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N91-30214**CALCULATION OF GALLIUM-METAL-ARSENIC PHASE DIAGRAMS****J. D. Scofield
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Dayton OH****ABSTRACT**

Electrical contacts and metallizations to GaAs solar cells, intended for satellite array and other space-based applications, must survive at high temperatures for several minutes under specific mission scenarios. The determination of which metallizations or alloy systems that are able to withstand extreme thermal excursions with minimal degradation to solar cell performance can be predicted by properly calculated temperature constitution phase diagrams. Alternately, the thermodynamic behavior of metal-GaAs systems could only be accomplished by performing hundreds of controlled reactions and experimentally determining compound formation, diffusion couples, eutectic points, and finally, electrical/mechanical performance degradation. A method for calculating a ternary diagram and its three constituent binary phase diagrams is briefly outlined and ternary phase diagrams for three Ga-As-X alloy systems are presented. Free energy functions of the liquid and solid phases are approximated by the regular solution theory. The three binary systems comprising the boundaries of a ternary phase diagram are utilized to calculate the binary regular solution parameters. The free energy functions for the ternary system liquid and solid phases are then written as a combination of the binary regular solution parameters. Liquidus and solidus boundaries, as functions of temperature and composition, for the ternary diagrams are calculated from these free energy functions. Phase diagrams calculated using this method are presented for the Ga-As-Ge and Ga-As-Ag systems.

INTRODUCTION

This research effort was initiated to determine an alloy system which is chemically stable when exposed to extreme temperature excursions, exceeding 873 K, while functioning as electrical contact metallization to GaAs. The theoretical portion of this investigation has been the calculation and utilization of temperature constitution phase diagrams to determine suitable alloy compositions, which will be in equilibrium with the (p) or (n)GaAs solar cell emitter when the device is thermally stressed. Large

numbers of binary phase diagrams have been determined experimentally and are readily available in the open literature [1-4]. However, only a few of the possible ternary alloy systems have been experimentally investigated. The vast numbers of possible ternary alloys, and the extensive experimental effort that would be required to satisfactorily determine a ternary phase diagram, prompted us to utilize computational methods to calculate the equilibrium phase boundaries for selected alloy systems. Mathematical representations for the liquidus and solidus phase boundaries were derived through an application of the heterogeneous phase equilibrium principle [5-6] to ternary alloy systems. The analytical expressions were developed with the following assumptions made: (a) the liquid and solid phases can be described by the theory of a regular solution [6], (b) the regular solution parameter is a linear function of the absolute temperature, (c) the free energy function of the ternary phases can be represented by a linear combination of the binary regular solution parameters [7], (d) the binary compounds have a fixed composition and have no solubility for any of the elemental constituents, and (e) the Neumann-Kopp rule is obeyed [8].

BINARY ALLOY SYSTEMS

The development of an expression representing the thermodynamic equilibrium in a binary alloy system was accomplished for two distinct phase boundary conditions. The first representation describes the equilibrium between a binary liquid phase and a terminal solid solubility phase. The second case treats the equilibrium between a binary liquid phase and an intermediate binary compound. The equations describing these two cases are utilized in conjunction with the experimentally determined elemental and binary alloy data to calculate the values for the binary regular solution parameters. In order to obtain a quantitative measure as to the correctness of the computational method, the calculated values for the regular solution parameters were used to generate the boundaries for the liquidus and solidus phases of binary systems and then compared to the experimentally obtained values for the phase equilibrium boundaries.

EQUILIBRIUM BETWEEN A BINARY LIQUID PHASE AND A BINARY TERMINAL SOLID SOLUBILITY PHASE

In developing the mathematical relations to express the thermodynamic equilibrium between a binary liquid phase and a terminal solid solubility phase the following procedure and principles were utilized:

1. Apply the principle of heterogeneous phase equilibrium.
2. Represent the partial molal free energy terms of each of the elemental components as functions of the standard state free energies of the pure elements, the activity coefficients, the

mole fractions of the components, and the absolute temperature.

3. The difference between the standard state free energies of the liquid and solid states of each of the elements is expressed in terms of their heats of fusion and melting temperatures. The difference between the heat capacities of the liquid and solid phases is assumed to be zero.
4. Use the regular solution model of alloying behavior to obtain expressions for the activity coefficients of the elemental components.

A straightforward application of these steps results in the expressions for the boundaries of the phase diagram.

