States of Partial Order in YBa$_2$Cu$_3$O$_z$

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A Monte Carlo simulation has been performed on a previously proposed model of oxygen ordering in YBa$_2$Cu$_3$O$_z$: a two-dimensional Ising model with isotropic first-neighbor and anisotropic second-neighbor effective pair interactions in the "chain plane." At low temperatures, states of partial order are observed in agreement with experimental findings. Such states of quasi-one-dimensional order are a consequence of the asymmetric nature of the interactions.

The nature of the tetragonal-to-orthorhombic transition in the YBa$_2$Cu$_3$O$_z$ compound is now fairly well understood (see, for example, the recent review by Beyers and Shaw[1] and references cited therein), but the low-temperature (< 500 °C) behavior of the system remains puzzling. Various states of oxygen ordering have been reported,[2-8] and it is not clear which of these represent true equilibrium states. The purpose of this Letter is to examine the conditions under which such ordered states may occur. The analysis is based on a previously proposed paradigm of ordering in YBa$_2$Cu$_3$O$_z$: a two-dimensional Ising model of occupied and unoccupied oxygen sites with isotropic first- and anisotropic second-neighbor effective pair interactions.[9-14] It will be shown, with the help of a Monte Carlo simulation, that the anisotropic character of the model is essential: Symmetric models[15,16] cannot account for the observed states of order.

Oxygen ordering, responsible for the tetragonal-to-orthorhombic transition, takes place on the (001) mirror plane of the YBa$_2$Cu$_3$O$_z$ unit cell, the "chain" plane. The structure of this plane can be represented by three interpenetrating sublattices:[9] two (α and β) of oxygen sites, which may be occupied or vacant, and one of Cu (always occupied). To simplify the thermodynamical treatment, only three effective pair interactions (EPI's) will be considered: the first-neighbor interaction, which couples the two sublattices and is expected to be the dominant one, and two second-neighbor interactions, V_2 which is mediated by the Cu ions and V_3 which is not. Such ordering interactions are expected to converge rapidly with pair spacing,[17] hence this scheme should suffice to represent the main features of the system. It may be argued[18] and V_1 should be positive (favoring unlike O-□ pairs) and V_2 negative (favoring like O-O and □-□ pairs), while Coulomb repulsion between parallel O-Cu-O chains suggests $V_3 > 0$.

The YBa$_2$Cu$_3$O$_z$ system is known to contain three distinct phases which differ by the oxygen arrangement on the mirror plane: the tetragonal phase (T) at stoichiometry $z = 6$, which is nonsuperconducting, the orthorhombic phase, ortho I (or OI, for short), at stoi-

chiometry $z = 7$, which has a 90-K superconducting transition and a second orthorhombic phase, ortho II (or OII, for short), at stoichiometry $z = 6.5$, which features cell doubling, has a 60-K transition, and for which ample experimental evidence is now available. In the framework of the present model all three structures have been proven to be ground states of the asymmetric Ising model,[10] and the conditions for stability of OII have been determined rigorously. The EPI's must obey the following inequalities: $V_1 > 0$ and $V_2 < 0$ (precisely what is expected on physical grounds) and $0 < V_3 < \frac{1}{2} V_1$.

The cluster-variation method (CVM) was used to calculate two phase diagrams with EPI's within the specified range.[12-14] For comparison, a Monte Carlo calculation was performed with the following parameters: $V_1 > 0$, $V_2/V_1 = -0.5$, and $V_3/V_1 = +0.50$. At high temperatures, agreement with previous CVM calculations[12] was quite satisfactory. At low-temperature simulations, around $\tau \equiv k_B T/V_1 = 0.2$ ($k_B T$ has its usual "Boltzmann constant, absolute-temperature" meaning), spurious specific-heat maxima occurred in and around the OII phase field. The highest disordering temperature of OII is $\tau \approx 1.0$, or about $T \approx 700$ K. Examination of computer printouts revealed that these specific-heat anomalies corresponded to states of somewhat irregularly spaced parallel O-Cu-O chains.

