

Short-range order in III-V ternary alloy semiconductors

Masaya Ichimura and Akio Sasaki

Department of Electrical Engineering, Kyoto University, Kyoto 606, Japan

(Received 27 May 1986; accepted for publication 27 August 1986)

Atom arrangements in III-V ternary alloy semiconductors are discussed using a thermodynamic analysis in which the elastic strain caused by mixing is considered as the mixing enthalpy. In calculating the strain energy, both bond-stretching and bond-angle distortion are taken into account, and Martin's microscopic elastic constants are used. The results show that there is a preference for ordering but not for clustering in III-V ternary alloy semiconductors. Values of short-range order parameters which represent the degree of ordering are obtained for several alloy semiconductors.

I. INTRODUCTION

It is a great advantage of III-V alloy semiconductors that their properties can be designed to some extent by varying the composition of binary compound semiconductors. Some material parameters can be obtained rather accurately by linear interpolation from binary compounds, but others deviate from the linear relation. Moreover, there are some phenomena observed only in alloy semiconductors such as alloy scattering of carriers¹ and alloy broadening of luminescence linewidth.²

Most theoretical studies of such phenomena are based on the virtual-crystal approximation or assume that the atom arrangement is completely random. For example, although the probability of alloy scattering depends on the order parameters of the atom arrangement, these parameters are usually assumed to be zero.¹ Short- or long-range order has been observed for many metal alloys such as CuAu.³ It is very important to investigate whether such deviations from randomness exist in III-V alloy semiconductors, since the deviations may affect many aspects of the material properties.

In this paper, we propose a model for the evaluation of the short-range order of atom arrangement in III-V ternary alloys. The quasichemical potential has been used to consider the deviation from random atom arrangement.³⁻⁶ However, the quasichemical approach has not been justified yet

for III-V ternary semiconductors, whereas it was pointed out by some authors that the calculated strain energy has close correlation with the mixing enthalpy determined by experiments.⁷⁻¹⁰ Thus, we consider that the mixing enthalpy is caused by elastic strain. On the basis of these considerations, we showed in the previous work that the structure with some degree of long-range order is stable below a certain temperature.¹¹ Here, we show that there is some degree of short-range order in the atom arrangement of III-V ternary alloy semiconductors.

II. FORMALISM OF FREE ENERGY

A. Enthalpy

Some papers have given the calculated strain energy of III-V ternary alloys using macroscopic elastic constants.^{7,8} However, the strain energy becomes about four times greater than those determined by experiments when the calculation is based on a strict virtual-crystal model.⁷ Recently, Mikkelsen⁹ and Fukui¹⁰ independently pointed out that the strain energy calculated from microscopic elastic constants derived by Martin¹² agrees well with the measured mixing enthalpy. Thus, Martin's microscopic elastic constants are used in our analysis. We choose a tetrahedral cell as the basic figure and take both bond-length deviation and bond-angle distortion into account. Five types of cells of $A_x^{III}B_{1-x}^{III}C^V$ or $C^{III}A_x^VB_{1-x}^V$ crystal are shown in Fig. 1. As in past analysis,¹³ it was assumed in the calculation for the strain energy of each cell that atoms in a mixed sublattice occupy the position defined by the virtual-crystal approximation (VCA) and that the atom of the common element moves to minimize the strain energy of the tetrahedron. This assumption can be justified by the extended x-ray absorption fine-structure (EXAFS) measurements.¹⁴ The strain energy of each cell for a whole composition range was calculated by extending the past analysis,¹³ and the results for an (InGa)As alloy are given in Fig. 2 as the functions of the average composition.¹¹ At a given average composition, the strain energy is minimum for the cell whose composition is closest to the average composition. For example, type-2 and -3 cells have the lowest strain energy among five cells for the average composition $x = 0.5$ and $x = 0.75$, respectively. Figure 2 is not exactly symmetric about $x = 0.5$ due to the difference between the elastic constants of InAs and GaAs.

