Stability of $2\sqrt{2}\times 2\sqrt{2}$ oxygen ordered superstructures in $YBa_2Cu_3O_{6+x}$

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We have compared the ground-state energy of several observed or proposed ''$2\sqrt{2}\times 2\sqrt{2}$ oxygen ordered superstructures'' [''herringbone'' structures (HS's)], with those of ''chain superstructures'' (CS's) (in which the O atoms of the basal plane are ordered in chains), for different compositions x in $YBa_2Cu_3O_{6+x}$. The model Hamiltonian contains (i) the Madelung energy, (ii) a term linear in the difference between Cu and O hole occupancies which controls charge transfer, and (iii) covalency effects based on known results for t-J models in one and two dimensions. The optimum distribution of charge is determined, minimizing the total energy, and depends on two parameters which are determined from known results for $x=1$ and $x=0.5$. We obtain that on the O lean side, only CS's are stable, while for $x=7/8$, a HS with regularly spaced O vacancies added to the $x=1$ structure is more stable than the corresponding CS for the same x. We find that the detailed positions of the atoms in the structure and long-range Coulomb interactions are crucial for the electronic structure, the mechanism of charge transfer, the stability of the different phases, and the possibility of phase separation. [S0163-1829(98)02501-6]

I. INTRODUCTION

The ordering of oxygen atoms in the basal plane of $YBa_2Cu_3O_{6+x}$, and its relation with electronic properties, particularly the superconducting critical temperature T_c, has been a subject of great interest. Overviews are contained in Ref. 1. For the sake of brevity, we denote the superstructures of unit cell multiple of $2\sqrt{2}\times 2\sqrt{2}$ as HS's (for ''herringbone'' structures, although this name is strictly valid for $x=\frac{1}{2}$ only). By the end of the last decade, for x near 0.5 evidence of ordering in chains was found, while for x near 0 or 1, HS's were reported,[2–7] the charge distribution in superconducting planes[8] and in the Cu ions of the basal planes[9,10] was determined, and an explanation of these experiments was presented using a lattice-gas model based on Coulomb repulsions, and the appropriate extension to this system of the three-band Hubbard model H_{3b}.[11] Optical[9,12] and nuclear quadrupole resonance[10,13] (NQR) experiments give strong evidence that twofold-coordinated Cu atoms are in an oxidation state Cu^+, while threefold and fourfold-coordinated Cu atoms are Cu^{2+}. Qualitatively, this fact is easy to understand in terms of H_{3b}:[14] The energy necessary to add a d hole to an n-fold-coordinated Cu^+ (surrounded by n O^{2-} ions) is $\epsilon_{Cu}-2nU_{pd}$, where U_{pd} is the Cu-O hole-hole repulsion. Provided that the hole Fermi energy of the superconducting CuO_2 planes lies between $\epsilon_{Cu}-4U_{pd}$ and $\epsilon_{Cu}-6U_{pd}$, only twofold-coordinated Cu atoms remain Cu^+, and the remaining holes go to the CuO_2 planes (and to O atoms of the chains). This mechanism not only provides the holes for superconductivity of the chain superstructures (CS's), but also reduces their energy.[14] For $x\sim 0.5$, annealing at room temperature produces an increase of T_c due to an increase in the amount of twofold-coordinated Cu ions.[16–18]

In spite of this qualitative understanding of the relation between O ordering and charge transfer, and the success of lattice-gas models in explaining the basic features of the thermodynamics of O ordering at temperatures above room temperatures,[11,19–22] a fully self-consistent theory of the atomic and electronic structure of $YBa_2Cu_3O_{6+x}$ is still lacking, and several controversial issues remain. Schleger *et al.* showed that it is necessary to add electronic degrees of freedom to lattice-gas models in order to explain the observed $\partial x/\partial\mu$, where μ is the O chemical potential.[23] The strong-coupling approaches to the electronic structure are able to treat adequately the on-site Cu Coulomb repulsion U_d and to explain the observed dependences of the hole count in the planes n_H (from which T_c can be inferred[24]), and the amount of Cu^+.[1,22,24–26] However, these agreements are obtained within a region of parameters of the model, which is not fully justified, and Coulomb repulsions beyond ~ 2 Å are neglected. On the other hand, *ab initio* calculations, as a consequence of the large value of U_d and the neglect of correlations, fail to describe the semiconducting phases (they predict a metal) and the neglected correlation energies are much larger than the lattice-gas model parameters which determine the structure.[1]

