OXYGEN ORDERING AND SUPERCONDUCTIVITY IN YBa$_2$Cu$_3$O$_z$

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Abstract

The tetragonal-to-orthorhombic oxygen ordering transitions in the YBCO superconducting compound can be described by means of a two-dimensional Ising model with opposite-sign second-neighbor effective pair interactions. Phase diagrams calculated by means of various approximations of the Cluster Variation Method are found to be in remarkable agreement with recent experimental findings. At low temperatures, two-dimensional ordering gives way to quasi-one-dimensional states of order as described by the linear chain Ising model with repulsive pairwise interactions. Diffraction patterns calculated for these structures are in striking agreement with those observed by electron diffraction. The low-temperature states of order are predicted to be stable, in agreement with recent results obtained at Argonne. Computed Cu-O correlations indicate how the superconducting transition temperature may be enhanced by low-temperature oxygen ordering.
Introduction

The compound YBa$_2$Cu$_3$O$_y$ (YBCO) was the first one discovered whose superconducting transition temperature ($T_c$) exceeded the technologically important limit of 77 K. [1] At stoichiometry $y=7$, $T_c$ is about 93 K, but drops progressively to very low values as oxygen is removed. Oxygen gain or loss occurs mostly on the so-called basal planes, or chain planes, those containing the Cu1 sites and O1 (normally occupied) and O5 (normally vacant) oxygen sites. Not only oxygen content but oxygen arrangements influence $T_c$, hence a careful study of oxygen ordering is critical to an understanding of the mechanism of superconductivity in this material.

The Model

Most oxygen-ordering phenomena in YBCO can be mapped onto a two-dimensional Ising model consisting of two interpenetrating square sublattices, the sites ($\alpha$:O1, $\beta$:O5) of which may be occupied or empty. [2] A third (identical) sublattice is fully occupied by Cu. In the simplest approximation, three effective pair interactions are defined: $V_1$ between nearest neighbor sites, $V_2$ between next nearest neighbor (nnn) sites bridged by Cu (the b direction), and $V_3$ between nnn sites along the a direction of the orthorhombic cell. When $\alpha$ and $\beta$ sublattices are equally occupied, the structure has tetragonal symmetry; $\alpha/\beta$ sublattice ordering produces orthorhombic structures. Ground state analysis [3] reveals that eight ordered superstructures are stabilized by these three interactions at stoichiometries $y=7$ or $y=6.5$ (or 7.5). Two of these structures have been observed in YBCO: one is the orthorhombic structure (Ortho I) at $y=7$, consisting of parallel O-Cu-O chains, the other is the Ortho II structure consisting of alternating "full" (O-Cu-O) and "empty" (V-Cu-V; V=vacancy) chains. Another predicted ground state superstructure, of tetragonal symmetry [4], has been observed in Ca-substituted compounds. [5] The YBCO structures are stabilized when the following inequalities are verified [4]: $V_2 < V_3 < V_1$. As expected, the Cu-mediated interaction $V_2$ must be attractive (negative) and $V_3$ must be repulsive (positive) due to Coulomb interaction between O ions. First-principles calculations [6] confirm these conclusions. The Ca-substituted structure is stabilized by a similar set of inequalities but with $V_1 < V_3$. Other, more complex structures with larger unit cells can be stabilized when the $V_1$, $V_2$, $V_3$ scheme of effective interactions is extended. In all cases, the nnn interactions must have opposite signs, producing an Ising model with unique, highly anisotropic properties. Models which do not possess this characteristic anisotropy are unphysical and cannot reproduce the correct features of the system, claims to the contrary notwithstanding.

Phase Diagrams

A pseudo-binary (oxygen-vacancy) phase diagram was calculated by the Cluster Variation Method (CVM) with interactions $V_2/V_1 = -1/2$, $V_3/V_1 = +1/2$. [7] The high-temperature tetragonal-to-orthorhombic transition was found to be of second-order type, as expected. The first complete and consistent CVM phase diagrams were calculated independently by Zubkus et al. [8] and by Kikuchi and Choi [9], with parameters taken from [7]. These authors showed that only second-order transitions existed at very low temperature and that a new phase, now called anti-Ortho I [10], must be present for low oxygen concentrations and low temperature.

