must also consider the possibility that the stoichiometric and off-stoichiometric CaCu₅ type compounds have merged into one large homogeneity region which, at elevated temperatures, extends primarily towards high Co-concentrations (Buschow & van der Goot, 1968, 1969). Upon annealing at low temperatures the off-stoichiometric compound then decomposes into stoichiometric RCo_5 and R_2Co_{17}. X-ray studies on quenched samples of various compositions between RCu_5 and RCu_7 show that such a situation does not apply to the copper compounds in which R = Gd, Tb or Dy. This is most convincingly demonstrated for the case in which R = Gd, where an orthorhombic compound $GdCu_6$ is observed (Buschow & van der Goot, 1970). An annealed $GdCu_6$ sample consists entirely of the orthorhombic phase notwithstanding whether the sample was quenched after annealing or not.

We prepared in addition a sample of the formula composition $GdCu_{6.5}$ and annealed it for 3 weeks at 700°C. At this temperature the phase $GdCu_7$ is still stable. After quenching of the sample from this temperature, microscopic and X-ray investigations showed the presence only of a mixture of the phases $GdCu_6$ and $GdCu_7$. The lattice constants of the phase $GdCu_7$ corresponding to this two-phase region are $a = 4.961$ and $c = 4.156$ Å. Within experimental error (± 0.005 Å) these values are close to those listed in Table 3 for $GdCu_7$ and, apart from the microscopic observation, show that the compound $GdCu_7$ has only a relatively small region of homogeneity.

X-ray observations on annealed and quenched samples of various composition between YCu_5 and YCu_7 show that is is not unlikely that the phases YCu_5 and YCu_7 form part of one relatively large homogeneity region and indeed give rise to a situation similar to that observed in some rare earth cobalt systems. A detailed investigation of this point will be the object of a forthcoming study.

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The Structure of the α Form of Uranyl Hydroxide

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The crystal structure of α-$UO_2(OH)_2$ has been determined from single-crystal X-ray diffraction data. α-$UO_2(OH)_2$ is orthorhombic, space group *Cmca* or *C2cb*, with $a = 4.242$ (1), $b = 10.302$ (1) and $c = 6.868$ (1) Å. Least-squares refinement based on the 199 independent observed reflexions in the range $0 < (\sin\theta/\lambda) < 0.81$ in space group *Cmca* gives a value of $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ of 0.063. Slight deviations of the oxygen atoms from the levels $x = 0$ and $x = \frac{1}{4}$, which are allowed in the alternative space group *C2cb*, were not detectable with these data. Each uranyl group is surrounded by six hydroxyl oxygen atoms in puckered hexagonal configuration. The hexagons are condensed into infinite hexagonal sheets, stacked in layers perpendicular to **b**. There are weak interlayer hydrogen bonds and probable hydrogen atom positions are deduced.

Introduction

The orthorhombic α- and β- forms of uranyl hydroxide have been prepared from UO_3 and water under hydrothermal conditions (Dawson, Wait, Alcock & Chilton, 1956). β-$UO_2(OH)_2$ consists of $UO_2(OH)_4$ octahedra, joined at the corners to form infinite $UO_2(OH)_2$ sheets, which are linked by O–H$\cdots$O (uranyl) hydrogen bonds (Roof, Cromer & Larson, 1964). The thermal expansion of the β form is anisotropic (Bannister & Taylor, 1970). Harris & Taylor (1962) showed that β-$UO_2(OH)_2$ transforms rapidly into α-$UO_2(OH)_2$ on application

of pressure, and considered that the effect was a simple displacement transformation (Buerger, 1951), involving only minor distortions of the β-UO$_2$(OH)$_2$ structure. As a sample of α-UO$_2$(OH)$_2$ was available, an X-ray crystal structure analysis of the substance was carried out.

Experimental

A mixture of the α and β forms of UO$_2$(OH)$_2$ was supplied by B. W. Edenborough, Department of Chemical Engineering, University of New South Wales. The crystals formed from a uranyl nitrate solution heated under hydrogen at 290°C and 10·6 MN.m^{-2} pressure. When prepared under hydrothermal conditions the α and β forms both have the formula UO$_2$(OH)$_2$ (Harris & Taylor, 1962).

