Conclusion

The neutron diffraction results are found to support the conclusions of Jones & Roberts. In particular, they offer direct structural evidence that the $MgFe_2O_4$ sample is incompletely inverted and also that the aluminium ions in $MgFeAlO_4$ are, certainly very largely, in *B* sites. It is thus possible to explain the steady variation of unit-cell dimensions (Nicks, 1951) as aluminium is substituted for iron in $MgFe_2O_4$. The Al^{3+} ions in these mixed ferrites enter the *B* sites, causing progressive reversion of Mg^{2+} into *A* sites. The final product is $MgAl_2O_4$ which, as always assumed and recently demonstrated directly by neutron diffraction (Bacon, 1952), has a 'normal' structure with Al^{3+} in *B* sites.

The present study arose as part of an investigation of certain ferrites at the Post Office Research Station, Dollis Hill, and was carried out at the Atomic Energy Research Establishment, Harwell.

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The X-ray Scattering from a Hindered Rotator. II

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The Laue–Bragg scattering from a group of atoms undergoing hindered rotation has been derived for a generalized potential function; this should permit treatment of a non-sinusoidal potential function as well as the non-classical rotator provided its probability distribution is known. The diffuse scattering from a hindered rotator is derived, and shown to be very sensitive to the degree of hinderance. A method of deriving the scattering from a spacially hindered rotator is also presented.

Introduction

The amplitude of Laue–Bragg scattering has previously been derived (King & Lipscomb, 1950) for hindered rotation of an atom, or group of atoms, about a fixed axis. A simple sinusoidal potential function was used for which the constants refer to each individual atom. It is useful to generalize the potential function to express the potential of the rotating group as a whole, and in order to provide for non-sinusoidal potential functions. The amplitude of Laue–Bragg scattering has been calculated for this more general potential function, assuming a classical rotator with Maxwell–Boltzmann distribution in the probability function of the rotation angle. A method of using this potential function in order to include the case of a distribution of quantum-mechanical rigid rotators is suggested.

The diffuse scattering from a hindered rotator has not previously been studied theoretically. The development indicated in the second part of the present paper for the case of a simple sinusoidal potential function indicates that the diffuse scattering should be very sensitive to the hindering potential, and quite different from that of a free rotator or that from atoms in fixed positions.

In the third part of this paper a general expansion is given which simplifies discussion of the spacially hindered rotator. Fortunately, most known examples

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of spacially hindered rotation occur in crystals of high symmetry, which, it will be observed, simplifies further the discussion of this relatively complicated case of hindered rotation.

1. Effect of generalized potential on a hindered axial rotator

Let the desired potential function of the rotating group of atoms be approximated as a series,

$$V = -\tfrac{1}{2}V_0 - \sum_{n=1}^{N} \tfrac{1}{2}V_n \cos(n\theta-\varphi_n)\,, \tag{1}$$

where V_0, V_n and φ_n are constants, and N must be chosen sufficiently large to give a reasonable approximation to the desired potential function. It will be observed that V_0 is arbitrary, and that only those V_n consistent with the axial symmetry of the expected potential function are different from zero.

Although the probability function

$$P(\theta) = \frac{\exp(-V/kT)}{\int_0^{2\pi} \exp(-V/kT)d\theta} \tag{2}$$

is evaluated here for a classical distribution of energy over various angles θ, a suitable modification can be proposed if $P(\theta)$ is known for the quantum mechanical distribution. The procedure would then be to choose the constants V_n in such a way that when V is substituted into equation (2) the quantum mechanical distribution is thereby obtained. Indeed, if the exponential functions are developed in series, as indicated in the previous paper, the constants V_n can be evaluated by the usual methods for orthogonal functions.

