Table 5. *Equations for least-squares planes*

C(1), C(2), C(3), C(4), C(5), C(6)	$0·0166x-0·0404y+0·9990z=0·7706$	0·01 (1)
C(16), O(8), O(9), C(15)	$-0·1285x-0·6146y+0·7783z=-2·8031$	0·01 (2)

favourably with the corresponding values of 1·44 (2) and 1·56 (2) reported by Hirai *et al.* (1969) for these distances.

The least-squares plane through the carbonyl carbon atom C(16) and its three bonded neighbours O(8), O(9) and C(15) is given by equation (2) in Table 5. All the individual atomic deviations are smaller than 0·02 Å making the arrangement planar. The two C=O bond lengths of 1·23 Å [C(19)–O(9)] and 1·19 Å [C(16)–O(7)] fall within the accepted range for this distance (Sutton, 1965).

As expected, the sp^2-carbon–oxygen bond length [C(16)–O(8)] of 1·36 Å is slightly smaller than the average value of 1·43 (1) Å in the case of the sp^3C–oxygen bonds C(8)–O(4), C(9)–O(4), C(9)–O(5), C(10)–O(5), C(10)–O(6), C(13)–O(6), C(17)–O(8) and C(7)–O(2) (McPhail & Sim, 1966). The mean sp^3C–sp^3C distance of 1·53 (2) Å agrees satisfactorily with the value of 1·545 Å in diamond.

The chain pattern previously mentioned in which separate molecules are linked together through hydrogen bonding also gives rise to the shortest contact distance observed, *viz.* 3·05 Å between N and O(9) whose parent molecules are related by the twofold screw axis at $a=\frac{1}{2}$ and $c=\frac{1}{2}$.

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The Crystal Structure of α-CF_4

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The crystal structure of tetrafluoromethane in a low-temperature phase has been studied with polycrystalline specimens. A monoclinic tetramolecular cell has been found which has the following parameters at 10°K: $a=8·435\pm0·005$, $b=4·320\pm0·002$, $c=8·369\pm0·005$ Å, $\beta=119·40\pm0·05°$; the unit-cell volume and X-ray density are $V=265·7\pm0·5$ Å^3 and $\varrho=2·119\pm0·005$ g.cm^{-3}. The calculation of the structure factors and their comparison with the experimental intensities of reflexions have been carried out on the basis of the packing model of CF_4 molecules in a lattice. The space group $P2_1/c$ has been found.

Introduction

The crystal structures of most of the carbon tetrahalides have not been determined unambiguously, thus complicating studies and understanding of the physical properties of this class of materials. Reliable investigation of the structure of these crystals is impeded by the lack of single crystals and the requirement for performing experiments at low temperatures. Crystals grown in a high-temperature phase are usually destroyed (Rudman & Post, 1966) because of a large volume jump at a phase transition. Therefore, the data on the structures of some carbon tetrahalides have either been obtained recently (CCl_4: Rudman & Post, 1966; Weir, Piermarini & Block, 1969; Post, 1959) or are very contradictiory (CBr_4, CI_4: Finbak & Hassel, 1937; Ormont, 1950).

The primary data on the α-CF_4 structure ($T < 76{\cdot}2\,^\circ K$) were obtained by the analysis of the Raman and infrared spectra (Founier, Savoie, Bessette & Carbana, 1968). According to these papers in a low-temperature phase tetrafluoromethane molecules are strictly ordered and form a lattice of tetragonal space group S_4^1 ($P\bar{4}$) or S_4^2 ($I\bar{4}$). Subsequent X-ray studies (Greer & Meyer, 1969; Gasan, Prokhvatilov & Erenburg, 1970) have shown that α-CF_4 has a monoclinic lattice and the discrepancy with the work of Founier, Savoie, Bessette & Carbana (1968) seems to be due to the ambiguity of the spectroscopic data.

Since the lattice parameters of α-CF_4 (Gasan, Prokhvatilov & Erenburg, 1970) differ from those of Greer & Meyer (1969), additional studies have been carried out in which the lattice parameters, the atomic coordinates and the space group have been found.

