a one-to-one relationship between crystals in two different orientations. It rather requires an integral relationship between an *infinite* number of crystal orientations.

An exhaustive description of all possible kinds of sample symmetry cannot be given by a normal point symmetry group. It rather requires black–white Shubnikov groups.

The specific case of centrosymmetric crystals is especially important in texture analysis in metallurgy since the basic metals, crystallizing in f.c.c., b.c.c. and h.c.p. lattices, are centrosymmetric. The determinability condition $l =$ even for this case has attracted much attention in the last few years.

The non-centrosymmetric crystal classes are more important in mineralogical and geological problems. Applications of the present considerations to non-centrosymmetrical crystal classes have not yet been reported. Investigations in this direction are presently being carried out and will be published elsewhere.

References

BUNGE, H. J. (1969). *Mathematische Methoden der Textur-analyse.* Berlin: Akademie-Verlag.

BUNGE, H. J. & ESLING, C. (1979a). *C. R. Acad. Sci. Ser. B,* **289,** 163–164.

BUNGE, H. J. & ESLING, C. (1979b). *J. Phys. (Paris) Lett.* **40,** 627–628.

BUNGE, H. J. & ESLING, C. (1981). *J. Appl. Cryst.* **14,** 253–255.

BUNGE, H. J., ESLING, C. & MULLER, J. (1980). *J. Appl. Cryst.* **13,** 544–554.

ESLING, C., BECHLER-FERRY, E. & BUNGE, H. J. (1981). *J. Phys. (Paris) Lett.* **42,** 141–144.

ESLING, C., BUNGE, H. J. & MULLER, J. (1980). *J. Phys. (Paris) Lett.* **41,** 543.

JURA, J., LÜCKE, K. & POSPIECH, J. (1980). *Z. Metallkd.* **71,** 714–728.

LÜCKE, K., POSPIECH, J., VIRNICH, K. H. & JURA, J. (1981). *Acta Metall.* **29,** 167–185.

MATTHIES, S. (1979). *Phys. Status Solidi B,* **92,** K135–K138.

MATTHIES, S. (1980). *Krist. Tech.* **15,** 431–444.

MATTHIES, S. (1981). *Krist. Tech.* In the press.

MATTHIES, S. & POSPIECH, J. (1980). *Phys. Status Solidi B,* **97,** 547–556.

PATERSON, M. S. & WEISS, I. E. (1961). *Geol. Soc. Am. Bull.* **72,** 841–882.

SHUBNIKOV, A. V. & BELOV, N. V. (1964). *Coloured Symmetry.* Oxford: Pergamon Press.

WEISSENBERG, K. (1922). *Ann. Phys. (Leipzig),* **69,** 409–435.

WENK, H. R., WAGNER, F., ESLING, C. & BUNGE, H. J. (1981). *Tectonophysics.* In the press.

Numerical Structure Factor Calculation of Orientationally Disordered Molecules

BY D. HOHLWEIN

Institut für Kristallographie der Universität Tübingen, Charlottenstrasse 33, D-7400 Tübingen, Federal Republic of Germany

Abstract

The structure factor of librating or orientationally disordered molecules with isotropic Gaussian distribution functions is calculated exactly by numerical integration. The computer program with an example is described. The results are compared with approximation methods which correspond to a cumulant expansion of the structure factor. The application to the refinement of the plastic phases of C_2Cl_6 and SF_6 is shown. The influence of anharmonic distributions is considered. The method is compared to the analysis with spherical cubic harmonics.

1. Introduction

There are many crystal structures which contain groups of atoms where the binding forces within a group are higher than those to the surrounding atoms. Such groups are called 'rigid molecules' if the internal vibration frequencies are considerably higher than the external or lattice mode frequencies. With this definition charged groups are included also.

For rigid molecules the thermal motion can be treated in a good approximation as the motion of a rigid body. But, also, disorder which is not of thermal origin can then be regarded as positional or orientation-

al disorder of a rigid body. In both cases the number of parameters needed to describe the disorder of the atoms is reduced. This can be very important because the disorder will in general reduce the number of observable reflections (more exactly: the intensity contribution of the disordered group to the Bragg reflections) and only a limited number of parameters can then be refined.

The thermal motion of a rigid molecule in a crystal can be described in the harmonic approximation by three tensors: **T** for the center-of-mass translational motion, **L** for the libration or torsional vibration and **S** for correlated translation and libration (Schomaker & Trueblood, 1968). The authors mentioned have shown how the conventional anisotropic temperature parameters of the atoms in a molecule can be calculated from the **T**, **L** and **S** tensors and *vice versa*. Most structure determinations start with the individual temperature parameter despite the advantage of less parameters in a direct **T**, **L**, **S** refinement (Pawley, 1972).

