Apart from the hydrogen bonds there are some intermolecular distances shorter than the van der Waals contacts. At Se there are two carbon contacts close to 3·72 Å, which is only slightly below the sum of the van der Waals radii, 3·85 Å. There is also a carbon–carbon intermolecular contact of 3·64 Å, which is slightly below the sum of the van der Waals radii for carbon (3·70 Å).

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The Structure of γ-Uranyl Dihydroxide, $UO_2(OH)_2$*

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γ-Uranyl dihydroxide, $UO_2(OH)_2$, is monoclinic, space group $P2_1/c$ with $a=5\cdot560$ (3), $b=5\cdot522$ (3), $c=6\cdot416$ (3) Å, and $\beta=112\cdot71$ (9)°. The observed density is 5·55 g.cm^{-3} and the computed value is 5·56 g.cm^{-3} for two formula weights. The structure was solved with 317 independent reflections recorded with an automatic diffractometer utilizing both double filter and $\theta/2\theta$ scan techniques. A least-squares refinement based on F gave an R value of 6·1 %. The configuration about a uranium atom is a distorted octahedron composed of two O(1) (uranyl) and four O(2) (secondary) oxygen atoms. Each O(2) atom is shared between two octahedra leading to puckered sheets of secondary oxygen atoms distributed within the *bc* plane. Each O(1) oxygen atom is associated with only one octahedron within a layer but is hydrogen-bonded to an O(2) oxygen atom in an adjacent layer. The structure is very similar to the orthorhombic β-$UO_2(OH)_2$. Postulated coordinates for the β modification at 280°C indicate that the β and γ forms can be related by a shear involving one-half of the hydrogen atoms. Grinding experiments demonstrate the existence of a shear effect.

Introduction

Three crystallographic modifications of uranyl dihydroxide, $UO_2(OH)_2$, have been prepared from the uranium trioxide–water system. The crystal structure of the α form was reported by Taylor (1971). Roof, Cromer & Larson (1964) published the structure of the β modification and subsequently, Bannister & Taylor (1970) reported on the results of a study of the structure and anisotropic thermal expansion of β-$UO_2(OH)_2$. A neutron powder diffraction study by Taylor & Hurst (1971) confirmed the hydrogen locations proposed in the β form by Roof *et al.* and in the α modification by Taylor. The preparation of a third form of uranyl dihydroxide and the identification of its symmetry and cell dimensions from an X-ray powder pattern has been described by Cordfunke & Debets (1964) who referred to this phase as the ε modification. As the existence of only three forms of uranyl dihydrate has been confirmed, the present phase will be regarded as γ-$UO_2(OH)_2$. The structure of γ-$UO_2(OH)_2$ and its relation to β-$UO_2(OH)_2$ will be presented here.

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Experimental studies

Crystals of γ-$UO_2(OH)_2$ were prepared by hydrolysis of uranyl nitrate solution with $La(OH)_3$ at 85°C (Hoekstra & Siegel, 1972). Cell dimensions, refined by diffractometer measurements, were found to be: $a=5·560$ (3), $b=5·522$ (3), $c=6·416$ (3) Å and $\beta=112·71$ (9)°. These dimensions are virtually identical with values reported by Cordfunke & Debets. The observed density is 5·55 g.cm^{-3} leading to two formula weights and a computed density of 5·56 g.cm^{-3}. Reflections $h0l$ with $l=2n$, and $0k0$ with $k=2n$ are observed, indicating space group $P2_1/c$. For this space group, the two uranium atoms can be placed in the special positions 000 and $0\frac{1}{2}\frac{1}{2}$ and the oxygen atoms in two sets of the fourfold general positions.

The linear absorption coefficient based on Mo $K\bar{\alpha}$ ($\lambda=0·71069$ Å) is 552 cm^{-1}, therefore necessitating the use of a small crystal in order to minimize absorption effects. A rhomb with edges ranging from 0·003 to 0·006 cm in length was found to be satisfactory and accordingly was used for data collection.

