Suppression of superconductivity in the oxide systems $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ (R = Sm, Gd, and Tm)

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Superconductivity in the 90-K range is observed in most of the orthorhombic $RBa_2Cu_3O_{7-y}$ compounds (R being rare-earth elements and Y). However, the isostructural Pr compound is not superconducting, either due to the 4+ state of Pr whereby the extra electron from Pr fills the Cu-O band, or due to the hybridization of the Pr $4f$ states with the O $2p$–Cu $3d$ states, or due to a combination of the two. The compounds $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ (R = Sm, Gd, and Tm; $0.0 \leq x \leq 1.0$) have been prepared and examined for superconductivity. It is observed that the critical Pr concentration required to suppress superconductivity depends on the R ion, varying from $x \simeq 0.32$ in the Sm-Pr system to $x \simeq 0.6$ in the Tm-Pr system. Band filling due to Pr^{4+} is expected to be nearly the same in all the compounds and cannot solely account for the strong dependence of the critical Pr concentration on R. Instead, the hybridization mentioned above may explain these results. The T_c data are analyzed on the basis of the Abrikosov-Gor'kov pair-breaking theory due to magnetic Pr^{3+} ions.

INTRODUCTION

Most of the orthorhombic $RBa_2Cu_3O_{7-y}$ (R being rare-earth elements and Y) compounds exhibit superconductivity with transition temperature (T_c) in the 90-K range, indicating that even strongly magnetic rare-earth ions have very weak or no interaction with the superconducting electrons presumed to reside in the Cu-O network.[1] The exceptions to this behavior are the compounds with Ce, Pr, and Tb. While the Pr compound is orthorhombic and isostructural to the superconducting $RBa_2Cu_3O_{7-y}$ compounds, Ce and Tb compounds do not even form in the same structure.[2] The nonformation of the Ce and Tb compounds in the orthorhombic structure type and the absence of superconductivity in $PrBa_2Cu_3O_{7-y}$ have been attributed to the capability of these rare-earth ions to show a stable valence state other than 3+. The Pr compound is semiconducting down to very low temperatures.[3-5] Moreover, it exhibits magnetic ordering of the Pr moments with Néel temperature (T_N) of about 17 K (Refs. 4–6)—much higher than the T_N of 2.24 K of the isostructural Gd compound.[7] The electronic specific-heat coefficient, γ, of $PrBa_2Cu_3O_{7-y}$ is also extremely large.[4-5,8]

In order to understand the behavior of $PrBa_2Cu_3O_{7-y}$, the system $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$, has been studied in great detail by various techniques.[3,5,6,8-19] In the latter system, as the Pr concentration x increases, the T_c decreases and eventually superconductivity disappears around $x \simeq 0.55$. Magnetic-susceptibility, Hall-effect, and structural studies[9,10,12] suggest that the Pr ions may have a valence greater than 3+. Therefore, it has been thought that the extra electron contributed by Pr (relative to other trivalent rare-earth ions) neutralizes a hole in the Cu-O network, rendering the system nonsuperconducting. On the other hand, x-ray-absorption-edge and other spectroscopic measurements[13,14] suggest a valence

close to 3+ for the Pr ions and also provide evidence for strong hybridization of the Pr $4f$ states with the electronic states of the Cu-O network. The hybridization accounts well for the high values of the electronic specific-heat coefficient and may also be responsible for the relatively high magnetic ordering temperature of the Pr moments in $PrBa_2Cu_3O_{7-y}$. The suppression of T_c in $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ as a function of Pr concentration can be understood on the basis of the Abrikosov-Gor'kov theory of pair breaking which has been taken to imply appreciable interaction of magnetic Pr ions with the superconducting electrons residing presumably in the Cu-O network.[5,8,11,16]

