Ground states of a ternary fcc lattice model with nearest- and next-nearest-neighbor interactions

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The possible ground states of a ternary fcc lattice model with nearest- and next-nearest-neighbor pair interactions are investigated by constructing an eight-dimensional configuration polytope and enumerating its vertices. Although a structure could not be constructed for most of the vertices, 31 ternary ground states are found, some of which correspond to structures that have been observed experimentally.

I. INTRODUCTION

Alloy phase diagrams are of considerable interest in materials science and condensed matter physics. They serve as guidelines to determine processing conditions and are often needed to explain the properties and behavior of a material with a given environmental history. From decades of experimental results, a relatively accurate picture has now been compiled for most binary alloy systems.[1,2] From the theoretical side, first-principles theorists are trying not only to reproduce some of these well-known phase diagrams, but also to understand their topology in terms of microscopic models for the energy and the entropy. Using a powerful combination of quantum mechanics and statistical mechanics, *ab initio* alloy theory has advanced to the point where the topology of simple phase diagrams can be reproduced, starting from only the atomic numbers of the constituents.[3-10]

Whereas binary systems have been studied extensively, both experimentally and theoretically, much less is known for three-component systems. No systematic compilation of ternary phase diagrams exists (although one has been started[11]) and only a few attempts have been made to compute ternary phase diagrams with first-principles models.[12,13] An essential part of a first-principles phase diagram computation is the prediction of the ground states in the system. In this paper we will present general ground-state results for ternary systems. Using a lattice model with only nearest- and next-nearest-neighbor pair interactions, we will attempt to predict which ordered fcc superstructures can exist in

three-component systems. In the binary case, only nine distinct ground-state structures are possible with this interaction range.[14-17] This number increases drastically when extending the interaction range to the fourth nearest-neighbor distance.[18,19] A recent study on the ground states in a ternary bcc lattice model indicated that only a few real ternary structures could be stabilized with nearest- and next-nearest-neighbor pair interactions.[20]

II. FORMALISM AND METHOD

The zero-temperature energy of an alloy that is restricted to order on an underlying fcc lattice can be conveniently mapped onto a lattice model Hamiltonian.[21] In the binary case, a spin variable, σ_i, takes on the value $+1$ (-1) when site i is occupied by an A (B) atom. Although the energy of binary alloy depends on the configuration of all the spins, represented by $\{\sigma\}$, it can be expanded exactly in a basis of local cluster functions[22]:

$$E(\{\sigma\}) = \sum_\alpha V_\alpha \sigma_\alpha \qquad (1)$$

with the cluster function σ_α defined as the product of all the spins on sites in cluster α:

$$\sigma_\alpha = \prod_{i \subset \alpha} \sigma_i \ . \qquad (2)$$

The expansion coefficients V_α are effective cluster interactions (ECI) and have been found to converge rapidly with distance and cluster size. The practicality of Eq. (1)

lies in its rapid convergence: once the values of the ECI have been determined, the energy of a given configuration can be obtained by summing a few local cluster functions around each lattice site.

The transfer to an Ising-like Hamiltonian does not imply that the alloy is modeled on a static, fixed lattice. The spin configuration $\{\sigma\}$ only reflects the state of connectivity of the atoms, but not their exact positions. $E(\{\sigma\})$ could, for example, be parametrized so that it gives the energy of a configuration $\{\sigma\}$ where atoms have been allowed to relax to their lowest-energy position, which need not coincide exactly with the lattice position. The effect of relaxation on ground-state energies has been shown to be substantial and significant errors can be introduced when neglecting it.[23][24][25] We recently indicated how, in a similar way, the effect of high-temperature vibrations can be included in expansion (1).[21][26]

To describe ordering in a ternary system a three-state occupation variable is needed. The obvious choice is a spin-1 model, although more symmetric state variables in the complex plane can be used as well.[27] In the following we will adopt the simple three-state spin model and represent A, B, or C occupation of a lattice site by the spin value $+1$, 0, and -1, respectively (see Fig. 1).

