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The Crystal Structure of Trigonal U_3O_8*

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The orthorhombic form of U_3O_8 is stable to about 400° C. At this temperature, U_3O_8 transforms to a trigonal modification. The unit-cell dimensions are $a = 6{\cdot}801 \pm 0{\cdot}001$, $c = 4{\cdot}128 \pm 0{\cdot}001$ kX. For one molecule in the cell the calculated density at the transition temperature is 8·41 g.cm.$^{-3}$. With the assumed oxygen positions, the space group becomes $P\bar{3}\text{–}C_{3i}^1$. This leads to $U_I\text{–}6\,O_I = 2{\cdot}31$ Å, $U_{II}\text{–}6\,O_I = 2{\cdot}31$ Å, and $U_{II}\text{–}2\,O_{II} = 2{\cdot}06$ Å.

Introduction

Investigations of the uranium–oxygen system in the composition range $UO_{2{\cdot}5}$ to U_3O_8 have led to the production of at least two polymorphic forms of U_3O_8 at elevated temperatures: one is an orthorhombic structure and the other an oxygen-deficient trigonal form. Only the latter phase will be reported here.

U_3O_8 will lose oxygen in a vacuum even at moderate temperatures. As it is convenient to perform the high-temperature studies with an evacuated capillary of U_3O_8, it is apparent that the sample will become more and more deficient in oxygen as the temperature is increased.

Experimental

The high-temperature X-ray camera is the model HC-101 unit manufactured by Central Research Laboratories and is capable of producing temperatures up to 1000° C. The camera diameter is 114·6 mm., and five separate diffraction patterns can be recorded on one film by means of a moving film carrier.

Diffraction patterns were obtained in 75° C. intervals. Following each photograph, the sample was allowed to cool to room temperature before a new pattern, at a higher temperature, was obtained. Room-temperature photographs, following such thermal cycling, indicated clearly that the composition corresponded to an oxygen:uranium ratio of less than 8/3.

The sample was contained in a narrow thin-walled quartz capillary. Copper radiation, filtered with nickel foil, was used throughout the investigations.

Results

Upon heating U_3O_8 to 365° C., the orthorhombic lattice was found to undergo somewhat rapid changes in size. The variations of the *a*, *b* and *c* axes with temperature are shown in Fig. 1. The temperature coefficients of expansion and the dimensional changes arising from the loss of oxygen account for these curves. Between 445° C. and 600° C., the pattern undergoes some changes and a noticeable sharpening of the diffraction maxima can be observed at large angles. Furthermore, the cell size remains essentially constant over this temperature range.

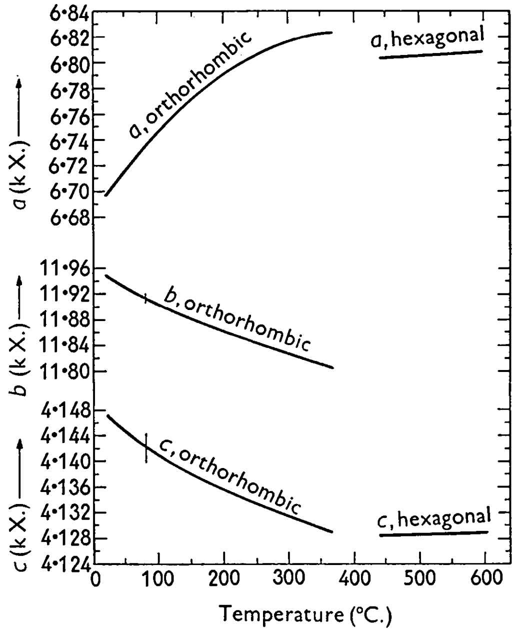

Fig. 1. The variation of α-U_3O_8 and trigonal U_3O_8 cell dimensions with temperature.

The new pattern can be referred to a hexagonal cell, with the following cell constants:

$$a = 6{\cdot}801 \pm 0{\cdot}001, \quad c = 4{\cdot}128 \pm 0{\cdot}001 \text{ kX}.$$

This leads to a calculated X-ray density of 8·41 g.cm.$^{-3}$ for one molecule in the cell.

The structure

The observed and calculated values for $\sin^2\theta$ are given in Table 1. The calculated values include correc-

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* Chemical and crystallographic studies describing the region $UO_{2{\cdot}5}$ to U_3O_8, upon which this work is based, are reported by Hoekstra, Siegel, Fuchs & Katz (1955).

