

**Theoretical analysis of the concentration and distribution of carriers in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$**

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(Received 17 May 1989)

An ionic model and the total-energy method are used to calculate the density and distribution of carriers in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  systems and, in particular, to understand the relationship between the density of carriers and the density of oxygen vacancies in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . It is shown that the density of carriers is normally  $1-x$  per unit cell and the carriers are holes on the oxygen ions in the  $\text{CuO}_2$  planes. In addition, for the  $1+$  valence copper ions  $\text{Cu}^+$  present in the  $\text{CuO}$  plane, the density of  $\text{Cu}^+$  is normally  $x$  per unit cell.

In order to understand the high- $T_c$  superconductivity in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , a study of the concentration and spatial distribution of carriers in the lattice is very important. For  $x=0$ , there is one hole in every unit cell,<sup>1</sup> and it is generally accepted that the hole is present in the  $\text{CuO}_2$  plane. It follows that in the  $\text{CuO}$  basal plane ( $\square$  denotes oxygen vacancy), the valence of copper ions is  $2+$  and that of oxygen  $2-$ , while in the  $\text{CuO}_2$  plane the charge distribution can be represented as  $[\text{CuO}_2]^{1.5-}$ . In another paper by one of the authors and co-workers,<sup>2</sup> this distribution was presented from the point of view of electrostatic screening. It has been demonstrated by many experiments<sup>3</sup> that for  $[\text{CuO}_2]^{1.5-}$  the holes occur on  $\text{O}^{2-}$  ions rather than  $\text{Cu}^{2+}$  ions. This was first proposed by Emery<sup>4</sup> and has been discussed by many theorists.<sup>5</sup> This has also been confirmed by the authors<sup>6</sup> in the calculation of the parameters of the extended Hubbard model for La-Sr-Cu-O and Y-Ba-Cu-O. However, there remains an important question: what is the relationship between the density of carriers and the density of oxygen vacancies for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ? In particular, experiments<sup>7</sup> indicate that the  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  is a conductor and has a superconducting transition temperature  $T_c \sim 50-60$  K. On the contrary, from the simple chemical model, all of the copper ions have a valence of  $2+$  and all oxygen  $2-$  and no extra holes; therefore it should be an insulator. From the electronic spectra, in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with  $x \neq 0$ , evidence of  $\text{Cu}^{3+}$  ions has not been observed, but the presence of  $\text{Cu}^+$  has evidently been confirmed. Which sites are  $\text{Cu}^+$  ions on? What is the relationship between  $\text{Cu}^+$  and hole concentration? Recently many experiments and theoretical discussions<sup>8</sup> have demonstrated that oxygen vacancies are ordered at low temperature in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x \neq 0$ ). As suggested by Tranquada *et al.*<sup>9</sup> for each oxygen vacancy occurring, only one hole is removed from the  $\text{CuO}_2$  plane as a  $\text{Cu}^{2+}$  ion in  $\text{CuO}$  plane is converted to  $\text{Cu}^+$ . Thus, in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x \neq 0$ ) the number of holes per unit cell is equal to  $1-x$ . We feel that the assumption of Tranquada *et al.* is reasonable, but requires theoretical support.

As the authors emphasized in Ref. 6, because of the electron correlation, especially the on-site electron corre-

lation, a discussion held on the ionic aspect is more realistic for high-temperature copper oxide superconductors. We have used the model developed by Watson and others to treat ionic solids.<sup>10</sup> The Madelung potential is given by

$$V_i(r) = \begin{cases} -V_i, & r < Q_i / -V_i, \\ Q_i / r, & r > Q_i / -V_i, \end{cases} \quad (1)$$

where  $-V_i$  is the Madelung potential constant for the electrons on the  $i$ th ion site, and  $Q_i$  is the net charge of the  $i$ th ion (see Fig. 1).

