Journal of Alloys and Compounds, 213/214 (1994) 268–277
JALCOM 4100

Crystallographic phase transitions in actinide metals as a function of pressure

Olle Eriksson[a], J.M. Wills[b], Per Söderlind[a], Joost Melsen[a], R. Ahuja[a], A.M. Boring[b] and B. Johansson[a]

[a]*Department of Physics, Uppsala University, Box 530, Uppsala (Sweden)*
[b]*Center for Materials Science and Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545 (USA)*

Abstract

We present first-principles calculations of the equilibrium volumes and crystal structures of the light actinides (Th–Pu). The calculated equilibrium volumes for f.c.c. Th, b.c.t. Pu, α-U, and β-Np are found to agree reasonably well with the experimental data, and when comparing the total energies of the b.c.c., f.c.c., b.c.t., α-U, and β-Np structures we obtain the correct crystal structures for all studied systems. Also, the calculated equilibrium volumes for Th–Pu, using a hypothetical f.c.c. structure, have been calculated and it is demonstrated that although spin–orbit coupling is included in these calculations the calculated equilibrium volume of Pu is smaller than for Np, in disagreement with experiment. Moreover, the calculated tetragonal elastic constant, C', is shown to be negative for b.c.c. U, b.c.c. Np, b.c.c. Pu and f.c.c. Pu. Thus, our zero temperature calculations suggest that the b.c.c. structure is unstable for these elements and that f.c.c. Pu is also unstable. This is in conflict with experiment and we are led to the conclusion that temperature effects must be of crucial importance for stabilizing cubic structures in U, Np, and Pu. Further, as a function of decreasing volume we predict a crystal structure sequence f.c.c. → b.c.t. → f.c.c. in Th, a sequence α-U → b.c.t. → b.c.c. in U, and a sequence β-Np → b.c.t. → b.c.c. in Np. Also, a sequence of transitions in Sc as a function of decreasing volume have been calculated, namely h.c.p. → f.c.c. → ω → β-Np → b.c.c.

1. Introduction

During the last two decades research on the light actinides has shown that the 5f electrons in Th–Pu are delocalized [1, 2]. Based upon this picture, many physical and chemical properties have been explained. The present paper is mainly devoted to the equilibrium volumes and the crystal structures and how these two properties can be understood assuming itinerant 5f electron states. Therefore, our introductory discussion of earlier actinide research will be focused on work concerning structures and volumes. As an example of this we mention the results of Skriver and coworkers [2] who demonstrated that the equilibrium volumes of the light actinides were well reproduced by first-principles calculations which assumed a hypothetical f.c.c. structure. Especially, the parabolic trend of the volumes as the series is traversed was very well reproduced by the calculations. This trend is in accord with the simple Friedel model for delocalized electron [3]. However, since the light actinides have a less than half-filled f shell it is the bonding orbitals which are filled and therefore one would expect the volumes to be strictly decreasing (parabolically) when moving towards the heavier elements. Interestingly, Pu shows an exception to this expectation since its volume is larger than the volume of Np. Skriver *et al.* [2] found that the disagreement between the scalar-relativistic calculations and experiment was largest for Pu, and later work by Brooks [4] showed that by performing fully relativistic calculations, solving the Dirac equation for the crystal, the increased volume of Pu compared with Np was reproduced and the agreement between experimental and calculated volumes was good. It was thus suggested that the increased volume in Pu relative to Np was due to the relativistic spin–orbit effect [4, 5]. We will discuss some of our own subsequent efforts concerning this question below.

The low temperature crystal structures of these elements are even more puzzling; Th crystallizes in the f.c.c. structure, Pa in the b.c.t. structure, U in an orthorhombic structure with two atoms per cell, Np in an orthorhombic structure with eight atoms per cell, and finally Pu in a monoclinic structure with 16 atoms per cell. Thus, as one moves across the series the structures become less symmetric and more open, an effect we will discuss below. Also, by applying an external pressure on Th it was demonstrated that the b.c.t.

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SSDI 0925-8388(94)04100-I

structure was stabilized [6]. This complex behaviour of the crystal structures has motivated us to investigate this property for the series of elements Th–Np, both at ambient conditions as well as at compressed volumes, by means of total energy calculations using a potential of a general shape (the structure of Pu is still too complex to allow for a theoretical calculation using the present technique). Very few all-electron, total energy calculations aimed at extracting energy differences between various structures for the actinides have been presented. However, Skriver considered the stability of the f.c.c. and b.c.c. structures for the light actinides [7] and found that Th correctly favours the f.c.c. structure whereas Pa, U, Np and Pu have a lower energy in the b.c.c. structure. Also, the electronic structures of α-U [8], α-Np [9] and β-Np [9], as well as of α-Pu [10], have been calculated.

With increasing temperature the light actinides undergo structural phase transformations and finally, before melting, they attain the b.c.c. structure [11, 12]. The elastic constants for these allotropes have been measured and we will report on our attempts to calculate the tetragonal shear constant, C', for b.c.c. U, b.c.c. Np, b.c.c. Pu and f.c.c. Pu by means of our zero temperature calculations. Similar studies for the transition metals have given successful results [13] and it is of interest to see if this description also works for f electron systems.

In contrast to the complicated crystal structures found for the light actinides the transition metals display the well known structural sequence h.c.p. → b.c.c. → h.c.p. → f.c.c. as the 4d and 5d series are traversed. There are very few exceptions to this well understood behaviour. However, the occurrence of the ω-structure in Ti, Zr, and Hf at elevated pressures is one exception. Another exception is the experimental observation of a β-Np structure found in Sc at compression [14]. The β-Np structure is orthorhombic and has four atoms per cell and is found in Np in the temperature interval 278–540 K [15]. Both the β-Np and α-Np structure can be looked upon as heavy distortions of the b.c.c. structure [15]. The discovery that this structure is stable for a d transition element is interesting and seems most anomalous since this is a type of structure which has only been found for f electron systems. This has motivated us to investigate the stability of this structure compared with the stability of the h.c.p. and b.c.c. structure of Sc as a function of volume.

