JOURNAL OF SOLID STATE CHEMISTRY **102**, 299–305 (1993)

The Crystal Structure of α- and β-$Cs_2U_2O_7$

F. C. MIJLHOFF AND D. J. W. IJDO

Gorlaeus Laboratories, Leiden University, P.O. Box 9502,
2300 RA Leiden, The Netherlands

AND E. H. P. CORDFUNKE

Netherlands Energy Research Foundation ECN, P.O. Box 1,
1755 ZG Petten, The Netherlands

Received January 27, 1992; in revised form June 1, 1992; accepted June 3, 1992

The structure of anhydrous β-$Cs_2U_2O_7$ has been redetermined. The compound is stabilized by water, and the structure of the stable compound in air, α-$Cs_2U_2O_7 \cdot 0.4D_2O$, has been determined with neutron powder diffraction data. Infrared spectra show these D_2O molecules to be chemically bonded. © 1993 Academic Press, Inc.

1. Introduction

Cesium uranates have attracted much interest as possible reaction products in nuclear-fuel elements during fission. For this reason the system Cs_2O–UO_3 was investigated systematically, and as a result a large number of compounds in this system have been described (*1, 2*). In addition, their physico-chemical properties, including the crystal structures (*3*), have been determined. Thus, van Egmond reported two monoclinic structures of $Cs_2U_2O_7$ which would have a reversible phase transition at ≈300°C (*3, 4*). However, since then it appeared that this transition is due to dehydration, and that α-$Cs_2U_2O_7$ is stabilized by a small amount of water. For this reason we reinvestigated the α- and β-$Cs_2U_2O_7$ structure by neutron and electron diffraction. The results are presented in this paper.

2. Experimental

β-$Cs_2U_2O_7$ was prepared by heating a stoichiometric mixture of Cs_2CO_3 and UO_3 in a gold boat at 600°C in dry oxygen for 16 hr. The sample was then homogenized, and an X-ray pattern was taken to judge the progress of the reaction. The sample was heated again and the procedure repeated until the reaction was completed. The sample was then cooled down to room temperature in dry oxygen.

When a sample of β-$Cs_2U_2O_7$ is annealed in moist oxygen below 300°C the so-called α-$Cs_2U_2O_7$ is obtained. This observation was used to prepare a deuterated sample of the α-phase by passing argon, which was saturated with D_2O at a pressure of 10 mm Hg, over the β-phase at about 250°C. The resulting product was the α-phase.

The uranium content in the sample was

0022-4596/93 $5.00

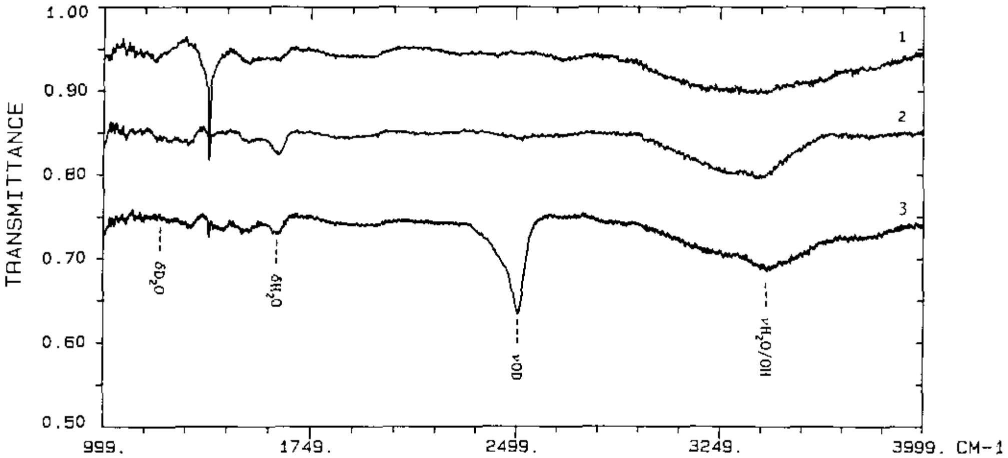

FIG. 1. Infrared spectra of $Cs_2U_2O_7$: (1) β-$Cs_2U_2O_7$, (2) α-$Cs_2U_2O_7 \cdot 0.4H_2O$, and (3) α-$Cs_2U_2O_7 \cdot 0.4D_2O$. The –OD stretch vibration at 2500 cm^{-1} is clearly seen, whereas the corresponding –OH vibration in (2) disappears in the broad absorption band at 3300–3600 cm^{-1} due to the presence of trace amounts of absorbed moisture.

