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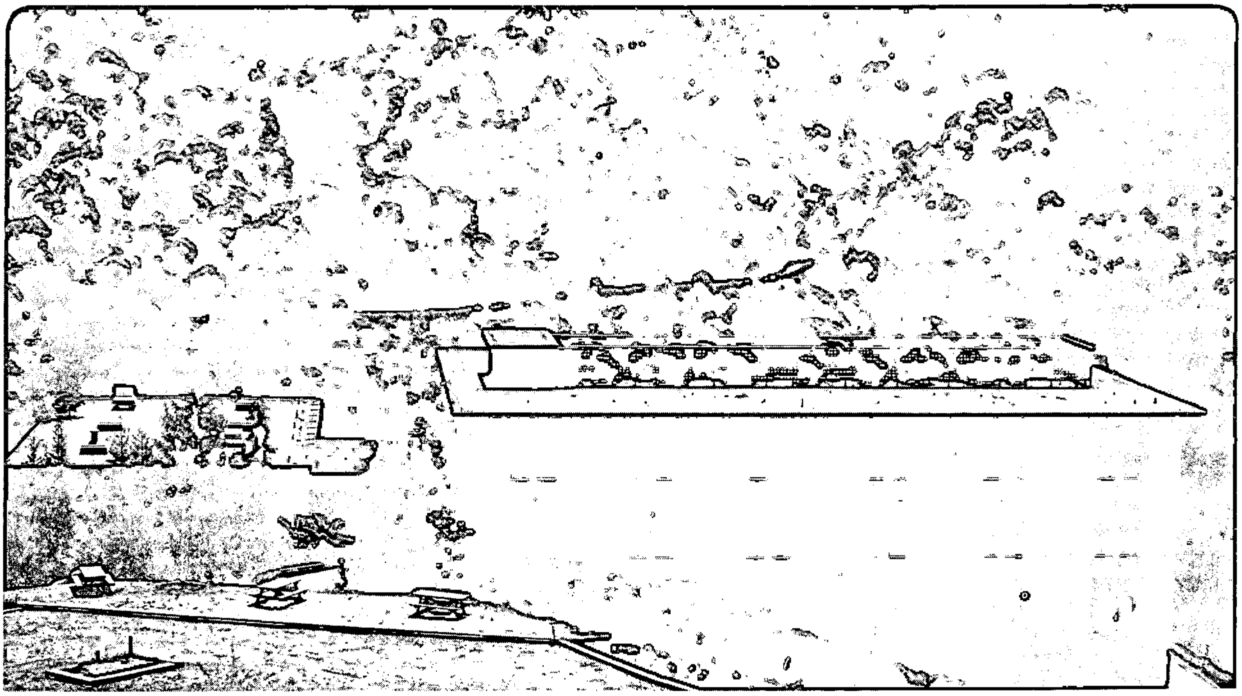

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THE SPECIFIC HEAT OF $YBa_2Cu_3O_7$

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Experimental evidence suggests that substantial fractions of typical $YBa_2Cu_3O_7$ samples are non-superconducting; that the non-superconducting inclusions are of dimensions of a lattice parameter; that the non-superconducting inclusions are associated with Cu^{2+} magnetic moments; and that the linear term in the specific heat is not an "intrinsic" property but is associated with the presence of these Cu^{2+} magnetic moments and impurity phases. A preliminary result on the effect of heat treatment on the volume fraction of superconductivity is presented.

I. INTRODUCTION

A major problem in the interpretation of experimental data on high-T_c superconductors (HTSC) is the sample-to-sample variation in measured properties: It is often not at all clear which properties are "intrinsic", characteristic of "ideal" material, and which are associated with impurities or other defects. In the case of specific heat (C) measurements, unlike e.g., spectroscopic or transport property measurements, the data give true volume averages of the bulk properties. In the particular case of $YBa_2Cu_3O_7$ (YBCO), for which measurements of C are much more extensive than for other HTSC, correlations among the sample-dependent parameters suggest that the sample dependence is a consequence of incomplete transitions to the superconducting state[1]. In fact, it seems that for many samples, even those prepared by methods expected to give good superconducting material, and thought to be good superconducting material on the basis of other criteria, the volume fraction of superconductivity (f_s) may be as low as 50%. The data suggest that the non-superconducting regions are small, of the order of the lattice parameters in size (which could make them important in determining critical currents) and that they are associated with the presence of Cu^{2+} magnetic moments that are present in low concentrations (n_2) that are measured quantitatively by the magnetic field dependence of the low-temperature specific heat. The same data also suggest an interpretation of the low-temperature "linear term" in the specific heat and point to a criterion for recognizing the values of parameters characteristic of "ideal" material. In this paper the evidence for these conclusions is summarized, and some preliminary data on the effect of heat treatment of a sample on n_2 and f_s are reported.

