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Plane-wave pseudopotential study of the light actinides

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Norm conserving pseudopotentials have been generated for the light actinides (Th-Np) and the plane waves + pseudopotential formalism has been used to study their crystal structures at zero temperature as a function of pressure. The often complex alpha phases of these elements have been fully relaxed, and we have used a thorough treatment of spin-orbit coupling. The zero-pressure zero-temperature equilibrium volumes and bulk moduli are consistent with previous all-electron full-potential calculations, and, up to uranium, in excellent agreement with experiment. This is also the case for cell parameters and pressure-induced phase transitions. It is likely that, from neptunium on, a more careful treatment of electronic correlations and/or relativistic effects is necessary to reproduce the experimental data with the same precision.

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I. INTRODUCTION

The actinide series is generally divided in two parts, the so-called ''light'' and ''heavy'' actinides, in relation to their $5f$ electrons behavior. The light actinides, from thorium to neptunium, exhibit f-electron bonding at ambient conditions. The f bands are narrow and highly directional, which results in very complicated open crystal structures, with low symmetry, such as α-U or α-Np. Upon increasing pressure, the f bands broaden and the light actinides undergo phase transitions to more close-packed and symmetric structures. As for the heavy actinides, starting from americium, the f electrons are strongly localized and do not contribute to bonding at ambient pressure. The resulting structures are more compact. The f bonding character reappears under pressure, and gives rise to open high pressure phases, such as Am-IV, which is closely related to α-U.[1] Plutonium is at the interface between the two series, and exhibits characters from both: in the equilibrium structure at ambient conditions (monoclinic α-Pu), the f electrons contribute to bonding, whereas in the higher temperature δ-Pu phase [face-centered cubic (fcc)] they are localized.

Heavy actinides are still out of reach of electronic structure calculations based on density functional theory (DFT) using local density approximation (LDA), even with gradient corrections (GGA). In this formalism, electron correlation is treated in an averaged way and cannot describe strongly localized states, for which new theories, which go beyond LDA, such as LDA+U or dynamical mean field theory (DMFT) are necessary.[2] For example, using LDA, the calculated equilibrium volume for δ-Pu is underestimated by as much as 25%. In the case of americium,[3] the equilibrium volume discrepancy for the equilibrium fcc phase is as large as 30%, whereas the high pressure AmIV structure, where f electron delocalization has occurred, is correctly treated at the GGA level.

This correlation problem appears to be less crucial for the light actinides. Yet, they still are a challenge for electronic structure calculations. First, for such heavy elements, relativistic effects are expected to become important, and a rigourous treatment of these should be included, at least at the scalar-relativistic level. Second, the complicated crystal structures have many internal degrees of freedom and their relaxation, necessary criterion of a correct theoretical structure, is difficult.

Numerous all-electron calculations, using various technical formalisms [full-potential linearized augmented plane-wave (FLAPW),[4,5] full potential linear muffin tin orbitals (FP-LMTO)[6]] are available for the light actinides series. But, in all cases, the structures have not been fully relaxed (only partially in some cases, not at all in the others, the cell parameters being taken as the experimental ones, if not a fake fcc).

We have chosen here to explore an alternative approach : the combination of pseudopotentials and plane waves basis sets,[7] which is one of the most popular methods for electronic structure calculations, within density-functional theory (DFT). The plane wave basis is one of the simplest and most natural formalism to implement for crystals. In particular, it allows for the global relaxation of large cells and ab initio molecular dynamics calculations.

Till recently, the pseudopotential formalism had been neglected for f elements, because one has to describe relatively localized electronic f states. In terms of plane waves, this means that one needs huge basis sets and the calculations used to be computationally demanding, if not unaffordable.

In a previous paper,[8] we have shown that it was possible to study pressure induced phase transitions in cerium, another f-pathological element by these techniques. Recently, ultrasoft pseudopotentials have been used by Pickard *et al.*[9] to study some lanthanide and actinide compounds and Crocombette *et al.*,[10] using one of our pseudopotentials for uranium, have studied point defects in uranium dioxyde.

The approach here is systematic. We have built norm-conserving pseudopotentials for all the light actinides and we have studied their fully relaxed crystal structures, and their phase transitions under pressure.

The paper is organized as follows. Section II details all the technical details for the pseudopotential generation and the plane waves calculations. Sections III to VI are devoted to elements from Th to Np. In Sec. VII, we detail the influ-

TABLE I. Cutoff radii in atomic units chosen for the pseudopotential generation.

