# KINEMATICAL AND DYNAMICAL DIFFRACTION THEORIES

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## INTRODUCTION

Dynamical theory is the name given to the theory of diffraction of a wave by a perfect crystal. It differs from the kinematical, or geometric, theory used in structure determination problems in that it takes into account the influence of matter on the wave. Although it is as old as the discovery of X-ray diffraction, it has only been widely used for the past twenty years or so. This is due partly to the fact that before that time no perfect enough crystals were available to test it and partly to the fact that it became necessary in order to interpret the contrast of defect images in electron microscopy and X-ray or neutron topography. These techniques were, at least for the former two, developped more than twenty years ago, the latter beeing more recent. Very interesting optical problems related to the energy propagation arise at the vicinity of BRAGG's condition, both in perfect crystals for fundamental reasons and in crystals containing isolated defects since they enable these defects to be visualized. A concice bibliography on geometrical and dynamical theories is given in (1).

## I.- PRINCIPLE OF THE KINEMATICAL, OR GEOMETRICAL THEORY

The principle of the kinematical or geometrical theory is to consider a spatial distribution of identical scattering centers and to assume that the amplitude of the incident wave is constant at each of these centers. The total amplitude diffracted in a given direction is therefore obtained by summing the amplitudes scattered by each center taking simply into account the phase relationships between them. This is only possible if the interaction between the incident wave and the scattering centers is so weak that partial reflections can be neglected. This approximation is no more valid for large perfect crystals and it is precisely the aim of the dynamical theory to take the above mentioned interaction into account.

Let O and P be two identical scattering centers and $\vec{k}_o = \vec{s}_o/\lambda$ the wave vector of an incident plane wave (fig. 1). Each center scatters this incident wave in every

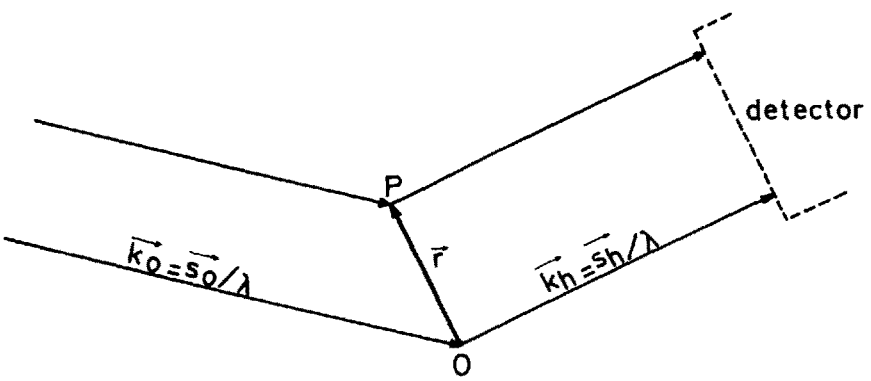



Fig. 1

direction. Let us consider one of them and place a receptor at a distance which is very large with respect to $\overrightarrow{OP} = \vec{r}$. We can assume that the receptor receives plane waves emitted at O and P and let $\vec{k}_h = \vec{s}_h/\lambda$ be their wave vector. Their phase difference is given by :

$$(1) \qquad \phi = \frac{2\pi}{\lambda} (\vec{s}_h - \vec{s}_o).\vec{r} = 2\pi\, (\vec{k}_h - \vec{k}_o).\vec{r} = 2\pi\, \overrightarrow{\Delta k}.\vec{r}$$

If a is the amplitude scattered by each center in the direction of $\vec{k}_h$, the total amplitude diffracted by n centers is equal to :

$$A(\Delta\vec{k}) = a \sum_{i}^{n} e^{-2\pi i\, \Delta\vec{k}.\vec{r}_i}$$

where $\vec{r}_i$ is the position vector of the ith center.

If we now consider a continuous distribution of centers and if $\rho(\vec{r})\ d\tau$ is the number of centers contained in volume element $d\tau$, the total diffracted amplitude is equal to :

$$(2) \qquad A(\vec{\Delta k}) = a \int \rho(\vec{r})\ e^{-2\pi i\ \vec{\Delta k}.\vec{r}}\ d\tau$$

If the distribution of centers extends over an infinite volume, this amplitude is equal to :

$$(3) \qquad A_\infty\ (\vec{\Delta k}) = a\ \mathcal{F}[\rho(\vec{r})]$$

where $\mathcal{F}[\rho(\vec{r})]$ is the Fourier transform of $\rho(\vec{r})$.

