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# Thermodynamic assessment of the Cu–Ge binary system

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ABSTRACT

The Cu–Ge binary system was assessed thermodynamically using the CALPHAD method through Thermo-calc® software package based on the evaluation of all available experimental data from the published literature. The solution phases, including liquid, fcc, hcp and diamond (Ge), were described by the substitutional solution model, of which the excess Gibbs energies were expressed with the Redlich–Kister polynomial. Due to their narrow homogeneity ranges, all intermetallic compounds, $\varepsilon$-$Cu_{0.765}Ge_{0.235}$, $\theta$-$Cu_{0.735}Ge_{0.265}$ and $\eta$-$Cu_{0.75}Ge_{0.25}$, were modeled as stoichiometric compounds. A set of self-consistent thermodynamic parameters formulating the Gibbs energies of various phases in the Cu–Ge binary system was obtained finally. A good agreement is achieved between the calculated results and the reported experimental data.



## 1. Introduction

Transition metal (TM) germanides have attracted much attention in the high-speed complementary metal oxide semiconductor (CMOS) technology because of their low room-temperature resistivity, high thermal stability and good adherence to silicon substrates [1–5]. The germanides including Cu–Ge [1], Cr–Ge [2], Co–Ge [3], Ni–Ge [4] and Ti–Ge [5] have been considered recently in Ge-based CMOS to minimize the sheet resistance and to achieve low contact resistances on gate source and drain areas. Interface reactions between TM and Ge are critically important for the reliability of microelectronic devices. Reliable thermodynamic information on the relative stabilities of TM-germanides is essential to control the interfacial microstructure evolution and thus to design optimal processing. On the other hand, Au-based alloys containing Ge are of interest for novel high temperature lead-free solder alloys [6–9]. For example, the Au–Ge binary system is characterised by a deep eutectic reaction with its temperature of around 360 °C, making it interesting for high temperature Au-based solders. These potential solders can react with substrates such as Cu, Ni, Si or others. Therefore, phase diagrams of the related binary and ternary systems are crucial to better understand interface reactions between Au–Ge-based solders and Cu substrate. Recently, thermodynamic properties and phase diagrams of the Cr–Ge and Ni–Ge binary systems have been assessed by Liu and Du [10,11]. The purpose of the present work was to evaluate the measured phase diagram and thermodynamic data of the Cu–Ge binary system using the CALPHAD method [12,13] and Thermo-calc® software package [14] and then to obtain a consistent and reliable thermodynamic description of this binary system.

## 2. Experimental information

### 2.1. Phase diagram data

The available crystallographic data and phase equilibria of the Cu–Ge binary system in the published literature up to 1980 had been reviewed critically by Olesinski and Abbaschian [15]. The liquidus of the Cu–Ge phase diagram was measured firstly by Schwarz and Elstner [16] and afterwards by Reynolds and Hume-Rothery [17] using thermal analysis. The solidus of the fcc phase in the Cu-rich part was determined by Hume-Rothery et al. [18] using the metallographic method. Owen and Rowlands [19] and Hume-Rothery et al. [20] measured the phase boundaries of the fcc and hcp solid phases using metallographic analysis and X-ray diffraction method, respectively. The experimental phase diagram data in the Cu–Ge binary system reported by Schwarz and Elstner [16], Reynolds and Hume-Rothery [17], Hume-Rothery et al. [18,20], Owen et al. [19] are compatible and consistent with each other. According to the experimental results mentioned above, Olesinski and Abbaschian [15] evaluated the compositions and temperatures of all invariant reactions in the Cu–Ge binary system as given in Table 1.

The solubility of Ge in the fcc solid phase was measured by Owen et al. [19] and Hume-Rothery et al. [20] using metallographic analysis and X-ray diffraction method, respectively. However, no experimental information concerning the solubility of Cu in diamond (Ge) phase could be found in the literature. Therefore, the solubility of Ge in fcc solid phase was taken into account, while the solubility of Cu in diamond (Ge) phase was neglected in the present optimization.

Based on the measurements by Schwarz and Elstner [16], Reynolds and Hume-Rothery [17], Hume-Rothery et al. [18,20], Owen et al. [19], there are three intermetallic compounds, $\varepsilon$, $\theta$ and $\eta$. The compositions of the three intermetallic compounds have been examined by Reynolds and Hume-Rothery [17] in the composition range from 22 to 30 at.% Ge. Rather narrow homogeneity ranges of three intermetallic compounds $\varepsilon$, $\theta$ and $\eta$ within 23.0–23.8 at.% Ge, 26.1–26.5 at.% Ge and 23.0–25.1 at.% Ge, have been observed, respectively. Due to their limited sol-

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**Table 1**
Invariant reactions in the Cu–Ge binary system.

