Thermodynamic re-assessment of the Pu-U system and its application to the ternary Pu-U-Ga system

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Abstract

Phase diagram and thermodynamic properties of the Plutonium-Uranium (Pu-U) system have been successfully re-assessed using the CALPHAD method with input from *ab initio* electronic-structure calculations for the bcc phase (β -U, ϵ -Pu). Results and methodology are discussed and compared with previous assessments. In addition, the already assessed Pu-Ga (Gallium) and U-Ga data are combined to build the Pu-U-Ga thermodynamic database. The predictions made using this database indicate that a small amount of U impacts the (δ -Pu) Pu-Ga phase stability by precipitating the complicated η and ζ phases that exist in the Pu-U system. Finally, the present investigation provides guidelines for further experimental studies.

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1. Introduction

The thermodynamic properties of actinide alloys are important because of their applications in nuclear power plants as fuels (metallic and MOX fuels), and this presents many associated materials challenges [1]. Among these challenges, the phase stability of actinide alloys versus chemical and temperature changes is crucial in understanding and predicting fuel behavior under normal, hypothetical (*e.g.*, aging, extending life time of materials) or even off-normal (accidental) conditions.

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The Plutonium-Uranium (Pu-U) binary system, which is one of the possible metal alloy fuels, was first studied by Ellinger *et al.* [2] in 1959, and still remains as one of the most complete and reliable experimental works (Fig. 1). Beyond the characterization of the solubility limits of Pu and U in pure phases (the bcc phase (ϵ -Pu/ γ -U) forms a continuous solid solution across the entire composition range of the phase diagram), Ellinger *et al.* revealed two new eta (η) and zeta (ζ) complex phases, with wide homogeneity ranges. Later on, the Pu-U phase diagram was constructed by Peterson and Foltyn [3], based mainly on the works of Ellinger *et al.* [2], and with data from U-rich region from the experiments of Calais *et al.* [4]. However, the phase boundaries were just hand drawn by means of overlapping the associated measured data points. Finally, several experimental studies have been dedicated to the β -U/ γ -U phase boundaries [5], the solidus/liquidus curves [6], and more generally to the characterization of phase boundaries [7].

Based on these previous experimental investigations, a complete thermodynamic assessment of the Pu-U phase diagram was attempted by Leibowitz *et al.* [8, 9]. The greatest difficulty reported was assessing the intermediate η and ζ phases. The resulting U-rich region of the assessed phase diagram presents reactions with intermediate phases that differ from the experiments. Subsequently, Kurata [10] reported the most complete assessment using the Parrot module of the Thermo-Calc code in 1999 (Fig. 2). This phase diagram is, in general, in better agreement with the experimental data than the one proposed by Leibowitz *et al.* [9]. However, Kurata noted some disagreements between experiments and simulations in the high-temperature part of the phase diagram. The calculated liquidus is slightly lower than most of the available experimental data, and the calculated phase boundaries between bcc (ϵ -Pu, γ -U) and η phases are shifted to a slightly higher temperature than the experimental ones. In 2010, Kurata revisited the Pu-U phase diagram to make consistent the high-temperature phase boundaries in the Pu-U-Zr system with those in the Pu-U binary system [11]. The resulting phase diagram is given in Fig. 3. In spite of the fact that the upper part of the Pu-U system seems in a better agreement with experimental data, the calculated eutectoid temperature among the ζ , η and β -Pu phases departs by $\sim 100^\circ\text{C}$ from the experimental one. Finally, Turchi and Landa [12] noted a difference between the 1999 and 2010

Kurata’s assessments [10, 11] for the bcc heat of formation of Pu-U alloys at $T = 0$ K.

40 The energetic values obtained from *ab initio* calculations are in better agreement with the 1999 assessment [10] (tendency to phase formation) by comparing with the most recent assessment [11] (tendency to phase separation), as shown in Fig. 4.

Thus, this work is based on a coupling between *ab initio* energetics [12, 13] and phenomenological thermodynamics models - based on the CALPHAD (CALculation
45 of PHase Diagrams) approach [14, 15, 16] - and the use of the Thermo-Calc software¹ [17, 18], together with experimental data [2, 4, 6, 7, 19, 20] to re-assess the Pu-U phase diagram with a focus on improving both the high- and low-temperature regions.

Then, as the experimental determination of phase diagrams on actinide alloys are costly, time-consuming and challenging, a preliminary phase diagram is calculated for
50 the Plutonium-Uranium-Gallium (Pu-U-Ga) system. Indeed, the high-temperature δ phase of Pu, which corresponds to the manufactured phase, can be retained at room temperature by alloying plutonium with a few atomic percent of so-called “ δ -phase stabilizing” elements such as aluminum (Al), americium (Am), cerium (Ce), gallium (Ga) and scandium (Sc) [21, 22, 23, 24]. However, alpha decay of Pu induces an in-
55 crease in U content with time, and the δ -phase stability of Pu-Ga alloys as a function of U remains unknown. Therefore, the purpose of this work is to capitalize on the development of a new *ab initio* aided CALPHAD thermodynamic database to predict the phase stability of more complicated alloys, such as Pu-U-Ga. Finally these predictions provide useful guidance for well-chosen experiments to further validate the proposed
60 thermodynamic database.

The paper is organized as follows. Computational details are given in Section 2. The Pu-U thermodynamic assessment as well as the Pu-Ga and U-Ga thermodynamic descriptions are detailed in Section 3, leading to the predicted Pu-U-Ga ternary phase diagrams. Accompanying discussions and guidelines for further studies are given
65 in Section 4.

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¹Thermo-Calc is a product of Thermo-Calc AB.

