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Thermodynamic assessment of the Au–Ga system

Jinming Liu, Cuiping Guo, Changrong Li, Zhenmin Du*

Department of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China

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ABSTRACT

The Au–Ga system was critically assessed by means of CALPHAD technique. Based on the experimental data in the literature, the excess Gibbs energies of the solution phases (liquid, fcc, orthorhombic) were modeled with the Redlich–Kister equation. The intermetallic compounds αAu_7Ga, βAu_7Ga_2, $\beta' Au_7Ga_2$, γAu_7Ga_3 and $\gamma' Au_7Ga_3$, which have homogeneity ranges, were treated as the formula $Au_7(Au,Ga)$, $(Au,Ga)_7Ga_2$, $(Au,Ga)_7(Au,Ga)_2$, $(Au,Ga)_7(Au,Ga)_3$ and $(Au,Ga)_7(Au,Ga)_3$, respectively, using a two-sublattice model with Au and Ga or Au on the first sublattice, Au and Ga or Ga on the second one. The two compounds AuGa and $AuGa_2$ were treated as stochiometric compounds. A set of self-consistent thermodynamic parameters of the Au–Ga system was obtained.

1. Introduction

The Gold-based materials have gained increasing attention in recent years because of its potential application, as amorphous alloys with concentration range from 30 to 80 at.% Ga [1] and as wire bond, flip chip and off wafer interconnections due to its corrosion resistance, ability to form metallurgical bonds by soldering or cold welding, and ease of fabrication [2–4]. The thermodynamic descriptions of relevant alloy systems containing gallium are of crucial importance for understanding the physical properties, chemical behavior and the technological applications of the alloys or compounds.

This work deals with an assessment of the thermodynamic description of the Au–Ga system by means of the CALPHAD (CALculation of PHAse Diagram) technique.

2. Literature review

The gold–gallium phase diagram was firstly investigated by Weibke and Hesse [5] and Pfisterer [6], using microscopic, X-ray and differential thermal analyses. Four intermetallic compounds, β with a homogeneity range of 26.5–29.2 at.%Ga, γ with a homogeneity range of 29.8–30.8 at.% Ga and two stochiometric compounds AuGa and $AuGa_2$ were reported. Later on, Owen and Roberts [7] had a careful investigation of the Au–Ga system using lattice-spacing measurements and modified the solid solubility value of Ga in fcc(Au) [5,6]. Based on the above experimental information, the Au–Ga phase diagram was firstly reviewed by Elliott and Yazawa [8], in which the phase boundary of the Au-rich terminal solid solution phase was uncertain. Subsequently, Müller and Merl [9] and Cooke and Hume-Rothery [10,11] re-investigated the Au–Ga system. The maximum solid solubility value of Ga in fcc(Au) is more than 10 at.% using the electrical resistivity measurement by Müller and Merl [9]. Three new compounds αAu_7Ga, $\beta' Au_7Ga_2$ and $\gamma' Au_7Ga_3$ were determined by Cooke et al. [10], which are different from the compounds reported by Weibke and Hesse [5] and Pfisterer [6]. Seven intermediate compounds αAu_7Ga, βAu_7Ga_2, $\beta' Au_7Ga_2$, γAu_7Ga_3, $\gamma' Au_7Ga_3$, AuGa and $AuGa_2$ were also confirmed by Wallace and Kitchingman [12], Frank [13] and Puselj and Schubert [14].

Based on the experimental data measured by Cooke et al. [10,11], Moffatt [15] and Massalki and Okamoto [16] re-reviewed the Au–Ga phase diagram, respectively. Recently, Mouani et al. [17] re-investigated the phase diagram of Au–Ga system when they investigated the Au–Ga–Te ternary system. Comparison with the results of Cooke et al. [10], the main difference is the temperature of the peritectic reaction liquid + fcc → αAu_7Ga, which is 696 K [17] instead of 688 K [10].

The mixing enthalpies of the liquid phase in the Au–Ga system were measured by many researchers [18–23]. Beja [18], Bergman et al. [19], Prede et al. [20], Itagaki et al. [21], Gather et al. [22] and Hayer et al. [23] determined the mixing enthalpies of liquid at the temperature range of 750–1660 K. These results obtained by Predel et al. [20] and Gather et al. [22] are less exothermic than those determined by Beja [18] and Hayer et al. [23].

The enthalpy of fusion of $AuGa_2$ at 749 K using direct reaction calorimetry and the enthalpies of formation of AuGa and $AuGa_2$ at 298 K using enthalpimetric analysis were measured by Bergman

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* Corresponding author. Tel.: +86 10 6233 3772; fax: +86 10 6233 3772.
E-mail address: zmdu2@hotmail.com (Z. Du).

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Table 1
Thermodynamic parameters of the Au–Ga system[a].

