# The Au-Ge (Gold-Germanium) System
196.9665          72.59

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## Equilibrium Diagram

The equilibrium phases of the Au-Ge system are: (1) the liquid, L; (2) the fcc terminal solid solution, (Au), having about 3 at.% solid solubility of Ge in Au; and (3) the diamond-type cubic terminal solid solution, (Ge), with a negligible solid solubility of Au in Ge (less than $13.6 \times 10^{-4}$ at.%. The phase diagram is of a simple eutectic form (Fig. 1). The eutectic temperature and composition are 361 °C and 28.0 at.% Ge, respectively.

The solidus and the solvus boundaries of the (Au) phase in Fig. 1 have been drawn according to the tentative thermodynamic model derived here. The calculated liquidus boundaries lie mostly within the scatter of experimental data (Fig. 2).

### Table 1  Eutectic Composition and Temperature of Au-Ge Alloys

| Reference | Composition, at.% Ge | Temperature, °C | Note |
|---|---|---|---|
| [35Sch], [37Ein] | 24.0 | 359.0 | No details |
| [45Jaf] | 27 | 356.0 | Thermal |
| [45Owe] | ··· | 363 | From [L + (Au)]/(Au) and (Au)/[(Au) + (Ge)] intersection |
| [75Pre] | 28 | 357 | Thermal |
| [77Leg] | 27 | 364 | Thermal |
| [81Eva] | 28 | 362 ± 1 | Thermal |
| Assessed | 28 | 361 | ··· |

## Fig. 1  Assessed Au-Ge Phase Diagram with Selected Experimental Data
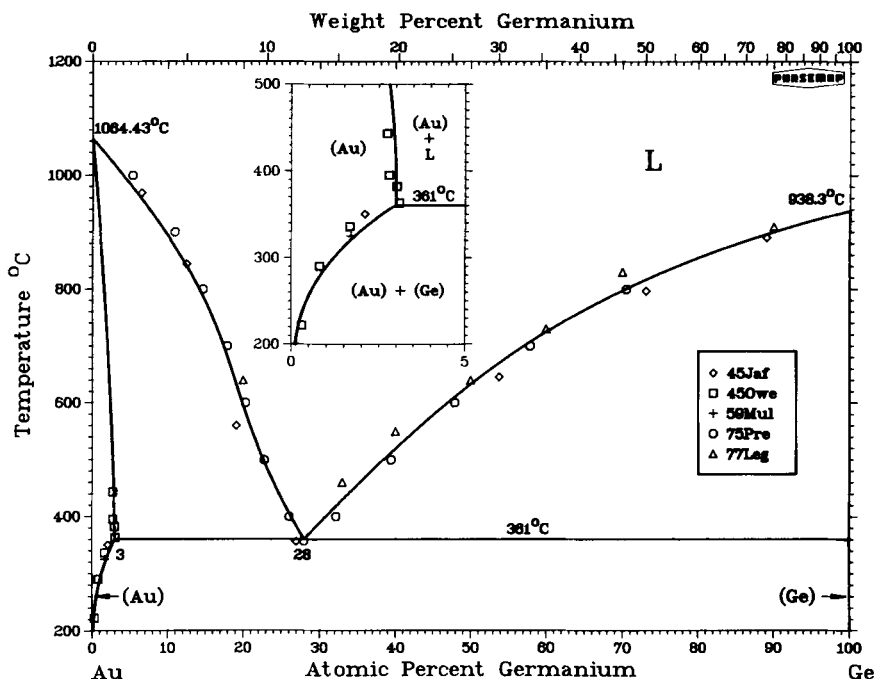


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## Fig. 2   Comparison of the Assessed Line Diagram and Diagram Based on Thermodynamic Calculation
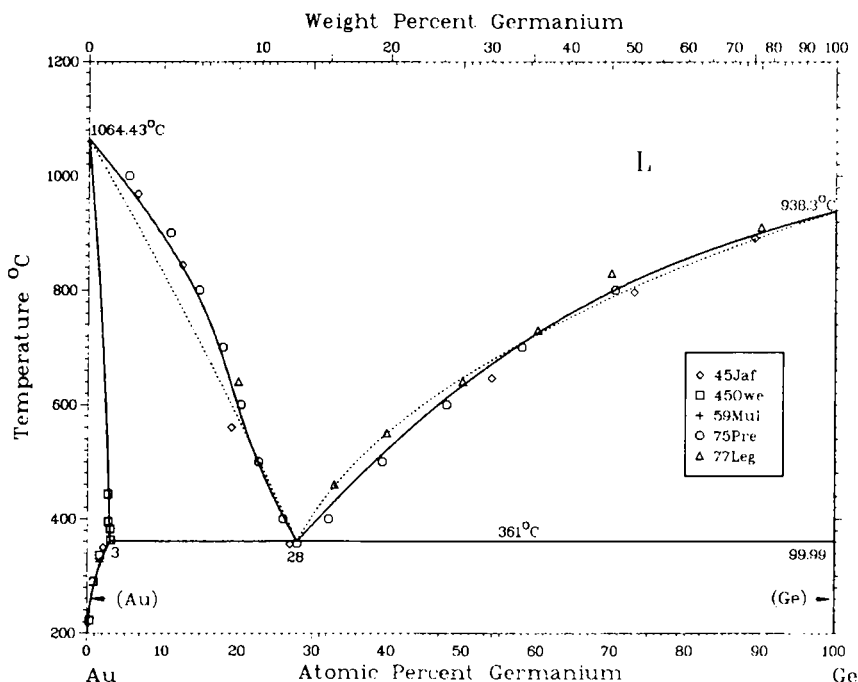


.... ≡ calculated, and——— ≡ assessed liquidus (Fig. 1). The assessed solidus and solvus boundaries of the (Au) phase in Fig. 1 are based on the calculated results (present model).

