Thermodynamic assessments and inter-relationships between systems involving Al, Am, Ga, Pu, and U

A. Perron^{a,*}, P. E. A. Turchi^a, A. Landa^a, B. Oudot^b, B. Ravat^b, F. Delaunay^b

^aLawrence Livermore National Laboratory, Livermore, CA 94550, USA

^bCEA-Centre de Valduc, 21120 Is sur Tille, France

Abstract

A newly developed self-consistent CALPHAD thermodynamic database involving Al, Am, Ga, Pu, and U is presented. A first optimization of the slightly characterized Am-Al and completely unknown Am-Ga phase diagrams is proposed. To this end, phase diagram features as crystal structures, stoichiometric compounds, solubility limits, and melting temperatures have been studied along the U-Al $\rightarrow$ Pu-Al $\rightarrow$ Am-Al, and U-Ga $\rightarrow$ Pu-Ga $\rightarrow$ Am-Ga series, and the thermodynamic assessments involving Al and Ga alloying are compared. In addition, two distinct optimizations of the Pu-Al phase diagram are proposed to account for the low temperature and Pu-rich region controversy. The previously assessed thermodynamics of the other binary systems (Am-Pu, Am-U, Pu-U, and Al-Ga) is also included in the database and is briefly described in the present work. Finally, predictions on phase stability of ternary and quaternary systems of interest are reported to check the consistency of the database.

1. Introduction

Plutonium stands out from the other elements of the periodic table by its unusual properties [1]. For instance, plutonium has six allotropes that exhibit very different densities and mechanical properties (from 19.86 g/cm³ for the brittle simple monoclinic α phase, stable at room temperature, to 15.92 g/cm³ for the ductile face-centered-cubic δ phase, stable at high temperature) in a small temperature range (since the melting point

*Corresponding author

Email address: perron1@llnl.gov (A. Perron)

is at 640°C). The high-temperature δ phase of Pu can be retained at room temperature by alloying plutonium with a few atomic percent of “ δ -phase stabilizing” elements such as aluminum (Al), americium (Am), cerium (Ce), gallium (Ga), indium (In), or
10 scandium (Sc). The phase stability and phase transformations in Pu-Ga alloys versus temperature and pressure have been thoroughly studied and have been summarized in two review papers [2, 3]. However, alpha and beta decays of Pu induce an increase in U and Am content with time (transmutation products). As mentioned by Hecker and
15 Martz, "the most important concern about the in-growth of actinide transmutation products in plutonium is their potential effect on the delicate balance of phase stability" [4]. Because the experimental determination of phase diagrams for actinide-based alloys are costly, time-consuming, and challenging, the development of modeling methods becomes crucial.

In this framework, the phenomenological CALPHAD method — based on the de-
20 velopment of self-consistent thermodynamic databases — has proved its efficiency by reproducing the Pu-Ga phase diagram [5, 6] and explaining the martensitic transformation and reversion paths in Pu-Ga alloys [7, 8]. Recently, the phase diagram and the thermodynamic properties of the Pu-U system have been re-assessed using the CAL-
25 PHAD method with input from *ab initio* electronic-structure calculations, and combined with the Pu-Ga and U-Ga assessments to build a self-consistent Pu-U-Ga thermodynamic database [9]. The prediction of phase stability trends in the Pu-U-Ga system revealed that the complex η and ζ phases (from the Pu-U system) are promoted by U, thus leading to a decreased stability of the desired δ phase. In the same spirit alluded to
above, the goal of this work is to develop a consistent CALPHAD-type thermodynamic
30 database that includes three actinide elements (Am, Pu, and U) and two δ -stabilizer elements (Al, Ga) to study the phase stability and the phase transformations of Pu alloys stabilized with Al or Ga as functions of Am and/or U content (transmutation products). Therefore, the CALPHAD database must include 10 binary systems: i) the actinide
binaries (Am-Pu, Am-U, Pu-U) and the alloying elements binary system (Al-Ga); and
35 ii) the binaries involving actinides and alloying elements (Am-Al, Am-Ga, Pu-Al, Pu-Ga, U-Al, U-Ga). Please note that the category (i) binaries are noted in alphabetical order and those of category (ii) follow the actinide-alloying element notation. The as-

sessments of the Am-Pu [10], Am-U [11], Pu-U [9], Al-Ga [12], Pu-Ga [5, 6], U-Al [13, 14], and U-Ga [15] will be briefly presented to keep the paper self-contained. The
40 assessment of the Pu-Al system will be detailed, and the more challenging Am-Al and Am-Ga systems assessments will be proposed for the first time. To this end, phase diagram features such as crystal structures, stoichiometric compounds, solubility limits, and melting temperatures have been studied along the U-Al $\rightarrow$ Pu-Al $\rightarrow$ Am-Al, and U-Ga $\rightarrow$ Pu-Ga $\rightarrow$ Am-Ga series, and the thermodynamic assessments compared
45 (Al versus Ga alloying). As for the ternary and quaternary systems, predictions can be made from the binaries and will be discussed but new experiments are needed to refine and further validate the database.

The paper is organized as follows. The thermodynamic models are described in Section 2 while the Am-Pu, Am-U, Pu-U, and Al-Ga assessments are reported in Sec-
50 tion 3. Then, the Pu-Al assessment is given in Section 4. In addition, the assessment of the Am-Al and Am-Ga systems are detailed in Section 5. Finally, predictions for higher-order systems such as the Pu-U-(Al, or Ga) and Pu-Am-(Al, or Ga) ternary systems, and the Pu-U-Am-Al and Pu-U-Am-Ga quaternary systems are discussed in Section 6 before concluding this paper in Section 7.

55 2. Thermodynamic modeling

The aim of the CALPHAD method — CALculation of PHase Diagrams, more recently defined as Computer Coupling of Phase Diagrams and Thermochemistry¹ — is to model the Gibbs energy associated with each structure and each phase exhibited by any given alloy system [16, 17, 18]. CALPHAD is an iterative method, based on
60 models, that adjusts the parameters describing the Gibbs energies of various phases in a system to fit the available thermodynamic and phase diagram data. Once such parameters have been assessed, they are compiled in a thermodynamic database that can be used for computational thermodynamic predictions of multi-component materials. Indeed, the strength of the CALPHAD method lies in the fact that the assessed databases

¹www.calphad.org

65 should be self-consistent, and thus can be combined to predict the thermodynamic behavior of multi-component systems.

For the unaries, the Gibbs energy function for the element X (X = Al, Am, 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:

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

70 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 -Al (fcc_A1), α -Am (double hexagonal close-packed, dhcp_A3'), α -Ga (orthorhombic_A11), α -Pu (simple monoclinic) and α -U (orthorhombic_A20), and T is the absolute temperature. In the present study, the empirical parameters (a to g in Eq. 1) are taken from the data compiled by Dinsdale [19].
75 The crystal structure data and transformation temperatures of the pure elements are reported in Table 1.

