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Analysis of Orientationally Disordered Structures. II. Examples: Solid CD_4, *p*-D_2 and ND_4Br

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In a number of examples a new method of analysing orientational structures of molecular crystals is illustrated. An application to solid heavy methane demonstrates a close analogy to magnetic structures. In the case of solid *p*-D_2, structure factors are calculated on the basis of the rotational wave functions of the individual molecules and a comparison with neutron diffraction data is performed. Finally several solid phases of ND_4Br, representative of the ammonium halides, are investigated and a better understanding of the orientational order in the NaCl-type phase is achieved.

I. Introduction

In the foregoing paper (Press & Hüller 1973; hereafter referred to as paper I) a new method of analysing orientational structures of molecular crystals has been developed. It is the purpose of the present paper to illustrate this method by applying it to several molecular solids. These examples will also help in the decision as to whether the method is useful in a specific case.

As has been pointed out in paper I, orthonormal surface harmonics most favourably apply to the analysis of neutron diffraction data from plastic crystalline phases. Plastic crystals (Timmermans, 1961; Pawley, 1972) possess an ordered centre-of-mass lattice and a very low entropy change at the melting point. Unfortunately very little neutron diffraction data about such solids is presently available, probably because Debye–Waller factors and, additionally, rotational form factors in general cause an extremely rapid decrease of intensities (paper I), and thus relatively poor diffraction patterns are obtained. Yet recently a growing interest in plastic crystalline phases and plastic phase transitions (Pawley, 1972) has developed and an increasing number of measurements may be expected.

Our interest in the analysis of orientationally disordered or ordered structures was aroused by the investigation of the solid phases of CD_4 (Press, Dorner & Will, 1970; Press, 1972). In our opinion some better understanding of the diffraction patterns has developed with the application of cubic harmonics. Therefore, as a first example, phases I and II of CD_4 will be treated in § II. In addition, solid methane seems to be well suited for illustrating the analogy between orientational order–disorder transitions and magnetic systems. In § III the low–temperature structure of *p*-deuterium (Mucker, Harris, White & Erickson, 1968) is investigated. In this simple case an explicit relation may be established between the wave function of the free molecule and the rotational formfactor $F^{\rm rot}(\mathbf{R})$. Neutron data on phases I, II and IV of ND_4Br (Levy & Peterson, 1953) are reanalysed in § IV: ND_4Br has attracted much attention in the last few years. The phases under consideration are distinguished by particularly simple centre-of-mass structures with just one molecule per primitive cell. The new method of data analysis provides a much simpler description of the orientational order in the high-temperature phase than has previously been given.

In paper I the structure factor was written

$$F(\mathbf{Q})=\sum_j \exp\,(i\,.\,\mathbf{Q}\,.\,\mathbf{R}_j^0) \times \exp\,[-W_j(\mathbf{Q})]\,.\,F^{\rm rot}(\mathbf{Q})\quad . \tag{1.1}$$

$\mathbf{Q}$ is the momentum transfer of the neutrons which may be expressed in terms of the Miller indices *hkl* and the lattice constant a_0 (the examples given in the following all have cubic structures) as

$$\mathbf{Q}=(2\pi/a_0)\,.\,(h,k,l)\,. \tag{1.2}$$

$\mathbf{R}_j^0$ denotes the (equilibrium) centre-of-mass position of the *j*th molecule in the cell; $\exp\,[-W_j(\mathbf{Q})]$ is the Debye–Waller factor. The rotational form factor $F^{\rm rot}(\mathbf{Q})$ of a molecular shell is expressed in terms of the cubic harmonics $K_{l'm}(\Omega_Q)$ (von der Lage & Bethe, 1947; Altmann & Cracknell, 1965:

$$F^{\rm rot}(\mathbf{Q})=4\pi\sum_{l'm} i^{l'}je'(\mathbf{Q}\,.\,\varrho)\,.\,\tilde{c}_{l'm}\,.\,K_{l\,m}'(\Omega_Q)\,. \tag{1.3}$$

$j_{l'}(\mathbf{Q}.\varrho)$ is a spherical Bessel function of argument $Q.\varrho$, where ϱ is the radius of the molecular shell under consideration and the $\tilde{c}_{l'm}$ are the expansion coefficients of the cubic harmonics. Ω_Q denotes the polar coordinates of the scattering vector $\mathbf{Q}$ which will be expressed as

$$\Omega_Q=(h,k,l)/\sqrt{h^2+k^2+l^2}=(h_1,k_1,l_1)\,. \tag{1.4}$$

The cubic harmonics $K_{l'm}(\Omega)$ which are invariant under the operations of the tetrahedral group (von der Lage & Bethe, 1967) are listed in Table 1 up to the order $l'=8$ [the cubic harmonics may also be expressed as linear combinations of spherical harmonics (Altmann & Cracknell, 1965)]. The index m of $K_{l'm}$ does not have the physical meaning of a component of angular momentum. The assignment of $2l'+1$ different numbers to m is therefore arbitrary. For functions having tetrahedral symmetry $m=1$ has been chosen.

