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Effect of oxygen pressure and temperature on the tetragonal-orthorhombic transition in a model $YBa_2Cu_3O_{7-y}$

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Abstract. Employing a layered oxygen lattice gas in equilibrium with an external source of O_2 as a model for the basal planes of $YBa_2Cu_3O_{7-y}$, we analyze the tetragonal-to-orthorhombic (T-O) phase change in this system as it is driven by the absorption of oxygen. We describe the dependence of oxygen ordering with temperature for both mean-field and Kramers-Wannier approximations. We discuss the value of the lower limit for the oxygen content of the orthorhombic phase.

Resumen. Con el empleo de un gas en una malla laminar de oxígeno en equilibrio con una fuente externa de O_2 como modelo de los planos basales de $YBa_2Cu_3O_{7-y}$, analizamos la transformación tetragonal-ortorrómbica producida por la absorción de oxígeno. Describimos la dependencia en temperatura del ordenamiento de oxígeno empleando ambas aproximaciones de campo medio y de Kramers–Wannier y discutimos la posición del límite inferior para el contenido de oxígeno de la fase ortorrómbica.

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A major development following the discovery of superconductivity as high as 92°K in the perovskite-based $YBa_2Cu_3O_{7-y}$ compound [1] has been the determination of its structural phase transition [2]. The orthorhombic room-temperature structure transforms upon heating under an oxygen atmosphere to a tetragonal structure with reported transition temperatures ranging from 620°C to 700°C when oxygen pressure changes from 0.02 to 1 atm [3]. This system displays variations in oxygen content $7 - y$ that strongly influences both the crystal structure and the superconducting properties [2]. Samples with $y = 1$ have been found to be tetragonal and nonsuperconducting [2]. Also, initial studies indicated that the T-O transition occurs near to a constant value of $y = 0.5$ [2, 3] and that in the orthorhombic phase the superconducting transition temperature T_c decreases as oxygen is removed and the structural transformation is approached. Other reports allocate the range $0.88 < y < 1$ for the tetragonal phase [4] and describe the variation of T_c for orthorhombic samples with oxygen content in the range $0 < y < 0.7$ [5]. A more precise determination of the locus of the T-O transition in temperature-composition space, including the lower limit of oxygen content for the orthorhombic phase has not, to our knowledge, been reported at present. The nature of the transition has been observed to be of the 2nd order with small hysteresis probably accounted for by the formation of twin boundaries [6]. X-ray and neutron powder diffraction measurements [2] have established the existence of two inequivalent Cu sites resulting in both two-dimensional and one-dimensional Cu-O sublattices perpendicular to the c axis of the unit cell. In the latter case, Cu-O chains form along the b axis in the basal plane separated by ordered oxygen vacancies along the a direction. This vacancy arrangement is responsible for the orthorhombic structure of the unit cell [2, 7].

Taking into account this close association between structure and superconductivity it is of interest to understand in detail the nature of the structural inestability in this system. Here we report calculations on a model for oxygen ordering [7] and absorption [8] that is given some of the salient features of the $YBa_2Cu_3O_{7-y}$ ("123") high-temperature superconductor. We reproduce the effects of temperature and oxygen partial pressure on the T-O transition and find that a lower limit to the oxygen content for the orthorhombic phase with $y_{\max} < 1$ is implied by the short-range concentration fluctuations of the two-dimensional order-disorder transition in the Cu-O basal planes.

