

Cluster expansions of alloy energetics in ternary intermetallics

C. Wolverton*

Department of Physics, University of California at Berkeley and Lawrence Berkeley Laboratory, Berkeley, California 94720

D. de Fontaine

Department of Materials Science and Mineral Engineering, University of California and Lawrence Berkeley Laboratory, Berkeley, California 94720

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Ternary alloy energetics are examined for substitutional systems by a formal cluster expansion. In contrast to the binary-alloy problem, several distinct basis sets are possible for the ternary cluster expansion. Several of these sets of ternary basis functions are examined and compared, and relationships are derived between the expansion coefficients, or effective cluster interactions, expressed in various bases. The method of direct configurational averaging (DCA) (based on a tight-binding, linearized muffin-tin-orbital Hamiltonian) is extended to treat ternary alloy systems. Using the DCA, ternary, fcc-based effective pair and triplet interactions are computed for the Rh-V-Ti, Pd-Rh-V, and Ag-Pd-Rh systems, and convergence of the expansion is examined. By combining the cluster expansion with the results of the DCA computations, formation energies are obtained for the completely disordered state as a function of alloy composition. Both pair and triplet interactions are seen to be crucial towards obtaining quantitatively converged energetics.

I. INTRODUCTION

The study of phase stability in substitutional alloy systems is of great technological interest. Due to the inherent complexities of the full multicomponent alloy problem, the majority of the theoretical work to date has focused on binary alloys. However, most alloys of practical importance are multicomponent (ternary, quaternary, etc.). Due to the enormous number of possible combinations of the constituents, the experimental survey of ternary alloys is much less thorough than that of binary systems. Thus, an extension of theoretical and computational techniques to ternary systems is a crucial step towards making a predictive theory which is of use in alloy design. Additionally, many important problems may be expressed as simplifications of the full ternary problem: dilute additions to a binary system, pseudobinary alloys, substitutional defects and vacancies in a binary system, dilute binary additions to a pure metal with vacancies, etc.

Much of the theoretical work on binary-alloy systems is formulated in terms of an extended "Ising-like" model, or more generally, a cluster expansion. The cluster expansion of binary-alloy properties then provides a formal framework for the study of alloy energetics with respect to substitutional rearrangements of atoms, with the energy being parametrized by effective pair and multisite interactions. Several techniques have been developed to compute these effective cluster interactions (ECI's) from electronic-structure calculations.¹⁻⁴ In particular, the method of direct configurational averaging⁴ (DCA) provides a straightforward means to compute the coefficients of the expansion, the effective cluster interactions (ECI's), with no adjustable or experimentally determined parameters. For binary alloys, knowledge of the ECI's for a

given alloy system can lead to predictions of such properties as stable ground-state structures, energies of metastable and disordered states, and phase equilibrium and diagrams. In this paper, we demonstrate the extension of the cluster expansion and DCA to the case of ternary alloys.

Many ambiguities arise in the ternary problem which are not present in the binary case. Consider the ternary formation energy of a structure γ :

$$\Delta E_{\text{FORM}}(\gamma) = E(\gamma) - [c_A E_A^0 + c_B E_B^0 + c_C E_C^0], \quad (1.1)$$

where the superscript 0 indicates the pure elements, and c_A , c_B , and c_C are the concentrations of A , B , and C atoms in γ . Only two of these concentrations are independent due to the constraint $c_A + c_B + c_C = 1$. The formation energies for *binary* alloys [given by Eq. (1.1) with $c_C = 0$] gives a measure of the energy of a given phase relative to the phase-separated pure elements. In the binary case, the *sign* of the formation energy, $\Delta E_{\text{FORM}} > 0$ (< 0) is often a qualitative indication that at low temperatures the alloy will tend to phase separate (order). For a ternary phase, ΔE_{FORM} of Eq. (1.1) gives the energy of γ relative to a completely phase-separated state of pure A , B , and C . However, the sign of ΔE_{FORM} does not fully specify (not even qualitatively) the ordering tendencies of the alloy: $\Delta E < 0$ implies that γ has a lower energy than $(A) + (B) + (C)$, but, in fact, γ may have a higher energy than $(A, B) + (B, C)$, for example. It is necessary, at the very least, to perform a stability analysis of the completely disordered state, which for multicomponent systems is not as straightforward as for binaries.⁵ What is really essential is not only ΔE , but also the *curvature* of ΔE with respect to the two independent concentrations. Therefore, to describe the gross ordering ten-

dencies of a ternary alloy even at a qualitative level, at least three parameters are required, corresponding to the ordering tendencies of A - B , B - C , and A - C pairs of atoms in the alloy. Depending on the signs of these three parameters, a ternary alloy may be placed into one of four categories:^{6,7} (I) All three parameters are positive, indicating ordering, (II) Two are positive, and one is negative, indicative of phase separating tendencies, (III) One parameter is positive, and two are negative, and (IV) All three are negative. The preceding discussion is but one example of how the ternary alloy is more complicated than its binary counterpart. However, as shown below, the cluster expansion of alloy energetics can take into account not only the gross qualitative features, but also quantitative detail of ternary-alloy phase stability.

To model the substitutional ternary alloy, consider a system of N lattice sites, to which each is assigned an A , B , or C atom. The description of a ternary-alloy system is facilitated by a generalized "Ising-like" model in which the atom at site i is designated by the variable $\sigma_i = (\tau_A, \tau_B, \tau_C)$ depending on whether the atom is A , B , or C , respectively. Any configuration of the system may be completely specified by the N -dimensional vector, $\sigma = (\sigma_1, \sigma_2, \dots, \sigma_N)$. Sanchez, Ducastelle, and Gratias⁸ have shown that within this "Ising-like" framework, a complete orthonormal basis of functions may be defined in the space of all 3^N configurations. However, the basis functions of Sanchez, Ducastelle, and Gratias are not the only reasonable choice, and hence, in Sec. II (and Appendix A), we examine several possible choices of basis functions, highlighting their advantages and disadvantages. In particular, relations are derived between the ECI's expressed in various bases. Section III contains a description of the ternary method of direct configurational averaging, and specifically contains details of extensions of the binary method necessary to compute the ternary ECI's. The results of the ECI calculations are shown in Sec. IV for three transition-metal systems, Rh-V-Ti, Pd-Rh-V, and Ag-Pd-Rh. Also shown in this section are the formation energies of the completely disordered states for each of the three alloys, all as a function of the alloy composition. Some general conclusions and three appendices follow.

II. TERNARY CLUSTER EXPANSIONS —BASIS FUNCTIONS

A. Chebychev polynomials

We begin by defining the occupation variables, $(\tau_A, \tau_B, \tau_C) = (+1, 0, -1)$. The domain of the point variable σ_i has three values. Therefore, to fully specify a function of σ_i , it is necessary to choose three *point* functions, products of which form the corresponding *cluster* functions. To define functions which are complete in the space of all 3^N configurations, the inner product of two functions of configuration $f(\sigma)$ and $g(\sigma)$ is defined as

$$\langle f(\sigma), g(\sigma) \rangle = \frac{1}{3^N} \sum_{\{\sigma\}} f(\sigma) g(\sigma), \quad (2.1)$$

where the summation runs over all 3^N configurations. An

intuitive set of three point functions (from which the orthonormal basis is constructed) is the first three polynomials of σ_i : $\{1, \sigma_i, \sigma_i^2\}$. Cluster functions formed from products of the set $\{1, \sigma_i, \sigma_i^2\}$, although not orthogonal, have been proposed as a possible basis of functions for describing the ternary-alloy problem⁹⁻¹¹ as well as treating the spin-1 problem of He³-He⁴ mixtures through the Blume-Emery-Griffiths Hamiltonian.¹² The effect of the nonorthogonality of this basis on the cluster expansion coefficients is discussed in Appendix A. The set $\{1, \sigma_i, \sigma_i^2\}$ may be made orthonormal with respect to the inner product of Eq. (2.1) through the Gram-Schmidt process. The resulting three functions are the first three Chebychev polynomials of the discrete variable σ_i :

$$\Theta_0(\sigma_i) = 1, \quad \Theta_1(\sigma_i) = \sqrt{3/2} \sigma_i, \quad \Theta_2(\sigma_i) = \sqrt{2} (1 - \frac{3}{2} \sigma_i^2). \quad (2.2)$$

For a cluster of lattice points $\alpha = \{1, 2, \dots, |\alpha|\}$ and a vector of indices $(s) = \{n_1, n_2, \dots, n_{|\alpha|}\}$ the cluster function is defined as

$$\Phi_\alpha^{(s)} = \Theta_{n_1}(\sigma_1) \Theta_{n_2}(\sigma_2) \cdots \Theta_{n_{|\alpha|}}(\sigma_{|\alpha|}). \quad (2.3)$$

(The superscript s will be in parentheses to distinguish it from a power.) The cluster functions of Eq. (2.3) are not only orthonormal with respect to the scalar product operation of Eq. (2.1), but they also satisfy a completeness relation. Therefore, any function of configuration may be exactly expanded in terms of the Chebychev cluster functions of (2.3).⁸ In particular, the internal energy as a function of configuration $E(\sigma)$ may be written

$$E(\sigma) = \sum_\alpha \sum_{(s)} m_\alpha V_\alpha^{(s)} \bar{\Phi}_\alpha^{(s)}(\sigma), \quad (2.4)$$

where the summation over α is over all clusters of lattice points which are symmetrically distinct, and the summation over (s) is over all possible values $n_1, n_2, \dots, n_{|\alpha|} \neq 0$. Thus, (s) in Eq. (2.4) is a vector of integers (each of which is either one or two) which specify the specific type of Chebychev polynomial associated with each site in the cluster α . The energy of (2.4) is per atom, with the multiplicity m_α being the number of clusters α per lattice site. The orbit of a cluster α is defined as the set of all clusters that are related to α by a symmetry operation of the lattice. All clusters in an orbit have the same effective interaction $V_\alpha^{(s)}$, and the orbit-averaged cluster functions $\bar{\Phi}_\alpha^{(s)}$ are simply the cluster functions of Eq. (2.3) averaged over all the symmetry-equivalent clusters of the lattice. Note that in the right-hand side of Eq. (2.4), only the cluster functions $\bar{\Phi}_\alpha^{(s)}$ are functions of configuration. The expansion coefficients $V_\alpha^{(s)}$ are thus configuration independent and are commonly referred to as effective cluster interactions (ECI's). Due to the orthonormality of the cluster functions, the ECI for a cluster α and set of indices (s) is given by the inner product of the cluster function $\Phi_\alpha^{(s)}$ with the energy:

$$V_\alpha^{(s)} = \langle \Phi_\alpha^{(s)}, E(\sigma) \rangle. \quad (2.5)$$

Consider the case of α representing a pair of lattice sites (1,2): There are three types of distinct effective pair

interactions (EPI's) depending upon whether the indices (s) take on the values (11), (12), or (22). There are actually four sets of indices (s) for pairs, but we consider throughout this paper the case in which all lattice sites are equivalent (as is the case for most of the common lattice types, e.g., fcc, bcc, hcp). Under this condition, the EPI with (s)=(12) is equal to the one with (s)=(21). Thus, for an n th nearest-neighbor (NN) pair of lattice points, there are three independent effective pair interactions, $V_n^{(11)}$, $V_n^{(12)}$, and $V_n^{(22)}$. The explicit forms of these pair interactions are given by combining (2.5) with (2.2) and (2.3):

$$\begin{aligned} V_n^{(11)} &= \frac{1}{6}(E_{AA} + E_{CC} - E_{AC} - E_{CA}), \\ V_n^{(12)} + V_n^{(21)} &= \sqrt{3}/9(-E_{AA} + E_{AB} + E_{BA} - E_{BC} \\ &\quad - E_{CB} + E_{CC}), \\ V_n^{(22)} &= \frac{1}{18}(E_{AA} - 2E_{AB} + E_{AC} - 2E_{BA} + 4E_{BB} \\ &\quad - 2E_{BC} + E_{CA} - 2E_{CB} + E_{CC}), \end{aligned} \quad (2.6)$$

where E_{IJ} is the average energy of all the ternary configurations with an I atom at site 1 and a J atom at site 2. The brackets, which are oftentimes used around each E_{IJ} are dropped for notational convenience, but one should always keep in mind that this is a configurationally averaged quantity. Note also that in (2.6), the sum of the coefficients of E_{IJ} is equal to zero.

