Thermodynamics of Oxygen Ordering in $YBa_2Cu_3O_z$

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The ordering in the Cu-O basal plane of $YBa_2Cu_3O_z$ is investigated as a function of oxygen content and temperature. A phase diagram is calculated by application of the cluster variation method to an asymmetric two-dimensional Ising model. The interaction parameters selected guarantee the stability of the experimentally observed double-cell structure around $z = 6.5$. The transition temperatures at various oxygen partial pressures are in good agreement with experiment. The pair probabilities along the Cu-O chains show a plateau with varying oxygen concentration, not unlike the dependence of T_c on oxygen content.

It is by now well established[1-4] that $YBa_2Cu_3O_z$ can exist in at least two different structures, depending on the overall oxygen content and the ordering of the oxygen atoms in the Cu-O basal plane. In the tetragonal ($P4/mmm$) phase the oxygen sites are occupied at random and the material is not superconducting. The high-T_c (92 K) compound possesses orthorhombic ($Pmmmm$) symmetry and contains O-Cu-O chains, believed to be responsible for superconductivity in this and related oxides. Near $z = 6.5$ an ordered double-cell phase has been observed by transmission electron microscopy[3] and x-ray diffraction[4]; its superconducting transition temperature T_c appears to drop to about 60 K.[2]

In previous work,[5,6] the stability of these structures was derived rigorously on the basis of a two-dimensional Ising model with symmetric first-neighbor interaction V_1 and asymmetric second-neighbor interactions V_2 and V_3, the first one linking oxygen sites through the Cu ions, the second one linking those without an intermediate Cu, as shown in Fig. 1(a). Effective pair interactions can in principle be calculated by the imposition of an ordering perturbation on a completely disordered (three dimensional) medium, in the spirit of the generalized perturbation method.[7] However, since no electronic structure calculations for the completely disordered material have been performed, the V_n were considered as parameters, and various stability regions were mapped out.[5,6] For simplicity, these interactions were assumed to be both concentration and temperature independent. The model thus features two phenomenological parameters, the ratios V_2/V_1 and V_3/V_1, with $V_1 > 0$ to insure nearest-neighbor ordering. Ordered structures with twice and four times the original square unit cell were found to occur for various ranges of these parameter ratios.[6] In particular for $V_1 > 0$, $V_2 < 0$, and $0 < V_3 < V_1$, the ordered arrangement of filled and vacant sites in the basal plane is predicted to be that shown in Fig. 1(a) for planar concentration of oxygen $c_0 = 0.50$ ($z = 7.0$) and that

shown in Fig. 1(b) for $c_0 = 0.25$ ($z = 6.5$). In the latter figure, cell doubling is seen to occur along the a direction of the simple orthorhombic structure (the Cu-O-Cu chains lie along the b direction). Such is the structure reported by Van Tendeloo, Zandbergen, and Amelinckx[3] and by Fleming et al.[4] The purpose of the present Letter is to present, for the first time, a two-dimensional Ising-model phase diagram with these two structures as ground states. Accordingly, canonical values $V_1 = 1$, $V_2 = -0.5$, and $V_3 = 0.5$ are used since they guarantee the existence of the proper ordered superstructures, thus ensuring that the phase diagram will have the correct topology.

The statistical thermodynamical model used is the cluster variation method (CVM).[8] Previous work along similar lines[9-13] did not differentiate between V_2 and V_3 and therefore did not contain the cell-doubling phase. The calculations were performed in the four- and five-point cluster approximation of the CVM, leading to en-
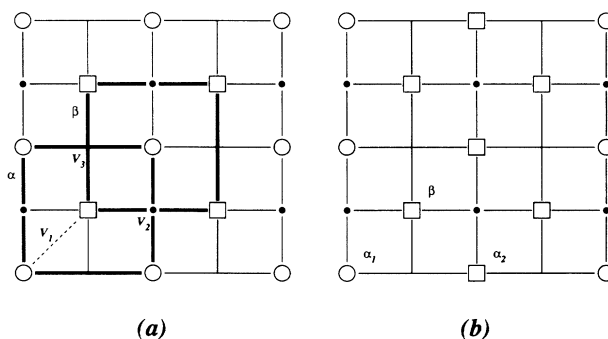