The phase diagram, calculated [10] with parameters $V_1$, $V_2$ and $V_3$ obtained from first-principles LMTO-ASA electronic structure calculations [6], is shown in Fig. 1. The four structures mentioned above are illustrated by portions of Monte Carlo simulation outputs: small black dots in the inserts are Cu atoms, large dark ones are oxygen atoms, open circles are empty oxygen sites. Ortho I (O1) is shown with two vacancies, Ortho II (OII) contains no defects, and anti-Ortho I (OII) is shown to consist of a random dispersion of a few filled stable chains in a predominantly empty background, the opposite of off-stoichiometric OII which consists of a dispersion of empty chains in a predominantly full background. The symmetry of OI or OII is orthorhombic, whereas that of the tetragonal structure (T), consisting of small segments of fluctuating chains in orthogonal orientations, is tetragonal, though locally orthorhombic. The CVM phase diagram, in this and earlier calculations [7-9] and in unpublished ones using larger cluster approximation [11-12], predicts narrow two-phase regions on the left border of the Ortho II phase region. This appears to be an artifact of the
Figure 1 - Phase diagram using the CVM approximation for parameters calculated by Sterne and Wille (full lines). Experimental points (filled circles) from Andersen et al. Inserted structure diagrams were obtained from Monte Carlo simulations (small filled circles in inserts denote copper ions, large filled circles denote oxygen ions, and open circles denote vacant sites).
approximation, as Monte Carlo simulations [13] yield only second-order transition throughout. The existence of the OI phase and of second-order transitions at very low temperatures is required by symmetry [10] and is not an artifact of the CVM. Other models, predicting a wide miscibility gap between T and OI structures, with possible spinodal mechanism, are in error.

The extensive experimental data of Andersen et al. [14] for the tetragonal-to-orthorhombic transitions are shown as filled circles in Fig. 1. The agreement is extraordinarily good given the fact that the calculated phase diagram was obtained with no adjustable parameters. In essence, the phase diagram of Fig. 1 was calculated only from the knowledge of the atomic numbers and positions of the atoms and knowledge of the lattice parameters of the tetragonal unit cell. The lower concentration (c) scale in Fig. 1 is that of oxygen content (average) in the chain plane. If all vacant oxygen sites in the three-dimensional structure are assumed to lie in this plane, then the parameters c and z (top scale) are linearly related by z = 6 + 2c.

**Branching Phases**

Other structures are expected to be stable at low temperature in the region roughly delineated by the dashed-line box in Fig. 1. The reasoning is as follows: longer-range attractive interactions along chains (b direction) do not produce new structures but repulsive interactions along the a direction may produce additional ordered superstructures at low temperatures. We know that interaction V3 must be positive because of repulsive Coulomb interactions between nnn O atoms, and because Ortho II has been shown to be a stable structure. [15] It follows that the second nearest interaction V4 between chains in the a direction must also be positive (repulsive), and so on. In fact, we expect [16] a set of monotonically decreasing "convex" interactions along a: V4, V5, V6, ... At low temperature, the strongly negative V2 interaction makes for very stable long O-Cu-O and V-Cu-V chains, so that, roughly in the area of the box in Fig. 1, we expect parallel-like chains to be mutually repulsive, theoretically out to infinite chain spacings. The ground state problem of infinity repulsive objects along a line has been solved exactly [17-18], and a simple algorithm determines uniquely the sequences of stable "branching phases" which result. [16] Some of the predicted structures and their respective diffraction patterns (one-dimensional structure factors) are indicated in Fig. 2, a and b. The notation is "1 = full chain," "0 = empty chain," the angle brackets enclosing the periodically repeating unit. For example, <1> is Ortho I, <10> is Ortho II, <110> may be called Ortho III, etc. Successive branching levels are expected to occur at successively lower temperatures, the complex structures with very long periods becoming stable only at temperatures so low that oxygen mobility will prevent their formation for kinetic reasons.

It is important to note that, because a structure is difficult to observe, or cannot be observed in all its expected regularity, it does not mean that such a structure is metastable, or transient, or is characterized by short-range order only. Actually, all of these branching phases must be stable, at least at low enough temperatures. Diffuse diffraction patterns are then due more generally to imperfect long-range order rather than stable short-range order (from fluctuations). The calculated diffraction patterns of Fig. 2b are in remarkable agreement [16] with electron diffraction patterns observed by Beyers et al. [18] on off-stoichiometric YBCO.

We have also calculated phase diagrams featuring Ortho III (<110>), the simplest and lowest-level branching phases. [19] For that, it was necessary to add interaction V4, arbitrarily taken to be 0.17 V3, and, for simplicity, the sites of sublattice B were assumed to be always unoccupied. A two-dimensional CVM calculation produced a phase diagram very similar to one published by Zübkus et al. [20] That phase diagram exhibited some incongruous features, such as the OI phase region subsisting to absolute zero for concentrations below OIII stoichiometry. This undesirable feature was clearly an artifact of the two-dimensionality of the model. A more complete three-dimensional CVM calculation based on pyramidal and prismatic clusters gave a much more realistic phase diagram, with an OIII phase region separated from OI and OII by two-phase regions, as required by the Landau rules, the OIII unit cell in the a direction being three times as long as that of OI.
Figure 2 - (a) Branching algorithm for quasi-one-dimensional ordered superstructures stabilized by long-range convex interactions. Concentration scale includes both basal plane coverage (c) and stoichiometric index (z). Symbols 1 and 0 indicate filled and empty chains, respectively.

