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High-Temperature Heat Capacity of (U,Am)O_{2±x} Oxides

DE LA RECHERCHE À L'INDUSTRIE



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Context and Objectives

In the frame of **minor actinide recycling** in sodium cooled fast reactors, (U,Am)O₂ are promising transmutation targets. Data on their thermal properties are mandatory to predict the behavior of these compounds in reactor under both normal and accidental conditions. For instance, the **heat capacity (C_p)** plays a crucial role by determining the quantity of heat that can be accumulated in the material. Several studies have been reported on the enthalpy increments and the heat capacity of UO₂ from room temperature (RT) up to its melting, but very few experimental data exist for Am binary oxides and U-Am mixed oxides. Measurements of the enthalpy increments from room temperature of AmO₂ were performed by Nishi *et al.* [1], but these were limited to 1080 K. For mixed uranium-amercurium dioxide, only one set of high temperature enthalpy increments has been reported in the literature, by Vălu *et al.* [2]. In this work, we extended the investigation of the (U_{1-y}Am_y)O_{2±x} system to higher americium contents: five compositions with Am/(Am+U) ratio equal to 0.3, 0.4, 0.5, 0.6 and 0.7 were investigated.

Experimental set-up & procedure

The enthalpy increment measurements were performed at the JRC-Karlsruhe facility, using a nuclearized (= in glove box) Setaram Multi Detector High Temperature Calorimeter (MDHTC 96 type) operating in **drop mode** (scheme in Fig. 1). The samples were introduced on the top of the experimental chamber. The furnace was programmed to reach and keep the target temperature of measurement T₂, at which the heat flow signal was stabilized during 7 hours. After this period, a “cold” sample was dropped into the detector, causing a small thermal shock. The additional heat provided to the system in order to re-stabilize T₂ is proportional to the enthalpy increment of the sample. Before and after each sample, small ingots of high purity Pt (99.99%) were dropped to be used as reference materials. These allowed determining the sensitivity S of the calorimeter. The enthalpy increment was hence calculated as:

$$\Delta_{T_a}^{T_m} H_m = \frac{\int \phi_s d\tau}{S} \cdot \frac{M_s}{m_s} + Q_\alpha,$$

Where Q_α is the heat generated by the sample itself from the α-decay of ²⁴¹Am.

The experiments were performed under purified Argon (oxygen content ~1 ppm) atmosphere for the samples with Am/(Am+U) ≤ 0.5 and under air for the highest Am contents, in order to try to keep the O/M ratio close to the stoichiometric value of 2.0.

