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Authors
Phillips, N.E.
Emerson, J.P.
Fisher, R.A.
et al.

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by

N.E. PHILLIPS[*+], **J. P. EMERSON**[*+], **R.A. FISHER**[*+],

J. E. GORDON[*§], **B. F. WOODFIELD**[*+] and **D. A. WRIGHT**[*+]

**Lawrence Berkeley Laboratory*
University of California
Berkeley, CA 94720

+Department of Chemistry, University of California
Berkeley, CA 94720 (address for mail)

§Department of Physics, Amherst College
Amherst, Massachusetts 01002

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N. E. Phillips[*+], J. P. Emerson[*+], R. A. Fisher[*+], J. E. Gordon[*§], B. F. Woodfield[*+], and D. A. Wright[*+]

[*]Lawrence Berkeley Laboratory, Berkeley, CA 94720
[+]Department of Chemistry, University of California, Berkeley, CA 94720 (address for mail)
[§]Department of Physics, Amherst College, Amherst, MA 01002

Specific heat measurements, including measurements in magnetic fields and at both low temperatures and near T_c, on a number of $YBa_2Cu_3O_7$ samples have revealed several correlations among strongly sample dependent parameters. These correlations suggest that the sample dependence of the parameters reflects a sample dependence of the volume fraction of superconductivity, which is in turn correlated with a low concentration of Cu^{2+} moments. The correlations give a criterion for recognizing the values of the parameters characteristic of the fully superconducting material. Preliminary results on the effects of sample heat treatment are reported. New data on the "linear term" is presented and discussed.

1. INTRODUCTION

The sample-to-sample variation in the properties of high-T_c materials is a general and serious problem in connection with attempts to recognize intrinsic properties and distinguish them from effects associated with impurity phases or other defects. The specific heat (C) is unique among commonly measured properties in giving a true volume average of bulk properties, and therefore can play a special role in understanding the sample dependence [1]. Measurements at LBL on a variety of $YBa_2Cu_3O_7$ (YBCO) samples, including a number made in other laboratories, have revealed correlations between a number of sample-dependent parameters that suggest that the volume fraction of superconductivity (f_s) is strongly sample dependent (and therefore probably a major factor in the variation of properties in general) and that the non-superconducting regions are associated with a low concentration (n_2) of Cu^{2+} magnetic moments [2,3]. In addition to measurements on a large number of samples, recognition of these correlations required a unique combination of measurements in magnetic fields (H) and at both low temperatures and near T_c -- all made on the same samples.

2. SPECIFIC HEAT-DERIVED PARAMETERS RELEVANT TO THE VOLUME FRACTION OF SUPERCONDUCTIVITY

Two of the parameters derived from C that are relevant to the determination of f_s are defined in Fig. 1: $\Delta C(T_c)/T_c$, here defined by a simple entropy-conserving construction, is a measure of the magnitude of the specific heat anomaly at T_c; ΔS is a measure of the effect of a magnetic field of 7T on that anomaly. These are both parameters that might be expected to be proportional to f_s. The other parameters of interest in this connection are derived by an analysis of the low-temperature C into its components: the lattice contribution (C_ℓ); the "linear term" (C_e); a contribution associated with Cu^{2+} magnetic moments (C_m);, and a hyperfine contribution (C_h) that occurs only for $H \neq 0$. The analysis of C into these four components is illustrated for a typical YBCO sample in Fig. 2. The linear term has a field dependence that can be represented by

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

where the H-proportional term corresponds to the mixed-state electron specific heat that is well known in conventional type II superconductors and its coefficient, $d\gamma^*/dH$, should also be proportional to f_s. For $H=0$ the contribution of the Cu^{2+} moments appears as the high-temperature tail of a broadened Schottky-like anomaly produced by the distribution of internal fields; for an applied field $H=7T$, which is large compared with the internal fields, it is well approximated by the Schottky anomaly labeled $C_m(7T)$ in Fig. 2. The quality of the fit to the 7T data is indicated by comparison of the experimental points, from which the other contributions have been subtracted, with the Schottky curve. The amplitude of the Schottky curve determines n_2.

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 if the value for a fully superconducting, $f_s = 1$, sample were known:

$$\frac{d\gamma^*/dH}{[d\gamma^*/dH]_{f_s=1}} = \frac{\Delta C(T_c)}{[\Delta C(T_c)]_{f_s=1}} = \frac{\Delta S}{[\Delta S]_{f_s=1}} = f_s. \tag{2}$$

Since none of the denominators in Eq. 2 is known, a least-squares procedure that gave equal weight to each of the parameters was used to derive the most consistent <u>relative</u> 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 $d\gamma^*/dH$, $\Delta C(T_c)/T_c$ and ΔS, and therefore supports the suggestion that each is a measure of f_s.

There is also a correlation of f_s with n_2, shown in Fig. 4, that provides the basis for putting f_s on an <u>absolute</u> basis. It shows that f_s decreases with increasing n_2 suggesting that the Cu^{2+} moments are in some way associated with a defect that suppresses the transition to the superconducting state, and that extrapolation back to $n_2 = 0$ should identify the point on the f_s axis at which the <u>absolute</u> value of f_s is $f_s = 1$ (see Fig. 4). With this identification the values of $d\gamma^*/dH$, $\Delta C(T_c)/T_c$, ΔS and all other specific-heat derived parameters, for a fully superconducting sample, are determined. The correlation of n_2 with f_s, i.e., with the superconductivity-related parameters $d\gamma^*/dH$, $\Delta C(T_c)/T_c$ and ΔS, shows that these Cu^{2+} moments must be located, at least in substantial measure, on the YBCO lattice. However, that correlation (Fig. 4) is clearly less precise than those among $d\gamma^*/dH$, $\Delta C(T_c)/T_c$ and ΔS themselves (Fig. 3) suggesting that, as expected, <u>some</u> of these moments are in impurity phases.

