Silver – Indium – Antimony

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Introduction

The experimental base on this system was laid by [1965Gub, 1969Kuz, 1971Kuz] and later assessed by [1988Sch]. In the early study of [1965Gub] a sample of composition Ag_3InSb was fused directly from the elements, studied by thermal analysis and metallography and found not to be a single phase material. Using the same technology [1969Kuz] confirmed this in studies of 14 samples along the vertical section InSb-Ag up to 71.9 at.% Ag (70 mass% Ag). However, the primary crystallization is interpreted by [1965Gub] to be InSb whereas for the same sample composition an unidentified ternary phase was reported to crystallize first by [1969Kuz]. Further, the temperatures of primary and eutectic crystallization disagree [1965Gub, 1969Kuz]. The later published study by [1971Kuz] is not helpful in this respect as the published isopleth based on DTA, X-ray analysis and metallography is virtually identical to that of [1969Kuz].
[2004Liu] reinvestigated the system using differential scanning calorimetry (DSC), metallography and electron probe microanalysis (EPMA). They also modeled the system using the CALPHAD approach. In contradiction with [1971Kuz] they reported that there is no ternary compound in the system. The ζ phase extends in the ternary from the Ag-In to the Ag-Sb side and corresponds to one of the ternary compounds mentioned by [1971Kuz]. According to [2004Liu] the second ternary compound mentioned by [1971Kuz] is the (Sb) solid solution with very small amounts of Ag and In.

Binary Systems

None of the phase diagrams published on Ag-In reflects fully the present knowledge. The Ag-In binary system published in 1990 by [Mas2] shows an unlikely asymmetric ζ/ζ+γ boundary. Further, [2001Mos] investigated phase boundaries in the Ag-In system using diffusion couples, DSC and metallography. They determined for the ζ phase a narrower homogeneity range than reported earlier. However, the α' and the β phases were not taken into account when they constructed the phase diagram, although DSC peaks belonging to these phases were determined. Therefore, combining data from [Mas2, 2001Mos and 1970Cam] results in a new binary Ag-In phase diagram, given in Fig. 1.
The In-Sb binary system is accepted from [Mas2] and Ag-Sb from [1993Oka] which actually is the work of [1992Fes].

Solid Phases

[2004Liu] determined that no ternary compound exists in this system. The ζ phase extents continuously from the edge binary Ag-In system to the Ag-Sb side. Very small Ag solubility in InSb was determined by [1971Kuz] and confirmed by [2004Liu]. The solid phases are listed in Table 1.

Invariant Equilibria

[2004Liu] omitted in their computer calculations the β phase in the Ag-In binary system and arrived at two ternary eutectic (E) and three ternary transition (U) reactions. The β phase has been re-introduced here on the basis of the accepted binary systems. This generates a new four-phase equilibrium of unknown type and temperature which is connected with p_1, p_2 and e_1 binary reactions. It has been assumed and shown in the reaction scheme given by Fig. 2. The invariant reactions and the changing composition of the liquid phase associated with the phase reactions are given in Table 2.

Liquidus Surface

The liquidus surface of the system, omitting the β phase, was calculated by [2004Liu] based on experimental work of [1971Kuz] along the InSb-Ag vertical section and on their own DSC work along the

AgIn-Sb vertical section. In Fig. 3 the β phase is added the liquidus surface has been slightly modified in order to meet the accepted binary phase boundaries.

Isothermal Sections

Sections at 350 and 400°C given in Fig. 4 and Fig. 5, are based on those calculated by [2004Liu]. They determined two tie lines in the InSb + ζ phase field and one tie line in (Sb) + ζ having almost the same composition at both temperatures. No three-phase samples were reported. Although calculated sections are close to the experimental results of [1971Kuz] and [2004Liu], slight corrections such as the homogeneity range of the ε phase have been done in agreement with the accepted binaries. The three-phase fields are drawn by dashed lines, since tie lines are not sufficient to describe boundaries.

