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The Structures of Fluorides X. Neutron Powder Diffraction Profile Studies of UF_6 at 193°K and 293°K

J. C. TAYLOR AND P. W. WILSON

Chemical Technology Division, Australian Atomic Energy Commission, Research Establishment, Private Mail Bag, Sutherland, New South Wales, Australia, 2232

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Neutron diffraction studies on polycrystalline UF_6 have been carried out at 193°K and 293°K. At both temperatures, UF_6 is orthorhombic with the space group *Pnma* (D_{2h}^{16}) and $Z = 4$. Measured lattice parameters are $a = 9.924\ (10)$ Å, $b = 8.954\ (9)$ Å, $c = 5.198\ (5)$ Å at 293°K and $a = 9.843\ (11)$, $b = 8.920\ (10)$, $c = 5.173\ (6)$ Å at 193°K. The neutron diffraction patterns were analyzed by the least-squares profile-fitting technique. The final values of $R = \sum_i (|I_{o_i} - I_{c_i}|)/\sum I_{o_i}$ over the pattern points, where I_{o_i} is a background corrected measured intensity, were 0.081 at 193°K and 0.133 at 293°K.

On cooling, the hexagonal close-packing tends to become more regular, and the F–F distances external to a UF_6 octahedron contract. The octahedra are nearly regular with a mean U–F distance of 1.98 Å, a mean F–F edge of 2.80 Å, and a F–U–F angle of 90.0° at 193°K.

Introduction

The structure of the important compound UF_6 was first determined by Hoard and Stroupe (*1*) using single-crystal X ray methods. The structure was found to be layered, with the fluorine atoms in hexagonal close-packing and the uranium atoms arranged in octahedral holes. It was not certain from this work whether the structure differed significantly from an idealized model with perfectly regular close-packing. A recent neutron diffraction powder study at 294°K (*2*) confirmed the X ray structure and significant deviations from the idealized positions were found.

Studies of UF_6 at room temperature are difficult because UF_6 has a high vapor pressure (~12 kPa) at this temperature, and constant sublimation and recrystallization in the sample give rise to preferred orientation effects. These effects increase with time and introduce systematic errors into the intensity data. To overcome this problem, it was thought worthwhile to carry out a neutron diffraction study of UF_6 at 193°K, where the vapor pressure of UF_6 is small.

The structure at room temperature was also reexamined because the diffracted intensities in the spectrometer used in the previous study (*2*) had been increased tenfold by the installation of a graphite analyzing crystal.

Experimental and Results

The sample of UF_6 was prepared as previously outlined (*2*) and contained in a Kel-F tube. For the 193°K work, the sample was placed in an evacuated aluminium cryostat, which has been described previously (*3*), the coolant being dry ice. In this study, the inner heat shield was not used and the temperature was probably warmer than the nominal value of 193°K.

The sample was sublimed into the Kel-F tube using methods previously described (*4*). The tube was completely filled in an attempt to prevent sample sublimation during a run. Using dry-box methods, the stopper attached to the Kel-F tube for the tube filling sublimation was exchanged for one suitable for attachment to the cryostat. The sample was quickly cooled before sublimation and reorientation could take place.

No diffracted intensity due to aluminium was observed, but a peak due to the Kel-F was found at 10–12° 2θ. The cryostat was rotated at 2π rad/sec since rotation of the

TABLE I

CRYSTAL DATA FOR UF_6 AT 293°K AND 193°K[a]

Temperature	a (Å)	b (Å)	c (Å)	Unit-cell volume (Å^3)	D_x g·cm^{-3}
293°K	9.924 (10)	8.954 (9)	5.198 (5)	461.9 (8)	5.06 (1)
193°K	9.843 (11)	8.920 (10)	5.173 (6)	454.2 (8)	5.15 (1)

[a] Orthorhombic space group *Pnma* (D_{2h}^{16}), $Z = 4$, M.W. = 352.02, $D_m = 4.93$ g·cm^{-3} at 335.5°K.

