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On the Effect of a Secondary Structure upon the Interference of X-rays

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Laue's dynamic theory of x-ray interference is shown to be applicable, with only a few minor changes, to crystals having a very general type of secondary structure. It is thus applied for the purpose of obtaining a quantitative estimate of the effect of such a structure upon the nature of the x-ray interference maxima. The estimate is relative insofar as it compares the intensities of respectively the "secondarily" and the "primarily" reflected interference beams and applies only in the region where the latter have been, or can be observed. In this region the "two-dimensional lattice" type of secondary structure is found to give rise to a fine structure which, with the present insufficient resolving power, would be manifested experimentally as a weak, diffuse background. The secondary structure of this type produces *no broadening* of the primary lines. The existence of this type of structure, therefore, is not inconsistent with the sharpness of the interference maxima obtained from such crystals as calcite, and a possible objection to the existence of the secondary structure in such crystals is removed. The extinction effect is briefly considered, but absorption is not taken into account, except with a few qualitative remarks.

ARGUMENTS against the existence of a secondary structure[1] in crystals have been raised from time to time in the literature on the basis of the nature of the x-ray interference patterns. For instance,[2] it has been argued that the sharpness of the x-ray interference lines from such crystals as calcite is not consistent with the presence of a secondary structure. This argument, if theoretically tenable, would be very weighty on account of the reliability and great accuracy of the x-ray spectroscopy; and its consequences would be far reaching in the theory of the solid state.[3] For this reason, and also in view of the possibility of enlisting the aid of the x-ray spectroscopist in the detection and analysis of secondary structures, it is desirable to obtain a quan-

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[1] Not to be confused with a "mosaic structure." For the sense in which these terms are here used, see F. Zwicky, Phys. Rev. **40**, 63 (1932).

[2] M. Siegbahn, *Spektroskopie d. Röntgenstrahlen*, 2d Ed., p. 60 (1931).

[3] As pointed out by Siegbahn, in reference 2, we would have as an immediate effect that Zwicky's explanation of the discrepancy between the values of the electronic charge obtained respectively by direct measurement and by x-ray analysis would be rendered unsatisfactory. (See F. Zwicky, Proc. Nat. Ac. **16**, 211 (1930)). There is, however, at present some controversy as to whether or not this discrepancy is significant.

titative estimate of the effect of such structures upon the interference of x-rays.[4]

Laue's dynamic theory of x-ray interference[5] is directly applicable to crystals having a very general type of secondary structure. In fact, the formulae developed by Laue remain formally the same when his theory is applied to crystals having such a structure; only the symbols involved must be given a slightly different interpretation. In order to prove this proposition we shall have to review briefly the physical background of Laue's theory.

Laue's theory in contradistinction to Ewald's[6] earlier theory and Waller's[7] modification thereof, is based on the supposition that the negative electric charges are distributed in an arbitrary manner over the entire lattice cell. It contains Ewald's theory as a special case when certain restrictions are placed on a group of symbols whereby the concentration of the said charges at the lattice points is accomplished.

His theory owes its simplicity and elegance to the following ingenious considerations.

First he shows that it is permissible to assume that for small displacements the displacement of the negative charges at any point in the lattice cell is proportional to the electric field strength at that point. The proportionality factor is calculable in principle, but since it does not enter directly into the theory, it is not necessary to go into the question as to how this factor may be calculated.

Secondly, on account of the large masses with which the positive charges are associated, these do not take any appreciable part in the scattering of the x-rays. They may therefore be distributed in any manner whatsoever over the lattice cell, provided we specify that they shall not be displaced by the electric vector. The positive charges, in fact, may be distributed in such a way that when there is no disturbing field they exactly neutralize everywhere the negative charges. A field then produces in every point of space a polarization which is proportional to the field strength at that point. The magnitude of the polarization is characterized by a proportionality factor varying from point to point within the crystal. By thus distributing the positive charges we therefore arrive at a fictitious body whose dielectric constant varies with the coordinates. In the real body, with its positive charges concentrated in the immediate neighborhood of the lattice points, the electromagnetic wave field is exactly the same. The fact that the two bodies differ electrostatically is of no consequence for our purpose.

In order to obtain the solution of the interference problem it is now only

[4] Darwin, (See reference 15), has already calculated the effect of one type of imperfections in crystals. The type of secondary structure which will be considered here, however, is essentially different from Darwin's imperfections.

[5] M. v. Laue, Erg. d. ex. Naturwiss **10,** 133 (1931).

