

Structure of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ and its electronic properties

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An improved model for the structure of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ is proposed. The phase diagram is calculated using the Kikuchi approximation, with the interaction energies of nearest-neighbor atom pairs computed by a universal-parameter tight-binding method. The Ge atoms are taken to be randomly distributed in order to avoid phase segregation in the computation of the metastable phase diagram of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$. There is a metastable order-disorder transition point at $x_c=0.36$, which agrees well with experiment. The contribution of the order-disorder transition to band-gap bowing is also calculated.

I. INTRODUCTION

Metastable compounds of the form $(A^{\text{III}}B^{\text{V}})_{1-x}C_{2x}^{\text{IV}}$ have been studied both experimentally and theoretically.¹⁻⁶ For small x , these alloys have a zinc-blende crystal structure characteristic of III-V compounds, while for large x , these alloys have diamond crystal structure characteristic of group-IV elements. At a critical composition x_c , the alloy undergoes an order-disorder transition between the zinc-blende and diamond crystal structures.⁵

Anomalous V-shaped bowings of the direct band gap^{3,7} ϵ_0 as a function of composition x have been observed in $(\text{GaAs})_{1-x}\text{Ge}_{2x}$. Several theoretical treatments^{3,4,8-15} were proposed to model the order-disorder transition of these materials and its effect on the electronic structure of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$. There has been some controversy regarding the nature of the short-range order. Newman and co-workers^{3,4} investigated the order-disorder transition by thermodynamic methods, assuming that the transition point is associated with the minimum of the energy-gap versus composition curve. Koiller, Davidovich, and Osório¹³ and Gu, Newman, and Fedder¹⁵ considered the correlation between first neighbors to improve upon the mean-field theory of the order-disorder transition in the alloys $(A^{\text{III}}B^{\text{V}})_{1-x}C_{2x}^{\text{IV}}$ using the Kikuchi approximation. Another category of the theoretical treatments assumed that there are no so-called "wrong" Ga-Ga and As-As bonds. D'yakonov and Raikh⁸ discussed the order-disorder transition in the context of the site percolation model of Ga and As on the diamond crystal structure with the restriction that no Ga-Ga or As-As nearest-neighbor pairs were allowed. The value of x_c is associated with the site percolation threshold in the diamond lattice, $x_c=1-p_c=0.57$, which is considerably higher than the experimental value. Still other workers⁹⁻¹² suggested a kinetic growth mechanism for the phase transition under the assumptions that there are no wrong bonds, and that the other interactions (between bonds Ga-As, Ge-Ge, As-Ge, and Ge-As) are taken to be identical. Davidovich *et al.*¹⁶ analyzed the electronic energy of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ as a function of both the short-range and long-range orders. They found

that the pair-interaction energies from their computation is different from those determined by Gu, Newman, and Fedders from extended x-ray-absorption fine structure (EXAFS) data and leads to a higher transition temperature at $x_c=0.3$ than the actual sample preparation temperature. They thus proposed a more general growth simulation.¹⁴ But there are some unknown parameters in this growth model. Additionally, there is the unrealistic assumption in both the thermodynamic and growth models that the Ge-Ga and Ge-As pairs, as well the Ga-Ga and As-As pairs, are taken to have the same interaction energies. In fact, Ge-As and Ge-Ga pairs are known to have different interaction energies. Harrison and Kraut¹⁷ have calculated the energies of substitution and solution of semiconductors using a universal-parameter tight-binding method. It can be seen from their results that the interaction energies of As-Ge and Ga-Ge, as well as Ga-Ga and As-As are clearly different. The relationship between cellular-automaton-based growth models and equilibrium-thermodynamic models of the material structure was explored by Bar-Yam, Kandel, and Domany.¹⁸ Recently, Osório, Froyen, and Zunger¹⁹ performed first-principles local-density total-energy calculations to extract pairwise energies and electrostatic interactions and used the pair approximation of the cluster-variation method to compute equilibrium phase diagrams. The resulting phase diagram shows that phase separation is the stable thermodynamic state at temperatures below the melting point.

