

Theory of X-Ray plane wave multiple diffraction

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1. INTRODUCTION

Despite the fact that a real coherent wave is a spherical monochromatic wave rather than a plane monochromatic wave, the theory of X-ray diffraction in single crystals as it has been developed by Ewald and Laue:

- P. P. Ewald, *Zur Begründung der Kristalloptik*.
 - . Teil 1. - Ann. Phys., 1916, vol. 49, N. 1, p.1-38;
 - . Teil 2. - Ann. Phys., 1916, vol. 49, N. 2, p. 117-143;
 - . Teil 3. - Ann. Phys., 1917, vol. 54, N. 23, p. 519-556, N. 24, p. 557-597;
 - . Teil 4. - Z. Kristall., 1937, vol. A97, N. 1/2, 1-27.
- M. Laue, *Ergebnisse der Exakten Naturwissenschaften*,
 - . vol. 10, Berlin, Julius Springer, 1931, p. 133-158.

considers the plane monochromatic waves.

The reason is easy to understand taking into account that the single crystal is a macroscopically homogeneous object. Therefore the plane wave being scattered coherently conserves its form to a great extent. The other reason is a small value of interaction between X-rays and atoms of the crystal. So we need to take into account a large piece of crystal containing many atoms along the X-ray path for obtaining the significant effect.

The procedure of summation over all atoms is simplest for a plane wave. One more reason is that X-rays have very small wavelength, so it is hard radiation. For such a radiation the geometrical optics works good and the plane wave can be considered as an approximation for each ray. An initial formulation of the theory, given by Ewald, was based on the model of crystal as a periodic lattice of dipoles. Laue introduced the model of crystal as a volume with a periodic distribution of complex susceptibility which plays the role of scattering amplitude for X-rays. Such a model allows us to introduce the Maxwell's equations and considers the periodic solutions which was called later Bloch waves.

2. BLOCH THEOREM AND THE STRUCTURE OF WAVE FIELD IN CRYSTAL

The Bloch theorem reads that we cannot consider a plane monochromatic wave

$$\mathbf{E}_0(\mathbf{r}, t) = \mathbf{E}_0 \exp(i\mathbf{k}_0\mathbf{r} - i\omega t) \quad (1)$$

with a wave vector \mathbf{k}_0 and a frequency ω to be alone inside the crystal. The solution of Maxwell's equation inside a medium having a periodic structure must be the Bloch wave

$$\mathbf{E}(\mathbf{r}, t) = \sum_{\mathbf{h}} \mathbf{E}_{\mathbf{h}}(\omega) \exp(i\mathbf{k}_{\mathbf{h}}\mathbf{r} - i\omega t), \quad \mathbf{k}_{\mathbf{h}} = \mathbf{k}_0 + \mathbf{h} \quad (2)$$

where \mathbf{h} is the reciprocal lattice vector and the sum is taken over all the reciprocal lattice vectors of the crystal including the value $\mathbf{h} = 0$. Just such a wave satisfies the translational symmetry of the crystal when any function must have a property $f(\mathbf{r} + \mathbf{a}) = f(\mathbf{a})$ where \mathbf{a} is one of the three lattice parameters (parameters of the unit cell).

The induced current density $\mathbf{j}(\mathbf{r}, t)$ of the Maxwell's equation

$$\left(\text{grad}^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \mathbf{E}(\mathbf{r}, t) = \frac{4\pi}{c^2} \frac{\partial \mathbf{j}(\mathbf{r}, t)}{\partial t} \quad (3)$$

is also the Bloch wave

$$\mathbf{j}(\mathbf{r}, t) = \sum_{\mathbf{h}} \mathbf{j}_{\mathbf{h}}(\omega) \exp(i\mathbf{k}_{\mathbf{h}}\mathbf{r} - i\omega t). \quad (4)$$

In a frame of linear optics the coefficients of such an expansion are expressed, in general case, through the Fourier components of the complex susceptibility tensor $\chi_{\omega}^{\alpha\beta}(\mathbf{k}_{\mathbf{h}}, \mathbf{k}_{\mathbf{g}})$ of the crystal and the electric field coefficients, namely,

$$j_{\mathbf{h}}^{\alpha}(\omega) = \frac{\omega}{4\pi i} \sum_{\beta, \mathbf{g}} X_{\omega}^{\alpha\beta}(\mathbf{k}_{\mathbf{h}}, \mathbf{k}_{\mathbf{g}}) E_{\mathbf{g}}^{\beta}(\omega). \quad (5)$$

Here \mathbf{g} is other reciprocal lattice vector and $\alpha, \beta = x, y, z$ are the vector indexes. The nonlinear optics, like Laser optics, is impossible for X-rays up to now and will not be considered.

Substituting Eq.(2) and Eq.(4) into Eq.(3) and taking into account Eq.(5) one obtains the infinite set of linear algebraic equations instead of differential equation

$$[k_{\mathbf{h}}^2 - K^2] E_{\mathbf{h}}^{\alpha}(\omega) = K^2 \sum_{\beta, \mathbf{g}} X_{\omega}^{\alpha\beta}(\mathbf{k}_{\mathbf{h}}, \mathbf{k}_{\mathbf{g}}) E_{\mathbf{g}}^{\beta}(\omega) \quad (6)$$

where $K = \omega/c$ as before. To obtain the understanding what kind of equation we have here we need to analyze first the coefficients which are, in general, Fourier components of the crystal susceptibility.

3. SUSCEPTIBILITY (KINEMATICAL SCATTERING AMPLITUDE)

3.1 Rayleigh scattering

Let us consider the structure of the susceptibility tensor $X_{\omega}^{\alpha\beta}(\mathbf{k}_{\mathbf{h}}, \mathbf{k}_{\mathbf{g}})$. It allows us to understand better possible phenomena of X-ray diffraction. A modern science calculates the Fourier components of the susceptibility tensor considering the induced current density in a frame of quantum mechanics theory as a quantum mechanical average of the current density operator over the wave function of the crystal disturbed by electric field. Since the interaction between the X-rays and medium is small, the first order of the perturbation theory is enough (linear optics). We shall consider only elastic processes which don't change the frequency of the radiation. The inelastic processes cannot lead to coherent phenomena. In general case, the susceptibility turns out to be the complex value. The real part describes the *scattering processes* while the imaginary part describes the *absorption processes* which lead to decreasing the intensity of X-ray beam.

The main process which gives a large contribution is the *Rayleigh scattering* on the inhomogeneous electron density. This process is classic and it can be calculated to a great extent from the Newton mechanics. Let us consider first this way of derivation. One electron contributes the value ev to the induced current density, where e is the electron charge and v is the additional contribution to the electron velocity due to the electric field. The velocity has a direction along the direction of amplitude of electric field. We may obtain the value of velocity from the Newton equation. However, we shall keep the complex form of Fourier transformation to be consistent with Maxwell's equation where the same form of Fourier transformation is used. So we obtain

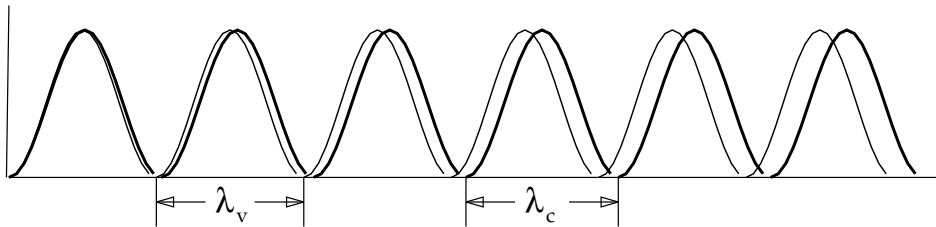


FIG. 1. Wavelength of X-rays in crystal is greater than in vacuum

$$m \frac{dv}{dt} = eE(\omega) \exp(-i\omega t), \quad v(\omega) = \frac{ie}{m\omega} E(\omega). \quad (7)$$

Therefore the induced current of one electron is

$$j(\omega) = \frac{ie^2}{m\omega} E(\omega). \quad (8)$$

As a result, we calculate the susceptibility per one electron as

$$X(\omega) = \frac{4\pi i}{\omega} \frac{j(\omega)}{E(\omega)} = -\frac{4\pi e^2}{m\omega^2}. \quad (9)$$

This formula shows the frequency dependence of the susceptibility and the property that the current has the same polarization as the electric field. In case of homogeneous electron density we may estimate the value of zero Fourier component of susceptibility.

The second consequence is that the susceptibility is negative. Once again in case of quasi homogeneous electron density in the medium this property leads to the fact that the speed of light in a medium becomes larger than in vacuum as it is shown on the Fig.1. In the volume filled by electrons the wavelength of X-rays becomes $\lambda_c = \lambda_v / \sqrt{\epsilon} \approx \lambda_v / (1 + \chi_0/2)$.

