very high angles, and only become significant if the film is photometered to this order of accuracy. These quantities may be compared with the centroid displacement and variance which have been determined previously (Pike, 1957, 1959; Langford, 1962) for a diffractometer with various collimator geometries.

Unlike most geometrical effects, the error arising from axial divergence does not extrapolate to zero at $2\theta=180°$. In the accurate determination of lattice parameters, therefore, it is necessary to evaluate the contribution to each diffraction maximum. If the centroid and variance are used as measures of position and breadth, the axial-divergence error is directly additive to errors from other aberrations (Pike,1957; Parish & Wilson, 1959).

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Neutron Diffraction Investigation of U_3O_8*

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A polycrystalline sample of orthorhombic U_3O_8 has been investigated by neutron diffraction in order to resolve discrepancies between previous single-crystal X-ray and powder neutron investigations. The space group is $Amm2$ (C_{2v}^{14}). The uranium atoms are surrounded by six oxygen atoms in close contact at distances between 2·07 and 2·23 Å, with a seventh oxygen atom at 2·44 Å for the U(1) atom and at 2·71 Å for the U(2) atom.

Introduction

The structure of the orthorhombic form of U_3O_8, first proposed by Zachariasen (1945), has been redetermined independently by an X-ray investigation on single crystals (Chodura & Malý, 1958) and by a neutron-diffraction investigation on powdered material (Andresen, 1958). The results from the two methods differ in many details, although the overall features are quite similar (Fig. 2). Because the investigation of Andresen made use of a neutron diagram with a rather poor resolution, it seemed worth while to repeat it, using an improved resolution, in order to get a set of experimental data more sensitive to the details of the structure.

Experimental

A high purity sample of U_3O_8 powder was mounted on the powder diffractometer at the Petten HFR. The sample was contained in a cylindrical aluminum sample holder of 0·05 mm wall thickness and 24 mm diameter. Monochromatic radiation with a wavelength of 1·092 Å was obtained from a copper (200) plane. Soller slits of 10′ angular divergence were mounted in front of the BF_3 detector and between the reactor and the monochromator. The experimental data of Table 1 were obtained in about one week with the reactor operating at 20 MW. The intensities were brought to an absolute scale by scaling from a nickel powder diagram, obtained under identical conditions. The diagram is reproduced in Fig. 1.

Results and discussion

From an X-ray diagram the unit-cell dimensions of the sample were found to be $a=4{\cdot}14_8$, $b=11{\cdot}96_6$ and $c=6{\cdot}71_7$ Å. The axes have been chosen in accordance with the usual designation of the space group, derived below. To avoid confusion, all space groups mentioned have been referred to these axes.

The unit cell is in accordance with Andresen's data, whereas Chodura & Malý report an a axis of double length derived from weak layer lines on rotation

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† Actually there is one weak intensity at 25·3° 2θ that cannot be indexed on the present cell. Nor, however, does it fit with an a axis of double length. It has been neglected.

Table 1. *Observed and calculated structure factors in barns per unit cell*

hkl	jF_c^2		jF_o^2
020	1·0		
011	2·7	3·7	3·1
100	107·4	107·4	101·2
031	136·0		
120	0·3	136·3	134·6
111	0·6		
002	60·0	60·6	61·9
040	1·1	1·1	< 1·8
022	2·6	2·6	< 1·8
131	5·4		
102	4·0	9·4	9·4
140	11·1	11·1	16·2
122	30·6	30·6	40·3
051	77·4	77·4	92·4
042	49·2	49·2	48·1
013	72·4	72·4	82·4
200	364·5	364·5	369·3
060	242·8		
151	96·0	338·8	350·3
142	56·6		
220	1·8		
211	4·9		
033	505·7		
113	67·9	636·9	652·9
160	95·4	95·4	101·4
231	253·9		
133	223·9		
202	112·7	590·5	587·6
062	183·1		
240	1·8	184·9	192·3
222	3·9		
004	72·5	76·4	76·0
071	14·9	14·9	15·1
053	24·6	24·6	24·9
024	42·4	42·4	48·8
162	12·5	12·5	13·6
104	1·3	1·3	< 6·2
171	1·4	1·4	< 6·4
251	134·6		
153	2·4		
242	85·9	223·0	258·2
213	126·9		
124	11·1	138·1	139·2
080	0·1	0·1	< 6·7
044	3·9	3·9	< 7·0
260	434·3	434·3	403·2
233	902·4		
180	4·9	907·3	910·1
300	90·7		
144	20·2	111·0	117·0
082	40·4		
073	43·8	84·2	56·9
320	0·3		
311	0·5	0·8	< 8·1
015	23·6	23·6	28·0
262	335·8	335·8	328·3

