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**Crystallographic Phase Transitions in
Actinide Metals as a Function of Pressure**

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ABSTRACT: We present first-principles calculations of the equilibrium volumes and crystal structures of the light actinides (Th - Pu). The calculated equilibrium volumes for fcc Th, bct Pu, α -U, and β -Np are found to agree reasonably well with the experimental data, and when comparing the total energies of the bcc, fcc, bct, 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 fcc 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 bcc U, bcc Np, bcc Pu, and fcc Pu. Thus, our zero temperature calculations suggest that the bcc structure is unstable for these elements and that fcc 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 fcc \rightarrow bct \rightarrow fcc in Th, a sequence α -U \rightarrow bct \rightarrow bcc in U, and a sequence β -Np \rightarrow bct \rightarrow bcc in Np. Also, a sequence of transitions in Sc as a function of decreasing volume have been calculated, namely hcp \rightarrow fcc \rightarrow ω \rightarrow β -Np \rightarrow bcc.

I. 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 who demonstrated that the equilibrium volumes of the light actinides were well reproduced by first-principles calculations which assumed a hypothetical fcc structure.² 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 electrons.³ However, since the light actinides have less than a 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. found that the disagreement between the scalar-relativistic calculations and experiment was largest for Pu,² and later work by Brooks⁴ showed that by performing fully-relativistic calculations, solving the Dirac equation for the crystal, the increased volume of Pu compared to Np was reproduced and the agreement between experimental and calculated volumes was good.⁴ 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 fcc structure, Pa in the bct structure, U in an orthorhombic structure

with 2 atoms per cell, Np in an orthorhombic structure with 8 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 bct 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 complex 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 fcc and bcc structures for the light actinides⁷ and found that Th correctly favours the fcc structure whereas Pa, U, Np, and Pu have a lower energy in the bcc structure. Also, the electronic structure 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 bcc 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 bcc U, bcc Np, bcc Pu, and fcc Pu by means of our zero temperature calculations. Similar studies for the transition metals have given successful results¹³ 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 hcp \rightarrow bcc \rightarrow hcp \rightarrow fcc 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 4 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 viewed upon as heavy distortions of the bcc 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 to the stability of the hcp and bcc structure of Sc as a function of volume.

The rest of this paper is organized as follows. In section II we describe the details of the calculations and in section III we discuss our results for the equilibrium volumes. Results on the crystal structures are discussed in section IV and in section V we present our calculations for Sc. Finally section VI contains concluding remarks.

II. 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 fcc structure for Th - Pu. Also, the bcc, fcc, bct, 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 bcc, fcc, bct, and the β -Np structure. The more complex structure of α -Np is computationally too cumbersome presently and therefore we use the β -Np structure as a representative of the low temperature phase of

Np. For the fcc structure we used 60 points of the irreducible part of the Brillouin zone, for the bcc structure 59 points, for the bct 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 bcc U, bcc Np, bcc Pu, and fcc Pu. These calculations required many more k-points and to be specific we used 150 points for the bcc structure and 275 points for the fcc structure.

III. Equilibrium Volumes

In Fig.1 we display our calculated equilibrium volumes for Th - Pu using a hypothetical fcc structure. Notice that the fcc 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 of our inclusion of the relativistic spin-orbit coupling we do not obtain an increased volume for Pu compared to Np. This is in disagreement with the results of Brooks⁴ as well as in disagreement with experiment. Although our failure of not obtaining 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 Hamiltonian using an l,s basis^{20,17}), we speculate that the reason for the unusual volume of Pu is due to its open and low symmetry structure. Another explanation for this may be that the LDA is introducing 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 bct Pa, α -U, and β -Np. It should be noticed here that the volumes of these low temperature structures differ by as much as $\sim 2-6\%$ from the fcc volumes. Furthermore, the agreement between the experimental and theoretical volumes is $\sim 5-15\%$, which is comparable 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.

In Fig.2 we display the calculated f occupation for Th - Pu in the fcc 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.

IV. Crystal Structures

In Fig.3 we display the energy differences between the bcc, fcc, bct, and α -U structure for Th, Pa, U. Results for Np are also shown but for Np the α -U structure is replaced by the β -Np structure. For the bct structure we optimized the c/a ratio for two of the elements namely Pa and Np. The so obtained c/a ratios 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 bct structure) start out being higher in energy for Th but that with increasing f 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 bct 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 minima, one at 1.915 and one at 0.856. The minimum at 0.856 has the lowest energy. The occurrence of two minimii of the Bains path at $c/a \sim 0.82$ and ~ 1.8 is interesting, since it is known that f -electrons systems which crystallize in the bct structure have c/a ratios which are close to these two widely different values. For instance the c/a ratios of bct-Ce, bct-Th, bct-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 fcc and bcc Np are mechanically unstable, since in Fig.3 there is not even a local minimum of the energy curve around $c/a=1$ (=bcc structure) or around $c/a=\sqrt{2}$ (=fcc structure), whereas experimentally it is observed that at elevated temperatures the bcc structure becomes stable. This will be discussed more below.

The reason for finding open, low symmetric structures in these elements thus seems to be correlated with the increased f -electron population (as was suggested by Hill²² and also by Skriver⁷) 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 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 (fcc) is also anomalous. Th has 4 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 all are hcp. In order to investigate this possibility we have calculated the total energy of Th using only s, p , and d partial waves whereas we omitted the f states. At the equilibrium volume we find that the bcc structure is stable and not the expected hcp 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 $hcp \rightarrow \omega \rightarrow bcc$ with increasing pressure. This has previously been demonstrated to be caused by an $s \rightarrow d$ transfer.²³ Due to the large core in Th the d -occupation is sufficiently large to stabilize the bcc structure. However by increasing the volume one can lower the d occupation and correspondingly one would expect first the ω structure and then the hcp structure. In Fig.5 we show the energy difference between the bcc, hcp, and ω structure and the expected behaviour is found. Namely, starting from low d -occupation (large volumes) the crystal structure is hcp, 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.*, $hcp \rightarrow \omega \rightarrow bcc$. 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 fcc structure is then stabilized and is ~ 10 mRy lower in energy than the bcc structure (see Fig.3). Thus, we can claim that the innocent looking fcc phase in Th is in fact an anomaly and its existence provides strong evidence of itinerant f electrons.

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 with 2 in order to distinguish the two 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 by comparing with earlier work.⁹ Also, the main peak of the occupied part of the DOS is not at the Fermi level but is situated ~ 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.7a) and in the xz -plane (Fig.7b). 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 what one finds 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 what one finds in close packed structures. A similar behaviour has been reported for α -U.²⁴ Also, the electron density displayed in Fig.7b suggests that this structure is of a layered type since there is a region between layers where the electron density is very low.

We now proceed with a discussion of the high temperature bcc structure in U, Np, and Pu as well as of the fcc structure of δ -Pu. The aim of this part of our study was to 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 bcc U, bcc Np, bcc Pu, and fcc 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.

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 show that Th undergoes an fcc \rightarrow bct 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 bcc, fcc, bct, and α -U structures of Th, Pa, and U as a function of compression, as well as the total energy of the fcc, bcc, bct, and β -Np structures of Np as a function of compression. The energy differences between these structures are displayed in Figs.8 a (Th), b (Pa), c (U), and 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 fcc \rightarrow bct at 16.9 \AA^3 and 1.1 Mbar in acceptable agreement with the experimental data for Th.⁶ However our calculations also predict a second transition from bct back to fcc at even higher pressures and this second transition has not yet been observed. For U our calculations predict a sequence of transitions α -U \rightarrow bct \rightarrow bcc with decreasing volume. Also for Np we predict a sequence of crystallographic phase transitions, namely β -Np \rightarrow bct \rightarrow bcc as the volume decreases and the pressure increases.

The reason for stabilizing symmetric, close packed structures in itinerant f -electron systems have been discussed before²⁵ and is also elaborated on at 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 latter term stabilizes close packed, symmetric structures. The onset of more close 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 bct and then to bcc.

V. 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 hcp. As mentioned above, under compression it has been measured to exhibit a primitive tetragonal (pt) structure with 4 atoms per cell, a structure very similar to the β -Np structure²⁷. This is a most unexpected behaviour since transition metals normally display the fcc, bcc, or hcp structure, depending on pressure or temperature. This has motivated us to investigate the total energies of Sc in the bcc, fcc, hcp, pt, and in the ω -structure ($c/a = 0.61$).