3. SOME EFFECTS OF HEAT TREATMENT ON THE VOLUME FRACTION OF SUPERCONDUCTIVITY

The interpretation of the sample-to-sample variation of the properties of YBCO as reflecting a corresponding variation of f_s raises an obvious question: How is f_s affected by sample preparation techniques? As part of an effort to answer this question, a ceramic sample of YBCO has been subjected to a series of heat treatments—two successive quenches into liquid nitrogen after heating to 200°C (comparable quenches have occasionally been used to fix the oxygen stoichiometry); a rapid cooling through the tetragonal/orthorhombic (T/O) transition (actually from 950°C to 350°C); and finally, "reconstitution" by annealing at 950°C and slow cooling to 350°C—with intermediate measurements of f_s, n_2, and resistivity (ρ). Since the superconducting properties are also sensitive to oxygen content, the oxygen stoichiometry was monitored by high temperature susceptibility measurements which showed that no significant changes occurred. Table I gives the value of f_s determined by $\Delta C(T_c)$, n_2 and, for comparison, $f_s(n_2)$, the value of f_s derived from n_2 and its relation to f_s shown in Fig. 4.

The first quench reduced f_s from 0.85 to 0.78; increased n_2, but by a larger relative amount; and changed ρ dramatically, increasing its magnitude and altering the T-proportional behavior (see Fig. 5). (Changes in ρ of this kind have been attributed to changes in oxygen content, but evidently they can be produced by the quench itself when a quench is used to fix the oxygen stoichiometry.) The second quench, and the rapid cooling through the T/O transition produced further reductions in f_s but no significant increases in n_2. The second quench caused a small further increase in ρ; reheating to 950°C, even with rapid cooling through the T/O transition, restored ρ to its original value. Apparently the defects that changed ρ, that were produced in the first quench, were completely repaired by heating to 950°C. Finally, after reconstitution at 950°C and slow cooling to 350°C, f_s increased and n_2 decreased, but the volume fraction of superconductivity remained lower than in the original sample [4].

4. THE LINEAR TERM

There has been a great deal of interest in the zero-field contribution to the linear term, $\gamma^*(0)$ in Eq. (2), because it has no counterpart in conventional superconductors. In early measurements [5] it was shown that impurity phases, particularly $BaCuO_2$, could make significant contributions to $\gamma^*(0)$, but it was often concluded that there was an "intrinsic" contribution as well. It has also been suggested [2] that $\gamma^*(0)$ could be accounted for by a sum of two contributions produced by, respectively, the impurity phases and the normal regions associated with the Cu^{2+} moments present in concentration n_2. That suggestion was based on using the concentration of Cu^{2+} moments in impurity phases (n_1) as a measure of the contribution of those phases to $\gamma^*(0)$. The moments that order below 1K in zero applied field, affect the superconducting properties (see Fig.4), and contribute to the Schottky anomaly in Fig. 2, are present in concentration n_2; most of those that are present in impurity phases, in concentration n_1, order at higher temperatures and do not contribute to the Schottky anomaly. Both kinds contribute to the Curie-Weiss term in the high temperature susceptibility, which therefore determines the total concentration, $n=n_1+n_2$. Since n_2 is determined by the low-temperature in-field C, both n_1 and n_2 are known. An analysis of $\gamma^*(0)$ based on the relation of $\gamma^*(0)=\gamma_0+\gamma_1 n_1+\gamma_2 n_2$, where γ_0 is an intrinsic contribution, led to the conclusion that γ_0 was less than 1mJ/K^2·mole, and negligible to within the accuracy of the data. The conclusion was that the data could be explained without invoking an intrinsic contribution. The figure showing the n_1- and n_2-proportional contributions is reproduced here as Fig. 6.

In connection with the interpretation of the linear term in YBCO, it is noteworthy that, in spite of continued attention to sample quality, it seems that no sample has shown a value of $\gamma^*(0)$ significantly less than 4mJ/K^2·mole. Measurements from other laboratories do not provide the values of n_1 and n_2 necessary to test the decomposition of $\gamma^*(0)$ into two components, but five new measurements at LBL have been added to those of Fig. 6 and are included in Figs. 7 and 8 where the two components are shown separately for greater clarity. Figs. 7 and 8 represent a comparison of the new data with the old, based on the parameters derived in the earlier analysis -- <u>not</u> a new analysis that includes the new data as well as the old. The points for the two Zn-doped samples were included in the original analysis because the data for those samples fit all the relevant correlations. However, the larger number of points for low values of n_2 (see Fig. 7) now emphasizes a discrepancy between those points and an extrapolation from the low-n_2 points such as that represented by the dashed line. A new analysis with the Zn-doped points excluded gives in addition to the n_1- and n_2-proportional components, an intrinsic contribution, $\gamma_0 \sim 2$ mJ/K^2·mole, which is to be compared with an upper limit of less than 1mJ/K^2·mole from the original analysis. For that reason, and for the perhaps more compelling reason that the directly measured minimum $\gamma^*(0)$ remains in the vicinity of 4mJ/K^2·mole, the possibility of an intrinsic γ_0 must be recognized.

