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The X-ray Scattering from a Hindered Rotator. III

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The average structure factor for a three-dimensional hindered rotator is derived by using a group-theoretical generalization of spherical harmonics. The final relation is general, and is easily specialized for the usual potential fields expected in the more symmetrical crystals.

Introduction

Previous discussions of Laue–Bragg and diffuse scattering by the hindered rotator (King & Lipscomb, 1950; Atoji, Watanabé & Lipscomb, 1953), cover only the rotation about a single axis fixed relative to the crystal axes. There are, however, many crystals of high symmetry in which various degrees of hindered three-dimensional rotation, or of local order which can be treated approximately equivalently, occur in fairly symmetrical potential fields. In the expectation that the behavior of an actual hindered rotator, with local order, may be reduced to one of essentially independent hindered rotators, we have derived a general theory for the average structure factor of a three-dimensional rotator in terms of parameters which allow a smooth transition from fixed orientation, through hindered rotation, to completely free rotation. We may expect that intensities of diffraction can be measured precisely enough for discriminating between different physical models by their dependence on the effective hindering potential, which occurs in the expression for the average amplitude of scattering.

As in the previous discussions, surface spherical harmonics are employed in the mathematical expansion, but now their general behavior under general rotation transformations are needed. Although Hultgren (1932) discussed this problem, his results are not used here because of lack of separation of variables in our equations. The results of Sato (1951) are applicable, but are not used because of the complexity of the analysis. Matrix representation for the three-dimensional rotation transformation of the surface spherical harmonics is well known (Wigner, 1931, p. 164), but it is the more extensive study of Takahashi (1952) by means of group-theoretical considerations which leads beautifully to the results given below.

The molecular structure factor

The molecule is considered rigid; it contains axes x', y', z' which make Eulerian angles θ, φ, ψ with the crystal axes x, y, z, here taken orthogonal. The polar coordinates of the molecular axes are θ and φ; and ψ is the angular parameter of molecular rotation around the z' axis. We shall consider a single molecule at the origin, and expand its probability distribution in terms of generalized surface spherical harmonics, where the constants, e_{jn}, in the expansion are to be determined eventually by comparing observed and calculated X-ray data. These same constants, e_{jn}, could also be derived from a molecular model and assumed force fields, and then be compared with the values obtained experimentally.

The hindering potential for atom j with the polar coordinates, θ_j, φ_j with respect to the crystal axes, x, y, z, can be expressed as

$$V(\theta_j, \varphi_j) = \sum_{n=0}^{\infty} e_{jn} Y_n(\theta_j, \varphi_j)$$

$$= \sum_{n=0}^{\infty} e_{jn} \sum_{m=0}^{n} (A_{mn} \cos m\varphi_j + B_{mn} \sin m\varphi_j) P_n^m(\cos \theta_j) \,. \quad (1)$$

For the coefficients, A_{mn} and B_{mn}, we substitute as follows:

$$\left.\begin{aligned} A_{mn} &= \{(-1)^m H_{mn} + H_{-m,n}\} \sqrt{\left\{\frac{(n-m)!}{(n+m)!}\right\}} \,, \\ B_{mn} &= i\{(-1)^m H_{mn} - H_{-m,n}\} \sqrt{\left\{\frac{(n-m)!}{(n+m)!}\right\}} \,; \end{aligned}\right\} \quad (2)$$

we then have

$$V(\theta_j, \varphi_j) = \sum_{n=0}^{\infty} e_{jn} \sum_{m=-n}^{n} H_{mn} Y_n^{om}(\Gamma_j) \,, \quad (3)$$

where $Y_n^{om}(\Gamma_j)$ is related to the generalized surface spherical harmonic, $Y_n^{km}(\Gamma)$.* From the representative matrix of the generalized surface spherical harmonics, we have

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* $Y_n^{km}(\Gamma)$ is defined for $0 \leq \theta \leq \pi$ by the relation

$$Y_n^{km}(\Gamma) = e^{ik\psi + im\varphi} P_n^{km}(\cos \theta) \,. \quad (4)$$

