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## UF4 and the High-Pressure Polymorph HP-UF4

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**Abstract:** A laboratory-scale synthesis of UF<sub>4</sub> is presented that utilizes the reduction of UF<sub>6</sub> with sulfur in anhydrous hydrogen fluoride. An excess of sulfur can be removed by vacuum sublimation, yielding pure UF<sub>4</sub>, as shown by powder X-ray diffraction, micro X-ray fluorescence analysis, infrared and Raman spectroscopy, as well as magnetic measurements. Furthermore, a single-crystalline, high-pressure modification of UF<sub>4</sub> was obtained in a multi-anvil press at elevated temperatures. The high-pressure polymorph HP-UF<sub>4</sub> was characterized by means of single-crystal and powder X-ray diffraction, as well as by magnetic measurements, and presents a novel crystal structure type. Quantum-chemical calculations show the HP-modification to be 10 kJ/mol per formula unit higher in energy compared to UF<sub>4</sub>.

#### Introduction

The first synthesis of uranium tetrafluoride was likely published in 1861, starting from  $U_3O_8$  and hydrofluoric acid, yielding UF<sub>4</sub> and  $UO_2F_2$  (Equation 1).<sup>[1]</sup>

$$U_3O_8 + 8 HF \longrightarrow UF_4 + 2 UO_2F_2 + 4 H_2O$$
 (1)

Since the Manhattan Project, uranium tetrafluoride has been a key intermediate in the enrichment of the <sup>235</sup>U isotope, which is used for the production of nuclear weapons and fuels.<sup>[2–5]</sup> UF<sub>4</sub> is commonly referred to as "green salt", which is converted by various fluorination agents to volatile UF<sub>6</sub> for the enrichment process. The <sup>235</sup>U isotope is then enriched, for example, by gas centrifugation, reconverted to UF<sub>4</sub> and usually further processed to UO<sub>2</sub>, which is a common nuclear fuel.<sup>[3]</sup> Uranium tetrafluoride can be reduced with Ca or Mg for the production of uranium metal.<sup>[4–6]</sup> Enriched uranium metal, or its alloys with aluminum, are also used as targets for the production of <sup>99</sup>Mo, which decays to the valuable <sup>99m</sup>Tc isotope, which is used in medical diagnostics.<sup>[7]</sup>

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Furthermore, enriched UF<sub>4</sub> can be used in Generation IV reactors, most notably in Molten Salt Reactors (MSR) or in the advanced Molten Salt Fast Reactors (MSFR).<sup>[8,9]</sup>

Various methods for the synthesis and technical production of UF<sub>4</sub> have been reported and extensively reviewed.<sup>[3,4,10]</sup> Thus, only a short overview will be given here. In principle, there are two main approaches for the synthesis of UF<sub>4</sub>, a wet and a dry chemical process. The first is based on the reduction of a uranyl(VI) salt in aqueous medium to U(IV), followed by the precipitation of uranium tetrafluoride hydrates upon addition of hydrofluoric acid. Suitable reducing agents are for example tin(II) chloride, sodium dithionite, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, or sulfur dioxide in the presence of Cu<sup>2+</sup> ions.<sup>[10–12]</sup> To obtain neat UF<sub>4</sub>, the UF<sub>4</sub> hydrates have to be dried either in vacuo or in a stream of hydrogen fluoride at temperatures of up to 500 °C. So, due to hydrolysis (by the H<sub>2</sub>O molecules of crystallization), usually UO<sub>2</sub> is obtained as a side product that cannot be easily separated from UF<sub>4</sub>.<sup>[3,10]</sup>

The most important process for the production of  $UF_4$  is probably the dry-chemical hydrofluorination of  $UO_2$  (Equation 2).<sup>[3,6]</sup>

$$JO_2 + 4 HF \longrightarrow UF_4 + 2 H_2O$$
 (2)

The reaction is carried out at temperatures between 250 and 600 °C and water released during the reaction is constantly removed to prevent the hydrolysis of UF<sub>4</sub>. The obtained UF<sub>4</sub> usually contains a small percentage of UO<sub>2</sub> and UO<sub>2</sub>F<sub>2</sub>, the latter due to UO<sub>3</sub> impurities in the starting material (Equation 3).<sup>[3]</sup> By adding a few percent of H<sub>2</sub> to the gas stream, U(VI) as well as oxidic impurities can be significantly reduced.

$$UO_3 + 2 HF \longrightarrow UO_2F_2 + H_2O$$
 (3)

The synthesis of UF<sub>4</sub> is also possible through the reduction of UF<sub>6</sub>, which, however, has been of little technical interest.<sup>[3,13]</sup> Suitable reducing agents are for example, H<sub>2</sub>, HCI, HBr, N<sub>2</sub>H<sub>4</sub>, and NH<sub>3</sub>. On a small scale H<sub>2</sub> has been used in a technical process for the reduction of depleted UF<sub>6</sub> to UF<sub>4</sub> and HF. The UF<sub>4</sub> is then further reacted with oxides like B<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> producing valuable BF<sub>3</sub> or SiF<sub>4</sub> and uranium oxides (Equation 4).<sup>[13]</sup>

$$3 UF_4 + 2 B_2O_3 \longrightarrow 3 UO_2 + 4 BF_3$$
 (4)

Based on a report from 1911 on the reaction of pure UF<sub>6</sub> with sulfur, yielding US<sub>2</sub>, UF<sub>4</sub> and possibly SF<sub>4</sub>, we investigated the reduction of UF<sub>6</sub> with sulfur in anhydrous HF (aHF), which yields UF<sub>4</sub>.<sup>[14]</sup> The obtained UF<sub>4</sub> was further reacted in a multi-anvil press under high temperature and pressure to obtain a single-crystalline high-pressure modification of UF<sub>4</sub>.

