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An Electron Diffraction Study of the Structures of Sulphur Hexafluoride below 94 K

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Abstract

Single-crystal electron diffraction patterns were obtained from SF₆ crystals condensed in an environmental cell in a 200 kV transmission electron microscope. Between 50 ± 5 K and 94 K the lattice was found to be hexagonal, with $a = 8.01$ (12) and $c = 4.83$ (7) Å. Consideration of the packing of SF₆ molecules shows that this phase is isostructural with UCl₆, having space group $P\bar{3}m1$ with $Z = 3$. At lower temperatures ($T < 50 \pm 5$ K) this structure was found to distort slightly to a C face-centred monoclinic (or conceivably even lower symmetry) lattice with $a = 8.01$ (12), $b = 13.9$ (2), $c = 4.83$ (7) Å and $\beta = 92.5$ (5)° with $Z = 6$. These observations are correlated with previous NMR and Raman-scattering results.

Introduction

Sulphur hexafluoride belongs to a group of transition-metal and Group VIa hexafluorides which all have broadly similar structural properties (Taylor, 1976). With the exception of the actinide hexafluorides they condense initially into an orientationally disordered body-centred cubic structure, which is characterized by rapid molecular reorientation and low barriers to molecular self-diffusion. At lower temperatures a phase transition occurs to a lower-symmetry structure. The crystallography of the low-temperature phase of several transition-metal hexafluorides has been determined

(Levy, Taylor & Wilson, 1975). They have been found to be isostructural with UF₆ (Levy, Taylor & Wilson, 1976), being orthorhombic, with space group $Pnma$ and $Z = 4$. It appears, however, that no low-temperature crystallographic work has been carried out on SF₆ or any of the other Group VIa hexafluorides.

SF₆ condenses at 222.4 K and undergoes a phase transition to the low-temperature phase at 94 K. Neutron diffraction (Taylor & Waugh, 1976; Dolling, Powell & Sears, 1979) and NMR (Blinic & Lahajnar, 1967) studies of the high-temperature phase confirm the b.c.c. structure and the orientational disorder of the molecules. Some orientational order is present since the S–F bonds tend to be aligned along $\langle 100 \rangle$ directions.

NMR of the low-temperature phase (Garg, 1977) suggests that molecules occupy two inequivalent lattice sites, with a fraction of $\sim \frac{1}{4}$ of the molecules still undergoing quite rapid reorientation while the rest are orientationally more ordered. The results of a study of the Raman spectrum (Gilbert & Drifford, 1972) appear to confirm the presence of two inequivalent lattice sites.

In the present work, selected-area electron diffraction was used to study the low-temperature phase of SF₆. The advantage of this method over X-ray or neutron diffraction lies in the fact that the diffraction pattern is collected from an area of crystal only $\sim 1 \mu\text{m}^2$ in size. Hence single-crystal patterns could be obtained even though it was not possible to prepare crystals larger than a few μm in diameter. Because of the dynamical nature of electron diffraction, it was not possible to determine the structure factors. However, having found the unit-cell dimensions, it was possible to determine the approximate atomic positions from consideration of the packing of SF₆ molecules.

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Experimental conditions

The liquid-helium-cooled stage fitted to a JEOL 200A transmission electron microscope has been described previously (Tatlock, Spain, Raynerd, Sinnock & Venables, 1980). Subsequent improvements allowed samples to be cooled to a minimum temperature of 12 K. This stage may be used in conjunction with an environmental cell for the study of condensed gases. The side-entry specimen rod, incorporating the environmental cell, is shown in Fig. 1. The specimen may be tilted by up to $\pm 30^\circ$ about the rod axis.

The cell itself consists of two electron-transparent windows separated by a distance of 0.5 mm. The space between the windows is isolated from the microscope-column vacuum and may be filled with gas at a maximum pressure of ~ 30 kPa. The upper window consists of a Pioloform film of thickness ~ 500 Å laid over a 200 mesh copper electron microscope grid. A 100 Å layer of aluminium is evaporated over the Pioloform to prevent charging in the electron beam at low temperatures. Two different types of lower window were used during the course of this work. The first type was similar to the upper window, with a layer of 300 Å of aluminium on Pioloform. Single-crystal patterns could then be obtained superimposed on the polycrystalline aluminium ring pattern, allowing the crystal lattice parameters to be measured. The second type consisted of a Pioloform film, to provide a gas-tight seal, laid over a graphite film supported on a copper grid with 20 μm holes. The graphite provided mechanical strength to support the crystal and sufficiently high thermal conductivity to allow thin crystals to be grown away from the grid bars.

