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CALCULATION OF PHASE DIAGRAMS FOR METAL-GAAS SYSTEMS



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| This report describe computer model for t Regular solution the energy functions for for the Au, Ag, and | s the analytical meth he calculation of Met ory of alloying behav the ternary systems Ge metals with GaAs h | ods utilized ir al-Ga-As ternar ior has been us of interest. T ave been calcul | the development of a y phase diagrams. The ed to model the free Ternary phase diagrams lated and are presented |
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NOTATION

| С | Intermediate compound phase | | | | | |
|--|--|--|--|--|--|--|
| G _C | Molal free energy, intermediate compound phase | | | | | |
| G_{1C}, G_{2C} $G_{1L}^{o}, G_{2L}^{o}, G_{3L}^{o}$ | Partial molal free energies, intermediate compound phase Standard state free energies, liquid phase | | | | | |
| $G_{1S}^{o}, G_{2S}^{o}, G_{3S}^{o}$ | Standard state free energies, solid phase | | | | | |
| G_{1L}, G_{2L}, G_{3L} | Partial molal free energies, liquid phase | | | | | |
| G ₁ S, G ₂ S, G ₃ S | Partial molal free energies, solid phase | | | | | |
| ΔH_{C} | Heat of fusion, intermediate compound | | | | | |
| $\Delta H_{f1}, \Delta H_{f2}, \Delta H_{f3}$ | Heats of fusion, elements 1, 2, 3 | | | | | |
| L | Liquid phase | | | | | |
| L12, L13, L23 | Regular solution parameters, liquid phase | | | | | |
| In | Natural logarithm | | | | | |
| N _{1C} , N _{2C} | Mole fractions, compound phase | | | | | |
| N _{1L} , N _{2L} , N _{3L} | Mole fractions, liquid phase | | | | | |
| N ₁ S, N ₂ S, N ₃ S | Mole fractions, solid phase | | | | | |
| R | Gas constant | | | | | |
| S | Terminal solid solubility phase | | | | | |
| S12, S13, S23 | Regular solution parameters, solid phase | | | | | |
| Т | Absolute temperature | | | | | |
| T_1, T_2, T_3 | Melting temperatures, elements 1, 2, 3 | | | | | |
| Т _С | Melting temperature, intermediate compound phase | | | | | |
| YIL, Y2L, Y3L | Activity coefficients, liquid phase Accession For | | | | | |
| Y15, Y25, Y35 | Activity coefficients, solid phase 9740 240 Unannounced Just 15 Lost 1 on | | | | | |

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CALCULATION OF PHASE DIAGRAMS FOR METAL-GaAs SYSTEMS

1. INTRODUCTION

The purpose of this research is to determine alloy compositions for electrical contacts to gallium arsenide which will be chemically stable for temperatures up to 873K. As part of this research, we utilized the temperature constitution phase diagrams of ternary gallium arsenic metal systems to determine alloy compositions for the electrical contact materials which are in thermodynamic equilibrium with gallium arsenide. Although the phase diagrams have been experimentally determined for a large number of binary systems¹⁻⁴, by comparison only a few of the possible ternary alloy systems have been experimentally investigated. The number of possible ternary systems and the experimental effort required to adequately determine a ternary phase diagram prompted us to utilize computational methods to calculate the phase boundaries for selected ternary alloy systems. The analytical expressions for the liquidus and solidus phase boundaries of ternary alloy systems. In developing these analytical expressions, the following assumptions were made:

- The liquid and solid phases can be described by the theory of a regular solution⁶.
- The regular solution parameter is a linear function of the absolute temperature.
- The free energy function of the ternary phases can be represented by a linear combination of the binary regular solution parameters⁷.
- The binary compounds have a fixed composition and have no solubility for either of the elemental constituents.
- The Neumann-Kopp rule is obeyed, i.e. the difference between the heat capacities of the liquid and solid phases is zero⁸.

2. BINARY ALLOY SYSTEMS

The equations describing the thermodynamic equilibrium in binary systems were developed for two cases. The first case treats the equilibrium between a binary liquid phase and a binary terminal solid solubility phase. The second case treats the equilibrium between a binary liquid phase and an intermediate binary compound. These relations, together with experimental data for the elements and the binary alloys, were utilized to calculate the values for the regular solution parameters. As a check on the computations, the calculated values of the regular solution parameters were utilized to compute the liquidus and solidus boundaries for the binary systems and these values were compared to the experimental values for the phase boundaries.

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2.1 <u>The Equilibrium Between a Binary Liquid Phase and a Binary Terminal Solid Solubility</u> Phase

The procedure for developing the analytical expressions for the liquidus and solidus boundaries consists of the following steps⁹:

- 1. Apply the principle of heterogeneous phase equilibrium. This principle states that the partial molal free energy of each of the elemental constituents in all of the separate phases must be equal at equilibrium.
- 2. Express the partial molal free energy terms of each of the elemental constituents as functions of the standard state free energy of the pure elements, the activity coefficients, the mole fractions of the elemental constituents, and the absolute temperature.
- 3. Express the difference between the standard state free energies of the liquid and solid states of each of the elements in terms of their heats of fusion and melting temperatures, with the assumption that the difference between the heat capacities of the liquid and the solid phases is zero.
- 4. Utilize the regular solution model of alloying behavior to obtain expressions for the activity coefficients of each of the constituents.

These steps lead to the analytical expressions for the phase boundaries of the phase diagram.

The thermodynamic equilibrium between a binary liquid phase and a binary terminal solid solubility phase is expressed by the two simultaneous equations (See Appendix A),

$$\Delta H_{f1} \left(1 - \frac{T}{T_1} \right) = R T \ln \left(\frac{N_{1S}}{N_{1L}} \right) + S12 N_{2S}^2 - L12 N_{2L}^2$$
(1a)

and

$$\Delta H_{f2} \left(1 - \frac{T}{T_2} \right) = R T \ln \left(\frac{N_{2S}}{N_{2L}} \right) + S12 N_{1S}^2 - L12 N_{1L}^2$$
(1b)

The left-hand side of Equations (1a) and (1b) depend only on the temperature of the alloy system and the properties of the elemental constituents. The first term on the right-hand side of each of each of these equations represents the ideal solution contribution to the chemical equilibrium, and these terms are independent of any particular elemental components. The terms containing the factors, S12 or L12, depend on the alloying effects and are specific to a particular alloy system.

