Orten der Bor-Atomrümpfe noch negative Werte (Tabelle 3), was zeigt, dass die in unserem Modell noch nicht berücksichtigten verschmierten Skelettelektronen von den Bor-Atomrümpfen abzuziehen sind. Tabelle 3 zeigt, dass die Differenzsynthese bei den terminalen Wasserstoffatomen dagegen positive Funktionswerte hat, obwohl als Atomrümpfe bereits ungeladene H-Atome eingesetzt wurden. Berücksichtigt man noch die Bindungselektronen E_t, so ergibt sich, dass die H-Atome eine erhebliche negative Teilladung tragen müssen.

Die Berechnungen wurden teils mit eigenen Programmen, teils mit dem Programmsystem X-Ray 63 (Stewart, 1966) ausgeführt, Fig. 5 mit Programm *ORTEP* von Johnson (1967).

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The Hydrogen Atom Locations in the α and β Forms of Uranyl Hydroxide

By J. C. Taylor and H. J. Hurst

Australian Atomic Energy Commission Research Establishment, Lucas Heights, Australia

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The hydrogen atoms in the α and β forms of uranyl hydroxide have been located by neutron diffraction and nuclear magnetic resonance methods. Least-squares refinement of the neutron powder data gives a discrepancy factor, $R=[\sum\omega(F_o^2-F_c^2)^2]^{1/2}/[\sum\omega(F_o^2)^2]^{1/2}$, of $0\cdot10$ for the α form and $0\cdot06$ for the β form. The uranyl hydroxide layers in both forms are linkedwith O(hydroxyl)–H···O(uranyl) hydrogen bonds of length $2\cdot76(8)$ Å in the α form and $2\cdot80(6)$ Å in the β form.

Introduction

A broadline n.m.r. study of 'β-$UO_3.H_2O$' was made by Porte, Gutowsky & Boggs (1962). These authors obtained a second moment of $1\cdot9$ gauss^2, and because of the lack of a water signal they inferred that the compound was a hydroxide. X-ray single-crystal analyses have been carried out on α-$UO_2(OH)_2$ (Taylor, 1971) and β-$UO_2(OH)_2$ (Roof, Cromer & Larson, 1964; Bannister & Taylor, 1970). The uranyl coordination is puckered hexagonal in α-$UO_2(OH)_2$ while the uranium coordination is octahedral in β-$UO_2(OH)_2$. In the X-ray analyses of both phases, it was proposed that the $UO_2(OH)_2$ sheets were linked with O(hydroxyl)–H··· O(uranyl) hydrogen bonds, although the hydrogen atoms were not directly located. The β form transforms to the α form on cooling or application of pressure (Harris & Taylor, 1962; Taylor, 1971).

As these phases are not readily obtainable as very large single crystals, neutron powder diffraction and n.m.r. studies have been carried out to locate the hydrogen atoms.

Table 1. *Crystal data*

Phase	*a*(Å)	*b*(Å)	*c*(Å)	Space group	D_x(g.cm^{-3})	V(Å^3)	Z	F(000)	F.W.
α-$UO_2(OH)_2$	4·242(1)	10·302(1)	6·868(1)	*Cmca* or C_{2cb}	6·73	300·1	4	504	304·1
β-$UO_2(OH)_2$	5·6438(1)	6·2867(1)	9·9372(2)	*Pbca*	5·73	352·6	4	504	304·1

Experimental

A sample of pure β-$UO_2(OH)_2$, prepared under hydrothermal conditions, was supplied by Dr B. W. Edenborough, of the Department of Chemical Engineering, University of New South Wales. The β phase was identified both by X-ray powder diffraction (unground) and crystal morphology. The α-$UO_2(OH)_2$ sample, prepared by cooling the β phase to liquid nitrogen temperature and allowing it to warm to room temperature, was characterized by X-ray diffraction and morphology. The transformation was complete. Crystal data are shown in Table 1.

Neutron diffraction powder patterns ($\lambda = 1·036$ Å) were collected at room temperature on the AAEC research reactor HIFAR, using the elastic diffraction technique (Caglioti, 1970). The diffractometer was fitted with an aluminum analysing crystal, which reduced the incoherent background scattering of hydrogen. α crystals, which were plate shaped, were mixed with a Krylon spray coat binder to reduce preferred orientation. β crystals, which were bipyramidal, were not treated in this way.

