# First-order structural phase transitions in a lattice-gas model for $YBa_2Cu_3O_{6+x}$

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Recent experiments indicate that the structural phase transitions in the high-temperature superconductor $YBa_2Cu_3O_{6+x}$ may be first order at low temperatures. The oxygen ordering in the Cu-O basal planes of this material may be described by a lattice-gas model introduced by Wille *et al.* [Phys. Rev. Lett. **60**, 1065 (1988)]. However, as recent numerical studies show, this model does not exhibit first-order transitions. Here, we extend the model to include weak attractive interactions (2% of the nearest-neighbor interactions) between next-nearest-neighbor oxygen chains, and we study the extended model using transfer-matrix finite-size scaling. We find that these weak interactions produce tricritical points and first-order transitions at low temperatures, which are in good agreement with experiments for the structural order-order phase transitions. Furthermore, we predict a tricritical point and first-order transitions at low temperatures on the order-disorder branch of the phase diagram. We also present the phase diagram.

Recent experiments[1,2] indicate that the structural order-order phase transition in the high-temperature superconductor $YBa_2Cu_3O_{6+x}$ may be first order at temperatures below 220 K. A lattice-gas model describing the structural phase transitions in this system has been introduced by Wille *et al.*[3-9] As discussed in earlier papers,[3-9] this model reproduces the experimentally observed phases. With the oxygen concentration in the Cu-O basal planes $\theta = x/2$, the phases are a tetragonal phase with $\theta \simeq 0$ (denoted by tetra-0 in Ref. 9) and two orthorombic phases with $\theta \simeq \frac{1}{4}$ and $\theta \simeq \frac{1}{2}$ (denoted by ortho-$\frac{1}{4}$ and ortho-$\frac{1}{2}$, respectively). However, at $T = 0$, the Wille *et al.* model exhibits an infinite number of ground states with $0 < \theta < \frac{1}{4}$ and $\frac{1}{4} < \theta < \frac{1}{2}$ that are degenerate with the ortho-$\frac{1}{4}$ and tetra-0 ground states at the order-disorder transition and with the ortho-$\frac{1}{4}$ and ortho-$\frac{1}{2}$ ground states at the order-order transition, respectively.[9] Furthermore, there are no first-order transitions in this model.[8,9]

Here we present a finite-size scaling transfer-matrix study of an extension of the model by Wille *et al.* The technical details of the calculations performed here were presented in a recent paper by Aukrust *et al.*[9] In a system with antiferromagnetic order, weak attractive interactions that connect sites only on the same sublattice can increase the free-energy gap between the thermodynamically stable phases on each side of the transition and the lowest-lying fluctuations. It is well known that such interactions can cause otherwise second-order phase transitions to become first order at low temperatures.[10-13] We therefore included weakly attractive interactions between next-nearest-neighbor oxygen chains in the Cu-O basal planes in the Hamiltonian. The effect of these interactions is to lower the energies of the tetra-0 and ortho-$\frac{1}{4}$ states with respect to the states with $\theta < \frac{1}{4}$, and to lower the energies of the ortho-$\frac{1}{4}$ and ortho-$\frac{1}{2}$ states with respect to the states with $\frac{1}{4} < \theta < \frac{1}{2}$, thereby lifting the low-temperature degeneracy. The modified Hamiltonian is

$$\begin{aligned}\mathcal{H} - \mu\theta N = &-\Phi_{\mathrm{NN}} \sum_{\langle \mathrm{NN} \rangle} c_i c_j - \Phi_{\mathrm{Cu}} \sum_{\langle \mathrm{NNN_{Cu}} \rangle} c_i c_j \\ &-\Phi_{\mathrm{V}} \sum_{\langle \mathrm{NNN_V} \rangle} c_i c_j - \mu \sum_i c_i \\ &-\Phi_{\mathrm{CC}} \sum_{\langle \mathrm{CC} \rangle} c_i c_j , \end{aligned} \tag{1}$$

where the $c_i$ are the site occupation variables for the oxygen atoms, with $c_i = 1$ if the site $i$ is occupied and $c_i = 0$ if site $i$ is empty. The oxygen chemical potential is $\mu$ and $N$ is the total number of oxygen sites. The term $\Phi_{\mathrm{CC}} \sum_{\langle \mathrm{CC} \rangle} c_i c_j$, in particular, denotes the sum over interactions between oxygen sites located on next-nearest-neighbor oxygen chains. Analogous to $\Phi_{\mathrm{Cu}}$, which couples oxygen sites via the shortest bond that can be drawn through a copper atom, $\Phi_{\mathrm{CC}}$ couples oxygen sites via the second shortest through-copper bonds. The first four sums on the right-hand side (rhs) of Eq. (1) define the original model by Wille *et al.*[3-7] The interactions are shown in Fig. 1.

