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Crystal Chemical Studies of the 5*f*-Series of Elements. XVII. The Crystal Structure of Neptunium Metal

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On the basis of powder diffraction patterns neptunium metal is found to be orthorhombic. The unit cell containing eight atoms has dimensions $a_1 = 4{\cdot}723 \pm 0{\cdot}001$, $a_2 = 4{\cdot}887 \pm 0{\cdot}002$, $a_3 = 6{\cdot}663 \pm 0{\cdot}003$ Å. The calculated density is $\varrho = 20{\cdot}45 \pm 0{\cdot}03$ g.cm.$^{-3}$. The space group is *Pmcn*, and the atomic positions are:

$$4 \text{ atoms in } \pm(\tfrac{1}{4}, y_1\, z_1)\ (\tfrac{1}{4}, \tfrac{1}{2}-y_1, z_1+\tfrac{1}{2}) \text{ with } y_1 = 0{\cdot}208 \pm 0{\cdot}006,\ z_1 = 0{\cdot}036 \pm 0{\cdot}006; \text{ and}$$

$$4 \text{ atoms in } \pm(\tfrac{1}{4}, y_2, z_2)\ (\tfrac{1}{4}, \tfrac{1}{2}-y_2, z_2+\tfrac{1}{2}) \text{ with } y_2 = 0{\cdot}842 \pm 0{\cdot}006,\ z_2 = 0{\cdot}319 \pm 0{\cdot}006\,.$$

The structure can be regarded as a heavily deformed cubic body-centered structure. The deformation is such that the coordination number is reduced from eight to four, the bond length being 2·60–2·64 Å. The four short bonds are of covalent type and have a strength about halfway between a single and a double bond.

It is concluded that there is at most one 5*f*-electron per atom in neptunium metal.

Neptunium metal was first prepared by Sherman Fried in 1945 (Fried, 1945, p. 6; Fried & Davidson, 1949). The preparation, which was on the 50 μg. scale, was made by the reaction of barium vapor on NpF_3 at 1200° C. Fried made two density measurements and obtained values of 17·9 and 17·6 g.cm.$^{-3}$. This writer obtained very weak X-ray diffraction patterns of Fried's preparation. The quality of the patterns was, however, too poor to justify attempts at interpretation.

Preparations of neptunium metal on the 1 mg. scale were later made by Westrum & Eyring (1951). These workers determined the melting point as 640±1° C. They report the density to be 19·5±0·5 g.cm.$^{-3}$. Individual density determinations ranged from 19·2 to 20·1 g.cm.$^{-3}$, except for one metal sample which gave values of 16·9 and 17·4 g.cm.$^{-3}$. X-ray diffraction examination of the preparations of Westrum & Eyring was made by D. Templeton who observed only the diffraction lines of NpO.

During recent months new preparations of neptunium metal on the 0·5 mg. scale have been carried out by James C. Wallman. The results presented in this paper have been obtained using Wallman's preparations.

Experimental difficulties

It is difficult to get good X-ray diffraction patterns of small samples of neptunium metal. The linear absorption coefficient is very high for Cu *Kα* radiation (about $7{\cdot}5 \times 10^3$ cm.$^{-1}$), and because of the complexity of the pattern it was not feasible to use radiation of shorter wave length and hence of smaller resolving power. Since the reductions were carried out high above the melting point, the resulting metal samples were in the form of nearly spherical globulets. As a consequence of the high absorption only a very small fraction of such a globulet contributes to the X-ray diffraction patterns. In order to improve the intensity of the pattern it was therefore necessary greatly to increase the surface area of the sample. To do so by filing was clearly out of the question because of the oxidation difficulties in so small a sample. However, a large increase in surface area, and a corresponding increase in the diffraction intensity, was attained by flattening the globulets into thin disks (Zachariasen, 1952).

The metals of the 5*f*-elements oxidize quite readily in air at room temperature. In a span of minutes a coating of the monoxide has formed and grown so thick that the X-rays do not penetrate the layer. For this reason (and also to minimize the risk of losing precious samples and to keep radioactive substances isolated as a health measure) the metal preparations were contained in thin-walled, flat-bottomed glass capillaries.