For the case of a triplet of points (1,2,3) labeled by the

symbol n , there are, in principle, eight possible distinct ECI's, at least four of which are necessarily distinct by symmetry: $V_n^{(111)}$, $V_n^{(112)}$, $V_n^{(122)}$, and $V_n^{(222)}$. [The use of n to label both pairs and triplets should cause no confusion because the vector (s) contains two elements for pairs and three for triplets.] The definitions of the four triplets have many terms (a maximum of $3^3=27$) and are given explicitly in Appendix B. The cancellation of the coefficients also holds for the triplet interactions, and is a specific example of a more general cancellation property which is proved in Appendix C for an arbitrary cluster interaction (provided $|\alpha| > 1$) in an M -component system. The "cancellation theorem" of Appendix C guarantees that even in multicomponent alloys, ECI's are not real interactions or potentials, but rather small differences of these real potentials which nearly cancel.

In computing alloy energetics, it is often necessary to give energies relative to some reference point, as in the formation energy of Eq. (1.1). By using a combination of the cluster functions for the pure elements, the expansion of Eq. (2.4), and the relation between the point cluster functions and the concentrations,

$$\bar{\Phi}^{(1)} = \sqrt{3/2}(c_A - c_C); \quad \bar{\Phi}^{(2)} = \sqrt{2}(1 - \frac{3}{2}[c_A + c_C]), \quad (2.7)$$

one obtains the following formula for the formation energy of a given ternary structure including only effective pair and triplet interactions in the energy expansion:

$$\begin{aligned} \Delta E_{\text{FORM}}(\sigma) \approx & \sum_n^{\text{pairs}} m_n \left\{ V_n^{(11)} \left[\bar{\Phi}_n^{(11)} - \left(1 - \frac{\bar{\Phi}^{(2)}}{\sqrt{2}} \right) \right] + 2V_n^{(12)} \left[\bar{\Phi}_n^{(12)} + \frac{\bar{\Phi}^{(1)}}{\sqrt{2}} \right] + V_n^{(22)} \left[\bar{\Phi}_n^{(22)} - \left(1 + \frac{\bar{\Phi}^{(2)}}{\sqrt{2}} \right) \right] \right\} \\ & + \sum_n^{\text{triplets}} m_n \left\{ V_n^{(111)} (\bar{\Phi}_n^{(111)} - \frac{3}{2}\bar{\Phi}^{(1)}) + 3\tilde{V}_n^{(112)} \left[\bar{\Phi}_n^{(112)} + \frac{1}{\sqrt{2}} - \frac{\bar{\Phi}^{(2)}}{2} \right] \right. \\ & \left. + 3\tilde{V}_n^{(122)} \left[\bar{\Phi}_n^{(122)} - \frac{\bar{\Phi}^{(1)}}{2} \right] + V_n^{(222)} \left[\bar{\Phi}_n^{(222)} - \frac{1}{\sqrt{2}} - \frac{3}{2}\bar{\Phi}^{(2)} \right] \right\}, \end{aligned} \quad (2.8)$$

where we define

$$\begin{aligned} \tilde{V}_n^{(112)} &= \frac{1}{3}[V_n^{(112)} + V_n^{(121)} + V_n^{(211)}], \\ \tilde{V}_n^{(122)} &= \frac{1}{3}[V_n^{(122)} + V_n^{(212)} + V_n^{(221)}]. \end{aligned} \quad (2.9)$$

The use of $\tilde{V}_n^{(112)}$ and $\tilde{V}_n^{(122)}$ in (2.8) reduces the number of terms involving triplets in the formation energy from eight to four, and amounts to implicitly assuming

$$\bar{\Phi}_n^{(112)} = \bar{\Phi}_n^{(121)} = \bar{\Phi}_n^{(211)}, \quad (2.10)$$

and similarly for $\bar{\Phi}_\alpha^{(122)}$ and permutations. There are two cases in which (2.10) is exact: (1) for the completely disordered state,

$$\bar{\Phi}_\alpha^{(112)} = \bar{\Phi}_\alpha^{(121)} = \bar{\Phi}_\alpha^{(211)} = [\bar{\Phi}_\alpha^{(1)}]^2 \bar{\Phi}_\alpha^{(2)},$$

regardless of the lattice points which make up the triplet, and (2) for a system in which all lattice sites are equivalent, triplets which contain three equivalent bonds

satisfy (2.10) independent of the configuration. In fcc, the triplet composed of three nearest-neighbor bonds is an example of such a triplet. It should be noted that the approximation in Eq. (2.10) is made only to reduce the number of computations. There is no problem in principle with computing separately each of $V_n^{(112)}$, $V_n^{(121)}$, and $V_n^{(211)}$. Also, all of the numerical results in this paper involving triplet interactions are for the completely disordered state, in which case (2.10) is exact.

B. Pair probabilities

In addition to the Chebychev functions, the cluster probabilities provide a basis for the ternary cluster expansion. In particular, we examine the expansion in probabilities up to and including pairs of atoms. In Eq. (2.7), the orbit-averaged point functions are expressed in terms of point concentrations, or point probabilities (the proba-

bility of finding a given type of atom at any site). The orbit-averaged pair functions may similarly be expressed in terms of pair probabilities. Define the pair probability, or pair concentration y_n^{IJ} as the probability of finding an n th nearest-neighbor I - J pair in a given configuration. There are six probabilities necessary to specify the occupation of n th nearest-neighbor pairs of sites in a ternary-alloy structure: y_n^{AA} , y_n^{AB} , y_n^{AC} , y_n^{BB} , y_n^{BC} , and y_n^{CC} . The orbit averages $\bar{\Phi}_n^{(11)}$, $\bar{\Phi}_n^{(12)}$, and $\bar{\Phi}_n^{(22)}$ may be written

$$\begin{aligned}\bar{\Phi}_n^{(11)} &= \frac{3}{2}[y_n^{AA} + y_n^{CC} - 2y_n^{AC}], \\ \bar{\Phi}_n^{(12)} &= \sqrt{3}/2[-y_n^{AA} + 2y_n^{AB} - 2y_n^{BC} + y_n^{CC}], \\ \bar{\Phi}_n^{(22)} &= \frac{1}{2}[4 - 3y_n^{AA} - 12y_n^{AB} - 6y_n^{AC} - 12y_n^{BC} - 3y_n^{CC}].\end{aligned}\quad (2.11)$$

By combining (2.11), (2.7), and the normalization conditions,

$$\begin{aligned}c_I &= y_n^{IA} + y_n^{IB} + y_n^{IC}, \quad I = A, B, C \\ 1 &= y_n^{AA} + 2y_n^{AB} + 2y_n^{AC} + y_n^{BB} + 2y_n^{BC} + y_n^{CC},\end{aligned}\quad (2.12)$$

one may write the six orbit-averaged cluster functions 1 , $\bar{\Phi}_n^{(1)}$, $\bar{\Phi}_n^{(2)}$, $\bar{\Phi}_n^{(11)}$, $\bar{\Phi}_n^{(12)}$, and $\bar{\Phi}_n^{(22)}$ in terms of the six probabilities y_n^{IJ} . (The inverse of this transformation is given by Cenedese and Gratias¹³ with the coefficients of the inverse transformation being the “ v -matrix” elements used in cluster variation method calculations.¹⁴) Rewriting (2.7) with the orbit averages expressed in terms of pair probabilities, the formation energy of a given ternary phase including only pair interactions in the energy expansion is given by

$$\Delta E_{\text{FORM}}(\sigma) = -4 \sum_n^{\text{pairs}} [W_n^{AB} y_n^{AB} + W_n^{BC} y_n^{BC} + W_n^{AC} y_n^{AC}].\quad (2.13)$$

The coefficients of the pair probabilities are linear combinations of the Chebychev pair interactions, and have the form

$$W_n^{IJ} = \frac{1}{4}[E_{II} + E_{JJ} - E_{IJ} - E_{JI}],\quad (2.14)$$

with E_{IJ} defined in Eq. (2.6). W_n^{IJ} is then a second type of EPI defined for the ternary system, and just as in the Chebychev scheme, there are three distinct types of interactions for a given pair of lattice sites, W_n^{AB} , W_n^{AC} , and W_n^{BC} . By comparing (2.14) and (2.6), it is easily shown that the two types of EPI's are linearly related:

$$\begin{pmatrix} V_n^{(11)} \\ V_n^{(12)} \\ V_n^{(22)} \end{pmatrix} = \begin{pmatrix} 0 & 0 & \frac{2}{3} \\ -\frac{2\sqrt{3}}{9} & \frac{2\sqrt{3}}{9} & 0 \\ \frac{4}{9} & \frac{4}{9} & -\frac{2}{9} \end{pmatrix} \begin{pmatrix} W_n^{AB} \\ W_n^{BC} \\ W_n^{AC} \end{pmatrix}.\quad (2.15)$$

From the definition of (2.14), one can see that W_n^{IJ} has the same form as the binary EPI's, however, the terms on the right-hand side of (2.14) are averaged over all ternary configurations. Just as in the binary case, the coefficients W_n^{IJ} have the simple physical interpretation: $W_n^{IJ} > 0$ (< 0) corresponds to an ordering (phase-separating) ten-

dency between I - J pairs. However, from (2.15), it is clear that an equivalent amount of information is contained in the EPI's of the pair-probability and Chebychev bases.

The Chebychev and pair-probability bases are but two examples of bases for ternary cluster expansions. Three alternate bases are discussed and related in Appendix A: (1) The nonorthogonal basis formed by products of the set $\{1, \sigma_i, \sigma_i^2\}$, (2) The orthonormal complex basis of functions¹³ constructed from the choice $(\tau_A, \tau_B, \tau_C) = (\omega, 1, \omega^*)$, where $\omega = e^{2\pi i/3}$, and (3) The basis of orthonormal functions defined with respect to a restricted inner product over all ternary configurations consistent with a given ternary composition.

III. DIRECT CONFIGURATIONAL AVERAGING FOR TERNARY SYSTEMS

The method of direct configurational averaging (DCA) for computing ECI's directly from their definition has been described in detail elsewhere^{4,15} for the case of binary alloys. DCA is readily generalized to multicomponent alloys, and the extensions necessary for bulk ternary alloys are demonstrated here.

As in the binary case, a given ternary-alloy configuration is described by the two-center, orthogonal, tight-binding Hamiltonian

$$H_{\text{alloy}} = \sum_{i,\lambda} |i,\lambda\rangle \varepsilon_i^\lambda \langle i,\lambda| + \sum_{i \neq j} |i,\mu\rangle \beta_{ij}^{\mu\nu} \langle j,\nu|,\quad (3.1)$$

where the Latin indices designate the lattice sites and the Greek indices label the orbitals. The ε 's are the on-site energies and the β 's are the hopping integrals. The hopping integrals are assumed to depend only on the species at the site(s) in question, and the vector joining the two atoms:

$$\beta_{ij}^{\mu\nu} = \beta_{I(i)\mu, J(j)\nu}(\mathbf{r}_i - \mathbf{r}_j),\quad (3.2)$$

where $I(i)$ and $J(j)$ indicate the type of atoms ($I, J = A, B$, or C) at sites i and j . The hopping integrals between like atoms, $\beta_{I\mu, I\nu}$, are obtained from the pure elements. The hopping between unlike atoms is then given by the geometric mean of the appropriate pure element integrals:¹⁶

$$\beta_{I\mu, J\nu} = \sqrt{\beta_{I\mu, I\nu} \beta_{J\mu, J\nu}}, \quad I, J = A, B, \text{ or } C.\quad (3.3)$$

Self-consistency is achieved by shifting the on-site energies of the pure elements B and C by orbital-independent amounts δ_B and δ_C , respectively. The three quantities, \bar{E}_F (the configurationally averaged Fermi level), δ_B , and δ_C are determined from the three constraints imposed by requiring each of the three configurationally averaged atoms to be neutral. Typically, averages over 20 configurations are used in the self-consistency procedure, and approximately ten iterations are needed before δ_B and δ_C are found so as to satisfy the configurationally averaged-neutrality constraints within 0.01–0.02 elec-

trons. The alloy Hamiltonian is then constructed from the matrix elements of the pure elements [which are obtained from linearized muffin-tin orbital (LMTO) calculations via the screening transformation of Andersen and co-workers^{17,18}] along with (3.3), and the values of δ_B and δ_C .

