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Calculated structural stabilities of U, Np, Pu and Am; new high-pressure phases for Am and Pu

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Abstract

The high-pressure phase of americium Am IV recently found experimentally, which is a primitive-orthorhombic structure with four atoms in the unit cell, is also found to be stable theoretically at high pressure in Am by a calculation using the full-potential linearized augmented-plane-wave (FPLAPW) method. The possibility of the Am IV structure being a stable high-pressure phase of U, Np or Pu, like in the case of Am, is examined using the FPLAPW method by comparing the total energy as a function of volume with ten other crystal structures. The results indicate that the Am IV structure is not a high-pressure phase for U and Np, but it is for Pu, for which it is proposed that the sequence under pressure is α -Pu \rightarrow Am IV \rightarrow body-centred cubic. Our calculations are reliable, because they give theoretically the stability of the crystal α -phases of U, Np, Pu under ambient conditions. The normal-pressure phase of Am is modelled by our fully relativistic muffin-tin orbital method with unhybridized 5f electron states.

1. Introduction

Very recently, an experimental study of americium under pressure was carried out [1, 2]. It was found that the normal-pressure double-hexagonal-close-packed (dhcp) phase (Am I) transforms at 61 kbar to a face-centred-cubic (fcc) phase (Am II), then at 100 kbar to a face-centred-orthorhombic structure (Am III) and finally at 160 kbar to a primitive-orthorhombic structure (Am IV), with four atoms in the unit cell (uc), which is stable up to a least 1 Mbar.

It is known that the series of actinide metals, corresponding to the progressive filling up of the 5f electronic subshell, must be split in two. At normal pressure in the first subseries, from Pa to Pu, the 5f electrons bind in the manner of d electrons in transition metals; in the other subseries, starting with Am, the 5f electrons are localized, similarly to electrons in deep atomic layers and, like the 4f electrons of lanthanides, do not take part in metallic bonding.

It has been proposed [1, 2] that the phase transition in Am from the fcc phase to the low-symmetry structures Am III and Am IV is consistent with the delocalization of the 5f electrons under pressure.

In a previous study [3] we reproduced the localized character of the 5f electrons of Am at normal pressure, in the fcc crystal structure, with our fully relativistic muffin-tin orbital (MTO) band-structure method. Since the local density approximation (LDA) of the density-functional theory (DFT) is known to overestimate the extent of the localized orbitals and hence the effects of interatomic hybridization and overlap, we neglect these terms in the matrix elements. We treat here the localized phases of Am (Am I and Am II) in the fcc structure alone, because the body of experimental data is consistent for this structure. The transition from dhcp to fcc involves only a few meV and we do not consider this transition here.

The high-pressure phases Am III and Am IV are treated with the 5f electrons delocalized. We use a full-potential linear augmented-plane-wave (FPLAPW) code [4] to calculate the total energies as functions of volume to determine the stabilities of Am III and Am IV in comparison to nine other possible crystal structures.

In a recent paper [5] we have studied the structural stabilities of Np and Pu by comparison of the total energies calculated in different crystal structures. Precisely four crystal structures were examined for Np and seven for Pu. Here, in a more systematic manner, eleven structures are compared for Np and Pu like for Am; moreover uranium is also studied.

The eleven structures compared are fcc, like Ac and Th, body-centred cubic (bcc), hexagonal close packed (hcp, ideal c/a ratio) and also the other normal-pressure α -phases of the first series of actinide metals [6]: body-centred tetragonal (bct) α -Pa, orthorhombic α -U, orthorhombic α -Np, monoclinic α -Pu. Moreover, also examined are the high-temperature β -Np and γ -Pu phases [6]. β -Np is tetragonal and γ -Pu is face-centred orthorhombic like the Am III structure [2] but with slightly different axial ratios c/a and b/a . Finally we look at the high-pressure phases: the orthorhombic Am IV structure [2] and the body-centred monoclinic (bcm) structure α'' -Ce seen to be present at around 70 kbar in Ce [7, 8].

