

X-ray and Neutron Diffraction by Nematic Liquid Crystals*

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An expression for the neutron (or X-ray) diffraction cross section for a nematic liquid crystal is derived. From this expression it is deduced that such diffraction experiments may be used to measure the nematic order parameter. It is further shown that scattering recorded at temperature close to the nematic-isotropic transition may show weak pretransitional effects even at finite values of the scattering wave vector.

Introduction

In a number of recent experiments neutron (Pynn, Otnes & Riste, 1972; Riste & Pynn, 1973) and X-ray (Brown, Doane & Neff, 1971; McMillan, 1973) diffraction pat-

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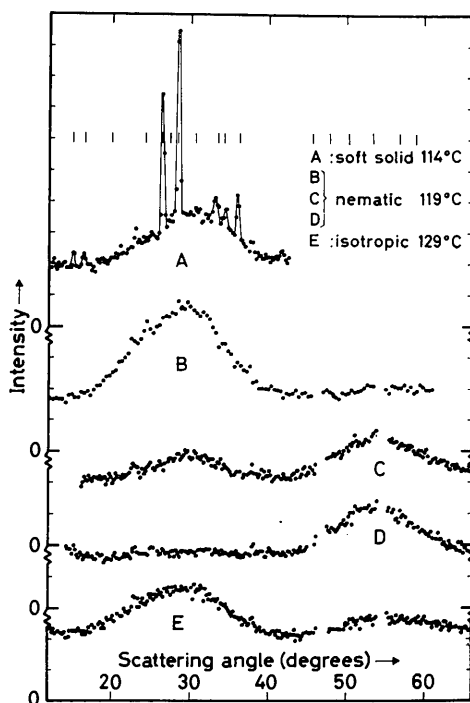


Fig. 1. Neutron diffraction patterns obtained with deuterated *p*-azoxyanisole with incident neutrons of wavelength $\lambda=1.863$ Å. Patterns *B* through *E*, obtained with fluid samples, display one or two broad peaks centered around $Q \sim 1.8$ Å⁻¹ (scattering angle of $\sim 30^\circ$) and $Q \sim 3.0$ Å⁻¹ (scattering angle of $\sim 53^\circ$). As pattern *A* shows, these peaks begin to develop in the solid phase at a temperature slightly below the 117°C solid-nematic transition temperature. Pattern *B* was obtained with \mathbf{Q} perpendicular to the preferred nematic axis while, for pattern *D*, \mathbf{Q} was parallel to the preferred axis. Patterns *C* and *E* were recorded with nonaligned and isotropic-liquid samples respectively. [These data are taken from Pynn *et al.* (1972).]

terns have been measured in the nematic and isotropic liquid phases of certain liquid crystals. Results obtained from neutron-scattering experiments with *p*-azoxyanisole (PAA) show, in both the nematic and isotropic liquid phases, that the structure factor $S(Q)$ has two broad peaks. These peaks, which are centered at $Q \sim 1.8$ Å⁻¹ and $Q \sim 3.0$ Å⁻¹, have intensities which depend on the temperature of the sample and, when the latter is in the nematic phase, on the relative orientation of the scattering vector \mathbf{Q} and the unique axis of the sample (see Fig. 1). Of these experimental results only the presence of the (second) peak in $S(Q)$ at $Q \sim 3.0$ Å⁻¹ has so far been satisfactorily explained (Pynn, 1973). This peak is caused by structure in the form factor of the PAA molecules and therefore reflects the distribution of atomic positions within each molecule. More detailed analysis of the data has been hampered by the lack of availability of suitable algebraic expressions on which such analysis can be based. In order to address this problem we derive in this paper an expression for the diffraction cross section. Besides providing a qualitative explanation of several experimental observations this expression should allow values of the nematic order parameter to be deduced from diffraction data. Various simplifications of the expressions derived in this note are open to experimental verification.

