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# Structural properties of plutonium from first-principles theory

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First-principles theory is shown to account for the unique low-temperature crystal structure of plutonium metal ($\alpha$-Pu). Also the observed, and debated, upturn of the equilibrium volume between neptunium and plutonium is reproduced and found to be a consequence of the different crystal structures for these two metals. Thus it is shown that density-functional theory is able to accurately describe bonding properties of $5f$ electrons in an outstandingly complex system, where also relativistic effects are large. The electronic structure for $\alpha$-Pu and for plutonium in competing close-packed crystal structures are also presented. Moreover, an explanation for the occurrence of the highly complex $\alpha$-Pu structure is given. The mechanism is described in terms of a Peierls distortion in conjunction with a narrow $5f$-band width. The energy gained from the splitting of the $5f$ bands outweighs the electrostatic energy which favors the high symmetry structures found for most other metals. At lower volumes we predict that plutonium should become bcc. [S0163-1829(97)01304-0]

## I. INTRODUCTION

Plutonium ($_{94}$Pu) metal is one of the heaviest metals known and it belongs to the series of metals that are referred to as the actinides. Plutonium metal, which is not found in nature, has since the first sample was prepared, been shown to have a number of spectacular physical and chemical properties. The phase diagram is particularly interesting with five allotropes discovered early ($\alpha$, $\beta$, $\gamma$, $\delta$, and $\epsilon$), and a sixth phase that was found later ($\delta'$),[1] see Fig. 1. The latest discovered solid phase ($\zeta$) (Ref. 2) has a yet unknown complex crystal structure. Thus plutonium has as many as seven different crystalline forms[1] which is more than any other metal. The $\alpha$, $\beta$, and $\gamma$ phases, stable up to about 380 K, 460 K, and 570 K, respectively, are very complex structures. This is in contrast to the simple structures of $\delta$-Pu (fcc, face centered cubic) and $\epsilon$-Pu (bcc, body centered cubic), which are frequently found in other metals. The $\alpha$ phase is especially interesting with a unique open and low symmetry (monoclinic) crystal structure. In this allotrope there are 16 atoms per unit cell and the atomic arrangement seems to reflect covalent chemical bonding, where the nearest neighbor distance between certain atoms is very small and between others very large.[1,3] The crystal structures of the light actinides ($_{90}$Th$-_{94}$Pu) display increasingly distorted crystal structures, with plutonium showing the most extreme complexity in this respect. This fact has been of great scientific interest for decades and a good understanding of this behavior has only recently emerged. For plutonium, however, there has not been presented any reliable theory for the crystal structure and in this paper we address from *ab initio* theory the peculiar crystallographic properties of this material. We would also like to give additional background to the complexity of this element and thus mention that other physical and chemical properties of plutonium are also very unusual.[4] For instance, two of the allotropes, $\delta$ and $\delta'$ (bct, body centered tetragonal), contract rather than expand when heated, whereas the low-temperature $\alpha$ phase shows the largest thermal expansion among the elemental transition metals.[4] Also other properties, like the thermal and electrical conductivity, are anomalous for this spectacular material.[4] Based upon these remarkable properties, it has been speculated that plutonium cannot be related to other metals and that a rather

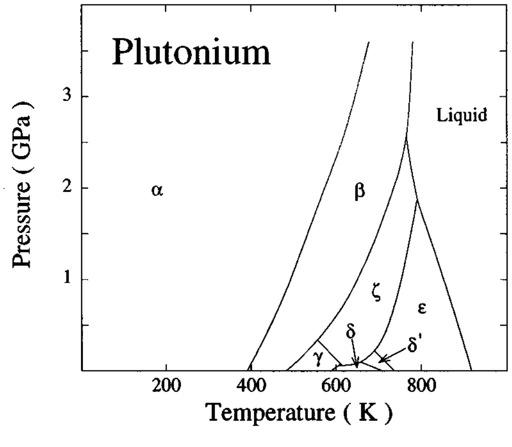

FIG. 1. The experimental (Ref. 1) phase diagram for plutonium.

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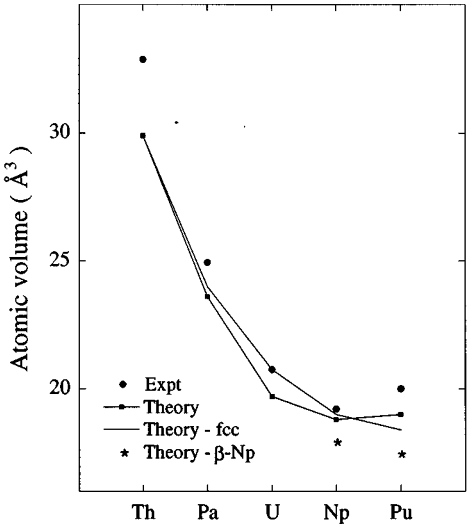