If, furthermore, the distribution $\rho(\vec{r})$ is triply periodic, that is if we are dealing with a perfect crystal, it can be written :

$$(4) \qquad \rho(\vec{r}) = \rho_o(\vec{r}) \ * \sum_{u_i v_i w_i} \delta(\vec{r}-\vec{r}_i)$$

where $\rho_o(\vec{r})$ is the distribution within the unit cell and

$$\vec{r}_i = u_i\vec{a} + v_i\vec{b} + w_i\vec{c}$$

is the position vector of a cell. Using (3) and (4), we obtain :

$$(5) \qquad A_\infty\ (\vec{\Delta k}) = \ aF(\vec{\Delta k}) \sum_{h,k,\ell} \delta(\vec{\Delta k}-\vec{h})$$

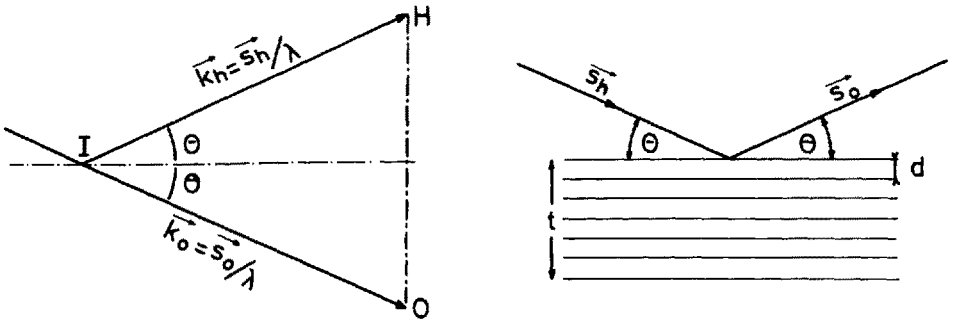
where $\vec{h} = h\vec{a}^* + k\vec{b}^* + \ell\vec{c}^*$ is a reciprocal lettice vector and $F(\vec{\Delta k})$ is the Fourier transform of $\rho_o(\vec{r})$. It is called the structure factor. The amplitude distribution $A_\infty$ is concentrated at the reciprocal lattice nodes. It is therefore only necessary to consider the values $F_{hk\ell}$ of $F(\vec{\Delta k})$ at these points. They are equal to

$$(6) \qquad F_{hk\ell} = \int_{\text{one cell}} \rho(\vec{r})\ e^{-2\pi i\ \vec{h}.\vec{r}}\ d\tau$$

and

$$(7) \qquad A_\infty(\vec{\Delta k}) = a \sum_{h,k,\ell} F_{hk\ell}\delta(\vec{\Delta k}-\vec{h})$$

The fact that the diffracted amplitude is only different from zero if $\vec{\Delta k}$ is a reciprocal lattice vector is equivalent to BRAGG's law. (fig. 2)




$\vec{OH}$ : reciprocal lattice vector

d : lattice spacing
t : crystal thickness
θ : Bragg angle

reciprocal space

direct space

$$\frac{OH}{2} = \frac{1}{\lambda} \sin\theta \; ; \quad OH = n/d \qquad 2d \sin\theta = n\lambda$$

Fig. 2

Actually, the crystal is finite. If $y(\vec{r})$ is a step function equal to 1 inside the crystal and to zero outside, the diffracted amplitude is equal to :

(8) $\quad A(\vec{\Delta k}) = a \; \mathcal{F}t \; [\rho(\vec{r}) \; y(\vec{r})]$

If $Y(\vec{k})$ is the Fourier transform of $y(\vec{r})$, the amplitude distribution in reciprocal space is given by :

(9) $\quad A(\vec{\Delta k}) = A_{\infty} \; (\Delta k) \; * \; Y(\vec{\Delta k})$

Equations (7) and (9) show that the amplitude distribution is now a continuous function, triply periodic in reciprocal space. Around each reciprocal lattice point h,k,ℓ, it is equal to

(10) $\quad A(\vec{\Delta k}) = a \; F_{hk\ell} \; Y(\vec{\Delta k} - \vec{h})$

and the corresponding intensity to

(11) $\quad I = |a|^2 |F_{hk\ell}|^2 |Y|^2$

It can be shown, for instance, that in the case of an infinite crystal slice of thickness t (fig. 2), the interference function $|Y|^2$ is proportional

to

$$\frac{\sin^2 (\pi X t/d)}{\pi^2 X^2}$$

where $X = 2d\Delta\theta \cos\theta/\lambda$, d is the lattice spacing and $\Delta\theta$ the departure from BRAGG's law of the incident plane wave.