II. CORRELATIONS AMONG SPECIFIC-HEAT-DERIVED PARAMETERS: THE VOLUME FRACTION OF SUPERCONDUCTIVITY

Some of the relevant parameters are derived from low-temperature specific-heat data, and others from data near T_c. In the former case there are four contributions to C that must be taken into account:

1. **The "linear term", $C_e(H)$.** This is a field-dependent temperature-proportional term of the form.

$$C_e(H)/T=\gamma^*(H)=\gamma^*(0)+H(d\gamma^*/dH), \tag{1}$$

where H is the applied magnetic field. The zero field contribution, $\gamma^*(0)$, has no counterpart in conventional superconductors. In part for that reason, and in part because it corresponds to a prediction of an early version of the RVB theory[2], it has received a great deal of attention. The H-proportional term, however, has an analogue in conventional superconductivity where it is associated with flux penetration in the mixed state. For a sample that is only partially superconducting, $d\gamma^*/dH$ should therefore be proportional to f_s.

2. **A contribution associated with Cu^{2+} magnetic moments, $C_m(T)$.** For $H=0$, in the vicinity of 1K, there is a sample-dependent "upturn" in C/T that is the high-temperature tail of a broadened Schottky anomaly associated with Cu^{2+} moments that order near 0.1K. In an applied field of 7T, these moments order under the influence of that field producing a Schottky anomaly near 3K that determines their concentration, n_2.

3. **The lattice specific heat, $C_\ell(T)$.** This is represented by the usual low-temperature expansion in odd powers of the temperature,

$$C_\ell=B_3T^3+B_5T^5+ ---. \tag{2}$$

4. **A hyperfine contribution, $C_h(T)$.** This term is associated with the interaction of nuclear magnetic moments with H. For the temperatures of interest it is accurately represented by

$$C_h=A_{-2}(H/T)^2. \tag{3}$$

The analysis of data below 10K for a typical YBCO sample into these four components is represented in Fig. 1. The solid curves represent the four components in both zero field and 7T. The experimental points associated with the $C_m(7T)$ curve are the measured data from which the other three contributions have been subtracted to give an impression of the accuracy with which the Schottky anomaly and n_2 are determined. They also give an impression of the overall accuracy of the fits, and in particular of that with which $C_e(7T)-C_e(0)$ and $d\gamma^*/dH$ are determined.

The analysis of the data for $H=0$ and 7T near T_c is illustrated in Fig. 2. The dashed lines represent the determination of the equivalent discontinuity in C at T_c [$\Delta C(T_c)$] by a simple entropy-conserving construction, but more elaborate analyses that use analytical expressions for the broadening of the transition by sample inhomogeneities and fluctuations give essentially the same values for $\Delta C(T_c)$. The other relevant parameter, ΔS, is defined by the shaded area in Fig. 2. It is a measure of the effect of the 7T field on the entropy of the specific-heat anomaly. (The total entropy change must, of course, be zero, and the equality of ΔS and $\Delta\gamma^* T_x$ -- $\Delta\gamma^*$ is, to the necessary accuracy, constant for $T<T_x$ -- corresponds to that requirement.) For a partially superconducting sample, both $\Delta C(T_c)$ and ΔS should also be proportional to f_s.

Thus, the measured parameters include three that should be proportional to f_s, and in principle any one of them could be used to calculate f_s for a sample if the value for a fully superconducting, $f_s = 1$, sample were known:

$$\frac{d\gamma^*/dH}{[d\gamma^*/dH]_{f_s=1}} = \frac{\Delta C(T_c)}{[\Delta C(T_c)]_{f_s=1}} = \frac{\Delta S}{[\Delta S]_{f_s=1}} = f_s \tag{4}$$

Since none of the denominators in Eq. 3 is known, a least-squares procedure that gave equal weight to each of the parameters was used to derive the most consistent relative values of f_s. The results are shown in Fig. 3, where the values of the three parameters define a single value of f_s for each sample, and each parameter has been scaled by a factor (the same for all samples) chosen to minimize the deviations from a common line through the origin. In addition to giving relative values of f_s, this construction demonstrates the mutual proportionality of $d\gamma^*/dH$, $\Delta C(T_c)$ and ΔS.

