<table>
<thead>
<tr>
<th>Title</th>
<th>On the Diffuse Scattering of X-Rays by a Partially Ordered Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Matsubara, Takeo</td>
</tr>
<tr>
<td>Citation</td>
<td>Bulletin of the Institute for Chemical Research, Kyoto University (1963), 41(2-4): 131-158</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1963-10-10</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/75973">http://hdl.handle.net/2433/75973</a></td>
</tr>
<tr>
<td>Type</td>
<td>Departmental Bulletin Paper</td>
</tr>
<tr>
<td>Textversion</td>
<td>publisher</td>
</tr>
</tbody>
</table>

Kyoto University
On the Diffuse Scattering of X-Rays by a Partially Ordered Crystal*

Takeo MATSUBARA**

Received January 22, 1963

A general discussion is given for the diffuse scattering by a crystal containing irregular atomic arrangements of various types. As examples, detailed calculations are given for the intensity of diffuse scattering caused by lattice vibrations, order-disorder arrangements of atoms in binary alloys, and orientational disorder in molecular crystals. An anomalous behaviour of diffuse scattering near the critical temperature of a phase transition is pointed out and discussed quite generally on the basis of crystal statistics.

I. INTRODUCTION

X-rays scattered by a crystal with ideally periodic structure give rise to a normal Laue-Bragg diffraction pattern, whereas if the crystal contains some dynamical or static irregularity, an anomalous Laue pattern, or the so-called diffuse scattering, is observed. Because of its ability to provide powerful tools in an examination of the dynamical behaviour of crystals, diffuse scattering is becoming more important in investigations of various phenomena in crystal physics. It is the aim of this paper to present a general survey of the theory of diffuse scattering.

There are many different origins and causes of irregularities or fluctuations in the regular periodicity of crystals. We may cite the following as being main causes:

1) Thermal vibrations of lattices.
2) Disorder arrangements of atoms in alloy systems.
3) Free or hindered rotations of molecules in crystals.
4) Orientational disorder in complex molecular crystals.
5) Various lattice defects.
6) Various kinds of microdomains.

We feel it is important to clarify common and particular features in diffuse scattering for each cause; and to give a basis for the analysis of observed data.

II. GENERAL REMARKS

We assume that an incident X-ray wave with wave vector \( k_0 \) is scattered by a single crystal. If the direction of the scattered wave is given by a wave vector

---

* This paper is a translation of two papers which appeared in the Japanese Journal, X-Rays, 5, 102 (1949) and 6, 15 (1950). The author is very grateful to Mrs. F. Yonezawa and Mr. C.J. Thompson for their kind help in the translation.

** 松原武生
Takeo MATSUBARA

$k$, the intensity of the scattered X-ray wave is proportional to the square of the absolute value of

\[ F(b) = \int \rho(r) \exp[-2\pi i (b \cdot r)] \, dv, \tag{2.1} \]

where $b = k - k_0$, $\rho(r)$ is the electron density at position $r$, and $V$ is the volume of the crystal. By dividing the crystal up into its $N$ unit cells, the integral can be written as a sum of $N$ integrals; each integral being over a unit cell. In an irregular crystal (the case we are interested in), the $N$ integrals may be different and may even vary with time. To take irregularities into account explicitly, we write (2.1) in the form:

\[ F(b) = \sum_{i=1}^{N} f_i(b) \exp[-2\pi i (b \cdot r_i)], \tag{2.2} \]

where the $i$-th unit cell (volume $v_i$) is at position $r_i$, and $f_i(b)$ is defined by:

\[ f_i(b) = \int_{v_i} \rho(r + r_i) \exp[-2\pi i (b \cdot r)] \, dv. \tag{2.3} \]

If $f_i(b)$ is a function of time, its time variation over the oscillation period of the X-ray must be small, so that the intensity of the scattered wave may be determined from the instantaneous values of $f_i(b)$, $i=0,1,2, \ldots, N-1$ at each time point. The intensity $I$ of the scattered wave at a given time is therefore

\[ I = I_0 \left| F(b) \right|^2, \tag{2.4a} \]

where

\[ \left| F(b) \right|^2 = \sum_{i=0}^{N-1} \sum_{k=0}^{N-1} f_i^*(b) f_i(b) \exp[2\pi i (b_0 \cdot r_{kl})]. \tag{2.4b} \]

$I_0$ is the Thomson factor and $r_{kl} = r_k - r_l$. The observed intensity of the scattered wave is actually a time-average of (2.4a) over some time interval, long compared with the oscillation period of the X-rays. For the purpose of computation we will assume that the time-average can be replaced by a statistical mechanical average in phase space. This can certainly be done in the cases of; lattice vibrations, molecular rotations, and order-disorder arrangements of atoms in alloys. However, these are not the only cases: for example, when a crystal contains some unknown irregularity, we have no a priori information about the distribution of the values of the $f_i(b)$'s which will in general vary from cell to cell; we must guess the distribution from the observed values of $\left| F(b) \right|^2$. In such a case we will assume that there exists a suitable statistical ensemble such that the observed value of $\left| F(b) \right|^2$ (which we denote by $\left| F(b) \right|^2_{\text{obs}}$) is equal to the average over this ensemble. To summarize: either the ensemble is determined from the nature of the irregularity, or the irregularity is characterized by the ensemble itself.

The observed value of $\left| F(b) \right|^2$ can then be written as

\[ \left| F(b) \right|^2_{\text{obs}} = \langle \left| F(b) \right|^2 \rangle, \tag{2.5} \]

and the observed intensity $I_{\text{obs}}$ as
Diffuse Scattering of X-Rays

\[ I_{\text{obs.}} = I_0 \langle |F(b)|^2 \rangle \]
\[ = I_0 \sum_{l=0}^{N-1} \sum_{k=0}^{N-1} \langle f_k^*(b) f_l(b) \rangle \exp[2\pi i (b \cdot r_{kl})]. \quad (2.6) \]

The ensemble average \( \langle f_k^*(b) f_l(b) \rangle \) is generally dependent on \( r_{kl} = r_k - r_l \); however, since the correlation between two cells at \( r_k \) and \( r_l \) is negligible for large \( r_{kl} \), we have

\[ \lim_{|r_{kl}| \to \infty} \langle f_k^*(b) f_l(b) \rangle = \langle f(b) \rangle^2. \quad (2.7) \]

Thus, by writing

\[ \langle f_k^*(b) f_l(b) \rangle = \langle f(b) \rangle^2 + \omega(r_{kl}), \quad (2.8) \]

\( I_{\text{obs.}} \) can be written in the form

\[ I_{\text{obs.}} = J_0 + J_1 + J_2, \quad (2.9) \]

where

\[ J_0 = I_0 \langle |f(b)|^2 \rangle^2 \sum_{k,l} \exp[2\pi i (b \cdot r_{kl})], \quad (2.10a) \]
\[ J_1 = N I_0 \langle |f(b)|^2 \rangle^2 - \langle |f(b)|^2 \rangle^2, \quad (2.10b) \]
\[ J_2 = I_0 \sum_{k \neq l} \omega(r_{kl}) \exp[2\pi i (b \cdot r_{kl})]. \quad (2.10c) \]

\( J_0 \) gives rise to normal Laue spots corresponding to the “average structure”; \( J_1 \) comes from the term \( h = l \) in the sum and gives rise to a diffuse halo; and \( J_2 \) is due to the “correlation term” \( \omega(r_{kl}) \), and gives rise to anomalous Laue spots. The easiest way to see that these conclusions are reasonable is to consider (2.9) as the weight distribution of scattering power in reciprocal space. For if we draw a vector \( -k_0 \) from the origin of the reciprocal lattice and then draw another vector \( k \) from the top of \( -k_0 \), the scattering vector \( b = k - k_0 \) is obtained by connecting the origin to the top of the vector \( k \) (see Fig.1) and the intensity of the scattered wave is determined from the weight function of (2.9) associated with the vector \( b \). Further, if the fundamental translation vectors are \( a_1, a_2 \) and \( a_3 \), and the total number of unit cells with volume \([a_1 a_2 a_3]\) is \( N_1 \cdot N_2 \cdot N_3 \), then \( J_0 \) is proportional to the Laue function

\[ L(b) = \sum_{k,l} \exp[2\pi i (b \cdot r_{kl})] = \prod_{i=1}^{3} \frac{\sin^2[N \pi (b \cdot a_i)]}{\sin^2[\pi (b \cdot a_i)]}, \quad (2.11) \]

which is non-zero only in the immediate neighbourhoods of points determined by the Laue conditions:

\[ A_i = (b \cdot a_i) = h_i = \text{integer}, \quad i = 1, 2, 3. \quad (2.12) \]

By introducing the fundamental translation vectors \( b_1, b_2 \) and \( b_3 \) of the reciprocal lattice through

\[ b_1 = (a_2 \times a_3) / \delta, \quad b_2 = (a_3 \times a_1) / \delta, \]
\[ b_3 = (a_1 \times a_2) / \delta, \quad \delta = [a_1 a_2 a_3], \quad (2.13) \]

the points in reciprocal space satisfying (2.12) are
and $L(b)$ takes the value $N^2$ at these points. The second contribution, $J_1$, is usually a slowly varying function of $b$ with a weight function extending throughout the reciprocal space. In particular, when $f(b)$ is a function of $|b|$ only, $J_1$ has an evenly distributed weight on the cone with axis vector $k_o$ and semi-angle $-\langle k_o \cdot b \rangle$; in this case a ring shape halo will be observed. Finally, since the "correlation term" $\omega(r_{kl})$ is a function of $|r_k - r_l|$ only, $J_1$ and $J_2$ may be combined to give

$$J(b) = J_1 + J_2 = \sum_{kl} \omega(r_{kl}) \exp[2\pi i (b \cdot r_{kl})]$$

$$= N \sum_{l} \omega(r_l) \exp[-2\pi i (b \cdot r_l)].$$  \hfill (2.15)\

$J(b)$, a more slowly varying function of $b$ than $L(b)$, contributes finite values to (2.9) at reciprocal lattice points other than the $B(h_1 h_2 h_3)$. We thus observe abnormal Laue spots; the spots being abnormal in the sense that they violate the Laue conditions (2.12).

