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### Authors

deFontaine, D.

Ceder, G.

Asta, M.

et al.

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D. deFontaine, G. Ceder, M. Asta, and R. McCormack

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# ENERGETICS AND STATISTICS OF ORDER IN ALLOYS WITH APPLICATION TO OXIDE SUPERCONDUCTORS

D. de FONTAINE<sup>1,2</sup>, G. CEDER<sup>3</sup>, M. ASTA<sup>1,4</sup> and R. McCORMACK<sup>2</sup>

<sup>1</sup>Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA

<sup>2</sup>Department of Materials Science and Mineral Engineering,  
University of California, Berkeley, CA 94720, USA

<sup>3</sup>Department of Materials Science and Engineering,  
Massachusetts Institute of Technology, Cambridge, MA 02139, USA

<sup>4</sup>Department of Physics, University of California, Berkeley, CA 94720, USA

## ABSTRACT

Now that first-principles calculations of ordering transformations are becoming increasingly accurate, the deficiencies of earlier mean field methods are becoming increasingly apparent. New techniques, based on cluster expansions, are now alleviating many of the earlier problems and are producing very satisfactory results. These ideas will be illustrated for the case of oxygen ordering in the  $\text{YBa}_2\text{Cu}_3\text{O}_z$  superconducting compound, for which a very simple two-dimensional Ising model has been developed. The model features nearest-neighbor repulsive effective pair interactions and anisotropic (attractive/repulsive) next-nearest-neighbor interactions. CVM (cluster variation method) calculations based on this model have produced a phase diagram in remarkable agreement with experimentally determined phase boundaries. Monte Carlo simulations have confirmed the validity of the model and have provided a rationalization for the influence of oxygen order on the value of  $T_c$  (superconducting transition temperature) in off-stoichiometric compounds.

## INTRODUCTION

The study of order-disorder phenomena in crystalline alloys has progressed considerably over the last ten years or so. No longer is the field confined to finding increasingly sophisticated methods of calculating critical temperatures and critical exponents in somewhat physically artificial but mathematically tractable systems. Today, effort is placed on investigating ordering in real systems, so that the emphasis is shifting away from the pure mathematical problem of, say, Ising model statistical mechanics, to the more physical problem of the quantum mechanics of interacting atoms. More importantly, the most fundamental task is that of combining the quantum and statistical mechanics into one coherent whole so that a free energy may be constructed from which all thermodynamic alloy properties may be deduced. It has been apparent for some time that the basic building block for a theoretical treatment, combining both statistics and energetics of ordering, is the *cluster* of lattice points.

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The notion of cluster is introduced quite naturally when one attempts to describe the state of order of a crystalline solid solution. For a binary system (atoms A,B), one may attach a pseudo-spin variable  $\sigma_p$  at each lattice point (p), equal to +1 if the point is occupied by an A atom, -1 if by a B. Such detailed information is not available experimentally, of course, and would in any case be of no use theoretically. Instead, one seeks averages of site occupancies. The problem is, which averages?

In this article, we shall describe briefly the principle of the cluster method, then apply it to the case of oxygen ordering in the superconducting compound  $\text{YBa}_2\text{Cu}_3\text{O}_z$  (YBCO). It will be shown that oxygen ordering is intimately related to the phenomenon of superconductivity itself.

## CLUSTER EXPANSION

In 1982, Sanchez, Ducastelle and Gratias [1] showed that products of pseudo-spins on the sites of lattice-point clusters

$$\varphi_\alpha(\sigma) = \sigma_p \sigma_{p'} \dots \sigma_{p''} \quad (1)$$

form a complete set of orthonormal functions over the space of all possible  $2^N$  configurations of a system of N lattice points. In Eq. (1),  $\alpha$  denotes the cluster of points  $\{p, p', \dots p''\}$ ; in principle, all possible clusters of points must be considered. In more recent publications [2,3], some of the present authors showed that other choices of cluster functions and of configuration space also produce possible sets of orthonormal functions.

Regardless of the particular choice of basis sets, it follows that any function of configuration  $\{\sigma\}$  can be expanded in the set  $\varphi_\alpha(\sigma)$ , the expansion is unique, and the (generalized) Fourier coefficients of the expansion are obtained in the standard way by taking scalar products of the function in question with the corresponding cluster function.

The energy  $E(\sigma)$ , being a function of configuration, can therefore be expanded in this manner. The expectation value  $\langle E \rangle$  of the energy at given temperature and concentration can then be written as

$$\langle E \rangle = E_0 + \sum_{\alpha \neq 0} E_\alpha \xi_\alpha \quad (2)$$

In this equation, originally derived by Sanchez [4],  $E_0$  is a configuration-independent energy,  $\xi_\alpha$  are expectation values  $\langle \varphi_\alpha(\sigma) \rangle$  of cluster variables, i.e., *multisite correlation functions*, and  $E_\alpha$  are so-called *effective cluster interactions* (ECI), the generalized Fourier coefficients referred to above.

