

X-ray Thermal Scattering in the Model Q -function Description. Linear Lattice Approximation

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Kinematical scattering from a crystal deformed by a progressive elastic wave was recalculated using the Q -function approach. A more general treatment, presented here, yields a new evaluation of the relative intensities of the satellite spots. Under the assumption of the adiabatic and harmonic approximations it was then possible by means of the central limit theorem to generalize calculations for the whole spectrum of elastic waves, however, for a model restricted to the chain crystal. The resulting Q -function consists of Gaussian curves, diffusing lattice points in the vector space. If amplitudes of elastic waves are defined by energy distribution among different modes of vibration, the appropriate Q -function becomes in general temperature-sensitive. For the low temperature region it is represented by Gaussian curves of practically constant variance, not depending on temperature. The calculated diffraction pattern is almost the same as given by the simple DW theory of independent atomic motions. For the high temperature region the variances of Gaussian curves are represented by the parabolic function, which strongly depends on temperature. An appropriate diffraction pattern displayed, each time, features common to the TDS, a sudden decrease as well as broadening of the Bragg peaks. The latter effect in the present treatment is a simple consequence of the harmonic model of a crystal. The Q -function method accounts for the TDS peaking at the Bragg positions and seems to offer some possibilities for explaining the existence of the inversion temperature.

Introduction

The Q -function, otherwise known as the generalized Patterson function, has been proved to be a powerful tool in evaluating results for paracrystals and imperfect crystals (Hosemann & Bagchi, 1962). It was proposed recently (Bagchi, 1970, 1971; Keller, 1970) that an approach *via* the Q -function is deemed valid for any kinematical discussion of irregularities and defects of the real crystal lattice. Examples, however, of its applications to the treatment of X-ray thermal scattering are rather scarce and inconsequential. The main advantages of the method used here result from the fact that it enables one to substitute a dynamical problem of individual collisions between X-ray photons and lattice phonons for a static problem of the X-ray coherent scattering from a lattice distorted by elastic thermal waves.

While the thermal elastic waves (in the assumed approximation) are independent in physical space, it follows immediately from the Q -function properties that their images depend strongly on each other in vector space and consequently they cannot be treated separately in intensity space. It will be shown here that every conceivable elastic wave contributes in its own specific way to the resulting distortion, as described by the Q -function, in an amount which depends on the allocation of available thermal energy to the corresponding mode of vibration. In other words, scattering is seen as a multiple phonon process during which, in any single collision, some

phonons are created or some annihilated. However, the average distribution of energy among different modes of vibration remains constant. This distribution of energy, depending on quantum mechanical considerations of temperature, defines in turn the Q -function, which becomes temperature sensitive itself.

The resulting approach is justified theoretically by the first Born approximation for the scattering of X-rays from a system of interacting particles. Under the assumption that energy transfer is negligible with regard to the energy of scattered photons, it is possible to express the differential cross section in terms of a pair distribution function as discussed by van Hove (1954). In this respect the Q -function denoting the average density distribution as seen from a particle of the system represents merely a particular, time-independent, case of the van Hove function.

The whole subject will be treated kinematically under harmonic and adiabatic approximations in a coherent model of scattering as follows:

1. The single phonon X-ray scattering
2. The multiple phonon X-ray scattering in linear lattice approximation.

Single phonon X-ray scattering

The single phonon X-ray scattering will be treated firstly as a basic phenomenon from which a subsequent generalization may be extended to the many-phonon processes. According to the static approximation, X-ray diffraction may be treated as arising from a crystal deformed by a single sinusoidal travelling wave.

Firstly, an instantaneous Q -function will be found

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for a case of deformation resulting from a stationary 'frozen' wave. Then, the motion of this wave will be accounted for, yielding a time-averaged Q -function. Thus two averaging operations, the former over space and the latter over time, will be carried out. The importance of the adapted sequence of operations for the X-ray thermal scattering was emphasized a long time ago by Jahn (1942).

It should be noted that the early calculations of the intensity function for a crystal deformed by a stationary wave have been performed in the usual way (averaging of the amplitude in the Fourier space) by Dehlinger (1927) whose calculation did not comply with mathematical rules for multiplying out infinite series. The calculation was subsequently repeated by Kochendörfer (1939) and an attempt was made to improve it by including neglected nonlinear terms. In this respect the calculation given below represents an exact solution for an arbitrary traveling wave and is not restricted to the linear case.

A crystal of any shape and size deformed by an elastic sinusoidal plane wave defined by its wave vector \mathbf{k} (where $|\mathbf{k}| = \frac{2\pi}{\lambda}$, $\lambda = \text{wavelength}$), and its polarization amplitude vector \mathbf{a}_k , may be described by the time dependent charge density function $\varrho(\mathbf{x}, t)$ in physical space (t time variable, \mathbf{x} vector variable) as follows:

$$\varrho(\mathbf{x}, t) = \varrho_a(\mathbf{x}) * \sum_n \delta[\mathbf{x} - \mathbf{x}^n - \mathbf{a}_k \cos(\mathbf{k} \cdot \mathbf{x}^n - \omega_k t - \Delta_k)] \quad (1)$$

In the above expression an assumption has been made that only one atom occupies every lattice point. It is described by the function $\varrho_a(\mathbf{x})$ which, in the adiabatic approximation, does not depend on time being simply convoluted (*):

$$g(x) * g(x) \equiv \int_{-\infty}^{+\infty} g(x)g(u-x)dx = h(u) \quad (2)$$

with the lattice peak function. The latter is defined by a sum of Dirac delta generalized functions (δ) the positions of which in physical space are governed by two agents: (i) the periodicity of the crystal assumed to be regular, with a parameter equal to unity and defined by a set of constant vectors \mathbf{x}^n of integer components $[n_1, n_2, n_3]$; (ii) the displacement resulting from the existence of the propagating wave given by the expression:

$$\mathbf{a}_k \cos(\mathbf{k} \cdot \mathbf{x}^n - \omega_k t - \Delta_k) \quad (3)$$

where ω_k and Δ_k represent the cyclic frequency and the phase shift respectively. The summation extends over all N atoms of the scattering crystal.

The instantaneous Q -function $q(\mathbf{u}, t)$ in vector space (\mathbf{u} vector variable) is obtained by the auto-correlation operation (*):

$$g(x) * g(x) \equiv \int_{-\infty}^{+\infty} g(x)g(u+x)dx = h(u) \quad (4)$$

as follows:

$$\begin{aligned} q(\mathbf{u}, t) &= \varrho(\mathbf{x}, t) * \varrho(\mathbf{x}, t) \\ &= \left\{ \varrho_a(\mathbf{x}) * \sum_n \delta[\mathbf{x} - \mathbf{x}^n - \mathbf{a}_k \cos(\mathbf{k} \cdot \mathbf{x}^n - \omega_k t - \Delta_k)] \right\} \\ &\quad * \left\{ \varrho_a(\mathbf{x}) * \sum_m \delta[\mathbf{x} - \mathbf{x}^m - \mathbf{a}_k \cos(\mathbf{k} \cdot \mathbf{x}^m - \omega_k t - \Delta_k)] \right\} \\ &= \{ \varrho_a(\mathbf{x}) * \varrho_a(\mathbf{x}) \} \\ &\quad * \left\{ \sum_n \delta[\mathbf{x} - \mathbf{x}^n - \mathbf{a}_k \cos(\mathbf{k} \cdot \mathbf{x}^n - \omega_k t - \Delta_k)] \right. \\ &\quad \left. * \sum_m \delta[\mathbf{x} - \mathbf{x}^m - \mathbf{a}_k \cos(\mathbf{k} \cdot \mathbf{x}^m - \omega_k t - \Delta_k)] \right\} \\ &= q_a(\mathbf{u}) * \sum_n \sum_m \delta\{\mathbf{u} - (\mathbf{x}^m - \mathbf{x}^n) + 2\mathbf{a}_k \\ &\quad \times \sin[\frac{1}{2}\mathbf{k} \cdot (\mathbf{x}^m - \mathbf{x}^n)] \sin[\frac{1}{2}\mathbf{k} \cdot (\mathbf{x}^m + \mathbf{x}^n) - \omega_k t - \Delta_k]\} \\ &= q_a(\mathbf{u}) * \sum_u \sum_v \delta[\mathbf{u} - \mathbf{u}^v + 2\mathbf{a}_k \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{u}^v) \\ &\quad \times \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{u}^w - \omega_k t - \Delta_k)] \quad (5) \end{aligned}$$