![Diagram of the reciprocal lattice space](image)

**Fig. 1.** A section of the reciprocal lattice space. A great circle is the reflection sphere, and the reciprocal lattice points are shown by black points; the weight of the diffuse scattering power concentrates about each of the latter. Small circles represent these regions of this concentration. For the example given in this figure two normal Laue spots and six anomalous Laue spots appear.

We may summarize in the following way: In an ideally periodic crystal, the weight of scattering power in reciprocal space is concentrated at discrete points $B(h_1 h_2 h_3)$. If an irregularity or randomness is present in the lattice, a diffusion of the weight into reciprocal lattice points other than the $B(h_1 h_2 h_3)$ takes place. If, based on some model assumption for the irregularity, we could calculate the degree of this diffusion of weight, and if at the same time we could observe the extent of the diffusion experimentally, we would know the nature of the irregularity. In general however, it is not easy to calculate $\omega(r)$ theoretically and to
obtain a compact expression for \( J(b) \). The remainder of this section will be devoted to a discussion of general features arising out of (2.15): soluble examples will be given in later sections.

The qualitative behaviour of \( J(b) \) in reciprocal space can be seen with the help of the following arguments: In most cases we are interested in \( \omega(r) \) is a slowly varying function of \( b \); in such cases the \( b \)-dependence of \( J(b) \) comes mainly from the factors \( \exp[2\pi i(b \cdot r)] \) which are periodic functions of \( b \), invariant under the transformation \( b \rightarrow b + B(h_1h_2h_3) \). This means that \( J(b) \) is an almost periodic function of \( b \) with different amplitudes varying slowly from point to point. On the other hand, since the Laue function is proportional to \( N^2 \) and the function \( J(b) \) is proportional only to \( N \), it is necessary for the observation of diffuse scattering that the sum \( \sum_i \omega(r_i) \exp[2\pi i(b \cdot r_i)] \) should take large values at some points in reciprocal space. That is, the most important contributions to diffuse scattering come from the immediate neighbourhoods of points at which \( J(b) \) is a maximum. Although the detailed behaviour of \( J(b) \) depends on the nature of the correlation term \( \omega(r) \), it is reasonable to assume that the maxima of \( J(b) \) will occur at the reciprocal lattice points (including superstructure points) of a crystal which is deviated slightly from an ideal periodic arrangement. It is this consideration that enables us to predict the directions for which strong diffuse scattering appears (see Fig.1).

A question that may be raised is whether or not it is possible to derive \( \omega(r) \) directly from the observed value of \( J(b) \). Since \( \omega(r) \) is a function of \( r \) and \( b \), it is in general not possible; however, if \( \omega(r,b) \) is separable, that is

\[
\omega(r,b) = g(b) \cdot \omega'(r),
\]

we have

\[
J(b)/Ng(b) = \sum_i \omega'(r_i) \exp[-2\pi i(b \cdot r_i)] = \Xi(b),
\]

which is a function of \( b \) only. In this case, \( \omega'(r) \), which is just the Fourier transform of \( \Xi(b) \), can be obtained directly from the experimental data.

### III. EFFECT OF LATTICE VIBRATIONS

The randomness caused by thermal vibration of the lattice is the most common origin of diffuse scattering. It is not surprising therefore that much work has been done on this problem.\(^{19}\) In this section we give a brief review of this effect from the standpoint stated in the previous sections.

For simplicity, we take a simple lattice composed of one kind of atom. \( f_i(b) \) in (2.8) may then be written in the form

\[
f_i(b) = f(b) \exp[-2\pi i(b \cdot u_l)],
\]

where \( u_l \) is the displacement of the \( l \)-th atom and \( f(b) \) is the atomic form factor. According to Ott\(^{20}\) the following relations hold in the harmonic approximation:
\[<f_k^*(b)f_l(b)> = |f(b)|^2 \exp \begin{bmatrix} 2\pi i \{(b \cdot u_k) - (b \cdot u_l)\} \end{bmatrix} \]
\[= |f(b)|^2 \exp [-M] \exp \left[8\pi^2 <(b \cdot u_k)(b \cdot u_l)>\right] \quad (3.2)\]

where
\[M = 8\pi^2<(b \cdot u)^2>\]
is the so-called Debye-Waller temperature factor. Since \(<(b \cdot u_k)(b \cdot u_l)>\rightarrow 0\) as \(r_{kl} \rightarrow \infty\), the correlation defined by (2.8) becomes in the present case
\[\omega(r_{kl}) = |f(b)|^2 \exp [-M] \{\exp[8\pi^2<(b \cdot u_k)(b \cdot u_l)>] - 1\}. \quad (3.3)\]

We now introduce \(3N\) normal coordinates and express the \(u_k\) in terms of them thus:
\[u_k = \sum_{j=1}^{3N} \sum_q A_j(q) e_j(q) \exp[2\pi i(q \cdot r_k)] \quad (3.4)\]

where, \(q\) is a wave vector, the \(e_j(q)\) are unit vectors in the directions of polarization, and the \(A_j(q)\) are the amplitudes. The averages indicated \(<\ldots>\) may be taken independently with respect to each normal coordinate: for example
\[P(r_{kl}) = 8\pi^2<(b \cdot u_k)(b \cdot u_l)> \]
\[= 8\pi^2 \sum_j \sum_q <A_j(q)^2>(b \cdot e_j(q))^2 \exp[2\pi i(q \cdot r_{kl})], \]
\[M = 8\pi^2<(b \cdot u_k)^2> = P(0) \]
\[= 8\pi^2 \sum_j \sum_q <A_j(q)^2>(b \cdot e_j(q))^2. \]

If we adopt the approximation; \(\exp[P(r)] \approx 1 + P(r)\), \(J(b)\) is given by
\[J(b) = 8\pi^2 |f(b)|^2 \exp [-M] \sum_j \sum_q <A_j(q)^2>(b \cdot e_j(q))^2 L(b - q) \]
\[- |f(b)|^2 (1 - \exp[-M]), \quad (3.6)\]

where \(L(k)\) is the Laue function defined by (2.11). From (3.6) and the properties of \(L(k)\) we may conclude that the diffuse scattering caused by lattice vibrations has an intensity, for the direction
\[b = q + B(h_1h_2h_3) \quad (3.7)\]
proportional to
\[8\pi^2 |f(b)|^2 \exp [-M] \sum_j [<(b \cdot e_j(q))^2<A_j(q)^2>]. \quad (3.8)\]

If \(\nu_j(q)\) is the frequency for the normal coordinate \((j, q)\), then
\[<A_j(q)^2> = [2\pi^2 m \nu_j(q)]^{-1} E(\nu_j(q)), \quad (3.9)\]

where
\[E(x) \equiv -\frac{x}{\exp(x) - 1} + \frac{1}{2} x. \]

Since \(\nu(q) \sim 0\) for \(q \sim 0\), we see from (3.7), (3.8) and (3.9) that \(J(b)/|f(b)|^2\) takes its maximum value at \(q = 0\); that is, at the reciprocal lattice point \(b = B(h_1h_2h_3)\),
as predicted in section 2.

We conclude this section by calculating the correlation function $P(r)$ under the continuum approximation of Debye: if $v$ is the velocity of sound ($\frac{\mathbf{q}_0}{\mathbf{v}}=v/v$) and if $\mathbf{b}$ and $\mathbf{r}$ are assumed to be parallel to the $z$-direction, then, after replacing the sum over $\mathbf{q}$ by the corresponding integral over $\mathbf{q}$, we have

$$P(r) = \left(\frac{2\pi b^2 V}{\beta_m v^2}\right) \int_0^{r_{\text{max}}} d\nu \int_0^{\nu_{\text{max}}} d\theta E(h\nu/kT) \cos(2\pi \nu \cos \theta/v)$$

$$= \left(\frac{2\pi b^2 VkT}{\beta_m v^2}\right) \frac{1}{r} \int_0^{\nu_{\text{max}}} E(x) \sin \mu x \frac{x}{x_m} dx$$

where

$$\mu = \frac{2\pi kT \nu}{\hbar v}, \quad x_m = \frac{\hbar \nu_{\text{max}}}{kT} = \frac{\theta_0}{T}.$$

The function $P(r)$ is sketched in Fig. 2.

![Fig. 2. A sketch of the curve for the $P(r)$ function at a high temperature. $a$ is the lattice constant. The broken curve is $1/r$.](image)

VI. DIFFUSE SCATTERING CAUSED BY RANDOM ARRANGEMENT IN AN ALLOY SYSTEM

It is a problem of pure statistical mechanics to calculate the intensity of diffuse scattering caused by thermal disturbances in equilibrium. By introducing suitable variables $x_1$ ($l=1,2,\ldots,N$) to describe the state of randomness of the unit cells, the scattering power of the $l$-th unit cell may be assumed to be a function of $x_l$:

$$f_l(b) = f(b;x_l).$$

Further, if we denote the probability of realizing the microscopic state $(x_1,\ldots,x_N)$ by $W(x_1,\ldots,x_N)$, then by Boltzmann's theorem

$$W(x_1,\ldots,x_N) = \exp[-E(x_1,\ldots,x_N)/kT],$$

where $E(x_1,\ldots,x_N)$ is the energy of the system in the state $(x_1,\ldots,x_N)$. The statistical average of $f_l^*(b)$ and $f_l(b)$ may then be written in the form

$$<f_l^*(b) f_l(b)> = \sum W(x_1,\ldots,x_N) f^*(x_l) f(x_l) / \sum W(x_1,\ldots,x_N).$$

(4.1)
where the sums are to be taken over all possible values of the \( x_i \)'s. Expression (4.1) can be written more simply if we introduce the quantity \( P_{kl}(x,x') \), the probability of the \( k \)-th and \( l \)-th cells being in states \( x \) and \( x' \) respectively, through

\[
P_{kl}(x,x') = \sum W(x_1, \ldots , x_N) / \sum W(x_1, \ldots , x_N),
\]

(the primed sum indicates that \( x_k \) and \( x_l \) are to be excluded in the summation): (4.1) becomes

\[
\langle f_k f_l \rangle = \sum_{x,x'} P_{kl}(x,x') f_k(x) f_l(x').
\]

In order to obtain the intensity \( J(b) \) it is necessary to calculate \( P_{kl} \) as a function of \( r_{kl} \). This is the well known "propagation of order" problem. In this section we will study this problem for a simple case.