In our calculations the hcp structure is correctly found to be stable at the equilibrium volume. We also optimized the energy of the hcp 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 \AA^3 , *i.e.*, $\sim 10\%$ too small in comparison to the experimental volume, which is a typical accuracy for the local density approximation. We now turn to the crystal structure stabilities and to begin with we first optimized the c/a ratio as well as the positional parameter, u , of the pt structure. This was done at the experimental transition volume for the pt structure, *i.e.*, at 17.4 \AA^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 pt 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 bcc, fcc, hcp, ω -, and pt structures as a function of volume. Notice that we first find a transition to the fcc structure at $V = 18.9 \text{ \AA}^3$, corresponding to $\sim 24 \%$ of the equilibrium volume. Further, in the volume-range of ~ 16.6 to 12.5 \AA^3 , the ω -phase stabilizes, which then transforms into the β -Np-like structure. This structure finally transforms into the bcc structure at $\sim 6.8 \text{ \AA}^3$. This agrees fairly well with the experimental observation of a hcp \rightarrow pt transition at $\sim 17 - 18 \text{ \AA}^3$. The experimental investigation did not cover the volume range which according to our calculations would stabilize the bcc structure and we hope our results will stimulate experimental work. Also, there are no experimental indications of an fcc 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 hcp and the fcc or ω -structure is quite low.

We will now elaborate a bit further on the stabilization of the β -Np structure in Sc. The densities of state for the bcc and pt structure at 25.0 \AA^3 and 7.8 \AA^3 have therefore been given in Fig. 11 (a) and (b), respectively. Notice first that at the lower volume the d partial DOS is broader in the pt structure than in the bcc structure. Furthermore, the shape of the bcc 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 pt structure is modified quite dramatically when the volume is lowered. We especially note that at the compressed volume the pt 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 pt 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 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.

VI. Conclusions

Above we have given examples of crystallographic phase transitions in both f as well as d -electron materials and showed that both close packed as well as 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 example of 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 pt 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 pt Sc at low volumes (Fig.11b) is an example of 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, bcc) structures if the volume is sufficiently low. Moreover, it seems plausible to expect a pt 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 $\beta\text{-Np}$ structure. Moreover, our calculations of the equilibrium volumes, where we used a hypothetical fcc 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 $\alpha\text{-Np}$ and $\alpha\text{-Pu}$.

Finally, zero temperature calculations of the tetragonal elastic constant for bcc U , bcc

Np, bcc Pu, and fcc Pu yield negative values and thus shows 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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Table I

Calculated elastic constants for bcc U, bcc Np, bcc Pu, and fcc Pu.

	C' (kbar)
bcc U	-600
bcc Np	-346
bcc Pu	-720
fcc Pu	-480

FIGURE CAPTIONS

- 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 (open circles, solid lines) and from a hypothetical fcc structure (open circles, dashed lines).
- Fig. 2 Calculated f -occupation number for the fcc structure.
- Fig. 3 Energy differences between the fcc, bcc, bct, and α -U structure for Th - U. For Np the α -U structure is replaced by the β -Np structure. The fcc structure is the reference line and is set equal to zero.
- Fig. 4 Calculated Bains path for Np.
- Fig. 5 Calculated energy differences between hcp, bcc, and the ω -structure for Th, as a function of volume. The bcc 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 Ry and the Fermi level is at zero energy and is marked by a dotted line. The full drawn curve is the total DOS, the dashed and dotted lines are the f -projected DOS for the two different atom types.
- Fig. 7 Electron density for β -Np for a cut in the xy-plane (a) and the xz-plane (b).
- Fig. 8 Energy difference between fcc, bcc, bct, and the α -U structure for Th (a), Pa (b), and U (c). 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.
- 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 bcc, fcc, hcp, ω -, and β -Np structures for Sc as a function of volume. The fcc energy is the reference level and is set equal to zero.

Fig. 11 Density of states for Sc in the bcc and pt structures at 25.0 \AA^3 (a) and 7.8 \AA^3 (b).
Energies are in Rydbergs and the Fermi level is at zero energy and is marked with a vertical line.

