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THERMOCHEMICAL PROPERTIES OF SOME LIQUID III-V ALLOYS

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SUMMARY

Heat contents of the Ga-P ,In-P ,Ga-As and In-As systems were measured by a drop-calorimeter in the respective concentration ranges of X_P=0.02 to 0.1, X_P=0.05 to 0.5, X_{As}=0.05 to 0.5 and X_{As}=0.05 to 0.5, and in the temperature ranges of 800 to 1550K. The enthalpies of fusion for InP, GaAs and InAs were determined as 44.09 ±0.09, 53.36±0.10 and 37.92 ±0.14kJ g-atom^{-1}, respectively, at the corresponding melting points of 1340 ±1, 1514 ±1 and 1221 ±1K. A thermodynamic analysis method was applied to calculate thermodynamic quantities such as the Gibbs free energies of mixing in the liquid Ga-P, In-P, Ga-As and In-As systems. An optimization of experimental data for these systems were carried out, and the coefficients for the excess Gibbs free energies of mixing for the liquid phase were derived in this study.

INTRODUCTION

The III-V systems (i.e. Ga-As, In-As, Ga-P and In-P) are of considerable technological interest due to the semiconducting properties of the compounds GaAs, InAs, GaP and InP. A knowledge of the phase equilibria and thermodynamic properties of these systems is of importance for growth of III-V crystals by liquid phase epitaxy (LPE) or by other means. Conventional methods such as vapour pressure measurement ,gas equilibration and e.m.f measurement are convenient for determining the thermodynamic properties of mixtures, but they are not applicable to the III-V systems at high temperature due to the significantly high vapour pressure as well as a complexity of the vapour species. The thermodynamic quantities of liquid binary systems can be obtained by the calorimetric method using a thermodynamic analysis method which was developed by Oelsen (ref.1). Following a study on the Fe-S system (ref.2), this method was conducted for the Ga-P, In-P, Ga-As and In-As systems in the present study,using a drop-calorimeter as an experimental apparatus. Based on the obtained thermodynamic data, a set of coefficients are established with which thermodynamic quantities including the Gibbs free energy of mixing can be derived.

PRINCIPLES OF THE THERMODYNAMIC ANALYSIS METHOD

Using a thermodynamic analysis method (ref.1), integral molar quantities

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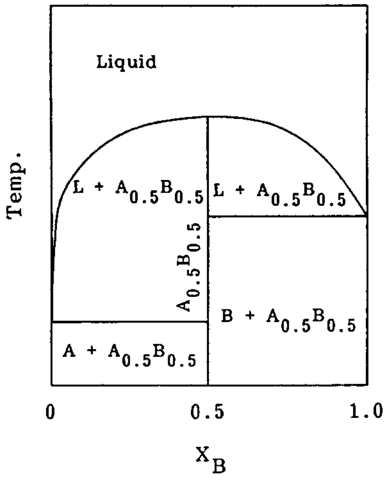

Fig. 1. Schematic illustration of phase diagram for the III-V alloy system.

such as the Gibbs free energy of mixing and heat of mixing at a given temperature are obtained as a function of composition on the basis of a heat content-temperature-composition ternary diagram, and the partial molar quantities are derived by use of a tangent-intercept method. The principles of thermodynamic analysis method are summarized as follows. The heat content, J_T, is defined as

$$J_T = H_T - H_\theta \tag{1}$$

where H_T and H_θ are the enthalpies of a specimen at T K and a specified reference temperature, θ K, respectively. On the basis of the second law of the thermodynamics, we can obtain the following equation :

$$T\int_{1/\theta}^{1/T} J_T \, d(1/T) + H_\theta - TS_\theta = H_T - TS_T \tag{2}$$

By applying eq.(2) to the pure components A,B and a mixture of the mole fraction X of the component A, the Gibbs free energy of mixing, $\Delta G^{mix}_{X,T}$, at T K is given by eq.(3).

