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## Thermodynamic modeling of the Pb–U and Pb–Pu systems

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### ABSTRACT

The thermodynamic assessments of the Pb–U and Pb–Pu binary systems were carried out using the CALPHAD (calculation of phase diagrams) method based on experimental data for thermodynamic properties and phase equilibria. The Gibbs free energies of the liquid, bcc, fcc, ( $\alpha$ U), ( $\beta$ U), ( $\delta$ 'Pu), ( $\gamma$ Pu), ( $\beta$ Pu) and ( $\alpha$ Pu) phases were described by a subregular solution model with the Redlich–Kister equation, and those of the intermetallic compounds ( $\text{Pb}_3\text{U}$ ,  $\text{PbU}$ ,  $\text{PbPu}_3$ ,  $\text{Pb}_3\text{Pu}_5$ ,  $\text{Pb}_4\text{Pu}_5$ ,  $\text{Pb}_5\text{Pu}_4$ ,  $\alpha\text{Pb}_2\text{Pu}$ ,  $\beta\text{Pb}_2\text{Pu}$  and  $\text{Pb}_3\text{Pu}$ ) by a two-sublattice model. The thermodynamic parameters for the two binary systems were optimized to consistently reproduce the available experimental data with satisfactory agreement.

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### 1. Introduction

A good understanding of nuclear materials is important to develop a safe nuclear reactor with high efficiency [1,2], and the investigation of phase diagrams is essential for the development of new nuclear materials. Our goal is to develop a database of thermodynamic data and phase diagrams for nuclear materials. However, traditional methods of materials research solely based on experimental investigations are far from being suitable for probing nuclear materials properties because of the stringent experimental conditions. A better approach is to investigate first the relevant phase diagrams of nuclear materials that are crucial for the development of advanced nuclear fuels. The present authors, therefore, have been conducting thermodynamic assessments in nuclear material systems using CALPHAD (calculation of phase diagrams) technique [3–9]. As a part of this thermodynamic database, the present work focuses on thermodynamic assessment of the Pb–U and Pb–Pu phase diagrams based on the CALPHAD method from available experimental data. Uranium (U) and plutonium (Pu) are the most common fissile elements in the nuclear fuel, and lead (Pb) is a primary coolant and spallation target material for the next generation of accelerator-driven systems (ADS) [10–12]. Thus, it is important to evaluate the interaction between metal fuel and lead coolant. In this work the phase diagram and the thermodynamic data for the Pb–U and Pb–Pu systems are assessed.

### 2. Thermodynamic model

#### 2.1. Modeling procedure

Optimization of the thermodynamic parameters describing the Gibbs free energies of each phase is carried out using the PARROT module of the Thermo-Calc software [13], a computer program that can accept different types of data, such as thermodynamic quantities and phase equilibria. Each selected data is given a certain weight and the weight can be changed until a satisfactory description for most of the selected data is achieved. The information on stable phases and the used models for the Pb–U and Pb–Pu systems is listed in Table 1.

#### 2.2. Solution phases

The Gibbs free energies of the solution phases of the Pb–Me (Me:Pu, U) systems were described by a subregular solution model [14]. The molar Gibbs free energy of each solution phase in the Pb–Me system was given as follows:

$$G_m^\phi = \sum_{i=\text{Pb,Me}} {}^0G_i^\phi x_i + RT \sum_{i=\text{Pb,Me}} x_i \ln x_i + {}^E G_m^\phi, \quad (1)$$

where  ${}^0G_i^\phi$  is the molar Gibbs free energy of pure component  $i$  with respect to their respective reference state  $\phi$  phase, which was taken from the SSOL4 database [15].  $R$  is the gas constant,  $T$  is the absolute temperature in Kelvin, and  $x_i$  denotes the mole fraction of component  $i$ . The term  ${}^E G_m^\phi$  is the excess energy, which was expressed by a Redlich–Kister polynomials [16] as:

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**Table 1**  
The stable phases and the models used for the Pb–U and Pb–Pu systems.