The diffraction cross section

The diffraction cross section for neutrons scattered by a molecular system can be written as the sum of two terms (Pynn, 1973), a single-molecule term denoted $d\sigma/d\Omega)_s$, and an interference term $d\sigma/d\Omega)_d$. The latter may be written as

$$\left(\frac{d\sigma}{d\Omega}\right)_d = \sum_i \sum_{i' \neq i} \sum_{j, j'} a_j a_{j'} \times \langle \exp\{-i\mathbf{Q} \cdot (\mathbf{R}_i - \mathbf{R}_{i'}) - i\mathbf{Q} \cdot \mathbf{D}_i \cdot \mathbf{u}_j + i\mathbf{Q} \cdot \mathbf{D}_{i'} \cdot \mathbf{u}_{j'}\} \rangle_T \quad (1)$$

where

\mathbf{R}_i is the center-of-mass coordinate of the *i*th molecule, \mathbf{D}_i is a matrix which rotates a space-fixed coordinate system [see Pynn (1973)] to the body-coordinate system of the *i*th molecule.

\mathbf{u}_j is the coordinate, measured in the body-coordinate system, of the j th nucleus of a molecule, a_j is the bound scattering length of the j th nucleus, \mathbf{Q} is the neutron scattering vector and $\langle \dots \rangle_T$ denotes a thermal average.

An analogous expression applies to X-ray scattering when the sum over a_j is replaced by an integral over the electron distribution of a molecule.

An expression for the single molecule term $d\sigma/d\Omega_s$ has been given previously (Pynn, 1973; de Gennes, 1972) as

$$\frac{d\sigma}{d\Omega}_s = \sum_I (-1)^I \sum_{JJ'} a_j a_{j'} j_{2I}(Q v_{JJ'}) P_{2I}(\cos \theta_{JJ'}) (4I+1) \times P_{2I}(\cos \theta_Q) \langle P_{2I}(\cos \beta_i) \rangle_T \quad (2)$$

where

$$v_{JJ'} = |\mathbf{u}_j - \mathbf{u}_{j'}|, \quad \cos \theta_{JJ'} = \mathbf{u}_j \cdot \mathbf{u}_{j'} / |\mathbf{u}_j \cdot \mathbf{u}_{j'}|,$$

$j_l(x)$ and $P_l(x)$ are respectively a spherical Bessel function and a Legendre polynomial,

θ_Q is the angle between \mathbf{Q} and the nematic preferred axis

and

β_i is the angle between a molecular long axis and the nematic axis.

Equation (2) has been used (Pynn, 1973) to explain the existence of the peak at $Q \simeq 3.0 \text{ \AA}^{-1}$ in the neutron diffraction pattern of PAA. However, the part of the diffraction cross section represented by this equation cannot explain the peak at $Q \simeq 1.8 \text{ \AA}^{-1}$. To provide such an explanation it is necessary to analyze the interference term given by equation (1).

In order to simplify equation (1) let us define $n(\mathbf{R}_i, \Omega_i) d\mathbf{R}_i d\Omega_i$ as the number of molecules which lie in the element $d\mathbf{R}_i d\Omega_i$ of configuration space at position (\mathbf{R}_i, Ω_i) in this space. Here Ω_i is an abbreviation for the Euler angles $(\alpha_i, \beta_i, \gamma_i)$ (Rose, 1957) which define the orientation of the i th molecule and \mathbf{R}_i denotes the position of the center of mass of this molecule. In terms of $n(\mathbf{R}_i, \Omega_i)$ [which we henceforth denote $n(i)$]. Equation (1) takes the form

$$\frac{d\sigma}{d\Omega}_d = \int d^3 R_i \int d^3 R_{i'} \int d\Omega_i \int d\Omega_{i'} \alpha_i(\mathbf{Q}) \alpha_{i'}(\mathbf{Q}) \times \langle n(i)n(i') \rangle_T \exp(-i\mathbf{Q} \cdot \mathbf{R}_{ii'}) \quad (3)$$

where

$$\alpha_i(\mathbf{Q}) = \sum_j a_j \exp\{-i\mathbf{Q} \cdot \mathbf{D}_i \cdot \mathbf{u}_j\} \quad \text{and} \quad \mathbf{R}_{ii'} = \mathbf{R}_i - \mathbf{R}_{i'}$$