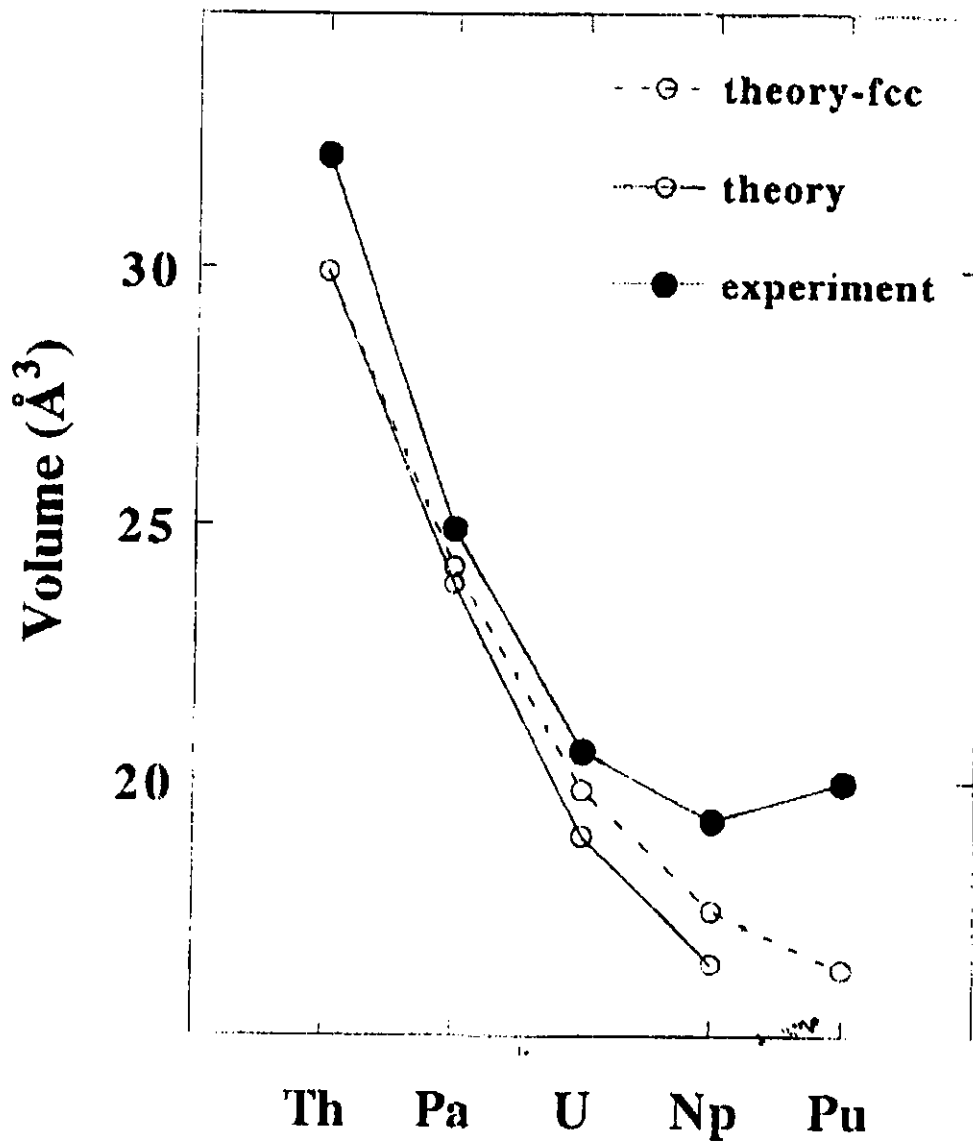


Fig. 1

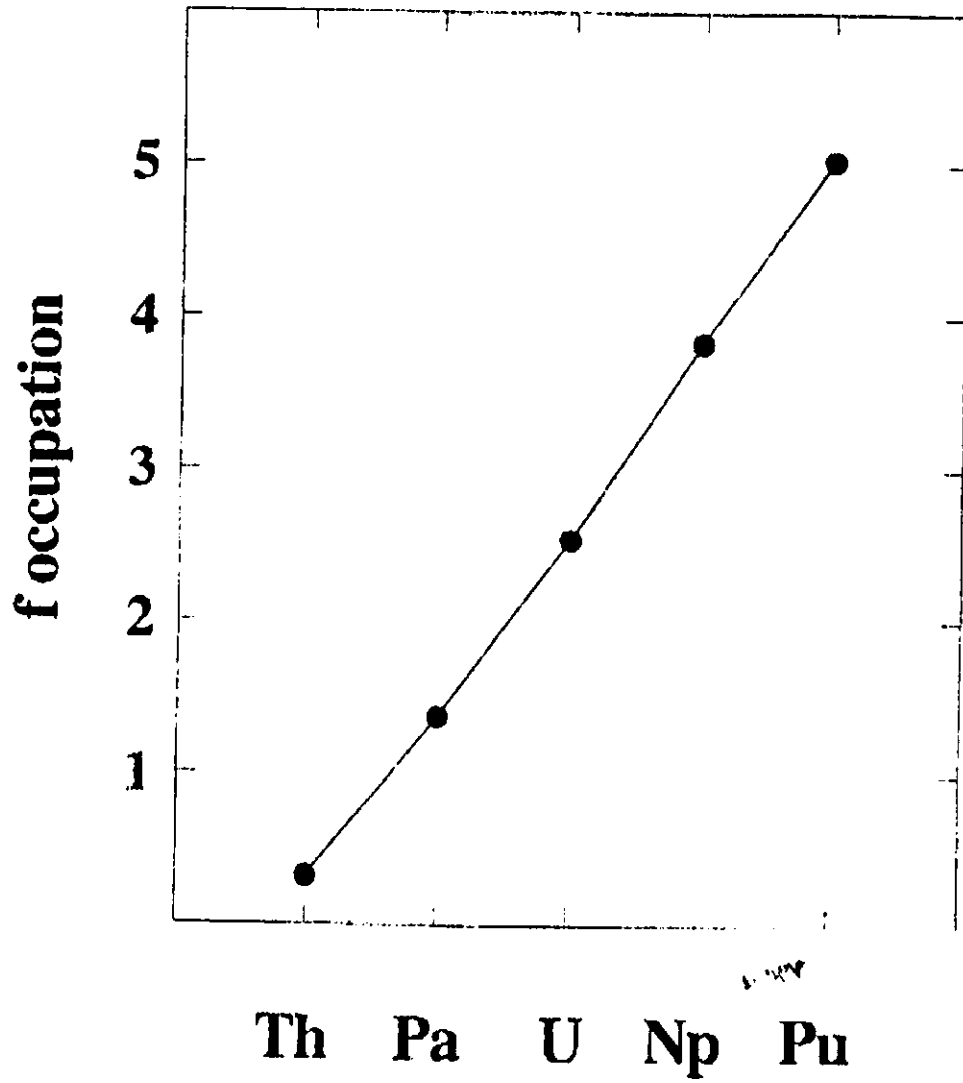


Fig. 2

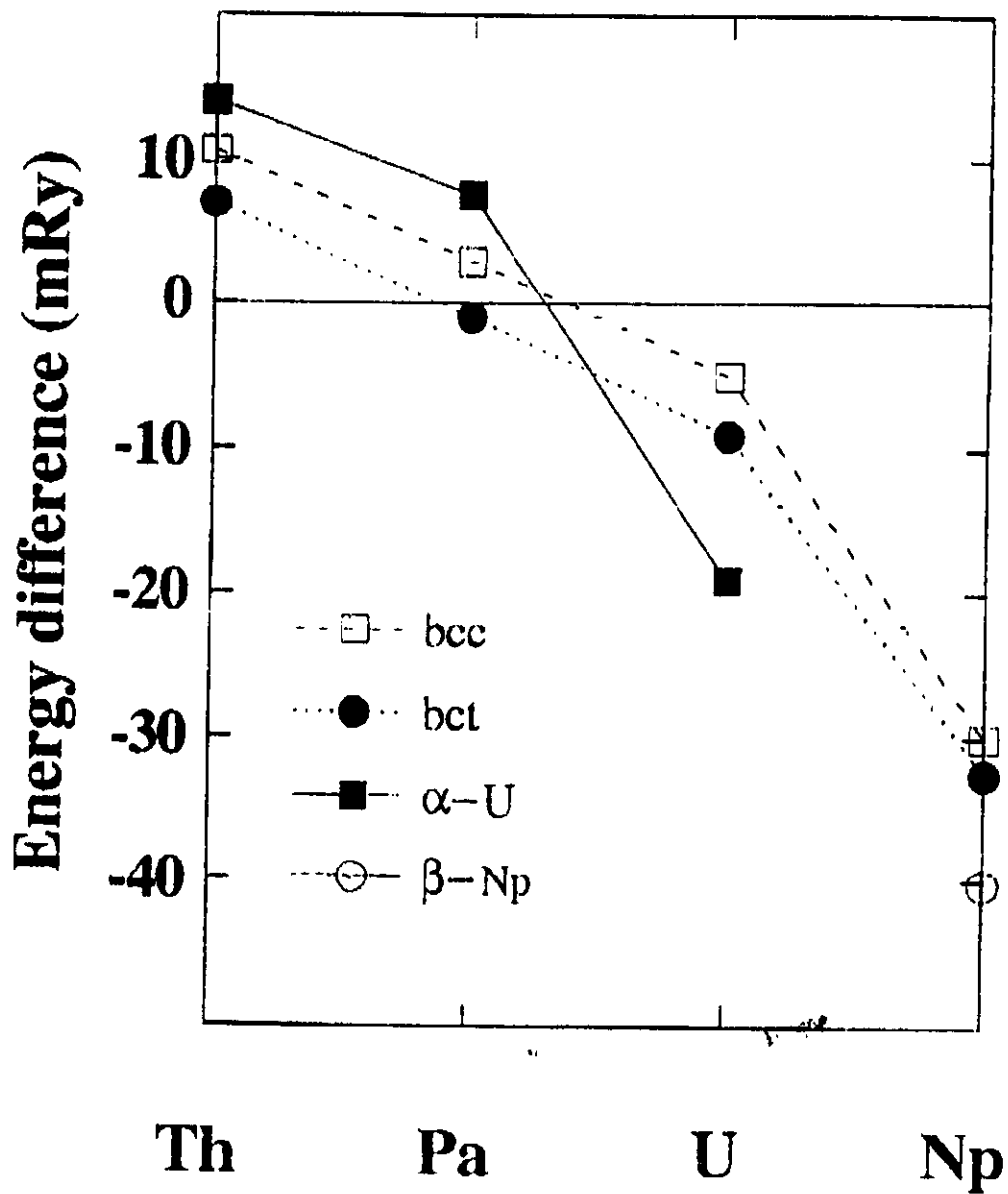


Fig. 3