A controversial issue is the stability of HS's. While it is

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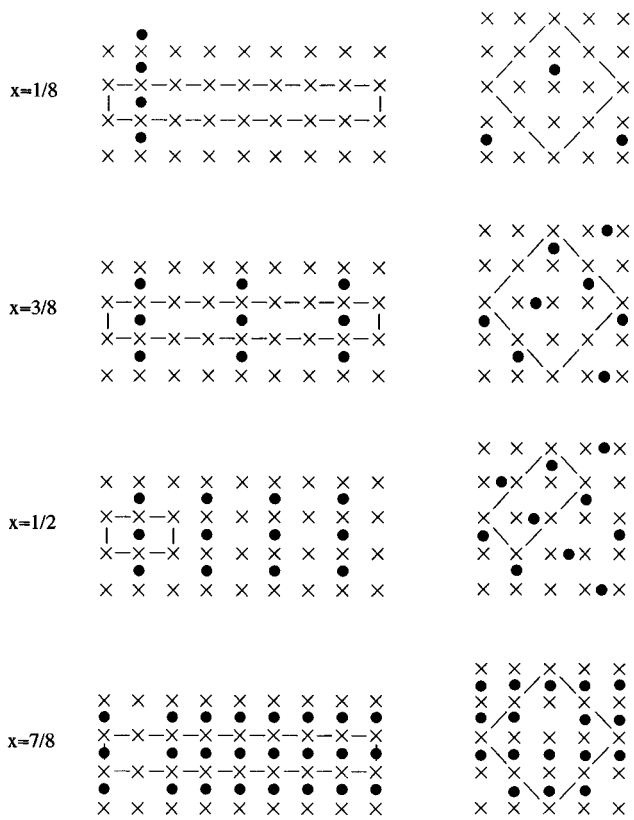

FIG. 1. Oxygen-ordered superstructures of the basal plane considered in this work, for different oxygen contents x. Left: CS, of unit cell $1\times n$. Right: HS, of unit cell $2\sqrt{2}\times 2\sqrt{2}$. Crosses denote Cu(1) atoms and solid circles represent O(4) atoms in the notation of Refs. 43 and 44.

clear that at room temperatures, the CS's disappear in the semiconducting region,[13] the experimental and theoretical situation does not at present disclose unambiguously the nature of the ground state. The HS's observed by transmission electron microscopy,[2,3] were proposed to be metastable.[3] Synchrotron radiation studies for $x\sim 0.2$ provided strong evidence of the presence of $\sim 0.2\%$ of a parasitic phase $BaCu_3O_4$,[27] which is able to explain the x-ray-diffraction pattern observed for $x\sim 3/8$, ascribed previously to O ordering.[28] This pattern is also fully compatible with the superstructure of minimum Coulomb repulsion between equally charged O atoms, among all those with unit cell $2\sqrt{2}\times 2\sqrt{2}$ (Ref. 28) (see Fig. 1). On the other hand, neutron-scattering experiments for $x\sim 3/8$,[29] which are more suitable to study O ordering due to the comparatively larger O cross section,[30] are so far only explained in terms of an O-ordered superstructure of unit cell $2\sqrt{2}\times 4\sqrt{2}$.[30,31] On the theoretical side, there is no general physical argument from which one can discard or confirm HS's,[1,30,32,33] except under too restrictive hypothesis,[33] as we will show in Sec. III. The model which obtained these superstructures[11,34] is based on Coulomb repulsions between any two O ions, with metallic and dielectric screening and a parameter ΔE, which favors CS's, to take into account the relation between charge transfer and Cu coordination mentioned above.[1,32] ΔE has been calculated using an extended Hubbard model, but the result is too sensitive to the parameters of this model, not known with enough precision. For large but reasonable ΔE, the ground state of the structural model is a CS for any O content x.[1,32]

Because of the very low or vanishing density of carriers, the Madelung energy is a fundamental ingredient in the physics of $YBa_2Cu_3O_{6+x}$ (Refs. 35–38) and other[38] high-T_c systems. In $YBa_2Cu_3O_{6+x}$, O-O repulsions at distances of at least 8 Å are necessary to explain observed split diffuse diffraction peaks,[39] and O-O repulsions at distances ~ 27 Å are required to stabilize several of the observed CS's.[32] Also, the model of Ref. 11, based on Coulomb repulsions, seems to be able to explain qualitatively the experimental data gathered on $YBa_2Cu_3O_{6+x}$,[1] including the structure transformation kinetics if supplemented by long-range elastic energies.[40] Here we generalize previous works considering the Madelung energy, allowing for the possibility of charge transfer and finding the optimum distribution of charges by minimization of the total energy. Effects of covalency are also included. Neglecting the latter, our approach is equivalent to the exact solution, in the limit of zero hopping and infinite on-site Coulomb repulsions, of the appropriate model of the Hubbard type for the system. The effect of correlations, essential for Cu-O charge transfer,[14] is adequately retained. The main shortcomings of the approach are the neglect of core-core repulsive energy (which amounts to 10% of the Madelung energy and stabilizes the lattice) and screening effects.

