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Stability analysis of special-point ordering in the basal plane in $YBa_2Cu_3O_{7-\delta}$

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It is shown that the Cu-O basal plane of $YBa_2Cu_3O_{7-\delta}$ can undergo three types of ordering wave instabilities at the *k* points $\langle 0,0\rangle$, $\langle \frac{1}{2},0\rangle$, or $\langle \frac{1}{2},\frac{1}{2}\rangle$, depending on the values of the effective pair interactions between filled and empty oxygen sites. The $\langle 0,0\rangle$ instability gives rise to the observed chains of oxygen atoms along either the *a* or the *b* axis of the crystals. The $\langle \frac{1}{2},0\rangle$ and $\langle \frac{1}{2},\frac{1}{2}\rangle$ instabilities produce doubling and quadrupling of the unit cell, respectively. Comparison with experiments suggests the necessity for interactions beyond nearest neighbors.

The structure of the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ has recently been refined in a series of neutron powder diffraction analyses.[1-3] This structure, as reported also by x-ray diffraction,[4] consists of a stack of three perovskite cells with a Ba-Y-Ba sequence along the *c* axis. Of crucial importance in the neutron refinement is the presence of ordered chains of oxygen atoms along the *b* axis of the basal plane with oxygen vacancies along the *a* axis to give an orthorhombic cell of $a \simeq 3.822$ Å and $b \simeq 3.885$ Å with $c \simeq 3b \simeq 11.68$ Å.

The importance to superconductivity of the ordered O-Cu-O chains along $\langle 010\rangle$ has been discussed by Massidda, Yu, Freeman, and Koelling,[5] and has been demonstrated by Schuller *et al.*[6] who showed, via x-ray scattering, that there is an orthorhombic-tetragonal phase transition at ~750 °C presumably associated with a disordering of the oxygens between the two chains along with a possible oxygen loss. When a powder sample was rapidly quenched from above 750 °C the tetragonal state was preserved and the superconducting T_c was reduced from 92.5 to ~50 K. This work has recently been extended by Jorgensen and co-workers[7,8] who studied in detail the chain disorder and oxygen loss (on both chains) and the attendant consequences for superconductivity. At the orthorhombic-tetragonal transition $\delta \simeq 0.5$.

We present here a stability analysis of the ordering in the Cu-O basal plane of the $YBa_2Cu_3O_{7-\delta}$ structure. Our objective is to assign to the possible two-dimensional (2D) ordered states stability boundaries based on the relative strengths of the relevant pairwise (Ising) interaction energies and thereby to investigate the energetics of the ordering transition in this material.

Consider the Cu-O basal plane of the perovskite-based structure in Fig. 1. There are two types of oxygen sites, O(4) and O(5),[1-4] occupying two interpenetrating sublattices, say α and β, respectively. Although drawn as squares (dashed outlines) these sublattices have rectangular symmetry *mm*. The formation of O-Cu-O rows can be considered as an ordering reaction of filled (O) and vacant (□) sites on the oxygen framework. Our problem can then be treated as an Ising model with oxygen sites interacting by effective pairwise forces.

The strongest interaction is expected to be the nearest-neighbor one, V_1, which couples the two sublattices. It is also necessary to include two second-neighbor-interactions, V_2 which is mediated by the Cu ion, and V_3 which is not. Both V_2 and V_3 connect sites on the same sublattice as in Fig. 1. The signs and strengths of the effective pair interactions will, of course, depend on the electronic structure of the full three-dimensional crystal. We adopt the usual convention that $V_r > 0$ favors "ordering" of the *r*th pair (unlike site occupation), and $V_r < 0$ favors "clustering" (like-site occupation), where

$$V_r = \frac{1}{4}[V_r(\mathrm{O}-\mathrm{O}) + V_r(\square-\square) - 2V_r(\mathrm{O}-\square)] \; . \tag{1}$$

We may then perform an ordering stability analysis of the 2D Ising problem by formally expanding the free energy to second order in the configuration variables. In a

