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On the crystal structure of protactinium metal.

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The structure of protactinium has been determined by Zachariasen (1952) from powder data. The crystallographic description of this structure is that it is tetragonal with $a_1 = 3{\cdot}925$, $a_3 = 3{\cdot}238$ Å, space group $I4/mmm$, two atoms per unit cell. In this structure each atom has eight neighbors at 3·212 and two at 3·238 Å. Zachariasen pointed out that if the axial ratio had an ideal value of $\sqrt{\frac{2}{3}} = 0{\cdot}817$ instead of the observed value of 0·825, each metal atom would have ten neighbors at exactly the same distance.

Table 1. *Diffraction data*

	Observed		Calculated					
					Pa			
			PaO_2	PaO	Tetragonal		Orthorhombic	
	I	$\sin^2\theta$	$\sin^2\theta$	$\sin^2\theta$	*hkl*	$\sin^2\theta$	*HKL*	$\sin^2\theta$
1	*vw*	0·0599	0·0588					
2	*ms*	0·0731		0·0725				
3	*w*	0·0787	0·0784		110	0·0772	020 200	0·0757 0·0767
4	*vs*	0·0975		0·0966	101	0·0953	111	0·0957
5	w^+	0·1567	0·1568		200	0·1544	220	0·1525
6	*wm*	0·1945		0·1933				
7	*vvw*	0·2174	0·2156					
8	*vw*	0·2293			002	0·2268	002	0·2302
9	*s*	0·2511			211	0·2497	131 311	0·2471 0·2492
10	*ms*	0·2679		0·2658				
11	*vw*	0·2917		0·2899				
							040	0·3029
12	*ms*	0·3064			112 220	0·3040 0·3088	022 400, 202	0·3059 0·3070
13	*m*	0·3841		0·3866	202 310	0·3812 0·3860	240 420, 222	0·3796 0·3827
14	w^-	0·4051			301	0·4041	331	0·4006
15	*w*	0·4599		0·4590				
16	w^+	0·4841		0·4832				
17	*w*	0·536			222	0·536	042 402	0·533 0·537
18	*w*	0·550			103	0·549	151	0·550
19	w^+	0·557			321	0·559	511, 113	0·556
20	w^-	0·580		0·580				
21	*m*	0·613			312	0·613	440, 242 422	0·610 0·613
					400	0·618		
22	*w*	0·652		0·652				
							060	0·681
					330	0·695	600	0·691
23	*s*	0·704			213	0·703	351	0·703
24		0·712			411	0·713	133, 531 313	0·708 0·710
25	w^-	0·772		0·773	420	0·772	260 620	0·758 0·766
26	*wm*	0·842		0·846	402	0·844	442	0·840
27	w^-	0·860			303	0·858	333	0·861
28	*vw*	0·872		0·870				
29	vw^-	0·905			004	0·907	062	0·911
30	*w*	0·921			332	0·922	602, 004	0·921

The ideal structure may also be described as stacking of closest packed hexagonal layers, the second layer lying over the first such that each atom in it touches two atoms in the first layer (rather than three as in cubic or hexagonal closest packing). The third layer then lies directly over the first, the stacking sequence thus being $[AB]A\ldots$ Because of the relation of the first layer to the second the symmetry of the structure is not hexagonal, but tetragonal. The structure may, nevertheless, be described with a hexagonal unit cell, with atoms at (0, 0, 0) and ($\frac{1}{2}$, 0, $\frac{1}{2}$). The corresponding orthohexagonal cell is in reality the face centered tetragonal cell related in the usual way to the ideal body centered tetragonal cell described by Zachariasen. Denoting the axes of the face centered cell as A_i and those of the body centered cell as a_i, the following relations obtain for the ideal structure:

$$A_1=a_1-a_2,\quad A_2=a_1+a_2,\quad A_3=a_3;$$
$$a_1=a_2=\sqrt{\tfrac{3}{2}}a_3,\quad A_1=A_2=\sqrt{3}A_3\,.$$