Phase	Thermodynamic parameters	
	Temperature (K)	$\mathrm{GHSER}_{\mathrm{Au}=}$
	298.15–929.4	$-6938.856+106.830098T-22.75455T\ln(T)$
		$-3.85924T^2+0.379625\times10^{-6}T^3-25097T^{-1}$
	929.4–1337.3	$-93586.481+1021.69543T-155.7067449T\ln(T)$
		$+87.56015\times10^{-3}T^2-11.518713\times10^{-6}T^3+10637210T^{-1}$
	1337.3–1735.8	$+314067.829-2016.378254T+263.2522592T\ln(T)$
		$-118.216828\times10^{-3}T^2+8.923844\times10^{-6}T^3-67999832T^{-1}$
	1735.8–3200.0	$-12133.783+165.272524T-30.9616T\ln(T)$
		$\mathrm{GHSER}_{\mathrm{Ga}}=$
	200.0–302.9	$-21312.331+585.263691T-108.2287832T\ln(T)$
		$+227.155636\times10^{-3}T^2-118.575257\times10^{-6}T^3+439954T^{-1}$
	302.9–4000.0	$-7055.643+132.73019T-26.0692906T\ln(T)$
		$+0.1506\times10^{-3}T^2-0.040173\times10^{-6}T^3-118332T^{-1}$
liquid		model: $(\mathrm{Au,Ga})_1$
		$G(\mathrm{liquid,Au})=$
	298.14–929.4	$+5613.144+97.444232T-22.75455T\ln(T)$
		$-0.00385924T^2+3.79625\times10^{-7}T^3-25097T^{-1}$
	929.4–1337.33	$-81034.481+1012.30956T-155.706745T\ln(T)$
		$+0.08756015T^2-1.1518713\times10^{-5}T^3+10637210T^{-1}$
	1337.33–1735.8	$+326619.829-2025.76412T+263.252259T\ln(T)$
		$-0.118216828T^2+8.923844\times10^{-6}T^3-67999832T^{-1}$
	1735.8–3200.0	$+418.217+155.886658T-30.9616T\ln(T)$
		$G(\mathrm{liquid,Ga})=$
	200.0–302.91	$-15821.033+567.189696T-108.228783T\ln(T)$
		$+0.227155636T^2-1.18575257\times10^{-4}T^3$
		$+439954T^{-1}-7.0171\times10^{-17}T^7$
	302.91–4000.0	$-1389.188+114.049043T-26.0692906T\ln(T)$
		$+1.506\times10^{-4}T^2-4.0173\times10^{-8}T^3-118332T^{-1}$
		${}^0L^{\mathrm{liq}}=-68557.9+8.0891T$
		${}^1L^{\mathrm{liq}}=-24134.3+1.6021T$
		${}^2L^{\mathrm{liq}}=-13523.4$
orthorhombic		model: $(\mathrm{Au,Ga})_1$
		$G(\mathrm{orthorhombic,Au})=+\mathrm{GHSER}_{\mathrm{Au}}+5000.0$
		$G(\mathrm{orthorhombic,Ga})=+\mathrm{GHSER}_{\mathrm{Ga}}$
fcc		model: $(\mathrm{Au,Ga})_1$
	298.14–3200.0	$G(\mathrm{fcc,Au})=+\mathrm{GHSER}_{\mathrm{Au}}$
		$G(\mathrm{fcc,Ga})=$
	200.0–302.91	$-17512.331+575.063691T-108.228783T\ln(T)$
		$+0.227155636T^2-1.18575257\times10^{-4}T^3+439954T^{-1}$
	302.91–4000.0	$-3255.643+122.53019T-26.0692906T\ln(T)$
		$+1.506\times10^{-4}T^2-4.0173\times10^{-8}T^3-118332T^{-1}$
		$+1.64547\times10^{23}T^{-9}$
		${}^0L^{\mathrm{fcc}}=-39969.7-20.1065T$
		${}^1L^{\mathrm{fcc}}=-17540.0+33.9116T$
		${}^2L^{\mathrm{fcc}}=-9010.4$
$\alpha\mathrm{Au_7Ga}$		model: $(\mathrm{Au})_7(\mathrm{Au,Ga})_1$
		$G^{\alpha\mathrm{Au_7Ga}}_{\mathrm{Au:Ga}}=+7\mathrm{GHSER}_{\mathrm{Au}}+\mathrm{GHSER}_{\mathrm{Ga}}-51431.6-23.6786T$
		$G^{\alpha\mathrm{Au_7Ga}}_{\mathrm{Ga:Ga}}=+8\mathrm{GHSER}_{\mathrm{Ga}}+40000.0$
		${}^0L^{\alpha\mathrm{Au_7Ga}}_{\mathrm{Au,Ga:Ga}}=-281981.2-45.4550T$
		${}^1L^{\alpha\mathrm{Au_7Ga}}_{\mathrm{Au,Ga:Ga}}=-980.3$
$\beta\mathrm{Au_7Ga_2}$		model: $(\mathrm{Au,Ga})_7(\mathrm{Ga})_2$
		$G^{\beta\mathrm{Au_7Ga_2}}_{\mathrm{Au:Ga}}=+7\mathrm{GHSER}_{\mathrm{Au}}+2\mathrm{GHSER}_{\mathrm{Ga}}-122095.7+0.9250T$
		$G^{\beta\mathrm{Au_7Ga_2}}_{\mathrm{Ga:Ga}}=+9\mathrm{GHSER}_{\mathrm{Ga}}+45000.0$
		${}^0L^{\beta\mathrm{Au_7Ga}}_{\mathrm{Au:Au,Ga}}=-22653.9-36.2242T$
		${}^1L^{\beta\mathrm{Au_7Ga}}_{\mathrm{Au:Au,Ga}}=-7423.5$
$\beta'\mathrm{Au_7Ga_2}$		model: $(\mathrm{Au,Ga})_7(\mathrm{Au,Ga})_2$
		$G^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Au:Ga}}=+7\mathrm{GHSER}_{\mathrm{Au}}+2\mathrm{GHSER}_{\mathrm{Ga}}-126079.1+7.2684T$
		$G^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Au:Au}}=+9\mathrm{GHSER}_{\mathrm{Au}}+45000.0$
		$G^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Ga:Au}}=+2\mathrm{GHSER}_{\mathrm{Au}}+7\mathrm{GHSER}_{\mathrm{Ga}}+216079.1-7.2684T$
		$G^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Ga:Ga}}=+9\mathrm{GHSER}_{\mathrm{Ga}}+45000.0$
		${}^0L^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Au,Ga:Ga}}={}^0L^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Au,Ga:Au}}=-210032.1+14.0000T$
		${}^1L^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Au,Ga:Ga}}={}^1L^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Au,Ga:Au}}=-30023.0$
		${}^0L^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Au:Au,Ga}}={}^0L^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Ga:Au,Ga}}=-64420.4+16.9223T$
		${}^1L^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Au:Au,Ga}}={}^1L^{\beta'\mathrm{Au_7Ga_2}}_{\mathrm{Ga:Au,Ga}}=-29300.0$

Table 1 (*Continued*)

Phase	Thermodynamic parameters	
	Temperature (K)	$\mathrm{GHSER}_{\mathrm{Au}=}$
$\gamma \mathrm{Au}_7\mathrm{Ga}_3$		model: $(\mathrm{Au, Ga})_7(\mathrm{Au, Ga})_3$ $G^{\gamma \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Ga:Au}} = 342209.9 - 1149.4232T + 233.7T\ln(T) + 0.0384T^2 - 130630T^{-1}$ $G^{\gamma \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Au:Ga}} = -242209.9 + 1149.4232T - 233.7T\ln(T) - 0.0384T^2 + 130630T^{-1}$ $G^{\gamma \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Au:Au}} = +10\mathrm{GHSER}_{\mathrm{Au}} + 50000.0$ $G^{\gamma \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Ga:Ga}} = +10\mathrm{GHSER}_{\mathrm{Ga}} + 50000.0$ ${}^{0}L^{\gamma \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Au,Ga:Ga}} = {}^{0}L^{\gamma \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Au,Ga:Au}} = -285033.5 + 13.7746T$
$\gamma' \mathrm{Au}_7\mathrm{Ga}_3$		model: $(\mathrm{Au, Ga})_7(\mathrm{Au, Ga})_3$ $G^{\gamma' \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Au:Ga}} = -248515.3 + 1161.0879T - 233.7T\ \ln(T) - 0.0384T^2 + 130630T^{-1}$ $G^{\gamma' \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Ga:Au}} = 348515.3 - 1161.0879T + 233.7T\ \ln(T) + 0.0384T^2 - 130630T^{-1}$ $G^{\gamma' \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Au:Au}} = +10\mathrm{GHSER}_{\mathrm{Au}} + 50000.0$ $G^{\gamma' \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Ga:Ga}} = +10\mathrm{GHSER}_{\mathrm{Ga}} + 50000.0$ ${}^{0}L^{\gamma' \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Au,Ga:Ga}} = {}^{0}L^{\gamma' \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Au,Ga:Au}} = -303431.8 + 30.1461T$ ${}^{0}L^{\gamma' \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Au:Au,Ga}} = {}^{0}L^{\gamma' \mathrm{Au}_7\mathrm{Ga}_3}_{\mathrm{Ga:Au,Ga}} = 75621.4 - 67.2495T$
AuGa		model: $(\mathrm{Au})_1(\mathrm{Ga})_1$ $G^{\mathrm{AuGa}}_{\mathrm{Au:Ga}} = -58793.5 + 236.3332T - 47.46T\ \ln(T) - 0.00686T^2 + 33480T^{-1}$
AuGa_2		model:$(\mathrm{Au})_1(\mathrm{Ga})_2$ $G^{\mathrm{AuGa}_2}_{\mathrm{Au:Ga}} = -89043.7 + 368.1044T - 72.36T\ \ln(T) - 0.009435T^2 + 95400T^{-1}$

[a] In J mol^{-1} of the formula units.

et al. [19]. Prede et al. [20,24] investigated the enthalpies of formation of AuGa and AuGa_2 at 706 and 700 K and the enthalpies of formation of fcc phase over the range 0.03–0.10 at.% Ga at 703 K using liquid tin solution calorimetry. The enthalpy increments of $H_m(T) - H_m(298\,\mathrm{K})$ and heat capacities of three compounds $\gamma\mathrm{Au}_7\mathrm{Ga}_3$ at the composition $\mathrm{Au}_{0.692}\mathrm{Ga}_{0.308}$, AuGa at the composition $\mathrm{Au}_{0.5}\mathrm{Ga}_{0.5}$ and AuGa_2 at the composition $\mathrm{Au}_{0.34}\mathrm{Ga}_{0.66}$ were measured by Wallbrecht et al. [25] in the temperature ranges between 235 and 700 K using differential scanning calorimetry. Durrwachter et al. [26] determined the core level binding energy shifts in the liquid alloy $\mathrm{Au}_x\mathrm{Ga}_{1-x}$ using X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS) core level spectra.

