The Structure Factor of Orientationally Disordered Crystals: the Case of Arbitrary Space, Site, and Molecular Point Group

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Dedicated to Professor Heinz Jagodzinski on his 65th birthday

Abstract

The rotational form factor will be derived for the most general case of crystal, site and molecular symmetry (including non-crystallographic molecular point groups). Linear combinations of spherical harmonics adapted to the proper symmetry are used throughout. Their number as well as the number of free parameters of the orientational probability function is computed. Rules are given about how many parameters can be determined independently. Their number depends on the geometry of the molecule. The paper also includes the case of several symmetrically equivalent orientationally disordered molecules per unit cell.

1. Introduction

Orientational disorder in crystals containing rigid molecules has been known since the early thirties: Kracek, Posniak & Hendricks (1931) observed in $NaNO_3$ that 'the rotational degree of freedom of the nitrate group about an axis normal to the plane of the group is apparently the one excited in the region 150 to 280° (C)'. Bijvoet & Ketelaar (1932) offered an explanation of the scattering in terms of the form factor of rotating atoms which is expressed by the Bessel function J_0. A much more detailed mathematical analysis of the scattering from the one-dimensional (*i.e.* axial) and the three-dimensional hindered rotator was given in a series of papers by King & Lipscomb (1950), Atoji, Watanabé & Lipscomb (1953) and Atoji & Lipscomb (1954). These authors applied a hindering potential to calculate the orientation probability which, in turn, was used for the average structure factor $\bar{F}$. Atoji (1958) suggested a spherical Fourier method: the scattering density at a cubic lattice site was described by the 'cubic harmonics' introduced by Von der Lage & Bethe (1947), *i.e.* by symmetry-adapted spherical harmonics. Kurki-Suonio & Meisalo (1967) applied functions of this kind adapted to tetrahedral and cubic symmetry for an analysis of the non-spherical electron

distribution in atoms. Press & Hüller (1973) and Press (1973) gave a calculation of the rotational form factor of a molecule from first principles: the scattering-length density is described in a molecular frame first, and then in a frame fixed within the crystal. The connection between the two is managed by an orientational probability density function, the mathematical form of which depends on both the molecular and the site symmetry. The analysis was extended recently by considering the consequences of the fact that the orientational distribution function has to be positive definite (Hüller & Press, 1979). Correlations between the orientation and the position of a molecule have been included in the theory also (Press, Grimm & Hüller, 1979). A review of experimental work applying the method is given by Hüller & Press (1979). Amoureux & Bee (1980) found it necessary in their analysis of adamantane to apply cubic harmonic functions up to 12th order. A group-theory method for deriving a complete set of symmetry-adapted basis functions has been given recently by Yvinec & Pick (1980). It was applied to neutron scattering and orientational dynamics in plastic molecular crystals (Pick & Yvinec, 1980).

The present paper originated from experimental work on the plastic phase of hexachloroethane (Gerlach, 1979; Gerlach, Hohlwein, Prandl & Schulz, 1981). In the course of the analysis it turned out that orientationally disordered molecules of low symmetry at a high-symmetry lattice site have an orientational probability density with a larger number of free parameters than, say, a cubic molecule at a cubic site which apparently is the only case which has been treated systematically in the literature so far.

Some basic definitions will be given in § 2. § 3 contains the derivation of the rotational form factor of a molecule with arbitrary point group at a site with arbitrary site (point) group. The meaning of the free parameters is also given. Methods of group representation theory allow the computation of the number of free parameters (§ 4). Not all of them can be determined uniquely (§ 5), which will be demonstrated

with an example (§ 6). Finally, we shall give the modifications to the formulation which are necessary when the point group of the crystal and the site group are different.

2. Mathematical preliminaries and nomenclature

We will use the following symbols and definitions:

G: space group of the crystal;

$G_0;P;\Pi$: point group of G; point site group of the lattice site on which the center of mass of the molecule is located; molecular point group;

$P_{l\nu}(\theta,\varphi)$, $\Pi_{l\nu}(\theta',\varphi')$: symmetry-adapted functions (SAF) for the point groups P and Π, respectively;

$\mathscr{M}^l_{\gamma\tau}(P,\Pi;\omega)$: mixed rotator functions.

The SAF's are defined in terms of spherical harmonics $Y_{lm}(\theta,\varphi)$:

$$P_{l\nu}(\theta,\varphi) = \sum_{m=-l}^{+l} Y_{lm}(\theta,\varphi)\, P^l_{m\nu} \qquad (1)$$

$$\Pi_{l\nu}(\theta',\varphi') = \sum_{m=-l}^{+l} Y_{lm}(\theta',\varphi')\, \Pi^l_{m\nu}. \qquad (2)$$

