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URL : <http://dx.doi.org/10.1016/j.jallcom.2005.05.038>

**To cite this version :**

Wang, Jianhua and Lu, Xiao-Gang and Sundman, B. and Su, Xuping ( 2006)  
[\*Thermodynamic reassessment of the Au-Te system.\*](#) Journal of Alloys and  
Compounds, vol. 407 (n° 1 - 2). pp. 106-111. ISSN 0925-8388

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# Thermodynamic reassessment of the Au–Te system

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## Abstract

The Au–Te binary system has been thermodynamically reassessed using the CALPHAD method. The excess Gibbs energy of the liquid phase was formulated with the Redlich–Kister expression and the AuTe<sub>2</sub> intermetallic phase was treated as a stoichiometric compound. A set of self-consistent thermodynamic parameters for each phase has been obtained. Good agreement is reached between the calculated and experimental results. Additionally, the standard formation enthalpy and enthalpy of fusion of AuTe<sub>2</sub> intermetallic phase have also been calculated.

*Keywords:* Thermodynamic properties; Au–Te system; Phase diagram; CALPHAD

## 1. Introduction

In electrical industry, Au–Te alloy can be used as Au/Te bilayer thin films [1] and Au/Te/Ni thin films for Ohmic contacts to n-type GaAs [2], which possess the lowest contact resistivity. The phase diagram of the Au–Te binary system is well known experimentally and only one intermediate compound exists. There are also experimental data on thermodynamic for this system. The system was previously assessed by Berman and Castanet [3]. Okamoto and Massalski [4] summarized the thermodynamic data before 1979 and gave some suggestions for future experimental research. The previously assessed results were reasonably consistent with the experimental data of the phase boundaries and thermodynamic properties in the Te-rich region. But in the Au-rich region, the consistency between the phase boundaries and thermodynamic properties was poor. The shape of the liquidus in the Au-rich region was difficult to obtain. Following the assessments of this system, new thermodynamic data presented. In view of this, the thermodynamic reassessment of

Au–Te binary system was performed in the present work. A set of self-consistent description of the phase relation and thermodynamic data was obtained by means of the CALPHAD technique [5].

## 2. Thermodynamic models

### 2.1. Solution phases: liquid, fcc and hexagonal phase

The Gibbs energy of the pure element is described relative to the standard element reference (SER), i.e. the enthalpy of the pure element in its stable states at 298.15 K [6].

For fcc (Au) and the hexagonal (Te) phases, no solubility is considered. The liquid phase is described using a substitutional model for which the Gibbs energy of expression is:

$$G_m^\phi = x_{\text{Au}} {}^0G_{\text{Au}}^\phi + x_{\text{Te}} {}^0G_{\text{Te}}^\phi + RT(x_{\text{Au}} \ln x_{\text{Au}} + x_{\text{Te}} \ln x_{\text{Te}}) + {}^E G_m^\phi \quad (1)$$

where  ${}^0G_{\text{Au}}^\phi$  and  ${}^0G_{\text{Te}}^\phi$  are the molar Gibbs energies of the pure elements Au and Te with the structure  $\phi$  in non-magnetic states, respectively, adopted from the work of Dinsdale [6]. The variables  $x_{\text{Au}}$  and  $x_{\text{Te}}$  denote the mole fraction of Au and

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Te, respectively.  ${}^E G_m^\phi$  is the excess Gibbs energy, expressed in the Redlich–Kister polynomial [7] as:

$${}^E G_m^\phi = x_{\text{Au}} x_{\text{Te}} \sum_i {}^i L_{\text{Au,Te}}^\phi (x_{\text{Au}} - x_{\text{Te}})^i \quad (2)$$

where  ${}^i L_{\text{Au,Te}}^\phi$  is the binary interaction parameter evaluated in the present work. It can be temperature dependent and given as follows:

$${}^i L_{\text{Au,Te}}^\phi = A_i + B_i T + C_i T \ln T \quad (3)$$

In order to model the temperature dependence of the enthalpy of mixing of liquid Au–Te alloys in this system, at least  $C_0$  should be non-zero.

## 2.2. Intermetallic compound

The intermetallic compound  $\text{AuTe}_2$  in the Au–Te system is treated as stoichiometric compound because of its very narrow homogeneity range. It is assumed that the Neumann–Kopp rule is valid for this compound. The Gibbs energy of  $\text{AuTe}_2$  phase is formulated as:

$$G^{\text{AuTe}_2} = {}^0 G_{\text{Au}}^{\text{fcc}} + 2 {}^0 G_{\text{Te}}^{\text{hex}} + a + bT$$

where  ${}^0 G_{\text{Au}}^{\text{fcc}}$  and  ${}^0 G_{\text{Te}}^{\text{hex}}$  are Gibbs energies of pure elements of Au and Te in fcc and hexagonal structure, respectively. The parameters  $a$  and  $b$  are optimized in the present work.

