

Fig. 3. Close contacts at ends of molecules ( $y$  projection).

The centre of symmetry at the molecular midpoint is between atoms C(9) and C(9'), Fig. 2. The shortest H...H distances between adjacent chains are of five kinds and are very closely similar in length. Atom H2(9) lies  $p=2.68$  Å from H3(9) and  $s=2.60$  Å from H3(7). The distances  $p$  and  $s$  for the whole chain range between 2.67<sub>8</sub> and 2.68<sub>4</sub> Å and 2.57 and 2.61 Å respectively. Because of the centre of symmetry at the molecular midpoint H2(7'), H2(9') are related in the same way. However, if we move down the chain towards C(1),

the hydrogen atoms lying beneath H2(9') and H3(9') are all attached to even-numbered carbon atoms. These hydrogen atoms show similar non-bonded distances to those on neighbouring chains. Thus distance  $r$ , typified by H2(8)–H3(8), is 2.69 Å and  $t$ , typified by H2(8)–H3(9'), is 2.64 Å. The distances  $r$  range between 2.68 and 2.69 Å, distances  $t$  between 2.62 and 2.64 Å.

The fifth type of close contact between adjacent chains is  $q$ , typified by H3(9)–H3(9'), 2.59 Å. These  $q$  distances range between the latter value and 2.69 Å.

There are three types of H...H contact between the ends of the chains. Two of these of length 2.68 and 2.73 Å are between H1(1) terminal hydrogen atoms and the other of length 2.71 Å is between H1(1) of one chain and H3(2) of another (Fig. 3).

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## A Neutron Diffraction Study of the Anisotropic Thermal Expansion of $\beta$ -Uranyl Dihydroxide

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Neutron diffraction powder patterns were taken to obtain positional parameters for all the atoms in  $\beta$ - $\text{UO}_2(\text{OH})_2$  at six temperatures from 21 to 260°C. The results confirm that the strongly anisotropic thermal expansion of this material is caused by the rotation of oxygen octahedra in the structure. These octahedra also undergo temperature-induced shape changes, which may be attributed to the effects of hydrogen bonding in the structure.

### Introduction

In a previous publication (Bannister & Taylor, 1970), it was shown that the thermal expansion of  $\beta$ - $\text{UO}_2(\text{OH})_2$  is anisotropic, with a large contraction in  $a$ , a large expansion in  $b$  and a smaller cyclic change in  $c$ . The anisotropy reaches a saturation level at 260°C. It was

proposed that the effect is caused by a rotation of the U–O(2) (hydroxyl oxygen) bonds about [110], their inclination to that direction being unchanged. At saturation, the O(2) atoms reach their maximum possible intrusion into holes in the structure, and the O(2) plane of the oxygen octahedra surrounding each uranium atom has its maximum tilt with respect to the (001)

plane. In this model, based on X-ray diffraction and hot-stage optical microscopy, the octahedra were assumed to remain undistorted in shape, and possible effects of hydrogen bonding were ignored.

The hydrogen bonding scheme has since been elucidated by the powder neutron diffraction study of Taylor & Hurst (1971). In the present work, neutron powder patterns have been obtained at six temperatures from 21 to 260°C, in order to obtain a direct measurement of the crystal structure changes which lead to the anisotropic thermal expansion.

### Experimental

The sample of pure  $\beta$ - $\text{UO}_2(\text{OH})_2$  was prepared by heating uranyl nitrate solution under hydrogen at 10.6 MN.m<sup>-2</sup> pressure and at 290°C. The crystals were block-shaped, bounded by {111} and (001) faces, and were about 200–300  $\mu\text{m}$  thick.

