Low-temperature specific heat of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system

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Low-temperature specific-heat C measurements as a function of temperature T between 0.5 and 30 K are reported for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ compounds with $x=0$, 0.2, 0.3, 0.4, 0.6, 0.8, and 1.0. The Pr contribution to the specific heat of all of the samples can be described as the sum of a Pr nuclear Schottky anomaly of the form $C_N(T)=AT^{-2}$, a linear term $C_L(T)=\gamma T$, and a Pr magnetic anomaly. For compounds with $x\leq 0.6$, which are metallic and superconducting, the Pr magnetic specific-heat anomaly has the same temperature dependence as a Kondo anomaly. For the compounds with $x\geq 0.8$, which are insulating, the magnetic specific-heat anomaly is consistent with antiferromagnetic ordering of the Pr ions with Néel temperatures T_N of 10.9 and 15.7 K for $x=0.8$ and 1.0, respectively. For $T<T_N$, the antiferromagnetic specific-heat anomaly has the form $C_M(T)=MT^3$, characteristic of three-dimensional antiferromagnetic magnons.

I. INTRODUCTION

The thirteen compounds with the chemical formula $RBa_2Cu_3O_{7-\delta}$ ($\delta\approx 0.1$) that form in the orthorhombic *Pmmm* crystal structure, where $R=Y$ or a lanthanide element except Ce, Pm, and Tb, are all metallic and superconducting with critical temperatures $T_c\approx 92-95$ K, except for $PrBa_2Cu_3O_{7-\delta}$, which is neither metallic nor superconducting.[1] In an attempt to obtain information about the singular behavior of Pr in this group of compounds, three independent experiments on the pseudoquaternary system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ were initially performed.[2–4] These experiments revealed a gradual transition from metal to insulator as x was increased from 0 to 1, and a monotonic decrease of T_c from 92 K at $x=0$ to 0 K at $x\approx 0.6$. More recent experiments on the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system indicate that the transition from metallic to insulating behavior is more abrupt and occurs near $x\approx 0.55$ where the superconductivity disappears.[5,6]

Two possible mechanisms for the suppression of T_c in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system have been considered. The first mechanism involves the filling of mobile holes in the conducting CuO_2 planes by electrons donated by the substituted Pr ions with a valence greater than +3, the valence of the Y ions.[2–4] Magnetic-susceptibility,[4,7] Hall-effect,[8] thermoelectric-power,[9] muon-spin-resonance (μSR),[10] and neutron-diffraction[11] measurements, as well as Ca substitution[12] experiments, are consistent with a Pr valence that is substantially larger than +3. The second mechanism is pair breaking due to spin-dependent exchange scattering of mobile holes in the CuO_2 valence band by Pr ions.[12–16] This would be expected for Pr ions with a nearly integral valence of $\sim +3$ or $\sim +4$ which carry well-defined magnetic moments that are strongly exchange coupled to the spins of the holes in the conducting CuO_2 planes. A large antiferromagnetic exchange interaction could be generated by hybridization of the localized Pr $4f$ states and CuO_2 valence-band states.[12,13,16] Evidence for Pr $4f-CuO_2$ valence-band hybridization was inferred from the anomalous pressure dependence of T_c in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system .[13] Valence-band resonant photoemission studies of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system indicate extensive Pr $4f-O$ $2p$ and Pr $4f-Cu$ $3d$ hybridization and a valence of Pr close to +3 (Refs. 17 and 18), while x-ray-absorption near-edge structure (XANES) measurements[19] on $PrBa_2Cu_3O_{7-\delta}$ are consistent with a valence of +3 for Pr. According to electron-energy-loss-spectroscopy measurements of the O 1s absorption edges in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, the total number of holes on O sites is independent of x,[20] suggesting that the Pr ions are trivalent and localize, rather than fill, mobile holes in the CuO_2 planes. The mechanism for localizing the mobile holes would presumably be associated with the Pr $4f-CuO_2$ valence-band hybridization. Recent measurements of the Pr $L_{\text{I-III}}$ x-ray-absorption edge reveal the existence of a small amount ($\sim 10\%$) of Pr^{4+} character.[21,22] Band-structure calculations[23] support the occurance of Pr $4f-CuO_2$ valence-band hybridization in the $Y_{1-x-y}Pr_xCa_yBa_2Cu_3O_{7-\delta}$ system.