	6s	6p	6d	5f
Th	1.37	1.55	2.25	1.00
Pa	1.27	1.53	2.23	1.05
U	1.26	1.52	2.20	1.26
Np	1.24	1.50	2.05	0.90

ence of spin-orbit coupling, and finally we conclude in Sec. VIII.

II. DETAILS OF THE CALCULATION

A. Pseudopotential generation

The physical idea behind the pseudopotential approximation is to replace the true atomic potential by an effective potential that accurately mimics the effect of the chemically inert core states on the valence states, explicitely treated in the calculation. There are several recipes to construct pseudopotentials and to ensure their transferability to very different chemical environments, while being computationally efficient. We have chosen here the non-local norm-conserving Troullier-Martins[11] technique, which has proven to be one of the most efficient and reliable, if not one of the cheapest computationally.

In this approach, one has to choose which states are to be pseudized and an atomic reference configuration on which to generate the all electron potential and wavefunctions. Then, for each angular momentum, one has to choose a cutoff radius for pseudization, beyond which the pseudo wave function is set equal to the true wave function. Within the cutoff radius, the pseudo wave function is continued by a polynomial form which obeys continuity equations.

After numerous tests, we concluded that, for the light actinides, it was necessary to treat as valence states the $6s$, $6p$, $6d$, $5f$, and $7s$ electrons, and that pseudopotentials built from an ionic reference configuration with an empty $7s$ orbital, and a single projector per angular momentum were optimum. Classically, the cutoff radii were taken close to the outermost maximum of the corresponding all electron wave functions. The angular momentum component $l=0$ was taken as the local part. In Table I, we list the cutoff radii for each angular component of each element.

With these pseudopotentials, the valence levels of the isolated atoms, both neutral and ionized, were reproduced within 0.05 eV (0.3 eV for the $7s$ state), as compared to the all electron scalar-relativistic calculation. Using the pseudopotential generator developped by Giannozzi,[12] we have generated for each element two pseudopotentials: one using the local density approximation (LDA) to DFT, with the exchange-correlation potential of Ceperley and Alder[13] as parametrized by Perdew and Zunger[14] and the second using gradient corrections (GGA) to LDA according to the recipe of Perdew, Burke and Erzerhof (PBE96).[15]

TABLE II. Equilibrium volume and bulk modulus of Th in the fcc structure.

	V_{eq} (Å^3/at)		B (GPa)	
	LDA	GGA	LDA	GGA
FLAPW (Ref. 4)	29.56	32.46	61.0	56.7
Pseudopotentials	29.75	32.23	65.1	54.2
Experiment (Refs. 21,22)	32.81		58	

For spin-orbit calculations, GGA pseudopotentials with components for each channel $l+\frac{1}{2}$ and $l-\frac{1}{2}$ were generated with Martins' generator.[16] The valence states, atomic configurations and cutoff radii were kept identical.

B. Structure calculations

All the plane waves calculations, were performed with the ABINIT code.[17] It relies on an efficient fast Fourier transform algorithm[18] for the conversion of wave functions between real and reciprocal spaces, on the adaptation to a fixed potential of the band-by-band conjugate gradient method[7] and on a potential-based conjugate gradient algorithm for the determination of the self-consistent potential.[19]

All our pseudopotentials need a 120 Ry energy cutoff for the plane-waves expansion of wave functions. With this cutoff, energy differences are converged within 1 mRy/at. A Gaussian smearing of 0.02 Ry has been applied for Brillouin Zone integrations, which results in a metallic correction less than 0.1 mRy/at. In the electonic structure calculation, the exchange-correlation functional was consistent with the one used for the pseudopotential generation.

For all the crystalline structures we have optimized the irreducible Brillouin zone sampling. We used 35 special k points for fcc, 35 for bcc, 56 for bct, 64 for hcp, 64 for α-U, 27 for α-Np, and 40 for β-Np.

When necessary, the stuctures were fully relaxed at each volume, and the energy versus volume curves were fitted by a Birch-Murnaghan equation of state to calculate equilibrium volumes and bulk moduli. Spin-orbit coupling has been introduced in the spirit of Hemstreet *et al.*[20] Details are given elsewhere.[40]

III. THORIUM

Thorium has a special place among the actinides. It is the first element in the series and the $5f$ band is beginning to be filled. The equilibrium structure is face-centered cubic and is quite simple and symmetric, as compared to the other light actinides. Cerium, the first $4f$ element has also an fcc equilibrium structure. But contrarily to cerium, thorium does not exhibit phase transitions towards structures where the f electrons would be localized (e.g., γ-Ce, which is also fcc).

