

THEORETICAL STUDY OF LATTICE VIBRATION EFFECT ON THE PHASE STABILITY OF A III-V SEMICONDUCTOR ALLOY

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ABSTRACT

Lattice vibration effect is incorporated into the conventional first-principles scheme based on the Debye-Gruneisen model, and the phase diagram of GaP-InP pseudo-binary system is calculated. The obtained phase diagram is not significantly modified by the lattice vibration effect.

1. INTRODUCTION

Designing of a semiconductor alloy with optimized properties is one of the central concerns in advanced technologies. In view of the numerous combinations of III-group and V-group elements, it is desirable to develop a non-empirical scheme to predict a phase diagram of a given system.

We note two major streams in this direction. One is the "semi-empirical" scheme in which experimental data are utilized in the mold of a simple thermodynamic model. CALPHAD method [1] is one of the typical examples in this category. The key element of this method is the thermodynamic data bank of which contents are constantly updated. Since the mathematical tool is based on a simple thermodynamic model, the extension of the method to a complicated system such as a multi-component system or a system with a non-cubic structure is fairly easily achieved. The method, however, heavily depends upon the reliability and quality of existing experimental data. Hence, when the data are not available as in the case for which the equilibrium condition is hardly achieved, the method would face serious difficulty.

The other method is "non-empirical" scheme which is founded on rigorous principles of physics with minimum input of adjustable parameters and experimental data. The extreme case in this category is the "first-principles calculation" in which the inputting parameter is limited only to an atomic number of constituent elements. The mathematical procedure is, in general, quite sophisticated and consists of two major computational steps; one is to calculate the internal energy of the system based on quantum mechanics and the other is to obtain an entropy term based on statistical physics. Since the model can be operated without any empirical data, the method

can be applied to any condition to which conventional experimental technique is hardly accessed. In fact, global investigation of a phase diagram [2-6] was recently carried out for a series of pseudo-binary III-V semiconductor alloys based on the non-empirical method, and the possible origin of an ordering reaction observed in a thin film on a substrate materials [20-22] has been partly elucidated.

Most of the first-principles calculation of the phase stability conducted so far [2-9], however, have assumed a static lattice. The description of the free energy of the system is, therefore, based only on atomic configurational contributions, and vibrational effects are not explicitly incorporated. Since the lattice vibration is closely related to the lattice softening (or hardening) through thermal expansion, the neglect of this effect may result in an error in calculated thermodynamic quantities such as solubility, transition temperature etc. and, hence, a phase diagram.

Although various sophisticated theories of the lattice phonon have been advanced most of them are not compatible with the present framework of the first-principles calculation. In contrast, Moruzzi et al. [10] calculated Debye temperature, Bulk modulus, Gruneisen constant etc. of a pure metal based on the simple Debye-Gruneisen model, and this was later extended to an alloy system by Becker et al. [11] to derive a phase diagram of Nb-Ru-Zr from the first-principles.

The major objective of the present study is to derive a phase diagram of a III-V semiconductor alloy by including the lattice vibration effects. As an initial attempt, our interest is limited to GaP-InP system and main focus is placed on the comparison with the one previously obtained without the vibration effect. Detailed discussions of the obtained results will be reported in a separate issue. The organization of this report is as follows. In the next section, brief outline of the theoretical background is introduced. Since the major technique of the first-principles calculation has been amply demonstrated in the previous reports [2-9] and the details of the lattice vibration effect are also reported by Moruzzi et al. [10], only the essential parts are reproduced. The reader interested in the mathematical details should consult the previous papers cited as references. The calculated results are demonstrated and discussions follow in the last section.

2. CALCULATION PROCEDURES

Many of the III-V semiconductor alloys have zincblend structure which is viewed as two fcc lattices, one is occupied by III-group elements only and the other by V-group elements only, displaced from each other by one-quarter of a body diagonal as is shown in Fig.1. The space lattice is fcc, hence the pseudo-binary phase equilibria of III-III-V (III-V-V) is

virtually regarded as the binary phase equilibria of III-III (V-V) system on a sublattice immersed in the environment of V(III) group element. The techniques developed for the fcc system can be, therefore, directly extended.

The first-principles method starts with the total energy calculation $E_i(r)$ of a set of selected ordered compound specified by i as a function of lattice parameter r . The ordered compounds adopted in this study are Ga_4P_4 ($i=0$), Ga_3InP_4 ($i=1$) and $GaIn_3P_4$ ($i=3$) with $L1_2$ structure on the cation sub-lattice, $Ga_2In_2P_4$ ($i=2$) with $L1_0$ structure on the same sub-lattice and In_4P_4 ($i=4$).