There is also a correlation of f_s with n_2, shown in Fig. 4, and that correlation provides the basis for putting f_s on an absolute basis. It shows that f_s decreases with increasing n_2 suggesting that the Cu^{2+} moments either suppress the transition to the superconducting state themselves, or they are associated with another defect that has that effect. In any case, the extrapolation back to $n_2 = 0$ should identify the point on the f_s axis at which the absolute value of $f_s = 1$ (see Fig. 4). With this identification the values of $d\gamma^*/dH$, $\Delta C(T_c)$, ΔS and all other specific-heat derived parameters, for a fully superconducting sample, are determined.

III. THE "LINEAR TERM"

The proposed interpretation of the linear term is based on a distinction between two kinds of Cu^{2+} moments: The Cu^{2+} moments included in n_2 order well below 1K in zero field and are located on the YBCO lattice, as shown by their effect on the superconducting properties. In addition, there are Cu^{2+} moments, with concentration n_1 located in impurity phases, notably $BaCuO_2$. They order at much higher temperatures in zero field, ~ 12K, and do not contribute to the field dependence of C_m near 3K that determines n_2. However, both kinds of Cu^{2+} contribute to the Curie-Weiss term in the high-temperature magnetic susceptibility. Since that term gives the total concentration $n = n_1 + n_2$, both n_1 and n_2 are determined.

Soon after the discovery[3] of the linear term in YBCO it was shown[4] there was a very large, approximately linear, term in the specific heat of $BaCuO_2$, a common impurity in YBCO samples. It was clear that $BaCuO_2$ could contribute significantly to the linear term observed in YBCO samples; n (rather than n_1, because n_2 had not been determined) was sometimes taken as a measure of the concentration of $BaCuO_2$; and correlations of $\gamma^*(0)$

with n such as that shown in Fig. 5 were taken as evidence that $\gamma^*(0) \neq 0$ even in the absence of $BaCuO_2$, and there was an "intrinsic" contribution to $\gamma^*(0)$ associated with the superconducting state. Later, when n_2 was determined separately, it was shown[5] that $\gamma^*(0)$ was well represented by

$$\gamma^*(0)=\gamma_1^* n_1+\gamma_2^* n_2 \tag{5}$$

which is also represented, for the same data, in Fig. 5. Thus, the experimental data are well represented as the sum of n_1-proportional $BaCuO_2$ contributions and n_2-proportional contributions associated with the Cu^{2+} moments that are present on the YBCO lattice.

Even though the suppression of the superconducting transition may be by another defect that also produces a Cu^{2+} moment as a secondary effect rather than by the Cu^{2+} moment acting directly, it is interesting to compare this effect with the case of gapless superconductivity associated with magnetic impurities in conventional superconductors. In the latter case, the linear term in C increases linearly, and $\Delta C(T_c)$ decreases linearly, with increasing concentration of moments -- in exact analogy with the effect of n_2 on $\gamma^*(0)$ and $\Delta C(T_c)$ in YBCO. There is, however, a conspicuous difference in gapless superconductivity where T_c also decreases linearly with increasing concentration of moments, while for the YBCO samples considered here, T_c is unchanged with increasing n_2. This difference has been attributed to the fact that for HTSC the coherence length (ξ) is short, of the order of a lattice parameter, and a defect acts locally to suppress superconductivity on that length scale, without affecting the superconducting properties elsewhere.

IV. PROPERTIES CHARACTERISTIC OF THE "IDEAL" MATERIAL

With the extrapolations of measured parameters to $f_s=1$ that are made possible by the results presented in Sec. II, the superconducting state properties can be analyzed to obtain information about the nature of the superconducting state. In particular, the specific-heat anomaly at T_c has been analyzed[6] with the "α-model"[7] to obtain information about the strength of the coupling. In that model, the ratio of the 0-K energy gap to T_c, $2\Delta_0/k_BT_c \equiv \alpha$, is taken as an adjustable parameter, but a BCS temperature dependency for the gap is assumed. Fits to the specific-heat anomaly give $\alpha=6.8$, whereas the BCS weak-coupling value is 3.5 -- a clear indication of <u>strong coupling</u>. However, since it is data near T_c that is being used in the fit, it should be kept in mind that it is the temperature dependence of the gap near T_c, rather than Δ_0, that gives this indication.

