A Computational Study of Oxygen Ordering in YBa$_2$Cu$_3$O$_z$ and its Relation to Superconductivity

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An *ab initio* model to study oxygen ordering in the high temperature superconductor YBa$_2$Cu$_3$O$_z$ is presented. The phase diagram computed with this model contains several ordered structures and is in excellent agreement with the known experimental information. At high temperature, an orthorhombic structure transforms by a second order reaction into a tetragonal structure. At low temperature, a branching algorithm generates an infinity of ordered structures all consisting of long O$-$Cu$-$O chains. By looking at the kinetic evolution of quenched samples in a Monte Carlo simulation it was possible to clarify how annealing of the material can influence its superconducting transition temperature.

1 INTRODUCTION

In spite of the fact that superconductivity in YBa$_2$Cu$_3$O$_z$ was only discovered in 1987, this system may qualify as the most studied material of this decade. Although its superconducting transition temperature (T_c) has been surpassed by other compounds, YBa$_2$Cu$_3$O$_z$ still offers the best possibilities for elucidating the intricate connection between the structure and superconducting properties in high-T_c oxides. One of the interesting features of YBa$_2$Cu$_3$O$_z$ is that small structural variations can be induced by changing the oxygen content or the temperature at which the material is annealed. As these structural changes affect superconductivity, they can be used systematically to probe the relation between superconductivity and structure.

Figure 1 shows the unit cell of YBa$_2$Cu$_3$O$_7$. Between each Y and Ba on lies a buckled CuO$_2$ sheet which we will refer to as the "CuO$_2$ plane" or the "CuO$_2$ sheet". It is now believed that superconductivity is localized in these planes. The structural variations that have received most interest occur in the Cu$-$O plane between the Ba ions. This plane coincides with a mirror plane of the structure and can accommodate a variable oxygen content. We will refer to this plane as the "chain plain." When fully oxidized, the stoichiometry of the material is YBa$_2$Cu$_3$O$_7$ and all the oxygen in this plane lines up with Cu to form O$-$Cu$-$O chains, making the symmetry of the unit cell orthorhombic (shown in Figure 1). Neutron diffraction studies have revealed that, upon reducing the oxygen content, oxygen is predominantly taken out of the chain plane [1, 2, 3]. The structural evolution as a result of removing oxygen atoms depends on temperature. When, at high temperature, the oxygen content is sufficiently reduced from $z = 7$, the chain
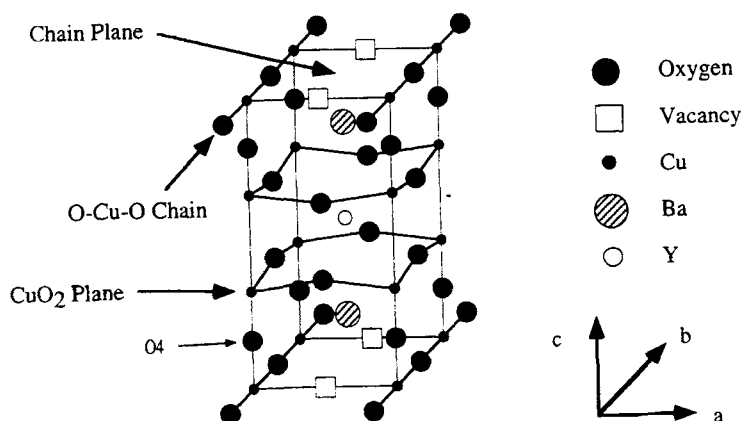
Figure 1 The unit cell of the $YBa_2Cu_3O_z$ structure contains two "buckled" planes with composition CuO_2 located between an Y and a Ba ion. Oxygen off-stoichiometry is accommodated in the plane between two Ba ions. For $z = 7$ half of the oxygen sites are filled in this plane and the oxygen atoms form long chains with Cu. In the tetragonal phase all sites in the chain plane are occupied with equal probability.

