

SUPERLATTICE ENERGETICS AND ALLOY THERMODYNAMICS OF GaAs/Ge

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(Received 14 December 1990 by A. A. Maradudin)

We re-examine the validity of the three-dimensional bulk thermodynamic description for the zinc-blende-to-diamond transition observed in $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ alloys. We use interaction parameters extracted from first-principles local-density total-energy calculations for $(\text{GaAs})_p/(\text{Ge}_2)_p$ superlattices and a cluster-variation solution to the corresponding Ising-like hamiltonian. The resulting phase diagram obtained with such a realistic energy model fails to account for the observed critical composition in the relevant temperature range, suggesting that, contrary to a previous view, the transition is *not* driven by *bulk* thermodynamics.

1. Introduction

The $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ alloy is a member of the new class of *non-isovalent* $(A^{\text{III}}B^{\text{V}})_{1-x}C_{2x}^{\text{IV}}$ semiconductor solid solutions, which exhibits remarkable structural and optical properties.¹ Unlike the more common *isovalent* (III-V)/(III-V) or IV/IV alloys, the non-isovalent constituents $A^{\text{III}}B^{\text{V}}$ and C^{IV} are mutually insoluble in the solid state,² even if they are size-matched (e.g., GaAs and Ge). This reflects the existence of local bonding arrangements that violate the octet rule, i.e., the Ga-Ge and Ge-As bonds (whose total number of valence electrons deviates by $\Delta Z_v = \pm 1$ from that in normal octet Ga-As and Ge-Ge bonds) and possibly Ga-Ga and As-As ("wrong bonds" whose total number of electrons deviates by $\Delta Z_v = \pm 2$ from the octet bonds). Despite their equilibrium segregating behavior, however, homogeneous $(A^{\text{III}}B^{\text{V}})_{1-x}C_{2x}^{\text{IV}}$ alloys can be prepared by non-equilibrium growth methods.³⁻⁶ Such homogeneous phases constructed from constituents of different lattice symmetries exhibit an interesting phase transition: The two interpenetrating fcc sublattices constituting the diamond-like structure of Ge can be occupied in $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ either by Ga or by As atoms. If these sublattices are occupied *equally* by Ga and As we have the pseudo-diamond

(D) structure; if, however, a sublattice is preferentially occupied by one of the two species, we have the pseudo-zinc-blende (ZB) structure, manifested by a [200] diffraction peak,^{6,7} forbidden in the diamond structure. Such a ZB \leftrightarrow D transition was observed in $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ at a composition $x_c \approx 0.3$ for samples grown by molecular beam epitaxy⁶ at 430°C and at $x_c \approx 0.4$ for samples grown by sputtering techniques.⁷

In addition to the simple percolation approach,⁸ producing $x_c = 0.572$, there are two other rather diverging points of view on the nature of the ZB \leftrightarrow D transition: growth models⁹⁻¹¹ and three-dimensional (3D) bulk thermodynamic models.^{12,13}

In "growth models"⁹⁻¹¹ one is attempting to directly produce a description of the atomic structure of the alloy without minimizing any explicit energy functional. This is done by defining a set of "growth rules" that dictate the preferences of incoming atoms to bond to specific substrate atoms; once bonded, atoms are assumed immobile. These growth rules are not justified *a priori* by way of an energy argument, but rather in terms of their success in producing an atomic structure that mimics *ex post facto* some of the properties of the experimentally observed structures. As a result, growth models produce structures that reflect the "deposition history," are orientation-dependent but generally temperature-independent.

In 3D "bulk" thermodynamic models,^{12,13} one defines an interaction hamiltonian that specifies the configurational dependence of the energy of the system and solves it in any of the available statistical-

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mechanics lattice models. The basic premise is that the atomic structure at a given (x, T) reflects a (local or global) minimum of a physically recognizable hamiltonian. In this approach, the *sequence* of growth does not enter (as atoms are assumed to be sufficiently mobile to attain any lattice configuration that leads to a minimum free energy) and the *orientation* of growth does not alter the results (as a 3D symmetry is postulated). Hence, the results depend naturally on temperature but not on orientation.