(a)   *(b)*

FIG. 1. Ground states in the Cu-O basal plane. Filled circles, Cu atoms; open circles, oxygen atoms; squares, vacant sites. (a) At $c_0 = 0.50$ two sublattices α and β are present. (b) At $c_0 = 0.25$ a cell-doubling phase gives rise to sublattices α_1, α_2, and β. Pair interactions V_1, V_2, and V_3 are sufficient to stabilize these structures.

tropy expressions containing 25 linearly independent correlation functions for the single-cell phase and 41 for the double cell. It has been established previously[13] that this gives very accurate phase diagrams; for example, the CVM result at $V_2 = V_3 = 0$ is only 4% higher than the exact Onsager solution for the transition temperature at zero field. Moreover, since the CVM is formulated in terms of correlation functions, it contains a wealth of information about ordering parameters, not easily accessible to other methods.

The resulting CVM phase diagram is shown in Fig. 2. Under the assumption of constant effective pair interactions, it is symmetric about the oxygen concentration $c_0 = 0.50$ $[c_0 = \frac{1}{2}(z - 6)]$. The single-phase regions are denoted by two-dimensional space-group symbols: $p4mm$, corresponding to the three-dimensional tetragonal phase ($P4/mmm$), and $p2mm$I and $p2mm$II for the single- and double-cell orthorhombic phases, respective-
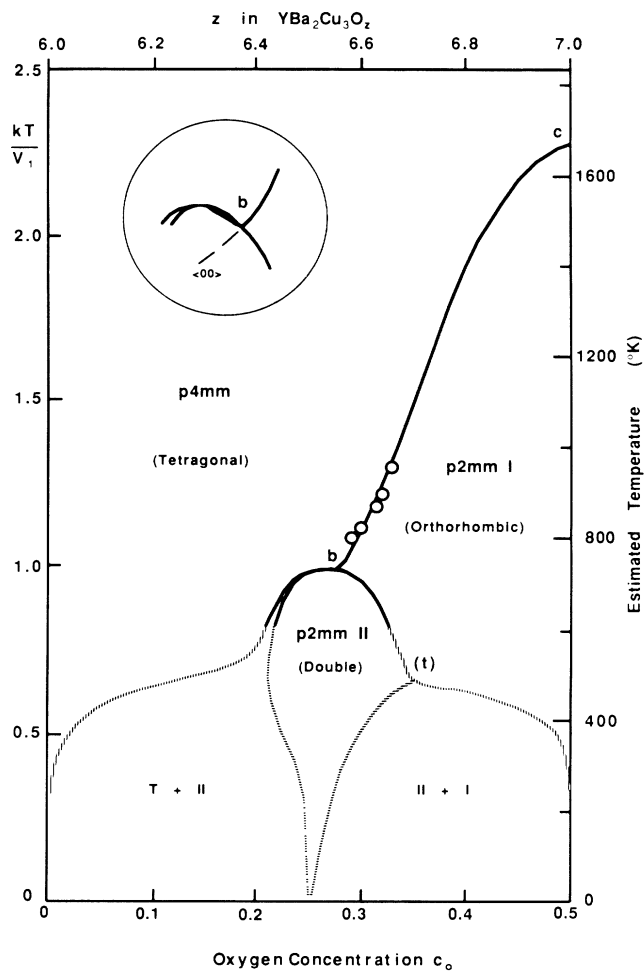

FIG. 2. Phase diagram obtained from CVM calculation; dotted lines are conjectured extensions. The diagram contains a bicritical point (b) and a tricritical point (t). Circles: experimental data of Specht et al. (Ref. 14).

ly. The high-temperature tetragonal phase is separated from the ordered single-cell phase by a line of second-order transitions (line b-c). Since the minimization of the CVM free energy becomes ill posed at low temperatures, no calculated data are available at temperatures below $kT/V_1 \cong 0.8$, but conjectured extrapolations are indicated by dotted lines. Point b appears to be a bicritical point, and a schematic representation of phase equilibrium lines in its vicinity is shown in the inset of Fig. 2: Two lines of second-order transitions (c-b and t-b) meet two first-order phase boundary lines, the separation of which is shown in an exaggerated manner in the inset. The second-order transitions are allowed by the Landau rules. The thin dashed line indicates the metastable $\langle 00 \rangle$ ordering instability or spinodal.[15] Other instability limits may be constructed in the vicinity of the bicritical point,[16] a topic which will be investigated further in a future publication.[17]

