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# Calculation of enthalpies of formation of actinide nitrides

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## Abstract

We report on the results of ab initio electronic structure calculation of total energies of AnN (An = Ac, ..., Am), the respective elemental An-metals and the nitrogen molecule using density functional theory (FP APW + lo method and generalized gradient approximation). The obtained energies are further complemented by low temperature heat capacity data and the enthalpies of formation $\Delta_f H^0_{298}$ are eventually evaluated. While the cohesive energies of AnN reveal an increasing dependence on atomic number from ThN to AmN – a trend similar to that of An-metals – the subtle differences between AnN and An result in enthalpies of formation which show strong negative irregularities at ThN and PaN from a linear downward trend. These are ascribed to substantial covalent contribution of 6d and 5f electrons to chemical bonding.

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## 1. Introduction

The actinide nitrides are considered as promising advanced fuel materials for fast breeder reactors, whose development and commercialization may be expected in the future once the fossil fuels and uranium for thermal reactors become scarce [1]. Alternatively, they are envisaged as target materials for transmutation of plutonium or minor actinides, either in the fast reactor cores or in accelerator-driven systems. Considering the breeding ratio, appropriate thermophysical properties (thermal conductivity, melting point) and reprocessing feasibility (solubility in nitric acid), actinide nitrides represent a compromise between oxide and metal fuels. Compared to currently used mixed oxide fuels, a nitride fuel providing a higher energy neutron spectrum can respond more flexibly to requirements such as conversion/breeding ratio, actinide burning and long core life [1]. High thermal conductivity enables a potentially better performance allowing a higher actinide content in the target. The metallic fuels offer similar advantages, however, the phase relations between the active material and zirconium added to control the anisotropic swelling, are complex. By contrast, actinides form an isostructural series of mononitrides (AnN) with a simple rock-salt type structure and a complete solid solubility in the whole composition range. In addition, a few nitrogen rich compounds $Th_3N_4$, $\alpha$-$U_2N_{3+\delta}$ and $\beta$-$U_2N_3$ have been identified.

In view of the prospective use of AnN as advanced fuel materials knowledge of their thermal properties is of crucial importance for modelling the fuel behavior at elevated temperatures. Among the thermal character-

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istics the thermodynamic properties such as standard enthalpies of formation, entropies and heat capacities are essential in order to predict the phase stability including the melting points and vaporization behavior. Since the available experimental information on basic thermodynamic data of AnN is very scanty, a modelling using the advanced first principle techniques of electronic structure calculation represents, apart from the indispensable experimental effort, a valuable tool for accessing these properties and to understand the trends in their evolution along the series, including the correlations with the fundamental parameters characterizing chemical bonding. In the present paper we address this issue and bring the results of enthalpies of formation of light AnN evaluated from ab initio band structure calculation energies combined with lattice and electronic excitation energies assessed from experimental low temperature heat capacity data (if available).

## 2. Calculation technique

In crystalline solids, the most important contribution to the enthalpy of formation originates from the difference in cohesive energies between a given compound and its constituent elements, all in the structural modifications being stable at the reference temperature and pressure. The additional contributions – the lattice and electronic excitation energies – represent in general only a small part (typically 0.5–2.0%) of the enthalpy of formation at the ambient temperature, $\Delta_f H^0_{298}$. For solids they are involved in the integral of the isobaric heat capacity from 0 K to the reference temperature. The effect of the elastic energy $\int V \mathrm{d}P$ is even less significant for $P^0 = 101.3$ kPa and can be neglected considering the accuracy of the experimental or theoretical techniques of $\Delta_f H^0_{298}$ determination.