Recently, T_c was measured as a function of Pr concentration x and Ca concentration y in the $Y_{1-x-y}Pr_xCa_yBa_2Cu_3O_{7-\delta}$ system in the range $0\leq x,y\leq 0.2$.[12] The variation of T_c with x and y has been interpreted[12] in terms of the combined effects of (1) the filling and generation of mobile holes in the CuO_2 planes by nearly tetravalent Pr ions and divalent Ca ions, respectively, and (2) pair breaking due to spin-dependent exchange scattering of mobile holes in the CuO_2 valence band by the Pr ions.[12–16] A phenomenological model based up on these two mechanisms has been developed[12,24,25] which can account for the dependence of T_c on x and y in the $Y_{1-x-y}Pr_xCa_yBa_2Cu_3O_{7-\delta}$ system[12] as well as the anomalous pressure dependence of T_c previously reported for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.[13]

The Pr $4f-CuO_2$ valence-band hybridization could facilitate the transfer of Pr localized $4f$ electrons to the CuO_2 planes and generate a large negative exchange interaction that is not present for the other R ions in the $RBa_2Cu_3O_{7-\delta}$ compounds. In metals, the negative exchange interaction between transition metal, rare earth, and actinide solutes with partially filled $3d$, $4f$, or $5f$ electron shells which carry well-defined magnetic moments and the conduction-electron spins, is known to give rise to the Kondo effect.[26] Especially noteworthy are metals containing trivalent Ce solutes which often exhibit the Kondo effect with attendant anomalies in the physical properties. Like trivalent Ce ions, tetravalent Pr ions have one f electron in the $^2F_{5/2}$ state, and, in a metallic environment with a negative exchange interaction between the Pr magnetic moments and the conduction electrons, would be expected to produce a Kondo effect. Although the number of mobile holes available to compensate the Pr magnetic moments in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system is relatively small (~ 2 orders of magnitude lower than in a normal metal), a similar situation is encountered in the Ce monopnictides,[27] where a well-defined coherent Kondo lattice ground state was found to form in spite of the small number of conduction electrons per Ce ion. We therefore thought it would be informative to measure the specific heat of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system to see if there are any anomalies traceable to Pr $4f-CuO_2$ valence-band hybridization in the metallic state and how they differed from those in the insulating state. Preliminary accounts of the present work have been reported elsewhere.[16,24,28]

II. EXPERIMENTAL DETAILS

The specimens of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ were prepared by solid-state reaction of the appropriate amounts of high purity (99.99% or better) Y_2O_3, Pr_6O_{11} $BaCO_3$, and CuO. All of the oxides were dried overnight at 800 °C prior to use. The powders were weighed, ground in an agate mortar, placed as a powder in an Al_2O_3 crucible, and fired in air at 900 °C for 2 days. The resultant powder was then reground and fired for 2–3 days four times with intermediate grindings. Subsequently, the powder was pressed into pellets which were fired in oxygen for four days at 980 °C and then slow cooled at 1 °C/min to 540 °C, where they remained overnight before a final slow cool at 1 °C/min to room temperature. All specimens were annealed together in an atmosphere of flowing oxygen. Oxygen contents were determined by iodometric titration to be 6.95 ± 0.02. Structural analysis by means of x-ray diffraction indicated that the specimens had the *Pmmm* orthorhombic crystal structure for all values of x.

Low-frequency (~ 16 Hz) ac electrical resistivity measurements on the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ specimens revealed that they exhibit metallic behavior (positive ρ versus T slopes) in the concentration range $0 \le x \le 0.6$ as well as superconductivity. The values of the superconducting transition temperature $T_c \equiv T_c(0.5)$ and the transition width $\Delta T_c \equiv T_c(0.9) - T_c(0.1)$, where $T_c(0.n)$ is the temperature at which the resistivity drops to $0.n$ of its extrapolated normal-state value, are listed in Table I. The increase of ΔT_c with x is typical of substitutional systems and presumably reflects the slope of the T_c versus x curve and gradients in the Pr concentration. The moderate increase of ΔT_c with x and the absence of any structure in the resistive transition curves indicates that the Pr concentration gradients are small. The $x=0.6$ specimen exhibits a reversal of the metallic behavior at $T < 100$ K, where the resistance is reminiscent of charge-carrier localization. This sample exhibits a full transition to the superconducting state by ~ 1.4 K, which is probably due to filaments of Y-rich material, since a recent study[5,6] indicates that T_c vanishes at $x \cong 0.55$. The $x=0.8$ and 1 specimens have negative temperature coeficients of electrical resistivity $(1/\rho)(d\rho/dT)$ for all temperatures in the range $1.2 \le T \le 300$ K. Specific-heat measurements were performed between 0.5 and 30 K using a ^{3}He semiadiabatic calorimeter with the heat-pulse technique.