The analytical representation for the thermodynamic equilibrium between a binary liquid phase and a terminal solid solubility phase is given by the two simultaneous equations:

$$\Delta HF_1 \times (1 - T/T_1) = R \times T \times \ln(N_{1S}/N_{1L}) + S12 \times N_{2S}^2 - L12 \times N_{2L}^2 \quad (1a),$$

and

$$\Delta HF_2 \times (1 - T/T_2) = R \times T \times \ln(N_{2S}/N_{2L}) + S12 \times N_{1S}^2 - L12 \times N_{1L}^2 \quad (1b),$$

where HF_1 and HF_2 are the heats of fusion for element 1 and element 2 respectively; $L12$ is the liquid phase regular solution parameter for alloy 1-2; $S12$ is the solid phase regular solution parameter for alloy 1-2; N_{1L} , N_{2L} , N_{1S} , and N_{2S} are the mole fractions of element 1 and element 2 in the liquid and solid phases; R is the gas constant; T is the system temperature; and T_1 and T_2 are the melting temperatures of the two component elements.

The regular solution parameters, $L12$ and $S12$, are assumed to be linear functions of the absolute temperature as shown below:

$$L12 = \alpha + \beta T \quad (2a)$$

and

$$S12 = \chi + \delta T \quad (2a),$$

where the slope and intercept constants are determined from a fit of the data to a linear function of the absolute temperature.

EQUILIBRIUM BETWEEN A BINARY LIQUID PHASE AND A BINARY COMPOUND PHASE

The relationship developed for describing composition of the liquid boundary which is in equilibrium with an intermediate binary compound was developed by following the following steps:

1. The molal free energy of the compound is expressed in terms of the compound composition and the partial free energies of its solid elemental components.
2. Heterogeneous phase equilibrium principles are used to describe the partial molal free energies in terms of the elemental components of the liquid phase which are in equilibrium with the compound.
3. The molal free energy of the compound is expressed in terms of the absolute temperature, standard state free energies, mole fractions, and the activity coefficients of the components in the liquid phase.
4. The molal free energy of the liquid phase, which has the same composition as that of the compound, is described using the same variables as in Step 3 above.
5. The heat capacity differences between the compound and the liquid are assumed to be zero. The molal free energy differences of the compound and the liquid phase are expressed in terms of the heat of fusion and temperature of the compound. The free energy difference between the liquid and solid phases at the equilibrium melting temperature is zero.
6. Regular solution theory is used to define the relations for the activity coefficients of each component of the liquid phase.

The resulting equation which describes the equilibrium between the binary liquid phase and the binary compound is given by the relation [9],

$$\begin{aligned} \Delta H_C \times (1 - T/T_C) &= R \times T \times (N_{1C} \times \ln(N_{1C}) + N_{2C} \times \ln(N_{2C})) \\ &\quad - R \times T \times (N_{1L} \times \ln(N_{1L}) + N_{2L} \times \ln(N_{2L})) \\ &\quad + N_{1C} \times L_{12} \times N_{2C}^2 + N_{2C} \times L_{12} \times N_{1C}^2 \\ &\quad - N_{1C} \times L_{12} \times N_{2L}^2 - N_{2C} \times L_{12} \times N_{1L}^2. \end{aligned} \quad (3)$$

RESULTS FOR BINARY ALLOY SYSTEMS

Gallium-Germanium

To demonstrate the validity of this computational method of

calculating equilibrium phase diagrams, the gallium-germanium (Ga-Ge) system is discussed in detail as an example and compared to empirical data from the literature. Equations (1a) and (1b) were utilized to obtain the binary regular solution parameters. Elemental values for the melting temperatures and the heats of fusion were taken from the compilation of Hultgren [10] and are listed in Table 1. Temperature and composition values for the liquidus and solidus boundaries, required for these calculations, are from the experimental efforts of Keck and Broder [11], Greiner and Breidt [12], and Thurmond and Kowalchik [13].

Table 1

Values for the Heats of Fusion and Melting Points of Selected Elements

Element	Heat of Fusion (Cal/gm-at)	Melting Point (K)
Silver (Ag)	2700	1234
Arsenic (As)	2600	1090
Gallium (Ga)	1335	303
Germanium (Ge)	8100	1210

At several temperatures the values for the regular solution parameters were calculated. These data points were fit to a linear function of the temperature by the method of least squares. Calculated values for the slope and intercept for the Ge-Ga and other selected binary systems are shown in Table 2. As a check on the computations, phase boundaries for the Ge-Ga binary system were calculated and compared to experimental values from Hansen [14]. Figure 1 shows the liquidus and solidus boundaries calculated for the Ga-Ge system. Ge solubility in Ga is very small and the region of terminal solubility is almost coincident with pure Ga. The composition calculated for the eutectic of Ga-Ge is located close to the melting point of pure Ga, which is in agreement with experimental results. The calculated and experimental liquidus boundary difference is less than 1 atomic percent over the complete composition and temperature range. Ge solidus boundary calculations also show the same retrograde solubility characteristic that has been experimentally observed. Maximum Ga solubility in solid Ge occurs near 650°C for both calculated and experimental boundaries.

