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X-ray powder diffraction study of the high pressure behaviour of uranium dioxide

U. Benedict

Commission of the European Communities, Joint Research Centre, European Institute for Transuranium Elements, Postfach 2266, D-7500 Karlsruhe, F.R.G.

G. D. Andreetti

University of Parma, Via M. D'Azeglio 85, 43100 Parma, Italy

J. M. Fournier

Université de Grenoble et Centre d'Etudes Nucléaires de Grenoble, 85 X, 38041 Grenoble Cedex, France

and A. Waintal

Université de Grenoble et CNRS-Grenoble, 166 X, 38042 Grenoble Cedex, France

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Résumé. — Le comportement du bioxyde d'uranium sous des pressions jusqu'à 40 GPa a été étudié par diffraction X sur poudre dans des cellules à enclumes de diamant. L'oxyde cfc se transforme progressivement en UO_2 II, phase moins symétrique, entre 29 et 38 GPa. Lorsqu'on diminue la pression, la transformation inverse se fait seulement entre 15 et 5 GPa. Il s'agit probablement d'une transformation purement structurale qui n'est pas liée à une délocalisation d'électrons 5f.

Abstract. — Uranium dioxide was studied by X-ray powder diffraction under pressure in diamond anvil cells up to 40 GPa. A gradual transition to a low symmetry high pressure phase (UO_2 II) occurs in the range 29 to 38 GPa. On pressure release, UO_2 II is conserved by hysteresis below 15 GPa, but retransforms completely to fcc UO_2 I above 5 GPa. The transformation is likely to be a purely structural one which is not due to delocalization of 5f electrons.

1. Introduction. — Information on the electronic structure of the actinide dioxides was gained recently both from the experimental [1, 2] and the theoretical [3] point of view. The electronic structure essentially consists of a 2p-derived valence band separated from a 6d-7s conduction band by a gap, of about 5 eV in UO_2 , in which lies the Fermi level. Going from thorium to plutonium, the 5f levels decrease in energy : there is no occupied 5f state in ThO_2 — nothing is known about PaO_2 — there are 2 occupied 5f states in the gap for UO_2 and, arriving at PuO_2 , the 5f states are down in the valence band [4].

The very interesting problem of the valence phase transition observed in some lanthanide monochalcogenides [5] is due to the coexistence of two conditions :

— narrow 4f levels allowing a well defined valence state,

— proximity of a 4f level to the Fermi level allowing a 4f electron promotion into the conduction band under moderate changes (pressure or alloying).

Most uranium compounds are metallic and it is by now recognized that 5f states form bands which hybridize with the conduction band. However, in the case of UO_2 , 5f states are localized in the band gap of this semiconductor and the proximity of the 5f levels to the empty conduction band is indicated by electrical measurements, photoemission measurements and band structure calculations.

Thus a valence phase transition in UO_2 under pressure might occur, with a resulting change from semiconducting to metallic behaviour. Preliminary electrical resistivity measurements [6] indicate that the resistivity is decreasing under pressure. It seemed worthwhile to study the high pressure behaviour of uranium dioxide by X-ray diffraction (XRD) methods.

2. Experimental. — A first series of measurements was made at the CNRS in Grenoble up to 13 GPa using a diamond anvil high pressure X-ray apparatus. A high power rotating anode was used to increase the X-ray flux [7]. NaCl was used as a marker and classical diffraction patterns were recorded by the Debye-Scherrer method.

The measurements were extended to higher pressures at the Joint Research Centre (JRC) Karlsruhe with equipment allowing pressures of at least 40 GPa. Uranium dioxide powder was obtained from a sintered pellet by grinding in an agate mortar. The lattice parameter of the powder was 547.11(5) pm. This corresponds to $\text{UO}_{2.00}$. The reddish-brown colour of the powder also indicated that the O/U ratio was 2.00.

Three series of measurements were made in Karlsruhe. The first series was carried out with the pure UO_2 powder and thus allowed observation of the pure UO_2 spectra without any overlapping marker lines. Finely ground CsCl was mixed with the UO_2 powder in the second series as a marker which undergoes no phase transformation below 40 GPa; the highest pressure applied was 38.6 GPa. Overlapping of certain CsCl lines with lines of UO_2 introduced some uncertainty at particular pressures, thus a third series up to 16.9 GPa was carried out with NaCl as a marker. NaCl also produces line coincidences with UO_2 lines, but at different pressures and for different energies, and thus constitutes a good check for the determinations of the second series.

The sample was contained in a hole of 0.2 mm diameter (0.25 mm for the series with NaCl) in the centre of an Inconel gasket between the diamond anvils of a high pressure cell [8]. A 4 : 1 methanol-ethanol mixture was added to allow for hydrostatic pressure conditions. The 0.2 mm hole did not widen up even for the highest pressures applied.