$P_n^{km}(\cos \theta)$ can be regarded as a generalized associated Legendre function; $P_n^{om}(\cos \theta)$ and $P_n^{ko}(\cos \theta)$ are the associated Legendre functions in Ferrer's definition, multiplied by a constant, e.g.

$$P_n^{om}(\cos \theta) = (-1)^m \sqrt{\left\{\frac{(n-m)!}{(n+m)!}\right\}} P_n^m(\cos \theta) \,. \quad (5)$$

We also utilized the relations

$$\left.\begin{aligned} (-1)^{m-k} P_n^{km}(\cos \theta) &= P_n^{-k-m}(\cos \theta) \,, \\ (-1)^{k+m} P_n^{k-m}(\cos \theta) &= P_n^{-km}(\cos \theta) \,. \end{aligned}\right\} \quad (6)$$

$$Y_n^{km}(\Gamma_2) = \sum_{h=-n}^{n} Y_n^{kh}(\Gamma_1) Y_n^{hm}(\Gamma)\,, \tag{7}$$

and further, applying (7) to (3),

$$V(\theta_j, \varphi_j) = \sum_{n=0}^{\infty} e_{jn} \left[\sum_{m=-n}^{n} H_{mn} \left\{ \sum_{h=-n}^{n} Y_n^{oh}(\Gamma'_j) Y_n^{hm}(\Gamma) \right\} \right]. \tag{8}$$

Here Γ refers to the parameters for the molecular orientation, θ, φ, ψ, and Γ'_j refer to the known atomic coordinates θ'_j, φ'_j, with respect to the cartesian molecular axes x', y', z'. Note that the $Y_n(\theta_j, \varphi_j)$'s have unique forms for given potential symmetries. Assuming the total hindering potential energy of a molecule containing μ atoms is less than kT, the probability function for molecular orientation is then

$$\begin{aligned} W(\theta, \varphi, \psi) &= \exp\left\{ -\sum_{j=1}^{\mu} \frac{V_j(\theta_j \varphi_j)}{kT} \right\} \\ &= 1 + \frac{1}{kT} \sum_{n=0}^{\infty} \sum_{m=-n}^{n} H_{mn} \sum_{h=-n}^{n} \left\{ \sum_{j=1}^{\mu} e_{jn} Y_n^{oh}(\Gamma'_j) \right\} Y_n^{hm}(\Gamma) \\ &\quad + \mathbf{O}\left\{ \left(\frac{1}{kT} \right)^2 \right\} + \dots\,. \end{aligned} \tag{9}$$

The higher terms can also be expressed as linear combinations of the $Y_n^{km}(\Gamma)$. The average structure factor is then

$$\bar{F} = \sum_j f_j \int_\Gamma W(\theta, \varphi, \psi) \times \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) d\Gamma \Big/ \int_\Gamma W(\theta, \varphi, \psi) d\Gamma\,, \tag{10}$$

where $\mathbf{h}$ is the reciprocal-lattice vector and f_j and $\mathbf{r}_j$ are the scattering factor and position vector of atom j, $d\Gamma$ equals $\sin\theta d\theta d\varphi d\psi$, and integration is carried out from 0 to π for θ and from 0 to 2π for both φ and ψ. Define $\alpha_j = 2\pi|\mathbf{h}|\,|\mathbf{r}_j|$, and ω_{hj} as the angle between $\mathbf{h}$ and $\mathbf{r}_j$. Then the Legendre expansion of the exponential is

$$\exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) = \sum_{p=0}^{\infty} i^p (2p+1) j_p(\alpha_j) P_p(\cos\omega_{hj})\,, \tag{11}$$

where $j_p(\alpha_j) = \sqrt{\left(\frac{\pi}{2\alpha_j}\right)} \cdot J_{p+\frac{1}{2}}(\alpha_j)$ is the spherical Bessel function. Using (7), we find

$$\begin{aligned} P_p(\cos\omega_{hj}) &= \sum_{q=-p}^{p} Y_p^{oq}(\Gamma_h) \overline{Y_p^{oq}(\Gamma_j)} \\ &= \sum_{q=-p}^{p} \left[Y_p^{oq}(\Gamma_h) \sum_{l=-p}^{p} \{\overline{Y_p^{ol}(\Gamma'_j) Y_p^{lq}(\Gamma)}\} \right]. \end{aligned} \tag{12}$$