The theoretical treatment is presented in Sec. II. Section III contains the results and Sec. IV is a discussion.

II. MODEL

The ground-state energy of the system per Y atom is described as

$$E=E_{\mathrm{Mad}}+E_{\Delta}+2E_{\mathrm{pl}}+E_{\mathrm{ch}}. \tag{1}$$

E_{Mad} is the Madelung energy as a function of Cu and O charges. E_{Δ} is the energy required by the charge-transfer process $Cu^{+}+O^{-}\rightarrow Cu^{2+}+O^{2-}$ in the absence of interatomic repulsions. E_{pl} describes the kinetic and magnetic energy gain due to covalency in the superconducting CuO_2 planes (assumed equal for both planes of the unit cell), and E_{ch} is the corresponding term for the CuO_{2+x} subsystem containing the basal plane.

The Madelung energy can be written as[41]

$$E_{\mathrm{Mad}}=\frac{e}{2N}\sum_i \beta_i Z_i,\quad \beta_i=e\sum_j \alpha_{ij}Z_j, \tag{2}$$

where e is the elementary charge, N the number of Y atoms in the supercell, Z_i the charge of the ith atom in the supercell, and β_i the electrostatic potential at the position of this atom. Because of charge neutrality $\Sigma_i Z_i=0$, the geometrical coefficients α_{ij} can be shifted by an arbitrary constant. We have chosen it in such a way that $\alpha_{ii}=0$ for all i. Then for $i\neq j$

$$\alpha_{ij}=\frac{1}{r_{j,\mathbf{0}}-r_{i,\mathbf{0}}}+\sum_{\mathbf{T}\neq\mathbf{0}}\left(\frac{1}{r_{j,\mathbf{T}}-r_{i,\mathbf{0}}}-\frac{1}{r_{i,\mathbf{T}}-r_{i,\mathbf{0}}}\right). \tag{3}$$

Here $\mathbf{T}$ labels the translation vectors which map the superlattice onto itself and $r_{k,\mathbf{T}}=\mathbf{T}+r_{k,\mathbf{0}}$ is the position of the kth atom of that supercell obtained from the one lying at the

origin by a translation **T**. The sum over **T** is evaluated by the Ewald's method.[42] For simplicity we have assumed that the lattice parameters $a=b$ (taking the average between them), and we have taken the positions of the atoms from three different O contents: $x=7$,[43] $x=0.45$,[44] and $x=0$.[44] We also assume that all Y ions are Y^{3+}, all Ba ions are Ba^{2+}, all Cu ions of the superconducting planes [Cu(2) in the notation of (Refs. 43 and 44)] have the same charge, and all O atoms of these planes [denoted O(2) and O(3) (Refs. 43 and 44)] related by translations of the primitive 1×1 cell have the same charge. This simplifies considerably the problem, allowing us to express part of the sums in i and j of Eqs. (2) and (3), in terms of the coefficients α_{ij}^{0} of the primitive unit cell, reducing appreciably the number of α's which should be calculated. Neglecting an unimportant constant we can write

$$E_{\Delta}=3\Delta(Z_{\mathrm{Cu}}-2), \tag{4}$$

where Z_{Cu} is the average charge of all Cu atoms. In principle, Δ is the difference between the ionization potential of Cu^{+} and the (negative) electron affinity of O^{-}. However, it should also contain information of steric effects (short-range repulsions), the energy gain of a *local* Zhang-Rice singlet[30] (not included in $E_{\mathrm{pl}}+E_{\mathrm{ch}}$), and the kinetic energy of the Cu hole. We keep Δ as a parameter, assumed independent of x and determined in such a way that the charge distribution in $YBa_2Cu_3O_{6.5}$ agrees with experiment.