The cohesive energies belong to the ground state properties of chemical substances and, as such, they can be accessed by the current first principle computation techniques based on density functional theory (DFT), which yields the minimum of total cohesive energy $E_t$ (referred to a state of free electrons and nuclei) based on the self-consistent electron density. In the recent years the widely used local density approximation (LDA) for the treatment of exchange-correlation energy has been improved by taking into account the gradient terms of the electron density. This generalized gradient approximation (GGA) partly corrects for the well known shortcoming of LDA which overestimates the binding energy due to incomplete cancellation of self-interaction. This correction is in particular important in systems with strongly varying electron density (such as actinide compounds) where GGA tends to improve total energies [20] and thus the derived cohesive and elastic properties. Among the methods for performing electronic structure calculations of crystals the full potential linearized augmented plane wave (LAPW) technique and its recent modification APW + lo ('lo' stands for local orbitals) proved to give highly accurate and satisfactory results over a wide range of crystalline solids.

In the present study we used the APW + lo basis set for solving Kohn-Sham equations and the GGA parametrization scheme by Perdew et al. [19] as implemented in the WIEN2k program package [5]. In all AnN and An cases the parameter $R_{\min} \cdot K_{\max} = 8.0$ for the plane wave basis set expansion was applied, where $R_{\min}$ is the smallest muffin-tin radius and $K_{\max}$ is the truncation limit for the length of reciprocal lattice vector in the wave function Fourier expansion. This corresponds to an energy cut-off of 301 eV for AnN ($R_N = 0.9$ Å) and ~119 eV for An ($R_{An} \sim 1.4$ Å). The $k$-space summation within the first Brillouin zone was performed on a grid of 2000 points. Both $K_{\max}$ and the number of $k$-points were sufficient to achieve a self-consistent total energy value with an accuracy better than 0.1 mRy. A limit charge difference $\int |\rho_n - \rho_{n-1}| \mathrm{d}r < 0.0001$ was applied as a criterion for terminating the iteration process. The total energies revealed to be relatively sensitive to the selected radius of the muffin-tin sphere of the actinide atom ($R_{Ac}$) defining a boundary between two types of basis functions (radial functions times spherical harmonics inside the spheres and plane waves in the interstitial region). Hence, the energies were minimized with respect to $R_{Ac}$ for all AnN and An-metals.

All calculations were carried out as spin-polarized, however, a zero net spin moment was found for AcN, ThN and PaN, and all metallic elements from Ac to U. Since the main objective of this study are the cohesive energies and enthalpies of formation attaining, respectively, the values in the order of $10^3$ and $10^2$ kJ mol$^{-1}$, we neglect the energy differences between the different magnetic states (typically less then 1 kJ mol$^{-1}$) for this purpose and consider all spin-polarized structures as ferromagnetic. For the same reason, the valence states were treated only within a scalar-relativistic approach leaving out the spin–orbit (s–o) coupling term, which is mainly confined to the muffin-tin radius and is supposed to be canceled to a great extent when the differences in total energies between AnN and An are evaluated. This assumption was tested for ThN, UN, PuN and the relevant metals upon applying the second variational procedure on the scalar-relativistic eigenstates within the atomic spheres of An, as implemented in WIEN2k [5]. The resulting enthalpies of formation and cohesive energies of AnN did not differ by more than 5 kJ mol$^{-1}$ from the pertinent non s–o values, although the total energies with and without s–o interaction differed substantially (≈100 kJ mol$^{-1}$).

The enthalpies of formation of AnN(cr) were evaluated using the total energies obtained directly from band structure calculations. As stated above, the ground state energy difference between AnN(cr) and the respective elements An(cr) and $\frac{1}{2}N_2(g)$ represents the major part of $\Delta_f H^0_{298}$. Since the molecular species cannot be treated directly within WIEN2k, the $N_2$ dimer was simulated by constructing a sufficiently large tetragonal unit cell (space group P4/mmm, $a = 4.50$ Å, $c = 5.60$ Å), locating $N_2$ in the vertices along the $z$-axis (N-positions $(0, 0, \pm 0.0981)$) and performing the calculation for a single $k$-point at the origin of the first Brillouin zone. The accuracy of the resulting total energy was tested by carrying out an analogous calculation for a nitrogen atom placed into fcc unit cell (Fm3m, $a = 15$ Å) and evaluating the dissociation energy of $N_2$. The obtained value $\Delta_{dis}H^0_0$ $(N_2/2) = 462.2$ kJ mol$^{-1}$ is in fair agreement with $470.2 \pm 0.4$ kJ mol$^{-1}$ assessed in [8] and the ab initio value $E_t(N_2)$ can be thus used for the evaluation of $\Delta_f H^0_{298}$(AnN).

