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DISCLAIMER

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ABSTRACT

New specific heat measurements on $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$, x=0, 0.1, 0.2, 0.3 and 1, $0.3 \leq T \leq 65K$, and including measurements in magnetic fields to 7T are reported. The combination of low-temperature and in-field data allows the separation of previously unrecognized hyperfine and magnetic ordering contributions from the low-temperature linear term, $\gamma_0 T$. The value of γ_0, 200 mJ/mole Pr.K^2 for x=0.1, 0.2 and 0.3, is substantially lower than deduced from earlier measurements, but the determination of a cut-off temperature of ~50K for this contribution adds to the appearance of "heavy-fermion-like" behavior.

Among the compounds prepared by substitution of a rare earth (R) for Y in $YBa_2Cu_3O_{7-\delta}$ (YBCO) with the retention of the superconducting orthorhombic phase, the Pr-substituted materials exhibit unique properties. For the others (Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu substituted), T_c is essentially unaffected by the substitution[1-4], and, although the magnetic R^{+3} ions order at temperatures of a few K, there is no evidence of ordering of Cu moments. For the Pr-substituted materials, the corresponding properties are dramatically different. For $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-\delta}$ ($Y_{1-x}Pr_x$BCO), T_c decreases nearly linearly with increasing x and superconductivity disappears for $x \geq 0.55$.[5-7] For $x > 0.55$, the materials are magnetic insulators with the Cu moments in the CuO_2 planes antiferromagnetically ordered.[8,9] For x = 1, that ordering occurs at $T_{N1} = 270K$, and a second magnetic ordering,[8-10] for which the associated entropy change[10] is ~Rln2, occurs at $T_{N2} = 17K$. Neutron diffraction line shapes and intensities[8] indicate that the second ordering is of Pr moments, but ordering of Cu moments on the CuO chains[9] is not completely ruled out. If it is Pr that orders, T_{N2} is a factor of 10 higher than expected[10] on the basis of scaling the T_N values for other RBCO's. (Substitution of Ce and Tb for Y have not produced the orthorhombic phase, presumably because they assume the +4 valence state under the strongly oxidizing conditions required for synthesis, while the orthorhombic structure requires the +3 state.)

The explanations for the anomalous x dependence of T_c in $Y_{1-x}Pr_x$BCO can be summarized by two models. In one[6,10-12], Pr is primarily in the +4 state and one electron that is removed from the Pr fills holes in the conducting CuO_2 planes. In the other[13-17], Pr is primarily in the +3 state and the hybridization of the Pr-4f and O-2p orbitals (which is critically dependent on the 4f energy and occurs to a significant degree only for Pr) produces the effect on T_c by a pair-breaking mechanism. The second model would also account for the relatively strong Pr-Pr interactions implied by the high value of T_{N2}.

The first specific heat (C) measurements[10] on $Y_{1-x}Pr_xBCO$ showed very large low-temperature contributions that were approximately proportional to T. They were interpreted as large values of the 0-K Sommerfeld constant, $\gamma_0 \sim 400$ mJ/mole Pr.K^2, and evidence of heavy-fermion behavior, although the possibility of a magnetic ordering contribution to C was also recognized. This Communication is a preliminary report on new measurements of C for x=0, 0.1, 0.2, 0.3 and 1 that extend to lower temperatures and include measurements in magnetic fields (H) to 7T. The emphasis is on the low-temperature, in-field, small-x data that clearly reveal a hyperfine contribution that is important for T<1K and a previously unrecognized H-dependent magnetic ordering contribution with a maximum at temperatures ranging from ~0.4K for x=0.1 to T~2K for x=0.3. When these contributions to C are taken into account, there remains a large, H-independent $\gamma_0 T$ term that extends to approximately 50K. The coefficient, $\gamma_0 \sim 200$ mJ/mole Pr.K^2, although substantially smaller than that deduced from the earlier measurements, is still much larger than the usual values for metals, and the determination of the 50-K cut-off temperature constitutes a significant additional contribution to the appearance of "heavy-fermion-like" behavior.

