RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 45, NUMBER 6 1 FEBRUARY 1992-II

Ion-size effect on T_c in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems (R = Nd, Eu, Gd, Dy, Y, Er, and Yb)

Yunhui Xu and Weiyan Guan
Institut für Schicht und Ionentechnik der Forschungszentrum Jülich, Gesellschaft mit beschränkter Haftung,
Postfach 1913, D-5170 Jülich, Germany

(Received 31 October 1991)

We observed that the superconducting-transition temperature (T_c) of the oxides $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) decreases monotonically with increasing Pr concentration x. At constant x, T_c decreases approximately linearly with increasing radius of the R ions. We suggest that in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems the hybridization between $4f$ states of the Pr ion and the conduction-band states is R-ion-radius dependent.

Although crystallographically identical to all the other rare-earth-based superconductors, $PrBa_2Cu_3O_{7-y}$ is a semiconductor and not superconducting. The $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ system is particularly interesting since it is isostructural to $YBa_2Cu_3O_{7-y}$ superconductor, yet the superconductivity is strongly suppressed as a function of Pr concentration.[1,2]

The suppression of T_c has been attributed to two possible mechanisms. The first mechanism involves the filling of mobile holes in the conducting CuO_2 planes. The substitution of Pr ions with a valence greater than 3+ implies that suppression of superconductivity results from a reduced number of carriers in the CuO_2 sheets.[2] However, this idea was later questioned. X-ray-absorption near-edge structure[3,4] and valence-band resonant photoemission[5] indicated a Pr valence close to 3+. According to electron-energy-loss-spectroscopy measurements[6] of the $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ system, the total number of holes on O sites was shown to be independent of x. This suggests that the Pr ions are trivalent and localize, rather than fill, mobile holes in the CuO_2 planes. Recently, Norton *et al.*[7] discovered superconductivity at 34.9 K in $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{7-y}$ epitaxial thin films and suggested that hole localization and/or filling contributes substantially to the suppression of superconductivity by Pr in $PrBa_2Cu_3O_{7-y}$.

The second mechanism is pair breaking due to spin-dependent exchange scattering of mobile holes in the CuO_2 valence band by magnetic Pr ions. The correspondence of the T_c vs x data to the theoretical predictions based on the theory of Abrikosov and Gor'kov[8] (AG) has been interpreted as evidence for pair breaking.[9,10] Spin-polarized band-structure calculations[11] for $RBa_2Cu_3O_{7-y}$ (R = Y, Gd, Pr) confirm the magnetic pair-breaking mechanism.

In order to achieve a better understanding of superconductivity suppression by Pr ions it would be useful to study other $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems in order to be sure that we are dealing with universal behavior. Several groups[4,12-15] reported experimental results of the $(Gd_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ and $(Eu_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$. The results of these investigations indicate that Pr is more effective in suppressing superconductivity in $(Gd_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ and $(Eu_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ than in $(Y_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$. In this paper, we report the variation of T_c with x in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) systems. The results show that T_c monotonically decreases with increasing Pr concentration, x, for all studied systems. However, the T_c suppression rates, dT_c/dx, are very different for various systems. We have found an ion-size dependence for T_c. At a constant concentration of Pr ($x > 0.1$) T_c decreases approximately linearly with increasing radius of R ions.

The ceramic $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) systems with x between $x = 0$ and $x = 0.6$ were prepared using a conventional solid-state reaction method. Stoichiometric amounts of high-purity CuO, $BaCO_3$, Pr_6O_{11}, and R_2O_3 (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) powders were mixed, ground, and fired at 915 °C for about 24 h in air, followed by slow cooling in the furnace. The resultant powder was milled again and pressed into pellets which were then heated at 925–930 °C for 3 days in flowing oxygen, followed by annealing at 680 and 400 °C in flowing oxygen each for 10 h before a slow cool to room temperature.