With the specimen rod inserted into the microscope, the cell is clamped inside a copper cooling block. A small cryostat situated in the back pumping line of the microscope contains liquid helium, which is pumped (through the top of the objective-lens pole piece) to the cooling block and to radiation shields around the specimen. The specimen temperature may be altered by changing the helium flow rate and by the use of a small heater situated close to the specimen. The specimen

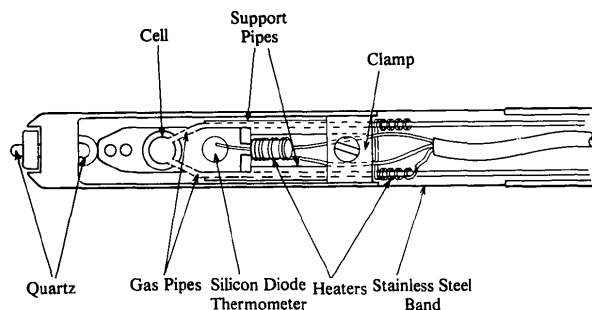


Fig. 1. The specimen rod. Electron-transparent windows (not shown) seal against the top and bottom of the cell using indium seals.

temperature is monitored using a silicon diode thermometer.

SF_6 gas (nominal purity 99.99%, from Matheson Ltd) was introduced to the cell at a pressure of 7 kPa and slowly cooled. Crystals condensed on the lower window at 175 K and were thinned by pumping gas from the cell, while being observed at low magnification. Crystals several μm across were formed which were sufficiently thin for transmission electron microscopy. Single-crystal diffraction patterns were obtained from these crystals using conventional selected-area diffraction techniques.

Electron diffraction patterns

Diffraction patterns obtained in the temperature range 50 ± 5 K to 94 K could be indexed in terms of a hexagonal lattice with $a = 8.01(12)$ and $c = 4.83(7)$ Å. This lattice can also be described as a C face-centred orthorhombic lattice with $b = \sqrt{3}a = 13.9(2)$ Å, a and c remaining the same. Since we have only determined the axes with limited precision it is possible that this is the true crystal lattice. The most characteristic feature of these diffraction patterns is a tripling of the spacing of a (211) plane of the b.c.c. lattice. Examples, which are indexed in terms of the orthorhombic lattice, are given in Fig. 2.

At lower temperatures ($T < \sim 50$ K) small distortions in interplanar angles were observed, in that angles which are 90° on a hexagonal or orthorhombic cell become distorted by up to 3° . These distortions could be measured to $\pm \frac{1}{2} - 1^\circ$ accuracy. Measurements were made on some 40 individual crystallites at temperatures in the range $15 < T < 90$ K. The values of these distortions are plotted against temperature in Fig. 3. The considerable scatter in the results arising from the large errors involved in the measurement makes difficult the precise determination of the temperature at which the onset of the distortion occurs. A further scatter in the results arises from the fact that equivalent directions in the hexagonal lattice become inequivalent in the distorted phase. Observations on individual crystallites over a range of temperatures showed the onset of the distortion at ~ 50 K and did not show any change in the size of the distortion below this temperature, within the limited precision available.

