

## Suppression of superconductivity in $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ and $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ systems

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The superconductive and magnetic properties of compounds in  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  ( $0 \leq x \leq 1.0$ ) and  $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  ( $R = \text{Y}$  and rare-earth elements) have been investigated by means of x-ray-diffraction, electrical-resistivity, and magnetic-susceptibility measurements. No obvious discrepancies were found between  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  and  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  from the structural and magnetic analysis. The depression of  $T_c$  by the Pr concentration can be described by the Abrikosov and Gor'kov pair-breaking-like relation, while the critical concentration  $x_c$  is considerably lower in  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  than in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ . In the  $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  system, the  $\Delta T_c$  [ $\Delta T_c = T_c(R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}) - T_c(R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y})$ ] strongly depends on the ionic radius of rare-earth elements. This suggests that the hybridization between Pr 4*f* states and conduction bands may play an important role in the quenching of superconductivity in the  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$  system.

### I. INTRODUCTION

It has been found that most magnetic rare-earth-element substitutions for Y in the 90-K high- $T_c$  superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  with the exception of Ce, Pr, Pm, and Tb, have no significant effect on the superconductivity.<sup>1-3</sup>  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$  forms the same orthorhombic structure as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  and other rare-earth compounds, however it is strangely not superconducting.<sup>4</sup> The quenching of superconductivity in  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$  has been a puzzle ever since the material was synthesized. Numerous extensive works have been carried out on the  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  system to solve the question mentioned above.<sup>4-22</sup> The effect of the Pr ion on the superconducting properties may help our understanding of the interplay between magnetism and superconductivity and provide insight as to the origin of the superconductivity in the high- $T_c$  superconductors.

If Pr is trivalent, it is not easy to understand why the substitution of Pr for Y in the 90-K superconductor should have such a profoundly negative effect on the superconductivity, while other rare-earth elements with local moments (such as Gd, Dy, Er, etc.) do not. Therefore, it was proposed that the superconductivity of  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  is destroyed by the presence of the tetravalent Pr ions.<sup>4</sup> When Y is replaced by Pr, some of the electronic holes are neutralized by the extra conduction electrons donated by the tetravalent Pr ions, thereby reducing the electronic hole concentrations believed to be crucial for the high- $T_c$  superconductivity.<sup>5</sup> These tetravalent or mixed-valent Pr and/or hole-filling effects are supported by several experiments, which include magnetic susceptibility,<sup>6,7</sup> Hall effect,<sup>8</sup> thermoelectric power,<sup>9</sup> heat capacity,<sup>7,10,11</sup> and chemical substitution.<sup>12</sup> However, at the same time, the depression of superconductivity in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  versus  $x$  following an Abrikosov-Gor'kov (AG) pair-breaking curve was also observed.<sup>10,12,13</sup> On the other hand, the trivalent Pr ion in the  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$  compound was concluded by some other experimenters using structure investigation,<sup>10,14,15</sup>

x-ray-absorption spectroscopy,<sup>16,17</sup> resonant photoemission,<sup>18</sup> and the Raman spectrum.<sup>19</sup> Moreover, apart from the tetravalency, electron energy-loss spectroscopy<sup>20</sup> suggested that Pr localizes mobile holes, while Ba core-level spectra<sup>21</sup> have been interpreted to indicate that a portion of the conduction holes are localized at Ba sites. The strong hybridization between Pr 4*f* states and conduction bands was proposed on the basis of critical magnetic field,<sup>13</sup> x-ray absorption,<sup>16</sup> photoemission spectroscopy,<sup>17</sup> high-pressure transport measurements,<sup>22</sup> and spin-polarized electronic-structure calculation.<sup>23</sup> All of the above studies found a suppression of superconductivity in  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ .