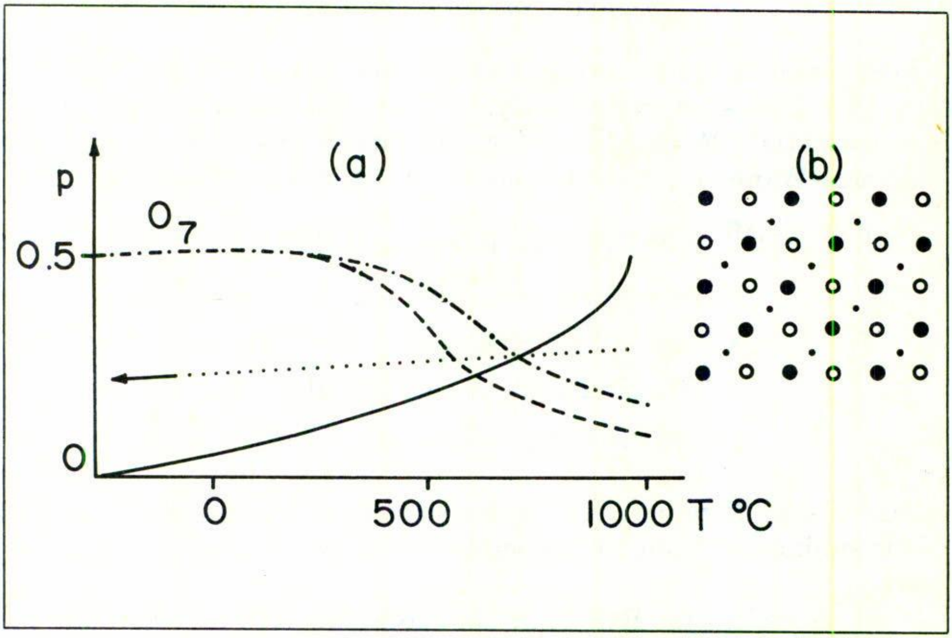

FIGURE 1. (a) Phase diagram for the model oxide. The full line is the locus of the orthorhombic-tetragonal transition in mean-field aproximation, the dotted line is that for the Kramers-Wannier method with 4-site clusters, the dashed and the dashed-dotted lines correspond to isobars of 2% and 100% oxygen, respectively. (b) Ordering of oxygen (•) and oxygen vacancies (∘) in the copper (·) basal planes of orthorhombic $YBa_2Cu_3O_{7-y}$.

Our model layered oxygen lattice gas [7, 8] consists of a set of two-dimensional arrays for oxygen positions as shown in Fig. 1. They represent the basal planes of the 123 compound. The effect of the in-plane copper atoms is modelled letting every oxygen atom feel an attractive potential V and by giving them an (effective) nearest-neighbor repulsion U. The corresponding mean-field grand potential term (per site) is

$$\begin{aligned}\Omega_0^{\mathrm{MF}} = kT\{&n\ln n + m\ln m + (1-n)\ln(1-n)\\ &+(1-m)\ln(1-m)\} + Unm - (\mu + V)(n+m),\end{aligned} \tag{1a}$$

where n and m are the average oxygen occupancies of the $(1/2,0,0)$ and $(0,1/2,0)$ sites, respectively, and μ is the (labile) oxygen chemical potential. When describing the lattice gas according to the Kramers-Wannier approximation [9] the expression for Ω_0 is

$$\begin{aligned}\Omega_0^{\mathrm{KW}} = \Omega_0^{\mathrm{MF}} + 2kT\{&S_{nnmm}\ln S_{nnmm} + 2S_{nmm}\ln S_{nmm}\\ &+ 2S_{nnm}\ln S_{nnm} + S_{nn}\ln S_{nn} + S_{mm}\ln S_{mm}\\ &+ 4S_{nm}\ln S_{nm} + S_n\ln S_n + S_m\ln S_m + S\ln S\\ &- 2[B_{nm}\ln B_{nm} + B_n\ln B_n + B_m\ln B_m + B\ln B]\}\\ &- U/4[B_n + B_m - B_{nm} - B + 4nm]\end{aligned} \tag{1b}$$

where S and B represent four-site squares and two-site bonds, and their subindexes indicate the sublattice to which occupied sites belong.

