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Reinvestigation of the crystal structure of UF_6 by single-crystal X-ray diffraction

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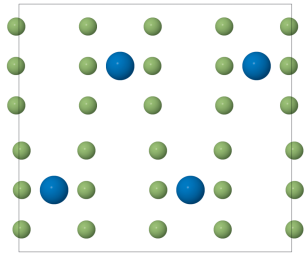
Single-crystals of hexafluoridouranium(VI), UF_6, were obtained by sublimation. A re-refinement of the crystal structure using low-temperature (100 K) single-crystal X-ray data was carried out considering all U^{ij} terms of the displacement parameters of the U and F atoms, leading overall to a significantly improved structural model. UF_6 crystallizes in the orthorhombic space group *Pnma* with the F atoms forming a double hexagonal closest packing of *ABAC* stacking with U atoms in one-sixth of the voids. The UF_6 molecules deviate only slightly from octahedral point-group symmetry.

3D view



Structure description

Uranium hexafluoride is likely the most important material in the nuclear energy sector for isotope enrichment of the fissile isotope ^{235}U. UF_6 was probably first synthesized by Henri Moissan (1900) by reacting fluorine gas with uranium metal. However, at that time he was unable to further characterize the resulting white smoke. Later, Otto Ruff and coworkers succeeded in obtaining UF_6 and describing its properties (Ruff, 1909; Ruff & Heinzelmann, 1911). Ruff reported shiny, colorless, crystals with monoclinic symmetry without giving further details (Ruff, 1909). Reports on the crystal structure of UF_6 appeared well after the Manhattan Project. The first one, a single-crystal X-ray diffraction study of a crystal mounted in a glass capillary (Hoard & Stroupe, 1958) led to lattice parameters a = 9.900 (2), b = 8.962 (2), c = 5.207 (2) Å, V = 462.0 Å^3 at T = 298 K in space group *Pnma* (no R values reported). In 1973, the space group and structure model were confirmed by powder neutron diffraction at 294 K using the previously reported lattice parameters (Taylor *et al.*, 1973) without giving R values. In 1975, another structural study of UF_6 at 193 and 293 K by powder neutron diffraction was carried out (Taylor & Wilson, 1975), confirming that it has orthorhombic symmetry at both temperatures [a = 9.843 (11), b = 8.920 (10), c = 5.173 (6) Å, V = 454.2 (8) Å^3 at T = 193 K, $R = \Sigma(|I_o - I_c|)/\Sigma I_o$ = 0.081; a = 9.924 (10), b = 8.954 (9), c = 5.198 (5) Å, V = 461.9 (8) Å^3 at T = 293 K,

Table 1
Selected geometric parameters (Å, °).

U1—F1	1.983 (4)	U1—F3^{i}	1.984 (3)
U1—F2	1.982 (4)	U1—F4	1.975 (3)
U1—F3	1.984 (3)	U1—F4^{i}	1.975 (3)
F1—U1—F3	90.12 (11)	F4^{i}—U1—F2	89.92 (11)
F2—U1—F1	179.95 (14)	F4—U1—F2	89.92 (11)
F2—U1—F3	89.91 (11)	F4—U1—F3	90.20 (13)
F4^{i}—U1—F1	90.05 (11)	F4—U1—F3^{i}	179.56 (11)

Symmetry code: (i) $x, -y+\frac{1}{2}, z$.

$R = \Sigma(|I_o - I_c|)/\Sigma I_o = 0.133$]. Levy *et al.* (1976) reported a single-crystal neutron diffraction study at 293 K with a = 9.92 (5), b = 8.97 (5), c = 5.22 (3) Å (V not reported), and gave an R value of 0.041. The latest report refers to a powder neutron diffraction study at 77 K, which led to lattice parameters a = 9.654 (3), b = 8.776 (4), c = 5.084 (3) Å, V = 430.7 (3) Å^3 and an $R = \Sigma(|y_o - y_c|)/\Sigma y_o$ value (y_o and y_c are the background-corrected pattern intensities) of 0.069 (Levy *et al.*, 1983).

As all of these structure refinements, with the exception of the single-crystal neutron diffraction study by Levy *et al.* (1976), used isotropic displacement parameters for all atoms, we reinvestigated the crystal structure of UF_6 based on single-crystal X-ray diffraction data at 100 K. Refinement of all U^{ij} terms of the displacement parameters of the U and the four F atoms allowed for a more precise structural model.

