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

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N.E. Phillips, R.A. Fisher, J.E. Gordon, S. Kim, A.M. Stacy, M.K. Crawford, and E.M. McCarron III

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DISCLAIMER

SPECIFIC HEAT OF $YBa_2Cu_3O_7$: ORIGIN OF THE "LINEAR" TERM, VOLUME FRACTION OF SUPERCONDUCTIVITY

Norman E. Phillips, R. A. Fisher, J. E. Gordon[+], S. Kim and A. M. Stacy

Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

M. K. Crawford and E. M. McCarron III

E. I. du Pont de Nemours and Co., Inc., Central Research and Development Department, Experimental Station, Wilmington, Delaware 19880-0356

ABSTRACT

It is shown that there is no evidence for a contribution to the "linear" term in the specific heat of $YBa_2Cu_3O_7$ that is characteristic of the superconducting state: the observed linear term is the sum of the previously recognized contribution from impurity phases and a second contribution associated with localized magnetic moments in the $YBa_2Cu_3O_7$ lattice that appear to produce normal regions by a pair-breaking mechanism. Estimates of several parameters related to the strength of the coupling are given. The model proposed has implications for the "weak-link" effect, and provides a quantitative measure of the volume fraction of normal material.

PACS numbers: 65.40.-f, 74.30.Ek, 74.30.Ci, 74.70.Ya

One of the interesting features of the high-T_c Cu-oxide superconductors is the occurrence of a "linear" term, $\gamma(0)T$, in the specific heat, C, at low temperature and in zero field. This term is consistent with the RVB theory[1], and also suggests more generally the absence of the energy gap that is characteristic of conventional superconductors. For these reasons it has attracted considerable attention, but there is still no consensus as to its origin or significance. For $YBa_2Cu_3O_7$, the most intensively investigated of these materials, impurity phases that are likely to be present, most notably $BaCuO_2$, can make significant contributions to $\gamma(0)$.[2] These phases contain Cu^{2+} magnetic moments that order near 10K producing a very high value of C at temperatures of a few K -- in just the relatively narrow window of temperature[3] in which $\gamma(0)$ is determined. However, the nature of the correlation of $\gamma(0)$ with estimates of the concentration of these phases, and the fact that values of $\gamma(0) \lesssim 4$ mJ/mole•K^2 have not been observed, have been taken as evidence that there is an intrinsic contribution to $\gamma(0)$ that is characteristic of the superconducting state.[3,4]

In this Letter we summarize correlations between several parameters[5] for a number of $YBa_2Cu_3O_7$ samples. The combination of measurements required to establish these correlations -- C, at low T and near T_c, and in magnetic fields; the magnetic susceptibility, χ, from below T_c to high T -- is unique to this work. In particular, it permits the independent determination of the concentrations of two types of magnetic moments: n_1, the concentration of the moments in impurity phases that order near 10K; and n_2, the concentration of Cu^{2+} moments in the $YBa_2Cu_3O_7$ lattice that order only below 1K. The correlations suggest that there is no evidence for a non-zero $\gamma(0)$ in the limit that <u>both</u> n_1 and n_2 are zero, i.e., that there is no contribution to $\gamma(0)$ that is characteristic of the pure superconducting state. Furthermore, various measures of the volume fraction of superconductivity and their correlations with n_2 point to the operation of a pair-breaking mechanism that suppresses the transition to the superconducting state, leaving parts of the sample normal and thus producing a previously unidentified contribution to $\gamma(0)$. A preliminary report on this work has been presented.[6]

For most $YBa_2Cu_3O_7$ samples, and for <u>all</u> that have been studied below 1K, there is a zero-field "upturn" in C/T that is transformed[7] into a Schottky-like anomaly near 4K in a field of 7T. It is evidently associated with magnetic moments that order below 1K in zero field. The Schottky anomaly is quantitatively consistent with Cu^{2+} moments, and determines their concentration, n_2. Since n_2 correlates with parameters characteristic of the superconducting state (see below), those moments must be located, at least in substantial measure, on the $YBa_2Cu_3O_7$ lattice. The <u>total</u> concentration of Cu^{2+} moments, $n=n_1+n_2$, is derived from the high-T Curie-Weiss term in χ.