System	Phase	Prototype	Strukturbericht designation	Modeling phase	Used models
Pb–U	(Pb)	Cu	A1	(Pb, U)	Subregular solution model
	Pb <sub>3</sub> U	AuCu <sub>3</sub>	L1 <sub>2</sub>	(Pb) <sub>3</sub> (U) <sub>1</sub>	Two-sublattice model
	PbU	PbU	–	(Pb) <sub>1</sub> (U) <sub>1</sub>	Two-sublattice model
	γU	W	A2	(Pb, U)	Subregular solution model
	βU	βU	A <sub>b</sub>	(Pb, U)	Subregular solution model
	αU	αU	A20	(Pb, U)	Subregular solution model
	Liquid	–	–	(Pb, U)	Subregular solution model
Pb–Pu	(Pb)	Cu	A1	(Pb, Pu)	Subregular solution model
	PbPu <sub>3</sub>	AuCu <sub>3</sub>	L1 <sub>2</sub>	(Pb) <sub>1</sub> (Pu) <sub>3</sub>	Two-sublattice model
	Pb <sub>3</sub> Pu <sub>5</sub>	Si <sub>3</sub> W <sub>5</sub>	D8 <sub>m</sub>	(Pb) <sub>3</sub> (Pu) <sub>5</sub>	Two-sublattice model
	Pb <sub>4</sub> Pu <sub>5</sub>	Ga <sub>4</sub> Ti <sub>5</sub>	–	(Pb) <sub>4</sub> (Pu) <sub>5</sub>	Two-sublattice model
	Pb <sub>5</sub> Pu <sub>4</sub>	–	–	(Pb, Pu) <sub>5</sub> (Pb, Pu) <sub>4</sub>	Two-sublattice model
	βPb <sub>2</sub> Pu	–	–	(Pb) <sub>2</sub> (Pu) <sub>1</sub>	Two-sublattice model
	αPb <sub>2</sub> Pu	Ga <sub>2</sub> Hf	–	(Pb) <sub>2</sub> (Pu) <sub>1</sub>	Two-sublattice model
	Pb <sub>3</sub> Pu	AuCu <sub>3</sub>	L1 <sub>2</sub>	(Pb) <sub>3</sub> (Pu) <sub>1</sub>	Two-sublattice model
	εPu	W	A2	(Pb, Pu)	Subregular solution model
	δ'Pu	In	A6	(Pb, Pu)	Subregular solution model
	δPu	Cu	A1	(Pb, Pu)	Subregular solution model
	γPu	–	–	(Pb, Pu)	Subregular solution model
	βPu	–	–	(Pb, Pu)	Subregular solution model
	αPu	–	–	(Pb, Pu)	Subregular solution model
	Liquid	–	–	(Pb, Pu)	Subregular solution model

$${}^E G_m^\phi = x_{\text{Pb}} x_{\text{Me}} \sum_{m=0}^n m L_{\text{Pb,Me}}^\phi (x_{\text{Pb}} - x_{\text{Me}})^m, \quad (2)$$

The  $x_{\text{Pb}}$  and  $x_{\text{Me}}$  are the mole fractions of Pb and Me components, and  $m L_{\text{Pb,Me}}^\phi$  is the interaction energy between Pb and Me atoms, and was expressed as:

$$m L_{\text{Pb,Me}}^\phi = a_m + b_m T. \quad (3)$$

The parameters  $a_m$  and  $b_m$  were evaluated from experimental data in the present work.

### 2.3. Stoichiometric intermetallic compounds

The Pb<sub>3</sub>U, PbU, PbPu<sub>3</sub>, Pb<sub>3</sub>Pu<sub>5</sub>, Pb<sub>4</sub>Pu<sub>5</sub>, αPb<sub>2</sub>Pu, βPb<sub>2</sub>Pu and Pb<sub>3</sub>Pu compounds were treated as stoichiometric phases. The Gibbs free energy of formation per mole of formula unit (Pb)<sub>m</sub>(Me)<sub>n</sub> can be expressed by a two-sublattice model [17] by the following equation with reference to the pure elements in their non-magnetic state:

$$\Delta G_f^{\text{Pb}_m\text{Me}_n} = {}^0 G_{\text{Pb}_m\text{Me}_n}^{\text{ref}} - m {}^0 G_{\text{Pb}}^{\text{ref}} - n {}^0 G_{\text{Me}}^{\text{ref}} = a' + b'T, \quad (4)$$

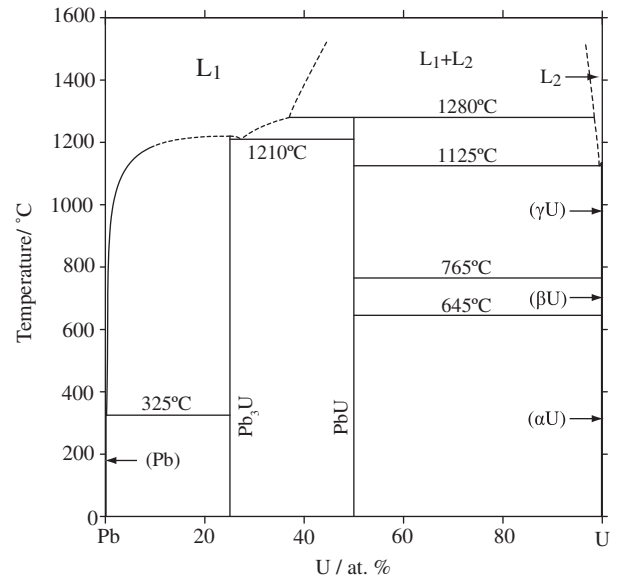
where  $\Delta G_f^{\text{Pb}_m\text{Me}_n}$  denotes the standard Gibbs free energy of formation of the stoichiometric compound with reference to the pure elements. The terms  ${}^0 G_{\text{Pb}}^{\text{ref}}$  and  ${}^0 G_{\text{Me}}^{\text{ref}}$  are the molar Gibbs free energy of pure element Pb and Me with its defined reference structure in a non-magnetic state. The parameters  $a'$  and  $b'$  were evaluated in the present optimization.

