versus $(\sin\theta)/\lambda$ and a smooth curve was drawn. This is represented in Table 5.

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Friedel's Law in the Dynamical Theory of Diffraction

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The significance and validity of Friedel's law are critically discussed by means of the dynamical theory of diffraction. It is proved that in some cases diffraction phenomena are not invariant under the operation of inversion exerted on the crystal; this means that Friedel's law fails. The cause of the failure is not the effect of absorption, but is found in the dynamical relation of reflexions which are excited simultaneously.

1. Introduction

Friedel's law (Friedel, 1913) was originally proposed as an empirical rule for the diffraction phenomena of X-rays by crystals. The law implies:

> Intensities of reflexions of indices (hkl) and $(\bar{h}\bar{k}\bar{l})$ are equal to each other. (Form I)

This rule can be readily derived from the kinematical theory of diffraction, because the structure amplitudes $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ are generally complex conjugate to each other and the integrated intensity of the diffraction spot given by this theory is proportional to $|F|^2$. The same law is expected to hold similarly for electron and neutron waves when the diffraction takes place in accordance with the kinematical theory.

Friedel's law is sometimes expressed in another form (e.g. Zachariasen, 1944):

> The diffraction phenomena of waves by a crystal are invariant under an inversion of the crystal with respect to the incident beam. (Form II)

The relation between Form I and Form II is critically discussed in § 2. Form II implies that any indication of the *sense* of polar axes in crystals never appears in diffraction phenomena.*

The break-down of Friedel's law can only occur when the scattering of waves by the atoms is accompanied by phase shifts. In the case of X-rays, this effect was experimentally detected on zincblende, by utilizing anomalous dispersion for zinc atoms, by Nishikawa & Matsukawa (1928), Coster, Knol & Prins (1930), and Geib & Lark-Horowitz (1932).

Now let us consider Friedel's law in the dynamical theory. In this theory, Friedel's law expressed in Form I has no definite meaning except when a certain restriction is imposed, as explained in § 2. Therefore we must refer to Form II. The proof of the validity of Friedel's law in the dynamical theory was given by Ewald (1925) in the case of single reflexion, and by Laue (1948*a*, *b*) for general cases in which simultaneous reflexions take place.

On the other hand, the present authors (Miyake & Uyeda, 1950) have found an effect by which the sense of polar axes of zincblende can be determined solely by an electron diffraction pattern from this crystal in which two strong diffracted beams are present. Later, Kohra and the present authors (Kohra, Uyeda & Miyake, 1950; Kohra, 1954) showed that the principal feature of the phenomenon is rendered by the dynamical theory of diffraction without taking into account the effect of absorption.

Our observation and theoretical explanation seem to contradict Laue's theory, and this contradiction cannot be considered trivial. The purposes of the present paper are to reinvestigate the meaning of Friedel's law and to find where it holds and where it fails. Our theoretical interpretation in the case of zincblende is discussed again and is confirmed; thus it is proved that Friedel's law does not hold in some cases in the dynamical theory, even when absorption is not taken into account. Although our treatment applies equally to the theories of X-ray, electron and neutron diffraction, the discussion is developed only for electron diffraction.

2. The meaning of Friedel's law in the dynamical theory

(*a*) *Plus and minus crystals*

Let us first consider a plane parallel slab of a non-centrosymmetrical crystal of infinite lateral extension and thickness $2H$. We will call it *the plus crystal*. The electric potential therein may be written

$$\overset{+}{V}(\mathbf{r}) = \sum_m \overset{+}{V}_m \exp\left[2\pi i(\mathbf{h}_m\mathbf{r})\right]; \qquad (1)$$

m represents a set of three indices $(m_1m_2m_3)$, $\overset{+}{V}_m$ the Fourier coefficient of $\overset{+}{V}(\mathbf{r})$, and $\mathbf{h}_m$ the position vector of a reciprocal-lattice point

$$\mathbf{h}_m = m_1\mathbf{b}_1+m_2\mathbf{b}_2+m_3\mathbf{b}_3; \qquad (1a)$$

here $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are the axes reciprocal to those of the crystal lattice $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$.

Next, consider another crystal which is obtained from the plus crystal by an operation of inversion about the centre of the slab. The new crystal is called *the minus crystal* and its potential is given by

$$\overset{-}{V}(\mathbf{r}) = \sum_m \overset{-}{V}_m \exp\left[2\pi i(\mathbf{h}_m\mathbf{r})\right] \qquad (2)$$

with the relation

$$\overset{+}{V}{}^*_m = \overset{-}{V}_m\,. \qquad (3)$$

Since $\overset{+}{V}(\mathbf{r})$ and $\overset{-}{V}(\mathbf{r})$ are real, we have

$$\overset{+}{V}{}^*_m = \overset{+}{V}_{-m},\ \overset{-}{V}{}^*_m = \overset{-}{V}_{-m}\,. \qquad (4)$$

The wave function of an electron with the total energy E in a stationary electric potential $V(\mathbf{r})$ is given by

$$\Psi = \exp\left[-2\pi iEt/h\right]u(\mathbf{r})\,, \qquad (5)$$

where $u(\mathbf{r})$ obeys the Schrödinger equation for stationary states, namely

$$\nabla^2u(\mathbf{r})+(8\pi^2m/h^2)\left[E+eV(\mathbf{r})\right]u(\mathbf{r}) = 0\,. \qquad (6)$$

For the potential $V(\mathbf{r})$, we put

$V(\mathbf{r}) = 0,\ z > H$ (upper free space),
$V(\mathbf{r}) = \overset{\pm}{V}(\mathbf{r}),\ H > z > -H$ (inside the crystal),
$V(\mathbf{r}) = 0,\ -H > z$ (lower free space),

where the z axis is taken to be normal to the surface of the crystal slab.