Unprimed coordinates $\mathbf{r} = (r,\theta,\varphi)$ refer to an orthogonal coordinate system Σ fixed in the crystal, primed ones $\mathbf{r}' = (r',\theta',\varphi') \equiv (r,\theta',\varphi')$ to an analogous system Σ' fixed in the molecule. The origin of Σ and Σ' coincide, therefore r and r' are identical. Indices l and m have their usual meaning. Greek indices like γ,τ (used later) label irreducible representations of the point groups in question. In principle there are $2l + 1$ indices γ for a given l. But only very few or even none of them, depending on l, refer to totally symmetric SAF's belonging to the so-called unit representation. Since in what follows we will need only totally symmetric SAF's, all Greek indices used from now on refer to unit representations (see § 4). $P^l_{m\nu}$, $\Pi^l_{m\nu}$ are unitary matrices of dimension $2l + 1$. They can be chosen in such a way that the SAF's are real functions. Again, we will need only those columns of the matrices which refer to totally symmetric SAF's. SAF's for all crystallographic point groups may be obtained from Bradley & Cracknell (1972). 'Index picking rules' for the selection of linear combinations of Y_{lm} for crystallographic point groups have also been given by Kurki-Suonio (1977). One should, however, bear in mind molecules with non-crystallographic point groups, e.g. with a fivefold axis of symmetry. They also might form orientationally disordered crystals. In these cases the totally symmetric SAF's may be calculated by projection operator techniques (Bradley & Cracknell, 1972) or, in simple cases, by inspection. Their number $n(\Pi,l)$, for a few non-crystallographic point groups, will be given in

Table 2(b); Table 2(a) contains the same information for crystallographic point groups.

Spherical harmonics Y_{lm} can be transformed from the primed to the unprimed coordinate system by using Wigner's $\mathscr{D}$ functions (Wigner, 1959; Edmonds, 1964)

$$Y_{lm}(\theta',\varphi') = \sum_{m'=-l}^{+l} Y_{lm'}(\theta,\varphi)\mathscr{D}^l_{m'm}(\omega). \qquad (3)$$

Here $\omega = (\alpha,\beta,\gamma)$ is the set of Eulerian angles transforming Σ into Σ' (Edmonds, 1964). We write down the integral representation

$$\mathscr{D}^l_{m'm}(\omega) = \int Y^*_{lm'}(\theta,\varphi)Y_{lm}(\theta',\varphi')\, \mathrm{d}\tau \qquad (4)$$

with $\mathrm{d}\tau = \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\varphi$ and the orthogonality relations:

$$\int \mathscr{D}^{*l_1}_{m'_1 m_1}(\omega)\, \mathscr{D}^{l_2}_{m'_2 m_2}(\omega)\, \sin\beta\, \mathrm{d}\beta\, \mathrm{d}\alpha\, \mathrm{d}\gamma$$

$$= \frac{8\pi^2}{2l_1 + 1}\, \delta_{l_1 l_2}\, \delta_{m'_1 m'_2}\, \delta_{m_1 m_2}. \qquad (5)$$

In complete analogy with (3)–(5) we now introduce mixed rotator functions $\mathscr{M}^l_{\gamma\tau}(\omega) \equiv \mathscr{M}^l_{\gamma\tau}(P,\Pi;\omega)$:

$$\Pi_{l\tau}(\theta',\varphi') = \sum_{\nu=1}^{n(P,l)} P_{l\nu}(\theta\varphi)\mathscr{M}^l_{\gamma\tau}(\omega) \qquad (6)$$

$$\tau = 1, \ldots, n(\Pi,l)$$

$$\mathscr{M}^l_{\gamma\tau}(\omega) = \int P^*_{l\nu}(\theta,\varphi)\Pi_{l\tau}(\theta',\varphi')\, \mathrm{d}\tau \qquad (7)$$

$$\int \mathscr{M}^{*l_1}_{\gamma_1 \tau_1}(\omega)\, \mathscr{M}^{l_2}_{\gamma_2 \tau_2}(\omega)\, \sin\beta\, \mathrm{d}\beta\, \mathrm{d}\alpha\, \mathrm{d}\gamma$$

$$= \frac{8\pi^2}{2l_1 + 1}\, \delta_{l_1 l_2}\, \delta_{\nu_1 \nu_2}\, \delta_{\tau_1 \tau_2}. \qquad (8)$$

From the definitions (1), (2), (3), and by equations (4) and (7), the mixed rotator functions can be written in terms of Wigner functions:

$$\mathscr{M}^l_{\gamma\tau}(\omega) = \sum_{m'm=-l}^{+l} \mathscr{D}^l_{m'm}(\omega)\, P^{*l}_{m'\nu}\, \Pi^l_{m\tau}. \qquad (9)$$

From equations (5) and (9) the function of lowest order is found to be a constant: $\mathscr{M}^0_{11}(\omega) = 1$ for an arbitrary pair of point groups P,Π.

