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and J.W. Morris, Jr.

September 1987

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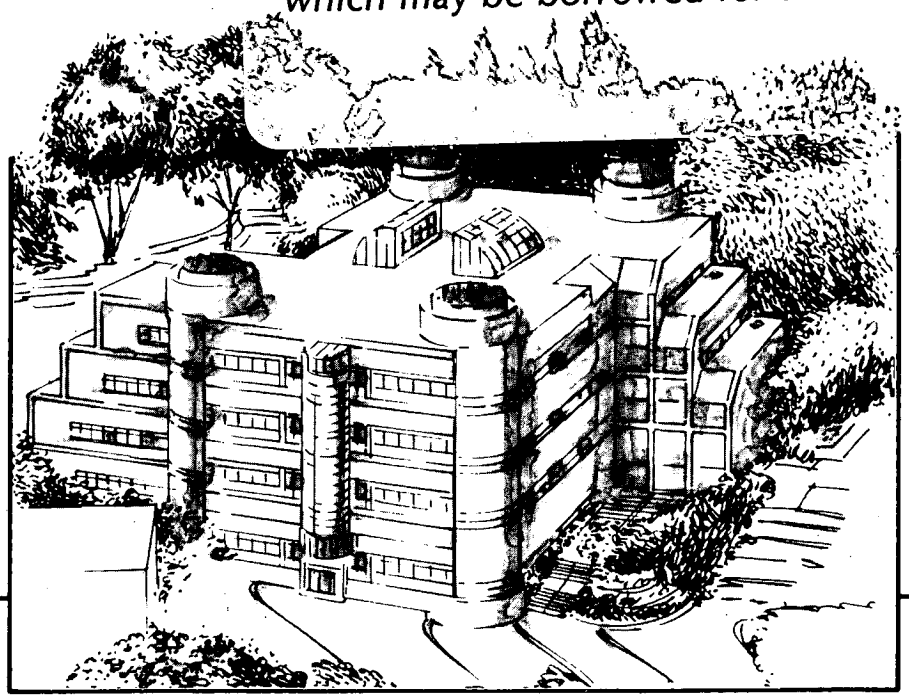

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Recent high temperature x-ray [1], neutron diffraction [2-4] and electron microscopic studies [5] have shown that the superconducting oxide $YBa_2Cu_3O_{6+\delta}$ has two common structures, one based on a tetragonal cell with nominal composition $YBa_2Cu_3O_6$ and the second based on an orthorhombic cell with the nominal composition $YBa_2Cu_3O_7$. The two phases differ in the distribution of oxygen atoms and vacancies over the vacant sites in the basal plane of the modified perovskite structure of $YBa_2Cu_3O_6$, which is illustrated in Figure 1a. In the tetragonal phase (T) these sites are vacant or contain a random distribution of oxygen atoms and vacancies. In the fully ordered orthorhombic structure (O), which is shown in Figure 1b, the oxygen atoms and vacancies fill alternate lines of sites parallel to [010].

The evidence suggests that the oxide is invariably in the T-phase at sufficiently high temperature, and transforms to the O-phase on cooling if the oxygen content is high enough [4]. The transformation is critical since only the O-phase exhibits high temperature superconductivity [6]. It is therefore important to clarify the phase fields of the two structures. If we confine our attention to the low-temperature portion of the phase diagram then an appropriate mean-field model should provide a reasonable approximation for the T-O equilibrium [7-9]. The

physical parameters required to make the model quantitative can be estimated from the results of recent experimental work. We use this procedure in the following to estimate the T-O equilibrium in $YBa_2Cu_3O_{6+\delta}$ as a function of oxygen concentration and temperature, or, alternately, as a function of temperature and oxygen partial pressure.

Since we are concerned with the ordering of oxygen atoms and vacancies in the basal plane of the oxide against a constant background structure, we consider the base-centered tetragonal Bravais sublattice of sites shown in Figure 2a (the "basal sublattice"). The sites of this sublattice are located at vector positions $\mathbf{R} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$, where $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ ($|\mathbf{a}_3| \sim 3|\mathbf{a}_1|$) are the unit translation vectors of the $YBa_2Cu_3O_{6+\delta}$ unit cell, x and y are both integers or half-integers, and z is an integer. The ordering of oxygen atoms over the sublattice can be described by the distribution [9]

$$n(\mathbf{R}) = n(x,y,z) = c + \eta\cos(\mathbf{k}^{\bullet}\cdot\mathbf{R}) = c + \eta\cos(2\pi x) \qquad (1)$$

where $n(\mathbf{R})$ is the probability that an O atom occupies the site at $\mathbf{R}$, c is the fraction of sublattice sites filled by O-atoms, and η is the long-range order parameter. The occupation probability $n(\mathbf{R})$ takes the two values, $n_1=c+\eta$ and $n_2=c-\eta$ on the sublattice sites. In the fully ordered state, $c=\eta=1/2$, $n_1=1$ and $n_2=0$, which orders the sublattice as shown in Figure 2b and generates the orthorhombic structure ($YBa_2Cu_3O_7$) shown in Figure 1b. The concentration wave that orders the basal sublattice involves the single wave-vector $\mathbf{k}^{\bullet} = (2\pi/a)(100)$. Since $3\mathbf{k}^{\bullet}$ is not a reciprocal lattice vector of the basal sublattice, the order transition satisfies the Lifshitz rule (see [8]) and may be of second order.

