

## Hole Filling and Pair Breaking by Pr Ions in $\text{YBa}_2\text{Cu}_3\text{O}_{6.95 \pm 0.02}$

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Measurements of the superconducting critical temperature  $T_c$  are reported for the  $(\text{Y}_{1-x-y}\text{Ca}_y)\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  system as a function of  $x$  and  $y$ . The  $T_c$  vs  $y$  curves at fixed values of  $x$  can be resolved into two contributions: (1) the counteracting effects of generation and filling of holes in the  $\text{CuO}_2$  sheets by  $\text{Ca}^{2+}$  and  $\text{Pr}^{4+}$  ions, respectively, and (2) the depairing of superconducting electrons via exchange scattering of the mobile holes in the  $\text{CuO}_2$  sheets by the Pr magnetic moments.

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The existence of superconductivity at  $\sim 92$  K in  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds, where  $R = \text{Y}$  or a lanthanide element, shows that the magnetic moments of the lanthanide ions have a weak effect on the superconducting electrons believed to reside in the  $\text{CuO}_2$  sheets only  $\sim 2$  Å away.<sup>1</sup> An intriguing exception,  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , departs from this behavior since it is neither metallic nor superconducting.<sup>2-4</sup> In an effort to gain an understanding of the origin of the nonmetallic character of  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , numerous investigations of the  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  system have been carried out. With increasing Pr concentration  $x$  the superconducting transition temperature  $T_c$  decreases monotonically and vanishes at  $x \approx 0.5$ . Applied pressure enhances  $T_c$  at a rate comparable to that observed for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with  $x \leq 0.3$ , while for higher concentrations superconductivity is rapidly depressed.<sup>5</sup> Low-lying excitations in the specific heat<sup>6-8</sup> result in enormous values of the electronic specific-heat coefficient  $\gamma$  [ $\sim 750$  mJ/(mole Pr)  $\text{K}^2$  near  $x = 0.4$ ], typical of heavy-fermion rare-earth and actinide systems. Magnetic,<sup>4,9</sup> Hall-effect,<sup>9</sup> and structural studies<sup>10</sup> suggest a valence state for the Pr ion that is greater than +3 and hence imply that suppression of superconductivity results from a reduced number of carriers in the  $\text{CuO}_2$  sheets. On the other hand, spectroscopic<sup>11</sup> measurements indicate that the Pr valence is  $\sim +3$ , and signatures of hybridization between the valence-band states and Pr ions are observed. The close correspondence of the  $T_c$  vs  $x$  data to the theoretical predictions based on the theory of Abrikosov and Gor'kov<sup>12,13</sup> has been interpreted<sup>7,14</sup> as evidence for magnetic pair-breaking effects.

In this Letter, we report the variation of  $T_c$  with  $x$  and  $y$  in the  $(\text{Y}_{1-x-y}\text{Ca}_y)\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.95 \pm 0.02}$  system with constant oxygen stoichiometry. It is of extreme importance to keep the oxygen stoichiometry constant since variations of it are well known to strongly affect  $T_c$ . The substitution of Ca for Y adds holes to the unit cell and serves as a direct chemical probe of the effect of Pr substitution. If Pr is in a mixed-valence state and does indeed fill holes, then the addition of Ca at constant Pr

concentration should counteract the hole filling and increase  $T_c$ . If the only effect of Pr substitution were to fill holes in the  $\text{CuO}_2$  planes, then  $T_c$  could, in principle, be restored to that of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . Our results show that in a narrow window of Pr concentration ( $x \leq 0.2$ ), it is possible to separate the influence on  $T_c$  of hole filling and pair breaking. A simple quantitative analysis of our data reveals that Pr has an effective valence close to +4 and yields  $|\mathcal{J}| \approx 41$  meV for the magnitude of the exchange interaction parameter.