The stationary-crystal stationary-counter method, using balanced filters (Y–Zr), was compared with the 2θ scan technique (utilizing a Zr filter only) over a range of intensities for those reflections with $k+l=2n$. No substantial difference was found so that data were collected initially using the double-filter technique. However, the 2θ scan was considered desirable for the weaker reflections and for these cases the data were collected at a scan rate of 2°/min. A diffraction maximum was recorded on a strip chart recorder, line width and background carefully assessed, and the integrated intensity evaluated with a planimeter. Reflections too weak to measure were given intensity values corresponding to a lower limit of evaluation. These intensities were then normalized relative to the remaining reflection data to give a total of 317 observations to be used in the analysis. Data were collected on a G. E. Automatic XRD 490 for scattering angles up to $2\theta=50°$. The intensities were corrected for absorption using the Wehe, Busing & Levy (1962) single-crystal absorption correction program. Lorentz and polarization corrections were applied in the usual manner.

Structure factors were computed with uranium positions at 000 and $0\frac{1}{2}\frac{1}{2}$ and a least-squares refinement carried out with the Busing, Martin & Levy (1962) *ORFLS* least-squares program in order to establish overall temperature and scale factors. For these calculations, the scattering curve for uranium was obtained from values given in *International Tables for X-ray Crystallography* (1962). The anomalous dispersion correction $\Delta f'=-9·19$ reported by Cromer (1965) was included in evaluating the uranium contribution. (The imaginary contribution $\Delta f''=9·09$ subsequently produced a negligible effect on the structure factors.)

A three-dimensional Fourier synthesis was then carried out using the uranium contribution to the intensities. This analysis was derived from a modified version of the Sly & Shoemaker (1960) Fourier program. The plot displayed distinct secondary peaks which could be attributed to the oxygen atoms. A difference Fourier synthesis with the uranium atoms removed showed related peak positions. A unique set of oxygen coordinates could be determined which simultaneously accounted for the intensities of the weak reflections and led as well to established configurations and U–O bond distances. The contributions of these oxygen atoms, based on the O^{2-} scattering curve of Tokonami (1965), was added to the uranium scattering to derive F_{cal} for a least-squares analysis. The final conventional reliability index R is 6·1% based on anisotropic temperature factors for uranium and isotropic factors for oxygen. However, if 13 intense reflections with high backgrounds are eliminated because of uncertainties in evaluating the true intensities, the R factor reduces to 5·1%. In this refinement, all reflections with the exception of these 13 were given unit weight. Extinction corrections were found to be without effect. The exceptionally high linear absorption coefficient and attendant errors in correcting for the absorption is the probable reason. Final coordinates and thermal parameters are presented in Table 1. Observed and computed structure factors are listed in Table 2. Bond distances and angles were computed with the Busing, Martin & Levy (1964) *ORFFE* program and are given in Table 3.

Table 1. *Position parameters and temperature factors*

Standard deviations are given in parentheses.

	U	O(1)	O(2)
x	0	0·3026 (33)	0·1716 (31)
y	0	0·1696 (34)	0·7320 (31)
z	0	0·1072 (29)	0·2955 (28)
B (Å^2)		2·66 (31)	2·29 (29)
β_{11}	0·0114 (5)		
β_{22}	0·0055 (4)		
β_{33}	0·0067 (3)		
β_{12}	−0·0005 (3)		
β_{13}	0·0070 (3)		
β_{23}	0·0002 (2)		

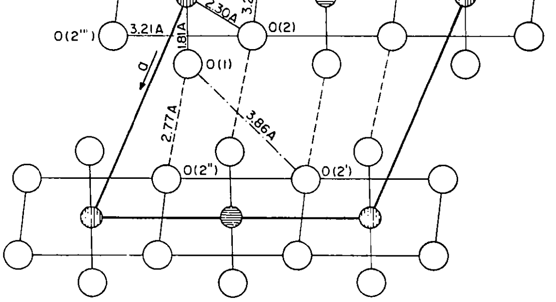

Fig. 1. Projection of the structure of γ-$UO_2(OH)_2$ in the ac plane.

