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The composition-wave theory of oxide structures is used to interpret the
equilibrium structures of YBa$_2$Cu$_3$O$_{6+\delta}$, predict its equilibrium phase diagram,
describe the transient ordered states that are most likely to appear during
decomposition, and discuss the probable transformation paths and
microstructures that follow from them. The results are in reasonable
agreement with experiment.

INTRODUCTION

Research on the complex perovskite YBa$_2$Cu$_3$O$_{6+\delta}$ has shown that it has two pri-
mary structures, one (T) based on a tetragonal cell with the stoichiometric composition
YBa$_2$Cu$_3$O$_6$, and the other (O) on an orthorhombic cell with the stoichiometric composition
YBa$_2$Cu$_3$O$_7$ (Figure 1). The two structures differ in the distribution of oxygen atoms and
vacancies over the lattice sites on the basal plane of the unit cell, which form a base-cen-
tered sublattice (the "basal sublattice"). In the T-phase oxygen atoms and vacancies are
randomly distributed; in the fully ordered orthorhombic O-phase the oxygen atoms are
confined to alternate rows parallel to [100]. In addition, fine domains of more complex
ordered phases are occasionally found in orthorhombic YBa$_2$Cu$_3$O$_{6+\delta}$. These micro-
domains do not grow to macroscopic size, and hence appear to be unstable or metastable
transient states during low-temperature decomposition.

Recently one of us [1] has shown that the structures of the common oxide phases
can be understood and predicted through the method of concentration waves. In this ap-
proach the oxide is treated as an interstitial compound that forms through the ordering of
atoms and vacancies on the lattice and interstitial sites of a host lattice of simple symmetry.
The theory has been applied to YBa$_2$Cu$_3$O$_{6+\delta}$, and produced interesting results concerning
its structure, its probable phase diagram, its microstructure, and its transient states [2-4].
The present paper summarizes some of those results.

THE EQUILIBRIUM STRUCTURES OF YBa$_2$Cu$_3$O$_{6+\delta}$

The structure of YBa$_2$Cu$_3$O$_{6+\delta}$ is based on a perovskite that can be made by placing
a mixture of Cu atoms and vacancies on the sites of an FCC lattice sites and a mixture of Y,
Ba and O in the octahedral interstices. As discussed in reference [1], the perovskite struc-
ture results when both lattices are ordered in an L1$_2$ pattern by the star of the vector $k_1 =
(2\pi/a)(100)$, where a is the lattice parameter of the parent FCC cell. The structure of
YBa$_2$Cu$_3$O$_{6+\delta}$ is achieved by a 1-dimensional secondary ordering governed by the
wavevector $k_2 = (2\pi/a)(00\frac{1}{2})$, which triples the unit cell in the c-direction and introduces a
three-layer periodicity in all planes parallel to (001). The stoichiometric formula of the or-
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derived phase is \( \text{YBa}_2\text{Cu}_3\text{O}_6 \) (Figure 1a). In this phase all basal plane oxygen sites are vacant; by symmetry, the unit cell is tetragonal.

![Image of unit cells](image)

Figure 1: The unit cells of (a) \( \text{YBa}_2\text{Cu}_3\text{O}_6 \); (b) \( \text{YBa}_2\text{Cu}_3\text{O}_7 \). B-vac signifies a vacancy on the basal sublattice. Lattice distortions not shown.

The orthorhombic \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) phase (the O-phase) is derived from the T-phase by placing oxygen atoms in vacant sites on the basal plane. These sites form a base-centered tetragonal Bravais lattice, the "basal sublattice". Since the oxygen content is not sufficient to fill the sites of the basal sublattice, the Nernst principle requires that at sufficiently low temperature the oxide is at least metastable with respect to ordering or decomposition into stoichiometric structures. The preferred ordering wave can be inferred from the nature of primary ordering in the system; the concentration wave that accomplishes the greatest reduction in the energy is, by definition, the concentration wave that generates the primary structure. Since the perovskite cell of \( \text{YBa}_2\text{Cu}_3\text{O}_6+\delta \) is generated by the star of the wavevector \( \mathbf{k}_1=(2\pi/a)(100) \), this wavevector is the most likely choice to govern tertiary ordering. There is only one ordered distribution that is based on this vector and has only two values on the available sites of the basal sublattice:

\[
n(\mathbf{r}) = c + \eta \cos(\mathbf{k}_1 \cdot \mathbf{r}) = c + \eta \cos(2\pi x) \tag{1}
\]

where \( n(\mathbf{r}) \) is the probability that an oxygen atom is located at the site, \( \mathbf{r} \), of the basal sublattice, \( c \) is the fraction of basal-plane vacancies that is filled by oxygen atoms and \( \eta (\leq c) \) is the long-range order parameter. The coordinate \( x \) in the second form is either an integer or half-integer. When \( c = \eta = 1/2 \) equation (1) generates the \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) cell shown in Figure 1b. The structure is orthorhombic and is characterized by rows of O-atoms along the [010]-directions that alternate with rows of vacant sites. An examination of the unit cell shows that the ordering described by equation (1) is already present on all other planes that are perpendicular to the c-axis; hence the same order wave governs every sublattice. Since
$3k_1$ is not a reciprocal lattice vector of the basal sublattice the ordering reaction may be second order, as recent experimental observations seem to show [5]. The order parameter is a function of concentration and temperature.

