High-pressure crystal structures of actinide elements to 100 GPa

High-pressure crystal structures of actinide elements to 100 GPa

A Lindbaum[1], S Heathman[2], T Le Bihan[3], R G Haire[4], M Idiri[2] and G H Lander[2]

[1] Institute for Solid State Physics, Vienna University of Technology, Wiedner Hauptstrasse 8-10/138, A-1040 Wien, Austria
[2] European Commission, JRC, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany
[3] European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France
[4] Oak Ridge National Laboratory, PO Box 2008, MS–6375, Oak Ridge, TN 37831, USA

Abstract
The structural behaviour of the actinide metals with pressure is being studied using diamond-anvil cells and the high-brilliance and angle-dispersive techniques now available at the ID30 beamline of the European Synchrotron Radiation Facility. A review is given of recent work at room temperature and up to 100 GPa. The results illustrate clearly the difference between the earlier metals (Pa, U) and those further across the actinide series (Am, Cm, and Cf). The complex structures at atmospheric pressure of the lighter actinides are a consequence of itinerant 5f electrons, and these metals show less compressibility (i.e. exhibit larger bulk moduli) and few (if any) phase transitions under pressure. In contrast, the transplutonium metals do not have 5f electrons contributing to their cohesive energies at atmospheric pressure, are therefore 'soft' (have lower bulk moduli), and show multiple phase transitions before their 5f electrons become itinerant. After delocalization of their 5f electrons due to pressure, they acquire structures displayed by the light actinides.

1. Introduction

The science of the actinide series presents one of the most significant challenges of the periodic table. Most are man-made and all are radioactive, but their solid-state-physics properties are poorly known and exceedingly complex. The dominating factor in defining their physical and chemical properties is the role of the 5f electrons in their bonding. We illustrate the importance of such bonding in figure 1, by plotting the atomic volumes of the elements at room temperature and pressure; a figure that has been shown in papers for several decades. The initial large decrease in the atomic volume going from Th to Pa to U arises due to additional
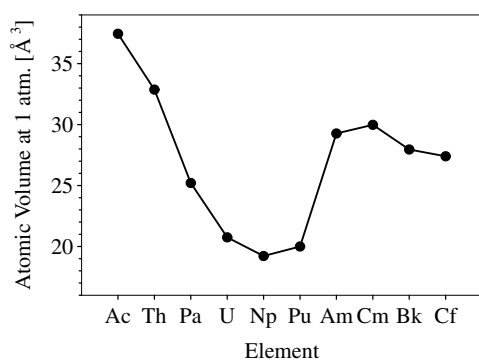
Figure 1. Atomic volumes of actinide metals at atmospheric pressure and 25 °C.

electrons being placed into the valence shell (either 6d/5f in the case of Pa, or 5f in the case of U) [1, 2]. The 5f-electron states are then described as being *itinerant*. For Np and Pu metals, we deduce that their 5f states are also itinerant, but a tendency for localization is beginning. At Am, the large increase in its volume is almost certainly a sign that its 5f states are *localized*. This trend continues for the remaining elements discussed here, with the small decrease in their atomic volumes mirroring that appearing in the second half of the rare-earth series [3], and due to the increased screening of the f states, as the 5f electron count increases. Although these concepts appear relatively simple, calculations of either the volumes or the crystal structures as a function of pressure are far from straightforward. Indeed, controversy still surrounds the best methods to be used for these calculations. This is particularly true for the case of Pu, which exhibits six allotropes as a function of temperature before melting [1–3], and in the fcc δ-Pu phase which has a substantially larger atomic volume than found for the low-temperature, α-phase. The extent (if any) of localization of the 5f states in Pu continues to be a subject of controversy [4–7].

Pressure is a key experimental parameter in demonstrating this change in the character of the 5f states across the actinide series. In the case of the higher actinides, one expects pressure to drive the 5f electrons into a bonding state, and their structures to become those of the Pa–Pu metals. Increasing the volume of the lighter actinides is not feasible for bulk samples. However, for Pu at the monolayer level (where the interatomic spacing can relax in vacuum), a remarkable localization of these states is seen by means of photoemission [8], and this is consistent with our concepts.