Table 2. *Observed and calculated structure factors*

h	k	ℓ	F_o	F_c
0	2	0	103.3	100.7
0	4	0	110.5	105.6
0	6	0	75.7	71.1
1	0	0	140.2	160.1
1	1	0	1.9	1.8
1	2	0	119.1	125.3
1	4	0	102.8	103.1
1	5	0	7.3	9.3
1	6	0	67.7	66.4
2	0	0	101.7	101.2
2	1	0	25.8	28.9
2	2	0	128.5	132.7
2	3	0	7.9	-8.8
2	4	0	89.4	88.4
2	5	0	3.6	2.1
2	6	0	62.3	63.9
3	0	0	104.5	106.6
3	1	0	3.8	5.3
3	2	0	103.5	105.5
3	3	0	2.9	1.3
3	4	0	68.7	71.4
3	5	0	3.6	-1.0
4	0	0	84.8	86.9
4	1	0	13.2	-13.8
4	2	0	85.5	83.2
4	3	0	8.8	6.2
4	4	0	65.5	64.7
5	0	0	68.0	68.4
5	1	0	3.0	-3.4
5	2	0	64.6	64.8
5	3	0	3.3	3.9
6	0	0	62.9	59.2
6	1	0	3.3	3.4
0	1	1	131.6	162.8
0	2	1	15.8	-16.8
0	3	1	103.7	103.0
0	4	1	7.7	9.0
0	5	1	88.5	86.5
0	6	1	3.4	-2.9
1	1	1	107.0	129.1
1	2	1	8.4	-9.2
1	3	1	98.6	115.0
1	4	1	2.7	5.0
1	5	1	64.7	79.8
2	1	1	103.6	115.9
2	2	1	12.1	13.6
2	3	1	93.4	96.6
2	4	1	10.4	-7.4
2	5	1	64.0	73.3
2	6	1	3.8	2.6
3	1	1	95.1	100.6
3	2	1	2.9	1.7
3	3	1	69.7	75.8
3	4	1	3.4	-0.9
3	5	1	60.4	64.2
4	1	1	81.3	74.6
4	2	1	3.2	-3.6
4	3	1	72.5	70.8
4	4	1	3.7	3.6
5	1	1	62.6	58.8
5	2	1	3.3	1.9
5	3	1	61.5	56.8
0	0	2	119.2	123.1
0	1	2	33.6	-32.6
0	2	2	124.5	135.2
0	3	2	4.5	6.7
0	4	2	85.5	86.1
0	5	2	3.2	1.3
0	6	2	68.4	69.9
1	0	2	93.9	106.2
1	1	2	15.8	-16.5
1	2	2	100.8	117.6
1	3	2	7.3	9.9
1	4	2	79.3	89.4
1	5	2	3.2	-4.5
1	6	2	52.2	59.4
2	0	2	109.0	122.7
2	1	2	4.2	4.8
2	2	2	78.2	84.2
2	3	2	2.8	3.0
2	4	2	71.7	80.0
2	5	2	3.4	-3.7
3	0	2	95.0	98.3
3	1	2	2.8	0.5
3	2	2	69.1	70.8
3	3	2	3.1	-2.6
3	4	2	63.6	66.5
4	0	2	65.9	62.4
4	1	2	3.3	3.6
4	2	2	70.7	66.5
4	3	2	3.6	-3.1
5	0	2	56.0	48.8
5	1	2	3.6	4.1
0	1	3	113.2	112.3
0	2	3	7.1	-7.9
0	3	3	108.9	103.7
0	4	3	3.0	2.8
0	5	3	71.8	70.1
1	1	3	88.4	98.2
1	2	3	3.7	5.1
1	3	3	89.9	95.3
1	4	3	3.1	-2.5
1	5	3	59.9	63.1
2	1	3	90.9	91.1
2	2	3	2.8	1.2
