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Superconductivity and magnetism in $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

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Measurements of the electrical resistivity ρ as a function of temperature T, and low-temperature specific heat C as a function of T and magnetic field H, have been performed for Pr concentrations $0 \le x \le 1$ in the $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system ($\delta \approx 0.05$). The superconducting critical temperature $T_c(x)$ in the metallic phase ($0 \le x \lesssim x_c \approx 0.5$) was determined from the resistivity $\rho(x,T)$, while the Néel temperature $T_N(x)$ in the insulating phase ($x_c \lesssim x \le 1$) was inferred from specific-heat anomalies due to antiferromagnetic (AFM) ordering of the Pr ions. The effect of "chemical" pressure on $T_c(x)$ in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system is opposite to that of applied hydrostatic pressure. The Pr contributions to the specific heat in the insulating phase have the form $C(T)=MT^3$ for $T<T_N$, characteristic of three-dimensional AFM magnons. In contrast, the Pr contribution to $C(T)$ in the metallic phase takes the form of a broad anomaly that can be described by a spin-$\frac{1}{2}$ Kondo model. The entropy associated with the Pr specific-heat anomalies in both the metallic and insulating phases is close to R ln2, indicative of a doublet ground state for Pr in the crystalline electric field and a Pr valence close to 4+.

I. INTRODUCTION

The compound $PrBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.1$) is the only isostructural member of the series of $RBa_2Cu_3O_{7-\delta}$ ($R=$ a rare-earth element except Ce, Pm, and Tb) compounds[1,2] that is nonmetallic and nonsuperconducting. The superconducting critical temperature T_c, which varies from ~90 to 95 K throughout the $RBa_2Cu_3O_{7-\delta}$ ($\delta<0.1$) series, is strongly depressed by the partial substitution of Pr for the R element. Studies of superconductivity in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system by a number of groups[2-5] revealed that T_c decreases monotonically with x and vanishes at a critical concentration $x_c \approx 0.5$–0.6 near the metal-insulator transition. The small discrepancies in the value of x_c reported in the literature may be due to differences in sample preparation or the oxygen content, which are known to affect T_c. Recent experiments[6] on the $Y_{1-x}Pr_xBa_2Cu_3O_{6.95}$ system show that T_c drops abruptly to zero near $x_c=0.55$.

A number of investigations, using a variety of experimental techniques, have been performed to elucidate the T_c depression mechanism in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system. The various explanations are based on inferred values of the valence of Pr ions in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. Spectroscopic studies[5,7-10] suggest that the valence of Pr is close to +3, with the formal valence estimated to be no larger than 3.1+.[10] This would suggest that the depression of T_c is due to magnetic pair breaking involving a strong exchange interaction between the Pr magnetic moments and the mobile holes in the CuO_2 planes. A large negative exchange interaction could be produced by hybridization between the Pr localized $4f$ electron states and CuO_2 valence band states. On the other hand, magnetic susceptibility[4,6] and specific heat[11,12] measurements can be interpreted in terms of a Pr valence close to 4+. This gives support to an alternate mechanism[2] for the depression of T_c specifically, the filling of holes in the conducting CuO_2 planes. Of course, pair breaking and hole filling could be simultaneously operable mechanisms for depressing T_c in the nearly tetravalent Pr situation.

A comparison between $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.05$) and oxygen-depleted $YBa_2Cu_3O_{7-\delta}$ in terms of μSR magnetic penetration depth[13] and normal-state ^{63}Cu NMR Knight shift[14] measurements implies that hole filling is the main effect in the depression of T_c. The dependence of T_c on pressure in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (Ref. 15) and on x and y in $Y_{1-x-y}Pr_xCa_yBa_2Cu_3O_{7-\delta}$ (Ref. 16) are consistent with a mechanism for the depression of T_c in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ that involves the combined effects of pair breaking and hole filling. Lopez-Morales *et al.*[17] proposed that the determination of the valence of Pr in $PrBa_2Cu_3O_{7-\delta}$ depends on whether an experiment measures properties associated with the Pr—O bond (that would yield Pr^{4+}) or the charge near the Pr site (that would indicate Pr^{3+}).

Evidence for antiferromagnetic (AFM) ordering of Pr with a Néel temperature $T_N \approx 16$ K in $PrBa_2Cu_3O_{7-\delta}$ was found in the magnetic susceptibility[18,19] and specific-heat data.[12] Neutron-diffraction measurements[18] indicate a simple three-dimensional commensurate AFM structure in the Pr sublattice with $T_N \approx 17$ K. The magnetic ordering is unusual in comparison to other $RBa_2Cu_3O_{7-\delta}$ compounds[20] because of the high value and lack of magnetic field dependence of T_N.[11] However, the magnetic behavior of Pr in $PrBa_2Cu_3O_{7-\delta}$ has several features in common with its behavior in other Pr oxides such as PrO_2 which has a comparable $T_N \approx 14$ K (Ref. 21) and $PrBaO_3$ which shows magnetic ordering below $T_N \approx 12$ K, possible due to a canted antiferromagnetic structure.[22] In the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, T_N decreases monotonically with Y concentration $(1-x)$, according to specific heat[11,12,23] and zero-field muon-spin-relaxation measurements.[24]

Specific-heat anomalies in superconducting $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ have been attributed to heavy-fermion behavior,[25] or to an "unknown" magnetic anomaly.[26] The occurrence of Kondo-like specific-heat anomalies has recently been reported[12] for superconducting $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ compounds. Upper critical-field measurements on $Gd_{0.55}Pr_{0.45}Ba_2Cu_3O_{7-\delta}$ are also consistent with a negative exchange interaction.[27] All of these observations support the hypothesis of hybridization of the Pr localized $4f$ and the CuO_2 valence-band states, resulting in a negative exchange interaction between the Pr magnetic moments and the spins of the mobile holes in the CuO_2 planes.