The rest of this paper is organized as follows. In section 2 we describe the details of the calculations and in section 3 we discuss our results for the equilibrium volumes. Results on the crystal structures are discussed in section 4 and in section 5 we present our calculations for Sc. Finally section 6 contains concluding remarks.

2. Details of the calculations

The self-consistent, fully relativistic calculations were performed, using a full-potential linear muffin-tin orbital scheme [16]. The local density approximation (LDA) was used, with the Hedin–Lundqvist density functional for the exchange-correlation potential. The basis set of wave-functions for the valence electrons comprised 6s, 6p, 7s, 7p, 6d and 5f partial waves. The tails of the basis functions are linear combinations of Hankel and Neumann functions with nonzero kinetic energy [17, 18]. We used two sets of energy parameters, one with energies appropriate for the valence band states and the other appropriate for the semi-core states. Integration over the Brillouin zone was done using a 'special-point' sampling [19].

As mentioned above, we performed total energy calculations in order to obtain the equilibrium volume assuming a hypothetical f.c.c. structure for Th–Pu. Also, the b.c.c., f.c.c., b.c.t. and α-U structures were considered for Th, Pa and U in an investigation of the structural stabilities. For Np we performed calculations for the b.c.c., f.c.c., b.c.t. and the β-Np structure. The more complex structure of α-Np is computationally too cumbersome at present and therefore we use the β-Np structure as a representative of the low temperature phase of Np. For the f.c.c. structure we used 60 points of the irreducible part of the Brillouin zone, for the b.c.c. structure 59 points, for the b.c.t. structure 80 points, for the α-U structure 16 points, and finally for the β-Np structure 18 points.

In addition we have performed calculations of the tetragonal elastic constant, C', for b.c.c. U, b.c.c. Np, b.c.c. Pu and f.c.c. Pu. These calculations required many more k-points and to be specific we used 150 points for the b.c.c. structure and 275 points for the f.c.c. structure.

3. Equilibrium volumes

In Fig. 1 we display our calculated equilibrium volumes for Th–Pu using a hypothetical f.c.c. structure. Notice that the f.c.c. volumes display a parabolic trend in agreement with the results of Skriver *et al.* [2]. Our present calculations incorporate relativistic terms such as the mass velocity term, the Darwin shift, and the spin–orbit coupling. Despite our inclusion of the relativistic spin–orbit coupling we do not obtain an increased volume for Pu compared with Np. This is in disagreement with the results of Brooks [4] as well as with experiment. Although our failure to obtain a larger volume for Pu than for Np might be due to our implementation of the relativistic effects (we did not solve the Dirac equation but diagonalized the relativistic

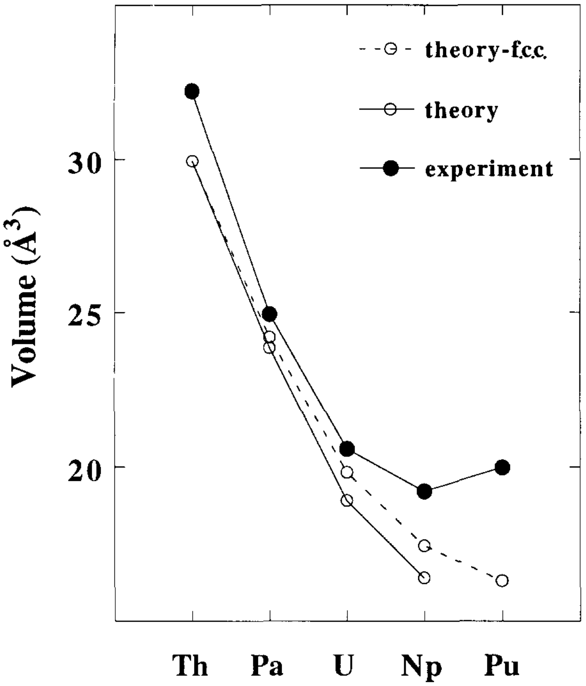

Fig. 1. Calculated and experimental data for the equilibrium volumes of the light actinides. The calculated data were obtained from both the low temperature structures (–o–) and from a hypothetical f.c.c. structure (– –o– –).

Hamiltonian using an 1,s basis [17, 20], we speculate that the reason for the unusual volume of Pu is due to the openness and low symmetry of its structure. Another explanation for this may be that the LDA introduces these errors in Pu and that a gradient correction to the exchange-correlation potential will improve the theoretical volume. In Fig. 1 we also show the calculated equilibrium volumes for b.c.t. Pa, α-U and β-Np. It should be noticed here that the volumes of these low temperature structures differ by as much as approx. 2–6% from the f.c.c. volumes. Furthermore, the agreement between the experimental and theoretical volumes is about 5–15%, which is comparable with or slightly worse than the corresponding agreement found for d electron elements. Also, the agreement between experiment and theory is not worse for Pa or U than for Th, and from this comparison it seems that LDA calculations work as well for d electron systems as for f electron systems. However, the calculated volume of β-Np shows the largest deviation from the experimental value. Before any conclusions can be drawn about the accuracy of LDA calculations for the actinide metals it is desirable to study the low temperature phase of Np and Pu, namely α-Np and α-Pu. Two interesting questions can be answered by doing this. Is the upturn between Np and Pu reproduced by such calculations? And does the calculated equilibrium volume reproduce experiment for Np and Pu with the same accuracy as for Th? If this is the case one can conclude that LDA calculations work for f electron elements with approximately the same accuracy as for d electron elements. Such studies are planned.

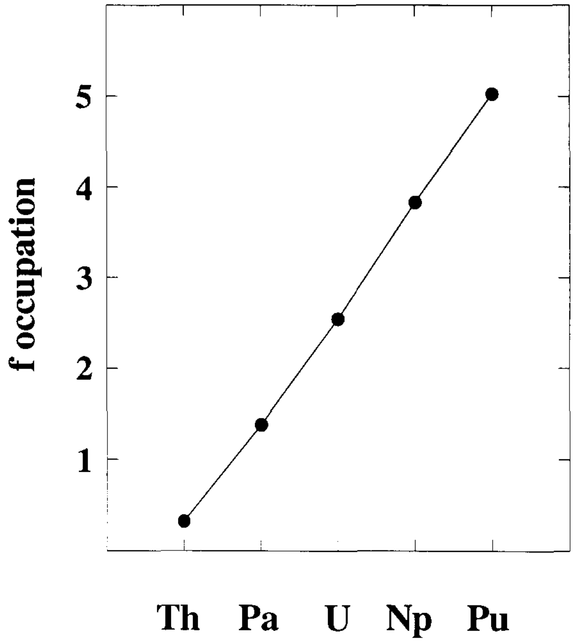

Fig. 2. Calculated f occupation number for the f.c.c. structure.

