ELSEVIER

Thermochimica Acta 314 (1998) 175–181

thermochimica acta

Measurement of activity of gallium in liquid Ga–Sb–Sn alloys by emf method with zirconia as solid electrolyte

I. Katayama*, Y. Fukuda[1], Y. Hattori, T. Maruyama[2]

Department of Materials Science and Processing, Faculty of Engineering, Graduate School of Osaka University, Yamadaoka 2-1, Suita, Osaka 5650871, Japan

Received 3 June 1997; accepted 4 August 1997

Abstract

The emf of galvanic cells with zirconia solid electrolytes was measured to determine the activity of gallium in liquid Ga–Sb–Sn alloys in the 1050–1150 K temperature range along three lines of constant antimony-to-tin mole ratio. A mixture of Ga and Ga_2O_3 was used as a reference electrode. The activity curves of Ga show negative to positive deviations from the ideal behavior with increasing Sn concentrations in the lower concentration range of Ga; whereas in the concentration range $X_{Ga} \geq 0.6$, the activity of Ga in the ternary alloys shows positive deviations from the ideal behavior. Isoactivity curves at 1073 K, in the ternary Ga–Sb–Sn alloys, were derived by combining the activity data for Ga–Sb and Ga–Sn alloys. The shape of the curves is simple in the Ga-poor region, but shows a wavy form with increasing Ga concentration. Isovalue curves in the excess free energies of mixing in the ternary alloys are derived by the Darken method. The results are in agreement with values derived by using the Chou method on the Sb-poor side, but the agreement is not good in the Sb-rich region. © 1998 Elsevier Science B.V.

Keywords: Activity; Electromotive force method; Gallium–antimony–tin alloy; Liquid alloy; Thermodynamics

1. Introduction

Many studies have been carried out on alloy systems related to semiconducting compounds which are of interest from both, the scientific and technological points of view. An accurate knowledge of the thermodynamic properties and phase diagrams of these systems is essential. Some of the binary systems have been studied extensively, but the experimental data for ternary and/or multicomponent systems are not adequate. The present measurements were made in the course of our program of experimental thermodynamic studies on materials related to groups III–V and II–VI compounds at high temperatures by using an emf method [1] to determine the activity of gallium in the liquid Ga–Sb–Sn alloys.

Activities of gallium in the liquid Ga–Sb [1–4] and Ga–Sn [1,5–7] alloys at 1073 K show moderately negative and positive deviations from Raoult's law. For Ga–Sb alloys, activity data obtained by Anderson et al. [2] – who originally used zirconia solid electrolyte emf method – agree well with our values; [1] except in the higher gallium concentration range. Recent results of Zajaczkowski and Botor [4], using

---

*Corresponding author. Fax: 81-6-879-7522; e-mail: katayama@mat.eng.osaka-u.ac.jp

[1] Present address: Murata Manufacturing Co. Ltd., Tenjin 2-26-10, Nagaokakyo, Kyoto 617, Japan.

[2] Present address: Tokai Rika Co. Ltd., Toyota-Noda 1, Oguchi, Tambagun, Aichi 480-01, Japan.

0040-6031/98/$19.00
PII S0040-6031(97)00464-4

the Knudsen method, show excellent agreement with our values. Bergman et al. [3] obtained slightly smaller activity values in the middle concentration region from mass-spectrometric study. For Ga–Sn alloys, our data [1] obtained by the emf method with zirconia solid electrolyte show excellent agreement with those of Danilin et al. [5], obtained by the fused salt emf method. Two groups calculated the activity of gallium based on Bergman's data by mass spectrometry. One group is that of Anderson and Ansara [7], using the Lukas program and the other that of Suzuki and Risold [8], using the Thermo-Calc method. These are in good agreement with our experimental values, but on a closer look, slightly higher than the original Bergman's data. Predel [9] obtained slightly higher values at 513 K, based on his calorimetric data and phase diagram. For ternary Ga–Sb–Sn alloys, there are no literature data to be compared with. In this study, emf measurements of an electrochemical cell with zirconia as solid electrolyte were performed along the three pseudo-binary lines of Sb_ySn_{1-y}–Ga to obtain the gallium activity in the 1050–1150 K range in the entire composition range of Ga–Sb–Sn alloys. The reference electrode used was Ga, Ga_2O_3.