The compound $EuBa_2Cu_3O_{7-\delta}$ is superconducting with $T_c \approx 94.7$ K and the Eu ions are trivalent with a nonmagnetic $J=0$ ground state. Therefore, the $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system constitutes an alternative nonmagnetic environment for the Pr ions, providing another opportunity to study the metal-insulator transition, depression of T_c, and evolution of Pr and Cu AFM as a function of carrier concentration in high-T_c oxides.

II. EXPERIMENTAL DETAILS

Samples of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with $x=0$, 0.05, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1 were prepared by solid-state reaction. Stoichiometric quantities of high-purity (99.99% or better) Eu_2O_3, Pr_6O_{11}, $BaCO_3$, and CuO powders were dried, outgassed, and ground in an agate mortar. The resultant power was reacted in air for three weeks with at least seven intermediate regrindings. Subsequently, the powders were pressed into pellets and annealed in an atmosphere of oxygen for two days at ~960 °C, followed by slow cooling (1 °C/min) to 450° C, where they remained for 18 h before the final slow cool at room temperature (1 °C/min).

Powder x-ray diffraction data were taken with Cu K_α radiation using a rotating anode Rigaku diffractometer at 0.01° intervals in the 20–60° range of 2θ. Lattice parameters were calculated from diffraction peak positions by a least-squares method. Oxygen contents were determined by iodometric titration, assuming that the valences in the presence of excess I^- in acidic solution are $+1$, $+2$, $+3$, and -2 for Cu, Ba, (Eu, Pr), and O, respectively.

Low-frequency (~16 Hz) electrical-resistivity $\rho(T)$ measurements were performed by means of a standard four-probe technique using silver paint contacts. Specific-heat measurements were carried out in the 0.5–30 K range in a ^{3}He semiadiabatic calorimeter using the heat pulse technique. Measurements of specific heat in a magnetic field were made using a Ge resistance thermometer with a calibrated temperature-dependent magnetoresistance.

III. RESULTS

Oxygen content and lattice parameters. The oxygen content $(7-\delta)$ vs Pr concentration data shown in Fig. 1 (a) for $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ indicate that $(7-\delta)$ is almost constant. X-ray diffraction measurements on all of the samples reveal that they have the orthorhombic *Pmmm* crystal structure with no evidence of impurity phases. The variation of the lattice parameters with Pr concentration is presented in Fig. 1(b).

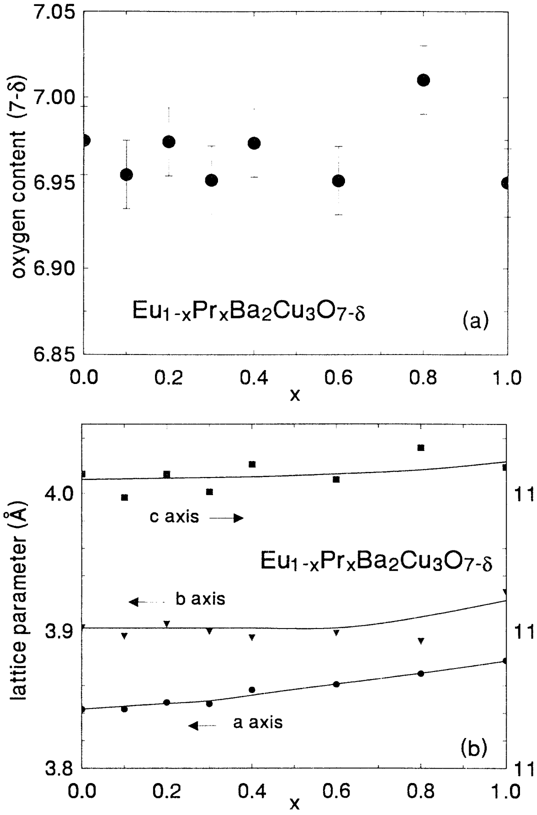

FIG. 1. (a) Oxygen content $(7-\delta)$ and (b) lattice parameters a, b, and c vs Pr concentration x for $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

Electrical resistivity. Displayed in Figs. 2(a) and 2(b) are representative electrical sensitivity $\rho(T)$ data for $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ in the form of plots of ρ vs T for $0 \leq x \leq 0.4$ [Fig. 2(a)] and $\log(\rho)$ vs T^{-1} for $0.6 \leq x \leq 1$ [Fig. 2(b)]. The $\rho(T)$ curves for specimens with $x \lesssim 0.3$ (the data for $x=0.05$ have been omitted for clarity) have metallic character, whereas the $\rho(T)$ curve for $x=0.4$ is metallic at high temperature but becomes nonmetallic close to T_c. For $x \geq 0.6$, $\rho(T)$ exhibits semiconductorlike behavior and the samples do not become superconducting. The general trends in the temperature dependence of ρ as a function of Pr concentration are similar to those found for the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.[2,4,25] The temperatures T_n at which the resistivity drops to $n=10\%$, 50%, and 90% of its extrapolated normal-state value are summarized in Table I. The superconducting critical temperature is defined as $T_c \equiv T_{50\%}$.