On the boundary surfaces of the crystal, we have the boundary conditions

$$u(\mathbf{r}) \text{ and } \partial u(\mathbf{r})/\partial z \text{ are continuous at } z = H \text{ and } z = -H\,. \qquad (7)$$

In each of the three spaces, $u(\mathbf{r})$ is a superposition of component plane waves. In the upper free space, we assume present an incident wave of given amplitude A and given wave vector $\mathbf{K}_0$, expressed by

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* Friedel's law has sometimes been interpreted as if it implies that the presence or absence of the centre of symmetry in crystals cannot be known from the diffraction phenomena alone; but this interpretation is not correct. Friedel's law excludes knowledge about the sense of polar axes only; it does not concern itself with the presence or absence of the centre of symmetry. In some cases the presence or absence of the centre of symmetry can be concluded from diffraction patterns, although the sense of polar axes remains unknown. For example: (i) In favourable cases the space group of crystals can be uniquely determined from extinctions alone. (ii) Centrosymmetrical and non-centrosymmetrical crystals present different features in the intensity statistics of reflexions (Wilson, 1949*a*, *b*). (iii) By applying the dynamical theory, Kambe & Miyake (Kambe & Miyake, 1954; Miyake & Kambe, 1954) discussed the effect of the relative phase angle of two structure amplitudes on diffraction patterns, and they showed that a method is available in principle to determine the existence or absence of the centre of symmetry in crystals.

$$A \exp [2\pi i(\mathbf{K}_0\mathbf{r})] \,, \tag{8}$$

where

$$|\mathbf{K}_0| = K_0 = \sqrt{\{(2m/h^2)E\}} \,.$$

Under the actual experimental condition, this wave should be the only one in the free spaces which travels towards the crystal; the other components in these spaces must emerge outwards from the crystal. These others correspond to diffracted waves (reflexions) which may be observed in experiments.

(*b*) *Formulation of Friedel's law*

In this subsection, the relation between Form I and Form II is made clear. Form I is stated as an empirical rule and it involves ambiguities because the meaning of the word *intensities* can be interpreted in many ways (see below). On the other hand, Form II involves no ambiguity, but it is not suitable for comparison with experiments. In the following, we start from Form II and rewrite it in more convenient forms.

Form II can be rewritten as far as observable quantities are concerned as follows: *The directions and the intensities of all corresponding reflexions* (*hkl*) *are equal to each other for the plus and minus crystals, provided the intensity and the direction of the incident beam are kept unchanged* (Form II′). In the dynamical theory (see § 4), as well as in the kinematical theory, the directions of all corresponding reflexions are equal to each other for the plus and the minus crystals. Therefore, Friedel's law in Form II′ holds if the intensities of the corresponding reflexions are equal to each other. The word *intensities* should be interpreted to include profiles of intensity curves, because according to the dynamical theory reflexions take place within certain angular ranges even when the crystals are thick.

Let us assume that Form II′ holds and let us exert an operation of inversion on one of the crystals, *say* the minus crystal, and exert simultaneously the same operation on the incident beam which falls upon it. (The inversion does not apply to the axial system of reference.) Then we obtain the plus crystal and an incident beam in the direction opposite to that originally assumed. Since the indices (*hkl*) for the minus crystal are transformed into the indices ($\bar{h}\bar{k}\bar{l}$) for the new plus crystal, we can rewrite Form II′ as far as intensities are concerned as follows: *The intensities of* (*hkl*) *and* ($\bar{h}\bar{k}\bar{l}$) *for a fixed crystal are equal to each other provided the directions of the incident beams which excite these reflexions are opposite to each other* (Form I′).

Form I′ goes over into Form I if the restriction imposed on the directions of the incident beams is omitted. Such a restriction can be omitted when the kinematical theory is applicable and the crystal is sufficiently thick; in such cases Bragg reflexions appear under sharp angular conditions and only integrated intensities, which are independent of the directions of the incident beam, can be observed. However, when reflexions possess profiles of finite widths, the restriction is important. In the dynamical theory, profiles are generally finite and, furthermore, intensities vary with azimuthal settings of incident beams, especially when more than two reflexions are excited simultaneously. Therefore, the restriction is inevitable and cannot be omitted in Form I′. In the following sections discrimination between the holding and the failure of Friedel's law in the dynamical theory must be made by applying Form II, II′ or I′.

If Form II, II′ and I′ hold by interpreting the word *intensities* as detailed profiles, we say that Friedel's law holds strictly. When, however, profiles of intensities oscillate rapidly with changes of the direction of incident beam so that only averaged profiles are observable, *intensities* may be interpreted as averaged profiles from an experimental point of view. When reflexions are so sharp that only integrated intensities are observable, *intensities* may be interpreted as integrated intensities. In some cases Form II, II′ and I′, may hold by interpreting intensities as the averaged profiles or the integrated intensities. In such cases we say that Friedel's law holds loosely. When the law holds strictly it holds also loosely; but not vice versa.