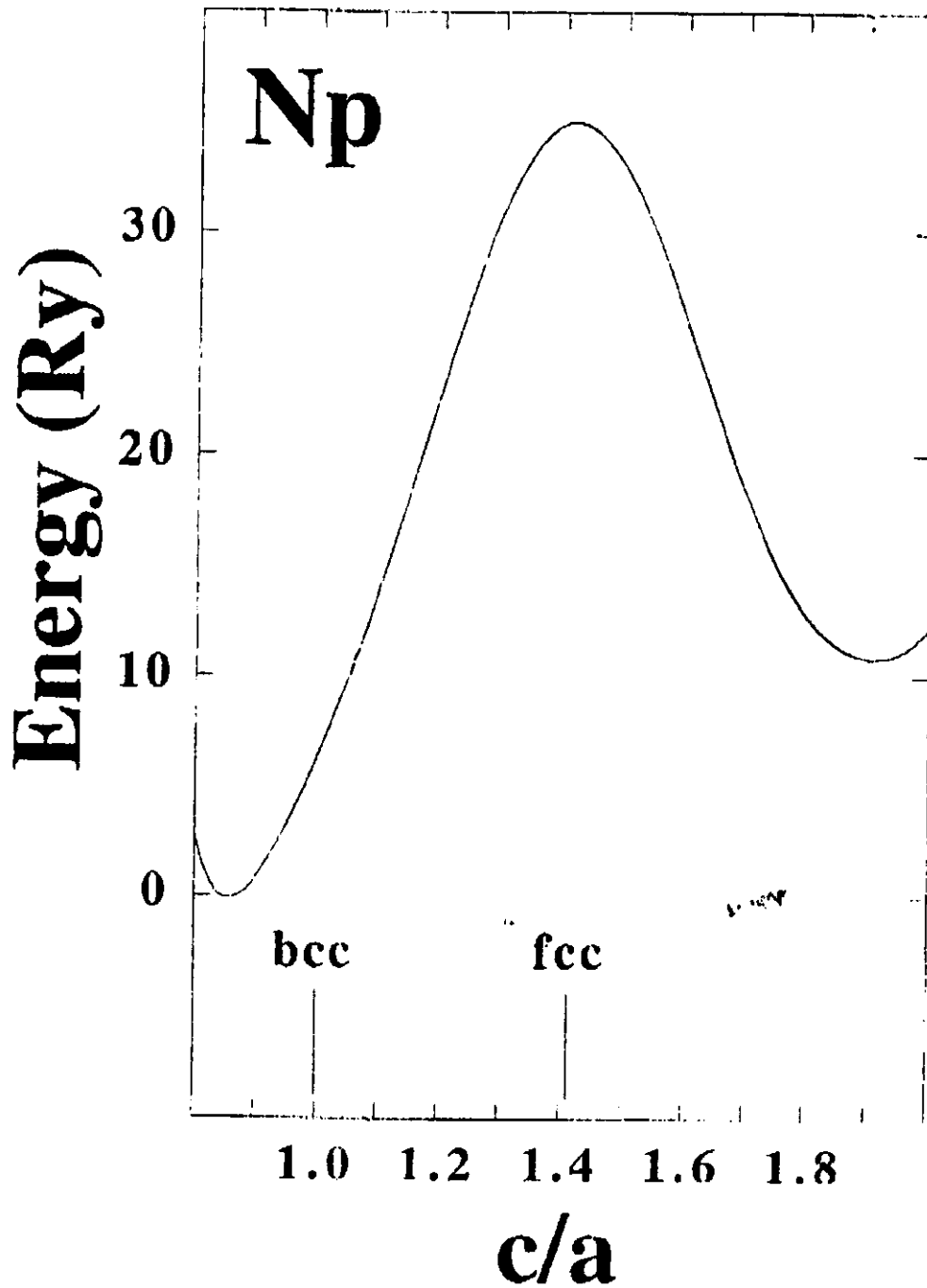


Fig. 4

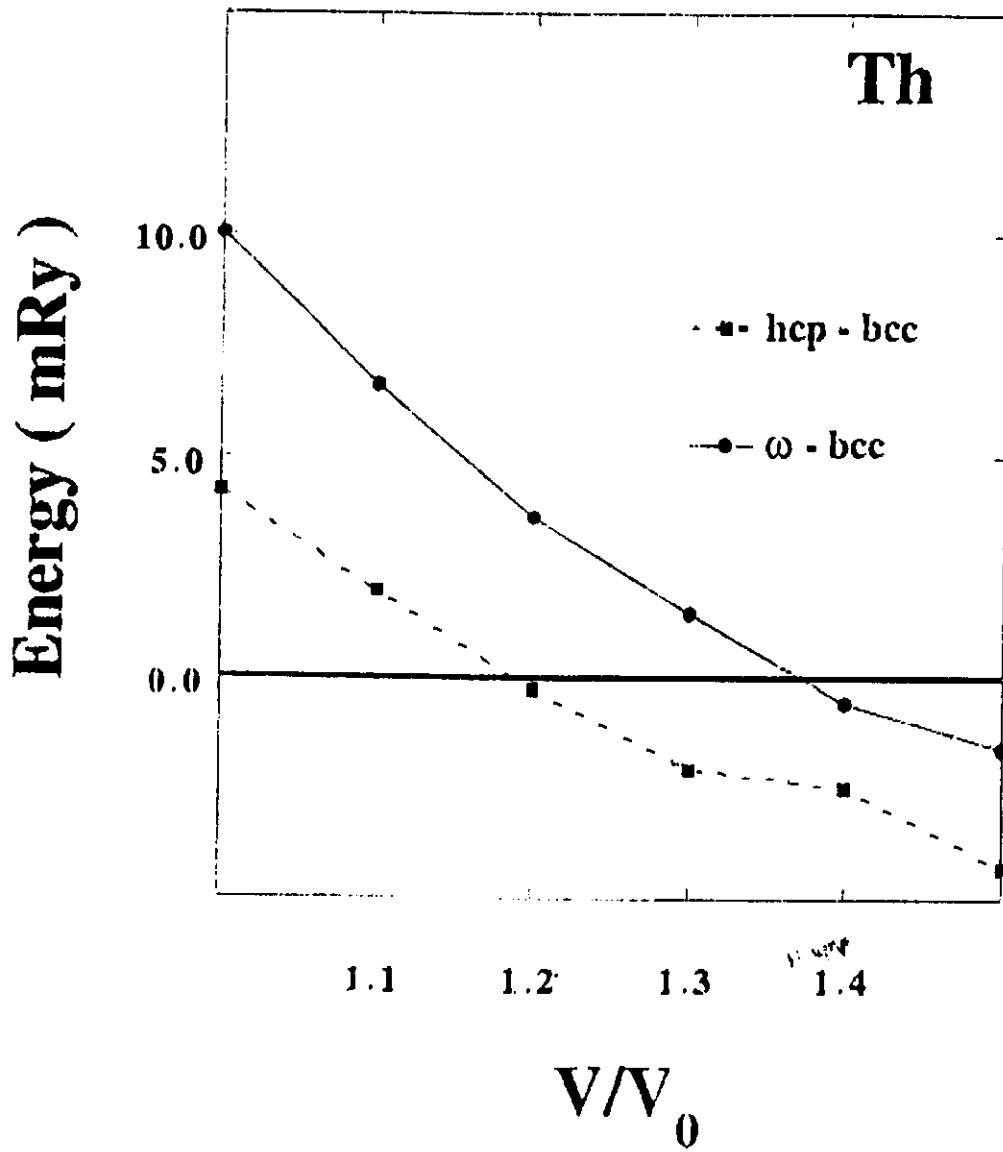
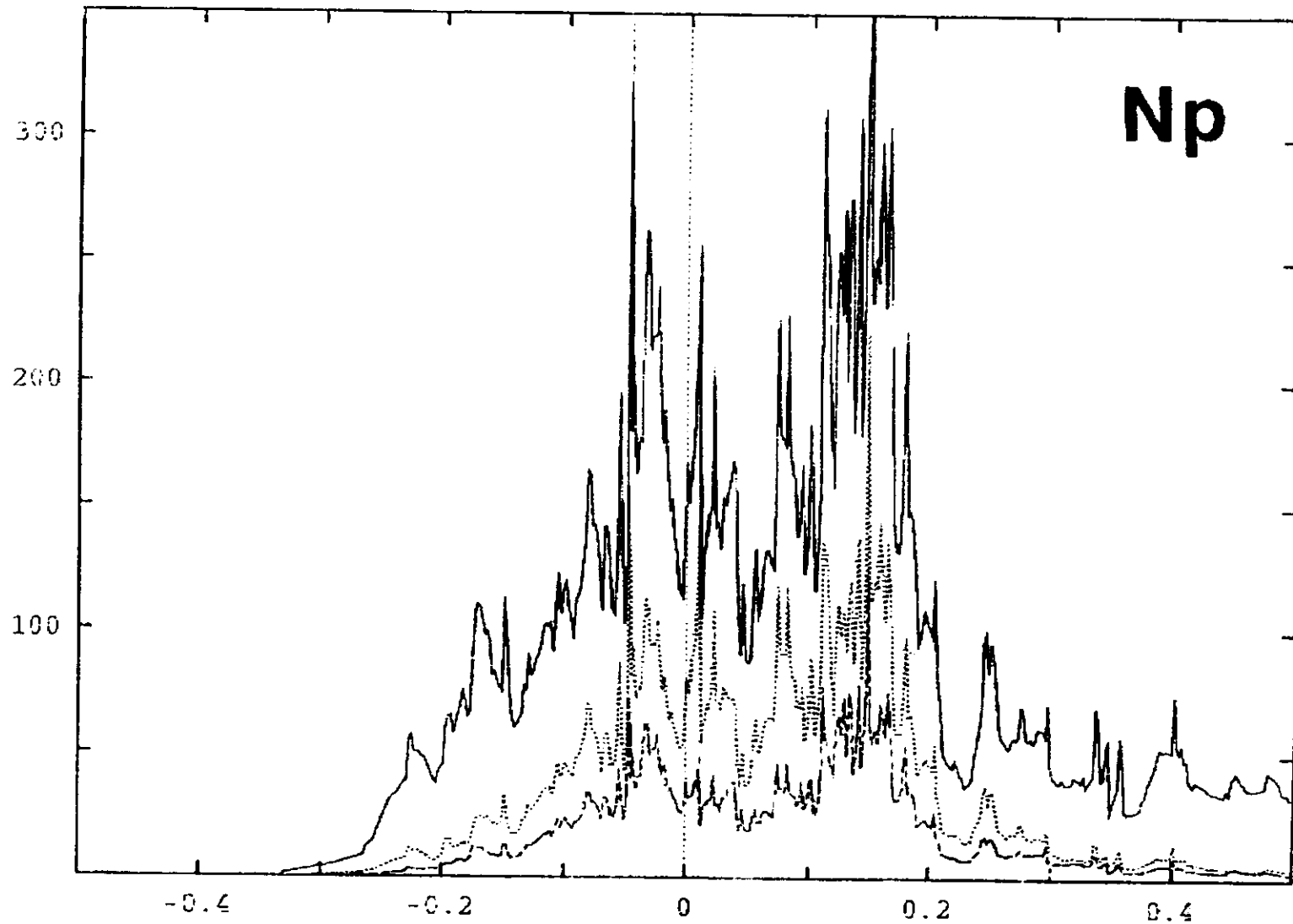
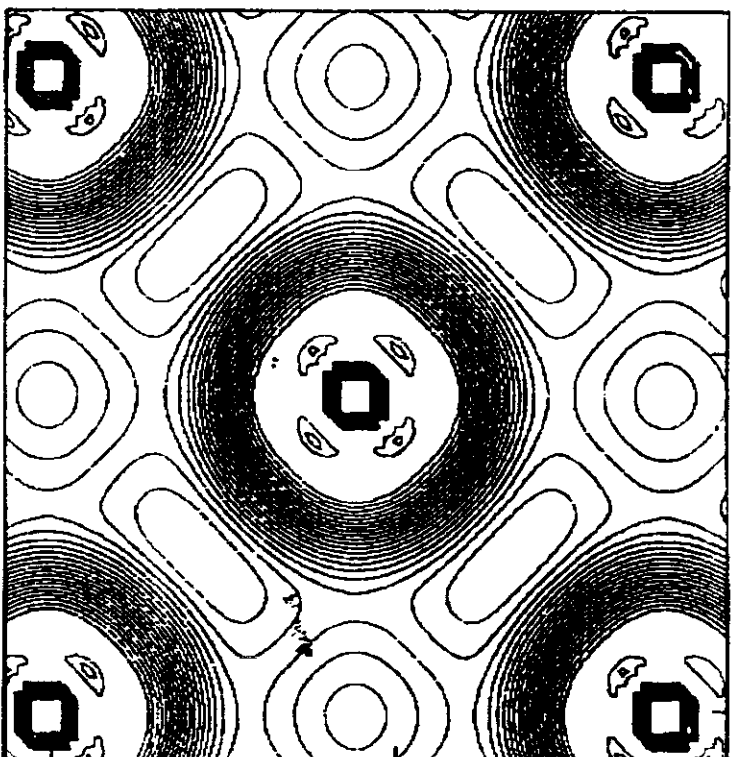


