

Electronic theory of ordering in $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ alloys

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The electronic energy of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ alloys is investigated as a function of the degree of short-range order in these ternary systems. The generalized cluster Bethe-lattice method, with a minimal sp^3 set of orbitals, is used in the calculation. The results are parametrized in terms of nearest-neighbor pair interaction energies which are independent of the degree of short-range or long-range order and consistent with known defect energies. This confirms the validity of previously used Ising-like Hamiltonians for such systems. The theory allows a critical examination of both the thermodynamic and growth models proposed for the zinc-blende–diamond transition observed in these alloys. The transition temperature calculated from the pair interaction energies is much higher than actual sample preparation temperatures, indicating that kinetics must determine the observed structure. However, previous kinetic models have essentially neglected Ge correlations which are shown to be important.

I. INTRODUCTION

Metastable homogeneous alloys of GaAs with Ge have recently been produced by different epitaxial growth techniques.^{1–3} Among the $(A^{III}B^V)_{1-x}C_{2x}^{IV}$ alloys, these are particularly interesting due to the gap-versus-composition variation² which covers a range of energies with potential application in infrared optical devices. In addition there is practically no lattice-parameter mismatch between the constituents.

A zinc-blende–diamond order-disorder transition has been predicted^{2,4,5} and observed^{3,6} to occur at a critical concentration x_c of the group-IV element. The zinc-blende structure, where the group-V and group-III species preferentially occupy different sublattices is favored for $x < x_c$. In the disordered (diamond) phase $x > x_c$ the sublattice occupations are equal. There has been considerable controversy regarding the mechanism responsible for this order-disorder transition.

In the first discussion of the phase transition, Dyakonov and Raikh,⁴ approximated it as the site percolation problem of Ga and As on the diamond lattice with the restriction that no Ga-Ga or As-As nearest-neighbor (NN) pairs were allowed. This led to a value of $x_c = 1 - p_c = 0.57$, which was considerably higher than the experimental one. (Here p_c is the site percolation threshold in the diamond lattice.) Newman and Dow⁵ proposed a thermodynamic model based on the assumption that x_c is also associated with the minimum of the energy-gap versus composition curve which occurs at $x_c = 0.3$. In this model a macroscopic number of the homoelement

(so-called “wrong”) Ga-Ga and As-As NN pairs are present at all concentrations. This number is reduced by improving the statistics^{7,8} beyond the mean-field approximation used in Ref. 5. To make it vanish would require an infinitely repulsive interaction energy for Ga-Ga and As-As NN pairs. However, as shown by Gu *et al.*,⁸ for infinite interactions, no phase transition occurs below the percolation concentration.

Further theoretical work,^{9,10} based on the experimentally observed value of $x_c \approx 0.3$ for films of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ and $(\text{GaSb})_{1-x}\text{Ge}_{2x}$ (Refs. 3 and 6, respectively) grown epitaxially on (100) GaAs surfaces, suggested a kinetic mechanism for the phase transition in which it was again postulated that no Ga-Ga or As-As pairs are allowed. This same assumption was used in Ref. 6 to fit the EXAFS data for $(\text{GaSb})_{1-x}\text{Ge}_{2x}$, while Newman *et al.*⁸ also obtained a fit for the same data using a thermodynamic model in which “wrong” bonds were present.

It is evident that there is a strong interplay between (i) the short-range order in the atomic arrangements in $(\text{GaAs})_{1-x}\text{Ge}_{2x}$, (ii) the long-range order, and (iii) the electronic properties of this alloy.^{4–13} Information about the effective electronic interaction energies between the different atoms is clearly crucial to any appraisal of the different models proposed for ordering in this system.

In this work we investigate the electronic energy of the $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ alloy as a function of the degree of short-range order (SRO) among the three different species. The calculation is performed using the generalized^{14,15} cluster Bethe-lattice method (CBLM),¹⁶ which is

a real-space tight-binding approach for the calculation of the alloy density of states (DOS). This is obtained from a configurational average over a cluster of atoms embedded in an effective medium with the Bethe-lattice topology, such that the SRO and long-range-order (LRO) correlations can be naturally incorporated both in the cluster and in the effective medium regions. The generalized CBLM has been previously applied to metallic alloys,^{14,15} and also to Ge-Si alloys¹⁷ with a simplified Hamiltonian.

As compared to other tight-binding approaches for the calculation of alloy DOS,¹⁸ the CBLM has the advantage of naturally incorporating atomic correlation effects, a feature that few other methods can handle.¹⁹ One alternative approach is to obtain energies for disordered semiconductor alloys by averaging, with appropriate weights, first-principles results for the energies of ordered compounds. For example, for In_xGa_{1-x}P alloys, the disorder is restricted to a single fcc sublattice and band-structure calculations of only five compounds must be performed.²⁰ In the ternary alloy we are treating here, each species can occupy any sublattice, which would require in principle band-structure calculations of more than 20 ordered compounds to be performed. Moreover, the degree of SRO cannot be varied independently from the LRO and the method relies on interpolation between very different structures.

II. THEORY

A. Statistics of site occupation

The CBLM incorporates in a natural way correlations in the occupations of NN sites which, in the zinc-blende lattice, belong to different sublattices, α and β . We generalize the usual parametrization for binary alloys with SRO (Ref. 15) to treat three species with (possibly) different sublattice occupations, i.e., LRO. The three species in the alloy are labeled by 0, +1, and -1.