#### **Results and Discussion**

The reaction of UF<sub>6</sub> with an excess amount of S<sub>8</sub> in aHF proceeds quickly at the melting point of aHF (-83.37 °C). Initially, a bluish supernatant HF solution is formed, indicating the presence of the  $[UF_6]^-$  ion.<sup>[15]</sup> After a few minutes of reaction time at room temperature, a brown supernatant HF solution is obtained that is accompanied by the precipitation of a grayish solid, which indicates the formation of mixed uranium(IV/V) fluorides, such as  $U_2F_9$  and  $U_4F_{17}$  (see Figure S1).<sup>[3]</sup> After two to three days of reaction time at room temperature, a green solid and a colorless supernatant HF solution results.

The fluorination process of sulfur in this reaction is probably quite complex, with the possible intermediate formation of sulfur difluoride, SF<sub>2</sub>, thio-thionyl fluoride, SSF<sub>2</sub>, and disulfur difluoride, S<sub>2</sub>F<sub>2</sub>.<sup>[16,17]</sup> These low valent sulfur fluorides are either unstable towards disproportionation in the presence of aHF or unstable at room temperature (S<sub>2</sub>F<sub>2</sub>).<sup>[16,17]</sup> Uranium hexafluoride is also known to oxidize H<sub>2</sub>S at 25 °C in the gas phase or when liquid H<sub>2</sub>S is used both as a solvent and reactant.<sup>[18]</sup> In both cases UF<sub>4</sub>. SF<sub>4</sub>, and HF are formed. Besides that, it has been reported that no reaction between UF<sub>6</sub> and SF<sub>4</sub> takes place at temperatures up to 300 °C.<sup>[19]</sup> At a temperature of 500 °C the formation of SF<sub>6</sub> has been observed. In comparison to that it has been shown that PuFe reacts with SF<sub>4</sub> at 30 °C.<sup>[19]</sup> Furthermore, the reaction between gaseous UF<sub>6</sub> and sulfur was reported to be slow up to at least 130 °C, with SF<sub>4</sub> being the fluorination product.<sup>[20]</sup> This reaction could be accelerated by increasing the pressure with N<sub>2</sub>, but in both cases several heating cycles had to be performed to obtain quantitative yields. It is likely from the afore-mentioned reactions that SF<sub>4</sub> is the main product of the reaction between S<sub>8</sub> and UF<sub>6</sub> in the presence of aHF. The overall reaction can then be described by Equation 5.

$$2 \text{ UF}_6 + 1/8 \text{ S}_8 \longrightarrow 2 \text{ UF}_4 + 1/8 \text{ SF}_4$$
 (5)

The removal of HF and other volatiles from the reaction mixture using vacuum distillation yields sulfur-containing UF<sub>4</sub>, due to the excess of sulfur used. The remaining sulfur was removed in vacuo at 350 °C. The phase purity of the UF<sub>4</sub> was checked by a Rietveld refinement of a powder X-ray diffraction (PXRD) pattern recorded at 293 K (see Figure 1 and Table S1). The following lattice parameters were refined: a = 12.815(1) Å, b = 10.806(1) Å, c = 8.3804(2) Å,  $\beta = 126.26(1)^{\circ}$ , V = 935.71(3) Å<sup>3</sup>, C2/c (no. 15), mS60,  $\beta$ -ZrF<sub>4</sub> structure type.<sup>[21]</sup> The determined values are in good agreement with so far reported data, see Table 1. Based on X-ray diffraction, UF<sub>4</sub> was obtained as a phase-pure product.

Table 1. Reported lattice parameters of ZrF<sub>4</sub>-type UF<sub>4</sub>. RT stands for room temperature.

Radiation type	т/к	a/Å	b/Å	c/Å	β/°	Reference
Neutron	300	12.7941(2)	10.7901(2)	8.3687(2)	126.25(2)	[22]
X-ray	RT	12.79(6)	10.72(5)	8.39(5)	126.2(5)	[23]
X-ray	RT	12.73(1)	10.753(7)	8.404(8)	126.33(5)	[24]
X-ray	RT	12.760(4)	10.768(2)	8.399(2)	126.32(2)	[25]
X-ray	RT	12.801(1)	10.799(1)	8.374(1)	126.30(1)	[26]
X-ray	293	12.815(1)	10.806(1)	8.3804(2)	126.26(1)	this work



**Figure 1**. Observed and calculated powder X-ray diffraction patterns of ZrF<sub>4</sub>-type UF<sub>4</sub> after Rietveld refinement.<sup>[21]</sup> The observed pattern is shown in blue, the calculated one in red. The calculated reflection positions are indicated by the vertical bars below the patterns. The curve at the bottom represents the difference between the observed and calculated intensity. Profile *R*-factors:  $R_p = 3.15\%$ ,  $wR_p = 4.51\%$ , GOF = 2.13. Further details on the structure determination are available from the Supporting Information.

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We attempted the detection of a potential sulfur content of our powder samples by micro X-ray fluorescence analysis ( $\mu$ XRF). No sulfur-containing impurities (like S<sub>8</sub> or US<sub>2</sub>) were detected in the sample after the sublimation. Furthermore, infrared and Raman spectra were recorded (see Figure S2 and Figure S3). In the measured IR spectrum, a weak band at 612 cm<sup>-1</sup> and a partly resolved broad band with a maximum at approximately 430 cm<sup>-1</sup> can be seen, which are in agreement with previous reports on UF<sub>4</sub>.<sup>[27,28]</sup> Possible oxygen-containing species like UO<sub>2</sub>, UO<sub>3</sub>, and UO<sub>2</sub>F<sub>2</sub> show bands at 450, 700-950, and 1020 cm<sup>-1</sup>, respectively.<sup>[3,29]</sup> Such bands are absent.