The basic structural parameters of most of AnN(cr) and An(cr) were adopted from [2]. However, the lattice cell constants $a = 5.513$ Å and $a = 4.956$ Å for AcN and PaN, respectively, were optimized by finding the minimum of $E_t$. The An-metals were considered in their α modifications stable at room temperature with the exception of Np and Pu, whose more symmetric cubic γ-Np and δ-Pu allotropes were examined in calculations. The resulting enthalpies of formation were transformed to the appropriate reference state of the α modifications using the corresponding enthalpies $\Delta_{tr}H^0_{298}$ for α-Np → γ-Np and α-Pu → δ-Pu transformations (Table 1) evaluated from the data collected in [21]. In the case of Pu the heat capacity of the metastable δ-Pu in the range 298.15–593.1 K was assessed from the data obtained on δ-Pu stabilized by 3.3 at.% of Ga [22].

Since the low temperature heat capacity has been measured for ThN [9], UN [24] and PuN [11], the contribution of lattice and electronic excitations were included in $\Delta_f H^0$(AnN) only in these three cases by evaluating $\int_0^{298} C_p \mathrm{d}T$ for AnN and An, and taking $[H^0(298.15) - H^0(0)]$ for $N_2(g)$ from [8]. As seen from Table 1 they represent only minute corrections to $\Delta_f H^0$(AnN).

## 3. Results and discussion

The total energies $E_t$ of AnN obtained by DFT calculations are measured with respect to unbound electrons and atomic nuclei and attain the values in the order of $10^4$ Ry differing in $10^3$ Ry between the individual series members. Hence, it is useful to express them as cohesive energies $E_c$ referred to isolated atoms in order to have a reasonable comparison with the constituent elemental metals and to get insight into the trends in $\Delta_f H^0$. This comparison is demonstrated in Fig. 1, where the dissociation energy of $N_2$ represents only an additive constant and the upper curve essentially reflects the evolution of $E_c$ of An(cr). As a basis for the evaluation of $E_c$(AnN) the assessed sublimation enthalpies of α-An(cr) given in [15] were considered.

As seen from Fig. 1, the cohesive energies of both An(cr) and AnN(cr) reveal first an abrupt drop from Ac to Th and then gradually increase up to Am. This is a different behavior compared to lanthanide (Ln) metals whose cohesion decreases nearly linearly due to higher exchange stabilization in the gaseous state having divalent configuration ($s^2f^{n+1}$), while in the condensed

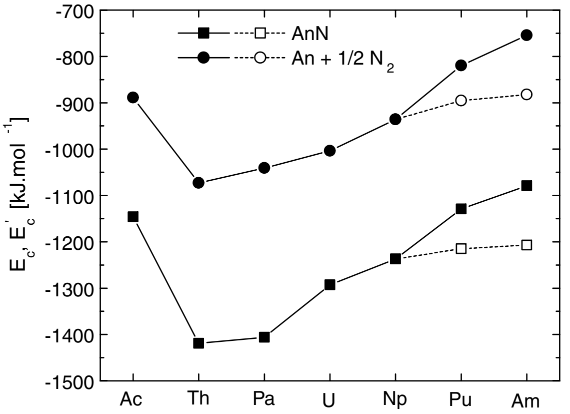

Fig. 1. The cohesive energies $E_c$ (full symbols) and the corrected values $E_c'$ (open symbols) of AnN(cr) compared to the sum of the cohesive energies of α-An(cr) and $\frac{1}{2}N_2(g)$.