Based on the density functional theories, the effective single-electron equation can be written as

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{eff}}\right) A_i = E_i A_i,$$

$$V_{\text{eff}} = V_{\text{Coulomb}} + V_{\text{ex}} + V_{\text{corr}}.$$

Adding the Madelung contribution, the equation becomes

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}} + V_i(r)\right] A_i = E_i A_i. \quad (2)$$

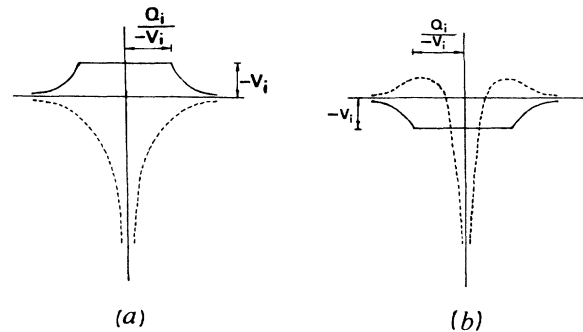
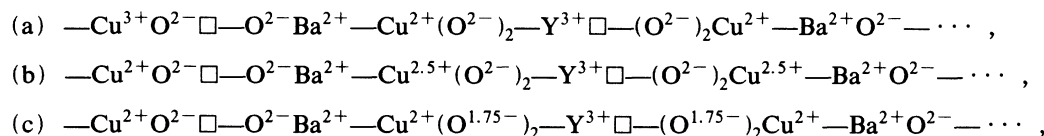


FIG. 1. The Madelung potential (solid line) and ionic potential (dashed line) (a) for  $\text{Cu}^{2+}$  ion and (b) for  $\text{O}^{2-}$  ion.  $(-V_i)$  is the electrostatic interaction for the electrons at the site of the  $i$ th ion due to the rest of the ions in the crystals.  $(Q_i)$  is the net charge of the  $i$ th ion, i.e., for  $\text{Cu}^{2+}$   $Q_i=2$  and for  $\text{O}^{2-}$   $Q_i=-2$ .

It can be solved self-consistently, and then we can calculate the total energy involving exchange energy and correlation energy (the sum of the total energy of the ions in a unit cell is the total energy of the system per unit cell). Such a calculation can be called a quasichemical



where the symbol “—” denotes that the layers are subsequently arranged along the  $c$  axis, and the ions between two “—” symbols denote the ions in one layer, for example,  $\text{—Cu}^{3+}\text{O}^{2-}\square\text{—}$  in the basal layer and so on. We assume that in the basal plane the oxygen vacancies are full-

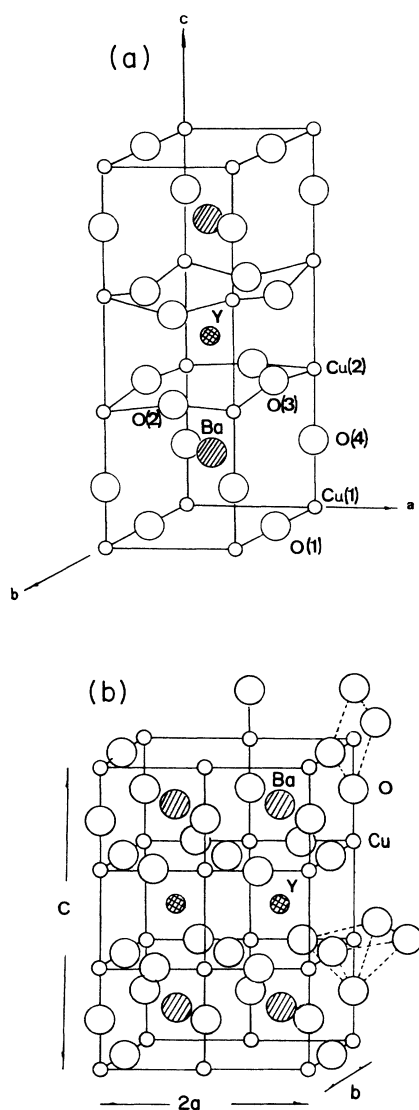


FIG. 2. The three-dimensional crystal structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (one unit cell) and  $\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{13}$  (double unit cells).

