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Thermodynamic instability of ordered (001) $AlGaAs_2$ in bulk form

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Recent tight-binding calculations of bulk electronic total energies by Koiller, Davidovich, and Falicov (KDF) [Phys. Rev. B **41**, 3670 (1990)] indicated the tendency for $Al_{1-x}Ga_xAs$ alloys to form ordered structures. The stablest structure they predicted was the monolayer $(AlAs)_1(GaAs)_1[001]$ superlattice, which was recently observed in homogeneous vapor-phase growth. In light of these results we have examined the possibility that bulk energetics can explain this ordering. We have subjected KDF's tight-binding total-energy calculations and, separately, our own first-principles pseudopotential total-energy calculations to a statistical-mechanics analysis of order-disorder transitions. We find that bulk thermodynamics is inconsistent with the observed ordering; hence, explanations must be sought elsewhere (e.g., surface thermodynamics or kinetic effects).

I. INTRODUCTION: POSSIBLE ORIGINS OF SPONTANEOUS ORDERING IN SEMICONDUCTOR ALLOYS

Isovalent $A^{\rm III}_{1-x}B^{\rm III}_xC^{\rm V}$ semiconductor alloys with zinc-blende constituents $A^{\rm III}C^{\rm V}$ and $B^{\rm III}C^{\rm V}$ were found to order spontaneously in homogeneous vapor-phase growth into a variety of superlattice-like structures.[1-7] Unlike the more familiar spontaneous ordering of metallic alloys (e.g., $Cu_{1-x}Au_x$, $Cu_{1-x}Pt_x$), disordered $A^{\rm III}_{1-x}B^{\rm III}_xC^{\rm V}$ semiconductor alloys are known[8] to have *positive* mixing enthalpies (suggestive of repulsive interactions); hence, until recently[9] they were not expected, on theoretical grounds, to exhibit any ordered phases. Depending on the constituents AC and BC and on growth conditions, these ordered $(AC)_p(BC)_p$ superstructures with layer repeat period p and orientation G were found to take up the ordered tetragonal CuAu-like structure [$p=1$ and $G=(001)$], or the chalcopyrite structure [$p=2$ and $G=(201)$], or the trigonal CuPt-like structure [$p=1$ and $G=(111)$]. The lattice-matched $Al_{1-x}Ga_xAs$ system orders in the CuAu-like structure,[1] whereas lattice-mismatched systems tend to order either in (201)-oriented structures [$GaAs_{1-x}Sb_x$ (Ref. 2) and $Ga_{1-x}In_xAs$ (Ref. 3)] or, more often, in the CuPt-like structure [e.g., $GaInP_2$ (Ref. 4), Ga_2PAs (Ref. 5), Ga_2AsSb (Ref. 6), and $AlInAs_2$ (Ref. 7)]. Unlike "artificial" ordering, created by sequential (shutter-controlled) exposure of a substrate to $A+C$, then $B+C$, etc., this spontaneous ordering occurs[1-7] when $A+B+C$ are mixed homogeneously.

Of central interest here is the understanding of the *type* of ordering mechanism at play here. A few possibilities come to mind.[10]

(i) The ordering reflects *bulk thermodynamics;* that is, the ordered phase has the lowest free energy even in the already-grown bulk form.

(ii) The ordering reflects thermodynamic *epitaxial stabilization;* that is, the ordered phase has the lowest free energy only when it is coherent with a substrate; beyond a critical thickness, it loses this stabilization.

(iii) The ordering reflects *surface thermodynamics;* that is, the ordered phase has the lowest free energy only when it possesses a free surface during growth (due to favorable surface reconstruction). When covered by subsequent layers, this (bulk-unstable) structure is "frozen-in" metastably.

(iv) The ordering reflects *growth kinetics;* that is, the ordered phase is not a minimum free-energy structure under any of the above circumstances, but constitutes instead a transient structure of the growth dynamics.

In analogy with the situation in metallic alloys, substantial theoretical effort has been focused on either validation or elimination of the first possibility of bulk ordering, which we address here. The pertinent thermodynamic quantities are the bulk (bk) mixing enthalpy of the disordered (D) alloy,

$$\Delta H^{(D)}_{\rm bk}(x)=H^{(D)}(x)-xH_{AC}-(1-x)H_{BC}\ , \qquad (1)$$

and the bulk formation enthalpy of the ordered structure of type S,

$$\Delta H^{(S)}_{\rm bk}(X_S)=H^{(S)}(X_S)-X_SH_{AC}-(1-X_S)H_{BC}\ , \qquad (2)$$

both taken with respect to the energies of equivalent amounts of the solid binary constituents at their equilibrium zinc-blende structures. Here, $H^{(D)}$ and $H^{(S)}$ are the equilibrium total energies of the disordered and ordered bulk systems, respectively. Three main situations can be recognized for bulk ordering.

(a) *Unstable ordering in bulk* occurs when the structure S is less stable than its constituents,

$$\Delta H^{(S)}_{\rm bk}>0\ , \qquad (3a)$$

or even with respect to the disordered alloy of the same composition,

$$\Delta H^{(S)}_{\rm bk}(X_S)>\Delta H^{(D)}_{\rm bk}(X_S)\ . \qquad (3b)$$

This leads, at low temperatures, to phase separation (the true thermodynamic ground state in this case), followed by possible formation of the homogeneous disordered alloy at higher temperatures.