TABLE. I. Superconducting critical temperatures $T_c \equiv T_c(0.5)$ and transition widths $\Delta T_c \equiv T_c(0.9) - T_c(0.1)$, where $T_c(0.n)$ is defined as the temperature where the resistivity drops to $0.n$ of its extrapolated normal state value, and least-squares fitting parameters for the specific heat of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ compounds. The fittings for the samples with $x \le 0.6$ include nuclear Schottky, linear, and Kondo contributions. For the samples with $x \ge 0.8$, the fittings include nuclear Schottky, linear, and antiferromagnetic magnon contribution. Table entries include values for the Kondo temperature T_K, the critical exponent α, the coefficent γ of the linear term, the coefficent A of the nuclear Schottky anomaly, and the coefficient M of the antiferromagnetic magnon contribution.

x	T_c (K)	ΔT_c (K)	A (mJ K/Pr mol)	γ (mJ/Pr mol K^2)	α	T_K (K)	M (mJ/Pr mol K^4)
0	92.2	0.7					
0.2	73.3	2.7	0±10	247±10	3±0.05	0.5±0.1	···
0.3	62.5	3.9	0±10	235±10	3±0.05[a]	2.1±0.1[a]	···
0.4	45.3	2.8	15±10	101±10	3±0.05	15.4±0.1	···
0.6	9.0	9.6	69±5	141±10	5±0.05	8.5±0.1	···
0.8			71±5	130±10	···	···	7.7±0.2
1.0			74±5	94±10	···	···	4.8±0.2

[a]For this sample the best fits are obtained with an entropy removal of only $0.6R$ ln2 (see text).

III. RESULTS AND DISCUSSION

Shown in Fig. 1 are specific heat C versus temperature T data for the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples with $x=0$, 0.2, 0.4, 0.6, 0.8, and 1.0 in the temperature range $0.5 \leq T \leq 25$ K. The same data, with the addition of data for a sample with $x=0.3$, are displayed in Fig. 2 as plots of C/T versus T^2.

Of all of the superconducting samples investigated, only the sample with $x=0.6$ had a value of T_c (~ 9 K) within the temperature range of the specific-heat measurements. However, no specific-heat jump could be discerned from the $C(T)$ data in Fig. 1 for the $x=0.6$ specimen, which is probably due to the fact that this sample does not exhibit bulk superconductivity, as discussed above. There are pronounced peaks in the $C(T)$ data in Fig. 1 at temperatures of 10.9 and 15.7 K for tha samples with concentrations $x=0.8$ and 1.0, respectively. Apparently, these peaks are associated with antiferromagnetic ordering of Pr^{4+} ions; for $PrBa_2Cu_3O_{7-\delta}$, antiferromagnetic ordering of the Pr^{4+} ions has been inferred from a feature in the magnetic susceptibility[16] and demonstrated directly by means of neutron-scattering studies[29] which reveal a magnetic structure consisting of simple antiferromagnetic arrays of Pr^{4+} moments in the basal planes aligned along the c axis. The maximum Néel temperature for antiferromagnetic ordering of the Pr ions ($T_N \approx 17$ K) is nearly an order of magnitude larger than the maximum Néel temperature for antiferromagnetic ordering of the other $RBa_2Cu_3O_{7-\delta}$ compounds ($T_N \approx 2.25$ K for $R=$Gd), which may be another manifestation of hybridization between the Pr localized $4f$ states and the CuO_2 valence-band states.[16]

The $C(T)$ data in Fig. 1 for the samples with lower Pr concentrations exhibit broad anomalies which manifest themselves as large gradual upturns in the C/T versus T^2 curves (Fig. 2). The C/T versus T^2 curves are reminiscent of the behavior of heavy fermion materials in which the electronic specific-heat coefficient $\gamma(T) \equiv C(T)/T$ increases with decreasing temperature and attains a value near 0 K as high as ~ 1 J/mol K^2. The steeper upturn in $C(T)/T$ at lower temperatures appears to be associated with a Pr nuclear Schottky anomaly.

