



## On the valence fluctuation in the early actinide metals



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### ARTICLE INFO

#### Article history:

Received 1 September 2015

Received in revised form

10 November 2015

Accepted 17 November 2015

Available online 15 December 2015

#### Keywords:

Valence fluctuations

Actinides

X-ray emission spectroscopy

Density functional theory

### ABSTRACT

Recent X-ray measurements suggest a degree of valence fluctuation in plutonium and uranium intermetallics. We are applying a novel scheme, in conjunction with density functional theory, to predict 5f configuration fractions of states with valence fluctuations for the early actinide metals. For this purpose we perform constrained integer f-occupation calculations for the  $\alpha$  phases of uranium, neptunium, and plutonium metals. For plutonium we also investigate the  $\delta$  phase. The model predicts uranium and neptunium to be dominated by the  $f^3$  and  $f^4$  configurations, respectively, with only minor contributions from other configurations. For plutonium (both  $\alpha$  and  $\delta$  phase) the scenario is dramatically different. Here, the calculations predict a relatively even distribution between three valence configurations. The  $\delta$  phase has a greater configuration fraction of  $f^6$  compared to that of the  $\alpha$  phase. The theory is consistent with the interpretations of modern X-ray experiments and we present resonant X-ray emission spectroscopy results for  $\alpha$ -uranium.

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### 1. Introduction

The electronic structures of the actinide metals and actinide-based compounds and alloys remain subjects for intense discussions and research. As regards the metals, the conventional view has been that the early actinides, thorium–plutonium, possess relatively weakly correlated f electrons so that a valence-band picture of these states is appropriate. This view is certainly correct for  $\alpha$ -Pu while the situation in  $\delta$ -Pu has been debated for many years. Of course, the late actinide metals (americium and beyond) have 5f states that are best described as localized and atomic like. Many experimental and theoretical approaches have been applied to better understand the nature of the electronic structure and the 5f electrons in particular. For a review see Moore and van der Laan [1].

The concept of fluctuating valence configurations has recently been expanded by X-ray emission and absorption studies [2,3] that have been able to assign weights (or fractions) to these configurations for actinides and their intermetallics. Because of the numerous successes of density-functional-theory (DFT)

calculations for the actinide metals [4] we have leveraged this framework in conjunction with a novel scheme that includes constrained electronic configurations to illuminate the possibilities of valence fluctuations in the early actinide metals (uranium through plutonium).

The idea is to perform constrained calculations that represent integer occupation f configurations and then determine their respective fractions such that the resulting multiconfigurational state, averaged over the fluctuations, reproduces the unconstrained DFT result. The scheme is currently limited to study up to three integer configurations with unknown fractions,  $a$ ,  $b$ , and  $c$ . These three unknowns can be determined from solving this set of linear equations for the configurations  $f^\alpha$ ,  $f^\beta$ , and  $f^\gamma$ :

$$a + b + c = 1 \quad (1)$$

$$a\alpha + b\beta + c\gamma = \xi \quad (2)$$

$$ap^\alpha + bp^\beta + cp^\gamma = 0 \quad (3)$$

Here,  $\xi$  is the unconstrained (non-integer) DFT f occupation,  $p^\alpha$ ,  $p^\beta$ , and  $p^\gamma$  are the electronic pressures associated with configurations  $f^\alpha$ ,  $f^\beta$ , and  $f^\gamma$ . These pressures are calculated at the equilibrium volume of the unconstrained calculations and Eq. (3) thus ensures that the valence fluctuations do not produce a net hydrostatic

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pressure. Of course, another condition is that these fractions cannot be negative, i.e.,  $a, b,$  and  $c \geq 0$ .

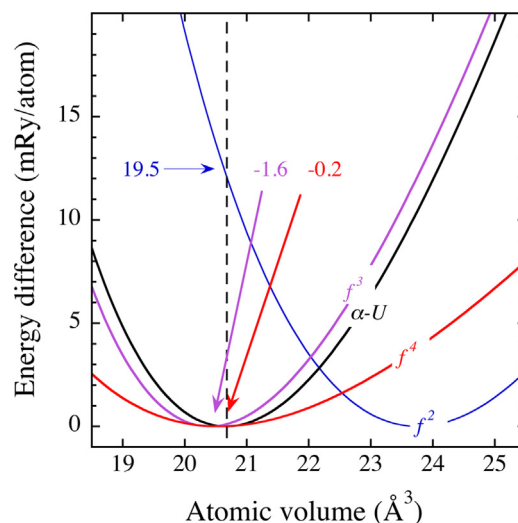
In principal, one may choose another quantity than the electronic pressure ( $p$ ) in Eq. (3), such as atomic volume, atomic density, or total energy, to help determine the fractions  $a, b,$  and  $c$ . Our choice is made because the pressures better represent the instantaneous homogenous distribution of all configurations on each atom than the atomic volumes or densities do. The volume (and density) is rather a reflection of the electronic pressure and a relaxation process. The reason the energy is not applied in lieu of the pressure is purely technical, as the constrained treatments do now allow for a comparison of their total energies as discussed below.

The integer,  $f^i$  ( $i = 2, 3, 4, 5, 6$ ), configurations are modeled simply by constraining the overall number of valence electrons. A conventional treatment for plutonium, for example, include 16 valence electrons (6s, 6p, 7s, 7p, 6d, and 5f states) and with a 5f-band occupation of about 5.3 (see Table 1). Reducing the number of valence electrons to 15.2 reproduces the integer  $f^5$  configuration while increasing it to 16.4 results in an  $f^6$  configuration. The integer occupations of the 5f states are found by trial and error. We simply vary the valence-band occupation until the sought after 5f state results from the electronic structure. The s, p, and d states remain nearly unaffected by these variations and in the present model we assume that their occupations are not changing.

