STUDIES OF RADIOACTIVE COMPOUNDS:
III—URANO-URANIC OXIDE (U_3O_8)[1]

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ABSTRACT

Weissenberg films of U_3O_8 crystals prove the existence of two hexagonal cells whose axes of reference coincide in direction; dimensions $a=3.93$, $c=4.14$kX (cell contents $1/3[U_3O_8]$) and $a=3.86$, $c=4.14$kX. Powder photographs indicate the large cell is always present. It is suggested that the "two cell" phenomenon is due to the introduction of oxygen into a portion of the structure. This oxygen may be either in a state of solid solution or in chemical combination necessitating the change of some U^{4+} to U^{6+}.

The compound U_3O_8 is well known in the field of chemistry and has been variously called, including urano-uranic oxide, uranosoic oxide and the green oxide of uranium. It is described (Friend, 1926) as an amorphous powder varying in colour according to its mode of preparation from green to black; the streak is always green. According to both Friend (1926) and Mellor (1932) the compound has not been observed in crystalline form. It is insoluble in water and in dilute acids but in concentrated mineral acids it dissolves slowly forming a mixture of uranous and uranyl salts. The specific gravity is given by Mellor (1932) as 7.31 and by Grønvold (1948) as 8.34.

Urano-uranic oxide is reduced to UO_2 by heating in hydrogen. It is formed when any of the uranium oxides or hydrated oxides or any of the uranium salts with a volatile base or acid is calcined at a red heat (Mellor, 1932). Thus it is readily produced upon heating many uranium-bearing minerals. During the present study of uranium minerals the *x*-ray powder pattern of U_3O_8 was repeatedly obtained from heating experiments. An investigation of the uranium compounds available in the chemical laboratory of this department revealed a quantity of U_3O_8 in the form of a crystalline powder. This enabled the writer to undertake the single crystal study described below.

The origin of the material used is not known. It is a black powder which under high magnification is seen to consist of laths approximately 0.1 mm. in length, showing several prismatic faces. The size of the crystals made it impossible to carry out morphological measurements but it was possible to orient them on the *x*-ray goniometer for rotation about the axis of elongation.

A series of sharp rotation, zero and first layer Weissenberg *x*-ray photographs about the axis of elongation was obtained from one of the

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[1] Extracted from a Ph.D. thesis.

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laths. These photographs clearly illustrate hexagonal symmetry and indicate the Laue class 6/*mmm*. Measurements gave the following dimensions of the hexagonal unit cell:

$$a=3.93\text{kX}$$
$$c=4.14$$

There are no systematic extinctions with the possible exception of a condition in (000*l*). Because of the extremely small dimensions of the crystals they could not be rotated about a direction normal to the *c* axis to observe these reflections. The compound therefore, is provisionally placed in the maximum symmetry space group *C6mmm*, of the Laue class 6/*mmm*.

The Weissenberg photographs are complicated by the presence of a complete set of extra reflections which may be interpreted as belonging to a second cell with slightly smaller *a* dimensions ($a=3.86$kX). These reflections on the single crystal photographs are generally weaker than those of the larger cell but some exceptions were observed. They appear on powder photographs as well and hence cannot be due to twinning. The two cells if such is the case, are so oriented that the *c* axes coincide in direction and length while the *a* axes coincide in direction but differ slightly in length. Suggestions as to the origin of this "two cell" structure are given later in this paper.

Grønvold (1948) determined the unit cell of U_3O_8 as orthorhombic base-centered with the following dimensions:

$$a=6.703, \qquad b=3.969, \qquad c=4.136\text{kX}$$

This determination was made from *x*-ray powder photographs only and the presence of diffraction lines from the two cells resulted in this orthorhombic interpretation. The diffraction lines of the powder pattern can be made to fit Grønvold's orthorhombic cell by taking the smaller $d(10\bar{1}0)$ spacing as $d(200)$ and the larger one as $d(110)$ of the orthorhombic cell. In the same way all of the other lines may be made to fit the orthorhombic cell approximately. However the single crystal photographs obtained during this study leave no doubt of the hexagonal symmetry of urano-uranic oxide.

