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Orientational Disorder in the Plastic Phases of SF_6 and CBr_4

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The coherent, elastic neutron scattering from polycrystalline samples of SF_6 and CBr_4 in their plastic phases has been measured. The powder line component of the neutron distributions has been analysed in terms of Debye-Waller factors to give information about the orientational disorder in the solids. An extensive diffuse scattering component is also observed in CBr_4. The scattering calculated for a simple model of the molecular disorder in CBr_4 agrees reasonably well with this observed diffuse scattering, but improvements in the model are clearly necessary.

INTRODUCTION

Many molecular solids crystallise from the liquid into a solid phase in which the molecular centres of mass occupy well-defined sites on a regular crystalline lattice, while the molecular orientations about the centres of mass are very ill-defined. The molecules may execute large amplitude oscillations or complete reorientations, leading to an effective orientational disorder of static or dynamic character. These solids have at least one solid-solid phase transition, and the high temperature, orientationally disordered or "plastic" phase often has cubic symmetry. Sulphur hexafluoride (SF_6) and carbon tetrabromide (CBr_4) are two simple molecules which solidify from the melt into a plastic phase and have a single phase transition at lower temperature. The plastic phase of SF_6 exists from its melting point (223 K) to 96 K and the crystal lattice in this phase is body-centered cubic. Below 96 K the crystal becomes a "normal" ordered solid whose detailed structure is not yet known. The plastic phase of CBr_4 exists from its melting point (365 K) to 319 K and its crystal lattice is face-centered cubic. The crystal structure at room temperature has recently been determined.[1] It is monoclinic (space group C2/c) with 32 molecules in the unit cell.

In the present paper we describe coherent, elastic neutron scattering measurements on polycrystalline samples of these molecular solids in their plastic phases. The discrete components of the scattered neutron distributions are analysed in terms of Debye–Waller factors, to give information about the orientational disorder in the solids. Extensive diffuse scattering is also observed in CBr_4, and this is compared with the scattering calculated from a simple model for the molecular orientational disorder.

EXPERIMENTAL DETAILS

The polycrystalline sample of SF_6 was prepared by rapid condensation of the gas into a quartz container held in liquid nitrogen. The sample was transferred to a variable temperature cryostat suitable for neutron diffraction measurements. The cryostat was rotated continuously during the measurements to minimize any effects due to grain size or preferred orientation, and the temperature was maintained below 110 K to minimize possible annealing in the sample. The neutron diffraction measurements were made on the N5 spectrometer at the NRU reactor, Chalk River. The monochromator and analyser were Si(113) and Be(002) reflections respectively and the wavelength, λ, was 1.57 Å. The analyser was used to reduce the background due to inelastically scattered neutrons. The scattering angle 2θ was varied from 20° to 125° and measurements were made at temperatures of 96.5, 98, 100 and 110 K. After subtraction of the empty container background the integrated intensities of 19 Debye–Scherrer powder lines were measured at each temperature, the corresponding Miller indices ranging from (110) to (620). The powder lines were all well-defined (although several were very weak) and there was little evidence of diffuse elastic scattering between the powder lines.

The neutron diffraction measurements on polycrystalline CBr_4 were made with Ge(113) and Cu(002) as monochromator and analyser respectively. Otherwise the experimental conditions were identical to those used for the measurements on SF_6. Scans were made at temperatures of 320 and 345 K. In contrast to the results from SF_6, in CBr_4 only two Debye–Scherrer lines were clearly observed and these were identified as (111) and (200). The remaining powder lines were extremely weak, indicating a dramatic decrease in intensity at larger scattering angles. Further, a rather broad intense diffuse scattering peak was observed at a momentum transfer $Q \sim 2$ Å^{-1} [$Q = (4\pi/\lambda)\sin\theta$] and additional diffuse scattering was apparent at larger scattering angles. This is in further contrast with the results from SF_6. More precise measurements of the weak Debye–Scherrer lines and the diffuse scattering were not possible because of the significant background scattering