The tetrahedral rotator functions introduced by James & Keenan (1958), and the cubic rotator functions applied by Press & Hüller (1973) coincide with the $\mathscr{M}$'s defined here if the appropriate cubic point groups are used for P and Π. From (9) it is clear that only the Wigner functions $\mathscr{D}^l_{m'm}(\omega)$ are necessary for a calculation of the $\mathscr{M}$'s since the unitary matrices $P^l_{m\pm\nu}$, $\Pi^l_{m\tau}$ are tabulated anyhow (Bradley & Cracknell, 1972). From a practical point of view it is hardly

necessary to go beyond $l = 10$ (or 12 as a maximum) at the present time, because the experimental data known so far for orientationally disordered crystals do not allow one to determine higher expansion coefficients (see §§ 4, 5, 6). The experimental situation might, however, be improved by the application of, for example, high-resolution methods.

3. Scattering-length density and its Fourier transform

Here we will briefly derive the rotational form factor introduced by Press & Hüller (1973) in terms of the functions defined in § 2. The nuclear scattering length b used in this paper may be replaced by the form factor f for X-ray experiments in the final expressions (27) and (27') as long as non-spherically distributed electrons can be neglected.

In a rigid molecule the atoms of the chemical species s with scattering length b_s are distributed, according to the molecular symmetry Π, on shells of radius $r'_s = r_s$ with coordinates

$$\mathbf{r}'_{si} = (r_s, \theta'_{sl}, \varphi'_{si}),$$

where the index i labels symmetrically equivalent atoms. The scattering-length density $b(\mathbf{r}')$ in a molecular frame Σ' is then

$$b(\mathbf{r}') = \sum_{s,l} b^{sl}(\mathbf{r}'), \tag{10}$$

with

$$b^{sl}(\mathbf{r}') = \frac{b_s}{r'^2} \delta(r' - r_s) \delta(\cos\theta' - \cos\theta'_{sl}) \times \delta(\varphi' - \varphi'_{sl}) \tag{11}$$

and

$$\int b^{sl}(\mathbf{r}') \, d\tau' = b_s. \tag{12}$$

$b(\mathbf{r}')$ is invariant under all operations of the molecular point group Π, and so the SAF's $\Pi_{l\tau}(\theta' \varphi')$ are the 'natural' functions for a description in terms of spherical harmonics:

$$b(\mathbf{r}') = \sum_{s,l} \sum_{l\tau} b^{si}_{l\tau}(r) \Pi_{l\tau}(\theta' \varphi') \tag{13}$$

with

$$b^{si}_{l\tau}(r) = \int b^{si}(\mathbf{r}') \Pi_{l\tau}(\theta' \varphi') \, d\tau', \tag{14}$$

where we have assumed that real SAF's have been chosen.

Combining (11) and (14) we may express (13) as

$$b(\mathbf{r}') = \sum_{sl\tau} \frac{b_s}{r^2} \delta(r - r_s) \bar{\Pi}^s_{l\tau} \Pi_{l\tau}(\theta' \varphi') \tag{15}$$

with

$$\bar{\Pi}^s_{l\tau} = \sum_i \Pi_{l\tau}(\theta'_{sl} \, \varphi'_{si}). \tag{16}$$

The expansion (15) is, among all conceivable expansions in the $Y_{lm}(\theta' \varphi')$, distinguished by the fact that it needs the smallest number of shell structure constants $\bar{\Pi}^s_{l\tau}$. The index τ in (16) runs over all totally symmetric SAF's for a given l (Tables 2a, 2b). By using (6) a particular molecular orientation given by the Eulerian angles ω and $b(\mathbf{r}')$ is expressed in the unprimed system Σ

$$b(\mathbf{r}) = \sum_s \frac{b_s}{r^2} \delta(r - r_s) \sum_{l\nu\tau} \bar{\Pi}^s_{l\tau} P_{l\nu}(\theta\varphi) \mathcal{M}^l_{\nu\tau}(\omega). \tag{17}$$

In the system fixed in the crystal the averaged scattering-length density $a(\mathbf{r})$ must be invariant under the site group P

$$a(\mathbf{r}) = \sum_{sl\nu} a^s_{l\nu}(r) P_{l\nu}(\theta\varphi) \tag{18}$$

and $a^s_{l\nu}(r)$ may be written as

$$a^s_{l\nu}(r) = b_s \, c^s_{l\nu} \, \delta(r - r_s)/r^2. \tag{19}$$

It is the quantity $c^s_{l\nu}$ which is determined directly from an experiment. Following Press & Hüller (1973) we introduce a probability density function $f(\omega)$ for the orientation of Σ' with respect to Σ:

$$f(\omega) = \sum_{l\nu\tau} M^l_{\nu\tau} \mathcal{M}^l_{\nu\tau}(\omega). \tag{20}$$

The $M^l_{\nu\tau}$ are constants. The number of $M^l_{\nu\tau}$'s will be determined in § 4. A consequence of the normalization condition for $f(\omega)$ [$\int f(\omega) \, d\omega = 1$] is that the lowest-order constant is fixed: $M^0_{11} = 1/8\pi^2$.

