Phase diagram and critical properties of a two-dimensional lattice-gas model of oxygen ordering in $YBa_2Cu_3O_z$

N. C. Bartelt and T. L. Einstein
Department of Physics and Center for Superconductivity Research, University of Maryland, College Park, Maryland 20742-4111

L. T. Wille
Department of Physics, Florida Atlantic University, Boca Raton, Florida 33431-0991
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Using transfer-matrix finite-size scaling, we investigate a square lattice-gas model for the oxygen ordering in $YBa_2Cu_3O_z$, which reproduces the experimentally observed orthorhombic and double-cell ordered phases. Contrary to the results of cluster-variational methods of calculation, the phase boundary between the (disordered) tetragonal and double-cell phases is continuous, as is the boundary between the orthorhombic and double-cell phases. Critical properties of the model can be understood by drawing an analogy with the Ashkin-Teller model; numerical results are consistent with this picture. At low temperature and low oxygen concentration, there is complicated behavior, possibly indicative of a second orthorhombic phase.

I. INTRODUCTION

A two-dimensional statistical mechanical model has recently been proposed[1] for the ordering of oxygen atoms in the Cu-O basal plane of $YBa_2Cu_3O_z$. This model is designed to reproduce the experimentally observed structures: the high-oxygen-content orthorhombic phase, the double-cell phase, and the low-oxygen-content tetragonal phase. The detailed temperature- (oxygen-) content phase diagram for this model has been estimated using the cluster variational method (CVM).[1,2] Work on this model and its relevance to physical systems has just been reviewed.[3] In this paper we estimate the phase diagram using the transfer-matrix scaling approach. Compared to CVM this approach is typically more accurate, especially in two dimensions; also it allows critical behavior to be classified.

In the proposed lattice-gas model, the oxygen atoms can occupy sites on a discrete square lattice and have only pairwise interactions in the Cu-O basal plane. The lattice appropriate for this plane is shown in Fig. 1. In this model, the energy of the system increases by E_1 when a pair of nearest-neighbor sites are simultaneously occupied. If next-nearest-neighbor sites are occupied, the energy is changed by E_2 or E_3, depending on whether there is a copper atom (closed circle) between the next-nearest-neighboring sites. Notice that the direction of the E_2 and E_3 bonds alternates from site to site.

In the particular model proposed by Wille *et al.*,[1] E_1 and E_3 are repulsive (positive), while E_2 is attractive (negative), with $E_3=0.5E_1$ and $E_2=-E_3$. The attractive E_2 stabilizes the oxygen "chains," which are characteristic of the high oxygen content ($c=0.5$) orthorhombic phase [Fig. 1(a)]. The repulsive E_3 is necessary for the intermediate-oxygen-content ($c=0.25$) double-cell phase [Fig. 1(b)].

II. ANALOGY WITH ASHKIN-TELLER MODEL: LANDAU CLASSIFICATION

As a first step in the analysis of the phase diagram for this system, we describe the connection between it and the phase diagram for the Ashkin-Teller model. In Fig. 2 we have divided the lattice into four sublattices: A, B, C, and D. In the orthorhombic phase either the A and C or the B and D sublattices are preferentially occupied. In the double-cell phase one of the four sublattices is preferentially occupied. This leads one to introduce three different local order parameters:

$$\begin{aligned} s&=(n_A-n_B)-(n_C-n_D)\,,\\ t&=(n_A-n_D)-(n_C-n_B)\,,\\ p&=(n_A+n_C)-(n_B+n_D)\,, \end{aligned} \tag{1}$$

where n_A, n_B, n_C, and n_D are local sublattice occupancies. These three order parameters describe all the critical fluctuations of the system (at fixed total-oxygen content). In the orthorhombic phase $\langle s\rangle=\langle t\rangle=0$, but $\langle p\rangle\neq 0$; the two possible ordered states have the same absolute value of $\langle p\rangle$ but differ in sign. In the double-cell phase $\langle s\rangle$ and $\langle t\rangle$ are nonzero; the four combinations of $\langle s\rangle=\pm 1$, $\langle t\rangle=\pm 1$ correspond to the four ground states of the double-cell phase. In the disordered phase—where tetragonal symmetry is regained—$\langle s\rangle$, $\langle t\rangle$, and $\langle p\rangle$ are all zero.