The ternary EPI's [see, for example, Eqs. (2.6), (2.14), and Appendix B] defined with respect to various bases are all of the form

$$V^{(s)} = -\frac{1}{\pi} \left\langle \text{Im} \int_{-\infty}^{\bar{E}_F} \sum_{k=1}^{\nu} \ln \prod_{I,J,\dots,K}^{A,B,C} [\bar{g}_k^{IJ\dots K}(E)]^{c_{IJ\dots K}^{(s)}} dE \right\rangle, \quad (3.4)$$

where ν is the number of orbitals to be peeled ($\nu=9$ in the case s, p , and d orbitals), and the brackets denote a simple configurational average (not a thermal or ensemble average). The elements $\bar{g}_k^{IJ\dots K}$ are the top left, energy-dependent matrix elements of a partial "Green-matrix": the inverse of the k th principal submatrix of $(EI - \mathbf{H}_{IJ\dots K})$, where $\mathbf{H}_{IJ\dots K}$ represents the Hamiltonian corresponding to an $IJ\dots K$ cluster of atoms at the sites of the ECI, with arbitrary configuration elsewhere. By k th principal submatrix, we mean the original matrix with the first $k-1$ rows and columns eliminated. Each of the partial Green-matrix elements are obtained by performing recursion²⁰ on the tight-binding LMTO Hamiltonian. Between 10 and 20 configurations are used in the averaging of (3.5).

It is noteworthy that the average over all ternary configurations is equivalent, in the thermodynamic limit, to the average over all equiatomic configurations. Define η to be the ratio of the number of configurations at a composition specified by (c_A, c_B, c_C) divided by the total number of configurations, 3^N . Using Stirling's approximation, η can be written as

$$\eta = [3(c_A)^{c_A}(c_B)^{c_B}(c_C)^{c_C}]^{-N}. \quad (3.6)$$

In the limit of $N \rightarrow \infty$, $\eta = 1$ if $c_A = c_B = c_C = \frac{1}{3}$, and $\eta = 0$ otherwise. Thus, we see that only equiatomic configurations need be kept in the averaging procedure of (3.5).

IV. COMPUTATION OF TERNARY ECIS AND FORMATION ENERGIES

Any theory of ternary-alloy properties must, in the limit of any of the concentrations going to zero, correctly reduce to the corresponding binary alloy. Thus, we examine three ternary systems for which many of the binary subsystems have been studied previously (using a binary cluster expansion): Rh-V-Ti, Pd-Rh-V, and Ag-Pd-Rh. With the exception of V-Ti, all possible binaries formed from the two ternary systems, Rh-V-Ti and Pd-Rh-V, have been examined previously^{4,21,22} using the binary-DCA: Rh-V, Rh-Ti, Pd-V, and Pd-Rh. Note that two of the ternary systems contain Rh-V binary alloys and two contain Pd-Rh alloys. Also, only the case of fcc-based alloys is treated, although, in principle, there is

no problem in extending these calculations to alloys based on other parent lattices. The formalism of orbital peeling,¹⁹ which has been incorporated in the computation of binary ECI's (Refs. 4 and 15) may also be applied to ternary ECI's. The ECI (3.4) is then given by

Total-energy calculations were performed for all the constituents of the ternary systems including Ag, Pd, Rh, V, and Ti, all in the fcc structure using the first-principles method of linear muffin-tin orbitals in the atomic-sphere approximation²³ (LMTO-ASA), based on the local-density approximation.^{24,25} The computations were performed semirelativistically (including scalar relativistic corrections, i.e., excluding spin-orbit terms), the exchange-correlation potential of von Barth and Hedin²⁶ was used, and combined correction terms^{23,27} were included. The basis set was composed of $l=0, 1$, and 2 orbitals. Convergence of the total energy with respect to k -point sampling was well within 0.1 mRy/atom, with the number of irreducible k points typically being 165. The equilibrium volume for each pure metal was calculated by fitting the total-energy calculations to a cubic polynomial in volume. For each alloy, the equiatomic volume was obtained by assuming a linear variation with composition [for example, in Pd-Rh-V, the alloy volume used in the calculations is given by

$$\Omega_{\text{eq}}(\text{Pd-Rh-V}) = \frac{1}{3}[\Omega_{\text{eq}}(\text{Pd}) + \Omega_{\text{eq}}(\text{Rh}) + \Omega_{\text{eq}}(\text{V})],$$

where $\Omega_{\text{eq}}(A)$ is the calculated equilibrium volume of A]. The pure element LMTO-ASA calculations were each performed again at the alloy volume, and the LMTO Hamiltonians were subsequently cast into the tight-binding (TB) representation in two-center form using the screening transformation of Andersen and co-workers.^{17,18} Including the first-order terms of this formalism, the TB Hamiltonians have nonzero hopping integrals only between first- and second-NN pairs of atoms. With these matrix elements, the self-consistent alloy Hamiltonian was constructed as described in Sec. III. As an example, the parameters used in the Pd-Rh-V calculations are shown in Table I. The self-consistent potentials, δ_B and δ_C , were calculated using configurational averages of 20 randomly chosen, equiatomic configurations. A basis set of s, p , and d orbitals and ten levels of recursion (corresponding to 20 moments of the density of states) were used throughout the calculations discussed in this section and the recursion system size of 891 atoms was chosen so as to give ten exact moments of the density of states, and ten approximate moments.

For Rh-V-Ti, ECI's were calculated for first- through fourth-NN pairs on the fcc lattice, both in the Chebychev basis ($V_n^{(s)}$) and pair-probability basis (W_n^{IJ}). In each basis, the same 12 randomly chosen equiatomic configurations were used in the averaging process, and the transformation of Eq. (2.15) was verified exactly (within the numerical precision of the computations), serving as a check to our calculations. The pair-probability first- and second-NN pair interactions ($W_1^{\text{Rh-V}}$, $W_1^{\text{Rh-Ti}}$, $W_1^{\text{V-Ti}}$, $W_2^{\text{Rh-V}}$, $W_2^{\text{Rh-Ti}}$, and $W_2^{\text{V-Ti}}$) are shown for the Rh-V-Ti system in Figs. 1(a) and 1(b) as a function of the Fermi level. The first-NN EPI's [Fig. 1(a)] indicate a strong ordering tendency between Rh-V pairs and Rh-Ti pairs, just as found both experimentally^{28,29} and theoretically^{4,30} in the binary systems. V-Ti pairs are indicated to have a very slight tendency towards phase separation. (Experimentally, the V-Ti system shows a weak phase separating tendency at low temperatures,²⁸ but this is for bcc-based solid solutions.) Each of the NN EPI's exhibits two zeros as a function of band filling as is characteristic of the canonical d -band binary transition-metal alloy Hamiltonian in the absence of off-

diagonal disorder. Of course, the computations in Fig. 1 include both off-diagonal disorder and s , p , and d orbitals. The second-NN EPI's [Fig. 1(b)] are all smaller in magnitude, have more oscillations as a function of Fermi level, and are of opposite sign from their NN counterparts. Each of $W_2^{\text{Rh-V}}$, $W_2^{\text{Rh-Ti}}$, and $W_2^{\text{V-Ti}}$ have magnitudes smaller than 0.5 mRy/atom (without multiplicity) thus suggesting that in the ternary case, as in the binary case, the NN EPI's are mainly responsible for gross ordering tendencies, as they dominate all other ECI's.

To investigate the convergence of the ternary energy expansion of Eq. (2.4) more thoroughly, ECI's in the Chebychev basis were computed for four triplets in addition to the four pairs mentioned above. Each of the triplets contains two NN bonds, with the third leg of the triangle being an n th NN bond, with $n=1,4$. For example, the triplet ECI, $V_1^{(s)}$ corresponds to a triplet composed of three NN bonds, while $V_4^{(s)}$ indicates a linear triplet with two NN bonds and one fourth-NN bond. In sum, this corresponds to 28 ECI's for each system studied ($3 \times 4 = 12$ pair interactions and $4 \times 4 = 16$ triplet interactions). In order for the cluster expansion to have any chance at convergence, the ECI's must decrease to zero in two instances: (1) As any of the points of a given cluster is moved away from the other points, and (2) As the number of points in the cluster increases. The calculated ECI's are shown in Figs. 2(a), 2(b), and 2(c) for Rh-V-Ti,

TABLE I. Matrix elements, potentials, and Fermi level (all in Ry) of the alloy Hamiltonian for fcc equiatomic Pd-Rh-V. Integrals corresponding to hoppings between like pairs of atoms are given in Slater-Koster form for first- and second-nearest-neighbor separations.

Matrix elements	Pd	Rh	V
Hopping integrals (NN)			
$ss\sigma$	-0.081 235	-0.083 881	-0.085 910
$pp\sigma$	0.327 409	0.335 259	0.325 382
$pp\pi$	-0.040 926	-0.041 907	-0.040 673
$dd\sigma$	-0.061 405	-0.071 689	-0.069 466
$dd\pi$	0.026 264	0.030 662	0.029 711
$dd\delta$	-0.002 404	-0.002 807	-0.002 720
$sp\sigma$	0.162 445	0.167 036	0.166 536
$sd\sigma$	-0.067 974	-0.074 632	-0.074 349
$pd\sigma$	-0.138 664	-0.151 612	-0.147 028
$pd\pi$	0.033 015	0.036 098	0.035 007
Hopping integrals (2nd NN)			
$ss\sigma$	-0.003 357	-0.003 466	-0.003 550
$pp\sigma$	0.014 733	0.015087	0.014 642
$pp\pi$	0.000 000	0.000 000	0.000 000
$dd\sigma$	-0.004 254	-0.004 966	-0.004 812
$dd\pi$	-0.000 370	-0.000 432	-0.000 418
$dd\delta$	0.000 000	0.000 000	0.000 000
$sp\sigma$	0.006 630	0.006 818	0.006 797
$sd\sigma$	-0.003 343	-0.003670	-0.003 657
$pd\sigma$	-0.007 704	-0.008 423	-0.008 168
$pd\pi$	-0.000 550	-0.000 602	-0.000 583
On-site energies			
s	0.213 672	0.269 292	0.404 234
p	1.169 485	1.235 969	1.244 110
t_{2g}	-0.229 698	-0.158403	0.091 330
e_g	-0.242 645	-0.173 518	0.076 683
Shifts	0.000	0.001	-0.048
Fermi level		-0.048 605	

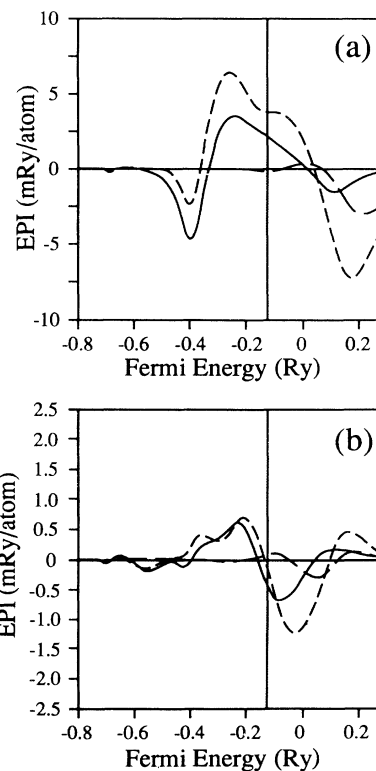


FIG. 1. Rh-V-Ti effective pair interactions, W_n^{IJ} , of Eq. (2.14) for (a) nearest-neighbor pairs and (b) next-nearest-neighbor pairs versus Fermi energy. The calculated Fermi level is shown as a solid vertical line. $W_n^{\text{Rh-V}}$ —solid curves; $W_n^{\text{Rh-Ti}}$ —short dashed curves; $W_n^{\text{V-Ti}}$ —long dashed curves.

