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The Ag + Au + Pb system: Determination of the liquidus surface

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Abstract

The liquidus surface of the Ag + Au + Pb system has been determined by differential thermal analysis. In the temperature range 973–298 K, experiments were performed along the four following sections: $x_{Au}/x_{Pb} = 1/3$ with $0 < x_{Ag} < 0.50$; $x_{Au}/x_{Ag} = 1/4$ and 1/1 with $0.30 < x_{Pb} < 1$; and $x_{Pb} = 0.4$ with $0 < x_{Ag} < 0.54$. These results allow the liquidus surface and the ternary eutectic valley to be proposed.

Keywords: DTA; Gold; Lead; Liquidus; Silver

1. Introduction

This research is part of a systematic study of the thermodynamic properties of the ternary systems Ag + Au + M with M being Ge, Si, Sn and Pb [1–4].

As shown in Fig. 1, the limiting binary systems of Ag + Au + Pb alloy present: (i) a typical complete solubility of the components in both the liquid and solid phase (Ag–Au); (ii) a single eutectic point (Ag–Pb); and (iii) three definite compounds (Au–Pb). From a critical analysis of the thermodynamic properties of formation of these binary alloys, weak inter-bondings in the ternary melt alloys can be predicted and the existence of ternary intermetallic compounds seems improbable.

So, the approximate shape of the liquidus surface may be predicted with a good degree of probability in a large ternary molar fraction range, except in the Pb-rich region where a ternary eutectic valley may be expected.

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The first solid–liquid equilibrium temperatures were given by Hager and Zambrano [5] in the high-temperature range. Using these results, a liquidus surface was proposed by Prince [6]. In spite of some determinations of the excess functions of formation of the Ag–Au–Pb system, no thermodynamic assessment has been published.

Consequently a new study of the Ag–Au–Pb alloy was undertaken using calorimetry and thermal analysis. In this article, some of the results obtained by differential thermal analysis are reported. The aim of the present research was the determination of the liquidus surface and the localization of the eutectic valley for ternary alloys in the Pb-rich region.

2. Bibliography survey

Very little information is published on the Ag + Au + Pb system. The first thermodynamic study of Ag + Au + Pb alloy was by Hager and Zambrano in 1969 [5]. From potentiometric measurements performed between 1044 and 1303 K, valuable data for the activity of lead and the liquidus surface were determined. The solid–liquid equilibrium temperatures of seven alloys were determined (results are given in Table 1) and the 1200 K liquidus isotherm was deduced.

In contrast, the phase diagrams of the limiting binary systems are well known.

(a) Ag–Au. This system consists of a continuous series of solid solutions, and the liquidus and solidus lines are very close (about 1.5 K at $x_{Ag} = 0.5$) [7, 8].

(b) Ag–Pb. The phase diagram published by Hansen [7] is of eutectic type with limited solid solubility at both the Ag and Pb sides of the diagram. The coordinates of the eutectic point are: $x_E = 0.953$ and $T_E = 577$ K.

(c) Au–Pb. For this system, the phase diagram published in the Bulletin of Alloy Phase Diagrams [9, 10] is from Bhattacharyya and Reynolds [11]. Recently, new thermodynamic data were proposed [12]; they have been criticized by Okamoto [13]. Three intermetallic compounds were formed by peritectic reaction: Au_2Pb at 707 K, $AuPb_2$ at 526 K and $AuPb_3$ at 494.5 K. In the Pb-rich region, a eutectic reaction takes place at 485.5 K.