Table 1
The difference in total energies $\Delta E_t$ between AnN(cr) and the sum of An(cr) and $\frac{1}{2}N_2(g)$ as obtained from band structure calculation (γ-Np and δ-Pu considered), the difference in lattice and electronic excitation energies $\int_0^{298} \Delta C_p \mathrm{d}T$ (unknown for Ac, Pa, Np, and Am), enthalpy of transformation $\Delta_{tr}H^0_{298}$ of γ-Np and δ-Pu to the respective α-forms, and the resulting enthalpies of formation $\Delta_f H^0_{298}$, all in kJ mol$^{-1}$

| | AcN | ThN | PaN | UN | NpN | PuN | AmN |
|---|---|---|---|---|---|---|---|
| $\Delta E_t$ | −256.8 | −345.7 | −365.3 | −289.4 | −312.2 | −322.0 | −324.6 |
| $\Delta\int C_p \mathrm{d}T$ | – | −2.2 | – | −1.6 | – | −2.4 | – |
| $\Delta_{tr}H^0_{298}$ | – | – | – | – | 10.9 | 12.5 | – |
| $\Delta_f H^0_{298}$ | −256.8 | −347.9 | −365.3 | −291.0 | −301.3 | −311.9 | −324.6 |

state the Ln atom is essentially trivalent. Indeed, if the cohesive energies [15] are corrected by the promotion energies $\Delta E(s^2f^{n+1} \rightarrow s^2df^n)$ [6], a nearly constant value is obtained along the Ln-metal series. By contrast, in An-metals even the corrected values $E'_c$ (only Pu(g) and Am(g) are divalent for light An) are far from being constant and reveal a deep minimum at Th (Fig. 1). This effect is definitely caused by an involvement of An-5f in chemical bonding compared to the well localized Ln-4f electrons. The covalent contribution of 5f electrons gradually decreases from Th to Am and, consequently, $E'_c$ approaches a value typical for Ln and the first member of the An series- actinium (≈−405 kJ mol$^{-1}$).

For AnN-series the covalent contribution of 5f and 6d states is even more pronounced, particularly for ThN and PaN. It is worth to note that the minimum of cohesive energy corresponds to a minimum in the position (center of gravity) of the valence band of predominantly N-2p character. This lowering is caused by an increased hybridization with 5f and 6d states due to covalent mixing, which stabilizes the bonding states of the valence band. The second notable feature is a progressive participation of An-5f states in the multi-band structure around the Fermi level ($E_F$), a gradual band narrowing and the extending spin polarization, which starts at UN and develops up to a complete band gap opening between spin-up and spin down states at AmN. This behavior suggests a strong tendency to 5f localization when approaching the center of the series. In contrast to An(cr) the corrected curve $E'_c$ for AnN(cr) does not saturate to the value corresponding to AcN, but is by ≈60 kJ mol$^{-1}$ lower for AmN. Such a stabilization can be ascribed to an increasing influence of Madelung contribution to the cohesive energy as a result of a strengthening ionic character towards the half-filled 5f sub-shell.

The effect of increasing ionic character of the bonding on the stabilization of AnN(cr) compared to purely metallic bond in An(cr) is clearly seen on the evolution of enthalpies of formation shown in Fig. 2. The calculated values of $\Delta_f H^0_{298}$ follow a straight line with a negative slope from UN to AmN. Moreover, this linear trend can be fairly extrapolated to AcN. However, the values for ThN and PaN reveal large deviations from the indicated trend due to the covalent stabilization discussed above. Note that this reinforced stability coincides with the occurrence of a paramagnetic ground state and a relatively low filling of the bands at $E_F$. Although this band structure has a prevailing 5f character, it is just its low energy tail which shows a strong 6d admixture attaining a maximum for ThN and PaN.

