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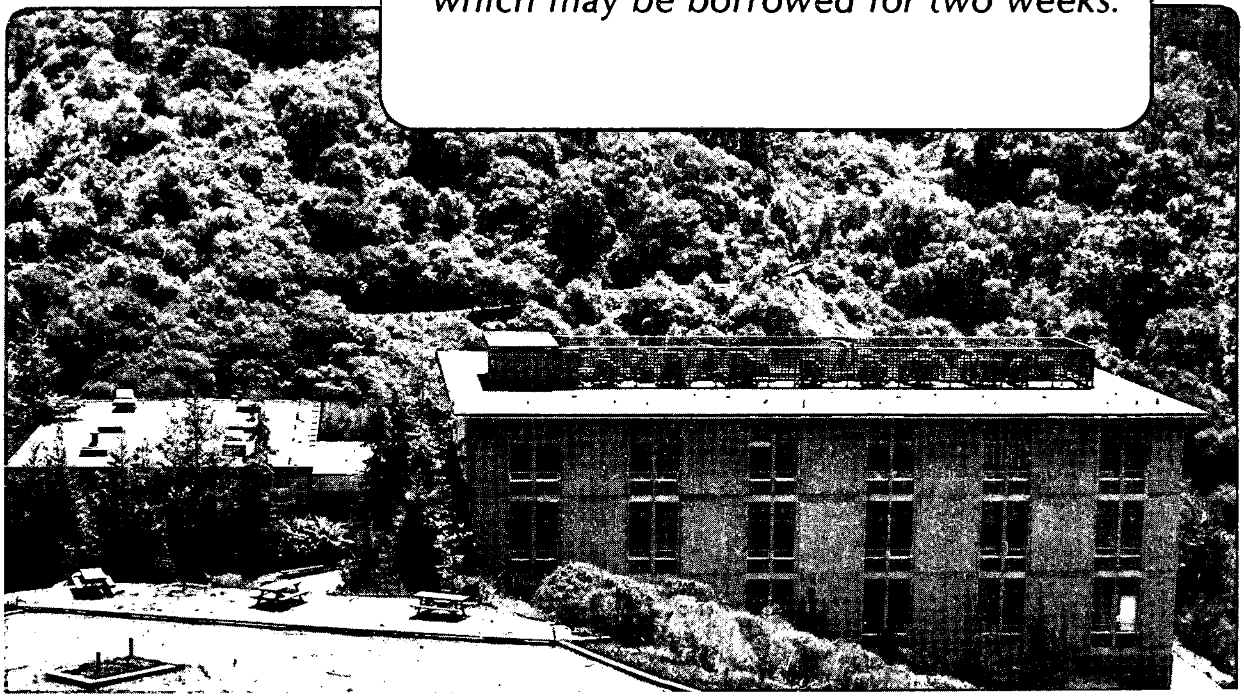

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SPECIFIC HEAT OF THE HIGH-T_c OXIDE SUPERCONDUCTORS: A REVIEW

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ABSTRACT

In this paper we review the specific heat measurements on La_2CuO_4, $La_{2-x}M_xCuO_4$ (M=Ca, Sr and Ba), $YBa_2Cu_3O_7$ and the Bi-Ca-Sr-Cu-O and Tl-Ca-Ba-Cu-O systems. Tables of properties derived from the data are presented. Results on $RBa_2Cu_3O_7$ (R=rare earth elements other than Y) are summarized, as are results on $YBa_2(Cu_{3-x}M_x)O_7$ (M=Zn, Cr, Fe or Ni). The difficulties of analyzing the specific heat data, and specifically the separation of the contributions associated with magnetic impurities, are discussed. It is tentatively concluded that the data near T_c are consistent with BCS theory, although they show evidence of fluctuation effects. It is also concluded that the low-temperature zero-field data on a majority of the high-T_c oxide superconductors provide evidence of an <u>intrinsic</u> term that is proportional to T, a result which is inconsistent with a gap in the electronic density of states.

Key words: High-T_c superconductivity, specific heat

1. INTRODUCTION

1.1. High-T_c Oxide Superconductors

The first known example of a superconducting oxide with the perovskite structure, predicted [1] and discovered [2] by Cohen and colleagues in 1964, was $SrTiO_3$. However, the critical temperature (T_c) was relatively low, and interest in the superconductivity was associated primarily with its electronic structure, that of a degenerate semiconductor. The discovery, in 1975, of superconductivity in $BaPb_{1-x}Bi_xO_3$ with $T_c \approx 13K$ by Sleight et al. [3] first suggested that such oxide systems might be of interest in the search for high T_c's. That lead was followed by a number of groups, but it was not until mid-1986 that Bednorz and Muller [4] reported a sharp drop in the resistivity of $La_{1.85}Ba_{0.15}CuO_4$ at 30K, and suggested that it was an indication of a transition to the superconducting state. The occurrence of superconductivity was soon confirmed by Meissner effect measurements [5,6] and was also shown to be a general property of the system $La_{2-x}M_xCuO_4$ with M=Ca,Sr,Ba (LCCO, LSCO, LBCO) and x within a small range of values near 0.15 [7-9]. The parent compound, La_2CuO_4 (LCO) is also a superconductor [10-13] under special conditions of preparation. In March 1987, superconductivity was reported by Chu and his colleagues [14] in the Y-Ba-Cu-O system, with $T_c \approx 90K$. The superconducting phase was later identified as $YBa_2Cu_3O_7$ (YBCO). The compounds RBCO, in which Y is replaced by a rare earth (R) other than Ce, Pr, Pm and Tb, are also superconductors with similar values of T_c. Within the past several months, and approximately a year after the discovery of superconductivity in YBCO, a number of new superconducting compounds have been discovered in the Bi-Ca-Sr-Cu-O (BCSCO) [15] and Tl-Ca-Ba-Cu-O (TCBCO) [16] systems with T_c ranging from 80 to 125K. It has also been shown that alkali-metal doped LCO, i.e., $La_{2-x}A_xCuO_4$ (LACO), where A = Na or K, are superconducting with T_c~40K and ~4K, respectively [17]. In the first non-Cu containing oxide superconductors discovered since $BaPb_{1-x}Bi_xO_3$, Mattheiss et al. [18] found T_c~22K and ~15K in $(Ba,K)BiO_x$ and $(Ba,Rb)BiO_x$, respectively. Cava et al. [19] have prepared a compound in the first of those systems, $Ba_{0.6}K_{0.4}BiO_3$, with T_c~30K. All of these oxide superconductors have crystal structures that are closely related to those of the perovskites, i.e., modifications of the basic ABX_3 structure [20].

1.2. Specific Heat Measurements: Potential and Problems

In general, specific heat (C) data provide the most reliable basis for distinguishing between bulk and filamentary superconductivity. For bulk superconductors they also provide much interesting and useful information about the transition to, and the nature of, the superconducting state: Measurements in magnetic fields (H) that exceed the upper critical field (H_{c2}), i.e., in the normal state, give the density of electronic states at the Fermi energy [$N(E_F)$], and the Debye characteristic temperature (θ_o), both of which are important in the conventional theory of superconductivity. The former is derived from the term proportional to T, the "linear" term (γT) in C and the latter from the T^3 term in C. The lattice specific heat (C_l), comprised of the T^3 and higher-order, odd-power terms, also gives some information about phonon dispersion. By subtracting C_l from zero-field data, one obtains the superconducting-state electronic specific heat (C_{es}). For a conventional superconductor C_{es}, and particularly the discontinuity in C at T_c [$\Delta C(T_c)$], give information about the strength of the electron-phonon coupling. For the oxide superconductors the temperature dependence of C_{es} might be useful in recognizing certain novel mechanisms of superconductivity, if they are at work (some non-BCS mechanisms could give the usual BCS result).

For the oxide superconductors, however, the interpretation of C is complicated by a number of problems: 1) the transitions are often broad, and possibly incomplete; 2) T_c is in a temperature region in which C_l is very large and does not have a simple temperature dependence; 3) the upper critical fields are so high that it is not practical to obtain normal-state data, except possibly _very_ near T_c; 4) an upturn in C/T exists at low temperatures (evidently due to magnetic impurities and not an intrinsic property of the materials) which complicates interpretation of the data for most samples for $T \le 4$K. Some of these problems are illustrated in Figs. 1 and 2 by typical data for YBCO [21]. In Fig. 1, the solid curve, a smoothed representation of zero-field C data, makes clear the small (percentagewise) size of the anomaly at T_c, and the insets show in more detail the anomaly at T_c and the low-temperature upturn in C/T. (In this particular example the transition seems to take place in a broadened, but also stepwise fashion.) In Fig. 2, data below 10K are shown in a plot of C/T vs T^2, a representation frequently used to estimate graphically the linear term and the cubic term (B_3T^3) in C. The solid line represents the linear and cubic terms obtained by making a least-squares fit to the data with a power series that includes $\gamma T+B_3T^3$ and, in addition, a T^5 term for the effects of phonon dispersion and T^{-2} and T^{-3} terms to approximate the high-temperature limit of the upturn in C/T. This line corresponds to the best values of γ and B_3, but, as is to be expected, <u>it is everywhere below the experimental data</u>. A typical attempt to derive γ and B_3 graphically is represented by the dashed line, which gives an underestimate of γ and an overestimate of B_3 (which in turn leads to an underestimate of θ_o.). Fig. 2 also illustrates an unexpected result of the measurements -- a non-zero value of γ in zero applied field (see Sections 2.2 and 3).

Furthermore, as might be expected for complicated materials that have been the object of such intense interest in the very short period of time since their discovery, inconsistent data have been reported by different investigators -- a fact that probably arises in large part from problems with sample purity and methods of preparation. Nearly all measurements of specific heat have been made on ceramic samples. Only very small single crystals have been grown, which precludes their use in most calorimeters, although very interesting data have been obtained in a few cases. Thus, while the results reported in this Review have already provided much useful information about high-T_c superconductivity, the definitive specific heat data probably still await the availability of better quality, better characterized samples.

1.3. Scope and Organization of this Review

During the span of approximately one year there have been more than 100 publications on specific heat measurements in the high-T_c superconducting oxide systems. This Review will summarize the results of the fairly extensive measurements that have been made on LCO, LMCO, YBCO, RBCO and of some of the first measurements on BCSCO and TCBCO. At the present we know of only one measurement on $BaPb_{1-x}Bi_xO_3$ [22], and none on LACO, $(Ba,K)BiO_x$ or $(Ba,Rb)BiO_x$.

The Review is organized into sections according to topic: In Section 2, there is a summary of the expected contributions to C, the notation used to represent them, their temperature and magnetic field dependences, and tables of some of the major parameters derived from the data, with references. Section 3 is focused on the properties and parameters related to the low-temperature data -- the linear term, particularly its value in zero field, but also its field dependence; the low-temperature upturn in C, and correlations between it and the zero-field linear term; and the T^3 term. In Section 4 the temperature region near T_c is discussed; values of $\Delta C(T_c)$ and its relation to γ and $N(E_F)$ are summarized. The anomaly in C in the vicinity of 220K is covered in Section 5; the effect of substitutions, for both Y and Cu, in YBCO in Section 6; and the lattice specific heat in Section 7. Section 8 lists papers to be published for which we have been unable to obtain preprints. In Section 9 a discussion of non-calorimetric determinations of γ and band structure calculations of the electron density of states are given. A summary of the state of the understanding of the specific heat measurements is given in Section 10.

2. SUMMARY OF SPECIFIC HEAT CONTRIBUTIONS AND TABLES OF RESULTS

2.1. Component Specific Heat Contributions; Notation; Expected Temperature and Field Dependences; Analysis of the Specific Heat into Components

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 moments with a magnetic field, which is either an applied field or, in the case of an ordered magnetic material, an internal field produced by the ordered electronic moments. In either case, a contribution arising from the interaction of a nuclear quadrupole moment with an internal electric field gradient is possible, but it is usually small compared with the magnetic contribution associated with a magnetic field of a few T or more.

For almost all samples of the oxide superconductors there is an additional contribution (C_i) apparently associated with magnetic impurities. In zero-field, this impurity contribution usually manifests itself as an upturn in C/T that starts at a temperature of a few K and increases with decreasing T, presumably taking the form of a Schottky-like anomaly at temperatures below 1K. However, in extreme cases the maximum in C may occur above 1K. For magnetic fields of a few T or more, the maximum always occurs above 1K.

In addition to the subscripts l, e, h and i, a second set of subscripts, n, m and s will be used, when useful, to distinguish the normal, mixed and superconducting states. For specific heat contributions that vary with H, and for parameters derived from them, the value of the magnetic field will be indicated in parentheses following the symbol, but again, only when useful.

The expected H and T dependences are: $C_l = B_3T^3 + B_5T^5 + \ldots$, independent of H and the same for all states; $C_{en} = \gamma T$; $C_{es} \approx a \exp(-b/T)$; and, for a conventional superconductor in a magnetic field that exceeds the lower critical field (H_{c1}), $C_{em} = \gamma(H)T + B_3'(H)T^3 + \ldots$, and $C_h = A(H)T^{-2}$ with $A(H) \propto H^2$ (other terms in the expansion are assumed to be negligible for the cases discussed here). As noted above, $C_i(0)$ may take the form $A(0)T^{-2}$ at temperatures near and above 1K. However, more generally it has a "Schottky-like" form governed both by the applied field (H), and by internal interactions, and an adequate approximation to the high temperature tail (at whatever temperature it occurs) may require terms in odd negative powers of T as well as even.

2.2 Outline of the Analysis of C into Component Contributions

In most reports of measurements of C, no attempt has been made to analyze the data to separate C_e and C_l except at low-temperature or near T_c (see Section 4 for exceptions). The zero-field low-temperature data, which include C_l, C_e and C_i, are normally analyzed to extract a linear term $[\gamma(0)T]$ and the coefficients of one or more terms in C_l, i.e., B_3, B_5, etc. For a conventional superconductor and a complete transition to the superconducting state, C_{es} would be essentially zero (for $T \leq T_c/10$) and such an analysis would give $\gamma(0) = 0$. The (initially) surprising result of these analyses, however, was $\gamma(0) \neq 0$. The origin of the non-zero $\gamma(0)$ is still uncertain, and is one of the most interesting questions related to the high-T_c superconductors. In some cases measurements in a magnetic field have been analyzed to separate C_l, C_e and C_i, and $\gamma(H)$ and $B_3'(H)$ have been determined. Near T_c, $\Delta C(T_c)$ has been estimated by entropy-conserving extrapolations from above and below T_c to obtain the "ideal" sharp discontinuity expected for conventional superconductors. At intermediate temperatures C_{es} is the quantity of interest, but it cannot be extracted from C in a straightforward way both because it is small compared with C_1 and because C_1 cannot be determined independently from measurements in the normal state (as is possible in the case of conventional superconductors).

2.3. Results of Measurements and References

The one measurement [22] on $BaPb_{1-x}Bi_xO_3$ gave $\gamma \approx 0.75$ mJ/mole K^2 and $B_3 \approx 0.25$ mJ/mole K^4 ($\theta_o \approx 340K$). No anomaly was observed at T_c, although magnetic susceptibility (χ) data showed a Meissner effect. For other oxide superconductors, values of some of the parameters derived from C and references are given in Tables I to VI. The units of tabulated quantities are in K, T and mJ/mole. Following the usual practice, however, the value of θ_o is derived from the formula $B_3 = (12/5)\pi^4 R \theta_o^{-3}$ <u>using the value of B_3 per g-at.</u>, i.e., the value of B_3 divided by the total number of atoms in the chemical formula.

3. LOW TEMPERATURE SPECIFIC HEAT

With few exceptions, all low-temperature specific heat measurements on the high-T_c materials show two common features: an upturn in C/T, and $\gamma(0) \neq 0$. The C/T upturn is almost certainly not an intrinsic property since its magnitude depends critically on sample preparation. It probably has its origin in the onset of ordering in magnetic impurity phases, since its magnitude is correlated with other measures of the amount of such phases, and the zero-field upturn becomes a Schottky-like anomaly in high magnetic fields [25-27,62,72,82]. On the other hand, $\gamma(0)$ is not as easy to account for. It could arise from a variety of sources acting separately or in combination: 1) Part of the sample could remain normal, even at the lowest temperatures. 2) Acoustic and thermal measurements below 0.5K for YBCO and LMCO have indicated the possible presence of tunneling or two-level systems (TLS) [40,50,129]. The TLS, which might be associated with oxygen vacancies, could produce a $\gamma(0)T$ term in C, as observed for TLS in other systems. Some evidence for tunneling in YBCO has also been found from the time dependence of C and from the thermal conductivity at low temperatures [130]. 3) Any mechanism producing gapless superconductivity, would lead to a term linear in T for the specific heat. In particular, the resonant-valence-bond (RVB) model proposed by Anderson [131] has received considerable attention in this respect. 4) Various impurity phases in the material (such as $BaCuO_{2+x}$) have large "pseudo-linear" terms in C [25,82,114,116,118]. The specific heats for various possible impurity phases are shown in Figs. 3 and 4 for H=0. Measurements of C for these materials have not been made in magnetic fields, although they would be of interest in connection with testing further the possibility that $\gamma(0)$ is associated with these impurities, and therefore with measurements of the variation of $\gamma(H)$ with field.

The departure of C_1 from T^3 behavior near 5K (see Sections 2 and 7) coupled with the upturn in C/T makes the common practice of visually fitting a C/T vs T^2 plot with a straight line an unreliable method to obtain B_3 and $\gamma(0)$. Accurate values for these parameters can be obtained by fitting the specific heat data by a series in T that takes into account both the upturn in C/T and departures of C_1 from T^3, e.g.,

$$\ldots + A_{-3}T^{-3} + A_{-2}T^{-2} + \gamma(0)T + B_3T^3 + B_5T^5 + \ldots \quad (3.1)$$

(The T^5 and higher order terms can also be represented by appropriate Einstein functions and the T^{-3} and T^{-2} terms, which represent the upturn in C/T, can be replaced by the high-temperature part of a Schottky anomaly.) To check for consistency of the fit and the uniqueness of the parameters derived, both the number of terms and the temperature range of the fit should be varied.

A sufficiently high magnetic field causes the C/T upturn at H=0 to become a Schottky-like anomaly (actually a superposition of Schottky functions resulting from a distribution of the local internal fields), which in an applied field of 7T, for example, has a broadened maximum in C/T near ~3.5K. (Since the coherence lengths for the high-T_c materials are very short, ~20Å or less, compared to the penetration depths, ~2000Å, magnetic fields inside the materials are essentially uniform for $H>H_{c1}$.) Even when a magnetic field produces a Schottky-like anomaly, there still is a C/T upturn at low temperatures as a result of the coupling of the field to nuclear moments, e.g., ^{63}Cu and ^{65}Cu.

For $H_{c1}<H<H_{c2}$, a superconductor is in the mixed state for which C_{es} is characterized by $\gamma(H)T + B_3'(H)T^3$ terms in C [132]. For specific heat measurements in a constant field, the data can be fitted by the expression:

$$A_{-2}(H)T^{-2} + n_i C_{Sch} + \gamma(H)T + B_3(H)T^3 + B_5T^5 + \ldots . \qquad (3.2)$$

Here the $A_{-2}(H)T^{-2}$ term is the hyperfine component of C. The Schottky specific heat (C_{Sch}) is characterized by a spin (usually assumed to be 1/2), an internal magnetic field (g=2 is assumed) and the amount of magnetic material (n_i), which can be estimated from the height of the maximum or the entropy of the anomaly. By a comparison of the parameters derived for H≠0 with those for H=0, $B_3'(H)$ and $\partial\gamma(H)/\partial H$ can be obtained.

3.1. LMCO

Figures 5 and 6 show C/T vs T for LCCO and LSCO, respectively, in

H=0, 3.5 and 7T [26,27]. The small C/T upturn in H=0 indicates only a low concentration of magnetic impurities, in sharp contrast to most YBCO (see Fig. 2), BCSCO and TCBCO samples which frequently have very large upturns (see Sections 3.2,3.3). A small anomaly is evident in 3.5T for the LSCO sample, which has a larger impurity content than does the LCCO sample. The upturns in C(H)/T are the result of hyperfine interactions, and at higher temperatures the near parallel displacement of the C(H)/T curves indicate the increase of γ(H) with H in the mixed state. Figure 7 shows a decomposition of the same LSCO data analyzed into components which were found from a least-squares fit of Eq. 3.2 [26,27]. At higher T, the departure from a constant value for C_e(H) is a result of the $B_3'(H)T^3$ term of the mixed state. A magnetic impurity concentration of $\sim 3\times 10^{-4}$ moles/mole sample is responsible for the two Schottky curves labeled C_i(H).

Figure 8 displays C/T vs T^2 for the $La_{2-x}Ba_xCuO_4$ system (with no C/T upturns) investigated by Kumagai et al. [30]. From x=0 to 0.02 the samples were antiferromagnetic and $\gamma(0)=0\pm0.5$ mJ/mole K^2. For x>0.02 to 0.04 the material was a non-magnetic insulator and γ(0) increased with increasing x, and appeared to saturate at a value between 4-5 mJ/mole K^2 in the superconducting region for x≥0.05 to 0.15. These results suggest an intrinsic origin for γ(0) and lend support to the RVB model. Similar results have been obtained for the $La_{2-x}Sr_xCuO_4$ system by Kato et al. [29] with $\gamma(0)\sim 1$ to 2 mJ/mole K^2. For LCO, the parent compound, values of γ(0) have been observed which range from 0 to 2 mJ/mole K^2. This spread in values could be due to sample-to-sample variations in antiferromagnetic order, or to other variations in sample quality.

(Antiferromagnetic ordering in LCO, found by Shirane et al. [133] in neutron scattering measurements, and by Kato et al. [29], suggests that for $\gamma(0)=0$ the LCO samples must be antiferromagnetic. For a single crystal investigated by them, the antiferromagnetism had been suppressed and $\gamma(0)=1$ mJ/mole K^2.)

All of the LMCO compounds show hyperfine contributions for the specific heat in fields [26,27]. For LCO the hyperfine component was equal to that expected for Cu and La. This was also the case for one LCCO and one LSCO sample, but for another LSCO sample and two LBCO samples the measured hyperfine terms were smaller. A value of $C_h(H)$ that is smaller than expected suggests some type of shielding, internal hyperfine fields opposed to the applied field, or very long relaxation times.

3.2. YBCO

The specific heat at low temperatures for a typical sample of YBCO [72] is shown as a plot of $[C-C_1]/T$ vs T in Fig. 9 for H=0, 3.5 and 7T. At H=0, the C/T upturn is about an order of magnitude greater than the corresponding upturns for LMCO samples. (From the Schottky-like anomaly in 7T the impurity content can be estimated to be about 0.004 moles/mole YBCO.) The various components of C(H) -- as obtained from least-squares fits to the data [62] -- are shown in Fig. 10. While the $\gamma(H)T$ terms for the mixed state are found, the $B_3'(H)T^3$ terms are not, in contrast to the LMCO results. [$B_3'(H)$ for YBCO may be smaller than for LMCO since $[H_{c2}]_{T=0}$ is larger.]

Because of the Schottky-like anomalies that are observed in magnetic fields, it is likely that the C/T upturn in H=0 is not an intrinsic property but is connected with magnetic impurity phases -- most probably $BaCuO_{2+x}$. It has also been suggested that a finite $\gamma(0)$ is connected, at least in part, with these impurity phases [25,82,84,114,116,118]. (For a sample with an impurity content of ~0.08 moles/mole YBCO, $\gamma(0) \approx 20$ mJ/mole K^2 [26,27]. Similar large values for $\gamma(0)$ have been reported elsewhere [83,114,117].) Depending on the preparation procedure, $BaCuO_{2+x}$ may have a large upturn in C/T and/or a large "pseudo-linear" term in C -- see Fig. 4 and Refs. [25,84,114]. In Fig. 11 C/T vs T^2 is plotted for three samples of YBCO [87,88]. As the upturn in C/T decreases, $\gamma(0)$ also decreases; however, as the upturn vanishes, $\gamma(0) \rightarrow 4.5$ mJ/mole K^2. Eckert et al. [114,117] have investigated the upturn in C/T and $\gamma(0)$ as a function of Cu^{2+} impurity content (as determined from magnetic susceptibility measurements above T_c) for both superconducting and non-superconducting samples of YBCO. For some of these samples, both superconducting and non-superconducting, a linear correlation was found between $\gamma(0)$ and Cu^{2+}/Cu_{total} with a zero intercept for zero Cu^{2+} content. However, a number of the superconducting samples did not show such a correlation when $Cu^{2+}/Cu_{total} < 0.05$, and suggested that although a "pseudo-linear" term from magnetic impurities can account for a large fraction of the observed $\gamma(0)$, other mechanisms may be responsible for an intrinsic $\gamma(0)$ of ~4 mJ/mole K^2. (X-ray diffraction showed the presence of $BaCuO_{2+x}$ for samples with $Cu^{2+}/Cu_{total} > 0.05$, the lower limit of detectability by such an analysis.) Fig. 12 is a plot of $\gamma(0)$ vs n_i (obtained from the Schottky-like anomalies in 7T) for a number of samples of YBCO [62] and one for TCBCO [120]. The straight line through the data has a slope which is consistent with $BaCuO_{2+x}$ as the impurity phase, while the intercept suggests an intrinsic $\gamma(0)$ of 7 mJ/mole K^2, somewhat larger than the ~4 mJ/mole K^2 quoted above. (The consistency of the point for TCBCO with the others in Fig. 12 may be coincidental.)

A systematic study has been made of the effect of oxygen content on specific heat for $YBa_2Cu_3O_{7-x}$ by Ramirez et al. [25] and Ayache et al. [70]. The results are illustrated in Fig. 13 [25]. The C/T upturn increases as the oxygen content is reduced, while θ_o remains nearly constant. Ayache et al. [70] find $\gamma(0)$ to be essentially constant at 10 mJ/mole K^2 for x=0 to 1, while Ramirez et al. [25] report that for x=0 and 0.3, $\gamma(0)$ is 4.2 and 3.5 mJ/mole K^2, respectively, and 6.3 mJ/mole K^2 for x=0.7. [A $\gamma(0)$ arising from tunneling states involving oxygen might be expected to change with oxygen content. In particular, as x is increased one might expect $\gamma(0)$ to decrease, which is not what is observed.]

Measurements of specific heat on a mosaic of single crystals have been made by von Molnar et al. [81]. Their data are plotted in Fig. 14 as C/T vs T^2 for both superconducting and non-superconducting samples. No upturn in C/T was observed (although their data did not extend below 1.8K); however, a finite $\gamma(0)$ was found which did not depend strongly on whether the samples were superconducting or non-superconducting. In contrast to the ceramic samples, however, there was more than a factor of two change in B_3 between C_n and C_s.

In a magnetic field all YBCO samples show hyperfine components arising mainly from Cu. These hyperfine components are smaller than expected. This result could be explained by the long relaxation times that have been observed for some of the Cu nuclei in nuclear resonance experiments [134]. In principle, accurate specific heat measurements might give the numbers of Cu nuclei associated with the different relaxation times. Another field-dependent effect has been observed in YBCO: Specific heat measurements made in a magnetic field show time-dependent effects which depend on whether the field is applied before or after the sample is cooled [135].

3.3. BCSCO and TCBCO

Plots of the specific heat in H=0 and 7T for TCBCO and BCSCO [120] are shown in Figs. 15 and 16, respectively. For TCBCO, C is similar to that observed in YBCO -- an upturn in C/T at H=0, a Schottky-like anomaly in 7T and a finite $\gamma(0)$. On the other hand, for BCSCO, which also exhibits an upturn in C/T and a Schottky-like anomaly, $\gamma(0)=0$ to within the experimental uncertainty. This is seen clearly in Fig. 17 where C_i has been subtracted. Kumagai and Nakamura [121] have also observed $\gamma(0)=0$ for a BCSCO sample with no upturn in C/T. Similar results have been reported by Sera et al. [122] who did observe a small upturn.

The fact that, within experimental error, BCSCO has no linear term in its specific heat, while this term is present in TCBCO and the other high-T_c materials, deserves further study. One significant difference between BCSCO and TCBCO may be that the latter contains Ba. The Tables in Section 2 show that LBCO has a higher $\gamma(0)$ than either LSCO or LCCO. This fact suggests that Ba impurities contribute to the non-zero value of $\gamma(0)$. This suggestion is clearly supported by the work on YBCO (see Section 2.3), but that work also indicates that even after contributions to $\gamma(0)$ from $BaCuO_{2+x}$ are accounted for, there remains an intrinsic $\gamma(0)$. More reliable data concerning the presence or absence of an intrinsic

$\gamma(0)$ in BCSCO and TCBCO, as well as in the other oxide superconductors, are essential. Should such an intrinsic term prove to characterize the high-T_c compounds, it would constitute perhaps the most fundamental empirical difference between these materials and other superconductors.

For both the BCSCO and TCBCO samples $C_h(H)$ is smaller than expected for Cu and Bi or Tl hyperfine components [120]. The data suggest that only Bi or Tl are contributing to $C_h(H)$. However, because of the large low-temperature tail of the magnetic impurity anomaly, the measurements do not extend to low enough temperatures to make an unambiguous evaluation.

4. SPECIFIC HEAT NEAR T_c

Measurement of $\Delta C(T_c)/T_c$ for the high-T_c oxide superconductors has proved difficult for the reasons cited in Section 1.2. Furthermore, fluctuation effects, which have their origin in very small coherence lengths, complicate the interpretation of [C(0)-C(H)]. Nevertheless, there have been numerous estimates of the "ideal" sharp values of $\Delta C(T_c)$.

For most of the high-T_c materials $\gamma(0)\neq 0$, and, as discussed in Section 3, there is evidence that a non-zero $\gamma(0)$ may be an intrinsic property of at least some of the high-T_c superconductors. However, another possibility is that $\gamma(0)$ is not intrinsic, but rather provides a measure of that fraction of the sample which remains normal (γ_n). In that case, $\gamma(0)$ and the observed $\Delta C(T_c)$ are related: If γ_n is assumed constant for all $T\leq T_c$, and γ is assumed to be the same throughout the sample, then:

$$\gamma(0)=f_n\gamma \qquad (4.1)$$

and

$$\Delta C(T_c)/T_c = f_s\beta\gamma T_c, \qquad (4.2)$$

where $f_s=(1-f_n)$. If γ is known from other measurements (see Section 9), or if β is taken as 1.43 (the weak-coupling BCS limit), Eqs. (4.1) and (4.2) can be solved for f_n and β or γ, respectively.

The value of γ can also be related to H_{c2} since empirically $\gamma(H)$ has been shown to be approximately linear in H in the accessible part of the region $H_{c1}\leq H\leq H_{c2}$ [136], consistent with the behavior of conventional type-II superconductors. It follows that

$$[H_{c2}]_{T=0} = [\gamma-\gamma(0)]/[\partial\gamma(H)/\partial H]. \qquad (4.3)$$

Therefore, if $[H_{c2}]_{T=0}$ is known, γ can be derived from

$$\gamma=\gamma(0) + [\partial\gamma(H)/\partial H][H_{c2}]_{T=0}, \qquad (4.4)$$

and using Eqs. (4.1) and (4.2), β can be derived.