$a(\mathbf{r})$ then takes the form

$$a(\mathbf{r}) = \int f(\omega) \, b(\mathbf{r}) \, d\omega \tag{21}$$

with $d\omega = \sin\beta d\beta d\alpha d\gamma$. From (8), (17), (20) and (21) we obtain

$$a(\mathbf{r}) = \sum_s b_s \, \delta(r - r_s)/r^2 \sum_{l\nu\tau} \frac{8\pi^2}{2l + 1}$$
$$\times P_{l\nu}(\theta\varphi) M^l_{\nu\tau} \bar{\Pi}^s_{l\tau}. \tag{22}$$

The expansions (18) and (22) for $a(\mathbf{r})$ must be identical. Therefore the experimental constants $c^s_{l\nu}$ are given by

$$c^s_{l\nu} = \frac{8\pi^2}{2l + 1} \sum_\tau M^l_{\nu\tau} \bar{\Pi}^s_{l\tau}. \tag{23}$$

In the rigid-molecule approximation all the $\bar{\Pi}^s_{l\nu}$ are numbers which can be calculated from the molecular geometry. So the $M^l_{\nu\tau}$ are free parameters which ultimately can be determined from the experiment.

In an analysis of the Bragg scattering one needs the average structure factor $\bar{F}(\mathbf{Q})$ of the unit cell. We will, at first, assume that the cell contains only one molecule, the center of mass of which coincides with the origin of Σ.

Then

$$\bar{F}(\mathbf{Q}) = e^{-\beta Q^2} a(\mathbf{Q}) \tag{24}$$

with

$$a(\mathbf{Q}) = \int a(\mathbf{r}) e^{i\mathbf{Q}\mathbf{r}} \, d^3 r, \tag{25}$$

where β is the temperature factor of the whole molecule. $a(\mathbf{Q})$ is the rotational form factor of the molecule. Terms coupling translational and rotational degrees of freedom as discussed recently by Press, Grimm & Hüller (1979) have been omitted.

With the expansion

$$e^{i\mathbf{Q}\mathbf{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{\nu=1}^{n(P,l)} i^l j_l(Qr) \times P_{l\nu}(\theta\varphi) P_{l\nu}(\Theta\Phi), \tag{26}$$

where j_l is a spherical Bessel function and the other symbols are given by $\mathbf{r} = (r,\theta,\varphi)$ and $\mathbf{Q} = (Q,\Theta,\Phi)$, we obtain

$$a(\mathbf{Q}) = 4\pi \sum_{sl\nu} i^l j_l(Qr_s) b_s \, c_{l\nu}^s \, P_{l\nu}(\Theta\Phi). \tag{27}$$

4. The number of symmetry-adapted functions

For the crystallographic point groups the SAF's are tabulated in a condensed, symbolic form (Bradley & Cracknell, 1972). For a further discussion of (23) we will also need, however, their number $n(\Pi,l)$ for non-crystallographic point groups. The general expression for $n(\Pi,l)$ is

$$n(P,l) = \frac{1}{h} \sum_{g \in P} \chi^{(l)}(g). \tag{28}$$

Here the sum runs over all the h different group elements g. For a rotation by an angle of $2\pi n/N$ corresponding to the operations of an N-fold axis the character $\chi^{(l)}(g)$ is (Bethe, 1929)

$$\chi^{(l)}(n,N) = \sigma_l \sin(2l+1)\frac{n}{N}\pi / \sin\frac{n}{N}\pi, \tag{29}$$

with

$$\sigma_l = 1 \qquad \text{for proper rotations}$$

$$\sigma_l = (-1)^l \qquad \text{for improper rotations.}$$

Since the characters $\chi^{(l)}(g)$ are the same for all the conjugate elements belonging to one class, $n(P,l)$ may be easily computed from the knowledge of the classes of P (Ljubarski, 1962) and from (29).

Algebraic expressions for the non-cubic groups are given in Table 1, numerical results, together with the $n(P,l)$ for the cubic groups extracted from Bradley & Cracknell (1972) are compiled in Tables 2(a) and 2(b).

The old Schoenflies notation is used in Tables 1 and 2(b) because, apparently, there is no Herrmann–Mauguin nomenclature for non-crystallographic point groups in common use. In solid-state physics and in theoretical chemistry only Schoenflies symbols are applied (Ljubarski, 1962; Hochstrasser, 1966) to them.

Two particularly simple cases will be considered separately, because they occur rather often in conjunction with rotationally disordered molecules. $C_{\infty v}$ is the point group of linear molecules like OH⁻, CN⁻. For every l there is only one SAF, namely $Y_{lm=0}(\theta'\varphi')$. Similarly, linear molecules with an inversion center like H_2, N_2, D_2 obey $D_{\infty h}$ symmetry. In this case only the $Y_{lm=0}(\theta'\varphi')$ with even l's are allowed SAF's.

