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Phase diagram of the superconducting oxide $YBa_2Cu_3O_{6+\delta}$

A. G. Khachaturyan, S. V. Semenovskaya, and J. W. Morris, Jr.
Center for Advanced Materials, Lawrence Berkeley Laboratory, Berkeley, California 94720
and Department of Materials Science, University of California, Berkeley, California 94720
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The superconducting oxide $YBa_2Cu_3O_{6+\delta}$ is found in two structures: a tetragonal structure (T) that is stoichiometric when $\delta=0$, and an orthorhombic (O) structure stoichiometric when $\delta=1$. Assuming that only these phases appear in the phase diagram of the oxide as temperature (t) and δ are varied, it is shown that the phase diagram must have one of two relatively simple forms. The first has a T field at high t and low δ, an O field at lower temperature and high δ, and a $T+O$ two-phase field that separates the two at low t. The second has these features, and also includes an $O+O'$ two-phase field that results from a miscibility gap in the O phase. A mean-field model is fit to the experimental data, and suggests that the second type of diagram is correct. The calculated phase diagram is presented. The variation of the oxygen partial pressure with δ and t is also discussed.

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 (T) based on a tetragonal cell with the stoichiometric composition $YBa_2Cu_3O_6$ and the other (O) on an orthorhombic cell with the stoichiometric composition $YBa_2Cu_3O_7$ [Fig. 1(a)]. 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 the base-centered sublattice (the "basal sublattice") shown in Fig. 1(b). In the T phase oxygen atoms and vacancies are randomly distributed over the sites of the basal sublattice. In the fully ordered orthorhombic O phase the oxygen atoms in the basal sublattice are confined to alternate rows parallel to [100]. Since only the O phase exhibits high-temperature superconductivity[6] it is important to clarify the phase fields of the two structures. It is the purpose of the present note to estimate the phase diagram of the nonstoichiometric oxide $YBa_2Cu_3O_{6+\delta}$ as a function of the temperature and the oxygen fraction (δ) on the basal sublattice.

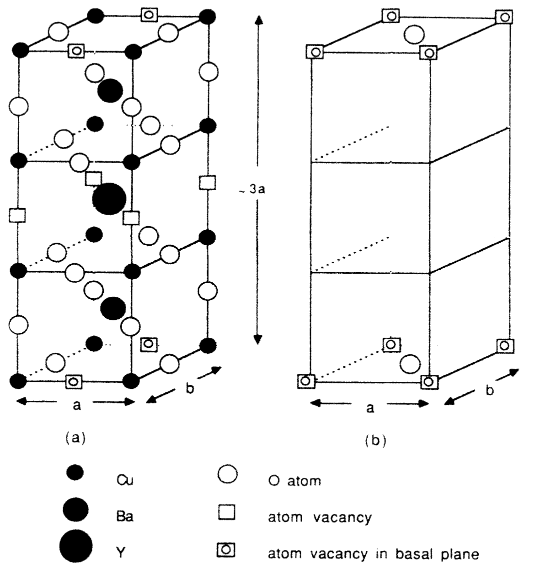

FIG. 1. (a) The structure of the orthorhombic $YBa_2Cu_3O_7$. (b) The sites of the basal sublattice $YBa_2Cu_3O_{6+\delta}$ showing the oxygen and vacant positions in the ordered orthorhombic phase.

The available experimental data suggest the qualitative form of the phase diagram. The T phase is preferred at elevated temperature, and transforms to the O phase on cooling if the oxygen content is sufficiently high.[4] The structural transformation is congruent and apparently of second order. However, it follows from the third law of thermodynamics (the Nernst principle) that a nonstoichiometric O phase cannot be preferred at low temperature. It must eventually decompose into a mixture of perfectly ordered phases. If we assume that only the T and O phases exist, since these are the only ones that have been found, then when $0<\delta<1$ the equilibrium state in the low-temperature limit must be a two-phase mixture of T and O. The phase diagram may then take either of two possible 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. 2(a)] the $T\rightarrow O$ ordering line terminates in a tricritical point where it bifurcates into two solvus lines that encircle the low-