### 2.4. Non-stoichiometric intermetallic phases

The Pb<sub>5</sub>Pu<sub>4</sub> phase in the Pb–Pu binary system was treated as a non-stoichiometric intermetallic phase, because there was a significant composition range in the Pb<sub>5</sub>Pu<sub>4</sub> phase at higher temperatures [18]. The Gibbs free energy of the Pb<sub>5</sub>Pu<sub>4</sub> phase was also described by a two-sublattice model [17]. The Gibbs free energy of formation per mole of formula unit (Pb, Pu)<sub>5</sub>(Pb, Pu)<sub>4</sub> can be expressed as the following equation with reference to the pure elements in their non-magnetic state:

$$\begin{aligned} G_m^{\text{Pb}_5\text{Pu}_4} = & y_{\text{Pb}}^{\text{I}} y_{\text{Pb}}^{\text{II}} {}^0 G_{\text{Pb:Pb}} + y_{\text{Pb}}^{\text{I}} y_{\text{Pu}}^{\text{II}} {}^0 G_{\text{Pb:Pu}} + y_{\text{Pu}}^{\text{I}} y_{\text{Pb}}^{\text{II}} {}^0 G_{\text{Pu:Pb}} + y_{\text{Pu}}^{\text{I}} y_{\text{Pu}}^{\text{II}} {}^0 G_{\text{Pu:Pu}} \\ & + 5RT (y_{\text{Pb}}^{\text{I}} \ln y_{\text{Pb}}^{\text{I}} + y_{\text{Pu}}^{\text{I}} \ln y_{\text{Pu}}^{\text{I}}) + 4RT (y_{\text{Pb}}^{\text{II}} \ln y_{\text{Pb}}^{\text{II}} + y_{\text{Pu}}^{\text{II}} \ln y_{\text{Pu}}^{\text{II}}) \\ & + 5y_{\text{Pb}}^{\text{I}} y_{\text{Pu}}^{\text{I}} \left[ y_{\text{Pb}}^{\text{II}} \sum_n L_{\text{Pb, Pu:Pb}} (y_{\text{Pb}}^{\text{I}} - y_{\text{Pu}}^{\text{I}})^n + y_{\text{Pu}}^{\text{II}} \sum_n L_{\text{Pb, Pu:Pu}} (y_{\text{Pb}}^{\text{I}} - y_{\text{Pu}}^{\text{I}})^n \right] \\ & + 4y_{\text{Pb}}^{\text{II}} y_{\text{Pu}}^{\text{II}} \left[ y_{\text{Pb}}^{\text{I}} \sum_n L_{\text{Pb:Pu, Pb}} (y_{\text{Pb}}^{\text{II}} - y_{\text{Pu}}^{\text{II}})^n + y_{\text{Pu}}^{\text{I}} \sum_n L_{\text{Pu:Pu, Pu}} (y_{\text{Pb}}^{\text{II}} - y_{\text{Pu}}^{\text{II}})^n \right], \end{aligned} \quad (5)$$

where  $y_i^{\text{I}}$  and  $y_j^{\text{II}}$  are the site fractions of component  $i$  and  $j$  ( $i, j = \text{Pb, Pu}$ ) located on sublattice I and II, respectively, and the parameters  ${}^0 G_{ij}$  represents the Gibbs free energy of the compound phase when the two sublattices are occupied by element  $i$  or  $j$ .  $L_{i:\text{Pb, Pu}}$  and  $L_{\text{Pb, Pu}:j}$  are the interaction parameter between Pb and Pu in the second or first sublattice, when the other sublattice is occupied by element  $i$  or  $j$ .  ${}^0 G_{ij}$ ,  $L_{i:\text{Pb, Pu}}$  and  $L_{\text{Pb, Pu}:j}$  were evaluated in the present work.



