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COMPARATIVE THERMODYNAMIC INVESTIGATION OF BINARY Ga–Bi SYSTEM
Experimental determination of enthalpies of mixing and activity estimation for liquid Ga–Bi alloys

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The results of experimental and analytical thermodynamic investigation of binary Ga–Bi system are presented in this paper. Integral molar enthalpies of mixing for liquid Ga–Bi alloys were obtained using quantitative differential thermal analysis. Activities of bismuth in the entire composition range and temperature interval 573–1073 K, were calculated by Zhang–Chou's method for binary systems having two liquid or solid coexisting phases in combination with other Chou's method developed for simple eutectic systems. Activities of gallium were derived from Gibbs–Duhem equation. Comparison between experimental, calculated values and existing literature data shows good agreement.

Keywords: activity, enthalpy of mixing, Ga–Bi liquid alloys, quantitative DTA, thermodynamics

Introduction

Having in mind that interfacial phase transitions, like surface and grain boundary melting, surface freezing or wetting transitions are of actual interest in different fields [1, 2], Ga–Bi alloys became recently a subject of numerous investigations [3–5], because such phase transitions have been observed in this gallium-based binary system.

For better understanding of these phenomena, an accurate knowledge of the thermodynamic properties and phase diagram is essential. The Ga–Bi system, given in Fig. 1 [6], is typical for miscibility gap existence, and below the monotectic line (495 K, x_{Ga}=0.385) a Ga-rich liquid coexists with a solid Bi phase. At temperature 302.48 K and composition x_{Bi}=0.0022 eutectic occurs in this system, also.

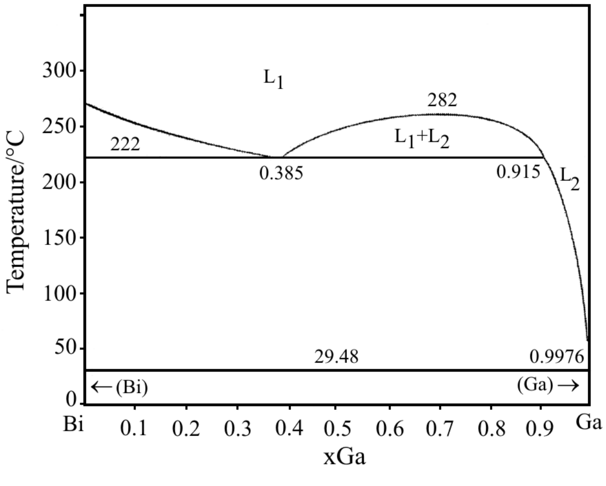

Fig. 1 Phase diagram of Ga–Bi system [6]

While Ga–Bi phase diagram is well known, thermodynamic properties of this system are not so numerous. The heats of mixing of liquid Ga–Bi alloys were measured by using high temperature calorimeters by Predel *et al*. [7], Gambino *et al.* [8] and Moser and Rzyman [9]. Yatshenko and Danilin [10] measured activities using a fused salt emf method at temperatures 680 and 870 K. Gambino *et al.* [11] determined heats of mixing of liquid Ga–Bi alloys and Katayama *et al*. [12] measured activities of gallium by emf method using zirconia as solid electrolyte at 1073 K. There is also a theoretical thermodynamic consideration of Ga–Bi alloys by Akinlade *et al*. [13], done in order to correlate the bulk and surface properties of mixing in Ga–Bi-In system. The most recent thermodynamic study of Ga–Bi system is given by Katayama *et al*. [14], who calculated Redlich–Kister polynomial equation parameters for Ga–Bi system in the 1000–1200 K temperature range, while Khairulin *et al*. [15], used X-ray analysis for liquid alloys and determined the diffusion coefficient and borders of the liquid miscibility gap.

Results of thermodynamic analysis of Ga–Bi alloys obtained by quantitative differential thermal analysis (DTA) [16–18] and thermodynamic calculation methods [19–20] are presented in this paper. Compari-

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son with existing literature data was also done, in order to evaluate the accuracy of applied methods.

Experimental

Quantitative differential thermal analysis [16–18] was used for experimental determination of enthalpies of mixing for liquid Ga–Bi alloys. This technique has been described in details in [16].