formation loses macroscopic coherence and the compound transforms to a phase with tetragonal symmetry. At the exact stoichiometry of this phase, $YBa_2Cu_3O_6$, no oxygen is present in the basal plane. This orthorhombic-tetragonal transition is a second order phase transition [3] and several researchers have determined the critical oxygen concentration at which the transition occurs as a function of temperature [4] [5]. At low temperature, the situation seems different. Using a low temperature oxygen reduction technique [6], Cava found evidence for a distinct phase between $z = 6.6$ and $z = 6.7$. The characteristic superstructure intensity of this new phase is located at (1/2 0 0) in reciprocal space [7], indicating a doubling of the unit cell along the a-axis (the axis perpendicular to the chains). We will call this phase Ortho II (OII) to distinguish it from the regular orthorhombic phase, Ortho I (OI). In addition to the (1/2 0 0) reflection, several other superstructure reflections of type (h 0 0) have been found by Beyers *et al.* [8]: (2/5 0 0), (0.37 0 0) and (1/3 0 0). These superstructure reflections suggest that, at low temperature, oxygen is not removed randomly from the chain plane, but rather in a way so as to promote ordered arrangements of oxygen atoms and vacant sites. Some of the oxygen-vacancy superstructures corresponding to the previously indicated reflections have been observed by high resolution electron microscopy [9].

The superconducting transition temperature is a strong function of the oxygen content of the material. Upon reducing the oxygen content at low temperature from $z = 7$, T_c decreases as illustrated in Figure 2: For $7 < z < 6.85$, T_c remains approximately constant at 90 K. Then there is a sharp decrease and for $6.7 < z < 6.5$, T_c is again roughly constant at 60 K [6, 8, 10]. Finally, for oxygen contents lower than $z \approx 6.4$ the material is a non-superconducting insulator.

Oxygen *content* is not the only factor which controls T_c in the $YBa_2Cu_3O_z$ system. Quenched and annealed samples with the same composition show remarkable differences in the temperatures at which they become superconductors.
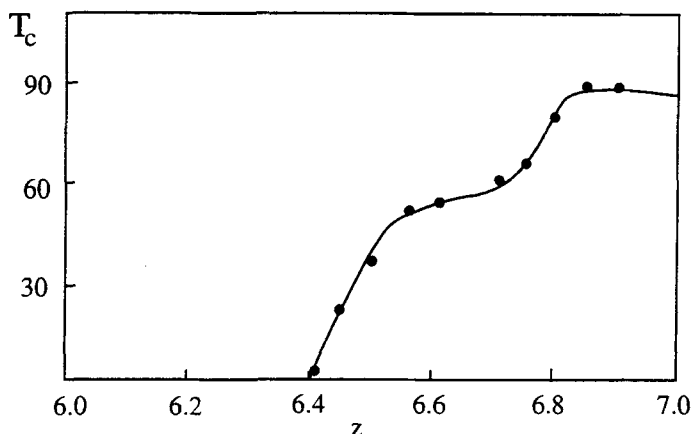
Figure 2 T_c versus oxygen content (z) (Redrawn from Beyers 1989[8]).

The results in Figure 2 are taken from annealed samples. When the material is quenched from high temperature, the observed T_c is always lower and the plateaus are less extended than for annealed material [11, 12]. In most studies, only the 60 K plateau is affected by annealing, although one group [13] claims that both the 90 K and 60 K plateau disappear when samples are quenched fast enough. Veal *et al.* [14], Jorgensen *et al.* [15] and Claus *et al.* [11] recently demonstrated that the effect of annealing on T_c is especially dramatic for specimens with oxygen content near the insulator-superconductor transition. These investigators monitored the super-conducting transition temperature of a sample with oxygen content $z = 6.44$ quenched to room temperature after annealing at 800 K. Their results are redrawn schematically in Figure 3. Annealing at room temperature produces an increase in T_c of more than 20 K! Great care was taken in these experiments to prevent oxygen uptake. The strong increase in T_c can thus only be due to structural rearrangements.

In this paper we will review a model that has been used to predict the oxygen phase diagram and structure of the $YBa_2Cu_3O_z$ as a function of temperature and composition. Where experimental results are available the model leads to very good agreement with experimental data. Part of the intent of this manuscript is to illustrate how computational modelling provides information and insight in areas where experimental results are lacking or conflicting. In addition, as will be illustrated in section 4, an accurate model for the atomic-scale structure can lead to a detailed understanding between the properties of $YBa_2Cu_3O_z$ and its oxygen content and thermal treatment.

