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Thermochimica Acta 314 (1998) 79–86

thermochimica acta

Thermodynamic assessment of the ternary system Bi–In–Pb

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Received 8 October 1997; accepted 27 November 1997

Abstract

Phase diagram information and thermodynamic properties of mixing of the ternary system Bi–In–Pb have been determined by different authors. By means of an optimisation procedure, the results derived from thermodynamic assessments for the three limiting binary systems are used to evaluate the thermodynamic quantities of mixing of the ternary solution phases.

Keywords: Thermodynamic; Assessment; Phase diagram; Bi–In–Pb; Optimisation

1. Introduction

The phase diagram of the Bi–In–Pb system, which displays low temperature eutectics, has been investigated by several authors. Contradictory results were obtained. In the present contribution, a thermodynamic assessment is performed using all available experimental phase diagram and thermodynamic data for the ternary system.

2. Previous assessments

2.1. System Bi–In

The Bi–In system exhibits three stoichiometric compounds, BiIn, $BiIn_2$, and Bi_3In_5, in addition to the liquid, (Bi) and (In) phases. In the latter two phases, no appreciable solubility exists. A BiIn-ϵ phase has also been identified but its stability range is not well established. BiIn, $BiIn_2$ are congruent melting compounds, the corresponding temperatures of fusion being 383.15 and 362.65 K, respectively.

The thermodynamic parameters are taken from the SGTE [1] solution database.

2.2. System Bi–Pb

The Bi–Pb system exhibits an fcc-A1 lead-rich solution and an intermetallic hcp-A3 phase (sometimes designated as ϵ-Pb_3Bi) formed by peritectic reaction at 460.15 K. There is no appreciable solubility of lead in bismuth. A eutectic reaction occurs at 398.15 K as well as a eutectoid reaction at the lower temperature of 227.15 K.

The thermodynamic assessment was performed by Lukas [2].

2.3. System In–Pb

The In–Pb system exhibits three solid solutions, fcc-A1, In-rich tetragonal-A6 and an intermediate

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0040-6031/98/$19.00
PII S0040-6031(98)00237-8

InPb-α phase. No intermetallic compound exists in this system. Two peritectic reactions occur at 445.15 and 432.15 K. The liquidus in the In-rich region exhibits a minimum which is well represented by the assessment due to Bolcavage et al. [3]. To combine the results of their assessment with the SGTE unary data for fcc-A1 Pb and tetragonal-A6 In, the lattice stabilities for fcc-A1 In and InPb-α Pb were modified.

2.4. System Bi–In–Pb

No thermodynamic assessment has been performed for the Bi–In–Pb system.

3. Experimental information

3.1. Phase diagram

Stel'mack et al. [4,5] have established, by Differential Thermal Analysis (DTA), seven polythermal sections of both the Pb–Bi–InBi and the In–Pb–InBi sub-systems. They also determined the isopleth for the section InBi–Pb. From these results, they constructed the liquidus projection over the entire composition range. The phase diagram characteristics that they observed are the following:

- the Pb–InBi section is quasi-binary and presents a eutectic reaction at 349.15 K:

$$e_1: \quad \text{liquid} \rightleftharpoons (\text{Pb}) + \text{InBi}$$

- the quasi-ternary system Bi–Pb–InBi presents two invariant reactions: the ternary eutectic E_1 at 343.15 K and the quasi-peritectic P_1 at 346.15 K:

$$E_1: \quad \text{liquid} \rightleftharpoons (\text{Bi}) + \text{hcp} + \text{InBi}$$

$$P_1: \quad \text{liquid} + \text{hcp} \rightleftharpoons (\text{Pb}) + \text{InBi}$$

- the quasi-ternary system In–Pb–InBi presents the quasi-peritectic reaction U_1 at 347.15 K:

$$U_1: \quad \text{liquid} + \text{InBi} \rightleftharpoons (\text{Pb}) + \text{In}_2\text{Bi}$$

Liao et al. [6] also used DTA to determine isopleths for selected constant Bi/In ratios and constant Pb contents. They only published the diagrams corresponding to $x_{Bi}/x_{In}=1$ and 9, $x_{Pb}=0.2$ and 0.6.

