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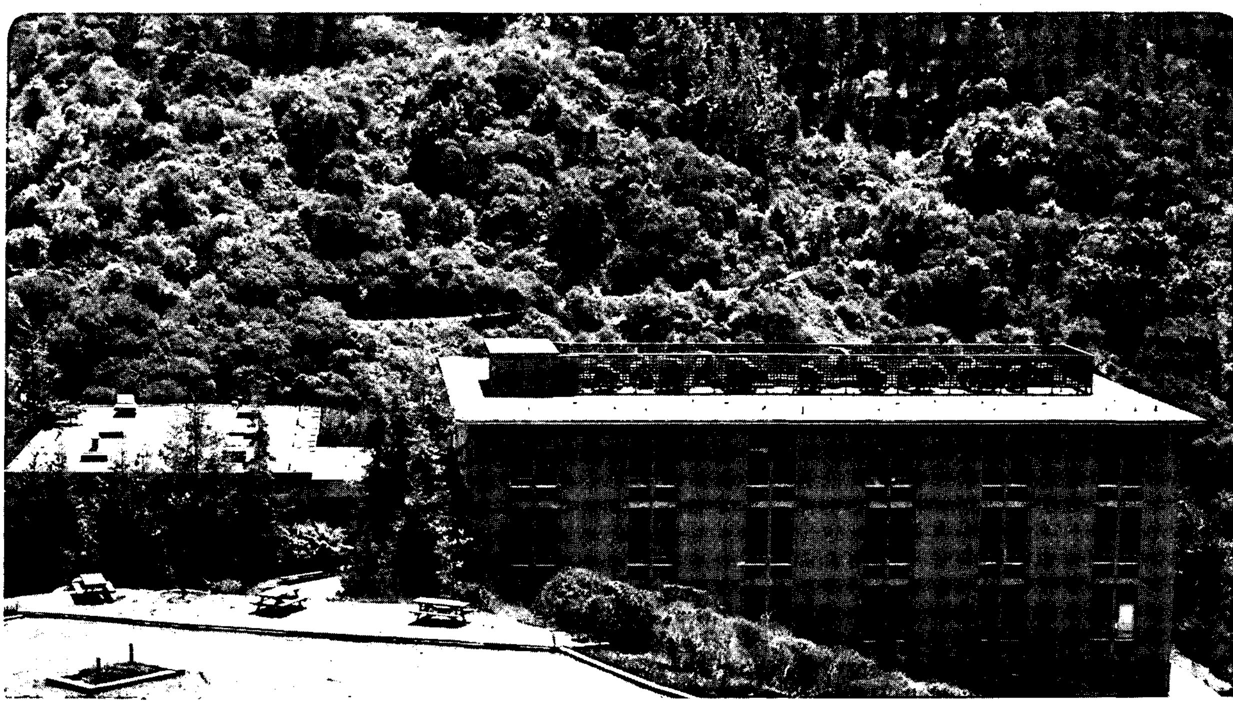

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LOW-TEMPERATURE SPECIFIC HEAT MEASUREMENTS ON METALS: APPLICATION TO HIGH-T_c SUPERCONDUCTORS

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LOW-TEMPERATURE SPECIFIC HEAT MEASUREMENTS ON METALS: APPLICATION TO HIGH-T_c SUPERCONDUCTORS

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The main features of the specific heats of normal metals and conventional superconductors, and the types of information that can be derived from specific heat data are summarized. The complications in extending this approach to high-T_c superconductors are outlined. It is shown that the properties of the superconducting state in $YBa_2Cu_3O_7$, and, more generally, probably in high-T_c materials, are correlated with a concentration of Cu^{2+} magnetic moments that can be derived from specific heat data. These correlations are of both practical and fundamental interest. They provide a criterion that should be useful in evaluating processing techniques for the production of high-quality bulk superconductors, and the values of parameters that are relevant to the nature of the superconducting state.

Introduction

Specific heat measurements can provide the values of a number of parameters related to, for example, the vibrational and electronic properties of metals. These parameters are of fundamental importance in predicting and understanding many properties of metals that are related to phase transitions, magnetism, superconductivity, etc. In principle more detailed information can often be obtained from "spectroscopic" types of studies that characterize the vibrational and electronic excitations more directly, but those methods are often limited in applicability by requirements of sample quality that are difficult to meet, and they are quite generally more difficult and time consuming. The advantages of the specific heat approach then are generality and simplicity. The disadvantages have to do with limitations on the detail in which information is provided, and also with the fact that (except when thermal equilibrium times are long) the specific heat sees all of the excitation modes, vibrational, magnetic, electronic, etc., and separation of the different contributions may be difficult. It is for the latter reason that many specific heat measurements are limited to temperatures below 20K or so -- in that region of temperature the different specific heat contributions have relatively simple temperature dependences and are therefore relatively amenable to analysis.

In the following sections the contributions to the specific heat (C), their dependences on temperature (T) and their relation to parameters characteristic of the associated excitation spectrum are summarized, first for normal metals, and then for "conventional" superconductors. Differences, some obvious and well established, others more speculative, between conventional superconductors and the recently discovered oxide, high-T_c

superconductors (HTSC) are introduced, and some information derived from specific heat measurements that is relevant to an understanding of HTSC -- on both the fundamental, theoretical and practical, materials-related levels -- is described.

Specific Heat of Normal Metals

The two contributions to the specific heat that are common to all metals are the lattice specific heat (C_ℓ) associated with the excitation of the vibrational modes of the lattice, or phonons, and the electronic specific heat (C_e) associated with excitation of the conduction electrons. [Additional subscripts n and s, will be used, when useful, to distinguish between the normal and superconducting states, and the value of the magnetic field (H) will occasionally be given in parentheses following the symbol for a component of the specific heat or a parameter derived from one.]

The Debye model provides a convenient, and frequently used, starting point for a discussion of the lattice specific heat. In that model the lattice is replaced by an elastic continuum with constant (frequency-independent) sound velocities. The number of normal modes in the frequency interval ν to $\nu + d\nu$ is then proportional to ν^2, with a proportionality constant determined by the sound velocities (or elastic constants). The specification of the frequency spectrum is completed by introducing a cut-off frequency (ν_{max}) that is chosen to limit the number of normal modes to the correct value (3x the number of atoms) and, therefore, to fix the high-temperature limit of C_ℓ at the classical value 3R. The Debye characteristic temperature, $\theta \equiv (h/k_B)\nu_{max}$, where h is Planck's constant and k_B is the Boltzmann constant, can be calculated from the elastic constants. It is the single parameter that appears in the Debye specific heat function, $C_D(T/\theta)$, and completely determines the temperature dependence of C_ℓ through the relation $C_\ell(T)=C_D(T/\theta)$. At low temperatures $C_D(T/\theta)$ can be expanded in odd powers of the temperature,

$$C_\ell = B_3T^3 + B_5T^5 + B_7T^7 + ... \qquad (1)$$

with, e.g., $B_3=(12/5)\pi^4R\theta^{-3}$. For $T<\theta/10$, the first term in Eq. 1 is an adequate approximation for most purposes. At higher temperatures the deviations from the T^3 temperature dependence, which are a direct consequence of the introduction of the cut-off frequency, are negative.

For a harmonic lattice, lattice-dynamic theory gives an expression of the same form as Eq. 1, with the relation between B_3 and the elastic constants unchanged. It is customary to define a 0-K Debye temperature, θ_0, by

$$B_3 \equiv (12/5)\pi^4R\theta_0^{-3}. \qquad (2)$$

However, the higher order terms in Eq. 1 now reflect the frequency dependence of the sound velocities (phonon dispersion) and the associated structure in the frequency spectrum. B_5 is almost always positive, and deviations from a T^3 dependence become significant at temperatures as low as $\theta_0/100$. The deviations of C_ℓ from the Debye function are often represented by an effective, temperature-dependent, Debye temperature (θ_T) that is defined by equating the measured C to $C_D(T/\theta_T)$. The deviations from the Debye function are usually substantial (1). In most cases, they are the normal consequence of ordinary phonon dispersion, although other more exotic effects are often invoked. C_ℓ is independent of magnetic field, and is unchanged in the transition between the normal and superconducting states.

The conduction electrons are governed by Fermi-Dirac statistics which permit only two electrons, with opposite spin directions, in any energy level (state). At the absolute zero of temperature the states are filled to the Fermi energy (E_F) which is often represented by the corresponding characteristic temperature, the Fermi temperature (T_F), $T_F = E_F/k_B$. Since T_F is typically of the order of 10^5K, only a relatively small number of levels near E_F are accessible to thermally excited electrons at moderate or low temperatures. The normal-state electronic specific heat is proportional to T, and the coefficient of proportionality (γ) measures the "density of electronic states", the number of states per unit of energy, at E_F [$N(E_F)$].

$$C_{en} = \gamma T = (1/3)\pi^2 k_B^2 N(E_F) T. \tag{3}$$

$N(E_F)$ is determined in part by the periodic electric field in the lattice, and in part by electron-electron interactions. Current theory and computational techniques permit accurate calculations of the effect of the lattice, and give $N_{bs}(E_F)$, the "bare" or band-structure density of states. The most important electron-electron interaction is indirect, via the lattice: the negative electric charge on one electron produces a distortion of the positively charged lattice (or excites a lattice vibration or phonon) which in turn interacts with another electron. The strength of this indirect electron-electron interaction, usually referred to as the "electron-phonon" interaction, is represented by λ, and modifies the band structure density of states by the factor $1+\lambda$. Thus, γ is composed of band-structure and electron-phonon enhancement components: $\gamma_{bs} = (1/3)\pi^2 k_B^2 N_{bs}(E_F)$ and $\gamma - \gamma_{bs} = \lambda(1/3)\pi^2 k_B^2 N(E_F)$.

