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Oxygen configurations and their effect on charge transfer in off-stoichiometric $YBa_2Cu_3O_z$

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The relationship between oxygen structure, charge transfer (hole count), and oxygen content in the $YBa_2Cu_3O_z$ superconductor is studied by combining Monte Carlo simulation with existing electronic-structure calculations. The present model proposes an expansion of the hole count in terms of oxygen configuration variables for states of an arbitrary degree of order. Configurations are obtained by Monte Carlo simulation on a two-dimensional asymmetric next-nearest-neighbor Ising model. Calculations of hole count as a function of oxygen content suggest that oxygen ordering is, at least in part, responsible for the observed plateau structure of T_c versus the oxygen content z. The fact that, in the present model, the hole count does not exhibit two well-defined plateaus indicates that the value of T_c is not simply related to the amount of charge transfer. Previous models, which claim to predict the 90- and 60-K plateaus on the basis of either electronic-structure or oxygen order considerations, are shown to agree with experimental findings for (partially) fortuitous reasons.

INTRODUCTION

Despite the great effort expended towards an understanding of the mechanisms of high-temperature superconductivity, an all-encompassing theory does not yet exist. The complex behavior of a system like $YBa_2Cu_3O_z$ typifies the issues that theorists must come to terms with, and in that sense, it is an ideal system to study from a theoretical standpoint. Several issues have been clarified with respect to $YBa_2Cu_3O_z$, namely, that T_c is strongly correlated with the carrier concentration and that the superconducting current consists of holes.[1-4] In addition, superconductivity is believed to occur in the CuO_2 sheets, with the rest of the structure acting as a charge reservoir.[5]

One feature of $YBa_2Cu_3O_z$ which is of special interest is the nonlinear variation of T_c as a function of oxygen off-stoichiometry z. Several groups have shown[6-8] that in annealed samples there are two distinct "plateau" regions around O_7 and $O_{6.5}$ at 90 and 60 K, respectively. Numerous investigators[1,2,4,5,9-17] have attempted to correlate the observed plateau behavior with the variation of hole count (number of holes in the CuO_2 plane per unit cell) as a function of oxygen content. This is also the objective of the present investigation; we shall treat the thermodynamics of oxygen ordering using the asymmetric next-nearest-neighbor Ising (ASYNNNI) model, and we shall associate a relative charge transfer to copper atoms surrounded by different oxygen configurations by making use of existing electronic-structure calculations.

Theoretical calculations of the pseudobinary phase diagram of $YBa_2Cu_3O_z$ from $O_{6\rightarrow 7}$,[18] which are supported by a great deal of experimental evidence,[7,19-21] have shown the system to be quite complicated: It not only undergoes a high-temperature orthorhombic-tetragonal ($O \rightarrow T$) phase transition, but also has a series of low-temperature ordered oxygen superstructures which must appear at equilibrium. The primary orthorhombic phases of interest are ortho-I (OI) with stoichiometry O_7 and ortho-II (OII) with stoichiometry $O_{6.5}$, although branching phases which are a combination of these two have also been shown to exist.[6,20-23] The predicted phase diagram, with experimental points superimposed, is shown in Fig. 1 (branching phases are not included).[18,19] Aside from these structural phenomena, the system undergoes electronic changes as oxygen is removed; maintaining charge balance requires the density of holes to decrease.

It is tempting to ask whether there is any correlation between the $O \rightarrow T$ phase transition and the plateau behavior of T_c; quenching experiments show that there is not. Rapidly quenched samples of $YBa_2Cu_3O_z$ have undergone the $T \rightarrow O$ transition, but do not have the distinct plateau structure of annealed (equilibrium) samples;[24-26] they show an almost linear decrease in T_c with concentration of oxygen. However, Veal *et al.*[27] and Claus *et al.*[28] have shown that T_c increases by as much as 30 K during room-temperature aging of these quenched samples. Monte Carlo simulation, performed by the present authors,[29] of these aging experiments has shown that the increase in T_c at constant oxygen content is correlated with the occurrence of time-dependent oxygen ordering. A Monte Carlo study by Poulsen *et al.*[30] presents dynamical scaling arguments which also support the correlation between ordering and the aging experiments. Hence, the formation of ordered superstructures has a definite influence on the superconducting behavior of this system.

It is clear that any model of the superconducting be-

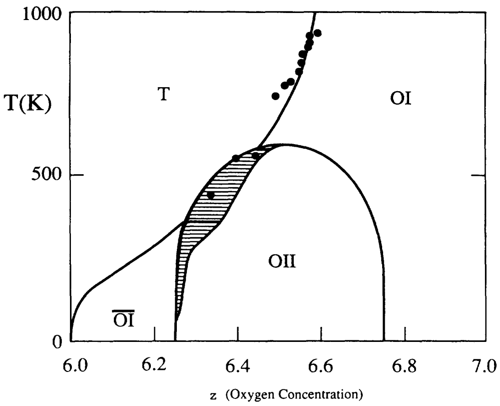


FIG. 1. Pseudobinary phase diagram for $YBa_2Cu_3O_z$ basal plane computed using *ab initio* interactions. Experimental points from Ref. 19 are superimposed.

havior of $YBa_2Cu_3O_z$ must reflect both the structure and the electronic properties of the system. Despite this fact, many theoretical studies seem to make unjustified simplifications in one subject area or the other. Electronic-structure calculations performed by Zaanen *et al.*[15] and Latgé, Anda, and Moran-Lopez[12] make assumptions concerning the oxygen-defect structure of the material that are not wholly consistent with either what has been observed experimentally or predicted theoretically.[23] Phenomenological studies which examine the system more from a structural standpoint, specifically the work of Poulsen *et al.*,[17] also make assumptions that cannot be justified readily. We present a brief overview of these and several other methods in Sec. I, followed by a discussion in Sec. III.

The procedure proposed herein is to expand the hole concentration in the CuO_2 plane as a function of oxygen configuration variables. The values of the oxygen configuration variables are obtained from Monte Carlo simulations on a two-dimensional Ising model that accurately describes equilibrium oxygen ordering in the basal or "chain" plane of $YBa_2Cu_3O_z$.[18,31] Since the state of oxygen order has been shown to affect the electronic properties of the system, a configuration expansion should be valid in the study of hole concentration in $YBa_2Cu_3O_z$. The method is described in detail in Sec. II, followed by a discussion of the results in Sec. III. A brief discussion of the calculation of T_c will also be given in Sec. III.

I. PREVIOUS METHODS OF CALCULATION

Two basic methods of computation will be reviewed briefly in this section: electronic-structure calculations and phenomenological calculations based on simple charge-transfer models. The purpose of this discussion is to examine these methods and to identify the fundamental concepts contained within them.

A. Electronic-structure calculations

The electronic structure of $YBa_2Cu_3O_z$ as a function of oxygen content was calculated by Zaanen *et al.*[15] using a proposed oxygen-defect structure and a tight-binding model based on density-functional calculations. The structural model used involves a $YBa_2Cu_3O_z$ unit cell which is doubled along the *a* direction. In the model, the two chains in this unit cell are inequivalent. For $z > 6.5$, one chain is always filled, and the oxygen vacancies are uniformly dispersed as far apart as possible in the other chain (with a uniform frequency). For $z < 6.5$, the filled chain is replaced by an empty one and the other chain is diluted as in the previous case. At $z = 6.5$, the unit cell has one filled and one empty chain. This statistical model has also been used by other investigators.[12,13] The results of the calculations of Zaanen *et al.*[15] show plateaus in the hole count versus oxygen content that are consistent with the observed 60- and 90-K plateaus in T_c. The basic conclusion of this model was that chain fragments longer than some critical length are responsible for both interlayer charge transfer and the plateaus in T_c. The rather artificial nature of the statistical model adopted will be discussed in more detail in Sec. III.

