

this figure, the unshared O atoms are in the staggered conformation, whereas (b) and (c) represent two possible eclipsed forms. Further classification of the discussed group of compounds is based on the value of the $X-O-X$ interbond angle which, in theory, can vary from 102 to 180° (Clark, 1972). Usually it falls within the range 110–155°. The $Mo_2O_7^{2-}$ ion described in the present paper is close to the configuration in Fig. 3(c) with a twist angle of 12° and Mo–O–Mo angle of 161°.

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Solid-State Phase Transition in Carbon Tetrabromide.

II. The Crystal Structure of Phase I

BY M. MORE, J. LEFEBVRE AND R. FOURET

Laboratoire de Physique des Solides, Equipe de Dynamique des Cristaux Moléculaires associée au CNRS (n° 465), Université de Lille I, BP 36, 59650 Villeneuve d'Ascq, France

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Phase I of CBr_4 (above 47°C) is cubic, space group $Fm\bar{3}m$, with $a = 8.82 \text{ \AA}$, $Z = 4$. The molecules are orientationally disordered and the structure is described by the use of symmetry-adapted functions. The orientational probability is discussed in terms of these functions.

Introduction

The high-temperature phase of CBr_4 (above 47°C) is 'plastic' with the molecules orientationally disordered.

As a first approximation, the disorder can be interpreted by assuming that the molecule occupies at random any one of N distinguishable orientations, the mean symmetry being cubic (Frankel model). If one neglects correlations, thermal entropy, *etc.*, the transition entropy is approximately $\Delta S_t = R \ln N$.

In CBr_4 , $\Delta S_t = 4.98 \text{ cal K}^{-1} \text{ mol}^{-1}$ (Marshall, Staveley & Hart, 1956; Hildebrand & Scott, 1950).

Guthrie & McCullough (1961) suppose that the orientational disorder corresponds to the 10 distinguishable orientations of the combined T_d and C_{3v} symmetry ($R \ln 10 = 4.58 \text{ cal K}^{-1} \text{ mol}^{-1}$).

In a previous paper (More, Baert & Lefebvre, 1977), we reported that one can expect six different molecular orientations corresponding to D_{2d} local symmetry.

However, a classical refinement of the high-temperature-phase diffraction data, based on a Frankel model with six equilibrium positions, has failed.

In this paper, we report the structure refined by the use of symmetry-adapted functions. This method takes

into account the rotational motions and it is shown that no well defined equilibrium positions exist for the atoms.

Experimental

Because of the high absorption for X-rays, neutrons were used. A powder experiment at the H12 spectrometer at the Saclay Reactor failed because of rapid sublimation (Meriel, 1977). Thus single-crystal neutron diffraction was necessary.

Sample preparation

A single crystal was grown from vapour at 52°C in a sphere of quartz (0.3 cm³) and set in an aluminium furnace. The temperature was controlled by a thermistor and, to prevent sublimation, a temperature gradient was applied.

Data collection

Data were collected at 52.0 ± 0.5°C on the H9 spectrometer (Saclay). A monochromatic beam (λ = 1.197 Å) was used. ω-2θ scans were made for all Bragg intensity measurements with a step size of 0.1° in 2θ. Background measurements were made for each Bragg position after removing the sample from the furnace. 24 reflexions were measured; only 16 have significant values. True absorption (μ = 0.09 cm⁻¹) was neglected. Since it is probable that the intense 111 and 200 reflexions suffer from extinction, they were omitted from the refinement.

Analysis of the data

Crystallographic data

The lattice constant is $a = 8.82 \pm 0.01$ Å and the crystal is face-centred cubic with $Z = 4$.

Structure determination

Because the present experimental data are limited and the disorder cannot be considered as static, a conventional least-squares refinement was not possible. Thus we have developed computer programs to fit the data by a method given by Seymour & Pryor (1970) and Press & Hüller (1973).

According to this last paper, the rotational form factor for the Br atoms is written

$$F^{\text{rot}}(\mathbf{Q}) = \int_{\text{cell}} \exp(i\mathbf{Q}\mathbf{r})a(\mathbf{r}) \, d\mathbf{r},$$

where \mathbf{Q} is the momentum transfer and $a(\mathbf{r})$ is the scattering-length density of Br which may be expanded into symmetry-adapted functions.

$$a(\mathbf{r}) = a(\theta, \varphi)(r - \rho)b_{\text{Br}}/r^2,$$

and

$$a(\theta, \varphi) = \sum_l \sum_m c_{lm} K_{lm}(\theta, \varphi),$$

where $\rho = \text{C-Br}$ length, b_{Br} is the scattering length of Br, θ, φ are the polar angles of \mathbf{r} , and K_{lm} are cubic harmonics (von der Lage & Bethe, 1947; Altmann & Cracknell, 1965).

