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First-principles phase stability, bonding, and electronic structure of actinide metals

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ABSTRACT

The actinide elemental metals are scarce, often toxic and radio active, causing challenges for both experiments and theory while offering fascinating physics. For practical purposes they are the prevalent building blocks for materials where nuclear properties are of interest. Here, however, we are focusing on fundamental properties of the actinides related to their electronic structure and characteristic bonding in the condensed state. The series of actinides is naturally divided into two segments. First, the set of lighter actinides thorium through plutonium, often referred to as the early actinides, displays a variation of the atomic volume reminiscent of what is seen in transition metals, suggesting a gradual occupation of bonding $5f$ states. Second, the heavier (late) actinides, Am and onwards, demonstrate volume behaviors comparable to the rare-earth metals that implies nonbonding $5f$ states. Arguably, one can distinguish plutonium metal as special case lying between these two subsets because it shares some features from both. Therefore, we discuss the early actinides, plutonium metal, and the late actinides separately applying first-principles density-functional-theory (DFT) calculations. The analysis includes successes and failures of the theory to describe primarily phase stability, bonding, and electronic structure.

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1. Introduction

The series of actinide metals exhibit behaviors unlike any other elemental solids in the Periodic Table. Properties such as equilibrium volume (or density), crystal structure, phase stability, thermal and electrical transport, anisotropy, among others, make these materials exotic in comparison to most metals. Because of their scarcity, nuclear instability, toxicity, and regulatory requirements, experimental work is generally challenging to say the least. Nevertheless, great strides have been made in recent years to illuminate their nature from various experimental angles [1].

Theoretically, the actinides pose challenge as well due to complexities of the electronic and crystal structures and importance of relativistic effects. Hence, the actinides have received increasing attention alongside technical developments of electronic band-structure methods [2] within the framework of DFT [3]. These techniques have since evolved to better meet the challenges and accurately account for relativistic effects including spin-orbit interaction [4] and complex crystal structures [5]. In recent years refinements of pseudopotential approaches, utilizing efficient plane-wave implementations, have demonstrated some

success for actinides, at least for the ground-state phases of Th-U [6].

The DFT band-structure approach is in principle only appropriate when dealing with bonding electrons that can be well described by band states. In the early actinide metals this is indeed the case as we explain in Fig. 1. Here we plot the tabulated room temperature equilibrium volumes (full lines, no symbols) for the $5d$ transition metals, $4f$ lanthanides, and $5f$ actinides [7], together with two opposing models for the $5f$ character. The “ $5f$ fully bonding” model assumes band (delocalized) states, while in the other, “ $5f$ nonbonding”, they are confined to core states with no band formation and interatomic bonding. Clearly, the former concept is justified for the earlier actinides Th-Np with plutonium showing a slight deviation. At the same time, the nonbonding model reproduces the behavior of the heavier actinides Am-Bk. These results thus confirm the notion that the early actinides have bonding (itinerant) $5f$ electrons while the later do not. This perception [8] was early founded on the fact that the $5d$ transition metals in Fig. 1 behave as the early and the $4f$ lanthanides as the late actinides.

From Fig. 1 it is evident that the early and late actinides fall into two categories with respect to their atomic volumes and thus bonding strength of their $5f$ electrons. One of them, plutonium, appears to not quite fit either simplistic approach, particularly the δ -Pu (face-centered cubic, fcc) phase whose volume lies squarely in the middle between that predicted by the two bonding schemes.

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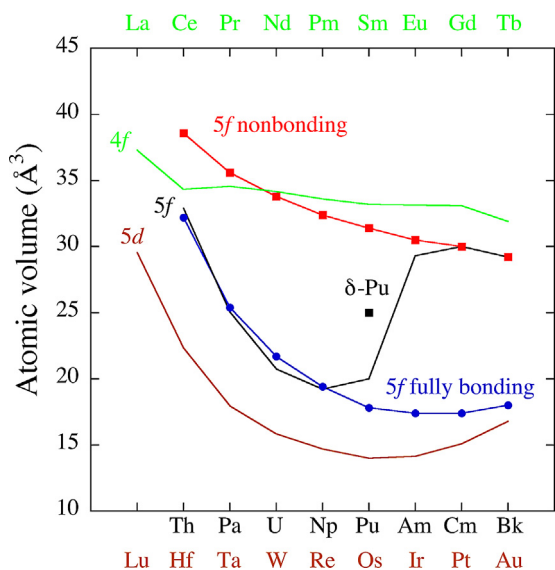


Fig. 1. Measured atomic volumes of the actinide metals are shown with a black line (5f), a brown line for the 5d transition metals, and a green line for the lanthanides (4f). The blue “5f fully bonding” and red “5f nonbonding” curves show results from model calculations, assuming face-centered cubic structure, where the 5f electrons are treated as part of the valence band and localized to nonbonding core states, respectively. (For interpretation of the references to color in this legend, the reader is referred to the web version of the article.)

