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Linear-programming method for obtaining effective cluster interactions in alloys from total-energy calculations: Application to the fcc Pd-V system

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We developed a method for obtaining effective cluster interactions in substitutional binary alloys from first-principles total-energy calculations. The method reproduces not only the formation energies, but also the ground-state line and relative energies of different structures. These quantities are crucial if the energy parametrization is to be used to compute the temperature-composition phase diagram of the alloy system. We applied the method to the Pd-V alloys, and obtained insight into the energetics of this complex alloy system. We showed that pair cluster interactions of long range (seventh or eighth nearest neighbor) are necessary to reproduce the ground-state line of the fcc Pd-rich superstructures.

I. INTRODUCTION

The ability to predict thermodynamic properties of multicomponent materials from first principles is an important step towards the understanding of phase stability in alloys. Because the electronic, vibrational, and configurational degrees of freedom in an alloy occur on very different time scales, the most successful approach in alloy theory has been to progresssively integrate out the excitations occurring on the smallest time scales.[1] After this process, only the relevant variables needed to characterize the system are retained. The Born-Oppenheimer approximation is generally accepted to be valid for removing the electronic degrees of freedom, by assigning a well-defined electronic (free) energy to every atomic configuration. Recently,[2] we also showed that, by coarse graining the alloy partition function over all the vibrational states for a given substitutional state, the total free energy of an alloy can be obtained in the phase space of a lattice model. Most of the emphasis in alloy theory has therefore been on the description of the energetics of substitutional states. In this paper, we propose a method to obtain an accurate configurational energy parametrization for substitutional alloys from first-principles total-energy calculations.

The dependence of the energy on the configurational state in a substitutional alloy can be described with a cluster expansion.[3] Given a lattice of all atomic sites, the occupancy of site i can be labeled with a spinlike variable σ_i [$\sigma_i = +1(-1)$ when an $A(B)$ atom sits on site i]. The configuration of a substitutional binary alloy with N sites can then be described with a vector $\{\sigma\}$ of N components. The energy can be expressed as

$$E(\{\sigma\}) = \sum_{\alpha} m_\alpha V_\alpha \langle \sigma_\alpha \rangle \ , \tag{1}$$

where $\langle \sigma_\alpha \rangle$ are the lattice averages of the cluster functions, defined as the product of the spin variables on the cluster α of lattice points, V_α are the effective cluster interactions (ECI), m_α is the number of clusters of type α per lattice site, and the sum is over all possible clusters α of lattice sites. The practical extension of the cluster expansion to ternary systems[4,5] and certain quaternary systems[6] has been shown recently. Sanchez, Ducastelle, and Gratias[3] proved that the expansion (1) is formally exact due to the fact that the cluster functions form a complete basis in the space of functions of configuration. When the energy of the alloy is mainly determined by the local environments (as is the case in metal alloys), the cluster expansion can be truncated, and a few pair and multisite interactions of short range are enough to parametrize the energy with enough accuracy. Then, the description of the energy of any of the 2^N configurational states of the alloy is reduced to the knowledge of a few ECI. These ECI can then be used to find the ground states of the system and to compute its phase diagram. Throughout this paper, the energy of an ordered structure computed with the total-energy method is going to be referred to as the *direct energy,* while the value obtained with the cluster expansion is going to be referred to as the *cluster expanded energy.* The challenge is, of course, to obtain an accurate energy parametrization, in which the features of the direct energies are well reproduced by the cluster expanded energies.