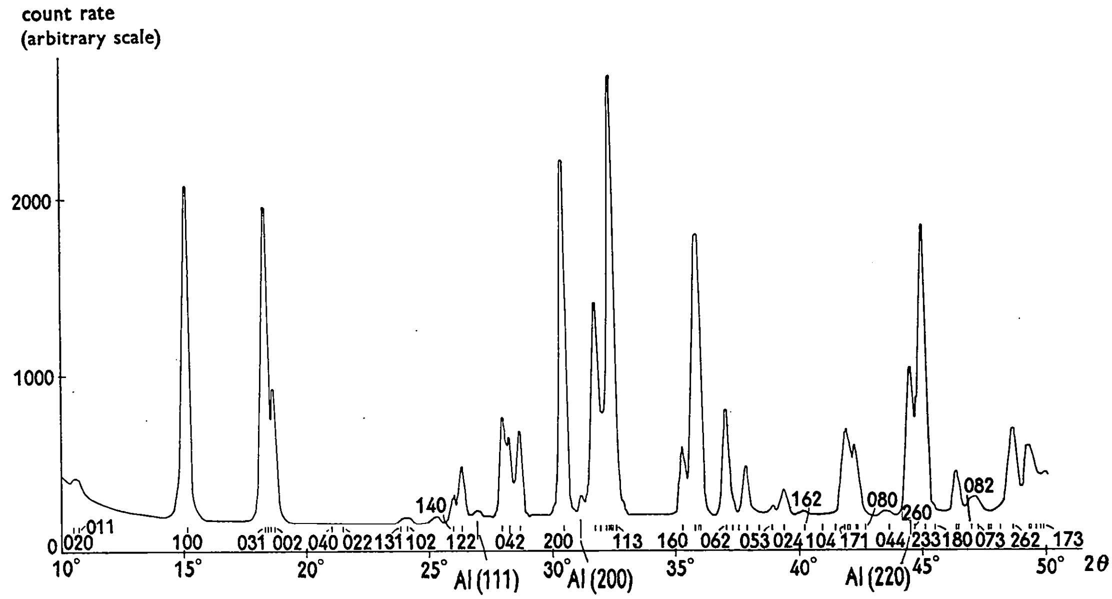
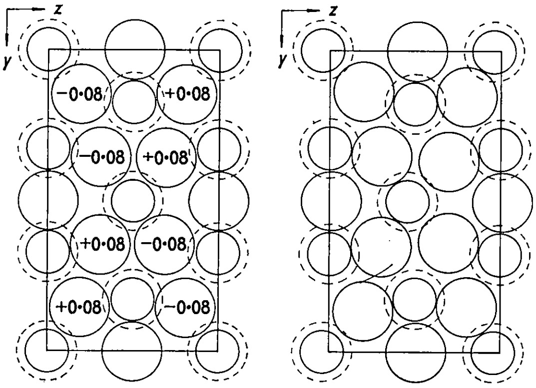


Fig. 1. Neutron diffraction pattern of U_3O_8.

photographs. In the present diagram no trace is found of lines to be expected for a double axis, even though some of these should give considerable intensity contributions†. It is therefore assumed that the unit cell of Chodura & Malý does not apply to the sample used in this investigation.

Chodura & Malý also noticed some splitting of their reflexions, indicating that their sample was partly monoclinic. The resolution of the neutron pattern is insufficient to reveal the existence of a monoclinic fraction and hence the sample was considered nearly enough orthorhombic to warrant a description in an orthorhombic space group. The space group given by Andresen is *A*222 (D_2^6), while Chodura & Malý used *Amma* (D_{2h}^{17}). Halving the *a* axis reduces the latter space group to *Amm*2 (C_{2v}^{14}). Andresen's structure is given in Fig. 2 together with that of Chodura & Malý, the latter slightly modified because of transition from *Amma* to *Amm*2.



