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Critical assessment and optimization of the Ag–Au–Pb system

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ABSTRACT

By means of an optimization procedure, the ternary Ag–Au–Pb system has been assessed. All available experimental data of the ternary system and the results derived from thermodynamic descriptions for the three limiting binary systems are used. For the Ag–Au and Au–Pb systems, optimized Gibbs energy expressions were taken from the literature. A new assessment of the binary Ag–Pb system based on our calorimetric investigations is presented in this paper.

Calculated phase diagrams and some calculated thermochemical functions for the binary Ag–Pb and the ternary Ag–Au–Pb systems are compared with experimental data.

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1. Introduction

Ternary systems based on gold and silver metals have received more attention due to their numerous applications in the metallurgy, dental industry, etc. Knowledge of the reliable thermodynamic properties and precise phase diagram is important in considerations of process design and control. A few data exist for the Ag–Au–Pb ternary system. However, the boundary binary systems: Ag–Au, Ag–Pb and Au–Pb have been well studied. Optimization programs are now widely used to obtain consistent and reliable data for binary and multicomponent systems. Discrepancies in the available data can often be resolved, and interpolations and extrapolations can be made in a thermodynamically correct manner.

The purpose of this study is to check the consistency between the different types of experimental data from various literatures and to provide a critical assessment of the Ag–Au–Pb system. The thermodynamic description is performed according to the Calphad method using the Thermo-Calc code [1].

2. Bibliographic data

2.1. Ag–Au binary system

Phase diagram. The Ag–Au phase diagram exhibits a continuous solution both in the liquid state and in the solid state. The liquidus has been determined by several workers [2–8] and their data are in good agreement. The solidus is also well established, except for the data from Janecke [2] and Raydt [3]. The liquidus and solidus lines are very close; the difference is never more than 2 K at any given concentration.

A thermodynamic analysis based on several phase boundaries and thermochemical data available prior to 1990 was carried out by Hassam et al. [9]. Their thermodynamic parameters yield satisfactory results and are accepted in this work.

Thermodynamic properties. The enthalpy of mixing in the liquid phase has been measured calorimetrically by Kawakami at 1473 K [10], Oriani and Murphy at 1396 K [11], Itagaki and Yazawa at 1373 K [12], Rakotomavo at 1373 K [13], Miane at 1700 K [14], Topor and Kleppa [15] and Fitzner et al. at 1375 K [16]. The results exhibit negative deviation from ideal behaviour, except for those of Kawakami [10] close to zero. The recent calorimetric results of Fitzner et al. [16] agree reasonably with the values of Topor and Kleppa [15], Oriani and Murphy [11] and Miane [14], but are more exothermic than those obtained by Rakotomavo [13] in the composition ranges from $x_{Ag} = 0.4$ to about 0.7.

The data of Itagaki and Yazawa [12] differ considerably from the previous measurements.

Fitzner et al. [16] have measured the enthalpy of mixing by in situ mixing technique which is a better method to determine the liquid–liquid heats of mixing at high temperature than the "solid drop" technique. Their values seem to be the most reliable and are in good agreement with the calculated data [9].

Using the EMF method, Oriani [17] and Wagner and Engelhardt [18] determined thermodynamic activities of components in liquid Ag–Au at 1344 and 1358 K, respectively. The activities of Ag at

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1358 K in the liquid alloy have been also determined from mass spectrometer measurements by Ginsberg [19]. All measurements agree well and are reviewed by Hultgren et al. [20]. The activity values show a negative deviation from Raoult's law.

The solid Ag–Au alloys have been the subject of many thermodynamic investigations. Experimental data were already critically evaluated by Hultgren et al. [20] and Hassam [21].

2.2. Ag–Pb binary system

Phase diagram. The Ag–Pb phase diagram has been explored many times and a detailed review can be found elsewhere [22]. The Ag–Pb system is a simple eutectic formed by a liquid and two fcc phases (Ag and Pb). The assessed phase diagram [22] is in good agreement with the selected liquidus data [23–26]. The calculated eutectic composition and temperature are 95.5 at.% Pb and 577.15 K, respectively. The mutual solid solubility of Ag and Pb were reported by several authors [27–30]. The experimental data show close agreement for the solid solubility of Pb in Ag in the temperature range 573.15–873.15 K, a 0.3 at.% solubility was reported at 473.15 K [29]. The solid solubility of Ag in Pb is very restricted; the maximum solubility has been reported as 0.19 at.% at the eutectic temperature [30].

Lee et al. [31] and Lukas [32,33] carried out the thermodynamic modeling and the calculation of phase diagram. Another thermodynamic description has been done and the parameters describing the Gibbs energies of all the phases are available in the SGTE database [34]. Two models were considered: the first one with temperature dependent enthalpy of mixing [33,34] and the second one with temperature independent values [31,32]. The phase diagrams calculated according to these two assessments are very close each other and calculations did not allow us to settle the question of temperature dependence of the enthalpy of mixing.

Thermodynamic properties. By calorimetry, the enthalpy of mixing of Ag–Pb liquid were measured by Kawakami at 1323 K [35], Kleppa at 723 K [24], Himmelstjerna at 773 K [36], Ehrlich at 1248 K [37], Kozuka et al. at 1273 K [38], Castanet et al. [39] at 1280 K, Itagaki and Yazawa [40] at 1243 K, Hultgren and Sommelet at 1250 K [41]. These works report positive deviation from ideal behaviour. However, Kawakami [35] observed large positive enthalpy of mixing. His results and those of Himmelstjerna [36] show considerable scatter. The values of Castanet et al. [39] and Kozuka et al. [38] obtained almost at the same temperature agree reasonably but differ considerably from those of Itagaki and Yazawa [40]. Data given by Hultgren and Sommelet [41] are less endothermic than those of Castanet et al. [39]. Although these results can present some doubts, the enthalpy of mixing seems to be temperature dependent.

Thermodynamic activities in liquid alloys have been determined by the emf method [42–46], and the vapour pressure measurements [47–49]. These results are reviewed by Hultgren et al. [20] except for those of Iwase et al. [45] and, Jacob and Jeffes [46]. The data of Iwase et al. [45] and Hager and Wilkomirsky [42] are in good agreement.

As available data on the enthalpy of mixing are inconclusive, we carried out calorimetric measurements at two temperatures and experimental details and results are presented in Section 3. In addition, heat capacity of liquid alloys were measured for the eutectic alloy Ag–Pb ($x_{Pb} = 0.955$).

2.3. Au–Pb binary system

Phase diagram. The Au–Pb phase diagram shows six stable phases: five solid phases – Au_2Pb, $AuPb_2$, $AuPb_3$, fcc Au and Pb, and a liquid phase. The Cu_2Mg-type cubic phase Au_2Pb, the $CuAl_2$-type bct phase $AuPb_2$ and the αV_3S-type tetragonal phase are stoichiometric compounds and decompose peritectically. The mutual solubility of Au and Pb is very low. The liquidus has been determined several times. All these results are more or less in agreement with each other. Phase equilibrium information was subsequently reviewed by Okamoto and Massalski [50,51] and Okamoto [52]. Recently, Wang et al. [53] carried out the thermodynamic assessment by the CALPHAD method. The calculated phase diagram is in good agreement with the selected experimental data. Four invariant reactions occur in the Au-Pb system: three peritectic reactions at 707, 526 and 495 K, respectively, and one eutectic reaction at 488 K. Wang et al. [53] reported also that, the decomposition temperature of the $AuPb_3$ is about 380 K, and the $AuPb_2$ is stable up to 495 K.