An approximate expression for the correlation function $\langle n(i)n(i') \rangle_T$ may be obtained by writing this function as the product of two terms. The first of these terms, denoted $n_{ev}(i, i')$, represents excluded volume effects. $n_{ev}(i, i')$ takes the value zero if molecules i and i' overlap and approaches unity as the molecular separation becomes infinite. At such large separations $\langle n(i)n(i') \rangle_T$ becomes equal to the product of two single-

molecule, orientation distribution functions. Thus one may write

$$\langle n(i)n(i') \rangle_T = \frac{1}{64\pi^4} \varrho^2 n_{ev}(i, i') \times \sum_{k_1 k_2} G_{k_1 k_2}(R_{ii'}) P_{k_1}(\cos \beta_i) P_{k_2}(\cos \beta_{i'}) \quad (4)$$

where ϱ is the molecular number density and $G_{ij}(r)$ is a function which describes correlation between values of the director throughout the sample. At temperatures which are not close to the isotropic-nematic transition the function $G_{k_1 k_2}(R_{12})$ takes the form

$$G_{k_1 k_2}(R_{12}) = n_{k_1} n_{k_2} \quad (5)$$

where n_k is an expansion parameter in the following representation of the single-molecule distribution function (Pynn, 1973)

$$\langle n(\beta_i) \rangle_T = \sum_k n_k P_k(\cos \beta_i) \quad (6)$$

Here we choose $n_0 = 1$ [which explains the $\frac{1}{64}\pi^4$ factor in equation (4)] and note that n_2 is proportional to the usual nematic order parameter. When correlated director fluctuations exist as, for example, close to the nematic-isotropic transition, an extra term [say of the Ornstein-Zernike form (Stinson & Litster, 1970)] must be added to equation (5) to account for these fluctuations.

Proceeding with the evaluation of equation (3) one first expands $n_{ev}(i, i')$ in the form

$$n_{ev}(i, i') = \sum_{l_1 l_2 m} n_{l_1 l_2}^m(R_{ii'}) \bar{Y}_{l_1 m}^*(\beta_i \alpha_i) \bar{Y}_{l_2 m}(\beta_{i'} \alpha_{i'}) \quad (7)$$

where \bar{Y} is a spherical harmonic evaluated in the coordinate system which has $\mathbf{R}_{ii'}$ as a polar axis. Substituting equations (4) and (7) in equation (3) and expanding all exponentials as Rayleigh series, one finds (see Appendix for more details) that eleven of the twelve integrations of equation (3) can be performed to yield the following expression for $d\sigma/d\Omega_d$:

$$\begin{aligned} \frac{d\sigma}{d\Omega}_d &= \varrho \sum_{l_1 l_2} \sum_{m_1 m_2} \sum_{j_1 j_2} \sum_{k_1 k_2} \beta_{j_1}(Q) \beta_{j_2}(Q) \\ &\times (i)^{l_1 + j_1 + j_2} (-1)^{l_1 + j_1} (-1)^{m_1 + m_2} \\ &\times [(2l_1 + 1)(2l_2 + 1)]^{1/2} \left\{ \int r^2 dr n_{l_1 l_2}^m(r) G_{k_1 k_2}(r) j_l(Qr) \right\} \\ &\times C(j_1 j_2 j; \bar{m}_1 m_2) C(j_1 j_2 j; 00) C(jlk; \bar{m}_1 + m_2, m_1 + \bar{m}_2) \\ &\times C(jlk; 00) \\ &\times C(l_1 l_2 l; \bar{m}_1 m_2) C(l_1 l_2 l; \bar{m} m) C(l_1 k_1 j_1; \bar{m}_1 0) \\ &\times C(l_1 k_1 j_1; 00) \\ &\times C(l_2 k_2 j_2; m_2 0) C(l_2 k_2 j_2; 00) P_k(\cos \theta_Q) \end{aligned} \quad (8)$$