determined titrimetrically (5), and cesium gravimetrically with kalignost. From the results obtained (U 54.72 ± 0.11%; Cs 30.83 ± 0.03%) the composition was calculated to be $Cs_2U_2O_7 \cdot 0.4D_2O$, assuming all the uranium present in the hexavalent state.

Infrared Measurements

The presence of bound H_2O in the α-structure could be made visible in the infrared spectra of the α- and β-phases. The spectra (Fig. 1) were recorded with a Bomen FT DA_3 spectrometer. The characteristic –OD stretching frequency at 2500 cm^{-1} is clearly present in the deuterated sample, whereas the stretching frequency of molecular D_2O vibrations at 1200 cm^{-1} is lacking.

Structure Determination

The X-ray pattern of both compounds could be indexed as a monoclinic *C* face-centered unit cell. No other phases were observed. These results were confirmed by electron diffraction using a Siemens Elmiscope 102 at 100 kV. The α-phase was beam-sensitive and no observation of superstructure or incommensurate modulations could be made, although on grounds of the fractional water content it might have been expected.

Since no single crystals could be grown,

TABLE I

LATTICE PARAMETERS, FRACTIONAL ATOMIC COORDINATES, AND THERMAL PARAMETERS OF β-$Cs_2U_2O_7$ AT 300 K

Space group *C2/m*. *Z* = 2 formula units per cell. Cell constants: a = 14.5293(9) Å, b = 4.3233(3) Å, c = 7.4899(5) Å, β = 113.852(1)°.

	x	y	z	B_{iso} (Å^2)
Cs	0.3994(3)	0	0.5868(7)	1.29(12)
U	0.1469(3)	0	−0.0076(5)	0.02(7)
O(1)	0.2003(4)	0	0.2562(7)	1.59(14)
O(2)	0.4108(4)	1/2	0.2755(6)	1.31(14)
O(3)	0.3104(3)	0	0.0030(6)	0.64(18)
O(4)	0	0	0	0.83(24)

R_p 3.24%, R_{wp} 4.34%, S 1.74

TABLE II

ATOMIC DISTANCES (Å) IN β-$Cs_2U_2O_7$ AT 300 K

Cs–Cs	3.648(11)	U–O1	1.807(6)
Cs–O1	2.951(6)	–O2	1.835(5)
	3.087(6) 2×	–O3	2.345(7)
–O2	3.233(6) 2×	–O3	2.245(2) 2×
	3.323(6) 2×	O4	2.158(5)

about 30 g of $Cs_2U_2O_7$ and $Cs_2U_2O_7 \cdot 0.4D_2O$ were prepared and powder diffractograms recorded at the High Flux Reactor at Petten, the Netherlands. A wavelength of about 2.57 Å from the (111) planes of a copper monochromator was used with a 30-ft collimation. The collected data were corrected for absorption, using $\mu R = 0.22$. A small preferred orientation was present for $Cs_2U_2O_7$.

The structures reported by van Egmond were used as initial models and refined by the program DBW 3.2S version 8802 (*6*).

3. Results

Anhydrous β-$Cs_2U_2O_7$

The final refinement was made using 124 reflections. The variables include a scale factor, three halfwidth parameters defining Gaussian peak shape, the counter zero error, an asymmetry parameter, six background parameters, the unit cell dimensions, atomic position parameters, isotropic thermal parameters, and a preferred orientation parameter. Refinement in space group *C*2/*m* gave the same result as proposed by van Egmond (*4*). The final coordinates are listed in Table I. Selected atomic distances are summarized in Table II; agreement be-

