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# CLUSTER EXPANSION OF fcc Pd-V INTERMETALLICS

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**ABSTRACT.** A cluster expansion is used to compute fcc ground states from first principles for the Pd-V system. Intermetallic structures are not assumed but derived rigorously by minimizing the configurational energy subject to linear constraints. A large number of concentration-independent interactions are calculated by the method of direct configurational averaging. Agreement with the fcc-based portion of the experimentally-determined Pd-V phase diagram is quite satisfactory.

## 1. Introduction

In recent years, first-principles total electronic energy calculations have been remarkably successful in predicting heats of formation, lattice parameters, and elastic moduli of simple intermetallic compounds at their stoichiometric compositions and at zero Kelvin. Performing similar calculations for off-stoichiometric compositions, in disordered or partially ordered states, has obviously not progressed as rapidly, as it is required to solve combined quantum and statistical problems at a high level of accuracy.

One aim of such calculations is to derive, virtually from first principles, reasonable temperature-composition phase diagrams for binary metallic systems, say. Thermodynamic quantities, such as free energies, entropies, enthalpies, states of order may then be deduced as by-products of the calculations.

Over the last ten years or so, it has become apparent that the preferred way of investigating *alloys* computationally (ordered or disordered) is through the medium of expansions in cluster functions. The theoretical framework is rigorous, flexible and completely general, and is essential for formulating both the energy (E) and the configurational entropy (S), hence the free energy ( $F = E - TS$ ).

The cluster expansion method can also be used to tackle the difficult problem of ground state determination. Predicting, without guesswork, which superstructures of a given lattice have minimum energy, is essential and is a topic which has perhaps not received as much attention lately as it deserves. In this article, we shall address precisely this problem, and, after having outlined the basic theory, we shall apply the cluster methods to the ground state determination of fcc superstructures in the Pd-V system.

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## 2. Cluster Expansions

It was back in 1951 that Kikuchi [1] introduced the idea of *clusters* in the statistical thermodynamics of the Ising model as a way of improving systematically on the currently known approximations of the configurational entropy. Since the free energy was obtained, in Kikuchi's method, by minimizing a functional with respect to cluster variables, he called his hierarchy of approximations the *cluster variation method* (CVM). Its application to the calculation of phase diagrams was suggested by Van Baal [2] in 1973, and the use of the method has expanded considerably ever since.

The cluster method is now viewed as far more general than the early practitioners of the CVM probably envisaged. Today, clusters (on a lattice) are considered as the essential building blocks for any description of alloy properties which depend on configuration. This approach was first described in 1982, in a remarkable paper by Sanchez, Ducastelle and Gratias [3]. Although these authors treated the general multicomponent case, we shall here summarize results for binary systems only. An alternative and very elegant method of treating multicomponent systems was suggested by Finel [4] and was very recently described in a very clear and comprehensive review article by Inden and Pitsch [5].

In a binary alloy (AB) let the pseudo-spin variable  $\sigma_p = +1$  ( $-1$ ) stand for an A (B) atom at lattice site  $p$ . Consider now a set of lattice points  $\{p, p', p'' \dots\}_\alpha$  which we shall denote as "the cluster  $\alpha$ ." It was shown [6,7] that *cluster functions*  $\varphi_\alpha(\sigma)$  can be constructed so as to form an orthonormal set in the space of  $2^N$  configurations,  $N$  being the total number of lattice points. A convenient choice [3] is the direct product of  $\sigma$  variables on the cluster points:

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

The set  $\{\varphi_\alpha\}$  is orthonormal in the sense that the scalar product  $\langle \varphi_\alpha(\sigma), \varphi_\beta(\sigma) \rangle$ , defined as the normalized sum of the product  $\varphi_\alpha \varphi_\beta$  over all configurations, is unity if the two clusters  $\alpha$  and  $\beta$  coincide, zero otherwise. It follows that any function of configuration,  $f(\sigma)$ , say, can be expanded in the set of cluster functions

$$f(\sigma) = \sum_{\alpha} f_{\alpha} \varphi_{\alpha}(\sigma) \quad (2)$$

with generalized Fourier coefficients given by

$$f_{\alpha} = \langle \varphi_{\alpha}(\sigma), f(\sigma) \rangle \quad (3)$$

Of particular interest is the expectation value of the function  $f(\sigma)$ , obtained by taking an ensemble average of Eq. (2) at given  $T$  and chemical field  $\mu$  (difference of chemical potentials  $\mu_B - \mu_A$ ):

