

Predicting structural energies of atomic lattices

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The complexity of current *ab initio* quantum-mechanical calculations of the total energy of given distributions of atoms on a periodic lattice often limits explorations to just a few configurations. We show how such a small number of calculations can be used instead to compute the interaction energies of a generalized Ising model, which then readily provides predicted energies of many more interesting configurations. This is illustrated for AlAs/GaAs systems.

I. INTRODUCTION

The prediction of the stable crystal structure of a given compound has traditionally been carried out either through phenomenological Pauling-type approaches,¹ or by crystal-packing algorithms with semiclassical atom-atom potentials,² or more recently, by directly searching the minimum of the quantum-mechanical total energy of the ion-plus electron system.³ While the latter *ab initio* approach has the advantage of directly reflecting the way in which the electronic structure selects certain equilibrium crystal configurations, it is also, by far, the most difficult. Involving repeated (“self-consistent-field”) solutions of a Schrödinger equation within some basis of M orbitals per atom, it requires as many as $(MN)^3$ operations for each N -atom configuration, yielding also an enormous amount of intermediate data (e.g., NM eigenvalues) whose informational content for the problem at hand is rather small (one value of the total energy per trial structure). Since even the more restricted problem of finding the ground state of a substitutional *binary AB* alloy involves as many as 2^N possible configurations on a crystal lattice with N sites, this approach³ has been limited in the past to study, just a few, $O(10)$ structures with a small number of atoms per unit cell. We show here how one can simply and accurately explore in an *ab initio* fashion the total energy of the various lattice configurations of a binary substitutional alloy, given the total energies of only $\sim O(10)$ lattice configurations. This is done by extracting, from a limited number of such quantum-mechanical calculations, the “building blocks” of cohesion: the contributions of N_f different clusters of atoms to the “glue” holding the solid together. After establishing convergence of the total-energy expansion in terms of N_f clusters, we can predict energies of new structures (which are often too difficult to calculate directly) by assembling these building blocks in different geometrical ways. The effort involved is just linear in N_f ; comparison of the predicted energies with those obtained (when possible) by direct calculations demonstrates the accuracy of this approach. This opens a practical way for exploring quantum mechanically the stability of a large number of *lattice configurations*, including ordered superstructures and random alloys.

II. METHOD

The idea of a “cluster expansion” of a physical property $P(\sigma)$ of any given configuration σ of A and B atoms on a N site lattice is not new. It is the cornerstone of all Ising-type Hamiltonians in statistical mechanics.⁴ Indeed, one can rigorously⁵ expand any lattice property $P(\sigma)$ in terms of the contributions p_f of all elementary clusters or “figures” f (i.e., a given selection of k_f sites out of the total N sites) as

$$P(\sigma) = \sum_{f=1}^{2^N} \Pi_f(\sigma) p_f, \quad (1)$$

where $\Pi_f(\sigma)$ is the product of the “spins” \hat{S}_i at the vertices of f ($\hat{S}_i = +1$ if site i is occupied by atom B , and $\hat{S}_i = -1$ if occupied by A ; we assume that there are no “broken bonds” or vacancies). This sum can be reduced by including in it only the symmetry inequivalent figures F , replacing $\Pi_f(\sigma)$ by its sum $ND_F \bar{\Pi}_F(\sigma)$ over the equivalent figures in the lattice:

$$P(\sigma) = N \sum_F D_F \bar{\Pi}_F(\sigma) p_F, \quad (2)$$

where D_F is the average number of figures F per site. Each figure $F = (k, m)$ has k vertices, separated by up to an m th neighbor distance, e.g., $F = (2, m)$ denotes pairs $(2,1)$, $(2,2)$, $(2,3)$, etc. between first, second, and third neighbors, respectively, while $F = (3, m)$ and $F = (4, m)$ denote the corresponding three-body (triangular) and four-body terms. Many previous applications of the Ising-type Hamiltonian of Eq. (2) have not calculated $p_{k,m}$ from a microscopic theory. Instead, it was often postulated that a given set of interactions describe some generic physical systems; nearest-neighbor pair interaction models⁴ ($k=2, m=1$) are one of the popular idealizations of Eq. (2). The general expansion (2) can, however, be made useful for predicting structural energies of solids to the extent that a reasonably rapidly convergent series of interactions $\{p_{k,m}\}$ can be calculated *a priori*. Knowledge of just a few such building blocks would then suffice to describe many more structures.