The x-ray-diffraction patterns show that all samples have the layered orthorhombic perovskitelike structure and contain no extra peaks due to impurity phases within the experimental error. We have not included an analysis of the oxygen stoichiometry. However, it has been reported by several groups that the praseodymium content does not influence oxygen content y essentially ($y \simeq 0$).[6]

T_c was determined from resistivity measurements. The resistivity were measured by standard four-probe technique on rectangular bars sliced from the as-grown sintered pellets to which Al-foil electrical leads had been attached with silver-paste epoxy, using a lock-in amplifier SR530 operating at a frequency of 130 Hz.

In Figs. 1 and 2 plots of the normalized transition temperature $T_c/T_c(0)$ as a function of Pr concentration x for $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) are shown. T_c is defined as the temperature at which the resistivity drops to 50% of the extrapolated normal-state value. The $T_c(0)$ for the undoped $RBa_2Cu_3O_{7-y}$ superconductors were 95.0 (R = Nd), 94.8 (R = Eu), 95.7 (R = Gd), 95.2 (R = Dy), 93.5 (R = Y), 93.2 (R = Er), and 91.5 (R = Yb). These T_c values show that magnetic rare-earth ions do not have a pair-breaking effect on superconductivity.[16]

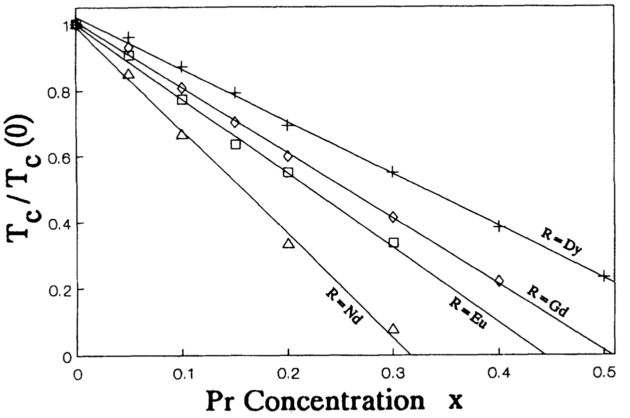

FIG. 1. Normalized superconducting transition temperature $T_c/T_c(0)$ vs Pr concentration x for $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems. △, R=Nd; □, R=Eu; ◇, R=Gd; and +, R=Dy.

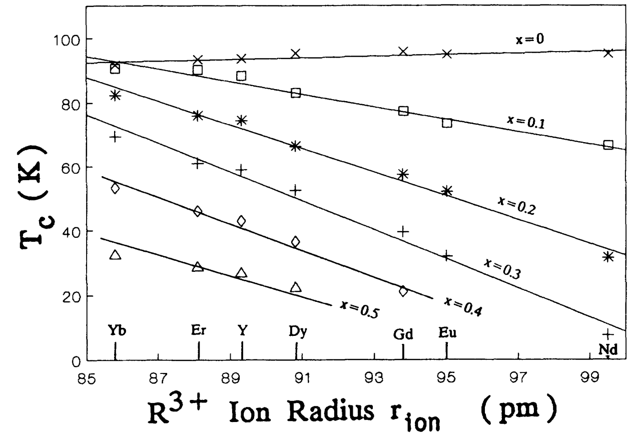

FIG. 3. Superconducting transition temperature T_c (midpoint) vs ion radius of the R ions, r_{ion}, in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems (R=Nd, Eu, Gd, Dy, Y, Er, and Yb).

