

Phase equilibria in heterogeneous systems with $A_xB_{1-x}C_yD_{1-y}$ alloys

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The $A_xB_{1-x}C_yD_{1-y}$ alloys are the conventional materials of the semiconductor heterostructures for the optoelectronics device applications. The liquid phase epitaxy is one of the methods for preparation of the $A_xB_{1-x}C_yD_{1-y}$ -based heterostructures. The liquid phase epitaxial processes are fulfilled near thermodynamic equilibrium. Therefore, information on the phase diagram and miscibility gap is necessary for the liquid phase epitaxy growth of the $A_xB_{1-x}C_yD_{1-y}$ alloys. The phase equilibria in the heterogeneous systems with the $A_xB_{1-x}C_yD_{1-y}$ alloy in the regular solution model are presented. The heterogeneous equilibria are considered as minimum condition of the Helmholtz free energy of the system that is presented as a canonical ensemble. The strictly regular approximation is used for description of all phases. The interactions between the nearest and next nearest atoms as well as the oscillation movement of the atoms are taken into account. The supposition on random distribution of the cations and anions in their sublattices is used for the configurational entropy. The numerical estimations are fulfilled for the phase diagram consisting of the (*In, Ga, Sb, As*) liquid solution and the $In_xGa_{1-x}Sb_yAs_{1-y}$ alloy lattice matched with the *GaSb* substrate. The obtained theoretical estimations are in good agreement with the available experimental results.

Keywords: LPE; Semiconductors; Quaternary alloys; Phase diagrams; In, Ga, Sb, As.

1. Introduction

Conductor electronic devices [1]. Growth of this kind of the alloys is accomplished by a variety of methods that include metalorganic vapor phase epitaxy, molecular beam epitaxy and liquid phase epitaxy (LPE) [2]. LPE is often recognized due to the high purity of the synthesized material, possibility of formation of the layers with thickness more than 10 μm and simplicity of the experimental apparatus [3]. In any case, the epitaxial growth of the quaternaries requires the previous knowledge of the corresponding phase diagrams and the mixing properties in the solid state.

The strictly regular approximation (SRA) is used for description of the phase diagrams and the miscibility gap of the $A_xB_{1-x}C_yD_{1-y}$ alloys [4-6]. SRA is based on the supposition of random distribution of the cations and the anions in their sublattice sites. The crystal lattice of the $A_xB_{1-x}C_yD_{1-y}$ alloy consists of cation and anion sublattices, where both sublattices consist of the atoms of two types. Therefore, any atom of the $A_xB_{1-x}C_yD_{1-y}$ quaternary alloy can has the atoms of two types at the nearest surroundings. There are four kinds of the bonds *AC*, *AD*, *BC* and *BD* corresponding to the binary compounds. Therefore, the $A_xB_{1-x}C_yD_{1-y}$ quaternary alloys are called the quaternary alloys of four binary compounds. The relations between the concentration of the atoms (*x* and *y*) and bonds (x_{AC} , x_{AD} , x_{BC} , and x_{BD}) are written by three equations

The III-V quaternary alloys of the type $A_xB_{1-x}C_yD_{1-y}$ are important systems that are used in modern semic

$$x_{AC} + x_{AD} = x,$$

$$x_{AC} + x_{BC} = y, \quad (1)$$

$$x_{AC} + x_{AD} + x_{BC} + x_{BD} = 1$$

Thus, there is absent a one to one correspondence between the elemental *x* and *y* and chemical x_{AC} , x_{AD} , x_{BC} and x_{BD} compositions of the $A_xB_{1-x}C_yD_{1-y}$ quaternary alloys. One atomic composition *x* and *y* of the $A_xB_{1-x}C_yD_{1-y}$ quaternary alloy can correspond to a vast set of chemical compositions x_{AC} , x_{AD} , x_{BC} and x_{BD} . Exchange of the lattice sites between the different cations or anions can lead to the solid state reaction between the bonds which is written as



where z_1 is the coordination number of the nearest neighbors of the $A_xB_{1-x}C_yD_{1-y}$ alloy. Number *n* in the solid state reaction depends on the nearest surroundings of the cations or anions that participate in exchange of the lattice places as it can see on the figure 1. The solid state reaction varies the numbers of the bonds in the $A_xB_{1-x}C_yD_{1-y}$ quaternary alloy.