Then

$$F^{\text{rot}}(\mathbf{Q}) = 4\pi b_{\text{Br}} \sum_l \sum_m i^l j_l(Q\rho) c_{lm} K_{lm}(\Omega_Q),$$

where Ω_Q denotes the polar angles of the scattering vector \mathbf{Q} in a coordinate system defined by the crystallographic axes, and $j_l(Q\rho)$ are the spherical Bessel functions.

If we neglect correlations between translational and rotational motions, $F^{\text{rot}}(\mathbf{Q})$ is simply weighted with the Debye-Waller factor corresponding to the centre of mass motion. Then the structure factor is

$$F(\mathbf{Q}) = \exp[-W(\mathbf{Q})] F^{\text{rot}}(\mathbf{Q}).$$

Table 1. Observed and calculated structure factors

Reflexions 111 and 002 were omitted from the refinement.

hkl	F_o	F_c	
		Isotropic term only	All terms
111	1.507	1.720	2.120
002	1.263	1.208	1.506
220	0.152	0.208	0.152
311	0.106	0.063	0.095
222	0.141	0.068	0.193
004	0.395	0.191	0.406
331	0.242	0.300	0.196
224	0.468	0.408	0.458
333	0.676	0.422	0.655
115	0.424	0.422	0.462
440	0.056	0.382	0.089
006	0.365	0.321	0.372
442	0.319	0.321	0.302
335	0.217	0.207	0.212
622	0.113	0.192	0.141
444	0.183	0.141	0.169
551	0.000	0.111	0.043
117		0.111	0.084
553		0.061	0.040
800		0.046	0.020
733		0.042	0.019
644		0.040	0.013
066		0.037	0.031
822		0.037	0.016

Owing to the symmetry invariance of $a(\theta, \varphi)$ the cubic harmonics belong to the totally symmetric representation A_1 ($m = 1$) and only a few coefficients c_{1l} are different from zero.

For one molecule at the lattice origin, the structure factor is

$$F(\mathbf{Q}) = \exp(-\frac{1}{2}Q^2\langle u^2 \rangle) \{ b_C + 4b_{Br} [j_0(Q\rho) + c'_{41} j_4(Q\rho) K'_{41}(\Omega_Q) - c'_{61} j_6(Q\rho) K'_{61}(\Omega_Q) + c'_{81} j_8(Q\rho) K'_{81}(\Omega_Q) + \dots] \}$$

$\langle u^2 \rangle$ is an isotropic mean-squared amplitude, and $b_C = 0.665$ and $b_{Br} = 0.68$ (in units of 10^{-12} cm) are the scattering lengths of C and Br. The 4π coefficient drops out by the use of $c'_{lm} = c'_{lm}/\sqrt{(4\pi)}$ and K'_{lm} with omission of the common factor $1/\sqrt{(4\pi)}$ of the cubic harmonics.

The data were fitted to this model with the following parameters: a scale factor, the C-Br length, a Debye-Waller factor (the same for the C atom and the centre of mass) and the three coefficients c'_{41} , c'_{61} , c'_{81} .

The first fit was made with the isotropic term $j_0(Q\rho)$. The weighted reliability factor R_w is 40.0% with $\rho = 1.89$ Å and $\langle u^2 \rangle = 0.16$ Å² for the 14 retained reflexions. The last fit with all coefficients leads to $R_w = 6.5\%$ with $\rho = 1.89$ (2) Å, $\langle u^2 \rangle = 0.20$ (4) Å², $c'_{41} = 0.077$ (3), $c'_{61} = -0.846$ (33), $c'_{81} = 0.018$ (1).

Table 1 shows the observed and calculated structure factors for these two fits.

Discussion

On the sphere of radius ρ , the scattering-length density of Br depends on θ and φ through

$$a(\theta, \varphi) = \frac{1}{4\pi} [1 + c'_{41} K'_{41}(\theta, \varphi) + c'_{61} K'_{61}(\theta, \varphi) + c'_{81} K'_{81}(\theta, \varphi) + \dots]$$

We have represented this function in the plane $(1\bar{1}0)$ (Fig. 1) and on a stereographic projection of the sphere of radius ρ (Fig. 2). The density is a maximum in the $[110]$ directions and we consider the $[111]$ directions which are absolute minima to be the reorientation axes.

If $a(\theta, \varphi)$ and $b(\theta', \varphi')$ are the angular part of the scattering-length density referred to the (x, y, z) crystal axes and to the (x', y', z') molecular coordinate system respectively (Fig. 3), we have

$$a(\theta, \varphi) = \int d\omega f(\omega) b(\theta', \varphi'),$$

where $f(\omega)$ is the probability that the molecule is in an orientation specified by the Euler angles ω . Because of the site and molecule symmetries, we have

$$f(\omega) = \frac{1}{8\pi^2} \sum_l (2l+1) A^{(l)} U_{11}^{(l)}(\omega),$$

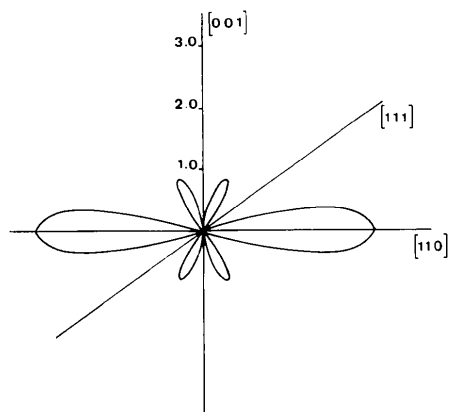


Fig. 1. Angular dependence in the $(1\bar{1}0)$ plane of the Br density on a sphere of radius $\rho = C-Br$.