where $\bar{m} = -m$ and the C functions are Clebsch-Gordon coefficients (Rose, 1957). In equation (8) we have defined

$$\beta_k(Q) = \sum_j a_j j_k(Q u_j) P_k(\cos \theta_j) \quad (9)$$

as a molecular form factor, where θ_j is the angle between \mathbf{u}_j and the long molecular axis. Since molecules are assumed to be end-to-end symmetric (or alternatively neither end is preferred!) the sets of l, j and k indices in equation (8) are even integers. In deriving equation (8) [and (2)] it has been assumed that molecular correlations are independent of the Euler angle γ_i ; that is $\langle n(i)n(i') \rangle_T$ is not changed by rotation of either of molecules i and i' about its long axis.

Equations (2) and (8) give an expansion of the total scattering cross section in terms of $P_k(\cos \theta_Q)$ where $k=0, 2, 4, \dots$. One might hope that even in the aligned nematic state only terms with $k \leq 2$ would be significant. Such a simplification is evidently open to experimental test.

In its present form equation (8) is too complex to permit qualitative deductions about the form of neutron diffraction patterns obtained with liquid crystals, even if one makes the assumption that only terms involving $P_0(\cos \theta_Q)$ and $P_2(\cos \theta_Q)$ contribute. Furthermore, equation (8) is, in general, too cumbersome for use by an experimentalist who wishes to extract pertinent information from his data. To simplify matters somewhat it is useful to identify terms which one expects to be important.

Past analysis (McMillan, 1973) of X-ray scattering data obtained with liquid crystals has been based on the assumption that the electron distribution within a molecule is effectively isotropic. If this were the case, $\beta_0(Q)$ would be the only non-zero member of the set of form factors defined by equation (9) and equation (8) would simplify to:

$$\begin{aligned} \frac{d\sigma}{d\Omega}_d^{(1)} &= \varrho \sum_{l_1 l_2} \sum_m |\beta_0(Q)|^2 (-i)^l (-1)^m \\ &\times [1/(2l_1 + 1)(2l_2 + 1)]^{1/2} \\ &\times \left\{ \int r^2 dr n_{l_1 l_2}^m(r) G_{l_1 l_2}(r) j_l(Qr) \right\} \\ &\times C(l_1 l_2 l; 00) C(l_1 l_2 l; \bar{m} m) P_l(\cos \theta_Q). \end{aligned} \quad (10)$$

In this approximation the anisotropy (dependence on θ_Q) of the liquid structure factor obtained with an aligned nematic is a result of the departure from sphericity of the molecular shape. This gives rise to terms of the type $n_{ij}^m(r)$ for which i and j are not both zero and hence to a dependence of the cross section on $P_{l \neq 0}(\cos \theta_Q)$. This is analogous to the result obtained by McMillan (1973) from his excluded-volume arguments. Other calculations (Pynn, 1973) have shown however that, at least for neutrons, part of the structure and anisotropy of the diffraction patterns obtained with PAA can be attributed to form factors $\beta_k(Q)$ for which k is non-zero. Since one might expect $\beta_k(Q)$ with $k \neq 0$ to be smaller and less rapidly varying than $\beta_0(Q)$ one may include such terms approximately by retaining only the most rapidly varying term of the set $n_{ij}^m(r)$. Thus we make the approximation of setting $l_1 = l_2 = 0$ in equation (8) when j_1 and

j_2 are not both zero. This gives a second contribution to $d\sigma/d\Omega)_d$ of the form

$$\begin{aligned} \frac{d\sigma}{d\sigma}_d^{(2)} &= \varrho \sum'_{l_1 l_2} \beta_{l_1}(Q) \beta_{l_2}(Q) (i)^{l_1 + l_2} (-1)^{l_1} \\ &\times |C(l_1 l_2 l; 00)|^2 \\ &\times \left\{ \int r^2 dr n_{00}^0(r) G_{l_1 l_2}(r) j_0(Qr) \right\} P_l(\cos \theta_Q) \end{aligned} \quad (11)$$

where the prime on the sum indicates the exclusion of the $l_1 = l_2 = 0$ term. Equation (11) ascribes asymmetry of the liquid structure factor of nematics to an asymmetric distribution of scattering centers within each molecule.