Pd-Rh-V, and Ag-Pd-Rh, respectively, and demonstrate both these convergence properties. For all three systems, the second-, third-, and fourth-NN EPI's are significantly reduced as compared to the NN EPI, indicating an extremely rapid convergence of the expansion with respect to separation of pairs. The EPI's have decayed practically to zero by the fourth-NN pair. Also, in each system, the largest triplet ECI's are an order of magnitude smaller than the largest pair interactions, thus demonstrating the convergence of the expansion with respect to the sequence of pairs, triplets, quadruplets, etc. However, in Rh-V-Ti and Ag-Pd-Rh, and to a lesser extent, in Pd-Rh-V, the triplet interactions do not decay rapidly as the third leg of the triplet goes from first-NN to fourth-NN ($n=1$ to $n=4$). As seen in the binary cluster expansion, the linear triplet corresponding to $n=4$ can be sizeable, and we see the same effect here in the ternary cluster expansion. Also, in Rh-V-Ti, the triplet interaction $V_3^{(111)}$ is the largest of the interactions, which is especially relevant when it is considered that the multiplicity of this cluster is 24 (compared, for example, to $m_\alpha=6$ for the NN pair). We shall see below that although the triplet interactions are relatively small in magnitude, they can, when taken collectively, contribute significantly to the formation energy of a given configuration.

It is interesting to note the amount of computational

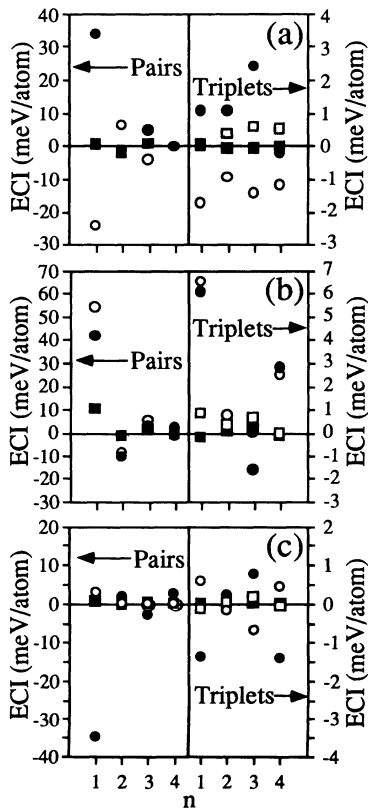


FIG. 2. Chebyshev-basis effective pair and triplet interactions for (a) Rh-V-Ti, (b) Pd-Rh-V, and (c) Ag-Pd-Rh. Filled circles— $V_n^{(111)}$ and $V_n^{(111)}$; open circles— $2V_n^{(12)}$ and $3\tilde{V}_n^{(112)}$; filled squares— $V_n^{(22)}$ and $V_n^{(222)}$; open squares— $3\tilde{V}_n^{(122)}$.

labor involved in obtaining the sets of ECI's in Figs. 2(a)–2(c). The computations involve a two-step procedure: the self-consistency process (based on configurationally averaged neutrality) followed by the calculation of the ECI's. In the self-consistency calculations, local densities of states are calculated for $N_a=3$ types of atoms, with each of these atoms having $N_v=9$ orbitals. Configurational averages are made over $N_{c1}=20$ configurations and it typically takes $N_i=10$ iterations to obtain self-consistency. For the ECI calculations, we compute a large number ($N_E=28$) of ECI's, each of which contains many terms (an average of approximately $N_t=30$). There are again $N_v=9$ orbitals to be “peeled” and the configurational averages are made over a conservative $N_{c2}=10$ configurations. Thus, the total number of Green-function matrix elements which are required for each ternary system to be studied is given by the sum of the self-consistency calculation and the ECI calculation: $N_a \times N_v \times N_{c1} \times N_i + N_E \times N_t \times N_v \times N_{c2} \approx 85\,000$ matrix elements, each of which is computed using ten levels of recursion on a 1000-atom cluster. (The preceding estimate ignores the computational cost of the total-energy LMTO-ASA calculations used to obtain the pure element Hamiltonian matrix elements, although these computations are relatively cost free.) Additionally, because each of the 85 000 Green-function matrix elements are computed independently of one another, these calculations are ideally suited for implementation on a massively parallel computer architecture. Thus, it is clear that these ternary calculations are quickly approaching the limitations of current computational resources, and extensions to quaternary and higher-order multicomponent systems, although relatively straightforward in principle, could prove to be intractable in practice.

The versatility of the cluster expansion is made manifest in considering the formation energy of the completely disordered state. The energy of the disordered state is computed on an equal footing with the ordered states, and the form of the energy in terms of the concentrations of A and C atoms is given by combining Eqs. (2.7), (2.8), and the cluster functions of the completely disordered state, which are completely uncorrelated (for example, $\overline{\Phi}_n^{(12)} = \overline{\Phi}^{(1)}\overline{\Phi}^{(2)}$).

For a *binary* cluster expansion, clusters with an even (odd) number of points have cluster functions that are even (odd) about equiatomic concentration. Consequently, triplet and other odd-body interactions do not contribute to the binary equiatomic formation energies as the corresponding cluster functions have a node at $c = \frac{1}{2}$. Thus, if only EPI's are kept in the expansion, the resulting formation energies would be completely symmetric about $c = \frac{1}{2}$, with triplet (and/or other odd-body) interactions being responsible for any asymmetries. It is of interest to extend this sort of analysis to ternary systems. If we define the function $\varphi^{(s)}$ as the cluster functions of the Chebyshev basis corresponding to the completely disordered state minus the composition weighted average of the cluster functions of the pure elements, then the formation energy of the completely random state may be written as

$$\Delta E_{\text{FORM}} = \sum_{\alpha} \sum_{(s)} m_{\alpha} V_{\alpha}^{(s)} \varphi^{(s)}. \quad (4.1)$$

In Fig. 3, we show the seven functions, $\varphi^{(s)}$, for all distinct values of (s) corresponding to pairs and triplets. Linear combinations of these seven functions make up ΔE_{FORM} of the completely disordered state. In a ternary system, the two-dimensional composition space is usually shown in the form of a Gibbs triangle. The vertices of the triangle represent the three pure elements, and the sides of the triangle indicate the three binary systems. Several features of Fig. 3 are noteworthy: (1) The function $\varphi^{(11)}$ has a nonzero contribution primarily for compositions near the binary A - C edge of the Gibbs triangle, consistent with the observation that $V_n^{(11)} (\propto W_n^{A-C})$ is an ECI with the same form as the binary A - C EPI [see Eqs. (2.6) and (2.15)]. (2) In the binary cluster expansion, formation energies are completely symmetric about equiatomic compositions when only pair functions are considered. However, the ternary pair function, $\varphi^{(12)}$, is odd near the A - C binary edge, and thus any $V_n^{(12)} \neq 0$ will result in formation energies of pseudobinary $A_c C_{1-c}$ alloys (with small additions of B) which are asymmetric about $c = \frac{1}{2}$. (3) All functions $\varphi^{(s)}$ for which there are an even (odd) number of functions of type 1 in (s) are even (odd) under the transformation $(A, B, C) \rightarrow (C, B, A)$. This is simply due to the fact that $\bar{\Phi}^{(1)}$ and $\bar{\Phi}^{(2)}$ are odd and even under this transformation, respectively, and $\varphi^{(s)}$ involve products of $\bar{\Phi}^{(1)}$ and $\bar{\Phi}^{(2)}$. (4) Again, in contrast to

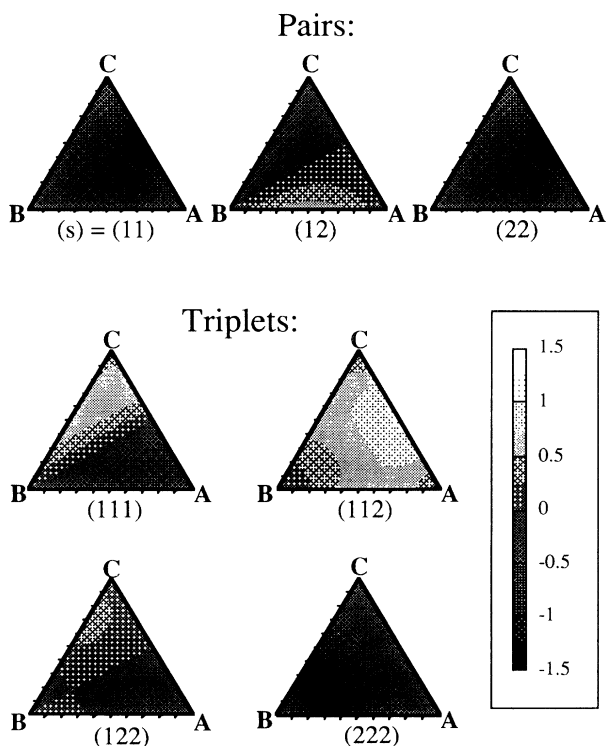


FIG. 3. The functions $\varphi^{(s)}$ for all distinct values of (s) corresponding to pairs and triplets. Linear combinations of these functions serve to make up the formation energy of the completely disordered state.

the binary cluster expansion, there is no composition (other than the trivial case of the pure elements) for which every triplet function $\varphi^{(s)}$ has a node. (5) The functions $\varphi^{(s)}$ themselves do not decrease in magnitude as one goes from pairs to triplets, etc. Thus, the convergence of the expansion lies solely in the properties of the ECI's, and not in the basis functions.

By combining the calculated ECI's of Fig. 2(a) with the cluster functions of Fig. 3, the formation energies of the completely random state are plotted in Fig. 4 for the Rh-V-Ti system using first only the 12 calculated *pair* interactions of the Chebychev basis, and then the complete set of 28 calculated *pair and triplet* ECI's. From Fig. 4, it is clear that the formation energies of binary Rh-Ti and Rh-V alloys are negative, indicative of ordering alloys, while the V-Ti binary exhibits very small, positive formation energies, indicating a very weak phase-separating tendency. These tendencies of ordering/phase separation are exactly those inferred from the NN EPI's of Fig. 1(a), again indicating that the qualitative ordering effects are dictated by the NN EPI. The signs of the NN EPI's, and consequently, the formation energies, are such as to place the Rh-V-Ti system in category II of Meirjering's classification of ternary systems.^{6,7} The effect of the triplet ECI's is clearly seen from Fig. 4(b), and while these multiplet interactions do not change qualitatively the or-

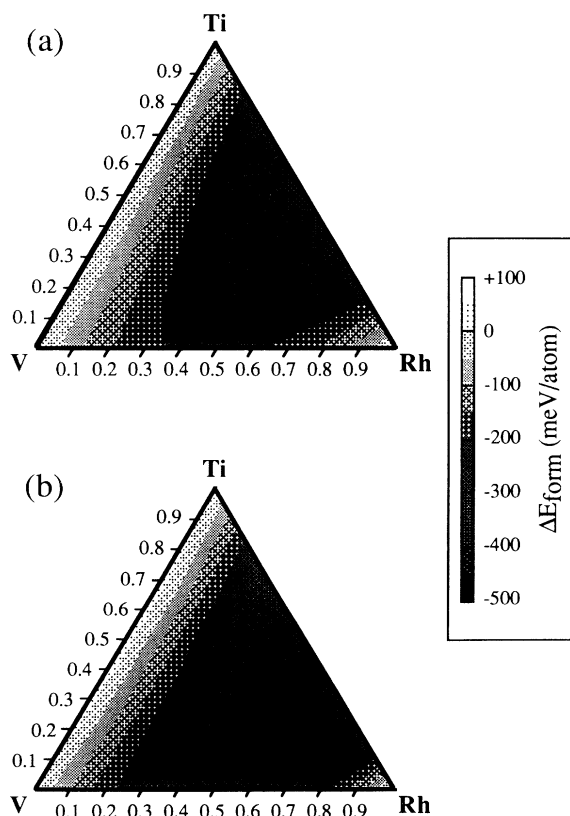


FIG. 4. Formation energies of completely disordered Rh-V-Ti alloys calculated from the ternary cluster expansion using (a) the 12 effective pair interactions of Fig. 2(a) and (b) all 28 calculated effective pair and triplet interactions.

dering tendencies, they do have a quantitative effect and serve to provide negative contributions to the formation energies of Rh-rich alloys.

The formation energies of disordered Pd-Rh-V alloys are shown in Figs. 5(a) and 5(b). As in Fig. 4, the formation energies are plotted both with [Fig. 5(b)] and without [Fig. 5(a)] triplet ECI's in the cluster expansion. As was the case in Rh-V-Ti, the Pd-Rh-V system exhibits two ordering binaries—Pd-V and Rh-V—and one weakly phase-separating binary—Pd-Rh, again placing the Pd-Rh-V system in category II of Meirjering's classification of ternary systems. There is a thin strip of positive formation energies along the Pd-Rh binary edge, but with small additions of V to these binary alloys, the formation energy becomes negative. This, however, does not imply that an ordering tendency develops between Pd and Rh pairs, but rather that Pd-Rh alloys with small additions of V energetically prefer ordering to *complete* phase separation. However, from the negative curvature of the energy parallel to the Pd-Rh edge, we expect an instability toward phase separation into Pd-rich and Rh-rich (possibly ordered) solutions.^{5,31,32} The triplet interactions in this system again do not dramatically change the ordering characteristics of the system, but do tend to add positive contributions to the formation energies, particularly for V-rich alloys.