The $T_c/T_c(0)$ vs x data shown in Figs. 1 and 2 indicate that T_c decreases monotonically with increasing Pr concentration for all studied $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems. However, the T_c suppression rates, dT_c/dx, are different for various $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems. For example, at the same Pr concentration, $x=0.3$, $T_c=69.5$ K for $Yb_{0.7}Pr_{0.3}Ba_2Cu_3O_{7-y}$ (Fig. 2) but $T_c=7.5$ K for $Nd_{0.7}Pr_{0.3}Ba_2Cu_3O_{7-y}$ (Fig. 1). This indicates that Pr is extremely more effective in suppressing superconductivity in $(Nd_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ than in $(Yb_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$. The experimental data of $T_c(x)$ can be divided into two groups and we present them in Figs. 1 and 2 separately. The results for $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ with R=Nd, Eu, Gd, and Dy shown in Fig. 1 demonstrate an approximately linear Pr concentration dependence of T_c. The results for samples with R=Y, Er, and Yb shown in Fig. 2 demonstrate a more complicated Pr concentration dependence of T_c, especially in the low-Pr-doping regime ($x<0.1$).

We find a systematic ion-radius (R_{ion}) dependence of T_c for studied $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems. At constant x the T_c vs r_{ion} curves are displayed in Fig. 3. Clearly, the Pr ion is more effective in suppressing T_c in the $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ system where the R ion has a larger ion radius. As the Pr concentration x is kept constant we find that the T_c of $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ approximately linearly decreases with increasing radius of the R ions in the higher-Pr-doping regime ($x>0.1$).

The linearly extrapolated values of critical Pr concentration x'_{cr} (the x values of the intersections of the extrapolated lines with the x axis in Figs. 1 and 2) are 0.32, 0.45, 0.51, 0.64, 0.67, 0.69, and 0.75, for R=Nd, Eu, Gd, Dy, Y, Er, and Yb, respectively. These extrapolated x'_{cr} are larger than x_{cr} at which superconductivity disappears (no attempt has been made to determine the exact values of the x_{cr}). The magnitude of x'_{cr} roughly scales with the R-ion size, r_{ion}, for the studied $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems. This is illustrated in Fig. 4.

Figures 3 and 4 clearly show that the suppression of superconductivity in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems is related to the Pr concentration and the ionic size of the R ion of the matrix.

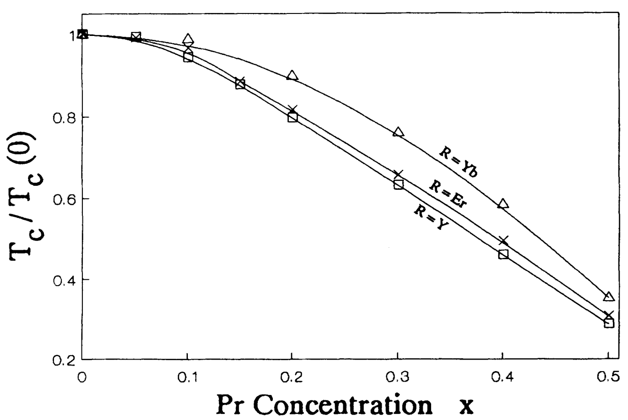

FIG. 2. Normalized superconducting transition temperature $T_c/T_c(0)$ vs Pr concentration x for $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems. □, R=Y; ×, R=Er; and △, R=Yb.

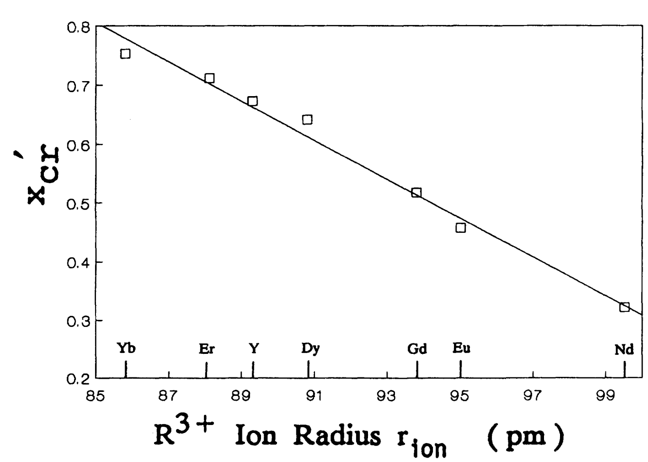

FIG. 4. Linear extrapolated critical concentration of Pr ions x'_{cr} vs ionic radius of the R ions, r_{ion}, in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems (R=Nd, Eu, Gd, Dy, Y, Er, and Yb).