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## Table 2   Experimental Data on the Au-Ge Liquidus Boundaries

| Reference | Composition, at.% Ge | Temperature, °C |
|---|---|---|
| [45Jaf] ..................... | 6.5 | 969 ± 15 |
| | 12.5 | 844 |
| | 19.1 | 560 |
| | 27.0 | 356 |
| | 53.8 | 646 |
| | 73.1 | 797 |
| | 89.1 | 891 |
| [75Pre](a) .................. | 5.3 | 1000 |
| | 10.9 | 900 |
| | 14.7 | 800 |
| | 17.9 | 700 |
| | 20.3 | 600 |
| | 22.8 | 500 |
| | 26.1 | 400 |
| | 28.0 | 357 |
| | 32.2 | 400 |
| | 39.4 | 500 |
| | 47.9 | 600 |
| | 57.9 | 700 |
| | 70.5 | 800 |
| | 89.2 | 900 |
| [77Leg](b) ................. | 20 | 640 |
| | 33 | 460 |
| | 40 | 550 |
| | 50 | 640 |
| | 60 | 730 |
| | 70 | 830 |
| | 90 | 910 |

(a) From liquidus curves smoothed by [75Pre] (42 data points). (b) From Fig. 11 in the original paper.

## Table 3   Solid Solubility of Ge in Au(a)

| Reference | Composition, at.% Ge | Temperature, °C | Method |
|---|---|---|---|
| [45Owe]....... | 2.74 | 443 | Lattice parameter |
| | 2.79 | 395 | |
| | 3.02 | 382 | |
| | 3.08 | 363 | |
| | 1.66 | 336 | |
| | 0.81 | 290 | |
| | 0.30 | 222 | |
| [45Jaf] ........ | 2.1 | 350 | Lattice parameter |
| | <0.3 | RT | |
| [59Mul] ....... | 1.7 | 325 | Electrical resistivity |
| Assessed ...... | **3.0** | **361** | |

(a) See Fig. 1.

**Liquidus and Eutectic Point.** The eutectic temperature $(T_e)$ of 359.0 °C and composition $(X_e)$ of 24.0 at.% Ge were first reported by [35Sch] and [37Ein] without any details in the literature. Subsequently, the values of $T_e$ and $X_e$ were obtained by [45Jaf], [75Pre], [77Leg], and [81Eva] according to thermal analyses (Table 1). [45Owe] obtained $T_e = 363$ °C from the intersection of the (Au)/[L + (Au)] and (Au)/[(Au) + (Ge)] boundaries, as determined by lattice parameter measurements. The presently assessed values of $T_e = 361$ °C and $X_e = 28.0$ at.% Ge have been estimated from the three most recent results (Table 1).

The liquidus boundaries were determined by Jaffee, Smith, and Gonser [45Jaf], Predel and Bankstahl [75Pre], and Legendre and Souleau [77Leg], who employed conventional thermal analysis (Table 2, Fig. 1).

The assessed boundaries in Fig. 1 have been drawn according to these experimental results. The melting points of Au and Ge have been adopted as 1064.43 °C and 938.3 °C, respectively, from [81BAP].

**Liquid.** X-ray diffraction patterns showed the existence of short-range ordering in the liquid Au-Ge alloys [73Dut, 76Wag]. The closest interatomic distance appears to be 0.267 nm in both the 25 at.% Ge liquid alloy at 425 °C and the 50 at.% Ge liquid alloy at 663 °C [76Wag]. The changes in the slopes of viscosity isotherms showed possible $Au_2Ge$ molecular associations in the liquid [69Abr], whereas the thermodynamic models by [80Sch3] and [82Som2] assumed $Au_3Ge$-type associations. There are no other data on this subject.

**Terminal Solid Solution (Au).** Solid solubilities of Ge in (Au), or $\alpha$, were determined by lattice parameter measurements by Owen and Roberts [45Owe], as well as by [45Jaf]. [59Mul] determined the solubility limit from their own electrical resistivity measurements and from those of [32Lin] (Table 3). Both the solidus and solvus boundaries in Fig. 1 have been drawn according to the thermodynamic model discussed below. The solidus shows a slight retrograde solubility.

**Terminal Solid Solution (Ge).** The maximum solid solubility of $13.6 \times 10^{-4}$ at.% Au in Ge was reported on the basis of radioactive $^{198}$Au tracer measurements in a coevaporated film of 250 $\mu$m thickness on a substrate held at 405 °C [60Bak]. (The atomic concentrations, expressed in the original papers as the numbers of Au atoms/cm$^3$ have been converted here to at.% Au, assuming $4.42 \times 10^{22}$ Ge atoms per cm$^3$ derived from the lattice parameter of pure Ge (Table 4).) The solubility

decreases with the decreasing thickness of the film, showing that the higher growth rate results in a higher Au concentration [60Bak]. Indirect electrical investigations, such as the Hall coefficient, sheet resistance, or junction capacitance measurements, by [59Tyl], [62Sye], [64Kod], and [72Bel] showed much lower solubility of Au in Ge in the order of $1 \times 10^{-4}$ at.% (Fig. 3), showing that not all the Au atoms dissolved in Ge are electrically active (substitutional) [60Bak]. Figure 3 shows that there are inconsistencies among the electrically measured solubilities, probably because of different specimen preparation methods [64Kod]. Two different distribution coefficients were proposed: $k = 8.2 \times 10^4 \exp(-2.67 \times 10^4/T)$ $(T > 973$ K$)$ by [64Kod], and $k = 4.0 \times 10^2 \exp(-21\,000/T)$ by [68Dor] (the latter derived from the data of [64Sye] and [59Tyl]). The boundary in Fig. 3 has been drawn according to the equation of [68Dor]. The boundary calculated by [66Kuz1, 66Kuz2] is in good agreement with this equation. The distribution coefficient at the melting point of Ge was estimated earlier to be $3 \times 10^{-5}$ [53Bur], $1.5 \times 10^{-6}$ [55Dun], and $1.3 \times 10^{-5}$ [60Tru] (the latter from the data of [59Tyl]). [64Kod] proposed another distribution coefficient for $T < 973$ K because of the very high observed solubility of Au in Ge, in comparison with the expected solubility from the high-temperature distribution coefficient.