If the crystal is oscillated in the incident beam around the normal to the $\vec{k}_o$, $\vec{k}_h$ plane and the variations of the diffracted intensity are recorded in a detector, the shape of the rocking curve obtained (Fig 3) and in particular its half width only depends on the crystal thickness. The value of the maximum is proportional to the square of the modulus of the structure factor.

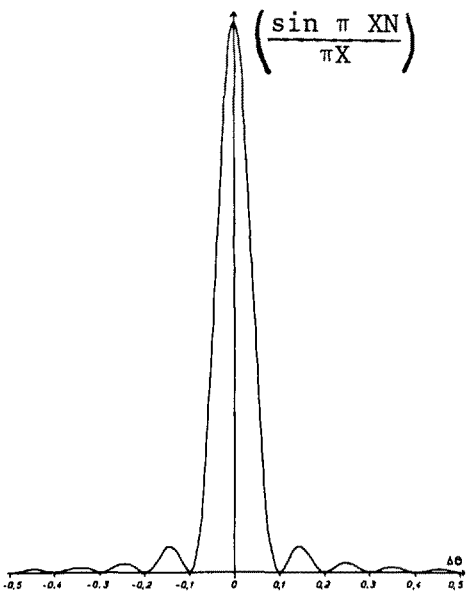



Fig. 3

Rocking curve for a thin crystal - Geometrical theory

The quantity which is actually used in practice is the total intensity received in the detector as the crystal is rocked : it is called integrated intensity. It is proportional to the area under the curve of figure 3. Its calculation shows that it is proportional to $|F_{hk\ell}|^2$ and to the crystal volume bathed in the incident beam. Its expression is only applicable to small enough crystals or to the so called "ideally imperfect" crystals which are made of small incoherent domains which can be considered to diffract the incident beam independantly. How "small" the crystal should be for the geometrical theory to be a good approximation is determined by the dynamical theory.

## II.- PRINCIPLES OF THE DYNAMICAL THEORY

Dynamical theory is really a part of general optics and started out from optics. Its foundations were laid by P.P. EWALD even before the discovery of X-ray diffraction by M. von LAUE, W. FRIEDRICH and P. KNIPPING(2) in 1912 : the topic given him for his thesis by SOMMERFELD was the interpretation of double refraction in terms of the diffraction of an electromagnetic wave by a triply periodic anisotropic arrangement of isotropic dipoles. His work led to the formulation of the dynamical theory published in 1917 (3).

Independantly, another approach to the dynamical theory was developped by C.DARWIN in 1914 (4). It is based on the resolution of recurrence equations which state the balance between partially transmitted and partially reflected waves at each lattice plane. Its results are the same as those of the EWALD theory but it is not quite so convenient for the study of the energy propagation. It is very useful for the interpretation of optical phenomena related to dynamical diffraction as will be shown further on.

The formulation of the dynamical theory of X-ray diffraction which is widely used nowadays is that due to M. von LAUE and was derived in 1931 from EWALD's theory (5). It is based on the solution of Maxwell's equations in a medium with a triply periodic continuous electric susceptibility. Since the interaction with protons can be neglected, only electrons need be taken into account and a classical calculation shows that the electric susceptibility is equal to :

$$(12) \qquad \chi(\vec{r}) = -\frac{R\lambda^2}{\pi}\,\rho(\vec{r})$$

where $R$ is the classical radius of the electron and $\rho(\vec{r})$ the electronic density.

In a crystal, $\rho(\vec{r})$ and $\chi(\vec{r})$ are triply periodic and can be expanded in Fourier series :

$$(13) \qquad \chi(\vec{r}) = \sum_{h,k,\ell} \chi_h \exp 2\pi i\, \vec{h}.\vec{r}$$

with $\chi_h = -\frac{R\lambda^2}{\pi V} F_{hk\ell}$

where $V$ is the volume of the unit-cell and the structure factors $F_{hk\ell}$ are proportional to the coefficient of the Fourier expansion of the electronic density (eqs. (7) and (8)).