The samples studied were essentially single-phase, polycrystalline material. They were characterized by field-cooled magnetization, x-ray diffraction, Raman spectroscopy and resistivity measurements. Thermal gravimetric analysis showed the materials to be nearly fully oxygenated ($\delta = 0.05 \pm 0.02$). Details of their preparation and characterization have been published previously.[13,18] Specific heats of ~20g samples were measured using a semi-adiabatic heat pulse technique for $T<30K$ and a continuous heating technique for $T>30K$. The precision of the data is ~0.2%.

Representative specific heat data are shown in Figs. 1-4. Results for $x=0.3$ are emphasized because the different contributions are most clearly delineated for that sample. Data for $x=0$ are included because they are taken as a "background" contribution in evaluating the magnetic ordering and $\gamma_0 T$ contributions, on the assumption that the lattice and impurity (e.g., $BaCuO_2$) contributions are approximately the same in all samples. Figure 1 gives an overview of the data for $x=0.3$, $H=0$ and 7T. The magnetic ordering is indicated by the broad maxima in C/T near 1 and 5K, for $H=0$ and 7T respectively. The upturns in C/T at $T<0.5K$ correspond to a strongly H-dependent hyperfine field. In Fig. 2, data are shown for the $x=0.1$ sample, the only one (except the $x=0$ sample) for which the superconducting transition is clearly evident in C. The entropy-conserving construction in the lower inset gives $\Delta C(T_c)/T_c$~8 mJ/mole.K^2, about 10% of the value expected for a fully superconducting sample of YBCO, and suggestive of a substantially lower value of the electronic density of states or gapless superconductivity. (A small volume fraction of superconductivity seems to be ruled out by the 40% Meissner effect.) For this sample the magnetic ordering and hyperfine contributions are superimposed for H=0, but clearly separated for H=7T. Analyses of the 7-T, low-temperature data into $\gamma_0 T$ and T^{-2} -proportional hyperfine terms are shown in Fig. 3 for x=0, 0.1, 0.2 and 0.3. The x dependence of the γ_0 values is well represented by the sum of an x=0 value, 7.6 mJ/mole.K^2, which is typical of YBCO samples, and an x-proportional term corresponding to γ_0=200 mJ/mole Pr.K^2.

The separation of the various low-temperature contributions to C is shown in Fig. 4 for x=0.3, as ΔC/T vs T where ΔC is the excess of C over the hyperfine and "background" (x=0) contributions. The H=0 value of γ_0 is not well determined at low temperature because it is small compared with the hyperfine and/or magnetic ordering contributions, but the 7-T value of γ_0, which is well determined by the construction in Fig. 2, is represented by the horizontal line at ΔC/T=210 mJ/mole Pr.K^2. (The fact that the lowest temperature 7-T data point falls below that line is misleading -- the discrepancy is a small part of the total C, and within the precision of the data.) For both H=0 and H=7T, ΔC/T is close to the 7-T value of γ_0 in the region 20-40K, and drops below that value at higher temperatures. Thus, taken together, the zero-field and 7-T data suggest a $\gamma_0 T$ contribution that is only weakly H-dependent and extends to a cut-off temperature of ~50K, and an H-dependent magnetic ordering contribution that produces the maxima in ΔC/T near 1 and 5K. The weak H dependence of γ_0 is understandable even if the $\gamma_0 T$ contribution is magnetic in origin if the cut-off temperature is a measure of the strength of interaction underlying the contribution. The associated entropy, the area below the line at ΔC/T=210 mJ/mole Pr.K^2

and below T=50K, is ~Rln4 (per mole Pr). The x=0.1 and 0.2 data are consistent with these results with respect to both entropy and cut-off temperature. The entropy of the magnetic ordering anomaly, the area between the line and the data is ~(1/2)Rln2 (per mole Pr) for both H=0 and H=7T. Within the experimental uncertainty it has the same value in 7T for x=0.1 and 0.2. (For H=0 and x=0.1 and 0.2, the data do not determine the magnetic ordering contribution.) The small "bump" in $\Delta C/T$ near 40K occurs in the vicinity of the superconducting transition, but its field independence suggests another origin. In fact, it corresponds to only ~1% of the total C, and could be just an artifact associated with the assumption that the background C is the same for x=0 and 0.3. Furthermore, it is not observed for x=0.1 or 0.2. The failure to observe an anomaly in C associated with the superconducting transition (there is a 35% Meissner effect in the x=0.3 sample) is consistent with the trend established by typical x=0 samples and the x=0.1 sample, and with the possible explanations cited in connection with the x=0.1 sample. The values of γ_0 reported here are lower than those derived from earlier measurements[10,19] because they are based on an analysis that took into account the magnetic contributions to C identified by the combination of lower-temperature and in-field data; not because there is any great discrepancy in the data. The origin of the differences in the values of γ_0 can be seen in Fig. 1: in the interval $5 \lesssim T \lesssim 12K$, C/T is relatively constant, and fits with a sum of T and T^3 terms, illustrated in the inset to Fig. 4, lead to the higher values of γ_0 reported earlier.