The site probabilities, p_K^γ ($\gamma = \alpha, \beta$; $K = 0, \pm 1$), give the fraction of sites of sublattice γ occupied by species K . They are therefore normalized in each sublattice:

$$\sum_{K=0,\pm 1} p_K^\gamma = 1. \quad (1)$$

The six site probabilities are completely specified in terms of only four macroscopic parameters, because of the two restrictions implied by (1). Two parameters describe the total concentrations:

$$x = \frac{p_0^\alpha + p_0^\beta}{2}, \quad (2)$$

the total concentration of species 0, and

$$\Delta = p_1^\alpha + p_1^\beta - p_{-1}^\alpha - p_{-1}^\beta, \quad (3)$$

the difference in concentrations of +1 and -1. The remaining two describe the degree of LRO:

$$M = [(p_1^\alpha - p_1^\beta) + (p_{-1}^\beta - p_{-1}^\alpha)]/2, \quad (4)$$

which measures ordering of species 1 on sublattice α and -1 on sublattice β , and

$$M' = p_0^\alpha - p_0^\beta, \quad (5)$$

which measures ordering of species 0 on sublattice α .

The pair probabilities $p_{KL}^{\alpha\beta}$ give the fraction of α - β bonds with a K atom on the α site and an L atom on the β side. They are related to the site probabilities by the sum rules

$$\sum_K p_{KL}^{\alpha\beta} = p_L^\beta \quad \text{and} \quad \sum_L p_{KL}^{\alpha\beta} = p_K^\alpha, \quad (6)$$

and therefore

$$\sum_{K,L} p_{KL}^{\alpha\beta} = 1. \quad (7)$$

The correlation in the occupation of neighboring sites is described in terms of generalized SRO parameters $\{\sigma_{KL}\}$ which are defined by

$$p_{KL}^{\alpha\beta} = p_K^\alpha p_L^\beta (1 + \sigma_{KL}). \quad (8)$$

Note that $\sigma_{KL} = 0$ applies when species K and L are not correlated, while $\sigma > 0$ ($\sigma < 0$) indicate a tendency of species K and L to be surrounded by (segregated from) each other. The constraints in (6) and (7) imply that only four independent SRO parameters, together with the four long-range parameters (2)–(5), are needed to completely specify the pair statistics of a ternary alloy on two sublattices.

For the special case of an alloy of type $(A^{III}B^V)_{1-x}C_{2x}^{IV}$, we label the group-IV element 0 and the group-III and -V elements -1 and +1, respectively. Then $\Delta = 0$ and since the group-IV element is expected to have no preferred sublattice, $M' = 0$. There are thus just two parameters x and M which describe the concentration and LRO. When $M = 0$, there is no LRO and the alloy has the diamond symmetry. The case $M \neq 0$ implies zinc-blende-type ordering. These two symmetries have been distinguished experimentally by electron microscopy³ and x-ray diffraction⁶ techniques.

The further assumption of cation-anion symmetry reduces the number of independent SRO parameters to three. We choose them to be

$$\sigma_{11} = \sigma_{-1-1} \equiv \sigma_1, \quad (9a)$$

$$\sigma_{00} \equiv \sigma_0, \quad (9b)$$

and

$$\sigma_{10} = \sigma_{0-1}. \quad (9c)$$

For a system with no LRO ($M = 0$), $\sigma_{KL} = \sigma_{LK}$, in which cases (6) and (9) imply

$$\sigma_{\pm 1,0} = \sigma_{0,\pm 1} = -\frac{x\sigma_0}{1-x} \quad (10)$$

leaving only σ_0 and σ_1 as independent SRO parameters. The physically accessible ranges of these parameters, derived in Appendix A, are presented in Fig. 1.

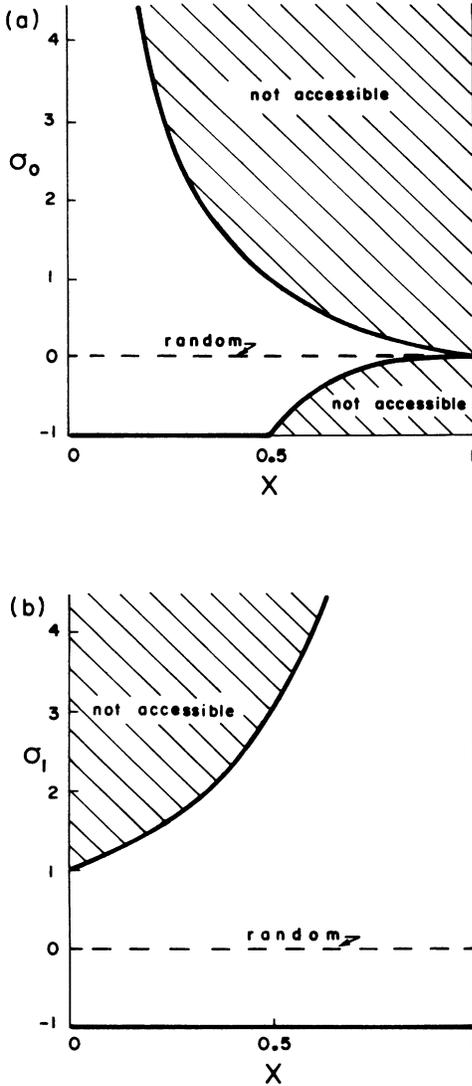


FIG. 1. Accessible regions in the (σ_0, x) and (σ_1, x) parameter space for disordered $(A^{III}B^V)_{1-x}C_{2x}^{IV}$ systems.