Using this approach, Newman and collaborators¹² have applied a mean-field solution to the three-species (Ga, As, Ge) lattice-statistics problem retaining only nearest-neighbor interactions between neutral atoms (isomorphic to the spin-1 Blume-Emery-Griffiths model¹⁴). If Ga—Ga and As—As bonds are allowed, an energy parameter of the model can be adjusted to give a ZB \leftrightarrow D transition at $x = 0.3$. Without such bonds,^{12b} however, the order-disorder transition occurs only at $x > 0.57$. In this model, a critical concentration as low as 0.3 requires the presence of $\Delta Z_v = \pm 2$ bonds, but independent evidence for their existence remains controversial.^{10,15,16} Indeed, extended x-ray absorption fine structure results for the related $(\text{GaSb})_{1-x}\text{Ge}_{2x}$ alloy can be fitted with^{12b,c} or without¹⁷ the assumption of existence of $\Delta Z_v = \pm 2$ bonds.

Three main questions surround the application of 3D thermodynamic models to $(A^{\text{III}}B^{\text{V}})_{1-x}C_{2x}^{\text{IV}}$ alloys:

(a) *Selection of values for interaction energies.* In the Newman *et al.* approach the hamiltonian is parametrized in terms of *reduced energies* (in units of $k_B T$) so that specific values (or temperatures) remain unknown. However, a "cluster—Bethelattice" tight-binding calculation¹⁸ and a pseudopotential structural-expansion model¹⁹ have obtained values of 0.15 to 0.16 eV for the average energy of Ga—Ge and Ge—As bonds in $(\text{GaAs})_{1-x}\text{Ge}_{2x}$. Using this value in the thermodynamic models leads to a transition temperature that is an order of magnitude too high compared with the experimental growth temperatures.

(b) *Physical content of the interaction hamiltonian.* In all previous applications^{12,13,16} it has been assumed that the interactions in the system consist of short-range concentration-independent energies between neutral atoms, so that the usual nearest-neighbor spin-1 Ising model¹⁴ may be applied. However, unlike *isovalent* alloys, where such approaches are appropriate, *non-isovalent* alloys can exhibit significant charge-transfer effects with their attendant electrostatic interactions, neglected previously. This becomes clear when one realizes that a Ga—Ge bond has a deficiency of 1/4 of an

electron (hence, behaving as an acceptor) and that a Ge—As bond has an excess of 1/4 of an electron (hence, behaving as a donor) and that transfer of a charge q from donor to acceptor states can reduce the electronic energy by the effective band-gap energy qE_g . Furthermore, the charge transfer produces an intra-bond Coulomb repulsion energy as well as an inter-bond long-range (Madelung) energy. Previous models of the ZB \leftrightarrow D transition have neglected all these electrostatic terms. This problem is well known in the theory of non-isovalent *impurities* such as anti-sites in GaAs,²⁰ where such compensating charge transfer reduces the calculated formation energy of an anti-site pair from 6.3 to 1.7 eV.

(c) *Accuracy of the statistical solutions to a given hamiltonian.* The critical temperature for the spin-1/2 Ising model found from a simple (site-approximation) mean-field solution exceeds the near-exact series-expansion result²¹ by as much as 48 %. This mean-field approximation can be considerably improved using the cluster-variation method (CVM) pair approximation,²² which leads to a critical temperature in the spin-1/2 Ising model that is just 6.7 % above the correct result.

Since the appropriateness of a 3D bulk thermodynamic description of the ZB \leftrightarrow D transition in $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ is clouded by the factors (a)–(c) above, we decided to reinvestigate the problem. The above mentioned problems (a)–(c) are treated as follows: (a) The interaction energies are extracted from first-principles self-consistent total-energy calculations²³ on prototype non-isovalent systems. (b) A realistic description of all three electrostatic effects is included. We use both Ising-like (pairwise) and electrostatic inter-bond (effective three- and four-body) interactions. The $\Delta Z_v = \pm 2$ bonds are disallowed and isolated ions are permitted to occur. (c) The phase diagram is calculated in the CVM pair approximation. We find that the phase diagram resulting from the use of realistic interaction energies shows that a 3D equilibrium thermodynamic interpretation for the ZB \leftrightarrow D transition fails to account for the observed x_c in the relevant temperature range.

