

Reliable First-Principles Alloy Thermodynamics via Truncated Cluster Expansions

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In alloys cluster expansions (CE) are increasingly used to combine first-principles electronic-structure calculations and Monte Carlo methods to predict thermodynamic properties. As a basis-set expansion in terms of lattice geometrical clusters and effective cluster interactions, the CE is exact if infinite, but is tractable only if truncated. Yet until now a truncation procedure was not well defined and did not guarantee a reliable truncated CE. We present an optimal truncation procedure for CE basis sets that provides reliable thermodynamics. We then exemplify its importance in Ni₃V, where the CE has failed unpredictably, and now show agreement to a range of measured values, predict new low-energy structures, and explain the cause of previous failures.

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Cluster expansion (CE) is increasingly used as a valuable tool for predicting and interpreting thermodynamic effects in a wide class of materials and problems, including precipitation [1–4], solubility limits [5], ionic diffusion [6], surface alloying [7] and patterning [8], vacancy [9] and chemical [3,10] ordering. As a means for multiscaling based on density-functional theory (DFT) electronic-structure energetics, the CE is a basis-set expansion in n -body clusters (associated with n Bravais lattice points) and effective cluster interactions (ECI) that specify configurational energies. Except for implicit DFT errors in the energy database, the CE is exact for an infinite basis, but impractical if not vastly truncated [11,12]. Although there are many successes, a truncated CE can and has unpredictably failed.

We present a new method for an optimal truncation of the basis set that gives reliable thermodynamics. We then detail its importance in face-centered-cubic (fcc) Ni₃V, a system with order-disorder transition from disordered A1 phase to ordered D0₂₂ phase at T_c of 1318 K [13]. Previous CE for Ni₃V [14–16] had errors of 40% to 1000% for a range of thermodynamic properties, prompting a search for missing physics [16]. We show that our new method allows more reliable predictions, including that of key low-energy configurational excitations. As a synopsis, we compare in Table I our CE results, along with the previous ones, with experimental values of T_c and $\Delta E_{\text{SRO}}^{L_1-L_2-D0_{22}}$, the energy difference between D0₂₂ and metastable L₁ structures, as assessed from the short-range order (SRO) measurements [17,19]. The new CE now agrees with a range of experimentally assessed values (more below). We find that prior failure in Ni₃V is due to inappropriate truncation of the cluster basis set and overfitting to get the ECI—underscoring again the need for careful application of basis-set methods. We have tested this new CE method on a few cubic and noncubic binaries and ternaries and found it to be especially important when multibody ECI are significant.

Cluster Expansions.—Any alloy configuration may be represented by a set of occupation variables $\{\xi_p^\alpha\}$, with $\xi_p^\alpha = 1(0)$ if the site p is (is not) occupied by an α atom. Composition c^α is the thermal average and the site average of $\{\xi_p^\alpha\}$ with $0 \leq c^\alpha \leq 1$. The energy of any atomic configuration σ can be written in a CE [11] using the n -body ECI $V_f^{(n)}$:

$$E_{\text{CE}}(\sigma) = V^{(0)} + \sum_{n,f,d} V_f^{(n)} \bar{\Phi}_{fd}^{(n)}(\sigma). \quad (1)$$

Sums are over symmetry-*distinct* (n, f) and symmetry-*equivalent* ($d = 1, \dots, D_f^{(n)}$, the degeneracy) clusters. A CE basis can be also presented as a product of orthonormal Chebychev polynomials based on ξ_p^α [11]. The n -site correlation function $\bar{\Phi}_{fd}^{(n)} = \langle \xi_{p'} \xi_{p''} \dots \xi_{p^{(n)}} \rangle$ is given by an ensemble average over the fixed sets $\{p\}_{fd}^{(n)}$ defining the n -body clusters of type (f, d) , see Fig. 1. When evaluated above T_c , $\bar{\Phi}^{(2)}$, for example, are related to the SRO. If the ECI are known, then the energy of any configuration can be predicted.

