

## Charge distribution in $Y_{1-x}Pr_xBa_2Cu_3O_7$ : A valency model for the depression of $T_c$

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We have carried out an evaluation of cation valences in  $Y_{1-x}Pr_xBa_2Cu_3O_7$  (YPBCO) on the basis of the fractional-valency ionic crystal model to investigate the causes of  $T_c$  suppression with Pr doping. Through comparison with the case of  $YBa_2Cu_3O_{7-x}$ , we have quantitatively estimated the extent to which the  $T_c$  depression can be accounted for in terms of the decrease in hole concentration in the  $CuO_2$  planes, paying special attention to the difference in the fourth ionization potential between Y and Pr. We have found that the valency of Pr is higher than that of Y by about 0.3 in YPBCO, thus reducing the Cu valency in the  $CuO_2$  planes with the Pr substitution, but that this effect can quantitatively explain no more than about one-third of the  $T_c$  depression. Accordingly, it is suggested that those effects neglected in the present model, such as a further decrease in mobile hole concentration due to the Pr-O hybridization, the localization of carriers due to disorder, and the magnetic pair breaking due to Pr spin, must play an important role in the mechanism of  $T_c$  suppression in YPBCO.

The puzzle that the superconductivity is suppressed upon substituting Y by Pr in the  $YBa_2Cu_3O_{7-\delta}$  (YBCO) system has attracted much interest<sup>1</sup> from the viewpoint of understanding the basic mechanisms of high- $T_c$  superconductivity in copper oxides. The elucidation of this issue is also important for the device applications utilizing YBCO/PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> (PBCO)/YBCO junctions.<sup>2</sup> Among a number of models<sup>1</sup> to explain this unique phenomenon in the  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  (YPBCO) system, the earliest one has presumed that the valence of the Pr ion is nearly +4,<sup>3-6</sup> which may cause the destruction of superconductivity through the back filling of holes in the  $CuO_2$  planes with the Pr substitution. Several spectroscopic measurements such as photoemission, x-ray absorption near-edge structure, Raman, ellipsometry, and electron-energy-loss spectroscopy have, however, confirmed<sup>1</sup> that the valence of the Pr ion is nearly +3 in the YPBCO system; a band-structure calculation<sup>7</sup> based on the linear muffin-tin orbital-atomic-sphere approximation method has also indicated that Pr<sup>3+</sup> is energetically more favorable than Pr<sup>4+</sup> in PBCO. On the other hand, more recent experimental<sup>8-11</sup> and theoretical<sup>12</sup> investigations have pointed out, through quantitative analyses, the significance of the decrease in mobile hole concentration in the  $CuO_2$  planes due to the Pr doping and have suggested a possibility that the Pr valence is intermediate between +3 and +4. In any case, a central issue in the YPBCO puzzle regarding what valence the Pr ion takes in YPBCO compounds still remains controversial.

The aim of the present work is fairly limited: On the basis of the fractional-valency ionic crystal model developed recently,<sup>13</sup> we carry out a quantitative analysis of the valence states of Cu, Y, and Pr ions in the YPBCO system and assess the extent to which the depression of  $T_c$  can be accounted for in terms of the valency difference between Y and Pr. The ionic crystal model has played an important role for the analyses of the charge distribution and the valence state of ions in high- $T_c$  copper-oxide su-

perconductors<sup>14,15</sup> on account of the high ionicity of interatomic bonds especially in the  $c$ -axis direction.<sup>16</sup> Compared with density-functional band-structure methods, this model calculation lays more emphasis on the ionic (rather than covalent) and the localized (rather than itinerant) characters of the electron system. In spite of its simple structure, this model has proven to be successful<sup>17</sup> in qualitatively explaining those conductive properties of high- $T_c$  and related oxides such as the magnitude of insulating gap, the electrical conductivity, and the hole's site preference in the  $CuO_2$  planes, with appropriate inclusion of electron correlation effects. An essential ingredient of the present approach in which the ionic charges are determined self-consistently is the difference in the fourth ionization potential between Y and Pr [61.8 versus 38.95 eV (Ref. 18)], which may work to enhance the valence of Pr relative to Y in YPBCO. We thus focus on the quantitative effects of this difference on the change in hole concentration in the  $CuO_2$  planes and on the variation of  $T_c$  with the Pr substitution.