To obtain the space dependence we need to consider the periodic distribution of number of electrons in space. In addition, we must take into account that the electron density of each atom takes part in the thermal vibrations of crystal lattice together with nuclei. Within the approximation of hard atoms the space Fourier components of the crystal electron density can be obtained as a sum of contributions from all atoms. The atoms may be considered approximately as having the same electron density as free atoms. It

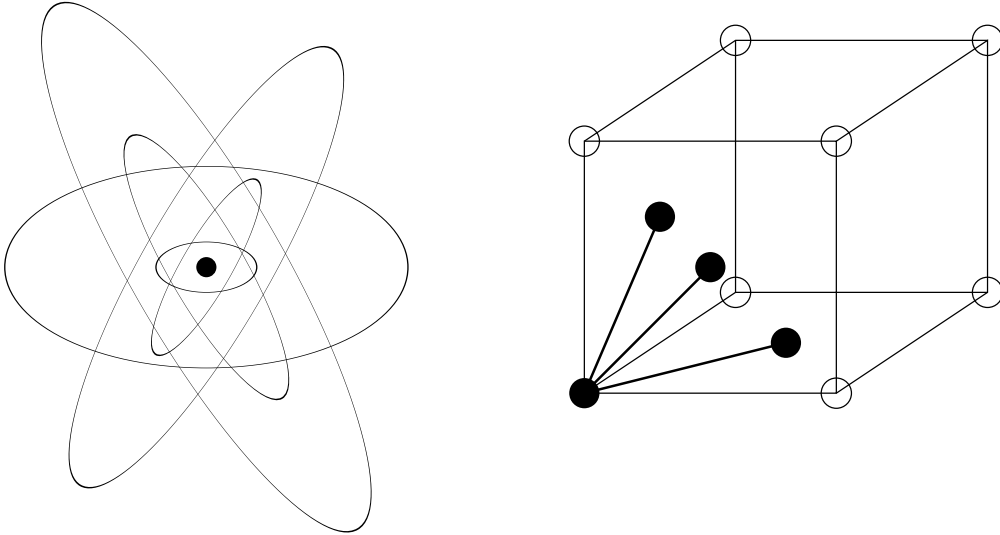


FIG. 2. The electron location may be divided on the electron location near the atom (left) and the location of atoms inside the unit cell(right)

is shown schematically in the Fig.2. In the case of face-centered cubic crystal lattice we have four atoms inside the unit cell. Such an approximation is rather good because all electrons of atom scatter the X-rays and the electrons of internal shells does not feel the influence of other atoms. As a result, the total expression of the Rayleigh contribution to the susceptibility can be written as

$$X_{\omega}^{\alpha\beta}(\mathbf{k}_{\mathbf{h}}, \mathbf{k}_{\mathbf{g}})|_{Rayleigh} = \delta^{\alpha\beta} \chi_{\mathbf{h}-\mathbf{g}}, \quad (10)$$

where

$$\chi_{\mathbf{h}} = -\frac{4\pi e^2}{m\omega^2 V_0} \sum_j f_j(\mathbf{h}) \exp(-i\mathbf{h}\mathbf{r}_j) \exp[-W_j(\mathbf{h})/2]. \quad (11)$$

Here the sum is carried out over the different atoms inside the unit cell of the crystal lattice (see Fig.2 for the face-centered cubic lattice), V_0 is the volume of the unit cell, therefore $1/V_0$ is a number of unit cells inside the unit volume, $f_j(\mathbf{h})$ is the space Fourier component of the electron density of atom having an index j on the reciprocal lattice vector \mathbf{h} (it is named usually atomic scattering factor or form-factor), \mathbf{r}_j is a coordinate of the j -th atom relative to an origin of the unit cell, $\exp[-W_j(\mathbf{h})]$ is the Debye-Waller factor which takes into account a random mean square displacement $\langle u_j^2 \rangle$ of the atom j from the equilibrium position inside the lattice $W_j(\mathbf{h}) = h^2 \langle u_j^2 \rangle$. The value $\langle u_j^2 \rangle$ depends on temperature.

3.2 Resonant scattering (photoelectron emission)

The expression of Eq.(11) is accurate in both classic and quantum mechanics. Let us introduce now the resonance (dispersion) contributions to the susceptibility, which is called, following to Laue, dispersion errors. The phenomenological theory of X-ray scattering considers the electron which moves over the circular orbit with a circular frequency ω_0 and is influenced by friction because it radiates. The corresponding Newton equation for one electron in this approach was taken in the form

$$m \left(\frac{d^2 x}{dt^2} + k \frac{dx}{dt} + \omega_0^2 x \right) = eE(\omega) \exp(-i\omega t), \quad (12)$$

where x is the electron coordinate, k is a friction coefficient. The velocity is $v = dx/dt$. The similar calculation as above leads to a following frequency dependence of the susceptibility

$$X(\omega) = -\frac{4\pi e^2}{m(\omega^2 - \omega_0^2 + ik\omega)} = X_0(\omega) [1 + A'(\omega) - iA''(\omega)] \quad (13)$$

where

$$X_0(\omega) = -\frac{4\pi e^2}{m\omega^2}, \quad A'(\omega) - iA''(\omega) = \frac{\omega_0^2(\omega^2 - \omega_0^2) - k^2\omega^2 - ik\omega^3}{(\omega^2 - \omega_0^2)^2 + k^2\omega^2}. \quad (14)$$

As it follows from Eq.(13) we obtain two additional terms in the expression of susceptibility compared to the pure Rayleigh scattering. One term add to a real part and it

is usually small compared to the amplitude of Rayleigh scattering. The second term is quite new because it is imaginary. In homogeneous medium this leads to the exponential decreasing of the amplitude of the radiation. The reason of this decreasing is just the absorption of coherent radiation due to incoherent rescattering of electron which leads to a friction. Therefore the imaginary part is proportional to a friction coefficient.

The approach described above is simple and it lies completely inside the classic mechanics including the expression for the friction force $F_{\text{fric}} = -mkv$. Such an expression is valid for our human life and it leads, for example, to a constant speed of the body moving under the constant external force, like gravitation $F_{\text{grav}} = mg$, instead of a constant acceleration g . The value of the constant speed is easy to calculate $v = g/k$. However, it is not clear that the electron undergoes the same friction force. Indeed, it is wrong. The friction force for the electron which radiates was calculated by Abraham using the Lorentz expression for the loss of electron energy per a unit time interval in the case of nonrelativistic speed of electron ($v \ll c$). This expression can be formally considered as a work of friction force for the same time interval. Such a condition leads to the formula

$$\left(-\frac{dU}{m dt}\right)_{\text{aver}} = \alpha \left(\frac{d^2x}{dt^2}\right)_{\text{aver}} = -\frac{1}{m} F \left(\frac{dx}{dt}\right)_{\text{aver}}, \quad \alpha = \frac{2e^2}{3mc^3} = 6.2 \cdot 10^{-24} \text{ s} \quad (15)$$

where we need to consider the average value over the long enough time interval compared to the period of electron oscillations. Taking the integral of the averaging procedure by part

$$\int dt \frac{du}{dt} f = u f - \int dt \frac{df}{dt} u$$

and neglecting the term without the integral because the movement of the electron is periodical, we arrive to the expression

$$\int dt \frac{dx}{dt} \left(\frac{1}{m} F - \alpha \frac{d^3x}{dt^3}\right) = 0, \quad F = \alpha m \frac{d^3x}{dt^3} \quad (16)$$

It is just the Abraham-Lorentz formula. Therefore the more accurate expression may be obtained from Eq.(14) with a use of relation $k = \alpha\omega^2$.

It is not essential if we consider the susceptibility in the frequency region just near the resonance. In this case we may put $\omega = \omega_0$ in all term which have no the resonance behavior. After that the Eq.(13) takes the approximate form

$$X(\omega) = -\frac{4\pi e^2}{m\omega_0 k} \frac{k/2}{(\omega - \omega_0 + ik/2)}, \quad k = \alpha\omega_0^2, \quad (17)$$

which describes the experiment and completely coincides with the same expression for the amplitude of nuclear resonant scattering where instead of k the variable Γ/\hbar is used.

However, in the region far away from the resonance this expression leads to a wrong dependence of linear absorption coefficient of X-rays due to the photoelectric resonant scattering (photo-effect) which is not verified in experiments

$$\mu = \frac{\omega}{c} X''(\omega) n = \frac{6\pi c^2}{\omega^2} \left[1 + \frac{(\omega^2 - \omega_0^2)^2}{\alpha^2 \omega^6}\right]^{-1} \neq CZ^4 \lambda^3 \quad (18)$$

The main reason of this fact is that the photoelectron emission is essentially quantum mechanical phenomenon. To describe it in a frame of classic mechanics we need to make an additional assumption about the electron properties. So we need to suppose that the electron has no definite frequency of the resonance but it is in a state with the definite energy E_e . The frequency of the resonance corresponds to transition of electron from the state with one energy to the state with another energy. However, the photoelectron emission corresponds to transitions from the finite energy state to the free states of electron where the density of energy values is nearly constant and very high so the states form a continuum.

Therefore we need to consider a continuous distribution of virtual oscillators each having the frequency ω_j inside the interval from ω_0 up to infinity and introduce the new function $f_0(\omega_j)$ as the virtual oscillator strength normalized on the total number of electrons having the energy E_e

$$Z_0 = \int_{\omega_0}^{\infty} d\omega_j f_0(\omega_j) \quad (19)$$

after that the formula for the linear absorption coefficient becomes

$$\mu = \frac{6\pi c^2}{\omega^2} \int_{\omega_0}^{\infty} d\omega_j \frac{f_0(\omega_j)}{\left[1 + (\omega^2 - \omega_j^2)^2 \alpha^{-2} \omega^{-6}\right]} \quad (20)$$

As a result of approximate calculation of the integral (the denominator can be reduced to the Lorentz function and then replaced by delta-function) we obtain for ω far from ω_0 that

$$\mu(\omega) = \frac{2\pi^2 e^2}{mc} f_0(\omega) \quad (21)$$

Therefore the frequency dependence of the absorption coefficient now is determined completely by new quantity - strength of the virtual oscillator. However, in the frame of classic mechanics we have no the equations to calculate this. So we may use only the experimental results - the normal practice for the phenomenological theory. A more detailed topic on this subject may be found, for example, in the book

- B. K. Agarwal, *X-Ray Spectroscopy, An Introduction*,

. Springer Series in Optical Science, vol.15, Springer-Verlag, Berlin, 1979.

where the following efforts to improve the classic approach are considered. Nevertheless the structure of the expression (13) for one electron is valid.