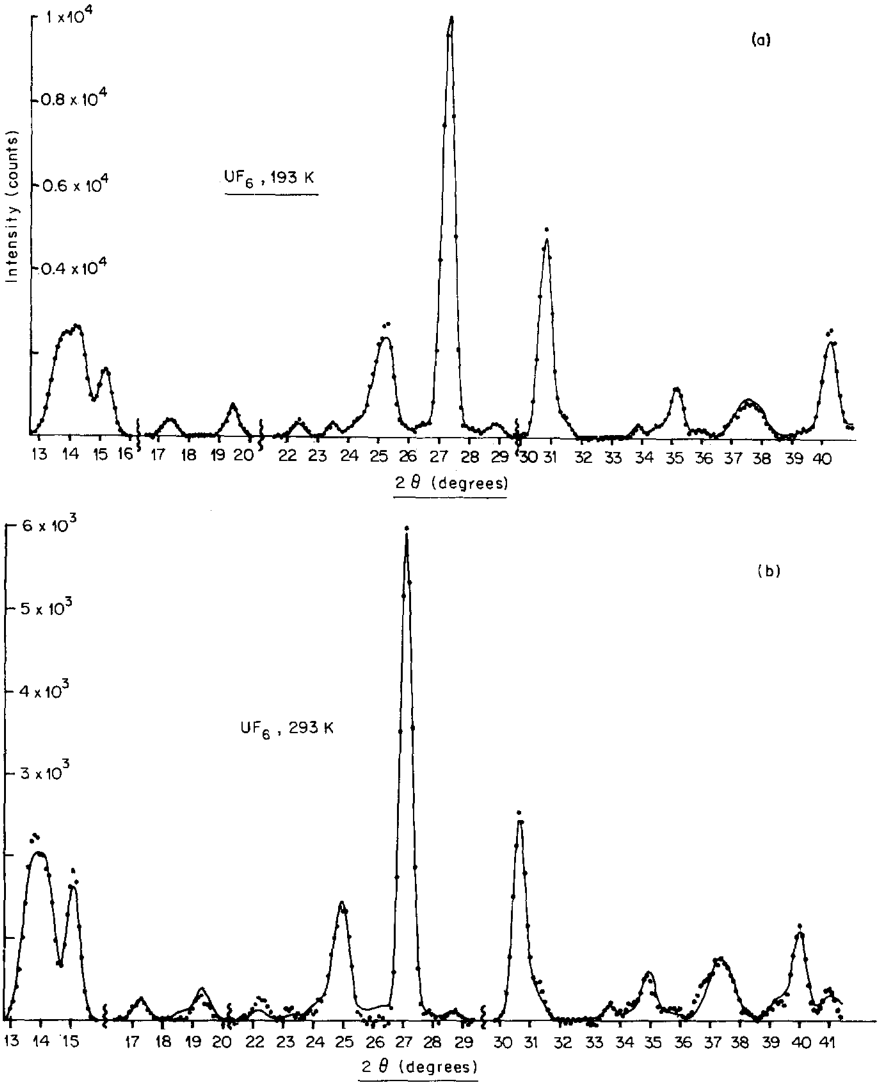

FIG. 1. Observed and calculated neutron powder pattern profiles of UF_6 at 193°K and 293°K.

TABLE II

POSITIONAL PARAMETERS FOR UF_6 AT 293°K AND 193°K AND THE IDEALIZED PARAMETERS DERIVED BY HOARD AND STROUPE (*1*) FOR PERFECT HEXAGONAL CLOSE-PACKING OF THE ANIONS

Atom	Parameter ($\times 10^4$)	293°K	193°K	Ideal
U	*x*	1290 (10)	1279 (6)	1250
	z	800 (29)	797 (15)	833
F(1)	*x*	159 (16)	118 (9)	0
	z	−2150 (31)	−2265 (16)	−2500
F(2)	*x*	2499 (22)	2488 (11)	2500
	z	3547 (50)	3968 (41)	4167
F(3)	*x*	186 (13)	162 (7)	0
	y	857 (11)	910 (8)	833
	z	2300 (22)	2356 (11)	2500
F(4)	*x*	2447 (14)	2452 (7)	2500
	y	1016 (31)	971 (23)	833
	z	−535 (55)	−864 (48)	−833
—	Overall *B* (Å)	3.2 (2)	1.9 (1)	

sample increased the intensity of the diffracted beam by a factor of 3 to 4.

Neutron diffraction patterns of UF_6 at 193°K and 293°K were collected with the cryostat in position on the AAEC research reactor HIFAR, to $\sin\theta/\lambda = 0.33$. The elastic diffraction technique (*5*) was used with a graphite analyzer and $\lambda = 1.077$ Å. Cell dimensions of UF_6 were determined at the two temperatures by a least-squares analysis of the neutron line positions. The lattice contractions on cooling were roughly isotropic, being 0.8% in *a*, 0.3% in *b*, and 0.5% in *c*. The lattice constants and other crystal data are given in Table I. As the wavelength was not measured precisely, the quoted errors do not reflect uncertainties in the wavelength. The neutron diffraction patterns for UF_6 at 193°K and 293°K are shown in Figs. 1(a) and 1(b).