$$\langle f \rangle = \sum_{\alpha} f_{\alpha} \xi_{\alpha} \quad (4)$$

where the  $\xi_{\alpha}$ , denoted *multisite correlation functions*, are ensemble averages of the corresponding cluster functions. Eq. (4) is important in that, in principle, it shows how to express any

macroscopic alloy property as an expansion in cluster correlation functions with coefficients calculated by Eq. (3). This cluster expansion technique, applied to the case of the energy  $E$ , has led to various methods for calculating macroscopic alloy parameters directly from quantum mechanical computations. One such method will now be described.

### 3. Effective Cluster Interactions

Let us apply the formalism of Eq. (4) to the expectation value of the internal energy  $E$ . It is necessary to calculate the expansion coefficients  $E_\alpha$ , generally called *effective cluster interactions* (ECI). These parameters are obtained from Eq. (3), with cluster functions given by Eq. (1). It would appear that the formalism requires the computation of energies as a function of alloy configuration,  $E(\sigma)$ , for all possible configurations. Actually, the sum of (4) converges fairly rapidly [7], so that only a few ECI's need to be calculated. As an example, let  $\alpha$  represent a pair of lattice sites,  $p$  and  $q$ , say. In that case, when the summation implied by the scalar product (3) is written out explicitly, the following single expression for effective pair ( $\alpha \equiv pq$ ) interactions is obtained [6-9]:

$$E_{pq} = \frac{1}{4}(W_{AA} + W_{BB} - W_{AB} - W_{BA}) \quad (5)$$

In Eq. (5),  $W_{IJ}$  represents the average energy of all configurations of the system with atom of Type I at  $p$  and J at  $q$ . The formalism can be extended to any reasonable size cluster: triplets ( $p,q,r$ ), quadruplets, etc. The physical meaning of the ECI's is thus quite clear:  $E_\alpha$  represents a linear combination of average energies of systems containing cluster  $\alpha$  in all of its possible configurations.

This definition of ECI's is perfectly rigorous, and, in this approach, leads to the following important properties:

- (a) Since the embedding medium is averaged over all possible configurations, and since all configurations of the embedded cluster are considered, the ECI's are *concentration independent*.
- (b) Since the ECI's, as per Eq. (5), consist of sums of very similar energies ( $W$ ), with equal number of positive and negative contributions, the  $E_\alpha$  are much smaller in magnitude than the "potentials"  $W$ .
- (c) As already anticipated in the pioneering work of Gautier and Ducastelle [10], the magnitude of the  $E_\alpha$  decreases rapidly with distance, in the case of pairs, and with the number of points in cluster [7]. This convergence property is responsible for making the whole notion of cluster expansion into a practical reality. It is important to note that no such convergence holds for the "potentials"  $W$  themselves. However, in taking sums and differences, as in Eq. (5), the long-range portions of the energies tend to cancel out.

This is not the only way to proceed: it has been shown recently [6,7] that orthonormal sets of functions on configuration space could be constructed by means of summations over configurations which conserve average concentration. The ECI's produced in this manner are thus necessarily concentration-dependent, but it was proved that, somewhat surprisingly, both concentration-dependent and -independent expansion schemes are in fact completely equivalent [6,7]. Of course, the coefficients of the expansions will have different numerical values, and the convergence rate of the two series may well differ.

The concentration-independent scheme presents definite advantages, not the least of which is the simplification of the search for ground states. This subject will be treated in Section 5, but first let us describe a method for actually computing concentration-independent effective cluster interactions.

#### 4. Direct Configurational Averaging

The most obvious way of computing ECI's ( $E_\alpha$ ) is by taking sums and differences of  $W$ 's, as in Eq. (5). The energies  $W$  themselves can be calculated by selecting an arbitrary configuration  $\sigma$  in a finite portion of the crystal (containing  $N$  atoms), computing the energy by suitable electronic structure techniques, then repeating the procedure over and over, with different configurations selected at random, keeping that on the chosen  $\alpha$ -cluster fixed. It has been shown that convergence to a true "random medium" is rather rapid [11]; usually about 20 to 50 configurations suffice [7].