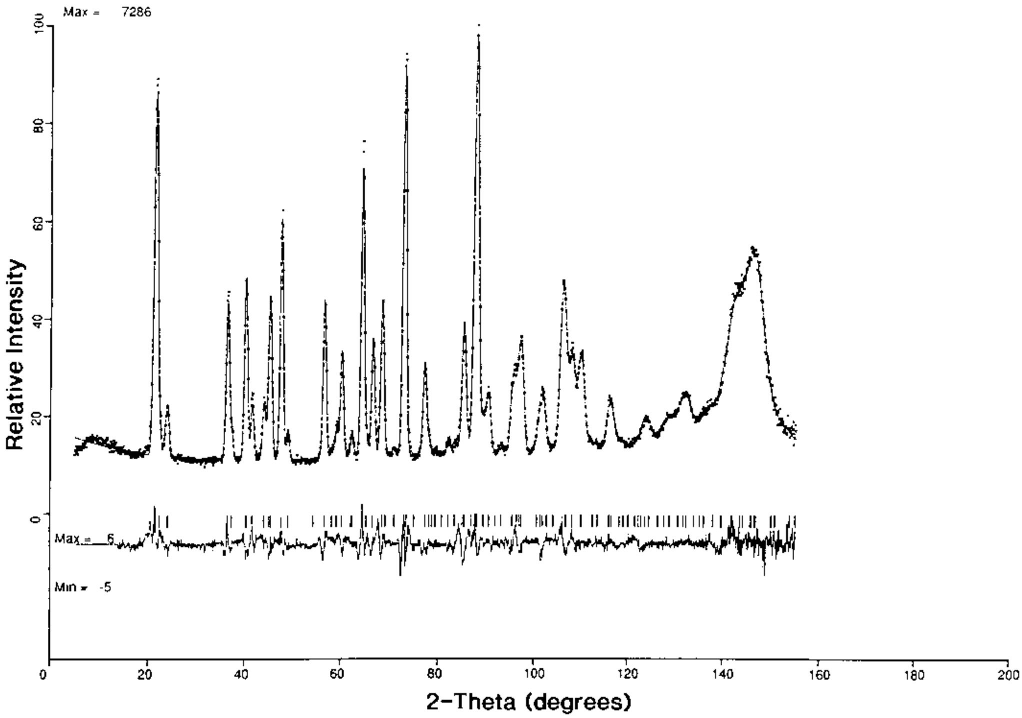

FIG. 2. Observed data (cross) and calculated (solid line) neutron powder diffraction profile of $Cs_2U_2O_7$ and difference curve. Tickmarks are at the positions of the Bragg reflections.

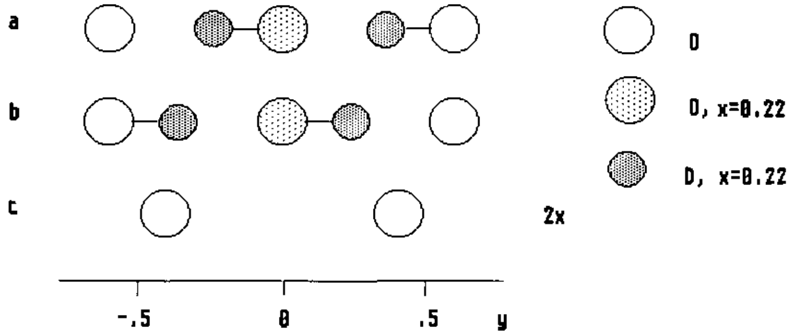

FIG. 3. Arrangement of O and D atoms along [010], used to generate the average structure for refinement.

tween observed and calculated profiles is shown in Fig. 2.

α-$Cs_2U_2O_7 \cdot 0.4D_2O$

The refinement included 124 reflections. Again, van Egmond's model was used as a starting model, to which water molecules had to be added. From the onset it was clear, that the α- and β-forms could only be different in minor aspects. The α-structure almost fitted the β-structure's data. Looking for voids in the structure to put water molecules in, it became obvious that they can only be inserted along the *b* axis, between the 0(4) atoms. As the infrared spectra suggest the presence of OD groups instead of D_2O molecules, the model is based on a distribution of OD groups along the line [0, *y*, 0], presumably forming linear deuterium-bonded chains. Taking the usual 0–D bond and hydrogen bond distances into account, filling every available site results in too long a *b* axis (~5.2 Å instead of the observed 4.275A). Therefore filling almost every