In the Au–Ga system, the activities of liquid were measured by Kameda et al. [27] at 973 and 1073 K and by Bergman et al. [19] at 1400 K using Knudsen method with mass spectrometry. The entropies of mixing of liquid in the Au–Ga system were measured by Bergman et al. [19] at 1400 K. The Gibbs energy of liquid in the Au–Ga system was measured by Bergman et al. [19] at 1400 K and Hayer et al. [23] at 1000 K combining with the excess Gibbs energy reported by Predel and Schallner [28].

3. Thermodynamic models

3.1. Unary phases

The Gibbs energy function $G_i^{\phi}(T) = G_i^{\phi}(T) - H_i^{\mathrm{SER}}\,(298.15\,\mathrm{K})$ for the element i (i = Au, Ga) in the phase ϕ (ϕ = liquid, face-centered cubic(fcc) and orthorhombic) is described by an equation of the following form:

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

where H_i^{SER} (298.15 K) is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER) state, fcc for Au and orthorhombic for Ga. The Gibbs energy of the element i, $G_i^{\phi}(T)$, in its SER state, is denoted by GHSER_i, i.e.,

$$\mathrm{GHSER}_{\mathrm{Au}} = {}^{0}G^{\mathrm{fcc}}_{\mathrm{Au}}(T) - H^{\mathrm{SER}}_{\mathrm{Au}}(298.15\,\mathrm{K}) \tag{2}$$

$$\mathrm{GHSER}_{\mathrm{Ga}} = {}^{0}G^{\mathrm{orth.}}_{\mathrm{Ga}}(T) - H^{\mathrm{SER}}_{\mathrm{Ga}}(298.15\,\mathrm{K}) \tag{3}$$

In the present work, the Gibbs energy functions are taken from the SGTE (Scientific Group Thermodata Europe) pure elements database compiled by Dinsdale [29] and listed in Table 1.

3.2. Solution phases

In the Au–Ga system, there are three solution phases: liquid, fcc and orthorhombic. Their Gibbs energies are described by the following expression:

$$G_m^{\phi} = x_{\mathrm{Au}}G_{\mathrm{Au}}^{\phi}(T) + x_{\mathrm{Ga}}G_{\mathrm{Ga}}^{\phi}(T) + RT(x_{\mathrm{Au}}\ \ln x_{\mathrm{Au}} + x_{\mathrm{Ga}}\ \ln x_{\mathrm{Ga}}) + {}^{\mathrm{E}}G_m^{\phi} \tag{4}$$

where R is the gas constant, x_{Au} and x_{Ga} are the mole fraction of Au and Ga, respectively, and ${}^{\mathrm{E}}G_m^{\phi}$ is the excess Gibbs energy, expressed by the Redlich–Kister polynomial [30].

$${}^{\mathrm{E}}G_m^{\phi} = x_{\mathrm{Au}}x_{\mathrm{Ga}}\sum_j {}^{j}L^{\phi}(x_{\mathrm{Au}} - x_{\mathrm{Ga}})^j \tag{5}$$

where ${}^{j}L^{\phi}$ is the interaction parameter between element Au and Ga, which is to be evaluated in the present work. Its general form is

$$L^{\phi} = a + bT + cT\ \ln(T) + dT^2 + eT^3 + fT^{-1} \tag{6}$$

In most cases, only the first one or two terms are used according to the temperature dependence on the experimental data.

3.3. Stoichiometric compounds AuGa and AuGa_2

AuGa has a structure of the MnP(B31)-type [11,14,31]. AuGa_2 has isotypic CaF_2(C1)-type structure [11,14,32]. In the present work, they are treated as stoichiometric compounds. The heat capacity for AuGa and AuGa_2 measured by Wallbrecht et al. [25] was expressed by following form:

$$C_p = a + bT + cT^{-2} \tag{7}$$

The Gibbs energy per mole of formula unit $\mathrm{Au}_m\mathrm{Ga}_n$ should be expressed as following:

$$G_m^{\mathrm{Au}_m\mathrm{Ga}_n} = p + qT - aT\ \ln(T) - \frac{1}{2}bT^2 - \frac{1}{2}cT^{-1} \tag{8}$$

where the parameters a, b and c of the Eq. (8) are obtained from the Eq. (7); the parameters p and q should be evaluated in the present work.

3.4. Intermetallic compounds αAu_7Ga and βAu_7Ga_2

The compound αAu_7Ga was reported to exist and have a structure of hexagonal Ni_3Ti-type by Cooke et al. [10,11]. On the basis of the phase diagram measured by Cooke et al. [10,11] and Mouani et al. [17], the intermetallic compound αAu_7Ga has a narrow homogeneity range about 12.7–14.2 at.% Ga. In the present work, it is treated as the formula $Au_7(Au,Ga)$ by a two-sublattice model [33,34] with Au on the first sublattice and Au and Ga on the second one. The Gibbs energy per mole of formula unit αAu_7Ga is given by the following expression:

$$\begin{aligned} G_m^{\alpha Au_7Ga} &= y_{Au} G_{Au:Au}^{\alpha Au_7Ga} + y_{Ga} G_{Au:Ga}^{\alpha Au_7Ga} + RT(y_{Au} \ln y_{Au} + y_{Ga} \ln y_{Ga}) \\ &\quad + y_{Au} y_{Ga} \sum_j {}^j L_{Au:Au,Ga}^{\alpha Au_7Ga} (y_{Au} - y_{Ga})^j \end{aligned} \qquad (9)$$

where y_{Au} and y_{Ga} are the site fraction of Au or Ga on the second sublattice; $G_{Au:Au}^{\alpha Au_7Ga}$ refers to Gibbs energy of pure Au in αAu_7Ga structure; $G_{Au:Ga}^{\alpha Au_7Ga}$ represents the Gibbs energy of the compound αAu_7Ga when the first sublattice is occupied by element Au and the second sublattice is occupied by element Ga, which is relative to the enthalpies of pure fcc for Au and orthorhombic for Ga in their SER states; ${}^j L_{Au:Au,Ga}^{\alpha Au_7Ga}$ represents the jth interaction parameters between the elements Au and Ga on the second sublattice.

The compound βAu_7Ga_2 has a hexagonal structure [12,13] and extends from ~20.4 to 22.1 at.% Ga [10,17]. It is treated as the formula $(Au,Ga)_7Ga_2$ by a two-sublattice model [33,34] with Au and Ga on the first sublattice and Ga on the second one. The Gibbs energy per mole of formula unit βAu_7Ga_2 is given by the following expression:

$$\begin{aligned} G_m^{\beta Au_7Ga_2} &= y_{Au} G_{Au:Ga}^{\beta Au_7Ga_2} + y_{Ga} G_{Ga:Ga}^{\beta Au_7Ga_2} + 7RT(y_{Au} \ln y_{Au} + y_{Ga} \ln y_{Ga}) \\ &\quad + y_{Au} y_{Ga} \sum_j {}^j L_{Au,Ga:Ga}^{\beta Au_7Ga_2} (y_{Au} - y_{Ga})^j \end{aligned} \qquad (10)$$

where y_{Au} and y_{Ga} are the site fraction of Au or Ga on the first sublattice; $G_{Ga:Ga}^{\beta Au_7Ga_2}$ refers to Gibbs energy of pure Ga in βAu_7Ga_2 structure; $G_{Au:Ga}^{\beta Au_7Ga_2}$ represents the Gibbs energy of the compound βAu_7Ga_2 when the first sublattice is occupied by element Au and the second sublattice is occupied by element Ga, which are relative to the enthalpies of pure fcc for Au and orthorhombic for Ga in their SER states; ${}^j L_{Au,Ga:Ga}^{\beta Au_7Ga_2}$ represents the jth interaction parameters between the elements Au and Ga on the first sublattice.