Specific heat. The specific heat $C(T)$ for the $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system in the temperature range 0.5–30 K exhibits systematic changes as shown in Fig. 3. The peak in $C(T)$ associated with the Pr AFM ordering in the insulating phase of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

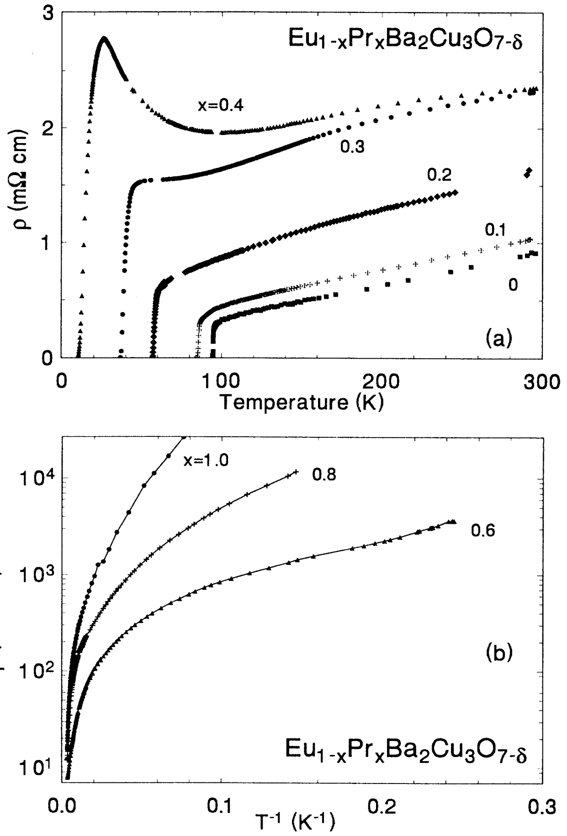

FIG. 2. (a) Electrical resistivity ρ vs temperature for superconducting $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. (b) Electrical resistivity ρ on a logarithmic scale vs inverse temperature T^{-1} for nonsuperconducting $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

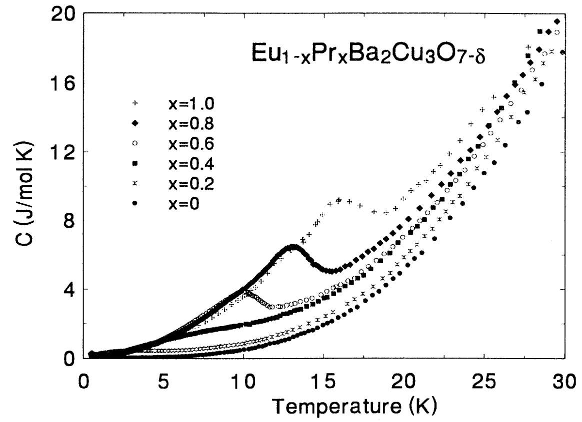

FIG. 3. Specific heat C vs temperature T for $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with $x=0$, 0.2, 0.4, 0.6, 0.8, and 1.

$(0.6 \leq x \leq 1)$ moves to lower temperatures with decreasing x; in the metallic-superconducting phase $(x \leq 0.4)$, the peak in $C(T)$ broadens considerably, but still shifts to lower temperature with decreasing x. The Pr contribution $\Delta C(T)$ to the low-temperature specific heat is shown in Fig. 4(a); $\Delta C(T) \equiv C_x(T) - C_0(T)$, where $C_x(T)$ is the measured specific heat for each composition x and $C_0(T)$ is the measured specific heat for $x=0$, assumed to consist of phonon and electronic contributions. The ΔC-vs-T curves for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ from Ref. 12 are shown in Fig. 4(b) for comparison. The differences between the

TABLE I. Temperatures corresponding to 10%, 50%, and 90% ($T_{10\%}$, $T_{50\%}$, and $T_{90\%}$, respectively) of the drop in resistivity from the extrapolated normal-state value for the superconducting samples in the $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system. We have defined the superconducting critical temperature as $T_c \equiv T_{50\%}$.

x	$T_0 \equiv T_{50\%}$ (K)	$T_{10\%}$ (K)	$T_{90\%}$ (K)
0	94.77	94.75	94.90
0.05	91.35	91.05	91.8
0.1	79.45	78.2	81.5
0.2	57.9	57.2	59.4
0.3	38.8	37.2	42.2
0.4	15	10.1	20.1