3. Experimental

Measurements between 300 and 1000 K were performed using a classical differential thermal analyser (Setaram, France). The cells employed were a Pyrex tube of about

Table 1
Liquidus temperatures from Hager [5]

x_{Pb}	x_{Ag}	x_{Au}	x_{Ag}/x_{Au}	T_{liq}/K
0.0940	0.76935	0.13665	5.63	1163
0.1980	0.68103	0.12097	5.63	1061
0.1000	0.6273	0.2727	2.30	1183
0.1000	0.4500	0.4500	1	1175
0.1000	0.2706	0.6294	0.430	1219
0.1000	0.1373	0.7627	0.18	1228
0.2000	0.1220	0.6780	0.18	1101

8 mm external diameter and 10 mm height. The bottom of the cells are shaped to fit the junction of the thermocouple (Pt–Pt + Rh 10 wt%); so the thermal detector is near the investigated alloy.

High purity metals (99.99 at% Au and Ag (wires)) and 99.999 at% Pb (ingot) from Koch and Light Ltd., London) were employed. The crucible was charged with about 0.1–0.3 g of metals (Ag, Au, Pb) and sealed under a high-purity argon atmosphere (from Air Liquide company). The alloying process was performed in an adjacent small furnace during several heating and cooling cycles, then maintained for one week at 473 K in the solid state.

The differential thermal analyser (DTA) was calibrated with the temperature of melting of pure metals (indium, tin, lead) and the temperature uncertainty was about ± 1.5 K.

4. Results

The experiments were performed with ternary alloys within the conditions (see Fig. 1): $x_{Au}/x_{Pb} = 1/3$ with $0 < x_{Ag} < 0.50$; $x_{Au}/x_{Ag} = 1/4$ and 1/1 with $0.30 < x_{Pb} < 1$; and in the section $x_{Pb} = 0.4$ with $0 < x_{Ag} < 0.54$.

The chosen range of composition is reliable to the maximal temperature of the apparatus ($T < 1000$ K). The liquidus temperatures reported in Table 2 allow the equilibrium lines for each investigated quasi-binary section to be drawn (Figs. 2–5).

Using isotherm lines, a representation of the liquidus surface is proposed (Fig. 6A).

For a better localization of the ternary eutectic valley, ten new alloys were prepared and analysed. Their molar fractions and the measured liquidus temperatures are gathered in Table 3 and reported in Fig. 6B.

Using the experimental data listed in Tables 2 and 3, the coordinates of points of the ternary eutectic valley were obtained by interpolation, see Table 4.

Analysis of the results obtained at temperatures below the liquidus temperature suggest the following comments. During the first investigations by thermal analysis, the most studied alloys, e.g. alloys the composition of which belongs to the quasi-binary sections $x_{Au}/x_{Ag} = 1/4$, $x_{Au}/x_{Pb} = 1/3$ with $0.03 < x_{Ag} < 0.20$, and the section $x_{Pb} = 0.40$, exhibit a thermal effect at 483 K. This temperature could correspond to the eutectic reaction

$$\text{liq.} \longleftrightarrow [Ag_{0.57}Au_{0.43}] + AuPb_3 + [Pb]$$

where [...] represents *solid solution.*

Referring to equilibrium phase conditions, at the ternary eutectic temperature, the liquid solidifies to the Ag–Au solid solution (containing 57 at% Ag, 43 at% Au), the $AuPb_3$ compound and a Pb-rich solid solution [6]. Therefore only alloys located in this triangle should show this eutectic reaction, if thermal equilibrium is attained. But according to our data, this eutectic reaction seems to take place inside and outside this tie-triangle (*ABC*, Fig. 1).