Table 1. *Cubic harmonics $K_{l1}(\Omega)$ which are invariant under the operations of the tetrahedral group (listed up to the order $l=8$)*

Ω denotes the polar coordinates either of the positional vector **r** or of the scattering vector **Q**. Functions in square brackets indicate functions with normalization factors omitted.

$K_{01}(\Omega)=1$

$K_{31}(\Omega)=\sqrt{105}xyz$

$K_{41}(\Omega)=(5\sqrt{21}/4)\,(x^4+y^4+z^4-\frac{3}{5})$

$K_{61}(\Omega)=(231\sqrt{26}/8)\,(x^2y^2z^2+\frac{1}{22}[K_{41}]-1/105)$

$K_{71}(\Omega)=\frac{11}{4}\sqrt{1365}xyz(x^4+y^4+z^4-5/11)$

$K_{81}(\Omega)=\frac{65}{16}\sqrt{561}(x^8+y^8+z^8-\frac{28}{5}[K_{61}]-\frac{210}{143}[K_{41}]-\frac{1}{3})$

The form factor $1/\sqrt{4\pi}$ is common to all harmonics and has been omitted. Introducing $c_{l'm}=\tilde{c}_{l'm}/\sqrt{4\pi}$, where c_{0l} relates directly to the integral scattering length of the atoms on a spherical shell, the factor 4π in equation (1.3) cancels and will also be omitted in the following. The first few expansion coefficients for an octahedron and a tetrahedron of zero librational amplitude are given in Table 2 (the integral scattering length is a common factor to all coefficients and has been extracted).

Table 2. *Expansion coefficients c_{l1}^T of a tetrahedron with zero librational amplitude and expansion coefficients c_{l1}^O of an octahedron with zero librational amplitude*

$c_{01}^T=1{\cdot}0$	$c_{01}^O=1{\cdot}0$
$c_{31}^T=\sqrt{35}/9$	$c_{41}^O=\sqrt{21}/2$
$c_{41}^T=-\sqrt{7}/3$	$c_{61}^O=\sqrt{26}/4$
$c_{61}^T=\sqrt{26}$	$c_{81}^O=\sqrt{33\,.\,17}/8$
$c_{71}^T=-\sqrt{465}/9$	
$c_{81}^T=\dfrac{\sqrt{33\,.\,17}}{27}$	

II. Solid methane (CD_4)

(*a*) CD_4 I

In its high-temperature phase (89·7°K $\geq T \geq$ 27·0°K) CD_4 has been found to crystallize in the space group *Fm*3*m* (Press *et al.*, 1970; Press, 1971, 1972), with four molecules in the face-centred cell (lattice constant $a_0=5{\cdot}85$ Å at 34·5°K). The methane molecules are essentially disordered; the site symmetry *m*3*m* is higher than the molecular symmetry $\bar{4}3m$. Complete disorder, that is, an isotropic distribution of the scattering length on a spherical shell (radius $\varrho \simeq 1{\cdot}09$ Å) is described by the cubic harmonic $K_{01}(\Omega)$. A question of interest concerns deviations from spherical symmetry, presumably due to angle-dependent hard-core repulsion. Hints of such deviations (then named 'partial order') have been detected in a neutron diffraction study – surprisingly at high temperatures (Press *et al.*, 1970; Press, 1972), while no visible indications were found at lower temperatures.

We have reanalysed our old data in terms of cubic harmonics. The structure factor reads

$$F(\mathbf{Q})=\exp\left(-\langle u^2\rangle Q^2/2\right).\{b_C+4\,.\,b_D\,.\,[j_0(\mathbf{Q}\,.\,\varrho)+c_{41}\,.\,j_4(Q\,.\,\varrho)\,.\,K_{41}(\Omega_Q)-c_{61}\,.\,j_5(Q\,.\,\varrho)\,.\,K_{61}(\Omega_Q)+\cdots]\}\,. \quad (2.1)$$

$\langle u^2\rangle$ is an isotropic mean-squared amplitude, $b_C=0{\cdot}665$ and $b_D=0{\cdot}62$ (in units of 10^{-12} cm) are the scattering lengths of the carbon and deuterium atoms respectively. A better fit of the data measured at 77°K is obtained, with a reduction of the *R* index from 14·5 to 11·5%. The results for the expansion coefficients are $c_{41}=0{\cdot}26\pm0{\cdot}04$ and $c_{61}=0{\cdot}0$ within the goodness of fit. The other previously determined parameters remain essentially unchanged. $c_{41}=0{\cdot}26$ probably provides an upper limit for the modulation of the density distribution by $K_{41}(\Omega)$. The data at 34·5°K, on the other hand, indicate complete disorder, since both coefficients vanish within the limits of accuracy.