While it is not *a priori* evident that the sum of equations (10) and (11) is an adequate approximation to the complete equation (8), the former equations do include a representation of the two physical effects which are expected to contribute to the anisotropy of $S(Q)$ for nematics. Thus, both anisotropic excluded-volume effects and the anisotropy of the molecular scattering power are included.

Qualitative deductions and suggestions for experiments

In the remainder of this paper the consequences of the expressions (8), (10) and (11) will be examined. Such deductions are facilitated by the availability of previous calculations (Pynn, 1974) of the coefficients $n_{ij}^m(r)$. In particular, these calculations showed that, for linear molecules, $n_{00}^0(r)$ has a form which is similar to the radial distribution function, $g(r)$, which pertains to a fluid of spherical molecules. However, in the linear-molecule case, $n_{00}^0(r)$ increases from zero to its first peak in an interval which corresponds to the difference between the length and breadth of a molecule. This form of $n_{00}^0(r)$ in conjunction with equations (10) and (11) and naive ideas about Fourier transforms indicate that one ought to expect a peak in $S(Q)$ at a value of $Q \simeq 2\pi/(\text{molecular width})$. This argument offers a somewhat rough and ready explanation of the appearance of the first peak (at $Q \sim 1.8 \text{ \AA}^{-1}$) in the neutron diffraction pattern of PAA.

Let us now consider a non-aligned nematic sample and set $G_{ij} = n_i n_j$, thereby ignoring correlated director fluctuations. Then equations (10) and (11) become, respectively,

$$\frac{d\sigma}{d\Omega}_d^{(1)} = \varrho \sum_{im} |\beta_0(Q)|^2 \frac{1}{(2l+1)^2} |n_l|^2 \left\{ \int r^2 dr n_{il}^m(r) j_0(Qr) \right\} \quad (12)$$

and

$$\frac{d\sigma}{d\Omega}_d^{(2)} = \varrho \sum_{i \neq 0} |\beta_i(Q)|^2 \frac{1}{(2l+1)} |n_l|^2 \left\{ \int r^2 dr n_{00}^0(r) j_0(Qr) \right\}. \quad (13)$$

For the special case of an isotropic liquid, $n_l = \delta_{l0}$ and only equation (12) gives a finite contribution to $d\sigma/d\Omega)_d$. Thus, ignoring the density difference be-

tween nematic and isotropic phases, one finds from equations (12) and (13) the important result that, to lowest order, the difference between scattering from an unaligned nematic and an isotropic liquid is proportional to n_2^2 which, in turn, is proportional to the square of the nematic order parameter. This conclusion remains correct for the total diffraction cross section since equation (2) gives a contribution which is independent of n_2 in both the isotropic and the unaligned nematic states. Thus, neutron (or X-ray) scattering may be used to measure the nematic order parameter at temperatures which are not too close to the nematic-isotropic transition, T_c .

The usefulness of the above method of determination of the nematic order parameter is restricted to those situations in which there is a discernable difference between intensities obtained, at some Q , from non-aligned nematic and isotropic samples. Neutron measurements indicate that, for PAA, this difference is essentially zero close to the $Q \approx 1.8 \text{ \AA}^{-1}$ peak (Riste & Bjerrum-Møller, 1975). This observation implies that the scattering obtained from the nematic phase is independent of the order parameter and that, in equation (8), one should use $G_{ij}(r) = n_0^2 \delta_{i0} \delta_{j0}$ for both nematic and isotropic phases at $Q \approx 1.8 \text{ \AA}^{-1}$. Actually this relation may apply over a wide range of Q values but this has not yet been confirmed experimentally. Nevertheless the observation of at least one case in which the scattering appears to be governed entirely by the short-range correlations expressed in $n_{ij}(r)$ is important since an alternative method of measuring n_2 can be established. In this case, measurement of diffracted intensity as a function of temperature should, in an aligned sample, yield a result which can be described by a temperature-independent term plus the contribution proportional to n_2 which appears in equation (2).