The average complex amplitude of scattering from an atom in hindered rotation may be derived by a method similar to that described previously (King & Lipscomb, 1950), with the result

$$\bar{g} \simeq f \exp(2\pi i\mathbf{h}\cdot\mathbf{k})\{J_0(a) + [2\sum_{n=1}^{N}\sum_{p=1}^{\infty} i^{pn}J_{pn}(a)I_p(b_n)\cos p(n\theta_h+\varphi_n)]/I_0(b_n)\}\,. \tag{3}$$

The term $J_0(a)$ is that for the free rotator, and the approximation involves neglect of products of more than one summation over the index p. Besides f, $\mathbf{h}$ and i, which have their usual meanings, $\mathbf{k}$ is the position vector from the origin to the center of rotation; $J_{pn}(a)$ and $I_p(b_n)$ are the Bessel and modified Bessel functions, respectively; $a = 2\pi|\mathbf{h}||\mathbf{v}| \sin\psi$, where $\mathbf{v}$ is the vector from the center of rotation to the instantaneous position of the atom, and ψ is the angle between the axis of rotation and $\mathbf{h}$; $b_n = V_n/(2kT)$; and θ_h is the angle between the projection of some standard reciprocal lattice vector $\mathbf{h}_s$ (selected conveniently, but otherwise arbitrarily) and the projection of $\mathbf{h}$ on the plane of rotation. The angles θ and φ_n are also measured in this plane from the projection of $\mathbf{h}_s$.

When the potential function applies to the rotation of the group of atoms as a whole, the amplitude of Laue–Bragg scattering can be most conveniently expressed in terms of the way in which the atoms are linked. The final result, obtained by averaging over all θ, is

$$\bar{F} = \overline{\sum_j g_j} \simeq \sum_j f_j \exp(2\pi_i\mathbf{h}\cdot\mathbf{k}_j)\{J_0(a_j) + [2\sum_{n=1}^{N}\sum_{p=1}^{\infty} i^{pn}J_{pn}(a_j)I_p(b_n)\cos p(n\theta+n\theta_{sj}-\varphi_n)]/I_0(b_n)\}\,, \tag{4}$$

where θ_{sj} is the angle, measured on the projection along the axis of rotation, between a standard atom (chosen arbitrarily) and the jth atom. The summation extends over the atoms of the group, and the result is a general expression for the molecular structure factor of a hindered axial rotator.

Some simplification for numerical calculations can be achieved for the simple* potential function $V = -\tfrac{1}{2}V_0 \cos n(\theta-\gamma)$, if use is made of the conclusion (Pauling, 1930; Pauling & Wilson, 1935, p. 292; Stern, 1931) that the transition between rotation and oscillation takes place at roughly the temperature $T = V_0/k$. The parameter $b = V_0/(2kT)$ then becomes $b \leq \tfrac{1}{2}$ for hindered rotation; the probability distribution can then be approximated by expansion of the exponential function, neglecting terms of order $b^2/2!$ or higher, as

$$P(\theta) = \frac{\exp[b\cos n(\theta-\gamma)]}{\int_0^{2\pi}\exp[b\cos n(\theta-\gamma)]d\theta} \simeq \frac{1}{2\pi}[1+b\cos n(\theta-\gamma)]\,. \tag{5}$$

For a group of atoms we find

$$\bar{F} = \Sigma_j f_j \exp[2\pi i\mathbf{h}\cdot\mathbf{k}_j][J_0(a_j) + i^n bJ_n(a_j)\cos n(\theta_{sj}+\gamma)]\,, \tag{6}$$

which can be further simplified for numerical calculation (cf. Atoji & Watanabe, 1950). The term in $J_0(a_j)$ corresponds to free rotation. The additional terms correct according to the degree of hinderance, and are shown in Fig. 1 as functions of a and Φ, where a is previously defined and $\Phi = \theta_{sj}-\gamma$.

2. Diffuse scattering from a hindered axial rotator

We shall assume a simple potential function $V = -\tfrac{1}{2}V_0 \cos n(\theta-\gamma)$, and no correlations among the rotations of individual groups. While the difference between diffuse scattering for the hindered rotator as compared with that for a free rotator would be enhanced by these correlations, no consideration has been made of these effects because of the wide variety of assumptions that could be made.