Pressure experiments on the actinides have been carried out for many years and multiple references up to 1992 are given in a review by Benedict and Holzapfel [3]. The primary technique for determining the structures is x-ray diffraction investigation. Diamond-anvil cells (DACs) have become quite sophisticated and the quantity of material (a few micrograms) is appropriate for obtaining excellent x-ray diffraction patterns. Earlier experiments were carried out with laboratory x-ray sources, and generally used the energy-dispersive method [3]. When transuranium samples could be studied at synchrotron sources, such experiments provided more intensity than possible with laboratory sources, but many experiments still used energy-dispersive techniques. Such techniques have a number of disadvantages:

 (a) fluorescence lines from the sample appear in the spectra, which can overlap with diffraction lines;
 (b) little is learned about preferred orientation in the small samples, as only *one* segment of the Debye–Scherrer cone is examined; and

(c) to compare intensities (even without preferred orientation) requires considerable faith in the calibration of both the incident photon spectrum *and* the detector's response.

For the most part, especially with relatively simple structures, this technique is reliable for *positions* of diffraction lines, but not for *intensities*. Thus, the dimensions and symmetry of the unit cell should be reliable, but atomic positions, which depend on intensities, will not.

The advent of third-generation synchrotron sources has led to a large increase in high-pressure work in biology, chemistry, and solid-state physics. Photon beams from undulator insertion devices provide enormous brilliance. This means that the intensity of the beam is concentrated into a very small area (i.e., square micrometres). Furthermore, the development of image plates and CCD detectors has allowed data to be gathered in seconds to minutes in angle-dispersive experiments, where the entire Debye–Scherrer cone is now accessible. It is the combination of these developments that has led to a revolution in the information obtainable in high-pressure diffraction experiments. As long as an average of the full Debye–Scherrer ring is available, then Rietveld analysis can be employed to obtain atomic positions and occupational parameters, and perhaps even anisotropic strains in the materials. The combination of these factors, together with the cooperation of the ESRF safety personnel in Grenoble, France, have allowed us to start the present programme on actinide metals at the ID30 beamline.

Since this is a review, we shall limit experimental details and instead refer to papers describing the experiments on Am [9], Pa [10], U [11], and Am–Cm alloy [12], which are either published or submitted for publication. It should be noted that all transplutonium samples have been supplied by the USDOE, and produced and loaded in pressure cells at Oak Ridge National Laboratory. Given the sensibility to the pressure diagram of Np and Pu, we shall not discuss their behaviour.

One other general remark on the compressibilities/bulk moduli determined previously by x-ray techniques is in order. We have recently examined in considerable detail the case of uranium (see [11] for full details) and have concluded that in the earlier work on this metal effects due to the freezing of the pressure-transmitting medium were not completely understood. This was discovered in part due to the higher quality of the data obtained with the new techniques. These effects vary from sample to sample, but are particular serious for α-U, given its lower symmetry. The result of not using the proper pressure-transmitting media is that many of the earlier moduli reported from x-ray studies on U are too high.

