Oxygen Ordering in the Basal Plane of YBa$_2$Cu$_3$O$_y$: Ground States

Joachim Stolze
Institut für Physik, Universität Dortmund, Postfach 500 500,
D-4600 Dortmund 50, Federal Republic of Germany
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The ground-state configurations of a lattice-gas model introduced by de Fontaine, Wille, and Moss for the distribution of empty and occupied oxygen sites in the Cu-O basal plane of the high-temperature superconductor YBa$_2$Cu$_3$O$_y$ are determined. It is shown rigorously that the configurations proposed earlier by Wille and de Fontaine basically exhaust the set of possible stable ground-state structures. States of partial order are excluded, except for special values of the interaction constants.

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The structural phase transitions of the high-temperature superconductor YBa$_2$Cu$_3$O$_y$ and the associated transitions between different ordered (or disordered) configurations of oxygen ions in the Cu-O basal plane ("chain plane") have been intensively investigated from both experimental and theoretical points of view (see Refs. 1 and 2 and references cited therein). The basal plane may be described as a square lattice of Cu ions with oxygen sites between adjacent Cu ions (see Fig. 1). The oxygen sites may be occupied or vacant, the concentration $f$ of occupied sites depending on the stoichiometry $z$ of the compound according to $f = (z - 6)/2$. In order to explain the various observed types of oxygen ordering in this plane, a lattice gas (or Ising) model was proposed, assuming short-range effective pair interactions between oxygen sites. An occupied site may be represented by an Ising spin $\sigma = + \frac{1}{2}$ ("up"), an empty site by $\sigma = - \frac{1}{2}$ ("down"). The Hamiltonian then is assumed to be given by

$$H = -2h\sum_{i} \sigma_{i} - 2J_{1} \sum_{NN} \sigma_{i} \sigma_{j} - 4J_{2} \sum_{NNN} \sigma_{i} \sigma_{j}$$

$$- 4J_{3} \sum_{NNNN} \sigma_{i} \sigma_{j},$$

in the lattice-gas picture. The sums denoted NN and NNN extend over all nearest-neighbor and next-nearest-neighbor bonds, respectively, where the prime denotes the next-nearest-neighbor bonds across a Cu ion and the double prime the remaining ones. The energy per oxygen site corresponding to (1) may be simply written as

$$H/N = -hm - J_{1}c_{1} - J_{2}c_{2} - J_{3}c_{3},$$

where $m$, $c_{1}$, $c_{2}$, and $c_{3}$ denote the relative Ising magnetization and the average spin correlations between nearest-neighbor pairs and the two kinds of next-nearest-neighbor pairs, respectively. All of these quantities are by definition restricted to the range $[-1, 1]$. The values of these parameters completely determined the energy of a spin configuration (oxygen-ion configuration). I shall now use a method$^4$ pioneered by Kanamori$^5$ to determine the range of possible combinations $(m, c_{1}, c_{2}, c_{3})$.

Subsequently, I shall demonstrate that the combinations of lowest energy correspond uniquely to certain simple spin configurations.

It is obvious that the quantities $m$, etc., are not independent of each other; it is, for example, impossible to imagine a spin configuration having $c_{1} = 1$ and $m = 0$ (at least if one assumes translational invariance, see below). Thus the set of possible combinations $(m, c_{1}, c_{2}, c_{3})$, which I shall denote by $S$, is certainly smaller than the four-dimensional cube $[-1, 1]^4$. Furthermore, it is important to note that the set $S$ is convex: Given two spin configurations $a$ and $b$, one may always construct an intermediate configuration corresponding to the parameter values $m = x m(a) + (1 - x)m(b)$ ($0 \leq x \leq 1$), etc., by building up two large $a$ and $b$ domains in the system, the domain-wall contributions being negligible in the thermodynamic limit. Assume now (this will be shown in a moment) that $S$ is not only convex but also bounded by (hyper)planes, that is, $S$ is a simplex (a convex polyhedron), and remember that the energy per site (2) is a