The Raman spectra of UF<sub>4</sub> obtained at different excitation wavelengths show bands at 473, 219, and 151 cm<sup>-1</sup>. The intensities of these bands are relatively low and UF<sub>4</sub> seems to be a very weak Raman scatterer.<sup>[28,30,31]</sup> In the Raman spectra, no bands attributable to sulfur species, such as S<sub>8</sub>, which is a strong Raman scatterer, could be observed.<sup>[32]</sup> Furthermore, no bands attributable to oxygen-containing species like UO<sub>2</sub>, UO<sub>3</sub>, and UO<sub>2</sub>F<sub>2</sub> could be observed in the Raman spectra.<sup>[3,33,34]</sup>

We were furthermore interested in obtaining a crystalline, highpressure modification of UF<sub>4</sub> since it had only been scarcely studied under high-pressure conditions.<sup>[30,35,36]</sup> The only reported crystal structure for ambient-pressure UF<sub>4</sub> to date is that of the  $\beta$ -ZrF<sub>4</sub> type, which is a structure type observed for several transition metals, as well as for some lanthanoid and actinoid tetrafluorides  $MF_4$  (M = Hf, Ce, Tb, Th, Pa, Np, Pu, Am, Cm, Bk).<sup>[22,23,37-41]</sup> In this structure type, each metal cation is coordinated by eight F atoms in a square-antiprismatic shape. The ZrF<sub>8</sub> coordination polyhedra share corners, which results in a 3D network that can be described with the Niggli formula  ${}^{3}_{\omega}[ZrF_{8/2}]$ . In contrast to UF<sub>4</sub>, there are several reports of crystallographic studies on high-temperature and high-pressure modifications of single-crystalline  $ZrF_4$ . The high-temperature modification  $\alpha$ -ZrF<sub>4</sub> has been obtained by sublimation of  $\beta$ -ZrF<sub>4</sub> under an argon atmosphere with a temperature gradient of 1020 K  $\rightarrow$  580 K.<sup>[42]</sup> It crystallizes in space group  $P4_2/m$  (no. 84), tP40, with a =7.896(1) Å, c = 7.724(1) Å, V = 481.6 Å<sup>3</sup>, Z = 8 (T = notreported).<sup>[42]</sup> Each Zr atom is coordinated by eight fluorine atoms, forming a polyhedron of square-antiprismatic shape. The ZrF<sub>8</sub> polyhedra share corners and edges, resulting in a 3D framework, which can be described with the Niggli formula  ${}^{3}_{*}[ZrF_{8/2}]$ . The high-pressure modification y-ZrF4 has been obtained by heating  $\beta$ -ZrF<sub>4</sub> at temperatures of 1173 to 1273 K under pressures of 4 to 8 GPa.<sup>[43,44]</sup> It crystallizes in the space group  $P2_1/c$  (no. 14), mP20, with a = 5.554(2) Å, b = 5.639(2) Å, c = 7.973(3) Å,  $\beta = 105.98(5)^{\circ}$ , V = 240.1 Å, Z = 4 (T = not reported).<sup>[43,44]</sup> The Zr atom has a similar coordination environment to  $\alpha$ -ZrF<sub>4</sub>, with edge and corner sharing  $ZrF_8$  square-antiprisms,  $\frac{3}{2}[ZrF_{8/2}]$ .

Up to now, only a few high-pressure studies on UF<sub>4</sub> have been published. It is reported that a hexagonal modification of UF<sub>4</sub> has been obtained by shock compression. Based on powder X-ray diffraction data recorded on a film, the authors assigned this modification to the Cu<sub>3</sub>P type structure (*hP*26, *P*6<sub>3</sub>*mc*) with *a* = 7.05 Å and *c* = 7.27 Å, and a site occupation factor of <sup>3</sup>/<sub>4</sub> for the uranium position. We note that this modification would be isotypic to UF<sub>3</sub> and the given composition UF<sub>4</sub> is only generated by an under-occupancy of U.<sup>[35,45]</sup> A cubic modification of UF<sub>4</sub> with *a* = 6.34(5) Å and *V* = 254.8 Å<sup>3</sup> (*T* = not reported) has been obtained by explosive compression, utilizing RDX (hexogen) as an explosive under conditions of 16 to 50 GPa and 400 to 1600 °C.<sup>[36]</sup> However, no further structural data were reported. Furthermore, a Raman spectroscopic study was conducted on UF<sub>4</sub> at a pressure of 4.7 GPa, assigning a phase transition at 2.2 GPa. The phase transition was observed by powder X-ray diffraction.<sup>[30]</sup>



Figure 2. Crystal structure of HP-UF4. Displacement ellipsoids are shown at the 90% probability level at 183 K.

Green HP-UF<sub>4</sub> single-crystals, with essentially the same color as regular UF<sub>4</sub>, were obtained in this study under a pressure of 9.5 GPa and a temperature of 600 °C in a multi-anvil press. HP-UF<sub>4</sub> is metastable at room temperature and all characterizations have been carried out under ambient pressure. This high-pressure modification of UF<sub>4</sub>, called HP-UF<sub>4</sub>, crystallizes in the monoclinic space group  $P_{2_1/m}$  (no. 11) with four formula units per unit cell, *mP*20. To the best of our knowledge, HP-UF<sub>4</sub> is a new structure type. See Table 2 for crystallographic details. The crystal structure of HP-UF<sub>4</sub> is shown in Figure 2.

