# Ordering and Decomposition in the High-Temperature Superconducting Compound $YBa_2Cu_3O_x$

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The method of concentration waves is applied to structural transformations in superconducting Y-Ba-Cu oxide. The method predicts an ordering reaction that results in a tetragonal-to-orthorhombic phase transformation, and also yields the correct structure of the $YBa_2Cu_3O_7$ orthorhombic ordered phase. The results suggest that at low temperature the off-stoichiometric orthorhombic phase is thermodynamically unstable with respect to secondary decomposition into a mixture of ordered orthorhombic and disordered tetragonal phases, whose microstructure can be anticipated.

The structure of the high-$T_c$ Y-Ba-Cu-O superconducting oxide has recently been determined by neutron diffraction[1,2] and is shown in an idealized form in Fig. 1. The results imply a stoichiometric composition: $YBa_2Cu_3O_7$. While the source of the high superconducting critical temperature is not fully understood, it is apparently associated with the ordering of the oxygen atoms in the basal plane of the unit cell into alternate rows of filled and empty oxygen sites. The asymmetric distribution of oxygen in the basal plane causes an orthorhombic distortion of the structure that is observed at low temperature. The structure transforms reversibly from tetragonal to orthorhombic symmetry at about $750\,°C$.[3-5]

Despite the significant research effort that has recently been devoted to the study of the superconducting oxide, important aspects of its structural and microstructural behavior remain unclear. This is due in part to the difficulty of determining the composition and distribution of the oxygen constituent, whose concentration varies from six to seven atoms per unit cell. It is the purpose of this Letter to identify some of the probable structural properties of the superconducting oxides from known theory that treats the behavior of similar systems. The results interpret the order and orthorhombic character of the oxide, suggest that off-stoichiometric oxides will likely decompose into similar but distinct oxides of different oxygen stoichiometries at low temperature, and point out the probable microstructures of the low-temperature state, which may have important consequences for its superconducting properties.

Recently one of us has shown that the structures of most of the common oxide phases can be understood and predicted by application of the method of concentration waves.[6,7] In this approach 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. As we shall describe in detail elsewhere, the same approach can be used to generate the observed structure of $YBa_2Cu_3O_7$. The perovskite structure on which it is based can be obtained from an fcc lattice by the placing of a mixture of Cu atoms and vacancies on the fcc lattice sites and a disordered mixture of Y, Ba, and O in the octahedral interstices. As discussed in Ref. 7, the perovskite structure results when both lattices are ordered by the star of the vector $k_1 = [2\pi/a](1,0,0)$, where $a$ is the lattice parameter of the parent fcc cell. A structure like that of $YBa_2Cu_3O_x$ is achieved by a layer secondary ordering governed by the wave vector $k_2 = [2\pi/a](0,0,\frac{1}{3})$, which is one of the preferred secondary ordering vectors identified in Ref. 7. The stoichiometric formula of the



YBa$_2$Cu$_3$O$_6$          YBa$_2$Cu$_3$O$_7$
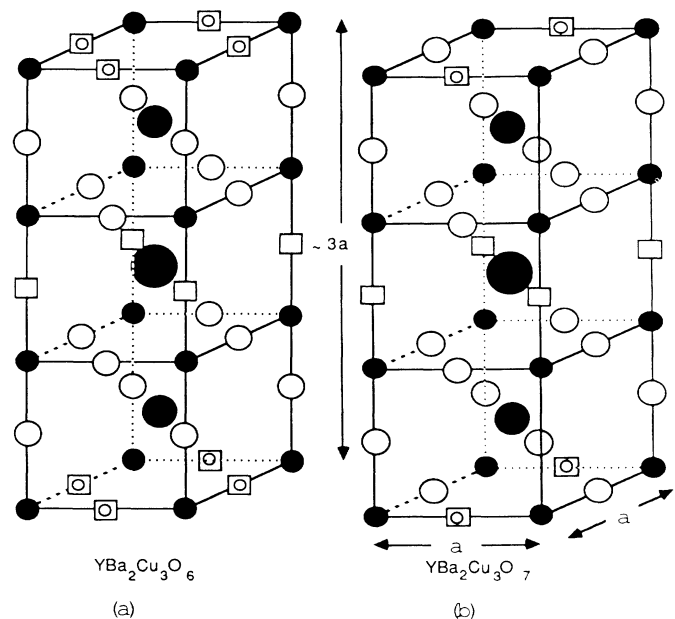
(a)                (b)

FIG. 1. (a) The structure of the tetragonal parent phase. (b) The structure of the orthorhombic ordered phase: small filled circles, Cu; medium filled circles, Ba; large filled circles, Y; open circles, O atoms; circles in squares, O-atom vacancies in basal planes; squares, O-atom vacancies.