2. Survey of experimental results

2.1. The light actinides, Pa and U

The pressure versus volume curves (compressibilities) for Pa and U are shown in figure 2, and a schematic overview of their different structures as a function of pressure is given in figure 3. Their structures at atmospheric pressure are body-centred tetragonal (Pa-I) and the orthorhombic α-uranium structure with space group $Cmcm$. Their bulk moduli are comparable (118(2) GPa for Pa, 104(2) GPa for U), and their pressure–volume curves are therefore similar (figure 2). In the case of Pa there is a single phase transition at 77(5) GPa to form the α-uranium structure, indicated as Pa-II in figure 2. There is only a small volume discontinuity of about 0.8% at the Pa-I to Pa-II transitions, suggesting that in both cases their valence band states are primarily itinerant, in agreement with theoretical predictions. Recent theoretical predictions [13] have indicated a transition to the α-U structure at ~25 GPa, with a high-pressure hexagonal-close-packed-type structure well above 100 GPa. The predicted bulk modulus for Pa is ~100 GPa [13]. Previously, the bulk modulus for this metal was reported
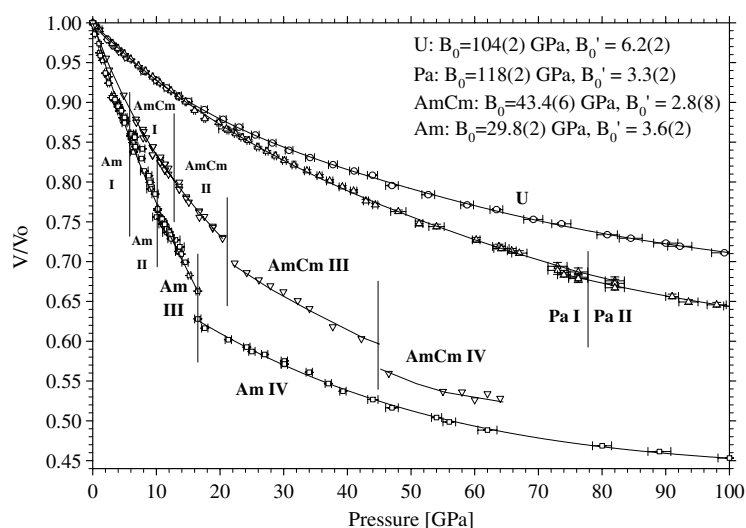
Figure 2. Relative volumes as a function of pressure for U [11], Pa [10], Am [9], and a 50% Am–Cm alloy [12]. The different phases and the bulk moduli are shown.
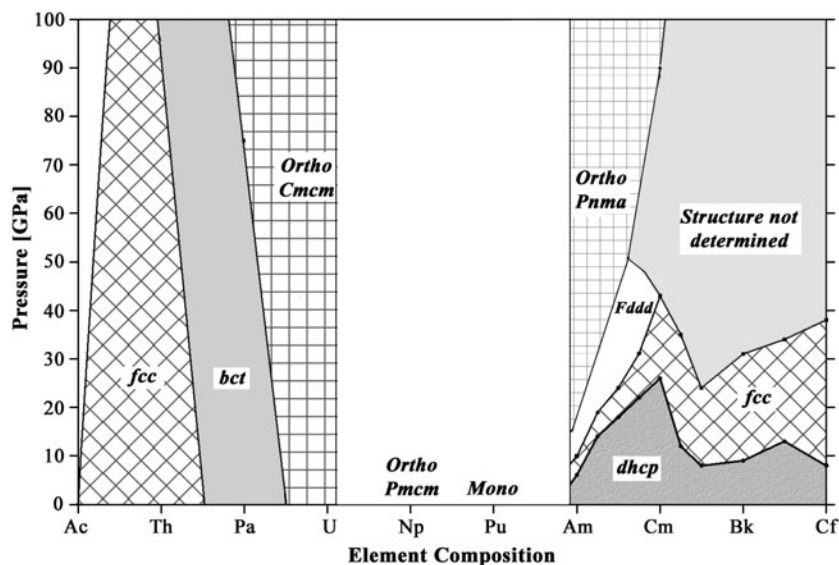

Figure 3. A schematic overview of the different structures of actinide metals as a function of pressure to 100 GPa, deduced from earlier work [3] and from data from our recent experiments. The pressure behaviours of Np and Pu are not shown.

as 157(5) GPa from energy-dispersive x-ray diffraction studies [14], but, as discussed above, this value is certainly too high.

In the case of uranium, there is no phase transition up to 100 GPa, again in agreement with theory [15]. The α-U structure is remarkably stable, a signature of the itinerancy of the 5f band states. Given that we are able to determine the atomic positional parameters, it is worth remarking that the y-parameter in the uranium position (4c sites of *Cmcm*: $0y\frac{1}{4}$) remains virtually unchanged as a function of pressure. Its ambient temperature and pressure value is 0.102(1) and at 100 GPa it refines to 0.101(1).
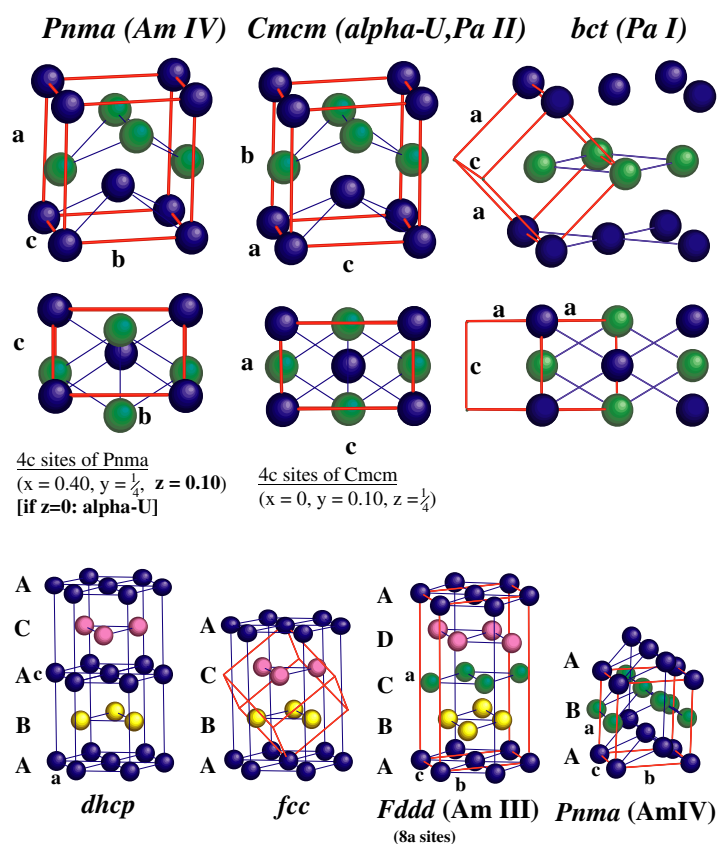
Pnma (Am IV)   Cmcm (alpha-U,Pa II)   bct (Pa I)