Zachariasen found that a deviation of about 1% from the value $\sqrt{\frac{2}{3}}$ for the ratio a_3/a_1 was required by his powder data. This distortion gives each atom eight closest neighbors at the corners of a square prism plus two more at a slightly longer distance above and below the centers of the squares. I wish to point out that the ideal structure may be distorted in a different way which agrees almost* as well with the powder data. If the value of A_2, rather than A_3, is changed from the ideal value, then the closest packing within each hexagonal layer is preserved, but the distance between layers is changed slightly. The symmetry of this second structure is orthorhombic, space group *Fmmm*, four atoms per unit cell, $A_1=5{\cdot}566$, $A_2=5{\cdot}603$, $A_3=3{\cdot}214$ Å ($A_1/A_3=\sqrt{3}$). The comparison of the values of $\sin^2\theta$ calculated (λ for Cu $K\alpha=1{\cdot}5418$ Å) for this structure with the observed values, and with those calculated for the tetragonal structure is shown in Table 1.

Even though the tetragonal structure is in better agreement with the data,† there would appear to be no strong basis for rejecting the orthorhombic structure altogether.* The orthorhombic structure predicts a rather more diffuse diffraction pattern, but the situation is complicated by the fact that the preparation from which the data were recorded was contaminated by two other phases which Zachariasen identified as PaO and PaO_2. His observed and calculated values of $\sin^2\theta$ for these substances are also included in Table 1.

In the orthorhombic structure each atom has six neighbors at 3·214 Å and four at 3·235 Å, the average distance being 3·222 Å. The ligancy is thus different from that in the tetragonal structure. The volume per atom is 25·1 Å³. There is an interesting relationship between the orthorhombic structure and the structure proposed by Zachariasen (1955) for γ plutonium. If the successive closest packed layers are stacked not in the sequence $[AB]A\ldots$ but in the sequence $[ABCD]A\ldots$ a different orthorhombic structure results, space group *Fddd*, 8 atoms per unit cell. The structure of γ plutonium has this symmetry, but with distortions (at 235 °C.) within each layer so that each atom has four neighbors at 3·288 Å and two at 3·159 Å, and with a contraction of the interlayer distance which reduces the four bond distances to atoms in adjacent layers to 3·026 Å.

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* See, however, the note which follows this one.

† If attention is centered on the first ten lines due to Pa only, Nos. 8, 9, 12, 14, 17, 18, 19, 21, 23, and 24, then the average difference between $\theta_{\text{calc.}}$ and $\theta_{\text{obs.}}$ is 0·07° for the tetragonal structure and 0·10° for the orthorhombic structure; the largest differences are 0·18° and 0·26° respectively.

* In the following note, Prof. Zachariasen reports the results of his reexamination of the photographs. He finds observed values of $\sin^2\theta$ which are smaller in an irregular fashion by up to 16×10^{-4} from those originally reported, and attributes the differences to film shrinkage. He then uses lattice constants for PaO and PaO_2 to correct, for absorption and sample size effects, the observed values for $\sin^2\theta$ for five lines which correspond to single Pa reflections. These corrected values differ by up to 25×10^{-4} from the original. Since the values of $\sin^2\theta$ for two of these lines (8 and 14) as calculated for the orthorhombic structure, differ from the new, corrected observed values of $\sin^2\theta$ by 36×10^{-4} and 22×10^{-4}, Prof. Zachariasen rejects the orthorhombic structure as incorrect. I prefer to think that the question of which structure is correct for Pa is open (with a bias, of course, in favor of the tetragonal one).

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On the crystal structure of protactinium metal.

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In the preceding note Donohue points out that the (110) planes of the tetragonal structure reported for protactinium metal show a nearly hexagonal distribution of atoms. This is true, as a direct consequence of the fact that the ratio $a_3:a_1$ is only about one per cent greater than $\sqrt{\frac{2}{3}}$.

The tetragonal body-centered structure can, of course, be described as tetragonal face-centered with

$$A_1=A_2=\sqrt{(2)}a_1,\quad A_3=a_3\,,$$

in which case (100) and (010) become the pseudo-hexagonal planes.

Donohue suggests that the protactinium structure may be orthorhombic, pseudo-hexagonal and pseudo-tetragonal, such that the ratio $A_1:A_3$ is exactly $\sqrt{3}$, but $A_1\neq A_2$. In other words it is proposed that the initially pseudo-hexagonal lattice plane (100) is made precisely hexagonal, whereas (010) remains pseudo-hexagonal. Although there is no obvious reason why the orthorhombic structure proposed by Donohue should be energetically more stable