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Pressure-induced phase transition in α-Pu

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Abstract

High purity α-Pu was studied by X-ray diffraction in a diamond anvil cell up to 62 GPa. A structural phase transition occurs around 40 GPa. The high pressure structure was indexed in a hexagonal lattice of space group $P6_3/m$, $a = 537.77$ pm, $c = 445.51$ pm at 62 GPa, $Z = 8$. The bulk modulus B_0 of α-Pu was determined as 43(2) GPa, with a pressure derivative $B_0' = 15(2)$.

1. Introduction

Two main subgroups can be distinguished in the series of the actinide metals according to the behaviour of the 5f electrons. The earlier actinides from protactinium to plutonium are a kind of 5f transition metal series with itinerant 5f electrons. This means that the 5f electrons are of a band type, hybridize with the conduction electrons and contribute to the metallic bond. From americium onwards, the 5f electrons become localized, having sharp energy levels, and do not participate in the bond. Physical properties of actinides and their compounds are strongly related to these differences in the nature of the 5f electrons. For instance, magnetic order can be observed when the 5f electrons are localized (curium, berkelium, californium), while actinide elements with itinerant 5f electrons can exhibit superconductivity (thorium, protactinium, uranium). Strengthening of the bond through the 5f contribution in the light actinide metals leads to crystal structures of low symmetry (α-Pu, for example, is monoclinic), small atomic volumes, high density and low compressibility. In contrast, in the second subgroup, crystal structures of high symmetry are observed: americium, curium, berkelium and californium have the d.h.c.p. structure at ambient pressure and temperature.

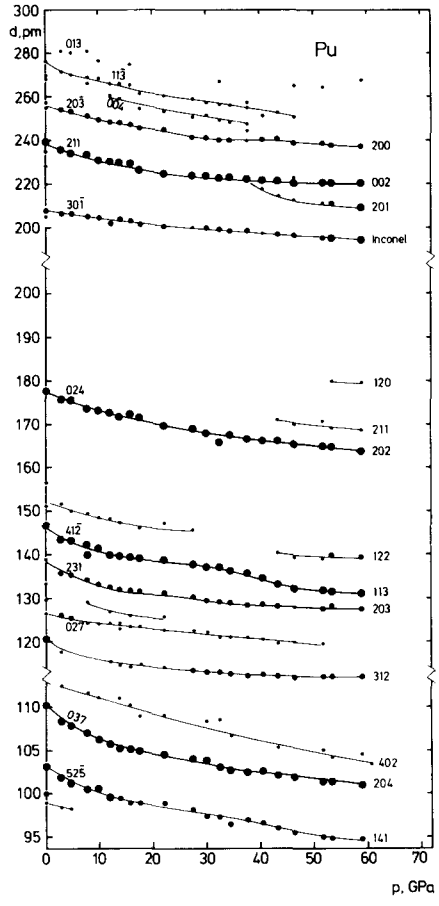

Fig. 1. Variation in d spacings with pressure for a sample of plutonium. Miller indices hkl are given on the left-hand side for the monoclinic α-Pu and on the right-hand side for the hexagonal high pressure phase. Indices were omitted for lines where indexing is not unambiguous. Diameters of the data points indicate relative intensities of the peaks: ●, strong; •, medium; ·, weak.

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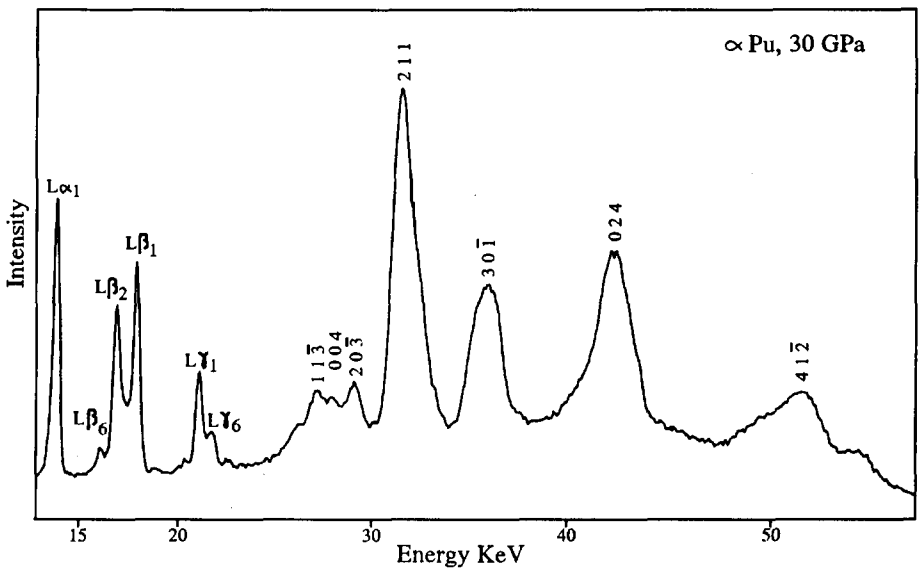

