Magnetic-field effect on the specific heat of $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$

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The specific heat of $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ ($x=0$, 0.04, and 0.08; $\delta\sim0.1$) in magnetic fields up to 8 T was studied. A depression of antiferromagnetic transition temperature T_N for Pr ions with Ga substitution becomes evident through broad specific-heat anomalies peaked at 17, 14, and 10 K for $x=0$, 0.04, and 0.08, respectively. Both the magnitude of the anomaly and the T_N values can be suppressed with magnetic field as often observed in conventional antiferromagnetic transitions. The specific-heat data above or below T_N increase with Ga substitution. In addition, by fitting them to $C=A/T^2+\gamma T+BT^3$ in the temperature range $0.6\leq T\leq5$ K, the linear term coefficient γ of the specific heat increases with x and decreases with magnetic field. These results suggest that the unusually large value of γ in $PrBa_2Cu_3O_{7-\delta}$ may be partially due to the strong magnetic correlation among Pr ions.

The absence of superconductivity and anomalous magnetic properties of $PrBa_2Cu_3O_{7-\delta}$ have received a great deal of interest since this compound was first synthesized. This compound forms the same orthorhombic structure as high-T_c $YBa_2Cu_3O_{7-\delta}$, but it is strangely not superconducting.[1] Meanwhile, an antiferromagnetic Pr ordering in $PrBa_2Cu_3O_{7-\delta}$ was observed below $T_N=17$ K by magnetic-susceptibility, specific-heat, and neutron-diffraction measurements.[2–4] Extensive experiments on the depression of T_c with increasing x in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ have been reported, and various mechanisms for the magnetic coupling interactions responsible for the high T_N in $PrBa_2Cu_3O_{7-\delta}$ have been proposed.[4–6] In general, $PrBa_2Cu_3O_{7-\delta}$ exhibits at least the following unusual magnetic properties compared to its isomorphic magnetic rare-earth compounds. (1) The value of $\mu_{\rm eff}$ derived from magnetic susceptibility is considerably lower than the expected value of $3.58\mu_B$ for the Pr^{3+} free ion.[1,2] (2) The magnetic ordering temperature $T_N=17$ K is about two orders of magnitude higher than expected if one scales the T_N for $GdBa_2Cu_3O_{7-\delta}$ ($T_N=2.2$ K) assuming either purely dipolar interactions or the Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange. (3) Unlike $\chi(T)$ for a conventional antiferromagnetic ordering, where the magnetic susceptibility decreases below T_N, the magnetic susceptibility of $PrBa_2Cu_3O_{7-\delta}$ increases below the apparent ordering temperature.[2,7] (4) In contrast to $GdBa_2Cu_3O_{7-\delta}$, the T_N of $PrBa_2Cu_3O_{7-\delta}$ remains essentially unchanged with Zn substitution but is suppressed substantially with Ga substitution, indicating that the magnetic coupling mechanisms in $GdBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ are different in nature.[7] (5) The Pr spins are arranged antiferromagnetically along all three crystallographic directions. However, the spin arrangement along the c axis changes from antiparallel to parallel by partial doping with Zn and Ga.[8,9] (6) In contrast to the suppression of T_N for $GdBa_2Cu_3O_{7-\delta}$ by magnetic field,[10] the T_N of $PrBa_2Cu_3O_{7-\delta}$ is basically field independent up to 5 T.[2] (7) The relatively high value [300 mJ/mol K^2 (Ref. 3) or 200 mJ/Pr mol K^2 (Ref. 11)] of the Sommerfeld constant γ determined from specific-heat measurements is comparable to that of heavy-fermion systems. Among these, it is of particular interest to study the correlation between the high T_N and the large γ in $PrBa_2Cu_3O_{7-\delta}$. In this work, we present the magnetic-field dependence of specific-heat data for $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ to examine the magnetic-field effects on γ as well as the correlation of γ and T_N.

Polycrystalline samples of $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ ($x=0$, 0.04, and 0.08; $\delta\sim0.1$) were synthesized by the standard solid-state-reaction method. Details of their preparation and characterization have been described elsewhere.[7] The specific heat of individual small samples ($\sim$2 mg) was measured in the temperature range 0.6–40 K with a ^{3}He thermal relaxation calorimeter using the heat-pulse technique[12] at fields of 0, 4, and 8 T. The samples were attached to a sapphire chip (sample holder in calorimeter), which has two separated silicon films deposited on it to serve as the heater and thermometer, respectively. The Si-film thermometer was calibrated against either a precalibrated germanium thermometer in zero field or a precalibrated capacitance sensor in field measurements. The chip was then connected to a constant-temperature copper block with a weak thermal link, for which thermal conductance κ was measured at each temperature and field by applying a small power $P=\kappa(T_{\rm sample}-T_{\rm block})$ to the chip. When the power was turned off, the sample temperature relaxed exponentially to the block temperature with a time constant $\tau=C/\kappa$. Thus the total heat capacity C was obtained. The uncertainty of this system estimated from measurements of reference sample Cu ($\sim$2.5 mg Cerac product 99.999%) in the temperature range 0.6–5 K is around 1%.