In the above expression symbol $q_a(\mathbf{u})$ is used for the autocorrelated atom charge density function, while symbols \mathbf{u}^v and \mathbf{u}^w are used for any difference and any sum respectively, of vectors \mathbf{x}^m and \mathbf{x}^n . The double summation extends now over the whole set ($U_{r,w}$) of vectors \mathbf{u}^v and the whole set (u_r) of vectors \mathbf{u}^r . Introducing the following substitutions:

$$\begin{aligned} 2\mathbf{a}_k \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{u}^v) &\equiv \mathbf{A}_v \\ \frac{1}{2}\mathbf{k} \cdot \mathbf{u}^w - \Delta_k &\equiv b_w \\ \sin(b_w - \omega_k t) &\equiv f_w(t) \quad (6) \end{aligned}$$

the Q -function may be expressed by the abbreviated form

$$q(\mathbf{u}, t) = q_a(\mathbf{u}) * \sum_r \sum_u \delta(\mathbf{u} - \mathbf{u}^r) * \delta[\mathbf{u} + \mathbf{A}_r f_w(t)] \quad (7)$$

The tridimensional Dirac delta $\delta(\mathbf{u} - \mathbf{u}^r)$ may be defined most generally as a product of three one-dimensional Dirac deltas, each of them on a different axis of any orthonormal coordinate system u'_1, u'_2, u'_3 :

$$\delta(\mathbf{u}-\mathbf{u}') \equiv \delta(u'_1 - u'_1) \delta(u'_2 - u'_2) \delta(u'_3 - u'_3). \quad (8) \quad \text{and}$$

Let

$$\begin{aligned} c_{ij} &= \cos(u_i, u'_j) \\ u_j &= c_{1j}u_1 + c_{2j}u_2 + c_{3j}u_3 \equiv c_{ij}u_i, \end{aligned} \quad (9)$$

where $i, j = 1, 2, 3$, then

$$\delta(\mathbf{u}-\mathbf{u}') = \delta(c_{i1}u_i - c_{i1}u'_i) \delta(c_{i2}u_i - c_{i2}u'_i) \delta(c_{i3}u_i - c_{i3}u'_i). \quad (10)$$

To obtain the time-averaged Q -function it will be necessary to integrate over one period of vibration T of the Q -function (7) or rather its last convoluted term:

$$\begin{aligned} \frac{1}{T} \int_{-T/2}^{+T/2} q(\mathbf{u}, t) dt &= q_a(\mathbf{u}) * \sum_{\mathbf{u}} \sum_{\mathbf{u}'} \delta(\mathbf{u}-\mathbf{u}') \\ &* \frac{1}{T} \int_{-T/2}^{+T/2} \delta[\mathbf{u} + \mathbf{A}_v f_w(t)] dt \end{aligned} \quad (11)$$

which, if given in arbitrary coordinate systems, is described by:

$$\begin{aligned} \frac{1}{T} \int_{-T/2}^{+T/2} \delta[\mathbf{u} + \mathbf{A}_v f_w(t)] dt &= \\ \frac{1}{T} \int_{-T/2}^{+T/2} \delta[c_{i1}u_i + c_{i1}A_v f_w(t)] \delta[c_{i2}u_i + c_{i2}A_v f_w(t)] \\ \times \delta[c_{i3}u_i + c_{i3}A_v f_w(t)] dt. \end{aligned} \quad (12)$$

It will be most useful to assume a coordinate system such that:

$$c_{i1}A_v = |A_v|, \quad c_{i2}A_v = c_{i3}A_v = 0. \quad (13)$$

In this system the integration is reduced to only the first of the deltas:

$$\begin{aligned} \frac{1}{T} \int_{-T/2}^{+T/2} \delta[\mathbf{u} + A_v f_w(t)] dt \\ = \frac{1}{T} \int_{-T/2}^{+T/2} \delta[u'_1 + |A_v| f_w(t)] dt \delta(u'_2) \delta(u'_3). \end{aligned} \quad (14)$$

The integration may be carried out with the help of the formula (Gel'fand & Shilov, 1964):

$$\int \delta[g(t)] h(t) dt = \sum_n \frac{h(t_n)}{|g'(t_n)|}, \quad (15)$$

where the summation is extended over all the solutions of the equation: $g(t) = 0$.

In this case

$$g(t) = u'_1 + |A_v| \sin(b_w - \omega_k t)$$

$$h(t) = 1.$$

Performing the necessary calculations and recalling that the function $g(t)$ has 2 simple roots in one period of vibration and that $|u'_1| \leq |A|$, we finally obtain

$$\begin{aligned} \frac{1}{T} \int_{-T/2}^{+T/2} \delta[u'_1 + |A_v| f_w(t)] dt \delta(u'_2) \delta(u'_3) \\ = \frac{\delta(u'_2) \delta(u'_3)}{\pi \sqrt{A_v^2 - (u'_1)^2}} = \frac{\delta(c_{i2}u_i) \delta(c_{i3}u_i)}{\pi \sqrt{A_v^2 - (c_{i1}u_i)^2}}. \end{aligned} \quad (16)$$

The similar expression for the diffusing function in vector space was discussed by Hosemann & Bagchi (1962).

The Q -function is given by the expression:

$$q(\mathbf{u}) = q_a(\mathbf{u}) * \sum_{\mathbf{u}} \sum_{\mathbf{u}'} \delta(\mathbf{u}-\mathbf{u}') * \frac{\delta(c_{i2}u_i) \delta(c_{i3}u_i)}{\pi \sqrt{A_v^2 - (c_{i1}u_i)^2}}. \quad (17)$$

The second sum in expression (17) may be now evaluated by means of the introduced function: $\omega(\mathbf{u})$. The latter is calculated by means of the autocorrelation operation of the shape function which confines the model of a scattering structure:

$$\omega(\mathbf{u}) = \int_{-\infty}^{+\infty} \sigma(\mathbf{x}) \sigma(\mathbf{u} + \mathbf{x}) d^3\mathbf{x}, \quad d^3\mathbf{x} = dx_1 dx_2 dx_3. \quad (18)$$

The shape function is defined in the usual way as follows:

$$\sigma(\mathbf{x}) \begin{cases} = 1 & \mathbf{x} \text{ belongs to the crystal space} \\ \text{if} \\ = 0 & \mathbf{x} \text{ does not.} \end{cases}$$

Analytically, after evaluation of the second sum, the whole time-averaged Q -function is rewritten in the following way:

$$\begin{aligned} q(\mathbf{u}) = q_a(\mathbf{u}) * \left\{ \sum_{\mathbf{u}} \omega(\mathbf{u}) \frac{\delta(c_{i2}u_i) \delta(c_{i3}u_i)}{\pi \sqrt{A_v^2 - (c_{i1}u_i)^2}} \right. \\ \left. * [\delta(\mathbf{u} + \mathbf{u}') + \delta(\mathbf{u} - \mathbf{u}')] + N \delta(\mathbf{u}) \right\}, \end{aligned} \quad (19)$$

where the set U'_v now contains only one vector out of any pair of conjugated vectors in a centrosymmetrical relationship: $\mathbf{u}' = -\mathbf{u}$.