FIG. 2. Measured and calculated room temperature atomic equilibrium volumes (Ref. 24) for the light actinide metals. The calculations were done both for the observed room temperature structures (curve labeled ''theory'') as well as for a hypothetical fcc structure (curve labeled ''theory-fcc'') and for Np and Pu also for the $\beta$-Np structure (stars labeled ''theory-$\beta$-Np'').

specific theory for plutonium is needed to describe its many facets.[5]

The electronic structure of plutonium also shows a very complex behavior. The actinide elements near $_{94}$Pu have the interesting property that for the earlier metals ($_{90}$Th, $_{91}$Pa, $_{92}$U, and $_{93}$Np) the 5$f$ electrons are delocalized,[6–10] whereas the heavier metals ($_{95}$Am and beyond) have 5$f$ electrons which are chemically inert, in analogy to the localized 4$f$ electrons in the lanthanide metals.[6–10] Hence plutonium is located at a position close to the border where, as a function of atomic number, a transition from delocalized to localized 5$f$ states appears.[6–10] This complex and intriguing scenario provides a great challenge for theory to accurately treat the electronic structure of plutonium. For instance, the appearance of $f$ states in the valence band of plutonium probably makes it hard to use theoretical band structure methods that utilize nonlocal basis functions (plane waves or similar) such as the pseudopotential methods. In addition to this the plutonium atom is very heavy, which means that relativistic effects need to be taken into account in the description of the electronic structure of plutonium metal.[10] In particular, the spin-orbit coupling cannot be neglected when such heavy metals are investigated. Because of the mentioned difficulties, an accurate total energy treatment of plutonium in its ground state ($\alpha$-Pu) has not been performed until now, to our knowledge.

One pronounced experimental evidence for the itinerant character of the 5$f$ electrons in the light actinide elements can be found from the trend displayed by their density (or volume) as one proceeds from $_{90}$Th to $_{94}$Pu, where the volume shows a parabolic decrease of the volume as a function of nuclear charge (Fig. 2). In contrast to this, from $_{95}$Am and onwards the metallic volumes are much larger ($\sim$ 50%) with a weak linear decrease with atomic number, similar to the lanthanide contraction (not shown). This behavior strongly suggests that the 5$f$ states for $_{95}$Am and the heavier actinides are localized.[6] The theoretically predicted[6] and observed[11] super conductivity of americium metal give much support to this view. The volume behavior of the early actinides ($_{90}$Th$-_{94}$Pu) on the other hand, is very similar to what is found for the nonmagnetic $d$-transition metals, and it can be understood from the filling of first bonding and then antibonding orbitals of the $d$ (or $f$ for the actinides) bands.[6] This implies that the lowest volume (highest density) would be found for the actinide metal with the highest number of bonding, and lowest number of antibonding electrons, i.e., for plutonium. Interestingly, from Fig. 2 we note that plutonium shows an additional anomalous behavior, namely, a somewhat *larger* volume than its preceding metal, neptunium ($_{93}$Np).

Intrigued by the complex electronic and crystallographic properties of $\alpha$-Pu we have performed first-principles, total energy calculations of this material over a wide volume range. By comparing the total energy of the $\alpha$ phase with the other structures found in the actinides as well as the structures found for the transition metals we aim to demonstrate that the delocalized 5$f$ states drive the peculiar crystal structure of $\alpha$-Pu. Furthermore we will show that at high pressures the bcc crystal structure becomes the most favorable for $_{94}$Pu. With the total energy dependence of the atomic volume for the eight studied structures we have been able to examine how the crystal structure influences the atomic equilibrium volumes for plutonium and it is our intention to show that the anomalous volume increase between $_{93}$Np and $_{94}$Pu is actually a consequence of the anomalous crystal structure of the $\alpha$ phase. In the following we describe our theoretical method in Sec. II. In Secs. III, IV, and V our results for the crystal structure, occupation numbers, and atomic volume, respectively, are presented and we conclude in Sec. VI.

## II. COMPUTATIONAL DETAILS

The reported results are obtained from electronic structure calculations for plutonium in eight different crystal structures: $\alpha$-Pu, $\alpha$-Np, $\beta$-Np, $\alpha$-U, bct, bcc, fcc, and hcp. The total energy of these structures was calculated as a function of volume. The present *ab initio* method solves the Dirac (for the core electrons) or a (modified) Schrödinger equation (for the valence and semicore). The total energy of the system was obtained within density-functional theory. In the density-functional approach, it is common to make the local density approximation for the exchange and correlation interactions between the electrons. Since the recently presented generalized gradient approximation (GGA) (Ref. 12) has been shown to significantly improve the accuracy of the results for $f$-electron metals,[13] we have chosen to adopt this approximation for the exchange and correlation energy functional in the present calculations. The relativistic effects are included in the Hamiltonian, and the spin-orbit interaction term is considered according to the recipe proposed by Andersen.[14] The wave functions are expanded by means of linear muffin-tin orbitals inside the nonoverlapping muffin-tin spheres that surrounds each atomic site in the crystal. The muffin-tin radius was consistently chosen such that the muffin-tin spheres occupied 41% of the total volume.