2. Simulation details

2.1. CALPHAD method

The aim of the CALPHAD method is to model the Gibbs energy [14, 15, 16]. This involves the selection of appropriate thermodynamic models for the Gibbs energy functions for any structure and any phase, and the maximum likelihood estimation of the model parameters using critically selected thermochemical and constitutive data as input. Once such functions have been assessed to reproduce phase diagrams and thermodynamic properties, they are compiled in a thermodynamic database that can be used for computational thermodynamic predictions of multi-component materials. To summarize, the Gibbs energy of each phase is modeled, and the model parameters are collected in a thermodynamic database.

For the unaries, the Gibbs energy function for the element X (X = Ga, Pu, U) in the pure phase ϕ is (for simplicity, the pressure dependence and the magnetic contribution are not shown here) generally written as:

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

where H_X^{SER} is the molar enthalpy of element X, at 298.15 K and 10^5 Pa, in its standard element reference (SER) state, *i.e.*, α -Pu (simple monoclinic) for Pu, α -U (orthorhombic_A20) for U, and α -Ga (orthorhombic_A11) for Ga, and T is the absolute temperature. In the present study, the empirical parameters (a to h) are taken from the data compiled by Dinsdale [25]. In the case of pure Pu, the six transitions, α -Pu (simple monoclinic) $\rightarrow$ β -Pu (body-centered monoclinic) $\rightarrow$ γ -Pu (face-centered orthorhombic) $\rightarrow$ δ -Pu (fcc) $\rightarrow$ δ' -Pu (body-centered tetragonal) $\rightarrow$ ϵ -Pu (bcc) $\rightarrow$ Liquid, are well described with transition temperatures of 124, 215, 320, 463, 483, and 640°C, respectively. Regarding the pure U phases, the α -U (orthorhombic_A20) $\rightarrow$ β -U (tetragonal) $\rightarrow$ γ -U (bcc) $\rightarrow$ Liquid, are also well determined with transition temperatures of 669, 776, 1135°C, respectively. Finally, the α -Ga (orthorhombic_A11) $\rightarrow$ Liquid is well reproduced at 30°C.

For stoichiometric compounds, the Gibbs energy can be written in its simplest form

as:

$$G^{A_X B_Y \dots} = \sum_I c_I {}^0G_I^{\phi_I} + a + bT \quad (2)$$

where $a + bT$ represents the Gibbs energy of formation ΔG^f of a specific compound formed from the pure elements considered in their states ϕ_I with compositions c_I . These states can be a given phase (structure), identical to the one of the compound, the SER state of each element (generally accepted), or any other reference states. The model parameters a and b represent the enthalpy and the entropy of formation of the compound, respectively [26]. In fact, the entropy of mixing for an ideal solution presented below for multi-component solution phases (Eq. 3) is equal to 0 for stoichiometric compounds, since there is no random mixing [27].

For multi-component solution phases, it has proven useful to distinguish three contributions from the concentration dependence to the Gibbs energy of a phase:

$$G_m^\phi = {}^0G^\phi + {}^{id}G^\phi + {}^{xs}G^\phi \quad (3)$$

where ${}^0G^\phi$ is the contribution from the mechanical mixing of the pure components, ${}^{id}G^\phi$ is the ideal mixing contribution (that corresponds to the entropy of mixing for an ideal solution), and ${}^{xs}G^\phi$ is the excess Gibbs energy of mixing due to non-ideal interactions (the so-called excess term). For a multi-component solution in a particular phase ϕ described with a single sublattice model, the three contributions to the total Gibbs energy reduce to:

$${}^0G^\phi = \sum_I c_I {}^0G_I^\phi \quad (4)$$

$${}^{id}G^\phi = RT \sum_I c_I \ln c_I \quad (5)$$

$${}^{xs}G^\phi = \sum_I \sum_{J>I} c_I c_J \sum_{k=0}^p {}^kL_{I,J}^\phi (c_I - c_J)^k \quad (6)$$

which can be summarize for a binary system (Pu-U, Pu-Ga, U-Ga):

$$\begin{aligned} G_{I,J}^\phi &= c_I {}^0G_I^\phi + c_J {}^0G_J^\phi \\ &+ RT [c_I \ln c_I + c_J \ln c_J] \\ &+ c_I c_J \sum_{k=0}^p {}^kL_{I,J}^\phi (c_I - c_J)^k \end{aligned} \quad (7)$$

where the excess molar Gibbs energy of mixing is expressed by a Redlich-Kister (RK) polynomial expansion (the sum of the terms $(c_I - c_J)^k$ is the so-called Redlich-Kister polynomial) [27, 28]. In these expressions, c_I is the composition of the alloy in species I , and ${}^kL_{I,J}^\phi$ is the k^{th} -order ($k \leq 2$ in the present assessment) binary interaction parameter, between species I and J , usually expressed as a first-order polynomial in temperature:

$${}^kL_{I,J}^\phi = {}^ka_{I,J}^\phi + {}^kb_{I,J}^\phi T \quad (8)$$

For a ternary system (Pu-U-Ga), the previous equations (Eq. 4-6) give:

$$\begin{aligned} G_{I,J,K}^\phi &= c_I {}^0G_I^\phi + c_J {}^0G_J^\phi + c_K {}^0G_K^\phi \\ &+ RT [c_I \ln c_I + c_J \ln c_J + c_K \ln c_K] \\ &+ c_I c_J \sum_{k=0}^p {}^kL_{I,J}^\phi (c_I - c_J)^k + c_I c_K \sum_{k=0}^p {}^kL_{I,K}^\phi (c_I - c_K)^k \\ &+ c_J c_K \sum_{k=0}^p {}^kL_{J,K}^\phi (c_J - c_K)^k \end{aligned} \quad (9)$$

Note that in Eq. 9, the Gibbs energy of a ternary- or higher-order solution phase is determined by extrapolation of the binary energies using Muggianu's method [29]. If necessary, a ternary term $c_I c_J c_K L_{I,J,K}^\phi$ can be added in order to describe the contribution of three-element interactions to the Gibbs energy [27]. Even if they are not used in the present study, more models based on multi-sublattices also exist for ordered phases having a range of solubility or exhibiting an order/disorder transformation [14, 15, 16, 27].