GaAs Liquidus Boundary

Experimental values are available for only a few compounds of interest [8,9], therefore two sets of computations were completed. In the first set, values for the heat of fusion, melting point, and composition of GaAs, and the composition and temperature of the liquid phase that is in equilibrium with the compound were used to calculate the regular solution parameter for the liquid phase.

Experimental values for GaAs were taken from References [14,15,19]. The regular solution parameter calculated from these values using Equation 3 is shown in Table 2.

Table 2

Calculated Binary Regular Solution Parameters

System	Liquid	Liquid	Solid	Solid	Ref.
	Intercept	Slope	Intercept	Slope	
Ag-As	-9256.9	.12305	134.12	-4.1037	[16]
Ag-Ga	-28,269	18.887	-25,839	15.932	[17]
As-Ga*	10,455	-11.608	---	---	[14,15]
As-Ga**	19,264	-11.233	---	---	[14,15]
As-Ge	-6200.4	4.688	16,816	-6.0467	[18]
Ga-Ge	210.23	-.54553	5945.4	-2.0719	[11-13]

* Calculated with the heat of fusion = 10,758 cal/gm-at.

**Calculated with the heat of fusion = 3,613 cal/gm-at.

The second set of computations involved using the same values for the melting point and composition of GaAs and the same liquidus boundary to determine values for the heat of fusion of GaAs and the regular solution parameter of the liquid phase. The GaAs heat of fusion calculation, in addition to those for other binary compounds, are listed in Table 3. The slope and intercept values are listed in Table 2.

Table 3

Heat of Fusion of Selected Binary Compounds

Compound	H _f Calculated	H _f Experimental
AsGa	3613	10,578
As ₂ Ge	7789	---
AsGe	8087	---

The heat of fusion value difference between the calculated and experimental results is considerable. Similarly, the values obtained for the regular solution parameter shows a significant disparity. In order to determine accuracy of subsequent calculations using these values, the liquidus boundaries were computed using the values obtained in the two sets of calculations. The resulting Ga-As phase diagram showing the comparison between the two sets of calculations are shown in Figure 2. Statistical analysis of the results shows that the maximum deviation between the computed and experimental boundaries is less than five atomic

percent arsenic. While the thermodynamic values are significantly different between the two approaches, the resulting liquidus boundaries for the calculated and experimental values are in satisfactory agreement.

TERNARY ALLOY SYSTEMS

Expressions describing the equilibrium in ternary systems were developed for two situations. First, the equilibrium between a ternary liquid phase and a ternary terminal solid solubility phase is represented by three simultaneous equations. Secondly, the expression for the equilibrium between a ternary liquid phase and a binary compound was formulated. The thermodynamic behavior is approximated by the binary regular solution parameters in both instances.

EQUILIBRIUM BETWEEN A TERNARY LIQUID AND A TERNARY SOLID SOLUBILITY PHASE

The assumptions and procedures for developing the relations describing the binary equivalent to this case were applied and the following three simultaneous equations were generated.

$$\Delta H_{f1} \times (1 - T/T_1) = R \times T \times \ln(N_{1S}/N_{1L}) + L12 \times N_{2L} \times (1 - N_{1L}) + L13 \times N_{3L} \times (1 - N_{1L}) - L23 \times N_{2L} \times N_{3L} \\ - S12 \times N_{1S} \times (1 - N_{2S}) - S23 \times N_{3S} \times (1 - N_{2S}) + S13 \times N_{1S} \times N_{3S} \quad (4a)$$

$$\Delta H_{f2} \times (1 - T/T_2) = R \times T \times \ln(N_{2S}/N_{2L}) + L12 \times N_{1L} \times (1 - N_{2L}) + L23 \times N_{3L} \times (1 - N_{2L}) - L13 \times N_{1L} \times N_{3L} \\ - S12 \times N_{1S} \times (1 - N_{2S}) - S23 \times N_{3S} \times (1 - N_{2S}) + S13 \times N_{1S} \times N_{3S} \quad (4b)$$

and

$$\Delta H_{f3} \times (1 - T/T_3) = R \times T \times \ln(N_{3S}/N_{3L}) + L13 \times N_{1L} \times (1 - N_{3L}) + L23 \times N_{2L} \times (1 - N_{3L}) - L12 \times N_{1L} \times N_{2L} \\ - S13 \times N_{1S} \times (1 - N_{3S}) - S23 \times N_{2S} \times (1 - N_{3S}) + S12 \times N_{1S} \times N_{2S} \quad (4c)$$

