electrons and one 5f-electron or with seven valence electrons and no electron in the 5f 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 5f 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 5f-Series of Elements. XVIII. Crystal Structure Studies of Neptunium Metal at Elevated Temperatures

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(*Received* 13 *June* 1952)

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

$$a_1 = 4{\cdot}897 \pm 0{\cdot}002,\quad a_3 = 3{\cdot}388 \pm 0{\cdot}002\ \text{Å}\,,$$

and the calculated density at this temperature is $\varrho = 19{\cdot}36$ 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 $u = 0{\cdot}375 \pm 0{\cdot}015$. 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 $a = 3{\cdot}52$ 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.

Observations on α-neptunium

The α form of neptunium metal was found to be stable up to 278° C., at which temperature it transforms into the β form to be discussed in the next section. The transition point may be given as 278±5° C.

The results on the unit-cell dimensions and calculated density of the orthorhombic α-Np are given in Table 1.

Table 1. *Unit-cell dimensions and calculated density of* α-Np

Temp. (°C.)	a_1 (Å)	a_2 (Å)	a_3 (Å)	ϱ (g.cm.$^{-3}$)
20	4·723±0·001	4·887±0·002	6·663±0·003	20·45
212	4·746±0·002	4·909±0·003	6·704±0·004	20·13
275	4·752±0·002	4·920±0·003	6·722±0·004	20·01

The values for room temperature are those reported earlier. The results of Table 1 correspond to the following values for the linear coefficients of thermal expansion in the 20°–275° C. range:

$$\alpha_{100} = 24\times10^{-6},\ \ \alpha_{010} = 25\times10^{-6},\ \ \alpha_{001} = 34\times10^{-6}\ .$$

The crystal structure of β-neptunium

The β phase of neptunium metal is stable in the range from 278° C. to at least 530° C. There is strong indication that the β form changes into a γ form at about 550° C.

X-ray diffraction data for β-Np, as obtained at 313° C., are listed in Table 2. The observed sine squares correspond to a primitive tetragonal translation group. The unit-cell dimensions and calculated density at various temperatures are shown in Table 3. The density is calculated on the basis of four atoms per unit cell. The values for 20° C. are obtained by extrapolation on the assumption that the expansion coefficients would be the same in the range 20°–282° C. as in the interval 282°–425° C.

The linear coefficients of thermal expansion for the interval 282°–425° C. are

$$\alpha_{100} = \alpha_{010} = 64\times10^{-6},\ \ \alpha_{001} \approx 0\ .$$

All reflections H_1H_20 are absent unless H_1 and H_2 are both even. This observation, together with the conclusion that the unit cell must contain four atoms, shows that the atomic positions must be:

$$2\,\text{Np(I)}\ \ \text{in}\ \ (0, 0, 0),\ (\tfrac{1}{2}, \tfrac{1}{2}, 0)\ ,$$
$$2\,\text{Np(II)}\ \ \text{in}\ \ (\tfrac{1}{2}, 0, u),\ (0, \tfrac{1}{2}, \bar{u})\ .$$

The space-group symmetry is $P42_1$.

The single parameter value is readily determined, particularly with the aid of the observed intensities in the back-reflection region. The value of u is

$$u = 0{\cdot}375\pm0{\cdot}015\ .$$

Table 2. *Diffraction data for* β-Np *at* 313° C.