Thermodynamic properties. Extensive measurements of the mixing enthalpy of the liquid alloys and the enthalpies of formation of the compounds employing the calorimetric method have been reported. The enthalpies of mixing appear to be strongly temperature dependent. The thermodynamic activities are also available in the literature. Experimental data prior to 2004 were already critically evaluated by Wang et al. [53] during the optimization of the Au–Pb system. Their analyses were considered in the present work. Recent calorimetric measurements [54] are in good agreement with the values calculated by Wang et al. [53]. Their thermodynamic description for Au–Pb system is selected in this work.

2.4. Ag–Au–Pb ternary system

Phase diagram. There is little experimental information available in the literature concerning the phase diagram or the thermodynamic data. The first thermodynamic study of Ag–Au–Pb ternary system was undertaken by Hager and Zambrano [55] using the galvanic cell method. Liquidus temperatures for seven alloys were determined. A 1200 K liquidus isotherm was deduced from the emf and Pb activity data. From these results, a liquidus surface was proposed by Prince et al. [56]. Using DTA measurements, Hassam et al. [57] have investigated the liquidus temperatures along four sections: $x_{Au}/x_{Ag} = 1/4$, 1, $x_{Au}/x_{Pb} = 1/3$ and $x_{Pb} = 0.4$. They reported two U-type reactions: $Liq + Au_2Pb = \alpha + AuPb_2$ (U_1) and $L + AuPb_2 = \alpha + AuPb_3$ (U_2), and one ternary eutectic: $L = Pb + \alpha + AuPb_3$ (E); α is a complete solid solution between Au and Ag. The comparison between the invariant reactions from Prince et al. [56] and the results of Hassam et al. [57] indicates a disagreement in the invariant compositions. For a better understanding of the phase equilibria in the four sections previously studied [57], Hassam and Bahari [58] reinvestigated recently, the ternary Ag–Au–Pb system, using DTA and X-ray powder diffraction analysis. They confirmed the three ternary invariants U_1, U_2 and E at 491, 487 and 482.5 K, respectively. These temperatures are in good agreement with those published by Prince et al. [56] except for U_1.

Thermodynamic properties. The only enthalpies of mixing of liquid ternary Ag–Au–Pb alloys available in the literature are those obtained recently by Hassam and Gheribi [54] at 973 K. Measurements were performed along three sections: $x_{Ag}/x_{Pb} = 1/4$, $x_{Au}/x_{Pb} = 1/4$ and 2/3 using a high temperature Calvet microcalorimeter.

3. Experimental investigations in the Ag–Pb binary system

3.1. Enthalpy of mixing

The enthalpy of formation of Ag–Pb liquid alloys were determined at 973 and 1065 K using a Calvet high temperature

Table 1
Experimental values of the molar integral enthalpy of mixing of the Ag–Pb system referred to liquid undercooled Ag and liquid Pb.

T = 973 K		T = 1065 K	
x_{Ag}	$\Delta_{mix}H_m$ (J mol^{-1})	x_{Ag}	$\Delta_{mix}H_m$ (J mol^{-1})
0.03335	511.51	0.02505	441.49
0.04349	615.34	0.05530	662.17
0.07133	1005.74	0.05811	926.24
0.08516	1102.07	0.09511	1376.12
0.11066	1429.89	0.11171	1329.04
0.12528	1508.70	0.13134	1717.59
0.15342	1801.94	0.16500	1834.31
0.16689	1871.65	0.16736	2013.8
0.19619	2085.85	0.20218	2247.15
0.20483	2129.36	0.21508	2212.13
0.23962	2301.49	0.23703	2444.69
0.24520	2344.12	0.26144	2526.74
0.28020	2460.54	0.27179	2596.7
0.28708	2511.77	0.30729	2657.59
0.32169	2560.93	0.30917	2693.03
0.32987	2604.70	0.34610	2734.65
0.36020	2594.29	0.35015	2762.61
0.37109	2624.70	0.38965	2830.75
0.39685	2598.14	0.42525	2836.50
0.40964	2575.12	0.45850	2802.63
0.43079	2554.38	0.49017	2731.95
0.44441	2569.96		

microcalorimeter (T < 1400 K) described elsewhere [59]. High purity metals Ag (4N) from Engelhard CLAL (Comptoir Lyon Alemand Louyot) and Pb (4N) from Alfa Aesar were employed in this study. The lead was scraped beforehand with a scalpel. The molar enthalpies of mixing were determined over the composition range $0 < x_{Ag} < 0.5$.

To synthesize alloys in the experimental cell, the direct drop method was applied [60]. The successive additions of small quantities of silver, stabilized at room temperature were dropped into the liquid lead maintained at the experimental temperature. All experiments were performed in high-purity argon (impurities < 5.5 vpm). The calorimeter was calibrated by additions of certified α-alumina from N.I.S.T [61] at the end of each experiment. The standard deviations of calibration experiments were about 0.1% and the uncertainties in the final values for the enthalpies of mixing were estimated to be 5%.

The experimental results referred to liquid undercooled Ag and liquid Pb are listed in Table 1 and are plotted in Fig. 1. The melting heat for silver is 10,578 J mol^{-1} at 973 K and 10,900 J mol^{-1} at 1065 K. The molar integral enthalpies are positive over the entire investigated composition range and increase with increasing temperature in agreement with the previous works. It is clear that in the range of temperature investigated, positive ΔC_P values in the

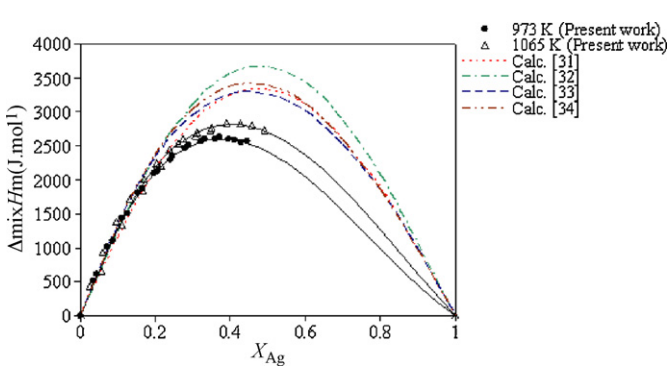

Fig. 1. Experimental integral molar enthalpies of mixing of liquid Ag–Pb at 973 and 1065 K. Comparison with the calculated data at 1065 K. Standard states: liquid undercooled Ag and liquid Pb.

liquid alloys are obtained. The variations of the enthalpy of mixing of Ag–Pb alloys are represented by the following equation.

$$\text{At 973 K}: \ \Delta_{mix}H_m(\text{J mol}^{-1}) = x_{Ag}(1-x_{Ag})(15524.07 - 11706.16x_{Ag})$$

$$\text{At 1065 K}: \ \Delta_{mix}H_m(\text{J mol}^{-1}) = x_{Ag}(1-x_{Ag})(15596.78 - 9580.40x_{Ag})$$

Our new enthalpy data show major inconsistency with the previous assessments [31–34] for x_{Ag} > 0.2 as it can be noted in Fig. 1. Based on that, a new assessment of the Ag–Pb system was performed in this work, using the present calorimetric measurements and the experimental data available in the literature.