Writing Eq. (2) for pure $\sigma = A$ and pure $\sigma = B$ and substituting back into Eq. (2) gives

$$P(\sigma) = [(1-x)P(A) + xP(B)] + \Delta P(\sigma), \quad (3)$$

where the *excess* property is

$$\Delta P(\sigma) = \sum_{m>0} \sum_{k>1} D_{k,m} [\bar{\Pi}_{k,m}(\sigma) - \eta] p_{k,m}, \quad (4)$$

and $\eta=1$ when k is even and $\eta=(2x-1)$ when k is odd. We see that this cluster expansion needs to capture only the *difference* $\Delta P(\sigma)$ between the property $P(\sigma)$ of some structure $A_{1-x}B_x$ and the linearly weighted sum over the same properties in the pure A and B lattices. Indeed, such differences are often much smaller than $P(\sigma)$ itself, e.g., for P =molar volume, Vegard's rule states that $\Delta P \approx 0$, for P =total energy, the formation enthalpy ΔP is often only $\sim 10^{-6}$ of P , and for P =optical band gap, the "bowing parameter" ΔP is usually less than 10% of P . Moreover, Bieber and Gautier^{6(a)} and Sluiter and Turchi^{6(b)} calculated $\Delta P(\sigma)$ of Eq. (4) for binary transition-metal alloys using an empirical tight-binding model Hamiltonian, finding that the $\{p_{2,m}\}$ series indeed converges rapidly.

A number of previous attempts at the problem tried to expand $P(\sigma)$ [rather than the smaller $\Delta P(\sigma)$], or² identified $p_{k,m}$ with interatomic interaction *potentials*. Depending on the type of solid, such potentials could be long ranged (e.g., Coulombic), rendering the series slowly convergent. Instead, we will identify the left-hand side of Eq. (4) with the excess total electron plus ion energy of a periodic structure σ , calculating this ΔP quantum mechanically by summing explicitly over all potentially long-range interactions. In practice, we will use the local-density formalism⁷ as implemented by the first-principles pseudopotential method,⁸ obtaining, thereby, the self-consistent Born-Oppenheimer energy of structure σ . Having integrated out the electronic degrees of freedom, we will then invert the problem, searching for a set of *effective* interaction energies (not potentials) $\{p_{k,m}\}$, which produce through Eq. (4) the independently calculated $\{\Delta P(\sigma)\}$ for a range of periodic structures $\{\sigma\}$. We will then consider a *hierarchy* of figures (k,m) , establishing how many are needed to accurately describe the excess energies of structures *outside* the set $\{\sigma\}$ used to determine $\{p_{k,m}\}$. To do so we perform the following.

TABLE I. Calculated formation energies (in meV/4 atoms) of various ordered $A_p B_q$ structures ($A = \text{AlAs}$, $B = \text{GaAs}$). The structures can be characterized as superlattices of repeat periods (p,q) in various orientations given in this table, except for the luzonite AB_3 (predicted energy, 10.31; direct calculation, 10.42) and A_3B (predicted energy 10.31; direct calculation, 10.16) which are not superlattices. We use the pseudopotential calculated excess energies of six structures, denoted by an asterisk (including pure AlAs and GaAs), to extract six interaction energies (in meV) $p_{0,1} = +5.2762$, $p_{1,1} = 0.0000$, $p_{2,1} = -0.8056$, $p_{2,2} = -0.0362$, $p_{2,3} = -0.0265$, and $p_{2,4} = -0.0025$. These six values were then used to predict, via Eq. (4), the energies of the remaining 21 structures. In each case we list the predicted value and below it the value obtained directly from the *ab initio* calculation. The standard deviation for 21 predictions is 0.13 meV, close to the relative precision (~ 0.1) of the underlying *ab initio* calculation.