(b) Metastable bulk ordering occurs when the ordered structure S is stabler than one of the two alternatives (phase separation and disordering), but is less stable than the others. For example,

$$0 < \Delta H_{\rm bk}^{(S)}(X_S) < \Delta H_{\rm bk}^{(D)}(X_S) \ . \tag{4}$$

Here, the true thermodynamic ground state corresponds again to phase separation, but, if the latter process is slow, the system may order in structure S. Once formed, this structure is thermodynamically stable toward disordering (up to a certain critical temperature).

(c) *Stable ordering in bulk.* This requires that structure S is stabler than its disproportionation products,

$$\Delta H_{\rm bk}^{(S)} < 0 \ , \tag{5a}$$

and other structures,[11] including the disordered alloy,

$$\Delta H_{\rm bk}^{(S)}(X_S) < \Delta H_{\rm bk}^{(D)}(X_S) \ . \tag{5b}$$

If S is such a "ground-state structure,"[11] it would occur in the phase diagram below a given critical (order-disorder) temperature.

Considering the simplest, lattice-matched $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$ system, three early calculations[12–14] suggested that this alloy will order stably in bulk in the observed[1] S = CuAu structure; hence this system was said to belong to the class described by Eq. (5a). Subsequently, however, these calculations were shown[12–14] to be either incorrect or incomplete, so condition (5a) is not supported by them. Very recently, Koiller, Davidovich, and Falicov[15] (KDF) found, on the basis of tight-binding calculations of the electronic energies, that AlGaAs_2 satisfies Eq. (5a) in the S = CuAu structure, and that this structure is also stabler than many alternative structures that they considered. This opens the possibility that the observed ordering[1] is driven by bulk thermodynamics, much like in many metal alloys. We have reexamined this possibility in light of this recent work. We find that while internally consistent, this tight-binding result conflicts with first-principles total-energy calculations that avoid many of the approximations made by KDF. We conclude, on the basis of highly precise pseudopotential calculations carried out in a manner parallel to the tight-binding work, that $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$ belongs to the class of "*unstable ordering in bulk*" [Eqs. (3a) and (3b)] for *all* ordered structures $\{S\}$. Hence, bulk thermodynamics cannot explain the observed ordering in $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$; explanations must be sought in other mechanisms,[10] such as surface thermodynamics [(iii) above] or kinetics [(iv) above].

II. STATISTICAL MECHANICS USING TIGHT-BINDING FORMATION ENTHALPIES

KDF considered a periodic supercell of composition $A_{8-n}B_nC_8$ $(0 \le n \le 8)$ consisting of eight zinc-blende primitive unit cells obtained by doubling the three face-centered-cubic (fcc) lattice vectors. Different occupations of the eight cation sites by A and B create 16 distinct structures[16] labeled S_i. The electronic structure of these

TABLE I. Average spin products $\overline{\Pi}_{km}(S)$ for the ordered structures $\{S\}$ of Ref. 15 (see Table III therein for definitions of structures and Table II here for the compositions). Here, k is the number of atoms interacting simultaneously and m is the separation, e.g., $(k,m)=(2,2)$ and (4,1) are two-body (pair) interactions between second fcc neighbors and the four-body (tetrahedron) interaction between first fcc neighbors, respectively. $(k,m)=(0,1)$ is the "empty" figure (normalization constant), and $(k,m)=(1,1)$ is the single-site figure. Note from Eq. (12) that the energy of the random alloy at $x=\frac{1}{2}$ is $J_{0,1}$. $D_{k,m}$ is the degeneracy of figure (k,m) per fcc site.

		$\overline{\Pi}_{k,m}(S)$															
(k,m)	$D_{k,m}$	S_1	S_2	S_3	S_4	S_5	S_6	S_7'	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}	S_{15}
(0,1)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
(1,1)	1	1	$\frac{3}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0	0	0	$-\frac{1}{4}$	$-\frac{1}{4}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{4}$	-1
(2,1)	6	1	$\frac{1}{2}$	$\frac{1}{6}$	0	0	$-\frac{1}{6}$	$-\frac{1}{6}$	0	0	$-\frac{1}{3}$	0	$-\frac{1}{6}$	$\frac{1}{6}$	0	$\frac{1}{2}$	1
(3,1)	8	1	$\frac{1}{4}$	0	$-\frac{1}{2}$	0	$-\frac{1}{4}$	0	0	0	0	0	$\frac{1}{4}$	0	$\frac{1}{2}$	$-\frac{1}{4}$	-1
(4,1)	2	1	0	0	-1	0	0	0	1	-1	1	0	0	0	-1	0	1
(2,2)	3	1	$\frac{1}{2}$	0	1	$-\frac{1}{2}$	$\frac{1}{2}$	0	-1	-1	1	$-\frac{1}{2}$	$\frac{1}{2}$	0	1	$\frac{1}{2}$	1
(2,3)	12	1	$\frac{1}{2}$	$\frac{1}{6}$	0	0	$-\frac{1}{6}$	$-\frac{1}{6}$	0	0	$-\frac{1}{3}$	0	$-\frac{1}{6}$	$\frac{1}{6}$	0	$\frac{1}{2}$	1
(2,4)	6	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
(2,5)	12	1	$\frac{1}{2}$	$\frac{1}{6}$	0	0	$-\frac{1}{6}$	$-\frac{1}{6}$	0	0	$-\frac{1}{3}$	0	$-\frac{1}{6}$	$\frac{1}{6}$	0	$\frac{1}{2}$	1
(2,6)	4	1	$\frac{1}{2}$	0	1	$-\frac{1}{2}$	$\frac{1}{2}$	0	-1	-1	1	$-\frac{1}{2}$	$\frac{1}{2}$	0	1	$\frac{1}{2}$	1