[6] P. P. Ewald, Series of papers starting with Ann. d. Physik **54,** 519 (1917). The general method embodied in Ewald's and Laue's works is more convenient for our purpose than the method employed by Darwin in a still earlier paper, C. G. Darwin, Phil. Mag. **27,** 315, 675 (1914).

[7] J. Waller, Uppsala Universitets Aarsskrift (1925).

necessary to solve Maxwell's equations for a medium having a triply periodic dielectric constant. In the case of the ideal crystal, as treated by Laue, the periodicities of the dielectric constant, ϵ, must conform with the periodicities of the primary lattice of the crystal. In the case of the crystal having a secondary structure, on the other hand, the *periodicities of* ϵ *must conform with the periodicities of the secondary structure.* The primary structure here appears as a very prominent higher harmonic. Instead of representing ϵ itself as a triply periodic Fourier summation it is more convenient for the purpose of calculation thus to represent the factor $\psi = 1 - 1/\epsilon$ which determines the polarization, $\mathcal{D}(1-1/\epsilon)$, $\mathcal{D}$ being the electric displacement vector of the electromagnetic field. If we understand by, $(\boldsymbol{a}_1^0, \boldsymbol{a}_2^0, \boldsymbol{a}_3^0)$ the primitive translations of the primary lattice, and by $(\boldsymbol{b}_1^0, \boldsymbol{b}_2^0, \boldsymbol{b}_3^0)$ the corresponding elementary vectors of the reciprocal lattice, we have for the ideal crystal:

$$1 - 1/\epsilon = \psi = \sum \psi_m e^{-j(\boldsymbol{b}_m \cdot \boldsymbol{r})} \tag{1}$$

where

$$\boldsymbol{b}_m = \sum_{\alpha=1}^{3} m_\alpha \boldsymbol{b}_\alpha^0; \; j = 2\pi(-1)^{1/2}.$$

m_α is an integer, and $\boldsymbol{r}$ is the independent variable radius vector measured from an arbitrary lattice point.

From the definition,

$$\boldsymbol{b}_k^0 = [\boldsymbol{a}_i^0 \times \boldsymbol{a}_j^0]/(\boldsymbol{a}_i^0 \boldsymbol{a}_j^0 \boldsymbol{b}_k^0) \tag{1a}$$

it follows immediately that each term in the series (1) is periodic with the three periods $(\boldsymbol{a}_1^0, \boldsymbol{a}_2^0, \boldsymbol{a}_3^0)$.

This is the starting point for Laue's theory. For crystals having a secondary structure Eq. (1) must be slightly modified. Let the periodicities of the secondary structure be $(\boldsymbol{D}_1^0, \boldsymbol{D}_2^0, \boldsymbol{D}_3^0)$. Let the corresponding reciprocal lattice be defined by,

$$\boldsymbol{B}_k^0 = [\boldsymbol{D}_i^0 \times \boldsymbol{D}_j^0]/(\boldsymbol{D}_i^0 \boldsymbol{D}_j^0 \boldsymbol{D}_k^0). \tag{2}$$

The polarization factor[8] now must be represented as follows:

$$1 - 1/\epsilon' = \phi = \sum \phi_m e^{-j(\boldsymbol{B}_m \cdot \boldsymbol{r})} \tag{3}$$

where

$$\boldsymbol{B}_m = \sum_{\alpha=1}^{3} m_\alpha \boldsymbol{B}_a^0.$$

By the definition (2) we are assured that each term in the series (3) is periodic with the three periods $(\boldsymbol{D}_1^0, \boldsymbol{D}_2^0, \boldsymbol{D}_3^0)$.

[8] This factor, as Laue points out, is akin to, and takes the place of the structure factor of the elementary theory; but only in so far as the polarization is proportional to the density of charge with a *constant* proportionality factor can it be said to be a measure of the distribution of charge.

Eq. (3) is formally the same as Eq. (1), the only differences being that ϕ and ϕ_m have replaced ψ and ψ_m, and $\boldsymbol{B}_m$ has replaced $\boldsymbol{b}_m$. From this it follows that any subsequent formula that may be derived on the basis of Eq. (3), in conjunction with Maxwell's questions, must be formally the same as the corresponding one derived by Laue on the basis of Eq. (1), since any subsequent development is of a purely mathematical nature. We can therefore write immediately in the place of Laue's fundamental Eqs. (I):[9]

$$\frac{K_m'^2 - k^2}{K_m'^2} \mathfrak{D}_m = \sum \phi_{m-q} \mathfrak{D}_{q[m]} \tag{I'}$$

where $\mathfrak{D}_m$ represents the electric displacement of the plane wave propagated in the direction of K_m' given by,

$$K_m' = K_0 + \boldsymbol{B}_m \tag{4}$$

and $\mathfrak{D}_{q[m]}$ represents the component of $\mathfrak{D}_q$ perpendicular to K_m'. k is the reciprocal of the vacuum wave-length.

