Ground-state analysis of ordered superstructures in the basal plane of $YBa_2Cu_3O_z$

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(Received 31 August 1987; revised manuscript received 25 November 1987)

Ordered superstructures consisting of occupied and empty oxygen sites in the Cu—O basal plane of $YBa_2Cu_3O_z$ have been determined. Pairwise interactions (V_1, V_2, V_3) between nearest- and next-nearest-neighbor sites are assumed and ordering maps are plotted as a function of V_2/V_1 and V_3/V_1 (in the ordering case: $V_1 > 0$). The ground state of this Ising model is determined by a direct enumeration method and the relation with experimentally obtained structures is discussed.

The crystal structure of the high-temperature superconductor $YBa_2Cu_3O_z$ ($z = 7-\delta$) has been investigated by x-ray,[1-4] neutron,[5-9] and electron diffraction and microscopy.[10,11] Both a tetragonal (*P4/mmm*) and an orthorhombic (*Pmmm*) phase have been identified: The latter is the superconducting one. It is now well documented that the superconducting properties depend critically on the presence of Cu—O chains parallel to the orthorhombic *b* axis. Furthermore, the oxygen content must be close to, or somewhat less than the stoichiometric value $z = 7$ ($\delta = 0$). The orthorhombic phase transforms on heating to the tetragonal phase at about 700 °C. The transition is marked by a disordering of oxygen ions and structural vacancies on the O sites of the Cu_2O basal plane. Other O sites, outside the basal planes, appear to be largely unaffected by the two-dimensional ordering. Hence we may take the concentration of filled sites in the basal plane to be $c_0 = (z-6)/2$. The study of the thermodynamics of this two-dimensional order-disorder transition is clearly crucial to the understanding of the superconducting properties of the compound of interest. The present contribution addresses the ordering ground states in the basal plane.

Ordering instabilities in two-dimensional *k* space were investigated in a previous publication.[12] The model shown in Fig. 1 was adopted. Were it not for the presence of Cu atoms this would be a simple square Ising model with cell edges at 45° to the horizontal axis in the figure. The Cu atoms, however, break the symmetry: The centers of alternate square cells are occupied by Cu in checkerboard fashion. Thus, there is a unique first-neighbor Ising pair interaction V_1, along cell edges, and two types of second-neighbor pair interactions along the diagonals V_2 and V_3; the first is mediated by Cu, but the other is not. Apart from modifying the strength of the pair interactions, the Cu ions play no further role in the ordering analysis. These effective pair interactions (EPI) V_r may be given an operational definition

$$V_r = \tfrac{1}{4}[W_r(\mathrm{O}-\mathrm{O}) + W_r(\square-\square) - 2W_r(\mathrm{O}-\square)] \ , \qquad (1)$$

where O denotes filled and □ denotes empty oxygen sites. Each quantity W_r on the right of the equal sign in Eq. (1) can in turn be defined as the total energy of the designated pair embedded in a medium consisting of a completely random distribution of O and □ sites.[13] It is important to note that the W_r must be obtained from a total-energy calculation and cannot be expressed in terms of pairs or assumed to be short ranged. The V_r on the other hand have been shown to converge rapidly in a large variety of systems.[13] Moreover, in the absence of any electronic structure calculations for the completely disordered state, it will be assumed that three-body and higher-order interactions are negligible as far as ground states are concerned. This assumption is justified *a posteriori* by the fact that all experimentally observed structures are reproduced by limiting the set of EPI's to V_1, V_2, V_3. It is seen that $V_r > 0$ favors unlike and $V_r < 0$ like pair formation. The EPI are expected to depend on the full three-dimensional nature of the system, that is, on the basal plane oxygen concentration c_o as well as the nature of the other metallic ions in the compound. The particular geometry of the basal plane was handled in our earlier paper[12] by subdividing the structure into three interpenetrating square sublattices: one for the Cu sites, and

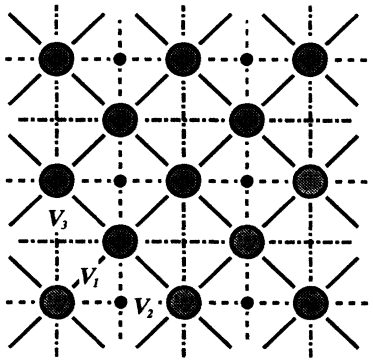

FIG. 1. Sublattices in the basal plane of $YBa_2Cu_3O_z$ structure. Black dots stand for Cu atoms; and shaded circles stand for O sites. Effective pair interaction V_1 couples the two oxygen sublattices α and β; V_2 and V_3 operate on one sublattice.

two for the O sites, the latter two being denoted by the labels α and β (see Fig. 1). The V_1 interaction then couples the α and β sublattices; V_2 and V_3 act on pairs of sites belonging to just one sublattice.