To find the phase diagram for the basal sublattice it is necessary to compute the Helmholtz free energy as a function of the concentration and order parameter. In the mean field approximation the part of the free energy that depends on the oxygen configuration on the basal sublattice can be written

$$F[\{n(\mathbf{R})\}] = (1/2)\Sigma_{\mathbf{R},\mathbf{R}'}W(\mathbf{R}-\mathbf{R}')n(\mathbf{R})n(\mathbf{R}') +$$

$$+ k_BT[\Sigma_{\mathbf{R}}\{n(\mathbf{R})\ln[n(\mathbf{R})]+[1-n(\mathbf{R})]\ln[1-n(\mathbf{R})]\}] \quad (2)$$

where k_B is Boltzmann's constant and $W(\mathbf{R}-\mathbf{R}')$ is the effective interaction between oxygen atoms on sites $\mathbf{R}$ and $\mathbf{R}'$ on the basal sublattice (note that this is total interaction, which does not include the effect of the crystal field imposed by the other atoms of the structure). If the oxygen distribution function, equation (1), is substituted into equation (2), F can be written as a function of c and η:

$$F[c,\eta] = (N/2)\{V(0)c^2 + V(\mathbf{k}^*)\eta^2 + k_BT[(c+\eta)\ln(c+\eta)+$$

$$(1-c-\eta)\ln(1-c-\eta)+(c-\eta)\ln(c-\eta)+(1-c+\eta)\ln(1-c+\eta)]\} \quad (3)$$

where

$$V(\mathbf{k}) = \Sigma_{\mathbf{R}}W(\mathbf{R})\exp(i\mathbf{k}\cdot\mathbf{R}) \quad (4)$$

is the Fourier transform of the two-body interaction energy and N is the total number of sites on the basal sublattice. The equilibrium value of the order parameter, η, for given values of T and c is that which minimizes the free energy, and is the solution to the equation

$$\ln\{[(c-\eta)(1-c-\eta)]/[(c+\eta)(1-c+\eta)]\} = 2V(\mathbf{k}^*)\eta/k_BT \quad (5)$$

The temperature, T_c, at which oxygen orders congruently on the basal sublattice to create the orthorhombic phase is given by the bifurcation point of equation (4):

$$T_c = -c(1-c)V(\mathbf{k}^*)/k_B \quad (6)$$

If the oxygen concentration, c, on the basal sublattice is less than 0.5, that is, if $\delta = 2c < 1$ in $YBa_2Cu_3O_{6+\delta}$, then the ordered, orthorhombic phase is off-stoichiometric after ordering, and, by the Nernst principle, is at least metastable at sufficiently low tempera-

ture. It must undergo either secondary ordering or decomposition to achieve a fully ordered state. As shown in reference [10] the behavior on cooling is governed by the minimum value of the potential

$$\tilde{V}(\mathbf{k}) = (1/2)[V(\mathbf{k})+V(\mathbf{k}-\mathbf{k}^{\bullet})] \tag{7}$$

Decomposition is preferred if the minimum value of $\tilde{V}(\mathbf{k})$ lies at the origin, $\mathbf{k} = 0$, while secondary ordering is preferred if $\min[\tilde{V}(\mathbf{k})]$ falls at $\mathbf{k} \neq 0$. Since the available neutron diffraction data on the oxide show only the Bragg peaks of the orthorhombic phase $YBa_2Cu_3O_7$, secondary decomposition is assumed.

We therefore wish to construct the equilibrium diagram for the compound $YBa_2Cu_3O_{6+\delta}$ on the assumption that oxygen orders on the basal sublattice, and the system then decomposes into two phases that differ in the oxygen concentration and degree of order. To do this we find the free energy, F, of the system as a function of the basal-plane oxygen concentration, c, for the range $0 \leqslant c \leqslant 0.5$ (which corresponds to $0 \leqslant \delta \leqslant 1$), find the range of temperatures over which the free energy curve divides into two stable branches, and locate the common tangent between the two branches. Solving equation (5) for the equilibrium long-range-order parameter, η, as a function of c and T, and substituting the result into equation (3), the free energy can be expressed in the dimensionless form

$$f = F/|V(\mathbf{K}^{\bullet})| = f(\tau,c,\xi) \tag{8}$$

where $\tau = k_BT/|V(\mathbf{k}^{\bullet})|$ and $\xi = V(0)/|V(\mathbf{k}^{\bullet})|$ is a dimensionless interaction potential. Since the system orders before decomposing, we expect $V(0) > 0$, $V(\mathbf{k}^{\bullet}) < 0$ and $\xi < 1$.

