We calculate the total energy of random Al$_{0.5}$Ga$_{0.5}$As alloys and ordered (AlAs)$_n$(GaAs)$_n$ superlattices through a series expansion in multi-atom interaction energies obtained from the local-density formalism. We find that the alloy is more stable than the monolayer ($n = 1$) superlattice at all temperatures, but it could order into longer-period ($n \geq 2$) superlattices below a critical temperature $T(n,G)$ calculated for various growth orientations $G$.

PACS numbers: 64.70.Kh, 64.60.My, 68.55.Rt

Large atomic diffusion activation barriers make uncertain whether artificially grown $(AC)_n(BC)_n$ semiconductor superlattices owe their apparent room-temperature stability to kinetic barriers inhibiting disordering into an A$_{0.5}$B$_{0.5}$C alloy, or to a genuine thermodynamic preference for order over disorder at room temperature. We present calculations of the total energy of ordered (AlAs)$_n$(GaAs)$_n$ superlattices and free energies of the random A$_{0.5}$Ga$_{0.5}$As alloy using series expansions in terms of multi-atom interaction energies calculated within the local-density formalism. We find that whereas both the random alloy and the superlattices have a higher energy than the phase-separated $AC + BC$ system [Fig. 1(a)], in the lattice-matched AlAs-GaAs system the random alloy has a lower free energy at all temperatures than the monolayer ($n = 1$) superlattice in any of the principal orientations $G = \langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$. However, (ii) longer-period superlattices ($n \geq 2$) have, below a critical temperature $T(n,G)$, a lower free energy than the random alloy of the same composition [Fig. 1(b)]. Hence, if complete phase separation is kinetically inhibited, ordering of the random alloy is thermodynamically possible below $T(n,G)$. (iii) For the lattice-matched AlAs-GaAs system, these ordering temperatures are lower than either room or growth temperatures. In contrast, in lattice-mismatched systems (e.g., GaAs-GaSb, GaAs-InAs), $T(n,G)$ is considerably higher (finite even for $n = 1$), consistent with recent observations of spontaneous ordering of these alloys.$^{2,3}$

In order to calculate the excess free energy $\Delta F = \Delta E - TS$ of ordered and disordered $A_1B_{1-x}C$ alloys, we first obtain the excess internal energy $\Delta E(\sigma,V)$ for atomic arrangements $\sigma$. Measured with respect to equivalent amounts of the end-point constituents $AC$ and $BC$ at their equilibrium volumes, this is

$$\Delta E(\sigma,V) = E(A_1B_{1-x}C;V) - xE(AC) - (1-x)E(BC).$$

We assume that $\Delta E(\sigma,V)$ can be written as a series of many-atom (not just pair) interaction energies $^4 F$

$$\Delta E(\sigma,V) = \sum_1^k \sum_m^n \xi_{k,m}(\sigma)J_{k,m}(V),$$

where $\xi_{k,m}(\sigma)$ is the occurrence frequency of $k$-atom "figures" whose fcc sites are separated by up to the $m$th nearest-neighbor distance and $J_{k,m}(V)$ is the corresponding interaction energy (e.g., $J_{3,2}$ is the energy due to simultaneous interaction between three cations comprising of one second-neighbor and two first-nearest-neighbor bonds. $J_{4,2}$ is the simultaneous interaction between four cations on a tetrahedron with one second-neighbor bond and five nearest-neighbor bonds). The central observations enabling calculation of the $J$'s are$^4$ that (i) while the set $\{\xi_{k,m}(\sigma)\}$ is generally unknown for arbitrary configurations $\sigma$, it reduces to a simple set of geometrical constants for ordered, periodic Landau-Lifshitz structures$^5$ (e.g., $A_nB_{4-n}C_4$, see Table I for
the expansion coefficients); and (ii) at the same time, \( \Delta E(s,V) \) can be independently calculated accurately for periodic structures with use of first-principles band-theory approaches. Specializing Eq. (2) to the set \( \sigma = \{ s \} \) and inverting this relation gives

\[
J_{k,m}(V) = \sum_{s=1}^{N} [\xi_{k,m}(s)]^{-1} \Delta E(s,V),
\]