2. Superlattice Energetics

We consider next the basic physical factors controlling non-isovalent interactions so that a realistic alloy hamiltonian can be developed. While there is no experimental evidence for the presence of $\Delta Z_v = \pm 2$ bonds, energy arguments suggest that if they occur in $(A^{\text{III}}B^{\text{V}})_{1-x}C_{2x}^{\text{IV}}$ alloys, they have a much smaller concentration than the $\Delta Z_v = \pm 1$ bonds. This can be estimated by contrasting the calculated average formation energy W

of the Ga—Ga and As—As ($\Delta Z_v = \pm 2$) bonds to the average energy δ of the Ga—Ge and Ge—As ($\Delta Z_v = \pm 1$) bonds. Different calculations^{18,19,24} indicate $W/\delta \approx 3-4$, with $\delta > k_B T_g$, where T_g is the growth temperature. Therefore, at thermodynamic equilibrium $\Delta Z_v = \pm 2$ bonds should occur much less frequently than $\Delta Z_v = \pm 1$ bonds. We hence omit them from the alloy hamiltonian.

We model the energy of a non-isovalent system containing both normal and $\Delta Z_v = \pm 1$ bonds by considering $(A^{III}B^V)_p/(C_2^IV)_p$ superlattices (SLs). The excess energies of such SLs were calculated²³ using the first-principles self-consistent pseudopotential method²⁵ for several orientations and repeat periods. The wave functions for semirelativistic pseudopotentials were expanded in plane waves with kinetic energies up to 15 Ry. The charge density was evaluated at the equivalent of two special k-points²⁶ in the irreducible part of the fcc Brioullin zone. (Larger equivalent sets were used for some of the longer-period SLs.) The excess energies can then be fitted by a sum of Ising-like nearest-neighbor interactions between neutral atoms and electrostatic terms due to charge transfer:²³

$$\Delta H = (N_D + N_A)\delta - \frac{1}{2}(N_D + N_A)E_g(0)q + \frac{1}{4}(N_D + N_A)(U_D + U_A)q^2 + E_{Mad}. \quad (1)$$

(For simplicity, we assume all charge transfers to be the same.)

The first term represents the total excess energy before charge transfer ($q=0$), where N_D and N_A are the total number of donor and acceptor bonds in the structure ($N_D = N_A$ for stoichiometric systems) and δ is the average excess energy of the $\Delta Z_v = \pm 1$ bonds before charge transfer occurs. Previous models^{12,13,18} have retained only this term. This predicts that the energy per $4p$ atoms of [001] and [110] SLs is 4δ while that of [111] SLs is 2δ . The three remaining terms on the right-hand side of Eq. (1) represent charge transfer effects:

(i) Transfer of a charge q from a donor to an acceptor state initially separated by a band gap of $E_g(q=0)$ produces to first order in q an energy gain of $qE_g(q=0)$. A total compensation energy gain of $-\frac{1}{2}(N_D + N_A)E_g(0)q$ therefore arises.

(ii) The excess or deficit of charges on the $\Delta Z_v = \pm 1$ bonds now produces an excess intra-bond Coulomb energy, both due to electrostatic and to exchange-correlation terms. This raises the energy by $\frac{1}{4}(N_D + N_A)(U_D + U_A)q^2$, where U_D and U_A are intra-bond Coulomb repulsions in the donor and acceptor bonds.