The computed T-O ordering curve and subsequent miscibility gap is plotted for several admissible values of the interaction parameter, ξ, in Figure 3. The calculated diagrams contain two-phase regions where the tetragonal (T) and orthorhombic (O) phases coexist, and, when $\xi > 0.286$, also contain a region near the top of the miscibility gap where

the O-phase decomposes into two orthorhombic phases (O′ and O″) with different compositions. At lower values of ξ the phase diagram contains a critical point at which the second order transition line bifurcates into two solvus lines that envelop the two-phase region, as is found in similar ordering systems [11]. In the mean-field approximation the temperature and concentration of the critical point are given by the relations [10]:

$$c_K = (1/2) - \{(1+\xi)/[12(1-\xi)]\}^{1/2}$$

$$T_K = - c_K(1-c_K)V(\mathbf{k}^*)/k_B \tag{9}$$

To identify the appropriate phase diagram for $YBa_2Cu_3O_{6+\delta}$ we require values for the interaction parameter, ξ, which fixes the shape of the diagram, and the potential, $V(\mathbf{k}^*)$, which sets the scale of temperature. We can approximate these from the available experimental data. Reference [4] reports that at $c = 0.25$ the primary ordering reaction occurs at $T = 700^oC = 993$ K. This result is consistent with equation (6) if $V(\mathbf{k}^*)/k_B = -5190$ K.

The interaction parameter, ξ, is more difficult to extract from the experimental data, but can be estimated from the solubility of O in the orthorhombic phase. According to reference [4] the composition of the orthorhombic phase saturates near $\delta = 0.9$ for samples exposed to a range of oxygen partial pressures. If we assume that this saturation effect is due to two-phase T-O equilibrium, that is, if we associate the saturation value with the oxygen content of the O-phase in two-phase equilibrium, then we can estimate the value of ξ. Letting the saturation point at $c = 0.45$ ($\delta = 0.9$) correspond to the equilibrium oxygen concentration in the O-phase at room temperature (293 K; $\tau = 0.0564$), then the approximate value of the interaction parameter is $\xi = 0.4$ (see Figure 3).

The phase diagram computed with the values $V(\mathbf{k}^*) = -5190$ K and $\xi = 0.4$ is plotted in Figure 4. The diagram displays two distinct types of two-phase equilibria: equilibrium between two orthorhombic phases of

different composition at T greater than about 380 K and equilibrium between orthorhombic and tetragonal (disordered) phases at lower T. The instability points are also marked on the diagram.

The instabilities govern the expected behavior of the oxide on quenching, which should phenomenologically resemble that of similar systems that are more fully understood. If the oxide is quenched into the two-phase region from the orthorhombic field (O) a spinodal decomposition into two orthorhombic phases (O′ and O″) is expected as soon as the temperature falls below the broken line. If the final temperature is below about 380 K the composition of the oxygen-depleted phase (O′) eventually reaches the dashed line on the left-hand side, at which point it spontaneously disorders into the tetragonal (T) phase to produce the final two-phase mixture. If an oxide is quenched into the two-phase region from the tetragonal (T) field congruent ordering initiates when its temperature falls below the dashed line on the left hand side of the diagram. The ordered phase either lies within the spinodal region of the phase diagram or falls into it on subsequent cooling. In either case it decomposes into two orthorhombic phases, and the oxygen-deficient phase disorders back into the tetragonal structure.

In addition to the phase diagram as presented in Figure 4, it is possible to estimate the phases present as a function of the oxygen partial pressure in equilibrium with the oxide from the condition that the chemical potential of oxygen be uniform throughout the system. Since the variable oxygen is that present on the basal sublattice, the chemical potential of oxygen in the solid can be written

$$\mu = \mu^{o} + (1/N)\partial F[c,\eta(c,t)]/\partial c \qquad (10)$$

where μ^{o} is the oxygen potential in the limit $c \rightarrow 0$ and N is the number of sites on the basal sublattice. If equation (4) is substituted into (10) under the constraint $\partial F/\partial\eta = 0$ the result is

$$\mu = \mu^{o} + V(0) + (1/2)k_{B}T\ln\{[c^{2}-\eta^{2}]/[(1-c)^{2}-\eta^{2}]\} \qquad (11)$$

Since oxygen exists as a diatomic molecule in the vapor ($O_2 \rightarrow 2O$) its chemical potential in the vapor depends on the root of the oxygen partial pressure, p, and can be written

$$\mu = \mu^{o}_{gas} + k_B T \ln(P)^{1/2} \tag{12}$$

Equating the left hand sides of (11) and (12) yields the condition of equilibrium

$$[V(0)c/k_B T] + (1/2)\ln\{[c^2-\eta^2]/[(1-c)^2-\eta^2]\} = \ln[p^{1/2}/K] \tag{13}$$

where $K = K(T) = \exp\{[\mu^{o}-\mu^{o}_{gas}]/k_B T\}$. Since the equilibrium value of the order parameter, η, is determined as a function of c and T by equation (5), equation (12) determines the oxygen concentration on the basal sublattice as a function of $\ln[p^{1/2}/K]$. Example curves are plotted in Figure 5.