The data given below were obtained using a sample consisting of five flattened globulets each weighing about 100 μg. The surfaces were carefully scraped free of oxide films immediately before the sample was placed in a capillary, evacuated and sealed. The radiation used was Cu *K* radiation filtered through nickel foil. Home-made cameras of 9 cm. and 19 cm. diameter of Bradley–Jay type with van Arkel mounting were used.

Except for the great improvement in quality, the X-ray diffraction patterns were the same as obtained with Fried's preparations in 1945. The sample was singularly free of NpO, the three strongest diffraction lines being barely visible.

Table 1 gives the observed intensities and sine squares for all diffraction lines up to $\sin^2\theta = 0{\cdot}600$.

Table 1. *Diffraction data for neptunium metal*

	$\sin^2\theta$		Intensity	
$H_1H_2H_3$	Calc.	Obs.	Obs.	Calc.
011	0·0382	—	—	0
110	0·0514	—	—	0·03
002	0·0534	—	—	0·07
111	0·0648	0·0654	20	1·21
012	0·0782	0·0792	30	2·34
102	0·0800	—	—	0·22
020	0·0994	0·1004	18	1·64
112	0·1048	0·1058	90	8·00
200	0·1064	0·1077	45	4·00
021	0·1128	0·1139	10	1·04
121	0·1394	0·1406	30	2·96
211	0·1446	—	—	0
013	0·1450	0·1453	8	1·04
022	0·1528	0·1526	12*	0·54
202	0·1598	—	—	0·14
113	0·1716	—	—	0
122	0·1794	—	—	0·01
212	0·1846	0·1859	45	4·68
220	0·2058	0·2077	35	3·28
004	0·2138	—	—	0·19
221	0·2192	0·2208	30	2·08
023	0·2196			0·60
031	0·2370	—	—	0·15
014	0·2386	—	—	0
104	0·2404	0·2420	45	6·34
123	0·2462	0·2482	8	0·96
130	0·2502	0·2523	25	1·50
213	0·2516			2·08
222	0·2592	0·2611	8	1·08
131	0·2636	0·2653	45	4·50
310	0·2641			0·03
114	0·2652			2·08
032	0·2770	—	—	0·07
311	0·2775	0·2789	8	1·21
302	0·2927	—	—	0·22
132	0·3036	0·3051	12	1·40
024	0·3132	—	—	0·40
312	0·3175	0·3195	100	8·00
204	0·3202	—	—	0·38
223	0·3260	0·3269	8	1·20
124	0·3398	0·3402	30	4·00
231	0·3434	—	—	0·30
033	0·3438	0·3457	30	4·28
214	0·3450	—	—	0
321	0·3521	0·3532	25	2·96
015	0·3588	—	—	0·22
133	0·3704	—	—	0·14
232	0·3834	—	—	0·14
313	0·3843	—	—	0
115	0·3854	—	—	0·03
322	0·3921	—	—	0·01
040	0·3974	—	—	0·03
041	0·4108	0·4118	8	0·46
224	0·4196	0·4204	8	0·80
400	0·4254	0·4271	30	4·00
025	0·4334	0·4391	35	1·92
141	0·4374			5·28
034	0·4374			1·06
233	0·4502	0·4512	70	8·56
042	0·4508			1·54
304	0·4531	0·4545	70	6·34
323	0·4599	0·4618	18	0·96
125	0·4600			3·68
330	0·4629	0·4643	15	1·50
411	0·4636			0
134	0·4640			0·64
215	0·4652			0·44
331	0·4763	0·4789	55	4·50
142	0·4774			2·20
314	0·4779			2·08
402	0·4788			0·14
006	0·4810			1·17
412	0·5036	0·5066	45	4·68
240	0·5038			0·06
016	0·5058			3·76
106	0·5076	—	—	0·46
332	0·5163	0·5188	18	1·40
241	0·5172			0·92
043	0·5176			1·10
420	0·5248	0·5262	25	3·28
116	0·5324	—	—	1·12
421	0·5382	0·5412	25	2·08
225	0·5398			3·84
234	0·5438	0·5443	18	2·12
143	0·5452	—	—	0·01
324	0·5525	0·5533	25	4·00
242	0·5572	0·5583	30	3·08
035	0·5576			0·54
413	0·5704	0·5729	12	2·08
422	0·5782	0·5807	8	1·08
026	0·5804			0·56
333	0·5831	—	—	0·14
135	0·5842	—	—	0·03
206	0·5874	0·5884	8	2·34
315	0·5981	—	—	0·03