Weissenberg photographs of α-UO$_2$(OH)$_2$ with Cu $K\alpha$ radiation showed orthorhombic symmetry and room-temperature lattice constants were derived from a least-squares analysis of a number of high angle reflexions (see Table 1). The reflexions with (eee) and (ooo) parity were strong, indicating an F-centred uranium arrangement. Only 9 weak reflexions with mixed indices were observed on the photographs, namely the 112, 132, 021, 023, 025, 041, 043, 061 and 081 reflexions. The systematic absences, h0l for l odd and hk0 for h odd, with C-face centring, indicated either the centric space group Cmca (No. 64) or the non-centric space group C2cb (No. 41). The crystal data are collected in Table 1.

Table 1. *Crystal data for* α-UO$_2$(OH)$_2$

Orthorhombic, space group, Cmca or C2cb

$a = 4\cdot242$ (1) Å	$V = 300\cdot1$ Å^3
$b = 10\cdot302$ (1)	F.W. $= 304\cdot1$
$c = 6\cdot868$ (1)	$Z = 4$
($\lambda = 1\cdot5405$–Cu $K\alpha_1$	$D_x = 6\cdot73$ g.cm^{-3}
$1\cdot5443$–Cu $K\alpha_2$)	$F(000) = 504$ e$^-$

The crystals were lath-shaped, with dominant plate faces {010} and poorly-defined edge faces {111}. Three-dimensional X-ray diffraction data were collected on a General Electric XRD-5 set fitted with a single-crystal orienter and scintillation counter. Zr-filtered Mo $K\alpha$ radiation was used. The linear absorption coefficient for Mo $K\alpha$ radiation was 656 cm^{-1}, ensuring that absorption effects in the platy crystals would be severe.

A set of data to $2\theta = 70°$ was collected on a crystal of thickness 24μm and volume $6\cdot8 \times 10^{-8}$cm^3. For this crystal, the transmission factors T calculated by the

program CDRABS (A.A.E.C. neutron diffraction program library, written by G. W. Cox & M. M. Elcombe) varied from 0·046 to 0·220. A further set of data to $2\theta = 50°$ was collected on a crystal of thickness 18μm and volume $1\cdot1 \times 10^{-8}$cm^3 ($0\cdot21 < T < 0\cdot35$). Although the reduction in size reduced the variation in T, the intensities from the latter crystal were weak for $2\theta > 30°$. The two sets of data were combined into one set after absorption corrections had been applied, by averaging after scaling through the common reflexions.

Structure analysis

The structure was solved from a difference Fourier synthesis calculated from the uranium contribution alone. A model in space group Cmca was obtained from this map, and it was refined with unit weights and isotropic Debye–Waller temperature factors to

$$R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0\cdot081.$$

The least-squares program used was ORFLS (Busing, Martin & Levy, 1962). The function minimized was $\sum[\omega(F_o - F_c)^2]$ with $\omega = 1$. The anomalous dispersion terms $\Delta f'(\text{U}) = -9e$ and $\Delta f''(\text{U}) = 9e$ (Cromer, 1965) for uranium and the SCF scattering curve with exchange for neutral oxygen and the TFD curve for neutral uranium (International Tables for X-ray Crystallography, 1962) were included.

When the refinement was continued to allow for anisotropic thermal vibration, the temperature factors of the oxygen atoms O(1) became non positive-definite. Consequently anisotropic thermal parameters for the uranium atom only were determined, and the temperature factors of the oxygen atoms were held at the isotropic values. R then refined to 0·063. Extinction corrections were not applied as the effects of extinction appeared to be much smaller than residual absorption errors. The final Cmca parameters are given in Table 2.

Refinement was also carried out in the non-centric space group C2cb in which the oxygen atoms are allowed to diverge from the levels $x = 0$ and $x = \frac{1}{2}$. The refinement also proceeded to $R = 0\cdot063$, with anisotropic temperature factors for uranium and isotropic temperature factors for the oxygen atoms. Within the experimental errors, the C2cb parameters were not significantly different from the Cmca values. Although it is possible that the space group is C2cb, the deviations from Cmca are so slight as to be undetectable with the present data. All tabulated data, therefore, are from the Cmca refinement. The final observed and calculated structure factors are given in Table 3.