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

$$G^{A_xB_y\cdots} = \sum_{I=A,B,\dots} x_I {}^0G_I^{\phi_I} + a + bT \quad (2)$$

with x_I the mole fraction of component I , and 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 . 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 crystal structure data of the stoichiometric compounds, taken from [20, 21, 22, 23, 24, 25], are reported in Tables 2-3. In the present study, the Gibbs energy of the binary stoichiometric phases is calculated using Eq. 2 where a and b are the parameters to optimize. This equation can be compared with Eq. 3 (multi-component solution phases) considering that there is no random mixing for a stoichiometric compound and that the excess Gibbs energy of mixing is modeled by $a + bT$. This last assumption, due to the lack of experimental data on stoichiometric compounds, is the
85 Neumann-Kopp approximation (*i.e.* the heat capacity of the stoichiometric compounds will be the weighted average of the heat capacities of the pure elements).
90

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, and ${}^{xs}G^\phi$ is the excess Gibbs energy of mixing due to non-ideal interactions. 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:

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

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

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

where R is the gas constant and the excess molar Gibbs energy of mixing is expressed by a so-called Redlich-Kister (RK) polynomial expansion [26]. Note that ${}^kL_{I,J}^\phi$ is the k^{th} -order binary interaction parameter between species I and J , and is usually expressed as a first-order polynomial in temperature:

$${}^kL_{I,J}^\phi = {}^ka_{I,J}^\phi + {}^kb_{I,J}^\phi T \quad (7)$$

In the present study, the liquid and solution phases are described as random mixtures of elements by Eqs. 4-6 (single sublattice model). Finally, the Gibbs energy of a ternary- or higher-order solution phase (Eq. 6) is determined by extrapolation of the binary energies using Muggianu's method [27], *i.e.* within the assumption that possible higher-order many-body interaction parameters can be ignored.

3. The Am-Pu, Am-U, Pu-U, and Al-Ga systems

It is worth noting that the use of *ab initio* energetics during the CALPHAD assessment entails a better description of the thermodynamic properties of actinide alloys. Indeed, as the process of parameter optimization and error minimization involved in

the CALPHAD method is an inverse problem with infinite degrees of freedom [28],
 115 some input from *ab initio* calculations (for instance, the heat of formation) can be used
 to constraint the optimization process but also to validate the resulting thermodynamic
 database not only from a diagrammatic representation, but also from a reliable ener-
 getic basis. Regarding the actinide binary systems (Am-Pu, Am-U, and Pu-U), the *ab*
initio calculated heats of formation of the bcc phase (Am-Pu, Am-U and Pu-U) as well
 120 as of the fcc phase (Am-Pu and Am-U) have been used successfully to assess the Am-
 Pu [10], Am-U [11], and Pu-U [9] systems (details on the methodology can be found
 in these references). The corresponding phase diagrams are reported in Figs. 1a-c.

Regarding the Am-Pu system (Fig. 1a), the calculated high-temperature phase dia-
 gram gives complete solubility between δ -Pu (fcc) and β -Am (fcc), and between ϵ -Pu
 125 (bcc) and γ -Am (bcc). The complete mutual solubility of the bcc phase is still a sub-
 ject of debate. Indeed, slightly different assessments of this phase diagram have been
 proposed previously [29, 30] and disagree with the bcc phase stability (the bcc solid
 solution is confined to the Pu- and Am-rich edges). Because of the limited availability
 of experimental data for this binary system, it is difficult to close the debate. However,
 130 the *ab initio* informed assessment (Fig. 1a) is in accordance with the most recent ex-
 perimental findings of Shushakov *et al.* [31]. A more detailed discussion can be found
 in Refs. [10, 11].

As for the Am-U system (Fig. 1b), the phase diagram is characterized by a liquid
 miscibility gap and a poor solubility of Am and U in all solid solutions. The γ -U phase
 135 (bcc) is the only one presenting a phase stability region. For more details about this
ab initio informed thermodynamic assessment and its comparison with the literature
 [29, 32], please refer to Ref. [11].

As regards to the Pu-U system (Fig. 1c), the phase diagram has been successfully
 assessed in the entire range of alloy composition and temperature [9]. This system is
 140 characterized by a continuous bcc solid solution across the entire composition range
 at high temperature, and the existence of complex η and ζ phases. However, the au-
 thors noted that experimental data are needed to characterize the crystallography, phase
 stability and thermodynamic properties of these complex phases. More details and a
 comparison with previous assessments [33, 34] can be found in Ref. [9].

Finally, the Al-Ga binary system has been added to the present database by using the thermodynamic assessment of Ansara *et al.* [12]. This phase diagram (Fig. 1d) is rather simple and exhibits one invariant reaction (eutectic) around room temperature with a small solubility of Ga in fcc-based Al.

4. Assessment of the Pu-Al system

The Pu-Al phase diagram originally proposed by Schonfeld in 1957 [35] and followed by the one of Bochvar *et al.* in 1958 [36] generated a dispute similar to the one discussed in the case of the Pu-Ga phase diagram [37]. The phase boundaries of the low temperature Pu-rich part of the diagram were the contended features. In the American version [35] the δ phase is indicated stable at low temperature whereas in the Bochvar *et al.* version [36] an eutectoid reaction $\delta \rightarrow \beta + \text{AlPu}_3$ at 175°C is proposed. Later on (in 1962), Ellinger *et al.* presented a revised Pu-Al phase diagram [38] — quite similar to the one proposed by Schonfeld — that has been considered as the reference by Kassner and Peterson in 1989 [39]. The long-standing controversy between the American and Russian version of the Pu-Al phase diagram was finally put to rest in 1999 in favor of the Russian version [40], which exhibits an eutectoid decomposition of the δ -Pu phase into the α -Pu phase plus the AlPu stoichiometric compound [37].

However, the phases involved in the low-lying eutectoid decomposition is also subject to debate. Adler predicted the existence of an eutectoid decomposition in Pu-Al at low temperature using a thermodynamic model [41]. This prediction involves the precipitation of the AlPu_3 phase (Option 1) instead of the AlPu phase (Option 2) characterized by Timofeeva [40]. It is interesting to note that, prior to long annealing at atmospheric pressure, the use of pressure and plastic deformation was used by Timofeeva to "precondition" plutonium alloys and enhance the kinetics of the δ -phase decomposition. On the contrary, the results of Adler seem underpinned by the experiments performed by Ellinger [38] where the AlPu phase was found to have decomposed into the AlPu_3 and the Al_2Pu phases after being aged at room temperature for 10 years. In addition, the eutectoid decomposition of the fcc phase involving the AlPu_3 compound is consistent with the other group IIIA Pu-M (M = Ga, In, Tl) systems [41].