In addition, an antiferromagnetic order of Pr in  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$  was observed below  $T_N = 17$  K by magnetic susceptibility,<sup>10,11</sup> heat capacity,<sup>10,11</sup> and neutron-diffraction<sup>24</sup> measurements.  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$  exhibits several unusual magnetic properties compared to its isomorphic magnetic rare-earth compounds. These include an ordering temperature  $T_N = 17$  K about 2 orders of magnitude higher than expected from either the dipolar or the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction alone, a low ordered moment, and a field-independent magnetic transition temperature. These properties suggest that the mixed-valent character of Pr ions affects not only the electronic and superconducting properties of the Cu-O layers, but also the magnetic interaction mechanism between the rare-earth ions.<sup>11,12</sup> In this work, we begin with the study of the superconductivity and magnetic properties in  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  to explore the similarities and differences between  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  and  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  systems. Then we present the superconducting data of  $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  to look for the possible mechanism for quenching of superconductivity in  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ .

### II. EXPERIMENTAL DETAILS

The systems  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ ,  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ , and  $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  were synthesized by stan-

standard solid-state reaction. Starting from high-purity  $R_2O_3$ ,  $BaCO_3$ ,  $CuO$ , and  $Pr_6O_{11}$ , powders were mixed and fired in air at  $950^\circ C$  for 24 h. The reacted samples were pressed into pellets and heated in air at  $950^\circ C$  for 24 h. This process was repeated at least four times with intermediate grinding. These pellets were then heated in flowing oxygen at  $950^\circ C$  for 48 h, followed by an additional anneal at  $450^\circ C$  for 12 h. Finally the samples were slowly cooled in oxygen over several hours to room temperature. Long reaction times at high temperature and thorough grinding appear to be essential in achieving single-phase samples. Samples were prepared at the same time in the same furnace as much as possible to ensure the same sample history. It is noted that the compound of  $LaBa_2Cu_3O_{7-y}$  was prepared differently using the procedure of Wada *et al.*<sup>25</sup> All samples were stored in dry oxygen to prevent deterioration due to the absorption of water and carbon dioxide. Oxygen contents ( $\sim 0.02$ ) were determined by iodometric titration techniques.<sup>26</sup> Most specimens had oxygen contents scattered between 6.90 and 6.97. Samples were checked by powder x-ray diffraction and showed single-phase oxygen-deficient perovskitelike structures. The lattice parameters were calculated from the diffraction peak positions by the method of least-squares fitting. Electrical-resistivity  $\rho(T)$  measurements were performed on rectangular specimens cut from sintered pellets employing the standard four-probe method with silver paint contacts attached to electrical leads. Data were taken from 300 K down to 10 K. The dc magnetic susceptibility for each sample was measured with a SQUID magnetometer (Quantum Design) over the temperature range 2–300 K. A field of 20 Oe was used to measure the magnetic shielding effect and a field of 5 kOe was used to measure the susceptibility above  $T_c$  from which the Curie-Weiss temperature  $\Theta$  and effective magnetic moment  $\mu_{eff}$  were derived.

### III. RESULTS AND DISCUSSION

#### A. Superconductivity and magnetic properties of $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$

A tabulated summary of the lattice parameters  $a$ ,  $b$ ,  $c$ , and the unit cell volume  $V$  for single phase  $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$  with  $y \sim 0.1$  is shown in Table I. The lattice constants for the end members  $GdBa_2Cu_3O_{7-y}$  and  $PrBa_2Cu_3O_{7-y}$  are consistent with