At low temperatures the behavior of the x=1 sample is qualitatively different from that of the x=0.1, 0.2 and 0.3 samples. For PrBCO in H=0 at $T \lesssim 1.5K$, $C = D/T^2 + \gamma_0 T + AT^3$

with D=61 mJ.K/mole, γ_0=102 mJ/mole.K^2 and A=6.99 mJ/mole.K^4. The parameters D, γ_0 and A are all strongly H dependent. The H-dependence of the Pr hyperfine field (calculated on the assumption that contributions from the Cu nuclei are negligible) is shown for the x=0.3 and 1 samples in Fig. 5. For all Pr-containing samples, the hyperfine field is ~100T at H=7T. However, for PrBCO, the hyperfine field is substantially higher than that for x=0.3 at H=0, and the field dependence is weaker and qualitatively different. For x=0.1 and 0.2, the hyperfine contribution cannot be separated from the magnetic ordering contribution at H=0, and no measurements were made for 0<H<7T.

In summary, the Pr-related contributions to C are: (1) H- and x-dependent hyperfine contributions; (2) H- and x-dependent, magnetic-ordering contributions, exemplified by the broad maxima in C/T in Fig. 1 and the maxima in ΔC/T in Fig. 4; and (3) a heavy-fermion-like γ_0T contribution that extends to a cut-off temperature of ~50K.

The hyperfine fields are in principle dependent on the crystal field levels and therefore the valency of the ion. In the absence of detailed calculations, however, it is not possible to distinguish between a Pr^{+4} J_z = $\pm 1/2$ ground state and low-lying states of higher J_z, or a Pr^{+3} singlet ground state with exchange-induced mixing of higher states.

The temperatures of the magnetic ordering contributions for x=0.1, 0.2 and 0.3 are qualitatively consistent with the expected effect of dilution on the 17K ordering anomaly for x=1, and with the recent phase diagram determined by Cooke et al.,[9] who used muon spin rotation to follow the Pr antiferromagnetic ordering to x=0.4 where it was observed near 2 K. The strong field dependence of the heat capacity anomaly at 1 K in the x=0.3 sample is consistent with antiferromagnetic ordering.

Although smaller than deduced from earlier measurements,[10,19] the value of γ_0 is still large compared with those typical of ordinary metallic systems, and may be associated with hybridization of the Pr-4f and O-2p electrons. Many authors[15-26] have pointed out that some hybridization is necessary in order to explain several of the anomalous features in these materials. In addition to the strong dependence of T_c on pressure[25] and an anomalous thermopower,[21] there is other evidence of strong coupling between the Pr local moments. This coupling is evident both in the temperature at which the magnetic ordering is observed[10] (17K for x=1), which is too high with respect to the other rare earths, as well as the pair breaking behavior implied by the critical field results.[13,14] This pair breaking is distinct from that proposed by Kebede et al.,[10] which is of the Abrikosov-Gorkov type,[27] and does not require the magnetic ions to be coupled. In the absence of conduction electrons to mediate the RKKY interaction, some form of hybridization is required to provide a superexchange interaction between the Pr ions. Hybridization of the Pr-4f electrons with those of copper and oxygen has also been proposed by Torrance et al.[26] as a mechanism which causes a localization of the conducting holes in the copper-oxygen planes. This would be consistent with the insulating behavior found at high x.[10,14] As x increases, percolative paths vanish and the material ceases to conduct. In the low-x region, however, the material would not be substantially affected, and this mechanism alone would not explain the absence of superconductivity when the material is still metallic. It has sometimes been argued that the presence of hybridization is consistent only with a +4 or mixed-valent state. In fact, the Pr ion can hybridize out of either the +4 or +3 states, but is much more likely to do so from the +3 state, since one of the two remaining 4f electrons is loosely bound. In the +4 state, which would correspond to one of these electrons being placed in a different location, presumably in the CuO_2 planes, the remaining 4f electron is more strongly bound, and would not tend to hybridize. The possibility of the Pr ion hybridizing out of the +3 valence state may be what distinguishes Pr from the other rare earths for which the f electrons are bound more securely in the +3 state.

