

Ordering of isovalent intersemiconductor alloys

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(Received 9 June 1988)

Recent observations of spontaneous long-range ordering in alloys of isovalent semiconductors, despite independent evidence for repulsive interactions in these systems, are interpreted in terms of first-principles total-energy calculations for ordered compounds and cluster-variation-method calculations for the disordered phase.

Solid $A_xB_{1-x}C$ alloys of isovalent semiconductor constituents AC and BC are known¹ to universally exhibit in their high-temperature disordered (D) phase positive mixing enthalpies $\Delta H^{(D)} = H[A_xB_{1-x}C] - xH[AC] - (1-x)H[BC]$. At sufficiently low temperatures, phase separation of such alloys into their binary constituents is often observed.¹ Similar effects are observed in many other isovalent octet alloys, e.g., those formed between alkali halides.² These phenomena have led to the widely held view¹⁻⁶ that the microscopic interactions between the local bonding configurations in an isovalent octet alloy (e.g., between A_4C and B_4C clusters in zinc-blende alloys) are fundamentally repulsive, and hence that no long-range-ordered isovalent compounds between AC and BC (such as those common in intermetallic phases, e.g., ordered CuAu-I) are to be expected in semiconductor physics. Since artificial $(AC)_n(BC)_m$ short-period superlattices can be viewed as ordered intersemiconductor compounds, this would imply that such isovalent superlattices are fundamentally unstable and owe their (temporary) existence to artificially imposed layer-by-layer growth processes. Zunger and co-workers⁷⁻⁹ showed, however, that the microscopic strain energy associated with packing on a lattice atoms A and B of dissimilar sizes can lead to (i) $\Delta H^{(D)} > 0$ even if the microscopic interaction between A and B is attractive,^{7,9} and (ii) a preference at low temperatures of ordered (O) over disordered arrangements⁸ even if the formation enthalpy of the ordered compounds $\Delta H^{(O)} = H[ABC_2] - 0.5H[AC] - 0.5H[BC]$ is positive. In either case, long-range-ordered phases which are stable⁹ (case i) or metastable⁸ (case ii) with respect to phase separation could exist at sufficiently low temperatures, since $\Delta H^{(O)} < \Delta H^{(D)}(x=0.5)$. Subsequently, ordered intersemiconductor phases were observed to occur spontaneously in lattice-matched epitaxial-growth experiments¹⁰⁻¹³ (see Fig. 1 for crystal structures).

In this work we calculate $\Delta H^{(O)}$ and $\Delta H^{(D)}$ for two prototype pseudobinary alloys in which ordering has been observed—one with a small size mismatch (AlAs-GaAs, with relative lattice parameters $\Delta a/a = 0.1\%$) and one with a large size mismatch (GaAs-GaSb, where $\Delta a/a = 7.5\%$). We explore the factors controlling the relative stabilities of three types of 50%-50% ordered structures (Fig. 1) as well as the disordered phase.

Self-consistent total-energy calculations for AlGaAs₂ and Ga₂AsSb in the three ordered structures, and the binary constituents provide $\Delta H^{(O)}$. These were performed

using the all-electron general-potential linearized augmented-plane-wave method¹⁴ (LAPW) within the local-density-functional formalism. The total energy was minimized with respect to the lattice parameter, as well as atomic positions within the unit cell. (Cubic geometry was retained for all the structures; the error introduced by this constraint is estimated to be about 2 meV per 4 atoms.) A precision of at least 3 meV per 4 atoms was secured by using precisely equivalent basis sets, muffin-tin radii, and sampling \mathbf{k} points for all structures.