Expansion of the scalar product for the ECI's [2,3] produces exact formulas for "point" interactions [ $\alpha = (p)$ ],

$$E_p = \frac{1}{2}(W_A - W_B) \quad (3a)$$

for "pair" interactions [ $\alpha = (p,q)$ ],

$$E_{pp} = \frac{1}{4}(W_{AA} + W_{BB} - W_{AB} - W_{BA}) \quad (3b)$$

and so on. In these formulas,  $W_I$  is rigorously shown to be the average energy of all configurations of the system having atom of type I (A or B) at point p, and  $W_{IJ}$  is the average energy of all configurations having atom of type I at p and J and q. Various averaging processes have been suggested for calculating the W energies from first principles. One such method, the Direct Configurational Averaging method, is described elsewhere [3,5].

The correlation functions required in Eq. (2) are obtained at thermodynamic equilibrium by minimizing an appropriate free energy functional F expressed in terms of these variables. The formalism used is that of the Cluster Variation Method (CVM), originally proposed in 1951 by Kikuchi [6]. In this approach, the energy is that of Eq. (2) and the configurational entropy is expressed by means of logarithms of cluster probabilities, the latter being themselves expressed as linear combinations of the correlations  $\xi_\alpha$ . The CVM has yielded excellent results, for instance for *ab initio* computation of phase diagrams [7]. Here, we shall apply the method to oxygen ordering in YBCO. Before doing so, however, let us emphasize how the cluster approach differs from earlier ones.

### CRITIQUE OF MEAN FIELD METHODS

Because of their extreme simplicity, mean field models are quite popular, even today. By "mean field" we denote that class of models which includes the regular solution (or sub-regular) models (for "clustering" systems), the Bragg-Williams (BW) model (for "ordering" systems with sublattices), or the concentration wave model, which is *identical* to the BW model: merely, the mean-field energy is Fourier-transformed, which changes nothing in the nature of the approximation. Let us denote collectively these models by the acronym BW.

It is often stated that these models behave poorly because of their inadequate entropy formulation. This is true: the entropy is a "point" approximation, hence is the lowest form of the hierarchy of CVM approximations; hence, the BW entropy typically tends to overestimate the configurational entropy by a factor of two or more. The major fault of the BW approximation lies with the energy, however, which is expanded as products of average concentrations (system average or sublattice average), rather than as averages of products. As a consequence, the BW model cannot (a) account for short-range order, (b) handle frustration effects such as ordering on an fcc or triangular lattice, and (c) distinguish between various lattice geometries: BW approximations merely count the number of sublattices, but the geometrical relationship between them is ignored. Such models produce exactly the same phase diagrams in either one, two or three dimensions and, in particular, incorrectly predict phase transitions on one-dimensional systems.

It is not surprising that all of these serious deficiencies should be encountered in BW models: the mean field energy is simply not included in the exact formulation of Eq. (2) and Eqs. (3a, 3b, ...). Thus, there is no justification at all for replacing averages of products by products of averages.

The concentration wave method [8], of course, does no better: it simply replaces a product of sublattice averages by a product of Fourier transforms of the same averages, while maintaining the "point" approximation for the configurational entropy. It is sometimes stated that, since long-range interactions are included implicitly in the concentration wave (CW) formalism, and since the mean field approximation is correct in the limit of infinite range interactions, therefore the CW formalism is acceptable for ordering in metallic systems, say. That argument is triply fallacious.

(a) Long-range interactions are of course included in the CVM as well, they are merely more difficult to handle computationally. Moreover, as mentioned earlier, the CW model is identical to the Bragg-Williams, and represents not the slightest improvement on it.

(b) It is true that for "clustering" (ferromagnetic) systems with monotonically decaying infinite-range *negative* interactions, the second-order transition at *zero field* (average concentration 1/2) approaches the exact value. For ordering (antiferromagnetic) systems, of interest for this Workshop, no such limiting property exists. For example, no amount of long-range ordering interactions will ever produce a BW (or CW) phase diagram on an fcc lattice which even approaches the right overall *shape*, let alone the approximately correct numerical values for the transitions.

(c) As first shown by Ducastelle and Gautier [9], *effective* pair (cluster) interactions *do* decay rapidly in magnitude with distance. Recent numerical studies have confirmed the rapid convergence properties of the effective interactions, particularly in transition metal alloys [2,3,10]. In fact, the first pair interaction is responsible for over 90% of the *ordering energy* in typical cases, although the latter is but a small part of the total *cohesive energy*. The latter cannot be expressed in terms of "pair potentials" at all.

