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 Å^3. 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.

By W. H. ZACHARIASEN, *Department of Physics, University of Chicago and Argonne National Laboratory, Chicago 37, Illinois, U.S.A.*

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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 than the simpler tetragonal structure reported by the writer, the suggestion put forth by Donohue is an interesting one. The writer has therefore reexamined the original films to test whether or not the experimental data can be interpreted in the manner proposed by Donohue.

The particular film (♯5480), upon which the original paper of the writer was based, has been remeasured three times, and a second film (♯5473), only slightly less good, was remeasured twice. Special care was taken to ascertain that there was no shrinkage of the, by now thoroughly 'aged', films during each independent set of measurements. No such film shrinkage was observed.

Table 1 gives the sine squares obtained for film ♯5480 with the lines numbered as in the original paper. Lines no. 24–30 were more difficult to measure precisely and have not been included. No corrections have been applied to the data of Table 1. The glancing angles are measured to better than ±0·03° so that the sine squares of Table 1 are accurate to $\pm 6\times10^{-4}$ apart from systematic errors due to absorption and sample size effects. Film ♯5473 gave identical results within the experimental error.

Table 1. $\sin^2\theta$ *for film* ♯5480

Line no.	Obs.	PaO and PaO_2	$\Delta\times10^4$
1	0·0589	0·0588	1
2	0·0726	0·0723	3
3	0·0778	—	—
4	0·0963	—	—
5	0·1557	—	—
6	0·1940	0·1929	11
7	0·2168	0·2158	10
8	0·2278	—	—
9	0·2500	—	—
10	0·2663	0·2653	10
11	0·2904	0·2893	11
12	0·3054	—	—
13	0·3831	—	—
14	0·4043	—	—
15	0·4594	0·4582	12
16	0·4838	0·4823	15
17	0·5352	—	—
18	0·5497	—	—
19	0·5575	—	—
20	0·5801	0·5787	14
21	0·6121	—	—
22	0·6520	0·6511	9
23	0·7034	—	—
24	0·7110	—	—

At large angles there is excellent agreement with the sine square values reported in the original paper; but at smaller angles the new values are systematically smaller than the old. This is probably due to film shrinkage error in the original measurements which were made on freshly developed film.

Lines no. 1 and 7 are due only to PaO_2 for which a precise value $a=5{\cdot}505\pm0{\cdot}001$ Å is known (Sellers *et al.*, 1954). Similarly lines no. 2, 6, 10, 11, 15, 16, 20 and 22 are due only to PaO. The uncorrected sine squares give $a=4{\cdot}957\pm0{\cdot}003$ Å for PaO (using $\lambda=1{\cdot}542$ Å for the unresolved α_1, α_2 doublet), but there is a small, systematic increase in a with glancing angle as a consequence of absorption and sample size effects. The extrapolation to $\theta=90°$ gives $a=4{\cdot}965\pm0{\cdot}003$ Å. The sine squares calculated with this latter value and with $a=5{\cdot}505$ Å for PaO_2 are shown in Table 1. The correction Δ to be applied to the observed sine squares is obviously zero at $\sin^2\theta=0$ and $\sin^2\theta=1$, and the PaO and PaO_2 data of Table 1 provide the experimental points for obtaining Δ as function of $\sin^2\theta$, with the aid of which the observed sine squares for the other lines in the diffraction pattern can be corrected.

Some lines in the film, nos. 8, 9, 14, 18, 19 correspond to single Pa reflections (on the basis of the tetragonal indexing). These lines are indeed sharper than neighboring other lines. The observed sine squares for these reflections as obtained from the remeasurements of films ♯5473 and 5480 are listed in Table 2 together with the corrected mean values. The resulting cell dimensions for Pa are

$$a_1=3{\cdot}932\pm0{\cdot}003\text{ Å},\quad a_3=3{\cdot}238\pm0{\cdot}003\text{ Å}\,.$$

The last column of Table 2 lists the sine squares calculated with these values.

Table 2. $\sin^2\theta$ *for single* Pa-*lines*

Line no.	Observed Film ♯ 5473	Observed Film ♯ 5480	Mean Corrected	*HKL*	Calculated
8	0·2275	0·2278	0·2268	002	0·2268
9	0·2498	0·2500	0·2489	211	0·2489
14	0·4039	0·4043	0·4028	301	0·4027
18	0·5498	0·5497	0·5484	103	0·5486
19	0·5581	0·5575	0·5565	321	0·5565

Thus the more careful remeasurements of the films have led to slight revisions in the values for the lattice constants, but otherwise confirmed the original tetragonal structure.

Table 3 shows the same lines as in Table 2, now indexed on the basis of the equivalent face-centered tetragonal cell and also according to Donohue. Since Donohue's proposed indexing presupposes a precise ratio $A_1:A_3=\sqrt{3}$, all but line 9 represent single reflections and any two reflections determine the cell dimensions. The last two columns of Table 3 give the calculated sine squares for Donohue's proposed structure, using first lines 8 and 14, and then lines 18 and 19 for the determination of the constants. Irrespective of how one proceeds, Donohue's indexing leads to discrepancies with the sine square

Table 3. *Test of orthorhombic structure*

Line no.	$\sin^2\theta$ (corr.)	Indices Tetr. F.C. Zachariasen	Indices Orthorh. F.C. Donohue	$\sin^2\theta$ (calc.) Orthorh. F.C. Donohue	
8	0·2268	002	002	(0·2268)	0·2304
9	0·2489	311=131	311≠131	0·2464, 0·2516	0·2493, 0·2470
14	0·4028	331	331	(0·4028)	0·4006
18	0·5484	113	151	0·5645	(0·5484)
19	0·5565	511=151	511=113	0·5488	(0·5565)

observations many times greater than the maximum possible error. Furthermore, line 9 is sharp and not diffuse as required by Donohue's indexing.

