Journal of Alloys and Compounds, 182 (1992) 103–114
JALCOM 123

Miscibility gap in II–VI alloy semiconductor systems

H. Ohtani, K. Kojima*, K. Ishida and T. Nishizawa
Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980 (Japan)

(Received August 12, 1991)

Abstract

A thermodynamic calculation and analysis of the nature and extent of miscibility gaps in ternary and quaternary systems of II(Zn, Cd, Hg)–VI(S, Se, Te) alloy semiconductors is presented. The Gibbs energy of the zincblende-type phase has been described using a sublattice model and the interaction energies in the pseudobinary systems have been estimated from the difference in lattice constants of the components. The origin of miscibility gap in the quaternary systems is discussed.

1. Introduction

Multicomponent alloy semiconductors are being used increasingly in optoelectronic devices because their lattice constants and thereby their band gap energies are easily alterable by proper selection of alloy composition. It is also known that in some systems a two-phase separation occurs because of the presence of a miscibility gap, causing severe problems during production. An extensive study of such miscibility gaps has been carried out for III–V systems, while a systematic analysis on this subject has not been undertaken for the II–VI systems. Thus in the present work a thermodynamic calculation of the phase equilibria in the quaternary II–VI alloy crystals was made and the origin of the miscibility gap islands was investigated from a thermodynamic point of view.

2. Thermodynamic analysis

2.1. *Description of Gibbs energy*

18 ternary and 15 quaternary systems composed of II–VI compounds (ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe and HgTe) are included in the present analysis. Almost all these compounds have the zincblende type of structure which consists of two sublattices, one occupied by group II atoms and the other by group VI atoms. CdS and CdSe are exceptions, in that they exhibit the wurtzite-type structure.

---

*Present address: NKK, Ltd, Fukuyama Works, Fukuyama 721, Japan.

0925-8388/92/$5.00

The Gibbs energy of (A, B, C)X-type compound is expressed using the sublattice model [1] as follows:

$$\begin{aligned} G^S = {}& {}^0G_{AX}y_A + {}^0G_{BX}y_B + {}^0G_{CX}y_C \\ & + RT(y_A \ln y_A + y_B \ln y_B + y_C \ln y_C) \\ & + L_{AB}{}^X y_A y_B + L_{AC}{}^X y_A y_C + L_{BC}{}^X y_B y_C \end{aligned} \quad (1)$$

where ${}^0G_{ij}$ is the Gibbs energy of the binary compound ij. L represents the interaction energy between two species; $L_{AB}{}^X$, for instance, is the interaction energy between A and B atoms on the same sublattice when all the sites on the other sublattice are occupied by X atoms. y_i is the mole fraction of i on the sublattice in which i atoms are located.

The Gibbs energy of (A, B)(X, Y)-type compound is also described using the same sublattice model as follows:

$$\begin{aligned} G^S = {}& {}^0G_{AX}y_A y_X + {}^0G_{AY}y_A y_Y + {}^0G_{BX}y_B y_X + {}^0G_{BY}y_B y_Y \\ & + RT(y_A \ln y_A + y_B \ln y_B + y_X \ln y_X + y_Y \ln y_Y) \\ & + L_{AB}{}^X y_A y_B y_X + L_{AB}{}^Y y_A y_B y_Y + L_{XY}{}^A y_A y_X y_Y + L_{XY}{}^B y_B y_X y_Y \end{aligned} \quad (2)$$

where y parameters are related to each other as follows:

$$y_A + y_B = 1 \qquad y_X + y_Y = 1 \quad (3)$$

The same notation as eqn. (1) is applicable to ${}^0G$ and L parameters in eqn. (2).

