Thermodynamic Stability of $(\mathrm{AlAs})_n(\mathrm{GaAs})_n$ Superlattices and the Random $\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5}\mathrm{As}$ Alloy

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We calculate the total energy of random $\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5}\mathrm{As}$ alloys and ordered $(\mathrm{AlAs})_n(\mathrm{GaAs})_n$ 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 ($n\gtrsim 2$) superlattices below a critical temperature $T(n,\mathbf{G})$ calculated for various growth orientations $\mathbf{G}$.

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Large atomic diffusion activation barriers make uncertain[1] 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 $(\mathrm{AlAs})_n(\mathrm{GaAs})_n$ superlattices and free energies of the random $\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5}\mathrm{As}$ alloy using series expansions in terms of multi-atom interaction energies calculated within the local-density formalism. We find that (i) 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 $\mathbf{G}=[001]$, [110], and [111]. However, (ii) longer-period superlattices ($n\gtrsim 2$) have, below a critical temperature $T(n,\mathbf{G})$, a lower free energy then 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 $T(n,\mathbf{G})$. (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), $T(n,\mathbf{G})$ is considerably higher (finite even for $n=1$), consistent with recent observations of spontaneous ordering of these alloys.[2,3]

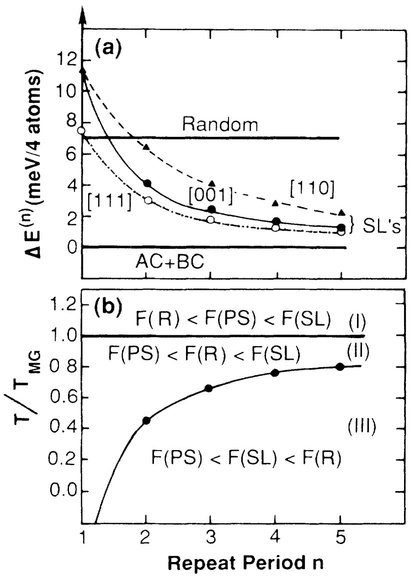

FIG. 1. (a) Internal energies of superlattices (as functions of n, in three orientations) and the $x=0.5$ random alloy, both given with respect to the phase-separated $AC+BC$ system. (b) Regions of stability and the relative order of free energies F for the random (R) $x=0.5$ alloy, the phase-separated (PS) system, and ordered superlattices (SL). If phase separation is kinetically inhibited, the next most stable phase below $T(n,\mathbf{G})$ (filled circles) is an ordered superlattice, rather than the random alloy.

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

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

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

$$\Delta E(\sigma,V)=\sum_k^K\sum_m^M \xi_{k,m}(\sigma)J_{k,m}(V), \qquad (2)$$

where $\xi_{k,m}(\sigma)$ is the occurrence frequency of k-atom "figures" whose fcc sites are separated by up to the mth 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 σ, it reduces to a simple set of geometrical constants for ordered, periodic Landau-Lifshitz structures[5] $\{s\}$ (e.g., $A_nB_{4-n}C_4$; see Table I for

TABLE I. 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 $\xi_{k,m}(\mathrm{R})$ for the random alloy at $x=0.5$ are also given.

	Space		Two-body				Three-body			Four-body		$\Delta E(s)$ [meV/(4 atoms)]	
Structure	group	Formula	$\xi_{2,1}$	$\xi_{2,2}$	$\xi_{2,3}$	$\xi_{2,4}$	$\xi_{3,1}$	$\xi_{3,2}$	$\xi_{3,3}$	$\xi_{4,1}$	$\xi_{4,2}$	LAPW	Fit
CuAu	$P\bar{4}m2$	ABC_2	−16	0	−32	0	0	0	0	0	−32	11.5	11.4
Chalc.	$I\bar{4}2d$	ABC_2	−16	−4	−16	−16	0	0	0	0	−16	9.8	9.7
CuPt	$R3m$	ABC_2	−12	−12	−24	0	0	0	0	−8	−24	7.5	7.5
Luz	$P\bar{4}3m$	A_3BC_4	−12	0	−24	0	16	0	48	−8	−24	8.4	8.6
Luz	$P\bar{4}3m$	AB_3C_4	−12	0	−24	0	−16	0	−48	−8	−24	8.7	8.6
Fam	$I\bar{4}2m$	A_3BC_4	−12	−2	−16	−8	16	8	32	−8	−32	7.3	7.7
Fam	$I\bar{4}2m$	AB_3C_4	−12	−2	−16	−8	−16	−8	−32	−8	−32	7.7	7.7
Random	$F\bar{4}3m$	$A_{0.5}B_{0.5}C$	−12	−6	−24	−12	0	0	0	−4	−24	...	7.0