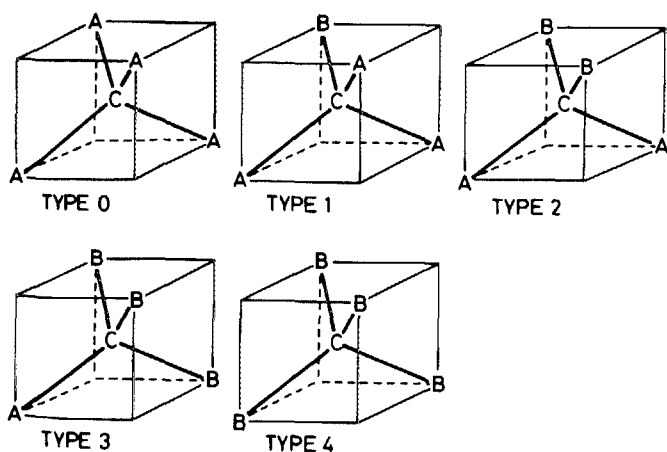


FIG. 1. Tetrahedron cells in a ternary III-V alloy semiconductor.

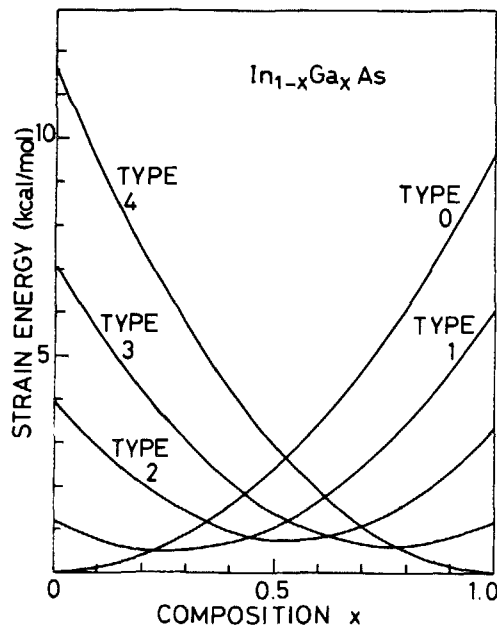


FIG. 2. Strain energies of five tetrahedron cells in $\text{In}_{1-x}\text{Ga}_x\text{As}$. Types of cells are illustrated in Fig. 1 where A and B atoms correspond to In and Ga , respectively.

The total strain energy, which corresponds to the mixing enthalpy in our analysis, is

$$H_m = \sum n_i \epsilon_i, \quad (1)$$

where n_i and ϵ_i are the number and the strain energy of type- i cells, respectively.

B. Entropy

If the atom arrangement is assumed to be completely random (regular solution model), then the entropy is written as

$$S = -k_B N [x \ln x + (1-x) \ln(1-x)], \quad (2)$$

where x denotes the composition of A atom as in $A_x B_{1-x} C$, k_B is the Boltzmann constant, and N is the number of atoms in the mixed sublattice. Although the entropy of the regular solution model is so simple, it is difficult to obtain an exact formula for the entropy as a function of the numbers of tetrahedra because one cannot treat them as independent entities: Each atom is shared by four tetrahedra and it is impossible, for example, that type-0 and -4 cells be neighbors. To obtain an approximate entropy, we use the method developed by Kikuchi.¹⁵ The number of type- i cells is expressed as $N\alpha_i q_i$, where q_i is the probability of appearance of a certain configuration of type- i cells and α_i is the number of different configurations having the same probability and given by the combination value of ${}_4C_i$. The q_i 's are normalized by the following equation:

$$\sum \alpha_i q_i = 1, \quad (3)$$

and are related to the composition of the A atom, x , as

$$x = q_0 + 3q_1 + 3q_2 + q_3. \quad (4)$$

The entropy of the face-centered-cubic lattice was de-

rived by Kikuchi,¹⁵ but the entropy of the ternary zinc-blende alloy is not the same as that of the face-centered lattice. In the zinc-blende structure, there are two kinds of tetrahedra: One includes an atom of the other group at the central position, and thus four nearest-neighbor pairs (bonds) and six second-nearest pairs (nearest cation-cation or anion-anion pairs) exist, as shown in Fig. 1. The other kind of tetrahedron does not include any bonds and thus only six second-nearest pairs exist. It is considered in the analysis that the strain energy is stored in the bonds between the nearest atoms. Therefore, the distribution of the latter tetrahedron can be excluded when considering the entropy of ternary alloys. Applying the procedure¹⁵ to derive the entropy to ternary zinc-blende alloys, we obtain

$$S = k_B N \left(3[x \ln x + (1-x) \ln(1-x)] - \sum \alpha_i q_i \ln q_i \right). \quad (5)$$

When atoms are distributed completely at random, $q_i = x^{4-i}(1-x)^i$. Equation (5) is reduced to Eq. (2) when the distribution becomes completely random.

C. Free energy and equilibrium state

The free energy F is given by $F = H - TS$ where H is the total enthalpy and T is the absolute temperature. From Eqs. (1) and (5), the free energy is obtained as

$$F = N \sum \alpha_i q_i \epsilon_i - N k_B T \left(3[x \ln x + (1-x) \ln(1-x)] - \sum \alpha_i q_i \ln(q_i) \right) + (\text{const}), \quad (6)$$

where (const) is the portion of a linear variation of the enthalpy. We obtain the values of q_i 's at the thermal equilibrium state from the condition for a minimum free energy:

$$\sum \frac{\partial F}{\partial q_i} \delta q_i = 0, \quad (7)$$

$$\sum \alpha_i \delta q_i = 0, \quad (8)$$

$$\delta q_0 + 3\delta q_1 + 3\delta q_2 + \delta q_3 = 0. \quad (9)$$

The second and the third equations are from Eqs. (3) and (4), respectively. The conditions are rewritten by using the Lagrange multipliers, a and b , as

$$\frac{\partial F}{\partial q_i} + a\alpha_i + b\gamma_i = 0 \quad (i=0-4), \quad (10)$$

where γ_i is the coefficient of δq_i in Eq. (9). The equilibrium values, q_i^{op} 's, can be calculated with the conditions of Eqs. (3) and (4). They are

$$q_i^{\text{op}} = c\eta_i t^{4-i} \left(c^{-1} = \sum \eta_i t^{4-i} \alpha_i \right), \quad (11)$$

where $\eta = \exp(-\epsilon_i/k_B T)$, and t is $\exp(-b/4k_B T)$ and satisfies the equation

$$(1-x)\eta_0 t^4 + (3-4x)\eta_1 t^3 + (3-6x)\eta_2 t^2 + (1-4x)\eta_3 t - x\eta_4 = 0. \quad (12)$$

To express the degree of the short-range order quantita-

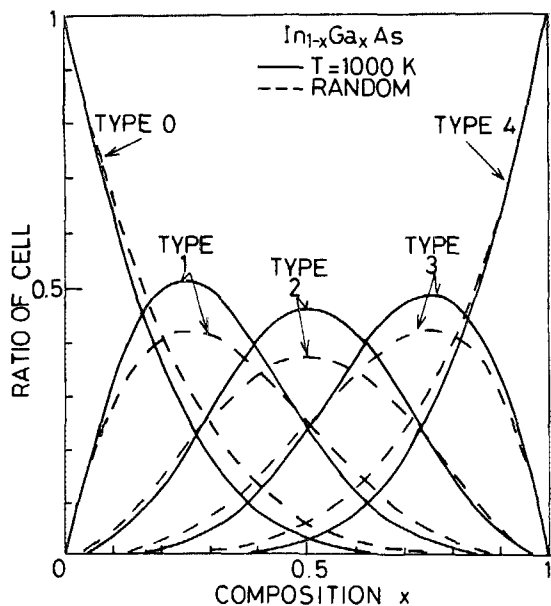


FIG. 3. Fractional values of five tetrahedron cells. Broken line: random arrangement. Solid line: at $T = 1000$ K for $\text{In}_{1-x}\text{Ga}_x\text{As}$.