We have calculated the equilibrium volume and the bulk modulus of thorium's fcc phase. The results are shown in Table II together with experimental results and all-electron FLAPW calculations. Our pseudopotential calculation

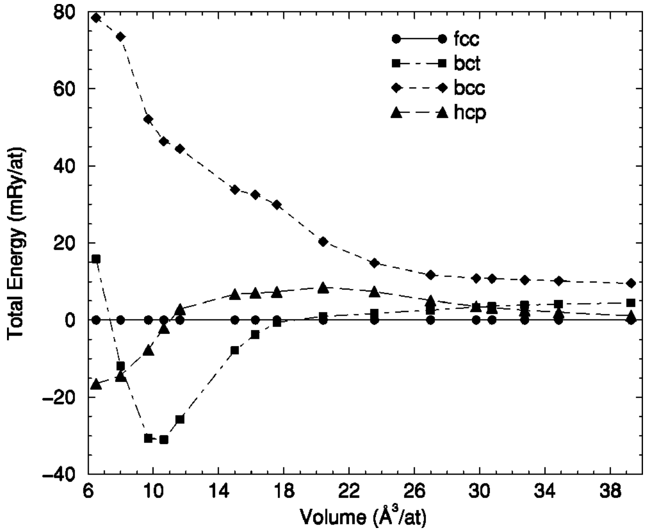

FIG. 1. Calculated GGA total energies for bcc, bct and hcp crystal structures of thorium relative to the total energy of the fcc structure, as a function of volume.

is in excellent agreement with the all-electron calculations done in the same approximation for the exchange-correlation functional. The improvement when GGA replaces LDA is clear. Our GGA results are very close to the experimental ones.[21,22]

We have also checked the relative stability with respect to fcc of some previously proposed high pressure phases: body centered cubic (bcc), body centered tetragonal (bct), and hexagonal compact (hcp). Our results, as a function of volume are shown on Fig. 1. The fcc phase is the most stable phase at the equilibrium volume of thorium as found experimentally.

We predict a first transition to bct at 18.5 Å^3/at ($V/V_0 = 0.57$) which corresponds to a pressure of 86 GPa. This value is consistent with the experimental results of Vohra and Akella[23] who evidenced the transition around 100 GPa ($V/V_0 = 0.534$) and with the all electron results of Eriksson *et al.*[24]

For the bct phase, we optimized the c/a parameter and we found that it remains equal to 1.65 on a wide pressure range. This is another similarity with cerium: thorium and cerium have the same value of c/a for the bct phase.

Upon further compression, for a much lower volume ($V = 8$ Å^3/at., $V/V_0 = 0.25$), the hcp structure becomes stable, a fact which was already predicted by Söderlind in all electron calculations.[25] However, this transition has never been observed experimentally.

IV. PROTACTINIUM

Protactinium is an element on which experimental results are very rare because of its radioactivity. The experimental zero temperature and zero pressure body centered tetragonal phase (with c/a = 0.82) is unique in the whole periodic table. The calculated equilibrium volume and bulk modulus of Pa are shown in Table III together with results from all electrons FLAPW calculations[4] and experiments.[26,27]

TABLE III. Equilibrium volume and bulk modulus of Pa in the bct structure.

	V_{eq} (Å^3/at)		B (GPa)	
	LDA	GGA	LDA	GGA
FLAPW (Ref. 4)	23.21	25.06	111	105
Pseudopotentials	22.83	24.60	115	92
Experiments (Refs. 26,27)	24.91		157	

The optimized c/a ratio at the equilibrium volume (Fig. 2) $c/a = 0.8$ turned out to be roughly constant up to the first transition. As in the case of thorium, the pseudopotential calculations are in very good agreement with all electron calculations done in the same approximation for exchange correlation.

The agreement with the experimental equilibrium volume is good when GGA is used. However, the calculated bulk modulus, although consistent with all electron results, differs from the experimental one by 40%. The agreement with experiment on bulk moduli for Th and U leads us to suggest that this experimental result may be wrong. To shed light on this point, new experiments would be welcome.

We have also studied the relative stabilities of several high pressure phases of protactinium. We checked the bct, fcc, bcc, hcp, and α-U structures. The α-U structure is described in the next section. We optimized the three internal degrees of freedom for this structure y, b/a, and c/a at each volume (Fig. 3).