| Invariant reaction | Type | $T$ (K) | Composition ($x^{L}_{Ge}$)) | Ref. |
|---|---|---|---|---|
| L + fcc ↔ hcp | Peritectic | 1097 | 0.175 | [15] |
| | | 1097 | 0.180 | This work |
| L ↔ ε-$Cu_{0.765}Ge_{0.235}$ | Congruent | 1020 | 0.220 | [15] |
| | | 1022 | 0.235 | This work |
| L ↔ hcp + ε-$Cu_{0.765}Ge_{0.235}$ | Eutectic | 1016 | 0.219 | [15] |
| | | 1021 | 0.232 | This work |
| L + ε-$Cu_{0.765}Ge_{0.235}$ ↔ θ-$Cu_{0.735}Ge_{0.265}$ | Peritectic | 971 | 0.303 | [15] |
| | | 971 | 0.320 | This work |
| L ↔ θ-$Cu_{0.735}Ge_{0.265}$ + (Ge) | Eutectic | 917 | 0.365 | [15] |
| | | 911 | 0.389 | This work |
| ε-$Cu_{0.765}Ge_{0.235}$ ↔ hcp + η-$Cu_{0.75}Ge_{0.25}$ | Eutectoid | 823 | – | [15] |
| | | 822 | – | This work |
| ε-$Cu_{0.765}Ge_{0.235}$ + θ-$Cu_{0.735}Ge_{0.265}$ ↔ η-$Cu_{0.75}Ge_{0.25}$ | Peritectoid | 909 | – | [15] |
| | | 948 | – | This work |
| θ-$Cu_{0.735}Ge_{0.265}$ ↔ η-$Cu_{0.75}Ge_{0.25}$ + (Ge) | Eutectoid | 887 | – | [15] |
| | | 885 | – | This work |

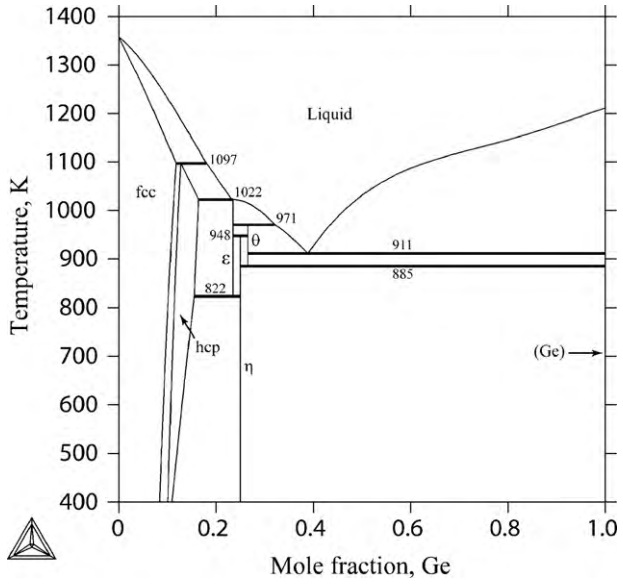


**Fig. 1.** Phase diagram of the Cu–Ge binary system calculated in the present work.

ubilities (<2 at.%), all intermetallic compounds, ε-$Cu_{0.765}Ge_{0.235}$, θ-$Cu_{0.735}Ge_{0.265}$ and η-$Cu_{0.75}Ge_{0.25}$, were treated as stoichiometric compounds in the present work.

### 2.2. Thermodynamic data

Predel and Stein [21] determined the enthalpy of mixing of the liquid Cu–Ge alloys by means of high-temperature calorimeter at 1423 K. With the same method, Takeuchi et al. [22] as well as Itagaki and Yazawa [23] measured the enthalpies of mixing of liquid Cu–Ge alloys at 1363 and 1373 K, respectively. The enthalpy of mixing of the liquid Cu–Ge alloys was determined at 1667 K by Sodeck et al. [24] with a Knudsen cell in combination with a mass spectrometer. Castanet [25] employed the high-temperature calorimeter to measure the enthalpy of mixing of the liquid Cu–Ge alloys referred to liquid Ge and solid Cu at 1348 K.

The activities of Cu and Ge in the liquid Cu–Ge alloys were measured by Sodeck et al. [24] using a Knudsen cell in combination with a mass spectrometer in the temperature range from 1540 to 1820 K. Alcock et al. [26] employed a Knudsen effusion cell and time-of-flight mass spectrometry to determine the activities of Cu and Ge in the liquid Cu–Ge alloys in the temperature range between 1350 and 1620 K. Using mass spectrometer method, Hager et al. [27] and Bergman et al. [28] measured the activities of Cu and Ge in the liquid Cu–Ge alloys at 1798 and 1700 K, respectively.

The activities of Cu and Ge in the solid solutions (fcc and hcp phases) at 1000 K were determined by Predel and Schallner [29] using the electromotive force (EMF) method. Jacob et al. [30] also measured the activities of Ge in the fcc solid solution phase at 1000 K through the reaction equilibrium method. The activities of Ge in the fcc solid phase at 1000 K reported by Predel and Schallner [29] and Jacob et al. [30] are in good agreement with each other and were thus used in the present optimization.

Predel and Stein [21,29] as well as Kleppa and King [31] determined the enthalpy of formation of the solid solution phases (fcc and hcp) in the Cu–Ge binary system using solution calorimetry at 1000 and 298 K, respectively. These experimental data are generally consistent and used in the present optimization. The enthalpy of formation of intermetallic compound η-$Cu_{0.75}Ge_{0.25}$ was also obtained by Predel and Stein [21] at 780 K, which is −7660 J/mol at 25 at.% Ge.