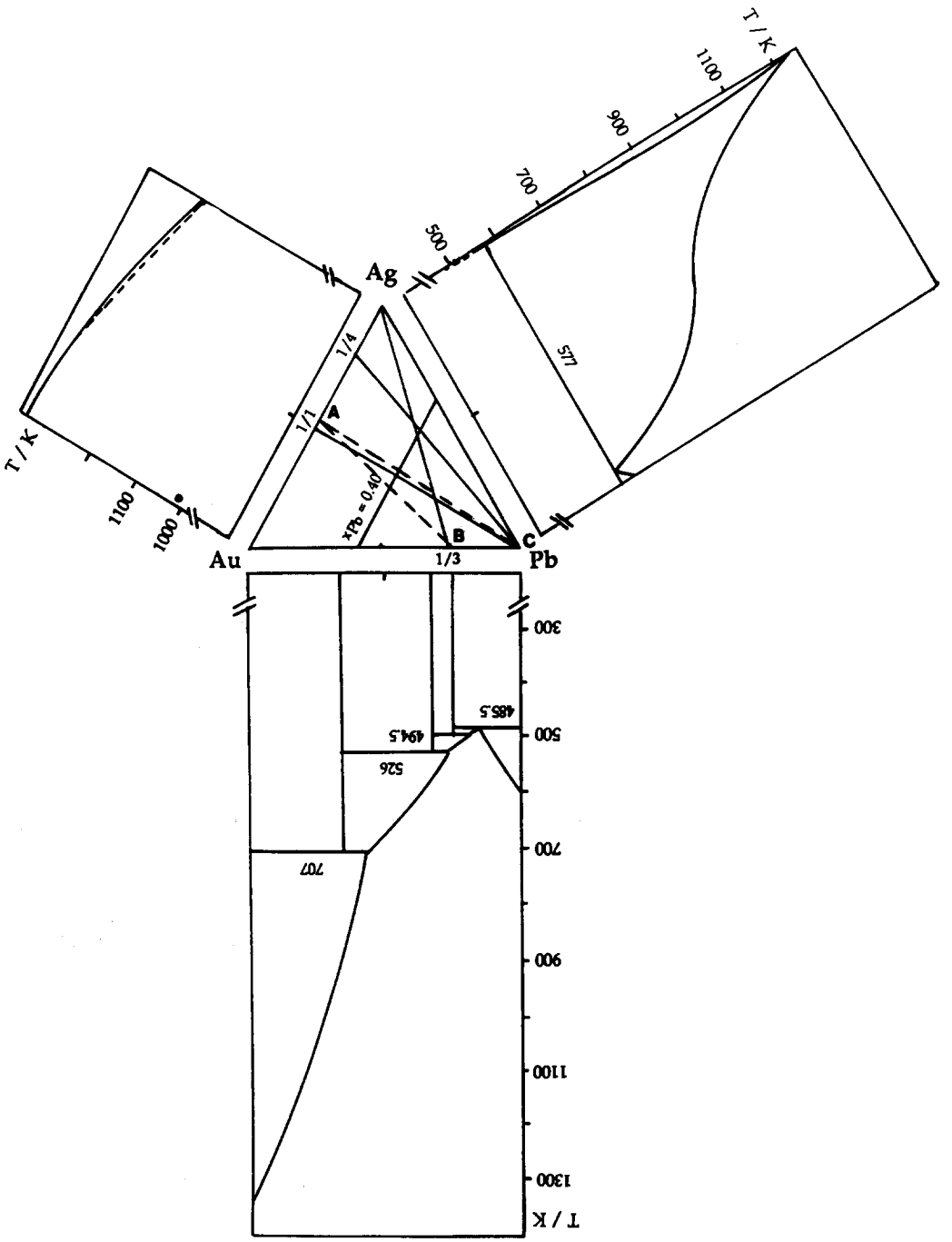

Fig. 1. Phase diagram of binary Ag–Au, Ag–Pb and Au–Pb systems from Refs. [7–10]. Quasi-binary lines along equilibrium temperatures have been measured.