In the present ionic crystal model, we express the total energy  $E$  of a system per unit cell as a sum of the Madelung energy  $E_M$  and the atomic (ionization) energy  $E_A$ . The Madelung energy is given by<sup>14</sup>

$$E_M = \frac{1}{2} \sum_{i,j} \tilde{c}_{ij} \alpha_i \alpha_j q_i q_j \quad (1)$$

in terms of the multiplicities  $\alpha_i$  and the charges  $q_i$  on inequivalent atomic sites  $i$  in the unit cell, with the charge neutrality condition,  $\sum_i \alpha_i q_i = 0$ . The coefficients  $\tilde{c}_{ij}$  can be calculated in advance<sup>14,19</sup> using the Ewald method once the crystal structure has been fixed. Here the dielectric constant has been set equal to unity, considering the consistency with the atomic energy as regards the cohesive energy<sup>13</sup> and the band gap<sup>17</sup> of metal oxides. The atomic energy is, on the other hand, expressed as a sum of the energies of the isolated ions on lattice sites:

$$E_A = \sum_i \alpha_i E_i(q_i), \quad (2)$$

where the functional form of  $E_i(q_i)$  is specified for each atomic species to account for the kinetic and potential energies of electrons relative to those for the neutral atom with  $q_i=0$  in the framework of the localized electron model.

The functional forms of atomic energies  $E_i(q_i)$  are usually constructed<sup>14,15</sup> so as to reproduce the experimental values of ionization potentials<sup>18</sup> and electron affinities of isolated atoms. Although there are a variety of schemes<sup>20</sup> interpolating  $E_i(q_i)$  over fractional values of  $q_i$ , we in this study rely on the following nonlinear expression for cations proposed in Ref. 13:

$$E_i(q_i) = a_i q_i^3 + b_i q_i^2 + c_i q_i, \quad (3)$$

where the coefficients  $a_i$ ,  $b_i$ , and  $c_i$  are determined according to the atomic energies at three integral values of  $q_i$  chosen appropriately, which are given by the sums of experimental ionization potentials. The merit<sup>13</sup> of this expression is that it is amenable to various optimization techniques employed for determining the charge distribution owing to the global and smooth interpolation considering the experimental  $E_i(q_i)$  behavior; it can then provide a stable fractional-charge distribution as a global minimum in the configuration space taking effective account<sup>20</sup> of itinerancy, covalency, and charge-transfer interaction usually neglected in the ionic crystal model. Given the crystal structure, the valency problem is thus reduced to that of finding an optimized local charge distribution  $\{q_i\}$  that minimizes the total energy  $E$  under the charge neutrality condition.

The present model calculation has been carried out as follows: We have employed the crystal structures of  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  for  $x=0.0, 0.2, 0.4, 0.6$ , and  $1.0$  obtained by means of neutron diffraction,<sup>8</sup> all of which are orthorhombic with the  $Pmmm$  space group. According to the notation in Ref. 8, we refer to the copper atoms on the CuO chain and in the CuO<sub>2</sub> plane as Cu(1) and Cu(2), respectively. We have taken into account the oxygen nonstoichiometry ( $-0.08 \leq \delta \leq 0.02$ ) and hence the occupancies of the O(4) site on the CuO chain and of the nearly vacant O(5) site out of the chain. The valences of O and Ba ions have been set equal to  $-2$  and  $+2$ , respectively, leaving four valences of Cu(1), Cu(2), Y, and Pr as parameters to be optimized. The present analysis exclusively aims at the description of interlayer charge transfer to which the ionic crystal model is reliably applicable,<sup>16</sup> and the valency change of CuO and CuO<sub>2</sub> planes is therefore represented by that of Cu(1) and Cu(2), respectively. This approximation has been adopted considering the difficulty in the ionic crystal model of describing the charge distribution between (energetically nearly degenerate) Cu and O sites in the CuO<sub>2</sub> planes<sup>13</sup> because of the overestimate of the magnitude of the charge-transfer gap.<sup>15,17</sup> The present model, thus, does not necessarily contradict the experimental fact that a considerable portion of holes doped into the CuO<sub>2</sub> plane enters the oxygen site. The atomic energies  $E_i(q_i)$  of cations are expressed

by Eq. (3) with the coefficients fitted to the experimental values<sup>18</sup> at  $q_i=1,2,3$  for Cu and at  $q_i=2,3,4$  for Y and Pr. We have used the average valency model<sup>13-15</sup> in the calculation of Y-Pr alloys, assuming that there is a charge of  $(1-x)q_Y + xq_{Pr}$  at the Y-Pr site, whose atomic energy is  $(1-x)E_Y(q_Y) + xE_{Pr}(q_{Pr})$ . Analogously, the oxygen sites have been assumed to have the charge  $-2p$  and the atomic energy  $pE_O(-2)$  when the occupancy of the O site is  $p$ . The optimization of four parameters  $\{q_i\}$  for Cu(1), Cu(2), Y, and Pr with respect to the total ener-