The complexity of the calculations for these various crystal structures increases with lack of symmetry, number of atoms in the uc and atoms being inequivalent. There is a single atom in the simplest uc for the fcc, the bcc and the bct structures. There are two equivalent atoms in the uc for the hcp, orthorhombic α -U and orthorhombic γ -Pu structures and two inequivalent atoms for bcm α'' -Ce. There are four equivalent atoms in the uc of the orthorhombic Am IV structure and four atoms of two types in tetragonal β -Np. In the uc of orthorhombic α -Np there are eight atoms of two types and in the most complex structure in the series of the actinide metals, the monoclinic α -Pu, there are 16 atoms of eight different types.

2. Methods of calculation

The reported results are obtained from electronic structure calculations for U, Np, Pu and Am in eleven different crystal structures. The total energy of these structures was calculated as a function of volume. When the 5f electrons are supposed to be delocalized we use the FPLAPW method [4] within the DFT with the generalized gradient approximation (GGA) [9] for the exchange–correlation energy functional. If the 5f electrons are supposed to be localized like in the Am I and Am II phases of americium we use our MTO method with unhybridized 5f electron states [3]. In all the calculations the semi-core states 6s and 6p have been taken account in the valence band.

With our MTO method [3] the solid is modelled by atomic spheres (AS) of volume equal to the crystal cells and inside each sphere the potential has spherical symmetry. This atomic sphere approximation (ASA) is well suited for the compact, cubic and hexagonal, crystalline structures. The one-electron MTO wavefunctions on the crystal lattice are linear combinations of the exact solutions ϕ of the Dirac equation in a spherical potential. The coefficients are solutions of a linear homogeneous system involving logarithmic derivatives of

the wavefunctions ϕ on the atomic sphere and ‘structure constants’ that only depend on the type of crystal lattice considered.

In the FPLAPW method [4, 10] there is no approximation as regards the crystal geometry; the charge density and electronic potential can have arbitrary shape but the wavefunctions are only variational approximations of the true wavefunctions obtained in the region of fixed energies E_v . The FPLAPW code [4] is fully relativistic for the core states and semi-relativistic with variational treatment of spin-orbit coupling for the valence band. To make a significant comparison between different crystal structures to determine which is the most stable for an actinide metal, the various parameters of the FPLAPW method, such as the choices of linearization energies, of muffin-tin radii and the truncations of bases and other expansions, are kept constant with the change of crystal structure.

In the LAPW method the crystal is divided into two regions: (I) ‘muffin-tin’ spheres centred on the ions where the potential has very strong variations and (II) an interstitial zone where the potential is almost constant. In the ‘full-potential’ method the potential and the electronic density are, like the wavefunctions, expanded in spherical waves inside (I) and in plane waves inside (II).

In the FPLAPW method the required precision in total energy is achieved by using a large plane-wave cut-off $R_{mt} K_{max} = 10$ and a k -point sampling in the Brillouin zone (BZ) of about 1000 points.

During the self-consistent cycle, the integration over the iBZ is done using ‘special-point’ sampling [11]. To obtain a good convergence for the total energy we take, in the irreducible part of the Brillouin zone (iBZ), 44 points in the bcc structure, 47 points in the fcc structure and 99 points in the bct structure which yield in each case 1000 points in the whole Brillouin zone (wBZ). For the more complex crystal structures, the more atoms a crystal cell contains, the fewer points necessary for the integration over the wBZ, which is smaller. We verify that the number of points in the wBZ multiplied by the number of atoms in the uc gives about 1000 points in the following structures. In the hcp structure we take 42 points in the iBZ yielding 500 points in the wBZ, in orthorhombic α -U 75 points in the iBZ yielding 405 points in the wBZ, in orthorhombic γ -Pu 64 points in the iBZ yielding 343 points in the wBZ and in the bcc α'' -Ce 135 points in the iBZ yielding 486 points in the wBZ. In the orthorhombic Am IV structure we take 45 points in the iBZ yielding 225 points in the wBZ and in the tetragonal β -Np structure 24 points in the iBZ yielding 175 points in the wBZ. Finally for orthorhombic α -Np we take 18 points in the iBZ yielding 144 points in the wBZ and for monoclinic α -Pu 15 points in the iBZ yielding 60 points in the wBZ.