Parameters characteristic of 12 samples, including two Zn-doped samples, are given in Table I. For one of the Zn-doped samples, the value of n is within the range of values for the undoped samples, and its properties are indistinguishable from those of the undoped samples. The solid triangles in Fig. 1 represent $\gamma(0)$ as a function of n. The correlation of $\gamma(0)$ with n is similar to that reported by the Geneva group[8] -- the data scatter widely, but the relation is approximately linear. A fit with $\gamma(0)=\gamma_0+\gamma' n$ gives $\gamma_0=2.5$ mJ/mole$\cdot$K^2 with an rms deviation of 34%. Taking n_1 and n_2 as independent variables, $\gamma(0)=\gamma_0+\gamma_1 n_1+\gamma_2 n_2$, gives $\gamma_0=0.1\pm0.8$ mJ/mole$\cdot$K^2, an rms deviation of 11%, and a value of γ_1 that is reasonable in relation to the properties[2] of $BaCuO_2$. The n_1- and n_2-proportional components of that fit are represented by the open circles and open squares in Fig. 1. Eliminating the γ_0 term does not appreciably affect the fit. Thus, for these samples, and within the experimental uncertainty, there is no evidence for a contribution to $\gamma(0)$ that is an intrinsic property of the superconducting state. The Geneva group[9] has reached a similar conclusion by applying a different, but apparently related, criterion to the samples studied there. For some samples, the absence of an upturn in C/T has been taken as showing the absence of extraneous contributions and the intrinsic nature of the observed $\gamma(0)$. However, impurity phases can contribute to $\gamma(0)$ without showing an upturn[2], and the observation of an upturn depends on the low-temperature limit of the measurements. We know of <u>no sample</u>[10] that is an obvious exception to the above correlation of $\gamma(0)$ with n_1 and n_2, and conclude that there is no evidence for an "intrinsic" contribution to $\gamma(0)$ for $YBa_2Cu_3O_7$.

The "ideal" value of the "jump" in C at T_c, $\Delta C(T_c)$, was determined by applying the usual entropy-conserving construction to data such as those shown in Fig. 2. The results are shown in Fig. 3 as $\Delta C(T_c)/T_c$ vs n_2. There is considerable scatter, which may reflect both the uncertainty in the determination of $\Delta C(T_c)$ and the possibility that some of the magnetic moments counted in n_2 are not on the $YBa_2Cu_3O_7$ lattice, but the relation is roughly linear. Since T_c is essentially constant, $\Delta C(T_c)$ also decreases roughly linearly with increasing n_2. Taken together with the $\gamma_2 n_2$ contribution to $\gamma(0)$, which is included in Fig. 3 for comparison, this behavior is strongly suggestive of the operation of a pair-breaking mechanism, an effect that is well established in conventional superconductors. As suggested by that comparison, the maximum value of $\Delta C(T_c)/T_c$, 77 $mJ/mole{\cdot}K^2$, the value characteristic of an ideal sample with $n_2=0$, was determined by fitting the data with a straight line, as shown in Fig. 3. For that purpose the point for sample 9, which showed a small Meissner effect but no measurable $\Delta C(T_c)$, was given zero weight because it seemed probable that $\Delta C(T_c)$ was not measurable only because the transition was too broad.