It is thus more reasonable to treat the problem, based on the calculated energies. Since we are primarily interested in the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ within the phase-separation region where the thermodynamic ground state of the system corresponds to a complete segregation of Ge atoms from the GaAs compound, we must have a method of dealing with the nonequilibrium nature of the alloy. Experimentally, phase separation can be inhibited if the crystal is quickly quenched in the highly mixed (due to secondary-ion bombardment) state. In order to eliminate phase separation, we assume that the Ge atoms are randomly distributed, instead of being segregated as is the case for phase separation. We thus take the same starting point as in the growth model. In the calculation

of the phase diagram of the alloy, we use results from Ref. 17 for the interaction energies of the nearest-neighbor pairs, instead of energies extracted from experimental data. Thus, our approach is of the first principle type.

In this paper we extend the thermodynamic approach to study the metastable phases of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ by taking into account the random distribution of the Ge atoms. The energy gap of the alloy is computed in the correlated virtual-crystal approximation.²⁰ The methods are described in Secs. II and III. In Sec. IV we show the calculated results of the structure and the electronic properties of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$. We summarize our results in Sec. V.

II. METHOD

In this section we describe the methods used to determine the structure of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$. We use the Kikuchi approximation²¹ with oriented-pair probabilities P_{ij} to include correlations. Because we are interested in the calculation both of an equilibrium phase diagram for $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ alloy and the metastable phase diagram, we have two versions of the Kikuchi approximation for the $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ alloy: one (described in Sec. II B) that uses the grand-canonical potential to calculate the phase diagram, and another (described in Sec. II C) that uses the Helmholtz free energy with the condition of a random distribution of the Ge atoms within the metastable phase region.

A. The pair interaction energies of the alloy

The alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ is modeled as a lattice gas, that is, an ideal zinc-blende crystal structure is divided into nominal cation and anion sites, and each site is assumed to be simply occupied by a Ga, As, or Ge atom. We use a notation similar to that of Ref. 15. Ga atoms are labeled "1," As atoms are labeled "2," and Ge atoms are labeled "3." The probability that an atom i occupies a cation or anion site is represented by P_i^c and P_i^a , respectively, and the oriented-pair probability that an atom i on a cation site is bonded to an atom j on an anion site is represented by P_{ij} .

The oriented-pair probabilities obey the sum rules

$$\sum_i P_{ij} = P_j^a \quad (1)$$

and

$$\sum_j P_{ij} = P_i^c, \quad (2)$$

which are statements of the conservation of probability. In the oriented-pair-probability notation, the energy of the alloy is given by

$$E = ZN \sum_{i,j} E_{ij} P_{ij}, \quad (3)$$

where $Z = 4$ is the coordination number, N is the number of sites in a sublattice, and the energies $E_{ij} = E_{ji}$ are the interaction energies of nearest-neighbor pairs.

The determination of the interaction energies E_{ij} together by theory and by experiment proves to be difficult. Recently, there have been some estimates for $A_x^{\text{III}}B_{1-x}^{\text{III}}C^{\text{V}}$ and $A^{\text{III}}B_{1-x}^{\text{V}}C_x^{\text{V}}$ semiconductor alloys²²⁻²⁵ and $(A^{\text{III}}B^{\text{V}})_{1-x}C_{2x}^{\text{IV}}$ semiconductor alloys.¹⁹ There also exist some microscopic quantum-mechanical theories for the isolated case of individual impurities.²⁶⁻²⁹ Most of these theories use a Green's function to represent the crystalline environment. Harrison and Kraut¹⁷ calculated the cohesive energies of elemental and compound semiconductors and the energies of substitution in semiconductors. Their technique is a tight-binding theory based on a universal parameter, and on individual bond energies with corrections (called metallization) due to coupling with neighbors. The universal-parameter tight-binding method did not depend on the lattice periodicity and is, therefore, directly applicable to our case, i.e., the total energy of systems with pair interactions.

In the universal-parameter tight-binding method,¹⁷ the interaction energies of nearest-neighbor atom pairs can be determined step by step by assembling free atoms into a bonded solid. The energy per bond is the sum of four terms: (1) the promotion energy to form sp^3 hybrids; (2) a bond formation energy between hybrids; (3) an overlap repulsive energy from the nonorthogonality of the two hybrids; and (4) a coupling energy of bonds to neighboring antibonds. We do not consider lattice relaxation in the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$, which is unimportant because of the small differences between the bond lengths of GaAs and the bond lengths of Ge. Thus we can obtain the interaction energies of nearest-neighbor pairs: $E_{11} = 0.075$ eV, $E_{12} = -2.09$ eV, $E_{13} = -1.29$ eV, $E_{22} = -3.66$ eV, $E_{23} = -2.86$ eV, and $E_{33} = -2.29$ eV.