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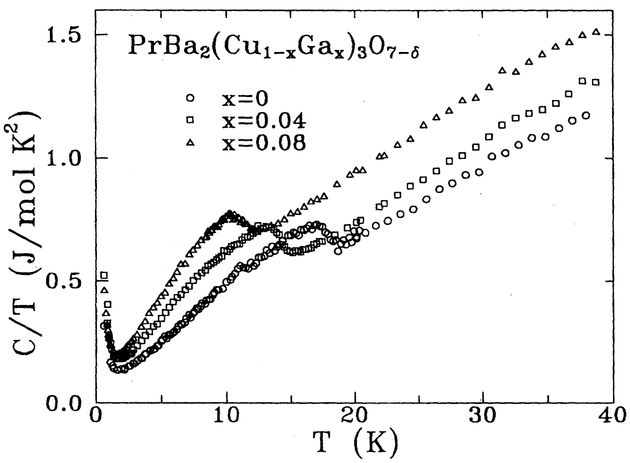

FIG. 1. Molar specific heat divided by temperature C/T as a function of temperature T for $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ with $x=0$, 0.04, and 0.08.

Molar specific-heat data for $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ with $x=0$, 0.04, and 0.08 are shown in Fig. 1 as C/T vs temperature T. An antiferromagnetic-ordering-induced maximum occurred at $T_N=17$ K for $x=0$, consistent with reported results.[2] Similar anomalies are also observed at 14 and 10 K for $x=0.04$ and 0.08, respectively. In contrast, there is just a minor deviation from the Curie-Weiss behavior in the temperature dependence of magnetic susceptibility.[9] Meanwhile, magnetic ordering has also been observed in neutron-diffraction experiments at about the same temperatures.[9] In fact, the T_N of $PrBa_2Cu_3O_{7-\delta}$ decreased substantially with Ga substitution but remained essentially constant with Zn substitution.[7] This is not yet completely understood. However, the T_N of $GdBa_2Cu_3O_{7-\delta}$ is more affected when the doping occurs in Cu-O_2 planes[13] (such as Zn) than in the Cu-O chains (such as Co).[14] It is recalled that the Cu-O_2 planes play a much more essential role than the Cu-O chains in the superconductivity of $YBa_2Cu_3O_{7-\delta}$.[15] Also, there exists a strong correlation between the quenching of superconductivity and the high T_N in Pr-based cuprates.[16] Therefore the Cu-O chains cannot be totally ignored in discussing the magnetic coupling mechanism for high T_N of $PrBa_2Cu_3O_{7-\delta}$. Figure 2 shows the C/T vs T for $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ in the vicinity of antiferromagnetic transitions for $x=0$, 0.04, and 0.08 with magnetic field $H=0$, 4, and 8 T. It is found that the transitions are broader than those for typical magnetic ordering transitions. The anomalies are suppressed by H in all three compounds. The T_N values determined from the peak position of each anomaly decrease from 17 to 15 K and from 14 to 11 K as H up to 8 T for $x=0$ and 0.04, respectively. These results are similar to those in conventional antiferromagnetic ordering, where an external field of a few tesla is usually sufficient to suppress its T_N by a few degrees. On the other hand, the T_N and the magnetic anomaly are almost field independent up to 5 T in magnetic-susceptibility measurements.[2]

The analyses for the linear term coefficient γ of molar specific heat in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ have been discussed by many groups.[2–4,11,17] In fact, the value of γ in this particular system depends on the different fitting temperature ranges, fitting terms, and interpretations,[2–4,11,17] while its origin remains to be identified. Though the value of γ determined for $PrBa_2Cu_3O_{7-\delta}$ differs significantly from different groups using various fitting procedures, it is commonly recognized to have a large value and heavy-fermion-like characteristics. For example, the sensitivity of γ to fitting procedure is highlighted by Li *et al.*[4] who obtained a value of 114 mJ/mol K^2 for $T<5$ K and an excess of 300 mJ/mol K^2 when extrapolated from $T>17$ K. However, in solids simple Debye T^3 behavior dominates the lattice contribution below about $\theta_D/50$, above which higher terms due to anharmonicity become significant. Thus, in this report, we fit the low-temperature ($0.6\leq T\leq 5$ K) specific-heat data of $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ to the equation $C=A/T^2+\gamma T+BT^3$, where the first term is the contribution from a nuclear Schottky anomaly and the third term is the sum of the lattice and three-dimensional antiferromagnetic magnon contributions. Figure 3 shows the agreement of the fit to the data (a) for $x=0$, 0.04, and 0.08 with $H=0$ and (b) for $x=0$ with $H=0$, 4, and 8 T. The fitting parameters A, γ, and B for various x and H are listed in Table I. It is found that the obtained γ value 118 mJ/mol K^2 for $x=0$ and $H=0$ is consistent with that obtained by Li *et al.*[4] using the same fitting