The quantitative forms of the phase diagrams given in Figures 4 and 5 are based on estimates from the experimental data, and are hence only approximate. However, the qualitative forms of the diagrams are a consequence of the $T \rightarrow 0$ ordering reaction and the Nernst principle and, barring the discovery of additional ordering reactions at low temperature, should be accurate. They suggest a series of reactions that should be observable, and that may permit a rather precise control over the microstructure of high-temperature superconducting oxide.

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FIGURE CAPTIONS

Fig. 1a. The structure of the $YBa_2Cu_3O_6$ tetragonal phase.

Fig. 1b. The structure of the $YBa_2Cu_3\ O_7$ orthorhombic phase.

Fig. 2a. The basal sublattice of oxygen vacancies occupied by ordering O atoms.

Fig. 2b. The ordered distribution of O atoms over the basal sublattice.

Fig. 3. Set of the calculated equilibrium diagrams for different values:

T - designates the disordered tetragonal phase.

O - ordered orthorhombic phase.

τ is reduced temperature.

Critical temperatures are shown by circles.

Numbers above the solvus curves indicate the value ξ.

(T+O) corresponds to the two-phase field.

Fig. 4. The calculated equilibrium diagram for ξ=0.4. Bold lines designate the second-order transition line tne the solvus lines. The dot-dash line shows the spinodal. The horizontal line separates the two phase (O+O') region of the two orthorhombic phases coexistance from the region (T+O) coexistance of the tetragonal and orthorhombic phases.

Fig. 5. The calculated dependence of O atom composition in the oxide on the oxygen pressure (ξ=0.4). Numbers 1,2,3 are related to the reduced temperatures τ=0.06188 (ordering and decomposition), τ=0.0866 (ordering without decomposition) and τ-0.1 (disordered field).

On the curve 1, the thin line designates the metastable states and the dash line corresponds to the unstable region.