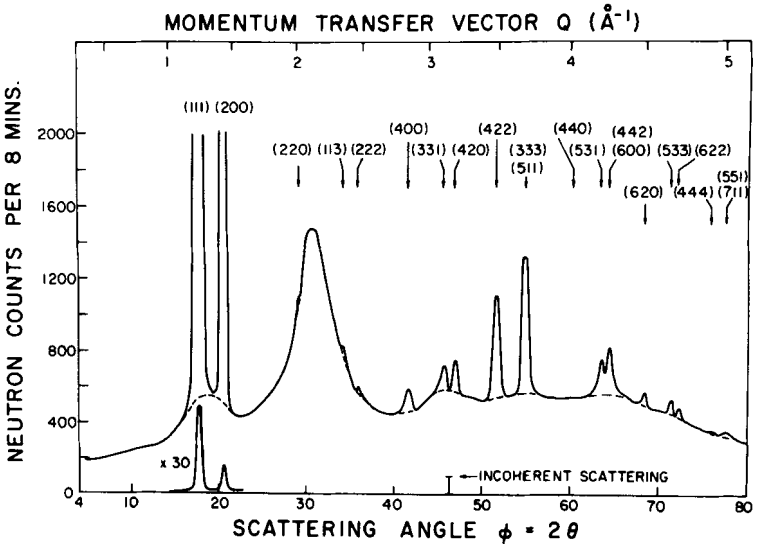

FIGURE 1 Coherent, elastic neutron scattering distribution from CBr_4 at 320 K. The neutron wavelength, $\lambda = 1.57$ Å. The dashed line shows the diffuse component of the distribution beneath the discrete powder lines.

from the quartz container. A new sample container was thus constructed from thin-walled vanadium tube, the inside of which was coated with a thin film of graphite[2] to protect it from corrosion by the CBr_4. The background scattering from this container was very weak and almost independent of scattering angle, thus enabling more details to be observed in the scattering from the CBr_4. The scattering neutron distribution measured at 320 K with this container is shown in Figure 1. The integrated intensities of 18 Debye–Scherrer lines, with Miller indices extending from (111) to (711), were measured at both temperatures.

In order to measure the diffuse scattering from CBr_4 the experimental configuration was changed. The analyser was removed, so the structure factor $S(\mathbf{Q})$ rather than the scattering law $S(\mathbf{Q}, \omega = 0)$ was measured; and a wavelength of $\lambda = 1.09$ Å was used to enable larger values of Q to be attained. The diffraction pattern between $Q = 0.5$ Å^{-1} and 9 Å^{-1} was measured at several temperatures. Figure 2 shows the diffuse scattering remaining after the discrete Debye–Scherrer line component of the distribution is subtracted. The scattering shows several broad peaks, the most prominent occurring at $Q = 2.1$ Å^{-1}. The oscillations in intensity continue as far as the largest experimentally accessible Q and the integrated intensity of the diffuse scattering is significantly greater than that of the powder line component. The diffuse scattering appears to be independent of temperature and is very

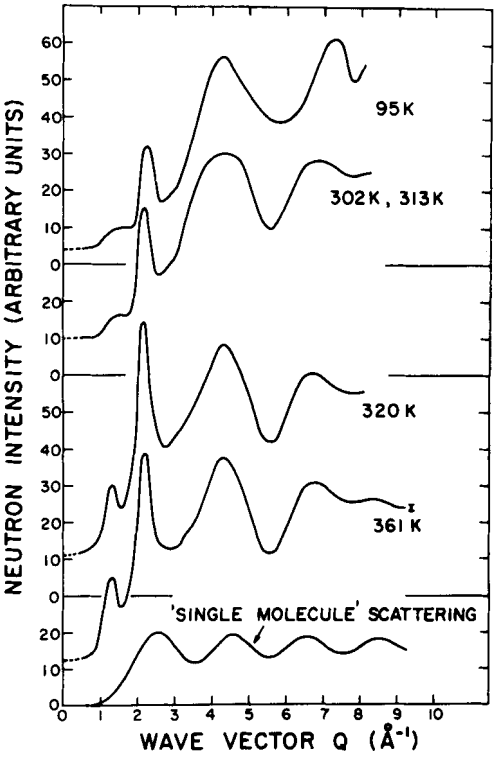

FIGURE 2 The temperature dependence of the diffuse elastic scattering from CBr_4. The neutron wavelength, $\lambda = 1.09$ Å, and the temperature of the plastic-normal transition for our specimen was 319 K. The curve labelled "single molecule scattering" is calculated from Ref. 6.