By means of the orthogonality relation of generalized surface spherical harmonics

$$\int_\Gamma Y_n^{hm}(\Gamma) \overline{Y_p^{lq}(\Gamma)} d\Gamma = \frac{8\pi^2}{2n+1} \delta_{np} \delta_{hl} \delta_{mq}\,, \tag{13}$$

the average structure factor can then be expressed as

$$\begin{aligned} \bar{F} = \sum_j f_j \Bigg[\frac{\sin\alpha_j}{\alpha_j} &+ \frac{1}{kT} \sum_{n=0}^{\infty} i^n j_n(\alpha_j) \sum_{m=-n}^{n} H_{mn} Y_n^{om}(\Gamma_h) \\ &\times \sum_{h=-n}^{n} \left\{ \sum_{j=1}^{\mu} e_{jn} Y_n^{oh}(\Gamma'_j) \right\} \overline{Y_n^{oh}(\Gamma'_j)} + \mathbf{O}\left\{ \left(\frac{1}{kT} \right)^2 \right\} + \dots \Bigg]. \end{aligned} \tag{14}$$

Using equations (2) and (6), we transform $\bar{F}$ to a more convenient form for computation:

$$\begin{aligned} \bar{F} = \sum_j f_j \Bigg[\frac{\sin\alpha_j}{\alpha_j} &+ \frac{1}{kT} \sum_{n=0}^{\infty} i^n j_n(\alpha_j) M_n^j \sum_{m=0}^{n} (A_{mn} \cos m\varphi_h \\ &+ B_{mn} \sin m\varphi_h) P_n^m(\cos\theta_h) + \mathbf{O}\left\{ \left(\frac{1}{kT} \right)^2 \right\} + \dots \Bigg], \end{aligned} \tag{15}$$

where M_n^j is

$$\begin{aligned} M_n^j = \sum_{h=0}^{n} \varepsilon_h \frac{(n-h)!}{(n+h)!} & \times \left[\left\{ \sum_{j=1}^{\mu} e_{jn} P_n^h(\cos\theta'_j) \cos h\varphi'_j \right\} P_n^h(\cos\theta'_j) \cos h\varphi'_j \right. \\ & \left. + \left\{ \sum_{j=1}^{\mu} e_{jn} P_n^h(\cos\theta'_j) \sin h\varphi'_j \right\} P_n^h(\cos\theta'_j) \sin h\varphi'_j \right], \end{aligned} \tag{16}$$

with $\varepsilon_h = 1$ when $h = 0$

and $\varepsilon_h = 2$ when $h \neq 0$.

Now, M_n^j may be regarded as the molecular shape factor, which depends upon the atomic coordinates relative to the appropriate molecular axes. The first term in (14) and (15) can be regarded as the explicit description of the free rotation of the molecule, while the degree of hindrance causes the remaining term as expressed by the factor $(1/kT)^n$.

The integrated intensity of Laue–Bragg scattering, J_1, from a crystal containing ν molecules with molecular centers at R_ν is thus

$$J_1 = I_e G |\bar{F}|^2 |\sum_\nu \exp(2\pi i \mathbf{h} \cdot \mathbf{R}_\nu)|^2\,, \tag{17}$$

where G is the Laue function and I_e is the scattering intensity from a single electron.

