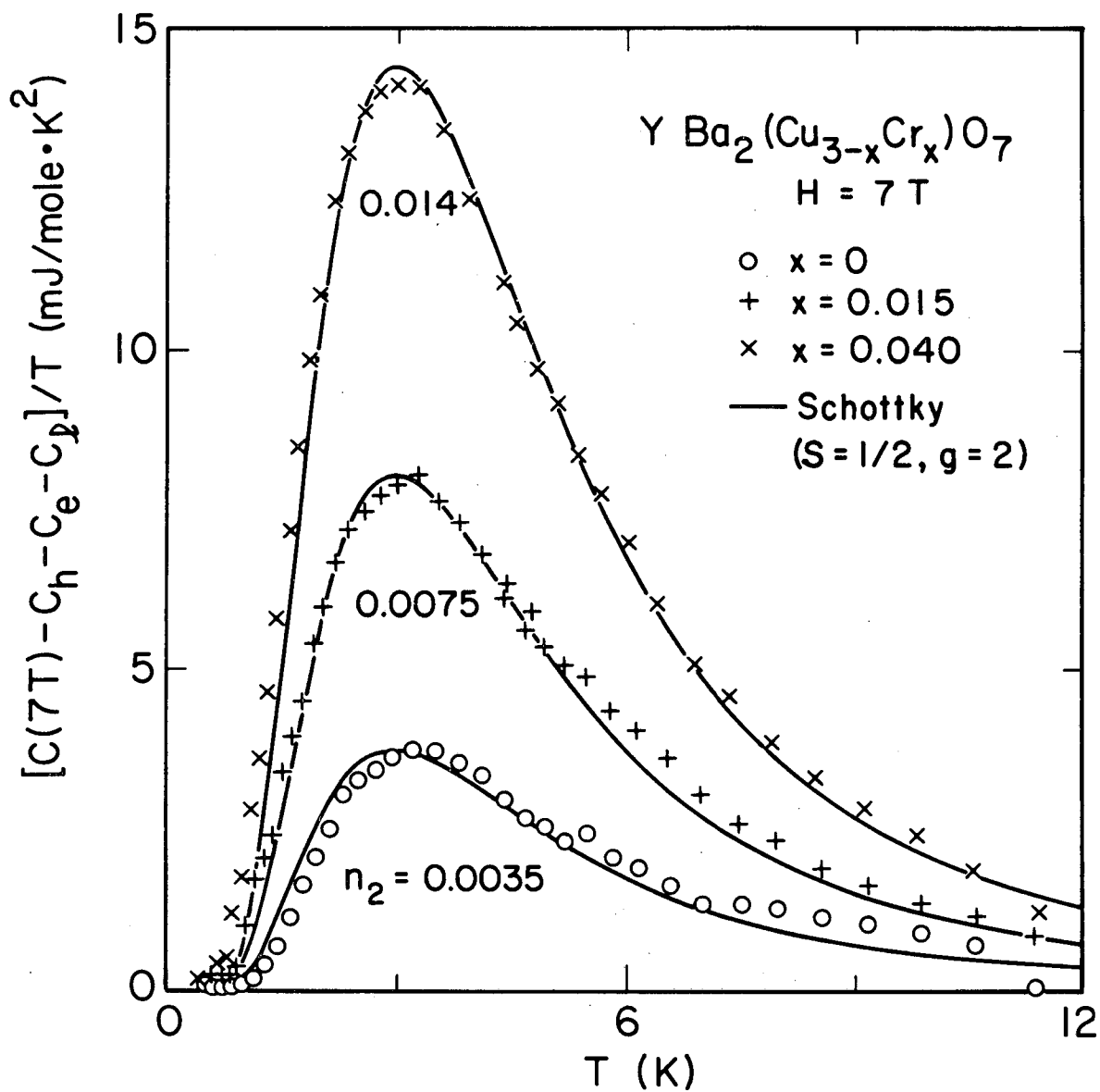
XBL 896-2289

Figure 39. The Meissner fraction for Cr-substituted YBCO samples (Kim et al. 1989).



XBL 885-1820A

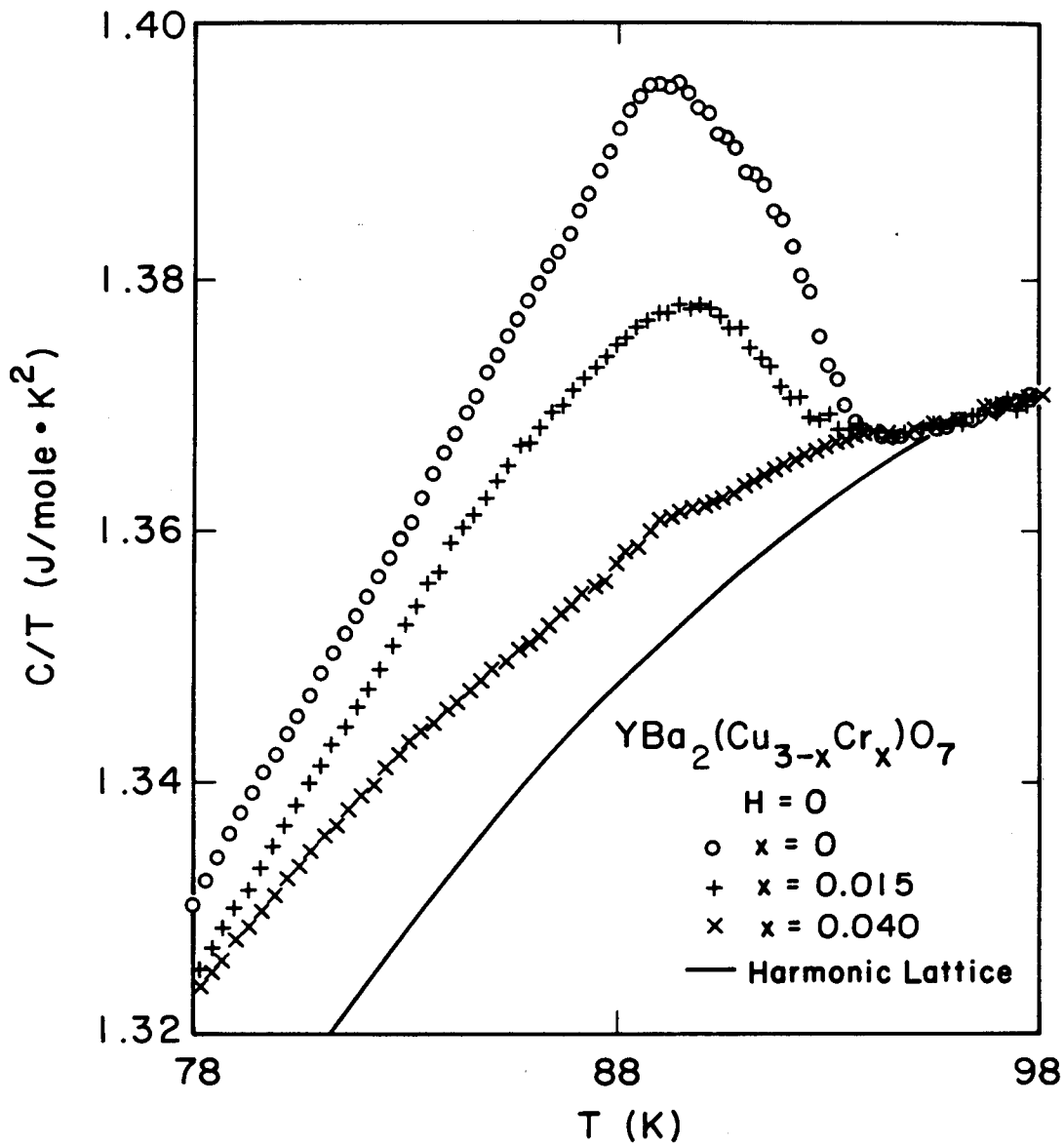
Figure 40. Low-temperature, zero-field specific heats of Cr-substituted YBCO samples (Kim et al. 1989).



XBL 896-2284 A

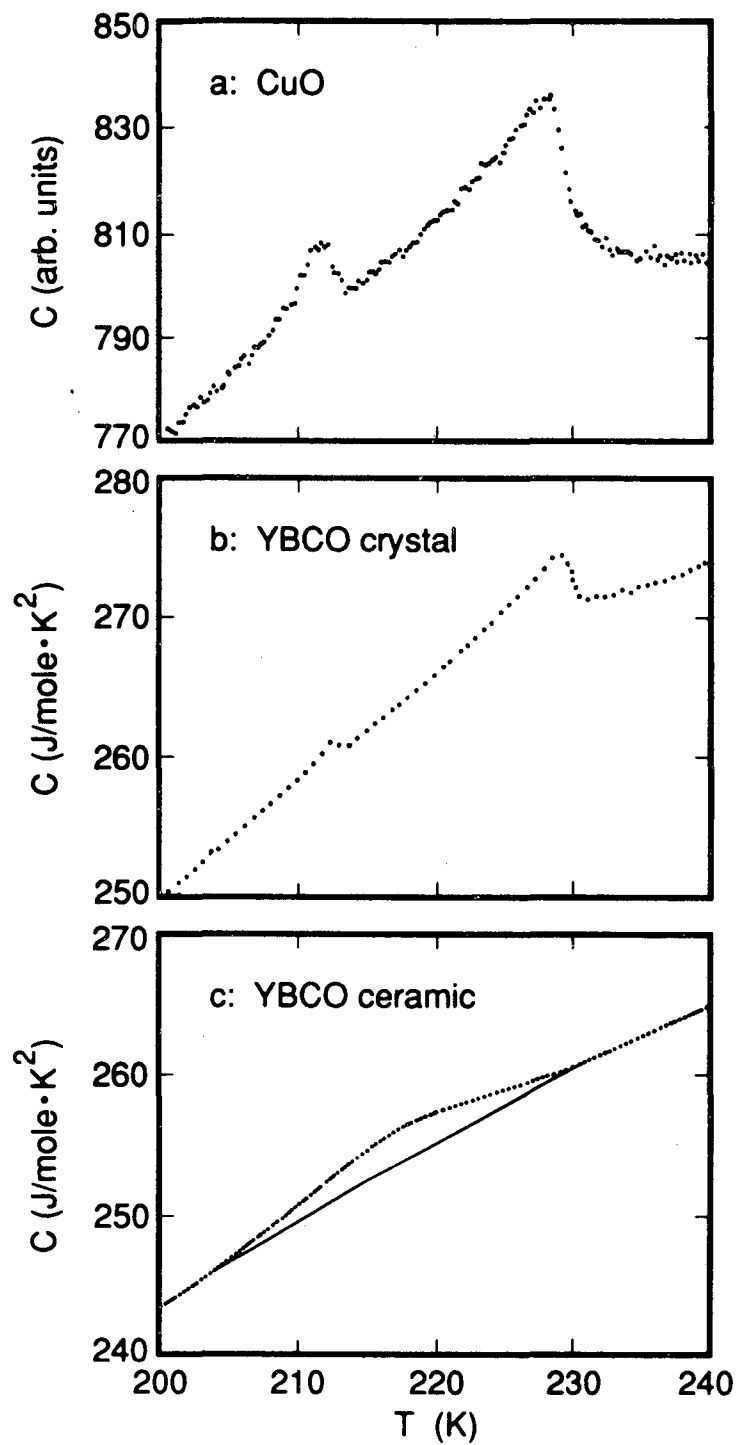
Figure 41. Schottky anomalies, represented by the curves, fitted to 7-T specific heat data for Cr-substituted YBCO samples (Kim et al. 1989).