Seventeen  $(\text{Y}_{1-x-y}\text{Ca}_y)\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{6.95 \pm 0.02}$  samples with compositions in the range  $0 \leq x \leq 0.2$  and  $0 \leq y \leq 0.2$  were prepared by solid-state reaction of appropriate mixtures of high purity (99.99%)  $\text{CuO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{CaCO}_3$ , and  $\text{BaCO}_3$ . The powders were mixed, ground, and fired at  $930^\circ\text{C}$  for 24 h in air. Four additional firings for 24-h intervals with intermediate grindings were performed; subsequently, we fired the specimens for two, four, and six days with intermediate grindings followed by a final grinding before the samples were pressed into pellets. The pellets were annealed in 1 atm of oxygen for two days at  $950$ – $960^\circ\text{C}$  followed by slow cooling at  $1^\circ\text{C}/\text{min}$  to  $450^\circ\text{C}$  where they remained for 18 h before a final slow cool to room temperature at  $1^\circ\text{C}/\text{min}$ . For all Ca and Pr compositions, x-ray diffraction patterns correspond to that of the orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  structure; peak intensities arising from  $\text{BaCuO}_2$  and other impurities were below 1% of the main diffraction peak intensity. Oxygen contents ( $\pm 0.01$ ) were determined by idometric titration<sup>15</sup> assuming that the valences in the presence of excess  $\text{I}^-$  in acidic solution are +1, +2, +3, and -2 for Cu, Ba (Ca), Y (Pr), and O, respectively. All specimens have oxygen contents scattered between 6.93 and 6.97.

For brevity, we show normalized electrical resistivity  $\rho(T)/\rho(85 \text{ K})$  and magnetic-susceptibility  $\chi/|\chi(20 \text{ K})|$  data for one Pr concentration,  $x = 0.20$ , in Figs. 1(a) and 1(b), respectively. The  $\rho(T)/\rho(85 \text{ K})$  data reveal that there is a distinct maximum in  $T_c$  vs Ca concentration  $y$  and that the transitions remain<sup>16</sup> very sharp; specifically, the substitution of 5% and 10% Ca for Y raises  $T_c$  by 1.7

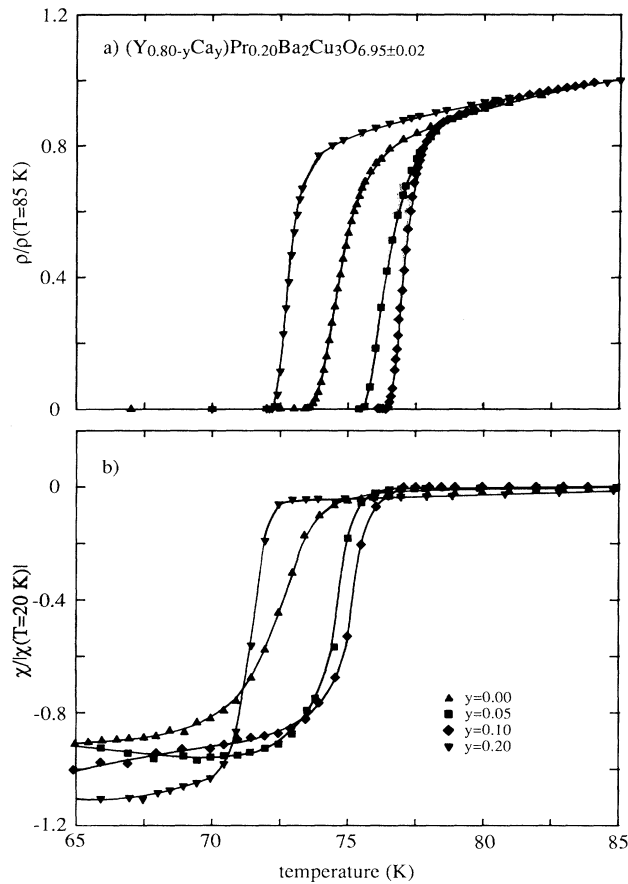


FIG. 1. (a) Normalized electrical resistivity  $\rho(T)/\rho(85 \text{ K})$  vs temperature for  $(Y_{0.80-y}Ca_y)Pr_{0.20}Ba_2Cu_3O_{6.95 \pm 0.02}$  specimens for values of  $y$  indicated. (b) Normalized Meissner fraction  $\chi/\chi(20 \text{ K})$  vs temperature at 1 Oe.

and 2.5 K, respectively, while 20% Ca decreases  $T_c$  by 1.9 K. The  $\chi/|\chi(20 \text{ K})|$  data shown in Fig. 1(b), which were taken by cooling through  $T_c$  in a constant field of 1 Oe, clearly corroborate the resistive data and indicate bulk superconductivity with over 19% flux expulsion for the 20%-Pr series. An upturn in  $\chi(T)$  below  $T_c$ , observed for several of the samples and evident in the data for the 50%-Ca specimen shown in Fig. 1(b), is presumably due to the polarization of the Pr magnetic moments by trapped magnetic flux in portions of the samples. Diamagnetic shielding measured by cooling the specimens below  $T_c$  in zero field and increasing the field to 50 Oe corresponds to volume fractions greater than 90% for these specimens.

