A 3 Scattering Theory: Dynamical Theory [1]

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1 Introduction

In order to describe the scattering of electrons and X-rays by crystals two theories are widely used. The first and the most common one is the so-called *kinematical theory*. Within the kinematical theory, it is assumed that the incoming wave of e.g. electrons or X-rays is scattered from the objects, which perform the scattering, e.g. atoms, only once. After such "once-scattering" the intensities of the scattered waves are added taking into account the phase differences of the scattered waves in order to form the intensities of the transmitted and reflected beams. What is neglected in the kinematical theory is the interaction of the "once-scattered" waves with each other and the matter. In terms of rigorous scattering theory, kinematical theory corresponds to the (1^{st}) *Born approximation*, discussed in detail in the proceeding's lecture by Prof. Stefan Blügel [1]. While kinematical theory works nicely in many cases, it is important to remember its limitations, namely, it works best when the crystals on which the incoming wave is scattered are small, thus, the interaction of the "once-scattered" wave with matter and other waves is negligible.

Very often, however, the diffraction of waves and particles on large crystals of very good crystalline quality is investigated, and the intensities of the transmitted and reflected beams are measured after the waves forming them traverse large regions of space filled with atoms. In this case the interaction between the scattered waves and atoms cannot be ignored anymore, and the so-called *multiple scattering* of waves inside the crystal, which technically corresponds to going beyond the Born approximation, has to be considered in order to explain observed phenomena which cannot be understood within the kinematic theory. Here, the situation can be essentially simplified if the perfect periodicity of the crystal is assumed. The foundations of the *dynamical scattering theory*, which goes beyond the kinematical scattering theory of diffraction along these lines, were set already by Darwin in 1914 [2]. On a more fundamental level the problem was treated by Ewald in 1917 [3] and later by Laue [4]. For electrons, the problem has been tackled further by Bethe [5]. Since then, many good books and reviews on the subject have been published, see e.g. the books of Zachariasen [6], Cowley [7] or Authier [8], or reviews by Slater [9], and Batterman and Cole [10]. In our manuscript, we mainly follow the review by Slater [9] and a beautiful review by P. H. Dederichs [11].

The present manuscript presents the simplest possible introduction into dynamical scattering, which is, however, mainly self-contained and can be understood without an advanced knowledge of quantum mechanics and solid state physics. The variety of effects which can be explained within the dynamical scattering theory is vast, and there are considerable differences for different types of radiation. There is, nevertheless, a common body of theory which lets us appreciate the main types of phenomena to be observed, and we present this in the simplest and most transparent form.

Below, summarized in Table I, we give an estimate of the most important for dynamical diffraction quantities. First, we give a typical energy E of neutrons, X-rays, electrons as well as for the case of low-energy-electron diffraction. Correspondingly, we also provide the characteristic wevelengths of different types of radiation λ. The most important for dynamical diffraction is the so-called *extinction length*, which is essentially the thickness of the crystal for which the kinematic theory breaks down. Note that for different types of radiation this thickness, denoted by d_{ext} in Table I, can change over five orders of magnitude. In particular, this means, that the dynamical theory is absolutely necessary for LEED, while it can be completely neglected for neutrons and it is not that important for X-rays, which can be more or less nicely described within the kinematic theory. Next, we provide the typical absorption length $1/\mu_0$, see sec-

	neutrons	X-rays	electrons	LEED
energy E	10 meV	10 keV	100 keV	100 eV
wavelength λ	1 Å	1 Å	0.05 Å	1 Å
extinction length d_{ext}	10^5 Å	10^4 Å	$10^2 - 10^3$ Å	5 Å
absorption length $1/\mu_0$	10^8 Å	10^5 Å	$10^3 - 10^4$ Å	10 Å
$1/\Delta\mu$	$> 10^8$ Å	$30 \cdot 10^5$ Å	$3 \cdot (10^3 - 10^4)$ Å	10 Å

Table 1: *Basic parameters for the diffraction of neutrons, electrons, X-rays and in the case low-energy electron diffraction (LEED).*

tion 4.1.1. We note, that the absorption length is essentially larger than the extinction length for neutrons and X-rays, while among all types of radiation neutrons are basically not absorbed at all by the medium. Finally, we give values for the absorption length in the case when the Bragg reflection is excited ($1/\Delta\mu$, where $\Delta\mu = \mu_0 \pm \mu_{\mathtt{G}}$, depending on the relative sign of μ_0 and $\mu_{\mathtt{G}}$, see section 4.1.1). This situation corresponds to the case of the so-called *anomalous transmission*, discussed in detail in section 4.1.1. We can observe from the Table I, that for the case of Bragg diffraction the absorption of the X-rays is reduced by a very large factor, known as the *Borrmann effect*, whereas the absorption of electrons is only slightly reduced.