If the model whereby the extra electron from Pr^{4+} fills the O $2p$–Cu $3d$ conduction band is applicable, then it would appear that the superconductivity in the $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ compounds should be suppressed to the same extent at about the same Pr concentration, irrespective of the rare-earth ion R since the number of holes is nearly the same (because of nearly the same T_c) and band structures are not expected to be very different for different $RBa_2Cu_3O_{7-y}$ compounds. Therefore, we have undertaken a systematic investigation to determine the critical Pr concentration required to suppress superconductivity in the $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ system. In this paper we present the results of such measurements on compounds with three representative rare earths, namely, a light rare earth (Sm), a heavy rare earth, (Tm), and the rare earth in the middle of the $4f$ series (Gd). We find that the critical Pr concentration required to suppress superconductivity depends on the ionic size of the R ion. Superconductivity is suppressed in the Sm-Pr system for a much lower concentration of Pr ($x \simeq 0.32$) while in the Tm-Pr system, a larger Pr concentration can be accommodated ($x \simeq 0.6$) before superconductivity is completely suppressed. The band-filling model alone is not able to explain such a strong dependence of critical Pr concentration in various $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ systems.

EXPERIMENTAL DETAILS

The samples of $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ (R = Sm, Gd, and Tm; $0 \le x \le 1$) were prepared by a standardized ceramic procedure to ensure nearly the same oxygen content in all the samples. Stoichiometric amounts of R_2O_3, Pr_6O_{11}, $BaCO_3$, and CuO were thoroughly mixed and heated at 900 °C for 24 h for the initial reaction. The resulting mixture was powdered, compacted, and reheated at tempertures ranging from 910 to 930 °C for 24 h. This process of powdering, compacting, and heating was repeated at least twice. The final sintering was carried out under a continuous flow of dry oxygen and the samples were cooled slowly (2 °C/min) to room temperature. In the case of Tm containing samples, additional sintering at 910 °C was necessary to obtain single-phase materials and to avoid phase separation which was evident in the resistivity measurements on samples sintered twice. Powder x-ray-diffraction patterns were obtained on a Sieman's x-ray diffractometer using Cu K_α radiation which revealed that all the $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ samples were single-phase materials crystallizing in the orthorhombic structure. The lattice parameters change little from one end to the other end. The homogeneity and the stoichiometry of the samples were determined using energy dispersive x-ray analysis. The samples were found to be homogeneous with metal compositions close to the starting values. Therefore, we shall use the nominal starting compositions as the correct composition for further discussions. Oxygen content was determined by the iodometric technique and was found to be stable in the range of 6.95 ± 0.02 in all the compounds. Four-probe dc resistivity measurements were made using a computer-controlled resistivity setup employing a closed-cycle refrigerator. The temperatures were monitored using a Lake-Shore temperature controller and a diode sensor. The ac-susceptibility measurements were carried out using the mutual inductance method.

RESULTS AND DISCUSSION

The results of dc resistivity (ρ) measurements are quite similar in all the three series of compounds. Typical $\rho - T$ plots for Sm-Pr and Tm-Pr systems are shown in Figs. 1 and 2. The $RBa_2Cu_3O_{7-y}$ compounds with R = Sm, Gd, and Tm exhibit superconductivity with a zero-resistance temperature (T_c) of 90 K, 90 K, and 89 K, respectively, in agreement with the results reported in the literature.[1] Reasonably sharp transitions are observed in all the superconducting compounds with transition width ΔT_c (defined as the temperature interval for 10% to 90% of the resistive transition) in the range of 1.2 K (for undoped samples) to about 10 K in the superconducting samples with the highest Pr concentration. The ΔT_c values are comparable to those observed in $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ compounds by Peng et al.[16] As R is partially replaced by Pr, the room-temperature resistivity increases, the zero-resistance temperature decreases, and with increasing Pr concentration the shape of the resistivity-temperature curve also changes. The $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ samples with x = 0.1, 0.2, and 0.3
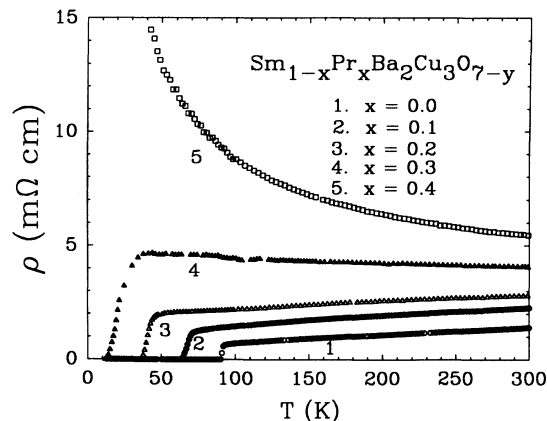