Temperature – Composition Sections

Isopleths along InSb-Ag and AgIn-Sb are given in Fig. 6 and Fig. 7, respectively. The vertical section InSb-Ag up to 71.9 at.% Ag (70 mass% Ag) was experimentally determined by [1971Kuz] and later calculated by [2004Liu] up to pure Ag. The Ag rich part of the diagram is described here by dashed lines, since there were no experimental data available on homogeneity ranges of (Ag) and ζ phase. [2004Liu] calculated also the AgIn-Sb section using their DSC results which were conducted on 4 samples. The temperatures determined for the invariant lines are consistent with the work of [1971Kuz]. In the Sb rich part of the diagram a calculated (Sb) + ζ two phase field exists up to 3.5 mass% Sb at 424°C which is not consistent with the calculated isothermal sections and EPMA analysis results. On the other hand the system was calculated down to 100°C but the results are not consistent with experimental works. Both isopleths are redrawn according to experimental results but the part calculated below 300°C was not taken into account.

Thermodynamics

[2001Ita] measured the activity of indium in the Ag-In-Sb system using a galvanic cell with zirconia solid electrolyte in temperature ranges between 697 and 1007°C. Isoactivity curves at 827 and 927°C are given in Fig. 8. They are derived from combining the activity data of the In-Sb and Ag-In binaries. The shape of the curves exhibits a slight bend to the Ag-Sb binary side.
[1987Gat] determined enthalpy of mixing of the ternary liquid in a heat flow calorimeter. The measured ternary mixing isoenthalpy curves are given in Fig. 9.

Miscellaneous

Surface tension and viscosity of liquid phase calculated on the basis of the thermodynamic modeling were given in the study of [2004Liu].

References

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Ag) < 961.93	*cF*4 $Fm\bar{3}m$ Cu	a = 408.57	at 25°C [Mas2]
(In) < 156.634	*tI*2 *I*4/*mmm* In	a = 325.3 c = 494.7	at 25°C [Mas2]
(Sb) < 630.755	*hR*6 $R\bar{3}m$ As	a = 430.84 c = 1127.4	at 25°C [V-C2]
InSb < 525.7	*cF*8 $F\bar{4}3m$ ZnS (sphalerite)	a = 647.84	[V-C2] up to 0.16 mass% Ag solubility at 350-400°C [2004Liu]
ε, Ag_3Sb < 562	*oP*8 *Pmmn* Cu_3Ti	a = 599 b = 485 c = 524	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ζ	*hP*2 $P6_3/mmc$ Mg		Solid solution from Ag-Sb to Ag-In
Ag_7Sb		a = 296.16 ± 0.3 c = 479.90 ± 0.3	Pure Ag_7Sb [V-C2]
Ag_3In		a = 295.63 c = 478.57	Pure Ag_3In [V-C2]
β 694 - 660	*cI*2 $Im\bar{3}m$ W	a = 336.82	Ag-In binary 25-30 at.% In [Mas2] High temperature phase
α' < 187	*cP*4 $Pm\bar{3}m$ $AuCu_3$	a = 414.4 ± 0.4	Ag-In binary 25 at.% In [Mas2], [V-C2]
γ, Ag_9In_4 < 301	*cP*52 $P\bar{4}3m$ Al_4Cu_9	a = 992.2 ± 0.4	[V-C2]
$AgIn_2$ < 167	*tI*12 *I*4/*mcm* Al_2Cu	a = 688.1 ± 0.4 c = 562.0 ± 0.4	[V-C2], [Mas2]