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Table 2.	Selected	crystallographic	data	and	details	of	the
single-crys	stal structu	re determination	of HF	P-UF₄	•		

	HP-UF₄
Empiric formula	UF4
Color and appearance	green plate
Crystal size / mm <sup>3</sup>	$0.02\times0.03\times0.03$
Molar mass / g⋅mol <sup>-1</sup>	314.02
Crystal system	monoclinic
Space group (No.)	<i>P</i> 2 <sub>1</sub> / <i>m</i> (no. 11)
a/Å	4.6015(2)
b/Å	6.9786(3)
c/Å	7.6271(3)
β/°	101.013(2)
V/Å <sup>3</sup>	240.41(2)
Ζ	4
$ ho_{calcd.}$ / g·cm <sup>-3</sup>	8.676
λ/Å	0.71073 (Mo- <i>K</i> α)
T/K	183
$\mu$ / mm <sup>-1</sup>	67.395
$\theta_{max}$	39.47
Range of Miller indices	$-8 \le h \le 8$
	-12 ≤ <i>k</i> ≤ 12
	−13 ≤ <i>l</i> ≤ 13
$R_{\rm int}, R_{\sigma}$	0.037, 0.015
$R(F)$ ( $I \ge 2\sigma(I)$ , all data)	0.015, 0.019
$wR(F^2)$ ( $I \ge 2\sigma(I)$ , all data)	0.028, 0.029
S (all data)	1.16
Data, parameter, restraints	1530, 53, 0
$\Delta \rho_{max}, \Delta \rho_{min} / e \cdot Å^{-3}$	2.83, -2.12

There are two symmetry-independent uranium atoms U(1) and U(2) in the structure of HP-UF<sub>4</sub>, both occupy the Wyckoff position 2e (*m*). U(1) is coordinated by eleven fluorine atoms, which form a polyhedron best described as a distorted mono-capped pentagonal antiprism, see Figure 3 and Figure 4. U(2) is coordinated by nine fluorine atoms, forming a polyhedron that can be described as a prismatoid composed of a pentagon and quadrangle in parallel orientation. The coordination spheres of the uranium atoms can also be described by the Niggli formulas  ${}^{3}_{4}[UF_{6/3}F_{5/2}]^{1/2-}$  for U(1) and  ${}^{3}_{4}[UF_{6/3}F_{3/2}]^{1/2+}$  for U(2), respectively. Atom coordinates and the isotropic displacement parameters are available from Table 3, anisotropic displacement parameters from Table S2. Selected atomic distances, *d*, and angles,  $\angle$ , are given in Table 4.

**Table 3.** Atomic coordinates and equivalent isotropic displacement parameters,  $U_{iso}$ , for HP-UF<sub>4</sub> at 183 K.

	1				
Atom	Wyckoff position	x	у	z	U <sub>eq</sub> / Ų
U(1)	2e	0.03554(3)	3/4	0.82749(2)	0.00233(3)
U(2)	2e	0.45712(3	3/4	0.34398(2)	0.00229(3)
F(1)	4 <i>f</i>	0.2048(4)	0.9198(3)	0.0933(2)	0.0064(3)
F(2)	4f	0.2975(4)	0.4259(2)	0.3961(2)	0.0046(3)
F(3)	2e	0.5525(6)	3/4	0.8844(3)	0.0068(4)
F(4)	4 <i>f</i>	0.7764(4)	0.5546(3)	0.2513(2)	0.0068(3)
F(5)	2e	0.1582(5)	3/4	0.5410(3)	0.0056(4)



**Figure 3.** A Section of the crystal structure of HP-UF<sub>4</sub>. Displacement ellipsoids are shown at the 90% probability level at 183 K. Symmetry transformations for the generation of equivalent atoms: F(1): #1 - x, -1/2 + y, 2 - z, #2 x, 3/2 - y, z, #3 - x, 2 - y, 2 - z, #4 x, y, -1 + z; #5 x, 3/2 - y, -1 + z; F(2): #1 1 - x, 1/2 + y, 1 - z, #2 1 - x, 1 - y, 1 - z, #3 x, 3/2 - y, z, #4 - x, 1 - y, 1 - z; #5 - x, 1/2 + y, 1 - z, F(3): #1 - 1 + x, y, z. F(4): #1 x, 3/2 - y, z, #2 1 - x, 1 - y, 1 - z; #3 1 - x, 1/2 + y, 1 - z.

Table 4. Selected interatomic distances d of HP-UF<sub>4</sub>.

	d/Å	Multiplicity
U(1)–F(1)	2.349(2)	2
U(1)-F(1)	2.674(2)	2
U(1)–F(2)	2.401(2)	2
U(1)–F(3)	2.335(3)	1
U(1)-F(3)	2.344(2)	1
U(1)-F(4)	2.414(2)	2
U(1)–F(5)	2.359(2)	1
U(2)–F(1)	2.358(2)	2
U(2)–F(2)	2.420(2)	2
U(2)–F(2)	2.434(2)	2
U(2)–F(4)	2.217(2)	2
U(2)–F(5)	2.222(2)	1

The fluorine atoms F(3), F(4), and F(5) are  $\mu_2$ -bridging between the uranium atoms with U–F distances in the range of 2.217(2) to 2.414(2) Å and U–F–U angles from 155.8(1) to 159.0(2)°. The fluorine atoms F(1) and F(2) are  $\mu_3$ -bridging between both uranium atoms with increased U–F distances of 2.349(2) to 2.674(2) Å and decreased U–F–U angles of 117.2(1) to 123.1(1)°, which may be explained by the different coordination numbers. Such  $\mu_3$ -bridging fluorine atoms are also present in U(IV) containing fluorido complexes like RbUF<sub>5</sub> and RbU<sub>3</sub>F<sub>13</sub>.<sup>[46]</sup> The average U–F distance for U(1) is 2.429 Å and for U(2) 2.342 Å.