(iii) Finally, an excess Madelung energy E_{Mad} results from the sum of screened long-range electrostatic interactions between compensating charges

$\{q_i\}$ (usually $\pm 1/4$, in units of the electron charge) which we place at the mid-points of the $\Delta Z_v = \pm 1$ bonds. These interactions are assumed to be screened, independently of distance, by the average static dielectric constant of the two end-point components.

It is convenient for a thermodynamic treatment of the problem to regroup the terms of Eq. (1) as

$$\Delta H = (N_D + N_A)J(q) + E_{Mad}, \quad (2)$$

where the effective pairwise energy is

$$J(q) = \delta - \frac{q}{2}E_g(0) + \frac{q^2}{4}(U_D + U_A) = \delta + \Delta J(q), \quad (3)$$

and $\Delta J(q)$ is the "bond charge-transfer energy."

Calculating E_{Mad} by Ewald's method, the parameters q (constrained to remain $< 1/4$), δ and $(U_D + U_A)$ of Eq. (1) were then obtained by fitting [for fixed values of $E_g(0)$] the formation energies calculated by the self-consistent pseudopotential method for eleven unrelaxed $(\text{GaAs})_p/(\text{Ge}_2)_p$ SLs. (Relaxation can decrease the formation energy by 4–14 %; its effects are not included in the energy model.) The degree of arbitrariness in the choice of $E_g(0)$ was of little consequence to the fit: Changes in $E_g(0)$ were offset by changes in $(U_D + U_A)$ so that both $\Delta J(q)$ and δ are relatively insensitive to $E_g(0)$ over a reasonable range of values, indicated in Fig. 1 by the shaded areas.

The resulting energy parameters for GaAs/Ge are $\delta = 0.162$ eV and, for a full charge transfer, $J(q=1/4) = 0.109$ eV. The accuracy of the fit is illustrated in Fig. 1, where the formation energies of SLs calculated by the pseudopotential method are compared with those obtained by the model. We find that all SLs have positive formation enthalpies ΔH , i.e., they are unstable at equilibrium towards disproportionation into Ge and GaAs, due to the presence of a large number of $\Delta Z_v = \pm 1$ bonds with their attendant energies $\delta > 0$. Charge transfer makes the SLs less unstable in that ΔH is below the $q=0$ limits indicated at the far right side of Fig. 1.

Analysis of the directly calculated pseudopotential total energies in terms of this model permits assessment of the significance of various physical contributions. While the excess Madelung energy can be either positive or negative, the bond charge-transfer energy, $\Delta J(q)$, is always negative, due to the prevalence of the $E_g(0)$ (compensation gain) term in Eq. (3) over Coulomb repulsions. Even when the excess Madelung energy is positive, it is never large enough to offset the gain in energy due to the bond charge-transfer term.

The energy of SLs with polar [001] interfaces can be lowered by reconstruction.²⁷ Four reconstructions were considered involving swapping of atoms

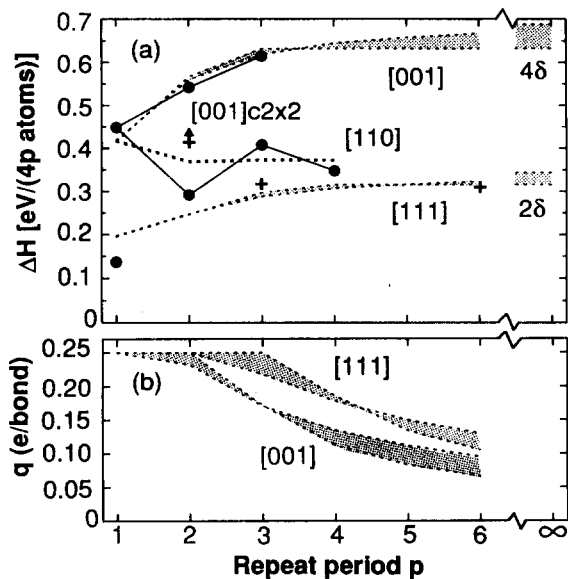


FIG. 1. Pseudopotential calculated²³ (solid circles and triangle) and modeled [dashed lines and crosses, from Eq. (1)] (a) $(\text{GaAs})_p/(\text{Ge}_2)_p$ superlattice formation enthalpies per $4p$ atoms and (b) inter-interface charge transfer. The reconstructed superlattices are obtained by swapping atoms between interfaces, as described in the text. The horizontal lines on the far right give the results without charge transfer for [001] and [110] SLs (4δ) and for [111] SLs (2δ). The model energies and charges correspond to a range of the input parameter $E_g(q=0)$ between 0.4 and 0.8. This gives a reasonably narrow spread in predictions, indicated by the shaded areas.