from which we obtain \( N \) interaction energies from calculations of the total energy functions of \( N \) structurally independent periodic systems. The set of \( N \) structures \( \{ s \} \) is selected so that (i) they exhibit at least all nearest-neighbor local arrangements around a common atom \( C \) expected to occur in the alloy [e.g., \( A_4 \) and \( B_4 \) in the zinc-blende structures, \( A_2B_2 \) in the layered tetragonal and chalcopyrite structures, \( A_3B \) and \( AB_3 \) in the layered trigonal, Luzonite, and Famatinite structures (see Table I)]; (ii) they include the lowest-energy structures; (iii) they exhibit ordering in all principal orientations: \([001]\) and \([110]\) for the layered tetragonal, \([111]\) for the layered trigonal, \([201]\) for chalcopyrite and Famatinite; (iv) the set \( \{ s \} \) is converged in the sense that the \( \{ J_{k,m} \} \) calculated from it can reproduce through Eq. (2) the independently calculated total energy \( \Delta E(s',V) \) of structures \( s' \) not included in the original set. The Landau-Lifshitz structures\(^{6-13}\) of Table I satisfy the first three requirements; we will show below by way of numerical calculation that they also satisfy the fourth requirement.

We have calculated \( \Delta E(\sigma = s) \) of Eq. (1) for nine ordered \( \text{Al}_n\text{Ga}_4-n\text{As}_4 \) structures (\( n=0,4 \) plus the seven structures indicated in Table I), using the local-density approach, as implemented by the general-potential, linear augmented plane-wave (LAPW) method.\(^5\) To assure an effective cancellation of random errors, we calculate all three terms of Eq. (1) using precisely equivalent basis sets, muffin-tin radii, and sampling \( k \) points. Since the equilibrium lattice constants \( a_{\text{AlAs}} \) and \( a_{\text{GaAs}} \) calculated, 5.661 and 5.690 \( \text{Å} \); low-temperature experimental

Table: Coefficients \( \{ \xi_{k,m}(s) \} \) of the expansion of the total energy (per 4 atoms) of ordered structures \( \{ s \} \) in terms of \( k \)-body, \( m \)-neighbor interaction energies \( J \) [Eq. (2)]. Here CuAu, Chalc., CuPt, Luz, and Fam refer to layered tetragonal, chalcopyrite, layered trigonal, Luzonite, and Famatinite, respectively (see Ref. 4d for pictures). Corresponding ensemble-averaged \( \xi_{k,m}(R) \) for the random alloy at \( x=0.5 \) are also given.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Space group</th>
<th>Formula</th>
<th>( \xi_{2,1} )</th>
<th>( \xi_{2,2} )</th>
<th>( \xi_{2,3} )</th>
<th>( \xi_{2,4} )</th>
<th>( \xi_{3,1} )</th>
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<th>( \xi_{3,3} )</th>
<th>( \xi_{4,1} )</th>
<th>( \xi_{4,2} )</th>
<th>( \Delta E(s) ) [meV/(4 atoms)]</th>
<th>LAPW</th>
<th>Fit</th>
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</thead>
<tbody>
<tr>
<td>CuAu</td>
<td>( P4m2 )</td>
<td>( ABC_2 )</td>
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<td>0</td>
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<td>0</td>
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<td>0</td>
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<td>9.8</td>
<td>7.5</td>
</tr>
<tr>
<td>Chalc.</td>
<td>( I42d )</td>
<td>( ABC_2 )</td>
<td>-16</td>
<td>-4</td>
<td>-16</td>
<td>-16</td>
<td>0</td>
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<td>-16</td>
<td>0</td>
<td>9.8</td>
<td>7.5</td>
<td>7.5</td>
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<tr>
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<td>( R3m )</td>
<td>( ABC_2 )</td>
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<td>-12</td>
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<td>-24</td>
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<tr>
<td>Luz</td>
<td>( P43m )</td>
<td>( AB )</td>
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<td>-24</td>
<td>0</td>
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<td>-24</td>
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<td>8.6</td>
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<tr>
<td>Luz</td>
<td>( P43m )</td>
<td>( AB )</td>
<td>-12</td>
<td>0</td>
<td>-24</td>
<td>0</td>
<td>-16</td>
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<td>-8</td>
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<td>8.7</td>
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<tr>
<td>Fam</td>
<td>( I42m )</td>
<td>( AB )</td>
<td>-12</td>
<td>-2</td>
<td>-16</td>
<td>-8</td>
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<td>8</td>
<td>32</td>
<td>-8</td>
<td>-32</td>
<td>7.3</td>
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<td>Fam</td>
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<td>( AB )</td>
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<td>-2</td>
<td>-16</td>
<td>-8</td>
<td>-16</td>
<td>8</td>
<td>-32</td>
<td>-8</td>
<td>-32</td>
<td>7.7</td>
<td>7.7</td>
<td>7.7</td>
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<tr>
<td>Random</td>
<td>( F43m )</td>
<td>( A_0.5B_0.5C )</td>
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<td>-24</td>
<td>-12</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>-24</td>
<td>...</td>
<td>7.0</td>
<td></td>
</tr>
</tbody>
</table>

