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Monoclinic phase of SF_6 and the orientational ordering transition

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The structure of the low temperature phase of SF_6 is described in terms of a monoclinic unit cell. The mechanism of the phase transition is discussed for this unit cell setting. It can be analysed in terms of three strain components, two molecular displacements and two molecular orientations.

1. Introduction

In a recent publication [1] we presented the results of a neutron powder diffraction study of the structure of the low temperature phase of SF_6. The results were interpreted in terms of a triclinic non-primitive unit cell with space group $P\bar{1}$. It has since been noted that it is possible to describe the same structure in terms of the monoclinic space group, $C2/m$, [2, 1 (note added in proof)], by a simple transformation of axes involving a rotation about the c-axis of approximately 60°. The refined coordinates of reference [1] are consistent with this higher symmetry. In this note, we present the results of our neutron diffraction study in terms of this monoclinic unit cell. The description of the transition mechanism given in reference [1] and the conclusions from the lattice energy calculations presented there remain unchanged within this new description. We simply re-express the main points of the transition mechanism in terms of the revised unit cell setting. The higher symmetry of the monoclinic space group introduces fewer symmetry breaking distortions than the triclinic space group. Consequently, the phase transition can be described in terms of only 3 independent strain distortions and 4 molecular motions.

2. Transformations among the unit cells

We have analysed the neutron powder diffraction data [1] in terms of the space group symmetry $C2/m$ and the results for the unit cell and structural parameters are given in table 1 (*a*), (*b*). The R-factors for the refinements in both monoclinic and triclinic space groups are compared in table 1 (*a*). The two descriptions of the crystal

Table 1 (*a*). The temperature dependence of the structural parameters for the low temperature monoclinic phase of SF_6. The figures in brackets are the errors from the refinements. At 18 K only unit cell parameters were refined. The *R*-factors for the refinements in the triclinic space group $P\bar{1}$ [1] are compared with those in the present monoclinic space group. The Euler angles are defined in [1] and, in that notation, $\phi_1 = \phi_2 = 0°$, $\psi_1 = \psi_2 = 90°$. The centre of mass coordinates for molecule 2 are orthogonal coordinates in Å (those of molecule 1 are 0, 0, 0).

Temperature/K		18	23	75	85
Wavelength λ/Å		4·1037	1·48018	1·83377	1·48018
R (per cent), *C*2/*m*		9·7	5·0	7·9	6·8
R (per cent), $P\bar{1}$		7·2	4·9	7·8	8·2
Lattice parameters					
a/Å		13·84(2)	13·8225(7)	13·953(5)	13·979(3)
b/Å		8·152(10)	8·1474(4)	8·198(3)	8·204(2)
c/Å		4·760(6)	4·7549(2)	4·801(2)	4·8125(9)
β/deg		95·59(1)	95·543(3)	95·15(1)	94·977(6)
Unit cell volume/Å^3		534·31	532·99	546·88	549·77
Euler angles (radians)					
molecule 1, θ_1		−0·5422	−0·550(4)	−0·53(1)	−0·566(8)
molecule 2, θ_2		0·8586	0·856(2)	0·856(6)	0·869(4)
Centre of mass	*x*	4·3667	4·396(2)	4·455(5)	4·462(4)
molecule 2	*y*	0·0	0·0	0·0	0·0
	z	1·9823	1·961(2)	1·955(5)	1·948(3)
S–F bond length (Å)			1·56626(9)	1·56638(5)	1·5624(3)

structure clearly give very similar fits to the data. The structure is shown in projection down the *b*- and *c*-axes in the figure.

The monoclinic cell vectors $\mathbf{a}_m$, $\mathbf{b}_m$, and $\mathbf{c}_m$ are related to the cubic cell vectors by

$$\mathbf{a}_m = a(-1, 2, -1),$$

$$\mathbf{b}_m = a(1, 0, -1),$$

$$\mathbf{c}_m = a(1, 1, 1)/2,$$

where *a* is the cubic unit cell length. The triclinic cell vectors, $\mathbf{a}_t$, $\mathbf{b}_t$ and $\mathbf{c}_t$ given in reference [1] are related to the monoclinic cell vectors by

$$\mathbf{a}_t = (\mathbf{a}_m + 3\mathbf{b}_m)/2,$$

$$\mathbf{b}_t = (-\mathbf{a}_m + \mathbf{b}_m)/2,$$

$$\mathbf{c}_t = \mathbf{c}_m.$$

The first stage of the phase transition mechanism involves a transition from a cubic to a hexagonal structure, with a contraction along ⟨111⟩. As described by Pawley and Dove [3], this involves the orientational ordering of 2/3 of the molecules so that they have orientations close to the average orientations in the cubic structure, but in such a way that the orientational frustration interactions of the disordered phase are minimized [4, 5]. These molecules are labelled 2 and 2′ in the figure. The

Table 1 (*b*). Fractional atomic positions derived from the structural parameters of table 1 (*a*).