2	3	3	69.5	70.5
2	4	3	3.2	0.6
2	5	3	55.0	60.2
3	1	3	71.1	72.1
3	2	3	6.9	-4.6
3	3	3	64.6	60.7
3	4	3	3.5	4.2
4	1	3	61.7	55.0
4	2	3	3.5	1.3
0	0	4	100.3	97.0
0	1	4	2.7	5.6
0	2	4	95.3	94.4
0	3	4	6.9	-6.2
0	4	4	75.3	79.6
0	5	4	4.1	3.7
1	0	4	78.0	83.0
1	1	4	11.7	13.5
1	2	4	85.8	87.0
1	3	4	3.1	-4.8
1	4	4	65.2	65.2
2	0	4	71.9	73.8
2	1	4	2.9	-2.0
2	2	4	70.1	72.6
2	3	4	3.2	0.9
2	4	4	52.3	53.4
3	0	4	59.4	56.8
3	1	4	3.9	-7.0
3	2	4	60.9	59.1
3	3	4	3.5	3.5
0	1	5	84.1	81.3
0	2	5	3.1	0.6
0	3	5	75.3	76.2
0	4	5	3.3	-0.9
1	1	5	76.4	74.6
1	2	5	3.3	4.2
1	3	5	62.3	61.1
1	4	5	5.1	-3.7
2	1	5	66.3	61.6
2	2	5	3.4	-1.5
0	0	6	75.3	69.0
0	1	6	3.3	-1.9
0	2	6	69.8	67.3
0	3	6	3.4	2.9
1	0	6	74.7	68.0
1	1	6	3.5	-0.4
1	2	6	55.3	52.6
1	1	-1	144.8	150.6
1	2	-1	16.3	-13.4
1	3	-1	118.6	113.8
1	4	-1	9.4	5.2
1	5	-1	84.1	81.7
1	6	-1	3.4	2.0
2	1	-1	120.7	119.9
2	2	-1	2.2	-0.7
2	3	-1	123.8	122.7
2	4	-1	2.9	2.0
2	5	-1	77.1	73.4
2	6	-1	3.7	0.3
3	1	-1	119.4	115.4
3	2	-1	7.6	7.4
3	3	-1	97.4	93.0
3	4	-1	3.4	-1.2
3	5	-1	72.2	72.0
4	1	-1	94.2	98.2
4	2	-1	2.9	-4.1
4	3	-1	70.9	74.1
4	4	-1	3.3	5.0
4	5	-1	63.0	65.8
5	1	-1	72.7	74.1
5	2	-1	3.1	-1.0
5	3	-1	67.3	68.3
5	4	-1	3.4	2.3
6	1	-1	57.8	59.5
6	2	-1	3.3	4.1
1	0	-2	155.5	142.7
1	1	-2	26.5	-22.7
1	2	-2	151.2	133.3
1	3	-2	5.4	6.8
1	4	-2	92.0	85.7
1	5	-2	3.2	0.6
1	6	-2	74.3	73.5
2	0	-2	122.7	117.9
2	1	-2	35.3	-31.0
2	2	-2	127.3	126.0
2	3	-2	13.9	11.9
2	4	-2	98.5	94.4
2	5	-2	3.1	-0.9
2	6	-2	67.4	64.0
3	0	-2	129.2	127.0
3	1	-2	9.2	5.3
3	2	-2	102.5	99.4
3	3	-2	8.9	4.5
3	4	-2	93.2	90.4
3	5	-2	3.4	-3.4
4	0	-2	125.6	118.2
4	1	-2	2.8	6.0
4	2	-2	82.5	81.7
4	3	-2	3.2	-2.2
4	4	-2	80.3	76.6
4	5	-2	3.8	3.3
5	0	-2	80.9	79.3
5	1	-2	3.1	1.8
5	2	-2	77.8	78.3
5	3	-2	3.4	-2.8
5	4	-2	63.2	63.9
6	0	-2	55.7	59.0
6	1	-2	3.3	3.9