In Fig. 2 we display the calculated f occupation for Th–Pu in the f.c.c. structure. Two features should be observed. First, the increase of the f orbital occupation is almost linear with increasing nuclear charge, in agreement with previous results [2, 4]. From this linear increase one can easily explain the parabolic volumes using the Friedel model [3]. Second, the stabilization of more open, low symmetry structures seems to be correlated with the filling of the f orbital. We will elaborate more on this in the next section.

4. Crystal structures

In Fig. 3 we display the energy differences between the b.c.c., f.c.c., b.c.t. and α-U structure for Th, Pa and U. Results for Np are also shown but for Np the α-U structure is replaced by the β-Np structure. For the b.c.t. structure we optimized the *c*/*a* ratio for two of the elements, namely Pa and Np. The *c*/*a* ratios obtained were 0.814 for Pa and 0.856 for Np. The experimental value for Pa is 0.83. Since the two calculated values are quite close we did not optimize the *c*/*a* ratio for Th and U but used the experimental *c*/*a* value for Pa, *i.e.* 0.83. Notice in Fig. 3 that for all four elements we obtain the correct crystal structure. Also, it may be observed that the low symmetry structures (α-U, β-Np and the b.c.t. structure) start out being higher in energy for Th but that with increasing f

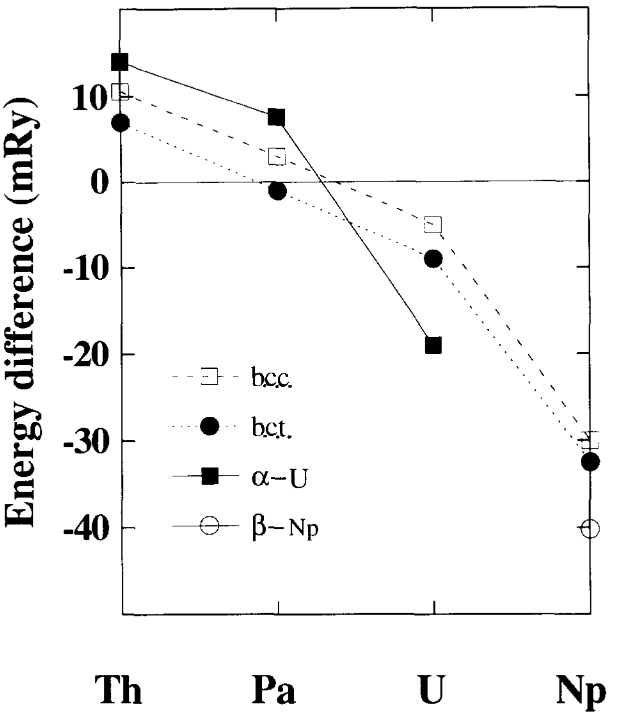

Fig. 3. Energy differences between the f.c.c., b.c.c., b.c.t. and α-U structure for Th–U. For Np the α-U structure is replaced by the β-Np structure. The f.c.c. structure is the reference line and is set equal to zero.

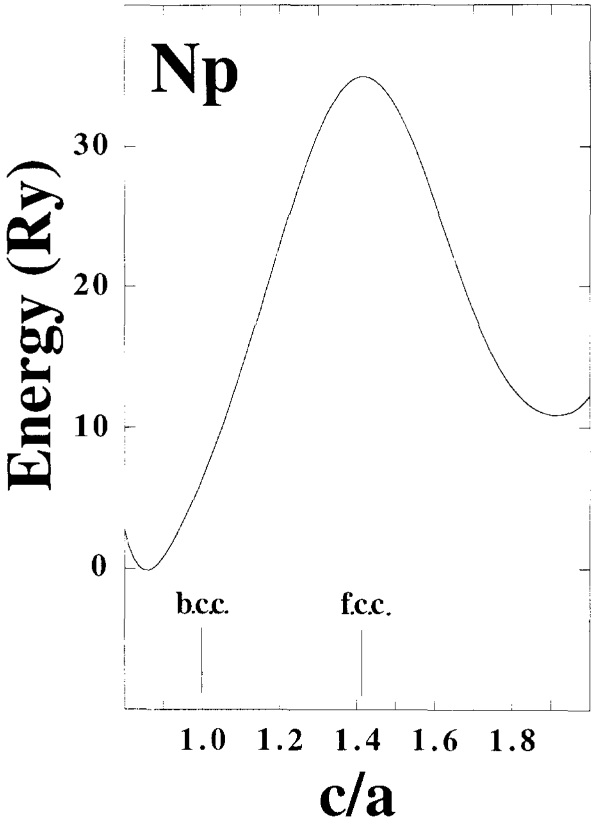

Fig. 4. Calculated Bains path for Np.

occupation (traversing the series) they become lower in energy. The trend of the crystal structures, namely that the observed structures gradually become more open and less symmetric as the actinide series is traversed, is thus correlated with the gradual filling of the f orbital (see also Fig. 2).

For Np we performed an additional analysis of the b.c.t. crystal structure and calculated the energy as a function of the c/a ratio using values between 0.8 and 2.0 (Fig. 4). We thus investigated the energies along what is normally referred to as the Bains path [21]. In Fig. 4 it is clear that we obtain two energy mimina, one at 1.915 and one at 0.856. The minimum at 0.856 has the lowest energy. The occurrence of two mimima of the Bains path at c/a of approx. 0.82 and approx. 1.8 is interesting, since it is known that f electron systems which crystallize in the b.c.t. structure have c/a ratios which are close to these two widely different values. For instance the c/a ratios of b.c.t.-Ce, b.c.t.-Th and b.c.t.-Sm are close to 1.8 whereas the c/a ratio of Pa is 0.83. Skriver performed a similar analysis on Ce, Th, and Pa and obtained very similar results [7]. It is also interesting that at zero temperature both f.c.c. and b.c.c. Np are mechanically unstable, since in Fig. 3 there is not even a local minimum of the energy curve around $c/a = 1$ (= b.c.c. structure) or around $c/a = \sqrt{2}$ (= f.c.c. structure), whereas experimentally it is observed that at elevated temperatures the b.c.c. structure becomes stable. This will be discussed further below.