Fig. 5

Fig. 6

DOS (States / Ry)





x

y

Plot 7.1

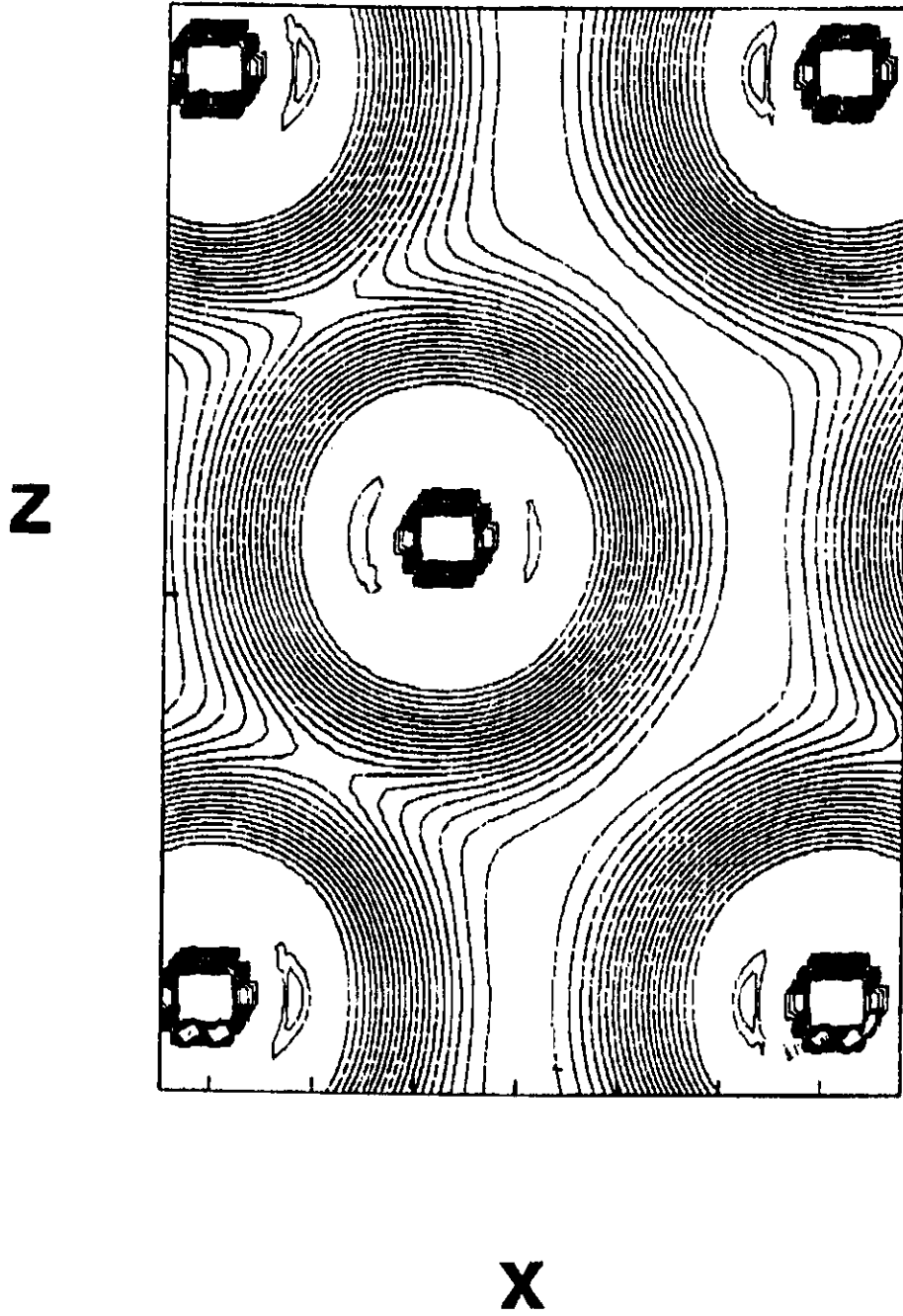


Fig. 7b

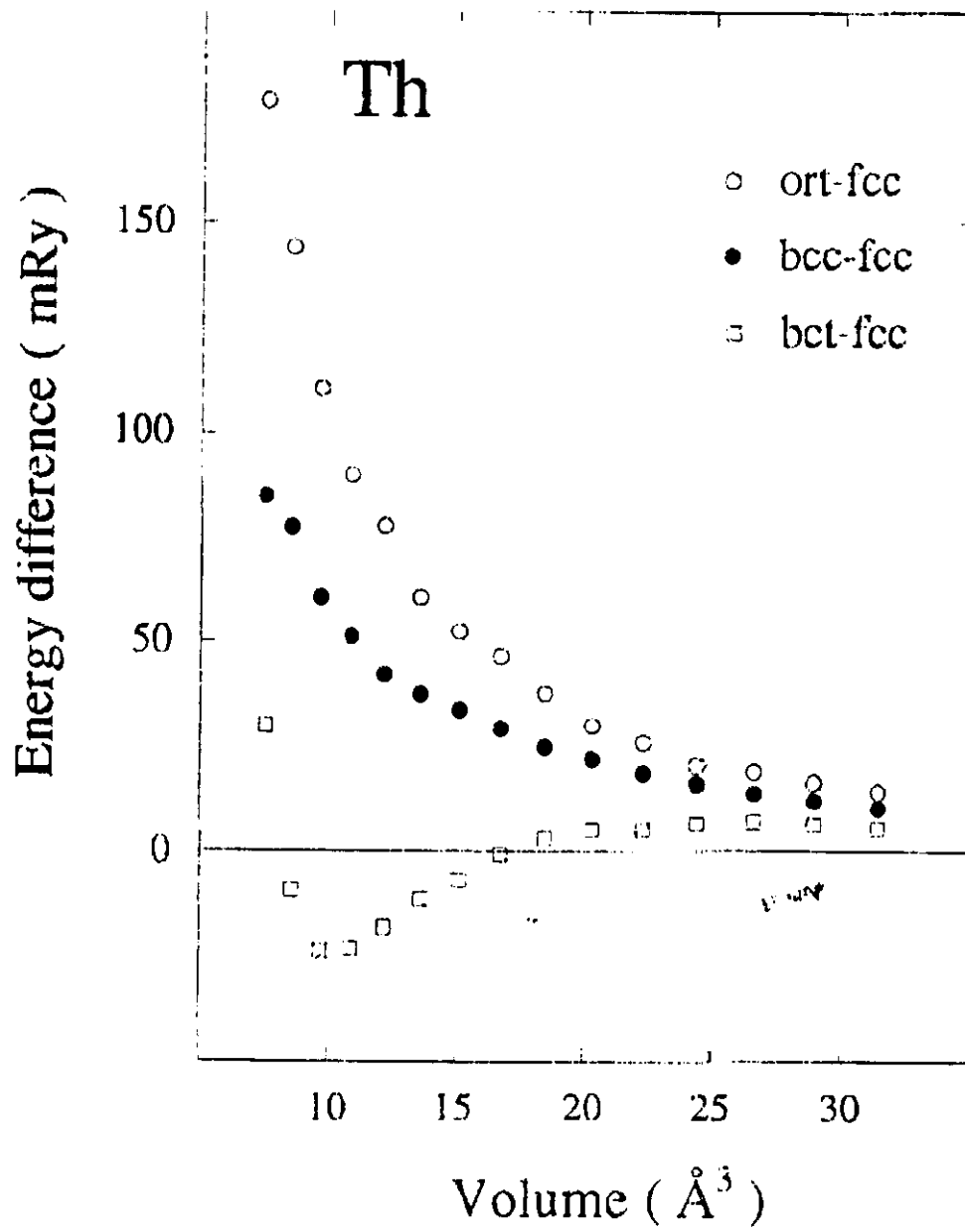