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

$$J_{k,m}(V)=\sum_{s=1}^{N}[\xi_{k,m}(s)]^{-1}\Delta E(s,V), \tag{3}$$

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 $\{J_{k,m}\}$'s 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[4b-4d,5] 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 $\mathrm{Al}_n\mathrm{Ga}_{4-n}\mathrm{As}_4$ 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.[6] 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_{AlAs} and a_{GaAs} (calculated, 5.661 and 5.690 Å; low-temperature experimental values, 5.659 and 5.652 Å) are similar, we fixed the lattice constant at 5.6569 Å so that the $J_{k,m}$ become volume-independent numbers. The next-to-last column of Table I gives the LAPW-calculated $\Delta E(s)$ values. For the two alternating monolayer superlattices for which independent calculations exist, we find good agreement {14.9 and 11.4 meV/(4 atoms) calculated by Bylander and Kleinman[7] for the layered tetragonal $\mathbf{G}=[001]$ and layered trigonal $\mathbf{G}=[111]$ structures, respectively}. Our method transcends many of the simplifying approximations used in contemporary models of phase diagrams,[4,8] e.g., use of a restricted tight-binding basis set, neglect of explicit Coulomb and exchange interelectronic terms, restricted (site-only) charge self-consistency, shape approximations on the potential and charge density, or truncation of K and M in Eq.(2) to small values.

Using the calculated $\Delta E(s)$ for nine Landau-Lifshitz structures and the expansion coefficients of Table I, we obtain from Eq. (3) nine interaction energies (the $J_{0,0}$, $J_{1,1}$, and all but $J_{3,3}$ and $J_{2,3}$ of Table I).[9] We find that the three- and four-body interaction energies are small (in meV): $J_{3,1}=-0.01$; $J_{3,2}=-0.005$; $J_{4,1}=0.01$; $J_{4,2}=0.01$. The largest contribution from these many-body terms to $\Delta E(s)$ is $32J_{4,2}$ (Table I), i.e., only ~0.3 meV/(4 atoms) or 3% of ΔE. We, hence, neglect these small terms in the following discussions. Retaining only the four largest pair interactions $J_{2,m}$, $m\leq 4$, in Eq. (2), a least-squares fit gives (in meV)

$$J_{2,1}=-0.713;\quad J_{2,2}=0.088;$$
$$J_{2,3}=0.000;\quad J_{2,4}=0.085. \tag{4}$$

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 AlAs-GaAs structures, we calculated $\Delta E(s')$ for a structure s' not included in the fit: An LAPW calculation for the

[001]-oriented $(\mathrm{AlAs})_2(\mathrm{GaAs})_2$ 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 σ 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 $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ 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 $\xi_{k,m}(\mathrm{R})$ 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: $\Delta E(\mathrm{R},x=0.5) = 7.0$ meV/(4 atoms). Since this energy is positive, the random alloy is *not* the $T=0$ ground state.