## 3. Experimental information

The liquidus of the Au–Te system were determined by Pellini and Quercigh [8] with conventional thermal analysis. Earlier observations by Rose [9] agree with Pellini and Quercigh in the general form of the liquidus. But Rose’s result on the melting point of Te is low and the data show more scatter than those of Pellini and Quercigh. Bergman and Castanet [3] determined the liquidus using the breaks on the isothermal enthalpy-of-formation curve versus mole fraction of Te. The eutectic temperatures and compositions were determined by Pellini [8], Rose [9], Pelabon [10] and Bergman and Castanet [3] using thermal analysis. The formation of the  $\text{AuTe}_2$  compound by alloying was first observed by Rose [9] using the thermal and microscopic methods. Coste [11] confirmed the existence of this phase by metallographic observations and electrochemical potential measurements in several Au–Te alloys. Cabri [12] confirmed that the solubility is less than 0.46 at.% Te and no solubility of Au in  $\text{AuTe}_2$  compound using the method of Lattice parameter measurements. Veale and Barrett [13] also estimated the solid solubility limits of this phase from the breaks of vapor pressure versus composition curves. The melting temperature of  $\text{AuTe}_2$  compound was determined by conventional and differential thermal analysis [3,8,9].

The enthalpy of mixing of liquid Au–Te alloys was determined by calorimetric measurements at 737 K [14], 751, 819,

Table 1

The optimized parameters describing the thermodynamic properties of the Au–Te system<sup>a</sup>

Liquid:

$${}^0 L_{\text{Au,Ni}}^{\text{Liq}} = -10472 + 63.941T - 9.329T \ln T$$

$${}^1 L_{\text{Au,Te}}^{\text{Liq}} = 6822$$

$${}^2 L_{\text{Au,Te}}^{\text{Liq}} = 8477$$

$\text{AuTe}_2$ :

$${}^0 G_{\text{Au,Te}}^{\text{AuTe}_2} - {}^0 G_{\text{Au}}^{\text{fcc}} - 2 {}^0 G_{\text{Te}}^{\text{hex}} = -11\,808 - 2.416T$$

<sup>a</sup> The values are given in SI units per mole of atoms.

872, 955, 1000 K [15], 737, 1103 and 1200 K [3], 769 K [16], and at 1281 K [17]. The agreement of the data between [3] and [17] is poor and the data at 1103 K is too negative. So the enthalpies at 1103 K and 1200 K [3] and 1281 K [17] were not used in the optimization. The enthalpy of mixing of liquid Au–Te alloys measured by Ishida et al. [16] for 60–100 at.% Te is in very good agreement with the results of Castanet et al. [14]. Bergman and Castanet [3] deduced an enthalpy versus composition expression from their data obtained at 737 K and the experiment results of [14,16]. Because of the qualitative agreements with the phase diagram and the preferable experimental method, the results of Castanet et al. [14], Bergman and Castanet [3] (except that at 1103 K and 1200 K), and Yassin and Castanet [15] were accepted for thermodynamic assessment.

Predel and Piehl [17] determined the activity of Te in liquid Au–Te alloys through almost the complete composition range from measurements of the partial vapor pressures. Yassin et al. [18] deduced the activity of Te from the measurements of the vapor pressure of Te over the Au–Te melts

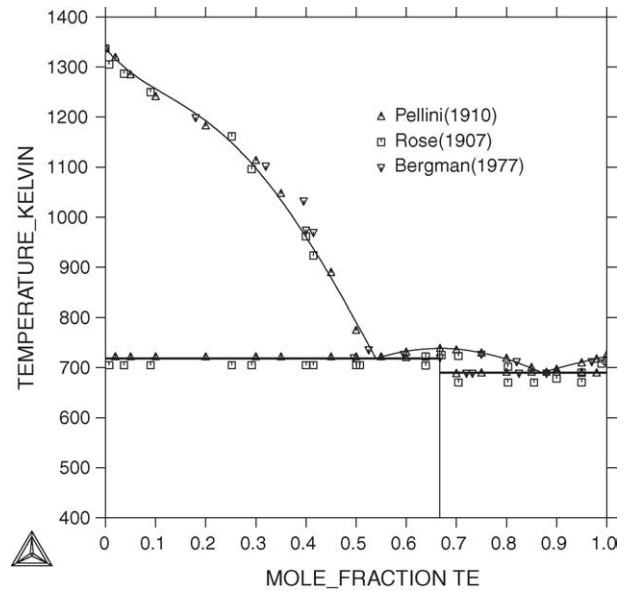


Fig. 1. The Au–Te phase diagram calculated from the present thermodynamic description in comparison with experimental measurements [10–15] and [18–20].