It can be proved that when the diffraction process is in accordance with the kinematical theory, Friedel's law holds strictly, even when the crystal is so thin that the widths of profiles are finite.

(*c*) *The case of zincblende*

In this subsection, we show that our observation in the case of zincblende (Miyake & Uyeda, 1950) violates Form II′. Our observation is as follows: The incident beam falls upon the cleavage surface (110) of the crystal in the [1$\bar{1}$0] or [$\bar{1}$10] azimuth, and reflexions (*hhl*) and (*hh$\bar{l}$*) are excited simultaneously. We observed that the intensities of these reflexions are not equal to each other, namely the relation

$$I_{(hhl)} = I_{(hh\bar{l})} \tag{A}$$

fails.

Let us consider the reflexions (*hhl*) and (*hh$\bar{l}$*) from the plus and the minus crystals. Since zincblende has a mirror plane parallel to (110), the minus crystal can be derived from the plus crystal not only by an inversion, but also by a rotation of 180° around the axis normal to (110). Then we have

$$\overset{+}{I}_{(hhl)} = \overset{-}{I}_{(hh\bar{l})},\ \overset{+}{I}_{(hh\bar{l})} = \overset{-}{I}_{(hhl)} \,. \tag{B}$$

When we assume the equality (*A*), then, combining (*A*) with (*B*), we get

$$\overset{+}{I}_{(hhl)} = \overset{-}{I}_{(hhl)},\ \overset{+}{I}_{(hh\bar{l})} = \overset{-}{I}_{(hh\bar{l})} \,. \tag{C}$$

Since, however, (*A*) fails in the present case, (*C*) must also fail. Thus our observation violates Form II′.

(*d*) *Meaning of complex conjugate wave functions in diffraction problems*

When a wave function $u(\mathbf{r})$ satisfies the Schrödinger equation for the plus crystal, then its complex conjugate function $u(\mathbf{r})^*$ satisfies the same equation. It is sometimes thought that the general validity of Friedel's law in the dynamical theory is based upon this relation (Laue, 1948*a*, *b*). Actually, however, this relation indicates nothing on the validity of the law, as is clear from the following consideration.

We assume that $u(\mathbf{r})$ for the plus crystal is composed of component waves such as are schematically represented in Fig. 1(*a*). The complex conjugate solution $u(\mathbf{r})^*$ is composed of component waves which travel in opposite directions, shown in Fig. 1(*b*). Now we apply simultaneously an operation of inversion upon the crystal and the wave field of Fig. 1(*b*). Then, since the crystal is transformed into the minus crystal, we have a possible solution for the minus crystal as is shown in Fig. 1(*c*). The scheme of Fig. 1(*c*), however, contains more than one entrant wave towards the crystal, contradicting the condition of diffraction experiments. It is obvious that such a solution has no relation to the present problem.†

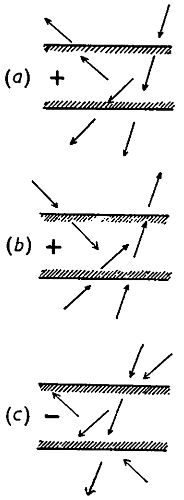

Fig. 1. Schematic illustration of (*a*) $u(\mathbf{r})$, (*b*) $u(\mathbf{r})^*$, and (*c*) the inversion of (*b*).

3. General procedure of solution of the diffraction problem

Although the dynamical theory of electron diffraction is widely known (e.g. Bethe, 1928; Thomson & Cochrane, 1939; Lamla, 1938*a*, *b*; Laue, 1948*b*), the following survey of the theory will be helpful.

A solution of the Schrödinger equation (6) for an electron in a crystal is given by a Bloch function

$$\psi(\mathbf{k}_0) = \exp\,[2\pi i(\mathbf{k}_0\mathbf{r})]\sum_m u_m \exp\,[2\pi i(\mathbf{h}_m\mathbf{r})]\,, \qquad (9)$$

where $\mathbf{k}_0$ represents the wave-number vector of the primary wave within the crystal. We can regard $\psi(\mathbf{k}_0)$ as a superposition of plane waves with amplitudes u_m and wave-number vectors

$$\mathbf{k}_m = \mathbf{k}_0 + \mathbf{h}_m\,. \qquad (9a)$$

By substituting (9) in the Schrödinger equation (6), we obtain the fundamental equations of diffraction

$$(\varkappa_0^2 - \mathbf{k}_m^2)u_m + \sum_n{}' v_n u_{m-n} = 0\,, \qquad (10)$$

where

$$\varkappa_0^2 = (2m/h^2)(E + eV_0),\ v_n = (2me/h^2)V_n\,, \qquad (11)$$

and $\sum_n{}'$ means the sum without the term $n = (000)$.

The vector $\mathbf{k}_0$ must satisfy the compatibility relation

$$\begin{vmatrix} \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots (\varkappa_0^2 - k_{-n}^2) & & v_{-n} & v_{-2n} & \cdots & \cdots \\ \cdots & v_n & (\varkappa_0^2 - k_0^2) & v_{-n} & v_{-m} & \cdots \\ \cdots & \cdots & v_n & (\varkappa_0^2 - k_n^2) & v_{n-m} & \cdots \\ \cdots & \cdots & v_m & v_{m-n} & (\varkappa_0^2 - k_m^2) & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{vmatrix} = 0\,. \qquad (12)$$

This defines the dispersion surface in reciprocal space; the wave points for $\mathbf{k}_0$ must lie on this surface.