Temperature/K			23	75	85
Molecule 1		x	0	0	0
	S	y	0	0	0
		z	0	0	0
		x	−0·0686	−0·0658	−0·0682
	F	y	0	0	0
		z	−0·2822	−0·2821	−0·2750
		x	0·0643	0·0647	0·0630
	F	y	0·1359	0·1351	0·1347
		z	−0·1222	−0·1178	−0·1236
		x	0·0643	0·0647	0·0630
	F	y	−0·1359	−0·1351	−0·1347
		z	−0·1222	−0·1178	−0·1236
Molecule 2		x	0·3318	0·3319	0·3313
	S	y	0	0	0
		z	0·4144	0·4088	0·4064
		x	0·4101	0·4100	0·4104
	F	y	0	0	0
		z	0·1974	0·1941	0·1959
		x	0·2534	0·2537	0·2523
	F	y	0	0	0
		z	0·6314	0·6235	0·6169
		x	0·3902	0·3893	0·3877
	F	y	0·1359	0·1351	0·1347
		z	0·5911	0·5838	0·5823
		x	0·3902	0·3893	0·3877
	F	y	−0·1359	−0·1351	−0·1347
		z	0·5911	0·5838	0·5823
		x	0·2733	0·2745	0·2750
	F	y	0·1359	0·1351	0·1347
		z	0·2377	0·2338	0·2305
		x	0·2733	0·2745	0·2750
	F	y	−0·1359	−0·1351	−0·1347
		z	0·2377	0·2338	0·2305

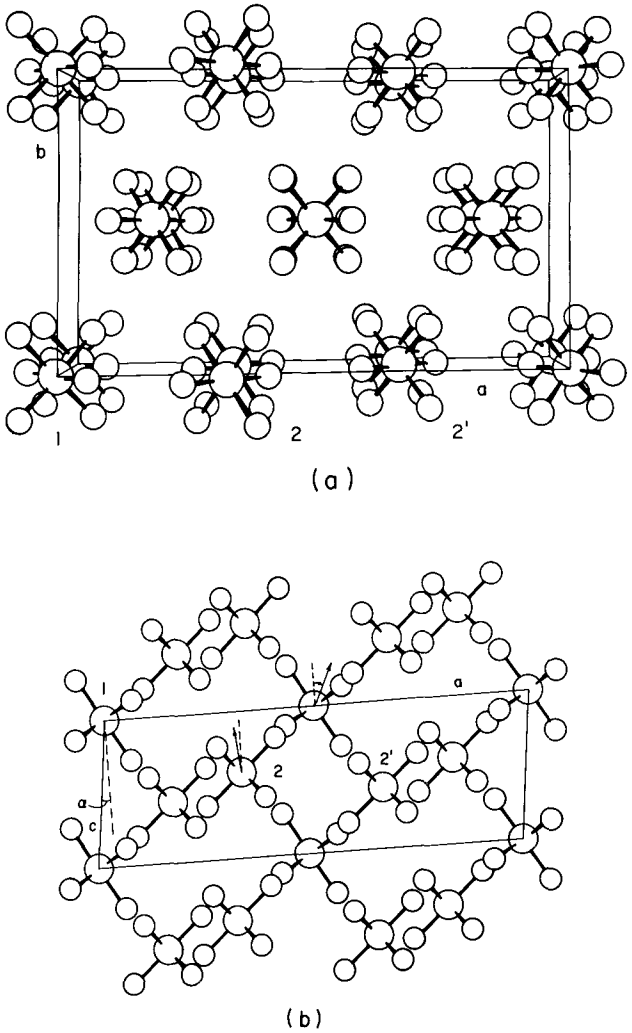
second stage involves a shear of the unit cell in the $\mathbf{a}_h - \mathbf{c}_h$ plane accompanied by the ordering of the remaining molecules (labelled 1 in the figure). Following the definitions given above and in [1], the monoclinic and hexagonal cell vectors are related by

$$\mathbf{a}_m = (\mathbf{a}_h - \mathbf{b}_h),$$

$$\mathbf{b}_m = (\mathbf{a}_h + \mathbf{b}_h),$$

$$\mathbf{c}_m = \mathbf{c}_h$$

and the relationship between the hexagonal, and cubic cell vectors is given in [1]. In our experiments these two stages were found to occur simultaneously, but in electron diffraction experiments [6] the hexagonal phase was observed as a separate, stable phase. Since the orientational ordering is coupled to spontaneous strains (see below), it seems possible that the stability of the different phases is dependent on local strains in the sample. Thus different phases may well be observed in samples prepared by different methods for different measuring techniques.



Low temperature monoclinic structure of SF_6. (*a*) Projection down *c*-axis showing perspective. (*b*) Projection down *b*-axis from infinity.

3. Discussion

The changes in the size and shape of the unit cell can be described by three strain components, e_1, e_2 and e_3, where

$$e_1 = 1 - 4\sqrt{2}c/(a + \sqrt{3}b),$$

$$e_2 = \tan(\beta - 90),$$

$$e_3 = (\sqrt{3}b - a)/(\sqrt{3}b + a)$$

and the unit cell parameters are those of the monoclinic phase. The contraction of the unit cell along c in the cubic to hexagonal transformation is specified by e_1, while e_2 and e_3 specify the hexagonal to monoclinic transformation. All three parameters can be considered to represent order parameters for the transformations.