in the following way: (i) Ga \leftrightarrow Ge vertical, (ii) Ga \leftrightarrow Ge staggered, (iii) Ge \leftrightarrow As vertical, and (iv) Ge \leftrightarrow As staggered swaps, where “vertical” (“staggered”) indicates swaps between atoms directly (not directly) above one another. The pseudopotential calculations found a value of 0.27 eV/(4 atoms) for the formation energy of the unreconstructed [001] $p=2$ SL, compared to 0.20 to 0.23 eV/(4 atoms) for the four [001] $p=2$ reconstructions. The average of these four reconstructions is represented by the solid triangle in Fig. 1(a). The model correctly reproduces the energy lowering attendant upon reconstruction and shows that it results primarily from a lowering of the Madelung energy. For [111] SLs, reconstruction is not guaranteed to lower the energy since the energy gain due to a more effective charge compensation and lower Madelung energy is offset by an increase (by 50 %) in the number ($N_A + N_D$) of $\Delta Z_v = \pm 1$ bonds. Our model results indicate a marginal stabilization of the reconstructed structures (with a Ga \leftrightarrow Ge or a Ge \leftrightarrow As vertical swap)

for $p=6$, but not for $p=3$, similarly to what was found²³ for GaP/Si.

In polar SLs the charge transfer decreases asymptotically as $1/p$ [Fig. 1(b)]. This can be explained as follows. Charge transfer between interfaces creates potential oscillations across the SL with amplitude proportional to the charge transfer q and repeat period p . Since this amplitude of oscillation should not exceed the band gap, q must scale with $1/p$ for large p . On the other hand, in structures where charged interfaces are absent, including non-polar [110] SLs and alloys, full charge transfer ($q = 1/4$) is expected.

3. Alloy Thermodynamics

In $(\text{GaAs})_{1-x}\text{Ge}_2x$ alloys no long-range order is expected to appear in the distribution of donor and acceptor bonds (even when the Ga and As atoms are organized in the ZB structure). Therefore, we have truncated the infinite sum of the Madelung energy beyond a certain range, thus making the hamiltonian of Eq. (2) amenable to an Ising-like description:

$$\Delta H \approx (N_D + N_A)J(q) + E_1 + E_2 + E_{3z} + E_{3h}, \quad (4)$$

where E_1 , E_2 , E_{3z} , and E_{3h} are the contributions to the Madelung energy from first-neighbor bond pairs, second-neighbor bond pairs, third-neighbor bond pairs along a zigzag chain and third-neighbor bond pairs in the same distorted hexagon, indicated in Fig. 2. These energy parameters can be expressed as

$$E_n = N_n \sum_{i,j,k,l} p_{(ij)(kl)}^{(n)} C_{(ij)(kl)}^{(n)}, \quad (5)$$

where N_n is the total number of n -th neighbor bond pairs on the lattice. The sum is taken over the possible occupations of n -th neighbor bond pairs by (i, j) on one bond, and (k, l) on the other. The

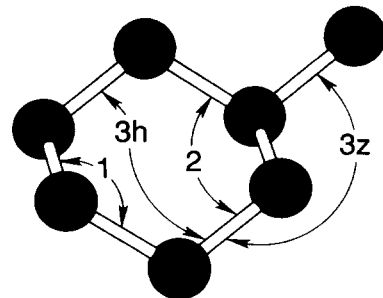


FIG. 2. Types of bond pairs, corresponding to the electrostatic interactions of Eq. (4).