3.5. Intermetallic compound $\beta' Au_7Ga_2$

The compound $\beta' Au_7Ga_2$ is formed peritectically at 682.8 K and exists unchanged down to room temperature, which has an orthorhombic structure [10] and has a homogeneity range of 21.3–24.8 at.% Ga [10,16,17].

In the present work, the intermetallic compound $\beta' Au_7Ga_2$ is treated as the formula $(Au,Ga)_7(Au,Ga)_2$ by a two-sublattice model [33,34]. The Gibbs energy per mole of formula unit $(Au,Ga)_7(Au,Ga)_2$ is given by the following expression:

$$\begin{aligned} G_m^{\beta' Au_7Ga_2} &= y'_{Au} y''_{Au} G_{Au:Au}^{\beta' Au_7Ga_2} + y'_{Au} y''_{Ga} G_{Au:Ga}^{\beta' Au_7Ga_2} + y'_{Ga} y''_{Au} G_{Ga:Au}^{\beta' Au_7Ga_2} \\ &\quad + y'_{Ga} y''_{Ga} G_{Ga:Ga}^{\beta' Au_7Ga_2} + 7RT(y'_{Au} \ln y'_{Au} + y'_{Ga} \ln y'_{Ga}) \\ &\quad + 2RT(y''_{Au} \ln y''_{Au} + y''_{Ga} \ln y''_{Ga}) + y'_{Au} y'_{Ga} (y''_{Au} \sum_j {}^j L_{Au,Ga:Au}^{\beta' Au_7Ga_2} \\ &\quad \times (y'_{Au} - y'_{Ga})^j + y''_{Ga} \sum_j {}^j L_{Au,Ga:Ga}^{\beta' Au_7Ga_2} (y'_{Au} - y'_{Ga})^j) \end{aligned}$$

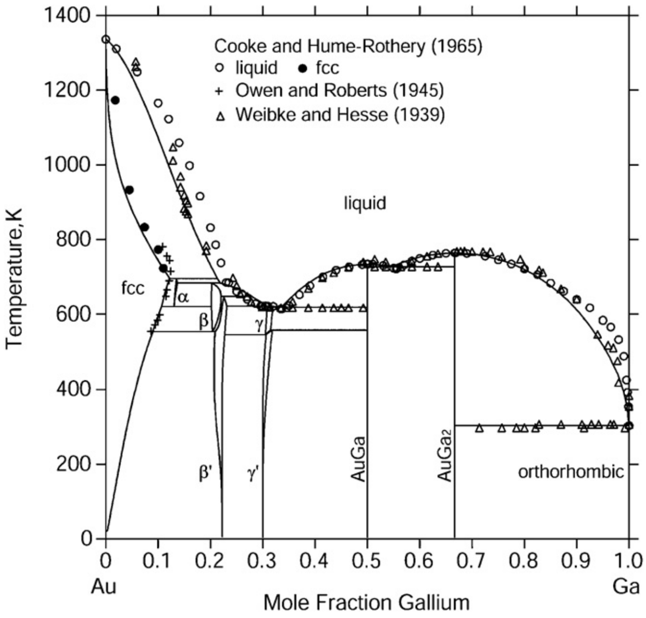

Fig. 1. Calculated Au–Ga phase diagram by the present thermodynamic description with experimental data measured by Weibke and Hesse [5], Owen and Roberts [7], Cooke and Hume-Rothery [10].

$$\begin{aligned} &\quad + y''_{Au} y''_{Ga} (y'_{Au} \sum_j {}^j L_{Au:Au,Ga}^{\beta' Au_7Ga_2} (y''_{Au} - y''_{Ga})^j \\ &\quad + y'_{Ga} \sum_j {}^j L_{Ga:Au,Ga}^{\beta' Au_7Ga_2} (y''_{Au} - y''_{Ga})^j) \end{aligned} \qquad (11)$$

where the parameters y'_i and y''_i are the site fractions of Au or Ga on the first and second sublattices, respectively; $G_{*:*}^{\beta' Au_7Ga_2}$ represents the Gibbs energies of the stable and unstable compounds when the first and second sublattices are occupied by only one element Au or Ga, respectively, which are relative to the enthalpies of pure fcc for Au and orthorhombic for Ga in their SER states; ${}^j L_{Au,Ga:*}^{\beta' Au_7Ga_2}$ and ${}^j L_{*:Au,Ga}^{\beta' Au_7Ga_2}$ represent the jth interaction parameters between the element Au and Ga on the first and second sublattice, respectively.

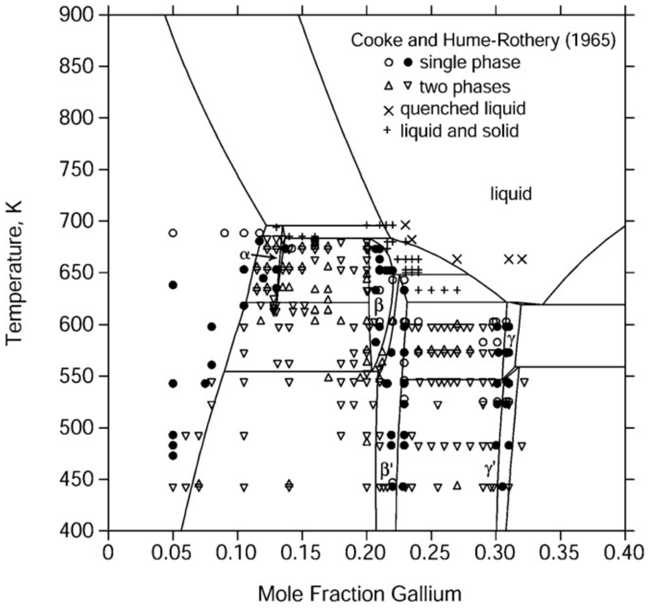

Fig. 2. Enlarged section of Fig. 1.

Table 2
Invariant reactions of the Au–Ga system.

Reaction	Present work				Cooke et al. [10]			
	T (K)	x(Ga)			T (K)	x(Ga)		
liq. + fcc(Au) → αAu_7Ga	696	0.2129	0.1222	0.1350	696[b]	0.228	0.124	0.138
liq. + αAu_7Ga → βAu_7Ga_2	683	0.2185	0.1369	0.2021	683[b]	0.231	0.142	0.205
αAu_7Ga → fcc(Au) + βAu_7Ga_2	621	0.1304	0.1067	0.2016	621	0.106	0.128	0.204
βAu_7Ga_2 → fcc(Au) + $\beta' Au_7Ga_2$	555	0.2038	0.0898	0.2087	555	0.205	0.085	0.213
liq. + βAu_7Ga_2 → $\beta' Au_7Ga_2$	648	0.2789	0.2206	0.2255	648	0.265	0.221	0.231
liq. → $\beta' Au_7Ga_2$ + γAu_7Ga_3	622	0.3079	0.2313	0.3087	620	0.285	0.248	0.298
liq. → γAu_7Ga_3 + AuGa	619	0.3362	0.3195	0.5000	612	0.336	0.310	0.500
liq. → γAu_7Ga_3	622	0.3086	0.3086	–	622	0.305	0.305	–
γAu_7Ga_3 → $\beta' Au_7Ga_2$ + $\gamma' Au_7Ga_3$	547	0.3048	0.2273	0.3063	547	–	–	–
γAu_7Ga_3 → AuGa + $\gamma' Au_7Ga_3$	559	0.3147	0.5000	0.3178	559	–	–	–
liq. → AuGa	734	0.5000	0.5000	–	734	0.500	0.500	–
liq. → AuGa + $AuGa_2$	727	0.5462	0.5000	0.6667	722	0.555	0.500	0.667
liq. → $AuGa_2$	764	0.6667	0.6667	–	764	0.667	0.667	–
liq. → $AuGa_2$ + orth. (Ga)	303	0.9992	0.6667	0.9999	303	1.000	0.667	1.000

[b] The invariant reaction temperatures were reported by Mounai et al. [17].