To maintain charge neutrality in the system (ionization does not take place) the number of protons in the nucleus is adjusted with the constrained number of valence electrons. This procedure ensures that the total energy is consistently calculated for a charge neutral system and thus allowing for determination of accurate electronic pressures. The absolute total energy itself, however, cannot be compared between the various configurations because of the difference in nuclear and valence charge.

The most accurate DFT calculations for the actinide metals involve so-called full potential all-electron treatments of the electronic structure and energy, see, for example [5]. For entirely technical reasons, full-potential methods usually accomplish the exact geometrical description of the electronic structure, “full potential”, by dividing the crystal into non-touching spheres centered at each atom site with an interstitial region in between. Because of this construct, the interstitial charge is not associated with an atomic orbital such as the 5f orbital and therefore this technicality underestimates the true 5f-band occupation a small amount as discussed in detail earlier [6]. To correct for this we employ calculations that do not utilize interstitial charges similar to those we have done previously for americium where the occupation numbers were the main focus [6]. From these non-full-potential electronic structures the integer 5f-occupation constraints were determined.

For the best possible electronic structure and total energy we utilize an accurate, fully relativistic, full-potential methodology [5,7] that includes the orbital-polarization correction as was done previously for plutonium [7,8]. The calculations for these actinide metals are identical, except for the crystal structures that are orthorhombic, Cmcm, primitive orthorhombic, Pnma, monoclinic,  $p2_1/m$ , and face-centered cubic, cF4, for  $\alpha$ -U,  $\alpha$ -Np,  $\alpha$ -Pu, and  $\delta$ -Pu, respectively [9]. The plutonium phases develop magnetic spin and



**Fig. 1.** Calculated total energies (shifted to zero for the energy minima) as functions of atomic volume for the constrained  $f^2$  (blue),  $f^3$  (purple), and  $f^4$  (red) configurations and  $\alpha$ -U. The vertical dashed line shows the equilibrium volume for  $\alpha$ -U ( $20.67 \text{ \AA}^3$ ). The electronic pressures ( $p^2$ ,  $p^3$ , and  $p^4$  in GPa) are indicated in the figure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

orbital moments that are anti-ferromagnetic ( $\alpha$ ) and paramagnetic ( $\delta$ ), described in detail by Söderlind and Sadigh [7].

The procedure to calculate the configurational fractions is illustrated for  $\alpha$ -U in Fig. 1. The total energies of  $\alpha$ -U subject to the constrained  $f^2$ ,  $f^3$ , and  $f^4$  configurations (also in the  $\alpha$ -U crystal structure) are plotted versus atomic volume. The  $\alpha$ -U equilibrium volume is  $20.67 \text{ \AA}^3$  (see Table 2) and is marked by a dashed vertical line. Because the equilibrium volumes of the  $f^3$  and  $f^4$  configurations are very close to that of  $\alpha$ -U, their respective electronic pressure at  $20.67 \text{ \AA}^3$  is quite small ( $-1.6$  and  $-0.2$  GPa). The  $f^2$  configuration, on the other hand, has a substantially larger equilibrium volume that implies a relatively large electronic pressure (19.5 GPa) at the  $\alpha$ -U equilibrium volume. The  $f^4$  state cannot compensate for the  $f^2$  configuration in terms of the electronic pressures and consequently the configurational fraction of  $f^4$  vanishes, see Table 1.

For both  $\alpha$ -Pu and  $\delta$ -Pu all ( $f^4$ ,  $f^5$ , and  $f^6$ ) valence configurations have fairly similar bonding characteristics leading to electronic pressure components ( $p^4$ ,  $p^5$ , and  $p^6$ ) that are small and close in magnitude. This is a prerequisite for valence fluctuations in our model. Clearly, the model depends on accurate calculations of these electronic pressure components. Fortunately, for the early actinide metals, the theoretical equilibrium volumes and bulk moduli are in very good agreement with experiments [9–14]: see Table 2. Both the  $\alpha$  and the  $\delta$  phases of plutonium are dominated by the  $f^5$  and  $f^6$  valence states in the model with relatively small amount of  $f^4$ . The  $f^5$  state is also more prevalent in the  $\alpha$  phase and this is in good quantitative agreement with the interpretations of earlier X-ray emission spectroscopy [2,3].

**Table 1**  
Calculated f-orbital occupancies ( $n_f$ ) and configurational fractions ( $f^i$ ) at ambient pressure.

Material	$n_f$	$f^2$	$f^3$	$f^4$	$f^5$	$f^6$
$\alpha$ -U	2.91	0.09	0.91	0	0	0
$\alpha$ -Np	4.16	0	0	0.84	0.16	0
$\alpha$ -Pu	5.31	0	0	0.11	0.49	0.40
$\delta$ -Pu	5.31	0	0	0.17	0.34	0.49

**Table 2**  
Atomic volume ( $\text{\AA}^3$ ) and bulk modulus (GPa). Experimental data are obtained at room temperature and shown in the parenthesis. The experimental bulk modulus for  $\delta$ -Pu is from a measurement of a  $\delta$ -Pu-2.3 at.% Ga alloy. All experimental data are taken from Refs. [9–14].

Material	Atomic volume	Bulk modulus
$\alpha$ -U	20.67 (20.75)	133 (119)
$\alpha$ -Np	19.16 (19.21)	157 (120)
$\alpha$ -Pu	20.30 (20.08)	45.0 (43)
$\delta$ -Pu	24.90 (24.82)	41.0 (30)

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