FIG. 1. Basal plane of the YBa$_2$Cu$_3$O$_y$ structure. The copper sites are all occupied; the oxygen sites may be occupied or empty. Also shown are the external field and the pair interactions acting on the Ising spins representing oxygen occupancy.
linear function of \(m, c_1, c_2, \) and \(c_3\). Thus the surfaces of constant energy are hyperplanes (with orientation determined by the coupling parameters \(h, J_1, J_2, \) and \(J_3\)) and the spin configurations of given energy are determined by the intersection of the appropriate energy surface with the simplex \(S\). States of minimum (or maximum) energy obviously correspond to “corners,” “edges,” or “faces” of the simplex. (See Fig. 2 for a two-dimensional example.) An “edge” or “face” ground state is obviously possible only for certain special values of the coupling parameters \(h, J_1, J_2, \) and \(J_3\) and corresponds to a locus of coexistence between two or more stable (with respect to small variations of the coupling parameters \(h, J_1, \) etc.) ground states (“corners”).

I shall now show that \(S\) is in fact a simplex, by deriving linear inequalities of the form

\[-1 \leq am + \beta c_1 + y c_2 + \delta c_3 \tag{3}\]

for the parameters \(m, \) etc. Consider a copper ion \(j\) and the four surrounding oxygen sites with their Ising spins \(\sigma_{j_1}, \ldots, \sigma_{j_4}\). Remembering that \(N_{Cu} = N/2,\) one may write

\[m = \frac{1}{N} \sum_j (\sigma_{j_1} + \sigma_{j_2} + \sigma_{j_3} + \sigma_{j_4}) \tag{4}\]

(The sum extends over all \(Cu\) sites so that every oxygen site is covered twice; see Fig. 1.) The quantity in parentheses in (4) assumes only integer values \(n, \) so that one may use the simple inequality \(|n| \leq n^2\) (note for later use that equality holds for \(n = 0, \pm 1\)) to write

\[|m| \leq \frac{1}{N} \sum_j |\sigma_{j_1} + \cdots + \sigma_{j_4}| \leq \frac{1}{N} \sum_j (\sigma_{j_1} + \cdots + \sigma_{j_4})^2 = \frac{1}{2} + c_1 + \frac{1}{2} c_2, \tag{5}\]

which is equivalent to the pair of inequalities

\[-1 \leq \pm 2m + 2c_1 + c_2. \tag{6}\]

Consideration of a nearest-neighbor square of oxygen sites not containing a Cu ion leads to an analogous pair of inequalities with \(c_3\) in place of \(c_2.\) A similar reasoning using a nearest-neighbor pair of oxygen sites leads to

\[-1 \leq \pm 2m + c_1. \tag{7}\]

Again it is obvious how to derive analogs of (7) with \(c_2\) or \(c_3\) in place of \(c_1.\) Finally, one may consider two nearest-neighbor bonds joining three of the four oxygen sites next to a copper ion to derive inequalities related to parts of \(c_1\) and \(c_2.\) Combining these, one arrives at

\[-1 \leq \pm 2c_1 + c_2, \tag{8}\]

where, again, \(c_2\) may be replaced by \(c_3.\)

The inequalities derived above, together with the trivial ones \(|m| \leq 1, \) etc.) describe a simplex with twelve corners which are listed in Table I.

I shall now describe spin (or oxygen ion) configurations corresponding to the parameter combinations of Table I (thereby ensuring that the desired set \(S\) is not only included in the simplex constructed above, as shown by the inequalities, but identical to it). Later I shall show that these spin configurations are basically determined uniquely by the parameter values listed in Table I.

