

THERMODYNAMIC ASSESSMENT OF THE Ag–Au–Bi AND Ag–Au–Sb SYSTEMS

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The aim of the action of COST 531 taking into account the eleven elements Ag,Au,Bi,Cu,In,Pb,Sb,Sn,Zr (solder), Ni and Pd (substrate) is the database assessment for candidates of lead free soldering process. We studied four of them forming the ternary systems Ag–Au–Bi and Ag–Au–Sb. First we determined experimentally their phase diagrams, then the integral enthalpy of mixing of the liquid phase along different sections at different temperatures by using a SETARAM device heat flow calorimeter of Tian-Calvet type. All these data were used to optimize the thermodynamic parameters of the different phases of both ternary systems.

Keywords: Ag–Au–Bi system, Ag–Au–Sb system, calphad method, enthalpy of formation, EPMA, heat flow calorimeter, phase diagram, solder, XRD

Introduction

Due to the physical properties of lead (high density, low melting point, malleability, corrosion resistance and impermeability), this metal was largely used from antiquity. With additions of some elements, lead forms alloys having also low melting points and used for welding and brazing, especially for electric and electronic materials. But for environmental reasons, even at low content, lead is responsible of important health diseases, so the European legislation has banned its use in 2008 [1]. This gave rise to the European action COST 531 (Coopération Scientifique et Technique) [2]. Our contribution through the Work Groups WG₁ and WG₂ was to determine a thermodynamic database at equilibrium including the Ag–Au–Bi–Sb elements. Its optimization needed the experimental determination of phase diagrams and thermodynamic properties. Some of our preliminary results have been previously presented at XXX and XXXI JEEP [3, 4]. First, we will briefly recall some experimental information.

Thermodynamic modelling

The molar Gibbs energy of the different solution phases (ϕ) is described with three terms:

$$G_m^\phi = G_{\text{ref}}^\phi + G_{\text{id}}^\phi + G_{\text{ex}}^\phi \quad (1)$$

The excess Gibbs energy is represented with the Redlich–Kister polynomial expansion [5]. For the binary systems:

$$G_m^\phi = \sum_{i=A,B} x_i^{\phi 0} G_i^\phi + RT \sum_{i=A,B} x_i^\phi \ln x_i^\phi + x_i^\phi x_j^\phi \sum_v L_{i,j}^\phi (x_i^\phi - x_j^\phi)^v \quad (2)$$

where $v_{L_{i,j}^\phi}$ is the binary interaction excess parameter of degree v between the elements i and j , and x_i^ϕ is the mole fraction of element i in phase ϕ .

The interaction parameters can be temperature dependent as follows:

$$v_{L_{i,j}^\phi} = v_{a_{i,j}^\phi} + v_{b_{i,j}^\phi} T + v_{c_{i,j}^\phi} T \ln T \quad (3)$$

For the ternary systems

$$G_{\text{ref}}^\phi = \sum_{i=A,B,C} x_i^{\phi 0} G_i^\phi \quad (4)$$

$$G_{\text{id}}^\phi = RT \sum_{i=A,B,C} x_i^\phi \ln(x_i^\phi) \quad (5)$$

The excess Gibbs energy is represented with a Redlich–Kister–Muggianu polynomial expansion [6] as:

$$G_{\text{ex}}^\phi = x_A^\phi x_B^\phi L_{A,B}^\phi + x_A^\phi x_C^\phi L_{A,C}^\phi + x_B^\phi x_C^\phi L_{B,C}^\phi + x_A^\phi x_B^\phi x_C^\phi L_{A,B,C}^\phi \quad (6)$$

The molar Gibbs energy of the stoichiometric Au₂Bi compound is expressed as follows:

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$$G_m^{\text{Au}_2\text{Bi}}(T) = a + bT + cT \ln T + \sum_{i=\text{Au,Bi}} x_i^{\text{Au}_2\text{Bi}^0} G_i(T) \quad (7)$$

The sublattice thermodynamic models are listed in Table 1. For the intermetallic compounds, the Wagner–Schottky law was applied [7]:

$$G_{B_p A_q}^\phi = G_{A_p A_q}^\phi + G_{B_p B_q}^\phi - G_{A_p B_q}^\phi$$

when the solubility of the elements Ag or Au in the rhombohedral terminal solid solution (Bi or Sb) was not reported in the literature, for simplicity we took pure solid Bi or Sb.