FIG. 1. Resistivity behavior of $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ compounds as a function of temperature for various values of x.

are superconducting with reduced T_c while the sample with $x = 0.4$ is not superconducting and, in fact, shows semiconducting behavior throughout the temperature range investigated. In contrast, the Tm-Pr system can accommodate a larger amount of Pr ($x \simeq 0.6$) before superconductivity is suppressed. In the Gd-Pr system, the critical Pr concentration is intermediate between the above two. The results of resistivity measurements are corroborated by the ac susceptibility (χ_{ac}) measurements. A typical plot of χ_{ac} versus temperature for the Gd-Pr system is shown in Fig. 3. The temperature where the resistance goes to zero corresponds closely to the onset of the diamagnetic signal. For the sake of discussion, we shall take T_c as the temperature where the resistance goes to zero.

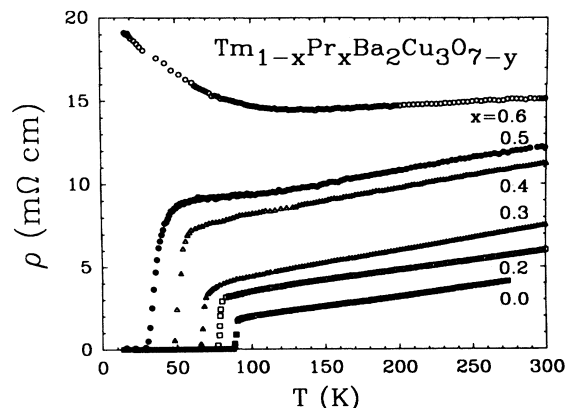Figure 4 shows the plot of reduced superconducting

FIG. 2. Resistivity behavior of $Tm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ compounds as a function of temperature for various values of x.
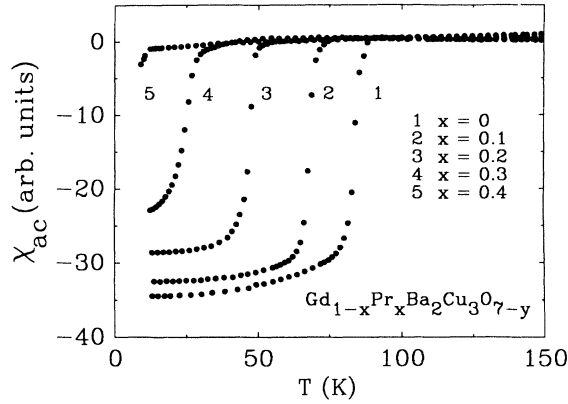
FIG. 3. ac susceptibility of $Gd_{1-x}Pr_xBa_2Cu_3O_{7-y}$ compounds as a function of temperature for various values of x.