Such a typical structure is shown in Fig. 1(a) where black dots denote Cu atoms, closed circles are oxygen atoms, and open circles are vacant sites. The structure was obtained by performing a Monte Carlo simulation on a 64×64 square network of oxygen sites at fixed chemical-potential field (normalized by V_1) of $\mu = -4.7$. Oxygen coverage in the plane is $c_O = 0.2265$ or stoichiometry index $z = 6.453$. The system was "quenched" from a high temperature of $\tau = 5.0$ and the iteration was pursued to 1200 Monte Carlo steps per site. O-Cu-O chains are seen to be fully formed and are stacked in such a way as to form regions of OII (alternating full-empty-full chains on the α sublattice) separated by slabs of ortho III (OIII, full-empty-empty-full cell-tripling structure). The corresponding intensity pattern, i.e., the amplitude squared of the Fourier transform, or oxygen
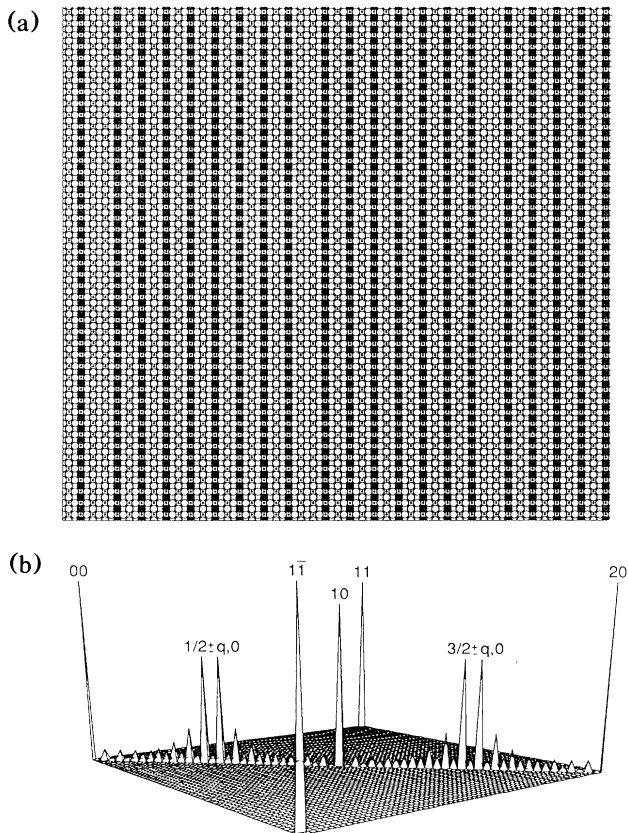
(a)

(b)

FIG. 1. (a) Chain configuration for a Monte Carlo system quenched from $\tau = 0.2$ at constant $\mu = -4.7$, after 1200 Monte Carlo steps per site. Closed circles denote oxygen ions, open circles are vacant sites, and black dots (perhaps not readily visible) indicate Cu ions. Concentration is $c_O = 0.2265$ or oxygen stoichiometry index $z = 6.453$. Structure is one of mixed OII and $\overline{OI}$ domains. (b) Fourier transform (amplitude squared) of configuration (a) showing characteristic split $(\frac{1}{2},0)$ peaks and (1.0) streaks of intensity.

structure factor of Fig. 1(a), is shown in Fig. 1(b). Diffraction maxima are located at $\langle 00 \rangle$, $\langle 20 \rangle$, and $\langle 11 \rangle$ which are the "Bragg peaks" in planar reciprocal-space notation, and at $\langle 10 \rangle$ which are the OI "reflections." The $\langle \frac{1}{2} 0 \rangle$ reflections are split into satellite peaks at $\langle \frac{1}{2} \pm q, 0 \rangle$, with q not necessarily a simple fraction. At an earlier stage of the simulation (500 Monte Carlo steps per site), the chains were often faulted and both α and β oxygen sublattice occupancy domains were observed (see Fig. 2). Chain-formation dynamics is discussed in more detail by Burmester and Wille.[19]

Another mode of "sample preparation" was also used in the simulations: First OI was produced at $\mu = -2.0$, then oxygen was extracted by imposing a chemical-potential field of $\mu = -3.2$, this procedure being equivalent to reducing the partial pressure of oxygen. After 8000 Monte Carlo steps ser site, a structure consisting of
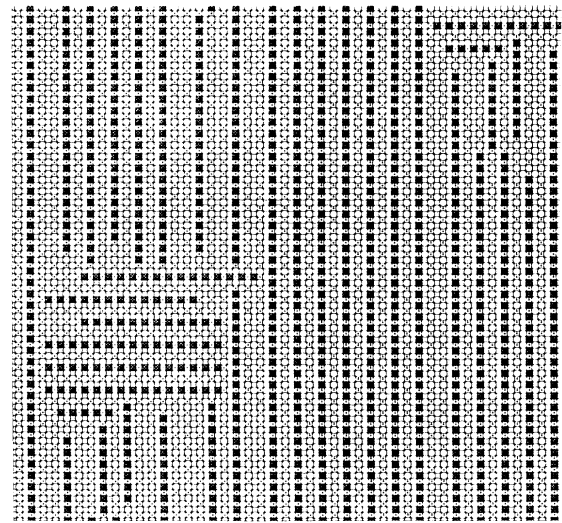