Optimization

The optimization of the thermodynamic parameters of the ternary systems was carried out with the Calphad method [8] with the Parrot module of the Thermocalc software [9]. The pure solid elements at 25°C (298.15 K) and $P=1.10^5$ Pa in their stable form were chosen as the reference state of the system. The

Scientific Group Thermodata Europe (SGTE) phase stability equations published by Dinsdale [10] were used for the thermodynamic functions of the pure elements in their stable and metastable states. We used the low-order systems available in the literature, except for Au–Bi [11] and Ag–Sb [12] that we had to re-optimize. For the binary and ternary systems, first the thermodynamic parameters of the liquid phase were optimized from the experimental integral enthalpy of mixing of that phase [13, 14] then the phase diagram data were introduced [15, 16]. A statistical mass was assigned to each experimental data according to its compatibility with the other ones.

Experimental

All the samples have been elaborated by the direct union of the elements Ag, Au, Bi/Sb with respective purity of 5N, 4N and 5N for Bi and Sb. The constituents are introduced into silica tubes, which

Table 1 Sublattice thermodynamic models used for the different binary and ternary systems

Systems	Phases	Modelling	Phases	Modelling
	Liquid		Rhombohedral_A7	
Ag–Au		:(Ag,Au) ₁ :		–
Ag–Bi		:(Ag,Bi) ₁ :		:(Ag,Bi) ₁ :
Au–Bi		:(Au,Bi) ₁ :		:(Bi) ₁ :
Ag–Sb		:(Ag,Sb) ₁ :		:(Sb) ₁ :
Au–Sb		:(Au,Sb) ₁ :		:(Sb) ₁ :
Ag–Au–Bi		:(Ag,Au,Bi) ₁ :		:(Ag,Au,Bi) ₁ :
Ag–Au–Sb		:(Ag,Au,Sb) ₁ :		:(Sb) ₁ :
	Fcc_A1		Hcp_A3	
Ag–Au		:(Ag,Au) ₁ :(Va) ₁ [*] :		:(Ag,Au) ₁ :(Va) _{0.5} :
Ag–Bi		:(Ag,Bi) ₁ :(Va) ₁ :		:(Ag,Bi) ₁ :(Va) _{0.5} :
Au–Bi		:(Au,Bi) ₁ :(Va) ₁ :		:(Au,Bi) ₁ :(Va) _{0.5} :
Ag–Sb		:(Ag,Sb) ₁ :(Va) ₁ :		:(Ag,Sb) ₁ :(Va) _{0.5} :
Au–Sb		:(Au,Sb) ₁ :(Va) ₁ :		:(Au,Sb) ₁ :(Va) _{0.5} :
Ag–Au–Bi		:(Ag,Au,Bi) ₁ :(Va) ₁ :		–
Ag–Au–Sb		:(Ag,Au,Sb) ₁ :(Va) ₁ :		:(Ag,Au,Sb) ₁ :(Va) _{0.5} :
	Bcc_A2		Au ₂ Bi	
Ag–Au		:(Ag,Au) ₁ :(Va) ₃ :		
Ag–Bi		:(Ag,Bi) ₁ :(Va) ₃ :		
Au–Bi		:(Au,Bi) ₁ :(Va) ₃ :		:(Au) _{0.66667} :(Bi) _{0.333333} :
Ag–Sb		:(Ag,Sb) ₁ :(Va) ₃ :		
Au–Sb		:(Au,Sb) ₁ :(Va) ₃ :		
Ag–Au–Bi		–		:(Au,Ag) _{0.66667} :(Bi) _{0.333333} :
			AgSb-ortho (ε)	
Ag–Sb				:(Ag,Sb) _{0.75} :(Ag,Sb) _{0.25} :
Ag–Au–Sb				:(Ag,Au,Sb) _{0.75} :(Ag,Au,Sb) _{0.25} :

Va* for vacancy

are then sealed under vacuum (10^{-2} Torr). The silica tubes are previously heated to burn out impurities and then cleaned in an ultrason tank containing ethanol. The sealed tubes containing the mixed elements are gradually heated in a furnace about 100°C above the melting point of Au (1064.43°C) during 20 mn. The samples are then slowly cooled until the annealing temperature (230°C) is reached. This later temperature is the lowest of the invariant reactions of the binary constitutive systems in order for the alloys to be entirely solid. With some samples, up to 8 or 10 months were necessary for the annealing [13].

