LIPSON, H. & COCHRAN, W. (1953). *The Determination of Crystal Structures*, S. 132, 250, 255. London: G. Bell.
MACGILLAVRY, C. H. & BIJVOET, J. M. (1936). *Z. Kristallogr.* **94**, 231, 249.
PAULING, L. (1933). *Z. Kristallogr.* **85**, 380.
PAULING, L. (1940). *The Nature of the Chemical Bond*, S. 179. London: Oxford University Press.
RIGAMONTI, R. (1947). *Atti acad. nazl. Lincei, Classe sci. fis. mat. e nat.* **2**, 446.
SILBERSTEIN, M. A. (1937). *C. R. Acad. Sci., Paris*, **205**, 909.
WELLS, A. F. (1950). *Structural Inorganic Chemistry*, 2nd ed., p. 70. Oxford: University Press.
WILSON, A. I. C. (1942). *Nature, Lond.* **150**, 152.

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The Structure of U_3O_8 Determined by Neutron Diffraction

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Neutron diffraction diagrams of the orthorhombic form of U_3O_8 show that the structure previously assumed on the basis of X-ray data must be in error. A modified unit cell is derived in which two of the uranium atoms are surrounded by a distorted octahedron of six oxygen atoms at distances of U_1–O_2 = 2·07 Å and U_1–O_4 = 2·18 Å. The other four are surrounded by seven oxygen atoms at distances U_2–O_3 = 2·07 Å, U_2–O_1 = 2·21 Å, U_2–O_4' = 2·17 Å and U_2–O_4'' = 2·42 Å. The symmetry conforms with the orthorhombic space group D_2^6–$C222$.

Introduction

In the determination of the structures of the uranium oxides based on X-ray data, one has had to rely greatly on spatial considerations for determining the oxygen positions. Utilizing the more favourable ratio between the coherent scattering amplitudes of uranium and oxygen for neutrons, $b_U = 0{\cdot}85 \times 10^{-12}$ cm. and $b_O = 0{\cdot}58 \times 10^{-12}$ cm., it was found of interest to check some of the proposed structures by means of neutron diffraction.

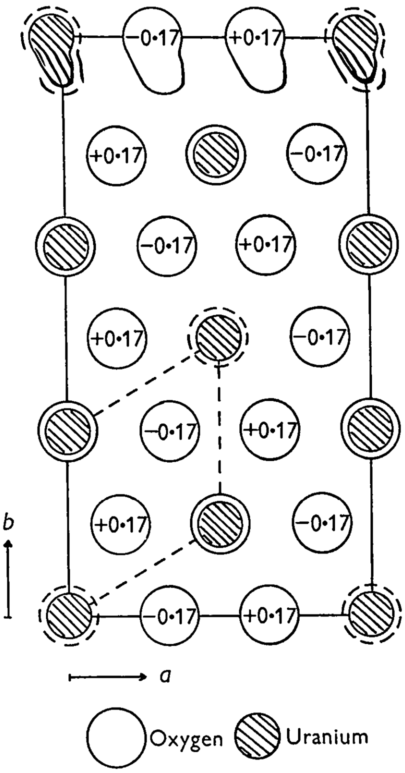

Fig. 1. *c* axis projection of previously assumed unit cell of U_3O_8.

For the orthorhombic form of U_3O_8 a structure has been proposed by Zachariasen (1945), based on the close relation with the α-UO_3 structure. Fig. 1 shows the projection along the *c* axis of the proposed unit cell, the dotted lines giving the outlines of the hexagonal UO_3 cell, whose dimensions are (Zachariasen, 1948) $a_0 = 3{\cdot}971 \pm 0{\cdot}004$ Å and $c_0 = 4{\cdot}168 \pm 0{\cdot}008$ Å. The *a* axis of the orthorhombic cell is somewhat less than $\sqrt{3}a_0$ being (Hoekstra *et al.*, 1955) $a = 6{\cdot}704$ Å, while $b = 11{\cdot}95$ Å and $c = 4{\cdot}142$ Å are very closely equal to $3a_0$ and c_0. Thus the only dimensional change taking place on transition from UO_3 to U_3O_8 is a slight contraction along the *a* axis. To obtain the correct composition the oxygen atoms in the positions $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ were removed as indicated by the dotted rings. The six uranium atoms of this unit cell are all surrounded by a staggered ring of six oxygen atoms, and four of them are in addition bonded to two oxygen atoms above and below at $z = \frac{1}{2}$, forming linear chains along the *c* axis.