Let us assume the incident wave in the upper space is given by (8). We decompose $\mathbf{K}_0$ and $\mathbf{k}_m$ (including $m = 0$) into tangential and normal components

$$\mathbf{K}_0 = \mathbf{T}_0 - \Gamma_0\mathbf{z}\,, \qquad (13)$$

$$\mathbf{k}_m = \mathbf{t}_m - \gamma_m\mathbf{z}\,, \qquad (14)$$

where $\mathbf{z}$ is the unit vector along the positive direction of z. Then the tangential continuity for the incident wave vector required by the boundary condition is rewritten as

$$\mathbf{T}_0 = \mathbf{t}_0\,. \qquad (15)$$

Let us define, for convenience, the ν-normal as follows: The straight line normal to the entrant surface which passes through the end point of the vector $-\mathbf{T}_0$ drawn from the origin of the reciprocal lattice.

The wave points for $\mathbf{k}_0$ are determined by the intersection of the ν-normal and the dispersion surface.

The factor $\varkappa_0^2 - k_0^2$ in (10) and (12) can be rewritten as

$$\varkappa_0^2 - k_m^2 = \beta_m^2 - \gamma_m^2\,, \qquad (16a)$$

where

$$\beta_m^2 = \varkappa_0^2 - t_m^2,\ \gamma_m = \gamma_0 - h_{mz}\,, \qquad (16b)$$

and h_{mz} is the z-component of $\mathbf{h}_m$. Since β_m is a known quantity, provided the incident wave vector is given, and h_{mz} is also known, the determinant (12) is a function of the unknown quantity γ_0.

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† Laue seemed to consider that the wave function including time for the minus crystal has the form $\exp\,(2\pi iEt/h)u(\mathbf{r})^*$ (Laue, 1948*b*). But this is only another way of representing the state $\exp\,(-2\pi iEt/h)u(\mathbf{r})$ for the plus crystal (see (5)).

We denote the possible roots of γ_0 by $\gamma_0^N (N = 0, \mathrm{I}, \mathrm{II}, \ldots)$. Corresponding to each γ_0^N, we are given a Bloch function $\psi(\mathbf{k}_0^N)$ with coefficients u_m^N, whose ratios are determined by the equation (10) and which can be normalized properly, say $u_0^N = 1$.

The wave function of an electron within the crystal, u_c, is given as a superposition of many Bloch functions

$$u_c = \sum_N \alpha_N \psi(\mathbf{k}_0^N) = \sum_N \alpha_N \sum_m u_m^N \exp\,[2\pi i(\mathbf{k}_m^N \mathbf{r})]\,, \quad (17)$$

where the sum $\sum\limits_N$ is over all possible wave points. The coefficients are determined by the boundary conditions (7).

We can write the waves in the upper and lower free spaces respectively as

$$u_U = A \exp\,[2\pi i(\mathbf{K}_0 \mathbf{r})] + \sum_s R_s \exp\,[2\pi i(\mathbf{K}_s' \mathbf{r})]\,, \quad (18a)$$

$$u_L = \sum_s D_s \exp\,[2\pi i(\mathbf{K}_s \mathbf{r})]\,, \quad (18b)$$

where the index s is used to represent the indices (m_1, m_2) corresponding to a row of reciprocal-lattice points normal to the surface of the crystal; specifically, $s = 0$ means $m_1 = 0$, $m_2 = 0$. Sometimes hereafter $m(m_1 m_2 m_3)$ is written as (s, m_3). The coefficients R_s and D_s are amplitudes of diffracted component waves and $\mathbf{K}_s'$ and $\mathbf{K}_s$ are their wave vectors. It is obvious that

$$|\mathbf{K}_s'| = |\mathbf{K}_s| = K_0\,,$$

and, by the requirement of the tangential continuity,

$$\mathbf{K}_s' = \mathbf{t}_s + \Gamma_s \mathbf{z}\,, \quad (19a)$$

$$\mathbf{K}_s = \mathbf{t}_s - \Gamma_s \mathbf{z}\,, \quad (19b)$$

where $\mathbf{t}_s$ means tangential component vector of $\mathbf{k}_{s, m_3}$ (m_3 is arbitrary), and Γ_s is given by $\Gamma_s = \sqrt{\{K_0^2 - t_s^2\}}$.

The conditions (7) at the upper and the lower surfaces, after eliminating R_s and D_s, give:

$$\left.\begin{aligned} \sum_N \sum_{m_3} \alpha_N (\gamma_{s, m_3}^N + \Gamma_s) u_{s, m_3}^N \exp\,(-2\pi i \gamma_{s, m_3}^N H) \\ = 2\Gamma_0 A \exp\,(-2\pi i \Gamma_0 H) \,.\, \delta_{0s}\,, \\ \sum_N \sum_{m_3} \alpha_N (\gamma_{s, m_3}^N - \Gamma_s) u_{s, m_3}^N \exp\,(2\pi i \gamma_{s, m_3}^N H) = 0\,, \end{aligned}\right\} \quad (20)$$

where $\delta_{0s} = 0$ for $s \neq 0$, and $= 1$ for $s = 0$. These relations hold for all s.