2.2. *Ab initio* input

CALPHAD is an iterative method, based on the equations of the the previous section, that adjusts the parameters describing the Gibbs energies of various phases in a system in order to construct a phase diagram that best fits the available experimental thermodynamic and phase diagram data for the system. On the one hand, one can see here the importance that the input from *ab initio* calculations (for instance, the heats of formation and transformation) can have when experimental data are sparse or missing. On the other hand, it is worth noticing that the process of parameter optimization and error minimization involved in the CALPHAD method is an inverse

problem with infinite degrees of freedom [30]. Thus, many possible combinations of values of user-defined parameters could produce phase boundaries and diagrams that perfectly coincide. Therefore, the use of *ab initio* energetics during the CALPHAD assessment constrains the optimization process, and validates the resulting thermodynamic database not only from a diagrammatic basis, but also from a reliable energetic basis.

Ab initio energetics of the bcc phase for actinide alloys have been calculated and are compatible with the general trends predicted for all actinide combinations that involve U, Np, Pu, and Am [13, 31, 32]. All the details about the *ab initio* methodology used in the present study can be found in [13]. In fact, complementary computational techniques have been previously used to compute the ground-state properties of the bcc Pu-U solid solution [13]: (i) a scalar-relativistic (SR) Green function technique based on the Korringa-Kohn-Rostoker (KKR) method within the atomic-sphere approximation (ASA), (ii) scalar-relativistic and fully-relativistic (FR) exact muffin-tin orbital methods (EMTO), and (iii) the all-electron full-potential linear muffin-tin orbital method (FPLMTO) that also accounts for all relativistic effects. Pertinent details of the computational methods are described in [13]. Both SR-KKR-ASA-CPA (Coherent Potential Approximation) and SR-EMTO-CPA methods gives a significantly larger equilibrium atomic volume than experimental data for Pu; on the contrary, the ones calculated within the fully-relativistic approaches (FR-EMTO-CPA and FPLMTO-SQS) are much closer. It was confirmed that a fully-relativistic treatment is necessary for an accurate determination of the energetics of all Pu-based alloys. Indeed, spin-orbit coupling becomes crucially important for calculating the excess thermodynamic characteristics of Pu-containing alloys. Thus, only the *ab initio* values obtained for the bcc phase of the Pu-U system within the framework of FR-EMTO-CPA formalism have been taken into account and are presented in Fig. 4. As observed, the calculated heats of formation at 0 K are negative and agree well with the Kurata's assessment of 1999 [10]. These values are very interesting because at $T = 0$ K, the heat of formation of bcc alloys resulting from *ab initio* calculations correspond to the T-independent terms that enter the expression for the excess Gibbs energy of random solution (*i.e.*, the coefficients ${}^k a_{I,J}^\phi$ in Eq. 8). This *ab initio* input to CALPHAD constrains the present

thermodynamic assessment by having to determine only the T-dependent terms (*i.e.*, the coefficients ${}^k b_{i,j}^\phi$ in Eq. 8), thus making it more trustworthy.

3. Results

170 3.1. Pu-U CALPHAD assessment

The Gibbs energies for the pure stable phases (α -, β -, γ -, δ -, δ' -, ϵ - and liquid Pu, and α -, β -, γ - and liquid U) are given by Dinsdale [25]. However, the Gibbs energies for “metastable” phases, such as the Gibbs energy of Pu for the α - and β -U phases and that of U for α -, β -, γ -, δ -, δ' -Pu phases, are not given in the SGTE database. These
175 functions have been evaluated by Kurata [10, 11] and are reported in Table 1. Even if these Gibbs energies (lattice stabilities) are hard to define, it is important to keep in mind that they are only used as reference and are associated with interaction parameters (Eq. 7). As mentioned by Kurata, although the interaction parameters optimized for these “metastable” phases do not directly represent the thermodynamic character
180 of the corresponding phases, the combination of the assumed Gibbs energies of the “metastable” phases and the optimized interaction parameters is considered adequate for the thermodynamic properties of the corresponding phases [10]. In the present study, the values determined by Kurata in 1999 can be taken with more confidence (Table 1). Moreover, the Gibbs energy function of U with the α -Pu structure was not taken
185 into account, because the solubility of U in the α -Pu phase is negligible (Fig. 1). Note that in the present text, the structure of pure elements (α -Pu, β -Pu...) and the alloy phases with the same structure (for instance, the δ -Pu solid solution) have the same notation to simplify the writing.