Neutron diffraction powder patterns ( $\lambda=1.08 \text{ \AA}$ ,  $10^\circ < 2\theta < 45^\circ$ ) were collected at 21, 130, 200, 220, 240 and 260°C on the AINSE neutron powder diffractometer on HIFAR, the A.A.E.C. research reactor. This machine is of conventional design (not fitted with an analyser). For the elevated temperature runs a 1 cm diameter vanadium can with an outer nichrome winding was used to contain the sample, and the temperature was measured using an iron-constantan thermocouple embedded in the sample centre. Temperature calibrations were not performed; thus it is possible that the thermocouple, being further from the winding than most of the specimen, indicated a temperature lower than the average sample temperature. Indicated temperatures remained steady to within  $\pm 2^\circ\text{C}$  in all runs. The vanadium can was surrounded by a 4 cm diameter glass jacket, which is normally evacuated but which in these experiments was left filled with air to prevent decomposition of the sample. A run with the can empty gave the f.c.c. peaks of the nichrome winding, and no  $\beta$ - $\text{UO}_2(\text{OH})_2$  peak affected by this pattern was used in calculations.

### Calculations and results

Integrated intensities were obtained for the peaks by subtracting the background contribution, and these were then converted to  $\sum F_{hkl}^2$  values by multiplying by the Lorentz factor  $\sin \theta \cdot \sin 2\theta$ . Each set of data was refined on  $F^2$  with statistical weights using the refinement procedure, starting parameters, scattering lengths and cell dimensions of Taylor & Hurst (1971) and the program *ORFLS* (Busing, Martin & Levy, 1962). Unobserved reflexions were also treated by the method described in Taylor & Hurst (1971). Each of the six refinements needed about 10 cycles. The computed

errors were doubled to allow for loss of statistical degrees of freedom due to overlap. The final parameters at each temperature are listed in Table 1,  $R$  values according to the formula  $R = \sum(F_o^2 - F_c^2) / \sum F_o^2$  in Table 2, the final observed and calculated  $F^2$  values in Table 3, and hydrogen bond data in Table 4.

Table 1. Final parameters for  $\beta$ - $\text{UO}_2(\text{OH})_2$  at 21, 130, 200, 220, 240 and 260°C

	Temperature				$B^*$
	(°C)	$10^3x$	$10^3y$	$10^3z$	
O(1)	21	120 (7)	484 (13)	349 (5)	1.8 (11)
	130	141 (6)	470 (5)	346 (2)	1.8 (4)
	200	160 (8)	460 (6)	344 (3)	2.6 (5)
	220	166 (6)	462 (4)	345 (2)	2.9 (4)
	240	156 (8)	439 (6)	329 (3)	2.6 (6)
	260	149 (5)	456 (3)	344 (2)	2.3 (4)
O(2)	21	210 (13)	317 (9)	084 (6)	
	130	220 (11)	294 (6)	094 (2)	
	200	241 (18)	297 (6)	089 (3)	
	220	291 (11)	279 (5)	094 (2)	
	240	250 (14)	266 (7)	104 (4)	
	260	238 (20)	273 (6)	104 (2)	
H	21	193 (18)	356 (11)	166 (9)	
	130	224 (12)	320 (6)	172 (5)	
	200	267 (20)	320 (8)	180 (8)	
	220	312 (17)	317 (6)	188 (6)	
	240	242 (20)	308 (8)	191 (7)	
	260	230 (25)	284 (8)	190 (3)	

\* Constant in overall Debye-Waller temperature factor  $\exp[-2B \sin^2 \theta / \lambda^2]$ .

The O–H distances in Table 4 are shorter than those found in other hydroxides by single-crystal neutron diffraction measurements, e.g.  $0.982 \pm 0.004 \text{ \AA}$  in  $\text{Ca}(\text{OH})_2$  (Busing & Levy, 1957) and  $1.005 \pm 0.004 \text{ \AA}$  on  $\text{AlO}(\text{OH})$  (Busing & Levy, 1958). The latter distances, however, were corrected for the apparent shortening due to thermal vibration, the hydrogen being assumed to ‘ride’ on its associated oxygen atom (Busing & Levy, 1964). Assuming  $B_H = 4.0 \text{ \AA}^2$  and  $B_O = 2.0 \text{ \AA}^2$ , the formulae of Busing & Levy (1964) give corrections of  $+0.03 \text{ \AA}$  (‘riding’ motion) or  $+0.09 \text{ \AA}$  (non-correlated motion of oxygen and hydrogen atoms). The present values, with these corrections, would be closer to the single-crystal values, but no corrections were applied because of the uncertainty in their magnitude, and the lower accuracy inherent in the powder method. The O–H...O distance of  $2.54 (6) \text{ \AA}$  at 240°C is unrealistically low, and arises from  $y$  and  $z$  parameters for O(1) which also appear to be low (Table 1). The data obtained at 240°C were checked, but the cause of the discrepancy was not identified. The parameters determined at 240°C, particularly the  $y$  and  $z$  parameters for O(1), should be regarded as suspect.