Experimental

Neutron powder diffraction diagrams were taken with the automatic diffractometer at the Kjeller reactor JEEP using a cylindrical sample holder of diameter 1 cm. and neutrons of wavelength 1·04 Å. The resolu-

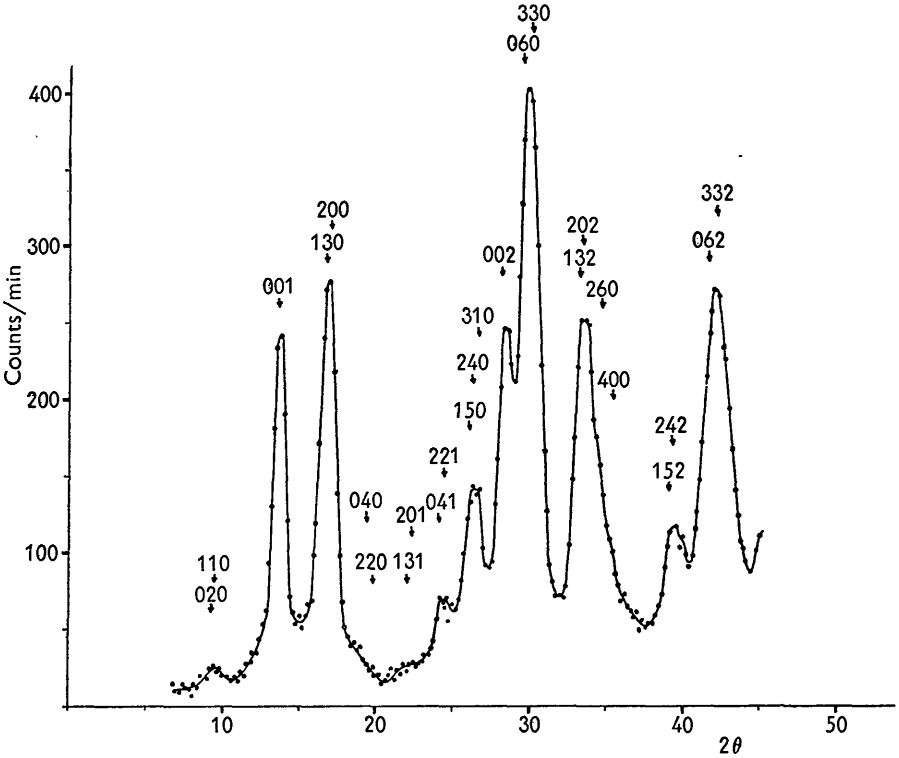

Fig. 2. Neutron diffraction diagram of orthorhombic form of U_3O_8. Instrumental background subtracted.

tion of this instrument is kept rather poor in order to gain intensity, and this causes a severe overlap of the peaks as seen in the diagram of Fig. 2. Still, enough characteristic features are visible in the low-angle region to allow one to draw decisive conclusions regarding the positions of the oxygen atoms. All the observed reflections could be indexed on a *c*-centred orthorhombic cell of the dimensions given above. It became, however, immediately evident that the structure given in Fig. 1 was not correct, and that a rearrangement of most of the oxygen atoms had to be undertaken. The model predicted for instance a strong (131) reflection, whereas at this point in the diagram hardly any peak is visible.

Discussion

From the X-ray data and the established close relation to the α-UO_3 structure it was obvious that only slight changes in the positions of the uranium atoms could be made. For the oxygens, however, a different arrangement was derived by the following reasoning. Since in the unit cell of Fig. 1 the oxygen atoms have retained their positions from the hexagonal UO_3 cell, no orthorhombic space group can be assigned to this cell. Effort was therefore directed towards changing positions so as to conform with the proper orthorhombic space group. In the X-ray data no systematic absences can be found outside those resulting from the *c*-centring. Possible space groups are then: *C*222, *Cmm*2, *Cmmm*, *Cmma*. From spatial considerations

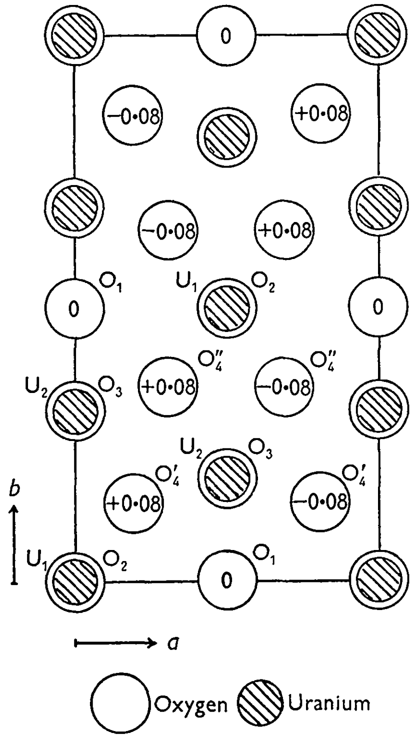

Fig. 3. *c* axis projection of the derived unit cell of U_3O_8.

the space groups involving symmetry planes can be considered unlikely, and so the correct space group is assumed to be D_2^6–$C222$.