Nonetheless, Fourier transform methods, handled properly, are useful as a diagonalization method in perturbation analyses of ordering instabilities [11]. It is best, however, to perform such analyses, i.e., to evaluate generalized susceptibilities, on the basis of a CVM free energy [12], rather than its BW counterpart. Short-range order intensity can be treated similarly [13]. A BW-based stability analysis may give the misleading impression that the unstable ordering wave corresponds to a minimum (in *k*-space) of the Fourier transform of the pair interaction energy,  $V(\mathbf{k})$ . This is not always the case, as the configurational entropy must play a role in determining the ordering wave as well. There are good indications, for example, that equilibrium ordering and spinodal ordering waves belong to different "special point ordering families" in the Pd-V system [14], an effect which can be explained in the CVM, but not in the BW context [14]. *A fortiori*, *k*-space stability analysis cannot predict the ordering wave spectra of stable ordered structures. Hence, the oft-quoted statement that "the most stable superstructure is generated by the star whose ordering wave vectors provide the absolute minimum of  $V(\mathbf{k})$ " [8] is quite simply incorrect.

The CVM is no panacea, however, and suffers from deficiencies of its own. Mainly, the CVM recognizes only a limited range of correlations, those corresponding to the largest clusters used in the CVM approximation. It therefore follows that second-order transitions, which are characterized by infinite-range correlations, are not treated very accurately by the CVM. Still, with reasonable large-cluster approximations, one can approach transition temperatures to within a few percent of the exact (or best known) value, as opposed to, typically, 100% error for the BW.

In closing these sections on general considerations, let us mention that excellent reviews of the CVM, its advantages and limitations, are to be found in the doctoral dissertations of A. Finel [15], M. Sluiter [16], and G. Ceder [17], and also in a recent review by Inden and Pitsch [18].

## YBCO OXYGEN ORDERING MODEL

The compound  $\text{YBa}_2\text{Cu}_3\text{O}_z$  (YBCO) was the first one discovered whose superconducting transition temperature ( $T_c$ ) exceeded the technologically important limit of 77 K [19]. At stoichiometry  $z=7$ ,  $T_c$  is about 93 K, but drops progressively to very low values as oxygen is removed. Oxygen gain or loss occurs mostly on the so-called basal planes, or chain planes, those containing the Cu1 sites and O1 (normally occupied) and O5 (normally vacant) oxygen sites. Not only oxygen content but oxygen arrangements influence  $T_c$ , hence a careful study of oxygen ordering is critical to an understanding of the mechanism of superconductivity in this material.

Most oxygen-ordering phenomena in YBCO can be mapped onto a two-dimensional Ising model consisting of two interpenetrating square sublattices, the sites ( $\alpha$ :O1,  $\beta$ :O5) of which may be occupied or empty [20]. A third (identical) sublattice is fully occupied by Cu. In the simplest approximation, three effective pair interactions are defined:  $V_1$  between nearest neighbor sites,  $V_2$  between next nearest neighbor (nnn) sites bridged by Cu (the  $b$  direction), and  $V_3$  between nnn sites along the  $a$  direction of the orthorhombic cell. These three interactions are precisely those defined in Eq. (3) although, in the present case, the actual computation of  $W_{II}$  energies was not carried out. Instead, the values of the effective pair interactions were obtained by parametrizing the energies of a number of two-dimensional superstructures and determining  $V_1, V_2, V_3$  by matrix inversion [21]. When  $\alpha$  and  $\beta$  sublattices are equally occupied, the structure has tetragonal symmetry;  $\alpha/\beta$  sublattice ordering produces orthorhombic structures. Ground state analysis [22] reveals that eight ordered superstructures are stabilized by these three interactions at stoichiometries  $z=7$  and  $z=6.5$ . Two of these structures have been observed in YBCO: one is the orthorhombic structure (Ortho I) at  $z=7$ , consisting of parallel O-Cu-O chains, the other is the Ortho II structure consisting of alternating "full" (O-Cu-O) and "empty" (V-Cu-V; V=vacancy) chains. Another predicted ground state superstructure, of tetragonal symmetry [23], has been observed in Ca-substituted compounds [24]. The YBCO structures are stabilized when the following inequalities are verified [23]:  $V_2 < 0 < V_3 < V_1$ . As expected, the Cu-mediated interaction  $V_2$  must be attractive (negative) and  $V_3$  must be repulsive (positive) due to Coulomb interaction between O ions. First-principles calculations [21] confirm these conclusions. The Ca-substituted structure is stabilized by a similar set of inequalities but with  $V_1 < V_3$ . Other, more complex structures with larger unit cells can be stabilized when the  $V_1, V_2, V_3$  scheme of effective interactions is extended (see below). In all cases, the nnn interactions must have opposite signs, producing an Ising model with unique, highly anisotropic properties. Models which do not possess this characteristic anisotropy are unphysical and cannot reproduce the correct features of the system, claims to the contrary notwithstanding.