In addition, it is possible to use the measured superconducting state parameters, corrected to $f_s=1$, to make rough estimates of γ, the coefficient of the normal-state electronic specific heat, a parameter that gives the density of electron states at the Fermi surface which is important to the interpretation of both normal- and superconducting-state properties. The α-model fit to the anomaly at T_c also gives a value for γ, $\gamma = 15$ mJ/mole$\cdot$K^2; an extrapolation of $d\gamma^*/dH$ to H_{c2} gives $\gamma = 18$ mJ/mole$\cdot$K^2; and extrapolation of $\gamma_2^* n_2$ to the value of n_2 at which superconductivity disappears gives $\gamma = 16$ mJ/mole$\cdot$K^2. Given the very rough nature of these estimates, their consistency has to be regarded as to some degree coincidental. Nevertheless, they may be as good as any available estimates of this important parameter. It is of interest to compare these estimates with calculations[8,9] of the "bare" or band-structure value, $\gamma_{bs} = 13\text{-}16$ mJ/mole$\cdot$K^2. The comparison suggests that the electron-phonon interaction (λ) given by $1+\lambda = \gamma/\gamma_{bs}$ is small, which suggests <u>weak coupling</u> if the conventional electron-phonon coupling is the mechanism. This discrepancy with the evidence from the anomaly at T_c that the coupling is strong is, however, just one of many associated with the value of λ and the nature of the coupling responsible for the superconductivity, and a definitive resolution of these discrepancies does not seem to be imminent.

V. AN EFFECT OF HEAT TREATMENT ON f_s AND n_2

Since the normal-state inclusions associated with, and measured by, n_2 are probably of dimensions comparable to a lattice parameter, they may be relevant to flux pinning and the critical current. It is thus of practical as well as theoretical interest to understand their relation to sample preparation procedures. Although many variations of sample preparation have been tried, very few have been accompanied by specific-heat measurements which are necessary to determine f_s and n_2. One result of recent work[10] at LBL is that these quantities can be varied by quenching a sample from 200°C to liquid nitrogen temperatures: That procedure resulted in a 10% reduction in f_s, consistent to within experimental uncertainty, with the changes in all the relevant parameters, n_2, $d\gamma^*/dH$, $\Delta C(T_c)$ and ΔS. This demonstrates the importance of details of sample preparation procedures in controlling the non-superconducting inclusions.

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FIGURE CAPTIONS

FIG. 1. Analysis of low-temperature data for C into its four components (see text for details).

FIG. 2. Analysis of data near T_c (see text for details).

FIG. 3. A demonstration of the mutual proportionality of $d\gamma^*/dH$, $\Delta C(T_c)$ and ΔS, and their use in determining relative values of f_s.

FIG. 4. The correlation of relative values of f_s with n_2, and the extrapolation to $n_2=0$ to determine the point at which $f_s=1$.

FIG. 5. Correlations of $\gamma^*(0)$ with concentrations of Cu^{2+} moments: $\gamma^*(0)$ with n (▾); $\gamma^*(0)$ with n_1 and n_2 separately (■,o), i.e., $\gamma^*(0)=\gamma^*_1 n_1+\gamma^*_2 n_2$.