Experimental

The experiments were made on a URS-50 IM diffractometer, using a helium cryostat and filtrated Cu $K\alpha$ radiation (Bol'shutkin, Gasan, Kucheryavii, Mironov-Kopisov, Mokrii, Prokhvatilov & Erenburg, 1970). Polycrystalline specimens of α-CF_4 were obtained by vacuum condensation of the vapour (99·95% purity) onto a copper plane substratum initially cooled down to 8 °K. Condensation of the gas volume (250 ml) required for obtaining a good diffraction picture was performed repeatedly with small successive portions. Specimen annealing was carried out for 1·5–2 hours at $T = 45\,^\circ K$ and controlled by X-ray photographs. The process of condensation and annealing permitted one to obtain an equilibrium homogeneous finely dispersed structure in the samples. Recrystallization was observed at $T > 63\,^\circ K$. In this region, in order to estimate the intensity, oscillation photographs were taken. During the exposure a specimen was made to oscillate at an angle of ±2° relative to the vertical axis, which was perpendicular to the X-ray beam. The intensities of Bragg reflexions were reliably observed up to the transition temperature.

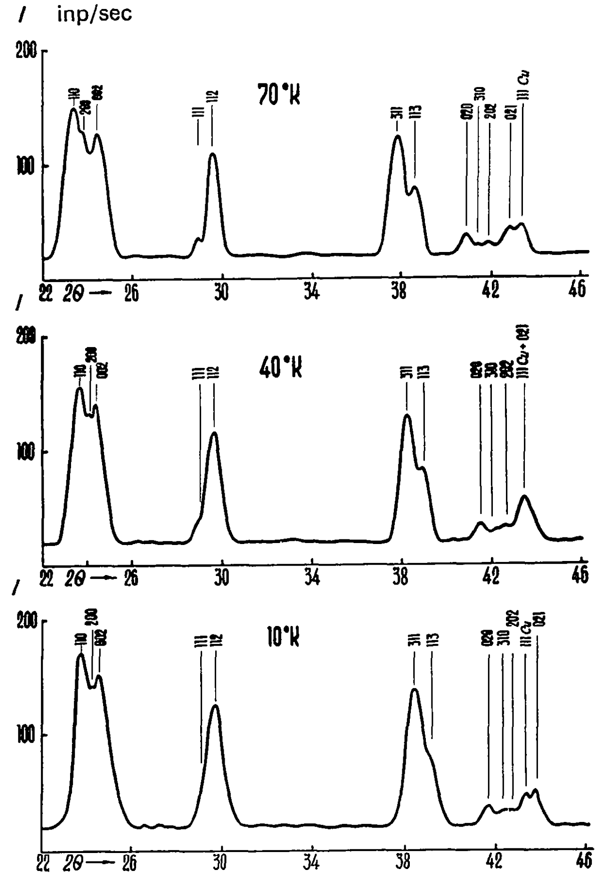

Fig. 1. Diffraction pictures of carbon tetrafluoride obtained with Cu $K\alpha$ radiation at different temperatures.

It has been observed that a fast single-stage condensation of the whole gas portion usually causes the formation of a texture in the samples which remains unchangeable while heating up to the transition temperature. Therefore, when growing the specimens from a gas phase, special attention must be given to the condensation procedure. As mentioned above, sample growing by layers prevents the formation of an unchangeable texture.

The temperature measurements were made with Ge and Pt resistance thermometers located near the substrate surface. Errors in the temperature measurements did not exceed 0·1 °K. Stabilization was accomplished to within ±0·05 °K. The intensity measurements of Bragg reflexions had an error of ~10%. Recording accuracy for angles of reflexion was equal to ±0·5′.

Results and discussion

Fig. 1 shows typical diffraction pictures of the low temperature phase of α-CF_4 at different temperatures. Like other plastic molecular crystals (Staveley, 1961), tetrafluoromethane is characterized by a considerable decrease of the Bragg reflexion intensities as the angle θ increases. At the angle $\theta > 40^\circ$ the reflexions are practically not observed. Because of the anisotropy of heat expansion with increasing temperature, lines which are superposed at low temperature become resolvable. Thus, at the angle $2\theta \simeq 24^\circ$ at $T > 65\,^\circ K$ we observed five lines instead of a triplet at 8 °K; at $2\theta \simeq 29$ and 38° we observed two lines instead of one, *etc.* This fact was used for estimation of the relative intensity and the number and positions of Bragg reflexions when determining the α-CF_4 structure, and was a criterion for proper indexing of the X-ray diffraction pictures.