2.2. *Evaluation of the Gibbs energy of formation of the binary compounds*

The Gibbs energy $\Delta_f G_{ij}$ of formation for the binary ij compounds with the zincblende structure are evaluated using the following thermodynamic data: (a) the enthalpies $\Delta_f H_{298}$ of formation and $(G_T - H_{298})/T$ function for ij compounds assessed by Mills [2] and (b) $(G_T - H_{298})/T$ function for liquid components i and j given by Hultgren *et al.* [3]. The $\Delta_f H_{298}$ values so evaluated using a least-squares fit are given in Table 1 for all the compounds. In the case of ZnSe and CdSe, however, the values shown in Table 1 are taken from Grytsiv *et al.* [4] and Pashinkin [5] respectively. The lattice parameters [6, 7] and the melting points of all the compounds are also included in Table 1. The lattice parameter for the metastable zincblende structure of CdSe was obtained by extrapolation of lattice parameter data from pseudobinary systems of CdSe–ZnSe [8] and CdTe–CdSe [9, 10]. It can be seen that large negative values for $\Delta_f H_{298}$ and high melting points go together. Since the compounds CdS and CdSe have the wurtzite crystal structure, the Gibbs energies of formation for the zincblende structure of these compounds were estimated from the following equations:

$$\begin{aligned} & \Delta_f G_{CdS}{}^Z = \Delta_f G_{CdS}{}^W + \Delta G_{CdS}{}^{W \to Z} \\ & \Delta_f G_{CdSe}{}^Z = \Delta_f G_{CdSe}{}^W + \Delta G_{CdSe}{}^{W \to Z} \end{aligned} \quad (4)$$

where $\Delta G_{\mathrm{CdS}}^{\mathrm{W}\to\mathrm{Z}}$ and $\Delta G_{\mathrm{CdSe}}^{\mathrm{W}\to\mathrm{Z}}$ are the Gibbs energy differences between the zincblende and wurtzite structures for CdS and CdSe respectively. These values are estimated by analyzing the experimental phase boundaries between the zincblende and wurtzite types of solutions in the systems of CdTe–CdSe [9] and CdTe–CdS [11, 12]. Figure 1 shows those pseudobinary phase diagrams in which the hypothetical transition temperature for CdTe to transform from zincblende structure to wurtzite structure is about 1280 °C. The solid phase equilibria in Fig. 1 are calculated using the values for $\Delta G_{\mathrm{CdS}}^{\mathrm{W}\to\mathrm{Z}}$ and $\Delta G_{\mathrm{CdSe}}^{\mathrm{W}\to\mathrm{Z}}$ given in Table 1 assuming that the interaction parameters in the zincblende and wurtzite phases in each system are equal.

2.3. *Evaluation of the interaction parameters*

Since experimental information on the miscibility gaps exists for the system ZnS–ZnTe [13] and CdS–CdTe [11] the interaction parameters $L_{\mathrm{STe}}^{\mathrm{Zn}}$ and $L_{\mathrm{STe}}^{\mathrm{Cd}}$ are obtained using those data and are given in the right-hand part of Table 2. $L_{\mathrm{STe}}^{\mathrm{Cd}}$ is the value for wurtzite and is assumed to be the same for the zincblende phase. For the other ij–ik systems where experimental information is not available on the miscibility gaps, the interaction parameters are estimated from the difference between the lattice constants of the binary compounds. Several models have been developed in order to estimate the interaction parameter using lattice constants [14–16], and they all lead to the following relation:

$$L_{\mathrm{jk}}^{\mathrm{i}}=K\left(\frac{\Delta a_{\mathrm{ij-ik}}}{\bar{a}_{\mathrm{ij-ik}}}\right)^{2} \tag{5}$$