Fig. 2. Diffraction pattern of monoclinic α-Pu at 30 GPa, energy dispersive, $\theta = 5°$.

TABLE 1. Diffraction data of hexagonal plutonium at 55 GPa ($a = 543.7$ pm, $c = 449.3$ pm, $c/a = 0.826 = 1.653/2$)

hkl	*d* (pm) (calculated)	*d* (pm) (observed; energy dispersive)	*d* (pm) (observed; PSD)	Relative intensities calculated			Relative intensities observed		
				ENDIX, 5°	ENDIX, 7°	LAZY PULVERIX	Energy dispersive, 5°	Energy dispersive, 7°	PSD
200	235.43	235.20	240	22 30	17 23	24	100	100	95
*111	232.62		236	8	6	8			100
002	224.65	224.30	225	29	23	30	56	38	90
201	208.55	208.70	210	100	100	100	44	30	30
*120	177.97	177.90	179	2	3	3	9	9	5
*211	165.47	165.50	w(sh)	1	2	1	w(sh)	48	2
202	162.57	162.50	164	13	28	16	48		26
*122	139.52	139.60				2	10	15	
220	135.93	135.90				15	w(sh)		
*113	131.22	131.40				<1	w(sh)		
*130	130.59	130.40				5	w(sh)	100	
203	126.40	127.00				21	41		
401	113.87	113.90				12			
312	112.91	112.90				5		34	
004	112.37	112.40				4			
402	104.28	104.00				3		7	
204	101.41	101.50				4		21	
*141	100.17	100.10				5			

w, weak; sh, shoulder. *,lines not compatible with an h.c.p. lattice. PSD, spectrum obtained with the position-sensitive detector. Programs: ENDIX, ref. 11; LAZY PULVERIX, ref. 12.

Because of the correlation between the crystal structure and the 5f electron configuration, the study of phase transformation under pressure is a way to observe the transition from a localised 5f state to itinerancy. High pressure X-ray diffraction allows such studies. With the heavier actinides from americium to californium, pressure induces phase transformations to structures of lower symmetry [1], accompanied by volume decreases from 6% to 21%. The decrease in symmetry, together with the observed decrease in atomic volume, indicate that these transitions correspond in fact to the delocalization of the 5f electrons. In the earlier actinides, which have their 5f electrons already in an itinerant state, pressure can thus not induce this type of phase transition. A phase transition in α-Pu was thus not expected, except for very high pressures.

Two previous high pressure X-ray diffraction studies of plutonium metal have been reported. Roof [2] studied

TABLE 2. Diffraction data of hexagonal plutonium at 62 GPa ($a = 537.8$ pm, $c = 445.5$ pm, $c/a = 0.828 = 1.657/2$)

hkl	*d* (pm) (calculated)	*d* (pm) (observed; energy dispersive)	Relative intensities observed	
			Energy dispersive, 5°	Energy dispersive, 7°
200	232.86	232.7	100	100
*111	230.62			
002	222.76	222.4	43	23
201	206.37	206.4	71	41
*120	176.03	176.7	11	14
*211	163.57			82
202	160.97	161.0	53	
*122	138.11	138.0	9	30
220	134.48		w(sh)	
*113	129.82			
*130	129.17	129.2	10	92
203	125.21	125.7		
401	112.65	112.5		
312	111.74	111.7		37
004	111.38	111.0		
402	103.28			
204	100.41			30
*141	99.08	99.0		

w, weak; sh, shoulder.
*Lines not compatible with an h.c.p. lattice.

plutonium up to 21 GPa and determined the compressibility data as $B_0 = 42.2(7)$ GPa and $B'_0 = 10.5(2)$. In a paper on high pressure study of thorium, Akella *et al.* [3] briefly mention a pressure-induced structural change of plutonium from monoclinic to h.c.p.