The α-$UO_2(OH)_2$ pattern (Fig. 1) showed 13 peaks in the range $2\theta = 0$–45° and was consistent with the X-ray systematic absences (Taylor, 1971). The 13 peaks covered 38 independent reflexions, of which 14 were unobserved; only 6 of the 24 reflexions in the peaks did not overlap. Above $2\theta = 45°$, the overlap became severe and this portion of the pattern was not used in the calculations. The β-$UO_2(OH)_2$ pattern (Fig. 1) showed 16 peaks in the range $2\theta = 0$–42°, including 58 independent reflexions of which 17 were unobserved. Only 4 of the 41 reflexions in the peaks were not overlapped.

The n.m.r. investigation was made with a JEOL JNM-W-40 broadline spectrometer and started with the β-$UO_2(OH)_2$ at room temperature. After cooling to 230°K, it was observed that the transition to α-$UO_2(OH)_2$ had occurred and the spectra were broader, reflecting the smaller unit-cell volume. An example of the first derivatives of the proton absorption signal for the α and β forms at room temperature is shown in Fig. 2. Further measurements over the temperature range 130 to 300°K showed no change in line shape.

Calculations

Neutron powder patterns

Values of $(F_{hkl}^2)_c$ for all possible reflexions to $2\theta = 45°$ for α and $2\theta = 42°$ for β were calculated with program *ORFLS* (Busing, Martin & Levy, 1962*a*), using Taylor's

Table 2. *Observed and calculated neutron powder intensities for* α-$UO_2(OH)_2$ *and* β-$UO_2(OH)_2$

The scale of the numbers is 10 times F_{hkl}^2 (absolute). Reflexions with brackets are superposed, while asterisks denote unobserved reflexions.

ALPHA

	h	*k*	*l*	F_o^2	F_c^2
	0	2	0	235	236
*	0	2	1	18	27
⎧	0	0	2	82	87
⎩	1	1	1	132	149
*	0	2	2	28	30
⎧	1	1	2	100	91
⎩	0	4	0	12	10
	1	3	1	52	42
	0	4	1	348	380
⎧	2	0	0	709	662
⎪	1	3	2	125	116
⎩	0	2	3	138	131
*	0	4	2	56	59
⎧	1	1	3	179	148
⎩	2	2	0	212	175
*	2	2	1	32	20
⎧	2	0	2	69	64
⎩	1	5	1	245	240
	1	3	3	418	448
⎧	0	0	4	12	13
⎪	0	6	0	4	5
⎪	0	4	3	124	148
⎩	2	2	2	18	22
*	0	6	1	81	65
⎧	2	4	0	20	7
*⎪	1	5	2	20	13
⎩	0	2	4	20	29
	2	4	1	333	279
*	1	1	4	44	4
	0	6	2	149	212
*	2	2	3	47	97
*	2	4	2	47	44
*⎧	1	3	4	19	29
⎩	1	5	3	19	0
*	0	4	4	111	128
⎧	0	6	3	28	30
⎪	3	1	1	78	81
⎩	1	7	1	505	525

BETA / BETA (*cont.*)

	h	*k*	*l*	F_o^2	F_c^2
	0	0	2	295	292
	1	1	1	224	231
*	1	0	2	4	26
*	1	1	2	3	0
	0	2	0	236	254
*	0	2	1	7	1
*	2	0	0	16	20
*⎧	0	2	2	3	0
⎩	1	2	1	3	1
*⎧	1	1	3	4	0
⎩	2	1	0	10	33
⎧	2	1	1	99	97
⎩	0	0	4	44	44
*	2	0	2	11	2
	1	2	2	273	243
⎧	2	1	2	19	19
⎪	0	2	3	111	114
⎩	1	0	4	548	556
⎧	1	1	4	34	30
⎪	1	2	3	104	97
⎩	2	2	0	202	191
*	2	2	1	7	3
	2	1	3	36	44
⎧	0	2	4	31	27
⎪	2	2	2	267	231
⎩	1	3	1	284	245
⎧	2	0	4	230	236
⎪	1	2	4	21	22
⎩	1	3	2	39	40
⎧	1	1	5	148	134
⎩	2	1	4	26	24
⎧	3	1	1	15	19
⎪	2	2	3	46	56
⎩	3	0	2	72	88
⎧	3	1	2	5	6
*⎪	1	3	3	5	17
⎪	2	3	0	11	3
⎩	0	2	5	11	13
⎧	2	3	1	86	85
⎩	0	0	6	0	0
⎧	1	2	5	138	144
⎪	2	2	4	38	37
⎪	3	2	1	9	10
⎪	2	3	2	8	9
⎪	1	0	6	0	0
⎪	3	1	3	475	476
⎪	2	1	5	90	94
⎩	0	4	0	714	727
⎧	0	4	1	26	26
*⎪	1	3	4	6	2
⎪	1	1	6	6	0
⎩	3	2	2	13	5
⎧	3	0	4	42	46
⎪	2	3	3	10	9
⎪	1	4	1	112	114
⎩	0	4	2	15	16
⎧	3	1	4	158	153
⎩	0	2	6	924	924