The regular solution parameters, S12 and L12, were assumed to be linear functions of the temperature, i.e.

$$L12 = \alpha + \beta T$$
 (2a)
and
$$S12 = \chi + \delta T,$$
 (2a)

where the quantities, α , β , χ , and δ , are constants determined from the fit of the data to a linear function of the absolute temperature.

2.2 Equilibrium Between a Binary Liquid Phase and a Binary Compound Phase

The procedure for developing the analytical relation to describe the composition of the liquid boundary which is in equilbrium with an intermediate binary compound consists of the following steps:

- i. Express the molal free energy of the compound in terms of the composition of the compound and the partial molal free energies of its solid elemental constituents.
- 2. Apply the principle of heterogenous phase equilibrium to express the partial molal free energies in terms of the elemental components of the liquid phase which are in equilibrium with the compound.
- 3. Express the molal free energy of the compound in terms of the absolute temperature and the standard state free energies, the mole fractions, and the activity coefficients of the components in the liquid phase.
- 4. Express the molal free energy of the liquid phase having the same composition as that of the compound in terms of the absolute temperature and the standard state free energies, the mole fractions, and the activity coefficients of the components in the liquid phase.
- 5. Assume that the difference between the heat capacities of the compound and the liquid phase is zero, and express the difference between the molal free energies of the compound and liquid phase in terms of the heat of fusion and melting temperature of the compound. At the equilibrium melting temperature, the free energy difference between the liquid and the solid phases is equal to zero.

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6. Utilize the regular solution theory to obtain expressions for the activity coefficients of each constituent of the liquid phase.

The equation which describes the equilibrium between the binary liquid phase and the binary compound is expressed by the relation (See Appendix C),

$$\Delta H_{C} \left(1 - \frac{T}{T_{C}}\right) = R T \left(N_{1C} \ln(N_{1C}) + N_{2C} \ln(N_{2C})\right)$$

$$- R T \left(N_{1C} \ln(N_{1L}) + N_{2C} \ln(N_{2L})\right)$$

$$+ N_{1C} L 12 N_{2C}^{2} + N_{2C} L 12 N_{1C}^{2}$$

$$- N_{1C} L 12 N_{2L}^{2} - N_{2C} L 12 N_{1L}^{2}.$$
(3)

2.2.1 Results for the Gallium-Germanium System

The gallium-germanium system is discussed in some detail as an example of this approach. The values for the binary regular solution parameters were obtained from the solution of Eqs. (1a) and (1b). The values for the heats of fusion and melting temperatures of the elements used are presented in Table 1 and were taken from the compilation of Hultgren¹⁰. The values for the temperature and composition of the liquidus and solidus boundaries which are required for these calculations are from the experimental investigations of Keck and Broder¹¹, Greiner and Breidt¹², and Thurmond and Kowalchik¹³.

Table 1Values 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 | |

The values for the regular solution parameter were calculated for each value of the temperature and these data were fitted by the method of least squares to a linear function of the

temperature. The values which were calculated for the intercept and slope for this system and other selected binary systems are presented in Table 2. As a check on the results of the computations, the phase boundaries were calculated for the binary system and compared to the experimental values which have been reported. The values calculated for the liquidus and solidus boundaries are presented in Figure 1. The solubility of germanium in gallium is very small and the terminal solubility region is almost coincident with pure gallium. The calculated eutectic composition of the gallium-germanium system is located close to the melting point of pure gallium and this result agrees with the experimental results. The difference between the calculated and experimental liquidus boundaries is less than 1 atomic percent over the entire temperature and composition range. The calculated germanium solidus boundary shows the same retrograde solubility feature that has been experimentally observed. The maximum solubility of gallium in solid germanium occurs near 650°C for both the calculated and experimental boundaries.

2.2.2 Results for the GaAs Compound Liquidus Boundary

Since experimental values for the heats of fusion have been reported for only a few compounds^{8,9}, two sets of computations were performed. In the first set of computations, the values for the composition, heat of fusion, and melting point of the gallium arsenide, and the temperature and composition of the liquid phase which is in equilibrium with this compound were utilized to calculate the value of the regular solution parameter for the liquid phase. The experimental values for the melting point and the heat of fusion of gallium arsenide were taken from the compilation of Tmar¹⁹. The experimental values for the temperature and composition of the liquid phase which are in equilibrium with gallium arsenide were taken from the experimental results of Hall¹⁴ and Koester and Thoma¹⁵. The regular solution parameter calculated from Equation 3 with these data is presented in Table 2.

In the second set of computations, the same values for the composition and melting point of gallium arsenide and the same liquidus boundary data were utilized to calculate the values for the heat of fusion of gallium arsenide and the regular solution parameter for the liquid phase. The calculated value for the heat of fusion for gallium arsenide and other selected binary compounds are presented in Table 3, and the slope and intercept for the regular solution parameters are presented in Table 2. A comparison between the experimental and calculated values for the heat of fusion of gallium arsenide and calculated values for the heat of fusion of gallium arsenide shows a considerable difference. Likewise, a comparison of the calculated results for the regular solution parameter also shows a significant difference.