In addition, *ab initio* calculations at T = 0 K are used to constrain the optimization
190 procedure. As observed in Fig. 4, the bcc heat of formation calculated from [11] is strongly positive - hence indicating a tendency toward phase separation (*i.e.*, existence of a miscibility gap at low temperature) - whereas the one calculated from [10] is negative - revealing a tendency toward phase formation. This tendency of bcc phase mixing is close to the *ab initio* calculated heat of formation. Thus, the *ab initio* calculated heat
195 of formation of the bcc solution phase (symbols), which is equal to the excess Gibbs

free energy at $T = 0$ K, can be fitted by a RK polynomial of first order (sub-regular solution model) with the Eq. 6, *i.e.*:

$${}^{xs}G^{bcc}(0\text{ K}) = c_I c_J ({}^0L_{I,J}^{bcc} + {}^1L_{I,J}^{bcc}(c_I - c_J)) \quad (10)$$

With $c_I = c_{Pu}$, $c_J = c_U$ and using $c = c_U$, Eq. 10 gives:

$${}^{xs}G^{bcc}(0\text{ K}) = c(1 - c)[{}^0L_{Pu,U}^{bcc} + {}^1L_{Pu,U}^{bcc}(1 - 2c)] = c(1 - c)L_{Pu,U}^{bcc} \quad (11)$$

In the present study, the RK description of the *ab initio* predicted excess Gibbs free energy at 0 K (in J/mole) is given by:

$$L_{Pu,U}^{bcc} = -4808 - 1389(1 - 2c) \quad (12)$$

Based on these calculated data and using the solidus and liquids lines determined experimentally [2, 6, 7], the bcc T-dependent terms of the mixing Gibbs energy are firstly assessed together with the interaction parameters of the liquid phase. The results are reported in Table 2. The liquidus and solidus curves presented in Fig. 5, resulting from the present assessment, are in good agreement with experiments. As observed experimentally [2], a continuous liquid-plus-solid region forms at high temperatures between ϵ -Pu and γ -U, and reveals a minimum at about 8 at.% U and 608°C (Table 3). This value is in quite good agreement with the experimental ones defined by Ellinger *et al.* (12 at.% U and 610°C) [2], Rosen *et al.* (9 at.% U and $624 \pm 2^\circ\text{C}$) [33] and Okamoto *et al.* (11 at.% U and 619°C) [6], and to the previous calculated ones by Leibowitz *et al.* (10 at.% U and 626°C) [9], Kurata in 1999 (9 at.% U and 618°C) [10] and in 2010 (8 at.% U and 619°C) [11]. As the minimum-melting reaction in the Pu-U system seems to be not well characterized, the weight in the present assessment was mainly put on the experimental data defining the solidus and liquidus curves, and not on the minimum-melting reaction itself during the assessment. In addition, two sets of Pu activity data in the liquid phase at 1200°C [19, 20] have been taken into account during the assessment. The resulting activity calculations at 1200°C are presented in Fig. 6, and compared with previous simulations [10, 11] and experiments [19, 20]. The Pu-activity curve is very similar to previous works and agrees with experiment, *e.g.*, exhibits a negative deviation from the ideal behavior (Raoult's law). Finally, metastable

phase diagrams considering only the liquid and bcc phases have been investigated. As expected regarding the interaction parameters in Table 2, the assessment from ref. [11] is the only one revealing a bcc miscibility gap at low temperature (Fig. 7). Thus, as a first step leading to the *ab initio* aided re-assessment of the Pu-U system, the high-
225 temperature region of the Pu-U phase diagram has been successfully optimized.

Then, the η , the β -U and the δ' -Pu phases are assessed by fixing the bcc parameters and using invariant lines involving the bcc phase (invariants 2 and 5 in Table 3), and data corresponding to the limits of the two-phase domains (bcc + η , bcc + β -U and bcc + δ' -Pu). Following the same procedure, the interaction parameters of the ζ
230 and the α -U phase are optimized using the invariants 3 and 4 (Table 3) with the accompanying phase boundaries (ζ + α -U, α -U + β -U and ζ + η domains). Finally, as the experimental data are very sparse in the Pu-rich region, the interaction parameters of Pu-phases are assessed as a function of the invariants (6-10 in Table 3). As reported in Table 3, present invariant temperatures are generally very close to those determined by
235 Ellinger *et al.* [2].

Regarding the U-rich region of the phase diagram, the η phase that is formed by a peritectoid reaction (invariant 2) agrees well with experiment for the bcc and η -phase compositions. However, the β -U assessed domain is wider than experimentally observed in [2]. The β -U phase reaches 27 at.% Pu from our calculation and only 20 at.%
240 Pu experimentally. This result is similar to the Kurata's assessment of 1999 in which the largest difference between experimental data and modeling is observed at the phase boundary between the η and β -U phases (the calculated η + β -U phase boundary is shifted closer to the Pu-rich region than the experimental boundary). Leibowitz *et al.* also indicated that their two-phase η + β -U field differs from the experiments but that
245 there are in effect no experimental data in that area [9]. Related to the same region, the bcc + β -U domain is not clearly defined yet. The present calculated width of this domain is between the Kurata's assessments of 1999 and 2010 [10, 11]. In parallel, and based on information from diffusion studies obtained during a private communication with M. C. Petri and M. A. Dayananda, Leibowitz *et al.* indicated that the two-phase
250 bcc + β -U field may be wider [9]. As a consequence, more experimental data are needed to characterize the η + β -U and bcc + β -U phase domains of stability. By low-

ering the temperature, the ζ phase is formed by a peritectoid reaction from the $\eta + \beta$ -U phases (invariant 3). This reaction is quite well described in the present assessment as well as in [11], contrary to the eutectoid reactions described in [9, 10]. Then, the
255 calculated eutectoid at 560°C (β -U $\rightarrow$ $\zeta + \alpha$ -U) is in good agreement with published data (invariant 4). Finally, the $\zeta + \alpha$ -U domain that extends down to room temperature is in better agreement with the experiments of Calais *et al.* [4] than the one assessed by Kurata in 2010 [11].