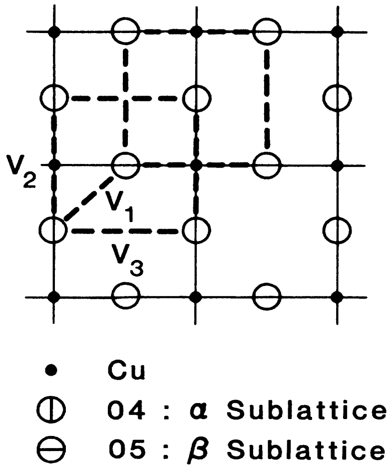

FIG. 1. Oxygen sublattices on the basal (*a-b*) plane of the $YBa_2Cu_3O_{7-\delta}$ structure. The effective pair interaction energies, V_1, V_2, and V_3, are indicated. V_2 and V_3 are both second-neighbor energies with V_2 mediated by Cu.

mean-field approximation the configuration entropy is site diagonal in the configuration variables so that all structural effects are determined by the pair interaction term written in its most general form as[9]

$$\phi=\frac{1}{2}\sum_{nn'}\sum_{mm'} v(\mathbf{R}_m+\rho_n-\mathbf{R}_{m'}-\rho_{n'})\sigma(\mathbf{R}_m+\rho_n)\times\sigma(\mathbf{R}_{m'}+\rho_{n'}) \ , \qquad (2)$$

where $\mathbf{R}_m$ designates a lattice vector and ρ_n a position inside the unit cell. The interaction parameters depend on the distance between lattice sites and the configuration variables σ denote site occupancy, i.e., +1 is filled, −1 is empty. The summations extend over all pairs of sites, compatible with the limited range of interactions v considered. The correspondence between these interactions and the more familiar V_1, V_2, and V_3 introduced above is established in Fig. 1.

The quadratic form (2) must now be diagonalized. This is done in three steps: As originally suggested by Khachaturyan,[10] translational symmetry is restored to the interactions by converting v to a matrix of elements $v_{nn'}$, the order of the matrix being equal to the number of sublattices considered, here equal to two. Equation (2) thus becomes

$$\phi=\frac{1}{2}\sum_{mm'}\sum_{nn'} v_{nn'}(\mathbf{R}_m-\mathbf{R}_{m'})\sigma_n(\mathbf{R}_m)\sigma_{n'}(\mathbf{R}_{m'}) \ . \qquad (3)$$

The second step consists of a lattice Fourier transform over N sites of a suitably large region:

$$\phi=\frac{N}{2}\sum_{\mathbf{k}}\sum_{nn'} V_{nn'}(\mathbf{k})\sigma_n(\mathbf{k})\sigma_{n'}(-\mathbf{k}) \qquad (4)$$

in which $V_{nn'}(\mathbf{k})$ is the Fourier transform of the effective pair interactions, $v_{nn'}$, and $\sigma_n(\mathbf{k})$ is the amplitude of an "occupancy wave" on sublattice n. In the third step, the diagonalization is completed by defining "normal modes" $\Gamma(\mathbf{k})$.

$$\sigma_n=\sum_{n'} U_{nn'}\Gamma_{n'} \ , \qquad (5)$$

where $\underline{U}$ is a unitary matrix diagonalizing $\underline{V}$. Let the eigenvalues of $\underline{V}$ be Λ_n. The fully diagonalized expression is thus

$$\phi=\frac{N}{2}\sum_{\mathbf{k}}\sum_{n} \Lambda_n(\mathbf{k})\,|\Gamma_n(\mathbf{k})|^2 \ . \qquad (6)$$

Instability will occur for that normal-mode wave vector $\mathbf{k}$ which will give the minimum Λ_n its lowest value.