(*a*) (*b*)

Fig. 2. The structure of U_3O_8 viewed along the *a* axis: (*a*) According to Andresen. (*b*) According to Chodura & Malý, modified as indicated in the text. In both (*a*) and (*b*) small circles designate uranium atoms ($x=0$), large circles oxygen atoms: dotted circles $x=0{\cdot}5$; full circles *x* as indicated in (*a*), $x=0$ in (*b*).

In the present investigation, the neutron intensities are again in agreement with a centring in the *a* plane. This, in combination with a short *a* axis, leaves only a choice from the space groups *A*222 (D_2^6), *A*2*mm* (C_{2v}^{11}), *Amm*2 (C_{2v}^{14}) and *Ammm* (D_{2h}^{19}). In projection along the *a* axis, all of these result in the plane group *cmm*, with the exception of *Amm*2 which gives *cm*1. This means that the U(1) atoms in projection along the *a* axis are either at 0,*z* (*Amm*2) or at 0,0 (all others). A superficial inspection of the 0*kl* X-ray intensities shows that the position 0, 0 is unlikely. The fact that the plane group *cmm* is incompatible with the data is further confirmed by calculating the neutron structure factors for the 0*kl* reflexions up to 015, using the parameters given by Andresen. The experimental values for all of these intensities can be obtained separately, although some have to be approximated by an estimate due to overlap. The fit between the observed and calculated data was rather poor. Using the calculated signs and the observed data, for those reflexions that gave calculated values equal to at least half the observed ones, a scattering-density projection is obtained (Fig. 3). It is evident that the peak at $\frac{1}{6}$, $\frac{1}{6}$, which should be a single oxygen atom in *cmm*, is composed of two atoms, related by false symmetry. Another prominent feature is the failure of the oxygen at 0, $\frac{1}{2}$ to show up, although its position was used in the calculation. The only possible conclusion seems then that the plane group has to be *cm*1 and hence the space group *Amm*2.

Assuming that the uranium positions of Chodura & Malý are approximately correct, the oxygen atoms were placed in such positions as seemed in agreement with the peaks of Fig. 3, reasonable distances being kept between all atoms. The structure was then refined by trial and error calculations on an Electrologica X 1 computer, shifting parameters independently until the minimum value of $\Sigma j|F_c^2-F_o^2|/\Sigma jF_o^2$ was obtained. (j = multiplicity of the reflexion).

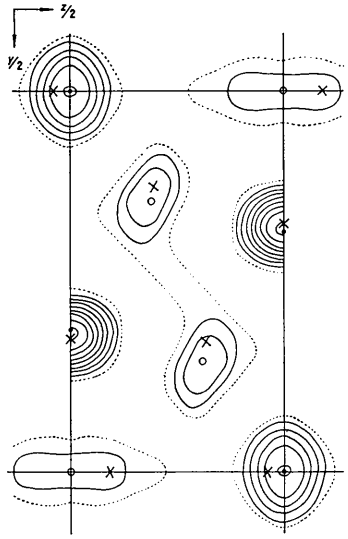


Fig. 3. Scattering-density projection along the *a* axis, assuming as space group *A*222. Positions used in calculation: black dots (U + O); open circles (O). Crosses indicate correct structure.

This minimum value was 4·25%. As there is considerable overlapping of reflexions in the pattern, this low value does not necessarily mean that the parameters are very accurate, but it may be considered as an indication that there are no fundamental errors in the selection of the coordinates and the space group. Separate isotropic temperature factors were introduced for uranium and oxygen ($2B_u=0{\cdot}46$ Å^2, $2B_o=1{\cdot}35$ Å^2).

Table 2. *Position parameters, as decimal fractions of the unit-cell sides*

	x	*y*	*z*
2 U(1) in (*a*)	0	0	0·962
4 U(2) in (*d*)	0	0·324	0
2 O(1) in (*b*)	0·500	0	0·962
4 O(2) in (*e*)	0·500	0·324	0
2 O(3) in (*a*)	0	0	0·598
4 O(4) in (*d*)	0	0·126	0·197
4 O(5) in (*d*)	0	0·328	0·327

The final list of observed and calculated values of jF^2 is given in Table 1, the final parameters in Table 2.

