Model for the order-disorder transition in $YBa_2Cu_3O_y$

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We present a model for the tetragonal-to-orthorhombic structural phase transition in $YBa_2Cu_3O_y$. We assume the transition involves only the oxygen atoms which form the $Cu-O$ chains in this compound and use an Ising-like Hamiltonian on a square lattice with nearest- and next-nearest-neighbor interactions to describe the system. Comparison of theoretical predictions with experimental results for site occupancy as a function of temperature and oxygen partial pressure shows good agreement.

With the discovery of superconductivity at liquid-nitrogen temperatures in the copper-oxide-based ceramics $RBa_2Cu_3O_y$ (where R is a rare-earth element and $6.5 < y < 7$),[1] the possibility of widespread commercial applications of superconductivity has emerged.[2,3] However, before commercial uses of these materials can be developed, reliable techniques need to be established for large-scale manufacture of high-quality superconducting material. One important consideration in the manufacture of these materials is the oxygen content. If the oxygen content is too low ($y < 6.5$) then the material has a tetragonal structure and is not a superconductor,[4,5] but for $6.5 < y < 7$ the material has an orthorhombic structure and is superconducting. These structures are illustrated in Fig. 1. In the ceramic processing technique usually used to prepare bulk samples of the superconductor

(see, e.g., Wu *et al.*[1]) the powder is sintered at about $900\,°C$ for several hours and then cooled. At this temperature the structure is tetragonal and the material transforms to the superconducting orthorhombic structure at about $700\,°C$ (depending on the oxygen atmosphere). The material must be cooled slowly through this transformation in order to allow the superconducting phase to form.[6] At the same time, the oxygen content increases from $y < 6.5$ to the optimum value of $6.8 < y < 6.9$.

Jorgensen and co-workers[4,5] and others[6,7] have studied the $YBa_2Cu_3O_y$ system in the region of this structural phase transition and have determined that (within the resolution of the experiment) the transition is a second-order order-disorder transition which involves the ordering of the oxygen atoms (denoted O) and vacancies (denoted V) to form the one-dimensional $Cu-O$ chains,
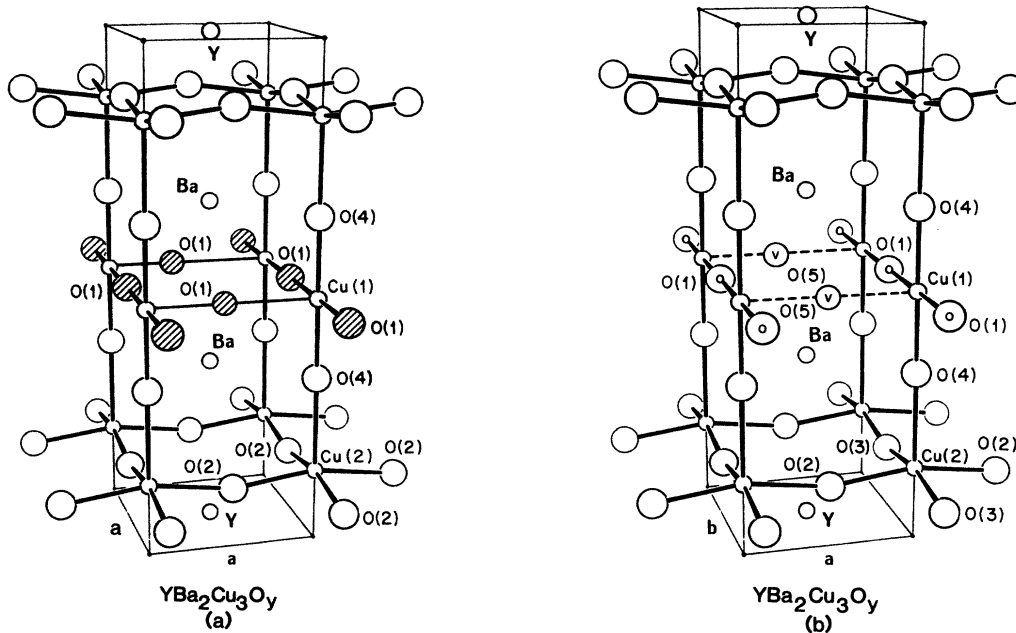

FIG. 1. The two structures of $YBa_2Cu_3O_y$. (a) The high-temperature tetragonal structure. The sites involved in the order-disorder transition are shaded. All four sites per unit cell are equivalent. (b) The low-temperature ordered orthorhombic structure, showing the $Cu-O$ "chains" running along the b direction. Only two of the relevant sites are occupied [O within a circle designated O(1) in text]; the other two relevant sites are generally vacant [V within a circle; O(5)].