Symmetry considerations

1. *Center of symmetry and mirror plane*

When the molecule has a center of symmetry, both h and n take on even integral values in M_n^j. When the hindering potential has a center of symmetry, m and n take on even integral values. An xz mirror plane makes the sine terms vanish in both (15) and (16).

2. *Diatomic molecule in a potential of symmetry T_d and O_h*

We choose the line connecting atoms A and B as the z' axis, whence the polar coordinates (θ'_A, φ'_A), become $(0, 0)$, and (θ'_B, φ'_B) become $(\pi, 0)$, so that $P_n^h(\cos\theta'_A) = 1$ and $P_n^h(\cos\theta'_B) = (-1)^n$ when $h = 0$, and zero otherwise. We now utilize the group theoretical results (Curdy, 1938) for a tetrahedral field to obtain,*

$$
\begin{aligned}
\bar{F} &= f_A\frac{\sin\alpha_A}{\alpha_A}+f_B\frac{\sin\alpha_B}{\alpha_B}\\
&+\frac{1}{kT}\Bigl[(e_{A0}+e_{B0})\Bigl(f_A\frac{\sin\alpha_A}{\alpha_A}+f_B\frac{\sin\alpha_B}{\alpha_B}\Bigr)\\
&+[(e_{A4}+e_{B4})\{f_Aj_4(\alpha_A)+f_Bj_4(\alpha_B)\}\{P_4(\cos\theta_h)\\
&+1/168\,P_4^4(\cos\theta_h)\cos 4\varphi_h\}-(e_{A6}+e_{B6})\{f_Aj_6(\alpha_A)\\
&+f_Bj_6(\alpha_B)\}\{P_6(\cos\theta_h)-1/360\,P_6^4(\cos\theta_h)\cos 4\varphi_h\}\\
&+(e_{A8}+e_{B8})\{f_Aj_8(\alpha_A)+f_Bj_8(\alpha_B)\}\{P_8(\cos\theta_h)\\
&+1/5940\,P_8^4(\cos\theta_h)\cos 4\varphi_h\\
&+1/3991680\,P_8^8(\cos\theta_h)\cos 8\varphi_h\}+\ldots\Bigr]\\
&-\frac{i}{kT}[(e_{A3}-e_{B3})\{f_Aj_3(\alpha_A)-f_Bj_3(\alpha_B)\}P_3^2(\cos\theta_h)\sin 2\varphi_h\\
&+(e_{A7}-e_{B7})\{f_Aj_7(\alpha_A)-f_Bj_7(\alpha_B)\}\{P_7^2(\cos\theta_h)\sin 2\varphi_h\\
&+1/1560\,P_7^6(\cos\theta_h)\sin 6\varphi_h\}+\ldots]+\mathbf{O}\Bigl\{\Bigl(\frac{1}{kT}\Bigr)^2\Bigr\}+\ldots.
\end{aligned}
\tag{18}
$$

The symmetry O_h causes the imaginary part of (18) to vanish. Thus for a simple hindering potential, it is not troublesome to obtain further terms.

3. *A simple example*

Let us assume hindering potentials, $V(\theta_A, \varphi_A) = -C_Axyz/r^3$ for atom A, and $-C_Bxyz/r^3$ for atom B of a diatomic molecule AB. This is a smoothed tetrahedral potential having maximum and minimum values at [111] and [$\bar{1}$11] plus the tetrahedral permutations. The average structure factor can be expressed as