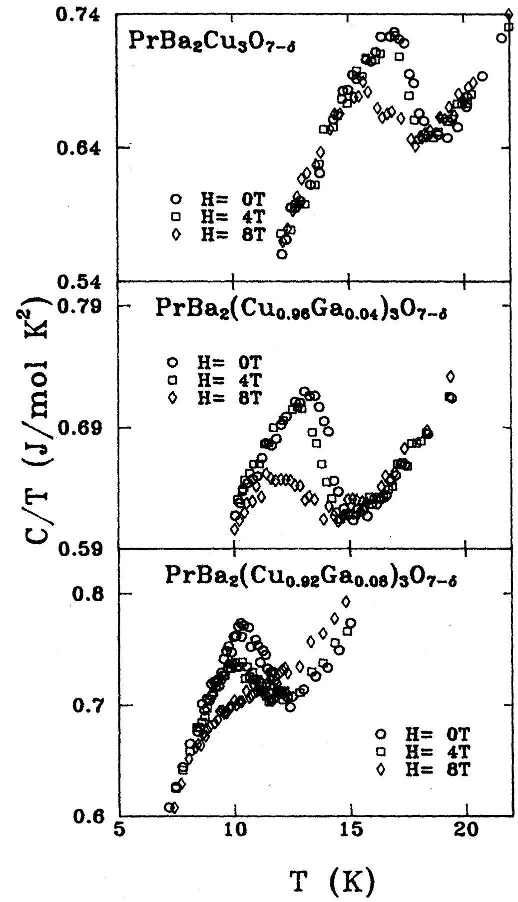

FIG. 2. C/T vs T of $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ in the vicinity of antiferromagnetic transition temperatures for $x=0$, 0.04, and 0.08 with $H=0$, 4, and 8 T.

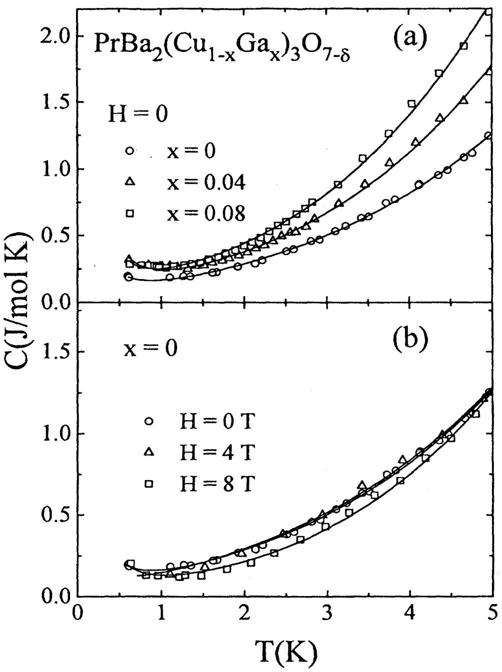

FIG. 3. Low-temperature ($0.6 \leq T \leq 5$ K) specific-heat data of $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ (a) for $x=0$, 0.04, and 0.08 with $H=0$ and (b) for $x=0$ with $H=0$, 4, and 8 T. The solid lines represent fits to the equation $C=A/T^2+\gamma T+BT^3$.

temperature limit. The γ value increases with Ga doping concentration for the same field. The enhancement of γ with various dopants has been observed in Fe-doped $Y_{1-x}Pr_xBa_2Cu_3O_7$ (Ref. 3) and Zn-doped $La_{1.85}Sr_{0.15}CuO_4$ (Ref. 18), which were thought to be associated with the atomic disorder or localization effects. On the other hand, the γ value decreases with increasing fields for all three samples in this work. The H dependence of the γ value suggests that it may be associated with low-energy magnetic excitations in the ordered state. It has been reported that[19] in heavy-fermion systems the γ values show little (<20%) or no change in a magnetic field up to 13 T. However, "false" heavy-fermion systems (i.e., those with a large low-temperature C/T value due to strong magnetic correlation) show a large change in specific heat with applied magnetic fields. Based on the above observations and arguments, the decrease of γ with magnetic field shown in Fig. 3 and Table I suggests that the large γ value in $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ may be partially due to a strong magnetic correlation between Pr ions.