Orientation formula	[111]	[001]	[110]	[201]	[113]
AB	CP	CA	CA	CA	CP
	10.74*	13.74*	13.74*	13.74*	10.74*
	10.74	13.74	13.74	13.74	10.74
AB_2	$\alpha 1$	$\beta 1$	$\gamma 1$	$\gamma 1$	$\gamma 1$
	7.39	9.57	11.39	11.39	11.39
	7.41	9.70	11.62	11.62	11.62
A_2B	$\alpha 2$	$\beta 2$	$\gamma 2$	$\gamma 2$	$\gamma 2$
	7.39	9.57	11.39	11.39	11.39
	7.50	9.88	11.66	11.66	11.66
AB_3	V1	Z1	Y1	F1	W1
	5.54	7.18	8.75	10.19	8.77
	5.49	7.12	8.68	10.31	8.78
A_2B_2	V2	Z2	Y2	CH	W2
	5.72	7.48*	10.64	13.50*	12.16
	5.65	7.48	10.48	13.50	12.13
A_3B	V3	Z3	Y3	F3	W3
	5.54	7.18	8.75	10.19	8.77
	5.55	7.22	8.65	10.13	8.74

(i) Define a set of N_s periodic crystals A_pB_q representing a range of compositions and atomic plane orientations \mathbf{G} ; Table I and its caption give 27 examples (including the binaries) for the fcc symmetry.

(ii) Calculate quantum mechanically from band-structure theory the excess total energy $\Delta E(s)$ of these N_s periodic structures. Here, the ion-ion, electron-ion, and electron-electron (Coulomb, exchange, and correlation^{7,8}) interactions are treated self-consistently in an *ab initio* fashion. The electron-ion terms are represented by nonlocal pseudopotentials;⁹ the wave functions are expanded in a basis set of $M \approx 150$ plane waves/atom, and all Hamiltonian matrix elements are computed by extending all integrals and lattice sums to convergence. Since for the example studied here ($A = \text{AlAs}$ and $B = \text{GaAs}$) the end-point compounds have equal molar volumes, all calculations are done at a fixed (theoretically obtained) equilibrium volume. Great care was exercised to assure that the calculated excess energies $\Delta E(s)$ have the same precision (within 0.1 meV/atom) for all structures; we use precisely equivalent basis sets, Brillouin-zone sampling,¹⁰ and stringent self-consistency conditions. These calculated energies $\Delta E(s)$ for all ordered structures (defined in Table I and its caption) are shown in Fig. 1; they exhibit a nonintuitive distribution of energies whereby certain atomic-plane orientations [e.g., (111)] have the lowest energies, others [e.g., (201)] have the highest ones.

(iii) To examine the expansion (4), we first fit all of the $N_s = 27$ calculated excess energies to a set of $N_f < N_s$ interactions $\{p_{k,m}\}$, systematically extending the range of

(k, m) to obtain convergence. Using only $N_f = 13$ terms produces an excellent fit¹¹ with the root-mean-square error of 0.097 meV, comparable to the intrinsic relative precision of the *ab initio* calculations. More importantly, these interactions $p_{k,m}$ show convergence with the size of F , e.g., the pair ($k=2$) energies decay with interatomic separation m : they are -0.8075 , -0.0279 , -0.0225 , -0.0051 , -0.0001 , and -0.0075 for $m=1, 2, 3, 4, 5$, and 6, respectively. The same is true for the three-body terms $p_{3,1} = +0.0075$, $p_{3,2} = -0.0021$, and $p_{3,3} = +0.0003$, while the four-body terms are rather small: $p_{4,1} = +0.0009$ and $p_{4,2} = -0.0034$.

(iv) Given this rapid convergence, we now select the figures that give the largest contribution $D_{k,m}p_{k,m}$ to the energy and use these to *predict* the energies of other structures. In addition to the normalization terms (0,1) and (1,1), we use the pair interactions (2,1), (2,2), (2,3), and (2,4) [the (2,4) pair has a higher multiplicity D_F than the (2,6) pair]. Using just these six figures and $N_s = 6$ structures, denoted in Table I by asterisks, we obtain by direct matrix inversion of Eq. (4) a set of six interaction energies, given in the caption of Table I. These are now used to *predict* the energies of the *remaining* 21 structures, whose energies were not used in the determination of the p_f 's. Table I shows that direct calculations on only 6 configurations can be used to predict the quantum mechanically calculated excess energies with useful precision: the prediction error (0.13 meV; a similar value is obtained by selecting other structures) is just slightly larger than the intrinsic precision of the *direct* calculation. This analysis shows that the informational content of the complex total-energy calculations on various $\text{Al}_p\text{Ga}_q\text{As}_{p+q}$ structures depicted by the symbols in Fig. 1 can be reduced to ~ 6 interaction energies and that these suffice to predict the structural energies of other configurations. Of course, the rate of convergence will depend, in general, on the chemical nature of the solid and may vary when long-range elastic or screened electrostatic interactions are present. Our previous studies¹² show that the same set of structures and interaction energies do apply, however, to many other III-V and II-VI intersemiconductor compounds. Applications to transition-metal alloys¹³ indicate that a similar convergence can be obtained. This opens the way for calculations of formation energies for lattice structures that are too complicated to be treated by direct *ab initio* methods. A few examples follow.