The diagram for $x_{In}/x_{Bi}=1$, which corresponds to the Pb–InBi section, is in disagreement with the one obtained by Stel'makh et al. [4]. Liao et al. observed that the phases formed after solidification were hcp and (Bi), whereas Stel'makh et al. observed InBi and (Pb). In Liao's study, no invariant reactions were detected.

Prince [7] critically assessed these two contradictory sets of results and more particularly for the section $x_{In}/x_{Bi}=1$. If the ternary equilibria suggested by Stel'makh et al. were acceptable for the partial system Bi–Pb–InBi, Prince stated that this was not the case for those existing in the partial system In–Pb–InBi because the phase Bi_3In_5 was not taken into account. Moreover, Stel'makh et al. based their interpolation on a version of the In–Pb system where a complete series of solid solution was assumed over the entire composition range, which is not the case.

By thermal analysis, metallography, and X ray diffraction performed on an alloy 18.65% Pb and 81.35% InBi ($x_{Pb}=0.15$ and $x_{InBi}=0.85$), Prince confirms the existence of InBi and (Pb) at low temperatures, which corresponds to the eutectic reaction in the Pb–InBi section observed by Stel'makh et al. But a second alloy (70% Pb, 30% InBi: $x_{Pb}=0.785$, $x_{InBi}=0.215$), heat treated for 300 h at 373 K, was found to be a single phase (Pb) solid solution, which contradicted the low solubility of InBi in Pb observed by Stel'makh et al.

Prince also showed the incompatibility of the equilibria suggested by Liao et al. [6] with the phase rule.

Bushanov et al. [8] determined the composition of the ternary eutectic at 343.15 K (liquid $\rightleftharpoons$ (Bi)+hcp+InBi) by describing the liquidus surfaces based on Stel'makh et al. [4,5] data, by polynomials of different order using a simplex grid planning.

Il'ves et al. [9] analysed the phase diagram along the quasi-binary section In_2Bi–Pb by different techniques (DSC, microscopic analysis, X ray diffraction). A eutectic reaction was characterised in that section at 346 K and corresponds to the reaction

$$e_2: \quad \text{liquid} \rightleftharpoons \text{In}_2\text{Bi} + (\text{Pb})$$

Their analyses are based on the accepted phase diagram for the Bi–In system, and differ notably from those of Stel'makh et al. [4,5] for the same section.

Il'ves et al. [9] also determined four invariant reactions, two of which had been determined previously by Stel'makh et al. [4], the eutectic reaction E_1, and the quasi-peritectic reaction P_1. The other two

are the following:

$$E_2: \quad \text{liquid} \rightleftharpoons In_2Bi + In_5Bi_3 + (Pb) \quad \text{at } 343.15\,K$$

$$P_2: \quad \text{liquid} + InBi \rightleftharpoons In_5Bi_3 + (Pb) \quad \text{at } 347.15 - 348.15\,K$$

Il'ves et al. also suggested three other possible invariant reactions:

$$U_2: \quad \text{liquid} + (Pb) \rightleftharpoons InPb\text{-}\alpha + In_2Bi$$

$$U_3: \quad \text{liquid} + InPb\text{-}\alpha \rightleftharpoons BiIn\text{-}\epsilon + In_2Bi$$

$$U_4: \quad \text{liquid} + (In) \rightleftharpoons \alpha + BiIn\text{-}\epsilon$$

3.2. Thermodynamic properties

Using DTA, Vecher et al. [10] measured the enthalpies of mixing of liquid alloys at 605 K along five sections: x_{Bi}/x_{In}=0.06, 0.3, 0.56, 1 and 5. Their results were represented graphically by iso-enthalpy curves. As no tables were produced, and due to the limited number of curves in their figure, the data were not used in the optimisation.