The Hamiltonian for the Ising model with sublattices α and β can be written[12]

$$H=\tfrac{1}{2}\sum_{m,m'}\sum_{n,n'} v(\mathbf{R}_m+\rho_n-\mathbf{R}_{m'}-\rho_{n'})\sigma(\mathbf{R}_m+\rho_n)\sigma(\mathbf{R}_{m'}+\rho_{n'}), \tag{2}$$

where $\mathbf{R}_m$ is a lattice vector and ρ_m is a position inside the unit cell; in the present case $\rho_n=(0,0)$ for sublattice α and $\rho_{n'}=(\frac{1}{2},\frac{1}{2})$ for sublattice β, for example. The pseudospin variables σ denote site occupancy, taking values $+1$ if a site is occupied by an O ion, -1 if it is empty. The summations run over all sites, taking into account the implicit cutoff due to the short range of the interactions. In the present case, the interactions v take the values V_1, V_2, V_3 as defined above (see Fig. 1).

In our previous paper,[12] a stability analysis was conducted by rewriting the Hamiltonian (2) in k-space representation, then expressing H as a sum of amplitude-squared of "normal concentration modes."[14,15] Ordering instabilities are expected for those k values for which the associated concentration wave has lowest energy (for unit amplitude). Instabilities are expected at so-called special points (SP) in k space where symmetry elements intersect (Lifshitz criterion). The SP relevant to the present problem are the Brillouin zone center $\langle 00\rangle$, and the zone boundary points $\langle\frac{1}{2}\,0\rangle$ and $\langle\frac{1}{2}\,\frac{1}{2}\rangle$. Which SP will have associated with it the lowest-energy wave will depend on the values of the normalized interaction parameters $x=V_2/V_1$ and $y=V_3/V_1$. For $V_1>0$ (nearest-neighbor ordering), regions were mapped out in x,y space where a given SP wave would lead to an ordering instability.[12]

Such a stability analysis gives information about incipient instability; ordering waves modulate the lattice and may give rise to fractional occupation of lattice sites. To ensure that actual crystal structures are described, with O or □ occupation at each site, combinations of ordering waves, belonging to different stars, may be required. It is then simpler to perform the analysis in direct space by seeking those combinations of $+1$ and -1 occupation variables σ which give H in Eq. (2) its minimum value for given interaction parameter ratios. There result ground-state maps which show regions in x,y space where a given ordered superstructure has minimum value for a selected stoichiometry c_0. To derive such maps we have generated all possible configurations on a 2×2 and a 2×4 lattice, containing 8 and 16 oxygen sites, respectively. Subsequently we determined which structure minimized the Hamiltonian (1) in the different regions of the xy plane. In view of the method used we cannot completely rule out the possibility of a ground state that is not compatible with the multiple unit cells that we chose. However, as will become clear from our results such a possibility appears extremely unlikely.

At concentration $c_0=0.50$, we find the ground-state map of Fig. 2. The boundaries of the ground-state regions agree exactly with those derived earlier for the stability analysis.[12] Hence we have indicated in each region both the unit cell of the ordered structure and the unstable wave vector. The appropriate two-dimensional space group symbol is also included. In the lower left corner of the figure, $\langle 00\rangle$ instability, a simple rectangular structure *p2mm* is found to be stable. One immediately recognizes the basal plane of the *Pmmm* orthorhombic structure of the high-T_c superconductor. As explained in the earlier paper, the $\langle 00\rangle$ instability places one type of symbol on one sublattice, say O on α and the other (□) on β, thus forming the one-dimensional Cu—O chains characteristic of the superconducting phase. The structure *p2mg*, depicted in the upper right corner can be produced by modulating each sublattice by a $\langle\frac{1}{2}\,\frac{1}{2}\rangle$ ordering wave. In the other two regions, the stability analysis predicts $\langle\frac{1}{2}\,0\rangle$ instabilities, but only one sublattice becomes modulated by the cell-doubling wave, the other sublattice remaining unmodulated. To produce a definite crystal structure two waves must operate simultaneously: $[\frac{1}{2}\,0]$ and $[0\,\frac{1}{2}]$, leading to a square quadruple cell with space group *p4mm*.