compounds was obtained by applying a four-orbital ($s+3p$) per atom nearest-neighbor tight-binding Hamiltonian to these 16-atom periodic crystals. The formation enthalpies were calculated from the definition of Eq. (2); the total energy $H(S_i)$ was approximated by summing the band energies of the 32 lowest doubly occupied valence band states, ε_j, at a single (zone-center) **k** point in the superlattice Brillouin zone,[17]

$$H(S_i)=\sum_j 2\varepsilon_j(\mathbf{k}=0)\ . \qquad (6)$$

The "double-counting"[18,19] electron-electron and ion-ion terms were neglected, as were direct interactions beyond first neighbors and charge self-consistency. The sums of occupied tight-binding band energies [Eq. (6)] often predict unreasonable equilibrium geometries;[19] KDF hence evaluated it at the experimental unit-cell volume. The resulting formation enthalpies of the ordered $\mathrm{Ga}_n\mathrm{Al}_{8-n}\mathrm{As}_8$ structures (defined in Table III of KDF) are shown in Fig. 1(a). Note that all structures were found by KDF to have *negative* formation enthalpies[20] with respect to the phase-separated $[(8-n)/8]$ AlAs$+(n/8)$ GaAs reference energy, and that the CuAu-like structure S_9 had the lowest overall energy. This suggests trends toward spontaneous ordering of the alloy in this structure. Virtually identical results were obtained[15] for $\mathrm{In}_n\mathrm{Ga}_{8-n}\mathrm{P}_8$.

This analysis does not address the possibility that other ordered structures (not spanned by different occupations of just the eight fcc sites considered by KDF) could have yet lower energies, nor does it provide the mixing enthalpy of the disordered alloy [hence, conditions (3b) and (5b) cannot be examined]. To address these questions, we subject the set of tight-binding formation enthalpies $\{\Delta H(S_i)\}$ to a cluster expansion.[21] The formation enthalpy $\Delta H(\sigma)$ of any of the 2^N configurations σ of atoms A and B on an N-site lattice (not just the eight-fcc-site lattice) can be rigorously expanded in a series of multiatom interaction energies J_f of "figures" f. Each figure consists of k vertices (the number of sites allowed to interact simultaneously), separated by up to mth neighbors, e.g., $(k,m)=(2,m)$ represents pair interactions between mth fcc neighbors, $(k,m)=(3,1)$ represents three-body nearest-neighbor (equilateral triangle) interactions, etc. Hence,

