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The Crystal Structures of α- and β-F_2 revisited

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Dedicated to Professor Wolfgang Bensch on the occasion of his 65th birthday

Abstract: The crystal structures of α-F_2 and β-F_2 have been reinvestigated using neutron powder diffraction. For the low-temperature phase α-F_2, which is stable below circa 45.6 K, the monoclinic space group *C*2/*c* with lattice parameters *a* = 5.4780(12), *b* = 3.2701(7), *c* = 7.2651(17) Å, *β* = 102.088(18)°, *V* = 127.26(5) Å^3, *mS*8, *Z* = 4 at 10 K can now be confirmed. The structure model was significantly improved, allowed for the anisotropic refinement of the F atom, and an F−F bond length of 1.404(12) Å was obtained which is in excellent agreement with spectroscopic data and high-level quantum chemical predictions. The high-temperature phase β-F_2, stable between circa 45.6 K and the melting point of 53.53 K, crystallizes in the cubic primitive space group $Pm\bar{3}n$ with the lattice parameter *a* = 6.5314(15) Å, *V* = 278.62(11) Å^3, *Z* = 8, *cP*16, at 48 K. β-F_2 is isotypic to γ-O_2 and δ-N_2. The centers of gravity of the F_2 molecules are arranged like the atoms in the Cr_3Si structure type.

Introduction

The crystal structures of the chemical elements belong to the fundamental knowledge of chemistry. Atom distances, bond lengths and angles can be determined precisely and the data serve as benchmarks for quantum chemistry. To our striking surprise the crystal structure of α-fluorine, the polymorph stable below circa 45.55 K, has so far only once been investigated, [1] and the β-allotrope, stable between the melting point (53.53 K) and the phase change temperature, also only once.[2,3] Both crystal structures were investigated using X-ray diffraction, for β-F_2 on single crystals grown from a mixture with argon and for α-F_2 only on powders as due to the phase change from β to α no single crystals could be obtained. Maybe it is not so surprising that the crystal structures of α- and β-F_2 have only been determined once as solid F_2 is still extremely reactive: In the case of the α-F_2 structure determination the authors reported several explosions when the solid F_2 reacted – due to the phase change at circa 45.6 K – with the copper ampoule that was used as the sample holder. [1] Additionally, the authors struggled with the strong X-ray reflection intensities of the Cu ampoule and the very weak reflections of α-F_2. The authors concluded that α-F_2 crystallizes in the monoclinic crystal system, probably in space group *C*2/*m*, but space group *C*2/*c* could not be ruled out. Years later, the original diffraction data were reinterpreted by Pauling and coworkers and space group *C*2/*c* was found to be more likely correct. All these assumptions were based on 36 collected reflections.[4] Thus, the space group of α-F_2 is still uncertain,[5] and the problems due to the Cu sample holder naturally had an influence on the determined atom positions, bond lengths and displacement parameters.

Up to 1964 fluorine was the only stable element of which no crystal structure and not even a powder pattern had been reported but *Lipscomb* and coworkers succeeded after significant efforts to obtain a proper single crystal of β-F_2 in a sealed glass capillary.[2,3] In those days diffraction intensities were measured visually, which was often ambiguous, and the reaction of F_2 with the residual moisture on the glass walls always led to the formation of HF. The authors faced the problem to distinguish between two likely cubic space groups, $P\bar{4}3n$ (No. 218) and $Pm\bar{3}n$ (No. 223), based on a total of 42 reflections which dropped significantly in intensity for higher diffraction angles. They chose the higher symmetric space group as they expected a disordered structure and explored in great efforts many structure models in this space group.[2,3] Neither the bond length of the F_2 molecules, and naturally not the anisotropic displacement parameters of the fluorine atoms could be refined.

We therefore reinvestigated the crystal structures of α- and β-fluorine using powder neutron diffraction and Rietveld refinement. We also selected Cu as a sample holder, as Cu can be thoroughly passivated with F_2. Aluminum would be almost transparent for neutrons and vanadium is almost exclusively an incoherent scatterer, but both cannot be passivated as thoroughly as Cu. Using neutron diffraction, the absorption by the Cu ampoule plays only a minor role and therefore the reflections of crystalline fluorine are much more easily detectable. Also in contrast to X-ray diffraction, the atom form factors for neutron scattering do not depend on the scattering angle and so the intensities of the reflections show a much less decrease (which may still happen due to absorption, texture, …) with increasing scattering angle. We therefore obtained models providing much more precise lattice parameters, atomic coordinates as well as bond lengths for the two polymorphs of fluorine.

