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RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

THE STRUCTURES OF FLUORIDES II - THE STRUCTURE OF URANYL FLUORIDE

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ERRATA SHEET

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Page 3 Line 12 change 'Z_f' to 'z_f'

Page 5 Lines 21, 23, 35 change 'Z_f' to 'z_f'

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THE STRUCTURES OF FLUORIDES-II
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ABSTRACT

A neutron powder diffraction study of UO_2F_2 has been carried out. Previous workers have proposed that line broadening in the diffraction pattern of UO_2F_2 is due to puckering of the hexagonal fluorine atom rings and consequent stacking disorders. It is shown that, in our samples, most of the line broadening is due to the effects of particle size and shape. The puckering of the layers, if present, must be determined from a neutron analysis of the deviation of the z-coordinate of the fluorine atom from the value 0.333, using reflexions for which h-k = 3n. There are only two resolved lines of this type in the pattern, making it difficult to decide whether the previously proposed complex disorder structures are better than a simple model where the layers are unpuckered. It is shown that single crystal studies will be necessary to distinguish between the alternative models.

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CRYSTAL MODELS; FLUORIDES; INTERATOMIC DISTANCES; LINE BROADENING; NEUTRON DIFFRACTION; PARTICLE SIZE; REFLECTION; SHAPE; SPACE GROUPS; STACKING FAULTS; STRUCTURAL MODELS; URANYL COMPOUNDS

CONTENTS

1. INTRODUCTION

There are two previous studies on the structure of UO_2F_2. The first study (Zachariasen 1948) was based on the X-ray powder diffraction pattern of UO_2F_2. A feature of the proposed structure derived from this study was the severe puckering by ± 0.6 Å of the fluorine atoms which formed a hexagonal ring system around the uranyl groups. Zachariasen noted that the X-ray lines were either sharp or diffuse and explained this in terms of a stacking disorder.

A later study (Atoji and McDermott 1970) was made using neutron diffraction techniques. In general this study confirmed the earlier X-ray powder diffraction study, but it was noted that the puckering of the hexagonal fluorine atoms rings was much less, ± 0.21 Å, than that suggested by Zachariasen. Since UO_2F_2 is an important chemical in the nuclear energy industry it was decided to re-examine these two differing results.

2. EXPERIMENTAL

To ensure an adequate supply of UO_2F_2 prepared under reproducible conditions, the UO_2F_2 used in this study was prepared in the laboratory. The starting product was UO_3 which had been prepared by thermal decomposition of $UO_4 \cdot 2H_2O$ (Stuart and Whateley, 1968). This is a particularly reactive form of UO_3. The UO_3 was placed in a nickel boat in a nickel reactor and heated to 310°C in a stream of anhydrous hydrogen fluoride and nitrogen (1:1) (Johnsson and Clewett, 1946). The UO_2F_2 so prepared was a fine pale yellow powder which was only slightly hygroscopic. To avoid hydrolysis of the sample all handling of UO_2F_2 was done in a dry box.

The sample prepared as above was a rather fine powder. Since UO_2F_2 is thermally unstable the particle size cannot be increased by either sublimation or sintering. Nor can the particle size be increased by using larger particle size UO_3 for the preparation. If this is done, there is a possibility that unreacted UO_3 will remain at the centre of each particle.

The UO_2F_2 sample was carefully sealed in a vanadium can, and a neutron diffraction powder pattern was measured on HIFAR, the AAEC research reactor, using the elastic diffraction technique (Caglioti 1970) with $\lambda = 1.081$ Å. The pattern (Figure 1) extended to $2\theta = 75^\circ$ ($\sin\theta/\lambda = 0.565$). The peaks were all broadened relative to the resolution function of the diffractometer, reflecting the small particle size. Least-squares analysis of the 2θ values of 9 reflexions gave $a = 4.201(1)$ and $c = 15.723(4)$ Å, for the triple hexagonal cell.

The work described above was repeated completely for two different preparations of UO_2F_2. This was done to ensure the preparation and subsequent neutron diffraction pattern could be reliably reproduced. The second pattern confirmed the features of the first and had a smaller particle size.