6	2	-2	67.3	67.1
1	1	-3	145.4	132.5
1	2	-3	2.5	-1.2
1	3	-3	97.1	91.8
1	4	-3	3.0	3.1
1	5	-3	82.1	79.5
1	6	-3	3.4	-1.3
2	1	-3	129.4	121.8
2	2	-3	14.9	-10.4
2	3	-3	107.8	100.1
2	4	-3	3.0	7.4
2	5	-3	80.2	77.9
3	1	-3	112.6	108.1
3	2	-3	8.4	6.9
3	3	-3	104.1	99.3
3	4	-3	3.0	-2.9
3	5	-3	70.6	71.9
4	1	-3	101.7	101.4
4	2	-3	8.3	6.5
4	3	-3	82.9	81.0
4	4	-3	3.3	-2.8
4	5	-3	65.2	67.0
5	1	-3	83.8	83.5
5	2	-3	3.2	-2.7
5	3	-3	71.8	73.1
5	4	-3	3.7	4.1
6	1	-3	66.8	66.5
6	2	-3	3.6	0.2
1	0	-4	132.4	131.9
1	1	-4	4.9	6.7
1	2	-4	89.2	87.8
1	3	-4	3.0	0.9
1	4	-4	86.4	84.3
1	5	-4	3.4	-1.5
2	0	-4	143.4	124.2
2	1	-4	2.7	1.4
2	2	-4	101.5	95.5
2	3	-4	8.2	-4.7
2	4	-4	84.9	84.0
2	5	-4	3.3	6.8
3	0	-4	92.2	91.9
3	1	-4	6.5	8.0
3	2	-4	109.4	107.1
3	3	-4	2.9	-4.2
3	4	-4	83.1	79.7
3	5	-4	3.5	4.7
4	0	-4	88.2	90.6
4	1	-4	9.4	6.5
4	2	-4	97.3	95.6
4	3	-4	4.3	1.3
4	4	-4	69.4	69.8
5	0	-4	84.8	86.6
5	1	-4	5.9	-6.7
5	2	-4	79.2	79.5
5	3	-4	3.4	5.1
6	0	-4	66.2	70.9
6	1	-4	3.5	-4.7
6	2	-4	65.3	66.7
1	1	-5	90.0	93.1
1	2	-5	6.9	7.4
1	3	-5	77.8	78.9
1	4	-5	3.4	-4.5
2	1	-5	101.8	99.2
2	2	-5	2.9	-0.5
2	3	-5	73.1	79.9
2	4	-5	3.3	1.2
3	1	-5	98.4	91.7
3	2	-5	3.1	-3.1
3	3	-5	90.9	88.0
3	4	-5	7.4	4.3
4	1	-5	89.9	87.7
4	2	-5	3.1	3.6
4	3	-5	80.6	80.6
4	4	-5	3.5	0.6
5	1	-5	79.6	83.1
5	2	-5	3.3	0.9
5	3	-5	65.2	67.3
6	1	-5	63.4	70.2
1	0	-6	71.5	72.1
1	1	-6	5.7	7.2
1	2	-6	79.4	79.6
1	3	-6	3.4	-1.8
2	0	-6	79.9	84.5
2	1	-6	3.0	-1.0
2	2	-6	75.6	81.5
2	3	-6	3.3	2.6
2	4	-6	57.3	62.1
3	0	-6	87.6	85.2
3	1	-6	8.8	-9.4
3	2	-6	83.3	81.0
3	3	-6	3.3	5.2
4	0	-6	85.9	83.4
4	1	-6	3.3	-0.4
4	2	-6	75.3	76.2
4	3	-6	3.5	3.1
5	0	-6	81.5	82.9
5	1	-6	3.4	4.8
5	2	-6	64.7	68.5
1	1	-7	61.0	63.4
1	2	-7	3.4	0.8
2	1	-7	66.1	71.9
2	2	-7	3.3	2.0
3	1	-7	67.7	75.0
3	2	-7	3.4	-1.8
4	1	-7	70.9	72.1