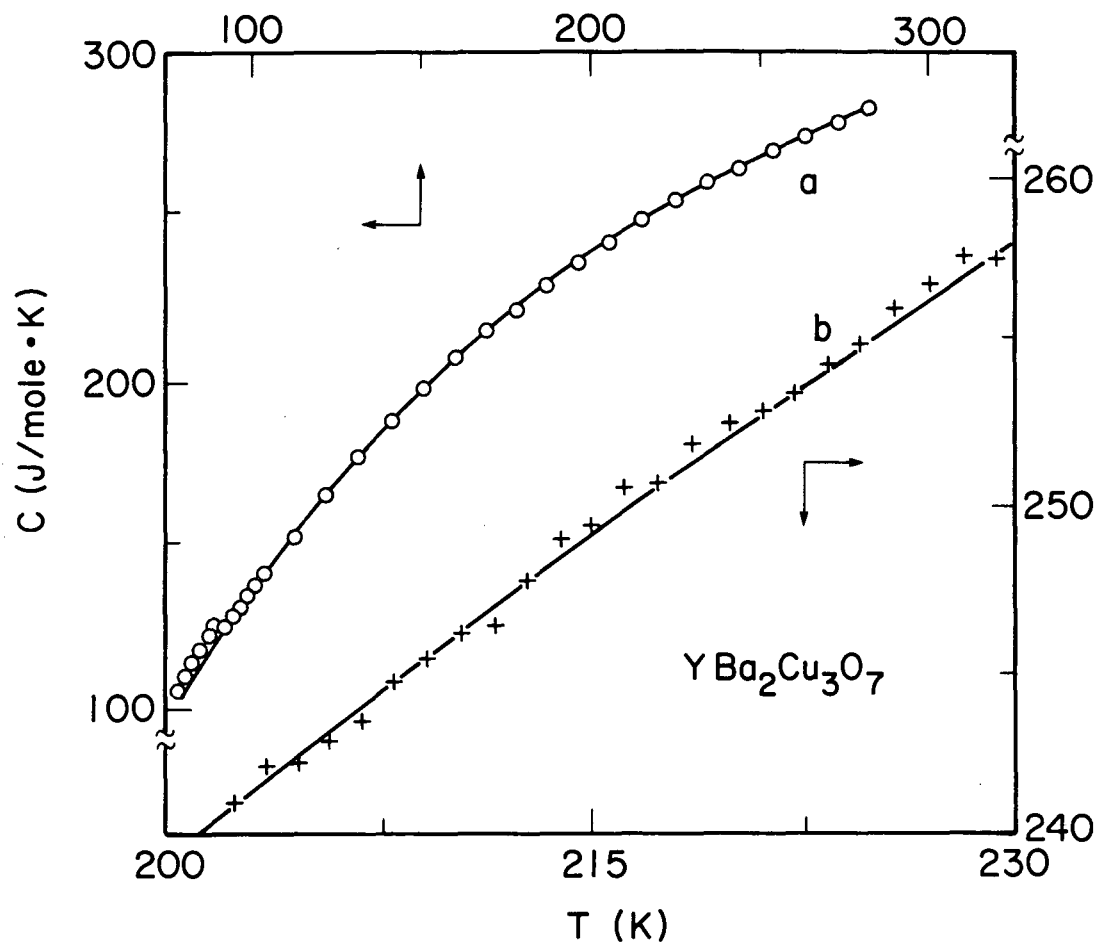
XBL 885-1819A

Figure 42. Specific heat anomaly at  $T_c$  for Cr-substituted YBCO samples. The solid curve is a harmonic-lattice fit to high-temperature data (Kim et al. 1989).



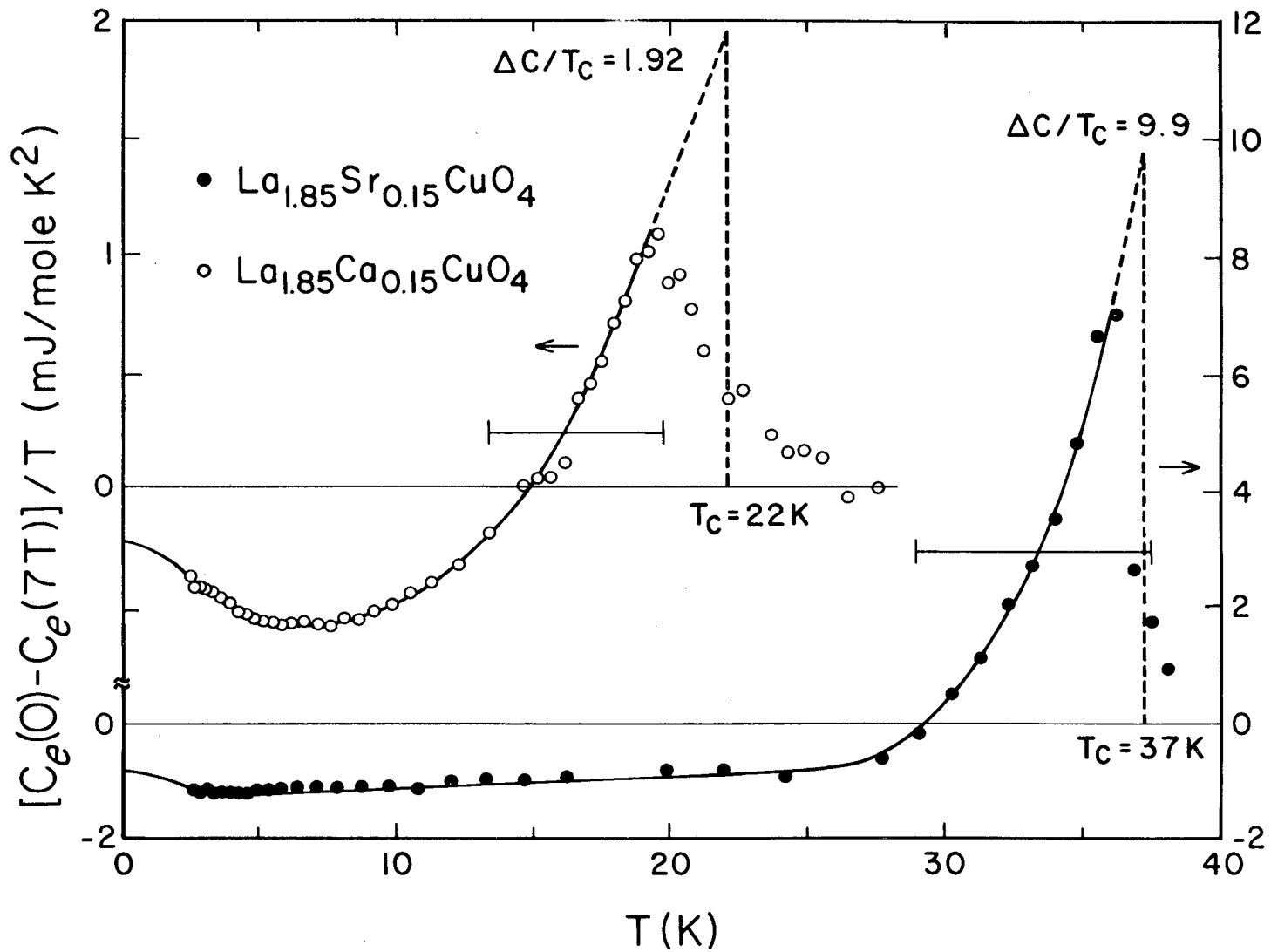
XBL 901-65

Figure 43. Comparison of the specific heats of CuO and single-crystal and polycrystalline samples of YBCO (Slaski et al. 1989b).