If there is an intrinsic linear term, it is possible that YBCO is unique among high-T_c superconductors in this respect, and that the linear term is associated with the Cu-O chains. The existence of a linear term associated with the Cu-O chains in YBCO has already been suggested, and its absence in other high-T_c superconductors is consistent with existing data on their specific heats. For both $(La, Sr)_2CuO_4$ and the Bi compounds there are no impurity phases with large pseudo-linear terms that are expected to make significant contributions to $\gamma^*(0)$, and the interpretation of the data is therefore much more straightforward than for YBCO. In the case of $(La, Sr)_2CuO_4$ at least one sample has shown a $\gamma^*(0)$ value less than 1mJ/K^2·mole, and a correlation of $\Delta C(T_c)/T_c$ with $\gamma^*(0)$ suggests that $\gamma^*(0)$ is zero for a fully superconducting sample; for the Bi compounds a number of samples have shown $\gamma^*(0)$ values that are substantially less than 1mJ/K^2·mole, and, within the experimental uncertainty, $\gamma^*(0)=0$ [9].

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Table I. Volume fraction of superconductivity determined from $\Delta C(T_c)$, $f_s = \Delta C(T_c)/78T_c$; and from n_2, $f_s(n_2) = 1 - n_2/0.012$.

Condition	f_s	n_2	$f_s(n_2)$
Original	0.85	0.0023	0.81
After first quench	0.78	0.0036	0.70
After second quench	0.73	0.0037	0.68
After rapid cool 950-350°C	0.62	0.0038	0.68
After reconstitution	0.73	0.0032	0.73

FIGURE CAPTIONS

Fig. 1 The specific heat anomaly at T_c.

Fig. 2 Analysis of low-temperature specific heat into its components.

Fig. 3 Mutual proportionality of $d\gamma^*/dH$, $\Delta C(T_c)/T_c$ and ΔS: Determination of relative values of f_s.

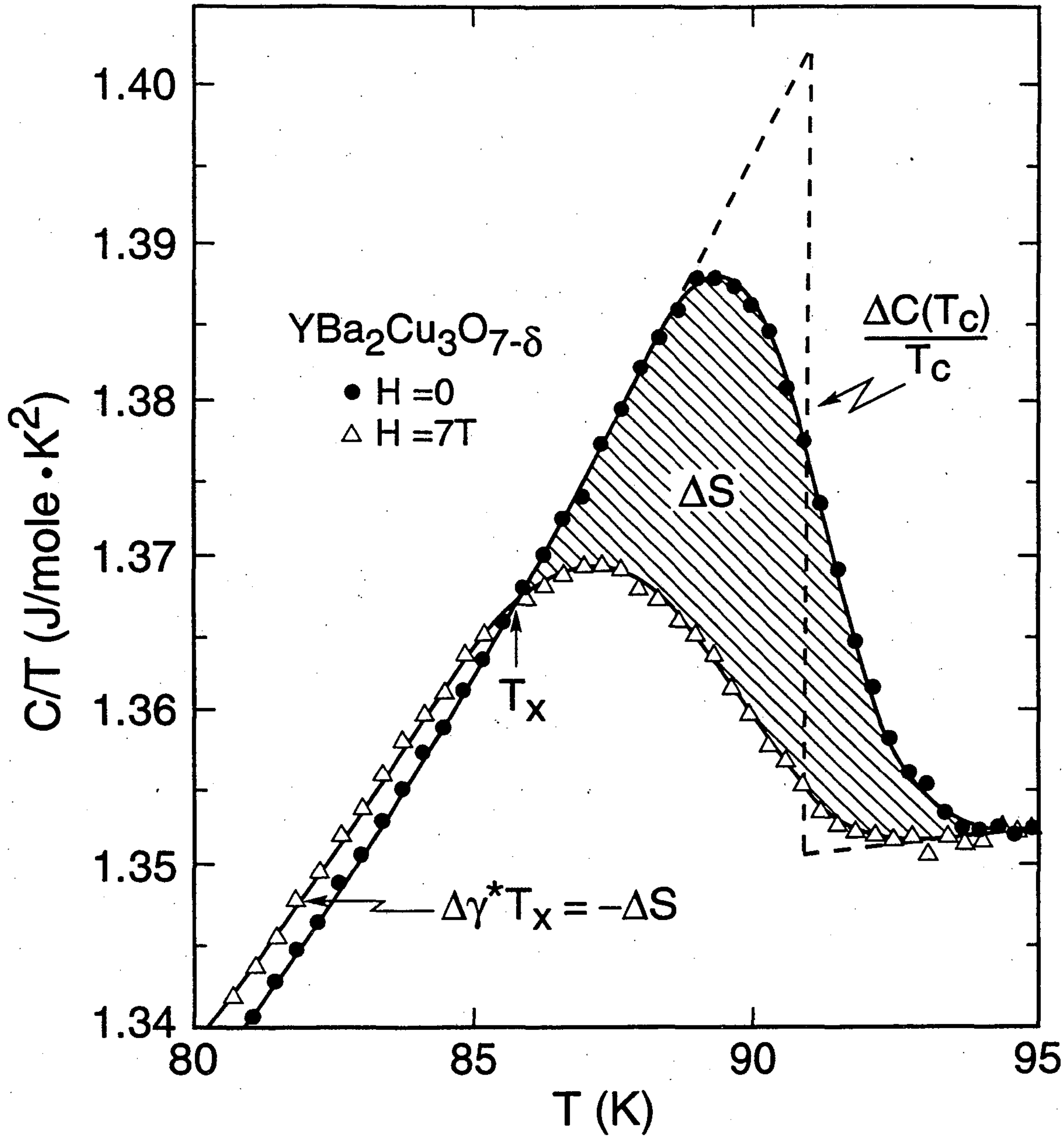
Fig. 4 Correlation of f_s with n_2.

Fig. 5 Resistivity vs. temperature, before and after quench.