Table 1 gives the experimental values of angles of reflexion, θ, and the calculated values: $Q_o = \frac{1}{d_o^2} = \frac{4\sin^2\theta_o}{\lambda_{cp}^2}$ where d_o are interplanar distances, $\lambda_{cp} = \frac{1}{3}(\lambda k\alpha_2 + 2\lambda k\alpha_1)$

Table 1. *Observed and calculated angles of reflexion, θ, squares of reciprocal lattice vectors, Q_1 and relative intensities, I, for α-CF_4 at* 10°K

			Calculated			Observed		
h	*k*	*l*	θ (°)	*Q*	*I*	θ (°)	*Q*	*I*
1	1	0	11·95	0·0721	119·8	11·92	0·0718	158·3
−1	1	1	11·99	0·0726	39·5			
2	0	0	12·11	0·0741	92·1	12·07	0·0736	98·6
0	0	2	12·21	0·0753	88·9	12·19	0·0751	134·0
−2	0	2	12·27	0·0760	60·0			
1	1	1	14·76	0·1092	8·8			
−1	1	2	14·86	0·1107	100·0	14·82	0·1102	100·0
1	1	2	19·31	0·1840	9·1	19·31	0·1840	103·5
−3	1	1	19·31	0·1841	103·2			
−3	1	2	19·39	0·1855	1·3	19·44	0·1864	57·0
−1	1	3	19·44	0·1864	58·1			
0	2	0	20·91	0·2143	4·3	20·90	0·2142	4·3
3	1	0	21·21	0·2203	5·0	21·23	0·2206	15·4
2	0	2	21·33	0·2227	12·7	21·38	0·2237	
−3	1	3	21·43	0·2246	0·01			
−4	0	2	21·45	0·2250	0·001			
−2	0	4	21·62	0·2285	0·02			
0	2	1	21·85	0·2331	11·9	21·85	0·2332	11·8
−2	2	1	23·64	0·2706	1·2			
2	2	0	24·46	0·2884	9·6	24·49	0·2892	19·4
0	2	2	24·51	0·2896	7·8			
−2	2	2	24·54	0·2903	0·01			
3	1	1	24·71	0·2941	7·7	24·68	0·2933	7·1
4	0	0	24·81	0·2963	0·002			
1	1	3	24·82	0·2964	11·3	24·79	0·2958	12·0
−1	1	4	24·97	0·2998	19·0	24·98	0·3002	19·1
0	0	4	25·03	0·3010	0·4			
−3	1	4	25·02	0·3013	1·0			
−4	0	4	25·16	0·3041	15·7			12·5
2	2	1	26·88	0·3439	5·5	26·81	0·3423	4·0
−2	2	3	27·04	0·3477	0·4			
0	2	3	28·52	0·3836	2·2	28·56	0·3846	2·0
3	1	2	29·40	0·4055	2·2	29·38	0·4050	3·0
−5	1	2	29·52	0·4086	0·4			
−5	1	3	29·62	0·4110	4·1	29·75	0·4144	6·0
−3	1	5	29·80	0·4156	3·5			
2	2	2	30·63	0·4370	3·4			
−4	2	2	30·73	0·4393	3·8			
−2	2	4	30·86	0·4428	13·0	30·97	0·4455	24·5
−5	1	1	30·90	0·4438	13·3			
1	1	4	31·00	0·4464	0·09			
−1	1	5	31·18	0·4508	4·9	31·23	0·4523	4·0
−5	1	4	31·17	0·4510	1·2			
−4	2	1	31·38	0·4562	9·5	31·52	0·4599	13·0
−4	2	3	31·52	0·4600	9·0			
1	3	0	33·06	0·5007	0·2			
−1	3	1	33·08	0·5012	7·6	33·09	0·5016	5·0
4	2	0	33·43	0·5107	1·9			
0	2	4	33·60	0·5153	7·8			
5	1	0	33·65	0·5166	0·5	33·72	0·5185	12·5
4	0	2	33·71	0·5182	3·8			
−4	2	4	33·71	0·5184	3·4			
2	0	4	33·84	0·5217	3·2	33·88	0·5229	10·0
−6	0	2	33·85	0·5221	5·1			
−6	0	4	34·06	0·5279	0·6			
−5	1	5	34·09	0·5287	0·3			
−2	0	6	34·19	0·5314	4·9	34·2	0·5316	6·0
−4	0	6	34·28	0·5337	1·1			
1	3	1	34·43	0·5379	0·6			
−1	3	2	34·48	0·5393	0·3			
3	1	3	35·03	0·5546	0·2			
−3	1	6	35·51	0·5676	4·2			
2	2	3	35·51	0·5677	1·0	35·60	0·5702	4·0
−2	2	5	35·79	0·5754	1·0			