The summation over all electrons must be performed taking into account two assumptions. First, the atoms usually have many electron shells with different energies. Second, for high energy X-rays only the electrons which move over the internal circular orbits are essential and these electrons are very localized. Therefore, we may neglect their spacial distribution. As a result, the phenomenological theory deals with the Fourier coefficients of susceptibility as follows

$$\chi_{\mathbf{h}} = -\frac{4\pi e^2}{m\omega^2 V_0} \sum_j [f_j(\mathbf{h}) + \Delta f_j'(\omega) - i\Delta f_j''(\omega)] \exp(-i\mathbf{h}\mathbf{r}_j) \exp[-W_j(\mathbf{h})/2]. \quad (22)$$

where $\Delta f'_j(\omega)$ and $\Delta f''_j(\omega)$ are the dispersion errors to the complex atomic scattering factor.

From the point of view of quantum mechanics this expression corresponds to

. E1-transition (electric dipole scattering).

It is accurate for the Rayleigh scattering which gives the main contribution to the real part of complex atomic scattering factor. It is also approximately valid for the photoelectron resonant scattering which gives the main contribution to the imaginary part of complex atomic scattering factor. However, in general, this expression is not valid because

. M1-transition (magnetic dipole scattering) and

. E2-transition (quadrupole scattering)

may play an apparent role in some phenomena. Simple estimations of relative value of these processes to electric dipole scattering gives $M1/E1 \approx v/c$, $E2/E1 \approx r/\lambda$, where v is the speed of electron, c is the speed of light, r is a radius of electron orbit, λ is a wavelength of the radiation.

Usually the approximation of Eq.(22) is enough in analysis of many phenomena of X-Ray diffraction in crystals. However, when considering the two-beam Borrmann effect and especially the multiple-beam anomalous transmission effect the approximation of Eq.(22) may lead to significant error. However in this cases only the imaginary part of the susceptibility needs to be improved. The more accurate expression for the imaginary part to the susceptibility from the dipole and quadrupole contributions to the photoelectric absorption may be written as follows

$$X_{\omega}^{\alpha\beta}(\mathbf{k}_{\mathbf{h}}, \mathbf{k}_{\mathbf{g}})''|_{photo} = \delta^{\alpha\beta} \chi_{\mathbf{h}-\mathbf{g}}''D + \left[\delta^{\alpha\beta} \frac{(\mathbf{k}_{\mathbf{h}}\mathbf{k}_{\mathbf{g}})}{K^2} + \frac{k_{\mathbf{g}}^{\alpha}k_{\mathbf{h}}^{\beta}}{K^2} \right] \chi_{\mathbf{h}-\mathbf{g}}''Q \quad (23)$$

where it is convenient to express the coefficients through the cross-section of the photoelectric absorption

$$\chi_{\mathbf{h}}''D,Q = \frac{1}{KV_0} \sum_j \sigma_j^{D,Q} \exp(-i\mathbf{h}\mathbf{r}_j) \exp[-W_j(\mathbf{h})/2] \quad (24)$$

where $\sigma_j^{D,Q}$ is a cross-section of dipole (D) or quadrupole (Q) terms of photo-electric absorption for the atom with the index j .

3.3 Other processes

In addition to *Rayleigh scattering* and *photoelectron resonant scattering* one has to consider the *Compton scattering* and *thermal diffuse scattering* (scattering of X-rays by phonons). For more complete information about a quantum mechanical calculation of the X-ray susceptibility it is useful to examine the article.

- Afanasev and Kagan, Acta Crystall., 1968, vol. A24, p.163

For our purpose it is convenient to write in explicit form the contribution of Compton scattering to the imaginary part of susceptibility.

The formula which takes into account the diffraction processes was considered for the first time in the article

- H. Sano, K. Ohtaka, Y.-H. Ohtsuki, J. Phys. Soc. Japan, 1969, vol. 27, p.1254.

This formula in general case of multiple diffraction may be written as

$$X_{\omega}^{\alpha\beta}(\mathbf{k}_h, \mathbf{k}_g)''|_{Compton} = \frac{8\pi r_0^2}{3V_0} \sum_j \exp(-i\mathbf{h}\mathbf{r}_j) \exp[-W_j(\mathbf{h})/2] G_j^{\alpha\beta}(\mathbf{k}_h, \mathbf{k}_g), \quad (25)$$

where

$$G_j^{\alpha\beta}(\mathbf{k}_h, \mathbf{k}_g) = \left\{ \delta^{\alpha\beta} f_j(\mathbf{h} - \mathbf{g}) - \frac{3}{8\pi} \int ds [\delta^{\alpha\beta} - s^{\alpha} s^{\beta}] \sum_{m,n} F_j^{(mn)}(K\mathbf{s} - \mathbf{k}_h) F_j^{(nm)}(\mathbf{k}_g - K\mathbf{s}) \right\} \quad (26)$$

Here \mathbf{s} is an arbitrary unit vector which shows the direction of outgoing scattered wave and integration is performed over all directions of this vector, $F_j^{(mn)}(\mathbf{k})$ is the transition amplitude which is defined as

$$F_j^{(mn)}(\mathbf{k}) = \langle m | \sum_e \exp(i\mathbf{k}\mathbf{r}_e) | n \rangle \quad (27)$$

where $\langle m | \dots | n \rangle$ means the matrix element between the occupied electron states of the atom and a summation is carried out over the all electrons of j -th atom. Similar to photoelectric resonant scattering the Compton scattering is also a pure quantum mechanical process. Therefore the formula written above is obtained in a frame of quantum mechanics theory. The atomic scattering factor which appeared in the formulas for Rayleigh and resonance scattering, can be written as a sum of the transition amplitudes which are diagonal over electronic states

$$f_j(\mathbf{h}) = \sum_m F_j^{(mm)}(\mathbf{k}). \quad (28)$$

The formulas derived above allows us to estimate the value of interaction, i.e. the value of scattered wave as compared to the initial wave. For example, the amplitude of forward scattering in Silicon χ_0 for X-rays of energy $E = \hbar\omega = 14.41$ keV ($\lambda = 0.86$ Å) equals

- $\chi_0' |_{Rayl} = -4.62 \cdot 10^{-6}$, Rayleigh scattering,
- $\chi_0'' |_{photo} = 3.52 \cdot 10^{-8}$, the photoelectric contribution to the imaginary part,
- $\chi_0'' |_{Comp} = 3.86 \cdot 10^{-10}$, the Compton contribution to the imaginary part.

One can see that these values are very small therefore the X-ray beam must illuminate the large volume of the crystal to obtain a significant scattering wave.

4. BRAGG CONDITIONS AND GEOMETRY OF MULTIPLE DIFFRACTION

The electric field induction $\mathbf{D} = \varepsilon\mathbf{E}$, where ε is a dielectric function ($\varepsilon = 1 + \chi$) satisfies by definition the Maxwell's equation

$$\text{div } \mathbf{D} = \mathbf{E} \text{ grad } \varepsilon + \varepsilon \text{ div } \mathbf{E} = 0 \quad (29)$$

therefore

$$\operatorname{div} \mathbf{E} = \mathbf{E} \operatorname{grad} \chi \quad (30)$$

which gives us the estimation of the longitudinal component of the electric field vector

$$E_{long} \approx \frac{\lambda}{a} \chi E \quad (31)$$

where λ is a wavelength, a is a crystal lattice parameter. The relation λ/a is less than unity for high-energy X-Rays. Since the susceptibility is very small, the longitudinal component of the electric field vector can be neglected in the linear approximation over χ which is rather good.

Considering the waves as transverse one, let us introduce for the plane wave with the wave vector $k_{\mathbf{h}}$ two unit vectors $e_{\mathbf{h}s}$ ($s = \pi, \sigma$) of polarizations. The the vector index α of the field can be expressed through the vector index of known vectors of polarizations

$$E_{\mathbf{h}}^{\alpha}(\omega) = \sum_{s=\pi,\sigma} E_{\mathbf{h}s} e_{\mathbf{h}s}^{\alpha} \quad (32)$$

that allows us to write the set of equations (6) through the scalar amplitudes

$$\frac{[k_{\mathbf{h}}^2 - K^2]}{K^2} E_{\mathbf{h}s} = \sum_{s', \mathbf{h}'} g_{\mathbf{h}\mathbf{h}'}^{ss'} E_{\mathbf{h}'s'}, \quad (33)$$

where

$$g_{\mathbf{h}\mathbf{h}'}^{ss'} = \sum_{\alpha\beta} e_{\mathbf{h}s}^{\alpha} X_{\omega}^{\alpha\beta}(\mathbf{k}_{\mathbf{h}}, \mathbf{k}_{\mathbf{h}'}) e_{\mathbf{h}'s'}^{\beta}. \quad (34)$$

The right-hand side of each equation in the set (33) has approximately the same value. These values are very small because the values $g_{\mathbf{h}\mathbf{h}'}^{ss'}$ are small. If the wave vector \mathbf{k}_0 is close to the wave vector in vacuum then the coefficient before E_{0s} is also small and the equation can be fulfilled with a large value of E_{0s} . As for the other coefficients, the value of difference $[k_{\mathbf{h}}^2 - K^2]$ normally is comparable with K^2 and therefore the value $E_{\mathbf{h}s}$ is comparable with χ_0 . This means that in usual case the difference of Bloch wave from the plane wave is very small.