Lattice parameter measurements showed no evidence for solid solubility of Au in Ge [65Ana].

## Crystal Structures

The only stable crystal structures are based on the terminal solid solutions (Au) and (Ge) (Table 4).

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**Fig. 3    Solid Solubility of Au in Ge Measured with Methods Related to Electrical Properties**
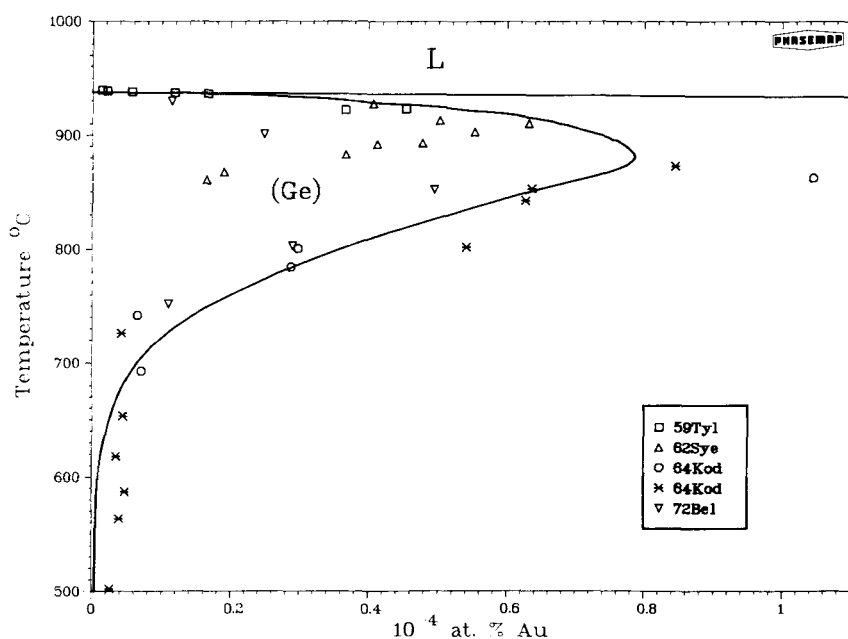


The solid line is drawn with the distribution coefficient, $k = 4.0 \times 10^2 \exp(-21\,000/T)$ [68Dor]. The equilibrium solubility may be larger (see text).

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The lattice parameters in the (Au) phase measured by [45Owe] are given in Table 4, where the lattice parameter of pure Au is adjusted to be 0.40784 nm for consistency.

## Metastable Phases

Two types of metastable phases ($\beta$ and $\gamma$) in splat-cooled Au-Ge alloys were first reported by Luo and Klement [64Luo1]. The crystal structure of the $\beta$ phase was identified as cph [64Luo1], with the single-phase range between 17.5 and 22.5 at.% Ge (Anantharaman, Luo, and
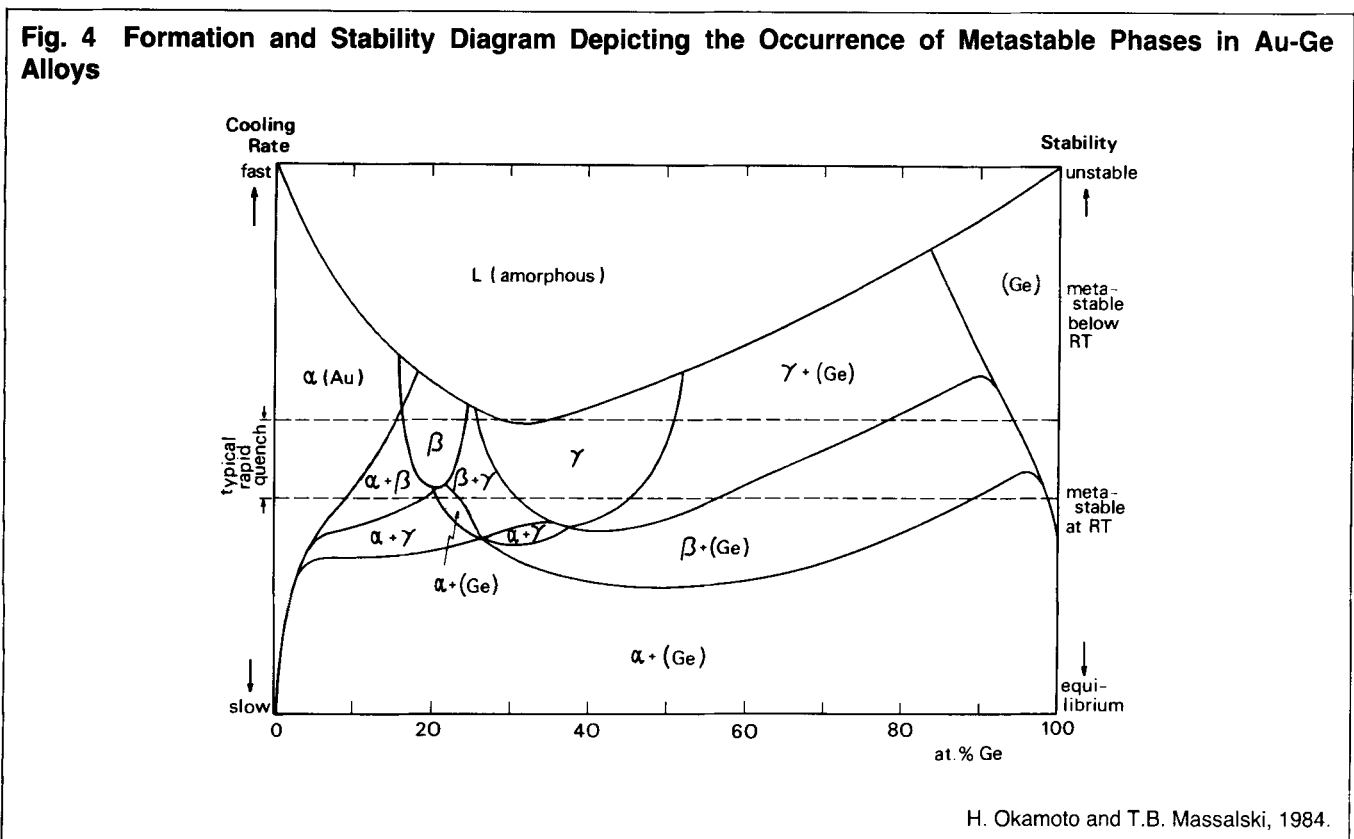
Klement [65Ana]), and the $\gamma$ phase was identified as bc tetragonal, with the single-phase range between 40 and 50 at.% Ge (Anantharaman, Luo, and Klement [66Ana]). Subsequently, the $\gamma$ phase has been identified with three types of tetragonal structures ($\gamma_1$, $\gamma_2$, $\gamma_3$) in a 27 at.% Ge alloy [70Ram]. However, [75Sco] could not confirm these results. All metastable crystal structures have been summarized in Table 4.