FIG. 2. Chain configuration for the Monte Carlo system of Fig. 1(a) but at an early stage of iteration (500 Monte Carlo steps per site).

mixed OII and OI slabs was obtained (Fig. 3). The average planar oxygen concentration was $c_O = 0.297$, corresponding to stoichiometry $z = 6.594$. Once again the chains were fully formed but the OI and OII mixing was rather irregular, giving rise to a diffraction pattern consisting of a diffuse streak centered on $\langle \frac{1}{2} 0 \rangle$ along the a direction. It is easy to rationalize how such a structure could come about. Because of periodic boundary conditions, complete O-Cu-O chains are infinite and thus very
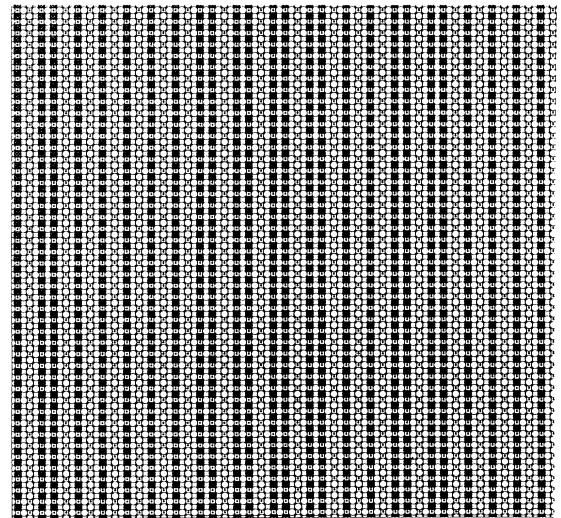

FIG. 3. Chain configuration for a Monte Carlo system initially in ortho-I state, equilibrated at $\mu = -3.2$. Concentration is $c_O = 0.297$ or $z = 6.594$. Structure is one of mixed OI and OII domains.

robust. Eventually a chain is broken by action of the chemical-potential field and it subsequently dissolves, thereby creating a slab of OII. The process is then repeated but in such a way that, at least for $c_O > 0.25$, no two empty chains form adjacent to one another. The reason for that is as follows: Fully formed chains on a single sublattice interact only through the effective V_3 interaction which is repulsive ($V_3 > 0$), thus favoring unlike nearest-neighbor parallel chains. Hence a mixed state of OI and OII domains results.

For $c_O < 0.25$ ($z < 6.5$), the situation is slightly different: The mixing is between OII and "antiortho-I" domains. The antiortho-I ($\overline{\text{OI}}$) 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. The $\overline{\text{OI}}$ phase is distinct from the tetragonal (T) one: T consists of short-range ordered chains distributed on both α and β sublattice, whereas $\overline{\text{OI}}$ has chains along a single sublattice only. Recent CVM calculations[20] indeed indicate that, at very low temperatures, T and OII phases are separated by an $\overline{\text{OI}}$ phase region.

This quasi-one-dimensional admixture of domains, OII+OI for $c_O > 0.25$, OII+$\overline{\text{OI}}$ for $c_O < 0.25$, gives rise, locally, to structures resembling the Magneli phases described by Khachaturyan and Morris (KM).[16] However, such structures are actually inconsistent with the miscibility gap of the KM model as we will demonstrate. First, we should point out that an equivalence between the "method of concentration waves" used by KM to construct the reported phase diagrams[15,16] and a two-dimensional Bragg-Williams model with first- and second-neighbor effective pair interactions can be rigorously demonstrated. A simple back-Fourier transform of the KM mean-field internal energy, for their chosen star values of $V(0)$ and $V(k_1)$, immediately yields the required values (in our notation) of V_1 and V_2 ($-V_3$), with ratio $V_2/V_1 = -0.4286\dots$. These values inserted into the Bragg-Williams model, as expected, reproduced exactly the KM phase diagram.[21]