We make use of a so-called double basis set since we allow two tails with different kinetic energy for each muffin-tin orbital with a given $l$-quantum number. The calculations were done for one, fully hybridizing, energy panel in which the values for $E_\nu$'s related to the valence orbitals $7s$, $7p$, $6d$, and $5f$, and to the semicore orbitals $6s$ and $6p$ were defined. Within the muffin-tin spheres, the basis set, charge density, and potential were expanded in spherical harmonics with a cutoff $l_{\max}=6$. Outside the muffin-tin spheres, in the interstitial region, the wave functions are Hankel or Neumann functions which are represented by a Fourier series using reciprocal lattice vectors. The same expansion is used to represent the charge density and the potential. This treatment of the wave function, charge density, and potential does not rely upon any geometrical approximations and the described type of computational method is usually referred to as a full potential linear muffin-tin orbital method (FP-LMTO). This so-called full potential method[15] has previously been successfully applied to many systems, including also some of the actinides,[16,17] proving its reliability.

In the calculation of the one-electron band structures the special $k$-point method has been used with various sampling densities of the $k$ points. In the $\alpha$-Pu and $\alpha$-Np structures 16 $k$ points of the irreducible part of the Brillouin zone (IBZ) were used whereas for $\beta$-Np the corresponding number was 18. This may seem to be relatively small numbers of $k$ points in the IBZ for these structures where the IBZ is 1/2, 1/2, and 1/4 of the full Brillouin zone (FBZ) for $\alpha$-Pu, $\alpha$-Np, and $\beta$-Np, respectively. However, an increase of the number of $k$ points to 32 ($\alpha$-Np) and 40 ($\beta$-Np) only lowered the total energy with about 0.1 mRy/atom at the theoretical equilibrium volume. The electronic structure for plutonium in the $\alpha$-U crystal structure (orthorhombic with 2 atoms/cell) was obtained using 100 $k$ points in the IBZ (1/8 of the FBZ). In the case of the more symmetric bcc, fcc, and bct structures the symmetry of the bct unit cell was consistently applied and a total number of 150 $k$ points were used in the IBZ for those (1/16 of the FBZ). For the hexagonal close-packed lattice, which we assumed to have an ideal $c/a$ ratio, we used 162 $k$ points in the IBZ (1/12 of the FBZ). To further investigate the convergence of the $k$-point sampling for the various crystal structures we chose the crystallographic parameters ($c/a$, $b/a$, and positional parameters) for $\alpha$-Np, $\beta$-Np, and bct in such a way that the structures described the bcc geometry. Close to the theoretical equilibrium volume these test calculations showed that the total energy difference between the structures was converged to about 1 mRy/atom.

## III. CRYSTAL STRUCTURES

This section focus on the crystal structures of plutonium at low temperatures and pressures, their origin and influence on the anomalously low equilibrium density exhibited by the plutonium metal. For that reason we have performed total energy calculations for ${}_{94}$Pu in the above mentioned eight crystal structures. As stated above we have chosen these structures since they represent typical structures found in the $d$-transition metals (bcc, fcc, and hcp) or in the actinides [bct ($\alpha$-Pa), $\alpha$-U, $\alpha$-Np, $\beta$-Np, and $\alpha$-Pu]. In order to find the theoretical equilibrium density for plutonium we have minimized the total energy with respect to volume for the mentioned eight crystal structures. The results from these calculations are shown in Fig. 3, where we plot the total energy for the different structures as a function of the atomic volume relative to the bcc total energy, which defines the zero energy level. In agreement with experiment our results confirm that the $\alpha$-Pu structure is the ground-state structure for plutonium. However, it is also interesting to notice that the energy for ${}_{94}$Pu in the $\alpha$-Np structure is very close. Notice in Fig. 3 that the $\alpha$-Pu, $\alpha$-Np, $\beta$-Np, $\alpha$-U, bct, and the bcc structures are all considerably lower in energy than the hcp and fcc structures.

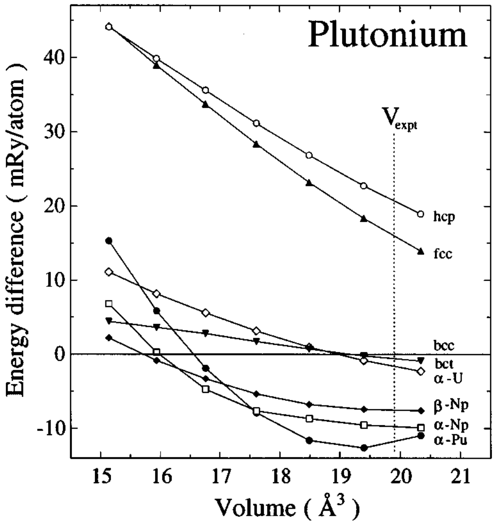

FIG. 3. Total energy for plutonium, calculated in the $\alpha$-Pu, $\alpha$-Np, $\beta$-Np, $\alpha$-U, bct ($c/a=0.85$), hcp (ideal $c/a$), and fcc crystal structures, relative to the bcc structure, as a function of volume.

