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Solid State Communications 133 (2005) 169–172
solid state communications
www.elsevier.com/locate/ssc

A high pressure distorted α-uranium (*Pnma*) structure in plutonium

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Received 6 September 2004; received in revised form 13 October 2004; accepted 18 October 2004 by A.K. Sood
Available online 2 November 2004

Abstract

Under pressure many rare earths and actinide metals transform to α-U type structure or its lower symmetry distorted forms. We have reinterpreted the diffraction data of Dabos et al. for Pu [S. Dabos et al. J. Alloys Compd. 190 (1993) 237] and find that an Am IV type distorted α-U structure in *Pnma* space group can explain its high pressure phase. The structures of both the high pressure Am IV type phase and α-Pu, the 0.1 MPa phase, are shown to have a distorted hcp topology. The upturn in the atomic volume of Pu at 0.1 MPa can also be rationalized on the basis of this proposal.

PACS: 61.50.Ks; 61.66.Pu; 62.50.+p; 64.70.Kb

Keywords: A. Pu; C. Structure; D. 5f Electrons; D. Phase transition; E. High pressure

The ambient temperature α-phase of plutonium metal crystallizes in a monoclinic structure with 16 atoms in a cell of space group $P2_1/m$ [1]. On heating to its melting point of 913 K, it exhibits five more phases [2]. However, under high pressure, only one phase transition has been reported in literature. Akela et al. alluded to a monoclinic to hcp transition under pressure in a publication on Th in 1988 [3]. However, Dabos et al. [4], in a study up to 62 GPa, showed that α-Pu transforms at 37 GPa to a hexagonal structure in space group $P6_3/m$ with $Z=8$. In this paper, I reinterpret the data of Dabos et al. and find that the structure of this high pressure phase can be assigned to a four atom distorted α-U structure type as found in Am IV under pressure and propose this to be its correct description.

α-U is an orthorhombic structure of the uranium metal at ambient conditions with space group, *Cmcm* having four atoms in 4c Wyckoff positions (000,1/2,1/2,1/2 ±(0,*y*,1/4)). The value of *y* is ~0.1 [5]. Under pressure, this structure has been found to occur, so far, in rare earths, Ce, Pr, Nd and the actinide, Pa [6–8]. A distorted form of this structure, in space group *Pnma* with four atoms at 4c sites (±(*x*,1/4,*z*)) occurs in Am from 16 GPa [9] and in an alloy of AmCm from 46 GPa [10]. Another form of the distorted α-U type structure in space group $P2_12_12_1$ has recently been seen to occur in Pr metal from 147 GPa [11]. Systems with α-uranium and these low symmetry type structures are regarded as having all the f-electrons participating in bonding and are less compressible compared to their preceding phases.

Dabos et al. [4] did X-ray diffraction studies under pressure on α-Pu by employing energy dispersive (ESD) technique up to 62 GPa, with one run in the angle dispersive mode using a position sensitive detector (PSD) having a 2θ range of only 16°. They have given in their paper the data for *d*-spacings and intensities only at 55 and 62 GPa. The comparison of the displayed diffraction patterns with those of Am-IV phase given by Lindbaum et al. [9] shows a one to one correspondence in the observed powder peaks (Fig. 1) and we were able to index all the Bragg peaks at 55 and 62 GPa to this structure. The fitted lattice constants at 55 GPa are $a\approx4.70$, $b\approx4.49$ and $c\approx2.76$ Å. These may be compared with the values: $a=5.093$, $b=4.679$ and

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doi:10.1016/j.ssc.2004.10.022

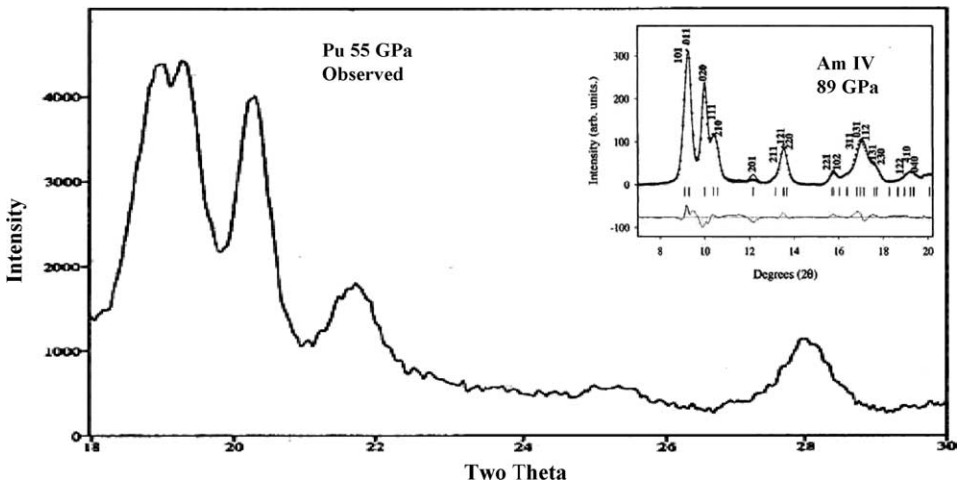

Fig. 1. A comparison of the observed diffraction pattern of Pu at 55 GPa [4] with that of Am IV at 89 GPa [9] shown as inset. Pu data is with Mo radiation while $\lambda = 0.3738$ Å for Am.

$c = 3.028$ Å for Am IV at 17.6 GPa [9]. Table 1 displays the observed and calculated d-spacings. The agreement between the two is excellent. Similar agreement was found for the data at 62 GPa. Since, we do not know the operating parameters of the X-ray generator in the experiments by Dabos et al., we could not calculate the intensities for the energy dispersive case. However, in Table 1, we give these for the angle dispersive mode. A good match could be obtained for the parameters $x \approx 0.45$ and $z \approx 0.105$ for the PSD data. The ESD intensity data also showed good qualitative agreement with the calculated ones (i.e., strong and weak observed reflections are calculated to be so). It may be also noted that the observation of the (201) peak rules out the α-U type structure.

Table 1
Observed and calculated diffraction date for *Pnma* structure of Pu at 55 GPa

d_{obs}(Å)		$h\,k\,l$	d_{cal} (Å)	I_{obs}		I_{cal}
ESD	PSD			(ESD 7°)	(PSD)	
2.352	2.40	1 0 1	2.380	100	95	100
	2.36	0 1 1	2.351		100	64
		2 0 0	2.352			56
2.243	2.25	0 2 0	2.245	38	90	76
2.087	2.10	1 1 1	2.103	30	30	15
		2 1 0	2.082	44		42
1.779	1.79	2 0 1	1.789	9	5	10
1.655		2 1 1	1.662	48	26	31
	1.64	1 2 1	1.633			69
1.625		2 2 0	1.623			39
1.396		2 2 1	1.399	15		10
1.359		3 0 1	1.362			7
1.314		0 3 1	1.316	100		11
1.304		3 1 1	1.304			24
1.270		1 1 2	1.270			45
		2 3 0	1.262			9
1.139		1 2 2	1.140	34		3
		4 1 0	1.137			17
1.129		0 4 0	1.122			9
1.040		4 2 0	1.041	7		1
		3 0 2	1.035			8
1.015		1 4 1	1.015	21		14
		2 4 0	1.013			8
		3 1 2	1.010			8
1.001		3 3 1	1.008			10