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The Crystal Structure of α-Fluorine

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The crystal structure of α-fluorine, stable below 45.6°K, has been studied by the theoretical analysis of the crystal energy and by the reinterpretation of the X-ray powder pattern reported by Meyer, Barrett, and Greer. It is concluded that the space group is $C2/c$, with eight F in the unit cell, cell dimensions $a = 5.50$ Å, $b = 3.28$ Å, $c = 7.28$ Å, $\beta = 102.17°$, in the general positions 8(f), with $x = 0.285$, $y = 0.317$, $z = 0.0997$.

X-ray powder patterns of α-fluorine, which is stable below 45.6°K, have been made by Meyer, Barrett, and Greer (*1*), who reported the structure to be monoclinic, with cell dimensions $a = 5.50$ Å, $b = 3.28$ Å, $c = 10.01$ Å, and $\beta = 134.66°$ at 23°K. They assigned to the crystal a structure involving layers of fluorine molecules tilted by 11° from the normals to the plane of the layers, in the *ac* plane. The structure, based on the space group $C2/m$, requires that there be two crystallographically nonequivalent kinds of fluorine atoms.

A theoretical study of alternative structures of crystalline fluorine was made by Nyburg (*2*) in the course of his application of the extended Hückel molecular-orbital method and the consideration of molecular multipole sums to various assemblies of Cl_2 molecules. We have found that a rather simple theoretical discussion, differing somewhat from that of Nyburg, leads to the conclusion that α-F_2 should have a stable monoclinic layer structure based on the space group $C2/c$ and, moreover, that this structure is in better agreement with X-ray powder patterns than the structure described by Meyer, Barrett, and Greer (*3*).

The axial ratio $a/b = 1.68$ is so close to the value $3^{1/2}$ as to suggest strongly that the crystal contains layers of fluorine atoms in hexagonal close packing. We may first discuss the stability of a layer of molecules tilted somewhat from orientations orthogonal to the plane of the layer. There are two reasonable directions of tilt: (a) along the *b* axis, in the direction of an adjacent atom, and (b) at 30° to this direction. The energy of van der Waals attraction between atoms would be a maximum when the number of atomic contacts is a maximum. Each fluorine atom has two neighbors in the *ab* plane at 3.28 Å and four at 3.20 Å. Tipping the molecules by 18° in the direction (a) from the position orthogonal to the plane gives each atom two additional neighbors at 3.30 Å and one at 3.15 Å. Tipping in the other proposed direction (b) leads to a less satisfactory result: two additional neighbors at 3.21 Å and two at a much larger distance, 3.51 Å. We conclude that the van der Waals stabilization of the hexagonal layer of molecules is greater for the tip (a) than for the other direction of tip.

With the molecules tipped in the direction towards adjacent molecules there are several ways of superimposing a second layer. The lower atoms of the upper layer of molecules are, of course, expected to fit into triangular sockets provided by the upper atoms of the lower layer. The trace of the direction of tip of the molecules of the upper layer may make the angles 0, 60, 120, or 180° with the trace of the tip for the lower layer. The values 60 and 120° are seen from the following argument to correspond to instability relative to 0 and 180°. The symmetry of a molecular layer with the molecular axes normal to the plane of the layer is hexagonal, and the orthohexagonal axes would have the ratio $b/a = 1.732\ldots$. With tipped molecules, the hexagonal axis of symmetry is no longer present, and the axial ratio is expected to differ from this value. The experimental value of b/a is 1.677, showing a 3% deformation from a hexagonal lattice. Two molecular layers with angle 0° or with angle 180° between the traces of the tip directions can be superimposed without being strained; but layers with angle 60 and 120° would have to be deformed in order to be superimposed, and in consequence would represent a less stable sort of superposition than for 0 or 180°.