5. The number of free parameters, and their determination

Returning to equation (23),

$$c_{l\nu}^s = \frac{8\pi^2}{2l+1} \sum_{\tau=1}^{n(\Pi,l)} \bar{\Pi}_{l\tau}^s \, M_{\nu\tau}^l,$$

$\gamma = 1, \ldots, n(P,l)$, $\tau = 1, \ldots, n(\Pi,l)$, $s = 1, \ldots, n_s$ (= number of shells), we realize that it actually represents, for fixed l, a system of linear equations for the

Table 1. *Algebraic expressions giving the number* $n(P,l)$ *of totally symmetric SAF's for non-cubic groups*

The expressions are also valid for non-crystallographic point groups.

P	$n(P,l)$
C_n	$2[l/n] + 1$
C_{nh}	$[l/n] + \frac{1}{2}[1 + (-1)^l] + (-1)^l \sum_{v=1}^{[l/n]} (-1)^{vn}$
D_n	$[l/n] + \frac{1}{2}[1 + (-1)^l]$
C_{nv}	$[l/n] + 1$
D_{nh}	$\frac{1}{2}\{[l/n] + 1 + (-1)^l [1 + \sum_{v=1}^{[l/n]} (-1)^{vn}]\}$
S_{2n}	$[l/n] + \frac{1}{2}[1 + (-1)^l] + (-1)^l \sum_{v=1}^{[l/n]} (-)^{v(n+1)}$
D_{nd}	$\frac{1}{2}\{[l/n] + 1 + (-1)^l [1 + \sum_{v=1}^{[l/n]} (-1)^{v(n+1)}]\}$
$C_{\infty v}$	1
$D_{\infty h}$	$\frac{1}{2}[1 + (-1)^l]$

$[l/n]$ = integer part of l/n.

determination of the unknown parameters $M^l_{\gamma\tau}$. There are N_{par} such parameters and

$$N_{par} = n(P,l)\, n(\Pi,l).$$

The system decays into $n(P,l)$ subsystems, the index γ being constant for each subsystem. Within each subsystem we have n_s equations for the $n(\Pi,l)$ unknown quantities $M^l_{\gamma\tau}$ (γ is fixed) and the unknown parameters are distinct in different subsystems. So we may set $\gamma = 1, 2, ..., n(P,l)$.

If the number of occupied shells is less than the number $n(\Pi,l)$ of totally symmetric Π functions, then

Table 2. *Numerical values of the n (P, l) for crystallographic and non-crystallographic point groups*

Groups marked with an L are the Laue groups: owing to the center of inversion they have only even-l SAF's. The heavy black dots indicate that *all* odd SAF's vanish.

In every column the string enclosed between two horizontal bars is obtained by adding the step Δ to the preceding string. Step widths Δ marked with an asterisk (Δ^*) indicate that $n(P,l)$ is increased by Δ^* only for even l: $n(P,l)=0$ for $l=2m+1$ in these cases.

(a) Crystallographic point groups

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	1	$\bar{1}$	2	m	$\frac{2}{m}$	222	mm2	mmm	4	$\bar{4}$	$\frac{4}{m}$	422	4mm	$\bar{4}2m$	$\frac{4}{m}mm$	3
		L			L			L			L				L	
Δ	2	4*	2	1	2*	1	1	1*	2	2	2*	1	1	1	1*	2
$l=0$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	3	●	1	2	●	0	1	●	1	0	●	0	1	0	●	1
2	5	$\bar{5}$	3	3	3	2	2	2	1	1	1	1	1	1	1	1
3	7	●	3	4	●	1	2	●	1	2	●	0	1	1	●	3
4	9	$\bar{9}$	5	5	5	3	3	3	3	3	3	2	2	2	2	3
5	11	●	5	6	●	2	3	●	3	2	●	1	2	1	●	3
6	13	13	7	7	7	4	4	4	3	3	3	2	2	2	2	5
7	15	●	7	8	●	3	4	●	3	4	●	1	2	2	●	5
8	17	17	9	9	9	5	5	5	5	5	5	3	3	3	3	5
9	19	●	9	10	●	4	5	●	5	4	●	2	3	2	●	7
10	21	21	11	11	11	6	6	6	5	5	5	3	3	3	3	7
11	23	●	11	12	●	5	6	●	5	6	●	2	3	3	●	7
12	25	25	13	13	13	7	7	7	7	7	7	4	4	4	4	9
13	27	●	13	14	●	6	7	●	7	6	●	3	4	3	●	9
14	29	29	15	15	15	8	8	8	7	7	7	4	4	4	4	9
15	31	●	15	16	●	7	8	●	7	8	●	3	4	4	●	11