probability $p_{(ij)(kl)}^{(n)}$ is the average fraction of n -th neighbor bond pairs occupied by (i, j) and (k, l) , and $C_{(ij)(kl)}^{(n)}$ is the corresponding inter-bond electrostatic interaction, given by

$$C_{(ij)(kl)}^{(n)} = \begin{cases} K^{(n)}, & \text{for like } \Delta Z_v = \pm 1 \text{ bonds;} \\ -K^{(n)}, & \text{for unlike } \Delta Z_v = \pm 1 \text{ bonds;} \\ 0, & \text{otherwise.} \end{cases} \quad (6)$$

The energy parameters $K^{(n)}$ can be calculated approximately from the average dielectric constant and the distances between bond centers; the resulting parameters for GaAs/Ge SLs or alloys are $K^{(1)} = 0.035$, $K^{(2)} = 0.020$, and $K^{(3)} = 0.017$ eV. As a test for the validity of the truncation in Eq. (4), we find that for ideal zinc-blende or diamond alloys in the infinite-temperature limit, the contribution from E_{3h} in Eq. (4) is typically only 5% of E_1 , so the truncation appears justified for alloys. This is due to the near charge cancellation of bonds in a shell of a sufficiently large radius.

The bulk equilibrium thermodynamics of homogeneous $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ solid alloys is described through the excess free energy $\Delta F = \Delta H - TS$, where the excess enthalpy ΔH includes the pairwise and inter-bond electrostatic terms of Eq. (2) and the configurational entropy S is expressed in the CVM pair approximation²² in terms of the pair probabilities $\{y_{ij}\}$ for occupation of nearest-neighbor sites by atomic species i and j . Constraints among the pair probabilities are introduced

by requiring (i) a fixed Ge composition, (ii) no sublattice ordering of Ge, and (iii) no Ga—Ga or As—As bonds [although similar results are obtained if requirement (iii) is relaxed and realistic values for $\Delta Z_v = \pm 2$ bond energies are used]. The number of independent variables is then reduced to three “correlation functions,”²⁸ defined as appropriate linear combinations of the $\{y_{ij}\}$.

At a given concentration x and temperature T , the CVM free energy ΔF is minimized with respect to the independent correlation functions to give their equilibrium values (and therefore any desired thermodynamic function). Since we include interactions of longer range than the size of the basic cluster, a “superposition approximation”^{28,29} is used that relates the $p_{(ij)(kl)}^{(n)}$ of Eq. (5) to the $\{y_{ij}\}$ by mean-field-like relations.

The resulting phase diagrams are displayed in Fig. 3 for (a) the uncompensated ($q = 0$) and (b) the compensated ($q = 1/4$) cases. The uncompensated case corresponds to the Blume-Emery-Griffiths spin-1 Ising model with pairwise interactions, while the compensated case includes also three- and four-site interactions. Phase diagrams for the uncompensated case have been presented previously by Gu *et al.*^{12b} with a temperature axis in units of the $A^{\text{III}}-B^{\text{V}}$ bond energy. We conclude the following from our results:

(i) In the infinite-temperature limit, the problem is reduced to a three-species correlated percolation problem. A second-order phase transition occurs