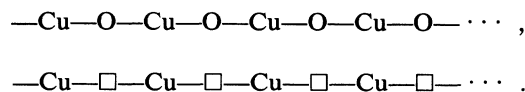
method, which emphasizes the difference of energies for different ionic charge distributions.

We calculated the following situations.

(i)  $x=0$ . This situation has been presented in Ref. 6. The possible distributions are

ly ordered into the  $a$  axis and there are a series of parallel  $\text{Cu—O—Cu—O—}\dots$  one-dimensional chains along the  $b$  axis. In distribution (a), holes are totally situated on the one-dimensional chains. The calculation results show that the total energy of this distribution is too high. In this paper we mainly discuss the (b) and (c) distributions. For (b), holes are present on  $\text{Cu}^{2+}$  ion sites in the  $\text{CuO}_2$  planes. There are two possible expressions: One is that half of the Cu ions remain on the 2+ valence; the other half of the  $\text{Cu}^{2+}$  ions are converted to  $\text{Cu}^{3+}$ . The other expression is that all of the  $\text{Cu}^{2+}$  ions uniformly become  $\text{Cu}^{2.5+}$ . In the latter situation holes are shared by the  $\text{Cu}^{2+}$  ions. In calculating the electron correlations of the two expressions there is a great difference between them, but for the quasichemical method used in this paper, there is not much difference. For (c), holes are present on  $\text{O}^{2-}$  ion sites in the  $\text{CuO}_2$  plane. There are also two types of expressions: One is that  $\frac{1}{4}$  of O(2) and O(3) become  $\text{O}^{1-}$ ; the rest retain a formal valence  $\text{O}^{2-}$ . The other is that holes are uniformly distributed among oxygen ions and every O(2) and O(3) becomes  $\text{O}^{1.75-}$ . In the discussion of total energy by the quasichemical method, these two expressions are not much different either.

(ii)  $x=0.5$ . We assume that the oxygen vacancies are fully ordered as illustrated in Fig. 2.<sup>11</sup> In the basal plane, two types of one-dimensional chains are possible,



The former is called full chain, the latter empty chain. We analyze two different charge distributions,

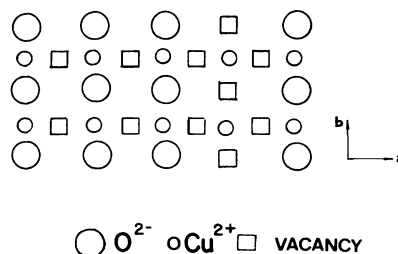
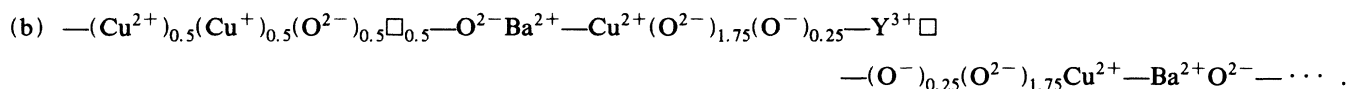
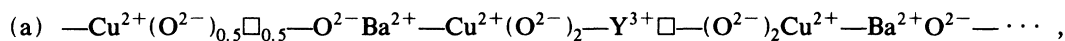


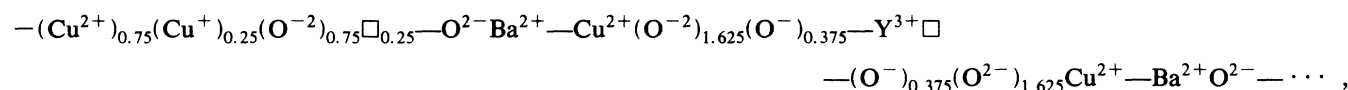
FIG. 3. Charge distribution with three full-chain orderings and one empty-chain ordering in the basal plane of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ .



For the (a) distribution, all of the Cu atoms are  $\text{Cu}^{2+}$ , and all of the O atoms are  $\text{O}^{2-}$ . It is consistent with the results of the simple chemical model that there is no extra hole, i.e., no  $\text{O}^-$ . For (b), Cu atoms on the twofold-coordinated sites of the empty chains have a valence of +, and fourfold-coordinated Cu atoms on the full chains have the formal valence 2+. The extra holes  $\text{O}^-$  are presented in the  $\text{CuO}_2$  planes with each unit cell having 0.5 hole, which is equal to the number of  $\text{Cu}^+$  ions.

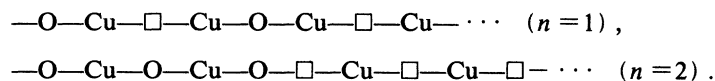
(iii)  $x=0.25$ , also assuming the oxygen-vacancy ordering.<sup>11</sup> There are several different distributions for the  $\frac{3}{4}$  oxygen occupation in the basal plane.

(a) For four unit cells, there are three full chains and one empty chain in the basal plane (see Fig. 3). It is similar to the situation of  $x=0.5$  with fourfold-coordinated  $\text{Cu}^{2+}$  on the full chains and twofold-coordinate  $\text{Cu}^+$  on the empty chains. The charge distribution is

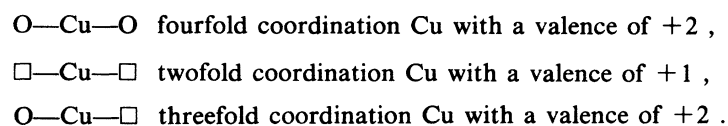


where the number of  $\text{O}^-$  is 0.75 within the  $\text{CuO}_2$  planes in every unit cell, and thus 0.375 per  $\text{CuO}_2$  plane, and 0.25  $\text{Cu}^+$  per basal plane.

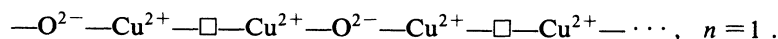
(b) For double unit cells, there are one full chain and one half-full chain in the basal plane. For the half-full chain, there are many different distributions with  $n$  oxygens locating side by side and  $n$  oxygen vacancies side by side when  $n$  varies ( $n=1, 2, \dots$ ):



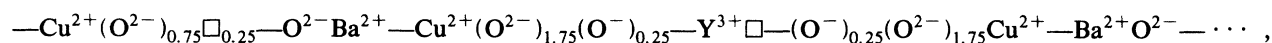
In addition to fourfold- and twofold-coordinated Cu atoms, there are Cu atoms in the threefold-coordinated sites of the half-full chains. The threefold-coordinated Cu sits between oxygen segment and oxygen vacancy segment. Then it can be represented as



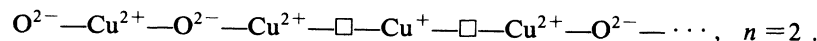
The calculations indicate that it will be unstable if threefold-coordinated Cu has the valence  $\text{Cu}^+$ . This is because on such site the Madelung potential is too high for  $\text{Cu}^+$  ions. It is similar to the unstable state of free  $\text{O}^{2-}$  ions. Thus, we take threefold-coordinated Cu with 2+ valence. The ordered half-full chains then become



The charge distribution is



where in  $\text{CuO}_2$  planes the number of  $\text{O}^-$  is 0.5 but not 0.75, and there is no  $\text{Cu}^+$  ion.



The charge distribution is

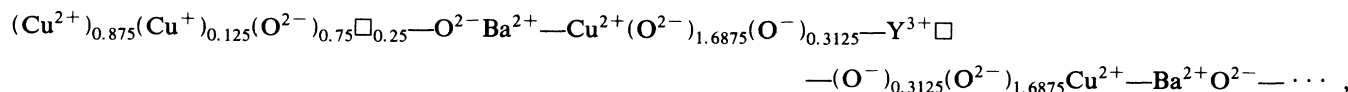


TABLE I. The total energy of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in the ionic model.