Table 2: Invariant Equilibria

Reaction	Type	T [°C]	Phase	Composition (at.%)		
				Ag	In	Sb
L, ζ, (Ag)	? (min)	500 - 600	-	-	-	-
L ⇌ ζ + InSb ?	e? (max)	417 - 450	-	-	-	-
L ⇌ (Sb) + ζ + InSb	E_1	417	L	45.54	21.14	33.32
L ⇌ InSb + $AgIn_2$ + (In)	E_2	144	L	2.34	97.33	0.33
L + ε ⇌ ζ + (Sb)	U_1	455	L	57.42	5.04	37.54
ζ + InSb ⇌ L + Ag_2In	U_2	197	L	6.05	93.01	0.94
L + Ag_2In ⇌ InSb + $AgIn_2$	U_3	167	L	4.57	94.91	0.52
L, β, ζ, (Ag)	?	?	-	-	-	-

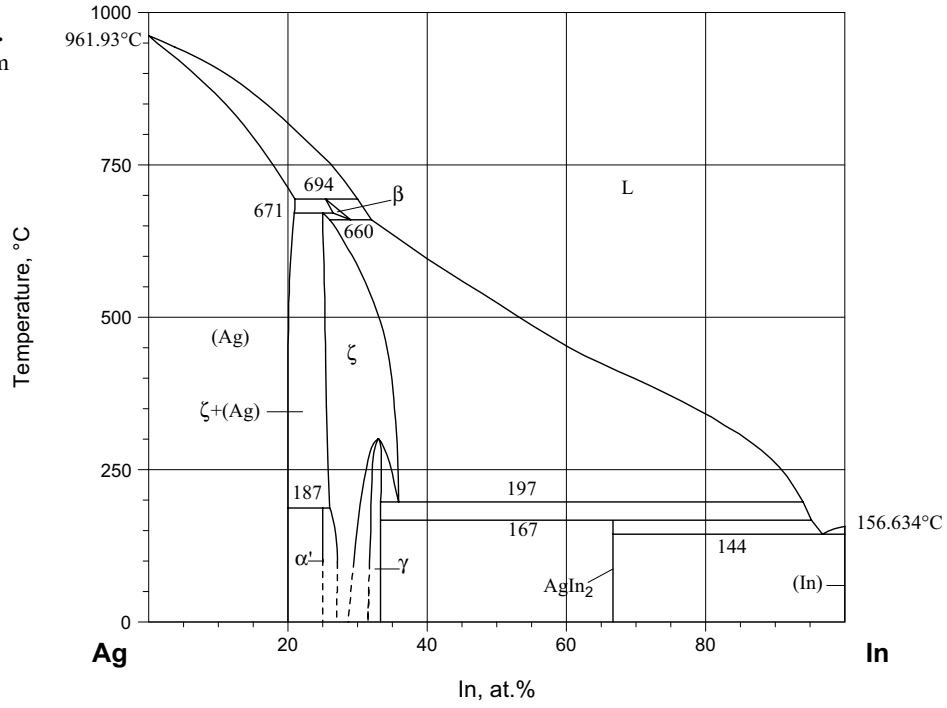

Fig. 1: Ag-In-Sb.
Ag-In binary system

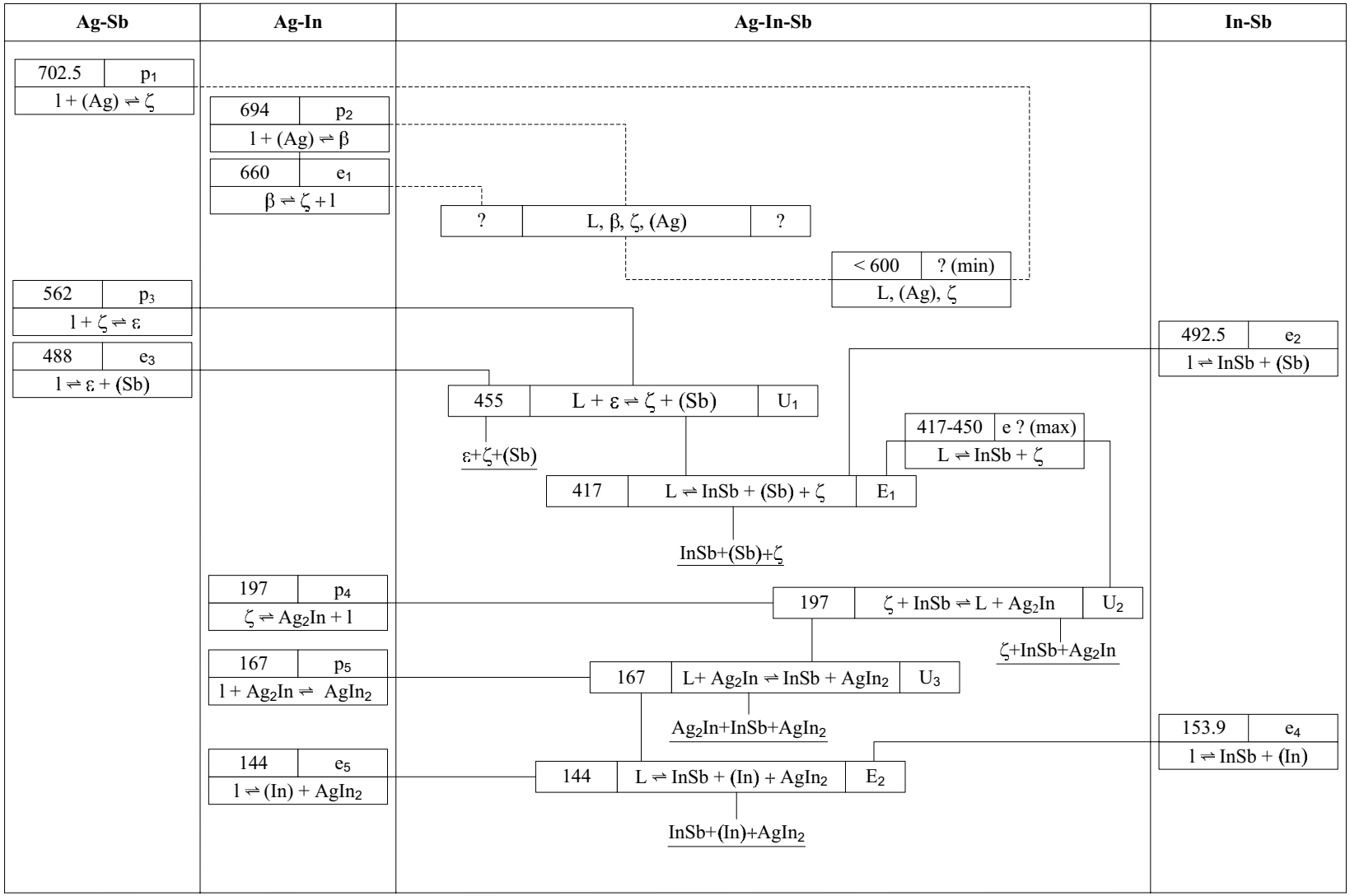

Fig. 2: Ag-In-Sb. Reaction scheme

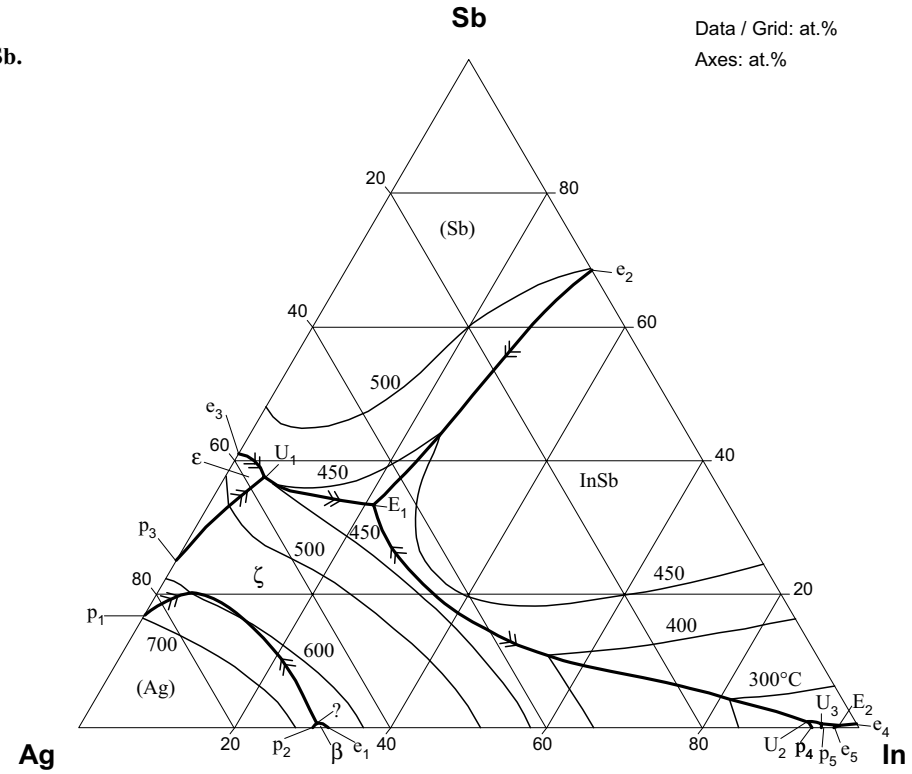