Gregorczyk and Jurzyk [11] used *emf* measurements to determine the chemical potentials of indium in the temperature range 673–873 K and derived the integral quantities by Gibbs–Duhem integration according to Darken's method. The concentration cell used was the following:

$$In(l)\,|\,0.01InBr + 0.99(0.60LiBr + 0.40KBr)\,|\,\times (Bi, In, Pb)(l)$$

Zheng and Kozuka [12] also measured chemical potentials of indium in the temperature range 923–1123 K with the solid electrolyte cell:

$$In,\ In_2O_3\,|\,ZrO_2 + Y_2O_3\,|\,(In, Bi, Pb),\ In_2O_3$$

The experimental phase diagram and thermodynamic information are listed in Tables 1 and 2.

Table 2
Experimental thermodynamic properties information

Ref.	Type of data	Exper. techniques
[10]	Enthalpies of mixing	DTA
[11]	Chemical potential of In	*e.m.f.* 673–873 K[a]
[12]	Chemical potential of In	*e.m.f.* 923–1123 K[a]

[a] Data used in the optimisation.

4. Thermodynamic modelling

The molar Gibbs energy for a binary substitutional phase φ is expressed by the following equation:

$$G_m^{\varphi} = \sum_{i=A,B} x_i^{\varphi}\,{}^{\circ}G_i^{\varphi} + RT \sum_{i=A,B} x_i^{\varphi} \ln(x_i^{\varphi}) + G^{\varphi,xs} \tag{1}$$

x_i^{φ} is the molar fraction of element i in the phase φ. ${}^{\circ}G_i^{\varphi}$ is the Gibbs energy of i in the same physical structure as φ.

The thermodynamic quantities can be referred to the enthalpies of the pure elements in their stable state at 298.15 K, ${}^{\circ}H_i^{SER}(298.15\,K)$, as follows:

$$G_m^{\varphi} - \sum_{i=A,B} x_i^{\varphi}\,{}^{\circ}H_i^{SER}(298.15\,K) = \sum_{i=A,B} x_i^{\varphi}({}^{\circ}G_i^{\varphi} - {}^{\circ}H_i^{SER}(298.15\,K)) + RT \sum_{i=A,B} x_i^{\varphi} \ln(x_i^{\varphi}) + G^{\varphi,xs} \tag{2}$$

Table 1
Experimental phase diagram information

Ref.	Type of data	Exper. techniques
[4]	Sections: Pb–InBi[a] and Pb–Bi–InBi[a]	DTA
[5]	Sections: Pb–Bi–InBi	DTA
[6]	Isopleths: x_{In}/x_{Bi}=1[a] and 1/9; x_{Pb}=0.6 and 0.2	DTA
[7]	Analysis of two alloys	DTA, metallography and X ray analysis
[8]	Determination of the ternary eutectic[a]	DTA
[9]	Isopleth: x_{In}/x_{Bi}=2[a]	DSC, microscopy and X ray analysis

[a] Data used in the optimisation.

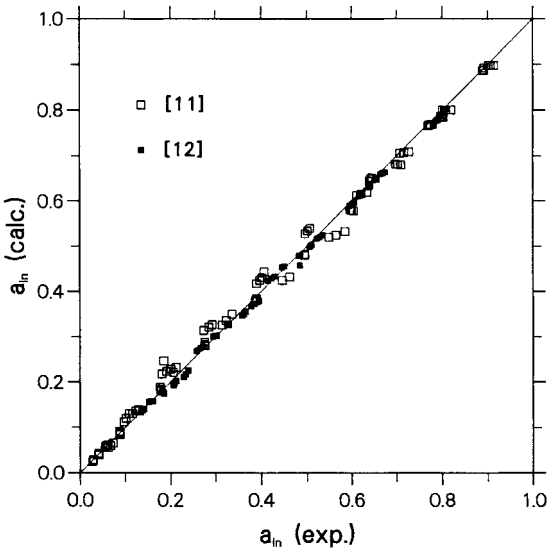

Fig. 1. Comparison between experimental and calculated activities.