The number of added holes in one of the two superconducting planes per unit cell is $h=2+Z_{\mathrm{Cu(2)}}+Z_{\mathrm{O(2)}}+Z_{\mathrm{O(3)}}$, where $Z_{\mathrm{Cu(2)}}$, $Z_{\mathrm{O(2)}}$, and $Z_{\mathrm{O(3)}}$ are the average charges of the Cu(2), O(2), and O(3) atoms of that plane. For the kinetic energy as a function of h, we take the form established from a high-temperature expansion of the t-J model, with $t=0.4$ eV, $J=0.1$ eV,[45] slightly generalized to give the correct magnetic energy for $h=0$:

$$E_{\mathrm{pl}}=-[\epsilon h+(1-h)(h+0.09192)\ \ \mathrm{eV}]. \tag{5}$$

ϵ represents the difference between the energy gain in forming a localized Zhang-Rice singlet in the planes with respect to forming it in perfect CuO_3 linear systems [involving the Cu(1) and O(4) atoms of the basal plane, and two O(1) apical atoms[43,44]]. It can also contain information of different steric effects in chains and planes. We keep ϵ as a parameter determined from the experimental charge distribution for $x=1$. Actually, a realistic one-band model for the cuprates contains also hoppings beyond nearest neighbors and three-site terms which determine the shape of the Fermi surface and are critical for the superconductivity,[46,47] but we expect that these terms do not affect E_{pl} very much.

E_{ch} is obtained by fitting exact results for the one-dimensional t-J model. The values $t=0.85$ eV, $J=0.2$ eV were determined from a low-energy reduction procedure which leads to excellent results for the optical conductivity of the chains.[48] The result is[48,33]

$$E_{\mathrm{ch}}=\{(J-2t)\sin[\pi(1-h_c)] -J(0.69+0.41h_c)(1-H_c)\}y_1-Jy_2, \tag{6}$$

where y_1 is the concentration of O(4) atoms belonging to perfect chains, y_2 is the concentration of isolated $O(4)^{2-}$ ions between two $Cu(1)^{2+}$ ions, and h_c is the number of holes per Cu, added to $(CuO_3)^{4-}$ perfect chains. This expression does not take into account doped, extremely short chains, or the correction corresponding to chains of intermediate length.

TABLE I. Charges (Z_i), potentials (β_i) at the different atomic sites, and different contributions to the total energy of $YBa_2Cu_3O_{6+x}$ for $x=1$, $\epsilon=2$ eV and $\Delta<46.05$ eV.

	Z_i	β_i (V)
Y	3	−29.39
Ba	2	−18.41
Cu(2)	2	−26.22
O(2)	−1.80	20.04
O(3)	−2	21.73
O(2)	−2	21.76
O(3)	−1.80	20.01
Cu(1)	2	−24.35
O(1)	−2	20.11
O(4)	−1.39	15.87
E	−291.32	eV
E_{Mad}	−288.59	eV
E_{Δ}	0	eV
E_{pl}	−1.24	eV
E_{ch}	−1.49	eV

The total energy E is minimized with respect to the charges in the subsystem CuO_{2+x} [containing Cu(1), O(1), and O(4) atoms] and the average Cu(2), O(2), and O(3) charges on both superconducting planes. Cu charges are allowed to vary between 1 and 2, and O charges between −2 and −1. This corresponds to the limit of very large on-site Coulomb repulsions.

III. RESULTS

First, we have applied our approach to stoichiometric $YBa_2Cu_3O_7$, a metallic state with a reasonably well-known, nontrivial charge distribution. This is difficult to obtain from the Madelung energy, because this concept was developed for insulators. In fact, if we neglect E_{pl} and E_{ch}, we obtain that all Cu ions are Cu^{2+}, and all O ions are O^{2-} except the chain O(4) atoms, the oxidation state of which is −1. In other words all holes go to the one-dimensional Cu(1)-O(4) chains which are not expected to conduct (due to defects or Peierls distortions) and the system is insulating. This is not bad as a first approximation. It is the best description of the observed charge distribution in terms of integer charges. Including all terms in the energy, with $\Delta<46$ eV and a reasonable $\epsilon=2$ eV, we obtain that 60% of the holes enter CuO chains and 20% are in each of the superconducting CuO_2 planes, in agreement with optical conductivity measurements[49] and estimations based on bond valence sums and other experiments.[50] The resulting charges, Madelung potentials β_i, and different contributions to the energy are included in Table I.

After checking that in general this gives lower energy, and to simplify the algorithm, we have constrained the minimization procedure distributing the holes on both superconducting planes in equal amounts between the O(2) atoms of

TABLE II. Same as Table I for the CS of $x=1/2$. The subscript of Cu(1) ions refers to its coordination, and that of apical O(1) ions is the coordination of its nearest neighbor Cu(1). Parameters are $\epsilon=2$ eV and $\Delta=31$ eV.