If α_N are known from (20), the amplitudes of diffracted waves, R_s and D_s for all s, are calculated from the following equations:

$$\left.\begin{aligned} \sum_N \sum_{m_3} \alpha_N (\gamma_{s, m_3}^N - \Gamma_s) u_{s, m_3}^N \exp\,(-2\pi i \gamma_{s, m_3}^N H) \\ = -2\Gamma_s R_s \exp\,(2\pi i \Gamma_s H)\,, \\ \sum_N \sum_{m_3} \alpha_N (\gamma_{s, m_3}^N + \Gamma_s) u_{s, m_3}^N \exp\,(2\pi i \gamma_{s, m_3}^N H) \\ = 2\Gamma_s D_s \exp\,(2\pi i \Gamma_s H)\,. \end{aligned}\right\} \quad (21)$$

$|R_s|^2$ and $|D_s|^2$ give detailed intensity profiles as functions of Γ_0, which decides the direction of the incident beam.

In the above equations the total number s is extended to infinity, and consequently the total number of N is also infinity; but from now on, for the sake of simplicity, we confine these numbers, assuming them to be respectively $\sigma + 1$ and $Z + 1$. Since the number $Z + 1$ is always twice the number $\sigma + 1$, as proved by Lamla (1938*a*, *b*), the relations (20) are just sufficient to determine all α_N uniquely, and the relations (21) are sufficient to determine R_s and D_s. We call the fundamental equations, after they are reduced to a finite number, the reduced fundamental equations.

4. Properties of wave function for plus and minus crystals

We will now briefly depict some simple but important mathematical properties of the Bloch functions for the plus and the minus crystals:

(*a*) A root γ_0 of the compatibility equation (12) is in general either real or complex. In the latter case its complex conjugate should also be a root, because, through the relation $v_m = v_{-m}^*$ according to (4), the complex conjugate to the determinant (12) can be obtained by exchanging rows and columns and by replacing γ_0 by γ_0^* in the determinant. We use new indices M and L or L' to indicate respectively a real and a pair of conjugate roots; for example, the real and the complex roots of γ_0 are written respectively as γ_0^M and γ_0^L or $\gamma_0^{L'}$. The letter N is also used as before for the general index of M and L or L'.

(*b*) The dispersion surfaces are the same for the plus and the minus crystals, because the determinant (12) for both crystals is the same, as is known by paying due regard to the relations (3) and (4). This amounts to having the same roots of γ_0 for the two crystals. Therefore the marks $+$ and $-$, which are used to discriminate between the quantities relevant to the plus and the minus crystals, can be omitted from γ_0.

(*c*) By substituting (16), the fundamental equations (10) and their conjugate complexes are rewritten as

$$\{\beta_m^2 - (\gamma_0^N - h_{mz})^2\} u_m^N + \sum_n{}' v_n u_{m-n}^N = 0\,,$$

$$\{\beta_m^2 - (\gamma_0^{N*} - h_{mz})^2\} u_m^{N*} + \sum_n{}' v_n^* u_{m-n}^{N*} = 0\,.$$

By comparing these equations, we get the following relations: When the crystal is centrosymmetrical (where v_m are all real)

$$u_m^M \text{ are real}\,, \quad (22)\,(\mathrm{i})$$

$$u_m^L = u_m^{L'*}. \quad (22)\,(\mathrm{ii})$$

When the crystal is non-centrosymmetrical

$$u_m^N \text{ are complex in general for real and complex } \gamma_0^N\,, \quad (23)\,(\mathrm{i})$$

$$u_m^L = u_m^{L'*} \text{ does not hold in general.}^\dagger \quad (23)\,(\mathrm{ii})$$

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† This means that the equality can hold in some special cases, but fails in others.

Examples of the failing of the equality in (23)(ii) are available from (28), (29) and (30) in §§ 5 and 6.

(*d*) The fundamental equations (10) for the plus and minus crystals are

$$\{\beta_m^2-(\gamma_0^N-h_{mz})^2\}\overset{+}{u}{}_m^N+\sum_n{}' \overset{+}{v}_n\overset{+}{u}{}_{m-n}^N=0\,,$$

$$\{\beta_m^2-(\gamma_0^N-h_{mz})^2\}\overset{-}{u}{}_m^N+\sum_n{}' \overset{-}{v}_n\overset{-}{u}{}_{m-n}^N=0\,.$$

By comparing these equations and by referring to (3), we get the following relations:

$$\overset{-}{u}{}_m^M=\overset{+}{u}{}_m^{M*}\,, \tag{24 (i)}$$

$$\overset{-}{u}{}_m^L=\overset{+}{u}{}_m^{L'*}\quad\text{or}\quad \overset{-}{u}{}_m^{L'}=\overset{+}{u}{}_m^{L*}\,. \tag{24 (ii)}$$

For non-centrosymmetrical crystals, we get from (23)(i) and (24)(i)

$$\overset{-}{u}{}_m^M=\overset{+}{u}{}_m^M \text{ does not hold in general,†} \tag{25 (i)}$$

and from (23)(ii) and (24)(ii)

$$\overset{-}{u}{}_m^L=\overset{+}{u}{}_m^L \text{ does not hold in general.†} \tag{25 (ii)}$$

Even for the absolute values of both sides of the above equations,

$$|\overset{-}{u}{}_m^L|=|\overset{+}{u}{}_m^L| \text{ does not hold in general.†} \tag{25 (iii)}$$

An example of the failure of the equality in (25)(iii) is provided by (30) in § 6.