where K is a coefficient depending on the modulus of elasticity, $\Delta a_{\mathrm{ij-ik}}$ is the lattice mismatch and $\bar{a}_{\mathrm{ij-ik}}$ is the average value of the lattice constants. Combining all the values obtained for the L parameters either from experiment or by estimation, a value for K in eqn. (5) is 1.97×10^{6} J mol^{-1} as shown in Fig. 2. The interaction parameters $L_{\mathrm{jk}}^{\mathrm{i}}$ for each pseudobinary system calculated using this K value are shown in the left-hand part of Table 2. Strictly speaking, the interaction parameters are not expected to be constant but should depend on temperature and composition. The composition dependence is self-evident, for example, from Fig. 1(b) where the miscibility gap has an asymmetric shape with a skew towards the component with a higher melting temperature. Asymmetric miscibility gaps have also been observed in the III–V systems [17], signifying the existence of this type of composition dependence of the interaction parameter in these systems as well. From the fact that the elastic modulus is directly proportional to the melting temperature, it can be safely said that the value of K in eqn. (5) should increase as one goes from the low melting compound side to the high melting compound side. However, in the present work, these types of temperature and composition dependences of the K values have not been considered. It is also worthwhile pointing out at this stage that the estimation

TABLE 1

The Gibbs energy of formation of binary compounds

Compound	a (nm)	T_m (K)	$\Delta_f H_{298}$ (kJ mol^{-1})	$\Delta_f G_{ij}$ (J mol^{-1})	$\Delta G^{W \to Z}$ (J mol^{-1})
ZnS	0.54093	1995	-205.0	$-215700+36.594T$	–
ZnSe	0.56676	1799	-169.0	$-175900-53.513T+12.47T \ln T$	–
ZnTe	0.60989	1570	-119.2	$-127500-112.39T+21.087T \ln T$	–
CdS	0.5832	1678	-149.4	$-157800+34.664T$	$1000+0.35T$
CdSe	0.6066	1537	-142.3	$-153600-3.4522T+5.8164T \ln T$	$-200+0.7T$
CdTe	0.6481	1371	-100.8	$-109100-107.82T+19.392T \ln T$	–
HgS	0.5851	1098	-49.3	$-53700+30.446T$	–
HgSe	0.6084	1043	-43.5	$-44650-51.733T+11.405T \ln T$	–
HgTe	0.6461	943	-31.8	$-28760-193.27T+30.668T \ln T$	–

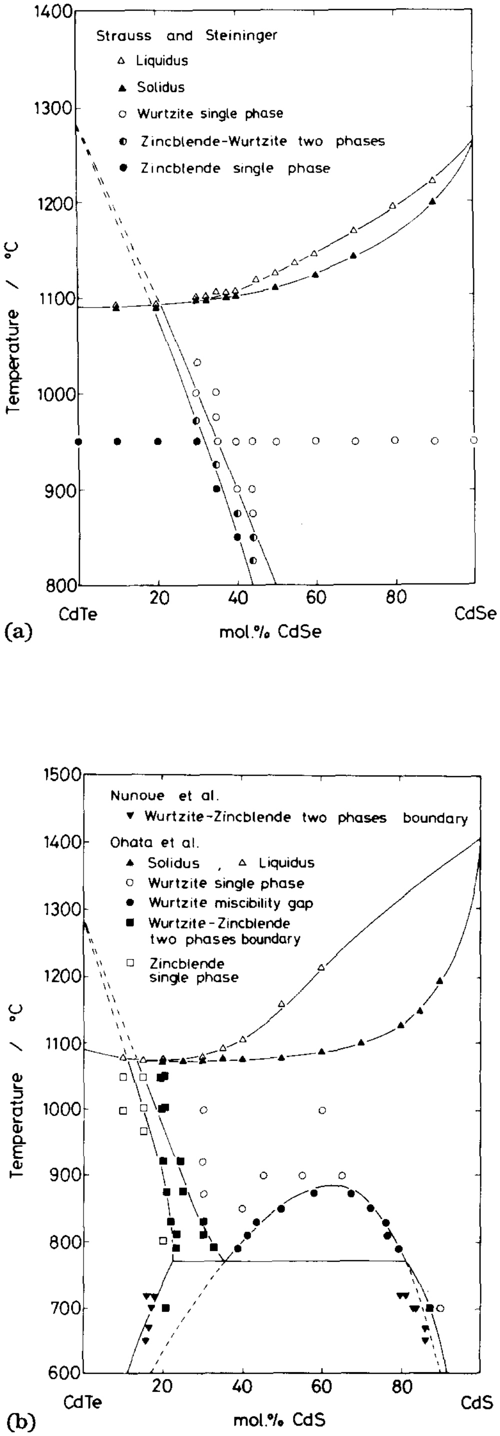
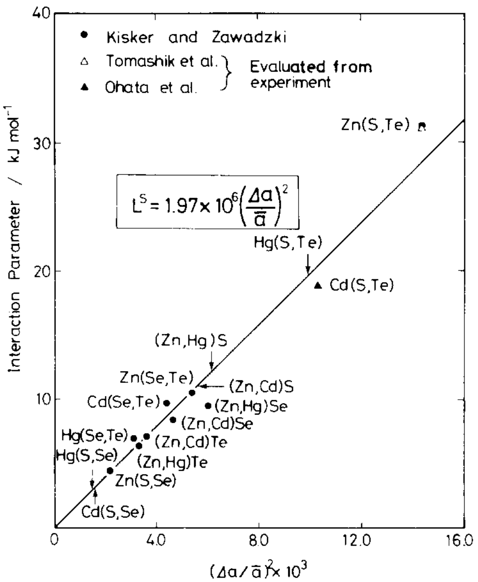