By eliminating $\vec{E}$, $\vec{B}$ and $\vec{H}$ in Maxwell's equations, the propagation is obtained :

$$(14) \qquad \Delta\vec{D} + \text{curl curl } \chi\vec{D} + 4\pi^2k^2\vec{D} = 0$$

This equation is actually very similar to the wave equation used in the case of particle waves, since Schrödinger's equation can be written

$$(15) \qquad \Delta\psi + 4\pi^2k^2 (1+\chi) \psi = 0$$

where $\chi$ is proportional to the crystal electric potential, for instance.

Equations (14) and (15) are both second order linear partial derivative equations and their solutions have very similar properties. They differ in the particular properties of the wave : electrons, neutrons or X-rays. Equation (14) is more complicated since electromagnetic waves are vector waves and this leads to polarization effects which are discussed in P. SKALICKY's paper (5). They will not be considered here and the discussion will be limited to that of equation (15).

The theory of electrons in solids also considers solutions of equation (15), but with the boundary conditions that the electrons should be limited to the inside of the crystal, which is written through BORN's cyclic conditions. The solutions provide the various possible values of the energy of the electrons for given values of their wave-vectors. In the case of diffraction, the boundary condition is that the wave inside the crystal should be matched at the surfaces with the incident and reflected waves, and the solutions provide the various possible wave vectors for a constant energy. The latter is equal to that of the incident wave. The solutions in both cases have great similarities since they are subsets of the same general solution, but with different boundary conditions. In particular, to the energy gap in band theory corresponds a gap between the branches of the dispersion surface in diffraction theory. The dispersion surface is the locus of the extremities of the wave-vectors which can propagate inside the crystal.

The solution of equation (15) when the interaction term $\chi$ is triply periodic is a combination of Bloch waves :

$$(16) \qquad \psi = \exp - 2\pi i \vec{k}_o.\vec{r} \sum_h \psi_h \exp 2\pi i \vec{h}.\vec{r}$$

It can also be written in the following way :

$$(16') \qquad \psi = \sum_h \chi_h \exp - 2\pi i \vec{k}_h.\vec{r}$$

(17)with $\vec{k}_h = \vec{k}_o - \vec{h}$

It shows that each particular solution of the wave equation is a wave field, that is a sum of plane waves of amplitude $\psi_h$ whose wave vectors can be deduced from one another by reciprocal lattice translations (fig. 4).

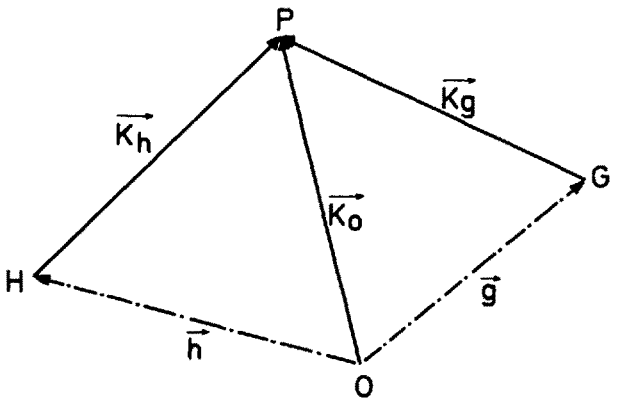



Fig. 4

The tie-point P characterizing a wave-field is the extremity of wave vectors $\vec{k}_o$, $\vec{k}_h$, $\vec{k}_g$ etc ... of the waves which constitute the wave field.

The propagation properties of X-rays in a perfect or nearly perfect crystal can be interpretated in terms of the optical paths of these wave fields inside the crystal. It is no more true, however, in the case of a highly distorted crystal, as is shown in the paper by F. BALIBAR (7). The wave field treatment is also only valid for an incident plane wave. It can be extended, with limitations, to incident wave packets or spherical waves by considering their Fourier expansion as has been done by N. KATO, but not to any kind of incident wave. This important point is also discussed by F. BALIBAR (7).