For conventional superconductors the operation of a pair-breaking mechanism and the associated occurrence of gapless superconductivity are characterized by linear relations between $\Delta C(T_c)$, n_2 and γ, as observed for $YBa_2Cu_3O_7$, but also by a linear decrease in T_c with increasing n_2 -- to $T_c=0$ for a value of n_2 comparable to that for which $\Delta C(T_c)=0$ -- and by a full Meissner effect, $-4\pi\chi_v=1$. The behavior of $YBa_2Cu_3O_7$ differs conspicuously from that of conventional superconductors in the n_2 dependence of T_c: for a value of n_2 for which $\Delta C(T_c)$ has decreased by more than a factor of 2, there is no significant change in T_c. The Meissner effect data are compared with $\Delta C(T_c)/T_c$ in Fig. 4. The vertical dashed line is at the maximum value of $\Delta C(T_c)/T_c$, and the sloping dashed line represents the Meissner effect that would be obtained if only a fraction of the sample proportional to $\Delta C(T_c)/T_c$ were superconducting <u>and the Meissner effect were not limited by pinning</u>. With the exception of the point for sample 9, for which $\Delta C(T_c)/T_c$ is probably underestimated, all the points fall below the sloping dashed line, and there is a trend to larger values of $-4\pi\chi_v$ with increasing $\Delta C(T_c)$. This behavior is consistent with a mixture of normal regions and superconducting regions in which the Meissner effect is limited by pinning, but it does not unequivocally rule out conventional gapless superconductivity. On the basis of the comparisons with pair breaking and gapless supercon- ductivity in conventional superconductors, we propose a somewhat different model, one that is also suggested by the very short coherence length, ξ: Superconductivity is suppressed by the pair-breaking interaction, but because ξ is small the result is a mixture of normal regions in the vicinity of magnetic moments, and superconducting regions with T_c unchanged elsewhere, rather than gapless superconductivity with T_c uniformly depressed everywhere. The n_2 dependence of $\Delta C(T_c)$ is a measure of the volume fraction of superconductivity. The observed linear relation between $\Delta C(T_c)$ and n_2 is reasonable for this model for values of n_2 that are not too high, but it does not have the theoretical basis for values of all n_2 that exist for gapless superconductors. The Meissner effect, and other measures of the volume fraction of superconductivity derived from C data, which correlate[5] with $\Delta C(T_c)$, are also consistent with the model.

The proposed interpretation and model have several implications for the nature of the superconducting state. An estimate of the normal-state γ can be obtained by extrapolating the straight-line n_2 dependences of $\gamma_2 n_2$ and $\Delta C(T_c)$ to the fully normal state. The result is γ=16 mJ/mole$\cdot K^2$, which is on the low side of the range of estimates obtained by other means but not unreasonable. Combining that value with $\Delta C(T_c)/T_c$ for the fully superconducting state gives $\Delta C(T_c)/\gamma T_c$=4.8, consistent with extreme strong coupling. The effectiveness of Cu^{2+} moments as pair-breaking centers -- a concentration of the order of one per hundred unit cells suppresses superconductivity completely -- provides additional evidence for singlet spin pairing.

Finally, the model has implications of interest for technical applications. It is widely believed that the low critical currents in bulk ceramic $YBa_2Cu_3O_7$ samples are associated with normal or weakly superconducting inclusions that separate the more perfectly superconducting regions -- the "weak-link" effect. The value of $\Delta C(T_c)$ provides a measure of the volume fraction of these inclusions, and shows that even for samples prepared by methods believed to give good superconducting material, there are substantial normal-state inclusions.

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TABLE I. Derived parameters characteristic of the samples. Samples 8 and 9 were Zn-doped, $YBa_2(Cu_{3-x}Zn_x)O_7$, with x=0.03 and 0.15, respectively. T_c is the temperature of onset of the Meissner effect, which was in every case sharp. n and n_2 are moles Cu^{2+} per mole $YBa_2Cu_3O_7$. $-4\pi\chi_v$ is the fractional Meissner volume measured in 1 mT and corrected for sample shape. Other quantities are in mJ-mole-K units.

	n	n_2	$\gamma(0)$	$\Delta C(T_c)/T_c$	$-4\pi\chi_v$	T_c
1	0.015	0.0014	4.6	59	0.51	91
2	0.031	0.0023	6.4	71	0.30	91
3	0.049	0.0028	8.3	75	0.30	91
4	0.047	0.0031	7.4	60	0.34	91
5	0.027	0.0035	6.95	53	0.50	92
6	0.0044	0.0044	5.0	38	0.48	91
7	0.035	0.0048	8.6	43	0.17	91
8	0.022	0.0060	11	32	0.17	89
9	0.101	0.0089	23	0	0.05	75
10	-	0.0036	7.2	60	-	-
11	-	0.0060	11	36	0.23	92
12	-	0.0074	7.9	37	0.24	91

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+ Permanent Address: Physics Department, Amherst College, Amherst, Massachusetts 01002.