The intensity of diffuse scattering (Zachariasen, 1945, p. 216)

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* Application of this discussion to the more general potential function is straightforward.

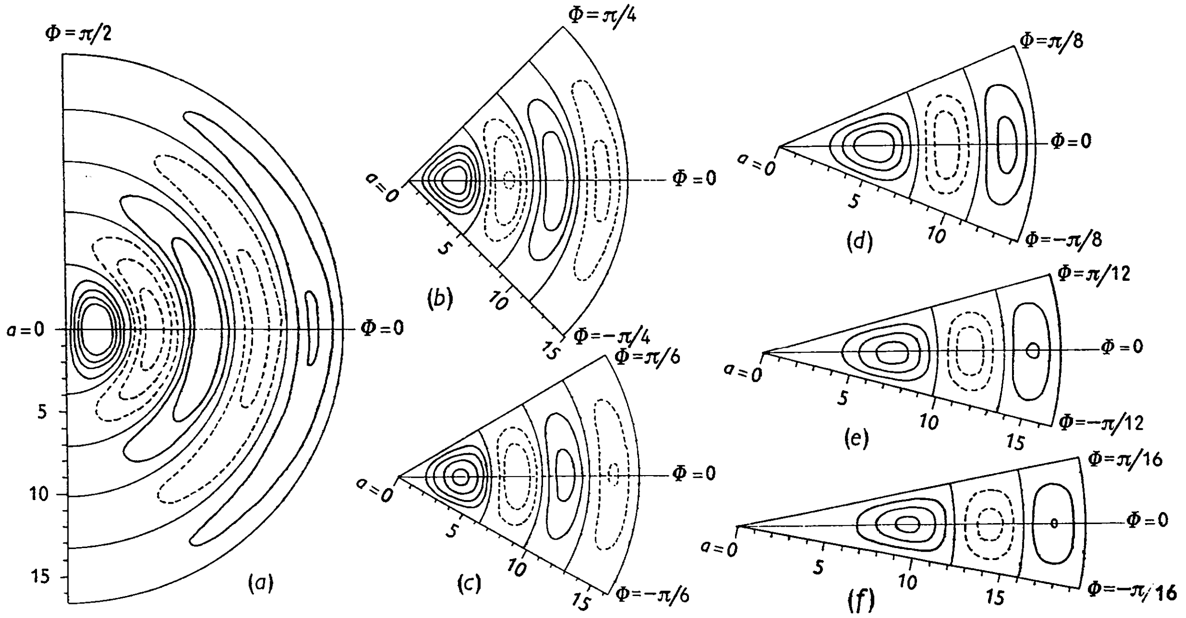

Fig. 1. The charts of $J_n(a)\cos n\Phi$. Contours are drawn at equal intervals. The outer contours show the zero value. (*a*) $J_1(a)\cos\Phi$. (*b*) $J_2(a)\cos 2\Phi$. (*c*) $J_3(a)\cos 3\Phi$. (*d*) $J_4(a)\cos 4\Phi$. (*e*) $J_6(a)\cos 6\Phi$. (*f*) $J_8(a)\cos 8\Phi$.

$$J_2 = K[\overline{|F|^2}-|\overline{F}|^2]\,, \tag{7}$$

where K is a constant for a given crystal, may be evaluated for a single rotating group in each unit cell. Define $\mathbf{k}_{jj'}=\mathbf{k}_j-\mathbf{k}_{j'}$, $\mathbf{v}_{jj'}=\mathbf{v}_j-\mathbf{v}_{j'}$, $\theta_{jj'}=\theta_j-\theta_{j'}$, $\alpha=a_j-a_{j'}\cos\theta_{jj'}$, $a_{jj'}=2\pi|\mathbf{h}||\mathbf{v}_{jj'}|\sin\psi$, $\beta=a_{j'}\sin\theta_{jj'}$, and $\varphi=\tan^{-1}(\beta/\alpha)$; these parameters are exemplified in Fig. 2 for ethane. Starting from