3. ANALYSIS OF DATA

The 22 peaks on the first pattern corresponded to 40 independent reflexions, and a further 12 independent reflexions had unobservably small intensity. On the triple hexagonal cell (Zachariasen, 1948), on which the following discussion is based, the reflexions were of the type $-h + k + \ell = 3n$, confirming the rhombohedral lattice.

By multiplication with the Lorentz factor $\sin\theta \sin 2\theta$ the integrated intensities were reduced to $\Sigma j_{hk\ell}$ values (where $j_{hk\ell}$ is the multiplicity of the reflexion $(hk\ell)$ and $F_{hk\ell}$ is the $(hk\ell)$ structure amplitude). The unobserved reflexions were estimated by assuming a constant minimum observable intensity over the pattern and correcting in a similar way. The neutron scattering lengths used were: $b_U = 0.85$, $b_O = 0.58$ and $b_F = 0.55$, in units of 10^{-12} cm. (Neutron Diffraction Commission 1969)

The geometrical structure amplitude in this case reduced to $\sum_n b_n \cos 2\pi\ell z$ for the n atoms in the cell. An initial calculation using the first three lines of the pattern and the Zachariasen parameters showed a lack of agreement between observed and calculated $F^2_{hk\ell}$ values.

The z(0) parameter was therefore reduced from 0.122 to 0.109, to reproduce the uranyl bond distance of 1.71(3) Å found in α - $UO_2(OH)_2$, which has a similar hexagonal sheet structure (Taylor 1971). An approximate value of z(F) was then determined by plotting for these three reflexions the quantity

$$R_1 = \frac{\Sigma(F_o^2 - F_c^2)}{\Sigma F_o^2}$$

versus z(F) with z(0) fixed at 0.109. The plot showed a minimum at z(F) = 0.325.

The model was then refined on F^2 by the method of least-squares using the program of Busing, Martin and Levy (1962a) and the complete data set. The weights used were $w_{hk\ell} = \left(\sigma\left(F^2_{hk\ell}\right)\right)^{-1}$ where $\sigma\left(F^2_{hk\ell}\right)$ is the estimated error in $F^2_{hk\ell}$. The treatment of the overlapped reflexions is described in Taylor and Hurst (1971). To allow for the reduced number of statistical degrees of freedom arising from the overlap, the errors calculated by the program were increased by a factor of two.

Refinement with individual atomic Debye-Waller temperature factors B led to $R_1 = 0.19$ and the parameters z(0) = 0.109(2), z(F) = 0.330(3), B(U) = 1.2(8), B(0) = 2.1(8) and B(F) = 2.1(8). By adding three more variables

(anisotropic vibration parameters β_{ij}, where the temperature factor is of the form $\exp - (\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)$), R_1 became 0.12 and the weighted R-factor

$$R_2 = \frac{\left(\Sigma w\left(F_o^2 - F_c^2\right)^2\right)^{1/2}}{\left(\Sigma w\left(F_o^2\right)^2\right)^{1/2}}, \text{ was } 0.10.$$

As an illustration of the sensitivity of the data to changes in z(0) and z(F), these parameters were changed to the Zachariasen values, all other parameters being left unchanged, and a set of F_c^2 values was calculated. For this set, R_1 increased to 0.74 and R_2 to 0.93, values obtainable for a random structure.

The final parameters for our refinement are given in Table I, the final F_o^2 and F_c^2 values in Table II, and the interatomic distances, calculated with the program ORFFE (Busing et al. 1962b), in Table III. As the value of Z_f was 0.332(2), the layers are unpuckered in this refinement.

4. THE STRUCTURE OF URANYL FLUORIDE

4.1 Comparison of Previous Models and the Model Proposed in this Study

The structure of UO_2F_2 as determined by Zachariasen is shown in Figure 2 and the associated data are summarised below.