Figure 3 shows ground-state configurations corresponding to an oxygen concentration of $c_0=0.25$ (or equivalently $c_0=0.75$). In that case, the stability analysis is no longer directly applicable and one expects to find more complicated structures made up of superpositions of ordering waves. As expected, the stable ground-state structures are made up of SP ordering waves belonging to different stars. In the first quadrant ($V_2>0, V_3>0$) of

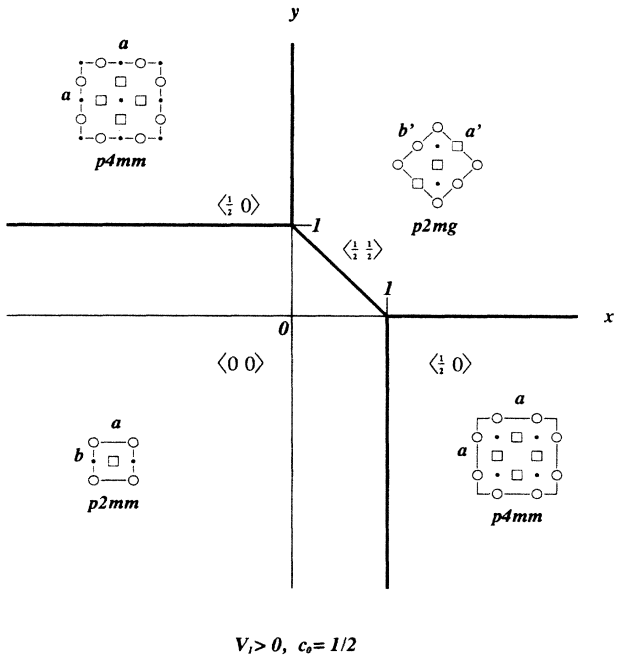

FIG. 2. Ground-state map ($V_1>0$) at $c_0=0.50$. Two-dimensional space group symbols are indicated along with corresponding special point wave.

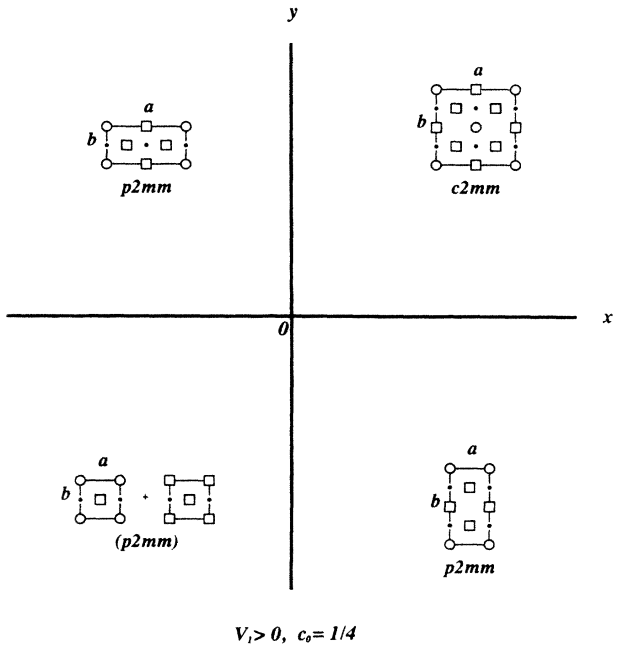

FIG. 3. Ground-state map ($V_1 > 0$) at $c_0 = 0.25$. Note that the structure in the upper right quadrant is infinitely degenerate (see text).

the xy map one sublattice is filled by □ symbols, and the other is modulated by a $\langle \frac{1}{2}\ \frac{1}{2} \rangle$ wave, producing the quadruple cell $c2mm$ structure shown. Actually, the ground state in that quadrant is infinitely degenerate: the O—□ diagonal chains may be translated parallel to themselves with no change in ground-state energy since only third-neighbor bonds are altered in the process. In the $(+,-)$ and $(-,+)$ quadrants, $p2mm$ cell doubling structures are produced by a combination of $\langle 00 \rangle$ and $[\frac{1}{2}\ 0]$ or $[0\ \frac{1}{2}]$ waves. Finally, the ground state in the $(-,-)$ quadrant can be regarded as produced by a $\langle 00 \rangle$ (very long wavelength) ordering wave placing □ symbols on sublattice α and a random mixture of □ and O on β. The β sublattice can then "phase separate" giving a structure composed of domains of $p2mm$ (ordered) and $p4mm$ (pure vacancy) units.

