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Atomic structure and ordering in semiconductor alloys

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Application of a first-principles local-density total-energy minimization method to both ordered and random models of a III-V semiconductor alloy shows a bimodal distribution of anion-cation bond lengths despite a close adherence to Vegard's rule and predicts ordered intermediate phases to be the thermodynamically stable low-temperature ground state, whereas the disordered phase is shown to be metastable.

Pseudobinary semiconductor alloys such as $A_x^{\mathrm{III}}B_{1-x}^{\mathrm{III}}C^{\mathrm{V}}$ have been known[1-3] to form as disordered (D) metastable phases with positive excess enthalpies of formation $\Delta H_D(x) = H(A_xB_{1-x}C) - xH(AC) - (1-x)H(BC)$, lattice parameters that are close to the composition (x) weighted average $a(x) \cong xa_{AC}^0 + (1-x)a_{BC}^0$ of the constituent AC and BC compounds[4] (Vegard's rule), and band gaps that are smaller than the composition weighted average[2,4] (positive "optical bowing"). Current theories of structure and stability of semiconductor alloys[1-3] have tacitly postulated that the low-temperature instability $\Delta H_D(x) > 0$ of the disordered phase follows from the inherent instability of (long-range) ordered intermediate compounds (e.g., ABC_2), and that optical bowing is largely disorder induced.[2] For instance, in Stringfellow's model[1] it is postulated that the enthalpy H of *any* phase, ordered or disordered, is a convex function of its lattice parameter $H = (-K/a^p)$ (where K is an empirical constant and $p > 0$). Hence, any phase with a lattice parameter intermediate between those of its constituent compounds will have $\Delta H > 0$. Similarly, in Van Vechten's model,[2] positive optical bowing accompanying compound formation is interpreted as a (destabilizing) upward shift of the valence-band energies, leading to $\Delta H > 0$ for either ordered or disordered compounds whose gaps are reduced relative to their average. All strain-minimizing models[3] necessarily lead to $\Delta H > 0$, as the strain energy is positive-definite.

Applying a first-principles local-density self-consistent total-energy minimization method[5] to both ordered and disordered models of a prototype semiconductor alloy ($\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$) we show the following: (i) Hitherto unrecognized *ordered (O)* intermediate phases (e.g., $\mathrm{GaInP_2}$) can be stable (i.e., $\Delta H_O < 0$) despite the fact that we predict them to obey Vegard's rule and to have positive optical bowing; (ii) both ordered and disordered intermediate phases are characterized by locally ordered and microscopically distorted anion positions,[6] leading to two unequal anion-cation bond lengths $R_{AC} \neq R_{BC}$ (bond alternation); and (iii) despite the stability of the ordered phases, substitutionally random semiconductor alloys nevertheless have a positive excess enthalpy $\Delta H_D(x) > 0$ as a result of the dominance of strain effects over chemical bonding effects. They are stable against disproportionation only at temperatures higher than T_C, when the disorder-induced excess entropy ΔS_D outweighs ΔH_D (hence, $T_C = \Delta H_D/\Delta S_D$).

Structural model. The four cations of type A and B can assume five different near-neighbor arrangements A_4C, A_3BC, A_2B_2C, AB_3C, and B_4C around the central anion C in a fourfold coordinated alloy $A_xB_{1-x}C$. Denote these structures by the number $n = 0$, 1, 2, 3, and 4 of the B-type cations, and the corresponding nearest-neighbor anion-cation bond lengths by $R_{AC}^{(n)}$ and $R_{BC}^{(n)}$. In general, these bond lengths (and the corresponding bond angles) could be deformed relative to the ideal bond lengths $d_{AC}^0 = (\sqrt{3}/4)a_{AC}^0$ and $d_{BC}^0 = (\sqrt{3}/4)a_{BC}^0$ of the constituent binary crystals AC and BC at their equilibrium lattice constants a_{AC}^0 and a_{BC}^0, respectively. Call these deviations $\Delta_{AC}^{(n)} = R_{AC}^{(n)} - d_{AC}^0$ and $\Delta_{BC}^{(n)} = R_{BC}^{(n)} - d_{BC}^0$. Extended x-ray absorption fine-structure (EXAFS) measurements[6] indicate that the A and B cations are very nearly distributed on the ideal fcc sites, with only a slight broadening in this distribution. Neglecting this small broadening, we have for each cation-cation separation $a/\sqrt{2}$ only a single independent displacement coordinate $\Delta^{(n)}$ per structure. We now evaluate the equilibrium (eq) values $\Delta_{\mathrm{eq}}^{(n)}(a)$, as well as the changes in total energy for both *ordered crystals* and for *randomly disordered alloys* sharing the same local structures.