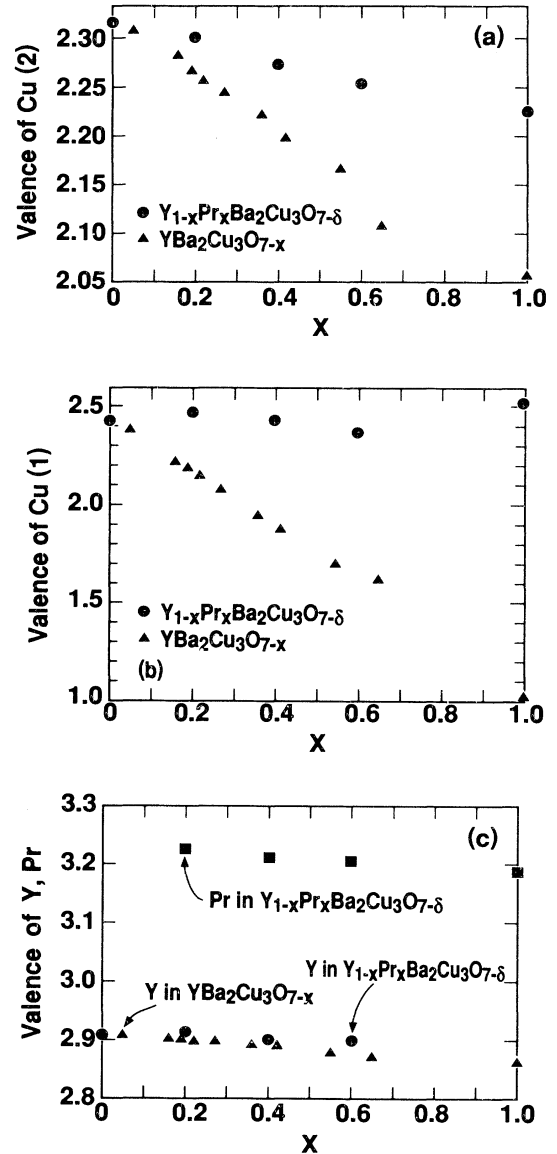


FIG. 1. (a) Valence of Cu(2) as a function of  $x$  in  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  (solid circles) and in  $YBa_2Cu_3O_{7-x}$  (solid triangles); (b) valence of Cu(1) as a function of  $x$  in  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  (solid circles) and in  $YBa_2Cu_3O_{7-x}$  (solid triangles); (c) valence of Y as a function of  $x$  in  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  (solid circles) and in  $YBa_2Cu_3O_{7-x}$  (solid triangles), and the valence of Pr as a function of  $x$  in  $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$  (solid squares).

gy  $E$  has then been carried out with the aid of the simplex method<sup>21</sup> under the charge neutrality condition.

Figure 1 shows the results for the valency changes of Cu(2), Cu(1), Y, and Pr in YPBCO as functions of the Pr content  $x$ . It is observed in Fig. 1(c) that the valences of Y and Pr slightly decrease with the increase in  $x$  but take nearly constant values of approximately 2.9 and 3.2, respectively, over the whole region of  $0 \leq x \leq 1$ . The difference between the two values, 0.3, primarily arises from the difference in the fourth ionization potential between Y and Pr (61.8 versus 38.95 eV) and is nearly identical to the values<sup>8,10</sup> estimated from the local bond lengths in the vicinity of the Pr ion. This valency difference necessarily brings about the decreases of Cu(2) and Cu(1) valences with the Pr substitution, or the hole filling in the  $\text{CuO}_2$  planes and the CuO chain, as observed in Figs. 1(a) and 1(b). Here it is noted, as regards Fig. 1(b), that the increase in the Cu(1) valence at  $x = 1.0$  is due to the enhanced occupancy of the O(5) site<sup>6</sup>; the experimental indication that the CuO chain in PBCO seems semiconducting<sup>9</sup> may then be ascribed to reasons other than the hole depletion, such as the disorder arising from oxygen vacancies and other defects.<sup>12</sup> As for the valence of Cu(2), which is directly associated with superconductivity, we find in Fig. 1(a) that it decreases by 0.062 at  $x = 0.6$  and by 0.091 at  $x = 1.0$  relative to at  $x = 0.0$ . Roughly speaking, the Y-Pr site thus deprives two  $\text{CuO}_2$  and one CuO planes in YPBCO of holes by approximately 0.1 $x$  per plane with the Pr substitution.