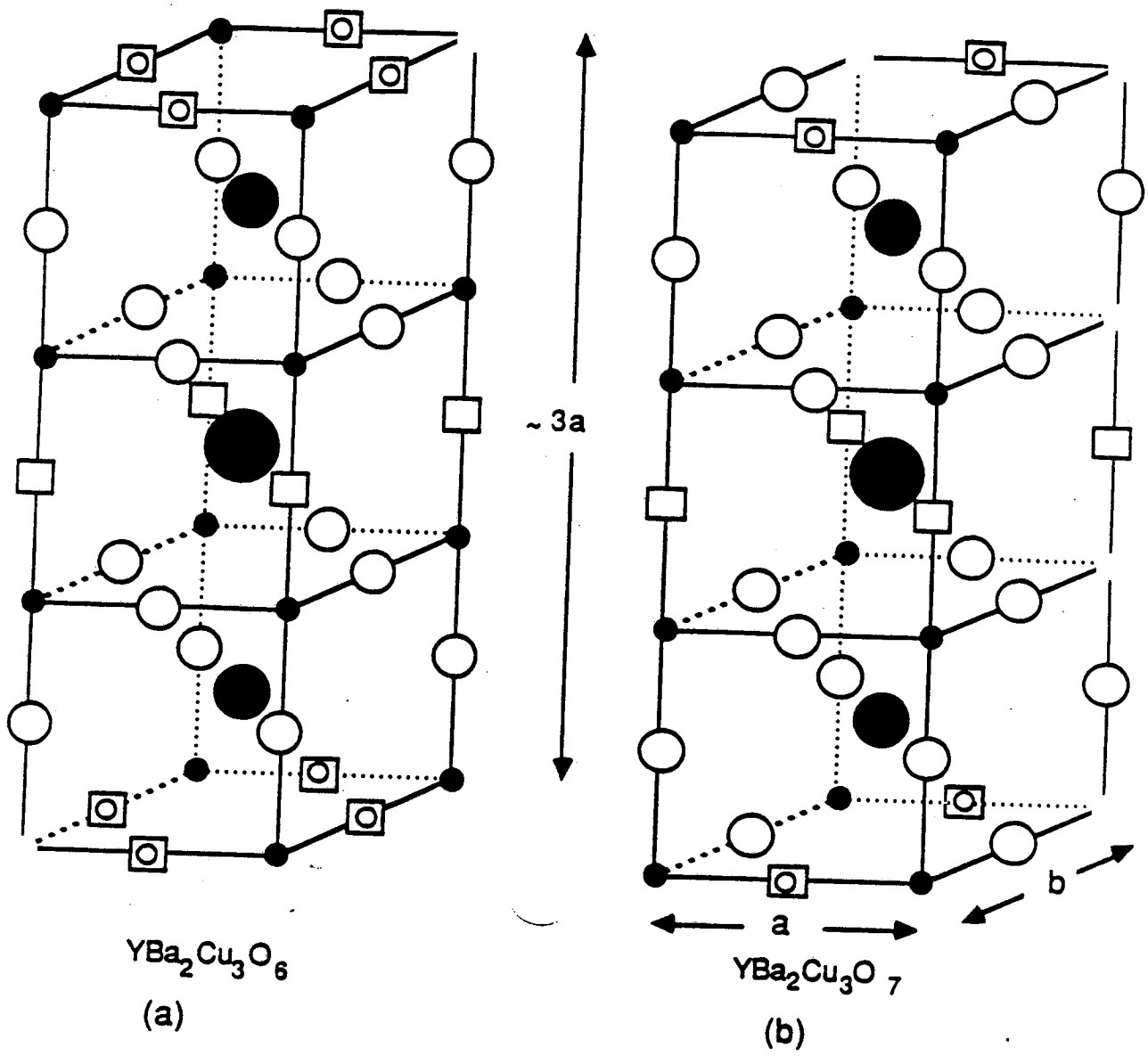
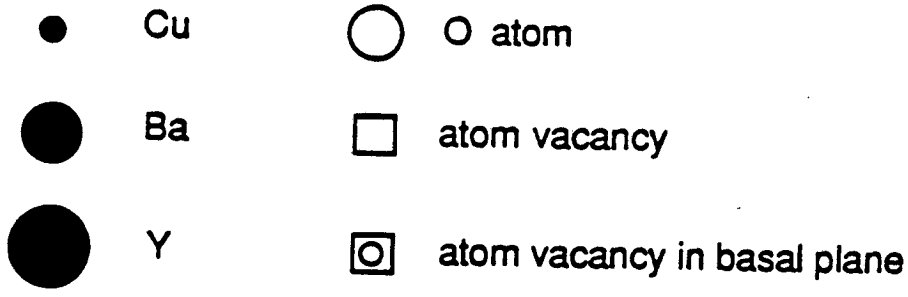


Fig. 1. (a) The structure of the $YBa_2Cu_3O_6$ tetragonal phase.
(b) The structure of the $YBa_2Cu_3O_7$ orthorhombic phase.



