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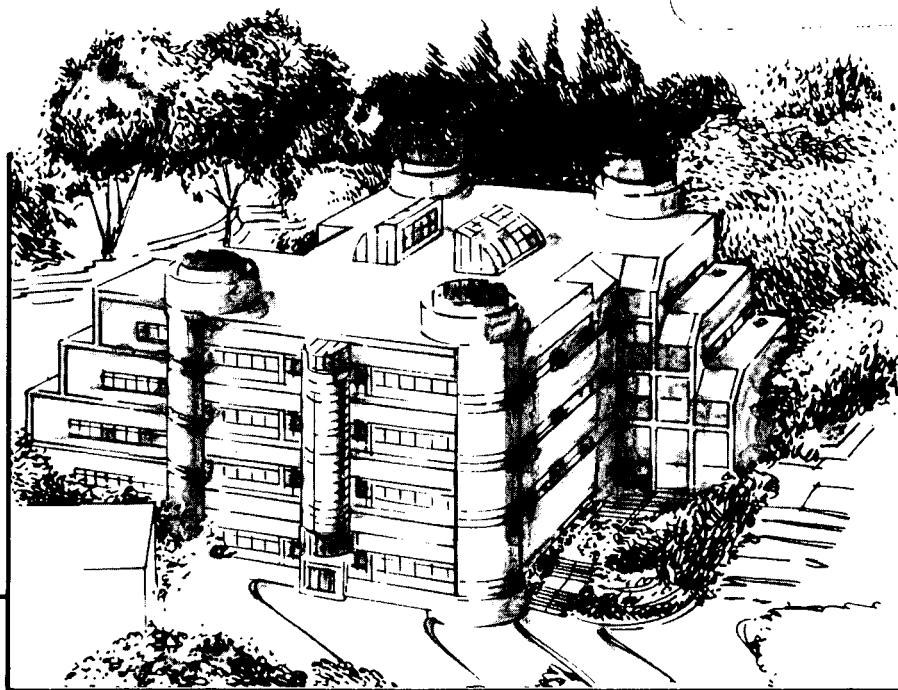
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**Comment on the Concentration-Wave Model for
Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$**

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Comment on the Concentration-Wave Model for Oxygen Ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$

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In previous work [1-3] we employed the concentration-wave method to study oxygen order in the basal planes of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$. We computed an approximate equilibrium phase diagram and predicted the appearance of Magneli-type order in rapidly cooled specimens. This work is criticized in a recent paper by de Fontaine, et al. [4]. The present note refutes that criticism and discusses the internal consistency of the method.

1. Introduction

Since the properties of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ are sensitive to the state of order in the oxygen-deficient basal plane of its unit cell, it is useful to explore the consequences of theoretical models that have been of value in the analysis of ordering in similar systems. One such model is the *concentration-wave method*, developed by Khachaturyan and others [5], which, in the form in which it is most often used for calculations, assumes a two-body interaction of arbitrary range and evaluates the free energy in the mean-field approximation. While the assumptions underlying this model are strong, its accuracy increases as the effective range of the interatomic interaction increases or the system becomes more perfectly ordered. It has consequently been particularly useful in the analysis of ordering reactions in non-stoichiometric oxides [6] for which more precise theories are unavailable.

In prior work [1-3] we used the concentration-wave method to study the tertiary reactions that establish an ordered oxygen distribution on the basal planes of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$. The model treated the redistribution of oxygen against the fixed background of the three-layer perovskite unit cell. The results included an estimate of the equilibrium phase diagram for the system as a function of temperature and δ , the oxygen concentration parameter [2], along with the theoretical suggestion that a sequence of ordered structures of the well-known Magneli type might appear when samples of intermediate oxygen content are cooled at a rate that prevents equilibrium decomposition [3]. The results were of some interest since both the (T+O) two-phase decomposition predicted by the phase diagram in ref. [2] and the Magneli-type ordering predicted by the analysis in ref. [3] have been observed in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ [7-12].

This work was, however, recently criticized by de Fontaine, Mann and Ceder in a paper that appeared in this journal [4]. The criticism claims that refs. [2] and [3] are inherently inconsistent in that the interatomic bonding function used to calculate the phase dia-

gram in ref. [2] rules out the appearance of the Magneli structures predicted in ref. [3]. It is the purpose of this note to refute that criticism.