The Q -function is depicted in Fig. 1. What is not shown on the picture, is that all the points are diffused by means of the autocorrelated atom charge density function $q_a(\mathbf{u})$.

To obtain the intensity function it is necessary to do the Fourier transform of the time-averaged Q -function. To shorten the used notation the whole operation will be indicated by a thick dash '—' over the function.

Recalling that:

$$\overline{q_a(\mathbf{u})} = f(\mathbf{s})^2, \left(|\mathbf{s}| = \frac{2 \sin \theta}{\lambda} \right)$$

is the square of the atomic scattering factor,

$$\begin{aligned} \frac{\delta(c_{i2}u_i)\delta(c_{i3}u_i)}{\pi\sqrt{A^2 - (c_{i1}u_i)^2}} &= \frac{\delta(\mathbf{u}'_2)\delta(\mathbf{u}'_3)}{\pi\sqrt{A^2 - (u'_1)^2}} \\ &= J_0(2\pi|A|s'_1) = J_0(2\pi|A|c_{i1}s_i), \\ &= J_0[2\pi|A| |\mathbf{s}| \cos(\mathbf{A}, \mathbf{s})] = J_0(2\pi\mathbf{A} \cdot \mathbf{s}) \end{aligned}$$

$$\overline{\delta(\mathbf{u} + \mathbf{u}^v) + \delta(\mathbf{u} - \mathbf{u}^v)} = 2 \cos(2\pi\mathbf{u}^v \cdot \mathbf{s}), \quad (20)$$

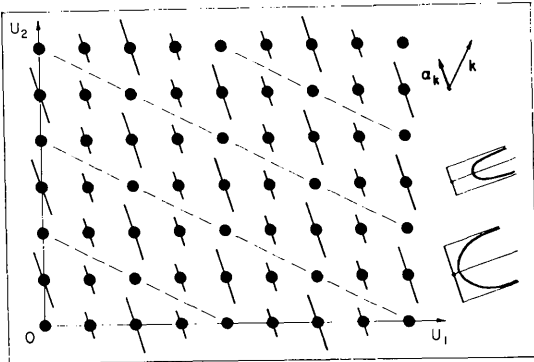


Fig. 1. A two-dimensional picture of the time-averaged Q -function obtained for a crystal distorted by a single elastic wave.

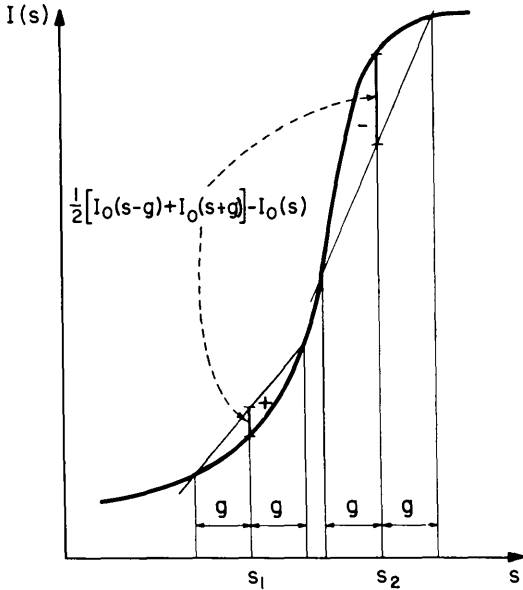


Fig. 2. The peak-flattening effect due to the distortion of a crystal by an elastic wave for a case when only a part of the crystal is illuminated by X-rays.

where $J_0(\mathbf{s})$ is the zero order Bessel function and, obviously, $s'_j = c_{ij}s_i$, we obtain, removing the restriction imposed on the vectors \mathbf{u}^v :

$$I(\mathbf{s}) = f(\mathbf{s})^2 \sum_{\mathbf{u}}^{U_v} \omega(\mathbf{u}^v) J_0[4\pi\mathbf{a}_k \cdot \mathbf{s} \sin(\frac{1}{2}\mathbf{k} \cdot \mathbf{u}^v)] \cos(2\pi\mathbf{u}^v \cdot \mathbf{s}). \quad (21)$$

This expression describes the scattering of X-rays from a crystal of any size and shape deformed by a single elastic travelling wave.

Now we can show that in the intensity pattern of a crystal deformed by an elastic wave, a sequence of satellite spots arranged in pairs may be observed. For that purpose we introduce a new wave vector $\mathbf{g} = \frac{1}{2\pi} \mathbf{k}$ and develop the Bessel function into a power series. The intensity function is then given by:

$$\begin{aligned} I(\mathbf{s}) &= f(\mathbf{s})^2 \sum_{\mathbf{u}}^{U_v} \omega(\mathbf{u}^v) \sum_{m=0}^{\infty} \frac{(-1)^m}{(m!)^2} (2\pi\mathbf{a}_k \cdot \mathbf{s})^{2m} \\ &\times \sin^{2m}(\pi\mathbf{u}^v \cdot \mathbf{g}) \cos(2\pi\mathbf{u}^v \cdot \mathbf{s}). \end{aligned} \quad (22)$$

Making use of the following easily proved identity:

$$\sin^{2m} \beta \cos \alpha = 2^{-2m} \sum_{n=-m}^m (-1)^n \binom{2m}{n+m} \cos(\alpha + 2n\beta) \quad (23)$$

we may further write

$$\begin{aligned} I(\mathbf{s}) &= f(\mathbf{s})^2 \sum_{\mathbf{u}}^{U_v} \omega(\mathbf{u}^v) \sum_{m=0}^{\infty} \sum_{n=-m}^m \frac{(-1)^{n+m}}{(m!)^2} \\ &\times \binom{2m}{n+m} (\pi\mathbf{a}_k \cdot \mathbf{s})^{2m} \cos[2\pi\mathbf{u}^v \cdot (\mathbf{s} + n\mathbf{g})]. \end{aligned} \quad (24)$$

Recalling that

$$f(\mathbf{s})^2 \sum_{\mathbf{u}}^{U_v} \omega(\mathbf{u}^v) \cos(2\pi\mathbf{u}^v \cdot \mathbf{s}) = I_0(\mathbf{s}) \quad (25)$$

represents the intensity function for an undistorted crystal and changing the order of summation, we obtain:

$$I(\mathbf{s}) = \sum_{m=0}^{\infty} \sum_{n=-m}^m \frac{(-1)^{n+m}}{(m!)^2} \binom{2m}{n+m} (\pi\mathbf{a}_k \cdot \mathbf{s})^{2m} I_0(\mathbf{s} + n\mathbf{g}). \quad (26)$$

After introducing identically the following quantity

$$\frac{(-1)^{n+m}}{(m!)^2} \binom{2m}{n+m} = \frac{(2m)!}{(m!)^2} \frac{(-1)^{n+m}}{(m-n)!(m+n)!} \equiv A_{nm} \quad (27)$$

we finally obtain the expression:

$$I(\mathbf{s}) = \sum_{m=0}^{\infty} \sum_{n=-m}^m A_{nm} (\pi\mathbf{a}_k \cdot \mathbf{s})^{2m} I_0(\mathbf{s} + n\mathbf{g}) \quad (28)$$

which is an exact description of X-ray scattering by a crystal of any shape and size, deformed by an arbitrary sinusoidal, traveling wave.

