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AN ASSESSMENT OF PHASE DIAGRAM AND THERMODYNAMIC PROPERTIES OF THE GALLIUM-INDIUM-ANTIMONY SYSTEM

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ABSTRACT The experimental thermodynamic and phase diagram data of the Ga-In-Sb ternary system have been critically assessed. A thermodynamic description that is consistent with the selected experimental data has been produced with the aid of ternary optimizing program TERGSS. Calculation of thermodynamic properties and phase diagrams were carried out using MTDATA.

I. Introduction

It is well known that III-V semiconductor compounds have an extremely important application in high speed and high frequency devices. In the III-V semiconductor family Ga-In-Al-Sb-As, there are ten ternary subsystems. By selecting different compositions within these subsystems, electrical and optical properties of the materials can be changed in order to satisfy different applications. In this work, the Ga-In-Sb system has been assessed as a first stage in the study of the Ga-In-Al-Sb-As system.

Since Liao et al[1] calculated the Ga-In-Sb system in 1982, new thermodynamic experimental studies have been undertaken by Aselage and Anderson[2], Chang et al[3], and Rugg and Bryant[4]. The three binary subsystems associated with the ternary Ga-In-Sb have also been assessed by Anderson & Ansara[5], and Ansara et al[6]. More recently, a thermodynamic analysis and calculation of the phase equilibria of the ternary system has been undertaken by Sharma and Mukerjee[7] although they had not used the most recent descriptions of the antimonide binary systems. It is also important to re-evaluate the ternary with the enthalpies of formation of the (Ga,In)Sb solid solution[4] which were not available to Sharma and Mukerjee, as it is from such measurements that the stability of the phase can be assessed.

The experimental phase diagram and thermodynamic data available in the literature for the Ga-In-Sb system have been critically assessed and by using unary data for the elements as recommended by SGTE[8], thermodynamic descriptions of the ternary liquid and (Ga,In)Sb phases which are consistent with the experimental data, have been produced. This was achieved with the aid of the ternary optimization program TERGSS kindly donated by Dr. H. L. Lukas[9,10] of the MPI Stuttgart.

II. Experimental data

II.I Phase diagram data

Measurement of the Ga-In-Sb liquidus has been made by Blom and Plaskett[11], Antypas[12] and Miki et al[13] using a weight loss method, and by Gorshkov and Goryunova[14], Ufimtsev et al[15], Woolley and Lees[16], and Joullié et al[17] using heating and cooling curve analysis. Direct visual observation of melting temperatures was used by Abrokwah and Gershenzon[18]. For thermal methods and direct observation, supercooling is considered to be the main source of uncertainty. In weight loss methods, there is no supercooling problem. However, there is a possibility of uncertainty with this method and with these types of systems, owing to equilibrium not being established. This method relies on the dissolution of a GaSb crystal into a melt until the liquid becomes saturated. An interface layer of the ternary compound in equilibrium with this liquid is then formed on the surface of the crystal. The liquidus composition is then determined by the weight loss of the

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crystal. However, the diffusion rates of the components are very low, and so there may be difficulties in attaining equilibrium. Also, no account is taken of diffusion of indium from the melt to the crystal which would have an effect on weight loss calculations.

An annealing technique was used by Gratton and Woolley[19], Blom and Plaskett[11], and Woolley and Smith[20] to measure the solidus/liquidus equilibria. X-ray studies of the annealed and quenched specimens revealed the compositions of the phases in equilibrium. Blom and Plaskett used a microprobe technique in preference to x-rays.

Gratton and Woolley extrapolated their solidus measurements to the liquidus curves as given by Blom and Plaskett, Joullié et al[17], and Antypas[12], in order to calculate the associated equilibria. As these derived liquidus data were heavily dependant on those of other workers they were not considered in this optimisation.

LPE methods were used by Antypas[12], Joullié et al[17],[21], Rode et al[22] and Miki et al[13] for the determination of the solidus compositions. Annealing techniques allow experimental conditions close to equilibrium thus allowing a better accuracy in the measurement of temperature than LPE methods, however, the uncertainty in composition is of the same order. By comparing all the experimental phase diagram data, it could be seen that there was general agreement between the data within the uncertainties assigned in this assessment.