At least three approaches have been used in the past to compute the ECI. The Connolly-Williams (CW) method takes advantage of the fact that if a few ECI are enough to parametrize the energy, then their values can be determined by fitting a truncated form of (1) to the direct energy of a small set of ordered structures. In its first formulation,[7] the CW method consisted in fitting the values of n ECI to the direct energy of n ordered arrangements on the lattice. These direct energies can, for example, be computed from first principles within the local density approximation. Subsequent improvements[8] used more ordered structures than ECI, and through a least-squares fit obtained a more stable set of ECI, avoiding the sometimes ill-conditioned inversions. When considering a set of p ordered structure with direct energies E_j, $j=1,\dots,p$, the n ECI ($n \le p$) are obtained by solving

$$\sum_{j=1}^{p} w_j \left[E_j - \sum_{\alpha=1}^{n} m_\alpha V_\alpha \langle \sigma_\alpha \rangle_j \right]^2 = \text{minimum} \ , \tag{2}$$

where w_j is the weight assigned to the jth structure. Because the cluster expansion requires only a one-to-one correspondence between atomic positions and lattice sites, it can also model configurations where the atoms relax away from their ideal lattice sites. In the CW method, the effect on the energy of the atomic relaxations is taken into account by relaxing the geometry of the ordered structures used in the fit. In some systems, strong elastic effects lead to a slow convergence of the cluster expansion. To deal with this convergence problem, the CW method has been further improved by considering long-range pair interactions in k space,[9] effectively allowing for infinite-range pair ECI.

The direct configurational averaging method uses recursion techniques to compute the local density of states and the ECI through a real space average, usually in the tight-binding approximation.[10] In this method, the ECI are computed one at a time, using their definition.[3] At its present stage, the method does not take atomic relaxations into account.

Finally, the coherent potential approximation can be used to describe the disordered system by an effective medium and the ECI are obtained perturbing this effective medium.[11] Although this method has been able to predict general trends, its ability to include atomic relaxations has not yet been proven.

Because atomic relaxations can play a very important role in determining the phase stability of an alloy system,[9] the CW method has gained popularity (of the three methods described above, CW is the only one that takes the effect of atomic relaxations into account). Although now widely applied, the least-squares fitting procedure used in the CW method to extract the value of the ECI from the direct energies of ordered structures has the following serious limitations: (i) The CW method only fits the ECI to the *absolute* direct formation energies of ordered structures. However, ground-state and phase-diagram predictions depend on subtle differences in direct formation energies of different ordered structures. (ii) The CW method does not necessarily reproduce the relative stability of the input structures one fits to (see, for example, Ref. 12). This may cause structures that were metastable with the direct energy calculation to become stable with the cluster expansion. These structures would be present in a phase diagram computed with the cluster expansion, whereas it is clear from the direct energy calculation that they should not be. (iii) The CW method is incapable of determining what truncation of the cluster expansion is needed to reproduce the desired features of the direct formation energies of the system.

The method we have developed overcomes the limitations of the CW method mentioned above. The philosophy of the method is to reproduce not only the direct formation energies, but also the ground states and relative values of the direct formation energies of a set of ordered structures. The new method only warrants that none of the metastable structures included in the fit will become ground states when their energies are computed with the cluster expansion. However, other structures not included in the fit may be ground states of the system. In the rest of this paper, we describe the new method, and then apply it to the study of the energetics of the Pd-V system.

II. DETERMINING THE EFFECTIVE CLUSTER INTERACTIONS

As in the regular CW method, the input quantities are the direct energies of a set of p ordered structures of A and B atoms arranged on a common parent lattice ($E_j, j=1,\ldots,p$). Each direct energy is assigned an error bar Δj, i.e., $E_j \pm \Delta_j$. This error bar can be determined either by the error of the method used to obtain the direct energy or by the maximum error accepted in the cluster expanded energy. The method also needs information about the ground-state line as obtained from the total-energy method, and relative direct formation energies of different structures that we wish the cluster expansion to reproduce. Each segment of the direct ground-state line is characterized by the two ordered ground-state structures at the ends of the segment and their energy. Finally, from the description of the unit cell of each ordered structure, the lattice averages of the cluster functions are easily computed ($\langle\sigma_\alpha\rangle_j$, $j=1,\ldots,p$, $\alpha=$empty cluster, point cluster, pairs, multiplets).