Results and Discussion

α-Fluorine

In α-fluorine there are four F_2 molecules per unit cell and the previous structure model is as follows: At 23 K, the lattice

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parameters were reported as a = 5.50(1), b = 3.28(1), c = 7.284(1) Å, β = 102.17(2)°, V = 128.4(5) Å^3, $mS8$, the calculated density was 1.97 g/cm^3, and the calculated molar volume 19.3 cm^3/mol.[1] The structure was reported to be very similar to α-O_2.[1,4] Each F_2 molecule is surrounded by six others in the shape of a distorted hexagon, so a hexagonally packed layer results. The main difference to α-O_2 was that the F_2 molecules are tilted, probably only by about 11°, away from the normal onto the planes of the hexagons. As the tilts are to alternate sides in consecutive hexagonal layers, the unit cell is approximately doubled in the c direction in comparison to α-O_2 (a = 5.403, b = 3.433, c = 4.247 Å, β = 117.841, V = 69.7 Å^3, $mC4$, T = 22 K).[6] It is said that this difference results from the antiferromagnetic ordering of the O_2 molecules, which is absent in case of F_2 molecules. α-O_2 crystallizes with an arrangement of the O_2 molecules similar to cubic closed packing.

We recorded powder neutron diffraction patterns of α-F_2 at 10 and 46 K. In the following, only the structural details of the 10 K measurement will be discussed. A Rietveld refinement was carried out (**Error! Reference source not found.**) and it unambiguously shows space group $C2/c$ (No. 15) to be correct as the refinement in space group $C2/m$ gave very poor results (see Supporting Information). The refined lattice parameters are a = 5.4780(12), b = 3.2701(7), c = 7.2651(17) Å, β = 102.088(18)°, V = 127.26(5) Å^3, $mS8$, Z = 4 at 10 K. Therefore, α-F_2 is not isotypic to α-O_2.[6] The crystal structure of α-F_2 is shown in **Error! Reference source not found.**. **Error! Reference source not found.** holds the atomic coordinates, Wyckoff positions, site symmetries and occupancies, as well as the isotropic displacement parameters, **Error! Reference source not found.** the anisotropic displacement parameters of the F atom of α-F_2. **Error! Reference source not found.** holds selected crystallographic details.

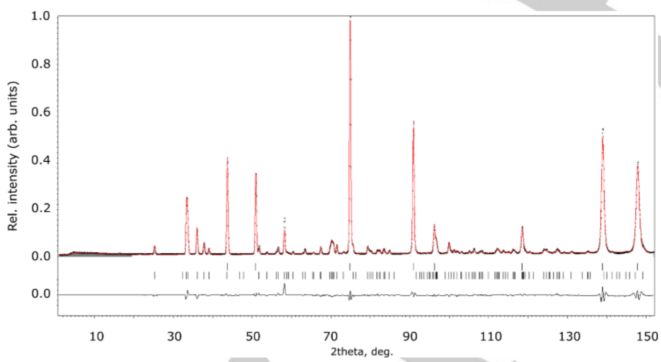

Figure 1. Powder neutron diffraction pattern of α-F_2 at 10 K. Black dots indicate measured intensity, fitted curve in red (Rietveld refinement for F_2, LeBail fit for Cu), difference curve in black. Tick marks indicate reflection positions, upper line for Cu, lower line for α-F_2. Excluded regions in grey. R_P = 0.054, wR_P = 0.076.

Table 1. Atom coordinates, Wyckoff position, site symmetry and occupancy, and isotropic displacement parameter of the F atom in α-F_2 in comparison to the literature.

Atom	Wyckoff position	Site symmetry	Site occupancy	x	y	z	U_{iso}	
F	8f	1	1	0.2740(14)	0.315(2)	0.0942(12)	0.0183(19)	This work
F	8f	1	1	0.285	0.319	0.100		[4]

Table 2. Anisotropic displacement parameters for the F atom in α-F_2.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F	0.006(3)	0.018(4)	0.032(3)	−0.002(4)	0.007(2)	0.003(5)