which are present in the orthorhombic structure (see Fig. 1). It has been conjectured that these chains are essential for superconductivity in this system.[8] In particular the transition involves only the oxygen atoms in the plane containing these chains and the Cu(1) sites. In the tetragonal structure each of the O(1) sites has the same probability of being occupied by an O atom. In the orthorhombic phase, the O(1) and O(5) sites are crystallographically inequivalent and the O(1) sites are preferentially occupied by oxygen. All the other atoms in the structure remain in essentially the same position. The orthorhombic distortion in this system is approximately 1.6% $(b/a \approx 1.016)$ and the other major change in the structure is a steady decrease in the c axis as the temperature decreases. (The change is about 2.5% from 900 to 0 °C, and is continuous through the transition.) The environments of the four oxygen sites per unit cell involved in the transition [2 O(1) and 2 O(5)] are basically unchanged.

As a first approximation to modeling the order-disorder transition in this system, we describe the configuration of oxygen atoms and vacancies in terms of a square planar array. The configurational Hamiltonian we use to describe the system is that of a binary alloy (of oxygen atoms and vacancies) on a square lattice of N sites with interactions between pairs of atoms on nearest- and next-nearest-neighbor sites. We call the model lattice the order-disorder lattice (see Fig. 2). We assume that the important interactions which drive the order-disorder transition are the nearest- and next-nearest-neighbor O-O and O-V interactions: all other interactions in the system do not change the configurational energy of the system and are assumed to be collected into potentials, denoted Λ, acting on each site of the square lattice. As shown by de Fontaine, Wille, and Moss,[9] who have described a similar model, there are actually two different next-neighbor interactions in the order-disorder lattice. One of these $(\mathcal{V}_1)$ is mediated by a Cu atom and the other $(\mathcal{V}_2)$ is a direct interaction between the sites of this lattice. In this paper we neglect this difference and assume that $\mathcal{V}_1 = \mathcal{V}_2 = \mathcal{V}$. The Hamiltonian we used to describe the order-disorder transition in this system is, therefore,[10]

$$H = -U\sum_{\langle ij \rangle} t_i t_j - \mathcal{V}\sum_{\langle ij \rangle}' t_i t_j + (2U+2\mathcal{V})\sum_{i=1}^{N} t_i + \Lambda\sum_{i=1}^{N} t_i \ ,$$

(1)

where $t_i = 1$ if the site i is occupied by an O atom and $t_i = 0$ if it is vacant. U and $\mathcal{V}$ are the effective nearest- and next-nearest-neighbor interactions and the sums $\sum_{\langle ij \rangle}$ and $\sum_{\langle ij \rangle}'$ are over all nearest- and next-nearest-neighbor pairs of sites in the order-disorder lattice, respectively. To describe the ordering in the system we divide the lattice into four sublattices, as illustrated in Fig. 2. We denote the sublattices 1, 2, 3, and 4 and use a greek letter to in-
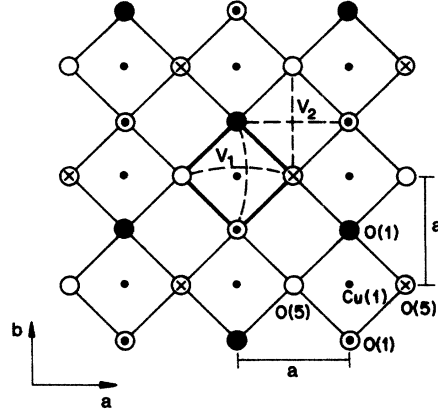

FIG. 2. The order-disorder lattice used to model the structural phase transition in YBa$_2$Cu$_3$O$_y$. The four sublattices are illustrated: $\odot$ is 1; $\otimes$ is 2; $\bullet$ is 3; $\bigcirc$ is 4. The positions of the Cu(1) atoms in YBa$_2$Cu$_3$O$_y$, and its crystal axes are indicated. The effect of these atoms is not included in our model (i.e., we assume $\mathcal{V}_1 = \mathcal{V}_2 = \mathcal{V}$). The basic cluster used in the calculation is a square of four nearest-neighbor sites: the nearest-neighbor interactions (bold lines; on edges of squares) and the next-nearest-neighbor interactions (dashed lines; square diagonals) are marked.

dex a quantity relating to a particular sublattice. We note that this model is isomorphic to an Ising antiferromagnet on a square lattice in an applied magnetic field.