$H_1H_2H_3$	$\sin^2\theta$ Calc.	$\sin^2\theta$ Obs.	Observed intensity*	$\lvert F\rvert^2p$
001	0·0516	—	—	0·1
101	0·0764	0·0769	*w*−	2·0
200	0·0991	0·1009	*w*	8·0
111	0·1012	0·1027	*m*	11·6
201	0·1507	—	—	0·4
211	0·1755	0·1773	*vw*	4·0
220	0·1982	0·2005	*w*	8·0
002	0·2064	0·2089	*vvw*	1·0
102	0·2312	0·2306	*vw*	4·0
221	0·2498	—	—	0·4
112	0·2560	0·2585	*vw*	4·0
301	0·2746	0·2777	Trace	2·0
311	0·2994	0·3018	*ms*	23·2
202	0·3055	—	—	4·0
212	0·3303	0·3323	*w*−	8·0
321	0·3737	0·3768	*vw*−	4·0
400	0·3964	0·3991	*vw*	8·0
222	0·4046	—	—	4·0
302	0·4294	0·4321	*vvw*	4·0
401	0·4480	—	—	0·4
312	0·4542	0·4563	*vw*	8·0
003	0·4644	—	—	2·9
411	0·4728	0·4747	*vw*−	4·0
103	0·4892	—	—	2·0
420	0·4955	0·4988	*w*+	16·0
331	0·4976			11·6
113	0·5140	—	—	0·4
322	0·5285	0·5305	*vw*+	8·0
421	0·5471	—	—	0·7
203	0·5635	0·5670	*vw*+	11·6
213	0·5883	0·5911	*vvw*	4·0
402	0·6028	0·6038	*vw*−	4·0
412	0·6276	0·6301	*vw*	8·0
332	0·6524	0·6560	*vvw*+	4·0
223	0·6626	0·6636	*vw*+	11·6
501, 431	0·6710	—	—	2·0+4·0
303	0·6874	—	—	2·0
511	0·6958	0·6979	*m*	23·2
422	0·7019	—	—	8·0
313	0·7122	—	—	0·7
521	0·7701	—	—	4·0
323	0·7865	—	—	4·0
440	0·7928	0·7950	*vw*	8·0
004	0·8256	—	—	0
502, 432	0·8258	0·8280	*w*	4·0+8·0
441	0·8444	—	—	0·4
104	0·8504	—	—	0
512	0·8506	0·8511	20	8·0
403	0·8608	0·8620	30	11·6
114	0·8752	0·8753	50	16·0
413	0·8856	0·8861	15	4·0
600	0·8920	0·8939	50	8·0
531	0·8940			23·2
333	0·9104	—	—	0·4
204	0·9247	—	—	0
522	0·9249	0·9249	16	4·0
601	0·9436	—	—	0·4
214	0·9495	—	—	0
423	0·9599	0·9601	100	23·2
611	0·9683	—	—	0·7
620	0·9910	0·9911	80	16·0

* Intensities are given as *s*=strong, *m*=medium, *w*=weak and *vw*=very weak except in the back-reflection region where the 2:1 ratio for the well-resolved $\alpha_1\alpha_2$-doublet permits quantitative intensity estimates.

The last column of Table 2 gives the values of the quantity $|F|^2p$ as calculated from the structure given above. F is the structure factor and p the multiplicity. The atomic scattering power was treated as a constant. All factors varying continuously with

Table 3. *Unit-cell dimensions and calculated density for* β-Np

Temp. (°C.)	a_1 (Å)	a_3 (Å)	ϱ (g.cm.$^{-3}$)
282	4·883±0·002	3·389±0·002	19·47
300	4·889	3·388	19·42
313	4·897	3·388	19·36
360	4·910	3·390	19·25
425	4·928	3·390	19·11
480	4·954	3·387	18·91
500	4·966	3·387	18·82
20	(4·799)	(3·388)	(20·16)

scattering angle having been omitted, calculated values of $|F|^2p$ should be compared with observed intensities only for neighboring reflections.

As in α-Np, each Np atom in the β-Np structure forms four strong bonds. The lengths of these and of secondary bonds are:

	20° C.	313° C.	500° C.
Np(I)–4 Np(II)	2·72 Å	2·76 Å	2·79 Å
–4 Np(II)	3·20	3·24	3·26
–2 Np(I)	3·39	3·39	3·39
–4 Np(I)	3·39	3·46	3·51
Np(II)–4 Np(I)	2·72	2·76	2·79
–4 Np(I)	3·20	3·24	3·26
–2 Np(II)	3·39	3·39	3·39
–4 Np(II)	3·50	3·56	3·61

The four strong bonds must be regarded as essentially covalent in character. A reasonable value for the single-bond radius of neptunium (with six valence electrons) is 1·40 Å. The 'strength' of each of the four short bonds, as defined by Pauling (1947), is then 1·35.