Moreover, a special hexagonal structure has been observed at high pressure in Pu [12] which contains eight atoms of two types in the uc (hex8-Pu). We take for this structure 15 points in the iBZ corresponding to 125 points in the wBZ.

When we compare the total energies as function of volumes between different crystal structures to determine the most stable, for the complex ones the internal crystallographic parameters and the axial ratios c/a , b/a are kept constant. For the α -Pa, α -U, α -Np and α -Pu structures we take the experimentally determined values at ambient temperature and pressure [6]. For the β -Np structure we use the values at ambient pressure and a temperature of 313 °C [6], for the γ -Pu structure those at ambient pressure and 235 °C [6]. For the Am III structure, which is like the γ -Pu structure but with slightly different axial ratios, we take the experimental values determined at ambient temperature and a pressure of 109 kbar [2]. For the Am IV structure we use the experimental values determined at ambient temperature and 890 kbar [2]. For the bcc α'' -Ce structure we take the values at ambient temperature and 69 kbar [8]. Finally, for the hex8-Pu structure, the values at ambient temperature and 550 kbar [12] are taken.

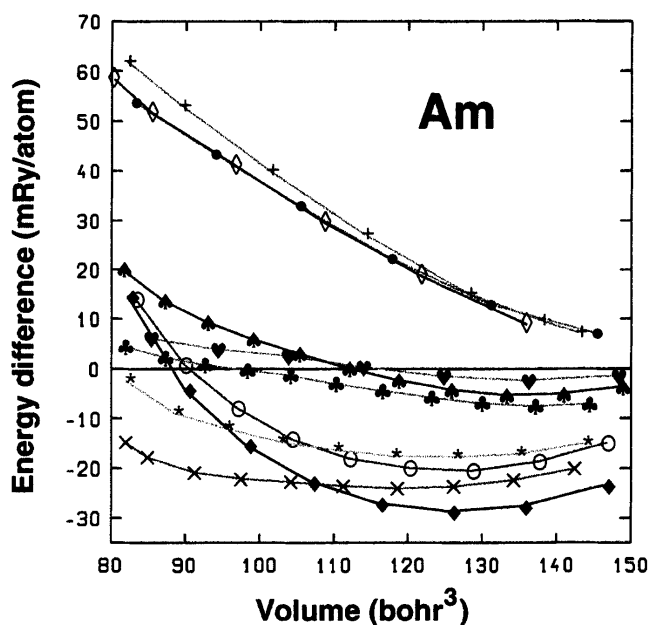


Figure 1. Total-energy differences for Am, calculated by the FPLAPW method in the α -Pu (\blacklozenge), Am IV (\times), α -Np (\circ), β -Np ($*$), Am III (\blacktriangle), α -U (\bullet), α -Pa (\blackheartsuit), α' -Ce (\diamond), hcp (\bullet) and fcc ($+$) crystal structures, relative to the bcc structure, as functions of volume.

3. Americium

The dhcp Am I and fcc Am II structures are modelled with our MTO method with unhybridized 5f electron states [3] and it is sufficient to do the calculation in the fcc structure as we have previously explained. We reproduce the localized character of the 5f electrons by removing the coupling between their states and other angular momenta. To do this, using the MTO method, we only have to cancel the corresponding matrix elements in our 'structure constants'. For the exchange–correlation energy functional we use the Hedin–Lundqvist formulation [13]. We obtain an equilibrium volume of 201.45 bohr³ close to the experimental value of 198.38 bohr³ [6]. For the bulk modulus we obtain 468 kbar in agreement with the experimental value of 450 kbar of Benedict [14], but not with the value of 299 kbar of Lindbaum *et al* [2].