In the approximation to the first and the second satellite pairs the intensity function after convenient (for the purpose of discussion) rearrangement may be given by:

$$I(\mathbf{s}) = I_0(\mathbf{s}) + 2\pi(\mathbf{a}_k \cdot \mathbf{s})^2 \{ [I_0(\mathbf{s} - \mathbf{g}) + I_0(\mathbf{s} + \mathbf{g})] - I_0(\mathbf{s}) \} + \frac{1}{2}(\mathbf{a}_k \cdot \mathbf{s})^4 \{ [I_0(\mathbf{s} - 2\mathbf{g}) + I_0(\mathbf{s} + 2\mathbf{g})] - I_0(\mathbf{s}) \} - 2\pi(\mathbf{a}_k \cdot \mathbf{s})^4 \{ [I_0(\mathbf{s} - \mathbf{g}) + I_0(\mathbf{s} + \mathbf{g})] - I_0(\mathbf{s}) \} + \dots \quad (29)$$

It is easy to see from the derived expression that every subsequent satellite pair is generated at the expense of the preceding pairs.

It may also be noticed that if the main reflection happens to be a broad peak, the intensity scattered by an elastic wave does not appear as a separate satellite spot (at least the most important first pair). In that case the broad peak in its convex part will be reduced in intensity, while in its concave part it will be increased, which results in a further flattening of the peak. The above situation occurs when only part of a crystal is illuminated by the X-rays. An appropriate change in the diffraction pattern is illustrated in Fig. 2.

On the other hand, if the main reflection is sharp and satellite spots occur separately, in order to compare their relative intensities it will be necessary to change the order of summation in the expression (28) and calculate coefficient factors of every intensity term:

$$I(\mathbf{s}) = \sum_{m=0}^{\infty} A_{0m}(\pi\mathbf{a}_k \cdot \mathbf{s})^{2m} J_0(\mathbf{s}) + 2 \sum_{n=1}^{+\infty} \sum_{m=n}^{+\infty} A_{nm}(\pi\mathbf{a}_k \cdot \mathbf{s})^{2m} \times [I_0(\mathbf{s} - n\mathbf{g}) + I_0(\mathbf{s} + n\mathbf{g})] \quad (30)$$

Every coefficient factor is an infinite series, which resembles the development of the Bessel function of the even order. If these are denoted by:

$$J_{2n}(x) = \sum_{m=n}^{\infty} B_{nm} \left(\frac{x}{2}\right)^{2m} \quad \text{and} \quad B_{nm} = \frac{(-1)^{n+m}}{(m-n)! (m+n)!} \quad (31)$$

it may be observed that the calculated series represent the Bessel function, every term of which is 'modulated' by the same factor which is equal to

$$\frac{(2m)!}{(m!)^2}$$

In conclusion, the present treatment of scattering from a sinusoidal wave, although being in general agreement with earlier papers with regard to the positions of satellite spots, differs from the previous calculations in the evaluation of the relative intensities as given in the paper of Kochendörfer (1939), by the proportion of the Bessel functions of all the orders:

$$I_{0\mathbf{g}}(\mathbf{s}) : I_{1\mathbf{g}}(\mathbf{s}) : I_{2\mathbf{g}}(\mathbf{s}) : \dots = J_0(x)^2 : J_1(x)^2 : J_2(x)^2 : \dots \quad (32)$$

The total integrated intensity of the main reflection and all its satellites is still equal to the intensity from the undisturbed lattice, which is easily seen from the identity

$$\sum_{n=-m}^{-m} A_{nm} = 0 \quad \text{for} \quad m \geq 1, \quad (33)$$

but the often cited expression (Daniel & Lipson, 1942) justifying the above fact:

$$J_0(s)^2 + 2 \sum_{n=1}^{\infty} J_n(s)^2 = 1 \quad (34)$$

cannot be thought to be relevant.

The multiple phonon X-ray scattering in linear lattice approximation

In this section an exact expression for the X-ray scattering from a crystal deformed by the thermal motion will be derived through a straightforward generalization of the results obtained previously for one elastic wave. In order to avoid calculational complications which have no bearing on the nature of the X-ray thermal scattering, we base our approach on a simple linear case. The essential relationship between a chain-lattice scatterer and its counterpart image in the intensity space will be examined as depending on a chosen set of parameters such as temperature factor, dynamical constant and crystal size. Since it is not possible to give exact solutions for the required intensity function in terms of a simple analytical expression, the whole subject will be treated numerically.

Only nearest neighbor interaction between atoms will be considered. The calculations are substantially simplified by assuming independence of motion for all elastic waves. The last assumption (harmonic approximation) permits the use of multiple convolutions and of the central limit theorem (CLT). This important theorem simultaneously provides an explanation accounting for the Gaussian form of the Debye-Waller factor.

The proposed Q -function description of the X-ray thermal scattering may be thought of as a numerical illustration of the theory developed by Born & Sarginson (1941), applied to a linear lattice. In its emphasis on the importance of the mean relative atomic displacements it is similar to the treatment recently presented in two papers by Borie (1970) and La Fleur (1970). But while the analytical approach given in these papers clearly neglects the averaged states of excitation of normal lattice vibrations, the dependence of these on temperature in the proposed approach is crucial for any discussion of the X-ray thermal scattering.

The second model to be considered will be a linear crystal deformed by elastic waves belonging to the whole spectrum of the first Brillouin zone. The amplitudes of the normal lattice vibrations are defined,

taking into account the proper energy distribution among different normal modes.

Generalizing the results for one elastic wave, the Q -function for a chain crystal deformed by independent waves may be given in harmonic approximation by the rewritten linear case equation (19):

$$q(\mathbf{u}) = q_a(\mathbf{u}) * \left\{ \sum_{\mathbf{v}}^{U'_v} \omega(\mathbf{v}) \frac{1}{\pi \sqrt{A_{1v}^2 - u^2}} * \dots * \frac{1}{\pi \sqrt{A_{Nv}^2 - u^2}} * [\delta(\mathbf{u} + \mathbf{v}) + \delta(\mathbf{u} - \mathbf{v})] + N\delta(\mathbf{u}) \right\} \quad (35)$$

where:

$$a_{\mathbf{k}} = a_n, \quad \mathbf{k} = \frac{2\pi n}{N}, \quad \mathbf{v} = v, \quad A_{uv} = 2a_{\mathbf{k}} \sin\left(\frac{1}{2}\mathbf{k} \cdot \mathbf{v}\right) = A_{nv}$$

are simply scalars.

and

$$\omega(\mathbf{v}) = N - v, \quad U'_v = N - 1.$$

It should be noted that if some value of A_{nv} equals zero then the respective term in the multiple convolution is just equal to $\delta(u)$ and may be cancelled out since the convolution with the Dirac delta is a unitary operation. Physically it means that an elastic wave does not change the distance between those pairs of atoms which, in the undeformed crystal, are separated by one or more wavelengths.