2. Experimental

2.1. Materials

The alloys used in this study were prepared from high-purity materials (Ga,99.9999 mass% purity from

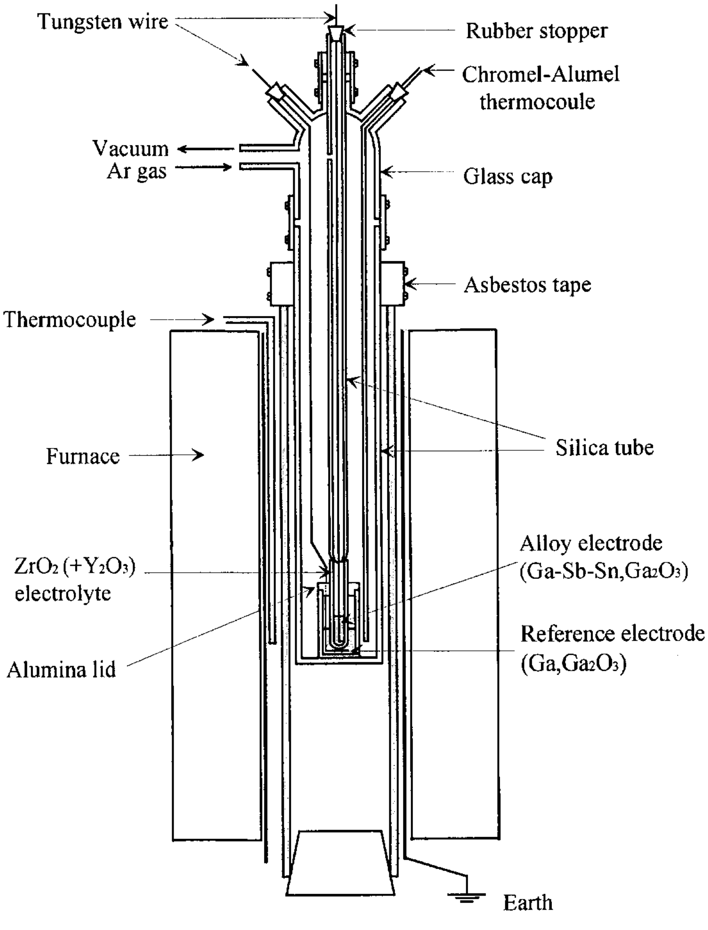

Fig. 1. Schematic diagram of cell arrangement for emf measurement.

Sumitomo Chemicals; Sb and Sn, 99.999% purity from Mitsubishi Materials). Ga_2O_3 powder added to the alloy electrode and reference electrode in a mass ratio of c. 1 : 9 was of 99.99% purity from Mitsubishi Materials. Zirconia solid electrolyte crucibles (0.92 ZrO_2+0.08 Y_2O_3, OD 8 mm, ID 5 mm and length 50 mm) were produced at Nikkato by the coprecipitation method.

2.2. Experimental apparatus and procedures

The experimental equipment used in this study is shown in Fig. 1. A glass cap with four branches, one of which was for a thermocouple, two were for lead wires from the electrodes, and the fourth for evacuation and argon flow, was connected to the upper part of the reaction tube with a rubber hosepipe. The reaction tube near the hosepipe was wound with a copper sheet connected to a water-cooled copper pipe. The reaction tube can be maintained in a vacuous state by the use of rubber stoppers, through which lead wires and thermocouple are held and pushed into the entrances of the glass branches.