Fig. 1. Phase diagrams for the (a) CdTe–CdSe and (b) CdTe–CdS pseudobinary systems.

TABLE 2

Interaction parameters in the pseudobinary system

Evaluation from lattice mismatch				Evaluation from phase diagram		
Compound	$(\Delta a/\bar{a})^2 \times 10^3$	Interaction parameter (J mol^{-1})	T_c (K)	Interaction parameter (J mol^{-1})	T_c (K)	Summit point composition mole fraction
ZnS–ZnSe	2.1751	4290	258			
ZnS–ZnTe	14.363	28300	1702	$21140+5.78T+(78.3-1.784T)(x_{ZnTe}-x_{ZnS})$	2029	$x_{ZnS}=0.5776$
ZnSe–ZnTe	5.3743	10600	637			
CdS–CdSe	1.5472	3048	183			
CdS–CdTe	11.113	21900	1317	$21460-3.05T+(-5330+7.75T)(x_{CdS}-x_{CdTe})$	1166	$x_{CdTe}=0.3742$
CdSe–CdTe	4.3760	8620	518			
HgS–HgSe	1.5245	3000	180			
HgS–HgTe	9.8189	19300	1161			
HgSe–HgTe	3.6124	7120	428			
ZnS–CdS	5.6558	11100	668			
ZnS–HgS	6.1548	12100	728			
CdS–HgS	0.1058×10^{-1}	21	1			
ZnSe–CdSe	4.6114	9090	547			
ZnSe–HgSe	5.0221	9890	595			
CdSe–HgSe	0.8779×10^{-2}	17	1			
ZnTe–CdTe	3.6903	7270	437			
ZnTe–HgTe	3.2246	6350	394			
CdTe–HgTe	0.9553×10^{-2}	19	1			



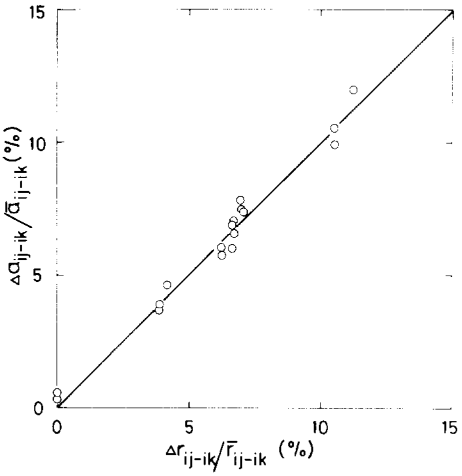


Fig. 2. Correlation between interaction parameter and misfit factor in the II–VI alloy semiconductor.