Wallbrecht [32] measured the heat capacity of the intermetallic compound η-$Cu_{0.75}Ge_{0.25}$ in the temperature range from 230 to 1000 K by differential scanning calorimetery. The measured heat capacity $C_p$ (unit: J/(mol K)) can be expressed as:

$$C_p = 24.03 + 0.00565T - 82316T^{-2} \quad (1)$$

However, no experimental information for other intermetallic compounds (ε-$Cu_{0.765}Ge_{0.235}$ and θ-$Cu_{0.735}Ge_{0.265}$) has been reported in the published literature up to now.

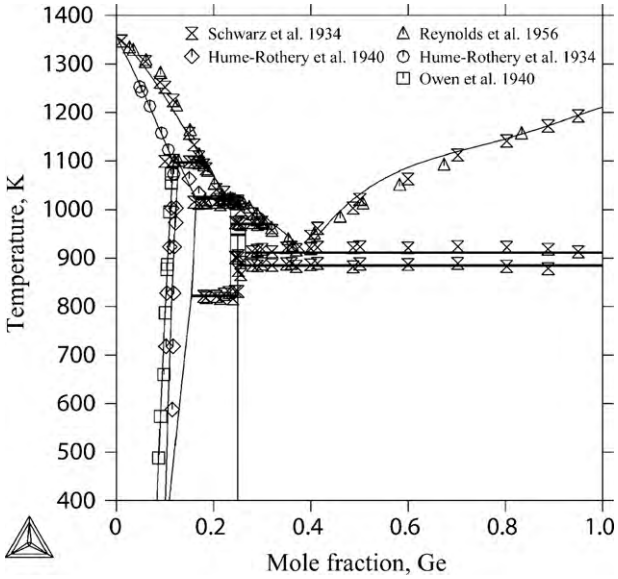


**Fig. 2.** Comparison of the calculated phase diagram of the Cu–Ge binary system with experimental data [16–20] in the present work.

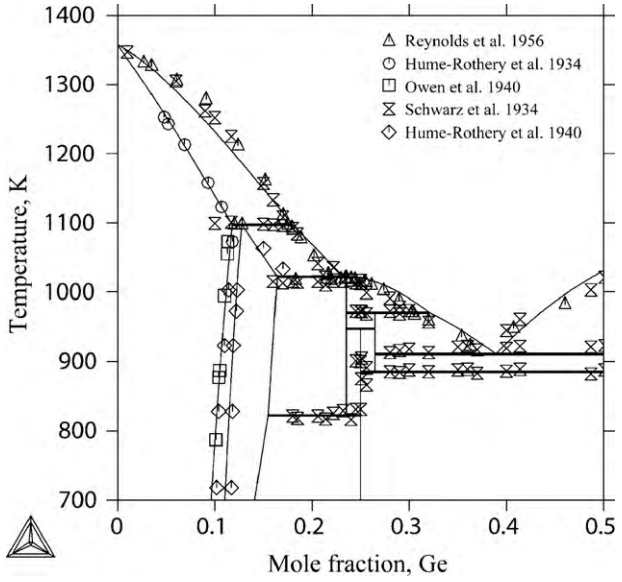


**Fig. 3.** Calculated phase diagram of the Cu–Ge binary system in the Cu-rich part with experimental data [16–20] in the present work.

## 3. Thermodynamic modeling

### 3.1. Pure elements

The stable forms of the pure elements at 298.15 K and 1 bar are chosen as the reference states of the system. For the thermodynamic functions of the pure elements in their stable and metastable states, the phase stability equations for the element $i$ in $\phi$ phase are given as:

$$^{0}G_i^{\phi}(T) = G_i^{\phi}(T) - H_i^{\mathrm{SER}} = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \quad (2)$$

where $H_i^{\mathrm{SER}}$ is the molar enthalpy of the so-called "standard element reference" (SER), i.e., the enthalpies of the pure elements in their defined reference phase at 298.15 K and 1 bar; $T$ is the absolute temperature in K; $G_i^{\phi}(T)$ is the absolute molar Gibbs energy of the element $i$ with structure of $\phi$; $^{0}G_i^{\phi}(T)$ is the molar Gibbs energy of the element $i$ with the structure of $\phi$ referred to the enthalpy of its stable state at 298.15 K and 1 bar. In the present work, the Gibbs energy functions of the pure elements Cu and Ge, $^{0}G_{\mathrm{Cu}}^{\phi}(T)$ and $^{0}G_{\mathrm{Ge}}^{\phi}(T)$ are taken from the Scientific Group Thermodata Europe (SGTE) database compiled by Dinsdale [33].