The lattice parameters of sample and marker were determined by energy dispersive X-ray diffraction. The diffraction angle $2\theta = 10.10^\circ$ was fixed by a conical slit which allows radiation to be collected from the whole diffraction cone and thus considerably increases the useful intensity on the detector. Details of this technique are given elsewhere [9].

The adjustment of the X-ray optics consists in first aligning the cone axis of the conical slit with the primary beam, and then, with the sample in the high pressure cell in position, adjusting the sample-slit distance to obtain maximum diffracted intensity. In the present case, the (200) line of a sodium chloride sample was used for finding the intensity maximum, and the diffraction angle given above was calculated from the known lattice parameter of sodium chloride, using the energy observed for the (200) line in the final position.

A ^{241}Am source was used for energy calibration of the detector. For the lattice parameter determination the peak positions were read directly with the cursor from the screen of the multichannel analyser. This procedure allowed for a precision of ± 0.5 channels out of the 1 024 channel range in the determination of the peak positions.

3. Results. — 3.1 FLUORITE TYPE UO_2 . — Table I shows the data obtained with the JRC equipment. The pressures given were determined from the equations of state calculated by Decker [10]. With the applied tube voltage of 59 kV, diffraction lines up to about 54 keV can be

Table I. — Lattice parameter, pressure and relative volume for fluorite type UO_2 . Columns Σh^2 give $h^2 + k^2 + l^2$ of the reflections used for calculating the lattice parameter in the preceding column. Errors in brackets (units of the last given decimal place). V/V_0 calculated from the individual lattice parameters with $a_0 = 547.11$.

a (marker), pm	Σh^2	p , GPa	$a(UO_2)$, pm	Σh^2	V/V_0
<i>a</i> : CsCl marker					
412.8	2 3 8	10^{-4}	547.0(9)	3 4 8 11 12 16 19	1
382.2	2 6	7.2(6)	541.6(7)	3 8 11 16	0.970
379.5	2 6	8.3(6)	540.5(6)	3 8 11 16	0.964
377.0	2 6	9.5(6)	538.5(5)	3 8 11 16	0.954
367.5	2 6	15.0(8)	536.3(9)	3 8 11 16	0.942
359.8	2 6	21.1(8)	533.3(4)	3 4 8 11 16	0.926
354.7	2 6	26.1(10)	530.6(9)	3 4 8 11 16	0.912
<i>b</i> : NaCl marker					
554.7	4	1.3	545.7	11	0.992
547.6	4 8	2.6(2)	544.2	11	0.984
538.6	4 8	4.6(2)	542.7	3 11	0.976
529.3	4 8	7.2(3)	542.3	3 11	0.974
521.5	4 8 12	9.9(4)	539.4	3 11	0.958
514.0	4 8	13.1(5)	538.2	3 11	0.952
506.4	3 4 8 12	16.9(6)	535.2	3 8 11	0.936

observed. Reflections missing in the Σh^2 columns of table I could not be used because they either were too weak or overlapped with others. It is seen from this table that more UO_2 lines can be used with the CsCl marker (4 to 5 lines up to the (400)) than when the NaCl marker is employed (where in general only the (111) and (311) reflections were available). Thus a standard deviation was only calculated for the UO_2 lattice parameters of the CsCl series and is given in the table. For the other lattice parameters, an error of ± 2 pm was assumed. The corresponding error on pressure determination is also given in the table ; it increases with pressure and is slightly smaller for NaCl, given the large $\Delta a/\Delta p$ of that marker substance.

Fitting of the data of table I to a second order Birch equation [11] yielded a bulk modulus $B_0 = 192(20)$ GPa and a pressure derivative $B'_0 = 9(4)$. If the fit is done with the fixed B_0 value of 212.7 GPa obtained from ultrasonic data [12] a pressure derivative of $B'_0 = 6.4(0.6)$ is obtained.

Figure 1 shows the variation of lattice parameters and volume with pressure in the fcc phase. There is good agreement between measurements made with the CNRS and the JRC equipment, and between measurements made with the two different marker substances.

3.2 FORMATION OF A HIGH PRESSURE PHASE. — In the first series of measurements without pressure marker, a gradual appearance of a high pressure phase, together with the gradual disappearance of the fluorite type phase, was observed. On pressure release, the sample retransformed to the pure fluorite type phase. These transformations have been shown to be reproducible by a number of further loadings and unloadings with different samples.