The pseudobinary GaSb-InSb phase diagram data of Woolley and Smith[20], and Woolley and Lees[16] have large differences from those of Gorshkov and Goryunova[14], and Ufimtsev et al[15]. Both Woolley and Smith and Gorshkov and Goryunova used the same annealing technique, but Woolley and Smith followed the heat treatment of their alloys by quenching, whereas Gorshkov and Goryunova did not. It is therefore more likely that the compositions determined by Woolley and Smith would reflect the equilibria at the annealing temperature than those determined by Gorshkov and Goryunova. The optimization result also shows that the data of Woolley and Smith fit other experimental data better than those of Gorshkov and Goryunova, or Ufimtsev et al. For these reasons Woolley and Smith's data were taken in this work and those of Gorshkov and Goryunova and Ufimtsev et al were omitted in the final optimisation. These same data were also disregarded in the work of Liao et al[1] and Blom and Plaskett[11].

II.II Thermodynamic data

Enthalpies of mixing of liquid alloys have been measured by Ansara et al[23] and Vecher et al[24] using direct reaction calorimetry and quantitative differential thermal analysis respectively. The agreement between the two sets of data is poor. In some cases, the differences are larger than 50% of the measured values. The experimental results of Vecher et al were presented in the form of an isothermal ternary section showing contours representing mixing enthalpies without indicating specific experimental measurements. This resulted in a fairly large uncertainty being ascribed to the data (+/- 20% in the enthalpies of mixing) owing to the difficulties in reading the data accurately.

The mixing enthalpies of pseudobinary liquid were measured only by Gerdes and Predel[25]. Enthalpies of mixing of the (Ga,In)Sb pseudobinary solid solution have been measured by Rugg and Bryant[4], and Mechkovskii et al[26] the latter calculating the enthalpies of mixing of the solution from the difference between the enthalpies of mixing of the binary Ga-Sb, In-Sb and ternary Ga-In-Sb liquids. The former calculated enthalpies of mixing from measured enthalpies of solution of the binary GaSb and InSb compounds, and pseudobinary alloys in tin and indium. The uncertainty in both sets of measurements of the enthalpies of mixing of the ternary solid solution are high, their small numerical values being comparable in magnitude to the experimental scatter. On comparing these two sets of results, it was found that they had opposing signs.

Partial Gibbs energies of gallium in the liquid phase have been measured by Aselage and Anderson[2], and Chang et al[3] using an electrochemical method. An experimental accuracy of 5% was given for the data by the authors. However, under comparison, it was evident that the temperature dependence of the emf was of opposing sign for the two sets of results. This implies that the uncertainty factors must be larger than quoted or one set of data are erroneous.

Table 1 gives a summary of the experimental data available in the literature together with the experimental techniques employed and their assigned uncertainties used in this assessment. The selected data and uncertainties were used in the subsequent ternary optimization.

Table 1 Assessed Uncertainties of Experimental Thermodynamic and Phase Diagram Data used in the Optimisation

Measurement	Author	Uncertainty (authors estimate)			Uncertainty (assessed)			Experimental Method
		x	T(K)	Value	x	T(K)	Value	
phase diagram	Gratton[19]		2		0.01	2		annealing (s)
	Antypas[12]				0.01	3		weight loss (l) LPE (s)
	Joullié[17]		4		0.01	3		DTA (l) LPE (s)
	Blom[11]				0.01	3		weight loss (l) annealing (s)
	Rode[22]				0.01	3		LPE (s)
	Miki[13]				0.01	3		weight loss (l) LPE (s)
	Abrokwah[18]				0.01	3		direct observation (l) LPE (s)
	Joullié[21]				0.01	3		LPE (s)
	Woolley[16,20]		5		0.01	3		thermal analysis (s+l) annealing (s)
enthalpy of mixing	Ansara[23]				0.01	4	20%	calorimetry (l)
	Gerdes[25]				0.01	2	20%	calorimetry (l)
	Rugg[4]					2	50%	calorimetry (s)
partial Gibbs energy Ga	Chang[3]	0.1%	1	3%	0.01	2	20%	emf method (l)
	Aselage[2]	0.1%	0.75	3%	0.01	2	20%	emf method (l)

III. Thermodynamic models for liquid and solid

Many thermodynamic models have been previously proposed to describe the thermodynamic properties of the ternary Ga-In-Sb liquid, for example the regular solution model, the sub-regular solution model, the associated solution model and other modified models[3],[13]. There has been no experimental evidence of association behaviour in the Ga-In-Sb liquid as has been found in II-VI systems[27]. If the uncertainties of the experimental data are taken into consideration, it can be found that the sub-regular model is adequate to describe both the Ga-In-Sb liquid and the (Ga,In)Sb pseudobinary compound.