2 THE ASYNNNI MODEL

Because all different structures that have been observed between composi-tion $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$ only differ by their arrangement of oxygen in the chain plain, one can model the equilibria between these structures with a

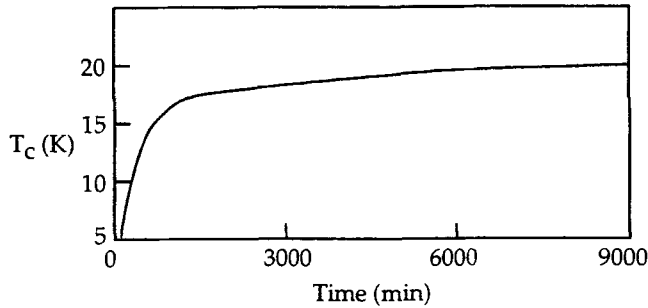**Figure 3** T_c as a function of annealing time at room temperature for $YBa_2Cu_3O_{6.44}$ (Redrawn from Veal *et al.* [14, 39]).

two-dimensional lattice model. This model, shown in Figure 4 and originally devised by de Fontaine, Wille and Moss [16] consists of all the possible sites where oxygen atoms can sit in the chain plane. It can be thought of as two interpenetrating rectangular sublattices. The regular orthorhombic structure (OI), shown in Figure 1, corresponds to having one sublattice filled with oxygen while the other sublattice is empty. In the perfect tetragonal-phase all sites in the model are vacant.

The energy of the different oxygen configurations is parameterized by three effective pair interactions (EPI): one nearest neighbor (NN) interaction (V_1) and two next nearest neighbor (NNN) interactions (V_2 and V_3). The asymmetry of the NNN interactions distinguishes the NNN pairs *with* and *without* a Cu atom in between and is essential to reproduce the experimentally observed ground states. The energy of an oxygen configuration in this model is given by the value of the Ising-like Hamiltonian:

$$H = \sum_{i,j}^{NN} V_1\sigma_i\sigma_j + \sum_{i,j}^{NNNa} V_3\sigma_1\sigma_j + \sum_{i,j}^{NNNb} V_2\sigma_1\sigma_j - \sum_i h\sigma_i \qquad (1)$$

where h is the chemical field (potential). The occupation variable σ_i takes on the value $+1$ (-1) when site i is occupied by an oxygen atom (vacancy). The second and third summation in Equation (1) are respectively over next-nearest neighbor pairs with and without a Cu atom in between. The effective pair interactions (EPI) are **not** plain oxygen-oxygen potentials. Rather, the EPI constitute a parameterization of the formation energy of the whole three-dimensional solid with a given oxygen configuration in the chain plane. Although the Hamiltonian in Equation (1) describes the configurational statistics of a two-dimensional array of oxygen sites, the influence of rest of the structure on the oxygen configuration is taken into account through the *value* of the EPI. This can be illustrated with V_2: Whereas a plain oxygen-oxygen interaction over this distance would be repulsive, the presence of the Cu atom makes V_2 attractive, reflecting the energetics of oxygen coordination around Cu. The *asymmetric-next-nearest-neighbor-interaction* (ASYNNNI) model shown in Figure 4, can thus best be described as a model that is three dimensional for the energy but two dimensional for the entropy.

It can be shown that the elements of Equation (1) correspond to the first terms in the cluster expansion of the total energy as a function of (oxygen) configuration
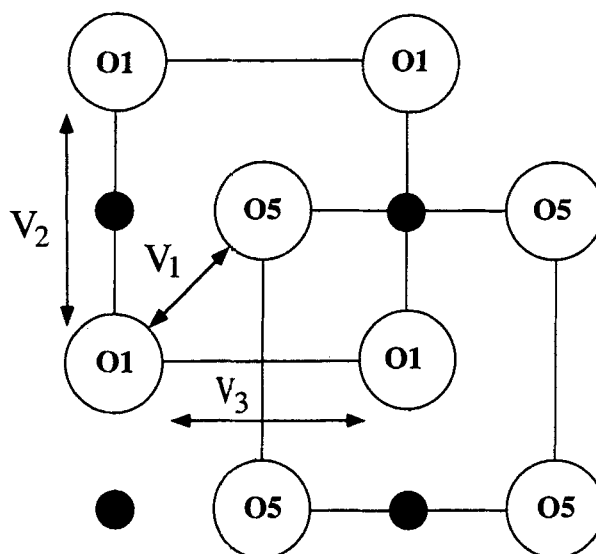
Figure 4 The ASYNNNI model, used to study oxygen ordering in the basal plane of $YBa_2Cu_3O_z$, consists of two interpenetrating rectangular sublattices (labelled O1 and O5) and three effective pair interactions. Large open circles are possible oxygen sites and small filled circles represent Cu atoms. The Cu sites are not part of the Ising model. They are only drawn to emphasize the fact that they reduce the symmetry on the oxygen lattice.