Ordered intermediate compounds. The local structures n that exist in alloys could also be realized in coherent periodic crystals with a unit cell of the form $A_{4-n}B_nC_4$, and a total energy (say, relative to separated atoms) of $E_{A_{4-n}B_nC_4}[a^{(n)},\Delta^{(n)}]$ per cell. For $n = 0$ and $n = 4$ these are the conventional zinc-blende structures ($F\bar{4}3m$, or $B3$). For $n = 2$ we take the $\mathrm{CuFeS_2}$-type ($I\bar{4}2d$, or $E1_1$) chalcopyrite structure[7] and the simple tetragonal lattice ($P\bar{4}m2$, with a CuAu-I cation sublattice), whereas for $n = 1$ and $n = 3$ we take the luzonite $\mathrm{Cu_3AsS_4}$-type ($P\bar{4}3m$, or $H2_4$, with a $\mathrm{Cu_3Au}$ cation sublattice) structure and the famatinite $\mathrm{Cu_3SbS_4}$-type ($I\bar{4}2m$, or $H2_a$, with a $\mathrm{Al_3Ti}$ cation sublattice) structures. For each ordered phase n we define its excess energy relative to its constituent binary compounds at equilibrium as

$$\Delta E^{(n)}[a^{(n)},\Delta^{(n)}] = E_{A_{4-n}B_nC_4}[a^{(n)},\Delta^{(n)}] - \left[\frac{4-n}{4}E_{AC}[a_{AC}^0] + \frac{n}{4}E_{BC}[a_{BC}^0]\right] . \quad (1)$$

We have minimized the two-dimensional function $\Delta E^{(n)}[a,\Delta]$ for $A = \mathrm{Ga}$, $B = \mathrm{In}$, and $C = \mathrm{P}$ for each of the five crystals n, obtaining thereby the ordered phases energies ΔE_O using the self-consistant local-density pseudopotential total-energy method.[5] The input to the calculation consists of the first-principles atomic pseudopotentials[8] of Ga, In, and P, and the Ceperley-Alder correlation functional.[9] A basis set consisting of 600–800 plane waves in these 8 atom unit cells and a strict self-consistency tolerance of 10^{-5} Ry assures a very precise convergence of $\Delta E^{(n)}$ to within better than 0.2 kcal/mole (a mole is taken in this paper as an atomic pair). We determined $\Delta_{\mathrm{eq}}^{(n)}$ for each value of a iteratively by displacing the atoms to obtain the equilibrium conditions of zero Hellmann-Feynman forces.[10]