We can also use the well-known three-component spin model of Blume, Emery, and Griffiths³⁰ to represent E :

$$E = J \sum_{i,j} S_i S_j - K \sum_{i,j} S_i^2 S_j^2 + L \sum_{i,j} (S_i^2 S_j + S_i S_j^2). \quad (4)$$

From the universal-parameter tight-binding theory, we find

$$4J = E_{11} + E_{22} - 2E_{12} = 0.595 \text{ eV},$$

$$4K = -E_{11} - E_{22} - 2E_{12} - 4E_{33} + 4(E_{13} + E_{23}) \\ = 0.325 \text{ eV},$$

and

$$4L = (E_{11} - E_{22}) + 2(E_{23} - E_{13}) = 0.595 \text{ eV}.$$

The three components of the spin S_i represent the occupation of one of the types of atoms on site i : $S_i = +1$ for a Ga atom, $S_i = 0$ for a Ge atom, and $S_i = -1$ for an As atom. We note that in Ref. 15, L is taken to be zero, while we have $L = 0.149$ eV, and, therefore, the occupancies of Ge atoms on the two sublattices are different.

B. The Kikuchi approximation

We use the Kikuchi approximation²¹ to compute the phase diagram in the pair-correlation approximation.

The equilibrium state of the system is derived by

minimizing the grand-canonical potential G defined as

$$G = E - TS - \sum_{i=1}^3 \mu_i N_i$$

$$= E - TS - \mu N x + \text{const} , \quad (5)$$

where the combined chemical potential μ is given by

$$\mu = 2\mu_3 - \mu_1 - \mu_2 , \quad (6)$$

and μ_i is the chemical potential of species i , E is the energy defined by Eq. (3), T is the absolute temperature, and S is the configurational entropy given by

$$S = Nk_B \left[-Z \sum_{i,j} P_{ij} \ln P_{ij} + (Z-1) \sum_{i,\alpha} P_i^\alpha \ln P_i^\alpha \right] , \quad (7)$$

where k_B is Boltzmann's constant. The grand-canonical potential G also depends parametrically on the oriented-pair probabilities P_{ij} , which are determined by minimization of G . Quantities such as the order parameter M and the composition x of the alloy (GaAs)_{1-x}Ge_{2x} are determined from the oriented-pair probabilities P_{ij} . The order parameter M , in fact, depends on the site probabilities P_i^α ,

$$M = (m_1 + m_2) / 2 \quad (8)$$

with

$$m_1 = P_1^c - P_1^a \quad (9)$$

and

$$m_2 = P_2^a - P_2^c . \quad (10)$$

The composition x is written in terms of P_{ij} by using a quantity a_{ij} that simply counts the number of Ge atoms in a bond,

$$x = \frac{1}{2} \sum_{i,j} a_{ij} P_{ij} \quad (11)$$

with

$$a_{ij} = (i-1)(i-2)/2 + (j-1)(j-2)/2 . \quad (12)$$

Following Kikuchi, the normalization condition for the oriented-pair probabilities P_{ij}

$$\sum_{i,j} P_{ij} = 1 \quad (13)$$

is used as a constraint for Lagrange's method of undetermined multipliers. Since the Ga and As atoms have the same composition, we have another constraint:

$$P_1^a + P_1^c = P_2^a + P_2^c \quad (14)$$

or written in terms of P_{ij}

$$\sum_{i,j} (b_{ij} - c_{ij}) P_{ij} = 0 , \quad (15)$$

where

$$b_{ij} = \frac{1}{2}(3-i)(2-i) + \frac{1}{2}(3-j)(2-j) , \quad (16)$$

$$c_{ij} = (3-i)(i-1) + (3-j)(j-1) . \quad (17)$$

We note that the constraint Eq. (15) is an extension beyond Ref. 15, where L was taken to be zero. After introduction of the Lagrange multipliers λ_1 and λ_2 associated with constraints (13) and (15), the minimization of G yields the following system of nonlinear algebraic equations:

$$P_{ij} = (P_i^c P_j^a)^{3/4} \exp \left[\frac{\lambda_1}{2} + \frac{1}{2} \lambda_2 (b_{ij} - c_{ij}) + \frac{\beta \mu}{2} a_{ij} - \beta E_{ij} \right] , \quad (18)$$