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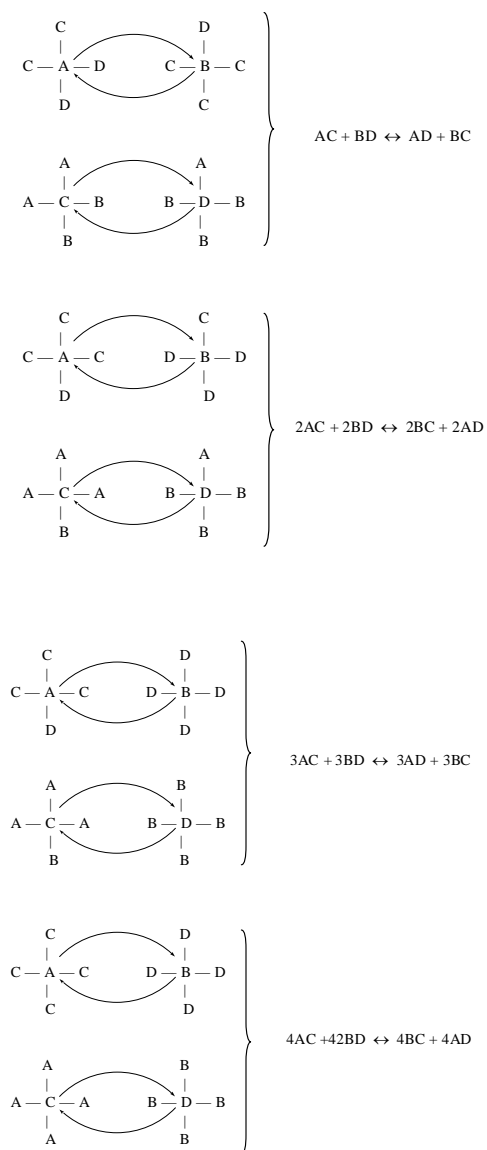


Figure 1. Solid state reactions in $A_x B_{1-x} C_y D_{1-y}$ quaternary alloys, ($z = 4$).

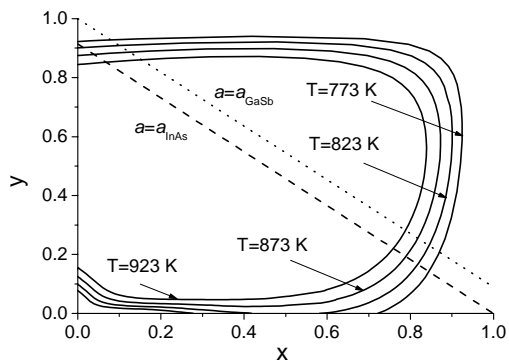


Figure 2. The miscibility gap of the $In_x Ga_{1-x} Sb_y As_{1-y}$ alloy at temperatures 773, 823, 873 and 923 K. The dashed lines correspond to the compositions of the alloys lattice matcher to $GaSb$ and $InAs$.

Usually, the Helmholtz free energy of the $A_x^{III} B_{1-x}^{III} C_y^V D_{1-y}^V$ alloy is expressed by the chemical potentials of the AC , AD , BC and BD binary components [7-9]. The chemical potentials of the binary components are introduced by a condition of the heterogeneous equilibrium between the $A_x^{III} B_{1-x}^{III} C_y^V D_{1-y}^V$ alloy and, the quaternary liquid solution. In this case, the chemical potential of the binary component is equivalent to the chemical potential of the cation-anion pair of the alloy. However, use of the chemical potentials of the binary components for the description of the $A_x^{III} B_{1-x}^{III} C_y^V D_{1-y}^V$ alloy leads to the problems. The Helmholtz free energy as well as the others thermodynamics potentials of the $A_x^{III} B_{1-x}^{III} C_y^V D_{1-y}^V$ alloy at the fixed temperature are the functions of three independent variables. The independent variables can be the quantities of the different atoms or some relations between them. In order to express the Helmholtz free energy of the $A_x^{III} B_{1-x}^{III} C_y^V D_{1-y}^V$ alloy by the chemical potentials of the cation-anion pairs, the one-to-one correspondence between the numbers of the different atoms or some relations between them and numbers of the different cation-anion pairs must exist. However, such correspondence between the variables is absent since the Jacobian of numbers of the pairs with respect to the numbers of the atoms is equal zero. As a result, the Helmholtz free energy of the $A_x^{III} B_{1-x}^{III} C_y^V D_{1-y}^V$ alloy [10] can be expressed as a function of any set of the cation-anion pairs consistent with the numbers of the atoms and stoichiometry. Hence, there is absent the one-to-one correspondence between the numbers of the cation-anion pairs and their “chemical potentials”. However, the chemical potentials of the species can be used in the description if the one-to-one correspondence between the numbers of the species and their chemical potentials is fulfilled [11]. Thus, the chemical potentials of the binary components cannot be used for the description of the $A_x^{III} B_{1-x}^{III} C_y^V D_{1-y}^V$ alloy.