reminiscent of the scattering which would be expected from a molecular liquid. It is the presence of this intense diffuse scattering in CBr_4 which suggests that the plastic phases of SF_6 and CBr_4 are different in character.

ANALYSIS

The intensities of the Debye–Scherrer lines have been analysed in terms of a Debye–Waller factor appropriate to the case of rigid molecules executing large amplitude librations. The structure factor for the Bragg reflection $\mathbf{B}(\equiv hkl)$ can be written as:[3]

$$F(\mathbf{B}) = \sum_k \exp(i\mathbf{B}\cdot\mathbf{r}_k)\exp(-\tfrac{1}{2}B^2\langle U_k^2\rangle)\sum_s F_s^{lib}(\mathbf{B}) \qquad (1)$$

where $\mathbf{r}_k$ is the equilibrium position of the centre of mass of molecule k in the unit cell, $\langle U_k^2 \rangle$ is the mean square translational displacement of this centre of mass, and $B = |\mathbf{B}|$.

$$F_s^{lib}(\mathbf{B}) = 4\pi b_s \sum_{lm} i^l j_l(BR_s) C_{lm} K_{lm}(\Omega_B) \tag{2}$$

where b_s is the coherent neutron scattering length of atom s,

R_s is the radius of the sth atomic shell in molecule k,

$j_l(x)$ is a spherical Bessel function of argument x,

$K_{lm}(\Omega_B)$ is a Kubic Harmonic whose argument Ω_B denotes the polar coordinates of the reciprocal lattice vector $\mathbf{B}$,

C_{lm} are the expansion coefficients of the Kubic Harmonic series.

The Kubic Harmonics are normalised such that the zeroth order term in the expansion ($l = 0$) describes atom s as uniformly distributed over a spherical shell of radius R_s. Such a distribution would correspond to a completely freely rotating molecule. Higher order terms in the expansion describe localisation of atoms s on this spherical shell and the magnitude of the coefficients C_{lm} measures the degree of localisation. The symmetry of the localisation represented by each term is specified by the order l of the term. The structure factors defined by Eqs. 1 and 2 are substituted into the standard expression for the intensity of Debye–Scherrer lines scattered from a polycrystalline specimen.[4] The disposable parameters in this expression are then $\langle U_k^2 \rangle$ and the coefficients C_{lm}. These parameters, together with a scale factor, are determined by fitting to the experimental integrated intensities. The molecular symmetry of SF_6 is octahedral and that of CBr_4 is tetrahedral. This high symmetry restricts the expansion to certain even order terms—for $m = 1$, $l = 0, 4, 5, 6, \ldots$.

The results of this analysis for SF_6 are shown in Table I. The dominant harmonic at all the temperatures is clearly that of fourth order, but both sixth and eighth order harmonics are also significant. The large, positive value for C_4 strongly favours localisation of the fluorine atoms on the $\langle 100 \rangle$

TABLE I

Kubic Harmonic analysis of the Debye–Scherrer line intensities from SF_6 ($C_0 \equiv 1$).

	Temperature (K)			
Coefficient C_l	96.5	98	100	110
C_4	1.47 ± 0.04	1.46 ± 0.03	1.36 ± 0.03	1.28 ± 0.03
C_6	0.32 ± 0.04	0.31 ± 0.04	0.36 ± 0.03	0.31 ± 0.04
C_8	0.80 ± 0.08	0.78 ± 0.07	0.73 ± 0.05	0.62 ± 0.07
$\langle U^2 \rangle$ Å^2	0.029 ± 0.003	0.029 ± 0.003	0.028 ± 0.002	0.027 ± 0.003

TABLE II

Kubic Harmonic analysis of the Debye-Scherrer line intensities from CBr_4 ($C_0 \equiv 1$). The values for 325 K are taken from Ref. 7.