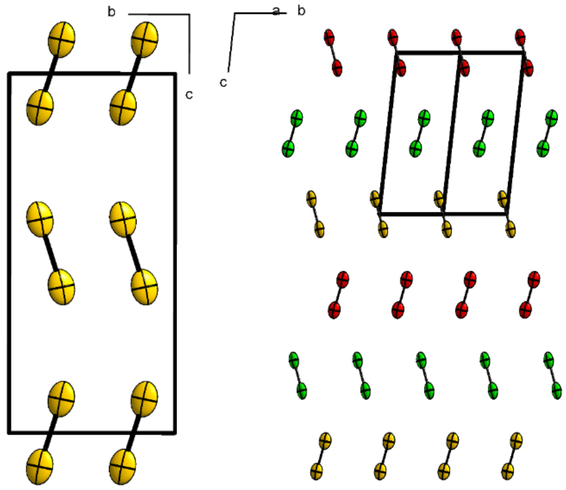

Figure 2. The crystal structure of α-F_2 (left, projection along a-axis). The F−F bond length is 1.404(12) Å. The different colors in the right picture indicate the hexagonally packed F_2 layers to show the relation to cubic closed packed structures (the centers of gravity of the F_2 molecules). Red corresponds e.g. to the A layer, green to the B layer, yellow to the C layer. Anisotropic displacement ellipsoids are shown at 70% probability level at 10 K.

Within the layers, the F_2 molecules are hexagonally close packed. These layers are parallel to the ab-plane. When viewed along the b-axis (**Error! Reference source not found.**, right), the ordering of the layers as ABC, and therefore the relationship to the cubic closed packing becomes obvious. Viewed along the a-axis, we observe a tilting of the F_2 molecules from the normal onto the ab-plane, best seen in **Error! Reference source not found.**, left, of

17.7(6)°. In α-O_2, this tilting angle is quite small (< 1°).[6] It is reported that these differences can be understood in terms of the larger quadrupole moment of the F_2 molecule and the lack of a magnetic interaction in comparison to O_2 molecules.[6,7] A F_2 molecule is surrounded by twelve F_2 molecules in the shape of a distorted cubeoctahedron, as expected for a structure that derives from the cubic closed packing. Within a layer, the centers of gravity of the F_2 molecules (on Wyckoff position 4*d*) are 3.1899(5) Å (4 times) and 3.2701(7) Å (2 times) apart, so the hexagon is slightly distorted. To the layer above and below, these distances lie in between 3.9834(8) and 4.0659(10) Å. The shortest intermolecular F···F distances are observed in between the layers with (two times) 2.849(11) and (one time) 2.985(10) Å. In the previous structure model, these F···F distances were reported as 2.82 Å (two times) and 2.87 Å (one time). Within the closed packed layer, the intermolecular F···F distances are (four times) 3.190(11) and (two times) 3.270(9) Å, which are in agreement with previously reported values of 3.20 and 3.28 Å.[4]

The F atoms occupy the 8*f* Wyckoff position. We observe the F−F distance as 1.404(12) Å. Previously, it had been fixed at 1.44 Å[1] or refined to 1.49 Å.[4] The F−F distance of the F_2 molecule in the gas phase at 0 K has been calculated using CCSD(T) level of theory with basis sets up to aug-cc-pV5Z to 1.411 Å.[8] From rotational and vibrational Raman spectra 1.4177(15) Å were obtained at room temperature and a pressure of 1 atm,[9] whereas others report a well agreeing value of 1.4168(5) Å.[10] Therefore it seems that the F−F bond length is only little influenced by the state of matter. This has been assumed previously based on IR and Raman data, where the stretch vibration of 898 cm^{-1} for solid F_2, and of 894 cm^{-1} for liquid F_2 have been reported.[11] In summary, the F−F bond length observed by us is in excellent agreement with theory as well as spectroscopic experiments.

As can be seen from **Error! Reference source not found.**, the anisotropic displacement ellipsoid of the F atom is elongated in the direction of the F−F bond, which may be due to vibration within the F_2 molecule and also due to librations between the F_2 molecules. The flattening of the anisotropic displacement ellipsoid may also be due to librations of the F_2 molecules.

Quantum chemical investigation of α-F_2

The harmonic and anharmonic stretching vibration of gas-phase F_2 have been reported to be 916.929(10) and 893.9416(18) cm^{-1}, respectively.[12] The corresponding frequencies from our *ab initio* CCSD(T)/aug-cc-pVTZ calculation are 916 and 892 cm^{-1}. The vibrational frequencies and the predicted F–F distance of 1.415 Å are therefore in very good agreement with the experiment. From systematic CCSD(T) studies on the F_2 molecule it is known that CCSD(T)/aug-cc-pVTZ benefits from some cancellation of errors in the case of F_2.[8]