The usual way[4] of classifying the possible continuous phase transitions of a particular model is to expand the Landau free energy in terms of the local order-parameter components: One constructs combinations of the mean order parameters, which are invariant under the symmetry operations of the original lattice. In this case translation of the lattice by the vector $\mathbf{t}_1$ of Fig. 2 causes the A and C sublattices to be interchanged. This causes s to go

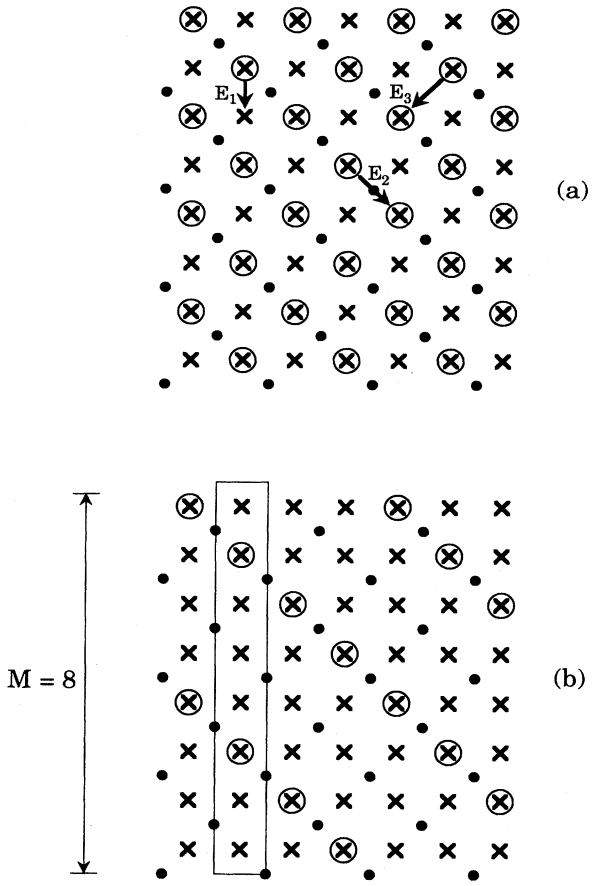

FIG. 1. The ordered phases and interactions of the lattice-gas model for oxygen atoms on a square grid, considered in this paper. X's denote the sites; if circled, oxygens occupy them. Dots denote copper atoms. (a) The orthorhombic phase. (b) The double-cell phase. In (a) the interactions of the lattice-gas model are indicated: Nearest-neighbor repulsions E_1 and diagonal, next-nearest-neighbor interactions E_2 or E_3, depending on whether or not there is a copper at the center of the cell. In (b) the column geometry and transfer direction of the transfer matrix are also shown.

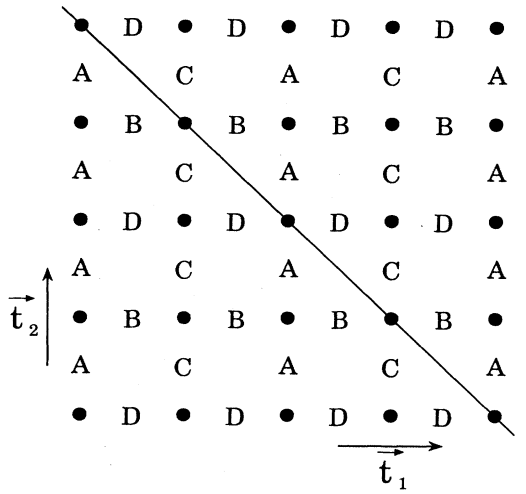

FIG. 2. The four sublattices ($X \rightarrow A$, B, C, and D) with which we define the local order parameters. The axes of this lattice are rotated 45° compared with Fig. 1.

to $-t$, t to go to $-s$, and p to be unchanged. Similarly, translation by $\mathbf{t}_2$ causes B and D to be interchanged, which causes s and t to be interchanged, with p unchanged. Reflection about the line drawn in Fig. 2 interchanges B with C and D with A, which gives $s \rightarrow -s$, $t \rightarrow t$, and $p \rightarrow -p$. Constructing the combinations of $\langle s \rangle$, $\langle t \rangle$, and $\langle p \rangle$, which are invariant to these operations, we find

$$F = r_1(\langle s \rangle^2 + \langle t \rangle^2) + u_1(\langle s \rangle^2 + \langle t \rangle^2)^2 + v_1\langle s \rangle^2\langle t \rangle^2 + r_2\langle p \rangle^2 + W\langle s \rangle\langle t \rangle\langle p \rangle + \cdots .$$

This free energy has the same structure as that for the Ashkin-Teller model.[5] In the Ashkin-Teller model s and t are Ising-type spins coupled by a four-spin term, and $p \equiv st$. Much is known about the critical behavior of the Ashkin-Teller model.[5] By analogy with this known behavior, the orthorhombic to tetragonal (disorder) transition should be Ising type (if second order), as should the double cell to orthorhombic transition. The double cell to tetragonal transition should be in the same universality class as the X-Y model with cubic anisotropy; that is, the critical exponents should vary as a function of chemical potential (or oxygen content). At the point where all the phases meet, the transition should be in the four-state Potts class.

III. TRANSFER-MATRIX SCALING

The direction of transfer of the transfer matrix is indicated in Fig. 1(b). Notice that this direction of propagation treats the two ground states of the orthorhombic phase symmetrically.[6] In order to treat the double-cell phase correctly, we used only strip widths, M, which are multiples of four.

Figure 3 shows the chemical-potential dependence of the absolute value of the four largest eigenvalues of the transfer matrix for $M = 12$ for a temperature where all three phases appear. At small chemical potentials μ (or low oxygen content) there is only one dominant eigenvalue. At intermediate μ the first four eigenvalues are comparable in magnitude. At high μ only the largest two eigenvalues are comparable in size.