The ternary mixing enthalpy for $x_{Au} = 0$ in the section $x_{Ag}/x_{Pb} = 1/4$ corresponds to the enthalpy in the Ag–Pb binary system for $x_{Ag} = 0.2$ at 973 K. Because the value used by Hassam and Gheribi [54] (2322 J/mol) is not obtained by a direct measure, our value (2109.2 J/mol) appears to be more accurate. In these conditions, the enthalpy of mixing of the ternary Ag–Au–Pb system in the section $x_{Ag}/x_{Pb} = 1/4$ must be evaluated again.

3.2. Heat capacity

No data on heat capacities of liquid alloys are available in the literature. Measurements were carried out for the eutectic alloy Ag–Pb ($x_{Pb} = 0.955$) in order to check the variation with temperature of the mixing enthalpy of the liquid phase.

The apparatus used in this investigation (D.S.C. 111, Setaram, Lyon-France) is designed as a Calvet microcalorimeter. A detailed description has been given by the Setaram Company and in previous publications. The experimental method used to determine the molar heat capacity of materials is the "stepped Cp method"; it has been described elsewhere [62,63]. Practically, if the temperature increases from T_1 to T_2 in the time range (t_2–t_1), the thermal disequilibrium between the experimental and reference cells observed, corresponds to the measurement of the variation in enthalpy during the same period. The heat capacity of the sample contained in the laboratory cell can be obtained as function of the temperature.

For C_p° measurements, the following procedure was adopted under the same conditions (constant rate, identical temperature, identical argon flow . . .):

The "zero" test with two identical empty containers, allows the thermal disequilibrium between the reference and laboratory cells to be determined.

The "experimental test" is performed with the sample in the experimental cell.

The "calibration test" is obtained either using a known mass of α alumina crystal [61]. The discrepancy between our experimental results and the reference data (N.I.S.T.) was always lower than 0.5%.

The metals Ag and Pb of about 500 mg were introduced in a silica tube and sealed under vacuum. They are then melted into the separate furnace and analyzed in a differential scanning calorimeter to control their homogeneity.

To measure the heat capacities, the samples were placed in a stainless steel cell. The experiments were performed under purified argon flow in the temperature range 623–973 K. A sequence includes a temperature step of 2 K at the 2 K min^{-1} rate followed by a stabilization of the temperature during 600 s. The experimental value of C_p° at T_{exp} is the mean value between ($T_{exp} - 1$) K and ($T_{exp} + 1$) K.

Temperatures were determined at ±0.5 K and molar heat capacities were measured with an accuracy of about 2%.

The experimental values of the molar heat capacity of eutectic alloy ($Ag_{0.045}Pb_{0.955}$) obtained are gathered in Table 2.

Table 2
Experimental heat capacity of Ag–Pb system at eutectic composition.

T (K)	C_p° (J/g K)	C_p° (J/K mol)	T (K)	C_p° (J/g K)	C_p° (J/K mol)	T (K)	C_p° (J/g K)	C_p° (J/K mol)
628.812	0.153	31.042	742.489	0.159	32.293	854.140	0.159	32.252
630.807	0.151	30.643	744.482	0.162	32.820	856.135	0.160	32.400
632.800	0.150	30.349	746.473	0.160	32.455	858.130	0.153	31.117
634.791	0.155	31.385	748.467	0.156	31.701	860.127	0.157	31.760
636.787	0.157	31.837	750.461	0.159	32.242	862.122	0.170	34.444
638.780	0.157	31.896	752.457	0.160	32.471	864.117	0.164	33.260
640.774	0.162	32.865	754.452	0.160	32.382	866.112	0.163	33.023
642.769	0.158	32.029	756.444	0.156	31.650	868.103	0.166	33.552
644.761	0.153	31.026	758.439	0.154	31.206	870.097	0.164	33.242
646.753	0.155	31.512	760.435	0.160	32.396	872.094	0.162	32.792
648.750	0.152	30.728	762.429	0.161	32.686	874.089	0.164	33.215
650.744	0.157	31.857	764.423	0.161	32.664	876.081	0.155	31.385
652.737	0.159	32.224	766.417	0.156	31.557	878.076	0.155	31.407
654.732	0.161	32.538	768.411	0.157	31.823	880.071	0.161	32.577
656.725	0.160	32.439	770.407	0.156	31.638	882.066	0.163	33.061
658.716	0.159	32.191	772.403	0.161	32.706	884.062	0.159	32.331
660.709	0.158	32.001	772.392	0.165	33.377	886.057	0.155	31.391
662.703	0.155	31.387	774.375	0.158	31.940	888.052	0.159	32.175
664.696	0.160	32.394	776.366	0.158	31.987	890.044	0.162	32.806
666.690	0.158	32.013	778.359	0.159	32.262	892.040	0.164	33.209
668.680	0.158	32.007	780.354	0.154	31.304	894.037	0.163	32.984
670.673	0.161	32.638	782.349	0.161	32.702	896.032	0.162	32.877
672.669	0.159	32.297	784.341	0.164	33.331	898.023	0.165	33.452
674.664	0.162	32.830	786.334	0.158	32.070	900.015	0.162	32.938
676.658	0.161	32.727	788.326	0.156	31.535	902.011	0.161	32.648
678.651	0.160	32.417	790.318	0.161	32.619	906.003	0.154	31.289
680.646	0.162	32.938	792.314	0.162	32.785	909.988	0.155	31.425
682.641	0.164	33.335	794.308	0.160	32.457	911.983	0.161	32.676
684.636	0.158	32.050	796.301	0.160	32.487	913.979	0.159	32.157
686.632	0.159	32.283	798.296	0.158	32.088	915.974	0.164	33.236
688.627	0.163	33.077	800.291	0.161	32.607	917.968	0.166	33.568
690.620	0.161	32.708	802.285	0.157	31.849	919.962	0.161	32.723
692.614	0.162	32.828	804.280	0.155	31.520	921.957	0.162	32.741
694.609	0.163	33.041	806.275	0.167	33.785	923.952	0.166	33.641
696.603	0.165	33.402	808.271	0.160	32.441	925.946	0.163	33.023
698.596	0.160	32.492	810.264	0.157	31.885	927.942	0.165	33.485
700.593	0.155	31.427	812.260	0.157	31.825	929.937	0.164	33.175
702.590	0.157	31.916	814.253	0.160	32.506	931.931	0.164	33.286
704.583	0.165	33.513	816.244	0.161	32.560	933.927	0.162	32.741
706.577	0.162	32.753	818.237	0.165	33.416	935.923	0.158	32.098
708.572	0.156	31.610	820.231	0.158	32.127	937.917	0.167	33.911
710.567	0.158	31.948	822.225	0.155	31.484	939.909	0.155	31.423
712.563	0.157	31.845	824.220	0.159	32.143	941.902	0.158	32.021
714.558	0.157	31.804	826.214	0.154	31.168	943.897	0.159	32.269
716.553	0.155	31.460	828.205	0.158	32.064	945.890	0.164	33.213
718.549	0.156	31.541	830.199	0.158	31.948	947.882	0.163	33.067
720.543	0.155	31.498	832.193	0.163	32.952	949.874	0.162	32.838
722.537	0.158	31.968	834.189	0.160	32.360	951.866	0.162	32.834
724.534	0.155	31.460	836.186	0.158	32.129	953.859	0.158	31.968
726.530	0.155	31.399	838.179	0.162	32.838	955.852	0.164	33.185
728.523	0.158	32.044	840.175	0.158	31.966	957.846	0.162	32.804
730.516	0.158	31.991	842.173	0.156	31.630	959.843	0.163	32.982
732.512	0.155	31.397	844.170	0.158	32.104	961.838	0.157	31.885
734.507	0.154	31.241	846.161	0.159	32.252	963.830	0.158	32.056
736.499	0.158	32.035	848.155	0.157	31.729	965.825	0.159	32.226
738.496	0.161	32.648	850.150	0.161	32.560	967.821	0.156	31.681
740.495	0.159	32.220	852.144	0.163	32.976	969.817	0.159	32.173