Space Group: $R\,\bar{3}\,m(D^5_{3d})$

Unit Cell Dimensions:

a = 5.767 Å, $\alpha = 42°47'$ (rhombohedral cell with one formula unit)

a_1 = 4.206 Å, a_3 = 15.693 Å (triple hexagonal cell)

Atomic Positions (referred to hexagonal cell):

Atom	Position	x	y	z
U	3(a)	0	0	0
F	6(c)	0	0	0.294(3) = z(F)
0	6(c)	0	0	0.122(6) = z(0)

The structure was determined by assuming a U-0 distance of 1.91 Å and interlayer 0-0 contacts of 2.65 Å. The fluorine atoms in the hexagonal ring system are puckered by ± 0.61 Å.

The structure of a uranyl fluoride layer, as determined in our refinement, is as shown in Figure 2, but with the following changes:

(a) The fluorine atoms are not puckered by ± 0.61 Å with respect to the uranium atoms, but are coplanar with them.

(b) The uranyl distance is 1.71(3) Å.

(c) There is no twofold choice in stacking sequence, the +A and -A vectors now being the same.

The F-F distances around the ring are 2.429(1) Å, the U-F distance is 2.428(1) Å, and the 0-F distances in the hexagonal bipyramid are 2.96(2) Å and 2.98(2) Å (Table III). The 0-0 interlayer contact is 3.03(3) Å. Each uranyl oxygen forms three contacts of this distance with uranyl oxygens of an adjacent layer, which form an equilateral triangle above or below it. Through the centre of this triangle is a fluorine atom distant 3.5 Å from the oxygen, but the latter interaction seems less important than the former in the packing scheme.

In the discrete $UO_2F_5^{3-}$ ion in $K_3UO_2F_5$ (Zachariasen 1954) the uranyl group (U-O = 1.76(3) Å) is surrounded equatorially by a planar and nearly regular pentagon of fluorine atoms, with U-F = 2.24(2) Å and F-F distances around the ring between 2.60 and 2.65 Å. The U-F bonds in UO_2F_2 are longer, allowing a sixth fluorine to be accommodated equatorially; however the situations are not strictly comparable as the $UO_2F_5^{3-}$ ion is discrete, whereas UO_2F_2 has a condensed ring system.

A condensed hexagonal sheet system also occurs in α - $UO_2(OH)_2$, but with oxygen atoms instead of fluorines (Taylor 1971). In α - $UO_2(OH)_2$ the uranyl distance is 1.71(3) Å, the U-O distances are 2.46(2) Å and 2.51(3) Å, and the O-O distances around the ring are 2.49(7) Å and 2.54(4) Å. In view of the comparable sizes of fluorine and oxygen atoms, the interatomic distances found in the present study of UO_2F_2 appear reasonable. The $UO_2(OH)_2$ sheets in α - $UO_2(OH)_2$ show a puckering of ± 0.25 Å; however this puckering is a direct consequence of interlayer hydrogen bonding forces as shown by Taylor (1971). As no such strong forces exist in UO_2F_2 to disturb the sheets, the α - $UO_2(OH)_2$ structure would not suggest a similar puckering in UO_2F_2.

4.2 Line Broadening in the Neutron Diffraction Pattern

Zachariasen (1948), in the X-ray diffraction pattern, and Atoji and McDermott (1970), in the neutron diffraction pattern, both observed a series of 'sharp' (h-k = 3n) and 'diffuse' (h-k $\neq$ 3n) lines. This would indicate a stacking disorder in planes perpendicular to the c-axis, and Atoji and McDermott (1970) derived a structural model based on incoherent domains of eight different ordered structures, four having the 3-layer cell (c = 15.7 Å) and four having a tripled nine-layer cell (c = 47 Å).

As shown in Section 3 of this report it is possible to fit the data to a much simpler model for the structure of UO_2F_2. It is therefore necessary to examine in detail the possible causes of line broadening and so see if the various observations are compatible.

The intrinsic broadening, b, of the spectrometer is 0.48(5)° 2θ at 12°, descending to a minimum of 0.30(2)° 2θ at 30° and rising to 0.55(5)° at 45°, as determined from previous patterns of substances giving sharp lines. In Table IV are listed the observed half-widths B of the strongest lines and particle sizes

D_{hkl}, perpendicular to the (hk$l$) plane calculated from the Scherrer equation (Klug and Alexander 1962). The width of the 'diffuse' (101) line was estimated by subtracting the smaller nearby (012) intensity.