The thermodynamic descriptions of the three binary systems were extrapolated into the ternary using Muggianu's[28] expression. The excess Gibbs energy of the liquid phase owing to ternary interactions of the three components was expressed by

$$G^E(l) = x(Ga)x(In)x(Sb)(a^l+b^lT) \qquad (\text{ J g-atom}^{-1}) \qquad (1)$$

The solid solution between the GaSb and InSb was treated as a pseudobinary solution rather than a true ternary, and thus the excess Gibbs energy was described by an expression equivalent to the Redlich-Kister formalism [29] used for the binary liquid phases

$$G^E(s) = x(GaSb)x(InSb)\,(a^s+b^sT) \qquad (\text{J mol}^{-1}\ (Ga_xIn_{1-x})Sb) \qquad (2)$$

III.I Unary and binary descriptions

The unary data for the pure elements have been taken from the SGTE[8] (see table 2) and are referred to the standard element reference (G-HSER). The interaction parameters of three binary sub-systems employed have been proposed by Anderson & Ansara[5], and Ansara et al[6](see table 3 and figs 1-3)

Table 2 Unary data for gallium, indium and antimony from SGTE[8]

$$G(T)-HSER = A + BT + CT\ln T + DT^2 + ET^3 + F/T + GT^7 + H/T^9$$

	A	B	C	D	E	F	G	H
Gallium								
orthorhombic								
200.00<T<302.92K	-21312.331	585.263691	-108.228783	0.22715564	-1.1857526E-4	439954	0.0	0.0
302.92<T<2900.0K	-7055.643	132.7302	-26.0692906	0.1506E-3	-0.040173E-6	-118332	0.0	1.645E+23
liquid								
200.00<T<302.92K	-15821.03	567.189696	-108.228783	0.22715564	-1.1857526E-4	439954	-7.017E-17	0.0
302.92<T<2900.0K	-1389.19	114.049043	-26.0692906	0.1506E-3	-0.040173E-6	-118332	0.0	0.0
Indium								
tetragonal-A6								
200.00<T<429.75K	-6978.89	92.338115	-21.8386	-5.72566E-3	-2.120322E-6	-22906	0.0	0.0
429.75<T<2900.0K	-7033.52	124.476588	-27.4562	5.4607E-4	-8.367E-8	-211708	0.0	3.53116E+22
liquid								
200.00<T<429.75K	-3696.798	84.701255	-21.8386	-5.72566E-3	-2.120321E-6	-22906	-5.59058E-20	0.0
429.75<T<2900.0K	-3749.81	116.857840	-27.4562	5.4607E-4	-8.367E-8	-211708	0.0	0.0
Antimony								
rhombohedral-A7								
298.15<T<903.78K	-9242.858	156.154689	-30.5130752	7.748768E-3	-3.003415E-6	100625	0.0	0.0
903.78<T<2900.0K	-11738.830	169.485872	-31.38	0.0	0.0	0.0	0.0	1.61685E+27
liquid								
298.15<T<903.78K	10579.470	134.231525	-30.5130752	7.748768E-3	-3.003415E-6	100625	-1.74847E-20	0.0
903.78<T<2900.0K	8175.36	147.455986	-31.38	0.0	0.0	0.0	0.0	0.0

Table 3a Thermodynamic parameters of Ga-In[5], Ga-Sb[6] and In-Sb[6] Liquid Phases

$$G^E = x(1-x)[(A_1 + A_2T + A_3T\ln T) + (B_1 + B_2T)(1-2x) + C_1(1-2x)^2]$$
$$(\mathrm{J\ g\text{-}atom^{-1}})$$

Phase	system		coefficients of G^E		
				T	TlnT
liquid	Ga(x)In(1-x)	A	4450.0	1.19185	0
		B	0	0.25943	0
		C	0	0	0
	Ga(x)Sb(1-x)	A	-13953.8	71.07866	-9.6232
		B	1722.9	-1.92588	0
		C	2128.3	0	0
	In(x)Sb(1-x)	A	-25631.2	102.9324	-13.45816
		B	-2115.4	-1.31907	0
		C	2908.9	0	0