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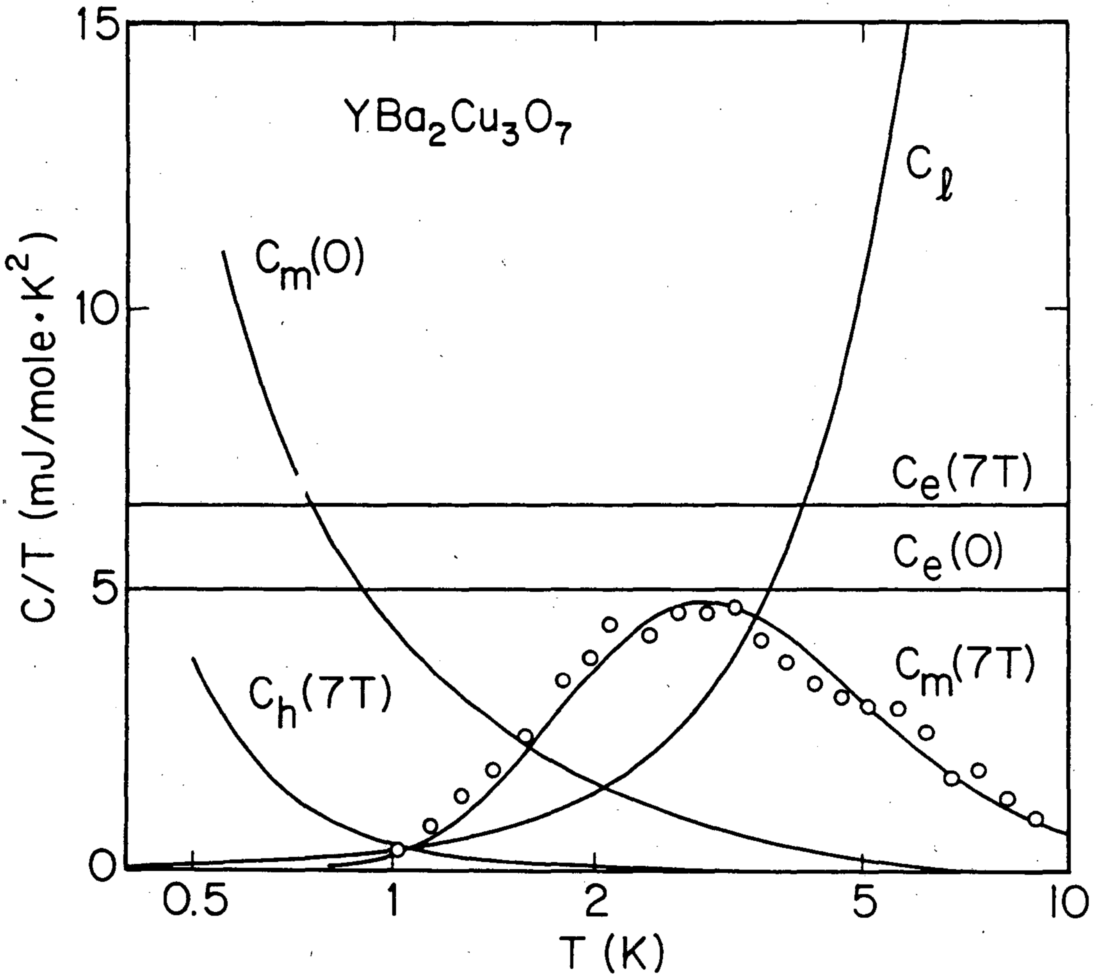