Information on the pressure range of this transformation was obtained by the measurements with the CsCl marker. In these measurements, lines of the high pressure phase were first observed at 29.4 GPa. The start of the transformation is thus between the pressure of the preceding measurement (26.1 GPa) and 29.4 GPa. Stepwise increase of pressure again gradually shifted the ratio

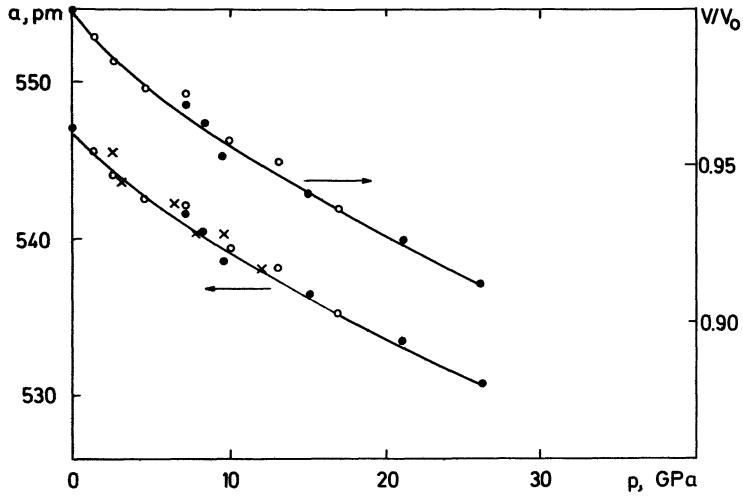


Fig. 1. — Lattice parameter and relative volume of fcc UO_2 versus pressure. ● with CsCl marker, JRC; ○ with NaCl marker, JRC; × with NaCl marker, CNRS.

of the two phases until at about 39 GPa the lines of the fluorite type phase had disappeared. This process is shown in figure 2 for the energy range of the (111) and (200) lines of fcc UO_2 .

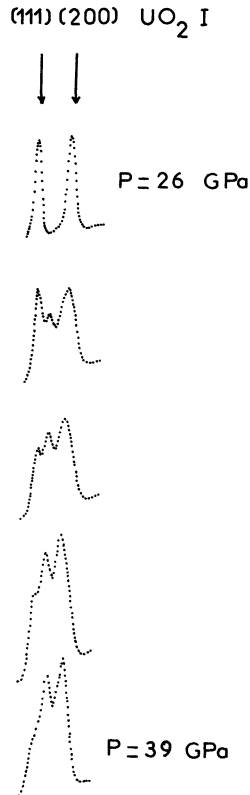


Fig. 2. — Gradual ingrowth of high pressure phase into UO_2 between 29 and 38 GPa (from top to bottom) as seen in the energy range of the (111) and (200) lines of fcc UO_2 . (Intermediate pressures not measured.)

On release of pressure, a marked hysteresis to transformation is observed. The high pressure structure expands down to 14.8 GPa without appearance of lines of the fluorite structure. Complete retransformation to the fluorite type structure occurred between two successive measurements at 14.8 and 4.8 GPa.

3.3 STRUCTURAL CALCULATIONS FOR THE HIGH PRESSURE PHASE UO_2 II. — The diffraction lines of UO_2 II at about 37 GPa are given in table II. Systematic calculations show that the best match is obtained in the orthorhombic space groups Pnma ($a = 593, b = 351, c = 656$ pm) and Cmcm ($a = 341, b = 670, c = 607$ pm), but that the match is not good enough to give a definite structure assignment. This has to wait until spectra of UO_2 II with more than 10 lines will be available, and until an adequate treatment of the relative intensities of energy dispersive spectra will be possible. The determination is also made difficult by the large difference in scattering power between uranium and oxygen; only the uranium positions are « seen » by the X-rays, but not the oxygen positions.

Table II. — Peak positions of the high pressure structure at about 37 GPa.

<i>d</i> , pm	303.8	289.4	272.0	208.4	189.43	175.65	168.59	158.11	148.21	132.30
intensity	w	s	s	w	s	m	s	s	vs	w

Nonetheless the agreement with calculated spectra is sufficient to conclude that the real structure of UO_2 II is very close to one of the above structures. In principle, one would favour Pnma as it is the space group of the $PbCl_2$ type. This structure type is 8% denser than the fluorite type and has a cation coordination of 9 with respect to 8 for the fluorite type. It is the high pressure form of $CaF_2, SrF_2, BaF_2,$ and $EuF_2,$ which are all of the fluorite type at 10^5 Pa, and is the normal