is the average wavelength of the X-ray radiation used, Q_o are scalar values which are equal to the square of a reciprocal lattice vector.

The analysis of Q_o by using quadratic forms of cubic, tetragonal and hexagonal lattices has shown that the low-temperature phase of tetrafluoromethane is of a lower symmetry. The investigation of Q_o with a computer by the Ito method (Azaroff & Buerger, 1961) has shown that α-CF_4 has a monoclinic lattice. The minimum discrepancy between the experimental values of Q_o and the values calculated from a quadratic form of the monoclinic lattice:

$$Q_c = h^2a^{*2} + k^2b^{*2} + lc^{*2} + 2hla^*c^* \cos \beta^*$$

(h,k,l are indices of the reflexion planes, a^*,b^*,c^*,β^* are parameters of the reciprocal lattice) has been obtained for a unit cell with the parameters $a = 8{\cdot}435 \pm 0{\cdot}005$, $b = 4{\cdot}320 \pm 0{\cdot}002$, $c = 8{\cdot}369 \pm 0{\cdot}005$ Å, $\beta = 119{\cdot}40 \pm 0{\cdot}05°$ at 10°K. The unit-cell volume $V_c = 265{\cdot}7 \pm 0{\cdot}5$ Å^3 indicates an arrangement in it of four molecules[†] with a volume $V_m = 41{\cdot}3$ Å^3. The packing coefficient of the molecules, $k = zv_m/v_c$, appeared to be equal to 0·63, and the density, ϱ, to $2{\cdot}199 \pm 0{\cdot}005$ g.cm^{-3}. The stacking coefficient obtained is somewhat larger than that of methane (0·58) and deuteromethane (0·6: Prokhvatilov, Gasan & Erenburg, 1970), indicating the lesser influence of zero librations on the structure formation of α-CF_4. On the basis of the unit cell found at 10°K a satisfactory indexing of X-ray diffraction pictures was possible in the whole range of the α-phase.

Table 2 gives the values of parameters and densities at different temperatures. In contrast to Greer & Meyer (1969) a monotonic change in the parameters is observed with temperature. Negative expansion is found only along **c** in the range $T > 60$°K. The density values, obtained near the transition temperature (Table 2), are in good accord with those Stewart & La Rock (1958) (1·94 g.cm^{-3}), if we take into account the volume jump at the transition which is equal to 2·0 cm^3 (Stewart, 1960).

In the carbon halide series there is a discrepancy between the absolute parameter values which is evidently due not only to molecule size, but also mainly to the nature of their ordering in the lattice. Unlike the data of Gasan, Prokhvatilov & Erenburg (1970), our lattice for α-CF_4 is isostructural with low-temperature modifications of other carbon halides. Monoclinic lattices of these materials are characterized by similar values of the parameter ratios and the angles of monoclinicity (Table 3). The proximity of the angels of monoclinicity to 120° allows one to distinguish body-centred lattices, with an angle β close to 90°, from base-centred ones of tetrahalides. Thus, for α-CF_4 we obtain the unit cell with parameters $a = 4{\cdot}184$, $b = 4{\cdot}320$, $c = 7{\cdot}348$ Å, $\beta = 90{\cdot}3°$. This seems to be responsible for the conclusions of Fournier, Savoie, Bessette & Carbana (1968) on tetragonality of the low temperature phase of α-CF_4.