However, near the surface inside the three-dimensional \mathbf{k}_0 -space the condition $[k_{\mathbf{h}}^2 - K^2]/K^2 \approx \chi_0$ may be fulfilled with $\mathbf{k}_{\mathbf{h}} = \mathbf{k}_0 + \mathbf{h}$ for any definite vector \mathbf{h} . When this condition is met, two plane waves have comparable values which will be much larger than all other plane waves. This allows us to omit all small waves and to consider a set of four equations for scalar values $E_{0\pi}$, $E_{0\sigma}$, $E_{\mathbf{h}\pi}$, and $E_{\mathbf{h}\sigma}$. Thus the two-beam approximation has to be considered which is called two-beam diffraction case

The condition $(\mathbf{k}_0 + \mathbf{h})^2 = K^2$ is known as the Bragg condition of two-beam diffraction. It is scalar equation for three coordinates of the vector \mathbf{k}_0 . The plane of vectors \mathbf{k}_0 and $\mathbf{k}_{\mathbf{h}} = \mathbf{k}_0 + \mathbf{h}$ may be called a scattering plane. The atomic planes normal to the reciprocal lattice vector \mathbf{h} are called reflecting planes. The vectors \mathbf{k}_0 and $\mathbf{k}_{\mathbf{h}}$ have the same projections on the reflecting planes $K \cos \theta_B$ while the reciprocal lattice vector has a modulus $h = 2K \sin \theta_B$. Here θ_B is the angle between the direction of waves and the reflecting plane. It is called Bragg angle. Taking into account that $K = 2\pi/\lambda$, $h = 2\pi/d$ where λ is

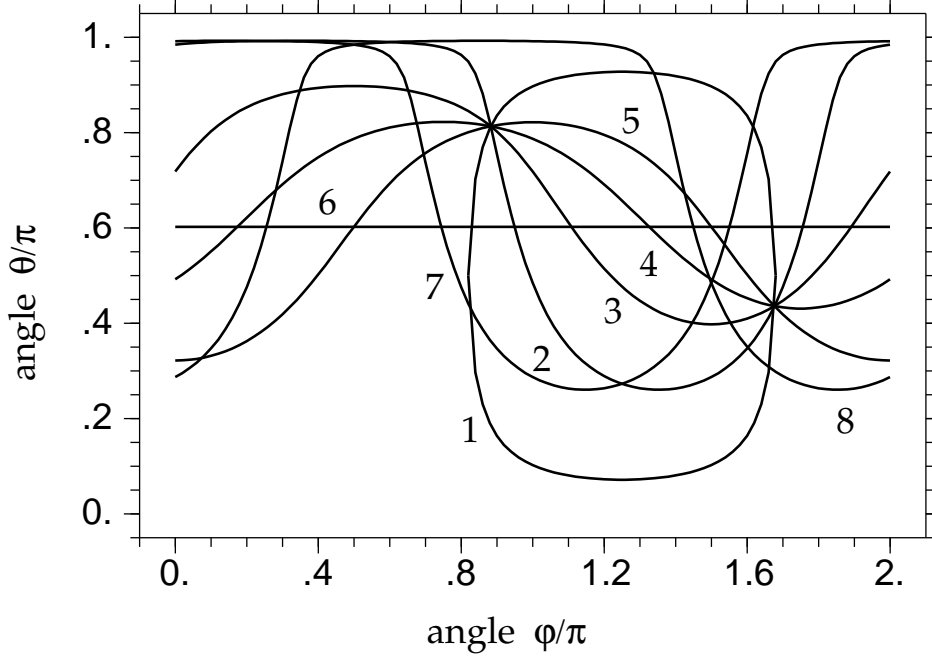


FIG. 3. The lines of Bragg conditions for different reciprocal lattice vectors of Si for $\lambda = 0.861\text{\AA}$, 1 = (220), 2 = (242), 3 = (044), 4 = ($\bar{2}$ 24), 5 = ($\bar{2}$ 02), 6 = (004), 7 = (422), 8 = ($\bar{4}$ 22)

a wavelength while d is an interatomic distance for the set of reflecting planes we may rewrite the Bragg condition in a scalar form

$$2d \sin \theta_B = \lambda \quad (35)$$

which allows to connect the direction of wave with the wavelength of the radiation.

The Eq.(35) defines only one angle of direction in the scattering plane while the values of second angle stay free. Using the spherical coordinates the vector \mathbf{k}_0 may be characterized as $k_{0x} = K \sin \theta \cos \varphi$, $k_{0y} = K \sin \theta \sin \varphi$, $k_{0z} = K \cos \theta$. For given frequency of the radiation the Bragg condition is fulfilled on the line inside the rectangle of angular coordinates. Taking into account that $K = 2\pi/\lambda$, $h = (2\pi/a)(h, k, l)$ in a cubic crystal lattice where a is a crystal lattice parameter, the Bragg condition can be written in the form

$$\frac{l \cos \theta + (\lambda/2a)(h^2 + k^2 + l^2)}{\sin \theta} = -(h \cos \varphi + k \sin \varphi). \quad (36)$$

Here the left-hand side depends only on θ , the right-hand side depends only on φ and the problem reduces to finding the possible θ values as a roots of equation for different φ values. There may be one or two roots. The functions $\theta_{hkl}(\varphi)$ are shown in Fig. 3 for several reciprocal lattice vectors of silicon and for ^{57}Fe nuclear resonant radiation with $\lambda = 0.861 \text{ \AA}$. One can see the line for (220) reciprocal lattice vector becomes closed. The

same diagram for $\lambda = 0.6 \text{ \AA}$ is shown on Fig. 4. It is of interest to analyze the difference between them as well as the similar properties. This will be done later.

In three-dimensional space the sphere $\mathbf{k}_0^2 = K^2$ is called Ewald's sphere. Each reciprocal lattice vector with the modulus less than $2K$ may be represented by its line not only inside the rectangle of angles but also by lines on the Ewald's sphere. When two different lines intersect each other the condition for three-beam diffraction arises similar two angular map.

In principle, the three-beam diffraction case exists always for any small enough wave length. Mathematically the conditions of three-beam diffraction are written as a set of two equations

$$(\mathbf{k}_0 + \mathbf{h}_1)^2 = K^2, \quad (\mathbf{k}_0 + \mathbf{h}_2)^2 = K^2$$

However, using this way one has to be careful and has to bear in mind about the crystal lattice symmetry. Just owing to the crystal lattice symmetry additional reciprocal lattice vectors may exist which satisfy the Bragg condition simultaneously with the selected reciprocal lattice vectors. On the graphics of Fig. 3 this situation is marked by the point of intersection of several lines simultaneously. The three beam case may be called *frequency insensitive* case because it is realized for each value of K larger than the value K_c , a radius of the circle which circumscribes the triangle drawn on the vectors \mathbf{h}_1 and \mathbf{h}_2 .

This case is convenient for the experiment because it is not necessary to select the special area of the frequency spectrum. That is why this case is called also the *systematic*

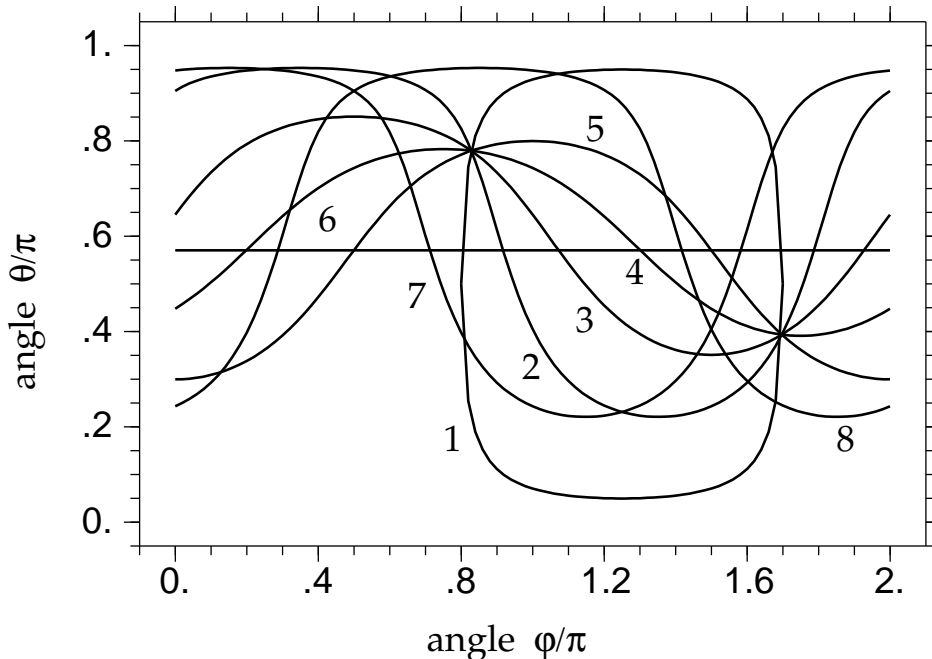


FIG. 4. The lines of Bragg conditions for different reciprocal lattice vectors of Si for $\lambda = 0.6 \text{ \AA}$, 1 = (220), 2 = (242), 3 = (044), 4 = ($\bar{2}$ 24), 5 = ($\bar{2}$ 02), 6 = (004), 7 = (422), 8 = ($\bar{4}$ 22)

multiple diffraction. The systematic or frequency insensitive multiple diffraction with a number of waves larger than 3 may exist only due to symmetry of the crystal lattice when the additional reciprocal lattice vectors as a linear combination of \mathbf{h}_1 and \mathbf{h}_2 have their ends on the same circle. Such the cases are therefore *lattice-vector coplanar*. The frequency insensitive case is characterized by the property that a small difference in K may be compensated by a small difference of angles without destroying the Bragg conditions. Fig.5 shows an example of such a systematic six-beam case in Silicon where five reciprocal lattice vectors (220), (242), (044), ($\bar{2}$ 24) and ($\bar{2}$ 02) are circumscribed by the same circle as a section of the Ewald's sphere. In the Fig.3 and Fig.4 this situation reveals itself by intersection of five lines at the same point.