Table IV showed that all these lines were broadened, including the (003), (110) and (113) lines which should be 'sharp'. Although the absolute particle sizes were not very accurate, because of the relatively large contribution of the instrumental broadening, b, the relative magnitudes should be meaningful (Klug and Alexander 1962) and they suggested that the UO_2F_2 particles were rod-shaped, with the longest dimension in the vicinity of the [110] direction. It was noted that the next longest dimension was in the [113] direction, which made the smallest angle (22°) with [110], and the shortest dimensions were in the [101] and [003] directions, which made larger angles with [110]. The neutron pattern thus strongly suggested that the line broadening in UO_2F_2 was at least largely due to diffraction by very small rod-shaped particles.

4.3 Electron Micrograph of UO_2F_2

An electron micrograph of a particle of UO_2F_2 is shown in Figure 3. This and all other pictures clearly showed clusters of rod-like particles with sizes in the diffraction broadening range.

4.4 Statistical Comparison of Simple and Disorder Models in UO_2F_2

The intensities of the reflexions with h-k = 3n are the same for the fluorine coordinates $(0.333 + \Delta Z_F)$ and $(0.333 - \Delta Z_F)$. These reflexions can thus be used to detect any deviations from planarity in the fluorine ring. Atoji and McDermott (1970) determined $\Delta Z_F = 0.0133 \pm 0.0015$ using integrated intensities of lines of this type derived from peak profiles by Gaussian analysis, but gave no values for the intensities used in this calculation, or their number.

On examining our pattern, which is similar to that of Atoji and McDermott, it was observed that there were only two fully resolved lines of this type available, the (003) and (116) reflexions. Of the remaining data, only the (006), (113), (009) and (119) reflexions could be estimated from the peak shapes, and these only roughly. These six intensities were used in an attempt to decide whether the neutron data precluded the existence of a planar fluorine ring.

Sets of structure factors for these 6 reflexions were calculated for $Z_F = 0.3333$ and $Z_F = 0.3466$, and these gave agreement indices of $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$ of 0.094 and 0.080. It was assumed that $B_u = 1.2$, $B_o = 2.1$, $B_F = 2.1$ Å^2, $Z_o = 0.109$ and the scale factor was varied. The two sets of structure factors obtained are given in Table V.

The R-factor ratio test of Hamilton (1965) can be applied in this situation. Hamilton (1965) has shown that if the R-factor ratio $R_o = \frac{R_1}{R_2}$ is less than $R_{b,n-m,\alpha}$ where b is the dimension of the hypothesis on which R_1 is based, n-m is the number of degrees of freedom of the system and α is the significance level, then the hypothesis cannot be rejected at this level.

We wish to test the hypothesis that the fluorine ring is planar. The R-factor ratio R_o is 0.094/0.080 = 1.175 and n-m is 6-1 = 5. The dimension of the hypothesis is 1. Table I of Hamilton (1965) gives

$$R_{1,5,0.05} = 1.524$$

$$R_{1,5,0.25} = 1.157$$

$$R_{1,5,0.50} = 1.051$$

The test suggests about a 25% probability of error if the hypothesis is rejected, and usual practice does not demand rejection of a hypothesis at this level. The data of Table V would not necessarily preclude the existence of a planar fluorine ring in UO_2F_2. The powder data of UO_2F_2 seem unsuitable for an unequivocal determination of slight deviations from planarity in the fluorine rings. A single crystal study of UO_2F_2 should satisfactorily distinguish between previously proposed disordered structures and the simple planar model.

5. CONCLUSIONS

The work described in Section 4 of this report showed that much of the line broadening seen in the present diffraction pattern of UO_2F_2 was due to particle size effects. Previously proposed structures of UO_2F_2 are very complex. It is difficult to conclusively demonstrate such complexity using an analysis of a powder pattern suffering from superposition such as given by UO_2F_2. Superposition of the powder lines prevents effective analysis of the intensities of the reflexions with h-k = 3n, necessary to demonstrate deviations from planarity in the fluorine rings. This will continue to be an inherent difficulty of the system since, to ensure sample purity, all preparations must be of small particle size. It has been shown that the simple model advanced in this report fits the data as well as previously advanced complex structures. However, the insensitivity of the diffraction patterns to changes in the z-parameters makes it impossible to conclusively state that either model is not correct.