Similarly to what is used in computations on binary systems, we can expand the energy of a ternary system in a complete basis of cluster functions. Sanchez, Ducastelle, and Gratias[22] suggested to use orthogonal Chebyshev polynomials in σ_i and σ_i^2. The orthogonality of the basis functions leads to a simple and powerful, definition of the ECI: they are the projection of $E(\{\sigma\})$ onto cluster function σ_α. This definition has been judiciously followed in one of the methods to compute these effective interactions from first principles[28][29] and its feasibility for ternary systems has recently been demonstrated as well.[30] In this ground-state study we will, however, choose a set of basis functions suggested by Inden and Pitsch,[31] and in a limited form by Taggart,[32] as this
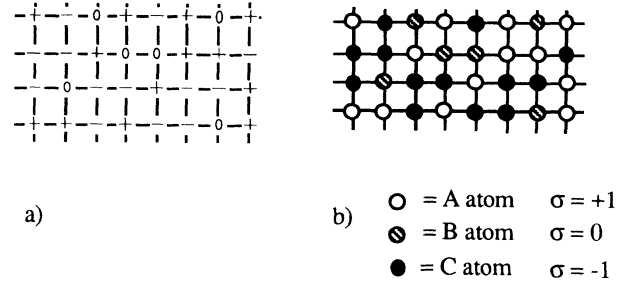

FIG. 1. The configuration of atoms (b) in a three-component system is represented by a three-state lattice model (a). A spin value of $+1$, 0, and -1, respectively, indicates the occupation of the lattice site by an A, B, or C atom.

basis is more apt for ground-state models. In the S basis, as we will refer to it, the cluster functions are simple products of σ_i and σ_j^2. Consider two figures β and γ on the lattice, with γ completely in β. The ternary cluster function $\Phi_{\beta,\gamma}$ is defined as

$$\Phi_{\beta,\gamma} \equiv \prod_{i\in\beta} \sigma_i \prod_{j\in\gamma} \sigma_j = \prod_{i\in\beta-\gamma} \sigma_i \prod_{j\in\gamma} \sigma_j^2 . \qquad (3)$$

The set of all cluster functions for all combinations (β,γ) forms a complete set in the space of all configurations. Although this basis is not orthonormal, it is desirable for ground-state work as the values of the cluster functions are always integer in the S basis.

In its most general form, the Hamiltonian of the ternary system can be expanded in the S basis as

$$E(\{\sigma\}) = \sum_\beta \sum_{\gamma\subseteq\beta} V_{\beta,\gamma}\Phi_{\beta,\gamma} . \qquad (4)$$

Limiting the effective interaction range to nearest-neighbor (NN) and next-nearest-neighbor (NNN) pairs, the last equation can be written explicitly:

$$E(\{\sigma\}) = V_\varnothing + \sum_i H^\sigma\sigma_i + \sum_i H^{\sigma^2}\sigma_i^2 + \sum_{i,j}^{NN} V_1^{\sigma\sigma}\sigma_i\sigma_j + \sum_{i,j}^{NN} V_1^{\sigma\sigma^2}(\sigma_i\sigma_j^2 + \sigma_i^2\sigma_j) + \sum_{i,j}^{NN} V_1^{\sigma^2\sigma^2}\sigma_i^2\sigma_j^2$$

$$+ \sum_{i,j}^{NNN} V_2^{\sigma\sigma}\sigma_i\sigma_j + \sum_{i,j}^{NNN} V_2^{\sigma\sigma^2}(\sigma_i\sigma_j^2 + \sigma_i^2\sigma_j) + \sum_{i,j}^{NNN} V_2^{\sigma^2\sigma^2}\sigma_i^2\sigma_j^2 . \qquad (5)$$