Equations (4a)-(4c) were solved to yield a solution, as a function of temperature, for the ternary Ga-As-Ge liquidus boundary which is in equilibrium with the Ge solid solubility phase. The binary regular solution parameters, which are used to estimate the alloying behavior of the ternary alloys, are those listed in Table 2. A 1000K isothermal section of the resulting ternary diagram is shown in Figure 3a and includes several tie-lines which connect the compositions on the liquidus boundary which are in equilibrium with the composition on the Ge solidus boundary. These calculations were repeated for the Ag-Ga-As system and an 800K isothermal plot of the liquidus and solidus boundaries is shown in Figure 3b.

EQUILIBRIUM BETWEEN A TERNARY LIQUID AND A BINARY INTERMEDIATE COMPOUND PHASE

An expression describing the equilibrium between a ternary liquid and a binary compound relates the heat of fusion and melting temperature of the binary compound, and the regular solution parameters, composition, and temperature of the ternary liquid phase. Following the steps outlined for the equivalent binary case given above, the following equation results.

$$\begin{aligned} \Delta H_C \times (1 - T/T_C) = & R \times T \times (N_{1C} \times \ln(N_{1C}) + N_{2C} \times \ln(N_{2C})) - R \times T \times (N_{1C} \times \ln(N_{1L}) + N_{2C} \times \ln(N_{2L})) \\ & + N_{1C} \times N_{2C} \times L_{12} - N_{1C} \times (L_{12} \times N_{2L} \times (1 - N_{1L}) + L_{13} \times N_{3L} \times (1 - N_{1L})) \\ & - L_{23} \times N_{2L} \times N_{3L} - N_{2C} \times (L_{12} \times N_{1L} \times (1 - N_{2L}) + L_{23} \times N_{3L} \times (1 - N_{2L})) \\ & - L_{13} \times N_{1L} \times N_{3L} . \end{aligned} \quad (5)$$

Equation (5) was solved as a function of temperature to yield the compositions of the Ga-As-Ge liquidus boundary which are in equilibrium with the compound GaAs. Figure (4a) shows the resulting diagram and the calculated liquidus boundary, which is the dominant liquid surface for this ternary system.

This liquidus surface has two intersections with the previously calculated ternary liquid boundary, which is in equilibrium with the Ge solid solubility phase, at a temperature of 873K. These two intersections define the compositional endpoints for which the liquid phase will be present. Figure 5a is a plot of the 1000K isothermal section and shows the liquid and solid boundaries with tie-lines connecting the liquid and solid phases at the two intersection endpoints mentioned above. Ternary compositions which fall between these two points will result in the presence of only two solid phases at equilibrium, the GaAs compound and the Ge alloy. There is however, a ternary eutectic involving GaAs, GeAs, and the Ge solid solubility phase and will act to lower the limit of the As-rich Ge solid solubility phase that is in equilibrium with GaAs.

These calculations were also performed for the Ag-Ga-As ternary system. The results of the previous section for the 800K computation, which determined the boundary between a ternary liquid phase that is in equilibrium with GaAs, is shown in Figure 4b. The results of this section were combined with the calculations reflected in Figure 4b and the resulting complete 800K Ag-Ga-As ternary diagram, showing liquidus and solidus boundaries with compositional tie-lines is presented in Figure 5b.

TERNARY EUTECTICS OF THE Ag-Ga-As SYSTEM

A eutectic point involving the ternary liquid phase, GaAs, GeAs, and a primary Ge solid alloy phase was calculated from the intersection of the three relevant ternary liquidus phase boundaries. These three boundaries are related to the equilibrium

between the ternary liquid phase and the GaAs compound, the GeAs compound, and the solid Ge alloy phase. The ternary liquid phase composition and temperature of the eutectic point and the composition of the solid Ge alloy phase in equilibrium with the GaAs and GeAs at this temperature is listed in Table 4. Of the three solid phases in this eutectic reaction the Ge solid solubility phase contains 99.78 atomic percent Ge, 0.16 atomic percent As, and 0.06 atomic percent Ga. Ge compositions on the solidus boundary containing a higher percentage of As will be in equilibrium with the GeAs compound.

The composition and temperature of the ternary liquid phase in equilibrium with the three compounds GaAs, GeAs, and GeAs₂ at the eutectic was determined from the intersection of the three liquidus surface boundaries described above but with the solid Ge alloy phase replaced by the compound GeAs₂ as the third liquidus boundary. These compositional values and eutectic temperature are also listed in Table 4.