Structure optimization of the α-F_2 (*C*2/*c*) solid state structure at the DFT-PBE0/TZVP level of theory with D3(BJ+ABC) dispersion corrections results in a true local minimum and a reasonable agreement with the experimental crystal structure determined by neutron diffraction. The lattice parameters *a* and *b* are underestimated by 2.2 and 3.3 %, respectively, while *c* and *β* are overestimated by 1.1 and 1.3 %, respectively (see Supporting information for full comparison of structural parameters). We also evaluated the cohesive energy of α-F_2, that is, the energy difference between solid α-F_2 and gas-phase F_2. Using a larger def2-TZVPP basis set, the cohesive energy is calculated to be – 3.9 kJ/mol (see Supporting Information for details). The absolute value 3.9 kJ/mol can be compared with the experimental sublimation enthalpy of F_2 adjusted to 0 K, which is 8.2 ± 0.3 kJ/mol.[13,14] Our quantum chemically calculated cohesive energy is in the same range as the experimental 0 K sublimation enthalpy, but somewhat underestimated. Müller *et al.* have shown that very good agreement with experiments can be reached using high-level quantum chemical methods.[15]

The harmonic vibrational frequencies of solid *α*-F_2 could only be calculated with the DFT-PBE0 method, which is not as accurate as CCSD(T) used for the F_2 molecule. In fact, previous benchmarks of several DFT methods have shown that hybrid DFT methods such as DFT-PBE0 overestimate the F−F bond strength and the F−F stretching frequency.[16] This can already be seen in the optimized F−F distance within the α-F_2 structure, which is underestimated by 1.8 % in comparison to the experiment (1.38 Å vs. 1.404 Å). The Raman frequency of the F−F stretching vibration in solid *α*-F_2 has been reported at 895 cm^{-1} and 894 cm^{-1} in previous studies.[11,17] Here the F−F stretching frequency predicted with DFT-PBE0 is 1096 cm^{-1}. Because there are two F_2 molecules in the unit cell, there are in fact two F−F stretching modes: An A_g-symmetric mode where the F_2 molecules are vibrating in the same phase and a B_g-symmetric mode where the F_2 molecules are vibrating in anti-phase. The frequency difference between these two modes is less than 0.5 cm^{-1} and the intensity of the B_g-mode is only 8% of the A_g-mode. In the experimental Raman spectrum measured with spectral slit width of ca. 0.5 cm^{-1} the low-intensity B_g-mode could not be distinguished from the A_g-mode.[17]

Even though the F–F stretching frequency calculated on the DFT-PBE0 level of theory is clearly overestimated, the calculated Raman and IR spectra enable comparisons of the low-energy librational modes with the experimental spectra.[17] Four librational modes have been observed in the lattice vibration region of the *α*-F_2 Raman spectrum: 93, 77, 55, and 44 cm^{-1}. In the calculated spectrum, the corresponding values are 101, 71, 58, and 16 cm^{-1}. The experimental IR spectrum showed librational modes at 80, 42.5, and 28 cm^{-1}. The corresponding DFT-PBE0 modes are 90, 41, and 32 cm^{-1}, with low absorbances of 0.02, 0.03, and 0.01 km mol^{-1}.

Structural optimization of *α*-F_2 in the alternative space group *C*2/*m* discussed above shows it to be essentially identical in energy and *C*2/*m* is also a true local minimum. However, the optimization yields much larger deviations of the predicted cell parameters in comparison to the experimentally determined ones. The deviation of the *b* axis increases from −3.3 to −4.6 %, the one of the *c* axis increases from 1.1 to 1.9 %, and for the angle *β* from 1.3 to 2.7 %. Only in the case of the lattice parameter *a*, the deviation decreases from −2.2 to −1.0 %. The predicted F–F distance however remains exactly the same as for the *C*2/*c* structure (1.38 Å).

β-Fluorine

In the previous single crystal X-ray structure determinations of β-F_2, fluorine gas was condensed into glass ampoules and flame sealed.[2,3] The authors reported difficulties due to the formation of HF with the H_2O residues on the glass. We therefore can conclude that also SiF_4 must have been formed during those experiments, as glass decomposition with fluorine is an autocatalytic process. Besides these experimental problems, the reflection intensities had been evaluated visually in those times, which of course can be very difficult. The authors of the previous single crystal structure study tried their very best in using many elegant models to describe the disorder of the F_2 molecules, and a section of the crystal structure with their final model is shown in **Error! Reference source not found.**. The F−F distance was given as 1.418 Å and 1.417 Å. In the previous structure model only a single F atom instead of a F_2 molecule was used as the center of gravity of almost spherically disordered F_2 molecules on Wyckoff position 2*a* ($m\bar{3}.$), which is at the corners and the center of the unit cell (**Error! Reference source not found.**). The F atoms on the 12*g* (*mm*2..) and 48*l* (1) positions, which are close to the faces of the unit cell, led only to an unsatisfactory disorder model as seen in **Error! Reference source not found.**.