$$\begin{aligned}\Delta G^{mix}_{X,T} = {} & T[\int_{1/\theta}^{1/T} J_T \, d(1/T) - (1 - X)\int_{1/\theta}^{1/T} J_{A,T} \, d(1/T) \\ & - X\int_{1/\theta}^{1/T} J_{B,T} \, d(1/T)] + \Delta H^{mix}_{X,\theta} - T\Delta S^{mix}_{X,\theta}\end{aligned} \tag{3}$$

where $\Delta H^{mix}_{X,\theta}$ and $\Delta S^{mix}_{X,\theta}$ are the heat and entropy of mixing at θ K, respectively. Thus, we can derive the Gibbs free energy of mixing solely from the heat contents of the specimen, J_T, if the values of $\Delta H^{mix}_{X,\theta}$ and $\Delta S^{mix}_{X,\theta}$ are known. The phase diagram of the III-V binary system, as shown in Fig.1, forms a

TABLE 1
Enthalpies and entropies of formation at 298K

Substance	ΔH^f_{298} (kJ mol^{-1})	Ref.	ΔS^f_{298} (J mol^{-1} K^{-1})	Ref.
GaP	-122.2	3	45.9	4
InP	-87.9	5	59.8	6
GaAs	-90.8	7	64.2	6
InAs	-62.0	8	74.7	9

stoichiometric compound at X_V=0.50 (V=P or As) and has no primary solid solution. Hence, the term, ($\Delta H^{mix}_{X,\theta} - T\ \Delta S^{mix}_{X,\theta}$), of eq.(3) is given by eq.(4) for mixtures, provided that a temperature below the eutectic is adopted as the reference:

$$\Delta H^{mix}_{X,\theta} - T\ \Delta S^{mix}_{X,\theta} = 1/2\ X\ \Delta H^{f}_{\theta} - 1/2\ T\ X\ \Delta S^{f}_{\theta} \tag{4}$$

where ΔH^f_θ and ΔS^f_θ are the molar enthalpy and entropy of formation of compound at θ K, respectively, and both are well established at moderate temperature, as listed in Table 1 (refs.3-9).

EXPERIMENTAL PROCEDURES

A drop-calorimeter was used as the experimental apparatus, details of which are given in a separate paper (ref.10). The samples were synthesized with gallium or indium (99.9999 purity) and stoichiometric compounds of GaP, InP, GaAs and InAs (99.9999 purity) in a vacuum-sealed silica container at high temperature. About 8g of sample was put into a vacuum-sealed silica ampoule (3g in weight) with an inner diameter of 20 mm and a height of 20 mm to avoid oxidation and evaporation of sample. The sample was held at the hot zone of the furnace and, after reaching thermal equilibrium, dropped into the calorimeter.

RESULTS

HEAT CONTENT FOR III-V BINARY SYSTEMS

Heat contents, $H_T - H_{298.15}$, for the Ga-P, In-P, Ga-As and In-As systems were measured by a drop-calorimeter in the concentration ranges of X_P=0.02 to 0.1, X_P=0.05 to 0.5, X_{As}=0.05 to 0.5 and X_{As}=0.05 to 0.5, and in the temperature ranges of 800 to 1550K. The results are shown three dimensionally in Fig.2 to 5. The deflection points in J_T – T curves correspond to temperatures of phase changes, and we can obtain the phase diagrams by projecting these points on the bottom X-T plane. The enthalpy of fusion for InP, GaAs and InAs were determined as 44.09 ±0.09, 53.36 ± 0.10 and 37.92 ±0.14kJ g-atom^{-1}, respectively, at the corresponding melting points of 1340±1, 1514 ±1 and 1221 ±1K.

THERMODYNAMIC QUANTITIES OF THE LIQUID III-V SYSTEMS

On the basis of eq.(3), the integral molar Gibbs free energy of mixing of the alloy systems can be obtained by integrating J_T over 1/T and combining with the values of enthalpy and entropy of formation of the compound at 298.15K, which are listed in TABLE 1. The values of $T[\int_{1/\theta}^{1/T} J_T d(1/T) -(1-X)\int_{1/\theta}^{1/T} J_{A,T} d(1/T) - X\int_{1/\theta}^{1/T} J_{B,T} d(1/T)]$ (θ=298.15K) obtained at intervals of 100 kelvins are shown in TABLE 2 to 5 for the respective binary alloy system.