* Coincidence with the 220-line of ThO_2. Traces of this substance, the crucible material, were present in the sample.

An additional forty resolved α_1 diffraction lines have been recorded in the range $0{\cdot}600 < \sin^2\theta < 0{\cdot}985$.

Interpretation of the diffraction pattern

All attempts to fit the observed sine squares in a reasonable manner to a cubic, hexagonal or tetragonal quadratic form failed. Accordingly it was next assumed that the quadratic form was of orthorhombic type. The assumption proved to be valid in as much as indexing of the pattern succeeded. A trial-and-error method developed by the writer during the war and used successfully on a great many unknown orthorhombic diffraction patterns led to the solution.

The resulting quadratic form is

$$\sin^2\theta = 0{\cdot}02659H_1^2+0{\cdot}02484H_2^2+0{\cdot}01336H_3^2\,.$$

The constants are based upon measurements for α_1 lines in the back-reflection region. Using $\lambda = 1{\cdot}5405$ Å for the Cu $K\alpha_1$ wave-length, one finds the following values for the periods of the orthorhombic lattice (at 20° C.):

$$a_1 = 4{\cdot}723\pm0{\cdot}001,\ a_2 = 4{\cdot}887\pm0{\cdot}002\,,$$
$$a_3 = 6{\cdot}663\pm0{\cdot}003\ \text{Å}\,.$$

The experimental density of $19{\cdot}5\pm0{\cdot}5$ g.cm.$^{-3}$ reported by Westrum & Eyring corresponds to 7·6 atoms per unit cell. Since the directly measured values are apt to be too low, it seems safe to assume 8 atoms in the orthorhombic unit cell. The calculated density (using 237·0 for the atomic weight of the neptunium isotope used) is $\varrho = 20{\cdot}45\pm0{\cdot}03$ g.cm.$^{-3}$.

It is seen from Table 1 that the translation lattice is primitive. One also notes, however, that, except at small scattering angles, most diffraction lines may be interpreted as reflections from two or more lattice planes. It is further seen that there are many absences which cannot be associated with space-group extinctions. Under these circumstances the proposed indexing of the diffraction pattern should be treated with skepticism unless and until the observed intensities can be accounted for.

Because of the paucity of uniquely indexed prism reflections it was difficult to extract information about the space-group symmetry. It was observed, however, that reflections $(0H_2H_3)$ occurred with H_2, H_3 and H_2+H_3 odd, and that reflections $(H_1H_2H_3)$ and (H_1+2,H_2,H_3) apparently had the same structure factor. These observations led to the conclusion that there are reflection planes normal to the X axis and that the neptunium atoms are lying in these planes. Holohedral symmetry was assumed, and the assumption is justified by the results obtained. Since the experimental data were incapable of yielding conclusive information as to the nature of the symmetry planes normal to the Y and Z axes, one was faced with the formidable task of seeking a structure based upon a space group in the set *Pm*--. It proved possible to eliminate, one by one, all of the space groups of this set except *Pmcn*.