Our MTO method gives directly the pressure as a function of volume with the values of the wavefunctions on the AS. The total energy, which is obtained by integration of the pressure, because of our localization procedure for the 5f electrons, cannot be directly compared with the total energies obtained by the DFT-GGA. We add to our MTO energies a constant energy to obtain a reasonable transition pressure with the delocalized 5f electron crystal structure of the lowest total energy.

In figure 1 we compare over a wide volume range the total energies, calculated with the FPLAPW method for Am, successively, in our eleven crystal structures. The α -Pu structure initially has the lowest energy in these calculations with delocalized 5f electrons, as was found previously [15], but for a pressure of 205 kbar there is a transition to the orthorhombic Am IV structure which remains stable up to at least 1 Mbar. The volumes for the transition are 109 and 106 bohr³ for the α -Pu and Am IV structures respectively—that is, a volume decrease of 2.6%.

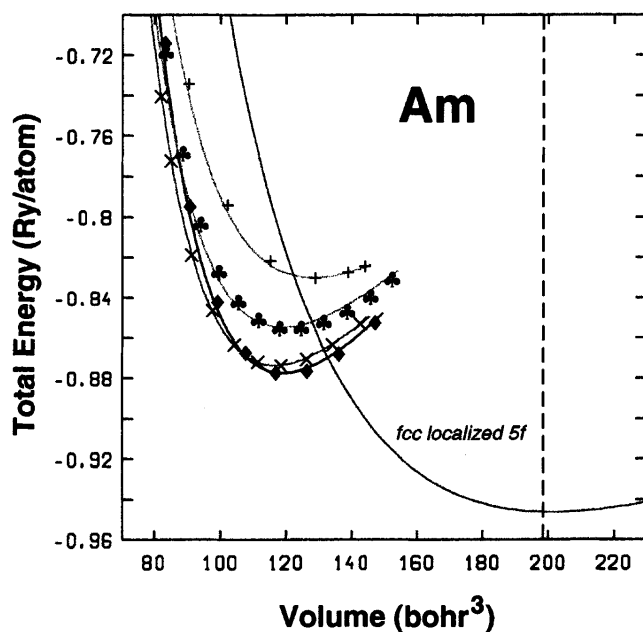
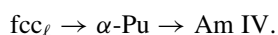


Figure 2. Total energies for Am, calculated by the FPLAPW method in the α -Pu (\blacklozenge), Am IV (\times), Am III (\clubsuit) and fcc ($+$) crystal structures, and total energies for Am calculated by the MTO method with localized 5f electrons in the fcc structure, as functions of volume. The room temperature equilibrium volume for Am is denoted by a vertical broken line.

While experimentally the face-centred-orthorhombic Am III structure is found to be stable [1, 2] between 100 and 160 kbar, this is not the case here, where its energy always stays greater than the energies of the α -Pu and Am IV structures.

In figure 2 we compare the total energy of the fcc structure with localized 5f electrons (fcc_ℓ) to the energies of the α -Pu, Am IV, Am III and fcc structures calculated with delocalized 5f electrons, as functions of volume. There are two phase transitions:



The first transition is for a pressure of 158 kbar. The volumes for the transition are 163 and 111 bohr³ for the fcc_ℓ and α -Pu structures respectively—that is, a volume collapse of 31.7%. In [15] the transition pressure found was 80 kbar and the volume collapse 25%, but the fcc_ℓ structure was modelled by calculations allowing spin and orbital polarization although Am is not magnetic. Experimentally [1, 2], the transition pressure between the fcc_ℓ and the Am III structure is 100 kbar, with only a 2% volume decrease, but the Am III \rightarrow Am IV transition follows at 160 kbar with a volume decrease of 7%.

From figures 1 and 2, the only possibility for being in agreement with experiment in finding the Am III phase stable in a volume range is to suppose that the 5f electrons are localized in this phase. To lower theoretically the energy of the Am III structure, we have to suppose that the 5f electrons are localized in this structure like in the fcc_ℓ structure. In figure 2 we see that the energy of the fcc_ℓ structure must be considerably lower than the energy of the fcc structure with delocalized 5f electrons to find a correct transition pressure with the α -Pu or Am IV structures and to obtain a correct equilibrium volume.