In this study the description of the solidus-liquidus phase diagram and the miscibility gap are described by the minimum condition of the Helmholtz free energy of the heterogeneous system.

2. The regular solution model for the $A_x B_{1-x} C_y D_{1-y}$ alloy

The regular solution model (RSM) for the $A_x B_{1-x} C_y D_{1-y}$ quaternary alloys is based on the supposition that any configuration of the solution can be described by the determination of number and geometric arrangements of the lattice sites which are occupied by the atoms of every type. Moreover, the energy of interaction between the atoms is determined by the interactions between the nearest and next nearest atoms. The energy of interaction between

the next nearest atoms depends on the type of atom situated between them.

In RSM, the vibrational movement of the atoms is determined by the bonds between the nearest neighbors.

The interaction energies of pairs and triads of the atoms as well as vibrational motion of the atoms are independent from their surrounding. The interaction between the next nearest atoms are determined by the interaction parameters between binary compounds AC , AD , BC and BD in the $A_xB_{1-x}C_yD_{1-y}$ quaternary alloy.

The thermodynamic functions and characteristics of the alloy can be described by the partition function of the ensemble representing the solution. The partition function is the most suitable function connecting the microscopic properties of the particles (molecules or atoms) with the thermodynamic (macroscopic) characteristics of the system such as the internal energy, the entropy etc. The solid solutions will be represented as the canonical ensemble where the numbers of the different types of cations and anions are the given values. Therefore, the partition function Q of the $A_xB_{1-x}C_yD_{1-y}$ quaternary alloy described as the canonical ensemble consisting of the $N=N_A+N_B$ cations and $N=N_C+N_D$ anions in RSM is written as

$$Q = Q_{conf} Q_{ac} Q_{int} \quad (3)$$

where Q_{conf} , Q_{ac} and Q_{int} are the configurational, acoustic and internal partition function, respectively, and the Helmholtz free energy F of the $A_xB_{1-x}C_yD_{1-y}$ regular solution according to the formula of the partition function is given as

$$F = E - TS = -k_B T \ln Q \quad (4)$$

The internal energy E and the entropy S are expressed as

$$E = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V \quad (5)$$

$$S = k_B \left[\ln Q + T \left(\frac{\partial \ln Q}{\partial T} \right)_V \right] \quad (6)$$

3. The heterogeneous system with $A_xB_{1-x}C_yD_{1-y}$ alloy as canonical ensemble

The heterogeneous system with $A_xB_{1-x}C_yD_{1-y}$ alloy is considered as canonical ensemble consisting of four types of atoms and two phases. Numbers of atoms in the phases of the system are connected by three constraints that are written as

$$\begin{aligned} \varphi_1 &= N - N^1 - N^2 = 0 \\ \varphi_2 &= N_A - N_A^1 - N_A^2 = 0 \\ \varphi_3 &= N_C - N_C^1 - N_C^2 = 0 \end{aligned} \quad (7)$$

The minimum condition of the Helmholtz free energy of the heterogeneous system is the condition of the stationary point of the Lagrange function, which is given as

$$L = F + \sum_{i=1}^n \lambda_i \varphi_i \quad (8)$$

where F is the Helmholtz free energy of the heterogeneous system and λ_i is the Lagrange undetermined multiplier. The condition of the stationary point of the Lagrange function is written as

$$\begin{aligned} \varphi_1 = 0, \quad \varphi_2 = 0, \quad \varphi_3 = 0 \\ \frac{\partial L}{\partial N_j^\beta} = 0 \end{aligned} \quad (9)$$

where j is the type of the particle participating in the exchange between the phases (cation, anion, cation-anion pair), β is number of the phase.

4. The liquid state-solid state equilibria

The phase diagram of the heterogeneous system consisting of the liquid phase (solution of the atoms A , B , C and D)–solid phase ($A_xB_{1-x}C_yD_{1-y}$ alloy) is considered.

There are four constraints between the numbers of the atoms in the liquid and solid phases in the heterogeneous system, that are given as

$$\begin{aligned} N_A^l + N_A^s - N_A &= 0, \\ N_B^l + N_B^s - N_B &= 0, \\ N_C^l + N_C^s - N_C &= 0, \\ N_D^l + N_D^s - N_D &= 0 \end{aligned} \quad (10)$$

The $N_i^l, N_A^s, N_j^l, N_C^s$ ($i = A, B; j = C, D$) are the reciprocally dependent variables, N_i and N_j ($i = A, B; j = C, D$) are the given values because the heterogeneous system is presented as canonical ensemble.