Equation (5) is the most general Hamiltonian for a three-state spin model with NN and NNN interactions. In a more restricted form it is known as the Blume-Emery-Griffith model used for the study of superfluidity in helium, liquid-crystal mixtures, and electronic conduction models.[33] As the effective interactions have the symmetry of the underlying lattice, Eq. (4) can be averaged over the whole lattice to get the energy per lattice site:

$$e(\{\sigma\}) = \sum_\beta{}' \sum_{\gamma\subseteq\beta}{}' V_{\beta,\gamma}m_{\beta,\gamma}\langle\Phi_{\beta,\gamma}\rangle . \qquad (6)$$

The primes indicate that the sums are only over the types of figures that are distinct, considering the symmetry of

the lattice. The coefficient $m_{\beta,\gamma}$ gives the number of (β,γ) figures per lattice site and the correlation function $\langle\Phi_{\beta,\gamma}\rangle$ is the average value of all the cluster functions defined on those clusters.

To find the ground states of our ternary system, Eq. (6) has to be minimized with respect to the values of the correlation functions. Although the energy is linear in the correlation functions, the ground-state minimization is nontrivial as the values of the correlations are restricted by the fact that they have to represent a physical state of ordering on the parent lattice. It is, for example, impossible for all correlations of a binary alloy on the fcc lattice to have the value -1. The difficulty in ground-

state studies lies in finding the exact constraints the lattice imposes on the correlation functions. Once these constraints are found, Eq. (6) can be minimized with standard linear programming techniques.[34]

One approach to finding these constraints, that has worked successfully for some binary problems, has been to require that the probability of an atomic configuration on a given cluster be between zero and one. Since this probability can be written as a linear function of the correlation functions on the cluster, these conditions impose linear inequality constraints between the correlation functions. Using only constraints on the tetrahedron and octahedron, for example, it is possible to exactly predict all binary fcc superstructures that can be stabilized with NN and NNN interactions.[14-17] We will follow a similar procedure to look at the possible ground states of a ternary fcc lattice model with NN and NNN interactions: First, we will express the probability functions for the configurations on the tetrahedron and octahedron in terms of the correlation functions that are defined on figures contained in these clusters. We will then eliminate, from the constraints, all the correlation functions for which no interaction appears in Eq. (5). The resulting set of inequalities limits the values of the correlation functions on the NN and NNN pair figures and on the point figure. The inequality constraints between the two-point correlation functions and six-pair correlation functions define hyperplanes in an eight-dimensional space. The values of the correlation functions are restricted to lie inside the polytope bounded by all constraints. The vertices of this configuration polytope are the possible ground states of Eq. (5). This can be easily understood by noting that the energy is a linear function of the correlations; hence, it will only reach an extremum at the boundary of the existence domain. The extreme points of a convex polytope are its vertices.

This procedure does not always yield acceptable results. As the inequality constraints are derived from configurations on a small cluster they might not be restrictive enough compared to inequalities resulting from the infinite system. In this method, the exact configuration polytope is thus always approached from the outside, and formulating constraints on a larger cluster may cut off some of the vertices that are obtained with smaller clusters. In that case, the vertex violated some of the constraints arising from the larger cluster, and it cannot correspond to a physical state of ordering. It is referred to as an *inconstructable* vertex. Conversely, every vertex for which a physical configuration can be found with the correct correlations will never be cut off when constraints are formulated on a larger cluster. Vertices of this type are *constructable* and correspond to real ground states of the system.

To find the constraints on the correlation functions, the probability $\langle X_\alpha(J) \rangle$, for configuration J to occur on cluster α, can be expanded linearly in the correlation functions (see the Appendix for a derivation of the expansion coefficients):

$$\langle X_\alpha(J) \rangle = {\sum_{\beta \subseteq \alpha}}' \; {\sum_{\gamma \subseteq \beta}}' \; Z_{\beta,\gamma}(J) \langle \Phi_{\beta,\gamma} \rangle \; . \tag{7}$$