2. Experimental details

Emission spectroscopic analysis of the plutonium used showed the main impurities to be as follows: [W] < 170 ppm, [Zn] < 133 ppm, [Fe] < 80 ppm. Turnings of the metal were obtained in a nitrogen atmosphere (20 ppm O_2, 6 ppm H_2O). The outer layer of the metal which could have been slightly oxidized was removed before the turnings were taken.

The lattice parameters of the sample at ambient pressure were determined by the conventional Debye–Scherrer method as $a = 617.9$ pm, $b = 480.6$ pm, $c = 1094$ pm, $\beta = 101.74°$, in good agreement with literature values. The cell volume obtained from these parameters was used as V_0 in calculating the relative volumes V/V_0 at pressure.

The compression studies were performed in a diamond anvil cell of the Syassen–Holzapfel type. The sample was loaded into the 0.2 mm diameter hole of an Inconel gasket. Silicone oil was used as the pressure-transmitting medium. The pressure was measured on a ruby splinter added to the sample, according to the ruby fluorescence method [4].

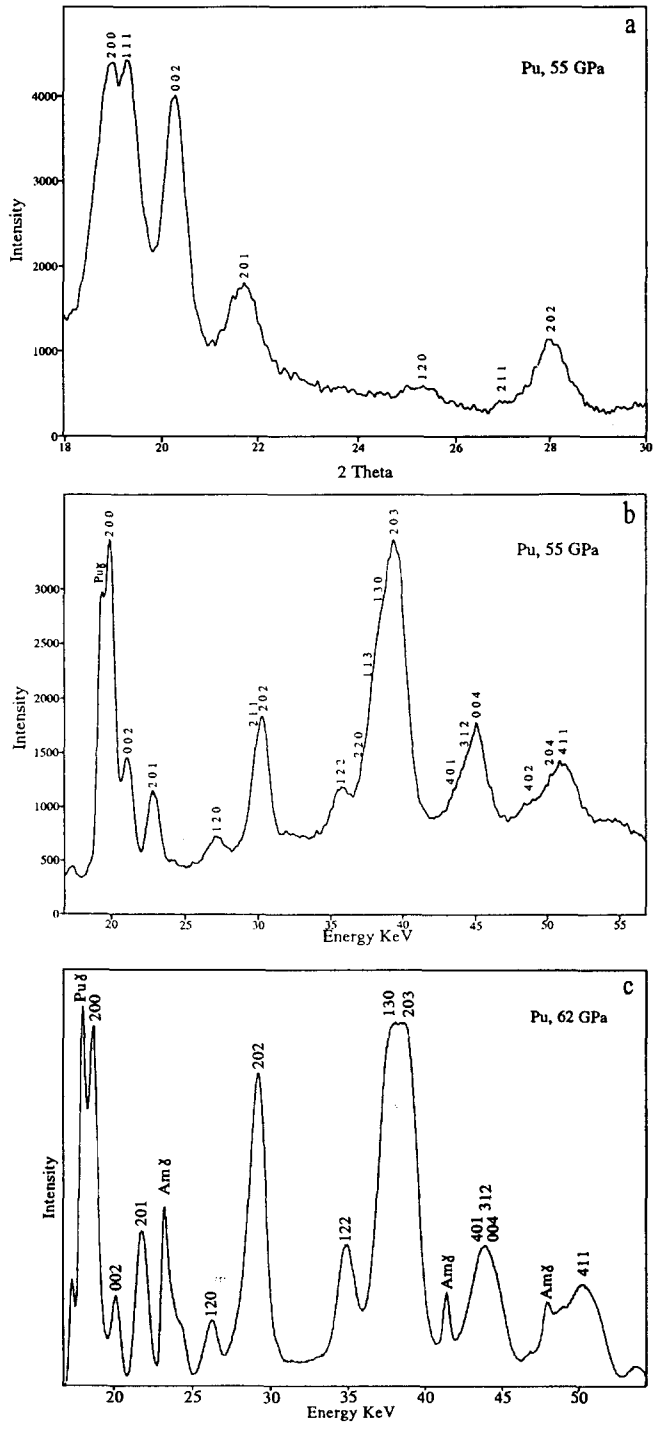

Fig. 3. Diffraction patterns of the hexagonal high pressure phase: (a) at 55 GPa, angle dispersive, Mo Kα radiation, position-sensitive detector; (b) at 55 GPa, energy dispersive, $\theta = 7°$; (c) at 62 GPa, energy dispersive, $\theta = 7°$.