For the semiconductor alloys, it has been well accepted that the pseudopotential method [12-14] is quite reliable to yield the total energy at the ground state. Based on the calculated ground state energy $E_i(r)$, the free energy of phase i at finite temperature T can be written in the following manner[10].

$$F_i(r,T) = E_i(r) - k_B T [D(\theta_D/T) - 3 \ln(1 - \exp(-\theta_D/T))] + (9/8) k_B \theta_D \quad (1)$$

where θ_D is the Debye temperature which is the function of Gruneisen constant and lattice parameter r , and $D(x)$ is the Debye function. It should be noted that the advantage of the method proposed by Moruzzi et al. is that all the parameters involved in the equation above are systematically derived only from the knowledge of the electronic energy contribution $E_i(r)$.

The next step is the employment of the Connolly-Williams's Cluster Expansion Method [15] operating on $F_i(r,T)$ to derive the effective interaction energies $v_j(r,T)$ of j -point cluster. Since the total energy calculation is performed for the five kinds of ordered compounds, five types of effective interaction energies $v_j(r,T)$, where j takes 0,1,2,3 and 4, are extracted. It is easily shown [16] that v_0 is the energy of the random solid solution at 50%, while v_j ($j \neq 0$) is the effective interaction energy for j -point nearest neighbor cluster.

For the calculation of a configurational entropy term, the Tetrahedron-Octahedron approximation [17,18] of the Cluster Variation Method [19] is employed. Then, together with the effective interaction energies $\{v_j(r,T)\}$, the free energy of the system Ω is given as the function of lattice constant r , temperature T and ten kinds of correlation function $\{\xi_j\}$ which describe the local atomic order [17].

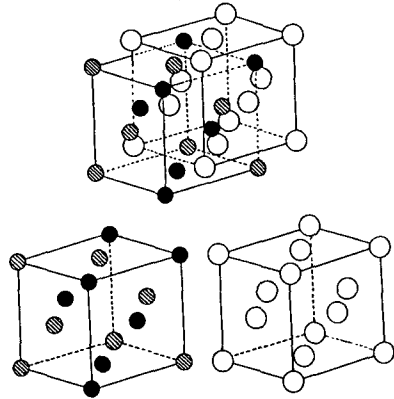


Fig. 1

$$\Omega = \sum_j v_j(r, T) \xi_j - TS(\{\xi_j\}) \quad (2)$$

The equilibrium state of the system is, therefore, obtained by minimizing the free energy with respect to both lattice parameter r and the set of correlation function $\{\xi_j\}$.

$$(\partial\Omega/\partial r)_{\{\xi_j\}} = 0 \quad \text{and} \quad (\partial\Omega/\partial\{\xi_j\})_r = 0 \quad (3)$$

Finally, the mechanical stability of the system is examined by calculating the second order derivative of the Ω with respect to the lattice constant r , which leads to the pressure-volume curve at temperature T . When the mechanical stability criterion is observed the system is stable with respect to the small volume fluctuation, while the system becomes inherently unstable and decomposes into two phases if the criterion is violated, which is indicated by a change of the sign of the slope of the pressure-volume curve. By converting two stable volumes to the compositions, one can obtain the phase boundaries. The repetition of this procedure for each temperature produces the phase diagram.

3. RESULTS AND DISCUSSIONS

The calculated heats of formation for the five kinds of ordered compounds are demonstrated as a function of lattice parameter r in Fig.2. For each compound, the dotted curve indicates the electronic energy at the ground state $E_i(r)$, while the solid curve represents the free energy at temperature $T=500\text{K}$. The lattice parameter corresponding to the minimum of each curve is equilibrium lattice constant r_0 for each phase. Two important features should be noted. One is that the heats of formation decreases due to the vibrational entropy contribution. The other is that the minimum of each curve