	Charge distribution	$E_{\text{tot}}$ (a.u.)/unit cell
$x=0$	(a) $\text{O}(1,2,3,4)_7^{2-}\text{Cu}(1)^{3+}\text{Cu}(2)_2^{2+}$	-24367.8317
	(b) $\text{O}(1,2,3,4)_7^{2-}\text{Cu}(1)^{2+}\text{Cu}(2)^{2+}\text{Cu}(2)^{3+}$	-24370.2857
	(c) $\text{O}(1)^{2-}\text{O}(2,3)_4^{-1.75}\text{O}(4)_2^{2-}\text{Cu}(1)^{2+}\text{Cu}(2)_2^{2+}$	-24377.5890
	(d) $\text{O}(1)^{2-}\text{O}(2)_2^{2-}\text{O}(3)^-\text{O}(3)^{2-}\text{O}(4)_2^{2-}\text{Cu}(1)^{2-}\text{Cu}(2)_2^{2+}$	-24377.400
	(e) $\text{O}(1)^-\text{O}(2,3,4)_6^{2-}\text{Cu}(1)^{2+}\text{Cu}(2)_2^{2+}$	-24374.9274
$x=0.25$	(a) $\text{O}(1)_{0.75}^{2-}\text{O}(2)_2^{2-}\text{O}(3)_{1.25}^{2-}\text{O}(3)_{0.75}^{2-}\text{O}(4)_2^{2-}\text{Cu}(1)_{0.25}^{+}\text{Cu}(1)_{0.75}^{2+}\text{Cu}(2)_2^{2+}$	-24360.3477
	(b) $\text{O}(1)_{0.75}^{2-}\text{O}(2)_2^{2-}\text{O}(3)_{1.5}^{2-}\text{O}(3)_{0.5}^{2-}\text{O}(4)_2^{2-}\text{Cu}(1)^{2+}\text{Cu}(2)_2^{2+}$	-24357.3880
	(c) $\text{O}(1)_{0.75}^{2-}\text{O}(2)_2^{2-}\text{O}(3)_{1.375}^{2-}\text{O}(3)_{0.625}^{2-}\text{O}(4)_2^{2-}\text{Cu}(1)_{0.125}^{+}\text{Cu}(1)_{0.875}^{2+}\text{Cu}(2)_2^{2+}$	-24358.7344
$x=0.5$	(a) $\text{O}(1)_{0.5}^{2-}\text{O}(2,3,4)_6^{2-}\text{Cu}(1)^{2+}\text{Cu}(2)_2^{2+}$	-24333.2215
	(b) $\text{O}(1)_{0.5}^{2-}\text{O}(2)_2^{2-}\text{O}(3)_{0.5}^{2-}\text{O}(3)_{1.5}^{2-}\text{O}(4)_2^{2-}\text{Cu}(1)_{0.5}^{+}\text{Cu}(1)_{0.5}^{2+}\text{Cu}(2)_2^{2+}$	-24343.2499

where in  $\text{CuO}_2$  planes the number of  $\text{O}^-$  is 0.625 and that of  $\text{Cu}^+$  0.125 in basal plane. Note that for distribution (a), it corresponds to  $n = \infty$ ; when  $n \neq \infty$ , the number of both  $\text{O}^-$  and  $\text{Cu}^+$  ions are smaller than that in the (a) distribution.

The results of calculations are presented in Table I.

(i) For  $x=0$ , the calculations indicate that the total energy of distribution (c) is the lowest. This confirms the model previously proposed by Emery.<sup>4</sup> The carriers are holes and are present in the  $\text{CuO}_2$  planes. In this situation, in the  $\text{CuO}_2$  planes, Cu atoms are  $\text{Cu}^{2+}$  with  $\frac{1}{2}$  spin, the holes are present on the oxygen ions, and they are the conductive carriers. There is one hole per unit cell. To compare with the experimental data of the electronic spectra, we calculate the transition energy of O 1s of this model, i.e., the energy of the

$$\text{O}^-(1s^2 2s^2 2p^5) + h\nu \rightarrow \text{O}^-(1s^1 2s^2 2p^6)$$

transition process. We obtain  $h\nu \sim 525$  eV (see Table II), which is consistent with the experimental value 528 eV (Ref. 3). This supports the idea that holes are present on

the oxygen sites.