A more accurate determination of the size and direction of the distortion may be made from patterns arising from twinned crystals where the distortion occurs in two opposite senses, leading to a splitting of diffraction spots (Fig. 4). These are consistent with a shear of (001) planes along the a axis of the orthorhombic lattice, leading to a C face-centred monoclinic lattice with lattice parameters as for the orthorhombic lattice and $\beta = 92.5(5)^\circ$. Further support for this monoclinic distortion is provided by the

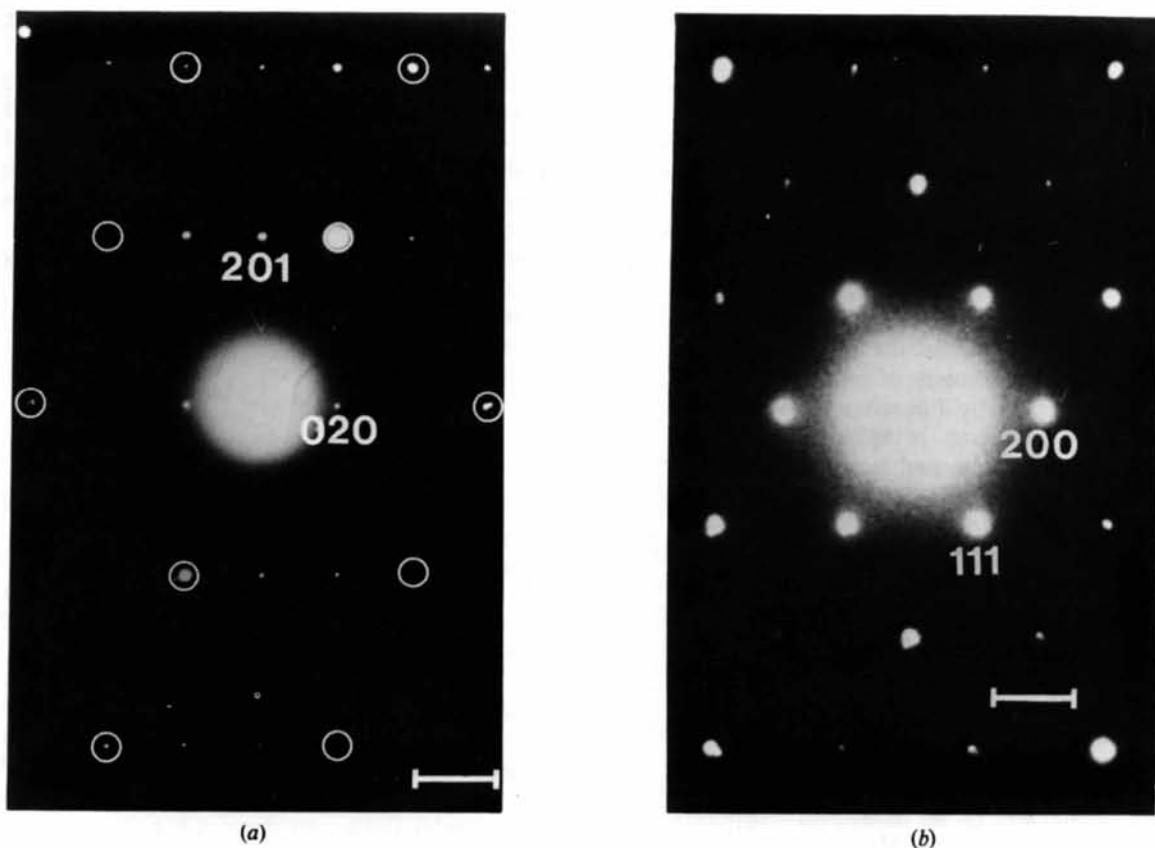


Fig. 2. Selected-area electron diffraction patterns from two SF_6 crystalites, indexed with respect to the orthorhombic lattice. (a) $T = 54$ K, (b) $T = 48$ K. Pattern (a) exhibits the tripling of the spacing of a (211) plane in the b.c.c. structure; the ringed spots are those present in the b.c.c. diffraction pattern. The 020 orthorhombic reflection is equivalent to the $10\bar{1}0$ hexagonal reflection and these have a d spacing of $3d(211)\text{b.c.c.}$ All the spots in pattern (b) are also present in the b.c.c. pattern. The bars represent 1 \AA^{-1} .