The orthorhombicity ($\Delta$) of the structure is the difference in length between the lattice parameters $a$ and $b$ in the basal plane, and should also be a function of $\eta$. It can be approximated by the linear relation $\Delta(\eta) = a - b = \gamma \eta$, where $\gamma$ is an expansion coefficient. The coefficient, $\gamma$, can be found experimentally from the maximum value of $\Delta$ in the O-phase; since $\Delta_{\text{max}} = \gamma \eta$, $\Delta(\eta)/\Delta_{\text{max}} = \eta/c$.

**THE EQUILIBRIUM PHASE DIAGRAM**

The phase diagram can be approximated with the help of the available experimental data. The T-phase is preferred at elevated temperature, and transforms to the O-phase on cooling if the oxygen content is sufficiently high [5]. The structural transformation is congruent and apparently of second order. However, it follows from the Nernst principle that a non-stoichiometric O-phase must eventually decompose into a mixture of perfectly ordered phases. If we assume that only the T and O phases appear at equilibrium, then when $0<\eta<1$ the equilibrium state in the low temperature limit is a two-phase mixture of T and O. The phase diagram may then take either of two forms at intermediate temperature, depending on whether the O-phase decomposes directly into a mixture of T and O or undergoes an intermediate spinodal decomposition into two orthorhombic phases of different composition (O+O'). In the former case (Fig. 2a) the T-O ordering line terminates in a tricritical point where it bifurcates into two solvus lines that encircle the low-temperature two-phase (T+O) field. This type of diagram is found in a number of binary systems; the relevant theory is well known [6,7]. In the second type of diagram (Fig. 2b) the T+O field is capped by a miscibility gap within which the O-phase separates into two orthorhombic phases (O+O') that have the same structure but different oxygen contents.

![Figure 2: The possible forms for the phase diagram of YBa$_2$Cu$_3$O$_{6+\delta}$](image)

Since the available experimental data is not definitive it is useful to explore the predictions of simple thermodynamic models that incorporate the O-O interaction on the basal sublattice. The specific O-O interaction is unknown, but must have a relatively long range since it enforces crystallographic registry between the oxygen distributions on (001) planes that are separated by three unit cells of the parent perovskite structure; the range of the in-
teraction must exceed 20 atomic coordination shells. Given the long range of the interaction it is possible to use the simple mean-field approximation, which is always asymptotically correct at low temperature where the long-range order parameter, \( \eta \rightarrow 1 \), and is also reasonable at temperatures only slightly below the ordering temperature when the effective range of the interaction, \( r_0 \), is large [8].

In the mean-field approximation the free energy of a structure that has a basal-plane oxygen concentration, \( c (=\delta/2) \), and order parameter, \( \eta \), is

\[
F(\delta, \eta, t) = \frac{N}{2} \left[ (V(0)c^2 + V(k_1)\eta^2) + k_BT[(c+\eta)\ln(c+\eta)+(c-\eta)\ln(c-\eta)+(1-c+\eta)\ln(1-c+\eta)+(1-c-\eta)\ln(1-c-\eta)] \right]
\] (3)

where \( t \) is the temperature, \( N \) is the number of sites on the basal sublattice, \( k_B \) is Boltzmann's constant, and \( V(k) \) is the Fourier transform of the interaction potential

\[
V(k) = \sum_r W(r)e^{-ik\cdot r}
\] (4)

where \( W(r) \) is the energy of an O-O pair on the basal sublattice that is separated by the distance \( r \). Minimizing equation (3) with respect to the long-range order parameter, \( \eta \), yields the free energy function, \( F(\delta, \eta, t) \), from which the phase diagram can be computed. The shape of the phase diagram depends on the ratio, \( \xi = V(0)/|V(k_1)|. \) When \( \xi \) is less than about 0.25 the phase diagram has the form given in Figure 2a, with a simple tricritical point. When \( \xi > 0.25 \) the diagram has the morphology given in Figure 2b; the O-phase has a miscibility gap above the tricritical point.