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| [| | | | | | | |
|---|------------------------|--------------------|------------------------|--------------------|-----------|--|--|
| | Liquid | | Solid | | | | |
| System | Intercept ¹ | Slope ² | Intercept ¹ | Slope ² | Reference | | |
| Ag-As | -9,256.9 | 0.12305 | 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 | -6,200.4 | 4.688 | 16,816 | -6.0647 | [18] | | |
| Ga-Ge | 210.23 | -0.54553 | 5,945.4 | -2.0719 | [11-13] | | |
| 1 Units = cal/gm-at | | | | | | | |
| 2 Units = cal./gm-at/°K | | | | | | | |
| * Calculated with the heat of fusion = $10,578$ cal./gm-at. | | | | | | | |
| ** Calculated with the heat of fusion = 3,613 cal./gm-at. | | | | | | | |

Table 2 Calculated Binary Regular Solution Farameters

| Table 3 | | | | | |
|---|--|--|--|--|--|
| Heat of Fusion of Selected Binary Compounds | | | | | |

| | Heat of Fusion | (cal./gm-atom) |
|--------------------|----------------|----------------|
| Compound | calc. | exp. |
| AsGa | 3,613 | 10,578 |
| As ₂ Ge | 7,789 | |
| AsGe | 8,087 | |

As a check on these calculations, the liquidus boundaries were computed utilizing the results from these two sets of calculations. The results from these two sets of computations and the experimental data for the liquidus boundary are presented in Table 4 and in Figure 2. A comparison of the results shows that the maximum deviation between the calculated and experimental boundaries is less than five atomic percent arsenic. Although the calculated values for the thermodynamic properties of gallium arsenide are significantly different for the two approaches, the differences between the calculated and experimental liquidus boundaries are in satisfactory agreement.

3. TERNARY ALLOY SYSTEMS.

The analytical relations describing the equilibrium in ternary systems were developed for two cases. In the first case, the equilibrium between a ternary liquid phase and a ternary terminal solid solubility phase was expressed by three simultaneous equations. In the second case, an expression was developed for the equilibrium between a ternary liquid phase and a binary compound phase. In both cases the thermodynamic behavior of the ternary phases was approximated by the binary regular solution parameters⁷.

3.1 The Equilibrium Between a Ternary Liquid Phase and a Ternary Terminal Solubility Phase

The steps described in Section 2.1 were applied to develop the equations of equilibrium between a ternary liquid phase and a ternary terminal solid solubility phase. This thermodynamic equilibrium is expressed by the three simultaneous equations (See Appendix B).

$$\Delta H_{f1} \left(1 - \frac{T}{T_{1}}\right) = R T \ln\left(\frac{N_{1S}}{N_{1L}}\right) + L12 N_{2L} (1 - N_{1L}) + L13 N_{3L} (1 - N_{1L})$$

$$- L23 N_{2L} N_{3L} - S12 N_{1S} (1 - N_{2S}) - S23 N_{3S} (1 - N_{2S})$$

$$+ S13 N_{1S} N_{3S} , \qquad (4a)$$

$$\Delta H_{f2} \left(1 - \frac{T}{T_{2}}\right) = R T \ln\left(\frac{N_{2S}}{N_{2L}}\right) + L12 N_{1L} (1 - N_{2L}) + L23 N_{3L} (1 - N_{2L})$$

$$- L13 N_{1L} N_{3L} - S12 N_{1S} (1 - N_{2S}) - S23 N_{3S} (1 - N_{2S})$$

$$+ S13 N_{1S} N_{3S} , \qquad (4b)$$

$$\Delta H_{f3} \left(1 - \frac{T}{T_3}\right) = R T \ln\left(\frac{N_{3S}}{N_{3L}}\right) + L13 N_{1L} (1 - N_{3L}) + L23 N_{2L} (1 - N_{3L})$$
$$- L12 N_{1L} N_{2L} - S13 N_{1S} (1 - N_{3S}) - S23 N_{2S} (1 - N_{3S})$$
$$+ S12 N_{1S} N_{2S} . \qquad (4c)$$

TABLE 4

| Temperature (°K) | Liquidus Boundary (atom-% As) | | | | |
|-----------------------|-------------------------------|-------------------------|--------|--|--|
| | experimental | calculated ¹ | | | |
| | | case 1 | case 2 | | |
| 731.1 | 0.004 | 0.007 | 0.043 | | |
| 767.1 | 0.023 | 0.016 | 0.074 | | |
| 827.1 | 0.053 | 0.057 | 0.168 | | |
| 866.1 | 0.114 | 0.117 | 0.269 | | |
| 926.1 | 0.34 | 0.32 | 0.52 | | |
| 964.1 | 0.56 | 0.56 | 0.76 | | |
| 984.1 | 0.70 | 0.73 | 0.92 | | |
| 1018.1 | 1.15 | 1.15 | 1.25 | | |
| 1064.1 | 2.07 | 2.00 | 1.86 | | |
| 1126.1 | 3.83 | 3.84 | 3.08 | | |
| 1162.1 | 5.20 | 5.37 | 4.06 | | |
| 1226.1 | 8.86 | 8.99 | 6.51 | | |
| 1262.1 | 11.2 | 11.5 | 8.41 | | |
| 1277.1 | 12.2 | 12.7 | 9.34 | | |
| 1346.1 | 19.0 | 18.9 | 14.9 | | |
| 1448.1 | 31.0 | 31.3 | 28.8 | | |
| 1473.1 | 35.0 | 35.6 | 33.8 | | |
| 1488.1 | 38.2 | 38.8 | 37.6 | | |
| 1453.1 | 68.2 | 68.0 | 70.3 | | |
| 1418.1 | 73.2 | 73.0 | 76.2 | | |
| 1338.1 | 78.4 | 81.9 | 85.8 | | |
| 1288.1 | 85.0 | 86.4 | 89.9 | | |
| ¹ See text | | - | | | |

CALCULATED AND EXPERIMENTAL BINARY LIQUID COMPOSITIONS IN EQUILIBRIUM WITH GALLIUM ARSENIDE

3.1.1 Results for the As-Ga-Ge System

The ternary liquidus boundary of the gallium arsenic germanium whose compositions are in equilibrium with the germanium solid solubility phase were calculated from Equations (4a) - (4c) as a function of temperature. The values for the binary regular solution parameters which were used to approximate the alloying behavior of the ternary alloys are listed in Table 2. The results of these computations for the 1000K isotherm are presented in Figure 3a. Associated with each composition on the liquidus boundary is a composition on the germanium solidus boundary with which it is in equilibrium. Several of the tie lines which connect these liquid and solid compositions are shown in Figure 3a. Similar computations were performed for the silver-arsenic-gallium system. The calculated results for the ternary liquidus and solidus boundaries of this system at 800K are presented in Figure 3b.