In both cases one has to correct for the positional parameters because the librational part of the thermal vibration is only approximated (ellipsoids): the movement of the atoms on a spherical surface is replaced by the movement along tangential planes. Correction factors to the structure factors have been calculated up to the second order of the libration angle (Willis & Pawley, 1970; Pawley & Willis, 1970), corresponding to a cumulant expansion (Johnson, 1969).

In this work the librational part of the movement — or static orientational disorder with the same distribution function — will be calculated exactly by numerical integration. We will confine ourselves to isotropic librations. The computer program and the results for an example are described. The above-mentioned approximations (Willis & Pawley, 1970) are compared with the exact (harmonic) model.

The application of the structure factor calculation to the refinement of the plastic phases of C_2Cl_6 and SF_6 is shown. The influence of an anharmonic potential is tested with an example. Further discussions and a comparison with the analysis in cubic harmonic functions (Kurki-Suonio, 1967; Seymour & Pryor, 1973; Press & Hüller, 1973) are given at the end. A preliminary account of the work has been presented at a conference (Hohlwein, 1980).

2. Theory

We assume one rigid molecule per unit cell. The molecule is specified by the equilibrium position of its center of mass and by a set of several well defined equilibrium orientations. The different orientations have probabilities which have to be consistent with the lattice site symmetry. We construct by superposition an averaged molecule with one orientation. In the following we will speak of one rigid molecule in a definite equilibrium position and keep in mind that this is in general an averaged molecule. As mentioned in the *Introduction* the harmonic movement of a rigid molecule can be described with the three tensors **T**, **L** and **S**. If the molecule has a center of symmetry, then the translational and librational movement will not be correlated (Schomaker & Trueblood, 1968). The structure factor can then be written (convolution theorem)

$$F(Q) = f_T(Q) \cdot F_{\text{lib}}(Q), \qquad (1)$$

with the molecular Debye–Waller factor f_T, the scattering vector $Q = k_1 - k_0$, the wavevectors of scattered and incident radiation k_1, k_0 ($k = k_0 = 2\pi/\lambda$) and the structure factor of a librating molecule F_{lib} with its center of mass at rest:

$$F_{\text{lib}} = \sum_{n=1}^{N} \sum_{\theta,\varphi} p_n(\theta,\varphi) f_n \exp\{i[Q \cdot r_n(\theta,\varphi)]\}, \qquad (2)$$

for N atoms of the molecule with scattering lengths f_n, equilibrium positions $r_n(0,0)$, the polar angles θ,φ which are defined for each atom with respect to its equilibrium position [z axis parallel to $r_n(0,0)$] and the probabilities $p_n(\theta,\varphi)$ that an atom n has turned away from its equilibrium position $r_n(0,0)$ to $r_n(\theta,\varphi)$.

For a harmonic and isotropic libration the probability distributions $p_n(\theta,\varphi)$ are equal and Gaussian in θ and we have:

$$F_{\text{lib}} = c \sum_{n,\theta,\varphi} \exp(-\theta^2/2\omega^2) f_n \exp\{i[Q \cdot r_n(\theta,\varphi)]\}, \qquad (3)$$

with the normalization constant c and the mean-square deviation ω^2 of the Gaussian distribution.

For a given unit cell, fractional coordinates x_n, y_n, z_n and the Miller indices h,k,l, equation (3) becomes:

$$F_{\text{lib}} = c \sum_{n,\theta,\varphi} \exp(-\theta^2/2\omega^2) f_n \exp\{2\pi i[hx_n(\theta,\varphi)$$
$$+ ky_n(\theta,\varphi) + lz_n(\theta,\varphi)]\}. \qquad (3a)$$

Expressions (3) or (3a) can be calculated by analytic approximation methods (§ 5) or — as suggested here — numerically with a computer program.

3. Calculation procedure

To evaluate equation (3a) the Fortran program *FLIB* was written.*

* A short description of the program has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36174 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Around the equilibrium positions of the atoms a (θ_j, φ_k) grid is generated. θ_j goes from 0 to θ_{max} equal to two times the half-width of the Gaussian distribution. φ_k runs from 0 to 2π. The step widths $\Delta\theta$ and $\Delta\varphi$ are chosen to be: $\Delta\theta = \theta_{max}/11$; $\Delta\varphi = \Delta\theta/\sin\theta$, so that the integration points are about equally distributed on the spherical surface.