The excess Gibbs energy $G^{\varphi,xs}$ of a binary solution is expressed by the Redlich–Kister equation [13]:

$$G^{\varphi,xs} = x_i^{\varphi} x_j^{\varphi} \sum_{\nu=1}^{n} {}^{\nu}L_{i,j}(x_i^{\varphi} - x_j^{\varphi})^{\nu} \qquad (3)$$

Table 3
Gibbs energy differences ${}^{\circ}G_i^{\varphi,T} - {}^{\circ}G_i^{ref,T}$ (in J.mol^{-1}) for the pure elements

Phase φ	Bi	In	Pb
Rhombohedral	0	...	...
Liquid	[14]	[14]	[14]
fcc-A1	[14]	162.061	0
hcp-A3	[14]	[14]	[14]
Tetragonal-A6	[14]	0	4493.235
BiIn-ϵ	[14]	−33+0.16 T	6100
InPb-α	[14]	0.31 T	1903.3−2.0602 T

The terms $L_{i,j}^{\varphi}$, which can be temperature dependent, are expressed by:

$${}^{\nu}L_{i,j} = {}^{\nu}A_{i,j}^{\varphi} + {}^{\nu}B_{i,j}^{\varphi}T + \cdots \qquad (4)$$

In a ternary system, when experimental information for ternary thermodynamic properties of mixing is available, an extra term expressing the interactions between the atoms can be added to Eq. (3). This term is expressed as follows:

$$x_{Bi}^{\varphi}x_{In}^{\varphi}x_{Pb}^{\varphi}L_{Bi,In,Pb}^{\varphi} = x_{Bi}^{\varphi}x_{In}^{\varphi}x_{Pb}^{\varphi}({x_{Bi}^{\varphi}}^{0}L_{Bi,In,Pb}^{\varphi} + {x_{In}^{\varphi}}^{1}L_{Bi,In,Pb}^{\varphi} + {x_{Pb}^{\varphi}}^{2}L_{Bi,In,Pb}^{\varphi}) \qquad (5)$$

Table 4
Gibbs energy of mixing of the solution phases (in J.mol^{-1})

Phase	Parameter	Bi–In [1]	Bi–Pb [2]	In–Pb [3]
fcc-A1	${}^{0}L_{A,B}$	7560.64	−2852.75−3.5832 T	4846.2−2.564 T
	${}^{1}L_{A,B}$	...	...	305.1
hcp-A3	${}^{0}L_{A,B}$		−4441.67−7.4411 T	6000
	${}^{1}L_{A,B}$		1725.26−4.0220 T	...
Liquid	${}^{0}L_{A,B}$	−7165.0−0.3754 T	−4330.3−2.0421 T +0.06542 T lnT	3771.4−0.963 T ...
	${}^{1}L_{A,B}$	1503.8−0.5418 T	1.53−1.02298 T	207.7
	${}^{2}L_{A,B}$	1221.15−1.65967 T	896.7−1.2644 T	...
	${}^{3}L_{A,B}$	−1627.0+2.764 T	...	...
Rhombohedral	${}^{0}L_{A,B}$	22500	3461.59+45.2234 T	...
Tetragonal-A6	${}^{0}L_{A,B}$	5646.8−26.868 T	...	−3118.2
	${}^{1}L_{A,B}$	...	...	3741.1
BiIn-ϵ	${}^{0}L_{A,B}$	4904.5−28.9743 T	...	...
	${}^{1}L_{A,B}$	−1386.4	...	...
InPb-α	${}^{0}L_{A,B}$	...	...	2580.3

The terms ${}^{i}L^{\varphi}_{Bi,In,Pb}$ can vary with temperature according to Eq. (4).

5. Optimisation

The thermodynamic properties of the ternary solution phases were derived from an optimisation procedure using the module PARROT developed by Jansson [15] contained in the Thermo-Calc databank system [16]. The experimental phase diagram and thermodynamic data which were used are indicated in Tables 1 and 2.