Latgé, Anda, and Moran-Lopez[12] use the same fragmented-chain model and a Hubbard-type Hamiltonian. Their results show a plateau in the hole count near stoichiometry $O_{6.5}$ (60 K) but *not* at high oxygen content (90 K), in contrast to the work of Zaanen *et al.*[15] Latgé, Anda, and Moran-Lopez[12] also performed calculations using randomly dispersed vacancies which predicted *no* plateaus in the hole count. These authors state that the plateau predicted by their model is produced by the fragmented-chain statistics that have been assumed in the Zaanen model.

Another set of calculations by Lambin[10] confirms the fact that there is a large difference between the electronic structure of ordered and disordered oxygen configurations. The basic prediction of Lambin is that ordered configurations of oxygen will give rise to a higher hole count than will disordered configurations. Other investigators have reported the same basic results.[9,12,13] In addition, Lambin predicts the hole counts for both ordered and disordered configurations to vary roughly linearly with concentration. Lambin uses the three ordered structures found in the theoretical phase diagram computation:[18,23] *O*I, *O*II, and *O*III. For the disordered structures, a simple probability distribution is assumed for the site occupancies. These calculations make no major assumptions (other than those made with respect to the validity of tight binding), but they do not take into account states of partial order.

B. Phenomenological correlations

This section will describe attempts at understanding the behavior of T_c versus z by assuming simple charge-transfer models. The basic idea in these models is that there is some fundamental structural unit which gives rise to charge transfer; this basic unit is regarded as either the oxygen environment of Cu in the "chain" plane, or the "minimal size cluster" (MSC) proposed by Poulsen *et al.*[17]

Cu(1) ions are found to be either two-, three-, or fourfold coordinated by oxygen. If it is assumed, as is generally done,[32–35] that the apical [O(4)] oxygen sites are always occupied, then these three coordinations correspond to V-Cu-V (V=vacancy), V-Cu-O, and O-Cu-O chain segments, respectively. These three configurations give rise to different oxidation states for Cu(1) atoms.

A schematic of the basal plane is shown in Fig. 2: Two types of oxygen sites exist [O(1) and O(5)] along with the Cu(1) atoms. Oxygen ordering in this plane has been studied extensively using an asymmetric next-nearest-neighbor Ising model.[31] The three effective pair interactions that were initially used are indicated as V_1, V_2, and V_3 in Fig. 2. Linear-muffin-tin-orbital (LMTO) calculations in the atomic sphere approximation (ASA) by Sterne and Wille[36] give the values for these interactions as 6.9, -2.4, and 1.1 mRy, respectively, a positive value denoting a repulsive or "ordering" interaction and a negative value denoting an attractive or "clustering" interaction. Formation of O-Cu-O chains is favored due to V_2, and nearest-neighbor oxygen atoms [occupied neighboring O(1) and O(5) sites] are unfavorable due to the highly repulsive nature of V_1. These interactions lead to the well-known O-Cu-O chains that form in the basal plane at low temperatures[6,7,18–23] and to the fact that one sublattice [O(5)] is usually completely empty while the oxygen resides in the other [O(1)]. Smaller (positive) interactions along the direction orthogonal to V_2, i.e., V_3, act as a repulsive force between the chains that are formed and tend to stabilize chain superstructures. Interactions V_1, V_2, and V_3 stabilize the OI and OII phases; the addition of V_4 stabilizes the OIII phase, the superstructure combination of OI and OII, at $z=6.67$.[23] Electron microscopy[21] and diffraction results[6] provide evidence supporting the existence of this phase.

Cluster-variation-method (CVM) calculations[23] have shown that the fraction of fourfold-coordinate Cu(1) sites decreases linearly with decreasing oxygen concentration, with a corresponding increase in the twofold fraction. The threefold fraction goes roughly to zero at the stoichiometry of any ordered phase since the O-Cu-O or V-Cu-V chains, at this point, become essentially infinite in length. Away from the stoichiometry of any ordered phase, chain ends are introduced, thus causing the threefold fraction to increase.

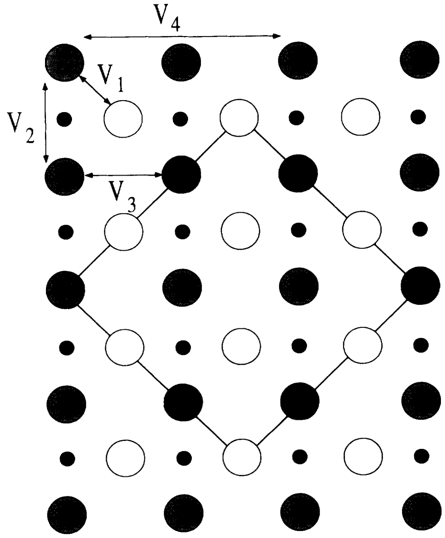


FIG. 2. Basal plane geometry. Shaded circles indicate O(1) sites, while open circles are O(5) sites. Small solid circles indicate Cu(1) atoms. Effective pair interactions are shown. The O-I MSC (see Sec. I B) is indicated by a box.

The purpose of examining the Cu(1) coordinations is that several studies[2,11,12] have shown that threefold and fourfold Cu(1) atoms probably exist as Cu^{2+}, while twofold Cu(1) atoms are Cu^{+}. Using these oxidation states and the fraction of Cu(1) in each of these states, it should be possible to make simple arguments concerning the hole count as a function of oxygen content. The CVM study[23] showed that the fraction of twofold Cu(1) atoms increases roughly as $7-z$ for $6.5<z<7$. If oxygen is present in $YBa_2Cu_3O_z$ as O^{2-}, then the removal of one oxygen atom destroys two holes. Using this simple model, it appears that for $6.5<z<7$, the hole count should decrease approximately linearly with oxygen content as $7-z$. Hence, this model, by itself, would not predict the existence of any plateaus in hole count for $6.5<z<7$.

The model proposed by Poulsen *et al.*,[17] hereafter referred to as the MSC model, has recently received a great deal of attention. In this model, only ordered oxygen domains (either OI or OII) exceeding a certain critical size can contribute to charge transfer. Indeed, Poulsen and co-workers state that examining Cu coordination alone does not produce any plateaus, which is consistent with the results previously described. The minimal size cluster for OI is 4×4 (see Fig. 2) and that for OII is 8×8; one defect is tolerated in each cluster to allow for thermal relaxation. The ASYNNNI model[31] was used by Poulsen *et al.* to perform a Monte Carlo simulation, and the occupation of the MSC's was calculated as a function of concentration. At this point, the ansatz was made that T_c is linearly related to the amount of charge transfer. Poulsen *et al.* assign a T_c of 93 K to OI domains and 58 K to OII domains, and the net T_c is just the weighted average of the T_c for the two types of domains:

$$T_c=93f_{OI}+58f_{OII} . \tag{1}$$

In Eq. (1), f_{OII} and f_{OII} represent the fraction of each type of domain at the given concentration (the "cluster probabilities" for OI and OII MSC's).