TABLE III

LATTICE PARAMETERS, FRACTIONAL ATOMIC COORDINATES, AND THERMAL PARAMETERS OF α-$Cs_2U_2O_7 \cdot 0.4D_2O$ AT 300 K

Space group *C*2/*m*. *Z* = 2 formula units per cell.
Cell constants: *a* = 14.5314(9) Å, *b* = 4.2739(2) Å, *c* = 7.6011(4) Å, β = 113.02(1)°.

	x	*y*	*z*	*n*	B_{iso}
Cs	0.3937(4)	0	0.5663(7)		2.04(10)
U	0.1438(3)	0	−0.0122(6)		1.22(7)
O(1)	0.1936(3)	0	0.2544(7)		1.29(6)[a]
O(2)	0.4139(3)	1/2	0.2725(7)		1.50
O(3)	0.3065(3)	0	0.0085(8)		1.50
O(4)	0	0.528(17)	0	1/2	1.50
O(5)	0	0	0	0.444(6)	1.50
D(1)	0	0.210(6)	0	0.222[b]	1.50
D(2)	0	0.344(12)	0	0.222[b]	1.50

R_p 3.58%, R_{wp} 4.82%, *S* 1.80

[a] Isotropic *B* of all O and D constrained as one parameter.

[b] *n* D-dependent: 1/2 *n* O(5).

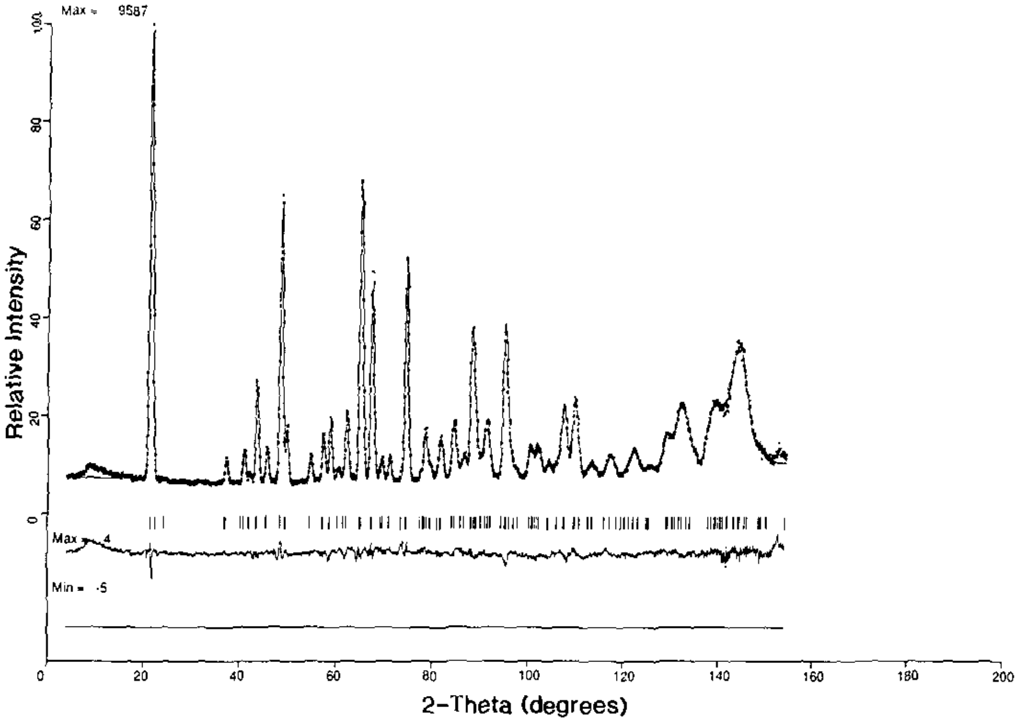

FIG. 4. Observed data (cross) and calculated (solid line) neutron diffraction profile of $Cs_2U_2O_7 \cdot 0.4D_2O$ and difference curve. Tickmarks are at the positions of the Bragg reflections.