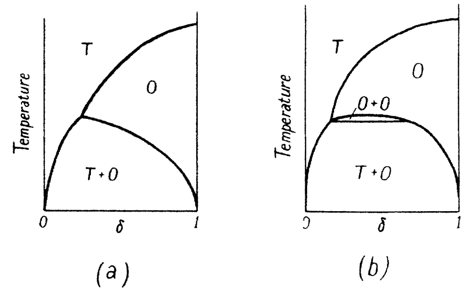

FIG. 2. The two possible forms for the phase diagram of $YBa_2Cu_3O_{6+\delta}$ assuming that only T and O phases appear.

temperature two-phase $(T+O)$ field. This type of diagram is found in a number of binary systems; the relevant theory is discussed by Landau[7] and by Krivolgaz and Smirnov.[8] In the second type of diagram [Fig. 2(b)] the two-phase $(T+O)$ 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.

Since the available experimental data do not distinguish between these two forms, it is useful to explore the predictions of simple thermodynamic models that incorporate the O-O interaction on the basal sublattice. While we do not know the details of the O-O interaction, it must have a relatively long range since it provides a crystallographic registry between the oxygen distributions on (001) planes that are separated by three unit cells of the parent perovskite structure; to enforce this registry the range of the interaction must exceed 20 atomic coordination shells. [Since the oxygen atoms replace vacancies on the basal sublattice, it is likely that their long-range interaction is largely elastic in which case it decays as $|r|^{-3}$ (Ref. 9)]. The long range of the interatomic interaction rules out the usual solution models that incorporate correlation effects, such as the Bethe[10] and cluster-variation[11] techniques, since these are mathematically intractable unless the range of interaction is very short. On the other hand, the long range of the interaction increases the accuracy of the simpler mean-field approximation.[12,13] The mean-field approximation is always asymptotically correct at low temperature where the long-range-order parameter $\eta \rightarrow 1$.[12] When the effective range of the interaction r_0 is large, the mean-field approximation is also reasonable at temperatures only slightly below the ordering temperature t_0 (Ref. 13) since its inaccuracy vanishes with the parameter $(v/r_0^3)[t_0/|\Delta t|]^{1/2}$, where v is volume per lattice site and Δt is the undercooling below t_0. It follows that if $r_0^3 \gg v$, as it appears to be, the mean-field model should provide a reasonable shape for the phase diagram.

The distribution of oxygen on the basal sublattice of $YBa_2Cu_3O_{6+\delta}$ is given by the relation[14]

$$n(\mathbf{r}) = c + \eta\cos(\mathbf{k}_0\cdot\mathbf{r}) = c + \eta\cos(2\pi x) \ , \qquad (1)$$

where $\mathbf{r} = (x,y,z)$ are the sites of the basal sublattice, $c(=\delta/2)$ is the concentration of oxygen on the basal sublattice, $\mathbf{k}_0 = (2\pi/a)(100)$ is the ordering wave that generates the orthorhombic phase, and a is the lattice parameter in the [100] direction. Defining the Fourier transform of the interaction potential,

$$V(\mathbf{k}) = \sum_{\mathbf{r}} W(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} \ , \qquad (2)$$

where $W(\mathbf{r})$ is the energy of an O-O pair on the basal sublattice that is separated by the distance $\mathbf{r}$, it can be shown[9] that the free energy of a configuration with given values of c and η depends only on the two parameters $V(0)$ and $V(\mathbf{k}_0)$ irrespective of the range of the interaction. In the mean-field approximation the free energy is given by the relation

$$F(c,\eta) = \frac{N}{2}\{[V(0)c^2 + V(\mathbf{k}_0)\eta^2] + k_B t[(c+\eta)\ln(c+\eta) + (c-\eta)\ln(c-\eta) + (1-c+\eta)\ln(1-c+\eta) + (1-c-\eta)\ln(1-c-\eta)]\} \ , \qquad (3)$$

