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Superconductivity in $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$: The role of apical oxygen in hybridization

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The structural and electric properties of $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ have been investigated as a function of x. X-ray powder-diffraction patterns indicate that a solid solution forms with x extending to about 1.4. It is found that the substitution of Sr for Ba results in a contraction in the c axis at the same rate as in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$. The oxygen content and T_c are found to remain essentially unchanged with increasing Sr. Our analysis suggests that the contraction in c arises mainly from the shift of the apical oxygen and from a shift of Ba(Sr) towards the CuO_2 planes. The apparent shift of the apical oxygen does not seem to influence the hybridization between the Pr $4f$ electrons and the valence band of the CuO_2 planes significantly. The hybridization is more sensitive to the bond length between the Pr and the oxygen located in the CuO_2 planes. T_c in this system appears to be controlled both by the shift of the apical oxygen and by the hybridization.

Many experimental studies have been undertaken to clarify the mechanism responsible for the nonsuperconductivity of $PrBa_2Cu_3O_{7-\delta}$. Studies on $Y_{1-x}Pr_xBa_2Cu_2O_{7-\delta}$ indicate that T_c is depressed rapidly with increasing x and that T_c goes to zero for $x_{cr} \approx 0.55$.[1-3] The valence of the Pr ions inferred from magnetic measurements,[4,5] Hall effect,[5] chemical substitution,[6] and muon-spin resonance[7] (μSR) is greater than +3 and possibly close to +4, implying that the depression of T_c results from hole filling in the CuO_2 sheets. On the other hand, Raman spectroscopy,[8] x-ray absorption,[9,10] electron energy-loss spectroscopy,[11] and inelastic neutron scattering[12] indicate that the valence of the Pr ions is close to +3.[13,14] The depression of T_c with increasing Pr was attributed to the enhanced hybridization between Pr $4f$ electrons and the CuO_2 valence band. Chemical substitution studies on $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ (Refs. 15–17) (where R is a rare earth) support this argument.

Though the hybridization mechanism seems plausible as an explanation of the depression of T_c, it remains unclear why $4f^2$ electrons of Pr^{3+} can interact with the conduction carriers of the CuO_2 planes in R-123 compounds while $Nd^{3+}(f^3)$ (immediately next to Pr in the Periodic Table) with a slightly smaller radius does not. Investigation of the superconducting $TlSr_2(Pr,Ca)Cu_2O_{7-\delta}$,[16] $Pr_{1.85}Ce_{0.15}CuO_4$,[17] and $Bi_2Sr_2Ca_{1-x}Pr_xCu_2O_{8+\delta}$ (Refs. 18 and 19) systems indicated that Pr^{+3} behaves just like other R^{+3} in these systems; no sign of hybridization effect has been observed. A careful structural examination of $RBa_2Cu_3O_{7-\delta}$ (Ref. 20) reveals that $PrBa_2Cu_3O_{7-\delta}$ is strictly isostructural with other superconducting R-123 compounds. The sole structural anomaly attributable to the presence of Pr^{+3} in the R-123 structure is a next-nearest-neighbor effect—an unusually short bond length between the in-plane copper and the apical oxygen, O(4) $[2q(0,0,z)]$. The role of the apical oxygen in determining the electronic properties has been reported in Y-123.[21-23] A high-resolution neutron powder-diffraction study of $YBa_2Cu_3O_{6.9}$ (Ref. 24) revealed a discontinuous shift of about 0.02 Å of the apical oxygen towards the CuO_2 sheets as the compound is heated through T_c into the nonsuperconducting temperature region. Hence the enhanced hybridization of $PrBa_2Cu_3O_7$ may arise from its unusually short apical Cu-O bond distance.

To verify this hypothesis a doped 123 system may be designed, so that the apical oxygen can shift along the c axis, while Pr^{3+} ions partially occupy the sites of R^{3+} and the R-123 structure remains. Such a system can allow us to study the effect of the apical oxygen on the hybridization as it shifts along the c axis. Previous studies[25–27] on $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ indicate that a solid solution forms with a solubility limit near $x = 1.25$, and that T_c decreases linearly with x. Anisotropic contractions of the lattice constants were also observed. Extended x-ray-absorption fine structure (EXAFS),[28] neutron diffraction,[29,30] and Raman scattering[30,31] have revealed that the contraction in the c axis results mainly from the rapid decrease in bond distance of Cu(2)-O(4) i.e., O(4) is displaced towards the CuO_2 planes with increasing Sr. It seemed that the Sr-doped $(Y,Pr)Ba_2Cu_3O_{7-\delta}$ system would be a useful system to study the role of the apical oxygen in hybridization. Since the T_c of $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_{7-\delta}$ is about 40 K, which allows us to observe its variations easily with Sr doping, we set the Pr-doping level at 0.4 in the present study.