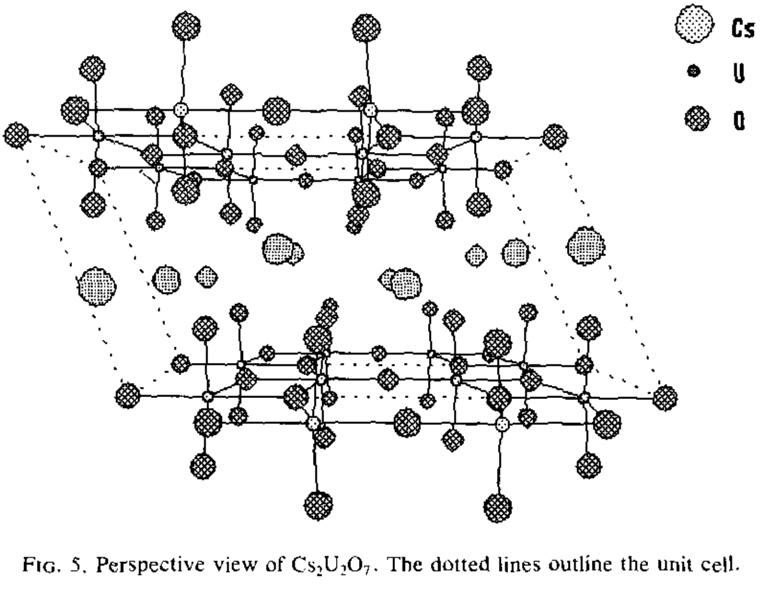

FIG. 5. Perspective view of $Cs_2U_2O_7$. The dotted lines outline the unit cell.

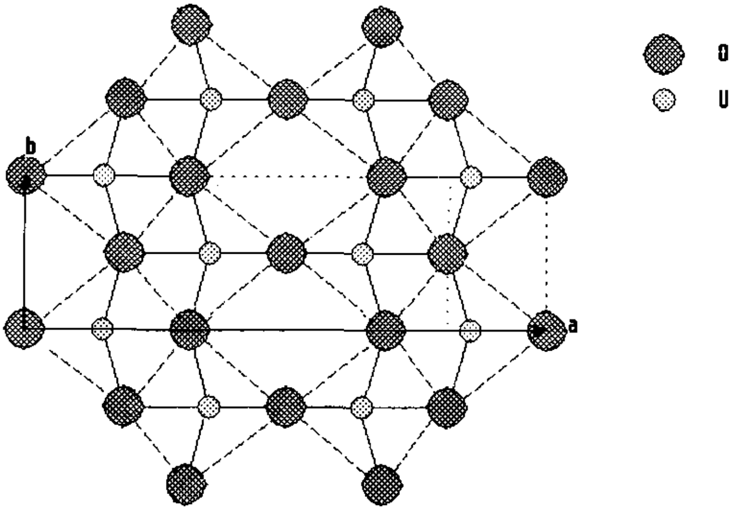

FIG. 6. [001] section of the $Cs_2U_2O_7$. U–O bonds are fully drawn, octahedron edges are dotted.

other site in a more or less random sequence of OD groups seems reasonable. This also explains why at most about 0.5 watermolecules per formula unit are found.

A model that refines satisfactorily, including these features, could be constructed. The water oxygen was put at (0, 1/2, 0) with an occupancy refining to 44%. The D atoms and 0(4) were added along the *b* axis as sketched in Fig. 3a. By symmetry the situation as in Figs. 3b and 3c is generated, and choosing suitable occupancy numbers results in fact in an average over these configurations. In fact, rather than doubling the *b* period, we represent the structure this way by its average. This may seem to be rather crude, but disorder along the sequence will prevent any more precise specification to be discriminated by the current method. The final coordinates are listed in Table III.

An alternative model having O(4) in the same position as in the water-free compound (0, 0, 0) could be ejected. The agreement between observed and calculated profiles is shown in Fig. 4.

Discussion

The structure of β-$Cs_2U_2O_7$ consists of layers of uranium in octahedral oxygen coordination. The Cs atoms are situated between these layers in an irregular seven coordination (Fig. 5). The UO_6 octahedra share *cis* edges, forming zigzag chains parallel [010]. The chains are connected by corner-sharing of octahedra as shown in Fig. 6. Because of the edge-sharing, the U–U distances are rather short, 3.62 Å. The metal coordination of the various oxygen atoms is quite different. The uranyl atoms O1 and O2 have one U and three respectively four Cs neighbors. O3 has three U atoms at a mean distance of 2.27 Å, O4 two at 2.20 Å. The temperature factor is rather high, suggesting a lack of perfect long-range order.