The only remaining structure based upon holohedral symmetry is accordingly:

$$\begin{aligned}&4 \text{ atoms Np(I)} \quad \text{in } \pm(\tfrac{1}{4}, y_1, z_1),\ (\tfrac{1}{4}, \tfrac{1}{2}-y_1, z_1+\tfrac{1}{2})\ ,\\ &4 \text{ atoms Np(II)} \quad \text{in } \pm(\tfrac{1}{4}, y_2, z_2),\ (\tfrac{1}{4}, \tfrac{1}{2}-y_2, z_2+\tfrac{1}{2})\ .\end{aligned}$$

Preliminary parameter values were obtained with the aid of reflections (H_1H_20) and (H_10H_3) in which the variables are partly separated. The final values were arrived at by calculating the intensities for all reflections in the entire angular range for many different sets of parameter values. The parameter values obtained as the final set in the successive approximations are:

$$\begin{aligned}y_1 &= 0{\cdot}208\pm0{\cdot}006 \qquad & z_1 &= 0{\cdot}036\pm0{\cdot}006\\ y_2 &= 0{\cdot}842\pm0{\cdot}006 \qquad & z_2 &= 0{\cdot}319\pm0{\cdot}006\end{aligned}$$

Because of the peculiar nature of the sample it was impossible to say much about the proper form of the absorption correction beyond the fact that it is a slowly varying function showing a monotonic decrease with increasing scattering angle. For this reason it is not feasible to compare intensities except for neighboring reflections. In calculating intensities it will accordingly suffice to use the simplified form

$$I \propto |F|^2 p/f^2$$

in which all factors varying continuously with scattering angle have been omitted. F/f is the structure factor, the atomic scattering power being treated as a constant, and p is the multiplicity factor. The intensities as calculated from the above equation are given in the last column of Table 1.

Discussion of the results

In describing the structure deduced for neptunium metal it is useful to point out at the outset that the atomic arrangement shows some similarity to that of a body-centered cubic structure. Were neptunium metal cubic body-centered the edge of the unit cube would be $a_c = 3{\cdot}375$ Å, on the assumption that this fictitious cubic form had the same density as the orthorhombic form. This cubic body-centered structure can be described by means of a cell of dimensions $\sqrt{2}.a_c$, $\sqrt{2}.a_c$, $2a_c$, and may be thought of as having space group symmetry *Pmcn* with the eight atoms per cell in the same two sets of fourfold positions as were found for the real form of neptunium metal. The following constellation shows the extent to which the neptunium metal structure may be regarded as a deformed cubic body-centered structure.

	Actual structure	Body-centered cubic structure
a_1	4·723 Å	4·773 Å
a_2	4·887 Å	4·773 Å
a_3	6·663 Å	6·750 Å
y_1	0·208	$\frac{1}{4}$
z_1	0·036	0
y_2	0·842	$\frac{3}{4}$
z_2	0·319	$\frac{1}{4}$

The deformation from cubic symmetry is considerable, and this is also illustrated in the following list of neighbor atoms and interatomic distances in the actual neptunium metal structure:

Np(I)–1 Np(II) = 2·60 Å
–1 Np(II) = 2·63 Å
–2 Np(II) = 2·64 Å
–1 Np(II) = 3·06 Å
–2 Np(I) = 3·16 Å
–2 Np(I) = 3·33 Å
–2 Np(II) = 3·35 Å

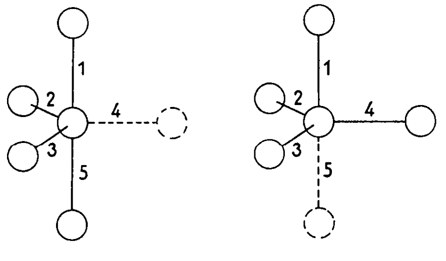
Np(II)–1 Np(I) = 2·60 Å
–1 Np(I) = 2·63 Å
–2 Np(I) = 2·64 Å
–1 Np(I) = 3·06 Å
–2 Np(I) = 3·35 Å
–2 Np(II) = 3·44 Å
–4 Np(II) = 3·53 Å

Were neptunium metal cubic body-centered each neptunium atom would have eight neighbors with Np–8 Np = 2·923 Å.

A comparison with the metals immediately preceding neptunium in the periodic system shows (see next section) that there is at most one 5*f*-electron in neptunium metal, and that hence six (and possibly as many as seven) electrons per atom may participate in bond formation. In NpF_6 the Np–F distance is about 2·10 Å. Using 0·72 Å for the covalent radius of fluorine, the single-bond radius of hexavalent neptunium is 1·38 Å. If all six electrons per atom participate in the formation of the four shortest bonds the expected bond length is 2·76 Å − 0·11 Å = 2·65 Å, using Pauling's empirical formula, as compared to the observed value of 2·63 Å. The conclusion seems inescapable that each of the four short bonds is a covalent bond and has a strength about halfway between a single and a double bond.