The patterns were analyzed with the profile-fitting technique of Rietveld (*6*). The computer program used was a modification of the Busing, Martin, and Levy (*7*) ORFLS program, which handled the profile refinement case (*8*). The lattice parameters were determined from a least-squares refinement of the line positions, separately from the profile refinement. The peak widths were measured from the pattern and not refined; the peaks were assumed to be Gaussian, a close approximation for the diffractometer used. The scattering lengths used were 8.5 fm for uranium and 5.5 fm for fluorine. The weights for the profile least-squares refinement were based on counting statistics. There were 84 independent reflexions in the range of the room-temperature pattern and 76 in the 193°K pattern. An overall isotropic Debye–Waller temperature factor was assumed. The final observed and calculated profiles at 193°K and 293°K are shown in Figs. 1(a) and 1(b). The final values of $R = \sum (|I_o - I_c|)/\sum I_o$ and $\chi = \{\sum w(I_o - I_c)^2/(NO - NV)\}^{1/2}$ were 0.081 and 1.15 for UF_6 at 193°K and 0.133 and 1.26 at 293°K. The weighted *R*-factors were 0.063 at 193°K and 0.095 at 293°K. The final positional parameters are given in Table II.

Discussion

At 193°K, where the low vapor pressure prevented recrystallization, very good agreement was obtained between the observed and calculated pattern profiles shown in Fig. 1(a), the value of $R = \sum_i (|I_{o_i} - I_{c_i}|)/\sum I_{o_i}$ being 0.081. The good fit indicated that systematic errors due to sublimation were not a serious problem at 193°K. For this reason, the 193°K results are considered more reliable than the 293°K results.

At 193°K, the UF_6 octahedron is only slightly distorted (Table IV). The scatter of the measured F–F edge lengths of the octahedron about the weighted mean value, 2.80 Å, is small and comparable with the calculated errors. This F–F separation is slightly greater than the ionic F^- diameter, 2.70 Å. The small variations in the F–F edges are due to the fact that the UF_6 octahedra are discrete, not sharing edges or faces with nearby octahedra. Similarly, the F–U–F angles are close to the mean value 90°, and the F–U–F diameters are close to 180°. The U–F(2) distance, 2.03 (2) Å, appears slightly longer than the U–F(1) (1.95 (1) Å) and U–F(3) (1.97 (1) Å) and U–F(4) (1.98 (2) Å) distances; an explanation of why this may occur was given in terms of U–U repulsions in the previous neutron study (*2*). The differences, however, are small and comparable with the experimental errors. The U–F distances are slightly smaller than the sum of the ionic radii, 2.08 Å. The F–F approaches external to an octahedron are larger than those within an octahedron by about 0.3 Å because of the clustering of the fluorine atoms around the uranium atoms, with a resultant expansion around the vacant octahedral holes.

TABLE III

DEVIATIONS $|\Delta|$ OF THE POSITIONAL PARAMETERS IN UF_6 FROM THE IDEALIZED POSITIONS OF HOARD AND STROUPE (*1*) FOR A PERFECTLY HEXAGONAL CLOSE-PACKED STRUCTURE

		$10^3|\Delta|$ (Å)	
Atom	Parameter	293°K	193°K
U	x	40 (10)	29 (6)
	z	16 (15)	17 (8)
F(1)	x	158 (16)	116 (9)
	z	182 (16)	122 (8)
F(2)	x	1 (22)	12 (11)
	z	324 (26)	104 (21)
F(3)	x	185 (13)	159 (7)
	y	24 (10)	71 (7)
	z	104 (11)	74 (6)
F(4)	x	53 (14)	47 (7)
	y	167 (28)	126 (21)
	z	153 (29)	18 (25)

TABLE IV

INTERATOMIC DISTANCES AND ANGLES IN UF_6 AT 293°K AND 193°K[a]