A CE can be truncated if there is rapid convergence of the ECI $V_f^{(n)}$ with increasing distance r (e.g., as measured by cluster radius of gyration or circumscribed sphere) and with increasing number of sites n in a cluster f , i.e., smaller n -body clusters are more physically important. Also $V_f^{(n)}$ for $n > n_0$ uncorrelated sites have their contributions to (1) suppressed by $\bar{\Phi}^{(n)} \sim c^n$, i.e., $V^{(n)} \bar{\Phi}^{(n)} \rightarrow 0$, and can be neglected. The magnitudes of $V^{(n)}$ typically

TABLE I. New truncated CE (CE₂ and CE₃) and experimental [17] values of T_c (kelvin) and the $\Delta E_{\text{SRO}}^{L_1-L_2-D0_{22}}$ (meV/atom) assessed from SRO, along with the former CE [14] and CPA [18] results. Details in text.

	CE ₂	CE ₃	Expt.	Old CE	CPA
T_c (K)	1335	1370	1318	1900	
$\Delta E_{\text{SRO}}^{L_1-L_2-D0_{22}}$	22 ± 16	17 ± 15	12 ± 5	101	7–12

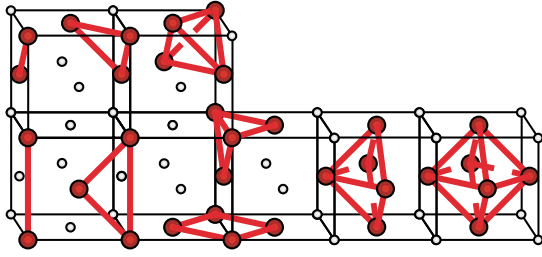


FIG. 1 (color online). The 2- to 6-body clusters for 1st and 2nd fcc neighbors. Including clusters up to 4-body in upper set (6-body in both sets) form a locally complete basis in the range of 1st (2nd) neighbors. These clusters form tetrahedron (tetrahedron-octahedron) approximations used in cluster-variation method [11].

become smaller for larger n , although for some systems ECI convergence is not rapid: such is Li_xNiO_2 where Jahn-Teller distortions control Li-vacancy ordering and ionic conduction and are reflected only in long-range multibody ECI [20]. For a truncated CE, ECI are obtained via *structural inversion* [21,22] at fixed c for c -dependent (canonical) ECI or versus c for c -independent (grand-canonical) ECI; these sets of ECI are related [23,24]. First, a set of N fully ordered (few atoms per cell) structures is *somehow* chosen and their DFT energies E_{DFT}^i ($i = 1 \dots N$) are calculated. Then, a set of M clusters ($M < N$) is *somehow* picked for use in (1) and Φ are calculated for each structure. A system of N linear equations (1) with M unknown ECI is solved by least-squares (LS) fitting—which unavoidably includes DFT errors in energy differences. As is obvious, the sets of structures and clusters used to get the ECI are not uniquely defined.

New Method.—Here we propose a method that, given a set of structural energies, unambiguously defines a set of clusters (and ECI) to provide an optimal truncated CE and yield reliable thermodynamics. First, we note that if $V^{(n)}(r > r_0^{(n)}) \equiv 0$, the truncated CE basis with local compact support that includes *all* clusters in $r_0^{(n)}$ is *locally complete* and exact; whereas, if $V^{(n)}(r > r_0^{(n)}) \approx 0$, this truncated CE is approximate and has an error. With no *a priori* knowledge of which clusters are required to represent well a given alloy, the CE error is minimal, in a Rayleigh-Ritz variational sense, if all admissible n -body clusters (basis functions) of smaller spatial extent ($r \leq r_0^{(n)}$) are included before the larger ones. In brief, having N E_{DFT}^i to be fitted, we can establish a variational CE basis by simple rules *ad vitam aut culpam* that implement easily computationally: (i) If an n -body cluster is included, then include *all* n -body clusters of smaller spatial extent. (ii) If a cluster is included, include *all its subclusters*. (iii) To prevent both underfitting and overfitting, *minimize* [25,26] the cross-validation (CV) error [27,28]:

$$CV^2 = \frac{1}{N} \sum_{i=1}^N (E_{\text{DFT}}^i - E_{\text{CE}'}^i)^2. \quad (2)$$