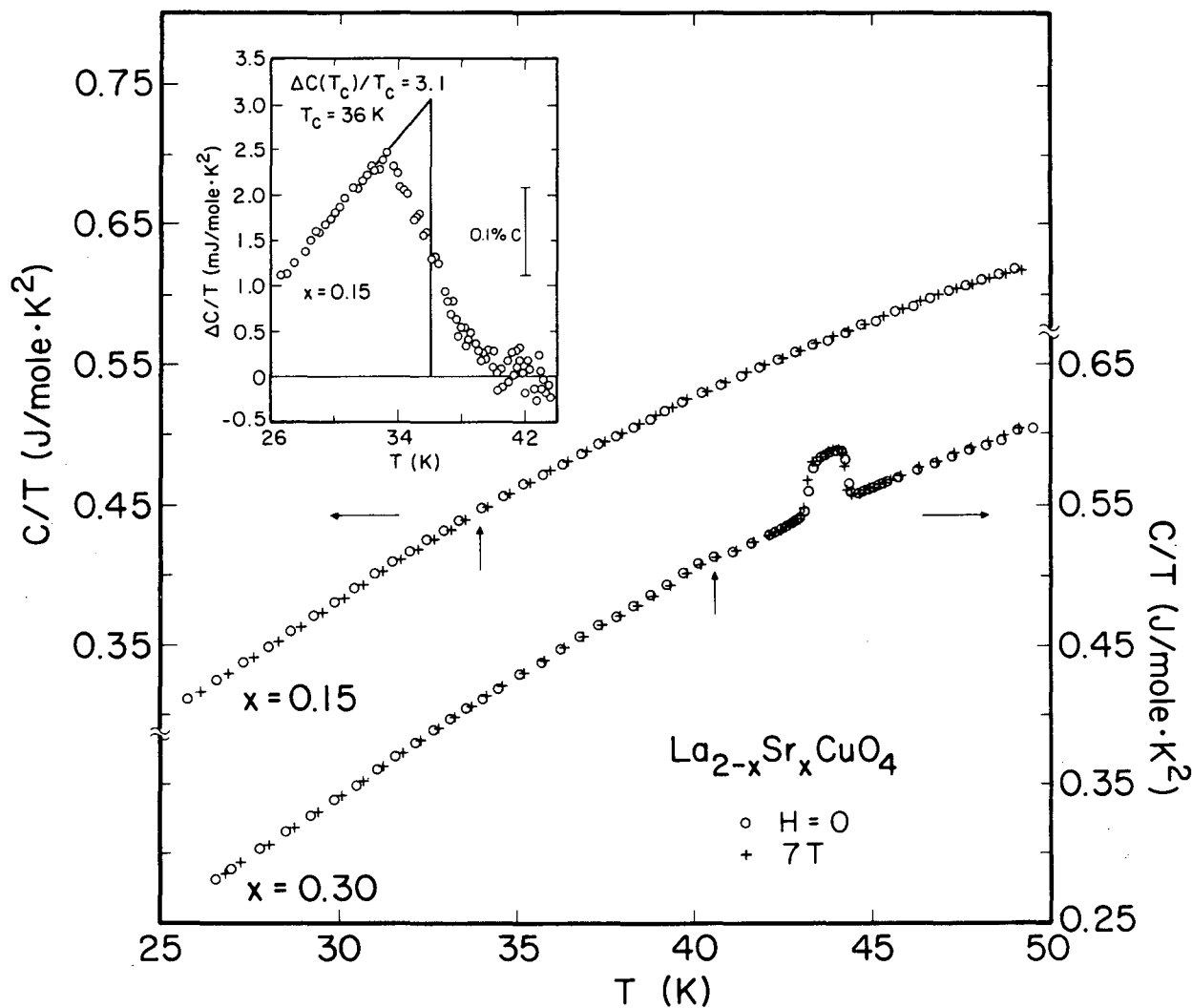
XBL 896-2281

Figure 44. Specific heat of a YBCO sample that does not show the 220K anomaly. Curve a and o's represent heat-pulse data; curve b and +'s represent continuous heating data. Both curves represent fits to the data by eq. (3) (Gordon et al. 1989b).



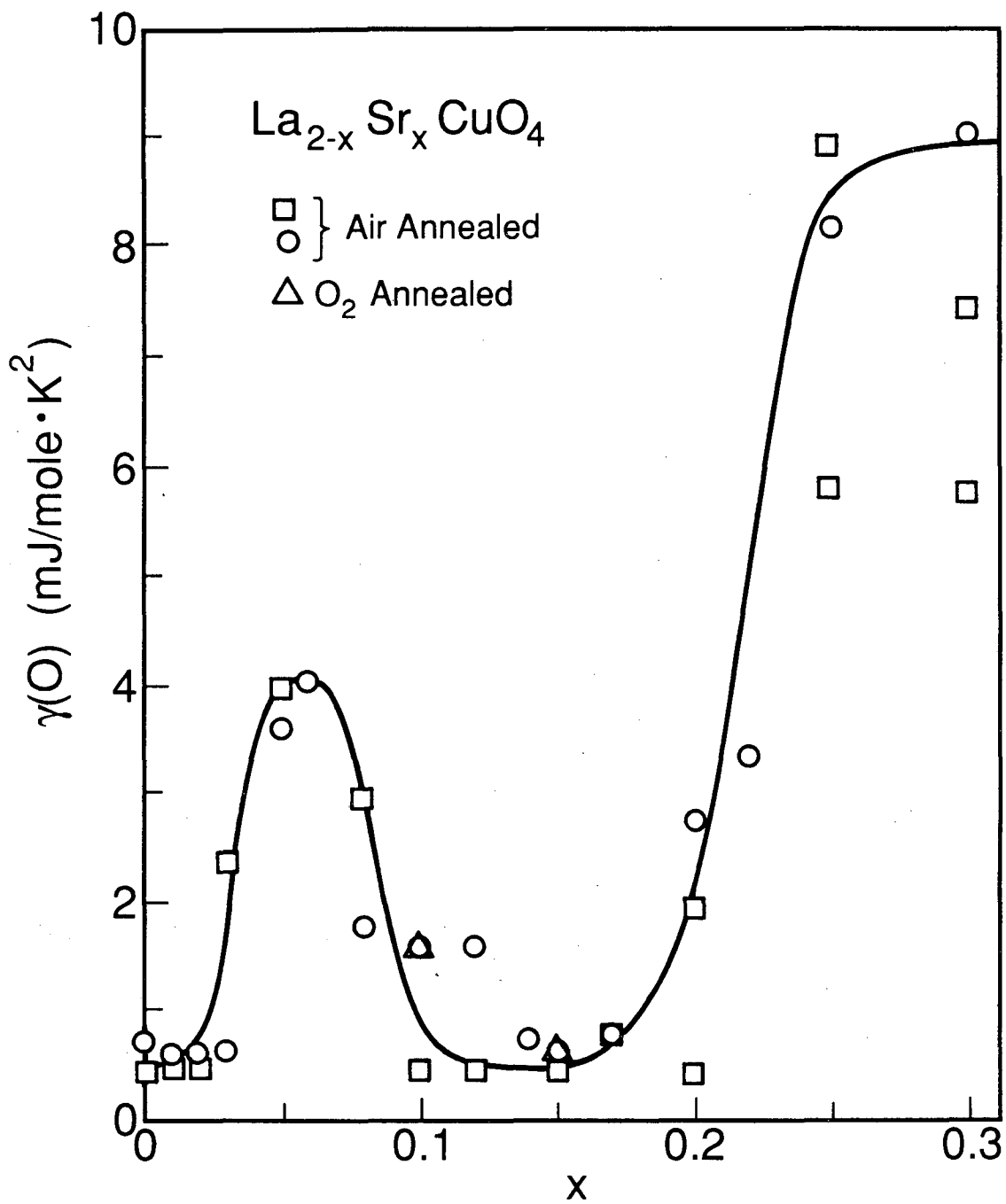
XBL 875-2027C

Figure 45. Differences in specific heat between zero field and 7T for (L,C)CO and (L,S)CO samples. The horizontal bars represent the 10-90% values of the Meissner effect (Phillips et al. 1987a).



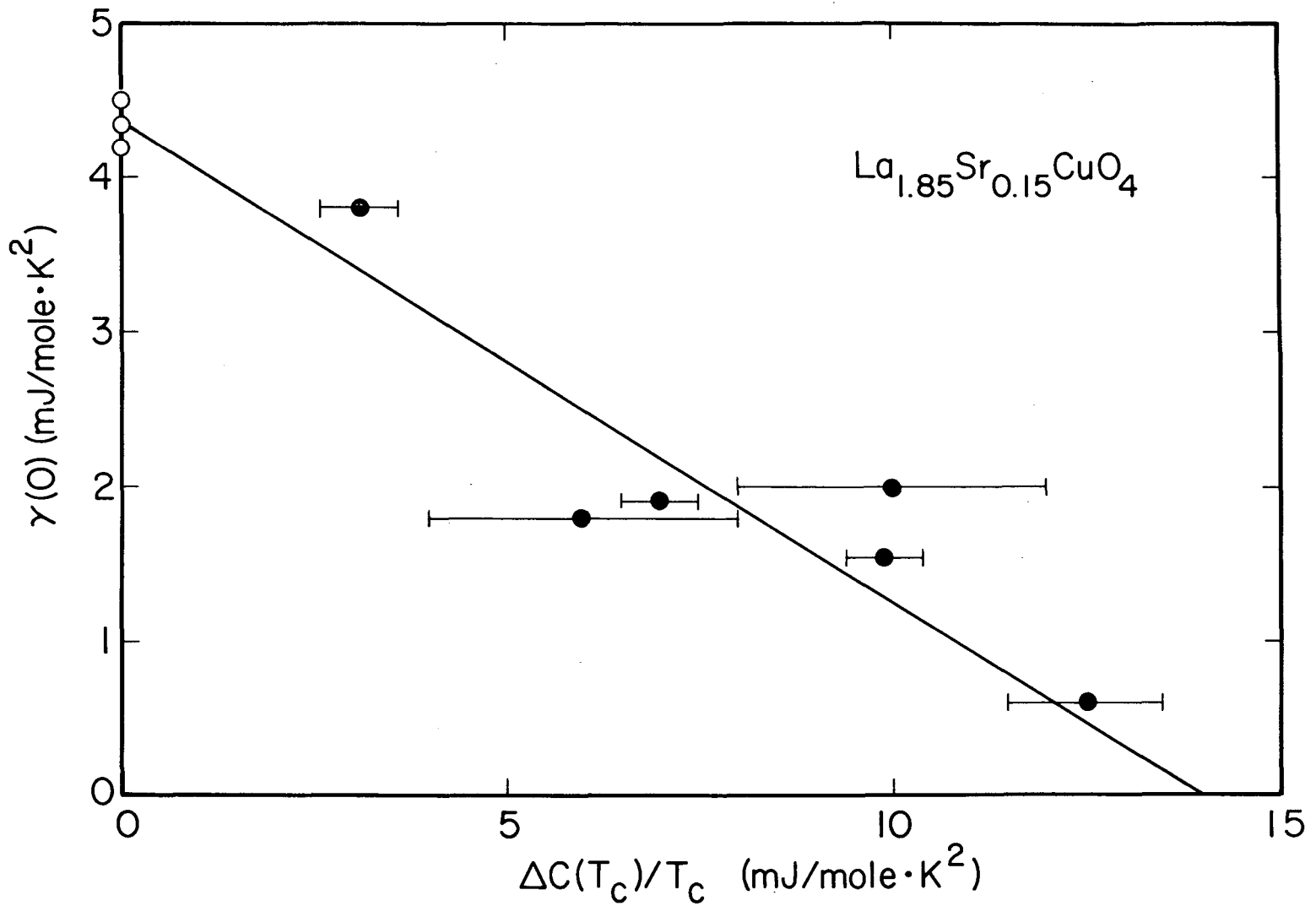
XBL 90-1-176

Figure 46. Specific heats of superconducting  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  and non-superconducting  $\text{La}_{1.7}\text{Sr}_{0.7}\text{CuO}_4$ , in both zero field and 7T. For the superconducting sample, the inset shows the difference in the specific heats between zero field and 7T; the arrow in the main figure marks the position of the maximum in the difference. For the non superconducting sample there is an anomaly in the specific heat near 44-45K, and a smaller feature, indicated by the arrow, near 41K (Amato et al. 1990b).