	293°K	193°K
U–F distances within octahedron		
Distance		
U–F(1)	1.90 (2)	1.95 (1)
U–F(2)	1.86 (3)	2.03 (2)
U–F(3) (2*x*)	1.99 (2)	1.97 (1)
U–F(4) (2*x*)	1.89 (2)	1.98 (2)
(Weighted) mean U–F	1.92	1.98
F(3)–F(3)	2.94 (2)	2.84 (2)
F(2)–F(3) (2*x*)	2.80 (2)	2.82 (2)
F(1)–F(3) (2*x*)	2.74 (2)	2.78 (1)
F(3)–F(4) (2*x*)	2.69 (2)	2.80 (2)
F(4)–F(4)	2.66 (6)	2.73 (4)
F(2)–F(4) (2*x*)	2.50 (2)	2.85 (2)
F(1)–F(4) (2*x*)	2.76 (3)	2.77 (2)
(Weighted) mean F–F	2.72	2.80
Angle		
F(3)–U–F(4) (2*x*)	87.6 (8)	90.4 (6)
F(3)–U–F(1) (2*x*)	89.5 (7)	90.3 (4)
F(3)–U–F(2) (2*x*)	93.1 (9)	89.8 (5)
F(3)–U–F(3)	95.1 (8)	92.2 (6)
F(4)–U–F(4)	89.5 (18)	86.9 (14)
F(4)–U–F(1) (2*x*)	93.6 (10)	89.4 (7)
F(4)–U–F(2) (2*x*)	83.7 (9)	90.5 (7)
(Weighted) mean F–U–F	90.0	90.0
F(2)–U–F(1)	176.2 (15)	179.8 (10)
F(4)–U–F(3) (2*x*)	175.9 (9)	177.3 (9)
Intralayer contact		
F(1)–F(3)	3.24 (2)	3.17 (1)
F(1)–F(3)	3.03 (1)	3.05 (1)
F(3)–F(3)	2.87 (2)	2.95 (1)
F(3)–F(3)	3.22 (2)	3.20 (1)
F(2)–F(4)	3.18 (2)	3.10 (2)
F(2)–F(4)	3.35 (5)	3.00 (4)
F(4)–F(4)	3.17 (3)	3.11 (2)
Mean	3.15	3.08
Interlayer contact		
F(4)–F(3)	3.24 (2)	3.17 (1)
F(4)–F(1)	3.23 (3)	3.11 (2)
F(4)–F(3)	3.20 (3)	3.23 (2)
F(4)–F(3)	3.10 (2)	3.03 (1)
F(3)–F(2)	3.08 (2)	3.07 (1)
F(2)–F(1)	3.24 (3)	3.10 (2)
F(2)–F(1)	3.22 (3)	3.04 (2)
Mean	3.19	3.11
U–U distances		
In mirror planes	5.267 (10)	5.227 (5)
	5.198 (5)	5.173 (6)
	6.032 (17)	5.988 (9)
Between mirror planes	5.706 (8)	5.688 (5)
	5.224 (11)	5.188 (6)
	6.758 (21)	6.719 (12)

[a] The F–F contacts are listed in the same order as in (*1*), where they may be identified in a diagram of the structure.

The structure may be viewed, perhaps preferably, not as a hexagonal close-packed array of fluoride ions with an orthorhombic arrangement of uranium ions in octahedral holes, but as an assemblage of UF_6 molecules, with the intermolecular F–F distances as van der Waals contacts. The results show that the orthorhombic structure persists down to 193°K.

At 293°K, the fit between observed and calculated profiles is not as good as at 193°K [Fig. 1(b)]. The standard deviations at 293°K are about twice those at 193°K. This is probably due to the preferred orientation resulting from sublimation and recrystallization. As mentioned above the room-temperature pattern was collected mainly to see whether the tenfold increase in intensity would lead to an improvement on the earlier results.

The results of the present study at 293°K compare favorably with the previous study at 294°K (*2*), while the e.s.d. of the present 293°K results are about half those found previously. However, preferred orientation effects may still be significant in the present 293°K data.

On cooling, the positional parameters appear to approach the ideal values, as the intermolecular distances contract (Tables II and III). Table III gives the deviations, in Å, of the atomic positions from the ideal parameters. The coordinates become more ideal as the F–F contacts within and without the octahedra tend to equalize with cooling, as seen in Table IV. The intra and interlayer contacts appear to decrease on cooling. These trends tend to be obscured by the lower reliability of the 293°K data. Although it appeared that in the reinvestigation of the structure of UF_6 at room temperature the preferred orientation errors were still significant, the main purpose of the work was achieved, i.e., a reliable parameter determination for UF_6 by the neutron diffraction profile method at lower temperatures, where crystal sublimation was greatly minimized.

Acknowledgment

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