Only correlation functions on figures in α appear in the expansion. The set $Z_{\beta,\gamma}(J)$ is often referred to as the v matrix. Requiring that $\langle X_\alpha(J) \rangle$ be positive gives the desired inequality constraints between the correlation functions. All probabilities sum to 1 by construction. On the tetrahedron, 14 distinct correlations and 15 atom configurations can be defined. For the octahedron there are 55 correlation functions and 56 distinct configurations. Combined, the two clusters define a polytope bounded by 71 distinct hyperplanes in a 60-dimensional space. The vertices of this polytope are the possible ground states that can be stable with interactions defined in the tetrahedron and octahedron clusters. What is needed, however, are the ground states that can be obtained when only NN and NNN pair interactions are present. To find the constraints between only the correlation functions that appear in Eq. (5), all other correlation functions need to be eliminated from the 71 constraints. This can be done by projecting the vertices of the polytope in the 60-dimensional space down to the eight-dimensional space spanned by the correlation functions of interest, and determining the convex hull of all the projected points. This procedure is not feasible in this case as the number of vertices of the full tetrahedron-octahedron polytope (in the 60-dimensional space) may be as many as 10^9.[34]

As an alternative, we determined the projections of polytopes derived from the constraints on the tetrahedron and octahedron onto the eight-dimensional space separately and then computed the intersection of these two polytopes. For the binary ground-state enumeration this gives exact results. Compare, for example, the results of Ducastelle[14] and Finel[16] with those obtained by Sanchez and de Fontaine.[17] The eight-dimensional projections of the tetrahedron and octahedron polytopes were characterized respectively by 36 and 699 faces. Six of the faces of the tetrahedral polytope also appear in the projection of the octahedral polytope so that the intersected polytope is defined by 729 hyperplanes. The vertices of this polytope are the possible ground states of the ternary NN-NNN fcc lattice model.

Enumerating the vertices of a polytope for which the bounding hyperplanes are given is a well-known problem in combinatorial geometry[35] that has received much attention for its applications in operations research. Most methods developed, however, are not practical to enumerate vertices of ground-state polytopes as these polytopes are usually characterized by a high degeneracy. Degeneracy in vertex enumeration techniques occurs when more than n hyperplanes go through a vertex on an n-dimensional polytope. To enumerate the vertices of our ternary ground-state polytope, both the double description algorithm[36] and the reverse search algorithm were used. The double description method is an incremental algorithm that computes all vertices of a polytope by sequentially adding each hyperplane to the polytope computed in the previous step. Although this method must store all vertices of the intermediate polytopes, it can deal with degeneracy quite well. The reverse search method was developed by two of the authors[37] and only requires storage space for the input data, making it very useful for

large problems. The drawback of the method is that many duplicates of the same vertex can be generated when degeneracy is present. While both methods successfully generated all vertices of the polytope, the double description method seems to be more appropriate for this computation because of the high degeneracy and moderate size of the inequality system. For larger systems, however, the reverse search method may become the only feasible algorithm for vertex enumeration.