The metals used in this work – gallium and bismuth were in granulated form (99.99 mass% purity), produced by Merck, Germany. The alloys in Ga–Bi system with x_{Ga}=0, 0.06, 0.264, 0.393, 0.506, 0.518, 0.649, 0.722, 0.833, 0.883, 0.948 and 1, were investigated experimentally. The volume of all samples was constant 0.2 cm^3. The heating rate in all cases was 10 K min^{-1}.

Theoretical basis

Quantitative differential thermal analysis

The main theoretical principle of DTA application in quantitative calorimetric determination [16–18] is given by following analytical expression

$$Q=gK_{\mathrm{s}}\int T\mathrm{d}t \tag{1}$$

where are Q – reaction heat, gK_{s} – calibration constant of the apparatus and $\int T\mathrm{d}t$ – area of DTA peak.

Every measurement run done in this work is characterized by appearance of two peak areas, recorded on single DTA curve. Obtained DTA peak areas are proportional to the corresponding heat effects.

The first DTA peak is due to the heat of melting of the metal with lower melting point. The total heat absorbed by the sample in the melting process and measured by DTA can be represented as:

$$\Delta H_{\mathrm{I}}=gK_{\mathrm{s}}(M_1)P_1 \tag{2}$$

where ΔH_{I} is heat of melting of metal M_1; $gK_{\mathrm{s}}(M_1)$ is calibration constant of the apparatus in respect to the metal M_1; P_1 is obtained peak area.

The second DTA peak includes two heat effects: heat of melting of metal with higher melting point and heat of mixing of two metals. The total heat effect proportional to the second peak area is:

$$\Delta H_{\mathrm{II}}=gK_{\mathrm{s}}(M_2)P_2+gK_{\mathrm{s}}(\mathrm{alloy})P_{\mathrm{mix.}} \tag{3}$$

where ΔH_{II} is total heat which include heat of melting of metal M_1 and heat of mixing of metals M_1 and M_2; $gK_{\mathrm{s}}(M_2)$ is calibration constant of the apparatus in respect to the metal M_2; P_2 is obtained peak area due to the heat of melting of metal M_2; gK_{s}(alloy) is calibration constant of the apparatus in respect to the alloy M_1–M_2; $P_{\mathrm{mix.}}$ is part of second peak area due to the heat of mixing of metals M_1 and M_2.

Thermodynamic calculation

The representative phase diagram for calculations done in this work is shown in Fig. 2.

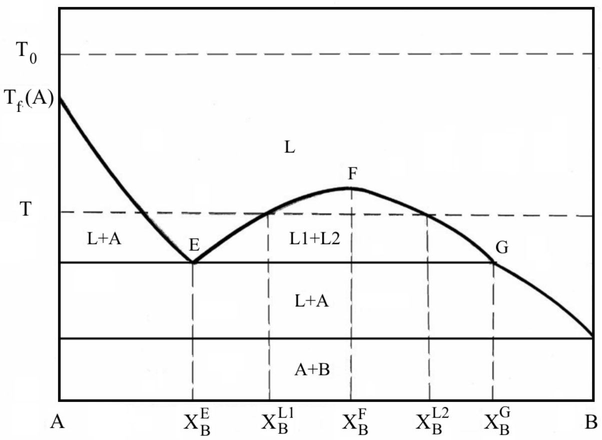

Fig. 2 The representative phase diagram A–B

Determination of activities of component A at temperature T_0 in the liquid mono-phase region and in the whole composition range is possible with application of different analytical methods [19, 20].

First of applied methods is developed for the simple eutectic systems [19] and in this work it is used for the compositions of Ga–Bi alloys outside of the miscibility gap. In the composition regions from x_{B}=0 to $x_{\mathrm{B}}=x_{\mathrm{B}}^{\mathrm{E}}$ and from $x_{\mathrm{B}}=x_{\mathrm{B}}^{\mathrm{G}}$ to x_{B}=1, activities of component A at the fixed temperature T_0 can be calculated by the following Eq. (4) [19]:

$$\ln\gamma_{\mathrm{A}}(x_{\mathrm{A}},T_0)=-\frac{\sigma}{\sigma_0}\left(\frac{\Delta_{\mathrm{fus}}G^0_{\mathrm{m,A(T)}}}{RT}+\ln x_{\mathrm{A}}\right) \tag{4}$$

where $\gamma_{\mathrm{A}}(x_{\mathrm{A}},T_0)$ activity coefficient of component A at investigated temperature T_0 and x_{A} mole fraction; $\Delta_{\mathrm{fus}}G^0_{\mathrm{m,A(T)}}$: melting molar Gibbs energy of component A at temperature T; T – temperature at the liquidus line for x_{A} mole fraction and:

$$\sigma=\frac{T}{1-T/\theta} \tag{5}$$

$$\sigma_0=\frac{T_0}{1-T_0/\theta} \tag{6}$$

$$\theta=\frac{H_{\mathrm{i}}}{S_{\mathrm{i}}^{\mathrm{E}}}=3000\,K \tag{7}$$

(Richardson assumption [21])

It should be added, that equation, similar to Eqs (5), (6), states for the conditions of composition presented in point *E* (Fig. 2): $\sigma_E = T_E/(1-T_E/\theta)$.