3.2 Equilibrium Between a Ternary Liquid Phase and a Binary Intermediate Compound Phase

The analytical representation which describes the equilibrium between a ternary liquid phase and a bin ry compound relates the composition, heat of fusion, and melting temperature of the binary compound, and the regular solution parameters, composition, and temperature of the ternary liquid phase. The steps described in Section 2.2 for the binary case were followed to obtain the equation for the ternary case. This thermodynamic equilibrium is expressed by the relation (See Appendix D),

$$\Delta H_{C} \left(1 - \frac{T}{T_{C}}\right) = R T \left(N_{1C} \ln(N_{1C}) + N_{2C} \ln(N_{2C})\right) - R T \left(N_{1C} \ln(N_{1L})\right)$$

$$+ N_{2C} \ln(N_{2L}) + N_{1C} L12 N_{2C} (1 - N_{1C})$$

$$+ N_{2C} L12 N_{1C} (1 - N_{2C}) - N_{1C} (L12 N_{2L} (1 - N_{1L}))$$

$$+ L13 N_{3L} (1 - N_{1L}) - L23 N_{2L} N_{3L}$$

$$- N_{2C} (L12 N_{1L} (1 - N_{2L}) + L23 N_{3L} (1 - N_{2L}))$$

$$- L13 N_{1L} N_{3L}$$
(5)

3.2.1 Results for the As-Ga-Ge System

The compositions of the gallium arsenide germanium ternary liquidus boundary whose compositions are in equilibrium with the compound, GaAs, were calculated from Eq. (5) as a function of temperature. The calculated liquidus boundary is shown in Figure 4a, and this liquidus boundary is the dominant liquidus surface for this ternary system.

At 873K, there are two intersections of this liquidus surface and the ternary liquidus surface which is in equilibrium with the germanium solid solubility phase in the arsenic gallium germanium system. The values for the liquid compositions of these two intersections and the values for the composition of the solid germanium alloy which are in equilibrium with each of these liquid compositions are listed in Table 5. These two intersections define the compositional endpoints at that temperature for which the liquid phase will be present. A plot of the liquidus and solidus boundaries at 1000K and the tie lines between the liquid and the solid phases at the intersection of the two liquidus boundaries is presented in Figure 5a. For compositions between these two endpoints only the two solid phases, the gallium arsenide compound and the germanium alloy, will be present at equilibrium. However, there is a ternary eutectic involving GaAs, GeAs.

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and the germanium solid solubility phase which will lower the limit of the arsenic-rich germanium solid solubility phase, which is in equilibrium with gallium arsenide.

Similar calculations were performed on the silver-arsenic-gallium ternary system. The calculated results for the liquidus boundary representing ternary liquid compositions which are in equilibrium with gallium arsenide at 800K are shown in Figure 4b. A plot of the liquidus and solidus boundaries at 800K and the tie lines between the liquid and the solid phases at the intersection of the two liquidus boundaries is presented in Figure 5b.

| | | Liquidus Atomic Percent | | Solidus Atomic Percent | | | | |
|----------|----------|----------------------------|-------|---------------------------|-------|-------|-----|-----------|
| System | Endpoint | As | Ga | Bal. | As | Ga | Bal | Temp (°K) |
| Ag-As-Ga | Ga-rich | 1.15 | 33.32 | Ag | >0.05 | 24.54 | Ag | 800 |
| Ag-As-Ga | As-rich | 18.08 | 11.92 | Ag | 9.9 | 3.2 | Ag | 800 |
| As-Ga-Ge | Ga-rich | 0.30 | 70.68 | Ge | >0.01 | 1.63 | Ge | 873 |
| As-Ga-Ge | As-rich | 58.46 | 0.24 | Ge | 0.08 | 0.01 | Ge | 873 |

Table 5Solid Alloy Compositions in Equilibrium with GaAs

3.2.2 Ternary Eutectics in the As-Ga-Ge System

The eutectic point involving the ternary liquid phase, the gallium arsenide, the germanium arsenide, and the primary solid phase germanium alloy was determined from the intersection of the three pertinent ternary liquidus phase boundaries. One of these boundaries is associated with the equilibrium between the ternary liquid phase and the compound GaAs. The second boundary is associated with the equilibrium between the liquid phase and the compound GeAs. The third boundary is associated with the equilibrium between the liquid phase and the compound GeAs. The third boundary is associated with the equilibrium between the liquid phase and the solid germanium alloy phase. The temperature and composition of the ternary liquid phase of the eutectic point and the composition of the solid germanium alloy which is in equilibrium with the two compounds GaAs and GeAs at this temperature are listed in Table 6. The composition of the germanium solid solubility phase (one of the three solid phases in this eutectic reaction) contains 99.78 atomic percent germanium, 0.16 atomic percent arsenic, and 0.06 atomic percent gallium. Germanium alloy compositions on the solidus boundary containing a higher percentage of arsenic will be in thermodynamic equilibrium with the GeAs compound.

The temperature and composition of the eutectic point involving the ternary liquid phase and the three compounds GaAs, GeAs, and GeAs₂, was determined from the intersection of the three pertinent liquidus surfaces. The three liquidus boundaries required to determine this eutectic point are the boundary between the ternary phase and the compound GaAs, the boundary between the liquid phase and the compound GeAs, and the boundary between the liquid and the compound GeAs₂. The calculated values of the eutectic temperature and composition for this ternary eutectic are also listed in Table 6.

Table 6 Calculated Ternary Eutectic Compositions in the Arsenic-Gallium-Germanium System

| | Liquidus Perc | | | |
|-------------------------------|------------------|------|-----|---------|
| Solid Phases | Temp (°K) | As | Ga | Balance |
| GaAs, GeAs,Ge | 1002 | 41.8 | 1.7 | Ge |
| GaAs, GeAs, GeAs ₂ | 1000 | 60.9 | 0.6 | Ge |

4. SUMMARY

The compositions of germanium and silver alloys which are in thermodynamic equilibrium with gallium arsenide were determined from the pertinent ternary alloy phase diagrams. The procedure for determining these alloy compositions consisted of:

- 1. Modeling the free energy functions of the binary and ternary phases utilizing the theory of a regular solution.
- 2. Developing the analytical expressions for the binary and ternary liquidus and solidus boundaries from these free energy functions.
- 3. Utilizing the melting temperatures and heats of fusion of the elemental components and the experimental values of the temperature and composition for the liquidus and solidus boundaries of the binary alloy systems to calculate the binary regular solution parameter.
- 4. Modeling the regular solution parameters for the ternary liquid and solid phases as a sum of the binary systems.
- 5. Calculating the compositions of the ternary liquidus and solidus boundaries as a function of temperature.