As for the Pu-rich region of the phase diagram, the two eutectoid reactions at high
260 temperature (5 and 6 in Table 3) are in quite good agreement with experiments. The chemical compositions of the phases are better described by the 2010 Kurata's assessment (Table 3). However, the experimental composition of the η phase is not clearly determined (see the dashed lines in Fig. 1). The resulting bcc + η region of the present assessment is better reproduced compared with the 1999 Kurata's assessment (too high)
265 but is not as good as the 2010 one [10, 11]. As for the $\delta + \delta'$ region, the calculated two-phase field is always very narrow compared with experiments [2]. This computed result is supported by the small enthalpy of transformation from δ - to δ' -Pu [9]; the calculated value (83.3 J/mole) from [25] is very close to the experimental one (84 J/mole) reported in [9]. By decreasing temperature, two peritectoid (7,8) and one eutectoid (9)
270 reactions involving the η phase occur (Table 3). Reactions 7 and 8 are not described in detail experimentally (Fig. 1). Indeed Ellinger *et al.* underlined that the β -Pu + η field is the only one for which no direct experimental evidence was obtained [2]. But, the present assessment is in agreement with these reactions. The eutectoid (invariant 9) is well described by the present assessment and in [10] whereas reactions 8 and 9,
275 involving the η phase, are out of the range in [11] (Table 3). According to the available experimental data, Kurata mentioned in 2010 that thermodynamic data for the η phase are required for improving the database [11]. Finally, the last eutectoid (reaction 10 in Table 3) is well reproduced in the present work and in [10] but not in [11] (ζ phase composition). All these results confirm the validity of the Kurata's assessment
280 of 2010 at high temperatures, and of the 1999 one at low temperatures with the present assessment combining the best of both assessments.

3.2. Pu-U-Ga predictions

The computation of any ternary, quaternary or higher-order system implies the critical evaluation and analysis of all underlying sub-systems. Thus, the thermodynamic
285 assessment of the Pu-U, Pu-Ga, and U-Ga binaries is necessary to estimate the thermodynamic properties of the Pu-U-Ga ternary phase diagram. The Pu-Ga and U-Ga thermodynamic properties and phase diagrams are reviewed below.

The thermodynamic assessment of the Pu-Ga system has been performed by Turchi *et al.* and a complete description of the literature, data, crystal structures and models
290 used is given in [26, 34]. This thermodynamic database has been successfully used to study martensitic transformation and reversion in Pu-Ga alloys [35, 36]. Thus, this database has been considered unchanged in the present work and the resulting Pu-Ga phase diagram is shown in Fig. 8.

The thermodynamic assessment of the U-Ga system was carried out by Wang *et al.*
295 in the framework of the CALPHAD method [37]. As reported by these authors, the experimentally determined U-Ga phase diagram consists of three intermetallic compounds (UGa_3 , UGa_2 and U_2Ga_3) and the liquid phase [38]. In addition, the existence of the UGa and U_3Ga_5 compounds were also mentioned in [39, 40, 41]. However, the phase stability of these compounds is unknown, and consequently has not been taken
300 into account during the assessment. The resulting phase diagram is plotted in Fig. 8.

Then, the thermodynamic data for the three binaries have been put together with consistency to study the ternary Pu-U-Ga alloy system. Let us recall that no experimental data are available for this ternary system. As a consequence, the solubilities of Ga in Pu-U intermediate phases (η and ζ), and of U in η -Pu-Ga phase are ignored. More-
305 over, contribution to the excess Gibbs energy from ternary interaction parameters is not considered. For instance, the interactions in the bcc phase - where the 3 elements are present - are based on the interactions from the binaries without any ternary correction. Finally, the PuGa_2 and UGa_2 compounds exhibit the same crystal structure (C32) and are considered as the same phase (XGa_2 with $\text{X} = \text{Pu}$ and/or U), meaning that Pu and U
310 mix on the same sublattice. However, the interaction parameters between Pu and U in XGa_2 (ternary solubility) can not be assessed without new experimental data. Because of the complexity of ternary systems in general, it is also anticipated that other com-

pounds that only form in the ternary system may exist. This implies that the isothermal sections that are presented below should be considered as representations if not in the stable equilibrium, at least in the metastable one [42]. Should more experimental data
 315 on solubilities and new compounds in the ternary system be available, it will be possible to introduce their thermodynamic description in the database. Isothermal sections of the Pu-U-Ga phase diagram are shown in Fig. 9.

The first compound to precipitate is UGa_2 (XGa_2). Then, by decreasing temperature, the U_2Ga_3 and UGa_3 are precipitating. This sequence of precipitation is in agree-
 320 ment with the U-Ga binary system (Fig. 8). On the Pu-Ga rich side, PuGa_2 (XGa_2) precipitates at high temperature, and is followed by PuGa_3 , PuGa , Pu_5Ga_3 and the numerous compounds revealed in the Pu-Ga binary system (Fig. 8). The Ga-rich corner (top of the isothermal sections presented in Fig. 9) remains liquid until about 30°C , as
 325 expected. It is interesting to note that the liquidus surface is continuously reduced to the Pu-rich corner (except for a tiny Ga-rich corner).