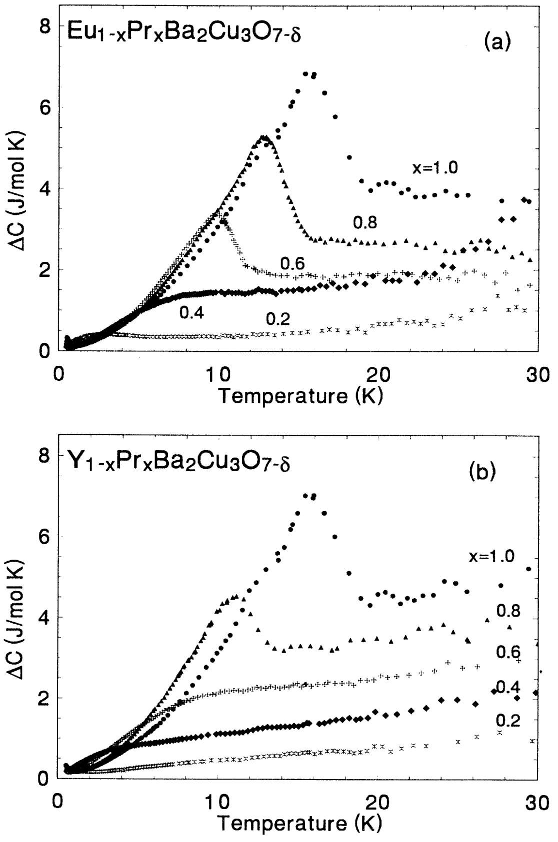

FIG. 4. (a) Pr contribution to the specific heat, $\Delta C(T) = C_x(T) - C_0(T)$, vs temperature T for $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. (b) Pr contribution to the specific heat, $\Delta C(T) = C_x(T) - C_0(T)$, vs T for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

two approximations based on $EuBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ for the background contribution $C_0(T)$ only have a sizable effect for $x=1$ and $T>20$ K. We believe that the Pr contribution to the specific heat for this sample [Fig. 4(a)] is better approximated by the data obtained from the Eu-based series since the atomic mass of Eu is closer than the Y mass to that of Pr.

IV. DISCUSSION

A. Superconducting and magnetic phase diagram

Whereas the variations of the lattice parameters with x do not exhibit any anomalies across the superconducting-nonsuperconducting transition at $x\approx 0.5$ in the $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, the rate of change of $\rho(296\text{ K})$ with x increases at this concentration as shown in Fig. 5. These results indicate that changes in Pr concentration affect the electronic density of states, or the number or mobility of the charge carriers.

The specific-heat anomaly in $\Delta C(T)$, which is sharp in the nonsuperconducting region, broadens markedly in the superconducting regime $x\leq 0.4$ in the $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system and $x\leq 0.6$ in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system.[12] Both systems show a monotonic decrease in T_c and an increase in the temperature T_M of the maximum in the specific heat with increasing x. However, as shown in the phase diagram of Fig. 6, striking differences appear in the slopes of the T_c and T_M-vs-x curves and, correspondingly, the values of the critical concentration x_c for the destruction of superconductivity and the appearance of the specific-heat anomalies associated with magnetic ordering of the Pr ions.

A consideration of the lattice parameters of $EuBa_2Cu_3O_{7-\delta}$ ($a=3.8429$ Å, $b=3.9023$ Å, $c=11.714$ Å), $YBa_2Cu_3O_{7-\delta}$ ($a=3.8229$ Å, $b=3.8865$ Å, $c=11.6821$ Å),[28] and $PrBa_2Cu_3O_{7-\delta}$ ($a=3.8783$ Å, $b=3.9281$ Å, $c=11.7186$ Å)[28] and the approximate Vegard's law variation of the three lattice parameters with x and y in the systems $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$,[28] and $Eu_{1-y}Y_yBa_2Cu_3O_{7-\delta}$,[29] implies that for a given Pr concentration x, the Pr ions may be regarded as being subjected to a negative chemical pressure in $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ relative to $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. The depression of T_c caused by Pr substitution in $YBa_2Cu_3O_{7-\delta}$ increases with increasing applied pressure for $x>0.3$.[15] The compression of the Pr site could increase the delocalization of the $4f$ electron thereby increasing the hole-filling or increasing the hybridization parameter, leading to more effective pair breaking. However, the increase of chemical pressure in going from $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ to $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ results in a decrease of the depression of T_c caused by Pr substitution. Figure 7(a) shows the effect of chemical pressure and Fig. 7(b)[15] shows the effect of hydrostatic pressure on T_c for different values of x. Noting that the ionic radius[30] of Eu^{3+} (1.066 Å) is greater than that of Y^{3+} (1.019 Å), the ionic radius of the rare earth has been taken to be proportional to $-P$ in Fig. 7(b). The apparent contradiction in the evolution of T_c with P and $-P$ for a given Pr concentration x may be resolved if the relative changes in parts of the structure relevant for superconductivity are similar for hydrostatic pressure and negative chemical pressure. The variation in T_c vs x between the Y- and Eu-based series [Fig. 7(a)] is possible related to structural differences, i.e., changes in the degree of orthorhombicity and the c-axis lattice parameter. The dependence of T_c on x for $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ systems with $R=$Er,[31] Gd,[27] Eu,[32] and Nd[33] and the trends as a function of ionic radii are in qualitative agreement with the results presented here, although possible differences in the oxygen content do not permit a quantitative comparison [a detailed study of $T_c(x)$ including other $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ systems is in progress and will be reported elsewhere].