3.6. Intermetallic compounds γAu_7Ga_3 and $\gamma' Au_7Ga_3$

The compounds γAu_7Ga_3 and $\gamma' Au_7Ga_3$ have orthorhombic structure [10,16], which are 21:3 electron compounds [11,35], and have homogeneity ranges 29.8–31 at.% Ga.

In the present work, the intermetallic compounds γAu_7Ga_3 and $\gamma' Au_7Ga_3$ are treated as the formula $(Au,Ga)_7(Au,Ga)_3$ by a two-sublattice model [33,34]. The Gibbs energy per mole of formula unit $(Au,Ga)_7(Au,Ga)_3$ is given by the following expression:

$$\begin{aligned} G_m^{\phi} = {} & y'_{Au}y''_{Au}G^{\phi}_{Au:Au} + y'_{Au}y''_{Ga}G^{\phi}_{Au:Ga} + y'_{Ga}y''_{Au}G^{\phi}_{Ga:Au} + y'_{Ga}y''_{Ga}G^{\phi}_{Ga:Ga} \\ & + 7RT(y'_{Au}\ln y'_{Au} + y'_{Ga}\ln y'_{Ga}) + 3RT(y''_{Au}\ln y''_{Au} + y''_{Ga}\ln y''_{Ga}) \\ & + y'_{Au}y'_{Ga}\Big(y''_{Au}\sum_j {}^{j}L^{\phi}_{Au,Ga:Au}(y'_{Au} - y'_{Ga})^j \\ & + y''_{Ga}\sum_j {}^{j}L^{\phi}_{Au,Ga:Ga}(y'_{Au} - y'_{Ga})^j\Big) \\ & + y''_{Au}y''_{Ga}\Big(y'_{Au}\sum_j {}^{j}L^{\phi}_{Au:Au,Ga}(y''_{Au} - y''_{Ga})^j \\ & + y'_{Ga}\sum_j {}^{j}L^{\phi}_{Ga:Au,Ga}(y''_{Au} - y''_{Ga})^j\Big) \end{aligned} \quad (12)$$

where ϕ represents γAu_7Ga_3 or $\gamma' Au_7Ga_3$; y'_i and y''_i are the site fractions of Au or Ga on the first and second sublattices, respectively; the parameter $G^{\phi}_{*:*}$ represents the Gibbs energies of the compound ϕ when the first and second sublattices are occupied by only one element Au or Ga, respectively, which are relative to the enthalpies of pure fcc for Au and orthorhombic for Ga in their SER state; ${}^{j}L^{\phi}_{Au,Ga:*}$ and ${}^{j}L^{\phi}_{*:Au,Ga}$ represent the jth interaction parameters between the element Au and Ga on the first and second sublattice, respectively. According to the heat capacities measured by Wallbrecht et al. [25], the Gibbs energy of γAu_7Ga_3 and $\gamma' Au_7Ga_3$ with stoichiometry at $G^{\phi}_{Au:Ga}$ is expressed similar to Eq. (8).

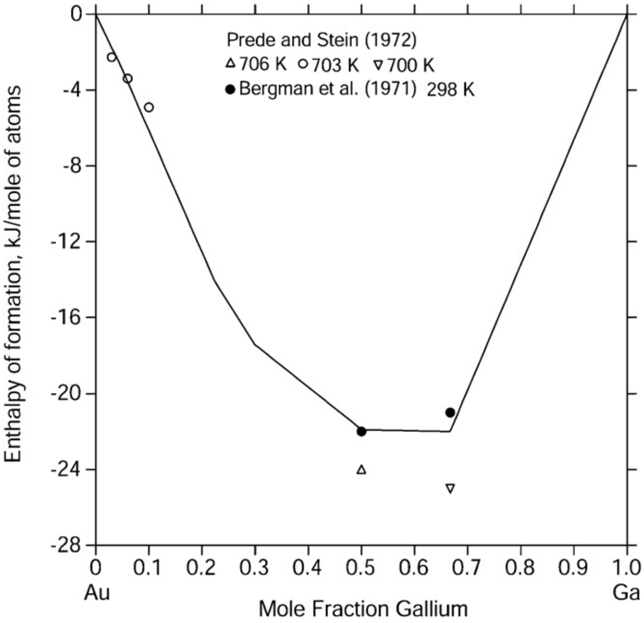

Fig. 3. Calculated enthalpies of formation at 298 K in the Au–Ga system and comparison with the experimental data [19,20,24]. The reference states for the elements are fcc for Au and orthorhombic for Ga.

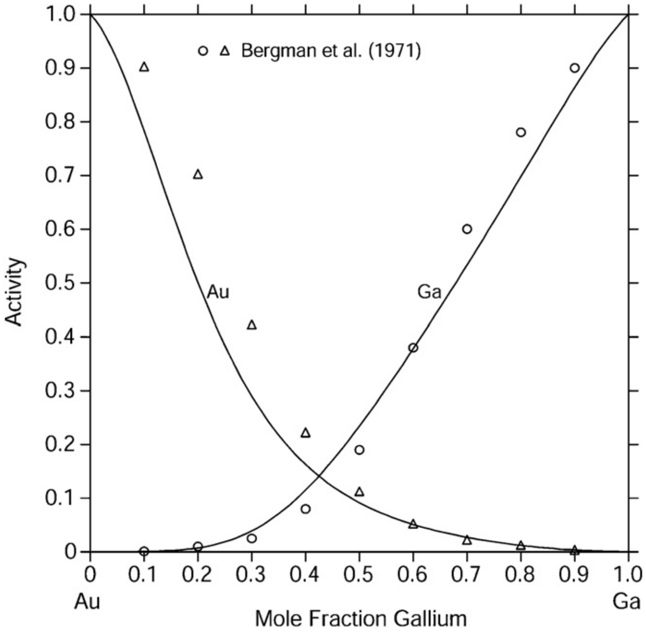

Fig. 4. Calculated activities of Au and Ga in liquid at 1400 K in the Au–Ga system and comparison with the experimental data [19]. The reference states of elements are liquid for Au and Ga.

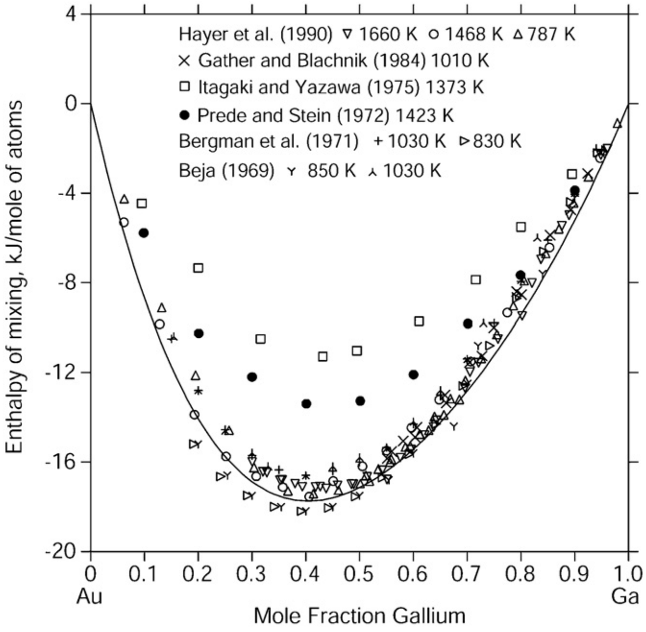

Fig. 5. Calculated enthalpies of mixing of liquid at 1468 K in the Au–Ga system and comparison with experimental data [18–23]. The reference states are liquid for Au and Ga.