4.1. LMCO

The LMCO superconductors usually do not show well-defined, sharp transitions in C at T_c. Thus $\Delta C(T_c)/T_c$ is difficult to obtain. This lack of sharpness may be largely a sample preparation problem, but in part it may be a consequence of the material's being a solid solution. In the LMCO system, by far the largest number of specific heat measurements have been made on LSCO, which has the best-defined $\Delta C(T_c)/T_c$. Only two measurements of C have been reported for LCCO [26,27,36] and they differ greatly. The original high-T_c material discovered by Bednorz and Muller [4], LBCO, seems to be unique, since with one exception [41], no anomaly in C vs T near T_c has been resolved. For that one case [41], specific heat measurements made after cooling LBCO from 300 to 25K, the temperature at which the resistance became zero, showed a discontinuity at T_c; however, measurements made after cooling from 300 to 5K showed no anomaly in C.

Loram and Mirza [137] used differential calorimetry to investigate LSCO and to obtain an estimate of C_{es} for all $T<T_c$. Their results are displayed in Fig. 18 as γ vs T (γ=C_{es}/T) for two samples. The principal advantage of this method is that, <u>provided a proper reference substance can be found</u>, a large fraction of the phonon specific heat can be compensated. However, in practice, to obtain C_{es}/T substantial corrections must be applied to the data. They are of the form: $\Delta C_b/T = \Delta C_l/T + \Delta C_i/T + \Delta\gamma + \Delta\gamma(0)$, where Δ stands for the difference between the sample and reference specific heats. Conventional measurements of C at low temperatures can be used to establish $\Delta\gamma(0)$ and $\Delta C_i/T$; however, $\Delta\gamma$, the difference between the normal state γ for the sample and that of the reference is difficult to assess and is assumed to be zero. The most difficult term to evaluate is $\Delta C_l/T$. Finally, the $\Delta C_b/T$ correction must be made to satisfy the condition $\Delta S = \int_0^{Tc}[C_{es}/T]dT = 0$. If these corrections can be made properly, then γ, $\Delta C(T_c)/T_c$ and β can be obtained and the energy gap parameter $[2\Delta(0)/kT_c]$ found by fitting C_{es} vs T to theory for $T<T_c$. From the C_{es} data the thermodynamic critical field (H_c) can also be calculated. The results show consistency with the BCS weak coupling limit. Using this same calorimetric technique, Loram et al. [34] also investigated LBCO, which showed only a very small anomaly. They interpret this result as implying that only a very small fraction of the conduction electrons were participating in the superconductivity.

One method of determining $\Delta C(T_c)$ that has been used for LMCO is to measure C near T_c both in H=0 and in a field which one hopes is high enough to lower the transition temperature by several degrees. The results obtained using this method are shown in Fig. 19 for LCCO and LSCO

[26,27]. In view of fluctuation effects near T_c, however, $[C(0)-C(7)]$ may be an underestimate of $(C_{es}-C_{en})$ -- see Section 4.2 for a discussion of such effects. In other cases visual extrapolations above and below the small anomaly at T_c have been used to estimate ΔC.

From the values given in Refs. [26,27] for $\partial\gamma(H)/\partial H$, $\Delta C/T_c$, and $\gamma(0)$, $[H_{c2}]_{T=0}$ can be calculated. If β is assumed to be 1.43, γ can be obtained from Eqs. (4.1) and (4.2). Eq. (4.3) can then be used to obtain $[H_{c2}]_{T=0}$ = 40T and 65T for LCCO and LSCO, respectively. These values are in reasonable agreement with values reported elsewhere [138].

Although most of the research effort is now concentrated on YBCO, BCSCO and TCBCO, specific heat measurements on high quality LMCO samples with sharper transitions might provide reliable values of parameters that would make a useful contribution to understanding high-T_c materials. In particular, a thorough specific heat study of LBCO to find if it is indeed different from the other LMCO materials would be worthwhile.

4.2. YBCO

The specific heat anomaly associated with the superconducting transition of YBCO has been more widely studied than that of any other substance. Between March 1987 and June 1988 there were more than 80 reported measurements -- not including those measurements made on samples in which rare earths have been substituted for Y and 3d elements for Cu (see Section 6). In almost all cases, it was found that the anomaly in C at T_c could be resolved. Fig. 1 provides an example: the anomaly near 90K is clearly visible even in this wide-temperature-interval plot [62]. In Fig. 20 the relation between the superconducting transition in C/T for YBCO and the corresponding ones for magnetic and resistivity measurements are compared [113].

As sample preparation techniques have improved, the specific heat anomalies at T_c have become increasingly sharper and higher. Figure 21 shows the evolution of measurements made by the Geneva group [113]. The data on the first samples are at the top of the figure and those obtained with later, and better, samples are shown at the bottom. Junod et al. [113] state that the citrate pyrolysis method of preparation provides samples with very narrow transition regions and large $\Delta C(T_c)/T_c$. Note that above T_c C/T increases with increasing T for some samples, decreases for others and is essentially constant in other cases. The reason for these sample-to-sample differences is not clear.

Loram and Mirza [100,101] have used differential calorimetry to obtain the electronic specific heat of YBCO. Their results for two samples are plotted as $\delta\gamma$ vs T in Fig. 22, where $\delta\gamma \equiv (C_{es}-C_{en})/T$. As noted in Section 4.1 where the method is described briefly, the authors do not measure $\delta\gamma$ directly, but rather calculate it by making corrections to the data for $C_{sample}-C_{reference}$. They also obtain values for γ and $\Delta C(T_c)/T_c$ (see Table V), and derive $\beta=4.1$, $2\Delta(0)/kT_c \approx 6\pm0.5$ and $H_c(0)=0.815T$.

To find $\Delta C(T_c)/T_c$, C_n must be estimated in some manner, and the most common method is by extrapolation of C from above and below T_c and construction of an idealized, sharp, entropy-conserving discontinuity. A variation of this extrapolation procedure is illustrated in Fig. 23 taken from the paper of Beckman et al. [92]. First γ is obtained from the data and the BCS relationship $\Delta C(T_c)/\gamma T_c=1.43$, and then γT is subtracted from C above T_c to obtain C_1. Below T_c, $C_{es}/C_{en}(T_c)$ is calculated from the

BCS theory which permits C_1 below T_c to be obtained. The smooth joining of C_1 above and below T_c demonstrates the correctness of the original choice of γ. Junod et al. [113] also use an extrapolation to obtain $\Delta C(T_c)/T_c$. For their better samples there is a region of temperature, both above and below T_c, where C/T is essentially linear in T. They argue that a reliable estimate of $\Delta C(T_c)/T_c$ is obtained by making linear extrapolations from above and below the anomaly and constructing an idealized sharp entropy conserving discontinuity at T_c. Their confidence in this procedure is due, in part, to the fact that their results are in agreement with values of $\Delta C(T_c)/T_c$ inferred from reversible magnetization measurements made near T_c.

Inderhees et al. [67] have assumed a Debye model with a temperature-dependent θ to estimate C_n, but they recognize that this is an over-simplification.

In another approach [127] to obtain C_n, a YBCO sample was irradiated with neutrons at 80K (to retard chemical reaction) until the discontinuity at T_c was eliminated. Before and after irradiation the specific heat above T_c agree to ±0.5%. Subtraction of C for the irradiated sample (assumed to be equal to C_n) from C before irradiation resulted in a variation of $\Delta C/T$ similar to that shown in Fig. 22 obtained by differential calorimetry [100,101].

Figure 24 is a plot of C(H)/T vs T in constant magnetic fields of 0, 3.5 and 7T [62]. Partial substitution of a 3d transition element for Cu suppresses $\Delta C(T_c)/T_c$ (see Section 6) and allows C_n to be estimated near T_c. The solid curve is from a cubic spline fit of the specific heat data for $YBa_2(Cu_{2.96}Cr_{0.04})O_7$ for which $\Delta C(T_c)/T_c = 0$ (see Fig. 34 of Section

6.2), and is assumed to represent C_n/T. (Note the similarity between the curve in Fig. 24 and that for $C_l/T = C_n/T-\gamma$ in Fig. 23.) Junod et al. [113] have questioned this assumption. They argue that it might be unjustified since the sharp change in $d(C/T)/dT$ at T_c could be evidence for a lattice rearrangement which is coupled to T_c. Nonetheless, if the solid curve in Fig. 24 is taken as representing C_l, it is clear, as was pointed out in Section 4.1, that using $[C(0)-C(7)]/T$ underestimates $\Delta C(T_c)/T_c$.

The effect of a magnetic field on C is different from that for a conventional type-II superconductor: As H is increased, the onset of the effect on C is shifted to lower temperatures only slightly while $\Delta C(T_c)/T_c$ is strongly suppressed. Thompson and Kresin [139] have pointed out that this behavior is a result of fluctuation effects which have their origin in the small coherence lengths for the high-T_c materials. Similar conclusions have been reported by Salamon et al. [91] from specific heat measurements on a twinned single crystal in fields from 0-6T. Their data, which exhibit an unusually sharp transition, are shown in Fig. 25.

Recently, Athreya et al. [140] have made magnetization measurements as a function of field near T_c, and have used these results to derive specific heats, which are in qualitative agreement with directly-measured values [62,91].

There are two measurements of C for YBCO near T_c that show unusual effects: In the first of these, two well-resolved superconducting transitions were observed [87,88], probably arising from inhomogeneities in the sample. For the second, Butera [119] reports a very sharp <u>first</u>

order transition (<<1K in width) at 90.3K with a second very sharp lambda-like anomaly between 86-87K. Neither of these features has been observed in other measurements on YBCO. While Junod et al. [113] have measured one sample [see panel (b) of Fig. 21] that has a small irregularity in C/T near 86K, this feature, which is attributed by the authors to a second superconducting phase, does not resemble the anomaly observed at that temperature by Butera [119].

From the measurements of $\partial\gamma(H)/\partial H$ reported in Ref. [62] and the procedure outlined in Section 4.1, $[H_{c2}]_{T=0}$ can be estimated to be ~180T, a value that is consistent with estimates made from magnetic measurements [141].

The effect of oxygen stoichiometry on $\Delta C(T_c)/T_c$ near T_c~90K has not been studied, except for one sample of $YBa_2Cu_3O_6$ in which superconductivity was completely suppressed [118].

In contrast to the time-dependent behavior (see Section 3.2) observed at low temperatures, measurements of C near T_c did not depend upon whether the field was applied before or after cooling the sample through T_c [135].

4.3. BCSCO and TCBCO

The Bi- and Tl-based high-T_c systems exhibit a number of superconducting phases [142]. Recent specific heat data [120] have confirmed the occurrence of bulk superconductivity in a Tl sample and in several Bi samples, each of which exhibited a Meissner effect.

In Fig. 26 the specific heat of Tl-Ca-Ba-$Cu_2O_{5.5}$ is displayed for fields of 0 and 7T. A clear but broadened anomaly with a sharp onset is observed near 115K. The 7-T field suppresses C/T near T_c, but it is not clear that [C(0)-C(7)]/T is equal to $[C_s-C_n]/T$. Consequently, only a lower bound can be placed on $\Delta C(T_c)/T_c$ (see Table VI).

Figure 27 is a plot of [C(0)-C(7)]/T vs T for a Bi-based sample. Meissner effect data indicated two superconducting transitions for this sample with flux expulsion ratios of ~10:1 (low-T to high-T). The two anomalies shown in Fig. 27 have areas which are roughly in this ratio. Once again, because of the uncertainties mentioned for the Tl compound, $\Delta C(T_c)/T_c$ can only be given a lower bound (see Table VI). Two other Bi samples also showed broadened anomalies. For one of these samples for which the Meissner effect indicated nearly equal proportions of two superconducting phases, the two transitions in C coalesced into one. For two other samples, magnetic data to the contrary, the bulk transitions are apparently too broad to be observed in the C data.

No value for $\partial\gamma(H)/\partial H$ could be derived for the TCBCO sample because of the relatively large amount of magnetic impurity present. For the Bi samples $\partial\gamma(H)/\partial H \sim 0.15$, but this is only a rough estimate, which when used with $\gamma \geq 17$ mJ/mole K^2 from Table VI, gives $[H_{c2}]_{T=0} \geq 110T$, a reasonable result.

5. THE SPECIFIC HEAT ANOMALY IN YBCO NEAR 220K

Since the 90K superconducting transition was first observed in YBCO, various phenomena suggestive of superconductivity at much higher temperatures, frequently in the range 200-240K, have been reported. Laegreid et al. [73,75-77,79] were the first to present calorimetic and elastic evidence for an ordering process near 220K. They found that the magnitude of the specific heat anomaly, illustrated in Fig. 28, was approximately proportional to $\Delta C(T_c)$ at 90K, and concluded that the most likely explanation of the anomaly lies in the ordering of the oxygen system of the Cu-O chains.

More recently, Calemczuk et al. [143] made measurements of elastic properties, resistivity and specific heat on YBCO and also observed an anomaly in the 200-240K temperature range in a superconducting sample but not in an insulating sample. They concluded that the anomaly was probably associated with a first-order structural change which corresponded to an ordering of the oxygen vacancies in the planes containing the Cu-O chains.

Both Laegreid et al. [144] and Calemczuk et al. [143] state that large hysteresis effects are observed when the samples are cooled. Furthermore, the cooling must be taken into the metastable region showing elastic hysteresis or no anomaly in specific heat is observed [144].

Junod et al. [113] have also made calorimetric measurements through the 220K region. While they have found an anomaly near 236K, they could account for it by the melting of a small amount of silicone grease used to attach the sample to the apparatus. (Neither Laegreid et al. [144] nor Calemczuk et al. [143] used silicone grease.) Ishikawa et al. [88] have measured specific heats to 300K and find no anomalous behavior between ~90 and 300K.

Since CuO has a specific heat anomaly near 230K due to antiferromagnetic ordering [145], it might be thought that a CuO impurity in YBCO could account for the 220K anomaly. However, the samples used by Laegreid et al. [144] have <<1% CuO, and those of Calemczuk et al. [143] were made in the same way as the non-superconducting YBCO, which showed no anomalous behavior. Thus it does not appear that antiferromagnetic ordering of an impurity phase can explain the 220K peak.

Superconducting $La_{2-x}Sr_xCuO_4$ undergoes a structural transition above T_c [146], and it is interesting to note that there appears to be an indication of this transition in the specific heat data of Junod et al. [47].

6. SUBSTITUTION OF OTHER ELEMENTS FOR Y OR Cu IN YBCO

The perovskite structure is a very versatile one since many elements can be used in the basic building unit, ABX_3 [20]. A substitution of one element for another often produces modified or distorted structures whose properties depend markedly on the nature of the substitution -- to which the high-T_c superconductors bear witness. In this section we discuss the effect of such substitutions on the superconductivity of YBCO, in particular the effect on C of the substitution of the rare earths for Y and other 3d transition elements partially substituted for Cu. The rare earths can also be substituted for La and the 3d transition metals for Cu in LMCO, both causing a decrease in T_c, which can be correlated with a decrease in the unit cell volume for the rare earth additions [147]. However, to our knowledge no specific heat measurements have been made on these materials.

6.1. RBCO

All of the rare earths with the exception of Ce, Pr, Pm and Tb can be substituted for Y in YBCO without an appreciable change in the superconducting properties near and above T_c. Figure 29 illustrates $\Delta C(T_c)/T_c$ for GdBCO [38], which may be compared to that for YBCO in Fig. 21. Similar results have been reported for DyBCO [104,108], ErBCO [109,112] and EuBCO [109] (see Table V). For temperatures well above T_c, the specific heats for RBCO [148] (R=Y, Eu, Gd, Dy and Er) vary by only ±2% in the temperature range 240-500K as shown in Fig. 30.

In marked contrast to the high temperature specific heat results, substitution of the rare earths for Y produces a quite different low temperature behavior. Three classes of specific heat are observed [52]: 1) for Ho, Tm and Yb, as illustrated in Fig. 31, crystalline electric field splittings of the rare earth ion energy level multiplet produces Schottky-like anomalies with no magnetic ordering above 0.45K; 2) when Nd, Sm, Gd, Dy and Er replace Y, long-range magnetic ordering, probably due to dipole-dipole interactions, results and leads to the specific heat anomalies shown in Fig. 32; and 3) non-magnetic EuBCO has a low-temperature specific heat similar to that for YBCO as displayed in Fig. 33. Investigation of the low temperature specific heats for RBCO has been extensive: Nd [52,53,63,149,150]; Sm [52,53,55,63,149,150]; Eu [52-55,63]; Gd [52,53,55,149-161]; Dy [52,53,63,104,149,150,157,159,162]; Ho [51,52,54,63,151,152, 157,159,162]; Er [52,53,63,150-152,155,157, 159,162,163]; Tm [51-54,63,157]; and Yb [52-54,63]. To our knowledge no measurements of specific heat have been made for LaBCO or LuBCO. Non-superconducting PrBCO has been measured [149] at low temperatures, and below 10K, C/T is nearly constant at about 200 mJ/mole K^2 with a very small upturn near 0.8K which has been interpreted as probably due to ordering in the nuclear system. Similar results have been obtained in another investigation of PrBCO where a magnetic ordering anomaly near 20K was observed [164]. Below 1K, HoBCO has a sharp upturn in C with an anomaly at 0.17K which is thought to arise from nuclear ordering [162]. For GdBCO, the specific heat has been investigated in magnetic fields at low temperatures. As is typical for an antiferromagnet, the maximum in the anomaly in C is shifted to lower T in a field of 1.7T, and disappears completely in 3.5T -- at least above 1.5K, the low-temperature limit of the measurements [161].

It is evident that in superconducting RBCO the electron system for R is acting essentially independently of that for the Cu-O system which is involved in the superconductivity. The specific heat of GdBCO, for example, has been measured in both the normal and superconducting states. It is found that the low-temperature results for the two states are identical within experimental error [155,156,160].

6.2. $YBa_2(Cu_{3-x}M_x)O_7$

While the substitution of rare earths for Y in YBCO is a straightforward procedure, the partial substitution (doping) of other 3d transition elements for Cu is much more complex. In YBCO there are two types of Cu sites (chains and planes), and it is not always evident where the doping has occurred or if it is random. A variety of techniques (thermo-gravimetric analysis, neutron diffraction, EPR, X-ray and Mossbauer measurements) have been used to help clarify the situation, but uncertainties still exist.

There has been a great deal of research into the effect of 3d doping on the superconductivity of YBCO and LMCO [165]. While there is disagreement on the magnitude of these effects, in general T_c and the Meissner effect decrease with increasing x. A number of possibilities have been suggested for this decrease [166]: 1) electronic effects which result from changes in the Cu-O electronic band structure, and which may cause localization and magnetic moment formation; 2) the doped 3d element may substitute mainly in the Cu-O chain sites causing the oxygen content to increase with an eventual change in crystal structure from orthorhombic to tetragonal; and 3) substitution of a paramagnetic ion in the Cu-O system can cause a breaking of Cooper pairs.

The effects of 3d doping on the specific heat near T_c and at low temperatures have been measured for Fe [115,118] (plane and chain site substitution), Zn [102] and Ni [102] (both probably plane site substitution) and Cr [62] (site substitution not known). A number of general statements can be made concerning the results: 1) $\Delta C(T_c)/T_c$ decreases and broadens as x is increased and finally disappears even when there is still an appreciable Meissner effect. This is demonstrated in Fig. 34 for the case of $YBa_2(Cu_{3-x}Cr_x)O_7$. 2) The low temperature upturn in C/T and $\gamma(0)$ both increase as x increases (see Fig. 35). 3) Doped YBCO is paramagnetic above T_c -- in addition to the paramagnetism arising from localized magnetic moments in impurity phases -- and this paramagnetism increases as x increases.

Disappearance of the anomaly near T_c, while the sample still shows a Meissner effect, probably results from the superconducting transition's becoming so broad and the associated anomaly so reduced in maximum height that the transition is masked by the large background lattice specific heat. The increased upturn in C/T at low temperatures could signal the onset of magnetic ordering of the localized magnetic moments induced by the 3d doping, while the increasing $\gamma(0)$ could result either from an increase in the fraction of normal state material, or from an increase in magnetic impurity phases. (For YBCO doped with Fe, Dunlap et al. [167] and Junod et al. [115] report broadened low temperature features in C which could be associated with the magnetic ordering of the Fe. Mossbauer measurements confirm that the Fe in $YBa_2(Cu_{2.94}Fe_{0.06})O_7$ orders at ~3K [168].) These features have not been observed in samples doped with Cr [62] or with Ni [102].

For $YBa_2(Cu_{3-x}Cr_x)O_7$ [62] the impurity content of the sample, as estimated from the Schottky-like anomalies in 7T (see Section 3), increases with increasing x. θ_o for both the Cr- [62] and Zn- [102] doped YBCO (x<0.3) is slightly smaller than that for the pure material.

7. LATTICE SPECIFIC HEAT

A knowledge of C_l is an important aid in understanding high-temperature superconductivity. As is noted in Section 2.3, if C_l is known accurately, then C_{es} can be determined from $C_{es}=C-C_l$. Furthermore, as Junod et al. [169] have pointed out, accurate determinations of C_l at temperatures where C_l/T^3 is no longer constant allow an evaluation of some of the parameters which enter into the Eliashberg Equation. Unfortunately, in the case of the high-T_c superconductors, no straightforward means of determining C_l is available. Except very near T_c, the magnetic fields necessary to suppress superconductivity are so large that they are unattainable in the laboratory. Moreover, according to [113], even if such fields were available, their appplication would alter the normal electron density of states (DOS). Thus , the determination of C_l must be made by means which are both indirect and, often, unreliable.

7.1. Lattice Specific Heat at Low Temperatures

The departures from a simple T^3 behavior of C_l can be dealt with in several ways. As noted in Sections 1, 2 and 3, the most straightforward is to assume that $C_l=B_3T^3+B_5T^5+\ldots$. For example, C_l data for YBCO can be fit to ~20K to within ~0.1% by such a power series expansion [62,72]. An alternative procedure for incorporating the higher-order contributions to C_l is to write $C_l=C_D+C_E$, where C_D is a Debye specific heat and C_E an Einstein term. For most of the oxide superconductors which have been measured, the characteristic temperature of C_E is of the order of 125K

[38,43,54,61]. This C_E corresponds to a peak which is evident in the neutron scattering determinations of the phonon DOS of both LSCO [43] and YBCO [170,171] (see Figs. 36 and 37). By allowing the number of Debye and Einstein modes to be variables, it is possible to obtain reasonably good fits to the zero field specific heat data of both substances for temperatures below ~40K, although in both instances the specific heat must include an additional $\gamma(0)T$ term (see Section 3). Figure 38 shows such a fit to the specific heat data for LSCO [43]. Gordon [172] has shown that if one assumes a small Gaussian or Lorentzian peak in the density of states at ~125K, rather than a single Einstein frequency, then this $\gamma(0)T$ term in YBCO can be regarded as arising from the finite intercept (at $T=0$) of the Gaussian or Lorentzian tail. The physical origin of such an intercept is, of course, unexplained by such a picture, although the oxygen tunneling model put forward by a number of authors [129] would provide one such mechanism.

Consistent with the idea of a lattice specific heat which contains both Debye and Einstein terms is the expectation that a graph of C_l/T^3 should have a maximum. Such a maximum is evident for LCO, YBCO and BCSCO as shown in Fig. 39 from Ref. [120]. In a discussion of the specific heat of A15 superconductors Junod et al. [169] pointed out that a graph of C/T^3 vs ln T mirrors a phonon spectrum plot of $F(\omega)/\omega^2$ versus $\ln\omega$, providing one chooses $\omega=4.928T$. Such an argument makes it clear that a peak in the phonon DOS at 125K will lead to a maximum in C_l/T^3 at $T\approx25K$. However, lest it be assumed that such behavior applies only to superconductors, it should be noted that Bijl [173] has tabulated C_l/T^3 data for a variety of materials. He plots $C_r = C_l/C_D$ (rather than C_l/T^3)

versus T/θ_o and finds that C_r usually has a maximum in the vicinity of $T/\theta_o \approx 0.05$ to 0.1. For the case of $\theta_o \approx 450K$, this result is consistent with a maximum in C_l/T^3 at 25K. Thus, although the lattice properties of the oxide superconductors may prove to be anomalous in a variety of ways, their low temperature departure from simple Debye theory does not seem noticeably out of the ordinary.

7.2. Calculation of the Lattice Specific Heat from DOS

In principle it is possible to calculate C_l if the phonon density of states is known. Ramirez et al. [43] have shown that the specific heat data up to 50K on $La_{1.85}Sr_{0.15}CuO_4$ are consistent with the phonon spectrum they obtain from inelastic neutron scattering studies (see Figs. 36 and 38). The somewhat more detailed results on the LSCO phonon DOS obtained by Rosseinsky et al. [174] presumably would also be in agreement with the measured specific heat data, although it should be noted that the additional small 4.3 meV Einstein peak assumed in [43] in order to obtain agreement between the measured and calculated specific heat is not evident in either group's DOS data.

Reeves et al. [38] and Gordon [172] have used the DOS from neutron scattering [170,171] to calculate the YBCO specific heat up to temperatures of the order of 200-300K. However, such calculations are sensitive to the way in which the DOS results are normalized. In [38] it is argued that the high energy neutron scattering data come predominantly from the oxygen ion motions, and that in order to obtain reasonable high temperature agreement between the calculated and measured specific heat data, it is necessary to cut off arbitrarily the measured phonon DOS at 60 meV. Because C_l constitutes 95% or more of the measured specific heat near T_c, even small uncertainties in a C_l calculated from the DOS data will make any values of C_{es} obtained from C-C_l(calc) quite unreliable.

The recent specific heat measurements of Heremans et al. [148] on RBCO superconductors extend to 500K. From their YBCO measurements these authors infer a θ of 606K, a value considerably higher than that obtained from the data either at helium temperatures or near T_c. Chaplot [175] has recently used an unscreened rigid-ion model to calculate the phonon DOS for YBCO. From his DOS he predicts a strongly temperature-dependent θ, a result which is consistent with the data reported in [148]. Kress and co-workers [176] also calculate a phonon DOS for YBCO and note that the specific heat calculated from their DOS agrees reasonably well with the specific heat data of Lang et al. [128]. Heremans et al. [148] state that their specific heat data, when combined with their thermal and electrical conductivity measurements, provide insight into the electron-phonon coupling mechanism in these materials. They argue that if superconductivity in the rare earth oxide materials is mediated by phonons, then the electron-phonon interaction must be strongly coupled. These authors use their data to estimate a value for the coupling constant (λ). For YBCO they obtain λ=6, and with this value, and their value of 606K for θ, they argue that the MacMillan Equation [177], would predict a value for T_c which is of the order of 150K.

8. ARTICLES TO BE PUBLISHED

A number of papers on the specific heat of high-T_c superconductors were presented at the International Conference on HTSC-M^2S held at Interlaken, Switzerland in February/March 1988 for which we have been unable to obtain preprints. The conference proceedings are to appear in Physica C in 1988, and meanwhile, for completeness, we present below the titles and authors of those papers.

1. Paper A2: "Electronic Properties of Oxide High Temperature Superconductors -- Transport Properties and Related Topics", K. Kitazawa, H. Takagi, S. Uchida, K. Kishio, S. Tajima and S. Tanaka.
2. Paper C11: "Electronic and Phononic Properties of High-T_c Oxide Superconductors", H. Rietschel, J. Fink, E. Gering, F. Gompf, L. Pintschovins, W. Reichardt, B. Renker, H. Schmidt, W. Weber and D. Ewert. [C was measured for $La_{2-x}Sr_xCuO_4$ ($0 \le x \le 0.25$) and $RBa_2(Cu_{3-x}M_x)O_{7-\delta}$ (R=Y and rare earths; M=Fe and Zn, $0 \le x \le 0.15$; $0 \le \delta \le 1$).]
3. Paper C15: "Heat Capacity and Equilibration Time Near T_c of $YBa_2Cu_3O_7$", A. V. Voronel, D. Linsky, A. Kisliuk and S. Drishlikh.
4. Paper B241: "Low-Temperature Specific Heat and Magnetic Susceptibility of $YBa_2(Cu_{3-x}M_x)O_{7-\delta}$", U. Ahlheim, R. Ahrens, B. Andraka, C. D. Bredl, R. Caspary, D. Ewet, H. E. Hoenig, T. Lechner, S. Riegel, H. Rietschel, H. Schmidt, H. Spille, F. Steglich, G. R. Stewart and G. Weber. [C was measured in the range 0.03-30K and 0-12T for M=Fe and Zn (x=0, 0.15 and 0.3) and δ=0.1 and 0.9. For all systems $\gamma(0)=12\pm6$ mJ/mole K^2.]
5. Paper B312: "Specific Heat of $YBa_2Cu_3O_{7-\delta}$ in Magnetic Fields up to 6T", T. Sasaki, N. Kobayashi, O. Nakatsu, S. Kawamata, T. Matsuhira, A. Tokiwa, M. Kikuchi, Y. Syono and Y. Muto. [C for two samples was measured with

$\gamma(0)$=4.6 and 9.2 mJ/mole K^2 and $\partial\gamma(H)/\partial H$ positive for both. In-field Schottky-like anomalies were observed.]

6. Paper 313: "Low Temperature Thermal Conductivity of $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ Compounds", B. Salce, R. Calemczuk, C. Ayache, E. Bonjour, J. Y. Henry, M. Raki, B. Barbara, P. Burlet, M. Covach and J. Rossat-Mignot.

7. Paper 316: "Low-Temperature Specific Heat of $REBa_2Cu_3O_7$ in Magnetic Fields up to 5T (RE=Y, Pr, Sm, Eu, Gd, Dy, Ho, Er, Yb and Lu)", H. P. van der Meulen, Z. Tarnawski, K. Kadowaki, J. C. P. Klaasse and J. J. M. Franse.

8. Paper B319: "Thermal Properties of Triple Oxides $LnBa_2Cu_3O_{7-\delta}$ Type", V. B. Lazarev, I. S. Shaplygin, K. S. Gavrichev, I. A. Konovalova, V. E. Gorgunov and E. A. Tistchenko [C was measured for Ln=Y, Gd and Ho.]

9. Paper B322: "Field Dependence of the Low Temperature Heat Capacity of High-T_c Superconductors", E. M. Forgan, C. Gibbs, C. E. Gough, C. Greaves, S. L. Lee and J. S. Abell. [C was measured for YBCO in the range 1-10K and 0-5T.]

10. Paper B323: "High T_c Superconducting Properties of $SmBa_2Cu_3O_{7-\delta}$: Thermal Properties", C. Escribe-Filippini, K. Konate, R. Buder, J. Marcus and C. Schlenker.

11. Paper 325: "Low-Temperature Thermal Properties of La_2CuO_4 and Superconducting $Ba_2YCu_3O_{7-\delta}$", A. Bernasconi, E. Felder, H. R. Ott and Z. Fisk. [C was measured in the range 0.04-15K.]