Table 5
Excess Gibbs energy of mixing (in J.mol^{-1}) of the ternary solution phases

Phase	Parameter
Liquid	${}^{0}L_{Bi,In,Pb}=-11184.30+3.397$ T
	${}^{1}L_{Bi,In,Pb}=25950.74-27.633$ T
	${}^{2}L_{Bi,In,Pb}=25950.74-27.633$ T
fcc-A1	${}^{0}L_{Bi,In,Pb}=8209.216$
	${}^{1}L_{Bi,In,Pb}=-13019.237$
	${}^{2}L_{Bi,In,Pb}=-13019.237$
Tetragonal-A6	${}^{0}L_{Bi,In,Pb}=20000.00$
	${}^{1}L_{Bi,In,Pb}=20000.00$
	${}^{2}L_{Bi,In,Pb}=20000.00$

The parameters $L^{\varphi}_{Bi,In,Pb}$ for the tetragonal-A6 and fcc-A1 phases were assumed to be temperature independent. To obtain a satisfactory agreement with the phase diagram data, a ternary interaction term was also necessary to represent the thermodynamic properties of the liquid phase. During the optimisation procedure, it was found that a better convergence of the system was obtained by using the data of Zheng et al. [12] rather than those of Gregorczyk et al. [11]. Nevertheless, even if the temperature range for the two sets of experiments was not the same, Fig. 1 shows that there is an overall agreement between the experimental and derived activity data.

The optimised thermodynamic parameters for the various phases in the Bi–In–Pb system are listed in Tables 3–6.

Table 6
Gibbs energy of the intermetallic compounds (in J.mol^{-1}) x_{Bi} Bi (rhombohedral-A7)+x_{In} In (tetragonal-A6)⇒$Bi_{x_{Bi}}In_{x_{In}}$

Compound	x_{In}	$G_C-\sum_i x_i^{\circ}G_i^T$ [1]
BiIn	0.5	−732.2−3.7906 T
$BiIn_2$	0.6666	−481.1−4.188 T
Bi_3In_5	0.625	−544.0−4.12287 T

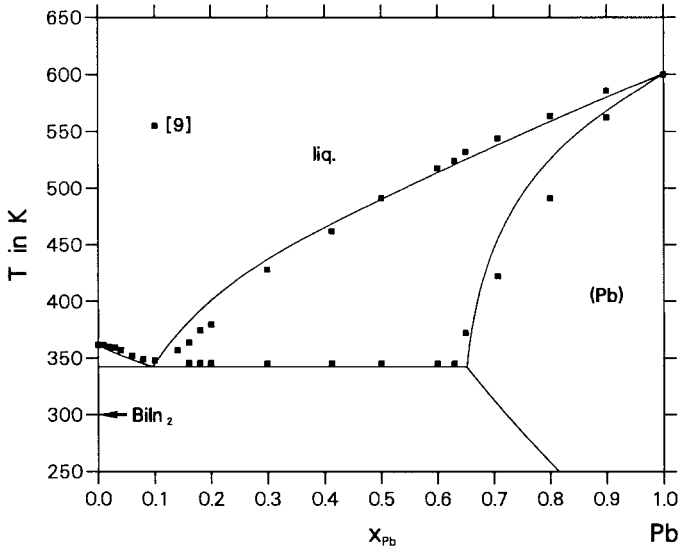

Fig. 2. Calculated isopleth $BiIn_2$–Pb.

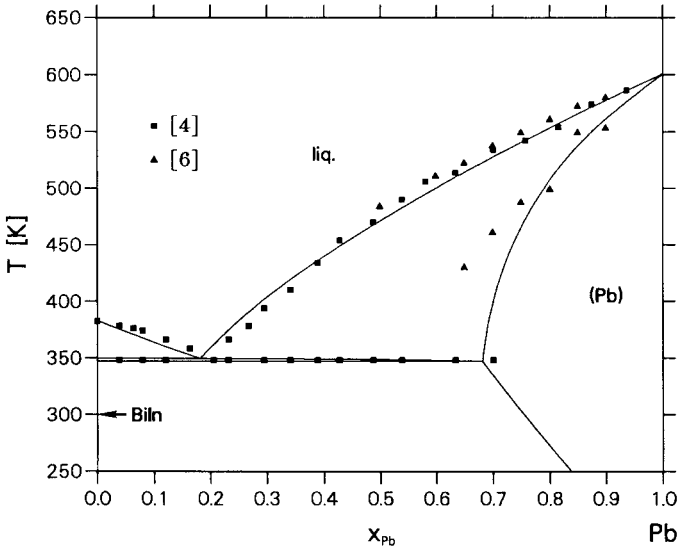

Fig. 3. Calculated isopleth BiIn–Pb.