Fig. 6 Original analysis of $\gamma^*(0)$ into $\gamma_1 n_1$ and $\gamma_2 n_2$ components.

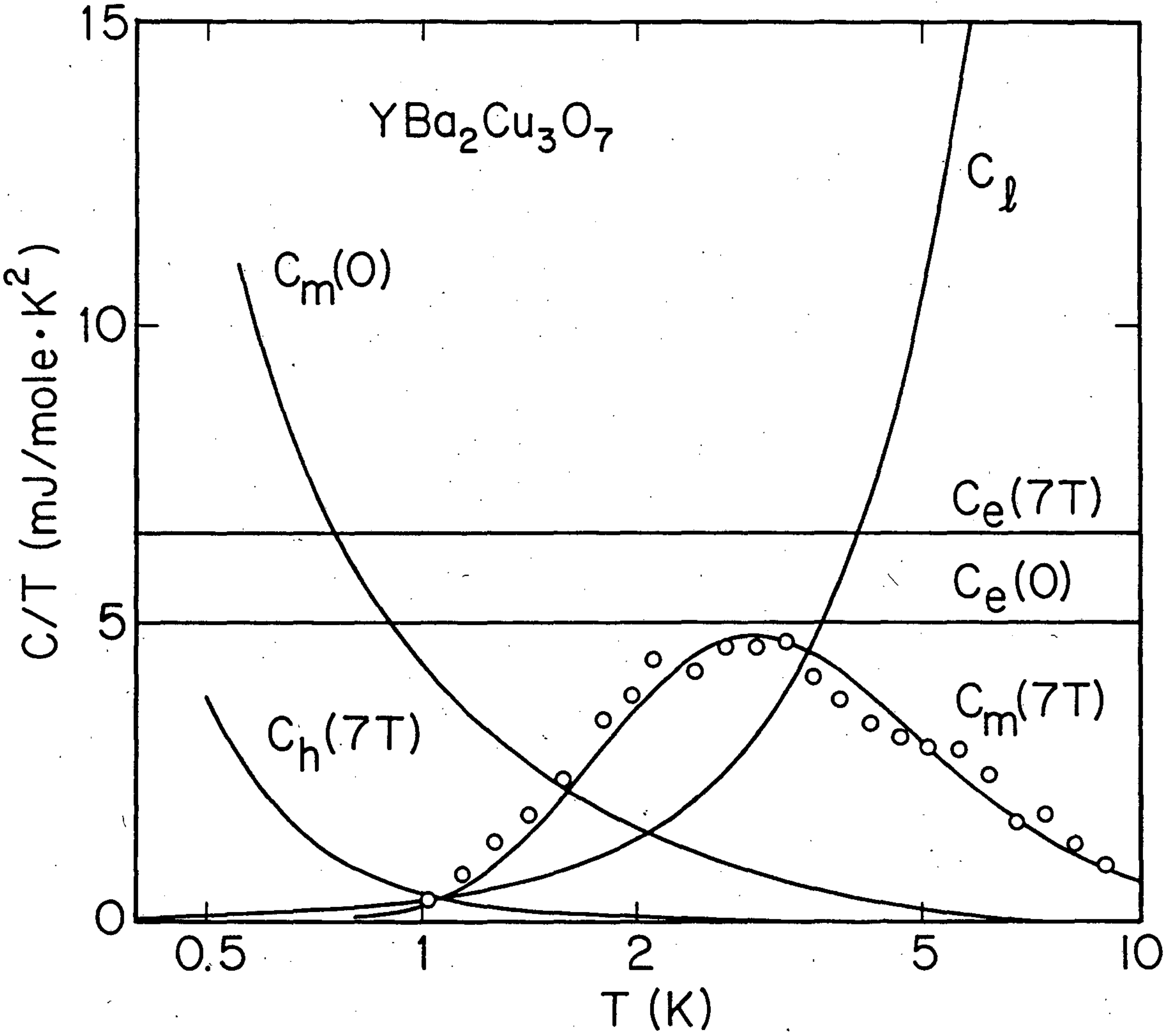
Fig. 7 $\gamma_2 n_2$ component of $\gamma^*(0)$; original analysis, but with new data added.

Fig. 8 $\gamma_1 n_1$ component of $\gamma^*(0)$; original analysis, but with new data added.