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TABLE I

STRUCTURAL PARAMETERS FOR UO_2F_2

Uranium in 3(a) with x = y = z = 0

$\beta_{11} = 0.008(10)$, $\beta_{33} = 0.005(1)$

Oxygen in 6(c) with x = y = 0, z = 0.109(2)

$\beta_{11} = 0.033(10)$, $\beta_{33} = 0.004(1)$

Fluorine in 6(c) with z = 0.332(2)

$\beta_{11} = 0.024(10)$, $\beta_{33} = 0.004(1)$

TABLE II

OBSERVED AND CALCULATED NEUTRON F^2 VALUES FOR UO_2F_2

h	k	λ	F_o^2	F_c^2	h	k	λ	F_o^2	F_c^2
0	0	3	145	150	*1	2	8	16	38
1	0	1	106	112	*2	0	11	21	7
0	1	2	16	21	⎧1	1	12	51	57
⎧1	0	4	29	36	⎩0	3	6	71	86
⎩0	0	6	88	101	*0	1	14	32	19
0	1	5	18	45	⎧2	2	0	416	458
1	1	0	709	684	⎩0	0	15	19	19
1	1	3	134	141	⎧2	1	10	60	45
*1	0	7	11	9	⎩2	2	3	136	115
⎧0	2	1	90	100	⎧1	3	1	70	72
⎪2	0	2	17	21	⎪0	2	13	4	8
⎪0	0	9	378	411	⎪3	1	2	18	20
⎩0	1	8	47	47	⎪0	3	9	285	273
⎧0	2	4	31	26	⎪1	2	11	10	7
⎩1	1	6	109	96	⎪1	3	4	10	8
*2	0	5	13	33	⎪2	2	6	81	81
1	0	10	62	57	⎩3	1	5	14	11
*0	2	7	21	9	*2	0	14	35	15
⎧2	1	1	92	89	*1	0	16	35	1
⎪1	2	2	19	20	*1	1	15	18	18
⎪1	1	9	380	358	*1	3	7	18	10
⎪2	0	8	48	42					
⎪0	1	11	12	8					
⎪0	0	12	70	61					
⎩2	1	4	20	18					
*1	2	5	11	23					
3	0	0	480	523					
⎧0	2	10	47	50					
⎪0	3	3	100	123					
⎩2	1	7	8	9					
*1	0	13	32	11					

* unobservably small reflexion

{ superposed reflexions

TABLE III

INTERATOMIC DISTANCES IN UO_2F_2

U-O (uranyl) = 1.71(3)
U-F in hexagonal sheets = 2.428(1)
F-F in ring = 2.429(1)
O-O (inter layer) = 3.03(3)
O-F (intra layer) = 2.96(2), 2.98(2)

TABLE IV

PARTICLE SIZES $D_{hk\ell}$, FROM THE NEUTRON PATTERN OF UO_2F_2

$hk\ell$	$b(^\circ 2\theta)$	$B(^\circ 2\theta)$	$D_{hk\ell}$ (Å)
003	0.48(5)	0.72(5)	155(50)
101	0.38(4)	0.80(5)	107(17)
110	0.30(2)	0.40(3)	348(165)
113	0.32(2)	0.50(3)	214(50)

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR SIX REFLEXIONS OF TYPE $h-k = 3n$, WITH $Z_F = 0.3333$ AND $Z_F = 0.3466$ RESPECTIVELY

$hk\ell$	F_o	F_c ($Z_F = 0.3333$)	F_c ($Z_F = 0.3466$)
003	13.0	12.5	13.1
006	12.3	10.9	10.7
113	12.7	11.4	12.0
009	20.2	23.9	23.4
116	11.1	10.1	9.8
119	20.9	21.5	21.2