For normal metals, measurement of the low-temperature specific heat, and its analysis into the components C_ℓ and C_e, gives the values of several important parameters. Perhaps the most important is $N(E_F)$ which has a fundamental role in determining many of the thermodynamic properties of metals,. including the critical temperature for superconductivity (T_c), a number of other phase transition temperatures and certain magnetic properties. In combination with band structure calculations, it also determines λ, which is also important in determining the properties of superconductors. The coefficients in Eq. 1 give information about the phonon spectrum which contributes to the determination of many of the same properties. Although that information is not very detailed, because C_ℓ is determined by an integration over the phonon spectrum, the single parameter θ_0 is often by itself useful.

"Conventional" Superconductors

The experimental discovery of the isotope effect, the dependence of T_c on isotopic mass (M),

$$T_c \propto M^{\alpha}, \tag{4}$$

with $\alpha \approx 0.5$ in most cases, provided the necessary clue to the understanding of the superconducting state. It showed that lattice vibrations, for which $\nu \propto M^{-12}$, were important, and led to the BCS theory of superconductivity. In that theory it is the electron-phonon interaction, the same interaction that gives the phonon enhancement of the normal-state electronic specific heat by the factor $1+\lambda$, that leads to the pairing of the electrons (with zero spin and zero angular momentum) that is fundamental to the nature of the superconducting state. The theory has been worked out in considerable detail for the "weak-coupling" case, $\lambda < 1$, but strong coupling effects are known and understood at least qualitatively. It is generally believed that almost all superconductors are to be understood on the basis of the phonon-mediated or BCS mechanism, the possible exceptions being heavy-fermion and high-T_c superconductors.

The BCS expression for T_c is

$$T_c \approx \theta e^{-1/NV} \tag{5}$$

where N and V are parameters closely related to $N(E_F)$ and λ. At T_c a gap (2Δ) appears in the energy levels of the conduction electrons at E_F. The gap increases with decreasing temperature and, at T=0 it is $2\Delta_0 = 3.53k_BT_c$ in the weak coupling limit, but the ratio $2\Delta_0/k_BT_c$ is larger in the case of strong coupling.

Figure 1 shows the electronic specific heat normalized to its normal-state value ($C_{en} = \gamma T$), and plotted against T/T_c for a BCS, weak-coupling superconductor. For all superconductors at $T < T_c$, the free energy is increased by the application of a magnetic field, and there is a critical magnetic field (H_{c2}), which is a function of the temperature, above which the normal state is thermodynamically stable (and realized in practice). In most cases the critical fields of conventional superconductors are small enough, of the order of 10^{-2} or 10^{-1}T, that the normal state can be retained to arbitrarily low temperatures and γ can be determined without ambiguity. The lattice specific heat is often only a small part of the total, and in most cases it can be determined by analysis of the normal-state data and subtracted from the total superconducting-state specific heat to obtain the electronic superconducting-state specific heat (C_{es}).

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

Because the specific heat is a true measure of bulk properties, specific heat measurements have played an important role in distinguishing bulk superconductivity from, e.g., filamentary superconductivity associated with impurity phases at grain boundaries. Resistivity measurements, and even magnetic susceptibility measurements, do not establish the existence of superconductivity throughout a sample. For a conventional superconductor an incomplete transition to the superconducting state would be indicated by the appearance of a linear term in the zero-field specific heat and a reduction in $\Delta C(T_c)$.

HIGH T_C SUPERCONDUCTORS

The intense interest in high-T_c superconductors (HTSC) stems from the confirmation, late in 1986, of the existence of superconductivity with $T_c \approx 30K$ in the Ba-La-Cu-O system. That discovery followed the report by Bednorz and Müller (3) of a drop in the electrical resistivity and their suggestion that it might be indicative of superconductivity. The earlier discovery of superconductivity at $T_c \approx 13K$ in $BaPb_{1-x}Bi_xO_3$ by Sleight et al. (4) had provided the first indication that these perovskite oxides might be of interest in connection with the search for high T_c's, but superconductivity, below 1K, had been predicted by Cohen (5) and discovered by Schooley et al. (6) in one compound of this class, $SrTiO_3$, even earlier. The work on the Ba-La-Cu-O system was quickly followed by the discovery of superconductivity in other alkaline earth-doped La_2CuO_4 samples (7, 8, 9) and, in March 1987, by the discovery of superconductivity in the Y-Ba-Cu-O system above liquid nitrogen temperatures, with $T_c \approx 90K$, by Wu et al. (10). Within another year superconductivity had been discovered in the Bi-Sr-Ca-Cu-O (11,12) and Tl-Ba-Ca-Cu-O (13, 14) systems with T_c's ranging from 80 to 125K. The most widely studied HTSC is $YBa_2Cu_3O_7$ (YBCO) with $T_c \approx 90K$, and it will be used to illustrate the features of HTSC in the following descriptions of specific heat measurements and their interpretation. Its properties can be taken as typical of those of the others for the purposes of this article.

The HTSC are highly anisotropic materials, characterized in most cases by CuO sheets in which each Cu atom is covalently bonded to four O atoms in the sheet, and, depending on the particularl structure, to other O atoms in the adjacent sheets. They differ significantly from conventional superconductors in the magnitude of the coherence length (ξ), the spatial distance over which the transition from the normal state to the superconducting state can occur. For conventional superconductors, $\xi \sim 10^{-1}$-1μ; for HTSC, $\xi \approx 10^{-3}$-$10^{-2}\mu$. The short coherence length, of the order of the lattice parameters in many cases, makes the properties HTSC very sensitive to defects.

The difference in values of ξ between conventional superconductors and HTSC arises from known differences in parameters such as E_F and carrier density; it is not an indication of a fundamentally different kind of superconductivity. However, the nature of HTSC, their crystal structure, the nature of the chemical bonding, the very high T_c's themselves, suggested that the origin of the superconductivity might be different from that of conventional, or BCS, superconductors in which the electrons are coupled by their interaction with the phonons. The discovery that the values of α, the exponent of M in the isotope effect, Eq. 4, are very small supported the possibility of the mechanism being different.

Specific heat measurements were among the earliest investigations undertaken on HTSC. A primary objective was to determine whether the superconductivity detected in electrical resistivity and magnetic susceptibility measurements was a bulk effect. Beyond that, the measurement of various parameters characterizing the superconducting state that might give information about the mechanism or the strength of the coupling were obvious goals. (If the origin of the superconductivity was not the electron-phonon interaction, the specific heat could be qualitatively different from that of a BCS superconductor, but not necessarily.)

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

For YBCO there can be inhomogeneities associated with oxygen stoichiometry and with the ordering of the O atoms. Other HTSC, e.g., those based on La_2CuO_4 with La partially replaced with Ca, Sr or Ba, are solid solutions. The inclusion of impurity phases is probably also a contributor to the breadth. The effect of small-scale defects of all kinds can be expected to be enhanced in HTSC relative to that in conventional superconductors because ξ is smaller and is comparable to the lattice parameters. Furthermore, there is the expectation, also based on the small value of ξ, that fluctuation effects should be important in determining the shape of the specific heat anomaly at T_c. Finally, the magnitude of the anomaly in C at T_c is strongly sample dependent. Thus, there are a number of unresolved issues bearing on the determination of the discontinuity in specific heat at T_c.

Figure 2 also shows the low-temperature "upturn" in C/T that is characteristic of virtually all samples of HTSC, at least those that have been studied below 1K. It is associated with electronic magnetic moments that order below 1K as shown by its magnetic field dependence. After appropriate correction for the upturn there is still a non-zero intercept of C/T at $T=0$. This "linear term", $\gamma(0)$, has attracted much attention. It was recognized very early (15) that it could be simply a manifestation of an incomplete transition to the superconducting state. However, independently of, and more or less simultaneously with, its experimental discovery, a linear term was predicted theoretically (16) as one of the consequences of the resonant valence bond (RVB) theory. In the RVB model the excitations from the superconducting ground state are qualitatively different from those in a conventional superconductor, and so is the thermodynamics. The development of an understanding of the origin of $\gamma(0)$ has, for these reasons, been a major goal of specific heat measurements on HTSC.

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

Analysis of Specific Heat Data for High-T_c Superconductors

In addition to the lattice and electronic contributions, there are two others that are relevant to a discussion of the specific heats of HTSC. As shown by its magnetic field dependence, the low-temperature upturn in C/T, which is apparent in Fig. 2, is associated with Cu^{2+} magnetic moments. Their contribution to C will be denoted C_m. In zero applied field, they order below 1K, and the upturn is the high-temperature side of a Schottky-like anomaly which can be approximated by the general expression

$$C_m(0) = \sum A_{-n} T^{-n}. \tag{6}$$

In an applied magnetic field, these Cu^{2+} moments order at a temperature determined by their interaction with the applied field, of the order of 4K for 7T, and produce a Schottky or Schottky-like anomaly, still denoted by $C_m(H)$, at that temperature. In that case, the zero-field upturn in C/T produced by the Cu^{2+} ions disappears and is replaced by the Schottky anomaly at a higher temperature. However, in a field of 7T, another, smaller low-temperature upturn appears. It is the hyperfine contribution (C_h) that arises from the interaction of nuclear magnetic dipole moments with the applied magnetic field or nuclear electric quadrupole moments with internal electric field gradients. It is given accurately by a Schottky anomaly, but it occurs at such a low temperature for the cases of interest here that only the first term of the high-temperature tail,

$$C_h(H) = D(H)T^{-2} \tag{7}$$

is of interest. In the case of magnetic moments $D(H) \propto H^2$.