Coupled with the calculated internal energies $\Delta E(\mathrm{O})$ of the ordered (O) short-period superlattices given in Table I, this leads to the following conclusions: (i) Since we find $\Delta E(\mathrm{R}) < \Delta E(\mathrm{O})$ and (neglecting *differences* in vibrational entropies) the excess free energies are $\Delta F(\mathrm{R}) = \Delta E(\mathrm{R}) - TS(\mathrm{R})$ and $\Delta F(\mathrm{O}) \simeq \Delta E(\mathrm{O})$, where $S(\mathrm{R}) > 0$ is the configurational entropy of the random alloy, we predict for $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ that $\Delta F(\mathrm{R}) < \Delta F(\mathrm{O})$ at *all temperatures*. In the absence of size mismatch, ordered monolayer ($n=1$) superlattices [with $\Delta E(\mathrm{O}) > 0$] are, hence, always of *higher* free energy then the the random alloy of the same composition. This suggests that the layered tetragonal ("CuAu-like") ordering observed by Kuan *et al.*[11] in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ 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" $\Omega = 4\Delta E(\mathrm{R},x=0.5) = 0.32$ kcal/mol (a mole of $A_{1-x}\mathrm{B}_xC$ unit), in reasonable agreement with the range[14] 0-1.6 obtained from the measured liquidus-solidus 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 $S(\mathrm{R},x)$ from random statistics, the calculated miscibility-gap (MG) temperature at $x=0.5$ (below which the components are immiscible) is $T_{\mathrm{MG}} = \Delta E(\mathrm{R})/S(\mathrm{R}) = 59$ K. No direct experimental value exists for T_{MG} in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ 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 $(AC)_n(BC)_n$ superlattices grown in different orientations. Table II gives the expansion coefficients $\xi_{2,m}(n,\mathbf{G})$ for the three orientations $\mathbf{G} = [001]$, [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 $2I[\mathbf{G}]$) past a critical repeat period $n_c(\mathbf{G})$: retaining $m \le 4$ gives $n_c = 2$ for the [001]- and [111]-oriented superlattices and $n_c = 4$ for the [110]-oriented superlattice. Hence, for $n \ge n_c$, one has (per 4 atoms)

$$\Delta E(n,\mathbf{G}) = 2I[\mathbf{G}]/n, \quad n \ge n_c, \tag{5}$$

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" ($I > 0$) 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 $I[111] = \frac{3}{4} I[100] = 2.7$ 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 $\xi_{2,m}(n,\mathbf{G})$ (per unit cell or $4n$ atoms) and the excess energy $\Delta E(n,\mathbf{G})$ [in meV/(4 atoms)] of $(AC)_n(BC)_n$ superlattices.

G	n	$\xi_{2,1}$	$\xi_{2,2}$	$\xi_{2,3}$	$\xi_{2,4}$	$\Delta E(n,\mathbf{G})$
[001]	$n=1$	−16	0	−32	0	11.4
	$n \ge 2$	−16	−16	−64	−32	3.6
[110]	$n=1$	−16	0	−32	0	11.4
	$n=2$	−24	−16	−48	−32	6.5
	$n=3$	−24	−16	−80	−40	4.1
	$n \ge 4$	−24	−16	−80	−48	2.9
[111]	$n=1$	−12	−12	−24	0	7.5
	$n \ge 2$	−12	−12	−48	−24	2.7

Comparison of $\Delta E(n,\mathbf{G})$ to the free energy $\Delta E(\mathrm{R}) - TS(\mathrm{R})$ 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

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

where $T_{\mathrm{MG}} = \Delta E(\mathrm{R})/S(\mathrm{R})$, and $A = 2I[\mathbf{G}]/S(\mathrm{R})$ for $n \geq n_c$ [Fig. 1(b)]. If perfect equilibrium conditions can be attained, the system will phase separate at $T < T_{\mathrm{MG}}$ 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, $T(\infty,\mathbf{G}) = T_{\mathrm{MG}}$ 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,[1] not that of the $n=1$ system.[11]) Whereas for $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, $T(n,\mathbf{G})$ is considerably lower than growth (and even room) temperature,[1] in lattice-*mismatched* alloys these temperatures are much higher[9]: in $\mathrm{GaAs}_{0.5}\mathrm{Sb}_{0.5}$, $T_{\mathrm{MG}} \simeq 1200$ K and $T(2,\mathbf{G}) > 500$ K for the chalcopyrite ($\mathbf{G}=[201]$) ordering. This is thermodynamically consistent with the recent observation of *spontaneous* metastable ordering in such alloys[2,3] during growth (although the precise value of the ordering temperatures is probably determined in real samples also by growth kinetics and surface steps[16]).

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