	Z_i	β_i (V)
Cu(2)	2	−26.73
O(2)	−1.91	20.34
O(3)	−2	21.15
O(2)	−2	21.16
O(3)	−1.91	20.32
$Cu_2(1)$	1	−12.23
$Cu_4(1)$	2	−24.94
$O_2(1)$	−2	20.18
$O_4(1)$	−2	20.14
O(4)	−1.37	15.59
E	−293.86	eV
E_{Mad}	−276.93	eV
E_{Δ}	−15.5	eV
E_{pl}	−0.71	eV
E_{ch}	−0.73	eV

one plane and the O(3) of the other, and have kept −2 the charge of the apical O(1) ions. The results depend significantly, but not dramatically, on ϵ: For $\epsilon=0$, the amount of holes in each plane is reduced to 14%. Instead, the positions of the Ba and apical O atoms are crucial. If the atomic positions are taken as those for $x=0$, for which the O(1) atoms are nearer and the Ba atoms more distant from the basal plane, we obtain a hole doping h of only 0.03 in each CuO_2 plane, while for the positions corresponding to $x=0.45$, the resulting doping is 0.14.

To establish bounds on Δ, we have calculated next the energy and charge distribution of both superstructures shown in Fig. 1 for $x=1/2$. The HS is the one which minimizes the Coulomb energy when all atoms related by symmetry operations of the tetragonal primitive unit cell have the same charge.[15,51,34] However, the ground state is the CS, the twofold- (fourfold-) coordinated Cu ions are mainly Cu^+ (Cu^{2+}),[9,12,10,13] and about 0.1 holes per Cu go to the superconducting CuO_2 planes,[8,50] in agreement with theory.[1,22] To satisfy this charge distribution, our model has to satisfy several constraints. One of them is $\Delta>\Delta'_{\min}=e(\beta_{O(p)}-\beta_{Cu(2)})-\partial E_{\mathrm{pl}}/\partial h$, where $\beta_{O(p)}$ is the lowest β_i of the occupied O atoms of the planes, and $\beta_{Cu(2)}$ is the potential at the twofold-coordinated chain Cu(1) atoms. If this constraint is not satisfied, the holes of the planes go to the twofold-coordinated Cu atoms and the system would be insulating. In Table II we give the resulting charges, β_i, and energies of the CS for $\Delta=31$ eV, slightly above $\Delta'_{\min}$. For larger values of Δ (not too large to avoid that fourfold-coordinated Cu^{2+} becomes Cu^+), the only change is that E and E_{Δ} decrease proportionally to $\Delta/2$. The resulting amount of holes in each CuO_2 plane (0.093 per Cu) is in very good agreement with experiment. The β_i at inequivalent O(1) atoms are surprisingly similar and a little bit smaller than the β_i of the O atoms of the CuO_2 planes. Holes prefer the latter because of the positive value of ϵ. However, a more realistic description should allow that a small amount of holes enter apical O(1) atoms, particularly for small ϵ.

TABLE III. Same as Table I for the HS (Ref. 27) for $x=1/2$, and $\Delta<40.29-\epsilon$.

	Z_i	β_i (V)
Cu(2)	2	−28.05
O(2)	−2	19.79
O(3)	−2	19.81
Cu(1)	2	−21.40
O(1)	−2	21.78
O(4)	−2	21.25
E	−294.03	eV
E_{Mad}	−293.93	eV
E_{Δ}	0	eV
E_{pl}	0	eV
E_{ch}	−0.1	eV

The experimental evidence indicates that threefold-coordinated Cu(1) atoms are Cu^{2+}, in particular optical experiments on quenched samples,[9,12] and NQR experiments in which Y is replaced by larger ions.[13] This is also suggested by the theoretical studies[1,22,33] and the argument on the interplay between charge transfer and structure[14] presented in Sec. I. An upper bound on Δ can be obtained requiring that in the HS for $x=1/2$, all Cu ions remain Cu^{2+} and no holes are transferred to the CuO_2 planes, so that the system remains semiconducting. This implies $\Delta<\Delta_{\max}=e(\beta_{O(p)}-\beta_{Cu(1)})-\partial E_{\mathrm{pl}}/\partial h|_{h=0}$. We obtain $\Delta_{\max}=38.29$ eV. It is interesting to note that in order for the present work to be consistent with the estimations of Ohta *et al.* for the charge transfer gap in several high-T_c superconductors[52] one should take $\Delta\sim3.5\times10.9$ eV$=38.15$ eV. The results for any $\Delta<\Delta_{\max}$ are presented in Table III. Comparison with the energy of the CS (Table II) establishes a better lower bound for Δ: In order for the CS to be the ground state, $\Delta>\Delta_{\min}=31.34$ eV.

