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THERMODYNAMICS OF OXYGEN-VACANCY ORDERING IN YBa$_2$Cu$_3$O$_z$

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The ordering in the Cu-O basal plane of YBa$_2$Cu$_3$O$_z$ is investigated as a function of oxygen content and temperature. Several phase diagrams are calculated by means of the Cluster Variation Method applied to asymmetric two-dimensional Ising models. The interaction parameters selected guarantee the stability of the orthorhombic structures near $z=7$, and, for certain choices, also include a double-cell phase around $z=6.5$. O-Cu-O correlations are investigated as a function of temperature and concentrations. Calculated orthorhombic to tetragonal transition temperatures and concentrations for various oxygen partial pressures are in excellent agreement with recent experimental data.

1. INTRODUCTION

The discovery by Bednorz and Müller (1), then by M. K. Wu et al. (2) of high-temperature oxide superconductors has fostered unprecedented interest in the condensed matter community. In particular, the compound YBa$_2$Cu$_3$O$_z$ ($z=7-8, 12\leq z\leq 0$) has been studied intensively, and its crystal structure has been determined accurately (3). It appears that, in the superconducting phase near $z=7$, the structure features O-Cu-O chains located in the perovskite basal plane and lying along the $b$ axis of the orthorhombic unit cell. This characteristic chain structure disappears in the non-superconducting tetragonal phase in which previously empty and filled oxygen sites are now occupied statistically by oxygen atoms. The presence of chains thus appears to be essential for superconductivity to occur, although the mechanism by which it does so is not known at present.

From the foregoing, it is clear that the orthorhombic to tetragonal transformation takes place by an order-disorder transition between filled and empty oxygen sites in the basal plane. As a sample is heated, disordering proceeds while, at the same time, oxygen is removed from the basal plane. Hence, the thermodynamics of YBa$_2$Cu$_3$O$_z$ can be mapped onto an open two-dimensional Ising model with interpenetrating sublattices. The fact that oxygen can be absorbed at crystallographic sites other than those of the basal plane is not taken into account in the idealized model.

The purpose of this short communication is to summarize recent results pertaining to the stated modelistic approach. The model will be defined, then a stability analysis will be described, followed by an enumeration of possible ground states of order. Finally, a phase diagram will be proposed, incorporating not only the well known tetragonal and orthorhombic phases, but also the more controversial double orthorhombic structure.

2. STABILITY AND GROUND STATES

Figure 1 shows the perovskite basal plane with oxygen sites marked by open circles and Cu atoms by filled circles. Effective pair interactions (EPI) are introduced between nearest neighbor sites ($V_1$) and between second neighbors, the latter interactions taking values $V_2$ or $V_3$ depending upon whether the sites are linked by a Cu atom or not, respectively. EPI's are defined by

$$V_n = \frac{1}{4} (V_{oo} + V_{oo} - 2 V_{oo})$$

and can be calculated, in principle, by taking linear combinations of energies of otherwise disordered (three

![Diagram](https://via.placeholder.com/150)

FIGURE 1
Model for perovskite basal plane with effective pair interactions $V_n$ indicated.

dimensional) crystals containing the designated pair (oxygen-oxygen, vacancy-vacancy,...) at the appropriate sites.

EPI's have not been calculated for this system as yet, but much can be learned about the model by considering the ratios $x=V_2/V_1$ and $y=V_3/V_1$ as phenomenological parameters. It was shown elsewhere (4) that, with the short range of effective interactions envisaged here,

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Ground states as a function of parameter ratios $x=V_2/V_1$ and $y=V_3/V_1$, for $V_1>0$ at oxygen concentrations (a) 0.50, (b) 0.25.

Oxygen-vacancy concentration waves may develop with wave vectors located at the three special points (5) $<00>$, $<1/20>$, $<01/2>$ and $<1/21/2>$ in $k$-space. Each of these four modes becomes unstable in regions of $(x,y)$ parameter space indicated in Fig. 2a, constructed for the case $V_1>0$ (required for first-neighbor ordering). The $<00>$ mode tends to fill one sublattice with oxygens and the other with vacant sites, creating, at stoichiometry $c_0=0.5$ [$c_0=1/2(z=6)$], the perfect chain structure of the orthorhombic phase. The corresponding planar unit cell is indicated in Fig. 2a and designated by its two-dimensional space group symbol $p2mm$. Other concentration modes operate in other sectors of the $(x,y)$ map, as shown in Fig. 2a.

