Phase diagram and low-temperature behavior of oxygen ordering in $YBa_2Cu_3O_z$ using *ab initio* interactions

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The phase diagram and oxygen ordering in $YBa_2Cu_3O_z$ are investigated, on a first-principles basis, by means of an asymmetric next-nearest-neighbor Ising model using Monte Carlo and cluster-variation-method statistics. It is shown that saturation of some pair-correlation functions at low temperature to a concentration-independent value makes the model quasi-one-dimensional. This correspondence between the two- and one-dimensional model explains some typical characteristics of the phase diagram at low temperature and provides a simple argument for the existence of a low-temperature, low-O-concentration, orthorhombic phase.

I. INTRODUCTION

Oxygen ordering in $YBa_2Cu_3O_z$ has received considerable attention as it may help to clarify the relation between oxygen content and T_c in this compound. Efforts have been made to relate the superconducting plateaus at 60 and 90 K to (micro)structural changes[1] involving the oxygen positions. It is therefore important to characterize the low-temperature oxygen superstructures. For $6 < z < 7$ most of the configurational changes take place in the Cu-O planes between the Ba ions. At least three distinct phases have been observed.[2,3] At high oxygen concentration ($z \approx 7$), a stable orthorhombic phase (*OI*) is present in which all O sits in O-Cu-O chains. The tetragonal phase (*T*) is one in which all available O sites are randomly occupied. For oxygen contents intermediate between *T* and *OI* a cell doubled orthorhombic phase (*OII*) has been observed. A two-dimensional Ising model with anisotropic next-nearest-neighbor (NNN) interactions (ASYNNNI model) has been used successfully to model the pseudobinary phase diagram for these superstructures of oxygen.[4,5] The basic lattice, consisting of two interpenetrating square sublattices (α and β), and effective pair interactions (V_1, V_2, and V_3) are defined in Fig. 1(a). The effective pair interactions and the applicability of the two-dimensional model to a three-dimensional system are discussed elsewhere.[6]

In terms of the interaction parameters, the conditions for the existence of *OII* were determined to be $V_2 < 0 < V_3 < V_1$.[7] A positive value implies that the interaction is repulsive, favoring unlike pairs. The cluster variation method (CVM) was then used to derive phase diagrams with parameter ratios ($V_2/V_1, V_3/V_1$) satisfying the stated inequalities.[8,9] Recently, Kikuchi[10]

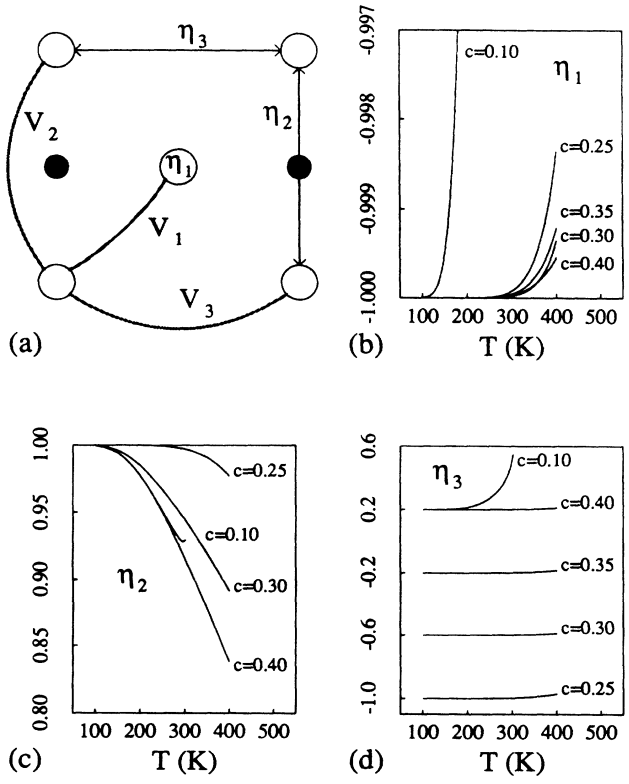

FIG. 1. (a) Centered square lattice with definition of interactions (V) and order parameters (η) used. (b) Average spin on the β sublattice as a function of temperature. (c) η_2 as a function of temperature. η_2 is the pair correlation for sites with Cu in between. (d) η_3 as a function of temperature. η_3 is the pair-correlation function for NNN neighbors without Cu in between.

extended these phase diagram calculations to low temperatures. The parameter ratios ($V_2/V_1=-0.5$, $V_3/V_1=0.5$) were those of Ref. 7. Transfer-matrix[11,12] calculations and Monte Carlo simulations[11,13,14] were also used to calculate phase diagrams for the same values of interaction ratios.