The upturn in C/T at low temperature and in zero field, i.e., $C_m(0)$, complicates the analysis of the low-temperature data, as illustrated in Fig. 3 for data for YBCO. Following a common convention the data are plotted as C/T vs T^2. The dashed line is a possible graphical fit to $C/T = \gamma(0) + B_3T^2$. However, an analytical fit by $C/T = A_{-3}T^{-4} + A_{-2}T^{-3} + \gamma(0) + B_3T^2 + B_5T^4$ leads to the substantially different values of $\gamma(0)$ and B_3 that are represented by the solid line. No doubt, some of the variation in reported values of $\gamma(0)$ and B_3 (and of θ_0) arise from such differences in the fitting procedure.

As noted above, the application of a magnetic field modifies $C_m(H)$, changing it from an upturn in the vicinity of 1K to a Schottky or Schottky-like anomaly at a temperature appropriate to the field and Cu^{2+} moments. It also produces an approximately linear-in-field increase in the linear term, $\gamma(H)T$, as expected for a superconductor in an applied field $H < H_{c2}$, and a hyperfine term $D(H)T^{-2}$. Some of these features are illustrated in Fig. 4 with data for an $La_{1.85}Ca_{0.15}CuO_4$ sample for which the concentration of magnetic moments is particularly low. The zero-field upturn is small; the Schottky anomalies are not conspicuous; and the field dependence expected for the mixed state, $\gamma(H)T$ linear in field, is clearly displayed. Similar data for a $La_{1.85}Sr_{0.15}CuO_4$ sample with a higher concentration of magnetic moments are shown in Fig. 5. In that case, $C_m(0) = A_{-2}T^{-2}$, and the approximately constant shifts in C/T with increasing field for T>5K, which are apparent in Fig. 4, are modified by Schottky anomalies that shift to higher temperatures in higher fields. The solid curves in Fig. 5 represent the sums of the C_h, C_m, C_e and C_ℓ contributions that are shown separately in Fig. 6. The latter figure also illustrates another feature: the deviations from constant C_e/T at $T>5K$ are approximately proportional to T^3, also as expected for a superconductor in a field $H<H_{c2}$.

Most YBCO samples have higher concentrations of magnetic moments than the samples represented in Figs. 4-6, and correspondingly larger values of C_m. An example of an analysis of the specific heat into its components similar to that of Fig. 6, but for a reasonably typical YBCO sample is shown in Fig. 7. In that case, $C_m(7T)$ is well represented by a Schottky anomaly, but for still higher concentrations of magnetic moments, as occur in some samples, the anomaly would be broadened.

The concentration (n_2) of the Cu^{2+} moments that produce the zero-field upturn in C/T and, in the presence of applied fields, the Schottky anomalies, can be determined from the Schottky anomaly. For the YBCO samples considered in this article, $n_2 \sim 10^{-2}$-10^{-3} moles/mole YBCO.

Figure 8 shows two constructions that have been used to estimate $\Delta C(T_c)$. The usual one, represented by the dashed lines, is a simple extrapolation from both $T<T_c$ and $T>T_c$ to a vertical line drawn to give the same entropy on the high temperature side of the anomaly as a smooth curve through the data. The height of the vertical line gives $\Delta C(T_c)/T_c$. (The dash-dot curve is a slightly different extrapolation, based on harmonic lattice dynamic expressions, of the high temperature data.) The solid curve is a fit by a superposition of BCS-like functions for C_{es} and $\Delta C(T_c)$ with a Gaussian distribution of T_c.

Both procedures give similar values of $\Delta C(T_c)$.

The sample-to-sample variation of $\Delta C(T_c)$ is represented in Fig. 9 for five YBCO samples. The lowest two sets of data are for "Zn-doped" samples, samples in which small amounts of Cu were replaced with Zn, a procedure known to suppress superconductivity. The other three samples were all prepared by methods expected to produce high-quality superconducting material, but the values $\Delta C(T_c)$ vary by a factor of 1.5 (and factors of two for similarly prepared samples are not at all unusual). The data for the different samples in Fig. 9 are labelled with the values of n_2, the concentration of Cu^{2+} moments determined from the low-temperature in-field Schottky anomalies. The correlation of the magnitude of the anomaly, and therefore $\Delta C(T_c)$, with n_2 will be developed more fully later. It shows that these moments influence the transition to the superconducting state and are therefore on the YBCO lattice, not in some impurity phase.

Interpretation of Specific Heat Measurements on High-T_c Superconductors

No doubt because of its possible theoretical significance, a great deal of attention has been focused on the zero-field linear term, i.e., on the value of the coefficient $\gamma(0)$ and on acquiring an understanding of its origin and significance.

For YBCO, the possible importance of impurity-phase contributions to $\gamma(0)$ was recognized in the early stages of the effort to determine the value, or the existence, of an intrinsic contribution (17, 18, 19). Examples of the specific heat for several possible impurity phases are compared with that of YBCO in Fig. 10, as reported by Kuentzler et al. (17), and similar data have been obtained by others (18, 19).

As is made clear in Figs. 6 and 7, there is a relatively narrow window in temperature in which the linear term is determined. Depending on the magnetic field and the magnitudes of C_h and C_m, it extends from about 0.3 to 10K, the temperatures at which it is about 10% of C. As shown in Fig. 10, $BaCuO_2$ can have a large approximately constant value of C/T, which is presumably associated with Cu^{2+} moments that order near 10K, in just that window of temperature. Systematic attempts to measure quantitatively the impurity phase contribution have usually been based on the use of the Curie-Weiss term in the high-temperature susceptibility to estimate the concentration of Cu^{2+} magnetic moments (n) which is then taken as a measure of the concentration of impurity phases, $BaCuO_2$ in particular. A correlation of $\gamma(0)$ with n is represented by the solid triangles in Fig. 11. It is similar to results reported by the Geneva group, Eckert et al. (19, 20). In part because the roughly linear correlations of $\gamma(0)$ with n, such as that portrayed in Fig. 11, extrapolate to non-zero values of $\gamma(0)$ for n=0, but perhaps more importantly because values of $\gamma(0) \lesssim 4$ mJ/mole$\cdot K^2$ have been reported only very rarely, it has frequently been concluded that there is an intrinsic contribution to $\gamma(0)$ of approximately 4-6 mJ/mole$\cdot K^2$ (see, e.g., Refs. 21 and 22).

The concentration n includes all Cu^{2+} moments, those in impurity phases that order, typically, near 10K (n_1), and those that produce the low-temperature upturn in C/T and which influence $\Delta C(T_c)$, showing that they are "on the YBCO lattice" (n_2). It has been shown (23) that $\gamma(0)$ is better represented by the sum of two terms, one proportional to n_1 and the other proportional to n_2, than by a constant plus a term proportional to n. That correlation is also represented in Fig. 11, by the open circles and open squares. The conclusion (23) is that $\gamma(0)=0$ in the limit $n_1=0$ and $n_2=0$ -- i.e., that there is no contribution to $\gamma(0)$ intrinsic to the ideal superconducting state. In this case also, Junod et al. (24) reached essentially the same conclusion by a different, related argument. At this time, although the role of the magnetic moments (concentration n_2) that produce the upturn in C/T in contributing to $\gamma(0)$ has yet to be elucidated in detail, it is reasonable to conclude that that contribution plus the impurity-phase (concentration n_1) contribution account completely for $\gamma(0)$.

The correlation of $\gamma(0)$ with n_2, i.e., of the $\gamma_2 n_2$ component of $\gamma(0)$ with n_2, is paralleled by a correlation of $\Delta C(T_c)$ with n_2, which was suggested by the data in Fig. 9 and which gives insight into the origin of the $n_2\gamma_2$ term. Figure 12 shows $\Delta C(T_c)/T_c$ vs n_2 for the same samples represented in Fig. 11. [Since T_c is essentially constant for these samples $\Delta C(T_c)$ is proportional to $\Delta C(T_c)/T_c$).] There is considerable scatter, reflecting no doubt uncertainties in the measurements of both $\Delta C(T_c)$ and n_2, but there is a pronounced trend to lower values of $\Delta C(T_c)$ with increasing n_2, and the relation is roughly linear. [The one point for which $\Delta C(T_c)=0$ was given zero weight in determining the straight line fit because there was reason to believe that a small fraction of the sample was superconducting, even though $\Delta C(T_c)$ was not measurable.] The obvious interpretation of Fig. 12 is that the volume fraction of superconductivity, which is measured by $\Delta C(T_c)$ decreases roughly linearly with increasing n_2. This permits, by extrapolation to $n_2=0$, an estimate of the value of $\Delta C(T_c)/T_c$ for an ideal, fully superconducting sample: $\Delta C(T_c)/T_c=77$ mJ/mole $\cdot K^2$. Furthermore, the value of $\Delta C(T_c)$ for any sample can be compared with that standard to obtain its volume fraction of superconductivity (f_s).

The combination of the correlation of $\Delta C(T_c)$ with n_2 and the $\gamma_2 n_2$ contribution to

$\gamma(0)$ is strongly suggestive of the operation of a pair-breaking interaction, an effect that is well known in conventional superconductors. The presence of a localized magnetic moment, such as a Cu^{2+} moment, introduces a perturbation which tends to unpair the spin-zero electron pairs characteristic of the superconducting state, and thereby to suppress the transition to the superconducting state. The well known consequences of this effect are a reduction in $\Delta C(T_c)$ and the creation of a linear term in the specific heat, both of which are linear in the concentration of magnetic moments. (The existence of the linear term has also given rise to the name "gapless" superconductivity.) There is, however, one striking difference between the behavior of YBCO and that of conventional superconductors: for the YBCO samples represented in Figs. 11 and 12, T_c is essentially constant; for the operation of a pair-breaking mechanism in conventional superconductors T_c also decreases linearly with increasing concentration of magnetic moments, at approximately the same rate at which $\Delta C(T_c)$ decreases. This difference can plausibly be related to the difference in values of ξ. In conventional superconductors, ξ, the distance over which the superconducting order can change, is long. As a consequence, even randomly distributed dilute magnetic moments act in unison suppressing superconductivity, and T_c, uniformly throughout the sample. By contrast, if the coherence distance is short, the magnetic moments in YBCO act individually, destroying superconductivity, i.e., creating normal regions, in their immediate vicinities, and leaving more remote regions of the sample unaffected, i.e., with the usual value of T_c.