$$\Delta H(\sigma)=N\sum_f \overline{\Pi}_f(\sigma)D_fJ_f\ , \qquad (7)$$

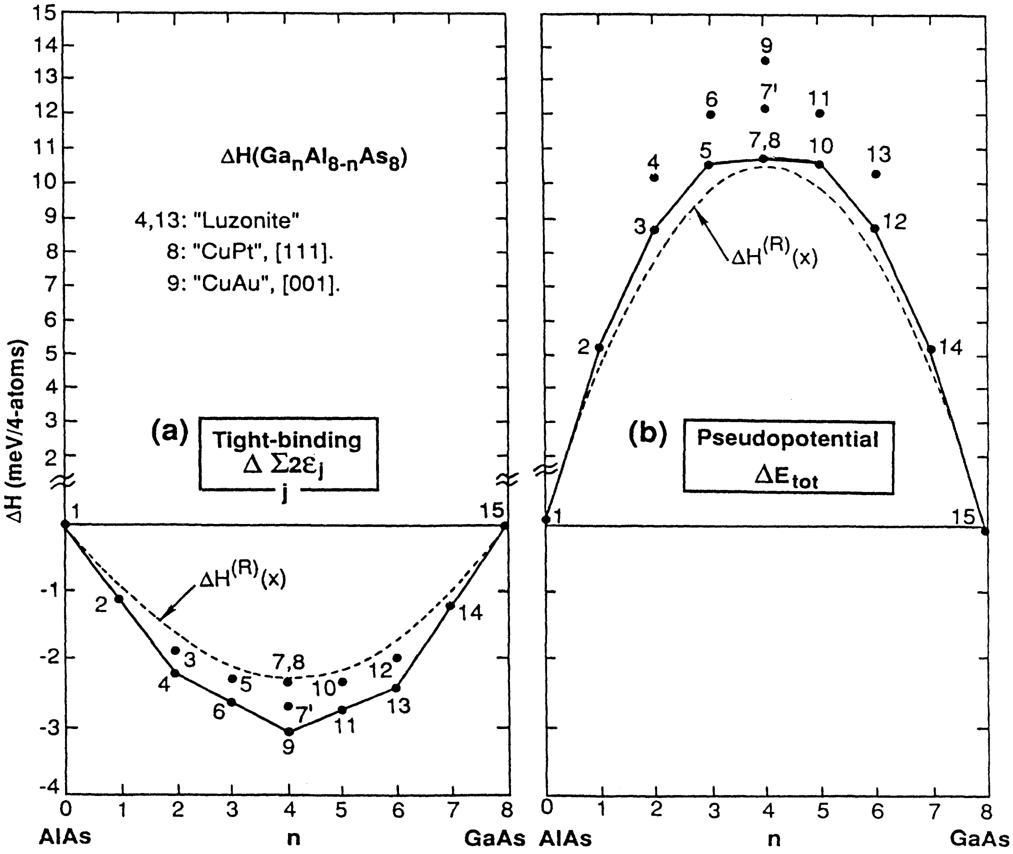

FIG. 1. Calculated formation enthalpies [Eq. (2)] of ordered $\mathrm{Ga}_n\mathrm{Al}_{8-n}\mathrm{As}_8$ compounds (solid circles) and the mixing enthalpies of the random alloy [Eq. (1) dashed lines] using (a) the tight-binding calculation of KDF [Eq. (6)], and (b) the self-consistent pseudopotential method [Eq. (6′)]. The values of the formation enthalpies for the stablest structure at each composition are connected by straight lines, to guide the eye. The numbered structures are defined in Table III of Ref. 15 (also see Ref. 16 of the present paper). Note the completely opposing trends (in signs and relative positions) in (a) and (b).

where the lattice-averaged product of spin variables of figure f is denoted $\overline{\Pi}_f(\sigma)$ and reflects the occurrence frequency of this figure in configuration σ. D_f is the degeneracy of this figure per fcc site. Table I gives $\overline{\Pi}_f(s)$ and D_f for the structures[16] considered by KDF. Assume now that this expansion converges reasonably rapidly and can be truncated after the inclusion of N_f terms. Specializing the truncated form of Eq. (7) to a particular set of N_s periodic structures $\{S_i\}$ gives

$$\Delta H(S_i)=N\sum_{f}^{N_f}\overline{\Pi}_f(S_i)D_f J_f \ . \tag{8}$$

Hence, as shown by Connolly and Williams,[22] knowledge of $N_s=N_f$ values of $\Delta H(S_i)$ gives N_s values of the interaction energies,

$$J_f=\frac{1}{ND_f}\sum_{S_i}^{N_s}[\overline{\Pi}_f(S_i)]^{-1}\Delta H(S_i) \ . \tag{9}$$

To check whether the truncation of the series after N_f terms is justified, we extract $\{J_f\}$ through Eq. (9) using but a small set of only $N_s=5$ (out of 16) structures considered by KDF. These $\{J_f\}$ values are then used to predict the energies of the *remaining* structures [not used in the inversion of Eq. (9)] from Eq. (8). Comparing the predicted energies to those calculated directly by tight-binding provides a measure for the convergence of the series.

We select a set of $N_s=5$ structures (indicated in Table II by an asterisk) and a corresponding set of $N_f=5$ interactions $J_{k,m}$. These are the normalization term $J_{0,1}$, the sites-only term $J_{1,1}$, and the fcc nearest-neighbor pair $J_{2,1}$, three-body $J_{3,1}$, and four-body $J_{4,1}$ interactions. (Note that the first fcc neighbor equals the second zinc-blende neighbor.) Inverting this 5×5 problem through Eq. (9) gives (in meV)

$$\begin{aligned}&J_{0,1}=-1.145,\ \ J_{1,1}=+0.05,\ \ J_{2,1}=+0.19\ ,\\&J_{3,1}=-0.006\,25,\ \ J_{4,1}=+0.002\,50\ .\end{aligned} \tag{10}$$

Using these five interactions, we then predict the energies of all remaining structures through Eq. (8). The results are compared in Table II to the values calculated directly by tight binding, showing excellent agreement (after an error in the definition of two structures was identified and confirmed by B. Koiller).[16] Virtually the same results [Eq. (10)] are obtained using *any* invertible set of five out of 16 structures. We conclude the following.

(i) The tight-binding formation enthalpies calculated by KDF are internally consistent in that knowledge of about five values suffices to predict the others. The compact set of five interaction parameters of Eq. (10) hence represents the full informational content of this calculation.