The last two columns of Table I demonstrate the good quality of the fit. To verify that this set of interaction energies is transferable to other substitutional \( \text{AlAs-GaAs} \) structures, we calculated \( \Delta E(s') \) for a structure \( s' \) not included in the fit: An LAPW calculation for the

The expansion coefficients; and (ii) at the same time, \( \Delta E(s,V) \) can be independently calculated accurately for periodic structures with use of first-principles band-theory approaches. Specializing Eq. (2) to the set \( \sigma = \{ s \} \) and inverting this relation gives

\[
J_{k,m}(V) = \sum_{s=1}^{N} [\xi_{k,m}(s)]^{-1} \Delta E(s,V),
\]

from which we obtain \( N \) interaction energies from calculations of the total energy functions of \( N \) structurally independent periodic systems. The set of \( N \) structures \( \{ s \} \) is selected so that (i) they exhibit at least all nearest-neighbor local arrangements around a common atom \( C \) expected to occur in the alloy [e.g., \( A_4 \) and \( B_4 \) in the zinc-blende structures, \( A_2B_2 \) in the layered tetragonal and chalcopyrite structures, \( A_3B \) and \( AB_3 \) in the layered trigonal, Luzonite, and Famatinite structures (see Table I)]; (ii) they include the lowest-energy structures; (iii) they exhibit ordering in all principal orientations: \([001]\) and \([110]\) for the layered tetragonal, \([111]\) for the layered trigonal, \([201]\) for chalcopyrite and Famatinite; (iv) the set \( \{ s \} \) is converged in the sense that the \( \{ J_{k,m} \} \) calculated from it can reproduce through Eq. (2) the independently calculated total energy \( \Delta E(s',V) \) of structures \( s' \) not included in the original set. The Landau-Lifshitz structures\(^{6-13}\) of Table I satisfy the first three requirements; we will show below by way of numerical calculation that they also satisfy the fourth requirement.

We have calculated \( \Delta E(\sigma = s) \) of Eq. (1) for nine ordered \( \text{Al}_n\text{Ga}_4-n\text{As}_4 \) structures (\( n=0,4 \) plus the seven structures indicated in Table I), using the local-density approach, as implemented by the general-potential, linear augmented plane-wave (LAPW) method.\(^5\) To assure an effective cancellation of random errors, we calculate all three terms of Eq. (1) using precisely equivalent basis sets, muffin-tin radii, and sampling \( k \) points. Since the equilibrium lattice constants \( a_{\text{AlAs}} \) and \( a_{\text{GaAs}} \) calculated, 5.661 and 5.690 \( \text{Å} \); low-temperature experimental
[001]-oriented (AlAs)$_2$(GaAs)$_2$ superlattice gives $\Delta E = 2.85$ meV/4 atoms, whereas using Eq. (2) with the data (4) gives 3.6 meV/4 atoms (see below). [Adding this superlattice to the nine structures and refitting gives similar values: $J_{2,1} = -0.758, J_{2,2} = 0.089, J_{2,3} = 0.022$, and $J_{2,4} = 0.112$. This fit produces $\Delta E(s)$ values which agree with those of Table I to within 0.1 meV and yields for the $n = 2$ superlattice $\Delta E = 2.85$ meV/4 atoms.] This demonstrated transferability shows that the expansion of Eq. (2) including up to fourth-neighbor pair interactions captures the essential energetics of substitutional AlAs-GaAs systems. The resulting interactions are repulsive ($J_{2,1} < 0$) between nearest fcc cations, and weaker, mostly attractive beyond this range. Consequently, under equilibrium conditions, all of our ordered Landau-Lifshitz structures [exhibiting $\Delta E(s) > 0$] are predicted to be unstable at $T = 0$ with respect to decomposition into AlAs + GaAs. However, since low-temperature phase separation (unlike ordering$^{1-3}$) is strongly inhibited kinetically in semiconductor alloys,$^1$ we will also study below the free energies of the next lowest thermodynamic states.