A shortcoming of the investigations of the structure of the CX_4-group materials, made by Rudman & Post (1966), Finbak & Hassel (1937) and Greer & Meyer (1969), is the absolute lack of data on the molecule orientations in the α-phases. In this paper, on the basis of the intensity studies and model arrangements, the coordinates of C and F atoms in the lattice have been obtained and the space group has been found. While constructing a structure model of the CF_4 low temperature phase, the following assumptions were made and experimental facts taken onto account.

1. It was considered that the CF_4 molecules in a crystal retain their sizes and forms characteristic of individual molecules, and their packing in the lattice corresponds to the close-packing principle (Kitaigorodskii, 1955).

2. Since the CF_4 molecules are of $\bar{4}3m$ symmetry, in the monoclinic cell they arrange one of the $\bar{4}$ axes along **b**.

Table 2. *Temperature dependence of lattice parameters, density and molar volumes of* α–CF_4

T(°K)	a (Å)	b (Å)	c (Å)	β (°)	ϱ (g.cm^{-3})	V_m(cm^3.mol^{-1})
10	8·435	4·320	8·369	119·40	$2{\cdot}199_2$	40·02
20	8·438	4·323	8·370	119·40	$2{\cdot}197_3$	40·05
30	8·451	4·331	8·372	119·39	$2{\cdot}189_0$	40·20
40	8·473	4·343	8·380	119·37	$2{\cdot}173_8$	40·48
50	8·500	4·359	8·391	119·26	$2{\cdot}154_4$	40·85
60	8·528	4·380	8·395	119·10	$2{\cdot}132_7$	41·26
70	8·565	4·409	8·388	118·86	$2{\cdot}106_6$	42·19
75	8·597	4·433	8·381	118·73	2·086	

Table 3. *Parameter ratio and monoclinicity angles of lattices of methane tetrahalides in* α–phase

	Parameter ratio of phase lattice			Angle of monoclinicity	
Material	a	b	c	β	References
CF_4	1·95	1	1·94	119·40	Present paper
CCl_4	1·75	1	1·72	111·0	Rudman & Post (1966)
CBr_4	1·72	1	1·97	125·3	Finbak & Hassel (1937)
CI_4	1·73	1	2	125·26	Finbak & Hassel (1937)

[†] Molecular radii of C and F required for calculation of a molecular volume have been taken from Kitaigorodskii (1955).

3. The absence of reflexions $h+k=2n+1$ ($n=0,1,2\cdots$) indicates an *ab* face-centred arrangement of the molecule similar to that at the origin, and the presence of the symmetry axis 2_1 which is parallel to **b** and lies in the *ab* plane at a distance of $\frac{1}{4}a$ from the origin.

4. The extinguishing of reflexions at $k=0$ for $l=2n+1$ is possible in the presence of a glide plane C which is perpendicular to **b**.

Fig. 2 shows the structure model of α-CF_4 constructed on the basis of the above. It was obtained by a superposition of close-packed planes {001} in which the $\overline{4}$ axes of the molecules are arranged parallel to **b** and the plane of the F(1)–C–F(2) bond is turned at an angle φ with respect to (001). Molecules of every second plane (001) were obtained by reflexion of the previous plane molecules relative to the plane C and displaced by $\frac{1}{2}$ C along **c** and, according to the close-packing principle, by a quantity ε along **b**. Such an arrangement of the CF_4 tetrahedral molecules in the monoclinic cell corresponds to the space group $P2_1/c$.

The calculation of the Bragg reflexion intensities confirmed the proposed structure for α-CF_4 and gave values for the parameters φ and ε. The intensities were computed taking into account the angular dependences of the atomic, absorption and P.L.G. factors. The parameters φ and ε varied between $\pm 45°$ and $\pm 0{\cdot}5$ respectively. A better agreement between the calculated and experimental intensities was found for $\varphi = 14{\cdot}19°$ and $\varepsilon = 0{\cdot}147$. A comparison of the calculated and experimental intensities is given in Table 1. After three cycles of refinement by the least-squares method the confidence coefficient of the structure appeared to be equal to $R=0{\cdot}15$. The coordinates of C and F atoms, given in the relative units, are presented in Table 4.