4c sites of Pnma
(x = 0.40, y = $\frac{1}{4}$, **z = 0.10**)
[if z=0: alpha-U]

4c sites of Cmcm
(x = 0, y = 0.10, z = $\frac{1}{4}$)

dhcp   *fcc*   *Fddd* (Am III) *Pnma* (AmIV)
                                    (8a sites)

Figure 4. Different structures as adopted by the actinide metals under pressure. The upper part of the figure shows the close relation between the bct structure of Pa-I, the *Cmcm* structure of α-U and Pa-II, and the *Pnma* structure of Am IV. The lower part of the figure shows the relation of the *Fddd* structure (Am III) and the *Pnma* structure (Am IV) with the close-packed dhcp and fcc structures.

(This figure is in colour only in the electronic version)

The close relationship between the bct structure of Pa-I and the orthorhombic *Cmcm* structure of α-U is shown in the upper part of figure 4. The main difference between the bct and the *Cmcm* structure is the buckling of the chains in the latter, which arises from the y-parameter of the 4c sites of *Cmcm*. When Pa-I adopts the *Cmcm* structure, its y-parameter (0.118(2) at 110 GPa) differs by less than 0.02 from that of α-U. Also shown in the upper part of figure 4 is how the *Cmcm* structure can be derived from the orthorhombic *Pnma* structure of Am IV by just shifting the atomic position z-parameter of the *Pnma* 4c sites to 0. This shows the close relation between the bct structure of Pa-I, the *Cmcm* structure of α-U and Pa-II, and the high-pressure phase of Am (Am IV).

2.2. The higher actinides, Am–Cf

As can be seen in figures 2 and 3, the behaviour of the transplutonium metals is more complex than that of the lighter actinides. As the pressure increases, their 5f states are driven from a

localized to an itinerant state. This is seen clearly in figure 2 in the case of Am. Initially its bulk modulus is ∼30 GPa and a very rapid decrease in the volume with pressure is observed. The (atmospheric pressure) dhcp structure transforms to fcc (see figure 3) at a relatively low pressure of 6 GPa. Then, there is a phase transition to the orthorhombic $Fddd$ structure at 11 GPa, which is also one of the phases adopted by Pu (γ-Pu). There is a small volume discontinuity of 2% at this transition, which is followed by a much larger collapse of 7%, when Am adopts the orthorhombic, $Pnma$ structure at 16 GPa. There is little doubt that these combined phase transitions represent delocalization of 5f states in Am [16–20].

The four different high-pressure structures of Am are shown in the lower part of figure 4, which permits one to envisage the transformation processes occurring under pressure. In principle, the structures can be viewed as being composed of close-packed hexagonal (Am I, Am II) or distorted close-packed hexagonal planes (Am III, Am IV) with a change in stacking sequence when going from one structure to the other. In the case of Am IV ($Pnma$ structure), there is an additional buckling of the hexagonal planes, given by the atomic position x-parameter of the space group, $Pnma$, which corresponds to the y-parameter of the $Cmcm$ structure of α-U and Pa-II ($1/2 - x_{Pnma} \approx 0.1$ corresponds to $y_{Cmcm} \approx 0.1$). As discussed above, a close relationship exists between the $Pnma$ structure of Am IV and the $Cmcm$ structure of α-U and Pa II (upper part of figure 4). The only difference between the two structures is the shifting of the buckled planes in case of the $Pnma$ structure, caused by a change from zero in the atomic position z-parameter of the $Pnma$ 4c sites.

Concerning the transamericium metals, high-pressure x-ray diffraction experiments have also been performed recently at the ESRF on $Am_{0.5}Cm_{0.5}$ [12], Cm, and Cf. In addition, an effort was made at ORNL some years ago to look at the pressure behaviour of Es [21], but intense radiation damage caused the sample to become amorphous after a few minutes. Publications on the Cm and Cf work will occur in the future.

In studies of the Am–Cm alloy, the same phase transitions as observed for Am are found [12], but they occur at higher pressures (see figures 2 and 3). Cm (as shown in figure 3) adopts the fcc structure, which changes to a structure *different* to the orthorhombic $Fddd$ structure of Am III. Cf also transforms to a structure different to that of Am III after formation of the fcc phase.