In the following, we assume that $\epsilon=2$ eV and $\Delta_{\min}<\Delta<\Delta_{\max}$ for all x. Using these criteria we derive conclusions regarding the stability of HS's in comparison with CS's. Let us begin with $x=1/8$, calculated with the atomic positions for $x=0$.[44] For CS's, all fourfold-coordinated Cu(1) ions remain Cu^{2+}, the twofold-coordinated ones are Cu^+, and most of the holes brought by the neutral O atoms entering the $x=0$ structure to form that of $x=1/8$ remain in their neighborhood: One hole is transferred to a nearest neighbor Cu^+ and only 0.09 additional holes per supercell are distributed in the planes. In other words the charge of the chain O(4) atoms is −1.090 and the doping of each superconducting plane is $h=0.0056$. The potential at the fourfold-coordinated Cu(1) atom in the supercell is −24.55 V, while those at twofold-coordinated Cu(1) atoms vary between −13.24 V and −12.36 V, with increasing distance to the Cu(1)-O(4) chain. The difference of more than 11 V is not taken into account in Hubbard-type models which do not include a large nearest-neighbor Cu-O repulsion U_{pd} in an appropriate way.[1,11,33] β_i at the chain O(4) atoms is 13.12 V. The β_i at the CuO_2 planes and apical O atoms have similar values as those reported in Tables I and II.

In the HS for $x=1/8$, all O ions are O^{2-} and all threefold-coordinated Cu(1) ions are Cu^{2+}. β_i at these atoms is −23.82 V, while at the remaining, twofold-coordinated $Cu(1)^+$ ions, it is ~-12 V. At the O(4) ions $\beta_i=-18.30$ V

and other β_i are similar as those in Table III. For $\Delta=\Delta_{\min}=31.34$ eV, the total energy of the CS is -296.33 eV, slightly less than that of the HS (-296.07 eV). Although the Madelung energy of the latter is less (-272.57 eV in comparison with -268.63 eV of the CS), the CS has lower energy because it ionizes half of the $Cu(1)^+$ ions of the $x=0$ structure, and thus pays less Δ. For larger values of Δ, the difference increases linearly with $\Delta/8$. Thus, the CS is the ground state for $x=1/8$.

Under some general conditions, using a multiband Hubbard model including U_{pd}, one of us has shown that HS-type superstructures have less energy in the semiconducting phase if no holes enter apical O(1) atoms.[33] What is the reason for the discrepancy with the present result? On the one hand, the effect of repulsions beyond nearest neighbors is important. For example, in usual Hubbard-type models, the energy necessary to add a hole in a chain O(4) atom with both nearest neighbors being Cu^{2+} is ϵ_p+2U_{pd} independently of the rest of the electronic and atomic structure. However, as explained above, this energy is 13.12 eV for the CS and 5.28 eV larger for the HS. On the other hand, to obtain the present charge distribution of the CS with the model of Ref. 33, $\epsilon_p<\epsilon_d+2U_{pd}$, is required, contrary to what is expected in CuO_2 planes[53,54] and one of the hypothesis of Ref. 33. As stated clearly in Ref. 33, that calculation was aimed to discuss the effects of covalency neglecting repulsions beyond nearest-neighbor Cu-O ones and assuming that these were small. However, we find that longer-range repulsions are essential.

Next, we analyze the superstructures corresponding to $x=3/8$ with atomic positions taken from data for $x=0.45$. The general trends of the charge distribution and potentials are similar to those of $x=1/8$. Twofold-coordinated Cu(1) ions remain Cu^+, while higher-coordinated Cu ions have an oxidation state Cu^{2+}. For CS's, the charge of chain O(4) atoms is -1.37 and the doping per Cu of the superconducting planes is $h=0.07$. The potential at the sites of two O(4) atoms of the unit cell is 15.01 V and 16.12 V at the remaining O(4) sites. The β_i at fourfold-coordinated Cu(1) sites are near -25 eV, and those at twofold-coordinated Cu(1) sites vary between -11.45 V and -13.17 V. For the HS, all O ions are O^{2-}, the β_i at O(1) atoms is near 20.8 V and those at fourfold- (twofold-) coordinated Cu(1) atoms are near -22 V (-10.35 V). We should note that keeping this charge distribution, there are at least two superstructures with less energy,[31] one of them which provides the best fit of the neutron-scattering data.[31,29] The difference between the Madelung energy of the superstructure of Fig. 1 and the lowest lying of the above-mentioned superstructures is 0.17 eV.[31] Including this correction, the energy of the lowest-lying superstructure of unit cell multiple of $2\sqrt{2}\times2\sqrt{2}$ for $\Delta=\Delta_{\min}=31.34$ eV becomes -294.62 eV, only slightly smaller than the energy for the CS (-294.56 eV). Since increasing Δ favors the CS by a term proportional to $3\Delta/8$, there is a crossing already at $\Delta_c=31.50$ eV, and for $\Delta_c<\Delta<\Delta_{\max}=38.29$ eV, the CS has lower energy. If the $x=3/8$ superstructures are analyzed with atomic positions corresponding to $x=0$ instead of $x=0.45$, the same trends are observed. Δ_c increases slightly to 31.85 eV. The doping of the planes for CS's is reduced to $h=0.02$. The energy decreases in ~0.6 eV for both structures. This difference becomes significant when one considers the possibility of phase separation: The structures with $x=3/8$ calculated with the positions for $x=0$ ($x=0.45$) (Ref. 44) are stable (unstable) against phase separation into phases with $x=1/8$ (calculated with the positions for $x=0$) and $x=1/2$ (calculated with the positions for $x=0.45$). Since we do not know exactly all atomic positions at the compositions of interest, we cannot draw definite conclusions regarding phase separation. However, as pointed out earlier,[55] the relaxation of the lattice is very important and favors phase separation.