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FIG 1

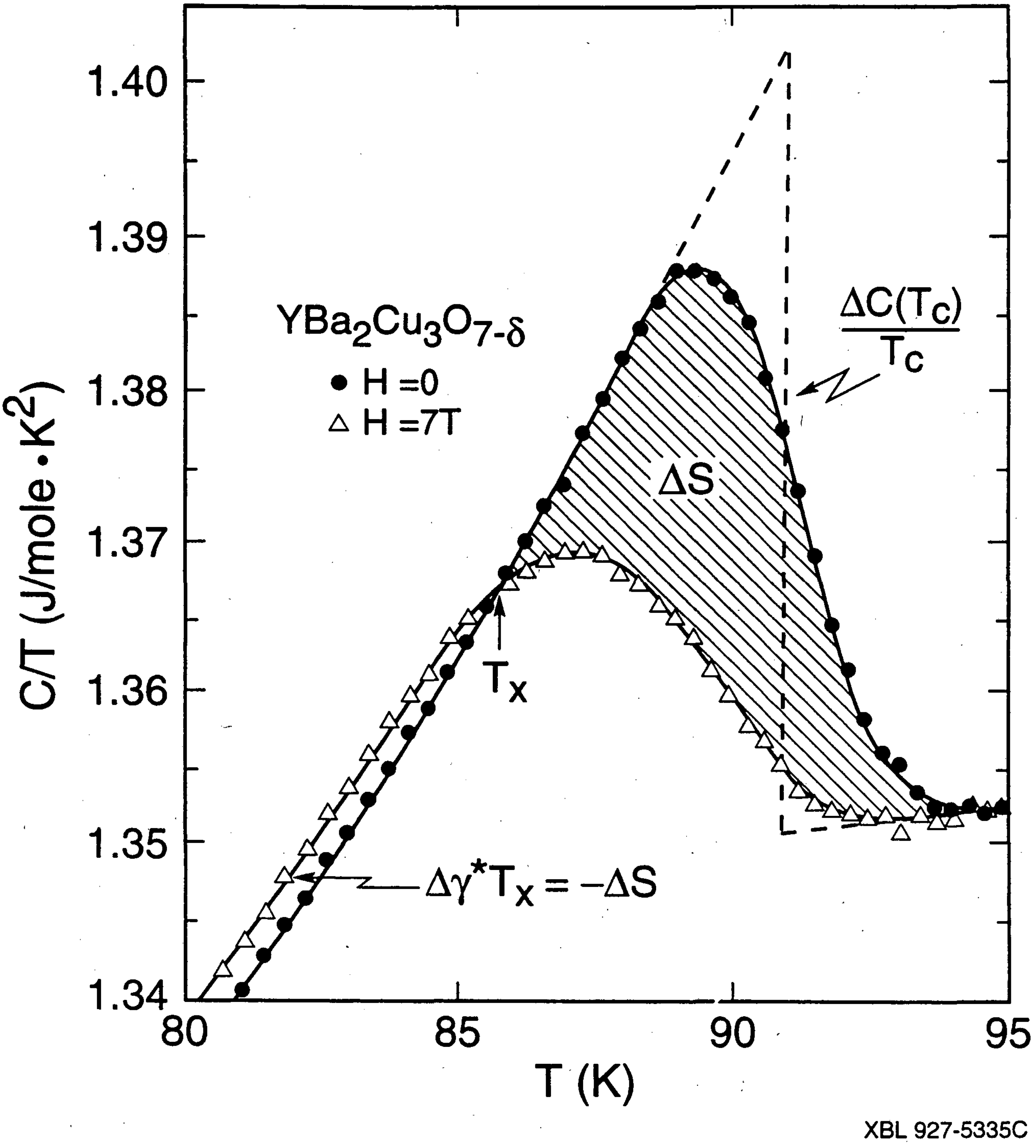

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FIG 2