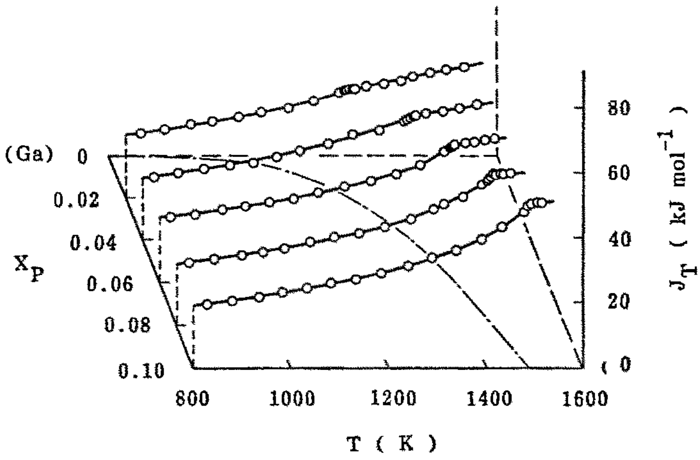

Fig. 2. J_T - X - T diagram for Ga-P system.

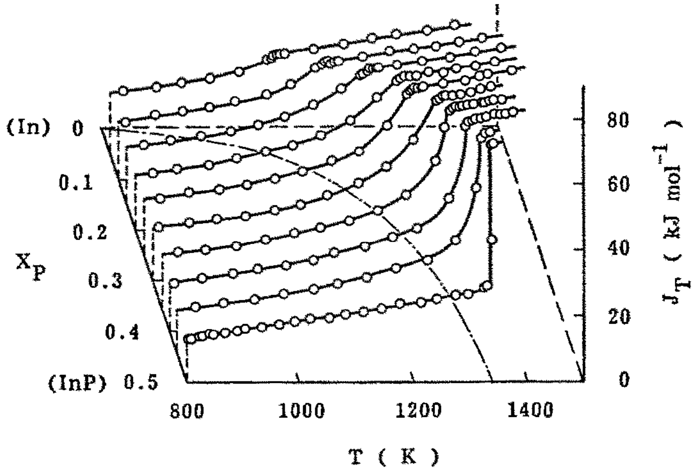

Fig. 3. J_T - X - T diagram for In-P system.

When pure liquid phosphorous and arsenic are chosen as standard state, $\int_{1/\theta}^{1/T} J_T \, d(1/T)$ of those alloying components can be calculated using the heat content data of the condensed phase (ref.3,11).

REDLICH-KISTER POLYNOMIALS

For the convenient use of ΔG^{mix} in calculating phase stability and vapour pressures of the III-V alloys and for its easy utilization in a thermodynamic data-base system, the obtained results were expressed using a Redlich-Kister

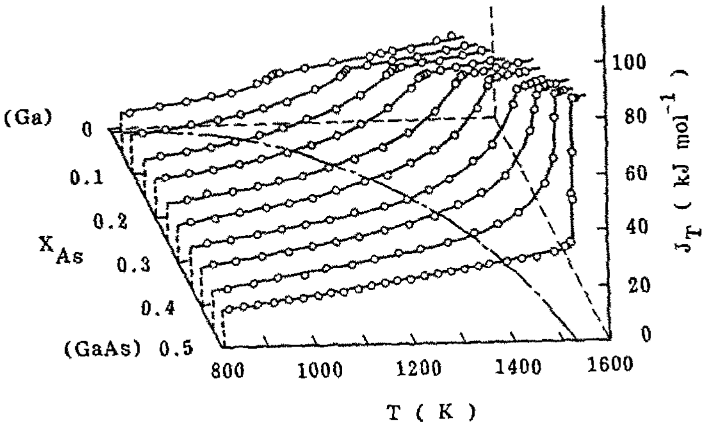

Fig. 4. J_T - X - T diagram for Ga-As system.