III. RESULTS

The ground-state polytope we found is highly degenerate and consists of 4862 vertices in the eight-dimensional space spanned by the correlation functions. Some of the vertices found correspond to structures that can be transformed into each other by permutations of the A, B, and C species. If these are considered to be the same structure, the total number of distinct structures is
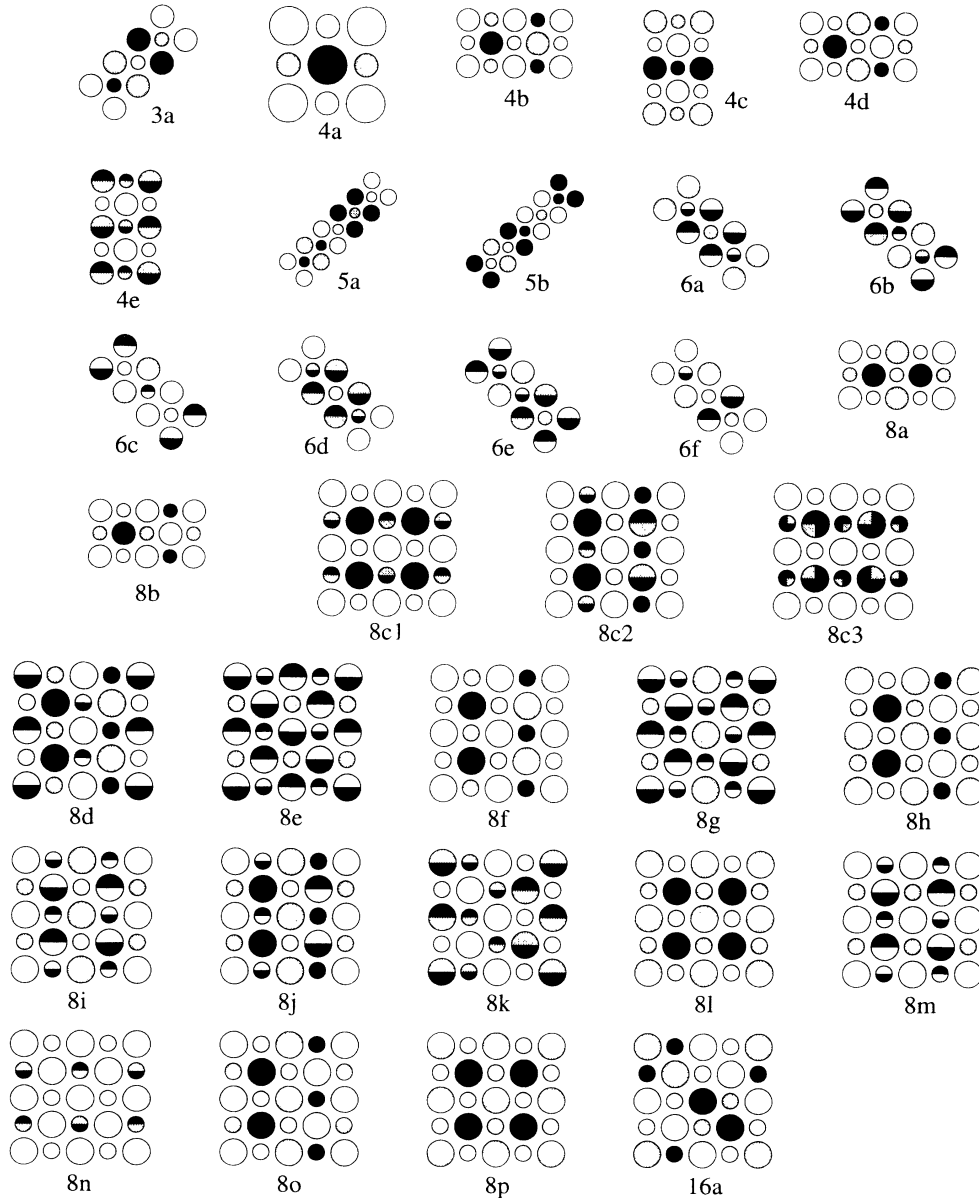

FIG. 2. {001} projections of the ternary ground-state superstructures of fcc with first and second nearest-neighbor interactions. White, grey, and black circles correspond to A, B, and C atoms, respectively. Large circles are in {00n} planes, and small ones in {00n + 1/2} planes. Half-shaded circles correspond to atoms alternating in the [001] direction, while circles with a shaded quadrant correspond to particles occupying every fourth site in the [001] direction. Rotations of the shaded parts indicate different {00z} planes. The structures are labeled with the number of atoms in their primitive unit cells and letters to distinguish between structures with the same number of atoms. Structures 8c1, 8c2, and 8c3 correspond to the same vertex in the configurational polytope and have the same energy for the range of interactions used.

TABLE I. Experimental prototypes have been found for three of the structures shown in Fig. 2.

