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Monte Carlo study of transient states of order in $YBa_2Cu_3O_z$

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Monte Carlo simulations of oxygen ordering in the $YBa_2Cu_3O_z$ system have been performed using a two-dimensional anisotropic Ising model. In agreement with experimental findings, transient phases are obtained at low temperatures. Observed structures are investigated, and the kinetics of their domain formation is described. The convergence of the system is seen to be exceptionally slow, and the rate of domain evolution is found to increase with decreasing oxygen content. The implications of these findings on the development of a complete theoretical ordering model for this system are discussed.

The tetragonal-orthorhombic structural phase transition in $YBa_2Cu_3O_z$ is caused by an ordering reaction involving the oxygen ions in the Cu-O basal plane. Upon ordering, parallel O-Cu-O chains are formed which are essential for the superconducting properties of the material: the disordered, tetragonal compound is nonsuperconducting, while the orthorhombic phase near $z=7$ is a 90 K superconductor. A large number of experimental results concerning this order-disorder transition have been obtained recently [for a review with many references to the original papers see Ref. 1], but theoretically the issue is still not completely resolved. Most treatments[2-12] have assumed that the problem can be reduced to a purely two-dimensional one involving occupied and vacant oxygen sites, although Khachaturyan *et al.*[13-15] have argued that the full three-dimensional nature of the material has to be taken into account for a correct description of the ordering process.

To some extent, theoretical studies have been hampered by the difficulty of distinguishing experimentally between stable and transient structures. Partial states of order in $YBa_2Cu_3O_z$ have been observed by transmission electron microscopy[16-18] and x-ray diffraction.[19] While these transient states have been described qualitatively,[13] proposed equilibrium models for this system have heretofore been unable to intrinsically reproduce this important experimental finding.[2-15] As was suggested in previous publications,[7-12] the equilibrium properties of the tetragonal to orthorhombic transition in $YBa_2Cu_3O_z$ can be described by means of a two-dimensional Ising model with isotropic nearest- and anisotropic next-nearest-neighbor effective interactions between oxygen sites in the Cu-O basal plane. To analyze the nonequilibrium properties of this model, Monte Carlo calculations were performed and the formation of the transient structures was found to occur in the course of the phase transformations in remarkable agreement with experiment. The object of the present communication is to examine some of the implications these findings have on the development of an adequate theoretical model for the equilibrium and kinetic ordering behavior of the $YBa_2Cu_3O_z$ system.

Experimentally, at least three distinct ordered phases have been observed in $YBa_2Cu_3O_z$, while the existence of others as a true ground state is still under active debate. A semiconducting tetragonal phase, henceforth called TetraI to distinguish it from the disordered tetragonal state, exists at stoichiometry $z=6$ and corresponds to a completely oxygen-depleted basal plane, the oxygen concentration in the basal plane, c_O, being to a good approximation given by $c_O=\frac{1}{2}(z-6)$. Near $z=7$, $c_O=\frac{1}{2}$, the orthorhombic structure (OrthoI) is known to have a 90 K superconducting transition temperature and it is now also generally accepted that a second, cell doubled, orthorhombic phase (OrthoII) exists at stoichiometry $z=6.5$, $c_O=\frac{1}{4}$, as a true ground state. This compound has a 60 K superconducting transition temperature and has been observed by means of various experimental techniques.[16-17,20-25] All three structures do indeed belong to the set of possible ground states admitted by the present model and the condition of their stability leads to the following effective-pair-interaction inequalities:[8] $V_1>0$, $V_2<0$, and $0<V_3<V_1$, exactly as previously derived elsewhere by bonding arguments.[26] In the proposed Cu-O basal plane model, the V_1 interaction couples nearest-neighbor oxygen sites, while the V_2 and V_3 interactions couple next-nearest-neighbor sites; the V_2 differing from the V_3 pair interaction to represent the action of the mediating Cu ion. It follows that models with $V_2<0$, $V_3<0$ will not include OrthoII as a stable phase and instead phase separation into OrthoI and TetraI is predicted.[8]