$$
\begin{aligned}
\bar{F} &= f_A\frac{\sin\alpha_A}{\alpha_A}+f_B\frac{\sin\alpha_B}{\alpha_B}\\
&-\frac{i}{30kT}(C_A-C_B)\{f_Aj_3(\alpha_A)-f_Bj_3(\alpha_B)\}P_3^2(\cos\theta_h)\sin 2\varphi_h\\
&-\frac{1}{210(kT)^2}(C_A^2+C_B^2)\Bigl(f_A\frac{\sin\alpha_A}{\alpha_A}+f_B\frac{\sin\alpha_B}{\alpha_B}\Bigr)\\
&-\frac{1}{110(kT)^2}(C_A^2+C_B^2)\{f_Aj_4(\alpha_A)+f_Bj_4(\alpha_B)\}\{P_4(\cos\theta_h)\\
&\qquad+1/168\,P_4^4(\cos\theta_h)\cos 4\varphi_h\}\\
&-\frac{1}{231(kT)^2}(C_A^2+C_B^2)\{f_Aj_6(\alpha_A)+f_Bj_6(\alpha_B)\}\{P_6(\cos\theta_h)\\
&\qquad-1/360\,P_6^4(\cos\theta_h)\cos 4\varphi_h\}+\mathbf{O}\Bigl\{\Bigl(\frac{1}{kT}\Bigr)^3\Bigr\}+\ldots.
\end{aligned}
$$

In most highly disordered crystals, the $1/(kT)^2$ terms are considerably less important, and terms of higher order are negligible.

The potential $V(\theta, \varphi) = -ax^2y^2z^2/r^6$ is a fairly sharpened octahedral potential giving maximum probabilities at the four body diagonal directions. This is one of the possible hindering potentials for face-centered packing of rotating diatomic molecules. The $1/(kT)$ term for this potential corresponds to the $1/(kT)^2$ term in (19) with different constants. Another possible packing of rotating molecules yields hexagonal symmetry. For C_{6h} symmetry, the linear combination of surface spherical harmonics, $P_6(\cos\theta)$, $P_6^6(\cos\theta)\times\{\cos 6\varphi \text{ or } \sin 6\varphi\}$, $P_8(\cos\theta)$, $P_8^6(\cos\theta)\{\cos 6\varphi$ or $\sin 6\varphi\}$ etc. are employed. For a general discussion of any symmetry, see Bethe (1929).

4. *Tetrahedral molecule in a potential of symmetry O_h*

For molecules of the type AB_4, having T_d symmetry, but disordered to O_h symmetry, the result is

$$
\begin{aligned}
\bar{F} &= f_A+4f_B\frac{\sin\alpha_B}{\alpha_B}+4f_B\frac{1}{kT}\Bigl[e_{B0}\frac{\sin\alpha_B}{\alpha_B}\\
&+28/27\,e_{B4}j_4(\alpha_B)\{P_4(\cos\theta_h)\\
&+1/168\,P_4^4(\cos\theta_h)\cos 4\varphi_h\}\\
&-128/81\,e_{B6}j_6(\alpha_B)\{P_6(\cos\theta_h)\\
&-1/360\,P_6^4(\cos\theta_h)\cos 4\varphi_h\}+\ldots\Bigr]+\ldots,
\end{aligned}
\tag{20}
$$

where the polar coordinates of the B atoms are chosen as $\theta_{B_i} = \cos^{-1}\{(-1)^{i-1}/\sqrt{3}\}$ and $\varphi_{B_i} = (2i-1)\pi/4\,(i = 1, 2, 3, 4)$, so that

$$
\begin{aligned}
&P_4(\cos\theta_B) = -7/18,\\
&P_4^4(\cos\theta_B)\cos 4\varphi_B = -140/3,\\
&P_6(\cos\theta_B) = 2/9,\\
\text{and}\quad &P_6^4(\cos\theta_B)\cos 4\varphi_B = -560.
\end{aligned}
$$

Then, $M_4^B = 28e_{B4}/27$ and $M_6^B = 32e_{B6}/81$.

When we know e_{B4} and e_{B6}, etc. from the $|\bar{F}|^2$ values using (20), the hindering potential can be estimated, at least approximately, from (1).

Finally, we shall not discuss the diffuse scattering, which has been extensively treated by Matsubara (1950) by different methods, except to point out its considerable dependence upon the hindering potential.

