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The Structures of Fluorides *XIII*: The Orthorhombic Form of Tungsten Hexafluoride at 193°K by Neutron Diffraction

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The positional parameters in the orthorhombic phase of solid tungsten hexafluoride WF_6, have been determined by total profile analysis of a neutron powder pattern taken at 193°K. WF_6 at 193°K is orthorhombic, with space group $Pnma$ (D_{2h}^{16}) and $a = 9.603$ (3), $b = 8.713$ (4), and $c = 5.044$ (3) Å at 193°K. The full matrix, least-squares refinement converged at $R = \sum (|y_0 - (1/c)y_c|)/\sum y_0 = 0.075$ where c is the scale factor and y_0 is one of the 306 background-corrected intensities in range of one or more Bragg reflections along the pattern. The refinement showed that, at this temperature, WF_6 has the orthorhombic UF_6 structure. The mean W–F distance is 1.81 Å, and the mean F–F separation between octahedra is 3.12 Å.

The results are compared with previous neutron profile studies of the orthorhombic phases of UF_6 and MoF_6 at 193°K, and with a neutron profile Kubic Harmonic analysis of the cubic form of WF_6 at 266°K. On the basis of these structural studies in this series of hexafluorides, reasons are given why MoF_6 and WF_6 have a high-temperature cubic phase, but UF_6 does not. Deviations from idealized h.c.p. coordinates in the orthorhombic phases are in a direction such that the fluorine atoms become strongly bonded to the metal atoms to form a molecular, rather than an ionic, lattice.

Introduction

The structural parameters in tungsten hexafluoride, WF_6, have not yet been measured by either X-ray or neutron diffraction techniques, possibly because of experimental difficulties in working with the compound. WF_6 is highly volatile and moisture-sensitive. It melts at 275.1°K and boils at 290.3°K. Like the other second- and third-row transition metal hexafluorides, solid WF_6 has a high-temperature, body-centered cubic phase, and a low-temperature phase of lower symmetry (*1*). The transition in WF_6 occurs at 264.7°K. Siegel and Northrop (*1*) found with X-ray powder photographs at 273 and 253°K that the cubic phase had a cell edge of 6.28 (2) Å and a calculated density of 3.99 g cm^{-3}, while the low-temperature form indexed on a cell of the UF_6 type (2), and had a calculated density of 4.56 (3) g cm^{-3}. The X-ray patterns were not suitable for structural analysis because of sublimation and recrystallization effects, but Siegel and Northrop concluded that the low-temperature form was probably isostructural with UF_6.

Further diffraction work seemed necessary to define the crystal structure of the low-temperature phase of WF_6. As WF_6 has a vapor pressure (*3*) of 31 kPa at 264.7°K and less than 0.1 kPa at 193°K, it was desirable to work at reduced temperatures to reduce sublimation effects. Single-crystal work did not seem practicable; it appeared that there was a major structural change at the transition and the cubic crystals would probably shatter on passing through it, thus WF_6 crystals would probably have to be grown at temperatures around 250°K. The problems of crystal growth, mounting, containment and maintenance at a desirable temperature (~193°K or less) on a single-crystal diffractometer seemed prohibitively difficult.

The recently developed technique of profile analysis (*4*), where structural parameters are fitted to the overall profile of a powder pattern, offered an alternative approach. In this method, each Bragg reflection is assumed to be Gaussian, and the whole pattern is the sum of all such Gaussians. The observations are the intensity measurements along the pattern, corrected for background. The profile method offers the maximum amount of information retrieval from a powder pattern, and in the case of neutron diffraction, approaches the precision of single-crystal methods for structures of moderate complexity (*5*). Profile analysis gives standard deviations which are about half those obtained by conventional integrated-intensity refinements (*6*).

Neutron powder profile analysis thus appeared to be a convenient means of circumventing the above problems associated with single-crystal studies on WF_6, and it seemed that reasonable precision could still be obtained with powders. Neutron diffraction would clearly be better than X-ray diffraction for this purpose as the W and F atoms have about the same thermal neutron scattering lengths, but only about one-tenth of the diffracted intensity in an X-ray pattern would be due to fluorine scattering. The experimental details and results of the present neutron powder profile study of WF_6 are given below.