Quite apart from the detailed validity of the model described in the preceding paragraph, the correlaton of $\Delta C(T_c)$ has implications for the processing of HTSC. It was recognized very early that the critical currents in polycrystalline samples are very much lower than in single crystals, and it is widely believed that the difference is a conseqence of normal or weakly superconducting regions at grain boundaries -- the "weak-link" effect, as it is called. It seems quite possible that the weak-link effect is associated with the normal regions represented by the $\gamma_2 n_2$ contribution to $\gamma(0)$ and that a measure of n_2, or much more effectively of $\Delta C(T_c)$, might be a useful criterion in the evaluation of processing procedures for bulk samples.

There are other implications of the model that would be of more fundamental interest. Fairly generally, the understanding of the properties of a sample, and the evaluation of parameters from experimental data depend on a value of f_s, which can be obtained from a specific heat measurements. The normal-state value of γ can be determined by extrapolating $\gamma_2 n_2$ to the value of n_2 at which superconductivity, i.e., $\Delta C(T_c)$, disappears. The result is $\gamma \approx 16$ mJ/mole$\cdot$K^2. Together with the value of $\Delta C(T_c)/T_c$ for a fully superconducting sample, this gives $\Delta C(T_c)/\gamma T_c \approx 4.1$, a value indicative of extreme strong coupling. However, a comparison of γ with the calculated band-structure value γ_{bs}(25, 26, 27) gives $\lambda < 1$, inconsistent with strong coupling via the phonons. These two results are suggestive of a non-phonon mechanism, a possibility also suggested by other lines of reasoning.

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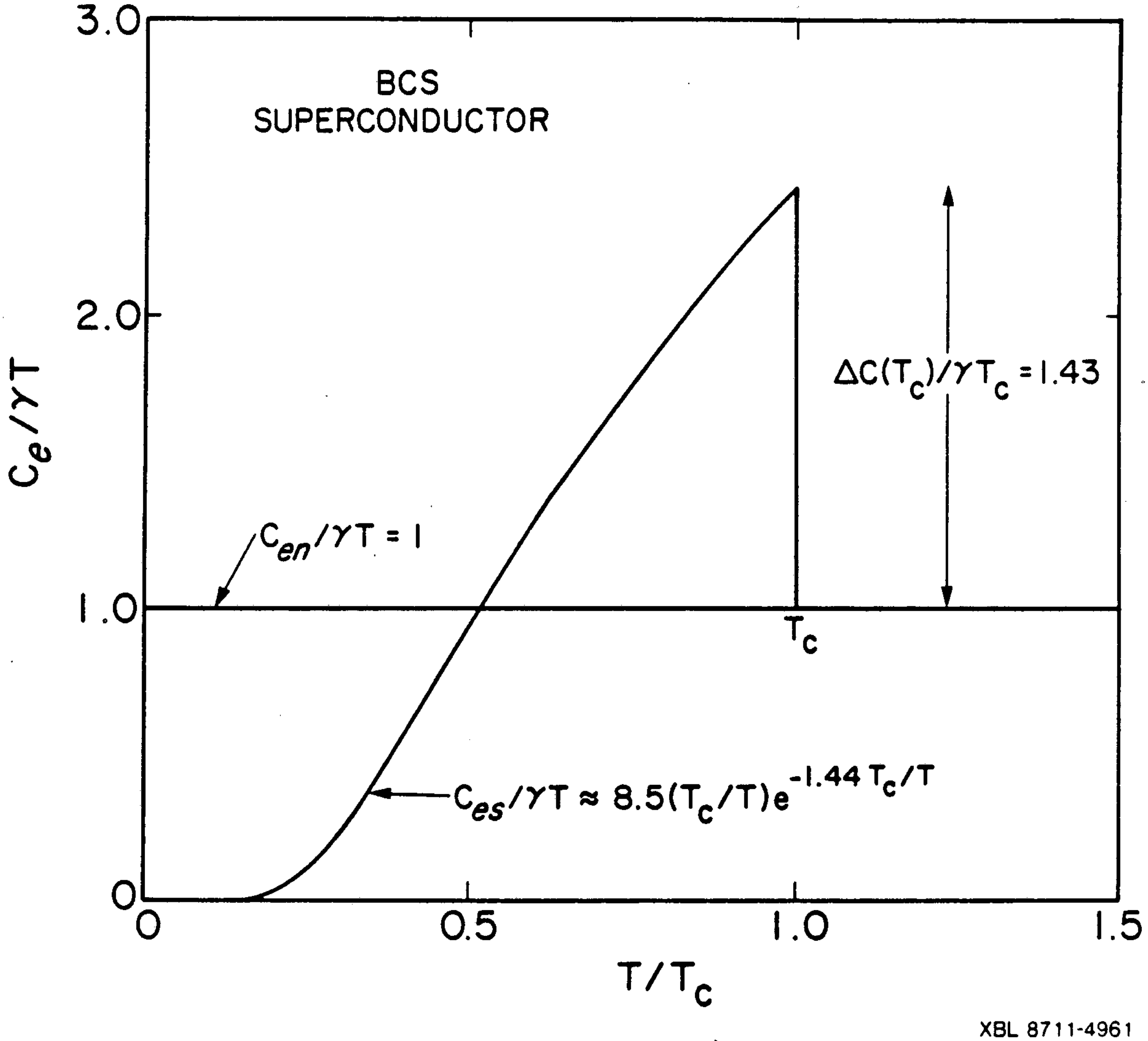

Figure 1. The electronic specific heat of a BCS superconductor in the weak-coupling limit.

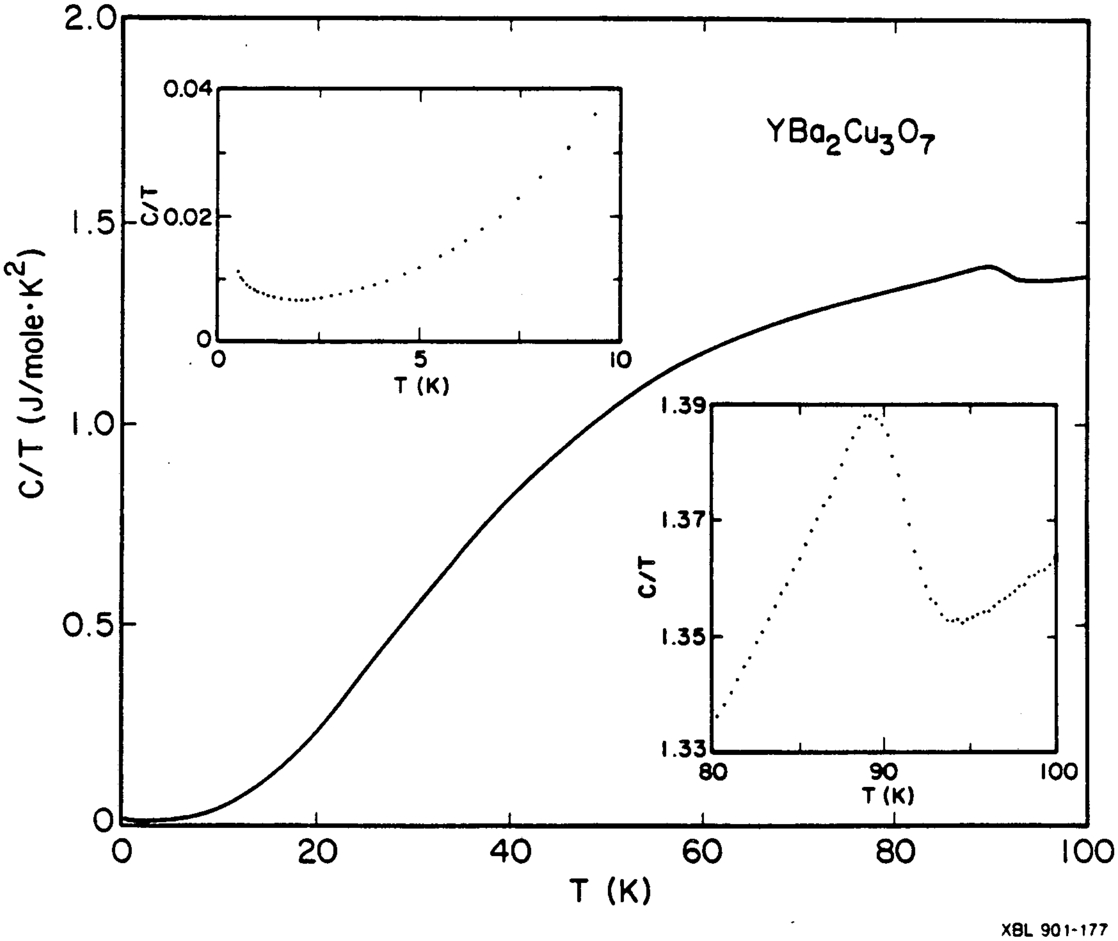

Figure 2. The total specific heat of a typical YBCO sample. The insets show actual data at low temperatures and in the vicinity of T_c.

