Acta Cryst. (1981). A**37**, 904–908

The Plastic Phase of Hexachloroethane, C_2Cl_6: A Neutron Powder and Single-Crystal Investigation

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(*Received* 23 *December* 1980; *accepted* 22 *April* 1981)

Abstract

Bragg intensity data extracted from energy-integrated neutron measurements were treated by a conventional split-atom model, with a series expansion in cubic harmonic functions, and by a Gaussian approximation for the molecular librations. The trigonal molecular axes are found to be smeared out close to cubic [111] axes with the Cl atoms near the [100] axes. With the three models mentioned consistent data are obtained for the root-mean-square translational amplitude: 0·4 Å, and the librational amplitude: 19·6°; both at 423 K. Data and results for three different temperatures are given.

1. Introduction

The process of melting and molten materials are usually not subjects crystallographers are very much interested in. The way, however, in which molecular crystals lose their translational and/or orientational order has recently found widespread interest. A new acronym ODIC (for: orientationally disordered crystals) has been suggested to replace the older term 'plastic crystal' or 'plastically crystalline state' introduced by Timmermans (1935) in order to describe the high ductility of some compounds consisting of globular molecules. This state is usually restricted to a temperature interval extending from the melting point to roughly 10 to 100 K below. The transition to the normal crystalline state at still lower temperatures very often proceeds *via* a first-order transformation. Orientationally disordered crystals are in a partially molten state. Their orientational order may be practically completely absent. They still have, however, long-range translational order: in most cases the lattice is f.c.c. or b.c.c.

C_2Cl_6 occurs in three solid modifications. Phase I is orthorhombic, and stable from 4 to 318 K (Hohlwein, Nägele & Prandl, 1979). The structure of phase II (Gerlach, 1979) is still unknown. The plastic phase III is stable from 344 K up to the melting point at 458 K. The transitions between the different phases are of first order, and single crystals are destroyed on heating and cooling through the I–II–III transformations.

Molecules of C_2Cl_6 have the point group $\bar{3}m$, and their plastic phase is b.c.c. with two molecules per unit cell. The molecular center of gravity is located at the lattice site 2(*a*) of space group $Im3m$ with $m3m$ site symmetry. There is therefore a discrepancy between the molecular and the average site symmetry, *i.e.* there must be some sort of disorder either in space or, *via* oscillations, rotations or rotational jumps, in time. C_2Cl_6 has been investigated earlier with X-rays by West (1934), Finbak (1937), and Atoji, Oda & Watanabe (1953). West and Finbak assumed that the $m3m$ site symmetry is caused by strong molecular vibrations. Atoji *et al.* discussed several disorder models with discrete lattice sites. The present paper is concerned with the interpretation of Bragg intensities extracted from energy-integrated neutron powder and single-crystal data. Several methods will be presented to analyze these data. In § 3 we apply the conventional crystallographic refinement with a split-atom model and the Schomaker & Trueblood (1968) **TLS** analysis of the thermal vibrations, librations and their coupling. § 4 deals with an analysis in terms of symmetry-adapted functions. A good survey about the principles and the recent applications of this method to other compounds is contained in a recent paper by Hüller & Press (1979). In § 5 we use a particularly simple Gaussian model to describe the scattering length density on the surface of a sphere.

Only time-independent properties of C_2Cl_6 will be dealt with here. Inelastic neutron scattering experiments which we have performed recently will be published elsewhere.

2. Experimental details

The powder neutron diffraction data were measured with the *P*14 diffractometer ($\lambda = 1·0296$ Å) at the FR2 reactor at Karlsruhe. The samples were contained in a cylindrical vanadium can (12 mm diameter, 50 mm

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height, 0·1 mm wall). In order to prevent single grains from growing we used a small amount of quartz wool in the sample container (Baharie & Pawley, 1977). The quartz glass did not produce any additional detectable scattering. In Fig. 1 we show a typical diagram. The heavy damping of the Bragg scattering which is characteristic for plastic crystals is clearly visible. Integrated intensities were obtained from Gaussian line fits. The two broad humps around $2\theta = 22$ and 46° are caused by the directional average of an anisotropic diffuse scattering which was observed in X-ray single-crystal photographs (Gerlach, 1979). This contribution is due to molecular disorder. As a by-product we obtain the temperature dependence of the lattice constant (Fig. 2) and the volume expansion

$$\frac{1}{V}\frac{\delta V}{\delta T} = 6 \pm 1 \times 10^{-4}\,\mathrm{K}^{-1}.$$