The formation and stability of the metastable $\beta$ and $\gamma$ phases appear to depend not only on the composition of the alloy and the cooling rate, but also on the history of

### Table 4   Au-Ge Crystal Structure and Lattice Parameter Data

| Phase | Approximate composition range, at.% Ge | Pearson symbol | Space group | Prototype | Lattice parameters at 25 °C, nm a | c | Comments | References |
|---|---|---|---|---|---|---|---|---|
| (Au) or $\alpha$ ....... | 0 to 3(a) | cF4 | Fm3m | Cu | (b) | ... | (c,d) | ... |
| | 0 | cF4 | Fm3m | Cu | 0.40784 | ... | (c) | [81Kin] |
| | 0.88 | cF4 | Fm3m | Cu | 0.40791 | ... | (c,e) | [45Owe] |
| | 1.82 | cF4 | Fm3m | Cu | 0.40798 | ... | (c,e) | [45Owe] |
| | 2.66 | cF4 | Fm3m | Cu | 0.40806 | ... | (c,e) | [45Owe] |
| | 6(f) | cF4 | Fm3m | Cu | 0.40816 | ... | (c) | [65Ana] |
| | ~15?(f) | cF4 | Fm3m | Cu | 0.4087 | ... | (c) | [80Sch1] |
| (Ge)........... | 100(a) | cF8 | Fd3m | C (diamond) | 0.56574 | ... | (g) | [81Kin] |
| **Other metastable phases** | | | | | | | | |
| $\beta$ ............. | 16 to 25(a) | hP2 | $P6_3/mmc$ | Mg | (h) | (h) | ... | ... |
| $\gamma$ ............. | 25 to 52(a) | (j) | ... | ... | (h) | (h) | ... | ... |
| **Pressure-stabilized phases** | | | | | | | | |
| Ge II........... | 100 | tI4 | $I4_1/amd$ | $\beta$Sn | 0.4884 | 0.2692 | ... | [63Jam], [83Kin] |
| Ge III......... | 100 | tP12 | ... | Ge III | 0.593 | 0.698 | ... | [63Bun], [64Kas], [83Kin] |

(a) Composition or approximate composition range from the phase diagram.   (b) See lattice parameters of 0 to 2.66 at.% Ge compositions.   (c) Metastable solubility range of 3 to 15 at.% Ge.   (d) See Fig. 1.   (e) Lattice parameter of pure Au was adjusted to 0.40784 [81Kin].   (f) Metastable.   (g) Metastable solubility range of 95 to 100 at.% Ge.   (h) See Table 7.   (j) Body-centered tetragonal.

### Fig. 4   Formation and Stability Diagram Depicting the Occurrence of Metastable Phases in Au-Ge Alloys



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the heat treatment of each alloy and some additional factors. Therefore, the experimentally observed aspects appear to be very complicated. A schematic formation and stability diagram for the metastable phases as shown in Fig. 4, which can be proposed on the basis of free energy relationships given in Fig. 5 (see the section on thermodynamics), may be used to clarify the observed complexity. This diagram (Fig. 4) shows schematically the composition dependence of the metastable phases obtainable at different cooling rates (left-hand-side coordinate) and the stability at different temperatures (right-hand-side coordinate). It is well to keep in mind that the cooling rates in the splat-cooled alloys are not uniform, or well controlled, throughout each specimen, and they may also be quite different for different measurements.

In addition, a part of the metastable phase formed by rapid quenching may decompose at an equally rapid rate into another phase. Therefore, the interval of time between specimen preparation and the X-ray experiment is an important factor (in many instances, this not specified in the literature).

The reported complex mixtures of equilibrium and metastable phases can be successfully explained according to Fig. 4. X-ray diffraction patterns of splat-cooled specimens have been interpreted in Table 5. The observed ranges of existence of each phase (including two-phase fields) are listed in Table 6. The observed composition ranges and lattice parameters of the $\beta$, $\gamma$, and several other unidentified phases reported by authors are given in Table 7. The (Au) phase precipitated

## Table 5  Phases Reported in Splat-Cooled Au-Ge Alloys

| Phase(a, b) | Composition, at.% Ge |
|---|---|
| (Au) or $\alpha$ | 8 |
| | 10 |
| $\beta$ + vw $\gamma$ + vvw $\alpha$ | 22.5 |
| $\beta$ + w $\gamma$ | 25 |
| w $\beta$ + $\gamma$ | 27.5 |
| $\gamma$ | 30 |
| | 39 |
| | 46 |
| $\gamma$ + vw (Ge) | 50 |
| $\gamma$ + w (Ge) | 53 |
| $\beta$ + (Ge) + w $\gamma$ | 60 |
| $\beta$ + vw $\gamma$ + (Ge) | 66 |
| $\beta$ + (Ge) | 70 |

(a) w = weak, vw = very weak, and vvw = very, very weak X-ray diffraction lines.    (b) From [64Luo2].