When these conditions are fulfilled the solution of Maxwell's equations for a medium having the dielectric constant specified in Eq. (3) is given by,

$$\begin{aligned} \mathfrak{D} &= e^{i\nu t} \sum \mathfrak{D}_m e^{-i(\boldsymbol{K}_m' \cdot \boldsymbol{r})} \\ \mathfrak{H} &= e^{i\nu t} \sum \mathfrak{H}_m e^{-i(\boldsymbol{K}_m' \cdot \boldsymbol{r})} \end{aligned} \tag{5}$$

$\mathfrak{H}$ being the magnetic field strength.

Each member of this triple sum represents a plane wave propagated in the direction of K_m' with the phase velocity

$$v = \nu / |K_m'|$$

ν being the frequency of the wave field which is assumed to be monochromatic. The index of refraction of the plane wave therefore is given by:

$$n = c/v = c|K_m'|/\nu. \tag{6}$$

It follows moreover from Maxwell's equations that the electric vector $\mathfrak{D}_m$ is perpendicular to the vector K_m' as well as to $\mathfrak{H}_m$. Hereby the number of unknowns, (components of $\mathfrak{D}_m$ perpendicular to K_m'), as well as the number of algebraic equations in (I') is reduced to $2N$ where N is the total number of vectors $\mathfrak{D}_m$, in general infinity.

Now to solve the infinite set of linear, homogeneous Eqs. (I') in general, not only is impracticable by the methods of existing mathematics but also is useless, since as Laue points out, only a finite number of the plane waves have an appreciable intensity. If, therefore, we follow the example set by Laue and neglect all the vectors $\mathfrak{D}_m$ except those that have an appreciable absolute value, the fundamental Eqs. (I') reduce to a finite set of linear, homogeneous equations which can be solved by ordinary methods. The criterion by which this reduction is brought about is the same as that employed by Laue in the case of the ideal crystal, and for practical purposes is

[9] See reference 5, p. 139.

most easily obtained by geometrical considerations in the reciprocal space. For a detailed account of the method, however, we shall refer to Laue's admirable paper.[5] Here we shall only consider the changes brought about in the reciprocal lattice by the introduction of the secondary structure. Although the following assumption is not necessary, we shall for simplicity assume that the secondary structure belongs to the same crystallographic group as the primary structure. Then we have:

$$\boldsymbol{D}_i^0 = M_i \boldsymbol{a}_i^0; \qquad (i = 1, 2, 3) \quad (7)$$

where

$$M_1 \sim M_2 \sim M_3 \sim M \qquad (7a)$$

are integral numbers all of the same order of magnitude. From Eqs. (1a) and (2) it then follows that,

$$\boldsymbol{B}_i^0 = \boldsymbol{b}_i^0 / M_i \qquad (8)$$

By this equation the relation between respectively the primary and the secondary reciprocal lattice is determined.

Now in order to obtain a quantitative estimate of the effect of the secondary structure it is necessary first to derive the relative magnitudes of the Fourier coefficients ψ_m and ϕ_m appearing respectively in Eqs. (1) and (3). From the general theory it is known that the secondary structure must be considered as a very slight modulation of the primary structure. In other words,

$$\psi_P > \phi_\pi$$

provided the triplet $\pi = (\pi_1, \pi_2, \pi_3)$ does not represent an integral multiple of the triplet $M = (M_1, M_2, M_3)$. In the latter case, that is when $\pi = Mq = (q_1 M_1, q_2 M_2, q_3 M_3)$, the exponential function by which ϕ_π is multiplied in the summation (3) is the same as the exponential function by which ψ_q is multiplied in the summation (1), and we have,

$$\psi_q \sim \psi_P \sim \phi_{Mq}.$$

A closer estimate is possible by sacrificing some of the generality. That is, if we exclude the type of secondary structure in which the individual blocks are tilted with respect to each other, it is clear that the ratio ϕ_π / ψ_P must be of the order of magnitude of the relative amplitude of deviation in lattice constant from the primary value. This amplitude of deviation is given particularly on the basis of the one,[10] but also on the basis of the other,[11] of the two general types of secondary structure lately propounded in the literature, as follows:

$$\Delta/a \sim a/D \sim 1/M.$$

Consequently the relative order of magnitude of the two Fourier coefficients is given by,

[10] F. Zwicky, Helv. Phys. Acta **3**, 287 (1930).
[11] F. Zwicky, Phys. Rev. **38**, 1772 (1931).

$$\phi_\pi/\psi_P \sim 1/M; \qquad (\pi \neq M_q) \quad (9)$$

where M usually is of the order of 50 or larger.