As argued by Lifshitz,[11] any k-space function, such as $V_{nn'}$ or Λ_n, must have certain symmetry—dictated extrema at points at which symmetry elements intersect. It was shown elsewhere[9] that, for any of the 230 crystallographic space groups, the group pertinent to the determination of these "special points" (SP) satisfying the Lifshitz criterion can be constructed as follows: Take the point group of the structure, include the inversion if it is not already present, and form the direct product of the resulting point group with the translation group of the reciprocal lattice. The SP are the Wyckoff positions[12] with fixed coordinates for the new space group. In the present case, the two-dimensional group of the disordered state (where all concentration amplitudes vanish) is $p4m$ and the SP are $\langle 0,0\rangle$, $\langle \frac{1}{2},0\rangle$, and $\langle \frac{1}{2},\frac{1}{2}\rangle$ with indices given by $\mathbf{k}=[k_1k_2]=2\pi[h_1h_2]/a_0$, a_0 being the lattice parameter of the square (disordered) sublattices. The search for minima in k space will be limited here to those three SP.

The Fourier transforms of the interaction parameters are given by

$$\begin{aligned} V_{11}(\mathbf{k})&=2V_2\cos(2\pi h_1)+2V_3\cos(2\pi h_2) \ , \\ V_{22}(\mathbf{k})&=2V_3\cos(2\pi h_1)+2V_2\cos(2\pi h_2), \qquad (7)\\ V_{12}(\mathbf{k})&=V_{21}(\mathbf{k})=2V_1\{\cos[\pi(h_1+h_2)]+\cos[\pi(h_1-h_2)]\} . \end{aligned}$$

In these equations, the V_r parameters are those defined in Fig. 1.

At the SP, the eigenvalues take on very simple forms:

$$\begin{aligned} &\langle 0,0\rangle: \ \Lambda_\pm(0,0)=2(V_2+V_3)\mp 4|V_1| \ , \\ &\langle \tfrac{1}{2},0\rangle: \ \Lambda_\pm(\tfrac{1}{2},0)=\mp 2|V_2-V_3| \ , \qquad (8)\\ &\langle \tfrac{1}{2},\tfrac{1}{2}\rangle: \ \Lambda_\pm(\tfrac{1}{2},\tfrac{1}{2})=-2(V_2+V_3) \ . \end{aligned}$$

In the search for minimum eigenvalues, only the upper sign needs to be considered. Depending on the relative values of V_1, V_2, and V_3, one SP eigenvalue will be lower than the other two. Following earlier work on the fcc and bcc lattices[13,14] and the hcp structure,[9] we may divide Eqs. (8) by V_1. Normalized interaction parameters $x=V_2/V_1$ and $y=V_3/V_1$ can then be used as coordinates in an "ordering instability map" which indicates the regions in interaction parameter space where a given SP wave will be most unstable. Boundaries between such regions are obtained by equating different SP eigenvalues. The resulting map is shown in Fig. 2 for the case $V_1>0$.

It is seen that the $\langle 0,0\rangle$ instability is favored for ordering first-neighbor and clustering second-neighbor interactions. Conversely, the $\langle \frac{1}{2},\frac{1}{2}\rangle$ instability is favored by

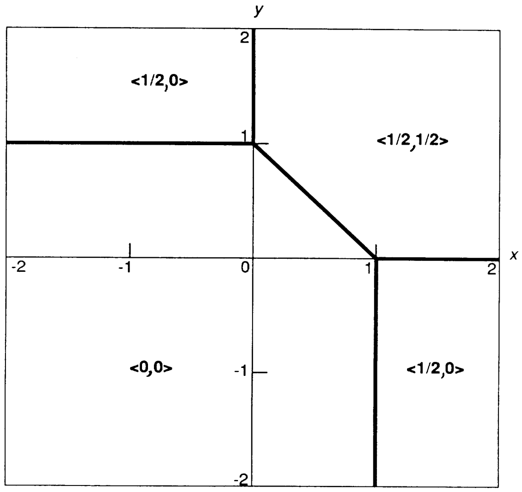

FIG. 2. Ordering instability map for $V_1>0$ (ordering first-neighbor interaction). Coordinates are the ratios $x=V_2/V_1$, $y=V_3/V_1$. While this map is appropriate for all c_0, the actual ground-state structure in each regime, at a particular stoichiometry, requires careful consideration (Ref. 15).

large ordering second-neighbor interactions, and $\langle \frac{1}{2},0\rangle$ is favored by V_2 and V_3 differing in sign.