To calculate $\Delta H^{(D)}$ we extract from total-energy calculations for nine $A_nB_{4-n}C_4$ ordered structures ($0 \leq n \leq 4$) the volume-dependent k -atom interaction energies^{8,15} $\{J_{k,m}(V)\}$, retaining $k \leq 4$ and $m \leq$ third neighbors. Using the cluster-variation method (CVM) and retaining up to four-body statistical correlations,⁸ we then solve approximately the fcc Ising model appropriate to the nine interactions $\{J_{k,m}(V)\}$ (with second- and third-neighbor effects resummed into nearest-neighbor terms¹⁵) to obtain the mixing enthalpy $\Delta H^{(D)}(x, T)$ of the disordered phase. Using an elastic valence-force-field (VFF) method, we

Name (ternary)	Layered tetragonal	Chalcopyrite	Layered Trigonal
Formula:	$n = 2; ABC_2$	$n = 2; ABC_2$	$n = 2; ABC_2$
Example: (ternary)	InGaAs ₂ -type	CuFeS ₂ -type	CrCuS ₂ -type (NaVS ₂)
Bravais Lattice:	Simple tetragonal	Body centered tetragonal	Rhombohedral
Space Group			
Int. Tables:	$P\bar{4}m2$	$I\bar{4}2d$	$R\bar{3}m$
Schoenflies:	D_{2d}^5	D_{2d}^{12}	C_{3v}^5
Number:	115	122	160

FIG. 1. Three possible structures for ordered ABC_2 compounds: The CuAu-I-like layered tetragonal structure (the AB sublattice has the CuAu-I structure), the chalcopyrite structure, and the CuPt-like layered trigonal structure (the AB sublattice has the CuPt structure).

also study a broad range of ordered isovalent systems, comparing their equilibrium strain energies.

Figures 2(a) and 2(b) show the calculated formation enthalpies $\Delta H^{(O)}$ of AlGaAs_2 [Fig. 2(a)] and Ga_2AsSb [Fig. 2(b)], along with the calculated low-temperature mixing enthalpies $\Delta H^{(D)}(x=0.5)$ of the corresponding disordered alloys. The following points are evident. (i) For both systems all of the ordered and disordered phases have *positive* excess enthalpies and so are unstable at low-temperature equilibrium (if attainable) with respect to decomposition into pure AC and pure BC .¹⁶ (ii) For *small size mismatch* (AlAs-GaAs), $\Delta H^{(D)} < \Delta H^{(O)}$, hence these ordered structures are also unstable with respect to disordering. The order of formation enthalpies in this case is $\Delta H^{(CA)} > \Delta H^{(CH)} > \Delta H^{(CP)}$, CA , CH , and CP denoting CuAu-I , chalcopyrite, and CuPt , respectively (Fig. 1). (iii) For *large size mismatch* (GaAs-GaSb), we find $\Delta H^{(D)}(x=0.5) > \Delta H^{(CH)}$ at all temperatures [and even $\Delta H^{(D)}(x=0.5) > \Delta H^{(CA)}$ above ≈ 700 K]; hence, at least the chalcopyrite-ordered structure could persist below some temperature T_c if phase separation is kinetically inhibited by low atomic mobilities below T_c . Neglect of vibrational contributions and use of random statistics to estimate the mixing entropy ΔS of the disordered phase then suggests $T_c = (\Delta H^{(O)} - \Delta H^{(D)}) / \Delta S \approx 425$ K. The order of formation enthalpies differs from that in (ii) above: $\Delta H^{(CP)} > \Delta H^{(CA)} > \Delta H^{(CH)}$. The total energy per atom $\Delta E^{(n)}$ of size-matched $(AC)_n(BC)_n$ superlattices scales as $2\sigma/n$, where σ is an orientation-dependent interface energy.¹⁷ Hence, while *short-period* superlattices such as CuAu-I (an $n=1$ superlattice in the $[001]$ direction) or CuPt (an $n=1$ superlattice in the $[111]$ direction) may have energies higher than the disordered phase (Fig. 2), beyond a critical repeat period n_c the opposite is true and metastable ordering is thermodynamically possible.