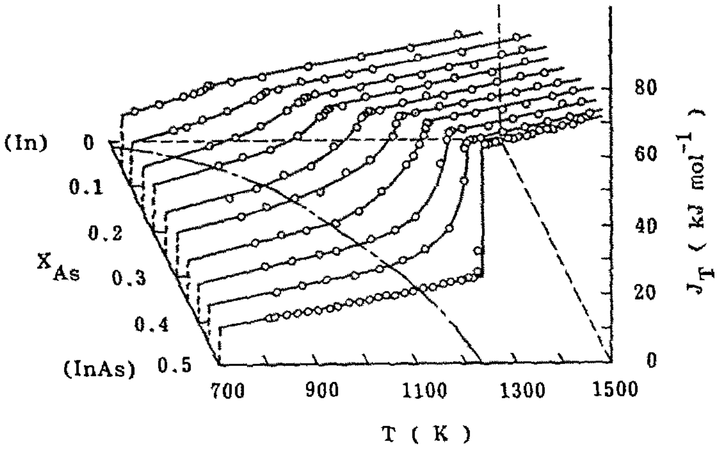

Fig. 5. J_T - X - T diagram for In-As system.

polynomial equation with the order of v.

$$\Delta G^E = X_i X_j \sum_{v=0}^{n} (X_i - X_j)^v L_{ij}^{(v)} (T) \tag{5}$$

$$\Delta G^E = \Delta G^{mix} - X_i R T \ln X_i - X_j R T \ln X_j \tag{6}$$

with $L_{ij}(T) = A_{ij} - B_{ij} T + C_{ij} T (1 - \ln T)$ where i is liquid Ga or In and j is liquid P or As. $L_{ij}(T)$ are non-linear functions of temperature, corresponding to the temperature-dependent values of the enthalpy and entropy

TABLE 2
$f(X,T) = T\ [\ \int_{1/\theta}^{1/T} J_T\ d(1/T) - (\ 1 - X\ ) \int_{1/\theta}^{1/T} J_{A,T}\ d(1/T) - X \int_{1/\theta}^{1/T} J_{B,T}\ d(1/T)\ ]$
for the Ga-P system.

T(K)	f(X,T) (kJ mol^{-1})				
	X_P				
	0.02	0.04	0.06	0.08	0.10
1300	-1.51	-3.01	-4.52	-6.02	-7.53
1400	-1.43	-2.87	-4.30	-5.73	-7.17
1500	-1.36	-2.72	-4.08	-5.44	-6.81
1600	-1.29	-2.58	-3.87	-5.16	-6.44

TABLE 3
$f(X,T) = T\ [\ \int_{1/\theta}^{1/T} J_T\ d(1/T) - (\ 1 - X\ ) \int_{1/\theta}^{1/T} J_{A,T}\ d(1/T) - X \int_{1/\theta}^{1/T} J_{B,T}\ d(1/T)\ ]$
for the In-P system.

T(K)	f(X,T) (kJ mol^{-1})									
	X_P									
	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
1200	-0.02	0.17	0.86	1.49	2.12	2.61	3.25	3.83	4.64	5.55
1300	-0.31	-0.45	0.01	0.52	1.11	1.76	2.89	3.74	4.83	6.27
1400	-0.61	-1.06	-0.89	-0.68	-0.36	-0.02	0.90	1.71	2.94	5.02
1500	-0.90	-1.68	-1.80	-1.88	-1.84	-1.80	-1.14	-0.55	0.51	2.43

TABLE 4
$f(X,T) = T\ [\ \int_{1/\theta}^{1/T} J_T\ d(1/T) - (\ 1 - X\ ) \int_{1/\theta}^{1/T} J_{A,T}\ d(1/T) - X \int_{1/\theta}^{1/T} J_{B,T}\ d(1/T)\ ]$
for the Ga-As system.

T(K)	f(X,T) (kJ mol^{-1})									
	X_{As}									
	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
1200	0.56	1.53	2.44	3.75	4.68	6.10	6.82	8.20	9.27	10.54
1300	0.42	1.78	2.16	3.86	5.06	6.89	7.89	9.69	11.03	12.69
1400	0.29	0.76	1.47	3.24	4.64	7.16	8.51	10.84	12.63	14.83
1500	0.15	0.34	0.77	2.45	3.64	6.28	7.87	10.99	13.62	16.98
1600	0.01	-0.08	0.06	1.66	2.62	5.21	6.67	9.70	12.26	16.07

TABLE 5
$f(X,T) = T\,[\int_{1/\theta}^{1/T} J_T\, d(1/T) - (1 - X)\int_{1/\theta}^{1/T} J_{A,T}\, d(1/T) - X\int_{1/\theta}^{1/T} J_{B,T}\, d(1/T)]$
for the In-As system.