An appropriate intensity function is obtained by means of the Fourier transform of the formula (35) as follows:

$$I_B(s) = f(s)^2 \left\{ \sum_{v=1}^{N-1} (N-v) \times \prod_{n=1}^{N-1} J_0 \left[4\pi a_n \sin\left(\frac{\pi v n}{N}\right) \right] 2 \cos(2\pi v s) + N \right\}. \quad (36)$$

It can be observed, recalling the results of the preceding section, that each wave forms its own diffraction pattern at the expense of the main maxima, conventionally called the Bragg peaks.

Alternatively, prior to the Fourier transform, we may apply the central limit theorem (CLT) of the theory of probability to the calculation of the multiple convolution of the diffusing functions in equation (35): The convolution of n functions is equal to a Gaussian function whose variance is the sum of the variances of the different functions plus the remainder which diminishes with increasing n in a certain way. The remainder term was discussed by Khinchin (1949).

Thus the multiple convolution of the diffusing functions may be approximated as follows:

$$\frac{1}{\pi \sqrt{A_{1v}^2 - u^2}} * \dots * \frac{1}{\pi \sqrt{A_{Nv}^2 - u^2}} \simeq \frac{1}{\sqrt{2\pi\epsilon_v}} \exp\left(\frac{-u^2}{2\epsilon_v^2}\right). \quad (37)$$

The variance of each convolution term is defined by:

$$\left[\frac{1}{\pi \sqrt{A_{nv}^2 - u^2}} \right]_{\text{VARIANCE}} = \frac{1}{2} A_{nv}^2 = \epsilon_{nv}^2 \quad (38)$$

and the resulting variance ϵ_v^2 is given by;

$$\epsilon_v^2 = \sum_{n=1}^{N-1} \epsilon_{nv}^2 = \frac{1}{2} \sum_{n=1}^{N-1} A_{nv}^2 = \sum_{n=1}^{N-1} 2a_n^2 \sin^2\left(\frac{\pi v n}{N}\right). \quad (39)$$

The amplitudes (a_n) of the normal lattice vibrations are defined, taking into account the proper energy distribution among different modes, by the relation:

$$\frac{1}{2} N m \omega_n^2 a_n^2 = \frac{1}{2} \hbar \omega_n \text{ctgh}\left(\frac{1}{2} \frac{\hbar \omega_n}{kT}\right), \quad (40)$$

where m is the mass of the atom and ω_n the cyclic frequency. The latter may be determined by means of one force constant β (nearest neighbor interaction) through the dispersion relation:

$$\omega_n = \omega_{\max} \sin\left(\frac{\pi n}{N}\right) = 2\sqrt{\frac{\beta}{m}} \sin\left(\frac{\pi n}{N}\right). \quad (41)$$

It will be convenient to introduce a temperature parameter:

$$\gamma = \frac{kT}{\hbar \omega_{\max}} \quad (42)$$

which is equal to unity at the Debye temperature.

The resulting Q -function is represented now by the Gaussian functions, the variances of which depend on the position in the vector space (denoted by the index v).

Introducing further a dynamical constant:

$$\epsilon^2 = \frac{\hbar}{\sqrt{\beta m}} \quad (43)$$

and defining the following function of the temperature parameter γ and the crystal size N (called below the variance distribution function) as:

$$\epsilon_v^2(\gamma, N) = \frac{1}{N} \sum_{n=1}^{N-1} \frac{\sin^2\left(\frac{\pi v n}{N}\right)}{\sin\left(\frac{\pi n}{N}\right)} \text{ctgh}\left[\frac{\sin\left(\frac{\pi n}{N}\right)}{2\gamma}\right] \quad (44)$$

the variances of the Gaussian functions are conveniently denoted by:

$$\epsilon_v^2 = \sum_{n=1}^{N-1} 2a_n^2 \sin^2\left(\frac{\pi v n}{N}\right) = \epsilon^2 \epsilon_v^2(\gamma, N). \quad (45)$$

The Q -function is then given by the equation:

$$q(u) = q_a(u) * \left\{ \sum_{v=1}^{N-1} \frac{N-v}{\sqrt{2\pi\epsilon_v}} \exp\left(\frac{-u^2}{2\epsilon_v^2}\right) * [\delta(u+v) + \delta(u-v)] + N\delta(u) \right\} \quad (46)$$

and the respective intensity function by:

$$I(s) = f(s)^2 \times \left[\sum_{v=1}^{N-1} (N-v) \exp(-2\pi^2 \epsilon_v^2 s^2) 2 \cos(2\pi v s) + N \right] \quad (47)$$

The averaging procedure and the resulting Q -function for the simplest case of equal amplitudes ($a_n = a$) are illustrated in Fig. 3.

The CLT approximation used is quite adequate. The difference between the intensity given by the Bessel form function (36) and the Gaussian form function (47) calculated for only nine waves, and the resulting variance $\epsilon_v = \epsilon = 0.01$ does not exceed 2.5%.

In view of the critical remarks expressed by Born

(1942) concerning the usual method of averaging the exponential expression:

$$\langle e^{-ip} \rangle \simeq \exp(\frac{1}{2} p^2) \quad (\text{James, 1950}) \quad (48)$$

by means of developing it in series, it may be said that the method used here is neither restricted to small values of the exponent p , nor to the Gaussian shape of the diffusing function (Warren, 1969).

The expression obtained for the intensity (47) is a linear version of the exact formula describing the X-ray scattering due to the thermal motion (Maradudin, Montroll & Weiss, 1963).

In the proportionality of ϵ_v^2 to:

$$\epsilon_v^2 \sim 2 \sin^2 \left(\frac{\pi v n}{N} \right) = 1 - \cos \left(\frac{2\pi v n}{N} \right) \quad (49)$$

we find the known Faxén (1918) factor which can be now interpreted as defining the contributions of differ-