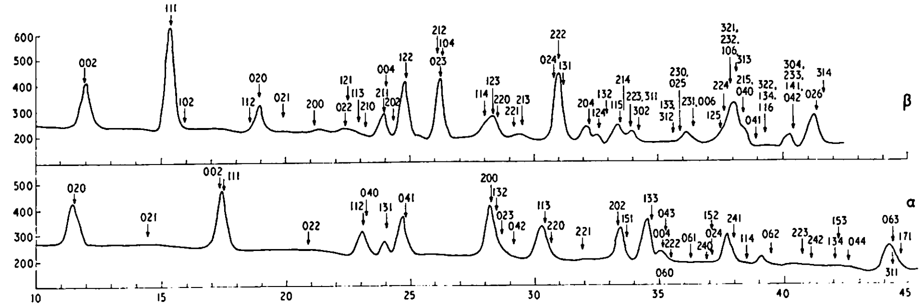

Fig. 1. Neutron diffraction powder patterns of α-$UO_2(OH)_2$ and β-$UO_2(OH)_2$.

(1971) model for α and the model of Bannister & Taylor (1970) for β, including the proposed hydrogen atoms. Scattering lengths were 0·85 for uranium, 0·58 for oxygen and −0·378 for hydrogen, in units of 10^{-12} cm (Bacon, 1962). Observed neutron intensities $(F^2_{hkl})_o$ were obtained from the powder patterns by applying the Lorentz factor $(\sin\theta \sin 2\theta)$ and an absorption correction; where one or more intensities overlapped, the separate observed intensities were obtained by multiplying the total intensity in the peak by the calculated intensity fraction for that component. The two models were then refined by least-squares techniques with the same program; new $(F^2_{hkl})_0$ values were determined for the overlapped reflexions after each cycle. The unob-

Table 3. *Final atomic parameters*

α-$UO_2(OH)_2$

	x	y	z	Reference
O(1) (uranyl)	0	158 (5)	109 (9)	*
	0	155 (3)	089 (5)	†
O(2) (hydroxyl)	½	−076 (7)	154 (10)	*
	½	−069 (3)	149 (5)	†
H	0	351 (10)	138 (15)	*
U	0	0	0	
		$B=2{\cdot}8$ (12) Å^2		*

β-$UO_2(OH)_2$

	x	y	z	Reference
O(1) (uranyl)	136 (6)	472 (8)	350 (4)	*
	154 (3)	464 (3)	342 (2)	‡
O(2) (hydroxyl)	203 (10)	304 (7)	091 (4)	*
	196 (3)	288 (3)	082 (2)	‡
H	206 (14)	344 (9)	172 (7)	*
U	0	0	0	
		$B=1{\cdot}4$ (8) Å^2		*

* This investigation.
† Taylor (1971).
‡ Bannister & Taylor (1970).

Table 4. *Interatomic distances and angles by neutron diffraction, compared with the X-ray values*

α-$UO_2(OH)_2$

	Neutrons	X-rays*
U——O(1) (uranyl)	1·79 (5) Å	1·71 (3) Å
U——O(2) (hydroxyl)	2·50 (4) (four)	2·46 (2)
U——O(2) (hydroxyl)	2·51 (7) (two)	2·51 (3)
O(2)–O(2) in ring	2·50 (7) (four)	2·54 (4)
O(2)–O(2) in ring	2·64 (14) (two)	2·49 (7)
O(1)–O(1) contact-intralayer	2·87 (8)	3·06 (5)
O(1)–O(1) contact-interlayer	3·21 (9)	3·13 (5)
O(2)–O(1) hydrogen bond	2·76 (8)	2·88 (4)
O(2)–H	0·76 (11)	
O(2)–H· · ·O(1) angle	178 (9)°	
Σs	5·1	5·9