The degeneracy of the leading eigenvalue in the limit of infinite system size is a signature of a symmetry breaking in the thermodynamic limit. In this case, the nature of the symmetry breaking can be determined from the symmetries of the associated eigenvectors. At high μ the eigenvector of the second largest eigenvalue changes sign when a column [see Fig. 1(b)] is reflected about one of the copper atoms. (For more details see the Appendix.) The largest eigenvalue of this type we denote λ_r. The asymptotic degeneracy of λ_r with the largest eigenvalue λ_0 is a sign of the symmetry breaking associated with an orthorhombic phase. As shown in Fig. 3, λ_0 and λ_r are nearly

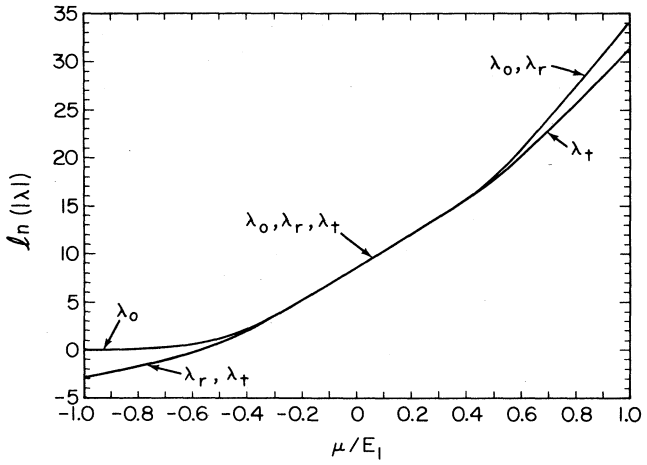

FIG. 3. The (logarithm of the) four largest eigenvalues of the transfer matrix at $T=0.175E_1/k_B$ as a function of chemical potential, for strip width $M=12$. For reasons discussed in the text, there are two eigenvalues with exactly the same value of $|\lambda_t|$; the other eigenvalues are of course never exactly degenerate; they only appear so on the scale of the figure.

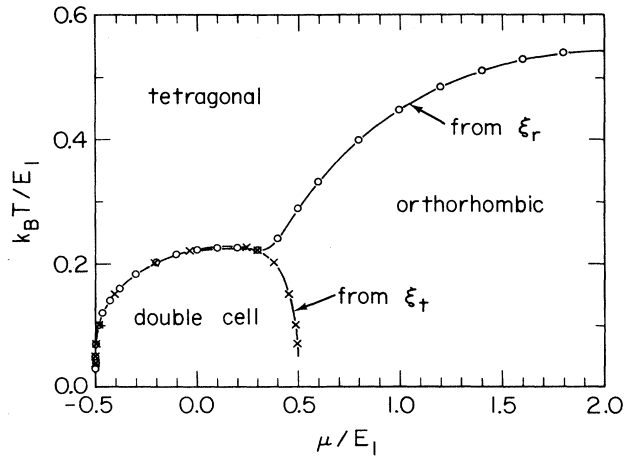

FIG. 4. Estimates of the temperature-chemical-potential phase diagram from transfer-matrix scaling. Solid lines: 8-12 scaling. ○'s: 12-16 scaling of ξ_r; ×'s: 12-16 scaling of ξ_t.

degenerate at high μ, signaling the presence of the high-oxygen-content orthorhombic phase. At intermediate chemical potentials there are two more large eigenvalues in addition to λ_r. These eigenvalues, which are exactly degenerate in magnitude (one is positive, the other negative—see the Appendix for an explanation), have eigenvectors that change sign when the lattice is displaced by two lattice constants. We call the magnitude of these eigenvalues λ_t. The asymptotic degeneracy of λ_r and λ_t with λ_0 (cf. Fig. 3) is a signature of the symmetry breaking associated with the double-cell phase.

Finite-size scaling theory predicts that when second-order phase transitions occur, the appropriate correlation length should grow linearly with strip width M,[7,8] for sufficiently large M. Thus one expects

$$\xi_{r,M}^{-1}=\ln\left[\frac{\lambda_{0,M}}{\lambda_{r,M}}\right]=\pi\eta_r/M \tag{2}$$

at the orthorhombic-to-tetragonal and double-cell–to–tetragonal phase transitions, and

$$\xi_{t,M}^{-1}=\ln\left[\frac{\lambda_{0,M}}{\lambda_{t,M}}\right]=\pi\eta_t/M \tag{3}$$

at the double-cell–to–tetragonal and double-cell–to–orthorhombic transitions. We estimated the phase boundaries with Eqs. (2) and (3) by using the standard method of finding where $\xi_M/M=\xi_N/N$ for two strip widths M and N. Notice we have two different estimates of the double-cell–to–tetragonal phase boundary from the two correlation lengths. If the correlations at critical points located in this way are conformally invariant,[9] then η_r and η_t can be identified with the exponents governing the long-range decay of correlation functions, i.e., anomalous dimensions times 2.[9,10] The question of whether the correlations at the transitions considered here are in fact conformally invariant will be discussed below.

