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THERMODYNAMIC EVALUATION OF THE Bi–Ge SYSTEM

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ABSTRACT

Available experimental information concerning thermodynamic properties and phase equilibria data has been compiled for the assessment of new self-consistent parameters of thermodynamic models for liquid and solid phases in the Bi–Ge system. These coefficients have been optimized using a program developed by Lukas et al., Calphad, 1 (1977) 225.

The phase diagram and the enthalpy of mixing of the liquid phase have been calculated and compared with the experimental values using the THERMODATA software.

A very satisfactory agreement has been obtained by using five optimized coefficients with a simple substitutional model for the liquid and the solid solution phases.

INTRODUCTION

This evaluation follows those of the Au–Sn, Au–Bi, Ag–Ge and Ag–Si systems, which have been previously assessed in the framework of a Scientific Group Thermodata Europ (S.G.T.E.) project in order to produce data for selected systems and to supply specialized data banks.

SHORT PRESENTATION OF THE DIFFERENT PHASES

According to the phase diagram reported by Hansen and Anderko [2], there is no compound in this system.

The various phases, with the symbols used, are listed below.

Solution phases

(1) Liquid phase (L).

(2) Terminal rich Bi solid solution with a rhombohedral (A7) structure isotypic with As. Stöhr and Klemm [3] reported that qualitative X-ray investigations indicated solid solubility of Ge in Bi of about 1.5 at.% Ge at

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$T = 523$ K, after annealing for several months at this temperature and quenching (rho).

(3) Terminal rich Ge solid solution with a diamond (A4) structure. In ref. 3 a solid solubility of Bi in Ge of about 2 at.% Bi was reported at $T = 523$ K using the previously described technique (dia).

EXPERIMENTAL INFORMATION

Phase diagram

The phase diagram of the Bi–Ge system is a simple eutectic. It is the result of thermal analysis work of Stöhr and Klemm [3] and Ruttewit and Masing [4]. In both cases, the data points of the liquidus curve have been taken from small diagrams and reported in ref. 2. The liquidus has also been determined by Thurmond [5], by calculation of the composition points based on the weight loss of massive ingots and by Schweitzer and Weeks [6] by chemical analysis of equilibrated specimens.

The solubility of Ge in liquid Bi, after refs. 5 and 6, has been reported by Elliott [7].

According to refs. 3 and 4, the eutectic consists of practically pure Bi at $T = 544.15$ K.

The eutectic composition has been calculated as 0.02 at.% Ge [5] and 0.03 at.% Ge [6]. Trumbore et al. [8] have determined the solid solubility of Bi in Ge by Hall effect measurements on diffusion specimens at $T = 1138$ K and have given approximate values at different temperatures. Solubilities are 2.3×10^{-5} at.% at $T = 1209$ K, 1.4×10^{-4} at.% at $T = 1183$ K (maximum), 8.0×10^{-5} at.% at $T = 1138$ K and 2.3×10^{-5} at.% at $T = 1033$ K. These values are very small compared with the value of 2 at.% at $T = 523$ K given in ref. 3. Similarly, the value of the solubility of Ge in solid Bi of 1.5 at.% at $T = 523$ K given in ref. 3 seems improbable.

Thermodynamic properties

Liquid alloys

The enthalpies of mixing of the liquid alloys of the binary system Bi–Ge have been determined directly with a high temperature calorimeter at $T = 1273$ K in the composition range $x_{Ge} = 0.1$–0.8 by Predel and Stein [9].

EVALUATION METHOD

The Gibbs energies of the different solution phases were described using a simple substitutional model. The excess Gibbs energies were derived by a

Redlich–Kister polynomial equation of the form

$$\Delta^{E}G = x_{Bi}x_{Ge}\sum_{\nu=0}^{n}(x_{Bi}-x_{Ge})L^{(\nu)}_{Bi,Ge}(T) \tag{1}$$

where the coefficients $L^{(\nu)}_{Bi,Ge}$ (T) are linear functions of the temperature

$$L^{(\nu)}_{Bi,Ge}(T) = a^{(\nu)}_{Bi,Ge} + b^{(\nu)}_{Bi,Ge}\cdot T \tag{2}$$

i.e. $a^{(\nu)}_{Bi,Ge}$ and $b^{(\nu)}_{Bi,Ge}$ correspond to the independent values of the enthalpy and the excess entropy of mixing.