Table 2. The temperature dependence of the strain components. The strains have been multiplied by 10^4. Standard deviations are given in brackets.

T/K	e_1	e_2	e_3
18	369 (15)	978·7 (1·8)	100·0 (9·5)
23	371·0 (0·5)	970·5 (0·5)	103·5 (0·5)
75	353·0 (4·8)	901·3 (1·8)	87·5 (2·6)
85	342·2 (2·4)	870·8 (1·0)	81·9 (1·6)

The values of these strain components as a function of temperature are given in table 2.

The parameter e_3 is closely proportional to $(e_2)^2$. This suggests that e_2 is the primary order parameter for the hexagonal to monoclinic transformation. The parameter e_3 is a secondary order parameter since it lowers the hexagonal symmetry only to an orthorhombic symmetry. The parameter e_2 however, specifies the complete symmetry breaking distortion. The weakest temperature dependence is shown by e_1 which is consistent with our suggestion of a two stage transition mechanism, with a weak coupling between the cubic to hexagonal and hexagonal to monoclinic transformations. The data of Cockcroft and Fitch [2] are also consistent with this analysis.

The transition can also be described in terms of the orientations and displacements of the molecules. In our two stage model, the orientation of molecule 2 orders in the cubic to hexagonal transformation so that one of its 3-fold axes lies in the direction of the c-axis [1, 3, 6], but in the subsequent hexagonal to monoclinic transformation the molecule is able to tilt by a rotation about the b-axis. The tilt of this axis from the normal to the a–b plane, together with the e_2 shear angle is given as a function of temperature in table 3.

It can be seen from the figure that the rotation angle is in the opposite direction to the shear direction. However, it is clear from table 3 that the magnitude of the rotation angle is approximately equal to that of the e_2 shear angle. Therefore the primary order parameter for the hexagonal to monoclinic transformation is a linear combination of the molecular rotation angle and the e_2 shear.

The other distortions associated with the phase transition are the orientation of molecule 1 (defined again as the tilt of the 3-fold axis from the normal to the a–b plane), the x displacement of molecule 2 (from $a/3$) and the z displacement of molecule 2 (from $c/3$). These distortions are given in table 4. The rotation angle of molecule 1 is not given with sufficient precision to be able to determine its temperature dependence. However, it is clear that the orientation of the 3-fold axis of this molecule is not as close to the hexagonal c-axis as is that for molecule 2. It thus

Table 3. The temperature dependence of the rotation angle of molecule 2 (deg) and of the shear angle $\alpha \equiv (\beta - 90°)$ (deg). Standard deviations are in brackets.

T/K	Rotation angle	$\beta - 90$
23	5·69 (11)	5·543 (3)
75	5·69 (34)	5·15 (1)
85	4·95 (23)	4·977 (6)

Table 4. The temperature dependence of the rotation angle of molecule 1 (deg) and of the x, z displacements of molecule 2 in fractional coordinates. Standard deviations are given in brackets.

T/K	Molecule 1 rotational angle	Molecule 2 x displacement	Molecule 2 z displacement
23	23·22 (22)	0·0016 (4)	0·0811 (10)
75	24·36 (68)	0·0015 (11)	0·0754 (26)
85	22·30 (45)	0·0019 (8)	0·0731 (17)

appears that the orientational ordering of molecule 1 is not associated with the intermediate hexagonal ordering. This is consistent with the computer modelling calculations [3] that suggest this molecule would remain disordered in the hexagonal structure, and would order during the hexagonal to monoclinic transformation. The x displacement of molecule 2, which is only associated with the hexagonal to monoclinic transformation, appears to represent only a small distortion. Although the distortion is observed consistently at all temperatures, its small size in comparison with the precision of the refinements means that we are unable to comment on its temperature dependence. The z displacement is more significant and within the errors is proportional to the e_1 strain component associated with the cubic to hexagonal transformation. It therefore seems to be associated primarily with this transformation rather than the hexagonal to monoclinic transformation.

4. Conclusion

The description of the structure of the low temperature phase of SF_6 in terms of a monoclinic rather than triclinic symmetry has facilitated the analysis of the phase transition in terms of three unique strain components, two molecular orientations, and two molecular displacements. The results are consistent with the two stage transformation mechanism proposed earlier [1]. The description still lacks a detailed analysis of the molecular orientational ordering associated with the cubic to hexagonal transformation (molecule 2) and with the hexagonal to monoclinic transformation (molecule 1). Presumably these two orderings are associated with the amplitudes of the symmetry breaking harmonics in the orientational distribution function, but this information is difficult to extract from powder diffraction refinements of low symmetry structures. This is particularly so in the present case, where there is evidence of strong diffuse scattering associated with residual disorder.

References

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