The formation energies of disordered Ag-Pd-Rh alloys are shown in Fig. 6. All formation energies are positive

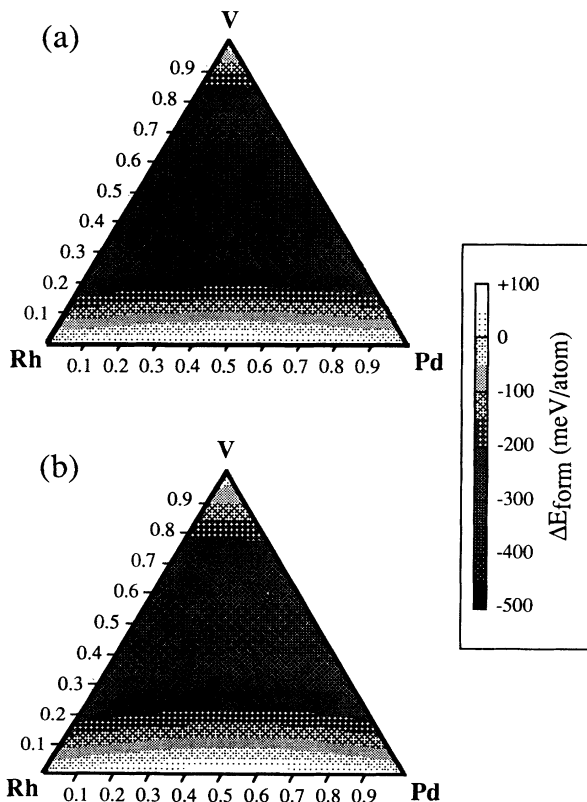


FIG. 5. Formation energies of completely disordered Pd-Rh-V alloys calculated from the ternary cluster expansion using (a) the 12 effective pair interactions of Fig. 2(a) and (b) all 28 calculated effective pair and triplet interactions.

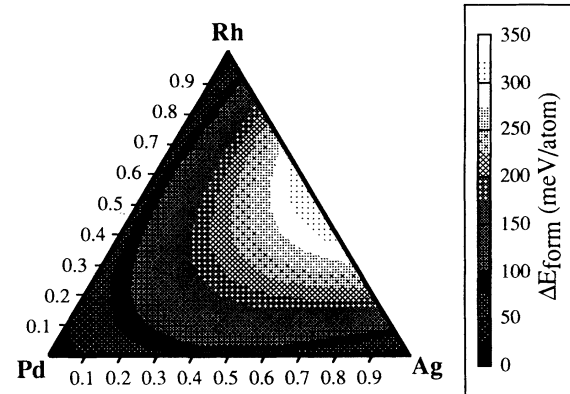


FIG. 6. Formation energies of completely disordered Ag-Pd-Rh alloys calculated using the 28 pair and triplet ECI's of Fig. 2(c).

throughout the Gibbs triangle, indicating that this alloy falls into class IV of Meirjering's ternary classification scheme. The binary Ag-Rh alloys have large, positive formation energies, consistent with the experimental phase diagram which shows this binary to be phase separating up to the melting points of both constituents. The results of Fig. 6 also show the Pd-Rh and Ag-Pd binary systems to have much weaker phase-separating tendencies. Again, the experimental evidence supports the predicted ordering tendencies, as Pd-Rh is observed to phase separate only at temperatures below 845 °C, which is also supported by a variety of previous binary-alloy calculations,^{22,33–35} while the experimental data for Ag-Pd down to 900 °C indicate complete miscibility. The formation energies of Ag-Pd-Rh have a striking similarity to the function $\varphi^{(11)}$ of Fig. 3, which is consistent with the fact that $V_1^{(11)}$ dominates all other pair and triplet ECI's in this system. The contribution to the formation energies from triplet ECI's is negligible in Ag-Pd-Rh.

In Figs. 7(a) and 7(b), we show specifically the contribution of the triplet interactions to the formation energies of disordered Rh-V-Ti and Pd-Rh-V alloys. As was already mentioned, the qualitative effects of the triplets are to add negative terms to the formation energies of Rh-rich Rh-V-Ti alloys and positive terms to V-rich Pd-Rh-V alloys. However, from Fig. 7 we see quantitatively that the triplet ECI's may be responsible for as much as 100 meV/atom of the formation energy ($\sim 7\text{--}8$ mRy/atom), and thus are absolutely essential to obtain a converged ternary cluster expansion for these two alloys.

The results in Fig. 7 might cause one to worry that the quadruplet ECI's may also be quantitatively important (although, presumably less important than the triplets). For binary cluster expansions, it has been shown that the quadruplet interactions are typically an order of magnitude less than the triplet ECI's, and thus, there is again good reason to expect them to be small in the ternary cluster expansion. To check some of these suppositions, we have compared directly in Table II the formation energies of equiatomic disordered binary alloys using both binary and ternary cluster expansions. For instance, the formation energies of a $\text{Rh}_{0.50}\text{V}_{0.50}$ alloy have been com-

puted using three sets of completely independent ECI's: (1) the ECI's of Ref. 4, calculated from the Rh-V binary cluster expansion, (2) the ternary ECI's calculated for the Rh-V-Ti system shown in Fig. 2(a), and (3) the ternary ECI's calculated for the Pd-Rh-V system shown in Fig. 2(b). (It is interesting to keep in mind that in the configurational averaging process, these three sets of ECI's are averaged over configurations at compositions $\text{Rh}_{0.50}\text{V}_{0.50}$, $\text{Rh}_{0.333}\text{V}_{0.333}\text{Ti}_{0.333}$, and $\text{Pd}_{0.333}\text{Rh}_{0.333}\text{V}_{0.333}$. It is only the basis functions of the expansion which yield the correct linear combinations of the ECI's so as to accurately describe $\text{Rh}_{0.50}\text{V}_{0.50}$ alloys.) The formation energies computed from these three sets of ECI's all agree to within 40 meV/atom (3 mRy/atom, or approximately 10% of the total formation energy), and the formation energies from the two ternary cluster expansions agree within 10 meV/atom (less than 1 mRy/atom). Similar comparisons for $\text{Rh}_{0.50}\text{Ti}_{0.50}$, $\text{Pd}_{0.50}\text{V}_{0.50}$, and $\text{Pd}_{0.50}\text{Rh}_{0.50}$ are likewise encouraging, with agreement being between 0 and 10%. For the Pd-Rh system, we also present comparison of the ternary cluster expansion results with two other distinct methods of obtaining the formation energies of disordered binary compounds: (1) the results obtained in Ref. 33, in which the authors use a combination of fully relaxed, scalar-relativistic linearized augmented-plane-wave (LAPW) calculations for ordered structures,

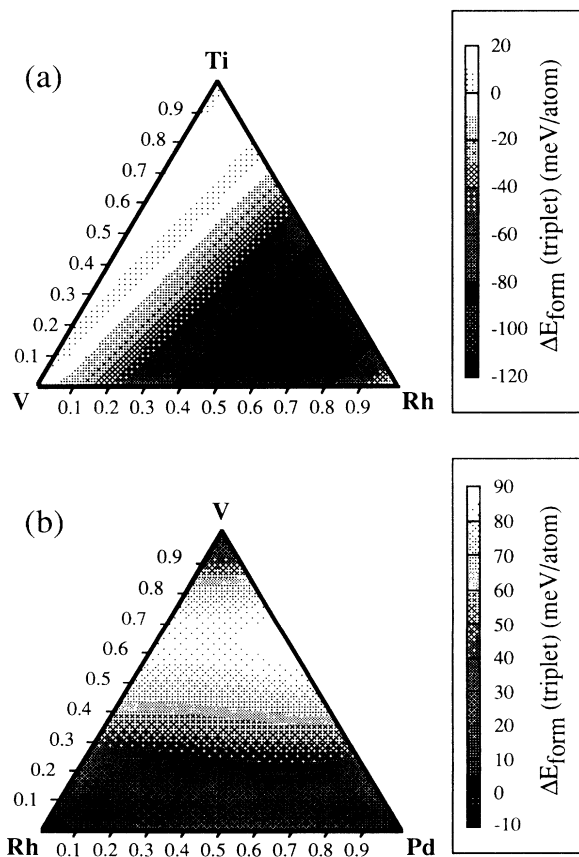


FIG. 7. Triplet contributions to the formation energy of completely disordered fcc solid solutions for the (a) Rh-V-Ti and (b) Pd-Rh-V systems.

TABLE II. Formation energies of completely disordered equiatomic binary fcc alloys, computed from the binary and ternary cluster expansions. The formation energies of the ternary cluster expansions were calculated using the Chebychev basis.

Alloy	Cluster expansion type (system)	ΔE_{FORM} (meV/atom)
$\text{Rh}_{0.50}\text{V}_{0.50}$	Binary (Rh-V)	-360 ^a
	Ternary (Rh-V-Ti)	-320
	Ternary (Pd-Rh-V)	-330
$\text{Rh}_{0.50}\text{Ti}_{0.50}$	Binary (Rh-Ti)	-450 ^a
	Ternary (Rh-V-Ti)	-460
$\text{Pd}_{0.50}\text{V}_{0.50}$	Binary (Pd-V)	-350 ^a
	Ternary (Pd-Rh-V)	-310
$\text{Pd}_{0.50}\text{Rh}_{0.50}$	Binary (Pd-Rh)	+80 ^b
	Binary (Pd-Rh)	+60 ^c
	Ternary (Pd-Rh-V)	+80
	Ternary (Ag-Pd-Rh)	+60
$\text{Pd}_{0.75}\text{Rh}_{0.25}$	Binary (Pd-Rh)	+60 ^b
	Binary (Pd-Rh)	+60 ^d
	Ternary (Pd-Rh-V)	+60
	Ternary (Ag-Pd-Rh)	+50

^aReference 4—DCA (TB-LMTO).

^bReference 22—DCA (TB-LMTO).

^cReference 33—Connolly-Williams method (LAPW).

^dReference 35—KKR-CPA.

along with the Connolly-Williams method for extracting the binary ECI's and (2) the calculations reported in Ref. 35, in which the Korringa-Kohn-Rostoker implementation of the coherent-potential approximation (KKR-CPA) was used to directly compute the self-consistent total formation energies of disordered Pd-Rh alloys. The comparison of the formation energies computed in this work with those of fully self-consistent total-energy computations leads to the conclusions that the ternary-alloy potentials have been accurately determined in the DCA computations, and that the one-electron energies provide a good quantitative description of formation energies for the alloys considered here. These comparisons are also a good indication that both the binary and ternary cluster expansions are well converged within pair, triplet, and, in the case of the binary cluster expansion, quadruplet ECI's.

V. SUMMARY AND CONCLUSIONS

The cluster expansion of alloy properties is extendable to multicomponent systems. In this paper, we have considered the case of ternary alloys and shown there are several possible choices for the basis functions of the expansion. In defining a complete set of functions in the space of all 3^N configurations of a system of N points, we have (in the main body of the text and Appendix A to follow) examined five possible basis sets, each with its own advantages and disadvantages. (1) *The Chebychev basis is*

an orthonormal and complete set of functions, but it may be numerically disadvantageous in certain situations because the orbit-averaged cluster functions are noninteger, oftentimes irrational numbers. The orthonormal characteristic of the basis leads to cluster expansion coefficients (ECI's, in the case of the energy expansion) which are easily defined for any cluster of lattice sites, but the ECI's are not physically very transparent. For calculations of the ECI's, the exact definitions are crucial when using the method of DCA, since the idea of this method is to compute the ECI's as closely as possible from their definition. Thus, the Chebychev polynomials provide a distinct advantage when used in conjunction with the DCA. However, if one uses other techniques, the advantages or disadvantages of the Chebychev basis may be unimportant. For instance, in the method of Connolly and Williams,¹ the ECI's are treated essentially as fitting parameters, thus the definition of the ECI's is really of no consequence, and any complete basis may be used equally well.