Eqs. (8) and (9) in conjunction with the formulae derived by Laue enable us to arrive at the desired estimates. The constructions in the reciprocal space are the same as those employed by Laue except that a number of lattice points are added in accordance with Eq. (8) as illustrated in Fig. 1.

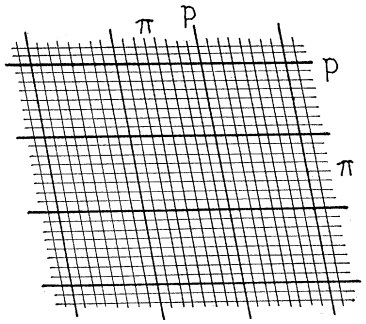

Fig. 1. Reciprocal lattice.

Associated with these additional lattice points are structure factors ϕ_π which bear the relation (9) to the factors ψ_P of the primary lattice points.

In the simplest possible case, that is when only one of the vectors $\mathcal{D}_m$, namely $\mathcal{D}_0$, has an appreciable absolute value, we obtain:

$$\mathcal{D}_\pi = (\phi_\pi/2\epsilon_\pi)\mathcal{D}_{0[\pi]}$$

$$\mathcal{D}_P = (\psi_P/2\epsilon_P)\mathcal{D}_{0[P]}.$$

Therefore, when the quantities ϵ_π and ϵ_P are roughly the same,[12] that is, when the "propagation sphere" passes at roughly the same distance from the secondary lattice point π as from the primary point p, and the geometrical status of the two points is otherwise roughly the same, our theory yields,

$$\mathcal{D}_\pi/\mathcal{D}_P \sim \phi_\pi/\psi_P$$

or by Eq. (9):

$$(\mathcal{D}_\pi/\mathcal{D}_P)^2 \sim 1/M^2. \qquad (10)$$

For the order of magnitude of M which we have indicated this ratio is very small. Nevertheless, when we consider the total or integrated energy scattered by the secondary structure we may arrive at a very sizable figure since the density of the secondary scattering centers in the reciprocal space is M^3 greater than that of the primary scattering centers. For the ordinary experimental setup, however, it is clear that this scattering from the secondary structure could be manifested only as an apparently diffuse background of radiation.

[12] See reference 5, Eq. (14a).

When more than one of the vectors $\mathfrak{D}_m$ have an appreciable absolute value we can usually write down relations similar in context to Eq. (10). Only in very particular cases do situations arise in which the plane wave created by interference from the secondary scattering centers is comparable in intensity with those produced under similar circumstances from the primary scattering centers. In these cases, however, the solid angular regions over which this intensity prevails is of the order $1/M^2$ for the secondary interference beams as compared with the primary ones. Therefore, again the experimental detection of the secondary interference beams would be very difficult.

We shall consider one such case somewhat more in detail, namely the practically very important Bragg reflection. This we shall do only in the symmetrical case, that is when the reflecting planes are parallel to the surface of the crystal. The more general case, where this condition is not fulfilled, presents no principally greater difficulties, but neither does it add any essentially novel features, so nothing is gained by its inclusion.

In the crystal of infinite thickness perpendicular to the reflecting planes the secondary as well as the primary structure will give rise to total reflection over certain angular regions. These angular regions are defined by the Eqs. IIIa and IVa derived by Laue,[13] equations which we shall reproduce here:

$$\chi_m = \chi_B + \psi_0/\sin 2\chi_B \tag{11}$$

$$\Delta\chi = 2(\psi_m\psi_{-m})^{1/2}/\sin 2\chi_B \tag{12}$$

where χ_B is the Bragg angle defined by the equation,

$$n\lambda = 2d\cos\chi_B$$

χ_m is the midpoint of the region of total reflection, and $\Delta\chi$ is the width of this region. In order to obtain the corresponding quantities for the reflection from the secondary structure it is only necessary to substitute ϕ_m for ψ_m and $D\sim Md$ for d. It follows immediately that,