In this paper we present structural and electrical properties of a series of $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ samples as a function of the Sr-doping level, x. We show that the shift of the apical oxygen towards the CuO_2 planes does not seem to influence the hybridization between Pr $4f$ electrons with the valence band of the CuO_2 sheets significantly in the present system.

A series of $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ samples with $x = 0.0$, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 were prepared by solid-state reaction of appropriate mixtures of high purity of Pr_6O_{11}, Y_2O_3, $SrCO_3$, and CuO. The powders were mixed, ground, and fired at 900 °C for 12 h in air. Two or three additional firings at 24 h intervals with intermediate grindings were performed before the samples were pressed into pellets. The pellets were then calcined at an elevated temperature, ranging from 930 to 970 °C with increasing Sr-doping levels. Phase identification and the measurement of lattice constants were performed on a MAC Science automatic diffractometer using Cu $K\alpha$ radiation at room temperature. High-purity Si was added to the samples as an internal standard to correct the positions of the diffraction lines. The lattice parameters were then calculated using a standard least-squares method. The electrical resistivity vs temperature was measured on rectangular bars cut from the sintered pellets employing the standard dc four-probe technique. The ac susceptibility was measured by an induction method. Data were collected from 300 down to 4.3 K. The oxygen content for all samples was measured by iodometric titration. Spectral-purity CuO was used as a standard. The measurement error is estimated to be less than 0.3%.

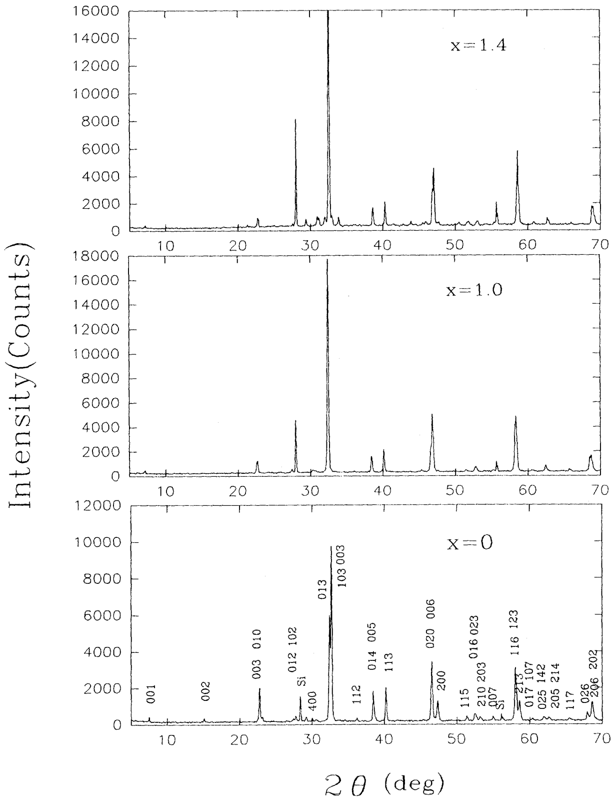

FIG. 1. Powder-x-ray-diffraction pattern of $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ for (a) $x = 0.0$, (b) $x = 1.0$, and (c) $x = 1.4$. High-purity Si was added as an internal standard to correct the positions of the diffraction peaks.

Powder-x-ray-diffraction patterns indicate that a solid solution forms in $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$. Figure 1 shows typical diffraction patterns for $x = 0$, 1.0, and 1.4. All samples with $x < 1.4$ are single phase. The appearance of unindexed diffraction peaks for the sample with $x = 1.4$ indicates that the solid solubility is less than 1.4. Since the highest intensity of the impurity contributions is less than 3% that of the main phase, the solubility is estimated to be close to 1.4. The lattice parameters for the Sr-free sample are in good agreement with the reported value.[1] Figure 2 shows the variation of lattice parameters with the doping level of Sr, x. As expected, the cell