**Table 2**
Thermodynamic parameters of the Cu–Ge binary system.

| Phase | Thermodynamic parameters[a] | Reference |
|---|---|---|
| Liquid | $^{(0)}L^{\mathrm{Liq}} = -22422.37 - 3.993T$<br>$^{(1)}L^{\mathrm{Liq}} = -37961.74 + 9.446T$<br>$^{(2)}L^{\mathrm{Liq}} = -19505.73 + 5.595T$ | This work |
| fcc (Cu) | $^{(0)}L^{\mathrm{fcc}} = -25790.38 + 15.129T$<br>$^{(1)}L^{\mathrm{fcc}} = -30213.96 - 12.245T$<br>$^{(2)}L^{\mathrm{fcc}} = -10601.97$ | This work |
| hcp | $^{(0)}L^{\mathrm{hcp}} = -31999.50 + 19.815T$<br>$^{(1)}L^{\mathrm{hcp}} = -26717.32 - 19.022T$<br>$^{(2)}L^{\mathrm{hcp}} = -14980.12$ | This work |
| Diamond (Ge) | $^{0}G_{\mathrm{Ge}}^{\mathrm{Dia.}}$ cited from SGTE database | [33] |
| $\varepsilon$-$Cu_{0.765}Ge_{0.235}$ | $G_m^{\varepsilon} = 0.765G_{\mathrm{Cu}}^{\mathrm{fcc}} + 0.235G_{\mathrm{Ge}}^{\mathrm{Dia.}} - 1991.34 - 6.816T$ | This work |
| $\eta$-$Cu_{0.75}Ge_{0.25}$ | $G_m^{\eta} = -11937.72 + 126.363T - 24.03T\ln T - 0.002825T^2 + 41158T^{-1}$ | This work |
| $\theta$-$Cu_{0.735}Ge_{0.265}$ | $G_m^{\theta} = 0.735G_{\mathrm{Cu}}^{\mathrm{fcc}} + 0.265G_{\mathrm{Ge}}^{\mathrm{Dia.}} - 1500.15 - 7.298T$ | This work |

[a] Gibbs energies are expressed in J/mol. The all lattice stabilities of Cu and Ge are given by Dinsdale [33].

### 3.2. Solution phases

The substitutional solution model is employed to describe the solution phases including liquid, fcc, hcp and diamond (Ge), respectively. The molar Gibbs energy of the solution phase $\phi$ ($\phi$ = liquid,

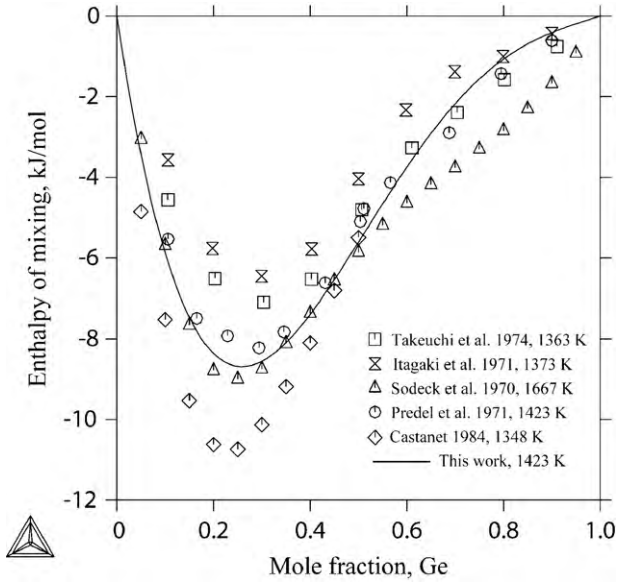


**Fig. 4.** Calculated enthalpies of mixing of liquid Cu–Ge alloys at 1423 K in comparison with experimental data [21–24] (Ref. states: liquid Cu and liquid Ge).

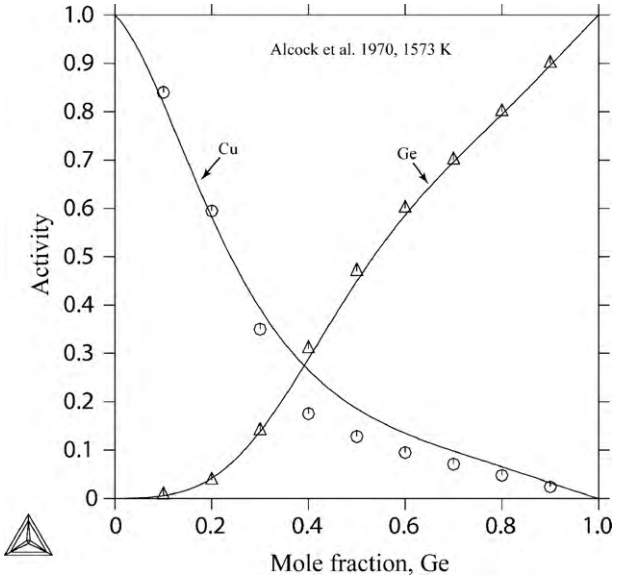


**Fig. 5.** Calculated activities of Cu and Ge with experimental data [26] at 1573 K (Ref. states: liquid Cu and liquid Ge).