[17, 18]. Cluster expansions like Equation (1) have been used successfully to compute phase diagrams and thermodynamic quantities in metallic systems from first principles [19, 20]. Given that the correct definition for the effective interaction is used, this expansion is always convergent.

For $YBa_2Cu_3O_z$, Sterne and Wille [21] extracted values for the effective interactions from quantum-mechanical total energy calculations of various ordered structure. The values found were: $V_1 = 6.5\,mRy$, $V_2 = -2.4\,mRy$ and $V_3 = 1.1\,mRy$. A positive (negative) interaction between two sites indicates repulsion (attraction) between oxygen atoms at those sites. It is already clear that the negative value of V_2 will cause oxygen to rearrange into $O-Cu-O$ chains. With the Sterne-Wille interactions, Equation (1) provides us with an accurate *ab initio* parameterization for the energy of various oxygen configurations. In the next section, results for the phase diagrams of this Hamiltonian will be shown.

3 OXYGEN SUPERSTRUCTURE PHASE DIAGRAMS

The Cluster Variation Method (CVM) was used to compute the oxygen ordering diagram of $YBa_2Cu_3O_z$ [22, 23]. The CVM is a hierarchy of analytical approximations used to compute free energy of a lattice Hamiltonian [24] and has the advantage that it is much faster than simulation methods like the Monte Carlo method. Although the CVM is a classical theory, and critical exponents are thus incorrectly reproduced, exact (or very well known) transition temperatures can be
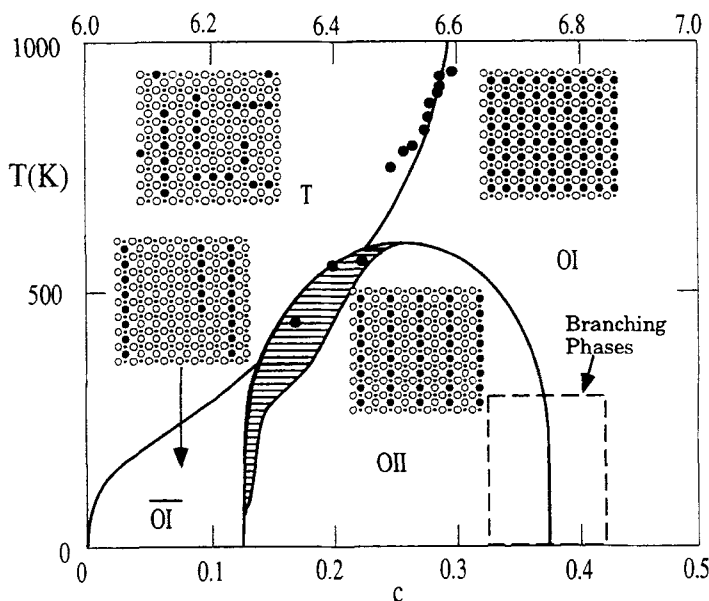
Figure 5 Pseudo-binary phase diagram as computed in the 4 and 5 point approximation of the Cluster Variation Method with the model of Figure 4 ($V_1 = 6.9$ mRy, $V_2 = -2.4$ mRy, $V_3 = 1.1$ mRy). Filled circles are experimentally measured transition points from Andersen *et al.* [4]. c is the concentration of oxygen in the chain plane and z gives the corresponding value of the stoichiometric index. The inserts are snap-shots of the structures obtained with Monte Carlo simulation. The dashed rectangle indicates where additional chain-ordered superstructures will appear as the results of long range interactions between the chains.

approached very closely [25]. The pseudo-binary phase diagram as computed [22] with the 4 + 5 point approximation of the CVM is shown in Figure 5. This diagram is similar to phase diagrams obtained with slightly different interactions [26, 27, 28] or with different methods [29, 30].