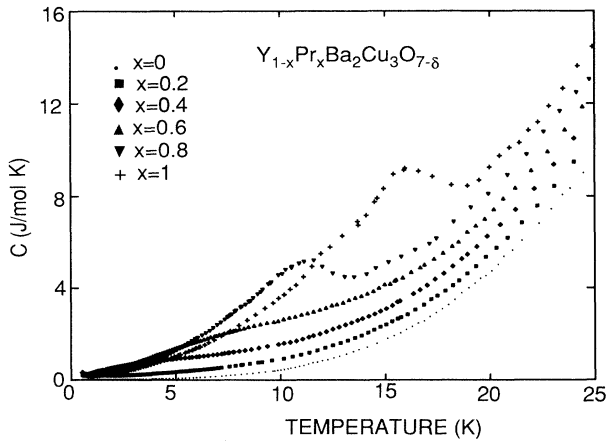

FIG. 1. Specific-heat C vs temperature T for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (with $x=0$, 0.2, 0.4, 0.6, 0.8, and 1.0) in the range $0.5 \leq T \leq 25$ K.

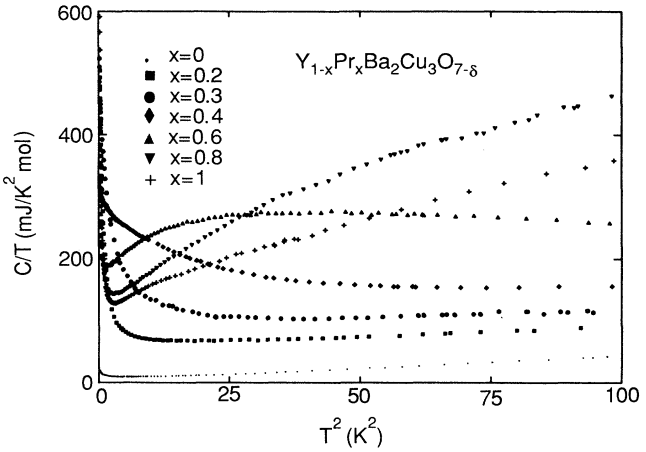

FIG. 2. Specific-heat C divided by temperature T, C/T, vs T^2 for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ in the range $0.5 \leq T \leq 10$ K.

The Pr contribution to the specific heat in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples was calculated as $\Delta C(T) = C_x(T) - C_0(T)$, where $C_x(T)$ is the measured specific heat for each composition x and $C_0(T)$ is the background contribution, the measured specific heat for $x=0$, assuming identical phonon contributions to $C(T)$ for $x \neq 0$ and $x=0$.

For Pr concentrations $x \leq 0.6$, the $\Delta C(T)$ data can be described as the sum of three contributions — a Pr nuclear Schottky anomaly $C_N(T)$, a linear term $C_L(T)$, and a Kondo anomaly $C_K(T)$; i.e.,

$$\Delta C(T) = C_N(T) + C_L(T) + C_K(T) \ . \tag{1}$$

The Pr nuclear Schottky anomaly is assumed to take the form

$$C_N(T) = AT^2 \ , \tag{2}$$

while the linear term is given by

$$C_L(T) = \gamma T \ . \tag{3}$$

For the Kondo specific-heat anomaly, we use an expression from a static scaling model[30,31]:

$$C_K(T) = (B/T^2)[1 + (T_K/T)]^{-\alpha} \quad (\alpha > 2) \ . \tag{4}$$

The parameter B in Eq. (4) can be obtained from the entropy $R \ln(2S+1)$; i.e.,

$$B = (1-\alpha)(2-\alpha)T_K^2 R \ln(2S+1) \ , \tag{5}$$

where R is the universal gas constant, T_K is the Kondo temperature, and the spin S is taken to be $\frac{1}{2}$, which is appropriate for Pr ions which are tetravalent[7] and have a doublet ground state in the presence of the crystalline electric field (CEF). Least-squares fits of Eq. (1) in the temperature range 0.5–10 K for $x=0.2$, 0.3, and 0.4, and