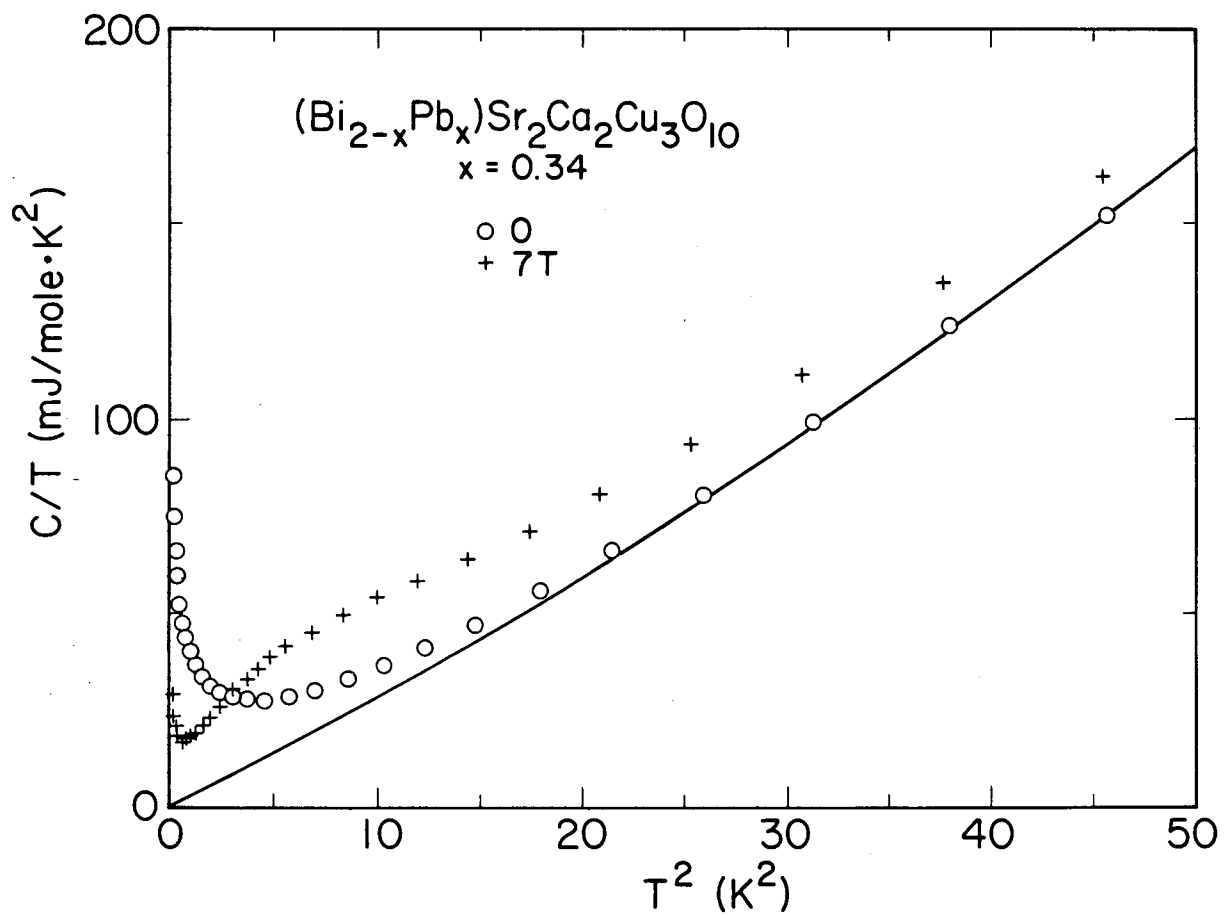
XBL 901-163

Figure 47.  $\gamma(O)$  for La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> (Wada et al. 1989a).



XBL 902-392

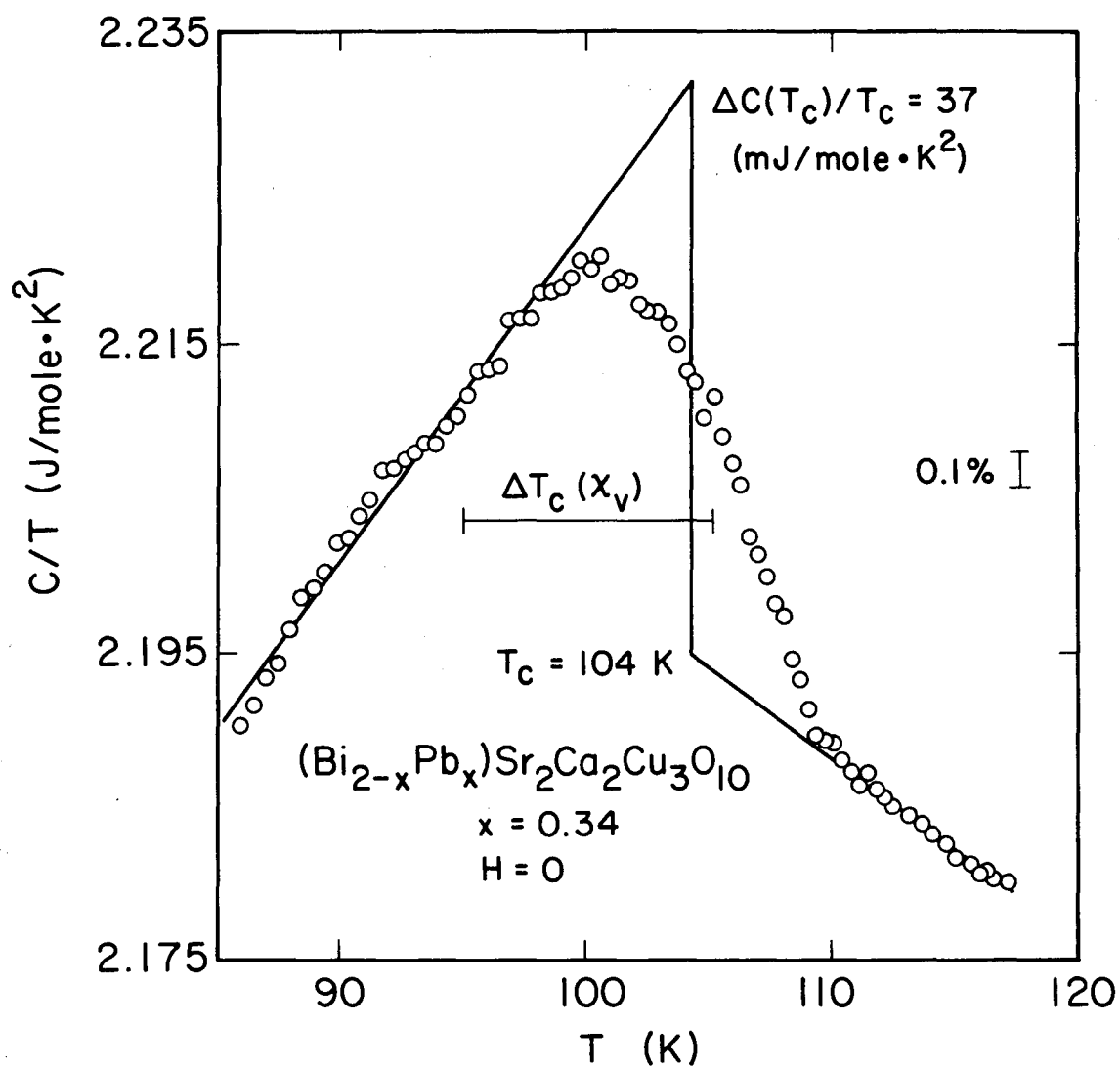
Figure 48.  $\gamma(0)$  vs  $\Delta C(T_c)/T_c$  for  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  (Amato et al. 1990b). See text for explanation and table 4 for references to original data.



XBL 896-2285 B

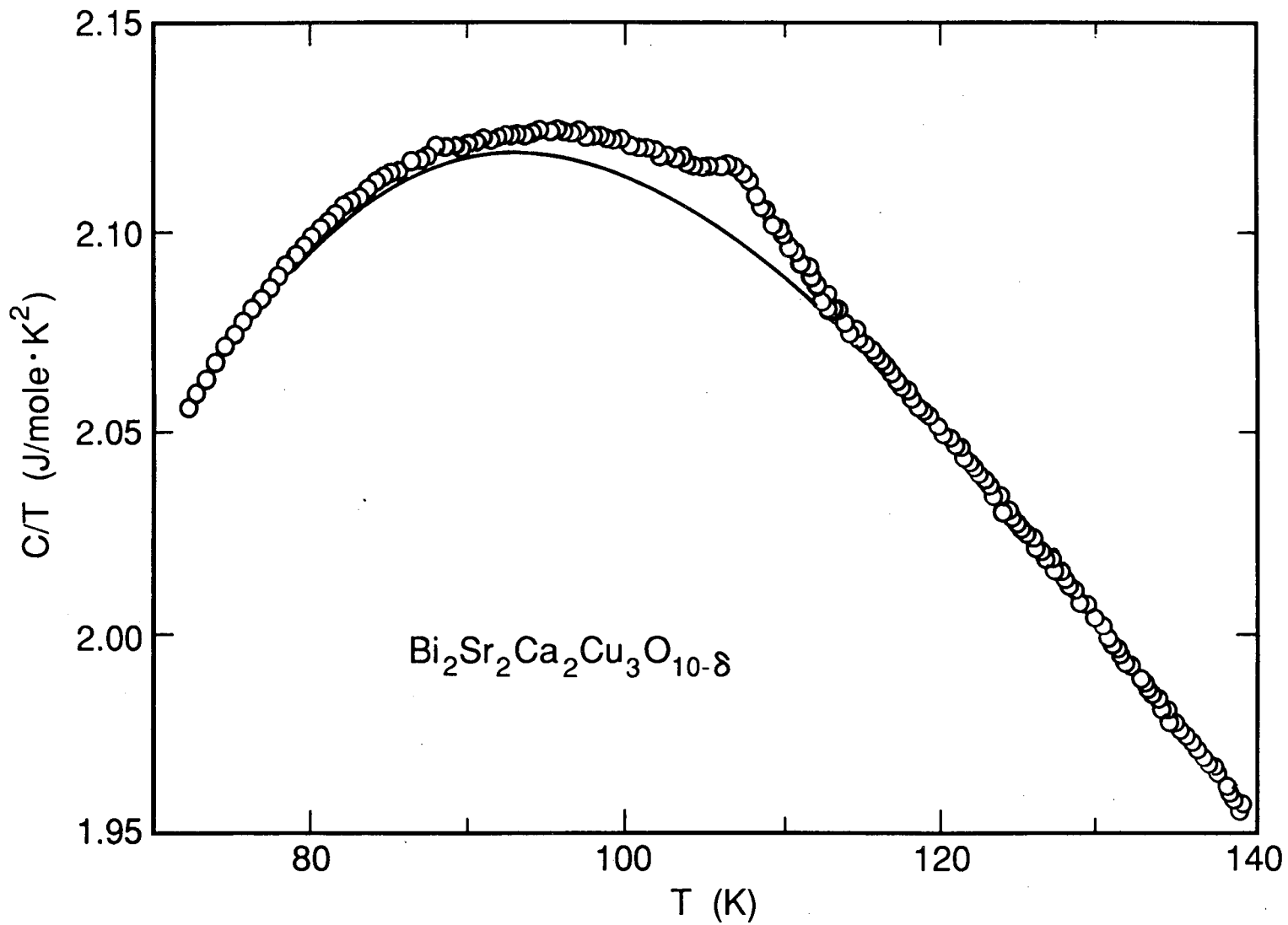
Figure 49. Specific heat of a Pb-stabilized, single-phase BSCCO (2223) sample (Fisher et al. 1989b).