The U atom (multiplicity 4, Wyckoff letter *c*, site symmetry *.m.*) is surrounded by six F atoms (F1 to F4) in a slightly distorted octahedral arrangement (Fig. 1, Table 1). The F1 and the F2 atoms likewise reside on a mirror plane (4 *c*, *.m.*), while the F3 and F4 atoms occupy a general position (8 *d*, 1). In the previous studies, the U—F bond lengths were reported to range from 1.88 (2) to 2.28 (4) Å with F—U—F angles from 88.0 (17) to 92.9 (17)° (Taylor *et al.*, 1973), from 1.95 (1) to 2.03 (2) Å at 193 K with angles from 86.4 (7) to 92.2 (6)°, from 1.86 (3) to 1.99 (2) Å with angles from 83.7 (9) to 95.1 (8)° (Taylor & Wilson, 1975), from 1.992 (3) to 2.004 (4) Å with angles from 89.42 (17) to 90.20 (11)° (Levy *et al.*, 1976), and as mean bond lengths of 2.023 (6) Å (77 K), 1.983 (6) Å (193 K), and 1.995 (2) Å (293 K) without reporting the bond angles (Levy *et al.*, 1983). It is interesting to note that the longest bond lengths were observed at the lowest temperature, underlining the need for a redetermination of the crystal structure. The U—F bond lengths determined in the present work are much more uniform, and the F—U—F bond angles are closer to the ideal values of 90 and 180° than determined in previous studies (Table 1). The deviations of the UF_6 molecule from O_h symmetry are thus small; its crystallographically imposed point symmetry is C_s (*m*).

The unit-cell parameters determined in this study (Table 2) are in good agreement with those given above, especially with those determined at 77 K (Levy *et al.*, 1983) which are a little smaller, as expected.

In the crystal structure, a single UF_6 molecule is surrounded by twelve others in the shape of a distorted anticuboctahedron if U···U distances from 5.0854 (4) to 5.1402 (4) Å are considered. Thus, the U atoms adopt a distorted arrangement similar to the Mg atoms in the Mg structure type. In a more detailed description, the U atoms occupy one-sixth of the octahedral voids of hexagonally close-packed layers of F atoms. The layers are parallel to the *bc* plane, with a stacking sequence along the *a*-axis direction of *ABAC*, representing a double hexagonal packing, *hc*. The close-packing of F atoms is only slightly distorted, as evidenced by the F···F distances. Those within a UF_6 molecule range from 2.791 (6) to 2.808 (4) Å, while the intermolecular distances are only slightly larger in the range from 2.900 (6) to 3.119 (6) Å. The crystal structure of UF_6 is shown in Fig. 2.

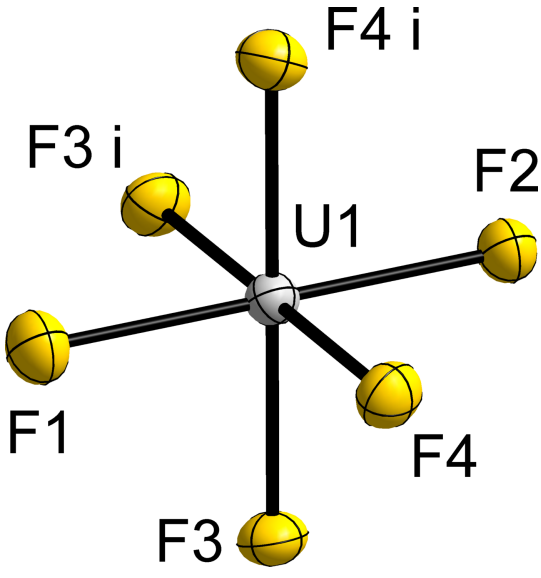


Figure 1
UF_6 molecule in the solid state. Atoms are shown with anisotropic displacement ellipsoids at the 70% probability level; the symmetry code refers to Table 1.

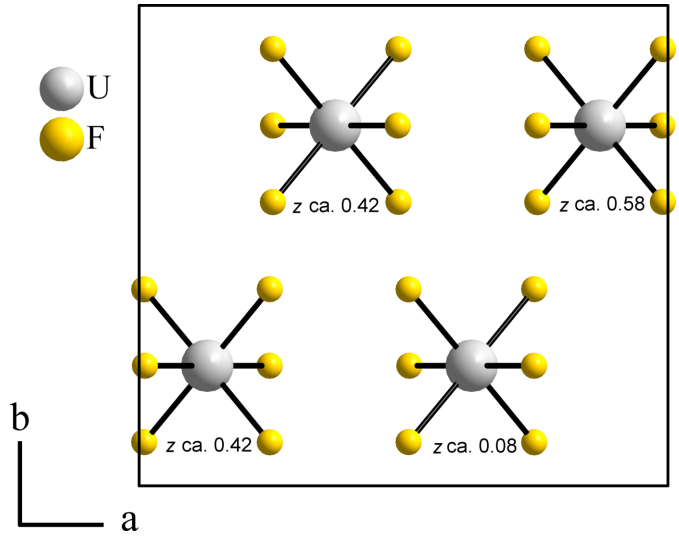


Figure 2
Crystal structure of UF_6 viewed along the *c* axis. Atoms are drawn as spheres with arbitrary radii. The *z* coordinates of the U atoms are indicated.