In previous work,[9-12] the cluster variation method (CVM) was employed to estimate high-temperature phase boundaries in a temperature–oxygen-concentration phase diagram. To clarify the low temperature behavior, a set of Monte Carlo calculations was initiated with the same parameters as were used for the CVM phase diagram:[11] $V_1>0$, $V_2/V_1=-\frac{1}{2}$, and $V_3/V_1=+\frac{1}{2}$. These simulations were performed in the grand canonical ensemble using Metropolis dynamics, in which the system is allowed to evolve at constant chemical potential, equivalent to constant partial pressure of oxygen, as is done in experiment. The Monte Carlo time scale is graduated by Monte Carlo Steps per site (MCS/site) each of which consists of a complete random "sweep" over all defined sites in the lattice. In this scheme, the change in energy associated with the occupation or deoccupation of oxygen at each site (a "spin flip") is determined. Energetically favorable flips are always accepted, while unfavorable exchanges are accepted according to a Boltzmann distribution. The Monte Carlo phase diagram results for this case, to be published later (see also Ref. 27), performed on 32×32, 64×64, and occasional 128×128 lattices, confirm the second-order transition at high temperatures found in the CVM and gives a transition temperature at $c_O=\frac{1}{2}$ that is only 5% lower than that calculated in the CVM. However, at low temperatures, the Monte Carlo calculation shows the OrthoII phase region appearing between the OrthoI and tetragonal phases in a continuous, second order fashion, contrary to the CVM results, but in agreement with recent transfer matrix work.[27,28] In fact, for this selection of parameters, the model belongs to the Ashkin-Teller universality class for which mean-field theories indeed may show erroneous first-order transitions.[28]

In addition to the equilibrium results, it was found that, for the current choice of parameters, the convergence of the Monte Carlo calculation was exceptionally slow. In particular, for very low temperature simulations [$T<0.35V_1/k_B\cong260$ K (Ref. 11)] performed with $<10^5$ MCS/site, additional specific-heat maxima occurred at chemical potentials fields (μ) intermediate between the TetraI$\rightarrow$OrthoII and OrthoII$\rightarrow$OrthoI second-order transition lines. Examination of correlated lattice configurations revealed that the anomalies corresponded to the formation of states of somewhat irregularly spaced parallel O-Cu-O chains [intermixed spacings of $(1\text{–}5)a_0$ observed] (see Fig. 1). These transient structures were seen to correspond directly with the set of "transient homologous structures" or "Magneli phases" described by Khachaturyan and Morris.[13] The generated structures were also found to correlate exactly with structures imaged by high-resolution transmission electron microscopy of low-temperature-annealed $YBa_2Cu_3O_z$ (Ref. 17) and were also consistent with reported electron diffraction evidence.[18,29] For Monte Carlo calculations performed at temperatures corresponding to the observed partial ordering, the order of the transitions has to be estimated very carefully. It is felt that thermodynamic effects induced by the partial ordering act to obscure the true nature of the transitions in this very low-temperature regime, and this may well explain the disagreement between various experiments concerning the structure of the low-temperature states.

The kinetic evolution of these transient states was investigated at various chemical potentials. It was found that short O-Cu-O chains rapidly (<10 MCS/site) nucleate throughout the lattice as a consequence of the attractive V_2 interaction, and, once formed, propagate in length while simultaneously inhibiting the formation of adjacent chains through the repulsive V_3 intra- and V_1 intersublattice interactions [see Fig. 2(a)]. Since these O-Cu-O chains nucleate simultaneously throughout the sample with mutually orthogonal orientations and occasional antiphase position, they quickly collide as they coarsen and further growth occurs only at the expense of equally stable adjacent phases and is thus extremely slow [see Figs. 2(a)–2(c)]. In this stage of its evolution the system tries to eliminate the excess free energy associated with the domain walls between regions where the *a* and *b* axis are interchanged. In the actual material these domains are rather regularly organized and separated by twin boundaries. However, the twinning process involves elastic interactions and will not be well described in the present rigid-lattice model. Nevertheless, very short 45° domain walls may be observed in Fig. 2(b) and considered as precursors of twin-boundary formation if elasticity were included. At chemical potentials favoring the incorporation of nonstoichometric oxygen, regions of OrthoI are found interspersed with regions of OrthoII which order in the Magneli fashion perpendicular to the orthorhombic "*a*" direction due to the repulsive V_3 interaction. As the chemical potential is decreased, less OrthoI appears in these partially ordered sequences and the system exhibits a series of transient phases at concentrations

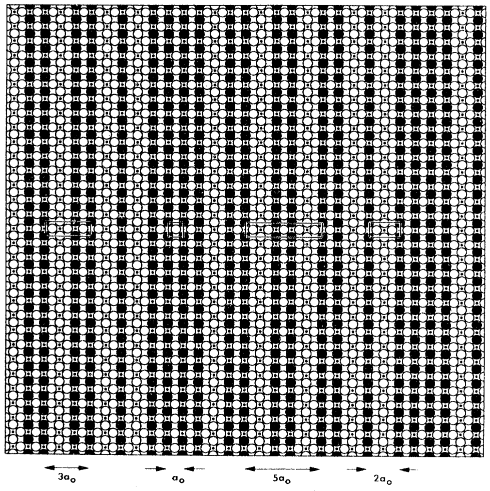

FIG. 1. A typical single-domain transient Magneli-type structure formed from a disordered, high temperature ($T=4.0V_1/k_B\cong3000$ K) structure with $\mu=-3.0$ after 10^5 MCS/spin at $T=0.2V_1/k_B\cong150$ K. OrthoI (a_0), OrthoII ($2a_0$), and transient "unit cells" present ($3a_0,5a_0$) are indicated ($c_O=0.34375$, $z=6.68$). Shaded circles represent oxygens, open circles indicate vacancies, and black dots represent Cu ions. Unit cells indicated correspond directly with those described by Khachaturyan and Morris.[13]