β-$UO_2(OH)_2$

	Neutrons	X-rays†
U——O(1) (uranyl)	1·69 (3) Å	1·81 (2) Å
U——O(2) (hydroxyl)	2·40 (5) (two)	2·27 (2)
U——O(2) (hydroxyl)	2·27 (5) (two)	2·32 (2)
O(2)–O(2) in octahedron	3·19 (2) (two)	3·20 (1)
O(2)–O(2) in octahedron	3·42 (4) (two)	3·30 (2)
O(1)–O(2) in octahedron	2·98 (6)	2·88 (3)
	2·93 (7)	2·98 (3)
	2·73 (6)	2·91 (3)
	2·89 (6)	2·93 (3)
O(2)–O(1) hydrogen bond	2·80 (6)	2·82 (3)
O(2)–H	0·84 (8)	
O(2)–H· · ·O(1) angle	165 (6)°	
Σs	6·4	5·7

* Taylor (1971)
† Bannister & Taylor (1970)

served reflexions were scaled after each cycle by comparison with the calculated intensities. At convergence, the value of

$$R=[\sum\omega(F_o^2-F_c^2)^2]^{1/2}/[\sum\omega(F_o^2)^2]^{1/2}\,,$$

including unobserved reflexions, was 0·10 for α-$UO_2(OH)_2$ and 0·06 for β-$UO_2(OH)_2$. The final observed and calculated intensities are given in Table 2, structural parameters in Table 3 and interatomic distances and angles, calculated with program *ORFFE* (Busing, Martin & Levy, 1962*b*), in Table 4.

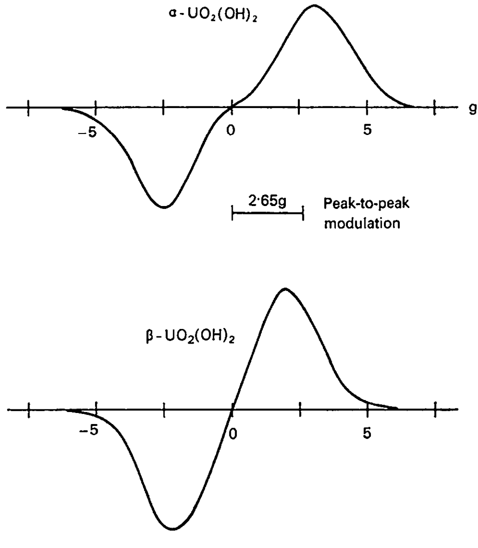

Fig. 2. First derivatives of proton absorption signals of α-$UO_2(OH)_2$ and β-$UO_2(OH)_2$.

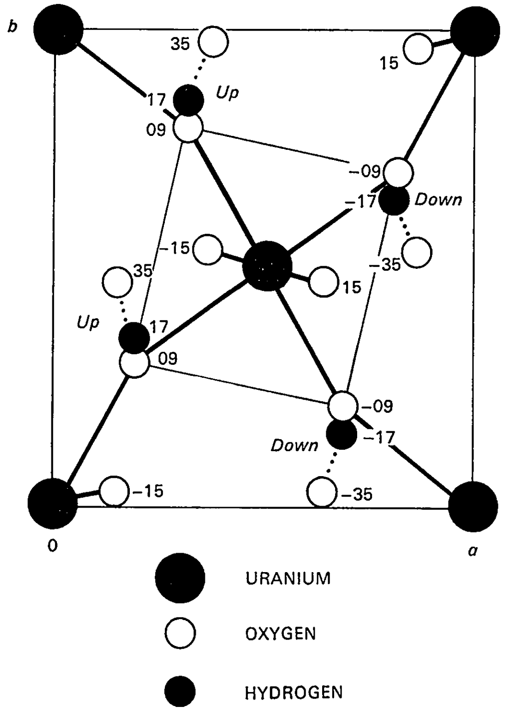

Fig. 3. Hydrogen bond scheme in β-$UO_2(OH)_2$.

The above refinement for α-$UO_2(OH)_2$ was carried out in space group *Cmca*. The systematic absences of the α form are also compatible with the space group C_{2cb}, where the hydrogen and oxygen x coordinates are allowed to deviate from the levels 0 and $\frac{1}{2}$ (Taylor, 1971). The X-ray data of Taylor (1971) were not accurate enough to detect any slight shifts from these levels.

Refinements of the neutron data were carried out in space group C_{2cb}, with the oxygen and hydrogen atoms displaced by 0·05 Å in all direction combinations. Oscillations around the 0 and $\frac{1}{2}$ levels occurred, but the x coordinates were always equal to 0 and $\frac{1}{2}$ within the experimental error. It was concluded that the neutron data also are not of sufficient accuracy to detect any deviations from space group *Cmca*.

Nuclear magnetic resonance pattern

The second moments of the spectra were obtained by a Simpson's rule integration of the derivative curve and were corrected for modulation broadening. Values of the second moments, computed to 99·99% convergence, are given in Table 5.