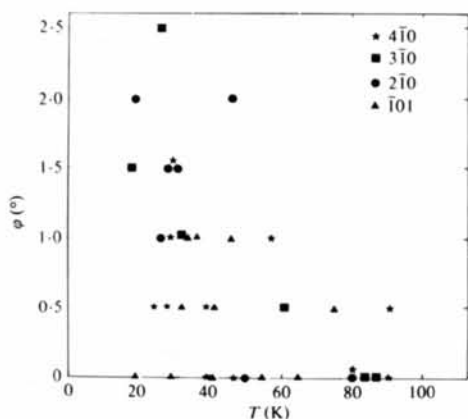


Fig. 3. Measured distortions from the orthorhombic lattice in individual diffraction patterns from four frequently observed crystal orientations. The angle ϕ is the difference between the measured angle and 90° .

fact that several $(10\bar{1})$ patterns (perpendicular to the distortion) show no evidence of the distortion at any temperature (Fig. 3). Those which are distorted are probably actually $(11\bar{2})$ which would be equivalent to $(10\bar{1})$ in the orthorhombic lattice in the absence of any distortion. Our limited accuracy does, however, mean that the distorted phase may have symmetry even lower than monoclinic.

Packing model

In discussing molecular packing, we shall initially consider only the undistorted hexagonal unit cell. The dimensions of this cell imply a density for the low-temperature phase of $(0.91 \pm 0.02)Z \text{ g cm}^{-3}$ where Z is the number of molecules per unit cell. The measured density of this phase is 2.68 g cm^{-3} (Klemm

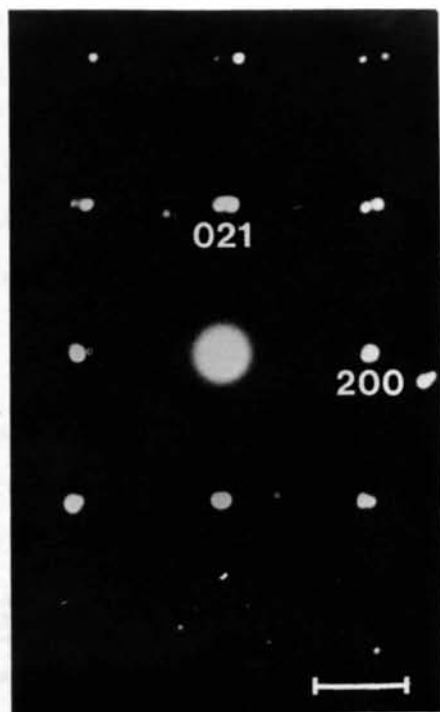


Fig. 4. Selected-area electron diffraction pattern from a twinned SF_6 crystal in the monoclinic phase. The 021 spot is split because of a distortion in opposite senses along the a axis of the orthorhombic lattice, while the 200 spot is not split. The bar represents 1 \AA^{-1} .

& Henkel, 1932). For $Z = 3$ we find a density of $2.73 \pm 0.06 \text{ g cm}^{-3}$. It is clear, therefore, that the experimentally determined unit cell must contain three molecules. This rules out the UF_6 structure, adopted by the low-temperature forms of MoF_6 and WF_6 , which has four molecules per unit cell.

Given the known octahedral molecular structure of the SF_6 molecule, this can only be achieved by almost hexagonal close packing of the F atoms, with S atoms filling some of the octahedral holes between the F atoms. This leads to the structure shown in Fig. 5(a). In this structure, molecule (1), centred at the origin, is rotated by 60° with respect to molecules (2) and (3) which are centred at $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, \bar{z})$, with $z \sim \frac{1}{2}$.

The structure thus produced belongs to space group $P\bar{3}m1$ (D_{3d}^3 , No. 164) with S atoms on positions (a) $(0,0,0)$ and (d) $(\frac{1}{3}, \frac{1}{3}, \bar{z})$, $(\frac{1}{3}, \frac{2}{3}, z)$ and F atoms on positions (i) $\pm(x\bar{x}z)$, $\pm(x, 2x, z)$, $\pm(2\bar{x}, \bar{x}, z)$ where x and z are determined by the S–F bond length. This is isostructural with UCl_6 (Zachariasen, 1948) and $\beta\text{-WCl}_6$ (Taylor & Wilson, 1974). It is also one of the possible structures predicted by Kihara (1975) for SF_6 on the basis of the packing of molecular models.