By looking at the Pu-U branch of the ternary isothermal sections (Fig. 9), the bcc phase starts to extend from the U-corner to the Pu-corner from 1100°C to 800°C . Then, the α -U, β -U, η and ζ phases appear along the Pu-U axis. Finally, the Pu-rich corner at
 330 room temperature is composed of pure α -Pu phase, Pu_3Ga compound and intermediate ζ phase. As problematic as the Pu-Ga phase stability is, it is of the greatest interest. We selected a Pu-U-Ga alloy composition equal to 1 at.% Ga and studied the influence of U on phase stability by varying composition from 1 to 10 at.% U. The calculated property diagrams - phase fraction versus temperature - are given in Fig. 10 for the
 335 corresponding alloys: $\text{Pu}_{.98}\text{U}_{.01}\text{Ga}_{.01}$ and $\text{Pu}_{.89}\text{U}_{.10}\text{Ga}_{.01}$. For the two compositions, the same phases (Liquid, bcc, η , ζ , δ -Pu, β -Pu, α -Pu and Pu_3Ga) are involved, and only their phase fractions vary. The high-temperature parts of the property diagrams are similar: the liquid phase transforms to the bcc phase. Then, the bcc phase fraction decreases and is replaced by the δ phase and the η phase. Note that the η -phase amount
 340 increases greatly with the U content (from about 18% at 400°C for 1 at.% U to 85% for 10 at.% U). Then, by decreasing temperature, the η phase is replaced by the ζ phase, and an increase in the δ -phase is observed. We note here the strong δ -stabilizing effect of Ga by comparing the stability domain of the δ phase in Fig. 10 with the stability

domain of the pure Pu δ -phase ($320 \rightarrow 464^\circ\text{C}$). It is also interesting to mention that
 345 beyond the phase transformations involving the Pu-phases (β -Pu, α -Pu and Pu_3Ga),
 the ζ phase is stable until room temperature and is stabilized by U: the ζ phase fraction
 is varying from about 4% (1 at.% U) to 35% (10 at.% U) at room temperature.

4. Discussion

The *ab initio* aided thermodynamic re-assessment of the Pu-U system was success-
 350 fully performed and has revealed some interesting features. The first point that can
 be mentioned is the re-entrant liquid phase observed in the metastable phase diagrams
 (Fig. 7). Surprisingly enough, all assessments indicate that liquid re-appears at very
 low temperature and U-composition. This result does not come from the assessed in-
 teraction parameters but from an internal inconsistency in the SGTE database for the
 355 pure elements [25] between Liquid-Pu and ϵ -Pu (bcc) already mentioned in [43]. This
 inconsistency is not the only one among the actinides (americium, neptunium, pluto-
 nium, uranium) described in the Dinsdale's database [25]. A summary of the driving
 forces (ΔG) leading to wrong re-entrant metastable phases are displayed on Fig. 11. As
 these phases do not appear during equilibrium calculations, they are not easily detected
 360 and one can ask about the interest in tracking these inconsistencies. The answer is that
 the metastable behavior between two phases (driving force) can reveal approximations
 in the definition of one or both of the unary phases. In the present study, the Pu pure
 phases have been considered unchanged but may have to be re-assessed in the future.

Then, the domain limits, the crystal structures, and the precipitation mechanisms re-
 365 lated to several phases of the Pu-U system were, and are still, uncertain (see the dashed
 lines in Fig. 1). For instance, Leibowitz *et al.* [9] mentioned internal inconsistencies in
 the $\eta + \zeta$ portion of the phase diagram (no reasonable way to extrapolate the two-phase
 $\eta + \zeta$ field to the Pu edge). The resulting U-rich region of their phase diagram presents
 reactions with intermediate phases that differ from experiments. However, the authors
 370 pointed out the lack of experimental data in these regions. Later, Kurata noticed that the
 largest difference between experimental data and these results is observed in the phase
 boundary between the η and β -U phases [10]. Finally, Kurata re-assessed this system

by changing the weight of the liquidus data to improve the fit to the experimental data [11]. This last adjustment led to changes in the stability regions of the ζ and η phases of Pu-U with a better agreement between experimental and calculated data at high temperature. Unfortunately, the low-temperature part of the phase diagram, including the α -U + ζ field, did not match the few available experimental data. Even if the present assessment combines favorably the high- and low-temperature regions of the phase diagram, all two-phase domains associated with α - and β -U phases (U-rich side) have to be considered with caution until more experimental data are made available.

As experiments on actinide materials are costly, time consuming and require special training, the use of the present thermodynamic database can help to guide experiments, and hence further contribute to a refinement of the thermodynamic database. For example, the variation of the molar enthalpy and heat capacity at constant pressure ($C_p = dH/dT$) for a Pu₄₀U₆₀ alloy are presented on Fig. 12. The molar enthalpy and its derivative, the transformation temperatures and the two-phase equilibrium domains can be simulated and directly compared with experiments like those based on differential thermal analysis and differential scanning calorimetry. It is important to underline that the η and ζ phases are mainly unknown. So far only a small amount of crystallographic data exists for the ζ phase (stable at room temperature) without any in-depth characterization of its physical properties [44, 45, 46]. It is important to emphasize that a better knowledge of the structures of the η and ζ phases may improve the way the excess Gibbs energy is modeled. As for the Pu-U binary system, characterization of the ζ phase has to be performed in the Pu-U-Ga ternary system to know if detrimental effects induced by the ζ -phase precipitation can occur during aging of Pu-based alloys. As calculated, only a small amount of U added to the Pu-Ga alloy stabilized in δ phase is enough to prompt the precipitation of the η and ζ phases (Fig. 10). The precipitation of intermetallics like the intermediate η and ζ phases is crucial. Indeed, these complex phases are not known but if we consider examples in traditional metallurgy, the precipitation of such complex phases like the σ phase in stainless steels (austenitic, duplex) has a detrimental effect on both mechanical (embrittlement) and corrosion behavior. Thus, the impact of U in Pu-Ga alloys should not be underestimated even at a small concentration of U.

Finally, it is interesting to note that the XGa_2 compound with $\text{X} = \text{Pu}$ and/or U (Fig. 9) presents a C32 crystallographic structure that is of interest in zirconium-based actinide alloys. Indeed, the U-Zr alloy exhibits the $\delta\text{-UZr}_2$ phase, which precipitates in a C32 (AlB_2 -type) crystal structure [47, 48]. It is worth recalling that the C32 structure is equivalent to the so-called ω -phase known to occur in pure elements, such as Zr [47], and in Zr- or Ti- based alloys. Thus, this XGa_2 compound should not be neglected in further development of the present thermodynamic database.