The four Np(II) atoms closest to a Np(I) atom are at the corners of a deformed tetrahedron, the bond angles being 102° and 125° (at 313° C.). The four close Np(I) atoms about a Np(II) atom lie at the corners of a square of edge 3·46 Å with the Np(II) atom 1·27 Å above the square so that the bond angles are 78°.

The probable existence of a third form of neptunium metal

Preliminary experiments strongly indicate the existence of a body-centered cubic form of neptunium metal (γ-Np) at temperatures immediately below the melting point. The transition point β-Np to γ-Np seems to be at about 570° C.

By the time the experiments at about 600° C. were performed, the surface of metal pieces of the original sample had become covered with a fairly thick layer of NpO which largely prevented the X-rays from reaching the underlying metal. With one single exception, all of the observed diffraction lines correspond to the lines of NpO. However, some of the NpO lines appear with greater than normal intensity. These abnormally strong NpO lines and the single line which cannot be ascribed to NpO correspond to the diffraction lines of a body-centered cubic lattice with $a = 3{\cdot}52$ Å (at 600° C.). The unit-cell edge of NpO at 600° C. is $a = 4{\cdot}979 \pm 0{\cdot}003$ Å and is thus $\sqrt{2}$ times as large as that of the cubic body-centered structure.

Clearly the evidence for the existence of γ-Np is not sufficiently convincing to merit universal acceptance. Further experiments in the interval 550°–640° C. will therefore be carried out as soon as a new metal sample becomes available.

The unit-cell edge of γ-Np extrapolated to 20° C. is about $a = 3{\cdot}43$ Å, and the extrapolated value of the interatomic distance is thus Np–8 Np = 2·97 Å. The calculated density at 600° C. is $\varrho = 18{\cdot}0$ g.cm.$^{-3}$, and at 20° C. $\varrho = 19{\cdot}3$ g.cm.$^{-3}$.

Structural relationships between the neptunium metal phases

The crystal structure of α-Np was described in a recent paper. The orthorhombic unit-cell contains eight atoms. The space group is *Pmna*, and the atomic positions are:

$$4\,\mathrm{Np(I)}\ \text{in}\ \ \pm(\tfrac{1}{4}, y_1, z_1),\ (\tfrac{1}{4}, \tfrac{1}{2}-y_1, z_1+\tfrac{1}{2})\,,$$
$$4\,\mathrm{Np(II)}\ \text{in}\ \ \pm(\tfrac{1}{4}, y_2, z_2),\ (\tfrac{1}{4}, \tfrac{1}{2}-y_2, z_2+\tfrac{1}{2})\,,$$

the parameter values being

$$y_1 = 0{\cdot}208 \pm 0{\cdot}006, \quad z_1 = 0{\cdot}036 \pm 0{\cdot}006\,,$$
$$y_2 = 0{\cdot}842 \pm 0{\cdot}006, \quad z_2 = 0{\cdot}319 \pm 0{\cdot}006\,.$$

Both the β-Np and the γ-Np structures can be described in terms of a cell containing eight atoms and resembling that of α-Np. When this is done, the atomic positions of all three forms may be described in a uniform way by means of the four parameters y_1, z_1, y_2, z_2 already used in describing the α-Np structure. The following comparison illustrates the degree of relationship between the three structures.

	α-Np (20° C.)	β-Np (313° C.)	γ-Np (600° C.)
a_1 (Å)	4·723	4·897	4·85
a_2 (Å)	4·887	4·897	4·85
a_3 (Å)	6·663	6·776	6·86
a_1:a_2:a_3	0·966:1:1·363	1:1:1·384	1:1:$\sqrt{2}$
y_1	0·208	0·250	0·250
z_1	0·036	0	0
y_2	0·842	0·750	0·750
z_2	0·319	0·313	0·250

In view of the close similarity between the β and γ forms it might have been expected that the axial ratio and the atomic positions of β-Np would approach those of γ-Np as the temperature increases towards the β–γ transition point. This is not the case. Thus the a_3:a_1 ratio deviates more from the ideal value of $\sqrt{2}$ at 500° C. than it does at 282° C.