Recent measurements on an x=0.3 sample by Ghamaty et al.[24] show some of the features reported here: γ_0 = 235 mJ/mole $Pr.K^2$ compared with the value 200 mJ/mole $Pr.K^2$ obtained in this work, but the measurements did not extend to temperatures high enough to determine the cut-off temperature, and a magnetic-ordering anomaly similar in magnitude to that reported here, but represented by a Kondo anomaly, which has a very different temperature dependence from that deduced in this work (although the low-temperature deviations of their data from the fitting expression are in the direction of consistency with this work).

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FIGURE CAPTIONS

Fig. 1 $H=0$ and 7-T data for $(Y_{0.7}Pr_{0.3})Ba_2Cu_3O_{7-\delta}$. $H=0$ data for $x=0$ are shown for comparison. (For $x=0$, the weak H dependence would not be apparent.)

Fig. 2 Data for $(Y_{0.8}Pr_{0.2})Ba_2Cu_3O_{7-\delta}$ in the vicinity of T_c and, in the upper inset, for $T \leq 6K$.

Fig. 3 Analysis of the low-temperature $H=7T$ data into T and T^{-2} terms.

Fig. 4 $\Delta C/T$ vs T, where ΔC is the magnetic ordering plus "heavy-fermion-like", $\gamma_0 T$, contributions to C. The inset shows C/T vs T^2 for $T<13K$.

Fig. 5 H dependence of the Pr hyperfine field for $x=0.3$ and 1.