Structure	Prototype	Space group	Pearson symbol	Atoms in unit cell
4a	Cu_2NiZn	$P4/mmm$	$tP4$	4
4c	$CdPt_2Zn$	$P4/mmm$	$tP4$	4
4b	Rh_2SnCo	$P4_2/ncm$	$tP16$	4

980. Nine of these have only two types of atoms and correspond to the ground-state structures of the binary problem.

To test the constructability of the 971 vertices with ternary composition, we developed a computer code that tries to build a structure with a given set of correlation functions. The only assumption made is that the primitive unit cell of the structure has less than a specified number of atoms. The code explores all the possible unit cells up to the maximal size. Setting the maximum size to 32 atoms, only 31 of the distinct vertices could be constructed. Two-dimensional projections of the unit cells of these structures are drawn in Fig. 2.

IV. DISCUSSIONS

Given the fact that no structures were found with more than 16 atoms in the primitive unit cell, and only one structure with more than 8 atoms, it is unlikely that many of the 940 vertices that we could not construct correspond to real structures with unit cells larger than 32 atoms. We will therefore consider all 940 vertices as inconstructable even though that has not entirely been proven. The vertices that can be constructed are true ground states of the NN and NNN Hamiltonian since they can never be removed by constraints derived from considering larger clusters. For some of the structures with small unit cells we have found experimental evidence in real ternary systems. Structure 4a, which is the only ternary ground state possible if the interactions are limited to the nearest-neighbor distance, has been observed in Cu_2NiZn.[38] The structure is similar to the binary $L1_0$, but with the minority atoms ordered in one of the (001) planes. A different secondary ordering occurs in structure 4c which corresponds to the $CdPt_2Zn$ phase. In this structure, Cd and Zn segregate each to their own (001) plane, alternating with pure Pt (001) planes. Structure 4b is the Rh_2SnX phase, where X can be Co, Cr, Fe, or V. This ordered phase can be considered as the antiphased variant of the Cu_2NiZn structure. Table I lists the space group, size of the primitive unit cell, and prototype for these three structures.

The search for prototypes corresponding to our ground states is hampered by the lack of detailed experimental information. For many ternary compounds the occupation of each site has not been determined unambiguously so that they cannot be compared with the pictures in Fig. 2. However, most often there is simply no experimental data available for a ternary system. Since the interaction range we considered here is not at all exceptional (most systems have significant effective interaction up to at least the second nearest-neighbor distance), many of the ground states in Fig. 2 should be found in real ternary

systems. Maybe this ground-state enumeration can assist experimentalists in their determination of the structure of a ternary fcc compound.

In contrast to the success of the tetrahedron-octahedron ground state analysis for the binaries, the ternary analysis produces a large number of inconstructable vertices, indicating that frustration effects on figures beyond the tetrahedron and octahedron need to be accounted for. The polytope method's applicability rests on the presumption that frustration effects between interactions can be sampled in the local environment around a lattice point. If this is not so, large clusters have to be used to formulate the correct constraints and the method quickly becomes infeasible. We have already found this to be the case for the binary ground-state problem as soon as one tries to go beyond the second nearest-neighbor interaction distance.[18] Considering that the problem presented here already tested the limits of vertex enumeration methods, it seems unlikely that the polytope method, in the form used here, will be tractable to solve the second nearest-neighbor ternary ground-state problem exactly. Many first-principles computations of the ECI have indicated that, in binary systems, interactions are typically significant up to the fourth nearest-neighbor distance, and there is no reason to believe that this will be any different in a ternary expansion. In this case, straightforward structure enumeration methods[18,39] might form the only acceptable alternative to obtain information on the possible ground states of a lattice model.