Experimental phase diagram data were obtained using X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and Electron Probe microanalysis (EPMA). Four vertical sections (isopleths) were studied at 20 at.% Ag, 50 and 80 at.% Bi, and the section with ratio Ag:Au=1:4 for the Ag–Au–Bi ternary system and 10, 70, 80 at.% Ag and 10 at.% Au for the Ag–Au–Sb ternary system.

The integral enthalpies of formation of the liquid alloys were measured with the high temperature calorimeter SETARAM HT1000. The experimental methodology was indicated in Zoro *et al.* [14].

Table 2 Reference (G) and optimized excess (L) thermodynamic parameters of the phases of the Ag–Au–Bi system. The a , b , and c parameters are defined in Eq. (3). The parameters GHSERAG, GHSEAU and GHSERBI are from [10]. [TW]=this work

Phase	System	$V_{L_{i,j,k}}^{\dagger}$	Ref.	ν	$a/\text{J mol}^{-1}$	$b/\text{J mol}^{-1} \text{K}^{-1}$	$c/\text{J mol}^{-1} \text{K}^{-1}$
Liquid	Ag–Au	L	[2]	0	–16402	1.14	0.0
	Ag–Bi	L	[2]	0	3340.81	39.16749	–5.9699
		L	[2]	1	–5485.45	–1.07133	0.0
		L	[2]	2	–3055.34	1.77449	0.0
		L	[2]	2	–3055.34	1.77449	0.0
	Au–Bi	L	[11]	0	2538.7930	–5.60093	0.0
		L	[11]	1	–157.76430	0.22601	0.0
		L	[11]	2	–4561.3797	4.19542	0.0
		L	[11]	3	–2539.0886	–1.14834	0.0
	Ag–Au–Bi	L	[TW]	0	24683.2871	0.0	0.0
L		[TW]	1	727.8594	0.0	0.0	
L		[TW]	2	869.3989	0.0	0.0	
Fcc_A1	Ag–Au	L	[2]	0	–15599	0.0	0.0
	Ag–Bi	L	[2]	0	25077.78	–12.0547	0.0
	Au–Bi	L	[11]	0	42000	0.0	0.0
	Ag–Au–Bi	L	[TW]	0	20.0705	0.0	0.0
		L	[TW]	1	50480.4216	0.0	0.0
Rhombohedral	Ag	G	[TW]	0	25000+GHSERAG		
	Au	G	[TW]	0	25000+GHSEAU		
	Bi	G	[10]	0			
	Ag–Au–Bi	L	[TW]	0	–506.6037	0.0	0.0
$(\text{Ag,Au})_2\text{Bi}$	Ag–Bi	G	[TW]	0	0.66667*GHSERAG+ 0.33333*GHSERBI		
		G	[11]	0	0.66667*GHSEAU+ 0.33333*GHSERBI+ 1725.6586+ 0.8409*T– 0.8986*T*LN(T)		
	Ag–Au–Bi	L	[TW]	0	–25884.4984	57.9688	0.0
		L	[TW]	1	–7570.1398	53.00	0.0
		L	[TW]	2	–11800.00	23.00	0.0

Results and discussion

Ag–Au–Bi system

The optimized thermodynamic parameters of the different phases are listed in Table 2. In Fig. 1, the

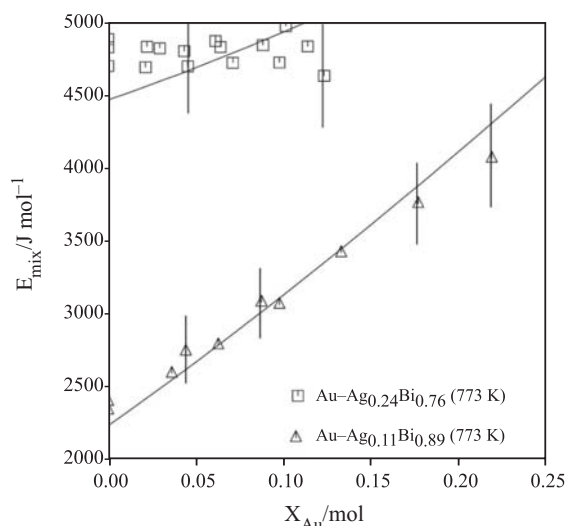


Fig. 1 Comparison of the calculated and experimental integral enthalpies of mixing of the liquid alloys $\text{Au–Ag}_x\text{Bi}_{1-x}$