In the composition interval involving two coexisting liquid phases L_1+L_2, activities of component A at the fixed temperature T_0 in the liquid mono-phase region can be obtained through the following Eq. [20]:

From $x_B = x_B^E$ to $x_B = x_B^F$ the formula for calculation of activity coefficient for component A at T_0 is given as:

$$\ln\gamma_A(x_A^{L_1}, T_0) = \ln\gamma_A(x_A^E, T_0) + \\ + \int_{\frac{\sigma_E}{\sigma_0}}^{\frac{\sigma}{\sigma_0}} \frac{1}{x_B^{L_1} - x_B^{L_2}} \left[x_B^{L_1}\sum{}^{L_2} - x_B^{L_2}\sum{}^{L_1}\right] \\ d\left(\frac{\sigma}{\sigma_0}\right) - \left(\frac{\sigma}{\sigma_0}\ln x_A^{L_1} - \frac{\sigma_E}{\sigma_0}\ln x_A^E\right) \tag{8}$$

and in the composition interval from $x_B = x_B^F$ to $x_B = x_B^G$:

$$\ln\gamma_A(x_A^{L_2}, T_0) = \ln\gamma_A(x_A^{L_1}, T_0) - \frac{\sigma}{\sigma_0}\ln\frac{x_A^{L_2}}{x_A^{L_1}} \tag{9}$$

where $\gamma_A(x_A^{L_1}, T_0)$ – activity coefficient of component A at temperature T_0 and $x_A^{L_1}$ mole fraction; $\gamma_A(x_A^E, T_0)$ – activity coefficient of component A at temperature T_0 and x_A^E mole fraction $\gamma_A(x_A^{L_2}, T_0)$ – activity coefficient of component A at temperature T_0 and $x_A^{L_2}$ mole fraction and:

$$\sum{}^{L_1} = x_A^{L_1}\ln x_A^{L_1} + x_B^{L_1}\ln x_B^{L_1} \tag{10}$$

$$\sum{}^{L_2} = x_A^{L_2}\ln x_A^{L_2} + x_B^{L_2}\ln x_B^{L_2} \tag{11}$$

where *T* is variable temperature along the line of miscibility boundary (Fig. 2).

After the determination of activities for component A in the entire composition interval, activities of component B can be derived using Gibbs–Duhem equation and α-function:

$$\ln a_B = \ln x_B - x_A x_B \alpha_A + \int_0^{x_A} \alpha_A \, dx_A \tag{12}$$

$$\alpha_A = \frac{\ln\gamma_A}{(1-x_A)^2} \tag{13}$$

where γ is the activity coefficient and x is the mole fraction.

Both applied methods are based on phase diagram informations and Richardson assumption [21–23]. Method for the binary systems with a miscibility gap has already been successfully applied to some other gallium based binary systems with a miscibility gap [24]. Comparison between experimental [25, 26] and calculated activities [24] for Ga–Pb and Ga–Tl systems shows that maximal deviation in activity values is ±0.06 in the case of Ga–Pb system and ±0.03 in the case of Ga–Tl system. Good mutual agreement between mentioned results indicates the possibility for the efficient application of this calculation method to Ga–Bi binary system. For that reason, mentioned methods have been adopted for thermodynamic investigation of single liquid phase region in Ga–Bi system.

Results and discussion

Determination of integral molar enthalpy of mixing

In the first part of applied experimental methodology, functional dependence between peak area and adequate heat effect are established. Calibration constants of the apparatus, gK_S for the pure metals were determined by recording a series of DTA curves for the melting process of pure metals with different masses. Using literature data for enthalpies of melting for gallium (5590 J mol^{-1})and bismuth (11300 J mol^{-1}) [27], polynomial dependences between melting enthalpies and masses of pure metals were determined.