6. Discussion

The calculated quasi-binary section Pb–In_2Bi confirms the diagram determined by Il'ves et al. [9] as shown in Fig. 2. Hence, the isopleths determined by S.I. Stel'makh et al. [5] are in complete disagreement.

Despite the general agreement between the experimental and calculated diagrams, some differences exist. The calculated section for $x_{Bi}/x_{In} = 1$ is not quasi-binary as reported by Stel'makh et al., and confirmed by Prince [7]. A three phase region liquid+BiIn+Pb exists in the temperature range 347–349.5 K (Fig. 3). This is due to the direction of the tie-lines between the liquid and the fcc-A1 phase. None of the tie-lines coincides with the line $x_{Bi}/x_{In} = 1$, as shown in the isothermal section represented in Fig. 4.

Figs. 5 and 6 represent two isopleths and Fig. 7 selected liquidus curves and monovariant lines. Table 7 lists the experimental and calculated invariant temperatures and the corresponding compositions for the various invariant reactions. Although the temperatures are generally in good agreement with the experimental values, (a maximum difference of 4 K is obtained except, for the peritectic reaction P_2), there are differences in the compositions.

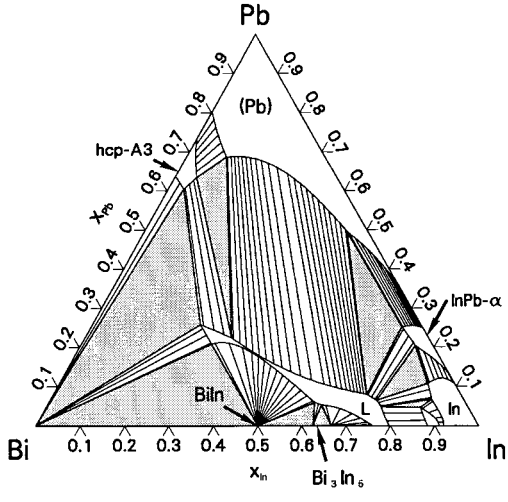

Fig. 4. Calculated isothermal section at 350 K.

The calculation confirms the three invariant reactions (U_2, U_3 and U_4) suggested by Ilv'es et al. The calculated characteristics of these reactions could be of help in further experimental investigations of their existence.

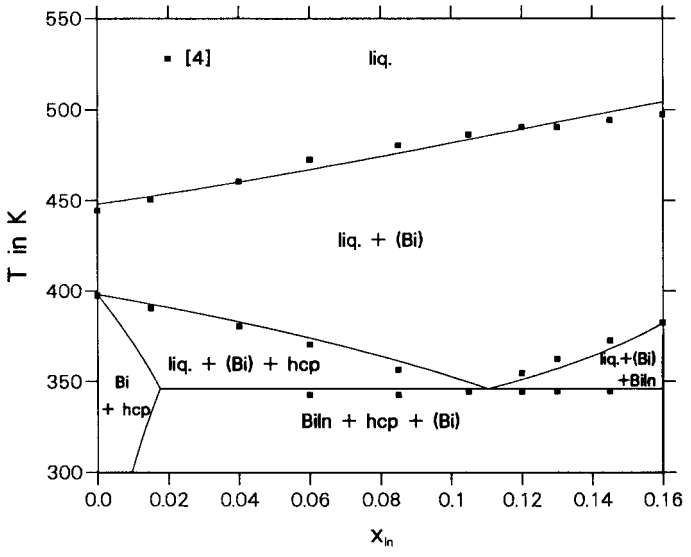

Fig. 5. Calculated isopleth corresponding to a section at 70 wt % Bi in the Pb–Bi–InBi partial system.