The temperature scale on Figure 5 is in absolute degrees Kelvin and the concentration (c, bottom scale) is the oxygen concentration in the chain planes and is related to the stoichiometric index z (top scale) by $z = 6 + 2c$. At high temperature, the tetragonal (T) and orthorhombic phase (OI) are separated by a second order transition line. The agreement with experimentally measured transition points (solid circles) [4] is remarkable, considering the fact that no adjustable parameters appear in the ASYNNNI model. Shown as inserts in the phase diagram are some snapshots of Monte Carlo simulations. The OI (top right) structure is dominated by the O—Cu—O chains. These chains are still present in the tetragonal structure (top left), but the chains run in both directions, making the overall symmetry of the structure tetragonal. So, the tetragonal structure does not correspond to a random arrangement of oxygen. This "short range order" of oxygen atoms has a stabilizing influence on the tetragonal phase and lowers its transition temperature by an order of magnitude from what one would expect from simple point-defect arguments: The energy cost for interchanging an oxygen and a vacancy (Frenkel pair) in the perfect OI structure is ≈ 1.2 eV ($\approx 15,000$ K!).

At low temperature, additional ordered phases appear: The cell-doubled OII (Orthorhombic II) phase occupies a major portion of the phase diagram. At its exact stoichiometry $z = 6.5$, half of the oxygen is removed from the chain plane and O—Cu—O chains alternate with vacancy-Cu-vacancy chains along the a-axis. Experiments [9] confirm the large stability domain of this phase. It can be seen that, at low temperature, orthorhombicity pertains to low oxygen concentrations by virtue of the $\overline{\text{OI}}$ phase. This phase can be regarded as the mirror image of OI in the sense that the roles of filled and empty chains on the occupied sublattice are interchanged. It is possible to show by symmetry arguments, that the $\overline{\text{OI}}$ *must* appear in the phase diagram [22].

The ordered structures in Figure 5 are stable with large amounts of off-stoichiometry, even down to zero K. A numerical investigation with the ASYNNNI model [22] showed that in the limit of $T \rightarrow 0°$K, this off-stoichiometry is not accommodated by extracting oxygen randomly from the chain plane. Instead, complete chains are eliminated when reducing the oxygen content. At low enough temperature, the symmetry of the YBa$_2$Cu$_3$O$_z$ compound is therefore always orthorhombic, since for **all oxygen contents**, the available oxygen lines up with Cu to form long chains. These chains order with the vacancy-Cu-vacancy chains under the influence of the interactions between them. In the ASYNNNI model, the only interaction between the chains is V_3. Its repulsive character is responsible for the ordering of O—Cu—O chains and vacancy-Cu-vacancy chains in the OII structure. At zero K, the problem of chain arrangement is a one-dimensional one, since chains are infinitely long. Only one chain-ordered structure, OII, appears in the phase diagram because the chain-to-chain interaction is truncated at V_3. This truncation is also the reason for the large width of the single-phase fields at $0°$K since for certain values of the chemical potential, the OI and OII phase have the same energy, just as any structure in which filled and empty chains are inter-dispersed so that no two empty chains are neighboring. Longer ranged interactions between the fully formed chains, however small, will break this degeneracy and may introduce new phases. For a reasonable interaction perpendicular to the chains, and beyond V_3, the changes in the phase diagram can be predicted with confidence [31, 32]: At high temperature, little will change to the phase diagram of Figure 5 since the tetragonal-orthorhombic phase transition is dominated by the strongly repulsive V_1. At low temperature, however, new phases will appear, all of which can be constructed from a structure branching algorithm [31, 32]: It is expected that, at a temperature depending on the interaction strength between chains, the phase boundary between OII and OI will become unstable with respect to the formation of a new phase. The unit cell of the new structure is merely the juxtaposition of the OI and OII unit cells. We refer to this phase as orthorhombic III (OIII). As it consists of a repeat of two O—Cu—O chains and one vacancy-Cu-vacancy chain its unit cell is tripled along the *a*-axis and the structure's stoichiometry is $z = 6.667$. At even lower temperature, the phase boundary between OII and OIII and between OIII and OI will again make way for phases with larger unit cells, and so on, *ad infinitum*. The branching phases may order through second or first order reactions. In the limit of zero temperature, an ordered structure exists for every rational value of the oxygen content. Since the branching will occur at successively lower temperatures, kinetics in the real YBa$_2$Cu$_3$O$_z$ system may not allow for homogeneous ordering of these superstructures over long distances. Only superstructures up to a certain branching level will thus be observed in experiments.