The finding that among the symmetric structures the bcc phase is energetically similar to the more open structures is quite interesting and deserves attention. First of all however, we note that the energy differences between the fcc, hcp, and bcc structures of the light actinides can be explained in the same way as was done for the transition metals, where the work of Skriver[18] and Duthie and Pettifor[19] showed that the occupation of the $d$ band is the important parameter for the transition metals. By evaluating the band energies for the transition metals, one was able to conclude that the shape of the $d$ density of states ($d$-DOS) in conjunction with the $d$-band occupation determined the crystal structures for those metals. With the same technique as for the $d$-transition metals (using canonical $f$ bands[20]) it has been shown that for $5f$ populations between 3 and 6 (Ref. 17) the bcc structure is lower in energy than the fcc and hcp structures. The reason for this is that for $5f$ occupations in this interval the Fermi level is situated between the two pronounced peaks in the canonical $f$-DOS for the bcc structure. Consequently this structure is very favorable for these $5f$ populations. The light actinides with $5f$ occupations in this interval (${}_{93}$Np$-{}_{94}$Pu, ${}_{92}$U has somewhat less than three $5f$ electrons) could be viewed as counterparts to the nonmagnetic bcc $d$-transition metals Nb, Mo, Ta, and W which all have $d$ occupations such that $E_F$ lies in between the two peaks of the bcc $d$-DOS. Thus, for the light actinides, ${}_{92}$U$-{}_{94}$Pu, canonical band theory[20] can be used to show that the bcc structure is

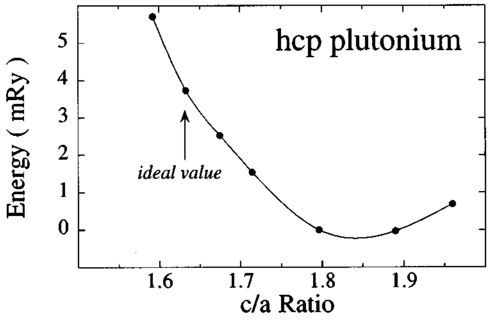

FIG. 4. Relative total energies for the hcp crystal structure of plutonium calculated as a function of the axial ratio $c/a$ at a volume of 18.2 Å$^3$ (i.e., a volume close to the theoretical equilibrium volume).

lower in energy than the fcc and hcp energies, in agreement with Fig. 3 as well as with the calculations of Skriver,[18] although for uranium the bcc and hcp energies are very close. However, this theoretical model is only useful when the comparison is restricted to close-packed (fcc or hcp) or nearly close-packed (bcc) structures.[18] This is because the electrostatic energies are very similar for these structures and can be essentially neglected when the comparison is restricted to these three phases. For other phases this difference in Madelung energy has to be considered explicitly together with overlap repulsion. The Peierls–Jahn-Teller distortion mechanism, favorizes low symmetry structures over high symmetry structures for narrow band systems, and must be considered in the present context. Taking into account both of these arguments it is natural to find crystal structures for uranium, neptunium, and plutonium at low temperatures and pressures that have low symmetry, and can be obtained through a distortion of the bcc parent lattice. For $_{92}$U (Ref. 21) and $_{93}$Np (Ref. 17) it has been shown theoretically that their equilibrium structures, which both for uranium and neptunium can be viewed upon as distorted bcc structures, transform to the bcc structure at sufficiently high pressure. Our present work shows that this also happens for plutonium (Fig. 3) but this prediction has not yet been observed. The basic explanation for the occurrence of the bcc structure in compressed plutonium metal is that a broadening of the $5f$ bands will eventually make the Peierls–Jahn-Teller distortion less important (since less energy can be gained by this mechanism for broader bands) which will favor more symmetric structures.[21]