B. The CBLM formalism

The application of the CBLM to alloys is discussed in detail in Refs. 14 and 15. There, the many-body alloy Hamiltonian incorporates, in a self-consistent scheme, one-electron (\mathcal{H}_{1e}), electron-electron corrections ($-\mathcal{H}_{e-e}$), and ion-ion interaction ($\mathcal{H}_{\text{ion-ion}}$) terms. In the present case of semiconductor alloys¹⁷ we restrict the Hamiltonian to the one-electron component

$$\mathcal{H} = \sum_{i,\mu} |i,\mu\rangle \varepsilon_{i,\mu} \langle i,\mu| + \sum_{i,\mu;j,\nu} |i,\mu\rangle v_{i\mu,j\nu} \langle j,\nu|, \quad (11)$$

where $|i,\mu\rangle$ represents the orbital μ of the species at site i . The matrix elements of \mathcal{H} are taken from the semiempirical parametrizations for ordered Ge and GaAs by Vogl *et al.*²¹ For the hopping energies between Ge-Ga and Ge-As, which are not calculated there, we take the geometric mean⁷ of Ge-Ge and Ga-As hopping ener-

gies. For Ga-Ga and As-As hopping energies we take the same values as given for Ga-As.⁵ The use of hopping energies for the ordered systems in the alloy may be justified²² in the present case, since there is no lattice-parameter variation between the constituents. Since we are interested in the ground-state electronic energy the basis of orbitals is restricted to the minimal set sp^3 , with all NN interactions incorporated.

The alloy CBLM is an approximation for calculating the configurationally averaged local density of states (LDOS) projected onto orbital μ at site i , $\mathcal{D}_{i\mu}(E)$, of an alloy specified by arbitrary values of the LRO and SRO parameters. The LDOS is related to the diagonal matrix element of the Green's function

$$\mathcal{D}_{i\mu}(E) = -\pi^{-1} \text{Im} \langle i,\mu | G(E) | i,\mu \rangle \quad (12)$$

which is calculated by solving Dyson's equation for a cluster of atoms embedded in an effective medium. The effective medium has the topology of a Bethe lattice with the coordination number of the crystals ($z=4$) and incorporates the same LRO and SRO properties as the alloy (Appendix B).

An improved configurational average for the effective medium is presented in Appendix B which is essentially the lowest in a hierarchy of approximations developed by Hubbard²³ for one-dimensional alloys. Calculations have been performed for single-site and five-site clusters, using both the traditional Kitter-Falicov (KF)^{14,15} and the improved Hubbard-type (HT) averaging techniques.

Previous work¹⁵ shows that the alloy CBLM is reliable for the evaluation of *changes* in *integrated quantities*, such as the total electronic energy and charge. Large errors should only be expected when the Fermi level lies near a strong structure in the alloy DOS not reproduced by the CBLM, but this is not to be expected for semiconductors. On the other hand, details in the LDOS such as the structure of the bands or the electronic gap are strongly dependent on the longer-range topology and fluctuations. Therefore the CBLM is not as accurate for the calculations of such properties.^{12,17}

Our calculations are limited to the study of the average electronic energy per site of the alloy as a function of the SRO parameters. This energy is

$$\mathcal{E} = \frac{1}{2} \sum_{I,\gamma} p_I^\gamma \sum_{\mu} \int_{-\infty}^{E_F} \mathcal{D}_{i\mu}^\gamma(E) E dE, \quad (13)$$

where the factor $\frac{1}{2}$ is due to the normalization (1) which implies $\sum_{K,\gamma} p_K^\gamma = 2$.

As discussed in Ref. 15, the contribution from $\mathcal{H}_{\text{ion-ion}} - \mathcal{H}_{e-e}$ in the total energy largely cancels out, but should be considered in more realistic calculations.^{15,24} However we find that, for a fixed composition, expression (13) yields satisfactory results, presented in Sec. III, for the behavior of the total energy with SRO.

III. RESULTS

A. Comparison between different approximations in the CBLM

Results for the average LDOS obtained for the single-site and five-site clusters with a KF-type effective medium

present the same overall structure. There are the same well-defined s , sp , and p regions in the valence band. Some states appear in the gap region whose weight in the DOS is about a factor of 2 smaller in the five-site cluster than in the single-site approximation.

The HT effective medium is consistent only with central clusters of at least five sites, and comparison of the average LDOS obtained in this approximation with the KF five-site cluster results shows no significant difference.

In the calculation of the average energy $\bar{\mathcal{E}}$, the Fermi level is determined for each alloy configuration by direct integration of the total DOS. Values of $\bar{\mathcal{E}}$ obtained for $x=0.5$ and typical SRO parameters from the different approximations are given in Table I. The segregated (Ge and GaAs separated) alloy results are the same in all approximations because no averaging is involved in this limit, therefore we take it as a reference value:

$$\Delta\bar{\mathcal{E}} = \bar{\mathcal{E}} - \bar{\mathcal{E}}(\text{segregated}) . \quad (14)$$

Analysis of Table I indicates that the KF five-atom cluster calculation and the HT approximation yield equivalent results to within less than 0.01 eV. This suggests that $\bar{\mathcal{E}}$ has already become insensitive to the form of the approximate effective medium. On the other hand, the more crude one-atom KF results for $\Delta\bar{\mathcal{E}}$ are quite different from the others. In the discussion below, the KF five-atom cluster scheme is used due to its reliability and greater computational simplicity as compared to HT.

B. The role of SRO

For a given alloy composition in the disordered phase ($x > x_c$, $M=0$), we calculate $\Delta\bar{\mathcal{E}}(\sigma_0, \sigma_1)$ in the range of allowed values for σ_0 and σ_1 shown in Fig. 1. The segregated situation corresponds to $\sigma_1 = -1$ (no Ga-Ga or As-As pairs) and $\sigma_{0,\pm 1} = \sigma_{\pm 1,0} = -1$ (no Ge-Ga or Ge-As pairs) which from (10) yields $\sigma_0 = (1-x)/x$. Increasing σ_1 means allowing Ga-Ga and As-As pairs to occur, while decreasing σ_0 means allowing Ge to form pairs with Ga and As.