2 Scattering of an electronic wave by a periodic perturbation: a preamble

We start with a simple picture of a wave of electrons, which is to be scattered, and which we can write as $e^{i(\omega_0 t - \mathbf{k}_0\mathbf{r})}$, where $\mathbf{k}_0$ is the propagation vector and $\mathbf{r} = (x, y, z)$ is the coordinate in real space. The wave which will do the scattering in a crystal we represent in a very simple way as $e^{-i\mathbf{G}\mathbf{r}}$, where $\mathbf{G}$ is some reciprocal vector of our crystal lattice. For simplicity, we assume in this section that the periodicity of the crystal is obeyed only along one direction, which is perpendicular to the surface of the crystal, onto which the wave $e^{i(\omega_0 t - \mathbf{k}_0\mathbf{r})}$ is incoming. Thus, $\mathbf{G} = (0, 0, G)$. This is a typical setup of the *Bragg diffraction* experiment, see Fig. 1. Generally speaking, the solution to this scattering experiment, that is, the decomposition of the total wavefunction in space into incident, scattered and the wavefunction inside the crystal can be obtained by finding a solution of the Schrödinger equation in $\mathbb{R}^3$, which satisfies certain boundary conditions. This solution must correspond to a constant energy $E = \hbar\omega_0$, meaning, that the wave inside the crystal, as well as incident and scattered waves have the same frequency. Let us first find the solution to the Schrödinger equation inside the crystal:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V_1\cos(\mathbf{G}\mathbf{r})\psi = i\hbar\frac{\partial\psi}{\partial t}. \tag{1}$$

Owing to the Bloch's theorem, valid inside periodic crystals, every solution of this equation can be characterized by a certain wave vector $\mathbf{k}$ from the Brillouin zone of the crystal (reciprocal space) [12], and the solution itself can be represented as:

$$\psi(\mathbf{r}, t) = \sum_{n=-\infty}^{+\infty} A_n e^{-i[\omega_0 t - (\mathbf{k}+n\mathbf{G})\mathbf{r}]}. \tag{2}$$

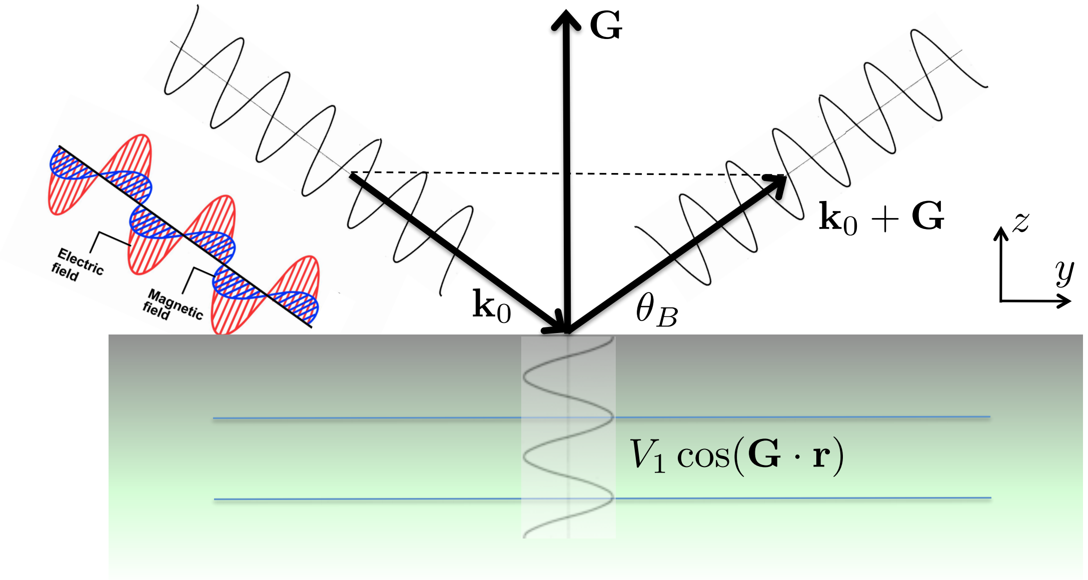

Fig. 1: *A setup of a simple diffraction experiment. An incoming wave with wave vector* $\mathbf{k}_0$ *and energy* $\hbar\omega_0$ *is scattered at a semi-infinite crystal, periodic along the* z*-direction. The wave on the left represents the case of X-ray radiation. In case of the Bragg scattering, the incoming wave is completely scattered into the reflected wave of the same energy and wave vector* $\mathbf{k}_0+\mathbf{G}$*, where* $\mathbf{G}$ *is the reciprocal vector corresponding to the periodicity of the lattice.*