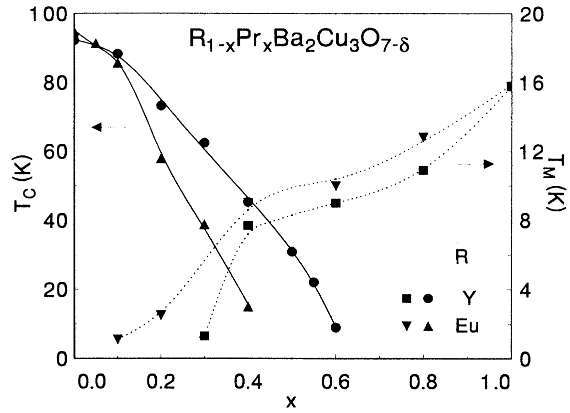

FIG. 6. Superconducting critical temperature T_c and temperature of the specific-heat maximum T_M vs Pr concentration x for $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ $R=$Y,Eu). The superconducting critical temperature T_c is defined as the midpoint of the resistive transition and T_M is identified with the Néel temperature for the samples with $X\geq 0.6$ in the insulating phase.

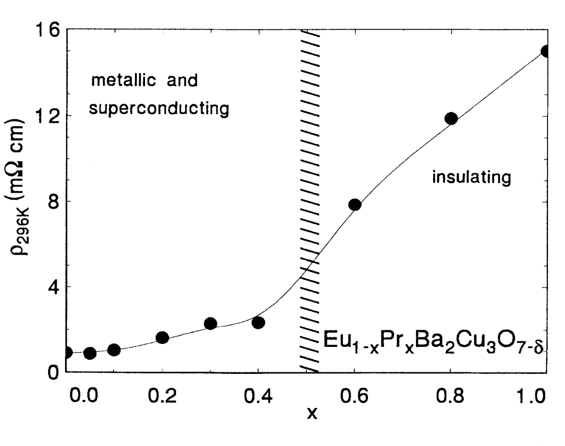

FIG. 5. Electrical resistivity ρ at 296 K vs Pr concentration for $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$.

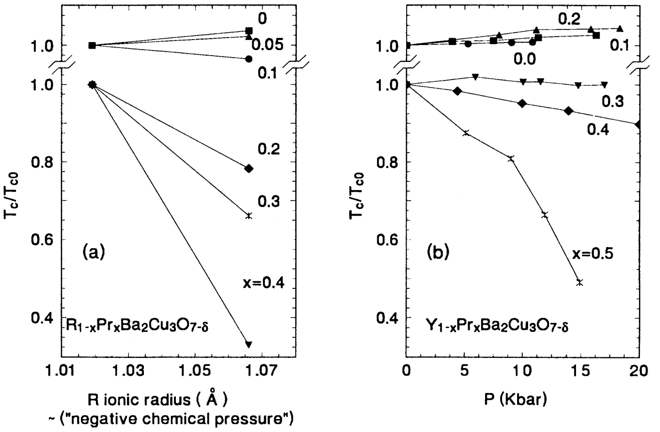

FIG. 7. Dependence of T_c on chemical (a) and hydrostatic (Ref. 15) (b) pressure on the Pr ions in $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($R=Y,Eu$) and $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, respectively. T_{C0} is the critical temperature of the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples at atmospheric pressure. The ionic radius of the R is assumed to be proportional to a negative chemical pressure on the Pr ions (see text).

The Pr AFM order in $PrBa_2Cu_3O_{7-\delta}$ is probably caused by the superexchange interaction, since there are few conduction electrons to mediate the Ruderman, Kittel-Kasuya-Yosida (RKKY) interaction and since T_N is too high to arise from dipole-dipole coupling. The sharp anomalies in the specific heat of the nonsuperconducting samples are apparently associated with AFM ordering of the Pr ions, since the anomaly at 15.7 K in $PrBa_2Cu_3O_{7-\delta}$ is coincident with the occurrence of AFM ordering at ~17 K according to neutron diffraction measurements.[18] We have, therefore, identified T_M with a Néel temperature T_N for these samples.

In addition to the decrease of T_N due to the dilution of the magnetic moments in the $R_{1-x}Pr_xBa_xCu_3O_{7-\delta}$ system, pressure should also affect the slope of T_N vs x, since it increases the overlap of the atomic wave functions involved in the superexchange interaction. The evolution of T_N with x shows an unusual chemical pressure effect upon replacing Y with Eu in $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ as shown in Fig. 6, where T_N is depressed faster with decreasing x for $R=Y$ than for $R=Eu$; i.e., for a given Pr concentration in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ and $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ systems, T_N is higher the higher the lattice parameter c. This curious behavior can be contrasted with the more intuitive behavior of magnetic ordering of Gd ions in $GdBa_2Cu_3O_{7-\delta}$. In this system, where $T_N=2.2$ K at ambient pressure, hydrostatic pressure, which increases the overlap of the Gd $4f$ orbitals with the wave functions of the CuO_2 planes, increases T_N,[34] while negative chemical pressure on the Gd ions depresses T_N. A comparison between $Y_{1-x}Gd_xBa_2Cu_3O_{7-\delta}$ (Ref. 35) and $Eu_{1-x}Gd_xBa_2Cu_3O_{7-\delta}$ (Ref. 36) reveals that the slope in the T_N-vs-x curve is steeper for the more relaxed lattice of Gd magnetic moments in the system.