Experimental

A sample of liquid WF_6 was prepared by direct fluorination of tungsten metal powder in a flow system (*7*). Using vacuum line techniques (*8*), the WF_6 was purified by distillation over NaF; then it was distilled into a 17 mm diameter Kel-F tube. This tube was attached to the inner jacket of a cryostat described previously (*9*). To ensure random orientation of the crystallites, the remelted sample was snap-frozen with liquid nitrogen, then allowed to warm to 193°K. This temperature was maintained with an acetone/dry ice slush bath.

A neutron diffraction powder pattern was collected on the AAEC research reactor HIFAR, to $2\theta = 45.70°$ with $\lambda = 1.083$ Å with steps of 0.1° 2θ (1° every 3 hr). The 2θ region from 10–12° was excluded from the calculations owing to the peak arising from the Kel-F tube; the Kel-F gave low background undulations thereafter. The total background level varied from 400–1000 counts per step, and the maximum background-corrected intensity from the WF_6 sample was 8334 counts. The number of independent Bragg reflections in the range of the pattern was 96, and there were 306 points along the pattern having a contribution from one or more Bragg reflections.

The profile refinement was carried out with the Rietveld program as modified by Hewat (*10*). The reflection halfwidths h, in deg 2θ were defined by the relation

$$h^2 = U\tan^2\theta + V\tan\theta + W$$

where U, V, W are halfwidth parameters, refined in the profile analysis. Also refined were the unit cell dimensions and instrument zero, z. The profile observations corrected for background, y_0, were assigned the statistical weights $w = (y_0)^{-1}$ in the full matrix, least-

TABLE I

CRYSTAL DATA FOR THE ORTHORHOMBIC FORM OF WF_6[a] AT 193 AND 253°K

	Lattice constants (neutron wavelength = 1.083 Å)				
Temperature	a (Å)	b (Å)	c (Å)	U (Å^3)	D_xg cm^{-3}
193°K[b]	9.603 (3)	8.713 (4)	5.044 (3)	422.0	4.69
253°K[c]	9.68	8.81	5.09	434.1	4.56

[a] MW = 297.84, space group *Pnma* D_{2h}^{16}, $Z = 4$.

[b] This work, neutron profile refinement.

[c] Ref. (*1*), X-ray powder.

TABLE II

POSITIONAL PARAMETERS ($\times 10^4$) FOR THE ORTHORHOMBIC FORM OF WF_6 AT 193°K, COMPARED WITH THE IDEAL PARAMETERS OF HOARD AND STROUPE FOR A PERFECT H.C.P. STRUCTURE.[a]

Atom	Parameter[b]	Value	Ideal
W	x	1247 (12)	1250
W	z	0999 (35)	0833
F(1)	x	0145 (10)	0000
F(1)	z	−1952 (23)	−2500
F(2)	x	2452 (12)	2500
F(2)	z	3717 (45)	4167
F(3)	x	0212 (7)	0000
F(3)	y	0967 (8)	0833
F(3)	z	2330 (15)	2500
F(4)	x	2357 (7)	2500
F(4)	y	1075 (17)	0833
F(4)	z	−0624 (39)	−0833

[a] Overall Debye–Waller factor = 3.14 (8) Å^2.

[b] Where a y-parameter is omitted, $y = 0.25$.

squares treatment. Preferred orientation and absorption corrections were not found to be necessary.