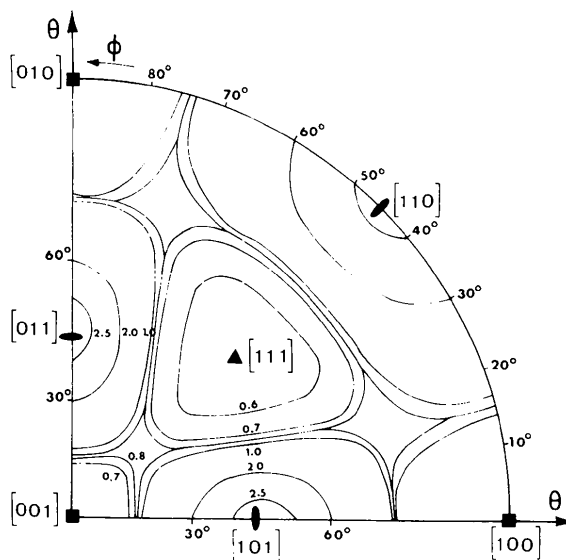


Fig. 2. Stereographic projection of the angular part of the Br density (in arbitrary units).

where the cubic rotator functions $U_{lm}^{(l)}(\omega)$ are defined by

$$K'_{l'm'}(\theta', \varphi') = \sum_{m''} K_{l'm''}(\theta, \varphi) U_{m''m'}^{(l)}(\omega)$$

(James & Keenan, 1959).

We obtain

$$a(\theta, \varphi) = \sum_l A^{(l)} b_l K_{11}(\theta, \varphi),$$

which we may compare with

$$a(\theta, \varphi) = \sum_l c_l K_{11}(\theta, \varphi).$$

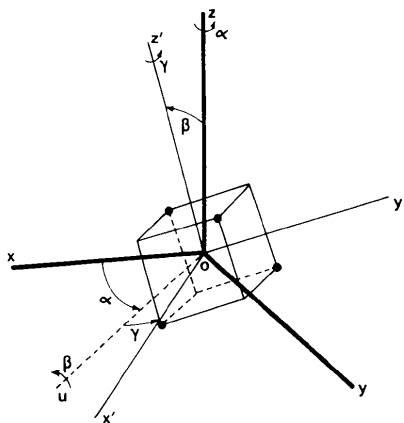


Fig. 3. Euler angles. In the (x', y', z') coordinate system, the molecular site has T_d symmetry. The lattice is referred to the (x, y, z) axes. The two systems are related by the Euler angles $\omega \equiv \alpha, \beta, \gamma$.

Therefore,

$$A^{(l)} = c_l/b_l.$$

For the molecular tetrahedron in the (x', y', z') coordinate system (Fig. 3) we have

$$b'_4 = -\sqrt{\left(\frac{7}{3}\right)}; \quad b'_6 = -\frac{4}{9}\sqrt{26}; \quad b'_8 = \frac{\sqrt{33 \cdot 17}}{27}.$$

Then

$$A_4 = -0.05, \quad A_6 = -0.373, \quad A_8 = 0.02.$$

A numerical calculation shows that $f(\omega)$ is a minimum when the molecular axes are parallel to the crystal axes and the maxima are obtained by 45° rotations round the crystal axes (e.g., $\alpha = \beta = 0, \gamma = 45^\circ$; $\alpha = \gamma = 0, \beta = 45^\circ$; ...).

It is clear that these results are consistent with those deduced from the phase II structure. Phase I can be regarded as six different molecules rotating around the $[111]$ axes. Each molecule has a maximum of orientational probability when it is in sites of D_{2d} symmetry.

The Debye-Waller factor $\langle u^2 \rangle = 0.20 \text{ \AA}^2$ corresponds to a large translational mean-squared displacement. We have measured the sound velocities; the mean values are approximately: longitudinal, $v_l = 1400$; transversal, $v_t = 800 \text{ m s}^{-1}$. In the Debye approximation

$$\langle u^2 \rangle = \frac{9kT}{M} \left[\frac{V}{18\pi^2} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \right]^{2/3} = 0.19 \text{ \AA}^2,$$

which is the same as the experimental value. Thus the correlations between translational and rotational motions are of great importance. Recently Rudman (1977) has shown that the transition in methylchloroform is due to a 0.5 \AA shift of the molecular centres. We were unable to determine precisely such a shift in CBr_4 but we think that the transition mechanism is probably the same.

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