## III.- FUNDAMENTAL EQUATIONS OF THE DYNAMICAL THEORY - PROPERTIES OF WAVE-FIELDS

If we put expansions (16') and (13) in equation (15), we obtain an equation with an infinite number of terms which is equivalent to an infinite set of linear equations :

$$(18) \qquad \psi_h = \frac{k_h^2}{k_h^2 - k^2} \sum_{h'} \chi_{h-h'} \psi_{h'}$$

when $\chi_{h-h'}$ is the Fourier coefficient corresponding to the $\vec{h}-\vec{h}'$ reciprocal lattice point.

Although it cannot be proved rigorously it is clear that only a limited number of terms of expansion (16') takes non negligible values , those which correspond to wave numbers $k_h$ very close to the wave number in vacuum, $k$ , in other words, those which are associated with reciprocal lattice points lying simultaneously close to the Ewald sphere. This number is usually big in the case of electron diffraction since the wave length is to small and the radius of the Ewald sphere so large, but small in the case of X-rays or neutrons.

The system (18) is linear and homogenous in $\psi_h$. For it to have a non trivial solution, its determinant should be equal to zero. This provides a relation between the values of the wave vectors of the plane wave components of the wave field and shows that the extremity, called tie-point, of these wave vectors, drawn from the various reciprocal lattice points (eq. 17, fig. 4) should lie on a certain surface which is the dispersion surface.

We shall limit ourselves to the two beam cases and consider what happens in the plane parallel to the wave vectors, $\vec{k}_o$ and $\vec{k}_h$, of the two waves. The system (18) reduces in this case to two equations :

$$(19) \qquad \begin{cases} 2X_o \psi_o - k \chi_{\bar{h}} \psi_h = 0 \\ -k\chi_h \psi_o + 2 X_h \psi_h = 0 \end{cases}$$

where $X_o$ and $X_h$ are respectively the distances of the tie-point P from the two spheres centered at the reciprocal lattice points O and H and with radius $n/\lambda$, $n = (1 + \chi_o/2)$ is the index of refraction (fig. 5)

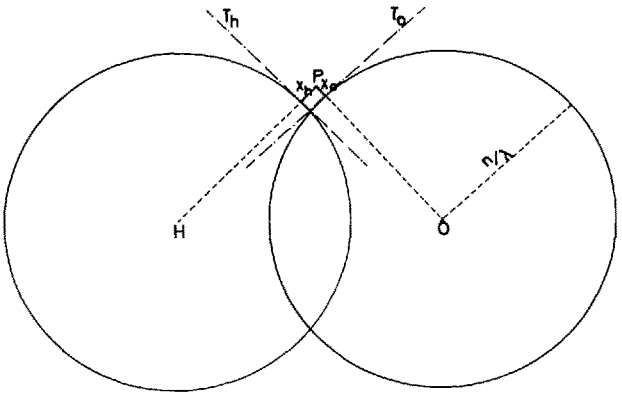



Fig. 5

If we equate the determinant of system (19) to zero, we obtain the following equation :

(20) $\quad X_o\, X_h = k^2\, \chi_h\, \chi_{\bar{h}}/4$

Since the values of $\chi_h$ and $\chi_{\bar{h}}$ are very small, of the order of $10^{-5}$, $X_o$ and $X_h$ are very small with respect to the radii of the spheres which can therefore be replaced by their tangential planes.

Equation (20) shows therefore that if we consider the $\vec{k}_o$, $\vec{k}_h$ plane, the tie-point lies on a hyperbola asymptotic to the tangents to the circles centered in O and H and with radii $k(1 + \chi_o/2)$ (fig. 6).

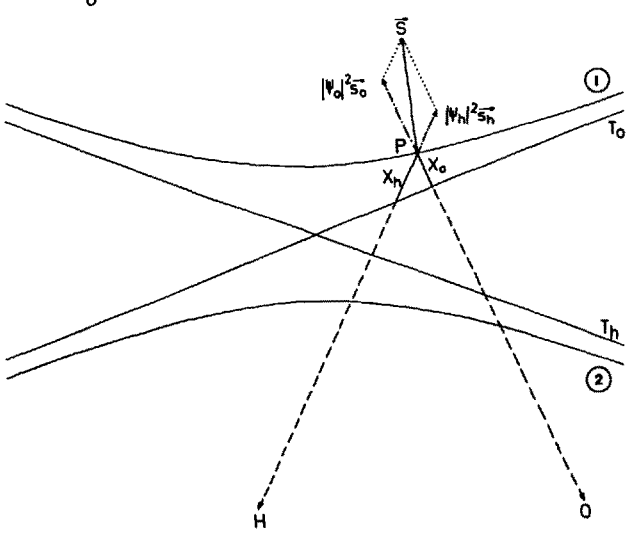



Fig. 6 : Dispersion surface

The diameter of this hyperbola is equal to :