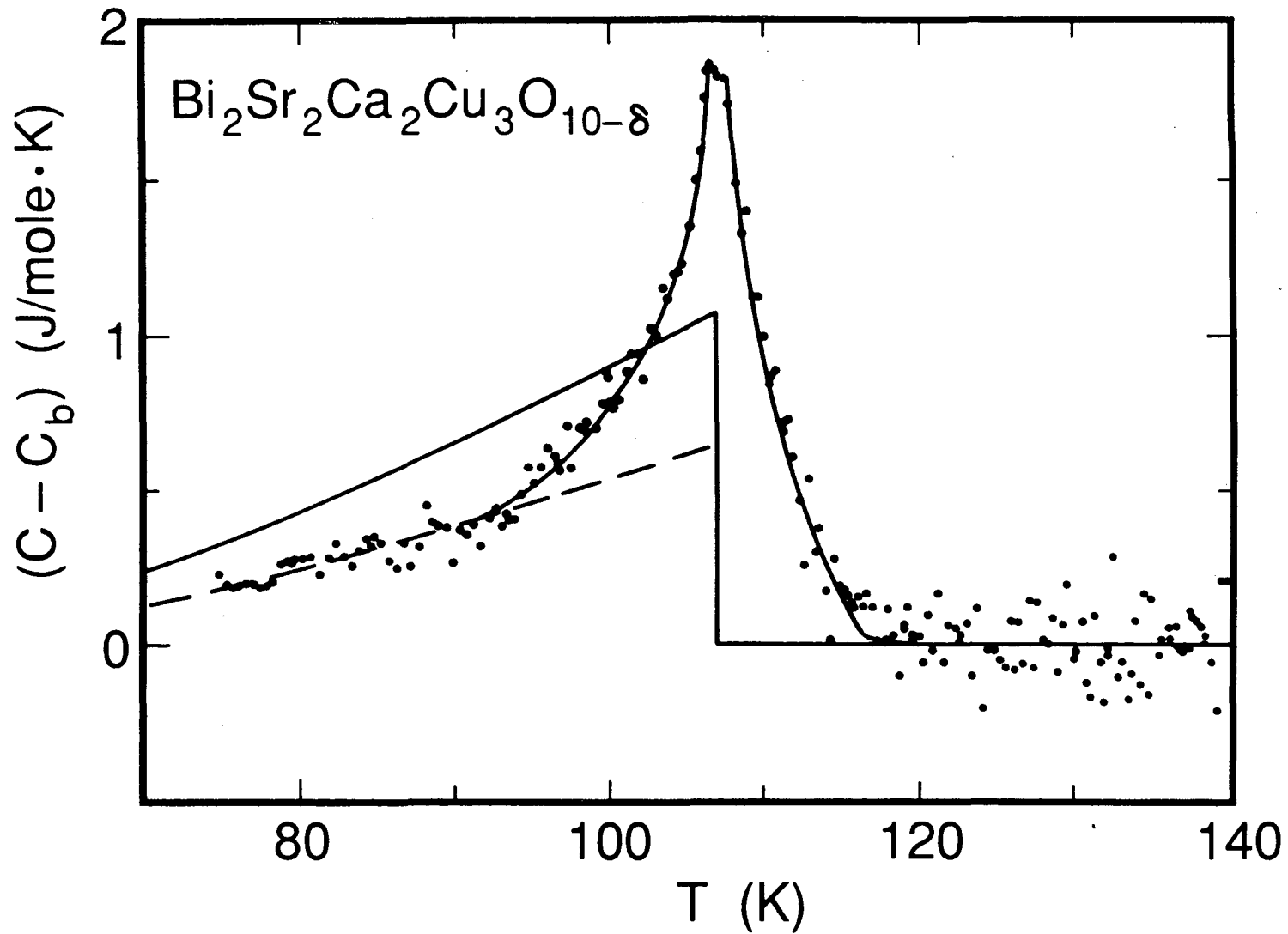
XBL 896-2286 B

Figure 50. Anomaly in specific heat at  $T_c$  of a Pb-stabilized, single-phase BSCCO sample (Fisher et al. 1989b).



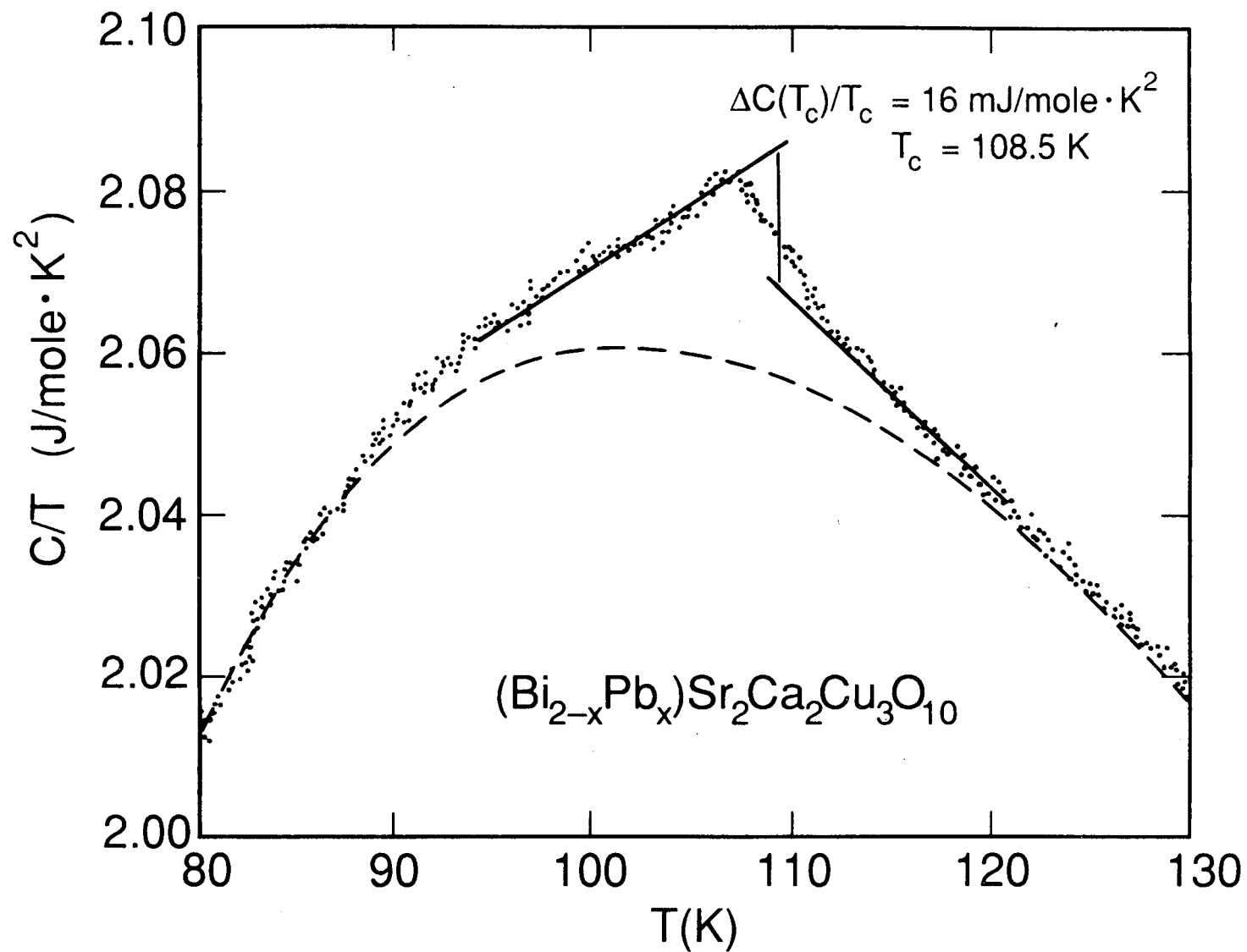
XBL 901-167

Figure 51. Anomaly in specific heat at  $T_c$  of a BSCCO (2223) sample. The solid curve is an approximation to the background specific heat, based on a polynomial interpolation between data well above and well below  $T_c$  (Schnelle et al. 1989).