(ii) The tight-binding enthalpies converge rapidly in a cluster expansion; they exhibit essentially only nearest-neighbor pair interactions ($J_{2,1}$), with further-neighbor terms (tested separately) as well as the three- and four-body terms being negligible. This fast convergence reflects the fact that the underlying tight-binding calculation limits the matrix elements only to first zinc-blende neighbors. The dominance of $J_{2,1}$ over other interactions

TABLE II. Formation enthalpies [in meV/(4 atoms)] for the 16 ordered structures considered by KDF. The structures are defined in Table III of Ref. 15; when available, we also give the conventional structural symbols. Note that the structure S_7' was omitted from Ref. 15 and that the energy quoted there for S_8 [-2.68 meV/(4 atoms)] actually corresponded to the structure S_7'. This is corrected here (Ref. 16). The cluster expansion [Eqs. (7)–(9)] based on five structures (denoted by asterisks) accurately predicts the directly calculated tight-binding result for all other structures. The interaction energies are given in Eq. (10).

Structure	Composition x in $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$	Formation enthalpies [meV/(4 atoms)] Tight binding	Cluster expansion
S_1 (AlAs)	0.0	0.00	0.00*
S_2	$\frac{1}{8}$	-1.10	-1.10
S_3	$\frac{1}{4}$	-1.86	-1.86
S_4 ($L1_2$)	$\frac{1}{4}$	-2.20	-2.20*
S_5	$\frac{3}{8}$	-2.28	-2.265
S_6	$\frac{3}{8}$	-2.62	-2.62
S_7	$\frac{1}{2}$	-2.32	-2.285
S_7'	$\frac{1}{2}$	-2.68	-2.67
S_8 (CuPt)	$\frac{1}{2}$	-2.32	-2.30
S_9 (CuAu)	$\frac{1}{2}$	-3.04	-3.04*
S_{10}	$\frac{5}{8}$	-2.34	-2.315
S_{11}	$\frac{5}{8}$	-2.72	-2.72
S_{12}	$\frac{3}{4}$	-1.96	-1.96
S_{13} ($L1_2$)	$\frac{3}{4}$	-2.40	-2.40*
S_{14}	$\frac{7}{8}$	-1.18	-1.20
S_{15} (GaAs)	1.0	0.00	0.00*

suggests that the occupation of the first fcc shell by Al or Ga decides the relative stabilities of different structures, as noted by KDF.

(iii) Knowledge of a converged set of interactions $\{J_f\}$ permits evaluation of ΔH for *any* configuration[21] σ. For the random (R) alloy, for example, we replace $\overline{\Pi}_f(\sigma)$ by its configurationally averaged value,

$$\langle \overline{\Pi}_{k,m}(R)\rangle=(2x-1)^k , \tag{11}$$

yielding the mixing enthalpy of the alloy,

$$\Delta H^{(R)}(x)=N\sum_{k,m} D_{k,m}(2x-1)^k J_{k,m} , \tag{12}$$

which is depicted in Fig. 1(a) by the dashed line. We see that the tight-binding calculation predicts that all of the ordered structures examined by KDF are stabler than the random alloy of the same compositions. Hence, both conditions (5a) and (5b) for "bulk stability" are satisfied for $S_9=\text{CuAu}$.

(iv) The set $\{J_f\}$ can be used to identify the true ground-state structure, not limiting the selection to the $2^4=16$ configurations considered by KDF. This is done by writing the Ising Hamiltonian corresponding to the tight-binding set of interactions of Eq. (10):

$$\hat{H}=\tfrac{1}{2}J_{2,1}\sum_{i,j}\hat{S}_i\hat{S}_j+\tfrac{1}{3}J_{3,1}\sum_{i,j,k}\hat{S}_i\hat{S}_j\hat{S}_k +\tfrac{1}{4}J_{4,1}\sum\hat{S}_i\hat{S}_j\hat{S}_k\hat{S}_l+J_{1,1}\sum_i\hat{S}_i+J_{0,1}N , \tag{13}$$

where $\hat{S}_i$ is the spin operator (1 if i is occupied by A; -1 if i is occupied by B). The ground states of this Hamiltonian were investigated previously for fcc lattices[11]. Rewriting (13) in terms of the alternative parameters[11(b)]

$$\begin{aligned}\omega&=-2J_{2,1} ,\\ \alpha&=\frac{4J_{3,1}+2J_{4,1}}{3J_{2,1}} ,\\ \beta&=\frac{-4J_{3,1}+2J_{4,1}}{3J_{2,1}} ,\end{aligned} \tag{14}$$

we can express the total energy of the AB alloy as

$$\hat{H}_{AB}=3\omega(1+\alpha)N_1+4\omega N_2+3\omega(1+\beta)N_3 , \tag{15}$$

where N_n is the number of tetrahedra whose four sites have n B atoms. In the limit where pair interactions dominate, $\alpha=\beta=0$. Cahn and Kikuchi[11(b)] give a ground-state diagram in the α versus β plane for $\omega>0$ (ferromagnet) and $\omega<0$ (antiferromagnet). The tight-binding results of KDF show that $\text{Al}_{1-x}\text{Ga}_x\text{As}$ behaves as an antiferromagnet with ground states $S_4=\text{Al}_3\text{GaAs}_4$ ($L1_2$-like), $S_9=\text{AlGaAs}_2$ ($L1_0$, or CuAu-like), and $S_{13}=\text{AlGa}_3\text{As}_4$ ($L1_2$-like) at compositions $x=\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$, respectively. The phase diagram hence has the same structure as that inferred for the $\text{Cu}_{1-x}\text{Au}_x$ metal alloy.[11(c),23]

Having established that the tight-binding calculations of KDF predict stable bulk ordering of the CuAu-like GaAlAs_2 structure in an internally consistent fashion, it remains to be seen if this prediction is also physically correct if one transcends approximations used in the tight-binding model.