In figure 3 we compare our theoretical isotherms with experiment [1, 2]. Our theoretical equilibrium volume in the fcc_ℓ phase is close to the experimental ones but we have a bulk

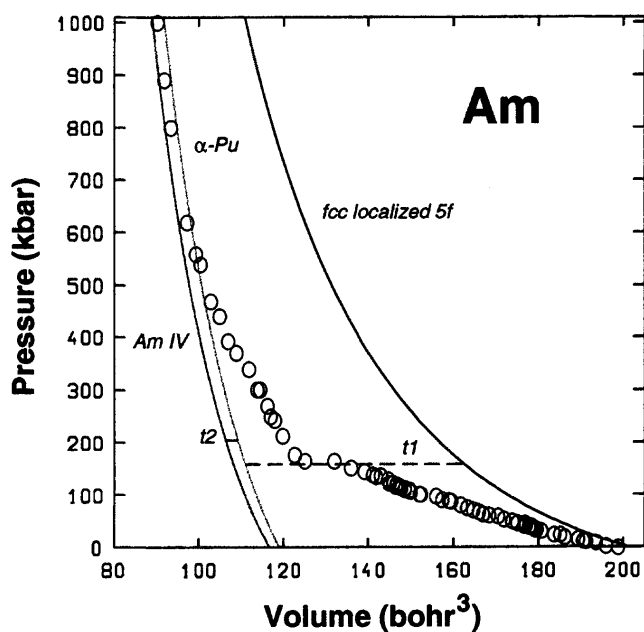


Figure 3. Pressures for Am, calculated by the FPLAPW method in the α -Pu and Am IV crystal structures and by the MTO method with localized 5f electrons in the fcc structure, as functions of atomic volume. The broken curve *t1* is the theoretical transition from fcc to α -Pu and the curve *t2* is that from α -Pu to Am IV; (O) experimental values [1, 2].

modulus greater than in the experiment; therefore our fcc_ℓ isotherm does not follow the experimental points. In [15] the bulk modulus found, 430 kbar, is also too great and the equilibrium volume of 169.39 bohr³ is too low. In [16] the fcc_ℓ phase of Am is modelled by the self-interaction-corrected local spin-density approximation; too-high values, 213.4 bohr³ and 395 kbar, for the equilibrium volume and the bulk modulus, respectively, were found.

From 600 kbar to 1 Mbar the experimental points in the Am IV structure are on our theoretical Am IV isotherm. In this volume range, around a 50% compression ($(V_0 - V)/V_0$, where V_0 is the experimental equilibrium volume) of Am, there is complete agreement between theory and experiment in finding the Am IV structure as the high-pressure phase of Am.

4. Plutonium

Experimentally, at ITU Karlsruhe, Pu was compressed in a diamond anvil cell up to 620 kbar [12] and only one phase transition was observed at about 400 kbar, α -Pu \rightarrow hex8-Pu.

In figure 4 we see that theoretically the energy of the hex8-Pu phase always stays greater than the energies of the α -Pu phase and no transition to the hex8-Pu phase occurs in our domain of study, i.e. up to a 40% compression ($(V_0 - V)/V_0$) of Pu. Therefore theory and experiment disagree, but the experimental system used for Pu, a simple x-ray tube [12], is not of the same quality as the one used for Am, synchrotron radiation [1, 2], so there is a greater possibility of error.

At ambient pressure the α -Pu phase is correctly calculated to be the most stable (figure 4) of the twelve crystal structures considered, but the energy difference from the α -Np phase is very small; consequently we have very soon, under pressure, the phase transition α -Pu \rightarrow