**Fig. 1.** The Pb–U phase diagram reviewed by Sheldon et al. [23].

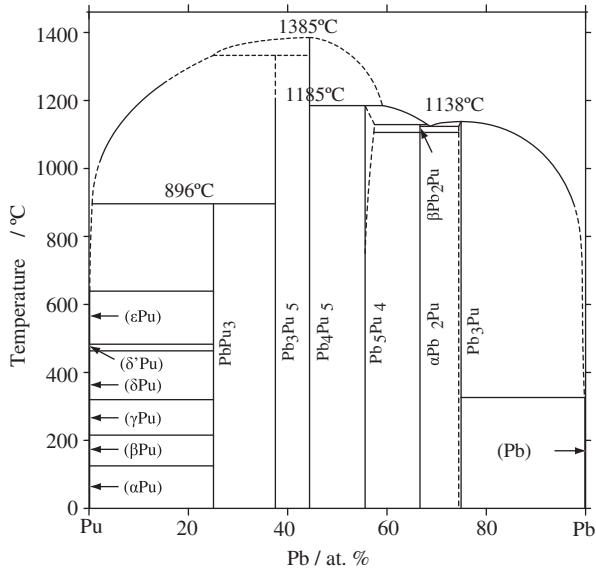


Fig. 2. The Pb–Pu phase diagram reviewed by Foltyn et al. [29].

### 3. Experimental information

#### 3.1. The Pb–U system

The phase diagram of the Pb–U system has been investigated by many researchers [18–23]. The first comprehensive investigation of the phase diagram in the Pb–U system was published by Teitel [19]. Teitel’s investigation [19] of the Pb<sub>3</sub>U phase gives a melting point in the 1210–1250 °C temperature range with a recommended value of 1220 °C. Teitel [19] also found that there is a liquid miscibility gap above 1280 °C and little solubility of U in the Pb phase or Pb in the U-rich phases ((αU), (βU), (γU)) by X-ray diffraction, metallographic observation and thermal analysis. However, the accurate solubility range of the liquid miscibility gap was not determined due to experimental difficulties.

Much later, the Pb–U phase diagram was reviewed by Sheldon et al. [23] as shown in Fig. 1. The reviewed phase diagram consists of five solution phases (liquid, (Pb), (αU), (βU), (γU)) and two intermetallic compounds (Pb<sub>3</sub>U and PbU). It also includes three eutectic reactions ( $L \leftrightarrow (Pb) + Pb_3U$ ,  $L \leftrightarrow Pb_3U + PbU$  and  $L \leftrightarrow Pb-U + (\gamma U)$ ), a

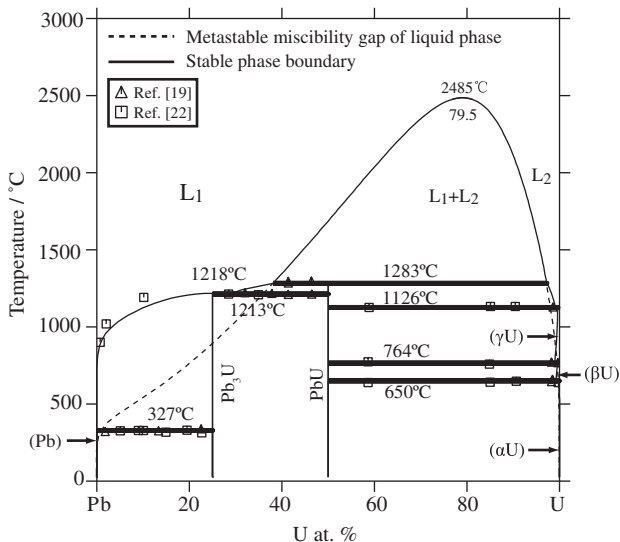


Fig. 3. Calculated Pb–U phase diagram with experimental data [19,22].

disputed syntectic reaction ( $L1 + L2 \leftrightarrow PbU$ ) and a phase separation in the liquid phase at higher temperatures.

In addition, the enthalpies and entropies of formation of the compounds (Pb<sub>3</sub>U and PbU) in the temperature range from 375 °C to 954 °C have been determined using vapour pressure measurement and EMF method respectively by many researchers [24–26]. Based on the above results, Chiotti et al. [27] calculated the enthalpies and entropies of formation of the compounds Pb<sub>3</sub>U and PbU phases.

#### 3.2. The Pb–Pu system

The most recent studies on the Pb–Pu system were reported by Wood et al. [18] and Nickerson [28] using differential thermal

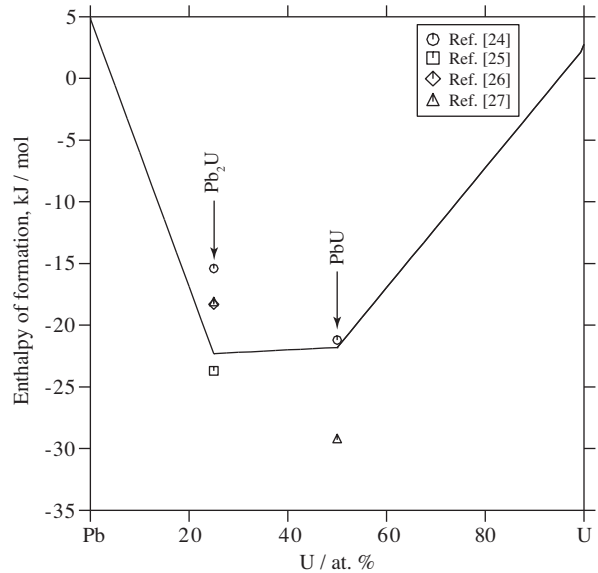


Fig. 4. Calculated enthalpies of formation of the intermetallic compounds at 677 °C in the Pb–U system compared with the experimental data [24–27]: the reference states are (αU) and fcc Pb phases.