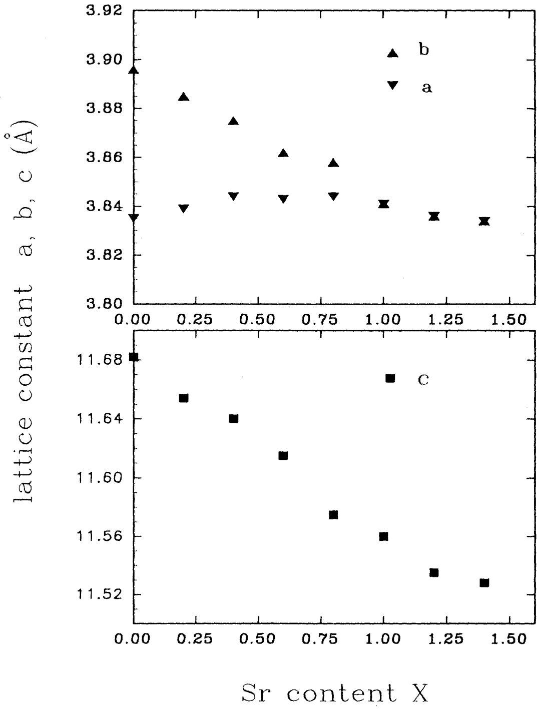

FIG. 2. Variation of lattice parameters a and c vs dopant concentration of Sr. Estimated standard deviation ≤ 0.002 Å for a and b, and ≤ 0.005 Å for c.

volume decreases with increasing x. However, the contractions of the cell parameters are anisotropic. The parameter c shows a linear decrease with a slope of about 0.13 Å/Sr atom. This value is identical with that observed in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$.[25,29] The result suggests that Sr ions indeed enter the unit cell and replace Ba ions. The variations of the cell parameters a,b, with x in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ are still controversial. Some researchers[29–31] reported that the substitution of Sr for Ba results in linear decreases for both a and b, without any tendency towards tetragonalization. But others[25,27] argued that b has a more rapid decreasing rate than a, leading to tetragonalization with increasing Sr. The disagreement may be due to the difference in synthesizing conditions. Nevertheless, the reported variations of T_c with x are similar, i.e., a linear decrease with a slope of about 10 K/Sr atom, so that any phase transition from orthorhombic to tetragonal that may occur does not have a significant effect on T_c. In the present system we found that the parameter b decreases from 3.895(1) Å ($x=0$) to 3.834(2) Å ($x=1.4$), while a varies nonmonotonically by a small amount. At about $x=1.0$, a and b become equal, indicating a phase transition from orthorhombic to tetragonal.

One striking feature in $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ is that T_c varies in a different way from $YBa_{2-x}Sr_xCu_3O_{7-\delta}$, where T_c is lowered with a rate of about 10 K/Sr atom with increasing Sr. Shown in Fig. 3 is the variation of T_c vs x for $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$, where T_c is defined as the temperature at which the resistivity corresponds to 50% of the extrapolated normal-state value while the transition width, indicated by vertical bars, is defined as the temperature difference between the 90 and 10% values. The variation of T_c over the entire compositional region from $x=0.0$ to 1.6 is within 8 K. Superconductivity continues to be observed until x reaches 1.8, with T_c as high as 44 K. Further substitution of Sr for Ba results in multiphases and a larger transition width, but T_c stays unchanged. This means that T_c does not decrease monotonically with doping Sr in the present system. In $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$, no obvious cusp is observed in the T_c-x curves similar to that reported in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$.[27] The variation of oxygen content, n, vs x for $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ is shown in Fig. 4. Fitting n vs x yields the equation $n=6.86+0.03x$. The value of the slope (0.03) is zero within the measuring error, showing that the oxygen content does not change with Sr doping in our specimens and that the variation of T_c cannot be associated with the change in n.

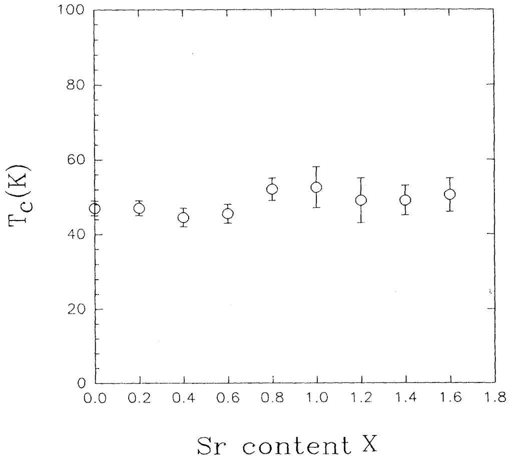

FIG. 3. Variation of T_c vs concentration of Sr in $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$. T_c is defined as the temperature at which the resistivity corresponds to 50% of the extrapolated normal state value while the transition width indicated by vertical bars is defined as the temperature difference between the 90 and 10% values.