The values used for the lattice stabilities of the pure elements where taken from the S.G.T.E. assessment [10] for the stable solid and liquid phases. The following values were used [10]

$${}^{0}G^{L}_{Bi} - {}^{0}G^{rho}_{Bi} = 11245.936 - 20.637366T - 5972582.889\times10^{-25}T^{7}$$

$298.15 < T < 544.52$

$${}^{0}G^{L}_{Bi} - {}^{0}G^{rho}_{Bi} = 11336.361 - 20.811775T - 166.491\times10^{23}T^{-9}$$

$544.52 < T < 3000.00$

$${}^{0}G^{L}_{Ge} - {}^{0}G^{dia}_{Ge} = 37141.633 - 30.684649T + 85676.079\times10^{-25}T^{7}$$

$298.15 < T < 1211.5$

$${}^{0}G^{L}_{Ge} - {}^{0}G^{dia}_{Ge} = 36791.565 - 30.381247T + 861075.152\times10^{23}T^{-9}$$

$1211.5 < T < 3200.00$

For the metastable phases (Bi dia and Ge rho), required to express the excess properties of mixing of the dia and rho solution phases, no value has been found in the literature for the lattice stabilities. For this reason, a value equal to $-30.0T$ (similar to Kaufman's [11]) for the difference between the liquid and the metastable phase was assumed and was combined with a linear approximation for the difference between the liquid and the stable phase, in order to obtain the difference between the stable and metastable solid [10,11]

$$\begin{aligned}{}^{0}G^{dia}_{Bi} - {}^{0}G^{rho}_{Bi} &= 11296.80 - 20.746345T + 30.0T\\ &= 11296.80 + 9.253655T\\ {}_{0}G^{rho}_{Ge} + {}^{0}G^{dia}_{Ge} &= 36944.72 - 30.495023T + 30.0T\\ &= 36944.72 - 0.495023T\end{aligned}$$

The different parameters of the solution phases were optimized using a program developed by Lukas et al. [1] which takes into account all the available information and accuracy.

RESULTS AND DISCUSSION

Table 1 shows the optimized parameters of the excess Gibbs energy for the liquid and the solid solution phases referred to the pure elements having

TABLE 1

Excess Gibbs energy for the liquid and solid solution phases of the Bi–Ge system

Phase	ν	$a^{(\nu)}_{\mathrm{Bi,Ge}}$ (J)	$b^{(\nu)}_{\mathrm{Bi,Ge}}$ (J K^{-1})
Liquid	0	12883.8	2.32905
	1	534.4	0
rho	0	100000.0	0
dia	0	87000.0 (1) Adjusted to reproduce the estimated value at $T = 1183$ K of ref. 8.	0
		95000.0 (2) Adjusted to reproduce the experimental value at $T = 1138$ K of ref. 8.	0

$\Delta^{E}G = x_{\mathrm{Bi}}x_{\mathrm{Ge}}\sum_{\nu=0}^{n}(x_{\mathrm{Bi}} - x_{\mathrm{Ge}})L^{(\nu)}_{\mathrm{Bi,Ge}}\ (T)$; $L^{(\nu)}_{\mathrm{Bi,Ge}}\ (T) = a^{(\nu)}_{\mathrm{Bi,Ge}} + b^{(\nu)}_{\mathrm{Bi,Ge}} \cdot T\ (\nu = 0, 1)$.

the same structure as the corresponding phase. A first-order polynomial equation was used for the liquid, and a zero-order polynomial equation was used for the solid solutions. The parameters of the solid solutions were estimated to reproduce a negligible solid solubility of Ge in Bi and a

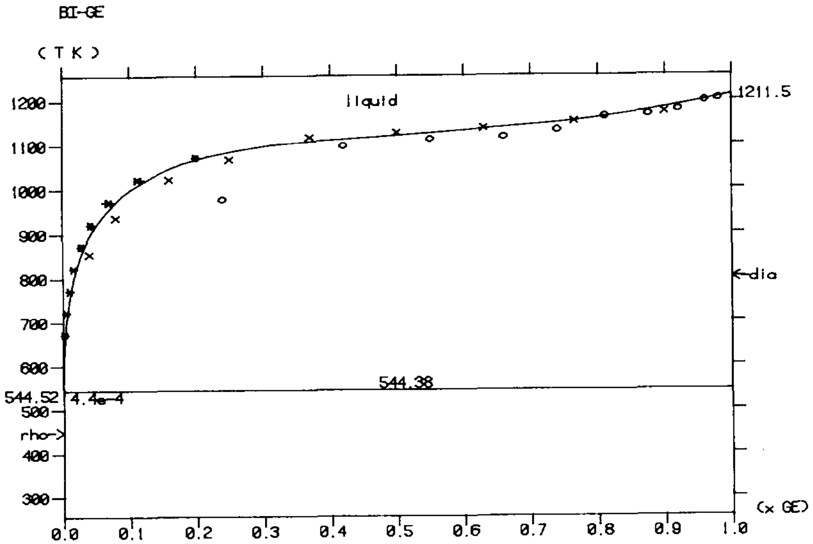

Fig. 1. Comparison between the calculated phase diagram of the Bi–Ge system and selected experimental data. Key: ○, Ruttewit and Masing [4]; ×, Stöhr and Klemm [3]; +, Thurmond [5]; *, Elliott [7].