ACKNOWLEDGMENTS

APPENDIX

Define the occupation operator $p_i(j)$ which takes the value 1 if the site i is occupied by an atom of type j and 0 otherwise. For a ternary alloy, $p_i(j)$ can be written as a linear combination of the σ_i and σ_i^2 operators[31,32]:

$$p_i(A) = \tfrac{1}{2}\sigma_i + \tfrac{1}{2}\sigma_i^2 ,$$

$$p_i(B) = 1 - \sigma_i^2 , \tag{A1}$$

$$p_i(C) = -\tfrac{1}{2}\sigma_i + \tfrac{1}{2}\sigma_i^2 .$$

If we define the transformation matrix U with columns and rows numbered as indicated in Eq. (A2),

col 0 col 1 col 2

$$
U = \frac{1}{2}
\begin{bmatrix}
0 & 1 & 1 \\
2 & 0 & -2 \\
0 & -1 & 1
\end{bmatrix}
\begin{matrix}
\rightarrow \text{row } -1 \\
\rightarrow \text{row } 0 \\
\rightarrow \text{row } 1
\end{matrix}
\qquad \text{(A2)}
$$

we can write the general formula for the occupation operator:

$$
p_i(j) = \sum_{k=0}^{2} u_{jk}\sigma_i^k = u_{j0} + \sum_{k=1}^{2} u_{jk}\sigma_i^k . \qquad \text{(A3)}
$$

In the last formula, the index i indicates the site, j the type of atom, and u_{jk} the element of matrix U. The occupation operators for configurations on larger figures can be easily written in terms of the cluster functions by multiplying the point operators. The following notation is adopted: α is the cluster on which the cluster configuration is considered; J specifies a given configuration on cluster α; $T_i(J)$ gives the spin value on site i when cluster α is in configuration J; $X_\alpha(J)$ is an operator that returns 1 when α is occupied with configuration J, 0 otherwise; $X_\alpha(J)$ is the product of the point operators on sites of cluster α:

$$
X_\alpha(J) = \prod_{i\in\alpha} p_i[T_i(J)] = \prod_{i\in\alpha}\left[\sum_{k=0}^{2} u_{T_i(J)k}\sigma_i^k\right] . \qquad \text{(A4)}
$$

By interchanging the summation and product and taking the lattice average we get

$$
\langle X_\alpha(J)\rangle = \sum_{k_1=0}^{2}\sum_{k_2=0}^{2}\cdots\sum_{k_n=0}^{2}\left[\prod_{i\in\alpha} u_{T_i(J)k_i}\right]\left\langle\left[\prod_{i\in\alpha}\sigma_i^{k_i}\right]\right\rangle . \qquad \text{(A5)}
$$

Using the definition of the cluster function [Eq. (3)], we can rewrite this as

$$
\langle X_\alpha(J)\rangle = \sum_{\beta\subseteq\alpha}\sum_{\gamma\subseteq\beta} z_{\beta,\gamma}(J)\langle\Phi_{\beta,\gamma}\rangle , \qquad \text{(A6)}
$$

where

$$
z_{\beta,\gamma}(J) \equiv \left[\prod_{i\in\alpha} u_{T_i(J)k_i}\right] \qquad \text{(A7)}
$$

and the clusters β and γ are defined as in Eq. (3). For all pairs (β,γ) in α that are equivalent under the symmetry of the lattice, the value of the correlation function is identical. If we call $\Omega_\alpha(\beta,\gamma)$ the orbit of all these symmetry equivalent figures in α, Eq. (A6) can be simplified by summing only over correlation functions that are not related by the symmetry of the lattice:

$$
\langle X_\alpha(J)\rangle = {\sum_{\beta\subseteq\alpha}}' {\sum_{\gamma\subseteq\beta}}' Z_{\beta,\gamma}(J)\langle\Phi_{\beta,\gamma}\rangle \qquad \text{(A8)}
$$

with

$$
Z_{\beta,\gamma}(J) = {\sum_{(\beta,\gamma)_i\subseteq\Omega_\alpha(\beta,\gamma)}}' z_{(\beta,\gamma)_i}(J) . \qquad \text{(A9)}
$$

$Z_{\beta,\gamma}(J)$ is usually called the v matrix. For large maximal figures, most of its elements are zero. For example, it can be seen from Eq. (A5) and (A2) that for all configurations J that have an A or C atom in α-β, the element $z_{\beta,\gamma}(J)$ will be equal to zero.