The phase diagram is fixed by the parameters, \( \xi \), which fixes the shape of the diagram, and \( V(k_1) \), which fixes the temperature scale. Their values can be estimated from the available experimental data [5], which suggests that the \( T \rightarrow O \) transition falls at 700°C (973 K) in a sample with \( \delta = 0.5 \), and a maximum solubility, \( \delta = 0.9 \) at room temperature. Fitting the parameter \( V(k_1) \) to the ordering temperature yields the value \( V(k_1) = -5190k_B \). The room temperature value \( \delta = 0.9 \) then gives \( \xi = 0.4 \). The predicted phase diagram is drawn in Figure 3. It is of the type 2b; two orthorhombic phases coexist at intermediate temperatures.

![Figure 3: The proposed phase diagram for YBa₂Cu₃O₆+δ](image-url)
Since the first publication of this approximate phase diagram it has received experimental support from a number of independent investigations. These document the low temperature decomposition into T+O [9,10], the spinodal decomposition of the orthorhombic phase [11,12], and the composition limit at room temperature [9,13,14].

**TRANSIENT ORDERED STRUCTURES IN ORTHORHOMBIC YBa2Cu3O6+δ**

The phase transformation behavior of YBa2Cu3O7-x is complicated by the appearance of intermediate ordered states which appear in the form of ultrafine ordered domains [15-17]. These ordered domains do not grow to macroscopic size, and hence appear to be unstable or metastable transient states that occur during low-temperature decomposition.

The appearance of intermediate ordered phases during the decomposition of non-stoichiometric mixed-valence oxides is reasonably common. Secondary ordering induced by the repulsion of nonstoichiometric vacancies always reduces the free energy at low temperature and is kinetically favored over decomposition since it is accomplished by short-range atom rearrangements. Secondary ordering will, therefore, often precede decomposition even if it leads to an end product with a higher thermodynamic potential. If the decomposition is spinodal, as it may be in mixed-valence oxides since charge balance does not constrain the stoichiometry, the decomposition path passes continuously through a range of compositions. Since each composition is compatible with the formation of an ordered phase with an appropriate symmetry and stoichiometry, a homologous series of ordered phases of varying composition may develop. Well-documented examples include TiO2-x, VO2-x, and MoO3-x.

The theory of secondary ordering in mixed-valence oxides has been developed in some detail [1]. It begins from the observation that an ordered phase has the lowest possible free energy if its atomic structure satisfies a "maximum amplitude principle", that is, if the amplitude of the dominant concentration wave that generates the ordered superstructure has the maximum value that is consistent with the given composition. The maximum amplitude criterion is satisfied when atoms and vacancies order in a layer structure of alternating filled and vacant planes with faults on every (2n+1)th plane. The motif of such a structure is $D_n A_{n+1}$; the concentrations of vacancies, $D$, and atoms, $A$, are $c_D = \frac{n}{2n+1}$ and $c_A = \frac{n+1}{2n+1}$, respectively. The maximum amplitude of the concentration wave generating the $n$th structure (i.e., the maximum of the diffracted intensity) is associated with the wave vector

$$k_0 = 2\pi \frac{n}{2n+1} \mathbf{H}$$

where $\mathbf{H}$ is the reciprocal lattice vector of the parent structure that specifies the ordered sequence of planes.

To identify the homologous series for YBa2Cu3O6+δ note that the chemical formula can be written YBa2Cu3O6(01-x $\square_x$) where the parenthetical expression describes the fractions of oxygen atoms and vacancies in the (001) basal plane. If a homologous series is formed, the stoichiometric formulae should be YBa2Cu3O7-$\frac{n}{2n+1}$. Substituting the integer series $n=1, 2, 3...$ into eq. (3) we obtain the possible homologous series of the transient secondary ordered oxides:

$$\text{YBa2Cu3O7-} \frac{1}{3}, \text{YBa2Cu3O7-} \frac{2}{3}, \text{YBa2Cu3O7-} \frac{3}{7}, ... \text{YBa2Cu3O7-} \frac{1}{2}$$

(6)
The associated superlattice reflections fall at the points $\frac{1}{3}H$, $\frac{2}{3}H$, $\frac{3}{3}H$, ..., $\frac{1}{3}H$, respectively. Since the dominant ordering vector is along $(100)$ filled and vacant $(100)$ planes should alternate in the homologous phases. In the basal plane the [010] filled by O atoms and vacancies alternate in the pattern: $\text{OO O O O O}$ for the $x = \frac{1}{3}$ structure, $\text{OO O O O O O O O O}$ for $x = \frac{2}{3}$, and $\text{O O O O O O}$ for $x = \frac{1}{2}$. The phases are all orthorhombic, but have orthorhombicity ratios that decrease with $n$. Given $H = H(100)$ the maximum intensity superlattice diffraction maxima are: $(\frac{1}{3}00) \ [\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}]$; $(\frac{2}{3}00) \ [\text{YBa}_2\text{Cu}_3\text{O}_{7-\frac{2}{3}}]$; $(\frac{3}{3}00) \ [\text{YBa}_2\text{Cu}_3\text{O}_{7-\frac{3}{5}}]$; ...; $(\frac{2}{2}00) \ [\text{YBa}_2\text{Cu}_3\text{O}_{7-\frac{1}{2}}]$. The diffraction peaks are shown schematically in Fig. 4. Since the members of the homologous series are not equally stable, some may form only at particular values of the temperature and composition. Others may not appear at all.