(*b*) CD_4 II

For phase II of solid CD_4(27·0°K $\geq T \geq$ 22·1°K) the cubic space group *Fm*3*c* has recently been found (Press, 1971, 1972), with 32 molecules in the face-centred cell ($a_0=11{\cdot}64$ Å at 24·5°K). The carbon atoms form a simple f.c.c. lattice as in phase I. Two different symmetry sites are occupied by the molecules: (i) six of eight molecules in the primitive cell, that is, six of eight sublattices are ordered [position (*c*) with point symmetry $\bar{4}2m$]; (ii) the molecules on the remaining two sublattices are orientationally disordered [positions (*a*) with point symmetry 432]; each molecular site is surrounded by a shell of antiferro-ordered nearest neighbours (James & Keenan, 1959) and therefore the octopole field vanishes.

The structure may be parametrized in the way described in paper I. The full expression for the structure factor is rather lengthy and an explicit formulation will not be given. As the site symmetry of the ordered tetrahedra is tetragonal, in principle symmetry-allowed harmonics in addition to the ones listed in Table 1 must be considered (*e.g.* one additional harmonic of order 2,4 or 5). On the other hand it may be concluded from Raman measurements in phase II (Chapados & Cabana, 1970), that such a tetragonal distortion of the ordered molecules is extremely small and may be neglected. The site symmetry is probably very nearly cubic, that is, the tetragonality of the crystalline field is rather weak. In the present example restriction to the harmonics with tetrahedral symmetry $[K_{l'1}(\Omega)]$ is possible only in coordinate systems related to the cubic axes by a 45° rotation around the fourfold axis at each molecular site (ordered molecules).

In the first step of refinement only six parameters have been included: scale factor, b_D, $\langle u^2\rangle$, ϱ_{CD_4} and the expansion coefficients c_{31} and c_{41} (for the ordered molecules). With the powder and single-crystal data the *R* values converged to 7·0 and 21·2% respectively, which essentially reproduces the values previously obtained with 9 parameters. Only the results for the expansion coefficients will be given:

Powder data: $c_{31}=1{\cdot}37\pm0{\cdot}10$ $c_{41}=0{\cdot}84\pm0{\cdot}10$
Single-crystal data: $c_{31}=1{\cdot}48\pm0{\cdot}15$ $c_{41}=0{\cdot}68\pm0{\cdot}11$.

In further steps of refinement higher-order harmonics, tetragonal distortion, and anisotropic thermal-motion parameters have been included. As the R index for the single-crystal data did not converge beyond 19%, the final parameters are apparently not very meaningful and will not be presented here. Thus, more precise data would be very helpful, especially to obtain rigorous evidence as to how far complete disorder can be attributed to the molecules at sites of octahedral symmetry.

The analogy between orientationally disordered and ordered solids and magnetic systems, pointed out in paper I, may be illustrated very nicely with the example of CD_4 I and CD_4 II. For simplicity isotropic (harmonic) Debye–Waller factors identical for all molecules and spherically symmetric density distributions for the disordered tetrahedra (in both phases) will be assumed.

The isotropic part in the density distribution of each molecule is responsible for the Bragg reflexions in phase I. In phase II it contributes to exactly the same Bragg peaks, which now are indexed $2h_{\rm I}\ 2k_{\rm I}\ 2l_{\rm I}$. In analogy with magnetic systems undergoing paramagnetic-to-antiferromagnetic transitions, additional superlattice reflexions arise in phase II, which are due to the orientational ordering. We may study this in more detail by writing down the structure factor $\tilde{F}(\mathbf{Q})$ for a pair of ordered CD_4 molecules which are connected by inversion symmetry.

$$\tilde{F}(\mathbf{Q})=[\exp(i\mathbf{Q}\,.\,\mathbf{R}_1)\,.\,F^{\rm rot}_{(1)}(\mathbf{Q}) + \exp(-i\,.\,\mathbf{Q}\,.\,\mathbf{R}_1)\,.\,F^{\rm rot}_{(2)}(\mathbf{Q})]\exp(-\langle u^2\rangle Q^2/2) \tag{2.2}$$

with

$$\mathbf{R}_1=(\tfrac{1}{4},0,0)\,.\,a_0$$

and

$$\mathbf{Q}=(2\pi/a_0)\,.\,(h,k,l)\,.$$

The rotational form factor $F^{\rm rot}_{(1)}(\mathbf{Q})$ reads:

$$F^{\rm rot}_{(1)}(\mathbf{Q})=4\,.\,b_D\sum_{l'm} i^{l'}\,.\,j_{l'}(Q\,.\,\varrho)\,.\,c^{(1)}_{l'm} \times K_{l'm}(\Omega_Q)=\sum_{l'}\,.\,\tilde{F}^{l'}_{(1)}(\mathbf{Q})\,. \tag{2.3}$$

Because of inversion symmetry and the parity of the cubic harmonics

$$\tilde{F}^{l'}_{(2)}(\mathbf{Q})=\tilde{F}^{l'}_{(1)}(-\mathbf{Q})=(-1)^{l'}\,.\,\tilde{F}^{l'}_{(1)}(\mathbf{Q})\,. \tag{2.4}$$