The $\Delta\bar{\mathcal{E}}(\sigma_0, \sigma_1)$ surface is depicted in Fig. 2 for $x=0.5$. There, we can clearly see the tendency of the electronic energy to increase when the system is forced away from the segregated situation. A somewhat surprising result is the fact that, within the precision we can rely on the KF

TABLE I. Average electronic energy relative to the energy of the segregated system ($\Delta\bar{\mathcal{E}}$) using different CBLM approximations for $x=0.5$ and typical values of the SRO parameters. KF(1) and KF(5) denote the Kittler and Falicov approximation for one-site and five-site clusters, respectively, and HT denotes first-order Hubbard-type approximation for a five-site cluster.

σ_1	σ_0	KF(1) (eV)	KF(5) (eV)	HT (eV)
-1.0	1.0	0.0	0.0	0.0
-0.5	1.0	0.099	0.064	0.066
-1.0	0.5	0.133	0.076	0.073
-1.0	0.0	0.391	0.146	0.142
0.0	0.0	0.373	0.264	0.260

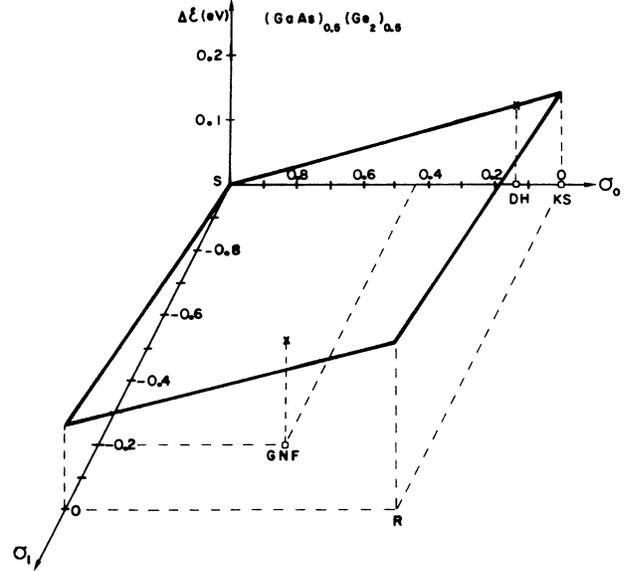


FIG. 2. Average electronic energy per site for the $(\text{GaAs})_{0.5}(\text{Ge}_2)_{0.5}$ disordered alloy as a function of the independent SRO parameters σ_0 and σ_1 . Point S indicates order appropriate for segregated Ge and GaAs and point R a random configuration. Other points indicate configurations studied by other authors: GNF, Ref. 8; KS, Ref. 9; and DH, Ref. 10, at $x=0.5$. Decreasing σ_0 from 1 increases the number of Ge-Ga and Ge-As pairs while increasing σ_1 from -1 increases the number of Ga-Ga and As-As pairs.

approximation, the $\Delta\bar{\mathcal{E}}(\sigma_0, \sigma_1)$ surface is a plane, i.e., the variation of $\Delta\bar{\mathcal{E}}$ with σ_0 and σ_1 is linear, a feature that is obtained in the whole range of compositions. Because the pair probabilities (8) are also linear in σ_{KL} , we may try a spin-model parametrization for the electronic energy of the same type assumed in previous thermodynamic calculations:^{7,8}

$$\bar{\mathcal{E}} = \frac{z}{2} \sum_{L,N} J_{LN} p_{LN}^{\alpha\beta} , \quad (15)$$

where $J_{LN} = J_{NL}$ are the interaction energies of L - N nearest-neighbor pairs. Using the relations in Sec. II A this may be rewritten as

$$\bar{\mathcal{E}} = R(x) + 2(1-x)^2 J \sigma_1 - 4x^2 K \sigma_0 , \quad (16)$$

where $R(x)$ is the energy of the completely random alloy ($\sigma_{MN}=0$),

$$4J = J_{11} + J_{-1-1} - 2J_{1-1} , \quad (17a)$$

and

$$2K = J_{10} + J_{-10} - J_{00} - J_{-1-1} . \quad (17)$$

The parameters J and K above are the same as those defined by Gu *et al.*⁸ The slopes of the $\Delta\bar{\mathcal{E}}(\sigma_0, \sigma_1)$ planes yield J and K , and we find $J = 0.26 \pm 0.01$ eV and $K = 0.15 \pm 0.01$ eV for all values of x .

C. The role of LRO and valence-band offsets

In the case of ordered compositions $x < x_c$ and $M \neq 0$, the validity of Eq. (15) requires

$$\mathcal{E} = R'(x, M) + 2[(1-x)^2 - M^2]J\sigma_1 - 4x^2K\sigma_0, \quad (18)$$

where R' is independent of σ_0 and σ_1 . Our numerical results show that the variation of $\Delta\mathcal{E}$ with σ_0 and σ_1 remains linear and the same numeric coefficients J and K obtained for $x > x_c$ yield a good fitting for (18) in this case.

As stated in Sec. IIB, the tight-binding parameters used in our calculations are taken from Vogl's model²¹ which does not consider absolute zeros of energy among different ordered systems, GaAs and Ge for example. Therefore the diagonal matrix elements for Ge are possibly shifted with respect to the ones for Ga and As. Calculations for the electronic energy $\mathcal{E}(\sigma_0, \sigma_1)$ have also been performed using in (11)

$$\varepsilon_{\text{Ge}, \mu} = \varepsilon_{\text{Ge}, \mu}^{(0)} + V, \quad (19)$$

with $\varepsilon_{\text{Ge}, \mu}^{(0)}$ taken from Vogl's parametrization and different values of V between 0.3 and 0.56 eV.^{25,26} The results for \mathcal{E} depend on V , but are always well fitted by expressions (16) or (18) with the same values of J and K . The only change is in $R(x)$ or $R'(x, M)$.