The reason for finding open, low symmetry structures in these elements thus seems to be correlated with the increased f electron population (as was suggested by Hill [22] and also by Skriver [7]) and the importance of the f orbitals for favouring these structures can be checked in our calculations by omitting the 5f states from the basis set. Such a calculation on for instance uranium yields the α-U structure as unstable, in disagreement with experiment, and only when including itinerant 5f states do we obtain the correct crystal structure of uranium. In this connection it is interesting to observe that the crystal structure of Th (f.c.c.) is also anomalous. Th has four valence electrons and if Th was a pure d electron material one would expect its crystallographic properties to resemble the isoelectronic transition metals, namely Ti, Zr and Hf, which are all h.c.p. In order to investigate this possibility we have calculated the total energy of Th using only s, p and d partial waves while omitting the f states. At the equilibrium volume we find that the b.c.c. structure is stable and not the expected h.c.p. structure. On closer inspection this is actually in good agreement with the isoelectronic metals Ti, Zr and Hf since these elements have a crystallographic sequence h.c.p. → ω → b.c.c. with increasing pressure. This has previously been demonstrated to be caused by an s → d transfer [23]. Owing to the large core in Th the d occupation is sufficiently large to stabilize the b.c.c. structure. However, by increasing the volume one can lower the d occupation and correspondingly one would expect first the ω structure and then the h.c.p. structure. In Fig. 5 we show the energy difference between the b.c.c., h.c.p. and ω structure, and the expected behaviour is found. Thus, starting from low d occupation (large volumes) the crystal structure is h.c.p., just as in Ti, Zr and Hf at ambient conditions. By increasing the d occupation (*i.e.* by lowering the volume) we obtain the same crystallographic sequence in Th as in Ti, Zr and Hf, *i.e.* h.c.p. → ω → b.c.c. Even though the f occupation found in Th is relatively small (see Fig. 2), it has a quite dramatic consequence for the crystal structure since the f.c.c. structure is then stabilized and is approx. 10 mRy lower in energy than the b.c.c. structure (see Fig. 3). Thus, we can claim that the innocent-looking f.c.c. phase in Th is in fact an anomaly and its existence provides strong evidence of itinerant f electrons.

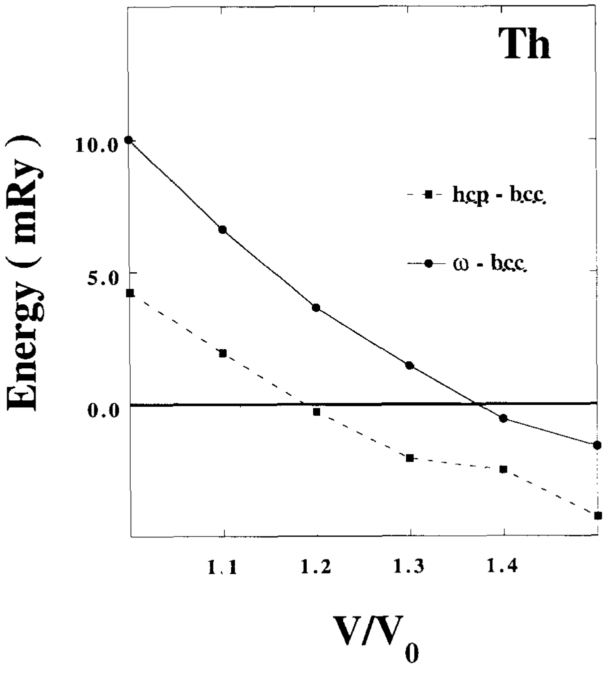

Fig. 5. Calculated energy differences between h.c.p., b.c.c. and the ω-structure for Th, as a function of volume. The b.c.c. structure is the reference level and is set equal to zero. V_0 is the experimental equilibrium volume.

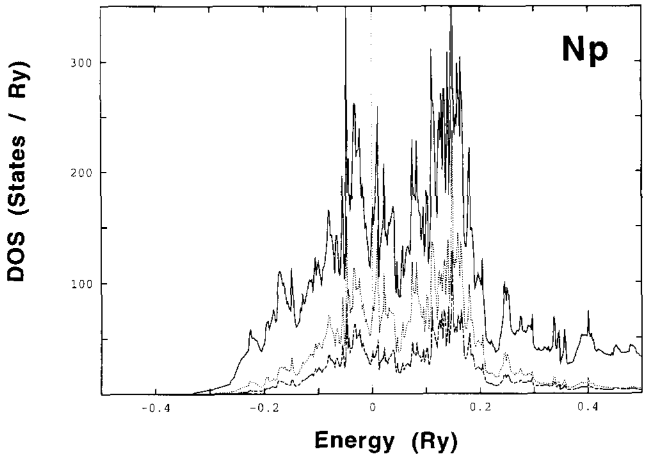

Fig. 6. Density of states (DOS) for β-Np. Energies are in rydbergs and the Fermi level is at zero energy and is marked by a dotted line. ——, Total DOS; – – –, · · ·, f-projected DOS for the two different atom types.