With the truncation of the cluster expansion symbolized by $\alpha_{\max}$, we impose the following constraints on the ECI:

$$\sum_{\alpha}^{\alpha_{\max}} m_\alpha V_\alpha \langle\sigma_\alpha\rangle_j \le E_j + \Delta_j\ , \quad j=1,\ldots,p\ , \tag{3a}$$

$$\sum_{\alpha}^{\alpha_{\max}} m_\alpha V_\alpha \langle\sigma_\alpha\rangle_j \ge E_j - \Delta_j\ , \quad j=1,\ldots,p\ , \tag{3b}$$

$$\sum_{\alpha}^{\alpha_{\max}} m_\alpha V_\alpha \left\{ \langle\sigma_\alpha\rangle_j - \frac{(\langle\sigma_1\rangle_b - \langle\sigma_1\rangle_j)\langle\sigma_\alpha\rangle_a + (\langle\sigma_1\rangle_j - \langle\sigma_1\rangle_a)\langle\sigma_\alpha\rangle_b}{\langle\sigma_1\rangle_b - \langle\sigma_1\rangle_a} \right\} \ge \varepsilon \quad \begin{matrix} j=1,\ldots,p\ , \\ j\neq a, j\neq b\ . \end{matrix} \tag{3c}$$

Equations (3a) and (3b) require that the cluster expanded energies be within the error bars of the direct energies. Equation (3c) imposes the linear constraints to reproduce the a-b segment of the direct ground-state line. $\langle\sigma_1\rangle_j$ is the lattice average of the point cluster function, related to the concentration through $\langle\sigma_l\rangle_j = 2c_j - 1$, and ε is a small number (smaller than the energy differences involved in the problem). Other constraints can be added

TABLE I. Formation energies of ordered structures in the Pd-V fcc system, as computed with the LMTO-ASA method (see text for details). K*n* structures refer to the *n*th structure in Ref. 22 and G*n* structures refer to possible ground-state structures reported in Ref. 23. The other structures are identified by either their prototype structure, their Strukturbericht notation, or a conventional name. For some structures, alternative names are shown. All the formation energies are in meV/atom. The composition is expressed by the chemical formula of the structure. The fourth column contains the reference number where a picture of the structure can be found.

Struc.	Energy	Comp.	Ref.	Struc.	Energy	Comp.	Ref.
CuPt	−240.2	PdV	11	$L1_0$	−364.9	PdV	11
A_2B_2	−242.6	PdV	11	G4*c* = *Z*2	−314.3	PdV	23
$MoPt_2$	−394.1	Pd_2V	11	$MoPt_2$	−179.8	PdV_2	11
DO_{22}	−349.7	Pd_3V	11	DO_{22}	−199.6	PdV_3	11
$L1_2$	−281.8	Pd_3V	11	$L1_2$	−201.4	PdV_3	22
Ni_4Mo=K15	−270.7	Pd_4V	22	Ni_4Mo=K15	−157.8	PdV_4	22
W8=K13	−236.6	Pd_5V	18	W8=K13	−145.5	PdV_5	18
Pt_8Ti=K4	−192.9	Pd_8V	22	Pt_8Ti=K4	−98.2	PdV_8	22
W1	−348.3	Pd_5V_3	18	W1	−289.3	Pd_3V_5	18
K8	−158.6	Pd_7V	22	K9	−197.9	Pd_7V	22
K12	−250.5	Pd_5V	22	K19	−344.0	Pd_5V_2	22
K21	−314.8	Pd_2V	22	K22	−304.1	Pd_2V	22
K29	−328.2	Pd_5V_3	22	K30	−331.1	Pd_5V_3	22
K33	−292.3	Pd_3V_2	22	K42	−205.3	Pd_2V	22
A_5B	−230.6	Pd_5V	11	G3*a*	−239.0	Pd_2V	23
G3*b*	−308.0	Pd_2V	23	G4*a*	−236.3	Pd_3V	23
G4*b*	−259.8	Pd_3V	23	G4*d*	−194.6	PdV	23
G4*e*	−253.2	PdV	23	G5*a*	−322.6	Pd_3V_2	23
G6*a*	−293.0	PdV	23	G6*b*	−206.0	Pd_5V	23
G6*c*	−306.6	PdV	23	G6*d*	−249.6	Pd_2V	23
G6*e*	−203.7	Pd_2V	23	G6*f*	−250.4	Pd_2V	23