It is of interest to consider a simple algorithm which allows us to find all additional reciprocal lattice vectors of the systematic diffraction. This algorithm was elaborated and written by author in the book

- Z. G. Pinsker, *Dynamical scattering of X-Rays in Crystal*, Springer, Berlin, 1978. The two reciprocal lattice vectors \mathbf{h}_1 and \mathbf{h}_2 define the plane in the reciprocal lattice. Let \mathbf{b}_1 and \mathbf{b}_2 be two minimal reciprocal lattice vectors in this place which correspond to nonzero structure factors. Each reciprocal lattice vector can be represented as a linear combination of these vectors $\mathbf{h} = \alpha\mathbf{b}_1 + \beta\mathbf{b}_2$. The Bragg condition for the vector \mathbf{h} looks like $(\mathbf{K}_c + \mathbf{h})^2 = K_c^2$ where K_c is a critical wave vector which lies at the same plane as the reciprocal lattice vectors. In terms of parameters α and β the condition can be written as

$$\alpha^2 - 2\alpha(A - C\beta) - \beta(B - D\beta) = 0 \quad (37)$$

where

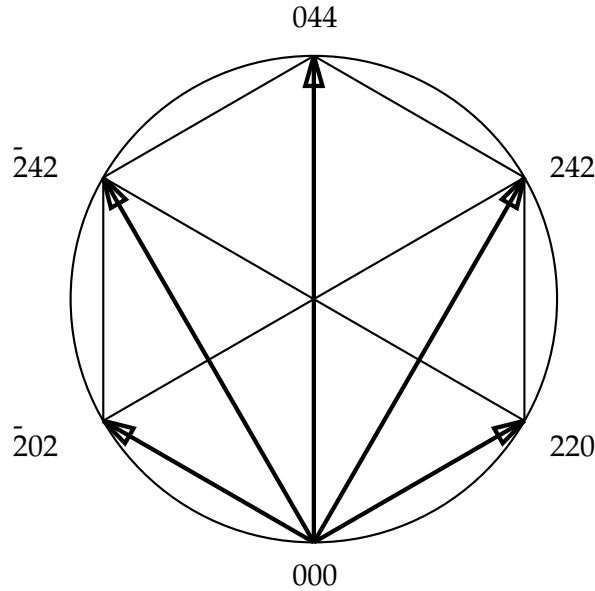


FIG. 5. The reciprocal lattice vectors of six-beam case in Silicon

$$A = -\frac{(\mathbf{K}_c \mathbf{b}_1)}{b_1^2}, \quad B = -2\frac{(\mathbf{K}_c \mathbf{b}_2)}{b_1^2}, \quad C = \frac{(\mathbf{b}_1 \mathbf{b}_2)}{b_1^2}, \quad D = \frac{b_2^2}{b_1^2}. \quad (38)$$

Here the coefficients C and D can be calculated directly while the parameters A and B may be found from the set of equations (37) with two set of values α_1, β_1 and α_2, β_2 which correspond to the reciprocal lattice vectors h_1 and h_2 . For each β value we have two values of α as a solution of Eq.(37)

$$\alpha_{1,2} = (A - C\beta) \pm \sqrt{(A - C\beta)^2 + \beta(B - D\beta)}. \quad (39)$$

We are interested only in integer values of α therefore the expression under a square root must be positive

$$E = (A - C\beta)^2 + \beta(B - D\beta) \geq 0 \quad (40)$$

The positive values of E correspond to β values which lie between the roots of equation $E = 0$. Examining all integer values of β inside this interval and calculating the α values from the formula (39) we must keep all integer values. If there are more than two solutions then the considering case is not the three-beam case and it has an additional symmetry.

The frequency sensitive cases may be of two kinds. First one is a particular case of the lattice-vector coplanar diffraction when $K = K_c$. In this case all reciprocal lattice vectors and all wave vectors lie in the same plane (plane of scattering). Therefore this case may be called *wave-vector coplanar* or simply the case of *coplanar diffraction*. This case of multiple diffraction similar to the two-beam diffraction is insensitive to the small change of wave vector direction in the plane normal to the scattering plane. On the other hand, the small difference of K value from K_c cannot be compensated by the angle difference and destroy the multiple diffraction on the set of two-beam diffractions. Therefore in the Chang's book

- Shin-Lin Chang, Multiple diffraction of X-Rays in crystals, Springer, Berlin, 1984. this case is called the *coincidental diffraction*. The second kind of frequency sensitive multiple diffraction is the four-wave case on three reciprocal lattice vectors which are not coplanar. The small difference of K in this case destroys the four-beam case on the set of three-beam cases. Once again the additional symmetry of the crystal may increase the number of waves. This case may be seen in the diagram of Fig.3 at $\theta = 0.7\pi$, $\varphi = 1.5\pi$ together with the six-beam case at two different angular positions. The diagram of Fig.4 shows the six-beam case but the frequency sensitive four-beam case does not exist here.

Now let us consider the case of n -beam diffraction on the reciprocal lattice vectors $\mathbf{h}_1, \mathbf{h}_2, \dots, \mathbf{h}_{n-1}$. We are interested in the small frequency bandwidth of the radiation near the value ω_b . Let us introduce the set of unit vectors \mathbf{s}_m , $m = 0, \dots, n - 1$, which define the directions of wave vectors having the modulus $K_b = \omega_b/c$ and satisfying exactly the kinematical Bragg conditions $\mathbf{s}_m = \mathbf{s}_0 + \mathbf{h}_m/K_b$, $s_m^2 = 1$ (see Fig.6). The wave vectors of the waves which take part in the diffraction interaction in air may be represented as

$$\mathbf{K}_m = K_b \mathbf{s}_m + \mathbf{q}_m, \quad (41)$$

The modulus of the additional vector \mathbf{q}_m is usually very small compared to K_b . It is convenient to use a local coordinate basis for each beam separately when representing

\mathbf{q}_m , namely, three mutually perpendicular unit vectors of polarizations \mathbf{e}_m^π , \mathbf{e}_m^σ and along the beam \mathbf{s}_m . The coordinates of the additional vector describe the angular deviation of the beam as well as the small relative change of the energy inside the bandwidth. In a linear approximation we obtain

$$\mathbf{q}_m/K_b = \Delta\theta_{1m}\mathbf{e}_m^\pi + \Delta\theta_{2m}\mathbf{e}_m^\sigma + \Delta\theta_\omega\mathbf{s}_m, \quad \Delta\theta_\omega = (\omega - \omega_b)/\omega_b, \quad (42)$$

We note that all the vectors \mathbf{K}_m have the same modulus $K_m^2 = K^2$ because the diffraction interaction is an elastic interaction which cannot change the energy of X-ray photon.

As it is shown in Fig.6, we may define the vectors \mathbf{e}_m^π and \mathbf{s}_m using the critical vector of coplanar diffraction \mathbf{K}_c and the unit vector of the normal to the reciprocal lattices plane \mathbf{n}_h as follows

$$\mathbf{s}_m = (\mathbf{K}_c + \mathbf{h}_m) \sin \theta_0 - \mathbf{n}_h \cos \theta_0, \quad \mathbf{e}_m^\pi = (\mathbf{K}_c + \mathbf{h}_m) \cos \theta_0 + \mathbf{n}_h \sin \theta_0 \quad (43)$$

while $\mathbf{e}_m^\sigma = [\mathbf{s}_m \times \mathbf{e}_m^\pi]$. Here θ_0 is an angle between the directions of the beams and $-\mathbf{n}_h$. The coplanar case corresponds to $\theta_0 = 90^\circ$.

In principle, each wave (for example, having the wave vector \mathbf{K}_i) may be treated as the incident wave. We define the geometrical parameters α_m describing the degree of deviation of m -th plane wave from the Bragg condition as

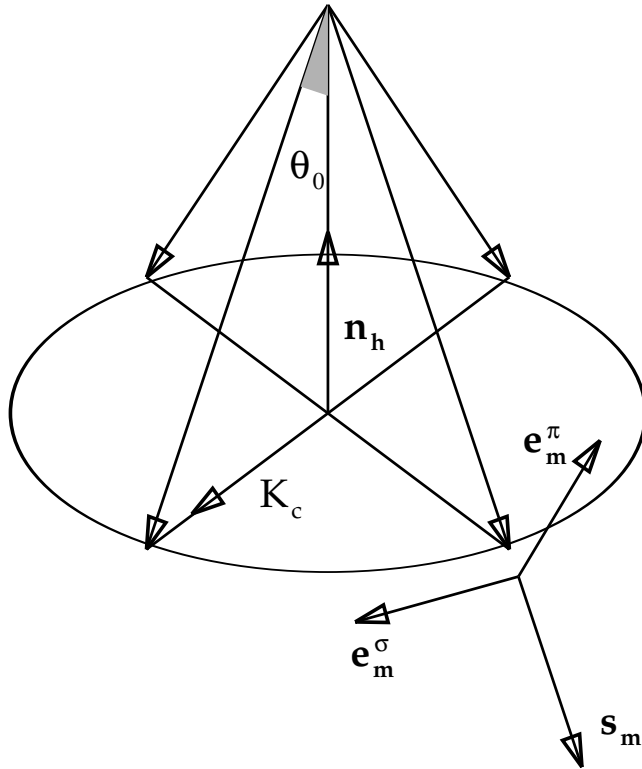


FIG. 6. The local coordinate system for a particular beam

$$\alpha_m = \frac{[(\mathbf{K}_i + \mathbf{h}_m - \mathbf{h}_i)^2 - K^2]}{K^2}, \quad m = 0, \dots, n-1. \quad (44)$$

The number of these parameters is n but $\alpha_i = 0$ because $K_i^2 = K^2$. Therefore only $n-1$ parameters having nonzero values. However in case of $n > 3$ the all parameters cannot be independent. We may express these parameters in terms of the vector \mathbf{q}_i which describes the small deviation of the vector \mathbf{K}_i from the reference wave vector. Taking into account that $\Delta\theta_{1i}$, $\Delta\theta_{2i}$ and $\Delta\theta_\omega$ are very small (of order 10^{-5}) we obtain in a linear approximation over a small value q/K that

$$\alpha_m(\mathbf{q}_i)/2 \approx \Delta\theta_{1i}(\mathbf{s}_m \mathbf{e}_i^\pi) + \Delta\theta_{2i}(\mathbf{s}_m \mathbf{e}_i^\sigma) - \Delta\theta_\omega[1 - (\mathbf{s}_m \mathbf{s}_i)]. \quad (45)$$

The coefficients before the small angular and frequency deviations allows us to estimate a degree of sensitivity of each Bragg condition. These parameters play a significant role in the diffraction problem as well as in the correspondence between the different wave vectors K_m of wave in air.