As described in Ref. 8, in our model we take into account the thermal expansion and elastic deformation of the lattice through a free energy term F_{el}. We also allow for crystal expansion due to absorption of oxygen, and the corresponding free energy term F_{exp} couples the oxygen occupancies to the elastic deformations. Finally, the lattice gas is set in equilibrium with a compressible gas containing O_2 with grand potential Ω_{gas} per unit volume. The expressions for these terms are given the forms:

$$F_{\mathrm{el}} = \tfrac{1}{2}\Sigma_{iklm}\lambda_{iklm}u_{ik}u_{lm} - \tfrac{1}{3}\Sigma_{ik}\alpha_{ik}u_{ik}(T - T_0), \tag{2}$$

$$F_{\mathrm{exp}} = -\epsilon_a[u_{aa}(n - p_0) + u_{bb}(m - p_0)] - \epsilon_c u_{cc}(p - p_0), \tag{3}$$

and

$$\Omega_{\rm gas} = kT\Big\{r(\ln r - 1) + s(\ln s - 1) - (r + s)\ln[1 - \sigma(r + s)]\Big\} - \mu_r r - \mu_s s, \qquad (4)$$

where u_{ik} is the strain tensor and where we regard the undeformed state of the crystal to be the equilibrium state at temperature T_0. We chose this state to have tetragonal symmetry so that the elastic modulus tensor λ_{ijkl} has six nonzero components and the thermal expansion tensor α_{ik} is diagonal with two different components. In Eq. (3) ϵ_a and ϵ_c are the compositional expansion tensor components, $p = (n + m)/2$ $(7 - y = 6 + 2p)$, and p_0 is the oxygen content at the basal planes at T_0. In Eq. (4) r and s are the number densities of O_2 and (say) N_2 molecules, with chemical potentials μ_r and μ_s, respectively. The molecules are given equal size $\sigma = 1$. As discussed in Ref. 8 the grand potential $\Omega = \Omega_0 + F_{\rm el} + F_{\rm exp} + \Omega_{\rm gas}$ can be seen to represent also a two-dimensional lattice gas with both 1st and 2nd neighbor interactions and subjected to a temperature-dependent external potential. In this equivalent system the 1st neighbor interaction is given by $U' = U - \epsilon_a H_b - \epsilon_c H_c/4$, the 2nd neighbor interaction by $U'' = -\epsilon_a H_a - \epsilon_c H_c/4$ and the external potential by $V' = V + (-\epsilon_a G_a - \epsilon_c G_c/2)T/T_0$, where H_a, H_b, H_c, G_a and G_c are constants.

We analize now some properties of the model and compare them with experiment. Since most reports of experimental determinations of crystal structure have been carried out varying temperature at constant oxygen partial pressure and our formalism is for constant chemical potentials, we need to know the dependence of μ with T, total pressure P and gas composition x. This is easily obtained when it is recalled that for the external gas $P = kT\{(r+s)/[1-\sigma(r+s)]\}$, and that $\mu_r = 4\mu$ since there is molecular oxygen in the gas and we are assuming that of the two types of Cu-O planes in the 123 compounds [2] only in the basal plane can oxygen be absorbed or removed. We obtain $\mu = (kT/4)\ln(xP/kT) + \sigma P/4$, where $x = r/(r + s)$ is the oxygen concentration in the gas. When the oxygen-oxygen 1st neighbor repulsions U' dominate over the effective 2nd neighbor interactions U'' oxygen vacancies order at low temperature producing the characteristic Cu-O chains observed in this system [3]. See Fig. 1. The transition is usually of the 2nd order but depending on whether U'' represents repulsions or attractions, the transition at even lower temperatures becomes either 1st order or new kinds of sublattice order develop [8].

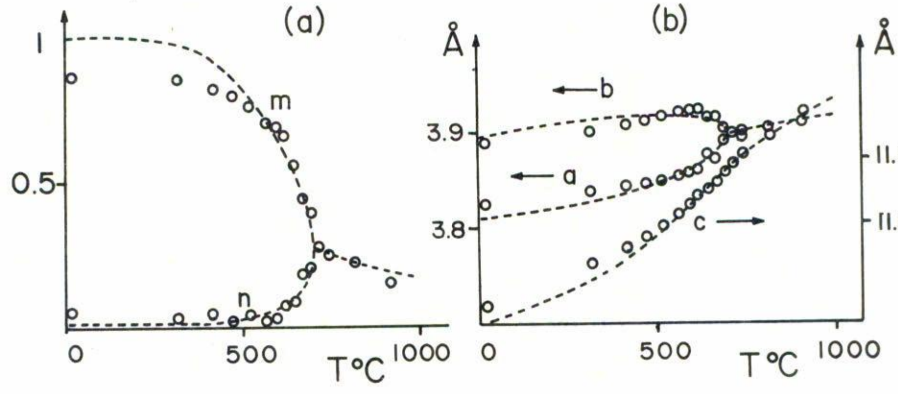

FIGURE 2. Temperature dependence of: (a) Sublattice oxygen site occupancies in the basal planes of $YBa_2Cu_3O_{7-y}$. (b) a- b- and c-lattice parameters for samples heated in 100% oxygen. The dashed lines are from mean-field approximation, and the points are from the experiments reported in Ref. 3.