The obtained enthalpies of formation are in excellent agreement with the experimental data in the case UN, for which a well established value $\Delta_f H^0_{298}(\mathrm{UN}) = -290.5 \pm 1.4$ kJ mol$^{-1}$ has been assessed based on calorimetric measurements [10,12]. Similarly, the value of $\Delta_f H^0_{298}(\mathrm{NpN}) = -(305.0 \pm 5.0)$ kJ mol$^{-1}$ derived from $N_2$ and Np vapor pressure data [18,17] compares quite well with our results. Unfortunately, relatively large discrepancies are encountered for PuN (−4.0%) and ThN (+6.0%), respectively. Since no direct experimental determination of $\Delta_f H^0_{298}(\mathrm{ThN})$ has been performed as yet (the experimental value in Fig. 2 was assessed from the oxidation calorimetry data on $Th_3N_4$ [23] dating from 1934 and $N_2$ decomposition pressure of $Th_3N_4$ [4,16]), the validation of our theoretical prediction requires further experimental work or, at least, performing a similar calculation for $Th_3N_4$ and comparing the theoretical value with the experiment [23].

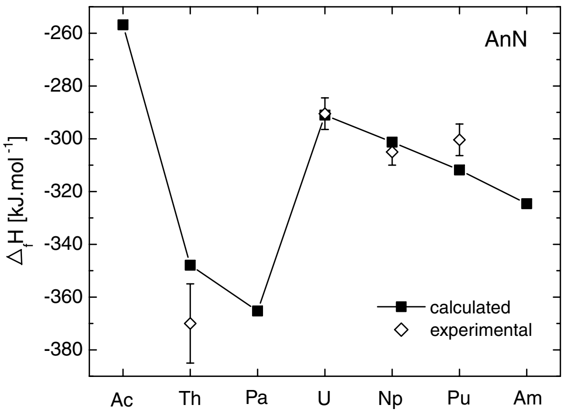

Fig. 2. The enthalpies of formation of AnN evaluated from total energies of AnN(cr), An(cr), and $N_2$(g).

Unlike ThN, PuN has been thoroughly examined by calorimetric [13] and high temperature equilibrium measurements [7,3,14] and the value $\Delta_f H^0_{298}(\mathrm{PuN}) = -(300.4 \pm 2.0)$ kJ mol$^{-1}$ is apparently well defined. One of the possible sources of this discrepancy might be the use of δ-Pu in calculation and the evaluation of $\Delta_{tr} H^0_{298}(\alpha\text{-Pu} \rightarrow \delta\text{-Pu})$ by using the $C_p$ of δ-Pu (3.3%Ga) instead of pure δ-Pu for the extrapolation in the temperature range 298.15–593.1 K. However, the value 12.5 kJ mol$^{-1}$ seems to be reasonable and could hardly be higher by ≈11 kJ mol$^{-1}$ – a correction needed to reproduce the experimental results. Secondly, as Pu seemingly appears at the crossover from itinerant to localized regime of 5f electrons, the correlation effects might play an appreciable role and one would need to go beyond DFT by applying LDA + U technique. If this is the case, it would indicate that the correlation effects stabilize Pu(cr) more than PuN(cr). Consequently, the evolution of $\Delta_f H^0_{298}$ would not follow the suggested linear downward trend in the whole range, but, instead, it would change the slope after NpN.

## 4. Summary

The enthalpies of formation of light actinide nitrides, whose main contribution arises from ground state cohesive energies of AnN(cr), An(cr) and $N_2$(g), were evaluated from total energies calculated by full potential APW + lo technique, and the accessory experimental data assessed from literature. The observed linear decrease of $\Delta_f H^0_{298}$ from AcN to AmN was attributed to the stabilizing effect of the Madelung term as the bonding becomes more ionic. The strong negative deviations from the linear trend encountered at ThN and PaN were accounted for by a substantial covalent contribution of 6d and 5f electrons, which is not present in AcN and is gradually reduced towards AmN. The existing discrepancies with experimental data observed for PuN and ThN still need to be clarified. One of the possible interpretations in the case of PuN is the increasing role of electron correlations which go beyond the used GGA method.

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