$$(21) \qquad \Lambda_o^{-1} = k\sqrt{\chi_h \chi_{\bar{h}}} \,/\, \cos\theta = R\lambda F_{hk\ell} / V \cos\theta$$

it is directly proportional to the strength of the interaction between the waves and matter.

The wave-fields defined by equation (16') are not simply a mathematical concept. They also have a physical reality and can actually be observed. Their physical reality is shown in particular by their propagation and absorption properties.

It can be shown either by calculating the POynting vector or the group velocity of a wave packet that the common direction of energy propagation of all the waves which constitute a wave field is along the normal to the dispersion surface at the tie-point associated with the wave field. In the two beam case, the propagation direction is given by that of the vector (fig. 6)

$$(22) \qquad \vec{S} = |\psi_o|^2 \vec{s}_o + |\psi_h|^2 \vec{s}_h$$

where $\psi_o$ and $\psi_h$ are respectively the amplitudes of the refracted and reflected wave components of the wave-field.

A very important property of the wave fields is that of anomalous transmission or BORRMANN effect (8). It can be readily understood by considering the interferences between the waves which constitute a wave field. In the two beam case, expansion (16) reduces to :

$$(23) \qquad \psi = \exp - 2\pi i \vec{k}_o.\vec{r} \; [\psi_o + \psi_h \exp 2\pi i \vec{h}.\vec{r}]$$

and the intensity of the wave-field is given by

$$(24) \qquad I = |\psi_o|^2 [1 + |\frac{\psi_h}{\psi_o}|^2 + 2 \frac{\psi_h}{\psi_o} \cos 2\pi \vec{h}.\vec{r}]$$

Equation (24) shows that a set of standing waves is formed. The nodes lie on planes such that $\vec{h}.\vec{r}$ should be constant, that is having the same spacing as that of the lattice planes. Depending on the sign of $\psi_h/\psi_o$ either the nodes or the antinodes lie on the planes of maximum electronic density. It can be shown that it is the nodes for wave fields where tie-points lie on branch 1 of the dispersion surface (fig. 6) and the antinodes for branch 2. There is therefore a minimum of electric field on the atoms for branch 1 wave-fields and thus a minimum of photoelectric

absorption and anomalous transmission. It is just the opposite for branch 2 wave fields. This effect is very sensitive to displacements of the atoms from their triply periodic equilibrium position. It is therefore reduced when temperature increases because of thermal vibrations, or when a high density of microdefects is present in the crystal.

## IV.- BOUNDARY CONDITIONS FOR AN INCIDENT PLANE WAVE - RELATION BETWEEN GEOMETRICAL AND DYNAMICAL THEORIES

There are two boundary conditions at the surfaces of the crystal which relate the waves inside and outside the crystal :

1/ - continuity of the tangential components of the wave vectors
2/ - continuity of the tangential components of the electric field and of the normal components of the electric displacement.

The first condition provides a geometrical construction to determine the wave fields which are actually excited inside the crystal by the incident wave : their tie-points lie at the intersections of the dispersion surface and the normal to the crystal surface drawn from the extremity of the wave vector in vacuum.

In transmission geometry (LAUE case), these tie-points lie on the two different branches of the dispersion surface and two wave fields are excited which propagate through the crystal. These wave fields interfere giving rise to fringes which were called "Pendellösung" fringes by P.P. EWALD because they are associated with periodic exchanges of energy between the refracted and reflected components of the wave-fields. The period of these fringes in direct space is equal to the parameter $\Lambda_o$ defined by equation (21) multiplied by a geometrical factor depending on the relative orientation of the normal to the crystal surface and the reflecting planes.