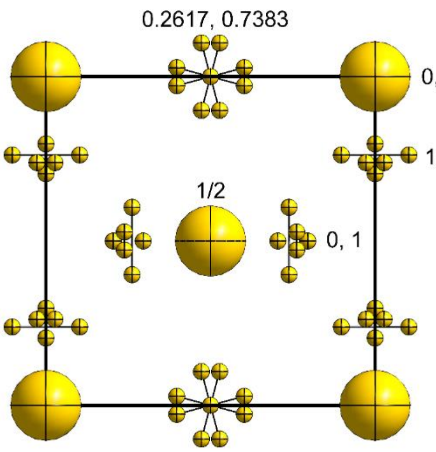

Figure 3. A section of the old structure model of β-F_2. Note the single F atom (a spherically disordered F_2 molecule) on the corners and in the center of the unit cell which is drawn with a diameter corresponding to the previously reported F−F atom distance of 1.418 Å. The radii of the other F atoms are chosen arbitrarily. The numbers shown correspond to the z coordinate and give the height of the center of gravities of the F_2 molecules in the cell.

We avoided the problems of single crystal growth of F_2 and its handling in glass, however we are therefore “only” able to obtain a structure model based on powder and not on single crystal diffraction. As can be seen from the powder neutron diffraction pattern of β-F_2 (**Error! Reference source not found.**), its reflections are of small intensity in comparison to the ones of the Cu sample holder. Additionally, the intensity of the reflections decreases rapidly with increasing scattering angle 2θ, which already indicates that “disorder”, vibrations and libration are present. This assumption is supported by the presence of the diffuse scattering in the powder diffraction pattern. We were therefore unfortunately unable to obtain high-angle diffraction data of sufficient signal to noise ratio for a better refinement.

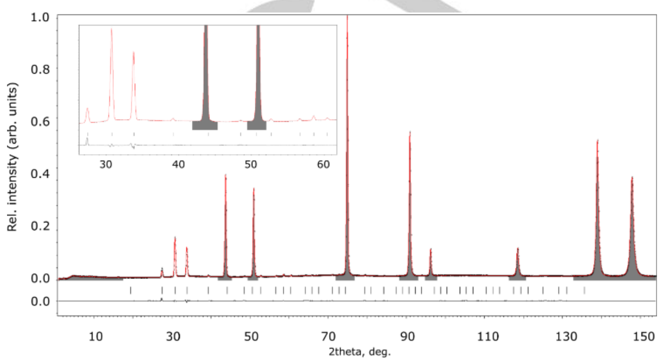

Figure 4. Powder neutron diffraction pattern of β-F_2 at 48 K. Black dots indicate measured intensity, fitted curve in red (Rietveld refinement for F_2, reflections of Cu had to be omitted (grey) from the refinement), difference curve in black. Tick marks indicate reflection positions for β-F_2. R_P = 0.014, wR_P = 0.020.

We investigated some different cubic space groups and employed various disorder models (see Supporting Information), but in the end, we agree with the literature and also describe the crystal structure of β-F_2 in the cubic primitive space group *Pm*$\bar{3}$*n* (No. 223) with the lattice parameter *a* = 6.5314(15) Å, *V* = 278.62(11) Å^3, *Z* = 8, *cP*16, at 48 K. Therefore, β-F_2 is isotypic to γ-O_2 and δ-N_2.[3,18,19] The crystal structure of β-F_2 is shown in **Error! Reference source not found.**. The structure model, which we find to be the most plausible one (Model 6 in the Supporting Information) is closest to the one established for δ-N_2.[19]

The crystal structure of β-F_2 can be derived from the tungsten structure type, in which the centers of gravity of the F_2 molecules occupy the positions of the W atoms. Additionally, half of the tetrahedral voids of the W structure type are filled with additional F_2 molecules in a manner that is known from the Cr_3Si structure type (*Pm*$\bar{3}$*n*, *cP*8). This leads to the formula $(F_2)_6(F_2)_2$ and thus *Z* = 8. For the description of the disorder we used three F atoms of which only F1 could be refined anisotropic. **Error! Reference source not found.** holds the atom coordinates, Wyckoff positions, isotropic displacement parameters and site occupation factors, **Error! Reference source not found.** contains the anisotropic displacement parameters of the F1 atom. In our structure model, three symmetry independent F_2 molecules are present in the unit cell, which will be denoted as F_2^1, F_2^2, and F_2^3. The centers of gravity of the F_2^1 and F_2^2 molecules lie both on Wyckoff position 2*a* ($m\bar{3}.$), which resides on the corners and in the center of the unit cell, whereas the F_2^3 molecule has its gravity center on Wyckoff position 12*h* (*mm*2..), which is in this case very close to 6*d* ($\bar{4}m.2$) at 1/4,1/2, 0.