## Table 6  Composition Ranges of Metastable Phases in Au-Ge Alloys

| Phase | Composition range(a), at.% Ge | Reference |
|---|---|---|
| (Au) | 0 to 22.5 | [64Luo1] |
| | 0 to 22.5 and 90 to 100 | [64Ana] |
| | 0 to 30 | [80Sch1](b) |
| $\beta$ | 10 to 30 and 56 to 95 | [64Luo1] |
| | 8 to 36 and 56 to 98 | [65Ana] |
| | 5 to 39 and 41 to 95 | [80Sch1](b) |
| | 20 to 80 | [82Liu] |
| $\gamma$ | 15 to 60 | [64Luo1] |
| | 15 to 80 | [65Ana] |
| | 22 to 80 | [80Sch1](b) |
| (Ge) | 50 to 100 | [65Ana] |

(a) Includes both single and two-phase fields.    (b) All of these ranges by [80Sch1] were determined quite possibly with a somewhat slower cooling rate than the typical quenching rate marked in Fig. 4.

## Fig. 5  Gibbs Free Energy at Room Temperature (15 °C)
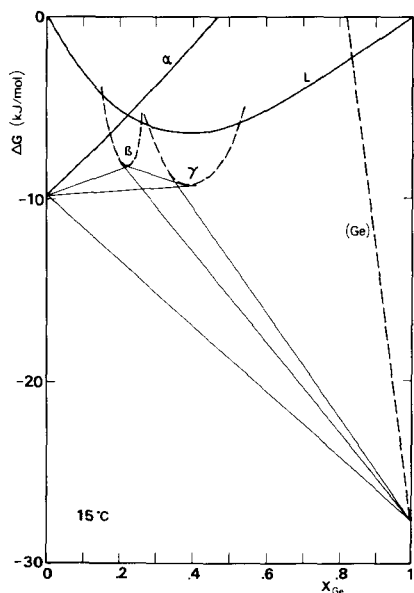


The $\Delta G$ functions for the liquid and the (Au) phase, and the (Ge) phase at $X_{Ge}=1$, are drawn to scale (present model). Dashed lines are schematic.    H. Okamoto and T. B. Massalski, 1984.

## Table 7  Lattice Parameter Data of Metastable Phases Present in Single-Phase Form with Other Coexisting Phases in Au-Ge Alloys

| Phase | Composition, at.% Ge | Lattice parameters, nm a | c | Reference |
|---|---|---|---|---|
| (Au) or $\alpha$ | 6 | 0.40816 | ··· | [64Luo1] |
| | ··· | 0.4087 | ··· | [80Sch1] |
| $\beta$ | ··· | 0.2844 | 0.4785 | [64Luo1] |
| | ··· | 0.2882 | 0.47512 | [80Sch1] |
| | 17.5 | 0.2885 | 0.4737 | [65Ana] |
| | 20 | ··· | ··· | [76Bun] |
| | 20 to 22 | 0.289 | 0.475 | [66Ana] |
| | 21 | 0.2876 | 0.4732 | [65Pre] |
| | 22.5 | 0.2885 | 0.4754 | [65Ana] |
| | 25 | ··· | ··· | [65Duw] |
| | 27 | 0.2885 | 0.4737 | [70Ram] |
| $\gamma$ | 40 | 1.1627 | 2.2491 | [65Ana] |
| | 40 | 1.163 | 2.249 | [82Liu] |
| | 40 to 50 | 1.163 | 2.249 | [66Ana] |
| | 41 | ··· | ··· | [76Bun] |
| | 50 | 1.1635 | 2.2525 | [65Ana] |
| | ··· | 1.15525 | 2.23328 | [80Sch1] |
| $\gamma_1$(a) | ··· | 0.413 | 3.854 | [70Ram] |
| $\gamma_2$(a) | ··· | 1.239 | 2.017 | [70Ram] |
| $\gamma_3$(a) | ··· | 1.297 | 1.247 | [70Ram] |
| ? | 20 | 0.328 | 0.527 | [82Liu] |
| | 27 | 0.4127 | 1.9270 | [69Ram] |
| | 27 | 0.8993 | 1.2469 | [69Ram] |
| | 27 | 1.6444 | 4.4982 | [70Ram] |
| | 40 | 1.6444 | 4.4982 | [65Ana] |

(a) Possibly based on $\gamma$; see text.

## Table 8  Decomposition of Metastable Phases in Au-Ge Alloys

| Reference | Specimen preparation | Composition range, at.% Ge | Reaction | Decomposition temperature, time |
|---|---|---|---|---|
| [73Kit] .................. | Vapor deposited | 8 to 20 | (Au), $\beta \rightarrow$ (Au) + (Ge) | 300 °C |
| [75Sco] .................. | Splat cooled | 27 | $\beta \rightarrow$ (Au) + (Ge) | 70 to 100 °C |
| | | | $\gamma \rightarrow$ (Au) + (Ge) | 125 °C |
| [78Aga] ................ | Splat cooled | 27 | $\beta \rightarrow$ (Au) + (Ge) | 100 °C, ~0.5 min |
| | | | | 300 °C, 5 min |
| | | | $\gamma \rightarrow$ (Au) + (Ge) | >50 °C |
| | | | | 100 °C, 200 min |
| [80Sch1]. ............... | Splat cooled | 20 to 60 | (Au), $\beta$, $\gamma \rightarrow$ (Au) + (Ge) | 125 °C |

out only from the Au-Ge alloys having more than 10 at.% Au and were prepared by coevaporation [78Dut].

The following features can be understood from Fig. 4. An alloy with 27 at.% Ge, subjected to different heat treatments, yielded the $\beta$ phase, as well as the (Au) and $\gamma$ phases, when the specimens were splat-cooled from 1000 or 1300 °C, or water quenched from 500 °C. However, the $\beta$ phase was not found in the specimen splat-cooled from 500 °C [75Sco]. A specimen splat-cooled from 800 °C consisted mainly of the $\gamma$ phase [78Aga]. Reported stabilities of each phase are listed in Table 8.