We next show that the order of formation enthalpies is determined by *structural* effects when $\Delta a/a$ is large, and by *chemical* effects when it is small. We begin by decomposing the formation enthalpy $\Delta H^{(O)}$ into three physically

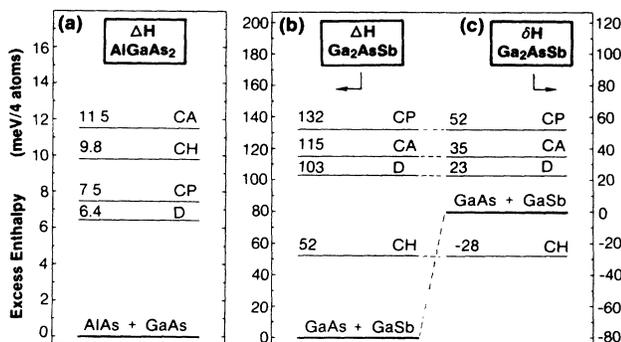


FIG. 2. Formation enthalpies for (a) bulk AlGaAs_2 and (b) bulk Ga_2AsSb in the three ordered structures of Fig. 1. Epitaxial formation enthalpies for Ga_2AsSb with substrate lattice constant $a_s = 5.89$ Å are shown in (c). Mixing enthalpies for disordered 50%-50% phases calculated from nine interaction parameters are also shown at (a) $T=80$ K and (b) and (c) $T=300$ K. The thick solid lines denote the zero of energy.

recognizable terms.⁷ These are (i) *volume deformation* (VD): compress and dilate the binaries from their equilibrium molar volumes (V_{AC} and V_{BC}) to the intermediate volume V , investing

$$\Delta E_{VD}(V) = [E_{AC}(V) - E_{AC}(V_{AC})] + [E_{BC}(V) - E_{BC}(V_{BC})]; \quad (1)$$

(ii) *charge exchange* (CE): combine AC and BC , at volume V , to form ABC_2 in a given ordered structure, retaining the unrelaxed atomic positions of (i); the associated energy is

$$\Delta E_{CE}(V) = E_{ABC_2}(V, \{u_0\}) - [E_{AC}(V) + E_{BC}(V)], \quad (2)$$

where $\{u_0\}$ denotes unrelaxed cell-internal atomic positions; and (iii) *structural (S) relaxation*: relax the cell-internal atomic positions $\{u\}$ (consistent with the space group symmetry) to minimize strain, allowing bond lengths and angles to approach “natural” values characteristic of the (unstrained) binaries; the associated energy is

$$\Delta E_S(V) = E_{ABC_2}(V, \{u_{rel}\}) - E_{ABC_2}(V, \{u_0\}). \quad (3)$$

The sum of these energies [(1)–(3)] at the equilibrium volume V_{eq} of ABC_2 is just the formation enthalpy of the ordered compound

$$\Delta H^{(O)} \equiv E_{ABC_2}(V_{eq}, \{u_{rel}\}) - [E_{AC}(V_{AC}) + E_{BC}(V_{BC})]. \quad (4)$$

Large $\Delta a/a$: Figure 3 depicts the energies of Eqs. (1)–(3) vs volume for GaAs-GaSb . We find that (i) the equilibrium cubic-cell volumes of the three structures are rather similar ($V_{CH} = 204.57$ Å³, $V_{CA} = 204.62$ Å³, and $V_{CP} = 205.11$ Å³), hence $\Delta E_{VD}(V_{eq})$ [Fig. 3(a)] does not distinguish much between these structures; (ii) the $\Delta E_{CE}(V)$ [Fig. 3(b)] are rather small and essentially volume independent; and (iii) in view of (i) and (ii), $\Delta E_S(V)$ [Fig. 3(c)] controls the order of formation enthalpies when $\Delta a/a$ is large, exhibiting $\Delta E_S^{(CP)} > \Delta E_S^{(CA)} > \Delta E_S^{(CH)}$, the same order as $\Delta H^{(O)}$ [Fig. 2(b)].