If b/a remains almost constant, c/a and y appear to vary considerably with increasing pressure, which is in contrast to what was assumed in a previous FPLMTO calculation[28] by Söderlind *et al*. The energy differences with respect to bct as a function of volume are shown on Fig. 4. According to our calculations, a transition from bct to α-U should occur around 46 GPa (volume of 18.7 Å^3/at.). This pressure is higher than the one calculated by Söderlind (25 GPa). More-

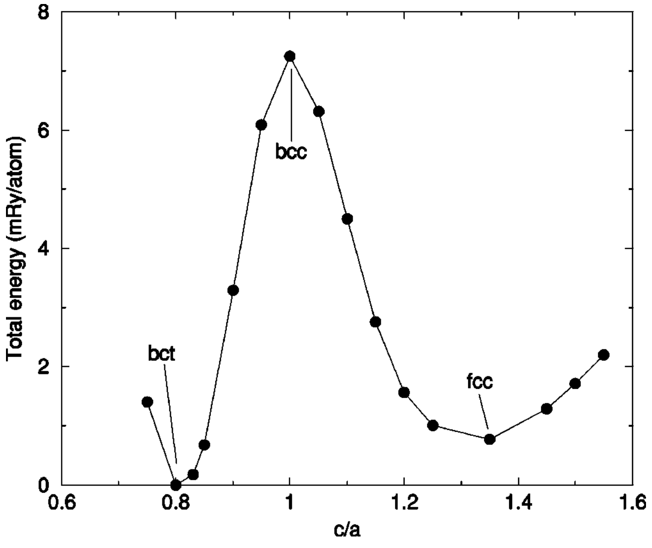

FIG. 2. Bains path for protactinium in GGA close to the equilibrium volume. The global minimum has been set to zero.

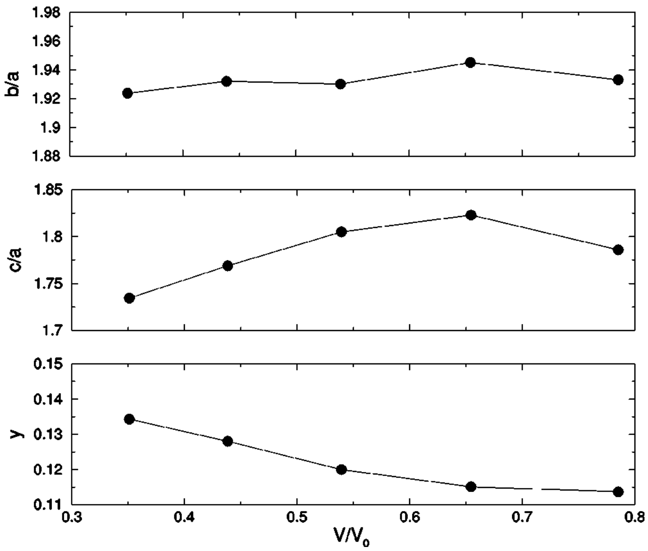

FIG. 3. Evolution ot the internal parameters of the α-U structure of protactinium versus volume with the GGA pseudopotential, in its stability domain.

over, the α-U structure remains stable to very high pressures, and, in contrast to all electron calculations, no further transition to a reentrant bct or hcp (Ref. 28) is evidenced, down to 8.5 Å^3/at. Yet, in the all electron calculations, the α-U structure was not optimized, which results here in stabilizing it on a wider pressure range.

V. URANIUM

In contrast to protactinium, uranium has been extensively studied, both theoretically and experimentaly. The low pressure and low temperature α phase is a base centered orthorombic structure with two atoms per cell, with atomic positions $(y,-y,-1/4)$ and $(-y,y,1/4)$ in units of the Bravais lattice vectors $(a/2,-b/2,0)$, $(a/2,b/2,0)$ and $(0,0,c)$. Four parameters are needed to describe it: a, b/a, c/a, and y. The experimental values of the parameters at equilibrium are[29] $a=2.858$, $b/a=2.06$, $c/a=1.73$, and $y=0.105$ at $V_0=20.71$ Å^3/at. The experimental bulk modulus is $B_0=135.5$ GPa. The α-U phase is experimentally stable up to at least 100 GPa.

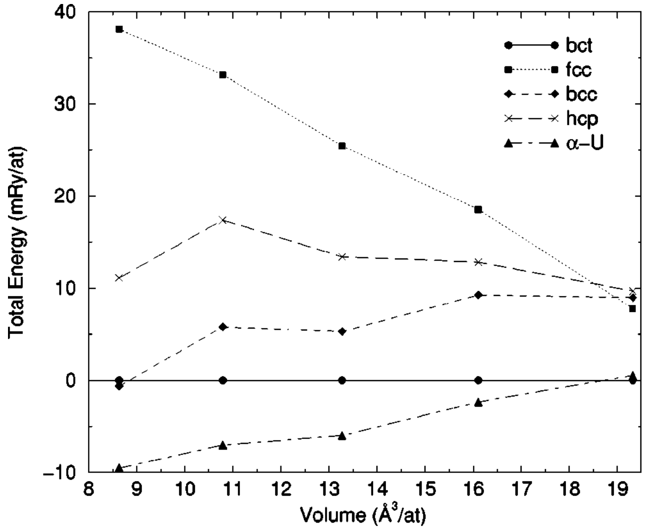

FIG. 4. Calculated GGA total energies for the fcc, bcc, hcp, and α-U crystal structures of protactinium relative to the total energy of the bct structure, as a function of volume.