We now proceed with a short discussion on the electronic structure and electron density distribution of β-Np, since this structure has not been considered before with the present technique. Thus in Fig. 6 we show the 5f partial and total density of states (DOS) of β-Np at a volume close to the experimental volume. Notice that since there are two atom types in β-Np we display two 5f partial DOS for the two different atom types. For illustrative purposes we have multiplied one of the two partial DOS by 2 in order to distinguish them better. The conclusion we draw from Fig. 6 is that the two partial DOS have very similar shape and that the total DOS is dominated by the 5f contribution, as would be expected from comparison with earlier work [9]. Also, the main peak of the occupied part of the DOS is not at the Fermi level but is situated about 0.1 Ry below. This finding was earlier reported by Boring *et al.* [9] and as a matter of fact our calculated DOS agrees well with the previous LMTO-ASA (atomic sphere approximation) calculation of Boring and coworkers [9]. It is interesting that from this point of view the ASA works well, despite the open nature of the β-Np structure. Next we display in Fig. 7 the electron density distribution for β-Np, for a cut in the *xy*-plane (Fig. 7(a)) and in the *xz*-plane (Fig. 7(b)). Notice that there is a considerable amount of charge piling up between atoms and that this charge density has a lot of structure in the interstitial region. This behaviour is drastically different from that found for standard close-packed systems where the interstitial charge is almost constant and without structure. The bonding of β-Np therefore seems to be much more covalent than that found in close-packed structures. A similar behaviour has been reported for α-U [24]. Also, the electron density displayed in Fig. 7(b) suggests that this structure is of a layered type since there is a region between layers where the electron density is very low.

We will now discuss the high temperature b.c.c. structure in U, Np and Pu as well as the f.c.c. structure of δ-Pu. The aim of this part of our study was to

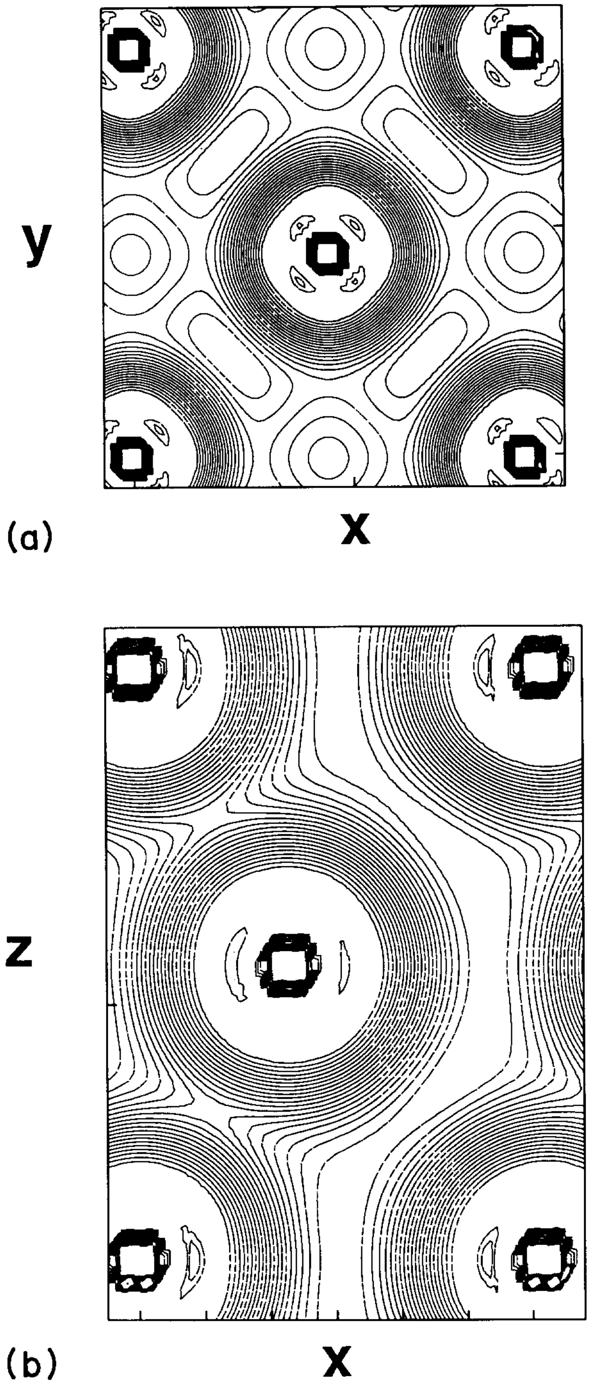

Fig. 7. Electron density for β-Np for a cut in (a) the xy-plane and (b) the xz-plane.

investigate the elastic constants of these phases by means of zero temperature calculations. In Table 1 we display our calculated tetragonal elastic constant, C'. Notice that for all four systems we calculate C' to be negative. This means that the crystal is mechanically unstable in that phase. This is in disagreement with the experimental observation of the existence of these structures and we conclude that the stabilization of b.c.c. U, b.c.c. Np, b.c.c. Pu and f.c.c. Pu at these volumes must originate from a crucial thermal contribution. It should be noted here that in this investigation we have treated the 5f electrons as paramagnetic and itinerant. The results presented above also suggest that the diffusion properties of these phases should show unusual behaviour.

TABLE 1. Calculated elastic constants for b.c.c. U, b.c.c. Np, b.c.c. Pu and f.c.c. Pu

	C' (kbar)
b.c.c. U	−600
b.c.c. Np	−346
b.c.c. Pu	−720
f.c.c. Pu	−480

We end this section with a discussion of the crystal structure stabilities of these elements as a function of compression. As mentioned above, experimental work shows that Th undergoes an f.c.c.→b.c.t. structural phase transition [6]. In Ref. 6 it was also mentioned that similar transitions might occur in other actinides. We have studied this theoretically by means of total energy calculations and have compared the total energy of the b.c.c., f.c.c., b.c.t. and α-U structures of Th, Pa and U as a function of compression, as well as the total energy of the f.c.c., b.c.c., b.c.t. and β-Np structures of Np as a function of compression. The energy differences between these structures are displayed in Figs. 8(a) (Th), 8(b) (Pa), 8(c) (U) and 8(d) (Np). As mentioned above we obtain the correct low temperature crystal structures for all four elements. Furthermore, we observe that Th undergoes a phase transition from f.c.c.→b.c.t. at 16.9 Å^3 and 1.1 Mbar, in acceptable agreement with the experimental data for Th [6]. However, our calculations also predict a second transition from b.c.t. back to f.c.c. at even higher pressures and this second transition has not yet been observed. For U our calculations predict a sequence of transitions α-U→b.c.t.→b.c.c. with decreasing volume. Also for Np we predict a sequence of crystallographic phase transitions, namely β-Np→b.c.t.→b.c.c. as the volume decreases and the pressure increases.