(2) *The cluster probability basis* was examined in the restricted case of only pair probabilities, and consequently, only pair interactions in the expansion. The EPI's in this basis have the same form as in the binary-alloy case, with the exception that the configurational averaging is over ternary configurations. Thus, the EPI's in the pair-probability basis are physically transparent in that the ordering or phase-separating tendencies between a pair of I - J atoms may often be determined simply from the sign of the NN EPI between I - J pairs. However, the cluster probability basis is not orthonormal, and thus, obtaining the exact definitions of the ECI's is nontrivial. In order to write a closed form expression for the ECI's in this nonorthogonal basis, one must write the expressions for the ECI's in an orthogonal basis (such as the Chebychev basis), and then project the nonorthogonal functions onto the orthogonal basis, thereby obtaining the linear combinations of the orthogonal expansion coefficients that serve to make up the ECI's of the nonorthogonal basis. In addition to the two sets of basis functions described in the main text, three more bases are considered in Appendix A: (3) *The 1 - σ - σ^2 basis* is another nonorthogonal basis which may, however, be numerically appealing due to the fact that the cluster functions are integers. (4) The complex basis formed from *the cubic roots of unity* has the desirable property that the permutations of (A, B, C) may be easily obtained by a combination of complex conjugations and rotations in the complex plane. However, it is seen in Appendix A that this basis is entirely equivalent to the Chebychev basis, and thus the complex basis offers no real practical advantage over the Chebychev polynomials. Additionally, the cluster functions and expansion coefficients of the cubic-roots-of-unity basis are complex quantities, and are consequently not physically transparent, to say the least. (5) The ternary orthonormal basis functions with a trace over configurations restricted to a given composition are also given in Appendix A. The advantages and disadvantages of each of these five bases of functions may or may not be important when attempting to use a given electronic-structure or statistical-mechanics technique. Therefore, it is to a certain extent a matter of choice as to which

basis is applicable for a given problem. Also, it has been shown here how one may transform the ECI's of each basis into any of the others, and thus, it may prove to be useful to solve certain aspects of a ternary problem in one basis, and other aspects in a different basis.

In using the DCA, we have seen how either the pair probability or Chebychev bases may be used effectively when considering pair interactions only, and when extending to multiplet interactions, the Chebychev interactions have been used to compute the formation energies of disordered configurations for Rh-V-Ti, Pd-Rh-V, and Ag-Pd-Rh alloys. The stability analysis of the ternary systems shows that the sign of the formation energy is not sufficient for correctly predicting the stability of these alloys, but rather one must also consider the curvature of the formation energies with respect to each of the independent compositions. To check the convergence of the cluster expansion, the binary formation energies computed from the ternary ECI's were checked against those obtained from binary cluster expansions. A good agreement was found between the results of the binary and ternary cluster expansions, indicating a rapid convergence of the expansion with only pair and triplet figures. The convergence does not come cheaply, however: It was necessary to retain 28 ternary ECI's in the expansion to recover binary formation energies in quantitative agreement with the binary cluster expansion. It is anticipated that both these types of qualitative and quantitative analyses based on ternary cluster expansions should provide a useful bridge between theory and experiment, and should serve as a guide to alloy designers.

ACKNOWLEDGMENTS

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APPENDIX A: ALTERNATE TERNARY BASIS FUNCTIONS

1. $\{1, \sigma_i, \sigma_i^2\}$

The set of the first three polynomials of σ_i

$$P_n(\sigma_i) = \sigma_i^n; \quad n = 0, 1, 2 \quad (\text{A1})$$

forms a basis of functions for the point variable σ_i . The functions $P_n(\sigma_i)$ are neither normalized nor orthogonal [with the definition $(\tau_A, \tau_B, \tau_C) = (+1, 0, -1)$], but they are complete in the sense that the Chebychev polynomials (a complete basis) may be expressed as linear combinations of P_n :

$$\begin{pmatrix} \Theta_0(\sigma_i) \\ \Theta_1(\sigma_i) \\ \Theta_2(\sigma_i) \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \sqrt{3/2} & 0 \\ \sqrt{2} & 0 & -\frac{3}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} 1 \\ \sigma_i \\ \sigma_i^2 \end{pmatrix} \quad (\text{A2})$$

or, in matrix notation, $\Theta = \mathbf{A}\mathbf{P}$. The functions $P_n(\sigma_i)$ may be advantageous in numerically intensive calculations due to the fact that these functions are always integer, whereas the same is not true of the Chebychev polynomials.

Products of (A1) yield the corresponding cluster functions

$$\Gamma_\alpha^{(s)} = \sigma_1^{s_1} \sigma_2^{s_2} \cdots \sigma_{|\alpha|}^{s_{|\alpha|}} \quad (\text{A3})$$

and so the cluster expansion in the basis of (A3) has the form

$$E(\sigma) = \sum_\alpha \sum_{(s)} m_\alpha X_\alpha^{(s)} \bar{\Gamma}_\alpha^{(s)}, \quad (\text{A4})$$

where the sum over (s) is all values of (s) on α for which $s_i \neq 0$; $i = 1, 2, \dots, |\alpha|$. m_α is the multiplicity of α and $\bar{\Gamma}$ is the orbit average of Γ . $X_\alpha^{(s)}$ are the coefficients in the cluster expansion (the ECI's in the Γ basis) but are *not* given by $\langle \Gamma_\alpha^{(s)}, E \rangle$ due to the nonorthogonality of Γ . The Chebychev polynomial cluster functions of Eq. (2.3) may be written in terms of $\Gamma_\alpha^{(s)}$ by forming tensor products of Eq. (A2). Then, by equating (2.4) and (A4) term for term, the following relation between the ECI's $V_\alpha^{(s)}$ and $X_\alpha^{(s)}$ is found:

$$X_\alpha^{(s)} = c(s) V_\alpha^{(s)} + \sum_{\beta \subset \alpha} \frac{m_\beta}{m_\alpha} \mu_{\beta\alpha} \sum_{(s')} d(s, s') V_\beta^{(s')}, \quad (\text{A5})$$

where the first summation on the right-hand side is over all clusters β which contain α . $\mu_{\beta\alpha}$ is the number of sub-clusters α in β and the constants $c(s)$ and $d(s, s')$ are determined from the tensor products of \mathbf{A} with itself. $c(s)$ has the simple form

$$c(s) = (\sqrt{3/2})^{n_1} \left[\frac{-3}{\sqrt{2}} \right]^{n_2}, \quad (\text{A6})$$

where $n_{1(2)}$ is the number of ones (twos) in (s) . Specific values of $d(s, s')$ are given in Table III for the case of EPI's renormalized by triplet terms. For the renormalization of α by β , let $(s') = (s'_1, s'_2, \dots, s'_{|\beta|})$ and $(s) = (s_1, s_2, \dots, s_{|\alpha|})$. Then, $d(s, s') = 0$ unless $s'_i = s_i$ ($i = 1, |\alpha|$) and $s'_i = 2$ ($i = |\alpha| + 1, |\beta|$). It is also important to note that $c(s)$ and $d(s, s')$ do not decay with increasing $|\alpha|$ and $|\beta|$, but rather grow. It is possible then

TABLE III. The coefficients $d(s, s')$ for renormalization of Eq. (A5) of pair interactions by triplets.

(s')	(s)		
	(11)	(12)	
(111)	0	0	0
(112)	$3/\sqrt{2}$	0	0
(122)	0	$-3\sqrt{6}$	0
(222)	0	0	$27/\sqrt{2}$

that the convergence of the ECI's, $X_\alpha^{(s)}$ is less rapid than $V_\alpha^{(s)}$ of the Chebychev basis.

2. Complex basis (cubic roots of unity)

Consider choosing for the domain of σ_i , the cubic roots of unity, i.e., $(\tau_A, \tau_B, \tau_C) = (\omega, 1, \omega^*)$, where $\omega = \exp(2\pi i/3)$. In the complex plane, the values of σ_i fall on the vertices of an equilateral triangle circumscribed in the unit circle. All the six permutations of the type $(A, B, C) \rightarrow (B, A, C)$ follow then easily from the point-group operations of the equilateral triangle (or the permutation group of order 3). For example, the permutation $(A, B, C) \rightarrow (B, A, C)$ would be accomplished by a rotation of $2\pi/3$ followed by complex conjugation and then a rotation of $-2\pi/3$. It is due to the conceptual simplicity of the transformation properties that one would wish to define a complex basis with the spin variables being given by the cubic roots of unity. We wish to define an orthonormal complex basis of functions in the space of all ternary configurations, and thus generalize the inner product of $f(\sigma)$ and $g(\sigma)$ as

$$\langle f(\sigma), g(\sigma) \rangle = \frac{1}{3^N} \sum_{\{\sigma\}} f(\sigma)^* g(\sigma). \quad (\text{A7})$$

The set of functions $\{1, \sigma_i, \sigma_i^2\}$ is *already* orthonormal with respect to (A7) when the complex domain is used, so no further manipulation is needed. Also, because $\sigma_i^2 = \sigma_i^*$, the basis of point functions is simply $\{1, \sigma_i, \sigma_i^*\}$. Products of the point functions form the *complex* cluster functions $\Lambda_\alpha^{(s)}$ with the values $s_i = 0, 1, 2$ corresponding to $1, \sigma_i, \sigma_i^*$, respectively. The energy is expanded (after orbit averaging) as

$$E(\sigma) = \text{Re} \left[\sum_\alpha \sum_{(s)} m_\alpha Y_\alpha^{(s)} \bar{\Lambda}_\alpha^{(s)} \right] \quad (\text{A8})$$

and due to orthonormality the ECI's, $Y_\alpha^{(s)}$, are given by

$$Y_\alpha^{(s)} = \langle \Lambda_\alpha^{(s)}, E(\sigma) \rangle. \quad (\text{A9})$$

For the complex effective pair interactions $Y_n^{(s)}$, the definition is given explicitly by the inner product of (A9) and may be compared with the definitions of the pair-probability-basis EPI's, W_n^{IJ} . After some algebra, one finds the following relation:

$$\begin{pmatrix} Y_n^{(11)} \\ Y_n^{(12)} \\ Y_n^{(22)} \end{pmatrix} = \frac{2}{9} \begin{pmatrix} 1 - \frac{i\sqrt{3}}{4} & -2 & 1 + \frac{i\sqrt{3}}{4} \\ 1 & 1 & 1 \\ 1 + \frac{i\sqrt{3}}{4} & -2 & 1 - \frac{i\sqrt{3}}{4} \end{pmatrix} \begin{pmatrix} W_n^{AB} \\ W_n^{BC} \\ W_n^{AC} \end{pmatrix}. \quad (\text{A10})$$

The three complex EPI's would generally contain six independent pieces of information through the real and imaginary parts. However, the information contained in $Y_n^{(s)}$ is equivalent to the three independent interactions W_n^{IJ} because of the three constraints imposed by $Y_n^{(11)} = Y_n^{(22)*}$ and $\text{Im}(Y_n^{(12)}) = 0$. Also, from the resulting transformations of Eqs. (2.15), (A5), and (A10), it is ap-

parent that the Chebychev, pair-probability, $\{1, \sigma_i, \sigma_i^2\}$ and complex-basis EPI's all contain the same information and it is possible to transform interactions calculated in any one of these bases into any of the others.

It is simple to verify that the complex basis is, in fact, equivalent to the Chebychev basis. Denote the complex spin variable by $\bar{\sigma}_i$ which takes on the values $(\omega, 1, \omega^*)$ and the real spin variable σ_i which has the domain $(+1, 0, -1)$. By inspection, the following relationship exists between the Chebychev polynomials and cubic roots of unity:

$$\Theta_2(\sigma_i) = \frac{1}{\sqrt{2}} \text{Re}(\bar{\sigma}_i); \quad \Theta_1(\sigma_i) = \frac{1}{\sqrt{2}} \text{Im}(\bar{\sigma}_i) \quad (\text{A11})$$

and thus the complex basis $\{1, \bar{\sigma}_i, \bar{\sigma}_i^*\}$ with $\bar{\sigma} = (\omega, 1, \omega^*)$ is completely equivalent to the basis $\{1, \gamma(\sigma_i), \gamma^*(\sigma_i)\}$ with $\sigma_i = (+1, 0, -1)$, where $\gamma(\sigma_i)$ is defined as

$$\gamma(\sigma_i) = \sqrt{2}[\Theta_2(\sigma_i) + i\Theta_1(\sigma_i)]. \quad (\text{A12})$$

In the Chebychev basis, the desirable transformation properties of the complex basis may be obtained by forming the complex function γ , taking tensor products of γ if necessary to obtain cluster functions, transform these new cluster functions in the complex plane according to the point-group operations of the equilateral triangle, and then return to the Chebychev polynomials by taking the real and imaginary parts of (A12). Thus, the complex basis offers no real practical advantage over the Chebychev basis in the ternary alloy problem as either may be easily transformed under permutations of (A, B, C) .