Fig. 9a

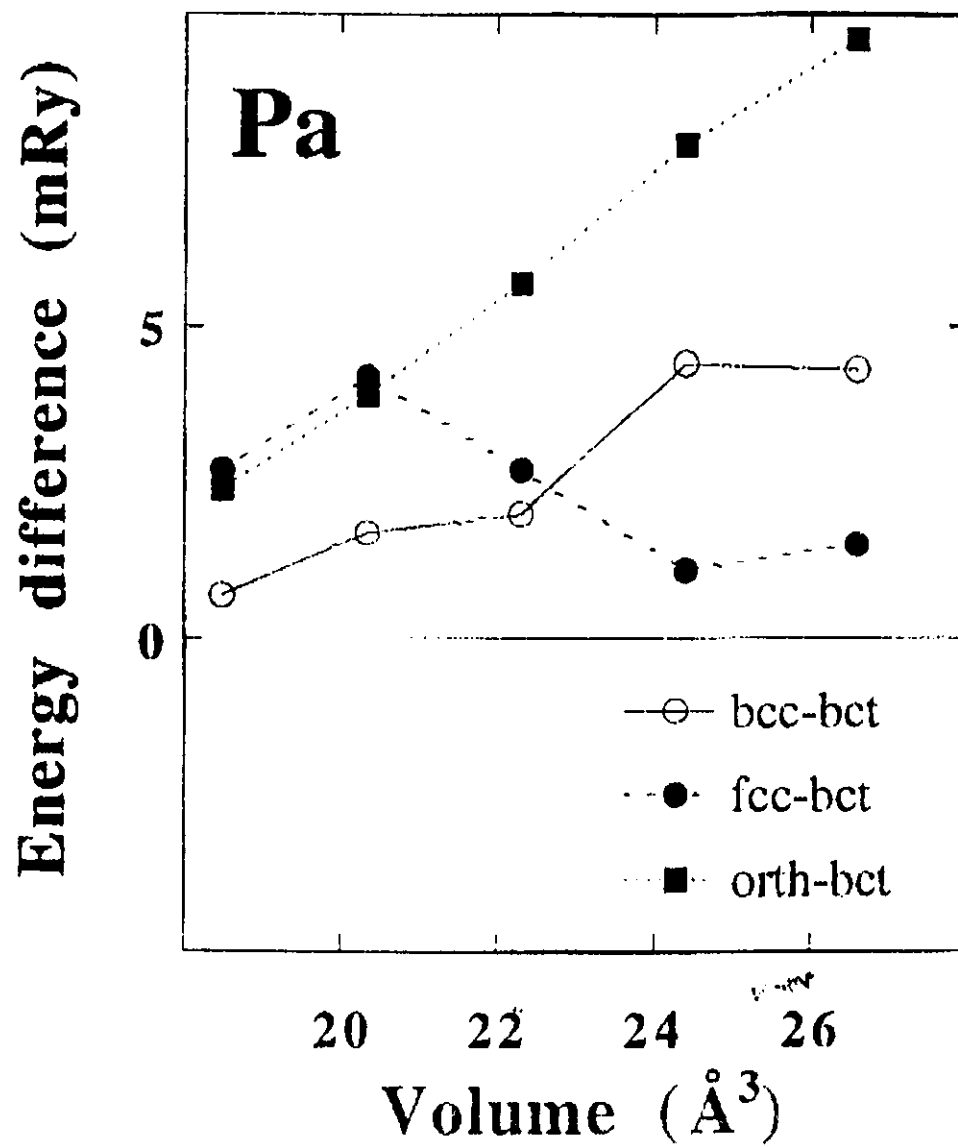


Fig. 8b

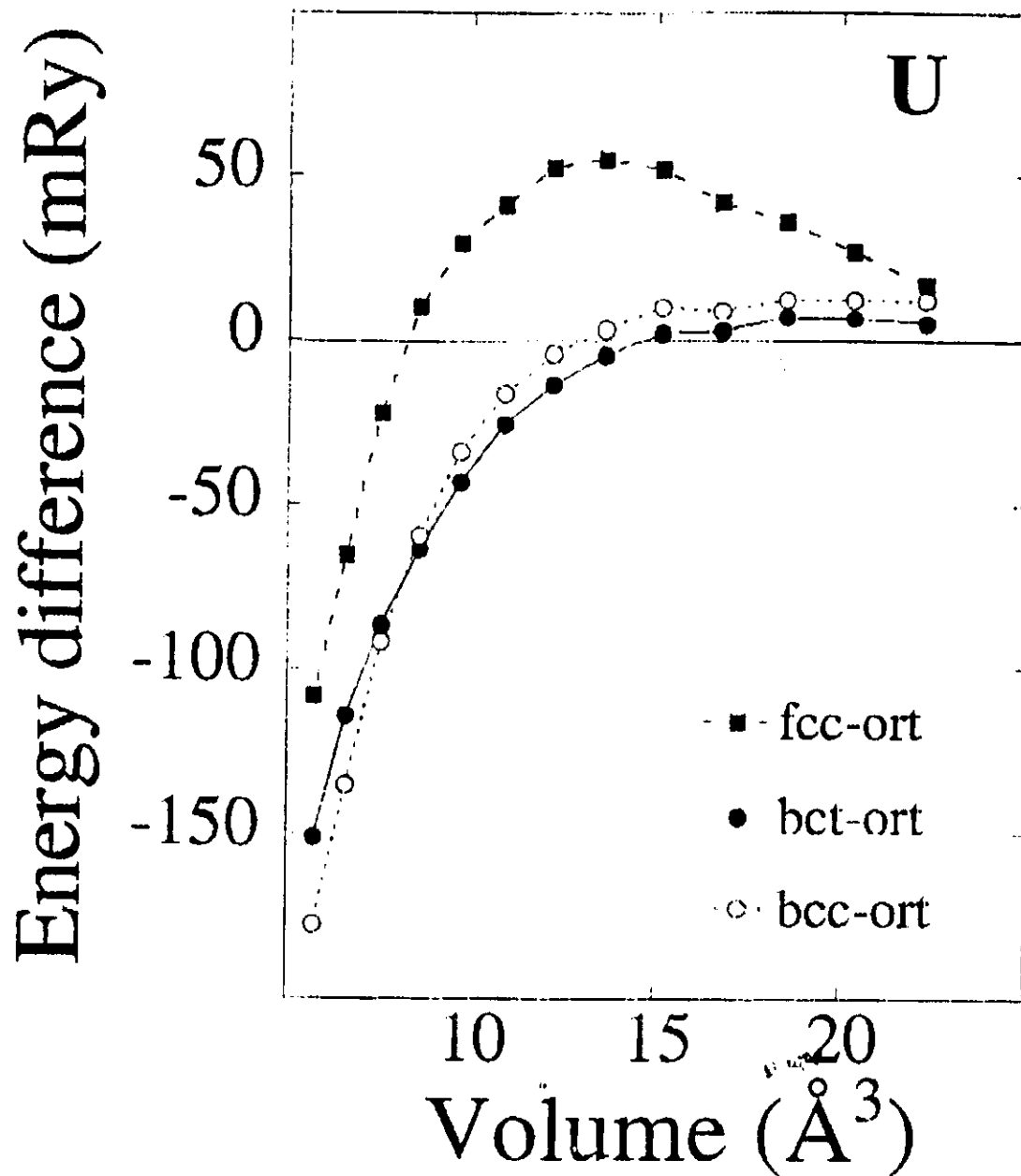


Fig. 8C

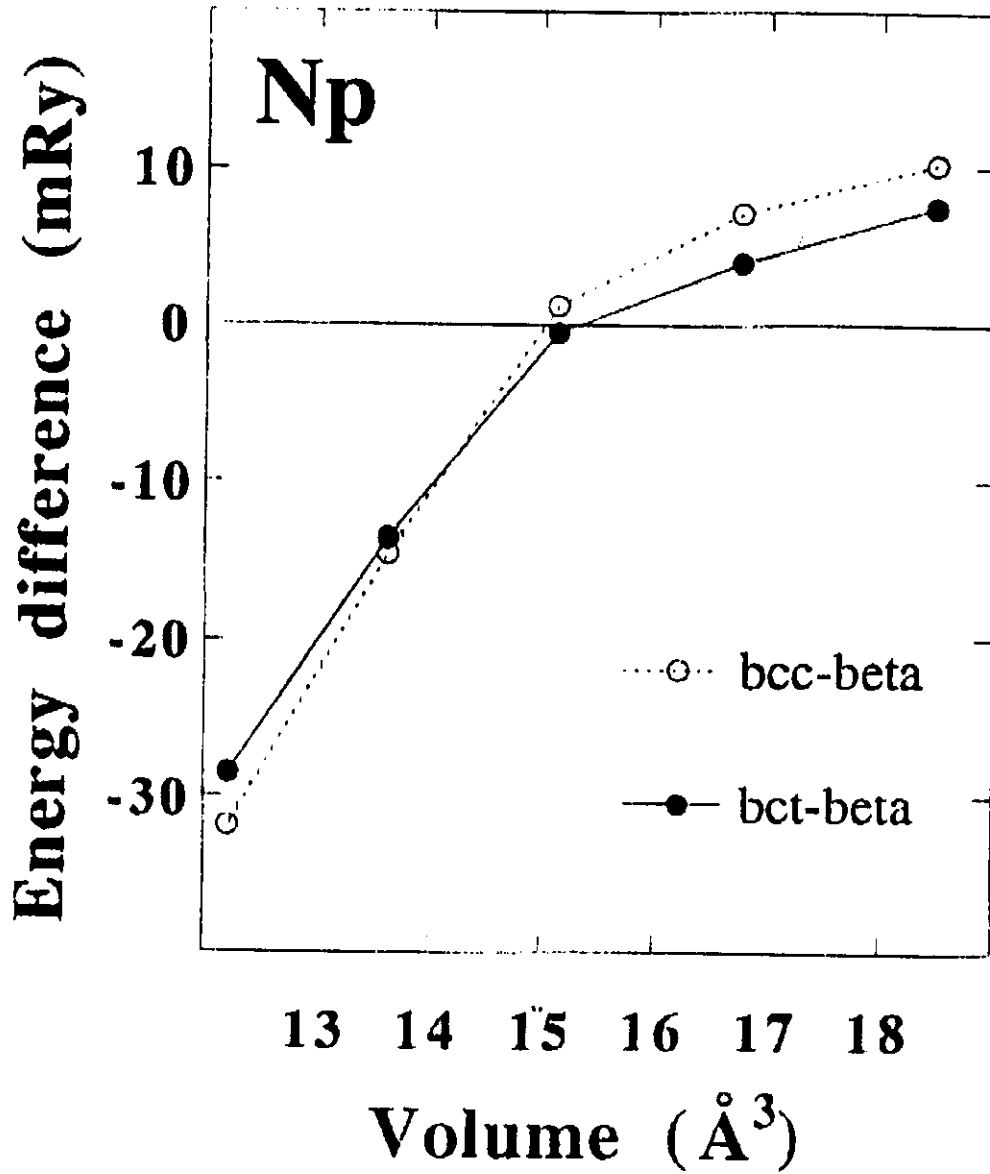