Inserting (2.3) and (2.4) into (2.2) we obtain

$$\tilde{F}(\mathbf{Q})=i^h[\sum_{l'}\{1+(-1)^{h+l'}\}\tilde{F}^{(1)}_{l'}(\mathbf{Q})] \times\exp(-\langle u^2\rangle Q^2/2)\,. \tag{2.5}$$

As may readily be seen, the above calculation is exactly the same for the two other pairs of ordered tetrahedra in the primitive cell. The curly bracket in equation (2.5) is non-zero only for even values of the sum $(l'+h)$, where h may be replaced by k and l, thus giving rise to two different kinds of superlattice reflexions: odd-parity harmonics contributing to the density distribution of ordered tetrahedra give rise to superlattice reflexions of indices hkl all odd only. On the other hand, superlattice reflexions of even indices are due to cubic harmonics of even parity only. These also contribute to the 'centre-of-mass' reflexions (the ones already present in phase I): solid CD_4 II is not strictly antiferro-ordered, therefore.

In the powder pattern of CD_4 II (Press, 1971, 1972) no superlattice reflexions at smaller scattering angles than that of the reflexions 531 have been observed ($Q_{531}=3{\cdot}15$ Å^{-1}). The reason for this is now well understood: first, reflexions of indices hkl all odd are systematically absent as a result of the diffraction symbol $F..c$ of the space group, second, the superlattice intensities arising from even-parity harmonics are proportional to $j_4^2(Q\,.\,\varrho)$ for small Q values and $j_4\,(Q\,.\,\varrho)$ increases very slowly with Q.

III. Low-temperature structure of *p*-deuterium

p-Deuterium and *o*-hydrogen possess two solid phases: a hexagonal high-temperature phase and below $T_c=4{\cdot}0\,^\circ$K(p-D_2) a cubic low-temperature phase. Theoretical considerations (Raich & James, 1966) as well as optical measurements (Hardy, Silveira & McTague, 1969) suggest an orientationally ordered low-temperature structure of space group *Pa*3 (No. 205 of *International Tables for X-ray Crystallography*, 1952). It is widely believed that the rotational quantum number J is a good quantum number even in the solid state. At low temperatures we are concerned with all p-D_2/o-H_2 molecules in the rotational ground state, labelled with $J=1$, $M=0$. The structure presumed stable down to absolute zero (*Pa*3) is described with an f.c.c. centre-of-mass lattice and the (rotational, quantization axes directed along body diagonals.

A neutron diffraction study of p-D_2 (enriched to 80%) (Mucker *et al.*, 1968) essentially confirmed the picture of an orientationally ordered low-temperature structure. Yet the presence of only 5 observed reflexions did not allow many detailed conclusions. Unfortunately, the 2 cubic primitive reflexions (210, 211), (i) indicating the correctness of the space group and – as we shall see later – (ii) being very susceptible to details of the rotational wavefunctions, were extremely weak and, in addition, strongly masked by background scattering originating from the aluminum sample chamber. In spite of the limited number of experimental data, we feel that solid hydrogen provides an extremely simple and interesting example for a structure analysis using cubic harmonics. Though such an application would be straightforward for both solid structures of p-D_2, discussion will be restricted to the low-temperature phase. As for o-H_2, everything is quite analogous, except that the rotational energy spacing is wider by a factor of two.

The structure factor is

$$F(\mathbf{Q})=\sum_{j=1}^{4}\cos\,(\mathbf{Q}\,.\,\mathbf{R}_j)\,.\,\exp\,[-W_j(\mathbf{Q})]\,.\,F^{\mathrm{rot}}_{(j)}(\mathbf{Q}) \tag{3.1}$$

with

$$F^{\mathrm{rot}}_{(j)}(\mathbf{Q})=2\,.\,b_{\mathrm{D}}\sum_{l'm}(-1)^{l'}\,.\,j_{2l'}(Q\,.\,\varrho)c_{2l'm}K^{(j)}_{2l'm}(\Omega_Q)\,. \tag{3.2}$$

The sum in (3.1) runs over the unit cell; R_j denotes the f.c.c. centre-of-mass coordinates [positions (*a*) of space group *Pa*3]. The site symmetry of the hydrogen molecules, according to the space group *Pa*3, is $\bar{3}$. We thus have only one symmetry-allowed harmonic of order 2, namely

$$K^{(1)}_{2A}(\Omega)=\sqrt{5}\,.\,(xy+xz+yz) \tag{3.3}$$

for one sublattice. There are two fourth-order harmonics, one of which $[K_{41}(\Omega)]$ is totally symmetric with respect to the operations of the cubic point group *m*3*m*. Since the D–D distance $2\varrho=0{\cdot}7416$ Å is extremely small, there will be little information on higher-order harmonics. This is due to the behaviour of the spherical Bessel functions $j_{l'}(\mathbf{Q}.\varrho)$ with small argument $\mathbf{Q}.\varrho$. Even to obtain information on the harmonics of order 4, measurements must be extended far out in reciprocal space to Q values of about 8 Å^{-1}. Thus, with the data at present available, we may restrict our attention to the factor in front of $K_{2A}(\Omega)$. If, furthermore, we assume that the anisotropy of the harmonic Debye–Waller factor is negligibly small (which should hold rather well because of the almost spherical electron distribution of the molecules), we arrive at a situation strictly analogous to the one met in connexion with antiferromagnets. With the above approximations, the structure factor reads