	Temperature (K)		
Coefficient C_l	320	345	325
C_4	0.06 ± 0.06	0.18 ± 0.08	0.077 ± 0.003
C_6	−0.75 ± 0.11	−0.84 ± 0.14	−0.85 ± 0.03
$\langle U^2 \rangle$ Å^2	0.166 ± 0.007	0.189 ± 0.008	0.20

axes. The positive coefficient of the sixth order term however favours localisation on ⟨111⟩ axes, while the eighth order term tends to localise the atoms on ⟨100⟩ and less strongly on ⟨111⟩ and ⟨110⟩ axes. The net result is that the fluorines are localised in the vicinity of the ⟨100⟩ axes, but with a distribution which leads to an effective librational amplitude of 12° to 15°. The temperature dependence of the coefficients suggests that as the temperature is lowered the localisation of the fluorines on the ⟨100⟩ axes increases. The crystal structure of the plastic phase of SF_6 is thus similar to that of a normal solid. It has a rather large value for the mean square translational displacement $\langle U^2 \rangle$ and a large "effective" librational amplitude.

The results of the Kubic Harmonic analyses for CBr_4 are given in Table II. The sixth order harmonic completely dominates the expansion, and the large negative coefficient shows that the bromines are strongly localised on the ⟨110⟩ axes. The four bromine atoms are distributed among these twelve sites. The crystal structure of the plastic phase of CBr_4 is thus highly disordered with an enormous value for $\langle U^2 \rangle$ and an effective librational amplitude of ~30°. There appears to be little temperature dependence of this structure near the phase transition.

In order to interpret the diffuse scattering from CBr_4 the structure factor $S(\mathbf{Q})$ is expressed as a sum of two terms.[5]

$$\begin{aligned} S(\mathbf{Q}) &= S_c(\mathbf{Q}) + S_d(\mathbf{Q}) \\ &= |\langle b(\mathbf{Q}) \rangle|^2 + \langle |\delta b(\mathbf{Q})|^2 \rangle \end{aligned} \tag{3}$$

where

$$\delta b(\mathbf{Q}) = b(\mathbf{Q}) - \langle b(\mathbf{Q}) \rangle$$

and

$$b(\mathbf{Q}) = \sum_{k,s} b_{k,s} \exp(i\mathbf{Q} \cdot \mathbf{r}_{ks}).$$

b_{ks} is the neutron scattering length of atom s in molecule k and $\mathbf{r}_{ks} = \mathbf{r}_k + \mathbf{r}_s$ where $\mathbf{r}_s$ is the position vector of atom s in molecule k, relative to the molecular centre of mass.

The coherent elastic scattering, $S_c(\mathbf{Q})$, arises from the mean value of $b(\mathbf{Q})$ while the diffuse scattering, $S_d(\mathbf{Q})$, arises from fluctuations in $b(\mathbf{Q})$. The fluctuations may be due to disorder in the scattering lengths b_{ks} (purely incoherent scattering), or due to positional disorder in the atomic position vectors $\mathbf{r}_{ks}$. It is the latter disorder with which we are concerned. If we assume that the CBr_4 molecules are rigid rotators of completely random orientation then $S_d(\mathbf{Q})$ can be calculated.[6] The oscillatory component of $S_d(\mathbf{Q})$ arising from the positional disorder of the Br atoms is shown as the curve labelled "single molecule scattering" in Figure 2. It can be seen that the positions of the observed oscillations agree quite well with those calculated for $Q \gtrsim 4\,\text{Å}^{-1}$, indicating that in this region the observed distribution is dominated by scattering from single molecules. The relative intensities of the observed