Linear dependences were calculated by least squares regression analysis and given together with uncertainty limits:

- for bismuth: total heat ±2.113 (J)=0.1727 (J/mm^2)× peak area (mm^2)
- for gallium: total heat ±1.254 (J)=0.1017 (J/mm^2)× peak area (mm^2)

Determined linear dependences were obtained for pure metals with masses up to 2 g. All investigated alloys were used with approximately same volume of 0.2 cm^3 and masses smaller of 2 g as given in Table 1.

Regarding to already determined fact about existence of a linear dependence of calibration constant on composition for eutectic systems [28], determination of gK_S values for all investigated alloys was done using following relation:

$$gK_s(\text{Ga–Bi alloy}) = x_{Ga}gK_s(\text{Ga}) + x_{Bi}gK_s(\text{Bi}).$$

The second part in the quantitative DTA is determination of the integral molar enthalpy of mixing. During the heating of prepared sample gallium melts at its melting point of 303 K, which is recorded as the first peak at the obtained DTA curve. Further, as heating process goes on, bismuth melts at its melting temperature of 545 K, and at the same time drops and mixes with melted gallium, which is recorded at the second peak in the obtained DTA curve. Characteristic examples of such DTA curves for some of the investigated samples are shown in Fig. 3.

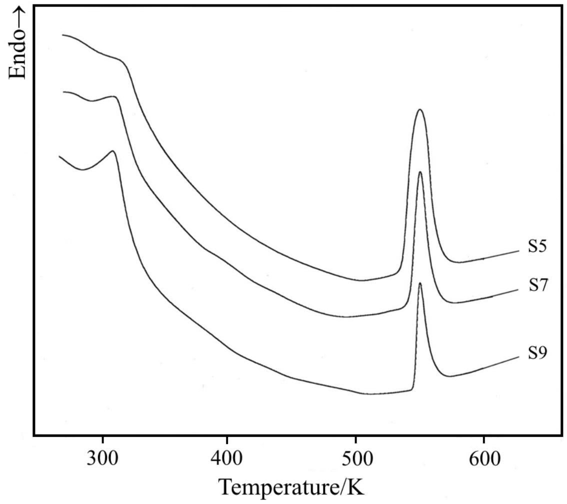

Fig. 3 Characteristic DTA curves for samples S5, S7 and S9

The parts of the second peak areas due to bismuth melting are computed using determined functional dependence between peaks surface and melting heat effect. Those parts were deduced from the overall surfaces of the second peaks to get the contribution of the mixing process.

In order to determine reproducibility and accuracy of the applied method, every experiment was repeated three times. For alloys with higher contents of bismuth, obtained results for integral molar enthalpies of mixing of Ga–Bi liquid alloys were found more scattered. Lower degree of reproducibility reached when larger masses of bismuth were dropping in liquid gallium indicates that the accuracy of the enthalpy of mixing depends of the molar fraction of alloys. Obtained enthalpies of mixing at the temperature of 545 K, together with the standard deviations, are given in Table 1.

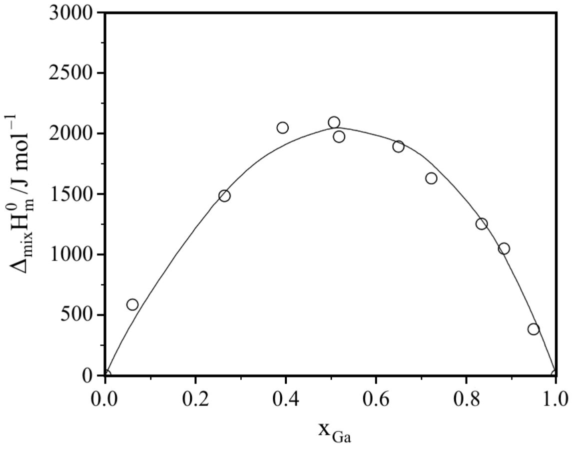

Fig. 4 Comparison of the values for integral molar enthalpies of mixing obtained by quantitative DTA and literature data [11]; ○ – this work and —– [11]

Table 1 Composition, masses and integral molar enthalpies of mixing for experimentally investigated Ga-Bi alloys

Alloy	x_{Ga}	Mass of the alloy/g	$\Delta_{mix}H^0_m$/J mol^{-1}
S1	0.060	1.9335	585±120
S2	0.264	1.8314	1484±278
S3	0.393	1.7615	2045±304
S4	0.506	1.6624	2090±320
S5	0.518	1.6702	1972±235
S6	0.649	1.5176	1891±190
S7	0.722	1.4590	1628±160
S8	0.833	1.3886	1251±102
S9	0.883	1.3762	1047±55
S10	0.948	1.2519	382±32

Comparison between values for the integral molar enthalpies of mixing obtained for Ga–Bi alloys by quantitative DTA and literature data [11] is presented graphically in Fig. 4. It can be noticed that results obtained by quantitative DTA are in accordance with literature data.