The results that Poulsen *et al.* obtain for T_c versus z are in almost exact agreement with the experimental data of Cava *et al.*[37,38] The results of Poulsen *et al.* are insensitive to the temperature at which the simulation is performed and are also robust with respect to the ASYNNNI model interaction parameters chosen. It would seem, then, that this model is indeed the solution to the perplexing question of T_c versus z. Unfortunately, we believe that some unwarranted assumptions were made and that the MSC model is too sensitive to the defect tolerances and cluster sizes.

II. OXYGEN-DEFECT STRUCTURES: STATISTICS AND CHARGE TRANSFER

The concept of examining finite domains (within a structure) with a given configuration is extended to a more general treatment, namely, that of expansion of the hole count in terms of oxygen configuration variables. This method rests on the determination of cluster probabilities: the probability that a given copper atom in the lattice is surrounded by a certain configuration of oxygen atoms and oxygen vacancies. These cluster probabilities are found using Monte Carlo simulation on the ASYNNNI model.

All of the Monte Carlo simulations are performed in the grand canonical ensemble (Glauber dynamics) using a 64×64 lattice (4096 sites) with periodic-boundary conditions. Each simulation was carried out for 1100 Monte Carlo steps (MCS), where one MCS involves attempting a spin flip on every site in the lattice. Examples of several structures are given in Fig. 3; the characteristic O-Cu-O chains are clearly visible, illustrating the asymmetry of the interactions. The results for the cluster probabilities were averaged over the last 100 MCS of the simulation using the results for every tenth step. This procedure reduces the amount of scatter, but does not affect the results significantly. The results were found to be essentially the same when the tests were run for 5000 MCS, with sampling over 1000 MCS. This relative insensitivity to the simulation length reflects the fact that lattices were seeded with concentrations that were known to be near the equilibrium concentration for the chosen chemical potential. Monte Carlo simulations were performed at a temperature of 300 K. At this temperature, all of the ordered phases of interest are stable and hence can be observed in the simulation. At lower temperatures, the degree of order will not increase or decrease, but the Monte Carlo simulation becomes more time consuming due to slow ordering kinetics. If the temperature of the simulations is increased, the cluster probabilities will change as some of the ordered phases become unstable (i.e., *O*II and *O*III).

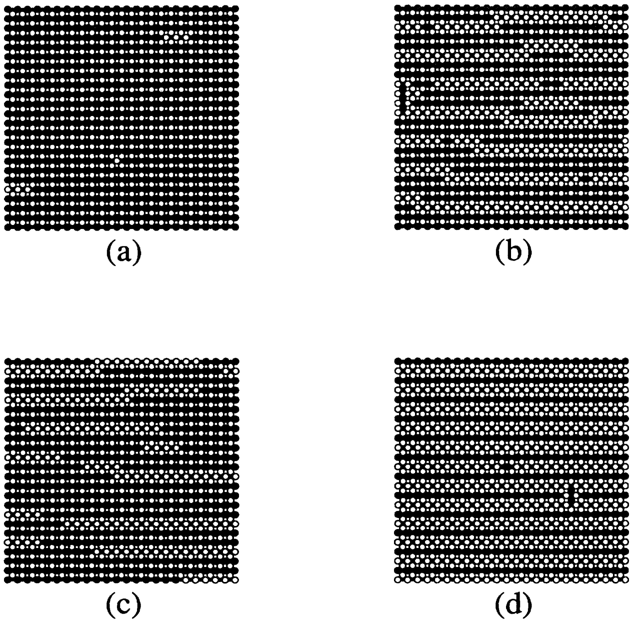

(a) (b) (c) (d)

FIG. 3. Lattices from Monte Carlo simulation at various concentrations (V_4 included). (a) *O*I phase; (b) *O*III phase; (c) Intermediate concentration between *O*I and *O*III; (d) *O*II phase.

Past studies have used the basic idea of cluster expansions to compute properties that are functions of configuration.[39,40] The general method is to expand a given property of configuration in a complete set of basis functions which can describe any configuration of the system. The coefficients in the expansion are then calculated for the chosen basis. This method has been used very successfully in expansions of the free energy[40–42] and has recently been shown to be rigorous when describing properties that are a function of configuration.[41–43] Since charge transfer (hole count) is clearly dependent on the oxygen configurations around copper atoms (Sec. I B), the hole count at oxygen stoichiometry z can thus be written as an expansion using a given set of configurations:

$$h(z)=\sum_{i=1}^{N} h_i f_i(z) \ . \qquad (2)$$

The sum extends over the number of clusters (N) being used in the expansion, f_i represents the fraction of *copper* sites surrounded by the *configuration* i of oxygen atoms and/or oxygen vacancies (hereafter referred to as the cluster probability), and h_i is what we refer to as the "hole coefficient" for that configuration. This study uses a cluster figure which consists of two unit cells in the basal plane and contains eight oxygen and three copper sites. The number of configurations considered on this cluster is 14: 6 ordered and 8 disordered. In the context of this study, "ordered" clusters are considered to be the clusters distinct by symmetry which are composed of only O-Cu-O and V-Cu-V chains; "disordered" clusters are all other configurations on the chosen eight-point cluster figure. This distinction between ordered and disordered clusters is not essential to the method; it is only used for simplicity. The configurations used are shown in Fig. 4 and will be referred to hereafter using the designations given in the third column . Clusters C_1 to C_6 in Fig. 4 are the ordered clusters and D_1 to D_8 are the disordered clusters. The copper atom which is used in the given configuration is the central atom, depicted by a small black circle in Fig. 4 (the first column). It should be noted that the expansion given in Eq. (2) is not an orthogonal expansion, but this is certainly not a requirement for the current calculations.

In order to demonstrate how cluster probabilities are computed for a given structure, a sample *O*II domain is shown in Fig. 5. In order to determine the cluster probabilities for any structure, it is necessary to examine all of the copper atoms and determine to which cluster (given in Fig. 4, first and third columns) these copper atoms correspond. In Fig. 5, the copper atom labeled 1 is in cluster C_2, while the copper atom labeled 2 is in cluster C_4. Examination of this structure shows that all of the copper atoms are in either of these two clusters, and the number of copper atoms of each type is the same. Hence, for the *O*II structure, the only nonzero cluster probabilities are $C_2=C_4=\frac{1}{2}$. Obviously, the procedure of cluster-probability determination becomes much more difficult for structures which possess an arbitrary degree of order.

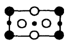
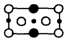
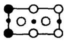
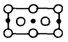
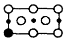
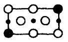
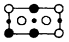
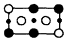
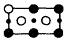
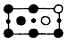
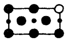
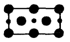
Cluster	Description	Designation	Hole Coefficient
	3 Chains	C_1	0.25
	2 Chains	C_2	0.18
		C_3	0.16
	1 Chain	C_4	0.096
		C_5	-0.010
	0 Chains	C_6	-0.02
	Disord. (1)	D_1	-0.12
	Disord. (2)	D_2	-0.29
	Disord. (3)	D_3	-0.15
	Disord. (4)	D_4	0.094
	Disord. (5)	D_5	0.19
	Disord. (6)	D_6	0.48
	Disord. (7)	D_7	-1.25
	Disord. (8)	D_8	0.046

FIG. 4. Configurations used in cluster expansion. Clusters are shown in the first column, with a brief description given in the second column. Shaded circles indicate oxygen atoms, open circles are vacancies, and small solid circles are Cu(1) atoms. The third column gives the designations used throughout the paper, and the fourth column indicates the hole coefficients.