Following Zernike\(^{19}\), we consider a binary alloy, composed of an equal number of "A" and "B" atoms arranged on a simple cubic lattice, and we assume that in the completely ordered state, the A and B atoms are arranged as in NaCl. With increasing temperature the "order" is gradually destroyed until at and above a certain temperature, where a phase change of the second kind takes place, the atomic arrangement becomes completely random, that is, the order is completely destroyed. We are interested here in the intensity variation of the scattered X-rays resulting from this change of order.

By denoting the atomic form factor of A(B) atoms by \( f_A(f_B) \) and introducing a variable \( x_i \) for each lattice site \( l \) with the property

\[
x_i = \begin{cases} +1 & \text{if site } l \text{ is occupied by an A atom,} \\ -1 & \text{if site } l \text{ is occupied by a B atom.} \end{cases}
\]

We have, noting that \( f_i(b,+1) = f_A \) and \( f_i(b,-1) = f_B \),

\[
\langle f_k f_l \rangle = f_A^2 P_{kl}(1,1) + f_B^2 P_{kl}(1,-1) + f_A f_B [P_{kl}(1,-1) + P_{kl}(-1,1)].
\]

Now from the definition of \( P_{kl}(x,x') \):

\[
\begin{align*}
P_{kl}(1,1) + P_{kl}(1,-1) &= 1/2, \\
P_{kl}(-1,1) + P_{kl}(-1,-1) &= 1/2, \\
P_{kl}(1,1) + P_{kl}(-1,1) &= 1/2, \\
P_{kl}(1,-1) + P_{kl}(-1,-1) &= 1/2,
\end{align*}
\]

so that three of the four quantities \( P_{kl}(\pm 1, \pm 1) \) can be written in terms of the fourth. Choosing \( P_{kl}(1,1) = P_{kl} \) as the independent quantity, \( \langle f_k f_l \rangle \) can be written simply as

\[
\langle f_k f_l \rangle = (f_A - f_B)^2 P_{kl} + f_A f_B.
\]

If we now define sublattice \( \alpha(\beta) \)-sites to be those sites which in the completely ordered state are occupied by A(B) atoms, we see that \( P_{kl} \) is related to the usual order parameter \( S \) defined in the following manner: If \( P_{\alpha\beta}(P'_{\alpha\beta}) \) is the probability of the \( l \)-th site being occupied by an A atom when the \( k \)-th \( \alpha \)-site (\( \beta \)-site) is occupied by an A atom, then \( S \) is defined implicitly through:

\[
P_{kl} = 1/4(1+S)P_{\alpha\beta} + 1/4(1-S)P'_{\alpha\beta}.
\]
Diffuse Scattering of X-Rays

In the limit \(|r_{kt}| \to \infty\), \(P_{kt}\) approaches the limiting value \(1/2(1+S)\) or \(1/2(1-S)\) according as the \(l\)-th site is an \(\alpha\)-site or a \(\beta\)-site and \(P_{kt}\) approaches the limiting value \(1/2(1-S)\) or \(1/2(1+S)\) according as the \(l\)-th site is an \(\alpha\)-site or a \(\beta\)-site. That is,

\[
\lim_{|r_{kt}| \to \infty} P_{kt}^{\alpha} = \frac{1}{2}(1 + (-1)^{\alpha}S),
\]

\[
\lim_{|r_{kt}| \to \infty} P_{kt}^{\beta} = \frac{1}{2}(1 - (-1)^{\alpha}S),
\]

where

\[
\varphi_{kt} = (l_1 - h_1) + (l_2 - h_2) + (l_3 - h_3).
\]

If we put

\[
P_{kt}^{\alpha} = \frac{1}{2} \left[ 1 + (-1)^{\alpha} \{ S + (1-S)t^{\alpha} \} \right],
\]

\[
P_{kt}^{\beta} = \frac{1}{2} \left[ 1 + (-1)^{\alpha} \{ -S + (1+S)t^{\beta} \} \right]
\]

then

\[
\lim_{|r_{kt}| \to \infty} t^{\alpha}_{kt} = 0,
\]

and (4.3) can be rewritten thus:

\[
\langle f_{kt} \rangle = \left( \frac{f_{A} + f_{B}}{2} \right)^2 + \left( \frac{f_{A} - f_{B}}{2} \right)^2 \varphi_{kt} (1 + (-1)^{\alpha}S) + \left( \frac{f_{A} - f_{B}}{2} \right) (1 - S^2) (-1)^{\alpha} 1/2(1-S^2(t^{\alpha}_{kt} + t^{\beta}_{kt})).
\]

Note that the third term on the right hand side of (4.7) corresponds to \(\omega(t)\) of section 2. Substituting (4.7) into the general expression (2.7) we then have

\[
\langle F(b) \rangle = \left( \frac{f_{A} + f_{B}}{2} \right)^2 L(A_1,A_2,A_3) + \left( \frac{f_{A} - f_{B}}{2} \right) S^2 L(A_1+1/2,A_2+1/2,A_3+1/2) + J(b).
\]

In this expression, the first term represents the weight function corresponding to a simple cubic lattice of atoms with average atomic form factor \(1/2(f_{A} + f_{B})\), the second term represents the “superstructure line” due to the partially ordered arrangement of \(A\) and \(B\) atoms with long range order parameter \(S\), and the last, the diffuse scattering term, is given by

\[
J(b) = N \left( \frac{f_{A} - f_{B}}{2} \right)^2 (1 - S^2) \sum_{i=1}^{3} t_{i} t_{j} t_{k} \exp \left[ -2\pi i \sum_{\nu=1}^{3} (A_{\nu} + 1/2) L_{\nu} \right],
\]

with

\[
t_{i} t_{j} t_{k} t_{i} = t^{\alpha}_{kt} + t^{\beta}_{kt}.
\]

Noting that \(t_{i}\) is real and positive, we can easily check that

\[
J(b)/(f_{A} - f_{B})^2 = \text{max. at the point } A_\nu + 1/2 = h_\nu \text{ (integer), } \nu = 1,2,3.
\]

These points correspond to the reciprocal lattice points of the superstructure line, which appears only below the critical point.

To determine the temperature dependence of \(J(b)\), it is necessary to calculate the \(t\)-dependence of \(t_{i} \) \((i=0, \ldots, N-1)\) for each temperature. This may be done
using Zernike's approximation. Before doing this however, the qualitative behaviour of $J(b)$ is given: Above the critical point (where $S=0$), there is "short range order" which influences local arrangements of atoms. As the temperature approaches $T_c$ from above, the short range order becomes more influencial, and in so doing gives rise to a weight of diffuse scattering power concentrated around the points $b = B(h_1+1/2,h_2+1/2,h_3+1/2)$. Finally, at the critical point, $T=T_c$, highly concentrated (intensity proportional to $N^2$) weights are formed at the "superstructure points".

Zernike\(^3\), assuming that the probabilities $P_l$, $l=0,1, \ldots, N-1$, are independent, has set up an infinite difference equation connecting the $P_l$'s. This equation can be written in terms of the quantities $t_l$ and the order parameter $S$ defined previously as

\[
32t*_{l_1l_2l_3} = K_1(\pm S) [t_{l_1}] + (1 \pm S) K_2(\pm S) [t_{l_1}t_{l_2}] + (1 \pm S)^2 K_3(\pm S) [t_{l_1}t_{l_2}t_{l_3}] + (1 \pm S)^3 K_4(\pm S) [t_{l_1}t_{l_2}t_{l_3}t_{l_4}] + (1 \pm S)^4 K_5(\pm S) [t_{l_1}t_{l_2}t_{l_3}t_{l_4}t_{l_5}],
\]

(4.9)

where $t_l$ represents $t$ for one of the 6 nearest neighbours of the point $(l_1l_2l_3)$, and $[ \ ]$ represents a sum over all possible combinations. The $K_n(S)$'s are polynomials in $S$ of degree $5-n$ with temperature dependent coefficients. For example

\[
K_1(S) = K_1(-S) = a_1 + 10a_3S^2 + 5a_5S^4.
\]

The $a$'s, which are defined in Zernike's paper, are not required here: all that is required here is the fact that $K_1(S)$ takes the value

\[
K_1(0)c = \frac{32}{6} \text{ at } T = T_c.
\]

As was proved by Zernike, except at the critical point, the $t_l$ for large $l$ are very small; so if we put (9.9) into the form

\[
32t*_{l_1l_2l_3} = K_1(S) \sum_{k=1}^{6} t_{l_k} + (1 \pm S) N^*_{l_1l_2l_3},
\]

(4.10)

the second term of the right hand side, which is the sum of all non-linear terms in $t$, can be regarded as a very small quantity, vanishing rapidly as $|l| \to \infty$. Now from the definition, $J(b)$ is proportional to the Fourier transform of $t$; that is, proportional to $I_k = \sum_l t_{l_1l_2l_3} \exp [-2\pi i \sum_{l}^{} (A_x+1/2) l_x]$