We have used the tight-binding method with parameters obtained from LMTO calculations for the pure elements of the binary alloy considered. On-site energies were determined by disallowing charge transfer, a reasonable assumption for transition metals, and the Shiba prescription was used for evaluating off-diagonal two-center hopping integrals [7,11]. Because the recursion method is used to calculate the density of states, it then turns out that the  $W$  potentials need not be calculated individually: the technique of "orbital peeling" [12] produces  $E_\alpha$  directly, so that taking a (small) difference of large numbers is not required. Generally, 10 recursion levels are used with a quadratic terminator.

The average medium, in the present case, was practically an fcc solution of 50% Pd and 50% V [13]. The tight-binding parameters were derived from pure fcc Pd and fcc V at a molar volume midway between that of equilibrium fcc Pd and fcc V at zero Kelvin. Effective cluster interactions were calculated for all pair and triplet and eight quadruplet clusters which belong to the set of subclusters of the 14-point fcc cube. Fig. 1 is a plot of the logarithm of the magnitude of the ratio of ECI  $E_\alpha$  to the first neighbor pair interaction for pairs (circles), triangles (crosses) and quadruplets (squares), as a function of the order of the largest pair in the cluster. Several distinct triplets and some quadruplets have the same largest pair, hence their representative points appear on the same vertical in Fig. 1. It is apparent that ECI's converge fairly rapidly with pair separation and with number of points in the cluster, although not monotonically. This set of 26 effective interactions represents, to date, the largest set of ECI's yet calculated for any alloy system. It is becoming increasingly clear, however, that large numbers of ECI's are required to describe adequately the properties of most alloy systems.

#### 5. Ground State Analysis

Predicting, for a given binary system, which intermetallic structures will have lowest energy, for all concentrations, at zero Kelvin, is an impossible task. Fortunately, most intermetallics of interest are superstructures of either fcc, bcc or hcp. Then, the problem of determining the lowest-energy *superstructures* of a given lattice is a simpler one which, in favorable cases, can be solved exactly. Each lattice must of course be handled separately: the ECI's calculated on different lattices will have different values. As for other intermetallic compounds, those which are *not* superstructures, they must be treated differently. For these "interloper" phases, their total energies must be calculated directly by appropriate electronic structure codes and compared to other, possibly

competitive structures. Here, we shall investigate only the minimum-energy fcc-based superstructures of the Pd-V system, for the calculated set of ECI's, over the whole Pd-V concentration interval. This set of structures constitute the set of *fcc ground states of order* for the system in question.