A. Computation of expansion coefficients

The hole coefficients in Eq. (2) (h_i) are found using electronic-structure parameters calculated by Lambin.[10] The results of Lambin are particularly useful in our study since he calculates hole counts for four ordered superstructures and for several disordered structures. The hole coefficients are then found by solving a system of linear equations where each equation resembles Eq. (2). For example, in the current study, 14 hole coefficients are needed, so we need at least 14 equations like Eq. (2) in order to solve the system by simple matrix inversion. In order to generate these equations, we need to know the cluster probabilities for a set of structures for which the hole count has been computed. This will be done for four perfectly ordered structures and a series of artificially generated structures which possess disorder.

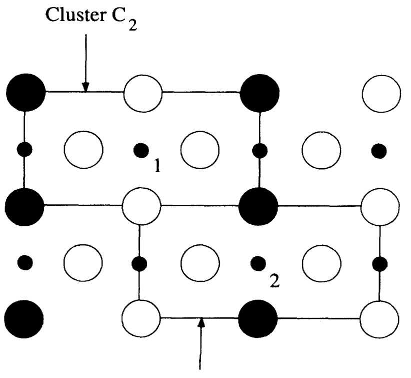


FIG. 5. Example of the determination of cluster probabilities for an *O*II structure. Shaded circles are oxygen atoms, open circles are vacancies, and solid circles are Cu(1) atoms. Cu(1) atom 1 is surrounded by cluster C_2, while Cu(1) atom 2 is in cluster C_4. These are the only two types of Cu(1) atoms in the *O*II structure, and there are equal numbers of them. The only nonzero cluster probabilities for *O*II are $C_2=C_4=\frac{1}{2}$.

Computation of the cluster probabilities (f_i) of the ordered clusters in perfectly ordered structures is relatively straightforward (as described previously) and can be done by inspection for *O*I, *O*II, *O*III, and the empty structure (at $z=6$). The hole counts for the ordered phases [h_{OI}, h_{OII} h_{OIII}, and h_E (h_{empty} at O_6)] are then written according to Eq. (2) as follows:

$$h_{OI}=h_1 \ , \tag{3}$$

$$h_{OII}=\tfrac{1}{2}(h_2+h_4) \ , \tag{4}$$

$$h_{OIII}=\tfrac{1}{3}h_2+\tfrac{2}{3}h_3 \ , \tag{5}$$

$$h_E=h_6 \ . \tag{6}$$

The values for h_{OI}, h_{OII}, h_{OIII}, and h_E are 0.25, 0.14, 0.17, and -0.02 holes per unit cell, respectively.[10] The hole coefficients for clusters C_1 and C_6 can be found by inspection from Eqs. (3) and (6): $h_1=0.25$ and $h_6=-0.02$.

In addition to these chain superstructure phases, Lambin also computed the hole count for a $2\sqrt{2}a\times2\sqrt{2}a\times c$ phase, originally proposed by Alario-Franco.[44] The calculation was performed by Lambin at $\delta=0.125$. The only nonzero cluster probabilities for this structure are for cluster C_1 and for several clusters containing five oxygen atoms on O(1) sites; these are found by examining the structure for $\delta=0.125$ given in Ref. 45. We will make the assumption at this point that the hole coefficients for all *disordered* clusters with the same number of oxygen atoms are the same. Hence, we can group these clusters containing five oxygen atoms together. The expansion for this structure is then written as

$$h_{\text{AF}}=\tfrac{1}{6}h_1+\tfrac{5}{6}h_5^d \ . \tag{7}$$

The hole coefficient h_1 is already known, and Lambin gives h_{AF} a value of 0.20 holes per unit cell. We can then solve for the hole coefficient of disordered cluster D_5; rearranging and solving Eq. (7) yields $h_5^d=0.19$.

At this point, three hole coefficients have been computed; it remains to compute the other eleven. This will be done by generating a system of equations of the form $\underline{A}\mathbf{x}=b$, and then solving for the vector $\mathbf{x}$. We have not used Eqs. (4) and (5) yet, so these are the first part of the matrix $\mathbf{A}$, but since there are 11 unknowns, we need at least nine more equations to solve for all coefficients. These remaining equations are based on the hole counts for the artificially generated structures used by Lambin; cluster probabilities for these structures are found using the same probability distributions as those that were used in Ref. 10.

After the cluster probabilities are computed, it is found that the resulting matrix **A** is singular and hence cannot be solved by matrix inversion. At this point, we elect to solve the associated least-squares problem: Find a vector **x** that minimizes the Euclidean length of the residual vector $\mathbf{r}=\underline{A}\mathbf{x}-\mathbf{b}$. Values of the vector **x** can be computed using the singular value decomposition (SVD) of the matrix $\underline{A}$.[46] The least-squares solution of the problem yields the hole coefficients given in the fourth column of Fig. 4. The SVD yielded a matrix of the fifth row, and the solution had a standard error of 1.95×10^{-2}.

The details of the computations performed are rather extensive and complicated. The interested reader is referred to the Appendix, where we present the specifics associated with all aspects of our computational method: disordered cluster-probability computation and the solution of the problem using the SVD of matrix $\underline{A}$.

B. Computation of cluster probabilities

The expansion coefficients (h_i) to be used in Eq. (2) have now been determined. All that remains is to determine the cluster probabilities (f_i) as a function of concentration. In the previous section on hole coefficient computation (Sec. II A), the cluster probabilities that were discussed were for either idealized or artificial structures; those are not to be used in the computation of the actual hole count. In order to find the hole count for a more physically realistic system, we generate cluster probabilities using Monte Carlo simulation on the ASYNNNI model, which allows the description of states which possess an *arbitrary* degree of order.

The Monte Carlo simulation is performed as described at the beginning of Sec. II. At each concentration, the fraction of copper sites which exist in the configurations given in Fig. 4 are found. A check was performed to ensure that these cluster probabilities summed to 1 (correct normalization), and this was found to be the case for all concentrations.

The ordered cluster probabilities shown in Figs. 6(a)–6(c) are given in symmetric pairs: Each cluster is paired with its O(1) sublattice "oxygen complement" [O(5) sites vacant]. The reason for this choice is to illustrate the fact that complementary cluster probabilities are mirror images of each other as a function of concentration. The trends illustrate exactly what one would expect: At the stoichiometry of any ordered phase (*O*I, *O*II, *O*III, and the empty structure at O_6) the dominant nonzero cluster probabilities are for those clusters which are used to construct the given phase; these probabilities sum to 1. Clusters C_1 and C_6 are shown in Fig. 6(a), with each having a probability of 1 at O_7 and O_6, respectively [Eqs. (3) and (6)]. Clusters C_2 and C_4 are given in Fig. 6(b) (right and left, respectively), with each having a probability of $\frac{1}{2}$ at *OII* stoichiometry [Eq. (4)]. At *O*III stoichiometry, Eq. (5) predicts that the probability for C_2 is $\frac{1}{3}$ and that for C_3 is $\frac{2}{3}$. Examination of Figs. 6(b) and 6(c) shows this to be the case.