With the range of interactions selected, ordered structures are found at stoichiometries $c_0=0.50$ and 0.25. Stable ordered structures (superstructures of the parent interpenetrating sublattices) are exactly six in number and are indicated in Figs. 2a and b (6). Of particular interest are the $p2mm$ cell-doubling structures predicted to be stable at $c_0=25$ (and $c_0=0.75$) for the indicated ranges of interaction parameter ratios (Fig. 2b). The structure with cell doubling along the $a$ axis, stable for $V_2/V_1<0, V_3>V_1>0$, is the one postulated by Van Tendeloo and co-workers (7) on the basis of high-resolution electron microscopy studies. This structure will be designated as "Ortho. III" ($p2mm$ II), as opposed to the usual superconducting phase "Ortho. I" ($p2mm$ I), found around $c_0=0.50$ at low temperature, with superconducting transition $T_c$ $\approx$ 90 K. It is here suggested that "Ortho II", at least in a short-range ordered state, is the phase found by Cava et al. (8) to exhibit a $T_c$ around 60 K. Clear evidence for cell doubling along the $a$ axis has been provided by the detailed single crystal x-ray diffraction work of Fleming and co-workers (9): diffraction maxima at $<1/20>$ are unmistakably present.

3. PHASE EQUILIBRIUM

The two-dimensional Ising model proposed here is an unusual one in that it has isotropic first neighbor ($V_1$) and anisotropic second neighbor ($V_2, V_3$) interactions. Not surprisingly, only isotropic cases had been studied heretofore, i.e. those cases whose representative points in parameter space lay along the diagonal $x=y$ ($V_2=V_3$). Both renormalization group (10) and Monte Carlo (11) methods had been used to investigate phase equilibria with $V_2=V_3=0.5V_1$. We used the Cluster Variation Method (CVM) with the same values of parameters in order to test the validity of the approximation. The centered square and lozenge clusters were used in the approximation, as explained in more detail elsewhere (12,13).

Good agreement was found with previous results (10,11) except that, as expected, the transition temperatures were calculated by the CVM to be a few percent too high. The resulting phase diagram, symmetric about $c_0=0.50$ (because constant pair interactions were used) features a line of second order transitions from $p4mm$ (disordered phase, corresponding to the tetragonal three dimensional structure) to $p2mm$ (Ortho. I) terminating in a tricritical point below which phase separation occurs.

If it is desired to obtain both the Ortho. I and Ortho. II ground states at $c_0=0.50 (z=7.0)$ and at $c_0=0.25 (z=6.5)$ respectively, then, from examination of Fig. 2, the $V_n$ interactions must be chosen such that $V_1>0, V_2<0, 0<V_3/V_1<1$. Two such calculations were performed, one
with \( x = -0.50, y = +0.50 \) (14), the other with same \( y \) but with \( x = -0.75 \). The phase diagram calculated with the latter values is shown in Fig. 3; topologically, both are identical although, with larger negative \( V_2 \), which contributes positively to oxygen ordering, the line of second order \( p4mm \rightarrow p2mm \) transition is a bit higher on the normalized temperature scale \((k_BT/V_1)\) for \( x = -0.75 \) than it for \( x = -0.50 \). The ratio of maximum Ortho I to Ortho II temperatures is somewhat lower for the larger (negative) \( x \), however.

The five filled circles in Fig. 3 represent second-order tetragonal-orthorhombic transition points determined experimentally at the Oak Ridge National Laboratory (15) for oxygen partial pressure \( P_{O_2} \) of 1, 0.2, 0.1, 0.02 and 0.005 atm, from the upper to the lower point. The point at 0.02 atm was fitted in the sense that it was used to determine the temperature scale. From this fit, the value of the nearest neighbor EPI was found to be \( V_1 = 0.047 \text{eV} \). Once the temperature scale was fixed (scale on right of Figure 3), all other experimental points were found to lie very closely to the calculated curve.