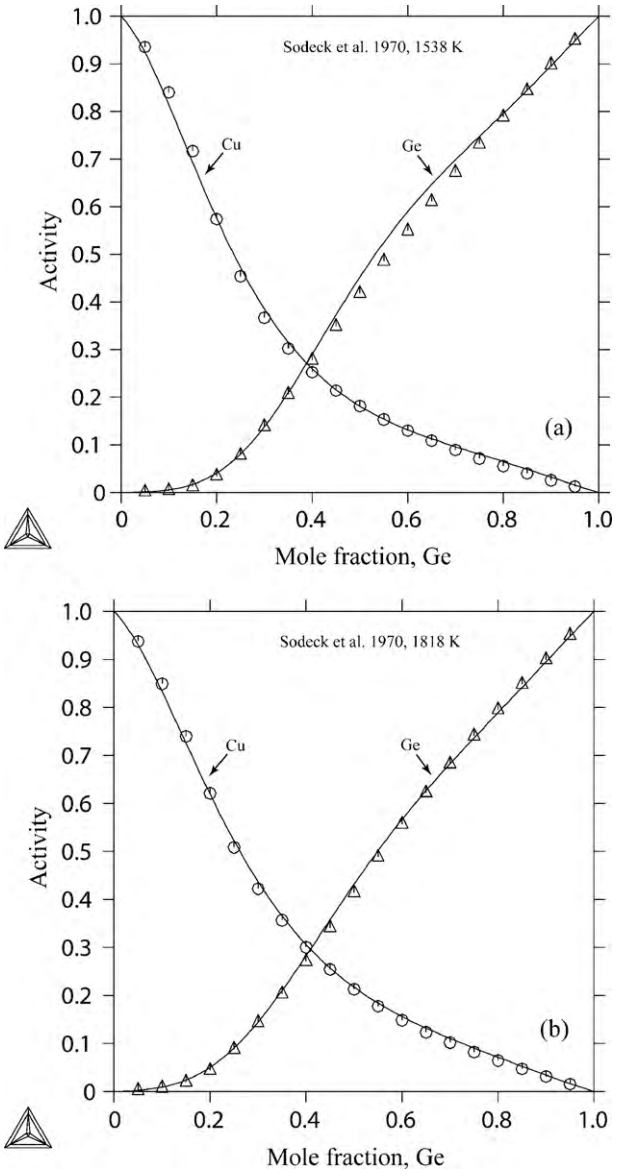


**Fig. 6.** Calculated activities of Cu and Ge with experimental data [24] (Ref. states: liquid Cu and liquid Ge). (a) 1538 K and (b) 1818 K.

fcc, hcp and diamond (Ge)) can be expressed as follows:

$$G_m^{\phi} = x_{Cu} \cdot {}^0G_{Cu}^{\phi} + x_{Cu} \cdot {}^0G_{Ge}^{\phi} + RT(x_{Cu} \ln x_{Cu} + x_{Ge} \ln x_{Ge}) + {}^EG_m^{\phi} \quad (3)$$

where $R$ is the gas constant, $x_{Cu}$ and $x_{Ge}$ are the mole fractions of Cu and Ge, respectively, and ${}^EG_m^{\phi}$ is the excess Gibbs energy expressed by the Redlich–Kister polynomial functions [34]:

$${}^EG_m^{\phi} = x_{Cu}x_{Ge}\sum_{i=0}^{n} {}^iL^{\phi}(x_{Cu} - x_{Ge})^i \quad (4)$$

where ${}^iL^{\phi}$ is the interaction parameter between elements Cu and Ge, which is formulated with a temperature dependence:

$${}^iL^{\phi} = A_i + B_iT \quad (5)$$

where $A_i$ and $B_i$ are model parameters to be optimized in the present work.

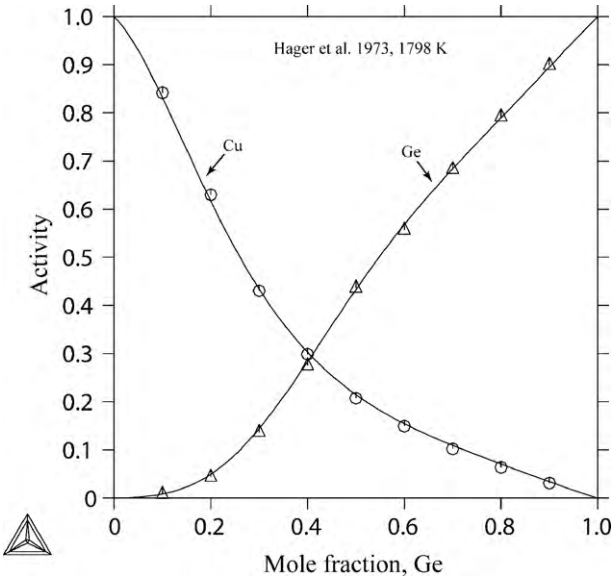


**Fig. 7.** Calculated activities of Cu and Ge with experimental data [27] at 1798 K (Ref. states: liquid Cu and liquid Ge).