For the end-point crystals GaP ($n=0$) and InP ($n=4$), we find calculated equilibrium lattice constants a^0_{GaP} and a^0_{InP} that are within 1.5% of experiments,[4] like in other recent calculations.[11] We find InP to have *weaker* bonds than GaP (the cohesive energy $-E_{\mathrm{InP}}[a^0_{\mathrm{InP}}]$ is smaller by 4 kcal/mole than that of GaP) and a *larger* degree of ionicity: its maximum charge density $\rho_{\max}=32.5e$/cell is both larger than that of GaP ($\rho_{\max}=31e$/cell, the experimental value is[12] $35\pm3e$/cell) and is drawn closer to the P site. For the intermediate compounds $n=1,2,3$, i.e., Ga_3InP_4, $Ga_2In_2P_4$, and $GaIn_3P_4$, respectively, we find equilibrium lattice constants $a^{(n)}_{\mathrm{eq}}$ that are within 0.5% of the calculated composition-weighted average values $\bar{a}(n)\equiv\frac{1}{4}(4-n)a^0_{\mathrm{GaP}}+\frac{1}{4}na^0_{\mathrm{InP}}$, confirming thereby quantum mechanically Vegard's rule $[a^{(n)}_{\mathrm{eq}}=\bar{a}(n)]$ for the ordered compounds. However, bond lengths do not average as lattice constants do [i.e., $\Delta_{AC}\neq(x-1)(d^0_{AC}-d^0_{BC})$]. We find very small equilibrium deformations $\Delta^{(n)}\leq0.01$ Å (solid circles in Fig. 1), indicating that throughout the composition range the bond lengths tend to stay very close to their values in the parent crystals. These results parallel the observed and calculated anion displacements in real chalcopyrites[7] and reflect the classical idea by Bragg[13(a)] and Pauling[13(b)] that bond radii are approximately conserved quantities in different chemical environments $[\Delta^{(n)}\cong0]$. What is new, however, in the present quantum-mechanical result relative to classical theory is that we predict the intermediate compounds to be not only stable relative to dissociation into free atoms, i.e., $(E_{A_{4-n}B_nC_4}<0)$, but to also be stable towards disproportionation into its constituent binary compounds [i.e., $\Delta E^{(n)}_{\mathrm{eq}}<0$, whereas classical additivity of bond energies[13(b)] would give $\Delta E^{(n)}\equiv0$ in Eq. (1)]. We illustrate the mechanisms leading to this stability by considering the process $(4-n)AC+nBC\rightarrow A_{4-n}B_nC_4$ in three steps. First, compress a^0_{InP} and dilate a^0_{GaP} to the equilibrium lattice $a^{(n)}_{\mathrm{eq}}$ of the intermediate compound. For $n=2$ we find that the energy is raised by the volume deformation (VD) contribution $\Delta E^{\mathrm{VD}}=0.87$ kcal/mole due to this uniform elastic strain. This is the only contribution considered in virtual crystal models[3] which grossly overestimate $\Delta E^{(n)}$. Second, bring together $4-n$ AC cells and n BC cells, both prepared at $a^{(n)}_{\mathrm{eq}}$, to form the crystal $A_{4-n}B_nC_4$, without relaxing the internal bond lengths and angles [i.e., $R^{(n)}_{AC}=R^{(n)}_{BC}=(\sqrt{3}/4)a^{(n)}_{\mathrm{eq}}$] to their equilibrium values. The energy change ΔE^{CE} reflects the ability of the $A-C$ and $B-C$ bonds, having, in general, different chemical electronegativities (CE), to exchange charge in the combined system. Figure 2(a) displays the corresponding difference in charge densities $\Delta\rho^{\mathrm{CE}}(\mathbf{r})=\rho[\mathrm{GaInP_2},a^{(2)}_{\mathrm{eq}},\text{ undistorted}]-2\rho[\mathrm{GaP},a^{(2)}_{\mathrm{eq}}]-2\rho[\mathrm{InP},a^{(2)}_{\mathrm{eq}}]$. It shows that charge flows from the less ionic Ga–P bond to the more ionic (but weaker) In–P bond, as Phillips' ionicity ($f_{\mathrm{GaP}}=0.327$, $f_{\mathrm{InP}}=0.421$) would suggest. We calculate a small positive $\Delta E^{\mathrm{CE}}=0.85$ kcal/mole, reflecting accumulation of extra charge on the weaker bond. (In general ΔE^{CE} could also be negative, if the more ionic bond, e.g., Ga–P, is stabler than the less ionic bond, e.g., Ga–As). In the final step we relax the internal bond lengths and angles to achieve equilibrium at $\Delta^{(n)}_{\mathrm{eq}}$, involving a structural (S) energy change of $\Delta E^{\mathrm{S}}=-3.2$ kcal/mole which stabilizes the system. Had we done this last step semiclassically by minimizing the bond bending and stretching[3] energies, using force constants of the *noninteracting* AC and BC compounds[14,15] (i.e., the valence force field, VFF approach) we would have obtained only a small energy stabilization of $\Delta E^{\mathrm{VFF}}=-0.7$ kcal/mole. This would have neglected deformation-induced