9. NON-CALORIMETRIC METHODS FOR DETERMINING γ

9.1 Magnetic Determination of γ by Susceptibility and Critical Field Measurements

A knowledge of γ is crucial to an understanding of the oxide superconductors. If it were possible to apply magnetic fields large enough to suppress completely the superconducting phase at low temperatures, one could determine γ calorimetrically. Since this is impossible, less direct methods of obtaining γ are of interest. Two methods utilizing magnetic measurements have been employed, and the early results on LSCO and YBCO have been summarized by Nevitt et al. [64]. One method obtains a value for γ from the temperature-independent paramagnetic susceptibility above T_c. In the free electron model γ is given by: $\gamma = 1/3(\pi k_B/\mu_B)^2 \chi_s$, where k_B is the Boltzmann constant, μ_B the Bohr magneton and χ_s is the measured temperature-independent susceptibility (χ_o), corrected for core diamagnetism. While the various experimental determinations of χ_o are in rough agreement, there is some disagreement about the magnitude of the core correction. Nonetheless, a number of workers (see [64] for references) agree that the susceptibility measurements for YBCO yield a value for γ of ~ 42 mJ/mole K^2 (~14 mJ/mole Cu K^2). In the weak coupling limit, BCS theory predicts that $\Delta C(T_c)/T_c = 1.43\gamma \approx 60$ mJ/mole K^2 for $\gamma \approx 42$ mJ/mole K^2. This value for $\Delta C(T_c)/T_c$ is in good agreement with the most recent calorimetric determinations for YBCO (see Table V).

Decroux et al. [46] have obtained a value of 12 mJ/mole K^2 for γ from their susceptibility measurements on LSCO. This value is somewhat smaller than that inferred from the measurements of Maletta et al. [178], but is larger than most of the γ values obtained from critical field measurements on LSCO.

A second method of inferring γ from magnetic measurements is to utilize the result that, for a type-II superconductor in the "dirty" limit, $(dH_{c2}/dT)_{Tc} = -4.48\gamma\rho$ T/K, where ρ is the normal state resistivity just above T_c measured in μohm cm, and γ is measured in ergs/cm^3 K^2 [179]. There is considerable uncertainty in determining $(dH_{c2}/dT)_{Tc}$ [64,180-182]. (See [183] for other recent references on H_{c2} measurements). The values of $(dH_{c2}/dT)_{Tc}$ for YBCO range, for example, from 1 to 5 T/K. There is also some variation in the values reported for ρ. Salamon and Bardeen [51] note that if one takes $\rho\approx200$ μohm cm, and $(dH_{c2}/dT)_{Tc} \approx 3$ T/K, then the resulting value for γ is consistent with that obtained from the susceptibility data. Van Bentum et al. [180] have recently obtained γ values for both LSCO and YBCO from their $(dH_{c2}/dT)_{Tc}$ measurements. They report values of 7 and 48 mJ/mole K^2 for LSCO and YBCO, respectively. Arberg et al. [184] report γ~17 mJ/mole K^2 for LSCO from their $(dH_{c2}/dT)_{Tc}$ measurements. These authors argue that this value, obtained assuming the "dirty" limit, is too high, and therefore calculate γ using the BCS relation in the "clean" limit. This calculation yields γ~7.5 mJ/mole K^2 and would therefore give a value for $\Delta C(T_c)/\gamma T_c$ which is close to the BCS weak-coupling value of 1.43.

It should be noted that the difficulty of extracting γ values from the magnetic data is beset with theoretical as well as experimental problems. Because of enhancement effects, a γ value obtained from the susceptibility data may not be the same as the γ which enters into the specific heat. Similarly, it is not certain that the oxide superconductors are type-II materials in the "dirty" limit [184,185]. Still, there is a rough consistency in the values of γ obtained from the two magnetic methods. In the case of YBCO, the magnetically-determined γ, when combined with the calorimetric determination of $\Delta C(T_c)/T_c$, would appear to indicate that this material can be regarded as a weakly coupled BCS superconductor. Marsiglio et al. [186] point out, however, that $\Delta C(T_c)/\gamma T_c \approx 1.43$ does not guarantee weak-coupling. These authors argue that as one enters the strong-coupling regime $\Delta C(T_c)/\gamma T_c$ first rises above 1.43 and then decreases again, possibly to values below 1.43.

9.2. Density of States at the Fermi Energy from Band Structure Calculations

Using band theory it is possible to calculate the "bare" electron density of states at the Fermi energy $[N_b(E_F)]$. If many-body enhancement effects are absent, then $N_b(E_F)=[3/\pi^2 k_B^2]\gamma$. If many-body effects are important then it is an enhanced DOS, $N(E_F)$, that is equal to $[3/(\pi^2 k_B^2)]\gamma$. $N(E_F)$ is related to $N_b(E_F)$ by $N(E_F)=(1+\lambda)N_b(E_F)$, where λ is an interaction parameter, the value of which is important in determining whether or not BCS theory in the weak-coupling limit is applicable to a given superconductor. A comparison of an experimentally-determined γ with a calculated $N_b(E_F)$ thus permits λ to be evaluated. Comparisons of $N_b(E_F)$ with γ are complicated by the matter of units. In the following discussion we use the relation $N(E_F) = 0.424\gamma = (1+\lambda)N_b(E_F)$, where γ is measured in mJ/mole Cu K^2 and $N(E_F)$ and $N_b(E_F)$ in states/ev Cu atom.[1] As might be expected for compounds as complex as

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[1] The relationship between $N(E_F)$ and γ can be written in various ways: $N(E_F)=0.424\gamma$ states/ev Cu atom, $N(E_F)=0.212\gamma$ states/ev Cu atom/spin direction, $N(E_F)=2.88\gamma$ states/Ry Cu atom/spin direction, where γ is in

the oxide superconductors, the calculated values of $N_b(E_F)$ vary over a considerable range. Since the values of γ obtained from magnetic measurements also vary, the estimates of λ have to be regarded as uncertain.

In the case of $La_{2-x}Sr_xCuO_4$ Krakauer et al. [187] find $N_b(E_F)$ to have a value of 2.1 states/ev atom (29 states/Ry cell) for $x=0.14$ and 1.18 states/ev atom for $x=0$. This value agrees with that reported for $LaCuO_4$ in references [188-191]. Freeman et al. [191] also obtain a value of 1.9 states/ev atom for $x=0.16$. They point out that their value for the $x=0.16$ compound, when combined with γ values obtained from magnetic measurements, leads to $\lambda=0.3\pm0.3$ -- a range of λ values which would imply that $La_{1.84}Sr_{0.16}CuO_4$ is essentially in the weak coupling limit.

The range of $N_b(E_F)$ values calculated for YBCO is wider than that for LSCO [192-196]. For example, Massidda et al. [192] obtain $N_b(E_F)=1.3$ states/ev Cu atom for YBCO, while Weber and Mattheiss [193] in one of their calculations obtain $N_b(E_F)=8$ state/ev cell. Massidda et al. [192] and Herman and co-authors [194] show that the calculated value of $N_b(E_F)$ depends strongly upon δ for $YBa_2Cu_3O_{7-\delta}$, although such a result may not be supported by the measurements of Junod et al. [113]. In [194] it is shown that, for a given δ, $N_b(E_F)$ increases with increasing oxygen-vacancy ordering. The authors argue that in the case of $YBa_2Cu_3O_{7+y}$, T_c

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mJ/mole Cu K^2. If there is one Cu atom/unit cell we can also write $N(E_F)=0.424\gamma$ states/ev cell. Since YBCO contains three moles of Cu per mole of compound or per unit cell, one must be careful in comparing the calculated $N_b(E_F)$ values with γ.

might be increased above 95K by preparing samples with $y>0$, and with highly-ordered oxygen vacancies.

The calculated values of $N_b(E_F)$ for YBCO, when combined with the magnetic determinations of γ, on the whole yield values for $\lambda>1$. For example, with $N_b(E_F)=2$ states/ev Cu atom and $\gamma\sim42$ mJ/mole K^2 (14 mJ/mole Cu K^2), one obtains $\lambda\sim2$, a result which would imply that YBCO is in the intermediate or strong coupling regime. Such a conclusion would seem to be at odds with the result $\Delta C(T_c)/\gamma T_c\sim1.43$, unless, as Marsiglio et al. [186] suggest, a value of 1.43 for $\Delta C(T_c)/\gamma T_c$ is not necessarily evidence for weak coupling.

10. CONCLUSIONS

Since the field of high-temperature superconductivity is a mere two years old, the conclusions to be drawn from the specific heat measurements made thus far have to be regarded as tentative. Perhaps the single most important, and the most surprising, result is that the high-T_c materials, with the possible exception of the bismuth compounds, have a non-zero value of $\gamma(0)$. While some part of the linear term in the low-temperature specific heat of many samples evidently arises from impurities, there is increasing evidence of an intrinsic non-zero $\gamma(0)$. There is evidence as well that this intrinsic $\gamma(0)$ is to be associated with the electrons rather than the lattice. In the case of LMCO, $\gamma(0)$ is of the order of 1-4 mJ/mole K^2. For YBCO this intrinsic $\gamma(0)$ appears to be of the order of 4-7 mJ/mole K^2. The apparent absence of an intrinsic $\gamma(0)$ in the Bi compounds is puzzling. In any event, any theory which seeks to explain high-temperature superconductivity must take account of the unexpected result that $\gamma(0)\neq0$ for a majority of the oxide superconductors. As has been pointed out, the RVB theory of Anderson [131] and others does predict such a result. The task of extracting $\gamma(0)$ from the low temperature specific heat data is complicated by the presence of an upturn in the zero field C/T at low temperature. There is considerable evidence that this upturn is not an intrinsic effect but is due to the existence of impurity phases. Thus, as sample preparation techniques improve, we can hope to obtain more reliable information about the value of $\gamma(0)$, as well as about the other contributions to the specific heat of these compounds.

Perhaps the second most striking feature of the specific heat measurements is the magnetic field dependence of C near T_c. Several groups [62,69,91] report that the principal effect of the application of a field is to broaden, and lower, the anomaly. However, the applied field does not appreciably lower the temperature at which the superconductivity begins. Salamon et al. [91] and Thompson and Kresin [139] argue that this magnetic field dependence is evidence for fluctuation contributions to the specific heat, although it is not certain whether the fluctuations are critical or Gaussian. It has long been known that there should be a fluctuation contribution to C in the vicinity of T_c. However, for conventional superconductors the coherence length is so large that this contribution is not experimentally observable. The high-T_c oxide superconductors may thus offer an opportunity to study the interplay between fluctuation effects and superconductivity which has not been previously available.

A third surprise which has emerged from the specific heat measurements on YBCO is the existence of an anomaly at ~220K. This specific heat peak has been observed by several groups, but is not present in the results of others. If this peak proves to be an intrinsic feature of YBCO, its possible relation to the superconducting properties remains to be clarified. However, there is now evidence that enhancing the ordering of oxygen vacancies in YBCO increases T_c. It is therefore plausible that if the peak at 220K corresponds to a partial order-disorder transition of these vacancies, then the size of the anomaly at 220K should correlate with the size of $\Delta C(T_c)/T_c$.

The specific heat results as yet provide only ambiguous evidence concerning the applicability of BCS theory in the weak-coupling limit. By combining γ values obtained from $(dH_{c2}/dT)_{Tc}$ data with the most recent calorimetric determinations of $\Delta C(T_c)/\gamma T_c$, it is possible to obtain $\Delta C(T_c)/\gamma T_c \sim 1.43$ for both LSCO and YBCO, but to do so one must assume the "clean" limit in calculating γ for LSCO and the "dirty" limit in the case of YBCO. If one assumes that the samples are 100% superconducting then the 1.43 value is consistent with the BCS weak-coupling prediction. If, however, one were to assume that the fraction of the sample which is superconducting is 50% or less -- as could be naively inferred from Meissner effect data -- then one would be forced to conclude that both LSCO and YBCO are in the strong-coupling limit. A comparison of γ with the $N_b(E_F)$ values obtained from band theory calculations allow the inference that LSCO, but not YBCO, is in the weak-coupling regime.

The fact that when Y in YBCO is replaced by other rare earth metals, the superconducting properties (in most cases) are only marginally affected, even though some of the RBCO materials undergo magnetic ordering at low temperatures, provides clear evidence that the rare earth atoms play no direct role in the superconductivity of this system. On the other hand even small percentage substitutions of Zn or transition metal elements for Cu reduce markedly, or suppress altogether, superconductivity in $YBa_2(Cu_{3-x}M_x)O_7$. Such substitutions also affect the low temperature specific heat -- $\gamma(0)$, C_1 and the upturn in C/T are all increased. Conversely, the substitutions appear to have little effect on C for $T>T_c$.

The specific heat measurements made thus far on the high-T_c oxide superconductors leave no doubt that superconductivity in these materials is a bulk phenomenon. Better thermal and magnetic measurements on higher quality samples, preferably single crystals, should help to clarify some of the ambiguities which remain in the interpretation of the results. With the exception of the non-zero value for $\gamma(0)$, however, it would be difficult to argue that the present specific heat results provide very strong evidence for a non-BCS behavior in the high-T_c materials.

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TABLE I. La_2CuO_4: Parameters derived from specific heat data (see Section 2.1 and the beginning of this section for units and definitions of symbols; mol. wt. 405.4).

H	A(0)	$\gamma(0)$	θ_o	Ref.
0	0.20^1	1.8	350	[23,105]
0		0	385	[24]
0-10	$+^2$	2^3	340^4	[25]^5
0-7	$0.17^{2,6}$	1.1^3	460	[26,27]
0		0.9±0.1	380±5	[28]
0		0.7±0.1	382±5	
0		0±0.2	402±5	[29]
0		0±0.5	460	[30,31]
0	+	1.0±0.1	320	[32]
0-7	$0.38^{2,6}$	0.22^3	430	[33]^7
0	0	1.12±0.14	406	[34]
0	+	$--^8$	396	[35]
0	+	0.2±0.2	280	[125]

[1] Interpreted as a hyperfine contribution from Cu.

[2] $A(H)>A(0)$.

[3] $\gamma(H)\approx\gamma(0)$.

[4] Estimated from the slope of C/T vs T^2 in Fig. 2.

[5] Composition $La_{1.98}Sr_{0.02}CuO_4$.

[6] There was a Schottky anomaly in 7T. A(7) was equal to that expected for the Cu and La hyperfine contributions.

[7] Data to be published.

[8] A linear term was not reported, but from Fig. 9 it appears small.

TABLE II. $La_{1.85}Ca_{0.15}CuO_4$: Parameters derived from specific heat data (see Section 2.1 and the beginning of this section for units and definitions of symbols; mol. wt. 390.5).

T_c	H	A(0)	$\gamma(0)$	$\Delta C(T_c)/T_c$	γ	θ_o	Ref.
18	0-5.7			~29	~20	270	[36]
22	0-7	0.02[1]	3.05[2]	1.92[3]	1.34(4.4)[4]	450	[26,27]

[1] A(H) was equal to that expected for the Cu and La hyperfine contributions.

[2] $\partial\gamma(H)/\partial H = 0.035$.

[3] $\Delta C(T_c)/T_c$ shifted to lower T with increasing H.

[4] The value of γ in parenthesis was determined after correcting for an assumed normal fraction as derived from $\gamma(0)$ (see Section 4).

TABLE III. $La_{1.85}Ba_{0.15}CuO_4$: Parameters derived from specific heat data (see Section 2.1 and the beginning of this section for units and definitions of symbols; mol. wt. 405.1).

T_c	H	A(0)	$\gamma(0)$	$\Delta C(T_c)/T_c$	γ	θ_o	Ref.
39	0	0	4	0		360	[37,38]
35	0		6±0.6	0		330±10	[39]
35	0		4	0		385	[24]
33	0-7	0.40[1]	3.6[2]	~0		430	[26,27]
34[3]	0-7	0.44[1]	3.5[2]	~0		410	
33	0	9.11	5.4	0		394	[40]
--[4]	0		5[5]			340	[30,31]
29	0	0	5.3±0.14	0.49±0.14[6]		418	[34][7]
34	0			20[8]	14		[41]

---

[1] A(H)<A(0). A(7) is much smaller than that expected for the Cu and La hyperfine contributions.

[2] $\gamma(H) \approx \gamma(0)$.

[3] This sample had a very small Meissner effect with a very broad ΔT_c.

[4] T_c not reported.

[5] A number of samples were investigated in the system $La_{2-x}Ba_xCuO_4$ in the range x=0 to 0.15. For x=0 $\gamma(0)=0\pm0.5$. In the antiferromagnetically ordered region for $x \leq 0.02$ $\gamma(0) \sim 0$. For insulating samples in the range x=0.02 to 0.04 $\gamma(0)$ is non-zero, and increases with increasing x, while in superconducting samples for $x \geq 0.05$ $\gamma(0) \sim 5$. (See Ref. [29] for similar results for $La_{2-x}Sr_xCuO_4$.)

[6] From the $\Delta C(T_c)/T_c$ discontinuity it was estimated that only ~6% of the electrons formed Cooper pairs.

[7] Differential specific heat measurements were made using La_2CuO_4 or non-superconducting $La_{1.85}Ba_{0.15}Cu_{0.9}Ni_{0.1}O_4$ as references.

[8] No $\Delta C(T_c)/T_c$ discontinuity was observed following cooling from 300 to 5K while a discontinuity was observed if the cooling was stopped at 25K.

TABLE IV. $La_{1.85}Sr_{0.15}CuO_4$: Parameters derived from specific heat data (see Section 2.1 and the beginning of this section for units and definitions of symbols; mol. wt. 397.7).

T_c	H	A(0)	$\gamma(0)$	$\Delta C(T_c)/T_c$	γ	θ_o	Ref.
38	0			7.6±1.8	5.3±1.5		[42]
37	0		2	10±2	7±1	430[1]	[43][2]
36	0		~12	0		360	[37]
31	0	+[3]	5±1	20±5	14±3.5	330	[44,45]
37	0	0.019	--[4]			350	[23,105]
--[5]	0		2.8	0		360	[39]
37	0	+	1.9	17±8	12±6	396	[46]
37	0	+[6]	1.6,4[7]	14±4[8]	10±3	401	[47]
38	0			15.4	11		[48]
37	0-8		1.4[9]	7[10]	5(7)[11]	370±20	[49]
37	0-7	0.16[12,13]	1.54[7,9]	9.9[10]	6.9(8.6)[11]	430	[26,27]
37	0-7	0.08[14]	3.8[7,15]	0		450	
36	0	0	4.0	0		439	[50]
35	0	0	3.35	~17	~12	376	[51-55]
--[5]	0		2-5[16]				[28]
--[5]	0		1.6±0.1[17]			450±5	[29]
41	0		4±2	33	23	400	[56][18]
30	0	+[19]	0.6±0.6			305±10	[57]
--[5]	0	0	0±0.5[20]			340	[31]
37	0	+	1.34			394	[35][18]
--[5]	0-4.5		0±1.4			360±20	[58][18]
--[21]	0	0	0[22]	+		350	[59][18]
37	0	+	1.8±0.2	6±2	4±1	285	[125]

[1] Estimated from the slope of C/T in Fig. 1.

[2] A correlation of specific heat with the density of states from neutron scattering was made.

[3] A peak was found in the specific heat at ~0.1K.

[4] No linear term, the data was fit using a $T^{1/2}$ term.

[5] T_c not reported.

[6] Very small upturn in C/T at the lowest T was observed.

[7] The smaller $\gamma(0)$ corresponded to the larger Meissner effect in the two samples investigated.

[8] Average for three samples.

[9] $\partial\gamma(H)/\partial H$ was positive and linear (0.11 for Ref. [49] and 0.109 for Refs. [26,27]).

[10] $\Delta C/T_c$ shifted to lower T with increasing H.

[11] Value of γ in parenthesis was determined after correcting for an assumed normal fraction as derived from $\gamma(0)$ (see Section 4).

[12] Schottky anomaly in 3.5 and 7T.

[13] A(3.5) was equal to that expected for the Cu and La hyperfine contributions; however, A(7) was only ~60% of that expected.

[14] A(7) was equal to that expected for the Cu and La hyperfine contributions.

[15] $\gamma(H)\approx\gamma(0)$.

[16] Samples with the larger $\gamma(0)$ values had smaller or non-observable $\Delta C(T_c)/T_c$.

[17] A number of samples were investigated in the system $La_{2-x}Sr_xCuO_4$ in the range $x=0$ to 0.15. In the antiferromagnetic region, for small x, $\gamma(0)$ was nearly zero. In the insulating region $\gamma(0)$ increased with increasing x to about 4, while in the superconducting region $\gamma(0)$ tended to become

smaller. (See Refs. [30,31] for similar results for $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$.)

18 Composition $La_{1.8}Sr_{0.2}CuO_4$.

19 The low temperature upturn in C/T was analyzed with two Schottky terms.

20 This work is similar to that of Ref. [29] with $x=0.1$ to 0.3. Finite $\gamma(0)$ was found only for $x>0.15$.

21 A bell-shaped anomaly was observed between 28 and 48K which was attributed to the transition to the superconducting state.

22 A C/T vs T^2 plot was drawn to give $\gamma(0)=0$ but the measurements did not extend below 5K.

TABLE V. $YBa_2Cu_3O_7$: Parameters derived from specific heat data (see Section 2.1 and the beginning of this section for units and definitions of symbols; mol. wt. 666.2).

T_c	H	A(0)	$\gamma(0)$	$\Delta C(T_c)/T_c$	γ	θ_o	Ref.
94	0	+	3.5	39±8	27±6	378	[47,60,61]
91	0-7.5	$+^{1,2}$	$\sim 20^{3}$				[26,27,62]
92	0-12	$+^{4,5}$	4.2^{6}			390^{7}	$[25]^{8}$
94	0	0	7.3			434	[50]
94	0	+	8.21			383	[51-55,63]
96	0			55	38		[64]
90	0-0.22	$+^{5}$	$\sim 8^{6,9}$	53	37		[65]
93	0			22	15		[66]
93	0	+	0	46	32		[38,67]
94	0			42^{10}	29		[38]
79	0-8		7.8^{11}	$\sim 26^{12}$	~18	384	[68]
93	0-8	$+^{5}$	$\sim 12^{6}$	69 ± 15^{12}	48±10	380	[69,70]
92	0			33±6	23±4	400	[71]
92	0-7	$+^{2,4}$	6.8^{13}	38^{12}	$27(34)^{14}$	450	[72]
90	0			12±2	8±1		$[73-80]^{15,16}$
92	0			18.3±0.4	12.7±0.3		
89	0			4±2	3±1		
92	0			16±2	11±1		
91	0			32±4	22±3		
92	0			37±3	26±2		
89	0	0	$\sim 9^{6}$			420	$[81]^{17}$
92	0	10.3^{18}	11.4^{19}				[82]

T_c	H	A(0)	$\gamma(0)$	$\Delta C(T_c)/T_c$	γ	θ_o	Ref.
91	0	+	12			390	[83,84][20,21]
91	0	+	19			371	
91	0	+	20			368	
90	0	207	20.1			377	[85]
89	0-4.3	+[4]	8.27±0.09[22]			465±2	[86]
89	0-4.3	+[4]	10.67±0.08[22]			500±2	
90	0-4.3	+[4]	11.97±0.07[22]			507±3	
90	0	+[23]	4.2-4.6			371-390	[87,88]
90	0			56	39		
89	0			62[24]	43		
89	0			16±3	11±2		[89,90][17,25]
90	0-6			42±2	29±1		[90,91][17,26]
92	0			59	41		[92]
94	0	+	5.5±0.5	48±2	34±1	389	[93,94]
90	0			39.5±3	28±2		[95]
91	0			43±7	30±5	336	[96]
91	0			44±11	31±8		[97]
90	0	+[27]	9.4			350	[98,99]
92	0	+[27]	9.9±0.9			352±2	[57]
90	0	+	5.5±2	33	23	400±25	[100,101][28]
90	0	+	5.2±2	33	23	400±25	
--[29]	0	+	16±3			400±25	
90	0	+	12	40±1	28±1	470	[102][30]
90	0	0.2	9			290	[103][17,31]

T_c	H	A(0)	$\gamma(0)$	$\Delta C(T_c)/T_c$	γ	θ_o	Ref.
92	0-7	+[2,4]	6.95[32]	47[12]	33(40)[14]	457	[62][33,34]
93	0			40[35]	28		[104]
--[36]	0	+	10.2			510	[106]
--[37]	0	+	16.4			450	
110	0			+[38]			[107]
92	0	+	7.74			397	[35]
93	0			43[35]	30		[108]
91	0			46[39]	32		
99	0			37	26		[109][40]
99	0			32[41]	22		
102	0			37[39]	26		
103	0			32[42]	22		
90	0	245	36.7	~22	~15	455	[110]
90	0	--[43]	27	0		410	[111]
90	0	--[43]	17	0		420	
90	0		5	0		315	
91	0			44	31		[112][39]
91	0			34	24		[113-118][44,45,46]
92	0			35	24		
91	0			36	25		
91	0	+	13.0	44	31	354	
--[36]	0			38	27		
91	0			45	31		
91	0	+	3.9	50	35	392	

T_c	H	A(0)	$\gamma(0)$	$\Delta C(T_c)/T_c$	γ	θ_o	Ref.
91	0			<20	<14		
92	0			53	37		
90	0			57	40		
90	0			56-59	39-41		
92	0	+	14.3			357	[114-118][44,45,46]
92	0	+	13.8			356	
92	0	+	11.7			387	
91	0	+	5.6			413	
92	0	+	63[47]			372	
92	0	+	14.1[48]			362	
--[49]	0	+	20.4			323	
--[49]	0	+	6.0			351	
93	0			60	42		[45]
90				62	43		[119][50]
84	0			29	20		[124]
--[36]	0	+	~4	68	48	~400	[126]
--[36]	0	+	~8	62	43	~360	[126][51]
93	0	~0[52]	~0[52]	33	23		[127][53]
91	0			41.2±5	28.8±3		[128]

---

[1] Cr impurity was present. There was a large Schottky-like anomaly in C/T near 0.5K which was moved to higher T in 7.5T.

[2] Hyperfine term in the highest field.

[3] $\partial\gamma(H)/\partial H \sim 0.3$.

[4] A Schottky-like anomaly was present in a magnetic field.

[5] A(0) increased as oxygen was removed.

[6] In the superconducting state $\gamma(0)$ was only weakly dependent on oxygen concentration.

[7] Estimated from the slope of C/T vs T^2 in Fig. 2.

[8] Specific heat of Cu containing impurity phases are reported: $Y_2Cu_2O_5$, Y_2BaCuO_5 and $BaCuO_{2+x}$. All but Y_2BaCuO_5 have a large $\gamma(0)$. (See also Refs. [84,114,116,118].)

[9] In the tetragonal phase there was a large increase in $\gamma(0)$.

[10] Gd substituted for Y.

[11] $\partial\gamma(H)/\partial H=0.65$.

[12] $\Delta C(T_c)/T_c$ shifted to lower T in a magnetic field.

[13] $\partial\gamma(H)/\partial H=0.20$.

[14] Value of γ in parenthesis was determined after correcting for an assumed normal fraction as derived from $\gamma(0)$ (see Section 4).

[15] The variation in the height of $\Delta C(T_c)/T_c$ was proposed as being due to an incomplete transition of the entire sample to the superconducting state -- perhaps due to oxygen content.

[16] A second anomaly was observed near 220K whose size correlates with $\Delta C(T_c)/T_c$ and the oxygen concentration. It was postulated that this anomaly has its origin in the ordering of the oxygen system related to the Cu-O chains.

[17] Single crystal (twinned).

[18] Attributed to Dy impurity.

[19] $\gamma(0)$ reported to be affected by the magnetic impurities.

[20] The three samples were made by oxalate coprecipitation, solid state and

organometallic precursor decomposition, respectively. $\gamma(0)$ for a thick film was 73 and $\gamma(0)$ for a powdered sample was 34. A sample which was not superconducting above 70K had $\gamma(0)=53$.

21 The low temperature specific heats for Y_2BaCuO_5, $Y_2Cu_2O_5$, CuO and $BaCuO_{2+x}$ are reported. $BaCuO_{2+x}$ had a large $\gamma(0)$ which was suggested as the source of the $\gamma(0)$ in YBCO. (See also Ref. [25] and Refs. [114,116,118] for similar measurements and conclusions.)

22 $\partial\gamma(H)/\partial H=0.45$.

23 Upturn in C/T was very small or zero for the three samples measured.

24 Double transition at T_c. Value of $\Delta C(T_c)/T_c$ reported for the lower temperature anomaly.

25 Transition at T_c was explained in terms of fluctuation effects. The low value of $\Delta C(T_c)/T_c$ was explained as being due to the presence of normal phases.

26 A magnetic field suppressed $\Delta C(T_c)/T_c$ and produced a small shift to lower T. The transitions were explained in terms of fluctuation effects.

27 Low temperature upturn in C/T was analyzed in terms of two Schottky terms.

28 Differential specific heat measurements were made using quenched non-superconducting samples as references. An energy gap was derived by fitting C_{es} for $T<T_c$.

29 Quenched sample having no superconducting transition.

30 Substitution of Zn for Cu suppressed T_c and $\Delta C(T_c)/T_c$ with a simultaneous increase in $\gamma(0)$. Application of a 3.5T field increased $\gamma(0)$ and lowered the upturn in C/T at low T. (See also Refs. [62,115,118].) Similar results were reported for Ni substitution.

31 Data have also been analyzed using $C=aT^{-2}+bT^2$ where the T^2 term was

interpreted as being due to twin boundary excitations (dyadons).

32 $\partial\gamma(H)/\partial H=0.16$.

33 Transitions for various fixed H at T_c were explained in terms of fluctuation effects. H suppressed $\Delta C(T_c)/T_c$.

34 Substitution of Cr for Cu suppressed T_c and $\Delta C(T_c)/T_c$ (see also Refs. [102,115,118]). C_1 was approximated from a sample where Cr substitution completely suppressed $\Delta C(T_c)/T_c$. A value of $\Delta C(T_c)/T_c$ of 38 reported in Ref. [72] was corrected to 52.

35 Dy substituted for Y.

36 T_c not reported.

37 $YBa_2Cu_3O_6$ (tetragonal sample). No superconducting transition.

38 Transition at T_c was observed but no analysis to obtain $\Delta C(T_c)/T_c$ was reported.

39 Er substituted for Y.

40 The T_c reported was the onset of the $\Delta C(T_c)/T_c$ discontinuity. All measurements were made using a differential calorimeter with the reference substances non-superconducting modifications of the superconducting substances.

41 $Y_{0.1}Eu_{0.9}Ba_2Cu_3O_7$. Evidence for a second transition below 90K was found.

42 Eu substituted for Y.

43 An anomaly was observed near 12K which the authors attributed to a low temperature superconducting phase; however, we feel it is more likely to be the magnetic transition in $Y_2Cu_2O_5$ or possibly $BaCuO_{2+x}$ (see also Refs. [25,84,114,116,118]) present as an impurity.

44 Specific heat of Cu containing impurity phases are reported in Refs. [114,116,118]: $YBa_3Cu_2O_7$, Y_2BaCuO_5, $BaCuO_{2+x}$ and CuO. All but CuO

had a finite $\gamma(0)$. (See also Refs. [25,84].)

45 Specific heats of $YBa_2(Cu_{1-x}Fe_x)_3O_7$ in the vicinity of T_c and at low temperatures are reported in Refs. [115,118]. Substitution of Fe for Cu lowered $\Delta C(T_c)/T_c$ and eventually eliminated it even though a relatively large Meissner effect still remained, while $\gamma(0)$ increased as the Fe concentration increased. (See also Refs. [62,102].)

46 $\gamma(0)$ was shown to depend on Cu^{2+} concentration.