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10. The sample described in Refs. 4 and 11 deserves special notice because it was unusually well characterized. C was measured from 2 to 10K, in fields to 3T. The reported $\gamma(0)$, 4.37 mJ/mole•K^2, was assumed to be intrinsic because no upturn in C/T was observed and an upper limit of 0.3 wt% was placed on the amount of $BaCuO_2$ (n_1=0.009). However, various possible non-intrinsic contributions could account for a significant fraction of $\gamma(0)$: The upper limit to the $BaCuO_2$ contribution is 1.4 mJ/mole•K^2; the reported 2 wt% of Y_2BaCuO_5 would contribute 0.3 mJ/mole•K^2; the reported anomalous field dependence of the T^3 term in C is equally well represented by the high-T side of a Schottky anomaly that corresponds to n_2=9.5x10^{-4} and a contribution to $\gamma(0)$ of 1.3 mJ/mole•K^2 (the upturn in C/T at 2K would be comparable to the precision of the data); and, finally, <u>the high-T χ data show that 8 to 12% of the Cu is present as Cu^{2+}</u> (n=0.24 to 0.36), i.e., as other phases of unknown properties.

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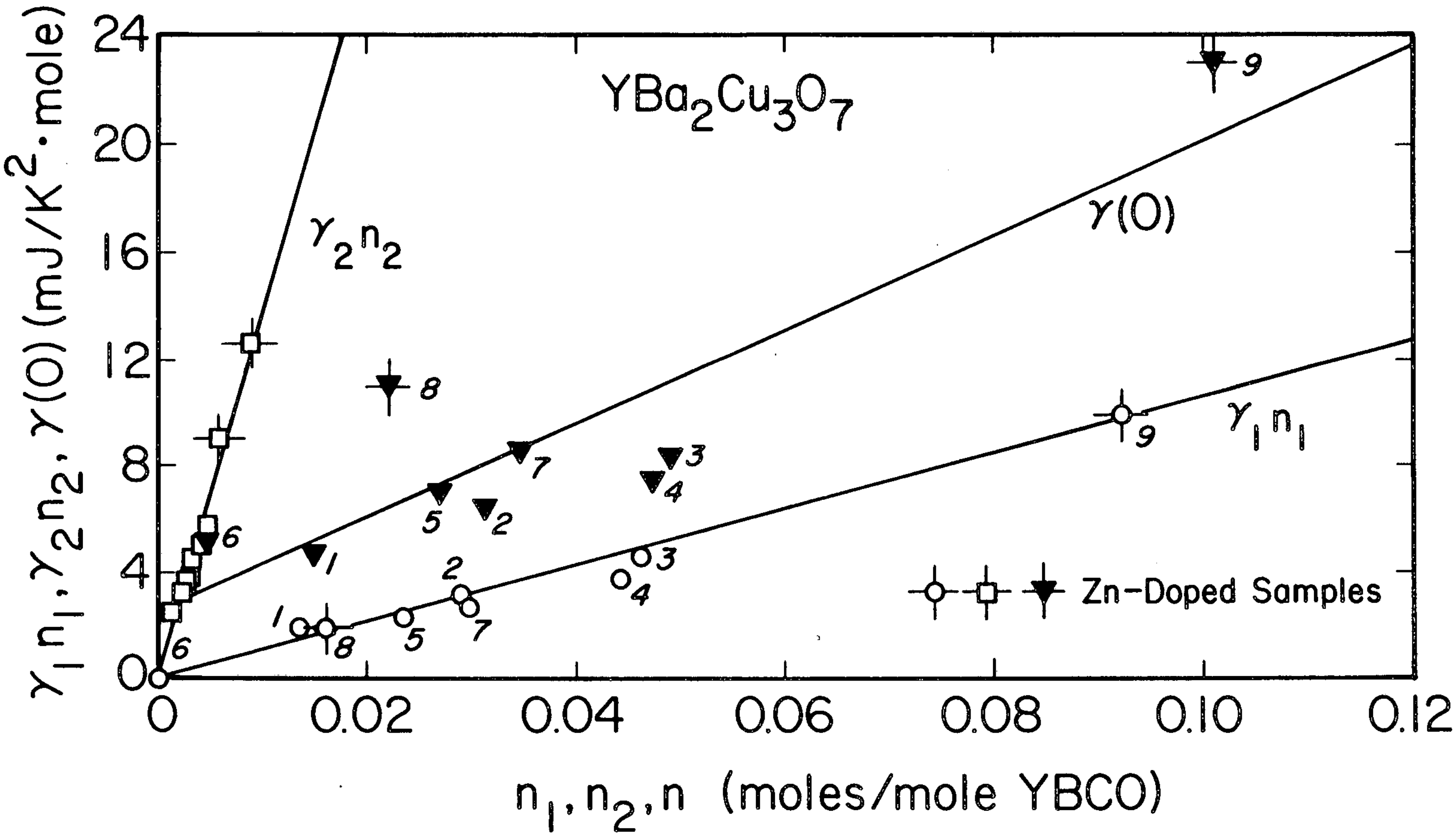
FIGURE CAPTIONS