From (24) and (25) we see that the relation between the Bloch functions for the plus and the minus crystals is not so simple for complex γ_0 as for real γ_0.

5. Examples in which Friedel's law holds

According to § 2(*b*) and § 3, Friedel's law in the dynamical theory is given by the relations

$$|\overset{+}{R}_s|^2=|\overset{-}{R}_s|^2,\ |\overset{+}{D}_s|^2=|\overset{-}{D}_s|^2\,. \tag{26}$$

Since $|R_s|^2$ and $|D_s|^2$ give detailed profiles of intensities, the law holds strictly when (26) is satisfied for all s.

In this and the following sections some practical examples are given where the law holds and where it fails. Although it is desirable to find general conditions under which the law holds or fails, we could not find them because no simple relations between $\overset{-}{u}{}_m^N$ and $\overset{+}{u}{}_m^N$ are available for non-centrosymmetrical crystals, as mentioned in § 4(*d*).

(*a*) *Example* 1. *The case where the Fourier coefficients (contained in the reduced fundamental equations) are all real*

Since this case is essentially equivalent to that of centrosymmetrical crystals, it is obvious that the law holds.

(*b*) *Example* 2. *The case where only a single reflexion is excited*

This case can be reduced to the foregoing case, because the only Fourier coefficient, appearing in the reduced fundamental equation, can be reduced to be real by a suitable transformation of the coordinate origin, provided that the lattice plane concerned is not parallel to the surface of the crystal slab. The above-mentioned restriction arises from our premise in choosing the origin at the mid-depth of the slab. A more general treatment can be given as follows:

When we assign the index s to the reflexion concerned, then the reduced fundamental equations are

$$\left.\begin{aligned}(\beta_0^2-\gamma_0^2)\overset{\pm}{u}{}_0^N+\overset{\pm}{v}_{-s}\overset{\pm}{u}{}_s^N&=0\,,\\ \overset{\pm}{v}_s\overset{\pm}{u}{}_0^N+(\beta_s^2-\gamma_s^2)\overset{\pm}{u}{}_s^N&=0\,,\end{aligned}\right\} \tag{27}$$

where u_0^N are normalized to unity. Solving (27), we have

$$\overset{\pm}{u}{}_s^N=\frac{-(\beta_0^2-\gamma_0^{N^2})}{\overset{\pm}{v}_{-s}}\,, \tag{28}$$

where $N=1, 2, 3$ and 4. Let us put

$$\frac{\overset{+}{u}{}_s^N}{\overset{-}{u}{}_s^N}=\frac{\overset{-}{v}_{-s}}{\overset{+}{v}_{-s}}=\frac{\overset{+}{v}_s}{\overset{-}{v}_s}\equiv\exp\,(2i\varepsilon_s)\,;$$

then ε_s corresponds to the phase factor of v_s. Since ε_s is independent of N, we can see at once from (20) that

$$\overset{+}{\alpha}_N=\overset{-}{\alpha}_N$$

and, in turn, from (21)

$$\overset{+}{R}_s\equiv\exp\,(2i\varepsilon_s)\overset{-}{R}_s,\ \overset{+}{D}_s=\exp\,(2i\varepsilon_s)\overset{-}{D}_s\,.$$

The equality of intensities required in (26) results at once from these relations. Then Friedel's law remains valid in the present case, as was formerly proved by Ewald (1925).

(*c*) *Example* 3. *The case where more than two strong rays exist without inter-relations*

According to the dynamical theory, the intensity of s-reflexion is determined not only by v_s but is influenced by $v_{s'}$ and $v_{s-s'}$, when another s'-reflexion occurs simultaneously, provided $v_{s-s'}$ does not vanish. The coefficient $v_{s-s'}$ inter-relates the intensities of s- and s'-reflexions. If all the inter-relating coefficients $v_{s-s'}$ are zero, the reduced fundamental equations become

$$\begin{aligned}(\beta_0^2-\gamma_0^2)\overset{\pm}{u}_0+\overset{\pm}{v}_{-1}\overset{\pm}{u}_1+\overset{\pm}{v}_{-2}\overset{\pm}{u}_2+\ldots+\overset{\pm}{v}_{-\sigma}\overset{\pm}{u}_\sigma&=0\,,\\ \overset{\pm}{v}_1\overset{\pm}{u}_0+(\beta_1^2-\gamma_1^2)\overset{\pm}{u}_1+0+\qquad\ldots+0&=0\,,\\ \overset{\pm}{v}_2\overset{\pm}{u}_0+0+(\beta_2^2-\gamma_2^2)\overset{\pm}{u}_2+0+\ldots+0&=0\,,\\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\,,&\end{aligned}$$

and we get

$$\overset{\pm}{u}{}_s^N = \frac{-\overset{\pm}{v}_s}{(\beta_s^2-\gamma_s^{N^2})} \,. \tag{29}$$

Let us put

$$\frac{\overset{+}{u}{}_s^N}{\overset{-}{u}{}_s^N} = \frac{\overset{+}{v}_s}{\overset{-}{v}_s} \equiv \exp\,(2i\varepsilon_s)\,,$$

where ε_s is the phase factor of $\overset{+}{v}_s$, and is independent of N, so that by a similar consideration as in the foregoing example, we can readily conclude that the law is valid also in this case.