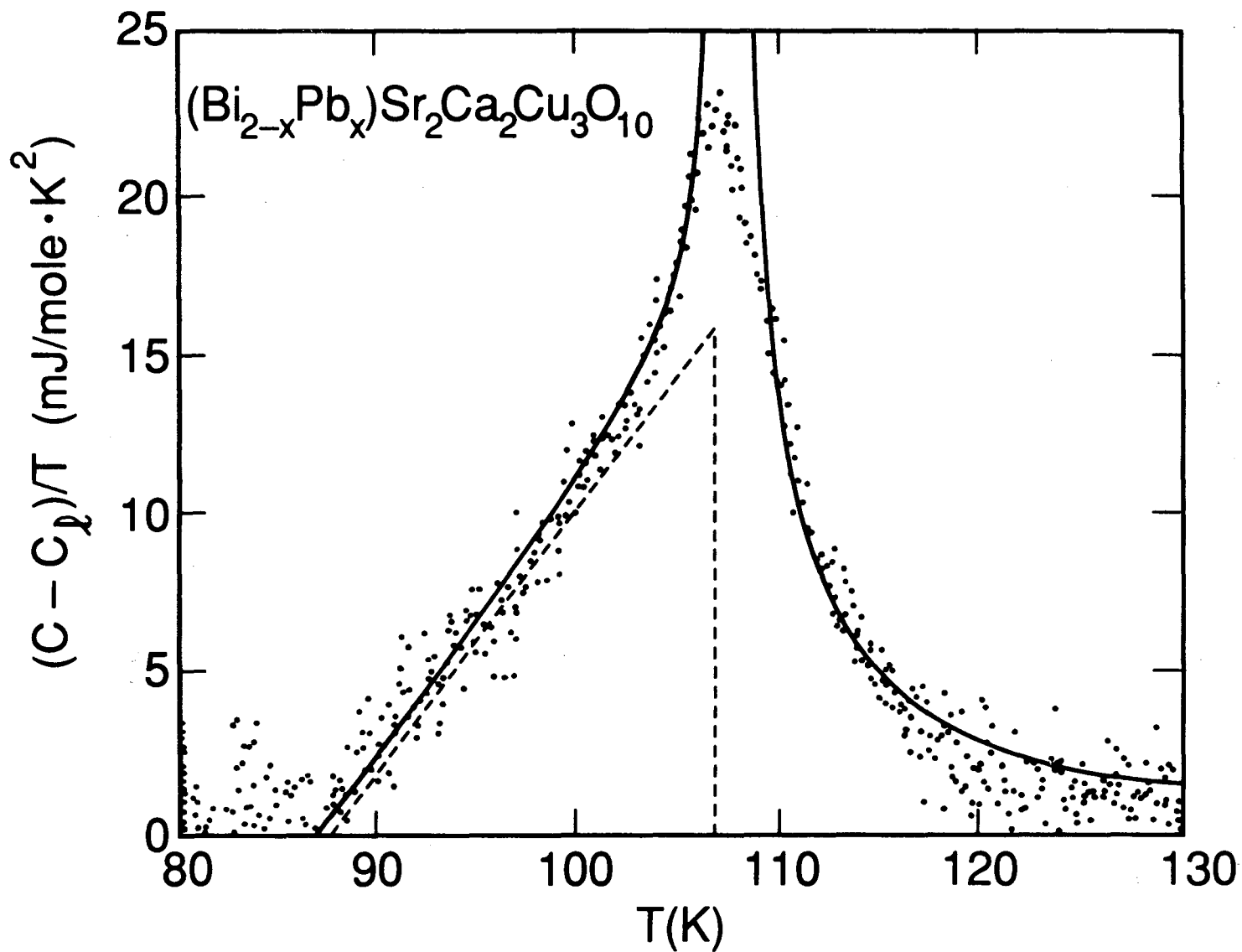
XBL 901-64

Figure 52. Specific heat anomaly for the sample of fig. 51, after subtraction of the background represented by the solid curve in that figure. The curves through the data are fits with exponential functions. The other solid curve is a BCS function scaled to give an entropy balance. The dashed curve is a BCS function scaled to fit the data near 80K (Schnelle et al. 1989).



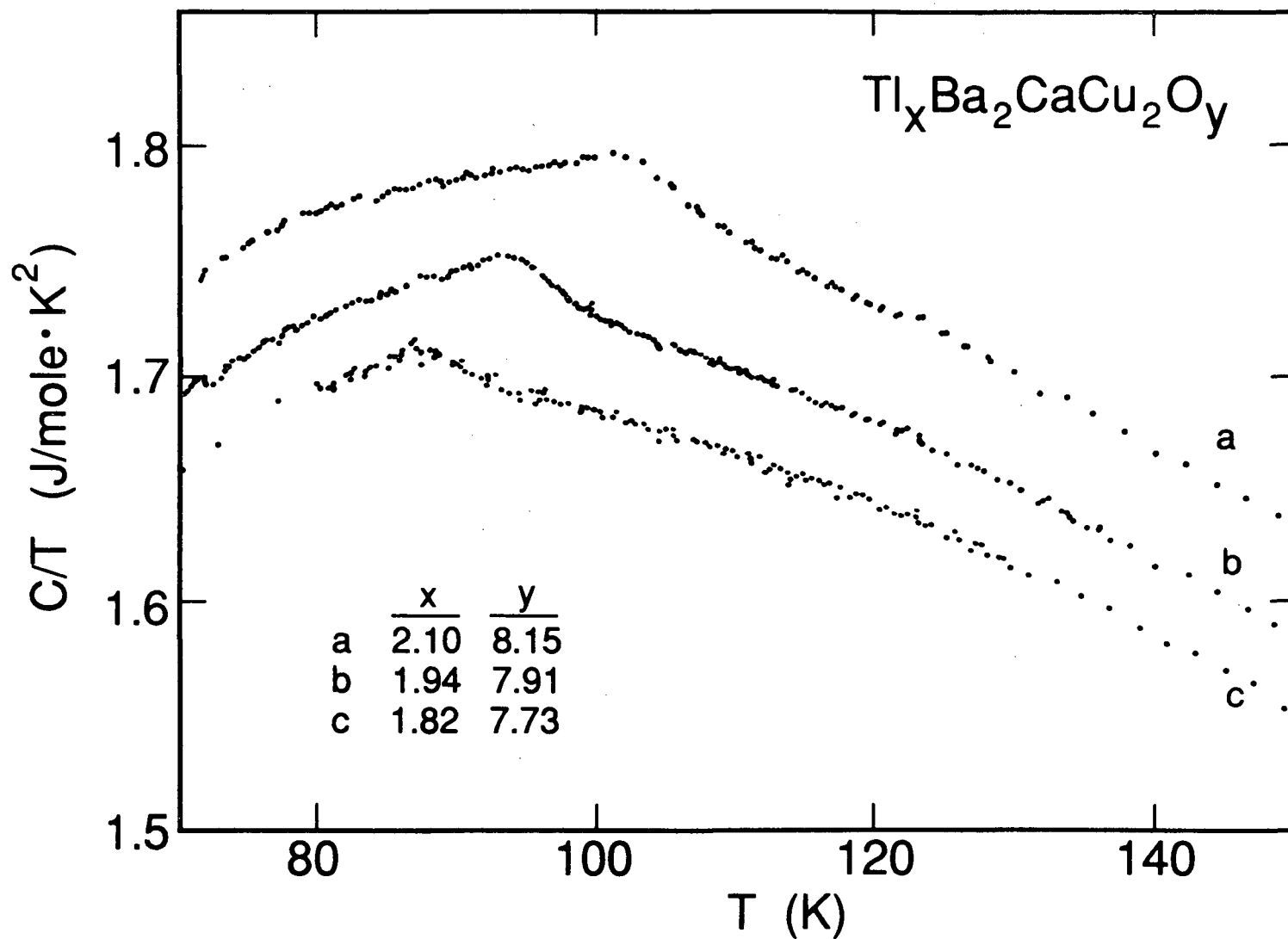
XBL 901-168

Figure 53. Anomaly in specific heat at  $T_c$  of a Pb-stabilized BSCCO (2223) sample. The dashed curve is an approximation to the background specific heat, based on an Einstein plus Debye function interpolation between data well above and well below  $T_c$  (Okazaki et al. 1990).



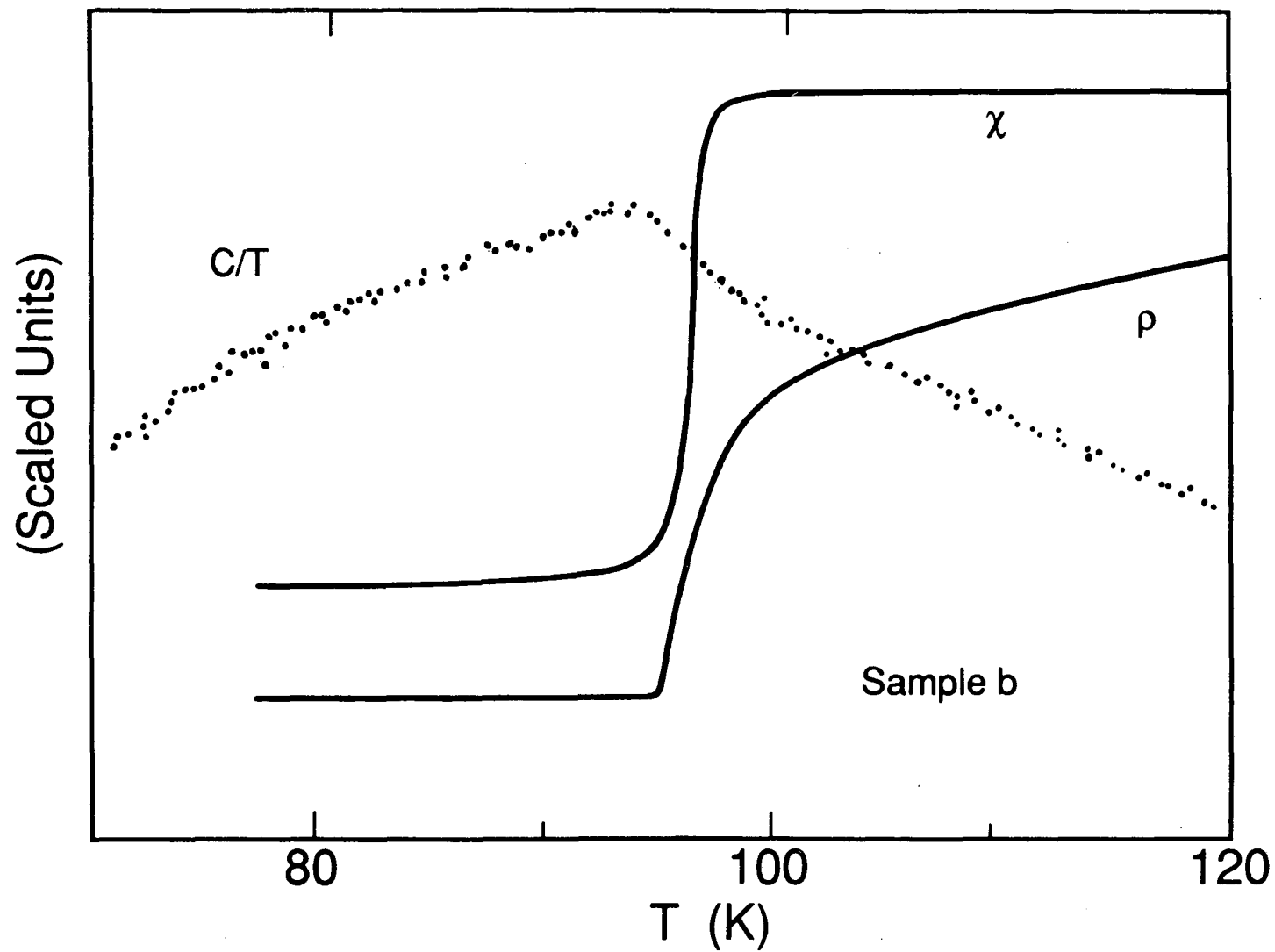
XBL 901-62

Figure 54. Specific heat anomaly for the sample of fig. 53, after subtraction of the background represented by the dashed curve in that figure. The solid curves represent the sum of a BCS function, represented by the dashed lines, and a two dimensional fluctuation contribution (Okazaki et al. 1990).