Table 2  
Experimental and calculated phase equilibria data in Au–Te system

Invariant reaction liquid	Reaction type	Experiment data			Calculated data	
		$T$ (K)	Te in liquid (at.%)	Ref.	$T$ (K)	Te in liquid (at.%)
Liquid = fcc (Au) + AuTe <sub>2</sub>	Eutectic	705	0.50	[9]	718.4	0.5394
		720	0.53	[8]		
		721		[3]		
		725	0.547	[10]		
Liquid = hex (Te) + AuTe <sub>2</sub>	Eutectic	670	0.857	[9]	689.9	0.8707
		688	0.887	[10]		
		689	0.88	[8]		
		690		[3]		
Liquid = AuTe <sub>2</sub>	Congruent	737		[8]	738.4	
		725		[9]		
		736		[3]		

in the 0.48–0.67 at.% Te. They also measured the heat content of four Au–Te alloys in the solid and liquid from 298 K to  $T$  ( $400\text{ K} < T < 900\text{ K}$ ) on heating (drop method) with the help of a high temperature Tian-Calvet calorimeter [19]. Anres et al. [20] measured the heat content of solid and liquid AuTe<sub>2</sub> from 298 K to  $T$  ( $471\text{ K} < T < 1022\text{ K}$ ) using the same method as Yassin et al. They obtained the enthalpy of formation of AuTe<sub>2</sub> compound at 298 K ( $-3.0\text{ kJ}$  per mole of atoms) and the enthalpy of fusion ( $19.1\text{ kJ}$  per mole of atoms). The enthalpy of formation of AuTe<sub>2</sub> compound at 728 K is  $-2.5\text{ kJ}$  per mole of atoms and the enthalpy of fusion at 737 K is  $18.6\text{ kJ}$  per mole of atoms, which were measured by direct reaction calorimetry [3]. The data for enthalpy of formation of AuTe<sub>2</sub> obtained from vapor pressure measurements by Andon et al. [21] and Veale and Barrett [13] are  $-4.74$  and  $-3.91\text{ kJ}$  per mole atoms, respectively, at 298 K.

#### 4. Assessment procedure

Most of the experimental data mentioned above were used in the thermodynamic evaluation. The optimization was carried out by using Thermo-Calc [22]. Each piece of the selected information was given a certain weight by personal judgment, and changed by trial and error during the assessment, until most of the selected experimental information was reproduced within the expected uncertainty limits.

The optimization was carried out step by step. The parameters for the AuTe<sub>2</sub> phase were first optimized using thermodynamic data of AuTe<sub>2</sub> compound. The liquid phase was then investigated by considering the thermodynamic data of the liquid Au–Te alloys and the data of liquidus correspond to fcc Au and hexagonal Te.

All the parameters were finally evaluated together using all thermodynamic and phase diagram data to give the best

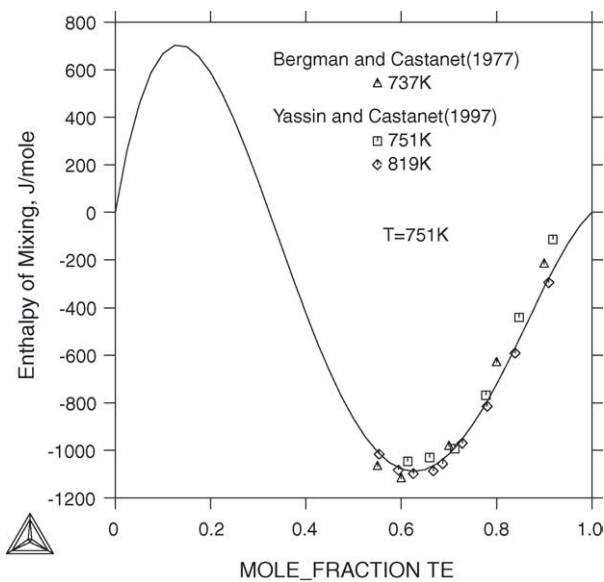


Fig. 2. The calculated enthalpy of formation of liquid Au–Te alloy at 751 K compared with various experimental measurements [3,15].