## PHASE DIAGRAM

A pseudo-binary (oxygen-vacancy) phase diagram was calculated by the CVM, first with phenomenological interactions  $V_2/V_1 = -1/2, V_3/V_1 = +1/2$  [25]. The high-temperature tetragonal-to-orthorhombic transition was found to be of second-order type, as expected. The first complete and consistent CVM phase diagrams were calculated independently by Zubkus et al. [26] and by Kikuchi and Choi [27], with parameters taken from [25]. These authors showed that only second-order transitions existed at very low temperature and that a new phase, now called anti-Ortho I [28], must be present for low oxygen concentrations and low temperatures.

The phase diagram, calculated [28] with parameters  $V_1, V_2$  and  $V_3$  obtained from first-principles LMTO-ASA electronic structure calculations [21], is shown in Fig. 1. The four structures mentioned above are illustrated by portions of Monte Carlo simulation outputs: small black dots in the inserts are Cu atoms, large dark ones are oxygen atoms, open circles are empty oxygen sites. In these simulated structures, Ortho I (OI) is shown with two vacancies, Ortho II (OII) contains no defects, and anti-Ortho I ( $\bar{O}I$ ) is shown to consist of a random dispersion of a few filled stable chains in a predominantly empty background, the opposite of off-stoichiometric OI which consists of a dispersion of empty chains in a predominantly full background. The symmetry of OI or  $\bar{O}I$  is orthorhombic, whereas that of the tetragonal structure (T), consisting of small segments of fluctuating chains in orthogonal orientations, is tetragonal, though locally orthorhombic. The CVM phase diagram, in this and earlier calculations [25-27] and in unpublished ones using larger cluster approximation [29-30], predicts narrow two-phase regions on the left border of the Ortho II phase region. This could be an artifact of the approximation, as Monte Carlo simulations [31] yield only higher-order transitions throughout. The existence of the  $\bar{O}I$  phase and of higher-order transitions at very low temperatures is required by symmetry [28] and is not an artifact of the CVM. Other



models, predicting a wide miscibility gap between T and OI structures, with possible spinodal mechanism, are in error.