The $T-\mu$ phase diagram generated with transfer-matrix scaling is shown in Fig. 4. Figure 5 shows the associated temperature-concentration phase diagram. Strips of width 8 and 12 were used to generate most of these phase diagrams. Strips of width 12 and 16 were used to check convergence; these results are shown by points in Figs. 4 and 5. Except at low concentrations on the temperature-concentration phase diagram, convergence is good; the complications in that regime will be discussed at the end of the next section.

The transition temperature at an oxygen content of $c=0.5$ can be found to high precision, as shown by the results listed in Table I. (In this case strip widths which are multiples of 2 were used because of the large distance from the double-cell phase.) CVM (Ref. 1) overestimates

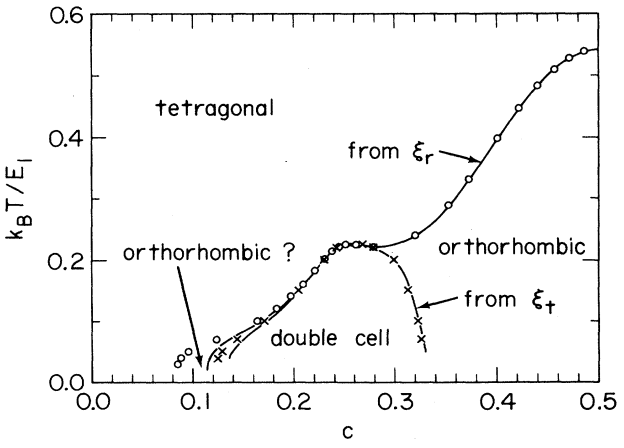

FIG. 5. Estimates of the temperature-concentration phase diagram. Solid lines: 8-12 scaling. ○'s: 12-16 scaling of ξ_r; ×'s: 12-16 scaling of ξ_t.

TABLE I. Sequence of estimates for T_c at a concentration of 0.5 ($\mu=2E_1$). The extrapolations come from a fit of the last three rows to a power law.

Strip widths	k_BT_A/E_1	ν	η_r
4–6	0.540 128 1	0.983 220	0.240 544 5
6–8	0.540 749 6	0.997 448	0.242 463 1
8–10	0.541 352 5	0.999 450	0.244 958 3
10–12	0.541 644 8	0.999 908	0.246 475 7
12–14	0.541 793 7	1.000 070	0.247 409 1
14–16	0.541 877 0	1.000 135	0.248 017 9
Extrapolations	0.5402	1.0002	0.2502

our extrapolated value of the transition temperature by about 5%.

Estimates of the critical exponent ν were obtained in the standard fashion.[7,11] The estimated values of ν at $c=0.5$ (i.e., $\mu=2E_1+2E_2+2E_3=2E_1$), listed in Table I are consistent with the Ising value of 1, again to high precision. (Since the lattice-gas Hamiltonian contains only pairwise interactions, there is "particle-hole" symmetry about $c=\frac{1}{2}$, so that the $\mu=2E_1$ isobar is vertical on a $T-c$ plot.) Figure 6 shows the variation of ν along the phase boundary determined by the length-like scaling of the correlation length associated with λ_r. Above $\mu\cong 0.5E_1$ (i.e., when $T\gtrsim 0.25E_1/k_B$ or $c\gtrsim 0.35$), the estimated values of ν are close to the Ising value of 1. At lower values of μ the estimate of ν begins to change dramatically. At $T=0.225E_1/k_B$, where examination of λ_t suggests that the double-cell phase starts to appear, the 8-12 estimate of ν drops to 0.70, close to the value of $\frac{2}{3}$ expected for the four-state Potts model. For lower T or μ, where the analogy with the Ashkin-Teller model suggests ν should be nonuniveral,[12] ν does seem to vary continuously. This variation is similar for the 8–12 and the 12–16 estimates, suggesting that it is not a finite-size effect.

Figure 7 shows the estimates of ν obtained from ξ_t. The behavior is roughly the same as in Fig. 6: Ising-type along the orthorhombic–to–double-cell boundary and continuously varying on the double-cell–to–tetragonal boundary. The convergence along the orthorhombic to double-cell phase is not very good; the larger strip widths, however, give results closer to the Ising value of 1.