47 Composition $Y_{0.9}Ba_{2.1}Cu_3O_7$.

48 Composition $Y_{1.1}Ba_{1.9}Cu_3O_7$.

49 Composition $YBa_2Cu_3O_6$ (non-superconducting tetragonal phase).

50 A lambda-like anomaly was observed in C between 86 and 87K in addition to the discontinuity $\Delta C(T_c)/T_c$ at 90K (reported as a first order transition).

51 Composition $YBa_{1.3}Cu_{4.2}O_{7-x}$.

52 A C/T vs T^2 plot appeared to have no upturn in C/T and $\gamma(0)=0$, however, T did not extend below ~2K.

53 The sample was irradiated with neutrons at 80K to suppress the superconductivity, and its specific heat assumed to be equal to C_n. At the lower temperatures an upturn in C/T was produced by the irradiation.

TABLE VI. Bi-Ca-Sr-Cu-O and Tl-Ca-Ba-Cu-O systems: Parameters derived from specific heat data (see Section 2.1 and the beginning of this section for units and definitions of symbols).

Composition	T_c	H	A(0)	$\gamma(0)$	$\Delta C(T_c)/T_c$	γ	θ_o	Ref.
$TlCaBaCu_2O_{5.5}$	114	0-7	+[1]	16	≥16[2]	≥11	270	[120]
$Bi_2CaSr_2Cu_2O_8$	84	0-7	+[1]	0[3]	--[4]		250	
$Bi_{2.15}Ca_{1.17}Sr_{1.68}Cu_2O_8$	80	0-7	+[1]	0[3]	--[4]		230	
$Bi_2Ca_2Sr_2Cu_4O_{11}$	110 95	0-7	+[1]	0[3]	--[5] ≥24[2]	≥17	250	
$Bi_2Ca_6Sr_2Cu_8O_{19}$	110 80	0-7	+[1]	0[3]	--[2,6]		290	
$BiCaSrCu_2O_{10}$	85	0	0	0±0.2			550	[121]
$Bi_4Ca_{2.4}Sr_{3.6}Cu_4O_y$		0	+	~0				[122][7]
Bi-Ca-Sr-Cu-O								[123][8]

---

[1] In 7T the sample-dependent upturn in C/T at H=0 became a sample dependent Schottky-like anomaly.

[2] The transition was suppressed in 7T, but the discontinuity was so broad that $\Delta C(T_c)/T_c$ can only be approximated.

[3] $\partial\gamma(H)/\partial H \sim 0.15$.

[4] No discontinuity in C was observed near T_c even though a Meissner effect was measured.

[5] The discontinuity in C/T near T_c=110K was too small to allow an estimate of $\Delta C(T_c)/T_c$ (only about 10% of the T_c=110K phase was present).

[6] The upper and lower transitions were coalesced into one broad transition (about 40% of the T_c=110K phase was present).

[7] Values quoted in Ref. [121] from a preprint.

[8] No preprint available.

FIGURE CAPTIONS

Fig. 1 Zero-field specific heat of YBCO (see text for discussion).

Fig. 2 C/T vs T^2 for YBCO. The solid line represents the T and T^3 terms from a least-squares fit of the data, while the dashed line represents the kind of fit that is likely to be obtained by fitting a straight line visually (see text for discussion).

Fig. 3 C/T vs T^2 for $Y_2Cu_2O_5$, $BaCuO_{2+\delta}$ and Y_2BaCuO_5 -- possible impurity phases in YBCO. (Taken from Ref. [25].)

Fig. 4 C/T vs T^2 for Y_2BaCuO_5, $Y_2Cu_2O_5$, $BaCuO_{2+x}$ (two forms) and CuO -- possible impurity phases in YBCO. $BaCuO_{2+x}{}^{(1)}$ was prepared in air and $BaCuO_{2+x}{}^{(2)}$ was prepared in oxygen. For comparison, YBCO is also shown. (Taken from Ref. [84].)

Fig. 5 C/T vs T for $La_{1.85}Ca_{0.15}CuO_4$ at H=0, 3.5 and 7T. The upturn in C(H)/T for $H\neq0$ is due to hyperfine interactions, and the field-dependent displacement at higher T is from the $\gamma(H) + B_3'(H)T^2$ terms in the mixed state. (See Refs. [26,27].)

Fig. 6 C/T vs T for $La_{1.85}Sr_{0.15}CuO_4$ at H=0, 3.5 and 7T. The data are similar to those shown in Fig. 5 except that in 3.5T an anomaly due to magnetic impurities is observed in the vicinity of 1-3K. In 7T it occurs at a higher temperature and is less conspicuous in the figure. (See Refs. [26,27].)

Fig. 7 C(H)/T vs T for $La_{1.85}Sr_{0.15}CuO_4$ showing a decomposition of the data in Fig. 6 into various components as derived from least-squares fits. (Taken from Refs. [26,27].)

Fig. 8 C/T vs T^2 for $La_{2-x}Ba_xCuO_4$ for various x (antiferromagnetic for $0\leq x\leq0.02$; non-magnetic insulator for $0.03\leq x\leq0.04$; superconductor for $0.05 \leq x \leq 0.15$). The solid lines are from least-square fits. (Taken from Ref. [30].)

Fig. 9	$[C-C_1]/T$ vs T for YBCO. The light lines are spline fits to the data, while the heavy lines represent $\gamma(H)$ at 0, 3.5 and 7T derived from least-square fits to the data. In 7T, below ~1K, the upturn in C/T is due to hyperfine components. (Taken from Ref. [72].)
Fig. 10	The analysis of C for YBCO into various components. (See Ref. [62].)
Fig. 11	C/T vs T^2 for three samples of YBCO showing the decrease in $\gamma(0)$ as the upturn in C/T decreases. (Taken from Refs. [87,88].)
Fig. 12	$\gamma(0)$ vs n_i for YBCO and one sample of TCBCO. The slope of the straight line is compatible with a $\gamma(0)$ contribution from $BaCuO_{2+x}$. The intercept implies an intrinsic $\gamma(0)$ of 7 mJ/mole K^2. (See Refs. [62,120].)
Fig. 13	C/T vs T^2 for $YBa_2Cu_3O_{7-x}$ for x=0, 0.28 and 0.70. (Taken from Ref. [25].)
Fig. 14	C/T vs T^2 for a single crystal mosaic of $YBa_2Cu_3O_{7-x}$. The open circles are data for x~0 (orthorhombic) while the other two sets of data are for x~1 (tetragonal). (Taken from Ref. [81].)
Fig. 15	C/T vs T^2 for TCBCO with $T \leq 10K$ and H=0 and 7T. The straight line represents the T and T^3 terms of the least-squares fit to the zero field data. (Taken from Ref. [120].)
Fig. 16	C/T vs T^2 for BCSCO for $T \leq 8K$ and H=0 and 7T. The straight line represents the T^3 term of the least-squares fit to the zero field data. (Taken from Ref. [120].)

Fig. 17 $[C(0)-A_{-3}T^{-3}-A_{-2}T^{-2}]/T$ vs T^2 for four BCSCO samples and one TCBCO sample. The straight lines represent the T^3 (T and T^3 for TCBCO) terms from least-squares fits to the data. (Taken from Ref. [120].)

Fig. 18 C_{es}/T, here denoted by γ, vs T for two samples of $La_{1.85}Sr_{0.15}CuO_4$. Differential calorimetry was used and γ calculated from the measured ΔC between sample and reference after corrections were applied -- see text for details. [See Ref. [137].)

Fig. 19 $[C_e(0)-C_e(7)]/T$ vs T for $La_{1.85}Ca_{0.15}CuO_4$ and $La_{1.85}Sr_{0.15}CuO_4$. The horizontal bars mark the 10-90% Meissner effect width. The low-temperature behavior is in qualitative agreement with expectation for the mixed state in 7T. The dashed lines represent entropy conserving constructions used to estimate ΔC at T_c. (Taken from Refs. [26,27].)

Fig. 20 Relationship between resistance (R), a.c. susceptibility (χ_{ac}), Meissner magnetization (M) -- field cooled in 17Oe -- and C/T for YBCO. The base-line represents R=0 and asymptotic low temperature diamagnetism for both χ_{ac} and M. (Taken from Ref. [113].)

Fig. 21 C/T vs T near T_c for YBCO. The solid lines are the idealized, sharp, entropy conserving constructions at T_c. The dashed line in (j) is a continuation of the normal state specific heat using the two-fluid model. T_c^{ind} is the transition width from χ_{ac}. (Taken from Ref. [113].)

Fig. 22 $(C_{es}-C_n)/T$, here denoted by $\delta\gamma$, vs T for two samples of YBCO.

Differential calorimetry was used and $\delta\gamma$ calculated from the corrected measured ΔC between sample and reference -- see text for details. (Taken from Refs. [100,101].)

Fig. 23 C/T vs T for YBCO in the vicinity of T_c. The solid line labeled C_{latt}/T represents the lattice part of the specific heat -- see text for details. (Taken from Ref. [92].)

Fig. 24 C(H)/T vs T for YBCO in fields of 0, 3.5 and 7T near T_c. The vertical line is the sharp entropy conserving construction representing the discontinuity at T_c. The lower solid curve is taken to represent C_n and is from a spline fit of C/T data for $YBa_2(Cu_{2.96}Cr_{0.04})O_7$ for which $\Delta C(T_c)/T_c \approx 0$ -- see Fig. 34 of Section 6.2. In-field data exhibit fluctuation effects. (See Ref. [62].)

Fig. 25 [C(0)-C(H)] vs T for single crystal YBCO showing fluctuation effects. The insert shows H=0, 1.5 and 4.5T data from which the differences were extracted. Note the similarity of this data to that in Fig. 24 for a ceramic sample of YBCO. (Taken from Ref. [91].)

Fig. 26 C/T vs T for TCBCO near T_c for H=0 and 7T. (See Ref. [120].)

Fig. 27 [C(0)-C(7)]/T vs T for a multiphase superconducting sample of BCSCO showing two anomalies corresponding to the double transition found by Meissner effect measurements. (Taken from Ref. [120].)

Fig. 28 ΔC vs T for a sample of YBCO showing the anomaly (from possible oxygen ordering) near 220K obtained by subtracting a quadratic background obtained from a fit above and below the anomaly.

(Taken from Ref. [73].)

Fig. 29 C/T vs T for $GdBa_2Cu_3O_7$ near T_c. (Taken from Ref. [38].)

Fig. 30 C vs T for RBCO from 230 to 490K where R=Gd,Er,Dy and Eu, and, for comparison, Y. (Taken from Ref. [148].)

Fig. 31 C vs T for RBCO with R=Ho,Tm and Yb, and, for comparison, Y. No magnetic ordering is observed above 0.45K although crystal field effects are present. (Taken from Ref. [52].)

Fig. 32 C vs T for RBCO, with R=Nd,Sm,Gd,Dy and Er, showing magnetic ordering. (Taken from Ref. [52].)

Fig. 33 C vs T for $EuBa_2Cu_3O_7$ which has a non-magnetic groundstate. The specific heat is similar to that for YBCO. (Taken from Ref. [52].)

Fig. 34 C/T vs T for $YBa_2(Cu_{3-x}Cr_x)O_7$ near T_c. For x=0.040 $\Delta C(T_c)/T_c$ is virtually completely suppressed. (An attenuated Meissner effect was observed for x=0.040 with an onset near 91K, and a very small anomaly in C/T -- nearly within the experimental precision -- may be present near 90K.) (See Ref. [62].)

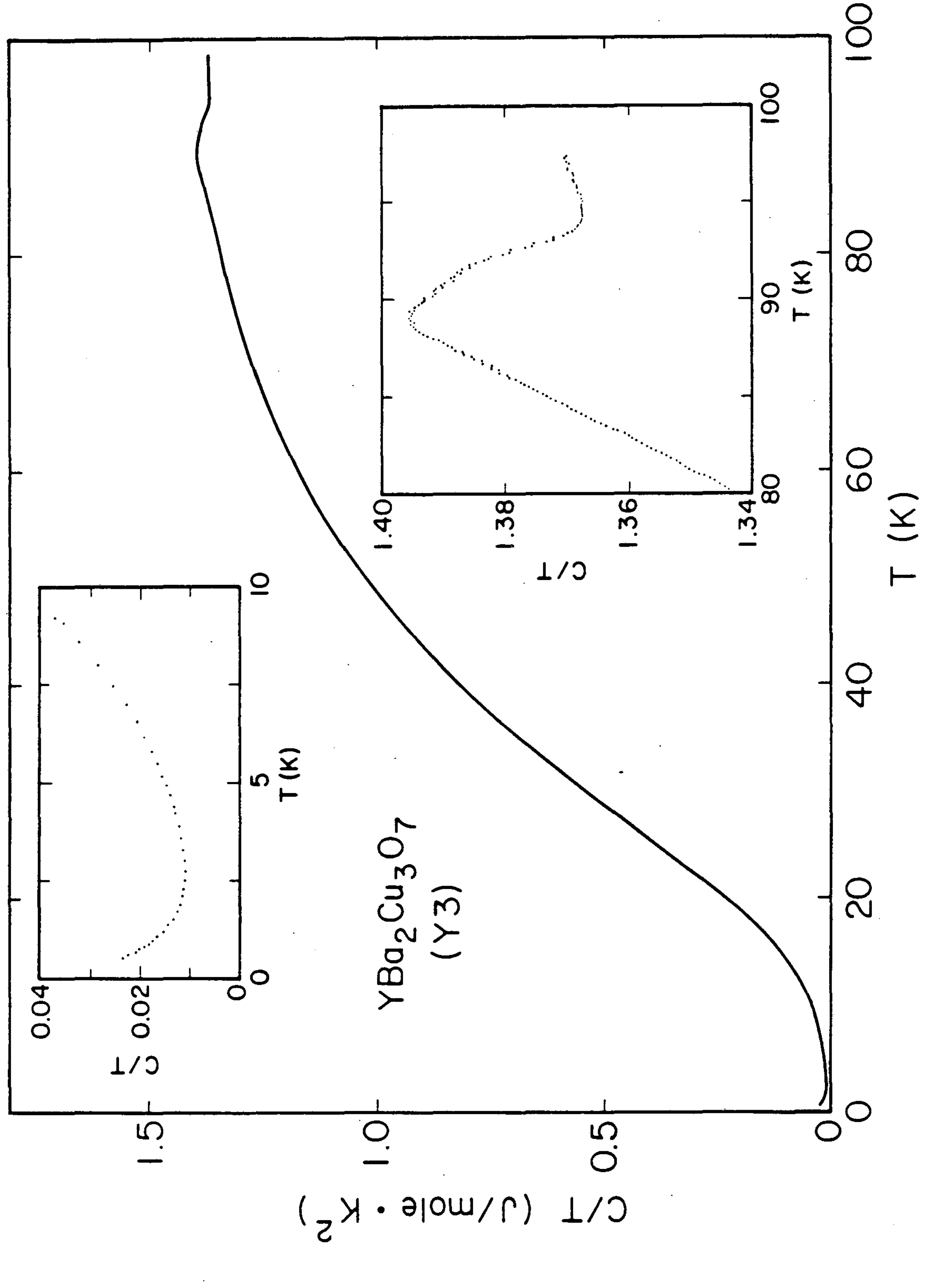
Fig. 35 C/T vs T for $YBa_2(Cu_{3-x}Cr_x)O_7$ at low temperatures. As x increases both $\gamma(0)$ and the upturn in C/T also increase. The lines are guides to the eye. (See Ref. [62].)

Fig. 36 (a) Neutron scattering spectrum for $La_{1.85}Sr_{0.15}CuO_4$. (b) The inelastic part of the spectrum shown in (a) after subtraction of an energy independent background. The solid line varies as ω^2 and the dashed line indicates the peaking structure near 10 meV. (Taken from Ref. [43].)

Fig. 37 Phonon density of states for YBCO as measured with inelastic neutron scattering. Below 9 meV the DOS varies as ω^2. (Taken from Ref. [170].)

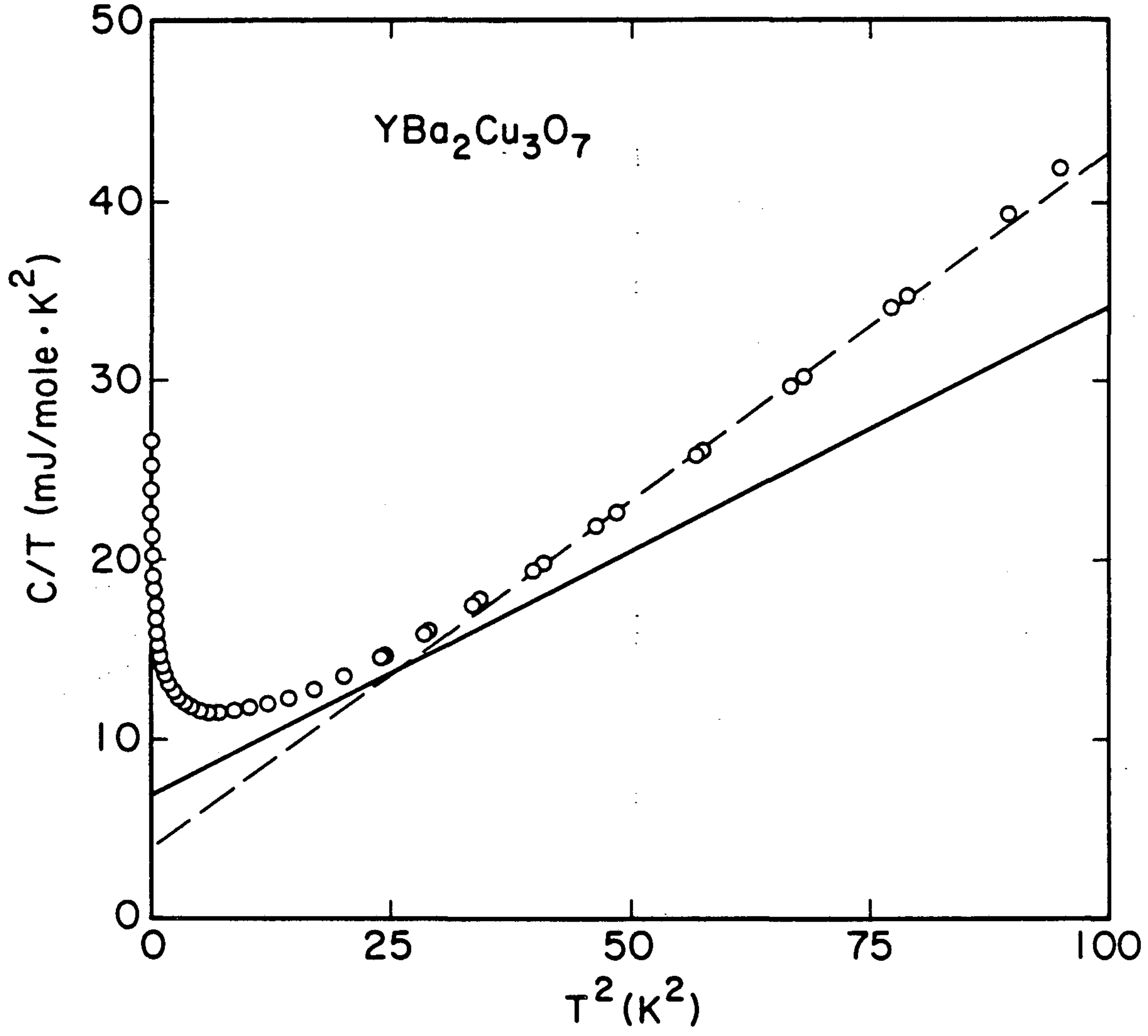
Fig. 38 C_l/T^3 vs ln [T(K)] for $La_{1.85}Sr_{0.15}CuO_4$. The 23K peak corresponds to an enhanced DOS at 10 meV (115K). The continuous lines labelled A, E_1 and E_2 are contributions from the acoustic (Debye) and two optical (Einstein) branches, respectively. The dashed line is the sum of these contributions and is in close agreement with the experimental data. The insert shows the phonon spectrum (drawn to scale) used to compute the contributions. (Taken from Ref. [43].)

Fig. 39 Comparison of the lattice specific heat for LCO, YBCO, TCBCO and BCSCO as C_l/T^3 vs log T(K). (Taken from Ref. [120].)