(b) Diffraction patterns (Fourier amplitude-squared) along (h00) for superstructures encountered by scanning the structure tree of (a) at level IV, oxygen content increasing from left to right.
Ordering and Superconductivity

In February 1990 we wrote [16]:

Although neither the theoretical branching temperatures nor the temperatures at which oxygen configurations are frozen in during sample preparation are known at present, the agreement between recent experimental findings and our theoretical model is really quite striking. We are thus tempted to rotate the plateau structure of the $T_c$ versus concentration curve to the existence of a theoretically infinite set of branching phases, the $T_c$ plateaus corresponding to states of quasi-one-dimensional order frozen in at a certain "generation" level. The number of plateaus and their range of oxygen content should depend critically on sample preparation. Recent experimental and theoretical work support these ideas. For example, Farneth et al. [21] report that the $T_c$ plateau for low-temperature vacuum-annealed samples of YBa$_2$Cu$_3$O$_z$ is sharply defined and entirely located at temperatures higher than the monotonically decaying $T_c$ versus oxygen-content curve for samples quenched from high temperatures. Lambin [22] has used a tight-binding model to show that the hole concentration for well ordered Ortho II and Ortho III phases should be higher than those for the corresponding disordered compounds. It is clear that chain formation minimizes the fraction of incorrectly coordinated copper ions in the basal plane. Hence, chain ordering can be regarded as a form of doping in this compound.

This conjecture received spectacular confirmation in the work of Argonne scientists on oxygen ordering at and below room temperature. [23,24] For quenched YBCO simple crystals of oxygen content $z=6.45$, it was found that $T_c$ increased markedly on subsequent aging, in fact by as much as $\Delta T = 27$ K. [23] During this process, it was ascertained [24] that oxygen content was not altered: the average occupancy on sites O1, O2, O3, O4 and O5 did not change, although the molar volume and lattice parameters contracted significantly, the $a$ more than the $b$. Such behavior can only be interpreted as being due to additional oxygen ordering.

Recent "quench and age" Monte Carlo simulations [25] based on the model described above, i.e., with $V_1$, $V_2$, $V_3$ parameters used in calculating the phase diagram of Fig. 1, have shed considerable light on the problem. Immediately after the essentially instantaneous "computer quench," $\alpha/\beta$ ordering takes place during a very short transient, so short that it is probably unobservable experimentally. Subsequently, ordering of chain segments parallel to themselves, so as to form the longest possible chains, takes place at a rate characterized by a lower time constant.

The oxygen coordination of Cu1 atoms was monitored continuously during simulated aging at room temperature for samples quenched from 800 K. In the chain plane, Cu can be 0-, 1-, or 2-fold coordinated, corresponding to 2-, 3-, or 4-fold three-dimensional coordination if it is assumed that O4 sites are always occupied. Three- and four-fold planar coordination are forbidden because of the strong $V_1$ nn repulsive interaction. Electronic structure calculations [26] reveal that (spatially) 3- and 4-fold coordinated Cu is mostly present as Cu**, and 2-fold coordinated Cu is present as Cu*. As a result, chain "healing," i.e., progressive elimination of chain ends, where Cu is 3-fold coordinated, gives rise to the following "reaction" in Kröger-Vink notation:

$$2\text{Cu}_{3x} \rightarrow \text{Cu}_{4x} + \text{Cu}_{2x} + h^*$$

thus creating holes ($h^*$), accompanied by an excess negative charge on 2-fold coordinated Cu. The increasing hole concentration should favor a high $T_c$, but oxygen loss tends to destroy holes by the following mechanism:
\[ O_0 \rightarrow V_O + \frac{1}{2}O_2(g) \]
\[ V_O^x \rightarrow V_O^* + 2e^- \]
\[ 2e^- + 2h^+ \rightarrow \phi \]

The first of these equations describes oxygen loss to the gas phase (g), the second describes ionization of vacancies and creation of electrons, the third describes electron-hole recombination.

Monte Carlo simulations [25] clearly show that the fraction of 2-fold or 4-fold coordinated sites increases with annealing time, that of 3-fold sites decreases. These trends reproduce those of the rise in \( T_c \) observed experimentally by the Argonne group. [23,24] Moreover, since it is argued that oxygen ordering promotes hole formation, and that oxygen loss destroys holes, these two conflicting tendencies may well produce non-monotonic decay of \( T_c \) as oxygen content is decreased, possibly giving rise to the "plateaus" observed in the \( T_c \) vs. oxygen curve.

**Conclusion**

The asymmetric two-dimensional Ising model described above has explained successfully many features of the YBCO system: the experimentally observed phases (tetragonal, Ortho I, Ortho II) are ground states of the model; the calculated phase diagram (with no adjustable parameters) agrees remarkably well with experimental data; the observed electron diffraction maxima correspond closely with calculated structure factors of additional "branching phases"; and Monte Carlo simulation reproduces correctly the trends in change in \( T_c \) with annealing time in off-stoichiometric samples. It may therefore be concluded that this simple model captures most of the physics of oxygen ordering in the YBCO and related systems.

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**References**

11. J. M. Sanchez, private communication to D. de Fontaine.