The partition function of the heterogeneous system is represented as the product of the partition functions of the liquid and solid phase, which is given as $Q = Q^l Q^s$. Hence, the Helmholtz free energy of the heterogeneous system is written as

$$F = -k_B T \ln Q = -k_B T \ln Q^l Q^s \quad (11)$$

The partition function of the liquid phase is written as

$$Q^l = \prod_{i,j=1}^2 \frac{\left[\sum_{i,j=1}^2 (N_i^l + N_j^l) \right]! q_i^{N_i^l} q_j^{N_j^l} \left[\exp \left\{ -\frac{u_{ii}^l}{k_B T} \right\} \right]^{(N_i^l)^2}}{N_i^l! N_j^l!} \exp \left\{ -\frac{u_{ij}^l}{k_B T} \right\}^{2N_i^l N_j^l} \exp \left\{ -\frac{u_{jj}^l}{k_B T} \right\}^{(N_j^l)^2} \left[\frac{z_1}{2 \sum_{i,j=1}^2 (N_i^l + N_j^l)} \right]^{z_1} \quad (12)$$

where q_i , q_j are the acoustic partition function of the i -th and j -th types of cations and anions, respectively, in the liquid state, u_{ii}^l , u_{ij}^l are the interaction energy between A atoms and A and B atoms in the liquid phase, respectively, N_i^l and N_j^l are the numbers of the i -th type of cations and j -th type of anions in the liquid phase, respectively, k_B is the Boltzmann constant and T is the absolute temperature.

The partition function of the solid phase is written as

$$Q^s = \prod_{i,j,l,m=1}^2 \frac{\left(\sum_{i=1}^2 N_i^s \right)! \left(\sum_{j=1}^2 N_j^s \right)! \left[\frac{1}{q_{ij}^s} \exp \left\{ -\frac{u_{ij}^s}{k_B T} \right\} \right]^{\xi_1}}{N_i^s! N_j^s!} \exp \left\{ -\frac{N_i^s u_{ijl}^s + N_m^s u_{jim}^s}{k_B T} \right\}^{\xi_2} \quad (13)$$

where $\xi_1 = \frac{2z_1 N_i^s N_j^s}{\sum_{i,j=1}^2 (N_i^s + N_j^s)}$, $\xi_2 = \frac{2z_2 N_i^s N_j^s}{\sum_{i,j=1}^2 (N_i^s + N_j^s)}$, q_{ij} is the

acoustic partition function of the molecules in the compound ij , z_2 is the coordination number of the next nearest neighbors, u_{ij}^s is the interaction energy between the nearest atoms in the compound ij , u_{ijl}^s and u_{jim}^s are the interaction energies between the nearest cation of the i -th

and l -th types with the intermediate anion of the j -th type, and, between the nearest anion of the j -th and m -th types with the intermediate cation of the i -th type, N_i^s and N_j^s are the numbers of the i -th type of cations and j -th type of anions in the solid phase respectively.

Then, the Helmholtz free energy of this system can be expressed as

$$F = \sum_{i,j,l,m=1}^2 \left\{ \frac{2N_i^s N_j^s}{\sum_{i,j=1}^2 (N_i^s + N_j^s)} \left[\frac{\mu_{ij}^{0s} + z_2 (N_i^s w_{ij-l}^s + N_m^s w_{ij-m}^s)}{\sum_{i,j=1}^2 (N_i^s + N_j^s)} \right] + k_B T \left[\frac{N_i^s \ln \frac{2N_i^s}{\sum_{i,j=1}^2 (N_i^s + N_j^s)} + N_j^s \ln \frac{2N_j^s}{\sum_{i,j=1}^2 (N_i^s + N_j^s)}}{\sum_{i,j=1}^2 (N_i^s + N_j^s)} \right] + N_i^l \mu_i^{0l} + N_j^l \mu_j^{0l} + \frac{N_i^l N_l^l w_{i-l}^l + N_i^l N_j^l w_{i-j}^l + N_j^l N_m^l w_{j-m}^l}{\sum_{i,j=1}^2 (N_i^l + N_j^l)} + k_B T \left[\frac{N_i^l \ln \frac{N_i^l}{\sum_{i,j=1}^2 (N_i^l + N_j^l)} + N_j^l \ln \frac{N_j^l}{\sum_{i,j=1}^2 (N_i^l + N_j^l)}}{\sum_{i,j=1}^2 (N_i^l + N_j^l)} \right] \right\} \quad (14)$$