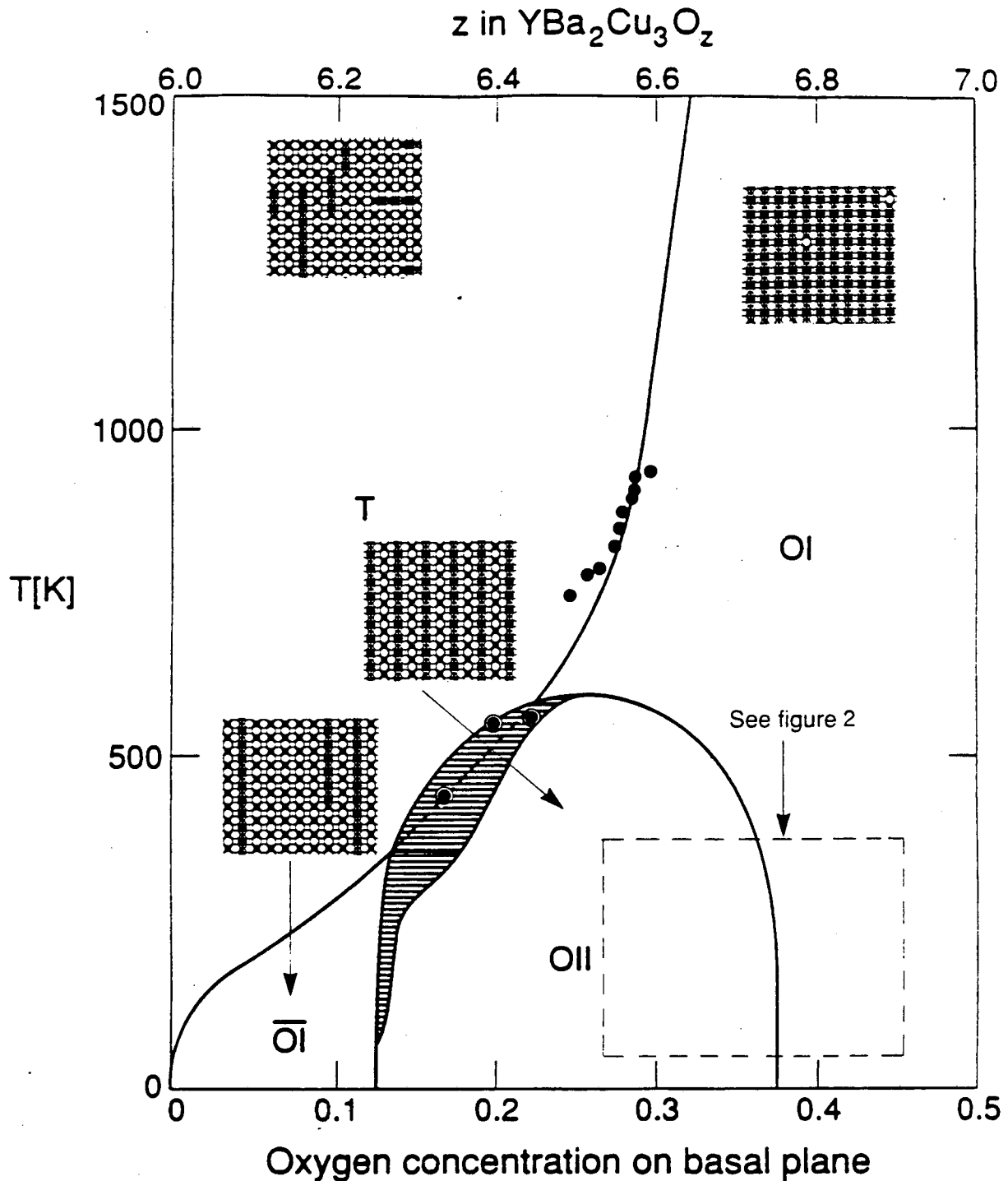


Figure 1. Phase diagram calculated by the CVM approximation, for parameters determined by Sterne and Wille [21] (full lines). Experimental points (filled circles) from Andersen et al. [32]. Inserted structure diagrams were obtained from Monte Carlo simulations (small filled circles in inserts denote copper ions, large filled circles denote oxygen ions, and open circles denote vacant sites).

The extensive experimental data of Andersen et al. [32] for the tetragonal-to-orthorhombic transitions are shown as filled circles in Fig. 1. The agreement is extraordinarily good given the fact that the calculated phase diagram was obtained with no adjustable parameters. In essence, *the phase diagram of Fig. 1 was calculated only from the knowledge of the atomic numbers and positions of the atoms and knowledge of the lattice parameters of the tetragonal unit cell.* The lower concentration (c) scale in Fig. 1 is that of oxygen content in the chain plane. If all vacant oxygen sites in the three-dimensional structure are assumed to lie in this plane, then the parameters c and z (top scale) are linearly related by  $z=6+2c$ .

Other structures are expected to be stable at low temperature in the region roughly delineated by the dashed-line box in Fig. 1. The reasoning is as follows: longer-range attractive interactions along chains (b direction) do not produce new structures but repulsive interactions along the a direction may produce additional ordered superstructures at low temperatures. We know that interaction  $V_3$  must be positive because of repulsive Coulomb interactions between nnn O atoms, and because Ortho II has been shown to be a stable structure [33]. It follows that the second nearest interaction  $V_4$  between chains in the a direction must also be positive (repulsive), and so on. In fact, we expect [34] a set of monotonically decreasing "convex" interactions along a:  $V_4, V_5, V_6, \dots$ . At low temperature, the strongly negative  $V_2$  interaction makes for very stable long O-Cu-O and V-Cu-V chains, so that, roughly in the area of the box in Fig. 1, we expect parallel-like chains to be mutually repulsive, theoretically out to infinite chain spacings. The ground state problem of infinitely repulsive objects along a line has been solved exactly [35-36], and a simple algorithm determines uniquely the sequences of stable "branching phases" which result [34]. Some of the predicted structures and their respective diffraction patterns (one-dimensional structure factors) are indicated in Fig. 2 of Ref. 34. Successive branching levels are expected to occur at successively lower temperatures, the complex structures with very long periods becoming stable only at temperatures so low that oxygen mobility may well prevent their formation for kinetic reasons.

It is important to note that, because a structure is difficult to observe, or cannot be observed in all its expected regularity, it does not mean that such a structure is metastable, or transient, or is characterized by short-range order only. Actually, all of these branching phases must be stable, at least at low enough temperatures. Diffuse intensity diffraction patterns are then due more generally to imperfect long-range order rather than to stable short-range order (from fluctuations). The calculated diffraction patterns are in remarkable agreement [34] with electron diffraction patterns observed by Beyers et al. [36] for off-stoichiometric YBCO.

We have also calculated phase diagrams featuring Ortho III, the simplest and lowest-level branching phases [37]. This structure may be described as a repeating unit of two filled chains and one empty one. To stabilize that phase, it is necessary to add interaction  $V_4$ , which was arbitrarily taken to be  $0.17 V_3$ , and, for simplicity, the sites of sublattice  $\beta$  were assumed to be always unoccupied. A two-dimensional CVM calculation produced a phase diagram very similar to one published by Zubkus et al. [38]. That phase diagram exhibited some incongruous features, such as the OI phase region subsisting to absolute zero for concentrations below OIII stoichiometry. This undesirable feature was clearly an artifact of the two-dimensionality of the model. A more complete three-dimensional CVM calculation based on pyramidal and prismatic clusters gave a much more realistic phase diagram, with an OIII phase region separated from OI and OII by two-phase regions, as required by the Landau rules, the OIII unit cell in the a direction being three times as long as that of OI. The relevant portion of the phase diagram is shown in Fig. 2.