Fig. 3. Relation between lattice mismatch and difference in tetrahedral covalent radii.

of the L parameters using this K value is extendable to other systems similar to these, as described in the next paragraph.

In the II–VI systems, as shown in Fig. 3, there exists a one-to-one correspondence between lattice mismatch and the difference $\Delta r_{ij\text{-}ik}$ in tetrahedral covalent radii calculated using the formula

$$\Delta r_{ij\text{-}ik} = \frac{2|r_j - r_k|}{2r_i + r_j + r_k} \tag{6}$$

where r_i, r_j and r_k are the Pauling [18] tetrahedral radii for i, j and k elements respectively. Since Pauling [18] has proposed a set of empirical values for the tetrahedral covalent atomic radii, not only for the group II and VI elements but also for other groups such as I, III and IV, it is reasonable to use eqn. (6) with the appropriate modifications as shown below:

$$L_{jk}^{\,i} = 1.97 \times 10^6 (\Delta r_{ij\text{-}ik})^2 \tag{7}$$

for estimating interaction parameters in other systems, where structures similar to zincblende or wurtzite occur, *i.e.* structures in which each atom is surrounded tetrahedrally by four other atoms.

3. Results and discussion

3.1. *Miscibility gaps in (A, B, C)X compounds*

Figure 4 shows the position of the calculated miscibility gap in Zn(S, Se, Te) system at 873 K. It is seen that the surface of the miscibility gap

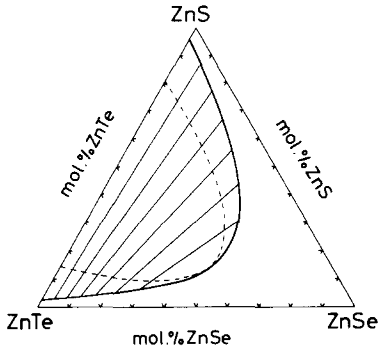
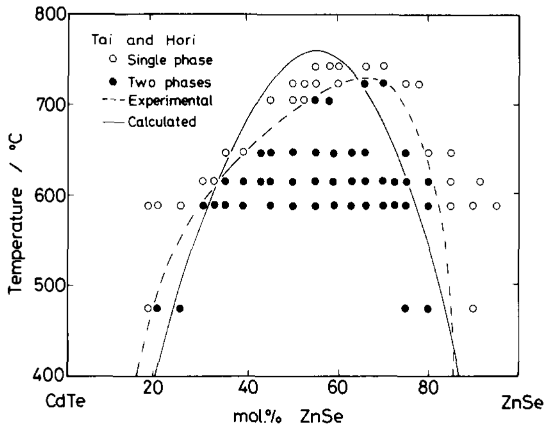


Fig. 4. Calculated miscibility gap in the Zn(S, Se, Te) system at 873 K.



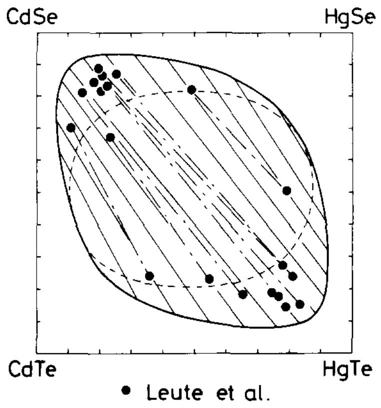


Fig. 5. Calculated miscibility gap in the CdTe–ZnSe system.

Fig. 6. Calculated miscibility gap in the (Cd, Hg)(Se, Te) system at 823 K.

extends from the ZnS–ZnTe pseudobinary side into the ternary. Although there is no experimental information on miscibility gaps available for this ternary, it seems reasonable to expect such a miscibility gap in this system because of the larger misfit factor arising from the size difference between sulphur($r_S = 1.04$ Å) and tellurium($r_{Te} = 1.32$ Å).