The stability of the localized 5f states increases in proceeding from Am to Cm to Bk to Cf, so the formation of other intermediate phases on the way to achieving 5f-electron delocalization is not surprising.

One experimental difficulty at higher pressures is appreciable line broadening that occurs in the diffraction patterns, and this complicates the identification of complex or mixed phases. In this respect, it will be very useful to have *ab initio* theory calculations to suggest potential intermediate structures.

3. Conclusions

Experiments using the capabilities of the ESRF, a third-generation synchrotron source, have allowed accurate determinations of the structures, compressibilities, and atomic positions of the actinides as a function of pressure up to 100 GPa. Despite the initially more complex structures of the light actinides, the pressures available to us do not produce differences in the state of their 5f electrons; they remain itinerant and bonding. This results in few if any phase transitions (one in Pa, none in U) and the metals have small compressibilities (i.e. relatively large bulk moduli). The structures of Np and Pu are even more complex but their behaviour with pressure is not discussed here. Instead, the reader is referred to a theoretical investigation [20], where it is predicted that for Pu a transition from the monoclinic α-Pu structure to the orthorhombic

Pnma structure (the same structure as found for Am IV, a derivative of the α-U phase) should occur at a volume compression of about 20%.

In contrast, for the transplutonium metals, the 5f states are *localized* at atmospheric pressure and their bulk moduli are smaller. The application of pressure on these metals leads to the delocalization of their 5f states, which generates structures known for the light actinides. The intermediate structures of Cm and Cf *en route* to forming their high-pressure structures are complex, and still being refined. We hope that the elucidation of these actinide phase diagrams will encourage the development of further theory and the evolution of a deeper understanding of this part of the periodic table and the bonding characteristics of these metals.

Acknowledgments

References

[1] Brooks M S S, Johansson B and Skriver H L 1984 *Handbook on the Physics and Chemistry of the Actinides* vol 1, ed A J Freeman and G H Lander (Amsterdam: North-Holland) pp 227–69
[2] Cooper N G (ed) 2000 *Los Alamos Science, Challenges in Plutonium Science* vol 1
[3] Benedict U and Holzapfel W B 1993 *Handbook on the Physics and Chemistry of the Rare Earths* vol 17, ed K A Gschneidner Jr, L Eyring, G H Lander and G R Choppin (Amsterdam: Elsevier) pp 245–300
[4] Boucher J, Siberchicot B, Jollet F and Pasturel A 2000 *J. Phys.: Condens. Matter* **12** 1723
[5] Wang Y and Sun Y 2000 *J. Phys.: Condens. Matter* **12** L311
[6] Söderlind P 2001 *Europhys. Lett.* **55** 525
[7] Savrasov S Y, Kotliar G and Abrahams E 2001 *Nature* **410** 793
[8] Gouder T, Havela L, Wastin F and Rebizant J 2001 *Europhys. Lett.* **55** 705
    Havela L, Gouder T, Wastin F and Rebizant J 2002 *Phys. Rev.* B **65** 235118
[9] Heathman S, Haire R G, Le Bihan T, Lindbaum A, Litfin K, Méresse Y and Libotte H 2000 *Phys. Rev. Lett.* **85** 2961
    Lindbaum A *et al* 2001 *Phys. Rev.* B **63** 214101
[10] Haire R G, Heathman S, Le Bihan T, Lindbaum A and Idiri M 2003 *Phys. Rev.* B **67** 13410
[11] Le Bihan T, Heathman S, Idiri M, Lander G H, Wills J, Lawson A and Lindbaum A 2003 *Phys. Rev.* B **67** 134102
[12] Le Bihan T, Haire R G, Heathman S, Idiri M and Lindbaum A 2002 *J. Nucl. Sci. Technol.* (Suppl. 3) 45
[13] Söderlind P and Eriksson O 1997 *Phys. Rev.* B **56** 10719
[14] Benedict U 1982 *J. Magn. Magn. Mater.* **29** 2287
[15] Söderlind P 2002 *Phys. Rev.* B **66** 085113
[16] Johansson B, Skriver H L and Anderson O K 1981 *Physics of Solids under High Pressure* ed J S Schilling and R N Shelton (Amsterdam: North-Holland) pp 245–62
[17] Brooks M S S 1983 *J. Phys. F: Met. Phys.* **13** 103
[18] Eriksson O and Wills J M 1992 *Phys. Rev.* B **45** 3198
[19] Söderlind P, Ahuja R, Eriksson O, Johansson B and Wills J M 2000 *Phys. Rev.* B **61** 8119
[20] Pénicaud M 2002 *J. Phys.: Condens. Matter* **14** 3575
[21] Haire R G 2002 private communication