Here we consider only two structures: the disordered phase (corresponding to the tetragonal structure) in which all sites have an equal probability of being occupied by O atoms; and an ordered phase (the orthorhombic structure) in which sites in two sublattices on opposite diagonals of each square [e.g., the O(1) sites in Fig. 2] are preferentially occupied by O atoms, with sites in the other two sublattices predominantly vacant. These will be the only phase found provided $\mathcal{V}/U < 2^{1/2}$.[9] In terms of the site occupation probabilities for each sublattice $n_\sigma = (4/N)\sum_{i \in \sigma} t_i$, these phases are identified by $n_1 = n_2 = n_3 = n_4$ (disordered) and $n_1 = n_3 \neq n_2 = n_4$ (ordered).

We solve this model using the cluster variation method[11,12] with a four-site square as the basic cluster (see Fig. 2). We follow the calculation and notation of Ref. 11. The clusters we have to consider, and the overlap correction numbers $[a^{(c)}]$ associated with them (see Ref. 11), are therefore the four-site square (4) $[a^{(4)} = 1]$, four three-site clusters $(3:\sigma\lambda\kappa)[a^{(3:\sigma\lambda\kappa)} = 0]$, four nearest-neighbor pair clusters (2:12), (2:23), (2:34), and (2:14) $[a^{(2:12)} = a^{(2:23)} = a^{(2:34)} = a^{(2:14)} = -1]$, two next-nearest-neighbor pairs (2:13) and (2:24) $[a^{(2:13)} = a^{(2:24)} = 0]$, and the four-site clusters $(1:\sigma)[a^{(1:\sigma)} = -\frac{1}{4}]$. The grand potential per site of the system Φ can now be calculated using Eq. (17) of Ref. 11. We obtain

$$\Phi = \beta\mu n_0 - \beta\Lambda n_0 - 2\beta(U+\mathcal{V})n_0 + \beta\mathcal{V}(2x_0^{(4)} + x_1^{(4)} + x_2^{(4)} + x_3^{(4)} + x_4^{(4)} + x_6^{(4)} + x_9^{(4)})$$

$$+ \frac{1}{2}\beta U[4x_0^{(4)} + 2(x_1^{(4)} + x_2^{(4)} + x_3^{(4)} + x_4^{(4)}) + x_5^{(4)} + x_7^{(4)} + x_8^{(4)} + x_{10}^{(4)}]$$

$$- \sum_{m=0}^{15} x_m^{(4)}\ln x_m^{(4)} + \frac{1}{2}\sum_{\substack{(\sigma\lambda)=(12), \\ (23),(34),(14)}}\sum_{m=0}^{3} x_m^{(2:\sigma\lambda)}\ln x_m^{(2:\sigma\lambda)} - \frac{1}{4}\sum_{\sigma=1}^{4}[n_\sigma\ln n_\sigma + (1-n_\sigma)\ln(1-n_\sigma)] \ .$$

(2)

Here n_0 is the concentration of oxygen atoms in the order-disorder lattice, μ is a chemical potential, $x_m^{(4)}$ and $x_m^{(2,\sigma\lambda)}$ give the probabilities of finding configuration m of the given cluster, and $\beta = 1/k_B T$. In this model $\mu = 0$ corresponds to $n_0 = 0.5$, and the concentration of oxygen decreases as μ decreases. To find the equilibrium state of the system the grand potential must be minimized with respect to the cluster probabilities, subject to certain constraints which are imposed by the requirement for self consistency. For example, the probabilities for the nearest-neighbor pair of sites with one site in each of sublattices 1 and 2 are related to the site occupancy probabilities by

$$x_0^{(2:12)} + x_1^{(2:12)} = n_1 ,$$ (3)

$$x_0^{(2:12)} + x_2^{(2:12)} = n_2, \text{ etc .}$$

We note that the concentration of O atoms in the order-disorder lattice is given by $n_0 = (\sum_\sigma n_\sigma)/4$ and is related to the value of y in $YBa_2Cu_3O_y$ by $y = 6 + 2n_0$. Also the chemical potential is related to the activity of oxygen in the system and varying μ in our model should have the same effect as varying the oxygen partial pressure in the experimental studies of this system.

We minimize the grand potential per site using the natural interaction method.[13] In this preliminary study of the system we have only considered the case of $U < 0$, which in most systems is the condition required to obtain alloy-type ordering.[14] Also, we have only considered values of the ratio $\mathcal{V}/U$ in the range $-1.5 < \mathcal{V}/U < 0$ (i.e., an attractive next-nearest-neighbor interaction). We find that an order-disorder transition occurs for all values of $\mathcal{V}/U$ we considered, and that for $\mathcal{V}/U \lesssim -1$ the transition is first order. For small negative values of $\mathcal{V}/U$ the transition is second order. However, it is extremely difficult to determine where the crossover occurs, particularly using the natural interaction method of solution.[10] We

are currently developing an alternative method of solution to study this region in more detail.