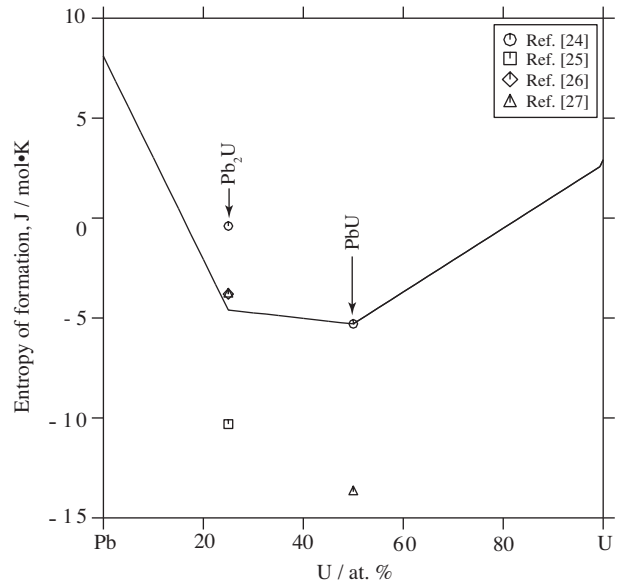
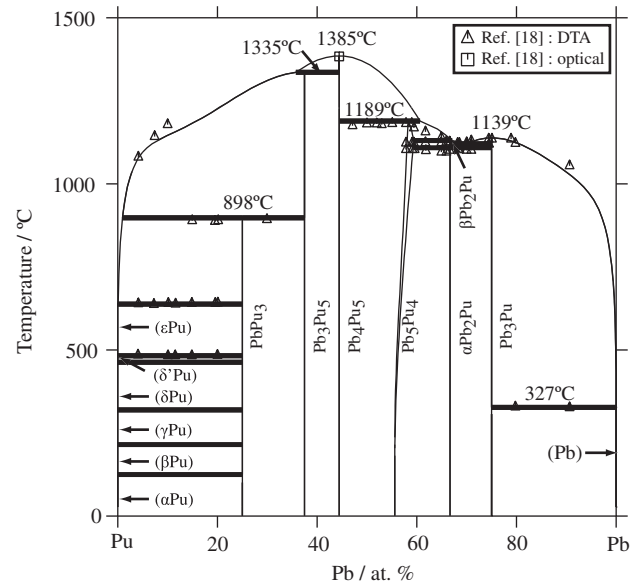


Fig. 5. Calculated entropies of formation of the intermetallic compounds at 677 °C in the Pb–U system compared with the experimental data [24–27]: the reference states are (αU) and fcc Pb phases.

**Table 2**  
Parameters for each phase of the Pb–U system optimized in this work.

Parameters in each phase (J/mol) with temperature $T$ in Kelvin	
Liquid phase, format (Pb, U) <sub>1</sub>	
${}^0L_{\text{Pb,U}}^{\text{Liq}}$	$= 81,158.96 - 47.628T$
${}^1L_{\text{Pb,U}}^{\text{Liq}}$	$= -21,756.49 - 16.5T$
${}^2L_{\text{Pb,U}}^{\text{Liq}}$	$= -20,700.2 + 9.61T$
${}^3L_{\text{Pb,U}}^{\text{Liq}}$	$= 17,000$
A2 $\gamma$ U phase, format (Pb, U) <sub>1</sub> (Va) <sub>3</sub>	
${}^0G_{\text{Pb,U}}^{\text{bcc}}$	$= -24,950 + 45T$
${}^1L_{\text{Pb,U}}^{\text{bcc}}$	$= 62,133 - 44T$
A <sub>b</sub> $\beta$ U phase, format (Pb, U) <sub>1</sub>	
${}^0G_{\text{Pb}}^{\beta\text{U}}$	$= {}^0G_{\text{Pb}}^{\text{fcc}} + 5000$
${}^0L_{\text{Pb,U}}^{\beta\text{U}}$	$= -26,820 + 50T$
${}^1L_{\text{Pb,U}}^{\beta\text{U}}$	$= 67,820 - 50T$
A20 $\alpha$ U phase, format (Pb, U) <sub>1</sub>	
${}^0G_{\text{Pb}}^{\alpha\text{U}}$	$= {}^0G_{\text{Pb}}^{\text{fcc}} + 20,000$
${}^0L_{\text{Pb,U}}^{\alpha\text{U}}$	$= 0$
A1 (Pb) phase, format (Pb, U) <sub>1</sub> (Va) <sub>1</sub>	
${}^0L_{\text{Pb,U}}^{\text{fcc}}$	$= 0$
Pb <sub>3</sub> U phase, format (Pb) <sub>0.75</sub> (U) <sub>0.25</sub>	
${}^0G_{\text{Pb,U}}^{\text{Pb}_3\text{U}}$	$= -22,300 + 4.6T + 0.75{}^0G_{\text{Pb}}^{\text{fcc}} + 0.25{}^0G_{\text{U}}^{\alpha\text{U}}$
Pb–U phase, format (Pb) <sub>0.5</sub> (U) <sub>0.5</sub>	
${}^0G_{\text{Pb,U}}^{\text{Pb-U}}$	$= -21,800 + 5.3T + 0.5{}^0G_{\text{Pb}}^{\text{fcc}} + 0.5{}^0G_{\text{U}}^{\alpha\text{U}}$