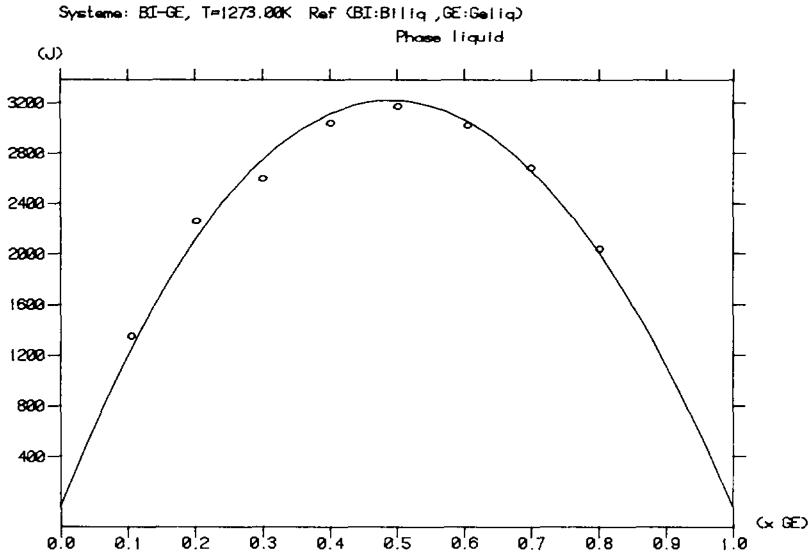

Fig. 2. Calculated enthalpy of mixing of the liquid phase of the Bi–Ge system at $T = 1273$ K compared with selected experimental data. Key: ○, Predel and Stein [9].

maximal estimated solid solubility of Bi in Ge equal to $x_{\mathrm{Bi}} = 1.4 \times 10^{-6}$ at $T = 1183$ K in the first case, and the experimental value $x_{\mathrm{Bi}} = 8 \times 10^{-7}$ at $T = 1138$ K (after ref. 8) in the second case.

Figure 1 shows the comparison between the calculated phase diagram and selected experimental data. The agreement is quite satisfactory. The calculated composition and temperature for the eutectic reaction are $x_{\mathrm{Ge}} = 0.00044$ and $T = 544.38$ K, which can be compared with the calculated values in refs. 5 and 6 of $x_{\mathrm{Ge}} = 0.0002$ and 0.0003 and experimental temperature $T = 544.15$ K.

The calculated solid solubility of Ge in Bi is $x_{\mathrm{Ge}} = 5.2 \times 10^{-8}$ at $T = 523$ K, and the calculated solid solubilities of Bi in Ge are $x_{\mathrm{Bi}} = 1.38 \times 10^{-6}$ at $T = 1183$ K, 1.71×10^{-7} at $T = 1209$ K, 1.95×10^{-6} at $T = 1138$ K, 9.7×10^{-7} at $T = 1033$ K and 2.84×10^{-9} at $T = 523$ K, in the first case. The agreement with the experimental values of ref. 8 is good at $T = 1183$ K, but the maximum appears at a lower temperature. If we adjust the parameter in order to reproduce the experimental value at $T = 1138$ K, the following calculated solubilities of Bi in Ge are derived: $x_{\mathrm{Bi}} = 6.0 \times 10^{-7}$ at $T = 1183$ K, 8.2×10^{-8} at $T = 1209$ K, 8.5×10^{-7} at $T = 1138$ K, 3.6×10^{-7} at $T = 1033$ K and 1.8×10^{-7} at $T = 523$ K.

Figure 2 shows the comparison between the calculated enthalpy of mixing of the liquid phase at $T = 1273$ K and the experimental data of ref. 9. The agreement is very good.

SUMMARY

A complete thermodynamic description of the Bi–Ge system is presented. Various solution phases of the system have been modelled and a set of self-consistent parameters has been obtained. Comparison between the available experimental information and the calculated values is quite satisfactory. Further experimental work needs to be undertaken in order to determine more accurately the solid solubilities in the solid state. Otherwise the "lattice stabilities" of Bi dia and Ge rho have to be evaluated by appropriate theoretical work.

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