where i and l are the types of cations A and B , j and m are the types of the anions C and D , μ_{ij}^{0s} , μ_i^{0l} , μ_j^{0l} are the chemical potentials of molecule of the ij binary compound in the alloy, atoms of the i -th and j -th types in the liquid state, respectively, $w_{i-l}^l = u_{ij}^l - \frac{u_{ii}^l + u_{jj}^l}{2}$ is the interaction parameter between the atoms of the i -th and j -th types in the liquid phase, $w_{ij-l}^s = u_{ijl}^s - \frac{u_{ji}^s + u_{jl}^s}{2}$ is the interaction parameter between the nearest i -th and l -th cations with the intermediate j -th anion, N_i and N_j are the numbers of the i -th type of cations and j -th type of anions, respectively.

After using the Lagrange method of the undetermined multipliers we obtain the system of three equations for description of the phase diagram that is given as

$$\begin{aligned}
\frac{\partial F}{\partial N^s} - \frac{\partial F}{\partial N_B^l} - \frac{\partial F}{\partial N_D^l} &= 0, \\
\frac{\partial F}{\partial N_A^s} - \frac{\partial F}{\partial N_A^l} + \frac{\partial F}{\partial N_B^l} &= 0, \\
\frac{\partial F}{\partial N_C^s} - \frac{\partial F}{\partial N_C^l} + \frac{\partial F}{\partial N_D^l} &= 0
\end{aligned} \tag{15}$$

The physical meaning of the equations is the following: two atoms of the III and V groups after the transition from the liquid phase to the solid phase or vice versa can form one, two or three types of the bonds.

Finally, the phase diagram of this two-phase system, consisting of the solid alloy and liquid solution in the macroscopic variables is written as

$$\begin{aligned}
&\mu_{BD}^{0s} - \mu_B^{0l} - \mu_D^{0l} - \\
& - (\mu_{AC}^{0s} + \mu_{BD}^{0s} - \mu_{AD}^{0s} - \mu_{BC}^{0s})xy + \\
& + xy[(2x-1)\alpha_{AC-BC}^s + (2y-1)\alpha_{AC-AD}^s] + \\
& + (x+y-2xy)(\alpha_{AD-BD}^s x + \alpha_{BC-BD}^s y) + \\
& + RT \ln \frac{(1-x)(1-y)}{x_B^l (1-x_A^l - x_B^l - x_C^l)} - \\
& - (x_A^l + x_C^l)(1-2x_B^l)(\alpha_{A-B}^l + \alpha_{B-C}^l) + \\
& + 2\alpha_{A-C}^l x_A^l x_C^l - x_B^l (x_A^l + x_B^l + x_C^l) \alpha_{B-D}^l - \\
& - (1-x_A^l - x_B^l - x_C^l)(1-x_B^l) \alpha_{B-D}^l - \\
& - (x_A^l + x_C^l)(2x_A^l + 2x_B^l + 2x_C^l - 1) \times \\
& \times (\alpha_{A-D}^l + \alpha_{C-D}^l) = 0
\end{aligned} \tag{16}$$

$$\begin{aligned}
&\mu_{AD}^{0s} - \mu_{BD}^{0s} - \mu_A^{0l} + \mu_B^{0l} + \\
& + (\mu_{AC}^{0s} + \mu_{BD}^{0s} - \mu_{AD}^{0s} - \mu_{BC}^{0s})y + \\
& + [\alpha_{AC-BC}^s y + \alpha_{AD-BD}^s (1-y)](1-2x) + \\
& + (\alpha_{AC-AD}^s - \alpha_{BC-BD}^s)y(1-y) + \\
& + RT \ln \frac{xx_B^l}{(1-x)x_A^l} - x_B^l (1-x_A^l) \alpha_{A-B}^l + \\
& + x_A^l (1-x_B^l) \alpha_{A-B}^l - \\
& - x_C^l \alpha_{A-C}^l - (1-x_A^l - x_B^l - x_C^l) \alpha_{A-D}^l + \\
& + x_C^l \alpha_{B-C}^l + (1-x_A^l - x_B^l - x_C^l) \alpha_{B-D}^l = 0
\end{aligned} \tag{17}$$

