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The structure of β - U_3O_8 . By B.O. LOOPSTRA, *Reactor Centrum Nederland, Petten, The Netherlands*

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The structure of β - U_3O_8 has been determined from neutron-diffraction powder data. The oxygen coordination is a pentagonal dipyramid for two uranium atoms; for the third it is a deformed octahedron.

At room temperature two crystalline forms of U_3O_8 are known. Normally the α -form is encountered, but under special circumstances the β -form is obtained (Hoekstra, Siegel, Fuchs & Katz, 1955). Unit-cell data for the two substances suggest a close structural relationship (Table 1). In this paper a structure determination of β - U_3O_8 is presented to permit a comparison with the structure of α - U_3O_8 (Loopstra, 1962).

β - U_3O_8 was prepared by heating α - U_3O_8 to 1350°C in air or oxygen, followed by slow cooling (100°C per day) to room temperature (Cordfunke, 1969). A coarsely crystalline product was obtained.

Neutron-diffraction powder data were collected at room temperature from a sample, contained in a thin-walled vanadium sample holder of 15 mm diameter. A wavelength of 2.5776(5) Å was employed. The range of observation was $0 < (\sin \theta)/\lambda < 0.361 \text{ \AA}^{-1}$, containing 85 possible reflexions. Soller slits of 10' divergence were placed between

Table 1. *Unit-cell data of α - U_3O_8 and β - U_3O_8 , obtained from X-ray powder diagrams*

Primed axes refer to the subcell. The value of a'/b' indicates the deviation from hexagonality (ideal value: 1.7321).

Phase	α	β
Space group	$C2mm (C_{2v}^{14})$	$Cmcm (D_{2h}^{17})$
a	6.716 (1) Å	7.069 (1) Å
b	11.960 (2)	11.445 (1)
c	4.1469 (5)	8.303 (1)
z	2	4
a'	6.716 (1) Å	7.069 (1) Å
b'	3.9868 (6)	3.8151 (5)
c'	4.1469 (5)	4.1515 (5)
a'/b'	1.6846 (2)	1.8529 (2)

the H.F.R. reactor and the Cu(111) monochromator, and between the sample and the detector.