A complete thermodynamic assessment of the Pu-Al system has been published by Turchi *et al.* [6] and reported by Okamoto in [21]. However, the CALPHAD model parameters have not been indicated in [6]. The present study reports a slightly modified version of the previous assessment [5, 6] to avoid any inverted liquid miscibility gap without changing the conclusions drawn in Refs. [5, 6]. The calculated Pu-Al phase diagram is presented in Fig. 2a (Option 1), and the optimized parameters are reported in Table 4. In addition, a second assessment has been performed to reproduce the Russian version of the phase diagram (Fig. 2b, Option 2). The experimental heat of formation of the Al₂Pu (-47.450 ± 3.349 kJ/mol), Al₃Pu (low temperature allotrope, -45.217 ± 2.523 kJ/mol), and Al₄Pu (-36.174 ± 2.009 kJ/mol) compounds [42, 43] are well reproduced by the CALPHAD assessments: -46, -45, and -36 kJ/mol, respectively (see Table 4). It is worth noting that only the Gibbs energies of the AlPu and AlPu₃ compounds differ between the two assessments (Table 4), and that no experimental heats of formation are available for these compounds. This difference is highlighted in terms of Gibbs energy minimization at 25°C (Fig. 2c) and 330°C (Fig. 2d). As observed, these two assessments are very close and it is difficult to differentiate them. Should more experimental data on this system be available, it would be possible to close the debate. However, based on the previous works reported in the literature, the $\delta \rightarrow \alpha\text{-Pu} + \text{AlPu}_3$ eutectoid decomposition (Option 1) is more likely valid.

5. Assessment of the Am-Al and Am-Ga systems

5.1. The U-Al $\rightarrow$ Pu-Al $\rightarrow$ Am-Al series

As limited experimental data are available regarding the Am-Al binary system [23], and no phase diagram is reported in the ASM Alloy Phase Diagram Database, the authors decided to study the trend along the U-Al $\rightarrow$ Pu-Al $\rightarrow$ Am-Al series to have some hints for this system assessment.

The phase diagram and thermodynamic properties of the U-Al system have been evaluated by Wang *et al.* who propose a consistent set of thermodynamic parameters [13]. Some modifications have been made by Kniznik *et al.* regarding the Al₄U compound [14], leading to a better agreement between the calculated results and most of

the experimental data found in the literature. The resulting phase diagram is reported in Fig. 3a. The U-Al system exhibits three different compounds: Al_2U , Al_3U , and Al_4U .
 205 The Al_2U stoichiometric compound (C15) melts congruently at 1621°C (highest melting temperature of the system). Then, the Al_3U (L1_2) and Al_4U (D1_b) precipitate from peritectic reactions at 1350 and 741°C , respectively. It is interesting to note that Al_4U is a non-stoichiometric compound. Finally, the $\gamma\text{-U}$ (bcc) phase exhibits some solubility in Al, and the eutectic reaction on the Al side of the phase diagram demonstrates
 210 no solubility of U in $\alpha\text{-Al}$ (fcc). By comparing to the Pu-Al phase diagram (present assessment, Option 1) presented in Fig. 3b, many similarities can be highlighted. First, the stoichiometry and the crystal structure of the three Al_xU_y compounds are observed in the Pu-Al system using the $\text{Al}_x\text{Actinide}_y$ notation: Al_2Pu (C15), Al_3Pu (L1_2 for the high-temperature polymorph), and Al_4Pu (Al_4U). As shown in Table 2, the crystal
 215 structures are similar, and the precipitation mechanisms equivalent: Al_2Pu melts congruently at 1529°C (highest melting temperature of the system), then Al_3Pu and Al_4Pu precipitate from peritectic reactions at 1442 and 949°C , respectively. In the Pu-rich region, the $\epsilon\text{-Pu}$ (bcc) exhibits an Al solubility similar to U-Al. In addition, the $\delta\text{-Pu}$ phase (fcc) presents a large solubility in Al which acts as a " δ " stabilizer. In the Al-rich
 220 region, the eutectic reaction is also present, and the fcc phase exhibits no solubility in Pu. Finally, in spite of the fact that the Pu-Al system contains more stoichiometric compounds (AlPu_3 , AlPu) and a polymorphic Al_3Pu compound (see Table 2), the general shape and features of this system are comparable with those of the U-Al system.

As for the Am-Al system, Radchenko *et al.* [23] did not determine the entire phase
 225 diagram but provided the most complete experimental data which — in addition to the review of Kassner and Peterson [22] — provide the benchmarks for this system. First, the Al_2Am and Al_4Am stoichiometric compounds have been characterized with the corresponding cubic lattice Laves structure (C15) and an orthorhombic lattice (similar to the Al_4U phase), respectively. This result confirms those published in Ref. [22].
 230 Then, AlAm_3 has been proposed with an ordered cubic structure and, in comparison with the Al-Ln (Ln = Lanthanides) systems, Radchenko *et al.* assumed the existence of both the AlAm and Al_3Am compounds. Even if no melting temperatures of the compounds have been determined, the melting temperature of Al_2Am has been charac-

235 terized as above 1600°C. No solubility has been detected in the α -Am phase (dhcp) and in the α -Al phase (fcc). Finally, the eutectic reaction on the Al-rich part of the phase diagram has been well characterized: $L \rightarrow \text{Al}_4\text{Am} + \alpha\text{-Al}$ at $643 \pm 3^\circ\text{C}$ and 98 at.% Al.

240 All the U-Al-type compounds, with their associated crystal structures, are reproduced in the Pu-Al system. Based on the few experiments on the Am-Al system which reveal the existence of the Al_2Am and Al_4Am compounds with crystal structures similar to the Al_2X and Al_4X ($\text{X} = \text{U}, \text{Pu}$) compounds, and the previous assumptions made by Radchenko *et al.* on the Am-Al system (existence of the AlAm_3 , AlAm and Al_3Am compounds), all the Al_xPu_y -type stoichiometric compounds should be present in the Am-Al phase diagram (see Table 2). However, no polymorphic transformations have been introduced. The assessment of the Am-Al system has been performed using the experimental data given in [23] and the parameter used for the Pu-Al and U-Al systems (as starting values to retain self-consistency between the systems). The assessed parameters are given in Table 5 and the resulting phase diagram is plotted in Fig. 3c. The congruent melting of Al_2Am is predicted at 1603°C ($>1600^\circ\text{C}$), and the eutectic reaction on the Al-rich region is well reproduced at 639°C and 98.3 at.% Al. The rest of the invariant lines of the predicted phase diagram are very similar to those observed in the U-Al and Pu-Al systems. Moreover, no Al solubility is predicted in the γ -Am phase (bcc), contrary to the β -Am phase (fcc). The Am-rich region should be considered with caution as no experimental data are available.

5.2. The U-Ga $\rightarrow$ Pu-Ga $\rightarrow$ Am-Ga series

255 Following the same methodology, and as no data are available for the Am-Ga system, the trend along the U-Ga $\rightarrow$ Pu-Ga $\rightarrow$ Am-Ga series was selected to identify some hints on this system assessment.