Table 2. *Final parameters for* α-UO$_2$(OH)$_2$

	Wyckoff notation	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	4(a)	0	0	0	0·0069 (6)	0·0024 (1)	0·0020 (2)	0	0	0·0001 (11)
O(1)	8(f)	0	0·155 (3)	0·089 (5)	$B = 1\cdot4$ (1) Å^2					
O(2)	8(f)	$\frac{1}{2}$	$-0\cdot069$ (3)	0·149 (5)	$B = 1\cdot5$ (1) Å^2					

Table 3. *Observed and calculated structure factors*

Reflexions with asterisks were omitted from the least-squares refinement.

	|Fo|	|Fc|
0,K,0		
K = 2	369	328
4	234	230
6	200	226
8	158	167
10	135	131
12	131	133
14	105	104
0,K,1		
K = 2	5	6
4	40	48
6	8	10
8	9	16
0,K,2		
K = 0 *	359	301
2	275	264
4	227	239
6	211	229
8	172	182
10	135	140
12	111	117
14	97	91
0,K,3		
K = 2	27	25
4	30	29
0,K,4		
K = 0	203	194
2	233	221
4	220	224
6	178	188
8	158	168
10	133	141
12	107	101
14	83	78
0,K,5		
K = 2	23	23
0,K,6		
K = 0	189	185
2	201	198
4	166	180
6	131	136
8	121	126
10	113	119
12	94	92
14	87	77
0,K,8		
K = 0	165	150
2	148	148
4	145	138
6	119	121
8	110	108
10	92	96
0,K,10		
K = 0	107	115
2	111	109
4	116	107
6	109	108
1,K,1		
K = 1 *	254	290
3	227	226
5	242	246
7	227	223
9	148	157
11	118	127
13	117	106
15	85	75
1,K,2		
K = 1	64	50
3	41	42
1,K,3		
K = 1 *	318	278
3	251	245
5	176	196
7	144	161
9	145	141
11	110	122
13	108	102
15	96	82
1,K,5		
K = 1	209	193
3	219	210
5	154	174
7	139	144
9	122	138
11	103	111
13	85	83
1,K,7		
K = 1	158	147
3	156	161
5	149	140
7	125	131
9	123	120
1,K,9		
K = 1	143	133
3	128	123
5	112	114
7	104	103
1,K,11		
K = 1	100	106
2,K,0		
K = 0	323	330
2	262	257
4	194	200
6	203	196
8	140	151
10	122	121
12	137	119
14	111	96
2,K,2		
K = 0	261	245
2	231	223
4	202	206
6	210	199
8	150	163
10	105	129
12	110	106
14	104	85
2,K,4		
K = 0	190	176
2	205	195
4	191	197
6	140	169
8	150	152
10	123	128
12	101	93
14	73	73
2,K,6		
K = 0	193	167
2	183	177
4	163	163
6	126	126
8	127	117
12	90	86
2,K,8		
K = 0	145	138
2	145	137
4	134	128
6	124	113
8	101	101
2,K,10		
K = 0	120	108
2	98	102
4	83	100
3,K,1		
K = 1	208	206
3	169	177
5	189	187
7	175	174
9	135	130
11	115	108
13	103	91
3,K,3		
K = 1	198	205
3	160	188
5	144	159
7	125	135
9	110	119
11	97	105
13	96	88
3,K,5		
K = 1	158	158
3	170	169
5	141	144
7	118	122
9	121	117
11	101	96
13	88	73
3,K,7		
K = 1	123	126
3	132	135
5	121	126
7	96	112
3,K,9		
K = 1	118	115
3	99	107
4,K,0		
K = 0	198	232
2	182	173
4	146	145
6	161	144
8	115	117
10	72	97
12	105	94
4,K,2		
K = 0	168	169
2	161	159
4	151	151
6	155	146
8	120	124
10	110	101
12	99	87
4,K,4		
K = 0	145	136
2	132	146
4	146	145
6	125	129
8	114	117
12	78	76
4,K,6		
K = 0	148	129
2	124	135
4	124	126
6	104	101
4,K,8		
K = 0	92	110
2	112	109
4	83	103
6	98	92
5,K,1		
K = 1	161	138
3	121	125
5	134	128
5,K,3		
K = 1	132	135
3	118	138
5	118	114
5,K,5		
K = 1	116	115
3	123	128
5	98	106
5,K,7		
K = 1	92	95
3	105	101
6,K,0		
K = 0 *	85	126
2	119	113
4	109	101
6	98	98
8	85	83
6,K,2		
K = 0	98	112
2	101	107
4	121	102
6	111	99
6,K,4		
K = 0	98	95
2	81	100
4	112	103