Multiplying both sides of (4.10) by $\exp [-2\pi i \sum_{l}^{} (A_x+1/2) l_x]$ and summing over $l$ we then have

\[
32I_k = [2K_1(S) \sum_{l=1}^{3} \cos 2\pi (A_x+1/2) l_x] I_k + (1 \pm S) \sum_{l}^{} N^*_{l_1l_2l_3}
\]

* Short range order, as usually defined (for instance say in Bethe's approximation) is related to our definition of $S$ through $\sigma = S^2 + 1/2(1-S^2)(t_{100} + t_{100})$. (140)
Diffuse Scattering of X-Rays

\[ \times \exp \left[ -2\pi i \sum_{\nu} (A_{\nu} + 1/2) l_{\nu} \right] , \]

or

\[ I_s = \frac{(1 \pm S)}{32 - 2K_1(S)} \left( \sum \cos 2\pi (A_{\nu} + 1/2) \right) \left( N_{s00}^* + 2N_{s100}^* \sum \cos 2\pi (A_{\nu} + 1/2) \right) + \ldots \],

and

\[ J(b) = \frac{N/4(1 - S^2)}{32 - 2K_1(S)} \left( \sum \cos 2\pi (A_{\nu} + 1/2) \right) \left( \sum N_\nu \exp \left[ -2\pi i \sum (A_{\nu} + 1/2) l_{\nu} \right] \right) , \]

where \( N_s \) is defined by

\[ N_s = 1/2 \left\{ (1 - S) N^*_s + (1 + S) N^- \right\} . \]

It is now easy to show that \( J(b) \) takes its maximum values at the point \( A_{\nu} + 1/2 = \text{integer} \).

Using Zernike's formula for \( K(S) \) in (4.14), the iso-diffuse surfaces \( J(b) / (f_A - f_B)^2 = \text{constant} \) can be calculated. The results are shown in Fig. 3. It should be noted that the temperature variation of \( J(b) \), which comes mainly from \( S \) and \( K(S) \), is particularly large near the critical point; since, in view of the fact

![Fig. 3. A set of iso-diffuse surface \((J(b) / (f_A - f_B)^2 = \text{const.})\) in a reciprocal unit cell for the diffuse scattering due to an alloy of the \( AB \)-type with simple cubic structure. There is a maximum of the weight at the centre. The centre is the point \( 1/2b_1 + 1/2b_2 + 1/2b_3 \) of the reciprocal lattice and corresponds to the position of the superstructure lines. The numerical values assigned to the curves are the relative values, taking the maximum value as unity. Right half: near the critical point. Left half: at a high temperature above the critical point.](141)
Takeo MATSUBARA

\[ K_1(0) = \frac{32}{6}, \] the denominator of (4.14) vanishes at the points \( A_r + 1/2 = \text{integer} \) when \( T = T_c \).

This anomalous behaviour (critical scattering) has been discussed phenomenologically by Landau. It will be proved quite generally in a later section that critical diffuse scattering must be expected at the critical point in a second order phase transition.

V. GENERAL THEORY

The theory of the binary alloy discussed in section 4, although suitable for an understanding of the mechanism of diffuse scattering, is not sufficiently general to be of much practical importance. In this section, Zernike's method, which was discussed and applied in previous sections, is extended to obtain a general expression for \( J(b) \), the intensity of diffuse scattering.

We first divide the crystal into \( N \) equivalent cells and assume that the division is performed in such a way that the disorder arrangements of the atoms in the crystal are effectively caused by correlations resulting from nearest neighbor cells interacting. We further assume that the state of the crystal can be described by a set of \( N \) variables \( x_i, i = 0, 1, \ldots, N-1 \), with \( x_i \) describing the state of the \( i \)-th cell. Next we construct a periodic space lattice by choosing from each of the \( N \) cells, \( N \) suitable lattice points \( r_l \) \( (l = 0, 1, \ldots, N-1) \). We emphasise that the space lattice provides us with nothing more than a frame of reference; effects resulting from displacement, or thermal motion, of the atoms will be included in the \( x \)-variables.

Using the notation of previous sections, the intensity of diffuse scattering of X-rays is

\[
I = \langle |F(b)|^2 \rangle = \sum_{k=0}^{N-1} \langle f^*(x_k)f(x_l) \rangle \exp[2\pi i (b \cdot r_k)],
\]

where \( f(x_l) \) is the scattering power of X-rays due to the \( l \)-th cell,

\[
\langle f^*(x_k)f(x_l) \rangle = \sum_{x,x'} P_{k l}(x,x') f^*(x)f(x'),
\]

and \( P_{k l}(x,x') \) is the probability of the \( k \)-th and \( l \)-th cells being in states \( x \) and \( x' \) respectively.

\( P_k(x) \), the probability of the \( k \)-th cell being in state \( x \), given by

\[
P_k(x) = \sum_{x'} P_{k l}(x,x') = \sum_{x'} P_{l k}(x',x), \text{ all } l,
\]

as satisfying \( \sum_x P_k(x) = 1, \) all \( k, l, \) may be used to decompose \( P_{k l}(x,x') \) thus:

\[
P_{k l}(x,x') = p_k(x)p_l(x') + \sigma_{k l}(x,x'),
\]

with

\[
\sum_{x} \sigma_{k l}(x,x') = \sum_{x} \sigma_{l k}(x,x') = 0, \text{ all } k, l.
\]
Diffuse Scattering of X-Rays

Substituting of (3.4) into (5.2) then yields:
\[
<f^*(x_k)f(x_l)> = \sum_{\alpha,\beta} \rho_\alpha(x)f^*(x)\rho_\beta(x')f(x') + \sum_{\alpha,\beta} \sigma_{\alpha\beta}(x,x')f^*(x)f(x').
\] (5.5)

If \(\sigma_{\alpha\beta}(x,x')\) is summed over \(k\) keeping \(r_{k\alpha}=r_k-r_l\) constant,
\[
\sum_k \sigma_{\alpha\beta}(x,x') \equiv N\sigma(x,x';r_l),
\] (5.6)
and if \(S(x,x')\) is defined by
\[
S(x,x') = \sum_k \sigma(x,x';r_k) \exp[-2\pi i (\mathbf{b} \cdot r_k)],
\] (5.7)
(5.5) and (5.1) may be combined to give
\[
I = \sum_\alpha \sum_i f(x) \rho_i(x) \exp[-2\pi i (\mathbf{b} \cdot r_i)] + N \sum_\alpha f^*(x)f(x')S(x,x').
\] (5.8)

The first term on the right hand side of (5.8) represents normal scattering (including that due to super-lattice structure), and the second term is equal to the intensity of diffuse scattering \(J(b)\). Note that if \(S(x,x')\) is determined experimentally as a function of \(b\), the corresponding expression for \(\sigma(x,x';r)\) is obtained by inverting (5.7).

Choosing the origin of our frame of reference arbitrarily from among the lattice points \(r\), we denote by \(P_k(x,x')\), the probability of the cell containing the \(k\)-th lattice point (position vector \(r_k\) measured from the origin) and the cell containing the origin being in states \(x\) and \(x'\) respectively. Thus
\[
\lim_{r_k \to \infty} P_k(x,x') = p_k(x),
\]
so that if we write
\[
P_k(x,x') = p_k(x) + R_k(x,x'),
\] (5.9)
\(\sigma(x,x';r_k)\) becomes
\[
\sigma(x,x';r_k) = p_k(x')R_k(x,x').
\] (5.10)
The previous arguments (5.4-6) are strictly valid only in the absence of long range order. If long range order exists, it is necessary to divide the crystal into sublattices, and distinguish \(P_k, p_k, R_k\) according to which sublattice they belong. Moreover, in this case, (5.6) must be averaged over the different sublattices. However, in the following it will be shown that apart from the averaging over sublattices, the two separate cases; presence of long range order, and absence of long range order, can be treated in essentially the same way: for the moment we consider the former.

We first assume there is a functional relationship between the probability \(P_k(x,x')\) associated with the \(k\)-th cell, and the probabilities \(P_i(x,x'), \ldots, P_z(x,x')\) associated with the \(z\) nearest neighbour cells of the \(k\)-th cell. For example, if
the \( P(x,x') \)'s are independent (Zernike) we may write

\[
P_k(x,x') = \sum_{x_1,\ldots,x_z} P_1(x_1,x') P_2(x_2,x') \cdots P_z(x_z,x') W(x_1,\ldots,x_z,x';x',x') \tag{5.11}
\]

where \( W(x_1,\ldots,x_z,x';x',x') \), a function of the temperature and the interaction potential between nearest neighbour cells, is the probability that a cell, and its \( z \) nearest neighbour cells are in states \( x' \) and \( x, \ldots, x_z \) respectively.

If we substitute (5.9) into (5.11) and expand, we obtain the equation determining the distribution of long range order,

\[
p_k(x) = \sum_{x_1,\ldots,x_z} p_1(x_1) \cdots p_z(x_z) W(x_1,\ldots,x_z;x',x') \tag{5.12}
\]

and

\[
R_k(x,x') = \sum_{t=1}^z \sum_{x''} R_{st}(x,x'') A_{st}(x'',x') + N_k(x,x'), \tag{5.13}
\]

where the non-linear term \( N_k(x,x') \) is the sum of terms consisting of products of two or more \( R(x,x') \)'s, and \( A_{st}(x,x') \) defined by

\[
A_{st}(x,x') = \sum_{x_1,\ldots,x_z} p_1(x_1) \cdots p_{t-1}(x_{t-1}) \cdots p_z(x_z) W(x_1,\ldots,x_{t-1},x_{t+1},\ldots,x_z;x',x') \tag{5.14}
\]

may be interpreted as the probability of a cell and \( t \)-th nearest neighbour cell being in states \( x \) and \( x' \) respectively, irrespective of the states of other cells.