$$\begin{aligned}
&\mu_{BC}^{0s} - \mu_{BD}^{0s} - \mu_C^{0l} + \mu_D^{0l} + \\
& + (\mu_{AC}^{0s} + \mu_{BD}^{0s} - \mu_{AD}^{0s} - \mu_{BC}^{0s})x + \\
& + [\alpha_{AC-AD}^s x + \alpha_{BC-BD}^s (1-x)](1-2y) + \\
& + (\alpha_{AC-BC}^s - \alpha_{AD-BD}^s)x(1-x) + \\
& + RT \ln \frac{y(1-x_A^l - x_B^l - x_C^l)}{(1-y)x_C^l} - \\
& - x_A^l \alpha_{A-C}^l - x_B^l \alpha_{B-C}^l - \\
& - (1-x_A^l - x_B^l - x_C^l)(1-x_C^l) \alpha_{C-D}^l + \\
& + x_C^l (x_A^l + x_B^l + x_C^l) \alpha_{C-D}^l + \\
& + x_A^l \alpha_{A-D}^l + x_B^l \alpha_{B-D}^l = 0
\end{aligned} \tag{18}$$

where $\alpha_{A-C}^l = z_1 w_{A-C}^l N_{Av}$ and $\alpha_{AC-BC}^s = z_2 N_{Av} w_{AC-BC}^s$ are the interaction parameter between the A and C atoms in the liquid phase and between the A and B cations with the intermediate C anion per mol of the alloy in the macroscopic form.

The value $\mu_{AC}^{0s} - \mu_{AD}^{0s} - \mu_{BC}^{0s} + \mu_{BD}^{0s}$ was estimated by

$$\begin{aligned}
&\mu_{AC}^{0s} - \mu_{AD}^{0s} - \mu_{BC}^{0s} + \mu_{BD}^{0s} = \\
& = \Delta h - T\Delta s + \int_{298.15}^T \Delta c dT - T \int_{298.15}^T \frac{\Delta c}{T} dT
\end{aligned} \tag{19}$$

where

$$\begin{aligned}
\Delta h &= h_{AC} - h_{AD} - h_{BC} + h_{BD}, \quad \Delta s = s_{AC} - s_{AD} - s_{BC} + s_{BD}, \\
\Delta c &= c_{AC}^P - c_{AD}^P - c_{BC}^P + c_{BD}^P, \quad h_{AC}, \quad s_{AC}, \quad \text{and} \quad c_{AC}^P
\end{aligned}$$

are the enthalpy, the entropy at the standard state and the specific heat capacity at constant pressure of AC, respectively. The magnitude of $\mu_{AC}^{0s} - \mu_{AD}^{0s} - \mu_{BC}^{0s} + \mu_{BD}^{0s}$ has the great importance for description of the thermodynamics characteristics and parameters of the $A_x B_{1-x} C_y D_{1-y}$ quaternary solution. This magnitude allows to describe the variation of the Helmholtz free energy of the $A_x B_{1-x} C_y D_{1-y}$ quaternary solution due to the reaction $nAC + nBD = nAD + nBC$, $n = 1, \dots, z_1$ (20)

The terms $\mu_{BD}^{0s} - \mu_B^{0l} - \mu_D^{0l}$, $\mu_{AD}^{0s} - \mu_{BD}^{0s} - \mu_A^{0l} + \mu_B^{0l}$ and $\mu_{BC}^{0s} - \mu_{BD}^{0s} - \mu_C^{0l} + \mu_D^{0l}$ were estimated by means of the following procedure

Table 1. The experimental results from [14] and theoretical estimation of the (In, Ga, Sb, As) liquid solution— $In_xGa_{1-x}Sb_yAs_{1-y}$ alloy phase diagram.

T (°C)	x	y	x_{In}^l	x_{As}^l	x_{Sb}^l	
517	0.21	0.82	0.609	1×10^{-3}	0.21	[14]
517	0.21	0.82	0.617	1.2×10^{-3}	0.28	Theor.
515	0.23	0.85	0.609	8.5×10^{-4}	0.21	[14]
515	0.23	0.85	0.614	1.1×10^{-3}	0.29	Theor.
515	0.15	0.83	0.59	1×10^{-2}	0.21	[15]

$$\begin{aligned} \mu_{BD}^{0s} - \mu_B^{0l} - \mu_D^{0l} &= \\ &= \mu_{BD}^{0s} - \mu_{BA}^{0l} - \mu_D^{0l} \approx RT \ln \gamma_{D(B)}^{0l} x_{D(B)}^{0l} \approx \\ &\approx \alpha_{B-D}^l + RT \ln x_{D(B)}^{0l} \end{aligned} \quad (21)$$