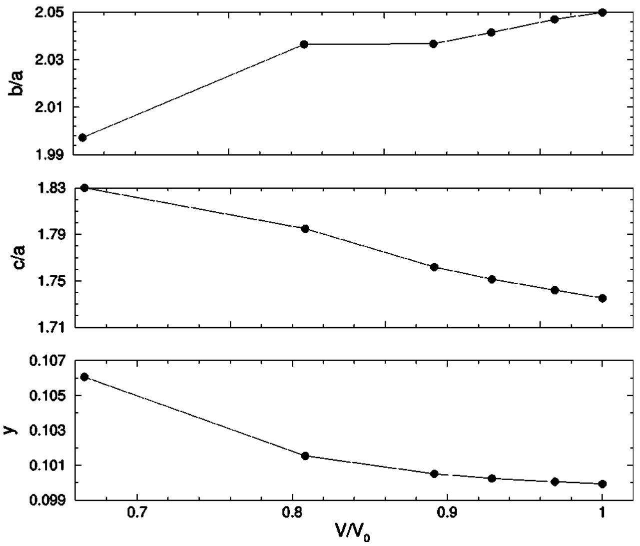

FIG. 5. Evolution ot the internal parameters of the α-U structure of uranium versus volume with the GGA pseudopotential.

We performed a total relaxation of the three parameters y, b/a, and c/a of this phase. Their evolution versus compression is detailed in Fig. 5 for the GGA pseudopotential.

For the equilibrium volume, our values are consistent with experiment. We find that c/a increases with pressure, whereas the corresponding decrease of b/a and y is smaller: from ambient pressure up to a 30% compression, the changes in axis ratios are about -3.4% for c/a, $+2.5\%$ for b/a, whereas y varies by as much as 5%. This is consistent with the experimental trends reported by Akella,[29] but in disagreement with their FPLMTO calculations hypothesis.

As already noticed for Th and Pa, the equilibrium volumes and bulk moduli for the LDA and GGA pseudopotentials are similar to the FLAPW ones, and the GGA ones are close to experimental values (Table IV).

We have also studied the relative stability of the α-U, fcc, bcc, bct, and hcp phases of uranium at zero temperature. For the bct phase, the c/a ratio was optimized to a value of 0.8. At low pressure, the α-U phase is the most stable phase as found experimentally. The energy differences versus volume, relative to the α-U phase, are presented in Fig. 6.

TABLE IV. Equilibrium volume (Å^3) and bulk modulus (GPa) of U in the α-U structure.

	V_{eq} (Å^3/at)		B (GPa)	
	LDA	GGA	LDA	GGA
FLAPW (Ref. 4)	18.93	20.38	176	149
Pseudopotentials	18.71	19.91	182	145
Experiment (Refs. 29,30)	20.56		135.5	

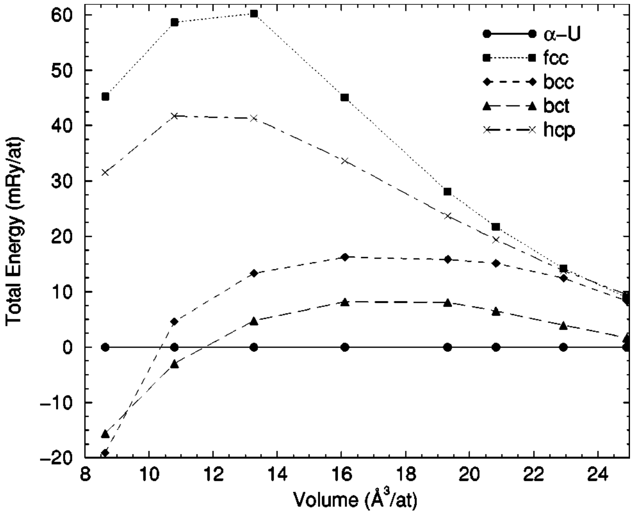

FIG. 6. Calculated total GGA energies for the bct, fcc, bcc, and hcp crystal structures of uranium relative to the total energy of the α-U structure, as a function of volume.