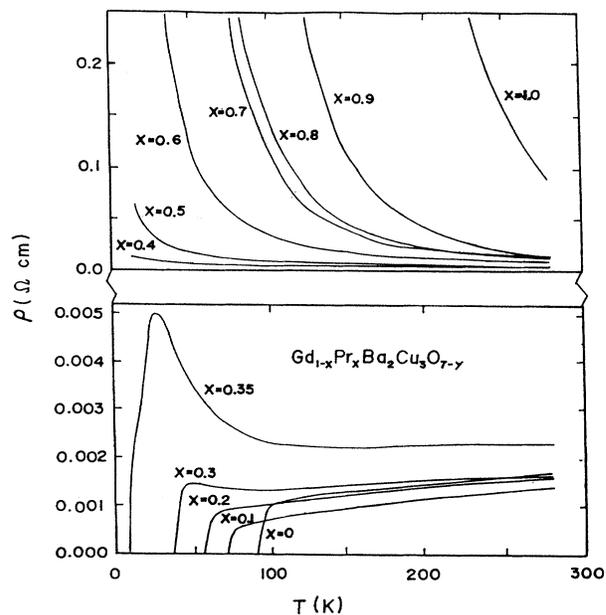


FIG. 1. Electrical resistivity  $\rho(T)$  for the series of  $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$  ( $0 \leq x \leq 1.0$ ) as a function of temperature  $T$ . For clarity, solid lines are drawn through the data points.

other published results.<sup>3,10,13</sup> The system remains orthorhombic for all  $x$  with a slight decrease in the orthorhombicity with increasing  $x$ . Electrical resistivity  $\rho(T)$  data for the series of  $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$  ( $0 \leq x \leq 1.0$ ) are shown in Fig. 1. For low dopant concentrations  $x \leq 0.3$ , the resistivity shows a metalliclike behavior; however, the resistivity curve at  $x = 0.35$  develops a broad maximum just above  $T_c$ . The magnetic shielding curves versus temperature are shown in Fig. 2. Superconducting transition temperatures determined from resistivity curves are consistent with those obtained from magnetization measurements. Superconducting transition temperature  $T_c$  and room-temperature resistivity  $\rho_{280 K}$  versus  $x$  for  $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$  are shown in Fig. 3. In the  $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$  system,  $T_c$  is depressed more than in the  $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$  system<sup>6,7,10,13</sup> by the Pr concentration. The value of the critical concentration  $x_{cr}$  required to suppress  $T_c$  to zero is estimated around 0.4. The room-temperature resistivity increases dramatically

TABLE I. Lattice parameters, superconducting transition temperature, and magnetic data for  $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$ .

$x$	$a$ nm	$b$ nm	$c$ nm	$V$ nm <sup>3</sup>	$T_c$ K	$\mu_{eff}$ $\mu_B$	$\Theta$ K	$\chi_0$ $10^{-4}$ emu/mol
0.0	0.3840	0.3899	1.1702	0.1752	91.5	7.79	-0.4	7.1
0.1	0.3845	0.3899	1.1701	0.1754	73.5			
0.2	0.3850	0.3895	1.1700	0.1755	58.0	7.06	-2.3	5.2
0.3	0.3857	0.3898	1.1699	0.1759	35.0	6.65	-16.1	1.5
0.35	0.3859	0.3899	1.1697	0.1760	15.5			
0.4	0.3862	0.3900	1.1698	0.1762		6.27	-4.6	4.5
0.6	0.3874	0.3898	1.1695	0.1766		5.51	-6.3	3.7
0.8	0.3885	0.3897	1.1690	0.1770		4.14	-6.7	4.2
1.0	0.3896	0.3903	1.1699	0.1779		3.02	-6.0	3.6