$z > 6.5$, the latter value corresponding to the equilibrium OrthoII structure. Although the resulting structures are similar, this mechanism differs from the phase separation and the spinodal decomposition between $z = 7$ and $z = 6$ predicted by Khachaturyan and Morris,[13] in that the stability of the OrthoII phase and the short range of the interactions in the current study lead to mixed phases of OrthoI and OrthoII between $z = 7$ and $z = 6.5$, and a mixture of OrthoII and TetraI between $z = 6.5$ and 6.

Within the range of chemical potentials favorable for the formation of transient states, the rate of the previously described domain evolution is found to increase with decreasing chemical potential. At high chemical potentials, the extra oxygen in the basal plane makes the resolution of conflicting domains extremely difficult as large amounts of energetically unfavorable spin flips are necessary for final growth to large, single orientation structures. Thus, typical microstructures at high chemical potentials within the transient phase range were found to consist of many small conflicting "Magneli" domains. As the chemical potential is decreased, the corresponding average concentration of oxygens also decreases and the

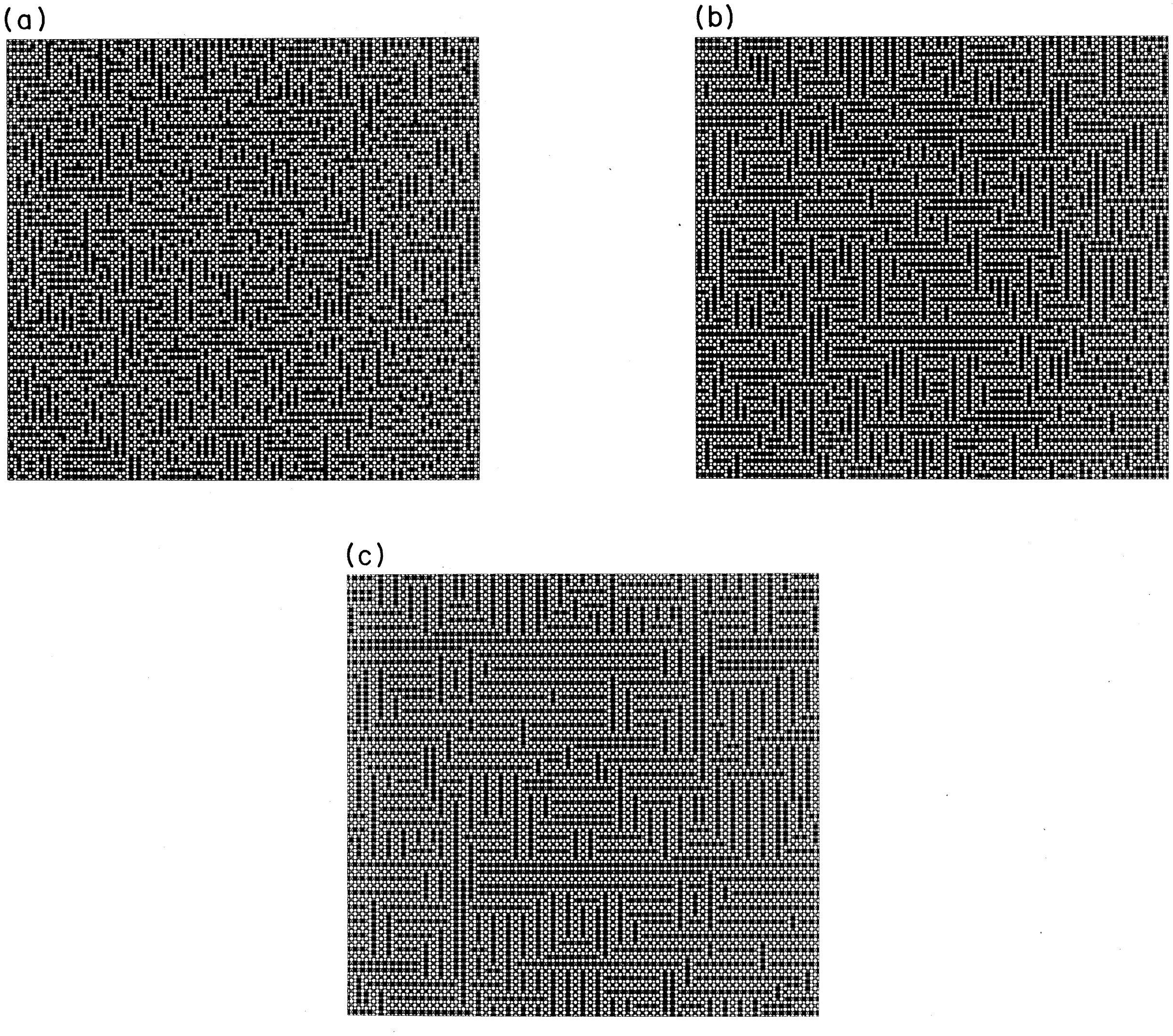

FIG. 2. Snapshot series illustrating domain coarsening at constant chemical potential ($\mu = -3.05$) and constant temperature ($T = 0.2V_1/k_B \cong 150$ K). These snapshots were obtained from the same kinetic series of Monte Carlo cycles initiated with a completely disordered structure obtained at high temperature ($T = 4.0V_1/k_B \cong 3000$ K) after 2.5×10^3 MCS/spin. Shaded circles represent oxygens, open circles represent vacancies, and black dots indicate Cu ions. (a) Lattice configuration achieved after 1 MCS/spin at $T = 0.2V_1/k_B \cong 150$ K ($c_O = 0.265$, $z = 6.530$). Many small O-Cu-O chain structures have nucleated throughout the sample but have yet to grow into conflicting positions. (b) Lattice configuration achieved after 10^2 MCS/spin at $T = 0.2V_1/k_B \cong 150$ K ($c_O = 0.291$, $z = 6.582$). Initial domains seen in (a) have coarsened into conflicting positions. Further domain growth occurs only at the expense of adjacent, equally stable phases. (c) Lattice configuration achieved after 10^5 MCS/spin at $T = 0.2V_1/k_B \cong 150$ K ($c_O = 0.266$, $z = 6.533$). Notice that, while slightly coarsened, the domain structure is still reminiscent of the frustrated structure in (b) reflecting the extremely slow evolution rate.