Fig. 1. $\gamma(0)$ and its components, $\gamma_1 n_1$ and $\gamma_2 n_2$, plotted against, respectively, n, n_1 and n_2, the concentrations of Cu^{2+} moments. Points are labeled with sample numbers (see Table I) which are in order of increasing $\gamma_2 n_2$. See text for other details.

Fig. 2. C/T in the vicinity of T_c for samples 1, 2, 5, 8 and 9.

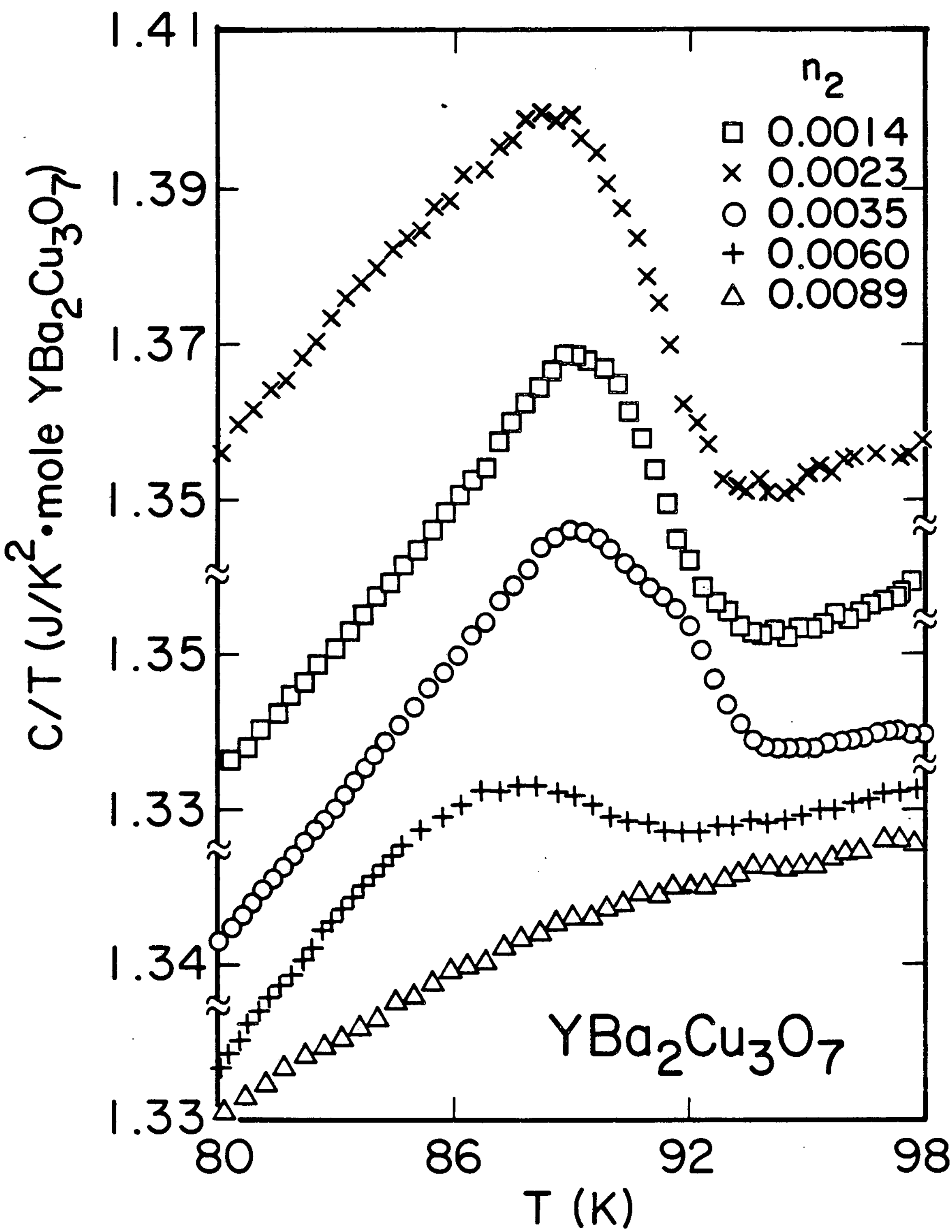
Fig. 3. $\Delta C(T_c)/T_c$ vs n_2. For comparison, $\gamma_2 n_2$ is reproduced from Fig. 1 on an expanded scale.