6. An example in which Friedel's law fails

We mentioned in § 2(*c*) that our observation in the case of zincblende violates Friedel's law. Although a theoretical interpretation of the observation according to the dynamical theory was given by Kohra, Uyeda & Miyake (1950), the essential points of the interpretation are given below from the present viewpoints.

In this case, Fourier coefficients v_n and v_m are complex conjugate to each other, and v_{n-m} is real and finite where n, m and $n-m$ stand respectively for (hhl), ($hh\bar{l}$) and (0, 0, 2l). The fundamental equations then become

$$\begin{aligned}
(\beta_0^2-\gamma_0^2)\overset{\pm}{u}_0+\overset{\pm}{v}_{-m}\overset{\pm}{u}_m+\overset{\pm}{v}_{-n}\overset{\pm}{u}_n &= 0\,,\\
\overset{\pm}{v}_m\overset{\pm}{u}_0+(\beta_m^2-\gamma_m^2)\overset{\pm}{u}_m+\overset{\pm}{v}_{m-n}\overset{\pm}{u}_n &= 0\,,\\
\overset{\pm}{v}_n\overset{\pm}{u}_0+\overset{\pm}{v}_{n-m}\overset{\pm}{u}_m+(\beta_n^2-\gamma_n^2)\overset{\pm}{u}_n &= 0\,.
\end{aligned}$$

According to the experimental condition (see § 2(*c*)), the incident ray is in the azimuth [1$\bar{1}$0], so that $\beta_n = \beta_m$ and $\gamma_n = \gamma_m$. Let us put

$$\eta \equiv \beta_n^2-\gamma_n^2 = \beta_m^2-\gamma_m^2\,.$$

Then, we obtain

$$\overset{\pm}{u}{}_n^N = \frac{-\overset{\pm}{v}_n\eta_N+\overset{\pm}{v}_m\overset{\pm}{v}_{n-m}}{\eta_N^2-\overset{\pm}{v}_{m-n}\overset{\pm}{v}_{n-m}}\,,\quad \overset{\pm}{u}{}_m^N = \frac{-\overset{\pm}{v}_m\eta_N+\overset{\pm}{v}_n\overset{\pm}{v}_{m-n}}{\eta_N^2-\overset{\pm}{v}_{m-n}\overset{\pm}{v}_{n-m}}\,, \tag{30}$$

and the number of wave points is six.

Because v_{n-m} is real and v_n and v_m are complex conjugate to each other, we have from (30) and (3)

$$\overset{+}{u}{}_n^N = \overset{-}{u}{}_m^N,\ \overset{+}{u}{}_m^N = \overset{-}{u}{}_n^N\,. \tag{31}$$

By (20) and (31) we know

$$\overset{+}{\alpha}_N = \overset{-}{\alpha}_N\,, \tag{32}$$

and from (21) and (32) we obtain the following result:

$$\overset{-}{R}_n = \overset{+}{R}_m,\ \overset{-}{R}_m = \overset{+}{R}_n,\ \overset{-}{D}_n = \overset{+}{D}_m,\ \overset{-}{D}_m = \overset{+}{D}_n\,. \tag{33}$$

If the amplitudes in (33) are squared, the relations (B) in § 2(*c*) are obtained.

For the validity of Friedel's law, the relations (26) are required, which, combined with (33), give

$$|\overset{+}{R}_n|^2 = |\overset{+}{R}_m|^2,\ |\overset{+}{D}_n|^2 = |\overset{+}{D}_m|^2. \tag{34}$$

The first of these relations is equivalent to the holding of (A) in § 2(*c*), which according to our observation fails. Our present problem is to make clear whether (34) holds or fails in the dynamical theory.

According to (21), $|\overset{+}{R}_n|^2$ and $|\overset{+}{R}_m|^2$ are respectively given by

$$|2\Gamma_n\overset{+}{R}_n|^2 = |\sum_N \overset{+}{\alpha}_N\overset{+}{u}{}_n^N(\gamma_n^N-\Gamma_n)\exp\,(-2\pi i\gamma_n^N H)|^2\,, \tag{35a}$$

$$|2\Gamma_m\overset{+}{R}_m|^2 = |\sum_N \overset{+}{\alpha}_N\overset{+}{u}{}_m^N(\gamma_n^N-\Gamma_n)\exp\,(-2\pi i\gamma_n^N H)|^2\,. \tag{35b}$$

These formulae are rewritten as

$$\begin{aligned}
|2\Gamma_n\overset{+}{R}_{n,m}|^2 = {} & \sum_N |\overset{+}{\alpha}_N|^2|u_{n,m}^N|^2|\gamma_n^N-\Gamma_n|^2\\
& + \sum_{N\neq N'}\sum \overset{+}{\alpha}_N\overset{+}{\alpha}{}_{N'}^{*}\overset{+}{u}{}_{n,m}^N\overset{+}{u}{}_{n,m}^{N'*}(\gamma_n^N-\Gamma_n)(\gamma_n^{N'}-\Gamma_n)^*\\
& \times\exp\,[-2\pi i(\gamma_n^N-\gamma_n^{N'*})H]\,,
\end{aligned} \tag{36}$$

where the suffix n, m means n or m. For further discussions, we study separately the following cases:

(*a*) γ_0^N *are real for all* N

Under this condition η_N are real for all N, and from (30) we have the relation

$$\overset{+}{u}{}_n^N = \overset{+}{u}{}_m^{N*} \quad \text{for all } N\,. \tag{37}$$

Then the single summation in (36) is invariant for the interchange of n and m. On the other hand, the double summation is not invariant for the interchange of n and m because

$$\overset{+}{u}{}_n^N\overset{+}{u}{}_n^{N'*} \quad\text{and}\quad \overset{+}{u}{}_m^N\overset{+}{u}{}_m^{N'*}$$

are not equal to each other. Thus Friedel's law does not hold strictly in this case. Since, however, the factor

$$\overset{+}{\alpha}_N\overset{+}{\alpha}{}_{N'}^{*}\exp\,[-2\pi i(\gamma_n^N-\gamma_n^{N'*})H]$$

oscillates very rapidly with the change of Γ_0, it is quite probable that the second term in (36) vanishes in the averaged intensity profile, which is calculated as

$$\overline{|R_s|^2} = \frac{1}{\Delta\Gamma_0}\int_{\Delta\Gamma_0}|R_s|^2 d\Gamma_0\,,$$

where $\Delta\Gamma_0$ means a small range of Γ_0 around a definite value. If such were the case, Friedel's law might hold loosely by interpreting *intensities* as averaged profiles of intensity. The vanishing of the second term is very probable, but we cannot prove it rigorously because of the complicated nature of α_N as function of Γ_0.

(b) *A pair of γ_0^N is complex*

Since our experimental condition is the Bragg case, a pair of γ_0^N become conjugate complex to one another when the Bragg condition is well satisfied by the lattice planes m and n. If we assign to these roots the indices $N = \mathrm{I}$ and II, we have

$$\gamma_0^{\mathrm{I}*} = \gamma_0^{\mathrm{II}},\ \eta_{\mathrm{I}}^* = \eta_{\mathrm{II}}\,.$$

Assigning $N = \mathrm{III}$, IV, V and VI to the other roots, which are assumed to be real, we obtain

$$\overset{+}{u}{}_n^{N*} = \overset{+}{u}{}_m^{N} \quad \text{for} \quad N = \mathrm{III, IV, V, VI}\,, \tag{38}$$

but from (30) we have

$$|\overset{+}{u}{}_n^{\mathrm{I}}| \neq |\overset{+}{u}{}_m^{\mathrm{I}}|,\ |\overset{+}{u}{}_n^{\mathrm{II}}| \neq |\overset{+}{u}{}_m^{\mathrm{II}}|\,. \tag{39}$$

These relations combined with (31) afford an example of (25) (iii) in § 4.

One of the waves associated with the complex conjugate roots γ_0^{I} and γ_0^{II} decreases and the other increases in penetrating deeper into the crystal. According to the boundary condition, the damped wave, say $N = \mathrm{I}$, predominates over all the other waves, provided the slab is sufficiently thick. Equations (35*a*) and (35*b*) then become respectively

$$|2\Gamma_n\overset{+}{R}_n|^2 = |\overset{+}{\alpha}_{\mathrm{I}}\overset{+}{u}{}_n^{\mathrm{I}}(\gamma_n^{\mathrm{I}}-\Gamma_n)|^2\,,$$

$$|2\Gamma_m\overset{+}{R}_m|^2 = |\overset{+}{\alpha}_{\mathrm{I}}\overset{+}{u}{}_m^{\mathrm{I}}(\gamma_n^{\mathrm{I}}-\Gamma_n)|^2\,,$$

and by (39) we have

$$|\overset{+}{R}_n|^2 \neq |\overset{+}{R}_m|^2. \tag{40}$$

Then, by (33), we have

$$|\overset{+}{R}_n|^2 \neq |\overset{-}{R}_n|^2,\ |\overset{+}{R}_m|^2 \neq |\overset{-}{R}_m|^2. \tag{41}$$

The profiles corresponding to $|\overset{+}{R}_n|^2$ and $|\overset{+}{R}_m|^2$ have been numerically calculated in former papers (Kohra, Uyeda & Miyake, 1950; Kohra, 1954) and the difference between them is clearly shown. They show no rapid oscillation and there is no distinction between detailed and averaged profiles. Thus Friedel's law fails in all respects in this case.

Summarizing the results of this section, we can state: Friedel's law does not hold strictly in any case under the assumed conditions. Although the law is likely to hold loosely with relation to the averaged profile in ranges where all the γ_0^N are real, it fails in every respect when a pair of γ_0^N is complex.

7. Conclusion

It is shown by the examples in §§ 5 and 6 that according to the dynamical theory of electron diffraction Friedel's law holds in certain cases, but fails in general, even when the effect of absorption is not taken into account in the theory. It must be emphasized that the cause of the failure is not the effect of absorption. The cause of the failure is found in the dynamical inter-relation of reflexions which are taking place simultaneously.

It is obvious that the failure is also to be expected theoretically in the case of X-rays, even when no anomalous dispersion accompanied by phase shift takes place. However, the experimental verification of the failure may be very difficult with X-rays because the coefficients of inter-relation are very small in that case. Similar remarks hold for neutron waves.

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