$E_{\text{CE}'}^{(i)}$ in (2) is *predicted* by a fit to $N - 1$ DFT energies *excluding* E_{DFT}^i , rather than to all N as in a LS fit. (This is an “exclude 1” CV, whereas an “exclude 0” CV is a LS fit.) While LS measures the error in reproducing known values of E_{DFT}^i , CV error estimates an uncertainty of *predicted* values. Both too few (underfitting) or too many (overfitting) parameters give poor prediction. The new rule 1, with well-established rule 2, now makes it easy to define uniquely all clusters in a truncated, variational CE basis by the number of n -body clusters (or the size of the largest n -body cluster) for each $n \leq n_0$. In particular, rules 1 and 2 permit a hierarchy of ranges for n -body clusters, i.e., $r_0^{(n)} \geq r_0^{(n+1)}$ for all n , giving a locally complete basis for strict equalities, while the inequality (e.g., more extended 2-bodies, less extended 3-bodies, even less extended 4-bodies, etc.) allows for fewer clusters. Because shorter-ranged and lower-order ECI are more important, rule 1 (rule 2) prohibits excluding more important ECI and transferring their weight to less important longer-ranged (higher-order) ones.

Once constructed, an optimal CE can be used to predict energy of any structure within the CV error. The CE is valid if the lowest structural energies (including the ground state) and fully disordered state energies are correct within the accuracy given by the CV error. A valid optimal CE provides reliable thermodynamics.

Application.— We now construct and assess the new canonical CE for Ni_3V based on 45 fully relaxed structural DFT energies, with relative accuracies of ~ 1 meV/atom [29]. A selected set of energies is given in Table II.

To examine effects of the new truncation method on prediction, we first limit the CE basis to pairs only and find that the pairs-only CV is minimal for 2 (nearest and next-nearest) pair interactions, see Fig. 2. Within this range, the symmetry-distinct clusters are two pairs, two 3-bodies, three 4-bodies, a 5-body pyramid, and a 6-body octahedron, see Fig. 1. The CE with two pair and two triplet interactions (denoted CE_2) with minimal CV of

TABLE II. Selected Ni_3V energies (meV/atom) from DFT and CE relative to $E_{\text{DFT}}^{D0_{22}}$, along with those of disordered state, its approximation by SQS_{16} [35], and (001) APB.

Structure	E_{DFT}	E_{CE_2}	δE_{CE_2}	E_{CE_3}	δE_{CE_3}
$D0_{22}$ ($1\frac{1}{2}0$)	0.0	7.1	7.1	10.5	10.5
$D0_{23}$ ($1\frac{1}{4}0$)	25.4	31.6	6.2	35.8	10.4
	33.7	31.6	-2.1	35.8	2.1
$L1_2$ (100)	101.2	56.1	-45.1	61.1	-40.1
	147.8	170.6	22.8	154.7	6.9
SQS_{16}	155.4	135.8	-19.7	152.0	-3.5
Disordered		109.8		115.1	
(001)APB	101.6	98.0	-3.6	101.1	-0.5
$L1_2$ - $D0_{22}$	101.2	49.0	-52.2	50.5	-50.7
$D0_{23}$ - $D0_{22}$	25.4	24.5	-0.9	25.3	-0.1