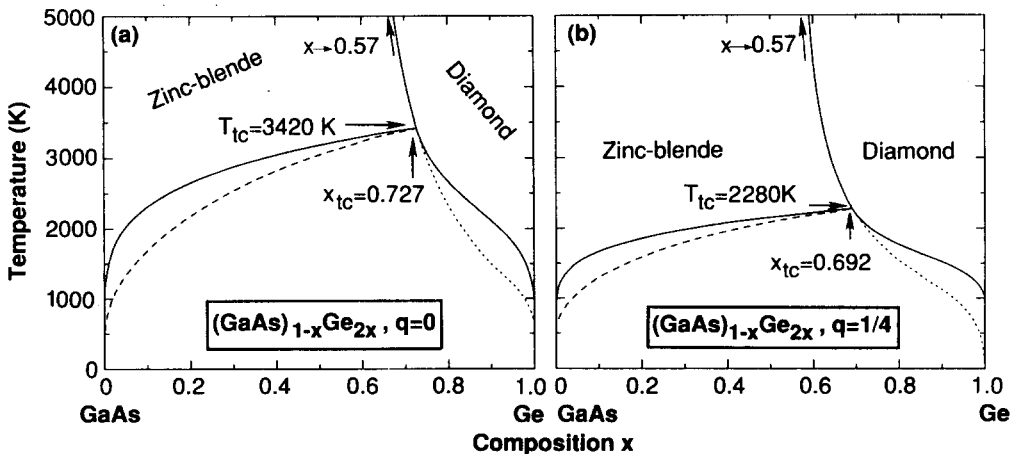


FIG. 3. Equilibrium phase diagram for the $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ alloy (a) without and (b) with charge transfer. The region below the tricritical point (x_{tc}, T_{tc}) and between the two full lines corresponds to phase separation into GaAs-rich zinc-blende and Ge-rich diamond phases. The dashed line is the spinodal of the zinc-blende phase, while the dotted line is the unstable continuation of the second-order transition line.

between the ZB and the D phases at $x \approx 0.57$. In contrast, phase diagrams for models that include $\Delta Z_v = \pm 2$ bonds^{12,13} show that this transition line terminates at $x = 0$ at a finite critical temperature T_c , so that only the D phase is stable for $T > T_c$. This feature enabled a low ($x_c = 0.3$ or 0.4) order-disorder concentration to be fitted in previous approaches by adjusting ratios of temperature to interaction energies. It was not determined, however, if the temperature where this fit is valid agrees with the experimental (growth) temperature ($T_g \sim 700$ K). While we have excluded $\Delta Z_v = \pm 2$ bonds, we note that if their energy were 3 to 4 times δ (as suggested by Refs. 18,19,24) their inclusion in our model would lead to insignificant changes in the phase diagrams below ~ 2000 K. Hence, the much disputed existence^{10,15-17} of so-called "wrong" ($\Delta Z_v = \pm 2$) bonds is actually irrelevant in a thermodynamic approach at the low temperatures where the ZB \leftrightarrow D transition is established.

(ii) As the temperature is lowered, x_c increases gradually, until a tricritical point (x_{tc}, T_{tc}) is reached, below which the transition becomes first-order. The presence of a tricritical point is a well-known characteristic of the Blume-Emery-Griffiths model.¹⁴

(iii) Below the tricritical point, the first-order transition is reflected in an (x, T) diagram by a phase-separation region, whose concentration range increases rapidly as the temperature drops until at $T = 0$ it occupies the whole $0 < x < 1$ interval. Two curves inside this phase-coexistence region are relevant for the discussion of possible metastable states. (a) The dashed line from $(x, T) = (0, 0)$ to (x_{tc}, T_{tc}) is the ZB-phase spinodal, where $\partial^2 F / \partial x^2 = 0$. To the right of this line, the single-phase ZB solution, although still a minimum of the CVM free energy, does not satisfy the condition $\partial \mu / \partial x > 0$ of thermodynamic stability, where $\mu = N^{-1} \partial F / \partial x$ is the chemical potential of Ge measured with respect to the average chemical potential of Ga and As. (b) The dotted line extending from $(x, T) = (1, 0)$ to (x_{tc}, T_{tc}) is the unstable continuation of the second-order phase transition. The ZB phase immediately to the left of this line is thermodynamically unstable ($\partial \mu / \partial x < 0$) with respect to long-range perturbations. Similar phase-transition lines have been denoted "metastable" in previous works^{12a,b} with the provision that long-range atomic interchanges are disallowed. We find that, even then, the transition occurs only very close to $x = 1$, in conflict with experiment.