When a given "ordering wave" (that with lowest eigenvalue) becomes unstable, the corresponding normal-mode amplitude will increase, thereby modulating the sublattice site occupation. Since the normal mode Γ_+ (corresponding to Λ_+) will always have lowest energy, we have by Eq. (5), with $\Gamma_- = 0$,

$$\sigma_1(\mathbf{k}) = u_{11}(\mathbf{k})\Gamma_+(\mathbf{k}) \ , \qquad \sigma_2(\mathbf{k}) = u_{21}(\mathbf{k})\Gamma_+(\mathbf{k}) \ , \tag{9}$$

where u_{11} and u_{21} are the components of the eigenvector corresponding to $\Lambda_+(\mathbf{k})$. At the $\langle 0,0\rangle$ SP, the eigenvectors are

$$[u_{11},u_{21}] = \frac{1}{\sqrt{2}}[1, -\mathrm{sgn}(V_1)], \qquad \mathrm{sgn}(V_1) = |V_1|/V_1 \ . \tag{10}$$

For the Brillouin-zone center instability, infinite-wavelength modulations will be placed on the α and β sublattices; for $V_1 > 0$ the two waves will be out of phase, i.e., there will be maximum concentration of filled sites on one sublattice and minimum on the other. For $V_1 < 0$, the two waves will be in phase. In the former case, the resulting structure, for average concentration of filled sites, $c_0 = \frac{1}{2}$ ($\delta = 0$), will have the observed[1-3] unit cell as depicted in Fig. 3. (This figure also shows a twin boundary as discussed below.)

For the zone-boundary instabilities $\langle \frac{1}{2},0\rangle$ and $\langle \frac{1}{2},\frac{1}{2}\rangle$ intrasublattice modulations are produced, leading to doubling and quadrupling of the original unit cell, respectively. For both cases, as a result of the vanishing of the off-diagonal element $V_{12}(\mathbf{k})$, the eigenvectors are [1,0] and [0,1]. Hence, by Eq. (9), we have for the $\langle \frac{1}{2},0\rangle$ case, $\sigma_1(\mathbf{k}) = \Gamma_+(\mathbf{k})$, $\sigma_2(\mathbf{k}) = 0$. The resulting structure may be interpreted as consisting of one sublattice modulated by a $\langle \frac{1}{2},0\rangle$ wave, with the other sublattice containing a random distribution of filled and empty sites. Actual ground-state structures corresponding to this SP instability will be described elsewhere.[15] For the $\langle \frac{1}{2},\frac{1}{2}\rangle$ case (for compositions near $c_0 = \frac{1}{2}$), since $\Lambda_+ = \Lambda_-$, *both* sublattices will be modulated by a $\langle \frac{1}{2},\frac{1}{2}\rangle$ wave, producing a structure with [1,1] rows populated alternately by filled and empty sites.

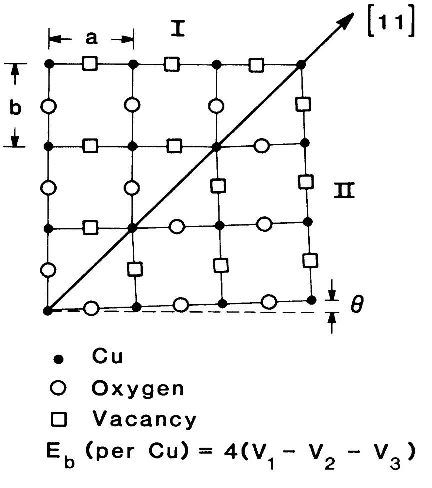

FIG. 3. Ground state ($V_1 > 0$) corresponding to the $\langle 0,0\rangle$ instability at $c_0 = \frac{1}{2}$ ($\delta = 0$). Included also is a schematic depiction of a twin boundary along the 2D [11], or 3D [110], direction across which the two ordered domains I and II with orthorhombic axes $a \neq b$ are matched. Note that the [11] directions in both domains are parallel and that "wrong" pairs of first and second neighbors are created across the boundary. The (positive) boundary energy E_b is noted, as is the tilt angle, $\theta = (b-a)/a$, between I and II.