If the correlations at the (two-dimensional) critical points are conformally invariant, the η's in Eqs. (2) and (3) yield estimates of anomalous dimensions of the correlations. A requirement of conformal invariance is that the correlation functions be isotropic at large distances. Because the orientational dependence of the interfacial free energy between the two (degenerate) ordered orthorhombic phases is fourfold symmetric, it is easy to imagine that the large-distance correlation functions are isotropic and thus that the correlations at orthorhombic-to-tetragonal critical points are conformally invariant. Indeed, as Fig. 8 and Table I show, the value of η_r on the orthorhombic-to-tetragonal phase boundary is consistent with the value of $\frac{1}{4}$, the anomalous dimension of the Ising (and four-state Potts) model. However, the interfacial free energies between pairs of the fourfold degenerate phases of the double-cell phase are only twofold symmetric. This anisotropy grows larger as the temperature decreases. Thus, it seems unlikely that the large-distance correlations of critical points involving the double-cell phase are conformally invariant. Thus it would be hazardous to associate an anomalous dimension with η_r in Fig. 8 at low chemical potentials, or with η_t shown for reference in Fig. 9. (On the other hand, if the correlations were conformally invariant, then the behavior of η_t at high μ would be inconsistent with the Ising designation of the transition between orthorhombic and double-cell phases.)

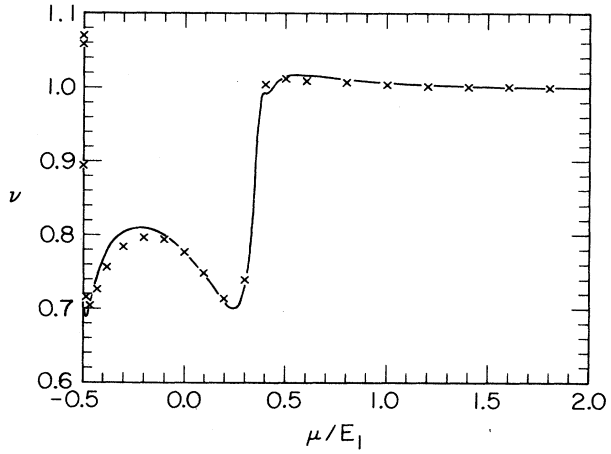

FIG. 6. Estimate of the critical exponent ν as a function of μ, using the correlation length ξ_r. Solid line: 8-12 scaling; ×'s: 12-16 scaling.

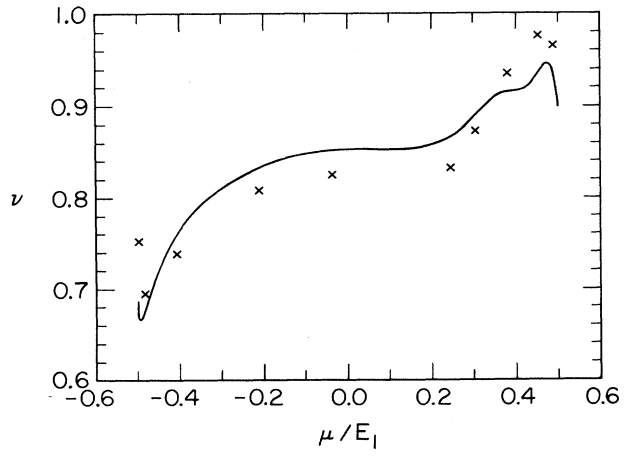

FIG. 7. Estimate of the critical exponent ν obtained using ξ_t. Solid line: 8-12 scaling; ×'s: 12-16 scaling.

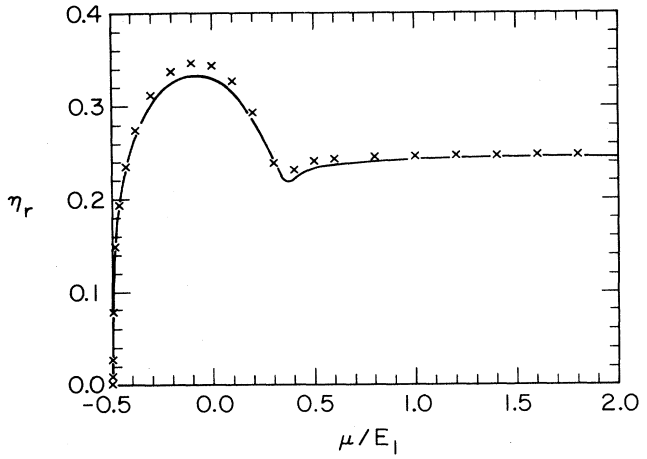

FIG. 8. Estimate of η_r from Eq. (2). For Ising transitions, one expects $\eta=\frac{1}{4}$. Solid line: 8-12 scaling; ×'s: 12-16 scaling. As discussed in the text, η_r should probably not be identified with a correlation-function exponent at small chemical potentials.

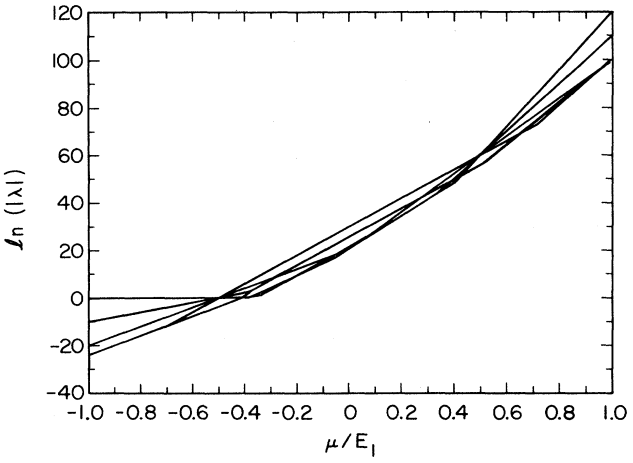

FIG. 10. The chemical-potential dependence, for $M=12$, of the seven largest eigenvalues that have eigenvectors which are even under reflection of a column about a copper site, and are even under translation of a column by two oxygen sites. The logarithm of the largest eigenvalue is proportional to the free energy.