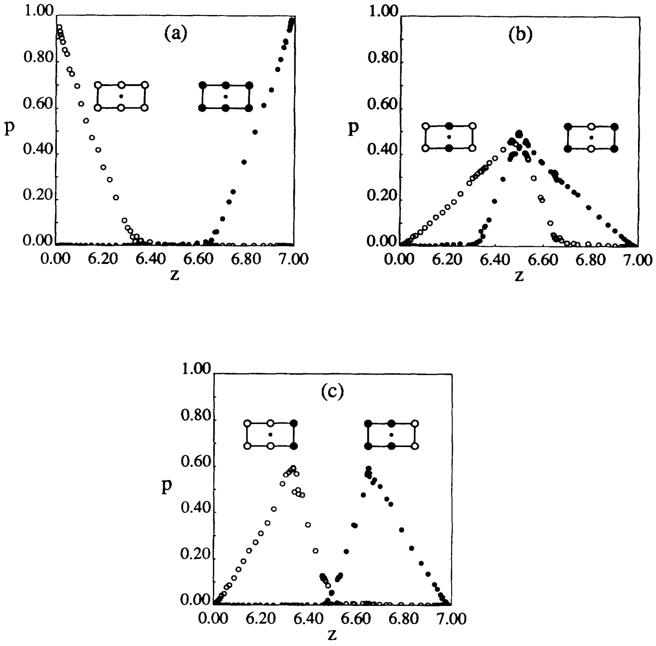


FIG. 6. (a)–(c) Cluster probabilities (p) vs concentration for ordered configurations. Solid circles correspond to the cluster on the right, while open circles correspond to that on the left.

Disordered cluster probabilities are given in Figs. 7(a) and 7(b). Complementary clusters D_1 and D_5 are given in Fig. 7(a), while cluster D_3 is shown in Fig. 7(b). Each of these clusters has its maximum probability when the stoichiometry is between any two of the ordered phases. All other disordered cluster probabilities (D_2, D_4, D_6 D_7, D_8) are zero across the concentration range. The fact that D_2 and D_4 vanish emphasizes the point that, at the

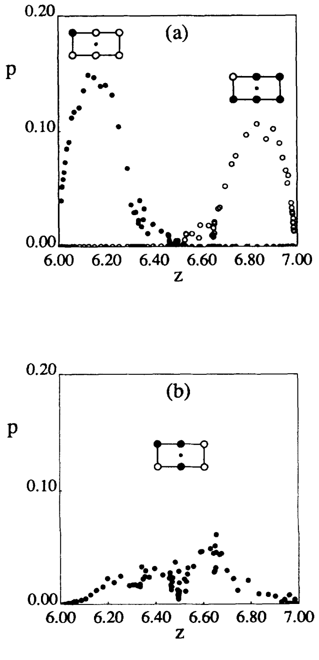


FIG. 7. (a)–(b) Disordered cluster probabilities (p) vs concentration for the clusters indicated.

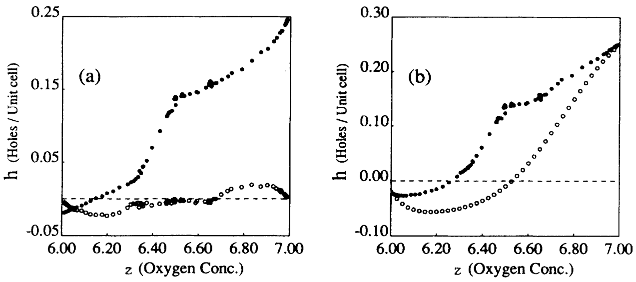


FIG. 8. (a) Relative contributions to the total hole count from ordered configurations (solid circles) and disordered configurations (open circles). (b) Total hole count (solid circles) found using cluster probabilities given in Figs. 7 and 8. Open circles show the total hole count for structures which are disordered on the O(1) sublattice.

temperatures of interest, the system prefers to form long O-Cu-O or V-Cu-V (V=vacancy) chains, with a minimum number of chain ends. Clusters D_6-D_8 have zero probability due to the highly repulsive nearest-neighbor oxygen interaction.

C. Computation of hole count as a function of concentration

The hole count as a function of concentration can now be computed from Eq. (2), using the cluster probabilities given by Figs. 6 and 7 and using the hole coefficients from Fig. 4. The relative contribution from the ordered and disordered configurations is shown in Fig. 8(a), where solid circles are the contribution from clusters C_1-C_6, and open circles are the contribution from clusters D_1-D_8.

The total hole count, which is the sum of the two curves in Fig. 8(a), is given in Fig. 8(b) (solid circles). At high oxygen content, no plateau in the hole count is predicted. Rather, the hole count initially decreases almost linearly with concentration. The initial decrease is followed by a region ($6.5<z<6.75$) where the decrease is much slower, which indicates that the 60-K plateau in T_c is probably due to a relatively constant hole count. For oxygen content less than $z=6.5$, the hole count decreases rapidly again, and goes to zero near $z=6.3$. The negative final value of the hole count reflects the fact that Lambin[10] obtains a negative value for $z=6$.

The open circles in Fig. 8(b) show the hole count for structures which are completely disordered on the O(1) sublattice. The cluster probabilities in this case are found as products of point probabilities (see Sec. II A), since all of the pair and multisite oxygen correlations vanish in the disordered phase. As has been observed in other theoretical investigations,[9,10,12] the hole count for the disordered structure is lower at all concentrations than the hole count for the ordered chain structures.

III. DISCUSSION

The fragmented-chain model of Zaanen *et al.*,[15] the MSC model of Poulsen *et al.*,[17] and the configuration expansion of the present model will now be discussed in turn.

A. Fragmented-chain model

The basic conclusion of Zaanen *et al.*[15] was that oxygen chains longer than some critical length are responsible for both interlayer charge transfer and the experimentally observed plateaus in T_c. This statement correctly asserts the importance of the oxygen chain statistics in the system, i.e., the number of chains longer than some critical length. In addition, the idea of a critical chain length recognizes the fact that shorter chains increase the fraction of threefold-coordinate copper atoms (chain ends), which in turn should reduce the amount of charge transfer. These ideas, put forth in the Zaanen fragmented-chain model, illustrate some important physics in the system, yet despite this fact, the plateaus they obtain in the hole count are somewhat fortuitous.

The oxygen-defect model of Zaanen *et al.* agrees at three points with *ab initio* phase diagram calculations performed by two of the authors:[18] the *O*I structure at $z=7$, the *O*II structure at $z=6.5$, and the empty structure at $z=6$. Away from the stoichiometry of these ordered phases, the two pictures diverge, and we believe that the fragmented-chain model of Zaanen and coworkers becomes unphysical. It is generally accepted that off-stoichiometry is accommodated in the chain plane, but there is no justification for assuming that within the chain plane vacancies only occupy half of the chains. Theoretical work[18] has pointed out that vacancies will form chains at low temperature; this is in stark contrast to the fragmented-chain model, which assumes a uniform dispersal of vacancies within a chain. In addition, recent work by two of the present authors[23] has shown that the fragmented-chain model artificially creates a plateau in the fraction of fourfold-coordinate copper atoms for $6.5<z<6.75$; more accurate CVM calculations do not predict this plateau in the copper coordination. In essence, then, the 60-K plateau calculated using the fragmented-chain model is an artifact created by this plateau in the fraction of fourfold-coordinate copper atoms; it is independent of the electronic-structure calculations.

The appearance of the limited 90-K plateau in the results of Zaanen *et al.* cannot be explained in a similar fashion. Examination of Zaanen *et al.*'s hole count for high oxygen content shows that this plateau is not nearly as well defined as the plateau centered at $z=6.5$ (60-K regime); a minor alteration in the fit curve could make this plateau disappear entirely. Additionally, Latgé, Anda, and Moran-Lopez[12] using a Hubbard-type Hamiltonian and the fragmented-chain model, predict *no* high oxygen content plateau in the hole count. This inconsistency shows that the fragmented-chain model does not necessarily explain the 90-K plateau.