The pair-breaking theory of Abrikosov and Gor'kov [8] for low values of paramagnetic impurity concentration x is given by

$$T_c(x) \simeq T_c(0) - [(\pi^2/4k_B)N(E_F)\mathcal{J}^2(g-1)^2J(J+1)]x\ , \tag{1}$$

where $N(E_F)$ is the density of states at the Fermi level, g and J, respectively, the Lande g factor and total angular momentum of the Hund's-rules ground state of the magnetic ion, and $\mathcal{J}$ is the exchange-interaction parameter. AG theory [Eq. (1)] predicts a suppression of T_c with paramagnetic impurity concentration x that is linear in the low-concentration regime.

The linear suppression of T_c vs x data for $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ (R = Nd, Eu, Gd, Dy) shown in Fig. 1 corresponds to the theoretical (AG) prediction [Eq. (1)]. These results can be interpreted as evidence for the magnetic pair-breaking effects by Pr doping, but the regime of linear dependence of T_c vs x is wider than that predicted by AG theory. Figure 2 shows that for $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ (R = Y, Er, Yb) the linear dependence of T_c vs x exists only in the higher-Pr-doping regime ($x > 0.1$). If one extrapolates the linear fit of $T_c(x)$ to the AG theory from the higher x regime ($x > 0.1$), in order to determine extrapolated $T_c'(0)$ one discovers that $T_c'(0)$ value would be > 100 K. In the case of R = Nd, Eu, Gd, and Dy (Fig. 1) $T_c'(0)$ linearly extrapolated from the high-x regime was identical with $T_c(0)$ measured for samples with $x = 0$.

In Eq. (1) there are two material parameters, $N(E_F)\mathcal{J}^2$ and the de Gennes factor $(g-1)^2J(J+1)$, which determine the T_c vs x dependence. $N(E_F)\mathcal{J}^2$ characterizes the hybridization between conduction electron states and local impurity states and their spin-dependent exchange interaction. The de Gennes factor is a characteristic of magnetic moment of impurity ion.

Of all the R^{3+} ions with partially filled $4f$ electron shells that form the orthorhombic $YBa_2Cu_3O_{7-y}$ structure Pr has the largest ionic radius and therefore the greatest amount of overlap between its $4f$ wave function and the wave functions of the neighboring oxygen and copper atoms. Thus, hybridization of the $4f$ states and the valence-band states would be expected to be strongest for Pr^{3+}. Since electrical conduction in these systems appears to be primarily confined to the CuO_2 planes the hybridization of the Pr $4f$ states with valence-band states should play a significant role for pair breaking and for determining $T_c(x)$ in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems. Hybridization could generate an appreciable exchange interaction between the Pr magnetic moments and the spin of the mobile holes in the CuO_2 planes with a large value of $N(E_F)\mathcal{J}^2$ in Eq. (1), in turn, causing suppression of T_c in the superconducting hosts.

Most of the R ions except Y and Eu in the ground states are magnetic. Our T_c data show that the dependence of T_c on x is not determined by whether the R ion is magnetic or nonmagnetic. Doping Pr ions in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems is more effective in suppressing superconductivity for R = Eu with zero moment of the Eu ions than for R = Er, Gd, and Dy with remarkable larger moments of Er, Gd, and Dy ions (Figs. 1 and 2) and is more effective for R = Y with zero moment of the Y ions than for R = Er with strong paramagnetic moment of the Er ions (Fig. 2). Apparently, the smaller spatial extension of $4f$ wave functions of R ions (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) does not lead to appreciable hybridization in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems which is similar to the situation in undoped $RBa_2Cu_3O_{7-y}$ systems.