	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
	$\bar{3}$	32	3m	$\bar{3}m$	6	$\bar{6}$	$\frac{6}{m}$	622	6mm	$\bar{6}2m$	$\frac{6}{m}mm$	23	m3	432	$\bar{4}3m$	m3m
	L			L			L				L		L			L
Δ	4*	2	1	2*	2	2	2*	1	1	1	1*	1	2*	1	1	1*
$l=0$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	●	0	1	●	1	0	●	0	1	0	●	0	●	0	0	●
2	1	1	1	1	1	1	1	1	1	1	1	0	0	0	0	0
3	●	1	2	●	1	2	●	0	1	1	●	1	●	0	1	●
4	3	2	2	2	1	1	1	1	1	1	1	1	1	1	1	1
5	●	1	2	●	1	2	●	0	1	1	●	0	●	0	0	●
6	5	3	3	3	3	3	3	2	2	2	2	2	2	1	1	1
7	●	2	3	●	3	2	●	1	2	1	●	1	●	0	1	●
8	5	3	3	3	3	3	3	2	2	2	2	1	1	1	1	1
9	●	3	4	●	3	4	●	1	2	2	●	2	●	1	1	●
10	7	4	4	4	3	3	3	2	2	2	2	2	2	1	1	1
11	●	3	4	●	3	4	●	1	2	2	●	1	●	0	1	●
12	9	5	5	5	5	5	5	3	3	3	3	3	3	2	2	2
13	●	4	5	●	5	4	●	2	3	2	●	2	●	1	1	●
14	9	5	5	5	5	5	5	3	3	3	3	2	2	1	1	1
15	●	5	6	●	5	6	●	2	3	3	●	3	●	1	2	●

Table 2 (cont.)

(b) Non-crystallographic point groups

Δ	1 C_5 2	2 C_{5h} 1	3 D_5 2	4 C_{5v} 1	5 D_{5h} 1	6 S_{10} 4*	7 D_{5d} 2*	8 C_8 2	9 C_{8h} 2*	10 D_8 1	11 C_{8v} 1	12 D_{8h} 1*	13 S_8 2	14 D_{8d} 1	15 $C_{\infty v}$ 0	16 $D_{\infty h}$ 0*
$l=0$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	1	0	0	1	0	●	●	1	●	0	1	●	0	0	1	●
2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
3	1	0	0	1	0	●	●	1	●	0	1	●	0	0	1	●
4	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
5	3	2	1	2	1	●	●	1	●	0	1	●	0	0	1	●
6	3	1	2	2	1	3	2	1	1	1	1	1	1	1	1	1
7	3	2	1	2	1	●	●	1	●	0	1	●	0	0	1	●
8	3	1	2	2	1	3	2	3	3	2	2	2	1	1	1	1
9	3	2	1	2	1	●	●	3	●	1	2	●	2	1	1	●
10	5	3	3	3	2	5	3	3	3	2	2	2	1	1	1	1
11	5	2	2	3	1	●	●	3	●	1	2	●	2	1	1	●
12	5	3	3	3	2	5	3	3	3	2	2	2	1	1	1	1
13	5	2	2	3	1	●	●	3	●	1	2	●	2	1	1	●
14	5	3	3	3	2	5	3	3	3	2	2	2	1	1	1	1
15	7	4	3	4	2	●	●	3	●	1	2	●	2	1	1	●

the parameters $M^l_{\nu\tau}$ cannot be determined uniquely: only linear constraint equations between the $M^l_{\nu\tau}$ can be formulated in this case.

For $n_s = n(\Pi,l)$ a unique solution in principle is possible provided the matrix of the particular subsystem is nonsingular, or

$$\det \bar{\Pi}^s_{l\tau} \neq 0, s = 1, ..., n_s = n(\Pi,l)$$

$$\tau = 1, ..., \qquad n(\Pi,l).$$

A necessary condition is that no two rows s and $s' \neq s$ be equal:

$$\bar{\Pi}^s_{l\tau} \neq \bar{\Pi}^{s'}_{l\tau}.$$

This condition would be violated, if two shells $(r_s \neq r_{s'})$ were occupied by the same number of atoms at the same angular positions: $(\theta'_{si},\varphi'_{si}) = (\theta'_{s'i},\varphi'_{s'i})$. The simplest conceivable example for this is a linear molecule A_2B_2. For $n_s > n(\Pi,l)$ the (sub-) system of equations can be solved with a least-squares algorithm.

The limitation of the method indicated here is a result of the expansion (20) of $f(\omega)$ (cf. Hüller & Press, 1979).

6. Example: C_2Cl_6

As an illustration we take C_2Cl_6. Crystals of this compound are orientationally disordered for $345 < T < 458$ K (Gerlach, 1979; Gerlach, Hohlwein, Prandl & Schulz, 1981). The structure is cubic with the space group $Im3m$ and with two molecules per unit cell. The centers of mass of the molecules occupy the 2(a) position (International Tables for X-ray Crystallog-

raphy, 1976). With the site symmetry $P = m3m$ and the molecular symmetry $\Pi = \bar{3}m$ (Morino & Yuwasaki, 1949), the number of totally symmetric SAF's is $n(P,l) = 1, 1, 1$ and $n(\Pi,l) = 1, 2, 3$ for $l = 0, 4, 6$, respectively (Table 2a). The carbon atoms form a dumbbell along the trigonal axis, and the chlorine atoms a trigonal antiprism. So we have two occupied shells. The SAF's $\Pi_{l\tau}(\theta'\varphi')$ together with the $\bar{\Pi}^s_{l\tau}$ are given in Table 3. From the analysis of § 5 we see that the two constants of fourth order M^4_{11}, M^4_{12} can be determined uniquely. This is not the case for the $M^6_{l\tau}$ ($\tau = 1, 2, 3$) or any constants of higher order l. As a trivial remark we add that in a hypothetical molecule containing only the chlorine atoms ($n_s = 1$) even the fourth-order constants cannot be determined separately.