3. Composition-dependent ternary basis functions and ECI's

For the binary cluster expansion, it has been shown that^{36,37} basis functions may be defined which are orthonormal and complete (in the thermodynamic limit, $N \rightarrow \infty$) with respect to an inner product which traces over all configurations of a system at a fixed composition. Generalizing to the ternary case gives the following *restricted* inner product:

$$\langle f(\sigma), g(\sigma) \rangle = \frac{1}{\rho_0(c_A, c_B, c_C)} \sum_{\{\sigma\}}^{c_A, c_B, c_C} f(\sigma)g(\sigma), \quad (\text{A13})$$

where the summation is for a fixed value of c_A, c_B , and c_C , and ρ_0 is given by

$$\rho_0(c_A, c_B, c_C) = \frac{N!}{(c_A N)!(c_B N)!(c_C N)!}. \quad (\text{A14})$$

Starting with the set of functions $\{1, \sigma_i, \sigma_i^2\}$ where σ_i has the domain $(+1, 0, -1)$, the Gram-Schmidt process gives the following orthonormal functions of point variable σ_i :

$$\begin{aligned} \Theta_0(\sigma_i) &= 1, \\ \Theta_1(\sigma_i) &= \frac{1}{\sqrt{\sigma^2 - \bar{\sigma}^2}} (\sigma_i - \bar{\sigma}), \\ \Theta_2(\sigma_i) &= \frac{1}{\sqrt{\beta}} [\sigma_i^2 - \bar{\sigma}^2 - \eta(\sigma_i - \bar{\sigma})], \end{aligned} \quad (\text{A15})$$

where we have defined

$$\begin{aligned} \eta &= \frac{\bar{\sigma}(1 - \bar{\sigma}^2)}{\sigma^2 - \bar{\sigma}^2}, \\ \beta &= \frac{(1 - \bar{\sigma}^2)}{\sigma^2 - \bar{\sigma}^2} [(\bar{\sigma}^2)^2 - \bar{\sigma}^2] \end{aligned} \quad (\text{A16})$$

with $\bar{\sigma} = \langle 1, \sigma \rangle$ and $\bar{\sigma}^2 = \langle 1, \sigma^2 \rangle$, both defined with respect to the restricted inner product of (A13). It should be noted that at equiatomic composition, $\bar{\sigma} = 0$ and $\bar{\sigma}^2 = \frac{2}{3}$, and the functions of (A15) reduce precisely to the Chebychev polynomials of Eq. (2.2), which must be true, since in the thermodynamic limit, a trace over all ternary configurations is equivalent to a restricted trace over all configurations at equiatomic composition. By forming products of the point functions of (A15), one forms a composition-dependent basis of cluster functions, and hence one can write an energy expansion in which the ternary ECI's are explicitly composition dependent.

APPENDIX B: TRIPLET ECI'S IN THE CHEBYCHEV BASIS

The definition of the ECI's in the Chebychev basis is given for a general cluster in Eq. (2.5). For a general cluster of three points, there are eight distinct ECI's corresponding to $(s) = (111), (112), (121), (211), (122), (212), (221),$ and (222) , at least four of which are distinct. The ECI's corresponding to $(s) = (111)$ and (222) are given by

$$\begin{aligned} V_n^{(111)} &= \frac{1}{18} \sqrt{3/2} (E_{AAA} - E_{AAC} - E_{ACA} - E_{CAA} + E_{ACC} + E_{CAC} + E_{CCA} - E_{CCC}), \\ V_n^{(222)} &= \frac{\sqrt{2}}{108} (-E_{AAA} + 2E_{AAB} - E_{AAC} + 2E_{ABA} - 4E_{ABB} + 2E_{ABC} \\ &\quad - E_{ACA} + 2E_{ACB} - E_{ACC} + 2E_{BAA} - 4E_{BAB} + 2E_{BAC} - 4E_{BBB} \\ &\quad + 8E_{BBB} - 4E_{BBC} + 2E_{BCA} - 4E_{BCB} + 2E_{BCC} - E_{CAA} + 2E_{CAB} \\ &\quad - E_{CAC} + 2E_{CBA} - 4E_{CBB} + 2E_{CBC} - E_{CCA} + 2E_{CCB} - E_{CCC}), \end{aligned} \quad (\text{B1})$$

where E_{IJK} is the average energy of all ternary configurations containing an IJK triplet of atoms at the specified sites. We also give the explicit definitions for $\bar{V}_n^{(112)}$ and $\bar{V}_n^{(122)}$:

$$\begin{aligned}
3\tilde{V}_n^{(112)} = V_n^{(112)} + V_n^{(121)} + V_n^{(211)} = \frac{\sqrt{2}}{36} & (3E_{AAA} + 2E_{AAB} + 2E_{ABA} + 2E_{BAA} \\
& + E_{AAC} + E_{ACA} + E_{CAA} - 2E_{ACB} - 2E_{BAC} - 2E_{CBA} \\
& - 2E_{ABC} - 2E_{CAB} - 2E_{BCA} + E_{AAC} + E_{ACA} + E_{CAA} \\
& + E_{ACC} + E_{CAC} + E_{CCA} + 2E_{CCB} + 2E_{CBC} + 2E_{BCC} - 3E_{CCC}) \quad (B2)
\end{aligned}$$

and

$$\begin{aligned}
3\tilde{V}_n^{(221)} = V_n^{(221)} + V_n^{(212)} + V_n^{(122)} = \frac{\sqrt{3}}{54\sqrt{2}} & (3E_{AAA} - 4E_{AAB} - 4E_{ABA} - 4E_{BAA} \\
& + E_{AAC} + E_{ACA} + E_{CAA} + 4E_{BBA} + 4E_{BAB} + 4E_{ABB} \\
& + 4E_{BCC} + 4E_{CBC} - 4E_{CCA} - 4E_{CAC} - 4E_{ACC} - E_{BBC} \\
& - E_{BCB} - E_{CBB} + 4E_{CCB} - 3E_{CCC}) . \quad (B3)
\end{aligned}$$

Explicit formulas for other ECI's [e.g., $V_n^{(112)}$] may be similarly obtained from (2.5).

APPENDIX C: GENERAL CANCELLATION THEOREM FOR MULTICOMPONENT ECIS

1. Defining some terms for the binary case

The basic idea of the cancellation theorem is that we wish to show that the coefficients in front of the ECI's "balance." For instance, in the case of binary pair interactions, the EPI is given by the familiar form

$$V_\alpha^{(11)} = \frac{1}{4}[E_{AA} + E_{BB} - E_{AB} - E_{BA}] , \quad (C1)$$

where α represents the cluster (a pair of atoms in this case) and the quantities E_{IJ} are the usual averaged "cluster energies." The vector (s) is superfluous in the binary cluster expansion, however, it is included here explicitly, as the generalization to multicomponent cluster expansions will be made below. From the definition in Eq. (C1), the number of A atoms in the definition may be "counted" in the following way: For each of the terms in the definition of the EPI, a sum is formed of the coefficients of the cluster energies which contain an A atom in the first site, and the coefficients of the cluster energies which contain an A atom at the second site. To be extremely explicit, this summed coefficient $N_\alpha^{(11)}(A)$ is

$$N_\alpha^{(11)}(A) = [\frac{1}{4} + 0 - \frac{1}{4} - 0] + [\frac{1}{4} + 0 - 0 - \frac{1}{4}] = 0 , \quad (C2)$$

where the first four bracketed terms are the coefficients of Eq. (C1) for an A atom in the first position, while the second four terms are the coefficients corresponding to an A atom being in the second position of the pair. Because both $N_\alpha^{(11)}(A)$ and $N_\alpha^{(11)}(B)$ are zero [which, of course, may be trivially verified from (C1)], there is a cancellation of terms in the pair interaction for the binary case, which was well known anyway. It is also interesting to note that in Eq. (C2) each of the brackets vanishes independently of the other. Thus, there is a cancellation of A atoms on site 1 and also on site 2. This property of cancellation individually on each site (or any subcluster) will also be seen below to be a general consequence of the orthonormal basis functions.

Because we wish to generalize this type of argument to

multicomponent alloys, we define the coefficients in terms of the cluster notation. For the binary case, there are only two cluster functions,

$$\Theta^{(0)}(\sigma_i) = 1; \quad \Theta^{(1)}(\sigma_i) = \sigma_i , \quad (C3)$$

where the point variable σ_i takes on two values $+1$ (-1) corresponding to whether an A or B atom is at the site specified by i . As shown in Ref. 8, the functions of (C3) obey the following orthogonality relation:

$$\sum_{\sigma=-1}^{+1} \Theta^{(s_1)}(\sigma) \Theta^{(s_2)}(\sigma) = \delta_{s_1, s_2} \quad (C4)$$

for any s_1 and $s_2 = 0, 1$.

For a system of N sites, the definition of the binary pair interactions between sites 1 and 2 is given by

$$V_\alpha^{(11)} = \frac{1}{2^N} \sum_{\{\sigma\}} \Theta^{(1)}(\sigma_1) \Theta^{(1)}(\sigma_2) E(\sigma) , \quad (C5)$$

which we may write as

$$V_\alpha^{(11)} = \frac{1}{4} \sum_{\sigma_1, \sigma_2 = -1}^{+1} \Theta^{(1)}(\sigma_1) \Theta^{(1)}(\sigma_2) E_{I_1 I_2} , \quad (C6)$$

where the cluster energy $E_{I_1 I_2}$ is defined above and I_1 and I_2 are either A or B depending on the occupation of sites 1 and 2, respectively. When all four terms of the summation of Eq. (C6) are explicitly written out, one recovers Eq. (C1), thus Eq. (C6) is just a "shorthand" way of writing down the cluster interactions. Now, an expression for $N_\alpha^{(11)}(I)$ may be written explicitly for the case of α representing a pair of sites, 1 and 2, and I being either A or B . Also, for notational convenience, write $\Theta^{(s)}(A_1) = \Theta^{(s)}(\sigma_1 = +1)$ and $\Theta^{(s)}(B_1) = \Theta^{(s)}(\sigma_1 = -1)$. In general, this is denoted $\Theta^{(s)}(I_1)$ and I_1 can be either A or B . With this notation, then, the coefficient $N_\alpha^{(11)}(I)$ is given by

$$\begin{aligned}
N_\alpha^{(11)}(I) &= \frac{1}{4} \left\{ \left[\Theta^{(1)}(I_1) \sum_{\sigma_2=-1}^{+1} \Theta^{(1)}(\sigma_2) \right] \right. \\
&\quad \left. + \left[\Theta^{(1)}(I_2) \sum_{\sigma_1=-1}^{+1} \Theta^{(1)}(\sigma_1) \right] \right\} \\
&= \frac{1}{4} \{ \Theta^{(1)}(I_1) \delta_{1,0} + \Theta^{(1)}(I_2) \delta_{1,0} \} = 0, \quad (C7)
\end{aligned}$$

where, in the second step, we have used Eq. (C4), the orthonormality condition between $\Theta^{(1)}$ and $\Theta^{(0)}=1$. Thus, the summed coefficient is zero, as seen above, and the cancellation for the pair interactions is satisfied for the binary case. Again, in Eq. (C7), it is seen that the first bracketed term vanishes as does the second, implying that the cancellation is not only complete, but also occurs on each individual site (e.g., there will be no terms like $[E_{AB} - E_{BA}]$, which would satisfy the cancellation in whole, but not on each individual site).