As the choice of a line background is rather subjective, and as there were few peaks, overlap, and high

Table 2. Values of  $R = \sum(F_o^2 - F_c^2) / \sum F_o^2$  at 21, 130, 200, 220, 240 and 260°C

Temperature °C	21	130	200	220	240	260
$R$	0.082	0.050	0.077	0.059	0.069	0.060

background, it was thought that systematic errors in the choice of background could have caused significant errors in the final parameters. Cycles were thus also calculated with backgrounds deliberately chosen too high; these showed that the results were sensitive to slight changes in the background values, and indicated that the program errors should be doubled again. All errors quoted in this paper are thus the program errors multiplied by a factor of four.

**Discussion**

*The crystal structure at 21 °C*

Positional parameters obtained in this work agree within the respective errors with the parameters found

in the neutron powder study of Taylor & Hurst (1971) which used the elastic diffraction technique (Caglioti, 1970). However, as discussed by Taylor & Hurst (1971), there is some disagreement between the neutron parameters and those obtained by single-crystal X-ray diffraction (Roof, Cromer & Larson, 1964; Bannister & Taylor, 1970). This disagreement probably reflects the systematic errors inherent in the two techniques. In the neutron work these errors arise from the superposition of reflexions and consequent lack of primary data, and from errors in choosing the background levels. These two factors increased the parameter errors by a factor of four (see previous section), and this factor has been included in the results listed in Tables 1 and 4.

Table 3. Observed and calculated  $F^2$  values at 21, 130, 200, 220, 240 and 260 °C ( $\times 10$ )

Brackets enclose reflexions superposed in a peak, and asterisks denote unobservably small reflexions.

21°		130°		200°		220°		240°		260°	
H	K	H	K	H	K	H	K	H	K	H	K
1	1	1	1	1	1	1	1	1	1	1	1

Systematic errors in our X-ray work are probably mainly due to errors in correcting for absorption, arising from errors in the measured crystal shape and size and possibly in the tabulated value of ( $\mu/\rho$ ) for uranium. In our refinement, we attempted to reduce the effect of these errors by omitting the worst-affected low-angle reflexions. Conceivable errors in crystal size could have caused the transmission factor to vary by 1.7 at low  $\theta$  to 1.3 at high  $\theta$ . Other possible sources of error are uncertainties in the uranium scattering curve, due to lack of precise knowledge of the uranium charge, and extinction. A later refinement of the X-ray data including an isotropic extinction correction has confirmed our earlier conclusion that the extinction effects were small and were outweighed by the absorption errors.

The shape and inclination of the octahedra in the crystal structure deserve more comment than they have received in previous publications (Roof, Cromer & Larson, 1964; Bannister & Taylor, 1970). The four O(2) atoms form not a square but a parallelogram, with the diagonals of unequal length ( $ac > bd$ ) and not at right angles to each other (the angle  $ahd \approx 86^\circ$ ) (Figs. 1 and 2). This distortion may be attributed to the hydrogen bonds extending from the O(2) atoms to O(1) atoms in neighbouring layers. As Fig. 1 suggests, the hydrogen bonds extending from O(2) atoms  $a$  and  $c$  tend to stretch the diagonal  $ac$  more than the hydrogen bonds from  $b$  and  $d$  stretch  $bd$ . The angle  $ahb$  exceeds the angle  $ahd$  because the hydrogen bonds from  $a$  and  $b$  extend to layers either side of the octahedron, whereas the bonds from  $a$  and  $d$  extend to the one layer. The hydrogen bonding to adjacent layers also twists the O(2) parallelogram in Fig. 1 clockwise about [001] and tilts it relative to the (001) plane.