The utility of the analysis of Eqs. (1)-(3) lies in the fact that the knowledge of a converged and transferable set $\{J_{k,m}\}$ affords simple calculations of the internal energies of more complex configurations $\sigma$ through evaluation of $\xi_{k,m}(\sigma)$ rather than by the more laborious direct self-consistent calculations of $\Delta E(\sigma)$. Coupled with simple models for the entropy, this permits modeling of the relative thermodynamic stability of alloys and longer-period superlattices.

The random Al$_{0.5}$Ga$_{0.5}$As alloy.—Calculations of spatial correlations for the Al$_{0.5}$Ga$_{0.5}$As alloy$^{9,10}$ have shown that (because of the small size and electronegativity difference between Ga and Al) this alloy is very nearly random (R) above room temperature. For random alloys, the ensemble-averaged expansion coefficients $\xi_{k,m}(R)$ are again simple constants; they are given in the last line of Table I. Equations (2) and (4) then give the excess energy of the 50%-50% random alloy: $\Delta E(R, R = 0.5) = 7.0$ meV/4 atoms. Since this energy is positive, the random alloy is not the $T \to 0$ ground state.

Coupled with the calculated internal energies $\Delta E(\sigma)$ of the ordered (O) short-period superlattices given in Table I, this leads to the following conclusions: (i) Since we find $\Delta E(R) < \Delta E(O)$ and (neglecting differences in vibrational entropies) the excess free energies are $\Delta F(R) = \Delta E(R) - TS(R)$ and $\Delta F(O) = \Delta E(O)$, where $S(R) > 0$ is the configurational entropy of the random alloy, we predict for Al$_x$Ga$_{1-x}$As that $\Delta F(R) < \Delta F(O)$ at all temperatures. In the absence of size mismatch, ordered monolayer ($n = 1$) superlattices [with $\Delta E(O) > 0$] are, hence, always of higher free energy than the random alloy of the same composition. This suggests that the layered tetragonal ("CuAu-like") ordering observed by Kuan et al.$^{15}$ in Al$_x$Ga$_{1-x}$As is not driven by bulk thermodynamics (but could be a consequence of surface thermodynamics$^{12,13}$ or kinetic factors not included in our theory). (ii) Our model predicts an "interaction parameter" $\Omega = 4\Delta E(R, x = 0.5) = 0.32$ kcal/mol (a mole of $A_1-B_2C_1$ unit), in reasonable agreement with the range$^{14}$ 0–1.6 obtained from the measured liquidus-solidsus phase diagram$^{14a}$ and diffuse x-ray scattering.$^{14b}$ but in conflict with the results of Shen, Bylander, and Kleinman.$^{15}$ (iii) If we estimate the mixing entropy $S(R, x)$ from random statistics, the calculated miscibility-gap (MG) temperature at $x = 0.5$ (below which the components are immiscible) is $T_{MG} = \Delta E(R) / S(R) = 59$ K. No direct experimental value exists for $T_{MG}$ in Al$_x$Ga$_{1-x}$As since it is well below conventional growth temperatures (800–1000 K).

**Longer-period superlattices.**—The expansion of Eq. (2) can be generalized to longer-period (AC)$_n$(BC)$_m$ superlattices grown in different orientations. Table II gives the expansion coefficients $\xi_{2,m}(n,G)$ for the three orientations $G = [001], [110]$, and [111], retaining up to fourth-neighbor pair interactions ($m = 4$). This shows that for each orientation, the excess energy per cell becomes constant (denoted below as $2I[G]$) past a critical repeat period $n_c(G)$: retaining $m \leq 4$ gives $n_c = 2$ for the [001]- and [111]-oriented superlattices and $n_c = 4$ for the [110]-oriented superlattice. Hence, for $n \geq n_c$, one has (per 4 atoms)

$$\Delta E(n, G) = 2I[G] / n, \quad n \geq n_c, \quad (5)$$

a relationship derived earlier by Wood, Wei, and Zunger$^{12}$ from different considerations. This scaling [Fig. 1(a)], indicating a greater stability per atom of longer (relative to shorter) period, "repelling" ($J > 0$) superlattices, simply reflects the fact that electronic and structural changes attendant upon the formation of an interface are limited to a certain distance from the interface. From Table II and Eq. (4), we find the interfacial energies $I[001] = 3.6$ meV, $I[110] = 5.8$ meV, and $I[111] = \frac{1}{2} I[100] = 2.7$ meV, suggesting the [110] interface to be the most unstable, whereas the [111] interface is the most stable in this sequence.