   

resulting ordered phase is $YBa_2Cu_3O_6$ [Fig. 1(a)]. In this phase all basal-plane oxygen sites are vacant; by symmetry, the unit cell should be tetragonal. It has been found experimentally[3,5] and is referred to as the $T$ phase in the following.

*Ordered structure of $YBa_2Cu_3O_7$.*—The orthorhombic $YBa_2Cu_3O_7$ phase (the $O$ phase) is derived from the $T$ phase by the placement of oxygen atoms in vacant sites on the basal plane. These sites form a base-centered tetragonal Bravais lattice, which we shall call 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 tertiary ordering or decomposition into stoichiometric structures. It has been shown[7] that, with a single known exception (the Magneli phases), the stable superstructures that arise from an ordering of this type are generated by concentration waves belonging to one star. This condition restricts the possible ordering vectors that can generate superstructures. The appropriate set for the base-centered tetragonal basal sublattice of the oxide can be shown to have the form $k_3 = (2\pi/a)(HKL)$, where

$$(HKL) = \{10L\}, \{\tfrac{1}{2} \tfrac{1}{2} L\}, \{\tfrac{1}{2} 0L\}, \{\tfrac{2}{3} 0L\},$$

$$\{\tfrac{1}{3} \tfrac{1}{3} L\}, \{\tfrac{1}{4} \tfrac{1}{4} L\}, \quad (1)$$

and $L = 0$, $\tfrac{1}{6}$, or $\tfrac{1}{12}$, and the indices relate to the parent cubic lattice. Under the assumption of a two-body effective interaction between the oxygen atoms, the preferred ordering wave from the list (1) is determined by the minimum of the $k$-space interaction potential

$$V(k) = \sum_r W(r) \exp(i k \cdot r), \quad (2)$$

where $W(r)$ is the effective interaction between oxygen atoms separated by the vector $r$, that is, the potential for rearrangement of the oxygen atoms in the presence of the three-dimensional background structure.

We cannot use this equation (2) directly since we do not know the effective O-O interaction in Y-Ba-Cu-O. However, 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 primary perovskite cell of Y-Ba-Cu-O is generated by the star of the wave vector $k_1 = (2\pi/a)(1,0,0)$, the vector $k_1 = (2\pi/a)(1,0,0)$ [or the degenerate vector $(2\pi/a) \times (0,1,0)$] should be the member of the set (1) that governs tertiary ordering. There is only one ordered distribution that is based on this vector and satisfies the condition[8] that it has only two values on the available sites of the basal sublattice of $YBa_2Cu_3O_6$ (the lattice of vacant sites designated in Fig. 1). The distribution function is

$$n(r) = c + \eta \cos(k_1 \cdot r) = c + \eta \cos(2\pi x), \quad (3)$$

where $n(r)$ is the probability that an oxygen atom is located at the site $r$ of the basal sublattice, $c$ is the fraction of basal-plane vacancies that is filled by oxygen atoms, and $\eta$ is the long-range order parameter. The coordinate $x$ in the second form is either an integer or half integer. When $c = \eta = \tfrac{1}{2}$, Eq. (3) generates the $YBa_2Cu_3O_7$ structure shown in Fig. 1(b). The structure is orthorhombic and is characterized by rows of O atoms along [010] directions that alternate with rows of vacant sites. (de Fontaine and Moss[9] provided an independent treatment of this ordering reaction on the basis of a two-dimensional model with second-neighbor interactions.)

An examination of the structure shown in Fig. 1 shows that the ordering described by Eq. (3) is already present on all other planes that are perpendicular to the $c$ axis of the unit cell. The ordering (3), hence, obeys the rule[8] that the same order wave appear on every sublattice.

The concentration wave that induces tertiary order involves the single wave vector $k_1$. 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.[10] The order parameter is a function of concentration and temperature, whose specific form is known for various approximate treatments of the free-energy function.[7,11,12]

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 the long-range order parameter. It can be approximated by the linear relation

$$\Delta(\eta) = a - b = \gamma \eta, \quad (4)$$

where $\gamma$ is an expansion coefficient, which follows via a Taylor expansion about the point $\eta = 0$. The linear term in (4) does not vanish as usual since the transformation $\eta \rightarrow -\eta$ reverses the $a$ and $b$ axes and, hence, the sign of $\Delta$. The coefficient $\gamma$ can be found experimentally from the maximum value of $\Delta$, the value in the stoichiometric $O$ phase. Since $\Delta_{max} = \gamma c$, $\Delta(\eta)/\Delta_{max} = \eta/c$.