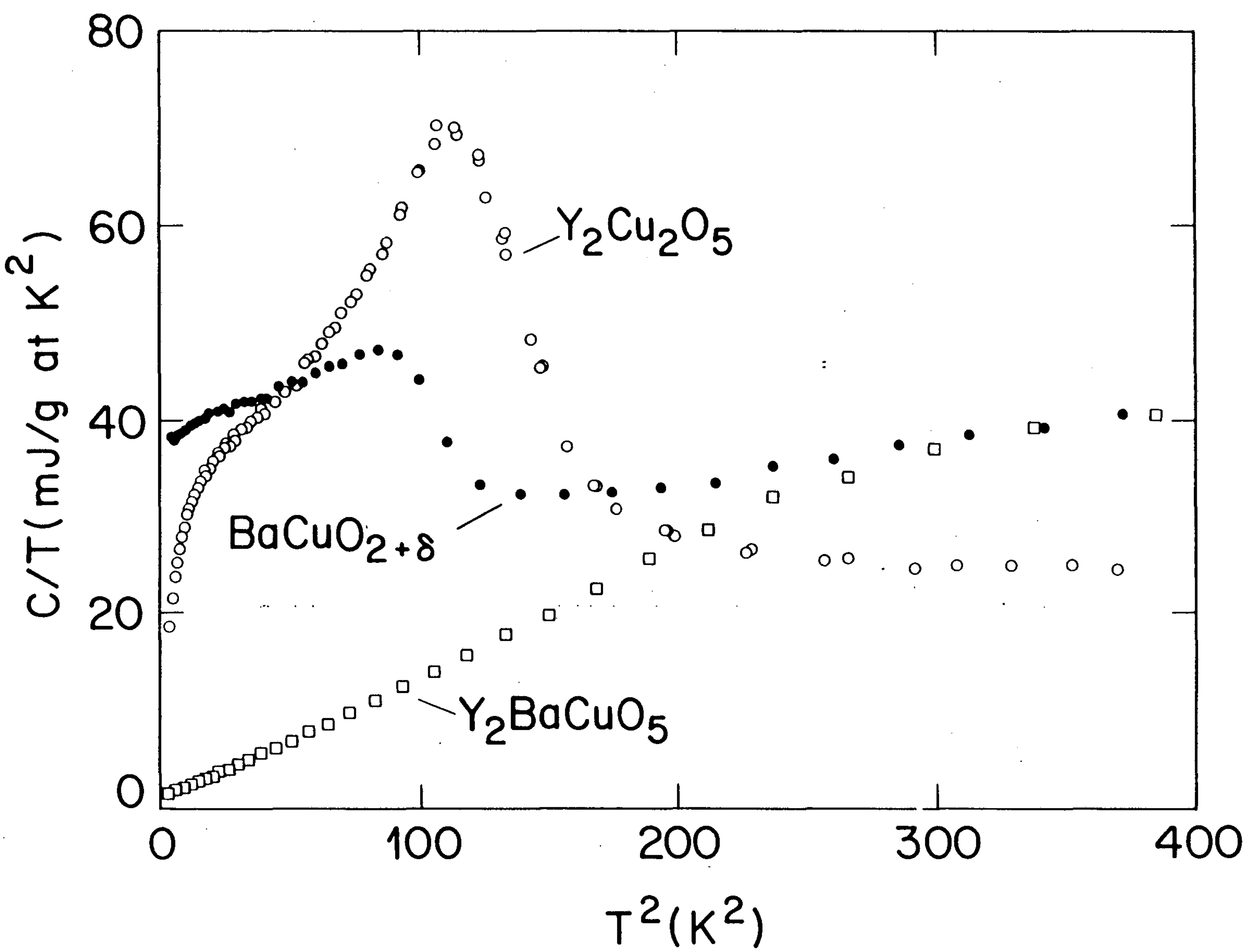
XBL 882-488

Fig. 1



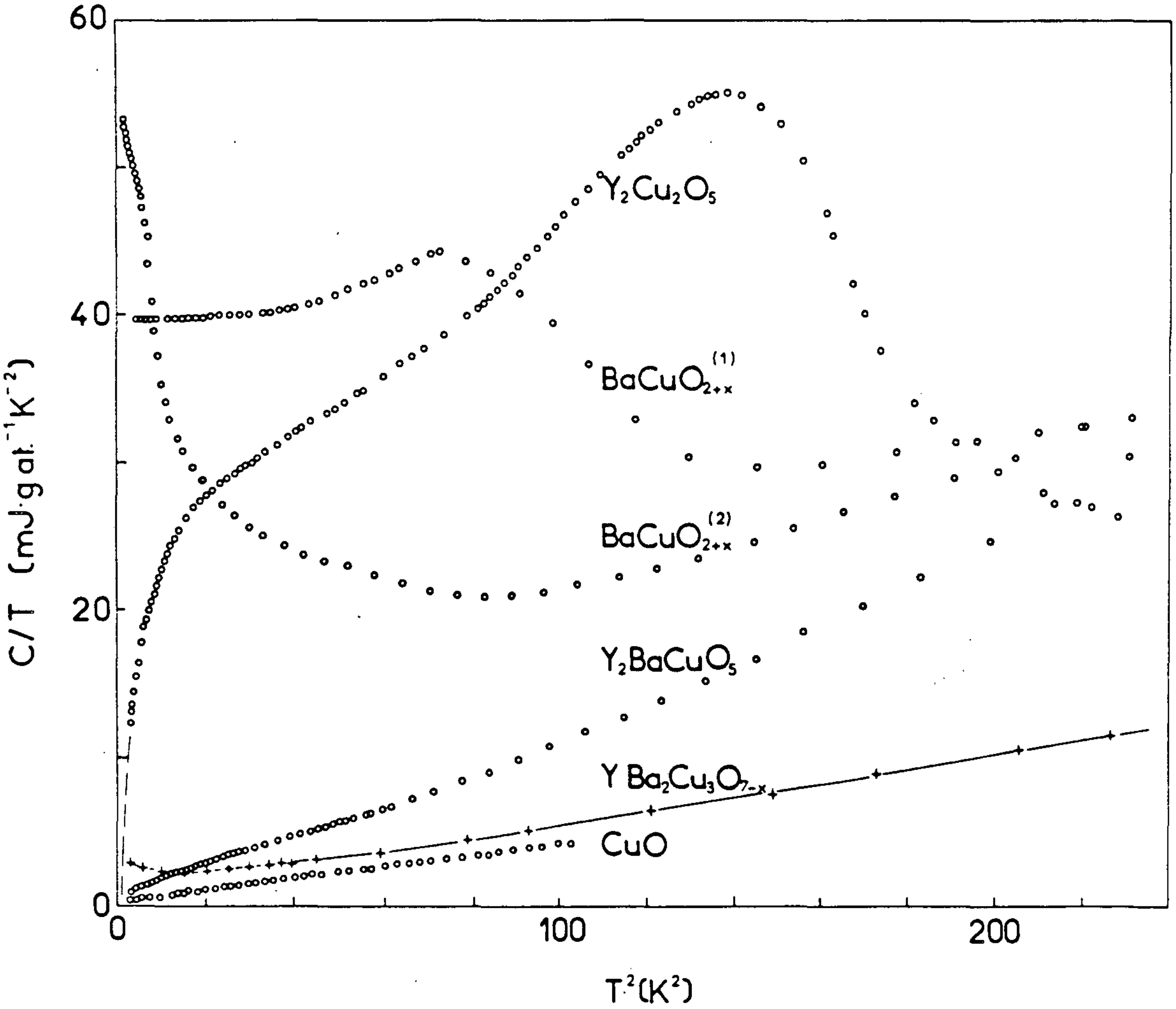
XBL 886-2091

Fig. 2



XBL 885-1777

Fig. 3



XBL 885-1761

Fig. 4

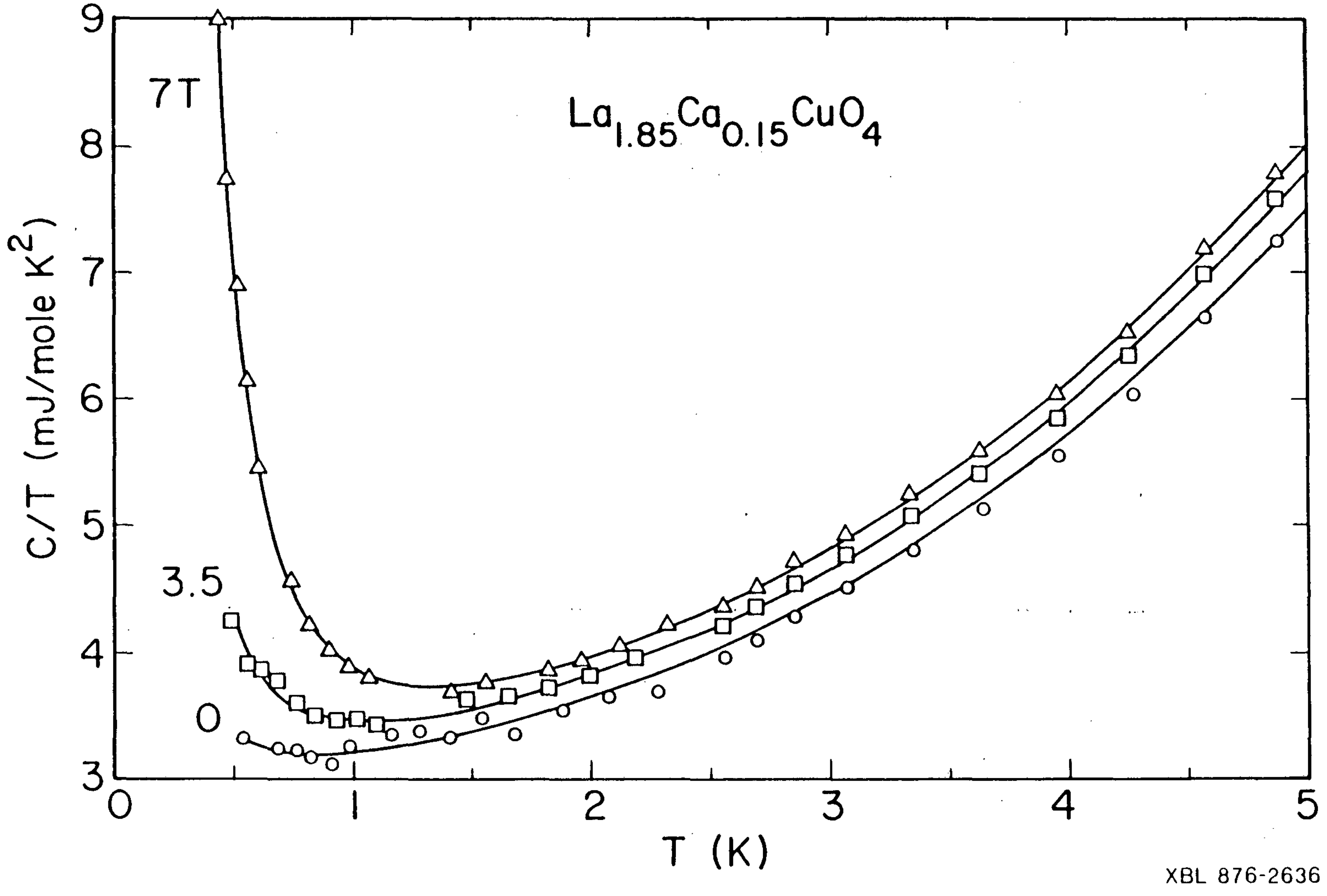
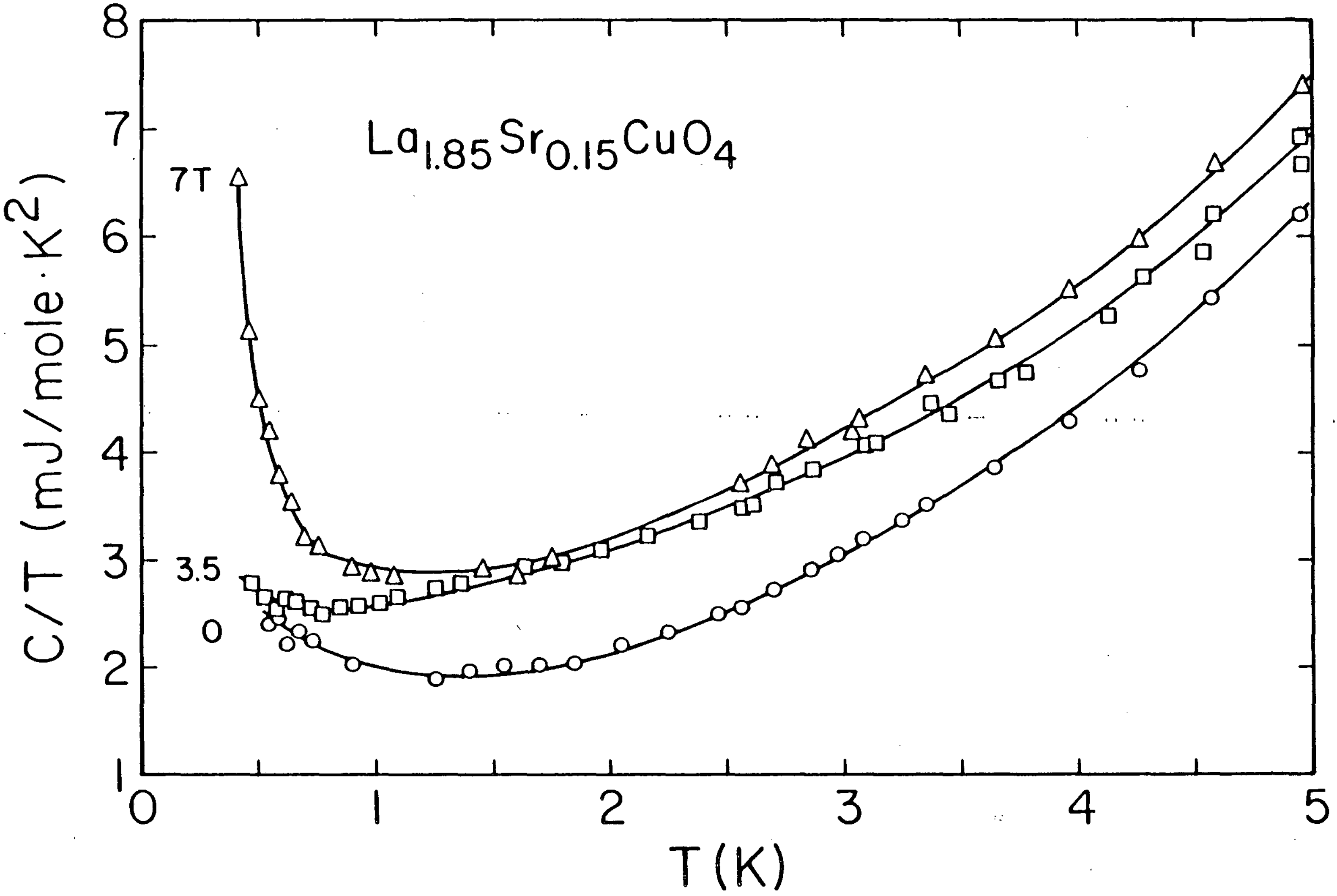
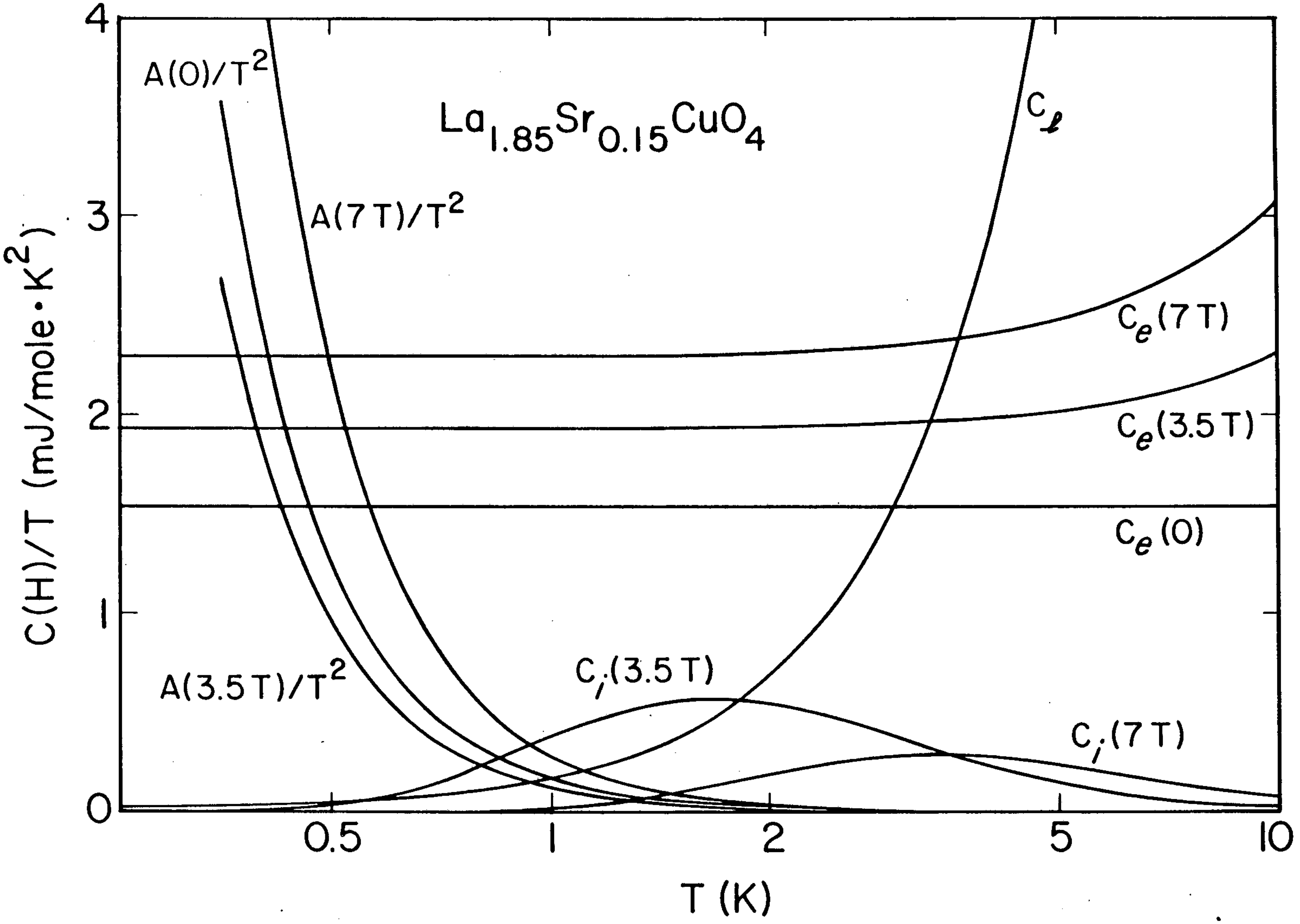

9
8
7
6
5
4
3
C/T (mJ/mole K²)
0
1
2
3
4
5
T (K)
7T
3.5
0
La1.85Ca0.15CuO4
XBL 876-2636