From the above discussion, that bcc is the most stable of the high symmetry structures of plutonium, it is not surprising to find that this phase becomes the stable one at high pressure. Fig. 3 confirms this picture and the transition to this phase occurs at about 20% compression ($V/V_0 \sim 0.8$). This result is also partially supported by very recent experimental findings for plutonium[22] which show that the metal transforms to a structure with higher symmetry at $V/V_0 \sim 0.8$, which was interpreted as a distorted hcp structure. We note here that the hcp and bcc structures can be viewed as distortions of each other, along the Burgers path.[23] The fact that the low-temperature structures of plutonium sometimes are compared to the hcp structure[22,24] has inspired us to also consider this structure in our calculations. In Fig. 4 we show the calculated total energy of the hcp structure as a function of $c/a$ ratio. Interestingly, a nonideal $c/a$ value ($c/a \sim 1.85$) optimizes the hcp structure. This optimized hcp structure has an energy close to the fcc energy at this volume (18.2 Å $^3$, i.e., close to the theoretical equilibrium volume) and this is in agreement with the hcp calculations by van Ek *et al.*[25] However, this phase is still much higher in energy than, for instance, the bcc energy. At elevated pressures the optimized hcp structure is also much higher in energy than the bcc structure (data not shown). The reason for the large $c/a$ ratio in the hcp structure is interesting, since normally one encounters $c/a$ ratios close to 1.63 (ideal packing). The distortion of the $c/a$ ratio of the hcp structure away from ideal packing is in line with the fact that the hcp and bcc structures are related via a so-called Burgers transformation path.[23] In the Burgers transformation, (1 1 0) planes of the bcc structure are shifted and followed by a Bain strain of the bcc lattice.[26] These displacements lead to a crystal structure with a hcp geometry, but the $c/a$ axial ratio of this hcp structure is larger than the ideal value and therefore, along a Burger transformation, a hcp structure with a $c/a > 1.63$ is closer to the bcc structure. This gives additional information for why a nonideal hcp structure has lower energy than the ideally packed hcp structure since the former structure is closer to the bcc structure which in turn is even lower in energy. We mentioned above that using a canonical band model for the $f$ bands one could argue that for $f$-band occupations between $3-6$, the bcc structure should be favored over the hcp and fcc structure.[17] Hence for metals with $5f$ populations within $3-6$ one should expect a nonideal $c/a$ axial ratio to optimize the hcp structure. Both neptunium and plutonium have $5f$ occupations within this interval, whereas uranium has somewhat less than three $5f$ electrons at ambient conditions. For neptunium the optimized $c/a$ axial ratio was calculated (FP-LMTO) to be larger than the ideal value ($c/a \sim$ 1.75) whereas for uranium the $c/a$ ratio was relatively close to the ideal value ($c/a \sim$ 1.70).[27]

In view of the structural properties of plutonium, discussed above, it is interesting to note (Fig. 5) that the $5f$ DOS for $\alpha$-Pu (upper panel) and bcc Pu (middle panel) are rather similar, with two broad features, one above and one below the Fermi level, whereas the hcp $5f$-DOS (lower panel) and fcc $5f$-DOS (not shown) are somewhat different. For $\alpha$-Pu (upper panel) we show the $5f$-DOS only for one of the 16 atoms of the cell since the difference between the various atoms is not significant for this discussion. The similarity in the $5f$-DOS for the bcc and $\alpha$-Pu structures indicates that $\alpha$-Pu is closer to the bcc structure than, for instance, the hcp or the fcc structures and this supports the arguments outlined above as well as the ones of earlier studies.[17] This observation further explains why many of the structures found in the light actinides ($_{92}$U$-_{94}$Pu in particular) may be viewed upon as distortions of the bcc structure. Our calculated DOS curve for $\alpha$-Pu in Fig. 5 may be compared with x-ray photoemission spectra of the valence band for this material.[28] The calculated DOS curve has a $\sim$ 2 eV (0.15 Ry) broad feature centered at $\sim$ 0.5 eV (0.04 Ry) binding energy. This is in acceptable agreement with the measured spectrum, showing a $\sim$ 2.5 eV broad feature centered at 0.5 eV binding energy.

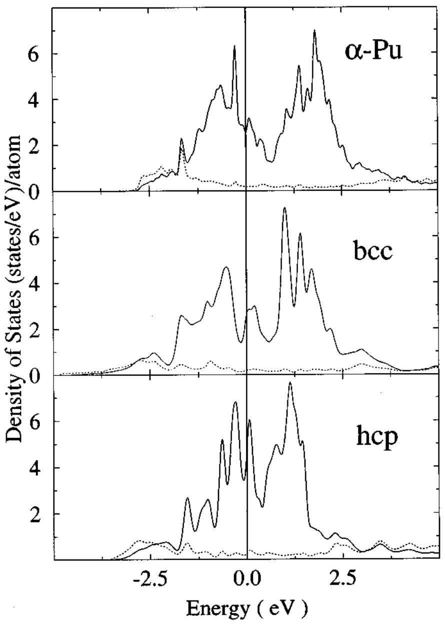

FIG. 5. $5f$ (full line) and $6d$ (dashed line) electron density of states (states/eV/atom) for $\alpha$-Pu (upper panel), bcc Pu (middle panel), and hcp Pu (lower panel) calculated at the experimental room temperature equilibrium volume (Ref. 24). The calculated density of states has here been convoluted with a Gaussian function of width 0.05 eV.