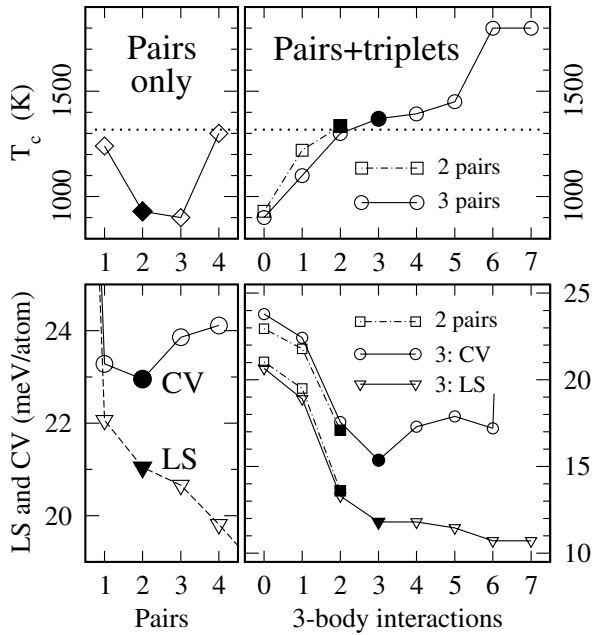


FIG. 2. (upper) The predicted and observed (dotted line) T_c (K), and (lower) the CV and LS errors (meV/atom) vs ECI truncation. Results are for CE with pairs only (left) and for 2 and 3 pairs with a number of 3-body ECI (right). The minimal CV and LS are given by solid symbols.

15.5 meV within this range gives T_c at 1335 K, near the observed 1318 K. Including tetrahedron does not significantly alter T_c , as expected for a 4-body cluster at $c = 1/4$, as $c^4 \ll 1$ and $V^{(4)}\Phi^{(4)} \rightarrow 0$. For optimal truncation, including the most compact 4-body cluster is necessary before including any other more extended 4-body or higher-order clusters. Within our set of 45 arbitrary structures only one (147.8 meV/atom in Table II) has contribution from the most compact 4-body cluster, so any CE including this cluster has formally infinite (thus not minimal) CV, so an optimal CE should contain pairs and triplets only. Indeed, the optimal CE (denoted CE_3), see Fig. 2, includes three pair and three triplet interactions and yields T_c of 1370 K, again near the observed value and well within the CV error of ± 15.2 meV. Both CE_2 and CE_3 are examples of the localized CE hierarchy allowed by rules 1–3. Notably, we find no failure or ill description of thermodynamics for optimal truncation embodied in the new rules; see Table I.

Moreover, we predicted from these optimal CE that Ni_3V has numerous metastable long-period superstructures (LPS) of the type $\langle 0 \frac{1}{2m} 1 \rangle$ with $m \geq 1$. The $D0_{22}$ ground state is $m = 1$, $D0_{23}$ is $m = 2$, and $L1_2$ is $m = \infty$, see Table II. We then confirmed by direct DFT calculations that over 23 metastable structures are between $D0_{22}$ and $L1_2$. Clearly, structural energy differences then will be sensitive to thermal antisites or partial-order, i.e., chemical environments that distinguish $D0_{22}$ from other low-energy structures.

The relative energies of $D0_{22}$ and $D0_{23}$, which can be viewed as $D0_{22}$ with (001) antiphase boundaries (APB), gives an estimate of the (001) APB energy per site of the antiphase plane: $E^{APB} = 4[E^{D0_{23}} - E^{D0_{22}}]$. In Table II, our calculated $E_{DFT}^{APB} = 101.6$ meV and CE_3 -predicted $E_{CE}^{APB} = 101.1$ meV agree at perfect long-range order. However, binaries with first-order transitions have order parameters η (defined in [18]) that jump from 0 to 0.7–0.9 at T_c . For partial-order below T_c as in experiment, we predict that $E_{CE}^{APB}(\eta)$ are 81, 65, and 50 meV for η 's of 0.9, 0.8, and 0.7, respectively. From superdislocation separation measurements, assessed values are 52 ± 20 meV at 273 K and 55 ± 18 meV at 900 K [17], with roughly constant $\eta < 1$ due to lack of kinetics.

The real-space Warren-Cowley SRO parameters α_{lmn} were calculated using our CE within Monte Carlo at $T = 1.04T_c$, as in experiment. The proper way to compare calculated SRO to experimental data is in [4]. Full details of the agreement between calculated and experimental α_{lmn} will be given elsewhere. However, the energetics associated with SRO given by $\Delta E_{SRO}^{L1_2-D0_{22}} \approx k_B T (\alpha^{-1}(100) - \alpha^{-1}(1\frac{1}{2}0)) / 16c(1-c)$ can be directly estimated from the calculated $\alpha(\mathbf{k})$ at $\{1\frac{1}{2}0\}$ and $\{100\}$ \mathbf{k} -points, as done experimentally [17]. We obtain 17 ± 15 meV for CE_3 at 1392 K, now in agreement with experiment [17] and coherent-potential approximation (CPA) results [18], see Table I. Our results confirm the CPA explanation for Ni_3V SRO energetics and the discrepancy between $T = 0$ K DFT results and measurements as arising from the strong dependence of $E^{L1_2}(\eta)$ on the state of partial order [18].