Table 2
Experimental liquidus temperatures along the quasi-binary sections $x_{Au}/x_{Ag} = 1/4$ and 1/1; $x_{Au}/x_{Pb} = 1/3$; and $x_{Pb} = 0.40$. The six new alloys studied are marked *

	x_{Ag}	x_{Au}	x_{Pb}	T_{liq}/K
$x_{Pb} = 0.40$	0.0601	0.5399	0.40	808*
	0.1199	0.4800	0.40	864*
	0.1800	0.4200	0.40	889*
	0.2400	0.3599	0.40	910
	0.3000	0.3000	0.40	917
	0.3600	0.2400	0.40	918
	0.4200	0.1800	0.40	920*
	0.4800	0.1200	0.40	921*
	0.5400	0.0600	0.40	913*
$x_{Au}/x_{Ag} = 1/4$	0.5020	0.1245	0.3735	929
	0.4800	0.1200	0.4000	923
	0.4000	0.1000	0.500	888
	0.3202	0.0800	0.5998	844
	0.2383	0.0595	0.7022	808
	0.1991	0.0498	0.7511	792
	0.1600	0.0400	0.8000	758
	0.1199	0.0299	0.8502	721
	0.0796	0.0199	0.9005	696
	0.0600	0.0150	0.9250	639
	0.020	0.005	0.9750	592
$x_{Au}/x_{Pb} = 1/3$	0.0055	0.2486	0.7459	570
	0.0344	0.2414	0.7242	714
	0.0501	0.2375	0.7124	743
	0.1516	0.2121	0.6363	804
	0.2001	0.1999	0.5999	828
	0.2489	0.1914	0.5597	849
	0.3119	0.1720	0.5161	880
	0.3549	0.1609	0.4842	896
	0.4077	0.1481	0.4442	908
	0.5020	0.1245	0.3735	929
$x_{Au}/x_{Ag} = 1/1$	0.3000	0.3000	0.4000	917
	0.2500	0.2500	0.5000	865
	0.2000	0.2000	0.6000	828
	0.1500	0.1500	0.7000	786
	0.1002	0.1002	0.7996	739
	0.0752	0.0752	0.8495	690
	0.0508	0.0508	0.8494	711
	0.0249	0.0249	0.9502	601
	0.0125	0.0125	0.9750	590

So, taking into account the critical remarks proposed by Prince [14], six new alloys have been studied. These alloys, marked by (*) in Table 2, are located on the $x_{Pb} = 0.40$ section and outside the range of composition $0.248 < x_{Ag} < 0.318$. They were annelaed at 473 K for one month, then a new thermal analysis was performed between 473 and 493 K. Before a new DTA run, these alloys were annealed again for six months at 473 K.

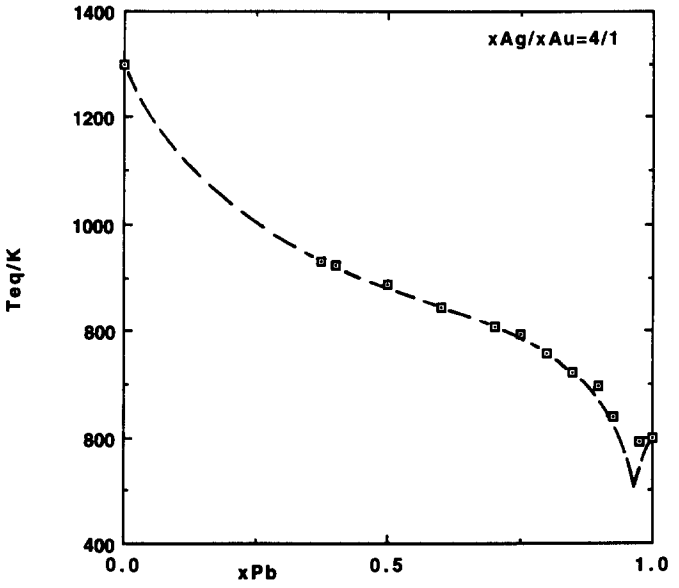

Fig. 2. Experimental liquidus temperatures along the section $x_{Au}/x_{Ag} = 1/4$.

