VOLUME 46, NUMBER 1

Magnetic-susceptibility and heat-capacity measurements on Pr-rich $PrBa_{2-x}Pr_xCu_3O_{7-y}$ compounds

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The compound $PrBa_2Cu_3O_{7-y}$, though isostructural to the 90-K superconducting compounds, $RBa_2Cu_3O_{7-y}$ (R=rare earth and Y), is semiconducting. Moreover, it orders magnetically with $T_N \sim 16$ K and also exhibits a large electronic specific-heat coefficient γ . We have prepared Pr-rich $PrBa_{2-x}Pr_xCu_3O_{7-y}$ ($0 \le x \le 1$) compounds to study the effect of excess Pr at the Ba site on the structure, magnetic ordering, and electronic specific-heat coefficient of this system. It is observed that singlephase compounds in the above series form up to $x \sim 0.8$. The stoichiometric $PrBa_2Cu_3O_{7-y}$ is orthorhombic but the compounds with excess Pr form in the closely related tetragonal structure. Magneticsusceptibility and heat-capacity measurements reveal that both T_N and γ decrease with increasing Pr concentration suggesting a common origin underlying the two.

The absence of superconductivity and the unusual magnetic properties of the compound $PrBa_2Cu_3O_{7-\nu}$ have attracted a great deal of attention (see, for instance, Refs. 1–17). Though isostructural to $RBa_2Cu_3O_{7-\nu}$ (R = rare earth or Y) compounds, most of which are superconducting with T_c in the 90-K range,¹⁸ this compound is semiconducting down to very low temperatures. The absence of superconductivity in $PrBa_2Cu_3O_{7-\nu}$ has been attributed to the capability of the Pr ions to show a stable valence state of other than 3+. The effective magnetic moment² of the Pr ions in $PrBa_2Cu_3O_{7-y}$ is $\sim 3\mu_B$, which is intermediate between that of Pr^{3+} (2.56 μ_B) and Pr^{4+} (3.56 μ_B) and is taken to imply an intermediate valence state of the Pr ions. Thus in the so-called bandfilling model, the additional electron from the Pr^{4+} ion (relative to other trivalent rare-earth ions) is thought to neutralize a hole in the CuO network rendering the system nonsuperconducting. However, x-ray absorptionedge studies⁴ reveal that the charge state of Pr is close to 3+, and the reduced magnetic moment can result¹⁵ due to crystalline electric fields acting on Pr³⁺ ions without invoking the intermediate valence state.

The Pr compound also exhibits magnetic ordering of the Pr moments with a Néel temperature (T_N) of ~16 K.^{7,9,10} This is much higher than the T_N of ~2.24 K of the isostructural Gd compound (see, for instance, Ref. 19). Moreover, the electronic specific-heat coefficient, γ , of PrBa₂Cu₃O_{7-y} is extremely large^{7,10,11} suggesting the presence of 4f electronic states near the Fermi level. This is indeed confirmed by x-ray photoemission spectroscopy (XPS) measurements.⁶ Therefore, in an alternate model, the absence of superconductivity in PrBa₂Cu₃O_{7-y} has been thought to be due to the strong hybridization between the Pr 4f electrons and the Cu 3d and O 2p electrons. Such a hybridization can lead to strong exchange interaction between the Pr spins and the conduction-electrons spins and may be responsible for the relatively high ordering temperature of the Pr moments in $PrBa_2Cu_3O_{7-\nu}$. The suppression of superconductivity in the $R_{1-x} Pr_x Ba_2 Cu_3 O_{7-y}$ (R = Y, Sm, Gd, and Tm) with increasing Pr concentration¹⁶ follows the Abrikosov-Gor'kov curve and the upper critical fields in $Y_{1-x} Pr_x Ba_2 Cu_3 O_{7-y}$ show a bell-shaped curve⁸ reminiscent of the exchange interaction mentioned above. It has been also suggested¹² that both band-filling and hybridization effects may be important in understanding the unusual behavior of $PrBa_2Co_3O_{7-\nu}$. Other models, such as the spin-polaron model,¹⁷ have also been proposed to explain the absence of superconductivity $PrBa_2Cu_3O_{7-\nu}$.