Single crystals were grown directly from the melt in a quartz-glass sphere of 6 mm diameter. A short capillary was attached to the sphere in order to improve the growth condition. Nevertheless, in all cases several grains were formed as could be seen from neutron Laue photographs. The largest was selected for collecting data with the *P*32 four-circle diffractometer (λ = 1·0272 Å) at the FR2 reactor. No overlap with other grains was observed. Integrated reflections were obtained from ω scans at 381 and 423 K. At both temperatures about 100 reflections were measured. Out of the 24 expected symmetry-independent reflections 11 were less than $2\sigma(I)$ at 381 K, and 14 at 423 K respectively. Absorption was not taken into account because the corrections would be less than 2%. All single-crystal as well as powder measurements are compatible with the space group *Im*3*m* (Atoji *et al.*, 1953).

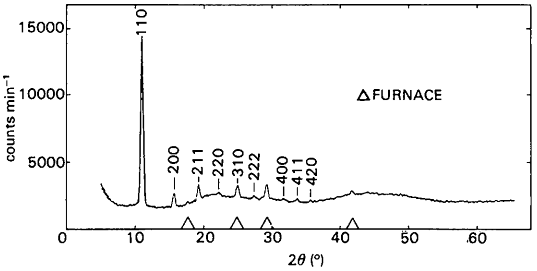

Fig. 1. Neutron powder diagram at 368 K.

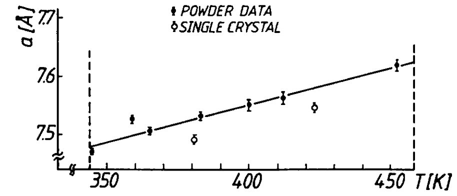

Fig. 2. Temperature dependence of the lattice constant.

3. Conventional analysis: split atoms and TLS analysis

Due to the different molecular and average site symmetry ($\bar{3}m$ *vs* $m3m$) hexachloroethane is necessarily disordered in the plastic phase. A closer inspection of the molecule (Fig. 3*a*) shows that the trigonal antiprism formed by the Cl atoms is not far from an octahedron: the elongation along the trigonal axis is only 0·12 Å. In an ideal octahedron the Cl positions would be on the axes of the cubic coordinate system with no difficulty arising from the site symmetry. Because of the small differences mentioned above we assume for the average structure a superposition of four molecules, the trigonal axes of which are parallel to the four cubic [111] directions. Carbon atoms will then occupy the 16(*f*) position (*x*,*x*,*x*) of *Im*3*m*, and chlorine atoms the 48(*k*) position (*x*,*x*,*z*). From the molecular geometry determined by gas electron diffraction (Morino & Yuwasaki, 1949; Swick, 1953) we find the following theoretical position parameters: $x_{\rm Cl} = 0{\cdot}0137$, $z_{\rm Cl} = 0{\cdot}2867$, $x_{\rm C} = 0{\cdot}0604$.

In the averaged unit cell there are always four chlorine atoms close to the *x*, *y* or *z* axes with a distance of only 0·147 Å. As the refinement showed, this distance is small compared with the librational amplitude of the molecule (0·75 Å; *cf.* Table 5). In order to reduce the number of free parameters we therefore assume only one atom in (0,0,*z*) with weight 1, instead of four atoms in (*x*,*x*,*z*) with weights 0·25. In addition, a fixed position and an isotropic temperature factor is used for the carbon atoms.