Table 3. *Interatomic distances and bond angles*

Standard deviations are given in parentheses.

Metal-metal	
U-U	4·233 (2) Å
Within octahedron	
U——(2)O(1)	1·81 (2) Å
U——(2)O(2)	2·30 (2)
U——(2)O(2″)	2·29 (2)
O(2)—O(2‴)	3·214 (3)
O(2′)—O(2‴)	3·28 (2)
O(1)—O(2)	2·92 (2)
O(1)—O(2′)	2·94 (2)
O(1)—O(2″)	2·95 (2)
O(1)—O(2‴)	2·88 (2)
O(2)—O(2‴)-O(2′)	90·3 (8)°
O(2‴)-O(2′)—O(2″)	89·7 (8)
O(1)—U——O(2)	89·5 (8)
O(1)—U——O(2′)	90·5 (8)
O(1)—U——O(2″)	91·4 (7)
O(1)—U——O(2‴)	88·6 (7)
Interlayer	
O(1)-O(2′)	3·86 (3) Å
O(1)-O(2″)	2·77 (2)

Experimental results

A projection of the structure of γ-$UO_2(OH_2)$ in the *ac* plane is shown in Fig. 1. The configuration about a uranium atom is a distorted octahedron with U–O distances as indicated. Each O(2) (secondary) oxygen atom shares between two octahedra so that puckered sheets of secondary oxygen atoms extend within the *bc* plane. These sheets form about $x=0$ and $x=a$, thereby leading to a layered structure.

Each O(1) (uranyl) oxygen is associated with only one octahedron within a layer but is undoubtedly hydrogen-bonded to the O(2) atom of an adjacent layer. Evidence for this is threefold: (1) the *bc* plane is on or near a cleavage plane; (2) the U–O(1) distance of 1·81 Å is ~0·1 Å longer than the conventional uranium (VI)–oxygen double bond value; (3) the O(1)–O(2″) distance of 2·77 Å is a reasonable value for hydrogen bonding. The striking similarity to β-$UO_2(OH)_2$, for which the hydrogen positions have already been established, is further indication that O(1)–O(2″) (and equivalent bonds as indicated by dashed bonding directions) constitute the hydrogen bonding oxygen atoms.

It is informative to compare the structure of γ-$UO_2(OH)_2$ with that of the β modification. β-$UO_2(OH)_2$ is orthorhombic with $a=5·6438$, $b=6·2867$, and $c=9·9372$ Å. (The Bannister & Taylor values are reported here in order to relate cell size to their axial values at elevated temperatures.) A pseudo monoclinic cell may be outlined in the orthorhombic cell as shown in Fig. 2. The uranium atom at 000 of the orthorhombic cell is now the origin of the pseudo cell. The *a′* axis is one half the orthorhombic *bc* face diagonal, the *b* axis, orthorhombic, remains unchanged, and the *a* axis, orthorhombic, is now normal to the plane of the pseudo cell. Primary and secondary oxygens of the β form referred to this monoclinic cell may be compared with corresponding oxygens in the γ modification by visual comparison of Figs. 1 and 2.

If, however, the uranium atom in the $0\frac{1}{2}\frac{1}{2}$ position of orthorhombic β-$UO_2(OH)_2$ is chosen as the origin of the pseudo monoclinic cell, octahedra with slightly different orientations about each uranium atom are developed, as shown by a second octahedron at the origin composed of dot–dashed circles and bonding directions. Only one such modified octahedron is displayed in Fig. 2. Dashed lines between layers connecting primary oxygen atoms of one layer to secondary oxygens of an adjacent layer represent hydrogen bonding directions. Numerical values associated with oxygen atoms in the figure represent heights of the respective atoms above and below the plane of the drawing. Room temperature values of the coordinate positions of the β form reported by Bannister & Taylor (X-ray data) have been used in order to derive these heights. (Coordinate positions reported by Roof *et al.* lead to only slight variations.) These may be compared with the corresponding heights observed in the γ modification.

In their high temperature study of β-$UO_2(OH)_2$, Bannister & Taylor observed that up to approximately 260 °C the *b* axis increases in length, the *a* axis decreases, and the *c* axis is virtually unchanged. From 260 to 317 °C all three lattice parameters increase by similar small amounts. They interpreted the anisotropic thermal expansion in terms of thermally induced rotation of oxygen octahedra surrounding the uranium atoms. This conclusion was deduced on the basis of the thermal motions of the O(2) (secondary) oxygen atoms which are directed into open channels of the structure. The rotation of an octahedron was assumed to occur without change in shape. On this basis they were able to derive parameters for oxygen positions in what they refer to as 'the fully distorted structure'. With these values, the two possible configurations of octahedra shown at the origin of Fig. 2 become more nearly coincident, with average heights of the secondary oxygens approximately 1·40 and 1·37 Å above or below the plane of the drawing. These values fall between the 1·28 and 1·48 Å heights for the γ form. The conclusions reached by Bannister & Taylor must, of course, be verified by high temperature structural studies. However, their arguments are sufficiently cogent to warrant additional structural comparisons with the γ modification.