- 6. Determining the compositions of any intersections of the ternary liquidus boundaries as a function of temperature. The compositions of these intersections are the limiting compositions for which the liquid phase will be present. Between these compositional limits only the solid phases will coexist.
- 7. Utilizing the tie lines between the ternary liquid and solid phases to determine the compositions on the ternary solidus surface which are in equilibrium with the ternary liquid phase at the points of intersection of the ternary liquidus surfaces.
- 8. These solid compositions represent the endpoints of the solid alloys for which only the two solid phases, the gallium arsenide and the terminal solid solubility phase will coexist.

The occurrence of ternary eutectics involving the terminal ternary solid solubility can be expected to limit the compositional range of terminal solid alloys which are in equilibrium with gallium arsenide. The ternary eutectic point involving the three solid phases, gallium arsenide, germanium arsenide, and the germanium solid solubility phase, was determined from the intersection of the ternary liquidus surfaces whose compositions are in equilibrium with each of these three solid phases. The composition of the germanium solid solubility phase which is one of the phases involved in the eutectic reaction was determined from the tie line between the ternary liquidus and solidus surface at the eutectic point. Solid germanium alloys containing a higher arsenic concentration than this eutectic component will be in thermodynamic equilibrium with germanium arsenide.

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Ge-Ga



Atomic Percent Ge

Figure 1. The temperature-constitution phase diagram for the gallium-germanium system. The calculated boundaries are represented by the solid lines and the experimentally reported results are represented by the '+' symbols.







Figure 2. The temperature-constitution phase diagram for the gallium-arsenide system. The experimentally reported results are presented by the 'X' symbols. The calculated liquidus boundaries are represented by the solid lines. The upper liquidus boundary labeled 1, is calculated with a calculated value for the heat of fusion for the gallium arsenide. The lower liquidus boundary was calculated with the experimental value for the heat of fusion.



Figure 3a. The calculated liquidus and solidus boundaries of the germanium-rich corner of the arsenic-gallium-germanium phase diagram. The liquidus and solidus boundaries are represented by the solid lines, and the tie lines connecting the liquidus and solidus compositions which are in equilibrium are represented by the dotted lines.

fiquade 300 k Datafile: terlipli



Figure 3b. The calculated liquidus and solidus boundaries of the silver-rich corner of the silver-arsenic-gallium phase diagram. The liquidus and solidus boundaries are represented by the solid lines, and the tie lines connecting the liquidus and solidus compositions which are in equilibrium are represented by the dotted lines.

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GafisGe 873. K DataFile: terf.plt



Figure 4a. The calculated liquidus boundary of the arsenic-gallium-germanium phase diagram representing ternary liquid composition at 873K which are in equilibrium with gallium arsenide.

Gafisfig - 300. K DataFile: ter4.plt



Figure 4b. The calculated liquidus boundary of the silver-arsenic-gallium phase diagram representing ternary liquid compositions at 800K which are in equilibrium with gallium arsenide.

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Figure 5a. Plots of the liquidus boundaries and their two intersections for the arsenicgallium-germanium phase diagram. The solid lines are the liquidus boundaries and the dotted lines represent the tie lines between the liquid and solid compositions which are in equilibrium.



Figure 5b. Plots for the liquidus boundaries and their two intersections for the silverarsenic-gallium phase diagram. The solid lines are the liquidus boundaries and the dotted lines represent the tie lines between the liquid and solid compositions which are in equilibrium.

Appendix A. The Equilibrium Between a Binary Liquid Phase and a Binary Terminal Solid Solubility Phase.

The quantitative criterion for thermodynamic equilibrium to exist between a binary liquid phase and a binary solid phase requires that the partial molal free energies of each elemental constituent in the two phases be equal. This requirement is expressed as follows,

$$G_{1S} = G_{1L} \tag{1a}$$

and

$$G_{1S} = G_{2L} \tag{1b}$$

The partial molal free energies are related to the standard state free energies of the pure components, the activity coefficients of the components, and the absolute temperature by the relations,

$$G_{1L} = G_{1L}^{0} + R T \ln(N_{1L}) + R T \ln(\gamma_{1L}), \qquad (2a)$$

$$G_{2L} = G_{2L}^{o} + R T \ln(N_{2L}) + R T \ln(\gamma_{2L}),$$
 (2b)

$$G_{1S} = G_{1S}^{0} + R T \ln(N_{1S}) + R T \ln(\gamma_{1S}), \qquad (2c)$$

and,

$$G_{2S} = G_{2S}^{o} + R T \ln(N_{2S}) + R T \ln(\gamma_{2S}).$$
(2d)

After substituting Equations (2a)-(2d) into Equations (1a) and (1b), the following expressions are obtained,

$$G_{1L}^{o} - G_{1S}^{o} = R T \ln(N_{1S}) + R T \ln(\gamma_{1S}) - R T \ln(N_{1S}) - R T \ln(\gamma_{1S})$$
(3a)

 $G_{2L}^{o} - G_{2S}^{o} = R T \ln(N_{2S}) + R T \ln(\gamma_{2S}) - R T \ln(N_{2S}) - R T \ln(\gamma_{2S}).$ (3b)

In the regular solution theory, the activity coefficients are related to the absolute temperature and the compositions of the liquid or solid phases by the expressions,

R T ln(
$$\gamma_{1L}$$
) = L12 N²_{2L}, (4a)

$$R T \ln(\gamma_{2L}) = L12 N_{1L}^2$$
, (4b)