2. General cancellation theorem for multicomponent systems

Consider an alloy system with M components. Then, there are M basis functions $\Theta^{(s)}$ with $0 \leq s \leq M-1$. The basis functions are assumed to satisfy a generalization of the orthonormality relation of Eq. (C4):

$$\sum_{\sigma} \Theta^{(s_1)}(\sigma) \Theta^{(s_2)}(\sigma) = \delta_{s_1, s_2}, \quad (C8)$$

where the summation over σ takes on all of the M values of the spin variables in the M component case. Now, for a given cluster, $\alpha = (\sigma_1, \sigma_2, \dots, \sigma_{|\alpha|})$, of $|\alpha|$ points (with $|\alpha| \geq 2$) and a given vector of basis functions, $(s) = (s_1, s_2, \dots, s_{|\alpha|})$, with $1 \leq s_i \leq M-1$ for all i , the ECI is given by (note that $s_i \neq 0$ for all i , because any $s_i = 0$ would give the cluster interaction for the cluster $\alpha - i$ which has already been counted in the cluster expansion sum over α):

$$V_\alpha^{(s)} = \frac{1}{M^{|\alpha|}} \sum_{\sigma_1, \sigma_2, \dots, \sigma_{|\alpha|}} \Theta^{(s_1)}(\sigma_1) \Theta^{(s_2)}(\sigma_2) \cdots \Theta^{(s_{|\alpha|})}(\sigma_{|\alpha|}) E_{i_1 i_2 \cdots i_{|\alpha|}}. \quad (C9)$$

And, the summed coefficient is given by a generalization of Eq. (C7):

$$\begin{aligned}
N_\alpha^{(s)}(I) &= \frac{1}{M^{|\alpha|}} \left[\sum_{i=1}^{|\alpha|} \Theta^{(s_i)}(I_i) \sum_{\substack{\sigma_1, \sigma_2, \dots, \sigma_{|\alpha|} \\ \neq \sigma_i}} [\Theta^{(s_1)}(\sigma_1) \Theta^{(s_2)}(\sigma_2) \cdots \Theta^{(s_{i-1})}(\sigma_{i-1}) \right. \\
&\quad \left. \times \Theta^{(s_{i+1})}(\sigma_{i+1}) \cdots \Theta^{(s_{|\alpha|})}(\sigma_{|\alpha|})] \right], \quad (C10)
\end{aligned}$$

which can be rewritten as

$$\begin{aligned}
N_\alpha^{(s)}(I) &= \frac{1}{M^{|\alpha|}} \left[\sum_{i=1}^{|\alpha|} \Theta^{(s_i)}(I_i) \sum_{\substack{\sigma_1, \sigma_2, \dots, \sigma_{|\alpha|} \\ \neq \sigma_i, \sigma_j}} \{ \Theta^{(s_1)}(\sigma_1) \Theta^{(s_2)}(\sigma_2) \cdots \Theta^{(s_{i-1})}(\sigma_{i-1}) \Theta^{(s_{i+1})}(\sigma_{i+1}) \cdots \Theta^{(s_{i-1})}(\sigma_{j-1}) \right. \\
&\quad \left. \times \Theta^{(s_{j+1})}(\sigma_{j+1}) \cdots \Theta^{(s_{|\alpha|})}(\sigma_{|\alpha|}) \} \sum_{\sigma_j} \Theta^{(s_j)}(\sigma_j) \right]. \quad (C11)
\end{aligned}$$

Each of the terms in Eq. (C11) contains the following factor:

$$\sum_{\sigma_j} \Theta^{(s_j)}(\sigma_j) = \delta_{s,0} = 0, \quad (C12)$$

which vanishes by Eq. (C8) because $s_j \neq 0$ for all j . Thus, we have proved the following result:

$$N_\alpha^{(s)}(I) = 0 \quad (C13)$$

independent of I , α (provided $|\alpha| \geq 2$), (s) , or M . Thus, the cancellation holds for an arbitrary ECI in an arbitrary multicomponent system. Also, because the sum in Eq. (C10) vanishes independently for every value of i , this general cancellation theorem also holds for summed coefficients on each site, or on each subcluster of α . The orthonormality of the basis functions (C8) is not necessary for the proof, only the much weaker condition of (C12) that each of the basis functions be orthogonal to unity (or, equivalently, the sum of the values of each basis function over its domain must be zero). Note that in the $\{1, \sigma_i, \sigma_i^2\}$ ternary basis of Appendix A, the function σ_i^2 is not orthogonal to unity, and thus, the ECI's in this basis are not written as closed form expressions, but rather as an infinite sum of ECI's which are defined with respect to an orthogonal basis, as in Eq. (A5).

- *Present address: National Renewable Energy Laboratory, Golden, CO 80401.
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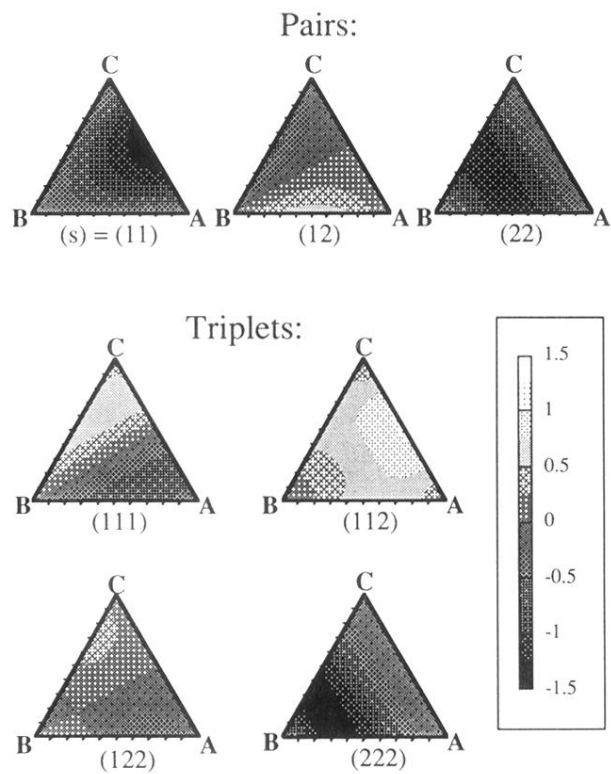


FIG. 3. The functions $\varphi^{(s)}$ for all distinct values of (s) corresponding to pairs and triplets. Linear combinations of these functions serve to make up the formation energy of the completely disordered state.

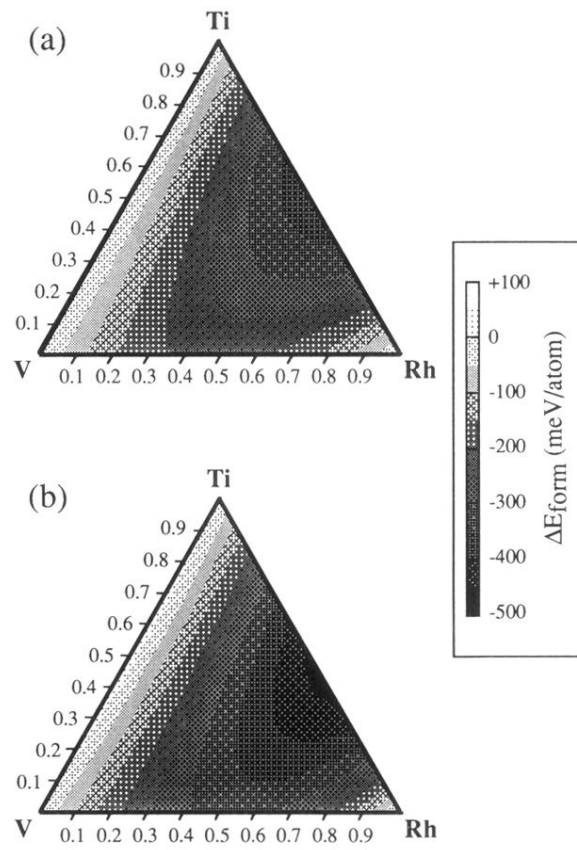


FIG. 4. Formation energies of completely disordered Rh-V-Ti alloys calculated from the ternary cluster expansion using (a) the 12 effective pair interactions of Fig. 2(a) and (b) all 28 calculated effective pair and triplet interactions.

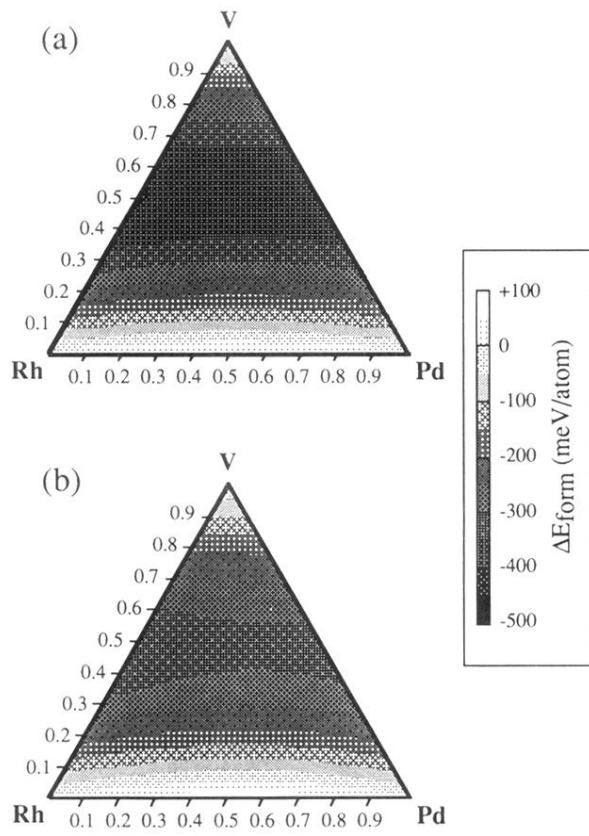


FIG. 5. Formation energies of completely disordered Pd-Rh-V alloys calculated from the ternary cluster expansion using (a) the 12 effective pair interactions of Fig. 2(a) and (b) all 28 calculated effective pair and triplet interactions.

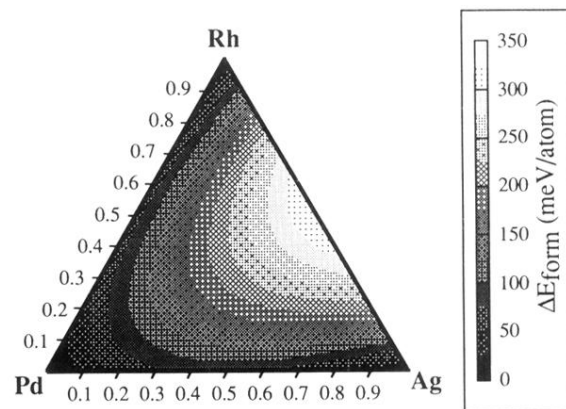


FIG. 6. Formation energies of completely disordered Ag-Pd-Rh alloys calculated using the 28 pair and triplet ECI's of Fig. 2(c).

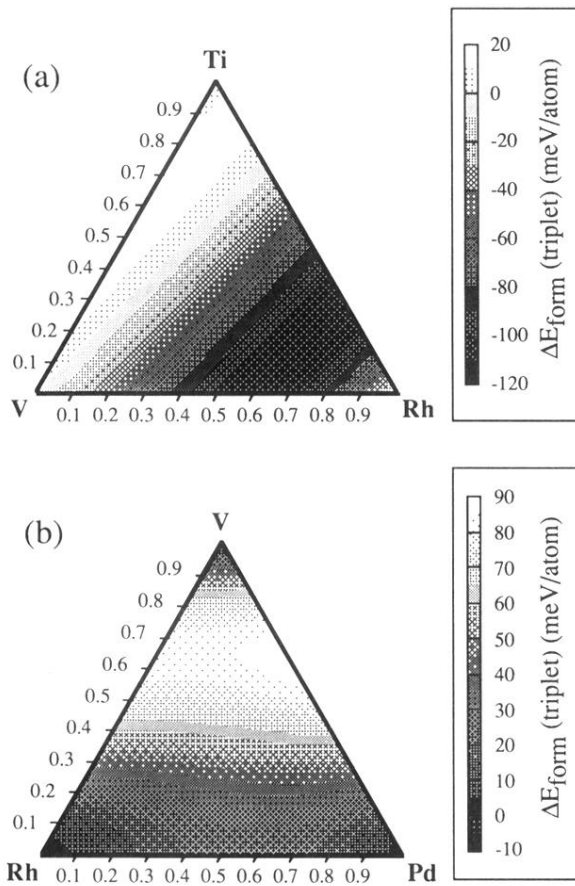


FIG. 7. Triplet contributions to the formation energy of completely disordered fcc solid solutions for the (a) Rh-V-Ti and (b) Pd-Rh-V systems.