Fig. 5



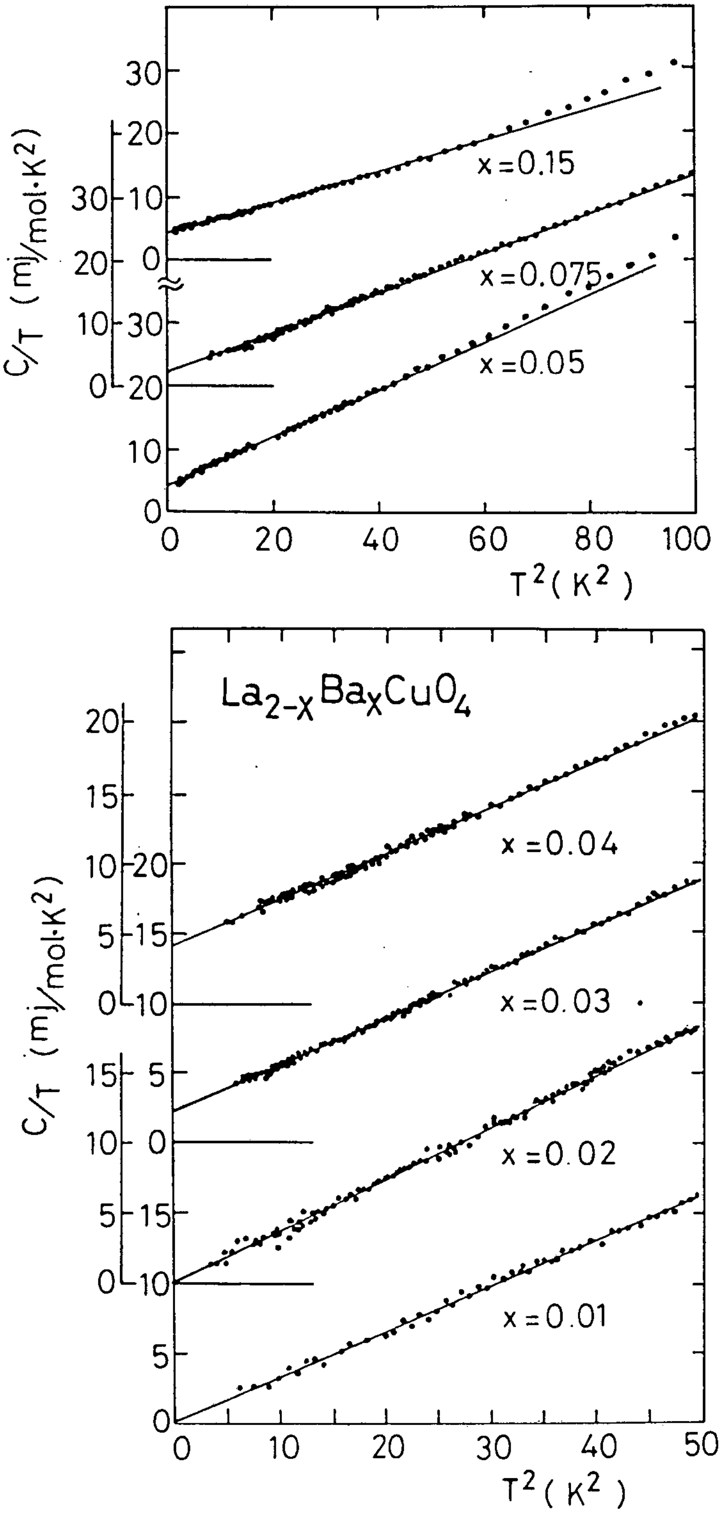
XBL 876-2634

Fig. 6



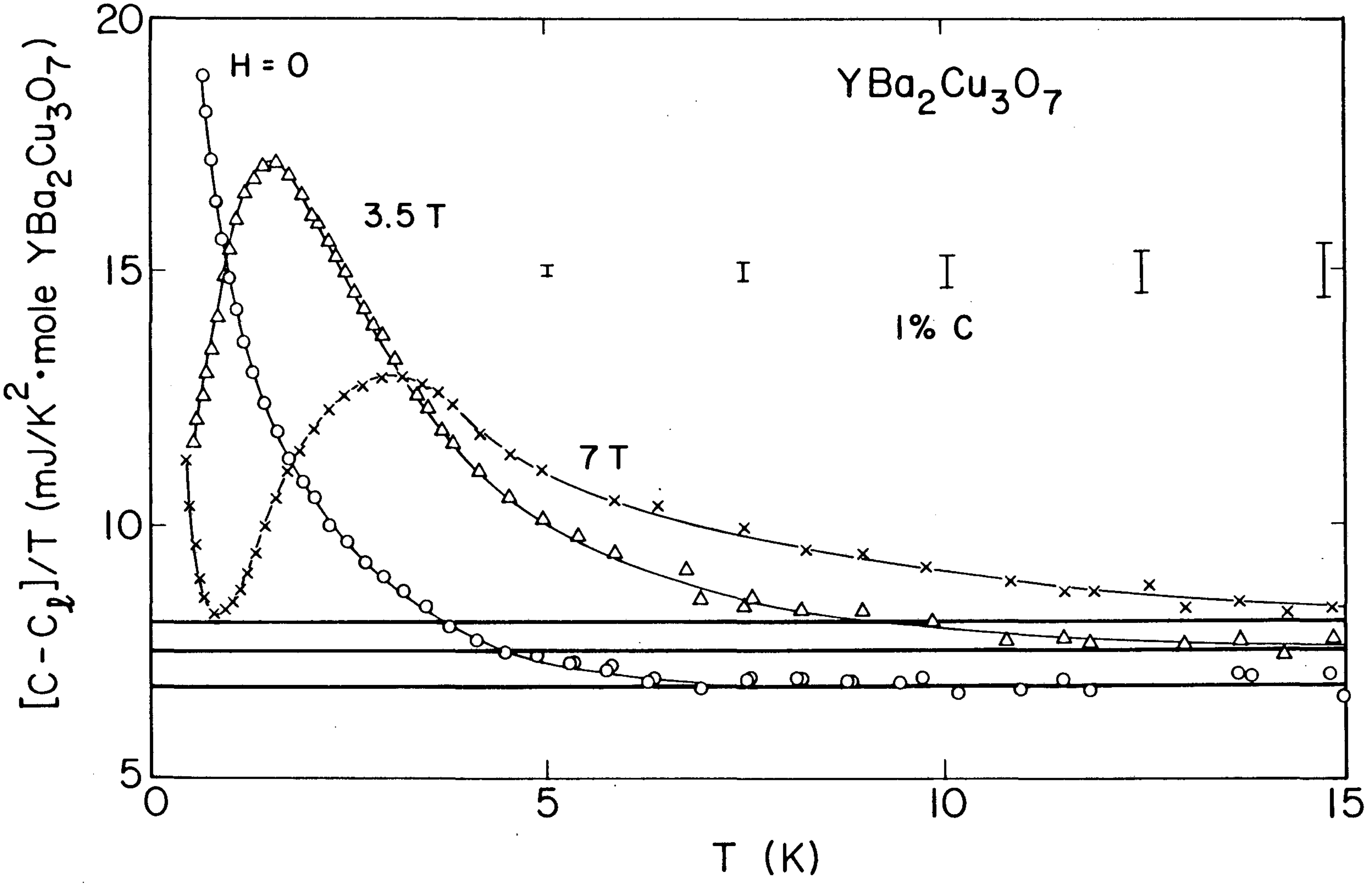
XBL 879-3963

Fig. 7



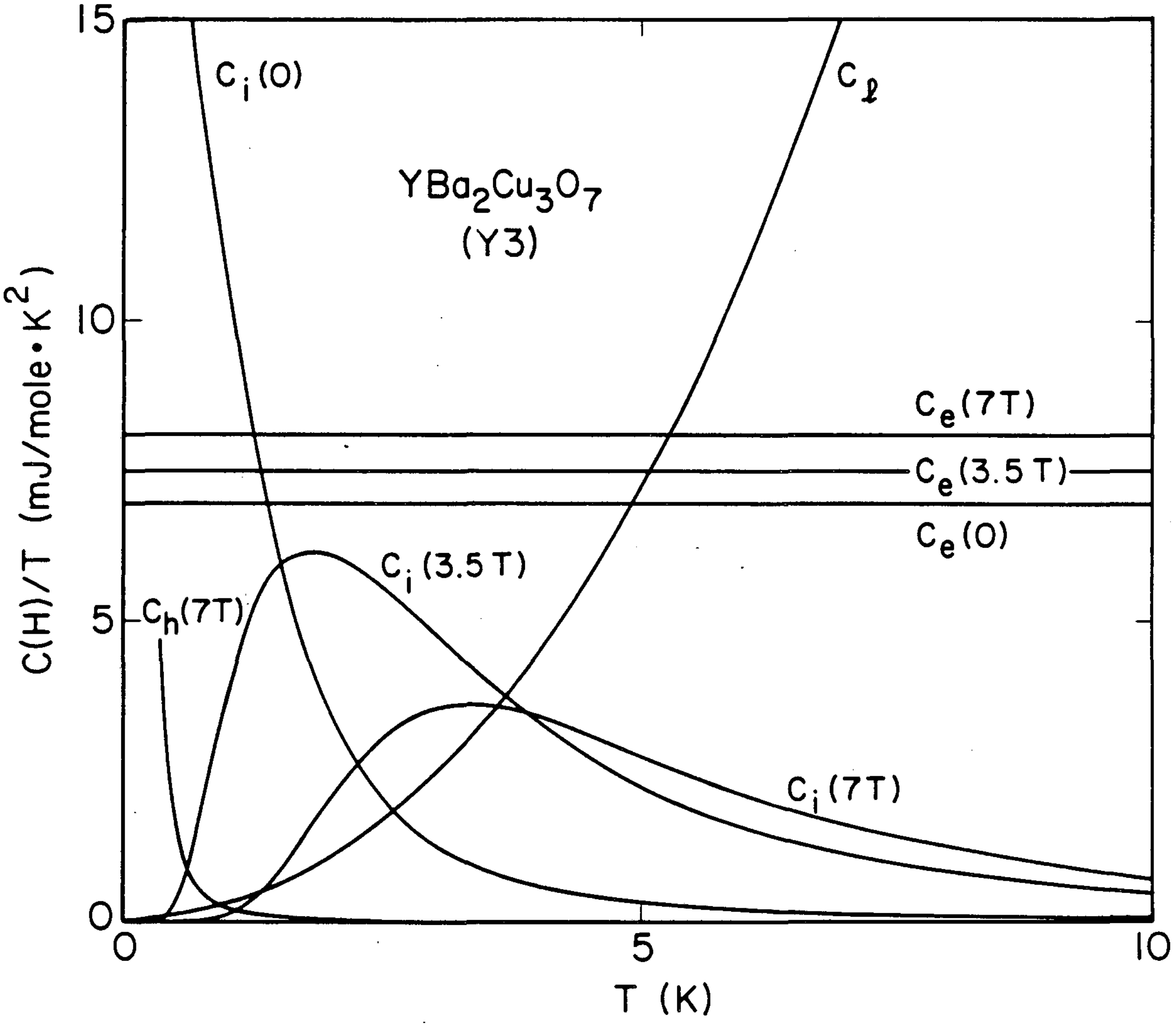
XBL 885-1771

Fig. 8



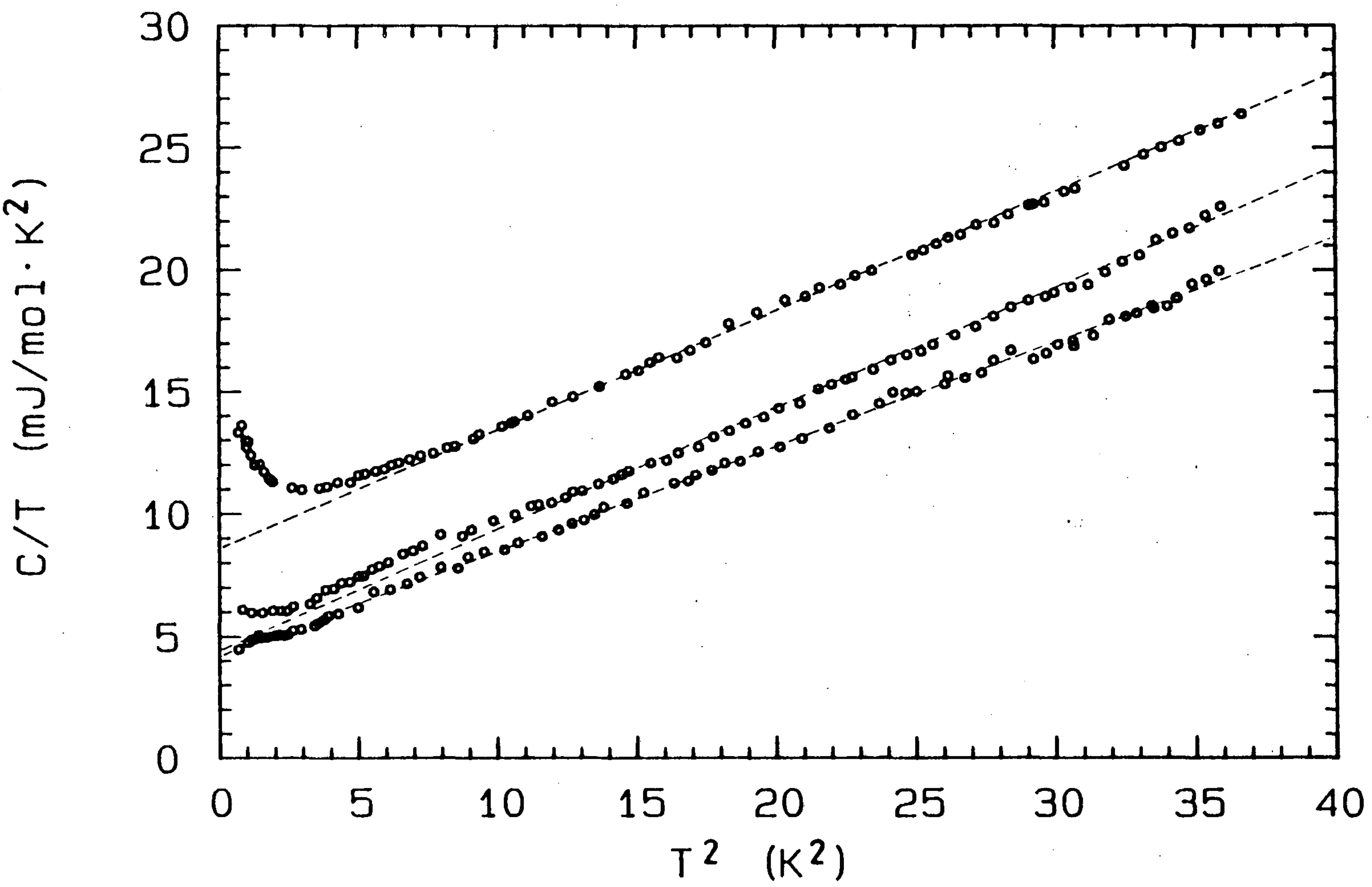
XBL 8710-4196

Fig. 9



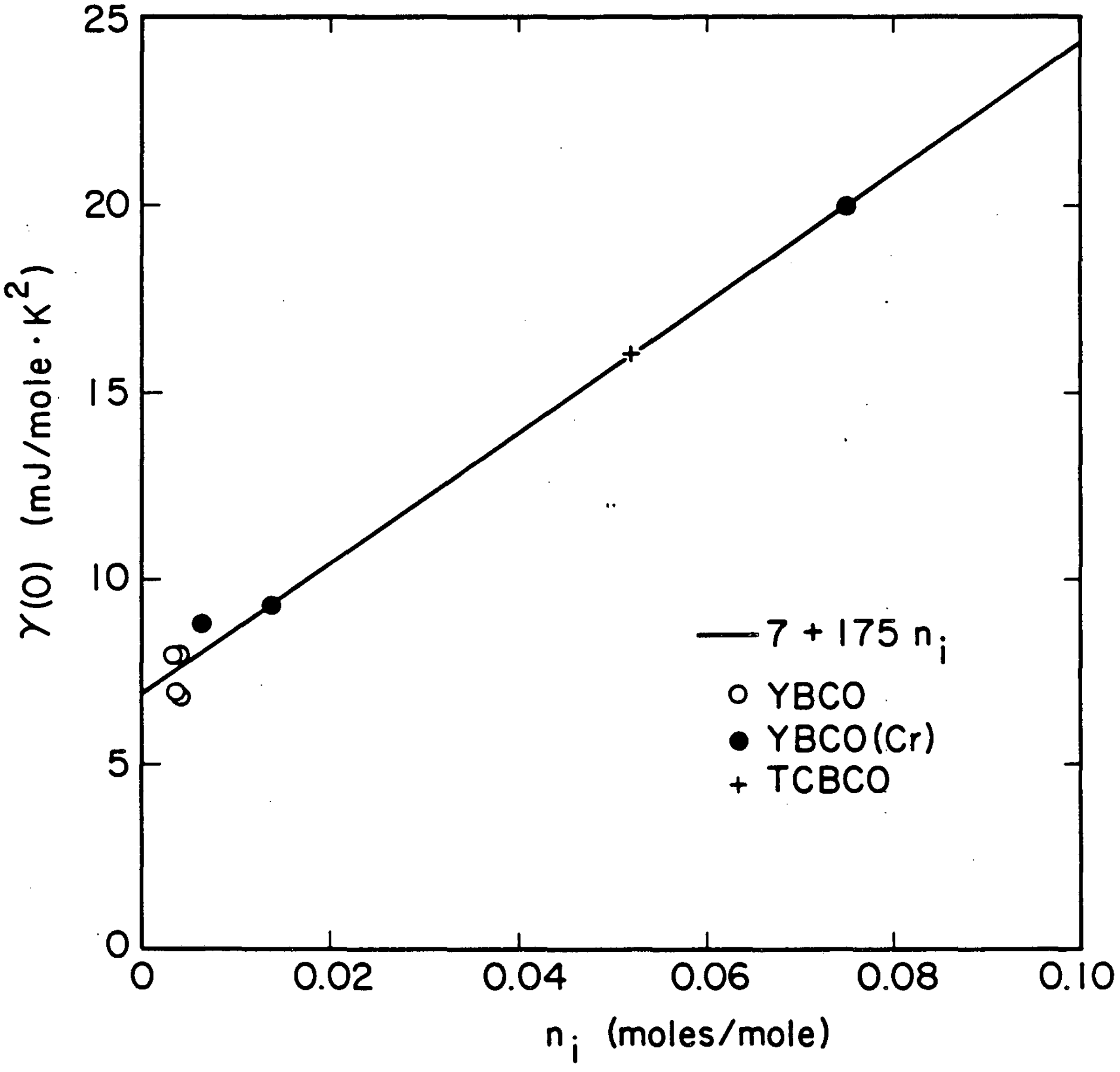
XBL 882-491

Fig. 10



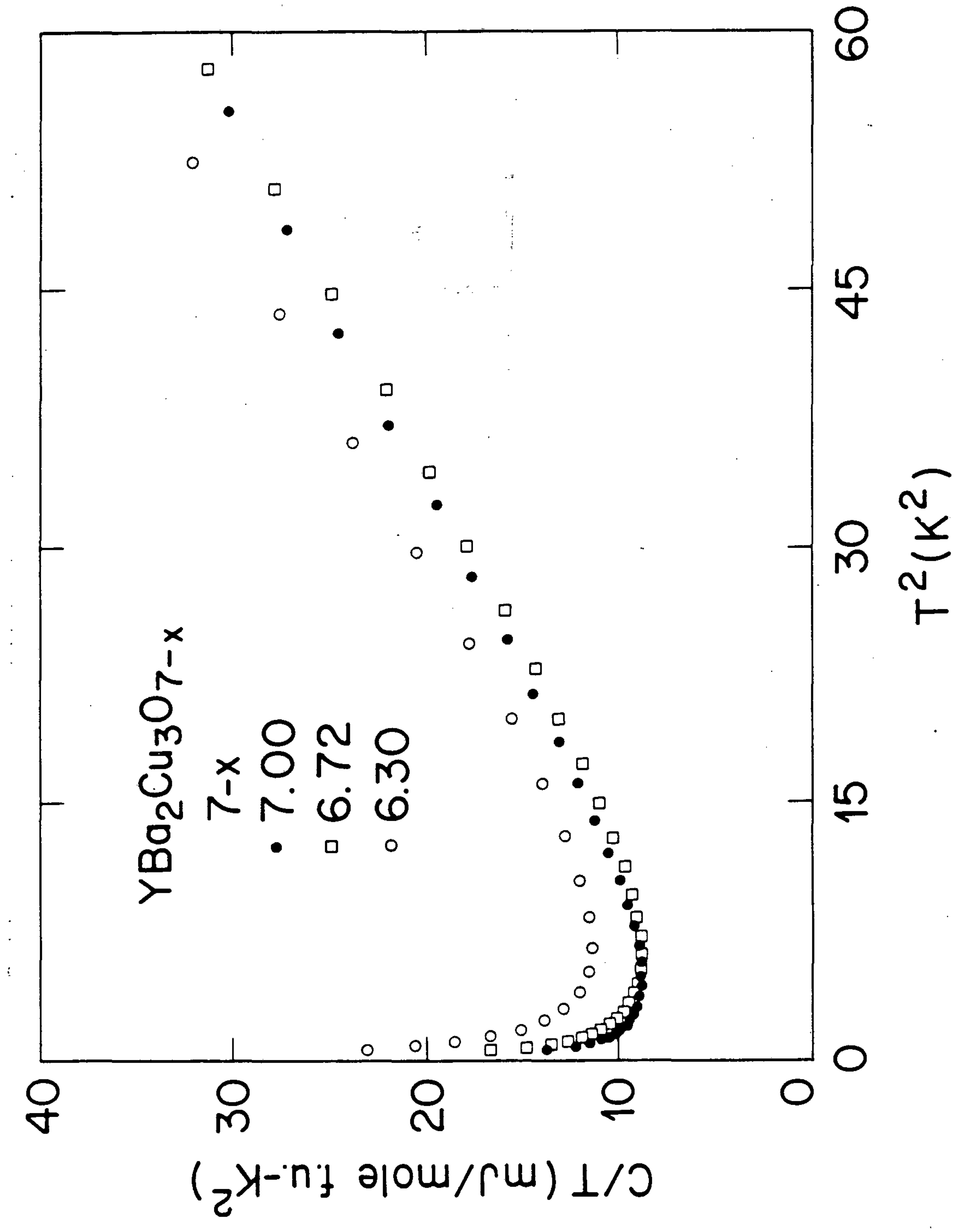
XBL 885-1763

Fig. 11



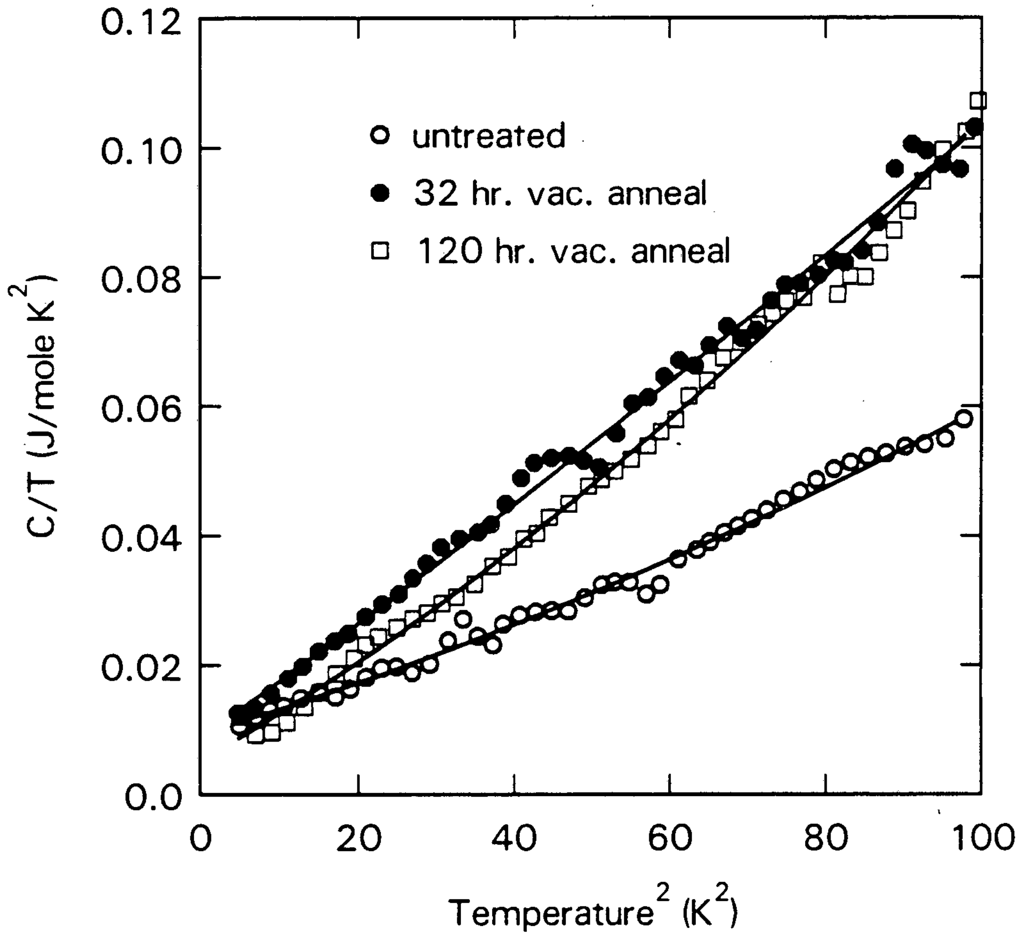
XBL 886-2092

Fig. 12



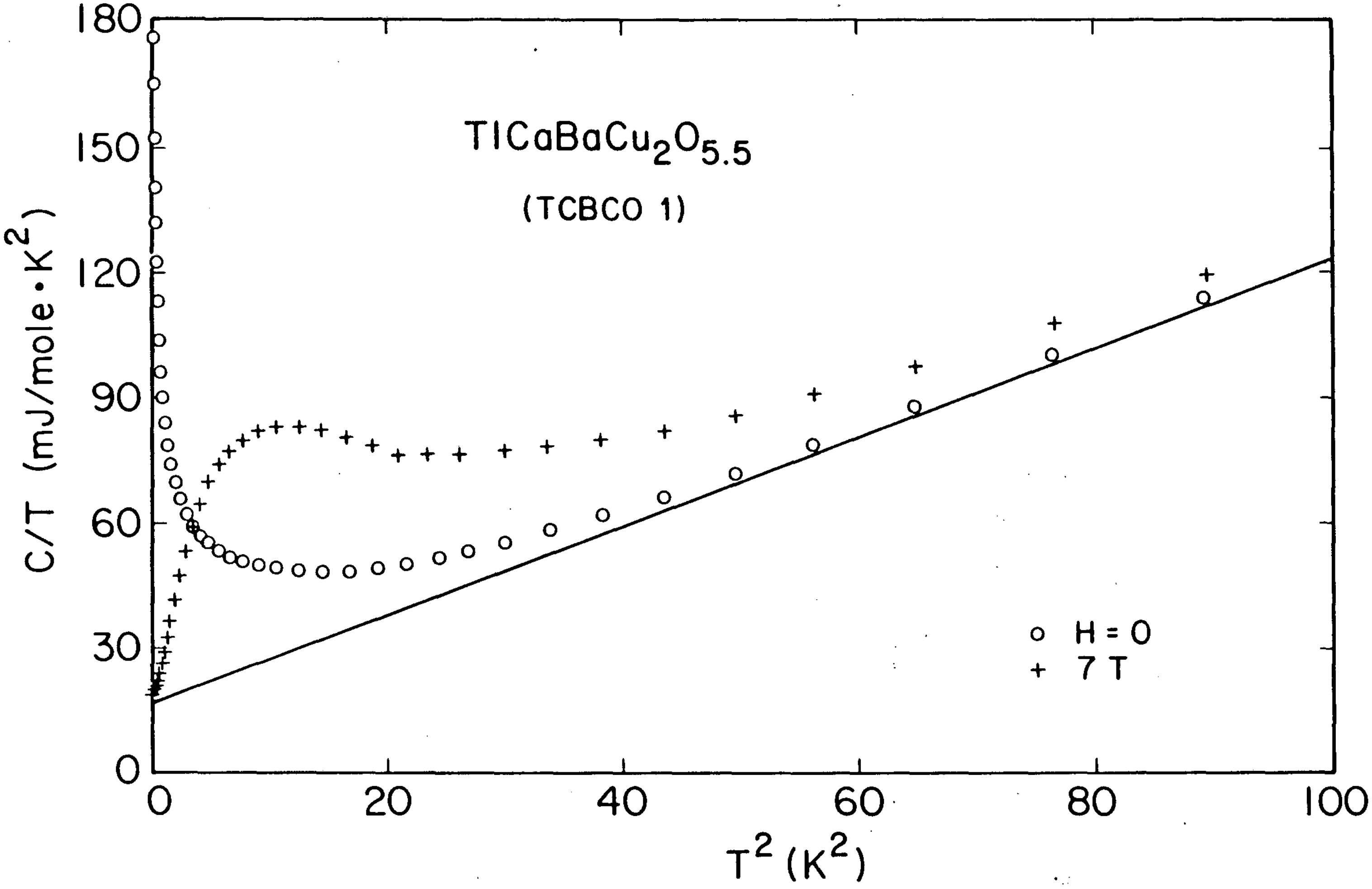
XBL 885-1767

Fig. 13



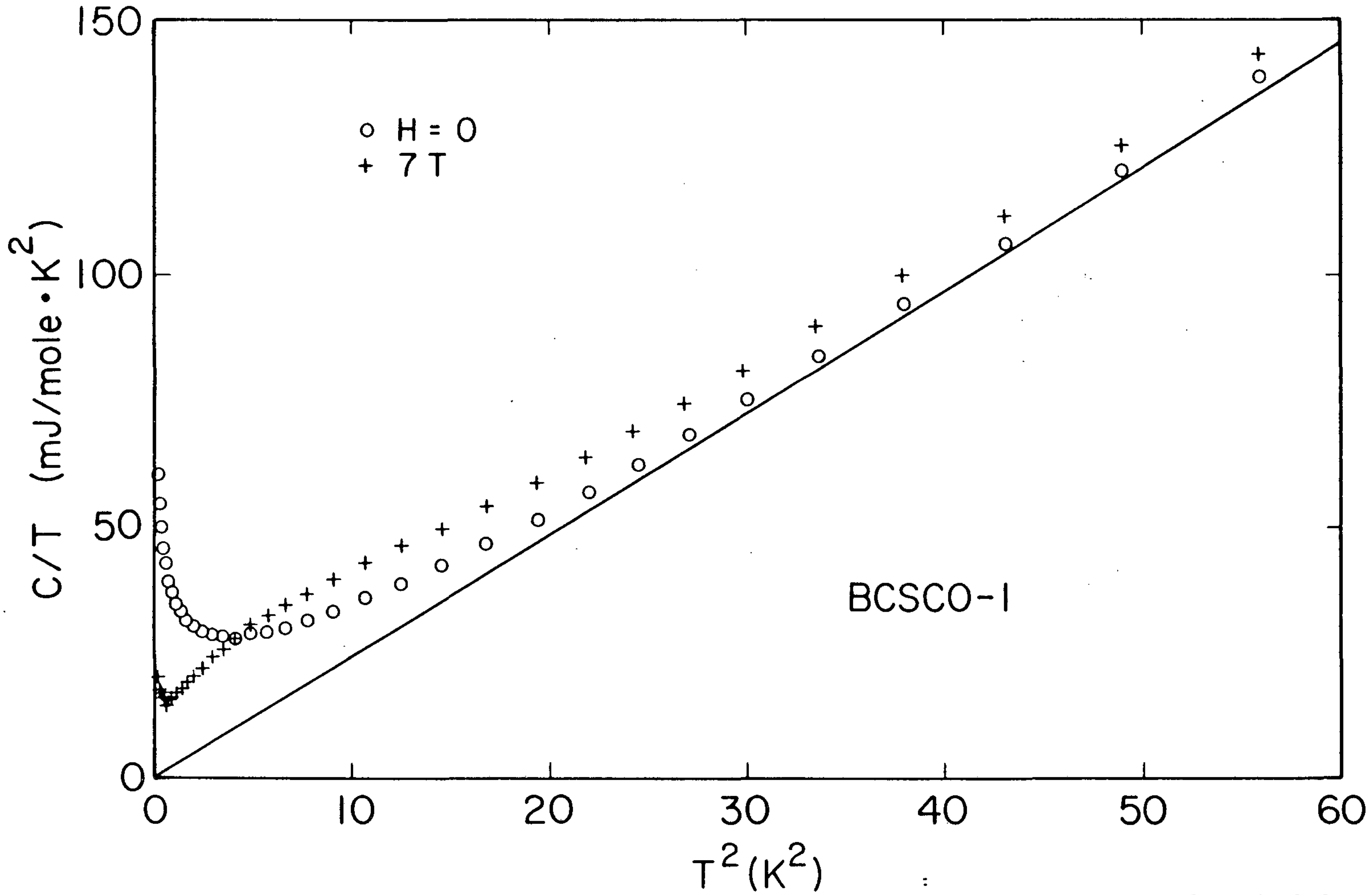
XBL 885-1760

Fig. 14



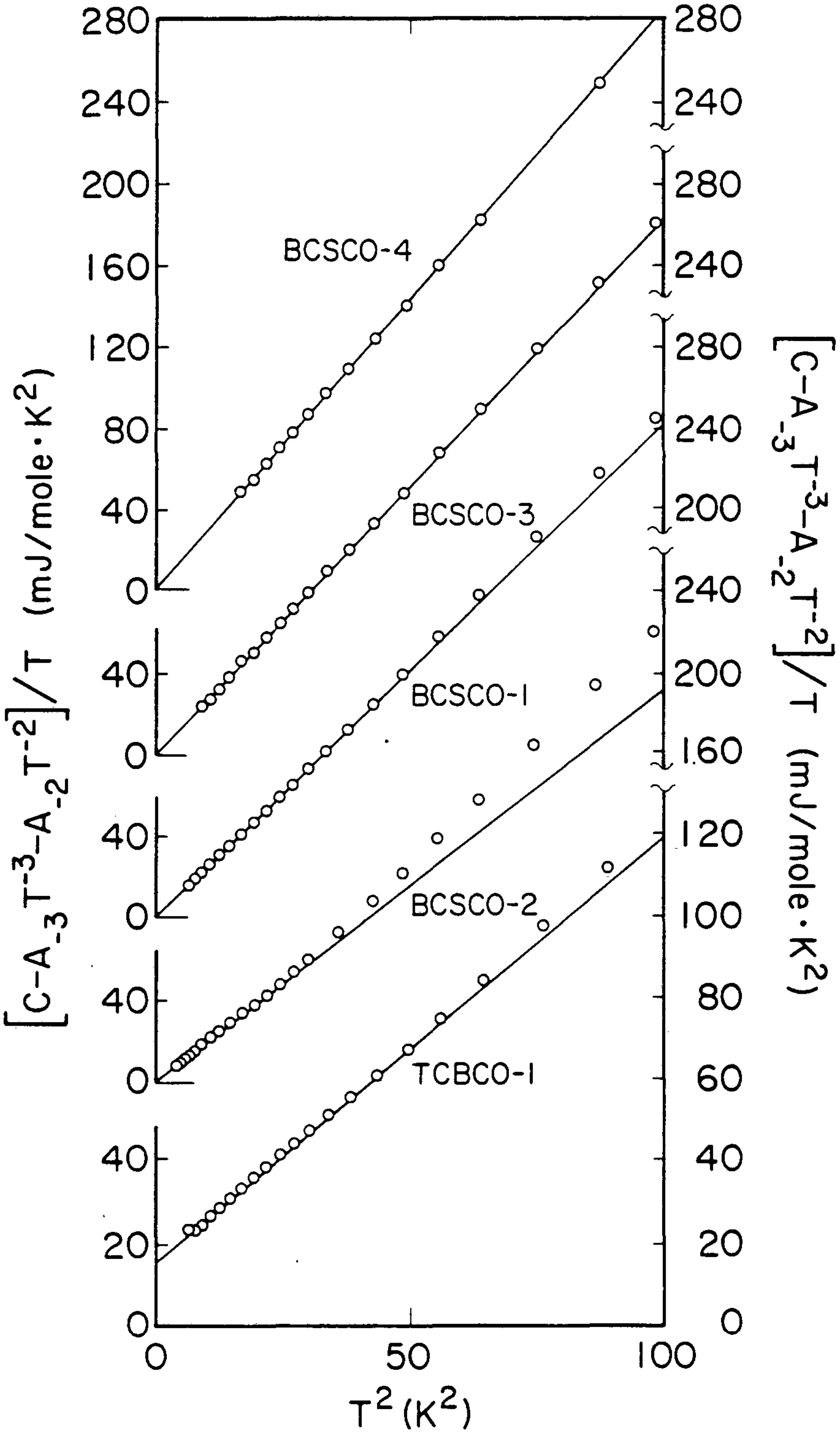
XBL 885-1543A

Fig. 15



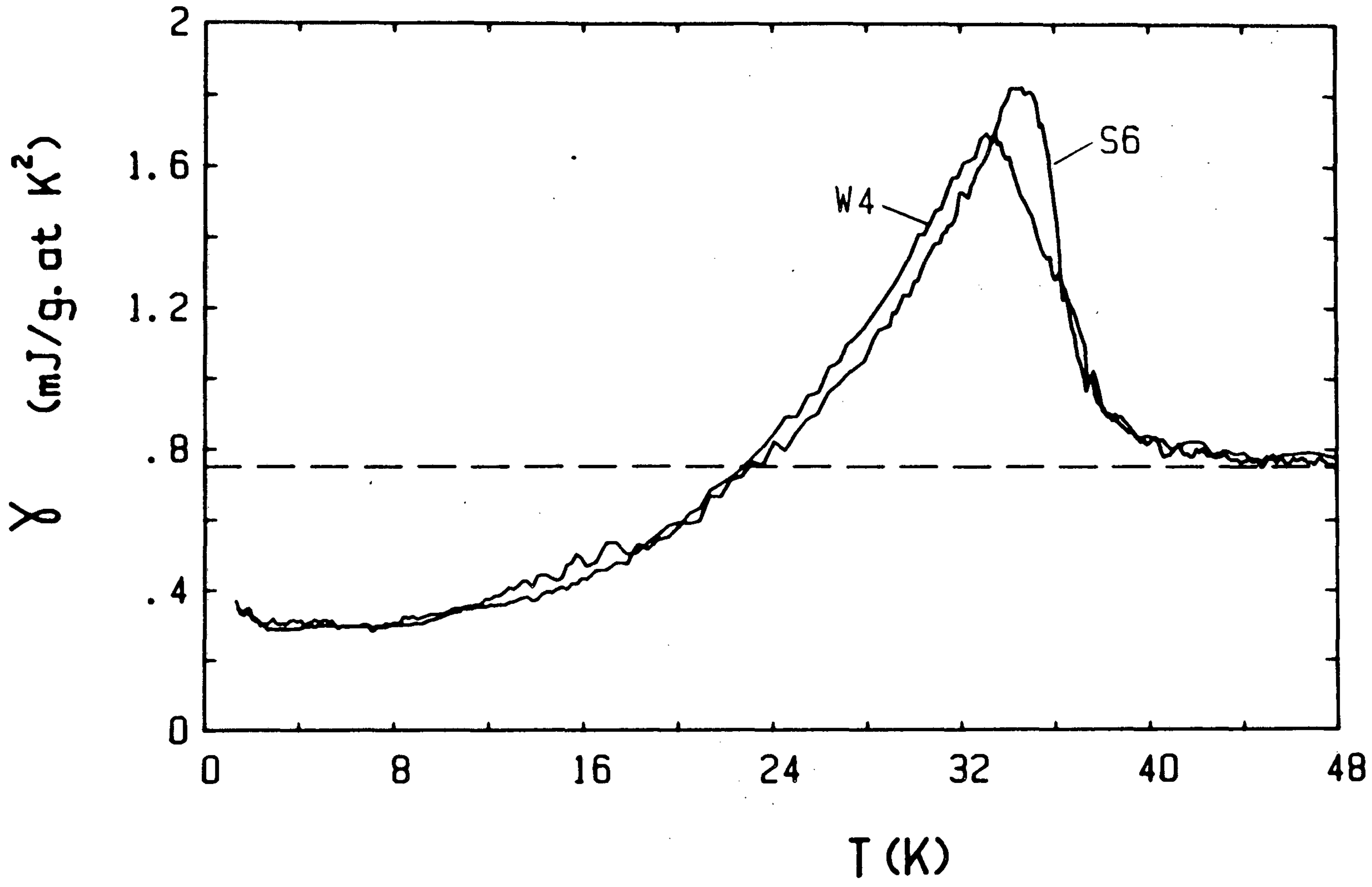
XBL 885-1548

Fig. 16