We believe that the ground-state analysis presented here is complete for the range of interactions considered and for $V_1 > 0$. Alternative plausible structures at these and other stoichiometries (such as $c_0 = 0.125$ or 0.375) are not stable under the limited set of interactions considered here. Higher-order interactions could stabilize these structures (and lift the degeneracy in the first quadrant of Fig. 3), but there seems to be no need for such interactions as far as the ordering in the basal plane of $YBa_2Cu_3O_z$ is concerned. The determination of ordered ground states for a novel type of Ising model is of intrinsic interest but it is, of course, the application to high-T_c superconductors which motivated the present study. In that regard, the basal plane structures expected are those formed for V_2 and V_3 less than V_1, in magnitude. Thus, the most likely structures to be encountered in practice are (a) the disordered (simple-cell) structure $p4mm$, corresponding to the three-dimensional tetragonal phase $P4/mmm$; (b) the simple-cell $p2mm$ structure, close to $c_0 = \frac{1}{2}$ stoichiometry ($z = 7$), corresponding to the orthorhombic phase $Pmmm$, and, possibly, (c) one of the double-cell $p2mm$ structures at stoichiometry $c_0 = \frac{1}{4}$ ($z = 6.5$) or $c_0 = \frac{3}{4}$ ($z = 7.5$).

Evidence for the cell-doubling structure has been obtained by electron microscopy and diffraction, although the observed $(\frac{1}{2}\ 0)$ diffraction spots are rather weak and diffuse.[10-12] No independent x-ray or neutron evidence for $(\frac{1}{2}\ 0)$ diffuse intensity is available, as far as we know. The existence of such a structure at equilibrium is quite plausible, however, since both simple-cell $p2mm$ (three-dimensional orthorhombic structure) and double-cell $p2mm$ are mutually compatible. If the effective pair interactions are concentration independent (which is by no means certain) it suffices to take, for the range of V's, the overlap of appropriate regions in the $c_0 = \frac{1}{2}$ and $c_0 = \frac{1}{4}$ maps, i.e., $V_1 > 0$, $V_2 < 0$, and $0 < V_3 < V_1$.

Given presently available structural information on $YBa_2Cu_3O_z$ or similar compounds, the following scenario appears to be a likely one: The stable low-temperature phase at or near $z = 7$ is the orthorhombic $Pmmm$ with basal plane ground state $p2mm$ (simple near-square cell), consisting of one filled, one empty sublattice, generated by out-of-phase $\langle 00 \rangle$ ordering waves[12] If the sample were to be heated at constant oxygen content, it would eventually transform to the tetragonal phase (simple cell, $p4mm$). Actually, at constant oxygen partial pressure, oxygen loss occurs progressively on heating,[9] so that, by the time the disordering temperature is reached, the system will be far from $c_0 = \frac{1}{2}$ stoichiometry, which may promote the $p2mm$ cell-doubling phase. For that phase, or for the simple-cell phase off stoichiometry, the disordering temperature is expected to be lower than that at stoichiometry. That is because only at $c_0 = \frac{1}{2}$ are the near-neighbor pair relations, required by the signs of V_1, V_2, V_3, strictly satisfied. The fact that very weak extra ordering spots were detected could mean that, at these high cooling rates required to retain the low oxygen content, the ordering kinetics are too slow to reach full equilibrium.

Note finally that the only basal plane structure that contains infinite [010] Cu—O chains is the $p2mm\langle 00 \rangle$ structure close to stoichiometry. At c_0 close to $\frac{1}{4}$ the $\langle 00 \rangle$ instability gives rise only to isolated chain structure domains. Since these chains appear to be essential for high-T_c superconductivity, transitions to either the disordered $p4mm$ or ordered cell-doubling $p2mm$ severely reduce the superconducting transition temperature.

The authors thank Dr. S. C. Moss, Dr. H. Zandbergen, and Dr. G. Van Tendeloo for many helpful discussions, and Mr. C. Burmester for programming assistance. This work was supported by The Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy, under Contract No. DE-AC03-76SF00098.

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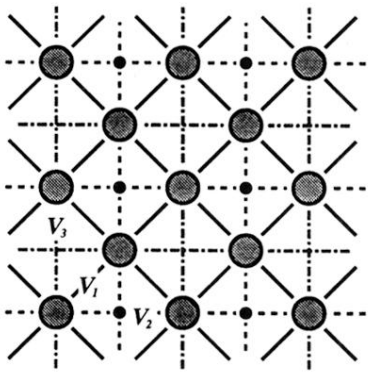

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