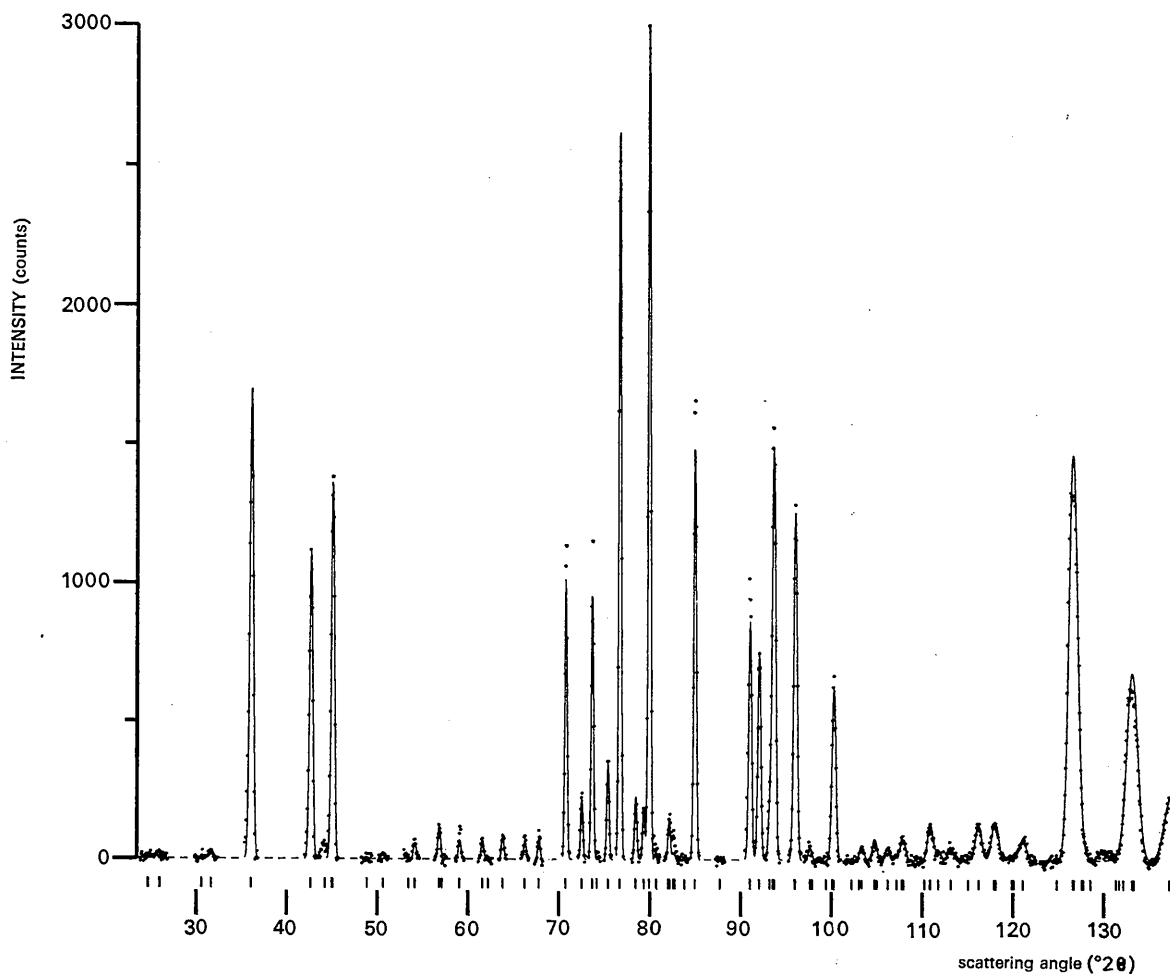


Fig. 1. Observed and calculated powder pattern. Dots: observed data, corrected for background. Full curve: calculated pattern.