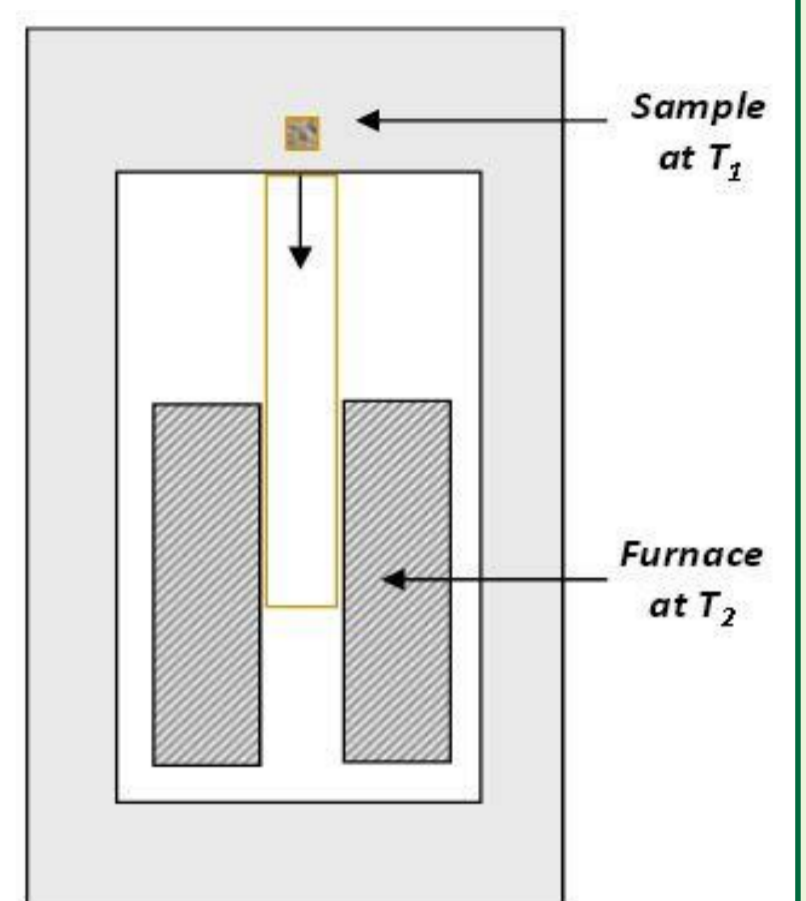


Fig. 1: Schematic representation of the Drop calorimeter

Experimental Results

The enthalpy increments for the five (U_{1-y}Am_y)O_{2±x} compounds were measured between 470 and 1750 K. The results are represented in Fig.2 (a) and (b), with a comparison to the literature data.

The two binary dioxides UO₂ and AmO₂ and the mixed compounds share a similar **enthalpy** trend with temperature. However, in the mixed dioxides with Am/(Am+U) > 0.4, the enthalpy increments seem generally higher than those of UO₂ and AmO₂ for T > 1100 K.

The **heat capacity** functions of the (U_{1-y}Am_y)O_{2±x} oxides were derived using a linear regression of all the enthalpy data. A **Maier-Kelley** polynomial relation was used for the fit:

$$C_p = a + b \cdot T + c \cdot T^{-2}$$

The results are shown in Fig. 2

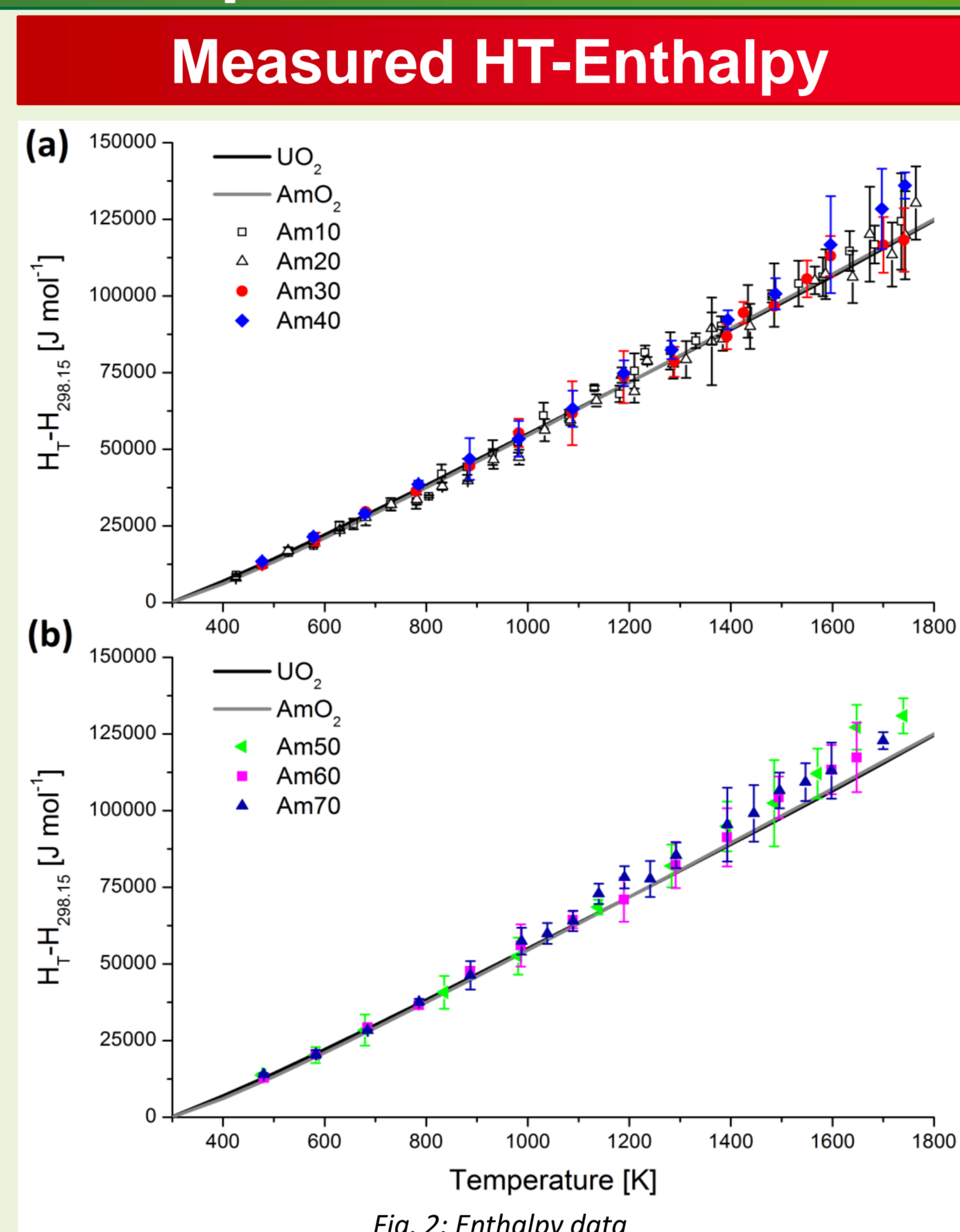