The alloy elements, weighed to give mixtures with desired compositions, and Ga_2O_3 powder were put in a zirconia crucible with a tungsten lead wire (0.5 mm diameter), and the crucible was settled in the reference electrode (Ga,Ga_2O_3), put in an alumina crucible in which another tungsten wire was settled as a lead wire. A calibrated Chromel–Alumel thermocouple settled by the cell was used to measure the cell temperature. The part of the one-end-closed silica reaction tube in the furnace was rapped with a stainless-steel sheet which was earthed.

After the cell was assembled in the homogeneous temperature region in the reaction tube that was settled in the vertical type electric-resistance furnace, the reaction tube was evacuated by a rotary oil pump and diffusion oil pump. Then, it was filled with purified argon gas. The argon gas from a gas tank was purified by passing through, glass tubes filled with silicagel, molecular sieves, activated alumina, an alumina tube filled with sponge titanium heated at 900°C and a glass tube with glass-wool and P_2O_5 powder. The flow rate of the argon gas was controlled with a slow-leak bulb. This operation was repeated twice or thrice. Subsequently, the temperature was raised to a desired value. The cell temperature was raised and lowered, alternatively, and controlled to ±1 K at each temperature with a thermocontroller (Thermo-let, Eiko Electric, TPC-A202C2) and a Pt-13RhPt thermocouple. The emfs of the cell and the cell temperature were measured with a digital voltmeter (Multi-Logging Meter AD-5311, A & D) with a printer.

3. Results

For the binary liquid alloys of Ga–Sb and Ga–Sn, the activity of gallium is reported in Ref. [1]. The emfs of cell I for the ternary alloys were measured.

$$(-)\mathrm{W,Ga,Ga_2O_3|ZrO_2(+Y_2O_3)|Ga–Sb–Sn(l),}\\ \mathrm{Ga_2O_3,W(+)} \qquad \text{(I)}$$

The compositions of the alloy are chosen for pseudo-binary system of $(Sb_ySn_{1-y})_{1-x}$–Ga_x, where y=0.25, 0.50 and 0.75; and x=0.1, 0.3, 0.5, 0.75 and 0.9.

After the cell temperature reached the desired value, it was held constant for ca. 12 h, and then the tungsten lead wire was dipped into the alloy electrode. Thereafter, it took about several tens of minutes to several hours to reach stable emf of the cell. On changing the temperature, equilibration at a new temperature took a very short period of time. The tungsten lead wire can be used to stir the alloy electrode to confirm the equilibrium emf.

The experimental results are shown in Fig. 2. As all the data points distribute around a linear line for each composition, the relations between emf (E/mV) and temperature (T/K) are obtained by least-squares regression analysis, and are listed Table 1.

Activities of Ga (a_{Ga}) in the alloys at 1073 K are calculated from Eq. (1).

$$-3EF = RT\ln a_{\mathrm{Ga}} (= \Delta\overline{G}_{\mathrm{Ga}}) \qquad (1)$$

where F is the Faraday constant, R the gas constant and $\Delta\overline{G}_{Ga}$/J mol^{-1} the partial Gibbs energy of mixing of Ga. Uncertainty limits in the activity values are derived from those in the emf values. The results are also shown in Table 1 with the values of activity coefficient of Ga ($\gamma_{Ga}=a/X$) and α-function of Ga ($\alpha_{Ga}=\ln\gamma_{Ga}/(1-X_{Ga})$).