Comparing the theoretical diffraction patterns for the ordered superstructures [31, 33] with electron diffraction patterns obtained from slowly cooled samples [8] gives excellent agreement.

The introduction of long ranged interactions complicates the computation of the phase diagram considerably. Although simple mean field theory, when formulated in k-space, has no problem handling long ranged interactions, we have found its results to be less than satisfactory [25]. Using the CVM it has only been possible to compute a phase diagram that includes the first branching phase (OIII) [34, 35]. The OIII phase was found to have a relatively high order-disorder transition temperature, even for small values of the chain-to-chain interaction beyond V_3.

The good agreement between experiments and computation for the $YBa_2Cu_3O_z$ system indicates that the two-dimensional ASYNNNI model with only three effective pair interactions is a viable model for the study of oxygen ordering on the chain plane of $YBa_2Cu_3O_z$. Motivated by the success in reproducing (and predicting) thermodynamic quantities for the system, we have also attempted to rationalize the kinetic behavior of the system and the relation between the superconducting transition temperature and oxygen content. By simulating the quench-and-anneal experiment of Veal and Jorgensen we will illustrate how atomic-scale simulations can be useful in understanding the behavior of a material. In the case of $YBa_2Cu_3O_z$, the results of the simulation will provide a rationalization for the observed increase in T_c during room temperature aging of quenched material.

4 SIMULATION OF ANNEALING AND ITS EFFECT ON Tc

The cluster expansion and lattice model technique for the computation of phase diagrams has been validated by the many diagrams that have already been derived with this approach. Recently, the success of the Ising-like models was justified on theoretical grounds as well [17]. Kinetic Ising models do not have the same fundamental basis as their thermodynamic counterparts. Putting this caveat aside, kinetic lattice models can still provide relevant qualitative information about the relaxation of a system to equilibrium [36]. In this section we will use the ASYNNNI model to simulate the aging experiments that have been performed on $YBa_2Cu_3O_z$. By tracing the microscopic origin of the increase in T_c, during the room temperature aging of quenched samples, one can hope to clarify the role oxygen ordering plays in superconductivity. Since the variations in T_c measured upon aging were most pronounced for oxygen deficient samples, with a maximum of $\Delta T_c \approx 27\,K$ for $z \approx 6.44$, we will concentrate on this composition.

The "computer experiments" were performed with a Monte Carlo (MC) simulation on a 64×64 two-dimensional lattice with periodic boundary conditions and oxygen content corresponding to $z = 6.44$. Kawasaki dynamics with nearest neighbor exchange were used in order to keep a fixed concentration of oxygen. Figure 6a shows the as-quenched state. Because quenching can be done infinitely fast in a Monte Carlo simulation, Figure 6a is also representative of the oxygen ordering at the temperature from which the system is quenched (800 K). As is typical for a structure in the tetragonal phase field, short O—Cu—O chains are oriented in both directions. Some "loose oxygen" can also be observed. After annealing for 3000 MC passes at room temperature the local structure has changed considerably (Figure 6b): The anneal has made O—Cu—O chains longer and most of the loose
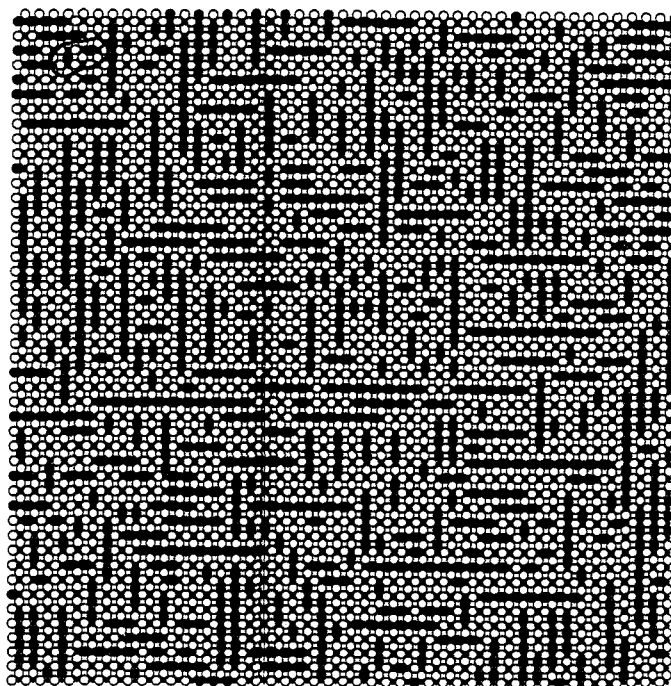
c = 0.22, Pass 0