$$|F|^2=\sum_j\sum_{j'}f_jf_{j'}\cos 2\pi\mathbf{h}\cdot(\mathbf{k}_{jj'}+\mathbf{v}_{jj'})\,,$$

we expand as follows,

$$2\pi\mathbf{h}\cdot\mathbf{v}_{jj'}=a_{jj'}\cos(\varphi+\theta_{sj}+\theta)\,,$$

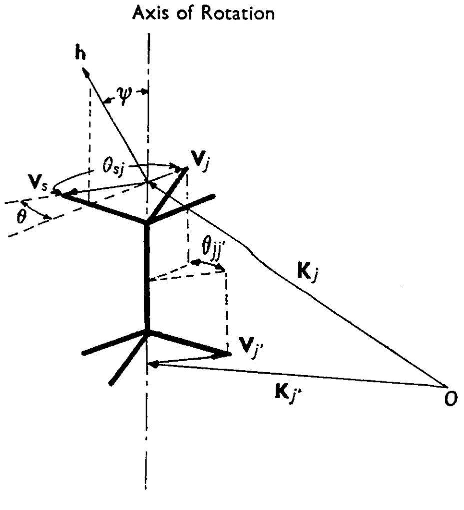

Fig. 2. Explanation of the notation, showing ethane as an example.

$$\cos(z\cos\varphi)=J_0(z)+2\sum_{m=1}^{\infty}(-1)^mJ_{2m}(z)\cos 2m\varphi\,,$$

$$\sin(z\cos\varphi)=2\sum_{m=1}^{\infty}(-1)^mJ_{2m+1}(z)\cos(2m+1)\varphi\,,$$

so that

$$\begin{aligned}\overline{|F|^2}=\sum_j\sum_{j'}f_jf_{j'}\{&\cos(2\pi\mathbf{h}\cdot\mathbf{k}_{jj'})[J_0(a_{jj'})\\&+\frac{2}{I_0(b)}\sum_{\substack{p=1\\pn=2m}}^{\infty}(-1)^{\frac{1}{2}pn}J_{pn}(a_{jj'})I_p(b)\cos pn(\varphi+\theta_{sj}+\gamma)]\\&-\sin(2\pi\mathbf{h}\cdot\mathbf{k}_{jj'})\frac{2}{I_0(b)}\\&\times\sum_{\substack{p=1\\pn=2m+1}}^{\infty}(-1)^{\frac{1}{2}(pn-1)}J_{pn}(a_{jj'})I_p(b)\cos pn(\varphi+\theta_{sj}+\gamma)\}\,,\end{aligned}$$

$$\begin{aligned}|\overline{F}|^2=\frac{1}{[I_0(b)]^2}\sum_j\sum_{j'}f_jf_{j'}\cos(2\pi\mathbf{h}\cdot\mathbf{k}_{jj'})&\\\times\sum_{p=0}^{\infty}\sum_{p'=0}^{\infty}\varepsilon_p\varepsilon_{p'}i^{pn}(-i)^{p'n}J_{pn}(a_j)J_{p'n}(a_{j'})&\\\times I_p(b)I_{p'}(b)\cos pn(\theta_{sj}+\gamma)\cos p'n(\theta_{sj'}+\gamma)\,,&\end{aligned}\tag{8}$$

where $\varepsilon_p=1$ when $p=0$, $\varepsilon_p=2$ where $p\neq 0$, and m is a positive integer.