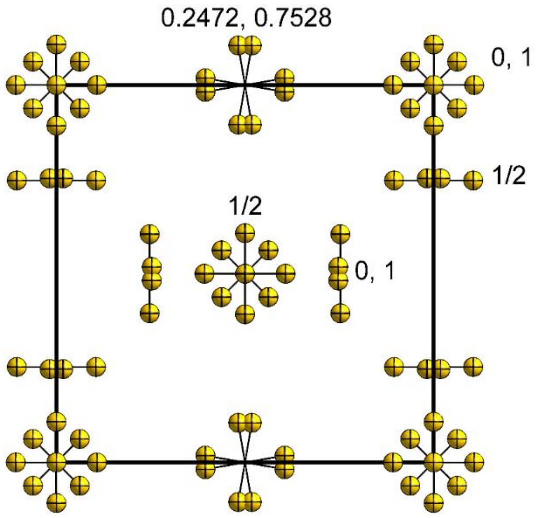

Figure 5. A section of the current model of the crystal structure of β-F_2 at 48 K. F atoms are shown isotropic with arbitrary radii. The numbers shown correspond to the z coordinate and give the height of the centers of gravity of the F_2 molecules in the cell.

Table 3. Atom coordinates, Wyckoff positions, site symmetries and occupancies, and isotropic displacement parameters of β-F_2 in comparison to the literature.

Atom	Wyckoff position	Site symmetry	Site occupancy	*x*	*y*	*z*	U_{iso}	
F1	16*i*	.3.	1/8	0.0620(3)	0.0620(3)	0.0620(3)	0.102(14)	This work
	2*a*	$m\bar{3}.$	1	0	0	0	–	[2]
F2	12*f*	*mm*2..	1/6	0	0	0.1075(5)	0.087(18)	This work
	–	–	–	–	–	–	–	[2]
F3	48*l*	1	1/4	0.018(5)	0.3952(9)	0.2472(18)	0.107(4)	This work
	48*l*	1	1/8	0.0275	0.3974	0.2617	–	[2]
	12*g*	*mm*2..	1/2	0.2046	0	1/2	–	[2]

Table 4. Anisotropic displacement parameters for the F1 atom in β-F_2.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F1	0.10(3)	0.10(3)	0.10(3)	−0.011(9)	−0.011(9)	−0.011(9)

Overall, the F1 and F2 atoms arrange around the 2*a* position in a shape similar to a rhombic dodecahedron. A section of the crystal structure showing the disorder model is available from **Error! Reference source not found.**. The F1 atoms (yellow in **Error! Reference source not found.**) form a cube with the F−F bonds of the F_2^1 molecules oriented along the space diagonals of the cube. A distance restraint had to be used for the refinement of the bond lengths preventing them from becoming unphysically short. This leads to (restrained) F^1−F^1 distances of 1.403(3) Å within the F_2^1 molecule. The F2 atoms form an octahedron (green in **Error! Reference source not found.**) around the 2*a* position with an F^2−F^2 distance of 1.404(6) Å for the F_2^2 molecules. As in total only a single F_2 molecule can occupy the space around the 2*a* position, the site occupation factors given in **Error! Reference source not found.** result. Unfortunately, we could not freely refine the occupancy ratio of the F_2^1 / F_2^2 molecules but had to fix it at 50 %. Overall, the disorder of the F_2^1 and F_2^2 molecules is reminiscent of a spherical disorder around the 2*a* position.

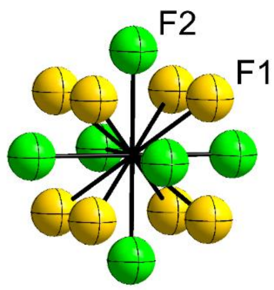

Figure 6. A section of the crystal structure of β-F_2 showing the used disorder model around the 2a position. The F1 atoms forming the cube are drawn yellow, the F2 atoms forming the octahedron are drawn in green. Isotropic displacement parameters are shown with arbitrary radii.

The disorder of the F_2^3 molecule with its center of gravity on Wyckoff position 12*h* (*mm*2..) can be described using only one F atom (F3). The (restrained) F^3−F^3 distances are 1.389(13) Å. In contrast to the previous structure model the refinement of the disordered F_2^3 molecules leads to a quite flat arrangement with all F3 atoms almost coplanar (**Error! Reference source not found.**). We also attempted the refinement with other positions for the F3 atom, however that always led to an insufficient structure model (see the Supporting Information for details).