III. APPLICATIONS

A. Random $\text{Al}_{1-x}\text{Ga}_x\text{As}$ alloys

We can predict the formation energy ΔE_R of a *random* $\text{Al}_{1-x}\text{Ga}_x$ alloy by replacing $\bar{\Pi}_{k,m}(\sigma)$ in Eq (4) by its configurationally averaged value $(2x-1)^k$. Using the interaction energies $\{p_f\}$ from the $N_s = N_f = 6$ set we get the excess energy of the random alloy depicted in Fig. 1 by the solid line. (Using instead the larger set with $N_f = 13$ interactions produces differences ≤ 0.05 meV.) The value at $x = \frac{1}{2}$ is within the experimentally determined range.¹⁴ A ground-state search¹⁵ with the Ising

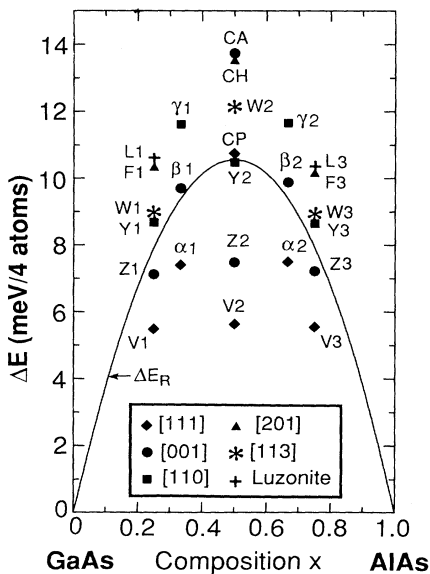


FIG. 1. *Ab initio* calculated formation energies of the various $\text{Al}_p\text{Ga}_q\text{As}_{p+q}$ ordered structures of Table I. The solid line gives the calculated energy ΔE_R of the random $\text{Al}_{1-x}\text{Ga}_x\text{As}$ alloy. The symbols refer to the structures defined in Table I.

Hamiltonian (4) using our interaction energies $\{p_{k,m}\}$ shows that the system will phase separate into AlAs+GaAs at $T=0$. Note that, despite this, some ordered structures have a lower formation energy than the corresponding random alloy at the same composition (Fig. 1), hence *metastable* ordering could exist.

B. Superlattices

It is possible^{12(a)} to predict from Eq. (4) the formation enthalpies of $(\text{AlAs})_p(\text{GaAs})_q$ superlattices as a function of the repeat periods (p, q) and layer orientation \mathbf{G} simply by calculating the geometrical correlation functions¹⁶ $\bar{\Pi}_f(p, q, \mathbf{G})$ and using the interaction energies that were determined previously from our fit (Table I). For repeat periods (p, p) we obtain the order of the formation enthalpies $\Delta E(111) < \Delta E(001) < \Delta E(110) < \Delta E(113) < \Delta E(201)$. In the few cases where our ΔE can be compared with direct *ab initio* superlattice calculations (for structures not included in our basis set), the agreement is good, e.g., for the $p=q=3(111)$ oriented superlattice the result obtained from our cluster expansion, 11.4 meV/cell, is in very good agreement with the extensive first-principles calculations of Bylander and Kleinman,¹⁷ yielding 11.6 meV/cell.