## IV. OCCUPATION NUMBERS

It was recently argued that the reason for the tendency towards open crystal structures in the actinides (and plutonium in particular) is primarily due to an increased population of the $6d$ band, which has a strongly itinerant character.[25] Furthermore it was suggested that the bonding in these structures was *not* dominated by the $5f$ band although the increased $5f$ bonding also encountered in these structures allowed for considerable lowering of the total energy. Here, and in our previous studies,[21] we argue that it is indeed the occupation of the $5f$ bands that is responsible for the open and complex structures in the actinide series. In Table I we present our calculated occupation numbers for plutonium in the eight investigated crystal structures at a volume close to the ($\alpha$-Pu) volume (19.4 Å$^3$). These numbers depend on the choice of muffin-tin radius in our computational method and could therefore not be compared directly with the results presented in the paper by van Ek *et al.*[25] However, a comparison of the population between the different structures (they all have the same muffin-tin radius) is still possible. In agreement with van Ek *et al.* we find that the $d$ occupation is somewhat larger for $\alpha$-Pu compared to the other structures, although the difference between the $\alpha$-Np and the $\alpha$-Pu structures is quite small. Our calculated $s$ occupation, however, is very much independent of the actual crystal structure, in disagreement with the results obtained by van Ek *et al.* Table I further reveals that the $f$ population is slightly enhanced for the most complex structures ($\beta$-Np, $\alpha$-Np, and $\alpha$-Pu). Considering the featureless shape of the $d$-DOS in Fig. 5 we conclude that the small increase in the $d$ population of the $\alpha$-Pu phase compared to the other structures is not the reason that this phase is the most stable. Note also that the bcc and hcp phases have very similar $d$ occupation (Table I) but the bcc total energy is much lower (Fig. 3). This thus illustrates that the occupation number of the $6d$ orbital is not the most important factor determining the chemical bonding and crystal structure of $\alpha$-Pu. Instead we argue, as has been done before,[6,9,10] that it is the $5f$ states which dominate the bonding and as discussed in the previous section it is the shape of the $5f$-DOS, the position of the Fermi level, and finally the electrostatic (Madelung) energy that are the most important factors for the determination of the crystal structure in the actinide materials, including plutonium.

TABLE I. Calculated occupation numbers for plutonium in eight crystal structures at an atomic volume 19.4 Å$^3$ and a 1.24 Å muffin-tin radius.

| Structure | $s$ | $p$ | $d$ | $f$ | Interstitial |
|---|---|---|---|---|---|
| bcc | 2.06 | 5.05 | 0.84 | 4.60 | 3.45 |
| fcc | 2.07 | 5.04 | 0.81 | 4.65 | 3.43 |
| hcp [a] | 2.07 | 5.04 | 0.82 | 4.65 | 3.42 |
| bct | 2.06 | 5.04 | 0.84 | 4.61 | 3.45 |
| $\alpha$-U [a] | 2.05 | 5.05 | 0.84 | 4.64 | 3.42 |
| $\beta$-Np [a] | 2.04 | 5.05 | 0.86 | 4.67 | 3.38 |
| $\alpha$-Np [a] | 2.04 | 5.05 | 0.92 | 4.70 | 3.29 |
| $\alpha$-Pu [a] | 2.02 | 5.02 | 0.98 | 4.74 | 3.24 |

[a] Average value per atom shown.

## V. ATOMIC VOLUMES

Next we analyze the equilibrium volume for plutonium. As mentioned in the introduction (Sec. I), plutonium shows an anomalous volume behavior since it has a *larger* atomic volume than its preceding metal, $_{93}$Np. This anomaly is important since it gives rise to appreciable effects on other properties of $\alpha$-Pu. For instance, it is the main reason for the extremely large thermal expansion of $\alpha$-Pu.[29] Suggested explanations for the upturn of the atomic volume for $_{94}$Pu, relative to the $_{93}$Np volume, are that the $5f$ electrons in plutonium show a tendency towards localization[25,30] (i.e., the $5f$ localization that dramatically lowers the density in americium has to some degree already begun in $_{94}$Pu) or that the relativistic spin-orbit splitting of the $5f$ band gives rise to this behavior. Fully relativistic calculations (based on the Dirac equation and with a spherical approximation for the charge density and potential) for fcc plutonium show that the relativistic spin-orbit coupling leads to a slightly decreased $5f$ bonding for $_{94}$Pu and consequently an increased equilibrium volume.[10] One purpose of the present section is to elaborate on this long-standing issue.