**TABLE II.** The expansion coefficients $\xi_{2,m}(n,G)$ (per unit cell or 4n atoms) and the excess energy $\Delta E(n, G)$ in meV/(4 atoms)] of (AC)$_n$(BC)$_m$ superlattices.

<table>
<thead>
<tr>
<th>G</th>
<th>n</th>
<th>$\xi_{2,1}$</th>
<th>$\xi_{2,2}$</th>
<th>$\xi_{2,3}$</th>
<th>$\xi_{2,4}$</th>
<th>$\Delta E(n, G)$</th>
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<tr>
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<tr>
<td></td>
<td>n ≥ 2</td>
<td>-12</td>
<td>-12</td>
<td>-48</td>
<td>-24</td>
<td>2.7</td>
</tr>
</tbody>
</table>

1507
Comparison of $\Delta E(n,G)$ to the free energy $\Delta E(R)$ $-T_S(R)$ of the random alloy shows that whereas the latter is more stable than the monolayer ($n=1$) superlattice at all temperatures, longer-period superlattices are predicted to be more stable than the random alloy below a critical temperature

$$T(n,G) = T_{MG} - \Delta E(n,G)/S(R) = T_{MG} - A/n,$$

where $T_{MG} = \Delta E(R)/S(R)$, and $A = 2I[G]/S(R)$ for $n \geq n_c$ [Fig. 1(b)]. If perfect equilibrium conditions can be attained, the system will phase separate at $T < T_{MG}$ into $AC + BC$ [formally equivalent to the $n \rightarrow \infty$ limit of a $(AC)_n(BC)_n$ "superlattice"]. At this limit we find, as expected, $T(\infty,G) = T_{MG}$ for all orientations. Since complete phase separation ($n \rightarrow \infty$) requires rearrangement of many bonds, it could be kinetically hindered at low temperatures, leaving the shorter-period $n > 1$ superlattice ordering (requiring lower activation barriers) as the next available thermodynamic state [region III in Fig. 1(b)]. In this case, once formed, the short-period superlattices have no thermodynamic incentive to disorder; they will persist even if there were no diffusion activation barriers for disordering. (Note, however, that this explains only the stability of $n > 1$ superlattices, not that of the $n = 1$ system.)

Whereas for $Al_xGa_{1-x}As$, $T(n,G)$ is considerably lower than growth (and even room) temperature, in lattice-mismatched alloys these temperatures are much higher: in $GaAs_{0.5}Sb_{0.5}$, $T_{MG} = 1200$ K and $T(2,G) > 500$ K for the chalcopyrite ($G = 201$) ordering. This is thermodynamically consistent with the recent observation of spontaneous metastable ordering in such alloys during growth (although the precise value of the ordering temperatures is probably determined in real samples also by growth kinetics and surface steps).

We are grateful to Dr. Kleinman for communicating to us his results of Ref. 15 prior to publication. This work was supported by the U.S. Department of Energy under Grant No. DE-AC02-77-CH00178.


8See review by P. Ducastelle, in Proceedings of the NATO Advanced Study Institute on Alloy Phase Stability, Crete, 1987 (to be published).

9L. G. Ferreira, S.-H. Wei, and A. Zunger, unpublished.


16Y.-T. Shen, D. M. Bylander, and L. Kleinman, Bull. Am. Phys. Soc. 33, 302 (1988), give $\Omega = 6.15$ kcal/mol, i.e., $T_{MG} = 1120$ K, well above the actually observed mixing temperatures. A revised calculation (private communication) gives $\Delta E_0(2.7) = 80$ meV/(4 atom), or $\Omega = 3.7$ kcal/mol, suggesting that the random alloy is the $T = 0$ ground state and will never disproportionate ($T_{MG} < 0$). Our results disagree with both of their conclusions.