C. Quantum wells

The cluster expansion can be used to extract the interfacial energy for the interesting case of $(BC)_\infty(AC)_p(BC)_\infty$ quantum wells, i.e., p layers of AC embedded in a continuous barrier made of¹⁸ BC . The results are shown in Fig. 2. We predict that a $[111]$ -oriented well is the most stable while the $[201]$ is the least stable in this series; the energy of the latter converges rather slowly to its asymptotic limit. The different behaviors versus p and, for fixed p , versus orientation \mathbf{G} can be understood in terms of the number of mixed A - B atom pairs at the interface for each geometry.¹⁶

D. Isovalent antiphase boundaries

Another interesting application is the determination of the energy of an antiphase boundary (APB) in a given ordered structure. We have considered an APB in which the atoms of the mixed sublattice (isovalent A and B atoms in $A_{1-x}B_xC$) are interchanged across the inter-

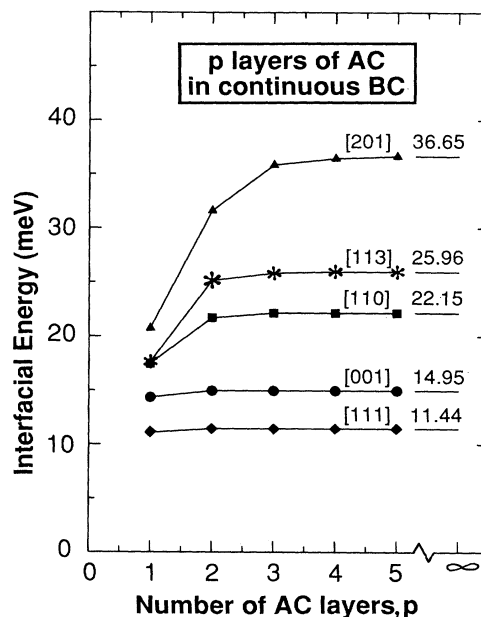


FIG. 2. Predicted interfacial energies of quantum wells consisting of p layers of AC embedded in a continuous BC barrier.

face. This type of APB was found to occur experimentally in high densities (mostly perpendicular to the growth direction), both in lattice-matched¹⁹ and in lattice-mismatched²⁰ ordered ternary compounds. Direct first-principles supercell calculations of such APB energies would be difficult, requiring $O(30-40)$ atoms/cell (Hamiltonian matrices of square dimensions of 6000×6000) in order to separate the contributions of two consecutive APB's. We have considered the effects of differently oriented APB's on the formation energy of the ordered CuPt (CP) structure (the monolayer GaAs-AlAs superlattice oriented along the $[111]$ direction) and of the ordered CuAu (CA) structure (monolayer superlattice along the $[001]$ direction). We define the APB energy $\delta_{\text{APB}}(\mathbf{G})$ as the difference between the energy of the (CP + APB) system and that of the perfect CP structure. Since there are two APB's per cell, the energy associated with each is

TABLE II. Calculated APB energies (in ergs/cm²) for differently oriented APB's in the CuPt ordered structure of AlGaAs₂. For nonstoichiometric APB's, the value given is the average of the energies of the two Ga and Al APB's [Eqs. (5) and (6)].

	Stoichiometric			Nonstoichiometric		
	CuPt					
orientation	$\bar{1}11$	001	110	$\bar{1}10$	$\bar{1}13$	111
energy	+1.658	-0.170	-2.388	+2.019	+0.679	-5.988
	CuAu					
orientation	101			110		
energy	-2.074			-2.375		

$$\delta_{\text{APB}} = \frac{1}{2}[\Delta E(\text{CP} + 2\text{APB}) - \Delta E(\text{CP})] \quad (5)$$

for stoichiometric APB's while for nonstoichiometric APB's we define an average APB energy as

$$\begin{aligned} \bar{\delta}_{\text{APB}} &= \frac{1}{2}(\delta_{\text{APB}_1} + \delta_{\text{APB}_2}) \\ &= \frac{1}{2}[\Delta E(\text{CP} + \text{APB}_1 + \text{APB}_2) - \Delta E(\text{CP})], \quad (6) \end{aligned}$$

where APB_1 refers to the Al APB and APB_2 to the Ga APB. The average energy for nonstoichiometric APB's can be found by selecting unit cells containing both types of APB's, so that the overall stoichiometry of the compound is preserved. Table II gives the APB energies of the CuPt and CuAu structures of AlGaAs_2 at the limit where the two APB's in each cell are sufficiently removed from each other so that E_{APB} no longer depends on their separation.