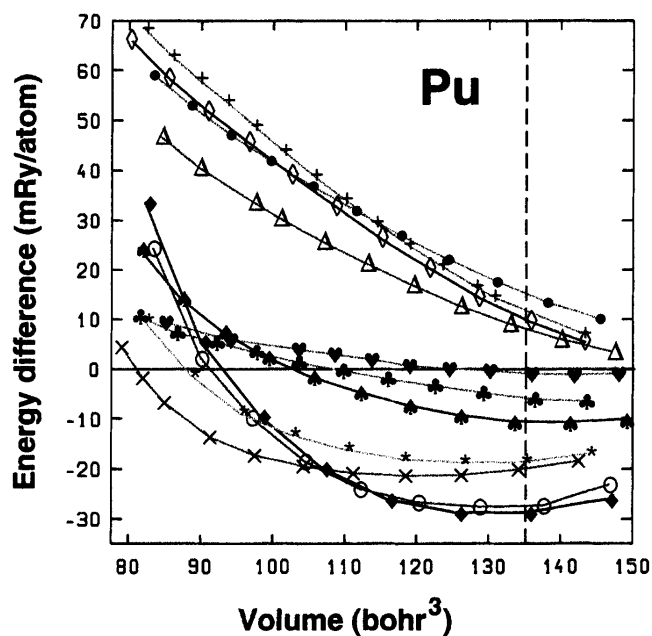


Figure 4. Total-energy differences for Pu, calculated by the FPLAPW method in the α -Pu (\blacklozenge), Am IV (\times), α -Np (\circ), β -Np ($*$), γ -Pu (\clubsuit), α -U (\bullet), α -Pa (\heartsuit), hex8-Pu (\triangle), α'' -Ce (\diamond), hcp (\bullet) and fcc ($+$) crystal structures, relative to the bcc structure, as functions of volume. The room temperature equilibrium volume for Pu is denoted by a vertical broken line.

α -Np which is followed very soon also by the transition α -Np \rightarrow Am IV. When the energy of the α -Np phase is the lowest among the crystal structures considered, there is a very small difference from the energy of the α -Pu phase. In view of this we think that, as indicated by experiment, there is in this volume range only one transition; theoretically it is α -Pu \rightarrow Am IV for about a 20% compression of Pu. Also the accuracy is not very good for the α -Pu phase because we obtain a theoretical equilibrium volume of 118.87 bohr³ instead of 135.15 bohr³ experimentally [6].

In figure 4 we see finally the transition Am IV \rightarrow bcc for a 39% compression of Pu. Therefore we propose the sequence α -Pu \rightarrow Am IV \rightarrow bcc under pressure for Pu. Previously, [5, 17, 18] α -Pu \rightarrow α -Np \rightarrow β -Np \rightarrow bcc was proposed theoretically, but we note in figure 4 that the energy of the Am IV structure is always lower than the energy of the β -Np structure and the range of stability of the α -Np structure is now very small with an energy too close to the α -Pu structure to be kept as a possible stable structure.

We notice also in figure 4 that the γ -Pu and the α'' -Ce structures for which the stabilities under pressure were never examined for Pu have their energies too high to be stable.

5. Neptunium

Experimentally, no phase transition was observed in Np below 520 kbar at ITU Karlsruhe [19].

In figure 5 at ambient pressure the α -Np structure is correctly calculated to be the most stable of the eleven crystal structures considered. We obtain an equilibrium volume of 125.6 bohr³ instead of 129.73 bohr³, obtained experimentally [6].