average domain size increases until the formation of single-domain structures is seen with relatively short annealing time ($< 10^4$ MCS/site). At low chemical potentials, corresponding to the OrthoII→TetraI transition ($\mu = -3.0$), very sparse transient single-domain structures with interchain spacings often greater than $3a_0$ are typically formed until the system finally transforms to the tetragonal structure. However, these low concentration chain states are probably structurally unstable and unlikely to be observed experimentally.[13] The observed chemical potential (concentration) effect on the kinetically achievable domain size is certainly a notable consequence of this anisotropic Ising model calculation and could form the basis of an experimental investigation. However, while Monte Carlo calculations do simulate the progression of a system towards its equilibrium state, stochastic kinetics, although similar, may not directly correspond to the kinetics of oxygen uptake and diffusion in this system.

In the present model the OrthoII structure is fourfold degenerate, since the *a* and *b* directions can be interchanged and the entire structure can be displaced by half a lattice vector along the *a* direction. Such degeneracies ($p = 4$) larger than the dimensionality of the system ($d = 2$) are known to give rise to extremely slow growth kinetics; in particular in the model under investigation the main reason for domain growth inhibition is the development of orthogonal chains. A few simulations were performed to investigate the effects of the fourfold degeneracy in the OrthoII structure in this calculation. The degeneracy was effectively halved by starting with a "biased" stoichometric OrthoI configuration, and then observing the formation of various transient and ground states at chemical potentials appropriate for the occurrence of mixed phases. It is found that in this way the system can very rapidly achieve single-domain structures with very short annealing time ($< 10^3$ MCS/spin). It would be interesting to check for correlated behavior experimentally under induced oxygen loss at low temperatures in single crystals of the orthorhombic $YBa_2Cu_3O_7$.

That this particular choice of interaction parameters leads to the reproduction of such a wide range of experimentally observed phenomena is notable. For a discussion of the range of interactions over which transient state formation abides, see de Fontaine, Mann, and Ceder.[30]

Transient phases are observed in this Monte Carlo simulation of oxygen ordering in the basal plane of $YBa_2Cu_3O_z$ in good agreement with previous theoretical[13] and experimental[16–18,19,29] work. Transient phase formation in this simulation appears to be a direct consequence of the choice of the OrthoII double-cell structure as a ground state, as reflected in the anisotropic next-neighbor interactions. Kinetic evolution of these states is found to be consistent with a second-order phase transition between OrthoI and OrthoII, leading to mixed phases corresponding to a series of transient structures associated with the calculated transitions.

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