4. Optimization

Most of the above experimental information was selected for the evaluation of the thermodynamic model parameters. In the present work, the phase relation and transformation temperatures based on the phase diagram of the Au–Ga system determined by Cooke and Hume-Rothery [10], the temperature of the peritectic reaction liquid + fcc → αAu_7Ga at 696 K [17] were adopted.

The optimization was carried out by means of the THERMO-CALC software [36], which can handle various kinds of experimental data. The program works by minimizing an error sum where each of the selected data values is given a certain weight. The weight is chosen by personal judgment and changed by trial and error during the work until most of the selected experimental information is reproduced within the expected uncertainty limits.

The optimization of the phase diagram of Au–Ga system was carried out in two steps. In the first step, these phases αAu_7Ga, βAu_7Ga_2, $\beta' Au_7Ga_2$, γAu_7Ga_3 and $\gamma' Au_7Ga_3$, are assumed to be stoichiometric compounds; in the second step, αAu_7Ga, βAu_7Ga_2, $\beta' Au_7Ga_2$, γAu_7Ga_3 and $\gamma' Au_7Ga_3$, are treated by a two-sublattice model [33,34], which are described in Sections 3.4–3.6. The parameters obtained from the first treatment were used as the starting values for the second treatment.

For the liquid and fcc solutions, the interaction parameters ${}^0L^{\text{liq}}$, ${}^1L^{\text{liq}}$ and ${}^2L^{\text{liq}}$, ${}^0L^{\text{fcc}}$, ${}^1L^{\text{fcc}}$ and ${}^2L^{\text{fcc}}$ in Eq. (6) can be reliably obtained from the experimental data.

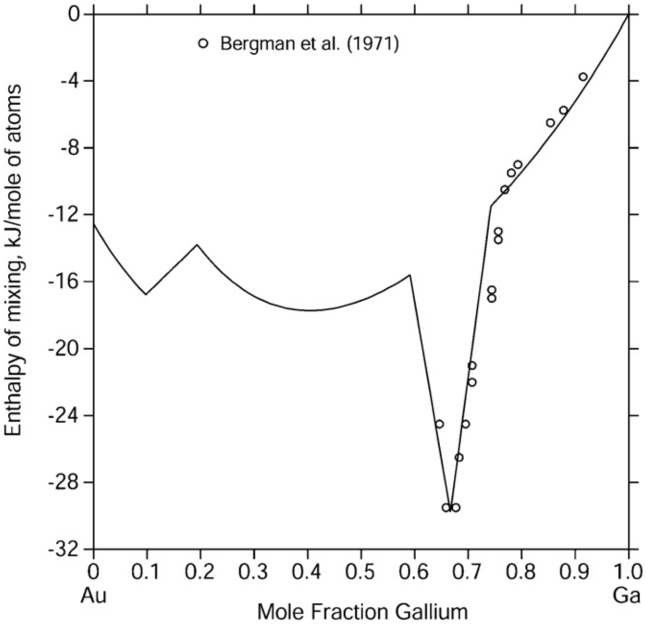

Fig. 6. Calculated enthalpies of mixing at 750 K in the Au–Ga system and comparison with experimental data [19]. The reference states are liquid for Au and Ga.

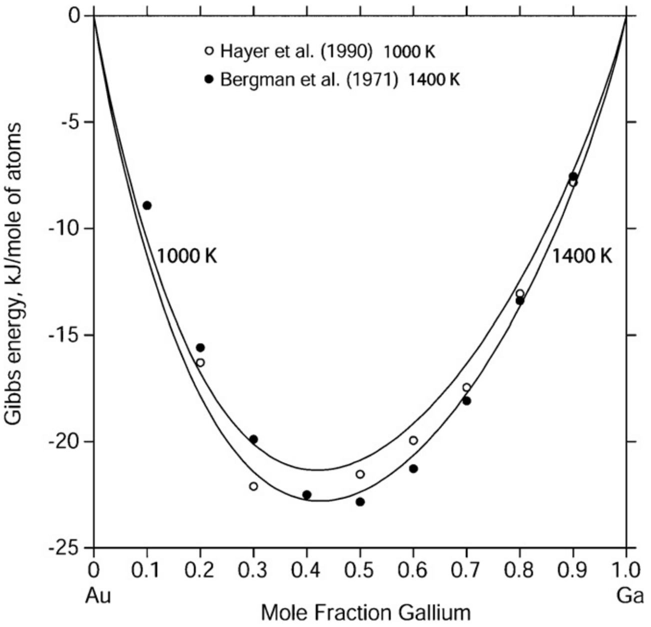

Fig. 7. Calculated Gibbs energies of mixing in the Au–Ga system and comparison with experimental data [19,23]. The reference states are liquid for Au and Ga.

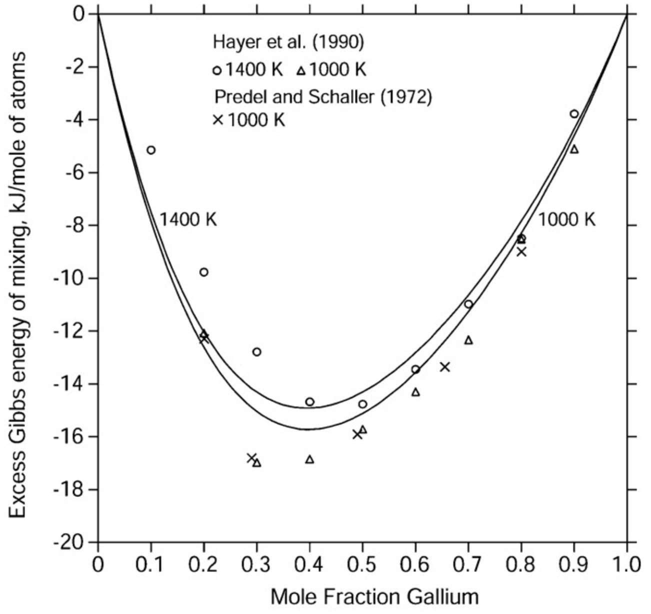

Fig. 8. Calculated excess Gibbs energies of mixing at 1000 and 1400 K and comparison with the experimental data [23,28]. The references are liquid for Au and Ga.

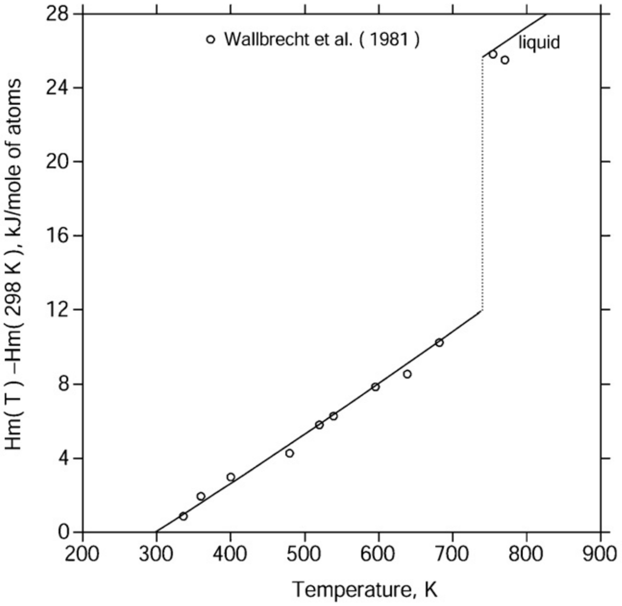

Fig. 9. Calculated $H_m(T) - H_m(298\,\mathrm{K})$ of phase AuGa in the Au–Ga system and comparison with the experimental data [25].