One basic conclusion that can be drawn from the studies of several investigators[9,10,12,13] is that there is a large difference between assuming ordered and random distributions of vacancies and that the choice of the ordered arrangement is crucial. This is the source of our objections to the fragmented-chain model. The (thermodynamically favorable) arrangement of oxygen into long O-Cu-O and V-Cu-V chains should produce the greatest amount of charge transfer, and hence a higher hole count. This is consistent with both the experimental work of Veal *et al.*[27] and Claus *et al.*[28] and with the theoretical studies by the present authors.[29]

B. MSC model

The main point that should be realized about the MSC model of Poulsen *et al.* is that it contains four explicit and an undetermined number of implicit fitting parameters which can be manipulated to describe the T_c versus z behavior. The implicit fitting parameters are the locations of the plateaus, which are given by the stoichiometry of the ordered clusters (OI) and OII, in the case of Poulsen *et al.*). The explicit parameters are the two coefficients in Eq. (1), which fix the plateau heights, and the defect tolerances for the OI and OII MSC's, which fix the width of each plateau. These parameters allow for a great flexibility, i.e., virtually any T_c curve could be fitted just by altering the plateau heights, widths, and locations.

Calculations performed by one of the authors[47] using codes provided by Poulsen has shown that the current MSC model fails when the OIII phase is included (i.e., it predicts a T_c near 0 K). This shows that the MSC model, as it stands, is truly a *minimal* model; charge transfer from other domains aside from those used in the MSC model is clearly important. The model could easily be corrected to account for this deficiency by simply adding another term for OIII in Eq. (1), although then one would need to add *two more* fitting parameters (a defect tolerance and a weighting factor for the OIII MSC).

The questions of MSC size and defect tolerance were not adequately addressed by Poulsen *et al.*, and another set of calculations was performed to assess the sensitivity of their model to these parameters.[47] As the MSC size is increased, the cluster-probability overlap (i.e., the concentration interval over which both OI and OII have nonzero probability) between the OI and OII MSC's decreases if the defect tolerance is kept fixed. This causes local maxima to develop in the behavior of T_c versus z. Hence, the tolerances must be increased to keep the amount of overlap constant. In addition, cluster overlap obviously decreases if no defects are allowed in the OI and OII domains. All of this essentially means that, in order to obtain plateaus using the MSC model, a finite set of configurations *must* be considered as having equivalent charge-transfer characteristics, and this finite set increases with the MSC size.

C. Configuration expansion

It has already been stated that the configuration dependence of charge transfer in this system allows us to use an expansion in oxygen configuration variables. For simplicity, our study uses a cluster figure which consists of two adjacent unit cells in the basal plane. This choice could be altered to allow for larger clusters, as long as the choice can be made consistent with the electronic-structure calculations. The only problem with expanding the size of the cluster figure is that the number of different possible configurations on this cluster rises exponentially with its size.

In a sense, Poulsen *et al.* performed a cluster expansion of their own, but with only two large clusters, OI and OII. Defect tolerance effectively expands this basis, collapsing all OI and OII clusters with either zero or one defect (17 and 65, respectively) into single OI and OII clusters. This "collapse" tends to lose information about the structure. The proposed method of cluster expansion uses a complete set of 14 basis clusters. The assumption that each disordered cluster with the same number of filled and empty sites has the same coefficient is a similar approximation, although it could be removed. Then, there would be no degeneracy for the disordered clusters, and the inversion problem would become more complicated due to the large number of variables. Treating each disordered configuration individually would especially be a problem if the cluster size were increased, in which case the degeneracies rise markedly. In the present model, it is unclear what effect this assumption concerning degeneracy has on the results, but in the model of Poulsen *et al.*, the effect is quite clear: The width of the plateaus in T_c versus z can be altered at will by changing the number of defects allowed in a given cluster.

The method of cluster expansion is exact up to the point where the expansion coefficients are determined. In order to find these coefficients, two things are required: determination of the disordered state cluster probabilities and the actual solution of the system of equations. Disordered cluster probabilities are found using the same distribution that Lambin used for the computation of hole counts of disordered structures. Whether or not this is a completely accurate description of the disordered state, it is consistent to use the same distribution for the cluster probabilities.

The solution to the system of equations is accomplished by solving a minimal least-squares problem with the SVD of the cluster-probability matrix. This method of solution is preferred when solving a linear system which involves a rank-deficient matrix, and it provides a minimal length solution vector which is unique. The hole coefficients determined by the least-squares method are merely the expansion coefficients which best represent the electronic-structure data using the chosen configurational basis. If the basis were expanded to treat more configurations as being distinct or contracted to treat more as equivalent, then the numerical values of the coefficients would change to reflect these basis function modifications.

An assumption in the determination of hole coefficients is that the *ab initio* hole counts, found by tight binding (TB), are an accurate representation for the system. The results found by the present model will only be as good as the electronic-structure parameters used to find the expansion coefficients. The question then becomes, how good is the tight-binding approach of Lambin[10] at describing $YBa_2Cu_3O_z$? This author readily acknowledges several shortcomings in the reproduction of the band structure, but claims that the essential details are present. Calculations by other authors[9,12] yield hole counts which are consistent with those of Ref. 10. The assumptions made in the cluster expansion model are consistent with those made by Lambin; hence one can conclude that the cluster expansion model should at least predict the correct trend in $h(z)$.

The central result of this paper is the hole count as a function of oxygen content. The solid circles in Fig. 8(b) predict the qualitative behavior of hole count correctly: The number of holes decreases with decreasing oxygen content. Unfortunately, no plateau at 90 K is predicted, contrary to the predictions of both the fragmented-chain and MSC models. The initial rapid decrease in hole count can be explained by the increase in the number of chain ends [threefold Cu(1) atoms]; this is reflected in the cluster probability for cluster D_5 [open circles, Fig. 7(a)]. As the oxygen content is further decreased, *O*III followed by *O*II ordering stabilizes the hole count by decreasing the number of chain ends. Hence, the curvature in the hole count decreases in the region $6.5 < z < 6.75$, creating a weak plateau. The rapid decrease in hole count past *O*II stoichiometry is again due to the rapid increase in the number of chains ends, which is reflected in cluster probability D_1 [solid circles, Fig. 7(a)]. The hole count for completely disordered structures [Fig. 8(b), open circles] clearly illustrates that disordered configurations yield a much lower hole count than do ordered configurations. No "plateau" in the hole count for $6.5 < z < 6.75$ is observed for the disordered structures because the stabilizing influence of the ordered structures (*O*II and *O*III) is not present. The lower hole count for completely disordered structures is consistent both with previous theoretical calculations[9,10,12,29] and with experimentally observed time-dependent ordering in quenched samples.