Figure 6a

oxygen atoms have attached themselves to a chain. Although the aging temperature (room temperature) is too low to allow for large scale rearrangements, the chains have started to order locally in the-cell-doubled pattern, typical of the OII phase. This is to be expected as the composition and aging temperature put the system in the stability domain of the OII phase.

It is easy to see how this ordering may enhance superconductivity: When two short chains merge into one larger chain, two chain ends are destroyed. In the process, two Cu atoms that were coordinated by three oxygen atoms are converted to one two-fold and one four-fold coordinated Cu. This process of two short chains merging to form one longer chain is illustrated in Figure 7. Note from the YBa$_2$Cu$_3$O$_z$ unit cell in Figure 1 that Cu atoms in the chain plane always have one oxygen above and below them so that the total Cu— coordination is the coordination in the chain plane plus 2. A Cu atom in an O—Cu—O chain is therefore four-fold coordinated, and one in a vacancy chain is two-fold coordinated. The differently coordinated Cu atoms will exist in different charge states. In the simplest chemical model for the valence states of Cu in YBa$_2$Cu$_3$O$_z$ one can assume that three and four-fold coordinated Cu ions are present as Cu^{2+} and that the less oxidized two-fold coordinated Cu is present as Cu$^+$. In this model, conversion of a three-fold coordinated Cu to a two-fold coordinated Cu will transform a Cu^{2+} to a Cu$^+$, producing an electron-hole as a result (reaction in
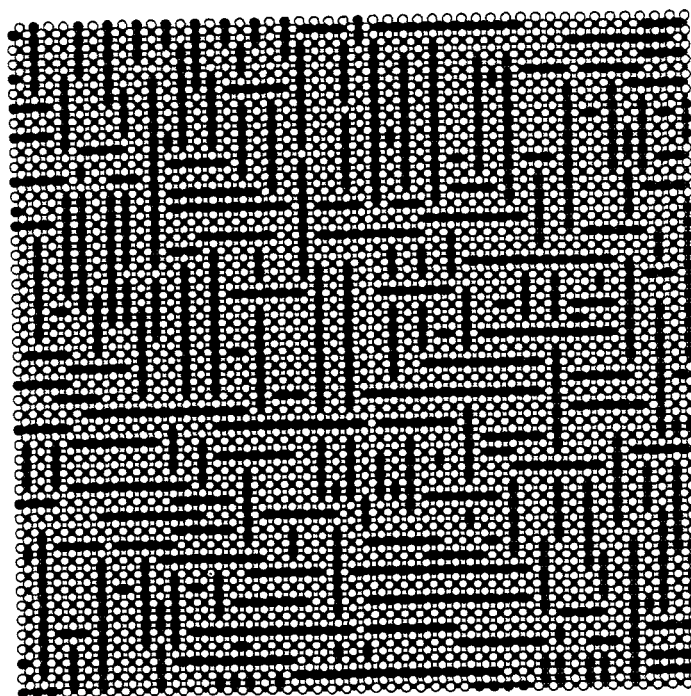
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c = 0.22 , Pass 3000