In order to obtain the isoactivity curve of Ga in the liquid Ga–Sb–Sn alloys, the activity data for

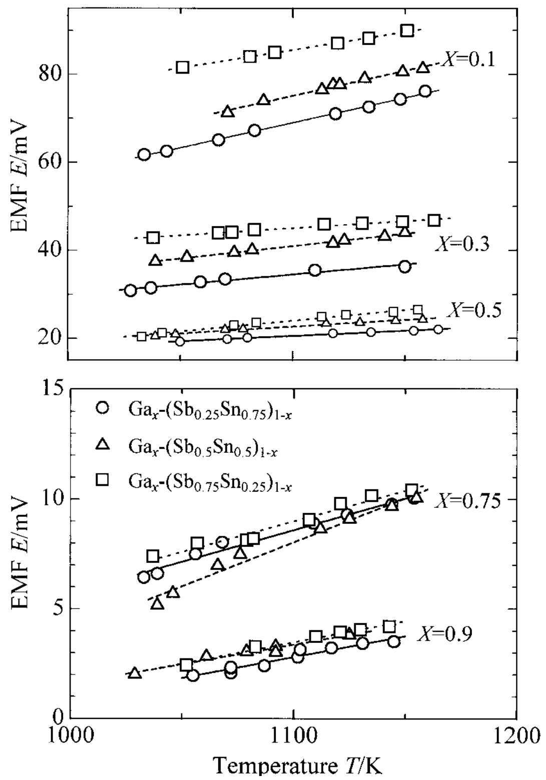

Fig. 2. Temperature dependence of the emf of cell (I).

liquid Ga–Sb [1] and Ga–Sn [1] alloys are used as the starting and end points, and the experimental data for the pseudo-binary systems of (Sb_ySn_{1-y})–Ga in this study are used. The result at 1073 K is shown in Fig. 3. The shape of the isoactivity curves is similar to those of Ga–Sb–Bi alloys [1] in the

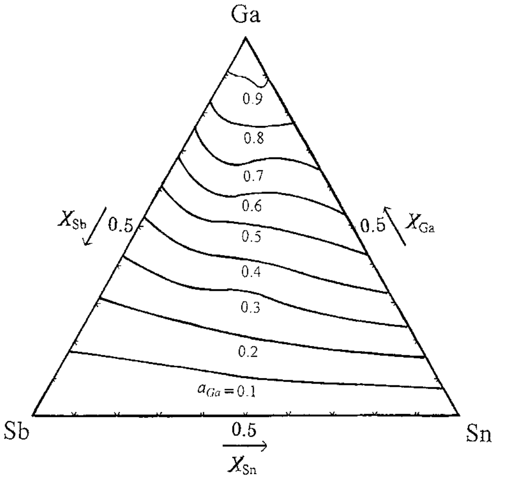

Fig. 3. Isoactivity curves of gallium in liquid Ga–Sb–Sn alloys at 1073 K.

Table 1
Temperature dependence of emf of cell; (−)Ga,Ga_2O_3|ZrO_2(+Y_2O_3)|Ga–Sb–Sn(l),Ga_2O_3(+) and thermodynamic quantities in the Ga–Sb–Sn system at 1073 K

X_{Ga}	E/(mV)=$a+bT\pm c$	E/(mV)	a_{Ga}	γ_{Ga}	α_{Ga}
(Ga–$Sb_{0.75}Sn_{0.25}$)					
0.1	$E=-4.54+0.0819T\pm0.12$	83.34±0.12	0.0669±0.0003	0.669	−0.496
0.3	$E=9.71+0.0321T\pm0.20$	44.15±0.20	0.239±0.002	0.797	−0.463
0.5	$E=-29.57+0.0487T\pm0.26$	22.69±0.26	0.479±0.005	0.958	−0.172
0.75	$E=-21.63+0.0278T\pm0.20$	8.20±0.20	0.766±0.006	1.021	0.333
0.9	$E=-17.84+0.0194T\pm0.09$	2.96±0.09	0.908±0.003	1.009	0.896
Ga–($Sb_{0.5}Sn_{0.5}$)					
0.1	$E=-50.73+0.1140T\pm0.35$	71.59±0.35	0.0979±0.0012	0.979	−0.026
0.3	$E=-21.12+0.0564T\pm0.16$	39.40±0.16	0.278±0.002	0.927	−0.155
0.5	$E=-11.84+0.0313T\pm0.19$	21.74±0.19	0.494±0.004	0.988	−0.048
0.75	$E=-36.10+0.0401T\pm0.26$	6.93±0.26	0.799±0.007	1.065	1.008
0.9	$E=-16.21+0.0178T\pm0.11$	2.89±0.11	0.910±0.004	1.011	1.094
Ga–($Sb_{0.25}Sn_{0.75}$)					
0.1	$E=-56.03+0.1136T\pm0.24$	65.86±0.24	0.118±0.001	1.180	0.204
0.3	$E=-25.38+0.0548T\pm0.18$	33.21±0.18	0.340±0.003	1.133	0.255
0.5	$E=-5.75+0.0239T\pm0.09$	19.89±0.09	0.524±0.002	1.048	0.188
0.75	$E=-23.15+0.0289T\pm0.19$	7.86±0.19	0.775±0.005	1.033	0.519
0.9	$E=-18.09+0.0190T\pm0.13$	2.30±0.13	0.928±0.004	1.031	3.053