4. Thermodynamic modeling and optimization

The substitutional solution model was used to describe the liquid and fcc-A1 (Au, Ag or Pb) phases. This model yields the following expression for the Gibbs energy:

$$G_m^\varphi = \sum_i x_i^\varphi {}^0G_i^\varphi + RT\sum_i x_i^\varphi \ln(x_i^\varphi) + G^{\varphi,xs} \quad (1)$$

in which x_i^φ is the molar fraction of element i in the phase φ, ${}^0G_i^\varphi$ represents the Gibbs energy of i in the same physical structure as φ taken from Dinsdale [64].

The thermodynamic quantities can be referred to the enthalpies of the pure elements in their stable state at 298.15 K, ${}^0H_i^{SER}(298.15\,\mathrm{K})$, as follows:

$$G_m^\varphi - \sum x_i^\varphi {}^0H_i^{\mathrm{SER}}(298.15\,\mathrm{K}) = \sum x_i^\varphi({}^0G_i^\varphi - {}^0H_i^{\mathrm{SER}}(298.15\,\mathrm{K})) + RT\sum x_i^\varphi \ln(x_i^\varphi) + G^{\varphi,xs} \quad (2)$$

Table 3
Evaluated thermodynamic parameters in the Ag–Au–Pb system (in J mol^{-1}).

System	Phase	Parameters	Ref.
Ag–Au	Liquid (L)	${}^{0}L^{L}_{Ag,Au} = -16,402 + 1.14T$	[9]
	Fcc-A1	${}^{0}L^{fcc}_{Ag,Au} = -15,599$	
Ag–Pb	Liquid (L)	${}^{0}L^{L}_{Ag,Pb} = -3746.161 + 113.1129T - 14.6377T\ln(T)$;	Present work
		${}^{1}L^{L}_{Ag,Pb} = -3423.095 + 1.0270T$;	
		${}^{2}L^{L}_{Ag,Pb} = 982.010 - 2.6091T$	
	Fcc-A1	${}^{0}L^{fcc}_{Ag,Pb} = 61,111.737 - 35.9004T$;	
		${}^{1}L^{fcc}_{Ag,Pb} = -23,560.202 + 31.5895T$;	
		${}^{2}L^{fcc}_{Ag,Pb} = -12,675.623$	
Au–Pb	Liquid (L)	${}^{0}L^{L}_{Au,Pb} = -17,577.988 + 105.97303T - 14.435179T\ln(T)$;	[54]
		${}^{1}L^{L}_{Au,Pb} = 2673.2826 - 5.379358T$	
	Fcc-A1	${}^{0}L^{fcc}_{Au,Pb} = 30,000$	
	Au_2Pb, $(Au)_{0.667}(Pb)_{0.333}$	${}^{0}G_{Au_2Pb} - 0.667{}^{0}G^{fcc}_{Au} - 0.333{}^{0}G^{fcc}_{Pb} = -3010 + 0.5T$	
	$AuPb_2$, $(Au)_{0.333}(Pb)_{0.667}$	${}^{0}G_{AuPb_2} - 0.333{}^{0}G^{fcc}_{Au} - 0.667{}^{0}G^{fcc}_{Pb} = -2800 + 1.45T$	
	$AuPb_3$, $(Au)_{0.25}(Pb)_{0.75}$	${}^{0}G_{AuPb_3} - 0.25{}^{0}G^{fcc}_{Au} - 0.75{}^{0}G^{fcc}_{Pb} = -1900 + 0.56T$	
Ag–Au–Pb	Liquid (L)	${}^{0}L^{L}_{Ag,Au,Pb} = 28136.926 - 25.170T$;	Present work
		${}^{1}L^{L}_{Ag,Au,Pb} = 23,906.324 - 58.049T$;	
		${}^{2}L^{L}_{Ag,Au,Pb} = 453.546 + 28.419T$	
	Fcc-A1	${}^{0}L^{fcc}_{Ag,Au,Pb} = 80608.231$; ${}^{1}L^{fcc}_{Ag,Au,Pb} = {}^{2}L^{fcc}_{Ag,Au,Pb} = 0$	
	Au_2Pb, $(Ag,Au)_{0.667}(Pb)_{0.333}$	${}^{0}G^{Au_2Pb}_{Ag:Pb} - 0.667{}^{0}G^{fcc}_{Ag} - 0.333{}^{0}G^{fcc}_{Pb} = 20,000$;	
		${}^{0}L^{Au_2Pb}_{Ag,Au:Pb} = -5000$	