We now multiply both sides of (5.13) by \( p_k(x) \), using (5.10) and the notation \( \sigma_k(x,x') \equiv \sigma(x,x';r_k) \), to get

\[
\sigma_k(x,x') = \sum_{t=1}^z \sum_{x''} \sigma_t(x,x'') A_{st}(x'',x') + p_k(x) N_k(x,x').
\]

If we further multiply this equation by \( \exp[-2\pi i(b \cdot r_i)] \) and sum over \( k \), we obtain (c.f.(5.7)) the linear integral equation for \( S(x,x') \)

\[
S(x,x') = \sum_{x''} S(x,x'') B(x'',x') + M(x,x') \tag{5.15}
\]

where the \( B(x,x') \) and \( M(x,x') \) are defined by

\[
B(x,x') = \sum_{t=1}^z \xi_t A_t(x,x'),
\]

\[
\xi_t = \exp[-2\pi i(b \cdot r_t)],
\]

and

\[
M(x,x') = \sum_k p_0(x) N_k(x,x') \exp[-2\pi i(b \cdot r_k)]. \tag{5.16}
\]

For a solution of (5.15) to exist, it is necessary that the series expansion for \( M(x,x') \) converges. This is obviously the case, since \( N_k \) rapidly approaches zero

\* Note that since \( \lim_{R_k \to \infty} R_k(x',x') = 0 \) ((5.9)), this term is small compared with the first term of (5.13) for large \( k \).
when \( k \) becomes large. Indeed, to obtain a reasonable approximation to \( N_k(x,x') \), it is sufficient to know its values at the origin and a few surrounding points.

All that remains to be done now is to solve (5.15) for \( S(x,x') \) and substitute the result in the expression for the intensity of diffuse scattering ((5.8)):

\[
J(b) = N \sum_{x,x'} f(x')f^*(x) S(x,x') . \tag{5.17}
\]

For simplicity we introduce matrix notation; i.e., \( T \) will denote an \( x \)-space matrix with elements \( T(x,x') \). Further, we define the trace of a matrix \( T \) (denoted by \( \text{Tr}(T) \)) by \( \text{Tr}(T) = \sum_x T(x,x) \) and note that the trace is invariant under a similarity transformation, i.e., if \( VV^{-1} = V^{-1}V = I \) (the unit matrix), \( \text{Tr}(VTV^{-1}) = \text{Tr}(T) \). In matrix notation then, (5.15) and (5.17) become

\[
S = SB + M , \tag{5.18}
\]
and

\[
J(b) = N \text{Tr}(FS) , \tag{5.19}
\]
where the matrix \( F \) is defined by

\[
F(x,x') = f(x)f^*(x') . \tag{5.20}
\]

We now observe, from (5.14) and (5.16) that the matrix \( B \) is symmetric, i.e., \( B(x,x') = B(x',x) \); this is sufficient to ensure the existence of a unitary matrix \( U \) such that

\[
UBU^{-1} = \Lambda \tag{5.21}
\]
is diagonal, i.e., \( \Lambda(x,x') = \delta(x-x')\lambda(x) \) (\( \delta(x-x') \) is the Kronecker symbol). Multiplying (5.18) on the left by \( UF \) and on the right by \( U^{-1} \), making use of (5.21), we get:

\[
UFSU^{-1} = UFSU^{-1} + UFMU^{-1} ,
\]
and solving for \( UFSU^{-1} \)

\[
UFSU^{-1} = UF MU^{-1}(I - \Lambda)^{-1} . \tag{5.22}
\]

Substitution into (5.19), remembering the invariance property of the trace, then yields

\[
J(b) = N \text{Tr}(UFSU^{-1}) = N \text{Tr}(UF MU^{-1}(I - \Lambda)^{-1}) , \tag{5.23}
\]
or, in expanded form:

\[
J(b) = N \sum_x \frac{m(x)}{1 - \lambda(x)} , \tag{5.24}
\]
where the \( m(x) \) are the diagonal elements of \( UF MU^{-1} \).

* When long range order exists, the crystal may have to be divided into several sublattices: If \( n \) is the total number of different sublattices, distinguished by indices \( \alpha, \beta, \gamma, \ldots \) and if \( B^\alpha, M^\alpha, \ldots \) are matrices corresponding to the \( \alpha \)-th sublattice, then (5.24) must be replaced by

\[
J(b) = \frac{N}{n} \sum_{\alpha} \left[ \sum_x m^\alpha(x) (1 - \lambda^\alpha(x))^{-1} \right] .
\]
Thus, if it is assumed that the probability distribution \( P(x,x') \) can be expanded as in (5.11), the calculation of the intensity of diffuse scattering reduces to a calculation of the \( m(x) \) (which include the effects of the non-linear terms in the \( N_k \)) and the eigenvalues \( \lambda(x) \) of the matrix \( B \) (which depends on the interaction potential between nearest neighbour cells). One advantage of writing \( J(b) \) in the form (5.24) is that its dependence on the direction of scattering \( b \) can be given in compact form. In the next section we shall give an example of calculation based on (5.24).

VI. EXAMPLE. DIFFUSE SCATTERING DUE TO ORIENTATIONAL DISORDER IN MOLECULAR CRYSTALS

When molecules (or radicals) making up a crystal can take different orientations, the usual result is what is known as orientational disorder. Such disordered configurations are known to give rise to diffuse scattering of X-rays. When only two orientations of each molecule are possible, the problem of calculating the intensity of diffuse scattering essentially reduces to the binary alloy calculation given in section 4. In this section then, we will use the results of the previous section to examine the case in which each molecule can take four possible orientations.

The low temperature phase of \( \text{N}_2 \) and the high temperature phases of \( \text{NaCN} \) and \( \text{KCN} \) may be regarded as real examples of this model. According to Ruhemann\(^9\), the \( \text{N}_2 \) crystal below 35.4°K has a face centred cubic structure (see Fig.4), with regularly arranged molecular axes taking four configurations ([111] and its associated directions). One might expect then that the observed specific heat anomaly\(^9\) in this crystal is brought about by the order-disorder effect in the molecular axes configurations. It has also been shown, by Bijvoet et al\(^7\), that \( \text{NaCN} \) and \( \text{KCN} \) crystals have a \( \text{NaCl} \) type structure at high temperature (above the critical point). In this temperature region, the CN ions are either rotating freely in the crystal or have their molecular axes distributed at random among the eight [111] directions. The empirical values of the specific heat and the size

\[ \text{Fig. 4. Crystal structure of solid N}_2. \]
of the CN⁻ ion suggest that a random distribution among the [111] directions is more probable than a free rotation. Since X-ray methods cannot distinguish the head of a CN⁻ ion from its tail, it is reasonable to consider the molecular axes configurations in these crystals to be distributed at random among four orientations just as in N₂. Keeping these examples in mind, we now consider in detail the '4-orientations' model.

Let us first suppose that each diatomic molecule making up a face centred cubic lattice (Fig.4) interacts with its 12 nearest neighbour molecules, and takes one of the four directions [111], [111], [111], [111]. Next introduce a variable \( x \) with values \( x=1,2,3,4 \), to describe these four directions, in the order stated above. The matrices of the previous section are then \( 4 \times 4 \). In the following, the lattice vectors of the face centred cubic lattice will be taken to be

\[
\mathbf{r}(l_1,l_2,l_3) = \frac{1}{2}(l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3)
\]  

(6.1)

where \( \mathbf{a}_i \), \( \mathbf{a}_j \), \( \mathbf{a}_k \) are the base vectors and the \( l_i \) are integers satisfying \( l_1 + l_2 + l_3 = \) even; and the 12 nearest neighbour lattice points of each point will be numbered as in Table 1 (c.f. Fig.5).

\[
\begin{array}{c|c|c|c}
\mu & 1 & 2 & 3 \\
\hline
l_1,l_2,l_3 & (l_1,l_2+l_3+1), & (l_1+1,l_2,l_3+1), & 9 (l_1+1,l_2+1,l_3), \\
\hline
6 & (l_1-1,l_2,l_3+1), & 10 (l_1-1,l_2+1,l_3), \\
\hline
7 & (l_1-1,l_2,l_3-1), & 11 (l_1-1,l_2-1,l_3), \\
\hline
8 & (l_1+1,l_2,l_3-1), & 12 (l_1+1,l_2-1,l_3). \\
\end{array}
\]

If we now define \( E(\mathbf{x}, x) \) to be the interaction energy between a molecule, in a state \( x \), and its \( \mu \)-th nearest neighbour, in a state \( x_\mu \); the probability \( W(x_1,x_2, \ldots x_{12}; x') \) of a molecule and its 12 nearest neighbours being in state \( x, \) and \( x_1, \ldots x_{12} \) respectively, is given by

(147)
Takeo MATSUBARA

\[ W(x_1, x_2, \cdots x_{12}; x) = Y(x) / \sum_{x=1}^4 Y(x), \]  

(6.2)

where \( Y(x) \) is defined by

\[ Y(x) = \exp \left[ - \sum_{\nu=1}^{12} E_{\nu}(x_{\nu}, x)/kT \right], \]  

(6.3)

\( k \) being Boltzmann's constant, and \( T \) the absolute temperature. The problem then is to obtain a solution of the simultaneous equations

\[ P_t(x, x') = \sum_{x_1, \cdots, x_{12}} P_1(x, x_1) \cdots P_{12}(x, x_{12}) W(x_1, \ldots, x_{12}; x') \]  

(6.4)

subject to the boundary conditions

\[ P_0(x, x') = \delta(x - x'), \]  

(6.5)

\[ P_t(x, x') > 0, \quad \sum_{x'} P_t(x, x') = 1 \]

of the form

\[ P_t(x, x') = P_t(x') + R_t(x, x') \]  