R T ln(
$$\gamma_{1S}$$
) = S12 N_{2S}², (4c)

and

$$R T \ln(\gamma_{2S}) = S12 N_1^2$$
(4d)

At the equilibrium melting temperature the liquid and solid phases coexist and the free energies of the liquid and solid phases are equal, and the free energy difference between the liquid and solid phases is expressed as a function of the temperature by the relations,

$$G_{1L}^{0} - G_{1S}^{0} = \Delta H_{f1} \left(1 - \frac{T}{T_1} \right)$$
 (5a)

and

$$G_{2L}^{o} - G_{2S}^{o} = \Delta H_{f2} \left(1 - \frac{T}{T_2} \right)$$
 (5b)

The substitution of Equations (4a)-(4d) and (5a) and (5b) into Equations (3a) and (3b) yields two simultaneous equations which express the temperature and composition dependence of the liquidus and solidus boundaries under equilibrium conditions for binary systems. The two equations resulting from these substitutions are,

$$\Delta H_{fl} \left(1 - \frac{T}{T_l} \right) = R T \ln \left(\frac{N_{1S}}{N_{1L}} \right) + S12 N_{2S}^2 - L12 N_{2L}^2$$
(6a)

$$\Delta H_{f2} \left(1 - \frac{T}{T_2} \right) = R T \ln \left(\frac{N_{2S}}{N_{2L}} \right) + S12 N_{1S}^2 - L12 N_{1L}^2.$$
 (6b)

The mole fractions of the elemental constituents of the liquid and solid phases are subject to the constraints,

$$N_{1L} + N_{2L} = 1$$
 (7a)

and

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$$N_{1S} + N_{2S} = 1.$$
 (7b)

Appendix B. The Equilibrium Between a Ternary Liquid Phase and a Ternary Terminal Solid Solubility Phase.

The quantitative criterion for thermodynamic equilibrium to exist between a ternary liquid phase and a ternary solid phase requires that the partial molal free energies of each elemental constituent in the two phases be equal. This requirement is expressed as follows,

$$G_{1S} = G_{1L}, \tag{1a}$$

$$G_{2S} = G_{2L}, \tag{1b}$$

and

$$G_{3S} = G_{3L}.$$
 (1c)

The partial molal free energies are related to the standard state free energies of the pure components, the activity coefficients of the components, and the absolute temperature by the relations,

$$G_{1L} = G_{1L}^{o} + R T \ln(N_{1L}) + R T \ln(\gamma_{1L}),$$
 (2a)

$$G_{2L} = G_{2L}^{o} + R T \ln(N_{2L}) + R T \ln(\gamma_{2L}),$$
 (2b)

$$G_{3L} = G_{3L}^{o} + R T \ln(N_{3L}) + R T \ln(\gamma_{3L}),$$
 (2c)

$$G_{1S} = G_{1S}^{o} + R T \ln(N_{1S}) + R T \ln(\gamma_{1S}), \qquad (2d)$$

$$G_{2S} = G_{2S}^{o} + R T \ln(N_{2S}) + R T \ln(\gamma_{2S}), \qquad (2e)$$

and,

$$G_{3S} = G_{3S}^{o} + R T \ln(N_{2S}) + R T \ln(\gamma_{3S}).$$
(2f)

After substituting Equations (2a)-(2f) into Equations (1a), (1b), and (1c), and rearranging, the following expressions are obtained,

$$G_{1L}^{o} - G_{1S}^{o} = R T \ln(N_{1S}) + R T \ln(\gamma_{1S}) - R T \ln(N_{1S}) - R T \ln(\gamma_{1S}), \qquad (3a)$$

$$G_{2L}^{o} - G_{2S}^{o} = R T \ln(N_{2S}) + R T \ln(\gamma_{2S}) - R T \ln(N_{2S}) - R T \ln(\gamma_{2S}),$$
(3b)

and

$$G_{3L}^{o} - G_{3S}^{o} = R T \ln(N_{3S}) + R T \ln(\gamma_{3S}) - R T \ln(N_{3S}) - R T \ln(\gamma_{3S}).$$
(3c)

In the regular solution theory, the activity coefficients are related to the absolute temperature and the compositions of the liquid or solid phases by the expressions,

$$R T \ln(\gamma_{1L}) = L12 N_{2L} (1 - N_{1L}) + L13 N_{3L} (1 - N_{1L}) - L23 N_{2L} N_{3L}, \qquad (4a)$$

R T ln(
$$\gamma_{2L}$$
) = L12 N_{1L} (1 - N_{2L}) + L23 N_{3L} (1 - N_{2L}) - L13 N_{1L} N_{3L}, (4b)

$$R T \ln(\gamma_{3L}) = L13 N_{1L} (1 - N_{3L}) + L23 N_{2L} (1 - N_{3L}) - L12 N_{1L} N_{2L}, \qquad (4c)$$

R T ln(
$$\gamma_{1S}$$
) = S12 N_{2S} (1 - N_{1S}) + S13 N_{3S} (1 - N_{1S}) - S23 N_{2S} N_{3S}, (4d)

$$R T \ln(\gamma_{2S}) = S12 N_{1S} (1 - N_{2S}) + S23 N_{3S} (1 - N_{2S}) - S13 N_{1S} N_{3S}, \qquad (4e)$$

and

$$R T \ln(\gamma_{3S}) = S13 N_{1S} (1 - N_{3S}) + S23 N_{2S} (1 - N_{3S}) - S12 N_{1S} N_{2S}.$$
(4f)

At the equilibrium melting temperature the liquid and solid phases coexist and the free energies of the liquid and solid phases are equal, and the free energy difference between the liquid and solid phases is expressed as a function of the temperature by the relations,

$$G_{1L}^{o} - G_{1S}^{o} = \Delta H_{f1} \left(1 - \frac{T}{T_1} \right)$$
 (5a)

$$G_{2L}^{o} - G_{2S}^{o} = \Delta H_{f2} \left(1 - \frac{T}{T_2} \right)$$
 (5b)

$$G_{3L}^{o} - G_{3S}^{o} = \Delta H_{f3} \left(1 - \frac{T}{T_3} \right)$$
 (5c)