Variation of R and R' with V makes attempts to derive further relations among the J_{LN} fruitless within the present level of approximation. More sophisticated calculations in which the diagonal matrix elements are determined self-consistently¹⁵ should remove this ambiguity. Such calculations should produce the same values for J and K found here since they are independent of V .

D. Simple defect energies and pair interactions

Although the CBLM is a tight-binding formalism, the energy integral (13) is not necessarily linear in the pair probabilities used in the intermediate steps of the calculation.¹⁵ Yet our CBLM results for the average electronic energy of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ alloys are fitted by a parametrization in terms of pair interactions over the whole composition range. This supports Harrison's theory of the two-center bond,²⁷ which is based upon a tight-binding theory with universal parameters,²² the so-called universal parameter tight binding (UPTB) method.²⁸

The plausibility of our results for J and K may be tested by comparison of the values they predict for simple defect energies in ordered systems with UPTB results²⁸ and also with first-principles²⁹ calculations. It should be noted that in the UPTB method the energy of a bonded solid is referred to free atoms, while in our calculation the reference configuration of the system is an alloy with specified SRO and LRO properties, say a segregated or a random alloy. Therefore we must only compare UPTB results with ours for defects whose creation does not involve free atoms in the initial or final state. Also, no free electrons or holes should be produced in the creation mechanism of the defect.

The antistructure defect or antisite pair in perfect GaAs is created by interchanging a NN Ga-As pair, causing each of the atoms to end up with three "wrong" bonds keeping one "right" bond. The formation energy of this defect in our approximation is given by $E_{\text{AsGa}}(\text{GaAs}) = 3(J_{11} + J_{-1-1}) - 6J_{-1-1} = 12J$. For an unbound pair, i.e., interchanging a non-nearest-neighbor Ga-As pair, each atom ends up with four "wrong" bonds, increasing the formation energy to $16J$.

Pair substitution of Ge_2 in GaAs is a defect formed in the segregated system by transferring a pair of Ge atoms into GaAs, one occupying a Ga site and the other a neighboring As site, the removed Ga and As atoms being returned to bulk GaAs. The energy required for this process is $E_{\text{Ge}_2}(\text{GaAs}) = 3(J_{10} + J_{-10}) - 6J_{00} = 6K + 3(J_{1-1} - J_{00})$, where the energy to remove a Ge_2 molecule from crystalline Ge ($-6J_{00}$) has been added. Analogously $E_{\text{GaAs}}(\text{Ge}_2) = 3(J_{10} + J_{-10}) - 6J_{1-1} = 6K - 3(J_{1-1} - J_{00})$. Thus the sum of these energies is $12K$.

In Table II our estimates are compared to the UPTB results. For the antisite pairs in GaAs, the results from first-principles calculations by Baraff and Schlüter²⁹ are also given. The defect energies are in excellent agreement with our values of J and K . The discrepancy with Baraff and Schlüter's result for the bound antisite pair is probably due to elastic relaxation effects which are not included in our approach or in the UPTB.

Note that the difference $E_{\text{Ge}_2}(\text{GaAs}) - E_{\text{GaAs}}(\text{Ge}_2) = 6(J_{1-1} - J_{00})$ gives us an independent relation between the pair interactions J_{LN} if we assume its value to be 0.28 eV as predicted by UPTB (Table II). This together with Eqs. (17) still requires three independent relations be-

TABLE II. Comparison of our estimates with previous calculations for the energy of formation of simple defects.

	Previous calculations (eV)	Present estimate (eV)
Bound antisite pair in GaAs	3.42 ^a , 1.7 ^b	3.1
Unbound antisite pair in GaAs	4.2 ^b	4.2
$E_{\text{Ge}_2}(\text{GaAs})$ (Ge_2 substitution in GaAs)	1.02 ^a	
$E_{\text{GaAs}}(\text{Ge}_2)$ (GaAs substitution in Ge)	0.74 ^a	
$E_{\text{Ge}_2}(\text{GaAs}) + E_{\text{GaAs}}(\text{Ge}_2)$	1.76 ^a	1.80

^aKraut and Harrison, Ref. 28.

^bBaraff and Schlüter, Ref. 29.

TABLE III. Calculated interaction energies of nearest-neighbor pairs within the assumptions described in the text.

$L-N$	J_{LN} (eV)
Ga-As	-0.26
Ge-Ge	-0.30
Ga-Ga	0.26
As-As	0.26
Ge-Ga	-0.13
Ge-As	-0.13

tween J_{LN} to yield the individual values of the six interactions between species. Because only relative values among them are relevant, we may choose the energy origin such that

$$J_{11} + J_{-1-1} + 2J_{1-1} = 0. \quad (20)$$

The assumption of cation-anion symmetry requires J_{11} and J_{-1-1} to be of the same order as well as J_{10} and J_{-10} . In order to get an estimate for the individual J_{LN} we impose, as previously done,^{7,8}

$$J_{11} = J_{-1-1} \quad (21a)$$

and

$$J_{10} = J_{-10}. \quad (21b)$$

Under these assumptions, we obtain the interaction energies given in Table III. Because of the choice (20), only the relative values among the J_{LN} are meaningful.

Parametrizations of alloy electronic energies in terms of pair interactions have been previously obtained within the CBLM for Cr-W, Cr-Mo, and Mo-W systems.³⁰ It should be noted that for these metallic alloys the effective pair interactions are concentration dependent.