tively, we use the short-range order parameter β , defined as¹⁶

$$\beta = 1 - P_{AB}/x, \quad (13)$$

where P_{AB} is the probability that an A atom occupies the second-nearest-neighbor site of a B atom. The second-nearest pair in the zinc-blende structure corresponds to the first-nearest pair on the fcc sublattice; the order parameter which has been used for a binary alloy A_xB_{1-x} can be applied to the mixed fcc sublattice of a zinc-blende structure of a ternary alloy $A_x^{\text{III}}B_{1-x}^{\text{III}}C$ or $C^{\text{III}}A_x^{\text{V}}B_{1-x}^{\text{V}}$. The value of β is negative when atoms tend to order, i.e., there is a preference for unlike second-nearest-neighbor pairs, and β is positive when like atoms tend to cluster.

The relation between β and q_i 's can be obtained by counting the number of $A-B$ pairs in each tetrahedron:

$$\beta = 1 - \frac{q_1 + 2q_2 + q_3}{x(1-x)}. \quad (14)$$

It can be proved by considering the number of $A-B$ pairs in the tetrahedra that the lower limit of β is $-\frac{1}{3}$ for ternary zinc-blende alloys.

III. SHORT-RANGE ORDER AND MIXING ENTHALPY OF THERMAL EQUILIBRIUM STATE

A. Atom arrangement

Figure 3 shows a relative number of various cells for an $(\text{InGa})\text{As}$ alloy. The broken lines represent a cell distribution in a random atom arrangement and the solid lines at $T = 1000$ K. As it is shown in the figure, the number of the cell whose composition is closest to the average composition increases from the number for the random arrangement. For example, at $x = 0.5$, the type-2 cell increases by a factor of 1.2, while type-0 and -4 cells decrease by a factor of 2 from the random distribution value.

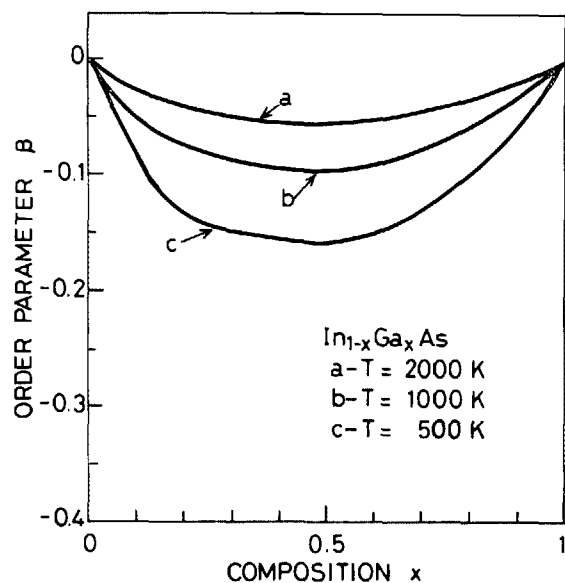


FIG. 4. Compositional dependence of the short-range order parameter β for $\text{In}_{1-x}\text{Ga}_x\text{As}$.

The compositional dependence of the short-range parameter is shown in Fig. 4. At any average composition, the parameter is negative, which indicates that short-range ordering is more probable than clustering. Figures 3 and 4 are slightly asymmetric about $x = 0.5$ because of the asymmetry of Fig. 1.