It is possible, in the case of the unusual chemical pressure effect on the Pr magnetic behavior, that the superexchange interaction is enhanced by the strong hybridization of the Pr $4f$ orbitals with the wave functions in the CuO_2 planes. This hybridization could change with subtle variations in the structure.

B. Specific-heat anomalies

The peaks in $C(T)$ of the nonmetallic samples [Figs. 4(a) and 4(b)] are associated with the AFM transition that occurs at 15.7 K for $PrBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0$). The low-temperature region ($1 \leq T \leq 4$ K) of these magnetic specific-heat anomalies for $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($x=0.6$, 0.8, and 1) varies as MT^3, characteristic of three-dimensional AFM magnons. The coefficient M has the values 9.4, 5.7, and 4.9 mJ/Pr mol K^4 for $x=0.6$, 0.8, and 1, respectively. Within the temperature range $1 \leq T \leq 4$ K, there is no evidence for an anisotropy energy gap greater than 0.1 K. Nevertheless the existence of such a gap cannot be confirmed because the low-temperature specific heat ($T \leq 1$ K) is dominated by the Pr nuclear Schottky anomaly.

The entropy associated with the anomalies in $C(T)$ due to AFM order estimated for these three nonmetallic samples is $\sim R$ ln2. This is consistent with a doublet ground state expected for a Pr $^{4+}$ ion in the orthorhombic crystalline electric field (CEF). If Pr is in the +3 state, the corresponding $^3H_4$ J multiplet would have a singlet or a quasitriplet ground state according to CEF calculations using the superposition model.[37] Nonmagnetic behavior or an entropy of R ln3 would then be expected for the Pr^{3+} state. Unfortunately, only broad features are observed in inelastic neutron scattering spectra of $PrBa_2Cu_3O_{7-\delta}$, which may be due to admixture of localized $4f$ and conduction electrons. These broad features make it difficult to determine the Pr CEF energy-level scheme directly.[38,39]

The specific-heat anomalies due to the Pr ions for the metallic superconducting samples have a symmetric bell shape on a logarithmic temperature scale (Fig. 8), reminiscent of a Kondo specific-heat anomaly. In fact, the specific-heat anomalies in metallic superconducting $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ compounds have been interpreted in terms of the Kondo effect.[12] In spite of the low number of carriers, hybridization between the Pr localized $4f$ states and CuO_2 valence-band states can generate a negative exchange interaction between the Pr localized magnetic moments and the mobile holes in the CuO_2 planes.

The entropy estimated for the specific-heat anomaly due to the Pr ions in $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with $x=0.1$, 0.2, and 0.4 is $\sim R$ ln2, the same as for the nonsuperconducting samples, and consistent with a Pr valence close to +4. The calculated entropy versus temperature is shown in Fig. 9 for an insulating and a metallic sample; the larger errors bars for the $x=0.1$ sample arise from the estimate of the entropy contribution between 0 and 0.45 K, our lowest measuring temperature.

As pointed out in the preceding section, the temperature of the maximum in $C(T)$ decreases more slowly with decreasing x in $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (Fig. 6) than in

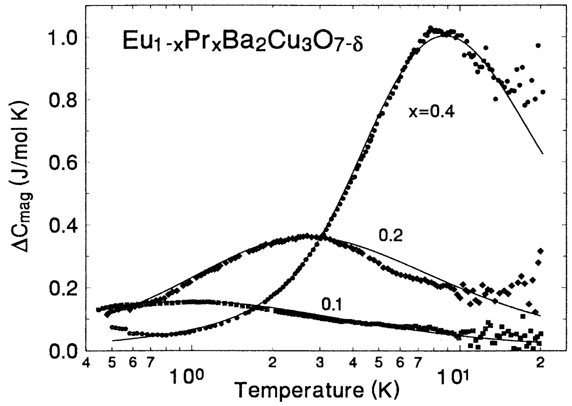

FIG. 8. Pr contribution to the specific heat for $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples with $x=0.1$, 0.2, and 0.4. The high temperature linear contribution was subtracted from the data; i.e., $\Delta C_{\mathrm{mag}}(T)=C_x(T)-C_0(T)-\gamma T$. The solid lines represent fits of Eq. (1) plus the linear term γT to the $\Delta C(T)$ data. The values for T_K, E, and γ used are listed in Table II.