It is known that the rare earths can be partially substituted at the Ba site to give rise to compounds of the type $RBa_{2-x}R_xCu_3O_{7-y}$ (R = La, Nd, Sm, Eu, Gd, and Dy).²⁰ The extent of such substitution depends on the size of the rare-earth ion involved and decreases with decreasing ionic radius. The superconducting transition temperature decreases with increasing rare-earth substitution at the Ba site. The T_c values in these compounds fall on a universal curve as a function of x suggesting that this decrease in T_c is not due to the magnetism of the rare-earth ion at the Ba site but rather due to electronic effects. Thus the magnetic rare-earth ions, both at the R site and at the Ba site, behave similarly in the sense that both of them have weak coupling with the conduction electrons. We have examined the Pr-rich, $PrBa_{2-x}Pr_{x}Cu_{3}O_{7-y}$ compounds to study the effect of excess Pr on the structure, superconductivity, and magnetism of these compounds. We find that Pr can be introduced at the Ba site to the extent of $x \sim 0.8$, i.e., up to the stoichiometry $PrBa_{1,2}Pr_{0,8}Cu_{3}O_{7-\nu}$, beyond which the samples are not single phase. Magnetic-susceptibility measurements reveal that the magnetic ordering temperature decreases

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The $PrBa_{2-x}Pr_xCu_3O_{7-y}$ samples with x = 0.0-1.0were prepared by the standard ceramic procedure. Stoichiometric amounts of Pr₆O₁₁, BaCO₃, and CuO were thoroughly mixed, pressed into pellets, and sintered at 930°C for 24 h. The resulting material was powdered, compacted, and reheated and this process was repeated several times with the final sintering being done in a flowing-oxygen atmosphere. Powder x-ray-diffraction patterns were obtained on a Sieman's x-ray diffractometer equipped with $CuK\alpha$ radiation, which showed that the $PrBa_{2-x}Pr_{x}Cu_{3}O_{7-y}$ samples with $0 \le x \le 0.8$ are single phase. Beyond x = 0.8, additional lines are observed in the x-ray patterns. As mentioned earlier, the stoichiometric $PrBa_2Cu_3O_{7-\nu}$ compound has the orthorhombic structure. However, as x or the Pr concentration increases in the $PrBa_{2-x}Pr_{x}Cu_{3}O_{7-y}$ series, the observed x-ray patterns can be indexed on the basis of a tetragonal unit cell. The lattice parameters, obtained from the least-squares fits of the observed d values are summarized in Table I. The lattice parameters and the unit-cell volume decrease with increasing Pr concentration. The oxygen content was determined to be in the range of 6.9-7.05. Susceptibility measurements were made in the temperature range 4.2-300 K in applied fields of 5 kOe using a setup based on the Faraday method. Specific-heat measurements were performed in the temperature range 4.2-25 K with a standard heatpulse technique using a small-sample calorimeter.²¹ The sample holder consisted of a sapphire substrate (with a mass of 40 mg) supported by 50- μ m thin constantan leads, with a nichrome film deposited on one side serving as a heater. The thermometer was a calibrated Ge resistor supported from the substrate by thin gold wires. The sample was attached to the other side of the substrate with a very thin layer of Ge varnish. The heat capacity of the sample holder constituted roughly 0.5% of the total at 4.2 K. Electricical resistivity measurements were

made using the four-probe dc method.