In Fig. 5, the temperature dependence of the short-range order parameter and that of the numbers of cells is shown for $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$. In the temperature range below 100 K, the entropy term, TS , is negligible compared with H_m . Since H_m is smaller at a higher ordered state, the atom arrangement becomes a higher order in a short range. In the temperature range between 10^2 and 10^4 K, the order parameter decreases logarithmically with temperature. The calculated results show little order at the temperature above 10^4 K because the entropy dominates over H_m , although $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ is no longer solid in this temperature range.

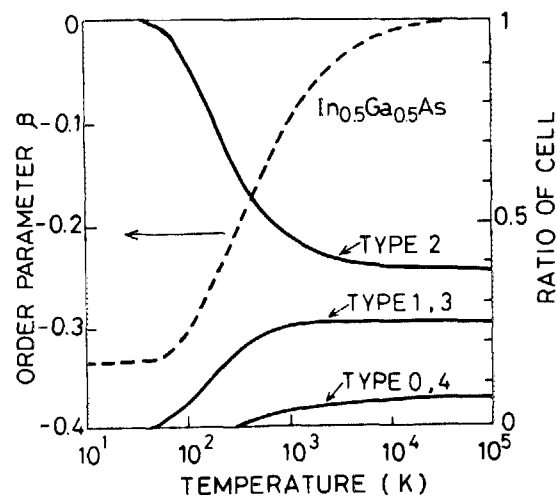


FIG. 5. Temperature dependence of short-range order parameter β and fractional values of tetrahedron cells for $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$.

TABLE I. Calculated values of the short-range order parameter β at $x = 0.5$, $T = 1000$ K, and the relative difference of lattice constants between two composite binary compounds.

| Material | $\beta(T = 1000 \text{ K}, x = 0.5)$ (10^{-2}) | $\Delta a/\bar{a}$ (%) |
|----------|---|---------------------------|
| (AlGa)As | 0 | 0.20 |
| (InGa)As | -9.72 | 6.92 |
| (InGa)P | -11.6 | 7.39 |
| (AlGa)Sb | -0.10 | 0.64 |
| (InGa)Sb | -7.56 | 6.11 |
| Ga(AsP) | -3.23 | 3.64 |
| Ga(AsSb) | -10.8 | 7.52 |
| Ga(PSb) | -18.8 | 11.15 |
| In(AsP) | -2.73 | 3.17 |
| In(PSb) | -17.0 | 9.88 |
| In(AsSb) | -9.36 | 6.72 |

The relation between β and the relative number of cells is almost the same among materials. However, the relation between β and temperature depends very much on materials. Table I lists the values of β at $T = 1000$ K for several ternary alloys of composition $x = 0.5$ and the relative difference between lattice constants of two composite compounds. The value of $|\beta|$ is large for the material with a large lattice mismatch, e.g., Ga(PSb), whereas it is null for lattice-matched alloys such as (AlGa)As.

B. Total strain energy

Figure 6 shows the total strain energy of the (InGa)As alloy as a function of composition rate x . The broken line represents the value for the random case and the solid line for the short-range ordering at $T = 1000$ K. Because of ordering, the cell having relatively high strain energy decreases compared with the random case, and therefore the total strain decreases.

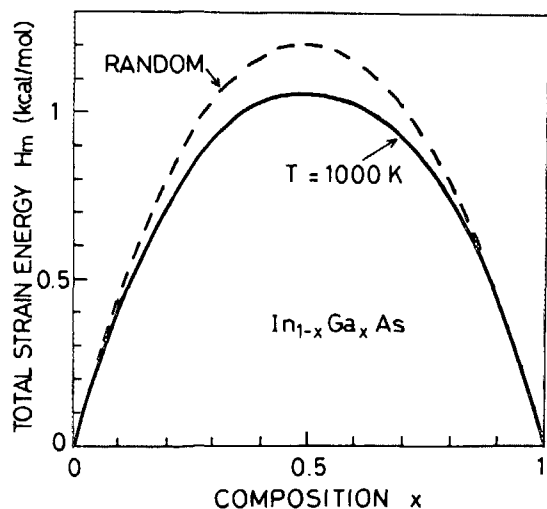


FIG. 6. Compositional dependence of the total strain energy (mixing enthalpy) for $\text{In}_{1-x}\text{Ga}_x\text{As}$. Broken line: random arrangement. Solid line: at $T = 1000$ K.