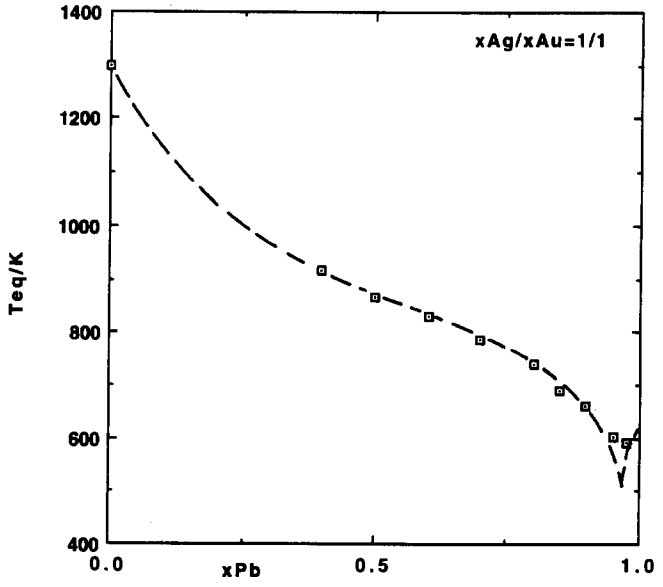

Fig. 3. Experimental liquidus temperatures along the section $x_{Au}/x_{Ag} = 1/1$.

In this case the thermal effect previously observed at 483 K disappeared. For three alloys ($x_{Ag} = 0.12, 0.18$ and 0.42), only one thermal effect was recorded at 486 K during the heating process. So outside the limits of the region $[Ag_{0.57}Au_{0.43}] + AuPb_3 + [Pb]$ the eutectic reaction does not appear on heating (Table 5).

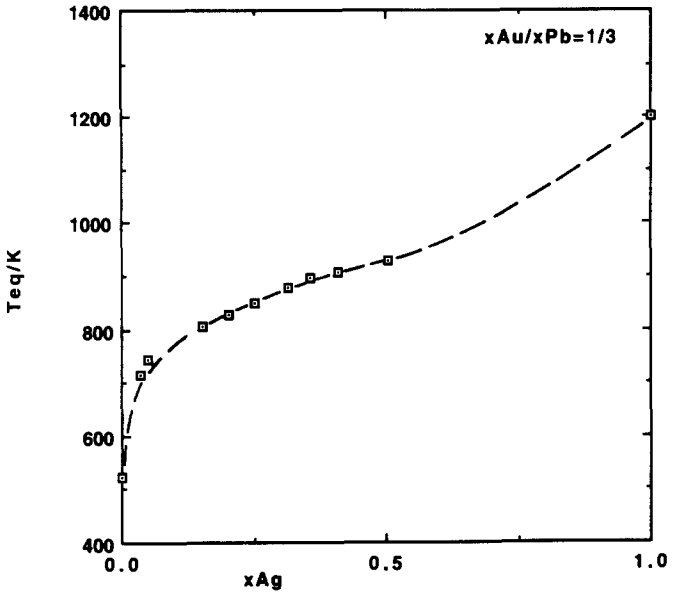

Fig. 4. Experimental liquidus temperatures along the section $x_{Au}/x_{Pb} = 1/3$.