We predict a transition towards the bct phase at a volume of 11.75 Å^3/at ($V/V_0 = 0.58$). Then, at a smaller volume ($V/V_0 = 0.47$), bcc becomes stable. The sequence of transitions is thus α-U→bct→bcc, in full agreement with Söderlind,[6] even if our transition pressures should be higher. As found in experiment, there is no transition below 100 GPa, and the α-U structure, as in Pa, seems to be remarkably stable.

VI. NEPTUNIUM

According to a somewhat schematic picture, one could say that with increasing Z, the f electrons tend to get more localized and the structures more and more complex, until the f electrons get fully localized and the structures relatively simpler.

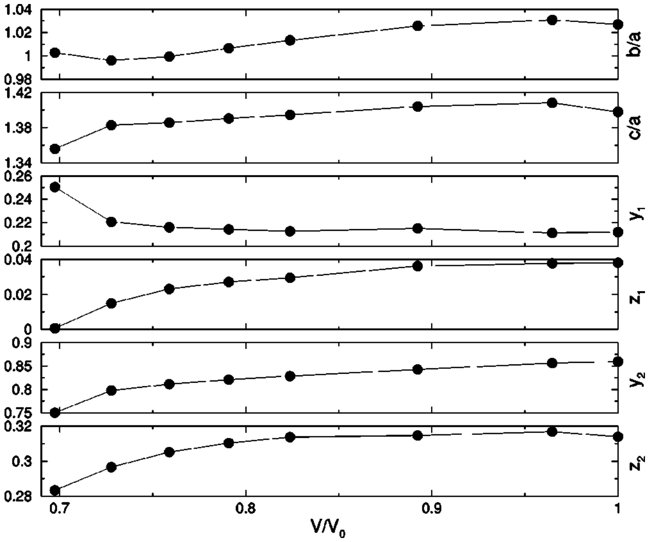

FIG. 7. Evolution with volume of the internal parameters of the α-Np structure of neptunium with the GGA pseudopotential.

TABLE V. Equilibrium volume (Å^3) and bulk modulus (GPa) of Np in the α-Np structure.

	V_{eq} (Å^3/at)	B (GPa)
FLAPW (Ref. 4)	18.44	196
Pseudopotentials	18.20	180
Experiment (Ref. 31,32)	19.20	120

Thus neptunium is experimentally found to crystallize at low pressure in three types of structure[33] : α-Np, β-Np, and γ-Np. α-Np is a simple orthorhombic structure with eight atoms/cell,[34] with atomic positions $\pm(1/4, y_1, z_1)$, $\pm(1/4, 1/2 - y_1, z_1 + 1/2)$, $\pm(1/4, y_2, z_2)$, $\pm(1/4, 1/2 - y_2, z_2 + 1/2)$. β-Np is tetragonal with 4 atoms/cell[35] [positions (0,0,0), (1/2,1/2,0), (1/2,0,u), and (0,1/2,$-u$) with $u = 0.375$] , and γ-Np is bcc.

For all this phases, we have performed a global relaxation of all the internal degrees of freedom, only for the GGA pseudopotential, as, due to the great number of degrees of freedom, the calculations were getting painful. Our results for the α-Np phase are reported on Fig. 7.

The cell parameters that we calculate for the equilibrium volume are $a = 4.66$ Å (exp. 4.723 Å), $b/a = 1.027$ (1.035), $c/a = 1.398$ (1.411), $y_1 = 0.212$ (0.208), $z_1 = 0.038$ (0.036), $y_2 = 0.86$ (0.842), $z_2 = 0.314$ (0.319).

The GGA equilibrium volume and bulk modulus are consistent with all electron results (Table V). The equilibrium volume is underestimated by 5% with respect to experiment[31,32] whereas the bulk modulus is strongly overestimated (50 %), as in FLAPW calculations.

Some authors[4] claim that temperature effects may soften the bulk modulus for Np. Yet, we think that we reach here the limits of our theory. As in plutonium,[36] subtle correlation effects could begin to occur in Np that are out of reach of LDA and even GGA. A thorough treatment of relativistic effects could also be necessary.