The refinement of this model was made with the program *CRYLSQ* (XRAY system, 1976). Only the single-crystal data were used. The weights were $w = 1/\sigma^2(F_o)$ with $\sigma^2(F_o) = \sigma_c^2(F_o) + (0{\cdot}02F_o)^2$, $\sigma_c(F_o)$ being the error of F_o due to the counting statistics. The quantity minimized was $\sum w(F_o - F_c)^2$. Scattering lengths ($b_{\rm C}$ = 6·65 and $b_{\rm Cl}$ = 9·58 fm) were taken from *International Tables for X-ray Crystallography*

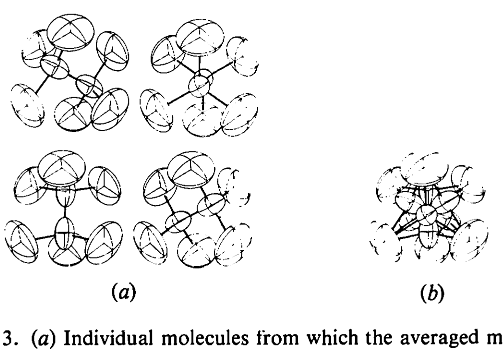
(*a*) (*b*)

Fig. 3. (*a*) Individual molecules from which the averaged molecule is formed [*ORTEP* plot (Johnson, 1965) at 423 K; parameters taken from the conventional refinement, Table 1]. (*b*) The averaged molecule (see text).

(1974). The computed parameters are given in Table 1.*

The thermal parameters were analyzed in terms of the tensors **T**, **L** and **S** describing the translations, librations and correlated librational–translational motions (Schomaker & Trueblood, 1968) of the averaged molecules. For this purpose we used the program *TLS*6 by Trueblood & Gantzel (1977). From symmetry reasons only T_{11} and L_{11} are nonzero (Table 2).

4. Analysis with cubic harmonic functions

We expand the average nuclear scattering lengths density $b(r_s,\theta_s,\varphi_s)$ of the carbon ($s = 1$) and the chlorine ($s = 2$) shells into a series of symmetry-adapted functions (Atoji, 1958; Press & Hüller, 1973; Press, 1973). The r_s are the distances between the molecular center of mass and the carbon and chlorine shells respectively. Following the latter authors, we obtain:

$$b(r_s,\theta_s,\varphi_s) = b_s[\delta(r - r_s)/r^2]\, p_s(\theta_s,\varphi_s),$$

$$p_s(\theta_s,\varphi_s) = \sum_{l=0}^{\infty} c_{l1}\, K_{l1}(\theta_s,\varphi_s),$$

with $r_1 = 0{\cdot}78$ Å and $r_2 = 2{\cdot}13$ Å. The K_{l1} are cubic harmonic functions introduced by Von der Lage & Bethe (1947). The first three, appropriate to the site symmetry $m3m$, are:

$$K_{01} = 1$$

$$K_{41} = (5 \times 21/4)K_4$$

$$K_{61} = (231 \times 26/8)K_6$$

with

$$K_4 = x^4 + y^4 + z^4 - 3/5$$

$$K_6 = x^2y^2z^2 + (1/22)K_4 - 1/10$$

and $x = \sin\theta\cos\varphi$, $y = \sin\theta\sin\varphi$, $z = \cos\theta$.

The structure factor for the distribution given above is:

$$F^s_{\rm rot}(\mathbf{Q},r_s) = 4\pi b_s \sum_l i^l j_l(Qr_s)\, c_{l1}(s)\, K_{l1}(\theta_Q\, \varphi_Q),$$

where the j_l are spherical Bessel functions (Abramowitz & Stegun, 1965) and θ_Q,φ_Q are the polar angles of the scattering vector **Q**. In our calculations we treated only the case with no correlation between the orientational distribution and the translational motion. Then the complete structure factor for the two shells (carbon and chlorine) is given by

$$F = \exp(-W)(F^1_{\rm rot} + F^2_{\rm rot}),$$

with an isotropic Debye–Waller factor $W(= 1/2Q^2 \times \langle u^2\rangle)$ for the whole molecule. Results of the refinement with the expansion coefficients $c_{l1}(s)$ as parameters are given in Table 3 for the single-crystal data and in Table 5 for the powder data.