The decision between 0 and 180° might be resolved by calculating the mutual van der Waals energy of adjacent layers. The fluorine molecule may be approximated as having polarizability represented by a prolate ellipsoid of revolution. The values of $\alpha_{\parallel} = 2.15$ Å^3 and $\alpha_{\perp} = 0.77$ Å^3 have been reported by Stevens and Lipscomb (*4*) from a perturbed Hartree–Fock calculation on the F_2 molecule. Somewhat similar values, $\alpha_{\parallel} = 1.87$ Å^3 and $\alpha_{\perp} = 0.96$ Å^3, are assigned to the molecule by considering it as consisting of two isotropically polarizable atoms the distance 1.44 Å apart, with the average polarizability given by the observed value of the index of refraction (*5*). The values of the van der Waals interaction energy for 0 and 180° calculated by the equation given by London[6] for two molecules with axially symmetric ellipsoids of polarizability were found to differ by only about 1 %. We conclude that adjacent layers might have either parallel (trace angle 0°) or alternating (trace angle 180°) directions of tip.

The successive molecular layers may follow one another in the sequence ABAB..., corresponding to hexagonal close packing, or ABCABC..., corresponding to cubic close packing. The structure based on cubic close packing of molecules with alternating tip leads to a unit with predicted axial lengths and monoclinic angle close to those observed, and with the space group, $C2/c$, that is strongly indicated by the absence of all reflections ($h0l$) with h and l odd (a criterion not required by the space group $C2/m$). The eight fluorine atoms are assigned to the general position 8(f) of $C2/c$, with predicted values of the coordinates $x = 0.28$, $y = 0.32$, $z = 0.10$, corresponding to bond length 1.44 Å and ± 18° tip of the molecules in the direction of the b axis, which makes similar van der Waals contacts between atoms nearly equal in length.

A least-squares refinement of the parameters, leading to $x = 0.285$, $y = 0.319$, $z = 0.100$, was then carried out with use of the experimental intensity values reported by Meyer, Barrett, and Greer. A comparison of the observed and calculated structure factors is given in Table I. The observed values, $|F_0|$, are obtained from Table 3 of Meyer, Barrett, and Greer.[1] The values $|F_c|$ are those for $x = 0.285$,

TABLE I

$(hkl)^a$	$2\theta_0$	$2\theta_c$	$\|F_0\|^b$	$\|F_c\| C2/c$	
002	24.88	25.01	8	14	
110		31.96		5	
$11\bar{1}$	33.01	33.06	47	47	
200	33.20	33.33	18	36	
111	35.59	35.72	22	33	
$20\bar{2}$	37.30	37.43	32	25	
$11\bar{2}$	38.53	38.66	14	18	
112	43.08	43.24	22	20	
202		46.42		4	
$11\bar{3}$		47.42		4	
004	51.25	51.33	16	24	
113	53.18	53.27	19	19	
$20\bar{4}$	55.54	55.59	18	14	
020	56.06	56.08	18	19	
$31\bar{1}$	57.57	57.64	48	35	39
021		57.68		17	
$11\bar{4}$		58.29		12	
310		58.71		9	
$31\bar{2}$	59.66	59.72	15	9	
022		62.33		8	
311	62.76	62.82	24	10	
$31\bar{3}$		64.77		11	
114		65.11		6	
$22\bar{1}$		65.55		5	
220	66.86	66.82	21	21	
204	69.26	69.17	40	23	35
$40\bar{2}$		69.33		22	
$22\bar{2}$		69.38		15	
312	69.80	69.69	37	13	37
023		69.70		23	
221		69.88		21	
400		69.99		15	
$11\bar{5}$	70.87	70.87	28	29	
$31\bar{4}$	72.37	72.45	14	12	
$22\bar{3}$	74.83	74.86	25	22	
222		75.67		2	
115		78.65		26	
313		79.01		22	
024		79.46		15	
$40\bar{4}$		79.84		1	
006	81.38	81.03	34	16	28
$20\bar{6}$		81.45		20	
402		81.75		10	
$31\bar{5}$	82.57	82.54	24	20	

[a] These are the hkl values for the conventional unit cell. They are related to the HKL assignments of Ref. (*1*) by the following transformations: $h = H$, $k = K$, $l = H + L$

[b] The multiplicity factor for the planes of type [$h0l$] and [$0k0$] has been included in the $|F_c|$'s. The $|F_0|$'s of Ref. 1 have also been multiplied by a constant scale factor of 0.79.