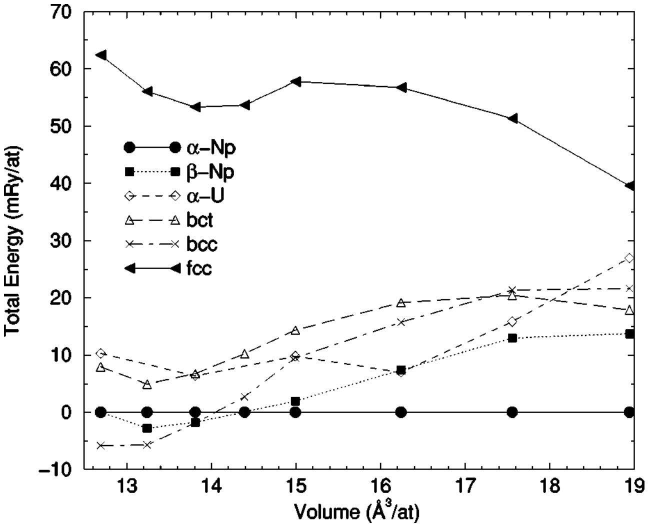

FIG. 8. Calculated total GGA energies for the β-Np, α-U, bct, fcc, and bcc crystal structures of neptunium relative to the total energy of the α-Np structure, as a function of volume.

TABLE VI. Equilibrium volumes (Å^3/at) for the light actinides in their α phases and in a reference fcc phase, with and without spin-orbit effects. In our calculations, the cells have been fully relaxed, except for Np (underlined result).

	fcc phase		α phase	
Method	GGA	GGA+SO	GGA	GGA+SO
		Th		
FP-LMTO (Refs. 39,38)		29.62		
FLAPW (Ref. 4)	32.46	32.28		
FLAPW (Ref. 5)		31.05		
This work	32.23	32.42		
Experiment (Ref. 21)	32.81			
		Pa		
FP-LMTO (Refs. 39,38)		23.71		23.32
FLAPW (Ref. 4)	25.50	25.57	25.06	24.92
FLAPW (Ref. 5)				23.95
This work	25.05	25.52	24.60	25.01
Experiment (Ref. 26)			24.91	
		U		
FP-LMTO (Refs. 39,38)		20.51		19.46
FLAPW (Ref. 4)	21.83	22.01	20.38	20.73
FLAPW (Ref. 5)				20.34
This work	21.31	21.98	19.91	20.33
Experiment (Ref. 29)			20.56	
		Np		
FP-LMTO (Refs. 39,38)		18.64		18.10
FLAPW (Ref. 4)	19.45	20.41	18.44	18.90
FLAPW (Ref. 5)				18.60
This work	19.34	19.97	18.20	19.83
Experiment (Ref. 34)			19.23	

TABLE VII. Bulk moduli (GPa) for the light actinides in their α phases and in a reference fcc phase, with and without spin-orbit effects. In our calculations, the cells have been fully relaxed, except for Np (underlined result).

	fcc phase		α phase	
Method	GGA	GGA+SO	GGA	GGA+SO
		Th		
FP-LMTO (Refs. 39,38)		61.5		
FLAPW (Ref. 4)	56.7	73.1		
FLAPW (Ref. 5)		57.7		
This work	54.2	55.1		
Experiment (Ref. 22)	58			
		Pa		
FP-LMTO (Refs. 39,38)		122		123
FLAPW (Ref. 4)	100	96	105	105
FLAPW (Ref. 5)				104.8
This work	93	92	92	93
Experiment (Ref. 27)			157	
		U		
FP-LMTO (Refs. 39,38)		148		172
FLAPW (Ref. 4)	125	99	149	124
FLAPW (Ref. 5)				147.5
This work	115	108	145	132
Experiment (Ref. 30)			135.5	
		Np		
FP-LMTO (Refs. 39,38)		161		170
FLAPW (Ref. 4)	137	140	196	158
FLAPW (Ref. 5)				201.7
This work	197	185	180	165
Experiment (Ref. 32)			120	

We have checked the relative stability of some high pressure phases of neptunium : β-Np, α-U, bct, bcc, fcc, with respect to α-Np. The results are shown on Fig. 8.

For a 21% compression (i.e., a volume of 14.4 Å^3/at.), we predict a transition towards β-Np. This is in disagreement with the FP-LMTO value of 10% proposed by Söderlind,[37] but is closer to the FLAPW value of Pénicaud (19%).[5] In their experimental work, Dabos *et al.*[32] found no transition under up to at least 20% compression, which is consistent with our results. At higher pressure, as already predicted by Söderlind[37] and Pénicaud,[5] bcc should become stable for a 23% compression factor.

VII. ROLE PLAYED BY SPIN-ORBIT COUPLING

Spin-orbit coupling should not be avoided in such calculations. After generating suitable GGA pseudopotentials, we have performed cell relaxations for the α phase of each element and for a reference fcc structure, and we have calculated the corresponding equilibrium volumes and bulk moduli. The results are summarized in Tables VI and VII, respectively, together with our calculations without spin-orbit coupling, all electron results and experimental data.

The α-Np phase of neptunium has not been relaxed in GGA+SO, because the calculations were computationally too demanding. We used the experimental parameters,[34,35] so as to compare with previous all-electron calculations.