Fig. 3: Ag-In-Sb.
Liquidus surface

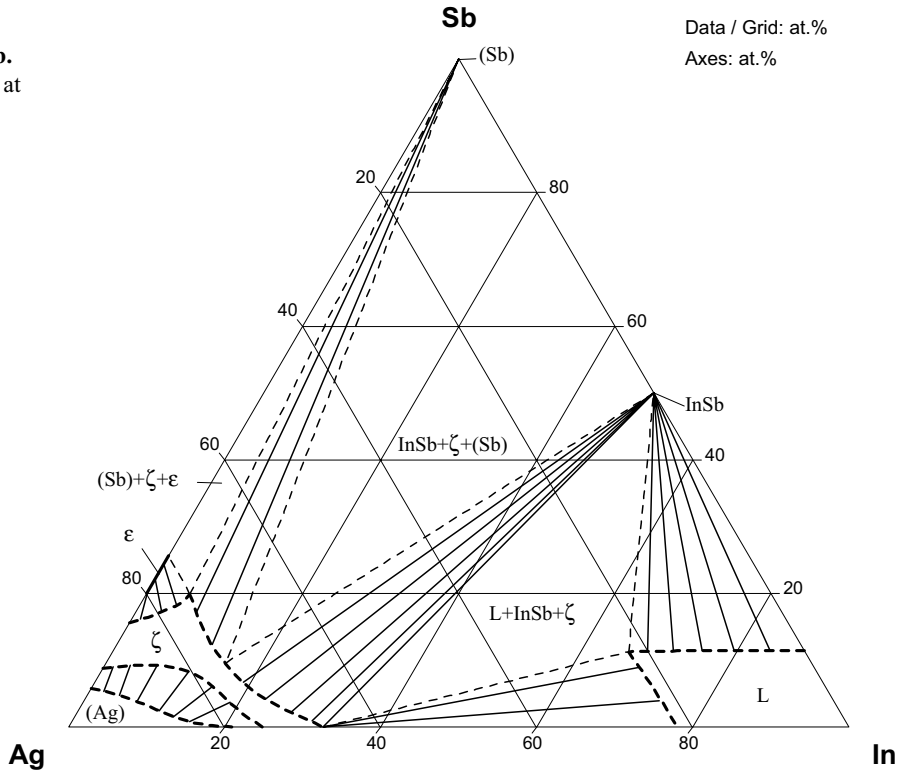

Fig. 4: Ag-In-Sb.
Isothermal section at 350°C

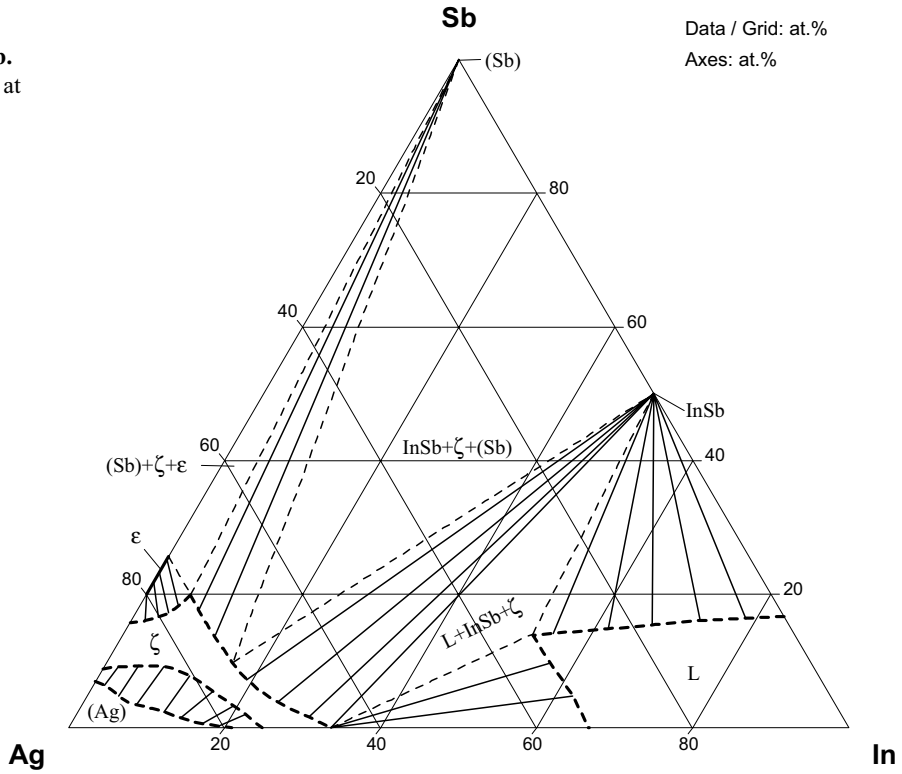

Fig. 5: Ag-In-Sb. Isothermal section at 400°C