The excess Gibbs energy $G^{\varphi,xs}$ can be expressed in Redlich-Kister-Muggianu formalism [65,66]:

$$G^{\varphi,xs} = x^{\varphi}_{Ag}x^{\varphi}_{Au}\sum_{\nu=0}^{n}{}^{\nu}L^{\varphi}_{Ag,Au}\left(x^{\varphi}_{Ag} - x^{\varphi}_{Au}\right)^{\nu} + x^{\varphi}_{Ag}x^{\varphi}_{Pb}\sum_{\nu=0}^{n}{}^{\nu}L^{\varphi}_{Ag,Pb}\left(x^{\varphi}_{Ag} - x^{\varphi}_{Pb}\right)^{\nu} + x^{\varphi}_{Au}x^{\varphi}_{Pb}\sum_{\nu=0}^{n}{}^{\nu}L^{\varphi}_{Au,Pb}\left(x^{\varphi}_{Au} - x^{\varphi}_{Pb}\right)^{\nu} + x^{\varphi}_{Ag}x^{\varphi}_{Au}x^{\varphi}_{Pb}\left(x^{\varphi}_{Ag}\,{}^{0}L^{\varphi}_{Ag,Au,Pb} + x^{\varphi}_{Au}\,{}^{1}L^{\varphi}_{Ag,Au,Pb} + x^{\varphi}_{Pb}\,{}^{2}L^{\varphi}_{Ag,Au,Pb}\right) \quad (3)$$

where, ${}^{\nu}L^{\varphi}_{i,j}$ and ${}^{\nu}L^{\varphi}_{i,j,k}$ are the interaction parameters between elements i and j and ternary parameters which can be temperature dependent as follows:

$${}^{\nu}L = {}^{\nu}A + {}^{\nu}BT + {}^{\nu}CTLnT \quad (4)$$

These parameters are derived from an optimization procedure, using the module Parrot developed by Jansson [67] included in the Thermo-Calc software [1].

All optimized binary and ternary thermodynamic parameters are given in Table 3.

4.1. Ag–Au and Au–Pb binary systems

The complete Ag–Au and Au–Pb systems have been assessed by Hassam et al. [9] and Wang et al. [53], respectively. As mentioned above, their thermodynamic descriptions are accepted in this work and are listed in Table 3.

4.2. Ag–Pb binary system

The calculated phase diagram is compared with the experimental results in Fig. 2. The agreement is very good. The calculated eutectic composition and temperature are $x_{Ag} = 0.045$ and 576.8 K, respectively. These values show excellent agreement with those assessed by Karakaya and Thompson [22].

The calculated thermodynamic quantities of the liquid alloy are presented in Figs. 3 and 4. We considered the temperature dependance of the enthalpy of mixing of the liquid phase, as can be seen, in Fig. 3. The calculated results are in good agreement with the selected experimental data. The molar integral enthalpies are positive and increase with increasing temperature in agreement with the data of heat capacity presented above.

The activities of Ag and Pb calculated at 1200 K are compared with available experimental data in Fig. 4. The agreement between calculated Pb activities and the experiments is satisfactory.

4.3. Ag–Au–Pb ternary system

Combining the Ag–Pb binary system assessed in the present work with the Ag–Au and Au–Pb binary systems optimized previously, the Ag–Au–Pb ternary system has been optimized based on available experimental information.

The calculated enthalpies of mixing along three sections at 973 K are compared with the experimental results in Fig. 5. The calcu-

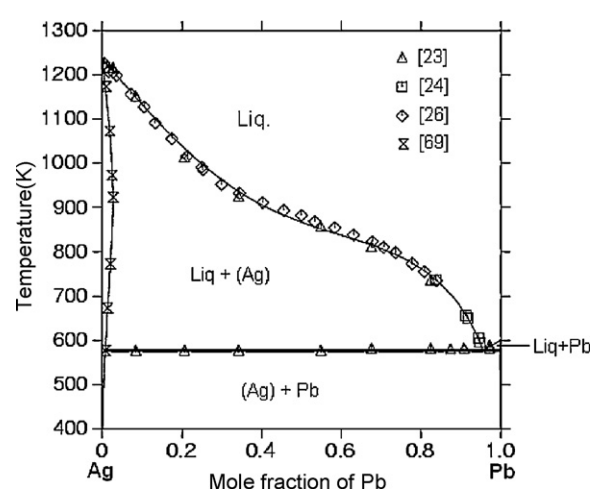

Fig. 2. Calculated phase diagram of Ag–Pb system compared with experimental data.

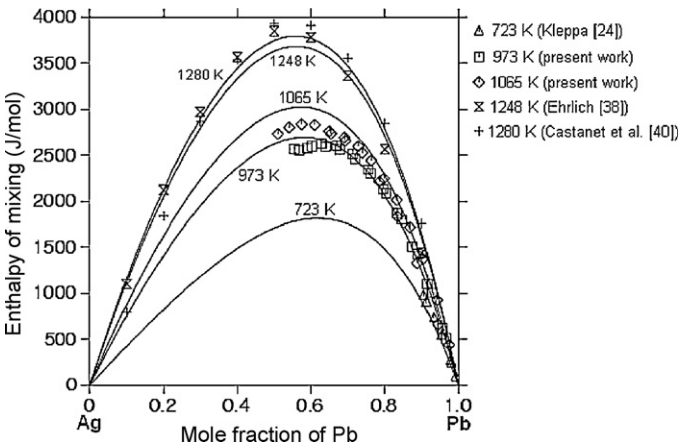

Fig. 3. Calculated mixing enthalpies of the liquid Ag–Pb system at different temperatures together with experimental data. Standard states: liquid undercooled Ag and liquid Pb.

lated results are reasonable and acceptable if one considers the experimental errors.

Fig. 6 shows the calculated isopleths of the Ag–Au–Pb ternary system compared with experimental data. The calculated liquidus is in good agreement with available experimental data [57,58]. The calculated phase boundaries are in general in accordance with experimental data obtained by Hassam and Bahari [58]. A little disagreement between calculated and experimental data can be found in the sections $x_{Ag}/x_{Au} = 4/1$ and $x_{Pb} = 0.4$ (see Fig. 6b and d) concerning the (Liq + α + Pb) and (Liq + α + Au_2Pb) three-phase regions, respectively.

The calculated isothermal liquidus lines and liquidus projection of the Ag–Au–Pb system are given in Fig. 7.

At 400 K, no liquid is involved in the phase equilibria. The triangulation of the ternary Ag–Au–Pb system is based on the $AuPb_2$, $AuPb_3$, Au_2Pb and (Pb) phases and the solid solution α between Ag and Au. Three three-phase regions were obtained: α + $AuPb_2$ + Au_2Pb, α + $AuPb_3$ + $AuPb_2$ and α + $AuPb_3$ + (Pb), as shown in Fig. 8.

A detailed compilation of the invariant reactions is shown in Table 4. Our calculated values are consistent with the results reviewed by Prince et al. [56].

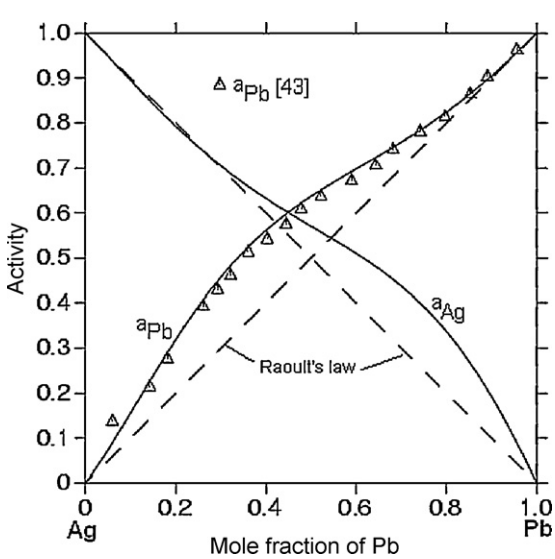

Fig. 4. Calculated and experimental activities in the liquid phase at 1200 K. Standard states: liquid Ag and Pb.