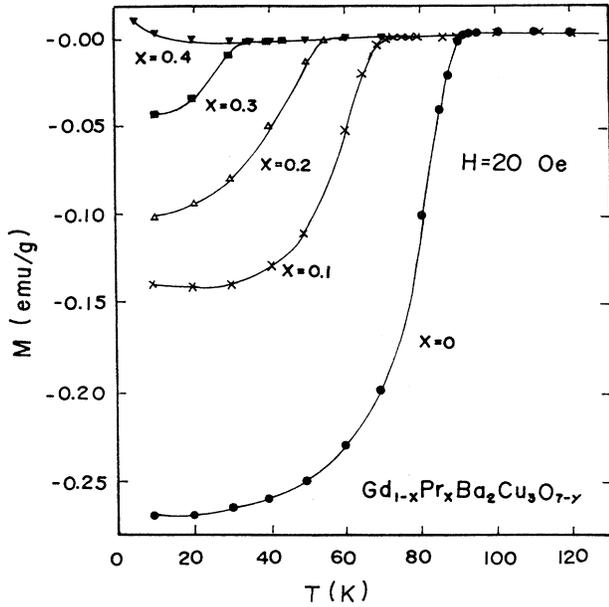


FIG. 2. Zero-field-cooled magnetization  $M$  vs temperature  $T$  as measured with a SQUID magnetometer in a field of 20 Oe. The solid lines are a guide to the eye.

as  $x > 0.4$ , indicating that semiconducting behavior accompanies the destruction of the superconducting phase. Nahm *et al.*<sup>27</sup> successfully explained the nonlinear depression of  $T_c$  by the increasing of Pr concentration in  $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$  using a simple BCS-like expression. This cannot be applied to the  $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$  case

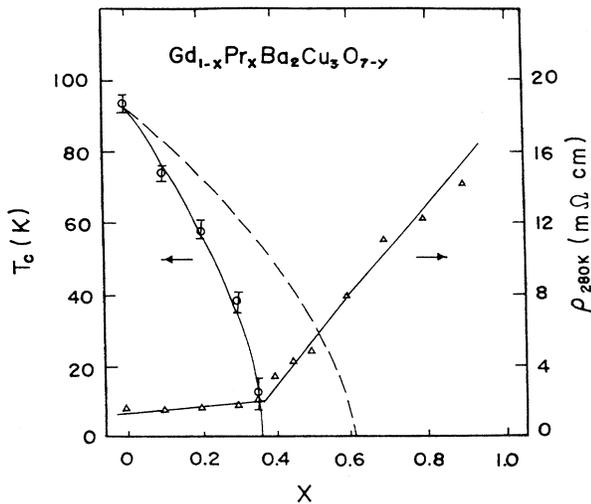


FIG. 3. Superconducting transition temperature  $T_c$  and room-temperature resistivity  $\rho_{280K}$  vs  $x$  for  $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$ .  $T_c$  is defined as the midpoint of the transition seen in  $\rho(T)$  and the transition width indicated by vertical bars is determined for the temperature interval between approximately 10 and 90% of the normal state  $\rho(T)$  evaluated just above  $T_c$ . The solid line is fitted to the Abrikosov-Gor'kov theory and the dashed line is reproduced from Ref. 10 for  $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ .

because the value of  $x_{cr}$  is too low. If  $YBa_2Cu_3O_{7-y}$  and  $GdBa_2Cu_3O_{7-y}$  have a similar structural and electronic character, clearly the hole-filling effect induced by the mixed valence of Pr ions is not the only mechanism for quenching of superconductivity in  $PrBa_2Cu_3O_{7-y}$ . The agreement between the measured  $T_c$  versus  $x$  and the Abrikosov-Gor'kov<sup>28</sup> pair-breaking relationship observed in  $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$  (Refs. 7, 10, and 13) is also found in  $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$  with an initial depression rate  $dT_c/dx = 180$  K per Pr fraction, and  $x_{cr} = 0.4$ . It may indicate that the Pr ions reduce  $T_c$  acting in some sense as Cooper pair breakers. However, some difficulties remain in explaining why only Pr suppresses superconductivity in  $RBa_2Cu_3O_{7-y}$  structure, while other rare-earth elements, some of which have higher magnetic moment, do not. In addition, paramagnetic pair breaking in conventional low- $T_c$  superconductors does not normally lead to the destruction of the metallic state at impurity concentration levels where  $T_c = 0$ . That means one would not expect to see the marked increase in room-temperature resistivity as paramagnetic impurities are introduced. Although the AG theory fits the experimental curve rather satisfactorily, we cannot rule out other possible mechanisms. From this point of view, the interpretation<sup>29</sup> of the depression of  $T_c$  in  $YBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ ,