4. Structure factor as a function of the libration angle

As an example we have calculated with the program *FLIB* the structure factor for an isotropically librating SF_6 molecule with the molecular center at rest.

The fluorine atoms of the molecule form a regular octahedron with the sulfur atom at its center. SF_6 has a plastic phase which is body-centered cubic (Dolling, Powell & Sears, 1979). Therefore, the equilibrium positions for the F atoms were chosen on the axis, *e.g.* (0,0,0·2712).

Fig. 1 shows the calculated structure factors for the first h,k,l reflections. The variation of the intensity with the libration angle is very irregular as a function of $\sin\theta/\lambda$. Therefore, the correlation with an isotropic translational temperature factor $[\exp(-B\sin^2\theta/\lambda^2)]$ will be small, at least for not-too-high libration angles.

5. Comparison with approximations

Approximations of the structure factor for an isotropic and harmonically librating rigid molecule up to the second order of the mean-square libration angle ω^2 have been given (Willis & Pawley, 1970). In the first approximation they found:

$$F_{\text{lib}} = \sum_n f_n \exp[i\mathbf{Q}\cdot\mathbf{r}_n(1 - \omega^2) - \tfrac{1}{2}Q^2 r_n^2 \omega^2 \sin^2\alpha_n], \quad (4)$$

with the angle α_n between $\mathbf{r}_n$ and $\mathbf{Q}$; the index n for the individual atoms is missing in the paper of Willis &
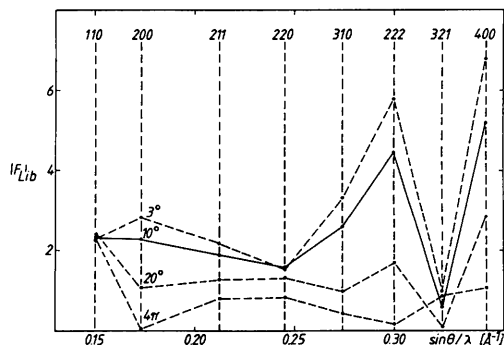
Pawley. In the second approximation they derived:

$$F_{\text{lib}} = \sum_n f_n \exp[i\mathbf{Q}\cdot\mathbf{r}_n(1 - \omega^2 + \tfrac{5}{12}\omega^4)]$$

$$\times \exp[-\tfrac{1}{2}Q^2 r_n^2(\omega^2 \sin^2\alpha_n$$

$$+ \omega^4 \cos^2\alpha_n - \tfrac{17}{12}\omega^4 \sin^2\alpha_n)]$$

$$\times \exp[i\tfrac{1}{2}Q^3 r_n^3 \omega^4 \cos\alpha_n \sin^2\alpha_n]. \quad (5)$$

For the above-mentioned example of SF_6 we have compared our numerically evaluated structure factors with the results of equations (4) and (5). The discrepancies are expressed as $R(F) = \sum_l |F_{1l} - F_{2l}|/\sum_l |F_{1l}|$ for the first 23 h,k,l reflections which are observable in the plastic phase of SF_6 (Dolling *et al.*, 1979). Fig. 2 shows the R values as a function of the libration angle ω. For $\omega = 10°$ the R value is already about 0·1. The second approximation does not improve the situation substantially. In the refinement of measured data the discrepancies will show up less clearly in the R factors because the libration angle can be refined to values different from the true values. An example for such a case will be contained in § 6. The errors in the numerical structure factor calculation due to the limited number of integration points are less than 0·02 in R.

6. Refinement of plastic phases

The program *FLIB* has been built into a standard least-squares program: *LIBLSQ*. For the center-of-mass motion we assumed an isotropic Debye–Waller factor, $\exp(-\tfrac{1}{2}Q^2 T^2)$. With this we analyzed the plastic phases of C_2Cl_6 and SF_6.

The results for C_2Cl_6 together with a comparison with other refinement models are in the following paper (Gerlach, Hohlwein, Prandl & Schulz, 1981). Therefore we mention here only one example of a refinement (Table 1). The R factor is quite satisfactory and is better or about equal to those of other models with more parameters. The approximation method [equation (4)] gives considerably different parameters and a higher R value.
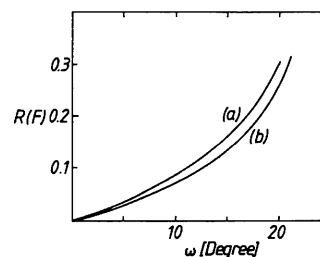

Fig. 1. Structure factor of an isotropically librating SF_6 molecule for the first h,k,l reflections. Libration angles $\omega = 3, 10, 20°$ and full rotation (4π).