The powder pattern of the material used for single crystal measurements showed the effects of preferred orientation due to the shape of the crystals. For measurement purposes a more general pattern was obtained from a sample of U_3O_8 supplied by Eldorado Mining and Refining (1944) Ltd. This pattern has been measured and indexed on the basis of the presence of two hexagonal cells. The information is presented in Table 1, and the photograph itself is reproduced in Fig. 1. In this case the diffraction lines indexed on the small cell are in general stronger than

TABLE 1. URANO-URANIC OXIDE (U_3O_8): *X*-RAY POWDER DATA[1]

Hexagonal—*C6mmm:* $a=3.93$, $c=4.14$kX (large cell)
$a=3.86$, $c=4.14$kX (small cell)

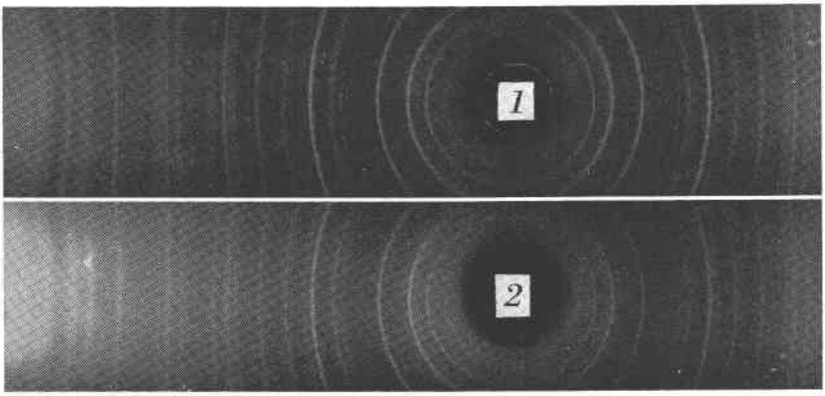
I (Cu)	*d* (meas.)	(*hkil*)	*d* (calc.)	*I* (Cu)	*d* (meas.)	(*hkil*)	*d* (calc.)
4	4.10kX	(0001)	4.14kX	2	1.431kX	$(11\bar{2}2)$	1.425kX
10	3.38	$(10\bar{1}0)$	3.40	3	1.415	$(11\bar{2}2)$*	1.412
7	2.61	$(10\bar{1}1)$	2.65	1	1.376	(0003)	1.380
3	2.06	(0002)	2.07	2	1.314	$(20\bar{2}2)$	1.323
5	1.971	$(11\bar{2}0)$	1.965	4	1.297	$(20\bar{2}2)$*	1.300
6	1.943	$(11\bar{2}0)$*	1.930	5	1.277	$(21\bar{3}0)$	1.286
2	1.782	$(11\bar{2}1)$	1.775	4	1.238	$(21\bar{3}1)$	1.228
8	1.760	$(11\bar{2}1)$*	1.749	3	1.219	$(21\bar{3}1)$*	1.202
5	1.702	$(20\bar{2}0)$	1.700	1	1.134	$(30\bar{3}0)$	1.133
4	1.673	$(20\bar{2}0)$*	1.670	2	1.123	$(11\bar{2}3)$	1.129
4	1.578	$(20\bar{2}1)$	1.574	5	1.100	$(30\bar{3}1)$	1.904
3	1.547	$(20\bar{2}1)$*	1.550			$(21\bar{3}1)$	1.093
½	1.501	—	—	5	0.991	$(30\bar{3}2)$	0.995

Note—Planes marked with an asterisk are indexed and spacings calculated on the small cell.

[1] For Ni filtered Cu radiation ($\lambda=1.5374$kX).

those of the large cell. This relationship was found in powder patterns of all samples of U_3O_8 which had been subjected to a high temperature.

In Fig. 2 is shown the powder diffraction pattern obtained from the product of heating uranyl nitrate at 220° C. in air for several days. This



FIGS. 1, 2.—*X*-ray powder photographs with Cu/Ni radiation ($\lambda=1.5374$kX); camera radius 57.3 mm.; actual size prints. Fig. 1. U_3O_8, "two cell" pattern. Fig. 2. U_3O_8, single cell pattern.

pattern shows only the lines of the large cell of U_3O_8 and is the only example obtained of a simple structure.