Table 4

Solid Phases	Temp. (K)	Liquidus Atomic %		Balance
		Ga	As	
GaAs, GeAs, Ge	1002	41.8	1.7	Ge
GaAs, GeAs, GeAs ₂	1000	60.9	0.6	Ge

Calculated Eutectic Compositions for the As-Ga-Ge System

Presented in Figure 6 is a representation of the complete As-Ga-Ge ternary phase diagram, including the three component binary diagrams which comprise the complete system. Visualization of the two eutectic points is enhanced by this representation. It is located by two distinct valleys which would form when the entire liquidus surface connecting the boundaries between the three binary diagrams is generated.

SUMMARY

Germanium and silver alloys compositions which are in equilibrium with gallium arsenide were determined from the appropriate ternary phase diagrams. The procedure for calculating these compositions consists of:

1. Modeling the free energy functions of the binary and ternary phases by an application of the theory of a regular solution.
2. Generating the representations for the binary and ternary liquid and solid boundaries from the calculated free energy functions.

3. Binary regular solution parameters are calculated from the melting temperatures, and heats of fusion elemental values and the experimental values for the binary liquidus and solidus boundaries.
4. Approximating the ternary liquid and solid regular solution parameters as a sum of the component binary systems.
5. The compositions of the ternary liquid and solid boundaries are calculated as a function of temperature.
6. Calculating the compositions at the intersections of the ternary liquidus boundaries as a function of temperature. These compositions are the limiting values for which the liquid phase will be present. Between these limits only the solid phases will be present.
7. Using the tie-lines between the liquid and solid phases to obtain the compositions on the ternary solidus surface that are in equilibrium with the ternary liquid phase at the intersection points.
8. The solid compositions resulting from Step 7 are the endpoints for which only two solid phases, GaAs and the terminal solid solubility phase will coexist.

Ternary eutectic involving the ternary terminal solid solubility will limit the compositional range of solid alloys that will be in equilibrium with GaAs. A ternary eutectic point involving the three solid phases was obtained from the intersection of the ternary liquidus surfaces whose compositions are in equilibrium with each of the three solid phases.

Experimental verification of the correctness of the ternary phase equilibrium model is currently being undertaken. Differential scanning calorimetry is the primary technique being utilized to verify the equilibrium reactions predicted. Additional analysis to determine composition and compound formation is to include TEM and SIMS techniques but have yet to be initiated. Initial calorimetry results would seem to indicate that the non-equilibrium solid state reactions will have equal importance in the development of a suitable alloy system for high temperature metallizations to GaAs.

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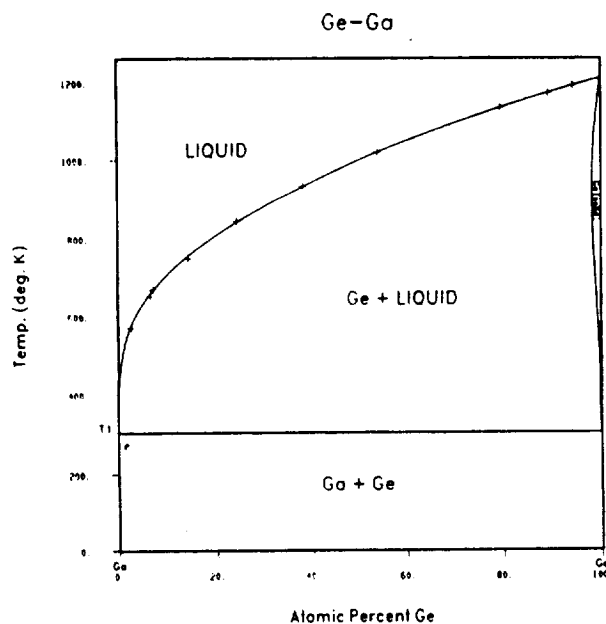


FIGURE 1

The temperature - constitution phase diagram for the Ga-Ge system. The calculated boundaries are represented by the solid lines and the experimentally reported results are shown as "+" symbols.