5. Conclusion

Based on an extensive literature search on phase stability properties, and by recasting the bcc phase *ab initio* energetics in the CALPHAD framework, the Pu-U phase diagram has been successfully re-assessed in the entire range of alloy composition and temperature. However, a lack of data still remains to characterize the phase stability of the complex η and ζ phases. In addition, the assessments of the Pu-Ga and U-Ga systems have been taken from previous investigations to assemble the Pu-U-Ga database (obtained so far without any data on the ternary system). Predicted isothermal sections and property diagrams have shown that Ga stabilizes the $\delta\text{-Pu}$ phase - as expected - and that U promotes the stability of the η and ζ phases, and therefore may impact swelling and mechanical integrity on aging. Both Pu-U and Pu-U-Ga phase diagrams and property diagrams can be used as guidelines to design experiments that are usually costly, challenging and time-consuming. Indeed, these preliminary diagrams can be used to identify composition and temperature ranges where maximum information can be obtained with minimum experimental effort to further improve and/or validate the proposed thermodynamic database.

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Tables

Table 1. Gibbs energies (lattice stabilities) in J/mole for the pure elements U and Pu.

Element	Phase	[10] - Present study	[11]
U	α -Pu	-	${}^0G_U^{\alpha-U} + 5000$
	β -Pu	${}^0G_U^{\alpha-U} + 2000$	${}^0G_U^{\alpha-U} + 5000$
	γ -Pu	${}^0G_U^{\alpha-U} + 2000$	${}^0G_U^{\alpha-U} + 5000$
	δ -Pu	${}^0G_U^{\alpha-U} + 2000$	${}^0G_U^{\gamma-U} + 5000$
	δ' -Pu	${}^0G_U^{\alpha-U} + 2000$	${}^0G_U^{\gamma-U} + 5000$
	η	${}^0G_U^{\beta-U} + 229.2$	${}^0G_U^{\beta-U} + 118.7$
	ζ	${}^0G_U^{\gamma-U} + 332.1$	${}^0G_U^{\alpha-U} + 337.8$
Pu	α -U	${}^0G_{Pu}^{\alpha-Pu} + 2026$	${}^0G_{Pu}^{\beta-Pu} + 652.7$
	β -U	${}^0G_{Pu}^{\delta-Pu} + 227.5$	${}^0G_{Pu}^{\delta'-Pu} + 209.6$
	η	${}^0G_{Pu}^{\delta-Pu} + 103.4$	${}^0G_{Pu}^{\gamma-Pu} + 51.1$
	ζ	${}^0G_{Pu}^{\epsilon-Pu} + 500$	${}^0G_{Pu}^{\beta-Pu} + 500$

Table 2. Interaction parameters (in J/mole or J/mole/K) for solution phases of the Pu-U system.

Phase	RK parameters	[10]	[11]	Present study
Liquid	${}^0L$	4751.6 - 12.0 T	32231 - 31.5 T	13839 - 19.6 T
	${}^1L$	-2284.3	-8980.2	-7093
bcc (ϵ -Pu, γ -U)	${}^0L$	-5062.3	19374 - 17.3 5 T	-4808 + 0.2 T
	${}^1L$	506.8	-4939.5	-1389
α -Pu	${}^0L$	-	5000	-
β -Pu	${}^0L$	-2550	5000	-4343
γ -Pu	${}^0L$	3620	4342.7	4090
δ -Pu	${}^0L$	3620	723.8	3136
δ' -Pu	${}^0L$	3000	495.4	2411
α -U	${}^0L$	-9581.4	6176.5	-12689 + 3.9 T
	${}^1L$	-	-	9712 - 11.8 T
β -U	${}^0L$	-4870.7	5287.3	-12577 + 8.9 T
η	${}^0L$	-5772.4 + 0.19 T	4049.1 - 1.5 T	-12970 + 8.3 T
	${}^1L$	-	-617.4 - 3.4 T	2690 - 3.5 T
ζ	${}^0L$	-64447.6 + 68 T	-6336.9 + 10.4 T	-87904 + 99.2 T
	${}^1L$	-4517.9 + 21.6 T	-19997 + 24.6 T	-23547 + 54.6 T
	${}^2L$	7968.5 + 4.8 T	12364 - 7.8 T	33907 -19.9 T

Table 3. Invariants (numbered from 1 to 10) of the Pu-U system.