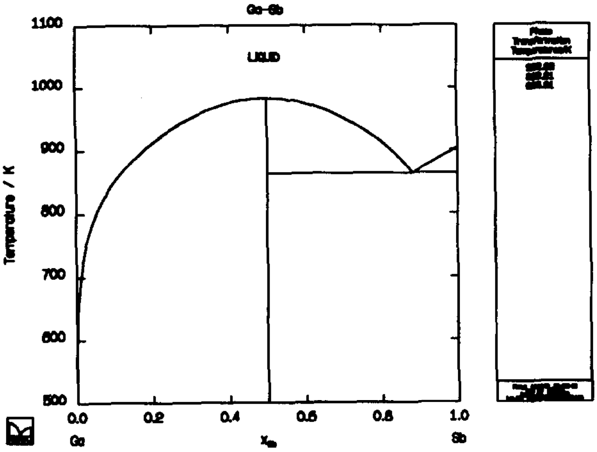


Figure 1
Assessed Ga-Sb Phase Diagram[6]

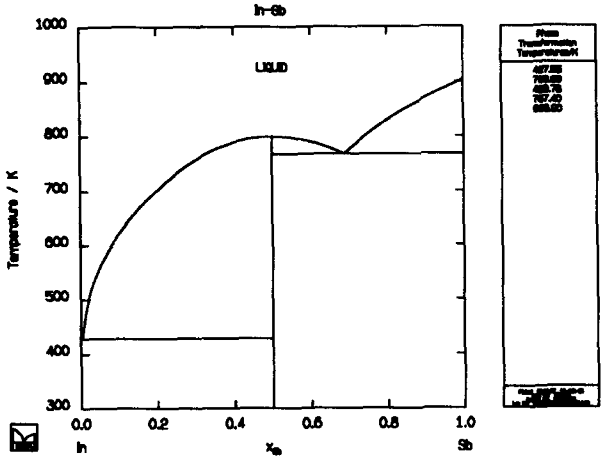


Figure 2
Assessed In-Sb Phase Diagram[6]

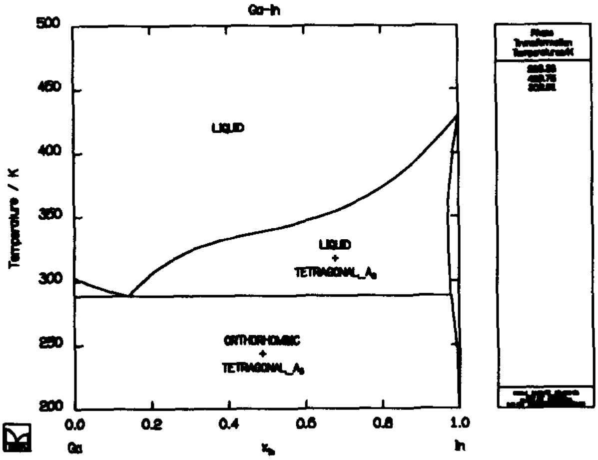


Figure 3
Assessed Ga-In Phase Diagram[5]

Table 3b. Thermodynamic Data for GaSb and InSb Binary Compounds.
G-HSER J mol^{-1}

	A	B	C	D	E	F	G	H
GaSb								
200.00<T<302.92K	-74031.389	720.3431	-133.356106	0.23214859	-1.215787E-04	540579	0	0
302.92<T<903.78K	-59774.701	267.809609	-51.1966138	0.00514355	-3.043588E-06	-17707	0	1.645E+23
903.78<T<2900.0K	-62270.673	281.140792	-52.0635386	-0.00260522	-4.0173E-08	-118332	0	1.6170145E+27
InSb								
200.00<T<429.75K	-47920.348	249.079082	-49.7645132	0.00202311	-5.123737E-06	77719	0	0
429.75<T<903.78K	-47974.978	281.217555	-55.3821132	0.00829484	-3.087085E-06	-111083	0	3.5311600E+22
903.78<T<2900.0K	-50470.95	294.548738	-56.249038	0.00054607	-8.367E-08	-211708	0	1.6168853E+27

Results and discussion

The ternary optimising program, TERGSS, was used to produce Gibbs energy coefficients for the ternary liquid and pseudobinary phases, that were consistent with the selected experimental data.