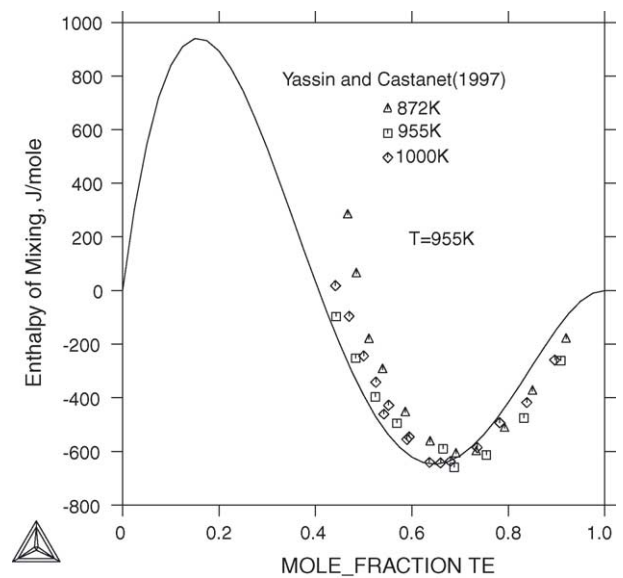


Fig. 3. The calculated enthalpy of formation of liquid Au–Te alloy at 955 K compared with experimental measurements [15].

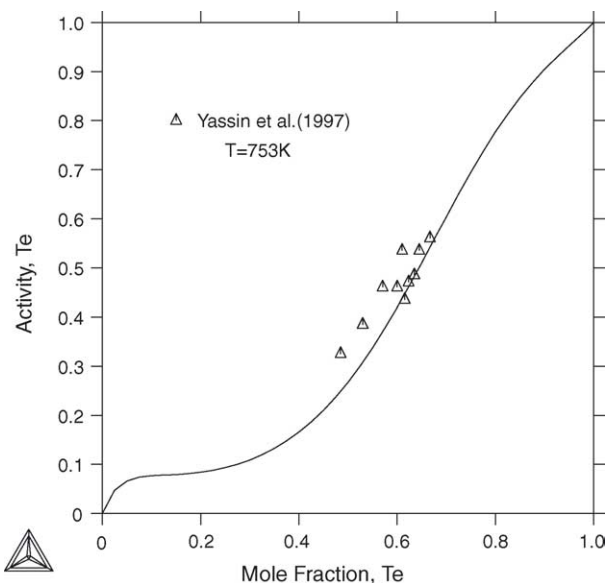


Fig. 4. The calculated activities of liquid Au-Te alloy at 753 K compared with experimental measurements [18].

description of the system. All evaluated parameters are listed in Table 1.

## 5. Results and discussion

The assessed Au-Te phase diagram is shown in Fig. 1. The calculated phase diagram is in good agreement with the experimental data reported by Bergman and Castanet [3], Pellini and Quercigh [8], and Rose [9]. All invariant equilibria in the system are reproduced and listed in Table 2. The temperatures and compositions of the two eutectic reactions

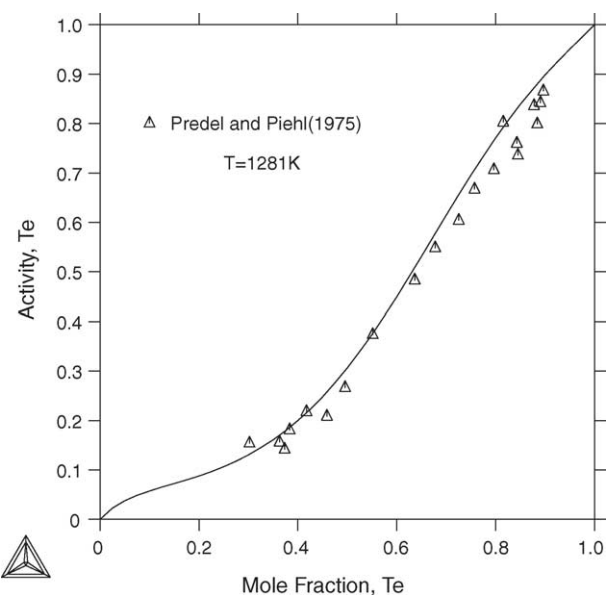


Fig. 5. The calculated activities of liquid Au-Te alloy at 1281 K compared with experimental measurements [17].