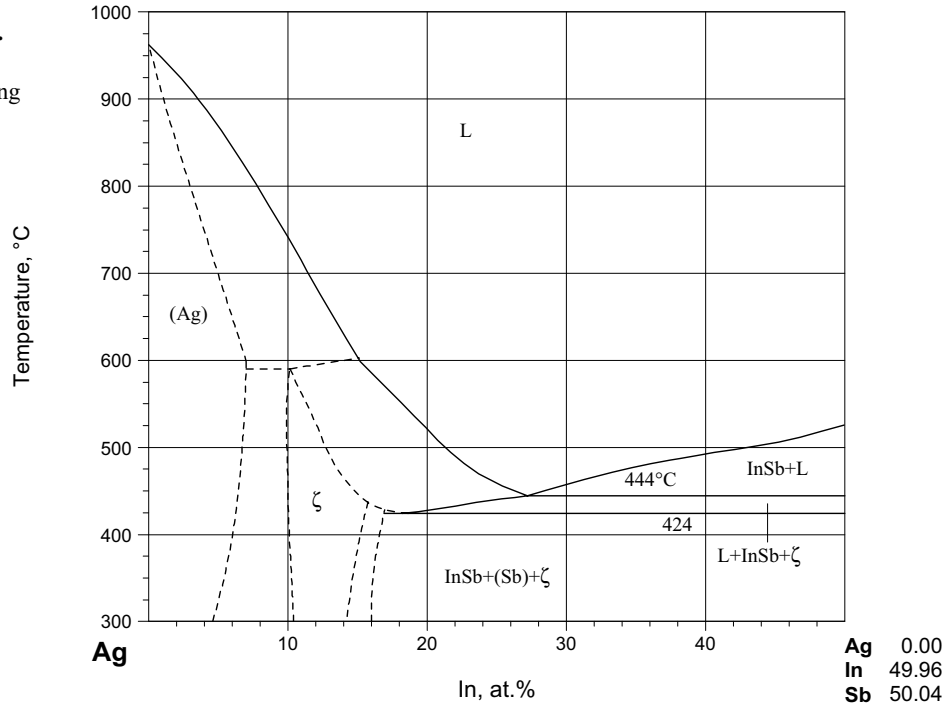

Fig. 6: Ag-In-Sb. Temperature - composition cut along Ag - InSb

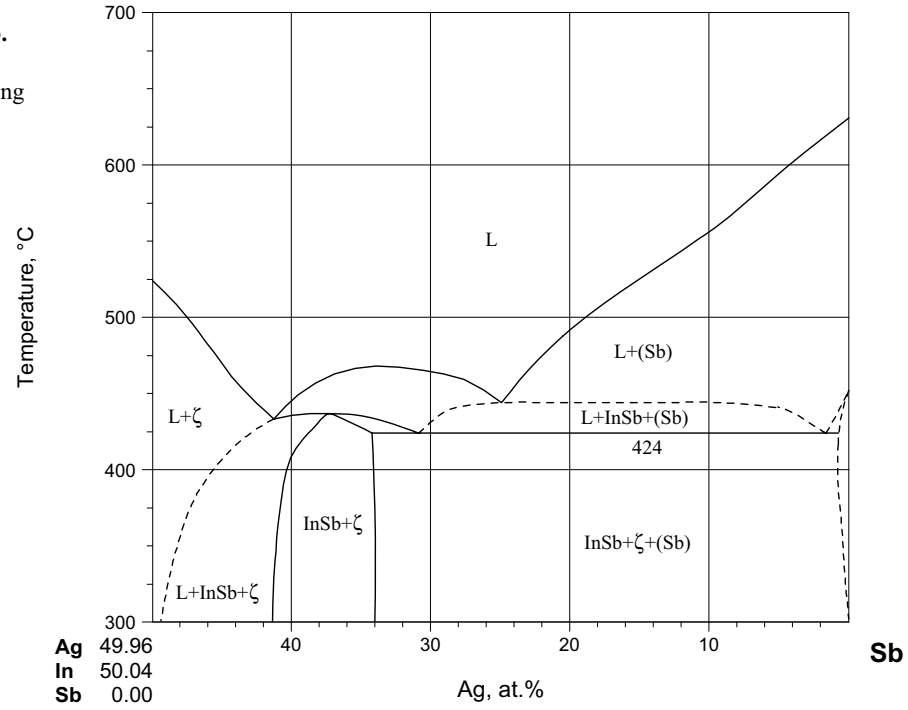

Fig. 7: Ag-In-Sb. Temperature - composition cut along AgIn-Sb