$$F(\mathbf{Q})=\sum_{j=1}^{4}\cos\,(\mathbf{Q}\,.\,\mathbf{R}_j)\,.\,\exp\,(-\langle u^2\rangle Q^2/2)\,.\,F^{\mathrm{rot}}_{(j)}(\mathbf{Q}) \tag{3.4}$$

$$F^{\mathrm{rot}}_{(j)}(\mathbf{Q})=2\,.\,b_D[j_0(Q\,.\,\varrho)-j_2(Q\,.\,\varrho)\,.\,c_{2A}\,.\,K^{(J)}_{2A}(\Omega_Q)]\,. \tag{3.5}$$

The spherically symmetric part of the density distribution is responsible for 'nuclear reflexions', giving rise to intensities proportional to $j_0^2(\mathbf{Q}.\varrho)$ at f.c.c. reflexions only. On the other hand, there are superlattice reflexions with $|F(Q)^2\sim j_2^2(\mathbf{Q}.\varrho)\mathrm{c}_{2A}^2\,.\,K^2_{2A}(\Omega._Q)$, indicating orientational order. We shall concentrate on this latter contribution. Fourth-order terms contribute to f.c.c. reflexions as well.

Accepting $J=1$ as a good quantum number, the scattering-length density at one molecular site may be written down immediately:

$$\begin{aligned}b^{(J)}(\Omega)&=2\,.\,b_{\mathrm{D}}\,.\,\psi^{(J)}_{1,0}(\Omega)\,.\,\psi^{(J)*}_{1,0}(\Omega)\\&=2\,.\,b_D\,.\,[1+2/\sqrt{5}\,.\,K^{(J)}_{2A}(\Omega)]\,.\end{aligned} \tag{3.6}$$

$\psi^{(J)}_{1,0}(\Omega)$ is the wave function of a hydrogen molecule with $J=1$, $M=0$. Inserting $c_{2A}=2/\sqrt{5}$ into equation (3.5) superlattice intensities smaller by about a factor 6 than those reported by Mucker *et al.* (1968) are obtained.

On the other hand, we may follow the description chosen by Mucker and coworkers in their calculation of the structure factor: they effectively used a rigid linear molecule performing only isotropic translational motions. With respect to the rotational aspects one is faced with a δ scatterer on a sphere. We may expand this in spherical harmonics and obtain a scattering-length density

$$b^{(J)}(\Omega)=2\,.\,b_{\mathrm{D}}\,.\,(1+\sqrt{5}\,.\,K^{(J)}_{2A}(\Omega)-\sqrt{7/3}\,.\,K_{41}(\Omega)\pm\cdots)\,. \tag{3.7}$$

This yields calculated structure factors in agreement with the ones reported by Mucker *et al.* (1968).

It must be concluded that either the experimental data are in error, perhaps for the reasons cited above, or that the assumption of J being a good quantum number is wrong, *i.e.* that higher-order terms in the Hamiltonian are very important.* In view of the wide separation of the $J=3$ from the $J=1$ state the latter possibility appears unlikely; deviations from $c_{2A}=2/\sqrt{5}$ hardly can be expected to account for a factor $\frac{5}{2}$.

IV. Ammonium bromide

Another group of orientationally disordered structures with properties quite different from those of the previously discussed systems, are the ammonium (phosphonium) halides. Arbitrarily, ND_4Br has been chosen as an example. In the early days of neutron diffraction, data on ND_4Br were collected by Levy & Peterson (1953) and to date represent the only available data on all solid phases. These data will be reanalysed in the following, applying the method developed in paper I.

ND_4Br possesses four solid phases

I: NaCl type (125 °C), disordered, space group *Fm*3*m*
II: CsCl type ($T\geq-38{\cdot}1$ °C), disordered, space group *Pm*3*m*
III: CsCl type (slightly distorted) ($T\geq-104$ °C) antiferro-ordered, space group *P*4/*nmm*
IV: CsCl type, ferro-ordered, space group $P\bar{4}3m$.

The tetragonal distortion of phase III leads to an additional complication which has little to do with the orientational structure. Phase III therefore will not be considered.