Table 4. *Atomic coordinates of the basis molecule of* CF_4 *relative to the symmetry centre of the* α*-phase lattice*

	x	*y*	*z*
C	0·250	0·323	0·250
F(1)	0·392	0·500	0·286
F(2)	0·289	0·500	0·394
F(3)	0·108	0·147	0·214
F(4)	0·211	0·147	0·106

Table 5. *Indexing of X-ray photographs of* α-CF_4 *at* 40 °K *carried out by* (*a*) *Greer & Meyer* (1969) *and* (*b*) *the authors*

(*a*)					(*b*)			
h	*k*	*l*	$2\theta°_{cal}$	$2\theta°_{obs}$	$2\theta°_{cal}$	*h*	*k*	*l*
−2	0	4	23·30					
0	0	2	23·81	23·74	23·79	1	1	0
					23·87	−1	1	1
−2	0	2	24·00	24·02	24·12	2	0	0
−1	1	2	24·37	24·35	24·44	0	0	2
					24·42	−2	0	2
−1	1	1	24·53		29·46	1	1	1
−1	1	3	29·59		29·66	−1	1	2
1	1	0	30·04					
−3	1	5	38·12					
−1	1	4	38·22					
−3	1	4	38·46	38·46	38·42	−3	1	1
					38·58	1	1	2
					38·56	−3	1	2
1	1	1	38·78	38·80	38·84	−1	1	3
−2	0	6	41·12					
−4	0	6	41·51		41·64	0	2	0
−3	1	6	41·60		42·22	3	1	0
2	0	0	42·41	42·42	42·64	2	0	2
−3	1	3	42·55		42·66	−3	1	3
					42·71	−4	0	2
					43·20	−2	0	4
0	2	0	43·51	43·54	43·54	0	2	1
0	2	1	45·18		47·04	−2	2	1
−4	0	8	47·64					
−3	1	7	48·22					
−2	2	3	48·18					
−1	1	5	48·68		48·70	2	2	0
0	0	4	48·74	48·76	48·88	0	2	2
−4	0	4	49·15			−2	2	2
1	1	2	49·41	49·42	49·28	3	1	1
					49·40	4	0	0
					49·64	1	1	3
−3	1	2	49·62					
−2	2	4	49·93		49·92	−1	1	4
0	2	2	49·82	49·92	49·90	−3	1	4
−2	2	2	50·30		50·10	0	0	4
					50·06	−4	0	4
−2	2	5	54·39		53·56	2	2	1
−2	2	1	55·12		53·88	−2	2	3
−3	1	8	57·13		56·94	0	2	3
−5	1	8	57·52		58·70	3	1	2
0	2	3	57·74		58·66	−5	1	2
−5	1	7	57·94		58·84	−5	1	3
−3	1	1	58·90	59·58	59·48	−3	1	5
−5	1	9	59·96		61·12	2	2	2
−1	1	6	60·65		61·10	−4	2	2
−5	1	6	61·18					
1	1	3	61·37	61·57	61·56	−2	2	4
−2	2	6	61·42		61·44	−5	1	1
					61·99	−5	1	4
					62·04	1	1	4
−4	2	6	61·68		62·37	−1	1	5
2	2	0	62·38		62·40	−4	2	1
−4	2	7	62·74	62·49	62·70	−4	2	3
−2	0	8	65·33		65·82	1	3	0
−4	2	8	66·48	65·88	65·84	−1	3	1
2	0	2	66·87		66·54	4	2	0
−5	1	5	66·99		67·12	0	2	4
−4	0	2	67·12		66·96	5	1	0
0	2	4	67·37	67·25	67·10	−4	2	4
					67·28	4	0	2
−4	2	4	67·71		67·24	−6	0	2
−3	1	9	67·93		67·72	2	0	4
					67·64	−6	0	4
					67·84	−5	1	5
−1	3	2	68·81	68·47	68·40	−2	0	6
−1	3	1	68·88		68·38	−4	0	6
					68·56	1	3	1
3	1	0	69·91		68·66	−1	3	2
−2	2	7	70·62		70·00	3	1	3
−1	3	3	71·33	70·93	70·92	−3	1	6