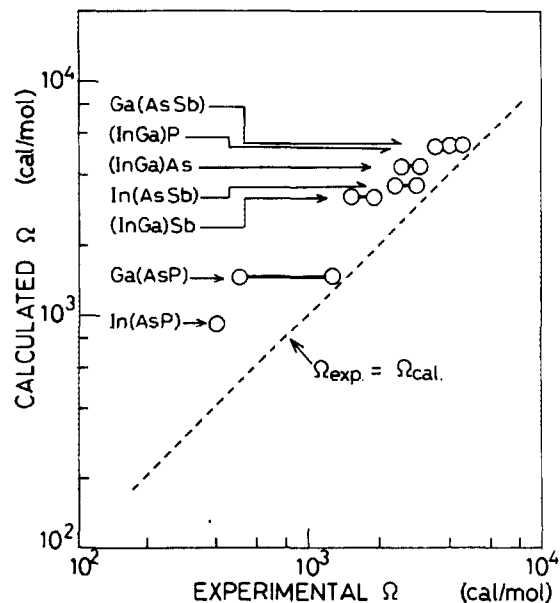


FIG. 7. Experimental values of interaction parameter, Ω_{exp} vs theoretical values of Ω_{cal} calculated from Eq. (15). The values of Ω_{exp} are taken from Refs. 8 and 18.

It should be noted that, in Fig. 6, the total strain energy or the mixing enthalpy is nearly proportional to $x(1-x)$. The relation of $H_m \propto x(1-x)$ has been used to explain the thermodynamical properties of binary or pseudobinary alloys including III-V ternary alloys,^{3,17} and the interaction parameter defined by $\Omega = H_m/x(1-x)$ has been determined from the experiment.^{17,18} When the quasicheical method is employed, it has been shown theoretically that $H_m \propto x(1-x)$ for a binary or pseudobinary alloy.³ The strain energy is also shown to be proportional to $x(1-x)$ when the macroscopic elastic constants are used.^{7,8} In the analysis described in Sec. II, the relation $H_m \propto x(1-x)$ does not appear explicitly in the equation, but the total strain energy shown in Fig. 6 follows this dependence of H_m on x . A similar compositional dependence of H_m is also obtained for other alloys. However, in a highly ordered state, the compositional dependence of H_m possess minimum values at $x = 0.25, 0.5$, and 0.75 , and becomes asymmetric about $x = 0.5$. Below but near the melting temperature, the relation $H_m \propto x(1-x)$ is almost satisfied. Because the melting temperatures of most of the alloys listed in Table I are around 1000°C , we determined the interaction parameter from our strain energy calculation by using

$$\Omega_{\text{cal}} = 4H_m \quad (T = 1000^\circ\text{C}, x = 0.5). \quad (15)$$

The values of Ω_{cal} are plotted against experimentally determined $\Omega, \Omega_{\text{exp}}$, in Fig. 7. Both agree qualitatively, although Ω_{cal} are larger than Ω_{exp} . This discrepancy would be due to the assumption that the atoms of mixed sublattice are at VCA positions. Because of this assumption, we consider only the relaxation of common atoms and neglect the relaxation of higher order which could reduce the strain energy further. Neglecting the temperature dependence of elastic constants would also lead to overestimating the strain energy. In addition, energetical interaction other than strain energy would also cause the reduction of mixing enthalpy.¹⁹

IV. DISCUSSION

Thermodynamical analysis in our study shows that there is some degree of ordering in the atom arrangement of III-V ternary alloys. If the compositional fluctuation or clustering occurs, the number of cells whose compositions are different from the average composition increases. However, as seen from Fig. 2, such cells have relatively high strain energy. In the equilibrium state, where the free energy becomes minimum, the cell having relatively high strain energy becomes less probable than that in the random case, as shown in Fig. 3. Thus, the compositional fluctuation is likely to be suppressed, if an alloy is grown or deposited in a quasi-equilibrium process.