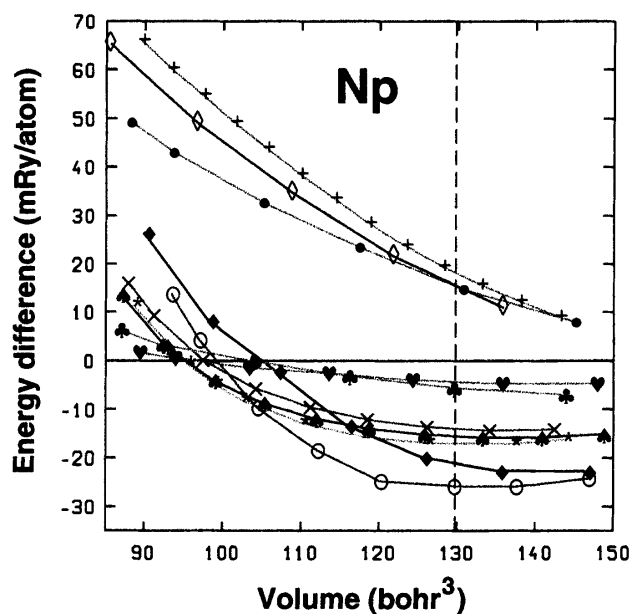


Figure 5. Total-energy differences for Np, calculated by the FPLAPW method in the α -Pu (\blacklozenge), Am IV (\times), α -Np (\circ), β -Np ($*$), γ -Pu (\blacktriangle), α -U (\bullet), α -Pa (\blackheartsuit), α'' -Ce (\diamond), hcp (\bullet) and fcc ($+$) crystal structures, relative to the bcc structure, as functions of volume. The room temperature equilibrium volume for Np is denoted by a vertical broken line.

Under pressure, as previously [5, 18, 20], the sequence α -Np \rightarrow β -Np \rightarrow bcc is obtained. The first transition is for a 19% compression ($(V_0 - V)/V_0$) of Np, the second transition for a 26% compression of Np.

The α -Pu, Am IV, γ -Pu and α'' -Ce structures for which the stabilities under pressure were never examined for Np have their energies too high to be stable. We also find the energies of the α -U structure higher than, but very close to, the energies of the β -Np structure in its range of stability, so the sequence α -Np \rightarrow α -U \rightarrow bcc is a possibility under pressure.

6. Uranium

Experimentally, the α -U structure remains stable up to 1 Mbar [21, 22].

In figure 6, at ambient pressure the α -U structure is correctly obtained as the most stable of the eleven crystal structures considered. We calculate an equilibrium volume of 137.34 bohr³, close to the experimental value of 140.03 bohr³ [6]. For the bulk modulus we obtain 1475 kbar, also close to the experimental values, 1355 kbar [21], 1387 kbar [22], 1470 kbar [19].

Theoretically, under pressure, as in figure 6, the α -U structure remains stable up to 1 Mbar, but for a higher pressure there is a transition to the bct α -Pa structure, for a 31% compression ($(V_0 - V)/V_0$) of U. At an even higher compression the transition bct \rightarrow bcc has been seen theoretically [18].

The never-examined α -Pu, Am IV, γ -Pu, α -Np and α'' -Ce structures for U have their energies too high to be stable.

In figure 7 we compare our theoretical isotherm in the α -U structure with experiments [21, 22].

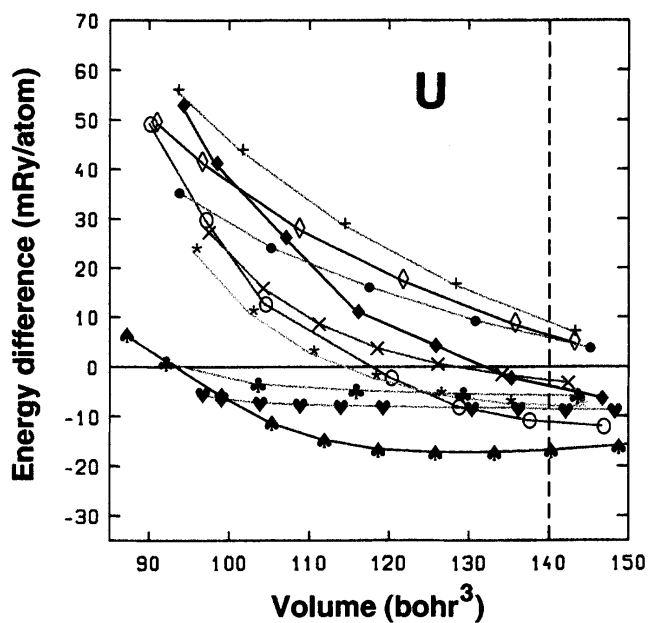


Figure 6. Total-energy differences for U, calculated by the FPLAPW method in the α -Pu (\blacklozenge), Am IV (\times), α -Np (\circ), β -Np ($*$), γ -Pu (\clubsuit), α -U (\spadesuit), α -Pa (\heartsuit), α'' -Ce (\diamond), hcp (\bullet) and fcc ($+$) crystal structures, relative to the bcc structure, as functions of volume. The room temperature equilibrium volume for U is denoted by a vertical broken line.