In this paper we clarify the uncertainties that still persist concerning the low-temperature behavior of the system and put the complete phase diagram on a more fundamental basis by performing CVM calculations with parameters obtained from a first-principles calculation.

II. PHASE DIAGRAM

Recently, Sterne carried out linear muffin-tin orbital (LMTO) calculations[15] on the $YBa_2Cu_3O_z$ system and derived the values of the pair interactions: $V_1=6.9$ mRy, $V_2=-2.4$ mRy, and $V_3=1.1$ mRy per pair. These values, which indeed verify the inequalities which guarantee the stability of the ortho II phase,[7] were used to calculate the O superstructure phase diagram shown in Fig. 2. As in previous studies,[8,9] calculations were performed in the 4 and 5 point cluster approximation of the CVM; Newton Raphson iteration was used for the free energy minimization. Low-temperature convergence problems were treated by minimizing under the constraint of constant (small) value of vanishing cluster probabilities.[16] The concentration (c, bottom scale) is the oxygen concentration in the Cu-O planes and is related to the stoichiometric index z (top scale) by $z=6+2c$. The high-temperature portion of the diagram agrees with that of previous calculations,[8,9] and need not be discussed further here. The low-temperature part is similar to Kikuchi's phase diagram:[10] In addition to the OII phase, a new phase, $\overline{O}$I, appears which we propose to call anti-ortho I. 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 (α in this case) are interchanged. We show below (Sec. III) by symmetry arguments that the $\overline{O}$I must appear in the phase diagram. The existence of this phase was missed by transfer-matrix calculations[11,12] which appeared to suffer from poor convergence at low temperatures. All transitions are found, by the CVM, to be of second order except for the $T\rightarrow O$II and $\overline{O}$I$\rightarrow O$I transition at intermediate temperatures. We have also checked the validity of the model by indicating some experimental points[17] for the OI$\rightarrow T$ transition. The agreement is striking, considering the fact that no fitting whatsover was performed. Recent experiments[2] confirm the large stability region of the OII phase.

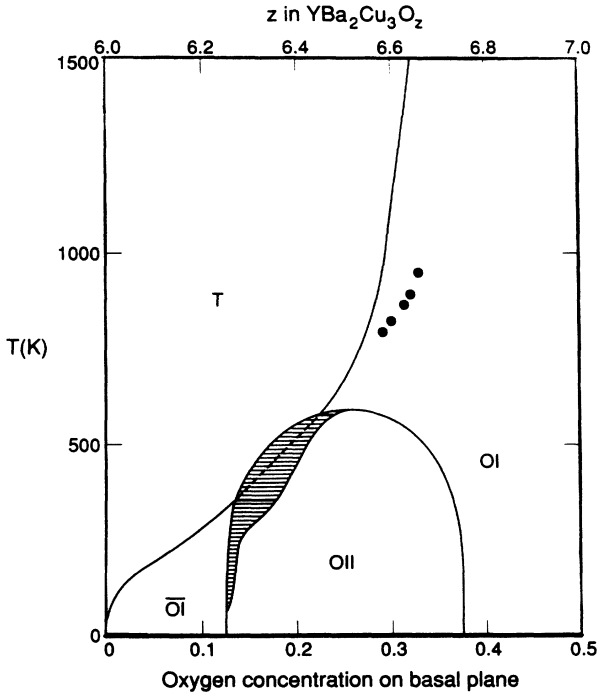

FIG. 2. Phase diagram calculated with a low-temperature version of the CVM. ($V_1=6.9$ mRy, $V_2=-2.4$ mRy, $V_3=1.1$ mRy).

III. REDUCTION TO ONE DIMENSION FOR $T\rightarrow 0$

To describe the oxygen vacancy ordering on the Cu-O planes we will make use of three-order parameters [Fig. 1(a)]. The first one, η_1, describes the occupancy of the β sublattice and ranges from -1 (all vacancies) to $+1$ (all oxygen). η_2 and η_3 are defined as the next-nearest-neighbor (NNN) correlation functions, *with* and *without* Cu in between, respectively. The variations of these order parameters with temperature, as calculated with the CVM, are given in Figs. 1(b)–1(d). The two correlations η_1 and η_2, saturate to concentration independent values at low temperature [Figs. 1(b) and 1(c)]. These values correspond to depletion of the β sublattice ($\eta_1=-1$) and formation of perfect O-Cu-O chains ($\eta_2=1$). Therefore, the ground state consists of an empty β sublattice and perfectly ordered O-Cu-O chains for every concentration between 0 and 0.5. The number and arrangement of the chains is determined by the concentration and by the sign of V_3. From the behavior of the correlation functions we can conclude that, at low-temperature, off stoichiometry in the system is accommodated by eliminating chains, instead of breaking them up.