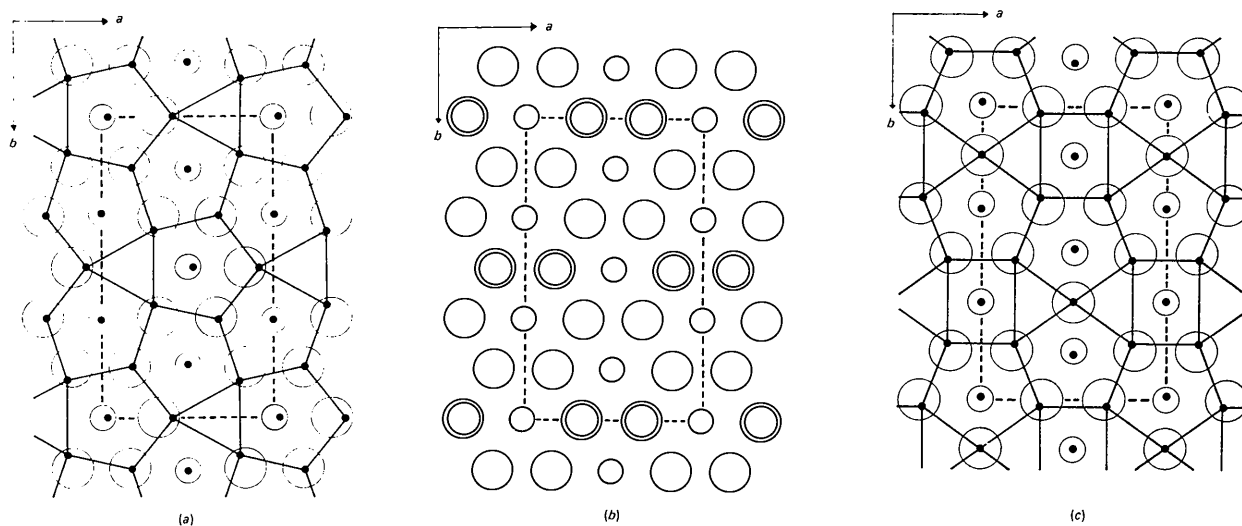


Fig. 2. Relationship between sections perpendicular to the c axis of α - U_3O_8 (a), 'ideal' UO_3 (b), and β - U_3O_8 (c). In (a) and (c) dots represent the actual positions, isolated dots uranium atoms, and dots connected by lines oxygen atoms; circles represent 'ideal' positions, small circles uranium atoms, and large circles oxygen atoms. Ideal positions are obtained from (b) by removing the right-hand atom from each pair of double-circled oxygen atoms to obtain α - U_3O_8 , while for β - U_3O_8 each pair is replaced by one atom halfway between. Note shift of origin by $b/3$ in (c). In (a) the section is at $z=0$, in (c) it is at $z=\frac{1}{3}$.

It was found that the neutron diffraction pattern was clearly related to that of α - U_3O_8 . Therefore a trial structure was sought which closely resembled the structure of α - U_3O_8 (Loopstra, 1962), but which at the same time would explain the occurrence of several sizable reflexions with $l \neq 2n$. Some models that readily suggested themselves were refined by preliminary least-squares computations, based on integral peak intensities. One model, which turned out to give good agreement, was refined by use of the profile-fitting technique described by Rietveld (1969). The resulting fit is displayed in Fig. 1. The final values of the parameters and their standard deviations are given in Table 2.

Table 2. Final least-squares parameters

	x	y	z
U(1)	4(c) 0 (-)	0.989 (1)	0.25 (-)
U(2)	4(c) 0 (-)	0.350 (1)	0.25 (-)
U(3)	4(c) 0 (-)	0.668 (1)	0.25 (-)
O(1)	4(a) 0 (-)	0 (-)	0 (-)
O(2)	8(f) 0 (-)	0.352 (1)	0.023 (1)
O(3)	4(c) 0 (-)	0.165 (1)	0.25 (-)
O(4)	8(g) 0.318 (1)	0.024 (1)	0.25 (-)
O(5)	8(g) 0.319 (1)	0.312 (1)	0.25 (-)

In Fig. 2 the structural relationship between α - and β - U_3O_8 is visualized. From a layer of hypothetical 'ideal' UO_3 [Fig. 2(b)] the idealized α form is derived by removing one oxygen atom from every third row as indicated in Fig. 2(a). (Holmberg, 1970). To obtain the idealized β form two oxygen atoms are replaced by one halfway between them [Fig. 2(c)]. Fig. 2(a) and (c) shows that the actual structures are only slightly distorted from the hypothetical ideal structures. In β - U_3O_8 the layers are stacked along the c axis such that a set of chains of U atoms, surrounded by oxygen atoms at the corners of a pentagonal dipyrmaid, is formed at $x=0$, $y=0$, and $x=\frac{1}{2}$, $y=\frac{1}{2}$. The other uranium atoms form chains in the c direction in which the oxygen coordination is alternately pentagonal dipyrmidal and distorted octahedral. All nearest neighbour groups of an octahedrally co-

ordinated U atom are pentagonal dipyrmidal. This situation may be compared with that in α - U_3O_8 , where all uranium atoms are pentagonal dipyrmidally coordinated.

In Table 3 the U-O distances shorter than 3.5 \AA have been collected. From these it may be seen that the oxygen bonding around U(3) cannot be described in terms of a uranyl group, in which case two distances would be considerably shorter than the others. It has been checked that this result is not due to a wrong choice of the z parameter of O(2): refinement starting from $z = -0.023$ leads to a positive parameter in a few cycles.

Table 3. Coordination of U atoms

Atom(1)-atom(2)	Number of equivalent distances	Distance
U(1)-O(1)	2	2.080 (1) \AA
U(1)-O(3)	1	2.021 (21)
U(1)-O(4)	2	2.287 (10)
U(1)-O(5)	2	2.398 (14)
U(2)-O(2)	2	1.888 (8)
U(2)-O(3)	1	2.112 (21)
U(2)-O(4)	2	2.368 (13)
U(2)-O(5)	2	2.295 (10)
U(3)-O(2)	2	2.275 (8)
U(3)-O(4)	2	2.087 (16)
U(3)-O(5)	2	2.088 (16)

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