The last comparison between the two types of superstructures we make is for $x=7/8$. Since we do not include covalent corrections for Cu(1)-O(4) chains of intermediate length present in the HS (see Fig. 1), we drop $E_{\rm pl}+E_{\rm ch}$ in this comparison. According to Table I, the magnitude of the neglected terms is ~3 eV. As in previous cases, only twofold-coordinated Cu ions are 1+ and the rest are Cu^{2+}. As a consequence of the neglect of covalency, all O atoms of CuO_2 planes are O^{2-}, and all chain O(4) atoms are O^-, except one of the four O(4) atoms of the $2\sqrt{2}\times2\sqrt{2}$ unit cell, nearest to the additional O(4) vacancy, which is O^{2-} (we have chosen it inside the short chain). For the CS, β_i at twofold-coordinated $Cu(1)^+$ is -9.14 V and that at fourfold-coordinated $Cu(1)^{2+}$ lies near -19.5 V. The potential at all apical O(1) [chain O(4)] ions lies near 22 V (16.7 V), with little variation with distance to the Cu(1)-O vacancy chains. For HS's, β_i at fourfold-coordinated $Cu(1)^{2+}$ ions is -23.10 V, except at the one nearest neighbor to the $O(4)^{2-}$, which amounts to -27.48 V. At the threefold-coordinated $Cu(1)^{2+}$ ion nearest neighbor to the $O(4)^{2-}$ ion, β_i is also -23.10 V, and at the other threefold-coordinated $Cu(1)^{2+}$ ion of the unit cell, $\beta_i=-18.73$ V. At the $O(4)^{2-}$ ions it is $\beta_i=17.57$ V. The potentials at the other O(4) sites (occupied by O^- ions) vary between 12.42 V and 14.57 V.

The energy of the HS for $x=7/8$ is $E=E_{\rm Mad}=-292.44$ eV. This is less than the energy $E=E_{\rm Mad}+E_\Delta$ for the CS, even at the largest possible $\Delta=\Delta_{\max}=38.29$ eV, for which $E=-291.40$ eV. Including $E_{\rm pl}+E_{\rm ch}$ this energy decreases to -292.92 eV, but in principle one expects a similar decrease for the HS. Also for $\Delta=\Delta_{\min}=31.34$ eV, even including $E_{\rm pl}+E_{\rm ch}$, the energy of the CS is -291.85 eV, larger than that of the HS. We conclude that our model supports the latter as the ground-state superstructure.

IV. DISCUSSION

We have studied the interplay between the electronic and atomic structures of $YBa_2Cu_3O_{6+x}$ by an approach based on the Madelung energy *and* the cost of the charge transfer process $Cu^+ + O^- \rightarrow Cu^{2+} + O^{2-}$. The effect of covalency is included as a correction. This approach is motivated by the fact that while first-principles calculations fail to describe the semiconducting systems, and the correlation energy they neglect is near 0.6 eV and depends on the oxygen ordering,[1] the strong-coupling models used so far[1,22,24–26] neglect long-range repulsions and depend on parameters which are not well known. A particular difficulty of these Hubbard-type models when applied to defects or systems with low symmetry (as the 1×8 or $2\sqrt{2}\times2\sqrt{2}$ unit cells) is that they require a large number of uncertain parameters (on-site energies at sites nonequivalent by symmetry, for example) to

describe the problem accurately enough. It is also difficult to include long-range repulsions in exact Lanczos diagonalizations of Hubbard-like models. This was done by Riera and Dagotto for a generalized three-band Hubbard model in one and two dimensions.[56] However, the two-dimensional results are incorrect due to subtleties in the use of boundary conditions, and in general different cluster sizes and shapes should be used.[57]