We view the suppression of T_c in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) as resulting from the pair-breaking effect by Pr doping. The conclusion concerning pair breaking is based on the facts that the Pr^{3+} ions have a magnetic moment of $3.58\mu_B$ and that the hybridization between the conduction electrons in the CuO_2 planes and local Pr ion states is strong. The latter feature is the major difference between the roles of the Pr and the R ions (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) on superconductivity suppression. The strong hybridization resulting in a large exchange interaction is a key parameter controlling the superconductivity suppression by pair breaking. We would like to emphasize that although the magnetic moment of the R ions is unfavorable to the superconductivity suppression, their ion sizes have a pronounced effect on T_c suppression. It is possible that the hybridization between the conduction electron states in CuO_2 planes and the local Pr states in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) depends on the presence of Pr and R ions in these systems. On the basis of our experimental T_c data we suggest that the spatial extent of the host R ion influences the hybridization between conduction and Pr $4f$ electrons. For R ions with a larger ionic radius, we observed a greater suppression of T_c. In this case, when we use Eq. (1) of AG theory to fit our experimental data of T_c, the de Gennes factor $(g-1)^2J(J+1)$ depends only on the Pr ion. In contrast, the parameters, $N(E_F)\mathcal{J}^2$, in Eq. (1) will change with individual R (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) ions, particularly, with their ionic radius. $N(E_F)\mathcal{J}^2$ is a function of the radius of the R ions.

To conclude, Pr doping is more effective in superconductivity suppression in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ (R = Nd, Eu, Gd, Dy, Y, Er, and Yb) systems with larger radius R ions. Both dT_c/dx and x'_{cr} are systematic, approximately linearly dependent on the radius of the R ions. This peculiar ion-size dependence of T_c is caused by the presence of both Pr and R ions in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems. It is possible that in $(R_{1-x}Pr_x)Ba_2Cu_3O_{7-y}$ systems the R ions may influence the hybridization between $4f$ states of Pr and conduction-band states, which influences the suppression of superconductivity. We think that the hybridization and the exchange interaction characterized by $N(E_F)\mathcal{J}^2$ in AG theory is dependent on the radius of the R ions.

The authors thank Professor Dr. Ch. Heiden for support and fruitful discussions, Dr. D. Guggi and Dr. M. Mück for experimental help, and Mr. F. Hutson for discussions.

---

[1] J. K. Liang *et al.*, Z. Phys. B **69**, 137 (1987).

[2] Y. Dalichaouch *et al.*, Solid State Commun. **65**, 1001 (1987).

[3] Y. Tokura *et al.*, Phys. Rev. B **38**, 7156 (1988).

[4] M. W. Shafer *et al.*, Phys. Rev. B **39**, 2914 (1989); D. D. Sarma *et al.*, Solid State Commun. **77**, 377 (1991).

[5] J. S. Kang *et al.*, J. Less-Common Met. **148**, 121 (1989).

[6] J. Fink *et al.*, Phys. Rev. B **42**, 4823 (1990).

[7] David P. Norton *et al.*, Phys. Rev. Lett. **66**, 1537 (1991).

[8] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1961)].

[9] J. L. Peng *et al.*, Phys. Rev. B **40**, 4517 (1989).

[10] Yunhui Xu and Weiyan Guan, Appl. Phys. Lett. **59**, 2183 (1991).

[11] G. Y. Guo and W. M. Temmerman, Phys. Rev. B **41**, 6372 (1990).

[12] H. Iwasaki *et al.*, Physica C **169**, 146 (1990).

[13] K. Latka *et al.*, Physica C **171**, 287 (1990).

[14] I. Das *et al.*, Physica C **173**, 331 (1991).

[15] Z. Tomkowicz *et al.*, Physica C **174**, 71 (1991).

[16] Yunhui Xu and Weiyan Guan, Appl. Phys. Lett. **53**, 334 (1988).