From the definition of $f(\omega)$ we may derive several marginal distributions, e.g.

$$f(\alpha\beta|\gamma) = \int f(\alpha\beta\gamma) \, d\gamma \qquad (30)$$

$$f(\alpha|\beta\gamma) = \int f(\alpha\beta\gamma) \sin\beta \, d\beta \, d\gamma. \qquad (31)$$

They can be used to visualize the distribution of the molecular axes. In the C_2Cl_6 case, for instance, the distribution of the threefold molecular axes is given by

$$f(\alpha,\beta|\gamma) = \frac{1}{4\pi} + M^4_{11} \mathscr{M}^4_{11}(\alpha\beta|\gamma) \qquad (32)$$

with

$$\mathscr{M}^4_{11}(\alpha\beta|\gamma) = \int \mathscr{M}^4_{11}(\alpha\beta\gamma) \, d\gamma$$

$$= \frac{4\pi}{3} \sqrt{\pi} \, P_{4a_1}(\beta,\alpha). \qquad (33)$$

Table 3. *The totally symmetric SAF's* $\Pi_{l\tau}$ $(\theta' \varphi')$ *for the point group* $\bar{3}m$ *and the molecular structure constants* $\bar{\Pi}^s_{l\tau}$ *for* C_2Cl_6 ($s = 1 \equiv C$; $s = 2 \equiv Cl$)

θ'_0 is the angle between the trigonal axis and the line between the molecular center of mass and one of the chlorine atoms.

	$\Pi_{l\tau}(\theta', \varphi')$	$\bar{\Pi}^1_{l\tau} = \bar{\Pi}^C_{l\tau}$	$\bar{\Pi}^2_{l\tau} = \bar{\Pi}^{Cl}_{l\tau}$
$l = 0$	$\Pi_{01}(\theta', \varphi') = \dfrac{1}{\sqrt{4\pi}}$	$\sqrt{\dfrac{1}{\pi}}$	$3\sqrt{\dfrac{1}{\pi}}$
$l = 4$	$\Pi_{41}(\theta', \varphi') = Y_{40}$	$3\sqrt{\dfrac{1}{\pi}}$	$\dfrac{9}{8}\sqrt{\dfrac{1}{\pi}}(32\cos^4\theta'_0 - 30\cos^2\theta'_0 + 3)$
	$\Pi_{42}(\theta', \varphi') = \dfrac{1}{\sqrt{2}}(Y_{43} - Y_{4\bar{3}})$	0	$-\dfrac{9}{4}\sqrt{\dfrac{70}{\pi}}\cos\theta'_0\sin^3\theta'_0$
$l = 6$	$\Pi_{61}(\theta', \varphi') = Y_{60}$	$\sqrt{\dfrac{13}{\pi}}$	$\dfrac{3}{16}\sqrt{\dfrac{13}{\pi}}(231\cos^6\theta'_0 - 315\cos^4\theta'_0 + 105\cos^2\theta'_0 - 5)$
	$\Pi_{62}(\theta', \varphi') = \dfrac{1}{\sqrt{2}}(Y_{63} - Y_{6\bar{3}})$	0	$-\dfrac{3}{16}\sqrt{\dfrac{2730}{\pi}}\cos\theta'_0\sin^3\theta'_0(11\cos^2\theta'_0 - 3)$
	$\Pi_{64}(\theta', \varphi') = \dfrac{1}{\sqrt{2}}(Y_{66} + Y_{6\bar{6}})$	0	$\dfrac{3}{32}\sqrt{\dfrac{6006}{\pi}}\sin^6\theta'_0$

Here the Eulerian angles α and β coincide with the polar angles φ, θ in Σ and $\mathcal{M}^4_{11}(\omega)$ has been derived from the $\mathcal{D}$ functions (Edmonds, 1964). $P_{4a_1}(\beta,\alpha) \equiv P_{4a_1}(\theta,\varphi)$ is the only SAF of the point group $m3m$ for $l = 4$.

7. More than one orientationally disordered molecule per unit cell

We next assume that the m symmetrically equivalent positions $R_j(j = 1, \ldots, m)$ of a lattice complex with multiplicity m are the centers of gravity of m orientationally disordered molecules. At each position R_j we define a local orthogonal coordinate system Σ_j which is adapted to the site group P. In general the Σ_j will not be parallel nor will they coincide with the crystal coordinate system Σ which is assumed to be orthogonal also. Σ and the Σ_j will coincide in a unique way only in symmorphic space groups, and then again only if $P = G_0$. This condition applies for the lattice complexes with the lowest multiplicity, e.g. for the $1(a)$ or $1(b)$ complex in $Pm3m$ and for $4(a)$ or $4(b)$ in $Fm3m$.