III. FIRST-PRINCIPLES PSEUDOPOTENTIAL RESULTS

A. Pseudopotential formation enthalpies

We have calculated the total energies of a set of ordered $\text{Al}_n\text{Ga}_m\text{As}_{n+m}$ structures using the first-principles pseudopotential approach[18] within the local-density formalism[24]. Since the excess energies in this system are $O(10)$ meV, we have very carefully tested all convergence parameters in the problem. In particular, we use a large set of plane-wave basis functions (with a cutoff energy of 15 Ry) and a substantial set of **k** points for Brillouin-zone integration, selected so that all structures are sampled exactly in an equivalent manner[25] (i.e., the set of **k** points for all structures is equivalent to 29 special zinc-blende **k** points in the irreducible portion of the zinc-blende Brillouin zone). The total energy can be written in momentum space[18] as

$$H(S)=\sum_{j,\mathbf{k}}2\varepsilon_j(\mathbf{k})-E_{ee}+E_{ii} , \tag{6$'$}$$

where the interelectronic term is

$$E_{ee}=\tfrac{1}{2}\sum_{\mathbf{q}\,(\neq 0)}V_{\text{Coul}}(\mathbf{q})\rho(\mathbf{q})+\tfrac{1}{4}\sum_{\mathbf{q}}\mu_{\text{xc}}(\mathbf{q})\rho(\mathbf{q}) , \tag{16}$$

and $V_{\text{Coul}}(\mathbf{q})$, $\mu_{\text{xc}}(\mathbf{q})$, and $\rho(\mathbf{q})$ are the Fourier transforms at the reciprocal-lattice vector $\mathbf{q}$ of the Hartree potential, the exchange-correlation potentials, and the valence (pseudo) charge density, respectively. The term E_{ii} represents[18] the ion-ion (Ewald) and part of the electron-ion energies. Since this term is common to the ordered structures and equivalent amounts of its zinc-blende constituents, the formation enthalpy of Eq. (2) can be written as

$$\Delta H(S)=\Delta\sum_{j,\mathbf{k}}2\varepsilon_j(\mathbf{k})+\Delta E_{ee} , \tag{17}$$

where Δ denotes differences between the respective quantities in $\text{Al}_n\text{Ga}_m\text{As}_{n+m}$ and equivalent amounts of its zinc-blende constituents. Comparing the tight-binding expression (6) of KDF to the complete expression in Eq. (17) used here, we note that the former lacks the excess interelectronic energy term ΔE_{ee}.

Table III gives the formation enthalpies obtained from the pseudopotential calculations, broken according to Eq. (17). We see the following trends.

(i) In contrast to the tight-binding results of KDF, we have

$$\Delta H(S_i)>0 \text{ (pseudopotential)} . \tag{18a}$$

(ii) The CuAu(S_9) structure is *higher* in energy than the CuPt(S_8) structure,

$$\Delta H(S_9)>\Delta H(S_8) \text{ (pseudopotential)} . \tag{18b}$$

These conclusions were carefully examined and found to hold within the numerical precision of the pseudopotential calculations.

TABLE III. Breakdown of the pseudopotential formation enthalpy $\Delta H(S_i)$ [in units of meV/(4 atoms)] into the band-structure term and an interelectronic term; see Eq. (17). The results are converged with respect to the **k**-point sampling.

Energy terms	CuAu S_9 $AlGaAs_2$	CuPt S_8 $AlGaAs_2$	$L1_2$ S_{13} $AlGa_3As_4$	$L1_2$ S_4 Al_3GaAs_4	Chalcopyrite $AlGaAs_2$
$\Delta\sum_{j,k} 2\varepsilon_j(\mathbf{k})$	10.93	9.60	5.49	5.93	12.93
ΔE_{ee}	2.81	1.14	4.93	4.23	0.57
ΔH	13.74	10.74	10.42	10.16	13.50

(iii) Trends (i) and (ii) are already evident from the excess band energies [first term in Eq. (17)]; while the excess interelectronic energy is significant, it does not reverse these trends.

We next predict the energies of all other structures $\{S_i\}$ considered by KDF by applying the cluster-expansion technique to the pseudopotential results.