The writer states without reservation that the orthorhombic structure for protactinium metal proposed in the preceding note must be rejected as incorrect because it does not fit the data.

Both of the original films are, of course, available on loan from the writer's collection.

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Crystal structures of $ZrBe_5$ and $Zr_2\,Be_{17}$.*

By ALLAN ZALKIN, RAY G. BEDFORD and DONALD E. SANDS,
Lawrence Radiation Laboratory, University of California, Livermore, California, U.S.A.

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An investigation of the Zr–Be system was undertaken to determine the number and compositions of the intermetallic compounds formed in this system. A variety of compositions of the elemental powders were weighed, mixed and heated to 1600 °C; these were crushed again and reheated. The resulting products were studied by X-ray diffraction powder methods using Debye–Scherrer techniques; both Cu $K\alpha$ (λ = 1·5418) and Cr $K\alpha$ (λ = 2·2909 Å) X-rays were used.

The resulting powder photographs showed four intermetallic phases. Two of these phases had been previously reported, $ZrBe_2$ (Nielsen & Baenziger, 1954) and $ZrBe_{13}$ (Baenziger & Rundle, 1949); two new phases hitherto unreported were found in the intermediate composition range, $ZrBe_5$ and Zr_2Be_{17}.

The structure of $ZrBe_5$ was determined from its powder pattern. The cell volume and the resulting intermetallic distances indicated the above formula. A powder pattern of a sample prepared using the above stoichiometry indicated a fairly pure $ZrBe_5$ phase. The Zr_2Be_{17} structure was determined from the close similarity of its powder patterns with those of Nb_2Be_{17}.

$ZrBe_5$

$ZrBe_5$ has a hexagonal cell with dimensions

$$a = 4{\cdot}564 \pm 0{\cdot}002, \quad c = 3{\cdot}485 \pm 0{\cdot}002\ \text{Å}\ .$$

There is one formula unit per unit cell. The X-ray density is 3·60 g.cm.$^{-3}$. The structure has the $CaZn_5$ type structure (Haucke, 1940). The space group is D^1_{6h}–$P6/mmm$ (*International Tables for X-ray Crystallography*, 1952). The atomic positions are:

1 Zr	(*a*)	0, 0, 0.
2 Be_{I}	(*c*)	$\frac{1}{3}, \frac{2}{3}, 0;\ \frac{2}{3}, \frac{1}{3}, 0.$
3 Be_{II}	(*g*)	$\frac{1}{2}, 0, \frac{1}{2};\ 0, \frac{1}{2}, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}.$

The interatomic distances are:

Zr–	6 Be	2·635 Å
	–12 Be_{II}	2·871
Be_{I}–	3 Zr	2·635
	– 6 Be_{II}	2·191
Be_{II}–	2 Zr	2·871
	– 4 Be_{I}	2·191
	– 4 Be_{II}	2·282

These distances are in good agreement with those found in the $ZrBe_2$ structure (Nielsen & Baenziger, 1954).

Zr_2Be_{17}

Zr_2Be_{17} has a rhombohedral cell with a = 5·694±0·005 Å and α = 83·02±0·02°. The triply primitive hexagonal cell has a = 7·548±0·004, c = 10·997±0·010 Å and c/a = 1·457. There are 3 formula units in the hexagonal cell. The X-ray density is 3·081 g.cm.$^{-3}$. This structure is isomorphous with the Nb_2Be_{17} type structure (Zalkin, Sands & Krikorian, 1959). The space group is $R\bar{3}m$.

Table 1 shows the first 15 lines of powder patterns of these two structures. Cr $K\alpha$ radiation were used to obtain these patterns. In the case of Zr_2Be_{17}, the hexagonal indices are used.

Table 1. *Powder patterns for* $ZrBe_5$ and Zr_2Be_{17}

$ZrBe_5$			Zr_2Be_{17}		
I	*hkl*	*d* (Å)	*I*	*hkl*	*d* (Å)
s−	100	3·953	*m*	101	5·619
m	001	3·485	*m*−	102	4·208
s+	101	2·614	*s*	110	3·773
m+	110	2·282	*w*+	003	3·666
m+	200	1·976	*w*+	201	3·132
s	111	1·909	*w*	202	2·809
w	002	1·743	*s*	113	2·629
m	201	1·719	*w*	104	2·534
m−	102	1·594	*w*+	211	2·411
m−	210	1·494	*w*	212	2·253
m	112	1·385	*m*−	300	2·179
m+	211	1·373	*w*	204	2·104
w−	300	1·318	*w*−	105	2·085
m	202	1·307	*m*+	220	1·886
m+	301	1·232	*m*+	303	1·873

w = weak; *m* = medium; *s* = strong.

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