Next consider the Magneli structures proposed by KM: $[(\text{O}\square)^j\text{O}]$, where O and $\square$ represent filled and empty chains on the α sublattice, respectively, where the square brackets denote periodic repetition and where the parentheses indicate that the OII element is to be repeated j times. Such structures are actually a subset of the well-known ground states of the one-dimensional Ising model and are stabilized by dominant positive (i.e., repulsive) first-neighbor pair interaction J_1 along the Ising line[22,23] which is the a direction in orthorhombic YBa$_2$Cu$_3$O$_z$. But, as mentioned above, for fully formed chains, the only relevant interaction is the interchain repulsive interaction V_3 which is precisely J_1. Hence, the presence of Magneli structures, stable or metastable, necessarily requires $J_1 \equiv V_3 > 0$. The KM phase diagram, however, is constructed with $V_2 = V_3 < 0$ so that this model is actually internally inconsistent, as was already noted earlier.[18] We checked by performing a

Monte Carlo simulation employing the "symmetric" KM interaction parameters $V_2 = V_3 = -0.4286 V_1$ and found, as expected, no Magneli-type ordered states, stable or otherwise. From the foregoing it is thus clear that the presence of states of partial order necessarily implies that ortho II (OII) must be a stable phase in the system.

At low temperature, the behavior of the proposed model with $V_2 > 0$ and $V_3 < 0$ is highly unusual: At $\tau \approx 0.2$, the interchain O-O correlation length is expected to become greater than the dimension of the Monte Carlo periodic cell so that spurious results may occur as discussed, for example, by Selke[24] in the context of the two-dimensional anisotropic next-nearest-neighbor Ising model. The system essentially can be mapped onto a one-dimensional Ising model with nearest-neighbor J_1 interaction for which only three ground states exist: the "ferromagnetic" (OI and $\overline{\text{OI}}$) and the "antiferromagnetic" (OII). Moreover, for $J_1 \equiv V_3 > 0$, any mixing of ferromagnetic and antiferromagnetic domains at fixed O concentration yields the same energy so that complete degeneracy prevails.

The mixing of domains appears to be not completely random, however. Indeed, at intermediate temperatures when the full two-dimensional character of the system is recognized by the Monte Carlo simulation, OI, $\overline{\text{OI}}$, or OII long-range order (LRO) is observed at equilibrium. At low temperature, the two-dimensional character of the model is not totally absent, especially during the early stages of chain formation (see Fig. 2) so that effective long-range (entropy-driven) interchain repulsion may occur. Resulting structures and their Fourier transforms are clearly reminiscent of ordered structures and diffraction patterns observed from YBa$_2$Cu$_3$O$_z$ samples annealed at low temperatures for long periods of time under reducing conditions with final oxygen stoichiometry of between about $z \equiv 6.4$ and 6.75:[25] Split diffraction peaks and diffusive streaks are seen about the $[\frac{1}{2}, 0]$ positions, but rather sharp peaks at positions $[\frac{1}{3}, 0]$ and $[\frac{2}{3}, 0]$ indicate, however, that actual longer-range repulsive interactions, beyond V_3, may be present along the a direction.

The small apparent volume fraction of OII observed in electron micrographs[6] can be explained[18] by the limited correlation existing between mirror planes along the c direction: OII domains phase shifted from plane to plane will tend to project as OI, thereby causing appreciable underestimation of the "areal" fraction of OII on each plane. For $z = 6.5$ samples well equilibrated at low temperatures, c-axis correlations can be extensive, however, and OII can be observed even in neutron-diffraction experiments.[26]

To conclude, states of partial order in YBa$_2$Cu$_3$O$_z$ have been obtained by a low-temperature Monte Carlo simulation in a two-dimensional Ising model with opposite-sign second-neighbor interactions. Such ordered states cannot arise in a symmetric model and are thus incompatible with a miscibility gap phase diagram.

Dimensionality plays an important role: States of partial order short-range order (SRO) arise because of the quasi- one-dimensional character of the model at low temperature and equilibrium LRO is found at high and intermediate temperatures. OII is a true equilibrium state on individual mirror planes, but appears as three-dimensional SRO when c-axis correlation is limited.

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