This means introducing a 2-fold axis along the c axis bringing each pair of oxygens previously related by the centre of inversion at (0, 0, 0) to the same level of z. To maintain reasonable distances between the oxygens slight changes in the x and y parameters are also needed. Rather little space is left for the oxygen atoms projected on the a axis, and we therefore assume that in the transition from UO_3 to U_3O_8 one of these is removed rather than the one at (0, 0, $\frac{1}{2}$), leaving the remaining one in the position ($\frac{1}{2}$, 0, 0). Correspondingly oxygens are left in the positions ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (0, $\frac{1}{2}$, 0). This is in accordance with the observation that the only dimensional change taking place in the transition is a contraction along the a axis.

The projection of the unit cell thus derived is shown in Fig. 3. To provide more room for the oxygen atoms at ($\frac{1}{2}$, 0, 0) and (0, $\frac{1}{2}$, 0) a slight translation of the neighbouring uranium atoms along the b axis seems reasonable and also leads to a better agreement for the X-ray data. For the neutron data all the changes mentioned produce a better agreement between observed and calculated intensities, and by trial a further refinement of the parameters was carried out bringing the percentage mean error of the integrated intensities down to 11·2%. This value cannot be given much weight since most of the peaks consist of two or more reflections as seen in Table 1, where the observed and calculated intensities are compared. However, assuming linear chains of uranium and oxygen atoms to run along the c axis through all uranium positions only 4 parameters have to be determined. In Table 1 the observed intensities have been normalized to the calculated ones. The temperature factor has been omitted since we are only dealing with low-angle reflections.

Table 1. *Observed and calculated intensities*

hkl	I_c		I_o	*hkl*	I_c		I_o
020	1·88	2·60	3·2	061	9·34	96·13	90·0
110	0·72			132	26·67		
001	41·18		44·9	202	20·16		
130	35·72	64·69	60·2	331	9·24		
021	0			260	11·20		
111	6·22			042	0·66		
200	22·75			222	4·20		
040	0·09		—	400	14·66		
220	0·77		—	170	6·99		
131	2·30	2·30	3·0	350	2·08		
201	0			420	0		
041	2·24	8·09	9·8	261	0·79		
221	5·85			401	2·35	36·12	35·7
150	6·79	33·22	27·9	171	0·70		
240	21·66			152	12·50		
310	4·77			242	14·26		
002	32·67		33·2	351	0·93		
060	26·95	109·4	117·7	312	2·69		
151	5·96			421	2·62		
022	0·78			080	0·07		
241	14·35			440	2·64	65·94	89·3
112	6·45			062	22·73		
330	46·17			332	36·65		
311	8·75			081	1·66		
				003	0·98		
				441	1·28		

The atomic parameters resulting from the refinement are given in Table 2. Each U_1 atom is bonded to six oxygen atoms forming the corners of a distorted octahedron at distances U_1–O_2 = 2·07 Å and U_1–O_4 = 2·18 Å. The other uranium atoms are surrounded by 7 oxygen atoms of which the 2 above and below are at the short distance U_2–O_3 = 2·07 Å, while the other 5 are close to the (001) plane forming a ring at distances: U_2–O_1 = 2·21 Å, U_2–O_4' = 2·17 Å, and U_2–O_4'' = 2·42 Å. The shortest O–O distance is 2·64 Å.

Table 2. *Atomic parameters in* U_3O_8

Space group D_2^6–$C222$

0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$; +

2 U_1^1 in a: 0, 0, 0;
4 U_2 in g: 0, y, 0; 0, $\bar{y}$, 0; y = 0·315
2 O_1 in b: 0, $\frac{1}{2}$, 0;
2 O_2 in d: 0, 0, $\frac{1}{2}$;
4 O_3 in h: 0, y, $\frac{1}{2}$; 0, $\bar{y}$, $\frac{1}{2}$; y = 0·315
8 O_4 in l: x, y, z; $\bar{x}, \bar{y}, z$; x = 0·19
$x, \bar{y}, \bar{z}$; $\bar{x}, y, \bar{z}$; y = 0·145
z = 0·08

Whereas the model of Zachariasen predicted one U^{4+} ion and two U^{6+} ions per molecule, the model suggested here favours the other alternative of 2 U^{5+} and 1 U^{6+} ion. This is in agreement with conclusions drawn by Haraldsen & Bakken (1940) from measurements of the magnetic moment.

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References

Haraldsen, H. & Bakken, R. (1940). *Naturwissenschaften*, **28**, 127.

Hoekstra, H. R., Siegel, S., Fuchs, L. H. & Katz, J. J. (1955). *J. Phys. Chem.* **59**, 136.

Zachariasen, W. H. (1945). Manhattan Project Report CK-2667.

Zachariasen, W. H. (1948). *Acta Cryst.* **1**, 265.