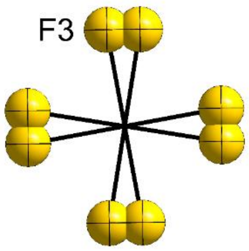

Figure 7. A section of the crystal structure of β-F_2 showing the used disorder model around the 12h position. Note that the symmetry-equivalent atoms shown almost reside within one plane. Isotropic displacement parameters are shown with arbitrary radii.

Of course all the F−F distances discussed here have to be interpreted with care due to the disorder as well as the applied distance restraint. As mentioned above, the F−F bond lengths seem to be rather independent of the physical state, thus the selected distance restraint is plausible.

Quantum chemical calculations on β-F_2

As quantum chemical calculations on the disordered β-modification are enormously demanding and highly difficult to carry out and other groups are successfully working since several years on this task,[20] we decided not to investigate this topic.

Conclusions

Using neutron diffraction and quantum chemical solid-state calculations we have shown α-F_2 to unambiguously crystallize in space group *C*2/*c*, *mS*8, with four F_2 molecules in the unit cell. The lattice parameters obtained at 10 K are *a* = 5.4780(12), *b* = 3.2701(7), *c* = 7.2651(17) Å, *β* = 102.088(18)°, *V* = 127.26(5) Å^3. The structure model was significantly improved, allowed for the anisotropic refinement of the F atom, and an F−F bond length of 1.404(12) Å was obtained.

β-F_2 crystallizes in space group $Pm\bar{3}n$ with the lattice parameter *a* = 6.5314(15) Å, *V* = 278.62(11) Å^3, *Z* = 8, *cP*16, at 48 K. The centers of gravity of the F_2 molecules are arranged like the atoms of the Cr_3Si structure type. β-F_2 is isotypic to γ-O_2 and δ-N_2. Due to the heavy disorder of the structure, only restrained F−F atom distances of 1.403(3), 1.404(6), and 1.389(13) Å could be refined, which still present a significant enhancement in comparison to previous structure models.

Table 5. Crystallographic details of α- and β-fluorine and a comparison to the literature data.

	α-F_2 (this work)	*α-F_2 [1]*	*α-F_2 [4]*	*α-F_2 (this work)*	*β-F_2 (this work)*	*β-F_2 ([2,3], single crystal)*
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	cubic	cubic
space group type, No.	*C*2/*c* (15)	*C*2/*c* (15) or *C*2/*m* (12)	*C*2/*c* (15)	*C*2/*c* (15)	$Pm\bar{3}n$ (223)	$Pm\bar{3}n$ (223)
Pearson symbol	*mS*8	*mS*8	*mS*8	*mS*8	*cP*16	*cP*16
a / Å	5.4780(12)	5.50(1)	5.50 *	5.5880(7)	6.5314(15)	6.67(7)
b / Å	3.2701(7)	3.28(1)	3.28 *	3.2870(4)	= *a*	= *a*
c / Å	7.2651(17)	7.284(1)	7.28 *	7.3407(9)	= *a*	= *a*
β /°	102.088(18)	102.17(2)	102.17 *	103.221(10)	90	90
V / Å^3	127.26(5)	128.4(5)	128.38 *	131.26(2)	278.62(11)	297(9)
Z	4	4	4	4	8	8
T / K	10	23	23	46	48	50
$\rho_{calc.}$ / g cm^{-3}	1.98	1.97	1.97	1.92	1.81	1.70(5)
*R*p, *wR*p	0.0538, 0.0761	–	–	0.0559, 0.0675	0.0135, 0.0198	–
$R_1(F)$	0.0645 [a]	–	0.20 [a]	–	0.1181 [a]	0.095 [b]
wR_2 (F^2)	0.0852 [a]	0.456 [a]	–	–	0.0980 [a]	0.176 [b]
d(F−F) / Å	1.404(12)	1.44 (fixed)	1.49 *	–	1.403(3), 1.404(6), 1.389(13) (all restrained)	1.418 (fixed)

[a] all data; [b] the details are not given

** no s.u. given*

Experimental Section

General: All operations with fluorine were carried out in a stainless steel, perfluoroelastomer (FEP) or Monel line. As an inert atmosphere either dry and purified argon (5.0, Westfalen AG, Germany) or helium (5.0, Westfalen AG, Germany) were used so that a possible contact of the inner surfaces of the apparatus and the fluorine with moisture or air was excluded. As vacuum pumps either “fluorine-resistant” two-stage rotary vane pumps (p_{min} = 10^{-3} mbar) or turbomolecular pumps (p_{min} = 10^{-7} mbar) were used. Fluorine was kindly donated by Solvay (> 99.9 %). 5.33 g of fluorine were condensed from a prepassivated nickel bottle into the prepassivated copper sample holder which was kept at 50 K so that all fluorine was condensed as a liquid.