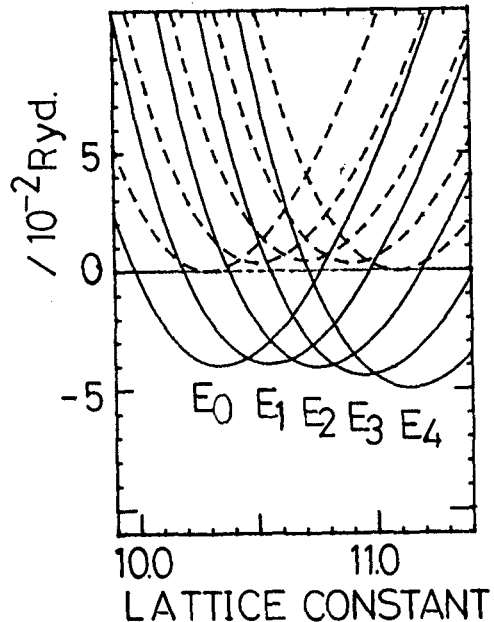


Fig. 2

shifts toward the right hand side, which suggests the thermal expansion. The thermal expansion coefficient which is defined as

$$\alpha(T) = (1/r_0)(dr_0/dT) \quad (4)$$

is calculated as a function of temperature for the binary ordered compounds and plotted in Fig.3. One can see that each curve demonstrates typical thermal expansion behavior i.e. a rapid raise in the low temperature region then linear increase in the high temperature portion. It is confirmed that the experimental values agree with the present results at least within the order of the magnitude.

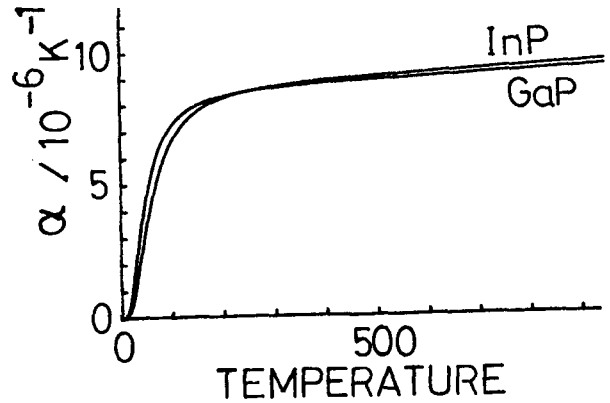


Fig. 3

Figure 4 indicates the effective interaction energies obtained by Connolly-Williams's Cluster Expansion Method. The $\{v_j(r)\}$ at $T=500$ and the ones extracted from the set of electronic energies $\{E_i(r)\}$ are shown by solid and dotted lines, respectively. It is noted that the v_0 and v_1 shift towards the right hand side due to the thermal expansion while pair interaction energy v_2 stays the same level. For the III-V systems, the multibody interactions v_3 and v_4 are quite small as compared with v_0 , v_1 and v_2 , which satisfies the convergency criterion of the Cluster Expansion Method.

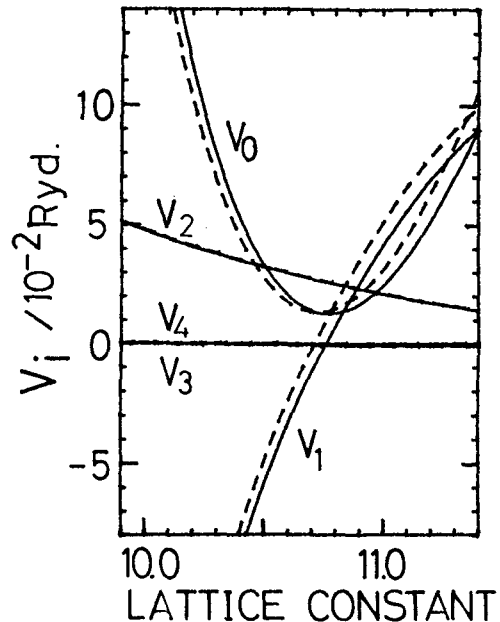


Fig. 4

The obtained phase diagrams are demonstrated in Fig.5. The dotted curve is the previous result calculated without the thermal vibration effect. The present calculation with the thermal vibration effects based on $\{v_j(r,T)\}$ is represented by solid line. One can confirm the phase separation tendency for this system.

As was pointed out previously [2-6], the origin of the

phase separation is the large elastic energy involved to form an alloy due to the size misfit of the constituent binary ordered compounds. In fact, the total heats of formation of the random solid solution is separated into the elastic energy contribution and chemical energy contribution by the method described in the previous reports [2-6] and demonstrated in Fig.6. Shown by solid lines and broken lines are ones estimated, respectively, at 1000K and based only on electronic contributions. For both cases, one can immediately see that the positive value of the total heats of formation is caused by the large elastic energy contribution which cancels the fairly large chemical driving force. It is noted that the thermal vibration effect does not affect each energy significantly, which is reflected in the calculated phase diagram in the Fig.5.