to require that relative stabilities of ordered structures be reproduced in the cluster expansion. Equations (3a)–(3c) are linear inequalities in the space of ECI, and can therefore be solved using any standard linear programming technique.[13] If the linear programming problem has a feasible solution in the space of ECI, then the cluster expansion with these ECI reproduces the required properties of the direct formation energies. If the volume of the polyhedron of feasible points is large, some of the constraints can be tightened to produce a better energy parametrization. If there is no feasible point, the truncation of the cluster expansion did not include enough terms to reproduce the direct energies. Then, we have two alternatives: (i) relax the constraints (increase the error bars or take out segments of the ground-state line), or (ii) include more ECI and look for a feasible point in the new space of interactions. Both of these alternatives can be carried out automatically by a computer program. One of the strengths of this method is, therefore, that it exactly recognizes whether a given truncation of the cluster expansion can reproduce the desired features of the direct formation energies.

The most important features of the substitutional excitation spectrum of the stable phases are determined by the distance of other metastable ordered structures to the ground line in the energy-composition plane. For metastable structures that are close to the direct ground-state line, a small relative error in the formation energy could imply a big relative error in its distance to the ground-state line, greatly altering the free energies of the stable phases and, therefore, the phase diagram. By requiring that the cluster expansion reproduce these distances, this problem can be avoided and a better description of the energetics of the system can be obtained. This can be done in the present method by introducing linear constraints of the form

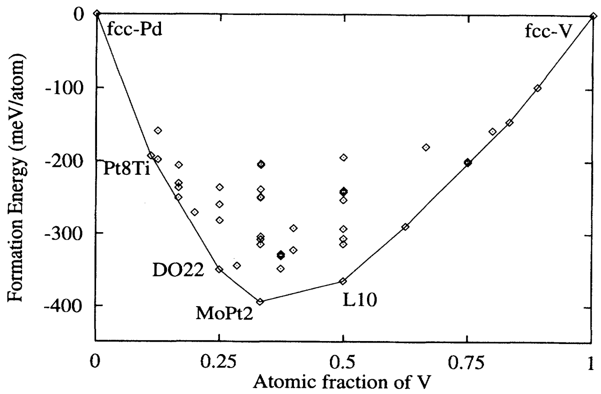

FIG. 1. Direct formation energies of the 42 ordered structures computed with the LMTO-ASA method. The ground-state line is shown and the ground-state structures on the Pd-rich side are labeled with their prototype structure (Pt_8Ti and $MoPt_2$) or Strukturbericht notation (DO_{22} and $L1_0$).