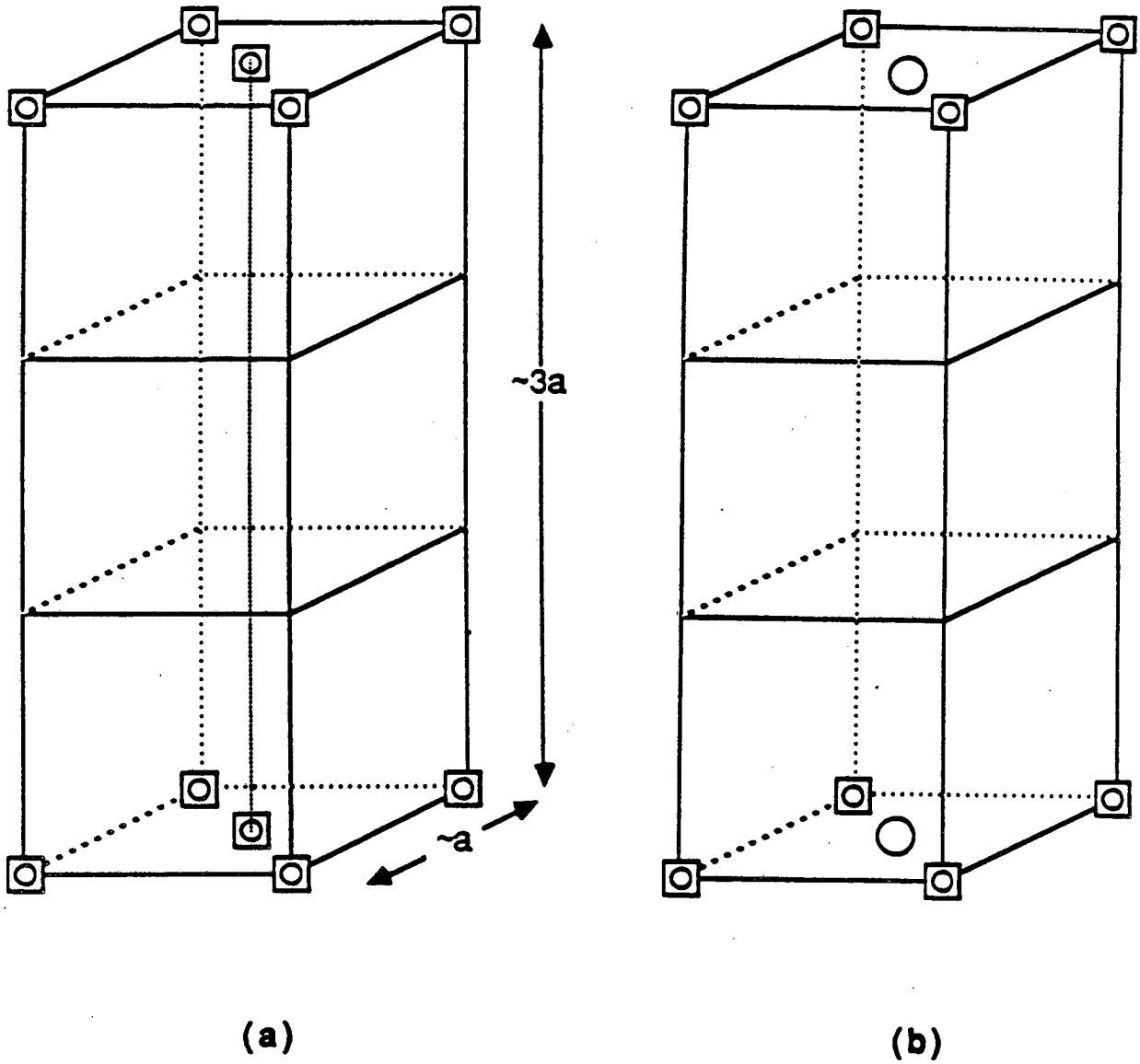


Fig. 2. (a) The basal sublattice of oxygen vacancies occupied by ordering O atoms. (b) The ordered distribution of O atoms over the basal sublattice.