$\beta$ (20 at.% Ge) and $\beta + \gamma$ (27 at.% Ge) are not stable at room temperature [76Bun]. Unidentified crystalline structures in 30, 40, and 50 at.% Ge alloys, found by ion-beam mixing [81Lau], might be $\gamma$ or (Au) + (Ge) phases (see Fig. 4). Amorphous alloys with more than 60 at.% Ge, made by ion-beam mixing, transformed into metastable crystalline structures in two to three days and decomposed into (Au) + (Ge) after about one week [82Liu]. The observed metastable crystalline structures were $\beta$ for 70 and 80 at.% Ge and an unidentified (probably $\gamma$, from Fig. 4) structure for the 60 at.% Ge alloy.

The $\gamma$ phase becomes a superconductor with its highest transition temperature of 1.63 K at 50 at.% Ge [64Luo2].

No reports are available on the metastable Au-Ge alloys related to the two metastable (pressure-stabilized) structures of pure Ge, namely Ge II (tetragonal $\beta$Sn-type) [63Jam, 83Kin] and Ge III ($tP$12) [63Bun, 64Kas, 83Kin].

## Amorphous Phase

Figure 4 also explains the behavior of the amorphous alloys, which can be made by coevaporating Au and Ge onto a substrate at 4 K in the range of 30 to 73 at.% Ge [71Str], onto a substrate at 4.2 K in the range of 23 to 60 at.% Ge [75Hau], onto a substrate at 15 to 20 K in the range of 5 to 40 at.% Ge [80Ngu1, 80Ngu2], and onto a dry-ice-cooled substrate in the range of 6 to 28 at.% Ge. Amorphous alloys can also be made with ion-beam mixing in the range of 30 to 80 at.% Ge [82Liu], as discussed previously. The (Au) and (Ge) phases were found to be coexisting with the amorphous phase in splat-cooled alloys with 5, 11, and 14 at.% Ge [80Ngu1, 80Ngu2]. Alloys containing 24, 28, and 30 at.% Ge can be made amorphous, having structures similar to the high-temperature liquids [76Wag]. Such amorphous alloys crystallized into a complex structure (probably a mixture of either $\beta + \gamma$ or (Au) + (Ge) from Fig. 4) above 250 K [80Ngu1]. The 34 and 39 at.% Ge amorphous alloys transformed into the $\gamma$ phase above 310 K [80Kgu2].

The composition dependence of the superconducting transition temperature in amorphous films deposited on a substrate held at 4 K shows a maximum of 3.6 K at 50 at.% Ge [71Str, 75Hau]. [70Ale] reported the transition temperature at 2.75 K in a laser-evaporated film with 50 at.% Ge and at about the same temperature as [64Luo2] (~1.63 K), after heating the specimen up to room temperature.

Metal-insulator transitions take place at about 18 at.% Ge in polycrystalline Au-Ge alloys and at about 6 at.% Ge in amorphous Au-Ge alloys [81Dod].

Models for the prediction of metastable phase formation, including the Au-Ge system, were proposed by [78Dan] and [81Pre].

## Thermodynamics

**Thermodynamic Data.** Figure 6 shows the $\Delta H$ (enthalpy of mixing) function of the liquid phase measured with the calorimetric method: at 1100 °C by Itagaki and Yazawa [71Ita] and by Hassan, Gaune-Escard, and Bros [81Has]; at 1150 °C by Predel and Stein [71Pre1]; and at 362 °C by Schluckebier and Predel [80Sch3]. The $\Delta H$ function was measured with the Knudsen cell method at 1400 °C by Hager, Howard, and Jones [73Hag]. The data points of [71Ita] have been plotted from the expression given in the original paper as $\Delta H = (-15\,620 + 1\,880\,X_{Ge})X_{Ge} (1 - X_{Ge})$, where $X_{Ge}$ is the atomic fraction of Ge in alloys. The $\Delta H$ values at 727 °C (not shown in Fig. 6) were given by [72Pre] for the range of 20 to 60 at.% Ge. The values are the same as those of [71Pre1] at 1100 °C for 30, 40, and 50 at.% Ge, and the value for 60 at.% Ge is the same as that of [71Pre1] for 70 at.% Ge. The excess free energy ($^E\Delta G$) for the liquid shows a minimum value of 14 kJ/mol at 30 at.% Ge, according to the emf measurements at 727 °C by [72Pre]. The specific heat trend with temperature obtained for a 28 at.% Ge alloy, given by [80Sch3], is approximately $C_p = -0.009\,T + 40$ J/mol·K between 600 and 1000 K.

Association models for describing the thermodynamic properties of the liquid were derived by [80Sch3] and [82Som1, 82Som2] from the $\Delta H$ values [71Pre1, 80Sch3] and the specific heats [80Sch3].

The partial quantities for the enthalpy of mixing and excess entropy of mixing of the (Au) phase were derived as $\Delta\overline{H}_{Ge} = -38.8$ kJ/mol and $^E\Delta\overline{S}_{Ge} = -29.12$ J/mol·K, respectively, by [75Pre] from the solubility data of [45Owe].

The $^E\Delta\overline{G}_{Ge}$ values of the (Au) phase at 727 °C were measured with the emf method by [74Pre] as $-67$ kJ/mol at 0 at.% Ge and by [74Jac] as $^E\Delta\overline{G}_{Ge} = -2.5$ kJ/mol,