Earlier magnetic-susceptibility measurements^{7,9} on stoichiometric $PrBa_2Cu_3O_{7-\nu}$ have shown that this compound orders magnetically at a temperature of ~ 16 K. This has been confirmed by neutron diffraction,⁹ heat capacity,¹⁰ and μ SR studies.¹³ Neutron-diffraction studies suggest a simple antiferromagnetic ordering of the Pr moments along the orthorhombic c axis with a Pr moment of $0.71\mu_B$. However, magnetic susceptibility does not exhibit a peak at the Néel temperature, typical of antiferromagnetic systems, but instead shows only a change in slope compared to the behavior expected from Curie-Weiss temperature dependence and continues to rise below T_N . This suggests that the magnetic ordering may not be of the simple antiferromagnetic type as inferred from neutron-diffraction measurements. The results of our low-temperature susceptibility measurements on $PrBa_{2-x}Pr_{x}Cu_{3}O_{7-y}$ compounds are shown in Fig. 1. The temperature, where a change in slope in susceptibility occurs, is taken to be the magnetic ordering temperature. For the parent compound this gives a T_N of 16.5 K, in good agreement with that reported in the literature.² Our susceptibility measurements suggest that the ordering temperature decreases with increasing Pr concentration, being 13 K for x = 0.2 and 8 K for x = 0.4 samples. The compound with x = 0.8 exhibits no deviation from the Curie-Weiss behavior down to 4.2 K, the lowest temperature of measurement.

The susceptibility of the $PrBa_{2-x}Pr_xCu_3O_{7-y}$ compounds can be fitted to the Curie-Weiss law with the addition of a temperature-independent term χ_0 , i.e.,

$$\chi = \chi_0 + \frac{C}{(T - \Theta_P)} \ . \tag{1}$$

The Curie-Weiss constant, C, is related to the effective magnetic moment μ_{eff} and Θ_P is the paramagnetic Curie temperature. The value of χ_0 was found to be small and nearly the same in all the compounds. The values of μ_{eff} and Θ_P are given in Table I. For the parent compound these are in agreement with those reported in the literature. As Pr is substituted at the Ba site, the μ_{eff} value initially shows a decrease which is most likely associated with the change from the orthorhombic to the tetragonal structure. With further increase of Pr concentration, the

TABLE I. Lattice parameters (**a**,**b**,**c**), unit-cell volume (V), effective paramagnetic moment per Pr (μ_{eff}), paramagnetic Curie temperature (Θ_P), and electronic specific-heat coefficient (γ) for Pr(Ba_{2-x}Pr_x)Cu₃O_{7-v} compounds.

x	a (Å)	b (Å)	c (Å)	$({\bf \mathring{A}}^3)$	$\mu_{ ext{eff}}\ (\mu_{B})$	$-\Theta_P$ (K)	γ (mJ/Pr mol K ²)
0.0	3.867	3.905	11.75	177.43	2.93	8.4	340
0.1	3.893		11.68	177.02	2.64	2.3	
0.2	3.895		11.69	177.35	2.75	10.7	300
0.3	3.893		11.68	177.02	2.75	8.5	
0.4	3.887		11.66	176.17	2.82	6.3	
0.5	3.879		11.63	174.99	3.05	22.6	
0.6	3.876		11.61	174.42	3.10	26.7	250
0.8	3.873		11.59	173.85	3.26	29.9	



FIG. 1. Inverse magnetic susceptibility vs temperature (low-temperature range) for $PrBa_{2-x}Pr_xCu_3O_{7-y}$ compounds with x = 0.0, 0.2, 0.4, and 0.8.

moment gradually moves towards the Pr^{3+} value. From the susceptibility measurements alone it cannot be ascertained whether or not the Pr ions at the regular site and those at the Ba site have the same paramagnetic moment and whether both are magnetically ordered below T_N .

Figure 2 shows the results of heat-capacity measurements some the samples on of the in $PrBa_{2-x}Pr_{x}Cu_{3}O_{7-y}$ series. A peak in the heat capacity (C) is observed at 15.5 K in the x = 0.0 sample and at 13.5 K in the x = 0.2 sample, indicating the magnetic ordering in these compounds in agreement with the susceptibility measurements. The compound with x = 0.6 does not appear to be ordered magnetically in the temperature range investigated consistent with the magneticsusceptibility results. Figure 3 shows a plot of C/Tversus T^2 . From the straight-line behavior of the plot above the respective magnetic ordering temperatures, the electronic specific-heat coefficient, γ , is determined to be (in units of mJ/Pr mol K²) 340 for x = 0, 300 for x = 0.2, and 250 for x = 0.6 samples.