For a binary or pseudobinary system whose mixing enthalpy is positive, the miscibility gap appears in the phase diagram in a certain temperature range³ and has been experimentally confirmed in some of III-V ternary alloys.²⁰ The immiscibility here denotes the macroscopic clustering. However, the results of our calculation show that the microscopic ordering is energetically preferable to microscopic clustering. In order to interpret this apparent contradiction, we consider two different cases. In the first case, a III-V semiconductor crystal of composition $x = 0.5$ is assumed to decompose into two separate crystals of $x = 0.4$ and 0.6 . Since the strain energy is maximum at $x = 0.5$ as shown in Fig. 6, the total strain energy is reduced by this decomposition. It should be noted that the lattice coherency is not retained between two crystals of $x = 0.4$ and 0.6 , and that their lattice constants are independent, determined by their respective composition. In the second case, we consider a small crystal of composition of $x = 0.4$ or 0.6 embedded in a large crystal of $x = 0.5$. In this case, the small crystal is distorted by surrounding crystals. If we take such strain into account, the strain energy of this small crystal of $x = 0.4$ or 0.6 is no longer smaller than that of the crystal of $x = 0.5$. Thus, such microscopic clustering is not energetically preferable as far as the lattice coherency is retained. As shown in these two cases, the strain energy acts on the atom arrangement differently depending on whether the coherency of the lattice is retained or not. In the case of macroscopic phase separation, the lattice coherency is broken, at least partly, and thermodynamical properties can be discussed by the conventional theory.

If there are crystal imperfections such as dislocations and a surface, the lattice coherency is locally broken. These defects could reduce the strain energy and therefore influence the atom arrangement. Since our analysis does not take the effect of defects into account, we cannot completely deny the possibility of the clustering accompanied with defects.

The atom arrangement in alloys has often been discussed on the basis of the quasichemical method.³⁻⁶ This method predicts the tendency for microscopic clustering for most of III-V ternary alloys. However, it is assumed that only the quasichemical interaction between the second-nearest-neighbor pair (cation-cation or anion-anion pair) causes the mixing enthalpy,^{5,6,17} and thus the change in the first-nearest-neighbor (cation-anion) interaction is neglected. Since the bond length between the first-nearest pair in an alloy is different from that in the corresponding binary com-

pound as revealed by the EXAFS measurement,¹⁴ it is obvious that there is a change in the first-nearest interaction or bond energy.²¹ This change is taken into account as the strain energy, which is large enough to explain the measured mixing enthalpy as shown in Fig. 7. Thus, the analytical method presented here would be more appropriate than the quasichemical method, although the chemical interaction should also be considered for the more accurate discussion.

Some authors⁷⁻¹⁰ calculated the strain energy of III-V ternary alloys using different methods. As mentioned earlier, the strict virtual-crystal model results in a strain energy four times larger than the measured mixing enthalpy.⁷ The values derived by the analysis using Martin's elastic constants agree very well with the measured ones.¹⁰ However, the analysis in Ref. 10 has assumed that the crystal of composition $x = 0.5$ is composed of type-2 cells only. It is difficult to expect such a complete order of atom arrangement at melting temperature or even at room temperature. The analysis in our study considers the strain energies of five different cells and their distribution. It could give a more realistic understanding of alloy semiconductors. Osamura, Nakajima, and Murakami calculated the strain energy using the continuum model.⁸ Their values of Ω agree well with the experimental values of Ω . Using this model, the long-range relaxation of strain, which is neglected in our analysis, can be easily taken into account. However, it will be difficult to discuss the atomic structure using the continuum model. Further study is needed to include long-range relaxation of strain into our model.