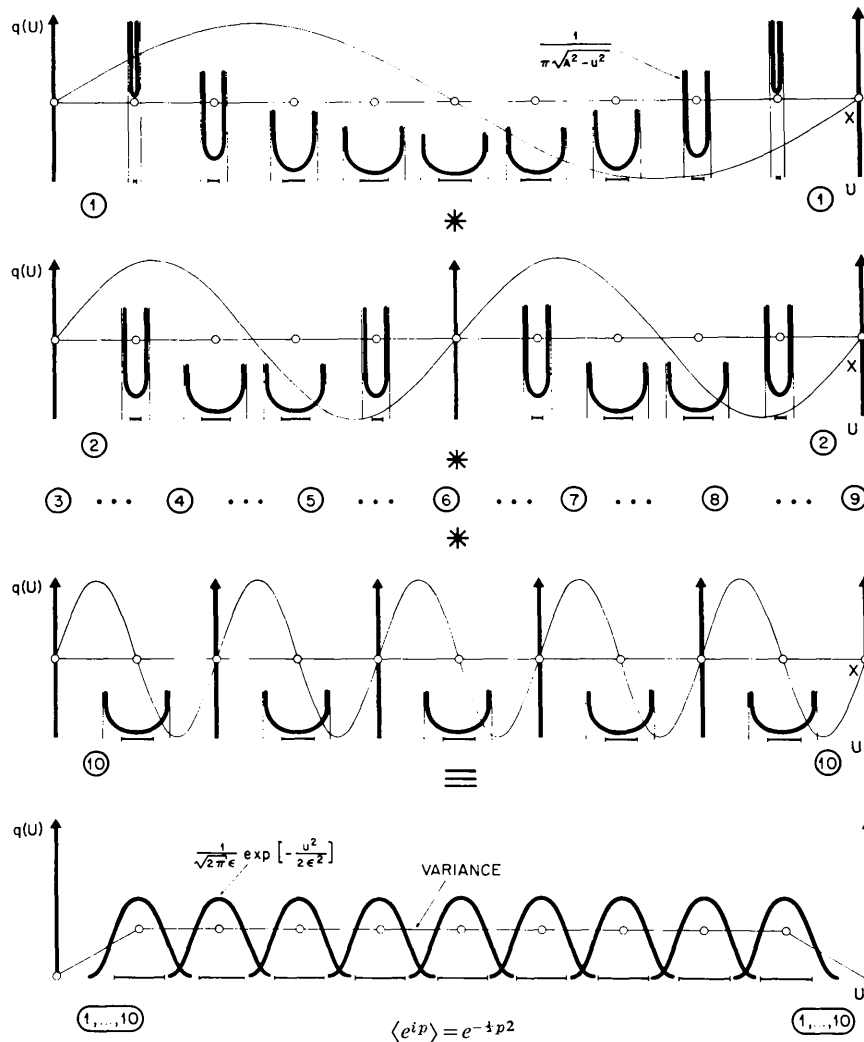


Fig. 3. Q -functions for a linear crystal deformed by a single elastic wave of length $\lambda = N, N/2, \dots, 2$ and the whole spectrum of waves within the first Brillouin zone, obtained by convoluting the diffusing functions along the vertical rows. The amplitudes of all waves are the same and the size factor is not shown on the Figure.

ent phonons, stemming from their wavelike character, to the resulting variance of the Gaussian function in vector space.

It would be most interesting now to examine the dependence of the variance distribution function (44), which determines the shape of the Q -function, upon the temperature parameter γ and the size factor N .

At high temperatures, the energy of each normal vibration may be put equal to kT :

$$\frac{1}{2}Nm\omega_n^2 a_n^2 = kT. \tag{50}$$

The variance of the Gaussian functions for this case is described by:

$$\epsilon_v^2 = \epsilon^2 2\gamma \frac{1}{N} \sum_{n=1}^{N-1} \frac{\sin^2\left(\frac{\pi v n}{N}\right)}{\sin^2\left(\frac{\pi n}{N}\right)} = \epsilon^2 2\gamma \left(v - \frac{v^2}{N}\right) \tag{51}$$

and the variance distribution function has a parabolic shape:

$$\epsilon_v^2(\gamma, N) = 2\gamma \left(v - \frac{v^2}{N}\right). \tag{52}$$

The largest breadth of the Gaussian curves occurs at the distance equal to one half the crystal size from the coordinate origin. It depends on the product of the temperature and size parameters:

$$\epsilon_{N/2}^2(\gamma, N) = \frac{1}{2}\gamma N. \tag{53}$$

The initial slope of the parabola, determined by the variance for $v=1$ according to

$$\epsilon_1^2(\gamma, N) = 2\gamma \tag{54}$$

is not related to the size factor N .

For low temperatures, and in the intermediate region, we carried out numerical calculations (for $N=10^1-10^4$). The results may be described by the half-empirical formula:

$$\left. \begin{aligned} v=1 \\ 1 < v \leq 0.1N \\ v=0.2N \\ v=0.3N \\ v=0.4N \\ v=0.5N \end{aligned} \right\} \epsilon_v^2(\gamma, N) = \epsilon_{N-v}^2(\gamma, N) = \begin{cases} 0.6366 \\ 0.733 \log N + 0.73 \\ \log(v/N) + 0.62 \\ 0.733 \log N + 0.091 \\ 0.733 \log N + 0.193 \\ 0.733 \log N + 0.245 \\ 0.733 \log N + 0.261 \end{cases} \tag{55}$$

The largest breadth of the Gaussian curves ($v=N/2$) occurs at the same position as previously but now it depends not at all on the temperature parameter γ and to a much lesser extent on the size factor N . The initial slope of the calculated curve ($v=1$) is a constant value.

The variance distribution function obtained for low temperature is very close to the constant value function characteristic for the model of the independent thermal motion of atoms discussed in the simple theory.

The important quantities $\epsilon_1^2(\gamma, N)$ and $\epsilon_{N/2}^2(\gamma, N)$ defining the shape of the Q -function for the entire region of the temperature parameter γ are represented in Fig. 4.

The typical intensity patterns were calculated with the help of equation (47) and two of them are shown in Fig. 5(a) and (b). In each case the calculated patterns displayed features which are common to X-ray thermal scattering. It may be observed from these curves that a continuous background is building up at the expense of the main peak. For low temperature curves ($\gamma=0.01$ and $\gamma=0.1$) only slight broadening occurs due to the fact that the variance distribution function of the Gaussian curves in the vector space is not exactly constant. On the contrary, for higher temperatures, the parabolic character of the variance distribution function results in a broadening and a decrease of the Bragg peaks which takes place just above Debye temperature. The latter phenomenon is usually interpreted as a manifestation of the anharmonic forces.

The curves presented in Fig. 5 (a) and (b), as well as many others calculated from the equation (47), were examined in terms of some of their characteristic features. Peak heights, half-peak bandwidth, and area under the peak, for eight orders of reflection ($s=0, \dots, 7$) were calculated for two cases, including and excluding the background intensity. The latter was taken as that part of the intensity function which fell under a straight line connecting the ordinates of the intensity function at its minimum points, as given by the relation: $s = n + \frac{1}{2}$, where $n=0, \dots, 7$.

After summarizing the results calculated for a broad range of values of ϵ (0.005–0.1), γ (0.00001–100.0) and N (10, 10^2 , 10^3 , 10^4), the following conclusions were reached:

1. A transition temperature, at which the change of the diffraction pattern giving rise to the characteristic TDS effects takes place, depends primarily on the variance distribution function $\epsilon_v^2(\gamma, N)$ and occurs approximately at the Debye temperature ($\gamma=1$).

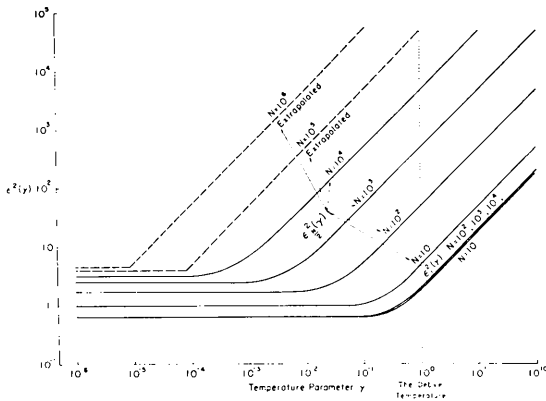


Fig. 4. Dependence of the variance distribution functions characterized by the smallest [$\epsilon_1^2(\gamma, N)$] and largest variance [$\epsilon_{N/2}^2(\gamma, N)$] on the temperature parameter (γ) and the size factor (N).

2. This transition temperature also depends on a numerical value of the force constant, ϵ , equal to an average displacement at the absolute zero of temperature. If, for instance, the transition temperature for $\epsilon=0.05$ coincides with the Debye temperature, then for $\epsilon=0.01$ it is shifted to higher temperatures by an order of magnitude ($\gamma=10.0$).

3. Peak broadening is not a linear function of the order of reflection.

4. The area under the peak, including the background, does not depend on ϵ and γ , and it always amounts to N . The above is consistent with results obtained by La Fleur (1970) and may be easily accounted for considering the form of the basic equation (47).