3.2. Miscibility gaps in (A, B)(X, Y) compounds

Experimental data on miscibility gaps in systems (Zn, Cd)(Se, Te) and (Cd, Hg)(Se, Te) reported by Tai and Hori [19] and Leute *et al.* [20] respectively are shown together with the present calculated results in Fig. 5 and Fig. 6. Even without the inclusion of any other interaction other than those from the pseudobinary systems, the agreement between experimental and calculated positions of miscibility gaps appears satisfactory. The position of the miscibility gap in the system (Cd, Hg)(Se, Te) shown in Fig. 6 indicates that the phase separation occurs towards the CdSe and HgTe ends which have the highest and lowest melting temperatures respectively among the four compounds.

Figure 7 shows the isothermal sections of the miscibility gaps in 15 quaternary systems. The numbers inside the diagrams denote the temperatures of the calculated sections. The summit points T_c of the miscibility gaps in (A, B)(X, Y) compounds are listed in Table 3. As mentioned in the previous section, miscibility gaps in (A, B, C)X type of compounds arise because of

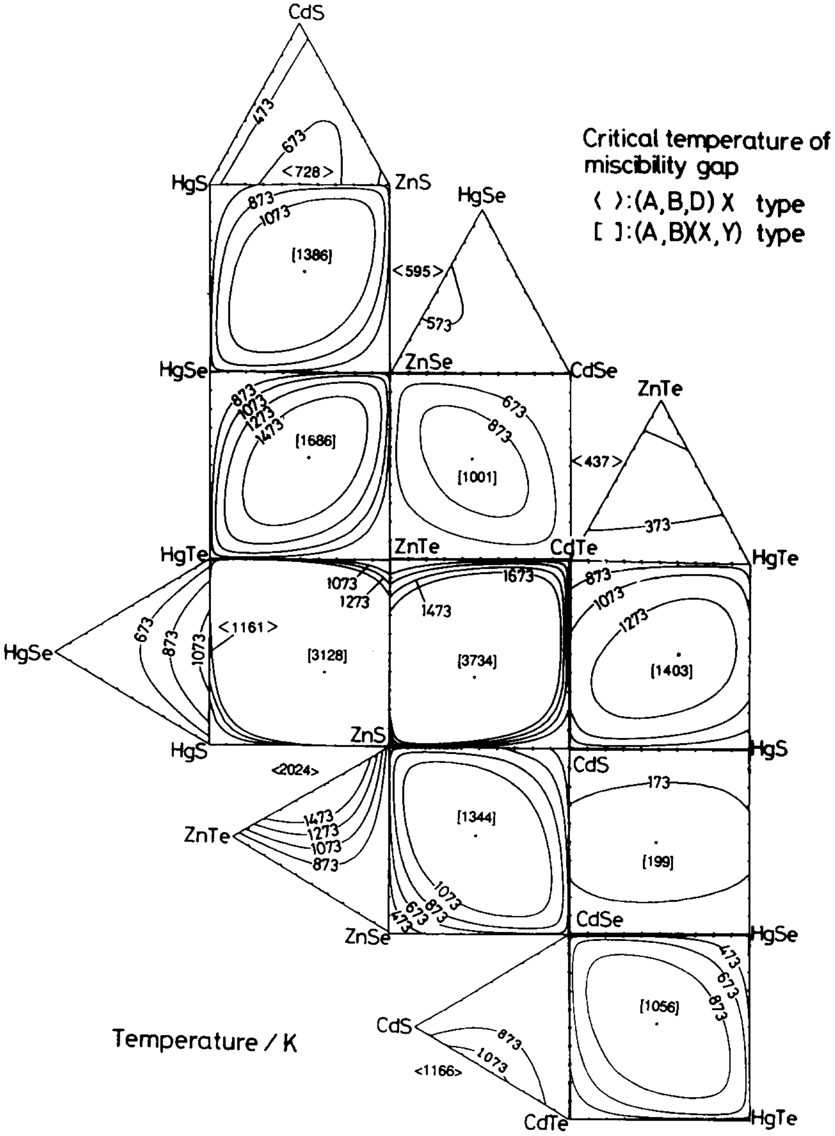
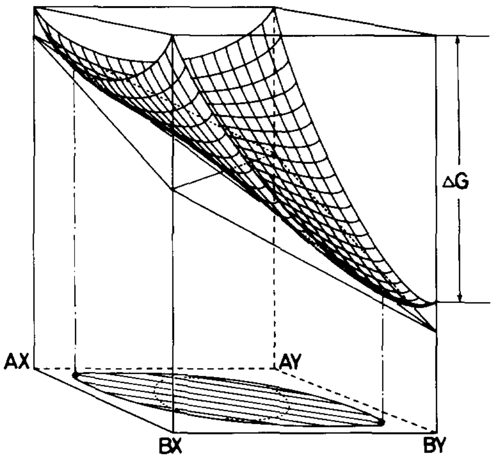