4. TRANSMISSION AND REFLECTION

Up to now we consider the crystal lattice medium as infinite. However, in a real situation the crystal is bounded and the main question is how the crystal influences the vacuum waves. Therefore we need to introduce the shape of crystal sample and the boundary conditions. It is natural that in the case of plane wave scattering the simplest boundaries are the planes and the simplest crystal shape is the plane parallel plate of thickness t_p . Fortunately this shape of the crystal is of great practical interest from the technological point of view. The plane of boundary of the crystal plate is characterized by the unit vector \mathbf{n} along the normal to the surface which makes an acute angle with the wave vector of the incident vacuum wave. Considering the n -beam case on the reciprocal lattice vectors $\mathbf{h}_1, \mathbf{h}_2, \dots, \mathbf{h}_{n-1}$ we may choose the incident wave as having any wave vector from a set $\mathbf{K}_0, \mathbf{K}_1, \dots, \mathbf{K}_{n-1}$. Let it be \mathbf{K}_i . Owing to a refraction at the boundary, the wave vector of the incident wave inside the crystal will differ from the vacuum wave vector by the small component normal to the boundary, namely, $\mathbf{k}_i = \mathbf{K}_i + \varepsilon \mathbf{n}/2$ where the multiplier $1/2$ is taken for a convenience. Assuming that all the parameters γ_m are large enough compared to $\sqrt{\chi_0}$ we arrive to a set of $2n$ equation

$$\left(\frac{\gamma_m}{K} \varepsilon + \alpha_m(\mathbf{q}_i)\right) E_{ms} = \sum_{m', s'} g_{mm'}^{ss'} E_{m' s'}, \quad \gamma_m = (\mathbf{s}_m \mathbf{n}) \quad (46)$$

where $m = 0, \dots, n-1$, $s = \pi, \sigma$.

To make a task more clear we introduce the new values $B_{ms} = \gamma_m^{1/2} E_{ms}$ and rewrite the equation in the form

$$\varepsilon B_{ms} = \sum_{m', s'} G_{mm'}^{ss'}(\mathbf{q}_i) B_{m' s'}, \quad (47)$$

where

$$G_{mm'}^{ss'}(\mathbf{q}_i) = \frac{K}{(\gamma_m \gamma_{m'})^{1/2}} (-\alpha_m(\mathbf{q}_i) \delta_{mm'}^{ss'} + g_{mm'}^{ss'}). \quad (48)$$

Here $\delta_{mm'}^{ss'}$ is the Kronecker symbol which equals unity if $m = m'$ and $s = s'$ and zero otherwise.

One can see that the equations (47) represent by themselves the eigen solution problem of the matrix $G_{mm'}^{ss'}$ having a rank $2n$. We shall call the matrix G the kinematical scattering matrix. Such a problem arises in any task investigated dynamical systems, for example, in the dynamical theory of the crystal lattice vibrations. Therefore we may use the standard mathematical methods to develop the dynamical theory of multiple diffraction. On the other hand, since even in three-beam case the rank of the matrix is 6 the analytical solution of the equation is not possible in general. Under these conditions the main purpose of the theory is to formulate the effective way of calculating all physical values measured in the experiment by means of computer, on one hand, and to formulate the general properties of the solutions, on the other hand. However, in some particular cases of high symmetry the analytical solutions are possible. These will be considered in another topic. Here we shall consider the general formulation of the problem which allows us to use a computer.

As well known, the eigen solution problem for the matrix of rank $2n$ has $2n$ solutions. We will distinguish them by the index j . On the other hand, to simplify the notation we will discard the polarization index s by incorporating it into m . So for each set of parameters value $\Delta\theta_{1i}$, $\Delta\theta_{2i}$ and $\Delta\theta_\omega = \Delta\omega/\omega$ we obtain $2n$ zones ε_j of refraction which may be used for drawing the dispersion surface and the matrix B_{mj} of the eigen vectors. We will suppose that the eigenvectors are normalized to unity. The total electric field inside the crystal is a linear combination of these eigen solutions

$$\mathbf{E}(\mathbf{r}, t) = \exp(i\mathbf{K}_0 \mathbf{r} - i\omega t) \sum_m \exp(i\mathbf{h}_m \mathbf{r}) E_m(z) \mathbf{e}_m. \quad (49)$$

where

$$E_m(z) = \gamma_m^{-1/2} \sum_j \lambda_j B_{mj} \exp(i\varepsilon_j z/2).$$

Here $z = \mathbf{n}(\mathbf{r} - \mathbf{r}_s)$, where \mathbf{r}_s is the position of the point on the entrance surface.

The quantity λ_j defines the degree of excitation of the j -th eigen solution. The set of values λ_j is determined from the boundary conditions. The boundary conditions depends essentially on the geometry of the beams relative to boundary of the crystal. In general case, some of the values γ_m may be negative while others are positive. The fraction of the diffracted waves exit from the crystal through the upper (entrance) surface if $\gamma_m < 0$. We call these waves Bragg-reflected waves. We will denote them by one index B . The waves leave the crystal through the lower (exit) surface when $\gamma_m > 0$. Such waves are called Laue-reflected waves. We will denote them by one index L .

Up to now we assumed that only one plane wave $\exp(i\mathbf{K}_i \mathbf{r} - i\omega t)$ falls on the crystal plate. However, it is convenient to generalize the problem in a way which may be useful in considering the multilayer systems. Namely, we may suppose that all waves of L -type are known on the entrance surface of the plate ($z = 0$) and all waves of B -type are known on the exit surface ($z = t_p$). In this case the structure of the wave field inside the crystal,

which is given by Eq.(49), stay the same but the boundary conditions take the more general form. We will denote the known values of the wave field at the boundaries as $E_m(z_m^{(i)}) = \gamma_m^{-1/2} D_m$ where $z_m^{(i)} = 0$ if γ_m is positive and $z_m^{(i)} = t_p$ if γ_m is negative, t_p is a crystal plate thickness. The task may be formulated as a calculation of the unknown values of the wave field of L -type at the exit surface and of B -type at the entrance surface. We will denote these values as $E_m(z_m^{(o)}) = \gamma_m^{-1/2} R_m$ where $z_m^{(o)} = 0$ if γ_m is negative and $z_m^{(o)} = t_p$ if γ_m is positive.

The boundary conditions assume the equality of the incoming wave from the both sides of the crystal to the total wave field inside the crystal. Since the difference in phases between different diffracted waves is very large, we may divide the total boundary condition on the $2n$ conditions separately for each beam and to write them as a matrix equation

$$\sum_j B_{mj} \exp(i\varepsilon_j z_m^{(i)}/2) \lambda_j = D_m \quad (50)$$

This is an equation for calculating all values λ_j which define the degrees of excitation of different eigen solutions of the crystal wave field.

The unknown values now can be calculated by means of formula

$$R_m = \sum_j B_{mj} \exp(i\varepsilon_j z_m^{(o)}/2) \lambda_j \quad (51)$$

We define the reflection coefficient $P_{m'm}$ for a scattering of particular wave m into the particular wave m' ($m' \neq m$) as a relation of outgoing to incoming flux densities. In our notation it is determined by the formula

$$P_{m'm} = \left| \frac{R_{m'}}{D_m} \right|^2 \quad (52)$$

The transmission coefficient is determined by the same expression with $m' = m$. The transmission of each beam of many-beam field can be considered.

To obtain the solution in explicit form we use the matrix notation. So the equations (47), (50) and (51) may be written as

$$B \cdot \varepsilon = G \cdot B, \quad X \cdot \lambda = D, \quad R = Y \cdot \lambda \quad (53)$$

where $\varepsilon \equiv \varepsilon_j \delta_{jj'}$ is a diagonal matrix while the definition of matrixes B , G , X and Y and vectors D , R , λ is evident. Now the solution of the boundary problem can be solved in terms of multiplicative inverse matrix as follows

$$R = Y \cdot X^{-1} \cdot D = M \cdot D, \quad M = Y \cdot X^{-1} \quad (54)$$

We will call the matrix $M \equiv M_{mm'}$ the dynamical scattering matrix. Its matrix elements depends on the crystal thickness t_p . It is clear that in the limit $t_p = 0$ we have $X = Y$ and $M = I$, where I is the identity matrix. It may be shown that for small values of t_p

$$M_{mm'} \approx \delta_{mm'} + i \frac{t_p}{2} \text{sgn}(\gamma_m) G_{mm'} \quad (55)$$

i.e. the dynamical matrix is simply proportional to the kinematic matrix. However, already for $t_p > (K\chi_0)^{-1}$ the matrix elements become nonlinear on t_p and rather complex.