The structure is in good agreement with the results of the earlier X-ray analysis by van Egmond (*3*).

The structure of $Cs_2U_2O_7 \cdot 0.4D_2O$, the so-called α-form, is very similar to that of the parent beta form. It differs mainly in the arrangement of the O and D atoms

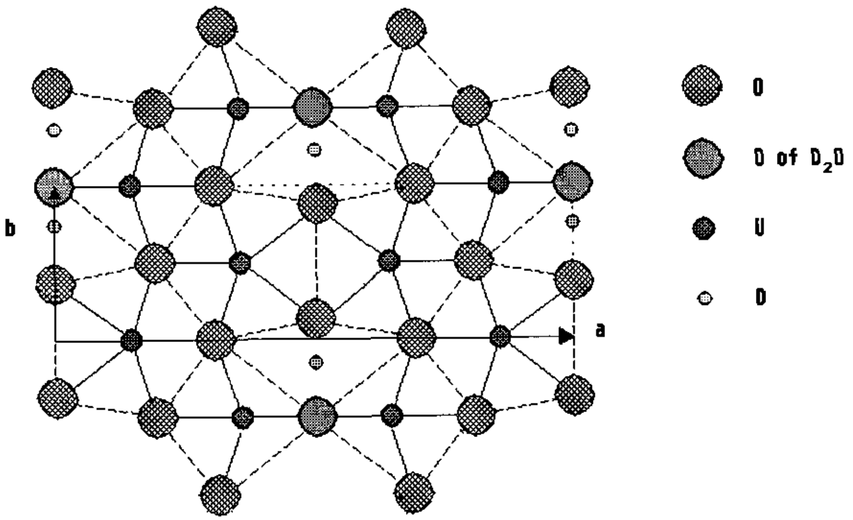

FIG. 7. Idealized [001] section of the structure of $Cs_2U_2O_7 \cdot 0.4D_2O$. U–O bonds are fully drawn, polyhedron edges are dotted.

in channels along [010]. Apparently, the uptake of water results in the insertion of OD groups, placed at 000 in almost every other period. In the process the O4 atoms are pushed together. They are found distributed around $y = 0.5$. An idealized representation of the [001] section is given in Fig. 7. At first sight one may be tempted to suspect a doubling of the *b* axis. Indeed, a refinement of such a model resulted in an *R* factor only 10% higher and might not be rejectable. Clearly, situations as in Fig. 7 are present locally, but long-range order is absent. It is interesting to see the uranium atoms now being coordinated by six as well as by seven oxygens. It should be mentioned, however, that the U–O4 distance in the case of seven coordination is exceptionally large, i.e., ~2.9 Å.

The occupation number of the D and additional O atoms agrees well with the gravimetric water content. The slight variability of the unit cell dimensions of $Cs_2U_2O_7$ reported by van Egmond may be understood as a consequence of the ability of β-$Cs_2U_2O_7$ to absorb foreign material such as water molecules.

References

1. E. H. P. CORDFUNKE, A. B. VAN EGMOND, AND G. VAN VOORST, *J. Inorg. Nucl. Chem.* **37,** 1433 (1975).
2. D. C. FEE AND C. E. JOHNSON, *J. Inorg. Nucl. Chem.* **40** (1978), 1375.
3. A. B. VAN EGMOND, Thesis, University of Amsterdam (1976).
4. A. B. VAN EGMOND, *J. Inorg. Nucl. Chem.* **38,** 2105 (1976).
5. W. A. LINGERAK, P. C. KONIJN, AND J. SLANINA, *in* "Proceedings of the 1st Annual Symposium on Safeguards and Nuclear Material Management," held by the European Safeguards Research and Development Association (ESARDA) at Brussels, 1979, p. 157, ESCARDA Secretariat, Ispra, without year.
6. Program DBW 3.2S, Wiles, Sakthivel and Young, School of Physics, Georgia Institute of Technology, Atlanta.