Substituting the Bloch wave into Eq. (1), we obtain a system of equations for the amplitudes A_n:

$$\left[\frac{\hbar^2}{2m}(\mathbf{k}+n\mathbf{G})^2 - \hbar\omega_0\right] A_n + \frac{V_1}{2}(A_{n-1} + A_{n+1}) = 0. \tag{3}$$

The system of equations above is completely identical to the system of equations for the coefficients of the wavefunction ψ expanded in the complete and orthonormal basis of quantum states $\{\psi_n\}$: $\psi = \sum_n A_n\psi_n$. Then, if the components of the Hamiltonian matrix $H_{nm} = \langle\psi_n|H|\psi_m\rangle$, wavefunction ψ solves the Schrödinger equation with energy E when the following system of equations is satisfied [13]:

$$(H_{nn} - E)A_n + \sum_{m\neq n} H_{nm}A_m = 0 \tag{4}$$

As follows from Eq. (3), in our case, the H_{nn} matrix elements are given by $\frac{\hbar^2}{2m}(\mathbf{k}+n\mathbf{G})^2 - \hbar\omega_0$, while the off-diagonal $H_{n,n\pm1}$ matrix elements assume the values of $V_1/2$.
In general, the system of equations Eqs. (3) and (4) has solutions only for certain values of E (or ω_0), if the Bloch vector $\mathbf{k}$ is given, which establishes the so-called dispersion relation $\omega_0(\mathbf{k})$ in a crystal. The wavefunction (2) with the vector $\mathbf{k}$ is the solution of the Schrödinger equation at energy E if the $\det(H_{nm} - E\delta_{nm}) = 0$. From this condition both $E(\mathbf{k}) = \hbar\omega_0(\mathbf{k})$ and the set of $\{A_n\}$ can be determined. The solution for $\{A_n\}$ for all n can be easily performed iteratively following Eq. (3) if, for example, A_0 and A_1 are pre-given. Effectively, the choice of A_0 and A_1 corresponds to the choice of the value of the wavefunction and its derivative when solving the second-order differential Schrödinger equation. It is known that generally, if arbitrary A_0 and

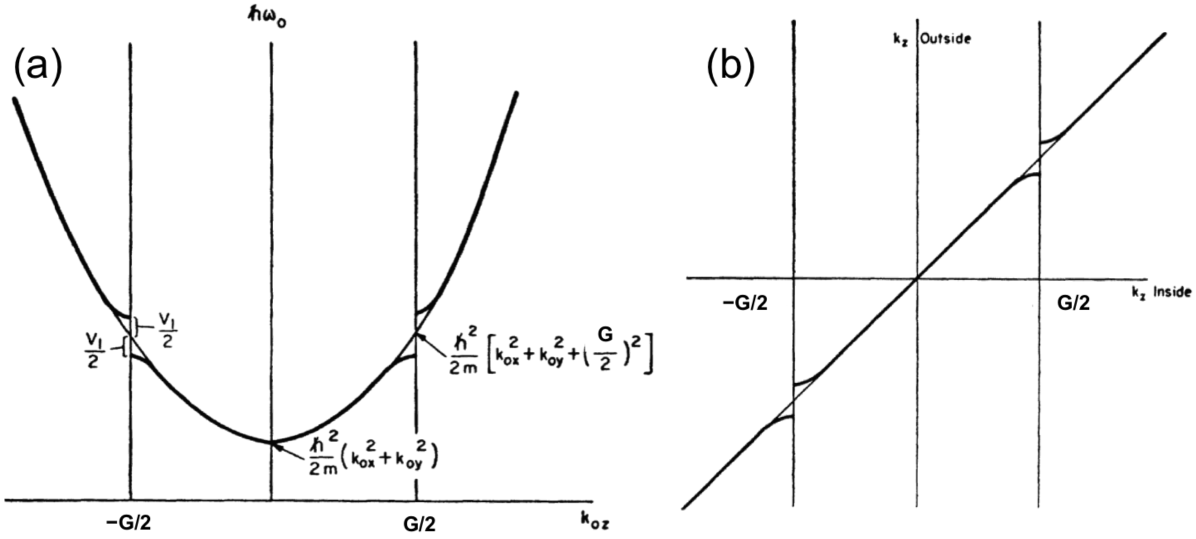

Fig. 2: *(a) Energy $\hbar\omega_0$ as a function of z component of the* $\mathbf{k}$*-vector for an electron wave inside the crystal. (b) The z component of the wave vector outside the crystal (k_{z0}) as a function of the z component of the wave vector inside the crystal (k_z). Taken from [9].*

A_1 are specified, the value of the wavefunction can be unbounded at infinity, however, upon an appropriate choice of ω_0 and A_1/A_0 ratio, the series (3) can be converged to provide a bounded wavefunction. Such frequencies ω_0 specify the energy spectrum of our system at $\mathbf{k}$.