4. PARTIAL PRESSURE CURVES

The reaction which consists of exchanging or removing an oxygen atom from the basal plane, replacing it by a vacancy, placing the oxygen atom in the gas phase and having it react there to form an oxygen molecule can be written symbolically as

\[
O = \text{O} + \frac{1}{2} O_2
\]

with standard free energy change per oxygen atom given by

\[
\Delta g^\circ = \frac{1}{2} \mu_{O_2}^\circ - (\mu_O^\circ - \mu_{O_2}^\circ)
\]

and corresponding enthalpy \((\Delta h^\circ)\) and entropy \((\Delta s^\circ)\) changes. The equilibrium condition for reaction (3) can be written in terms of chemical potentials as

\[
\mu_O = \mu_{O_2} + \frac{1}{2} \mu_{O_2}^\circ
\]

the subscripts in Eqs. (3) and (4) indicating an oxygen on a crystal site (O), a vacant site (\(\text{O}_\text{V} \)), and molecular oxygen in the gas phase \((O_2)\); the superscripts \((^\circ)\) denote 1 atm standard states.

The chemical potential \(\mu\) calculated by the CVM is the difference \(\mu_O - \mu_{O_2}\), so that, with

\[
\mu_{O_2} = g_{O_2}^\circ + k_BT \ln P_{O_2}
\]

we have

\[
\mu = \Delta h^\circ + T(k_B \ln P_{O_2}^{1/2} - \Delta s^\circ)
\]

Two points from the Oak Ridge data were used to determine the two parameters \(\Delta h^\circ\) and \(\Delta s^\circ\), assumed to be temperature independent. The result fit yielded quite reasonable values of \(\Delta h^\circ \approx 0.6 \text{ eV} \) and \(\Delta s^\circ \approx 10^{-3} \text{ eV/K} \).

The partial pressure curves of Fig. 3 were calculated with the values of \(\Delta h^\circ\) and \(\Delta s^\circ\) obtained from two experimental points along the 0.02 isobar. The calculated 1 atm \(P_{O_2}\) curve (b) misses the corresponding transition point only slightly, indicating that the overall fit is quite good. Two other \(P_{O_2}\) curves have been calculated with the same parameters, those labeled (a) for 390 atm and (d) for \(10^{-9}\) atm. For the latter, the reactions are so sluggish at these low temperatures that equilibrium will probably not be achieved.

5. PAIR CORRELATIONS

The CVM offers, as a by-product, equilibrium values of cluster probabilities at any temperature and concentration. In the present application, the (second neighbor) pair probability \(x_2^6(O-O)\), on the \(\alpha\) sublattice, is of particular interest since it measures how well the O-Cu-O chains are ordered. Figure 4a shows these pair probabilities computed, with \(x = -0.5\), \(y = +0.5\), at various concentrations for fixed temperature (estimated to lie around 650 K) just below the top of the Ortho II phase region (14). It is seen that ordering is almost complete.
(x_2^a=1) at c_0=0.5 (z=7), then the pair probability decreases practically linearly with decreasing oxygen content. As the second order transition from I to II is encountered (at about c_0=0.31), the \( \alpha \) sublattice (normally rich in oxygen) splits into two sub-sublattices, \( \alpha_1 \) and \( \alpha_2 \). The full curve in Fig. 4a represents the average of the \( x_2^a \) pair probabilities on \( \alpha_1 \) and \( \alpha_2 \). The dotted line represents the pair probability in the Ortho I metastable extension. This curve, which is also shown on an enlarged concentration scale in Fig. 4b (full curve) is computed as the average of the pair probability curves of the two sublattices \( \alpha_1 \) and \( \alpha_2 \). These two are shown as dotted lines in Fig. 4b and reach extreme values close to cell doubling stoichiometry, near \( c_0=0.25 \) (z=6.5).

It is tempting to relate the O-Cu-O pair probability curve with its plateau-like behavior to the plot of the value of the transition temperature \( T_c \) as a function of temperature as determined experimentally by Cava et al. (8). Thus, the Ortho II phase could well be the one observed to have superconducting \( T_c \) around 60 K, although, for kinetic reasons, it may be difficult for the structure to reach equilibrium long range order.

6. CONCLUSION

Phase equilibrium in YBa_2Cu_3O_7 has been mapped onto a two-dimensional Ising model with isotropic first neighbor and anisotropic second neighbor effective pair interactions. Stability analysis has shown the possibility of cell doubling and quadrupling and ground state analysis has predicted a total of seven ordered superstructures. Of these, one is the superconducting (90 K) orthorhombic phase (Ortho I) and another is the proposed Ortho II (60 K). Phase diagrams have been calculated and second order transition points are in excellent agreement with available experimental data. Pair probabilities along Cu-O chains show a plateau not unlike the experimentally observed dependence of \( T_c \) on oxygen content.

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