In order to use the transfer-matrix formalism with layers of manageable size, we consider only interactions that

 

connect nearest-neighbor transfer-matrix layers, as previously done by Kitatani and Oguchi in their study of the antiferromagnetic Ising model on a triangular lattice.[14] In the transfer matrix we therefore retain only those $\Phi_{CC}$ terms which correspond to the dotted lines in Fig. 1. This consequently means that the transfer matrix does not have the full rotational symmetry of the Hamiltonian in Eq. (1). However, we expect that this will not seriously alter the physical results. This is supported by the fact that, for a model in which the interactions between next-nearest-neighbor oxygen chains couple only sites which lie on the *same* transfer-matrix layer, we have obtained results very similar to the ones reported here.[15]

As in Refs. 3–9, we chose the interactions $\Phi_{NN} < 0$, and $\Phi_{Cu} = -\Phi_V = 0.5|\Phi_{NN}|$. To induce first-order transitions at *low* temperatures only, the interaction $\Phi_{CC}$ must be weakly attractive.[13] We chose $\Phi_{CC} = 0.02|\Phi_{NN}|$.

Second-order phase transitions were located by the Nightingale finite-size scaling criterion.[16,17] The finite-size scaling behaviors of the following three different quantities, described in detail elsewhere,[12,13,18–20] were used to locate tricritical points along the transition lines given by the Nightingale criterion: (1) the persistence length $\hat{\xi}_N$ (defined in Refs. 12 and 18); (2) the maximum of the nonordering susceptibility $\chi_N^{max}$ (as defined in Ref. 18); and (3) the eigenvalues of the operator $\Theta$, corresponding to the oxygen concentration $\theta$, in the space spanned by the eigenvectors corresponding to the three and four largest eigenvalues of the symmetric block of the transfer matrix for the order-disorder and order-order transition, respectively.[19,20]

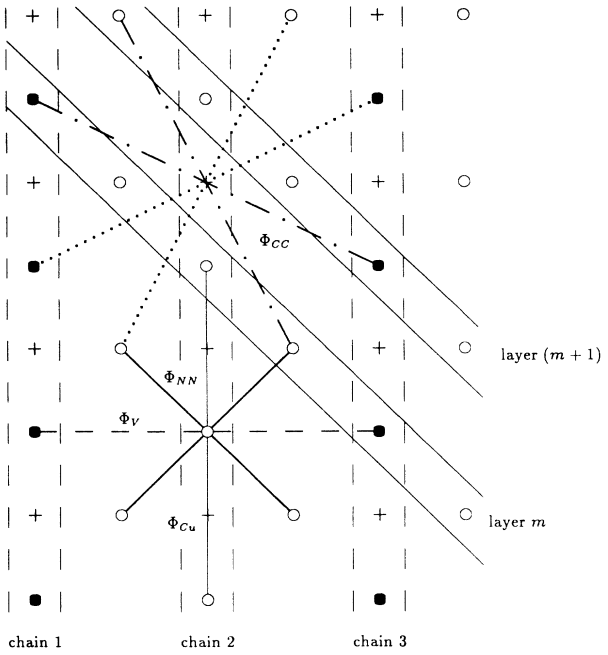


FIG. 1. The interactions for the lattice-gas model are shown over the ground state corresponding to the ortho-$\frac{1}{4}$ phase. The interactions of the Wille *et al.* model are $\Phi_{NN}$ for nearest-neighbor interactions (thick solid lines), $\Phi_V$ and $\Phi_{Cu}$ for next-nearest-neighbor interactions via a vacancy (dashed lines) and a copper atom (thin solid lines), respectively. The additional interaction added here is $\Phi_{CC}$, a next-nearest-neighbor oxygen chain interaction (dot-dashed and dotted lines). Also shown are two transfer-matrix layers and the possible locations for oxygen chains. Interactions between oxygen sites connected by dotted lines are not included in the transfer-matrix calculations. (+) Cu atoms; (■) occupied O sites; and (o) empty O sites.

Estimates for the tricritical temperatures obtained from the three methods are displayed in Table I. The estimates from the first two methods differ by roughly 10%. This difference is consistent with that observed in other lattice-gas models.[18] As was pointed out by Rikvold,[18] the scaling of $\hat{\xi}_N$ yields the more accurate estimate. The scaling for $\chi_N^{max}$ is more robust in cases where a complicated eigenvalue spectrum makes the choice of $\hat{\xi}_N$ ambiguous, but because of its coupling to the heat capacity it tends to yield slightly too high a value for $T_t$.