Figure 2 shows the calculated atomic volumes for the fcc and the $\alpha$-Pu structure and we compare them with the calculated equilibrium volumes for the other light actinides (evaluated both in the low-temperature structures as well as in a hypothetical fcc structure). The zero-temperature calculations are corrected for thermal expansion since the experimental data are measured at room temperature.[24] We have done this by means of the experimental thermal expansion coefficient (a correction using the theoretical thermal expansion coefficient[29] gave a very similar result). Notice that $_{94}$Pu in the fcc structure has a considerably lower volume than $_{93}$Np, and hence these isostructural calculations do not reproduce the observed behavior of the atomic volume mentioned in the introduction. This result is in agreement with earlier full potential calculations for plutonium in the fcc crystal structure.[16] The same conclusion can be drawn from calculations based on the $\beta$-Np structure. As is clear from Fig. 2, minimizing the total energy of Np and Pu in the $\beta$-Np structure with respect to volume leads to a larger equilibrium volume of Pu than for Np. However, when the true low temperature structures are considered ($\alpha$-Np and $\alpha$-Pu), the calculations indeed reproduce the experimental observation with an upturn of the atomic volume between these two metals. The reason for this anomaly of the $\alpha$-Pu volume is thus mostly due to its unique crystallographic properties. It has been argued from so-called full charge density calculations (albeit with a spherical potential)[30] that the structural properties of the $\alpha$ phase are not responsible for the rise in volume between $_{93}$Np and $_{94}$Pu. Our present calculations show that the crystal structures, in fact, are decisive for the equilibrium volume and that a consideration of the correct structures indeed reproduce the experimental trend. To exemplify the important influence that the structures have on the equilibrium volumes we observe that the difference in the equilibrium volume between bcc and fcc neptunium is about 7% (Ref. 17) and for plutonium this difference is almost as much as 10% (not shown). In the description of the parabolic trend displayed by the equilibrium volume of the light actinides it seems sufficient to use almost any crystal structure in combination with spherical potentials. However, in order to resolve the smaller features, such as the rise in atomic volume between neptunium and plutonium, the true crystal structure obviously needs to be considered.

We now put our results in context with previous theories attempting to explain the upturn of the $\alpha$-Pu volume. First we note that since we are able to describe accurately the crystal structure and equilibrium volume of plutonium, the electron correlation effects seem to be equally well described by the GGA in $\alpha$-Pu as they are in the other light actinides. The suggestion that the anomalous atomic equilibrium volume is a sign of an onset of localization, or a fingerprint of strong electron correlations,[25,30] not being accurately described by density-functional theory, thus seems less likely. The other argument, that the large volume of $_{94}$Pu is related to the relativistic spin-orbit effect,[10] is more plausible. In fact, we find that by neglecting this interaction in our calculations we obtain a slightly different volume (about 1%, not shown) for $\alpha$-Pu. However, the inclusion of the spin-orbit coupling did not affect the trend of the calculated atomic volumes for the light actinides. The mechanism shown in Ref. 10, that relativistic effects reducing the chemical bonding from the $5f$ shell, are also present in our calculations, thereby expanding the equilibrium volume. However, relativistic effects also influence the semicore states such that the sum of all the effects cause the equilibrium volume of $\alpha$-Pu to be rather insensitive to the treatment of the spin-orbit coupling. However, we find that the detailed electronic structure of for instance the $5f$ band is heavily influenced by the spin-orbit coupling, in agreement with the conclusion made by other researchers.[10,31]

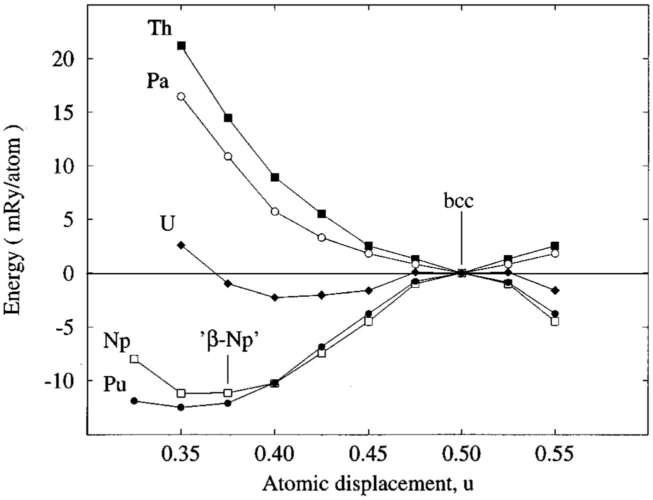

FIG. 6. Calculated total energy as a function of atomic position, $u$, for a crystal structure which is approximately the observed $\beta$-Np structure for $u=0.375$ and the bcc structure for $u=0.50$ (Ref. 17). The calculations are done for the light actinides $_{90}$Th$-_{94}$Pu close to their respective experimental equilibrium volumes and the energies are shifted so that the bcc total energy is equal to zero for each metal.