### 3.3. Intermetallic compounds

The three intermetallic compounds in the Cu–Ge binary system, $\varepsilon$-$Cu_{0.765}Ge_{0.235}$, $\theta$-$Cu_{0.735}Ge_{0.265}$ and $\eta$-$Cu_{0.75}Ge_{0.25}$, are treated as stoichiometric compounds $Cu_aGe_b$ because of their narrow homogeneity ranges measured by Reynolds and Hume-Rothery [17]. Since the heat capacity of $\eta$-$Cu_{0.75}Ge_{0.25}$ was determined by Wallbrecht et al. [32], the molar Gibbs energy of $\eta$-$Cu_{0.75}Ge_{0.25}$ (unit: J/mol) can be deduced using Eq. (1):

$$G_m^{\eta} = C + DT - 24.03T\ln T - 0.002825T^2 + 41158T^{-1} \quad (6)$$

where $C$ and $D$ are parameters to be optimized in the present work.

Due to the lack of heat capacities of the other two intermetallic compounds ($\varepsilon$-$Cu_{0.765}Ge_{0.235}$, $\theta$-$Cu_{0.735}Ge_{0.265}$) and with the Neumann–Kopp rule, their molar Gibbs energies can be expressed

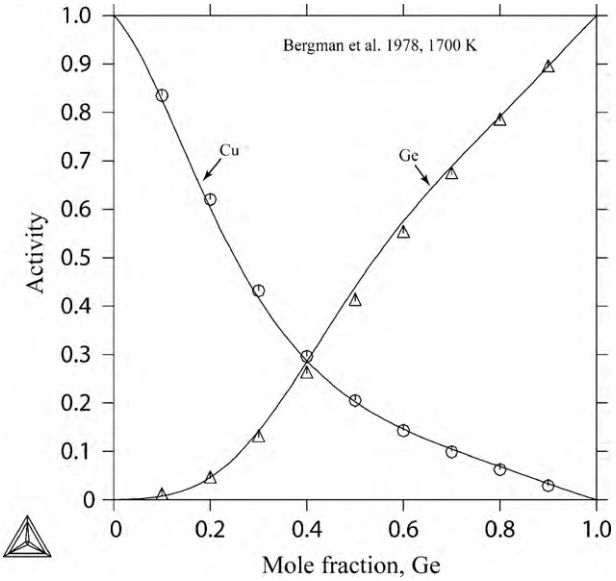


**Fig. 8.** Calculated activities of Cu and Ge with experimental data [28] at 1700 K (Ref. states: liquid Cu and liquid Ge).

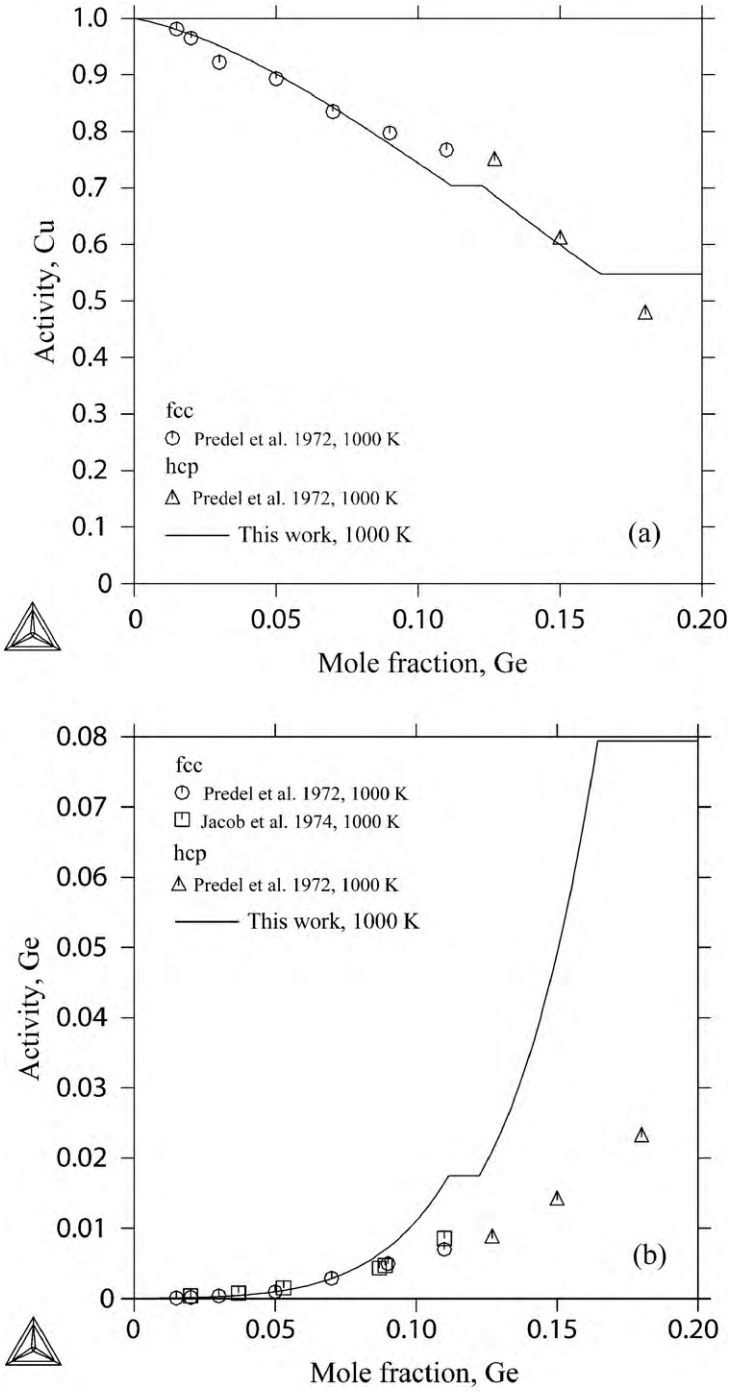


**Fig. 9.** Calculated activities of Cu and Ge in the fcc and hcp phases with experimental data [29,30] at 1000 K (Ref. states: fcc Cu and diamond Ge). (a) Cu and (b) Ge.