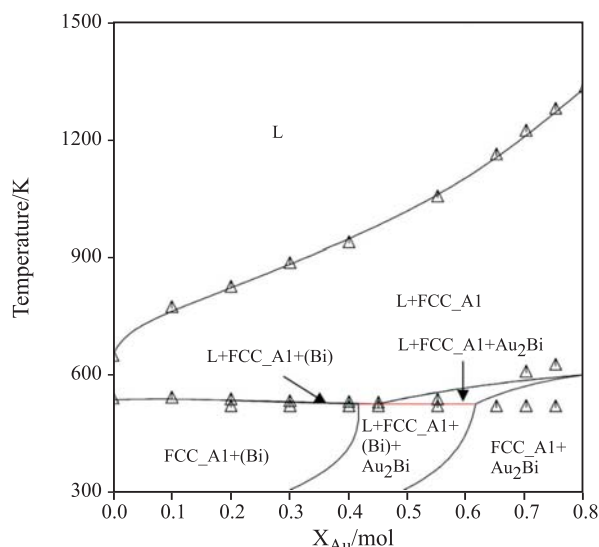


Fig. 2 Calculated and experimental isopleth section at 20 at.% Ag for the Ag–Au–Bi system. The experimental data (Δ) obtained by Zoro *et al.* [15] are included

experimental and calculated integral enthalpies of mixing of the liquid phase at 773 K of some $\text{Au–Ag}_x\text{Bi}_{1-x}$ or $\text{Ag–Au}_x\text{Bi}_{1-x}$ alloys are compared. A reasonable agreement is observed. The experimental reproducibility of the heat effect was better than $\pm 8\%$ [13]. For the calculation, all phases, apart from the liquid one, were suspended. The reference states were Ag, Au solid fcc and Bi liquid at $T=773$ K and 1 bar. We verified that the experimental and calculated integral enthalpies of mixing of the liquid alloys $\text{Ag–Au}_{0.1}\text{Bi}_{0.9}$ at 673 K and $\text{Ag–Au}_{0.11}\text{Bi}_{0.89}$ at 773 K are practically independent of the temperature.

The calculated and experimental isopleth section at 20 at.% Ag for the Ag–Au–Bi system is plotted in Fig. 2. The uncertainty bar on T is ± 5 K. A good agreement is noted. In Table 3, the calculated and experimental temperatures of the invariant reactions for the Ag–Au–Bi ternary system are compared. A satisfactory agreement is observed.

Ag–Au–Sb system

The optimized thermodynamic parameters of the different phases are listed in Table 4.

The experimental and calculated integral enthalpies of mixing of the liquid phase for different isopleth sections of the Ag–Au–Sb system are shown in Fig. 3. A good agreement is noted. The experimental and

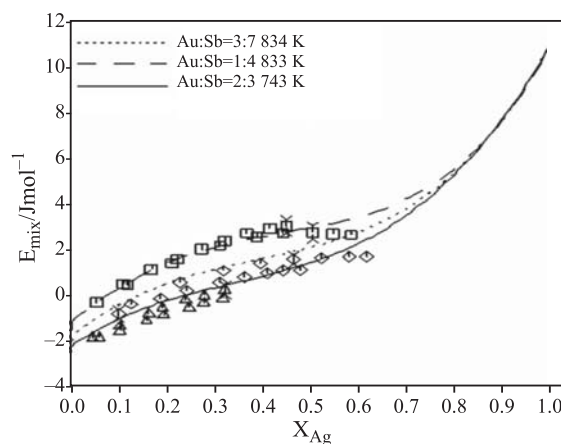


Fig. 3 Calculated integral enthalpy of mixing of the liquid phase for three isopleth sections of the Ag–Au–Sb system at different temperatures. The polygons represent our data [13]

Table 3 Calculated temperature compared with the experimental one for the invariant transitory peritectic reaction U in the Ag–Au–Bi ternary system. The experimental and calculated temperatures of the eutectic reactions of the binary systems Ag–Bi and Au–Bi are also given

Invariant reaction	Calculated T/K	Reference	Experimental T/K	Reference
U Fcc+L \leftrightarrow Au ₂ Bi+(Bi)	525.4	[TW]	516.0 \pm 0.5	[15]
e ₁ L \leftrightarrow FCC_A1+(Bi)	535.7	[TW]	535.4	[13]
e ₂ L \leftrightarrow Au ₂ Bi+(Bi)	514.0	[11]	515.1 \pm 0.1	[15]