In all cases, both for equilibrium volumes and bulk moduli, the results get closer to experiment. The effect of spin orbit coupling on equilibrium volumes (Fig. 9) and bulk moduli (Fig. 10) becomes noticeable from uranium on. In this case, the agreement with experimental data is perfect.

As for the bulk moduli, except for Pa (but we suspect, as already said, that the experimental value is wrong), the agreement with experiment is also very good. The only failure is for neptunium, where we can say that, even taking into account cell relaxation, it is doubtful that we could retrieve the experimental value within a few % as is the case for the other elements.

Our calculations are consistent with FLAPW results.[4,5] However, former FP-LMTO calculations[38,39] give quite different values which may be questionable, as already noticed by Jones.[4] The influence of spin-orbit coupling on the internal parameters of various structures will be detailed in a forthcoming paper.

VIII. CONCLUSION

We have generated norm-conserving pseudopotentials for the light actinides, which have enabled us to perform global

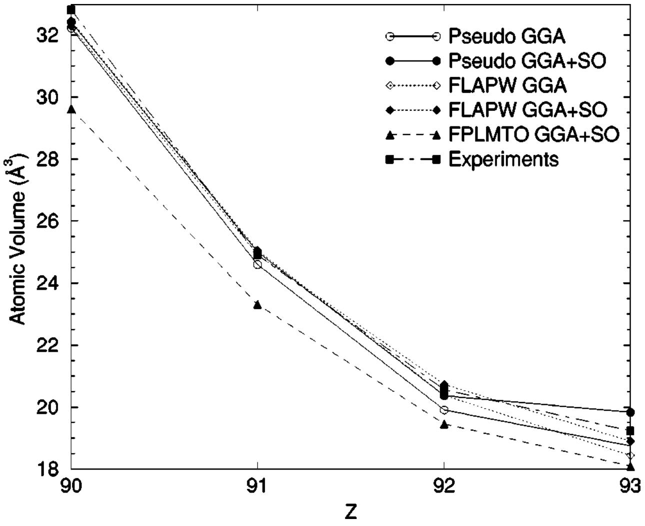

FIG. 9. Equilibrium volume in the α phase versus atomic number taking or not into account spin-orbit coupling. The FPLMTO results are from (Refs. 39,38) and the FLAPW from (Ref. 4).

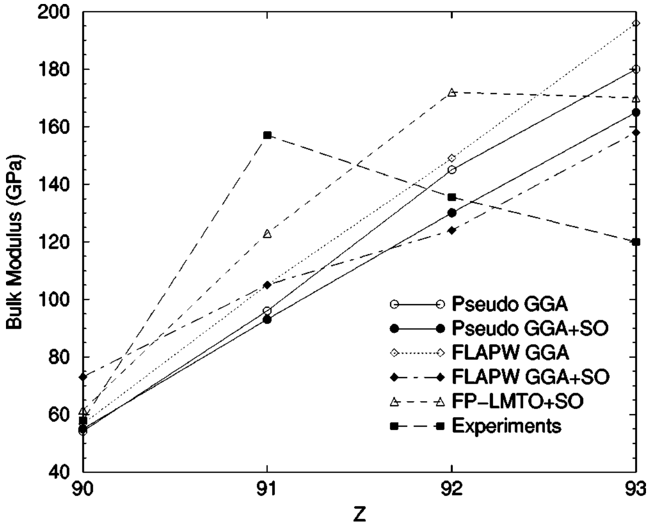

FIG. 10. Bulk modulus in the α phase versus atomic number taking or not into account spin-orbit coupling. The FPLMTO results are from (Refs. 39,38) and the FLAPW from (Ref. 4).

relaxations of the complex structrures of these elements. We have also performed a systematic study of their phase transitions under pressure. All our results compare favorably with previous all-electron calculations, with a better agreement with FLAPW results. As for equilibrium volumes and bulk moduli, our GGA results are very close to experiment up to uranium and, as previously noticed, GGA represents a significant improvement on LDA for these elements. We have also used for the first time to our knowledge a full treatment of spin-orbit coupling in a plane-waves formalism. Its role on the equation of state seems to become important starting from neptunium. It is interesting to note that all LDA/GGA-based calculations seem to converge, within a few % towards the same values for the equilibrium volumes and bulk moduli of the light actinides, and that these values start departing from experimantal data for neptunium. It is likely that new developments in the theoretical formalism (fully relativistic treatment, electronic correlations beyond LDA) cannot be avoided if one wants to describe with the same accurracy heavier elements, and especially the alpha phase of plutonium.

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