Fig. 8d

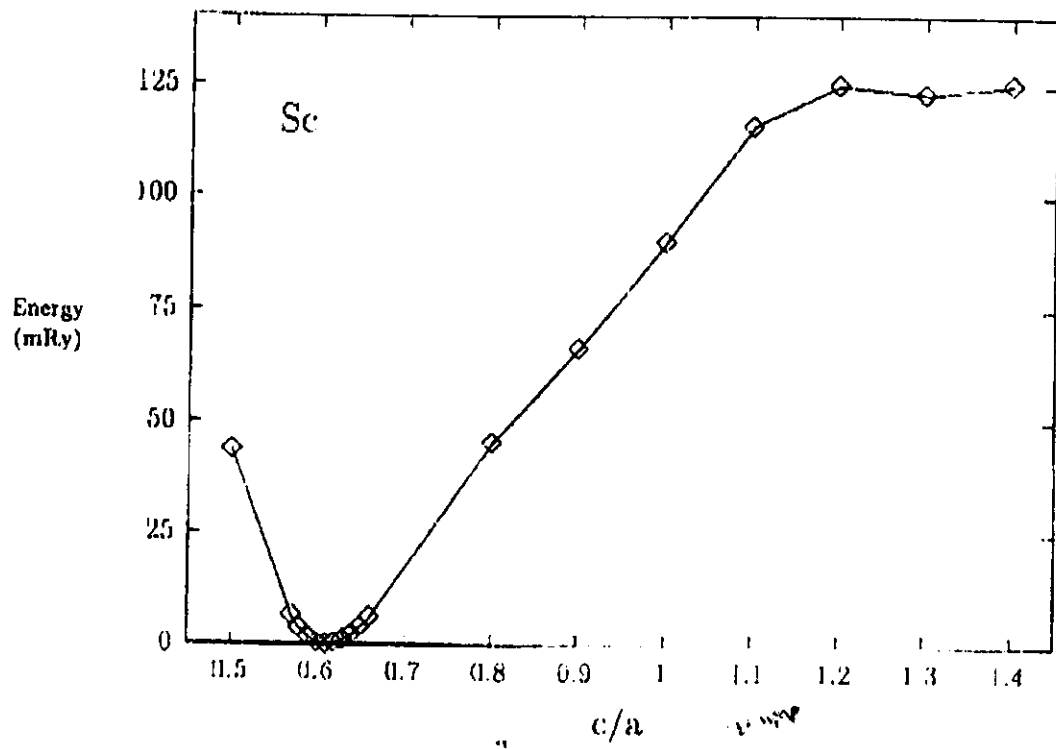


Fig. 9

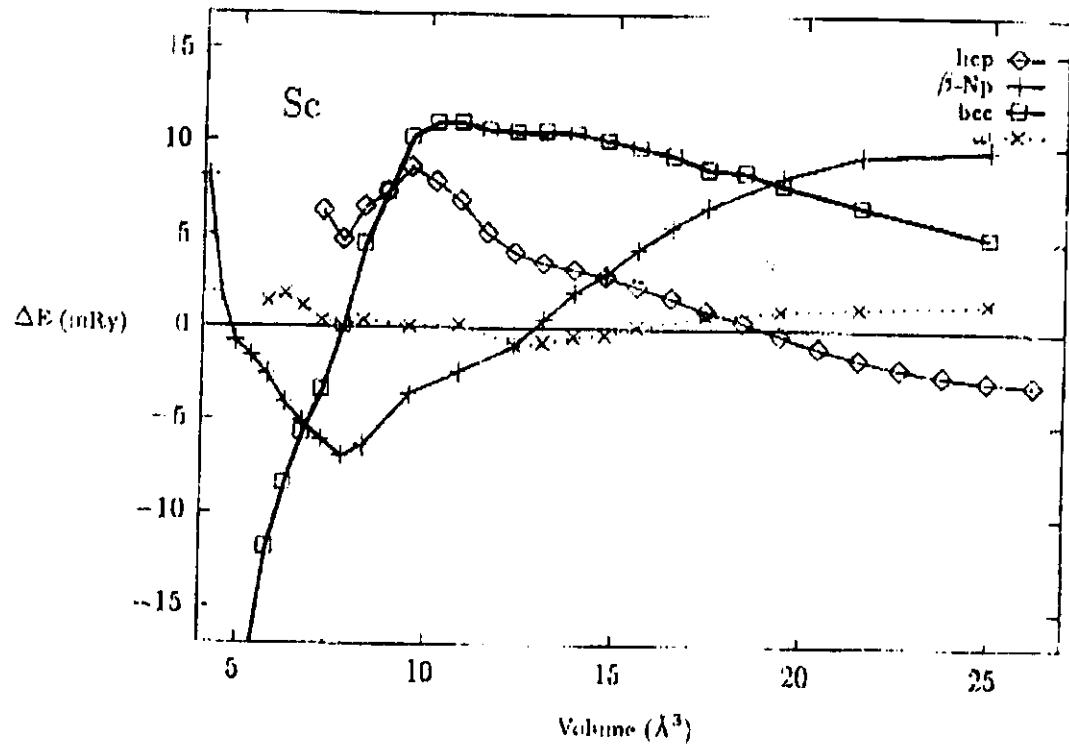
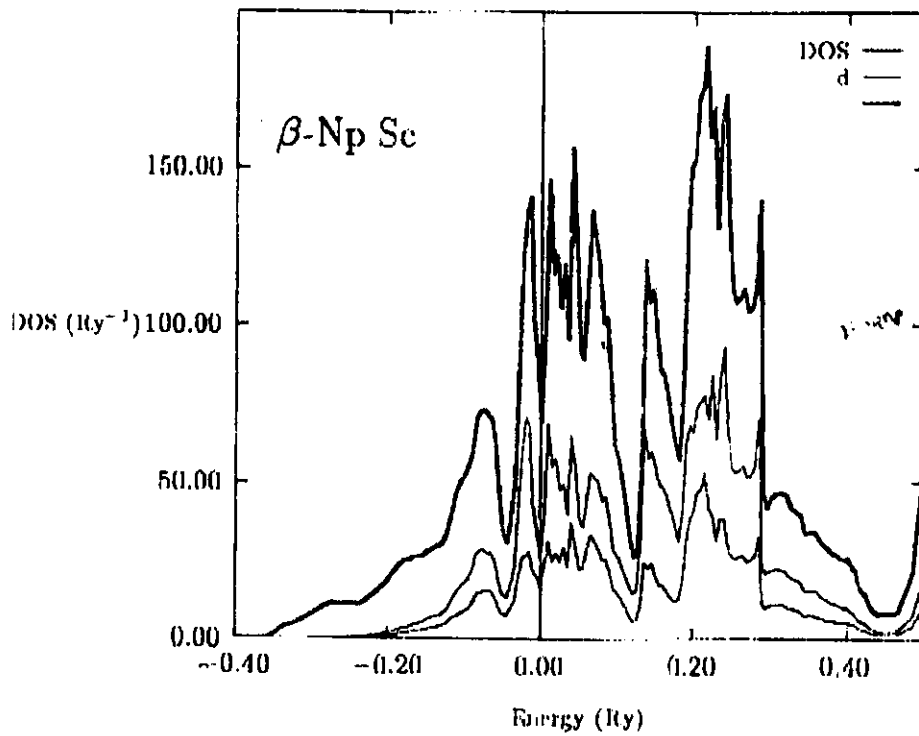