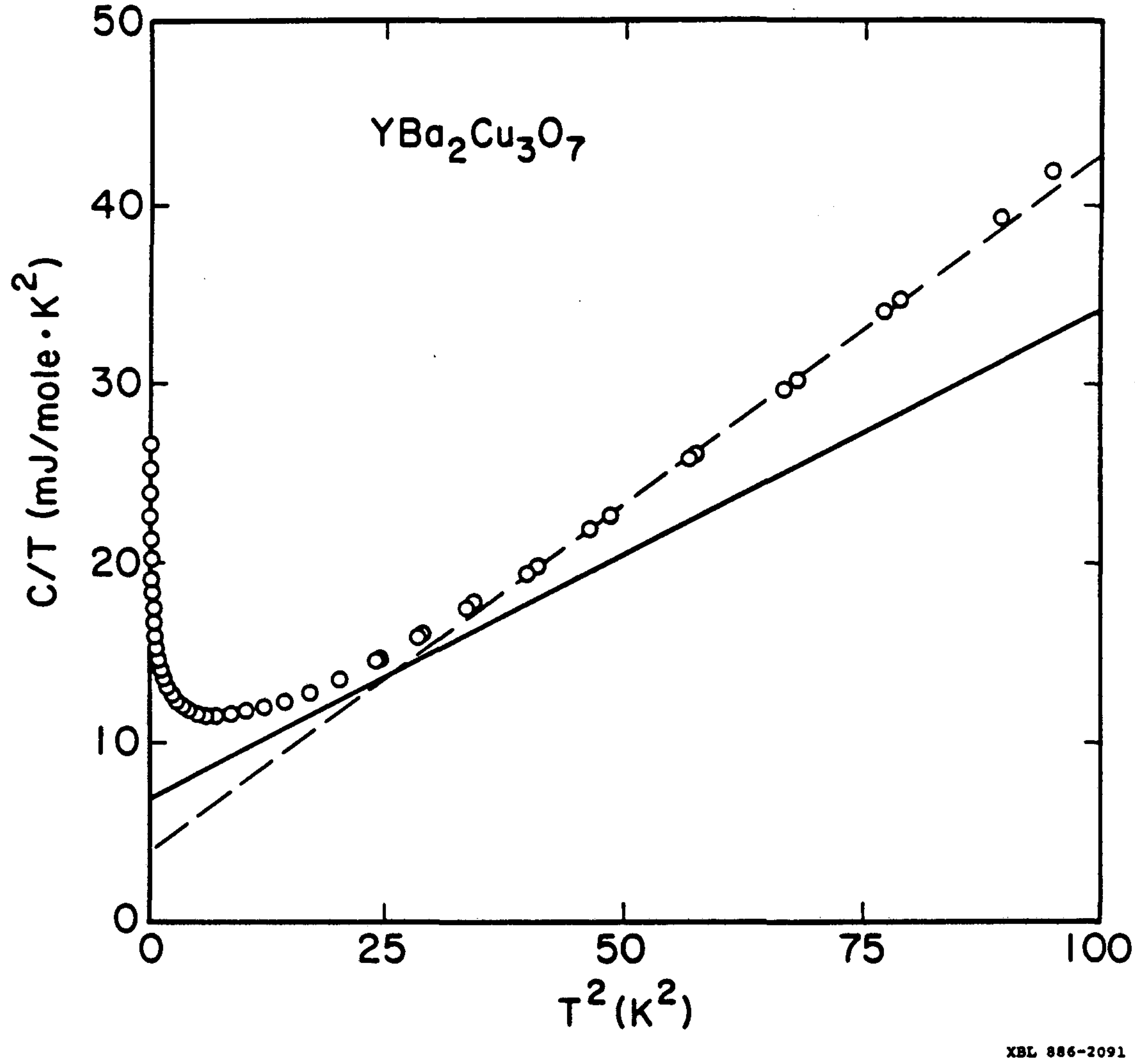

Figure 3. The dashed and solid lines represent the values of $\gamma(0)$ and B_3 for a YBCO sample derived by different methods, as described in the text.

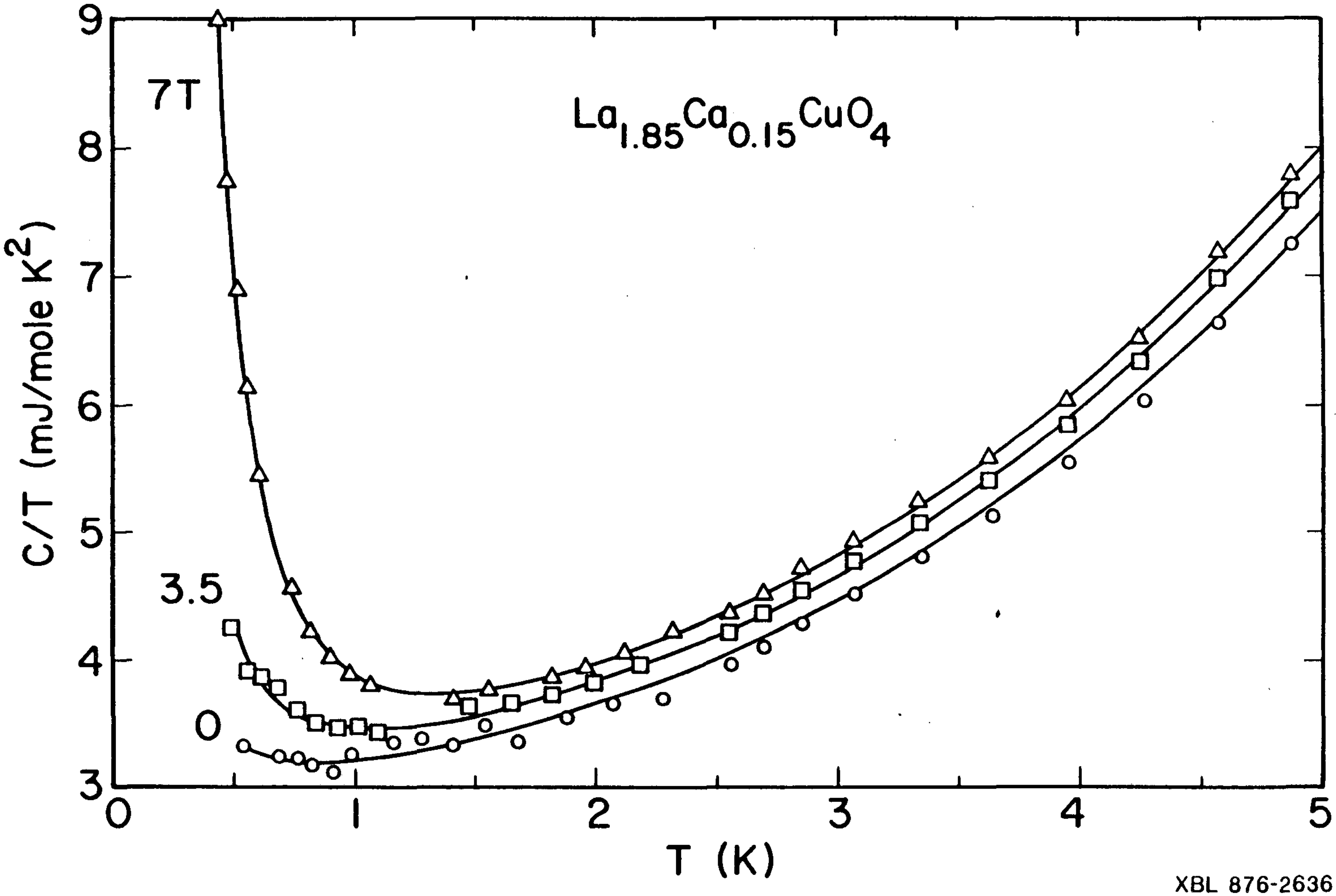

Figure 4. Data for an $La_{1.85}Ca_{0.15}CuO_4$ sample with a low concentration of magnetic moments in 0, 3.5 and 7T.