260 The thermodynamic assessment of the U-Ga system has been performed by Wang *et al.* [15] and is reproduced in Fig. 3d. This system exhibits three different stoichiometric compounds: Ga_3U_2 , Ga_2U , and Ga_3U . The Ga_2U compound (C32, see Table 3) melts congruently at 1355°C (highest melting temperature of the system), and the hexagonal β - Ga_2U (C32) transforms into the orthorhombic α - Ga_2U below the Curie temperature (-148°C). As the CALPHAD assessment is performed above room

temperature, the C32 structure is the only one considered for this compound. Ga_3U_2 and Ga_3U precipitate from peritectic reactions at 1260 and 1250°C, respectively. The γ -U (bcc) phase exhibits some solubility in Ga, but no U solubility in α -Ga is observed. This assessed diagram is in agreement with the review published by Okamoto in 1993 [24] but some uncertainties remain regarding the range of composition in which some of these compounds are stable. Indeed, the Ga_5U_3 and GaU compounds have been reported in [24] but the reaction types of formation and phase stability were missing. In 2008, Okamoto reported that the crystal structures of Ga_5U_3 , Ga_3U_2 , and GaU were the same and speculated that only one of these phases corresponds to the true equilibrium phase [44]. Based on the works of Salhov *et al.* [45], Okamoto concluded that Ga_5U_3 was the stable compound. This result is different from the determination of Wang *et al.* for their thermodynamic assessment [15]. Therefore, a slight modification of this assessment may be needed in the future. Ga and Al have a similar impact on U alloying (Figs. 3a,d): 3 compounds precipitate, the systems exhibit one high-temperature congruent melting, the γ -U (bcc) phase admits some Al and Ga solubility, and no solubility of U in the Ga or Al phases is observed.

For the Pu-Ga system (Fig. 3e) assessed by Turchi *et al.* [5, 6], the stoichiometry and the crystal structure of the three Ga_xU_y compounds are reproduced using the $\text{Ga}_x\text{Actinide}_y$ notation: Ga_3Pu_2 , Ga_2Pu , and Ga_3Pu . However, similarly to the Pu-Al system which exhibits more compounds than the U-Al system; the Pu-Ga system displays a greater number of compounds than the U-Ga system (Figs.3 d-e, Table 3). But the Ga_5U_3 stoichiometry suggested by Okamoto for the U-Ga system, instead of the Ga_3U_2 stoichiometry, is non-existent in the Pu-Ga system. In fact, only one compound has the same structure in both the U-Ga and Pu-Ga systems: Ga_2Pu (C32). This compound melts congruently at 1262°C (highest melting temperature of the system). Otherwise, the bcc (ϵ -Pu) and fcc (δ -Pu) phases admit good solubility in Ga (as for the Pu-Al system). Once again, the alloying effect of Ga and Al on Pu is very similar (a δ -phase stabilizer) even if the Pu-Ga phase diagram is more complex.

For the Am-Ga system, there are presently no available experimental data. The Ga_2X (X = U, Pu) compounds have the same crystal structure (C32), so the Ga_2Am compound is also assumed to be C32 (Table 3), similar to the Al_2X (X = U, Pu, Am)

series of compounds which exhibit the same crystal structure (C15). This compound should melt congruently and exhibit the highest melting temperature for the Am-Ga system. A relationship between the melting temperatures of these stoichiometric compounds has been discovered for the U-Al/Pu-Al and U-Ga/Pu-Ga systems :

$$\Delta T_m(Al_2U - Ga_2U) = 266^\circ C \quad (8)$$

$$\Delta T_m(Al_2Pu - Ga_2Pu) = 267^\circ C \quad (9)$$

Thus, the melting temperature of the Ga_2Am compound has been evaluated around $1337^\circ C$ ($T_m(Al_2Am) \approx 1603^\circ C$). The existence of other stoichiometric compounds are inferred from observations of the U-Al $\rightarrow$ Pu-Al $\rightarrow$ Am-Al series (all U-Al-type compounds are present in the Pu-Al system, and all Pu-Al-type compounds have been reproduced in the Am-Al system) to the U-Ga $\rightarrow$ Pu-Ga $\rightarrow$ Am-Ga series. Since the Ga_xU_y compounds have their equivalent in the Pu-Ga system (Ga_xPu_y), the Ga_xPu_y stoichiometries are reported in the Am-Ga system (Ga_xAm_y) (Figs. 3d-f). Al_4U , Al_4Pu , Al_4Am , and Ga_4Pu exhibit the same $D1_b$ structure (Al_4U -type), thus the Ga_4Am compound is assumed to have a $D1_b$ structure. The $GaPu_3$ compound exhibits a $L6_0$ structure at low temperature. This structure (Pb_3Sr prototype) is similar to the $AlPu_3$ compound. However, $GaPu_3$ is a dimorphic compound exhibiting a $L1_2$ structure at high temperature. In order to maintain consistency along the U-Ga $\rightarrow$ Pu-Ga $\rightarrow$ Am-Ga series, α - $GaAm_3$ and β - $GaAm_3$ are considered $L6_0$ and $L1_2$, respectively. The polymorphism of the remaining compounds (Ga_3Am_5 , $GaAm$, Ga_3Am_2 , Ga_3Am , Ga_7Am_2 , $Ga_{11}Am_3$, Ga_6Am , $Ga_{15}Am_2$) has been considered similar to those of the Pu-Ga system but with independent crystal structures (no similarities can be established for these compounds). Based on these relations and using the previous Pu-Ga assessment, a tentative assessment of the Am-Ga phase diagram is proposed. The assessed parameters for the Am-Ga system are reported in Table 6 — with the assumptions summarized in Table 7 — and the predicted phase diagram is shown in Fig. 3f.

Congruent melting of the Ga_2Am is predicted at $1338^\circ C$ (as calculated using Eqs. 8-9), and a eutectic reaction on the Am-rich region is proposed. In addition, no solubility of Ga in the γ -Am phase (bcc) is predicted and a good solubility in Ga for the β -Am phase (fcc) is proposed. The Ga-rich portion of the phase diagram is similar to U-Ga

and Pu-Ga diagrams (see Figs. 3d-f). The rest of the invariant lines of the predicted
 325 phase diagram are very similar to those observed in the Pu-Ga system. This phase dia-
 gram is entirely predicted and should be considered with caution since no experimental
 data are available.

The eutectic reactions in the Am-rich regions of the Am-Al and Am-Ga phase di-
 agrams are similar to those observed in the lanthanide-rich regions of phase diagrams
 330 involving Ln-Al and Ln-Ga. Moreover, all the Ln-Al and Ln-Ga systems exhibit the
 Al_2Ln or Ga_2Ln compounds. These compounds have the highest melting temperature
 for most of these systems (except for the Er-Al, Tm-Al, Lu-Al, Dy-Ga, Ho-Ga, Er-Ga,
 Tm-Ga, and Lu-Ga systems), consistent with the U-Al, Pu-Al, Am-Al, U-Ga, Pu-Ga,
 and Am-Ga systems. Generally, the Ln-Al and Ln-Ga phase diagrams look similar to
 335 the Am-Al and Am-Ga diagrams with the presence of numerous compounds, eutectic
 invariant lines on both sides of the phase diagrams, and no solubility on the Al/Ga-rich
 part of the phase diagram. These similarities originate from the electronic structure of
 these two peculiar series. Indeed, the Am element belongs to the actinide series, which
 is characterized by a progressive filling of the $5f$ -electron shell with increasing atomic
 340 number [46]. From thorium to plutonium, the lighter actinides are characterized by
 itinerant $5f$ electrons that contribute to the bonding. Starting with Am (and to some ex-
 tend, Pu, depending on the structure), the heavy actinides exhibit localized $5f$ electrons
 that contribute very little to the bonding. This specific behavior along the actinide series
 has been compared with both the d transition elements (delocalized $5d$ electrons) and
 345 the lanthanides (localized $4f$ electrons) [47]. Thus, the ground-state crystal structure
 of Am (heavy actinide) — dhcp (double-hexagonal close-packed) — is isotypic with
 many lanthanides (α -La, β -Ce, α -Pr, α -Nd, α -Pm). Because the data on Am-Al and
 Am-Ga are lacking, the comparison of the phase diagram features along the U-Al $\rightarrow$
 Pu-Al $\rightarrow$ Am-Al, and the U-Ga $\rightarrow$ Pu-Ga $\rightarrow$ Am-Ga series coupled with a comparison
 350 between the Am-Al/Ga and Ln-Al/Ga systems provides some justification for a better
 understanding of these systems.