Table 4. Hydrogen bond data for  $\beta$ - $\text{UO}_2(\text{OH})_2$  at 21, 130, 200, 220, 240 and 260 °C

Temperature (°C)	Bond lengths (Å)		Next O(1)-O(2) interlayer distance (Å)	Bond angle (°) O-H...O
	O-H	O-H...O		
21	0.86 (11)	2.88 (8)	3.50 (8)	171 (7)
130	0.79 (6)	2.78 (4)	3.33 (4)	158 (5)
200	0.93 (9)	2.78 (5)	3.37 (5)	147 (7)
220	0.97 (8)	2.85 (4)	3.22 (4)	145 (7)
240	0.90 (11)	2.54 (6)	3.11 (6)	160 (8)
260	0.86 (4)	2.71 (3)	3.20 (3)	148 (4)

Similar arguments may be applied to the positions of the O(1) atoms in the octahedra. In particular since the atoms *a*, *d* and *e* are all hydrogen-bonded to the layer above the octahedron whereas *b* and *c* are hydrogen-bonded to the layer below, the angles *ahc* and *dhe* are slightly less than the angles *che* and *bhe* respectively (Fig. 2).

#### Temperature-induced changes

As predicted in our earlier paper (Bannister & Taylor, 1970), increasing temperature causes the O(2) atoms to move to positions immediately above or below the  $\langle 110 \rangle$  diagonals in the unit cell (Fig. 1). The prediction was based on the observation that the thermal vibration ellipsoid for O(2) has a dominant axis, which is directed towards open channels in the crystal structure. With increasing temperature the O(2) atoms would thus be expected to move towards these channels. In this model no account was taken of the hydrogen atoms, but they are located so close to the O(2) atoms that the channels remain present and the argument is not affected.

The movement of the O(2) atoms was postulated to occur as a rotation of the U–O(2) bonds about  $[110]$ , their inclination to  $[110]$  remaining unchanged but with the tilt of the O(2) plane of each octahedron to (001) increasing to a maximum. The actual results are shown in Fig. 3. The angle between  $[110]$  and *hb*, the shorter of the two U–O(2) bonds, does remain constant to within about  $1^\circ$  up to  $260^\circ\text{C}$ , whilst the tilt of the O(2) plane to (001) increases by about  $7^\circ$ . Thus the original model, in which shape changes were ignored and the thermal expansion anisotropy was attributed entirely to changes in orientation of the octahedra, was essentially correct. Megaw (1968) concluded similarly that thermal expansion anisotropy in certain niobates was influenced more by changes in tilt of the  $\text{NbO}_6$  octahedra than by shape changes within the octahedra.

Although thermal expansion anisotropy in  $\beta\text{-UO}_2(\text{OH})_2$  is caused mainly by changes in orientation of the octahedra, they do also change in shape (Figs. 1 and 2). Up to  $220^\circ\text{C}$ , when the alignment of O(2) atoms along  $\langle 110 \rangle$  is complete, the diagonals of the O(2) parallelogram become even more dissimilar (Fig. 1) although the angle between them (*ahd*, Fig. 2) does not change. The O(1)–U–O(1) bond remains collinear by symmetry, but the bond length (*eh*) increases (Fig. 1) and it rotates in the opposite direction to the rest of the octahedron, leading to a rapid increase in the angle *ahc* and a decrease in *dhe* (Fig. 2). All changes tend to return to zero above  $220^\circ\text{C}$ .

Qualitative explanations for these shape changes involve the influence of hydrogen bonding between octahedra in neighbouring layers. As the O(2) parallelogram *abcd* rotates anticlockwise (Fig. 1), the hydrogen bonds pull the neighbouring O(1) atoms in the direction of movement of the O(2) atoms. Thus O(1) atoms *j* and *l* are caused to rotate anticlockwise in the plane

of projection about their bonded uranium atoms, and O(1) atoms *k* and *m* rotate clockwise. By symmetry, the U–O(1) bond *eh* thus rotates clockwise whilst the O(2) parallelogram *abcd* rotates anticlockwise. At the same time the tendency of the O(2) atoms to pull the O(1) atoms along behind them leads to an increase in the U–O(1) bond length.