Figure 6 Monte Carlo simulation of room temperature aging of the chain plane in $YBa_2Cu_3O_{6.44}$. The small filled circles are Cu atoms. The large filled circles are oxygen atoms and the open circles are oxygen vacancies.
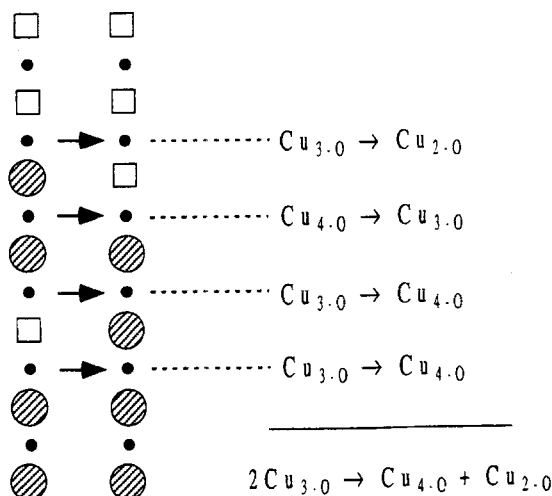a) As quenched structure
b) Structure after 3000 Monte Carlo passes.

Figure 7). This hole may join the electron-holes which constitute the superconducting carriers in the CuO_2 planes. The close correlation between the hole carrier density in the CuO_2 planes and T_c has been well documented in many oxide superconductors [37].

The mechanism by which annealing increases T_c is thus as follows: Annealing leads to local oxygen ordering, even at room temperature. The change in coordination of the Cu atoms as a result of ordering, induces charge transfer from the chain planes to the CuO_2 sheets which in turn, increases the superconducting transition temperature.

5 SUMMARY

The two-dimensional ASYNNNI model, with only three effective pair interactions, contains most of the essential information necessary to reproduce oxygen ordering in $YBa_2Cu_3O_z$. The strongly repulsive nearest neighbor interaction (V_1) and the attractive interaction mediated by Cu (V_2) are responsible for the orthorhombicity

$$Cu_{3.0} \rightarrow Cu_{2.0}$$

$$Cu_{4.0} \rightarrow Cu_{3.0}$$

$$Cu_{3.0} \rightarrow Cu_{4.0}$$

$$Cu_{3.0} \rightarrow Cu_{4.0}$$

$$2Cu_{3.0} \rightarrow Cu_{4.0} + Cu_{2.0}$$

Charge Balance:

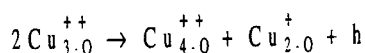$$2Cu_{3.0}^{++} \rightarrow Cu_{4.0}^{++} + Cu_{2.0}^{+} + h$$

Figure 7 When two short chains merge, two 3-fold coordinated Cu atoms are converted into a 2-fold and a 4-fold coordinated Cu. In the process a positive charge is released.

and the formation of O—Cu—O chains. V_3 is part of the repulsive interaction that causes the fully formed chains to order at low temperature into quasi-one-dimensional superstructures. All low temperature superstructures can be predicted exactly from a structure branching algorithm.

Using the cluster expansion to parameterize the energy of planar oxygen configurations in the $YBa_2Cu_3O_z$ structure, it was possible to compute a pseudo-binary phase diagram for oxygen ordering between the end members $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$. This diagram, computed with the Cluster Variation Method, is in excellent agreement with the available experimental data. In addition, some of the essential predictions of the ASYNNNI Model (character of the OI → T transition, orthorhombicity and chain formation at low temperature) are not very sensitive to the exact value of the effective interactions.

Oxygen ordering affects superconductivity in $YBa_2Cu_3O_z$ by reducing the average valence of the Cu ions and transferring positive charge to the CuO_2 sheets in the structure. This effect explains the sensitivity of the superconducting transition temperature in $YBa_2Cu_3O_z$ to the annealing treatment the material receives, and shows why less annealed samples have lower T_c's. Recently [38], the amount of charge transfer could be quantified for states with arbitrary degree of oxygen ordering by using the cluster expansion to parameterize the charge transfer. Combining this model with the configurational results of the ASYNNNI model, it was possible to attribute the 60 K plateau in T_c versus oxygen content to oxygen ordering. No oxygen ordering mechanism could be identified for the 90 K plateau.

The cluster expansion is thus a versatile and systematic technique to parameterize properties that depend on the substitutional configuration of atoms on a fixed lattice topology.

Acknowledgements

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