Fig. 3 shows the unit cell of the β form, with dimensions at 280 °C superimposed on the γ cell, and with the uranium atom at the origin of each unit cell common to both. The room temperature cell dimensions of β-$UO_2(OH)_2$ are given in parentheses. The coincidence in cell dimensions is striking; the major difference arises from the 10° increase of the β angle in the pseudo monoclinic cell. This angle is only slightly changed over the temperature range from 25 to 280 °C.

Room temperature values for bond distances in β-$UO_2(OH)_2$ are the same (within error) as those for the γ modification. If, indeed, the rotation of octahedra occur without change in shape, the configurations within a layer of both polymorphs are nearly the same and one structure is related to the other by a shear of about one ångström, together with a rearrangement of one-half of the hydrogen bonds and a slight rotation of the octahedra. It would then appear that two minima in energy exist permitting hydrogen bonding to either of two primary oxygen atoms.

Attempts to determine equilibrium conditions for the $\beta \leftrightarrow \gamma$ interchange have not been successful. As γ-$UO_2(OH)_2$ is the least dense modification of this compound [$\varrho(\alpha) = 6{\cdot}73$ g.cm^{-3}; $\varrho(\beta) = 5{\cdot}73$ g.cm^{-3}; and $\varrho(\gamma) = 5{\cdot}56$ g.cm^{-3}] it might be expected to show increased stability relative to the more dense forms at elevated temperatures. However, the thermoanalytical experiments show that the γ phase converts to β-$UO_2(OH)_2$ at approximately 125 °C and static heating experiments on the β form for four days at 100 °C have given no indication of reversibility in this reaction.

Taylor & Hurst (1971) have shown that β-$UO_2(OH)_2$ transforms to the α modification when cooled to −43 °C. We find that this transformation occurs slowly even at 0 °C and that γ-$UO_2(OH)_2$ undergoes a similar phase change. Thus, the thermal stability of the γ modification is limited to the 0–125 °C temperature interval.

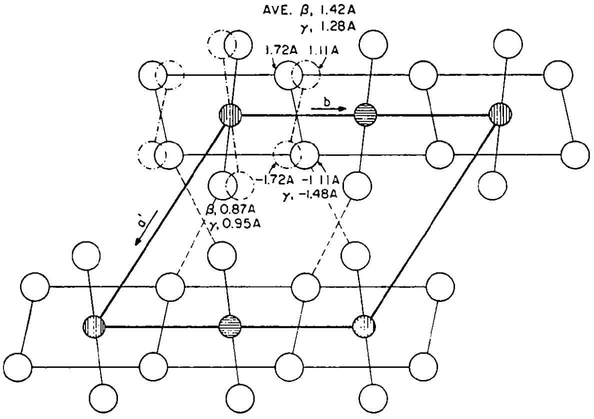

Fig. 2. Pseudo-monoclinic cell of β-$UO_2(OH)_2$ projected in the *bc* plane of the true orthorhombic cell. $a' = \frac{1}{2}(b^2 + c^2)^{1/2}$ and the *a* axis is normal to the plane of the drawing.

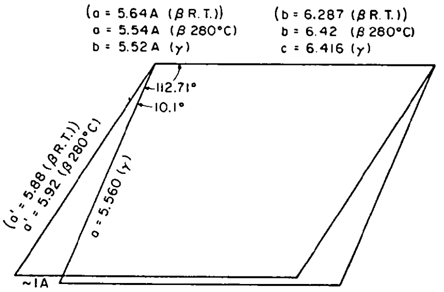

Fig. 3. Unit cell of γ-$UO_2(OH)_2$ superimposed on pseudo cell of β-$UO_2(OH)_2$ with a uranium atom chosen at the origin and common to both cells.