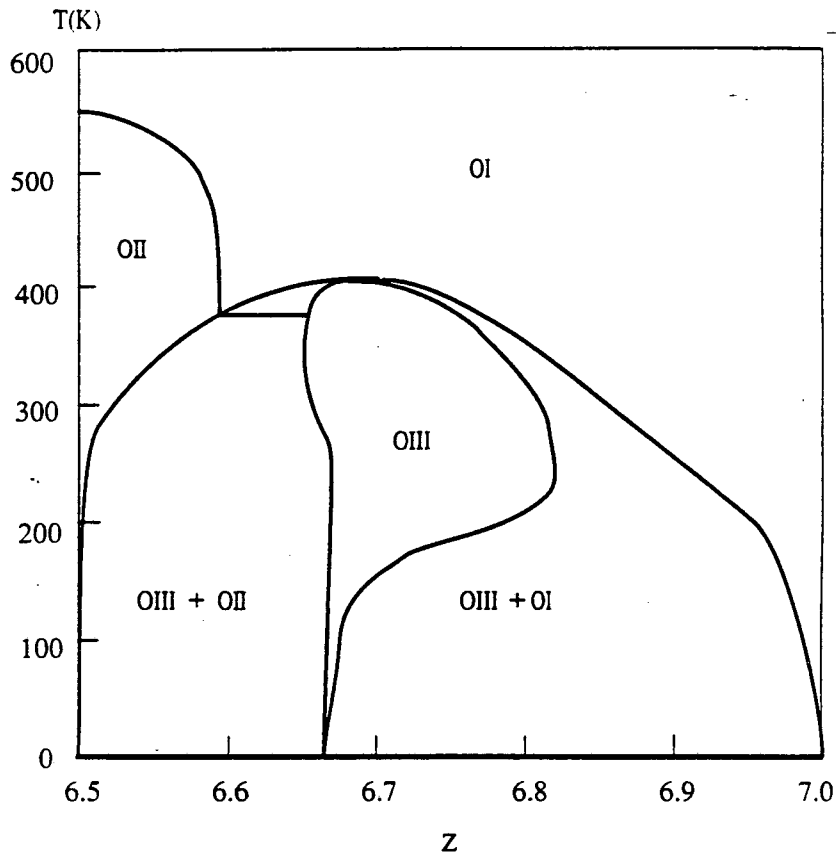


Figure 2. Portion of phase diagram corresponding roughly to boxed area of Figure 1. Ortho III phase is obtained by including a small repulsive  $V_4$  interaction along direction  $a$ .

## ORDERING AND SUPERCONDUCTIVITY

In February 1990 we wrote [34]:

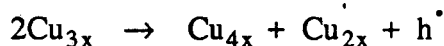
Although neither the theoretical branching temperatures nor the temperatures at which oxygen configurations are frozen in during sample preparation are known at present, the agreement between recent experimental findings and our theoretical model is really quite striking. We are thus tempted to relate the plateau structure of the  $T_c$  versus concentration curve to the existence of a theoretically infinite set of branching phases, the  $T_c$  plateaus corresponding to states of quasi-one-dimensional order frozen in at a certain "generation" level. The number of plateaus and their range of oxygen content should depend critically on sample preparation. Recent experimental and theoretical work support these ideas. For example, Farneth et al. [39] report that the  $T_c$  plateau for low-temperature vacuum-annealed samples of  $\text{YBa}_2\text{Cu}_3\text{O}_z$  is sharply defined and entirely located at temperatures higher than the monotonically decaying  $T_c$  versus oxygen-content curve for samples quenched from high temperatures. Lambin [40] has used a tight-binding model to show that the hole concentration for well ordered Ortho II and Ortho III phases should be higher than those for the corresponding disordered compounds. It is clear that chain formation minimizes the fraction of incorrectly coordinated copper ions in the

basal plane. Hence, chain ordering can be regarded as a form of doping in this compound.

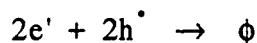
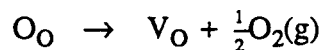
This conjecture received spectacular confirmation in the work of Argonne scientists on oxygen ordering at and below room temperature [41,42]. For quenched YBCO single crystals of oxygen content  $z=6.45$ , it was found that  $T_c$  increased markedly on subsequent aging, in fact by as much as 27 K [41]. During this process, it was ascertained [42] that oxygen content was not altered: the average occupancy on sites O1, O2, O3, O4 and O5 did not change, although the molar volume and lattice parameters contracted significantly, the more than the b. Such behavior can only be interpreted as being due to *additional* oxygen ordering.