(*a*) CsCl-*type structures*

Phases II and IV have a common centre-of-mass structure, with the N atoms at positions (0,0,0) and the Br atoms at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The difference concerns the

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* *Note added in proof:* Recently a detailed neutron-diffraction study of cubic *p*-D_2 has come to the knowledge of the author. The results confirm the quantum-mechanical picture in a convincing manner (R.L. Mills, T.L. Yarnell & A.F. Schuch, to be published).

orientational ordering of the NH_4 tetrahedra. In phase II the tetrahedra are distributed at random in two equivalent equilibrium orientations. The resultant site symmetry is $m3m$. In phase IV a long-range order of the tetrahedral orientations is established, and these are arranged in a ferro-ordered way (site symmetry $\bar{4}3m$). Order-parameter and orientational fluctuations have been described by a pseudo-spin model; that is, the two different orientations in phase II of ND_4Br are identified with the 2 possible states of a spin $S=\pm\frac{1}{2}$ (Garland & Renard, 1966).

In our concept the structure is parametrized in such a way as to provide a good means of analysing the critical behaviour of the order parameter in the ammonium halides. The orientational pdf of the D_4 tetrahedra or the corresponding scattering-length density is expanded in cubic harmonics and the following expression is obtained for the structure factor in phase IV:

$$F(\mathbf{Q})=A(\mathbf{Q})+iB(\mathbf{Q}) \tag{4.1}$$

with

$$\begin{aligned}A(\mathbf{Q})=&b_{\mathrm{Br}}\,.\,\exp\left(-\langle u(T)^2\rangle_{\mathrm{Br}}\,.\,Q^2/2\right)\exp\left[\mathbf{Q}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})\right.\\&\left.\times a_0(T)\right]+\exp\left(-\langle u(T)^2\rangle_{\mathrm{ND4}}\,.\,Q^2/2\right)\\&\times\{b_{\mathrm{N}}+4b_{\mathrm{D}}\,.\,\sum_{l'}j_{2l'}(Q\,.\,\varrho)\,.\,(-1)^{l'}c_{2l'm}(T)\\&\times K_{2l'm}(\Omega_Q)\}\end{aligned} \tag{4.2}$$

$$\begin{aligned}B(\mathbf{Q})=&4b_{\mathrm{D}}\,.\,\exp\left(-\langle u(T)^2\rangle_{\mathrm{ND4}}\,.\,Q^2/2\right)\\&\times\sum_{l'}j_{2l+1}(Q\,.\,\varrho)\,.\,(-1)^{l'}c_{2l'+1m}(T)K_{2l'+1m}(\Omega_Q)\,.\end{aligned} \tag{4.3}$$

The same expression applies to phase II of ND_4Br, with the difference that $B(\mathbf{Q})\equiv O$. As the molecular sites possess inversion symmetry in phase II, only harmonics of even order contribute in this phase. Because of the tetrahedral site symmetry in phase IV, harmonics of odd order, namely $1=3,7,9,11$ *etc.*, also become symmetry-allowed and will give rise to a finite $B(\mathbf{Q})$.

In the least-squares procedure the quantity $j\,.\,F^2(\mathbf{Q}_{hkl})$ has been refined (powder data: j is the multiplitity of each reflexion), as was originally done by Levy & Peterson. For lattice constants and scattering lengths the following values were used: $a_0(-195\,°\mathrm{C})=4·01$ Å, $a_0(23\,°\mathrm{C})=4·06$ Å and $b_{\mathrm{D}}=0·62$, $b_{\mathrm{N}}=0·94$, $b_{\mathrm{Br}}=0·68$ ($\times 10^{-12}$ cm). The refinement proceeded satisfactorily within the limits of experimental accuracy. The R index converges to 4·6% in case of phase II and to 4·6% in case of phase IV, with use of 6 and 9 parameters respectively. (In the original analysis 6 parameters were included yielding $R=5·4$% for phase II and $R=9·0$% for phase IV, without application of a numerical least-squares procedure.) Table 3 quotes the final parameters. Tables 4 and 5 compare measured and calculated values of jF^2. Reasonably precise information on the first few expansion coefficients c_{l1} is obtained. As to be expected in phase II, there are eight maxima of the D_4 density along lines connecting nitrogen atoms with nearest-neighbour bromine ions ([111] directions). The magnitude of the coefficients corresponds to a librational amplitude $\sigma_L=11°$. In phase IV the deuterium atoms are much better localized. A value $\sigma_L=6·5°$ at nitrogen temperature may be estimated [see Fig. 2(*b*) in paper I]. Due to this strong orientational localization, many coefficients c_{l1} are non-zero. Fortunately, the rate of convergence of the structure factor [equation (4.1) to (4.3) is enhanced by the small size of the ND_4 ions ($\varrho=1·03$ Å) and the high symmetry.