For the stoichiometric APB's in the CuPt structure we find that the $(\bar{1}\bar{1}1)$ and the $(\bar{1}10)$ oriented APB's increase the formation energy, while the (110) and (001) APB's reduce it, hence, they could occur spontaneously. This energy change increases with the APB density. Often a high APB density gives rise to a new ordered compound: for example, (110) APB's separated by two atomic planes in the CuPt structure generate a $2 \times 2(001)$ superlattice

(the Z2 structure of Table I), while a (001) APB separated by two double layers gives the Y2 structure (Table I) observed experimentally.²⁰ In the nonstoichiometric case, the presence of $(\bar{1}\bar{1}3)$ APB's is unfavorable, while the (111) APB's, generating new (111) superlattices with double-layer periods, reduce the CuPt formation energy.

For the ordered CuAu structure, we see that the two inequivalent (110) and (101) APB's lower its formation enthalpy. This is consistent with the observation¹⁹ of (110) APB's in spontaneously CuAu-type long-range ordered $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys.

In summary, we have shown that combining *ab initio* total-energy calculations on a few ordered structures with a statistical mechanical cluster expansion could be used to explore the stabilities of a wide range of configurational degrees of freedom in solids.

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¹Examples for phenomenological models of structural stability can be found in W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys* (Wiley Interscience, New York, 1972).

²See, e.g., I. M. Torrens, *Interatomic Potentials* (Academic, New York, 1972).

³Recent examples of *ab initio* structural calculations in solids can be found in *Electronic Structure, Dynamics and Quantum Structural Properties of Condensed Matter*, Vol. 121 of *NATO Advanced Study Institute, Series B: Physics*, edited by J. T. Devreese and P. Van Camp (Plenum, New York, 1985).

⁴See, e.g., D. de Fontaine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34, p. 73.

⁵J. M. Sanchez, F. Ducastelle, and D. Gratias, *Physica A* **128**, 334 (1984).

⁶(a) A. Bieber and F. Gautier, *Acta Metall.* **34**, 2291 (1986); (b) M. Sluiter and P. E. A. Turchi, *Phys. Rev. B* **40**, 11 215 (1989).

⁷W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

⁸J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).

⁹G. P. Kerker, *J. Phys. C* **13**, L189 (1980).

¹⁰S. Froyen, *Phys. Rev. B* **39**, 3168 (1989).

¹¹For $N_f = N_s$ one can invert Eq. (2) or (4) to obtain p_f , as shown by J. W. D. Connolly and A. R. Williams, *Phys. Rev. B* **27**, 5169 (1983) for nearest-neighbor fcc interactions; here,

we use a fit with $N_s > N_f$: the weights for the 27 structures are given by $w_s = (24/n_s)N_c$, where n_s is the number of inequivalent symmetry operations in the point group of the structure and N_c is the number of cations/unit cell.

¹²(a) S.-H. Wei and A. Zunger, *Phys. Rev. Lett.* **61**, 1505 (1988); (b) L. G. Ferreira, S. H. Wei, and A. Zunger, *Phys. Rev. B* **40**, 3197 (1989).

¹³Z. W. Lu, S. -H. Wei, L. G. Ferreira, and A. Zunger (unpublished).

¹⁴L. M. Foster, J. E. Scardefield, and J. F. Woods, *J. Electrochem. Soc.* **119**, 765 (1972); V. T. Bublik and V. N. Leikin, *Phys. Status Solidi A* **46**, 365 (1978).

¹⁵J. Kanamori and Y. Kakehashi, *J. Phys. (Paris) Colloq.* **38**, C7-274 (1977).

¹⁶E.g., $\bar{\Pi}_{2,m}(p, q, \mathbf{G}) = 1 - [2N_{2,m}(p, q, \mathbf{G})/D_{2,m}(p + q)]$, where $N_{2,m}(p, q, \mathbf{G})$ is the number of A-B atom pairs between m th neighbors at the interface.

¹⁷D. M. Bylander and L. Kleinman, *Phys. Rev. B* **38**, 7480 (1988).

¹⁸Using the $N_f = N_s = 6$ set, embedding AC in BC or BC in AC yields the same result. The difference in energy is, however, small: within the prediction error of the cluster expansion.

¹⁹T. S. Kuan, T. F. Kuech, W. I. Wang, and E. L. Wilkie, *Phys. Rev. Lett.* **54**, 201 (1985).

²⁰I. J. Murgatroyd, A. G. Norman, and G. R. Booker, *J. Appl. Phys.* **67**, 2310 (1990).