The results presented above show that Sr has a wide solid solubility range extending to about $x=1.4$ in $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$, over which T_c does not decrease, unlike the case of $YBa_{2-x}Sr_xCu_3O_{7-\delta}$. Moreover, based on neutron diffraction and Raman measurement, Kakihana *et al.*[30] inferred that the substitution of Sr for Ba does not cause a redistribution of charge between the planes and the chains in Sr-doped Y-123. The same conclusion should also be applicable to the present system. We discuss two possible mechanisms with opposite effects on T_c: a shift of the apical oxygen toward the CuO_2 sheets due to direct substitution of Sr for Ba, and an increase in Pr-O bond distance due to a leveling off in the corrugation of the CuO_2 sheets. We argue that the same contraction rate and the solid solubility in $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ and $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ suggest uneven contraction along the c axis for both systems. This means that the c axis contraction in the former system would result mainly from the shift of the Ba(Sr)-O sheets towards the CuO_2 sheets, as is the case with the latter system. This is easily understood since Y(Pr) is the next-nearest ion to the Sr(Ba) ion and since the contraction in the c direction takes place between the plane and the chain, while the distance between planes is left unchanged in the Pr-free system.[28,30] Partial substitution of Pr for Y should therefore not disturb the uneven contraction along the c axis due to the substitution of Sr for Ba. The shift of the apical oxygen towards the CuO_2 planes will bring about a strong interaction between the apical oxygen and the valence band of CuO_2 planes, leading to an increase of the Cu $3d_{z^2}$ component in the Cu $3d_{x^2-y^2}$ bond or decreased splitting of Cu $3d_{z^2}$ and Cu $3d_{x^2-y^2}$ orbitals if the crystal-field effect is considered.[32] These effects cause T_c to decrease, as observed in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$. On the other hand, Raman measurement[31] and neutron diffraction[29] indicate that the Y-O bond distance can increase slightly with substitution of Sr for Ba in Y-123. The increase in the Y-O bond distance may arise from the leveling off in the corrugation of the CuO_2 sheets since the ionic radius of Sr is smaller than that of Ba. A similar situation is expected for (Y,Pr)-123 upon Sr substitution for Ba. Since the hybridization is a strong inverse function of the interatomic spacing,[32,33] the increase in the Y(Pr)-O bond distance will undoubtedly weaken the hybridization between the Pr $4f$ electrons and Cu $3d$-O $2p$ valence band, and subsequently lead to an increase in T_c. It seems that the effects

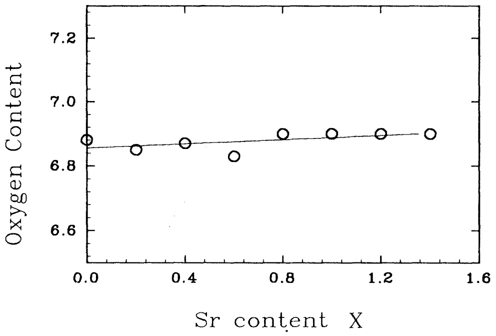

FIG. 4. Variation of oxygen content of $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ vs x, the concentration of Sr.

on T_c of the weakening hybridization and of the shift of apical oxygen counteract each other so as to prevent any significant change in T_c.

In view of the above argument we are led to suggest that the shift of the apical oxygen seems to have no significant effect on the hybridization, i.e., it does not make it stronger, as might be expected. However, the hybridization seems more sensitive to the Pr-O bond distance. This conclusion agrees well with the work by Neumeier *et al.*[34] They found that the T_c of $Y_{0.6}Pr_{0.4}Ba_2Cu_3O_{7-\delta}$ shows a rapid decrease with pressure with an initial slope of -0.21 K/kbar. Other studies, such as chemical substitution[15-17] and resonant photoemission spectroscopy,[35] strongly support this conclusion. At this stage, however, the origin of the hybridization between Pr 4f electrons and a Cu 3d-O 2p valence band is still unclear. From the present study we may infer that the unusual axial distance between Cu and the apical oxygen in $PrBa_2Cu_3O_{7-\delta}$ has no direct relation to the hybridization.

In conclusion, the substitution of Sr for Ba in the $Y_{0.6}Pr_{0.4}Ba_{2-x}Sr_xCu_3O_{7-\delta}$ results in a solid solution with x extending to about 1.4. The parameter c decreases with a slope of 0.13 Å/Sr atom at the same rate as in $YBa_{2-x}Sr_xCu_3O_{7-\delta}$. This would seem to imply that the contraction of the c axis results from the shift of the apical oxygen and of the Ba(Sr) ions towards the CuO_2 planes. The shift of the apical oxygen and the weakening hybridization have opposite effects on T_c, and, in fact, no large change is observed. The shift of the apical oxygen towards the CuO_2 planes does not seem to have any significant effect on the hybridization. The hybridization seems more sensitive to the bond distance between Pr and O in the CuO_2 planes.

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