$$\Delta\chi_\pi/\Delta\chi_P \sim |\phi_\pi| / |\psi_P| \sim 1/M. \tag{13}$$

For a somewhat divergent beam of incident, the apparent intensities of reflection are proportional to these widths. Again the intensity of reflection from the secondary structure is small compared with the intensity of reflection from the primary structure. Moreover, the interference maxima from the two structures ordinarily do not overlap[14] since ψ_P is of the order of magnitude 10^{-6} which hence is also the order of magnitude of the width $\Delta\chi_P$, whereas the distance between neighboring midpoints of the interference maxima is of the order $\lambda/2Md$ which is ordinarily very much larger than 10^{-6}. This type of secondary structure consequently produces no apparent widening of the primary lines, in contradistinction to the mosaic structure introduced by Darwin[15] to explain certain anomalies of x-ray reflection. Dar-

[13] See reference 5, p. 157.

[14] This is a point of considerable importance since otherwise it would be necessary to consider not only two of the rays $K_{m'}$ simultaneously but three.

[15] C. G. Darwin, Phil. Mag. **43**, 800 (1922).

win's type of mosaic structure is characterized by an angle of tilt between the elementary blocks. Such a contingency has not been taken into account in the present theory, and our results represent not a contradiction but rather a complement to those of Darwin. Whereas such an angle of tilt is apparently, in most cases, a necessary result of the energetic considerations which led to the second type of secondary structure,[11] the angle of tilt is not an adjunct of the secondary structure of the first kind.[10] In other words, our theory applies to the latter type of structure. Incidentally this was the type of structure employed by Zwicky[3] to explain the discrepancy between the values for the electronic charge obtained respectively by direct measurement and by x-ray analysis. If this discrepancy should turn out to be significant, Zwicky's explanation consequently will remain consistent with the great sharpness of the interference lines obtained from such crystals as calcite.

In spite of the weakness of the individual interference maxima arising from the secondary structure the total or integrated intensity obtained from this source when the crystal is turned through a certain finite angle may be quite appreciable, since the number of secondary interference maxima by the Bragg arrangement in general is M times greater than that of the primary maxima. Again, however, this "secondarily" reflected radiation would be manifested for experimental purposes, (with the employment of hard x-rays), as a diffuse background. This would be particularly true when the secondary structure is no longer ideal, but is degenerated into a mosaic structure, which is to be expected unless the crystal is grown under very carefully controlled conditions; for it is clear that the mosaic structure, in its effects, would bear a somewhat analogous relation to the ideal secondary structure, as the thermally agitated lattice, in its effects, bears to the ideal static one.

To complete the theory we shall consider briefly the effect of the finite thickness of the crystal. Total reflection, strictly speaking, is only obtained when the crystal is nonabsorbing and has an infinite thickness. When the crystal has a finite thickness some of the energy in the angular regions defined by Eqs. (11) and (12) is transmitted through the crystal. The energy of the transmitted beam drops off exponentially from the reflecting surface. The rapidity with which the intensity drops off depends on the coefficient in the exponent of the exponential factor. This coefficient, κ, which may be called the extinction coefficient varies from zero at one extremity of the angular region defined by Eqs. (11) and (12) through a maximum and back to zero at the other extremity. This maximum is given to a sufficiently close approximation by Laue's theory as follows:

$$\kappa_{\max} = k(\psi_m \psi_{-m})^{1/2}. \tag{14}$$

From this it is seen that the extinction coefficient is of the order M times greater for the primary interference beams than for the secondary ones. For crystals of finite thickness, therefore, the efficiency of reflection from the primary structure may be enormously greater than the efficiency of reflection from the secondary structure. Thus the relative intensity of the secondary interference beams is no longer given by the ratio $1/M$; this ratio now must

be multiplied by a factor containing exponential terms depending on the thickness of the crystal, and this factor may be very small when the crystal is thin although it reaches a value of unity asymptotically as the thickness is increased. Incidentally these considerations show that the intensity of the interference beams from the secondary structure must be reduced more by absorption than the primary beams, since the former traverse more of the crystal before they are reflected than the latter.

It should be noted that the present theory is only concerned with the *relative* intensities of the interference maxima for x-rays of the same wavelength. Nothing has been said about the absolute value of the Fourier coefficients involved, except in so far as they are known from measurements on the primary interference beams. It is therefore quite conceivable that measureable interference maxima from the secondary structure will be obtained when x-rays of sufficient softness to exclude the primary lines are employed. In this case, moreover, it is doubtful whether or not Laue's theory is applicable since the boundary solution, (i.e., the interference pattern from the cross grating forming the boundary of the crystal), might be expected to come within the region of observables.