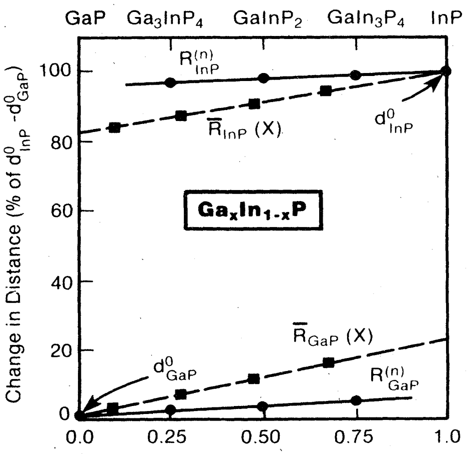

FIG. 1. Percent charge (in units of $d^0_{\mathrm{InP}}-d^0_{\mathrm{GaP}}$) of the near-neighbor bond lengths in ordered phases (●) and in random alloys (□).

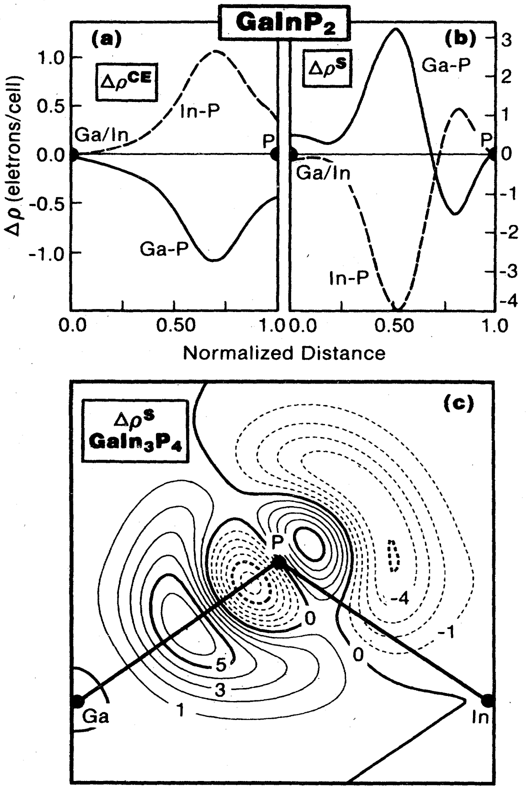

FIG. 2. Cation-electronegativity induced [$\Delta\rho^{\mathrm{CE}}$ in (a)], and structurally induced [$\Delta\rho^{\mathrm{S}}$ in (b)] changes in the electronic charge densities along the anion-cation bond in GaInP$_2$. (c) shows $\Delta\rho^{\mathrm{S}}$ for GaIn$_3$P$_4$, where solid (dashed) contours indicate gain (loss) of charge.