Fig. 4. Meissner volume vs $\Delta C(T_c)/T_c$.



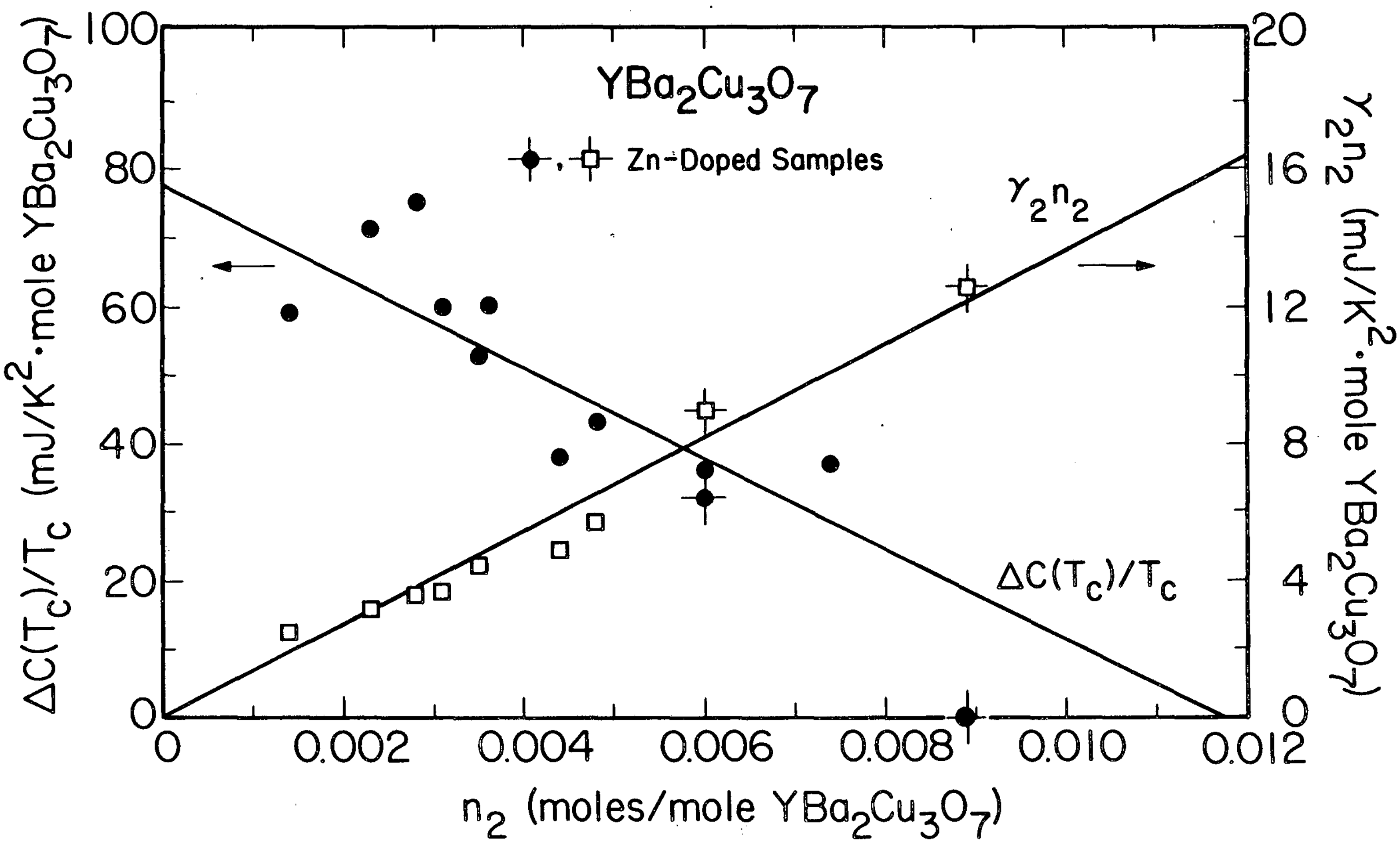
XBL 897-2700A

Fig. 1



XBL 8911-4190

Fig. 2



XBL 8911-4187

Fig. 3