**Fig. 6.** Calculated Pb–Pu phase diagram with experimental data [18].

No experimental thermodynamic data for the compounds in the Pb–Pu system is available, but Chiotti [27] calculated the Gibbs energy of formation of the Pb<sub>3</sub>Pu phase between 650 °C and 775 °C based on the data of Cafasso et al. [30].

#### 4. Optimized results and discussion

##### 4.1. The Pb–U system

The calculated Pb–U phase diagram with the experimental data [19,22] is shown in Fig. 3. This figure also shows the metastable liquid miscibility gap at lower temperatures with dashed lines. The calculated phase diagram was in agreement with the experimental data [19,22]. The calculated stable liquid miscibility gap region was between 38 and 97.2 at.% U, which agrees well with the experimental data [19]. The calculated critical composition and temperature of the liquid miscibility gap were 79.5 U at.% and 2485 °C, respectively. The calculated melting point of the Pb<sub>3</sub>U phase was 1218 °C, which agrees with the result of Teitel [19]. In the U-rich region, little solubility of Pb in the (βU) and

**Table 3**  
A comparison between the calculated invariant reactions and special points in the Pb–U system and the experimental results.

Reaction type	Reaction	U (at.%)			$T$ (°C)	Reference
Eutectic	$L \leftrightarrow (\text{Pb}) + \text{Pb}_3\text{U}$	~0	0	25	325	[23]
			0	25	327	This work
Congruent	$L \leftrightarrow \text{Pb}_3\text{U}$		25		1220	[23]
			25		1218	This work
Eutectic	$L \leftrightarrow \text{Pb}_3\text{U} + \text{PbU}$	27.2	25	50	1210	[23]
			28.6	25	50	1213
Syntectic	$L1 + L2 \leftrightarrow \text{PbU}$	37	98.5	50	1280	[23]
			38	97.2	50	1283
Eutectic	$L \leftrightarrow \text{Pb-U} + \gamma\text{U}$	99.5	50	100	1125	[23]
			99.1	50	99.6	1126
Eutectoid	$\gamma\text{U} \leftrightarrow \beta\text{U} + \text{PbU}$	~100	~100	50	765	[23]
			99.0	99.5	50	764
Eutectoid	$\beta\text{U} \leftrightarrow \alpha\text{U} + \text{PbU}$	~100	~100	50	645	[23]
			99.2	99.9	50	650
Critical	$L \leftrightarrow L1 + L2$		–	–	–	[23]
			79.5	–	2485	This work

( $\gamma$ U) phases is considered in the calculation. The calculated enthalpies and entropies of formation of the compounds at 677 °C are shown in Figs. 4 and 5, respectively, with the experimental data [24–27]. The experimental thermodynamic data obtained by different researchers differ somewhat from each other, and the calculated results of the present work are within the range of these values. The calculated enthalpies and entropies of formation of the PbU phase are in agreement with the experimental data of Alcock et al. [24], but slightly different from the calculated values of Chiotti et al. [27].

The complete set of the thermodynamic parameters describing the Gibbs free energy of each phase in the Pb–U system is given in Table 2, and all invariant reactions in the Pb–U system are

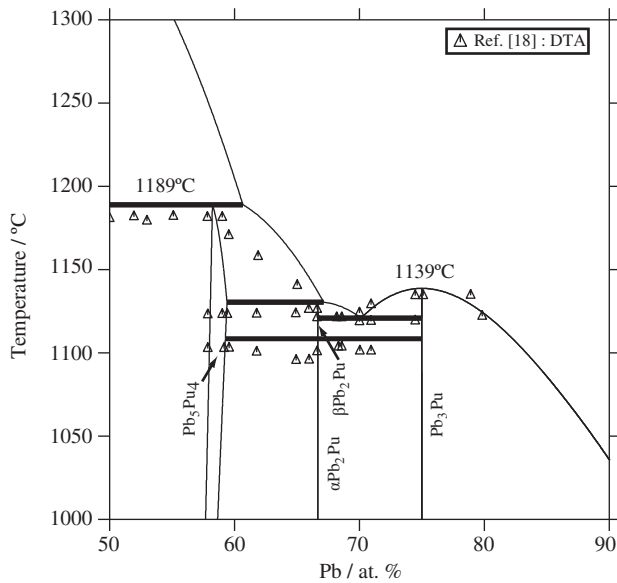


Fig. 7. Pb-rich portion of the calculated Pb–Pu phase diagram with experimental data [18].