For comparison, in the structure of ZrF<sub>4</sub>-type UF<sub>4</sub>, both uranium atoms are coordinated by eight fluorine atoms, forming distorted square antiprisms.<sup>[21]</sup> All fluorine atoms in this modification are  $\mu_2$ bridging between the uranium atoms with distances in the range of 2.230 to 2.354 Å. The average U–F distance for U(1) in ZrF<sub>4</sub>type UF<sub>4</sub> is 2.290 Å and for U(2) it is 2.266 Å. Comparing the average U–F distances of both modifications, those in HP-UF<sub>4</sub> are increased due to the higher coordination numbers, which is generally observed in high-pressure modifications.<sup>[47]</sup>

The overall structure of HP-UF<sub>4</sub> is a 3D network structure in which the UF<sub>9</sub> and UF<sub>11</sub> polyhedra share corners and edges. The UF<sub>9</sub> polyhedra are surrounded by two UF<sub>9</sub> and seven UF<sub>11</sub> polyhedra; the UF<sub>11</sub> polyhedra are surrounded by seven UF<sub>9</sub> and four UF<sub>11</sub> polyhedra. In HP-UF<sub>4</sub> the F···F distances are observed in a range

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from circa 2.37 to 2.89 Å and are thus shorter compared to ZrF<sub>4</sub>type UF<sub>4</sub> (2.56 to 3.08 Å). The nearest U–U distances in HP-UF<sub>4</sub> are in the range of 4.045(1) to 4.602(1) Å, those in ZrF<sub>4</sub>-type UF<sub>4</sub> are between 4.468 and 4.584 Å. The average U–U distances for the nearest U atoms are 4.382 Å for U(1) and 4.284 Å for U(2) in HP-UF<sub>4</sub>, the ones in ZrF<sub>4</sub>-type UF<sub>4</sub> are 4.507 Å for U(1) and 4.504 Å for U(2). These observations are in line with the expectations for a high-pressure structure.



**Figure 4**. Coordination environment of the two symmetry-independent uranium atoms in HP-UF<sub>4</sub>. Left: U(1) with eleven neighboring fluorine atoms; Right: U(2) with nine neighboring fluorine atoms. Uranium atoms are depicted in green and fluorine atoms in yellow. Displacement ellipsoids are shown at the 90% probability level at 183 K.

The U atoms in HP-UF<sub>4</sub> are approximately hexagonal close packed with the hexagonal layers perpendicular to the *b* axis. However, the F atoms do neither occupy octahedral nor tetrahedral voids but reside either on the faces ( $\mu_3$ -F) or on the edges ( $\mu_2$ -F) of these polyhedra.

The phase purity of the HP-UF<sub>4</sub> obtained was checked by powder X-ray diffraction, see Figure 5. No additional reflections resulting from crystalline impurities, such as the ambient pressure modification of  $ZrF_4$ -type UF<sub>4</sub> or Pt from the container material used during the synthesis, were observed. Thus, HP-UF<sub>4</sub> was prepared phase-pure based on powder X-ray diffraction. The following cell parameters were obtained after a Rietveld

refinement fit: a = 4.6080(1) Å, b = 6.9955(1) Å, c = 7.6364(1) Å,  $\beta = 101.07(1)^{\circ}$ , V = 241.58(1) Å<sup>3</sup>, T = 293 K. The lattice parameters obtained at 293 K show a good agreement with the single-crystal data obtained at 183 K, with a slight difference due to the different measurement temperatures and X-ray wavelengths.

The magnetic properties of ZrF<sub>4</sub>-type UF<sub>4</sub> and HP-UF<sub>4</sub> were investigated by means of temperature-dependent DC-magnetic measurements in a temperature range between 300 K and 5 K. The magnetic susceptibilities are shown in Figure 7. At temperatures between 100 to 300 K, the susceptibilities of both compounds can be fitted with a Curie-Weiss law (*C*/(*T* – *Θ*)). An effective moment,  $\mu_{eff}$ , of 3.67(1)  $\mu_B$  and 3.61(1)  $\mu_B$  per formula unit and a paramagnetic Curie constant  $\Theta$  of –160.8(7) K and – 147.1(2) K resulted from the fits of ZrF<sub>4</sub>-type UF<sub>4</sub> and HP-UF<sub>4</sub>, respectively.

The effective moments for ambient pressure UF<sub>4</sub> and HP-UF<sub>4</sub> are of similar magnitude. The obtained values resemble the effective atomic moment of 3.58  $\mu_B$  of a [Rd]5f<sup>2</sup> U<sup>4+</sup> cation with a <sup>3</sup>H<sub>4</sub> ground state indicating that crystal field effects contribute only to a small extent within this temperature region. This behavior is found for many U(IV) systems.<sup>[46,48–50]</sup> The negative values of  $\Theta$  of both compounds indicate an antiferromagnetic interaction between the U(IV) ions, although the course of the susceptibility at low temperatures does not display an explicit magnetic ordering.



**Figure 5.** Observed and calculated powder X-ray diffraction patterns of hp-UF<sub>4</sub> after the Rietveld refinement. The observed pattern is shown in blue, the calculated one in red. The calculated reflection positions are indicated by the vertical bars below the patterns. The curve at the bottom represents the difference between the observed and calculated intensity. Profile *R* factors:  $R_p = 1.98\%$ ,  $wR_p = 2.69\%$ , GOF = 5.31. Further details on the structure determination are available from the Supporting Information.

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Figure 6. Different plots of the temperature dependence of the molar susceptibility of a) ZrF4-type UF4 and b) hp-UF4 with an applied field of 0.1 T.