Finally, we discuss issues that led to previous poor Ni_3V results. For the range of ECIs included in our truncated CE basis sets, $\Delta E_{CE}^{L1_2-D0_{22}} \equiv [E_{CE}^{L1_2} - E_{CE}^{D0_{22}}] = 2[E_{CE}^{D0_{23}} - E_{CE}^{D0_{22}}] \equiv E^{APB}/2$, as verified in Table II. So for a truncated CE, $L1_2$ can be viewed also as a (001) APB in $D0_{22}$. Other LPS, e.g., with $E_{DFT} = 33.7$ meV/atom and $E_{DFT}^{D0_{23}} = 25.4$ meV/atom in Table II, also have indistinguishable energies within the truncated CE. This observation has great import in Ni_3V . Table II shows that $\Delta E_{CE}^{L1_2-D0_{22}}$ and $\Delta E_{DFT}^{L1_2-D0_{22}}$ are not equal. This implies again that there is a strong configurational dependence of partially ordered $L1_2$ energy on η , as indeed shown by CPA calculations [18]. Because $L1_2$ is highly metastable with respect to $D0_{22}$, a truncated CE will be suspect versus η (particularly for $\eta \sim 1$) unless all clusters that distinguish $L1_2$ from $D0_{22}$, and similar LPS, are included in the basis. In Refs. [14–16], $\Delta E_{CE}^{L1_2-D0_{22}}$ at 0 K was forced to coincide with $\Delta E_{DFT}^{L1_2-D0_{22}} = 101$ meV by overfitting and including certain 3- and 4-body clusters arbitrarily that created an invalid CE and hence inaccurate energetics. Our truncated CE properly describes the observed thermodynamics, but not high-energy and ill-described structures such as fully ordered $L1_2$ that are unimportant for thermodynamics, as evidenced in Table II. Of course, calculating more DFT structural

energies and properly extending the CE basis to include critical n -body clusters would describe everything more reliably.

Generally speaking, neglecting stronger interactions and assigning their weight to weaker and less physically important longer-range [or higher-order] ones, i.e., violating rule 1 [or rule 2], leads to inaccurate predictions of energetics. Overfitting (neglecting rule 3) results in large errors in predicted energies, which were not used in the fit. Combined violations can result in dramatic failures: for example, previous CE for Ni-V [14] overfitted energies (violating rule 3) and included, e.g., a longer-ranged 4-body before the most compact one (violating rule 1); hence the disagreement with experiment and CPA. Previous CE results are generally valid if only rules 1 and 2 were obeyed with no large overfitting; in such cases, minimizing the CV error leads only to a moderate improvement of accuracy. The optimal CE basis truncation presented has an error that is variational, which is not necessarily the case for other basis-set truncation and reduction methods.

In summary, the cluster-expansion method is a valuable first-principles tool for predicting and interpreting thermodynamic behavior in alloys. With convergence and reliability in mind, we presented a simple variational method for the optimal truncation of the cluster-expansion basis set. We presented the method as a set of rules that are computationally easy to implement. For a given set of DFT structural energies and no *a priori* knowledge of which clusters are needed to represent a particular alloy well, our truncation method provides a unique optimal choice of clusters based on their contribution to thermodynamics and variational reduction in error, avoids choosing clusters by intuition, and gives reliable thermodynamic predictions. We exemplified the importance of this new approach in fcc Ni₃V by predicting important new metastable structures and by showing agreement with order-disorder temperature, antiphase boundary energy, and short-range order energetics, all quantities missed by previous cluster-expansion applications. We also elucidated the origin of the previous failures. Without *a priori* information, the new cluster-expansion strategy allows reliable thermodynamic predictions in alloys.

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