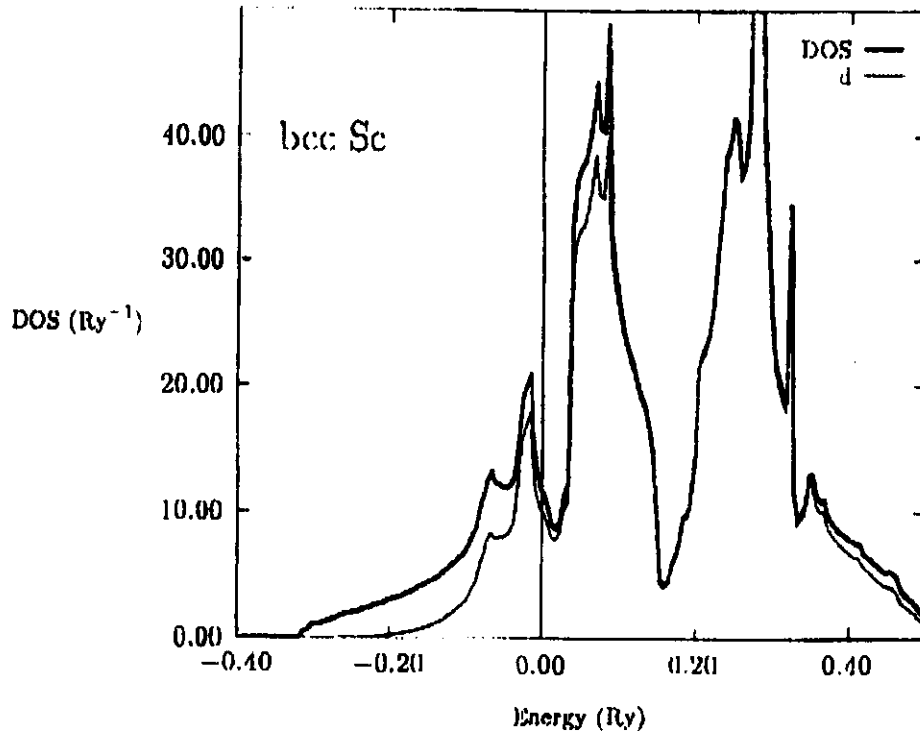


Fig. 22



Figure

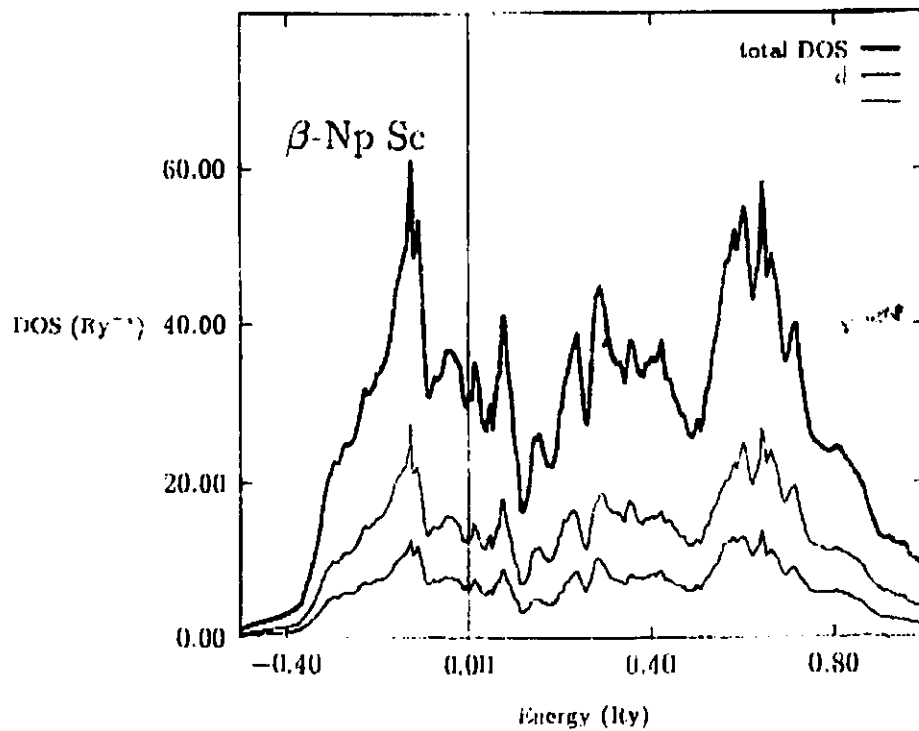
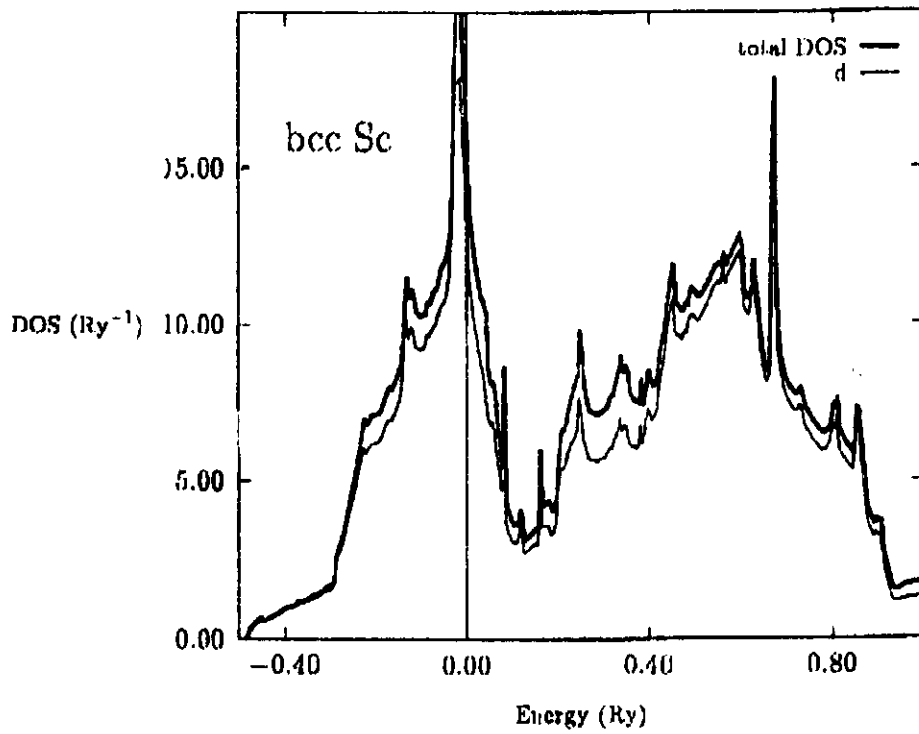


Fig. 11