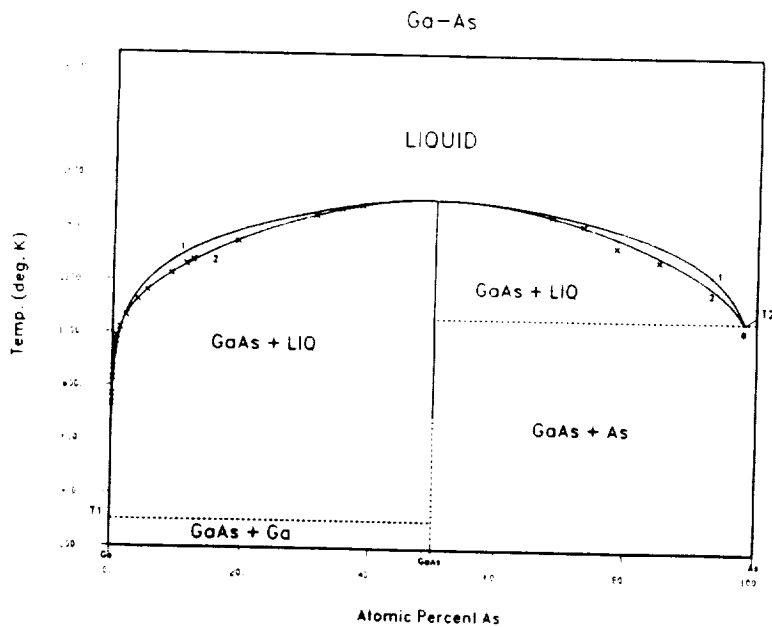


FIGURE 2

Temperature constitution phase diagram for the Ga-As system. Curve 1 is the calculated liquidus boundary and curve 2 the experimental boundary.

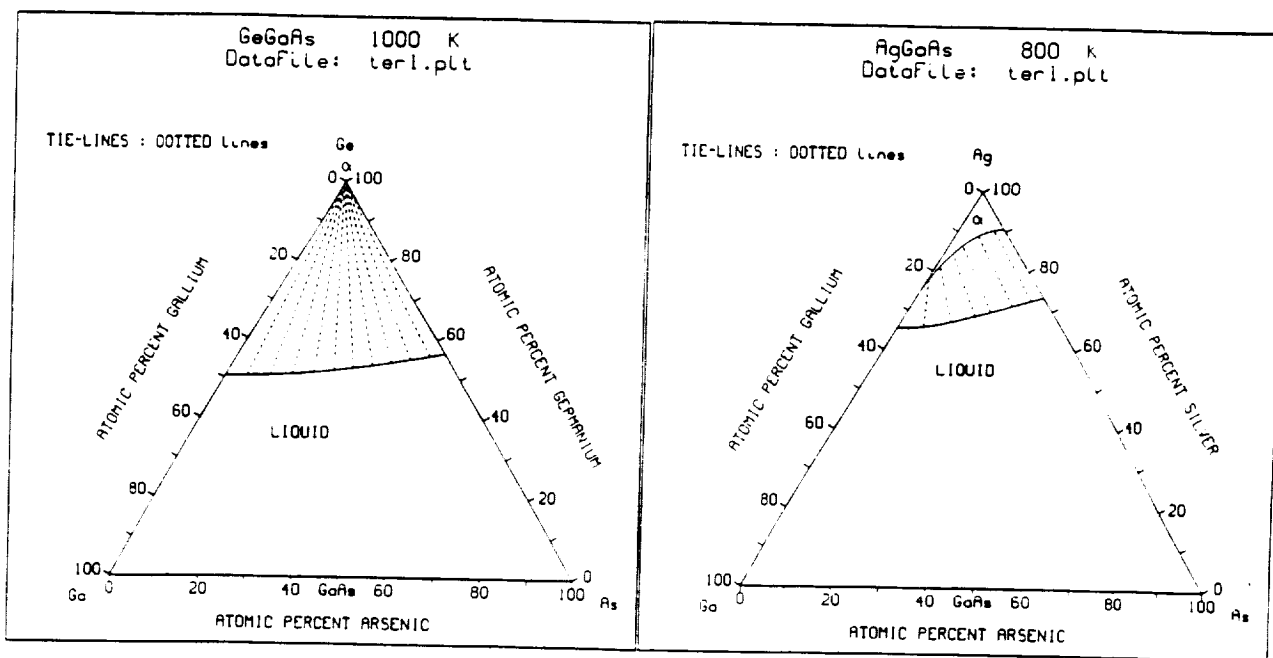


FIGURE 3a

FIGURE 3b

The Ge and Ag rich corners of their respective ternary phase diagrams. Tie-lines shown connect the liquid and solid compositions which are in equilibrium.