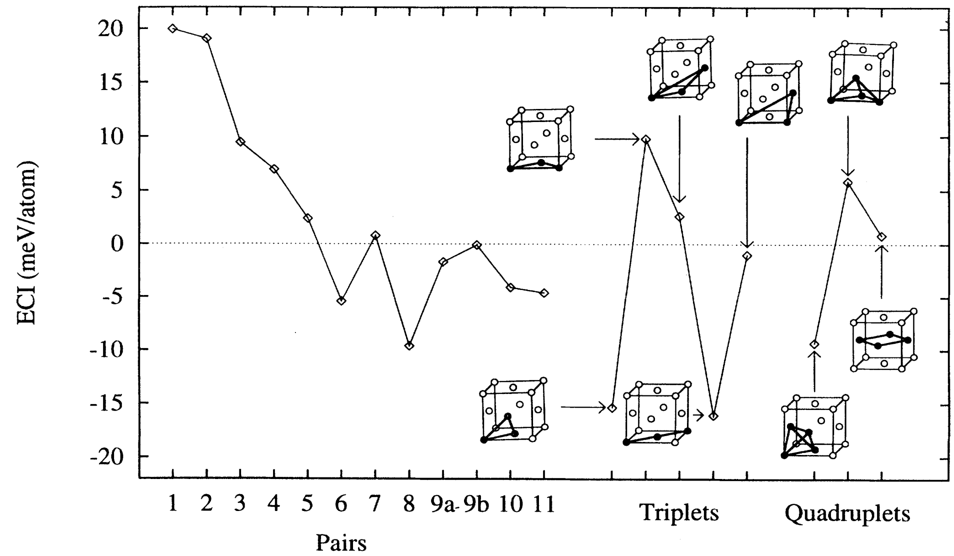

FIG. 2. Effective cluster interactions for the Pd-V system computed with the new method. The pairs are indicated with the shell number and pictures of the multiplets are shown by their ECI.

$$\Delta E_j-\delta_j \le \sum_{\alpha}^{\alpha_{\max}} m_\alpha V_\alpha \left\{ \langle\sigma_\alpha\rangle_j - \frac{(\langle\sigma_1\rangle_b-\langle\sigma_1\rangle_j)\langle\sigma_\alpha\rangle_a+(\langle\sigma_1\rangle_j-\langle\sigma_1\rangle_a)\langle\sigma_\alpha\rangle_b}{\langle\sigma_1\rangle_b-\langle\sigma_1\rangle_a} \right\} \le \Delta E_j+\delta_j \ , \tag{4}$$

where ΔE_j is the direct energy difference between structure j and the a-b ground-state tieline at the same composition, and δ_j is the error bar assigned to this quantity.

III. APPLICATIONS: ENERGETICS OF THE PD-V SYSTEM

To illustrate the method, we studied the Pd-V substitutional alloys on the fcc lattice. Much work has been recently reported on this alloy system.[14–20] Part of the theoretical interest in Pd-V alloys was motivated by a study indicating that relatively long-range interactions are needed to describe the energetics of the ordering processes.[14] Since we are studying the energy of substitutional arrangements on the fcc lattice, our studies are relevant for the Pd-rich concentrations of the system. On the V-rich side of the phase diagram, the stable phases are not based on the fcc lattice. We computed the formation energies of 42 ordered structures using the linear muffin-tin orbital–atomic-sphere approximation (LMTO-ASA) method.[21] The calculations were self-consistent and semirelativistic. We used equal atomic sphere radii for Pd and V, "combined corrections" to the ASA, and 17^3 points in the Brillouin zone for k-space integrations. The von Barth–Hedin form for the exchange and correlation potential was used. In these calculations, only global volume relaxations are taken into account. The size mismatch between Pd and V is only 3%, so the effect of other relaxations is expected to be small. Of the 42 structures, 18 coincide with the ones studied by Wolverton and Zunger[19] using similar techniques. The formation energies for these structures differ from the ones in Ref. 19 by less than 4 meV/atom, except for *W*1 (Pd_5V_3) and *W*1 (Pd_3V_5), for which the differences are 13.5 and −6.5 meV/atom, respectively. The energies of the other 24 structures have not been reported before, to our knowledge. The formation energies are shown in Table I and Fig. 1. Figures of the unit cells of these structures can be found in Refs. 11, 18, 22, and 23. Since we are interested in the energetics of Pd-rich configurations, we chose more structures on this side of the system.