The initial divergence between the lengths of the diagonals of the O(2) parallelogram probably has an explanation similar to that offered to support the difference in their room temperature values. As the parallelogram *abcd* rotates anticlockwise, its tilt to the (001) plane also increases. Thus the diagonals *ac* and *bd* become directed more closely towards the neighbouring planes to which these O(2) atoms are hydrogen-bonded. Since the hydrogen bonds tend to stretch *ac* more than *bd*, this increased tilt will lead to a lengthening of *ac* and a corresponding decrease in *bd*. This effect reaches its maximum value when the O(2)

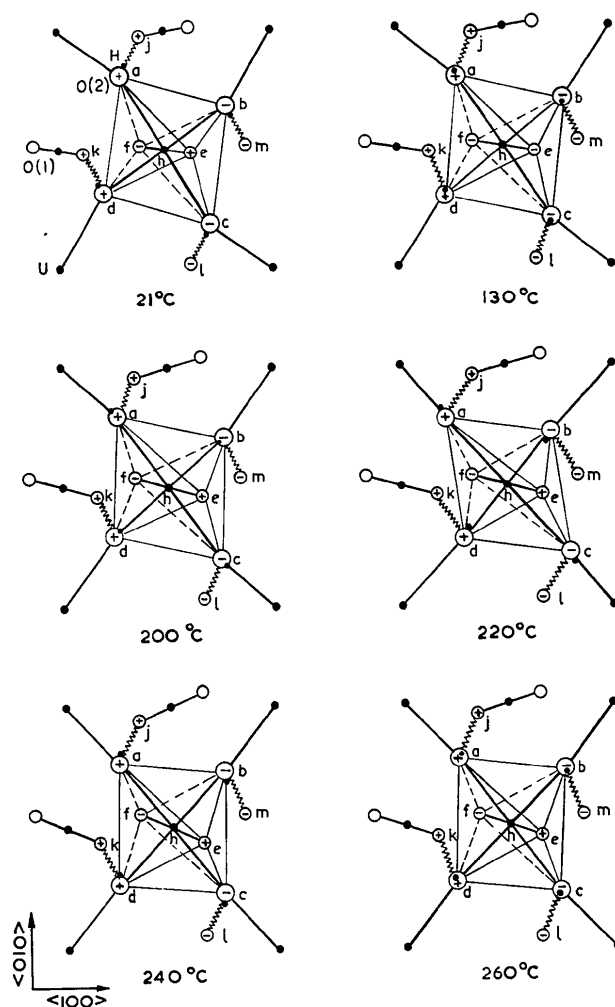


Fig. 1. The effect of temperature on the crystal structure of  $\beta\text{-UO}_2(\text{OH})_2$ , as seen in a (001) projection. Filled circles are hydrogen atoms (small) and uranium atoms (large), and open circles are O(1) atoms (small) and O(2) atoms (large).

atoms lie immediately above or below the  $\langle 110 \rangle$  diagonals of the unit cell. The general relaxation of all