Shown in Fig. 2(a) are  $T_c$  vs Ca-concentration- $y$  data, for four Pr concentrations in the range  $0 \leq x \leq 0.20$ . Maxima in the  $T_c$  vs  $y$  curves are clearly visible in both the  $x=0.15$  and 0.20 series at  $0.02 \lesssim y \lesssim 0.05$  and  $0.10 \lesssim y \lesssim 0.14$ , respectively. The monotonic decrease of  $T_c$  with  $y$  for  $x=0.10$  is consistent with the occurrence of a peak at  $y \lesssim 0$ . The horizontal shift of the peak in  $T_c$

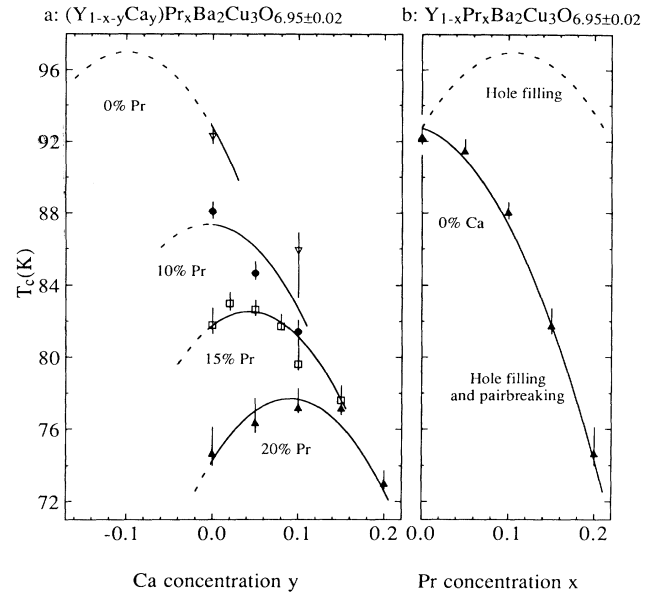


FIG. 2. (a) Superconducting transition temperature  $T_c$  vs Ca concentration  $y$  for four Pr concentrations  $x$ .  $T_c$  is defined as the temperature where the resistivity drops to 50% of the extrapolated normal-state value while the transition width is defined as the difference between the 90% and 10% values; data points indicate  $T_c$  and vertical bars indicate transition width. Curves formed by solid and dashed lines represent the equation  $T_c(x, y) = (97 \text{ K}) - (425 \text{ K})(0.1 - 0.95x + y)^2 - (96.5 \text{ K})x$ . The negative Ca concentrations are hypothetical and would correspond to tetravalent substitution. (b)  $T_c$  vs Pr concentration  $x$ . The dashed line represents the function  $T_c(x, y=0) + (96.5 \text{ K})x$  which describes pure hole filling and the solid line represents the function  $T_c(x, y=0)$  which includes hole filling and pair breaking.

vs  $y$  reveals that for increasing Pr concentrations, a larger number of Ca ions are required to obtain the maximum value of  $T_c$ . This implies that Pr contributes electrons that fill holes in the  $\text{CuO}_2$  planes and hence that its formal valence is greater than +3. The decrease in the magnitude of the maximum value of  $T_c$  with increasing Pr concentration reveals that Pr ions have a destructive effect on superconductivity in addition to filling holes in the  $\text{CuO}_2$  sheets.

In order to make a quantitative analysis of  $T_c$  vs  $y$ , we fit the data for  $x=0.10, 0.15$ , and  $0.20$  by the simple polynomial  $T_c(x, y) = T_{c0} - A(\alpha - \beta x + y)^2 - Bx$ , where  $T_{c0}$  is the maximum obtainable value of  $T_c$ ,  $-A(\alpha - \beta x + y)^2$  is an empirical term that represents the effect of hole generation by Ca( $y$ ) ions and hole filling by Pr( $x$ ) ions,  $-\alpha$  is an optimal hole concentration,  $\beta$  is the deviation of the effective valence of Pr,  $v(\text{Pr})$ , from +3 [i.e.,  $\beta = v(\text{Pr}) - 3$ ], and  $-Bx$  describes the overall depression of  $T_c$  with  $x$  due to pair-breaking interactions. The parameters  $\alpha$  and  $\beta$  can be determined from the values  $x_0$  and  $y_0$  that correspond to the maxima in Fig.