2. Discussion of the Concentration-Wave Method

Before considering the arguments advanced by de Fontaine, et al. it is useful to recall the essential features of the concentration-wave model as it was applied to $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (detailed discussions of the method are given in refs. [5,6]). Let the atoms within a crystalline solid interact through a two-body potential of arbitrary form and range. The energy of a particular configuration of atoms over an excess set of lattice sites is given by the Hamiltonian

$$H = \frac{1}{2} \sum_{\mathbf{r}\mathbf{r}'} W(\mathbf{r}-\mathbf{r}') c(\mathbf{r}) c(\mathbf{r}') \quad (1)$$

where $W(\mathbf{r}-\mathbf{r}')$ is the two-body interaction and $c(\mathbf{r})$ specifies the configuration; it has the value 1 at occupied lattice sites and the value 0 elsewhere. For oxygen ordering on the basal planes of $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ against a fixed background, $W(\mathbf{r}-\mathbf{r}')$ is the effective interaction between sites in the three-dimensional lattice of oxygen positions in the basal planes. Applying the mean-field approximation equation (1) yields the configurational energy

$$E = \frac{1}{2} \sum_{\mathbf{r}\mathbf{r}'} W(\mathbf{r}-\mathbf{r}') n(\mathbf{r}) n(\mathbf{r}') = \frac{1}{2N} \sum_{\mathbf{k}} V(\mathbf{k}) |\ln(\mathbf{k})|^2 \quad (2)$$

where $n(\mathbf{r})$ is the probability that an atom occupies the site \mathbf{r} , $n(\mathbf{k})$ is its Fourier transform, and $V(\mathbf{k})$ is the Fourier transform of the interaction potential, $W(\mathbf{r})$. The factor $|\ln(\mathbf{k})|^2$ is the squared amplitude of a concentration wave of wave vector \mathbf{k} , which is a plane wave in three-dimensional space. The Helmholtz free energy is obtained from equation (2) by adding the mean-field value of the configurational entropy.

To compute the full thermodynamics of ordering in the system described by equation (2) one needs to know the potential, $V(\mathbf{r})$, or, equivalently, its Fourier transform, $V(\mathbf{k})$. However, there are at least two important situations in which the free energy can be calculated from a knowledge of $V(\mathbf{k})$ at particular isolated points. These are cases in which the state of the system is dominated by one or more particular concentration waves. Only these generate appreciable values of $|\ln(\mathbf{k})|^2$. The others are gathered into the background mean field (though they can be treated more precisely by including fluctuations [5,6]). The method of calculation becomes exact in the limit of long-range order.

The first example arises in the computation of the low-temperature portion of the equilibrium phase diagram of a system that has a small number of known ordered equilibrium phases. Since only these rise to concentration waves with macroscopically significant amplitudes, only the plane waves that create these phases need be included in the free energy function, and only the associated values of $V(\mathbf{k})$ appear. As long as fluctuations are neglected (as they can be when the temperature is low and the long-range order parameter

large) one need not assume any particular values for the other $V(\mathbf{k})$ beyond the general criterion that they are, relatively, large enough that they do not generate equilibrium phases. We used this method to approximate the equilibrium phase diagram of $YBa_2Cu_3O_{6+\delta}$. Given the experimental data available at the time we assumed only two stable phases: the tetragonal T-phase of O_6 , in which any excess oxygen in the basal planes ($\delta > 0$) is disordered, and the orthorhombic O-phase of O_7 , in which the excess oxygen is ordered by the plane wave $\mathbf{k}_1 = \frac{2\pi}{a}(100)$, where a is the lattice parameter in the basal plane. Since \mathbf{k}_1 is a plane wave the ordering is three-dimensional and automatically provides the registry of oxygen order in the basal planes that is required by the symmetry of the O-phase. Since only two waves appear in the free energy function the equilibrium behavior is governed by the two parameters $V(0)$ and $V(\mathbf{k}_1)$, which were evaluated from the available experimental data to generate the diagram.

More recent experimental data [11,12] suggests that a second ordered phase may also appear in the phase diagram of $YBa_2Cu_3O_{6+\delta}$, though the data is ambiguous. This phase is one of the Magneli structures, and is characterized by oxygen ordering in the basal plane by the plane wave $\mathbf{k}_2 = \frac{2\pi}{a}(\frac{1}{2}00)$. If this phase is an equilibrium phase then it can easily be included in the computed phase diagram by retaining the term $V(\mathbf{k}_2)|\ln(\mathbf{k}_2)|^2$ in the energy expression and adding an appropriate correction to the mean field entropy. We shall discuss this modification of the phase diagram in a separate publication.