transition temperature (T_c/T_{c0}) versus x in $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ compounds, where T_{c0} corresponds to the zero-resistance temperature of the respective undoped $(x=0)$ $RBa_2Cu_3O_{7-y}$ samples. The data for $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$, taken from the literature,[5] with T_c as the midpoint of the resistive transition, are also plotted for comparison. It is to be noted that the depression of T_c for the same Pr concentration is stronger in the Sm system compared to that in the Gd and Tm systems. As mentioned earlier, the band-filling model would suggest nearly the same value of critical Pr concentration for the suppression of superconductivity independent of the rare-earth ion (R), which is not observed experimentally. Instead, we feel that the results may be understood in terms of the hybridization between the Pr $4f$ states and the O $2p$-Cu $3d$ states. The ionic size of Pr is much
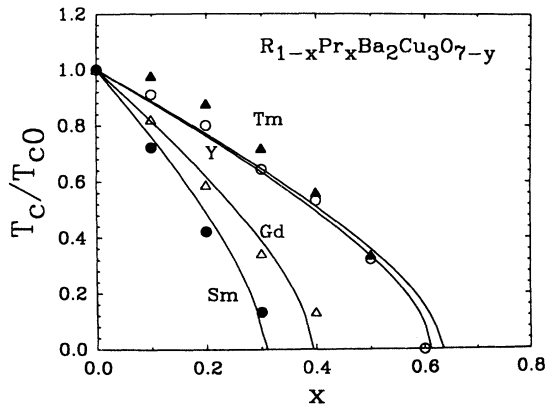

FIG. 4. Reduced T_c of $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ compounds as a function of x. Solid lines are fits based on Abrikosov-Gor'kov theory.

larger than that of Tm, but comparable to that of Sm. Therefore, the Pr ion is able to adjust its size by hybridization of the $4f$ electrons with the conduction electrons in the Cu-O network depending upon the lattice volume available. Since the ionic size of Pr is closer to that of Sm than to that of Tm, a situation similar to that in undoped Pr compound is easily obtained in the Sm-Pr system for relatively small Pr concentration and superconductivity is suppressed quickly. Alternatively, viewed from the Pr end, because of nearly the same ionic size of Pr and Sm, even a large amount of Sm does not substantially alter the hybridization present in the undoped Pr compound, so that superconductivity does not appear in the $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ system until a large fraction $(\sim 70\%)$ of Pr is replaced by Sm. On the other hand, the ionic sizes of Pr and Tm or Pr and Y are different and, therefore, the hybridization changes and these systems can accommodate more Pr than the Pr-Sm system. Thus our measurements favor a picture involving hybridization of the Pr $4f$ electrons with the O $2p$-Cu $3d$ electrons as a possible mechanism for the suppression of superconductivity. The actual situation may involve a combination of both the hybridization and the band-filling effects.[11] In fact, it has been shown[11] that the band filling alone initially raises the T_c in the Y-Pr system. This may be the reason for the deviation of the experimental T_c points in the Tm-Pr system from the Abrikosov-Gor'kov prediction (vide infra).

As mentioned above, there are many experimental observations[4-6,13,14] in the literature on $PrBa_2Cu_3O_{7-y}$ which also suggest strong hybridization of the Pr $4f$ states with the O $2p$-Cu $3d$ electronic states. These include the high magnetic ordering temperature of the Pr moments $(T_N=17$ K$)$, the large electronic specific-heat coefficient, and spectroscopic evidence of $4f$ character near the Fermi level. Besides, the bell-shaped upper-critical-field curves obtained in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ (Ref. 16) system indicate the presence of internal fields presumably arising due to the magnetic interaction of the Pr ions with the conduction electrons. These observations have prompted us to analyze the suppression of T_c in $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ $(R=$Sm, Gd, and Tm$)$ on the basis of the Abrikosov-Gor'kov (AG) pair-breaking theory,[20] according to which the T_c is given by the following expression:

$$\ln(T_c/T_{c0})=\psi(\tfrac{1}{2})-\psi[\tfrac{1}{2}+(2\pi T_c\tau_s)^{-1}] \qquad (1)$$

with

$$\tau_s^{-1}=2\pi n_I N(0)J_{sf}^2(g_J-1)^2 J(J+1) , \qquad (2)$$

where n_I is the concentration of pair-breaking magnetic impurities (which we take to be nearly trivalent Pr ions in this case), T_{c0} is the transition temperature in the absence of such impurities, ψ is the digamma function, $N(0)$ is the density of states at the Fermi level, g_J is the Landé g factor of the pair-breaking magnetic ion, and J is its total angular momentum and J_{sf} is the interaction constant for exchange interaction between the rare-earth spins S and