A chemical analysis of this oxide of uranium was carried out using standard methods of analysis. The analysis gave the following results:

U_3O_8	99.0%
Fe_2O_3, V_2O_4	0.4
Total	99.4%

A calculation of the specific gravity of U_3O_8 using the formula $G = MW \times 1.65/V$, where MW is the molecular weight of U_3O_8 and V is the volume of the larger cell gives the value 24.74. This is roughly 3 times the value reported by Mellor (1932) and Grønvold (1948) and it is evident at once that the unit cell derived in this investigation contains only $\frac{1}{3}$ U_3O_8. Grønvold's orthorhombic cell contains $\frac{2}{3}$ U_3O_8; he has suggested that this can be explained by a deficiency structure with some oxygen missing from an ideal UO_3 composition, or with interstitial oxygen in a UO_2 structure. The weakness in this explanation lies in the fact that the compounds UO_2 and UO_3 have *x*-ray powder patterns distinctly different from that of U_3O_8. A more reasonable suggestion in the opinion of the writer is that the *c* dimension of the hexagonal cell is actually 3 times as long as the measured value; the measured value is probably a strong pseudo-period resulting from the arrangement of the uranium atoms in the structure. This problem will be solved only when larger crystals of U_3O_8 are produced so that Weissenberg layer photographs about the *a* axis may be taken.

Experimental observations by Biltz & Müller (1927), and by Alberman & Anderson (1949) on the oxides of uranium have enabled the writer to put forward two suggestions as to the origin of the "two cell" structure of U_3O_8. Biltz & Müller (1927) obtained the dissociation isotherms between 438 and 650° C. of preparations varying in composition from UO_3 to U_3O_8 and found them to be continuous; they also found that the *x*-ray powder patterns of these preparations show the lattice of U_3O_8. They concluded that the solid phase in these experiments was a solid solution. Further experiments were carried out by measuring the densities of uranium oxides (at 25°C.) between $UO_{1.992}$ and $UO_{3.069}$. They state that between UO_2 and $UO_{2.226}$ oxygen is taken up without any change in volume of the oxide and that the composition $UO_{2.226}$ corresponds with the solution of urano-uranic oxide in the dioxide. (Evidently at this point the U_3O_8 pattern appears in *x*-ray powder patterns of the preparations.) Beyond this point the volume increases regularly with no discontinuity at the composition U_3O_8 ($UO_{2.66}$). From these experiments, it may be concluded that solid solution effects are important in determining the composition of the urano-uranic oxide structure. It is possible that the "two cell" structure is due to solid solution effects (with oxygen presumably) which have enlarged the *a* dimension of the unit cell. In accordance with this suggestion most specimens of urano-uranic oxide must contain two phases, one with more and one with less O than is indicated by the formula U_3O_8; the solution effect giving rise to the higher oxide may be confined to the outer boundaries of grains or crystals where solution of O is most likely. Thus the *x*-ray diffraction pictures would show the two cells. The U_3O_8 pattern obtained as the result of heating uranyl nitrate at 220° C., which is that of the large cell only can be explained as the result of the formation of urano-uranic oxide under highly oxidizing conditions (decomposition of a nitrate) which would encourage maximum solid solution of oxygen throughout the compound.

More recently, Alberman & Anderson (1949) have made an exhaustive study of the oxygen-uranium system between UO_2 and $UO_{2.3}$ and have found a somewhat analogous double cell phenomenon. In brief, they found that two distinct cubic oxides exist in this range; these are UO_2 (α phase, $a=5.457$kX) and $UO_{2.19}$ (β phase, $a=5.430$kX). The two components appear when oxides in this range of composition are annealed at high temperature. The explanation they offer is that oxygen enters the available interstitial positions in UO_2 in which it may be accommodated in 6-fold co-ordination with uranium, and with very little distortion of the structure. This introduction of oxygen atoms necessitates the change of a corresponding number of U^4 cations to the smaller U^6 cations. The net effect on the cell dimensions is determined by the interplay of sizes and charges of the substituted cations with the distortion caused by the interstitial anions. In this case the shrinkage effect due to the smaller U^6 cations is greater than the expansion effect of the interstitial oxygen anions and therefore the resultant cell is smaller. It is possible that an effect similar to that outlined above is taking place in U_3O_8 and thereby giving the "two cell" structure. If this explanation is correct it would suggest that most U_3O_8 preparations are a mixture of two similar uranium oxide structures with greater and less oxygen than the resultant U_3O_8.

The two suggestions offered for the "two cell" effect are similar in that both depend upon the introduction of O into the urano-uranic oxide structure. Biltz & Müller (1927) feel that this causes an increase in the cell size. Alberman & Anderson (1949) on the other hand have shown that in the case of the oxides UO_2 and $UO_{2.19}$, the latter has a smaller cell volume resulting from the change of valence of U^4 to U^6 necessitated by the introduction of O.

Further experimental work is necessary to arrive at the explanation of the "two cell" phenomenon. It is hoped that the additional information presented here will enable others to carry on the investigation.

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