Fig. 2: Enthalpy data

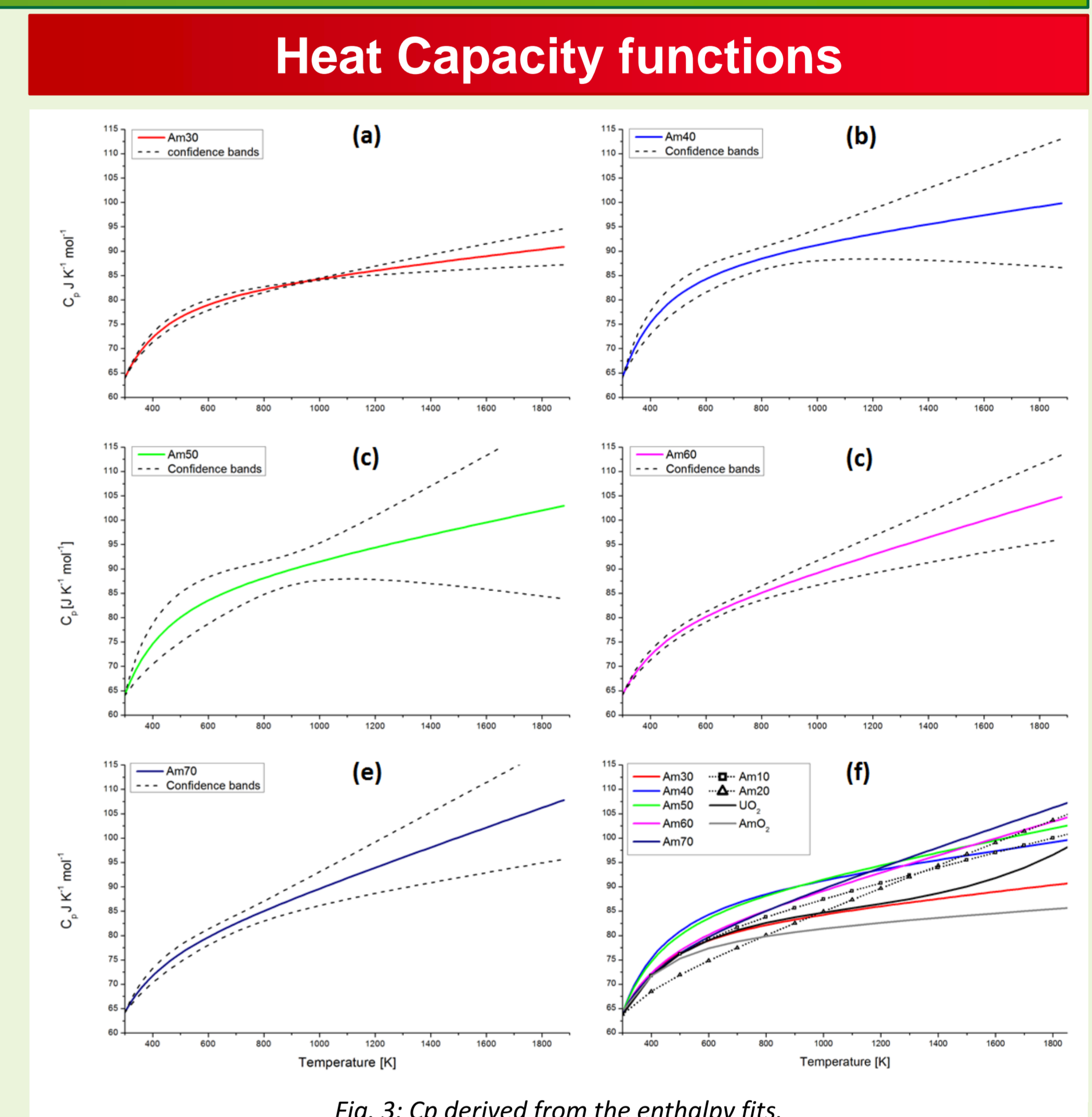


Fig. 3: Cp derived from the enthalpy fits.