Fig. 7. Calculated miscibility gap in the II–VI alloy semiconductor system.

TABLE 3

Summit point of miscibility gap in (A, B)(X, Y) compound

Compound (A, B)(X, Y)	T_c^{id} (K)	T_c (K)	y_B	y_Y
(Zn, Cd)(S, Se)	887	1344	0.4774	0.4658
(Zn, Cd)(S, Te)	1440	3734	0.4650	0.4141
(Zn, Cd)(Se, Te)	257	1001	0.4528	0.4623
(Zn, Hg)(S, Se)	906	1386	0.4768	0.4634
(Zn, Hg)(S, Te)	2014	3128	0.3640	0.4643
(Zn, Hg)(Se, Te)	1234	1686	0.4547	0.4557
(Cd, Hg)(S, Se)	93	199	0.4806	0.5008
(Cd, Hg)(S, Te)	847	1403	0.6100	0.5100
(Cd, Hg)(Se, Te)	833	1056	0.4809	0.4842



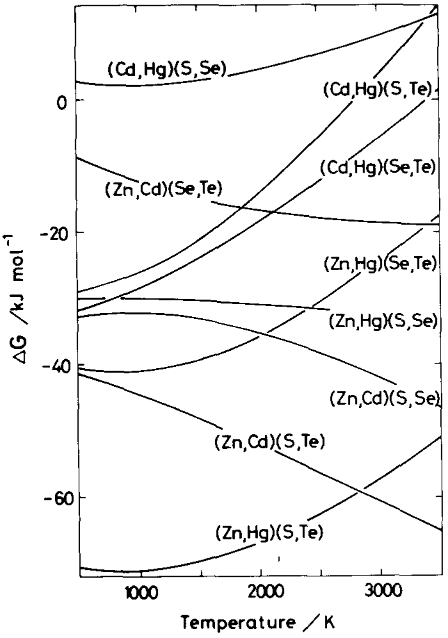


Fig. 8. Gibbs energy surface in the (A, B)(X, Y) compound.

Fig. 9. Variation in the ΔG parameter with temperature.

the atomic misfit factor in the constituent pseudobinary systems. In the (A, B)(X, Y) compounds miscibility gaps arise even when there are no miscibility gaps in all the constituent pseudobinary systems. The circumstances under which such miscibility gaps occur were investigated by Hillert and Staffansson [1] and Rudy [21], who pointed out that phase separation occurred mainly depending on the difference ΔG between the Gibbs energies of formation of the binary compounds, given by the expression

$$\Delta G = {}^0G_{AX} + {}^0G_{BY} - {}^0G_{AY} - {}^0G_{BX} \qquad (8)$$

A schematic Gibbs energy surface in (A, B)(X, Y) compounds is illustrated in Fig. 8 and the value of ΔG for every quaternary system is shown in Fig. 9. With a few exceptions, it is generally true to claim that, the larger the absolute value of ΔG, the higher is the summit temperature T_c of the miscibility gap in these compounds. For instance, the absolute values of ΔG are very high in (Zn, Cd)(S, Te) and (Zn, Hg)(S, Te) systems and so also are their summit temperatures. In order to clarify the effect of ΔG on the miscibility gap quantitatively, the critical temperature of the miscibility gap in (A, B)(X, Y) compound without taking the interaction parameter into account is estimated. The critical temperatures T_c^{id} for ideal solution behaviour is given by