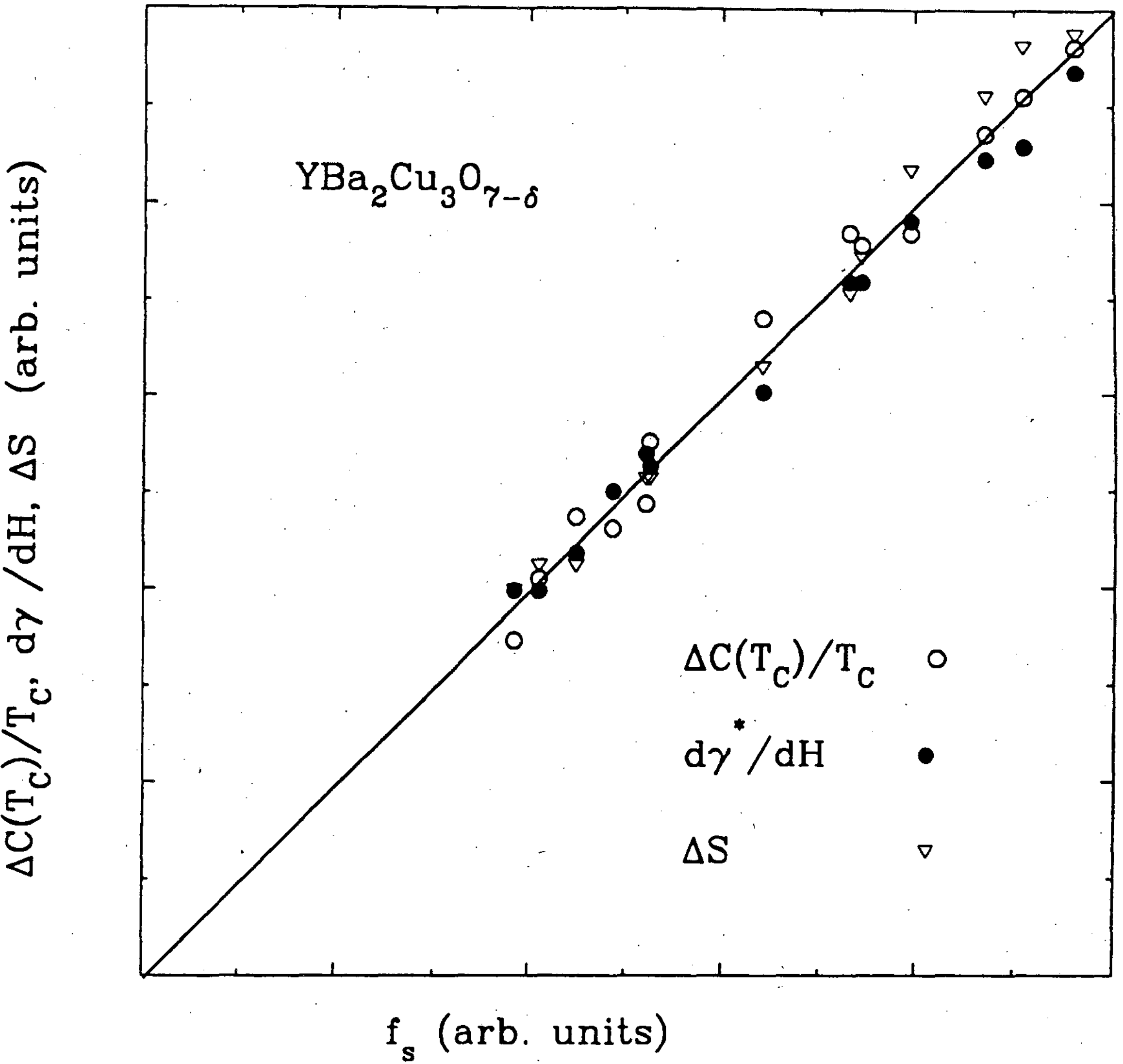
XBL 927-5335C

FIG. 1



XBL 904-1224