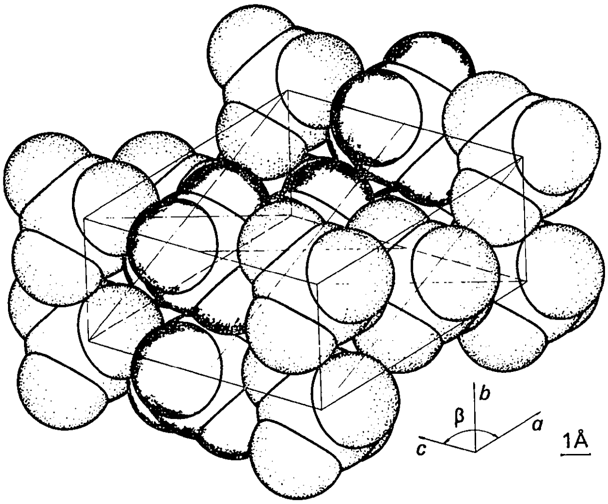

Fig. 2. Structural model of α-CF_4.

The distances between F–F neighbour molecules are within 3·03–3·18 Å at 10°K.

The analysis of our results and the data of Greer & Meyer (1969) has led to the conclusion that Greer & Meyer (1969) made an error when choosing values and directions of vectors for the monoclinic cell basis. It was for this reason that according to its structure type, α-CF_4 ceased to belong to the series of similar molecular crystals of the CX_4 group. Furthermore, they wrote that 'strange behaviour of the lattice parameters as the temperature changes' was observed in their experiments. In a wide temperature range (up to 40–50°K) the expansion coefficient is negative along **a** and **c**; along **b** a sign of the expansion coefficient changes twice before the transition.

Table 5 presents the comparison of the results of the indexing of experimental X-ray pictures at 40°K made on the basis of the cell proposed by Greer & Meyer (1969) (Q_c^a), and by us (Q_c^b). Better agreement between the experimental and calculated angles of reflexions is seen to be observed for Q_c^b, particularly in the range $2\theta > 40°$. It should be noted that Greer & Meyer (1969) present a considerably smaller number of experimental and calculated reflexions. Thus, in the range $2\theta = 22$–$24°$ they observe the triplet, the angular distance between the triplet lines being equal to $\sim$0·3°, while in reality, as follows from the calculation, there are five lines; as mentioned above, they become apparent in experiments at high temperatures. The first line calculated by the parameters of Greer & Meyer (1969) must occur at an angle which is smaller by 0·4° than that of the first experimental line, and its absence in the experiments may be to a large extent due to incorrect indexing, because its intensity should be considerable.

At the angle $2\theta \sim 29°$ we observe one line instead of a doublet; furthermore, according to the calculation of Greer & Meyer (1969) there must be an extra line at a larger angle than that of the observed line, while in the experiment it becomes apparent on the smaller angle side. We could continue to give examples of the inconsistency of indexing with the experimental results.

The intensity distribution of Bragg reflexion given by Greer & Meyer (1969) also does not correspond to a diffraction picture taken of an equilibrium specimen with homogeneous structure. We have found that a similar distribution of reflexion intensities is observed when the CF_4 films have a texture, and since in order to obtain the finely dispersed structure the specimens (Greer & Meyer, 1969) were considerably deformed plastically, texture formation is not excluded.

The space group C_c proposed for the α-CF_4 structure (Greer & Meyer, 1969) seems to be unlikely, because otherwise we should propose the non-parallelism of the molecule axes $\bar{4}$ to the **b** axis. In the latter case we obtain unequal distances between the F–F neighbour molecules arranged along the axis **b**; this seems to be disadvantageous energetically and to be inconsistent with the close-packing principle.

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