Expressions corresponding to the approximation, $b\leqq\frac{1}{2}$, as discussed above, are

for $n=2m$

$$\begin{aligned}J_2=K\sum_j\sum_{j'}f_jf_{j'}\cos(2\pi\mathbf{h}\cdot\mathbf{k}_{jj'})\{&[J_0(a_{jj'})\\&+(-1)^mbJ_n(a_{jj'})\cos n(\varphi+\theta_{sj}+\gamma)]\\&-[J_0(a_j)+(-1)^mbJ_n(a_j)\cos n(\theta_{sj}+\gamma)][J_0(a_{j'})\\&+(-1)^mbJ_n(a_{j'})\cos n(\theta_{sj'}+\gamma)]\}\,,\end{aligned}\tag{9}$$

and for $n = 2m+1$

$$J_2 = K \sum_j \sum_{j'} f_j f_{j'} \big(\cos (2\pi \mathbf{h} \cdot \mathbf{k}_{jj'})\{J_0(a_{jj'}) \\ -[J_0(a_j)+i^n bJ_n(a_j) \cos n(\theta_{sj}+\gamma)]\,[J_0(a_{j'}) \\ +(-i)^n bJ_n(a_{j'}) \cos n(\theta_{sj'}+\gamma)]\} \\ +\sin (2\pi \mathbf{h} \cdot \mathbf{k}_{jj'})(-1)^{m+1} bJ_n(a_{jj'}) \cos n(\varphi+\theta_{sj}+\gamma)\big)\,. \tag{10}$$

These expressions reduce, as they should, to that for disorder scattering of a free rotator as $b \to 0$:

$$J_2 = K \sum_j \sum_{j'} f_j f_{j'} \cos (2\pi \mathbf{h} \cdot \mathbf{k}_{jj'})[J_0(a_{jj'})-J_0(a_j)J_0(a_{j'})]\,. \tag{11}$$

The effect of hinderance of the rotation is illustrated in Fig. 3, which shows intensity contours for $b = \frac{1}{2}$ when $n = 2$ and $n = 4$, and for the free rotator, for which $b = 0$. These contours are calculated from equation (9) for a homonuclear diatomic molecule ($\theta_{jj'} = \pi$, $\varphi = 0$), i.e. $\mathbf{k}_{jj'} = 0$. The expression is

$$J_2 = 2Kf^2\{1+[J_0(2c)+(-1)^m bJ_n(2c) \cos n\theta_h] \\ -2[J_0(c)+(-1)^m bJ_n(c) \cos n\theta_h]^2\}\,, \tag{12}$$

where $n = 2m$, d_0 is the interatomic distance, and $c = 2\pi d_0 \sin \psi\, (\sin \theta)/\lambda$. The maxima shown by the hindered rotator and free rotator are about the same distance from the centers of the patterns, but the angular dependence differs considerably, and would be expected to be even greater if some correlation among different rotating groups is included. These features are similar to those shown by tetranitromethane (Oda, 1945).

3. The spacially hindered rotator

Again assuming the classical distribution, the average scattering amplitude from a single atom in spacially hindered rotation about a fixed point may be written as

$$\bar{g} = f \iint W(\theta, \varphi) \exp (i\alpha \cos \omega) ds\,, \tag{13}$$

where the integration extends over the surface (of element ds) of the unit sphere with origin at the center of rotation. Here

$$\alpha = 2\pi|\mathbf{h}||\mathbf{r}|\,,$$

and

$$\cos \omega = \cos \theta \cos \theta_h + \sin \theta \sin \theta_h \cos (\varphi-\varphi_h)\,,$$

where ω is the angle between $\mathbf{h}$ and the position vector $\mathbf{r}$ of the atom, and the polar angles of $\mathbf{h}$ and $\mathbf{r}$ are (θ_h, φ_h) and (θ, φ), respectively. The probability function, $W(\theta, \varphi)$, may be represented as

$$W(\theta, \varphi) = \frac{\exp [-V/kT]}{\iint \exp [-V/kT] ds}\,, \tag{14}$$

where $V = V(\theta, \varphi)$ is the hindering potential. We now expand the exponential functions in surface spherical harmonics $Y_n(\theta, \varphi)$, making use of a 'singular addition theorem' (Magnus & Oberhettinger, 1949, p. 21). The result is