The near volume and structure independence of ΔE_{CE} suggests that a strain-only model can be used to assess both *relative* energies $\Delta H^{(O)}$ and equilibrium volumes for large $\Delta a/a$. Such a model permits exploratory calculations for a *large number* of size-mismatched semiconductors to determine the generality of the LAPW results and the way in which ΔE_S leads to a particular order of stability. We use a Keating-type¹⁸ VFF model, which includes strain contributions due to bond stretching and bond bending. The parameters of the model are natural bond lengths and angles and bond-stretching and bond-bending force constants, all determined from measured lattice and elastic constants.^{19,20} This model has been shown to give good results in the prediction of equilibrium structural geometries and enthalpies of formation of strained structures.¹⁹

The elastic strain contributions to $\Delta H^{(O)}$ are plotted versus lattice mismatch, in Fig. 4 for 18 III-V ternary compounds in the structures of Fig. 1. The order of strain energies is *universally* $\Delta H^{(CP)} > \Delta H^{(CA)} > \Delta H^{(CH)}$, the same order obtained from the LAPW calculations for

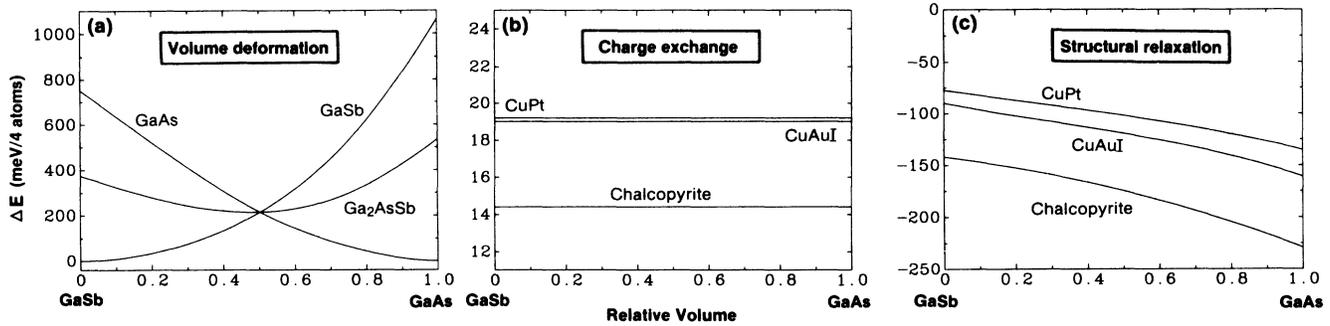


FIG. 3. Decomposition of the formation energy of ordered Ga_2AsSb into three components: (a) volume deformation [Eq. (1)], (b) charge exchange [Eq. (2)], and (c) structural relaxation [Eq. (3)].

GaAs-GaSb [Fig. 2(b)]. Since ΔE_{VD} does not distinguish the three ordered structures, and ΔE_{CE} is absent in VFF, the predicted order of stabilities of Fig. 4 must reflect relative strain-only structural relaxation energies. The order of ΔE_S reflects differences in the degree to which various ordered structures accommodate natural bond lengths and angles. In accommodating distinct $A-C$ and $B-C$ bond lengths, the displacement of the C atom in the chalcopyrite structure causes less bond-angle distortion (thus allowing less bond-length distortion) than in CuAu-I . The CuPt structure has large strain because it must accommodate in the same lattice two clusters, A_3BC and AB_3C , with different size. The emergence of chalcopyrite as the lowest energy form when $\Delta a/a$ is large is consistent with the fact that among I-III-VI₂ and II-IV-V₂ ordered adamantine ABC_2 semiconductors, none exists in the CuAu-I or CuPt form; instead, all have the chalcopyrite structure.²¹

Small $\Delta a/a$: Equations (1)–(3) show that for small $\Delta a/a$ one finds $\Delta E_{\text{VD}} \approx 0$ and $\Delta E_S \approx 0$, leaving ΔE_{CE} as the main contribution to $\Delta H^{(O)}$ (hence, VFF cannot be used in this limit). Modeling¹⁷ ΔE_{CE} in this limit as the excess Madelung electrostatic energy of ordered ABC_2 relative to AC and BC , one finds for structure λ (per four-atom cell)

$$\Delta E_M^\lambda = \frac{1}{d} \left[\frac{\alpha}{2} (\Delta q)^2 - 2\beta_\lambda (\Delta Q_\lambda)^2 \right], \quad (5)$$