The reason for stabilizing symmetric, close-packed structures in itinerant f electron systems has been discussed before [25] and is also elaborated upon in a parallel paper presented at this conference [26]. As demonstrated in Ref. 25, the crystal structures of the actinides can be understood as a Peierls distortion due to the narrow f states which are situated close to the Fermi level. However, if the volume is reduced and therefore the bandwidth is increased this effect becomes less important whereas the Madelung contribution to the energy will become increasingly important. This

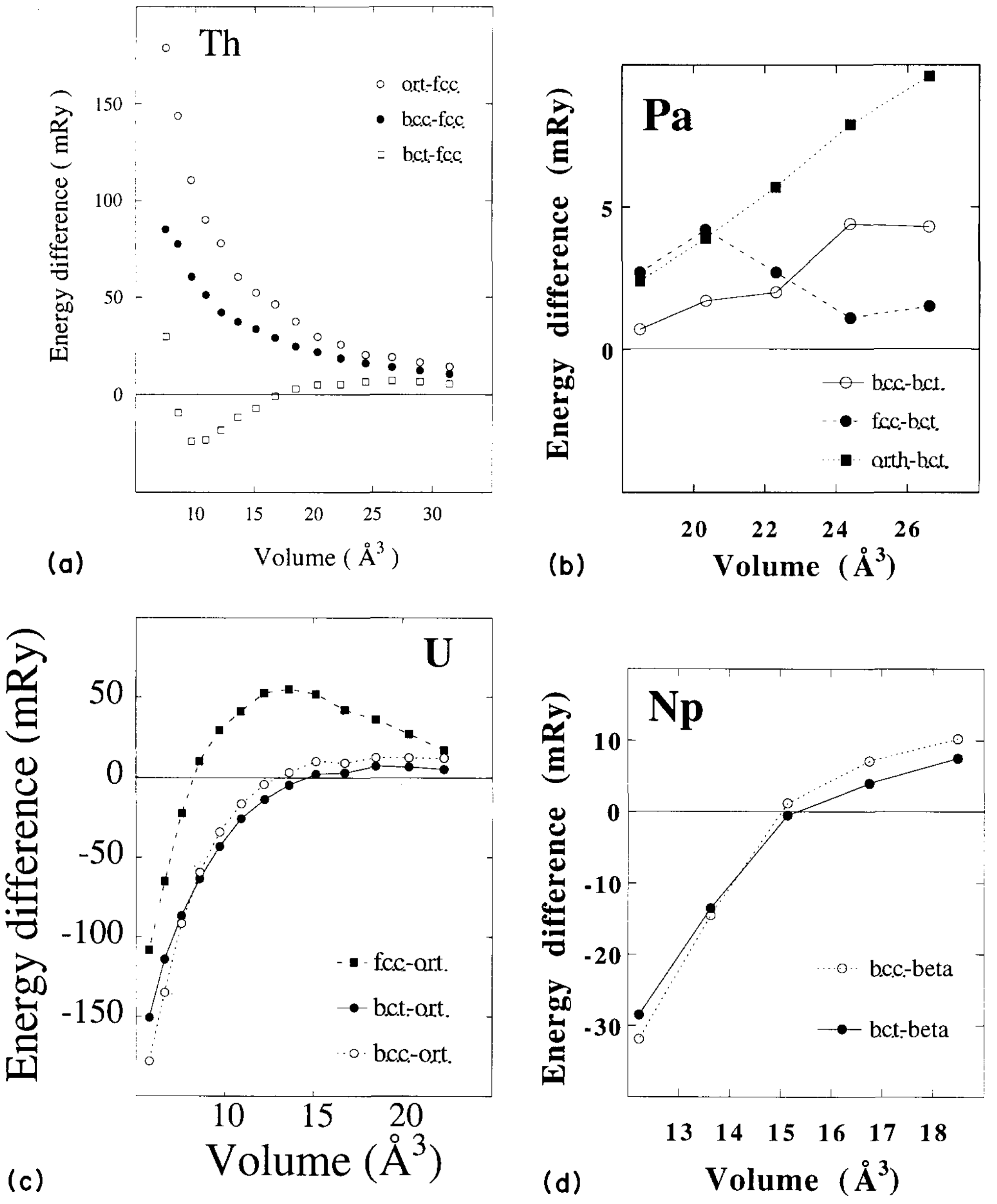

Fig. 8. Energy difference between f.c.c., b.c.c., b.c.t. and the α-U structure for (a) Th, (b) Pa and (c) U. The experimental structure is used as a reference level for each element and is set equal to zero. For Np (d) the α-U structure is replaced by the β-Np structure.

latter term stabilizes close-packed, symmetric structures. The onset of closer-packed structures of the actinides as a function of increasing bandwidth (decreasing volume) can thus be understood from the decreasing tendency of the narrow bands to give rise to open structures and the increasing importance of the Madelung energy to favour close-packed structures. In agreement with this argument our results show transitions with a gradual increase of the packing ratio and a gradual increase of the crystal symmetry, namely first from α-U (or β-Np) to b.c.t. and then to b.c.c.

5. Scandium under compression

In view of the discussion above, the occurrence of the β-Np structure (or a related structure) in Sc at elevated pressure is very interesting. Sc is the first 3d transition metal and it is often referred to as belonging to the rare earth elements, since it shows strong similarities to Y and La. Its ground state crystal structure is h.c.p. As mentioned above, under compression it has been measured to exhibit a primitive tetragonal (p.t.) structure with four atoms per cell, a structure very similar to the β-Np structure [27]. This is a most unexpected behaviour since transition metals normally display the f.c.c., b.c.c., or h.c.p. structure, depending on pressure or temperature. This has motivated us to investigate the total energies of Sc in the b.c.c., f.c.c., h.c.p., p.t., and in the ω-structure ($c/a = 0.61$).