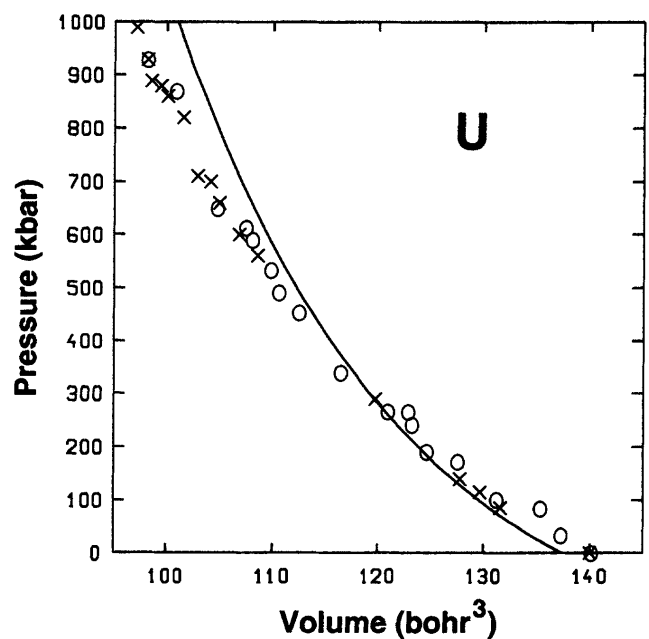


Figure 7. Pressure for U, calculated by the FPLAPW method in the α -U crystal structure, as a function of atomic volume; experimental values (\circ) from [21] and (\times) from [22].

7. Conclusions

For Am, Pu, Np, U we have examined using the FPLAPW method (WIEN97 code) [4] the stability under pressure of the high-pressure phase of americium, Am IV, recently found experimentally, which is a primitive-orthorhombic structure with four atoms in the uc, by comparing its total energy with those of ten other crystal structures, fcc, bcc, hcp, bct α -Pa, orthorhombic α -U, orthorhombic α -Np, monoclinic α -Pu, tetragonal β -Np, face-centred-orthorhombic γ -Pu or Am III and monoclinic α'' -Ce. We have chosen to plot the total energies relative to the total energy of the bcc structure, which is found to be the last structure for U, Np, Pu at small volumes and perhaps Am for a very high compression. The fcc, hcp, α'' -Ce structures have their energies always higher than the bcc one and cannot be stable for Am, Pu, Np and U. bct and γ -Pu have their energies always close to the bcc value, but becoming higher for small volumes. From Am, Pu, Np to U, the energy for the α -U structure is reducing, the energy of the α -Pu structure is increasing, etc; this explains why we obtain at ambient conditions the stability of the crystal α -phases of U, Np, Pu. Finally, the Am IV structure is found to be stable at high pressure for Am and Pu but not for Np and U.

In Am we have not found the Am III phase to be stable in any volume range. For this to happen, we think that the only possibility is to suppose that the 5f electrons are localized in the Am III phase like in the dhcp and fcc phases near ambient conditions, which are modelled by our fully relativistic MTO method with unhybridized 5f electron states in a fcc structure (fcc_ℓ).

In summary, we have found theoretically under pressure the following sequences:

- for Am: $\text{fcc}_\ell \rightarrow \alpha\text{-Pu} \rightarrow \text{Am IV}$, unless an Am III structure with localized 5f electrons exists;
- for Pu: $\alpha\text{-Pu} \rightarrow \text{Am IV} \rightarrow \text{bcc}$;
- for Np: $\alpha\text{-Np} \rightarrow \beta\text{-Np} \rightarrow \text{bcc}$ (α -U can be the stable structure instead of β -Np because its energy is very close);
- for U: $\alpha\text{-U} \rightarrow \text{bct} (\rightarrow \text{bcc [18]})$.

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