Close to T_c the approximation $G_{ij}(R_{12}) = n_i n_j$ becomes inadequate as a result of the existence of correlated fluctuations in the directions of local preferred axes (director fluctuations). In this case $G_{22}(R_{12})$ takes, in a mean-field treatment (Stinson & Litster, 1970; Fan & Stephen, 1970; de Gennes, 1971), the Ornstein-Zernike form, and is proportional to $(\exp -R_{12}/\xi)/R_{12}$ where ξ is a suitable correlation length. Let us consider the scattering at small Q at temperatures close to T_c . At small Q only $n_{ij}^m(r)$ at large r need be retained, but at large r , $n_{ij}^m(r) = 4\pi \delta_{i0} \delta_{j0} \delta_{m0}$. The contribution of equation (10) to the scattering is then independent of the nematic order parameter and of the direction of Q . Equation (11) gives however

$$\begin{aligned} \left. \frac{d\sigma}{d\Omega} \right|_a^{(2)} (Q \rightarrow 0) &= \varrho \sum_{l_1 l_2 l} \beta_{l_1}(Q) \beta_{l_2}(Q) (i)^{l_1+l_2} (-1)^{l_1} \\ &\times |C(l_1 l_2 l; 00)|^2 \\ &\times 4\pi \left\{ \int r^2 dr G_{l_1 l_2}(r) j_0(Qr) \right\} P_l(\cos \theta_Q). \end{aligned} \quad (14)$$

In view of the Ornstein-Zernike form proposed for $G_{22}(R_{12})$ it is clear that equation (14) predicts divergent scattered intensity at T_c if the isotropic-nematic transition is of second order. In practice this transition is usually only weakly first order and thus 'critical scattering' should be detectable and should be distributed (as a function of θ_Q) according to equation (14). Critical light scattering at T_c has indeed been observed (Stinson & Litster, 1970; Fan & Stephen, 1970) and it is perhaps worth noting that, in both light and neutron scattering experiments, this scattering is caused by the anisotropic scattering power of the molecules.

At finite values of Q , director fluctuations close to T_c contribute to the scattering *via* both equations (10) and (11). However, the major contribution still appears to arise from (11) because $n_{22}^m(r)$ approaches zero rapidly for values of r greater than a molecular length. Since the term $d\sigma/d\Omega|_a$ makes its greatest contribution to the diffraction pattern for values of Q which are less than that at the second peak (*i.e.* $Q \lesssim 3 \text{ \AA}^{-1}$ in PAA) one would not expect the intensity of this peak to vary strongly in the neighborhood of T_c . To estimate the likely effect in the vicinity of the first peak in $S(Q)$ it is convenient to approximate $n_{00}^0(r)$ by a unit step function which is zero for r less than a molecular breadth. With this approximation, the Ornstein-Zernike form for $G_{22}(R_{12})$ in conjunction with equation (11) predicts that

$$\left. \frac{d\sigma}{d\Omega} \right|_a \sim \left(Q^2 + \frac{1}{\xi^2} \right)^{-1} \{ \exp(-1/Q\xi) - 1 \} \quad (15)$$

for a non-aligned sample with Q in the neighborhood of the first diffraction peak.

It should be pointed out that the observation of the effects described by equations (14) and (15) in X-ray or neutron diffraction experiments may indeed not be feasible. As has been pointed out above, neutron experiments with PAA indicate that only the term involving G_{00} in equation (8) is of importance in the nematic phase of this material. If this is a universal result, equations (14) and (15) will represent interesting but probably unobservable phenomena.

In this paper an expression for the neutron diffraction cross section for a nematic material has been derived. This expression demonstrates the possibility of using neutron diffraction experiments to measure the nematic order parameter and should provide the framework for detailed quantitative calculations of diffraction patterns obtained with nematic materials.