If referred to local axes Σ_j, the rotational form factor $a_j(Q)$, given in (28), reads

$$a_j(Q) = 4\pi \sum_{sl\nu} i^l j_l(Qr_s)\, b_s\, c^s_{l\nu}\, P_{l\nu}(\Theta_j\, \Phi_j). \quad (27')$$

Table 4. *The calculation of the polar angles of* Q *in the local coordinate system* Σ_j *appropriate to the* $4(a)$ *site in the space group* $Pa3$

j	1	2	3	4
R_j	(000)	$(\tfrac{1}{2}\tfrac{1}{2}0)$	$(\tfrac{1}{2}0\tfrac{1}{2})$	$(0\tfrac{1}{2}\tfrac{1}{2})$
ξ_j	$\dfrac{(1\bar{1}0)}{\sqrt{2}}$	$\dfrac{(110)}{\sqrt{2}}$	$\dfrac{(\bar{1}10)}{\sqrt{2}}$	$\dfrac{(1\bar{1}0)}{\sqrt{2}}$
η_j	$\dfrac{(11\bar{2})}{\sqrt{6}}$	$\dfrac{(\bar{1}1\bar{2})}{\sqrt{6}}$	$\dfrac{(\bar{1}\bar{1}2)}{\sqrt{6}}$	$\dfrac{(11\bar{2})}{\sqrt{6}}$
ζ_j	$\dfrac{(111)}{\sqrt{3}}$	$\dfrac{(\bar{1}\bar{1}1)}{\sqrt{3}}$	$\dfrac{(\bar{1}\bar{1}1)}{\sqrt{3}}$	$\dfrac{(1\bar{1}1)}{\sqrt{3}}$
h_j	$\dfrac{h-k}{\sqrt{2}}$	$\dfrac{h+k}{\sqrt{2}}$	$\dfrac{-h+k}{\sqrt{2}}$	$\dfrac{-h-k}{\sqrt{2}}$
k_j	$\dfrac{h+k-2l}{\sqrt{6}}$	$\dfrac{-h+k-2l}{\sqrt{6}}$	$\dfrac{-h-k-2l}{\sqrt{6}}$	$\dfrac{h-k-2l}{\sqrt{6}}$
l_j	$\dfrac{h+k+l}{\sqrt{3}}$	$\dfrac{-h+k+l}{\sqrt{3}}$	$\dfrac{-h-k+l}{\sqrt{3}}$	$\dfrac{h-k+l}{\sqrt{3}}$
$\cos\Theta_j$	$\dfrac{1}{\sqrt{3}}\dfrac{h+k+l}{H}$	$\dfrac{1}{\sqrt{3}}\dfrac{-h+k+l}{H}$	$\dfrac{1}{\sqrt{3}}\dfrac{-h-k+l}{H}$	$\dfrac{1}{\sqrt{3}}\dfrac{h-k+l}{H}$
$\tan\Phi_j$	$\dfrac{1}{\sqrt{3}}\dfrac{h+k-2l}{h-k}$	$\dfrac{1}{\sqrt{3}}\dfrac{-h+k-2l}{h+k}$	$\dfrac{1}{\sqrt{3}}\dfrac{-h-k-2l}{-h+k}$	$\dfrac{1}{\sqrt{3}}\dfrac{h-k-2l}{-h-k}$

Θ_j, Φ_j are the angular coordinates of **Q** expressed in Σ_j. This can be easily obtained from the following relations:

$$\mathbf{Q} = 2\pi\,\mathbf{H}$$

and

$$\mathbf{H} = h\boldsymbol{\xi} + k\boldsymbol{\eta} + l\boldsymbol{\zeta}$$
$$= h_j\,\boldsymbol{\xi}_j + k_j\,\boldsymbol{\eta}_j + l_j\,\boldsymbol{\zeta}_j,$$

where $\boldsymbol{\xi},\boldsymbol{\eta},\boldsymbol{\zeta}$; $\boldsymbol{\xi}_j,\boldsymbol{\eta}_j,\boldsymbol{\zeta}_j$ are the unit basis vectors of Σ and Σ_j, respectively.

Let β_j be the anisotropic temperature factor appropriate to the local system Σ_j. Then the complete structure factor will be:

$$F(Q) = \sum_j e^{i\mathbf{QR}_j}\, e^{iQ\beta_j Q}\, a_j(\mathbf{Q}). \tag{34}$$

One could of course transform the $P_{l\nu}(\Theta_j\,\Phi_j)$, with (3), to the crystal system Σ. This procedure, however, would require all the Wigner functions $\mathcal{D}^l_{m'm}(\omega_j)$ in addition to the SAF's $P_{l\nu}(\Theta\Phi)$.

As an example the calculation of Q_j, Θ_j, Φ_j for the lattice site 4(a) of the space group $Pa3$ (International Tables for X-ray Crystallography, 1976) is given in Table 4.

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