$$\begin{aligned} \mu_{AD}^{0s} - \mu_{BD}^{0s} - \mu_A^{0l} + \mu_B^{0l} &= \\ &= \mu_{AD}^{0s} - \mu_A^{0l} - \mu_D^{0l} - \mu_{BD}^{0s} + \mu_B^{0l} + \mu_D^{0l} \approx \\ &\approx RT \ln \gamma_{D(A)}^{0l} x_{D(A)}^{0l} - RT \ln \gamma_{D(B)}^{0l} x_{D(B)}^{0l} \approx \\ &\approx \alpha_{A-D}^l - \alpha_{B-D}^l + RT \ln \frac{x_{D(A)}^{0l}}{x_{D(B)}^{0l}} \end{aligned} \quad (22)$$

$$\begin{aligned} \mu_{BC}^{0s} - \mu_{BD}^{0s} - \mu_C^{0l} + \mu_D^{0l} &= \\ &= \mu_{BC}^{0s} - \mu_B^{0l} - \mu_C^{0l} - \mu_{BD}^{0s} + \mu_B^{0l} + \mu_D^{0l} \approx \\ &\approx RT \ln \gamma_{C(B)}^{0l} x_{C(B)}^{0l} - RT \ln \gamma_{D(B)}^{0l} x_{D(B)}^{0l} \approx \\ &\approx \alpha_{B-C}^l - \alpha_{B-D}^l + RT \ln \frac{x_{C(B)}^{0l}}{x_{D(B)}^{0l}} \end{aligned} \quad (23)$$

where γ_i^{0l} is the activity coefficient of the i -th type of component in the binary system, and $x_{D(B)}^{0l}$ is the solubility of element D in solvent B .

6. The phase diagram of the $In_xGa_{1-x}Sb_yAs_{1-y}$ quaternary alloy

The estimation of the (In, Ga, Sb, As) liquid solution- $In_xGa_{1-x}Sb_yAs_{1-y}$ alloy phase diagram was fulfilled. The theoretical estimations using experimental data reported in [12, 13] are showed in Table 1 as well as the available experimental results from [14, 15]. The theoretical estimations of the phase diagram are in reasonable agreement with the experimental results from [14]. Table 1 demonstrates also the significant difference between the experimental results from [14, 15]. The concentrations of arsenic in the liquid phases differ in one order of magnitude for the close solid state compositions [14-15].

5. The solid state-solid state equilibrium

Description of the miscibility gap of the $A_xB_{1-x}C_yD_{1-y}$ quaternary alloys is carried out as the minimum condition of the Helmholtz free energy of the heterogeneous system consisting of two quaternary solid solutions (decomposed alloy) having the compositions x_1, y_1 and x_2, y_2 , respectively, and the average composition x, y .

The partition function of the heterogeneous system consisting of the $A_{x_1}B_{1-x_1}C_{y_1}D_{1-y_1}$ and $A_{x_2}B_{1-x_2}C_{y_2}D_{1-y_2}$ solid solutions and represented as the canonical ensemble or closed system where the numbers of the different types of cations and anions are given values is written as

$$\begin{aligned} Q &= \prod_{n=1}^2 \prod_{i,j,l,m=1}^2 \frac{(N_n!)^2}{N_{ni}! N_{nj}!} \left[q_{ij}^{z_i} \exp \left\{ -\frac{u_{ij}}{k_B T} \right\} \right]^{\frac{z_1 N_{nl} N_{nj}}{N_n}} \times \\ &\times \left[\exp \left\{ -\frac{N_{nl} u_{ijl} + N_{nm} u_{jim}}{k_B T} \right\} \right]^{\frac{z_2 N_{nl} N_{nj}}{2 N_n^2}} \end{aligned} \quad (24)$$

where $2N_n, N_{ni}, N_{nl}, N_{nj}$ and N_{nm} are the quantities of the atoms, cations and anions in the n -th phase of the heterogeneous system, respectively.

The Helmholtz free energy of the two-phase system in strictly regular approximation is given as

$$F = \sum_{n=1}^2 \sum_{i,j,l,m=1}^2 \left\{ \begin{aligned} &\frac{N_{ni} N_{nj}}{N_n} \mu_{ij}^0 + \\ &+ z_2 \frac{N_{ni} N_{nj}}{2 N_n^2} \left(N_{nl} w_{ij-lj}^s + N_{nm} w_{ij-im}^s \right) \\ &- k_B T \left(\begin{aligned} &2 N_n \ln N_n - \\ &- N_{ni} \ln N_{ni} - \\ &- N_{nj} \ln N_{nj} \end{aligned} \right) \end{aligned} \right\} \quad (25)$$

where $n = 1, 2$ is the number of the phase.