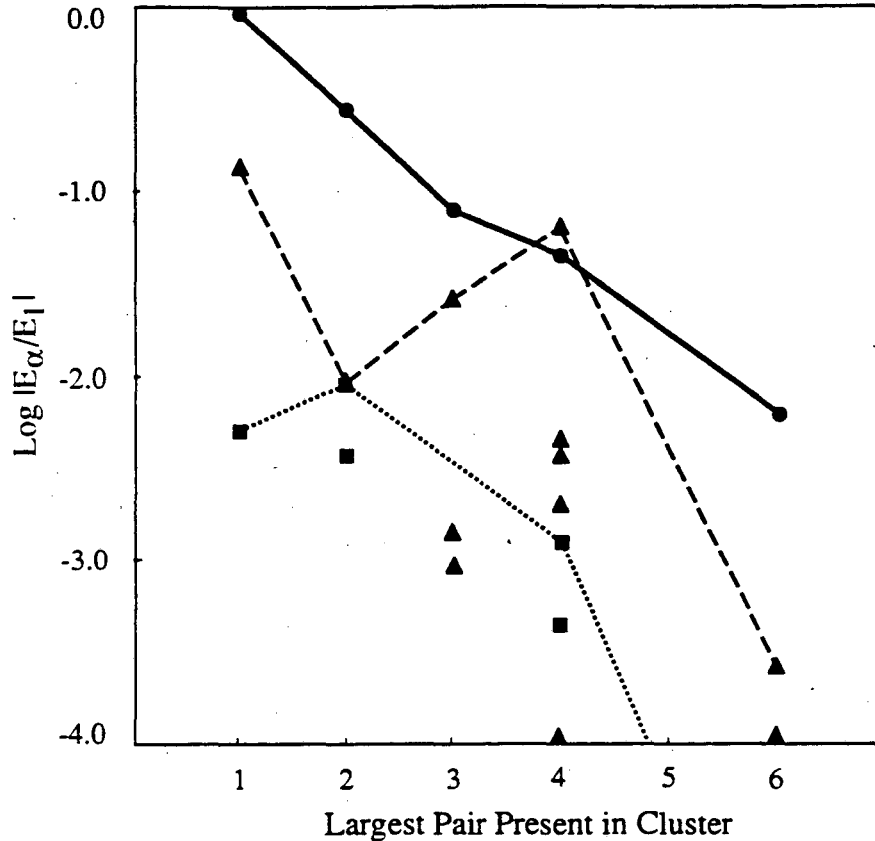


Figure 1. Logarithm of ECI's (normalized to nn pair interaction  $E_1$ ), as a function of largest pair distance in cluster, for three types of clusters: pairs (circle symbols), triplets (triangles), quadruplets (squares). Lines connect highest-energy ECI's for the three classes of clusters. Geometrically distinct triplets and quadruplets which have same largest pair are located on the same vertical.

Eq. (2), written for the energy  $E(\sigma)$ , is the one to minimize, but it must first be rewritten in a more convenient form. Many of the clusters ( $\alpha$ ) appearing in the summation are equivalent through the space group symmetry operations of the underlying lattice. The set of such clusters equivalent to a given one by symmetry is known as the orbit of the given cluster. Each distinct orbit (or its generating cluster) will be denoted by the index  $j$ . The total number of clusters in orbit  $j$  is then the total number of lattice translational symmetry operations times the number of equivalent clusters per lattice point, or multiplicity  $m_j$ . Let us also denote the "empty cluster" by the index  $j = 0$ . Then, the energy of a given stoichiometric superstructure, per lattice point, is, by Eq. (4), given by the linear form



$$e = e_0 + \sum_{j=1}^J m_j E_j \xi_j \quad (6)$$

where the brackets have been removed from  $\langle e \rangle$  since, at absolute zero of temperature, the expectation value is just the energy of the perfect structure. The variables  $\xi_j$  here are not strictly ensemble averages, but "orbit averages" of cluster functions; such averaging process must be taken into account since the symmetry of the ordered superstructure is generally lower than that of the parent lattice. The summation in Eq. (6) extends from the "point" cluster to some maximal cluster(s), denoted by the index  $J$ .

Simply minimizing the linear function (6) with given ECI's  $E_j$  will not do, since the parameters  $\xi_j$  must describe a real structure, or mixture of structures, on the lattice. Hence, a number of constraints (i.e., linear inequalities) on the domain of  $\xi_j$  must be imposed. The required constraints are usually derived from considerations of clusters (see Refs. [14] and [15] and references cited therein), but the most straightforward method is probably that suggested by Sanchez and one of the present authors [16] and described fully, for the case of pair interactions, by Finel [15] and in a recent review [5]. The handling of combinatorics of large clusters was treated even more recently in the Ph.D. dissertation of one of the present authors [17] and a more detailed application to the Pd-V system will be published elsewhere [13].

Briefly, the idea is the following: denote the probability of finding a given cluster, say a nearest-neighbor triangle of lattice points (equilateral triangle in fcc) populated by atoms in a certain configuration ( $\sigma \equiv \text{AAA}, \text{AAB}, \dots$ ) by the symbol  $x_j(\sigma)$ . This probability, or "dressed" cluster concentration, being a function of configuration, can be expanded in a set of cluster functions, as in Eq. (2) [17]. For simplicity, let distinct configurations on a given cluster be labeled by the index  $k$ . For the maximal cluster  $J$ , the concentrations of various configurations  $k$  are then given by [18]:

$$x_J(\sigma_k) = \rho_J^0 \left( 1 + \sum_{j=1}^J C_{kj} \xi_j \right) \quad (7)$$

where  $\rho_J^0$  is a normalization factor given by the reciprocal of the number of configurations on the cluster, i.e.,  $2^{-J}$ . The summation is over all subclusters  $j$  of the maximal cluster  $J$  and the coefficients  $C_{kj}$ , calculated by means of Eq. (3), are elements of a rectangular matrix, the so-called *configuration matrix* (or *C-matrix*). Often, more than one "maximal cluster" is used,  $J, J', J'', \dots$ , neither one being a subcluster of any other.