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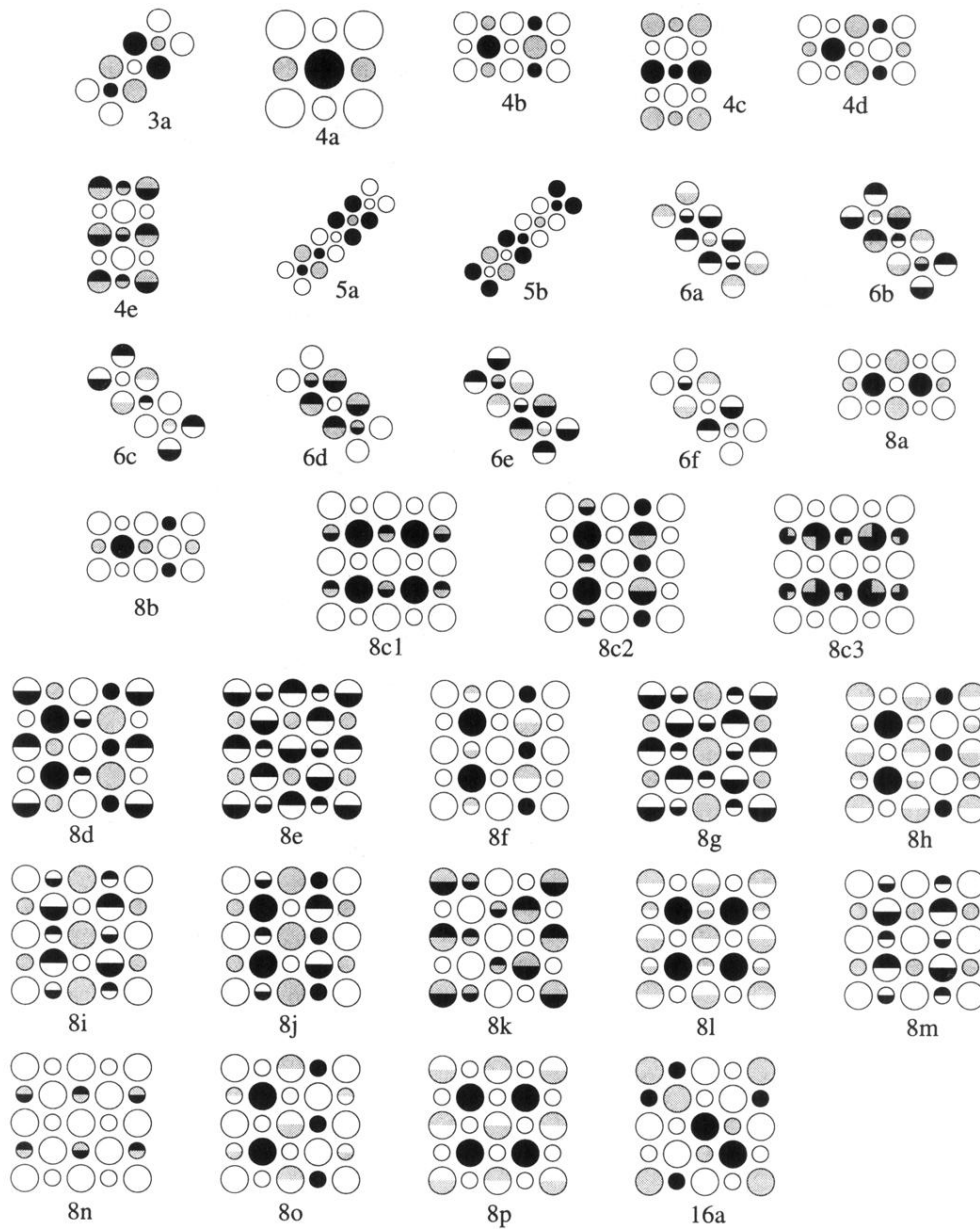
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