conduction electron spins s given by the Hamiltonian $H = -2J_{sf}\mathbf{S}\cdot\mathbf{s}$. Details of the analysis are similar to those given elsewhere.[21] The solid lines in Fig. 4 show a least-squares fit to the T_c data. The fit is reasonably good except for the low-concentration points in the Tm-Pr system. The values of $N(0)J_{sf}^2$ obtained from this analysis (in units of 10^{-3} eV states/atom spin) are 4.50 in the Sm-Pr system, 3.48 in the Gd-Pr system, 2.14 in the Tm-Pr system, and 2.23 in the Y-Pr system. Using a typical value of $N(0)=0.44$ states/eV atom spin, estimated in Ref. 11 from the specific-heat jump,[22] this leads to $|J_{sf}|$ values of 101, 89, 70, and 71 meV in the above-mentioned four systems in that order. The analysis shows an increase in the value of J_{sf} in going from the Tm-Pr system to the Sm-Pr system reflecting the increase in the hybridization. The values of J_{sf} obtained here in the oxide systems are comparable to those in rare-earth ternary borides,[23] rare-earth-based Heusler alloys,[21] etc. The hybridization between the $4f$ electrons of the light rare earths such as Ce, Pr, etc., and the conduction electrons is usually strong and can lead to large values of the exchange interaction constant J_{sf}.[24] It should, however, be remarked that the T_c data can also be explained on the basis of other models such as the spin-polaron model[19] employed by Wood.

In conclusion, studies on the $R_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ oxide systems with $R = $Sm, Gd, and Tm reveal that the critical Pr concentration required to suppress superconductivity depends on the rare-earth ion R. A simple band-filling model alone cannot account for this behavior. Instead, the results can be understood on the basis of hybridization between the Pr $4f$ states and the O $2p$–Cu $3d$ states. The results of T_c suppression are analyzed on the basis of AG theory, which yields the magnitude of the exchange constant, J_{sf}. The exchange constant is found to be larger in the Sm-Pr system compared to that in the Tm-Pr system consistent with the expected trend of hybridization.

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[1]See, for instance, D. W. Murphy, S. Sunshine, R. B. Van Dover, R. J. Cava, B. Batlogg, S. M. Zahurak, and L. F. Schneemeyer, Phys. Rev. Lett. **58**, 1888 (1987); Z. Fisk, J. D. Thompson, S. W. Cheong, R. M. Aikin, J. L. Smith, and E. Zirngiebl, J. Magn. Magn. Mater. **67**, L139 (1987).

[2]K. N. Yang, B. W. Lee, M. B. Maple, and S. S. Laderman, Appl. Phys. A **46**, 229 (1989).

[3]L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. U. Segre, and I. K. Schuller, Nature (London) **328**, 604 (1987).

[4]M. B. Maple, J. M. Ferreira, R. R. Hake, B. W. Lee, J. J. Neumeier, C. L. Seaman, K. N. Yang, and H. Zhou, J. Less Common Met. **149**, 405 (1989).

[5]A. Kebede, C. S. Jee, J. Schwegler, J. E. Crow, T. Mihalisin, G. H. Myer, R. E. Salomon, P. Scholttmann, M. V. Kuric, S. H. Bloom, and R. P. Guertin, Phys. Rev. B **40**, 4453 (1989).

[6]W. H. Li, J. W. Lynn, S. Skanthakumar, T. W. Clinton, A. Kebede, C. S. Jee, J. E. Crow, and T. Mihalisin, Phys. Rev. B **40**, 5300 (1989).

[7]See, for instance, B. D. Dunlap, M. Slaski, D. G. Hinks, L. Soderholm, M. Beno, K. Zhang, C. Segre, G. W. Crabtree, W. K. Kwok, S. K. Malik, I. K. Schuller, J. D. Jorgensen, and Z. Sungaila, J. Magn. Magn. Mater. **68**, L139 (1987).