Discussion and comparison to thermodynamic CALPHAD model

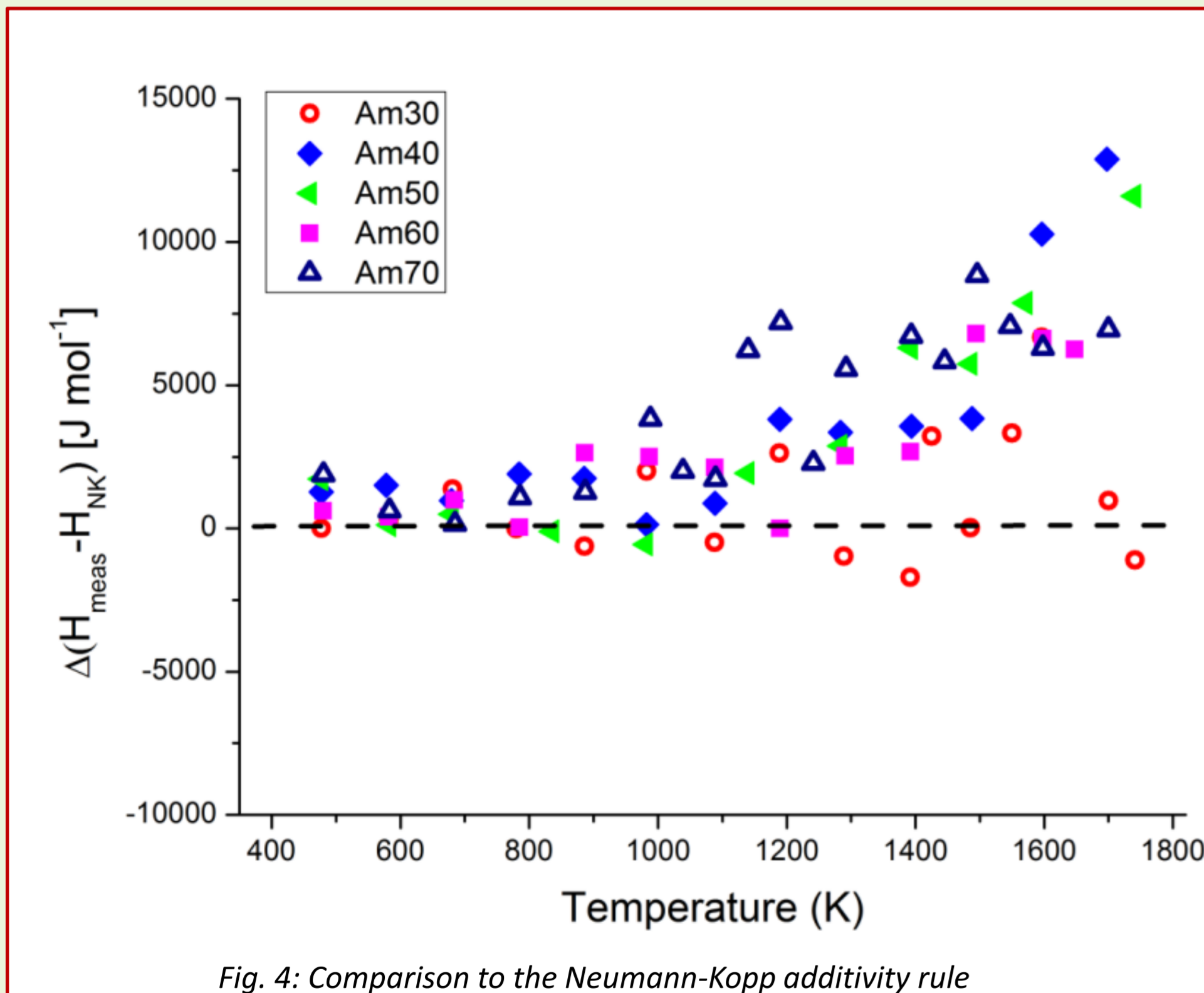


Fig. 4: Comparison to the Neumann-Kopp additivity rule

The experimental enthalpies H_{meas}(T) = H(T) - H(298.15) are compared to the ideal values obtained applying the **Neumann-Kopp rule** H_{NK}(T). For AmO₂, the extrapolation of the data fit by Nishi *et al.* [1] is used for T > 1100 K. The resulting difference Δ(H_{meas} - H_{NK}) is represented as a function of the temperature Fig. 4. The difference is randomly distributed around the zero-line for the U_{0.68}Am_{0.32}O_{2±x} compound and it can then be neglected. On the contrary, clear shifts toward positive values are observed above 1000 K for the other compositions with higher Am content. Moreover, the shifts increase with the temperature. The systematic nature of the phenomenon indicates the presence of an **excess contribution**.