6. Prediction for higher-order systems

The strength of the CALPHAD method lies in the prediction of the thermodynamic behavior of multi-component systems. As the 10 binary systems (Am-Pu, Am-U, Pu-U, Am-Al, Am-Ga, Pu-Al, Pu-Ga, U-Al, U-Ga, and Al-Ga) have been included in the present database, it enables the study of the phase stability of more complex systems based on the CALPHAD predictions. However, the contribution to the excess Gibbs energy from ternary interaction parameters is not considered in the present study. Thus, the interactions in multi-component systems are based on the interactions from the binaries without any ternary correction. This implies that the predictions presented for the ternary and quaternary systems should be considered as representations of systems if not in the stable equilibrium, at least in a metastable one. Should more experimental data or even *ab initio* calculations on the ternaries be available, it would be possible to introduce their thermodynamic description in the database.

First, the alloying effect of Al and Ga on Pu can be compared. Property diagrams for typical concentrations of 1 and 7 at. % Al or Ga are presented in Fig. 4. As observed and expected, Al and Ga act similarly as powerful δ -Pu phase stabilizers. The kinetics of the low-temperature eutectoid decomposition of the δ -Pu phase into α -Pu and GaPu_3 or AlPu_3 is very slow (several millenia [1, 5]). However, these diagrams should not be neglected as they represent the thermodynamic equilibrium and thus, highlight the underlying driving force acting to minimize the system energies.

The impact of the transmutation products (U and Am) of Pu on Al- and Ga-stabilized Pu-based alloys can be investigated. The effect of neptunium (Np) has not been taken into account in the present study. In spite of the fact that this element belongs to the actinide series U, Np, Pu, Am, and that Np is a transmutation product of Pu, the Np-Al system is unknown and the Np-Ga system has been poorly characterized (as reported in the ASM Alloy Phase Diagram Database: only Ga_2Np (C32) and Ga_3Np (L1₂) are indicated). In addition, the growth rate of Np as a transmutation product is quite low compared with Am and U [2]. Thus, the impact of U and Am on the Al- and Ga-stabilized Pu-based alloys are the only ones considered in this study.

For the Pu-U-Al and Pu-U-Ga systems, the calculated monovariant lines associ-

ated with the primary crystallization fields, and the isothermal liquidus projections are presented in Fig. 5. As observed, the $\text{Al}_2(\text{Pu},\text{U})$ and $\text{Ga}_2(\text{Pu},\text{U})$ compounds develop a large primary crystallization field. The Pu-U-Ga system is more complex due to the numerous Ga_xPu_y compounds and exhibits a larger bcc primary crystallization field but, overall, the systems are quite similar. For both systems, the last drops of liquid are concentrated on the Al and Ga corner, and on the Pu-U branch. In the Pu-Am-Al and Pu-Am-Ga systems, similar observations can be made (Fig. 6). However, one major difference is highlighted: the appearance of a fcc primary crystallization field. This fcc field is related to the predicted Am-Al and Am-Ga systems and should be characterized experimentally in more detail. Indeed, this can be crucial during the solidification process of Al- and Ga-stabilized Pu-based alloys. Thus, any alloy composition belonging to the fcc primary crystallization field presented in Fig. 6 is a good candidate to validate and refine the present thermodynamic database.

In order to have a better understanding of the impact of U and Am, several property diagrams have been plotted (Fig. 7). By comparing Fig. 4a ($\text{Pu}_{.99}\text{Al}_{.01}$) and Fig. 7a ($\text{Pu}_{.94}\text{U}_{.05}\text{Al}_{.01}$), a clear destabilization of the δ phase is observed with the formation of the two complex η and ζ phases of the Pu-U system. This result is similar to the one observed for the $\text{Pu}_{.98}\text{U}_{.01}\text{Ga}_{.01}$ and $\text{Pu}_{.89}\text{U}_{.10}\text{Ga}_{.01}$ alloys [9]. In order to balance the effect of U, one may try to add more Al (Fig. 7b). This will indeed enhance the stability of the δ -Pu phase rather than the η phase but will have no impact on the ζ -phase stability. Moreover, by adding Al, the liquidus temperature is shifted from 650°C ($\text{Pu}_{.94}\text{U}_{.05}\text{Al}_{.01}$) to 790°C ($\text{Pu}_{.88}\text{U}_{.05}\text{Al}_{.07}$) and induces the precipitation of Al_2Pu (C32) at high temperature.

As presented in Fig. 7c, Am operates as a δ stabilizer (by comparing with Fig. 4a and Fig. 7a). However, the poor miscibility of Am and Pu at room temperature induces the precipitation of the α -Am phase (dhcp). By adding more Al, see $\text{Pu}_{.88}\text{Am}_{.05}\text{Al}_{.07}$ (Fig. 7d), the precipitation of the dhcp phase can be avoided through the precipitation of the $\text{Al}(\text{Am},\text{Pu})_3$ compound and the fcc phase is even more stabilized. For this composition, the bcc phase does not appear during the solidification process (under equilibrium conditions). This prediction arises from the proposed Am-Al binary system (Fig. 3c), and is in agreement with Fig. 6a ($\text{Pu}_{.88}\text{Am}_{.05}\text{Al}_{.07}$ belongs to the fcc primary crystal-

lization field), but must be confirmed experimentally as it is of technological interest. Indeed, the diffusion properties of the bcc and fcc phases of Pu are very different and
415 lead to a strong coring effect during solidification [48].

Two property diagrams ($\text{Pu}_{.96}\text{U}_{.01}\text{Am}_{.02}\text{Al}_{.01}$ and $\text{Pu}_{.90}\text{U}_{.01}\text{Am}_{.02}\text{Ga}_{.07}$) of quaternary systems are presented in Fig. 8 to explore the impact of both transmutation products on the phase stability of Pu-based alloys. As observed, 1 at. % of U can lead to up to 10% of the complex η phase, while adding Ga, Al, and/or Am greatly stabilizes
420 the fcc phase. These first predictions using the newly developed self-consistent CALPHAD thermodynamic database confirm the role of Al, Ga, and Am as δ -Pu phase (fcc) stabilizers, and of U as a destabilizing element for the δ -Pu phase. Finally, the impact of Pu transmutation products (Am, U) should not be neglected — even at a small fraction and especially when complex phenomena such as diffusion under irradiation
425 occur — as they induce a strong phase separation for the Am-Pu system (Fig. 1a) at room temperature and for the Am-U system (Fig. 1b) across the whole phase diagram.