0.5–15 K for $x=0.6$, to the $\Delta C(T)$ data for $Y_{1-x}Pr_xBa_2CU_3O_{7-\delta}$ specimens are shown in Fig. 3 and can be seen to give a good description of the $\Delta C(T)$ data. For the Kondo specific-heat anomaly, the best fits were obtained with $\alpha=3$ and yielded values for T_K of 0.5, 2.1, and 15.4 K for $x=0.2$, 0.3, and 0.4, respectively. The $x=0.6$ sample was fitted with $\alpha=5$ and $T_K=8.5$. Equation (4) was derived[30] using the classical static scaling hypothesis for second-order phase transitions, extended to negative values of the critical temperature T_c (in our case $T_c=-T_K$). Within this description, the "critical exponent" α is restricted to values $\alpha>2$. We have taken $\alpha=3$ for the samples with lower Pr concentrations, in analogy to the case of the concentrated Kondo system $CeCu_6$.[30] Nevertheless, no universality has been found in the description of heavy fermion systems in terms of only one possible value of α. On the contrary, the best fits of Eq. (4) to the specific-heat data of the concentrated Kondo system $CeRu_2Si_2$ (Ref. 31) and $CePd_3B$ (Ref. 32) are obtained with the values $\alpha=3.5$ and $\alpha=4$, respectively. An even higher value of α is required to fit the data for the $x=0.6$ sample with Eq. (4). This could be related to the proximity of the $x=0.6$ sample to the critical value for the onset of the metallic behavior and superconductivity for which neither a Kondo picture nor long-range magnetic order may be appropriate. A more realistic approach may be one which incorporates the interplay between these two phenomena.

For all of the samples with $x\leq 0.6$, the entropy associated with the Kondo anomaly was taken to be R ln2 as noted in the description of the parameter B in Eq. (5). Nevertheless, the best fit (shown in Fig. 3) for the $x=0.3$ sample is achieved for a Kondo contribution that is only 60% of the one described by Eqs. (4) and (5), implying an entropy removal of only $0.6R$ ln2 for this sample. Taken at face value, this suggests that only 60% of the Pr ions in the sample have a magnetic ground state that is expected for the Pr^{4+} configuration. At the moment, we do not have an explanation for the puzzling behavior of this particular sample.

The values of T_K and the coefficients A and γ of the Pr nuclear Schottky and linear terms are given in Table I. The increase of T_K with Pr concentration x suggests that the magnitude of the exchange interaction J and, in turn, the amount of hybridization between the Pr $4f$ and CuO_2 valence-band states, increases with x. However, this increase of T_K could be illusory and the result of complications associated with Pr-Pr magnetic interactions, the strength of which increases with Pr concentration and becomes dominant for the nonmetallic and nonsuperconducting samples.

In the range of Pr concentrations $x\geq 0.8$, the $\Delta C(T)$ data can be described by the sum of three contributions, the Pr nuclear Schottky anomaly $C_N(T)$, the linear term $C_L(T)$, and an antiferromagnetic magnon term $C_M(T)$ with no activation energy (energy gap); i.e.,

$$\Delta C(T)=C_N(T)+C_L(T)+C_M(T)\ . \tag{6}$$

The Pr nuclear Schottky anomaly $C_N(T)$ and linear term $C_L(T)$ are given by Eqs. (2) and (3), respectively, while the antiferromagnetic magnon term $C_M(T)$ has the form

$$C_M(T)=MT^3\ . \tag{7}$$

Least-squares fits of Eq. (6) in the temperature range 0.5–4 K to the $\Delta C(T)$ data for the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ specimens with $x=0.8$ and 1.0 are shown in Fig. 4. The values of A, γ, and M for the samples with $x=0.8$ and 1.0 are given in Table I.