Copper was selected as the sample holder as it is the metal of choice in the work with F_2 if passivated properly. Nickel or Monel (a Ni-Cu-alloy) would be superior (also for working the metals), however Ni scatters and absorbs neutrons to a significantly higher extent compared to Cu. We did not dare to use the usual sample holder out of vanadium for neutron diffraction as it is not or not easily passivated, and explosions at the nuclear reactor providing the neutrons should be avoided. In addition to the sample holder, the capillary inside the cryostat stick, allowing for the transfer of F_2, was built out of stainless steel and was thoroughly passivated with F_2 in order to exclude any reactions.

Powder Neutron Diffraction: The powder patterns of F_2 were recorded in a pre-passivated copper ampoule of 12 mm outer and 10 mm inner diameter and of approximately 60 mm height at temperatures of 10 K, 46 K (both for α-F_2) and 48 K (and β-F_2) using the SPODI neutron powder diffractometer (λ = 1.5482 Å) at the research reactor FRM II.[21] After condensation of the fluorine it was cooled below the melting point. A first quick measurement was carried out at 50 K and the positions of the reflections confirmed the presence of the cubic β-phase of F_2. Due to the Cu sample holder, its reflections showed an inhomogeneous intensity distribution along their Debye-Scherrer rings which was due to texture of the Cu sample holder. The sample was then rapidly cooled to 10 K. A quick measurement at this temperature showed that the cubic β-phase was present no longer.

Refinement of α-F_2:

The structure solution and refinement of the crystal structure of α-F_2 were carried out using the Jana2006 software [22,23] and the SUPERFLIP algorithm.[24] For the Cu sample holder a LeBail refinement was used whereas the reflections of α-F_2 were treated with a Rietveld refinement. A manual background was chosen. The pseudo-Voigt functions were used to treat the peak shapes. The slight asymmetry was described by the divergence algorithm implemented in the Jana2006. https://www.ccdc.cam.ac.uk/. CSD 1874484.

Refinement of β-F_2:

The refinement of the crystal structure of β-F_2 was carried out similar to the procedure described above with the exception that the reflections of the Cu sample holder had to be excluded from the refinement. Several disorder models of the F_2 molecules were tested (see Supporting Information for details). https://www.ccdc.cam.ac.uk/. CSD 1874485.

Computational details: The quantum chemical calculations on solid alpha-F_2 were done with the CRYSTAL17 program package.[25] We applied the PBE0 hybrid density functional method and the weak intermolecular interactions were treated with the D3 dispersion correction of Grimme (Becke-Johnson damping and three-body correction).[26–30] A polarized triple-ζ-valence level basis set based on the molecular Karlsruhe def2-TZVP basis set was used for the fluorine atoms.[31,32] The full def2-TZVPP basis set was used for single-point calculations on the cohesive energy (see Supporting information). The reciprocal space of the primitive cell was sampled using an 8x8x4 Monkhorst-Pack-type *k*-point grid.[33] For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, and 16 were used. Both the atomic positions and lattice constants were fully optimized within the constraints imposed by the space group symmetry. Very tight optimization criteria were applied in the structural optimization: root-mean-square (RMS) of gradient 0.00003 a.u. (TOLDEG), RMS of estimated displacements 0.00012 a.u. (TOLDEX), and the maximum energy change between optimization steps 10^{-10} a.u. (TOLDEE). Default extra-large integration grid was used for the DFT exchange-correlation functional (XLGRID). The harmonic vibrational frequencies were obtained by using the computational scheme implemented in CRYSTAL.[34,35] The CFOUR program package was used to carry out *ab initio* CCSD(T) coupled-cluster calculations on the F_2 molecule with an augmented and polarized correlation-consistent triple-zeta-valence quality aug-cc-pVTZ basis set.[36–41] The structure of F_2 was fully optimized and both the harmonic and anharmonic vibrational frequencies were evaluated at the CCSD(T)/aug-cc-pVTZ level of theory.[42]

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Keywords: fluorine • crystal structure • neutron diffraction • quantum chemical calculations

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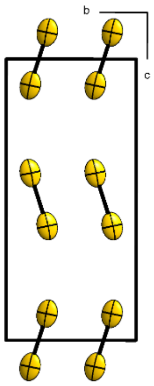

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