The large chemical energy implies that the system has intrinsically large driving force for the formation of solid solution. According to recent X-ray and electron diffraction studies, ordered phases have been observed for various III-V systems constrained on a substrate [20-22]. Although the origin of the ordering reaction should be considered based on various factors such as a surface effect and kinetics during growth, the energetics demonstrated in Fig.6 implies that if the elastic energy is relaxed by a certain mechanism, the chemical energy becomes dominant and the

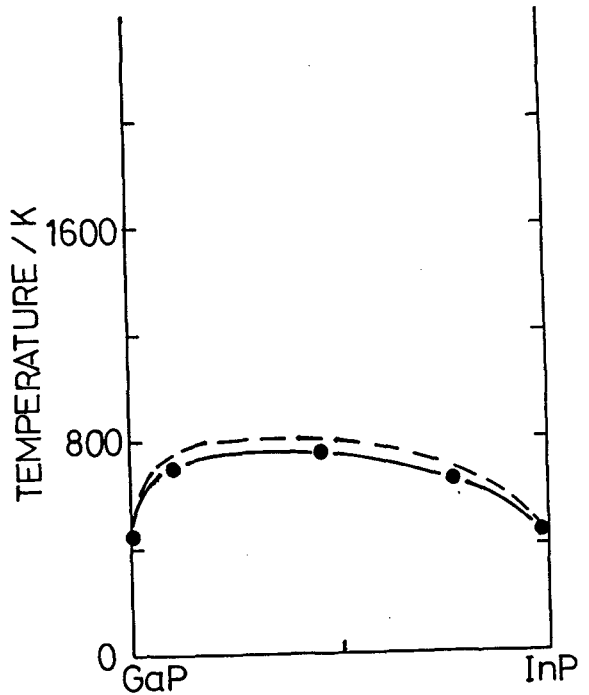


Fig. 5

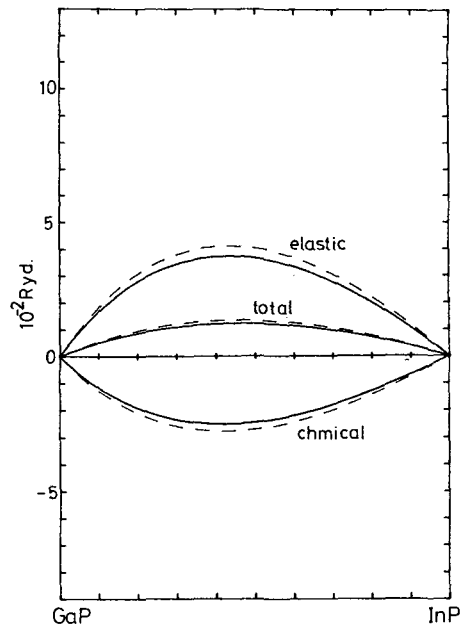


Fig. 6

mixing reaction becomes feasible. In fact, more detailed analysis including second nearest neighbour pair interaction reveals [3] that the formation of the $L1_1$ ordered phase is more stable than those of random solid solution and $L1_0$ ordered phase for GaAs-InAs system, which agrees with the experimental fact.

It has been pointed out [2-10] that the major deficiencies of the first-principles calculation conducted so far is the neglect of the local lattice distortion effect. If only a uniform distortion depending upon an alloy concentration is allowed, a solute element is forced to have an equivalent size of host element, which unnecessarily raises the internal energy and solubility is unreasonably suppressed. Such an error is anticipated to become serious for a system which has large difference in atomic size of constituent elements.

The theory of the relaxation energy due to the local distortion is proposed by Khachatryan [23] based on the harmonic approximation of lattice dynamics. According to this method, the essential quantity required to evaluate the relaxation energy is the Dynamical matrix which is, in principle, derived from phonon dispersion relation. The major stumbling block, however, is the fact that the local distortion alters the crystal symmetry and the conventional CVM for a cubic system is broken down for the locally distorted lattice. Moreover, the harmonic approximation does not leads to the thermal expansion. The method adopted in the present report, on the other hand, incorporates the lattice softening due to the thermal expansion within an approximation of uniform lattice displacement. Hence, the extra internal energy evaluated for a uniformly displaced lattice based on the electronic contribution at the ground state alone is, at least, partly relaxed. We believe that the most accurate result will be yielded by incorporating the local distortion effect in the vibrating lattice. This remains as a future work.

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