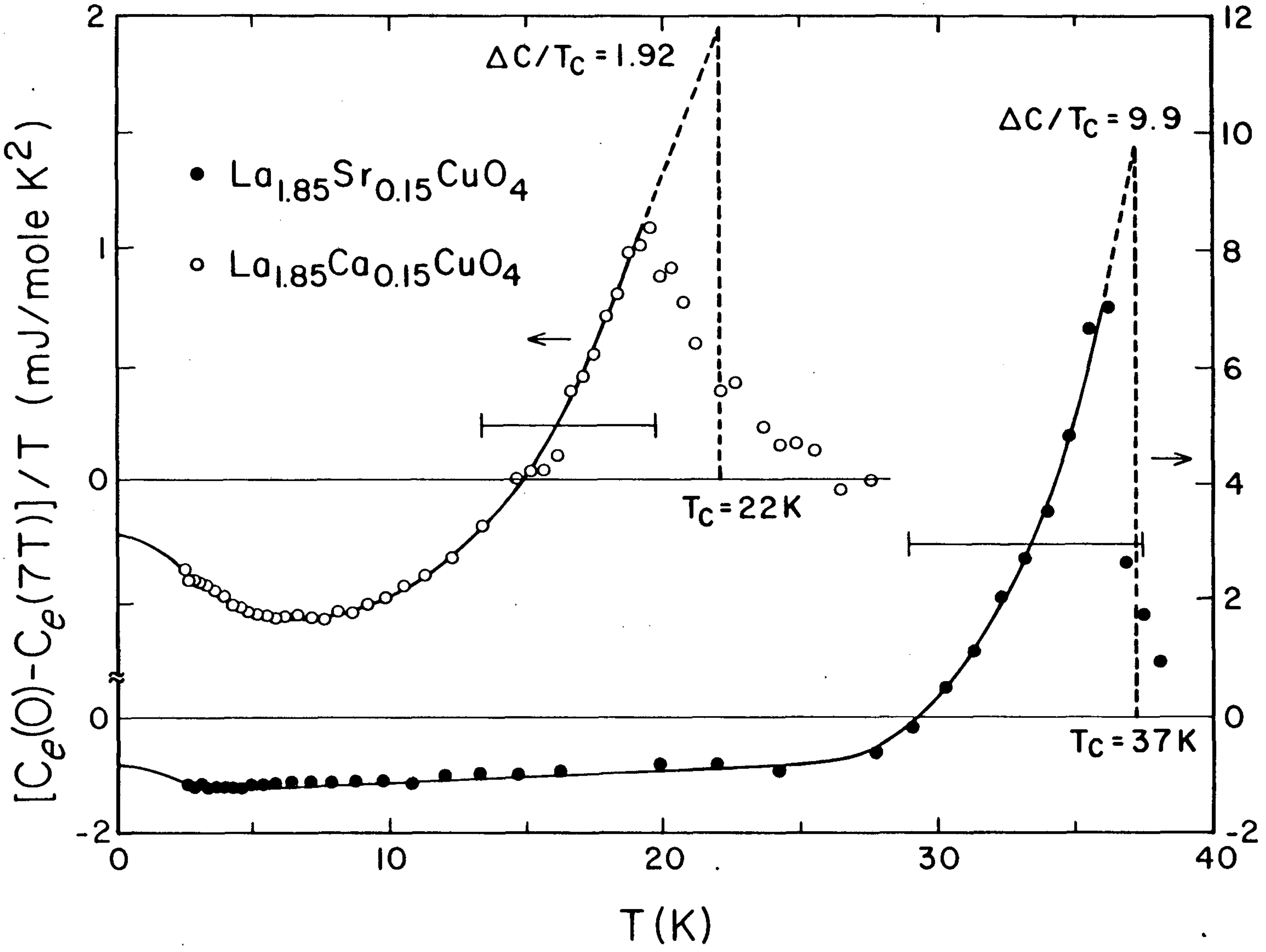
XBL 885-1817

Fig. 17



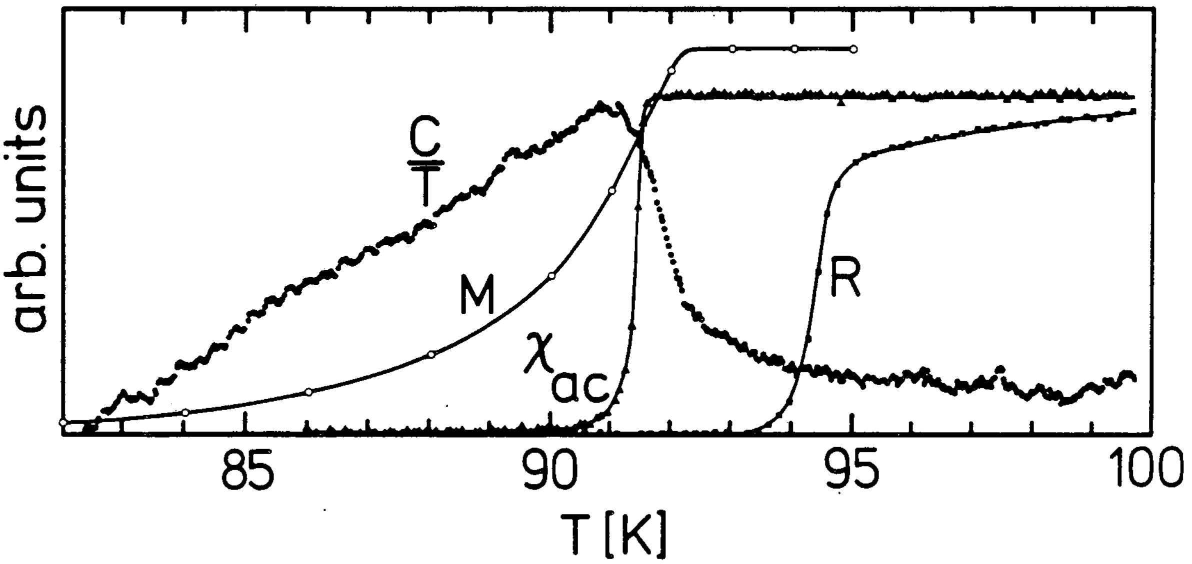
XBL 885-1769

Fig. 18



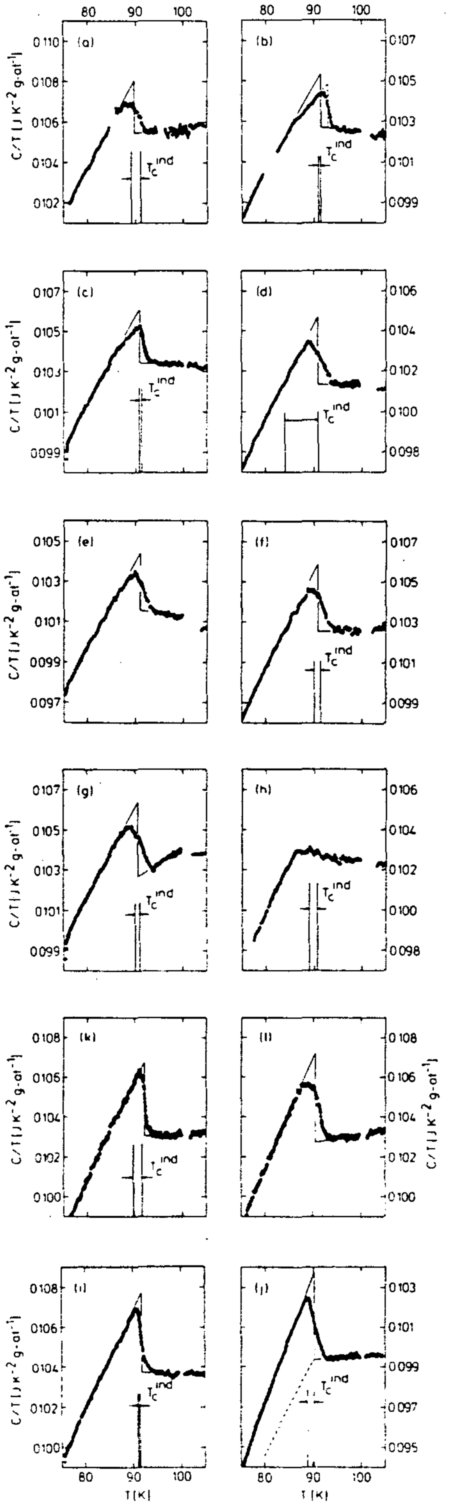
XBL 875-2027C

Fig. 19



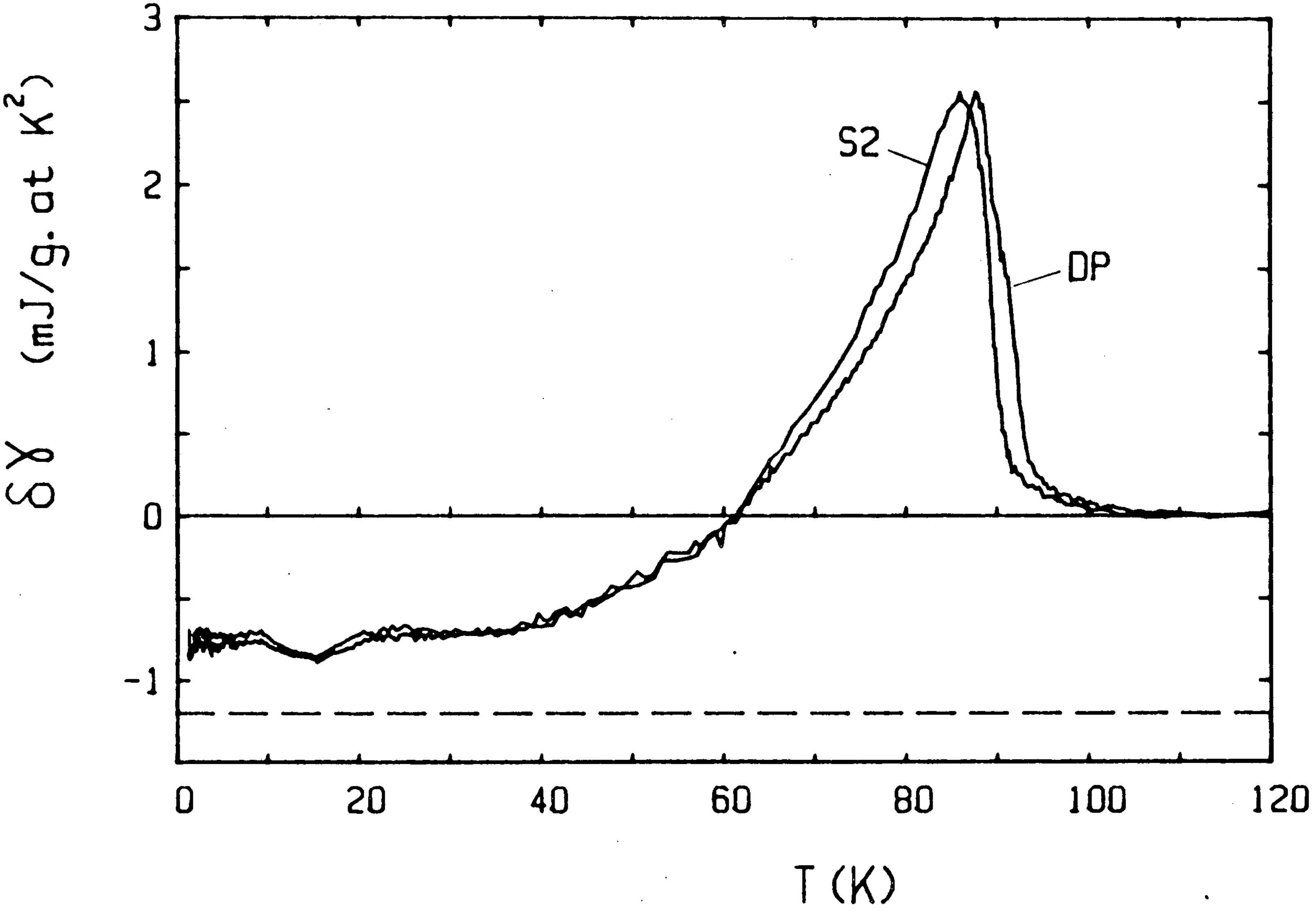
XBL 885-1765

Fig. 20



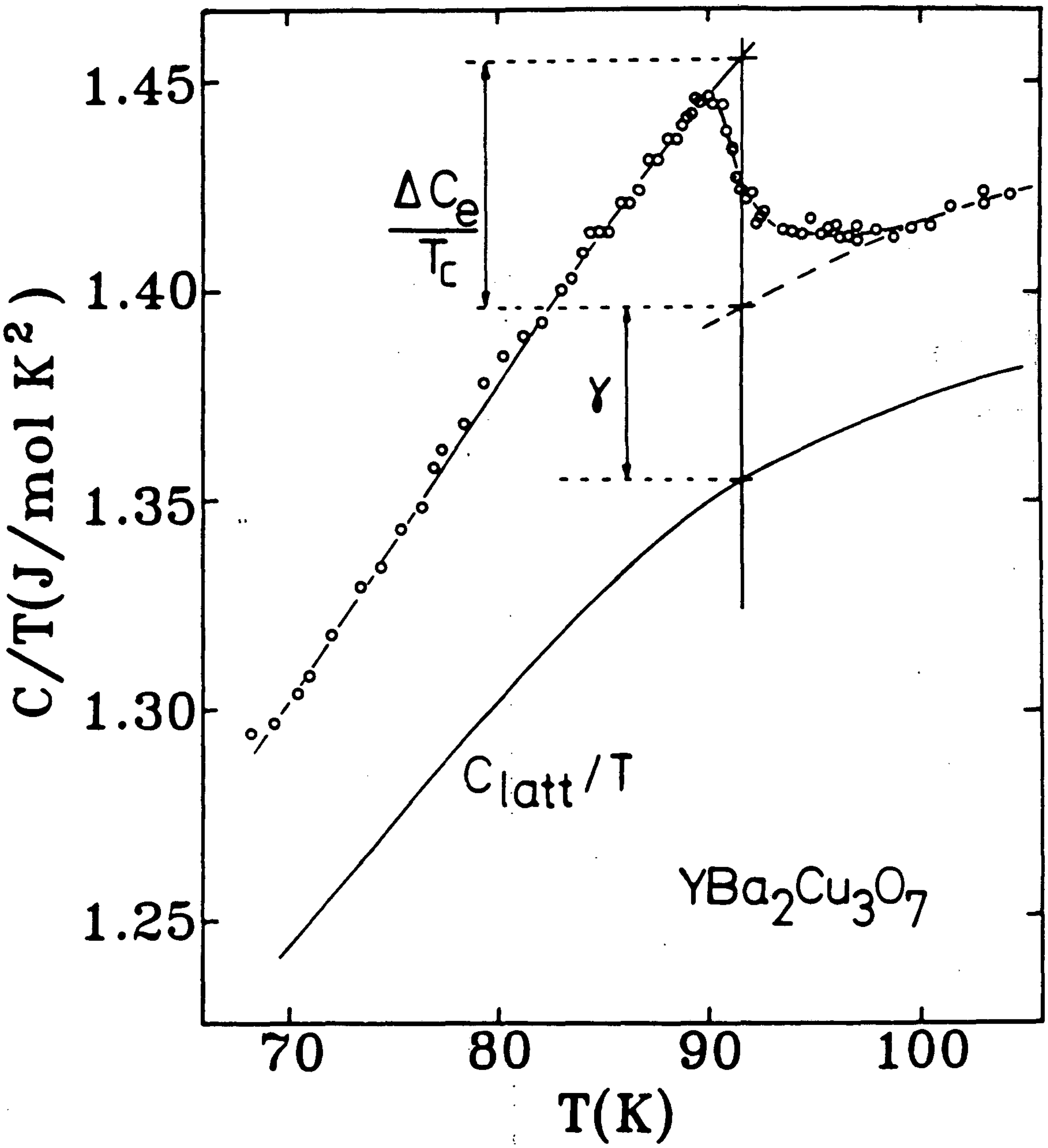
XBL 885-1766

Fig. 21



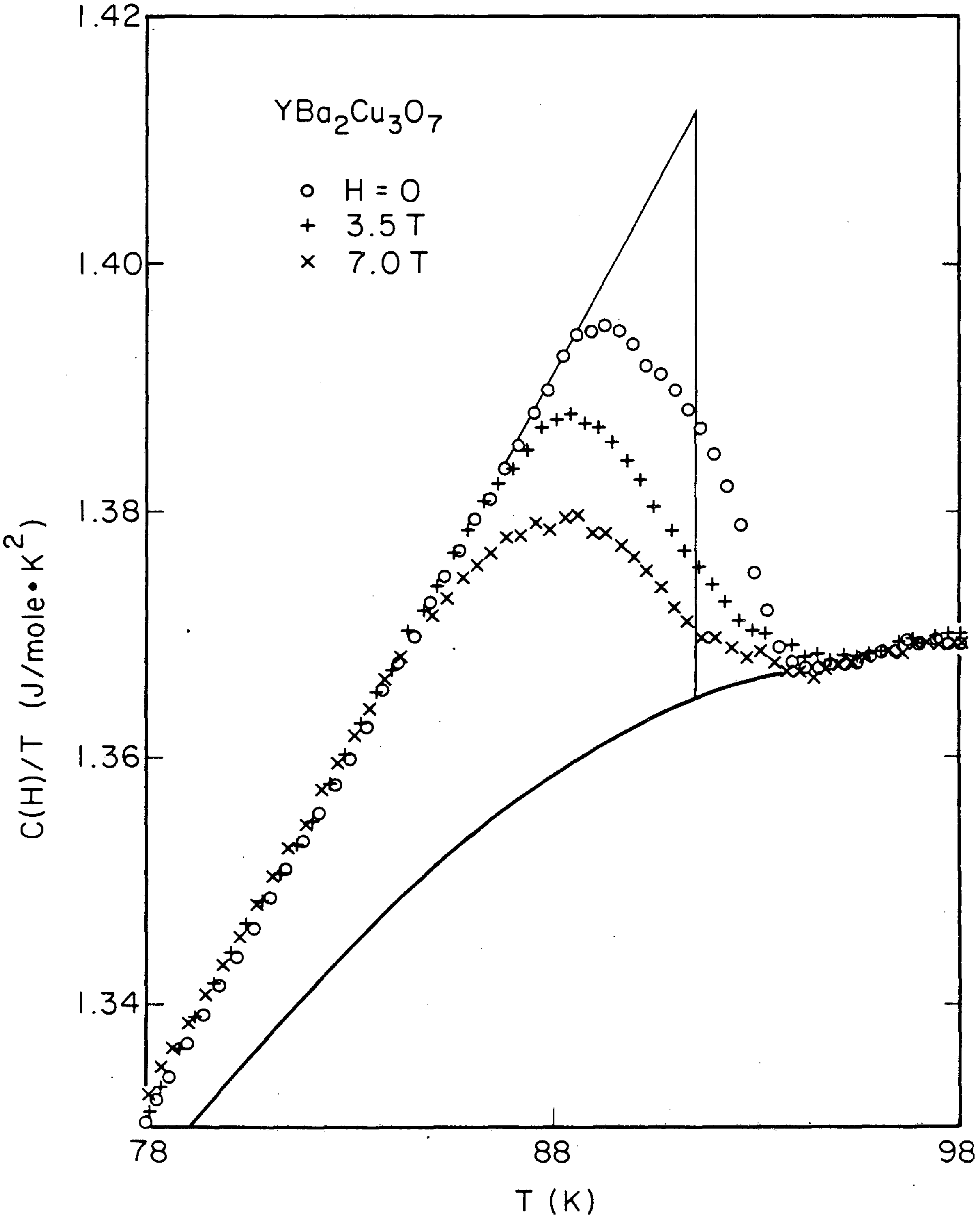
XBL 885-1770

Fig. 22



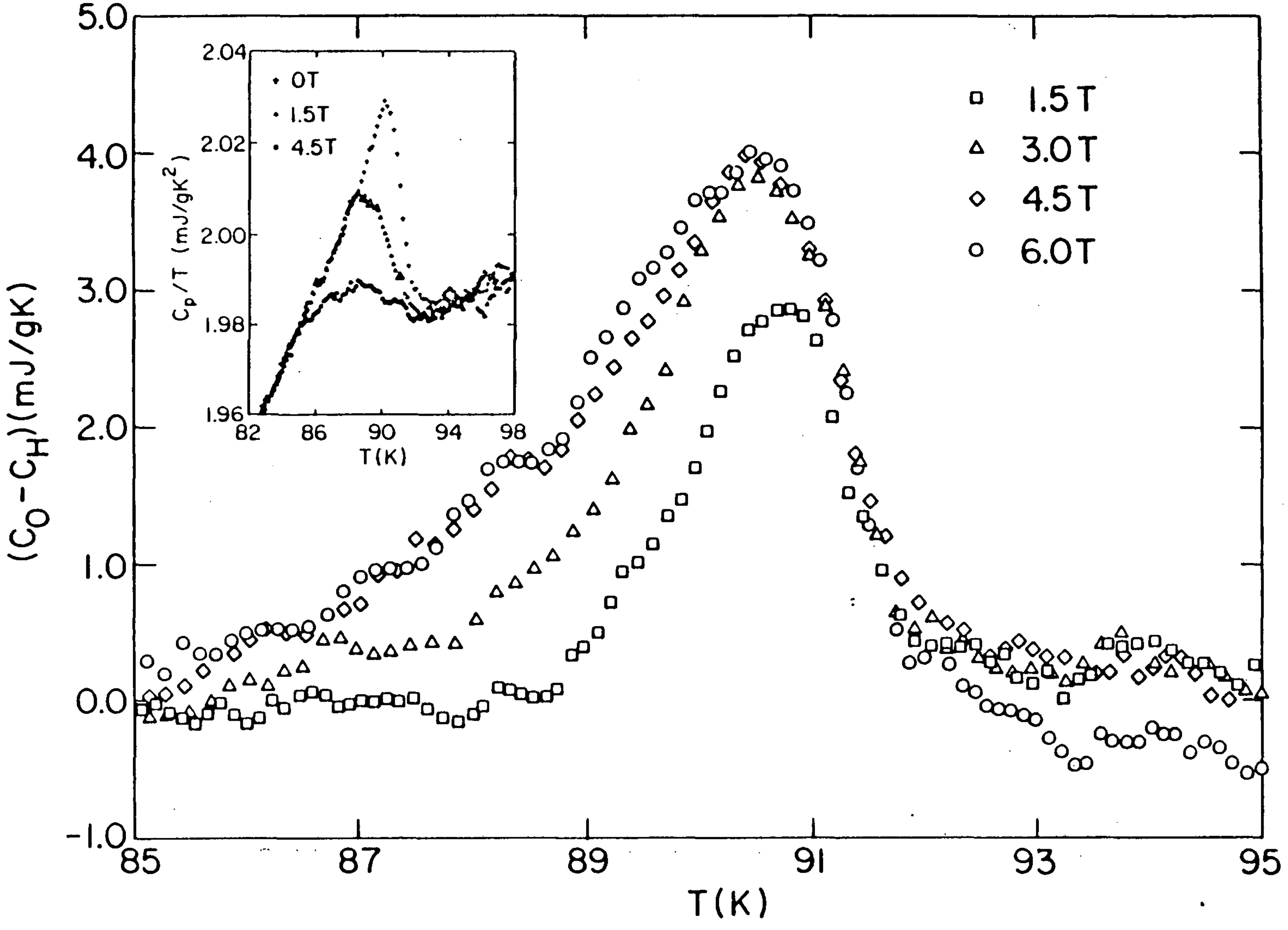
XBL 885-1764

Fig. 23



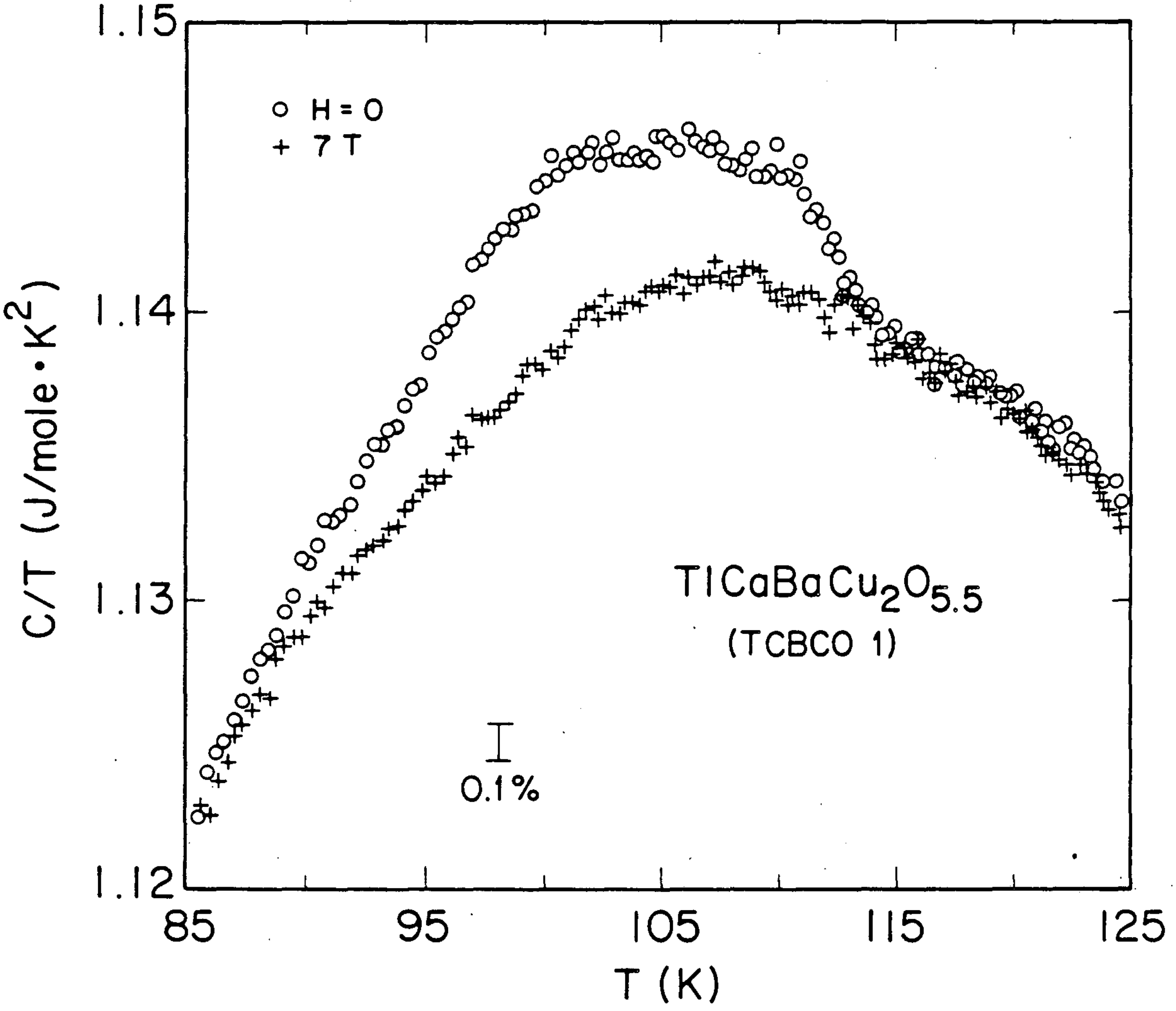
XBL 882-489 A

Fig. 24



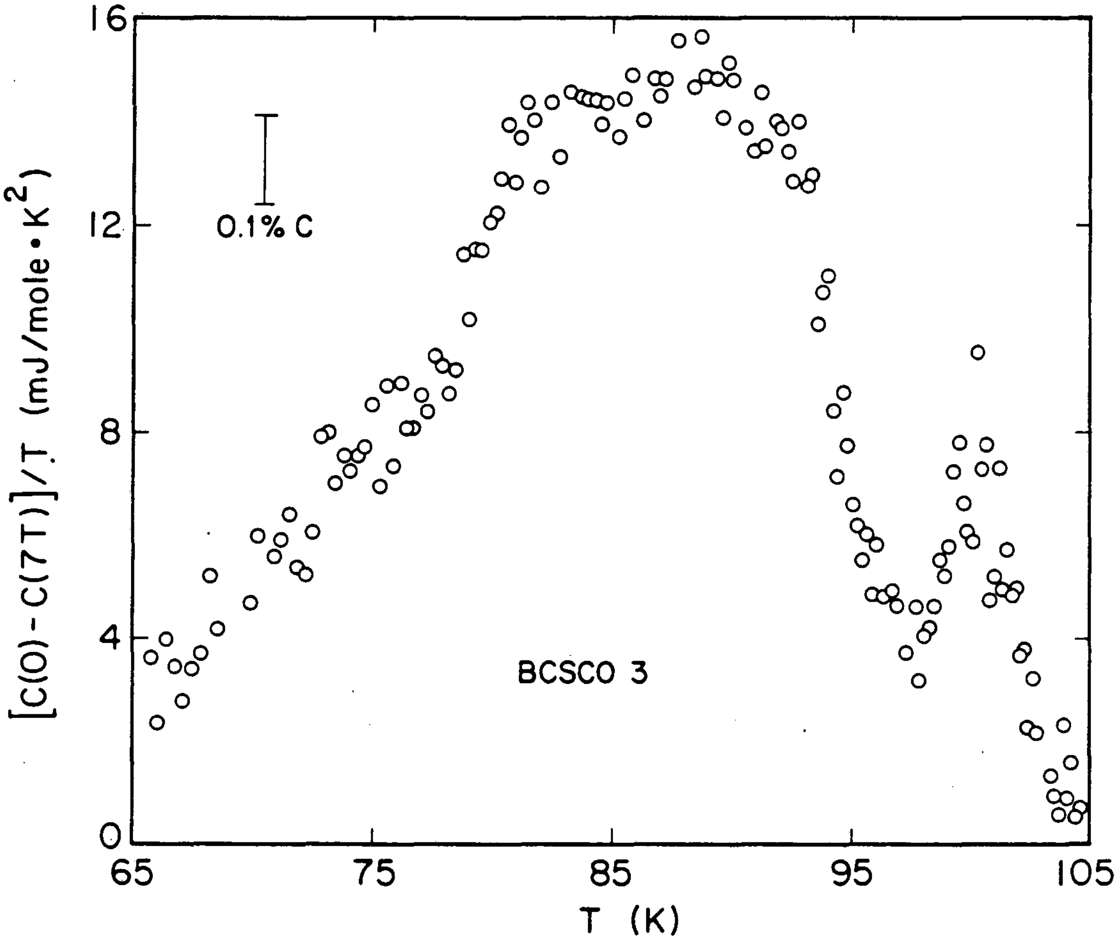
XBL 885-1757

Fig. 25



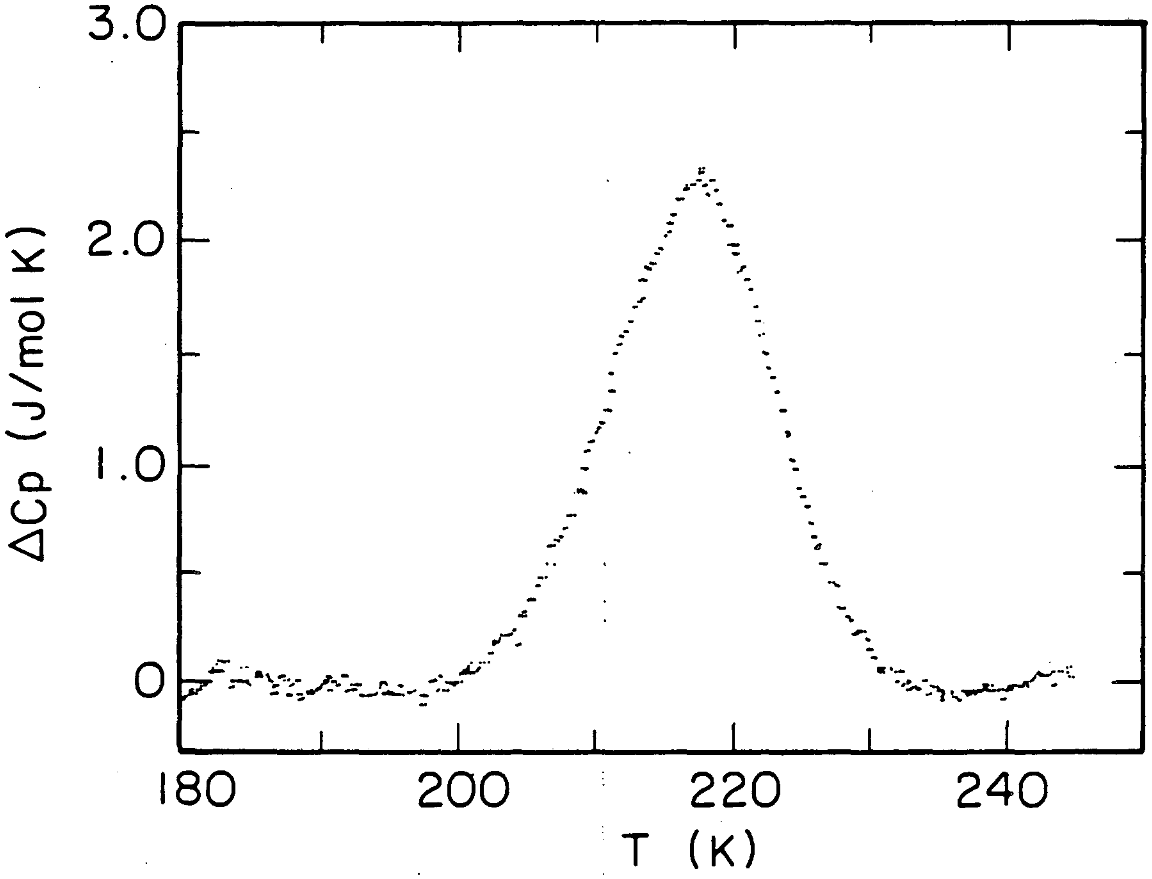
XBL 885-1544A

Fig. 26



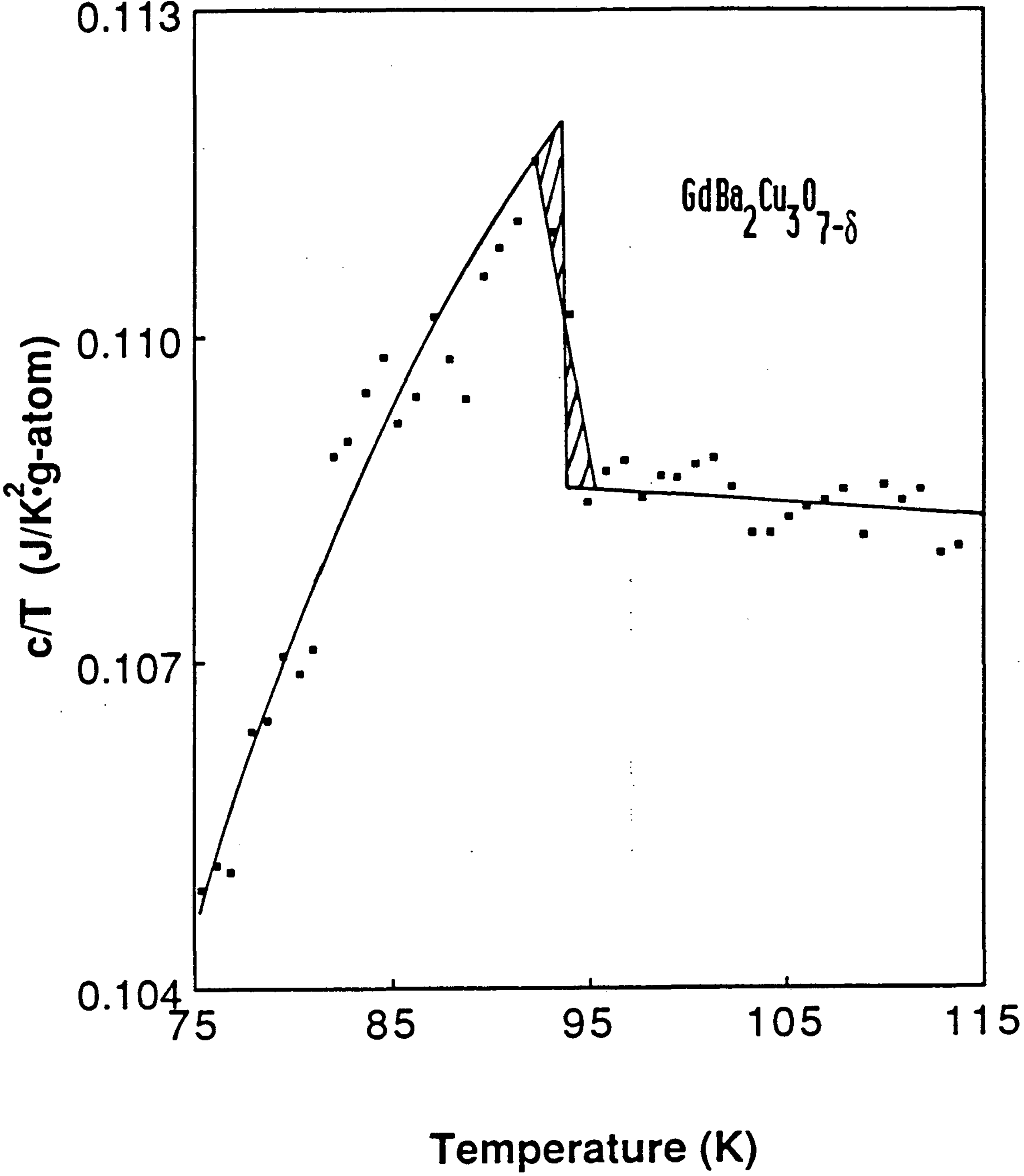
XBL 885-1541A

Fig. 27