Discussion

The $UO_2(OH)_2$ *layers*

The structure of α-$UO_2(OH)_2$ consists of parallel $UO_2(OH)_2$ layers at the levels $y=0$ and $y=\frac{1}{2}$. The layer at $y=\frac{1}{2}$ is illustrated in Fig. 1. The uranyl oxygen atoms deviate from this level by $\pm 1{\cdot}6$ Å while the hydroxyl oxygen atoms deviate from the level by $\pm 0{\cdot}7$ Å. The linear uranyl group [U–O(1)=1·71 (3) Å] is inclined at 70° to the plane $y=\frac{1}{2}$. Each uranyl group is surrounded equatorially by a hexagon of hydroxyl oxygen atoms, with U–O(2) distances of 2·51 (3) Å (two) and 2·46 (2) Å (four). In the equatorial plane of the uranyl group (not the plane $y=\frac{1}{2}$), the hydroxyl oxygen atoms are alternately up and down from the plane by either 0·2 Å (twice) or 0·3 Å (four times); the coordination of the uranyl group may be described as puckered hexagonal. In the hexagon, there are four O(2)–O(2) contacts of 2·54 (4) Å and two O(2)–O(2) contacts of 2·49 (7) Å. The O(2)–O(2)–O(2) angles are 117 (1)° (four) and 114 (3)° (two). The O(1)–O(2) contacts in the coordination polyhedron vary between 2·82 (3) and 3·16 (3) Å (Fig. 2).

The $UO_2(OH)_2$ layer is seen edge-on in the view down the *a* axis, Fig. 2. The hexagonal ring is seen to be puckered-hexagonal normal to the uranyl group. Fig. 2 illustrates the compact packing of the layers in this crystal. There are close O(1)–O(1) contacts of 3·06 (5) Å (intralayer) and 3·13 (5) Å (interlayer). These approaches would hinder the formation of a strong O(2)–H···O(1) hydrogen bond. The interlayer O(2)–O(1) distance is 2·88 (4) Å, indicating probable interlayer hydrogen bonding. These O(2)–O(1) vectors are nearly parallel to **b**. The hydrogen atoms are probably situated near the O(2)–O(1) line, distant 1Å from O(2); the assumed hydrogen locations are shown in Fig. 2. The easy cleavage of the crystals perpendicular to **b** is in accord with the layer structure.

Christ & Clark (1960) have proposed that puckered hexagonal $UO_2(OH)_2$ layers occur in the uranyl hydroxide minerals, with water molecules and cations occupying interlayer positions. In the minerals, the layers are separated by 7 to 8 Å, as compared with 5 Å in α-$UO_2(OH)_2$. Debets & Loopstra (1963) have proposed that the same $UO_2(OH)_2$ layer is the structural basis of the ADU-type compounds, with the ammonia and water molecules occupying interlayer

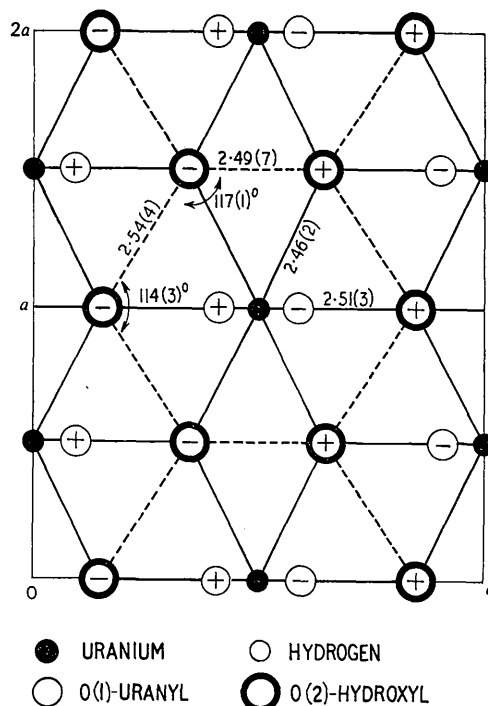

2a
2·49(7)
117(1)°
2·54(4)
2·46(2)
114(3)°
2·51(3)
a
0
c
+
−
● URANIUM
○ HYDROGEN
○ O(I)-URANYL
◯ O(2)-HYDROXYL

Fig. 1. The α-$UO_2(OH)_2$ layer at the level $y=\frac{1}{2}$.