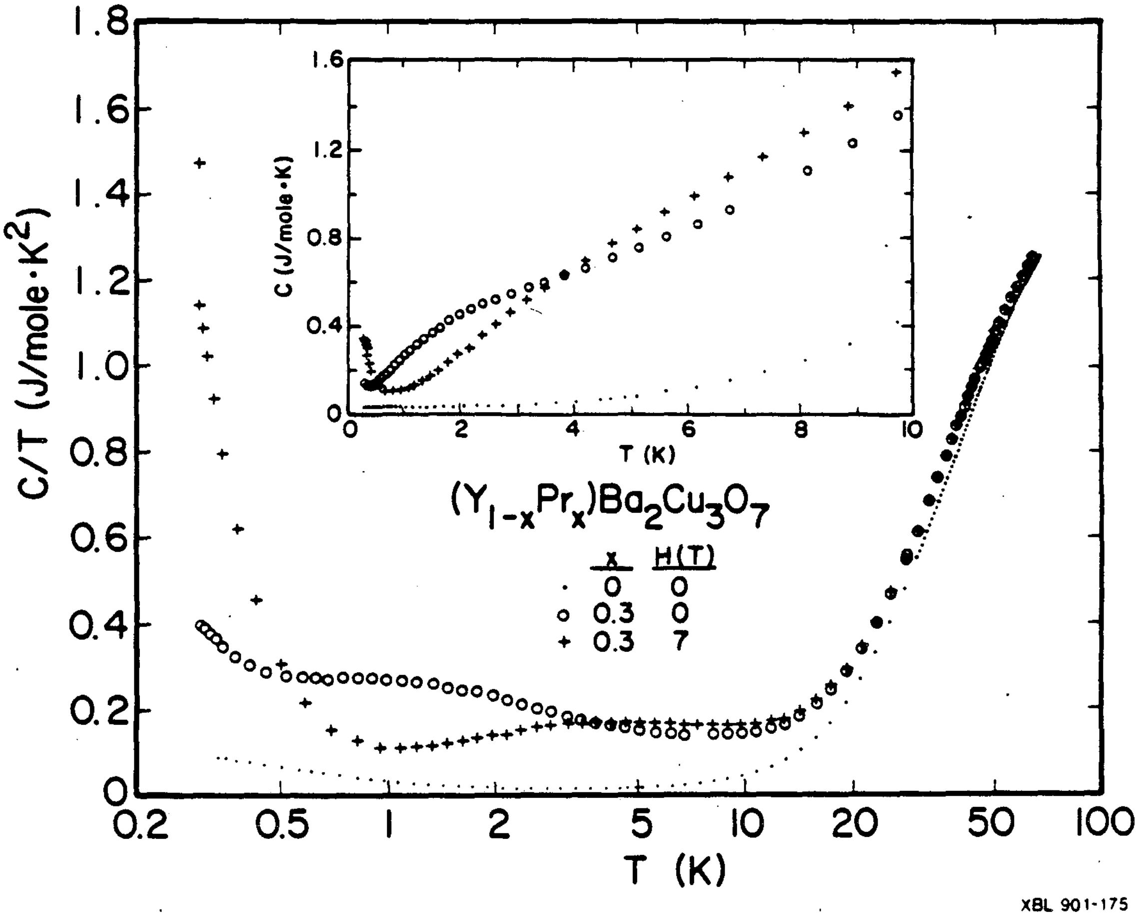
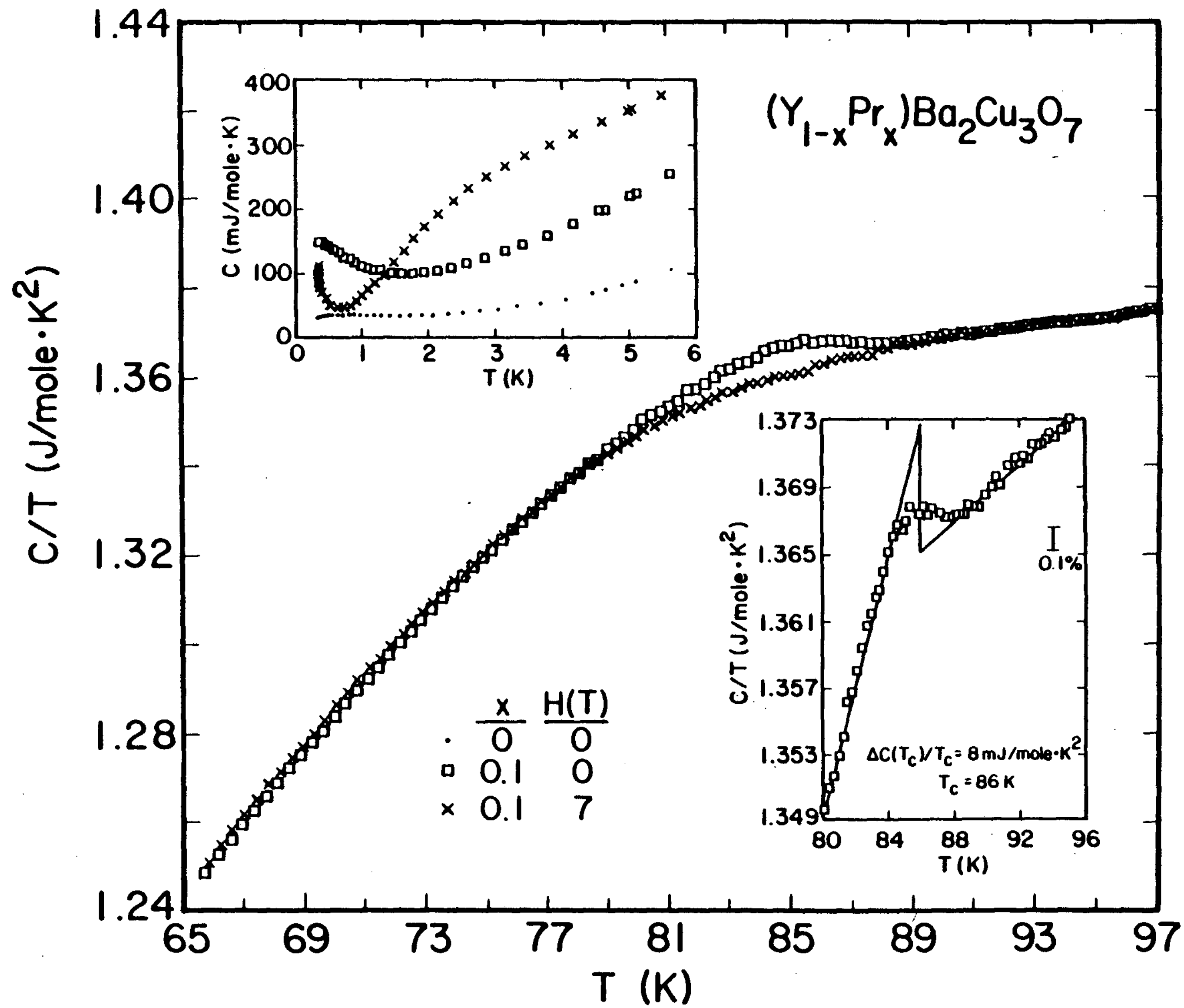