The present method describes a procedure for computing the hole count as a function of oxygen content. The information needed to convert Fig. 8(b) to $T_c(z)$ is the functional form of T_c as a function of hole count, $T_c(h)$. A great deal of work has been done in this area.[1,3,4,16,48] Two basic conclusions can be reached from past work: (1) A lower critical hole count exists for superconductivity and (2) a saturation regime exists beyond which T_c decreases with increasing hole count. The behavior of $T_c(h)$ is decidedly nonlinear, which makes the task of prediction much more difficult. Herein lies the essential problem in attempting to predict $T_c(h)$ from the results in Fig. 8(b). Small changes in the functional form of $T_c(h)$ have pronounced effects on $T_c(z)$. Reproduction of the experimental results thus becomes a fitting procedure of questionable merit. One very important piece of information can be derived from attempts to do exactly this, namely, that the saturation regime for $h > 0.22$ appears to allow for a plateau at 90 K, even though there is no plateau in the hole count. This implies that it is possible for a theory to predict no high oxygen content plateau in the hole count and yet still be consistent with the 90-K plateau observed in experiments.

CONCLUSION

The problems surrounding the understanding of the superconducting behavior of $YBa_2Cu_3O_z$ as a function of its oxygen stoichiometry are numerous, and many have attempted to come up with plausible models which correctly predict this behavior. It became clear after some work was done that oxygen ordering in this system was quite seminal. With this fact in mind, several groups were able to reproduce the famous plateau behavior of T_c as a function of oxygen content.

The fragmented-chain model of Zaanen *et al.*[15] recognized the importance of oxygen ordering, and the fact that a large number of chain ends (short, fragmented chains) reduced the amount of charge transfer in the $YBa_2Cu_3O_z$ system. Unfortunately, the plateau centered at $z = 6.5$ (60 K) that Zaanen *et al.* computed appears to be an artifact of the rather artificial oxygen-defect statistics that were assumed. Several other investigators[12,13] used the same fragmented-chain model; results were similar in all studies, except for the conspicuous absence of the 90-K plateau in the study of Latgé, Anda, and Moran-Lopez.[12] The MSC model of Poulsen *et al.*[17] also recognized the importance of oxygen ordering, specifically the existence of the two ordered oxygen structures, *O*I and *O*II. Despite its agreement with experiment, the MSC model is not as meaningful as it appears to be: The model succeeds due to a large number of adjustable parameters.

The current method of cluster expansion produces some interesting results, but it does not yield the plateau structure in the hole count that had been anticipated. We do not believe that this is a failure of the present model. The cluster-expansion method provides evidence to support two important conclusions: (1) the 90-K plateau is *not* due to a constant amount of charge transfer (plateau in the hole count) and (2) the 60-K plateau is a direct consequence of the formation of ordered oxygen structures (*O*II, *O*III, etc.).

Based on the above conclusions, it is clear that any correct prediction of hole count as a function of oxygen content will probably not give the predicted plateaus in T_c. In order to explain the plateau behavior of T_c, new attempts must be made to develop a theory which correlates charge transfer (hole count) with T_c. In general, it appears that such a theory must predict a nonlinear relationship between T_c and the amount of charge transfer, which experiments have already indicated to be the case.[3,4,16,48] In any case, the question of the relationship between oxygen structure, charge transfer (hole count), and T_c requires more concerted theoretical effort in the future.

ACKNOWLEDGMENTS

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APPENDIX: COMPUTATIONAL INFORMATION

1. Cluster-probability computation for artificial structures

Computation of the cluster probabilities for the artificially generated structures is accomplished by using the simple probability distribution given by Lambin for the O(1) and O(5) site occupancies. The probabilities that the O(1) and O(5) sites are filled with an oxygen atom are given by the following equations (for $6.5 < z < 7$):

$$x(\mathrm{O}(5)) = \frac{1-\sqrt{1-(2\delta)^2}}{4} \tag{A1}$$

$$x(\mathrm{O}(1)) = 1-\delta-x(\mathrm{O}(5)) , \tag{A2}$$

where $\delta = 7-z$. For this study, we would like these probabilities to fall between zero and 1, so we normalize to obtain true point probabilities:

$$\begin{aligned} P(\mathrm{O}(1)) &= \frac{x(\mathrm{O}(1))}{x(\mathrm{O}(1))+x(\mathrm{O}(5))} , \\ P(\mathrm{O}(5)) &= \frac{x(\mathrm{O}(5))}{x(\mathrm{O}(1))+x(\mathrm{O}(5))} . \end{aligned} \tag{A3}$$

The cluster probability for a given oxygen-vacancy configuration on the eight-point cluster figure is then found as a product of the point probabilities given in Eq. (A3). For example, in the point approximation, the probability of finding a copper atom surrounded by cluster C_1 is given by

$$P(C_1) = [P(\mathrm{O}(1))]^6[1-P(\mathrm{O}(5))]^2 , \tag{A4}$$

since the probability that an O(5) site is empty is given as $1-P(\mathrm{O}(5))$.

At this point, the situation becomes slightly complicated, since we want to make sure we treat the ordered clusters with a given number of filled sites as being distinct from the disordered clusters with the same number of filled sites. We can write an explicit form for a "disordered" hole count based on Eq. (2), differentiating between ordered and disordered clusters:

$$h^d(z) = \sum_{j=1}^{6} n_j^o f_j^o h_j + \sum_{k=1}^{8} P_k^d h_k^d , \tag{A5}$$

$$P_k^d = \sum_{i=\max(0,k-2)}^{k} (m_k - m_k^o \delta_{ki}) f_k^d . \tag{A5a}$$

In Eq. (A5), the summation over j corresponds to ordered clusters C_1-C_6 (denoted by a superscript o); n_j^o is the multiplicity of cluster C_j ($n_j^o=2$ for $j=3,5$ and 1 otherwise). The second summation in Eq. (A5) corresponds to the eight disordered clusters, D_1-D_8, with k indicating the number of oxygen atoms on the eight-point clusters figure (D_k). The summation over i in Eq. (A5a) indicates the number of O(1) sites that are filled. Hence, if the total number of filled sites is k, and the number of O(1) sites filled is i, then the number of O(5) sites filled is $k-i$. The multiplicity m_k of a given configuration is given by the product of two binomial coefficients, one for the six O(1) sites and one for the two O(5) sites:

$$m_k = \left[\begin{matrix}6\\ i\end{matrix}\right]\left[\begin{matrix}2\\ k-i\end{matrix}\right] = \frac{6!}{(6-i)!\,i!}\,\frac{2!}{[2-(k-i)]!\,(k-i)!} . \tag{A6}$$

The cluster probabilities for clusters C_1-C_6 in Eq. (A5) are given by equations analogous to Eq. (A4), where probabilities are computed for all O(5) sites being empty. Similarly, the cluster probabilities in Eq. (A5a) for the disordered hole coefficients (h_k^d) are given by

$$\begin{aligned} f_k^d = {} & [P(\mathrm{O}(1))]^i [P(\mathrm{O}(5))]^{k-i} [1-P(\mathrm{O}(1))]^{6-i} \\ & \times [1-P(\mathrm{O}(5))]^{2-(k-i)} . \end{aligned} \tag{A7}$$

In order to achieve a separation between the ordered and disordered clusters, it is necessary to subtract out the probabilities for the ordered clusters with k filled sites. In Eq. (A5a), this is accomplished by the correction term $m_k^o \delta_{ki}$, where δ_{ki} is the Krönecker delta and m_k^o is the number of ordered configurations with k filled sites. The Krönecker delta is used, since ordered configurations will exist only when the O(5) sites are empty, i.e., when $k=i$. The multiplicities m_k^o can be found using Fig. 4, including the factors n_j^o for each cluster: $m_k^o = 1,3$, and 3 for $k=6,4$, and 2, respectively. This process of separation is important because the whole purpose of the cluster expansion is to distinguish different configurations.