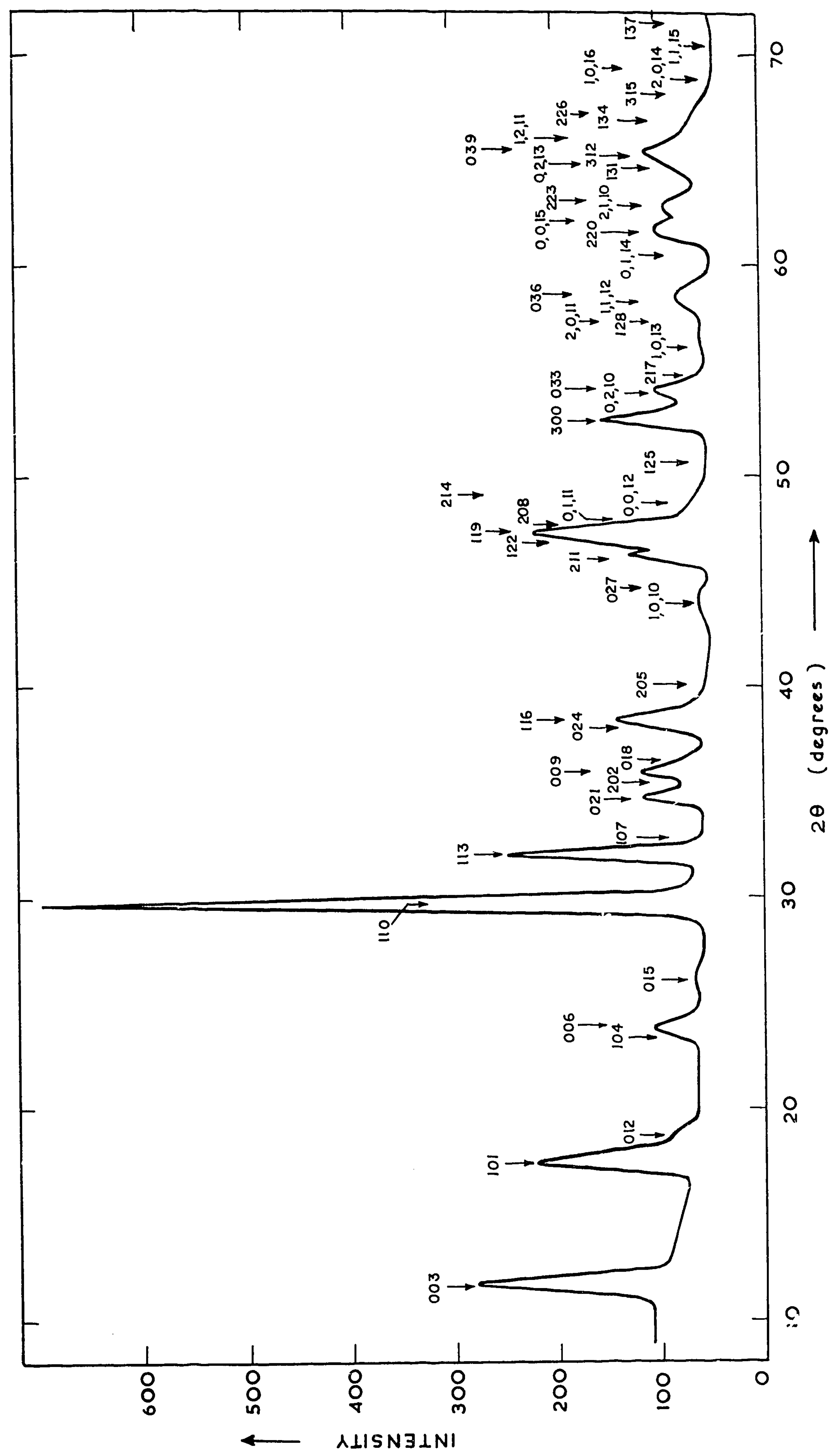

FIGURE 1. THE NEUTRON POWDER DIFFRACTION PATTERN OF UO_2F_2

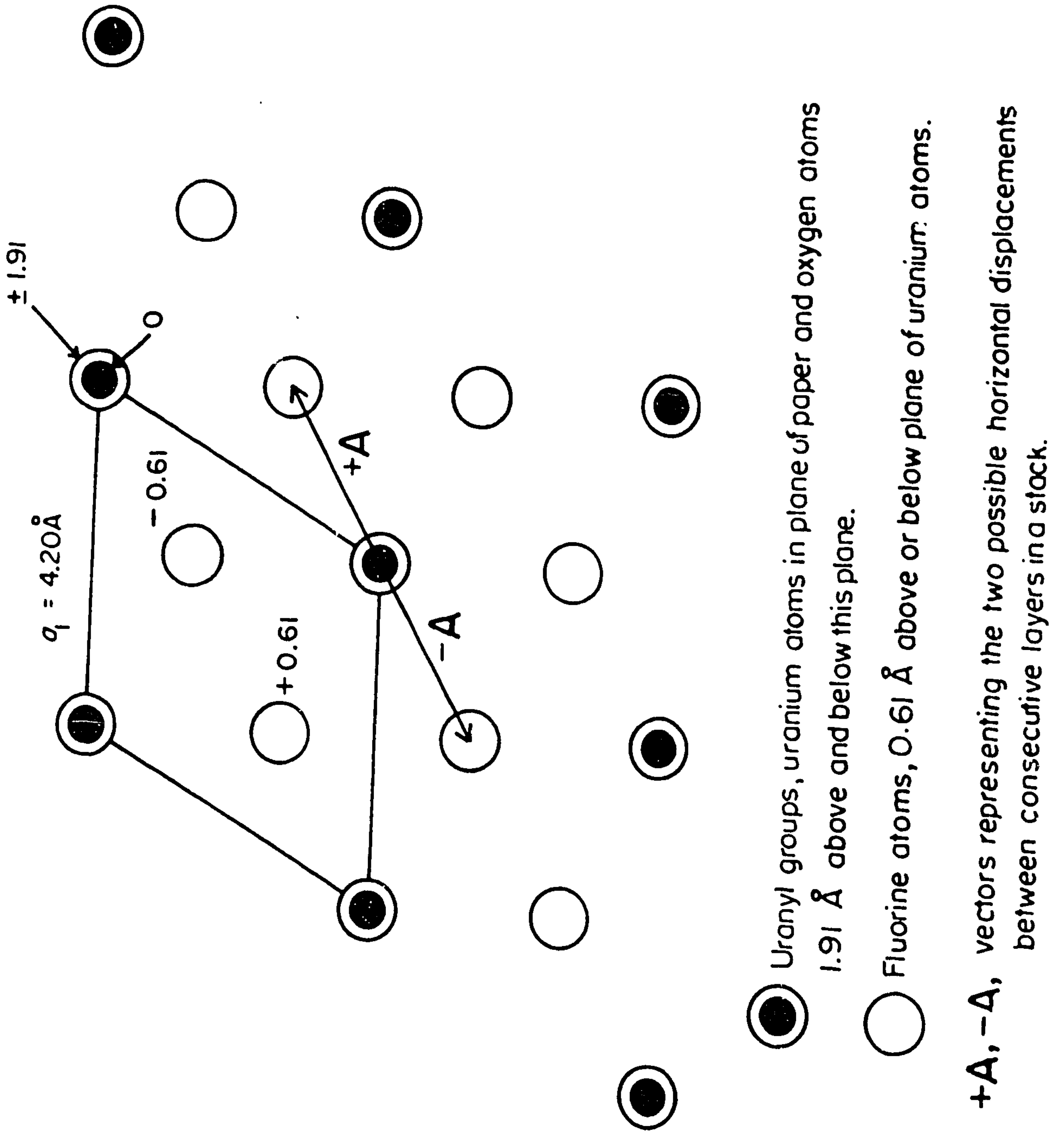

FIGURE 2. THE STRUCTURE OF UO_2F_2 AS PROPOSED BY ZACHARIASEN (1948)

FIGURE 3. ELECTRON MICROGRAPH OF UO_2F_2 SHOWING A TYPICAL CLUSTER OF ROD-SHAPED PARTICLES

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