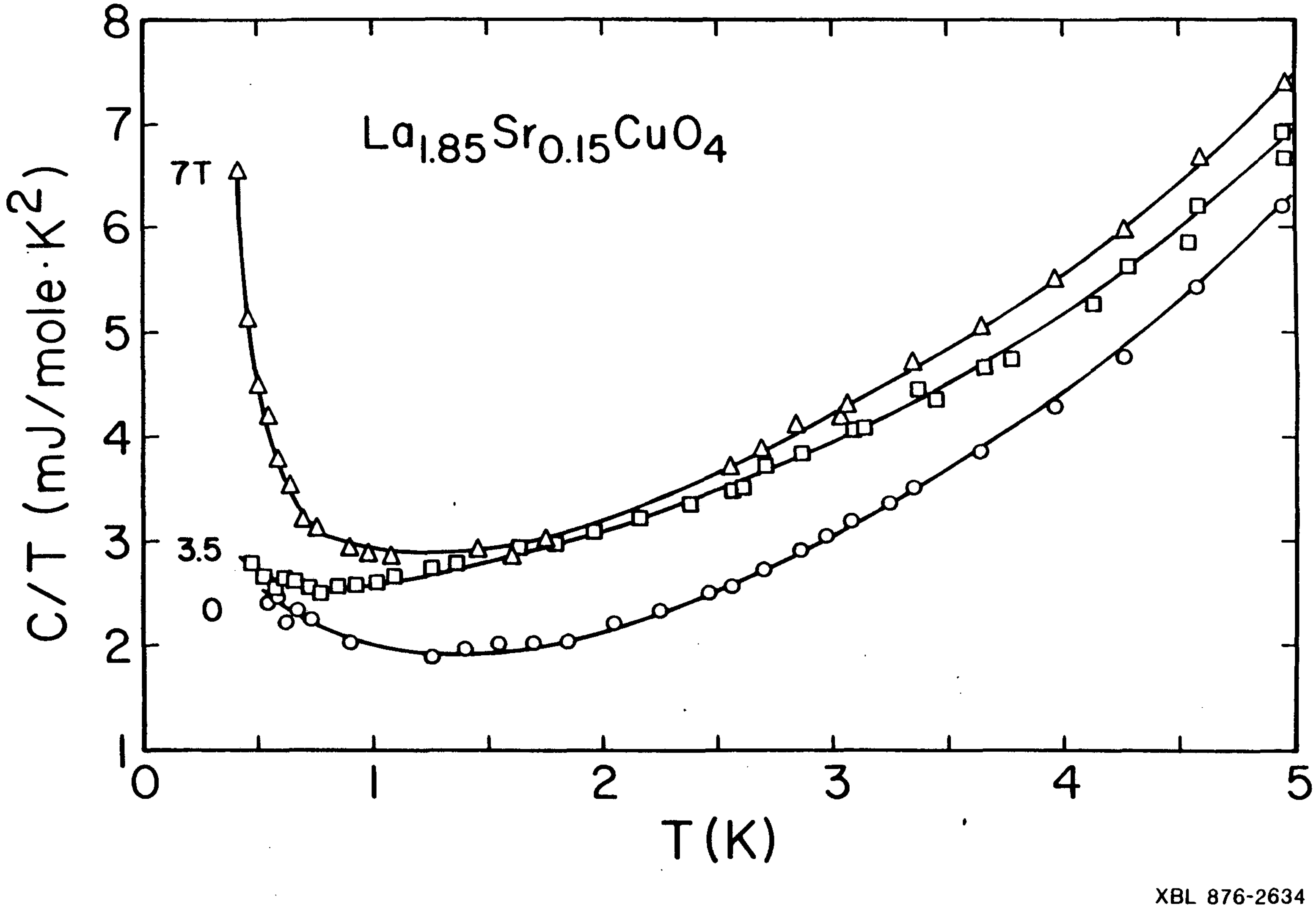

Figure 5. Data for an $La_{1.85}Sr_{0.15}CuO_4$ sample with a higher concentration of magnetic moments than the sample represented in Fig. 4. The curves correspond to analytical fits to the component contributions to the specific heat.

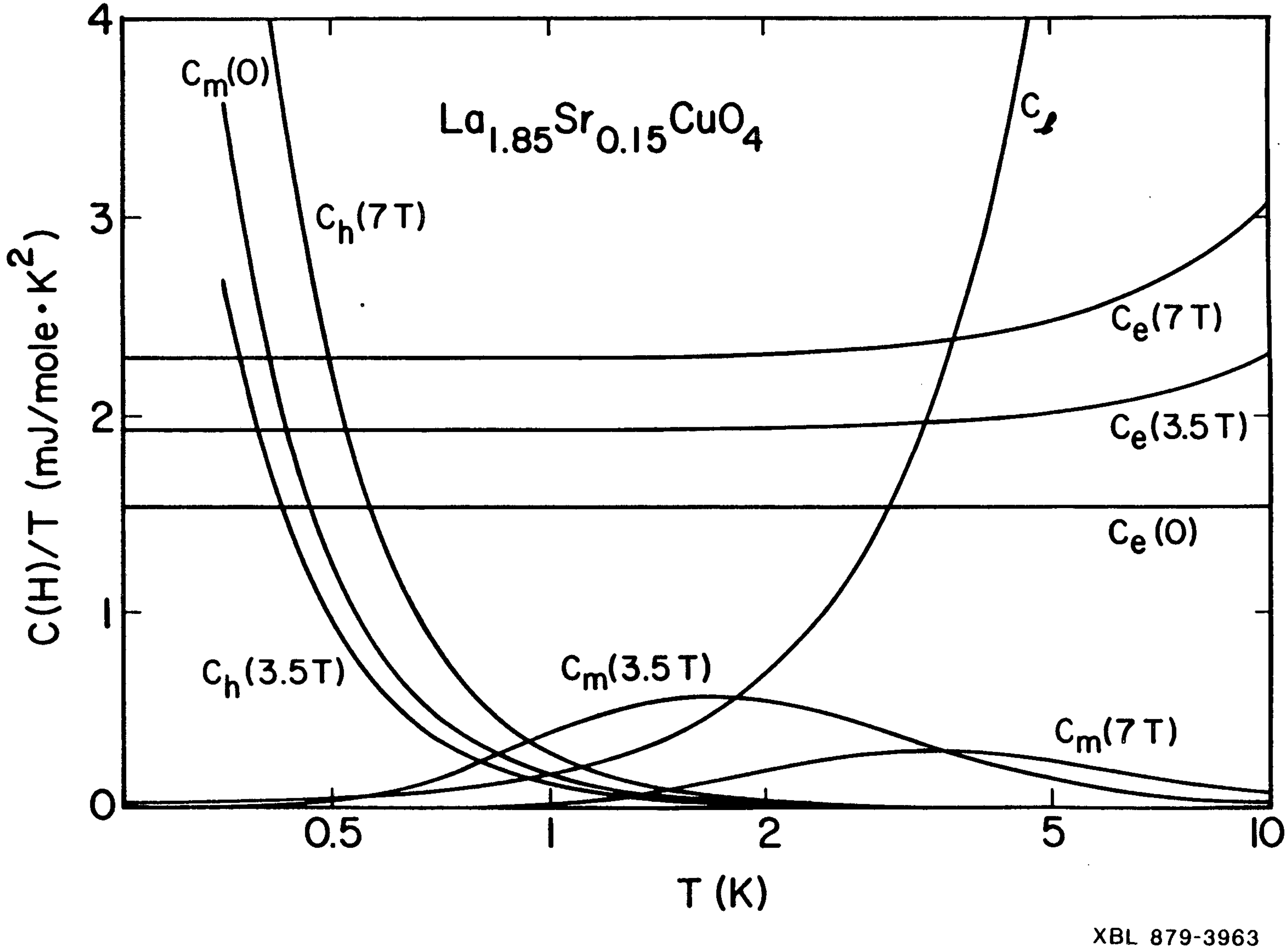

Figure 6. The component contributions to the total specific heat curves in Fig. 5.

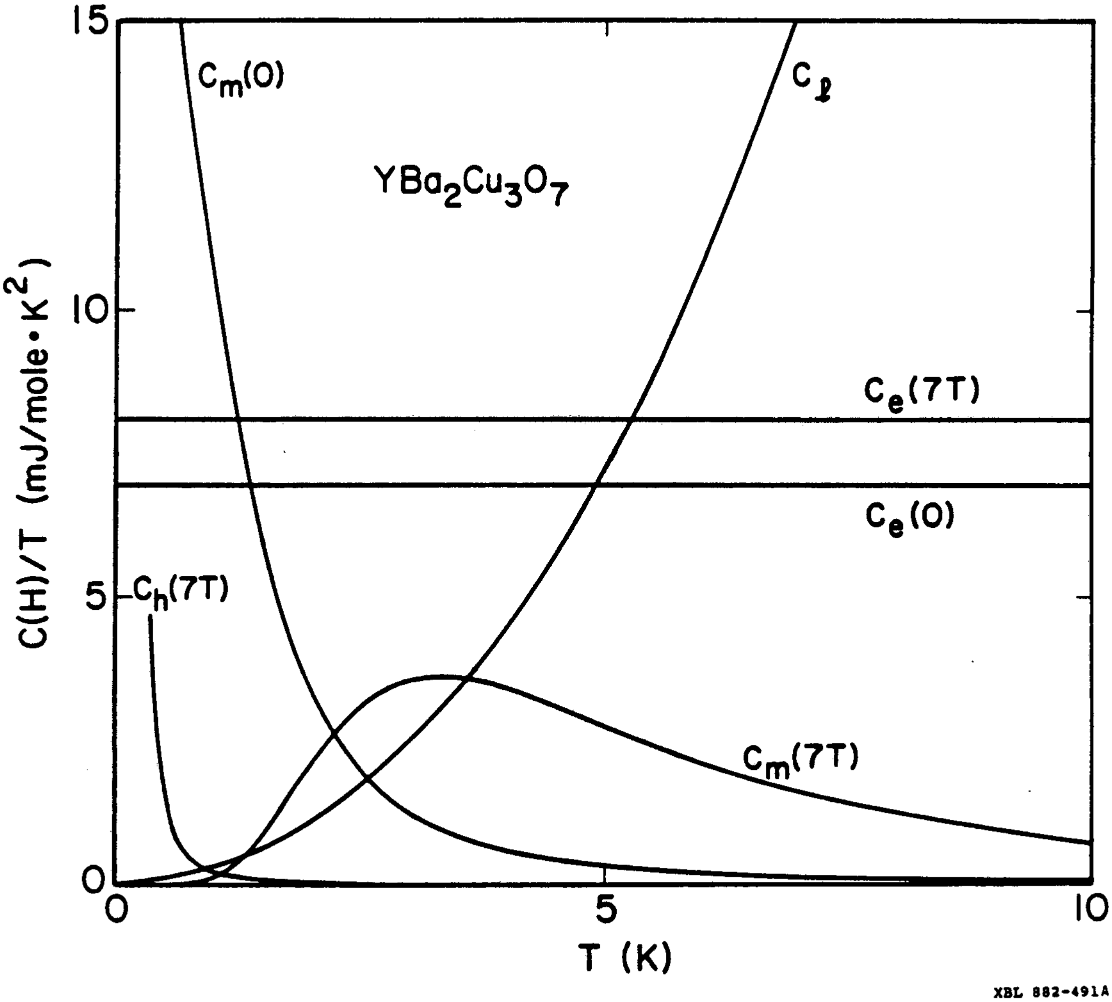

Figure 7. Components of the specific heat of a YBCO sample in 0 and 7T.