5. The established relationship between the modified model of the structure and its image in the intensity space leads one to the conclusion that the Debye-Waller factor may be rigorously defined only below the transition temperature. In view of the fact that each peak undergoes a change in its own specific way, the notion of a multiplying factor in connection with the intensity function appears to be rather meaningless.

It would now be of interest to examine an obvious paradox arising from the above conclusions as they relate, as often cited in literature, to the TDS contribution to the Bragg peak. If each elastic wave forms its own image in intensity space at the expense of the main peak, we may ask the question: in what way can this be reconciled with 'strong peaking of the TDS scattering at the Bragg positions'?

We apply the usual formulas defining the TDS scattering in terms of 'ordinary sharp crystalline reflections' and different order temperature diffuse scattering (Warren, 1969) to the recently discussed lattice case. The latter, rewritten in the notation used here, is given by the double series:

$$\begin{aligned}
 I(s) = & f(s)^2 \exp(-2\pi^2 \epsilon_0^2 s^2) \left[N + \sum_{v=1}^{N-1} (N-v) \cos(2\pi v s) \right] \\
 & + f(s)^2 \exp(-2\pi^2 \epsilon_0^2 s^2) \\
 & \times \left[N 2\pi^2 \epsilon_0^2 s^2 + \sum_{v=1}^{N-1} (N-v) 2\pi^2 \epsilon_{v2}^2 s^2 \cos(2\pi v s) \right] \\
 & + f(s)^2 \exp(-2\pi^2 \epsilon_0^2 s^2) \left[N \frac{(2\pi^2 \epsilon_0^2 s^2)^2}{2} \right. \\
 & \left. + \sum_{v=1}^{N-1} (N-v) \frac{(2\pi^2 \epsilon_{v2}^2 s^2)^2}{2} \cos(2\pi v s) \right] + \dots \quad (56)
 \end{aligned}$$

where

$$\epsilon_0^2 = \epsilon^2 \frac{1}{N} \sum_{n=1}^{N-1} \frac{1}{2 \sin\left(\frac{\pi n}{N}\right)} \operatorname{ctgh} \left[\frac{\sin\left(\frac{\pi n}{N}\right)}{2\gamma} \right] \quad (57)$$

enters into the conventional Debye-Waller factor, and

$$\epsilon_{v2}^2 = \epsilon^2 \frac{1}{N} \sum_{n=1}^{N-1} \frac{\cos\left(\frac{2\pi v n}{N}\right)}{2 \sin\left(\frac{\pi n}{N}\right)} \operatorname{ctgh} \left[\frac{\sin\left(\frac{\pi n}{N}\right)}{2\gamma} \right] \quad (58)$$

defines the (negative) variances of the previously discussed Gaussian curves in vector space.

The numerical value of the Debye-Waller factor as determined by (57) corresponds to the maximal variance of the Gaussian curves for $v=N/2$

$$\epsilon_0^2 \approx \epsilon^2 \frac{1}{N} \sum_{n=1}^{N-1} \frac{1 + (-1)^{n-1}}{2 \sin\left(\frac{\pi n}{N}\right)} \operatorname{ctgh} \left[\frac{\sin\left(\frac{\pi n}{N}\right)}{2\gamma} \right] = \epsilon^2_{N/2} \quad (59)$$

Comparing now the term yielding 'ordinary sharp reflections' with the exact expression for the intensity

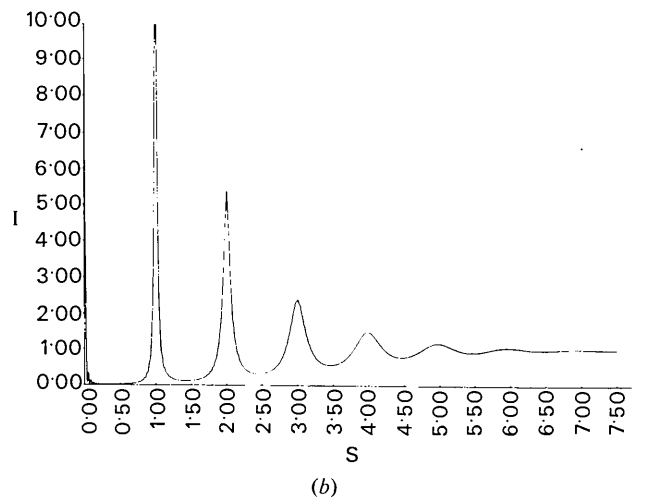
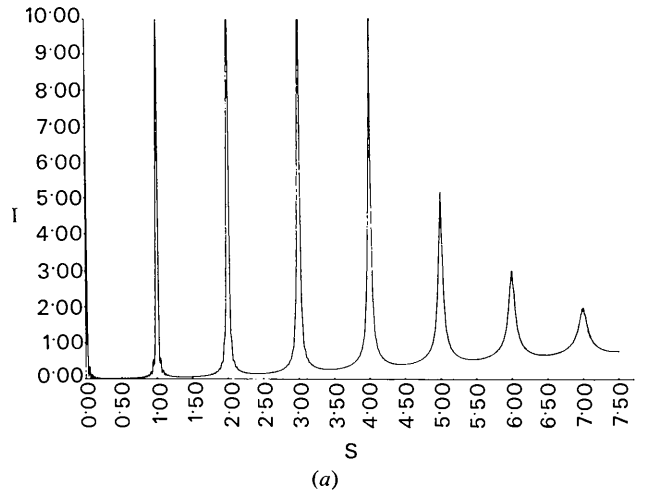


Fig. 5. Dependence of the intensity function $I(s)$ on the temperature parameter (γ) for the case of $N=100$ atoms, and dynamical parameter $\epsilon=0.05$. (a) $\gamma=0.1$; (b) $\gamma=1.0$.

as given by (47) we notice that only the middle terms of the former are properly described by the conventional DW factor where

$$M = \pi^2 \epsilon_0^2 s^2. \quad (60)$$

The greatest difference at higher temperatures exists for the first and last terms of the series (56). The 'averaged' conventional DW factor is much higher for these terms than the appropriate 'partial' DW factors (M_v) given by the relations:

$$M_v = \pi^2 \epsilon_0^2 s^2 \quad v = 1, \dots, N-1. \quad (61)$$

In this way the last terms of the basic expression (47), which contribute most to the main peak, are disproportionately weakened in the first 'crystalline' term of the series (56) and in consequence they must appear in the terms describing the TDS. The above fact seems to explain, at least qualitatively, the effect of so called TDS peaking at the Bragg positions.

The treatment outlined above, although limited to the linear case, clearly points out the inadequacies of the usual notions concerning the TDS scattering, as well as the difficulties in the commonly applied partition of the intensity function into the part defining 'crystalline reflection' and the part defining 'the TDS scattering'.

Discussion

As a conclusion to the remarks of the preceding section it should be emphasized that the shape of the variance distribution function (44) appears decisive in qualifying the intensity patterns arising from thermally deformed chain crystals. In fact its transformation from a flat curve at low temperatures into a parabolic form at high temperatures introduces characteristic changes in the intensity function as described above. They are quite similar to a sudden drop in the Bragg peaks and the TDS effects observed in the real crystals. The former is usually discussed in terms of anharmonic crystal forces. It is interesting to note however, that the parabolic shape of the function (44) was obtained under just the opposite assumption of strictly undisturbed propagation of every normal vibration across the whole chain crystal. If we were to include anharmonicity, this supposition would obviously become less and less justified as the temperature of a crystal is raised and nonlinear forces appear. The rigorous harmonic phase relationship, given by the Faxén factor (49), gradually breaks down. The last effect is probably most significant at the points of thermal fluctuations where atomic displacements from equilibrium are particularly large. For a chosen normal vibration this kind of disturbing phenomenon is equivalent to an apparent partition of a crystal into parts which vibrate more or less independently. The above effect, valid for all normal vibrations, is especially important for longer waves which contribute most to

the middle part of the parabolic function (44). The final result of this might be a flattening of this function which in the region of very high temperatures would more closely resemble the almost constant value function characteristic for very low temperatures, although on a much higher level. The latter conclusion seems quite compatible with the existence of the inversion temperature, as well as with the simple theory of independent atomic motions.