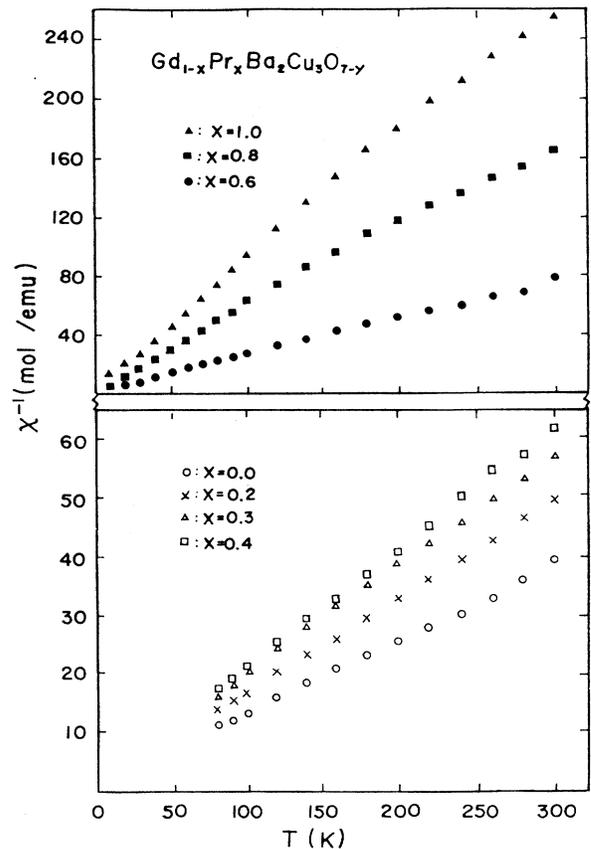


FIG. 4. Inverse magnetic susceptibility vs temperature for  $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$  in the normal state with  $x = 0, 0.2, 0.3, 0.4, 0.6, 0.8,$  and  $1.0$ .

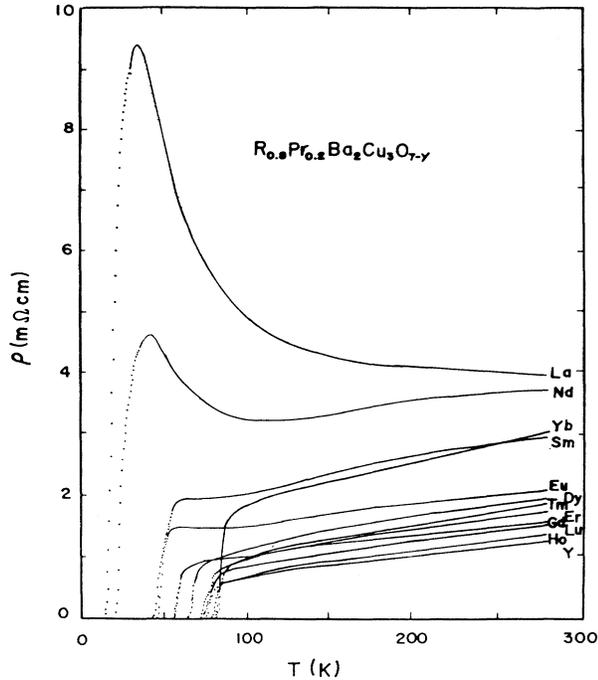


FIG. 5. Electrical resistivity  $\rho(T)$  for the series of  $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  ( $R = \text{Y}$  and rare-earth elements with the exception of Ce, Pr, Pm, and Tb) as a function of temperature  $T$ .

where the role of Zn substitution for Cu is to induce the localization of  $d$  holes within the Cu-O planes, may be applicable. Most recently, Fink *et al.* proposed that the effect of Pr substitution for Y is to localize the mobile holes.<sup>20</sup> This localization of mobile holes could account for the metal-insulator transition as  $x$  equals critical concentration  $x_{\text{cr}}$ .