5. Analysis with Gaussian librations

As in the conventional refinement one molecule with a well defined equilibrium position is generated by superposition of four molecules in different orientations. The distribution of the chlorine atoms is approximated by an octahedral arrangement.

This molecule is treated as a rigid body (Hohlwein, 1981). The site symmetry and the symmetry of this pseudo molecule are $m3m$ so that translation and libration of the molecule are uncorrelated. The structure factor is:

$$F = f_T\, F_{\rm lib},$$

Table 1. *Results of the conventional refinement [fractional coordinates* ($\times 10^4$) *and temperature factors* ($\times 10^2$) *at* (*a*) 381 K *and* (*b*) 423 K]

Data without errors were kept fixed.

	x	y	z	U_{11}	$U_{22} = U_{33}$	$R(F)$
C (*a*)	579	579	579	17 (1)	Isotropic	
(*b*)	579	579	579	44 (20)		
Cl (*a*)	2746 (40)	0	0	14 (2)	48 (4)	0·14
(*b*)	2681 (40)	0	0	21 (2)	61 (5)	0·11

Table 2. *Rigid-body analysis of the conventional refinement* (*cf.* Table 1) *with the translational and librational tensors* **T** *and* **L** *relative to the crystal axes*

	$T_{11}^{1/2}$ (Å)	$L_{11}^{1/2}$ (°)
381 K	0·38 (1)	16·1 (7)
423 K	0·47 (2)	17·5 (7)

Table 3. *Results of the refinement with cubic harmonic functions*

	$T_{11}^{1/2}$ (Å)	c_{41} (C)	c_{41} (Cl)	c_{61} (Cl)	$R(F)$
381 K	0·31 (3)	−2·3 (1·4)	0·98 (6)	0·18 (6)	0·07
423 K	0·37 (2)	−3·2 (1·3)	0·84 (3)	0·11 (4)	0·03
368 K (Powder)	0·34 (5)	−1·2 (4·6)	0·95 (5)	0·15 (8)	0·05

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* The observed and the calculated structure factors (and powder data) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36176 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

with the isotropic Debye–Waller factor f_T for the translational movement:

$$f_T = \exp(-Q^2 T_{11}/2),$$

and F_{lib} for the librating molecule. The libration is assumed to be Gaussian and isotropic. Then each atom is distributed around its equilibrium position on a spherical surface in the same manner. If we call the angle between the radius vectors of an atom (original at the center of mass of the molecule) in its equilibrium position and the actual position θ and the azimuthal angle φ, then the probability $p(\theta,\varphi)$ of finding an atom at the position θ and φ is:

$$p(\theta,\varphi) \propto \exp(-\theta^2/2L_{11}^2).$$

F_{lib} is calculated numerically (Hohlwein, 1981). For the θ integration a grid with 11 steps was used. The φ values were distributed as a function of θ according to the relation

$$\Delta\varphi = \Delta\theta/\sin\theta.$$

In this way the integration points have a constant density on the surface of the sphere. The integration area covered twice the half-width of the Gaussian function.

Besides the scale factor only two parameters have to be refined in this model: a normal isotropic temperature factor T_{11}, and L_{11} which is the mean-square libration angle of the harmonic librational movement (not an approximation as an ellipsoid as in the conventional analysis also called 'harmonic').

The results for the two temperatures are given in Table 4.

6. Discussion

Table 5 shows the comparable parameters of the different models.

Table 4. *Refinement with Gaussian librations*

	$T_{11}^{1/2}$ (Å)	$L_{11}^{1/2}$ (°)	$R(F)$
381 K	0·33 (2)	18·1 (7)	0·08
423 K	0·40 (2)	19·6 (3)	0·04
368 K (Powder)	0·35 (2)	18·5 (6)	0·05

Table 5. *Comparison of the results of the different refinement methods* [(*a*) *conventional refinement*, (*b*) *analysis with cubic harmonic functions, and* (*c*) *with Gaussian librations*]

	$T_{11}^{1/2}$ (Å)		$L_{11}^{1/2}$ (°)	
	381 K	423 K	381 K	423 K
(*a*)	0·38 (1)	0·47 (2)	16·1 (7)	17·5 (7)
(*b*)	0·31 (3)	0·37 (2)		
(*c*)	0·33 (2)	0·40 (2)	18·1 (7)	19·6 (3)

The translational temperature factors for Gaussian libration and cubic harmonic analysis are identical within the statistical errors. In the conventional refinement a part of the librational movement is obviously contained in the translational temperature factor.