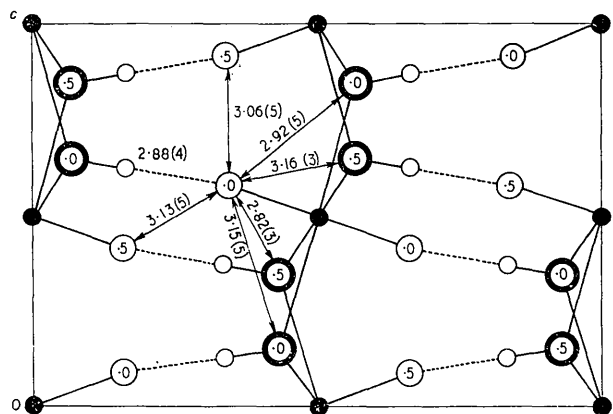
c
0
b
·5
·0
3·06(5)
2·92(5)
2·88(4)
3·16(3)
3·13(5)
3·15(5)
2·82(3)

Fig. 2. The α-$UO_2(OH)_2$ structure viewed in the **a** direction. The probable hydrogen atom locations are shown.

positions. The present analysis appears to be the first measurement of the stereochemistry of the puckered hexagonal layer.

Thermal motion

The data were not sufficiently accurate to permit a determination of the orientation of the oxygen atom thermal vibration ellipsoids. The r.m.s. components of the uranium atom vibration along the principal axes R_1, R_2 and R_3 of its vibration ellipsoid are 0·069 (5), 0·079 (4) and 0·114 (4) Å. R_3 makes angles of 90° with **a**, 3 (27)° with **b** and 87 (27)° with **c**, so the maximum vibration of the uranium atom is roughly in the direction of **b**. The r.m.s. components of the uranium atom in β-$UO_2(OH)_2$ along R_1, R_2 and R_3 are 0·071 (12), 0·102 (7) and 0·108 (5) Å (Bannister & Taylor, 1970). A reduction in thermal parameters is expected on going from the sixfold coordination in β-$UO_2(OH)_2$ to the eightfold coordination in α-$UO_2(OH)_2$.

The $\beta \rightarrow \alpha$ transformation

β-$UO_2(OH)_2$ transforms rapidly into α-$UO_2(OH)_2$ on application of pressure, for example with a spatula

(Harris & Taylor, 1962), or on cooling with liquid nitrogen. The present analysis of α-$UO_2(OH)_2$ has shown that during the transformation the number of oxygen atoms coordinated to the uranium atom increases from six to eight. The transformation occurs within the layers. The open octahedral structure of β-$UO_2(OH)_2$ collapses to give the puckered hexagonal sheets of α-$UO_2(OH)_2$ with an increase in density from 5·73 to 6·73 g.cm^{-3} and a decrease in cell volume from 352·6 to 300·1 Å^3, a major structural change. The transformation is not a simple displacement one as defined by Buerger (1951), as changes in the coordination number occur. It is similar to the martensitic transformations in metals and alloys. The transformation is normal in that the high-temperature form has the more open structure and lower coordination number.

Fig. 3 shows the coordination around one uranium atom in β-$UO_2(OH)_2$ with the α-$UO_2(OH)_2$ arrangement superimposed on it in an orientation suggested by Harris & Taylor (1962). Possible atomic movements as the β-structure collapses are indicated. Although this may be an oversimplification it gives an idea of the magnitude of the shifts involved. Further work is needed in order to clarify the mechanism of this transition.
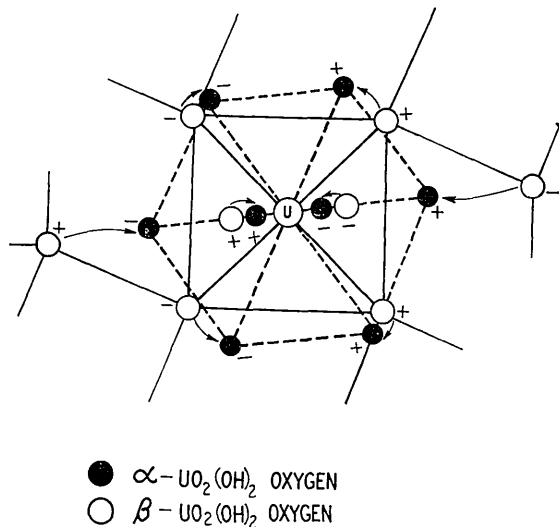

● α- $UO_2(OH)_2$ OXYGEN
○ β - $UO_2(OH)_2$ OXYGEN

Fig. 3. Possible movements around a uranium atom in the $\beta \rightarrow \alpha$ transition.

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