It is noted that the decrease in the ordering temperature in the $PrBa_{2-x}Pr_xCu_3O_{7-y}$ system is accompanied



FIG. 2. Specific heat (C) vs temperature (T) for some samples in the $PrBa_{2-x}Pr_xCu_3O_{7-y}$ series with x = 0.0, 0.2, and 0.6.

by a decrease in the electronic specific-heat coefficient. To understand this behavior it may be conjectured that the Pr ion at the Ba site behaves as a normal trivalent ion with a moment of $3.56\mu_B$ and a low value of γ while the Pr at the regular site continues to behave in the same manner as in $PrBa_2Cu_3O_{7-\nu}$. This would lead to an increase in μ_{eff} and a decrease in γ per Pr ion. However, this cannot account for the remarkable observation that T_N decreases with increasing Pr concentration. Disordered substitution of the excess Pr at the Ba site may cause some broadening of the magnetic transition rather than decrease in T_N of Pr ions at the regular sites. In this connection it may be of interest to study and compare the results with similar stable moment systems, though keeping in mind that the mechanisms giving rise to the high magnetic ordering in the $PrBa_2Cu_3O_{7-y}$ ($T_N \sim 16$ K) and the low magnetic ordering temperature, e.g., $T_N \sim 0.54$ K in $NdBa_2Cu_3O_{7-y}$, are presumably very different. Therefore, it is very likely that both the decrease in γ and T_N in the $PrBa_{2-x}Pr_{x}Cu_{3}O_{7-y}$ system have some other common origin. As mentioned earlier, in one of the mod-



FIG. 3. Plot of C/T vs T^2 for some samples in the $PrBa_{2-x}Pr_xCu_3O_{7-y}$ series with x = 0.0, 0.2, and 0.6.

els, the hybridization between the Pr 4f electrons and Cu 3d and O 2p conduction electrons is thought to be responsible for the suppression of superconductivity and give rise to magnetic ordering at 16 K. A decrease in the hybridization may result in the lowering of T_N of the Pr moments and also a decrease in the electronic specificheat coefficient. The crystal structure of $RBa_2Cu_3O_{7-\nu}$ compounds involves Cu-O planes puckered towards the rare-earth ions. This puckering is thought to be due to the charge imbalance of trivalent rare-earth ions and divalent Ba ions between which the Cu-O planes are situated. It is very likely that the puckering of the Cu-O planes is reduced when divalent Ba ions are replaced by Pr ions. Moreover, the orthohombic-to-tetragonal structural change points towards the fact that the linear Cu-O chains are affected by the substitution of Pr at the Ba site. It is possible that both these effects, namely, the changes in the puckering of the Cu-O planes and the disruption of the chains, the latter of which plays a supporting role in the superconductivity of the family of $RBa_2Cu_3O_{7-\nu}$

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compounds, may cause a reduction in the hybridization effects and hence a reduction in the magnetic ordering temperature and the γ values.

Finally, it is observed that, even in the x = 0.6 sample of the Pr-rich series, the electronic specific-heat coefficient is still large, implying sizable hybridization between the Pr 4f states and the electronic states in the CuO network which precludes superconductivity in this system. Resistivity measurements²² confirm that all the Pr-rich compounds show semiconducting behavior at low temperatures. Typical room-temperature resistivities of our PrBa_{2-x}Pr_xCu₃O_{7-y} samples (in units of m Ω cm) are 38, 47, 84, 100, and 167 for x = 0, 0.2, 0.3, 0.5, and 0.6, respectively, but show some sample dependence.

In conclusion, magnetic-susceptibility and heatcapacity measurements on Pr-rich $PrBa_{2-x}Pr_xCu_3O_{7-y}$ compounds show that both the magnetic ordering temperature and the electronic specific-heat coefficient γ decrease with increasing Pr concentration suggesting that both may have a common underlying origin.

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