It is of interest to examine the factors that shift the

values of  $x_{\text{cr}}$  from 0.6 in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  to 0.4 in  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ . The possibilities include the different magnetic properties and ionic radii of Y and Gd. Figure 4 shows the inverse magnetic susceptibility versus temperature for  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ . The magnetic-susceptibility data  $\chi(T)$  can be approximated by

$$\chi = \chi_0 + C/(T - \Theta), \quad (1)$$

where  $C$  is the Curie-Weiss coefficient, which is related to the effective magnetic moment  $\mu_{\text{eff}}$ . Values of  $\mu_{\text{eff}}$ ,  $\Theta$ , and  $\chi_0$  obtained by a nonlinear least-squares fit are also given in Table I. The temperature-independent susceptibility  $\chi_0$  and Curie-Weiss temperature  $\Theta$  are only weakly concentration dependent. The values of  $\mu_{\text{eff}}$  obtained for  $\text{GdBa}_2\text{Cu}_3\text{O}_{7-y}$  ( $7.79\mu_B$ ) and  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$  ( $3.02\mu_B$ ) are in good agreement with reported values.<sup>3,6</sup> Presumably the effective moment of the Gd ion is constant in the whole series of  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ ; the effective moment of the Pr ion can be estimated using the simple formula

$$x\mu_{\text{eff}}^2(\text{Pr}) = \mu_{\text{eff}}^2 - (1-x)\mu_{\text{eff}}^2(\text{Gd}). \quad (2)$$

The  $\mu_{\text{eff}}(\text{Pr})$  has values between  $2.41\mu_B$  and  $3.02\mu_B$ , which is smaller than the effective free-ion moment for  $\text{Pr}^{3+}$  of  $3.58\mu_B$ . As mentioned by some workers,<sup>15,22</sup> the relatively small effective moment of Pr obtained from the simple Curie-Weiss law most likely results from the strong crystalline electric field, which partially lifts the degeneracy of the Pr ion ground state. Except for the slight change of the Pr effective moment, the magnetic properties of Pr ions are almost identical in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  and  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ . Therefore, the magnetic property of Gd should not be the main reason for lowering the  $x_{\text{cr}}$  value. We propose that the difference between ionic radii of Gd and Y is the key factor resulting in the different degree of the suppression of  $T_c$ .

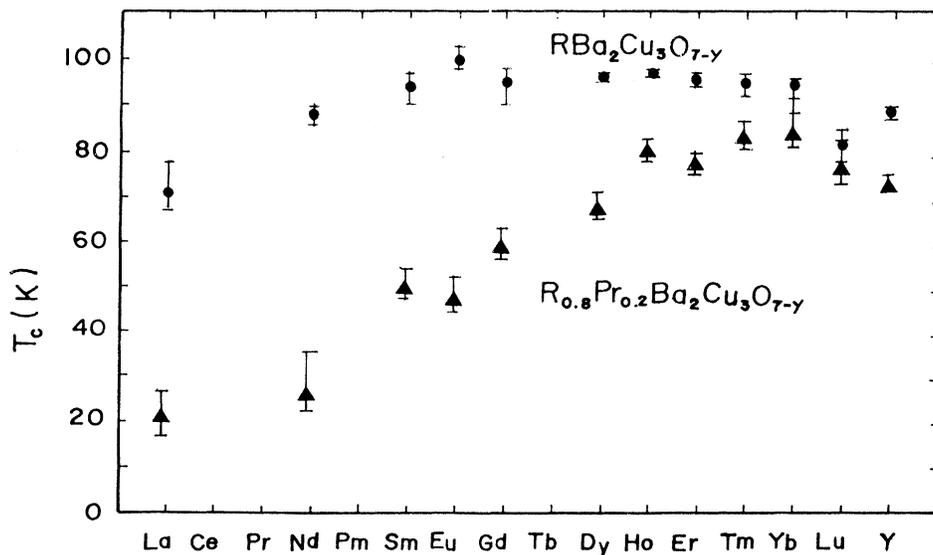


FIG. 6. Superconducting transition temperature  $T_c$  of  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  and  $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  ( $R = \text{Y}$  and rare-earth elements with the exception of Ce, Pr, Pm, and Tb). The transition width is indicated by vertical bars.