charge transfer. Figure 2(b) shows the self-consistently calculated deformation-induced charge transfer $\Delta\rho^{S}(\mathbf{r})=\rho[\mathrm{GaInP_2}, a_{\mathrm{eq}}^{(2)}, \text{distorted}]-\rho[\mathrm{GaInP_2}, a_{\mathrm{eq}}^{(2)}, \text{undistorted}]$ and Fig. 2(c) shows similarly $\Delta\rho^{S}(\mathbf{r})$ for $\mathrm{GaIn_3P_4}$. They indicate substantial charge redistributions: the stabler Ga–P bond (with a deep Ga pseudopotential) acquires *more* charge than it lost in the previous step to the In–P bond (with the shallower In pseudopotential). The corresponding polarization (pol) energy is $\Delta E^{\mathrm{pol}}\equiv\Delta E^{S}-\Delta E^{\mathrm{VFF}}=-2.5$ kcal/mole for $n=2$ and constitutes the main driving force for stability. The total excess energy of the ordered compound is $\Delta E_O=\Delta E_{\mathrm{eq}}^{(n)}=(\Delta E^{\mathrm{VD}}+\Delta E^{\mathrm{VFF}})+(\Delta E^{\mathrm{CE}}+\Delta E^{\mathrm{pol}})$. We find $\Delta E_{\mathrm{eq}}^{(2)}=-1.48$ kcal/mole for the chalcopyrite. The ordered simple tetragonal structure is only 0.1 kcal/mole less stable; similarly the luzonite and famatinite structures are also close to one another in stability. A few observations are in order. First, the closeness of the ordered phase energies ΔE_O for these polytype pairs suggests that all are likely to form kinetically at growth temperatures, but the choice of growth (i.e., substrate) orientation might discriminate them: the chalcopyrite is a (2,2) superlattice in the (2,1,0) direction whereas the simple tetragonal CuAu-*I*-like structure is a (1,1) superlattice in the (1,0,0) direction. We hence predict these particular superlattices to be *intrinsically* (not accidentally[1]) stable against alloy formation below an ordering temperature $T_O=(\Delta H_D+\Delta E_O)/\Delta S_D$. Second, these structures can be identified by their fingerprint diffraction beams. They are $(\pm1,0,0)$ and $(\pm1,\pm1,0)$ for luzonite and $(0,\pm1,\pm1/2)$ for chalcopyrite,[7] whereas both the famatinite and the simple tetragonal structures have in common the $(0,0,\pm1)$ and $(\pm1,\pm1,0)$ beams, but the former also has the $(\pm1,0,\pm1/2)$ beam. Third, our analysis suggests that alloys formed from closely lattice matched binaries with a large difference in bond stability in the direction of the charge flow (e.g., $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ with an $\sim0.1\%$ bond length mismatch but a large, 24 kcal/mole excess bond energy of AlAs over GaAs) will order readily below T_O as $(\Delta E^{\mathrm{VD}}+\Delta E^{\mathrm{VFF}})$ is a vanishingly small positive quantity but $(\Delta E^{\mathrm{CE}}+\Delta E^{\mathrm{pol}})$ is larger and negative. Ironically, it is this closeness in atomic sizes (i.e., "atom indistinguishability"), that also renders the same alloy *grown above* T_C as strongly disordered. An opposite example ($\Delta E_O>0$) is likely to be $\mathrm{GaSb}_x\mathrm{P}_{1-x}$. Finally, it is interesting to note[14] that whereas the chemical energy affects the value of ΔE_O, it has a negligible effect on the position of its minimum; i.e., $R^{(n)}$ can be calculated with useful accuracy from strain-minimizing models.[14]

We have calculated the changes in the lowest band gaps of $\mathrm{Ga}_{4-n}\mathrm{In}_n\mathrm{P}_4$ relative to the average of the calculated GaP and InP band gaps ("optical bowing") for $n=1$, 2, and 3. We find that most of the observed bowing[4,7] ($b\cong0.5$ eV) is accounted for by the calculated VD, CE, and S changes (0.45 eV). Hence, positive optical bowing can be produced by local bond relaxation effects[7] and need not reflect a thermodynamic instability of the compound.[2]

Random alloys. At the temperatures that semiconductor alloys are usually grown, entropy-favored disordered alloys are quenched in. We model the excess enthalpy of formation $\Delta H_D(x)$ of such substitutionally disordered alloys by assuming the $A_{4-n}B_n$ units to exist at each composition $x(\bar{a})$ with a random probabilities $P^{(n)}[x(\bar{a})]=\binom{4}{n}x^n(1-x)^{4-n}$ [Fig. 3(a)] leading to

$$\Delta H_D(x)=\sum_{n=0}^{4}P^{(n)}[x(a)]\Delta E^{(n)}[a,\Delta] \quad . \tag{2}$$

The properties of $P^{(n)}(x)$ and $\Delta E^{(n)}(a)$ are such that $\Delta H_D(1)=\Delta H_D(0)=0$.