Fig. 2. R factors as defined in the text between the numerical calculation $(FLIB)$ and the cumulant expansions of (a) equation (4), and (b) equation (5), for the case of an isotropically librating SF_6 molecule with libration angles ω.

Table 1. *Refinement of the plastic phases of* C_2Cl_6 *at 423 K* (a, b) *and* SF_6 *at 110 K* (c, d) *with LIBLSQ* (a, c) *and equation* (4) (b, d)

T (Å) is the translational temperature parameter, and ω (°) the librational angle.

	T	ω	R (F)
(a)	0·40 (2)	19·6 (3)	0·04
(b)	0·46 (3)	15·8 (7)	0·10
(c)	0·15 (1)	14·1 (5)	0·071
(d)	0·16 (2)	12·2 (5)	0·089

The plastic phase of SF_6 has already been analyzed with an approximation method [equation (4)] and with cubic harmonic functions (Dolling *et al.*, 1979). We have refined their diffraction data with the Gaussian model and the equilibrium positions described in § 4. Table 1 shows the results together with values of a refinement with the approximation method [equation (4)]. With the same number of parameters a better fit is achieved with the exact harmonic model.

7. Influence of the distribution function

If we regard the librating molecule as a single oscillator (Einstein model) then the Gaussian distribution follows from a harmonic potential V:

$$V(\theta) = D\theta^2 \qquad (6)$$

(for $\theta \ll 2\pi$) with a constant D. In the high-temperature approximation the distribution function $p(\theta)$ is:

$$p(\theta) = \exp(-V/kT) = \exp(-D\theta^2/kT), \qquad (7)$$

with the Boltzmann constant k and the absolute temperature T. The mean-square deviation ω^2 of the Gaussian distribution is then
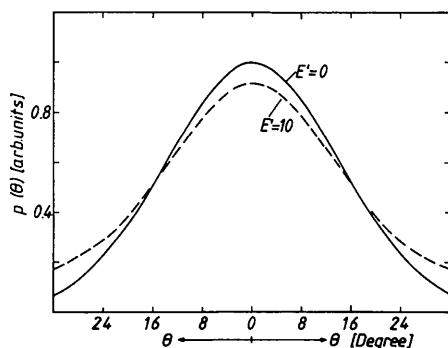
$$\omega^2 = kT/2D. \qquad (8)$$

Fig. 3. Angular distribution functions $p(\theta) = \exp(-D'\theta^2 - E'\theta^4)$ with $E' = 0$ and $E' = 10$ [equation (10), § 7]. For the plastic phase of SF_6 we found $E' = -6 \pm 6$.

The distribution function will be modified if the rotational potential contains higher-order terms, *e.g.* a quartic term (to preserve the isotropic case):

$$V(\theta) = D\theta^2 + E\theta^4, \qquad (9)$$

with constants D and E. Then

$$p(\theta) = \exp(-D\theta^2/kT - E\theta^4/kT)$$

$$= \exp(-D'\theta^2 - E'\theta^4). \qquad (10)$$

We note that reasonable potentials can be chosen in direct space without worrying whether the Fourier transform can be found analytically.

In order to estimate the accuracy of the Gaussian approximation we have refined the diffraction data of SF_6 in the plastic phase with free parameters D' and E' of equation (10). The final value of E' is -6 ± 6. Fig. 3 shows the distribution function for $E' = 0$ and $E' = 10$. Any deviation from the Gaussian distribution must be larger than shown in Fig. 3 before it can be detected with the limited amount of observable diffraction data.

8. Discussion and conclusion

The structure factors for an isotropic and harmonic librating molecule have been calculated previously with approximation methods only (§ 5). The second approximation already gives a complicated formula, equation (5), and is only good for relatively low libration angles. The advantage of a numerical calculation of the structure factors is that for such simple physical models exact values are obtained.

For the plastic phases of C_2Cl_6 and SF_6 the model of isotropic Gaussian librations is quite satisfactory. The model has a low number of parameters which is important as only 10 to 20 reflections are observable in these cases. From the Bragg reflections alone one cannot, of course, decide whether the Gaussian distributions are fully of dynamical origin or whether static components of orientational disorder are present.