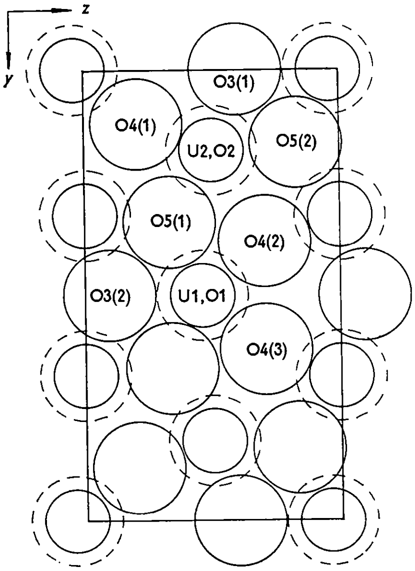


Fig. 4. The structure of U_3O_8 viewed along the a axis (representation as in Fig. 2). Numbers not in parantheses refer to parameters in Table 2 or equivalent sets; numbers added in parentheses allow reference to corresponding distances in Table 3.

The structure is shown in projection along the a axis in Fig. 4. From the list of interatomic distances (Table 3) it is seen that the U(1) and U(2) atoms are surrounded by six oxygen atoms at 2·07 to 2·23 Å. In addition, U(1) has a seventh oxygen atom at a somewhat larger distance (2·44 Å) while U(2) has its seventh atom at a much larger distance (2·71 Å). This seems in agreement with the assumption that U(1) may be identified with the U^{6+} ions and U(2) with the U^{5+} ions.

Table 3. *Interatomic distances*

	(Å)		(Å)		(Å)
U(1)–O(1)	2·07	O(1)–O(3)(2)	3·06	O(3)(1)–O(4)(1)	3·09
U(1)–O(3)(2)	2·44	O(1)–O(4)(2)	3·01	O(3)(2)–O(5)(1)	2·57
U(1)–O(4)(2)	2·18	O(1)–O(5)(2)	3·21	O(4)(1)–O(5)(1)	2·57
U(1)–O(5)(2)	2·23	O(2)–O(3)(1)	3·02	O(4)(2)–O(4)(3)	3·02
U(2)–O(2)	2·07	O(2)–O(4)(1)	2·97	O(4)(2)–O(5)(1)	2·55
U(2)–O(3)(1)	2·20	O(2)–O(4)(2)	3·42		
U(2)–O(4)(1)	2·12	O(2)–O(5)(1)	2·99		
U(2)–O(4)(2)	2·71	O(2)–O(5)(2)	3·02		
U(2)–O(5)(1)	2·16				
U(2)–O(5)(2)	2·20				

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The Crystal Structure of Lithium Hydrazinium Sulfate

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At room temperature, lithium hydrazinium sulfate, $Li(N_2H_5)SO_4$, is orthorhombic, space group $Pbn2_1$, with $a = 8·99$, $b = 9·94$, $c = 5·18$ Å, and $Z = 4$. The structure has been determined by X-ray diffraction and has been refined to give an R index $(\Sigma|F_o - F_c|/\Sigma|F_o|)$ of 0·11. The lithium and sulfur atoms are at the centers of tetrahedra of oxygen atoms. The tetrahedra share apices to form a three-dimensional framework containing channels running parallel to the c axis. The hydrazinium ions lie in these channels and are linked into infinite chains by hydrogen bonding between their NH_2 groups. The electrical properties of the crystal appear to be related to the movement of protons within this chain.

Introduction

The interesting electrical properties of lithium hydrazinium sulfate, $Li(N_2H_5)SO_4$, have been described briefly by Pepinsky, Vedam, Okaya & Hoshino (1958). The crystals are orthorhombic, space group $Pbn2_1$, and are ferroelectric at room temperature, with a spontaneous polarization along the c axis. The spontaneous polarization is found to increase with temperature in the range −10 to +70 °C. Cuthbert & Petch