Figure 3 shows schematically why $\Delta H_D(x)$ is positive for a disordered semiconductor alloy, although stable ordered intermediate phases (i.e., $\Delta E_{\mathrm{eq}}^{(n)}<0$) can exist for integer A/B ratios at lower temperatures. At any given composition, say $x=\frac{1}{2}$ [at which $\bar{a}(1/2)=a_{AC}^{0}/2+a_{BC}^{0}/2$], the $P^{(2)}(1/2)=37.5\%$ of the ABC_2 species present is seen to be near equilibrium in its $\Delta E^{(2)}(a)$ curve, contributing therefore a negative term to ΔH_D. However, the $P^{(0)}(1/2)=P^{(4)}(1/2)=6.25\%$ of the pure AC and BC species present at this concentration with $\bar{a}(1/2)$ (as well as the 25% each of the A_3B and AB_3 species) are strained relative to their equilibrium lattice constants a_{AC}^{0} and a_{BC}^{0}, contributing therefore positive terms to ΔH_D. The superposition of all five equations of states $\Delta E^{(n)}(\bar{a})$ [Fig. 3(b)], weighted with their probabilities $P^{(n)}[x(\bar{a})]$ [Fig. 3(a)] produce in this case a positive $\Delta H_D(x)$ curve [Fig. 3(c)]. Since we showed that $a_{\mathrm{eq}}^{(n)}\cong\bar{a}(n)$, the lattice mismatch $\delta^{(n)}(x)$ of each species in the alloy is

$$a_{\mathrm{eq}}^{(n)}-a(x)=(x-n/4)(a_{AC}^{0}-a_{BC}^{0})\equiv(x-n/4)\Delta a \quad .$$

For small Δa, the energy $\Delta E^{(n)}$ is second order in $\delta^{(n)}(x)$; hence, $\Delta H_D(x)\sim\Delta a^2$. This is exactly the scaling found empirically[1] to be necessary to explain the distribution of the experimentally measured ΔH_D values of most semicon-

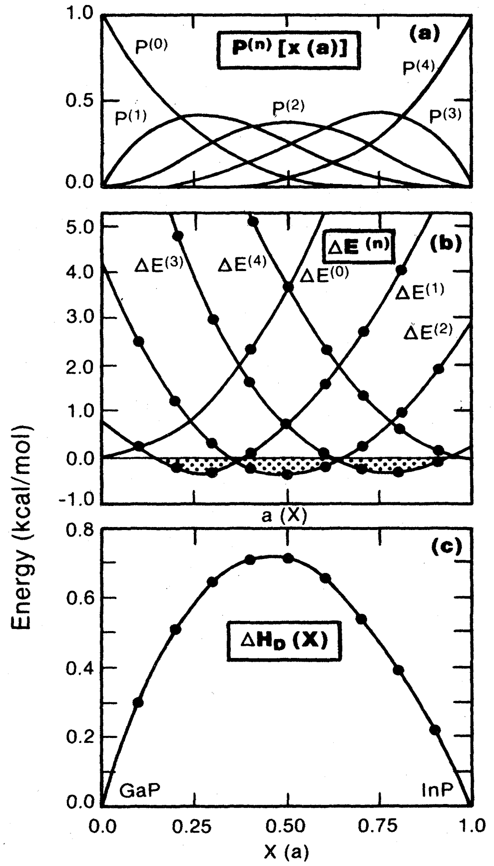

FIG. 3. Illustration of the way in which (a) the random occurrence probabilities $P^{(n)}(x)$ combine with (b) the equations of state $\Delta E^{(n)}$ (a) of the stable species n (stable areas highlighted by shading), to produce (c) a positive excess enthalpy $\Delta H_D(x)$.

ductor alloys. While we have assumed a perfectly random solid solution, the physical idea leading to $\Delta H_D(x) > 0$ (cf. Fig. 3) also suggests that in actual samples, the concentration fluctuations[3] (as well as clustering[1]) may be reduced through the Boltzman factor $\exp - [\Delta E^{(n)}(a)/kT]$, reflecting the smaller-than-random existence probability of the highly strained species. Our analysis simply predicts this tendency for homogenizations of the species to be enhanced as Δa increases, leading also to a temperaure dependence[1] and nonparabolicity in $\Delta H_D(x)$.