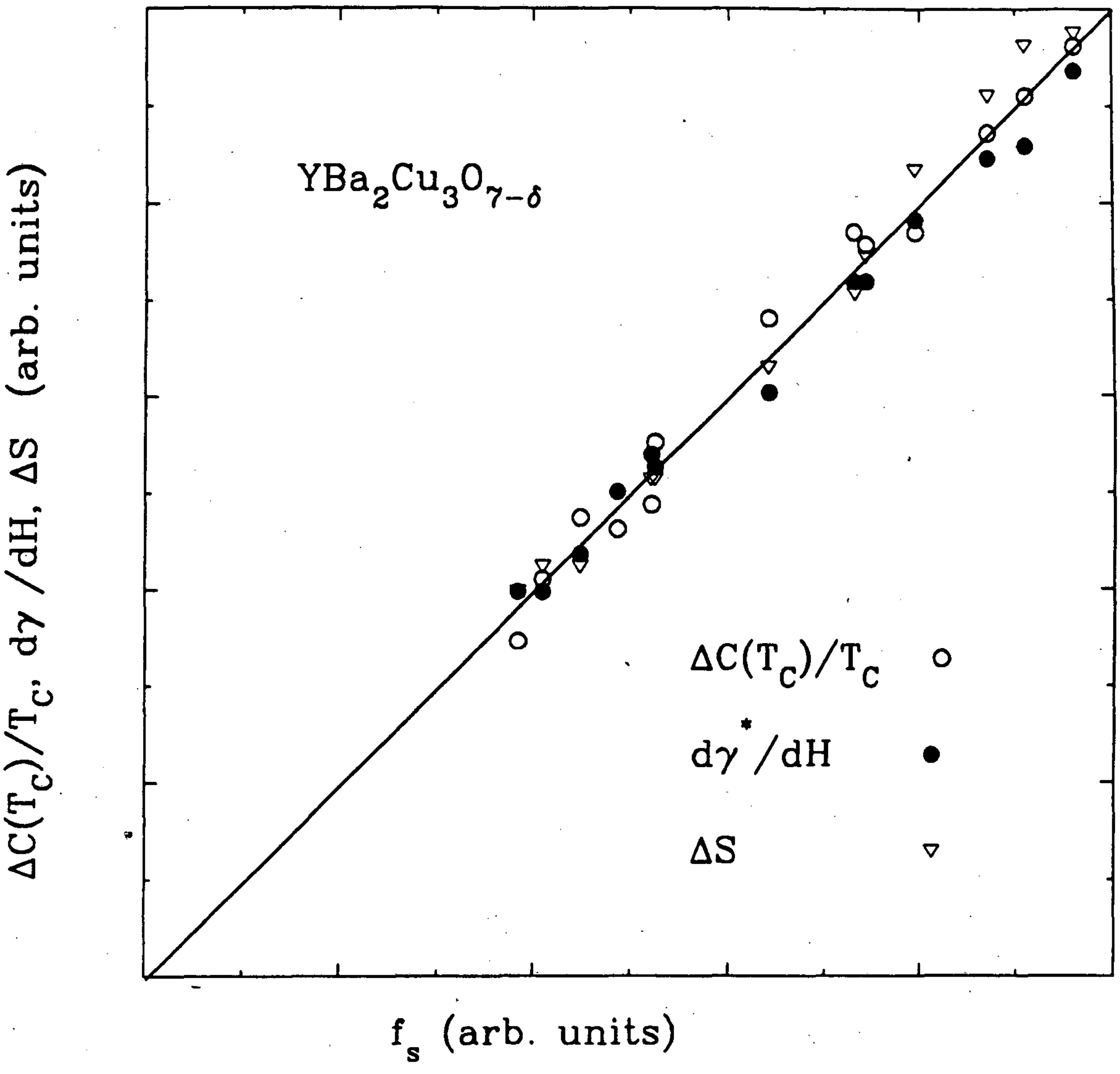

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FIG 3

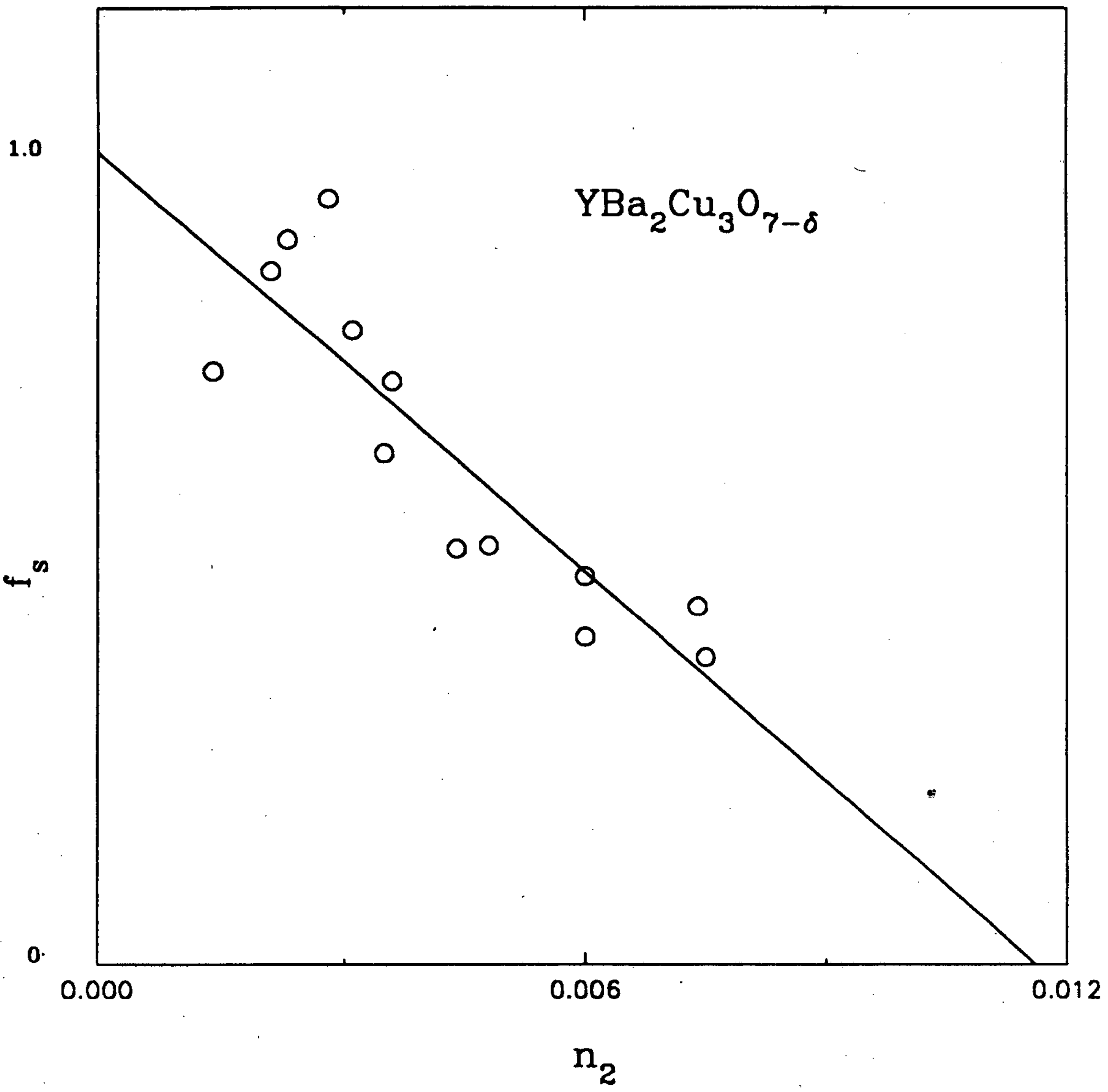

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FIG 4