7. Conclusion

The CALPHAD assessments of the Pu-Al system (two options), of the slightly characterized Am-Al phase diagram, and of the completely unknown Am-Ga system
430 (all presented in this study) have been performed, and permitted to develop a new self-consistent CALPHAD thermodynamic database involving Al, Am, Ga, Pu, and U. Predictions have been made on the impact of the transmutation products of Pu (U and Am) on Al- and Ga-stabilized Pu-based alloys. A phase stability study of ternary and quaternary systems highlights the δ -stabilizing effect of Al, Ga, and Am, and the
435 destabilizing effect of U (acting as a stabilizer for the complex η and ζ phases). Finally, guidance for experiments have been proposed to verify the existence of the fcc primary crystallization fields in the Pu-Am-Al and Pu-Am-Ga systems.

Acknowledgments

This work was performed under the auspices of the U.S Department of Energy
440 by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344.

This work was done as part of the international agreement on cooperation between DOE-NNSA and CEA-DAM in fundamental science supporting stockpile stewardship. A.P. gratefully acknowledges the financial support from the CEA-Centre de Valduc (France), the Post-doctoral program at LLNL, and Scott K. McCall for a thorough
445 reading of the manuscript.

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Tables

Table 1. Al, Am, Ga, Pu, and U crystal structures and their associated transformation temperatures (calculated using [19]).

Phase	CALPHAD Designation	Pearson symbol	Space group	Strukturbericht Designation	Prototype	Temperature (°C)
α -Al	FCC_A1	$cF4$	$Fm\bar{3}m$	A1	Cu	660
α -Am	DHCP	$hP4$	$P6_3/mmc$	A3'	α -La	769
β -Am	FCC_A1	$cF4$	$Fm\bar{3}m$	A1	Cu	1077
γ -Am	BCC_A2	$cI2$	$Im\bar{3}m$	A2	W	1176
α -Ga	Orthorhombic_A11	$oC8$	$Cmca$	A11	Ga	30
α -Pu	Alpha_Pu	$mP16$	$P2_1/m$	-	α -Pu	124
β -Pu	Beta_Pu	$mC34$	$C2/m$	-	β -Pu	215
γ -Pu	Gamma_Pu	$oF8$	$Fddd$	-	γ -Pu	320
δ -Pu	FCC_A1	$cF4$	$Fm\bar{3}m$	A1	Cu	463
δ' -Pu	Tetragonal_A6	$tI2$	$I4/mmm$	A6	In	483
ϵ -Pu	BCC_A2	$cI2$	$Im\bar{3}m$	A2	W	640
α -U	Orthorhombic_A20	$oC4$	$Cmcm$	A20	α -U	668
β -U	Tetragonal_U	$tP30$	$P4_2/mnm$	A_b	β -U	776
γ -U	BCC_A2	$cI2$	$Im\bar{3}m$	A2	W	1135

Table 2. Crystal structure data for stoichiometric compounds along the U-Al → Pu-Al
→ Am-Al series.

Compound	Pearson symbol	Space group	Strukturbericht Designation	Prototype	Ref.
Al ₂ U	<i>cF24</i>	<i>Fd$\bar{3}m$</i>	C15	Cu ₂ Mg	[20]
Al ₃ U	<i>cP4</i>	<i>Pm$\bar{3}m$</i>	<i>L1₂</i>	AuCu ₃	[20]
Al ₄ U	<i>oI20</i>	<i>Imma</i>	<i>D1_b</i>	Al ₄ U	[20]
AlPu ₃	<i>tP4</i>	<i>P4/mmm</i>	-	Pb ₃ Sr	[21]
AlPu	<i>cI58</i>	-	-	-	[21]
Al ₂ Pu	<i>cF24</i>	<i>Fd$\bar{3}m$</i>	C15	Cu ₂ Mg	[21]
α -Al ₃ Pu	<i>hR*</i>	<i>R$\bar{3}m$</i>	-	-	[21]
β -Al ₃ Pu	<i>hR*</i>	<i>R$\bar{3}m$</i>	-	-	[21]
γ -Al ₃ Pu	<i>hP*</i>	<i>P6₃/mmc</i>	-	-	[21]
δ -Al ₃ Pu	<i>cP4</i>	<i>Pm$\bar{3}m$</i>	<i>L1₂</i>	AuCu ₃	[21]
Al ₄ Pu	<i>oI20</i>	<i>Imma</i>	<i>D1_b</i>	Al ₄ U	[21]
AlAm ₃	-	-	-	ordered cubic	[23]
AlAm ₃	<i>tP4</i>	<i>P4/mmm</i>	-	Pb ₃ Sr	[this study]
AlAm	-	-	-	-	[23]
AlAm	<i>cI58</i>	-	-	AlPu	[this study]
Al ₂ Am	<i>cF24</i>	<i>Fd$\bar{3}m$</i>	C15	Cu ₂ Mg	[22, 23]
Al ₃ Am	-	-	-	-	[23]
Al ₃ Am	<i>cP4</i>	<i>Pm$\bar{3}m$</i>	<i>L1₂</i>	AuCu ₃	[this study]
Al ₄ Am	<i>o*</i>	-	-	-	[22, 23]
Al ₄ Am	<i>oI20</i>	<i>Imma</i>	<i>D1_b</i>	Al ₄ U	[this study]

Table 3. Crystal structure data for stoichiometric compounds along the U-Ga → Pu-Ga → Am-Ga series.