The temperature range used for the Curie-Weiss fits is shown in red. The low temperature magnetic susceptibilities of ZrF<sub>4</sub>-type UF<sub>4</sub> and HP-UF<sub>4</sub> are given in Figure 6. The susceptibilities of both compounds exhibit saturation effects. However, the saturation is more pronounced for HP-UF<sub>4</sub>. A saturation of the susceptibility at low temperatures is often observed in compounds containing U(IV) cations.<sup>[46,48-50]</sup> This effect is discussed in terms of crystal field effects that should stabilize a singlet ground state, which is populated with decreasing temperature. In case of ZrF<sub>4</sub>-type UF<sub>4</sub>, capacity,<sup>[51]</sup> heat magnetic,<sup>[52]</sup> and spectroscopic measurements^{[53]} reveal an energy difference  $\Delta$  between the ground state and the first excited state of about 10 cm<sup>-1</sup>. Due to the small energy difference, the saturation of the susceptibility and therefore the deviation from the Curie-Weiss law occurs only at low temperatures, e.g.  $k_{\rm B}T \approx \Delta$ . Leask and coworkers suggested the following fitting function (Equation 6) for the magnetic susceptibility of ZrF<sub>4</sub>-type UF<sub>4</sub> below 20 K, assuming, in line with spectroscopic measurements,<sup>[53]</sup> that only the first exited state is accessible within this temperature range.[52]

$$\chi(T) = p \cdot \frac{8N_{\rm A}\mu_{\rm B}^2}{k_{\rm B}} \cdot \frac{1}{\Delta} \cdot \frac{1 - \exp(-\Delta/T)}{1 + \exp(-\Delta/T)} + \mu_0 \tag{6}$$

In the equation,  $N_A$  is the Avogadro constant,  $\mu_B$  the Bohr magneton, and  $k_B$  the Boltzmann constant. The factor *p* accounts for a reduction of the magnetic susceptibility due to antiferromagnetic coupling,  $\Delta$  is the energy difference in K between the ground state and the first excited state and  $\mu_0$  is the temperature-independent susceptibility. Applying Equation 6 to our data, we can reproduce the results of previous studies finding an energy gap  $\Delta$  of 10.6(1) cm<sup>-1</sup> (see Figure 6). In the case of HP-UF<sub>4</sub>, we determine an energy gap  $\Delta$  of 21.9(2) cm<sup>-1</sup>, almost twice the value of ZrF<sub>4</sub>-type UF<sub>4</sub>. This is in line with the expected increase of crystal field effects as the average coordination number of the uranium atoms increases from eight in ZrF<sub>4</sub>-type UF<sub>4</sub> to nine and eleven (ten in average) in HP-UF<sub>4</sub>. Due to the higher energy difference between the ground state and the first excited state of HP-UF<sub>4</sub> the saturation of the magnetic susceptibility is more pronounced as in ZrF<sub>4</sub>-type UF<sub>4</sub> (see Figure 6).





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Using quantum chemical calculations, we optimized the structures of ZrF<sub>4</sub>-type UF<sub>4</sub> and HP-UF<sub>4</sub> with density functional theory (DFT) applying the hybrid functional PBE0. The results of the structural optimization of the magnetic ground state of ZrF<sub>4</sub>type UF<sub>4</sub> and a comparison with experimental data are collected in Table S3 and Table S4. The data concerning HP-UF<sub>4</sub> is summarized in Table S5 and Table S6. The calculated lattice parameters of the two compounds agree well with the experimental results. The difference is in the order of 1%. The experimental U-F distances (in the following given in brackets) are also well reproduced by the DFT calculations. In case of ZrF<sub>4</sub>type UF<sub>4</sub>, the calculated U-F distances range from 2.21 Å (2.230 Å) to 2.34 Å (2.354 Å).<sup>[21]</sup> The average distance of U(1) and U(2) to their coordinating fluorine atoms is calculated as 2.27 Å (2.290 Å and 2.266 Å, respectively). In case of HP-UF<sub>4</sub>, the calculated U-F distances range from 2.18 Å (2.217(2) Å) to 2.68 Å (2.414(2) Å). The average U-F distance of U(1) is 2.43 Å (2.429 Å) and of U(2) 2.32 Å (2.342 Å). This demonstrates that PBE0 calculations can reproduce the experimental structures of  $ZrF_4$ -type UF<sub>4</sub> and HP-UF<sub>4</sub> reasonably well.

We estimated the magnetic ground states of  $ZrF_4$ -type  $UF_4$  and HP- $UF_4$  performing single-point calculations with different starting spin-orientations. Details concerning the calculations are given in the Experimental Section. The results of the calculations are summarized in Table 5 and Table 6. We find an antiferromagnetic ground state for both structures in line with the negative paramagnetic Curie-temperatures determined from experiment. Comparing the two ground state energies,  $ZrF_4$ -type  $UF_4$  is about 10 kJ/mol per formula unit more stable than HP-UF<sub>4</sub>. This is expected from our experiments finding the  $ZrF_4$ -type  $UF_4$  to be the stable polymorph under normal conditions.

For both structures, the energy difference of the ground state magnetic structures to magnetic structures higher in energy is in the order of 10 meV to 20 meV. These small energy differences point to only weak antiferromagnetic coupling between the uranium atoms, reflecting that experimentally no magnetic ordering is found in the investigated temperature range between 5 K and 300 K.

As pointed out above, U(IV) systems are often discussed having a singlet ground state. However, our calculations reveal a triplet ground state with a spin magnetic moment of approximately 2  $\mu_B$  per uranium atom. This discrepancy could stem from neglecting spin-orbit interactions in our calculations. The typical magnitude of spin-orbit effects are discussed to be around 300 meV for actinoid ions.<sup>[54]</sup> It is thus likely that the degeneracy of the triplet ground state can be lifted by including spin-orbit interactions in our calculations driving UF<sub>4</sub> to the experimentally indicated singlet ground state.