B. Statistical mechanics using the pseudopotential formation enthalpies

The cluster expansion described in Eqs. (7)–(9) was repeated using the pseudopotential formation enthalpies. However, we find here that nearest-neighbor terms do not suffice; a precision of ≤ 0.1 meV/(4 atoms) in the expansion of ΔH of 27 ordered structures (whose unit cells are up to 4 times the primitive zinc-blende cell) requires that we extend the cluster expansion up to the sixth fcc neighbors. The 27 ordered structures have been chosen so that different compositions ($x=\frac{1}{4},\frac{1}{3},\frac{1}{5},\frac{2}{3},\frac{3}{4}$) and different atomic-plane orientations (short-period superlattices in the [111], [001], [110], [113], and [201] directions) are represented. We find (in meV)

$$J_{0,1}=5.2811,\quad J_{1,1}=-0.0119\ , \tag{19a}$$

while for the pair interactions,

$$\begin{aligned} &J_{2,1}=-0.8115,\quad J_{2,2}=-0.0252\ ,\\ &J_{2,3}=-0.0240,\quad J_{2,4}=-0.0050\ ,\\ &J_{2,5}=0.0022,\quad J_{2,6}\ =-0.0092\ . \end{aligned} \tag{19b}$$

The three- and four-body terms are small,

$$J_{3,1}=0.0068,\quad J_{4,1}=-0.0035\ . \tag{19c}$$

One notices that the dominant pair-interaction energy $J_{2,1}$ describing the pseudopotential results is "ferromagnetic" (A-B interactions are repulsive, indicating a trend toward phase separation). In contrast, the interactions describing the tight-binding results [Eq. (10)] are "antiferromagnetic" (A-B interactions are attractive, indicating a tendency towards ordering).

The cluster expansion for the pseudopotential total energies was used to predict the pseudopotential total energies of the structures $\{S_i\}$ calculated by KDF (the energies of S_4, S_8, S_9, and S_{13} were also calculated directly using the pseudopotential total energy—see Table III—and are in perfect agreement with the results of the cluster expansion). The results are depicted in Fig. 1(b), where we also give the energies of the random alloy calculated from Eq. (12) and the set (19).

Comparing Fig. 1(a) (tight binding) and Fig. 1(b) (pseudopotential) shows the following precisely reversed trends.

(i) The pseudopotential calculations yield $\Delta H(S)>0$ for all S values.

(ii) The random alloy is stabler than these ordered structures.

(iii) The CuPt(S_8) structure is stabler than CuAu(S_9); the same opposing trend exists in all other pairs of structures at the same composition (e.g., S_3 is stabler than S_{13}, etc).

(iv) Using the ground-state analysis of Ref. 11(a), the pseudopotential interaction energies [Eq. (19)] predict that the ground state corresponds to phase separation, not ordering. The CuAu structure satisfies the conditions (3a) and (3b) of "unstable ordering in bulk," whereas long-period $(AlAs)_p(GaAs)_p$ superlattices in all the orientations satisfy[26] condition (4) of "metastable bulk ordering."

Our first-principles results hence show that the $Al_{1-x}Ga_xAs$ system represents "*unstable ordering in bulk*" [Eqs. (3a) and (3b)], not "*stable ordering*" [Eqs. (5a) and (5b)] as suggested by the tight-binding study.

Other first-principles calculations indicate trends similar to those obtained in the pseudopotential study here. For example, the monolayer $(AlAs)_1(GaAs)_1$ superlattice in the (001) orientation (the CuAu-like structure S_9) has been studied by a number of authors. The best-converged results give, for $\Delta H(S_9)$ [in meV/(4 atoms)],

$$\begin{aligned} &\Delta H(S_9)=13.5\quad [\text{LAPW (Ref. 27)}]\ ,\\ &\Delta H(S_9)=15.1\quad [\text{pseudopotential (Ref. 28)}]\ , \end{aligned} \tag{20a}$$

while for the CuPt(S_8) structure,

$$\Delta H(S_8)=10.1\quad [\text{pseudopotential (Ref. 28)}] \tag{20b}$$

(here, LAPW denotes the linear augmented-plane-wave method). Given the large diversity in methods and numerical strategies used, the agreement with our results (Table III) is very good.

C. Likely source of error in tight-binding calculations

While the interelectronic energy E_{ee} [Eq. (16)] omitted in the independent-particle calculation of KDF [Eq. (6)] is numerically significant and can, on occasion, even reverse the order of stability of two structures (e.g., S_{13} and S_4 in Table III), it does not change the sign of $\Delta H(S)$. Similarly, the rather small charge transfer found in AlGaAs compounds[27,28] suggests that the lack of self-consistency in the tight-binding calculations of KDF will also not affect their conclusions. However, given the small magnitude of the electronic energies in these systems, it is possible that the use of a single **k** point ($\mathbf{k}=0$) in the supercell Brillouin zone [Eq. (6)] might introduce systematic errors. This $\mathbf{k}=\mathbf{0}$ sampling (inherent in the "small crystal approximation"[29] of Ref. 15) is equivalent in the 16-atom cell to the use of the zinc-blende **k** points $\Gamma+X+L$ with weights $\frac{1}{8}:\frac{3}{8}:\frac{1}{2}$. (This sampling scheme has been widely used before the advent of "special **k** points for Brillouin-zone integration"; see, e.g., Ref. 30). Since the wave functions are highly symmetric at these **k** points, they might not correctly represent the circumstances throughout the zone. To shed some light on this possibility, we have recalculated our pseudopotential total energies of Eq. (6′), (16), and (17) for the zinc-blende constituents, CuAu(S_9) and CuPt(S_8), using the **k**-point sampling $\Gamma+X+L$ used by KDF. The results are presented in Table IV in a manner analogous to those shown in Table III, where 29 zinc-blende-equivalent (special) **k** points were used. This comparison shows that, all other things being equal, the $\Gamma+X+L$ **k**-point sampling produces (i) $\Delta H(S)<0$, and (ii) $\Delta H(S_9)<\Delta H(S_8)$, exactly as obtained by KDF in their tight-binding study [Fig. 1(a)]. *This suggests that their conclusions on the tendencies of the electronic energy to drive "stable bulk ordering" in $Al_{1-x}Ga_xAs$ (Sec. II) are incorrect,* reflecting, most likely, poor **k**-point convergence inherent in their "small-crystal approximation."[29]