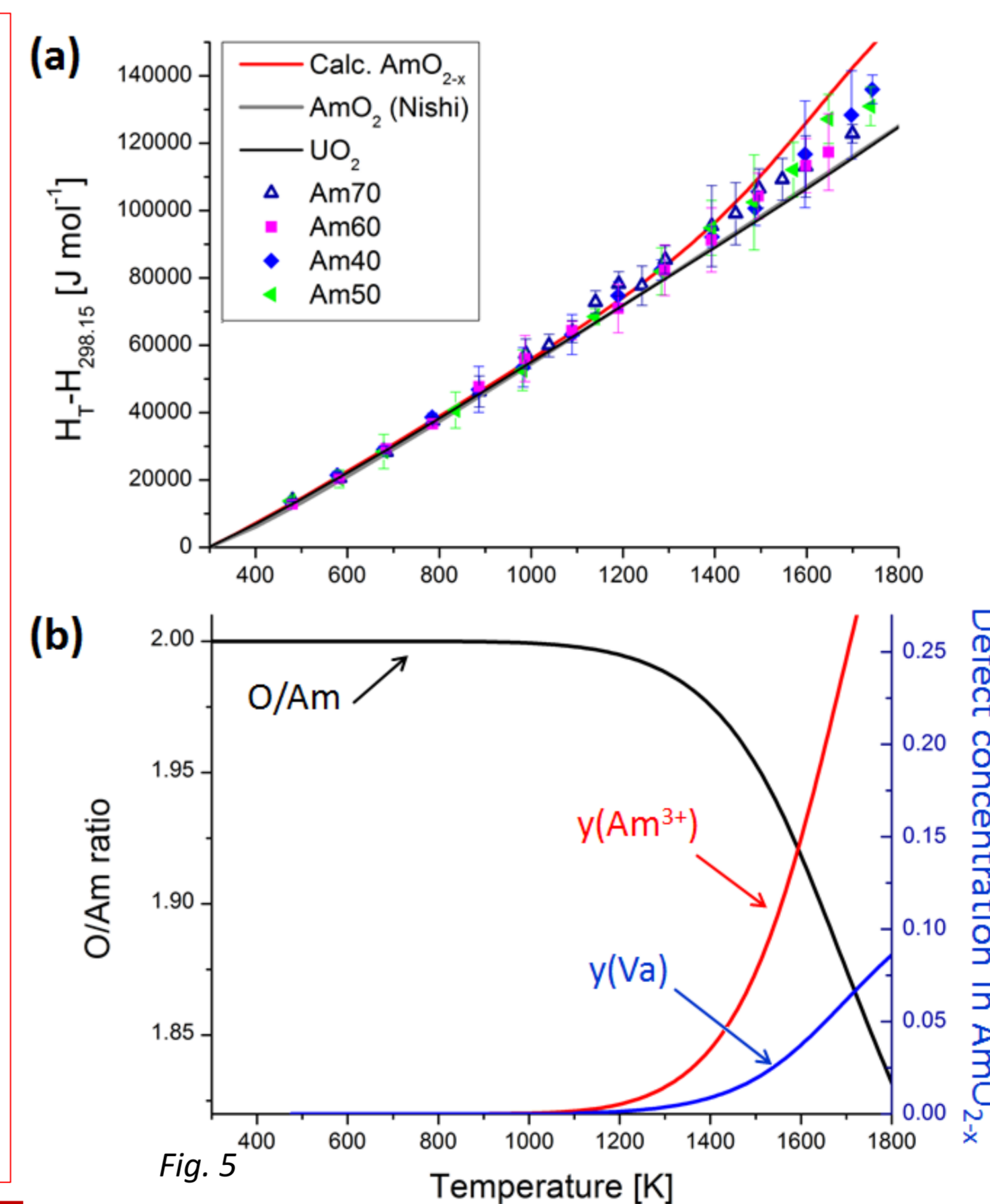


Fig. 5

The **Am-O CALPHAD model** of Epifano *et al.* [3] was adopted to perform thermodynamic calculations. The H(T) of AmO_{2-x} was computed as a function of T, including in the calculation a gas phase with pO₂ = 0.21 atm, hence simulating air. The results are shown in Figure 5(a). In Figure 5(b), the variation of the composition of the AmO_{2-x} phase with temperature is illustrated. Under air, the Am⁴⁺ → Am³⁺ reduction and the **O vacancy formation** start at ~1100 K. This causes the departure from the linearity of the H(T) function. Indeed, all the measured H(T) for the mixed (U,Am)O₂ samples are comprised between the UO₂ and the calculated AmO_{2-x} H curves

Conclusions and perspectives

Drop calorimetry measurements were performed in the 470 < T < 1750 K range and H increments data for U_{0.68}Am_{0.32}O_{2±x}, U_{0.61}Am_{0.39}O_{2±x}, U_{0.51}Am_{0.49}O_{2±x}, U_{0.42}Am_{0.58}O_{2±x} and U_{0.32}Am_{0.68}O_{2±x} were reported for the first time. The experimental data were fitted in order to derive the Cp functions. The obtained enthalpy data are higher than those of UO₂ and AmO₂ for T ≥ 1100 K and **Am/(Am+U) ≥ 0.39**. However, the available experimental data for AmO₂ are limited to 1080 K and the enthalpy function was extrapolated above this temperature. This extrapolation is not appropriate because it does not keep into account the effect of the **oxygen vacancy formation**, that occurs in AmO_{2-x} for T > 1100 K even under pure O₂. This leads to an increase of the enthalpy values, as confirmed by the thermodynamic computations presented in this work, which were in very good agreement with the experimental trend. Therefore, **the oxygen vacancy formation is responsible for the high enthalpy values** measured for the compositions with high Am content [4]. In fact, a reduction similar to that of AmO₂ can be supposed at high temperature. For further improvement of the interpretation of the results, the effect of O vacancies on the heat capacity needs to be further quantified.

[1] T. Nishi *et al.*, J. Nucl. Mater. 414 (2011) 109-113.

[2] Vălu *et al.*, J. of Alloys and Compounds 614 (2014) 144-150

[3] E. Epifano *et al.*, Inorg. Chem. 56 (2017) 7416-7432.

[4] E. Epifano *et al.*, J. Nucl. Mater. 494 (2017) 95-102



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