Initially, all the experimental thermodynamic and phase diagram data were given the same weight in the optimisation procedure based upon the assessed experimental uncertainties. Early results showed that some of the data were in obvious disagreement with the majority of the data. For this reason, the data of Vecher et al[24], Gorshkov and Goryunova[14], and the pseudobinary phase diagram data of Ufimtsev et al[15] were omitted from the data set. The enthalpies of mixing of the solid solution data of Mechkovskii et al[26] were also omitted as the optimisation suggested that values of an opposite sign to that of those data would be in closer agreement. Therefore, Rugg and Bryant's[4] data were accepted as their data had the appropriate sign.

The weight of the partial Gibbs energy data of Aselage and Anderson[2] was reduced to 50% of that given to the rest of the data. This was because these data comprised 40% of the total data set, and thus there may have been a tendency of the optimisation to be biased in favour of these data purely because of their number. A weight of 50% was also used for Ansara et al's data[23] as there was a certain degree of disagreement between these and the rest of the data. In the final result, there is about 20% discrepancy between these data and the optimized curves. Incidently, even though Vecher et al's data[24] were omitted, it is worth noting that these data lie on the opposite side of the optimised curve from that of Ansara et al's data.

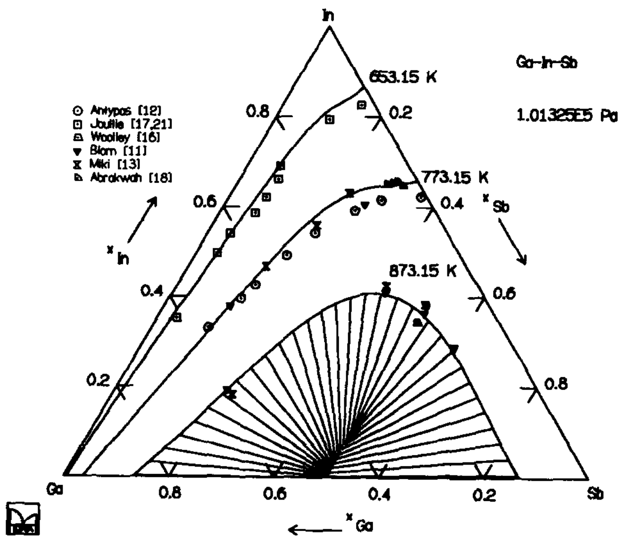
Table 4. Optimised Excess Gibbs Energy Coefficients for the Ga-In-Sb System

	a	b
liquid	-5072.76	-10.8842
(Ga,In)Sb	9093.00	-2.8698

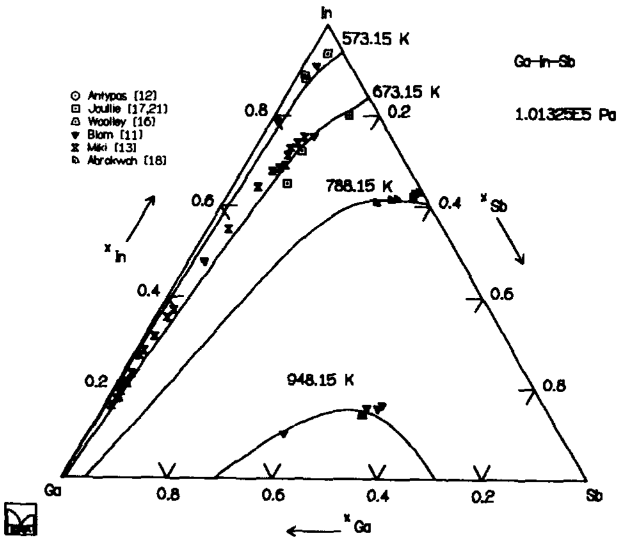
The resulting coefficients from the final optimisation are given in table 4. The phase diagrams with the tie-lines and experimental data (shown as fig.4-5) have been plotted using MTDATA[30] and the parameters in table 4. It can be seen that most of the phase diagram data are in agreement with the calculated liquid isotherms except for some near the In-Sb boundary, such as those of Antypas[12] at 773.15K and Joullié et al [17] at 653.15K. These data did not fit well because they conflicted with the description of In-Sb binary.