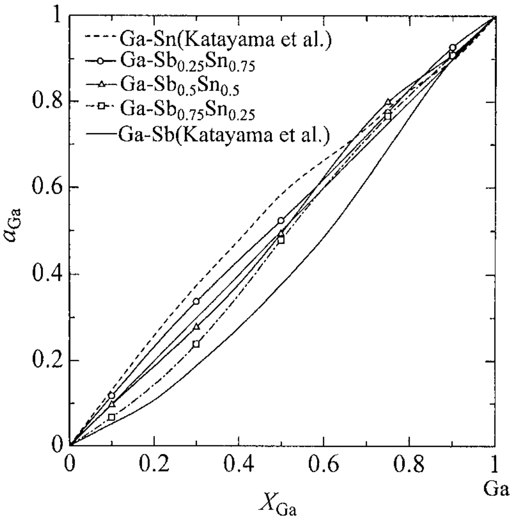

Fig. 4. Activity of gallium in the pseudo-binary Sb_ySn_{1-y}–Ga system at 1073 K.

lower concentration region of Ga, but in the Ga-rich and Sn-poor region the isoactivity curves go toward Sb side, contrary to the cases of Ga–Sb–Bi [1] and Ga–Sb–In [1] alloys. Fig. 4 shows the activity curves along the quasi-binary Sb_ySn_{1-y}–Ga (y=0.25, 0.5, 0.75) systems with those of the binary Ga–Sn and Ga–Sb systems. It can be seen that, at lower Ga concentrations, the activity of Ga changes from negative to positive deviations from the ideal behavior, with increasing Sn concentration; whereas, in the region of $X_{Ga}\geq 0.6$, the activity of Ga shows positive deviations in the ternary alloys studied.

4. Discussion

Recently, Chou [10] proposed a general solution model for predicting ternary thermodynamic properties only from the three related binary systems by using the selected binary compositions closely related to the ternary compositions. (For details, see Ref. [10].) As a result, excess Gibbs free energies of mixing ΔG^{XS} can be represented by Eq. (2).

$$\begin{aligned}\Delta G^{XS} = {} & \Delta G^{XS}_{12} X_1X_2/\{(X_1+\xi_{12}X_3)(X_2 \\ & + (1-\xi_{12})X_3)\} + \Delta G^{XS}_{31}X_3X_1/ \\ & \{(X_3+\xi_{31}X_2)(X_1+(1-\xi_{31})X_2)\} \\ & + \Delta G^{XS}_{23}X_2X_3/\{(X_2+\xi_{23}X_1)(X_3 \\ & + (1-\xi_{23})X_1)\} \end{aligned} \qquad (2)$$

where $X_{1(12)}=x_1+x_3\xi_{12}$; $X_{3(31)}=x_3+x_2\xi_{31}$; $X_{2(23)}=x_2+x_1\xi_{23}$, ξ_{ij} is the similarity coefficient, ΔG^{XS}_{ij} the excess Gibbs free energy of mixing in the i–j binary system, $X_{i(ij)}$ the mole fraction of component i in the i–j binary system and the range of $X_{1(12)}$ varies from x_1 to (x_1+x_3), and x_i the mole fraction of component i in the ternary system. In order to calculate the value of ΔG^{XS} from Eq. (2) binary data for Ga–Sb [1], Ga–Sn [1] and Sn–Sb [1] are fitted to the Redlich–Kister presentation by Eqs. (3) and (4).