Table 1. *Diffraction data*

hkl	$(\sin^2\theta)_o$	$(\sin^2\theta)_c$	I_o	I_c
001	0·03531	0·03531	164	164
110 101	0·05206	0·05202 0·05256	258	266 ~0
111	0·08685	0·08716	229	229
210	0·1207	0·1212	Weak	~0
002	0·1403	0·1404	62	31
211 102 300	0·1558	0·1562 0·1576 0·1557	125	~0 ~0 124
301 112	0·1915	0·1906 0·1920	214	162 126
220	0·2072	0·2074	56	65
310	0·2246	0·2245	Weak	~0
221	0·2419	0·2423	90	101
311 212	0·2596	0·2593 0·2608	Weak	~0
302	0·2954	0·2950	99	85
003	0·3150	0·3147	20	10
320	0·3280	0·3273	Weak	~0
222	0·3463	0·3464	71	68
410 321 312	0·3613	0·3615 0·3620 0·3636	58	56 ~0 ~0
113	0·3664	0·3660	63	50
411	0·3960	0·3959	89	80
330 501 322	0·4641	0·4640 0·4645 0·4660	29	22 ~0 ~0
303	0·4690	0·4688	62	29
331 412	0·4993	0·4986 0·5002	105	35 62
223	0·5202	0·5201	37	34
004	0·5577	0·5580	11	5
511 502	0·5667	0·5670 0·5687	Weak	~0 ~0
332	0·6018	0·6026	36	30
114	0·6089	0·6094	39	27
600	0·6177	0·6176	22	16
601	0·6519	0·6523	30	29
520 431	0·6681	0·6688 0·6694	31	25 ~0
413 512	0·6722	0·6738 0·6711	39	44 ~0
$521\alpha_1$	0·7021	0·7014	51	54
$521\alpha_2$	0·7065	0·7047	26	27
$304\alpha_1$	0·7101	0·7090	45	24
$304\alpha_2$	0·7132	0·7127	23	12
$602\alpha_1\alpha_2$ $224\alpha_1\alpha_2$ $333\alpha_1\alpha_2$	Not resolved in intensity			
$522\alpha_1$	0·8048	0·8046	64	66
$522\alpha_2$	0·8080	0·8085	32	33
$440\alpha_1$ $440\alpha_2$	0·8198 0·8235	0·8195 0·8234	51	12 6
$700\alpha_1$ $530\alpha_1$	0·8357	0·8365 0·8365	Faint	~0 ~0
$700\alpha_2$ $530\alpha_2$	0·8396	0·8404 0·8413	Faint	~0 ~0
$441\alpha_1\alpha_2$ $005\alpha_1\alpha_2$ $612\alpha_1\alpha_2$ $701\alpha_1\alpha_2$	Not resolved in intensity			
$414\alpha_1$	0·9121	0·9130	115	74
$414\alpha_2$ $115\alpha_1$	0·9171	0·9178 0·9177	156	38 36
$115\alpha_2$ $621\alpha_1$	0·9214	0·9229 0·9223	50	18 ~0
$621\alpha_2$	—	—	0	~0
$603\alpha_1\alpha_2$ $433\alpha_1\alpha_2$	Not resolved in intensity			
$442\alpha_1$	0·9564	0·9572	40	44
$442\alpha_2$	0·9606	0·9595	20	22
$710\alpha_1$	0·9711	0·9711	108	57
$710\alpha_2$ $702\alpha_1$ $532\alpha_1$ $523\alpha_1$	0·9759	0·9764 0·9743 0·9743 0·9768	158	29 ~0 ~0 147
$702\alpha_2$ $532\alpha_2$ $523\alpha_2$	0·9804	0·9788 0·9788 0·9817	52	~0 ~0 74

tions for the very heavy absorption within the sample.

The intensity distribution requires that the uranium atoms be located in the following positions:

$$0, 0, 0;\quad \tfrac{1}{3}, \tfrac{2}{3}, 0;\quad \tfrac{2}{3}, \tfrac{1}{3}, 0\,.$$

This will account for the main intensity features of the diffraction pattern. However, some discrepancies appear between observed and calculated intensities, and furthermore, a number of very weak maxima occur which are not accounted for on the basis of the uranium scattering. Because of the very great differences in scattering powers between the uranium and oxygen atoms, no attempt was made to determine the oxygen positions directly from the data; rather, the oxygen positions were assumed to be derivable from suggested positions in the room-temperature form of U_3O_8 and the intensity contributions from the oxygen atoms were then compared with the data.