The covalent character of the four short bonds having been established the question arises as to the directions of these bonds. As a convenient description it may be said that the bonds from a neptunium atom to its four neighbors are approximately directed towards four of the five corners of a trigonal bipyramid. However, these four corners are not the same for the bonds of a Np(I) and a Np(II) atom, as shown in Fig. 1(*a*) and 1(*b*). The bond angles (the numbering of the bonds referring to Fig. 1) are:

Bonds	Np(I)	Np(II)	α-U
1–2	84½°	90½°	90°
1–3	84½°	90½°	90°
1–4	—	79°	—
2–3	127°	127°	127°
3–4	—	116°	—
4–2	—	116°	—
2–5	89½°	—	90°
3–5	89½°	—	90°



(*a*) (*b*)

Fig. 1.

It is interesting to note that the configuration and bond angles in α-U structure are very nearly the same as for a Np(I) atom.

In many instances it is possible to correlate bond directions with directions of maximum overlapping of atomic wave functions. It is difficult to see that there is valid theoretical justification for interpreting observed bond directions for atoms near the end of the periodic system in this simple manner. Under these circumstances it seems advisable to refrain from proposing 'interpretations' which do not rest on reasonably sound theoretical basis. It seems certain, however, that there are six to seven bonding electrons per atom, four of them giving rise to directed σ-bonds and two or three being involved in π-bond formation, thus giving a considerable amount of double-bond character to the σ-bonds.

It is clear that a satisfactory explanation of the observations on the basis of the band theory of metals cannot be obtained with the present state of development of this theory for metals with several valence electrons per atom. It may be stated, however, that there is a prominent Brillouin zone (corresponding to the strong reflections (104), (131), (312)) containing six to seven electronic states per atom.

Metallic crystal radius

The metallic radius of neptunium in the idealized cubic body-centered structure is 1·46 Å, which corresponds to a value of 1·50 Å for the standard coordination number twelve. It is of interest to compare this radius with the experimentally determined values for the metallic radius of the preceding elements in the periodic system. Results are available for thorium, protactinium and uranium.

Thorium has the cubic close-packed structure with a radius of 1·79 Å. Protactinium has a unique structure with coordination number ten and a radius of 1·61 Å, giving a corrected radius of 1·63 Å for twelve coordination. The α-U structure is a distorted hexagonal close-packed configuration. There are four short bonds, two of length 2·76 Å and two of 2·82 Å. Further bond lengths are 3·27 Å (4 bonds) and 3·36 Å (4 bonds). In an idealized close-packed structure with the same density as α-U the crystal radius would be 1·54 Å. The structure of β-U is tetragonal, but has not been determined with sufficient accuracy to give reliable data for the interatomic distances. γ-U is cubic body-centered with U–8U = 3·01 Å (at room temperature), thus leading to the same radius of 1·54 Å for twelve coordination as the α form.

The rapid decline in metallic radius with atomic number from thorium to protactinium to uranium shows that in these metals there are respectively four, five and six valence electrons. The radius of 1·50 Å for neptunium is consistent either with six valence

Table 2. *Comparison of metallic radii*

Rb	2·48 Å	Cs	2·67 Å	Fr	(2·80) Å
Sr	2·15 Å	Ba	2·22 Å	Ra	(2·35) Å
Y	1·80 Å	La	1·87 Å	Ac	(2·03) Å
Zr	1·60 Å	Hf	1·59 Å	Th	1·79 Å
Nb	1·46 Å	Ta	1·46 Å	Pa	1·63 Å
Mo	1·39 Å	W	1·39 Å	U	1·54 Å
Tc	1·36 Å	Re	1·37 Å	Np	1·50 Å