as follows:

$$G_m^{\phi} = \frac{a}{a+b}{}^0G_{Cu}^{fcc} + \frac{b}{a+b}{}^0G_{Ge}^{Dia.} + E_{\phi} + F_{\phi}T \quad (7)$$

with $\phi = \varepsilon\text{-}Cu_{0.765}Ge_{0.235}$, $\theta\text{-}Cu_{0.735}Ge_{0.265}$ and where the parameters $E_{\phi}$ and $F_{\phi}$ are parameters to be optimized in the present work.

## 4. Results and discussion

Using the lattice stabilities of Cu and Ge cited from Dinsdale [33], the model parameters for various phases in the Cu–Ge binary system were optimized using the PARROT module in the Thermo-calc® software package developed by Sundman et al. [14]. This module works by minimizing the square sum of the differences between the experimental data and calculated values. During the optimization, each set of experimental data was given a certain weight. The weights were changed systematically during the optimization until most of experimental data was accounted for within the claimed uncertainty limits.

The model parameters of the liquid phase were optimized firstly because many experimental data such as mixing enthalpies, activities and related phase boundaries are readily available. This was followed by adjusting the parameters for terminal solution phases and intermetallic compounds. The evaluation was conducted one by one using the step-by-step optimization procedure. Finally, all

condensed phases were optimized simultaneously considering all of the selected experimental information.

Thermodynamic parameters for all condensed phases in the Cu–Ge binary system obtained finally in the present work are summarized in Table 2. The calculated temperatures and compositions of all invariant reactions are compared with the reported experimental data [15–17] in this binary system as given in Table 1.

Fig. 1 shows the calculated phase diagram of the Cu–Ge binary system in the present work. Comparison of the present calculated phase diagram with the experimental data measured by Schwarz and Elstner [16], Reynolds and Hume-Rothery [17], Hume-Rothery et al. [18], Owen et al. [19] and Hume-Rothery et al. [20] is given in Figs. 2 and 3. As can be seen, the calculated liquidus in the present work is in good agreement with most experimental data [16–20]. However, it should be noticed that the present calculated liquidus of the part at about 50 at.% Ge is somewhat higher than the experimental data [16,17]. The calculated maximum solubility of Ge in fcc (Cu) (11.8 at.% Ge) is in good agreement with the measured value (12.0 at.% Ge). The present calculated phase boundaries between the fcc and the hcp phase are consistent with the experimental data determined by Owen et al. [19] and Hume-Rothery et al. [20]. With regard to Table 1, the present calculated temperatures and compositions of invariant reactions associated with the liquid phase agree with experimental data reported in Refs. [15–20] within the experimental error. Note here that the calculated temperature of transformation for the intermetallic compound ($\eta$-$Cu_{0.75}Ge_{0.25}$), $\varepsilon$-$Cu_{0.765}Ge_{0.235}$ + $\theta$-$Cu_{0.735}Ge_{0.265}$ ↔ $\eta$-$Cu_{0.75}Ge_{0.25}$ at 948 K, deviates significantly from the corresponding measured value (909 K). However, it should be pointed out that this reaction temperature is very difficult to measure accurately because the compositions of three intermetallic compounds are very close to each other. On the other hand, from the thermodynamic point of view, such quite close compositions of three intermetallic compounds (less than 3 at.%) lead to rather small differences between their Gibbs energies, which in turn limits the range in which their thermodynamic parameters can be adjusted significantly. Therefore, the present authors suggest that the further experimental investigations need to be performed.

Fig. 4 compares the calculated enthalpies of mixing of the liquid Cu–Ge alloys at 1423 K with the experimental data obtained by Predel and Stein [21], Takeuchi et al. [22], Itagaki and Yazawa [23], Sodeck et al. [24] and Castanet [25]. From Fig. 4, the calculated enthalpies of mixing of the liquid Cu–Ge alloys agree with the experimental data measured by Predel and Stein [21], while they show obvious deviation from the experimental data reported by Takeuchi et al. [22], Itagaki and Yazawa [23], Sodeck et al. [24] and Castanet [25]. This deviation might be resulted from the following reasons. Firstly, there is an obvious discrepancy between the experimental data obtained by Takeuchi et al. [22], and Itagaki and Yazawa [23] in the narrow temperature range of 10 K. Secondly, the experimental data obtained by Sodeck et al. [24] are deduced from the measured partial molar quantities of the liquid alloys. It should be pointed out that larger error may exist in such deduced values of the enthalpy of mixing in comparison with the data obtained directly by using calorimetry. Thirdly, the experimental results reported by Castanet [25] are much more negative than the experimental data in Refs. [21–24] and are not comparable. Thus, the difference between the calculated values and experiment data in Ref. [24,25] is unavoidable. During the present optimization, the experimental data measured by Predel and Stein [21] was only used. Therefore, the calculated enthalpies of mixing of the liquid Cu–Ge alloys are reasonable and acceptable in the present work.