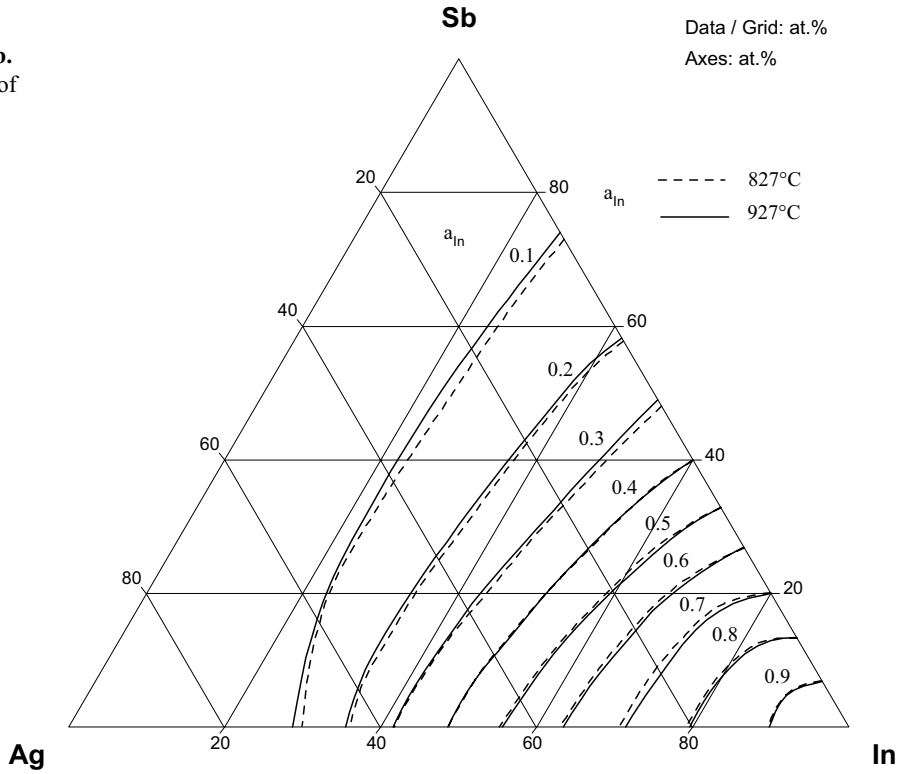

Fig. 8: Ag-In-Sb. Isoactivity curves of indium at 827 and 927°C

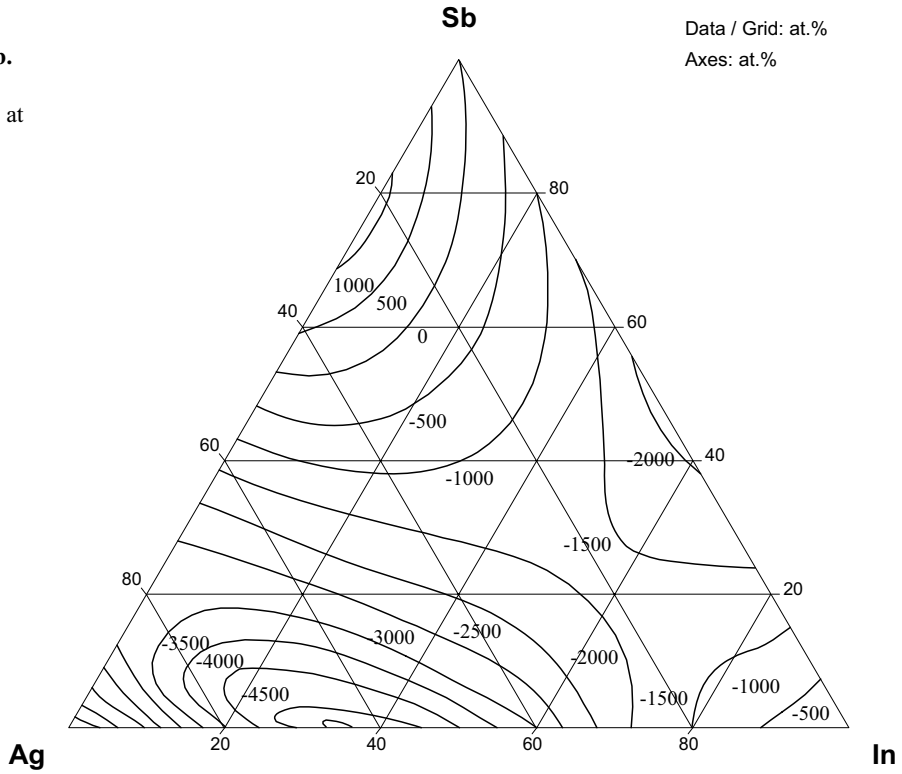

Fig. 9: Ag-In-Sb. Ternary mixing isoenthalpy curves at 980°C