with $\beta = (k_B T)^{-1}$, where the undetermined multipliers λ_1 and λ_2 are found by using the constraint Eqs. (13) and (15). Combining Eqs. (13) and (14), we find

$$P_{ij} = \frac{(P_i^c P_j^a)^{3/4} \exp[-\beta E_{ij} + \frac{1}{2} \beta \mu a_{ij} + \frac{1}{2} \lambda_2 (b_{ij} - c_{ij})]}{\sum_{i,j} (P_i^c P_j^a)^{3/4} \exp[-\beta E_{ij} + \frac{1}{2} \beta \mu a_{ij} + \frac{1}{2} \lambda_2 (b_{ij} - c_{ij})]} . \quad (19)$$

Equation (19) is the basis of the natural-iteration calculation described by Kikuchi. Starting with given values of μ and T , we guess initial values of the on-site probabilities P_i^α are then calculated using Eq. (19). New on-site probabilities P_i^α are found from Eqs. (1) and (2). In every iteration we use the Newton-Raphson method to compute the Lagrange multiplier λ_i . The procedure is continued until the difference between the previous values and newly determined values of the probabilities P_i^α are small. In this way, the phase diagram is found.

C. The modified Kikuchi approximation

Since we are primarily interested in the alloy (GaAs)_{1-x}Ge_{2x} within the phase-separation region, we must modify the Kikuchi approximation in order to study metastable phases. Following Ref. 15, the Helmholtz free energy is used

$$F = E - TS \quad (20)$$

instead of the grand-canonical potential, Eq. (5). The free energy of the alloy is given by

$$F = N \left[Z \sum_{i,j} E_{ij} P_{ij} + Z k_B T \sum_{i,j} P_{ij} \ln P_{ij} - (Z-1) k_B T \sum_{i,\alpha} P_i^\alpha \ln P_i^\alpha \right] . \quad (21)$$

Ge atoms are taken to be randomly distributed in order to study the metastable region. There are thus three constraint equations to represent the random distribution of Ge atoms,

$$\sum_j P_{3j} = x , \quad (22)$$

$$\sum_i P_{i3} = x , \quad (23)$$

and

$$P_{33} = P_3^a P_3^c. \quad (24)$$

In Ref. 15, only constraints (22) and (23) are used. That is, one uses the constraints of composition x instead of the chemical potential μ_i by simply choosing not to search for phase separation regions. Both the Ge atoms still tend to segregate, which is reflected in pair probabilities. Therefore, we add another constraint (24) which assumes that the Ge atoms to be randomly distributed. In terms of P_{ij} , we have

$$\sum_{i,j} d_{ij} P_{ij} - x = 0, \quad (25)$$

$$\sum_{i,j} e_{ij} P_{ij} - x = 0, \quad (26)$$

$$\sum_{i,j} f_{ij} P_{ij} - x^2 = 0, \quad (27)$$

where

$$d_{ij} = (i-1)(i-2)/2, \quad (28)$$

$$e_{ij} = (j-1)(j-2)/2, \quad (29)$$

$$f_{ij} = (i-1)(j-1)(i-2)(j-2)/4. \quad (30)$$

We then introduce five undetermined multipliers: λ_1 , λ_2 , λ_3 , λ_4 , and λ_5 . Minimizing the free energy with respect to P_{ij} , we find

$$P_{ij} = (P_i^c P_j^a)^{3/4} \exp \left[-\beta E_{ij} + \frac{\lambda_1}{2} + \frac{\lambda_2}{2} (b_{ij} - c_{ij}) + \frac{\lambda_3}{2} d_{ij} + \frac{\lambda_4}{2} e_{ij} + \frac{\lambda_5}{2} f_{ij} \right]. \quad (31)$$

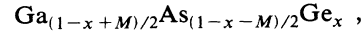
The undetermined multipliers λ_1 , λ_2 , λ_3 , λ_4 , and λ_5 are calculated by using constraints (13), (15), (26), (27), and (28). For fixed values of temperature and composition x , Eq. (31) forms the basis of Kikuchi's natural-iteration calculation. For each iteration we use the method of steepest descent to determine the undetermined Lagrange multipliers.

III. THE CORRELATED VIRTUAL-CRYSTAL APPROXIMATION

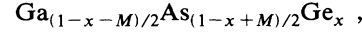
We use the correlated virtual-crystal approximation^{13,15} (CVCA) based on the Kikuchi approximation and the Vogl empirical tight-binding theory³¹ to find the band gap of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$.