IV. LOW-TEMPERATURE BEHAVIOR

All of the aforementioned analysis assumed that the phase boundaries are continuous, and the values of ν we obtain are consistent with the types of continuous transitions predicted by the Ashkin-Teller model. At zero temperature, however, there is, at least formally, a first-order transition: the dependence of the (free) energy (given by the logarithm of the largest eigenvalue of the transfer matrix) on chemical potential at a low temperature is shown in Fig. 10. From this it is clear that at zero temperature there are two discontinuities in slope: one at $\mu=-0.5E_1$ (corresponding to a jump between $c=0$ and $c=\frac{1}{4}$ another at $\mu=+0.5E_1$ (with a jump between $c=\frac{1}{4}$ and $c=\frac{1}{2}$). The question then arises of whether these discontinuities exist at finite temperature. This can be a difficult question to answer on the basis of numerical work on finite systems. However, Fig. 11 shows the dependence of the compressibility $\kappa\equiv k_B T(\partial c/\partial\mu)$ at a low temperature as a function of c for several M. The maximum compressibilities grow less quickly than linearly with M. This sublinear growth contrasts starkly with the expontial growth of the maximum compressibility with M expected at a first-order phase transition.[8] Similar behavior is seen along all the phase boundaries drawn in Figs. 4 and 5; all phase transitions seem continuous. This conclusion is consistent with the very careful Monte Carlo finite-size scaling studies of Aukrust *et al.*[13] and examination of the size dependence of the ordering susceptibilities.

It is perhaps not surprising that the zero-temperature "first-order" transition becomes continuous at finite temperature: We first note that at $\mu=-0.5E_1$ and again at

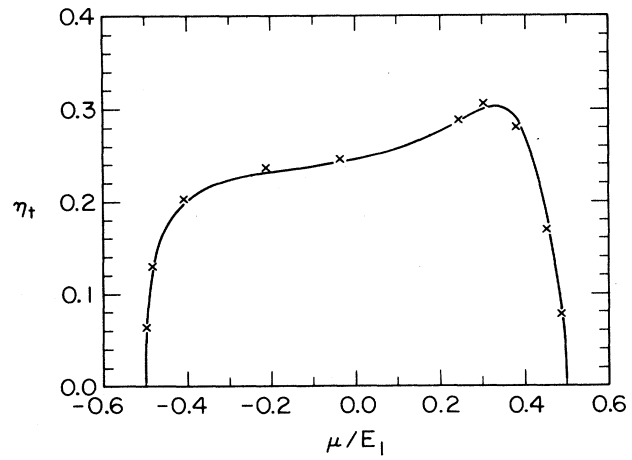

FIG. 9. Estimates of η_t from Eq. (3). Solid line: 8-12 scaling; ×'s: 12-16 scaling. As discussed in the text, η_t should probably not be identified with a correlation-function exponent.

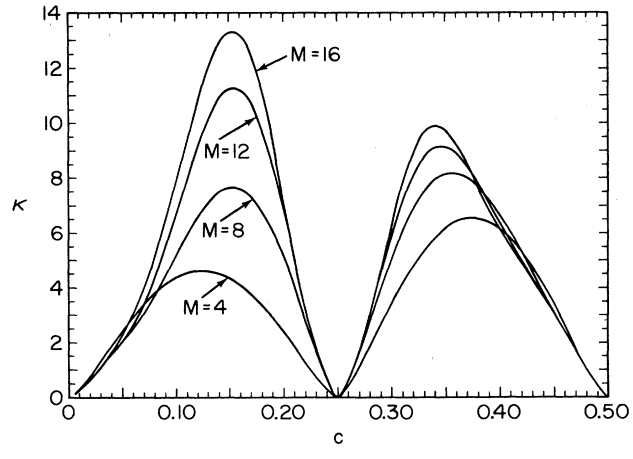

FIG. 11. The concentration dependence of the compressibility κ for different strip widths, M, at a temperature of $0.05E_1/k_B$. The slow increase of $\kappa_{\max}$ with M is inconsistent with the behavior expected at a first-order transition.