Energy-dispersive and angle-dispersive set-ups were used for collection of X-ray diffraction data. The energy-dispersive set-up [5] uses a double conical slit system

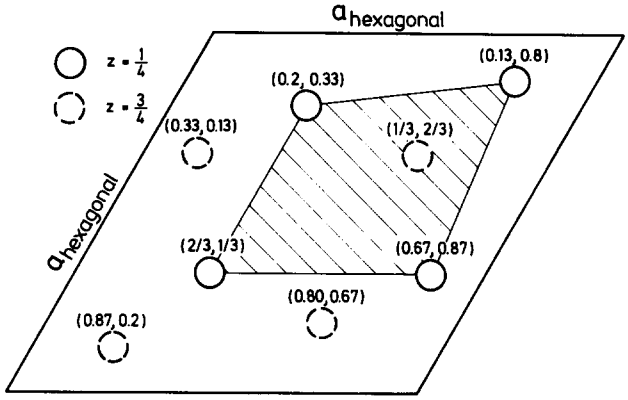

Fig. 4. Projection along c of the high pressure structure of plutonium. The shaded area represents a distorted h.c.p. cell.

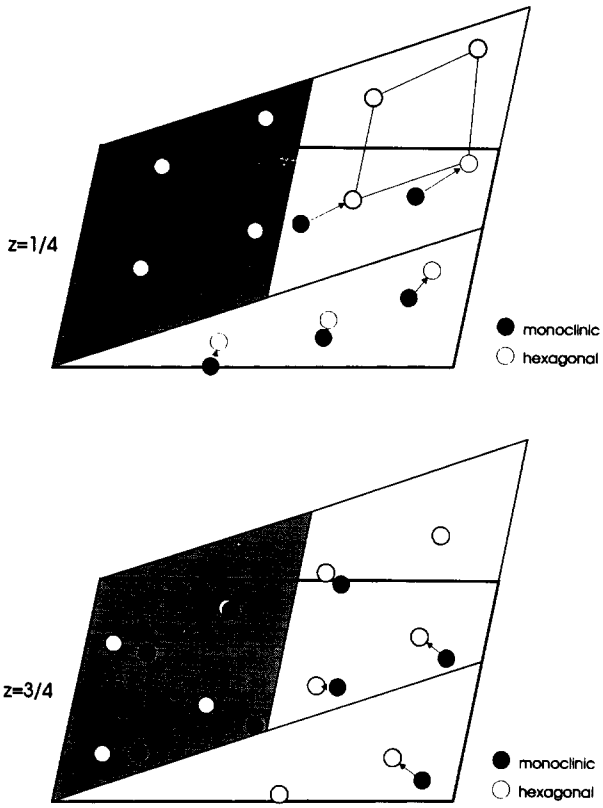

Fig. 5. Relationship between the high pressure structure of plutonium and that of α-Pu. The thick frame marks the monoclinic cell. The arrows indicate the shift of the atoms on transition from monoclinic to hexagonal.

which fixes two Bragg angles. This system allows the simultaneous collection of data under two angles ($\theta_1 = 5°$, $\theta_2 = 7°$) without moving the pressure cell. According to the Bragg equation

$$2d \sin \theta = hc/E$$

the energy E of a given set of lattice planes of spacing d decreases when θ increases. The useful energy range being limited by the maximum voltage that can be applied to the X-ray tube, a given lattice will generate more diffraction lines in this range for $\theta = 7°$ than for $\theta = 5°$. On the contrary, the larger angle can shift some of the lines corresponding to large d values into the energy range where they are superseded by the intense L fluorescence lines of the actinides. The spectra obtained at either angle are thus complementary information. The angle-dispersive set-up used a curved-wire position-sensitive detector of radius 150 mm (50C/R150, MBraun Co., Munich). Molybdenum radiation was used to minimize absorption in the diamonds and to have a sufficient number of diffraction lines within the 16° (2θ) angular range of the detector.