(6.6)

with

\[ \lim_{I \to \infty} R_t(x, x') = 0. \]

From such a solution we can construct the matrices \( A, M, B, \) etc., of the previous section, compute the eigenvalues \( \lambda_i \) of \( B \), the unitary matrix \( U \) which diagonalizes \( B \), etc., and consequently, calculate the intensity of scattered X-rays ((5.8) and (5.24)):

\[ I = I_{\text{Laue}} + J(b) \]  

(6.7)

with

\[ I_{\text{Laue}} = \sum_{t} f_t(x) P_t(x) \exp \left[ -2\pi i (b \cdot r_t) \right]^2, \]  

(6.8)

and

\[ J(b) = N \sum_{t=1}^{4} (U_{FMU}^{-1})_{tt} (1 - \lambda_t)^{-1}. \]  

(6.9)

The first task is to obtain solutions of (6.4) of the form (6.6). By taking the crystal symmetry into account, we can reduce the complexity of (6.4) considerably. To be precise, it can be shown that the number of free parameters in the problem can be reduced to 5, even when the most general interaction, \( E(x, x') \), is used: In Fig.6 the configurations of the molecules which give different energies are shown: the Boltzmann factor \( \exp \left[ -E(x, x')/kT \right] \) for these five configurations being denoted by \( A, B, C, D \) and \( E \). The 12, 4x4 matrices \( W_{\mu}(\mu = 1, 2, \ldots, 12) \) with elements \( \exp[-E_{\mu}(x, x')/kT] \) are, using the symmetry property, given by:
The only property used in writing down expressions (6.10) was the symmetry property; so that 12 matrices having the same symmetry properties as the $W$, must necessarily have the form (6.10): In particular, the matrices $R_{\mu}$, $A_{\mu}$ and $N_{\mu}$ ($\mu=1,2,\ldots,12$) over 12 neighbouring lattice points to the origin, have the forms (6.1). 

Even with five parameters, the problem is still a little too complicated for detailed calculations. To obtain results then, we use the following heuristic argument to reduce the number of free parameters to three.

If the distance $2d$, between two atoms of a molecule, is assumed to be small compared with the distance $l$, between two molecules; and the mutual interaction between molecules is assumed to be caused by a repulsion inversely proportional to the $n$-th power of the interatomic distance, the energies of the five configurations shown in Fig.6 can be calculated by expanding in powers of $\rho=d/l$. Thus:

\[ A = A_0(1 + 4n\rho^2 + \cdots), \]
\[ B = A_0(1 + 4n^2\rho^2 + \cdots), \]
\[ C = A_0(1 + 2n(n-1)\rho^2 + \cdots), \]
\[ D = A_0(1 - 4n\rho^2 + \cdots), \]
\[ E = A_0(1 - 4n^2\rho^2 + \cdots), \]

and to second order in $\rho$

\[ A = B, \quad \text{and} \quad D = E. \]  

(6.11)
In this approximation, we observe, that of the $4^{12}$ values of $W(x_1,\ldots,x_{12}; x')$, only 35 are distinct, and any of these 35 quantities can be written as a function of the parameter $\theta=C^2/AD$. It is then possible, dividing the crystal into four sublattices of simple cubic type, and using the symmetry property, to choose the $p_i(x) = (p_i(1), p_i(2), p_i(3), p_i(4))$ as in Table 2. In so doing, we obtain a solution of (6.4) which exhibits explicitly the long range order as shown in Fig.4.

**Table 2.**

<table>
<thead>
<tr>
<th>$p_i(x)$</th>
<th>when $l_i,l_j,l_k$ are all even</th>
<th>$l_i,l_j=\text{odd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(1/4(1+S_1),\ldots,1/4(1+S_6))$</td>
<td>$(1/4(1+S_1),\ldots,1/4(1+S_6))$</td>
<td>$(1/4(1+S_1),\ldots,1/4(1+S_6))$</td>
</tr>
</tbody>
</table>

By replacing the $P_i(x, x')$ in (6.4) by the $p_i(x')$ of Table 2, and using the sublattice division of Table 2, i.e.,

$$l-th \text{ lattice point } \mu=1,2,3,4 \quad 5,6,7,8 \quad 9,10,11,12$$

$$\alpha \quad \beta \quad \gamma \quad \delta$$

$$\beta \quad \alpha \quad \delta \quad \gamma$$

$$\gamma \quad \delta \quad \alpha \quad \beta$$

$$\delta \quad \gamma \quad \beta \quad \alpha$$

(6.12)

equations (6.4) can be reduced to 4 simultaneous equations of the form:

\begin{align*}
1/4(1+S_1) &= F(S_1,S_2,S_3,S_4;\theta), \\
1/4(1+S_2) &= F(S_2,S_3,S_4,S_1;\theta), \\
1/4(1+S_3) &= F(S_3,S_4,S_1,S_2;\theta), \\
1/4(1+S_4) &= F(S_4,S_1,S_2,S_3;\theta),
\end{align*}

(6.13a) (6.13b) (6.13c) (6.13d)

where $F$, considered as a polynomial in the $S_k$, is of degree 12:

$$F(S_1,S_2,S_3,S_4;\theta)=1/4 \left[ 1+ \sum_{n=1}^{12} \sum_{k=1}^{4} a_k^{(n)}(\theta) S_k^{n} \right].$$

(6.14)

Note that equations (6.12b, c, d) are obtained from (6.12a) by operating on the $S$ indices with the permutations

$$\begin{align*}
(12)(34) ; 
(13)(24) ; 
(14)(23) ,
\end{align*}$$

(6.15)

respectively.

The trivial solution of (6.13), namely, $S_1=S_2=S_3=S_4=0$, represents the state of complete disorder. A non-trivial solution which is valid for sufficiently large $\theta$ (that is, for sufficiently low temperatures) we assert, is:
Diffuse Scattering of X-Rays

\[ S_1 = 3S(\theta), \quad S_2 = S_3 = S_4 = -S(\theta). \quad (6.16) \]

(Three other, essentially identical solutions, may of course be obtained from (6.16) by operating on the S indices with permutations (6.15)). Since a solution of the form (6.16) is only valid in the low temperature region, one would expect \( S(\theta) \), in someway describes long range order. Indeed, if we substitute (6.16) into (6.13), we can obtain the explicit dependence of \( S(\theta) \). The result is shown in Fig.7.

![Fig. 7. Temperature dependence of the order parameter S.](image)

When \( \theta^{-1} = 0 \), i.e., \( T = 0 \), the lattice is perfectly ordered (\( S = 1 \): c.f. Table 2 and Fig.4). As the temperature increases, the ‘order parameter’ \( S(\theta) \) decreases, until at some temperature \( T_c \), which may be taken to be the critical temperature, \( S = 0 \). A peculiar property of \( S(\theta) \) in our approximation is its doubly valuedness for the temperature range around \( T_c \). Since we are mainly interested in discussing solutions of (6.4) exhibiting phase transitions, we will not attempt any detailed discussion on this point; suffice it to say that it is essentially due to the type of interaction assumed, and the face centred cubic structure of the lattice.

If we neglect terms in (6.13) of degree higher than the first in \( S \), we get

\[
\begin{align*}
S_1 &= a_1(\theta)S_1 + a_2(\theta)S_2 + a_3(\theta)S_3 + a_4(\theta)S_4, \\
S_2 &= a_2(\theta)S_1 + a_1(\theta)S_2 + a_4(\theta)S_3 + a_3(\theta)S_4, \\
S_3 &= a_3(\theta)S_1 + a_4(\theta)S_2 + a_1(\theta)S_3 + a_2(\theta)S_4, \\
S_4 &= a_4(\theta)S_1 + a_3(\theta)S_2 + a_2(\theta)S_3 + a_1(\theta)S_4.
\end{align*}
\]

For these equations to have no solutions other than the trivial one \( (S_1 = S_2 = S_3 = S_4 = 0) \), the \( a \)-coefficients must satisfy

\[
\begin{vmatrix}
a_1 & a_2 & a_3 & a_4 \\
a_2 & a_1 & a_4 & a_3 \\
a_3 & a_4 & a_1 & a_2 \\
a_4 & a_3 & a_2 & a_1
\end{vmatrix} = 0.
\quad (6.17)
\]

The solutions of (6.17) may be used to determine the critical point.

Now in (6.14), \( a_\nu \) is defined to be the coefficient of \( S_\nu \) in the equation obtained by replacing the \( P_\nu(x, x') \)'s in (6.4) by the \( p_\nu(x) \)'s of Table 2. For example,

\[
a_1 = \sum_{\nu=1}^{4} A_\nu(21) + \sum_{\nu=5}^{8} A_\nu(31) + \sum_{\nu=9}^{12} A_\nu(41),
\]

\[(151)\]
where the matrices \( A_p(x, x') \), introduced in the previous section and defined by
\[
A_p(x, x') = (1/4)^{11} \sum_{x_1, x_2, \ldots, x_{12}} \bar{W}(x_1, x_2, \ldots, x_{12}; x, x')
\]
has the same structure as the \( W \) matrices, (6.10). Moreover, from the assumption
\( A = B, D = E, \) and the normalization condition
\[
\sum_p A_p(x, x') = 1,
\]
\( A_p \) may be written in the form* (c.f. (6.10))
\[
A_p = \begin{bmatrix}
-1 & 1 & 1 & -1 \\
1 & -1 & -1 & 1 \\
1 & -1 & -1 & 1 \\
-1 & 1 & 1 & -1 \\
-1 & 1 & 1 & 1 \\
1 & 1 & -1 & -1 \\
1 & 1 & -1 & -1 \\
-1 & 1 & -1 & 1 \\
-1 & 1 & 1 & -1 \\
1 & 1 & 1 & -1
\end{bmatrix},
\]
\( p = 1, 2, 3, 4 \)
\[
A_q = \begin{bmatrix}
-1 & 1 & 1 & -1 \\
1 & -1 & -1 & 1 \\
1 & -1 & -1 & 1 \\
-1 & 1 & 1 & -1 \\
-1 & 1 & 1 & 1 \\
1 & 1 & -1 & -1 \\
1 & 1 & -1 & -1 \\
-1 & 1 & -1 & 1 \\
-1 & 1 & 1 & -1 \\
1 & 1 & 1 & -1
\end{bmatrix},
\]
\( q = 5, 6, 7, 8 \)
\[
A_r = \begin{bmatrix}
-1 & 1 & 1 & -1 \\
1 & -1 & -1 & 1 \\
1 & -1 & -1 & 1 \\
-1 & 1 & 1 & -1 \\
-1 & 1 & 1 & 1 \\
1 & 1 & -1 & -1 \\
1 & 1 & -1 & -1 \\
-1 & 1 & -1 & 1 \\
-1 & 1 & 1 & -1 \\
1 & 1 & 1 & -1
\end{bmatrix},
\]
\( r = 9, 10, 11, 12 \)