The quoted errors in Table I are due to numerical uncertainties in estimating the tricritical temperatures. They do not include finite-size effects, which are difficult to estimate.

In order to estimate the tricritical temperatures and the discontinuities in the oxygen concentration $\theta$ from the third method, one needs the tricritical indices $\tilde{\beta}$ and $\tilde{\nu}$, corresponding to the discontinuity in $\theta$ and the divergence of the correlation length, respectively, as the tricritical point is approached *parallel* to the transition line. In the case of the transition between the ortho-$\frac{1}{4}$ and the ortho-$\frac{1}{2}$ states, we estimated $\tilde{\beta}/\tilde{\nu}$, the tricritical temperature, and the coexistence gap from a power-law extrapolation utilizing the sum and the difference of the largest and smallest eigenvalues of the operator $\Theta$, determined from the three strip sizes $N = 4$, 8, and 12.[19] We obtained the tricritical temperature displayed in Table I and $\tilde{\beta}/\tilde{\nu} = 0.17$.

Since this transition belongs to the Ising universality class, $\tilde{\beta}$ and $\tilde{\nu}$ are known. Using the exponent relations given in Ref. 21 and the eigenvalue exponents in Ref. 22 one obtains $\tilde{\beta} = \frac{1}{4}$ and $\tilde{\nu} = \frac{5}{4}$, yielding $\tilde{\beta}/\tilde{\nu} = \frac{1}{5}$. Our estimate is somewhat lower than this value, possibly due to finite-size effects. These are especially evident for $N = 4$, where "wrap-around" effects occur since the interaction between the next-nearest-neighbor oxygen chains is too long ranged to fit on the lattice.

To circumvent this problem, an alternative method

TABLE I. Estimates are shown for the tricritical temperatures, $k_B T_t/|\Phi_{NN}|$, from finite-size scaling using the persistence length $\hat{\xi}_N$, the maximum of the nonordering susceptibility $\chi_N^{max}$, and the eigenvalues of the density operator $\Theta$, for $N = 4$, 8, and 12. See the text for a complete discussion.

| Scaled quantity | Tetra-0 to ortho-$\frac{1}{4}$ | Ortho-$\frac{1}{4}$ to ortho-$\frac{1}{2}$ |
|---|---|---|
| $\hat{\xi}_N$ | 0.106(5) | 0.092(2) |
| $\chi_N^{max}$ | 0.116(2) | 0.103(5) |
| $\theta_N^{\pm}$ | | 0.089(1) |

would be to utilize the tricritical temperature as estimated by the scaling of $\hat{\xi}_N$ to determine $\tilde{\beta}/\tilde{\nu}$ or to take its literature value directly (both of which are consistent) and use a two-point power-law extrapolation involving only the 8 and the 12 lattice strips to estimate the coexistence gap. However, we found that these methods lead to a coexistence gap whose slope is considerably different from zero near the tricritical point.

The order-disorder transition belongs to the universality class of the $XY$ model with cubic anisotropy, which has a two-dimensional order parameter and variable critical indices.[8,9] Using the same three-point power-law extrapolation described above for the order-order transition, however, does not lead to a coexistence gap that converges to zero. We believe this to be a result of the finite-size effects, especially for $N = 4$. To find $\tilde{\beta}/\tilde{\nu}$, we therefore used the two-point power-law extrapolation, utilizing $T_t$ obtained from the scaling for $\hat{\xi}_N$ described above. This led to $\tilde{\beta}/\tilde{\nu} = 0.36$ at a tricritical temperature of $k_B T_t/|\Phi_{NN}| = 0.1065$. The coexistence gap was then calculated from a two-point power-law extrapolation of the difference and a three-point power-law extrapolation of the sum of the largest and the smallest eigenvalue of $\Theta$.

Figure 2 shows the $\theta$-$T$ phase diagram for low temperatures. The coexistence gaps correspond to values of $\tilde{\beta}/\tilde{\nu} = 0.17$ and $\tilde{\beta}/\tilde{\nu} = 0.36$ at the order-order and order-disorder transition, respectively. The high-temperature part of the phase diagram is not shown, since the introduction of $\Phi_{CC}$ gives only an overall increase of the critical temperature between 3% and 9% compared to the Wille *et al.* model. The agreement between the 4/8 and the 8/12 scaling results for the lines of critical points is quite good, except at the order-order transition close to the tricritical point. The experimental data points by Specht *et al.*[23] were used to establish an estimated temperature scale on the right-hand vertical axis of the phase diagram by adjusting the value of $|\Phi_{NN}|$.