We have in the following chosen to divide the article into these segments, namely, the early actinides (Th–Np), plutonium, and the late actinides (Am–Cf), in Sections 3–5. Section 2 details technical aspects of the electronic-structure computations. We further discuss the high-temperature body-centered cubic (bcc) phase that is prevalent in all actinides in Section 6 before we offer some concluding remarks in Section 7.

2. Computational details

All calculations are performed within the framework of DFT and the necessary assumption for the unknown electron exchange and correlation functional is that of the generalized gradient approximation (GGA) [9]. Although newer varieties of this approximation have been proposed, the GGA remains the best choice for actinide metals [10]. Our particular implementation is based on the full-potential linear muffin-tin orbitals (FPLMTO) method that has recently been described in detail [11]. In addition to the choice of GGA, we have found that for actinides no geometrical approximations (full potential), full relativity including spin-orbit coupling, spin and orbital polarization, and a well converged basis set is generally needed for good accuracy. Specifically, we associate a set of semi-core states 6s and 6p and valence states 7s, 7p, 6d, and 5f to two kinetic energy parameters for a so-called double basis set. In all present calculations the sampling of k points in the Brillouin zone (BZ) for the appropriate summations are carefully checked for convergence. In the case of elastic-constant calculations, the converged number of k points in the irreducible BZ can sometimes be as high as several thousand but for most investigations a few hundred k points suffice.

Table 1

Calculated and measured single crystal elastic constants (GPa) for α -U. Values in parenthesis are extrapolations to zero temperature. Taken from Ref. [19].

Method	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{12}	c_{13}	c_{23}
DFT-GGA	287	241	316	140	105	96	43	17	110
Experiment	215 (210)	199 (215)	267 (297)	124 (145)	73.4 (94.5)	74.3 (87.1)	46.5	21.8	108

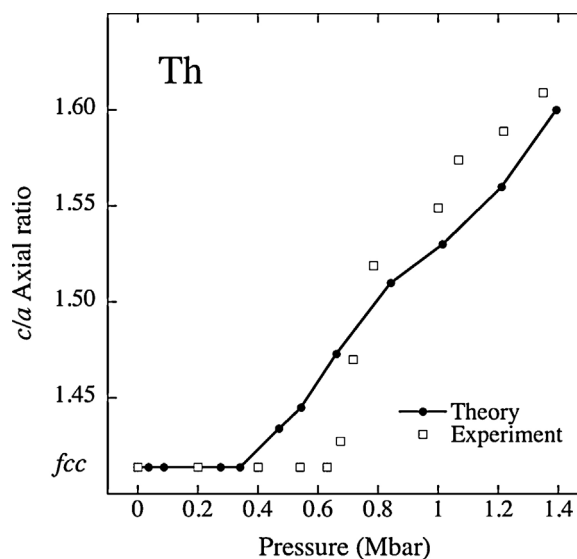


Fig. 2. Experimental data (open squares) and theoretical results (solid circle, solid line) for the c/a axial ratio in the tetragonal structure of Th as functions of pressure.

3. Early actinides: thorium through neptunium

As one proceeds through the actinide series both the crystal structure as well as the electronic structure become more complex. The reason for this is that more 5f electrons are being involved in the bonding up until americium and they are occupying narrow band states close to the Fermi level [12]. At this point a change of the 5f character, akin to a Mott transition [8], takes place as we discussed in the introduction. Consequently, the early actinides are governed predominantly by fully active (itinerant) 5f bonding and the band-formation description is appropriate. In fact, carefully performed electronic-structure calculations reproduce the nontrivial ground state [12,13] for these metals and also predict the correct structure-pressure relationships for Th, Pa, and U [14–17].

In Fig. 2 we plot the body-centered tetragonal (bct) c/a axial ratio of thorium, theory and experiment, to highlight the good agreement and accuracy of the DFT approach. The fcc to bct phase transition in Th was explained to be due to an increase of 5f-electron occupation with pressure [15]. Notably, in the case of thorium’s next neighbor protactinium, calculations [16] predate experiments [18] by several years predicting a high-pressure orthorhombic phase (Cmcm, α -U-type).

A materials crystal structure is obviously sensitively connected to details of the bonding and electronic structure. Similarly, elastic constants characterize strength, anisotropy, and symmetry of the chemical bonds and constitute an accurate account of the bonding aspects of the electronic structure. In Table 1 we list calculated [19] elastic constants for α -U and contrast them with experimental data. Notice that the elastic constants compare as well as one can expect for simpler metals from the d -transition series (about a 20% difference between DFT and measurements). Later DFT calculations for α -U confirm this conclusion [20–22] suggesting that the results are robust and rather insensitive to technical approximations within the application of DFT.

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