(ii) For  $x=0.5$ , it shows that the total energy of distribution (b) is the lowest. This confirms the model proposed by Tranquada and co-workers. In this situation, there is one oxygen vacancy in the basal plane in the "unit"  $\text{Y}_2\text{Ba}_4\text{Cu}_6\text{O}_{14}$ . For the two removed holes, one is removed from the basal plane leading from  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  and another is removed from the  $\text{CuO}_2$  planes. That is, in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x=0.5$ ) the number of carriers is 0.5 per unit cell. The charge distribution in  $\text{CuO}$  basal plane is illustrated in Fig. 4.

(iii) For  $x=0.25$ , it shows that the total energy of distribution (a) is the lowest. Distribution (b) has half-full chains, and its energy is somewhat higher. In the experimental samples, it might be predicted that distribution (a) retain dominant, mixing with distribution (b).

(iv) Because the Madelung potential is mainly determined by the near-neighbor charge distribution, in addition to the preceding calculations, we also calculated some localized situations and discussed the stability of different ionic valences. These calculations indicate that the following results are primarily correct: In the pyram-

TABLE II. The calculated transition energy of O 1s in the ionic model.

	$\text{O}(3)^-(1s^2 2s^2 2p^5) \xrightarrow{+h\nu} \text{O}(3)^-(1s^1 2s^2 2p^6)$	$P$ denotes the percentage on different sites of $\text{O}^-$ .			
	$\text{O}^{-1}(1s^2)$	$\text{O}^{-1}(1s^1)$			
	$V_{\text{Madelung}}$	$P$	$E_i(1s^2)$ (a.u.)	$E_i(1s^1)$ (a.u.)	$\Delta$ (eV)
$\text{O}_{6.5\text{II}}$	-0.70055	50%	-80.4159	-61.0830	525.85
	-0.50969	50%	-79.0298	-59.6533	527.04
$\text{O}_{6.75}$	-0.86273	$\frac{2}{3}$	-81.4261	-62.1241	525.01
	-0.53505	$\frac{1}{6}$	-79.2258	-59.8549	526.89
	-0.49286	$\frac{1}{6}$	-78.8973	-59.5173	527.14
$\text{O}_{7\text{II}}$	-0.75687	100%	-80.7840	-61.4631	525.53

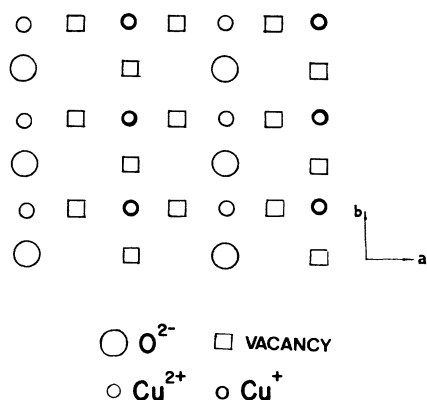


FIG. 4. Charge distribution in the basal plane of  $YBa_2Cu_3O_{6.5}$ .

idlike or the fivefold-coordinated  $CuO_2$  plane, the Cu ions have a valence of  $2+$  and extra holes occur on the  $O^{2-}$  sites. In the basal plane, the fourfold-coordinated Cu ions are also  $2+$  while in the oxygen-deficient basal plane the twofold Cu ions have a valence of  $1+$ . On the half-full chain, the copper ions on threefold-coordinates sites remain  $2+$  valence. We believe that this conclusion should be common for the layered perovskite copper-oxide superconductors besides  $YBa_2Cu_3O_{7-x}$ .

Finally, we wish to emphasize that a series of experiments<sup>12</sup> indicate that the major factor contributing to the superconducting transition temperature is the concentration of carriers in the  $CuO_2$  planes. Therefore it is very important to analyze the relationships among the carrier concentration, the chemical valence of copper and oxygen ions, and the oxygen vacancy concentration. We plan to use the quasichemical model or the ionic model presented by the authors to discuss more situations.

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