Deviations from a Gaussian distribution can be easily taken into account, as has been shown for a fourth-order (anharmonic) term in the rotational potential in § 7. Also, it will not be difficult to include anisotropic distributions. Distribution functions in direct space can often be more easily calculated from a physical model than the Fourier transforms.

The application to plastic phases of simple molecular crystals can be extended to more complicated structures where only a part of the structure is strongly librating or orientationally disordered. If the frame of the structure is relatively rigid there will be many observable reflections up to high diffraction angles. This can lead to long computing times if the *FLIB*

program is incorporated. However, a strongly librating group will contribute considerably to the reflections in the low-angle region only. Therefore, the structure refinement can be started with conventional anisotropic temperature factors. In a second step one can subtract from the observed F values calculated ones which are computed on the basis of the refined frame structure. The smaller number of relevant differences can then be used for a more detailed analysis of the strongly librating group with the *LIBLSQ* program.

For the structure determination of cubic plastic phases of simple molecules the cubic harmonic analysis has been widely adapted (*e.g.* Press, 1973; Levy, Sanger, Taylor & Wilson, 1974; More, Lefebvre & Fouret, 1977; Dolling *et al.*, 1979). In this method the scattering density on spherical shells around the molecular center is expanded in symmetry-adapted spherical surface harmonics. This procedure is analogous to a Fourier expansion in a Cartesian coordinate system and can be called spherical Fourier expansion (Atoji, 1958). The expansion coefficients are refined with a least-squares program. This method is very general as no equilibrium orientations of the molecule are required and only shell radii, the number of atoms in a shell and the site symmetry enter into the refinement. The small amount of information inevitably increases the number of free parameters. The way back from the scattering density distribution to the orientational distribution function is in general not unique (Prandl, 1981) and it is also difficult to constrain the parameters in such a way that the two distribution functions are everywhere positive or zero (Hüller & Press, 1979). Therefore, a good refinement can lead to an unphysical result. Another restriction of the method comes from the fact that the number of parameters has to be low as only a small number of Bragg reflections are observable in plastic crystals. For the favorable high-symmetry case of four identical Gaussian distributions on the poles of a sphere it has been demonstrated (Press & Hüller, 1973) that for a relatively large libration angle of $15°$ one still needs at least five expansion coefficients.

With these arguments we come to the conclusion that the cubic harmonic analysis should only be used as a method to find a suitable model for the orientational distribution function analogous to the use of Fourier and difference Fourier methods in normal structure analysis. A specific model will in general reduce the number of parameters and no further approximations are necessary if the structure factor is then calculated numerically as shown in this work. The parameters will then also have a direct geometrical or physical meaning.

References

ATOJI, M. (1958). *Acta Cryst.* **11**, 827–829.
DOLLING, G., POWELL, B. M. & SEARS, V. F. (1979). *Mol. Phys.* **37**, 1859–1883.
GERLACH, P., HOHLWEIN, D., PRANDL, W. & SCHULZ, F. W. (1981). *Acta Cryst.* A**37**, 904–908.
HOHLWEIN, D. (1980). DMG/AgKr-Tagung, Göttingen; *Z. Kristallogr.* **154**, 290–291.
HÜLLER, A. & PRESS, W. (1979). *Acta Cryst.* A**35**, 876–880.
JOHNSON, C. K. (1969). *Acta Cryst.* A**25**, 187–194.
KURKI-SUONIO, K. (1967). *Ann. Acad. Sci. Fenn. Ser. A* **4**, pp. 241–263.
LEVY, J. H., SANGER, P. L., TAYLOR, J. C. & WILSON, P. W. (1974). *Acta Cryst.* B**31**, 1065–1067.
MORE, M., LEFEBVRE, J. & FOURET, R. (1977). *Acta Cryst.* B**33**, 3862–3865.
PAWLEY, G. S. (1972). *Advances in Structure Research by Diffraction Methods*, Vol. 4, edited by W. HOPPE & R. MASON, p. 32. Oxford: Pergamon Press.
PAWLEY, G. S. & WILLIS, B. T. M. (1970). *Acta Cryst.* A**26**, 260–262.
PRANDL, W. (1981). *Acta Cryst.* A**37**, 811–818.
PRESS, W. (1973). *Acta Cryst.* A**29**, 257–263.
PRESS, W. & HÜLLER, A. (1973). *Acta Cryst.* A**29**, 252–256.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
SEYMOUR, R. S. & PRYOR, A. W. (1973). *Acta Cryst.* B**26**, 1487–1491.
WILLIS, B. T. M. & PAWLEY, G. S. (1970). *Acta Cryst.* A**26**, 254–259.