$$\Delta G^{XS} = X_iX_j\sum(X_i-X_j)^vL^{(v)}_{ij}(T) \qquad (3)$$

$$L^{(v)}_{ij}(T) = a^{(v)}_{ij} + b^{(v)}_{ij}T \qquad (4)$$

From the experimental data, ΔG^{XS}-values were calculated in the 1000–1200 K range at intervals of 50 K , and the fitting parameters, shown in Table 2, were obtained. By use of these parameters the experi-

Table 2
Parameters for excess Gibbs free energy of mixing in liquid binary systems in Eqs. (3) and (4)

i	j	v	$a^{(v)}_{i,j}$	$b^{(v)}_{i,j}$	Temperature range/K
Ga	Sb	0	−832.80	−6.6885	1000–1200
		1	5598.30	−6.6301	
		2	−120.56	−1.1081	
Sn	Ga	0	16792.00	−12.1380	1000–1200
		1	−15241.00	13.0650	
		2	5651.50	−5.2132	
Sb	Sn	0	−4855.50	−1.6688	1000–1200
		1	1092.70	−1.1787	
		2	1752.80	−0.7129	

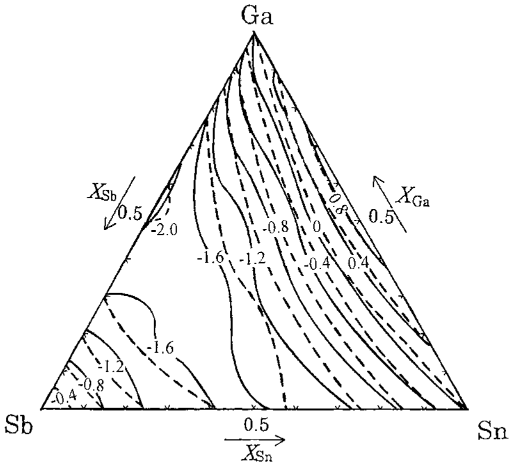

Fig. 5. Excess Gibbs energy of mixing of Ga–Sb–Sn alloys (ΔG^{XS}/kJ mol^{-1} K^{-1}) at 1073 K.; (———) this work; and (- - -) calculated values by use of Chou's model.

mental ΔG^{XS}-values of Ga–Sb alloys [1] can be reproduced with the maximum deviation of 127 J/mol(−8%), except X_{Ga}=0.9 where the largest deviation (211 J/mol) is found. The experimental data of Ga–Sn [1] are reproduced within ±27 J/mol(5%) in the entire composition range. The experimental data of Sb–Sn alloys [11] are reproduced with the maximum deviation of −46 J/mol (±8%). These values are applied to Eq. (2) and the obtained isovalues of ΔG_{XS} are shown in Fig. 5 as the dotted lines. The results in this study, presented as the solid lines, are obtained by use of the following Darken equation.

$$\Delta G^{XS} = (1 - X_{Ga})[\Delta G^{XS}(X_{Ga} = 0)]_{(X_{Sb}/X_{Sn}=k)} + RT(1-X_{Ga})\left[\int_{X_{Ga}=0}^{X_{Ga}=X_{Ga}} \alpha_{Ga}\mathrm{d}X_{Ga}\right]_{X_{Sb}/X_{Sn}=k} \quad (5)$$

Another equation by Darken can be used to calculate ΔG^{XS} based on the two binary data of Ga–Sb, Ga–Sn and ternary data along the pseudo-binary Sb_iSn_j–Ga system, but in view of the consistency between the binary data and derived values, Eq. (5) is used in this study. From this figure, it is found that the experimental data are in agreement with the derived values by using the Chou method on the Sb-poor side, but in the Sb-rich region the agreement is not good. One of the reasons may be based on the lack of the experimental data points in this region, but the precise reason is not clear.