Reaction type	Invariants	U (at.%)			T (°C/K)	Reference
1 Minimum-melting	Liquid $\leftrightarrow$ bcc	≈ 12.0	≈ 12.0		610 / 883	[2]
		8.9	8.9		618 / 891	[10]
		7.7	7.7		619 / 892	[11]
		8.1	8.1		608 / 881	Present work
2 Peritectoid	bcc + β -U $\leftrightarrow$ η	≈ 70	≈ 80	≈ 70.5	705 / 978	[2]
		72	74	72.6	700 / 973	[10]
		67.3	78.7	72.9	702 / 975	[11]
		69.6	73.2	71.2	707 / 980	Present work
3 Peritectoid	β -U + η $\leftrightarrow$ ζ	≈ 82	≈ 67.5	≈ 72	590 / 863	[2]
		74.7	73.2	71.4	595 / 868	[10]
		79.6	73.5	74.3	593 / 866	[11]
		75.8	74.0	74.1	588 / 861	Present work
4 Eutectoid	β -U $\leftrightarrow$ α -U + ζ	≈ 82	≈ 85	≈ 74	560 / 833	[2]
		82	86.2	74.6	566 / 839	[10]
		82.5	87.2	76.8	568 / 841	[11]
		83.1	87.4	76.3	560 / 833	Present work
5 Eutectoid	bcc $\leftrightarrow$ δ' -Pu + η	≈ 2.5	≈ 1.3	≈ 4.5	455 / 728	[2]
		1.4	0.4	2.1	459 / 732	[10]
		2.5	1.5	4.4	455 / 728	[11]
		1.4	0.4	2.0	457 / 730	Present work
6 Eutectoid	δ' -Pu $\leftrightarrow$ δ -Pu + η	≈ 1.2	≈ 0.3	≈ 4.0	442 / 715	[2]
		0.43	0.38	2.1	443 / 716	[10]
		1.31	1.26	4.1	440 / 713	[11]
		0.37	0.33	2.0	443 / 716	Present work
7 Peritectoid	δ -Pu + η $\leftrightarrow$ γ -Pu	≈ 0.2	≈ 2.0	≈ 0.3	320 / 593	[2]
		0.34	2.3	0.34	320 / 593	[10]
		0.28	1.3	0.29	320 / 593	[11]
		0.25	2.3	0.21	318 / 591	Present work
8 Peritectoid	γ -Pu + η $\leftrightarrow$ β -Pu	≈ 0.8	≈ 2.9	≈ 2.0	280 / 553	[2]
		0.48	3.6	1.8	279 / 552	[10]
		0.31	1.5	0.27	213 / 486	[11]
		0.26	3.3	1.6	281 / 554	Present work
9 Eutectoid	η $\leftrightarrow$ β -Pu + ζ	≈ 3.0	≈ 2.0	≈ 26.0	278 / 551	[2]
		4.2	2.1	27.0	272 / 545	[10]
		2.7	0.4	14.3	177 / 450	[11]
		3.5	1.7	31.0	279 / 552	Present work
10 Eutectoid	β -Pu $\leftrightarrow$ α -Pu + ζ	≈ 0.1	≈ 0	≈ 30.0	125 / 398	[2]
		0.25	0	26.0	124 / 397	[10]
		0.23	0.23	14.4	124 / 397	[11]
		0.04	0	27.1	124 / 397	Present work

Figure Captions and Figures

Figure 1. Experimental Pu-U phase diagram (Top) with a magnification of the Pu-rich region (Bottom), according to the results of Ellinger *et al.* [2].

Figure 2. (Color online) Phase diagram of the Pu-U system (Top) with a magnification of the Pu-rich region (Bottom) assessed by Kurata in 1999 [10]. The symbols ($\times$, $\square$, ∇ , $\diamond$, $\circ$) represent the experimental data taken from [2, 4, 6, 7, 20], respectively.

Figure 3. (Color online) Phase diagram of the Pu-U system (Top) with a magnification of the Pu-rich region (Bottom) assessed by Kurata in 2010 [11]. The symbols ($\times$, $\square$, ∇ , $\diamond$, $\circ$) represent the experimental data taken from [2, 4, 6, 7, 20], respectively.

Figure 4. (Color online) Heat of formation (in kJ/mole) of the bcc phase for the Pu-U alloy at $T = 0$ K as a function of U composition. The positive green line (diamond) corresponds to the 2010 Kurata's assessment [11] whereas the black (squares) and red (circles) negative lines correspond to 1999 Kurata's assessment [10] and the *ab initio* results [12, 13, 31], respectively.

Figure 5. (Color online) *Ab initio* aided CALPHAD assessment of the Pu-U system (Top) with a magnification of the Pu-rich region (Bottom). The symbols ($\times$, $\square$, ∇ , $\diamond$, $\circ$) represent the experimental data taken from [2, 4, 6, 7, 20], respectively.

Figure 6. (Color online) Calculated and measured activities at 1200°C: present assessment (red solid lines) and previous assessments from Kurata (blue short dashed lines and green long dashed lines) [10, 11]. The dotted lines (Raoult's law lines) represent the ideality of the liquid alloys assumed by Leibowitz *et al.* [9]. The experimental data, empty and filled circles (Pu activity) are taken from [19] and [20],

respectively. Reference state: Pu and U in the liquid state at 1200°C.

Figure 7. (Color online) Liquid + bcc metastable phase diagram of the Pu-U system
645 calculated from [11] (Top) with a magnification of the Pu-rich region at low
temperature (Bottom). A low-temperature bcc miscibility gap and a re-entrant liquid
phase are observed.

Figure 8. (Color online) Pu-Ga (Top) and U-Ga (Bottom) assessed phase diagrams
650 reproduced from data published in [26, 34] and [37], respectively.

Figure 9. (Color online) Predicted isothermal sections, based on the present
assessment, of the Pu-U-Ga phase diagram at 1100°C, 700°C, and room temperature.

655 **Figure 10.** (Color online) Calculated property diagrams for the ternary Pu-U-Ga with
the following compositions: $\text{Pu}_{.98}\text{U}_{.01}\text{Ga}_{.01}$ (Top) and $\text{Pu}_{.89}\text{U}_{.10}\text{Ga}_{.01}$ (Bottom).

Figure 11. (Color online) Calculated Gibbs energy differences (driving force), in
kJ/mole versus temperature (in °C), between various phases of pure actinides
660 according to the SGTE data [25].

Figure 12. Molar enthalpy (Top; in kJ/mole) and its derivative with respect to
temperature (Bottom; in kJ/mole/°C) versus temperature (in °C) for the $\text{Pu}_{.40}\text{U}_{.60}$ alloy.

Figure 2

Figure 3

Figure 4

Figure 6

Figure 7

Figure 8

Figure 10

Figure 11

Figure 12

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