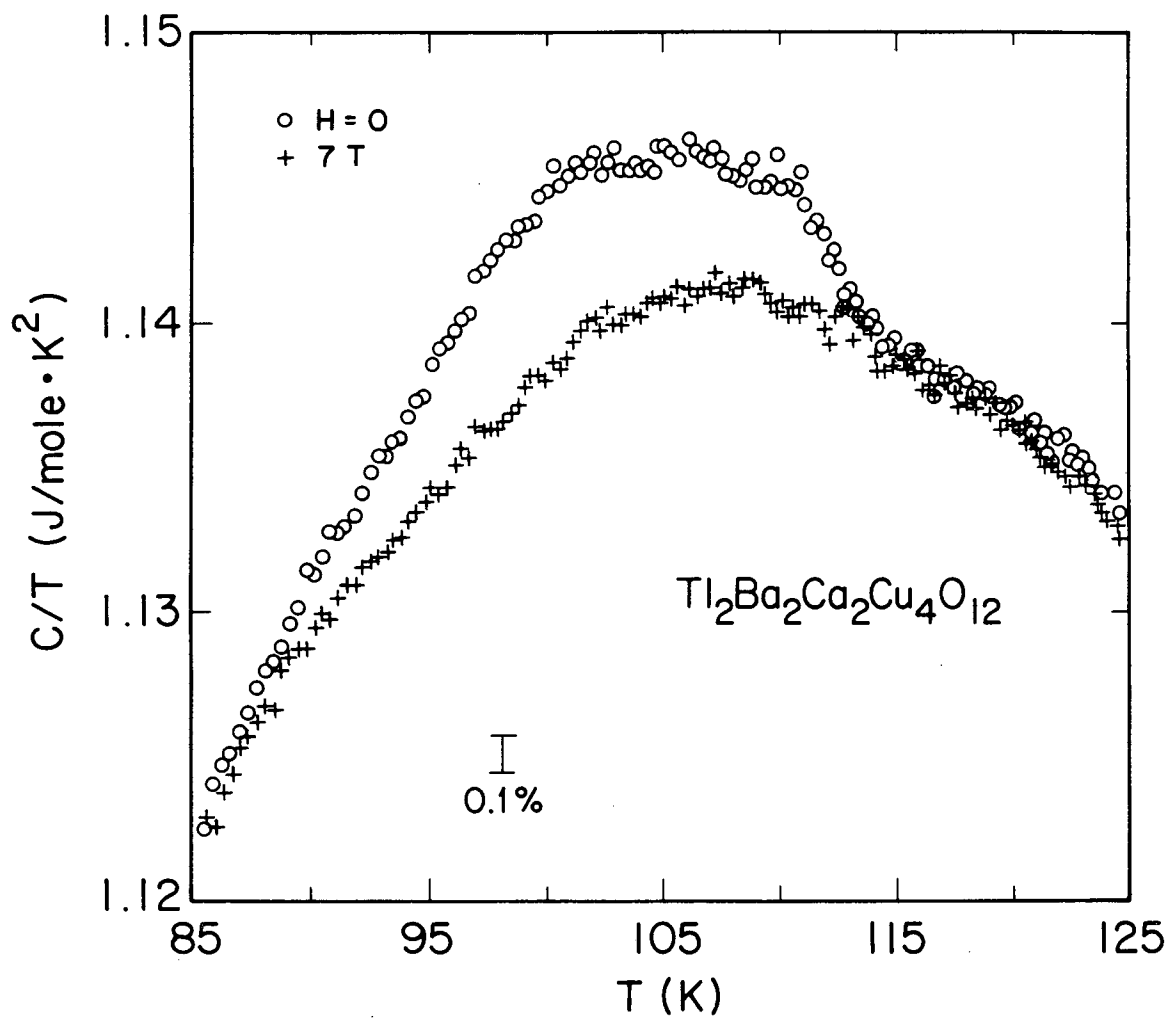
XBL 901-71

Figure 55. The effect of Tl content on the specific heat anomaly at  $T_c$  for a TBCCO (2212) sample (Atake et al. 1989c).



XBL 901-73

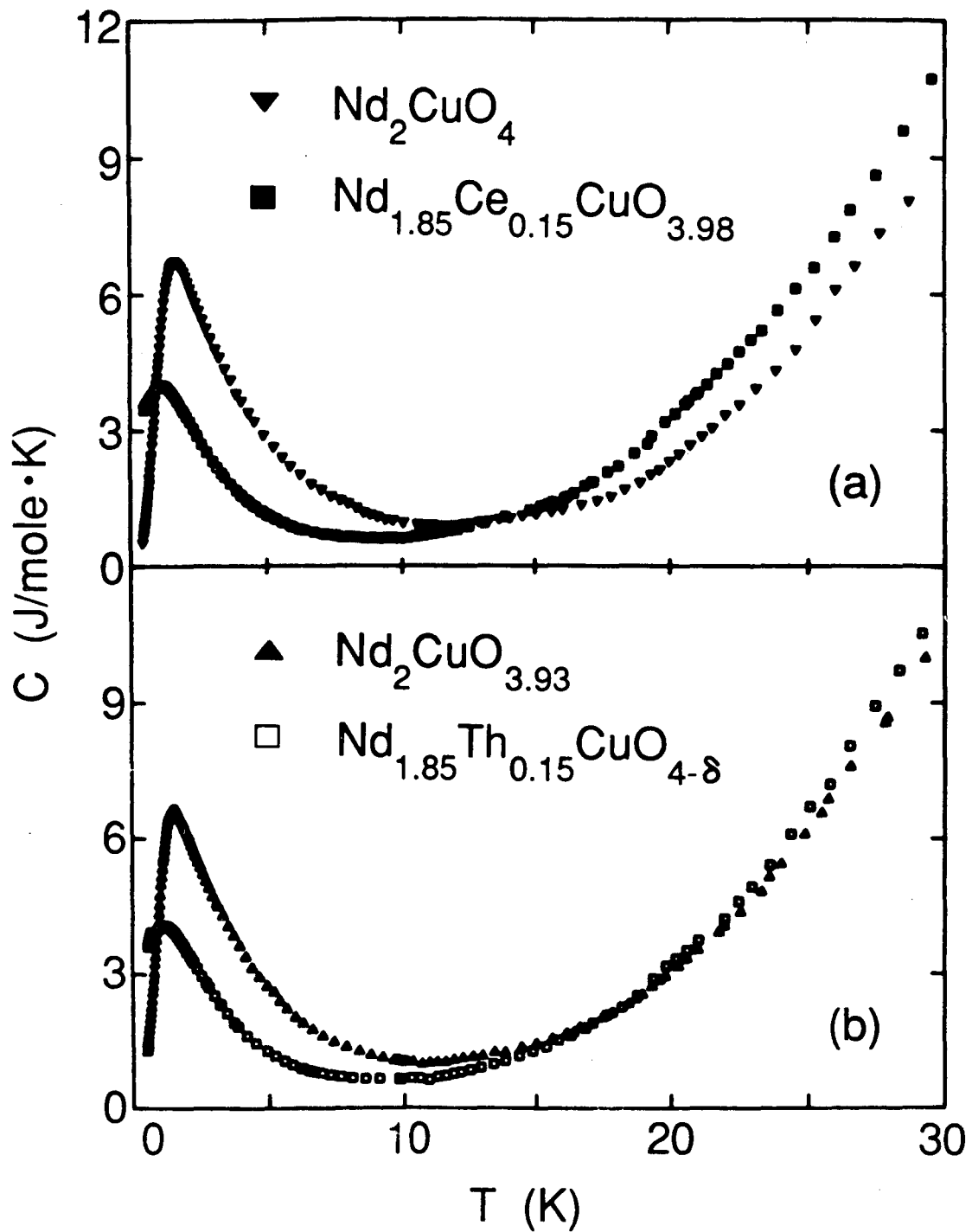
Figure 56. Comparison of the magnetic and resistive transitions with the specific heat of sample b, fig. 55 (Atake et al. 1989c).