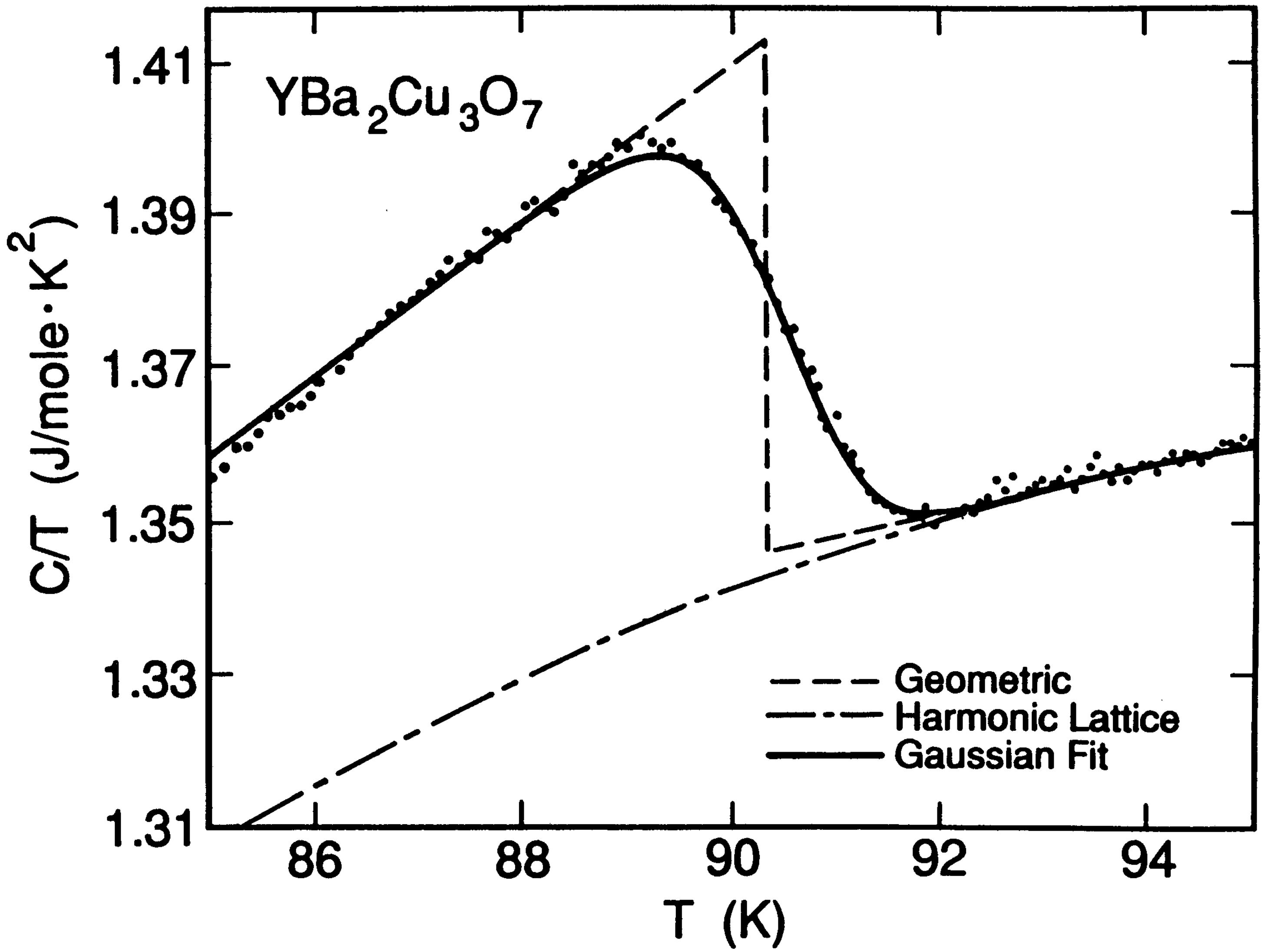

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Figure 8. Specific heat data for YBCO near T_c with several constructions used to determine $\Delta C(T_c)$ as described in the text.

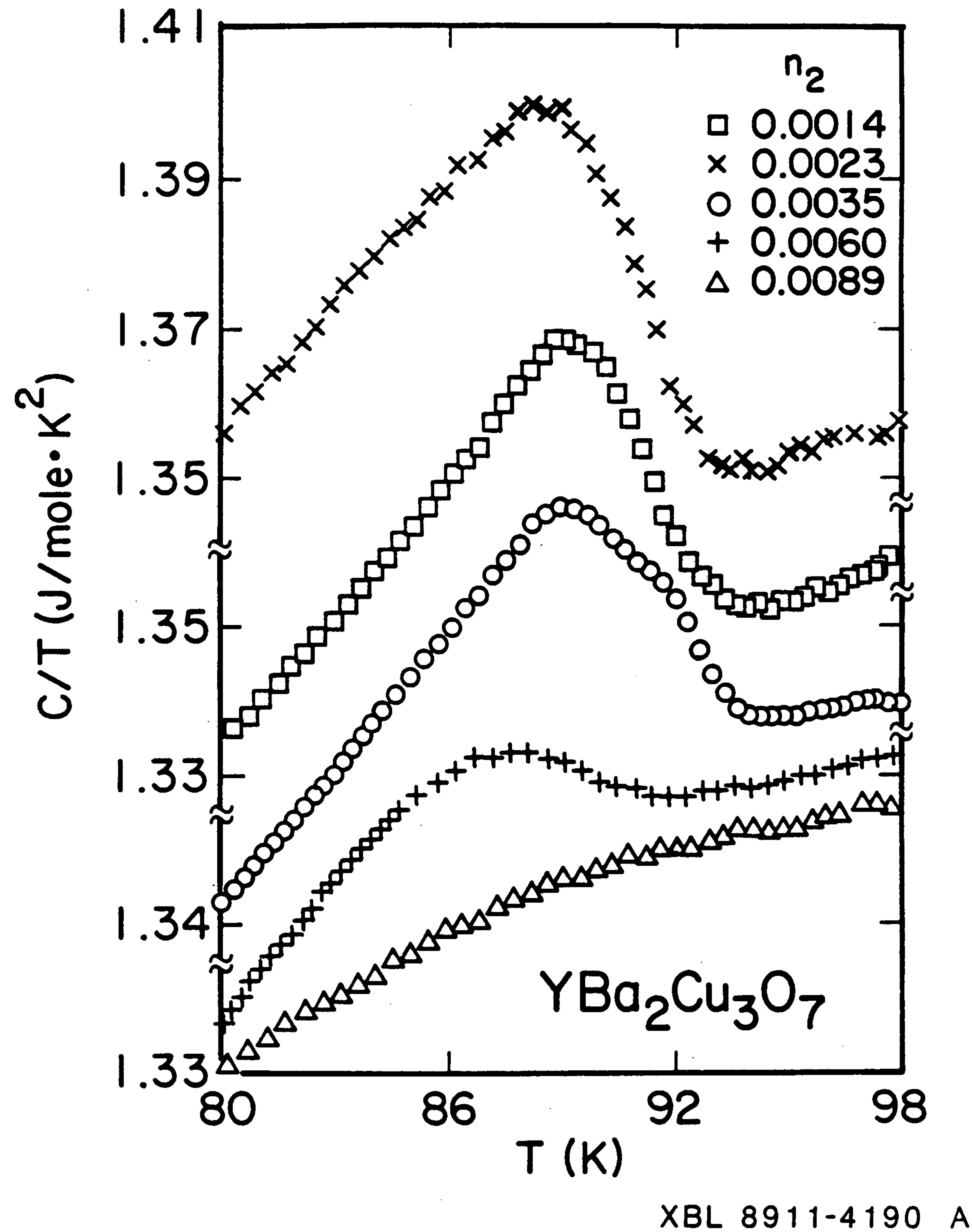

Figure 9. Specific heats, in the vicinity of T_c, for YBCO samples with different concentrations of Cu^{2+} moments on the YBCO lattice.