The method of generalization from one to many elastic waves, illustrated above for an example of a linear lattice can be easily extended to the case of any real crystal. One merely requires a knowledge of the crystal dynamics. By solving an appropriate set of secular equations we define numerical values of the \mathbf{a}_k vector. Then making use of the tridimensional CLT it can be shown that the diffusing functions in vector space are radially Gaussian as in the linear case, but circumferentially ellipsoidal. In that respect they resemble the known thermal ellipsoids. In the Q -function description, however, their dimensions, shapes and orientation depend in general on their positions in the vector space and, simultaneously, on the temperature. One might expect that in this case the Fourier transform of the whole space Q -function would be able to reveal the characteristic 'diffused diffraction' patterns which were first observed and accounted for in the works of Laval (1938, 1939).

Finally one might add that the Q -function methods indicate possibilities for the treatment of the thermal motion within the same mathematical formalism for other phenomena which also give rise to diffuse X-ray scattering, e.g. work hardening or alloying. In this generalized situation different physical modes of a structure might happen to have the same Q -function which might be seen as an extension of the Friedel law to the field of defects.

The author wishes to express his many thanks to Professor T. B. Massalski for encouragement, discussions and interest in connection with this work.

During the time this work was prepared the author was the recipient of a grant from the International Research and Exchange Board, New York, for which he expresses his sincere gratitude. Thanks are also due to Carnegie-Mellon University for providing facilities and partial support.

The author is particularly grateful to the reviewers of the original manuscript for their numerous and very helpful comments and discussion. Their help has made possible the present manuscript.

References

- BAGCHI, S. N. (1970). *Advanc. Phys.* **19**, 119.
- BAGCHI, S. N. (1971). *Int. Conf. on Small Angle Scattering*, Graz, Austria.
- BORIE, B. (1970). *Acta Cryst.* **A26**, 533.
- BORN, M. (1942). *Phys. Rev.* **61**, 377.

BORN, M. & SARGINSON, K. (1941). *Proc. Roy. Soc. A* **179**, 69.
 DANIEL, V. & LIPSON, H. (1941). *Proc. Roy. Soc. A* **182**, 378.
 DEHLINGER, U. (1927). *Z. Kristallogr.* **65**, 615.
 FAXÉN, H. (1918). *Z. Phys.* **54**, 615.
 GEL'FAND, I. M. & SHILOV, G. E. (1964). *Generalized Functions*. Vol. 1. New York: Academic Press.
 HOSEMAN, R. & BAGCHI, S. N. (1962). *Direct Analysis of Diffraction by Matter*. Amsterdam: North-Holland.
 VAN HOVE, L. (1954). *Phys. Rev.* **95**, 249.
 JAHN, H. A. (1942). *Proc. Roy. Soc. A* **179**, 320.
 JAMES, R. W. (1950). *Optical Principles of the Diffraction of X-rays*. London: Bell.
 KELLER, W. A. (1970). 28th Pittsburgh Diffraction Conference.
 KHINCHIN, A. I. (1949). *Mathematical Foundations of Statistical Mechanics*. New York: Dover.
 KOCHENDÖRFER, A. (1939). *Z. Kristallogr.* **101**, 149.
 LA FLEUR, P. L. (1970). *Acta Cryst. A* **26**, 674.
 LAVAL, J. (1938). *C. R. Acad. Sci. Paris*, **207**, 169.
 LAVAL, J. (1939). Thesis, Paris.
 MARADUDIN, A. A., MONTROLL, E. W. & WEISS, G. H. (1963). *Solid State Phys.*, Suppl. 3. New York: Academic Press.
 WARREN, B. E. (1969). *X-ray Diffraction*, pp. 36, 162. Massachusetts: Addison-Wesley.

Acta Cryst. (1972). A **28**, 338

Morphology of the Heesch Magnetic Groups and Associated Magnetic Aspects

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(Received 22 October 1971)

The structures of the 122 magnetic point groups (Heesch groups) and their relation to the structures of the 32 associated magnetic aspect groups, underlying point groups and invariant subgroups are studied and enumerated in a physically meaningful scheme. It is shown that in many instances the number of classes of a given group is simply related to the number of classes of an associated group, and these relations are given.

The concept of generalization of the crystallographic point and space groups through inclusion of an operation which reverses the value of a two-valued quantity was originally introduced by Heesch (1930). This concept has turned out to be a very useful one in the study of magnetic crystal structures (Donnay, Corliss, Donnay, Elliott & Hastings, 1958). There result, from the generalization of the 32 ordinary crystallographic point groups through the introduction of a change-of-color (black-white) operation and its identification with time reversal, 122 magnetic groups (Donnay & Donnay, 1959; Donnay, 1967) which have been called the Heesch groups (Riedel & Spence, 1960; Spence & van Dalen, 1968).

The group *A*, obtained from a given Heesch group *H* by replacing all improper rotations by the corresponding proper rotations, and by replacing all time-reversing proper and improper rotations by the corresponding improper rotations was introduced by Donnay & Donnay (1959) and was called the (magnetic) aspect group by Spence & van Dalen (1968). The importance of the magnetic aspect group derives from the fact that it is uniquely determinable by n.m.r. experiments.

The underlying point group *G* is obtained from *H* by replacing all time-reversing elements of *H* by the corresponding non-time-reversing elements. The invariant subgroup *S* is that group which is obtained by

deleting all time-reversing elements from *H*. In the case that *H* is one of the 32 grey or one of the 58 black-white Heesch groups, *S* is an invariant subgroup of *H* of index 2. In the case that *H* is one of the 32 colorless Heesch groups, the invariant subgroup *S* is equal to *H* itself.

The above definitions are summarized in Table 1. Throughout, time reversal will be denoted by single prime and improper rotations by a bar affixed to the appropriate symbols.

Table 1. *Relation between the elements of the Heesch group H, aspect group A, underlying point group G, and invariant subgroup S*

Operation in <i>H</i>	<i>H</i>	<i>A</i>	<i>G</i>	<i>S</i>
<i>n</i> -fold rotation	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>
<i>n</i> -fold time-reversal rotation	<i>n</i> '	<i>n</i> ̄	<i>n</i>	omit
<i>n</i> -fold improper rotation	<i>n</i> ̄	<i>n</i>	<i>n</i> ̄	<i>n</i> ̄
<i>n</i> -fold improper time-reversal rotation	<i>n</i> '̄	<i>n</i> ̄	<i>n</i> ̄	omit

Any group *A*, *G*, or *S* can be shown to be one of the ordinary 32 crystallographic point groups which can be classified as follows:

Type I: This type is comprised of the 11 pure rotation groups 1, 2, 3, 4, 6, 222, 32, 422, 622, 23, and 432 and will be designated by *R*.

Type II: These are the 11 groups obtained as the direct product group of a Type I group with the inver-