Starting positional parameters were obtained from previous profile refinements for UF_6(*11*) and MoF_6(*9*). The neutron scattering lengths (*12*) were taken as 4.8 fm for W and 5.6 fm for F, and an overall Debye–Waller temperature factor B was refined. The refinement proceeded satisfactorily, to values of the residuals

$$R_1 = \sum (|y_0 - (1/c)y_c|)/\sum y_0 = 0.075,$$

$$R_2 = (\sum w\,(y_0 - (1/c)y_c)^2 \sum w y_0^2)^{1/2} = 0.079,$$

These were close to the "predicted" (or statistically expected) R-factor

$$R_3 = ((N-P)/\sum w y_0^2)^{1/2} = 0.051,$$

where c is the scale factor, N the number of observations, and P the number of variable parameters. The refined instrumental parameters were $U = 5.49$ (54) deg^2, $V = -2.80$ (28) deg^2, $W = 0.59$ (4) deg^2 and $z = -0.02$ (1) deg. The profile cell dimensions are given, with other crystal data, in Table I and the structural parameters in Table II. The observed and calculated profiles are shown in Fig. 1.

Discussion

The present neutron profile refinement for orthorhombic WF_6 at 193°K has shown that WF_6 has the UF_6 structure (*2*) at this temperature. The observed and calculated profiles, Fig. 1, show good agreement between theory and experiment, as do the above R-factors. The parameters in Table II are the first measured for solid WF_6. The WF_6 structure is shown projected down the a-axis in Fig. 2.

The mean W–F distance in the octahedron (Table III) is 1.81 Å. This is less than the sum of the W and F ionic radii (*13*) pertinent to the present coordination, which is 1.91 Å. Thus, there is covalent character in the W–F bonds. The errors in the W–F bond lengths are not sufficiently low to permit a statement that the individual W–F bonds differ in length. The M–F distances in UF_6 and MoF_6 are also less than the ionic sums by about 0.10 Å (Table IV) so the amount of covalent character in the three M–F bonds is approximately equal. Thus the three compounds are better

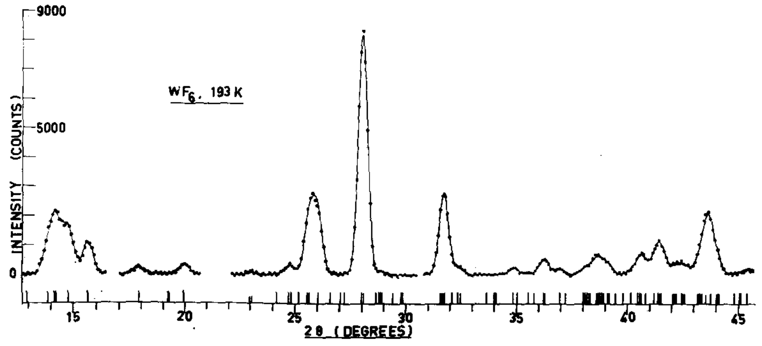

FIG. 1. Observed and calculated neutron diffraction powder profile for orthorhombic WF_6 at 193°K.

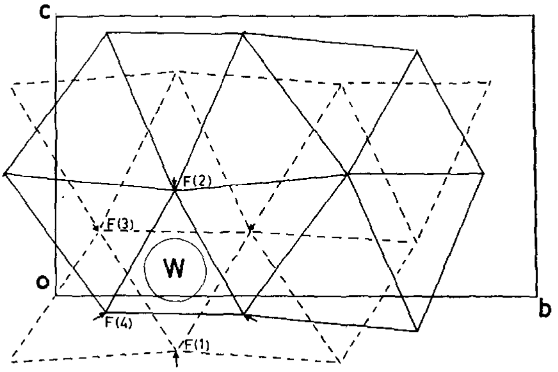

FIG. 2. The structure of WF_6 projected down the *a*-axis. Lines are drawn between atomic centers to illustrate the packing. The dashed lines outline the F layer at $x \sim 0$ and the solid lines the F layer at $x \sim \frac{1}{4}$. The ionic radius of W is drawn to scale. The small arrows indicate in direction and magnitude (in projection) the differences between the fluorine positions and those of an idealized h.c.p. structure.