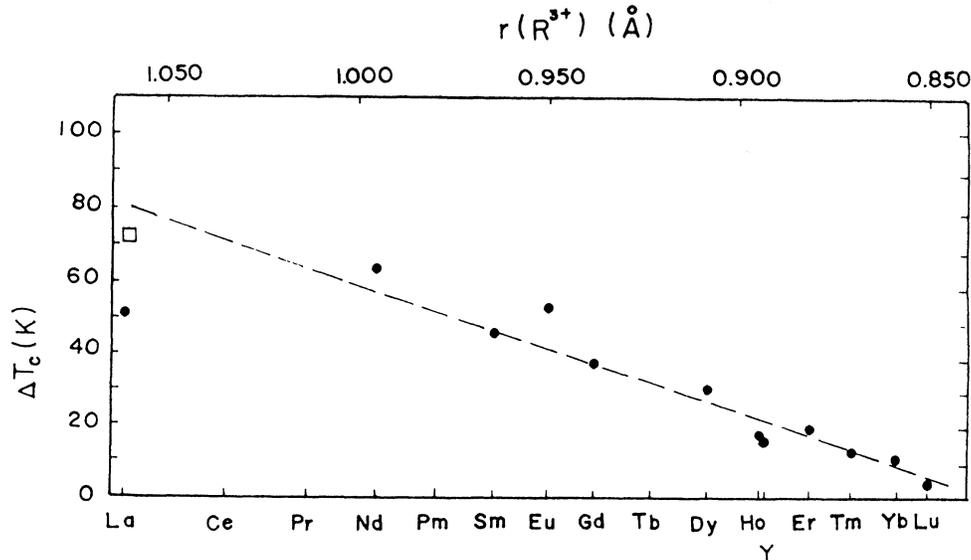


FIG. 7.  $\Delta T_c$ , as defined in the text, as a function of ionic radius  $r(R^{3+})$  of rare-earth elements. Values of  $r(R^{3+})$  are found in Ref. 30. The dashed line is a guide to the eye.

### B. Superconductivity in $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$

In order to study the ionic radius effect on the superconductivity in the  $R_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  system, samples of  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  and  $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ , where  $R = \text{Y}$  and rare-earth elements, with the exception of Ce, Pr, Pm, and Tb, were prepared. The electrical resistivity  $\rho(T)$  as a function of temperature  $T$  for  $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  is shown in Fig. 5. All resistivity curves with the exception of La and Nd compounds exhibit a metalliclike behavior with a sharp superconducting transition. The  $\text{La}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  and  $\text{Nd}_{0.8}\text{Pr}_{0.2}\text{Cu}_3\text{O}_{7-y}$  show a broad maximum just above  $T_c$ , which is very similar to what we see in  $\text{Gd}_{0.65}\text{Pr}_{0.35}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ . The superconducting transition temperatures  $T_c$  of  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  and  $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  are shown in Fig. 6. Values of  $T_c$  for  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  located at  $92 \pm 3$  K are consistent with well-documented results.<sup>3</sup> The resistivity curves and  $T_c$  values of  $\text{Y}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  are in good agreement with those previously reported.<sup>7</sup> It is noted that the  $T_c$  of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-y}$  is much lower than the result reported by Wada *et al.*<sup>25</sup> even though the same procedure of sample preparation was followed. Figure 7 shows the  $\Delta T_c$ , where