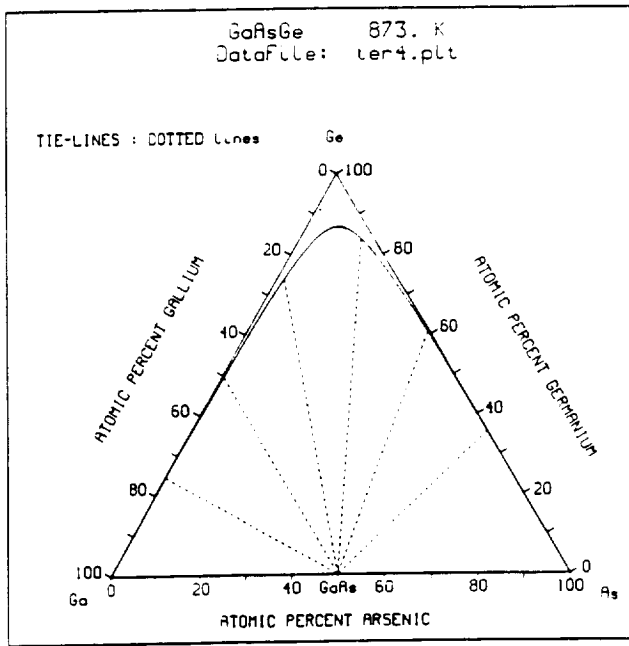


FIGURE 4a

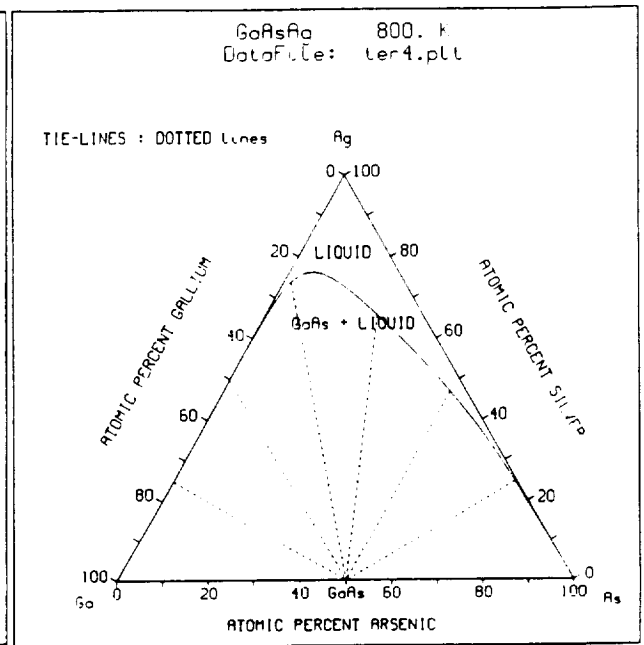


FIGURE 4b

Ga-As-Ge and Ga-As-Ag phase diagrams showing the ternary liquid composition which are in equilibrium with GaAs.