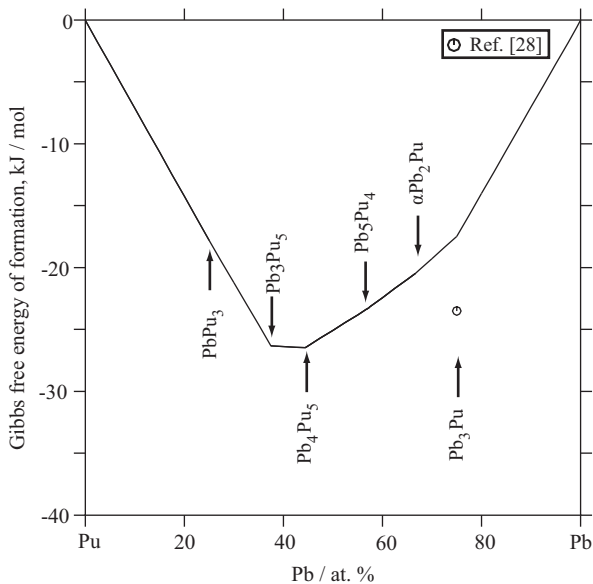


Fig. 8. Calculated Gibbs free energy at 727 °C in the Pb–Pu system compared with the calculated data from Chiotti et al. [27]: the reference states are liquid Pb and liquid Pu.

summarized in Table 3, where the experimental data [23] are also listed for comparison.

#### 4.2. The Pb–Pu system

The calculated phase diagram of the Pb–Pu system compared with all the experimental data [18] used in the present optimization is shown in Figs. 6 and 7. The calculated peritectic reaction,  $L + Pb_4Pu_5 \leftrightarrow Pb_3Pu_5$  is in agreement with the temperature reported in the work of Wood et al. [18] although their composition of the liquid phase is smaller than that evaluated in the present work. The temperature of transformation between the  $\alpha$ Pb<sub>2</sub>Pu and  $\beta$ Pb<sub>2</sub>Pu phases agreed with the experimental data [18] very well. In Fig. 7, the phase boundary between Pb<sub>5</sub>Pu<sub>4</sub> and liquid phase is slightly different from the result of Foltyn et al. [29], and this suggests further experimental work to validate the present conclusions. Fig. 8 indicates the calculated Gibbs free energies at 727 °C compared with those obtained by Chiotti [27].

The complete set of the thermodynamic parameters describing the Gibbs free energy of each phase is given in Table 4, and all invariant reactions and special points of the phase diagram are summarized in Table 5, where the experimental data [29] are with available.

Table 4

Parameters for each phase of the Pb–Pu system optimized in this work.

Parameters in each phase (J/mol) with temperature  $T$  in Kelvin

Liquid phase, format (Pb, Pu)<sub>1</sub>

$${}^0L_{Pb, Pu}^{Liq} = -77,296 + 25.000T$$

$${}^1L_{Pb, Pu}^{Liq} = -3563 - 0.503T$$

$${}^2L_{Pb, Pu}^{Liq} = 32,516 - 3.866T$$

A2  $\epsilon$ Pu phase, format (Pb, Pu)<sub>1</sub>(Va)<sub>3</sub>

$${}^0L_{Pb, Pu}^{\epsilon} = 50,000$$

A1 (Pb,  $\delta$ Pu) phase, format (Pb, Pu)<sub>1</sub>(Va)<sub>1</sub>

$${}^0L_{Pb, Pu}^{f_{cc}} = 0$$

A6  $\delta'$ Pu phase, format (Pb, Pu)<sub>1</sub>

$${}^0L_{Pb, Pu}^{\delta'} = 0$$

PbPu<sub>3</sub> phase, format (Pb)<sub>0.25</sub>(Pu)<sub>0.75</sub>

$${}^0G_{Pb, Pu}^{PbPu_3} = -23,120 + 0.100T + 0.25^0G_{Pb}^{fcc} + 0.75^0G_{Pu}^{zPu}$$

Pb<sub>3</sub>Pu<sub>5</sub> phase, format (Pb)<sub>0.375</sub>(Pu)<sub>0.625</sub>

$${}^0G_{Pb, Pu}^{Pb_3Pu_5} = -35,850 + 4.620T + 0.375^0G_{Pb}^{fcc} + 0.625^0G_{Pu}^{zPu}$$