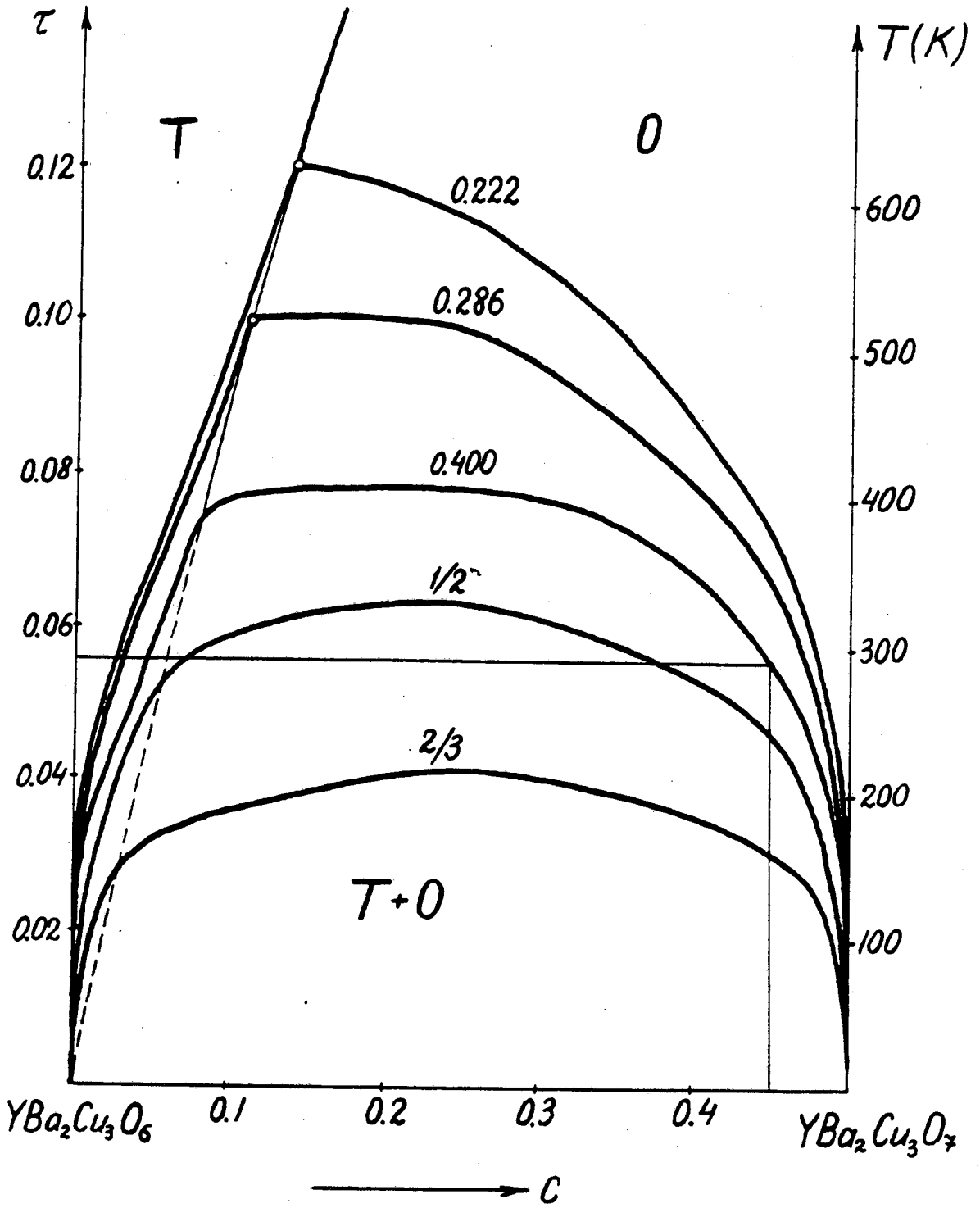


Fig. 3. Set of the calculated equilibrium diagrams for different values of the parameter ξ. T designates the disordered tetragonal phase. O designates ordered orthorhombic phase. τ is reduced temperature. The critical temperatures are indicated by circles. The numbers above the solvus curves indicate the value ξ. (T+O) labels to the two-phase field.

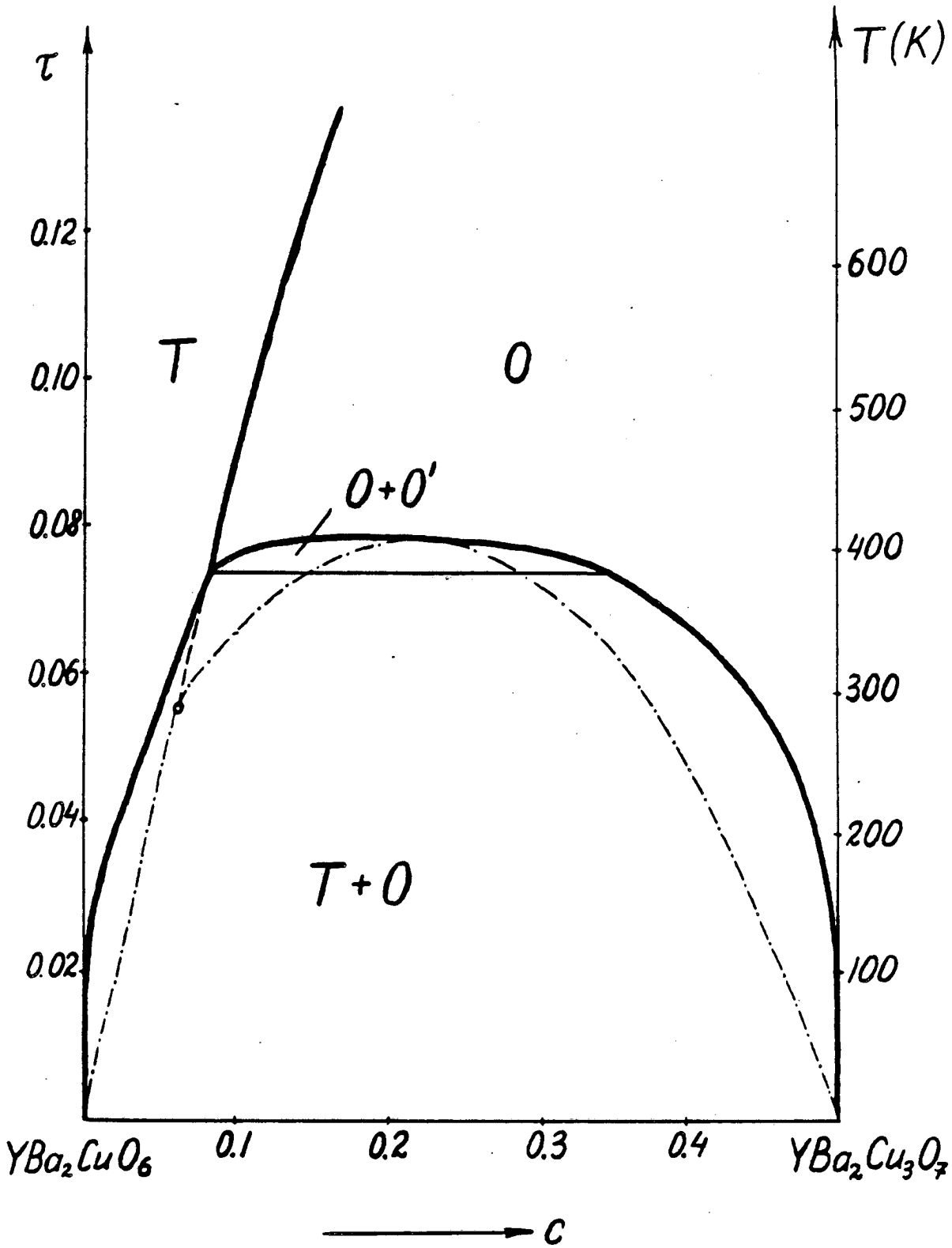


Fig. 4. The calculated equilibrium diagram for ξ=0.4. Bold lines designate the second-order transition line and the solvus lines. The dot-dash line shows the spinodal. The horizontal line separates the two phase (O+O') region of the two orthorhombic phases coexistance from the region (T+O) coexistance of the tetragonal and orthorhombic phases.