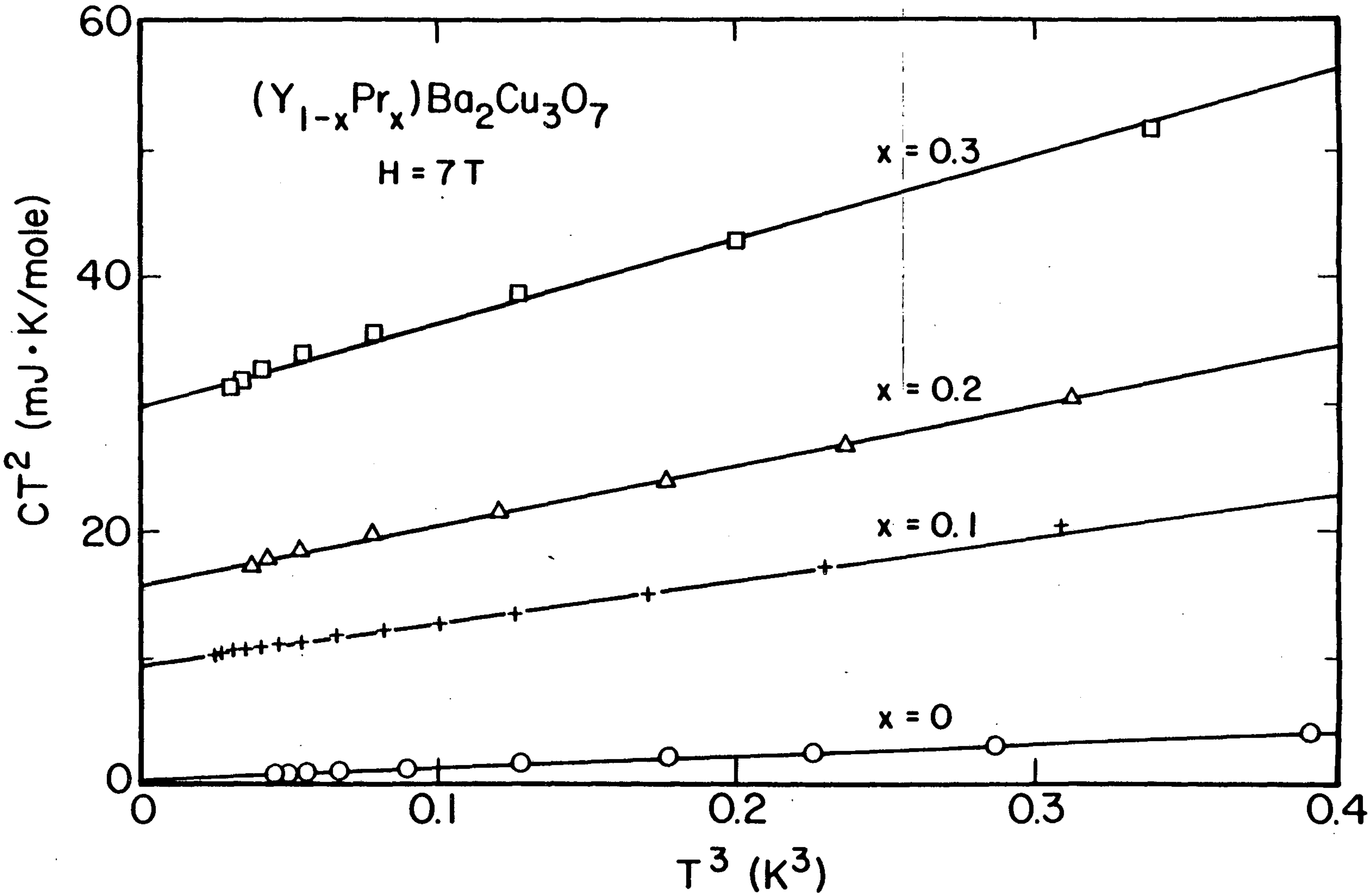