Recent "quench and age" Monte Carlo simulations [43] based on the model described above, i.e., with  $V_1, V_2, V_3$  parameters used in calculating the phase diagram of Fig. 1, have shed considerable light on the problem. Immediately after the essentially instantaneous "computer quench,"  $\alpha/\beta$  ordering takes place during a very short transient, so short that it is probably unobservable experimentally. Subsequently, ordering of chain segments parallel to themselves, so as to form the longest possible chains, takes place at a rate characterized by a lower time constant.

The oxygen coordination of Cu1 atoms was monitored continuously during simulated aging at room temperature for samples quenched from 800 K. In the chain plane, Cu can be 0-, 1-, or 2-fold coordinated, corresponding to 2-, 3-, or 4-fold three-dimensional coordination if it is assumed that O4 sites are always occupied (see Fig. 3). Three- and four-fold planar coordination are forbidden because of the strong  $V_1$  nn repulsive interaction. Electronic structure calculations [44] reveal that (spatially) 3- and 4-fold coordinated Cu is mostly present as  $Cu^{++}$ , and 2-fold coordinated Cu is present as  $Cu^+$ . As a result, chain "healing," i.e., progressive elimination of chain ends, where Cu is 3-fold coordinated, gives rise to the following "reaction" in Kröger-Vink notation:



thus creating holes ( $h^{\bullet}$ ), accompanied by an excess negative charge on 2-fold coordinated Cu. The increasing hole concentration should favor a high  $T_c$ , but oxygen loss tends to destroy holes by the following mechanism:



The first of these equations describes oxygen loss to the gas phase (g), the second describes ionization of vacancies and creation of electrons, the third describes electron-hole recombination.

Monte Carlo simulations [43] clearly show that the fraction ( $f_{n-Cu}$ , with  $n=2, 3$  or 4) of 2-fold or 4-fold coordinated sites increases with annealing time, that of 3-fold sites decreases. These trends (see Fig. 4) reproduce those of the rise in  $T_c$  observed experimentally by the Argonne group [41,42]. Moreover, since it is argued that oxygen ordering promotes hole formation, and that oxygen loss destroys holes, these two conflicting tendencies may well produce non-monotonic decay of  $T_c$  as oxygen content is decreased, possibly giving rise to the "plateaus" observed in the  $T_c$  vs. oxygen content curve.

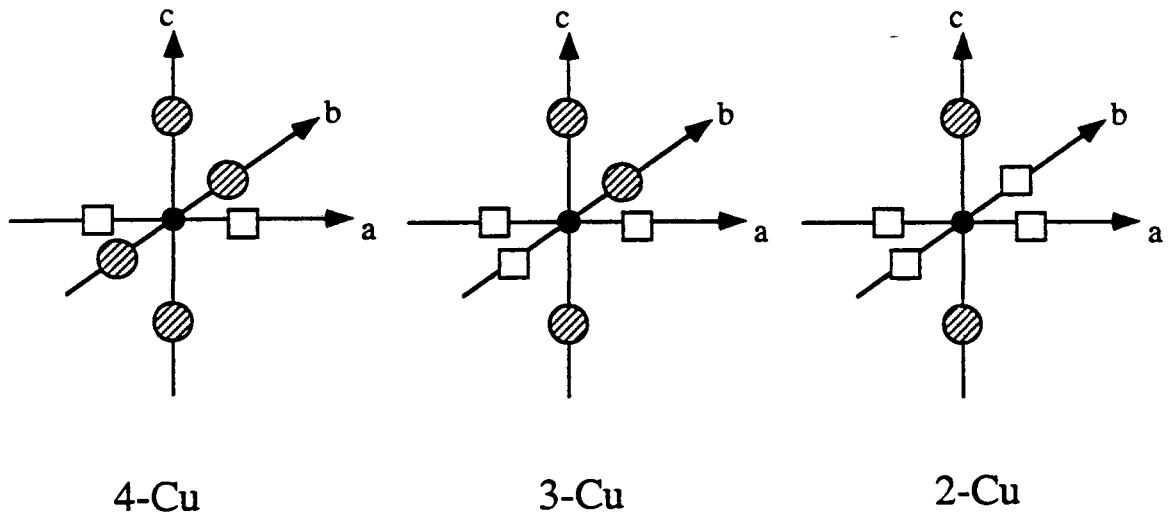


Figure 3. The important configurations of oxygen around a Cu1 atom. It is assumed that the axial oxygens (along the c-axis) are always in place.