The location of the tricritical point on the order-order transition line agrees well with that found in the experiments by You *et al.*,[1] who give $T_t$ in the range 220–240 K. However, this agreement is fortuitous in the sense that we chose $\Phi_{CC}$ only to give $T_t$ approximately one-half of the maximum critical temperature for the ortho-$\frac{1}{4}$ phase. We also predict a tricritical point on the order-disorder transition line. However, our value for its tricritical temperature appears to be slightly too high since one might have expected the experimental data point given by McKinnon *et al.*[24] to lie above the tricritical point rather than below it. This might be for several reasons: First, we did not adjust our value of $\Phi_{CC}$ in order to fit the location of the tricritical points to the available experimental data on the order-order transition line. Second, because of finite-size effects, especially on the smallest lattice $N = 4$, the coexistence gap and the tricritical temperatures could not be obtained very accurately.[25]

In summary, we have demonstrated that the lattice-gas model suggested by Wille *et al.*[3–9] exhibits first-

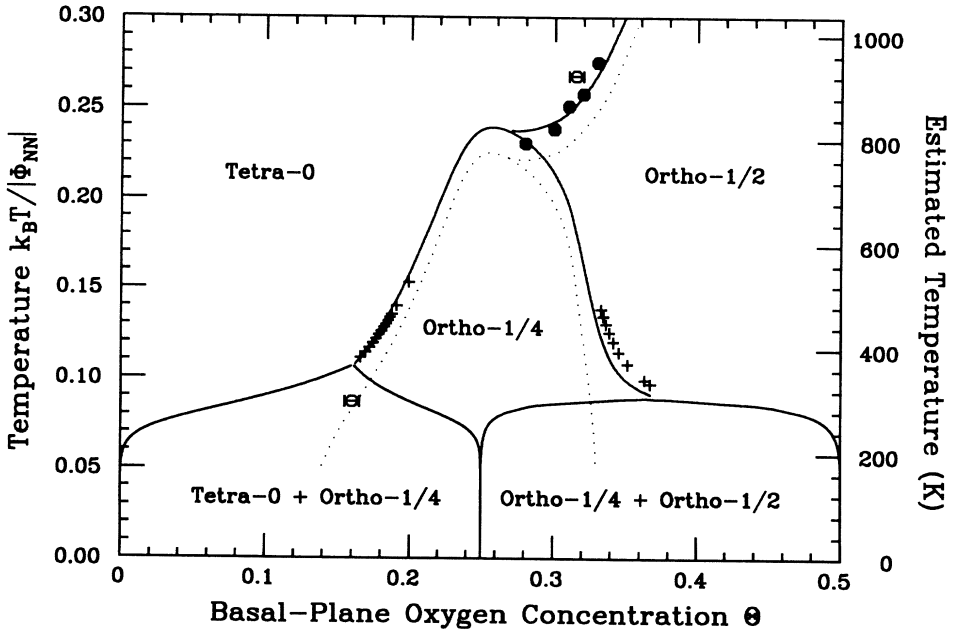


FIG. 2. The $\theta$-$T$ phase diagram at low temperatures is shown. The solid lines were obtained from 8/12 scaling. The + were calculated from 4/8 scaling. The dotted curve corresponds to the original model by Wille *et al.* ($\Phi_{CC} = 0$) obtained from 8/12 scaling (Ref. 9). Also shown are experimental points due to Specht *et al.* (Ref. 23) (solid circles) and McKinnon *et al.* (Ref. 24) (open circles with error bars). They were used to establish an estimated temperature scale on the right-hand vertical axis by adjusting the value of $|\Phi_{NN}|$.

order transitions at low temperatures on both the order-order and the order-disorder branches if one introduces weakly attractive interactions between next-nearest-neighbor oxygen chains. This might be helpful in explaining the possible first-order behavior of the structural order-order transition at low temperatures, observed experimentally[1,2] in the high-temperature superconductor $YBa_2Cu_3O_{6+x}$. Furthermore, if the mechanism of introducing first-order behavior into the Wille model presented here is correct then our prediction is that there should also be a tricritical point at approximately the same temperature on the order-disorder transition line. We also determined the locations of the tricritical points and the approximate shapes of the coexistence gaps associated with the first-order transitions at low temperatures. Moreover, using the location of the tricritical point as determined by the scaling of the persistence length, we were able to give an estimate for the unknown ratio of $\tilde{\beta}/\tilde{\nu}$ for the tricritical point on the tetra-0 to ortho-$\frac{1}{4}$ transition line.

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