1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
C/T (J/mole·K²)
0.2
0.5
1
2
5
10
20
50
100
T (K)
1.6
1.2
0.8
0.4
0
C (J/mole·K)
0
2
4
6
8
10
T (K)
(Y1-xPrx)Ba2Cu3O7
x H(T)
· 0 0
o 0.3 0
+ 0.3 7
XBL 901-175

FIG.1



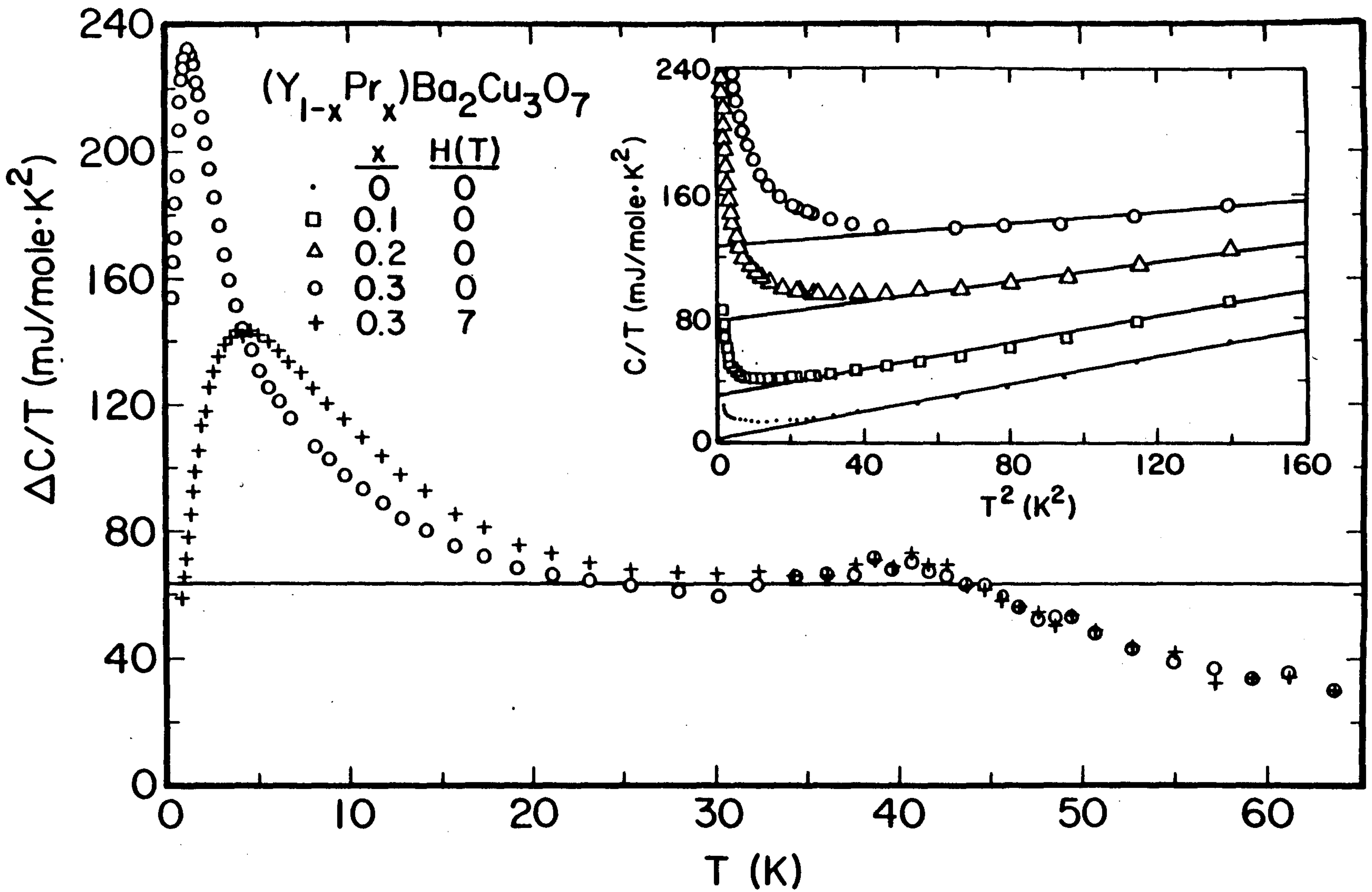
XBL 901-174

FIG. 2



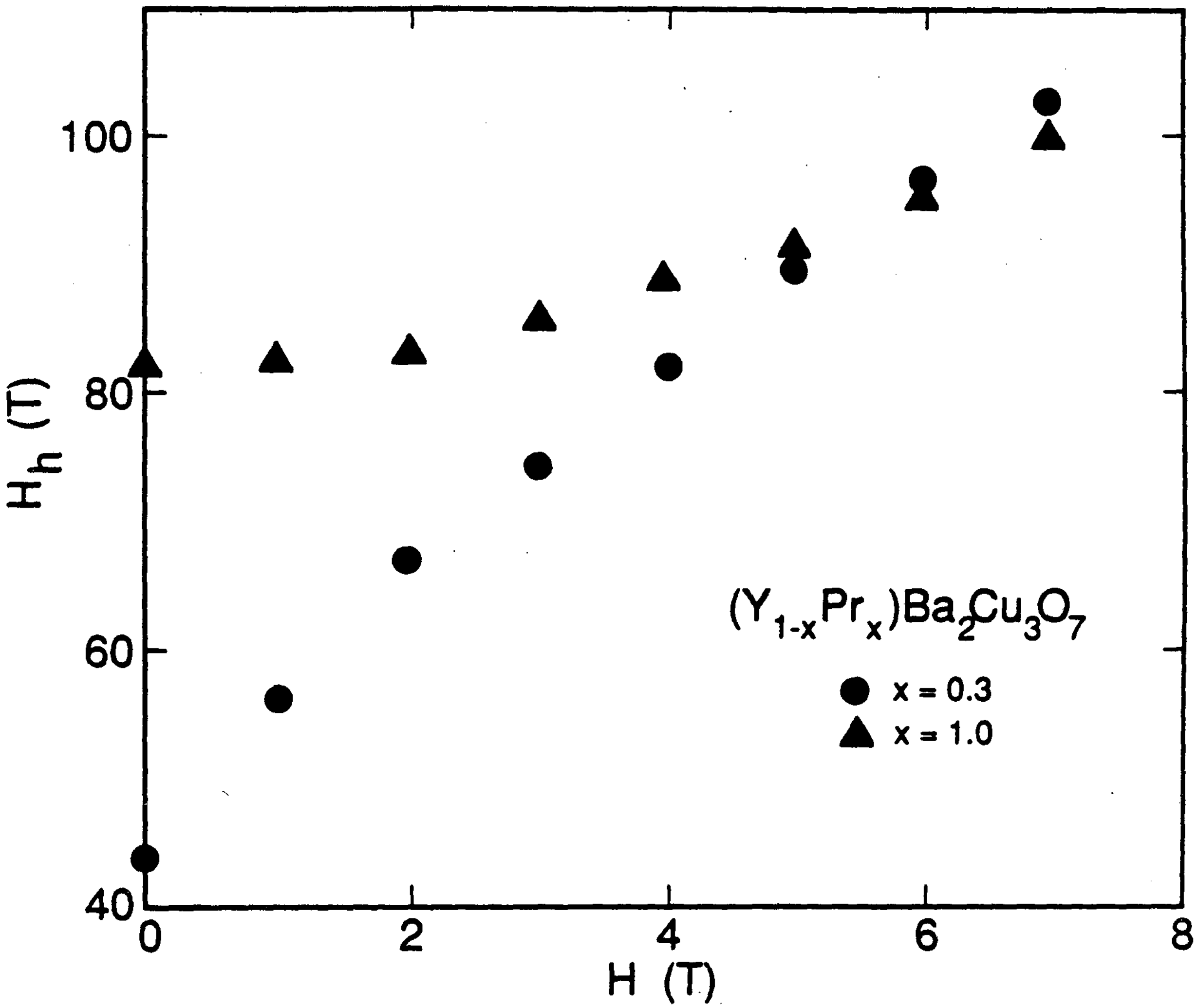
XBL 902-543

FIG. 3



XBL 909-3020

FIG. 4



XBL 909-3023

FIG. 5

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