XBL 885-1544 B

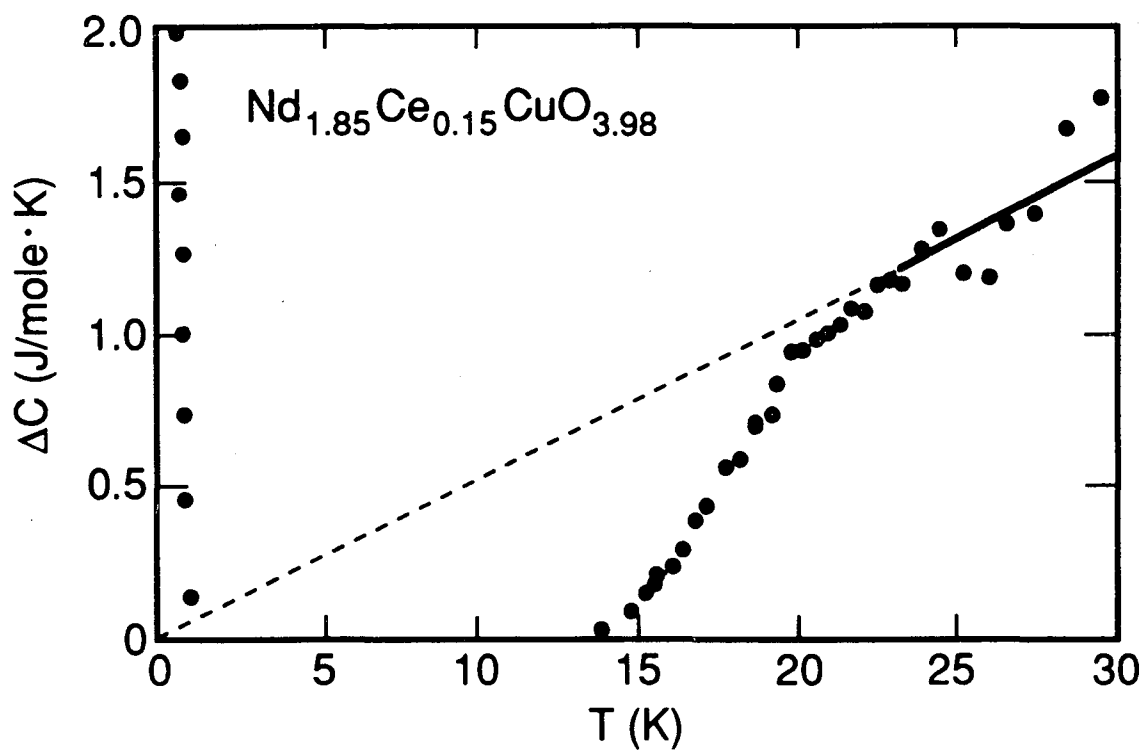
Figure 57. Effect of magnetic field on the specific heat anomaly at  $T_c$  for a TBCCO (2224) sample (Fisher et al. 1988c).





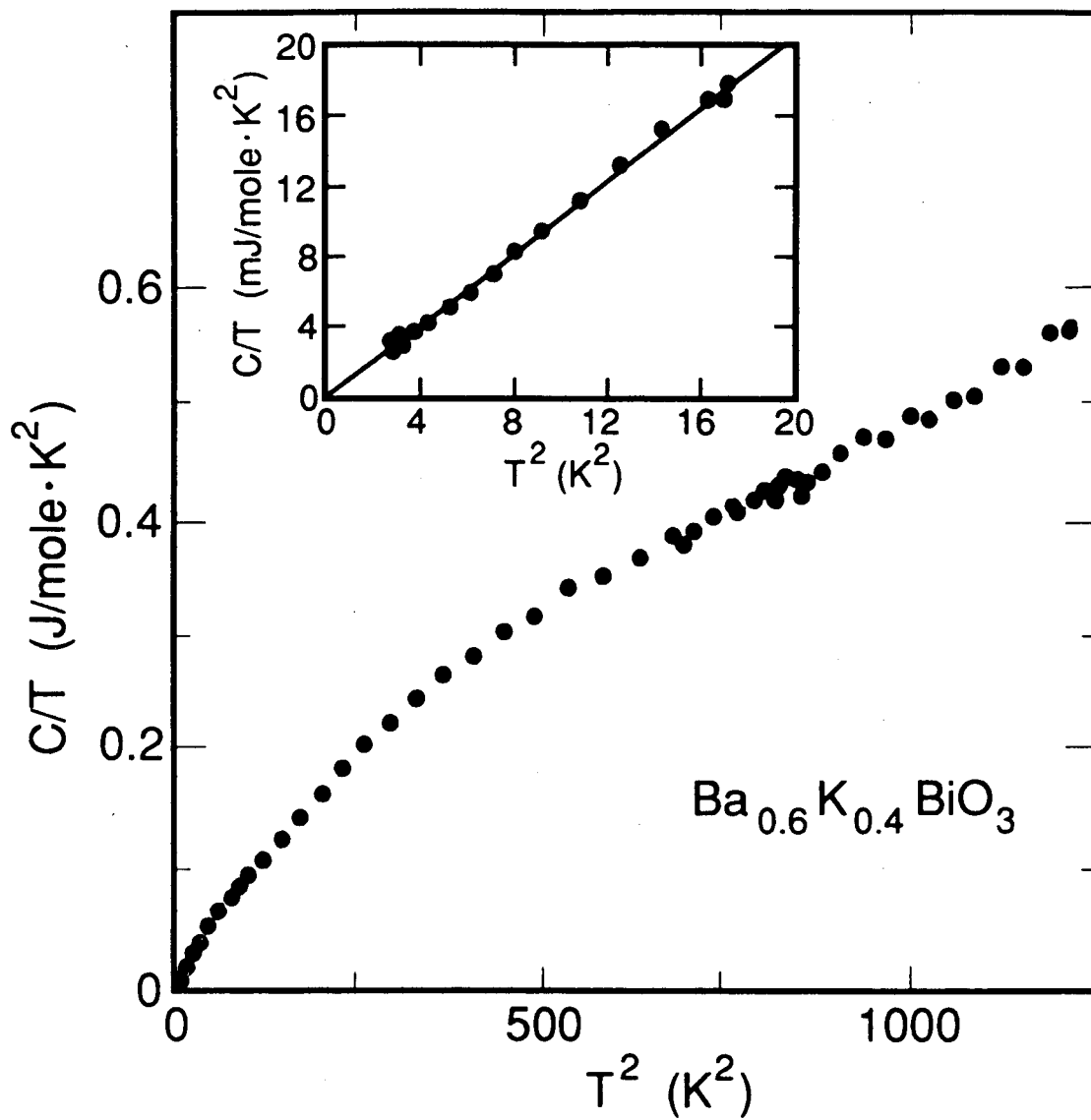
XBL 901-69

Figure 58. Specific heats of several electron-carrier HTSC and the corresponding parent compound (Ghamaty et al. 1989).



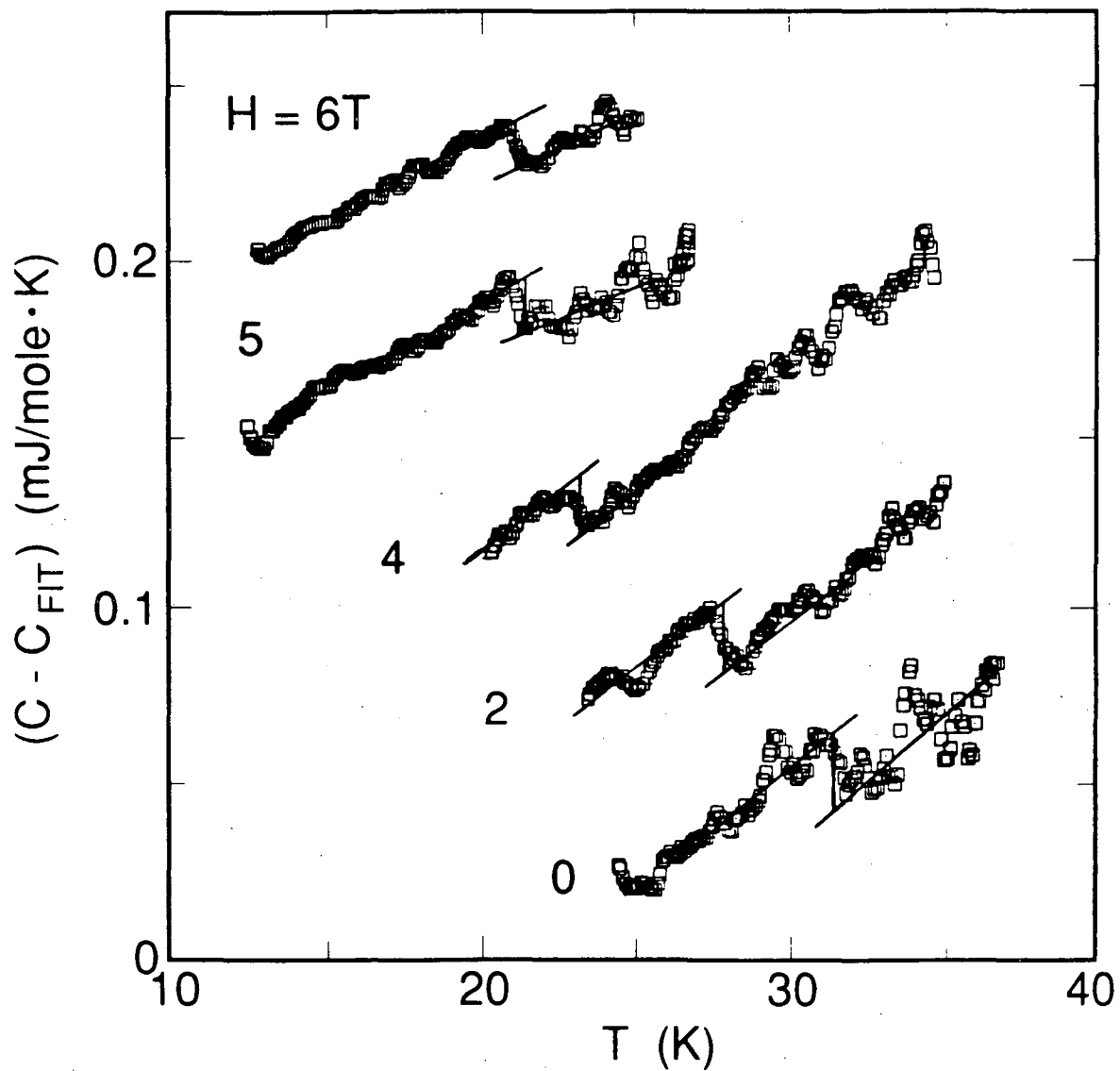
XBL 901-72

Figure 59.  $\Delta C = C(\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{3.98}) - C(\text{Nd}_2\text{CuO}_4)$  (Ghamaty et al. 1989).



XBL 901-75

Figure 60. The specific heat of polycrystalline  $(\text{Ba}_{0.6}\text{K}_{0.4})\text{BiO}_3$  (Hundley et al. 1989).



XBL 901-70

Figure 61.  $\Delta C(T_c)$  for magnetic fields 0 to 6T for single-crystal  $(\text{Ba}_{0.6}\text{K}_{0.4})\text{BiO}_3$ . The curves have been displaced for clarity (Graebner et al. 1989).

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