**Fig. 6  Enthalpy of Mixing for the Liquid Au-Ge Alloys with Selected Experimental Data**



Legend:
- ● 71Ita, 1100 °c
- △ 71Pre1, 1150
- ○ 73Hag, 1400
- ■ 80Sch3, 362
- ▼ 81Has, 1100
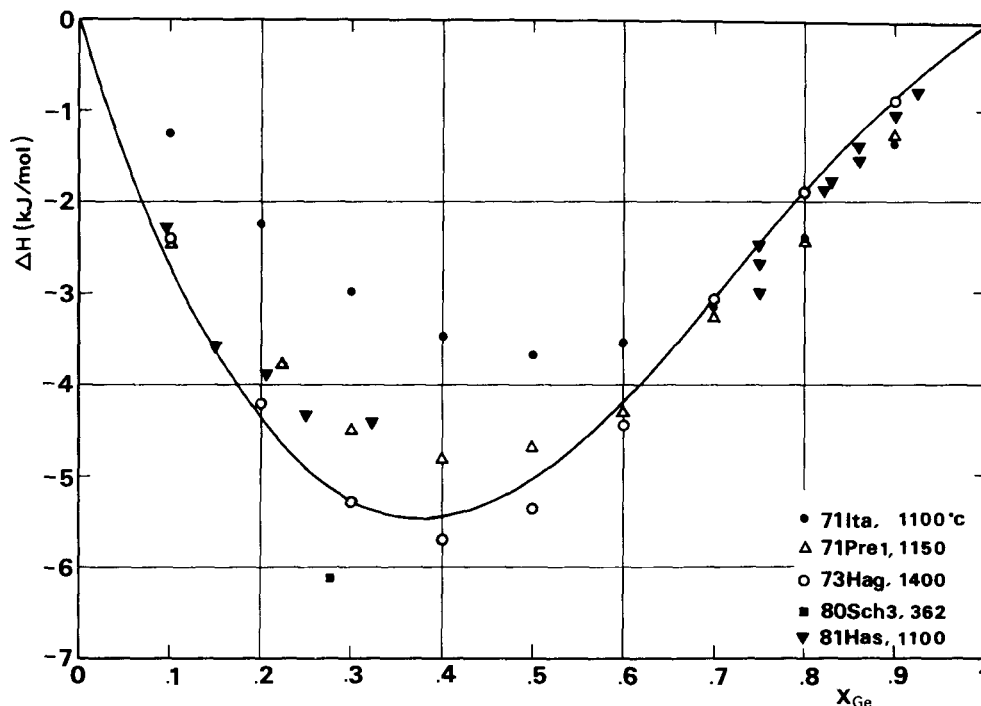
——— ≡ present model (temperature-independent).

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relative to pure solid Ge. Therefore, the difference between the lattice stability parameters of fcc Ge and diamond- cubic Ge may be in the order of 64 kJ/mol. The $^E\Delta G$ values of the (Au) phase at 727 °C are −0.59 kJ/mol at $X_{Ge}$ = 0.01 and −0.92 kJ/mol at $X_{Ge}$ = 0.02 [74Pre].

The enthalpy and the free energy of transformation of Ge from a stable diamond-cubic structure to a hypothetical fcc structure are $\Delta H$ = 54.4 kJ/mol at 1150 °C [71Pre1] and $\Delta G$ = 42 kJ/mol at 727 °C [71Pre2].

The thermodynamic properties of the (Ge) phase were estimated as $\Delta \overline{H}_{Au} \geqslant$ 188 kJ/mol and $^E\Delta \overline{S}_{Au} \geqslant$ 58.6 J/mol·K [68Dor]. These are large enough to approximate that the (Ge) phase has practically no solid solubility.

The enthalpies of transformation for the metastable $\beta$ and $\gamma$ phases are $\Delta H_\beta$ = +4.46 kJ/mol and $\Delta H_\gamma$ = +8.12 kJ/mol [80Sch2].

**Thermodynamic Parameters in the Present Evaluation.** Because of the abundant thermodynamic data available in various forms (with some inconsistencies), the following approach has been taken in the present evaluation.

The lattice stability parameters for the stable phases of pure Au and Ge ($^0G_{Au}^{(Au)}$ and $^0G_{Ge}^{(Ge)}$) are derived, as given in Table 9, by assuming the difference of the specific heats of solid and liquid is zero ($\Delta C_p$ = 0) for Au, which should give good results [79Tho], and $\Delta C_p$ = 5.9 × 10$^{-3}$ T + 6 J/mol·K for Ge from the $C_p$ values of solid and liquid Ge given by [77Bar]. The standard states are the liquid Au and the liquid Ge. The heat of fusion at the melting points are taken as $\Delta H$ = 12.55 kJ/mol for Au and $\Delta H$ = 36.94 kJ/mol for Ge [77Bar].

**Table 9  Lattice Stability Parameters in Present Model, J/mol**

| |
|---|
| $^0G_{Au}^{L}$ = 0 |
| $^0G_{Ge}^{L}$ = 0 |
| $^0G_{Au}^{(Au)}$ = −12 550 + 9.383 T |
| $^0G_{Ge}^{(Ge)}$ = −34 006 − 10.954 T + 6 T ln T − 0.00295 T² |
| $^0G_{Ge}^{(Au)}$ = $G_{Ge}^{(Ge)}$ + 42 000 |

**Table 10  Excess Free Energies of the Liquid Phase and (Au) Phase in Au-Ge Alloys, J/mol**

$$^E\Delta G^L = X_{Ge}(1 - X_{Ge})(25\,900\,X_{Ge} - 33\,000 - (54.13\,X_{Ge}^2 - 58.16\,X_{Ge} + 23.91)T)$$

$$^E\Delta G^{(Au)} = X_{Ge}(1 - X_{Ge})(12\,650 - 59.51\,T)$$

The lattice stability parameter of the hypothetical fcc Ge ($^0G_{Ge}^{(Au)}$) has been estimated as follows. For an assumed $^0G_{Ge}^{(Au)}$, the (Au)/[(Au) + (Ge)] solvus curve determines the excess energy of the (Au) phase, which has been taken to have the form of $(a + bT)X_{Ge}(1-X_{Ge})$. This $^0G_{Ge}^{(Au)}$ should give the experimentally obtained values as given in Table 3. If the free energy of transformation, $^0G_{Ge}^{(Au)} - ^0G_{Ge}^{(Ge)}$, of 42 kJ/mol at 727 °C [71Pre2], can be assumed to be temperature independent, the (Au)/[(Au) + (Ge)] phase boundary (Fig. 1) and the $^E\Delta G$ for the (Au) phase ($^E\Delta G$ = −0.92 kJ/mol at $X_{Ge}$ = 0.02) are derived consistently. The resulting lattice stability parameter $^0G_{Ge}^{(Au)}$, and the free energy of mixing, $\Delta G$, for the (Au) phase are given in Tables 9 and 10, respectively. The temperature dependence of $^0G_{Ge}^{(Au)} - ^0G_{Ge}^{(Ge)}$ can be calculated if the enthalpy of the transformation of Ge, given by [71Pre1], is taken into account. However, no reasonable $^E\Delta G$ function

for the (Au) phase can be obtained in this instance that would reproduce the experimental phase boundary.