V. CONCLUSIONS

We have presented a thermodynamical analysis which enables us to estimate the nonrandomness of the atom arrangement in III-V ternary alloy semiconductors. It has been considered that the mixing enthalpy is caused by the elastic strain. In calculating the strain energy, not only the bond-length deviation but also the bond-angle distortion have been taken into account using Martin's microscopic elastic constants. The values of the interaction parameter Ω obtained from our estimation of the strain energy agree qualitatively with the values determined from thermodynamical experiments. The results of our calculation show that, at a thermal equilibrium state, there is a preference for ordering, not for clustering, in most of the III-V ternary alloys. This does not contradict the tendency for macroscopic clustering if we note the strain energy reduction by the breakdown of the coherency of lattice.

ACKNOWLEDGMENTS

We would like to thank Dr. Y. Takeda and Dr. Sg. Fujita, and Sz. Fujita for stimulating discussions and encouragement. This work was partly supported by the Scientific Research Grant-in-Aid No. 60122004 for Special Project Research on "Alloy Semiconductor Physics and Electronics" from the Ministry of Education, Science and Culture.

¹For example, Y. Takeda, in *GaInAsP Alloy Semiconductors*, edited by T. P. Pearsall (Wiley, Chichester, 1982), Chap. 9, and references therein.

²E. F. Schubert, E. O. Gobel, Y. Horikoshi, K. Ploog, and H. J. Queisser, *Phys. Rev. B* **30**, 813 (1984).

- ³As review, R. A. Swalin, *Thermodynamics of Solids*, 2nd ed. (Wiley, New York, 1972).
- ⁴G. B. Stringfellow and P. E. Greene, *J. Phys. Chem. Solids* **30**, 1779 (1969).
- ⁵R. Kikuchi, *Physica* **103B**, 41 (1981).
- ⁶K. A. Jones, W. Porod, and D. K. Ferry, *J. Phys. Chem. Solids* **44**, 107 (1983).
- ⁷P. A. Fedders and M. W. Muller, *J. Phys. Chem. Solids* **45**, 685 (1984).
- ⁸K. Osamura, K. Nakajima, and Y. Murakami, *J. Jpn. Soc. Metall.* **36**, 744 (1972).
- ⁹J. C. Mikkelsen, Jr., *J. Electrochem. Soc.* **132**, 500 (1985).
- ¹⁰T. Fukui, *J. Appl. Phys.* **57**, 5188 (1985).
- ¹¹M. Ichimura and A. Sasaki, *Jpn. J. Appl. Phys.* **25**, 976 (1986).
- ¹²R. M. Martin, *Phys. Rev. B* **1**, 4005 (1970).
- ¹³T. Fukui, *Jpn. J. Appl. Phys.* **23**, L521 (1984).
- ¹⁴J. C. Mikkelsen, Jr. and J. B. Boyce, *Phys. Rev. B* **28**, 7130 (1983).
- ¹⁵R. Kikuchi, *Phys. Rev.* **81**, 988 (1951).
- ¹⁶J. M. Cowley, *Phys. Rev.* **77**, 669 (1950).
- ¹⁷M. B. Panish and M. Illegems, in *Progress in Solid State Chemistry*, edited by M. Reiss and J. O. McCaldin (Pergamon, New York, 1972), pp. 39–83.
- ¹⁸G. B. Stringfellow, *J. Cryst. Growth* **27**, 21 (1974).
- ¹⁹W. I. Wang, *J. Appl. Phys.* **58**, 3244 (1985).
- ²⁰L. M. Foster, *J. Electrochem. Soc.* **121**, 1662 (1974).
- ²¹T. Onda, R. Ito, and N. Ogasawara, *Jpn. J. Appl. Phys.* **25**, 82 (1986).