Entries No. 1 and No. 2 of Table I are obviously the “completely magnetized” phases of the Ising model, corresponding to oxygen-ion occupancy of zero and unity, respectively; No. 3 describes a phase in which occupied and empty oxygen sites alternate in a checkerboard fashion, leading to the much-discussed Cu-O-Cu-O chains. Corners 4 and 5 correspond to checkerboard patterns of \(2 \times 2\) blocks of up and down spins. (Observe that any configuration with \(c_2=1\) has an obvious counterpart with exchanged numerical values of \(c_2\) and \(c_3\), related to the original configuration by a shift of the whole oxygen-ion configuration with respect to the Cu-ion lattice.) Corner 6 is the last of the \(m=0\) (stoichiometry \(z=7\)) phases, corresponding to alternately occupied and empty nearest-neighbor rows of oxygen sites. The remaining entries of Table I correspond to \(m = \pm \frac{1}{2},\)

**TABLE I.** The twelve stable ground states of the model Hamiltonian (1) as characterized by their values of the relative magnetization \(m,\) the nearest-neighbor correlation \(c_1,\) and the two kinds of next-nearest-neighbor correlations, \(c_2\) and \(c_3.\)

<table>
<thead>
<tr>
<th>No.</th>
<th>(m)</th>
<th>(c_1)</th>
<th>(c_2)</th>
<th>(c_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2</td>
<td>\pm 1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>7,8</td>
<td>\pm \frac{1}{2}</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>9,10</td>
<td>\pm \frac{1}{2}</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>11,12</td>
<td>\pm \frac{1}{2}</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
that is, \( z = 6.5 \) or 7.5. Corners 7–10 represent configurations consisting of diagonal next-nearest-neighbor rows of occupied (empty) oxygen sites, separated by three diagonal rows of empty (occupied) sites. Finally, corners 11 and 12 correspond to isolated occupied (empty) sites, each surrounded by a "cage" of empty (occupied) nearest and next nearest neighbors. These configurations and the corresponding "ground-state phase diagrams" (for \( J_1 < 0 \)) were already discussed by Wille and de Fontaine; the OO and OII configurations of Ref. 1 correspond to corners 3 and 8, respectively.

In order to decide whether there is a unique correspondence between the "corners" listed in Table I and the spin configurations described above, one simply has to recall that a corner of the parameter simplex \( S \) is defined by the fact that several inequalities are fulfilled as equalities. One may then reconsider the design of these inequalities in order to see under which circumstances they are fulfilled as equalities. From (5) one concludes that equality in one of the inequalities (6) may hold only if for the nearest-neighbor squares of oxygen sites centered by Cu ions the quantity \( \sigma_3 + \cdots + \sigma_4 \) never changes sign and never exceeds the values \( \pm 1 \). A more physical way to state this rule is to say that (a) there is no Cu-centered square with four equal spins and (b) if in any such square there are three spins of a given direction, then no other square is allowed to have only one spin of this direction. Similarly one may convince oneself that equality in (7) implies the following rule: If there is one nearest-neighbor pair of up (down) spins in the system, then all nearest neighbors of a down (up) spin must be up (down). (There are some more rules of this type associated with the various modified inequalities described above.)

For a given entry of Table I, one may check which inequalities are fulfilled as equalities, and which rules the spin configuration has to obey accordingly. One may then consider an "empty lattice" and build up the spin configuration from a simple "seed," for example, a single up spin. This is especially easy for the corners 1, 2, 6 of Table I, as these are to a large extent determined by the values of the two kinds of next-nearest-neighbor correlations. As a more interesting example, I describe the construction of configuration No. 9. A single up spin fixes a diagonal row of up spins via \( c_3 = 1 \). Consider a nearest neighbor of one of these up spins and assume that it is down (assuming it to be up would lead to an equivalent configuration by a different argument). This fixes a diagonal row of down spins orthogonal to the first row of up signs. Now, as \( m > 0 \), there must exist some nearest-neighbor pairs of up spins, and according to (7) the nearest neighbors of down spins must be up. This fixes two diagonal up-spin rows of nearest neighbors of the diagonal down-spin row, and, via \( c_3 = 1 \), an infinity of diagonal up-spin rows orthogonal to the down-spin row. The remaining spins are fixed by the rule following from (7) with \( c_2 \) in place of \( c_1 \).