For $Ga_xIn_{1-x}P$, we find that the experimental[16] $\Delta H_D(x)$ curve for the disordered alloy, with a maximum at $\Delta H_D(1/2) = 0.72$ kcal/mole (experimental uncertainty in this value is around[1,16] 50%) is consistent with an excess stability of an ordered $GaInP_2$ of $\Delta E_{eq}^{(2)} = -0.3$ kcal/mole. Our calculation (yielding -1.5 kcal/mole) overestimates this stability due to "Brillouin zone effects,"[17] i.e., resonances between periodically arranged bonds present in the ordered compound but not in the alloy.

We can use our calculated bond lengths $R_{AC}^{(n)}(a)$ and $R_{BC}^{(n)}(a)$ for the ordered structure, to obtain their sample averages[15] $\bar{R}(x)$ in a disordered alloy

$$\bar{R}_{AC}(x) = \sum_{n=0}^{4} \omega_{AC}^{(n)} P^{(n)}[x(a)] R_{AC}^{(n)}(a) \quad , \tag{3}$$

where $\omega_{AC}^{(n)} = 4 - n$ (or $\omega_{BC}^{(n)} = n$) is the number of AC (or BC) bonds. A similar expression pertains to $\bar{R}_{BC}(x)$. The dashed lines in Fig. 1 show the calculated results, indicating a bimodal distribution similar to that observed for other alloys, but $\bar{R}(x)$, in a *random* alloy, deviates from the corresponding d^0 values significantly more than do the bond lengths $R^{(n)}$ in the *ordered* phases.

We conclude that the stability of the ordered structures arises from the fact that they are *strain reducing* (i.e., small $\Delta E^{\mathrm{VD}} + \Delta E^{\mathrm{VFF}}$), reflecting their ability to simultaneously accommodate the two dissimilar bond lengths in a coherent fashion[7] (solid circles in Fig. 1). When small, this allows the stabilizing chemical charge transfer terms to take over (the net electron flow is from the less stable bond to the more stable bond). Such ordered systems are predicted to have a Vegard-like lattice constant, much like their random analogs at the same concentration (hence the latter could be used as a convenient substrate for growing the former), a sharp bimodal distribution of bond lengths with displaced anions, and positive "optical bowing" (although with somewhat larger gaps than their random counterparts). In contrast, random alloys do not minimize strain: although the *average* bond lengths are still close to the ideal bonds (solid squares in Fig. 1), configurations with strained bonds are quenched in [Fig. 3(b)]. They are entropy stabilized over the ordered phase when grown at temperatures above T_C or (T_O); hence, annealing of these samples is not likely to order them readily. Upon quenching to lower temperatures they will either (a) disproportionate, (b) remain metastably disordered, or (c) order. Ordering and disproportionation can occur if sufficient atomic mobility remains at the lower temperature and the activation barriers posed, for example, by coherent strains,[1] are surmountable. The choice between these two reactions depends both on the relative values of T_C and T_O and on the relative size of their (unknown) activation barriers. While reaction (c) could hopefully be catalyzed chemically or by suitable photons, under normal conditions, reaction (a) (e.g., in GaP_xSb_{1-x}, showing a miscibility gap) or (b) (e.g., in $Ga_xAl_{1-x}As$) prevail upon cooling. However, if grown *from the outset* below T_O (about $\Delta E_O/k \cong 200\,^{\circ}\mathrm{C}$ below conventional growth temperatures) by growth techniques that assure sufficient surface mobilities at lower temperatures, ordered phases, presumably with appealing transport properties, are predicted to form.

Note added in proof: After the submission of this manuscript we have been informed by T. S. Kuan, T. F. Kuech, W. I. Wang, and E. L. Wilkie (unpublished), for which we are grateful, that low-temperature growth of $Al_xGa_{1-x}As$ for $x = \frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ has produced a novel ordered and stable crystalline phase showing CuAuI-like diffraction spots, confirming our theoretical predictions.

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