2(a) since  $(dT_c/dy)_0=0$  at the maximum which yields  $\alpha-\beta x_0+y_0=0$ . From the values  $(x_0=0.10, y_0=0 \pm 0.03)$ ,  $(x_0=0.15, y_0=0.03 \pm 0.02)$ , and  $(x_0=0.20, y_0=0.12 \pm 0.02)$ , we obtain  $\alpha=0.10+0.02$  and  $\beta=0.95 \pm 0.20$ . The parameters  $T_{c0}$  and  $B$  are obtained by fitting the maximum values of  $T_c$  by  $T_c(x_0, y_0) = T_{c0} - Bx$  which yields  $T_{c0}=97$  K and  $B=96.5$  K. The coefficient  $A$  is estimated to be 425 K by a best fit to the curvature of the peaks. The resulting equation for  $T_c(x, y)$  is given by

$$T_c(x, y) = 97 \text{ K} - (425 \text{ K})(0.1 - 0.95x + y)^2 - (96.5 \text{ K})x \quad (1)$$

and is represented by the solid and dashed lines in Fig. 2(a). The negative Ca concentration region corresponding to hole filling is inaccessible and is therefore depicted by dashed lines.

The description of both the shift in the peak and maximum  $T_c$  depression with  $x$  in the range  $0.1 \leq x \leq 0.2$  by Eq. (1) strongly supports our interpretation that doping of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with Pr influences  $T_c$  through two independent but simultaneously operating effects. Since Ca has a valence of +2 and hybridizes little, if at all, with the  $\text{CuO}_2$  valence-band states, the most important effect of Ca substitution is to dope the  $\text{CuO}_2$  planes with holes because the charge at the Y site must balance the charge in the two adjacent  $\text{CuO}_2$  planes. The interpretation that substitutions at the Y site do not result in charge transfer to the chains or a change in their structure is strongly supported by the fact that under the identical preparation conditions of this study the oxygen content is independent of the average valence at the Y sites and in the range of Ca and Pr concentrations considered. Since Ca creates holes, and Ca and Pr concentrations appear in Eq. (1) with nearly equal weight and opposite sign, it is evident that Pr fills holes and behaves as an ion with an effective valence of  $+3+\beta=+3.95 \pm 0.20$ .

The third term in Eq. (1), which describes the overall depression of  $T_c$  with  $x$ , must be attributed to a non-hole-filling effect of the Pr ions since it is independent of the Ca concentration  $y$ . A natural explanation of this effect is hybridization of the Pr  $4f$  states with the valence-band states associated with the  $\text{CuO}_2$  planes as discussed in Ref. 5. Hybridization could generate an appreciable exchange interaction between the Pr magnetic moments and the spins of the mobile holes in the  $\text{CuO}_2$  planes resulting in<sup>12,13</sup> a depression of  $T_c$  with paramagnetic impurity concentration that is linear in the low-concentration regime (concentrations corresponding to  $\sim 50\%$  reduction of  $T_c$ ).

Since we have been able to resolve  $T_c(x, y)$  into mobile-hole and pair-breaking contributions, we can use the pair-breaking contribution to estimate the magnitude of the exchange interaction parameter  $\mathcal{J}$ . This can be accomplished<sup>12,13</sup> by using a pair-breaking theory such

as that of Abrikosov and Gor'kov (AG) in which the exchange scattering rate is calculated to second order in  $\mathcal{J}$ , or one which takes into account the Kondo effect (exchange scattering calculated to higher order than  $\mathcal{J}^2$ ). Since we only seek an order of magnitude estimate of  $\mathcal{J}$ , we use the AG result which for low values of  $x$  is given by

$$T_c(x) \approx T_{c0} - \left[ \frac{\pi^2}{4k_B} N(E_F) \mathcal{J}^2 (g-1)^2 J(J+1) \right] x = T_{c0} - Bx, \quad (2)$$