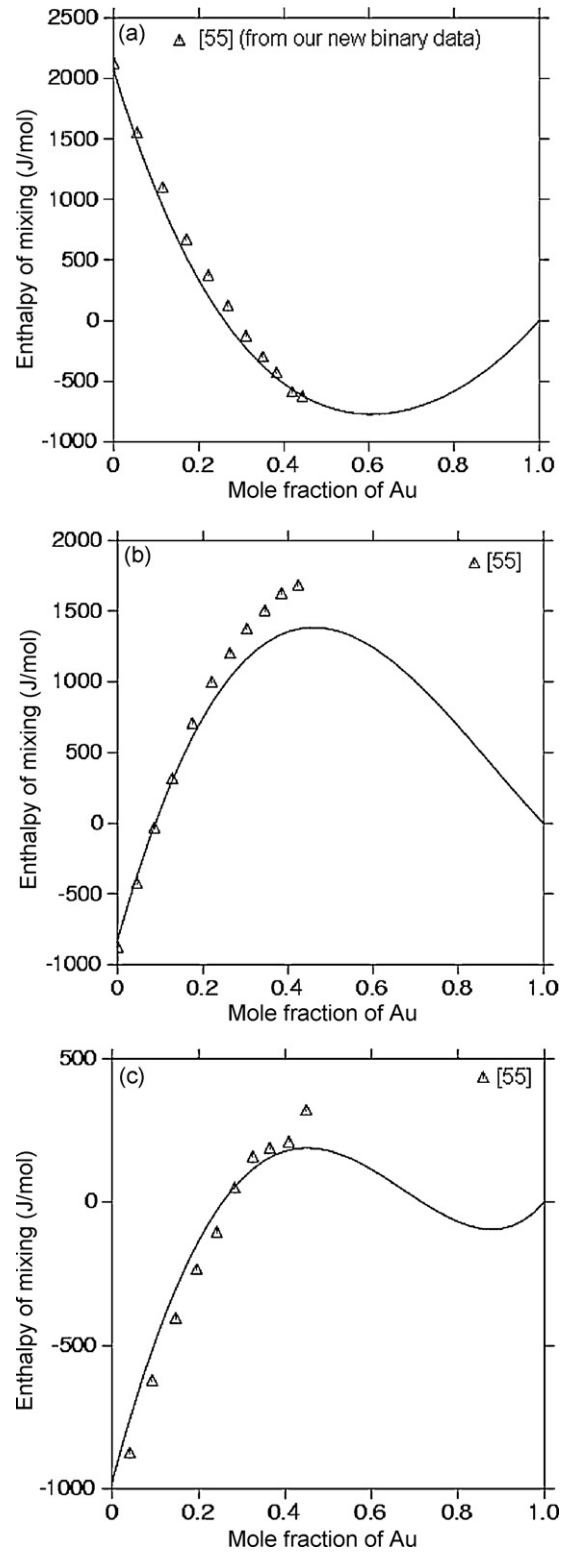

Fig. 5. Calculated mixing enthalpies of the liquid Ag–Au–Pb system at 973 K along three isoplethic sections compared with the experimental data. (a) $x_{Ag}/x_{Pb} = 1/4$; (b) $x_{Au}/x_{Pb} = 1/4$; and (c) $x_{Au}/x_{Pb} = 2/3$.

The major disagreement between the present work and that of Hassam and Bahari [58] concerns the temperature of the U-type reaction: L + Au_2Pb = α + $AuPb_2$ (U_1) reported as 524.5 and 491 K, respectively. No definite reason is found for that difference. This disagreement cannot only be explained by the insufficiencies of the thermodynamic model and optimization. Indeed, ther-

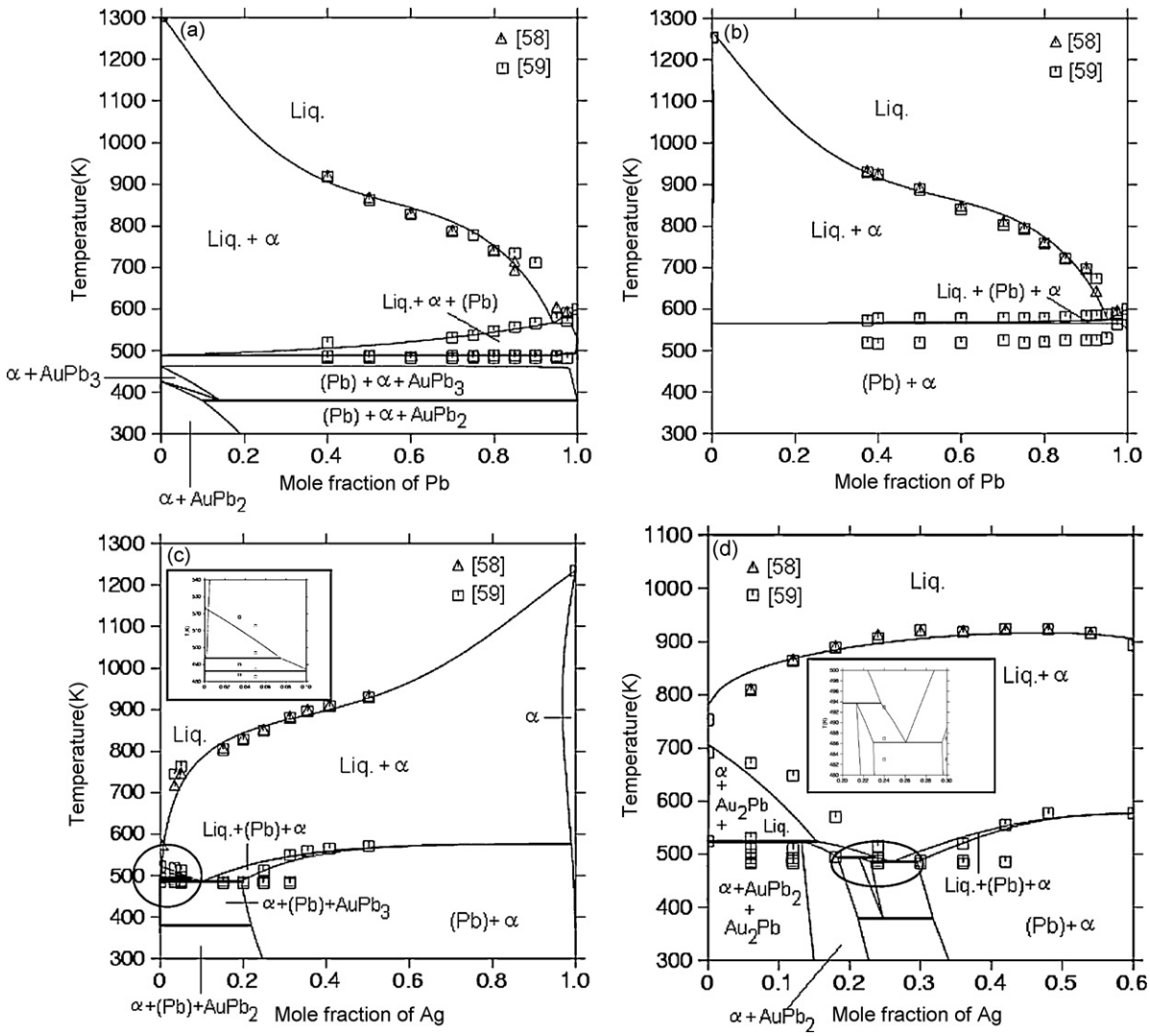

Fig. 6. Calculated four isopleths of Ag–Au–Pb system compared with the experimental data. (a) $x_{Ag}/x_{Au} = 1/1$; (b) $x_{Ag}/x_{Au} = 4/1$; (c) $x_{Au}/x_{Pb} = 1/3$; and (d) $x_{Pb} = 0.4$.