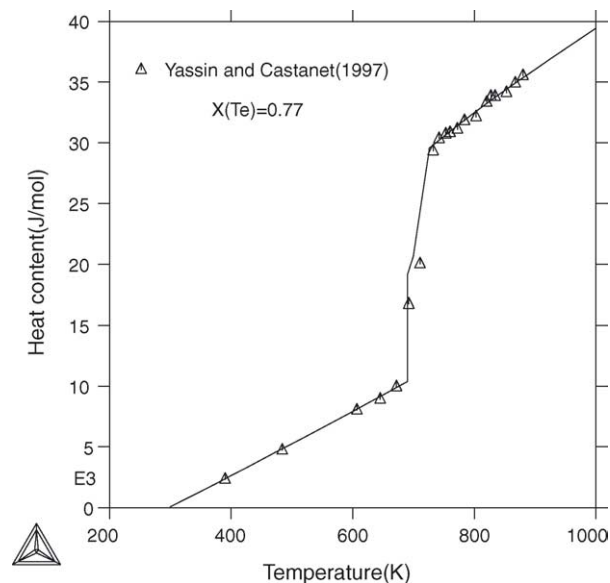


Fig. 6. The calculated Heat content of Au-Te alloy at 77 at.% Te compared with experimental measurements [19].

agree well with those given by [3,8-10]. The assessed congruent temperature of  $\text{AuTe}_2$  agrees well with those obtained by [3,8].

The assessed enthalpies of formation of liquid Au-Te alloys referring to liquid components at 751 K and 955 K are plotted in Figs. 2 and 3, respectively. Also shown in Figs. 2 and 3 are the data from Bergman and Castanet [3], and Yassin and Castanet [15]. The assessed activities of liquid Au-Te alloys at 753 K and 1281 K are plotted in Figs. 4 and 5, respectively. Also shown in Figs. 4 and 5 are the experimental data from Yassin et al. [18], and Predel and Piehl [17]. As can be seen, the calculation enthalpies and activities

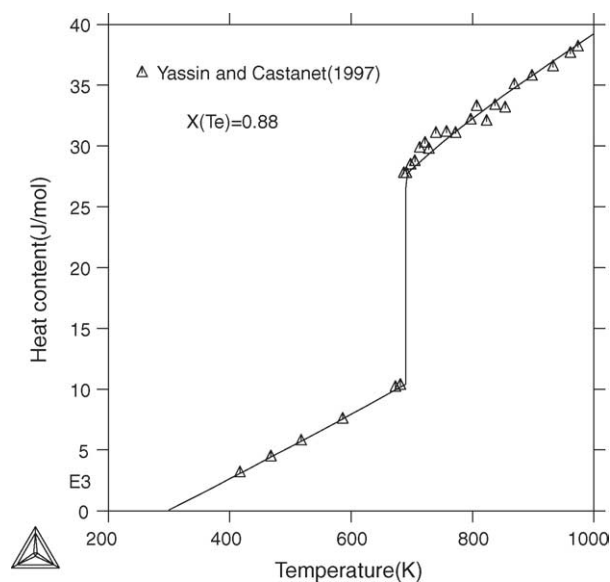


Fig. 7. The calculated Heat content of Au-Te alloy at 88 at.% Te compared with experimental measurements [19].

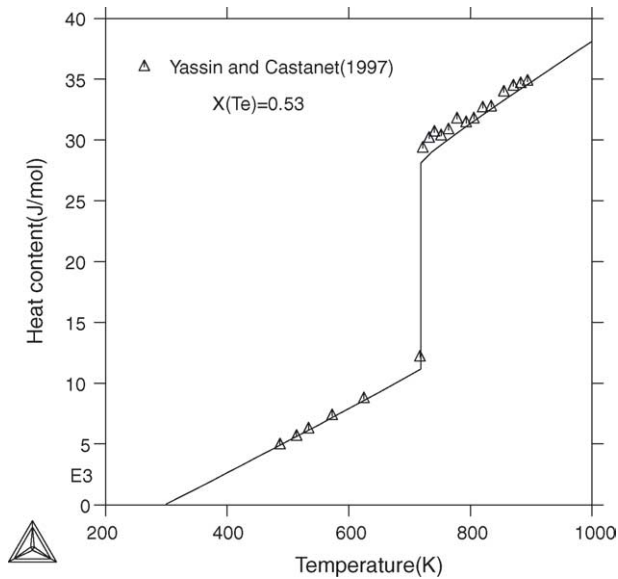


Fig. 8. The calculated Heat content of Au–Te alloy at 53 at.% Te compared with experimental measurements [19].