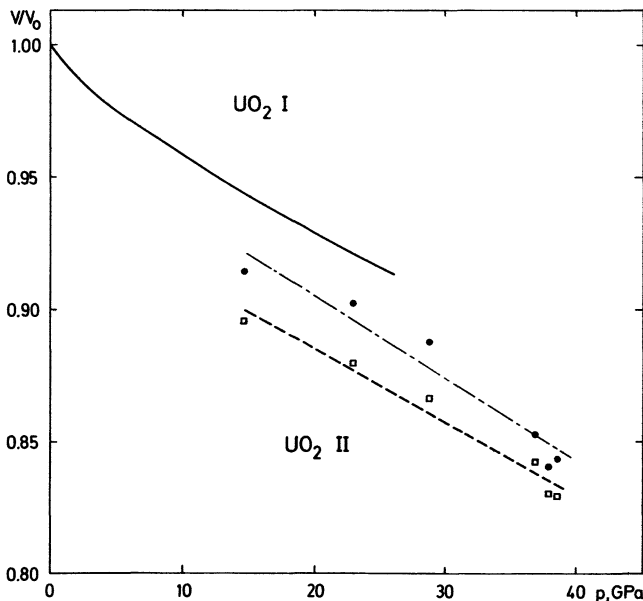


Fig. 3. — Equation of state for UO_2 I and UO_2 II. — UO_2 I; ● — — — UO_2 II, Pnma; □ — — — UO_2 II, Cmcm.

pressure form of the actinide chalcogenides ThS_2 , ThSe_2 , $\beta\text{-US}_2$, and $\beta\text{-USE}_2$. On the other hand, figure 3 shows that the volume difference between UO_2 I and UO_2 II is only 2.5 to 5 %, according to the space group chosen. This would be an argument against the PbCl_2 type.

4. **Discussion.** — 4.1 FLUORITE-TYPE UO_2 (UO_2 I). — The compression curve up to 26 GPa is normal, compressibility decreasing with increasing pressure. The obtained B_0 value at atmospheric pressure agrees well with the 213 GPa value obtained from the elastic constants.

Since the cohesive properties of UO_2 have been computed recently in the atomic sphere approximation [3], it is interesting to compare the experimental and computed equations of state in their form $3 PV (a/a_0)$. The two curves are reported in figure 4. The computed B_0 (300 GPa) is too large by 40 % leading to an increase of steepness but the overall agreement may be considered as good regarding the approximations used in the model.

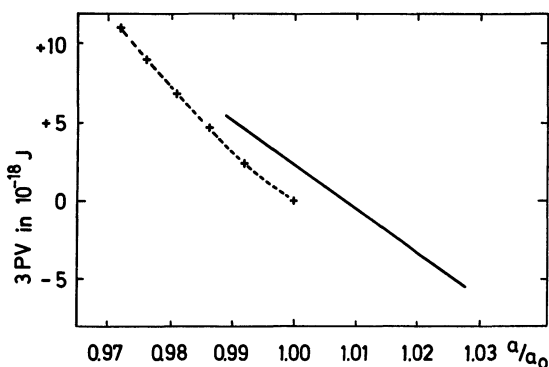


Fig. 4. — Comparison between experimental and calculated equations of state. + - - - - exp., this work ; ——— calculated [3].

4.2 HIGH PRESSURE UO_2 (UO_2 II). — A discontinuity in a plot of shock velocity vs. particle velocity observed in shock-wave experiments on UO_2 suggests a phase transition [13]. But the high stress corresponding to this discontinuity (about 54 GPa) leaves some doubt whether the author observed the same phase transition as the present authors.

Approximate U-U distances can be calculated from the space groups derived above for UO_2 II. Though two of the twelve U-U distances between nearest neighbours are in the transition range near 350 pm which has been considered by Hill [14] as separating localized from itinerant 5f behaviour, the average U-U distance is still distinctly above that transition zone. As Hill refers to that average distance for distinguishing localized from itinerant behaviour, this might indicate that the present phase transition is not accompanied by 5f delocalization. This view is also supported by preliminary results on thorium dioxide under pressure [15]. This compound, which has no 5f electrons in the ground state, also transforms to a high pressure allotrope in the same pressures range (around 40 GPa) as uranium dioxide. In addition, a phase transition linked to delocalization of f electrons can be considered as a Mott transition, and metallic properties are expected for the high pressure phase. Since in other cases, metallic lustre was observed in the sample under the microscope when a transformation to a metallic phase had occurred, the samples of UO_2 were always carefully observed. A metallic aspect was never found.

During writing, as yet unpublished results of similar work were communicated to the authors from the Geophysical Laboratory, Washington [16]. A comparison showed general agreement with the present work, but the relative volume of the high pressure phase, calculated as being

of the PbCl_2 type, agreed better with our calculation for Cmcm than with that for the space group Pnma of the PbCl_2 structure. Further study of the high pressure phase is certainly necessary.

There might be another transition in uranium dioxide which is linked to 5f delocalization, but this has to be sought at pressures higher than 65 GPa, UO_2 II having found to be stable to that pressure [16].

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