TABLE III

INTERATOMIC DISTANCES AND ANGLES IN TUNGSTEN HEXAFLUORIDE AT 193°K

In WF_6 octahedron

Distance		Angle	
W—F(1)	1.826 (15) Å	F(3)—W—F(4)	89.1 (6)° (2*x*)
W—F(2)	1.794 (24)	F(3)—W—F(1)	89.1 (6) (2*x*)
W—F(3)	1.796 (10) (2*x*)	F(3)—W—F(2)	94.1 (9) (2*x*)
W—F(4)	1.830 (16) (2*x*)	F(3)—W—F(3)	96.2 (8)
F(3)—F(3)	2.672 (13)	F(4)—W—F(4)	85.5 (13)
F(2)—F(3)	2.627 (10) (2*x*)	F(4)—W—F(1)	88.5 (9) (2*x*)
F(1)—F(3)	2.541 (9) (2*x*)	F(4)—W—F(2)	88.0 (8) (2*x*)
F(3)—F(4)	2.544 (14) (2*x*)	F(2)—W—F(1)	175.2 (15)
F(4)—F(4)	2.484 (30)	F(4)—W—F(3)	174.1 (11) (2*x*)
F(2)—F(4)	2.519 (18) (2*x*)		
F(1)—F(4)	2.550 (13) (2*x*)		

F–F contacts external to octahedron

In the ~h.c.p. F layer	Between ~h.c.p. F layers
F(1)—F(3) 3.18 (1) Å	F(4)—F(3) 3.16 (1) Å
F(1)—F(3) 3.05 (1)	F(4)—F(1) 3.19 (2)
F(3)—F(3) 2.92 (1)	F(4)—F(3) 3.21 (2)
F(3)—F(3) 3.20 (2)	F(4)—F(3) 3.11 (1)
F(2)—F(4) 3.14 (2)	F(3)—F(2) 3.02 (1)
F(2)—F(4) 3.11 (3)	F(2)—F(1) 3.06 (2)
F(4)—F(4) 3.15 (2)	F(2)—F(1) 3.11 (2)

W–W distances

In mirror plane	Between mirror planes
5.03 (1), 5.044 (3), 5.96 (2) Å	5.58 (1), 5.07 (1), 6.40 (3) Å.

TABLE IV

COMPARISON OF NEUTRON PROFILE RESULTS FOR ORTHORHOMBIC UF_6, MoF_6 AND WF_6 AT 193°K

Quantity	Value		
	UF_6[a]	MoF_6[b]	WF_6
$rM^+ + rF^-$; ionic sum (Å)	2.08	1.93	1.91
M—F observed (Å)	1.98	1.81	1.81
Ionic sum −(M—F) Å	0.10	0.12	0.10
Mean F—F in octahedron (Å)	2.80	2.56	2.56
Mean F—F without the octahedron (Å)	3.11	3.10	3.12
Debye–Waller factor B (Å^2)	1.9 (1)	2.5 (1)	3.14 (8)
rms amplitude of vibration = $(B/8\pi^2)^{1/2}$Å	0.155 (3)	0.179 (3)	0.200 (3)
Ionic radius ratio	0.564	0.451	0.436

[a] Ref. 11.
[b] Ref. 9.

described as an assemblage of interlocking MF_6 molecules, rather than a hexagonal close packed arrangement of fluorine ions with metal atoms in octahedral holes.

The mean F–F distance in the WF_6 octahedron is 2.56 Å (Table IV) and this is 0.10 Å less than the effective fluorine ionic diameter (*13*), 2.66 Å. This suggests that slight tensions are present in the octahedron, caused by the formation of the W–F bonds. The critical W–F distance, below which overcrowding of the fluorine atoms in the octahedron occurs, is $2.66/\sqrt{2} = 1.88$ Å (*14*); the W–F distances are less than this value. The fluorine atoms in the octahedra in MoF_6 at 193°K are also "touching" since the mean Mo–F distance is also 1.81 Å (Table IV), This is in contrast with UF_6, where the F–F distances in the UF_6 octahedron are 2.80 Å, larger than the fluorine ionic diameter, but equal to $\sqrt{2}$ times the mean U–F distance, 1.98 Å (Table IV). On proceeding from UF_6 to MoF_6 to WF_6, the ionic metal/fluorine radius ratios (Table IV) also approach the theoretical limit of 0.414 for transition to tetrahedral bonding.