At stoichiometries other than $\frac{1}{2}$, more complicated structures, made up of superpositions of ordering waves,[10] may be obtained which include secondary ordering on the depleted sublattice. Of course, significant deviations in oxygen content from $c_0 = \frac{1}{2}$ will also lower the transition temperature for ordering and may lead, as in many 3D ordering alloys, to a stabilization of the disordered state on cooling. This is particularly important in these oxides because of the oxygen volatility at elevated temperature and the sensitivity of superconductivity to oxygen content.[6,8]

Below the ordering transition, the effect of the observed[1-3] $\langle 0,0\rangle$ wave is to enrich one sublattice in filled sites (composition $c_0 + \Delta$, where Δ is some appropriate concentration wave amplitude) and delete the other sublattice correspondingly (composition $c_0 - \Delta$). In another region of the sample, the opposite ordering process may have been initiated. Between these two ordered regions ($\Delta \neq 0$) there will be a domain wall or twin boundary as depicted in Fig. 3 along the [11] direction. The twin-related domains are at an angle of $\theta \simeq (b-a)/a$ and are seen as rotationally split spots along $\langle 110\rangle$ in a single-crystal diffraction pattern.[16]

It is clear from Fig. 3 that first- and second-neighbor pairs are reversed across the twin boundary which is thereby an energetically costly interface, however favorable it may otherwise be in terms of lattice matching. It is straightforward with Eq. (1) to estimate the energy E_b of this boundary per Cu atom as $E_b/4V_1 = [1-(x+y)]$. From Fig. 2 we note that, over the entire regime of $\langle 0,0\rangle$ instability, E_b must always be positive because, for $V_1 > 0$, this regime lies below the line $(x+y) = 1$. The $\langle 110\rangle$ twin boundaries in $\mathrm{YBa_2Cu_3O_{7-\delta}}$ therefore always cost energy and may attempt, should they not anneal out, to assume a (metastable) configuration that minimizes the total boundary energy. For example, because the atom pairs across the boundary are unfavorable, the pairing can be thought of as repulsive; the $\langle 1\bar{1}0\rangle$ planar separation at the boundary may thus increase slightly over the normal $\langle 1\bar{1}0\rangle$ planar spacing and be modulated by the alternating O-O and □-□ pairs. If the two boundaries are sufficiently mobile they will also, under this repulsive interaction, tend to arrange themselves in a regularly spaced twin lattice.

We note finally that a detailed electron microscopy/diffraction study of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ by Zandbergen *et al.*[17] shows, on rapidly cooled specimens,[18] diffuse $(\frac{1}{2},0,0,)$ and $(0,\frac{1}{2},0)$ spots in the [001] zone pattern. This evidence for a $\langle \frac{1}{2},0\rangle$ instability is intriguing because a recent calculation[15] has predicted the stability of a ground-state structure at $c_0 = \frac{1}{4}$ ($\delta = 0.5$) which consists of a cell doubling along the [100] direction. Jorgensen and coworkers[7,8] find that the chain disordering of $YBa_2Cu_3O_{7-\delta}$ takes place at $\delta = 0.5$; rapid cooling of such a structure could thereby produce the observed ordering. We must, however, distinguish here between an ordering ground state which has superstructure spots at $(\frac{1}{2},0,0)$ [or $(0,\frac{1}{2},0)$] and the actual $\langle \frac{1}{2},0 \rangle$ regime in Fig. 2. In fact, if $V_r \neq f(c_0)$, the $\langle 0,0 \rangle$ instability must prevail at all c_0. The combined observations[7,8,17] then require a cell doubling structure for $c_0 = \frac{1}{4}$ within the regime $\langle 0,0 \rangle$ in Fig. 2 and this in turn requires appreciable values of V_2 and V_3 of *opposite* sign, i.e., higher neighbor effective oxygen-oxygen interactions are important in these compounds.

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