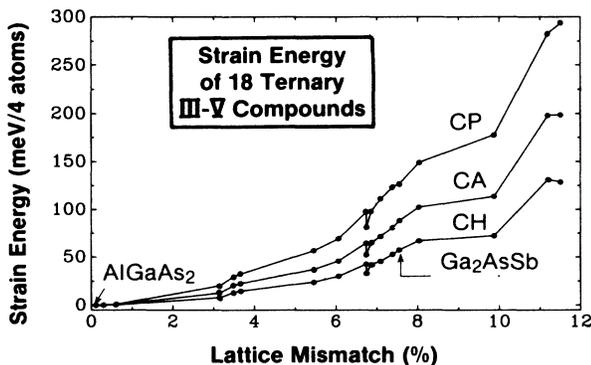


FIG. 4. Strain energy of 18 III-V ordered ternary semiconductor compounds in the three structures of Fig. 1, calculated via a valence-force-field model.

where d is the nearest-neighbor anion-cation bond length (unique when $\Delta a/a \rightarrow 0$), $\Delta q = q_A(AC) - q_B(BC)$ is the difference in the charges on A and B in the binary compounds, $\Delta Q = Q_A(ABC_2) - Q_B(ABC_2)$ is the corresponding difference in the ternaries, α is the Madelung constant for zinc-blende, and β_λ is a geometrical constant. The values of the constants are²² $\beta_{\text{CH}} = 0.1253$, $\beta_{\text{CA}} = 0.1220$, $\beta_{\text{CP}} = 0.1868$, and $\alpha = 1.6381$. Thus, (i) if ΔQ_λ is the same for the three ordered structures, we find²³ $\Delta E_M^{(\text{CA})} > \Delta E_M^{(\text{CH})} > \Delta E_M^{(\text{CP})}$, just the order of formation enthalpies found from the LAPW calculation for the lattice-matched system AlGaAs_2 [Fig. 2(a)]; (ii) in the absence of additional charge exchange in the ternary relative to the binaries ($\Delta Q_\lambda = \Delta q$), the excess Madelung energy is positive (destabilizing); (iii) only if $\Delta Q_\lambda/\Delta q$ exceeds the critical value $(\alpha/4\beta_\lambda)^{1/2}$ (1.83 for CuAu-I , 1.81 for chalcopyrite, and 1.48 for CuPt) is $\Delta E_M < 0$.

Most recent observations of ordering in semiconductor alloys are for films grown epitaxially on a substrate.^{10–13} The (sufficiently thin) film grows in atomic registry with the substrate (coherent growth), its lattice constants parallel to the substrate matching that of the substrate a_s , the third being free to adjust to accommodate strain. In most cases lattice-matched substrates are used, i.e., $a_s \approx a_{\text{eq}}(ABC_2) \approx a_{\text{eq}}(A_{0.5}B_{0.5}C) \approx a_{\text{avg}}$. While this choice exerts no strain on either the ordered ABC_2 or the disordered $A_{0.5}B_{0.5}C$ phases, it discourages phase separation into $AC + BC$ since *coherently grown constituents would be highly strained*²⁴ if Δa is nonzero. The epitaxial formation enthalpy is then calculated with respect to strained binaries:²⁴

$$\delta H^{(O)} = H[ABC_2, a_s] - H[AC, a_s] - H[BC, a_s]. \quad (6)$$

Figure 2(c) depicts δH for the GaAs-GaSb system lattice matched to $a_s = a_{\text{avg}} = 5.89 \text{ \AA}$. The destabilization of epitaxial GaAs and GaSb exposes the bulk-metastable chalcopyrite phase [Fig. 2(b)] as *epitaxially stable* [$\delta H^{(\text{CH})} < 0$]. This is consistent with recent observations of chalcopyrite-like and CuAu-I -like ordering in Ga_2AsSb ,¹¹ and possibly also in GaInAs_2 .¹³