Figure 3 shows the site occupancy probabilities as functions of reduced temperature for $\mathcal{V}/U = -0.4$ and $\mathcal{V}/U = -1.0$, both for $\bar{\mu} = \mu - \Lambda = -1.85|U|$. The individual data points are experimental data for the site occupancy probabilities in different oxygen atmospheres.[4] The theoretical result for $\mathcal{V}/U = -0.4$ (solid lines) fits the data quite well below the transition, while the prediction for $\mathcal{V}/U = -1.0$ (dashed lines) has a quite different shape and the transition may even be first order. It is quite likely that the on-site potential (Λ) varies appreciably with temperature as the c-direction lattice constant decreases with decreasing temperature. This could account for the apparent discrepancy between the experimental and theoretical results above the transition. The effect of variation of chemical potential is illustrated in Fig. 4, where curves for $\mathcal{V}/U = -0.2$ are plotted for $\bar{\mu}/|U| = -1.85$ and -1.8. We can see that changing the chemical potential does mimic the effect of the different oxygen atmospheres. In particular, when μ decreases the transition temperature decreases and the oxygen concentration at the transition also decreases. Both these observations are in agreement with the observed behavior of $YBa_2Cu_3O_y$.

The similarities between the experimental results and the theoretical predictions from the simple model we have presented suggest that the description of the order-disorder system we have used is reasonable. It should be noted that the cluster-variation method is generally a good approximation for studying order-disorder systems and gives an accurate prediction of the order of transitions in both body-centered-cubic and face-centered-cubic alloy systems.[10] Also, although we have effectively used a two-dimensional lattice model, we cannot use the exact Ising-model solution since, in the magnetic analogue of our model, we have an applied magnetic field ($\bar{\mu} \neq 0$).
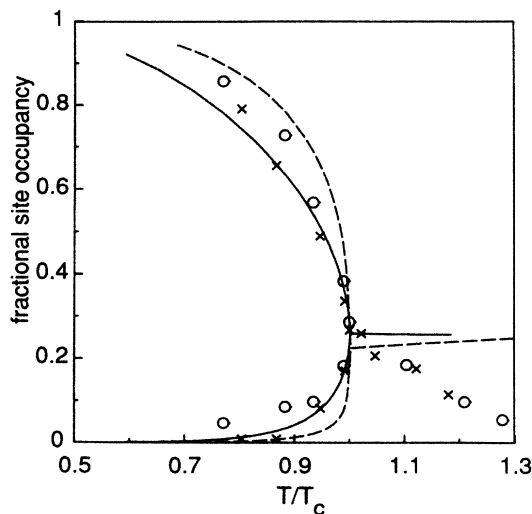

FIG. 3. Site occupancy probabilities predicted by our model as a function of T/T_c for $\bar{\mu} = \mu - \Lambda = -1.85|U|$ and two values of $\mathcal{V}/U$: (solid line) $\mathcal{V}/U = -0.4$; (dashed line) $\mathcal{V}/U = -1.0$. Individual data points (O is 2% O_2; × is 100% O_2) are experimental values from Jorgensen et al.[4] Each set of data is normalized to T_c for those data.
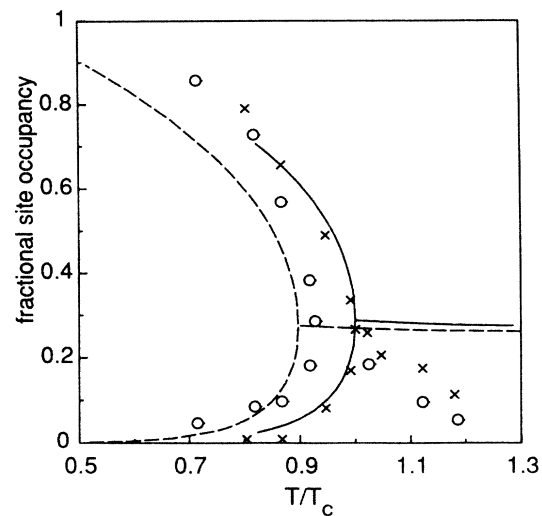
FIG. 4. Site occupancy probabilities as a function of T/T_c for $\mathcal{V}/U = -0.2$ and two values of $\bar{\mu}/|U|$: (solid line) $\bar{\mu}/|U| = -1.80$; (dashed line) $\bar{\mu}/|U| = -1.85$. For both curves T_c is the transition temperature for $\bar{\mu}/|U| = -1.8$. Experimental points are as in Fig. 3, with T_c the transition temperature in 100% O_2.

Further work, including experimental studies of the order-disorder transition in $YBa_2Cu_3O_y$, is currently underway and will be reported elsewhere.

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