Table 3. *Final parameters obtained in the various phases of solid* ND_4Br

	ND_4Br IV	ND_4Br II	ND_4Br I
Scale factor	0·998 (45)	0·98 (3)	1·08 (8)
$\varrho_{\mathrm{ND_4}}$	1·008 (10)	1·036 (10)	1·079 (56)
$\langle U^2\rangle_{\mathrm{Br}}$	0·0040 (18)	0·022 (2)	0·045 (19)
$\langle U^2\rangle_{\mathrm{ND_4}}$	0·0083 (20)	0·023 (1)	0·061 (15)
c_{41}	−1·30 (10)	−1·07 (5)	0·58 (20)
c_{61}	1·76 (11)	1·13 (11)	0·6 (1·4)
c_{81}	−0·60 (27)	–	–
c_{31}	1·75 (7)	–	–
c_{71}	−1·38 (31)	–	–
R index	4·6%	4·6%	5·1%

Table 4. *Neutron diffraction data from* ND_4Br II *at* 23 °C (*Levy & Peterson*, 1953)

hkl	jF^2_{obs}	jF^2_{calc}	*hkl*	jF^2_{obs}	fF^2_{calc}
100	17·2 ± 0·4	17·4	320	3·6 ± 1·8	2·7
110	65·3 ± 1·3	65·9	321	75·5 ± 6	74·6
111	3·5 ± 0·4	3·6	400	0 ± 1·0	0·1
200	6·0 ± 0·7	6·1	410	5·9 ± 3	4·0
			322		
210	0 ± 1·0	0·3	411	46·6 ± 5	48·0
211	31·2 ± 1·6	30·0	330		
220	18·9 ± 1·4	17·5	331	9·3 ± 5	8·6
221	7·6 ± 0·8	11·1	420	35·8 ± 6	34·9
300			421	5·0 ± 3	5·5
310	3·6 ± 1·8	3·8	332	17·6 ± 3	17·3
311	2·9 ± 1·5	2·3	422	17·3 ± 3	18·7
222	11·0 ± 1·7	11·5			

Table 5. *Neutron diffraction data from* ND_4Br IV *at* −195 °C (*Levy & Peterson*, 1953)

hkl	jF^2_{obs}	jF^2_{calc}	*hkl*	jF^2_{obs}	jF^2_{calc}
100	17·9 ± 0·4	18·9	320	5·8 ± 4	10·5
110	72·3 ± 1·4	75·0	321	163·2 ± 8	162·0
111	16·1 ± 0·8	14·3	400	0 ± 1	1·2
200	5·0 ± 0·6	6·5	410	27·4 ± 5	25·7
210	1·7 ± 1·0	0·2	322		
211	87·1 ± 2·4	81·3	411	118 ± 15	117·8
220	30·8 ± 2·0	28·6	330		
211	76·0 ± 3·5	81·0	331	33 ± 15	31·1
300			420	93 ± 15	94·5
310	4·1 ± 2·1	2·5	421	41 ± 15	40·0
311	13·3 ± 3·5	12·7	332	25 ± 10	26·8
222	41·5 ± 8	42·6			

In paper I criteria were discussed which may tell whether the present approach of analysing structures should be applied or not. In our opinion the ordered phases of the ammonium halides provide limiting examples; particularly at very low temperatures, where the addition of 2 more terms up to order $l'=10$ may be necessary, the situation becomes less favourable. Then it might be advisable not to use many parameters to study deviations from a Gaussian distribution on a sphere (or any other pdf), but to study other structural details such as higher cumulants, correlations between centre-of-mass and rotational motions and the non-rigidity of the molecules under consideration. Nevertheless in such situations the present method may still serve a complementary purpose and yield supplementary information, especially if precise experimental data are available. One general feature of the method should be kept in mind in this context: rather direct information on bond lengths is provided; there is no need of further corrections which often have to be applied when using conventional procedures (Busing & Levy, 1964).

As mentioned before, the above or similar expressions for the structure factor should be well suited for studying the critical behaviour of the order parameter(s) at the phase transitions in the ammonium halides. Examples of almost continuous transitions (at normal pressure) are the transitions from disorder to ferro-order in $ND_4Cl(NH_4Cl)$ or the disorder-to-antiferro-order transition in $ND_4Br(NH_4Br)$. The quantities to investigate are the expansion coefficients of odd order $c_{2l'+1m}$ or preferably the corresponding coefficients $A^{(2l'+1)}_{mm'}$ of the cubic rotator functions. The latter are defined in equation (3.6) of paper I and the connexion with the expansion coefficients of the cubic harmonics is given in equation (3.9) of the same paper.

Often it will be necessary to perform full structure analyses at a sequence of temperatures below the transition temperature as has recently been done (W. B. Yelon & D.G. Cox, to be published). This extra labour is due to the considerable variation of all temperature-dependent parameters, which is to be expected over the interesting range of temperatures. As far as magnetic phase transitions are concerned the situation is much simpler, since in general only variations of one parameter must be accounted for.