FIG. 2



XBL 9111-2461

FIG. 3

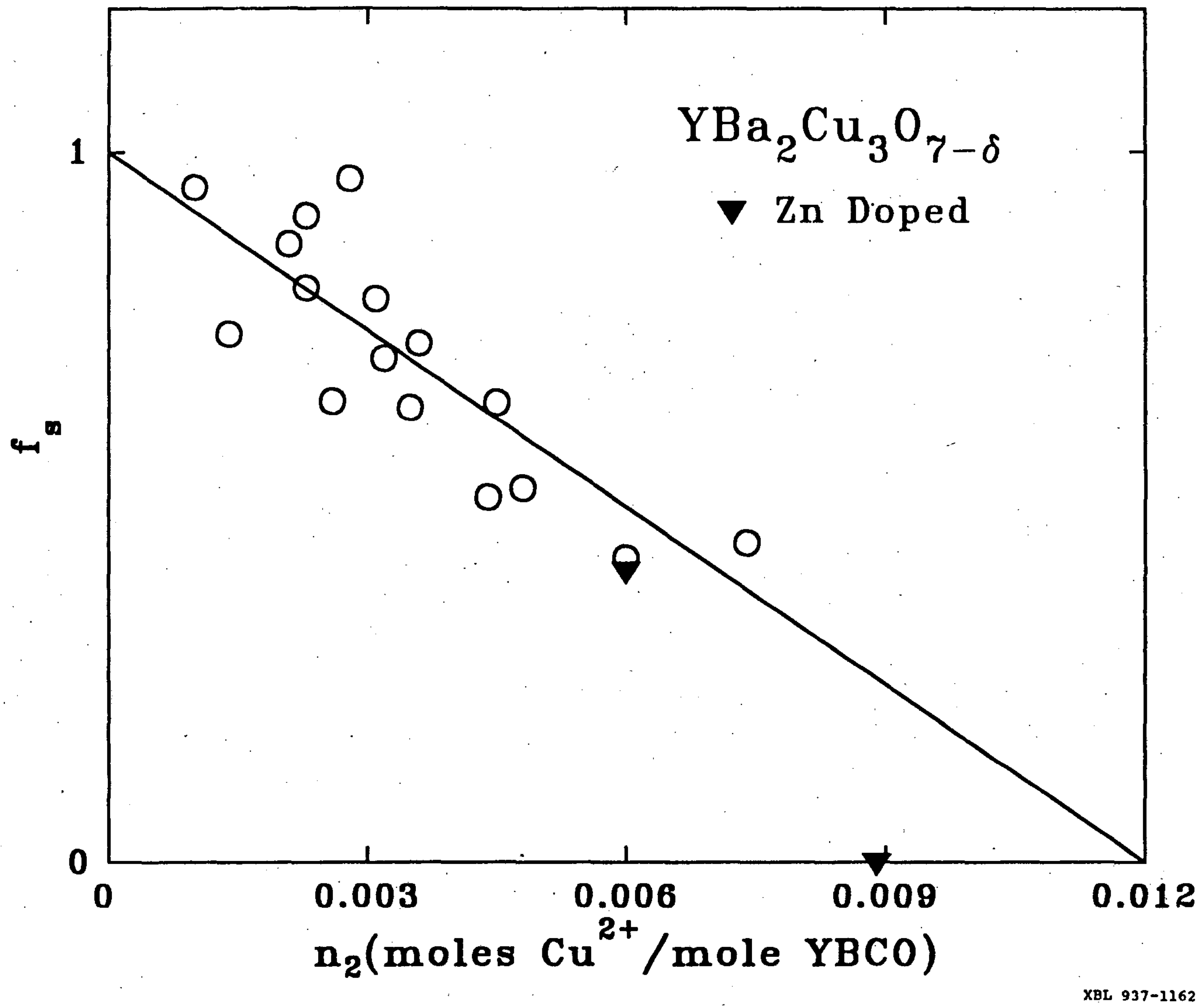