For the compounds $\beta'\mathrm{Au_7Ga_2}$, $\gamma\mathrm{Au_7Ga_3}$ and $\gamma'\mathrm{Au_7Ga_3}$, in the present work, they are treated as the formula $(\mathrm{Au,Ga})_m(\mathrm{Au,Ga})_n$ by a two-sublattice model [33,34]. It was shown by Ansara et al. [37] that for the Wagner-Schottky model and the sublattice formalism to be equivalent, the following parameter constraints should be hold:

$$G^{\mathrm{Au}_m\mathrm{Ga}_n}_{\mathrm{Au:Ga}} + G^{\mathrm{Au}_m\mathrm{Ga}_n}_{\mathrm{Ga:Au}} = G^{\mathrm{Au}_m\mathrm{Ga}_n}_{\mathrm{Au:Au}} + G^{\mathrm{Au}_m\mathrm{Ga}_n}_{\mathrm{Ga:Ga}} \tag{13}$$

The number of the parameters is reduced by the following assumption:

$${}^{j}L^{\mathrm{Au}_m\mathrm{Ga}_n}_{\mathrm{Au:Au,Ga}} = {}^{j}L^{\mathrm{Au}_m\mathrm{Ga}_n}_{\mathrm{Ga:Au,Ga}} \tag{14}$$

$${}^{j}L^{\mathrm{Au}_m\mathrm{Ga}_n}_{\mathrm{Au,Ga:Au}} = {}^{j}L^{\mathrm{Au}_m\mathrm{Ga}_n}_{\mathrm{Au,Ga:Ga}} \tag{15}$$

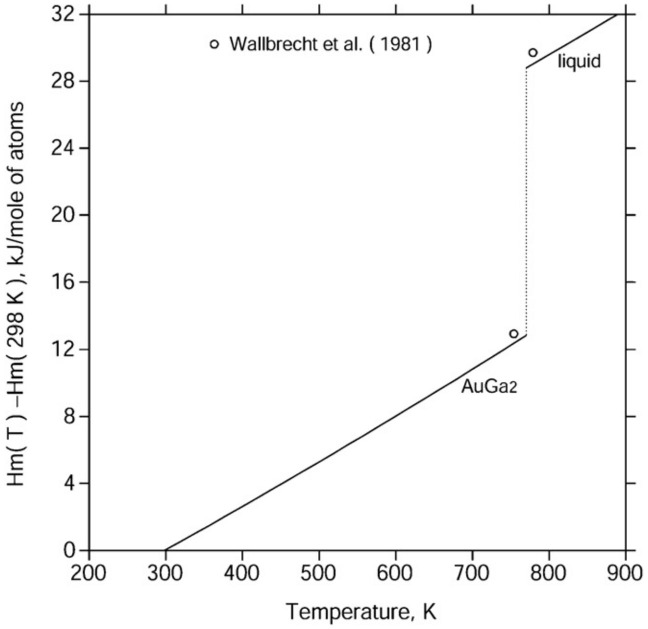

Fig. 10. Calculated $H_m(T) - H_m(298\,\mathrm{K})$ of phase $\mathrm{AuGa_2}$ in the Au–Ga system and comparison with the experimental data [25].

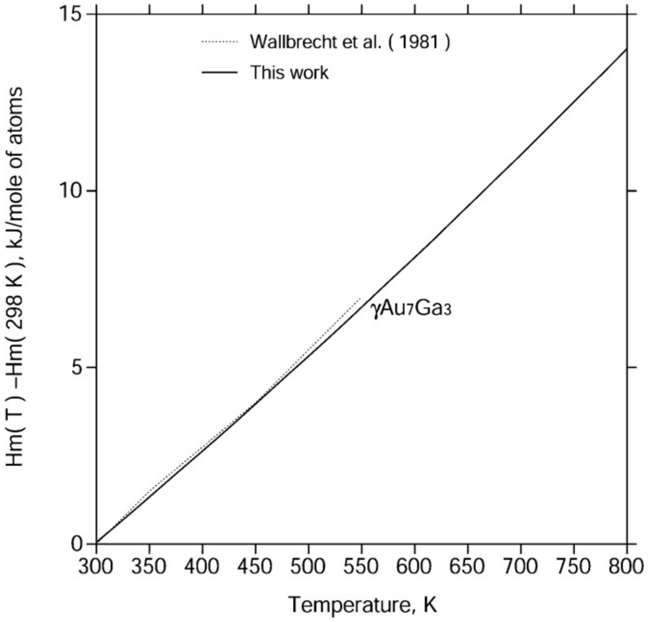

Fig. 11. Calculated $H_m(T) - H_m(298\,\mathrm{K})$ of phase $\gamma\mathrm{Au_7Ga_3}$ in the Au–Ga system and comparison with the experimental data [25].

5. Results and discussions

A thermodynamic description of the Au–Ga system obtained in the present work is shown in Table 1. The Au–Ga phase diagram calculated by means of the thermodynamic parameters is presented in Fig. 1 and nearly identical to the one reported by Weibke and Hesse [5], Cooke and Hume-Rothery [10], and Mouani et al. [17]. Fig. 2 is the enlarged section of Fig. 1.

The invariant equilibria of the Au–Ga system are listed in Table 2. As shown in the table, satisfactory agreement is obtained between the calculations and experiments, where there are some uncertainties in three invariant reaction temperatures: 2 K in

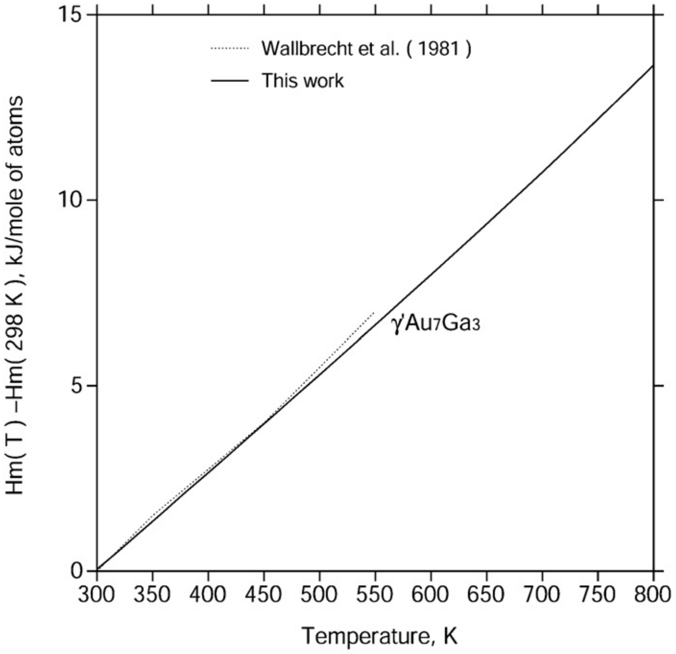

Fig. 12. Calculated $H_m(T) - H_m(298\,\mathrm{K})$ of phase $\gamma'\mathrm{Au_7Ga_3}$ in the Au–Ga system and comparison with the experimental data [25].