Since the  $x_j$  are probabilities, their values must be constrained to lie between 0 and 1. Then, only the lower constraint needs to be considered, since the upper one is guaranteed by the fact that cluster averages lie between  $-1$  and  $+1$ . Hence, from Eq. (7), we must have, for all maximal clusters, and for all cluster configurations  $k$ ,

$$\sum_j C_{kj} \xi_j \geq -1 \quad (8)$$

These linear inequalities define a convex region in multidimensional  $\xi$ -space, the so-called *configurational polyhedron*, which contains all realizable configurations on the lattice. The determination of ground states then consists of minimizing the energy (objective) function (6),

under the constraint of inequalities (8). This is a standard problem in linear programming and can be solved, when the ECI's are given, by the simplex algorithm. It follows that the vertices of the configuration polyhedron are the solutions sought, i.e., the ordered ground state superstructures, different vertices corresponding to different stoichiometries.

The C-matrix, which has more rows (configurations  $k$ ) than columns (subcluster types  $j$ ) contains all the geometric properties of the problem, and is used to transfer that information (lattice type, largest cluster(s), subclusters, symmetry equivalence) to both ground state and CVM codes. Unfortunately, the number of (sub)clusters and the number of configurations tend to increase exponentially with the number of points in the largest cluster retained in the energy (or entropy) approximation chosen. For example, in the 13-, 14-point fcc approximation (central lattice point and its twelve nearest neighbors, fcc cube itself), there are 742 distinct clusters, 554 configurations on the 14-point cluster and 288 on the 13-point cluster. Hence the C-matrix has  $842 \times 742$  elements! Clearly, the enumeration of all variables and constraints must be obtained by a suitable computer algorithm based on group theoretic considerations. One such algorithm has recently been developed by one of the present authors [17].

Despite the computer automation provided by the C-matrix code and the simplex algorithm, the 13-, 14-point fcc approximation lies pretty much at the limit of what can be done practically at present. We have used this approach to determine the fcc ground states of fcc Pd-V with, as input, the 26 effective cluster interactions calculated by the DCA method, as described above. The resulting ground state map is shown in Fig. 2, in which the *formation energies* (in eV/atom) are plotted as a function of concentration. Formation energies are defined as the actual ordered ground state energy compared to the linear combination of pure fcc Pd and fcc V at the same concentration. The ordered states of minimum energy are indicated by filled squares joined together by a dotted line representing the "convex hull" for this problem. Open squares represent ordered superstructures which narrowly miss being ground states. Their energies were calculated separately, through the use of Eq. (6), using known values of the  $\xi_j$  structural variables. The full curve in Fig. 2 is the calculated energy of the completely disordered Pd-V fcc solid solution, theoretically resulting from the infinite-temperature fcc solution quenched infinitely rapidly to zero Kelvin.

All other structures indicated have been derived rigorously and are guaranteed to be the true and only fcc ground states for the given set of interactions. The nomenclature used to describe the superstructures is a hybrid one, consisting of standard Strukturbericht (such as  $DO_{22}$ ) and prototype designations (such as  $MoPt_2$ ). The structures are determined as follows: the simplex algorithm automatically zeroes in on a vertex of the configuration polyhedron and returns all vertex coordinates ( $\xi_j$ ) appropriate to that structure. The investigator's task then consists in constructing an actual superstructure on the fcc lattice which has these  $\xi_j$  as structural variables. If a structure can be constructed from the vertex coordinates then it is guaranteed to be an absolute minimum energy structure, hence a true ground state.

In the past, ground state searches have often produced "non-constructible structures," which necessarily indicated that the set of constraints was too "loose," in some sense, i.e., incomplete. In the present search, fortunately (i.e., with the 13-, 14-point approximation and the 26 interactions chosen), all vertices turned out to correspond to "constructible" structures, including the very large-unit-cell  $HfGa_2$  structure, which could certainly not have been guessed at. For points on the convex hull (dotted line), a mixture of two phases, with structures given by the square symbols on either side, is the stable state.