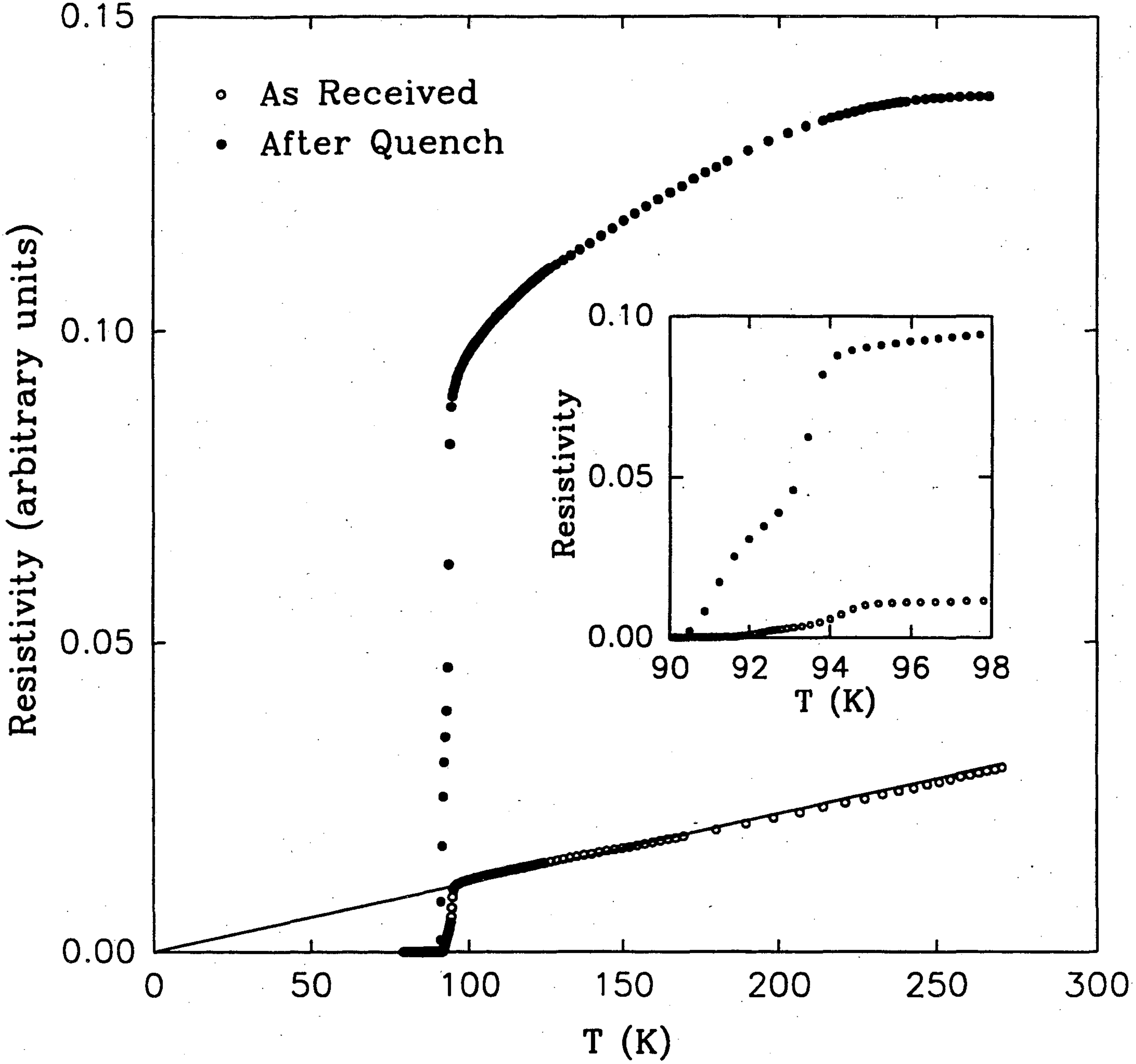
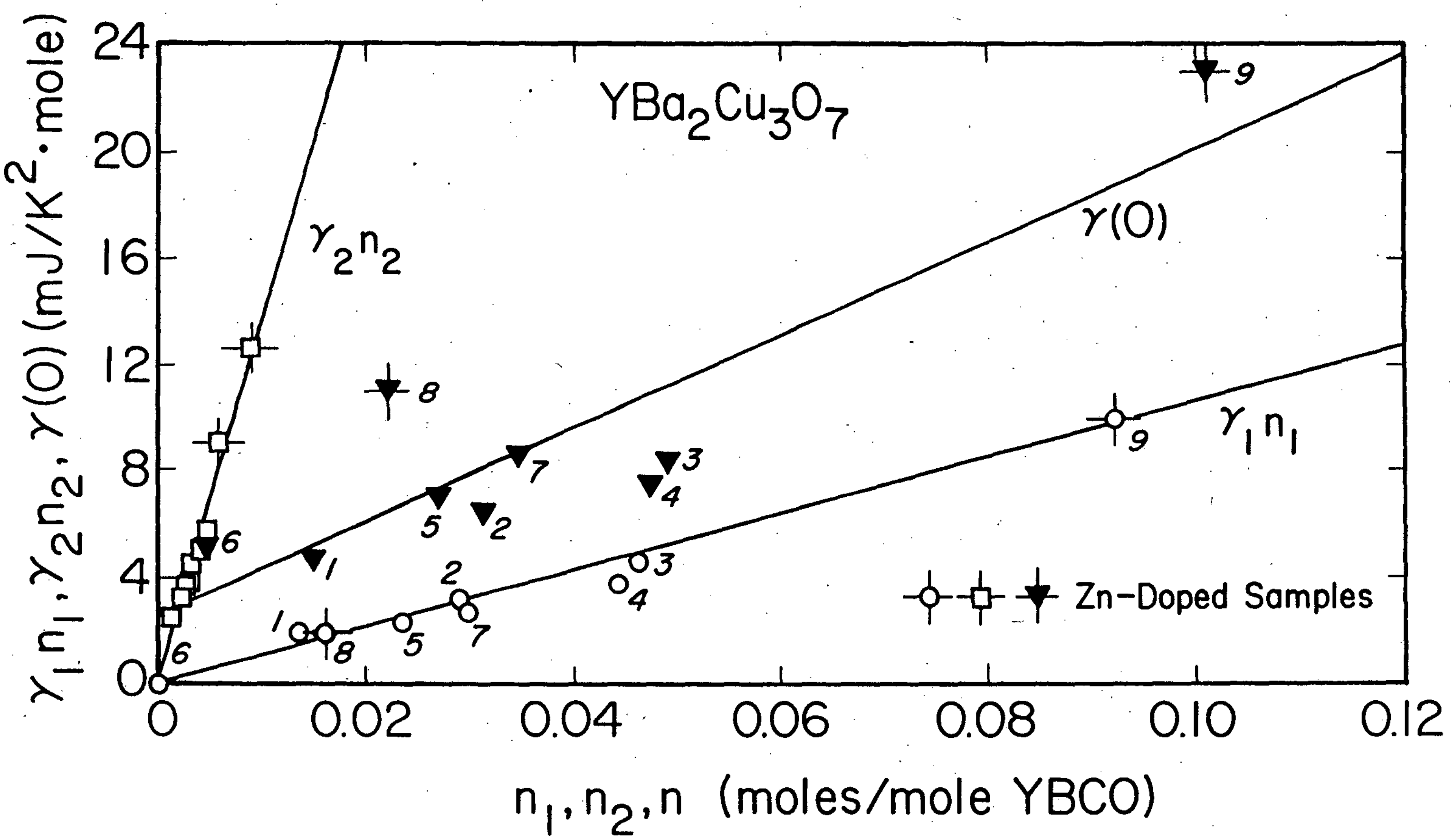