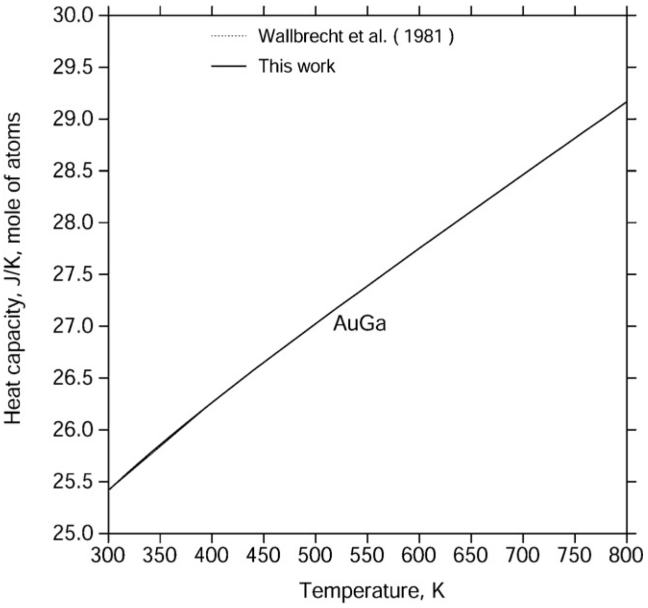

Fig. 13. Calculated heat capacities of phase AuGa in the Au–Ga system and comparison with the experimental data [25].

liq. → $\beta' Au_7Ga_2 + \gamma Au_7Ga_3$ [10], 7 K in liq. → γAu_7Ga_3 + AuGa [10], and 3 K [5] and 5 K [10] in liq. → AuGa + $AuGa_2$. In view of the estimated experimental errors (about 1–2 at.%), 39 of the 42 experimental invariant reaction compositions in the Au–Ga system are well reproduced.

Fig. 3 presents the calculated standard enthalpies of formation in the Au–Ga system at 298 K and comparison with the experimental data [19,20,24]. The reference states are fcc for Au and orthorhombic for Ga. Fig. 4 shows the calculated activities of Au and Ga in 1400 K with the experimental data [19]. Satisfactory agreement is obtained between the calculated results and the experimental data.

Fig. 5 is the calculated enthalpies of mixing in the Au–Ga system at 1468 K with the experiments [18–23]. Satisfactory agreement is obtained between the calculated results and the experimental data [18,19,22,23].

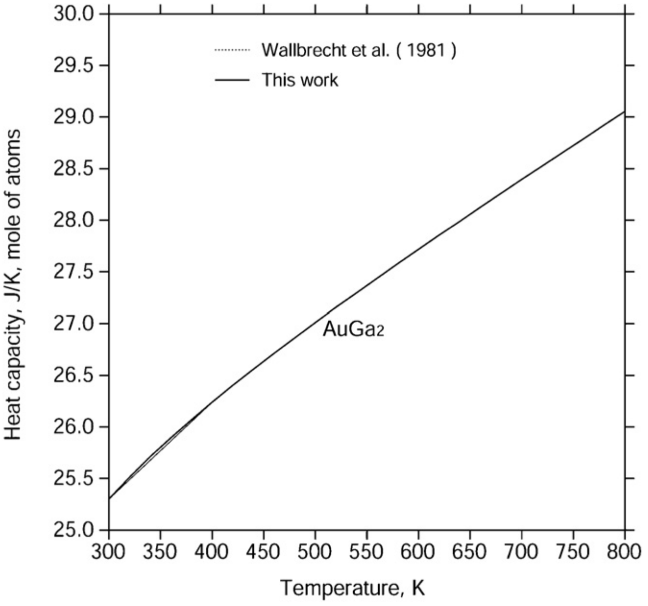

Fig. 14. Calculated heat capacities of phase $AuGa_2$ in the Au–Ga system and comparison with the experimental data [25].

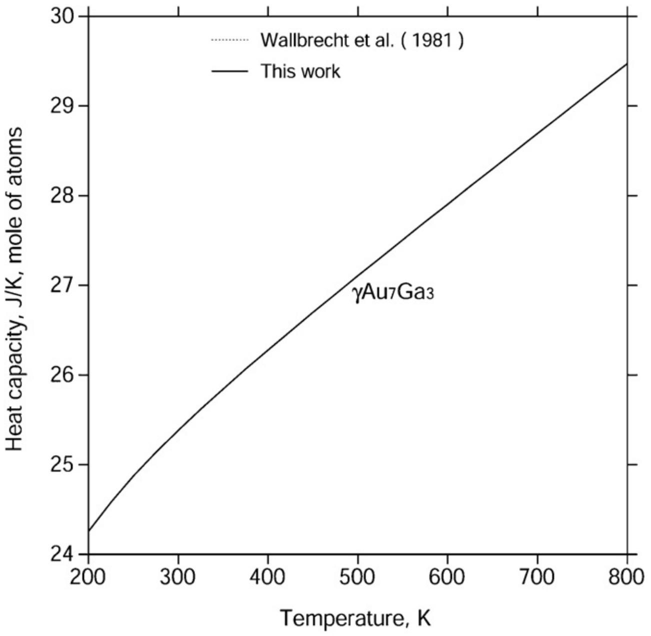

Fig. 15. Calculated heat capacities of phase γAu_7Ga_3 at $x_{Ga} = 0.308$ in the Au–Ga system and comparison with the experimental data [25].

Fig. 6 is the calculated enthalpies of mixing at 750 K in the Au–Ga system with the experimental data [19]. Fig. 7 is the calculated molar Gibbs energies of mixing at 1000 and 1400 K with the experimental data measured by Hayer et al. [23] at 1000 K and Bergman et al. [19] at 1400 K, respectively. Fig. 8 is the calculated excess Gibbs energy in the Au–Ga system at 1000 and 1400 K with the experimental data reported by Predel and Schallner [28] at 1000 K and Hayer et al. [23] at 1400 K, respectively. Reasonable agreement is obtained between the calculated results and the experimental data.

Figs. 9–12 are the calculated enthalpy increments of $H_m(T) - H_m(298\,K)$ for the compounds AuGa and $AuGa_2$ with extrapolated liquid, γAu_7Ga_3 and $\gamma' Au_7Ga_3$, and comparison with the experimental data [25], respectively. Good agreement

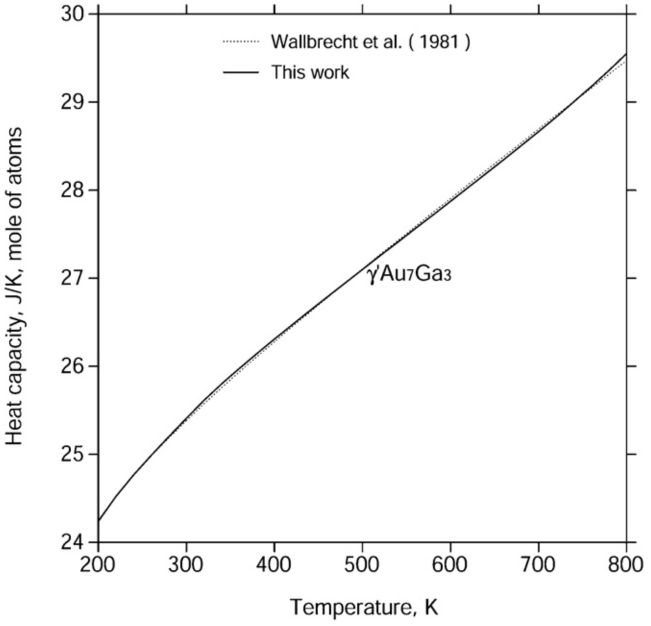

Fig. 16. Calculated heat capacities of phase $\gamma' Au_7Ga_3$ at $x_{Ga} = 0.308$ in the Au–Ga system and comparison with the experimental data [25].

is obtained between the calculated results and the experimental data [25].

Figs. 13–16 present the heat capacities of the compounds AuGa, $AuGa_2$, γAu_7Ga_3 and $\gamma' Au_7Ga_3$ with the experimental data [25], respectively. The calculated results well reproduced the experiments [25]. For $\gamma' Au_7Ga_3$ with a homogeneity range, the calculated heat capacities at $x_{Ga} = 0.308$ have a little deviations with the experiments [25], as shown in Fig. 16.

6. Conclusions

The phase relations and the thermodynamic description of the Au–Ga system were critically evaluated from the experimental information available in the literature. A set of consistent thermodynamic parameters was derived. With the thermodynamic description available, one can now make various calculations of practical interest.

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