TABLE 3. Lattice parameters and volume of plutonium as a function of pressure and bulk modulus and pressure derivative of α-Pu plutonium (equations 3 to 6 according to ref. 6). Volumes are unit cell volumes (10^3 nm^3)

Pu metal monoclinic

Pressure	a (pm)	b (pm)	c (pm)	$\beta°$	Volume	V/V_0
0.0	617.89	480.59	1094.22	101.74	318.13	1.0
2.9	606.04	471.16	1073.45	102.01	299.81	0.9424
4.6	602.5	468.05	1072.72	102.10	295.79	0.9298
7.8	599.48	461.54	1065.95	102.01	288.48	0.9068
10.1	596.51	460.80	1062.54	101.93	285.75	0.8982
12.2	593.48	456.85	1060.04	101.61	281.53	0.8849
14.0	593.69	455.90	1058.46	101.72	280.51	0.8817
15.7	593.00	457.15	1050.37	101.91	278.60	0.8757
17.4	591.75	456.79	1034.70	102.12	273.45	0.8596
23.0	590.49	457.35	1021.14	102.61	269.12	0.8459
27.7	585.21	451.89	1031.80	101.63	267.26	0.8401
30.3	584.08	447.89	1031.60	101.56	264.40	0.8311
32.8	585.04	447.92	1022.98	101.38	262.80	0.8261
34.6	581.52	448.57	1022.14	101.41	261.36	0.8215
37.5	580.23	446.70	1017.98	101.60	258.46	0.8124

High pressure phase ($P6_3/m$); atom positions for Pu1 are 0.666, 0.333, 0.25 and for Pu2 are 0.2, 0.333, 0.25

Pressure	a, b (pm)	c (pm)	Volume	V/V_0
43.6	564.08	445.85	122.86	0.7724
46.6	559.62	445.87	120.93	0.7603
52.0	554.12	444.80	118.28	0.7436
55.0	543.67	449.30	115.01	0.7230
62.0	537.77	445.51	111.58	0.7015

Equation	B_0 (GPa)	B_0'
1: Birch	42	18
2: Murnaghan	49	11
3: universal	43	14
4: H0L	44	15
5: H1L	40	16
6: general, MVL-(MNL)	43	15

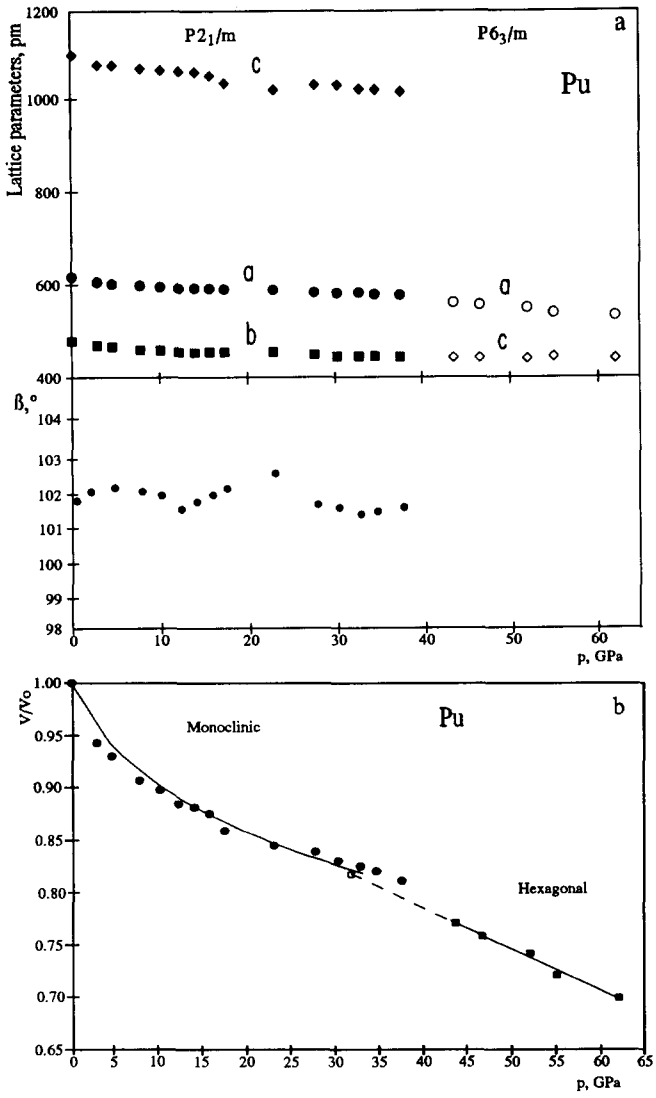

Fig. 6. Lattice parameters and relative volume of plutonium as a function of pressure: (a) lattice parameters a, b, c, β for the monoclinic phase and a, c for the hexagonal phase; (b) relative volume (□, high pressure phase on releasing pressure).

3. Results and discussion

The plutonium metal was studied at room temperature up to 62 GPa. No indication for chemical reaction of the sample (*e.g.* oxide formation) was observed in the diffraction spectra and under the microscope.