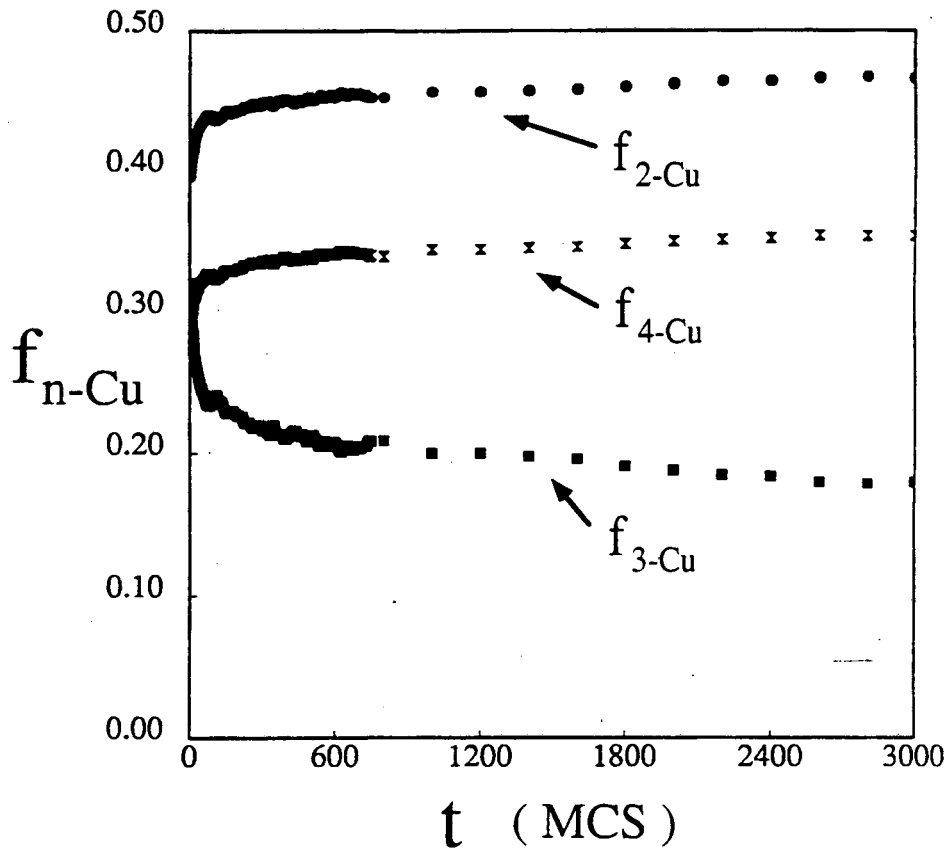


Figure 4. The fractions of 2-, 3- and 4-fold coordinated Cu atoms in the chain planes as a function of Monte Carlo time (MCS). The rapid initial rise (or decay) of  $n$ -fold coordinated functions corresponds to  $\alpha/\beta$  sublattice ordering. The slower evolution is due to "chain healing," i.e., gradual elimination of chain ends ( $3\times$  coordination).

Recently, Poulsen et al. [45] were able to reproduce the observed plateau structure by a Monte Carlo procedure, much like the one reported here. The counting algorithm was different, however; instead of monitoring Cu-coordination, these authors considered a relative population of two-dimensional "minimal-size clusters" of both Ortho I and Ortho II types. Upon careful analysis of their counting algorithm, it appears [46] that the good agreement with experiment obtained by Poulsen et al. is due to a very particular choice of rather artificial assumptions. Substituting another set of equally valid assumptions, differing but little from the original one, tends to destroy the plateau structure altogether. Clearly, a deep understanding of the relationship between superconductivity and oxygen ordering is still lacking.

## CONCLUSION

A new "first-principles thermodynamics" of alloys is emerging thanks to the unifying concept of *clusters*: both ordering energy and configurational entropy are expressed in terms of cluster functions, multisite correlations, cluster probabilities. Clusters provide the link between quantum and statistical mechanics and, by means of the cluster variation method, with classical thermodynamics itself. Calculated phase diagrams, such as the one for oxygen ordering in YBCO, have yielded excellent agreement with experimentally determined ones. By contrast, mean field models (BW, CW) produce phase diagrams which are not only quantitatively but even qualitatively in error.

The asymmetric two-dimensional Ising model described above has explained successfully many features of the YBCO system: the experimentally observed phases (tetragonal, Ortho I, Ortho II) are ground states of the model; the calculated phase diagram (with no adjustable parameters) agrees remarkably well with experimental data; the observed electron diffraction maxima correspond closely with calculated structure factors of additional "branching phases" (such as Ortho III); and Monte Carlo simulation reproduces correctly the trends in change in  $T_c$  with annealing time in off-stoichiometric samples. It may therefore be concluded that this simple model captures most of the physics of oxygen ordering in the YBCO and related systems.

## ACKNOWLEDGEMENTS

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LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
INFORMATION RESOURCES DEPARTMENT  
BERKELEY, CALIFORNIA 94720