Because of the coupling we enforced between the oxygen occupancies n and m and the elastic deformations u_{ik} the oxygen ordering transition is also a structural transition from a tetragonal to an orthorhombic symmetry. See Fig. 2. To particularize our model we determined the constants in the expressions for U', U'' and V' from neutron scattering data [3, 8]. A good fit to them in the temperature range 0°C to 900°C when the external gas is pure oxygen is given by $G_a = 0.0128$, $G_c = 0.0189$, $H_a = 0.0062$, $H_b = -0.0155$, $H_c = -0.0335$ with $T_0 = 715°C$ [8]. There are only left three adjustable parameters including the temperature scale in the model, which we choose to be the interactions and external potential of the equivalent 2-*d* lattice gas, U', U'' and V'. Once the values of these parameters are chosen, we calculate with them all the properties including those for different oxygen partial pressures. In Fig. 1 we show the locus of the T-O transition for both mean-field and the Kramers-Wannier approximations, together with absorption isobars of 2 and 100% oxygen atmospheres. (There $U''/U' = -0.01$). From the shape of the isobars (calculated only in mean-field) we note, in agreement with experiment [3], that oxygen can be absorbed or removed from the crystal only above ~ 350 to 400°C, but still well below the transition range of temperatures. We note too, that the lower limit for oxygen concentration in the orthorhombic phase (at $T = 0°K$) is $p = 0$ ($y_{\max} = 1$) for mean-field, and $p = 0.22$ ($y_{\max} = 0.56$) for four-site clusters in the Kramers–Wannier approximation. Changes in the value of the effective 1st to 2nd nearest neighbor interactions ratio U''/U' changes the locus of the T-O transition together with the value of p at $T = 0°K$. We have found that our model produces good fittings to the oxygen occupancies and to the lattice cell parameters with different sets of values for U', U'' and V'' [8]. When $U''/U' < 0$ this transition becomes 1st order below (a symmetrical tricritical point at) T_t (with $T_t \to 0$ when $U'' \to 0$) so that there is coexistence between a disordered phase with $p = 0$ and the ordered phase with $p = 1/2$ at $T = 0°K$.

A ground-state analysis for the pure 1st neighbor problem indicated a value of $p = 0.31$ at $T = 0°K$. Thus, accoding to our model the existence of a lower limit, $y_{\max} < 1$, for oxygen deficiency in the orthorhombic crystal at low temperature would be inherited directly from the properties of order-disorder transitions [10]. We note from Fig. 1a that the T-O transition locus obtained from the Kramers–Wannier approximation is a very steep function of composition. This result is in good accord with experiment because it explains why when cooling samples in different oxygen atmospheres with total pressures of 1 atm the transition appears to occur at a fixed composition of $7-y \sim 6.5$. It also explains why orthorhombic samples in the range $6 < 7-y < 6.3$ have not apparently been detected. In Fig. 2 we compare our results for oxygen occupancies and lattice parameters with experiment for samples cooled in 100% oxygen [8]. Other results for 20% and 2% oxygen atmospheres [3], not shown here, have similar agreement with experiment.

The consideration of a coupling between the oxygen-ordering and superconducting order parameters in an earlier version [7, 11] of this model oxide (where no elastic deformation term was included) permits the determination —within a Landau-Ginzburg theory— of the dependence of the superconducting transition temperature on the oxygen content of the sample. This coupling is likely to occur via the elastic deformations of the crystal and the model employed here may be useful in understanding the close connections that exist between oxygen content, structure and superconductivity in these materials. Work is in progress to update this lattice gas model to the fast growth of experimental evidence.

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