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[1] A temperature factor correction with $B = 6.0$ was used in converting $|F_{obs}|^2$ to $|F_0|$, and a scaling constant was introduced in the course of the least-squares refinement.

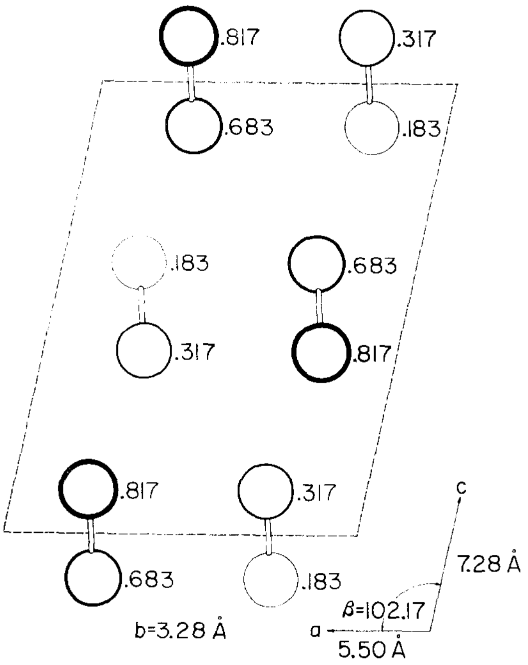

FIG. 1. The structure of α-F_2 projected along the *b* axis. The numbers give the values of *y*. The circles are drawn with radius 0.45 Å.

$y = 0.319$, and $z = 0.100$, obtained by omitting the superimposed reflections in the refinement process.[2] The *R* value $(\Sigma||F_0| - |F_c||/\Sigma|F_0|)$ thus obtained is 0.28, which dropped to 0.20 when all the observed reflections were included in the summation. The lines of multiple reflection were used in a second refinement, by reducing the $|F_0|$ values for the multiple lines in the same ratios as the $|F_c|$ values before refining, this breakdown being repeated until a self-consistent result was obtained. In this way the atomic parameters $x = 0.287$, $y = 0.319$, and $z = 0.100$ were obtained, with $R = 0.20$.

The general agreement between the calculated and observed $|F|$ for $C2/c$ is reasonably good, with $R = 0.20$. (The comparable value of *R* for the structure of Meyer, Barrett, and Greer is somewhat larger, 0.33.)

We conclude that α-F_2 has a monoclinic structure based on the space group $C2/c$ with the atoms in the eight general positions, and coordinates as given above. The bond length is 1.49 Å. Each fluorine atom has twelve nearest neighbors, in addition to the atom in the same molecule (Fig. 1). These neighbors lie at the following distances: in the *ab* plane, four at 3.20 Å and two at 3.28 Å; in the other plane of the molecular layer, one at 3.26 Å, one at 3.18 Å, and one at 3.38 Å; and in the adjacent molecular layer, two at 2.82 Å and one at 2.87 Å.

The fluorine atom in the F_2 molecule may be described as having van der Waals radius, in this crystal, of 1.62 Å for atomic contacts in the same molecular layer and 1.42 Å for contacts between layers. The difference between these values is undoubtedly due to the larger number of contacts in the molecular plane. The effective van der Waals radius of the fluorine atom in α-F_2 is larger than the conventional van der Waals radius, 1.35 Å (equal to the ionic radius), presumably because the forces of attraction are smaller for the fluorine crystal than for crystals with higher melting points, for which the ordinary van der Waals radius is intended. The superposition of the layers, with the molecules tipped in opposite directions, is that which leads to the maximum energy of van der Waals attraction between the layers.

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[2] We are grateful to Dr. S. Freer and Dr. R. Alden for the use of their crystallographic refinement program. The International Tables values of atomic form factors were used.