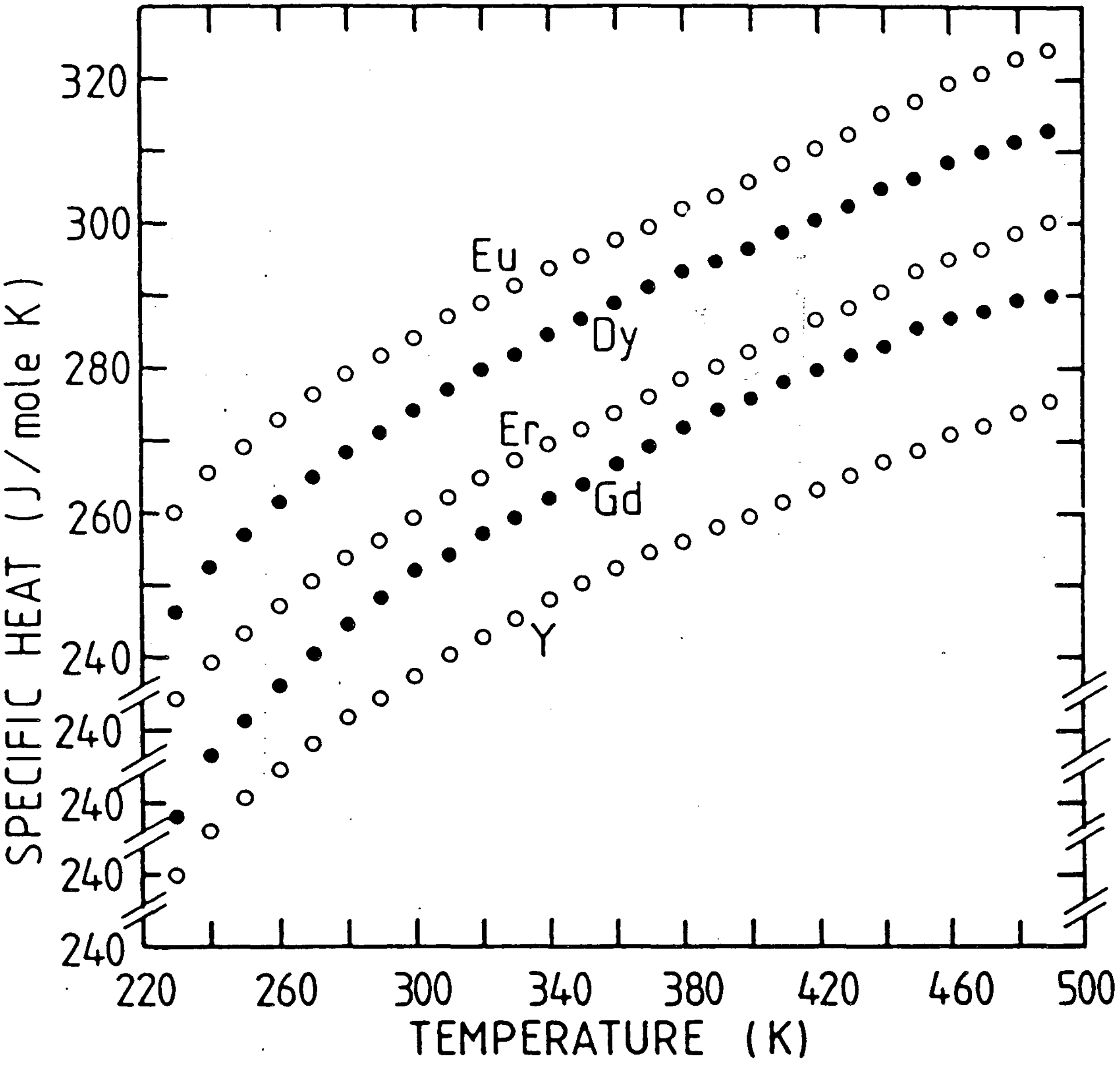
XBL 885-1768

Fig. 28



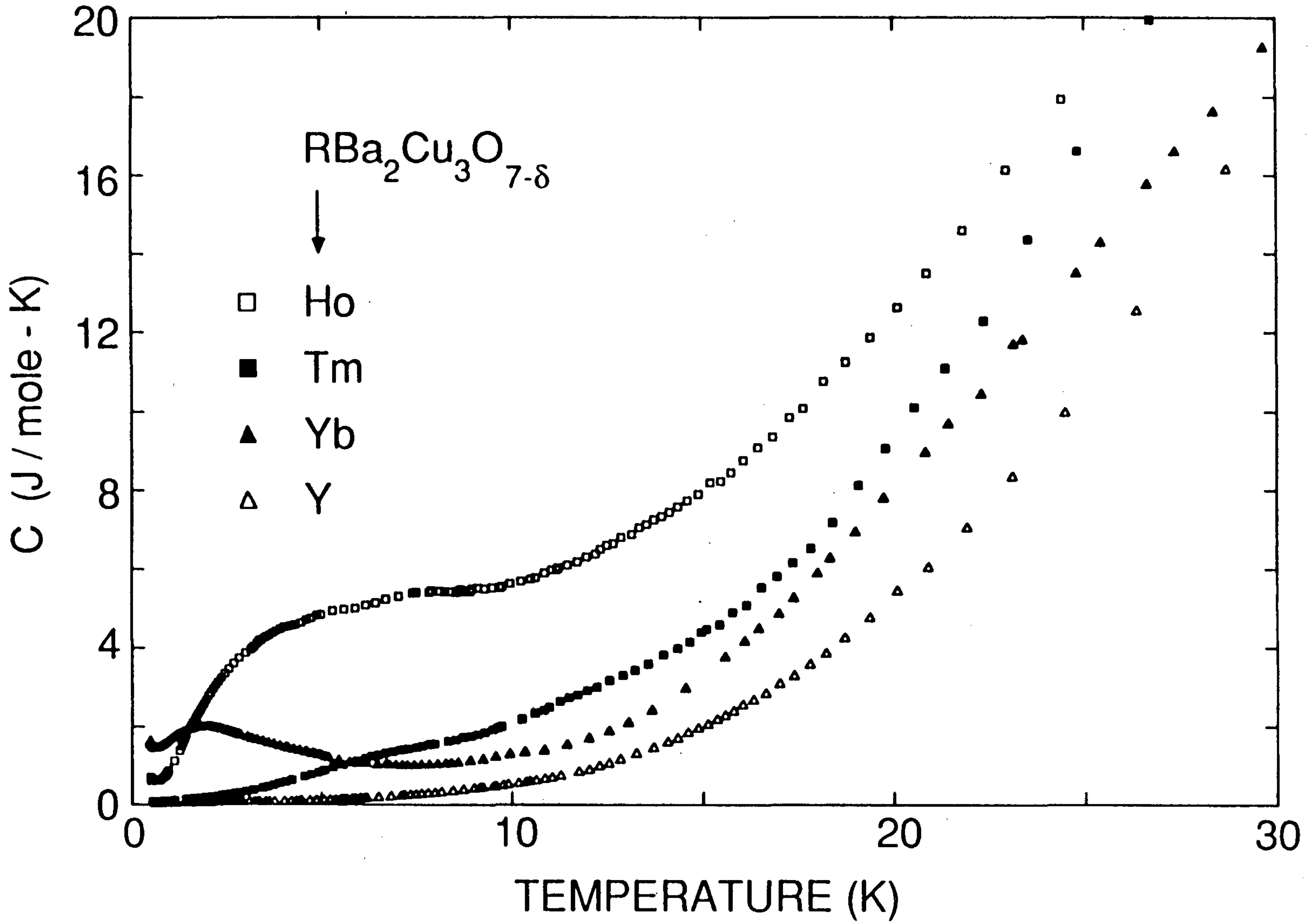
XBL 885-1758

Fig. 29



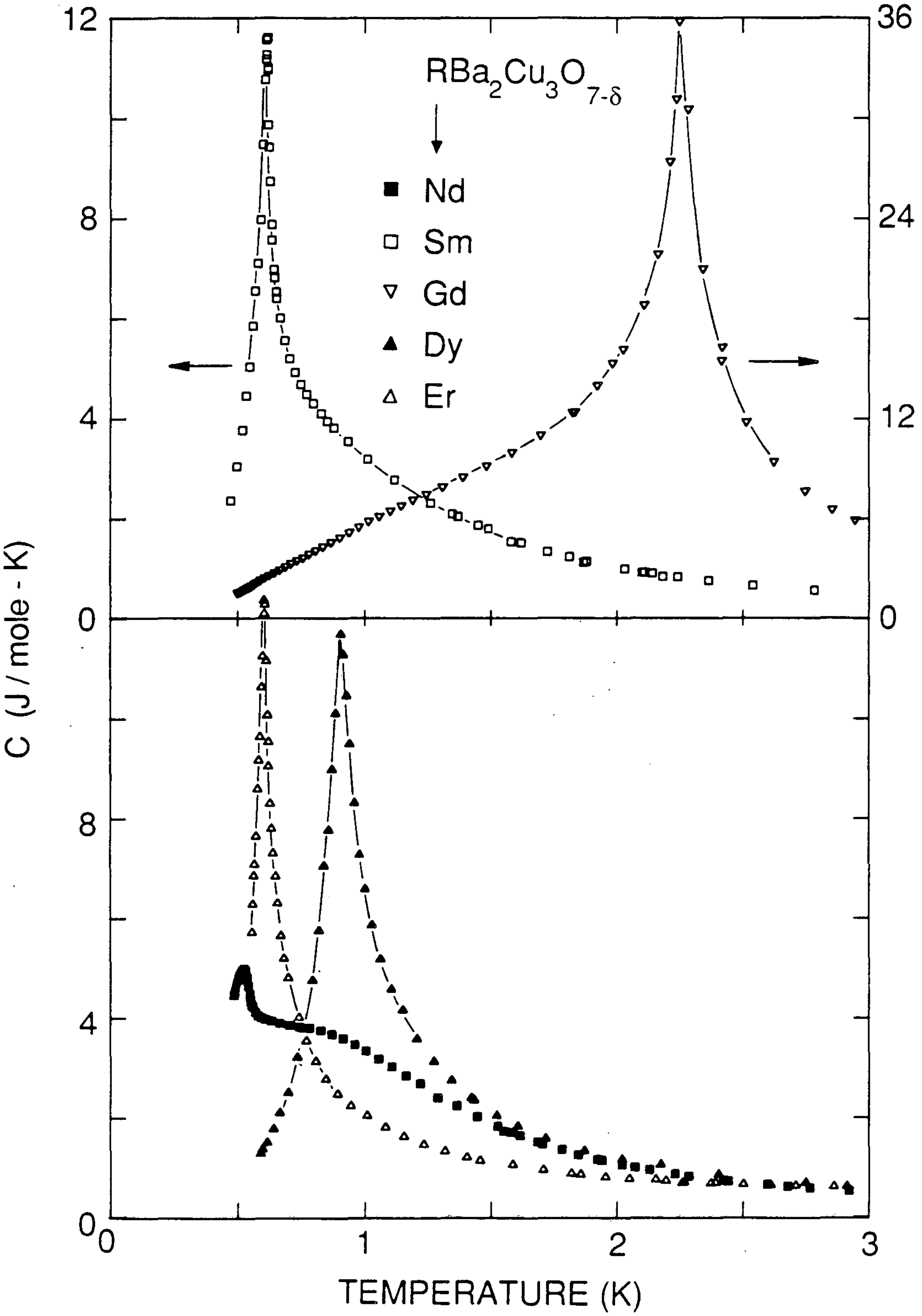
XBL 885-1762

Fig. 30



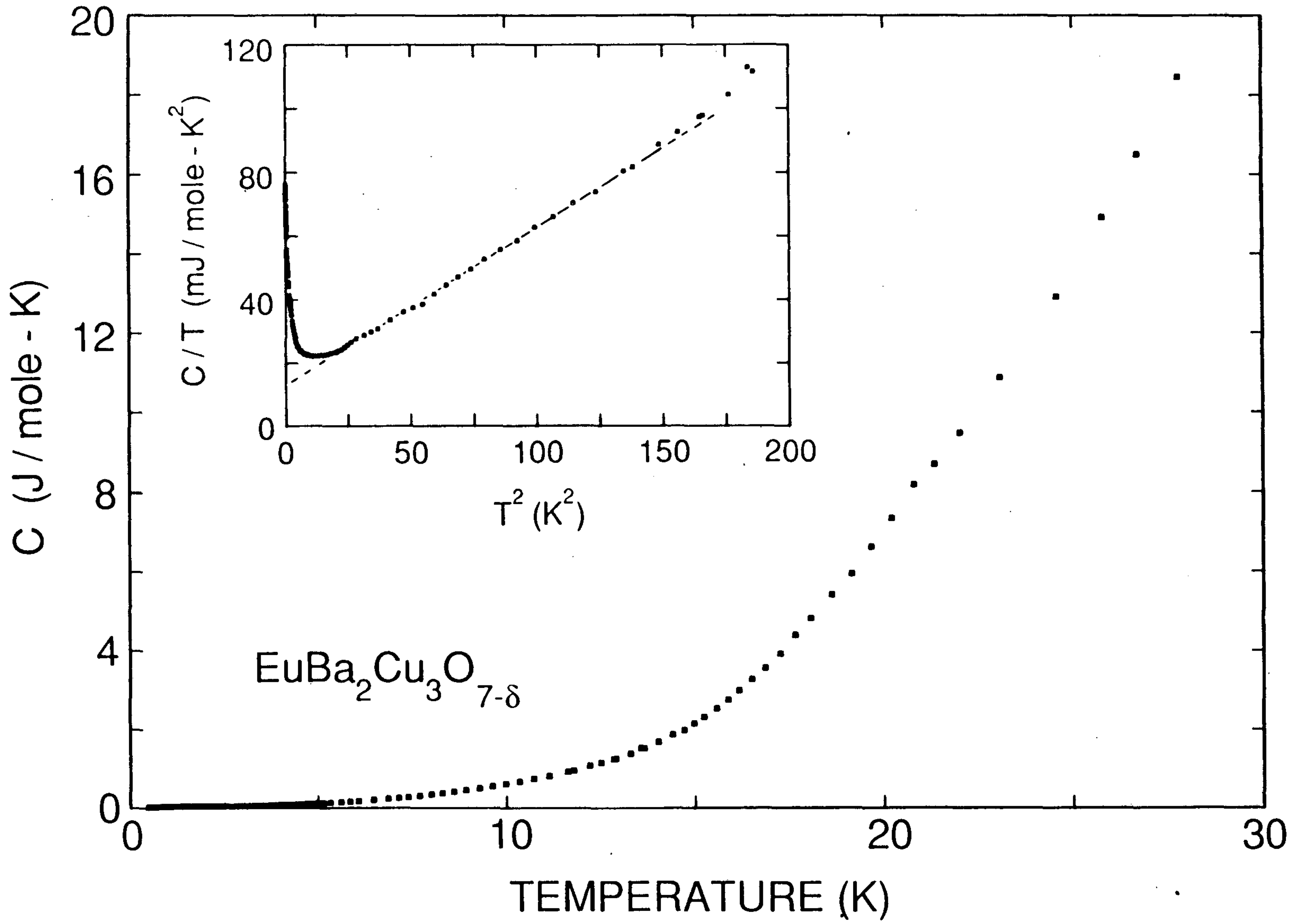
XBL 885-1772

Fig. 31



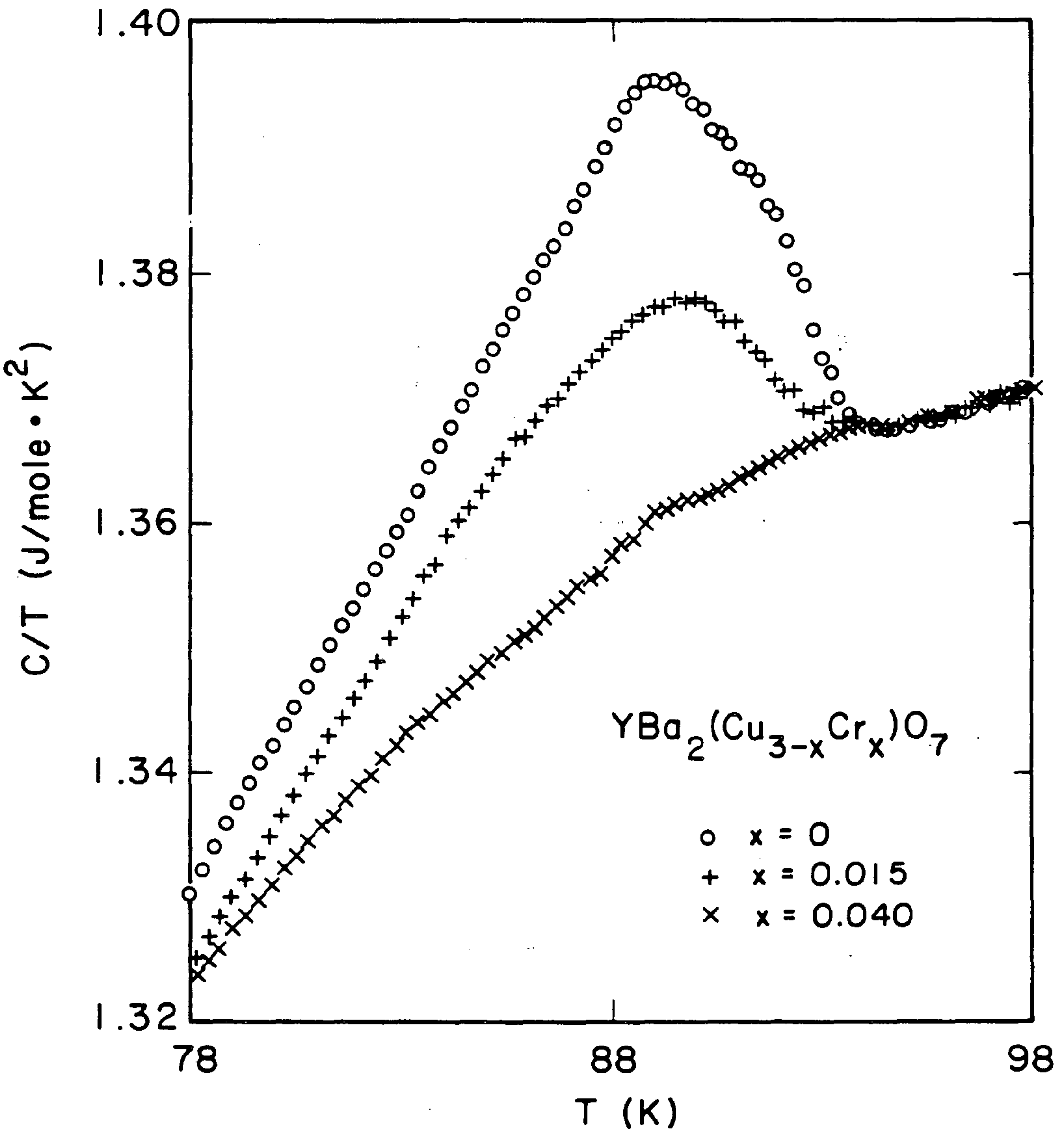
XBL 885-1774

Fig. 32



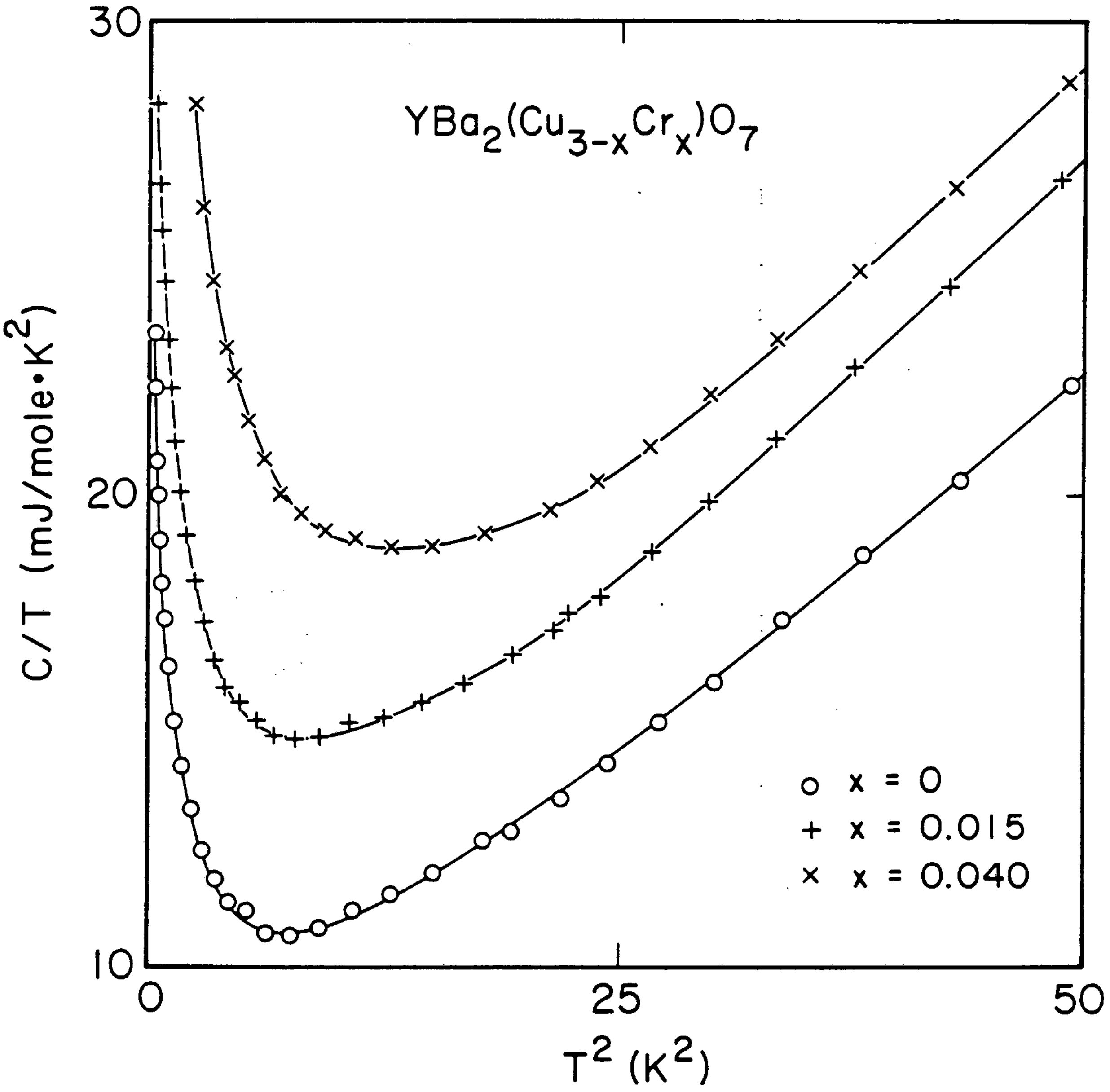
XBL 885-1773

Fig. 33



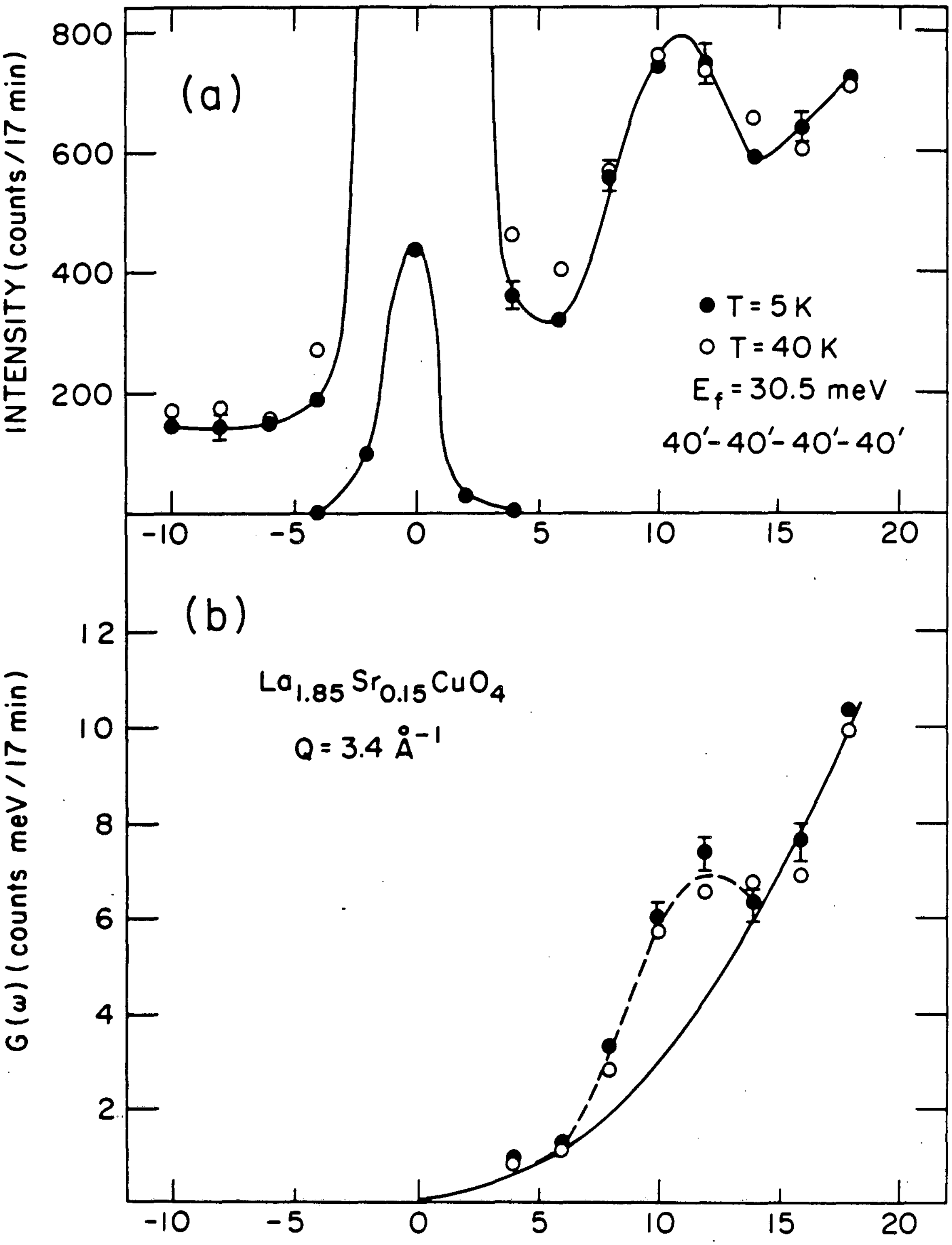
XBL 885-1819

Fig. 34



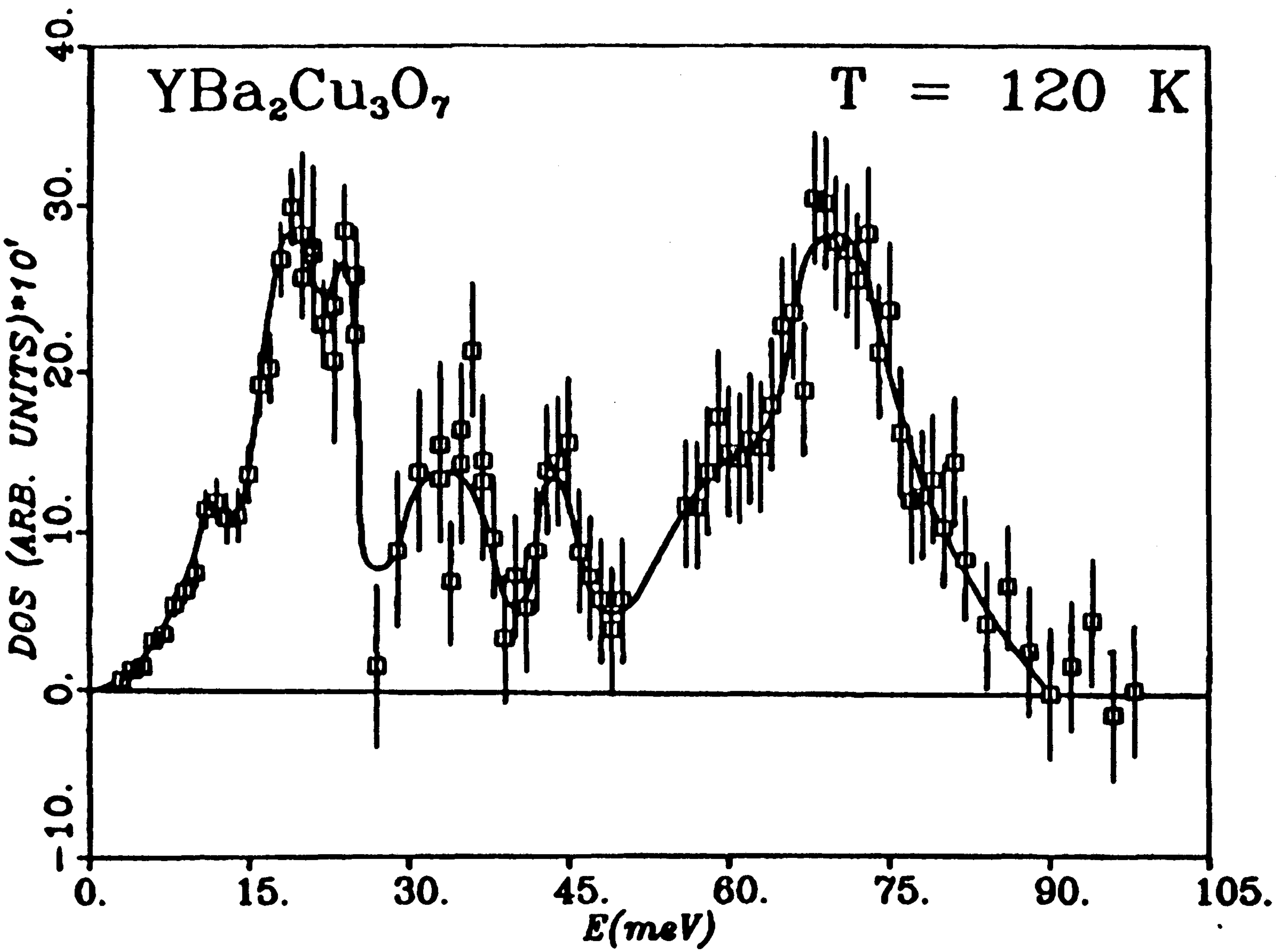
XBL 885-1820

Fig. 35



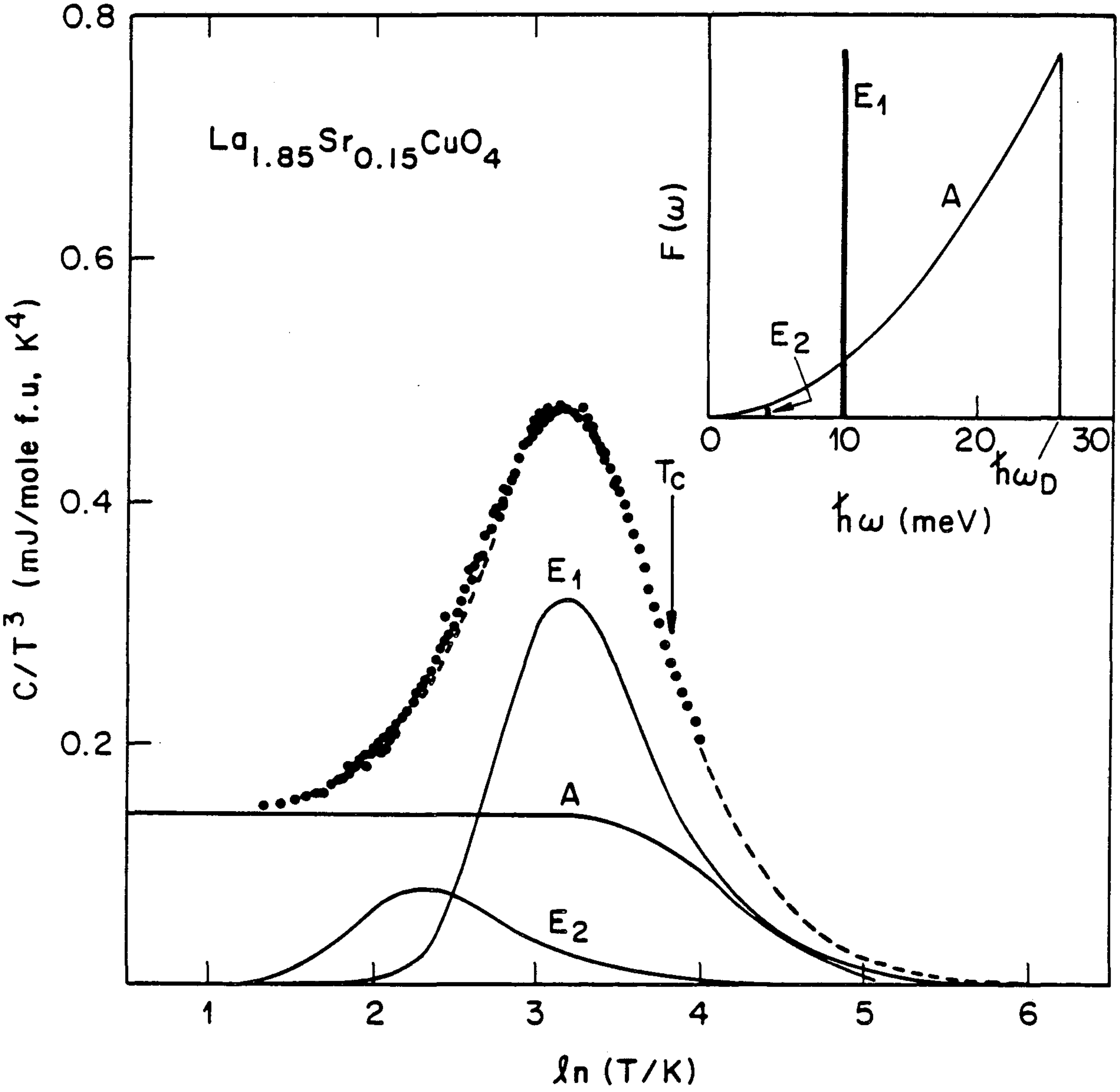
XBL 885-1775

Fig. 36



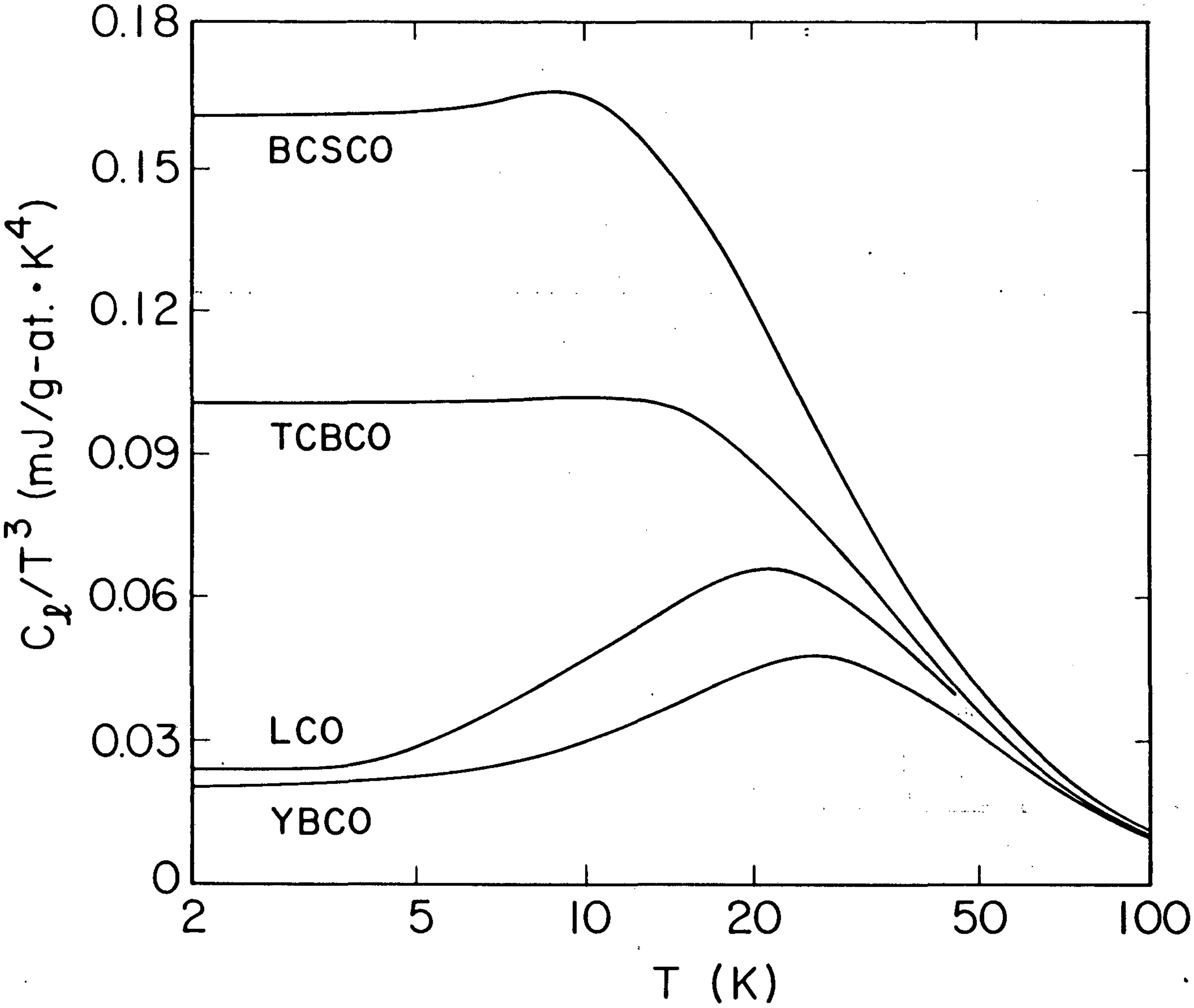
XBL 885-1759

Fig. 37



XBL 885-1776

Fig. 38



XBL 885-1818

Fig. 39

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