The existence of a T^3 term, characteristic of antiferromagnetic magnons, is consistent with the magnetic order observed in neutron-scattering studies.[29] The absence of a gap in the magnon spectrum associated with the strong

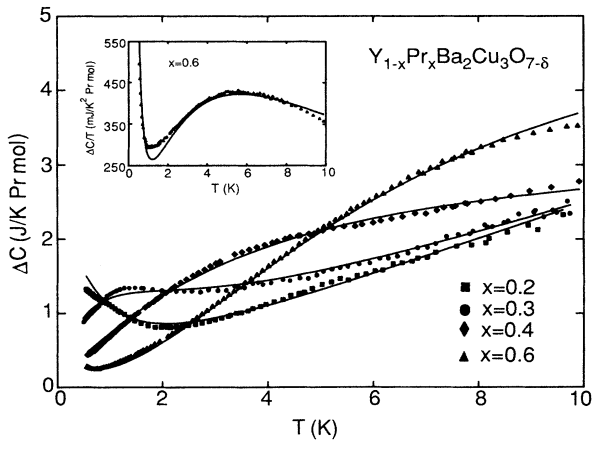

FIG. 3. Pr contribution to the specific heat, $\Delta C=C_x-C_0$, vs temperature T for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with $x\leq 0.6$. The inset shows $\Delta C/T$ vs T in a more extended temperature range for the sample with $x=0.6$. The solid lines represent fits which include nuclear Schottky, linear, and Kondo contributions (see text).

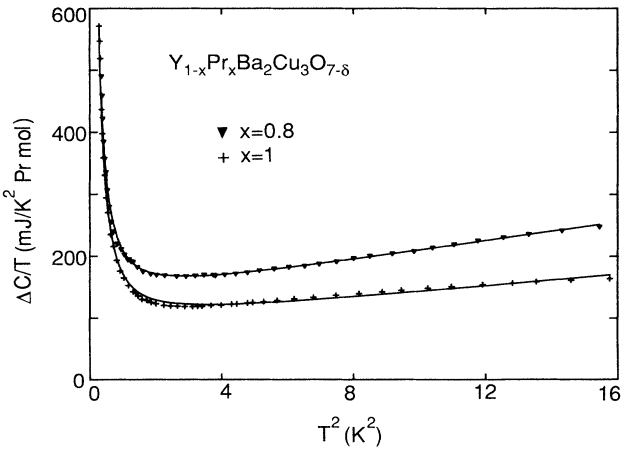

FIG. 4. Pr contribution to the specific heat, $\Delta C=C_x-C_0$, plotted as $\Delta C/T$ vs T^2, for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with $x=0.8$ and 1.0. The solid lines represent fits which include nuclear Schottky, linear and antiferromagnetic magnon contributions in the range $0.5\leq T\leq 4$ K.

anisotropy[33] of the antiferromagnetically ordered array of Pr moments along the c direction is surprising. However, it is possible that the exponential behavior characteristic of the anisotropy appears only at lower temperatures and has been obscured by the Pr nuclear Schottky anomaly. The coefficient M of the magnon term increases with decreasing Pr concentration; i.e., $M=4.8$ and 7.7 mJ/Pr mol K^4 for $x=1.0$ and 0.8, respectively. This behavior is consistent with the temperature dependence of the pronounced peak in the $C(T)$ data for these two samples. From the relation between the coefficients $M(x=1.0)$ and $M(x=0.8)$, we can obtain a relation between the cutoff energies $k_B\Theta_N(x=1.0)$ and $k_B\Theta_N(x=0.8)$ of the magnon spectrum; i.e.,

$$M(x=1.0)/M(x=0.8)=[n(x=1.0)/\Theta_N(x=1.0)]^3 \times[\Theta_N(x=0.8)/n(x=0.8)]^3, \quad (8)$$

where $n(x)$ represents the number of Pr atoms in each sublattice of the antiferromagnetic structure at Pr concentration x. Application of Eq. (8) yields the ratio $\Theta_n(x=1.0)/\Theta_N(x=0.8)=1.46$, which is comparable to the ratio $T_N(x=1.0)/T_N(x=0.8)=1.44$ between the Néel temperatures T_N estimated from the maximum of the specific heat for the two samples. This good agreement (within 2%) reflects the fact that the low-temperature excitations are actually related to the magnetic order observed at higher temperatures.

Figure 5 shows the evolution of the coefficient γ of the linear term and the coefficient A of the nuclear Schottky contribution as a function of Pr concentration for all of the samples. A noteworthy step occurs in the values of γ and A for concentrations near the threshold for the onset of metallic behavior and superconductivity.