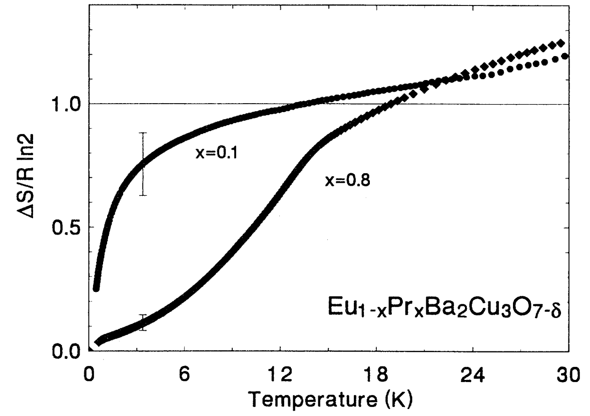

FIG. 9. Entropy ΔS per mol Pr, as a function of the temperature for a superconducting ($x=0.1$) and a nonsuperconducting ($x=0.8$) $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ sample.

$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ for both metallic and nonmetallic phases. This makes $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ particularly attractive for studying the dilute Pr regime and testing for the presence of a Kondo effect. The specific-heat anomaly due to Pr exhibits a maximum at ~ 1 K for $Eu_{0.9}Pr_{0.1}Ba_2Cu_3O_{7-\delta}$, whereas it occurs at a Pr concentration that is three times larger in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. This allows a study of the dilute Pr region where the antiferromagnetic interactions (present in the higher Pr concentration samples) should be considerably diminished, or even negligible.

The specific heat in the "resonant level model"[40] which describes the basic physics of the Kondo problem is given by

$$C(T)=k_B\frac{2S\Delta}{\pi k_B T}-2k_B\mathrm{Re}\left\{\frac{(\Delta+iE)^2}{(2\pi k_B T)^2}\left[(2S+1)^2\Psi'\left[1+\frac{\Delta+iE}{2\pi k_B T}(2S+1)\right]-\Psi'\left[1+\frac{\Delta+iE}{2\pi k_B T}\right]\right]\right\}, \tag{1}$$

where Ψ' is the derivative of the digamma function, $\Delta=k_BT_K$ is the width of the Lorentzian-shaped resonance at the Fermi level, $E=\mu\mathrm{H}$ is a shift introduced by a finite magnetic field, and S is the impurity spin. This description of the Kondo interaction yields a simpler expression for the specific heat (and with very similar results[41]) than the one obtained from the exact solution of the s-f exchange Hamiltonian for magnetic impurities in a metallic matrix.[42]

Using Eq. (1), assuming $S=\frac{1}{2}$ for a Pr doublet ground state in the CEF, and adding a γT term, a reasonable fit to the $\Delta C(T)$ data for $x=0.1$, 0.2, and 0.4 (solid lines in Figs. 8 and 10) could be obtained. The parameters γ, E/k_B, and T_K are given in Table II. The evolution of the parameter E and T_K with x can be understood as follows: The increase in E is possibly due to an increase in the molecular field[43] caused by increasing Pr-Pr magnetic interactions. The increase in the T_K may be caused by an increased hybridization with Pr concentration. However, the origin of the γT term, which was also observed in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ low-temperature specific heat,[12] is not readily apparent.

In spite of this, it is necessary to ascertain whether alternative explanations such as the formation of a spin glass or a distribution of Néel temperatures can account for the broad specific-heat anomaly in the metallic-superconducting samples. The evolution of the broad specific-heat anomaly with field (Fig. 10) rules out the possibility of its origin being due to a distribution of Néel temperatures since, in this case, the anomaly is expected to move to lower temperatures with increasing magnetic field.[44] The increase in the maximum of the specific-heat anomaly with field rules out the possibility of spin-glass behavior, since the maximum has been shown to decrease with field in spin glasses.[45]

The interpretation of the specific heat in terms of the Kondo effect explains the evolution of the maximum with

TABLE II. Summary of the least-squares fits of Eq. (1) plus a linear term γT to the $\Delta C(T)$ data for the superconducting samples of $Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, where T_K is the Kondo temperature and E the energy shift due to the molecular field (see text).

x	γ (mJ/mol Pr K^2)	E/k_B (K)	T_K (K)
0.4	112.5	18	7
0.2	90	3.75	4.5
0.1	40	0	2.1

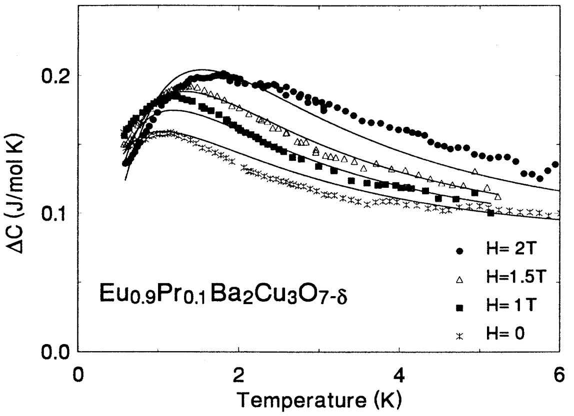

FIG. 10. Pr contribution to the specific heat, $\Delta C(T)=C_x(T)-C_0(T)$, for the $\mathrm{Eu_{0.9}Pr_{0.1}Ba_2Cu_3O_{7-\delta}}$ sample for various applied magnetic fields. The solid lines represent the calculated specific heat according to Eq. (1) for $T_K=2.1$ K and E appropriate for each internal magnetic field (magnetization corrected for demagnetizing factor), plus a linear term γT with a magnetic-field-independent $\gamma=4$ mJ/mol K^2.

field in a natural way as shown in Fig. 10, assuming a doublet ground state for Pr^{4+} with $S=\frac{1}{2}$ and $g=\frac{10}{7}$. The solid lines are derived from Eq. (1) and give a reasonable description of the data in applied magnetic fields up to $2\,T$.