[8]C. S. Jee, A. Kebede, D. Nichols, J. E. Crow, T. Mihalisin, G. H. Myer, I. Perez, R. E. Salomon, and P. Scholttmann, Solid State Commun. **69**, 379 (1989).

[9]Y. Dalichaouch, M. S. Torikachvili, E. A. Early, B. W. Lee, C. L. Seaman, K. N. Yang, H. Zhou, and M. B. Maple, Solid State Commun. **65**, 1001 (1988).

[10]A. Matsuda, K. Kinoshita, T. Ishii, H. Shibatu, T. Watanabe, and T. Yamada, Phys. Rev. B **38**, 2910 (1988).

[11]J. J. Neumeier, T. Bjornholm, M. B. Maple, and I. K. Schuller, Phys. Rev. Lett. **63**, 2516 (1989).

[12]J. J. Neumeier, T. Bjornholm, M. B. Maple, J. J. Rhyne, and J. A. Gotaas, Physica C **166**, 191 (1990).

[13]U. Neukirch, C. T. Simmons, P. Sladeczek, C. Laubschat, O. Strebel, G. Kaindl, and D. D. Sarma, Europhys. Lett. **5**, 567 (1988); E. E. Alp, G. K. Shenoy, L. Soderholm, G. L. Goodman, D. G. Hinks, and B. W. Veal, in *High-Temperature Superconductors*, edited by M. B. Brodsky, R. C. Dynes, K. Kitazawa, and H. L. Tuller, MRS Symposia Proceedings No. 99 (Materials Research Society, Pittsburgh, 1988), p. 177; L. Soderholm and G. L. Goodman, J. Solid State Chem. **81**, 121 (1989); S. Horn, K. Reilly, Z. Fisk, R. S. Kwok, J. D. Thompson, H. A. Borges, C. L. Chang, and M. L. denBoer, Phys. Rev. B **38**, 2930 (1988).

[14]J. S. Kang, J. W. Allen, Z.-X. Shen, W. P. Ellis, J. J. Yeh, B. W. Lee, M. B. Maple, W. J. Spicer, and I. Lindau, J. Less-Common Met. **24**, 25 (1989).

[15]I. Nowik, M. Kowitt, I. Felner, and E. R. Bauminger, Phys. Rev. B **38**, 6677 (1988).

[16]J. L. Peng, P. Klavins, R. N. Shelton, H. B. Radousky, P. A. Hahn, and L. Bernardez, Phys. Rev. B **40**, 4517 (1989).

[17]D. W. Cooke, R. S. Kwok, R. L. Lichti, T. R. Adams, C. Boekema, W. K. Dawson, A. Kebede, J. Schwegler, J. E. Crow, and T. Mihalisin, Phys. Rev. B **41**, 4801 (1990).

[18]A. P. Reyes, D. E. MacLaughlin, M. Takigawa, P. C. Hammel, R. H. Heffner, J. D. Thompson, J. E. Crow, A. Kebede, T. Mihalisin, and J. Schwegler, Phys. Rev. B **42**, 2688 (1990).

[19]R. F. Wood, Phys. Rev. Lett. **66**, 829 (1991), and references therein.

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

[21]S. K. Malik, A. M. Umarji, and G. K. Shenoy, Phys. Rev. B **32**, 4426 (1985).

[22]R. A. Fisher, J. E. Gordon, and N. E. Phillips, J. Supercond. **1**, 231 (1988).

[23]See, for example, *Ternary Superconductors*, edited by G. K. Shenoy, B. D. Dunlap, and F. Y. Fradin (North-Holland, New York, 1981).

[24]See, for instance, M. B. Maple, Appl. Phys. **9**, 179 (1976), and references therein; *Theoretical and Experimental Aspects of Valence Fluctuation and Heavy Fermions*, edited by L. C. Gupta and S. K. Malik (Plenum, New York 1987).