Table 3. *Metallic radii*

	Number of valence electrons					
Number of 5*f* electrons	1	2	3	4	5	6
0	Fr 2·80	Ra 2·35	Ac 2·03	Th 1·79	Pa 1·63	U 1·54
1	—	—	—	Pa 1·76	U 1·61	Np 1·52
2	—	—	—	U 1·74	Np 1·60	Pu 1·51
3	—	—	U 1·92	Np 1·72	Pu 1·59	Am 1·50
4	—	—	Np 1·89	Pu 1·70	Am 1·58	—
5	—	—	Pu 1·86	Am 1·69	—	—
6	—	—	Am 1·84	—	—	—

electrons and one 5*f*-electron or with seven valence electrons and no electron in the 5*f* subshell. As far as the metal goes, neptunium is thus to be considered either as a uranide element or as a homologue of technetium and rhenium. Table 2 compares the metallic radii of the series Fr–Np with other series in the periodic system. The radii given for Fr, Ra, Ac are extrapolated values. Table 3 gives the metallic radii to be expected for the elements Fr–Am for various numbers of 5*f* electrons.

It is interesting to note that Pa, α-U, β-U and Np all exhibit unique crystal structures. The formation of four strong bonds of covalent character observed for neptunium and the low-temperature form of uranium may be typical for the trans-protactinic metals.

Dr James C. Wallman is sincerely thanked for the loan of his metal preparations, and so is Miss Anne Plettinger for having taken the diffraction patterns.

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Crystal Chemical Studies of the 5*f*-Series of Elements. XVIII. Crystal Structure Studies of Neptunium Metal at Elevated Temperatures

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The orthorhombic room-temperature form of neptunium metal (α-Np) is found to be stable up to 278° C. Unit-cell dimensions and thermal expansion coefficients in the range 20°–278° C. are given.

At 278±5° C. α-Np transforms into β-Np, which is tetragonal. The tetragonal modification is stable up to about 540° C. At 313° C. the dimensions of the unit cell containing four atoms are

$$a_1 = 4\cdot897 \pm 0\cdot002,\ a_3 = 3\cdot388 \pm 0\cdot002\ \text{Å}\,,$$

and the calculated density at this temperature is $\varrho = 19\cdot36$ g.cm.$^{-3}$.

The atomic positions in the β-Np structure are:

2 Np(I) in $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$; 2 Np(II) in $(\frac{1}{2}, 0, u)$, $(0, \frac{1}{2}, \bar{u})$ with $u = 0\cdot375 \pm 0\cdot015$. As in α-Np, each atom forms four short bonds.

There is strong indication of a transition point at about 550° C. Above this point the metal seems to be cubic body-centered (γ-Np) with $a = 3\cdot52$ Å, and this phase is presumably stable up to the melting point at 640° C.

The structural relationships between the three forms of neptunium metal are discussed.

Introduction

The crystal structure of neptunium metal at room temperature was described in a recent paper (Zachariasen, 1952). The present paper gives the results of crystal structure studies of neptunium metal in the range from room temperature to the melting point, which is at 640° C (Westrum & Eyring, 1951). Owing to serious oxidation difficulties, the results applying to the range of 550°–640° C. are given with some reservation, and it is planned to re-examine this temperature range as soon as a new metal sample becomes available.

Experimental procedure

The sample of neptunium metal used in this investigation is the same as was described in connection with the crystal structure determination of the room-temperature form. The sample, which had been prepared by James C. Wallman, weighed about 0·5 mg, and consisted of several flattened pieces of metal. The metal pieces were contained in evacuated thin-walled glass capillaries. Fused silica served as capillary material in all experiments carried out at 350° C. and higher.

The diffraction patterns were all taken with Cu *K* radiation filtered through nickel foil. The high-temperature camera described by Buerger, Buerger & Chesley (1943) was used. The calibration curve relating temperature at the sample to power input to the heating coil was obtained using Jay's (1933) data for the thermal expansion of quartz and the known transition points for NH_4ClO_4 (236° C.), $KClO_4$ (297° C.), and quartz (575° C.).

Since more than one form of neptunium metal was found to exist, the room-temperature form will be designated as the α form.