IV. DISCUSSIONS AND CONCLUSIONS

The main controversy in the literature concerning metastable $(A^{\text{III}}B^{\text{V}})_{1-x}C_{2x}^{\text{IV}}$ alloys involves the origin and nature of the SRO. Both the thermodynamic models^{5,7,8} and the growth models^{9,10} rely on stated or implicit assumptions regarding the energies of interaction, in the bulk and in the growing surface, respectively, between the different types of atomic pairs. For example, they assume correlations which can only exist if certain pair interaction energies are large. Our results, obtained by fitting total energy versus SRO surfaces calculated using the CBLM, lead to a parametrization which yields reasonable estimates for simple defect formation energies (see Table II). This is an indication that the results are reliable for a semiquantitative discussion of the thermodynamic and growth models.

In the most recent thermodynamic model calculation, Gu, Newman, and Fedders (GNF)⁸ obtain a best fit for EXAFS data for $(\text{GaSb})_{1-x}\text{Ge}_{2x}$ using $K/J=3.5$ and $k_B T_S/J=2.15$, where K and J are as defined in Eqs. (17), and $T_S \approx 700$ K is the sample preparation temperature. Taking for the parameters J and K the values we calcu-

late for $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ implies $K/J=0.6$ and $k_B T_S/J \approx 0.23$. The first ratio is off by a factor of 6 and the second by an order of magnitude. While some variation of K and J with the cation species is possible, the changes are expected to be no more than a factor of 2. Phase diagrams obtained for different values of K/J in Ref. 8 as well as in previous thermodynamic calculations^{5,7} always require $k_B T_S/J \approx 2$ to get the order-disorder transition at $x_c \approx 0.3$. Thus, even allowing uncertainty in K/J , the calculated J is at least one order of magnitude too large to be consistent with the thermodynamic model.

Another difficulty with the thermodynamic model is that for MBE prepared $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ samples,³ growth temperatures of 700 and 820 K produce homogeneous and segregated samples, respectively. The thermodynamic phase diagrams^{5,7,8} indicate that, for a fixed composition, the system segregates at low temperatures while increasing T favors homogeneously mixed (ordered or disordered according to x) phase in contradiction with the MBE results.

The growth model offers a simple explanation for the phase separation of MBE samples³ grown at $T_S=820$ K. At this temperature there should be enough thermal energy ($k_B T_S \sim 0.07$ eV) not to allow Ge to bind on either Ga or As at the surface of the growing sample and therefore forming Ge segregated domains.

In the kinetic model of Kim and Stern (KS)⁹ it is implicitly assumed that on the growth surface $J_{11}=J_{-1-1}=\infty$ and all other pair interaction energies are taken to be finite and equivalent, as pointed out by GNF. This necessarily yields a random distribution for the Ge, i.e., $\sigma_0=0=\sigma_{\pm 1,0}=\sigma_{0,\pm 1}$ and $\sigma_1=-1$. The model of Davis and Holloway¹⁰ (DH) also implies $\sigma_1=-1$, but they consider Ga-As as bound molecules, i.e., each Ga(As) in the alloy has at least one As(Ga) NN. This induces correlation in the Ge, so that $\sigma_0 > 0$ and $\sigma_{0,\pm 1}=\sigma_{\pm 1,0} < 0$. In Fig. 2 the SRO parameters for $x=0.5$ in the GNF, KS, and DH calculations are indicated. Notice that in GNF, Ge is quite correlated ($\sigma_0=0.44$) while $\sigma_1=-0.2$ indicates a considerable fraction of "wrong" bonds. On the other hand, the KS and DH results are constrained to the $\sigma_1=-1$ axis. The germanium correlation in DH corresponds to $\sigma_0=0.14$.

The results obtained here for the bulk interaction energies indicate that different atomic affinities among the species could also be expected on the growing surface. As for the bulk, energetically Ge-Ga and Ge-As pairs might bind less easily than Ge-Ge, although they are all favored with respect to Ga-Ga and As-As. Growth simulations³¹ show that allowing σ_1 to increase from -1 destroys the order-disorder transition, while increasing σ_0 favors the ordered phase.

In summary, we have generalized the usual binary alloys parametrization¹⁵ for the statistics of site occupation to treat ternary alloys of the type $(A^{\text{III}}B^{\text{V}})_{1-x}C_{2x}^{\text{IV}}$ with SRO and LRO. The statistics is based on pair probabilities and is used in connection with the CBLM to study the electronic structure of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$. Three levels of approximation within the CBLM were tested for the

calculation of the electronic energy, and the five-atom cluster in a KF effective medium was considered satisfactory for the present purposes.

Analysis of the variation of the average electronic energy with the SRO parameters allows us to parametrize it simply in terms of pair interaction energies. Two independent combinations, J and K , are obtained that fit our results within ~ 0.01 eV for all compositions, all degrees of LRO and SRO, and different values of the valence-band offsets. The individual interaction energies are obtained by taking the pair interactions which are expected to be of the same order to be equal [Eqs. (21)]. Our calculation also confirms the validity of Ising-like (in this case, spin 1) models to treat $(\text{GaAs})_{1-x}\text{Ge}_{2x}$, with NN pair interaction energies which are independent of composition and of the degree of SRO and LRO.

Our study leads to the conclusion that the zinc-blende–diamond transition observed in these alloys is driven by the kinetics of growth, and that Ge correlations must be incorporated in realistic models.