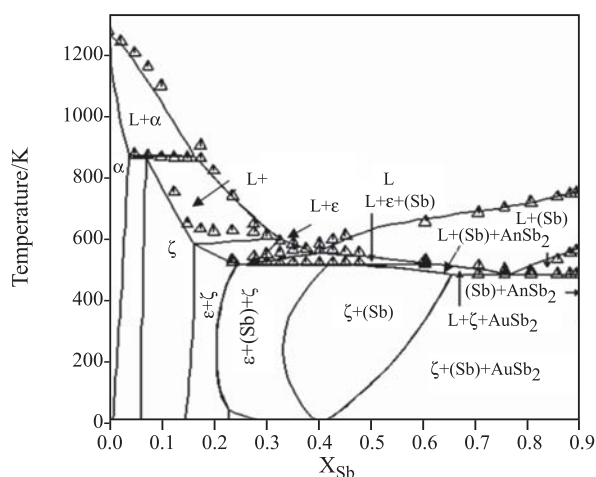
Ag–Au–Bi AND Ag–Au–Sb SYSTEMS

Table 4 Reference (*G*) and optimized excess (*L*) thermodynamic parameters of the phases of the Ag–Au–Sb system.
The parameters GHSERAG, GHSERAU and GHSERSb are from [10]

Phase	System	$v_{L_{ij}}^{\circ}$	Ref.	v	$a/\text{J mol}^{-1}$	$b/\text{J mol}^{-1} \text{K}^{-1}$	$c/\text{J mol}^{-1} \text{K}^{-1}$
Liquid	Ag,Au	L	[2]	0	-16402.0	1.14	
	Ag–Sb	L	[TW]	0	-964.4779	-7.9876	
		L	[TW]	1	-21481.357	7.1738	
		L	[TW]	2	-9992.0766	0.0	
	Au,Sb	L	[17]	0	-10288.0428	-14.7865	
		L	[17]	1	-2901.6678	-7.2503	
		L	[17]	2	1217.4360	-4.7490	
	Ag,Au,Sb	L	[TW]	0	-70007.00	10.002	
		L	[TW]	1	14955.980	-6.5513	
L		[TW]	2	10.0	-30.0		
Fcc_A1	Ag–Au	L	[2]	0	-15559.0		
	Ag,Sb	L	[TW]	0	-30164.027	66.4033	
		L	[TW]	1	8714.5741	-67.6783	
	Au–Sb	L	[TW]	0	31456.5511	-35.1097	
	Ag,Au,Sb	L	[TW]	0	-40000	13.30	
		L	[TW]	1	102555.776	-0.3686	
Hcp_A3	Ag–Au	L	[2]	0	-15559.0		
	Ag,Sb	L	[TW]	0	-24173.95	44.2101	
		L	[TW]	1	-2341.9664	-49.1982	
	Au–Sb	L	[17]	0	7580.0		
	Ag,Au,Sb	L	[TW]	0	-124000	34.0	
		L	[TW]	1	3000.0	0.6248815	
Bcc_A2	Ag,Au	L	[2]	0	-15599	0.0	0.0
	Ag,Sb	L	[TW]	0	30000	0.0	0.0
	Au,Sb	L	[17]	0	7580	0.0	0.0
AuSb ₂ phase: (Ag,Au) _{0.33333} :(Sb) _{0.66667} :							
			Ref.	v	$a/\text{J mol}^{-1}$	$b/\text{J mol}^{-1} \text{K}^{-1}$	$c/\text{J mol}^{-1} \text{K}^{-1}$
:Ag:Sb:	G	[TW]		0	0.33333*GHSERAG +0.66667*GHSERSB +2641.1228	0.0	0.0
:Au:Sb:	G	[17]		0	0.33333*GHSERAU +0.66667*GHSERSB -5721.6694	6.9350	-0.62
AgSb_ortho phase:(Ag,Au,Sb) _{0.75} :(Ag,Au,Sb) _{0.25} :							
			Ref.	v	$a/\text{J mol}^{-1}$	$b/\text{J mol}^{-1} \text{K}^{-1}$	
:Ag:Ag:	G	[TW]		0	5000+GHSERAG		0
:Au:Au:	G	[TW]		0	5000+GHSERAU		0
:Sb:Sb:	G	[TW]		0	5000+GHSERSB		0
:Ag:Au:	G	[TW]		0	0.75*GHSERAG+0.25*GHSERAU		0
:Au:Ag:	G	[TW]		0	10000+0.75*GHSERAU+0.25*GHSERAG		0