The fact that, to a good approximation, every oxygen at low temperature is bound in a O-Cu-O chain reduces the configurational problem to a one-dimensional one in which filled and empty chains on the not depleted (α) sublattice are represented by spin variables ± 1 on an Is-

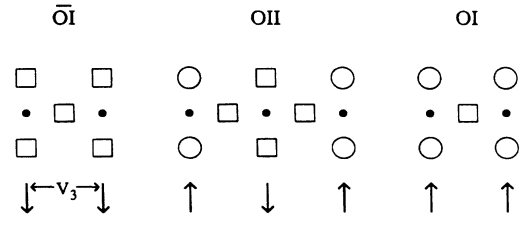

FIG. 3. For fully ordered chains and a "frozen out" sublattice the ordered structures can be mapped onto a one-dimensional model. Spin up (down) represents a completely filled (empty) O-Cu-O chain.

ing chain (Fig. 3) with NN effective interaction equal to V_3. The solutions for this 1D Ising problem are known exactly.[18] At $T=0$, the correspondence between the Ising chain and the 2D model is exact.

Using the fact that $\eta_1=-1$ and $\eta_2=1$, at low enough temperatures, the ASYNNNI Hamiltonian can be mapped onto the Ising chain Hamiltonian. The following relations are then obtained: $\varepsilon=V_3$ and $H_{1D}=H_{2D}+4V_1$, where H_{2D} is the field in the ASYNNNI model and ε and H_{1D} are, respectively, the antiferromagnetic interaction and the field in the one-dimensional Ising model. It is now possible to predict the ground states for the 2D model from the Ising chain solution with $\varepsilon>0$. In one dimension at $T=0$ the antiferromagnetic phase is stable in the absence of a field. The alternation of up and down spins corresponds in the ASYNNNI model to having every other row filled on the α sublattice. This is the OII phase (Fig. 3). When applying large positive (negative) fields, a ferromagnetic state with all spins up (down) is stable, the ASYNNNI equivalent of this being OI ($\overline{O\text{I}}$). In the Ising chain, at exactly $T=0$, these transitions occur for $H_{1D}=2\varepsilon(-2\varepsilon)$. Only at $T=0$ do these transitions create a discontinuity in the relation between concentration and field. Nevertheless, thermodynamically, only the limit for $T\to 0$ is important, and in this limit, the oxygen concentration associated with the $\overline{O\text{I}}\to O$II or OII$\to O$I transition has a definite value. To find these concentrations, we determined the zeroes of the NN correlation function in the Ising chain. This correlation is the 1D equivalent of η_3 and one can easily see that it is $+1$ in perfect OI or $\overline{O\text{I}}$ (ferromagnet) and -1 in perfect OII (antiferromagnet). The zero of this correlation approaches $T=0$ only for average spin 0.5 or -0.5 which fixes the $\overline{O\text{I}}\to O$II and OII$\to O$I boundaries at $c=0.125$ and $c=0.375$, independent of the value of V_1, V_2, and V_3. These phase boundary values make the 2D ground states completely symmetrical around $c=0.25$, in complete agreement with the CVM results of Fig. 2. From the symmetry, imposed by the 1D state, the stable phase must be $\overline{O\text{I}}$, at low temperature and low concentration, and not the tetragonal phase as previously believed.[7,8,10,11,12]

IV. THE MODEL AT LOW TEMPERATURE

The analogy between the ASYNNNI model at low temperature and the Ising chain with NN interactions is very useful for temperatures above $T=0$ as well, as the detailed comparison with CVM and Monte Carlo (MC) results will now show. The MC calculations were performed in the grand canonical scheme on square lattices with 4096 sites, with typically 20 000 MC steps per site. Perfect OI was used as starting configuration for each run. Figure 4(a) reveals that the functional dependence of planar oxygen concentration on chemical potential is quite similar for the 2D MC simulation (at $kT/V_1=0.3$) and in the Ising chain (at $kT/\varepsilon=0.2$). The rapid change in O concentration around $H_{2D}=-3.68V_1$ corresponds to the OII$\to$OI transition and can easily be mistaken for a first-order transition. Even more convincing may be Fig. 4(b) where the specific heat results from the 2D