A previous CVM calculation[13] for the symmetric case $V_2 = V_3$ showed good agreement with published Monte Carlo[18] and renormalization-group[19] calculations. In such diagrams, cell doubling is absent and second- and first-order transitions meet at a tricritical point, below which a very wide two-phase region is found. It follows that solubility of oxygen in $p4mm$ and vacancies in $p2mm$I must become vanishingly small at low temperatures. In the present asymmetric interaction case, the $p2mm$II phase region breaks up the $p4mm + p2mm$I two-phase field, but the low solubility character of low- and high-concentration phases is not expected to be altered. The (dotted) extrapolations in Fig. 2 have been constructed accordingly. It also follows that the line of second-order transitions between the ordered phases I and II must terminate, at low enough temperatures, at a tricritical point, for example, at the conjectured point marked t in Fig. 2. The presence of a low-temperature tricritical point allows the width of the $p2mm$II phase region to go to zero as the temperature is lowered since it is expected that, at 0 K, the double-cell phase will be stable only at the precise stoichiometry $c_0 = 0.25$ ($z = 6.5$).

The orthorhombic-to-tetragonal transition has been found experimentally to have second-order character. Transition temperatures and oxygen content for oxygen partial pressures of 5×10^{-3}, 2×10^{-2}, 10^{-1}, 2×10^{-1}, and 1 atm were determined recently by Specht et al.[14] These experimental points are shown as open circles in Fig. 2, with transition temperatures increasing monotonically with partial pressure. One point, that at 0.02 atm, was used to fit the temperature scale (see "Estimated temperature" in kelvins at the right-hand side of Fig. 2). All other points were then found to fall very nearly on the line b-c of calculated second-order transitions. Moreover, Specht et al. report an irreversible transformation below about 725 K with very sluggish kinetics.[14] Significantly, the transition is predicted to be a first-

order one between tetragonal and cell-doubling phases. The latter structure was not observed by Specht et al.,[14] however, because of the experimental difficulty of attaining thermodynamic equilibrium.

A large number of independent cluster correlation functions can be determined within the CVM. For example, point correlations are related to the fractional site occupancies x_0^α, x_0^β and $x_0^{\alpha_1}$, $x_0^{\alpha_2}$, and x_0^β for the single- and double-cell phases, respectively, the superscripts indicating sublattices, as illustrated in Figs. 1(a) and 1(b). Sublattice "point" probabilities essentially measure the degree of long-range order, whereas pair probabilities, such as nearest-neighbor, x_1, and next-nearest neighbor, x_2, measure short-range order (SRO). Here, x_1 refers to SRO between the α and β sublattices, while x_2 refers to SRO within a given sublattice in a given crystallographic direction. Of particular interest are x_2^q (for $p2mm$I) and $x_2^{\alpha_1}$ and $x_2^{\alpha_2}$ (for $p2mm$II), since these pair probabilities determine SRO along the O-Cu-O chains within the oxygen-rich sublattice, and hence must be intimately connected to superconducting properties.

Values of these x_2 probabilities are plotted in Fig. 3(a) as a function of oxygen concentration c_0 for the fixed temperature $kT/V_1 = 0.9$. As expected at this relatively low temperature, ordering is almost complete at $c_0 = 0.50$, then decreases practically linearly with decreasing oxygen concentration. The second-order transition from I to II is encountered at about $c_0 \cong 0.31$, at which point sublattices α_1 and α_2 must be distinguished. The full curve in Fig. 3(a) represents the average pair probability $\frac{1}{2}(x_2^{\alpha_1} + x_2^{\alpha_2})$, which exhibits a slope change at $c_0 \cong 0.31$, decreasing at first more slowly than would have been the case for the metastable extension of the I

FIG. 3. Second-neighbor oxygen-oxygen pair probabilities through Cu atoms at $kT/V_1 = 0.9$. (a) Full line, equilibrium probabilities; dashed line, metastable extension of single-cell phase. (b) Decomposition of double-cell probabilities: upper (lower) dashed line corresponds to oxygen-rich (-poor) sublattice; full line is the average value.