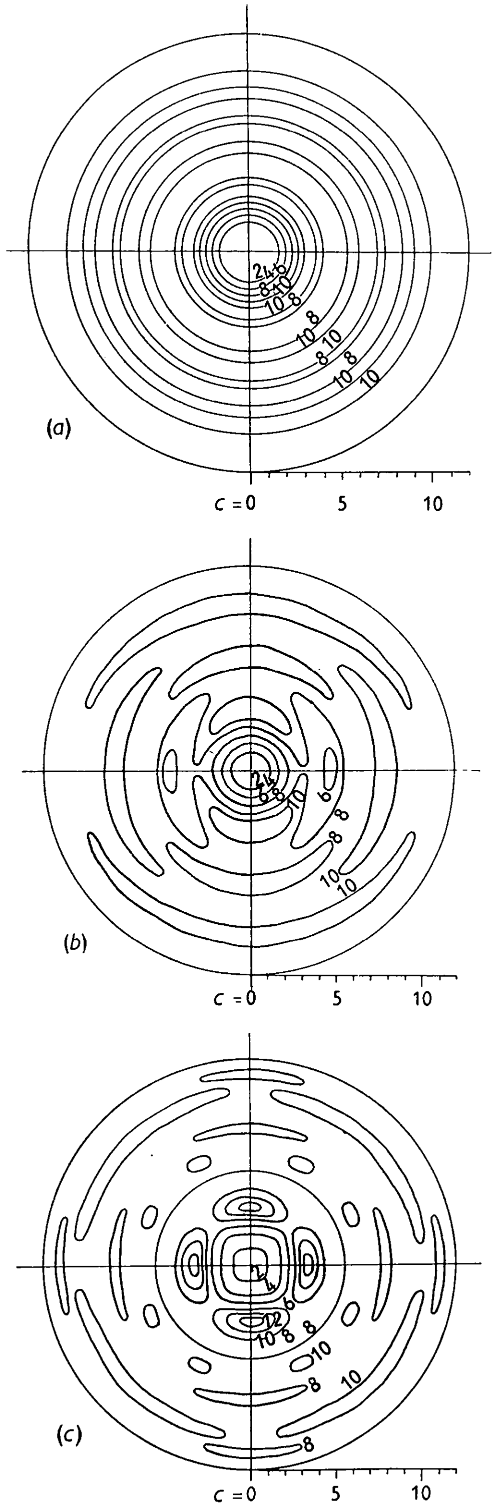

Fig. 3. A set of intensity contours of the expression

$$1+J_0(2c)+(-1)^m bJ_n(2c) \cos n\theta_h \\ -2[J_0(c)+(-1)^m bJ_n(c) \cos n\theta_h]^2$$

for a homonuclear diatomic molecule. For comparison the intensity contours for free axial rotation of the same molecule are shown, and correspond to the expression $1+J_0(2c)-2J_0^2(c)$.

(a) $b = 0$. (b) $n = 2$, $b = \frac{1}{2}$. (c) $n = 4$, $b = \frac{1}{2}$.

$$\exp\left[-V(\theta,\varphi)/kT\right] = \sum_{n=0}^{\infty} e_n Y_n(\theta,\varphi) = \sum_{n=0}^{\infty} e_n A_{0n} P_n(\cos\theta) + \sum_{n=0}^{\infty}\sum_{m=1}^{\infty} e_n(A_{mn}\cos m\varphi + B_{mn}\sin m\varphi)P_n^m(\cos\theta)\,, \quad (15)$$

and,

$$\exp\left[i\alpha\cos\omega\right] = \sum_{p=0}^{\infty} a_0 j_p(\alpha) P_p(\cos\omega)\,, \quad (16)$$

where $P_n(\cos\theta)$ and $P_n(\cos\omega)$ are the Legendre polynomials, $P_n^m(\cos\theta)$ are the associated Legendre functions, $a_p = i^p(2p+1)$, $j_p(\alpha) = \sqrt{[\pi/(2\alpha)]}J_{n+\frac{1}{2}}(\alpha)$ is the spherical Bessel function, and the e_n are the coefficients to be determined by the usual methods for orthogonal functions.