Pb<sub>4</sub>Pu<sub>5</sub> phase, format (Pb)<sub>0.4444</sub>(Pu)<sub>0.5556</sub>

$${}^0G_{Pb, Pu}^{Pb_4Pu_5} = -33300.8 + 2.130T + 0.4444^0G_{Pb}^{fcc} + 0.5556^0G_{Pu}^{zPu}$$

$\beta$ Pb<sub>2</sub>Pu phase, format (Pb)<sub>0.6667</sub>(Pu)<sub>0.3333</sub>

$${}^0G_{Pb, Pu}^{\beta} = -24,855 + 0.310T + 0.6667^0G_{Pb}^{fcc} + 0.3333^0G_{Pu}^{zPu}$$

$\alpha$ Pb<sub>2</sub>Pu phase, format (Pb)<sub>0.6667</sub>(Pu)<sub>0.3333</sub>

$${}^0G_{Pb, Pu}^{\alpha} = -24,960 + 0.386T + 0.6667^0G_{Pb}^{fcc} + 0.3333^0G_{Pu}^{zPu}$$

Pb<sub>3</sub>Pu phase, format (Pb)<sub>0.75</sub>(Pu)<sub>0.25</sub>

$${}^0G_{Pb, Pu}^{Pb_3Pu} = -21,600 + 0.230T + 0.75^0G_{Pb}^{fcc} + 0.25^0G_{Pu}^{zPu}$$

Pb<sub>5</sub>Pu<sub>4</sub> phase, format (Pb, Pu)<sub>0.5556</sub>(Pb, Pu)<sub>0.4444</sub>

$${}^0G_{Pb, Pu}^{Pb_5Pu_4} = -29,500 + 1.540T + 0.5556^0G_{Pb}^{fcc} + 0.4444^0G_{Pu}^{zPu}$$

$${}^0G_{Pb, Pu}^{Pb_5Pu_4} = 30,000 + {}^0G_{Pb}^{fcc}$$

$${}^0G_{Pb, Pu}^{Pb_5Pu_4} = 10,000 + {}^0G_{Pu}^{zPu}$$

$${}^0G_{Pu, Pb}^{Pb_5Pu_4} = 10,000 + 0.4444^0G_{Pb}^{fcc} + 0.5556^0G_{Pu}^{zPu}$$

$${}^0I_{Pb, Pb, Pu}^{Pb_5Pu_4} = -28,000 - 6.300T$$

$${}^0I_{Pu, Pb, Pu}^{Pb_5Pu_4} = 0$$

$${}^0I_{Pb, Pu, Pb}^{Pb_5Pu_4} = 0$$

$${}^0I_{Pb, Pu, Pu}^{Pb_5Pu_4} = 0$$

**Table 5**

A comparison between the calculated invariant reactions and special points in the Pb–Pu system and the experimental results.

Reaction type	Reaction	Pb (at.%)			T (°C)	Reference
Peritectic	L + Pb <sub>3</sub> Pu <sub>5</sub> ↔ PbPu <sub>3</sub>	~0.5	37.5	25	896	[29]
		0.9	37.5	25	898	This work
Peritectic	L + Pb <sub>4</sub> Pu <sub>5</sub> ↔ Pb <sub>3</sub> Pu <sub>5</sub>	25.5	44.4	37.5	1333	[29]
		35.7	44.4	37.5	1335	This work
Congruent	L ↔ Pb <sub>4</sub> Pu <sub>5</sub>		44.4		~1385	[29]
			44.4		1385	This work
Peritectic	L + Pb <sub>4</sub> Pu <sub>5</sub> ↔ Pb <sub>5</sub> Pu <sub>4</sub>	57.5	44.4	55.6	1185	[29]
		60.6	44.4	58.2	1189	This work
Peritectic	L + Pb <sub>5</sub> Pu <sub>4</sub> ↔ βPb <sub>2</sub> Pu	67.2	57.5	66.7	1129	[29]
		67.1	59.4	66.7	1130	This work
Eutectic	L ↔ βPb <sub>2</sub> Pu + PbPu <sub>3</sub>	68.8	66.7	75	1124	[29]
		70.1	66.7	75	1121	This work
Congruent	L ↔ PbPu <sub>3</sub>		75		1138	[29]
			75		1139	This work
Allotropic	αPb <sub>2</sub> Pu ↔ βPb <sub>2</sub> Pu		66.7		1106	[29]
			66.7		1108	This work

## 5. Conclusions

The phase diagrams and thermodynamic properties of the Pb–U and Pb–Pu binary systems were evaluated by combining the thermodynamic models with the available experimental information. A consistent set of optimized thermodynamic parameters has been derived for describing the Gibbs free energy of each solution phase and intermetallic compound in the Pb–U and Pb–Pu binary systems. Good agreement between the calculated results and most of the experimental data is achieved.

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