Several additional factors have also influence on accuracy of the obtained results and have to be pointed out. The effect of inhomogeneous alloying, caused by the difference of densities between two investigated metals and the absence of attraction between the elements, is one among them. Calculated uncertainty limits (obtained in a process of determination of calibration constants for pure metals), together with the approximetely taken linear dependence of calibration constant *vs*. the composition, may cause the additional uncertainty in the values of enthalpies of formation of the liquid Ga–Bi alloys.

Because of these factors it is considered that the maximal uncertainty in the measured mixing enthalpies was in the region of ±20%.

Calculation of activities

According to presented calculation procedure and using phase diagram of Ga–Bi system [6], values for activities of both components were calculated in temperature range 573–1073 K and presented in Table 2.

In the composition range outside of miscibility gap, activities of bismuth in the temperature range corresponding to the liquid mono-phase region were calculated in terms of the formula for simple eutectic systems Eq. (4). Starting data for such calculation process requires information about compositions along the liquidus line, extracted from phase diagram, and dependence between values of molar Gibbs energies of melting for bismuth and temperature (calculated from literature data [27]).

Table 2 Calculated activities for gallium and bismuth at different temperatures

Alloy composition	573 K		673 K		773 K	
x_{Ga}	a_{Bi}	a_{Ga}	a_{Bi}	a_{Ga}	a_{Bi}	a_{Ga}
0.9	0.575	0.927	0.418	0.922	0.328	0.919
0.8	0.651	0.899	0.525	0.884	0.445	0.867
0.7	0.674	0.895	0.578	0.857	0.520	0.828
0.6	0.691	0.887	0.625	0.826	0.579	0.784
0.5	0.713	0.861	0.667	0.779	0.636	0.724
0.4	0.743	0.814	0.713	0.714	0.695	0.649
0.3	0.793	0.729	0.776	0.620	0.763	0.549
0.2	0.849	0.584	0.841	0.481	0.834	0.415
0.1	0.918	0.366	0.915	0.288	0.912	0.242

Alloy composition	873 K		973 K		1173 K	
x_{Ga}	a_{Bi}	a_{Ga}	a_{Bi}	a_{Ga}	a_{Bi}	a_{Ga}
0.9	0.276	0.914	0.236	0.914	0.210	0.912
0.8	0.397	0.858	0.359	0.847	0.331	0.842
0.7	0.473	0.806	0.447	0.789	0.421	0.778
0.6	0.550	0.752	0.525	0.725	0.505	0.708
0.5	0.615	0.683	0.597	0.653	0.582	0.628
0.4	0.679	0.601	0.665	0.567	0.660	0.539
0.3	0.753	0.499	0.744	0.464	0.738	0.437
0.2	0.828	0.371	0.823	0.339	0.820	0.316
0.1	0.911	0.211	0.909	0.189	0.908	0.173

For the calculation of bismuth activities in the temperature range corresponding to the liquid mono-phase region and in the composition range inside miscibility gap by Eqs (8)–(9), only information about the relationship between temperatures along miscibility gap and alloy composition were used and no other extra thermodynamic properties were required.

Accuracy of such calculation method depends on: a) accuracy of input data, taken from represented phase diagram of the Ga–Bi system, and b) applicability of Richardson assumption [21] to investigated system. This assumption is just a particular case of the main equation in the theory of quasiregular solutions given by the following expression: $\Delta H_i = \theta \Delta S_i^E$ [22]. It was shown for the numerous binary systems [22], that this equation is satisfactorily characterized by a single value of θ equal to 3000 K.

Calculated activities of both components show large positive deviation from Raoult's law at lower temperatures and moderately positive deviation at higher investigated temperatures. Calculated activities of gallium at 573 K are compared with the experimental data [7] at 583 K, considering that a difference of 10 K is negligible for the activity value (Fig. 5a). Activities of gallium at 1073 K are graphically compared in (Fig. 5b) with the results by Katayama *et al.* [12], obtained by emf method, using zirconia as solid electrolyte.