$\mu = +0.5E_1$ there are at $T=0$ an infinite number of states on an infinite lattice that are degenerate in energy, corresponding to each configuration of the lattice with complete rows of oxygen atoms. (In the $-0.5E_1$ case, of course, there must be at least one empty diagonal between occupied diagonals.) In a finite system this degeneracy shows up clearly in the eigenvalue spectrum, shown in Fig. 10 for strip width $M=12$: Each of the eigenvalues that appear to cross through the points $\mu=\pm 0.5E_1$ corresponds to a particular configuration of a column, consistent with complete rows of oxygen atoms. The number of these states grows expontially with M. (In the problem of the equilibrium crystal shapes for Kossel crystals with short-ranged interactions, a similar degeneracy occurs because for ranges of orientations all surfaces with straight "steps" have equal energy, regardless of the position and number of the steps.) It has been argued[14] that at nonzero temperature, this type of degeneracy is broken by entropy, favoring the intermediate concentration configurations and rounding the discontinuity in the free energy (analogous to the rounding of the corner of the equilibrium crystal shapes.[15]

The scaling of ξ_t at higher concentrations than ξ_r, which is visible in Fig. 5 at low concentrations, intimates the possible existence of a low-concentration orthorhombic phase. Recent CVM calculations[2] also suggest the existence of this phase. Its existence does seem plausible: While the states which are degenerate at zero temperature, discussed earlier, do not break the translation symmetry of the lattice, they all break the rotational symmetry. The question then again is whether this broken symmetry extends to finite temperature. If there is a low-concentration orthorhombic phase, the critical properties of its phase transitions should be the same as that of the high-concentration orthorhombic phase: the sudden drop of ν, seen in Fig. 6, to ~ 0.68 and subsequent rise to a value close to 1 as the chemical potential nears $-0.5E_1$ appears to be a mirror image of the (Ashkin-Teller-type) behavior seen at higher chemical potentials.[12] We have found more definitive evidence for such a low-concentration phase in a slightly different lattice-gas-model (one in which an adsorbed $p(2\times 2)$ phase on a square lattice disorders through a low-coverage $c(2\times 2)$ phase.[16] Here, however, we find poor convergence of the location of the phase boundaries. (Compare the 8-12 and 12-16 estimates of the phase boundary in Fig. 5.) Moreover, the complexity of the eigenvalue spectrum discussed earlier, in particular the multiple degeneracy, does not occur in that model. Given the complexity in the eigenvalue spectrum at low temperatures, our calculations cannot be said to give definitive evidence for the existence of a low-coverage orthorhombic phase.

V. CONCLUSIONS

With transfer-matrix finite-size scaling we can accurately compute the phase diagram for this lattice-gas model of O ordering in $YBa_2Cu_3O_z$. The low-double-cell–to–orthorhomic and double-cell--to–tetragonal phase boundaries appear to be continuous: The structure of the phase diagram appears to be similar to that of the Ashkin-Teller model. There are suggestions of a low-oxygen-concentration orthorhombic phase.

Finally, it is interesting to investigate what these findings imply for the ordering behavior of the $YBa_2Cu_3O_z$ superconducting compounds. The model being studied has been constructed to possess just three phases. There have been some reports of other phases with larger unit cells, in particular, ones with reciprocal lattice vectors $\frac{1}{3}$ and $\frac{1}{5}$ as large.[3,17] If these correspond to stable phases, rather than transients, the model will have to be extended to include further neighbor pair or multisite interactions. As a test of the validity of the present model in describing "universal" properties of the real system, it would certainly be important to measure experimentally the critical exponents associated with the transitions. Moreover, the predicted continuous transition between the double-cell and single-cell phases disagrees with the work of You *et al.*,[18] where indirect evidence of phase separation is reported. Further experimental study of this situation is warranted.

ACKNOWLEDGMENTS

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APPENDIX: SYMMETRIES OF IMPORTANT EIGENVECTORS

Here we discuss the symmetry properties of the eigenvectors of the transfer matrix $\underline{T}$. Define two operators $\underline{R}$ and $\underline{P}$: $\underline{P}$ permutes the sites in a column [see Fig. 1 (b)]by two lattice units; $\underline{R}$ reflects a column of sites about one of the copper atoms. $\underline{P}$ obviously commutes with the transfer matrix, so eigenvectors of $\underline{T}$ are eigenvectors of $\underline{P}$. $\underline{R}$ does not commute with $\underline{T}$. However, $\underline{TR}=\underline{RPT}$. So suppose $\mathbf{x}$ is an eigenvector of $\underline{T}$ with eigenvalue λ with the property $\underline{P}\mathbf{x}=\mathbf{x}$. Then $\underline{T}(\underline{R}\mathbf{x})=\lambda(\underline{R}\mathbf{x})$. Thus $\underline{R}\mathbf{x}=a\mathbf{x}$. The eigenvalues of $\mathbf{R}$ are ± 1, so $a=1$ or -1. The maximum eigenvalue with $\underline{R}\mathbf{x}=\mathbf{x}$ and $\underline{P}\mathbf{x}=\mathbf{x}$, which is the largest eigenvalue of $\underline{T}$,[19] is labeled λ_0 in the text. The largest eigenvalue with $\underline{R}\mathbf{x}=-\mathbf{x}$ and $\underline{P}\mathbf{x}=\mathbf{x}$, which is associated with orthorhombic symmetry breaking, is labeled λ_r. Now suppose $\mathbf{x}$ is an eigenvector of $\underline{T}$ with eigenvalue λ but with $\underline{P}\mathbf{x}=-\mathbf{x}$. Then $\underline{T}(\underline{R}\mathbf{x})=-\lambda(\underline{R}\mathbf{x})$. Thus $\underline{R}\mathbf{x}$ is also an eigenvector of $\mathbf{x}$ with eigenvalue $-\lambda$; this leads to the twofold degeneracy in absolute value mentioned in the text. The largest eigenvalue with $\underline{P}\mathbf{x}=-\mathbf{x}$ is denoted λ_t in the text.