It is interesting to note that certain amount of disagreement was found between the extrapolated liquidus data of Gratton and Woolley[19] and the calculated curves. Sharma and Mukerjee[7] on the other hand, found a better fit of these data to their calculated curve. It is felt that this may be, because including such a large amount of data in their optimisation which were extrapolations to other experimental data, a bias had been imposed on their final result.

The GaSb-InSb pseudobinary phase diagram together with the experimental data of Woolley[20], and Blom and Plaskett[11] is shown in fig.6. This result has no obvious differences from that obtained using an associated solution model for the liquid[1]. Most of the solidus experimental data was found to fit with the calculated curve. However, an interesting feature of the calculation is the appearance of the miscibility gap in the (Ga,In)Sb solid solution. The critical temperature was calculated to be 466.3K. The presence of the miscibility gap has not been confirmed experimentally owing to sluggish diffusion rates at the relatively low temperature.



Figures 4 & 5
Calculated Liquidus Phase Boundaries
with Experimental Data



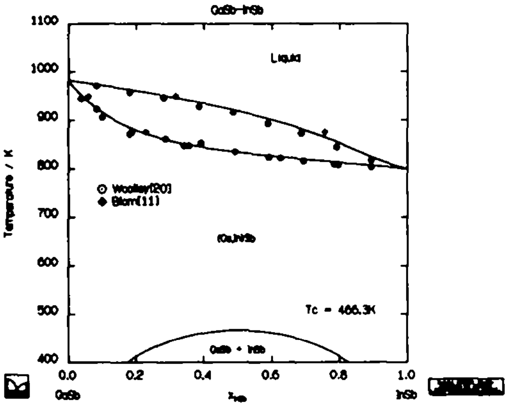


Figure 6
Calculated Pseudobinary Section Across the Ga-In-Sb system With Experimental Data

However, it could have profound implications for devices made from such materials as there is a possibility of their degradation with time. A similar temperature for Tc was proposed by Chang et al[3] (433K) resulting from their calculations. The level of agreement is acceptable considering the experimental difficulties encountered in measuring the enthalpies of mixing of the solid solution phase[4], which had a significant effect on determining the miscibility gap in this work. The measured enthalpies of mixing of the pseudobinary phase were found to fit well with the calculated curves. However, it was necessary to increase the weight of these data during the optimisation in order to produce well defined Gibbs energy coefficients.

There is a large discrepancy between calculation and experiment for the enthalpies of mixing of the liquid phase (see Fig.7). This is a consequence of the data not being in particularly good agreement with the phase diagram data. This is also shown in Liao et al's work.

Unexpectedly, the mixing enthalpy data of pseudobinary liquid could be fitted very well. These data are shown in figure 8 together with the calculated heat curve produced from the optimisation. The fact that this was not reflected in Sharma and Mukerjee's[7] work was probably mainly due to a typographical error in the original publication. However, their calculated curve still gives larger values for the heat of mixing than were found here.

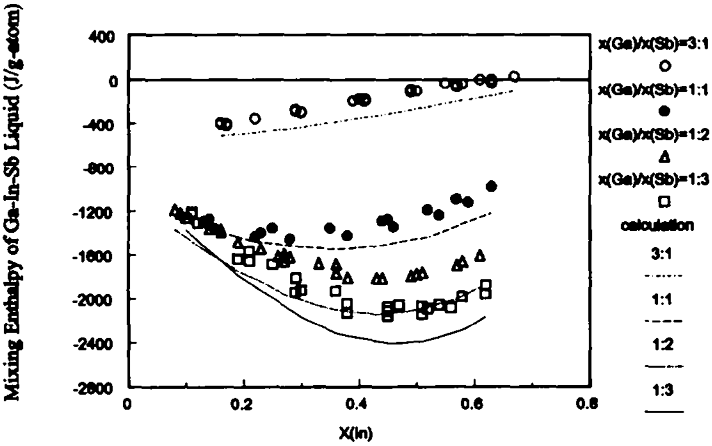


Figure 7.
Experimental Enthalpies of Mixing of the Liquid Phase at 995K[23]
Compared with Calculated Curves.