modynamic parameters used in this work accommodate all the reported binary and ternary data. For the ternary systems not presenting any very strong interactions as the Ag–Au–Pb system: no ternary compounds, weak values of enthalpies of mixing, etc., the ordinary substitutional solution model can be used and the Redlich–Kister polynomial is sufficient to describe the liquid and the disordered phases. In some cases, phase equilibria in a ternary system can be predicted satisfactorily from the only binary parameters.

The U-type reaction U_1 [58] has been experimentally put in evidence in the section $x_{Pb} = 0.4$ in the range $0 < x_{Ag} < 0.2$. However, the number of thermal effects observed in the samples $x_{Ag} = 0.0601$ and 0.1199 could let think about a metastable equilibrium, in spite of the long isothermal annealing periods. In these conditions, it is not excluded that the temperature of the invariant U_1 is higher than the one proposed (491 K).

Considering the pronounced tendency of supercooling for the Ag–Au–Pb alloys, further experiments on the ternary alloys, espe-

Table 4
Experimental and calculated values for the invariant reactions in the Ag–Au–Pb system.

Reaction	Type	T (K)	Composition		Ref.
			x_{Au}^{liq}	x_{Pb}^{liq}	
$L + Au_2Pb = \alpha + AuPb_2$	U_1	491	–	–	[59]
		522	0.2610	0.7337	[57]
		524.5	0.2597	0.7367	Present work (calc.)
$L + AuPb_2 = \alpha + AuPb_3$	U_2	487	–	–	[59]
		491	0.1861	0.8091	[57]
		493.7	0.1739	0.8218	Present work (calc.)
$L = (Pb) + \alpha + AuPb_3$	E	482.5	–	–	[59]
		485	0.1696	0.8253	[57]
		486.2	0.1519	0.8436	Present work (calc.)

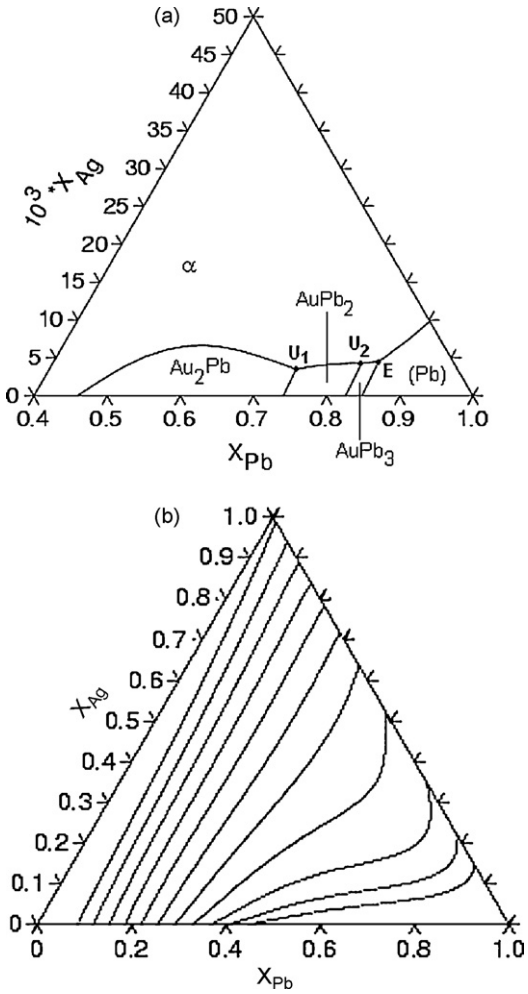

Fig. 7. Calculated (a) isothermal liquidus lines and (b) liquidus projection (723–1223 K, step: 50 K) of the Ag–Au–Pb system.

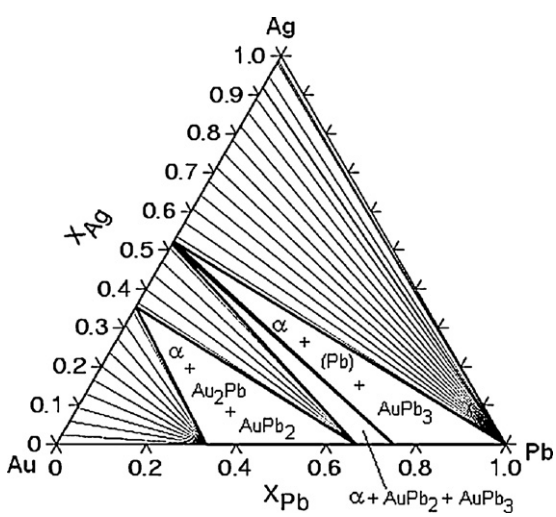

Fig. 8. Calculated isothermal section of Ag–Au–Pb system at 400 K.

cially examination of isothermal equilibria are necessary to resolve this discrepancy.

5. Conclusions

The enthalpies of mixing of liquid Ag–Pb alloys have been determined at 973 and 1065 K. The temperature-dependence of the enthalpy of mixing is stated. Combining the present results with experimental data available in the literature, the binary Ag–Pb system has been re-assessed. The thermodynamic properties and phase diagram calculated using the new optimized parameters are in good agreement with experimental data. A first thermodynamic description is proposed for the ternary Ag–Au–Pb system. Thermodynamic properties of liquid alloys, vertical sections, liquidus projection and an isothermal section at 400 K were calculated. A satisfactory agreement between the experimental and calculated data is obtained except for the temperature of the U-type reaction: $L + Au_2Pb = \alpha + AuPb_2$, which emphasizes the need for further experimental data.