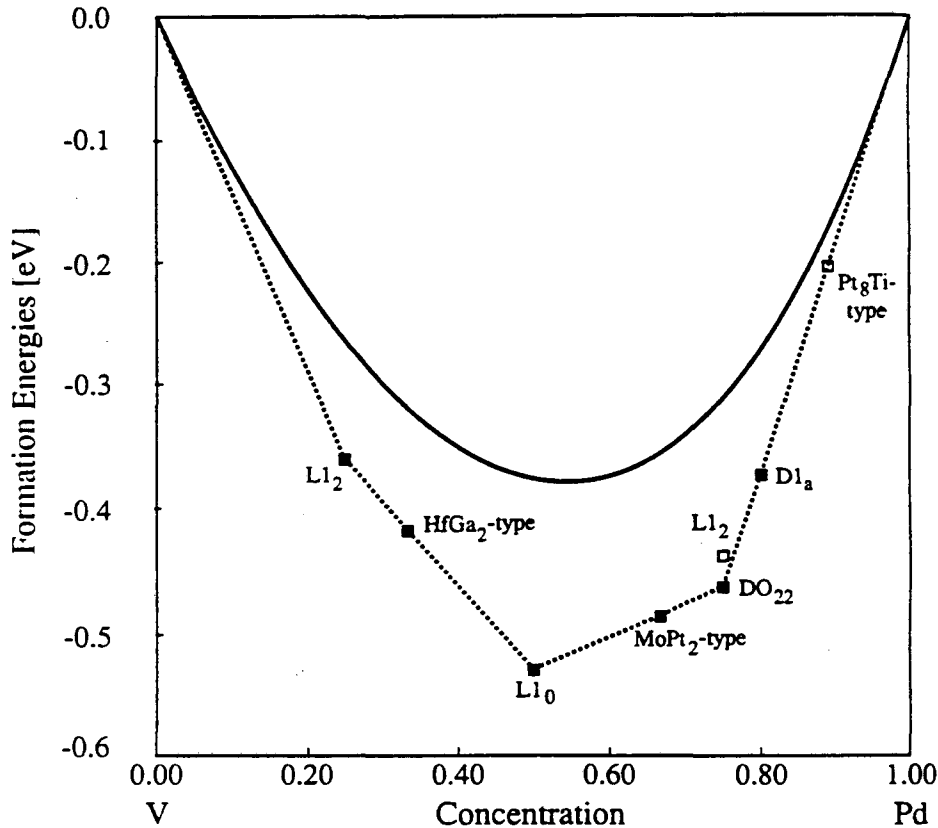


Figure 2. Formation energies for Pd-V fcc ground states as a function of Pd concentration.

## 6. Discussion

It must be emphasized that what has just been presented is a *true first-principles determination of lowest-energy structures*; *not a single adjustable or experimentally-derived parameter has been introduced*. Of course, this does not mean that the calculations were exact: local density and atomic sphere approximations were used to calculate tight-binding parameters of pure fcc Pd and V, the tight-binding Hamiltonian was used for the calculation of the ECI's, the Shiba prescription was used to determine off-diagonal hopping parameters, a limited number of recursion levels was used in the density of states calculation, a limited number of configurations was considered in the DCA method, elastic interactions and vibrational entropy were ignored, a limited number (though large, by current standards) of ECI's was calculated. However, the ground state structures were *derived* from these first-principles calculations without any preconceived notion of what the unit cells might be, only that they must be fcc superstructures. The same sort of calculation will also be performed with bcc superstructures at a later date. Then the two sets of ground states will be compared with one another.

Let us now investigate how well the present calculation compares to a previous one and to experimental evidence. Other ECI calculations on the fcc-based Pd-V system are those of Turchi et al. [19], who used the KKR-CPA-GPM scheme (Korringa-Kohn-Rostoker, Coherent Potential Approximation, Generalized Perturbation Method). The first four pair interactions calculated at

concentration 0.5 by the latter method [19] and by the present one (DCA) agree closely. Both studies show the importance of describing this system by interactions extending beyond the second-neighbor pair: truncating the inter-action set after the second-neighbor pair would stabilize the  $L1_2$  structure for  $Pd_3V$ , instead of the correct  $DO_{22}$ .