The procedure outlined above accomplishes the desired separation between ordered and disordered clusters when computing the hole count for the structures generated with a simple probability distribution. A careful analysis of all of the above manipulations shows that, indeed, the cluster probabilities in this "disordered" expansion [Eq. (A5)] sum to 1, as they should. Now that all of the disordered cluster probabilities can be computed (with correct normalization), we can compute the remaining 11 expansion coefficients.

2. Coefficient determination

The values of the coefficients for clusters C_1, C_6, and D_5 are known from Eqs. (3), (6), and (7). This leaves 11 unknowns, and hence we need at least 11 equations to solve for the remaining coefficients. The two ordered structures provided two of these [Eqs. (4) and (5)], and the remaining equations are found using Eq. (A5) for nine (or more) values of z between 6.5 and 7. The calculations made by Lambin for the disordered structures show that the hole count for these structures essentially falls on a line of the form

$$h^d(z) = -0.38(7-z)+0.25 . \tag{A8}$$

Now we have a basic problem of the form $\underline{A}\mathbf{x}=\mathbf{b}$, where $\underline{A}$ contains cluster probabilities, $\mathbf{x}$ represents the desired hole coefficients, and $\mathbf{b}$ contains the hole counts for the structures represented by the cluster probabilities in the columns of $\underline{A}$. For the current problem, the first two rows of $\mathbf{b}$ are given by the hole counts for OII and OIII (0.14 and 0.17), and the remaining rows (hole counts) are found using Eq. (A8) for evenly spaced values of z between 6.5 and 7. In this situation, the matrix $\underline{A}$ is found using Eqs. (4) and (5) for the first two rows, followed by Eq. (A5) for the remaining rows.

The problem at this point is to account for the fact that we already know the values of the coefficients for C_1, C_6, and D_5. This is accomplished by correcting the vector b using the values of the hole coefficients which have already been determined along with the corresponding cluster probabilities:

$$h_{\text{corr}} = h - 0.25 f_1^0 - 0.19 P_5^d + 0.02 f_6^0 \tag{A9}$$

This final correction allows us to solve for the 11 unknowns. Unfortunately, if we use the matrix $\underline{A}$ we have just constructed, it is found that it is singular (i.e., not invertible).

We can, however, solve the least-squares problem: Find a vector $\mathbf{x}$ such that the Euclidean length of the residual vector $\mathbf{r} = \underline{A}\mathbf{x} - \mathbf{b}$ is a minimum. Values of the vector $\mathbf{x}$ are computed using the singular value decomposition of the matrix $\underline{A}$ (see, for example, Ref. 46). The resulting coefficients are given in Fig. 4, fourth column. The matrix $\underline{A}$ was found to have a rank of 5 using the above tolerance. The standard error in the solution is defined as

$$\sigma = \left[\frac{\mathbf{r}^T \mathbf{r}}{\mathbf{d}} \right]^{1/2} , \tag{A10}$$

where $\mathbf{r}$ is the residual vector and d is the rank deficiency (full column rank minus actual rank $= 11 - 5 = 6$). The least-squares solution found a standard error of $\sigma = 1.95 \times 10^{-2}$.

In any problem in which the SVD is used, it is necessary to determine what singular values may be neglected (i.e., those which are effectively zero for the problem under consideration). In the current problem, we neglect singular values which are smaller than the largest singular value multiplied by the numerical tolerance in the vector $\mathbf{b}$ (which we assume to be 0.01 holes per unit cell). The SVD with a minimal least-squares approach produces a minimum length solution vector which *is* unique, despite the rank deficiency of the system.[46] Ideally, we would have liked a system with full column rank, but the electronic-structure calculations of Lambin were not performed for enough ordered structures to allow this.

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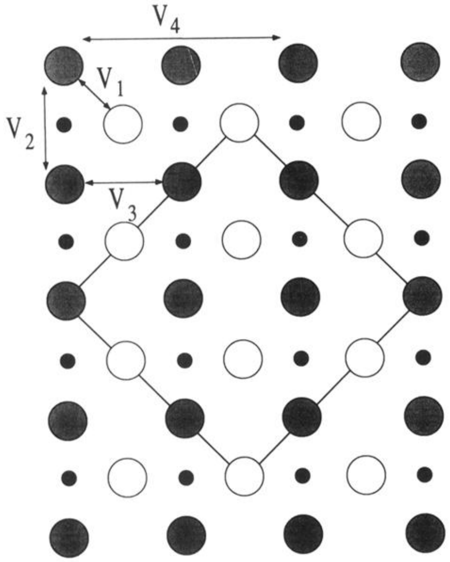

FIG. 2. Basal plane geometry. Shaded circles indicate O(1) sites, while open circles are O(5) sites. Small solid circles indicate Cu(1) atoms. Effective pair interactions are shown. The *O*-I MSC (see Sec. I B) is indicated by a box.

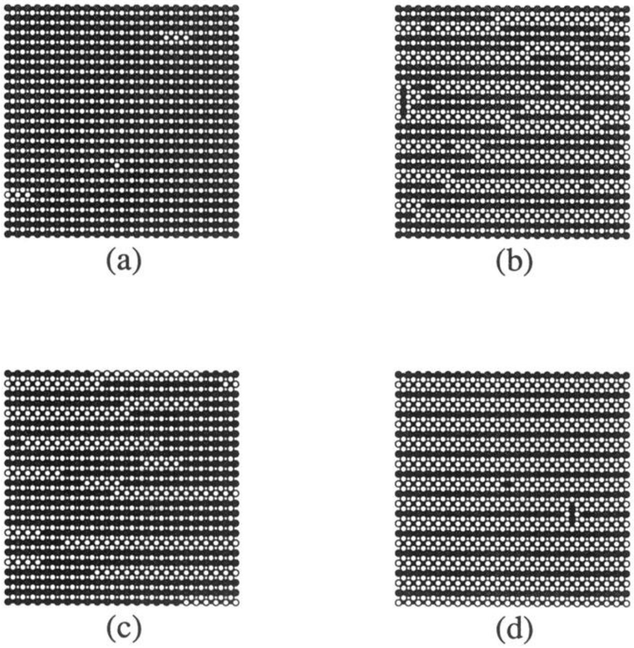

FIG. 3. Lattices from Monte Carlo simulation at various concentrations (V_4 included). (a) *O*I phase; (b) *O*III phase; (c) Intermediate concentration between *O*I and *O*III; (d) *O*II phase.

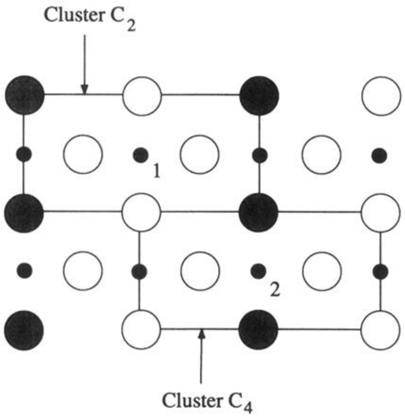

FIG. 5. Example of the determination of cluster probabilities for an *O*II structure. Shaded circles are oxygen atoms, open circles are vacancies, and solid circles are Cu(1) atoms. Cu(1) atom 1 is surrounded by cluster C_2, while Cu(1) atom 2 is in cluster C_4. These are the only two types of Cu(1) atoms in the *O*II structure, and there are equal numbers of them. The only nonzero cluster probabilities for *O*II are $C_2 = C_4 = \frac{1}{2}$.