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APPENDIX A: ALLOWED RANGES OF SRO PARAMETERS WHEN $\Delta = M' = M = 0$

The range of allowed σ_{KL} is determined from Eq. (6) using the constraint that $p_{KL}^{\alpha\beta} \geq 0$. This requires

$$\sigma_{KL} \geq -1. \quad (\text{A1})$$

For $\Delta = M' = M = 0$, the only two independent SRO parameters are σ_0 and σ_1 . Equation (10) relates $\sigma_{\pm 1,0} = \sigma_{0,\pm 1}$ to σ_0 . With Eq. (A1) it requires,

$$-1 \leq \sigma_0 \leq \frac{1-x}{x}. \quad (\text{A2})$$

The other dependent SRO parameters, $\sigma_{+1-1} = \sigma_{-1+1}$, are determined using Eqs. (6) and (8), giving

$$\sigma_{1,-1} = -\sigma_1 + \frac{2x^2\sigma_0}{(1-x)^2}. \quad (\text{A3})$$

Equation (A1) then implies

$$-1 \leq \sigma_1 \leq 1 + \frac{2x^2\sigma_0}{(1-x)^2}. \quad (\text{A4})$$

Thus the limits on σ_1 and σ_0 are not independent. However, Eq. (A4) does imply a further limit on the minimum allowed value of σ_0 such that the range of σ_1 is nonzero:

$$\max \left\{ -1, - \left[\frac{1-x}{x} \right]^2 \right\} \leq \sigma_0 \leq \frac{1-x}{x}. \quad (\text{A5})$$

Figure 1(a) shows the allowed range of σ_0 as a function of x . The allowed range of σ_1 depends on both σ_0 and x . Figure 1(b) shows the maximum range which occurs at the largest allowed value of σ_0 . The minimum allowed range occurs for the minimum σ_0 . For $x < \frac{1}{2}$, the minimum range is $-1 \leq \sigma_1 \leq 1 - 2x^2/(1-x)^2$ and for $x \geq \frac{1}{2}$ the minimum range shrinks to just -1 .

APPENDIX B: CBLM FORMALISMS FOR TETRAHEDRAL SEMICONDUCTOR ALLOYS

We define on-site and hopping matrices by its matrix described in (11)

$$[\tilde{\epsilon}(I)]_{\mu\nu} \equiv \langle i, \mu | \mathcal{H} | i, \nu \rangle, \quad (\text{B1})$$

$$[\tilde{v}_{ij}(I, J)]_{\mu\nu} \equiv \langle i, \mu | \mathcal{H} | j, \nu \rangle, \quad (\text{B2})$$

where it is understood that the species at nearest-neighbor sites i and j are I and J , respectively, and $\tilde{v}_{ij}(I, J)$ depends on $\delta_{ij} = \mathbf{r}_i - \mathbf{r}_j$, the relative position between the sites. In the zinc-blende structure the vector δ_{ij} has eight possible values: $\delta_1, \delta_2, \delta_3, \delta_4$ if i is in sublattice α , and $-\delta_1, -\delta_2, -\delta_3, -\delta_4$ if i is in sublattice β .

The Hermiticity of \mathcal{H} implies

$$\tilde{\epsilon}(I) = [\tilde{\epsilon}(I)]^\dagger, \quad (\text{B3a})$$

and

$$\tilde{v}_{ij}(I, J) = [\tilde{v}_{ji}(J, I)]^\dagger. \quad (\text{B3b})$$

Assuming real wave functions, the symmetry of s and p orbitals gives

$$[\tilde{v}_{ij}(I, J)]_{sp} = -[\tilde{v}_{ij}(J, I)]_{ps}. \quad (\text{B4})$$

Consider a cluster such that the central site (0) belongs to sublattice γ and is occupied by species I . Dyson's equation gives the matrix elements of the Green's function $G(E) = (E - \mathcal{H})^{-1}$ between the central site and any other site $\mathbf{r}_n \equiv n$ occupied by species K :

$$[E\vec{J} - \tilde{\epsilon}(K)]\vec{G}_{n,0} = \delta_{n,0}\vec{J} + \sum_{\lambda=1}^4 \tilde{v}_\lambda(K, L(\lambda))\vec{G}_{n_\lambda,0}. \quad (\text{B5})$$

Here, \vec{J} is the identity, the index λ labels the four nearest-neighbor vectors δ_λ relative to site \mathbf{r}_n and $L(\lambda)$ is the species at site $\mathbf{r}_n + \delta_\lambda \equiv n_\lambda$.

Suppose atom K belongs to sublattice α and is in the Bethe-lattice (effective medium) region. Then one of its nearest neighbors is closer to the origin than it is, as illustrated in Fig. 3. This is called the “parent” atom,¹⁴ and taken to be of species J on site n_λ . The $z-1=3$ other nearest neighbors are the “descendants” at sites $n_{\lambda' \neq \lambda}$ and of species $L(\lambda')$. From (B5)

$$[E\vec{J} - \tilde{\epsilon}(K)]\vec{G}_{n,0} = \tilde{v}_\lambda(K, J)\vec{G}_{n_\lambda,0} + \sum_{\lambda' (\neq \lambda)} \tilde{v}_{\lambda'}(K, L(\lambda'))\vec{G}_{n_{\lambda'},0}. \quad (\text{B6a})$$

Analogously, if K is on site \bar{n} belonging to sublattice β

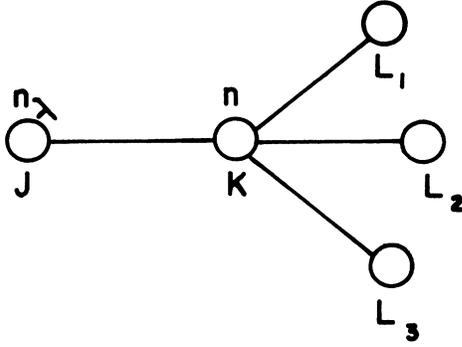


FIG. 3. Typical sites in the effective-medium (Bethe-lattice) region. Relative to site n , site n_λ belongs to the path leading to the cluster region and is called the “parent” site, while the three other sites are the “descendants.” Species are labeled as referred to in the text.

$$[E\vec{J} - \vec{\epsilon}(K)]\vec{G}_{\bar{n},0} = \vec{v}_{\bar{\lambda}}(K,J)\vec{G}_{\bar{n}_{\bar{\lambda}},0} + \sum_{\bar{\lambda}' (\neq \bar{\lambda})} \vec{v}_{\bar{\lambda}'}(K,L(\bar{\lambda}'))\vec{G}_{\bar{n}_{\bar{\lambda}'},0} \quad (\text{B6b})$$

where $\delta_{\bar{\lambda}} = -\delta_\lambda$.