The AT^{-2} term, attributed to the high-temperature tail of the nuclear Schottky anomaly, could be caused by electric quadrupolar and/or hyperfine-field interactions. In this high-temperature limit, the coefficient A is given by the sum of both quadrupolar A_q and hyperfine $A_{\rm hf}$ contributions. In the presence of internal fields, A_q is normally negligible in comparison to $A_{\rm hf}$.[33] In our case, the evolution of A with Pr composition could be explained by a sudden increase in the hyperfine field when crossing the metal-insulator phase boundary. For low-Pr-concentration samples, the Kondo screening of the Pr magnetic moments should produce a many-body singlet ground state and, therefore, negligibly small hyperfine fields, while for higher-concentration samples, the presence of magnetic order implies the existence of finite hyperfine fields $H_{\rm hf}$. The magnitude of $H_{\rm hf}$ can be estimated from the values of A using

$$A=(\tfrac{1}{3})R(g_I\mu_N H_{\rm hf}/k_B)^2 I(I+1)\ , \quad (9)$$

where R is the universal gas constant, k_B is Boltzmann's constant, μ_N is the nuclear magneton, I is the nuclear spin, and g_I is the nuclear spectroscopic splitting factor. From Eq. (9), we have obtained $H_{\rm hf}\approx 0$, 0, 40, 86, 87, and 89 T for $x=0.2$, 0.3, 0.4, 0.6, 0.8, and 1.0, respectively, neglecting possible electric quadrupolar interactions.

The linear term γT is usually attributed to the electronic contribution to the specific heat for which the coefficient γ is ordinarily a measure of the electronic density of states $N(E_F)$ at the Fermi level E_F. The existence of such an electronic term is unexpected at any Pr concentration, since an energy gap should open up in the density of states in both the metallic-superconducting and insulating phases. However, a finite γ could occur in the superconducting phase if the superconductivity were rendered "gapless" due to the presence of strong exchange scattering of conduction electrons (or holes) by the Pr magnetic moments. The magnitude of the coefficient γ would be expected to increase in proportion to the number of Pr exchange scattering centers, which is in accord with experiment. As shown in Fig. 5, the coefficient γ increases by a factor of ~ 2 upon going from the insulating to the metallic region, which could be interpreted as an increase in $N(E_F)$. However, any interpretation of the γT contribution to the specific heat in terms of mobile electrons (or holes) should be made with caution, since the thermal population of the excited Pr $4f$ levels in the CEF (Ref. 34) could give a contribution that has been neglected in the present analysis. In particular, the low-temperature part of this contribution could be enhanced for the low-Pr-concentration samples by the hybridization of the excited Pr $4f$ levels in the CEF with the conduction electrons (holes) as has been observed in other Kondo systems.[35] large γT contributions to the specific heat in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system have previously been reported by our group[16,28] and other groups.[7,36,37]

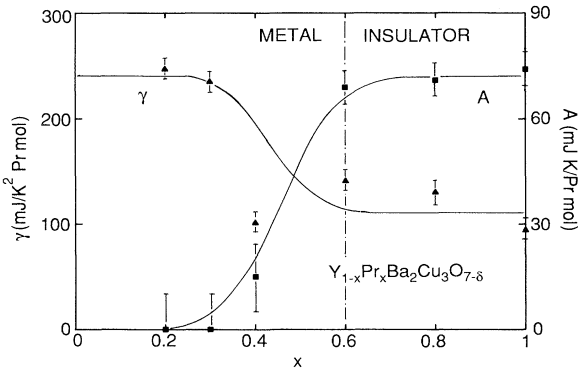

FIG. 5. Linear specific-heat coefficient γ and nuclear Schottky specific-heat coefficient A vs concentration x for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

IV. CONCLUDING REMARKS

Low-temperature specific-heat measurements as a function of temperature between 0.5 and 30 K have been performed on $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ compounds with $x=0$, 0.2, 0.3, 0.4, 0.6, 0.8, and 1.0. The specific heat of all of the samples can be described as the sum of a Pr nuclear Schottky anomaly of the form $C_N(T)=AT^{-2}$, a linear term $C_L(T)=\gamma T$, and a Pr magnetic specific