The substitution of Equations (4a)-(4f) and Equations (5a)-(5c), into Equations (3a)-(3c) yields three simultaneous equations which express the temperature and composition dependence of the liquidus and solidus boundaries under equilibrium conditions for ternary systems. The three equations resulting from these substitutions are,

$$\Delta H_{f1} \left(1 - \frac{T}{T_1}\right) = R T \ln \left(\frac{N_{1S}}{N_{1L}}\right) + L12 N_{2L} (1 - N_{1L}) + L13 N_{3L} (1 - N_{1L})$$

$$- L23 N_{2L} N_{3L} - S12 N_{1S} (1 - N_{2S}) - S23 N_{3S} (1 - N_{2S})$$

$$+ S13 N_{1S} N_{3S} , \qquad (6a)$$

$$\Delta H_{f2} \left(1 - \frac{T}{T_2}\right) = R T \ln \left(\frac{N_{2S}}{N_{2L}}\right) + L12 N_{1L} (1 - N_{2L}) + L23 N_{3L} (1 - N_{2L})$$

$$- L13 N_{1L} N_{3L} - S12 N_{1S} (1 - N_{2S}) - S23 N_{3S} (1 - N_{2S})$$

$$+ S13 N_{1S} N_{3S} , \qquad (6b)$$

and

$$\Delta H_{f3} \left(1 - \frac{T}{T_3} \right) = R T \ln \left(\frac{N_{3S}}{N_{3L}} \right) + L13 N_{1L} (1 - N_{3L}) + L23 N_{2L} (1 - N_{3L})$$
$$- L12 N_{1L} N_{2L} - S13 N_{1S} (1 - N_{3S}) - S23 N_{2S} (1 - N_{3S})$$
$$+ S12 N_{1S} N_{2S} . \tag{6c}$$

The mole fractions of the elemental constituents of the ternary liquid and solid phases are subject to the constraints,

$$N_{1L} + N_{2L} + N_{3L} = 1$$
(7a)

$$N_{1S} + N_{2S} + N_{3S} = 1.$$
(7b)

Appendix C

The Equilibrium Between a Binary Liquid Phase and a Congruently Melting Intermediate Binary Compound.

The quantitative criterion for the thermodynamic equilibrium to exist between a binary liquid phase and a solid compound phase requires that the partial molal free energies of each constituent in the two phases be equal. This requirement is expressed by the two relations,

$$G_{1C} = G_{1L}$$
(1a)

and

$$G_{2C} = G_{2L} \quad . \tag{1b}$$

The molal free energy of the solid compound phase is related to the partial molal free energies of its constituents by the expression,

$$G_{\rm C} = N_{\rm 1C} \,G_{\rm 1C} + N_{\rm 2C} \,G_{\rm 2C}.$$
 (2)

The molal free energy of the compound can also be expressed in terms of the partial molal free energies of the components in the liquid phase with which it is equilibrium by the substitution of equations 1a and 1b into equation 2. This substitution results in the expression,

$$G_{\rm C} = N_{\rm 1C} G_{\rm 1L} + N_{\rm 2C} G_{\rm 2L}.$$
 (3)

The partial molal free energies of the liquid phase are related to the standard state free energies of the pure components in the liquid phase, the composition variables, and the activity coefficients by the expressions,

$$G_{1L} = G_{1L}^{0} + R T \ln(N_{1L}) + R T \ln(\gamma_{1L})$$
(4a)

and

$$G_{2L} = G_{2L}^{o} + R T \ln(N_{2L}) + R T \ln(\gamma_{2L})$$
(4b)

The activity coefficients are related to the regular solution parameter of the liquid phase by the expressions,

$$R T \ln(\gamma_{1L}) = L12 N_{2L}^2$$
(5a)

$$R T ln(\gamma_{2L}) = L12 N_{1L}^{2}$$
 (5b)

The substitution of Equations (4a), (4b), (5a), and (5b) into Equation (3) yields an expression for the molal free energy of the compound in terms of the standard state free energies of the elemental components in their pure fiquid state, the regular solution parameter, and the temperature and composition of the liquid phase with which it is in equilibrium. The expression which results from these substitutions is as follows,

and

$$G_{C} = N_{1C} (G_{1L}^{o} + R T \ln(N_{1C}) + L12 N_{2L}^{2})$$

+ $N_{2C} (G_{2L}^{o} + R T \ln(N_{2L}) + L12 N_{1L}^{2}).$ (6)

The molal free energy of the liquid phase is related to the partial molal free energies of its constituents by the expression,

$$G_{L} = N_{1L} G_{1L} + N_{2L} G_{2L}.$$
 (7)

The substitution of Equations (4a), (4b), (5a), and (5b) into Equation (7) yields an expression for the liquid phase in terms of the standard state free energies of the elemental components in their pure liquid state, the regular solution parameter of the liquid phase, and the temperature and composition of the liquid phase. The equation which results from these substitutions is as follows,

$$G_{L} = N_{1L} (G_{1L}^{0} + R T \ln(N_{1L}) + L12 N_{2L}^{2})$$

+ $N_{2L} (G_{2L}^{0} + R T \ln(N_{2L} + L12 N_{1L}^{2}).$ (8)

The free energy function of a liquid phase which has the same composition as that of the compound phase is obtained by fixing the composition of the liquid phase at the same value as that of the compound phase. Thus, the free energy function of a liquid phase which has the same constitution as that of the compound is give by the relation,

$$G_{L} = N_{1C} (G_{1L}^{0} + R T \ln(N_{1C}) + L12 N_{2C}^{2})$$

+
$$N_{2C}$$
 (G_{2L}^{o} + R T ln(N_{2C} + L12 N_{1C}^{2}). (8)

The mole fractions which represent the composition of the liquid phase have the same value as that of the composition as the compound and are written with the subscript, C, to emphasize this point.