[1]L. T. Wille, A. Berera, and D. de Fontaine, Phys. Rev. Lett. **60**, 1065 (1988).

[2]R. Kikuchi and J. -S. Choi, Physica C-160, 347 (1989); (private communication).

[3]L. T. Wille, Phase Transitions (to be published).

[4]E. Domany, M. Schick, J. S. Walker, and R. B. Griffiths, Phys. Rev. B **18**, 2209 (1978); M. Schick, Prog. Surf. Sci. **11**, 245 (1981).

[5]P. Bak, P. Kleban, W. N. Unertl, J. Ochab, G. Akinci, N. C. Bartelt, and T. L. Einstein, Phys. Rev. Lett. **54**, 1539 (1985), and references therein.

[6]We performed some calculations with a transfer-matrix direction rotated by 45° from that indicated in Fig. 1. Similar results were obtained as those presented in this paper for $T \gtrsim 0.15 E_1/k_B$. However, the low-temperature regions on the temperature-concentration phase diagram were significantly displaced from those appearing in Fig. 5. Because the boundary conditions in this case break the degeneracies between the ground states of the ordered phases, we assume that these results are less reliable than those presented in Fig. 5.

[7]M. N. Barber, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1984), Vol. 8, p. 145.

[8]M. P. Nightingale, J. Appl. Phys. **53**, 7927 (1982).

[9]J. Cardy, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1987), Vol. 11, p. 55.

[10]M. E. Fisher, in *Collective Properties of Physical Systems,* edited by B. Lundqvist and S. Lundqvist (Academic, New York, 1974), p. 16.

[11]M. N. Barber, Phys. Rev. B **27**, 5879 (1983).

[12]Along the special line in the Ashkin-teller model, ν is expected to increase monotonically and continuously from $\frac{2}{3}$ as one moves away from the four-state Potts point. If the Ashkin-Teller quartic coupling is real, the upper bound of ν is 2, but more generally ν could increase withoug bound. [See, e.g., Fig. 4 of L. P. Kadanoff and A. C. Brown, Ann. Phys. (N.Y.) **121**, 318 (1979).] (Note that $\nu = \infty$ corresponds to a Kosterlitz-Thouless transition, i.e., the zero-anisotropy limit of an XY model with cubic anisotropy.) The turnover below $\mu/E_1 \sim -0.2$ in Fig. 6 could be due to the existence of the low-concentration orthorhombic phase, which would be associated with a second Ashkin-Teller model and a second four-state Potts point slightly above $\mu/E_1 = -\frac{1}{2}$.

[13]T. Aukrust, M. A. Novotny, P. A. Rikvold, and D. P. Landau (unpublished); (private communication).

[14]C. Rottman and M. Wortis, Phys. Rev. B **29**, 328 (1984); M. Wortis, in *Chemistry and Physics of Solid Surfaces VII,* edited by R. Vanselow and R. Howe (Springer, Berlin, 1988), p. 367.

[15]It is unclear how strict this analogy with equilibrium crystal shapes is. Taken strictly it would predict incommensurate phases with algebraic decay of correlations at low temperatures. To investigate the possibility of the existence of low-temperature (striped) incommensurate phases we examined the concentration dependence of the quantity

$$y_{\text{eff}} = -\ln[\xi(M-4)/\xi(M)]/\ln[(M-4)/M] \ .$$

In a phase with algebraic decay of correlation, y_{eff} should be equal to 1; i.e., if a phase with algebraic decay of correlations exists, it would show up as a plateau in the concentration dependence of y_{eff}. [See M. P. M. den Nijs, M. P. Nightingale, and M. Schick, Phys. Rev. B **26**, 2490 (1982).] We found no indication of such a plateau at any temperature, although with the relatively small strip widths (compared with the size of the double-cell unit cell) used, this effect might be difficult to detect.

[16]N. C. Bartelt, L. D. Roelofs, and T. L. Einstein, Surf. Sci. (Lett.) **221**, L750 (1989).

[17]R. Beyers and T. M. Shaw, Solid State Phys. **42**, 135 (1989).

[18]H. You, J. D. Axe, X. B. Kan, S. Hashimoto, S. C. Moss, J. Z. Liu, G. W. Crabtree, and D. J. Lam, Phys. Rev. B **38**, 9213 (1988).

[19]L. K. Runnels and L. L. Combs, J. Chem. Phys. **45**, 2482 (1966).