We conclude that (i) the ordered intersemiconductor structures of Fig. 1 are unstable in bulk equilibrium since, when $\Delta a/a$ is large, the positive volume-deformation energies overwhelm the negative structural-relaxation energies, whereas for small $\Delta a/a$ the positive excess electrostatic energies lead to instability. (ii) For large $\Delta a/a$, the

order of formation energies is $\Delta H^{(CP)} > \Delta H^{(CA)} > \Delta H^{(CH)}$, dictated by the availability of different types of strain-lowering structural degrees of freedom; for small $\Delta a/a$, the order is $\Delta H^{(CA)} > \Delta H^{(CH)} > \Delta H^{(CP)}$, consistent with the order of the electrostatic energies. (iii) For large $\Delta a/a$, the better accommodation of strain by ordered (relative to disordered) structures leads to $\Delta H^{(O)} < \Delta H^{(D)}$, hence, to metastable bulk ordering. This could become stable ordering under epitaxial conditions. Items (i) and (ii) suggest that recent observations of CuPt-like ordering in epitaxially grown Ga₂AsSb (Ref. 12) and GaInP₂ (Ref. 25) are a result of surface thermodynamic effects rather

than bulk thermodynamic effects. For small $\Delta a/a$, the dominance of chemical pair interactions leads to $\Delta H^{(D)} < \Delta H^{(O)}$, hence, no thermodynamic ordering (stable or metastable) is predicted at this limit; longer period superlattices can, however, be stabler than the disordered phase at low temperature.

We wish to thank David Wood for a number of useful discussions. This work was supported by the Office of Energy Research, Materials Science Division, U.S. Department of Energy under Grant No. DE-AC02-77-CH00178.

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¹⁶The slight stability ($\Delta E^{(2)} = -25$ meV per 4 atoms) obtained in Ref. 8 for GaInP₂ using nonrelativistic local pseudopotentials is in error. A fully structurally optimized all-electron semirelativistic LAPW calculation gives $\Delta E^{(Ca)} = 91$ meV per 4 atoms. This system is thus predicted to order metastably.

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²³Adding to Eq. (5) a term $-\gamma_c U(\Delta q)^2$ due to on-site Coulomb repulsion U (see Ref. 17), where $\gamma_{CH} = \gamma_{CA} = \frac{1}{4}$ and $\gamma_{CP} = \frac{3}{16}$, gives the same order $\Delta E_{CE}^{(CA)} > \Delta E_{CE}^{(CH)} > \Delta E_{CE}^{(CP)}$, as found for the ΔE_M^k when the ΔE_{CE}^k are positive.

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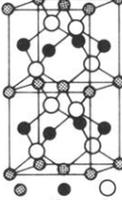
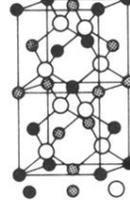
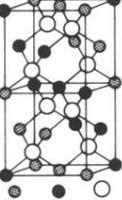
Name (ternary)	Layered tetragonal	Chalcopyrite	Layered Trigonal
Formula:	n = 2:ABC ₂	n = 2:ABC ₂	n = 2:ABC ₂
Example: (ternary)	 In Ga As InGaAs₂-type	 Cu Fe S CuFeS₂-type	 A B C CrCuS₂-type (NaV S₂)
Bravais Lattice:	Simple tetragonal	Body centered tetragonal	Rhombohedral
Space Group			
Int. Tables:	P4̄m2	I4̄2d	R3m
Schoenflies:	D ₅ ⁵ D _{2d} ⁵	D ₁₂ ¹² D _{2d} ¹²	C _{3v} ⁵
Number:	115	122	160

FIG. 1. Three possible structures for ordered ABC_2 compounds: The CuAu-I-like layered tetragonal structure (the AB sublattice has the CuAu-I structure), the chalcopyrite structure, and the CuPt-like layered trigonal structure (the AB sublattice has the CuPt structure).