Several samples of the same batch of plutonium metal were studied, most in the energy-dispersive mode and one in the angle-dispersive mode with the position-sensitive detector. The results of the different runs were in good agreement, although variations in relative intensities were observed. These are thought to be due to the sample size (of the order of 10 μg) which is not sufficient to guarantee completely random distribution of crystallites. Non-statistical distribution of crystallite orientations may also be at the origin of deviations from theoretical intensities that are observed for a few of the diffraction lines.

As an example, Fig. 1 shows the variation in interplanar distances for a sample which was taken up to 59 GPa in the energy-dispersive mode. The figure illustrates that new peaks appear above 40 GPa, but that most of the interplanar distances vary rather continuously around this pressure. Figure 2 shows a diffraction spectrum of monoclinic α-Pu at 30 GPa. Examples of spectra of the high pressure phase at 55 and 62 GPa are given in Fig. 3. Diffraction data of the high pressure phase for 55 and 62 GPa are given in Tables 1 and 2.

These diffraction data do not fit the h.c.p. structure proposed by Akella *et al.* [3] because the latter structure does not explain four weak to medium intensity diffraction lines (marked by an asterisk in Tables 1 and 2) that appear in most of our spectra. We propose instead another hexagonal structure which can be derived from the monoclinic α-Pu structure by slight shifts of the atomic positions and can be seen as a distortion of an h.c.p. cell:

$$a_{hex} = a_{mon}$$

$$b_{hex} = (1/4)(2c_{mon} - a_{mon})$$

$$c_{hex} = b_{mon}$$

A projection of the proposed structure along the c axis is shown in Fig. 4. The shaded area indicates how an h.c.p. cell has to be distorted to yield the proposed cell. The relative intensities are subject to slight changes inside the range of existence of the high pressure phase up to 62 GPa, which indicates that the atomic positions are still changing in this pressure range.

The space group is $P6_3/m$ (no. 176) with atoms in special positions 2d (2/3, 1/3, 1/4) and 6h (x, y, 1/4 with $x = 0.2$, $y = 0.333$), $Z = 8$. Only the point symmetry of the position 2d changes to 6, whereas the other atoms still have the point symmetry m. The lattice constants are $a = 543.7$ pm, $c = 449.3$ pm, $c/a = 0.826 = 1.653/2$, at 55 GPa, and $a = 537.8$ pm, $c = 445.5$ pm, $c/a = 0.828 = 1.657/2$, at 62 GPa.

The relationship between α-Pu and the high pressure structure is visualized in Fig. 5. On the basis of these structures, Table 3 and Figure 6 show lattice parameters and volume as a function of pressure. The volume decreases by 1%–2% at the phase transition. It is noteworthy that the volume of the high pressure phase exhibits an approximately linear decrease with pressure, indicating a value of the pressure derivative B'_0 close to zero. The transformation to a hexagonal cell is completed at 47 GPa. On pressure release, the high pressure phase was conserved down to about 32 GPa.

Table 3 also shows the results of fitting the pressure–volume data to different equations of state. The

agreement between the results applying different equations is remarkable. This allows us to adopt average values of $B_0 = 43(2)$ GPa and $B'_0 = 15(2)$.

4. Conclusion

In the present work we have described a hexagonal high pressure phase of plutonium which is formed from monoclinic α-Pu around 40 GPa. As outlined in Section 1, a low symmetry structure such as that of monoclinic plutonium is, according to a widely accepted although not rigorously proven correlation, taken as a strong indication of f itinerancy. Along the same lines, a hexagonal structure, having relatively high symmetry, should be correlated with more localized f electrons. According to this simple scheme, the degree of itinerancy should decrease at the monoclinic to hexagonal transition.

The situation found in plutonium parallels that in cerium and samarium where the monoclinic high pressure phase transforms to a more symmetric body-centred tetragonal structure with increasing pressure [7–9]. It seems difficult to explain this increase in symmetry by a loss of itinerancy of the 5f electrons. The present results, and the results obtained on cerium and samarium, show that the correlation between degree of symmetry and degree of itinerancy is more complicated than previously thought.

With the preceding actinide, neptunium, we have performed high pressure X-ray diffraction studies up to 52 GPa [10] and did not detect a phase transition in this pressure range. However, the present study on plutonium suggests that the neighbouring metal neptunium could well exhibit a phase transition at a pressure somewhat higher than 52 GPa. It thus seems useful to extend the study of the compression of neptunium to higher pressures.

Acknowledgments

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