Table	5.	Energy	difference	of	different	magnetic	structu	ires	of ZrF	4 <b>-UF</b> 4
( <i>C</i> 2/ <i>c</i> ,		<i>mP</i> 60)	(DFT-P	BE	0/TZVP).	Magne	etic	orde	ering:	AF
(antife	rroi	magnetic	), FR (ferri	ma	anetic). F	(ferromag	netic).			

Magnetic	Magnetic	$\Delta E$ / meV and	
	ordoring	per formula	Spin arrangement <sup>a</sup>
space group	ordening	unit	
Pc2/c (13.74)	AF	0	↓↑↓↑↓↑↓↑↓↑
C2 '/c' (15.89)	FR	12	<u> </u>
Pc2/c (13.74)	AF	13	↓↑↓↑↑↓↓↓↓↓
non magnetic	-	1313	_

<sup>a</sup> The atomic positions of the corresponding uranium atoms are listed in Table S7 in the SI.

**Table 5.** Energy difference of different magnetic structures of HP-UF<sub>4</sub> (*P*<sub>21</sub>/*m*, *mP*20) (PBE0/TZVP). Magnetic ordering: AF (antiferromagnetic), FR (ferrimagnetic), F (ferromagnetic).

Magnetic space group	Magnetic ordering	Δ <i>E</i> / meV and per formula unit	Spin arrangement <sup>a</sup>
<i>P</i> 2 <sub>1</sub> '/ <i>m</i> (11.54)	AF	0	↑↑↓↓
P21'/m (11.52)	AF	11	↓↑↓↑
P2 <sub>1</sub> '/m (11.54)	F	21	$\uparrow\uparrow\uparrow\uparrow$
non magnetic		1259	_

<sup>a</sup>The atomic positions of the corresponding uranium atoms are listed in Table S8 in the SI.

#### Conclusions

Based on powder X-ray diffraction, micro X-ray fluorescence analysis, IR and Raman spectroscopy, a route for the synthesis of UF<sub>4</sub> free from oxygen-containing impurities has been developed. The magnetic behavior was re-examined and shown to be consistent with previously reported values. A high-pressure modification HP-UF<sub>4</sub> was synthesized in a multi-anvil press. The compound is metastable under ambient temperature and pressure and its structure was determined by single-crystal X-ray diffraction. HP-UF<sub>4</sub> has a complex 3D network structure that is structurally not related to high-pressure modifications of ZrF<sub>4</sub>. To the best of our knowledge, it presents a novel structure type. The coordination numbers of the uranium atoms are nine and eleven, respectively. The magnetic behavior at high temperatures is similar to that of ambient pressure ZrF<sub>4</sub>-type UF<sub>4</sub>. The magnetic susceptibility shows saturation effects at low temperatures that is often observed for U(IV) systems. Quantum chemical solid-state calculations indicate HP-UF<sub>4</sub> to be 10 kJ/mol per formula unit less stable than ZrF<sub>4</sub>-type UF<sub>4</sub>.

#### **Experimental Section**

**General:** All operations were performed in either stainless steel (316L) or Monel metal Schlenk lines, which were passivated with 100% fluorine at various pressures before use. Preparations were carried out in an atmosphere of dry and purified argon (5.0, Praxair). Hydrogen fluoride (99%, Hoechst) was dried over K<sub>2</sub>NiF<sub>6</sub> prior to its use. The well-educated reader is aware that F<sub>2</sub>, HF, and UF<sub>6</sub> can be dangerous if not properly handled. Uranium compounds are radioactive and should therefore not be ingested. Sulfur is safe at ambient conditions.

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**Preparation of UF**<sub>4</sub> from the reaction of sulfur with UF<sub>6</sub>: In a typical reaction, sublimed S<sub>6</sub> (455 mg, 14.2 mmol) was placed in a perfluorinated ethylene propylene copolymer (FEP) reaction tube and heated in vacuo several times. Approximately 2 mL of anhydrous HF were added by vacuum distillation. The suspension was frozen with liquid nitrogen and UF<sub>6</sub> (3.27 g, 9.29 mmol) was distilled onto it. The reaction mixture was slowly warmed, and reaction began at the melting point of HF. The supernatant solution turned bluish for a few seconds, then brown with the formation of a greyish solid. After two to three days of reaction time at room temperature, a green solid formed, with a colorless supernatant HF solution (see Figure S1). The solvent and volatile reaction products were distilled into a separate FEP reaction tube and the crude product was transferred into a flame-dried glass Schlenk tube. The tube was attached to a vacuum line and residual S<sub>8</sub> was sublimed off in a fine vacuum at approximately 350 °C. The yield of UF<sub>4</sub> is quantitative with respect to UF<sub>6</sub>.

#### Preparation of the high-pressure modification of UF<sub>4</sub>:

UF4 was filled in crucibles, which are made of hexagonal boron nitride (HeBoSint® P100, Henze BNP GmbH, Kempten, Germany) and lined with a platinum foil (thickness 0.027 mm, Ögussa GmbH, Vienna, Austria). For the heating process the boron nitride crucible was surrounded by two thin graphite tubes, which are employed as a graphite resistance heater. The assembly was then placed inside the octahedral pressure medium made from 5% magnesium chromite doped magnesium oxide (Ceramic Substrates & Components Ltd., Isle of Wight, UK). In order to transfer the uniaxial load of the press onto the eight octahedral faces of the magnesium oxide octahedron, eight tungsten carbide cubes (ha-7%Co, Hawedia, Marklkofen, Germany) were used. As soon as the compression process (300 min) of the Walker-module to a maximum pressure of 9.5 GPa was finished, the sample was heated to T = 873 K within 10 min. After keeping this temperature constant for 15 min, the sample was steadily cooled to room temperature within 40 min. The completed heating process was followed by a decompression to ambient pressure within 700 minutes. Under strictly inert conditions, the surrounding crucible material has been easily removed from the crystalline sample. Further information about the multi-anvil technique and the construction of the various assemblies can be obtained from numerous references.[55-59]