Nevertheless, grinding experiments indicate that the shear relationship between the γ and β structures is real. Grinding crystals of the β form causes a conversion to the α form together with a minor amount of the γ modification. On the other hand, grinding of γ crystals also gives the α form, along with a small amount of the β-dihydroxide. This has been verified by infrared as well as X-ray observations. Continued grinding of either γ- or β-$UO_2(OH)_2$ eventually results in complete conversion to the α form.

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Die Strukturen einiger *p*-Halogenphenyl-diphenylphosphin-chalkogen.
III. *p*-Bromphenyl-diphenyl-phosphinsulfid

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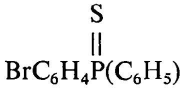
p-Bromphenyldiphenylphosphine sulphide is monoclinic, space group $P2_1/a$. The unit-cell constants are $a=17{\cdot}288$, $b=10{\cdot}970$, $c=9{\cdot}310$ Å, $\beta=108{\cdot}66°$. The structure has been determined by three-dimensional X-ray analysis and refined to a final R value of 0·051 for the 2634 reflexions recorded by an automatic single-crystal diffractometer with a 2θ scan.

Experimente

p-Bromphenyl-diphenyl-phosphinsulfid



$$\overset{\overset{\displaystyle S}{\|}}{BrC_6H_4P(C_6H_5)_2}$$

$BrC_6H_4P(C_6H_5)_2$ (Goetz, Nerdel & Wiechel, 1963) und die dazu analoge Chlorverbindung wurden untersucht, um im Vergleich mit den entsprechenden Oxiden (Dreissig & Plieth, 1971) den Einfluss verschiedener Chalkogene auf die Phosphor–Kohlenstoff-Bindungen zu ermitteln.

Die Verbindung bildet farblose, linealförmige Kristalle, die aus einer gesättigten Lösung in Äthanol durch langsames Abdunsten in befriedigenden Abmessungen erhalten werden konnten. Weissenbergaufnahmen um die Hauptwachstumsrichtung [010] zeigten die Raumgruppe $P2_1/a$. Die genauen Gitterkonstanten wurden auf einem automatischen Einkristall-Diffraktometer der Firma Siemens ermittelt:

$a=17{,}288\pm0{,}01$ Å	$\alpha=90°$
$b=10{,}970\pm0{,}008$	$\beta=108{,}66\pm0{,}03°$
$c=9{,}310\pm0{,}006$	$\gamma=90°$
$V=1672{,}8$ Å^3	$D_{\text{exp}}=1{,}46$ g.cm^{-3}
$Z=4$	$D_{\text{Rö}}$ 1,49 g.cm^{-3}

Es wurden auf dem Diffraktometer mit nickelgefilterter Cu $K\alpha$-Strahlung die Intensitäten von 2634 unabhängigen Reflexen im Bereich $4{,}5°\le\theta\le62°$ mit θ–2θ-scan gemessen. Wegen der hohen Temperaturbewegung wiesen 466 von ihnen eine Intensität kleiner als der statistische Fehler auf. Sie wurden als unbeobachtet eingestuft. Wegen des hohen Absorptionskoeffizienten ($\mu=56{,}4$ cm^{-1}) und der anisotropen Kristallform wurde eine Absorptionskorrektur nach Burnham (1962) vorgenommen. Die dabei ermittelten Transmissionskoeffizienten lagen zwischen 0,42 und 0,68.

Strukturbestimmung und Verfeinerung

Aus der Pattersonsynthese konnten die Lagen der drei Schweratome Brom, Phosphor und Schwefel ermittelt werden. Mit den Vorzeichen einer auf diese drei Atome gestützten Strukturfaktorberechnung wurde eine Foueiersynthese gerechnet, die eine eindeutige Bestimmung der 18 Kohlenstoffatomlagen gestattete. Die so ermittelten 21 Atome wurden zuerst isotrop und anschliessend anisotrop mit der Methode der kleinsten Quadrate verfeinert bis zu einem Zuverlässigkeitsindex von 6,7 %. Jetzt konnten in einer Differenzsynthese die Lage-