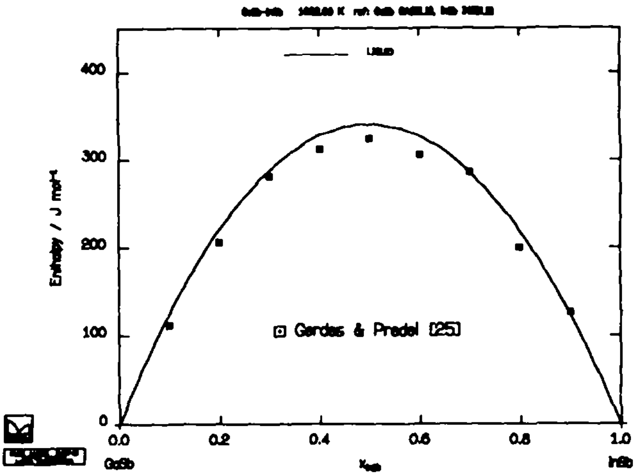


Figure 8.
Experimental Enthalpies of Mixing of the Pseudobinary Liquid Phase [25] at 1022K
Compared with Calculated Curve.

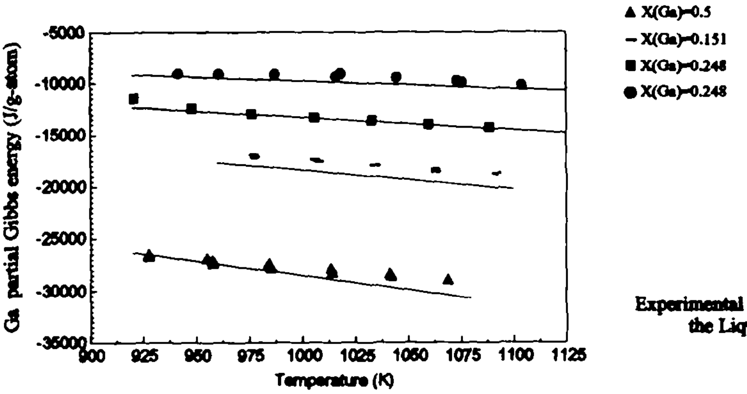


Figure 9
Experimental Partial Gibbs Energies of Gallium [2] in
the Liquid Phase with Calculated Curves

Figure 9 shows the calculated partial Gibbs energies of gallium in the liquid phase compared with the experimental data of Aselage and Anderson[2]. It can be seen that the temperature dependence of gallium partial Gibbs energy fits well with the calculated values. It was found that most of these data could be fitted well if 20% uncertainty in the partial Gibbs energy was allowed. In Sharma and Mukerjee's[7] work, only Chang et al's[3] data, which were found to be unreasonable here, were used. As a result, a bad fit was given for these data in their work.

A three phase equilibrium region has been found in the Sb-rich side at temperatures from 768K to 860K similar to that in the As-Ga-In phase diagram[31]. This is shown in figure 10. The implications of this with respect to device manufacture will be discussed in a future publication.

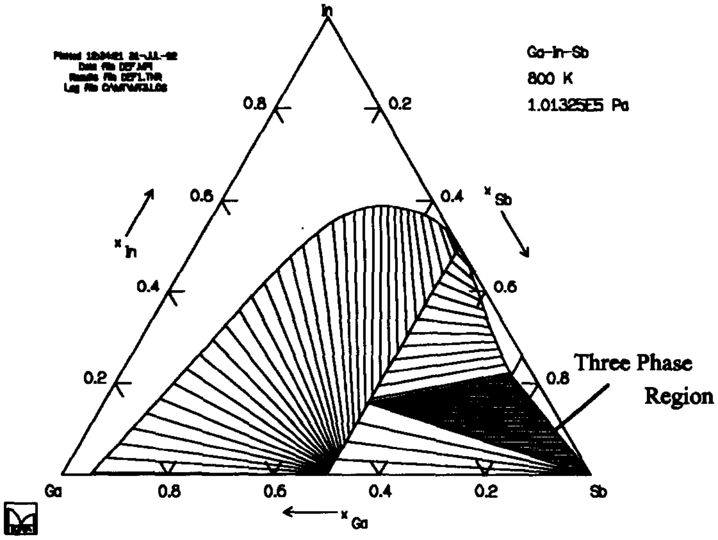


Figure 10
Calculated Isothermal Section of the
Ga-In-Sb System at 800°C Showing
Three Phase Region.

Acknowledgments

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