The present results help to explain why MoF_6 and WF_6 form disordered cubic phases whereas UF_6 does not. The Mo–F and W–F distances are both 0.17 Å shorter than the U–F distance. This leads to a large difference in the octahedral "volumes" $4/3\,\pi[(M - F) + rF^-]^3$, which are 130 Å^3 for MoF_6 and WF_6, and 152 Å^3 for UF_6. Since the F–F contacts not in an octahedron are constant for UF_6, MoF_6 and WF_6 at 3.11 Å, the volume difference suggests that librational motion of the octahedron should be less hindered in MoF_6 and WF_6 than in UF_6. This view is supported by the Debye–Waller factors at 193°K (Table IV) which give a significantly lower amplitude of thermal vibration in UF_6 than in MoF_6 or WF_6. A single-crystal neutron diffraction study of UF_6 has revealed an rms libration amplitude of the UF_6 molecule of $4\frac{1}{2}°$ at 293°K which must be regarded as hindered (*15*). From the foregoing arguments it is to be expected that the onset of the disordered cubic phase, where the MF_6 molecules are known to be undergoing fast reorientations (*16*), should occur at a higher temperature for UF_6 than for MoF_6 and WF_6. In fact, this onset is not reached before the triple point for UF_6, 337.2°K.

WF_6 may be regarded as derived from an "ideal" h.c.p. structure, and idealized coordinates may be derived for the atoms on this basis (*2*). Table V shows the deviations between the ideal and measured coordinates for UF_6, MoF_6 and WF_6 at 193°K. Because of the longer U–F bonds, the deviations from the ideal structure are only half as great for UF_6 as for MoF_6 and WF_6. The deviations are well correlated in direction and magnitude. Coordinates increased or decreased from the

TABLE V

DIFFERENCES IN Å BETWEEN THE IDEAL AND MEASURED POSITIONAL PARAMETERS IN UF_6, MoF_6 AND WF_6 AT 193°K[a]

Atom	Parameter	$\lvert\Delta\rvert \times 10^3$ (Å) UF_6[b]	 MoF_6[c]	 WF_6
M	x	29 (6) ↑	6 (11) ↓	3 (12) ↓
	z	17 (8) ↓	105 (18) ↑	84 (17) ↑
F(1)	x	116 (9) ↑	148 (13) ↑	139 (10) ↑
	z	122 (8) ↑	262 (15) ↑	276 (12) ↑
F(2)	x	12 (11) ↓	56 (16) ↑	46 (12) ↓
	z	104 (21) ↓	212 (36) ↓	227 (23) ↓
F(3)	x	159 (7) ↑	211 (11) ↑	204 (7) ↑
	y	71 (7) ↑	139 (10) ↑	117 (7) ↑
	z	74 (6) ↓	27 (10) ↓	86 (8) ↓
F(4)	x	47 (7) ↓	172 (10) ↓	137 (7) ↓
	y	126 (21) ↑	249 (18) ↑	211 (16) ↑
	z	18 (25) ↑	61 (21) ↑	105 (20) ↑

[a] Parameters increased or decreased from the ideal values are marked ↑ or ↓, respectively. Mean deviation: UF_6, 0.075 Å; MoF_6, 0.137 Å; WF_6, 0.136 Å.

[b] Ref. 11.

[c] Ref. 9.

ideal are indicated by ↑ or ↓. The directions of movement away from the ideal are shown in Fig. 2; the movement is always towards the metal atom and in such a way as to form MF_6 clusters along the mirror planes and gaps between molecules.

The W–F distance observed in the present study of the orthorhombic phase at 193°K agrees well with the results of a profile analysis of the cubic phase of WF_6 at 266°K (*17*), using Kubic Harmonic functions to describe the disordered fluorine distribution around the W atom. In the latter study the fluorine density was assumed to lie on the surface of a sphere with a radius equal to the W–F distance; the fluorine density over this surface was found to be not spherically symmetrical. The radius of the "sphere", found by least-squares analysis at 266°K, 1.84 (2) Å, was in good agreement with the mean W–F distance, 1.81 Å, observed in the present study.

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