If the ratio a/b for orthorhombic U_3O_8 is plotted as a function of temperature, it is found that this ratio approaches the value $\frac{1}{3}\sqrt{3}$ near 365° C. (the approximate transition temperature). This may indicate that the transformation from the orthorhombic to the hexagonal cell does not involve an abrupt change and suggests that the hexagonal cell may be derived from the orthorhombic form described by Zachariasen (1948, 1945). In fact, it is found that the cells are simply related, leading to the uranium positions cited above. Hence, if it is speculated that the oxygen atoms are related in a similar manner, the oxygen positions in the hexagonal cell become

$$\pm(\tfrac{1}{3}, 0, z);\quad \pm(\tfrac{1}{3}, \tfrac{1}{3}, \bar{z});\quad \pm(0, \tfrac{1}{3}, z);\quad \pm(\tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{2})\,.$$

The effect of the oxygen positions on the line intensities was determined crudely by observing the ratio I_o/I_c as a function of $\sin\theta$, with and without oxygen atoms, in order to determine if the addition of the oxygen contributions was found to produce a smooth curve. For the *hk*0 reflections, an improvement in the calculated intensities was indeed found. The oxygen contributions were always of the correct sign, although small. On the other hand, the z parameter could only be given an approximate value. The observed 00*l* intensities were always considerably greater than the calculated values, indicating, possibly, the existence of preferred orientation of the crystallites. This may account for some of the uncertainty in evaluating z. However, the value $z = 0{\cdot}1$ appears to be compatible with observations. The addition of the oxygen atoms with the coordinates given above produces a general improvement in the calculated intensities. The extent of the agreement is shown in Table 1, where the calculated intensities I_c include the oxygen contributions. The calculated intensities also contain heavy temperature and absorption corrections. The observed intensities I_o were taken from microphotometer tracings. At the large angles, the overlapping of the α_1 and α_2 maxima is generally so extensive that serious errors are introduced in the evaluation of the intensities and $\sin^2\theta$ values. As indicated in Table 1, a number of reflections could not be resolved in intensity.

Thus, with the assumption that the oxygen positions are assigned correctly, the space group becomes $P\bar{3}$–C_{3i}^1, with atoms in the following positions:

1 U_I in $(0, 0, 0)$;
2 U_II in $(\frac{1}{3}, \frac{2}{3}, z_1)$, $(\frac{2}{3}, \frac{1}{3}, \bar{z}_1)$, with $z_1 = 0$;
6 O_I in (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(\bar{y}, x-y, z)$, $(y, y-x, \bar{z})$,
  $(y-x, \bar{x}, z)$, and $(x-y, x, \bar{z})$ with $x = \frac{1}{3}$, $y = 0$,
  and $z = 0{\cdot}1$;
2 O_II in $(\frac{1}{3}, \frac{2}{3}, z_2)$, $(\frac{2}{3}, \frac{1}{3}, \bar{z}_2)$ with $z_2 = \frac{1}{2}$.

Each U_I is bonded to 6 O_I with O_I–6 O_I = 2·31 Å. Each U_II is bonded to 6 O_I with U_II–6 O_I = 2·31 Å and in addition to 2 O_II with U_II–2 O_II = 2·06 Å. The latter bonding produces endless U_II–O_II–U_II–O_II... chains along the c direction.

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A Method for Calculating Thermal Vibration Amplitudes from Spectroscopic Data

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It is shown how $(\overline{u_i^2})_{\text{int.}}$, the contribution from internal molecular vibrations to the mean square amplitude of thermal motion of an atom in a molecular crystal, may be calculated from the vibrational spectrum of the molecule itself and that of a molecule which differs from it only by the occurrence of a different isotope at position i.

In two previous papers (Higgs, 1953, 1955), which will be referred to as I, II respectively, the effect of thermal motion on the electron distribution in molecular crystals was discussed. The motion of an individual atom i was characterized by its mean square amplitude $\overline{u_i^2}$, a quantity identical apart from a numerical factor with the temperature parameter B_i commonly used by X-ray crystallographers (see II, equation (28)). It was stated in II that the calculation of $(\overline{u_i^2})_{\text{int.}}$, the contribution to $\overline{u_i^2}$ from internal vibrations of a molecule, is hampered by the unreliability (so far) of purely theoretical data on molecular force fields. In view of this fact it is perhaps worth while to point out that $(\overline{u_i^2})_{\text{int.}}$ may be calculated from spectroscopic data. The quantities involved in the formula which is to be derived are the fundamental vibration frequencies of the molecule itself and those of molecules differing from it only by their isotopic composition. Thus the necessary data consist of certain infra-red and Raman spectra or of the vibrational structure of certain ultraviolet spectra.

First, using the notation of II, we write down some properties of normal coordinates. The vibrational kinetic and potential energies of a molecule,

$$T = \tfrac{1}{2}\dot{\mathbf{y}}'\mathbf{G}^{-1}\dot{\mathbf{y}} \quad \text{and} \quad V = \tfrac{1}{2}\mathbf{y}'\mathbf{F}\mathbf{y}\,,$$

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[*] This work was done while the author was at the Wheatstone Physics Laboratory, King's College, Strand, London W. C. 2, England.