The applied magnetic field could also create a Zeeman splitting of the doublet ground state, and the thermal population of the excited level would generate a Schottky anomaly in the specific heat. While the temperature of the Schottky-anomaly maximum would increase with increasing field, its value C_m should remain constant and equal to $C_m=0.36$ J/mol K for the $x=0.1$ sample. Since the value of C_m does not remain constant in the data displayed in Fig. 10, this possibility can be ruled out. However, this effect has been observed for other $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ systems[46] with a doublet ground state in which the hybridization between the R $4f$ states and the $\mathrm{CuO_2}$ valence-band states is apparently very small and there is no evidence for Kondo-like anomalies.

V. CONCLUDING REMARKS

Measurements of $\rho(x,T)$ and $C(x,T,H)$ have been performed on $\mathrm{Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}}$ components for $0\le x\le 1$. The $T_c(x)$ curve, determined from $\rho(x,T)$ in the metallic phase, decreases monotonically with x to zero near the metal-insulator phase boundary at $x_c\approx 0.5$. The $T_N(x)$ curve was inferred from the peaks in the anomalies in $C(x,T)$ due to AFM order in the insulating phase. Chemical pressure has the opposite effect as applied hydrostatic pressure on the $T_c(x)$ and $T_N(x)$ phase boundaries. The compression of the Pr site could increase the delocalization of the $4f$ electron, thereby increasing the hole-filling effect or increasing the hybridization parameter, leading to more effective pair breaking. However, the increase of chemical pressure in going from $\mathrm{Eu_{1-x}Pr_xBa_2Cu_3O_{7-\delta}}$ to $\mathrm{Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}}$ results in a decrease of the depression of T_c caused by Pr substitution. The AFM anomalies in $C(x,T)$ can be described by the relation $C(T)=MT^3$ below T_N, a behavior that is characteristic of three-dimensional AFM magnons.

In the metallic phase, the Pr contribution to the specific heat takes the form of a broad anomaly, rather than the sharp anomaly due to AFM ordering that characterizes the insulating phase. The temperature dependence of the Pr specific-heat anomalies in the metallic region can be described well by a spin-$\frac{1}{2}$ Kondo anomaly with parameters that evolve as expected with x. The magnetic field dependence of the Pr specific-heat anomaly for $x=0.1$ conforms to the predictions of a spin-$\frac{1}{2}$ Kondo model, and is in disagreement with the variation expected for AFM ordering with a distribution of Néel temperatures or a spin glass. The temperature dependence of the entropy corresponding to the Pr specific-heat anomalies in both metallic and insulating phases indicate a value close to R ln2, implying a doublet ground state for Pr in the CEF which suggests a Pr valence close to +4.

The existence of a spin-$\frac{1}{2}$ Kondo effect in the specific heat of the $\mathrm{Eu_{1-x}Pr_xBa_2Cu_3O_{-7\delta}}$ system implies that there is an antiferromagnetic exchange interaction between the mobile holes in the $\mathrm{CuO_2}$ planes and the Pr^{4+} magnetic moments. Similar behavior was previously reported for the $\mathrm{Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}}$ system.[12] In spite of the low carrier density in these systems, Kondo spin compensation seems to be involved in the enhancement of the effective mass of the electrons. The existence of a Kondo effect is not readily detectable in other physical properties such as the electrical resistivity and thermoelectric power, which vanish in the superconducting state, and the magnetic susceptibility, due to complications introduced by the diamagnetism associated with the superconductivity and vortex lattice dynamics. A large antiferromagnetic exchange interaction would be expected for strong hybridization between the Pr localized $4f$ states and the $\mathrm{CuO_2}$ valence band states.

The specific-heat data are consistent with hole filling (or localization) and pair breaking as mechanisms which determine the behavior of T_c as a function of Pr concentration. Hole filling (or localization) is reflected in the $\rho(x,T)$ data which evolve from "metallic" for $0\le x\lesssim x_c$ to semiconductorlike in the range $x_c\lesssim x\le 1$. The strength of the exchange interaction $\mathcal{J}$ is difficult to estimate from the specific-heat data. The values of T_K, which range from ~2 K at $x=0.1$ to ~7 K at $x=0.4$, yield estimates for $|\mathcal{J}|$ of ~10 to ~100 meV; uncertainty in other parameters involved in the analysis preclude a more precise determination. However, this range of values overlaps the value of 41 meV obtained from an analysis of $T_c(x,y)$ in the $\mathrm{Y_{1-x-y}Pr_xCa_yBa_2Cu_3O_{7-\delta}}$ system,[16] although this analysis did not include higher-order exchange scattering associated with the Kondo effect. It is interesting to note that the values of T_K inferred from the specific-heat data vary nearly linearly with x between 0.1 and 0.4 and suggest a very small value near $x=0$.

A detailed study of the evolution of T_K and, in turn, $\mathcal{J}$

with x and the structural changes induced through chemical and hydrostatic pressure could be very illuminating.

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