(*b*) NaCl-*type structure*

In the cubic high-temperature structure of ND_4Br (and also of the other ammonium halides) the nitrogen atoms are at positions (0,0,0) and the bromine atoms at positions ($\frac{1}{2}$,0,0), *i.e.* positions (*a*) and (*b*) of space group *Fm*3*m*. The major problem again concerns the orientational order of the ND_4^+ ions. The situation is evident in phases II and IV, as there are eight nearest-neighbour Br^- ions surrounding each ND_4^+ group and there is an orientation where all four protons are close to halide neighbours. In phase I this coordination number reduces to six. Levy & Peterson (1953) have overcome the resultant difficulty by putting the deuterium atoms onto several equivalent (low-symmetry) positions or circles, both of which are occupied at random. Altogether eight different models have been tested, three of which satisfy the condition of a 'close approach between D and Br' (Levy & Peterson, 1953) and also give rather low *R* indices. It has not been possible to achieve any further selection between these three models – for obvious reasons: if the scattering-length density distributions corresponding to these models are expanded into cubic harmonics, differences show up in higher-order terms only. These differences are beyond the scope of this analysis because owing to the large values of the translational-motion parameters $\langle u^2\rangle$, the experimental observations are restricted to $Q\le 4{\cdot}5$ Å^{-1}. Hence only information on coefficients $c_{2l'1}$ with $2l'\le 6$ is obtained and an analysis in terms of our expansion procedure certainly seems preferable. The structure factor for phase I of ND_4Br is the same as given in equation (4.1) and (4.2) apart from constant factors due to the different choice of the unit cell ($a_0=6{\cdot}90$ Å at 200°C). $B(\mathbf{Q})$ vanishes identically because of inversion symmetry at the molecular sites.

As in § IV(*a*), the quantity $jF^2(\mathbf{Q}_{hkl})$ has been refined with unchanged values for the various scattering lengths. The *R* index converges to 5·1 % with inclusion of 6 parameters. Measured and observed data are listed in Table 6 and the final parameter values in Table 3. Estimated standard deviations are rather large, because only 10 experimentally observed reflexions were available. The ensemble-averaged density distribution produces maxima in the direction of the bromine ions (positive sign of c_{41}). Formally the averaged density distribution may be visualized as an octahedron performing librations with amplitudes as large as 20°.

Table 6. *Neutron diffraction data from* ND_4Br I *at* 200°C (*Levy & Peterson, 1953*)

hkl	jF^2_{obs}	jF^2_{calc}
111	6·7 ± 0·1	6·7
200	11·1 ± 0·1	11·2
220	6·8 ± 0·1	6·9
311	0·7 ± 0·35	0·55
222	4·0 ± 0·3	4·1
400	5·0 ± 0·2	4·7
331	1·0 ± 0·5	1·4
420	3·8 ± 0·2	3·4
422	2·9 ± 0·3	2·5
620	3·0 ± 0·45	3·4

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Freezing of Myoglobin Crystals at High Pressure

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A method is described for freezing sperm-whale myoglobin single crystals at a hydrostatic pressure of 2500 atm. Precession photographs show no damage to the lattice order of the frozen crystals.

1. Introduction

Crystallographic phase determinations in protein single crystals by means of nuclear γ-resonance scattering meet with considerable difficulties (Parak, Mössbauer & Hoppe, 1970). One of the problems is the low recoilless fraction (f factor) of the nuclear-scattering process at room temperature. For sperm-whale myoglobin it has been shown that at room temperature the probability of γ-resonance scattering at a ^{57}Fe nucleus is only 1 % of the theoretical value, which is equivalent to a scattering amplitude of 490 electrons (Parak & Formanek, 1971). To increase the recoil-free fraction one must cool the crystal. Unfortunately, freezing protein single crystals is a major problem since the crystal water expands during the liquid/ice phase transition, which usually destroys the single crystal.

Haas & Rossmann (1970) have published a method of freezing lactate dehydrogenase crystals by adding certain amounts of sugar to the mother liquid. In this way, they obtain during the freezing process some kind of glass, which does not rupture the crystal structure. The disadvantage of this method is the necessity to find for each protein the exact working conditions. Their aim was to reduce the radiation damage to the crystals during exposure to X-rays. They found that the rate of the radiation damage to the frozen crystals was ten times less than at room temperature. This effect should be expected for any freezing method.

In the following we describe a method of freezing sperm-whale myoglobin crystals. In order to prevent the damaging high volume change during the freezing process, one may work in a more suitable range of the water phase diagram. The so-called ice III and ice IX phases, which differ only in the ordering of the protons, exist at a pressure between 2100 and 3500 atm. The phase transition of water to the ice III phase is accompanied by a volume contraction in contrast to the expansion which occurs during the formation of the ice I at atmospheric pressure. Besides, the absolute alteration of the volume is considerably smaller (Whalley, Davidson & Heath, 1966; Whalley, Heath & Davidson, 1968; Riehl, Bullemer & Engelhard, 1969).

For these reasons, we have frozen sperm-whale myoglobin crystals at a hydrostatic pressure of 2500 atm and investigated the crystals at liquid-nitrogen temperature on a precession camera. The photographs can be taken at atmospheric pressure, because the high pressure phase is metastable at very low temperatures.

2. Experimental details

The high-pressure freezing equipment is shown in Fig. 1. Part 6 of Fig. 1 is removed at the beginning of the