The scattering density distribution of the chlorine atoms is shown in Fig. 4 for the cubic harmonic analysis. A comparison between the cubic harmonic and the Gaussian analysis along several directions on the sphere is given in Fig. 5. Both distributions have main maxima in the [00*l*] directions. The negative values of the scattering density which are found in the cubic harmonic analysis are non-physical and can be avoided only if constraints between the expansion coefficients are introduced. The method to do this described in the literature (Hüller & Press, 1979) is complicated, and so far has been worked out for higher molecular symmetry only. Also, if these constraints are introduced it will be difficult to refine a sufficient number of expansion coefficients as the number of observed reflections is very low.

In our case the method of Gaussian librations which gives a reasonable physical picture is quite satisfactory and has the advantage of a very small number of parameters.

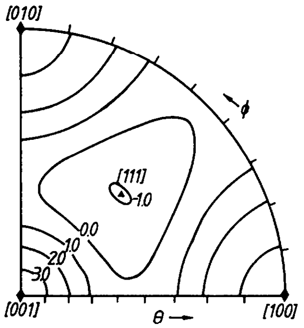

Fig. 4. The probability density $p_2(\theta_2,\varphi_2)$ of the Cl shell in a stereographic representation. Results of the 381 K single-crystal data refinement with cubic harmonic functions are shown.

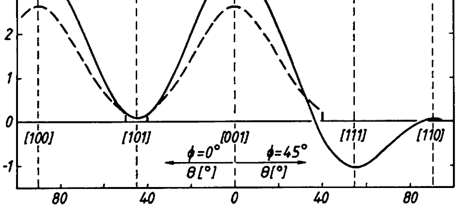

Fig. 5. A comparison of the Gaussian approximation (– – –) with the analysis by cubic harmonic functions (——) based on the 381 K single-crystal data.

The temperature variation of T_{11} and L_{11} between 381 and 423 K is consistent within the error limits with harmonic potentials.

It is obvious from our results that different models – at least the cubic harmonic and the Gaussian approximation – give comparable results as far as R values are concerned. The only way out of this difficulty is an increase of the signal-to-noise ratio in the measurements of Bragg data. The background cannot be reduced below the level given by the diffuse scattering due to the sample. So the only other way out which apparently has not been tried so far is high-resolution X-ray and neutron scattering.

This investigation has been supported financially by the Bundesministerium für Forschung und Technologie (project No. KNF 03-41E03P; 04-45E03I). We are indebted to the Kernforschungszentrum Karlsruhe for providing neutron diffraction facilities.

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Acta Cryst. (1981). A**37**, 908–913

Examination of Semiempirical Atom–Atom Potential Functions for Cl···Cl Non-Bonded Interactions

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(*Received* 30 *September* 1980; *accepted* 14 *May* 1981)

Abstract

Three semiempirical atom–atom potential functions suggested by different authors to describe non-bonded Cl···Cl interactions are examined *via* calculation of some thermodynamic properties of hexachlorobenzene, C_6Cl_6, and *p*-dichlorobenzene, $C_6H_4Cl_2$, crystals. All thermodynamic quantities are evaluated with the cell model as a statistical mechanical basis. The calculation results provide some evidence to support the existence of positional disorder in the high-temperature phases of *p*-dichlorobenzene.

0567-7394/81/060908-06$01.00

Introduction

In the present paper we test three potential functions suggested by different authors to describe non-bonded Cl···Cl interactions in the crystals of chlorinated benzenes. The test involves calculation of some thermodynamic quantities of hexachlorobenzene (HCB) and *p*-dichlorobenzene (DCB) crystals and subsequent comparison of the calculation results with experiment. As a statistical mechanical basis for the thermodynamic calculations we use a classical self-consistent-field approximation which is frequently called the cell