![Figure 4: Schematic diffraction pattern of the homologous series in YBa$_2$Cu$_3$O$_{7-x}$. The positions of the various phases are labelled by the index $h$ in (hkl).](image)

The recent reports of secondary ordering in orthorhombic YBa$_2$Cu$_3$O$_{6+\delta}$ are in at least qualitative agreement with the theory. Diffraction maxima at $(\frac{1}{3}00)$ ($n=1$) were observed by Chen [15]; the corresponding tripling of the period along the [100] direction was imaged by Van Tendeloo, et al. [16]. Werder, et al. [17] found $(\frac{2}{3}00)$ diffraction maxima ($n=2$). They also observed diffuse maxima at $(\frac{4}{2}00)$, whose source may either be the limiting structure at $n = \infty$, or the accumulation of diffraction intensity from structures with high values of $n$. The $(\frac{3}{3}00)$ maxima appeared when the composition of YBa$_2$Cu$_3$O$_{7-x}$ lay within the range $0.3 < x < 0.4$, in good agreement with the predicted stoichiometry $x = \frac{1}{2}$ of the YBa$_2$Cu$_3$O$_{7-x}$ homologous phase. The status of the other members of the homologous series at $n = 3, ..., \infty$ is not clear. They were not found either because they did not form or because when $n \geq 3$ the positions of the relevant diffraction maxima lay so close to one another and to the maximum at $(\frac{2}{2}00)$ that they were gathered into the broad, diffuse maximum about $(\frac{2}{2}00)$. 

6
Three aspects of the phase transformation behavior of YBa$_2$Cu$_3$O$_{6+\delta}$ can be inferred from the known behavior of similar systems: the microstructure of the orthorhombic phase, the microstructure of the mixed T+O state, and the appearance of transient ordered states during spinodal decomposition.

The orthorhombic distortion that accompanies ordering strains the parent lattice unless it occurs homogeneously in a single crystal. The microstructure that minimizes the internal strain is known from the established theory of similar systems [18]. The elastic strain is accommodated by dividing the crystal into parallel lamellae that are (110) twin-related domains. Evidence for this microstructure is given, for example, in the atomic resolution micrographs of Van Tendeloo, et al. [16]. If the subsequent transformation is direct decomposition into T+O, the elastic energy is minimized if the O-phase maintains the a-axis orientation of the parent lamellae. The result is a microstructure of the "tweed" type. If the microstructure is permitted to coarsen then strain-induced coarsening leads to a martensite-like structure in which colonies of (110) twin-related platelets form plates that are embedded in a matrix of T-phase. The habit of the plate is determined by the condition that the macroscopic shape change of the plate is an invariant plane strain, to eliminate the volume-dependent part of the elastic energy.

The spinodal transformation path is more complex. If orthorhombic YBa$_2$Cu$_3$O$_{7-x}$ be cooled to a temperature below the secondary spinodal shown by the dashed line in Fig. 3 it preferentially decomposes into two orthorhombic phases by the spinodal mechanism. The oxygen content of one of the decomposition products evolves towards YBa$_2$Cu$_3$O$_7$ (x decreases in the formula YBa$_2$Cu$_3$O$_{7-x}$) while the oxygen content of the other evolves towards the YBa$_2$Cu$_3$O$_6$ (x increases). The oxygen contents of the decomposing phases pass sequentially through the stoichiometric compositions of the Magneli-like phases at x = $\frac{n}{2n+1}$. Since the overall oxygen content of a macroscopic phase, which is controlled by bulk diffusion, evolves slowly compared to the relaxation time for secondary ordering, which requires only local atom jumps, the formation of a transient homologous phase is kinetically favored. Given the spatial variation in mean composition during spinodal decomposition, the homologous phase should not grow to macroscopic size before the local composition shifts to the next homologous phase in the series. The reduction of the oxygen content in the oxygen-lean O-phase during the decomposition reaction continues until it reaches the limit of stability with respect to disorder, and disorders spontaneously to create the equilibrium tetragonal phase.

The sequential formation of ordered phases is expected when x ≤ 0.5, where the homologous series terminates in the (100) phase (n = ∞) with the composition YBa$_2$Cu$_3$O$_{6.5}$. While a "mirror-image" series with x > 0.5 is possible, its stability is questionable because of the high vacancy concentration. When x > 0.5 we would expect direct decomposition into a two-phase mixture of T and O.

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