Let us consider the wave vectors of diffracted waves in air. Since the vector $\mathbf{K}_i = K_b \mathbf{s}_i + \mathbf{q}_i$ has an arbitrary value the other vectors cannot be arbitrary. These can differ from \mathbf{K}_i by the reciprocal lattice vector and the vector along the normal \mathbf{n} to the crystal surface. It is easy to verify that

$$\mathbf{q}_m = \mathbf{q}_i - \frac{K_b}{2\gamma_m} \alpha_m(\mathbf{q}_i) \mathbf{n}. \quad (56)$$

This equation allows us to obtain the correspondence between angular deviations of different beams from the reference values. For example,

$$\begin{aligned} \Delta\theta_{1m} = \Delta\theta_{1i} & \left((\mathbf{e}_m^\pi \mathbf{e}_i^\pi) - \frac{(\mathbf{e}_m^\pi \mathbf{n})(\mathbf{s}_m \mathbf{e}_i^\pi)}{(\mathbf{s}_m \mathbf{n})} \right) + \Delta\theta_{2i} \left((\mathbf{e}_m^\pi \mathbf{e}_i^\sigma) - \frac{(\mathbf{e}_m^\pi \mathbf{n})(\mathbf{s}_m \mathbf{e}_i^\sigma)}{(\mathbf{s}_m \mathbf{n})} \right) \\ & + \Delta\theta_\omega \left((\mathbf{e}_m^\pi \mathbf{s}_i) + \frac{(\mathbf{e}_m^\pi \mathbf{n})[1 - (\mathbf{s}_m \mathbf{s}_i)]}{(\mathbf{s}_m \mathbf{n})} \right) \end{aligned} \quad (57)$$

The formula is rather complicated. However, using the formulas of vector algebra

$$([\mathbf{a} \times \mathbf{b}][\mathbf{c} \times \mathbf{d}]) = (\mathbf{ac})(\mathbf{bd}) - (\mathbf{ad})(\mathbf{bc}), \quad [\mathbf{s}_m \times \mathbf{e}_m^\pi] = \mathbf{e}_m^\sigma \quad (58)$$

we may transform this relation to a more simple form

$$\Delta\theta_{1m} \gamma_m = \Delta\theta_{1i} (\mathbf{n}[\mathbf{e}_i^\pi \times \mathbf{e}_m^\sigma]) + \Delta\theta_{2i} (\mathbf{n}[\mathbf{e}_i^\sigma \times \mathbf{e}_m^\sigma]) + \Delta\theta_\omega \{ (\mathbf{n} \mathbf{e}_m^\pi) + (\mathbf{n}[\mathbf{s}_i \times \mathbf{e}_m^\sigma]) \}. \quad (59)$$

In the important particular case of coplanar diffraction all the vectors \mathbf{e}_m^π equal to each other while all the vectors \mathbf{e}_m^σ and \mathbf{s}_m lie at the same plane. Let us assume that the vector \mathbf{n} lies also at the plane of \mathbf{s}_m (usually called the scattering plane). In this case the relation (58) shows that $\Delta\theta_{1m} = \Delta\theta_{1i}$. Therefore the angular property of the beam in the plane normal to the scattering plane becomes not changed.

The second angular parameter can be expressed in similar way

$$\Delta\theta_{2m} \gamma_m = \Delta\theta_{1i} (\mathbf{n}[\mathbf{e}_m^\pi \times \mathbf{e}_i^\pi]) + \Delta\theta_{2i} (\mathbf{n}[\mathbf{e}_m^\pi \times \mathbf{e}_i^\sigma]) + \Delta\theta_\omega \{ (\mathbf{n} \mathbf{e}_m^\sigma) + (\mathbf{n}[\mathbf{e}_m^\pi \times \mathbf{s}_i]) \}. \quad (60)$$

In the above mentioned coplanar case when \mathbf{n} lies in the scattering plane we obtain

$$\Delta\theta_{2m} = \Delta\theta_{2i} \frac{\gamma_i}{\gamma_m} + \Delta\theta_\omega \frac{(\mathbf{n}[\mathbf{e}_m^\sigma - \mathbf{e}_i^\sigma])}{\gamma_m} \quad (61)$$

We note that the last term can be transformed to another form taking into account that

$$(\mathbf{n}[\mathbf{e}_m^\sigma - \mathbf{e}_i^\sigma]) = (\mathbf{e}_m^\pi [\mathbf{n} \times \mathbf{h}_{mi}]) / K_b = 2 \sin \psi_{mi} \sin \theta_{Bmi} = (\gamma_m + \gamma_i) \tan \theta_{Bmi}$$

where $\mathbf{h}_{mi} = \mathbf{h}_m - \mathbf{h}_i$, ψ_{mi} is an angle between \mathbf{n} and \mathbf{h}_{mi} , θ_{Bmi} is the Bragg angle corresponding to the reciprocal lattice vector \mathbf{h}_{mi} , i.e. $\mathbf{h}_{mi} = 2K_b \sin \theta_{Bmi}$. As a result the Eq.(61) can be written as follows

$$\Delta\theta_{2m} = \Delta\theta_{2i} \frac{\gamma_i}{\gamma_m} + \Delta\theta_\omega \left(1 + \frac{\gamma_i}{\gamma_m} \right) \tan \theta_{Bmi} \quad (62)$$

This formula shows that the last term corresponds to a change of the Bragg angle with a change of frequency. The formula is valid in case of two-beam diffraction as well.

5. SOLUTION IN THE CASE OF THICK CRYSTAL

The solution (54) determines formally the way of calculating the transmission and reflection coefficients. In the case of two-beam diffraction such an approach is enough because the corresponding equations can be solved analytically. In the case of multiple diffraction this approach is enough when all diffracted beams are of transmission type ($\gamma_m > 0$). However, in case of multiple diffraction when, at least, one of the beam is of Bragg-type ($\gamma_m < 0$) such a formulation is not enough for a thick crystal because it is impossible to solve the problem numerically. The reason of this fact is the properties of the eigenvalues. It is known that the real part of the matrix $g_{mm'}$ (see Eq.(48)) which describes the scattering is the Hermitian matrix. If all values $\gamma_m > 0$ then the matrix $G_{mm'}$ in nonabsorbing crystal is also Hermitian and therefore all eigenvalues are real values. However, when, at least, one of the value γ_m is negative the matrix becomes non-Hermitian and eigenvalues becomes complex values even in nonabsorbing crystal.

Moreover, inside the total reflection region the imaginary part ε'' of the eigenvalues ε is rather large. It is known and may be verified by computer calculations that $2n_B$ solutions have an imaginary part less than zero, $\varepsilon_j'' < 0$, while other $2n_L$ solutions have $\varepsilon_j'' > 0$. Here n_B is a number of beams of Bragg-type, n_L is a number of beams of Laue-type ($n = n_B + n_L$). The physics of this property of eigenvalues can easily be explained. The eigen states of the wave field inside the crystal may be characterized by the direction of the Poynting vector. The solutions having the negative imaginary part of the eigenvalue have simultaneously the direction of the Poynting vector (the direction of the energy flow) from a bottom to a top of the crystal plate, i.e. to the opposite direction compared to the direction of incident beam. We will call them the Bloch waves of Bragg-type. These waves become attenuated when moving in the opposite direction compared to the Bloch waves of Laue-type having the positive imaginary part of eigenvalues. We will use the same letters B and L for all values of j of Bragg-type and Laue-type correspondingly.

Taking into account this property of the eigenvalues one easily understand that in the limit of very large t_p some of the elements of the X and Y matrixes decrease infinitely while the rest elements become infinitely large. The computer calculation is impossible in this case. To obtain a solution suitable for computer processing we need to reformulate the scheme of calculation. To make this we make an order of the values of m according to decreasing values of γ_m and the values of j according to decreasing values of ε_j'' , and then we go over to the new notation L and B as described above. We also introduce the diagonal matrixes

$$E_{LL} = \exp(i\varepsilon_j t_p/2)\delta_{jj'}, \varepsilon_j'' > 0; \quad E_{BB} = \exp(i\varepsilon_j t_p/2)\delta_{jj'}, \varepsilon_j'' < 0 \quad (63)$$

Now the matrix equation $X \cdot \lambda = D$ can be written as follows

$$\begin{aligned} B_{LL} \cdot \lambda_L + B_{LB} \cdot \lambda_B &= D_L \\ B_{BL} \cdot E_{LL} \cdot \lambda_L + B_{BB} \cdot E_{BB} \cdot \lambda_B &= D_B \end{aligned} \quad (64)$$

where B_{LL} and B_{BB} are respectively $2n_L \times 2n_L$ and $2n_B \times 2n_B$ square matrixes, B_{LB} and B_{BL} are generally rectangular matrixes. In solving the system one has to bear in mind that only the square matrixes have multiplicative inverses. The matrix equation $R = Y \cdot \lambda$ in the new notation takes a form

$$\begin{aligned}
R_L &= B_{LL} \cdot E_{LL} \cdot \lambda_L + B_{LB} \cdot E_{BB} \cdot \lambda_B \\
R_B &= B_{BL} \cdot \lambda_L + B_{BB} \cdot \lambda_B
\end{aligned} \tag{65}$$