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Compound	Pearson symbol	Space group	Strukturbericht Designation	Prototype	Ref.
Ga ₃ U ₂	<i>oC32</i>	<i>Cmcm</i>	-	-	[24]
α -Ga ₂ U	<i>oC*</i>	<i>Cmmm</i>	-	-	[24]
β -Ga ₂ U	<i>hP3</i>	<i>P6/mmm</i>	<i>C32</i>	AlB ₂	[24]
Ga ₃ U	<i>cP4</i>	<i>Pm$\bar{3}m$</i>	<i>L1₂</i>	AuCu ₃	[24]
α -GaPu ₃	<i>tP4</i>	<i>P4/mmm</i>	<i>L6₀</i>	Pb ₃ Sr	[25]
β -GaPu ₃	<i>cP4</i>	<i>Pm$\bar{3}m$</i>	<i>L1₂</i>	AuCu ₃	[25]
Ga ₃ Pu ₅	<i>tI32</i>	<i>I4/mcm</i>	<i>D8_m</i>	W ₅ Si ₃	[25]
α -GaPu	<i>tI2</i>	<i>I4/mmm</i>	<i>A6</i>	In	[25]
β -GaPu	<i>cI2</i>	<i>Im$\bar{3}m$</i>	<i>A2</i>	W	[25]
Ga ₃ Pu ₂	<i>hP*</i>	-	-	-	[25]
Ga ₂ Pu	<i>hP3</i>	<i>P6/mmm</i>	<i>C32</i>	AlB ₂	[25]
α -Ga ₃ Pu	<i>hR16</i>	<i>R$\bar{3}m$</i>	-	-	[25]
β -Ga ₃ Pu	<i>hP8</i>	<i>P6₃/mmc</i>	<i>D0₁₉</i>	Ni ₃ Sn	[25]
γ -Ga ₃ Pu	-	-	-	-	[25]
Ga ₇ Pu ₂	<i>t**</i>	-	-	-	[25]
Ga ₁₁ Pu ₃	-	-	-	-	[25]
Ga ₄ Pu	<i>oI20</i>	<i>Imma</i>	<i>D1_b</i>	Al ₄ U	[25]
Ga ₆ Pu	<i>tP14</i>	<i>P4/nbm</i>	-	-	[25]
Ga ₁₅ Pu ₂	<i>t**</i>	-	-	-	[25]
α -GaAm ₃	<i>tP4</i>	<i>P4/mmm</i>	<i>L6₀</i>	Pb ₃ Sr	[this study]
β -GaAm ₃	<i>cP4</i>	<i>Pm$\bar{3}m$</i>	<i>L1₂</i>	AuCu ₃	[this study]
Ga ₃ Am ₅	-	-	-	Ga ₃ Am ₅	[this study]
α -GaAm	-	-	-	α -GaAm	[this study]
β -GaAm	-	-	-	β -GaAm	[this study]
Ga ₃ Am ₂	-	-	-	Ga ₃ Am ₂	[this study]
Ga ₂ Am	<i>hP3</i>	<i>P6/mmm</i>	<i>C32</i>	AlB ₂	[this study]
α -Ga ₃ Am	-	-	-	α -Ga ₃ Am	[this study]
β -Ga ₃ Am	-	-	-	β -Ga ₃ Am	[this study]
γ -Ga ₃ Am	-	-	-	γ -Ga ₃ Am	[this study]
Ga ₇ Am ₂	-	-	-	Ga ₇ Am ₂	[this study]
Ga ₁₁ Am ₃	-	-	-	Ga ₁₁ Am ₃	[this study]
Ga ₄ Am	<i>oI20</i>	<i>Imma</i>	<i>D1_b</i>	Al ₄ U	[this study]
Ga ₆ Am	-	-	-	Ga ₆ Am	[this study]
Ga ₁₅ Am ₂	-	-	-	Ga ₁₅ Am ₂	[this study]

Table 4. Optimized thermodynamic parameters (in J/mol or J/mol/K) for the Pu-Al system (present study). The standard element reference Gibbs energy functions (GHSER) are taken from [19]. Option 1 and 2 corresponds to Ref. [35] and Ref. [36], respectively (see text for more details).

Phase	Parameters
Liquid	${}^0G_{Al}, {}^0G_{Pu}$ [19] ${}^0L_{Al,Pu}$ -19000 - 40*T ${}^1L_{Al,Pu}$ -1000 - 30*T ${}^2L_{Al,Pu}$ -30000 + 10*T
BCC_A2 (ϵ -Pu)	${}^0G_{Al}, {}^0G_{Pu}$ [19] ${}^0L_{Al,Pu}$ -98000 + 10*T ${}^1L_{Al,Pu}$ -3500 - 28*T
FCC_A1 (δ -Pu, α -Al)	${}^0G_{Al}, {}^0G_{Pu}$ [19] ${}^0L_{Al,Pu}$ -94000 + 18*T ${}^1L_{Al,Pu}$ -1000 - 8*T
δ' -Pu	${}^0G_{Pu}$ [19]
γ -Pu	${}^0G_{Al}$ +4900 + GHSERAL ${}^0G_{Pu}$ [19]
β -Pu	${}^0G_{Pu}$ [19]
α -Pu	${}^0G_{Al}$ +5000 + GHSERAL ${}^0G_{Pu}$ [19] ${}^0L_{Al,Pu}$ +31500
AlPu ₃	$G_{Al:Pu}$ -16375 - 5.35*T + .25*GHSERAL + .75*GHSERPU (Option 1) -16300 - 5.45*T + .25*GHSERAL + .75*GHSERPU (Option 2)
AlPu	$G_{Al:Pu}$ -34128 - 2.159*T + .5*GHSERAL + .5*GHSERPU (Option 1) -38000 + 3.14*T + .5*GHSERAL + .5*GHSERPU (Option 2)
Al ₂ Pu	$G_{Al:Pu}$ -46000 + .667*GHSERAL + .333*GHSERPU
α -Al ₃ Pu	$G_{Al:Pu}$ -45000 + 7.5*T + .75*GHSERAL + .25*GHSERPU
β -Al ₃ Pu	$G_{Al:Pu}$ -28200 - 6.5*T + .75*GHSERAL + .25*GHSERPU
γ -Al ₃ Pu	$G_{Al:Pu}$ -25600 - 8.5*T + .75*GHSERAL + .25*GHSERPU
δ -Al ₃ Pu	$G_{Al:Pu}$ -24150 - 9.5*T + .75*GHSERAL + .25*GHSERPU
Al ₄ Pu	$G_{Al:Pu}$ -36000 + 5*T + .8*GHSERAL + .2*GHSERPU

Table 5. Optimized thermodynamic parameters (in J/mol or J/mol/K) for the Am-Al system (present study). The standard element reference Gibbs energy functions (GHSER) are taken from [19].

Phase	Parameters
Liquid	${}^0G_{Al}, {}^0G_{Am}$ [19] ${}^0L_{Al,Am}$ -50000 - 25*T ${}^1L_{Al,Am}$ -66000 + 20*T ${}^2L_{Al,Am}$ -45000 - 6*T
BCC_A2 (γ -Am)	${}^0G_{Al}, {}^0G_{Am}$ [19] ${}^0L_{Al,Am}$ -20000
FCC_A1 (β -Am, α -Al)	${}^0G_{Al}, {}^0G_{Am}$ [19] ${}^0L_{Al,Am}$ -48950
DHCP (α -Am)	${}^0G_{Am}$ [19]
AlAm ₃	$G_{Al:Am}$ -22500 + 5*T + .25*GHSERAL + .75*GHSERAM
AlAm	$G_{Al:Am}$ -37700 + 3*T + .5*GHSERAL + .5*GHSERAM
Al ₂ Am	$G_{Al:Am}$ -48000 + 2*T + .667*GHSERAL + .333*GHSERAM
Al ₃ Am	$G_{Al:Am}$ -50000 + 7*T + .75*GHSERAL + .25*GHSERAM
Al ₄ Am	$G_{Al:Am}$ -41500 + 6*T + .8*GHSERAL + .2*GHSERAM

Table 6. Optimized thermodynamic parameters (in J/mol or J/mol/K) for the Am-Ga system (present study). The standard element reference Gibbs energy functions (GHSER) are taken from [19].