5. Conclusions

The emf of the galvanic cells with the solid electrolyte ($ZrO_2(+Y_2O_3)$) was measured in the 1050–1150 K range to derive the activity of Ga for liquid Ga–Sb–Sn alloys by using of Ga,Ga_2O_3 as reference electrode. The following results have been obtained:

The activity curves of Ga show negative-to-positive deviations from the ideal behavior, with increasing Sn concentrations in the lower concentrations of Ga, and in the higher concentrations where $X_{Ga} \geq 0.6$, the activity of Ga in the ternary alloys shows positive deviations from the ideal behavior. Combining the binary data for Ga–Sn and Ga–Sn alloys with the ternary data in this study, isoactivity curves in the whole composition range of the ternary system are obtained. By using the Darken method, excess free energies of mixing in the ternary system can be calculated, and the results are compared with the model calculation proposed by Chou based on the three binary data.

Acknowledgements

The authors would like to express their appreciation to Prof. T. Iida for his interest in this work.

References

[1] I. Katayama, T. Nakai, T. Inomoto, Z. Kozuka, Mater. Trans. JIM. 30 (1989) 354 (for GaAs–InAs(s)); I. Katayama, T. Inomoto, Z. Kozuka, T. Iida, Mater. Trans. JIM. 32 (1991) 169 (for ZnTe–CdTe(s)); I. Katayama, T. Inomoto, Y. Kuwaki, Z. Kozuka, T. Iida, Netsu Sokutei 18 (1991) 53 (for Zn–Te); I. Katayama, J. Nakayama, T. Nakai, Z. Kozuka, Trans. JIM, 28 (1987) (for Ga–Sb(l), Ga–Te(l)); I. Katayama, J. Nakayama, T. Ikura, Z. Kozuka, T. Iida, Mater. Trans. JIM 34 (1993) 792 (for Ga–Sb–Bi); I. Katayama, J. Nakayama, T. Ikura, T. Tanaka, Z. Kozuka, T. Iida, J. Non-Cryst. Solids 156-158 (1993) 393 (for Ga–Sb–In); I. Katayama, T. Ikura, K. Maki, T. Iida, Mater. Trans. JIM 36 (1995) 41 (for Ga–Sb–Te); I. Katayama, K. Maki, M. Nakano, T. Iida, Mater. Trans. JIM 37 (1996) 988 (for Ga–Sn); I. Katayama, K. Maki, Y. Fukuda, A. Ebara, T. Iida: Mater. Trans. JIM 38 (1997) 119 (for Zn–Cd).

[2] T.J. Anderson, T.L. Aselage, L.F. Donaghey, J. Chem. Thermodyn. 15 (1983) 927.
[3] C. Bergman, M. Laffitte, Y. Muggianu, High Temp.-High Pressures 6 (1974) 927.
[4] A. Zajaczkowski, J. Botor, Z. Metall. 85 (1994) 472.
[5] V.N. Danilin, S.P. Yatsenko, Izv. Akad. Nauk SSSR, Metall 5 (1968) 14.
[6] C. Bergman, PhD Thesis, Universite de Provence, 1972.
[7] J. Anderson, I. Ansara, J. Phase Equilib. 13 (1992) 181.
[8] R.O. Suzuki, D. Risold in Kyoto University, personal communication.
[9] B. Predel, J. Less-Common Met. 7 (1964) 347.
[10] K.-C. Chou, CALPHAD 19 (1995) 315; (20) (1996) 395.
[11] T. Tanaka, I. Katayama, S. Akai, Y. Fukuda, Y. Hattori, T. Iida, Mater. Trans. JIM, to be published.