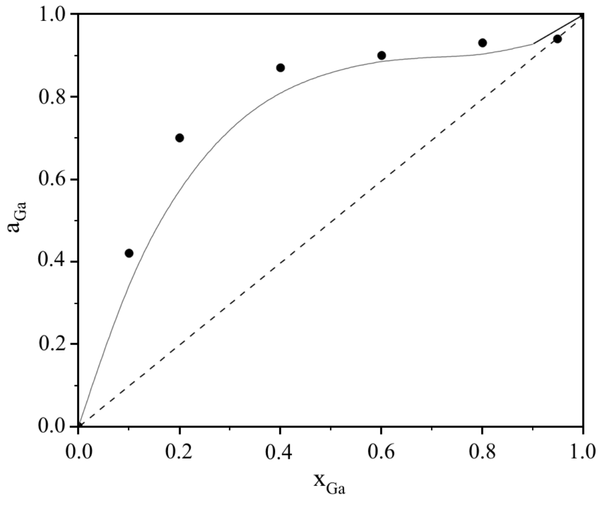

Fig. 5a Comparison between calculated activities and literature data at 573 K; • – Predel *et al.* [7], 583 K and –– – this work-calculation, 573 K

Based on calculated activities of gallium and bismuth, integral molar excess Gibbs energies are de-

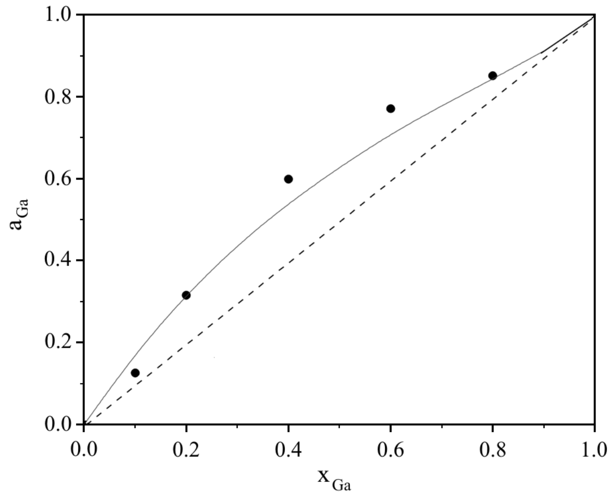

Fig. 5b Comparison between calculated activities and literature data at 1073 K; ● – Katayama *et al.* [12], 1073 K and —— – this work-calculation, 1073 K

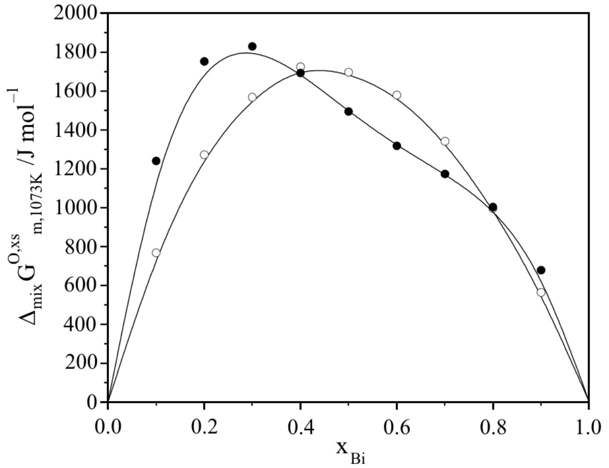

Fig. 6 Comparison between calculated integral molar exces Gibbs energies and literature data at 1073 K; —○— – this work-calculation and —●— –Katayama *et al.* [14]

rived at 1073 K and plotted in Fig. 6 with the data by Katayama *et al.* [14]. Obtained values from this work show reasonably agreement with literature data in spite of some differences in form of compared curves.

Conclusions

The integral mixing enthalpies of liquid Ga–Bi alloys have been determined using the quantitative DTA. Results satisfactorily agree with literature, which is an additional confirmation of this experimental technique as useful one in investigation of Ga-based binary alloys [29, 30]. Calculation method for binary systems having two liquid or solid coexisting phases in combination with method for simple eutectic systems were used for calculation of bismuth activities in whole composition range and in the temperature range 573–1073 K. Activities of gallium were derived from Gibbs–Duhem equation. Estimated activities were compared with experimentally obtained values at different temperatures.

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