where  $N(E_F)$  is the density of states at the Fermi level and  $g$  and  $J$  are, respectively, the Landé  $g$  factor and total angular momentum of the Hund's-rules ground state of the Pr ion. Using the value<sup>17</sup>  $N(E_F) \approx 11.5$  states/eV,  $g=0.86$ ,  $J=\frac{5}{2}$  for  $\text{Pr}^{4+}$ , and  $B=-96.5$  K/(Pr atom per unit cell) from Eq. (1), we obtain  $|\mathcal{J}| \sim 41$  meV. This value is comparable to that obtained from the depression of  $T_c$  for other superconducting hosts containing paramagnetic rare-earth impurities.<sup>18</sup> Strong hybridization is frequently observed for light rare earths like Ce and Pr since their  $4f$  wave functions are more spatially extended, leading to anomalously large<sup>12,18</sup> values of  $|\mathcal{J}|$  and, in turn, rapid depressions of  $T_c$  in superconducting hosts; e.g.,  $\text{La}_{1-x}\text{Ce}_x$ ,  $(\text{La}_{1-x}\text{Ce}_x)\text{Al}_2$ ,  $(\text{Zr}_{1-x}\text{Pr}_x)\text{B}_{12}$ , and  $\text{La}_{1-x}\text{Pr}_x$  (under high pressure). Apparently, the smaller spatial extent of the heavier rare-earth  $4f$  wave functions does not lead to appreciable hybridization and hence a significant depression of  $T_c$  in  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds.

A number of studies involving nonisovalent substitutions at the Y and Ba sites in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  have been performed<sup>19</sup> in which special attention has been given to the relation between  $T_c$  and the number of holes per  $\text{CuO}_2$  unit,  $p_{\text{sh}}$ . Electron doping is typically accomplished by substitution of a +3 ion for  $\text{Ba}^{2+}$ . However, this type of substitution often results in changes in oxygen stoichiometry and oxygen-chain ordering, thereby complicating simple interpretations in terms of changes in  $p_{\text{sh}}$ . In the present study, we have shown that a continuous decrease of the average charge at the crystallographic site sandwiched between the  $\text{CuO}_2$  sheets (Y site) causes  $T_c$  to go through a maximum in compounds where  $T_c$  is initially depressed by the presence of Pr. Since there is no change in oxygen stoichiometry and hence no evidence of charge transfer to the chains, the change in  $T_c$  may in this case be directly related to a change in the hole concentration in the sheets. The relation between  $p_{\text{sh}}$  and the dopant concentration  $y$  is hence given by  $p_{\text{sh}} = p_{\text{sh}}(y=0) + y/2$ , since two  $\text{CuO}_2$  sheets penetrate every unit cell. According to Eq. (1), in the limit  $x=0$ , the  $T_c$  of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  could be increased from its value of 92 to 97 K by decreasing the hole concentration  $p_{\text{sh}}$  to the value  $p_{\text{sh}}(y=0) - 0.05$ . Unfortunately, our attempts to increase  $T_c$  above 92 K by substituting tetravalent Th and Ce, which do not carry mag-

netic moments, in concentrations  $x \leq 0.05$  yielded multi-phase specimens. For  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  we have shown that in addition to changes in  $\rho_{sh}$ ,  $T_c$  is depressed with  $x$ , presumably due to the presence of magnetic moments on the Pr ions. More importantly, it has been possible to separate the effects of hole doping and pair breaking and hence to obtain valuable information concerning the intrinsic nature of both, resulting in the excellent description of the nonlinear dependence of  $T_c$  on  $x$  by Eq. (1) depicted in Fig. 2(b) by the solid line. Our data provide direct evidence for an optimal hole concentration in the  $CuO_2$  sheets for a single dopant (Ca) in  $(Y,Pr)Ba_2Cu_3O_{7-\delta}$  with fixed oxygen concentration, similar to that reported<sup>20</sup> for Sr-substituted  $La_2CuO_4$ . These results suggest that an optimal hole concentration is a characteristic feature of the layered copper-oxide superconductors which may serve as a useful reference in future efforts to understand high-temperature superconductivity.

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<sup>16</sup>Depending on exact composition, samples annealed at temperatures higher than 960°C show broadened resistive transitions and sometimes clear steplike features, indicating phase separation into Y-rich and Pr-rich regions. We note that this type of phase separation is not clearly visible in the x-ray spectra, and hence sharp superconducting transitions provide important evidence for single-phase compounds.

<sup>17</sup> $N(E_F)$  is estimated using the equations  $1.43\gamma = \Delta C/T_c$  and  $\gamma = 1/3\pi^2 N(E_F)k_B^2$  with  $\Delta C/T_c \approx 39$  mJ/mole K<sup>2</sup> taken from R. A. Fisher, J. E. Gordon, and N. E. Phillips, *J. Supercond.* **1**, 231 (1988).

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