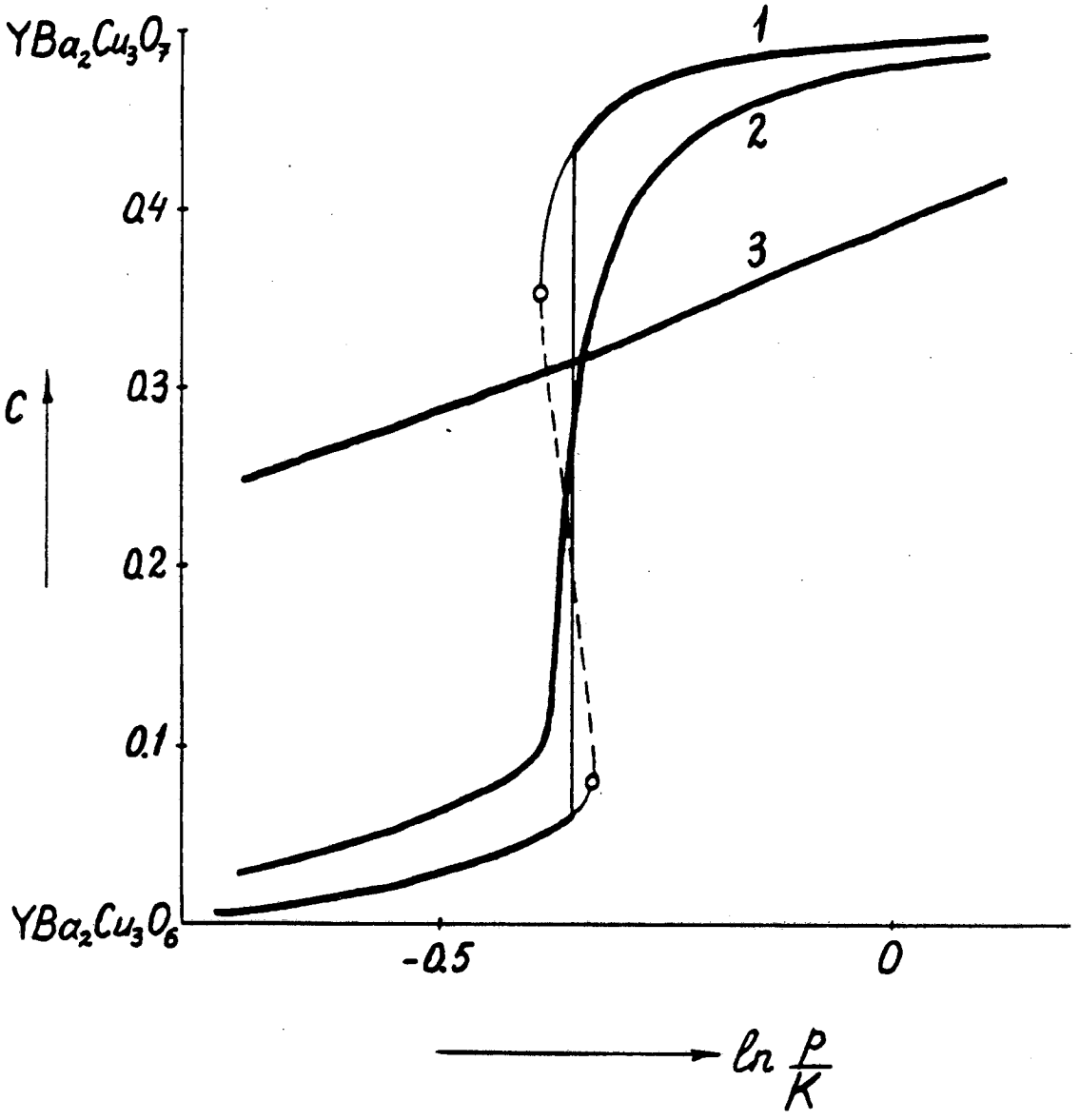


Fig. 5. The calculated dependence of O atom composition in the basal plane of the oxide on the oxygen pressure (ξ=0.4). Numbers 1,2,3 are related to the reduced temperatures τ=0.06188 (ordering and decomposition), τ=0.0866 (ordering without decomposition) and τ-0.1 (disordered field). On curve 1, the thin line designates metastable states and the dashed line corresponds to the unstable region.

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