In our calculations the h.c.p. structure is correctly found to be stable at the equilibrium volume. We also optimized the energy of the h.c.p. structure with respect to the c/a ratio and obtained a minimum for $c/a = 1.56$, in fair agreement with the experimental value of $c/a = 1.594$. Moreover, the equilibrium volume is found to be 22.6 Å^3, *i.e.* about 10% too small in comparison with the experimental volume, which is a typical accuracy for the LDA. We now turn to the crystal structure stabilities and to begin with we optimized the c/a ratio as well as the positional parameter, u, of the p.t. structure. This was done at the experimental transition volume for the p.t. structure, *i.e.* at 17.4 Å^3. The c/a ratio was varied between 0.5 and 1.4, whereas the u parameter was varied between 0.25 and 0.5. The lowest energy was found for $c/a = 0.61$ and $u = 0.39$ and these values were then used for calculating the total energy of the p.t. structure at other volumes. As an example of this optimization we display in Fig. 9 the calculated energy as a function of the c/a ratio, holding u fixed at 0.39. The minimum energy at $c/a = 0.61$ is clearly observed. In Fig. 10 we compare the energies of the b.c.c., f.c.c., h.c.p., ω-, and p.t. structures as a function of volume. Notice that we first find a transition to the f.c.c. structure at $V = 18.9$ Å^3, corresponding to about 24% of the equilibrium volume. Further, in the volume range of about 16.6 to 12.5 Å^3, the ω-phase stabilizes, which then transforms into the β-Np-like structure. This structure finally transforms into the b.c.c. structure at approx. 6.8 Å^3. This agrees fairly well with the experimental observation of a h.c.p.→p.t. transition at about 17–18 Å^3. The experimental investigation did not cover the volume range which according to our calculations would stabilize the b.c.c. structure and we hope that our results will stimulate experimental work. Also, there are no experimental indications of an f.c.c. or ω-structure. This might be due to the fact that our calculations are at zero temperature while the experiments were done at room temperature. We also note that for these volumes the calculated energy difference between the h.c.p. and the f.c.c. or ω-structure is quite low.

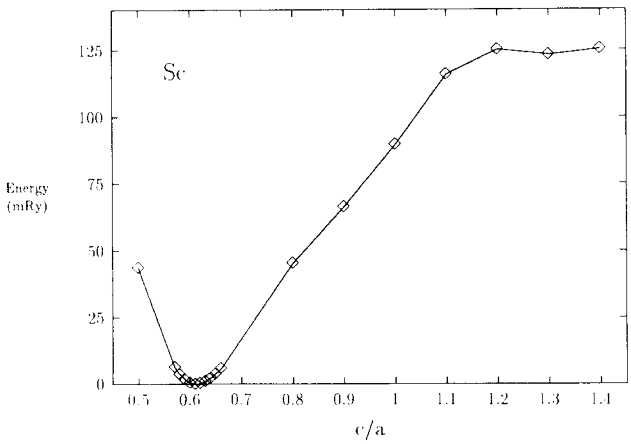

Fig. 9. Total energy of Sc in the β-Np structure as a function of the c/a ratio. The positional parameter u was kept fixed at 0.39.

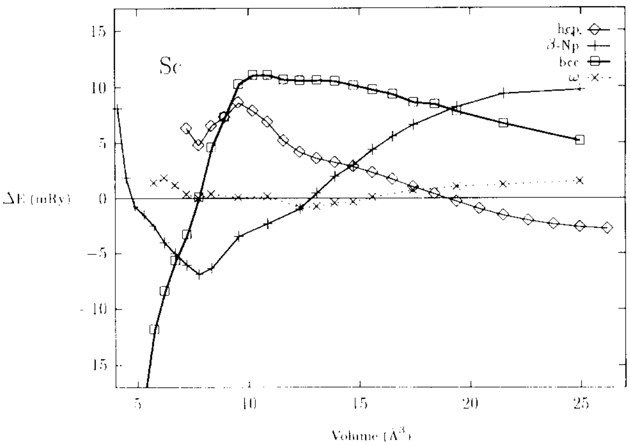

Fig. 10. Energy differences between the b.c.c., f.c.c., h.c.p., ω- and β-Np structures for Sc as a function of volume. The f.c.c. energy is the reference level and is set equal to zero.

We will now elaborate further on the stabilization of the β-Np structure in Sc. The densities of state for the b.c.c. and p.t. structure at 25.0 Å^3 and 7.8 Å^3 have therefore been given in Figs. 11(a) and 11(b) respectively. Notice first that at the lower volume the d partial DOS is broader in the p.t. structure than in the b.c.c. structure. Furthermore, the shape of the b.c.c. DOS is approximately the same for the two volumes, with the characteristic splitting into an e_g and t_{2g} peak. In contrast to this, the DOS of the p.t. structure is modified quite dramatically when the volume is lowered. We especially note that at the compressed volume the p.t. DOS is characterized by a dominating peak at 0.15 Ry below E_F, which is not the case for the DOS at the larger volume. This strong modification of the DOS as a function of volume is normally not found in d electron systems and therefore appears to be a quite unique effect. The DOS of Sc at low volume shows similarities to the DOS of β-Np (Fig. 6) which also has a dominating peak at lower energies. Clearly these peaks will cause the one-electron contribution to the total energy to favour the β-Np structure and the occurrence of the p.t. structure in Sc and Np can be understood from the shape of their DOS. This happens to take place for two systems which are quite different; the electronic structure of Np is dominated by f electrons whereas Sc is dominated by d electrons. Hence it seems that