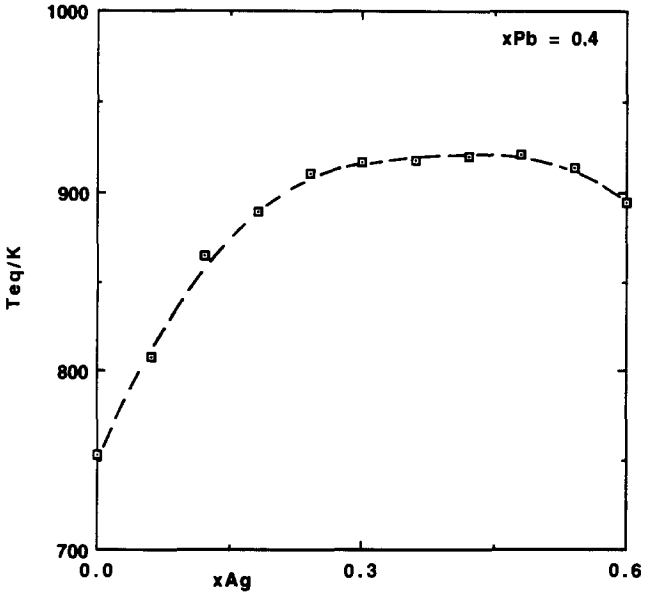

Fig. 5. Experimental liquidus temperatures along the section $x_{Pb} = 0.40$.