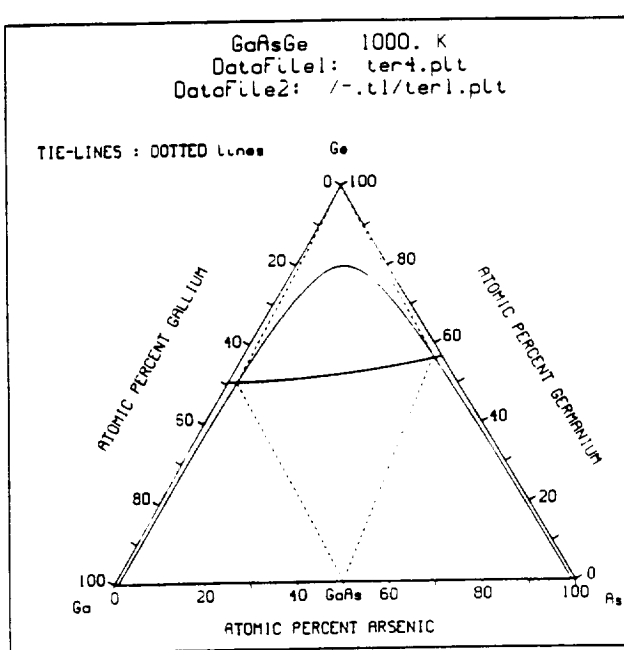


FIGURE 5a

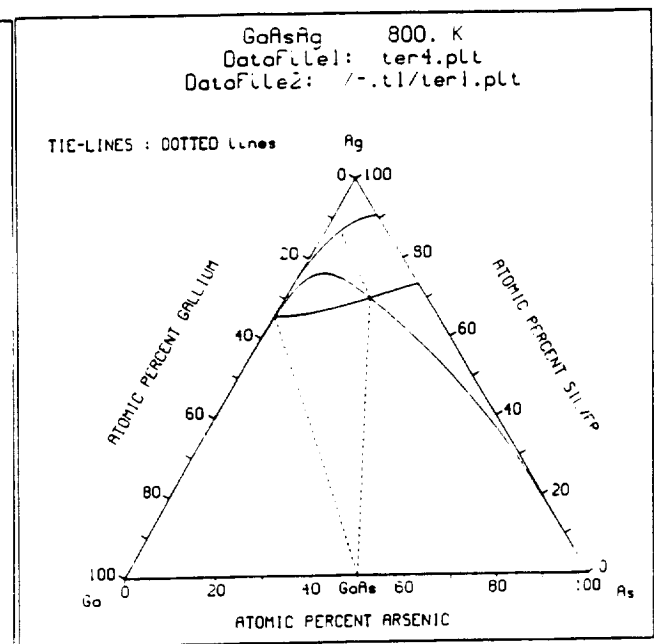


FIGURE 5b

Plots for the two liquid boundary intersections of the Ga-As-Ge and Ga-As-Ag ternary systems. Tie-lines show the liquid and solid compositions in equilibrium.

REPRESENTATION OF THE Ga-As-Ge SYSTEM

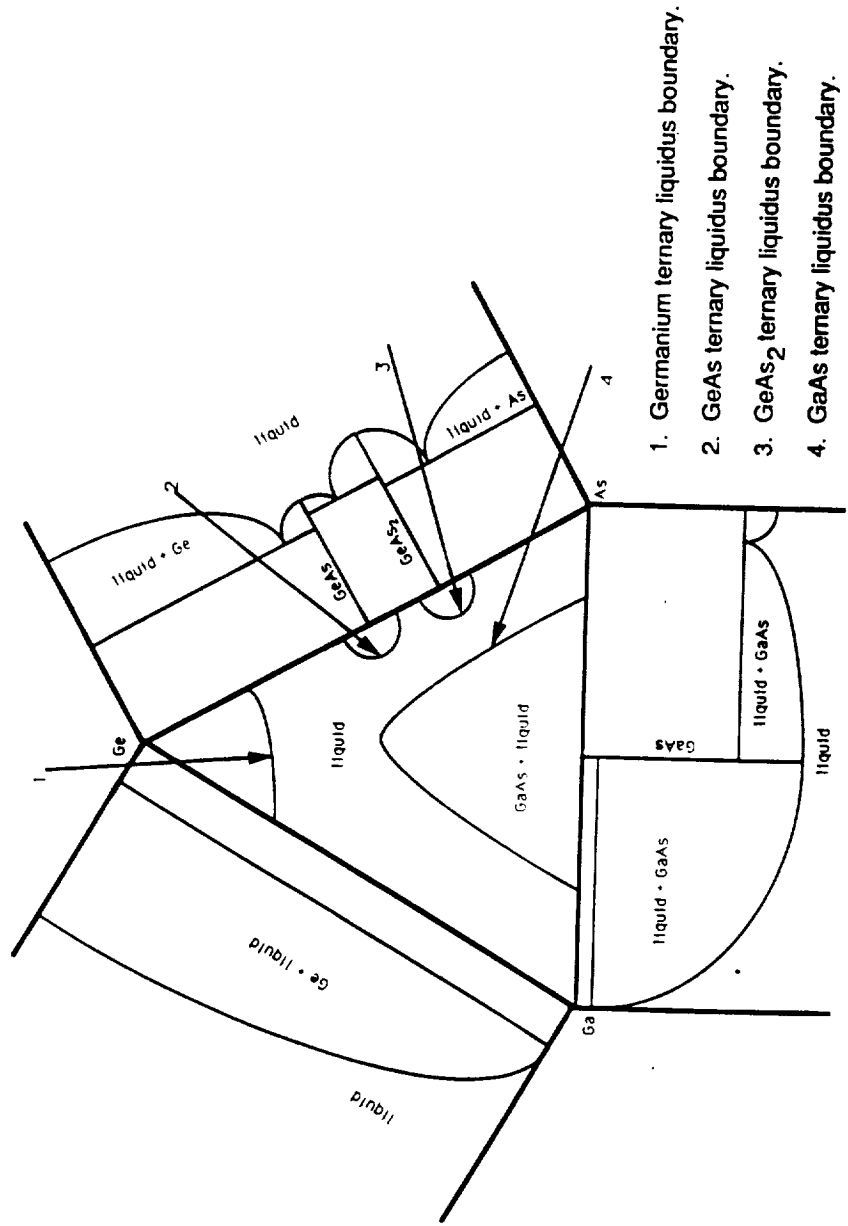


FIGURE 6

Ternary Ga-As-Ge phase diagram showing the 3 component binary diagrams.