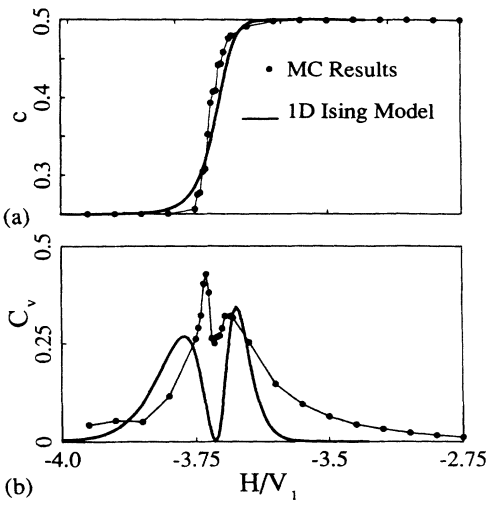

FIG. 4. (a) O concentration as a function of field from the MC simulation and the Ising chain equivalent. MC at $kT/V_1=0.3$. Ising chain at $kT/\varepsilon=0.2$. (b) Specific heat as function of field from MC and Ising chain results; temperatures as in (a).

Monte Carlo simulation and Ising chain solution are plotted for the same range of the external field. For fields around the OII$\to O$I second-order transition, two specific heat peaks occur. Previously, this phenomenon had been attributed[13] to formation of transient phases. These two peaks also show up in the antiferromagnetic Ising chain solution at the corresponding fields. They are simply a Schottky-type anomaly due to the ground-state degeneracy: For $H_{1D}=\pm 2\varepsilon$ any mixing of antiferromagnetic and ferromagnetic domains has the same internal energy and no energy can be absorbed by spin flipping (bond breaking). In the 2D MC result the dip in the heat capacity occurs exactly at the equivalent critical field $H_{2D}=4V_1\pm 2V_3$. It does not drop to zero because of the residual fluctuations in the fully formed chains and on the β sublattice. From analyzing the MC final lattice configurations and average concentrations, we located the OII$\to O$I transition at a field between the peaks; the same holds for the NN correlation in the 1D Ising chain. We believe that this shows that peaks in the heat capacity cannot be taken as a criterion for the OII$\to O$I transition and are no evidence for the presence of definite intermediate "phases"[13] in this model, stable or metastable. This does not exclude the existence of these phases in the $YBa_2Cu_3O_z$ system, but they are probably due to the nonzero interactions normal to the O-Cu-O chains beyond V_3. These interactions would, however, not affect the one-dimensional behavior, reported here. The intermediate phases can be deduced from the class of ground states of the 1D Ising model that maximize the number of unlike NN pairs. The appearance of these additional phases in the phase diagram is discussed elsewhere.[19]

The topology of the CVM phase diagram confirms the trend to one-dimensional behavior at low temperature. The surprising result that the two-phase region between

$T(\overline{OI})$ and OII at intermediate temperature collapses into a second-order line at low temperature was not anticipated in previous work[8] but it can be explained by relating again to the Ising chain: At low temperatures the saturation of some correlation functions drives the system into a pseudo one-dimensional state and a one-dimensional system[20] does not allow for two-phase regions, hence the closure of the two-phase region.

V. CONCLUSION

An oxygen superstructure phase diagram has been calculated by the CVM with a low-temperature modification. The input parameters V_1, V_2, and V_3 were derived from first principles LMTO calculations by Sterne[15] on the $YBa_2Cu_3O_z$ compound. The existence of a low-temperature, low-oxygen, orthorhombic phase, anti-ortho I, first discovered by Kikuchi,[10] was confirmed. It is now clear that this phase must exist for symmetry reasons: at low-temperature CVM calculations of sublattice, interchain and intrachain long-range order parameters clearly show that the asymmetric next-nearest-neighbor Ising (ASYNNNI) model must progressively evolve from two to one-dimensional behavior. Indeed, the 2D CVM calculations converge exactly to the 1D analytical solution indicating that at low temperature every oxygen atom sits in a fully formed O-Cu-O chain. Hence, there are no "free oxygens." The reason for this unusual behavior lies in the asymmetry of the next-nearest-neighbor interactions. Monte Carlo simulations confirm these findings, in particular the split specific heat maxima.

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