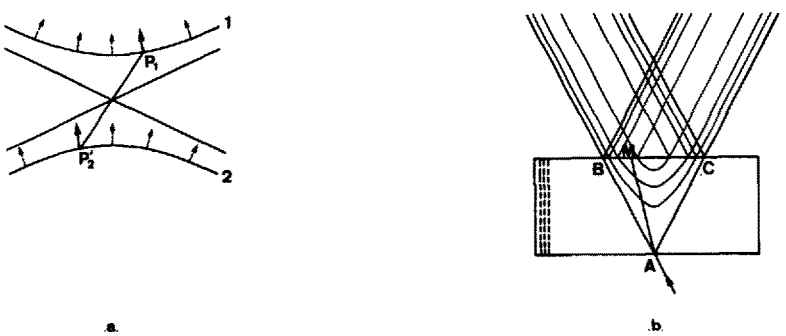
In reflection geometry (BRAGG case), the normal to the crystal surface intersects the dispersion surface either at two real points of the same branch or at two imaginary points. Two cases are to be considered : thick and thin crystals. In the thick crystal case, it can be shown that only one intersection point should be taken into account and there is total reflection of the incident wave. The width of the rocking curve is inversely proportional to $k \Lambda_o$ and, from equation (21), proportional to $\lambda^2 F_{hk\ell}$. In the thin crystal case, both intersection points must be taken into acaount and interferences occur between the corresponding wave fields. The total reflection domain disappears and oscillations appear in the rocking curve. The shape and width of the rocking curve tend asymptotically towards those given by the geometrical

theory as the ratio $t/\Lambda_o$ becomes much smaller than one (t is the crystal thickness). Equation (21) shows that this ratio is proportional to $t \lambda F_{hk\ell}$. For a given crystal thickness and a given reflection, this ratio is very small for a very small wavelength, for instance for $\gamma$-rays, and geometrical theory is a good approximation, while, for longer wave lengths such as CuK$\alpha$, the ratio may be large enough for dynamical theory to be necessary. In a similar way, for a given crystal thickness and a given wave length, dynamical theory may be necessary for the strongest, low order reflections, while geometrical theory is in general a good enough approximation for the weak high order reflections. Since the latter form the majority of reflections used for structure determinations, this explains why geometrical theory suffices for this purpose.

## V.- DIFFRACTION OF A SPHERICAL WAVE

The above discussion applies to an incident plane wave. Actually, it is not possible to generate a true plane wave for X-rays. Pseudo plane waves can be obtained with particular settings, but normally, X-rays are produced as spherical waves.

The diffraction of a spherical wave may be treated by generalizing the solutions (16) of the wave equation. This was done by S.TAKAGI (19) who considered that the amplitudes $\psi_h$ are slowly varying functions of position. The fundamental linear equations (18) are then replaced by partial derivative equations which admit analytical solutions for a spherical wave incident on a perfect crystal. Another method was used by N.KATO (10). He summed the diffracted waves associated to the plane wave components of the Fourier expansion of the spherical wave. This approach enables to keep the geometrical description provided by the dispersion surface. Each of its points is now simultaneously excited and wave fields are generated which propagate in all the directions which lie between the incident and reflected directions : they fill out a triangle, called the BORRMANN triangle (11) (fig. 7)




Reciprocal space Direct space

Fig. 7 - Diffraction of a spherical wave in transmission geometry

Among the optical properties related to the diffraction of a spherical wave, two important ones may be selected out :

1/ - Pendellösung fringes : two wave fields propagate along any path AM within the BORRMANN triangle (fig. 7) These tie-points lie on different branches of the dispersion surface and are actually at the extremities of a diameter (fig. 7).These wave fields give rise to interference fringes first observed by N.KATO and A.R. LANG (12) and interpreted by N.KATO (10). These fringes are only visible for non too absorbing crystals since branch 2 wave-fields are anomalously highly absorbed. They are sensitive to the presence of defects and microdefects and their presence is a good test of crystalline perfection.

2/ - Angular amplification : a narrow wave packet of angular width $\delta\theta$ within the incident wave generates inside the crystal a packet of wave-fields. If the angular width of the paths of these wave fields is $\delta\alpha$, the ratio $\delta\alpha/\delta\theta$ , or amplification ratio varies greatly within the BORRMANN triangle : it is equal to one on the sides and becomes very large, of the order of $\Lambda_o/\lambda$ in the center. The consequence is that for all the optical problems related to the propagation of wave fields in the central part of the BORRMANN triangle it is $\Lambda_o$ which should be considered as the wave length rather than $\lambda$.

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