It is of interest to note that the tendency to form four strong bonds persists to within 100° C. of the melting point. The directions of these four short bonds differ markedly for the two kinds of neptunium atoms and from the α structure to the β structure. Hence it is idle speculation to try to correlate the bond directions with directions of maximum overlapping of atomic wave functions.

The interatomic distances in the neptunium metal structure are so short (and the densities so high) that one must assume at least six valence electrons and at most one 5*f* electron.

Miss Anne Plettinger and Dr Stanley Siegel gave valuable aid in calibrating the high-temperature camera and Miss Plettinger also by taking some of the diffraction patterns of neptunium metal. Sincere thanks are due Dr James C. Wallman for the use of his metal samples and Dr Sherman Fried for having made the exceptionally thin-walled capillary of fused quartz.

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Acta Cryst. (1952). **5**, 667

On the Structure of the Paratungstate Ion

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(*Received* 10 *April* 1952)

The structure of the complex ion in $5Na_2O.12WO_3.28H_2O$ has been determined, using a new vector-algebraic method. The formula of the ion, $W_{12}O_{46}^{20-}$, has no direct relation to the analytical formula, which would require a $W_{12}O_{41}^{10-}$-ion for the paratungstate to be a neutral salt.

Crystals

The formula of sodium paratungstate has recently been determined as $5Na_2O.12WO_3.28H_2O$. The symmetry is triclinic, space-group $P\bar{1}$. Constants and estimated errors are:

$$\alpha=86^\circ\,0'\pm15',\ \beta=113^\circ\,20'\pm15',\ \gamma=94^\circ\,0'\pm15',$$
$$a=11{\cdot}77\pm0{\cdot}03,\ b=22{\cdot}19\pm0{\cdot}05,\ c=12{\cdot}44\pm0{\cdot}02\ \text{Å}\,.$$

There are 24 tungsten atoms in the cell (Saddington & Cahn, 1950). Single crystals of this paratungstate were prepared using the same procedure as the authors quoted. The crystal used for the X-ray investigation was prismatic with *c* as prism axis. Weissenberg photographs were taken with Cu *K* radiation and the *c* axis as rotation axis. Relative $|F|^2$ values were calculated from the estimated intensities with the help of Lu's curves (Lu, 1943). An appreciable absorption made the intensity values less valid. It was observed that reflexions with $h+k$ odd had very small intensities (the sum of their contributions was only 1·5% of the sum of all intensities). The point positions of the heavy tungsten atoms thus can be considered as corresponding to a *C*-centered unit cell, the larger dimensions being due to Na^+ and H_2O. The calculation of the three-dimensional Patterson function $P(x, y, z)$ then can be reduced to one-quarter of the unit cell. The functions $P(x, y_{n/60}, z)$ were computed on the X-RAC analogue computer for $y_n = 0\text{–}15$, and the structure was derived by a special method.

Method of structure determination

The method of structure determination is based on the relations imposed upon the Patterson function if the structure has a centre of symmetry. Fig. 1 shows the vectors obtained for two twofold positions. They evidently form a parallelogram, where the vectors between equivalent atoms are the diagonals. The vector equations are

$$A+B=a,\ A-B=b\,.$$

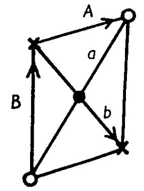

Fig. 1. Vector parallelogram produced by two twofold positions with a centre of symmetry.

Each pair of two twofold positions will give rise to such a parallelogram in the Patterson function.

This fact indicates a simple method of analyzing the $P(x, y, z)$ vectors. Their components are tabulated and all possible vector sums are calculated. If the resulting vector sum is equal to one of the vectors in $P(x, y, z)$, the first of the vector equations is evidently fulfilled. It then remains to see if the corresponding vector difference is also found in $P(x, y, z)$.