T(K)	f(X,T) (kJ mol^{-1})									
	X_{As}									
	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
1000	-0.55	-0.25	-0.18	0.09	0.74	0.78	1.45	1.85	2.19	2.41
1100	-0.89	-0.83	-1.07	-0.90	-0.04	0.28	1.32	2.07	2.56	2.92
1200	-1.14	-1.22	-1.70	-1.63	-0.98	-0.57	0.71	2.23	3.32	4.37
1300	-1.40	-1.61	-2.34	-2.38	-1.94	-1.70	-0.55	0.94	2.01	3.36
1400	-1.65	-2.01	-2.98	-3.13	-2.91	-2.84	-1.83	-0.36	0.55	1.68

TABLE 6
Coefficients of Redlich-Kister polynomials for Ga-P system.

Power	$L^{(v)} = A^{(v)} - B^{(v)}\,T + C^{(v)}\,T\,(1 - \ln T)$ (J mol^{-1})		
	$A^{(v)}$	$B^{(v)}$	$C^{(v)}$
v = 0	131482.0	120.140	10.1358
v = 1	18990.5	-477.279	12.6635
v = 2	-305208.0	346.795	8.1591
v = 3	34265.0	-447.075	29.4464

TABLE 7
Coefficients of Redlich-Kister polynomials for In-P system.

Power	$L^{(v)} = A^{(v)} - B^{(v)}\,T + C^{(v)}\,T\,(1 - \ln T)$ (J mol^{-1})		
	$A^{(v)}$	$B^{(v)}$	$C^{(v)}$
v = 0	-50121.9	-168.008	22.7663
v = 1	228153.0	-56.784	36.4515
v = 2	-484803.0	365.084	-118.6780
v = 3	533823.0	1262.810	-139.1890

TABLE 8
Coefficients of Redlich-Kister polynomials for Ga-As system.

Power	$L^{(v)} = A^{(v)} - B^{(v)}\,T + C^{(v)}\,T\,(1 - \ln T)$ (J mol^{-1})		
	$A^{(v)}$	$B^{(v)}$	$C^{(v)}$
v = 0	-13387.1	56.993	-6.2087
v = 1	64958.4	137.884	-14.5129
v = 2	-162561.0	-464.847	54.6299
v = 3	0	0	0

TABLE 9
Coefficients of Redlich-Kister polynomials for In-As system.

Power	$L^{(v)} = A^{(v)} - B^{(v)} T + C^{(v)} T (1 - \ln T)$ ($J\ mol^{-1}$)		
	$A^{(v)}$	$B^{(v)}$	$C^{(v)}$
v = 0	-38183.0	-22.884	2.8168
v = 1	-60899.5	-354.242	49.4759
v = 2	-39019.6	-345.959	50.3660
v = 3	0	0	0

of mixing. An optimization program written by Lukas et al.(ref.12) was used to obtain a set of coefficients for the excess Gibbs free energy of mixing, ΔG^E, which are listed in TABLE 6 to 9. It was clarified that the second order (v=2) and third order (v=3) expressions are enough for the Ga-As and In-As systems and the Ga-P, In-P systems, respectively. The mean square error of the regressed ΔG^E from the experimental values for Ga-P, In-P, Ga-As and In-As systems is determined as, respectively, ±8, ±17, ±28, ±21 J mol^{-1}.

CONCLUSIONS

A thermodynamic analysis method using a drop-calorimeter was applied to the liquid III-V systems to determine the integral Gibbs free energy of mixing. Based on the obtained free energy of mixing, the coefficients for describing the excess Gibbs free energy of mixing for these liquid alloy systems were derived, which will be useful for calculating the phase stability and thermodynamic properties of multi-component systems such as the Ga-In-As and Ga-In-P ternary systems.

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