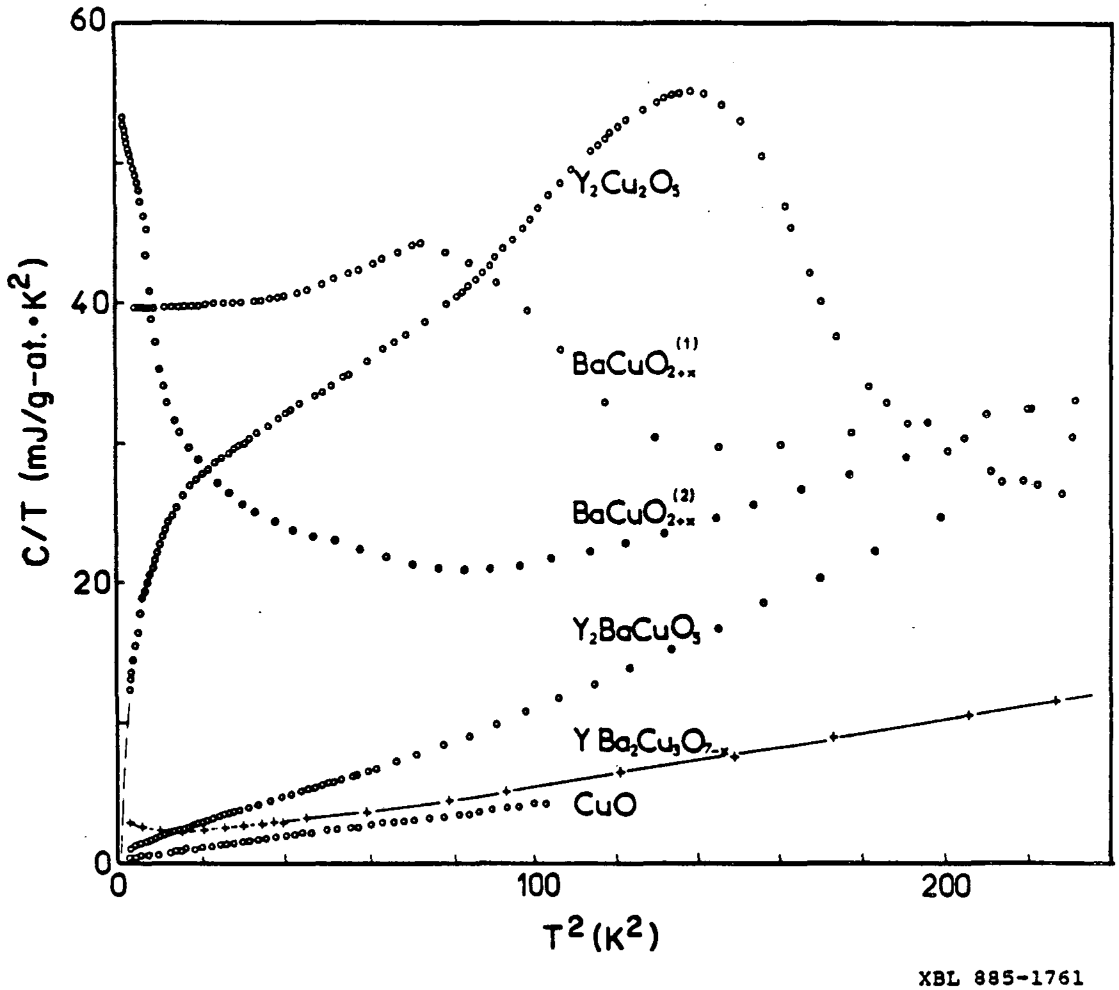

Figure 10. Specific heats of several compounds that might be present as impurities in YBCO compared with that of YBCO. The two samples of $BaCuO_2$ were prepared under different conditions. (Taken from Ref. 17.)

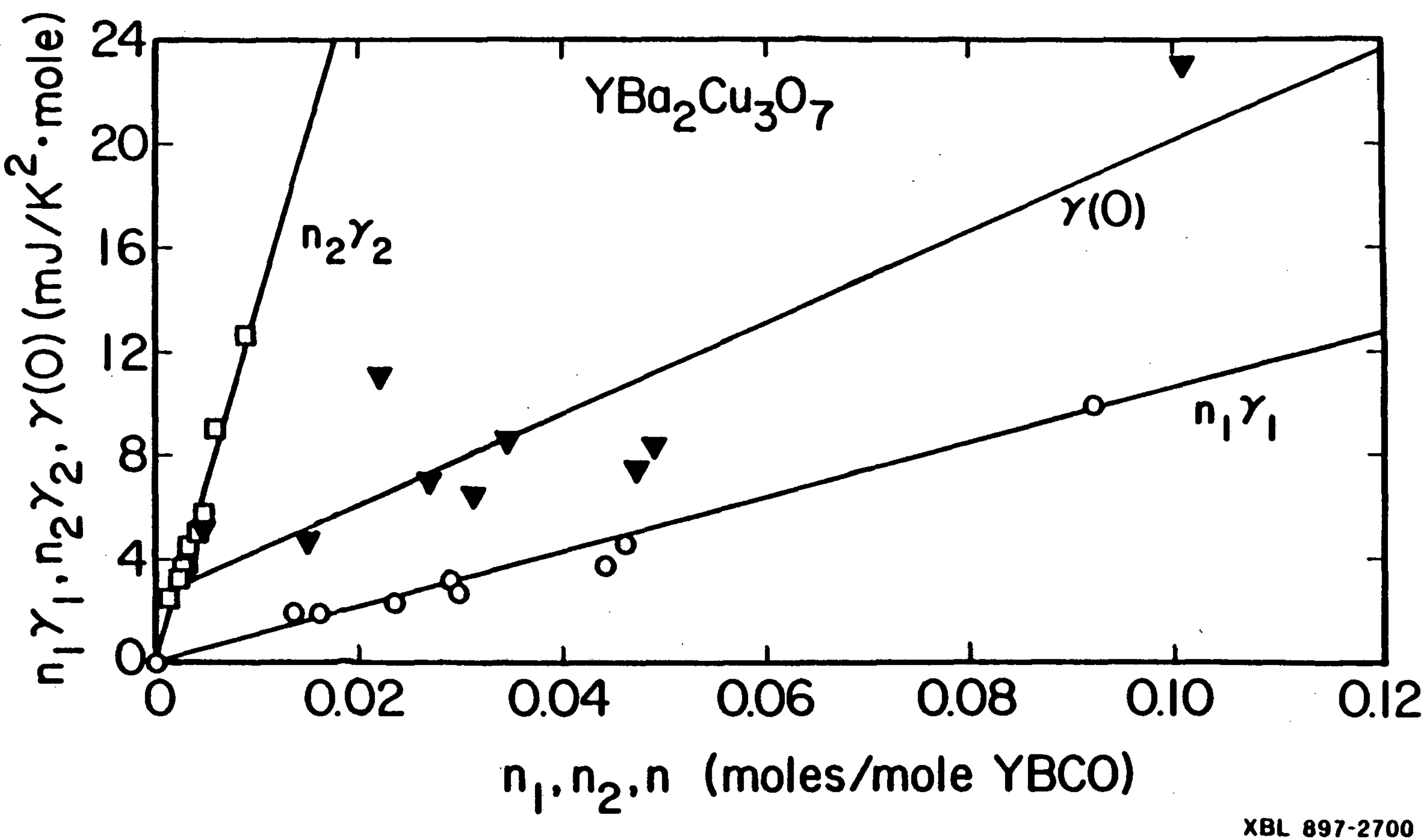

Figure 11. Values of $\gamma(0)$ for YBCO samples displayed in two different ways: solid triangles represent $\gamma(0)$ vs n, the total concentration of Cu^{2+} moments; open circles and squares represent $\gamma(0)$ decomposed into two components, proportional to the concentrations, n_1 and n_2, of two types of Cu^{2+} moments, $n = n_1 + n_2$.

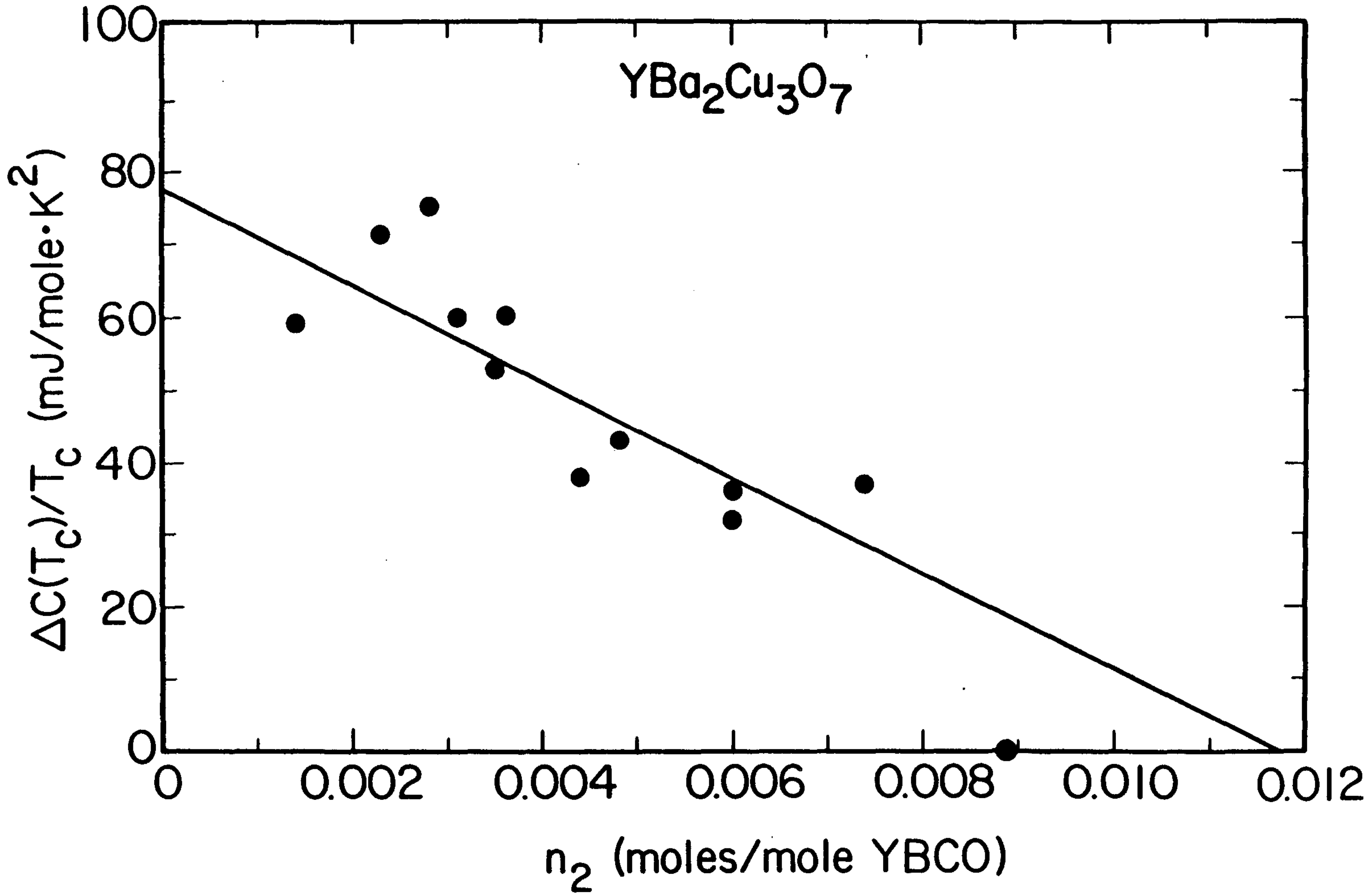

Figure 12. Correlation of $\Delta C(T_c)/T_c$ with n_2, the concentration of Cu^{2+} moments on the YBCO lattice.

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