Ordered superstructures can be classified according to the dominant *special-point ordering wave* [14,20]. In fcc, there are three ordering wave families  $\langle 100 \rangle$ ,  $\langle 1\frac{1}{2}0 \rangle$  and  $\langle \frac{1}{2}\frac{1}{2}\frac{1}{2} \rangle$ . The  $L1_2$  and  $L1_0$  structures belong to the  $\langle 100 \rangle$  family, the  $MoPt_2$ ,  $DO_{22}$  and  $D1_a$  belong to the  $\langle 1\frac{1}{2}0 \rangle$  family [20]. A glance at the ground state diagram of Fig. 2 clearly shows that the V-side is dominated by the  $\langle 100 \rangle$  wave, the Pd-side by the  $\langle 1\frac{1}{2}0 \rangle$ . Competition is close, however: the  $L1_2$  and  $DO_{22}$   $V_3Pd$  structures have almost the same formation energies. Also, there is experimental evidence [21] that the short-range order above the  $Pd_3V$  transition temperature is of  $\langle 100 \rangle$  type, whereas the long-range order ( $DO_{22}$ ) is of  $\langle 1\frac{1}{2}0 \rangle$  type. For a given binary system to belong to more than one special-point family, either concentration-dependent interactions must be used, or, as in the present case, multisite interactions must be taken into account. The latter approach allows for a rigorous ground state determination to be made through the linear programming algorithm, as explained above.

Obviously, the ground state diagram of Fig. 2 cannot do full justice to the actual Pd-V phase diagram [22]. In reality, vanadium is bcc and that side of the phase diagram must be dominated by that lattice and its superstructures or other non-superstructure phases. The Pd side is dominated by the fcc lattice, as expected, and it is found that the  $DO_{22}$  and  $MoPt_2$ -type structures are predicted correctly, respectively for  $Pd_3V$  and  $Pd_2V$ . The  $L1_0$  structure is not observed in the experimentally-determined phase diagram, but a B19 structure has been reported, and described as a "distorted  $L1_0$  phase" [23]. In Fig. 2, the  $D1_a$  ( $Pd_4V$ ) and  $Pd_8V$  structure points are located practically on the tie-line between  $DO_{22}$  and pure Pd so that it is difficult to predict whether those superstructures or phase mixtures will be the true observed ground states. Somewhat surprisingly, the  $D1_a$  is not observed experimentally at temperatures for which atomic mobility is high enough to produce equilibrium states, but  $Pd_8V$  has been observed by Cheng and Ardell [24] in high-energy proton-irradiated samples. The  $D1_a$  structure is the equilibrium one for  $Ni_4Mo$ , however. In Fig. 2, the vertical distance between a structure's formation energy and the full curve of the disordered-state energy represents the *ordering energy* (at zero Kelvin) and therefore gives a rough idea of the corresponding order-disorder transition temperature. It is therefore anticipated, from consideration of Fig. 2, that the ordering temperatures of the  $Pd_4V$  and, especially,  $Pd_8V$ , will be quite low, perhaps therefore unobservable, except under accelerated kinetic conditions such as those produced by irradiation. These two structures depend, for their stabilization, on interactions beyond the second neighbor pair.

## 7. Conclusion

We have presented a rigorous, first-principles ordered ground state determination of fcc-based Pd-V intermetallic structures. The structures were not selected *a priori*, then compared energetically with one another, as is usually done, but actually derived by an algorithm which guarantees minimum energy in the given context. The cluster expansion method was used here both for calculating the configurational energy and for obtaining the inequalities required by the linear programming technique.

The cluster method is an offshoot of the original cluster variation method but is now considered to be the fundamental technique for describing alloy thermodynamics in general: in principle, any

function of configuration can be expressed as an expansion in orthonormal cluster functions. This basic property establishes the link between quantum mechanics and statistical mechanics, hence with classical thermodynamics itself. Here, only ground state applications were discussed in detail, but phase diagrams can be calculated by the CVM, and all derived quantities such as long- and short-range order parameters, diffuse intensity [24], elastic moduli as a function of atomic configuration, etc.

Many practical problems remain to be solved, however. The Pd-V case shows clearly that reliable results can only be obtained if a fairly large number of effective cluster interactions is calculated. The number of cluster functions then tends to increase exponentially, rapidly making the problem completely intractable. Computer algorithms for deriving the configuration matrix are now available [17], without which the present computations could not have been performed. Still, the complexity of the problem can be overwhelming.

It is interesting to note that, originally, the cluster approach was proposed as a method to improve the reliability of the configurational *entropy* [1]. Today, the emphasis has shifted to the configurational *energy*: it is primarily the latter contribution to the free energy that dictates which cluster approximation is required, hence whether or not the problem is tractable by present theoretical means. Undoubtedly, better algorithms will be developed in future, thereby ushering in a true first-principles thermodynamics of materials.

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