Corners 11 and 12 are the only configurations which are not uniquely determined. It is easy to see that they consist of isolated spins of one direction, surrounded by nearest neighbors and next nearest neighbors of the other direction, and it is also easy to see that these building blocks may be stacked in more than one way. All configurations of this type consist of straight rows made up from the elementary building blocks; adjacent rows, however, may be in two different positions with respect to each other. (Starting from one of the minority spins in one row and running in a lattice direction perpendicular to the row, one may or may not meet another minority spin after two steps.) The degeneracy of this configuration thus is of the order of \( 2^{\sqrt{N/2}} \), leading to a subextensive ground-state entropy.

Up to now the discussion has been limited to situations of given magnetic field (given chemical potential). This point of view is certainly appropriate when the synthesis of the compound (at a given oxygen partial pressure) is discussed. It is, however, also interesting to study possible ground-state structures at fixed stoichiometry: Once the compound has been formed, the stoichiometry may be considered fixed, but the interaction parameters of the present phenomenological model may depend, for example, on pressure (via changes in electronic structure of the whole crystal), with the ground-state configuration changing accordingly. The configurations of given stoichiometry (given magnetization) correspond to the intersection of the simplex \( S \) with the plane \( m = \text{const} \). The situation is particularly simple at \( m = 0 \). In this case, the intersection of \( S \) with \( m = 0 \) has the corners 3–6 of Table I, plus the additional corner \( c_1 = 0, c_2 = c_3 = 1 \) which clearly corresponds to a "phase-separated" system with equal numbers of up and down spins, separated by a domain wall. The intersection of \( S \) with \( m = 1 \) plane has eight corners, namely 8, 10, and 12 from Table I, plus the \( m = 1 \) convex combinations of 1 and 2, 2 and 3, 2 and 4, 2 and 5, and 2 and 6, respectively (all numbers referring to Table I). For \( J_1 < 0 \) (which is the appropriate choice for \( YBa_2Cu_3O_y \)) it is easy to see that only the "2 and 3" combination may become an additional ground state, stabilized by the condition of fixed stoichiometry. From the inequalities which are fulfilled as equalities at this point one concludes that the corresponding spin configuration necessarily decomposes into two pure-phase domains.

To summarize, I have shown that the model for oxygen ordering in the basal plane of \( YBa_2Cu_3O_y \) proposed by de Fontaine, Wille, and Moss has only finitely many different stable ground-state configurations (apart from the degeneracies discussed above), namely, those discussed already in Ref. 6. In particular, there are only finitely many stable stoichiometries (\( z = 6.6, 6.5, 7, 7.5, 8 \)). Thus the partially ordered states recently observed in a low-temperature Monte Carlo simulation certainly do not represent stable ground states, but special forms of
coexistence between two or more "corner" states. For
given two-particle interactions (in the lattice-gas pic-
ture) the chemical potential has to be tuned to a special
value to obtain these ground states. For this single value
of the chemical potential, a continuum of stoichiometries
is possible, including the aperiodic arrays of chains ob-
served in Ref. 1 as well as the "Magneli-type" states dis-
cussed in Refs. 1 and 2. All of these states correspond to
points on edges connecting type-7 corners (see Table 1)
to type-1 or type-3 corners. As an obvious consequence
of this geometrical fact, Magneli phases cannot be stable
ground states of the present model; they might be stabi-
lized only by long-range or many-body interactions. The
interrupted-chain configurations observed in a recent
constant-stoichiometry Monte Carlo simulation must be
attributed either to the well-known technical (meta-
stability) problems of low-temperature Monte Carlo simu-
lations or to the physical effects (configurational entro-
py) of the assumed nonzero temperature; the correspond-
ing zero-temperature configurations should show separa-

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