In order to quantitatively estimate the extent to which such a decrease in hole concentration in the  $\text{CuO}_2$  planes affects the change of  $T_c$  in YPBCO, we have comparatively carried out analogous calculations for the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  system. The valency changes in Cu(2), Cu(1), and Y are plotted also in Fig. 1 as functions of the oxygen deficiency  $x$ , which have been calculated on the basis of the crystal-structure data by neutron diffraction (orthorhombic for  $0.05 \leq x \leq 0.55$  and tetragonal for  $0.65 \leq x \leq 1.00$ ).<sup>22</sup> The result for the valency change in Cu(2) reproduces (except for the overall upward shift by about 0.05) the generally accepted presumption,  $\text{Cu}^{2.25+} \rightarrow \text{Cu}^{2+}$ , showing a behavior analogous to the results evaluated by means of the strain-corrected bond valence sums<sup>23,24</sup> (BVS's); all these results exhibit a common kink structure at  $x \sim 0.5$ . In addition, we find in Fig. 1(b) that the result for the Cu(1) valence coincides with the BVS estimate<sup>24</sup> fairly well, giving another support for the quantitative reliability of the present model. It is then observed in Fig. 1(a) that the valency change in Cu(2) in YPBCO is no more than 30–40% of that in YBCO for the same  $x$ . It follows from this observation that we cannot explain the disappearance of superconductivity at  $x \sim 0.55$  (Ref. 1) in YPBCO only in terms of such a decrease in hole concentration in the  $\text{CuO}_2$  planes resulting from the valency difference between Y and Pr ions. To illustrate the situation more vividly, we plot in Fig. 2 the relationship between the Cu(2) valence and  $T_c$

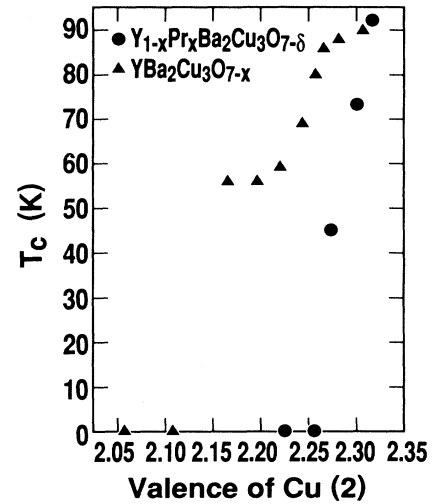


FIG. 2. Relationship between the valence of Cu(2) and  $T_c$  in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  (solid circles) and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (solid triangles). The values of  $T_c$  have been determined as the temperature where the resistivity drops to 50% of the extrapolated normal-state value in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  (Ref. 8) and by the onset of diamagnetism on a linear scale in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Ref. 22).

(Refs. 8 and 22) for both the YPBCO and YBCO systems. It is apparent in this figure that the degree of reduction in hole concentration in the  $\text{CuO}_2$  planes by which the superconductivity is fully destroyed in the case of YPBCO can depress  $T_c$  at most from about 90 to 60 K in YBCO, and hence that the present hole-filling model can account for no more than approximately one-third of the required  $T_c$  depression in YPBCO.

In conclusion, we have found on the basis of the fractional-valency ionic crystal model that the decrease in hole concentration in the  $\text{CuO}_2$  planes due to the valency difference between Y and Pr arising from the difference in the fourth ionization potentials can somewhat contribute to the  $T_c$  depression, but that this valency model alone cannot completely account for the suppression of superconductivity in the YPBCO system. To draw a complete picture for the mechanism of the  $T_c$  depression with the Pr substitution, therefore, one or all of those effects ignored in the present model, such as (1) a further decrease in mobile hole concentration due to the hole transfer from  $\text{O } 2p_\sigma$  to  $\text{O } 2p_\pi$  states resulting from the hybridization between Pr  $4f$  and the surrounding O  $2p$  orbitals,<sup>12</sup> (2) the localization of holes due to the disorder on, e.g., the Y-Pr site,<sup>1,12</sup> and (3) the magnetic pair breaking due to the Pr spin,<sup>1,5,7</sup> must play an important role.

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