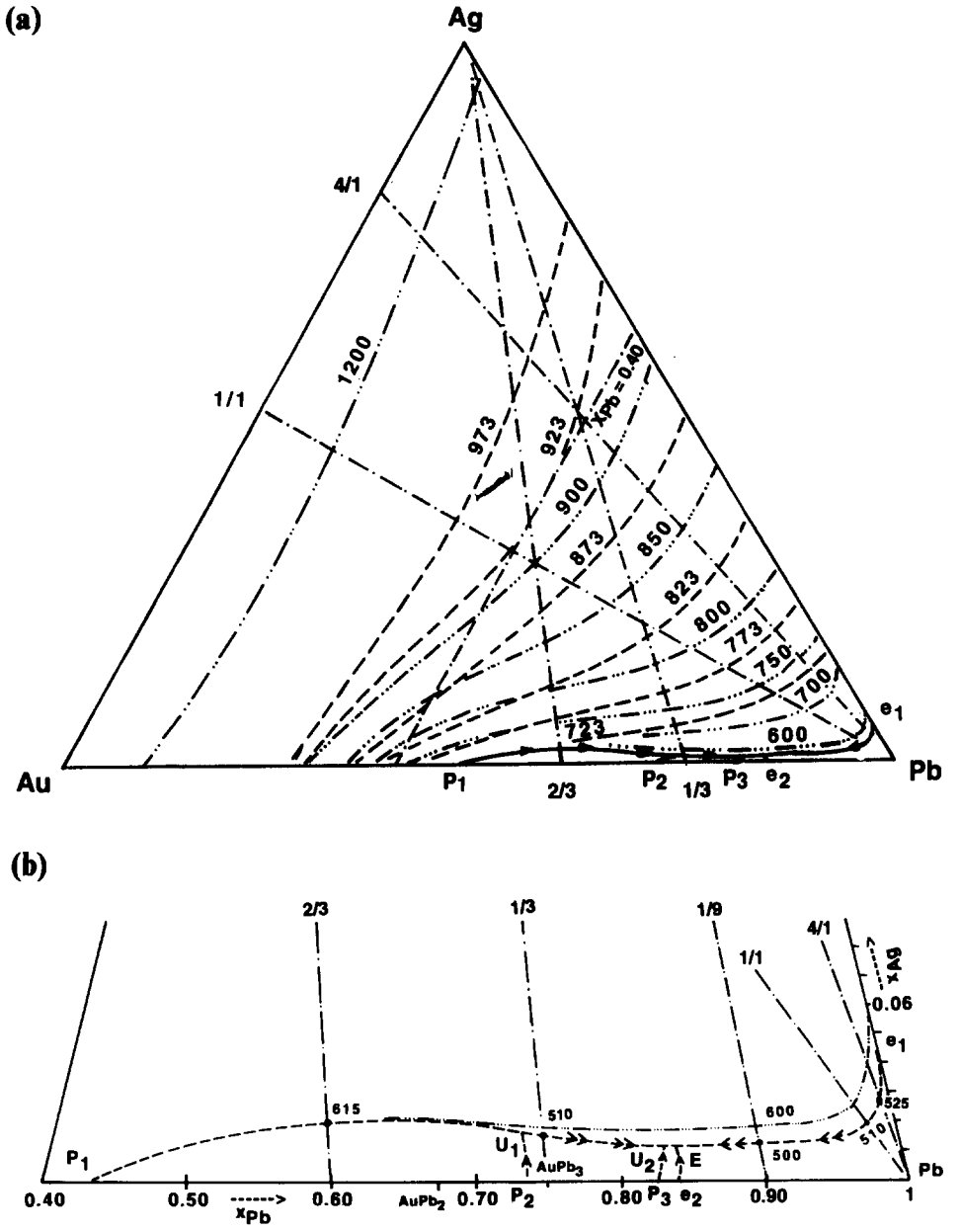

Fig. 6A. Liquidus surface of the Ag–Au–Pb system (isotherm lines).
B. Eutectic valley of the Ag–Au–Pb ternary alloy: enlarged part of 6A.

In this ternary system, there are three invariant reactions of the type: U_1, U_2 and E

U_1 Liq. + Au_2Pb = [Ag–Au] + $AuPb_2$

U_2 Liq. + $AuPb_2$ = [Ag–Au] + $AuPb_3$

E Liq. + (Ag–Au) = [Pb] + $AuPb_3$

Table 3
Temperatures obtained for ten alloys near the ternary eutectic valley

x_{Ag}	x_{Au}	x_{Pb}	T_{liq}/K
0.007	0.0993	0.8939	534
0.008	0.0992	0.8931	524
0.016	0.098	0.8860	524
0.022	0.0978	0.8801	551
0.032	0.0968	0.8710	623
0.013	0.3950	0.5925	647
0.0202	0.3918	0.5879	629
0.0297	0.3881	0.5822	646
0.036	0.3856	0.5784	652
0.037	0.3851	0.5777	656

Table 4
Coordinates of points of the ternary eutectic valley obtained by interpolation

x_{Au}/x_{Pb}	x_{Ag}	T_{liq}/K	x_{Ag}/x_{Au}	x_{Pb}	T_{liq}/K
1/9	0.013	500	1/1	0.960	510
1/3	0.015	510	1/4	0.965	525
2/3	0.021	615			

Table 5
T_1 and T_2, the temperatures of the thermal effects recorded on heating the samples annealed for one week at 473 K. T (*) are temperatures obtained on heating after the first annealing for one month and the second, for six months

x_{Ag}	T_1/K	T_2/K	T/K (*)
0.0601	483	487	–
0.1199	482	486	486.6
0.18	483	488	487.5
0.42	483	486	486.8
0.48	482	486.5	–
0.54	481	–	–

These three alloys (U_1, U_2 and E), the compositions of which are given in Table 6, were synthesized and held at 473 K for two weeks in the furnace. The equilibrium temperatures obtained by thermal analysis are also reported in this table: two thermal effects, at the U_1 and E compositions, and three at the U_2 composition, were obtained. These results are very different from those of Prince who obtained just one thermal effect for these alloys. The large difference between these two series of data can be explained either by an error in the composition during the preparation or by a metastable equilibrium reached at 473 K.

Table 6
Experimental temperatures of the invariant equilibria (U_1, U_2 and E). Prince's [6] data have been also reported

	x_{Ag}	x_{Au}	x_{Pb}	T/K [6]	T_{exp}		
					T_1	T_2	T_3
U_1	0.0053	0.2610	0.7340	522	524	492	–
U_2	0.0048	0.1861	0.8091	491	518	496	486
E	0.0051	0.1696	0.8253	485	502	–	487

5. Conclusion

Using a differential thermal analyser, liquidus temperatures have been determined in a large composition range. New experiments near the ternary eutectic reaction have been realized. All results allow the liquidus surface and the eutectic valley to be proposed. Determination of the enthaply of formation of the Ag + Au + Pb liquid alloy by direct calorimetry is in progress. From these data, the other thermodynamic properties will be deduced and the phase boundaries of this ternary alloy calculated.

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