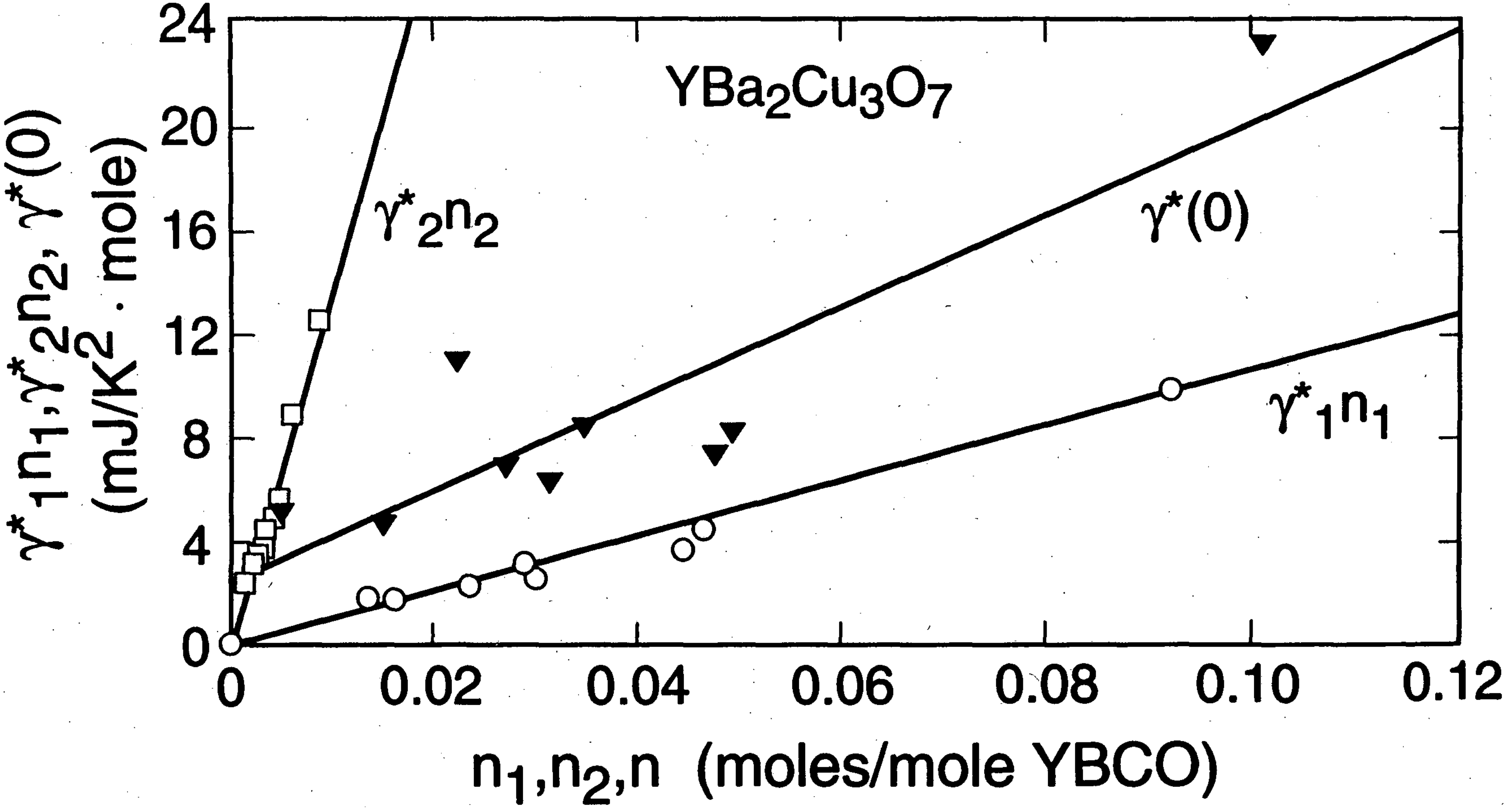

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FIG 5

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