of liquid Au–Te alloys at different temperature agree well with experimental data. Figs. 6–9 show the assessed heat content of Au–Te alloys at different compositions compared with their experimental measurements [19], the data are well reproduced. The assessed heat content of AuTe<sub>2</sub> compound is plotted in Fig. 10. The calculated heat content of AuTe<sub>2</sub> compound agrees well with the experimental data [20]. It can be seen that the Neumann-Kopp rule is valid for the AuTe<sub>2</sub> compound. The calculated enthalpy of formation of AuTe<sub>2</sub> is  $-3.936$  kJ per mole atoms, which is close to the result of Veale and Barrett [13] ( $-3.91$  kJ per mole atoms). The cal-

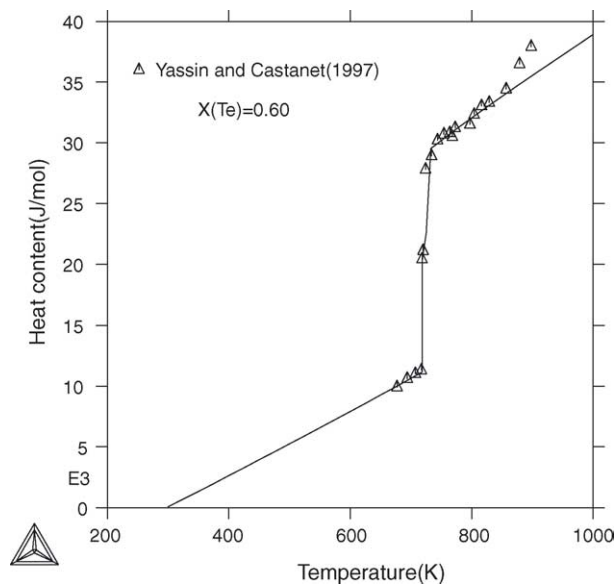


Fig. 9. The calculated Heat content of Au–Te alloy at 60 at.% Te compared with experimental measurements [19].

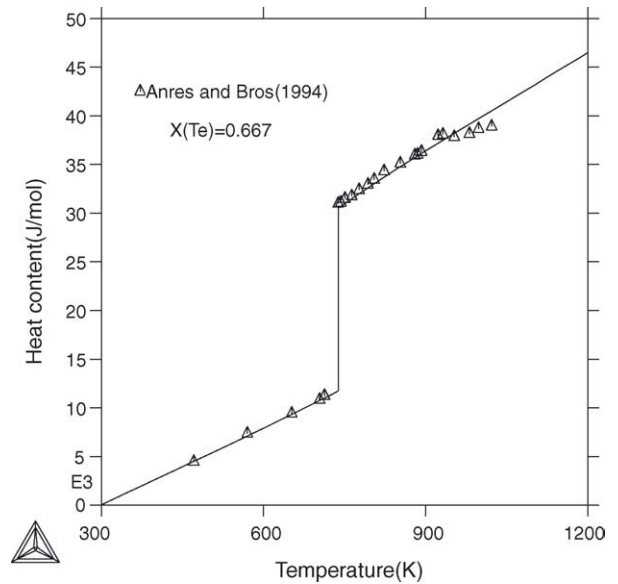


Fig. 10. The calculated Heat content of Au–Te alloy at 66.7 at.% Te compared with experimental measurements [20].

culated enthalpy of fusion of AuTe<sub>2</sub> is  $18.772$  kJ per mole of atoms, which is almost the same as the result obtained by direct reaction calorimetry [3] ( $18.6$  kJ per mole of atoms).

## 6. Conclusions

Based on the experimental information available in the literature, the phase relations and thermodynamic properties in the system Au–Te were evaluated. A consistent set of thermodynamic parameters was derived for describing the Gibbs energies of liquid phase and AuTe<sub>2</sub> in this system. The calculated phase equilibria agree well with the experimental data. The calculated enthalpy of formation and fusion of AuTe<sub>2</sub> compound is  $-3.936$  and  $18.772$  kJ per mole atoms, respectively.

## Acknowledgements

One of the authors (Jianhua Wang) is grateful for financial support by China Scholarship Council and Swedish Institute of Sweden government for his visit to the Royal Institute of Technology, where the present work was conducted. The authors are grateful to Dr. Huahai Mao and Dr. Lidong Teng for their support during this work.

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