D. Other intersemiconductor compounds

Tight-binding calculations that are analogous to those shown in Fig. 1(a) for $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$ were also performed by KDF (Ref. 15) for $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$, giving virtually identical results. Similar calculations[15] for $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ also predicted a minimum of $\Delta H(S)$ for the observed[31] rhombohedral (space group $R\overline{3}m$) ordered structure. In these two cases, the formation enthalpy consists of a "microscopic strain" (MS) term associated with elastic deformations of the positions of the A,B atoms of dissimilar size, plus a "chemical" (chem) term,

$$\Delta H(S)=\Delta E_{\mathrm{MS}}(S)+\Delta E_{\mathrm{chem}}(S)\ . \tag{21}$$

TABLE IV. Breakdown of the pseudopotential formation enthalpies $\Delta H(S)$ [in units of meV/(4 atoms)] in a manner analogous to Table III using, however, the $\Gamma+X+L$ **k**-point sampling of KDF instead of a converged set of 29 zinc-blende **k** points.

Energy terms	CuAu S_9 AlGaAs_2	CuPt S_8 AlGaAs_2
$\Delta\sum_{i,j} 2\varepsilon_j(\mathbf{k})$	-73.33	-21.22
ΔE_{ee}	47.48	5.31
ΔH	-25.85	-15.91

For the lattice-matched $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$ systems, we have $\Delta E_{\mathrm{MS}}=0$. KDF calculated only $\Delta E_{\mathrm{chem}}(S)$, finding it to be negative with a minimum at $S=\mathrm{CuAu}$ in $\mathrm{In}_{1-x}\mathrm{Ga}_x\mathrm{P}$ and $S=R\overline{3}m$ in $\mathrm{Si}_{1-x}\mathrm{Ge}_x$. In contrast, first-principles calculations for lattice-mismatched III-V alloys[21,32] show that $\Delta E_{\mathrm{chem}}(S)>0$ for $S=\mathrm{CuAu}$ and CuPt, and that this chemical energy hardly distinguishes between these two structures. It is possible that the limited Brillouin-zone sampling of KDF is again responsible for this difference. Note that the *total* enthalpy of Eq. (21) is positive for these systems, showing, therefore, no trends toward stable bulk ordering, i.e.,

$$\Delta H(\mathrm{GaInP}_2, S_9)=91\ \mathrm{meV/(4\ atoms)}\quad [\mathrm{LAPW\ (Ref.\,33)}]$$

and (22)

$$\Delta H(\mathrm{SiGe}, R\overline{3}m)=28\ \mathrm{meV/(4\ atoms)}\quad [\mathrm{pseudopotential\ (Ref.\,34)}]\ .$$

IV. SUMMARY AND CONCLUSIONS

We have examined the possibility that the observed[1] spontaneous ordering in $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$ reflects *bulk* thermodynamics and have drawn negative conclusions on the basis of combined pseudopotential total-energy calculations and statistical-mechanics models of the random alloy. The tight-binding calculations of Koiller, Davidovich, and Falicov[15] must be reexamined in light of these results. A useful conclusion reached is that the cluster-expansion method[21] can be used, in conjunction with either tight-binding or pseudopotential total-energy calculations, on a small number of periodic structures to predict accurately the energies of many more structures. Regarding the ordering classes defined in Sec. I, the status at present is as follows.

(i) Since the CuAu ordering in $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$ is not mandated by bulk thermodynamics, and since epitaxial effects are negligible in this system (on account of the close lattice match between AlAs and GaAs), ordering mechanisms in this system must be sought in nonbulk effects, e.g., surface[10] or kinetic effects.

(ii) In lattice-mismatched systems, we find[10,21,33] that "metastable bulk ordering" [Eq. (4)] exists for the $S=$chalcopyrite structure (however, the calculated order-disorder transition temperature for GaInP_2 is only[21] 463 K, while the growth temperature at which ordering was observed[4] is ~ 900 K). For AlInP_2 and AlInAs_2, we find[33] "stable bulk ordering" [Eq. (5a)], again for the chalcopyrite structure.

(iii) In contrast, the CuPt structure of all lattice-mismatched semiconductors is found[10,21,33] to belong to the "unstable bulk ordering" [Eq. (3)] class; hence, bulk thermodynamics is not the relevant mechanism. Surface-induced ordering[10] does explain the observed[4-7] CuPt structures in that reconstruction lowers the surface energy of CuPt well below that of the phase-separated and the chalcopyrite systems.

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