Table 5. *Nuclear magnetic resonance second moments* (gauss²)

		α-$UO_2(OH)_2$	β-$UO_2(OH)_2$
Experimental		4·6 (3)	2·4 (3)
Calculated	(*a*)	5·47	2·98
	(*b*)	5·29	3·15

The experimental values at room temperature are compared with the theoretical values calculated using the van Vleck equation and assuming that the only magnetic nuclei present are protons. Case (*a*) in Table 5 is for hydrogen positions determined by the powder neutron diffraction data and case (*b*) is for the X-ray models with linear bonds and an O–H distance of 1 Å.

Discussion

The neutron powder analyses confirmed the hydrogen locations proposed for α-$UO_2(OH)_2$ (Taylor, 1971) and β-$UO_2(OH)_2$ (Roof, Cromer & Larson, 1964). A diagram of the α-$UO_2(OH)_2$ structure with the proposed hydrogen atoms is given in Taylor's (1971) paper; the hydrogen bond scheme in β-$UO_2(OH)_2$ is shown in Fig. 3. The hydrogen atoms are ordered and link the uranyl hydroxide layers with O(hydroxyl)–H···O(uranyl) hydrogen bonds. Hydrogen bonds are of length 2·76(8) Å with an angle of 178(9)° in α-$UO_2(OH)_2$ and 2·80(6) Å with an angle of 165(6)° in β-$UO_2(OH)_2$. Further evidence to support hydrogen locations is the extreme sensitivity of the neutron data to hydrogen contribution. The R value for F^2 increases from 0·10 to

0·53 for α-$UO_2(OH)_2$ and from 0·06 to 0·43 for β-$UO_2(OH)_2$ when the hydrogen contribution is omitted from the calculations. Difference Fourier syntheses of the hydrogen density were calculated with the neutron data but were inconclusive, owing to the limited number of terms.

The X-ray and neutron parameters in Table 3 show general agreement, although some differences are greater than the experimental errors. This is probably due to the systematic errors inherent in the two methods. The neutron errors in Tables 3 and 4 have been doubled to allow for systematic errors in the choice of background; this doubling was suggested by check cycles calculated with the backgrounds deliberately chosen too high. More precise parameters must await single-crystal neutron studies. Bond-strength sums ($\sum s$) calculated from the curve of Zachariasen & Plettinger (1959) are given in Table 4 and approximate the uranium valence number of 6.

The agreement between observed and calculated second moments is reasonable and insensitive to slight changes in oxygen and hydrogen positions. Calculated values are higher than observed values in both cases, and this may be due to the thermal motion. There is no sign of the water molecule signal.

In attempting to explain the low second moment of 1·9 gauss^2 for the 'β-$UO_2.H_2O$' phase of Porte, Gutowsky & Boggs (1962), we have repeated their preparation. The hydrate $UO_2(OH)_2.H_2O$, identified with the standard pattern (Dawson, Wait, Alcock & Chilton, 1956), was refluxed in water at 100°C for 5 days and the product was heated for 3 hours at 105°C. X-ray photographs of the intermediate product gave an α-$UO_2(OH)_2$ pattern, which was unchanged on heating at 105°C. The second moment of our product was 2·6 gauss^2.

The difference between this value and the value of 1·9 gauss^2 of Porte, Gutowsky & Boggs (1962) is ascribed to varying degrees of rehydration. The α form prepared by this method is metastable with respect to the hydrate $UO_2(OH)_2.H_2O$ and is usually hydroxyl deficient with an (unrehydrated) formula $UO_2(OH)_{1 \cdot 6}$ (Dell & Wheeler, 1963). Moments of 2·6 gauss^2 and 1·9 gauss^2 correspond to the phase α-$UO_2(OH)_{1 \cdot 6}$ with unknown amounts of rehydration due to atmospheric moisture.

The α-$UO_2(OH)_2$ phase used in our study was prepared by a martensitic-type transformation of β-$UO_2(OH)_2$. The β phase has never been prepared in hydroxyl-deficient form; we have had the stoichiometry of our β crystals checked by differential thermal analysis (Dr W. I. Stuart, private communication), and the formula corresponds to β-$UO_2(OH)_{2 \cdot 0}$. Therefore, our α phase is also $UO_2(OH)_{2 \cdot 0}$ and the second moment of 4·6 g^2 corresponds to the stoichiometric phase. Stoichiometric α-$UO_2(OH)_2$ has also been prepared hydrothermally by Harris & Taylor (1962).

We wish to thank Dr W. I. Stuart for the differential thermal analyses and helpful comments.

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