TABLE I. Fitting parameters A, γ, and B to $C=A/T^2+\gamma T+BT^3$ in the temperature range $0.6 \leq T \leq 5$ K for $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$.

x	H (T)	A (mJ K/mol)	γ (mJ/mol K^2)	B (mJ/mol K^4)
0	0	44 ± 1	118 ± 2	5.5 ± 0.1
	4	40 ± 1	125 ± 4	5.3 ± 0.2
	8	53 ± 1	74 ± 2	7.1 ± 0.2
0.4	0	93 ± 2	146 ± 3	8.3 ± 0.2
	4	24 ± 1	151 ± 4	8.9 ± 0.3
	8	65 ± 2	90 ± 3	10.4 ± 0.3
0.8	0	77 ± 2	168 ± 5	11.4 ± 0.3
	4	24 ± 1	163 ± 5	12.4 ± 0.4
	8	75 ± 3	101 ± 4	14.3 ± 0.5

It is interesting to study the correlation between the anomalously high T_N and the large γ value in Pr-based cuprates. These parameters for six selected Pr-based compounds including Pr_2CuO_4, $PrBa_2Cu_2NbO_8$, $PrSr_2Cu_{2.7}Mo_{0.3}O_7$, and $PrBa_2(Cu_{1-x}Ga_x)_3O_7$ ($x=0$, 0.04, and 0.08) are listed in Table II for comparison. Where the Pr_2CuO_4 forms a T'-type structure consisting of only the square-planar CuO_4 arrangement with no apical oxygen atoms, the $PrBa_2Cu_2NbO_8$ and $PrSr_2Cu_{2.7}Mo_{0.3}O_7$ have a similar structure to $PrBa_2Cu_3O_7$ but with NbO_2 planes replacing the CuO chains and Sr-O replacing the Ba-O, respectively. Indeed, Pr_2CuO_4 seems to have very different structural and physical properties from the other five compounds. Thus Pr_2CuO_4 has no indication of a magnetic ordering transition and an effective magnetic moment $\mu_{eff}\sim3.51\mu_B$ close to the $3.58\mu_B$ for the free Pr^{3+} ion, as well as a metal-like γ value suggesting a nonmagnetic ground state.[20] In contrast, the anomalous properties of the other five compounds may be attributed to their unique magnetic and/or electronic structure characteristic of Pr ions. Furthermore, it is difficult to correlate the large γ value with the high T_N from the information listed in Table II. A high T_N ($\sim$12 K) with a small γ in $PrBa_2Cu_2NbO_8$ (Ref. 21) and a low T_N (<0.6 K) with a large γ in $PrSr_2Cu_{2.7}Mo_{0.3}O_7$ (Ref. 16) imply that the large γ value is not necessarily a result of the strong magnetic coupling (high T_N) between Pr ions. Moreover, a similar relation is also seen in an increase of γ with a decrease of the high T_N in $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$. Therefore the primary origin of large γ values in Pr-based cuprates is still unclear.

In summary, magnetic-field effects on the specific heat of

TABLE II. Antiferromagnetic transition temperature T_N, effective magnetic moment μ_{eff}, and linear term coefficient γ of specific heat for selected Pr-based compounds.

Compound	T_N (K)	μ_{eff} (μ_B)	γ (mJ/mol K^2)	Ref.
Pr_2CuO_4	not observed	3.51	1.5	20
$PrBa_2Cu_2NbO_8$	12	2.86	3.1	21
$PrSr_2Cu_{2.7}Mo_{0.3}O_7$	not observed	3.05	197	16
$PrBa_2Cu_3O_7$	17	2.97	114, 118	4, this work
$PrBa_2(Cu_{0.96}Ga_{0.04})_3O_7$	14		151	this work
$PrBa_2(Cu_{0.92}Ga_{0.08})_3O_7$	10		168	this work

$PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ are presented and discussed. Several features can be concluded from the present data. (1) A depression of T_N with x is clearly shown by the specific-heat anomalies, even though there is only a slope change in the χ-T curve. (2) The specific-heat anomalies are broader than those in typical magnetic transitions. However, both their magnitudes and the T_N values for $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ are suppressed by magnetic field, suggesting that the magnetic transition of this system is consistent with conventional antiferromagnetic ordering. (3) The low-temperature specific-heat data are slightly suppressed with magnetic field and the derived γ values show an significant decrease in the magnetic field up to 8 T. Therefore the large γ value in $PrBa_2Cu_3O_{7-\delta}$ may be partially induced by the strong magnetic correlation. (4) The increase of γ values with decrease of T_N in $PrBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ suggests that the origin of large γ values in these particular Pr-based cuprates needs further clarification.

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