At the equilibrium melting temperature of the compound, the free energy difference between the liquid and solid phases is equal to zero. At any other temperature, the free energy difference between the compound phase and a liquid phase at the same composition is given by the relation,

$$G_{L} - G_{C} = \Delta H_{C} \left(1 - \frac{T}{T_{C}} \right)$$
(10)

The substitution of Equations (6) and (9) into Equation (10) yields the relation,

$$\Delta H_{C} \left(1 - \frac{T}{T_{C}}\right) = R T \left(N_{1C} \ln(N_{1C}) + N_{2C} \ln(N_{2C})\right)$$

- R T $\left(N_{1C} \ln(N_{1L}) + N_{2C} \ln(N_{2L})\right)$
+ $N_{1C} L_{12} N_{2C}^{2} + N_{2C} L_{12} N_{1C}^{2}$
- $N_{1C} L_{12} N_{2L}^{2} - N_{2C} L_{12} N_{1L}^{2}$. (11)

This expression relates the mole fractions of the components, the heat of fusion, and the melting temperature of the compound, the mole fractions and the regular solution parameter of the liquid phase, and the temperature of the equilbrium between the two phases. The mole fraction of the elemental constitutents of the compound and the liquid phase are subject to the constraints,

$$N_{1L} + N_{2L} = 1$$
 (12a)

$$N_{1C} + N_{2C} = 1$$
 (12a)

Appendix D.

The Equilibrium Between a Ternary Liquid Phase and a Conquently Melting Intermediate Binary Compound.

The quantitative criterion for thermodynamic equilbrium to exist between a ternary liquid phase and a solid binary compound phase requires that the partial molal free energies of the elemental constituents in the two phases be equal. This requirement is expressed by the relations,

$$G_{1C} = G_{1L} \tag{1a}$$

and

$$G_{2C} = G_{2L} \tag{1a}$$

The molal free energy of the compound is related to the partial molal free energies of the elemental constituents by the expression,

$$G_{C} = N_{1C} G_{1C} + N_{2C} G_{2C}.$$
 (2)

The molal free energy of the compound can also be expressed in terms of the partial molal free energies of the liquid phase with which it is in equilibrium. The substitution of Equations (1a) and (1b) into Equation (2) results in the expression,

$$G_{C} = N_{1C} G_{1L} + N_{2C} G_{2L}.$$
 (3)

The partial molal free energies of the liquid phase are related to the standard state free energies of the pure components in the liquid phase, the activity coefficients, the mole fractions of the components in the liquid phase, and the absolute temperature by the relations,

$$G_{1L} = G_{1L}^{o} + R T \ln(N_{1L}) + R T \ln(\gamma_{1L})$$
(4a)

and

$$G_{2L} = G_{2L}^{o} + R T \ln(N_{2L}) + R T \ln(\gamma_{2L})$$
(4b)

The activity coefficients are related to the regular solution parameters of the liquid phase by the expressions,

$$R T \ln(\gamma_{1L}) = L12 N_{2L} (1 - N_{1L}) + L13 N_{3L} (1 - N_{1L}) - L23 N_{2L} N_{3L}, \qquad (5a)$$

$$R T \ln(\gamma_{2L}) = L12 N_{1L} (1 - N_{1L}) + L23 N_{3L} (1 - N_{2L}) - L13 N_{1L} N_{3L},$$
 (5b)

The substitution of Equations (4a), (4b), (5a), and (5b) into Equation (3) yields an expression for the molal free energy of the compound in terms of the standard state free energies of the pure elemental components in the liquid state, the regular solution parameter of the liquid state, and the temperature and composition of the liquid phase with which it is in equilibrium. The expression which results from these substitutions is as follows,

and

$$G_{C} = N_{1C} (G_{1L}^{o} + R T \ln(N_{1L}) + L12 N_{2L} (1 - N_{1L}) + L13 N_{3L} (1 - N_{1L})$$

- L23 N_{2L} N_{3L}) + N_{2L} (G_{2L}^o + R T ln(N_{2L}) + L12 N_{1L} (1 - N_{2L})
+ L23 N_{3L} (1 - N_{2L}) - L13 N_{1L} N_{3L}). (6)

The free energy function of a liquid phase which has the same composition as that of the compound phase is obtained by fixing the values of the mole fractions of the components of the liquid phase at the same values as those of the compound phase. Thus, the free energy function of a liquid phase which has the same constitution as that of the compound is given by the expression is given by the expression,

$$G_{L} = N_{1C} (G_{1L}^{0} + R T \ln(N_{1C}) + L12 N_{2C} (1 - N_{1C})) + N_{2C} (G_{2L}^{0} + R T \ln(N_{2C}) + L12 N_{1C} (1 - N_{2C})).$$
(7)

At the equilibrium melting temperature of the compound the free energy difference between the liquid and solid phases is equal to zero. At any other temperature the free energy difference is given by the relation,

$$G_{L} - G_{C} = \Delta H_{C} \left(1 - \frac{T}{T_{C}} \right)$$
(8)

The substitution of equations 6 and 7 into equation 8 yields the relation,

$$M_{C} \left(1 - \frac{T}{T_{C}} \right) = R T \left(N_{1C} \ln(N_{1C}) + N_{2C} \ln(N_{2C}) \right)$$
$$R T \left(N_{1C} \ln(N_{1L}) + N_{2C} \ln(N_{2L}) \right)$$

+
$$N_{1C} L12 N_{2C} (1 - N_{2C}) + N_{2C} L12 N_{1C} (1 - N_{2C})$$

- $N_{1C} (L12 N_{2L} (1 - N_{1L}) + L13 N_{3L} (1 - N_{1L}))$
- $L23 N_{2L} N_{3L})$
- $N_{2C} (L12 N_{1L} (1 - N_{2L}) + L23 N_{3L} (1 - N_{2L}))$
- $L13 N_{1L} N_{3L})$ (9)

This expression relates the composition, the heat of fusion, and the melting temperature of the compound, the compositon and regular solution parameter of the liquid phase with which it is equilibrium, and the absolute temperature of the alloy system. The mole fractions of the elemental constituents of the ternary liquid and the binary compound phases are subject to the constraints,

$$N_{1L} + N_{2L} + N_{3L} = 1$$
(10a)

$$N_{1C} + N_{2C} = 1$$
 (10b)