where N is the number of sites on the basal sublattice and k_B is Boltzmann's constant. Minimizing Eq. (3) with respect to the long-range-order parameter η yields the free energy function $F(c,t)$ from which the phase diagram can be computed. The shape of the phase diagram depends on the ratio $\xi = V(0)/|V(\mathbf{k}_0)|$. When ξ is less than about 0.25 the phase diagram has the form given in Fig. 2(a), with a simple tricritical point. When $\xi > 0.25$ the diagram has the form given in Fig. 2(b), and the O phase has a miscibility gap above the tricritical point.

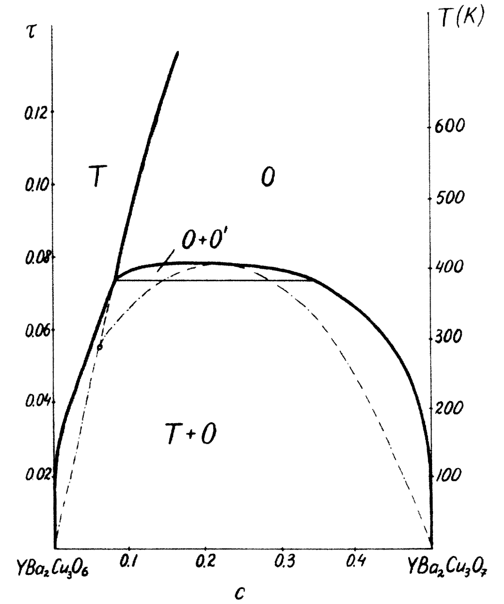

FIG. 3. The calculated $YBa_2Cu_3O_{6+\delta}$ phase diagram. The order-disorder transition and solvus lines are bold. The broken line shows the spinodal instability curve for decomposition of the O phase. The parameter $\xi = 0.4$. The left-hand axis shows the reduced temperature $\tau = k_B t/|V(\mathbf{k}_0)|$.

To determine the phase diagram we require numerical values for the parameters ξ, which fixes the shape of the diagram, and $V(\mathbf{k}_0)$, which fixes the temperature scale. We can approximate these from the experimental data given in Ref. 4. These workers found the $T \rightarrow O$ transition at 700 °C (973 K) in a sample with $c = 0.25$ $(\delta = 0.5)$, and report a maximum solubility, $c = 0.45$ $(\delta = 0.9)$ at room temperature, which we interpret as a concentration in equilibrium with residual T phase. Fitting the parameter $V(\mathbf{k}_0)$ to the ordering temperature yields the value $V(\mathbf{k}_0) = -5190k_B$. The value $\xi = 0.4$ then provides an oxygen concentration $c = 0.45$ in the O phase at room temperature. The predicted phase diagram is plotted in Fig. 3. Note that this diagram is of the type of Fig. 2(b). At intermediate temperature two orthorhombic phases, O

and O' coexist at equilibrium; at low temperature the equilibrium phases are T and O.

The presence of both ordering and decomposition reactions in the phase diagram has an important effect on the dependence of the oxygen concentration in $YBa_2Cu_3O_{6+\delta}$ on the oxygen partial pressure. The chemical potential of atomic oxygen in the oxide must equal that in the vapor phase. Since the latter is determined by the reaction $O_2 \rightleftharpoons 2O$, the chemical potential in the vapor phase is

$$\mu = \mu_g^0 + (k_B t)\ln\sqrt{p} \ , \tag{4}$$

where μ_g^0 is the reference chemical potential for the oxygen gas and p is its partial pressure. The chemical potential of oxygen in the solid can be found from Eq. (3). Using the equilibrium condition that $(\partial F/\partial \eta) = 0$ to evaluate the function $\eta(c,t)$, we have

$$\begin{aligned}\mu &= \mu^0 + \frac{1}{N}\left[\frac{\partial F(c,t)}{\partial c}\right] \\ &= \mu^0 + V(0)c + \left[\frac{k_B t}{2}\right]\ln\left[\frac{c^2-\eta^2}{(1-c)^2-\eta^2}\right] .\end{aligned} \tag{5}$$