$$\Delta T_c = T_c(R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}) - T_c(R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}),$$

as a function of ionic radius  $r(R^{3+})$  (Ref. 30) of rare-earth elements. If the  $T_c = 93$  K of  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-y}$  (Ref. 25) as indicated by an open square is taken into account, a closely linear relationship between  $\Delta T_c$  and the ionic radius of rare-earth elements can be obtained. The depression of  $T_c$  by Pr substitution in  $R_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  strongly depends on the host  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  compounds as shown in Figs. 6 and 7. The larger the ionic radius of rare-earth elements in host compounds is, the greater the decrease in  $T_c$  is at the

$x = 0.2$  concentration level. It is noted that the  $\Delta T_c$  does not depend significantly on the magnetic properties of rare-earth elements. To interpret these data, we discuss the relationship between the length of the  $c$  axis in  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  compounds and the ionic radius of  $R^{3+}$ . The increase of the  $c$  axis from 11.654 Å ( $\text{LuBa}_2\text{Cu}_3\text{O}_{7-y}$ ) to 11.785 Å ( $\text{LaBa}_2\text{Cu}_3\text{O}_{7-y}$ ) is less than that of the ionic radius from 0.85 Å ( $\text{Lu}^{3+}$ ) to 1.061 Å ( $\text{La}^{3+}$ ) (Ref. 30). This trend is also generally true for the whole series of  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  (Ref. 3) under the consideration of rare-earth contraction. This indicates that the separation between rare-earth atoms and Cu-O planes in  $\text{LaBa}_2\text{Cu}_3\text{O}_{7-y}$  is less than in  $\text{LuBa}_2\text{Cu}_3\text{O}_{7-y}$ . If the Pr 4*f* electrons tend to hybridize with conduction holes in the Cu-O planes, we expect that the hybridization between Pr 4*f* electrons and conduction holes in  $\text{La}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  is more pronounced than in  $\text{Lu}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  at the same Pr concentration levels. This is the result seen in Fig. 7. The larger the ionic radius of the rare-earth element in the host compounds  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  is, the stronger the depression of  $T_c$  is as Pr ions are introduced. Thus a strong hybridization between Pr 4*f* electrons and conduction bands in  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$  as found by total-energy calculations<sup>23</sup> and previously mentioned experiments,<sup>13,18,22</sup> is concluded from our results. Without this hybridization effect, either the hole filling or the localization of mobile holes alone, it is difficult to explain this ionic radius effect on the suppression of  $T_c$  in the  $R_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  system. Therefore the quenching of superconductivity in  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$  might be due to the strong hybridization that occurs between Pr 4*f* electrons and conduction holes in the Cu-O planes inducing a localization of the mobile holes. This strong hybridization may lead to the large crystalline electric fields resulting in the reduced magnetic moment. The localization of mobile holes causes the suppression of superconductivity and accounts for the

metal-insulator transition at  $x = x_{cr}$ . Of course, one can also argue that the localization of mobile holes, which suppresses  $T_c$ , follows a curve, which can be fitted quite well to an AG-like relation. Furthermore, this hybridization might be related to the unusual magnetic properties of  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$  at low temperatures. Studies of the low-temperature magnetic properties of  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  are currently in progress.

In conclusion, superconductivity and magnetic properties of  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  have been studied and compared to  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ . The nonlinear depression of  $T_c$  by the Pr concentration in  $\text{Gd}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  is observed with a considerably lower value of critical concentration  $x_{cr}$  than in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ . In the  $\text{R}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  system, the depression of  $T_c$  depends on the ionic radius of

rare-earth elements. A closely linear relationship between  $\Delta T_c$  and the ionic radius of rare-earth elements can be obtained. These results can be explained by assuming the strong hybridization between extended Pr 4f electrons and conduction bands in the Cu-O planes. This hybridization would play a significant role in the suppression of superconductivity in the mentioned  $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  systems.

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