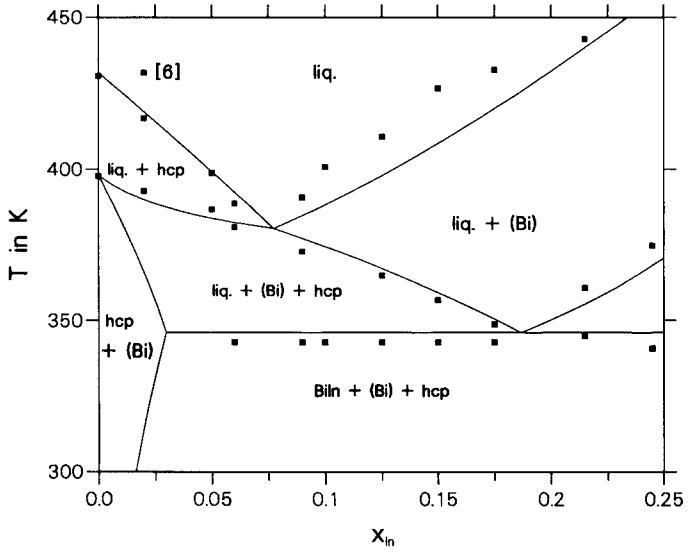

Fig. 6. Calculated isopleth corresponding to a section at 50 wt % Bi in the Pb–Bi–InBi partial system.

7. Conclusions

A consistent set of thermodynamic parameters for the ternary solution phases of the Bi–In–Pb system was obtained by means of a thermodynamic description. Although there is, in general, a very satisfactory agreement between the selected experimental data for the phase diagram, some differences still exist. Further experimental investigation of the phase diagram is desirable.

Table 7
Experimental and calculated values for the invariant reactions in the Bi–In–Pb system

Reactions	Type	T/K	x_{Bi}	x_{Pb}	Ref.
Liq. ⇌ (Pb)+InBi	e_1	349.15	0.395	0.166	[4]
		352.15	0.41	0.18	[8]
		347–349.5	–	–	Calculated
Liq. ⇌ (Pb)+$BiIn_2$	e_2	346	0.293	0.12	[9]
		342.22	0.301	0.096	Calculated
Liq. ⇌ (Bi)+hcp-A3+BiIn	E_1: ternary eutectic	343.15	0.515	0.180	[8]
		343.15	0.483	0.208	[5]
		346.02	0.491	0.240	Calculated
Liq. ⇌ (Pb)+$BiIn_2$+Bi_3In_5	E_2: ternary eutectic	343.15	...	...	[9]
		341.82	0.320	0.103	Calculated
Liq.+hcp-A3 ⇌ BiIn+(Pb)	P_1: quasi-peritectic	346.15	0.438	0.241	[5]
		348.62	0.445	0.219	Calculated
Liq.+BiIn ⇌ Bi_3In_5+(Pb)	P_2: quasi-peritectic	347.15–348.15	...	...	[9]
		342.04	0.333	0.110	Calculated

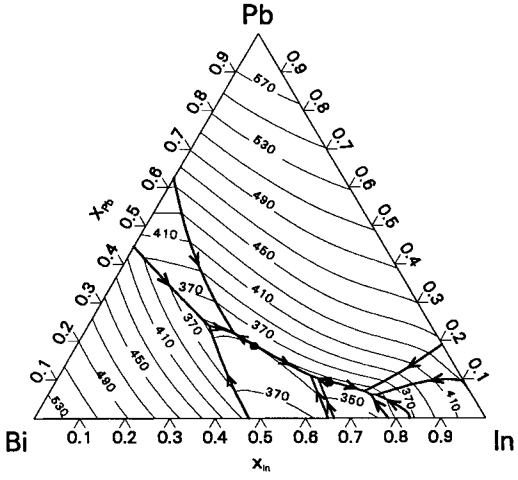

Fig. 7. Calculated liquidus isotherms (20 K step) and monovariant lines.

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