Now, with the use of such orthogonality relations as

$$\int_0^{2\pi}\int_{-1}^{1} Y_n(\theta,\varphi)P_p(\cos\omega)d(\cos\theta)d\varphi = \frac{4\pi}{2n+1}Y_n(\theta_h,\varphi_h) \text{ when } n = p$$
$$= 0 \text{ when } n \neq p\,, \quad (17)$$

equation (13) reduces to

$$\bar{g} = f\sum_{n=0}^{\infty} i^n e_n j_n(\alpha) Y_n(\theta_h,\varphi_h) A_{00}^{-1}\,. \quad (18)$$

It will be observed that when $V/kT = 0$ (that is when $n = 0$, $e_0 = 1$, and $A_{00} = 1$) equation (18) reduces to the expression $\bar{g} = f(\sin\alpha)/\alpha$, which is the mean amplitude for an atom in free spherical rotation about a fixed point chosen as the origin.

Fortunately, most crystals showing rotational disorder have high symmetry, which simplifies the application of these equations. Functions appropriate to the point symmetry O_h of the function $W(\theta,\varphi)$ have been discussed (von der Lage & Bethe, 1947; Nakamura, 1950), and the resulting amplitude of scattering from a single atom is given here as an example:

$$\bar{g} = f\left\{e_0\frac{\sin\alpha}{\alpha} + \frac{\sqrt{21}}{2}e_4 j_4(\alpha)\left[P_4(\cos\theta_h) + \frac{1}{168}P_4^4(\cos\theta_h)\cos 4\varphi_h\right] - \frac{\sqrt{26}}{4}e_6 j_6(\alpha)\left[P_6(\cos\theta_h) - \frac{1}{360}P_6^4(\cos\theta_h)\cos 4\varphi_h\right] + \ldots\right\}A_{00}^{-1}\,. \quad (19)$$

The average molecular structure factor of a spacially hindered rotator depends in a complicated manner on the way in which the atoms are linked and the specific assumptions concerning the potential function. As a possible example, however, the amplitude of scattering from a diatomic molecule having atomic scattering amplitudes f_1 and f_2 may be written as

$$\bar{\bar{F}} = \sum_{n=0}^{\infty} i^n\left[f_1 j_n(\alpha_1) + f_2 j_n(-\alpha_2)\right]e_n Y_n(\theta_h,\varphi_h)/A_{00}\,, \quad (20)$$

which is similar to equation ~~(18)~~ for an individual atom.

These expressions for hindered rotation are developed as modifications of the similar situations for free rotation, as represented by the first terms in the expansions. The additional terms depend mostly on temperature and the heights of potential barriers, and it is hoped that their evaluation will give some detailed information about crystalline fields in rotationally disordered crystals (Atoji, 1951). Besides modifications to include quantum mechanical rotation, and to study the effect of correlation on the intensities of Laue–Bragg and disorder scattering, it would also be desirable to develop the theory of scattering for oscillational disorders of groups of atoms starting from the perfectly ordered crystal as the first term, if a series development is promising. However, discussion of these cases of oscillational disorder as anisotropic temperature vibrations has been successful for hexamethylenetetramine (Shaffer, 1947).

We are indebted to Dr T. Matsubara for discussion of some of the mathematical aspects, and to the Office of Naval Research for financial aid of part of this research.

Note added 1 *August* 1952.—There is a close similarity between some of the mathematical techniques in the present paper and in a paper by Deas (1952), especially in the use of spherical harmonics when an average about a point is considered (cf. Atoji, 1951). Although a common basis of initial development also exists, both the problems considered, and the assumptions introduced in their development are, however, quite different.

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