The orthorhombic distortion that occurs on 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.[11] The elastic strain is accommodated by the division of the crystal into parallel plates that are (110) twin-related 90° domains. The microstructure is shown schematically in Fig. 2 and should be observed in congruently ordered $YBa_2Cu_3O_x$ at temperatures below the ordering temperature. (Evidence for this microstructure seems to be present in the atomic-resolution micrographs of Van Tendeloo *et al.*[5])

*Low-temperature decomposition.*—The tertiary-ordering reaction discussed above rearranges the oxygen atoms on the basal sublattice without changing their total concentration. It follows that an off-stoichiometric oxide remains off stoichiometric after cooling to below
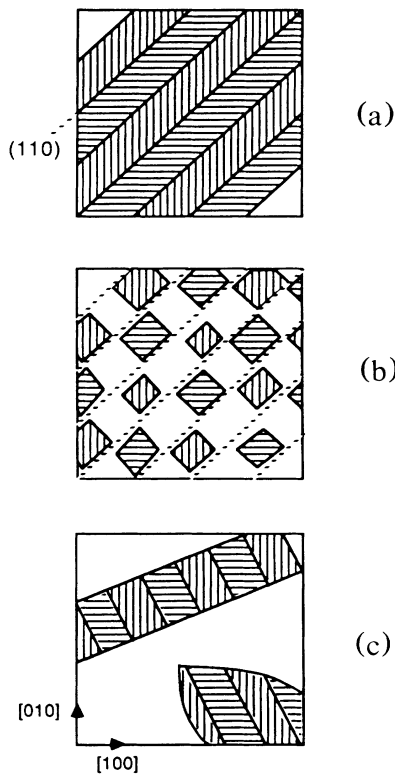
FIG. 2. Schematic picture of the expected microstructure of the two-phase state of $YBa_2Cu_3O_x$: (a) the (110) twin structure of the off-stoichiometric $O$ phase formed as a result of congruent ordering at the first stage of decomposition; (b) the "tweedlike" ⟨110⟩ aligned structure; (c) the morphology of colonies of twin-related (110) lamellae.
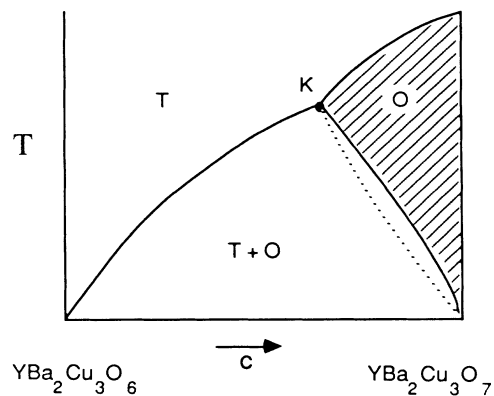


FIG. 3. Schematic drawing of the equilibrium diagram: $O$, ordered orthorhombic-phase field; $T$, disordered tetragonal-phase field. The dotted line designates the secondary spinodal curve for decomposition of the off-stoichiometric $O$ phase. $K$, critical point.

$T_c$. By the Nernst principle such an alloy cannot be stable at low temperature. If $V(0)+V(k_3) < 0$, it decomposes into a mixture of $T$ phase of composition close to $YBa_2Cu_3O_6$ and $O$ phase of composition near $YBa_2Cu_3O_7$. Otherwise it undergoes one or more additional ordering reactions before decomposing. Since there is no evidence for additional ordering reactions we consider the decomposition of the $O$ phase. The phase diagram that governs its decomposition is drawn schematically in Fig. 3. Landau[13] and Krivoglaz[12] have suggested ways of calculating the critical point $(T_K, c_K)$ at which instability with respect to congruent ordering is changed into instability with respect to decomposition.

The microstructure induced by a decomposition reaction of this sort is well known from the behavior of similar systems.[11] After ordering, the system consists of twin-related (110) lamellae of the $O$ phase. Each lamella undergoes secondary decomposition. To minimize the elastic energy the precipitates of $O$ phase maintain the $a$-axis orientation of the parent lamella and are hence aligned along ⟨110⟩ directions. The result is a microstructure of the "tweed" type, drawn schematically in

Fig. 2. If the microstructure is permitted to coarsen, then strain-induced coarsening leads to a martensitelike 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 decomposition of the off-stoichiometric oxide and the characteristic microstructures that result may be observable through high-resolution electron microscopy.

The decomposition reaction should have an important effect on the superconducting properties of the off-stoichiometric oxide. The decomposition has the consequence that near-stoichiometric $O$ phase is present in off-stoichiometric oxides, and so the critical temperature and critical field should not depend strongly on the overall stoichiometry. However, the decomposition also has the consequence that the $O$ phase in an off-stoichiometric oxide may be intimately embedded in a matrix of $T$ phase, which is believed to be semiconducting. The two-phase microstructure should have a profoundly deleterious effect on the critical current of off-stoichiometric material. The microstructure that results from a decomposition of this sort also interacts strongly with grain boundaries in polygranular structures, and may share responsibility for the low superconducting critical current observed in bulk polygranular material.

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