Equations (B6) may be approximately solved by the transfer-matrix ansatz:

$$\begin{aligned} \vec{G}_{n,0} &= \vec{\tau}_{KJ}(\lambda)\vec{G}_{n_\lambda,0}, \\ \vec{G}_{\bar{n},0} &= \vec{\tau}_{KJ}(\bar{\lambda})\vec{G}_{\bar{n}_{\bar{\lambda}},0} \end{aligned} \quad (\text{B7})$$

which relates the Green's function on K to that at the parent site, and similarly the Green's function on the descendants to that on K . It is easily shown that

$$\tau_{KJ}(\rho) = \vec{t}_\rho(K)\vec{v}_\rho(K,J), \quad (\text{B8})$$

where $\rho = \lambda, \bar{\lambda}$ and the reduced transfer matrices \vec{t} satisfy

$$\vec{t}_\lambda(K) = \left[E\vec{J} - \vec{\epsilon}(K) - \sum_{\lambda' (\neq \lambda)} \vec{v}_{\lambda'}(K,L(\lambda'))\vec{t}_{\lambda'}(L(\lambda')) \times \vec{v}_{\lambda'}(L(\lambda'),K) \right]^{-1}, \quad (\text{B9a})$$

$$\vec{t}_{\bar{\lambda}}(K) = \left[E\vec{J} - \vec{\epsilon}(K) - \sum_{\bar{\lambda}' (\neq \bar{\lambda})} \vec{v}_{\bar{\lambda}'}(K,L(\bar{\lambda}'))\vec{t}_{\bar{\lambda}'}(L(\bar{\lambda}')) \times \vec{v}_{\bar{\lambda}'}(L(\bar{\lambda}'),K) \right]^{-1}. \quad (\text{B9b})$$

Relations (B6)–(B9) imply

$$\left[E\vec{J} - \vec{\epsilon}(K) - \sum_{\lambda' (\neq \lambda)} \vec{\xi}_{\lambda'}(K,L(\lambda')) \right] \vec{G}_{n,0} = \vec{v}_\lambda(K,J)\vec{G}_{n_\lambda,0}, \quad (\text{B10})$$

where

$$\begin{aligned} \xi_{\lambda'}(K,L(\lambda')) &= \vec{v}_{\lambda'}(K,L(\lambda'))\vec{t}_{\bar{\lambda}'}(L(\lambda')) \\ &\times \vec{v}_{\bar{\lambda}'}(L(\lambda'),K) \end{aligned} \quad (\text{B11})$$

may be interpreted as the self-energy contribution to species K on sublattice α due to a descendant $L(\lambda')$ at site $n_{\lambda'}$.

The usual configurational averaging for the alloy CBLM proposed by Kittler and Falicov^{14,15} (KF) consists of eliminating the dependence of the partial self-energy on the “descendant” species by averaging (B11):

$$\Sigma_\lambda(K) = \langle \xi_{\lambda'}(K,L) \rangle_L = \sum_L \frac{p_{KL}^{\alpha\beta}}{p_K^\alpha} \xi_{\lambda'}(K,L) \quad (\text{B12a})$$

and analogously

$$\Sigma_{\bar{\lambda}}(K) = \sum_L \frac{p_{KL}^{\beta\alpha}}{p_K^\beta} \xi_{\bar{\lambda}'}(K,L). \quad (\text{B12b})$$

Note that in using (B12) in (B9), the configuration average of the inverse of a quantity is replaced by the inverse of its average. A better approximation is to take

$$\vec{t}_\rho(K) = \left\langle \left[E\vec{J} - \vec{\epsilon}(K) - \sum_{\rho' (\neq \rho)} \vec{\xi}_{\rho'}(K,L(\rho')) \right]^{-1} \right\rangle_{\{L(\rho')\}}, \quad (\text{B13})$$

where $\rho = \lambda$ or $\bar{\lambda}$ and the average is performed simultaneously over the species of the three descendants $\{L(\rho')\}$. Assuming K belongs to α , the contribution from descendants $\{L_1, L_2, L_3\}$ shown in Fig. 3 is weighted by $p_{KL_1}^{\alpha\beta} p_{KL_2}^{\alpha\beta} p_{KL_3}^{\alpha\beta} / (p_K^\alpha)^3$. This improved average of (B10) is equivalent to the averaging in Hubbard's first-order method²³ for one-dimensional chains. Higher-order versions of his method may also be generalized to the Bethe lattice because of its simple topology.

Within a given approximation, (B9) is solved iteratively for the transfer matrices and $\vec{G}_{00}(E)$ is obtained for a fixed configuration \mathcal{C} of the cluster. The matrix elements required for the density of states in (12) are obtained by averaging $\langle \vec{G}_{00}(E) \rangle_{\mathcal{C}}$ over all cluster configurations with species I at site 0. The numerical evaluation of the Green's function is significantly simplified by using group theory and the total energy integral (13) is also facilitated by deforming the contour of integration into the complex plane. These techniques are described in Ref. 15.

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