The solution of Eq.(64) must be found in the form that contains no increasing exponentials, namely, instead of matrix E_{BB} we must deal with the multiplicative inverse E_{BB}^{-1} . A simple calculation leads to the following result

$$\begin{aligned}
\lambda_L &= Z_{LL}^{-1} \cdot (D_L - B_{LB} \cdot E_{BB}^{-1} \cdot B_{BB}^{-1} \cdot D_B) \\
\lambda_B &= E_{BB}^{-1} \cdot Z_{BB}^{-1} \cdot (D_B - B_{BL} \cdot E_{LL} \cdot B_{LL}^{-1} \cdot D_L)
\end{aligned} \tag{66}$$

where

$$\begin{aligned}
Z_{LL} &= B_{LL} - B_{LB} \cdot E_{BB}^{-1} \cdot B_{BB}^{-1} \cdot B_{BL} \cdot E_{LL} \\
Z_{BB} &= B_{BB} - B_{BL} \cdot E_{LL} \cdot B_{LL}^{-1} \cdot B_{LB} \cdot E_{BB}^{-1}
\end{aligned} \tag{67}$$

A substitution of Eq.(66) into Eq.(65) gives the solution in the new form

$$R_L = M_{LL} \cdot D_L + M_{LB} \cdot D_B, \quad R_B = M_{BL} \cdot D_L + M_{BB} \cdot D_B \tag{68}$$

with the blocks of the dynamical scattering matrix as follow

$$\begin{aligned}
M_{LL} &= B_{LL} \cdot E_{LL} \cdot Z_{LL}^{-1} - B_{LB} \cdot Z_{BB}^{-1} \cdot B_{BL} \cdot E_{LL} \cdot B_{LL}^{-1} \\
M_{LB} &= B_{LB} \cdot Z_{BB}^{-1} - B_{LL} \cdot E_{LL} \cdot Z_{LL}^{-1} \cdot B_{LB} \cdot E_{BB}^{-1} \cdot B_{BB}^{-1} \\
M_{BL} &= B_{BL} \cdot Z_{LL}^{-1} - B_{BB} \cdot E_{BB}^{-1} \cdot Z_{BB}^{-1} \cdot B_{BL} \cdot E_{LL} \cdot B_{LL}^{-1} \\
M_{BB} &= B_{BB} \cdot E_{BB}^{-1} \cdot Z_{BB}^{-1} - B_{BL} \cdot Z_{LL}^{-1} \cdot B_{LB} \cdot E_{BB}^{-1} \cdot B_{BB}^{-1}
\end{aligned} \tag{69}$$

It is easy to verify directly that notwithstanding their unwieldy form these equations are rather convenient for calculating the case of any crystal thickness including the limit $t_c \rightarrow \infty$. These formulas were derived for the first time in the papers

- V. G. Kohn, J. Moscow Phys. Soc., 1991, vol. 1, p. 425,
- V. G. Kohn, Zh. Eksp. Teor. Fiz., 1994, vol. 105, p. 665
- (Sov. Phys. - JETP, 1994, vol. 78, p. 357)

For thick crystals the block M_{BL} is of most important which describes the reflected beams. A zero order of the perturbation expansion in small exponential leads to the approximate expression

$$\lim_{t_c \rightarrow \infty} M_{BL} = B_{BL} \cdot B_{LL}^{-1} \tag{70}$$

This is well known result which was obtained for the first time in the works

- V. G. Kohn, Phys. Stat. Sol. (a), 1979, vol. 54, p. 375,
- Shin-Lin Chang, Acta Crystall. A, 1979, vol. 35, p. 543.

On the other hand, the matrix M_{LL} describes the anomalous transmission effect of Laue beams under the existence of the Bragg beams. In the first order of the perturbation expansion we obtain from Eq.(69) the expression

$$\lim_{t_c \rightarrow \infty} M_{LL} = (B_{LL} - B_{LB} \cdot B_{BB}^{-1} \cdot B_{BL}) \cdot E_{LL} \cdot B_{LL}^{-1} \tag{71}$$

This result was obtained for the first time in

- A. G. Toneyan, V. G. Kohn, R. N. Kuz'min, *Kristallografiya*, 1984, vol. 29, p. 203
 . (Sov. Phys. - Crystallogr., 1984, vol. 29, p. 122)

The formulas obtained are valid in the two-beam case of diffraction as well. The comparison with analytical solution in case of two-beam diffraction allows us to understand the physical sense of these results. When all beams are of Laue type the index B has zero size and

$$X = B_{LL} = Z_{LL}, \quad Y = B_{LL}E_{LL} \quad (72)$$

so we arrive to the result of preceding section

$$M_{LL} = B_{LL} \cdot E_{LL} \cdot B_{LL}^{-1} = Y \cdot X^{-1} \quad (73)$$

It is of interest to demonstrate how these general formulas work in the case of two beam diffraction. In this case the different polarizations don't interact, therefore we can consider σ and π polarization separately. The polarization factors can be included in a notation of susceptibility therefore we will consider a simple scalar case of two-beam diffraction.

$$G_{mm'} = \begin{pmatrix} \chi_0 \gamma_0^{-1} & \chi_{\bar{h}} (\gamma_0 \gamma_h)^{-1/2} \\ \chi_h (\gamma_0 \gamma_h)^{-1/2} & (\chi_0 - \alpha) \gamma_h^{-1} \end{pmatrix}, \quad m, m' = 0, h \quad (74)$$

The matrix equation $B \varepsilon = G B$ leads to two equations

$$\begin{aligned} \varepsilon B_0 &= K \gamma_0^{-1} [\chi_0 B_0 + \chi_{\bar{h}} \beta^{1/2} B_h] \\ \varepsilon B_h &= K \gamma_0^{-1} \beta [\chi_h \beta^{-1/2} B_0 + (\chi_0 - \alpha) B_h] \end{aligned} \quad (75)$$

where $\beta = \gamma_0 / \gamma_h$. Let us introduce the notation $R = B_h / B_0$ and transform the equations to another form

$$\varepsilon = K \gamma_0^{-1} [\chi_0 + \chi_{\bar{h}} \beta^{1/2} R] = K \gamma_0^{-1} \beta [(\chi_0 - \alpha) + \chi_h \beta^{-1/2} R^{-1}]. \quad (76)$$

Now introducing the new notations

$$R = \frac{\xi}{\chi_{\bar{h}} \beta^{1/2}}, \quad y = \frac{1}{2} [\alpha \beta + \chi_0 (1 - \beta)] \quad (77)$$

we lead to the square equation for ξ

$$\xi^2 + 2y\xi - \beta \chi_h \chi_{\bar{h}} = 0, \quad \xi_{1,2} = -y \pm \sqrt{y^2 + \beta \chi_h \chi_{\bar{h}}}, \quad \varepsilon_{1,2} = K \gamma_0^{-1} [\chi_0 + \xi_{1,2}] \quad (78)$$

Let us consider the Bragg case when $\gamma_h < 0$ and therefore $\beta < 0$. In accordance with a general rule we will suppose that $\varepsilon_1'' > 0$, $\varepsilon_2'' < 0$, index $L = 1$, index $B = 2$. Using the normalized eigenvectors we have

$$B_{LL} = c_1, \quad B_{BL} = c_1 R_1, \quad B_{LB} = c_2, \quad B_{BB} = c_2 R_2, \quad c = (1 + R^2)^{-1/2} \quad (79)$$

Now we can obtain the general formulas in analytical form

$$\begin{aligned}
Z_{LL} &= c_1 - c_2 e^{-i\varphi_2} \frac{1}{c_2 R_2} c_1 R_1 e^{i\varphi_1} = c_1 [1 - X e^{i\varphi_1} e^{-i\varphi_2}] \\
Z_{BB} &= c_2 R_2 - c_1 R_1 e^{i\varphi_1} \frac{1}{c_1} c_2 e^{-i\varphi_2} = c_2 R_2 [1 - X e^{i\varphi_1} e^{-i\varphi_2}]
\end{aligned} \tag{80}$$

where for a convenience the notation $\varphi_{1,2} = \varepsilon_{1,2} t_p / 2$, $X = R_1 / R_2$ is introduced. Finally we obtain (the notation t, \bar{t}, r, \bar{r} is used in the theory on crystalline multilayer)

$$\begin{aligned}
M_{LL} = t &= e^{i\varphi_1} \frac{(1 - X)}{(1 - X e^{i\varphi_1} e^{-i\varphi_2})}, & M_{BB} = \bar{t} &= e^{-i\varphi_2} \frac{(1 - X)}{(1 - X e^{i\varphi_1} e^{-i\varphi_2})}, \\
M_{BL} = r &= R_1 \frac{(1 - e^{i\varphi_1} e^{-i\varphi_2})}{(1 - X e^{i\varphi_1} e^{-i\varphi_2})}, & M_{LB} = \bar{r} &= \frac{1}{R_2} \frac{(1 - e^{i\varphi_1} e^{-i\varphi_2})}{(1 - X e^{i\varphi_1} e^{-i\varphi_2})}
\end{aligned} \tag{81}$$

Please note:

(1) the formulas is written in the form where $\exp(i\varphi_2)$ does not appear because it is impossible to calculate this number in a thick crystal by computer for the reason that it is very large,

(2) $t \neq \bar{t}$, $r \neq \bar{r}$ We only have

$$\frac{t}{\bar{t}} = e^{i\varphi_1} e^{i\varphi_2} = \exp\left(\frac{K t_p}{2\gamma_0} [\chi_0(1 + \beta) - \alpha\beta]\right), \quad \frac{r}{\bar{r}} = R_1 R_2 = -\frac{\chi_h}{\chi_{\bar{h}}} \tag{82}$$

Even in two beam case some authors failed to write the correct formulas. On the other hand, the approach based on the dynamical scattering matrix allows to solve more complicated tasks of calculating many crystal systems under the conditions of multiple diffraction. The examples of such systems are considered in a separate topic.