$YBa_2Cu_3O_{7-\delta}$
▼ Zn Doped
f_s
1
0
0
0.003
0.006
0.009
0.012
n_2(moles Cu^{2+}/mole YBCO)
XBL 937-1162

FIG. 4



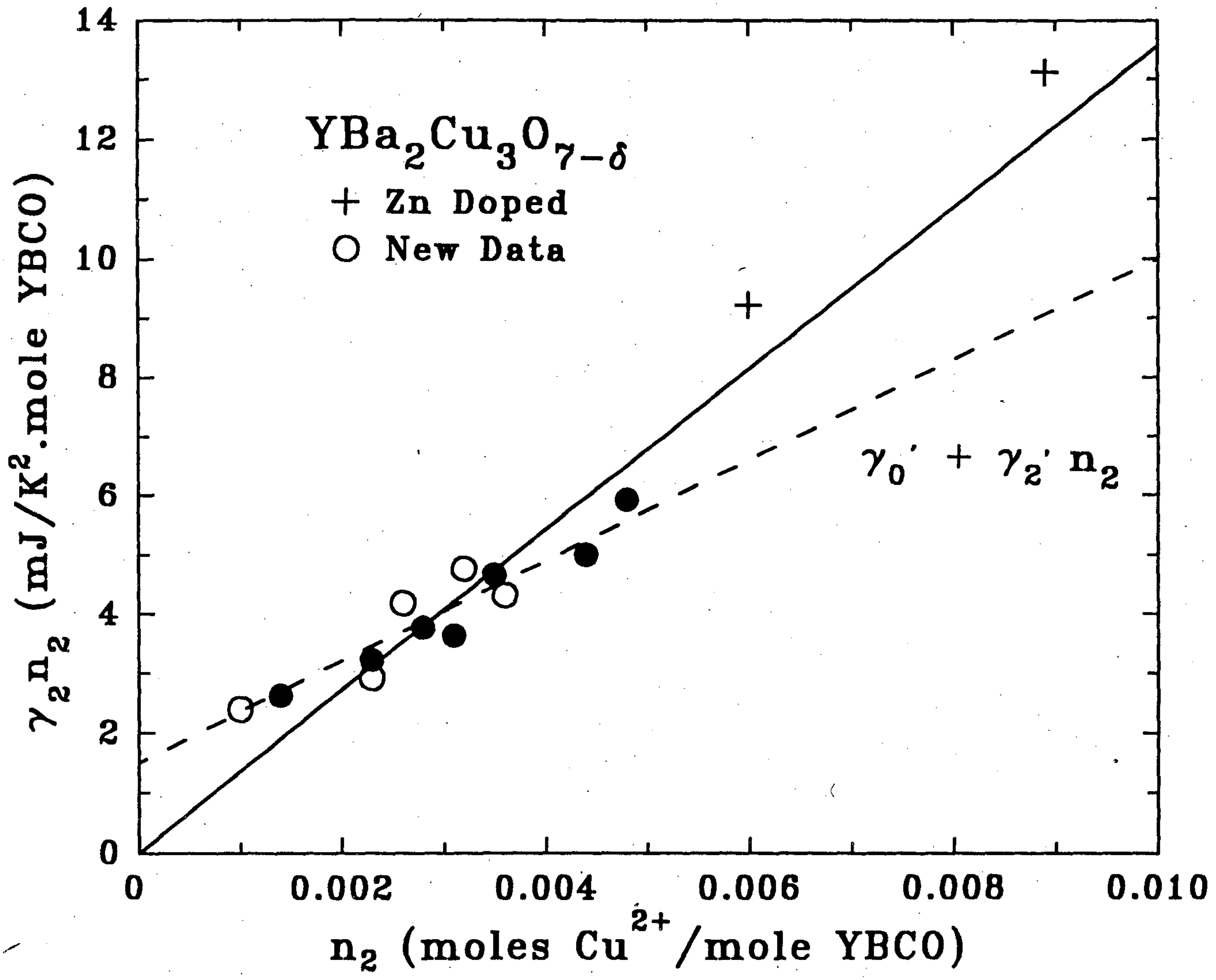
XBL 9212-2570

FIG. 5



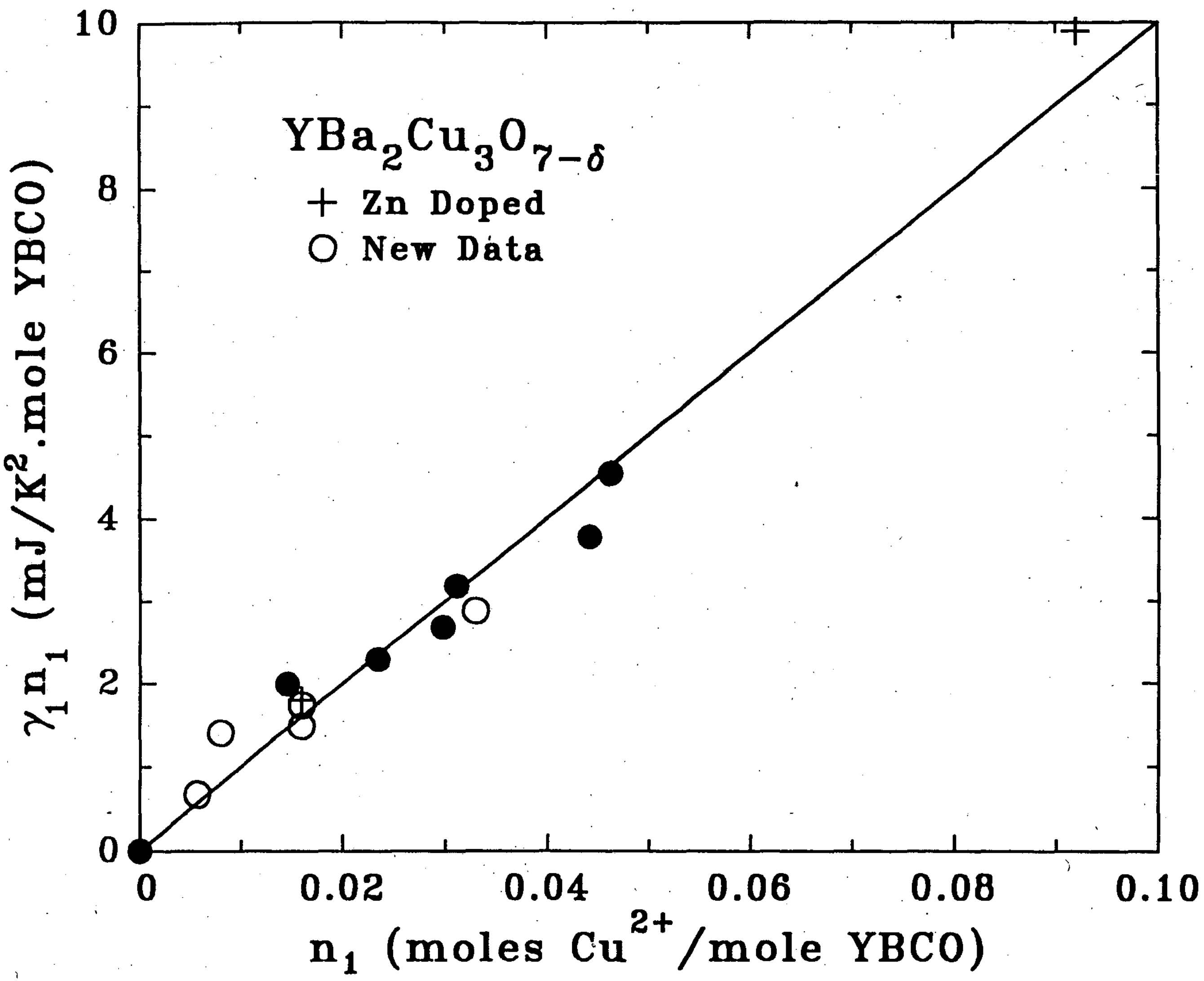
XBL 897-2700A

FIG. 6



XBL 937-1160

FIG. 7



XBL 937-1161

FIG. 8

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720