Synthesis and crystallization

UF_6 of natural isotope ratio was synthesized according to a literature procedure (Chemnitz *et al.*, 2021), and single crystals were obtained by slow sublimation at room temperature.

Refinement

Details of the data collection and structure refinement are given in Table 2.

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Table 2
Experimental details.

Crystal data	
Chemical formula	UF_6
M_r	352.02
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	100
a, b, c (Å)	9.6612 (8), 8.7786 (7), 5.0854 (4)
V (Å^3)	431.30 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	37.66
Crystal size (mm)	0.3 × 0.2 × 0.1
Data collection	
Diffractometer	Stoe *IPDS* II
Absorption correction	Multi-scan (*LANA*; Koziskova *et al.*, 2016)
T_{min}, T_{max}	0.0002, 0.001
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6472, 784, 681
R_{int}	0.042
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.743
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.054, 1.03
No. of reflections	784
No. of parameters	38
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.37, −1.68

Computer programs: *X-AREA* (Folkers-Karlsson *et al.*, 2026), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2022), *publCIF* (Westrip, 2010) and *OLEX2* (Dolomanov *et al.*, 2009).

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full crystallographic data

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Hexafluoridouranium(VI)

Crystal data

UF_6
M_r = 352.02
Orthorhombic, *Pnma*
a = 9.6612 (8) Å
b = 8.7786 (7) Å
c = 5.0854 (4) Å
V = 431.30 (6) Å^3
Z = 4
F(000) = 584
D_x = 5.421 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9312 reflections
θ = 4.0–32.3°
μ = 37.66 mm^{-1}
T = 100 K
Plate, clear colourless
0.3 × 0.2 × 0.1 mm

Data collection

Stoe IPDS II diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus, X-ray tube
Planar graphite monochromator
Detector resolution: 6.67 pixels mm^{-1}
rotation method, ω scans
Absorption correction: multi-scan (*LANA*; Koziskova *et al.*, 2016)
T_{min} = 0.0002, T_{max} = 0.001
6472 measured reflections
784 independent reflections
681 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 31.9°, θ_{min} = 4.2°
h = −14→13
k = −13→13
l = −7→7

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.054
S = 1.03
784 reflections
38 parameters
0 restraints
Primary atom site location: dual
$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.37 e Å^{-3}
$\Delta\rho_{min}$ = −1.68 e Å^{-3}
Extinction correction: SHELXL-2019/2 (Sheldrick, 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0038 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
U1	0.12887 (2)	0.250000	0.42275 (4)	0.01189 (11)
F1	0.0110 (4)	0.250000	0.7420 (8)	0.0199 (9)
F2	0.2469 (4)	0.250000	0.1039 (7)	0.0167 (8)
F3	0.0096 (2)	0.0910 (3)	0.2627 (6)	0.0174 (5)
F4	0.2471 (3)	0.0906 (4)	0.5800 (5)	0.0180 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.01144 (14)	0.01073 (13)	0.01350 (14)	0.000	−0.00002 (8)	0.000
F1	0.0201 (17)	0.022 (2)	0.018 (2)	0.000	0.0037 (16)	0.000
F2	0.0174 (16)	0.016 (2)	0.0164 (18)	0.000	0.0033 (14)	0.000
F3	0.0180 (11)	0.0131 (14)	0.0212 (13)	−0.0024 (11)	−0.0012 (11)	−0.0027 (11)
F4	0.0177 (11)	0.0158 (15)	0.0206 (14)	0.0025 (11)	−0.0004 (10)	−0.0010 (12)

Geometric parameters (Å, º)

U1—U1^{i}	5.1402 (4)	U1—F3	1.984 (3)
U1—U1^{ii}	5.1072 (4)	U1—F3^{iv}	1.984 (3)
U1—U1^{iii}	5.0854 (4)	U1—F4	1.975 (3)
U1—F1	1.983 (4)	U1—F4^{iv}	1.975 (3)
U1—F2	1.982 (4)		
F1—U1—F3^{iv}	90.12 (11)	F4^{iv}—U1—F2	89.92 (11)
F1—U1—F3	90.12 (11)	F4—U1—F2	89.92 (11)
F2—U1—F1	179.95 (14)	F4—U1—F3	90.20 (13)
F2—U1—F3	89.91 (11)	F4^{iv}—U1—F3^{iv}	90.20 (13)
F2—U1—F3^{iv}	89.91 (11)	F4^{iv}—U1—F3	179.56 (11)
F3^{iv}—U1—F3	89.39 (17)	F4—U1—F3^{iv}	179.56 (11)
F4^{iv}—U1—F1	90.05 (11)	F4^{iv}—U1—F4	90.21 (18)
F4—U1—F1	90.05 (11)		

Symmetry codes: (i) *x*−1/2, −*y*+1/2, −*z*+1/2; (ii) −*x*, *y*+1/2, −*z*+1; (iii) *x*, *y*, *z*+1; (iv) *x*, −*y*+1/2, *z*.