(iv) The main change in the phase diagram with compensation ($q = 1/4$) is a scaling of the tricritical temperature by a ratio of approximately $J(q = 1/4) / \delta$. The lowering of ΔH produced by

charge transfer depresses therefore T_{tc} from 3420 to 2280 K and decreases the area of phase separation. A second, more subtle, change is a slight decrease in the tricritical concentration (from 0.727 in the $q=0$ case to 0.692 when $q=1/4$). This effect is a direct consequence of inter-bond Madelung interactions. The excess Madelung energy is larger in the ZB phase than in the D phase, due to the presence of a larger number of Ga-Ge-Ga and As-Ge-As clusters, which have positive nearest-neighbor-bond repulsions. Madelung energy, therefore, increases the region of stability of the D phase, displacing the tricritical concentration to lower values. These changes, however, are not sufficient to produce a significant modification of the phase diagrams at temperatures below the eutectic point² ($T \approx 1140$ K) of the alloy.

(v) The different contributions to the excess enthalpy of the two phases are qualitatively similar to the ones found for $(\text{GaP})_{1-x}\text{Si}_{2x}$, for which a detailed discussion is given in Ref. 28. In particular, the Madelung and bond charge-transfer contributions reduce the D-phase excess enthalpy with respect to the ZB-phase result.

The fact that the bond charge transfer does not overwhelm the positive values^{19,23,24} of $J(q)$ implies that phase separation between the usual zinc-blende and diamond structures is the equilibrium state at low temperatures, in agreement with the known² near mutual insolubility of GaAs and Ge. It might be thought, however, that new ordered structures could be stabilized if strong first-neighbor inter-bond electrostatic interactions, in excess of what the dielectric constant approximation would grant, are introduced. Frustration effects, however, preclude the appearance of any new minimum-energy ordered configuration.

We do not find below ~ 2000 K any single-phase states that are metastable with respect to concentration fluctuations. In the CVM pair approximation, single phases are unstable between the ZB spinodal and the unstable phase transition curves. Furthermore, below melting temperatures the (unstable) phase transition occurs only very close to $x = 1$. These results lead us to conclude that a 3D bulk lattice thermodynamic approach is unlikely to explain the experimentally observed existence of ZB or D single-phase $(A^{\text{III}}B^{\text{V}})_{1-x}C_{2x}^{\text{IV}}$ alloys, prepared at temperatures below 800 K and covering the whole composition range.

Of course, a large number of configurations (including superlattices) that are intermediate in energy between phase-separated and single-phase alloys can be designed by placing arbitrarily sized domains of pure (or nearly pure) constituents in arrangements where most of the $\Delta Z_v = \pm 1$ bonds occur at the domain walls. High diffusion barriers

in the bulk imply that many of these structures are metastable in a broader sense than that considered in the previous discussion, i.e., they are likely to be local minima of the free energy in a configurational space constituted by *all* continuous degrees of freedom of the system. *Lattice* statistical models, however, independently of the mathematical approximations used, are unable to describe this type of metastability.

The failure of a *three-dimensional bulk* thermodynamic model opens the possibility that a *two-dimensional surface* thermodynamic model might be appropriate. Solid solutions of $(A^{III}B^V)_{1-x}C_{2x}^{IV}$ alloys produced by epitaxial-growth techniques could correspond to a minimum-free-energy *surface* configuration that is frozen in by subsequently deposited layers. This approach differs from 3D ther-

modynamic models^{12,13} in that explicit surface effects are included, so the resulting structure may depend on *orientation*. It differs also from previous growth models⁹⁻¹¹ in that minimum-energy structures are sought explicitly. Recent studies of such models for isovalent alloys by Froyen and Zunger³⁰ have shown that *surface reconstruction* (neglected in previous growth models) acts to select minimum-energy configurations that are absent in 3D thermodynamic models, but are observed experimentally.

Acknowledgments—This work was supported in part by the U. S. Department of Energy, Office of Energy Research, Basic Energy Science, Grant No. DE-AC02-77-CH00178. One of us (R. O.) would like to thank CAPES (Brazil) for a post-doctoral fellowship.

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