Virtual-crystal approximation²⁰ (VCA) simply estimates the curvature of the band gap of an alloy by averaging the band-structure parameters, such as on-site energies or off-diagonal matrix elements from the tight-binding approximation. When the alloy undergoes an order-disorder transition between two different crystal-line types, its long-range order is modified, necessitating a change in the standard VCA. In the Newman-Dow⁴ approximation, called there the mean-field VCA (MFVCA), the change in long-range order is handled through mean-field theory, with the band-structure parameters estimat-

ed by replacing the alloy with virtual cations and anions of the form



and



respectively. Koiller, Davidovich, and Osório¹³ improved upon this MFVCA by adding correlation. Their correlated VCA (CVCA) weights statistically (using on-site probabilities P_i^a and oriented-pair probabilities P_{ij}) the band-structure parameters of their host compounds GaAs and Ge. Gu, Newman, and Fedders¹⁵ gave an alternative approach. In our calculations, the band-structure parameters are estimated using the correlated VCA methods given in Ref. 15 and approximations made by Vogl, Hjalmanson, and Dow in their empirical tight-binding model and their "universal" model for III-V compounds and group-IV elemental semiconductors.³¹

IV. RESULTS

In Fig. 1 we present the calculated phase diagram, which is qualitatively equivalent to the ones presented in Ref. 15. Our results are also similar to those of Osório, Froyen, and Zunger,¹⁹ except that they have excluded As-As and Ga-Ga bonds. In the calculated phase diagram there are three regions: (1) ordered (zinc-blende) phase; (2) disordered (diamond) phase; and (3) phase separation. We study only those features of the phase diagrams of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ that occur below the melting temperature. In Fig. 1 it can be seen that the order-disorder transition line is rather high; the lowest point where the order-disorder transition line intersects the phase-separation boundary is 0.26 eV, which is higher than the melting point. Therefore this feature of the phase diagram probably cannot be observed experimentally. Since we use the calculated interaction energies of the nearest-neighbor pair to compute the phase diagram,

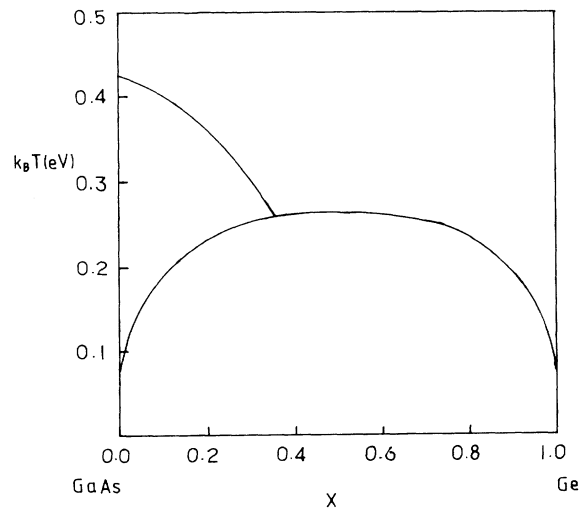


FIG. 1. The phase diagram of temperature vs composition x for $(\text{GaAs})_{1-x}\text{Ge}_{2x}$.

there is no unknown parameter. In the previous model,¹⁵ the Ge atoms have the same interaction energies with Ga and As atoms and, therefore, have the same occupancies in the nominal cation and anion sites. In our case, the interaction energies of Ge atom with Ga and As atoms are different, and Ge atoms thus have different occupancies in the nominal cation sites and the nominal anion sites. The order parameters m_1 and m_2 are also different, with m_1 being larger than m_2 . It can be seen from the calculated pair-correlated probabilities P_{ij} that the Ge atoms preferentially form pairs with Ga atoms rather than with As atoms. Since the experimental sample preparation temperature is lower than 1000 K, for most composition x , it is in the phase-separation region. Therefore, for our analysis the most useful information is contained in the metastable phase diagram shown in Fig. 2. It can be seen from Fig. 2 that the critical composition x_c at the sample preparation temperature is about 0.36, while experimentally it is about 0.3.⁵ Considering that there is no adjustable parameter, the fit between the theory and the experiment is rather good. The results of the computation of the oriented-pair correlation P_{ij} show that the number of As-As and Ga-Ga nearest-neighbor pairs is very small. Therefore, our results are also qualitatively compatible with the growth model which assumed that there are no As-As and Ga-Ga nearest-neighbor pairs. One significant advantage of our model is that we have adopted the less stringent assumption that the Ge atoms are randomly distributed, which is reasonable because experimentally the sample is quickly quenched in the highly mixed state to avoid phase separation (Ge segregation). In Ref. 15, there is a continuation of the critical line within the phase-separation region in the phase diagram which is computed by minimizing the Helmholtz free energy rather than the grand-canonical potential, but there only constraints (22) and (23) have been imposed. Since in that calculation the Ge atoms still tend to segregate, the phase-separation boundary is thus only implicitly eliminated and the calculated oriented-pair coordination P_{ij} still describes the phase separation. The continuation of the order-disorder transition line in the phase-separation regions describes the boundary between two different phase-separation regions, which corresponds to two types of instabilities: one is the disorder spinodal and