Figs. 5–8 present comparisons of the calculated activities of Cu and Ge in the liquid Cu–Ge alloys with the experimental data [24,26–28] at different temperatures. It can be seen that the calculated activities of Cu in liquid Cu–Ge alloys are in excellent

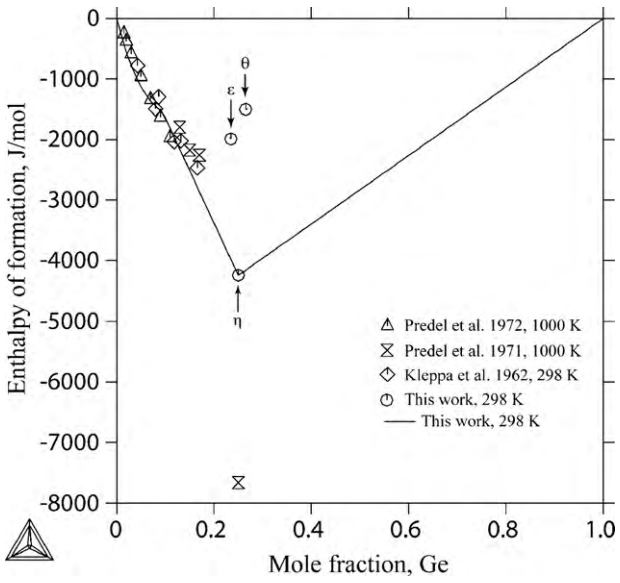


**Fig. 10.** Calculated enthalpies of formation of solid alloys and intermetallic compound in comparison with experimental data [21,29,31] at 298 K (Ref. states: fcc Cu and diamond Ge).

agreement with the experimental data measured by Sodeck et al. [24], Hager et al. [27] and Bergman et al. [28] at 1538, 1818, 1978 and 1700 K, respectively, while the discrepancy from the experimental data reported by Alcock et al. [26] at 1573 K was observed in the composition range from 30 to 70 at.% Ge. The calculated activities of Ge in liquid Cu–Ge alloys are in good agreement with all experimental data measured respectively by Sodeck et al. [24], Alcock et al. [26], Hager et al. [27] and Bergman et al. [28] at 1573, 1538, 1818, 1978 and 1700 K.

The comparison of the activities of Cu and Ge in the solid solution (fcc and hcp phases) between the calculated results and experimental values at 1000 K is shown in Fig. 9. It can be seen that the calculated activities of Cu and Ge in the solid fcc phase agree with the experimental data by Predel and Schallner [29] and Jacob et al. [30]. The calculated activities of Cu in solid hcp phase is in agreement with the experimental data by Predel and Schallner [29], while the calculated activities of Ge show the deviation from the experimental data reported by Predel and Schallner [30]. It is assumed that this discrepancy originates mainly from the experimental error because it is difficult to measure accurately the activities of components in solids. The purity of Ge used for measurements in Ref. [29] was not given in detail. It is only stated that the Ge was purified by zone melting technique, while the purities are given for all other elements used in these experiments. The larger experimental error for the activity of Ge might result from the contaminants in the Ge. Furthermore, the activity of Ge in the hcp phase measured in Ref. [29] is incompatible with the enthalpy of formation of the hcp phase determined in Refs. [21,29,31]. If a better agreement between the calculated activity of Ge in the hcp phase and the experimental data in Ref. [29] was achieved, the enthalpy of formation of the hcp phase would become too negative and deviate significantly from the experimental data given in Refs. [21,29,31].

The enthalpy of formation of solid alloys and intermetallic compounds in the Cu–Ge binary system at 298 K was calculated as presented in Fig. 10. As can be seen, the present calculated values in solid alloys are in excellent agreement with the experimental data measured by Predel and Stein [21,29] and Kleppa and King [31]. However, the calculated enthalpy of formation of the intermetallic compound $\eta$-$Cu_{0.75}Ge_{0.25}$ is −4245 J/mol, which is significantly different from the experimental data (−7660 J/mol) reported by Predel and Stein [21]. The solid fcc and hcp phases at 298 K would

not stable if the experimental data reported by Predel and Stein [21] was reliable. Obviously, the measured enthalpy of formation of the intermetallic compound $\eta$-$Cu_{0.75}Ge_{0.25}$ is too negative and is thus not reasonable. With regard to this discrepancy, the present authors suggest the further experimental investigations to measure directly and accurately the standard enthalpies of formation of intermetallic compounds in this binary system.

## 5. Conclusions

On the basis of the critical review for the experimental information on phase diagram and thermodynamic properties from the published literature, thermodynamic assessment of the Cu–Ge binary system has been performed using the CALPHAD method. A set of self-consistent thermodynamic parameters has been obtained, which can reproduce well most of the experimental data on thermodynamic properties and phase diagram within experimental uncertainties.

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