APPENDIX

In this Appendix we provide a few brief notes on the salient mathematical steps required for the derivation of equation (8) from equations (3), (4), and (7). The first step is to substitute (7) in (4) and to obtain an equation for $\langle n(i)n(i') \rangle_T$ in terms of the Y_{lm} which appear in (7). Since the Y_{lm} are spherical harmonics defined in a coordinate system which has $\mathbf{R}_{i'}$ as the polar

axis, these harmonics must be transformed to a space-fixed coordinate system before the integrations over the orientations of \mathbf{R}_i and $\mathbf{R}_{i'}$ [cf. equation (3)] can be performed. The required transformation is (Rose, 1957)

$$\bar{Y}_{lm'} = \sum_m D_{mm'}^l(\mathbf{R}_{i'}) Y_{lm} \quad (\text{A1})$$

where Y_{lm} is defined in the space-fixed system and where $D_{mm'}^l(\mathbf{R}_{i'})$ is a Wigner matrix whose arguments are the polar coordinates of $\mathbf{R}_{i'}$ in the space-fixed frame. The transformed expression for $\langle n(i)n(i') \rangle_T$ may now be plugged into equation (3) together with the Rayleigh expansion of $\exp(-i\mathbf{Q} \cdot \mathbf{R}_{i'})$, i.e.

$$\exp(-i\mathbf{Q} \cdot \mathbf{R}_{i'}) = 4\pi \sum_l (-i)^l j_l(QR_{i'}) \times \sum_m Y_{lm}^*(\mathbf{R}_{i'}) Y_{lm}(\mathbf{Q}) \quad (\text{A2})$$

Integration over the angular coordinates of \mathbf{R}_i and $\mathbf{R}_{i'}$, required by equation (3), may now be performed directly by making use of the rules given in Chapter 4 of Rose (1957).

Integration over the angular coordinates Ω_i and $\Omega_{i'}$ follows a prescription similar to that described above for the angular parts of the \mathbf{R}_i and $\mathbf{R}_{i'}$ integrations. The defining equation [cf. equation (3)] for $\alpha_i(\mathbf{Q})$ is first expanded as a Rayleigh series:

$$\alpha_i(\mathbf{Q}) = 4\pi \sum_j a_j \sum_{lm} (-i)^l j_l(Qu_j) Y_{lm}^*(\mathbf{Q}) Y_{lm}(\mathbf{D}_i \cdot \mathbf{u}_j) \quad (\text{A3})$$

In order to introduce the orientational coordinates Ω_i of the molecules, the Y_{lm} are rewritten in terms of a set of spherical harmonics, $\bar{Y}_{lm}(\mathbf{u}_j)$, which are defined in the body coordinate system of a molecule. The re-

quired transformation, which is similar to equation (A1), yields:

$$\alpha_i(\mathbf{Q}) = 4\pi \sum_j a_j \sum_{lmm'} (-i)^l j_l(Qu_j) \times Y_{lm}^*(\mathbf{Q}) D_{mm'}^{l*}(\Omega_i) \bar{Y}_{lm'}(\mathbf{u}_j) \quad (\text{A4})$$

where the argument of the rotation matrix is now the orientation Ω_i of the i th molecule. Integrations over Ω_i and $\Omega_{i'}$ may now be carried out and the resulting expression may be converted to that given by equation (8) by making use of the sum rules for the Clebsch-Gordon coefficients described in Chapter 3 of Rose (1957).

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Energy-Dispersive Spectroscopic Methods Applied to X-ray Diffraction in Single Crystals

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Two single-crystal energy-dispersive crystallographic methods (the fixed-crystal method and the rotating-crystal method) are described and investigated. Formulae for integrated intensities are derived for mosaic and perfect single crystals. Experimental results and a comparison between measured and calculated integrated intensities for a perfect germanium crystal are given. Special features and possible applications of the methods are discussed.

1. Introduction

Energy-dispersive X-ray diffractometry, since it was introduced by Giessen & Gordon (1968) and by

Buras, Chwaszczewska, Szarras & Szmid (1968), has been used almost exclusively for studies of powdered crystals. A few results on single-crystal diffraction have been published, dealing with escape peaks (Fukamachi,