The experimentally observed $\Delta H$ functions of the liquid phase are at variance, as shown in Fig. 6. When the specific heat of a 28 at.% Ge by [80Sch3] was considered, the calculated liquidus boundaries tended to have larger curvatures than the experimental results. The assumption that $\Delta C_p = 0$ (the difference in the specific heats of alloyed liquid and the weighted average of pure Au and Ge) resulted in a better model. Therefore, the $^E\Delta G$ function of the liquid phase has been assumed to be of the form of $^E\Delta G = \Delta H + (aX_{Ge}^2 + bX_{Ge} + c)T$. The $\Delta H$ function similar to that of [73Hag] (Fig. 6) gave the best fitting of the calculated curve to the experimental results. The $^E\Delta G$ function used in the present evaluation is given in Table 10.

**Thermodynamic Evaluation of the Phase Diagram.** The phase boundaries of the Au-Ge system have been calculated with the thermodynamic parameters mentioned above. The results are given in Fig. 2. The [L + (Au)]/(Au) and (Au)/[(Au) + (Ge)] boundaries in Fig. 1 have been drawn according to the calculated results. The liquidus boundaries show slight deviations from the experimental observations, especially on the L/[L + (Au)] side. Higher order approximation of the thermodynamic properties can certainly improve the observed consistency. However, such calculations have not been attempted.

The $^E\Delta G$ function for the (Au) phase (Table 10) gives $^E\Delta\overline{G}_{Ge} = -1.6$ kJ/mol at $X_{Ge} = 0$ and 1000 K, relative to the stable solid phase. This is comparable to the value of $-2.5$ kJ/mol by [74Jac]. On the other hand, the $\Delta G$ function of [72Pre] ($-14$ kJ/mol at 30 at.% Ge and 723 °C) is quite different from the present value of $-9.8$ kJ/mol at the same composition and temperature.

**Earlier Phase Diagram Calculations.** [60Thu] estimated the $^E\Delta G$ of the liquid phase in the form of $(a - bT)X_{Ge}$ $(1 - X_{Ge})$ from the L/[L + (Ge)] liquidus by [45Jaf], under the assumption that the $\Delta C_p$ for pure Ge is zero. The results are $a = -19.6$ kJ/mol and $b = -4.27$ J/mol·K.

[70Rao] estimated liquidus points quoted in [60Thu] using three parameters as $\ln \gamma_{Ge}/X_{Au}^2 = 0.6499 - 0.03995 \cdot X_{Au} - 2515.1/T$.

The (Au)/[(Au) + (Ge)] solvus was approximated by [79Kor] as $X_{Ge} = 0.0016 + \exp(-(\Delta H - T\Delta S)/RT)$, where $\Delta H = 64.245$ kJ/mol and $\Delta S = 35.953$ J/mol·K.

The eutectic composition was calculated assuming the same nucleation rates for pure Au and Ge and the growth rates proportional to the temperature differences between the melting points and the eutectic temperature [67Med, 69Sal]. If the coefficients for the growth rates are equal for Au and Ge, the calculated composition shows marked discrepancy with experiment [67Med].

The relation between the thermodynamic properties of simple eutectic-type alloys based on Ge, and the difference in electronegativities and in atomic radii of the components, is discussed by [77Bel].

## Suggestions for Future Experimental Research

In the opinion of the present evaluators, the following features of the present Au-Ge phase diagram may be considered at this time to be tentative, or in need of future research:

- Liquidus boundaries are not well established experimentally, resulting in disagreements of as much as 50 °C, as observed in recent reports (Fig. 1).
- Equilibrium solid solubility of Au in Ge (including both substitutional and interstitial Au atoms) is still not well determined. Figure 3 only shows the concentration of electrically active (substitutional) Au atoms.
- Thermodynamic properties of the liquid Au-Ge alloys are still uncertain. Especially useful for thermodynamic evaluations would be the temperature dependences of $\Delta H$ and $^E\Delta S$ functions measured with the same experimental setting.

The Au-Ge system, as contributed in a short version by R.P. Elliott and F.A. Shunk, was published in provisional form in the *Bulletin*, *1*(2), 51-54 (1980). The present evaluation reviews all bibliography and data on the Au-Ge system available in the literature through 1982 and includes information pertaining to crystal structures, metastable phases, and thermodynamics. The present authors have also performed a thermodynamic assessment of certain phase boundaries. The present evaluation may be considered as superseding the earlier work.

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*Indicates key paper.
#Indicates presence of a phase diagram.

# The Bi-Ti (Bismuth-Titanium) System

208.9804                    47.88

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The Ti-Bi phase diagram has been examined experimentally only for Ti-rich and Bi-rich alloys and is known only approximately. Special points of the diagram are summarized in Table 1 and crystal structures of the equilibrium phases are given in Table 2. According to [58Aue], the absorption of oxygen by pyrophoric Ti-Bi alloys is so rapid that assurance that a phase is not a ternary phase is usually difficult to obtain. Moreover, they noted that free Bi was almost always found in their samples, indi-

cating that reaching equilibrium also poses difficulties in this system.

The equilibrium solid phases of the Ti-Bi system are:

• The bcc ($\beta$Ti), cph ($\alpha$Ti), and (Bi) solid solutions. The solubility of the Ti in (Bi) is less than $5 \times 10^{-3}$ at.%, assuming that the solubility in solid (Bi) is less than in the Bi-rich liquid. The maximum solubilities of Bi in ($\beta$Ti) and ($\alpha$Ti) respectively are 10 and 0.5 at.% [60Obi].