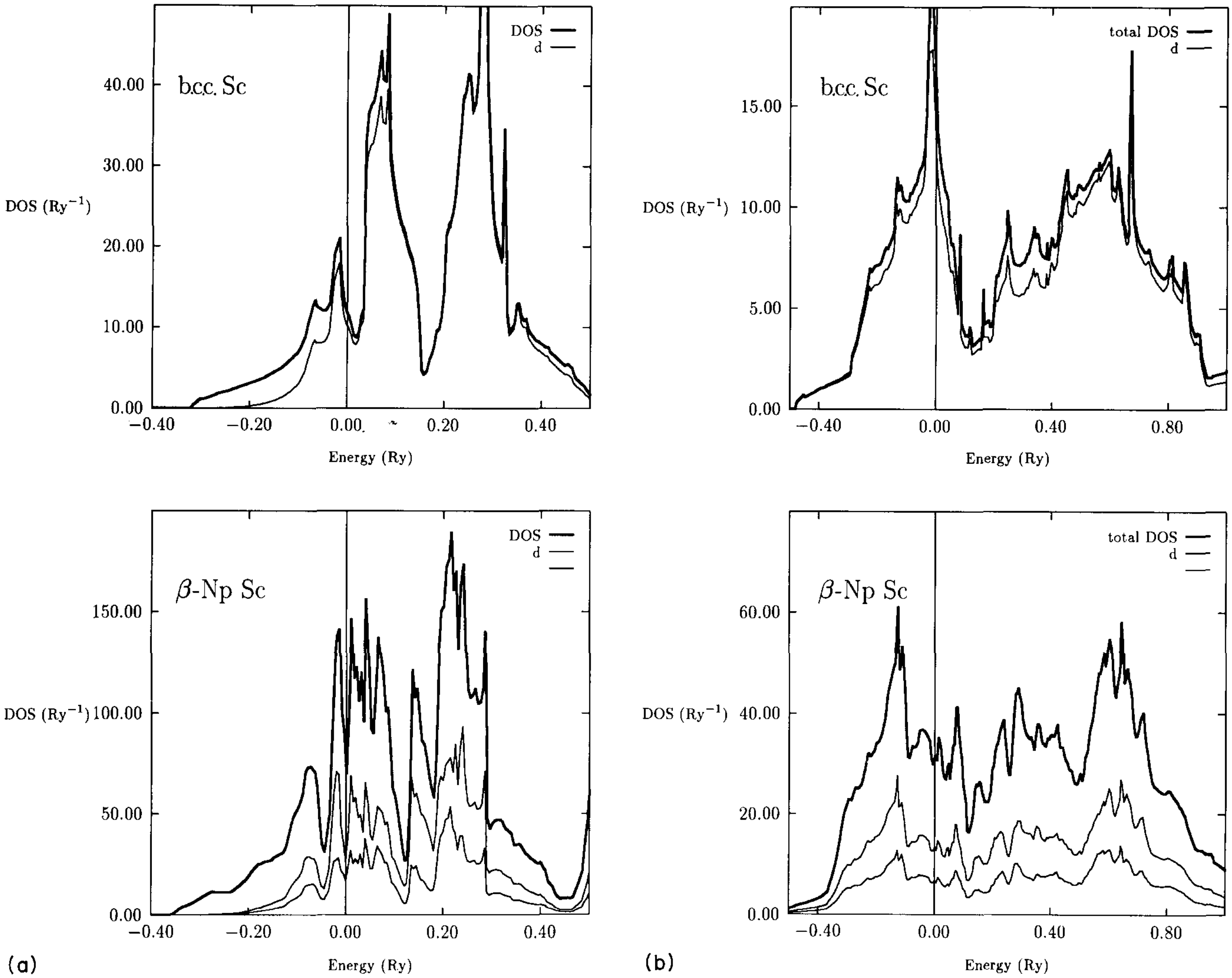

Fig. 11. Density of states for Sc in the b.c.c. and p.t. structures at (a) 25.0 Å^3 and (b) 7.8 Å^3. Energies are in rydbergs and the Fermi level is at zero energy and is marked with a vertical line.

the presence of f electrons is no prerequisite for the appearance of ‘exotic’ structures. The wide range of ‘exotic’ structures of p-bonded systems is another manifestation of this.

6. Conclusions

Above we have given examples of crystallographic phase transitions in both f and d electron materials and showed that both close-packed and open structures can be found in either type of system depending on the external boundary conditions. Various contributions to the total energy of a system have been shown to become increasingly or decreasingly important when the volume is increased or decreased. Let us now collect the main conclusions concerning the stabilization of open versus close-packed structures which can be drawn from our investigation. We start by listing the interactions which tend to stabilize the two types of structures.

Open structures:
- Peierls distortion
- Modification of the shape of the DOS
- Modification of the width of the DOS.

Close-packed structures:
- Madelung energy
- Modification of the shape of the DOS
- Modification of the width of the DOS.

The change in crystal structure of, for instance, U as a function of decreasing volume is an instance where the Madelung energy gradually increases in strength whereas the Peierls distortion effect becomes less important due to a broadening of the bands. Sc is an example of a different type since here the shape of the DOS of the p.t. structure is drastically modified when the volume is changed. This type of change is more unexpected and seems hard to predict and one has to perform energy band calculations in order to discover it. Furthermore, a distorted structure can sometimes give rise to broader bands than a symmetric structure since the atomic overlap between the nearest neighbours is increasing. However, when the crystal distorts each atom will have a reduced number of nearest neighbours and this will tend to narrow the bands. Therefore, one has to perform an energy band structure calculation in order to see which effect is dominating. The DOS of p.t. Sc at low volumes (Fig. 11(b)) is an instance where the effect of the increased overlap is stronger than the effect of the reduced coordination and the resulting DOS is therefore broadened.

Some of the above-mentioned effects are hard to predict without performing total energy calculations whereas some other effects are easier. For instance, the trend of the crystal structures shown by Th–Np leads us to speculate that even Pu and Ce will stabilize in close-packed (or rather close-packed, b.c.c.) structures if the volume is sufficiently low. Moreover, it seems plausible to expect a p.t. structure also in Y at high compression and we are currently investigating this.

Concerning the ground state properties at ambient conditions we have shown that our zero temperature calculations for Th–Np reproduce the experimental data for the crystal structures. The equilibrium volumes found for these systems are in reasonable agreement with experimental data. The worst agreement is found for Np but it should be observed that for this element we did not use the correct low temperature structure in the calculations but instead the β-Np structure. Moreover, our calculations of the equilibrium volumes, where we used a hypothetical f.c.c. structure throughout the series, do not reproduce the experimental finding that the volume of Pu is larger than for Np. We propose that this behaviour might be due to the unusual structures of α-Np and α-Pu.

Finally, zero temperature calculations of the tetragonal elastic constant for b.c.c. U, b.c.c. Np, b.c.c. Pu and f.c.c. Pu yield negative values and thus show that these allotropes are mechanically unstable against a tetragonal shear. This is in sharp contrast to experiment, since these structures are observed in nature and we conclude that temperature effects must be of crucial importance for stabilizing these structures.

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