Equating (4) and (5) yields the result

$$\left[\frac{1}{2}\right]\ln\left[\frac{c^2-\eta^2}{(1-c)^2-\eta^2}\right] + \left[\frac{cV(0)}{k_B t}\right] = \ln\left[\frac{\sqrt{p}}{K}\right] , \tag{6}$$

where $K = \exp[(\mu^0 - \mu_g^0)/k_B t]$. Equation (6) determines the oxygen concentration on the basal sublattice as a function of $\ln[\sqrt{p}/K]$. Figure 4 shows the predicted relation at three temperatures: a high temperature at which the system is disordered over the range of interest and the variation is monotonic, an intermediate temperature where the system orders without decomposing and the curve has an s shape, and a low temperature where the system decomposes, so that the curve has a discontinuity that corresponds to entry into the two-phase region.

The phase diagram derived above (Fig. 3) is only accurate to within the approximation introduced by the mean-field model and the uncertainty in the experimental data used to fit it. The model could be improved by introducing correlation effects according to the theory developed in Ref. 15, but even the first correlation correction introduces two more unknown energy parameters, and we do not presently have the data to evaluate them. The approximate diagram is valuable in its own right since it suggests the existence of important decomposition reactions that may be sought experimentally. However, it should be recognized that the phase diagram says nothing about the kinetics of the decomposition reactions. It is entirely possible that the kinetics are so slow that the decomposition is difficult to observe.

Finally we note that since the original submission of this paper several experimental groups have reported data that seems to confirm the decomposition of $YBa_2Cu_3O_{6+\delta}$ into $O+O'$ and $O+T$ mixtures. Hinks *et al.*[16] report neutron-diffraction data that are best fit with the assumption that the sample contains two orthorhombic phases with different compositions. You, Axe, Kan, and Moss[17] have interpreted recent synchrotron radiation data in a similar way. Brynestad *et al.*[18] report data that suggest the coexistence of orthorhombic and tetragonal phases. Lee, Fu, Johnson, Samwer, and Pietrokawsky[19] report preliminary data on the dependence of δ on the oxygen partial pressure that is in at least qualitative agreement with the predicted curve 1 shown in Fig. 4. These results support the qualitative form of the phase diagram given in Fig. 3, but are not yet sufficient to test or refine its quantitative features.

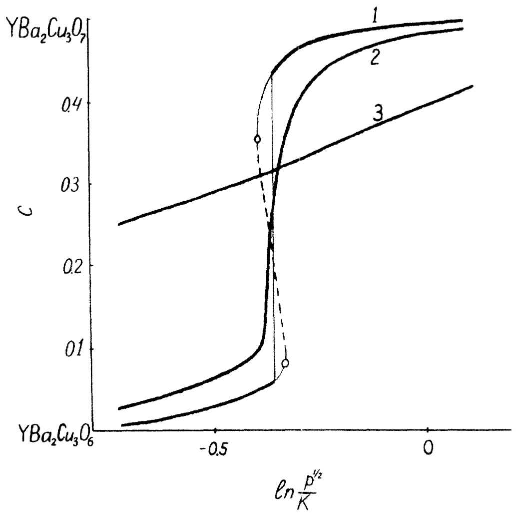

FIG. 4. The calculated dependence of the oxygen concentration on the basal sublattice as a function of oxygen partial pressure for three values of the reduced temperature $\tau = k_B t / |V(\mathbf{k}_0)|$. (1) $\tau = 0.06188$, $T \rightleftharpoons T + O \rightleftharpoons O$, the curve has a discontinuity that corresponds to the two-phase region (the thin line indicates the metastable region and the broken line the unstable region); (2) $\tau = 0.0866$, $T \rightleftharpoons O$, the curve has a simple s-shape; (3) $\tau = 0.25$, the system is disordered and the variation is monotonic.

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