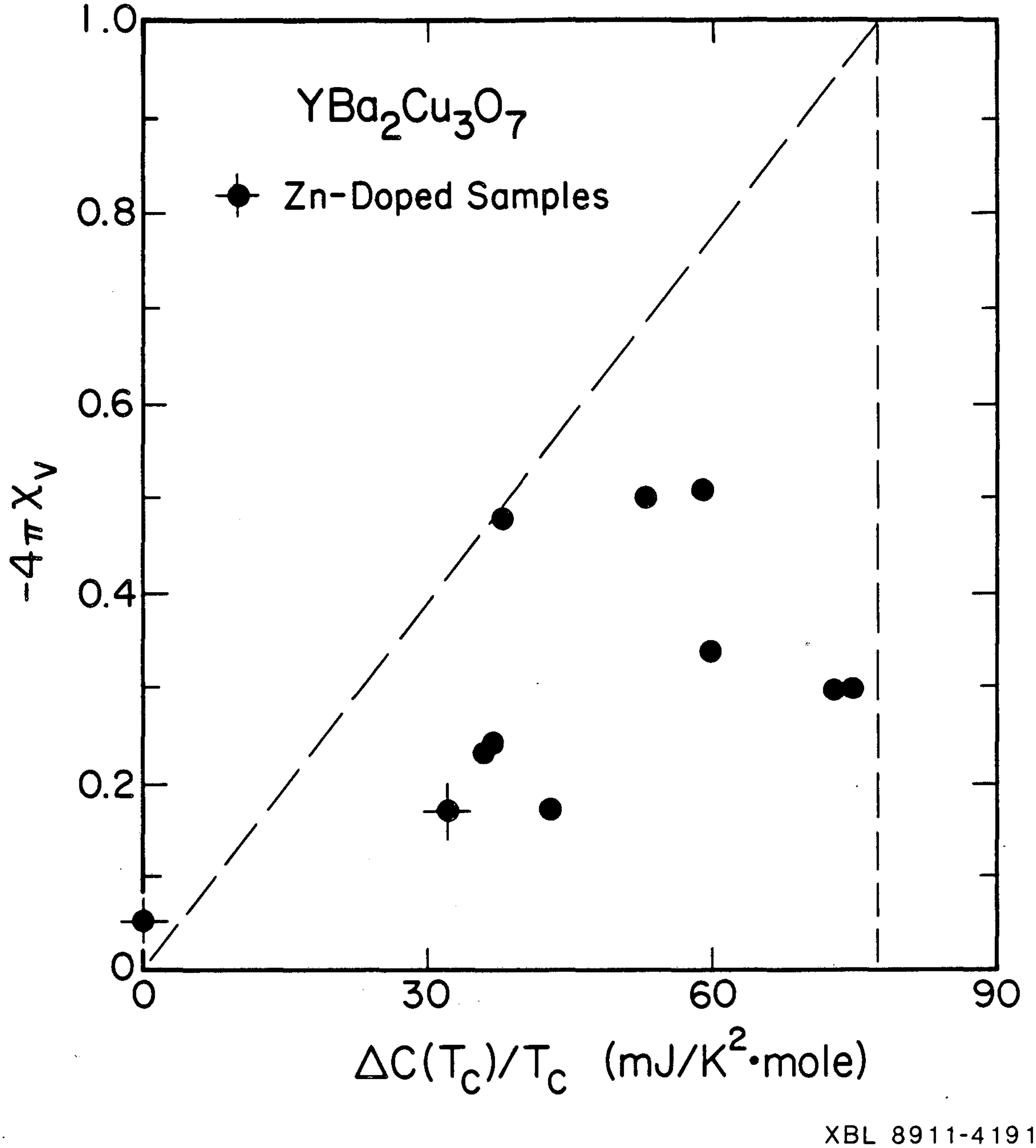

YBa2Cu3O7
Zn-Doped Samples
1.0
0.8
0.6
0.4
0.2
0
-4πχv
0
30
60
90
ΔC(Tc)/Tc (mJ/K2·mole)
XBL 8911-4191

Fig. 4

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