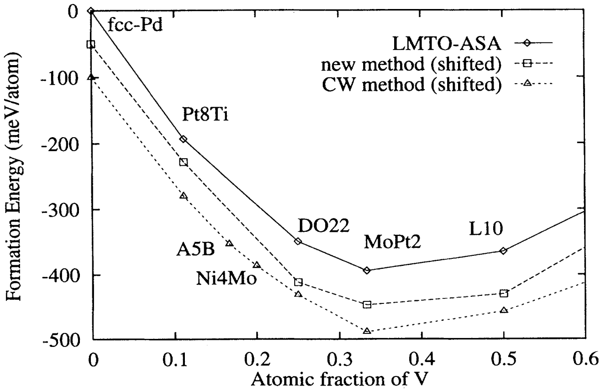

FIG. 3. Ground-state line on the Pd-rich side of the Pd-V system. The cluster expansion obtained with the new method reproduces the LMTO results, while the CW method produces two extra ground states (A_5B and Ni_4Mo) that are only metastable in the LMTO results. The curves obtained with the new method and with the CW method have been shifted down by 50 and 100 meV/atom, respectively, for clarity.

We first apply the method to find a suitable truncation of the cluster expansion that can reproduce the direct LMTO-ASA ground-state line. The ground-state structures, as obtained with the LMTO-ASA method, in the Pd-rich part of the system are fcc Pd, Pt_8Ti-type, DO_{22}, $MoPt_2$-type, and $L1_0$ (see Fig. 1). It is important to stress that we are not making use of the values of the direct formation energies in this stage. We are only asking what truncation of the cluster expansion can give the desired ground-state line. We find that the direct ground-state line cannot be reproduced with the ECI used for this system in the past.[14–20] These include pairs up to the fourth nearest neighbor, four triplets, and two quadruplets. By adding pair ECI, the direct ground-state line can be reproduced only when the seventh or eighth nearest neighbor is included. This result could not have been obtained with the CW method.

We decided to truncate the cluster expansion at the 11th nearest-neighbor distance, including five triplets and three quadruplets, for a total of 20 ECI (there are two ninth nearest neighbors not related by symmetry). The empty and point ECI are determined by requiring that the formation energies of fcc Pd and fcc V be zero. The set of 20 ECI is fitted imposing the following linear constraints: (i) the cluster expanded formation energies of the ground-state structures in the Pd-rich side should be within 15 meV/atom of the LMTO values; (ii) the ground-state line as predicted by the LMTO results on the Pd-rich side should be reproduced by the cluster expansion; (iii) the direct energy differences between the Pd-rich structures and the ground-state line should be well reproduced by the cluster expansion when this difference is relatively small; and (iv) the formation energy of the V-rich structures should be reproduced within 50 meV/atom. The resulting values for the ECI are shown in Fig. 2. These ECI capture the essential features of the energetics of the Pd-V system. Although the pair ECI decay with distance, the eight nearest-neighbor ECI is rather large. Our linear programming technique gives clear evidence that this is necessary to reproduce the LMTO ground-state line. Figure 3 shows that this set of ECI indeed reproduces the ground-state structures obtained with the LMTO method. The energy differences between the metastable Pd-rich structures and the ground-state line are shown in Fig. 4. It can be seen that the important low-lying structures are better fitted than the high-energy ones.

For comparison, we also used the CW method to fit the same set of ECI. Even with the 20 ECI used, the CW method failed to reproduce the ground-state line. Three of the structures (Ni_4Mo, A_5B, and K12) that were above the ground-state line in the direct LMTO results, were "pushed" below the ground-state line by the CW cluster expansion. Of course, a better CW fit could be obtained by adjusting the weights of the different structures in the least-squares fit [see Eq. (2)]. However, in the CW method, there is no systematic way of achieving this, and even more important, no *a priori* knowledge that a good fit is possible. The CW results are compared to the ones obtained with the new method in Figs. 3 and 4. Since the Ni_4Mo and A_5B structures are ground states of the CW energy parametrization, they would be stable phases in a phase diagram computed with these ECI, contrary to what the LMTO computations predict. The stability of the Ni_4Mo and A_5B phases, and a relatively poor fit to the low-energy metastable structures would greatly affect the topology of the phase diagram. This problem is naturally avoided in the new method, requiring that the direct ground-state line and the direct energies of structures close to it be well reproduced by the cluster expansion.