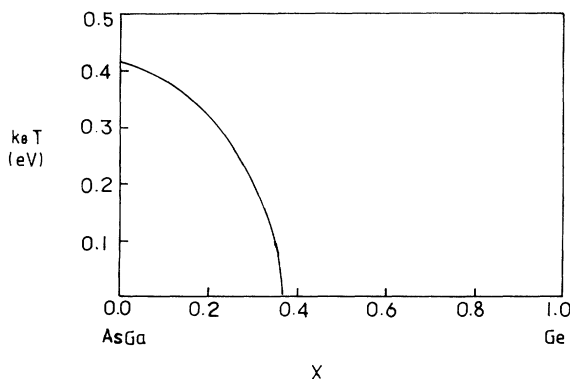


FIG. 2. The metastable phase diagram of temperature vs composition x for $(\text{GaAs})_{1-x}\text{Ge}_{2x}$.

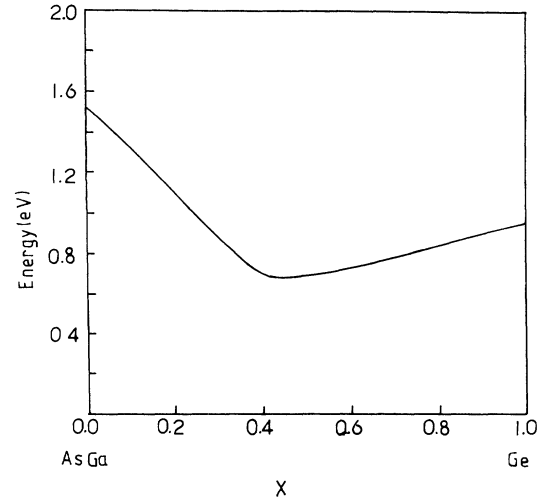


FIG. 3. Conduction-band edges as functions of x relative to the valence-band maximum at the Γ point of the Brillouin zone for $(\text{GaAs})_{1-x}\text{Ge}_{2x}$.

the other is the zinc-blende ordering spinodal. Two different decomposition mechanisms are thus expected from the solid solution in different composition regions.

Following the methods outlined in Sec. IV, we have calculated the bowing of the band gap of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ with the calculated oriented-pair correlation P_{ij} . A V-shaped bowing is again found in qualitative agreement with the results of the previous theory¹⁵ and also in agreement with experimental results. The band gap of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ is direct for $x \leq 0.75$, and becomes indirect at point L [$\mathbf{k} = \pi(1, 1, 1)/a_c$] for $x \geq 0.75$. (See Fig. 3.)

V. SUMMARY AND DISCUSSION

We have presented an improved model for the structure of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$. Using the interaction energies of the nearest-neighbor atom pairs computed by the universal-parameter tight-binding method, we have calculated the phase diagram based on the Kikuchi approximation. We have also computed the metastable phase diagram of the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$. The non-equilibrium nature of the alloy is accounted for by excluding thermodynamic states corresponding to phase separation, which cannot be achieved during the growth process. The Ge atoms are taken to be randomly distributed in order to avoid phase segregation. There is a metastable order-disorder transition point at $x_c = 0.36$. The calculated value of x_c gives an excellent fit to the experimental value. Since there is no adjustable parameter, our computation is of the first-principles type. Our approach also gives a united picture for both the thermodynamic model and the growth model. We have also calculated the contribution of the order-disorder transition to band-gap bowing.

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