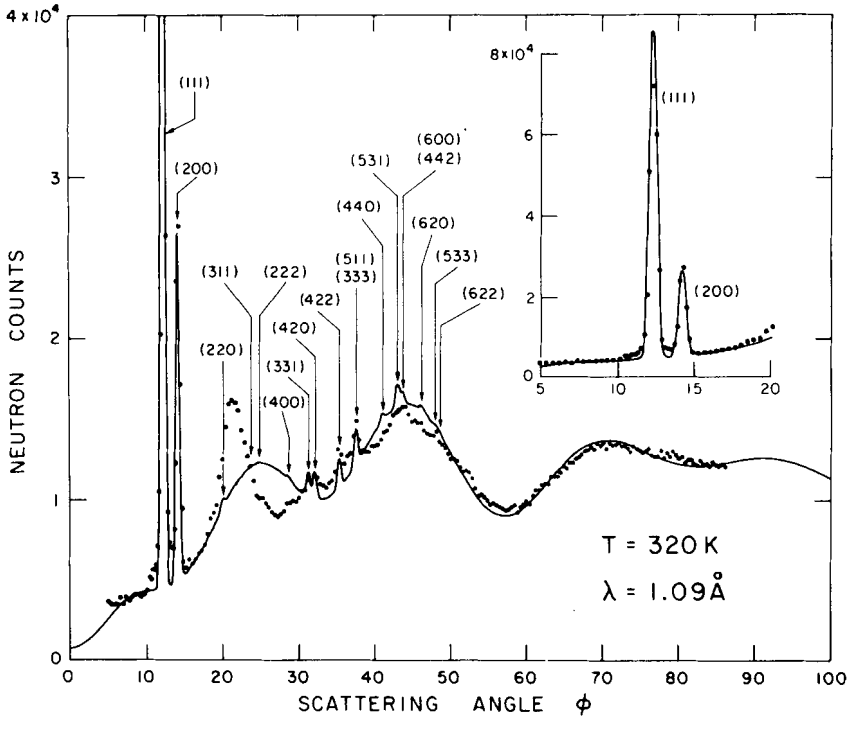

FIGURE 3 Comparison between the observed (dotted curve) and calculated (continuous curve) $S(\mathbf{Q})$ from CBr_4 at 320 K. The experimental neutron wavelength, $\lambda = 1.09$ Å. The calculated curve is from equation 3 (see Ref. 5) and assumes the CBr_4 molecule to be a rigid rotator of random orientation.

oscillations however are not well described by the "single molecule" calculation. For $Q < 4$ Å^{-1} significant discrepancies between the phases of the observed and calculated curves are evident. This suggests that correlations between neighbouring molecules, which are neglected in this calculation for $S_d(\mathbf{Q})$, are important in this region.

The *total* scattering distribution, $S(\mathbf{Q})$, has also been calculated from Eq. 3 for the same model of molecular disorder.[5] The calculation includes the effect of the translational Debye–Waller factor, specified by $\langle U^2 \rangle$ in Table II, and the Placzek correction has been applied to the term $S_d(\mathbf{Q})$. The calculated intensity is averaged to apply to a polycrystalline sample and is convoluted with the approximate neutron spectrometer resolution function. The result of this calculation is compared with the experimental $S(Q)$ at 320 K in Figure 3. Qualitatively the agreement is seen to be very good, with the relative magnitudes of the powder and diffuse components of the distribution calculated correctly. The oscillatory behaviour at large Q is also well reproduced by the calculation, but discrepancies clearly exist at small Q. The analysis of the powder line component given above shows that the approximation of randomly oriented molecules is not satisfactory: modifications to incorporate a more realistic Br distribution are clearly needed in order to improve the agreement.

The crystal structure of the plastic phase of SF_6 has been shown to be similar to that of a normal solid, but with large values for its mean square translational and librational displacements. Little evidence of diffuse scattering was observed. The magnitudes of the corresponding quantities in CBr_4 show its structure in the plastic phase to be an example of a highly disordered solid, and intense diffuse scattering was also observed. These differences in the crystal structures indicate that the plastic phases of SF_6 and CBr_4 are of significantly different character.

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