## VI. CONCLUSION

In summary we have demonstrated that the highly anomalous crystal structure of $\alpha$-Pu is reproduced by accurate density-functional calculations. We conclude that the peculiar crystallographic properties of this material are not a fingerprint of strong electron correlations or quasilocalization of the $5f$ states. We further conclude that the $5f$ band is dominating the bonding in these systems and that the $6d$ band is of less importance for the crystal structure. The spectacular crystallographic properties of this material are instead understood from delocalized $5f$ states, in the same way as for the earlier actinides, with the key ingredient being a Peierls distortion caused by the $5f$ bands. Let us investigate these arguments in some detail by comparing two similar, but yet different crystal structures, namely, the bcc and the $\beta$-Np structure. Both these structures yield low total energies for plutonium, see Fig. 3, but bcc has a very high symmetry as opposed to the $\beta$-Np structure. Nevertheless, they are very similar and an approximate one-parameter path can be defined between these structures.[17] When the parameter $u$ (an atomic position) is equal to 0.5 and 0.375 the structure becomes bcc and approximately $\beta$-Np, respectively. We have calculated the total energy for the light actinides (at their experimental equilibrium volume) for this path and the results are shown in Fig. 6. Notice that for uranium, neptunium, and plutonium the approximate $\beta$-Np structure is lower than the bcc structure which indicates that the Peierls distortion is effective in lowering the energy for these metals. Neptunium and plutonium, in particular, are more stable in the distorted $\beta$-Np type of structure and this follows from the fact that lowering the crystal symmetry results in fewer degenerate $5f$ bands in the vicinity of the highest occupied level. This can be illustrated by comparing the $5f$-DOS for the bcc and ''$\beta$-Np'' structures. In the upper panel of Fig. 7 the $5f$-DOS for the ''$\beta$-Np'' structure is shown and in the

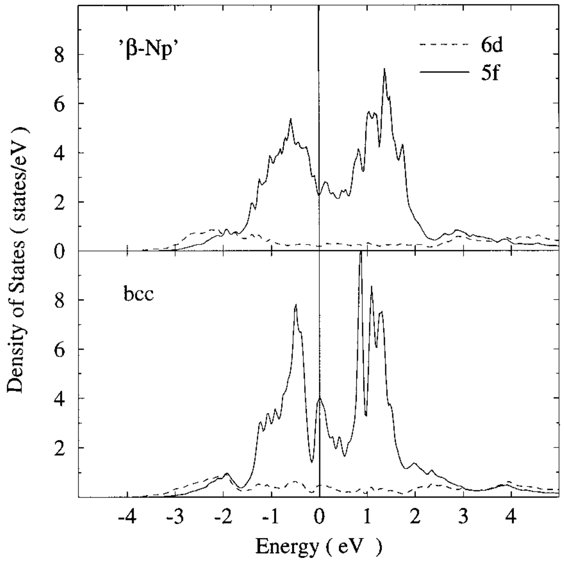

FIG. 7. Calculated $5f$ (full line) and $6d$ (dashed line) electronic density of states for plutonium in an approximate $\beta$-Np structure (upper panel) and in the bcc structure (lower panel). The density of states has here been convoluted with a Gaussian function of width 0.03 eV. Energies are in eV and the vertical line indicates the Fermi level.

lower panel the corresponding DOS for the bcc structure at an atomic volume of 20.4 Å$^3$. Notice that the "$\beta$-Np" $5f$-DOS is relatively low at the Fermi level. For the bcc case, in the lower panel, the $5f$-DOS at $E_F$ is larger and more weight of the DOS is found at higher energies. Furthermore the bcc $5f$-DOS has a peak at about 0.5 eV below the $E_F$, which is much less pronounced in the "$\beta$-Np" $5f$-DOS in the upper panel of Fig. 7. The lowered symmetry for the "$\beta$-Np" structure thus shifts electronic energy states away from $E_F$ to lower energies and consequently the band energy decreases. The $6d$-DOS, on the other hand, is very similar for these two crystal structures, and does not seem to be of any importance for the crystal structure. The results shown in Fig. 6 illustrate that an increased $5f$ occupation drives low symmetry structures. We compare Fig. 6 with Fig. 6 of Ref. 17, where a very similar study was performed for Np at ambient and compressed volumes. Curves of exactly the same shape as in Fig. 6 are found in Fig. 6 of Ref. 17. The reason for this is that compressing neptunium broadens the $5f$ band, reducing the effect of the Peierls–Jahn-Teller distortion. The same reduction is found when depopulating the $5f$ band by going from $_{93}$Np to $_{92}$U, $_{91}$Pa, and $_{90}$Th.

We have also predicted that the high pressure phase of plutonium will attain the bcc crystal structure and this transition is calculated to occur at about a 20% compression of this metal.

Finally, we have shown that the unique crystal structure of plutonium results in an anomalously large equilibrium volume at room temperature, which is larger than for the preceding metal, neptunium. Hence we demonstrate that although many of the ground-state properties of plutonium are anomalous the description of its $\alpha$ phase does not require a special theoretical approach, and that $\alpha$ plutonium is the last actinide metal with a delocalized $5f$ band.

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