Phase	Parameters
Liquid	${}^0G_{Am}, {}^0G_{Ga}$ [19] ${}^0L_{Am,Ga}$ -121696 - 4*T ${}^1L_{Am,Ga}$ -31927 - 5.288*T ${}^2L_{Am,Ga}$ +12711 - 7.134*T
BCC_A2 (γ -Am)	${}^0G_{Am}, {}^0G_{Ga}$ [19] ${}^0L_{Am,Ga}$ -20000
FCC_A1 (β -Am)	${}^0G_{Am}, {}^0G_{Ga}$ [19] ${}^0L_{Am,Ga}$ -100000
DHCP (α -Am)	${}^0G_{Am}$ [19]
α -Ga	${}^0G_{Ga}$ [19]
α -GaAm ₃	$G_{Am:Ga}$ -38934 + 11.093*T + .25*GHSERGA + .75*GHSERAM
β -GaAm ₃	$G_{Am:Ga}$ -38775 + 10.8425*T + .25*GHSERGA + .75*GHSERAM
Ga ₃ Am ₅	$G_{Am:Ga}$ -48393.75 + 9.5*T + .375*GHSERGA + .625*GHSERAM
α -GaAm	$G_{Am:Ga}$ -51489 + 5.0365*T + .5*GHSERGA + .5*GHSERAM
β -GaAm	$G_{Am:Ga}$ -50288.5 + 3.61*T + .5*GHSERGA + .5*GHSERAM
Ga ₃ Am ₂	$G_{Am:Ga}$ -54260 + 4*T + .6*GHSERGA + .4*GHSERAM
Ga ₂ Am	$G_{Am:Ga}$ -55500 + 2.67*T + .667*GHSERGA + .333*GHSERAM
α -Ga ₃ Am	$G_{Am:Ga}$ -59714.11 + 11.248*T + .75*GHSERGA + .25*GHSERAM
β -Ga ₃ Am	$G_{Am:Ga}$ -59713.12 + 11.247*T + .75*GHSERGA + .25*GHSERAM
γ -Ga ₃ Am	$G_{Am:Ga}$ -48682 + 2.025*T + .75*GHSERGA + .25*GHSERAM
Ga ₇ Am ₂	$G_{Am:Ga}$ -59000 + 17.8*T + .778*GHSERGA + .222*GHSERAM
Ga ₁₁ Am ₃	$G_{Am:Ga}$ -57000 + 16.1*T + .787*GHSERGA + .213*GHSERAM
Ga ₄ Am	$G_{Am:Ga}$ -53820 + 14.9*T + .8*GHSERGA + .2*GHSERAM
Ga ₆ Am	$G_{Am:Ga}$ -41000 + 12.4*T + .857*GHSERGA + .143*GHSERAM
Ga ₁₅ Am ₂	$G_{Am:Ga}$ -38000 + 22*T + .882*GHSERGA + .118*GHSERAM

Table 7. Assumptions made regarding the thermodynamic assessment of the Am-Ga system (present study). No experimental data are available to the authors' knowledge.

Phase	Assumption
Ga ₂ Am	<p>Crystal structure: C32 (as Ga₂U and Ga₂Pu, and also because Al₂U, Al₂Pu, and Al₂Am exhibit the same C15 crystal structure)</p> <p>Invariant line: Melts congruently and exhibits the highest melting temperature of the Am-Ga system (as Ga₂U in U-Ga, Ga₂Pu in Pu-Ga, Al₂U in U-Al, Al₂Pu in Pu-Al, and Al₂Am in Am-Al)</p> <p>Melting temperature: Estimated at 1337°C because of the following relationships: $\Delta T_m(\text{Al}_2\text{U} - \text{Ga}_2\text{U}) = 266^\circ\text{C}$, $\Delta T_m(\text{Al}_2\text{Pu} - \text{Ga}_2\text{Pu}) = 267^\circ\text{C}$ and $(T_m(\text{Al}_2\text{Am}) \approx 1603^\circ\text{C})$</p>
Other stoichiometric compounds	<p>Stoichiometry: As the Ga_xU_y compounds have their equivalent in the Pu-Ga system (Ga_xPu_y), the Ga_xPu_y stoichiometries are reported in the Am-Ga system (Ga_xAm_y). Similarly, all U-Al compounds are present in the Pu-Al system, and all Pu-Al compounds have been reproduced in the Am-Al system</p> <p>Crystal structure: Ga₄Am → D1_b structure as Al₄U, Al₄Pu, Al₄Am, and Ga₄Pu α-GaAm₃ and β-GaAm₃ are considered L6₀ and L1₂ as the dimorphic GaPu₃ compound (AlPu₃ compound is also L6₀)</p> <p>As no experimental data are available for the Am-Ga system, the polymorphism of the remaining compounds has been considered similar to the one observed for the Pu-Ga system but with independent crystal structures (no similarities can be established for these compounds)</p>

Figure Captions

Figure 1. (Color online) Predicted (a) Am-Pu [10], (b) Am-U [11], (c) Pu-U [9], and
650 (d) Al-Ga [12] phase diagrams using previous CALPHAD assessments and included
in the present database for completeness.

Figure 2. (Color online) Predicted Pu-Al phases diagrams according to the (a) Ref.
[35] (Option 1), and (b) Ref. [36] (Option 2) versions using the assessed parameters
655 reported in Table 4. The Gibbs energies of the different phases and compounds at
25°C (dotted lines) and 330°C (dashed lines) are reported in (c) and (d), respectively.
In (c-d), the blue domain is similar for both assessments whereas the black and red
domains correspond to Options 1 and 2, respectively.

Figure 3. (Color online) CALPHAD predicted phase diagrams resulting along the (a)
660 U-Al [13, 14] → (b) Pu-Al (present study, Option 1) → (c) Am-Al (present
assessment, interaction parameters given in Table 5) series; and along the (a) U-Ga
[15] → (b) Pu-Ga [5] → (c) Am-Ga (present assessment, interaction parameters given
in Table 6) series.

Figure 4. (Color online) CALPHAD predicted property diagrams for the (a)
665 $\text{Pu}_{.99}\text{Al}_{.01}$, (b) $\text{Pu}_{.93}\text{Al}_{.07}$, (c) $\text{Pu}_{.99}\text{Ga}_{.01}$, and (d) $\text{Pu}_{.93}\text{Ga}_{.07}$ binary systems.

Figure 5. (Color online) Calculated monovariant lines (in red) of the (a) Pu-U-Al, and
670 (b) Pu-U-Ga systems associated with the primary crystallization fields. In addition,
the black lines represent the isothermal liquidus projections based on the present
optimization.

Figure 6. (Color online) Calculated monovariant lines (in red) of the (a) Pu-Am-Al,
675 and (b) Pu-Am-Ga systems associated with the primary crystallization fields. In
addition, the black lines represent the isothermal liquidus projections based on the
present optimization.

Figure 7. (Color online) CALPHAD predicted property diagrams for the (a)
680 $\text{Pu}_{.94}\text{U}_{.05}\text{Al}_{.01}$, (b) $\text{Pu}_{.88}\text{U}_{.05}\text{Al}_{.07}$, (c) $\text{Pu}_{.94}\text{Am}_{.05}\text{Al}_{.01}$, and (d) $\text{Pu}_{.88}\text{Am}_{.05}\text{Al}_{.07}$ ternary
systems.

Figure 8. (Color online) CALPHAD predicted property diagrams for the (a)
685 $\text{Pu}_{.96}\text{U}_{.01}\text{Am}_{.02}\text{Al}_{.01}$, and (b) $\text{Pu}_{.90}\text{U}_{.01}\text{Am}_{.02}\text{Ga}_{.07}$, quaternary systems.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8