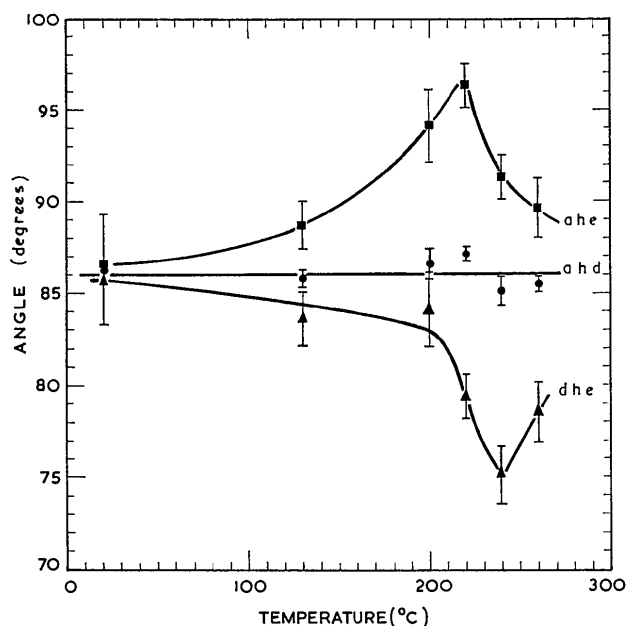


Fig. 2. The effect of temperature on the angles between bonds in the octahedra in  $\beta\text{-UO}_2(\text{OH})_2$ .

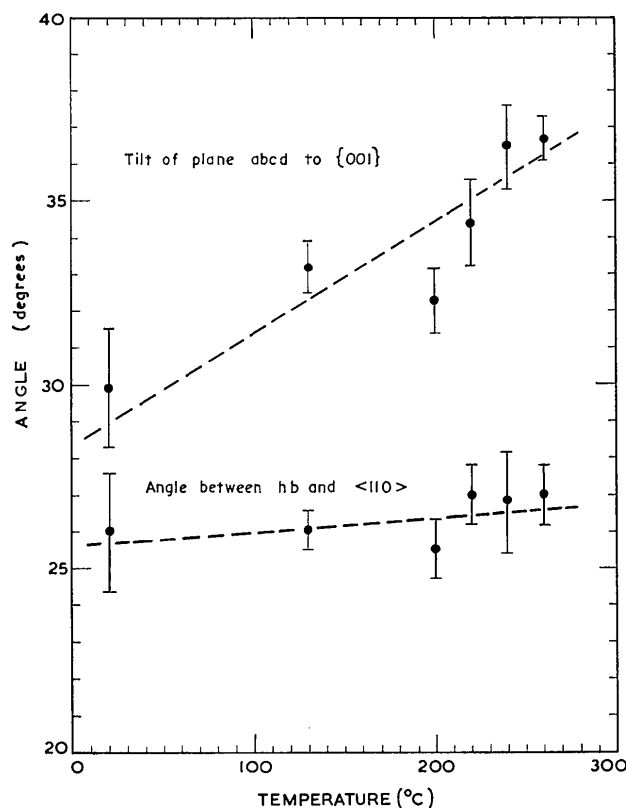


Fig. 3. The effect of temperature on the inclination of U-O(2) bonds to  $[110]$  and on the tilt of the O(2) plane to  $\{001\}$ . (In this Figure, 'between *hb* and  $\langle 110 \rangle$ ' should read 'between *hb* and  $[110]$ '.)

shape distortions which occurs at higher temperatures can probably be attributed to the influence of thermal vibrations eventually tending to outweigh the influence of the hydrogen bonds.

#### Hydrogen bond character

It was predicted previously (Bannister & Taylor, 1970) that the hydrogen bonds may become bifurcated at 260°C and above. This suggestion was based on O(1)-O(2) interlayer contact distances calculated from the simple model for the anisotropic thermal expansion, in which shape changes of the octahedra were not considered. However, Fig. 1 suggests, and Table 4 confirms, that the hydrogen bonds are definitely not bifurcated at 260°C. Bifurcation could have occurred if each U-O(1) bond had not rotated in the opposite direction to the rest of the octahedron. Thus it is still possible that, if the relaxation in shape distortion evident from 220 to 260°C continues at higher temperatures, bifurcation of the hydrogen bond could eventually occur. However it would be difficult to confirm by experiment, because thermal decomposition begins to occur above about 300°C.

#### Conclusions

Neutron diffraction of  $\beta\text{-UO}_2(\text{OH})_2$  powders at elevated temperature has confirmed that the strongly anisotropic thermal expansion of this material is caused by the rotation of oxygen octahedra in the structure. At the same time the hydrogen bonding between octahedra in adjacent layers leads to pronounced shape changes in the octahedra. Contrary to an earlier suggestion, bifurcated hydrogen bonds do not exist in the fully-distorted structure.

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