The z coordinates of the S atoms on positions (d) are not determined by symmetry considerations. A simple

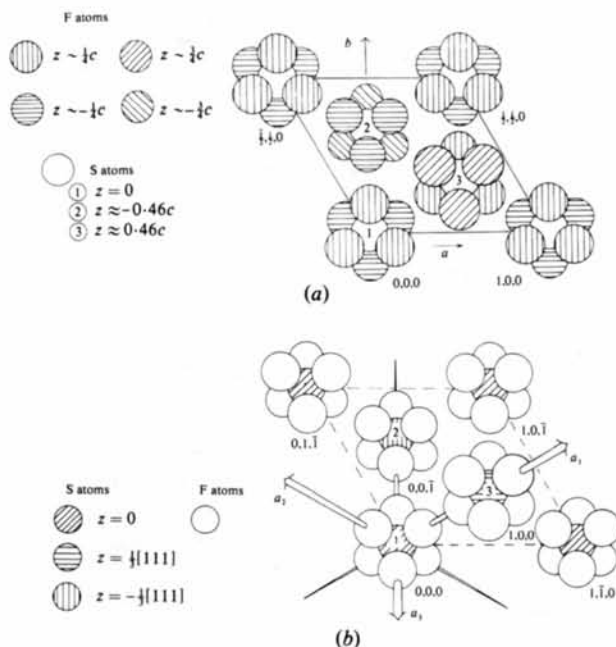


Fig. 5. (a) Packing model of the low-temperature structure. The F atoms are shaded to show their quasi-hexagonal close packing. (b) Projection down a $\langle 111 \rangle$ direction of the b.c.c. phase showing its similarity to the low-temperature structure. a_1 , a_2 and a_3 are the axes of the b.c.c. lattice.

potential calculation was therefore carried out to estimate these z coordinates. The molecules were positioned as described above, using the measured lattice parameters, and the potential was minimized by allowing the z coordinates of molecules (2) and (3) to vary. A Lennard-Jones atom–atom potential over nearest and second-nearest intermolecular neighbours was used. Lennard-Jones parameters for S–S, F–F and S–F interactions were taken from Downs, Gubbins, Murad & Gray (1979). This potential was minimized for $z = 0.46$. At this value of z , the intermolecular nearest-neighbour F–F distances range from 2.95 to 3.35 Å, compared with an intramolecular F–F separation of 2.21 Å.

Relationship to the high-temperature structure

Fig. 5(b) shows a projection down the $\langle 111 \rangle$ axis of the high-temperature b.c.c. structure, the F atoms pointing along $\langle 100 \rangle$ directions. It is clear that the symmetry of the low-temperature structure is obtained simply by rotating molecule (1) by 60° about the $\langle 111 \rangle$ axis (*cf.* Fig. 5a). Molecules (1), (2) and (3) then form the basis of the new structure with hexagonal lattice parameters $a = a \langle 1\bar{1}0 \rangle$ b.c.c. and $c = a/2 \langle 111 \rangle$ b.c.c. For the

orthorhombic indices $a = a \langle 1\bar{1}0 \rangle$ b.c.c., $b = a \langle 11\bar{2} \rangle$ and $c = a/2 \langle 111 \rangle$. The b.c.c. phase has lattice parameter $a = 5.79 \text{ \AA}$, implying hexagonal lattice parameters $a = 8.19$ and $c = 5.01 \text{ \AA}$. These are slightly higher than the measured values for the hexagonal phase in accordance with the measured density change for the phase transition.

The low-temperature distortion

An NMR study of solid SF_6 (Garg, 1977) showed that between 45 and 94 K, SF_6 molecules occupy two inequivalent lattice sites. Approximately $\frac{1}{4}$ of the molecules are orientationally ordered, while the rest are orientationally disordered. Raman-spectrum measurements (Gilbert & Drifford, 1972) also suggested the presence of two distinct lattice sites. In the present model of the low-temperature SF_6 structure, $\frac{1}{3}$ of the molecules [molecule (1) in Fig. 5(a)] experience a different site symmetry from the remainder. This appears, therefore, to be compatible with the above observations. Garg's (1977) work also showed, however, that the remaining fraction of molecules became ordered below 45 K. It appears likely that the distortion observed at low temperatures is connected with this increase in molecular ordering.

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