$$T_c^{id} = \left| \frac{\Delta G}{4R} \right| \qquad (9)$$

The calculated T_c^{id} is shown in Table 3, which reveals that ΔG has a significant contribution to the miscibility gap of (A, B)(X, Y) compound.

4. Conclusions

(1) Miscibility gaps in the II–VI zincblende-type alloy systems have been calculated using a sublattice model. The Gibbs energies of formation for all the constituent binary compounds have been evaluated from the thermochemical data in the literature. Hypothetical formation energies of zincblende CdS and CdSe have been estimated from knowledge of phase equilibria in the CdS–CdTe and CdSe–CdTe systems. Interaction parameters in the pseudobinary systems have been estimated using the differences in the lattice constants of the components.

(2) The origin of miscibility gap in the (A, B, C)X type of compound is mainly attributed to the difference between the lattice parameters of the component compounds, while in the (A, B)(X, Y) compounds it is attributed mainly to the difference in relative stabilities of the binary compounds.

Acknowledgments

This work was partly supported by Grant-in-Aids for Science Research from the Ministry of Education, Science and Culture, Japan. One of the authors (K.I.) would like to acknowledge the financial assistance by Murata Science Foundation.

References

1 M. Hillert and L.-I. Staffansson, *Acta Chem. Scand.*, *24* (1970) 3618.
2 K. C. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*, Butterworths, London, 1974.

3 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelley, *Selected Values of the Thermodynamic Properties of Binary Alloys*, American Society for Metals, Metals Park, OH, 1973.

4 V. I. Grytsiv, V. N. Tomashik and Z. F. Tashik, *Inorg. Mater.*, *15* (1979) 30.

5 A. S. Pashinkin, *Zh. Fiz. Khim.*, *38* (1964) 2690.

6 G. B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice*, Academic Press, New York, 1989.

7 P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, American Society for Metals, Metals Park, OH, 1985.

8 Ju. V. Zerdev and B. F. Ormont, *Z. Neorg. Khim. S.S.S.R.*, *5* (1960) 1796.

9 A. J. Strauss and J. Steininger, *J. Electrochem. Soc.*, *117* (1970) 1420.

10 H. Tai, S. Nakashima and S. Hori, *J. Jpn. Inst. Met.*, *40* (1976) 474.

11 K. Ohata, J. Saraie and T. Tanaka, *Jpn. J. Appl. Phys.*, *12* (1973) 1198.

12 S. Nunoue, T. Hemmi and E. Kato, *J. Electrochem. Soc.*, *137* (1990) 1248.

13 V. N. Tomashik, G. S. Oleinik and I. B. Mizetskaya, *Inorg. Mater.*, *14* (1978) 1119.

14 K. Osamura, K. Nakajima and Y. Murakami, *J. Jpn. Inst. Met.*, *36* (1972) 744.

15 G. B. Stringfellow, *J. Cryst. Growth*, *27* (1974) 21.

16 D. W. Kisker and A. G. Zawadzki, *J. Cryst. Growth*, *89* (1988) 378.

17 K. Ishida, T. Nomura, H. Tokunaga, H. Ohtani and T. Nishizawa, *J. Less-Common Met.*, *155* (1989) 193.

18 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, 1960, p. 244.

19 H. Tai and S. Hori, *J. Jpn. Inst. Met.*, *41* (1977) 33.

20 V. Leute, H. M. Schmidtke and W. Stratmann, *Ber. Bunsenges. Phys. Chem.*, *86* (1982) 732.

21 E. Rudy, *J. Less-Common Met.*, *33* (1973) 43.