References

[1] B. Sundman, B. Jansson, J.O. Anderson, CALPHAD 9 (1985) 153.
[2] E. Janecke, Metallurgie 8 (19) (1911) 597.
[3] U. Raydt, Z. Anorg. Chem. 75 (1912) 58.
[4] C. Wagner, Acta Met. 2 (2) (1954) 242.
[5] J.L. White, Trans. AIME 215 (1) (1959) 178.
[6] J.L. White, R.L. Orr, R. Hultgren, Acta Met. 5 (12) (1957) 747.
[7] J. Markali, P. Thoresen, Acta Chem. Scand. 15 (1961) 31.
[8] C.J. Cooke, M. Hume-Rothery, Acta Met. 9 (10) (1961) 982.
[9] S. Hassam, J. Agren, M. Gaune-Escard, J.P. Bros, Metall. Trans. A 21 (1990) 1877.
[10] M. Kawakami, Sci. Rep. Tohoku Univ. 19 (1930) 521.
[11] R.A. Oriani, W.K. Murphy, J. Phys. Chem. 62 (1958) 327.
[12] K. Itagaki, A. Yazawa, J. Jpn. Inst. Met. 35 (4) (1971) 389.
[13] J. Rakotomavo, Thèse Doct. Spec., Univ. de Provence, Marseille, 1979.
[14] J.M. Miane, Thèse Doct. Spec., Univ. de Provence, Marseille, 1979.
[15] L. Topor, O.J. Kleppa, Metall. Trans. A 15 (1984) 203.
[16] K. Fitzner, Q. Guo, J. Wang, O.J. Kleppa, J. Alloys Compd. 291 (1999) 190.
[17] R.A. Oriani, Acta Met. 4 (1) (1956) 15.
[18] C. Wagner, E. Engelhardt, Z. Physik. Chem. 159 (1932) 241.
[19] M.J. Ginsberg, Thesis, Univ. Pennsylvania USA, 1969.
[20] R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, Selected Values of the Thermodynamic Properties of Binary Alloys, ASM, Metals Park, OH, 1973.
[21] S. Hassam-Dalichaouch, Thèse Doct., Univ. Provence, Marseille, 1985.
[22] I. Karakaya, W.T. Thompson, Bull. Alloy Phase Diag. 8 (1987) 326.
[23] G.J. Petrenko, Z. Anorg. Chem. 53 (1907) 200.
[24] O.J. Kleppa, J. Phys. Chem. 60 (1956) 446.
[25] G.W. Preckshot, R.E. Hudrlik, Trans. AIME 218 (1960) 516.
[26] C.T. Heycock, F.H. Neville, Philos. Trans. R. Soc. Lond. Ser. A 189 (1897) 37.
[27] B.M. Glazov, P.A. Akopyan, Izv. Akad. Nauk SSSR Met. 1 (1975) 162.
[28] R.A. Akopyan, S.Kh. Mamedova, E.R. Kerimov, V.U.Z. Izv, Tsvetn. Metall. 6 (1983) 83.
[29] D.D. Pollock, Trans. AIME 239 (1967) 1768.
[30] K. Kusunoki, K. Tsumuraya, S. Nishikawa, Trans. Jpn. Inst. Met. 22 (1981) 501.
[31] B.Z. Lee, C.S. Oh, D.N. Lee, J. Alloys Compd. 215 (1994) 293.
[32] H.L. Lukas, unpublished optimization, (2000) in COST 531 database version 1.1, 2004.
[33] Landolt-Börnstein-Group IV Physical Chemistry Numerical Data Functional Relationships in Science Technology Binary Systems, 19 B1, Elements and Binary Systems from Ag–Al to Au–Tl, 2002, pp. 64–68.
[34] SGTE Solution Database, 1998.
[35] M. Kawakami, Sci. Rep. Tohoku Imp. Univ. 19 (1930) 521.
[36] H.O. Von Samson-Himmelstjerna, Z. Metallkd. 28 (1936) 197.
[37] K. Ehrlich, Inaugural Dissertation, Ludwig-Maximilians-Universität, München, 1965.
[38] Z. Kozuka, T. Oishi, J. Moriyama, Nippon Kihz. Gakk. 32 (1968) 136.
[39] R. Castanet, Y. Claire, M. Lafitte, J. Chim. Phys. 66 (1969) 1276.
[40] K. Itagaki, A. Yazawa, J. Jpn. Inst. Met. 32 (1968) 1294.
[41] R. Hultgren, P. Sommelet, Proc. First Intern. Conf. Calorimetry and Thermodynamics, Warsaw, 1969, p. 1027.
[42] J.P. Hager, I.A. Wilkomirsky, Trans. AIME 242 (1968) 183.
[43] J. Terpilowski, Arch. Hutnictwa 2 (1957) 289.
[44] V.N. Eremenko, Ukr. Khim. Zh. 23 (1957) 6.
[45] M. Iwase, K. Fujimura, T. Mori, Trans. Jpn. Inst. Met. 19 (1978) 377.
[46] K.T. Jacob, J.H.E. Jeffes, J. Chem. Thermodyn. 3 (1971) 433.
[47] A.T. Aldred, J.N. Pratt, Trans. Faraday Soc. 57 (4) (1961) 611.
[48] R.Zh. Khobdabergenov, V.I. Nesterov, E.T. Ivragimov, A.S. Shendyapin, E.I. Vasharatyan, E.I. Kalinin, Trans. Inst. Met. i Obogashch. Akad. Nauk Kaz. SSR 26 (1967) 37.
[49] A.P. Granovskaya, A.P. Lyubimov, Z. Fiz. Khim 27 (1953) 1437.
[50] H. Okamoto, T.B. Massalski, Bull. Alloy Phase Diagrams 1 (1980) 54.
[51] H. Okamoto, T.B. Massalski, Bull. Alloy Phase Diagrams 5 (1984) 276.
[52] H. Okamoto, J. Phase Equilib. 14 (1993) 648.

[53] J. Wang, H.S. Liu, Z.P. Jin, CALPHAD 28 (2004) 91.
[54] S. Hassam, A. Gheribi, Thermochim. Acta 464 (2007) 1.
[55] J.P. Hager, A.R. Zambrano, Trans. AIME 245 (1969) 2313.
[56] A. Prince, G. Petzow, G. Effenberg (Eds.), Ternary Alloys, vol. 1, Verlag Chemie, Weinheim, 1988, p. 190.
[57] S. Hassam, M. Gambino, J.P. Bros, Thermochim. Acta 257 (1995) 83.
[58] S. Hassam, Z. Bahari, J. Alloys Compd. 392 (2005) 120.
[59] J.P. Bros, J. Less-Common Met. 154 (1989) 9.
[60] M. Gambino, Thèse Doct. Ès Sc. Phys., Marseille, 1976.
[61] National Institute of Standards and Technology (NIST), US Department of Commerce, Gaithersburg, Washington, DC, 1989.
[62] M. Gambino, P. Rebouillon, J.P. Bros, G. Borzone, G. Cacciamani, R. Ferro, J. Less-Common Met. 154 (1989) 195.
[63] M Gambino, P. Gaune, W. Szczepaniak, Ber. Bunsenges. Phys. 93 (1989) 555.
[64] A.T. Dinsdale, CALPHAD 15 (4) (1991) 317.
[65] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 345.
[66] Y.M. Muggianu, M. Gambino, J.P. Bros, J. Chim. Phys. 72 (1975) 83.
[67] B. Jansson, Ph.D. Thesis, KTH, Stockholm, Sweden, 1984.