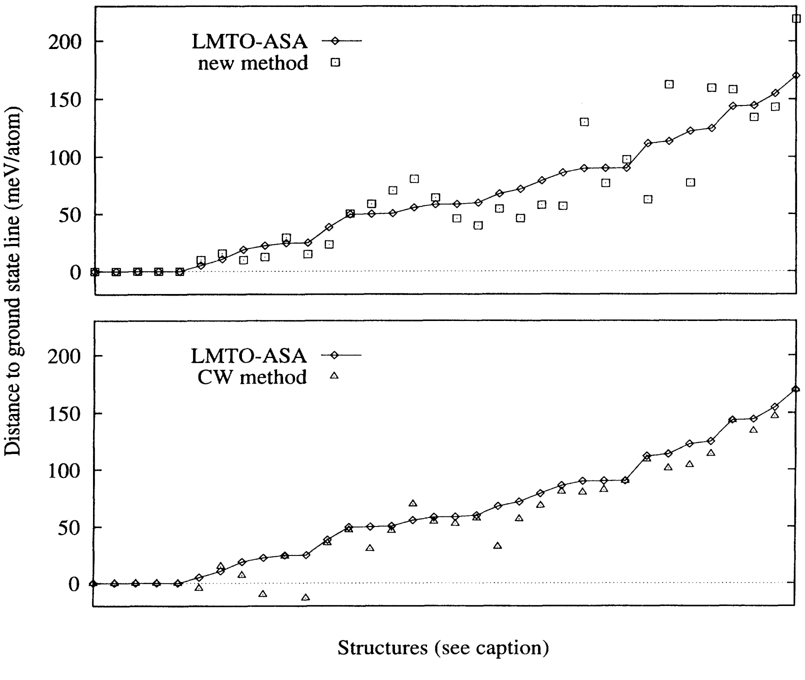

FIG. 4. Energy differences between the Pd-rich structures and the tielines defined by the sequence fcc-Pd, Pt_8Ti-type, DO_{22}, $MoPt_2$-type, and $L1_0$. On the abscissa, the Pd-rich structures are ordered in increasing distance to the tielines as obtained with the LMTO method. For the LMTO results and the energy parametrization of the new method these tielines define the ground-state line, and all the energy differences are positive. The energy parametrization obtained with the proposed method reproduces the ground states and fits the structures with energies close to the ground-state line better than structures with high energy. The CW results fail to reproduce the ground states (negative points in this plot) and the fits to the low-energy structures are worse than the ones obtained with the proposed method, while the high-energy structures are well reproduced.

Before using a cluster expansion (obtained with either the CW method or the new method) to compute the phase diagram of an alloy system, the ground states of the system should be computed with the same cluster expansion. If any of the ground-state structures is not within the set of structures used to derive the ECI, its cluster expanded energy should be checked against the direct energy method. If it is not a ground state in the direct energy method or if its energy is badly reproduced by the cluster expansion, the ECI should be recomputed including this structure in the set of structures the cluster expansion is fitted to.

IV. CONCLUSIONS

The proposed method to get ECI from the direct formation energies of ordered structures overcomes the limitations of the Connolly-Williams approach by taking into account the relative stabilities of different structures and the ground-state line of the alloy system. These relative energies can have a strong effect on the predicted phase diagram of the alloy system, especially for ordering systems with many structures close to or on the ground-state line. By applying the method to the Pd-V alloy system, we found that relatively long-range interactions (seventh or eighth nearest-neighbor pairs) are needed to reproduce the ground-state line obtained with the LMTO-ASA method. By truncating the cluster expansion at the 11th nearest-neighbor distance, we found a set of ECI that reproduces most of the subtle energy differences in the Pd-V system. The method can be easily extended to the *k*-space formulation,[9] and to volume-dependent ECI.

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