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* Expressions for $P_n^m(\cos\theta)$ in terms of $\cos k\theta$ or $\sin k\theta$ have been given for $n \leq 7$ (Jahnke & Emde, 1945; Sato, 1951). For $n = 8$, we have,

$$
\begin{aligned}
&P_8(\cos\theta) = (1/16384)\\
&\times(6435\cos 8\theta+3432\cos 6\theta+2772\cos 4\theta+2520\cos 2\theta+1225),\\
&P_8^4(\cos\theta) = (10395/1024)\\
&\times(65\cos 8\theta-104\cos 6\theta-36\cos 4\theta+40\cos 2\theta+35),\\
&P_8^8(\cos\theta) = (2027025/128)\\
&\times(\cos 8\theta-8\cos 6\theta+28\cos 4\theta-56\cos 2\theta+35).
\end{aligned}
$$

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An X-ray Diffraction Method for the Study of Substructure of Crystals

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A double-crystal diffractometer method using a Geiger counter and supplementary film technique has been described. The analysis of the multi-peaked rocking curves obtained from bent, coarse-grained aluminum established a correlation between intensity maxima and adjacent lattice regions giving rise to them. The tilt between adjacent subgrains was determined and the existence of substructural domains within the subgrain was shown.

1. Introduction

Various workers studying the subgrain structure of single-crystal and polycrystalline aluminum as well as other metals have obtained data concerning the subgrain size which vary greatly in order of magnitude (Tate & McLean, 1951–2; Perryman, 1954; Hunter & Robinson, 1953; Delisle, 1953; Hirsch & Kellar, 1952). Refined microscopic and X-ray techniques have revealed substructural entities which are considerably smaller than those disclosed by more conventional techniques. The possibility therefore arises that under certain conditions of specimen preparation various orders of magnitude of substructural entities may coexist. The possible coexistence of such different substructural entities is investigated in coarse-grained bent aluminum specimens by means of an X-ray diffraction technique.

2. Experimental method

(*a*) *Preparation of specimens*

The aluminum specimens studied were furnished through the courtesy of Mr M. Metzger of Columbia University. The specimens were of 99·993% purity, containing 0·004% Fe and 0·002% Cu. The coarse grains were obtained by the strain-anneal method. Specimen Al−1 was bent to a radius of curvature of 20·5 cm. and subsequently heated at 600° C. for 18 hr. Specimen Al−2 was bent to a radius of curvature of 2 cm. and recrystallized upon annealing at 645° C. for 21 hr. and etched with 7% HCl solution containing some copper. This solution has been shown to attack subgrain boundaries strongly (Metzger & Intrater, 1954).

(*b*) *X-ray method*

As the principal research tool in this investigation a modified X-ray double-crystal diffractometer shown in Fig. 1 was employed. The X-ray beam emerging from a copper-target tube is reflected from the cleaved surface of a calcite crystal mounted on an adjustable holder (A) next to the beam port. The rocking curve of the cleaved calcite crystal exhibited a width at half maximum intensity of 8 sec. of arc. In order to remove the $K\alpha_2$ component from the reflected radiation, the beam passes through a 41 cm. long collimator (B) bolted to the sturdy base plate (C).

The collimator is provided with adjustable slit systems (D) at both ends. By proper adjustment of the vertical exit slit the $K\alpha_2$ component of the emerging beam was eliminated. The specimen is mounted on a goniometer (E), the axis of rotation being coincident with the crystal surface. The goniometer is equipped with a micrometer screw (F) which permits vertical scanning of the specimen surface. The specimen is rotated by a worm gear (G) which is connected to a synchronous 2 r.p.m. reversible motor (H) by means of interchangeable reduction gears (I) providing for a variety of speeds of specimen rotation. Attached to the reduction-gear system is a revolution counter (J) which enables one to relocate readily the angular position of the specimen. The reflection intensities of the specimen are detected by a Geiger counter (K) mounted on a track (L) which can be rotated independently around the specimen axis. Provisions are made for tilting the Geiger counter to register non-equatorial reflections. Attached to the front of the Geiger-counter window is a frame with inserted film holder (M). By means of the screw (N) small film