The total numbers of the cations (anions) N , the A cations N_A and C anions N_C in the heterogeneous system, respectively, that are considered as the given values in the developed model. Therefore, there are three constraints for the numbers of the atoms in the heterogeneous system that are written as

$$\begin{aligned} N_1 + N_2 - N &= 0, \\ N_{1A} + N_{2A} - N_A &= 0, \\ N_{1C} + N_{2C} - N_C &= 0 \end{aligned} \quad (26)$$

After using the Lagrange method of the undetermined multipliers we obtain the next system of equations for the description of the boundary of the miscibility gap that are given as

$$\begin{aligned} \frac{\partial F}{\partial N_1} - \frac{\partial F}{\partial N_2} &= 0, \\ \frac{\partial F}{\partial N_{1A}} - \frac{\partial F}{\partial N_{2A}} &= 0, \\ \frac{\partial F}{\partial N_{1C}} - \frac{\partial F}{\partial N_{2C}} &= 0 \end{aligned} \quad (27)$$

The physical meaning of the equations is that the atoms of the *III* and *V* groups after the transition between the solid phases can form one, two or three types of the bonds and, thus, change the numbers of the bonds in the alloys.

In general case, taking into account the interaction parameters between the compounds in the $A_x B_{1-x} C_y D_{1-y}$ quaternary solution, the boundary of the miscibility gap is expressed in the macroscopic form by the next system of the equations

$$\begin{aligned} &-(x_1 y_1 - x_2 y_2) (\mu_{AC}^0 + \mu_{BD}^0 - \mu_{AD}^0 - \mu_{BC}^0) + \\ &+ RT \ln \frac{(1-x_1)(1-y_1)}{(1-x_2)(1-y_2)} + \\ &+ \sum_{n=1}^2 (-1)^{n+1} \left\{ \begin{aligned} &x_n y_n \left[(2x_n - 1) \alpha_{AC-BC} + \right. \\ &\left. + (2y_n - 1) \alpha_{AC-AD} \right] + \\ &+ (x_n \alpha_{AD-BD} y_n \alpha_{BC-BD}) \times \\ &\left. \times (x_n + y_n - 2x_n y_n) \right\} = 0 \end{aligned} \right. \end{aligned} \quad (28)$$

$$\begin{aligned} &(y_1 - y_2) (\mu_{AC}^0 + \mu_{BD}^0 - \mu_{AD}^0 - \mu_{BC}^0) + \\ &+ RT \ln \frac{(1-x_1)x_2}{x_1(1-x_2)} + \\ &+ \sum_{n=1}^2 (-1)^{n+1} \left\{ \begin{aligned} &(1-2x_n) \left[\alpha_{AC-BC} y_n + \right. \\ &\left. \alpha_{AD-BD} (1-y_n) \right] + \\ &\left. + (\alpha_{AC-AD} - \alpha_{BC-BD}) y_n (1-y_n) \right\} = 0 \end{aligned} \right. \end{aligned} \quad (29)$$

$$\begin{aligned} &(x_1 - x_2) (\mu_{AC}^0 + \mu_{BD}^0 - \mu_{AD}^0 - \mu_{BC}^0) + \\ &+ RT \ln \frac{(1-y_1)y_2}{y_1(1-y_2)} + \\ &+ \sum_{n=1}^2 (-1)^{n+1} \left\{ \begin{aligned} &(1-2y_n) \left[\alpha_{AC-AD} x_n + \right. \\ &\left. \alpha_{BC-BD} (1-x_n) \right] + \\ &\left. + (\alpha_{AC-BC} - \alpha_{AD-BD}) x_n (1-x_n) \right\} = 0 \end{aligned} \right. \end{aligned} \quad (30)$$

where 1 and 2 subscripts correspond to 1-st and 2-nd phases, respectively.

Thus, the miscibility gap of the $A_x B_{1-x} C_y D_{1-y}$ quaternary solution depends on the thermodynamic characteristics of the binary compounds AC , AD , BC and BD constituting the alloy. The miscibility gap is demonstrated in Fig. 2.

7. Conclusions

The statistical thermodynamics description of the phase equilibria in the quaternary heterogeneous system with the $A_x B_{1-x} C_y D_{1-y}$ alloy is presented. The liquid solution-alloy phase diagram and the miscibility gap are considered. The strictly regular approximation of the regular solution model was used. The fulfilled numerical estimations for the (*In*, *Ga*, *Sb*, *As*) liquid solution- $A_x B_{1-x} C_y D_{1-y}$ alloy phase diagram are in good agreement with the experimental results.

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