phase (dashed curve). Both dashed and full curves drop rapidly below $c_0 \cong 0.26$ corresponding to the maximum ordering temperature of the II-phase region. The dashed curve must change slope discontinuously as the metastable extension of the high-temperature ordering line (the $\langle 00 \rangle$ spinodal) is crossed, at about $c_0 \cong 0.23$, since SRO is now that pertaining to the (metastable) disordered state. As for the equilibrium SRO curve (full line), after dropping linearly in the narrow two-phase region, it rejoins the x_2 curve for the disordered state. Figure 3(b) shows the behavior of $x_2^{\alpha_1}$ (upper dashed line) and $x_2^{\alpha_2}$ (lower dashed line) in the cell-doubling region. The average is plotted as a full line, and corresponds to the full line in Fig. 3(a) over the same concentration range. The rapid decrease of the average pair probability appears to be due to the existence of a pronounced maximum in the O-Cu-O correlation on the α_1 sublattice. Correspondingly, the O-Cu-O correlations on the α_2 sublattice go through a minimum which would in fact be zero for perfect $p2mm$II ordering. It is important to note, however, that pair probabilities for oxygen atoms parallel to the a axis do not show any structure similar to Fig. 3.

It is tempting to relate the O-Cu-O pair probability curve with its plateau-like behavior to the plot of the value of the superconducting transition temperature T_c as a function of oxygen content as determined experimentally by Cava et al.[2,20] In particular, it is suggested here that the 60-K T_c phase observed in the range $z = 6.56$ to 6.7 ($c_0 = 0.28$ to 0.35) is indeed the predicted $p2mm$II phase, the cell-doubling character of which has been observed by electron microscopy[3] and x-ray diffraction.[4] If indeed the presence of O-Cu-O chains is closely related to the existence of a high T_c, it is reasonable to expect that the II-phase, containing, at stoichiometry, only half the density of chains of the I phase, should have a lower T_c than that of the single-cell phase.

To summarize, a CVM calculation was performed on a two-dimensional anisotropic Ising model with first-neighbor (V_1) and second-neighbor (V_2 and V_3) interactions. The ratios V_2/V_1 and V_3/V_1 were chosen so as to stabilize both single-cell ($p2mm$I) and double-cell ($p2mm$II) ordered ground states. It was subsequently found that, by our fitting the magnitude of V_1, experimentally determined[14] transition points could be made to fall very nearly on the calculated line of second-order transitions. Furthermore, the O-Cu-O cluster probability as a function of oxygen content, calculated at 725 K, exhibited a plateaulike behavior, not unlike the one observed by Cava et al.[2,20] for the concentration dependence of the superconducting transition temperature. The fact that the cell-doubling phase has not always been observed in bulk samples must be due to the very sluggish oxygen kinetics below 450 °C, which is the highest temperature at which this phase is expected to be stable according to the present calculation. Moreover,
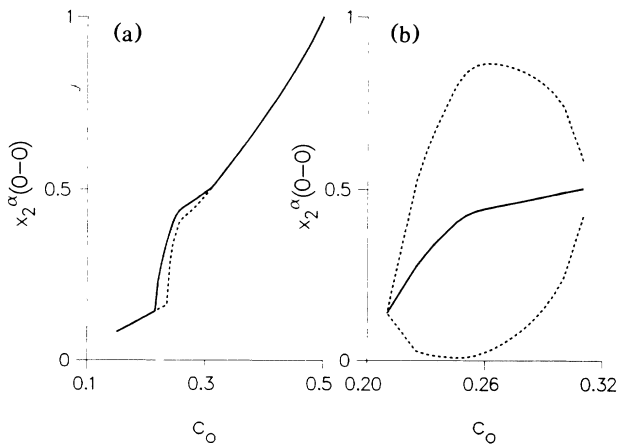
the plane-to-plane correlation may be highly imperfect in the three-dimensional solid. It must be emphasized that the choice of ratios V_2/V_1 and V_3/V_1 used in the computation is not expected to be the optimal one. Preliminary results indicate that, with slight changes of the interaction parameter ratios, the agreement between the calculated points can be improved further.[17]

Confirmation of the position of the second-order transition line would require experiments to be performed at high overpressure of oxygen and at high temperatures where, in fact, other "incoherent" phase changes may occur. The temperature scale on the left-hand side of Fig. 2 and the concentration scale at the bottom of the figure are those of the two-dimensional order-disorder model; the estimated temperature scale on the right-hand side depends on the parameter fit and is therefore approximate. The oxygen content scale (z) at the top of the figure is correct only under the assumption that all oxygen concentration changes occur exclusively in the "basal planes."

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