We addressed the issue of the stability of CS's of unit cell $1\times n$ (n integer) in comparison with $2\sqrt{2}\times 2\sqrt{2}$ type of superstructures (HS's). As mentioned in Sec. I, for $x<0.4$ and room temperature, the experimental evidence is against CS's. We mention here also photoconductivity experiments:[58–61] Illuminating semiconducting (non-CS) films, the resistivity decreases strongly as a consequence of pumping holes to the superconducting CuO_2 planes, and ordering in (presumably short) chains takes place[60] since these structures are energetically favored under the constraint of a sizable hole occupancy in the planes (this can be inferred from the information on the different potentials given in the previous section or the arguments given in Refs. 1 and 62). When illumination ceases, the resistivity returns to the original high values in times characteristic of oxygen diffusion (see Fig. 2 of Ref. 58), showing that the true equilibrium state is not a CS. Nevertheless, it is still possible that at lower temperatures a phase transition takes place (difficult to detect because of the sluggish oxygen kinetics at low temperatures) and the ground state is a CS. The present results support this statement. It is reasonable to expect that HS's are favored by entropy at moderate temperatures: For CS's, the cost in energy for a displacement of an O atom to their nearest available positions, breaking the chains, is high, while this is not the case for HS's.[31] In fact this entropy term is essential to explain the neutron-diffraction results for $x\sim 3/8$ (Ref. 29) in terms of a $2\sqrt{2}\times 4\sqrt{2}$ superstructure.[31]

The structural model of Aligia, Garcés, and Bonadeo[1,32,51] is based on Coulomb repulsions between any two basal-plane O(4) ions, screened by free carriers and dielectric polarization. Except for the high stabilization energy of the chains ΔE, CS's are unstable within this model for $x\sim 1/8$ because of the large cost in O-O Coulomb energy required to arrange the O(4) atoms in Cu(1)-O(4) chains. The present results show that the neglect of electronic screening in the semiconducting phase is incorrect: For $x=1/8$ and CS's, the resulting O(4) charge (~ -1) is screened by their nearest-neighbor $Cu(1)^{2+}$ ions, and the cost in Coulomb energy to build the CS is not so high. Instead, we obtain that the cost of putting a line of O *vacancies* in the $x=1$ structure is not so efficiently screened and thus, for $x\sim 1$, CS's are not favorable. Other results which should be revised concern the hole count in the planes and the 60-K plateau in the superconducting critical temperature.[1,11,22,24–26] The present results suggest that the role of apical O(1) atoms is not so important as previously assumed,[1,11,24] and that the positions of the atoms and relaxation of the lattice are crucial in the charge balance and also in a possible separation in phases with different oxygen contents.[55]

Dielectric screening and that of free carriers, neglected in the present approach, are likely to play an essential role in the problem. One of the attempts to include Madelung potentials in electronic calculations is that of Ohta, Tohyama, and Maekawa.[52] The authors screened those potentials by the optical dielectric constant (assumed 3.5 for all systems) to obtain different parameters of a multiband Hubbard model for the superconducting Cu-based perovskites. Using these parameters, they have obtained charge-transfer gaps, exchange constants, and other information in good agreement with experiment. One would be tempted to extend trivially this formalism to calculate the total energy of $YBa_2Cu_3O_{6+x}$, dividing all Madelung contributions by 3.5. This is clearly incorrect, since dielectric and metallic screening should *lower* the total energy of the system (increasing its absolute value) with respect to the unscreened case, in spite of the fact that the magnitude of the effective interaction between two defect charges at a distance large in comparison with the interatomic distance is reduced by dielectric or metallic screening.[1,32] A simple electrostatic calculation involving two charges surrounded by a small void sphere (to avoid divergences) in a dielectric medium shows that the interaction of the defect charges with the immediate neighborhood causes the largest reduction of the total energy. Local distortions around added or vacant O(4) atoms in $YBa_2Cu_3O_{6+x}$ were calculated by Baetzold[63] and are significant. In the semiconducting phase, for which the effect of free carriers can be neglected, a formalism which takes into account Madelung energies, atomic potentials, and atomic polarizations exists,[64] and might be applied to $YBa_2Cu_3O_{6+x}$ for $x<0.4$, as an extension and improvement of the present approach.

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