where \([1/4]\) denotes the \( 4 \times 4 \) matrix with all elements equal to \( 1/4 \). Using (6.19)
the \( a_k \) become:
\[
a_1 = 4 \{ A_p(11) + A_q(41) + A_r(31) \} = 3 \{ 1 + K(\theta) \},
\]
\[
a_2 = 4 \{ A_p(11) + A_q(41) + A_r(31) \} = 3 \{ 1 - K(\theta) \},
\]
\[
a_3 = 4 \{ A_p(31) + A_q(11) + A_r(21) \} = 3 \{ -K(\theta) \},
\]
\[
a_4 = 4 \{ A_p(31) + A_q(11) + A_r(21) \} = 3 \{ -K(\theta) \},
\]

and on substitution in (6.17) we get:
\[
11 \{ 4K(\theta) - 1 \} = 0.
\]
The critical point is defined by \( K(\theta_c) = 1/4 \), and the disordered state \( (S=0) \)
characterized by
\[
K(\theta) < 1/4, \quad \theta < \theta_c.
\]

It remains now to calculate \( J(b) \). Since for temperature \( T < T_c \) expression for
the \( R_l(x, x') \) (5.19) become too complicated to handle, we will restrict our
calculation to the high temperature phase \( (T > T_c) \).

When \( S = 0 \), substitution of \( P_l(x, x') = 1/4 + R_l(x, x') \) into (6.4) yield

\[ K(\theta) = (1/2)^3 \times \left[ \frac{2\theta^4}{1 + 3\theta^4} + \frac{1 + 14\theta^4 + 9\theta^4}{1 + 2\theta^4 + \theta^4} + \frac{3 + 18\theta^2 + 15\theta^4}{1 + 2\theta^4 + \theta^4} + \frac{8 + 24\theta^2 + 6\theta^4}{1 + 2\theta^4 + \theta^4} + \frac{3 + 10\theta^2 + 11\theta^4}{1 + 2\theta^4 + \theta^4} \\
+ \frac{36 + 60\theta^2 + 8\theta^4 + 108\theta^2}{1 + 2\theta^4 + \theta^4} + \frac{16 + 12\theta^2}{1 + 2\theta^4 + \theta^4} + \frac{32 + 24\theta^2 + 40\theta^4}{1 + 2\theta^4 + \theta^4} + \frac{36 + 72\theta^2}{1 + 2\theta^4 + \theta^4} + \frac{96 + 288\theta^2 + 192\theta^4}{1 + 2\theta^4 + \theta^4} \\
+ \frac{80 + 48\theta^2}{1 + 2\theta^4} + \frac{180 + 252\theta^2}{2 + 2\theta^4} + \frac{108}{4} \right] - 1. \]
Diffuse Scattering of X-Rays

\[ R_t = \sum_{\mu=1}^{12} R_\mu A_\mu + N_t, \quad (6.22a) \]

or, making use of \[ \sum_{x'} R_t(x,x') = 0 \]

\[ R_t = \sum_{\mu=1}^{12} R_\mu A'_\mu + N_t, \quad (6.22b) \]

where \( A'_\mu \) is defined by \( A'_\mu = A_\mu - [1/4] \), and \( A_\mu \) by (6.18). Equation (2.22b) can be solved by the method of successive approximations: We will however, content ourselves with the lowest order approximation for \( R \), viz., in (6.22b) we neglect all the non-linear terms \( N_t \) with the exception of the \( l=0 \) term. In this approximation, using the boundary conditions (6.5), the solution of (6.22b) is

\[ R_0 = I - [1/4] = \frac{1}{4} \begin{pmatrix} 3 & -1 & -1 & -1 \\ -1 & 3 & -1 & -1 \\ -1 & -1 & 3 & -1 \\ -1 & -1 & -1 & 3 \end{pmatrix}. \quad (6.23) \]

To calculate the intensity of diffuse scattering \( J(b) \) for \( S=0 \), we require the following preliminaries: First, the matrix (5.16)

\[ B = \sum_{\rho=1}^{12} \xi_\rho A_\rho', \quad \xi_\rho = \exp[-2\pi i(b \cdot r_\rho)] \]

from (6.19) and Table 1 is

\[ B = \begin{pmatrix} a & b & c & d \\ b & a & d & b \\ c & d & a & b \\ d & c & b & a \end{pmatrix}, \quad (6.24) \]

where

\[ a = -K(0) \{ \cos \pi h_2 \cos \pi h_3 + \cos \pi h_2 \cos \pi h_4 + \cos \pi h_3 \cos \pi h_4 \}, \]
\[ b = K(0) \{ \cos \pi h_2 \cos \pi h_3 + \cos \pi h_3 \cos \pi h_4 + \cos \pi h_4 \cos \pi h_2 \}, \]
\[ c = K(0) \{ \cos \pi h_2 \cos \pi h_3 + \cos \pi h_2 \cos \pi h_4 - \cos \pi h_3 \cos \pi h_4 \}, \]
\[ d = K(0) \{ -\cos \pi h_2 \cos \pi h_3 + \cos \pi h_2 \cos \pi h_4 + \cos \pi h_2 \cos \pi h_4 \}, \]

and \( h_1, h_2, h_3 \) are defined by

\[ (b \cdot a_i) = h_i, \quad i = 1, 2, 3. \]

The eigenvalues \( \lambda_i \) (i=1,2,3,4) of \( B \), and the unitary matrix \( U \) which diagonalizes \( B \), are easily shown to be

\[ \lambda_1 = 0, \]
\[ \lambda_2 = -4K(0)\cos \pi h_2 \cos \pi h_3, \]
\[ \lambda_3 = -4K(0)\cos \pi h_2 \cos \pi h_4, \]
\[ \lambda_4 = -4K(0)\cos \pi h_3 \cos \pi h_2, \quad (6.25) \]

and

(153)
It is next necessary to evaluate the matrix (5.16)

\[
M = \frac{1}{4} \sum_i N_i \exp[-2\pi i (\mathbf{b} \cdot \mathbf{r}_i)].
\]

If we neglect all the \( N_i \) except \( N_0 \) and \( N_{12} \), with \( \mu = 1, 2, \ldots, 12 \) representing the 12 lattice points surrounding the origin, we get

\[
M = \frac{1}{4} \{N_0 + \sum_{\varphi = 1}^{12} \xi_\varphi N_{\varphi}\}. \tag{6.27}
\]

Now, from (6.22a) and the symmetry property (Fig. 6), it can be shown that \( N_0 \), and the \( N_{12} \), have the same form as \( R_0 \), and the \( A_\varphi' \) respectively. That is, there exist scalar functions \( m_0(\theta) \) and \( m_1(\theta) \), such that

\[
N_0 = 4m_0(\theta)R_0, \quad N_{12} = m_1(\theta)A_{12}'. \tag{6.28}
\]

Substitution into (6.27) then yields

\[
M = \frac{1}{4} \{4m_0(\theta)R_0 + m_1(\theta)B\}. \tag{6.29}
\]

By comparing (6.23) and (6.24) we observe that \( R_0 \) is a special case of \( B \) (i.e., \( R_0 \) is obtained from (6.24) by the transformation \( a \rightarrow 3/4; b, c, d \rightarrow -1/4 \)), so that the unitary matrix (6.26) diagonalizes \( M \) as well as \( B \). Thus, if we denote the diagonal elements of \( UFU^{-1} \) by \( f_i \) \( (i = 1, 2, 3, 4) \) we have

\[
(UFU^{-1})_{ii} = f_i \quad (i = 1, 2, 3, 4)
\]

Having completed the necessary preliminaries, we are now in a position to calculate the scattering intensity (6.7)

\[
I = I_{\text{Laue}} + J(b).
\]

First, the Laue scattering intensity, \( I_{\text{Laue}} \), given by (6.8) may be put in matrix form, by introducing a matrix \( S_0 \) through

\[
S_0(x, x') = S_0^*(x)S_0(x'),
\]

with

\[
S_0(x) = \sum_k p_k(x) \exp[-2\pi i (\mathbf{b} \cdot \mathbf{r}_k)],
\]

thus:

\[
I_{\text{Laue}} = \left| \sum_k f(x)S_0(x) \right|^2 = \sum_{x, x'} f(x) f^*(x') S_0(x', x)
\]

(154)
From (6.1) and Table 2, it is possible to show that $S_0$ has the form

$$S_0 = Q P L(h_1, h_2, h_3),$$

where $L(h_1, h_2, h_3)$, the Laue function for the simple cubic lattice with base vectors $a_1, a_2$ and $a_3$, is proportional to $N^2$ when $(b \cdot a_i) = h_i$, $i = 1, 2, 3$; and zero otherwise, and $Q$ and $P$ are matrices of the form (6.24) with

$$a = 1, \quad b = \cos \pi h_2 \cos \pi h_3,$$
$$c = \cos \pi h_3 \cos \pi h_1, \quad d = \cos \pi h_1 \cos \pi h_2,$$

and

$$a = S_1^2 + S_2^2 + S_3^2, \quad b = 2(S_1 S_2 + S_3 S_4),$$
$$c = 2(S_1 S_3 + S_2 S_4), \quad d = 2(S_1 S_4 + S_2 S_3),$$

respectively.