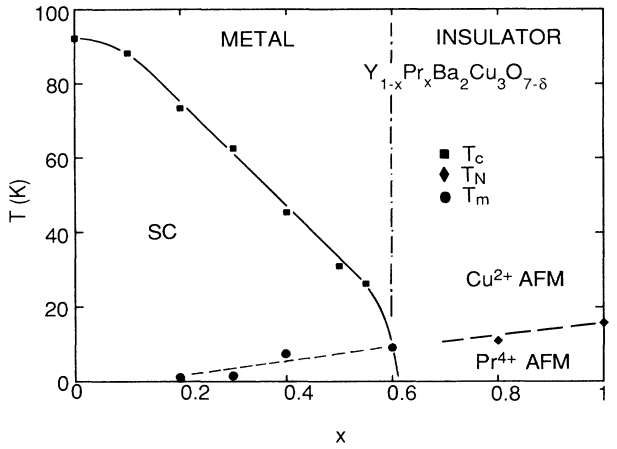

FIG. 6. Temperature vs Pr concentration x phase diagram for the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system. The superconducting critical temperature T_c corresponds to the midpoint of the resistive superconducting transition curve. The temperature of the maximum of the magnetic specific-heat anomaly is indicated by T_m for $x \leq 0.6$ and by T_N, the Néel temperature, for $x=0.8$ and 1.0. AFM = antiferromagnetic.

anomaly. For compounds with $x \leq 0.6$, which are metallic and superconducting, the Pr magnetic specific-heat anomaly has the same temperature dependence as a spin-$\frac{1}{2}$ Kondo anomaly. The occurrence of a Kondo effect is consistent with a negative exchange interaction between the Pr magnetic moments and the spins of the mobile holes in the CuO_2 planes, which, in turn, was anticipated from the Pr $4f$–CuO_2 valence-band hybridization we originally inferred from the pressure dependence of T_c and other properties of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.[13,16] The spin-$\frac{1}{2}$ character of the Kondo specific-heat anomaly indicates that the ground state of Pr in the CEF is a doublet, which suggests that the Pr valence is close to +4, since the ground state of the Pr^{3+} ion in the CEF should be a singlet. However, a Pr valence close to +4 is at variance with spectroscopic results which indicate a valence closer to +3, although there is growing spectroscopic evidence for substantial hybridization between Pr $4f$ states and the Cu $3d$ and O $2p$ states associated with the CuO_2 planes.[17,18,21,22] The resolution of this question is presently unclear. For the compounds with $x \geq 0.8$, which are insulting, the magnetic specific anomaly is consistent with antiferromagnetic ordering of the Pr ions with Néel temperatures T_N of 10.9 and 15.7 K for $x=0.8$ and 1.0, respectively. For $T < T_N$, the antiferromagnetic specific-heat anomaly has the form $C_M(T)=MT^3$, characteristic of antiferromagnetic magnons.

The specific-heat data presented here and other data reported in the literature for the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system reveal a rich temperature versus Pr concentration x phase diagram which is shown in Fig. 6. The data plotted in the figure represent the superconducting temperature T_c and the maximum of the magnetic specific-heat anomaly at low temperature, presumably associated with the Kondo effect for $x \leq 0.6$ and identified as T_m, and attributed to antiferromagnetic ordering of the Pr ions for $x \geq 0.6$, where it is associated with the Néel temperature T_N. Also indicated in Fig. 6 is the metal-insulator phase boundary which was estimated from the change in the temperature dependence of the electrical resistivity from metallic to semiconductorlike character. The metal-insulator phase boundary coincides with the onset of superconductivity, as well as the change in the shape of the specific-heat anomaly from a sharp peak, indicative of antiferromagnetic order, to a broad maximum we have interpreted in terms of the Kondo effect. Independent evidence for the occurrence of a Kondo effect is highly desirable since the broad anomalies in the specific heat of the superconducting samples could also be interpreted as a spin-glass type of behavior or as a distribution of Néel temperatures associated with the antiferromagnetic interactions between the Pr ions. Unfortunately, magnetic-susceptibility measurements are difficult to interpret because of complications introduced by the diamagnetism associated with the superconductivity and vortex lattice dynamics, and electrical resistivity and thermoelectric-power measurements are not very useful because these properties vanish in the superconducting state. Finally, the antiferromagnetic ordering of the Pr ions in the insulating region $0.6 \leq x \leq 1.0$ occurs in a background of antiferromagnetic ordering of the Cu(2) ions according to zero-field μSR (Ref. 38) and Mössbauer[39] experiments with Néel temperatures of the order of 200 K.

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