A second case in which the concentration-wave analysis of ordering is simple is when a disordered or off-stoichiometric ordered phase is cooled too rapidly to reach equilibrium by two-phase decomposition. In this case ordered phases that preserve the stoichiometry of the parent can form even if the associated values of $V(\mathbf{k})$ are too high to generate equilibrium phases; because of the compositional constraint the squared amplitudes, $|\ln(\mathbf{k})|^2$, of the concentration waves associated with the stoichiometric ordered phase can reach much higher values than those of equilibrium phases that have significantly different stoichiometric compositions. As discussed in ref. [3,6] the Magneli-type structures are stoichiometric at intermediate values of δ , and are expected to provide local minima in the value of the term $V(\mathbf{k})|\ln(\mathbf{k})|^2$ at these compositions. They are hence likely to appear in quenched samples.

3. Response to the Criticism of de Fontaine, et al.

De Fontaine, et al. argue [4] that the analyses presented in refs. [2] and [3] are internally inconsistent. (Actually, they refer only to references [1] and [3], but the model and phase diagram they purport to have analyzed does not appear in either of these papers; it is in ref. [2].) To make their point they consider the computed phase diagram [2], note that it is based on two interaction parameters, $V(0)$ and $V(\mathbf{k}_1)$, and conclude that it has "an equivalence" to a "two-dimensional Bragg-Williams model with first and second neighbor pair interactions". The reason they give for this conclusion is that "a simple back-Fourier transform of the KM mean field internal energy, for their chosen star values of $V(0)$ and $V(\mathbf{k}_1)$, immediately yields the required values of... V_1 and V_2 ".

This statement is mathematical nonsense. The internal energy is a number, and has no Fourier transform. It is equally meaningless to speak of the back-transform of the expression that determines the internal energy in ref. [2]. To compute an inverse Fourier transform one needs the function $V(\mathbf{k})$ over the Brillouin zone. The expression for the mean-field energy given in [2] includes only the two parameters $V(0)$ and $V(\mathbf{k}_1)$, which define the function $V(\mathbf{k})$ at only two isolated points of the continuum.

What we think de Fontaine, et al. mean is that they can find first- and second-neighbor potentials V_1 and V_2 which, when substituted into a two-dimensional Bragg-Williams model, produce a phase diagram like that given in [2]. (This statement is, at best, only partly true since a two-dimensional model cannot generate three-dimensional order, while a three-dimensional plane concentration wave automatically does.) Since they find that these values of V_1 and V_2 cannot stabilize the Magneli structures, they infer that our model is inherently flawed.

It should be clear from the previous section that this particular flaw is not in our model, but in their misrepresentation of it. The near-neighbor bonding function they assume is only one of a non-denumerably infinite set of functions $W(\mathbf{r})$ whose transforms yield the given values of $V(0)$ and $V(\mathbf{k}_1)$, and hence reproduce the phase diagram given in [2]. It is mathematically trivial to construct functions, $W(\mathbf{r})$, that give any finite set of pre-selected values for $V(\mathbf{k})$; one need only define functions, $V(\mathbf{k})$, that include these values and take their Fourier transforms. In fact, it is relatively easy to find physically plausible two-body potentials, $W(\mathbf{r})$, that simultaneously yield the required values of $V(0)$ and $V(\mathbf{k}_1)$, provide a strong minimum of $V(\mathbf{k})$ at \mathbf{k}_1 to motivate the equilibrium phase diagram given in reference [2], and predict ordering of the Magneli type on rapid cooling. As we shall show elsewhere, a simple screened Coulomb potential has these properties. We know of no physical or mathematical reason to adopt the peculiar choice of $W(\mathbf{r})$ that de Fontaine, et al. ascribe to us, and did not do so. While the analyses presented in refs. [2,3] did not require us to define a specific function $W(\mathbf{r})$, it is clearly stated in ref. [2] and in the theoretical development [6] that underlies ref. [3] that the interaction is long-range. It is, moreover, well known that a long-range interaction is essential to the accuracy of the mean-field methods we employed in these calculations.

While there is no known physical reason to assume a short-range O-O interaction in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$, as de Fontaine, et al. do, there are compelling reasons to assume a long-range interaction, as we did. A long-range interaction is not only necessary to assure the registry of the oxygen configuration in successive basal planes and to justify the appearance of Magneli-type order in a system that has the equilibrium phase diagram calculated in ref. [2], but it is also required by all theoretical studies known to us on bonding in oxides, including specific studies of the O-O interaction in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ [13,14].

In summary, the DCM criticism is invalid. It reflects a physical misunderstanding of the concentration-wave method and a mathematical misunderstanding of the nature of the Fourier transform.

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