Since $Q$ and $P$ have the same form as $B$ ((6.24)), they can be diagonalized by $U$ ((6.26)). Using this fact, the eigenvalues of $Q(Q)$, and $P(P)$, are easily shown to be

$$Q_1 = 1 + \cos \pi h_2 \cos \pi h_3 + \cos \pi h_3 \cos \pi h_1 + \cos \pi h_1 \cos \pi h_2,$$
$$Q_2 = 1 + \cos \pi h_2 \cos \pi h_3 - \cos \pi h_3 \cos \pi h_1 - \cos \pi h_1 \cos \pi h_2,$$
$$Q_3 = 1 - \cos \pi h_2 \cos \pi h_3 + \cos \pi h_3 \cos \pi h_1 + \cos \pi h_1 \cos \pi h_2,$$
$$Q_4 = 1 - \cos \pi h_2 \cos \pi h_3 - \cos \pi h_3 \cos \pi h_1 + \cos \pi h_1 \cos \pi h_2.$$ (6.33)

P1 = 1, P2 = P3 = P4 = $S^2$.

Combining them and remembering the invariance property of the trace, we get

$$I_{\text{Laue}} = \text{Tr}_F(U F U^{-1} U Q U^{-1} U P U^{-1}) L(h_1, h_2, h_3)$$
$$= [f_1 Q_1 + S^2 (f_2 Q_2 + f_3 Q_3 + f_4 Q_4)] L(h_1, h_2, h_3).$$ (6.34)

Of the two terms in (6.34), proportional to $f_1 Q_1$ and $S^2$, the former, with its weight concentrated at lattice points for which $h_1$, $h_2$ and $h_3$ are either all even or all odd integers, gives us the normal Laue pattern for the face centred cubic lattice. The latter, with its weight proportional to $S^2$ is a result of the superlattice structure caused by the presence of long range order. (Note that this term vanishes above the critical point.)

To conclude, the expression for $J(b)$ above the critical point, obtained from (6.9), (6.25), and (6.30) is:

$$J(b) = N \left\{ f_1 (m_0 - m_1 K \cos \pi h_2 \cos \pi h_3) \right\}$$
$$+ \left[ \frac{f_2 (m_0 - m_1 K \cos \pi h_2 \cos \pi h_3)}{1 + 4K(\theta) \cos \pi h_2 \cos \pi h_1} \right.$$
$$+ \frac{f_3 (m_0 - m_1 K \cos \pi h_2 \cos \pi h_3)}{1 + 4K(\theta) \cos \pi h_2 \cos \pi h_1} \right.$$
$$+ \frac{f_4 (m_0 - m_1 K \cos \pi h_2 \cos \pi h_3)}{1 + 4K(\theta) \cos \pi h_2 \cos \pi h_1} \right\}. \quad (6.35)$$

This expression has extrema for integral values of the $h_k$; the extrema being minima when the $h_k$ are either all even or all odd, and maxima otherwise. This means that the directions for which the diffuse scattering is strongest, are
Takeo MATSUBARA

concentrated about those points of reciprocal space which have intensity proportional to $S^2$ below the critical point ((6.34)). We note that, since $K(\theta_o)=1/4$, at least two of the three denominators in (6.35) approach zero as the temperature approaches $T_0$ from above. That is, for temperatures just above the critical temperature, the maxima of $J(b)$ are extremely sharp.

VII. GENERAL RELATIONSHIP BETWEEN PHASE TRANSITIONS AND DIFFUSE SCATTERING

Since diffuse scattering reflects directly the correlations of various disorder arrangements in the crystal, its observation provides us with useful information about the transition mechanism.

A particularly important case is the phase transition of the second kind that produces differences in the X-ray diffraction pattern in the high and low temperature phase, without changing the crystal structure. In such a case, one would expect the diffraction pattern in one phase to shift continuously into the other as the temperature passes through the critical temperature.

In reciprocal lattice space, the weight value of scattering power due to the super-lattice structure, dispersed in the high temperature phase, is observed to become concentrated around certain points below the transition temperature. That is, one should expect 'abnormal' changes in the distribution of weight in the neighbourhood of the transition point. This was illustrated in the examples of sections 4 and 6. In this section we will exhibit this abnormality for the general case.

Considering the crystal as an assembly of equally spaced, parallel plane nets, numbered $0,1,\ldots,N-1$, we introduce a set of variables $\{x_n; n=0,1,\ldots,N-1\}$ to describe the state of the crystal, each $x_n$ describing the state of a net. Then, if $d$ is the distance between neighbouring nets, $\mathbf{p}$ the unit vector normal to the plane nets, and $f(x_n)$ the "layer structure factor" of the net in state $x_n$, the average value of

$$|F(\varphi)|^2 = \sum_n f(x_n) \exp[2\pi i \varphi n]$$

is the weight value of X-ray scattering power at the reciprocal lattice point with position vector $(\varphi/d)\mathbf{p}$.

If we now choose the "layer unit" so that only nearest neighbour nets interact, the probability of nets $0,1,2,\ldots,N-1$ being in states $x_0, x_1, x_2,\ldots,x_{N-1}$ respectively, is given by

$$W(x_0, x_1, \ldots, x_{N-1}) = \exp \left[ -\frac{1}{kT} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N-2} E(x_i, x_{i+1}) \right]$$

with $E(x, x')$ the interaction energy between neighbouring nets in states $x$ and $x'$. The average of (7.1) over this distribution is then

$$\langle |F(\varphi)|^2 \rangle = \sum_{\varphi} \sum_{n,m} f^*(x_m) f(x_n) \exp[2\pi i (n-m)\varphi] W(x_0, x_1, \ldots, x_{N-1})$$

$$= \sum_{\omega} W,$$

(7.2)
Diffuse Scattering of X-Rays

where \( \sum_{x_0} \) denotes the sum over all configurations of \( x_0, x_1, \ldots, x_{N-1} \).

If we now define the matrix \( M \) by
\[
M(x, x') = \exp[-E(x, x')/kT],
\]
and expand \( W(x_0, x_1, \ldots, x_{N-1}) \) in terms of the orthonormal set of eigenfunctions \( \phi_1(x), \ldots, \phi_N(x) \) of \( M \), (7.1) becomes
\[
\begin{aligned}
\langle |F(\rho)|^2 \rangle &= \sum_{s} \lambda_s^N |g_{ss}|^2 \sum_{s} \lambda_s^N \phi_s(\rho) \\
&= \frac{1}{\sum_{s} \lambda_s^N} L(\rho) + \frac{1}{\sum_{s} \lambda_s^N} \phi_s(\rho),
\end{aligned}
\]
(7.3)

where \( \lambda_1 \geq \lambda_2 \geq \lambda_3 \geq \ldots \) are the eigenvalues of \( M \) corresponding to the eigenfunctions \( \phi_1(x), \phi_2(x), \phi_3(x), \ldots \).

\[
g_{st} = \sum_{x} \phi_s(x) f(x) \phi_t(x) = g_{ts},
\]
\[
L(\rho) = |\sum_{n} \exp[2\pi i n \rho]|^2,
\]
\[
\phi_s(\rho) = 2 \sum_{t \neq s} |g_{ts}|^2 \Re \left[ \sum_{n \geq m} \left( \frac{\lambda_t}{\lambda_s} \right)^{n-m} \exp[2\pi i (n-m) \rho] \right],
\]
(7.4)

\( \Re \) denotes 'real part of', and sums over \( t \) are to be extended over all eigenvalues \( \lambda \). The first term of (7.3) gives the normal Laue scattering, the second, diffuse scattering.

When \( N \) becomes large, the maximum eigenvalue dominates, and the second term in (7.3) becomes
\[
\sum_{s} \lambda_s^N \phi_s(\rho) \approx \Phi(\rho),
\]
(7.5)

where
\[
\Phi(\rho) = \sum_{t \geq 1} g_{tt}^2 \hat{\eta}(\rho | \frac{\lambda_t}{\lambda_1}),
\]
and
\[
\hat{\eta}(\rho | \tau) = \frac{1 - \tau^2}{1 - 2\tau \cos 2\pi \rho + \tau^2}.
\]

A plot of \( \hat{\eta}(\rho / \tau) \) as a function of \( \rho \) is given for several \( \tau \)-values, in Fig.8.

Significant information about \( J(\rho) \), the intensity of diffuse scattering, can be obtained by noting that when a phase transition of the type mentioned takes place, the degeneracy of the maximum eigenvalue (of \( M \)) depends on the phase. To be precise, about the critical point (where there is no long range order), the maximum eigenvalue is non-degenerate; whereas below the critical point (where there is long range order), the maximum eigenvalue is at least doubly degenerate \(^9\) (in the limit \( N \to \infty \)). Using these facts we can now describe the behaviour of \( J(\rho) \). Above the critical point \( \lambda_t < \lambda_1 \) for \( t > 1 \) so that small \( \tau \) dominates. In the
region of small $\tau, \vartheta$ is approximately constant (Fig. 8) so $J(\varphi)$ is well dispersed. Below the critical point $\tau \approx 1$ dominates: thus since $\vartheta$ has sharp peaks when $\tau \to 1$ and $\varphi = \text{integer}$, $J(\varphi)$ is concentrated about integral values of $\varphi$.

REFERENCES

(3) F. Zernike, Physica, 7, 565 (1940).
(4) L. Landau, Phys. Z. Sowjetunion, 12, 123 (1939).