Table 4 Continued

		Ref.	v	$a/\text{J mol}^{-1}$	$b/\text{J mol}^{-1} \text{K}^{-1}$
:Sb:Ag:	G	[TW]	0	$0.75*\text{GHSERSB}+0.25*\text{GHSERAG}+$ $10000+411.8398$	3.8229
:Ag:Sb:	G	[TW]	0	$0.75*\text{GHSERAG}+0.25*\text{GHSERSB}-$ 411.8398	-3.8229
:Au:Sb:	G	[TW]	0	$+0.75*\text{GHSERAU}+0.25*\text{GHSERSB}$	0
:Sb:Au:	G	[TW]	0	$10000+0.75*\text{GHSERSB}+0.25*\text{GHSERAU}$	0
:Ag,Sb:Ag:	L	[TW]	0	0	0
:Ag,Au:Ag,Sb:	L	[TW]	0	-35500	9.85857
:Ag:Ag,Sb:	L	[TW]	0	-5788.5398	0
:Ag:Ag,Au,Sb:	L	[TW]	0	-48000	0
:Sb:Ag,Sb:	L	[TW]	0	0	0
:Ag,Sb:Sb:	L	[TW]	0	10491.79	0
:Ag,Au:Sb:	L	[TW]	0	-11750	9.15

**Fig. 4** 10 at.% Au isopleth section of the Ag–Au–Sb system calculated and compared to our experimental data (Δ)[13]

calculated 10 at.% Au isopleth sections are compared in Fig. 4. A very good agreement is noted, except for the liquidus $L/(L+\alpha)$. In Table 5 are given the experimental and calculated reaction scheme. For a relatively slight change in the a optimized enthalpy term of the thermodynamic parameter G:Ag:Sb: of the phase (Ag,Au) Sb_2 (a decrease from 2641 J mol^{-1} (Table 2) to 150 J mol^{-1}), U_2 changes from 661.8 to 668.3 K and becomes peritectic (as observed experimentally) while U_3 changes from 663.1 to 664.7 K but remains eutectic (contrarily to the experiment). Taking into account the few experimental data concerning the U_3 reaction, further experimental determinations are therefore necessary to check the reaction scheme.

Table 5 Comparison of the experimental and calculated (*) invariant reactions for the Ag–Au–Sb system, by using the optimized thermodynamic parameters listed in Table 4

Invariant reaction	Type of reaction		Temperature/K		Phase	Composition/at.%	
	Calc.	Exp.	Calc.	Exp.		Au	Sb
					Calc.		
$L+\epsilon \leftrightarrow \zeta+(\text{Sb})$ $L+\epsilon \leftrightarrow \zeta+(\text{Sb})^*$	U	U_1	688.1	690	L ϵ ζ (Sb)	15.44 9.52 14.19 0	38.53 25.17 17.50 100
$L+(\text{Sb}) \leftrightarrow \zeta+\text{AuSb}_2$ $L \leftrightarrow (\text{Sb})+\zeta+\text{AuSb}_2^*$	E_1	U_2	661.8	662	L ζ (Sb) AuSb_2	25.04 24.12 0 31.17	39.43 15.79 100 66.67
$L+\zeta \leftrightarrow \alpha+\text{AuSb}_2$ $L \leftrightarrow \zeta+\alpha+\text{AuSb}_2^*$	E_2	U_3	663.1	650	L ζ α AuSb_2	38.74 40.68 56.68 32.84	36.34 10.57 0.29 66.67

Conclusions

By taking into account our recent experimental phase diagram data and thermodynamic properties of the Ag–Sb, Au–Bi, Ag–Au–Bi and Ag–Au–Sb systems and previous data available in the literature, we optimized both ternary systems, after having previously re-optimized the Ag–Sb and Au–Bi low order systems. A consistent set of thermodynamic parameters has been determined. A satisfactory agreement between experiments and calculation was found. In the Ag–Au–Sb system a change in the type of two invariant reactions U_2 and U_3 was calculated. These two transition ‘peritectic’ reactions may be degenerate, so additional experimental work is needed to confirm the reaction scheme.

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