**Powder X-ray diffraction**: Powder X-ray diffraction patterns were obtained with a StadiMP diffractometer (Stoe) using Cu-*Ka* radiation ( $\lambda = 1.54059$  Å), a germanium monochromator and a Mythen1K detector. The compounds were placed on adhesive tape (Scotch Tape, 3M) and measured in transmission geometry. The data were handled within the WINXPOW software.<sup>[60]</sup> Rietveld refinement was performed with the TOPAS program suite.<sup>[61]</sup>

Single-crystal X-ray diffraction: X-ray structure analysis of a singlecrystal of HP-UF4 was carried out with a D8 QUEST PHOTON 100 diffractometer (Bruker) with monochromated molybdenum radiation (Mo- $K_{\alpha}$ ,  $\lambda = 0.71073$  Å). Evaluation and integration of the diffraction data was carried out with the Bruker software package.[62] An empirical multi-scan absorption correction was applied. The structure was solved with Direct Methods (SHELXT 2014/5) in the space group P21/m (No. 11) and refined against F<sup>2</sup> (SHELXL 2014/7).<sup>[63,64]</sup> All atoms were refined anisotropically. Representations of the crystal structure were created with the Diamond software.<sup>[65]</sup> Further details of the crystal structure investigation can be obtained from the Cambridge Crystallographic Data Centre, Road, Cambridge, CB2 1EZ, United 12 Union Cambridge, Kinadom (https://www.ccdc.cam.ac.uk/structures/) on quoting the depository number CCDC-1896463

**Micro X-ray fluorescence**: Micro X-ray fluorescence spectra were obtained with a Tornado M4  $\mu XRF$  spectrometer (Bruker). A tungsten X-ray tube was used for the measurements.

**IR and Raman Spectroscopy**: The IR spectra were measured on an ALPHA FT-IR spectrometer (Bruker) equipped with a PLATINUM-ATR unit with a diamond window inside a glovebox. The spectra were processed with the OPUS software package.<sup>[66]</sup> The Raman spectra were collected with an InVia Qontor Raman microscope (Renishaw) equipped with laser wavelengths of 457, 532, 633 and 785 nm. The collected data were handled with the WiRE software.<sup>[67]</sup>

**Magnetic measurements:** DC-magnetic data were collected with the aid of the VSM option of a physical property measurement system (ppms) of LOT-Quantum Design. Temperature dependent magnetic data were recorded in the range from 1.8 K to 300 K with an applied field of 0.1 T. The collected data were corrected with respect to the diamagnetic moment of the sample holder, as well as to the diamagnetic contribution ( $\chi_{dia} = -7.9 \cdot 10^{-5} \mathrm{cm^3 mol^{-1}}$ ) of the sample derived from Pascal constants taking into account the composition of UF4, the result being the net paramagnetic data.<sup>[68]</sup>

#### **Quantum-chemical calculations**

We performed periodic density functional theory (DFT) calculations to calculate the energy difference of the two UF<sub>4</sub> modifications. We further wanted to estimate the magnetic ground state of these structures. The calculations were performed with the software package CRYSTAL17 that uses Gaussian-type atom-centered basis functions.<sup>[69]</sup> We applied the PBE0 hybrid functional and triple-zeta-valence + polarization (TZVP) level basis sets for the uranium and fluorine atoms.<sup>[70–72]</sup> The basis sets derived from the molecular Karlsruhe def2 basis sets were taken from our previous studies.<sup>[73]</sup> We applied a 5x5x5 Monkhorst-Pack-type *k*-points grid for the reciprocal space integration. For the evaluation of the Coulomb and exchange integrals (TOLINTEG) we used tightened tolerance factors of 8, 8, 8, 8, and 16. We performed the structural optimizations of the atomic positions and lattice constants within the constraints imposed by the respective space group symmetry and the default optimization convergence thresholds. We applied spin-unrestricted formalism using an antiferromagnetic spin orientation. We expect only minor effects of different spin orientations on the results of the optimization.

We estimated the magnetic ground states performing single-point calculations with different starting spin-orientations using the optimized structure obtained as above as input. For each UF<sub>4</sub> modification, we calculated a non-magnetic, a ferromagnetic, and two antiferromagnetic starting configurations. In case of ZrF<sub>4</sub>-type UF<sub>4</sub>, we could not find a stable ferromagnetic solution as the calculations always converged in a ferrimagnetic state. The antiferromagnetic spin-orientations were derived from the maximal magnetic subgroups of the space groups of the paramagnetic phases using a single magnetic propagation vector along the crystallographic *Server*.<sup>[74]</sup> The starting magnetizations were set with the input keyword FDOCCUP that defines initial f-orbital starting occupations. We found that for both spin orientations an initial occupation of (0 0 0 0 0 1 1) converged to the lowest energy.

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## **FULL PAPER**

#### Entry for the Table of Contents

## FULL PAPER

Uranium under pressure: The reaction of UF<sub>6</sub> with S<sub>8</sub> in anhydrous HF under oxygen-free conditions yields UF<sub>4</sub> of high purity. Subsequent treatment of the obtained UF<sub>4</sub> in a multi-anvil press yields the high-pressure modification HP-UF<sub>4</sub> in single-crystalline state, with unusual coordination environments for the uranium atoms. Both compounds are investigated by magnetic measurements and quantum-chemical calculations.



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UF4 and the High-Pressure

Polymorph HP-UF<sub>4</sub>