Usually, in the theory of the *X-ray diffraction* and *electron diffraction* one of the main approximations which is made is the smallness of the V_1 (or its equivalent for X-rays, see last section). This allows to use approximations which are equivalent to the perturbation theory expressions. In the drastic case of $V_1 = 0$ (free space) the solution is trivial: $A_0 = 1$, $A_n = 0, n > 1$, and $\hbar^2\mathbf{k}^2/2m = \hbar\omega_0 = \hbar^2{\mathbf{k_0}}^2/2m$. When V_1 is sufficiently small we can derive approximate expression for the energy:

$$\hbar\omega_0 = \frac{\hbar^2\mathbf{k}^2}{2m} - \frac{V_1}{4}\left[\frac{1}{\frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})^2 - \hbar\omega_0} + \frac{1}{\frac{\hbar^2}{2m}(\mathbf{k}-\mathbf{G})^2 - \hbar\omega_0}\right] \tag{5}$$

and the only surviving coefficients in the first order with respect to V_1 are:

$$A_{\pm 1} = -\frac{V_1}{2}A_0\frac{1}{\frac{\hbar^2}{2m}(\mathbf{k}\pm\mathbf{G})^2 - \hbar\omega_0} \tag{6}$$

While for most of the energies $A_0 \gg A_{\pm 1}$, in the particular case of the *Bragg scattering*, when $(\mathbf{k}\pm\mathbf{G})^2 = {\mathbf{k_0}}^2$, Eqs. (3) and (5) have no definite value. In this case, the degenerate perturbation theory should be used. Note that in our interpretation of the equations (3) the Bragg condition means the equality of the diagonal elements of the Hamiltonian matrix for $n = 0$ and $n = 1$. In this case, employing the degenerate perturbation theory we can show that at the point where the Bragg condition, $\mathbf{k} = \pm\mathbf{G}/2$, is met, exactly two energy solutions are possible:

$$\hbar\omega_0 = \frac{\hbar^2}{2m}\mathbf{k}^2 \pm \frac{V_1}{2}, \tag{7}$$

while there are two major participants in the Bloch wave: $A_0/A_1 = 1$. The solution $\hbar\omega_0$ as a function of $\mathbf{k}$ for the both considered above cases of the Bragg scattering and away from it, is shown in Fig. 2(a). We have to remark that without assuming that there are only two waves in the crystal in the vicinity of the Bragg point (as we shall see in the following, it is called the *two-beam approximation*), we can recover analogously the opening of the gaps in the spectrum at points $\pm n\mathbf{G}/2$, with the magnitude of the gap proportional to V_1^n. Thus, if V_1 is small, then the two-beam approximation is justified.

Lets try to interpret now the appearance of the gap in the energy spectrum of a perfect periodic crystal (through V_1 and $\mathbf{G}$) from the point of view of a simple diffraction experiment, depicted in Fig. 1. In this experiment a wave of electrons (X-rays etc.) of a certain energy $\hbar\omega_0$ and wavelength $\mathbf{k}_0$, is sent toward the (possibly even finite) film, while the intensities of the reflected (or even transmitted to the other side of the film) waves are measured. Theoretical treatment of this experiment lies in finding the solutions to the Schrödinger equation in the vacuum and in the film, which can be very complicated owing to the dynamical nature of scattering. Two necessary conditions have to be satisfied in order to uniquely solve the problem: (i) the solution of the Schödinger equation in each part of space is sought at an energy $\hbar\omega_0$, and (ii) the wavefunction and its normal space derivative have to be continuous at the boundaries of the crystal.

In our simple case, the boundary conditions, owing to the fact that we have periodicity in the crystal only along the z-axis, lead to an observation that the in-plane components of the wave vector have to be continuous: $k_x = k_{x0}, k_y = k_{y0}$, where $\mathbf{k}_0 = (k_{0x}, k_{0y}, k_{0z})$ and the wave vector of the wave inside the crystal $\mathbf{k} = (k_x, k_y, k_z)$. The z-components of the both wave vectors do not have to be the same however, and they are indeed different in the vicinity of $\pm\mathbf{G}/2$. This discrepancy is obvious looking at the energy dispersion in Fig. 2(a), in which the energy of the electrons inside the crystal as a function of k_z is given with the thick line, while the thin line stands for the energy of electrons as a function of k_{0z} in the vacuum. As we can see, in the vicinity of $\pm\mathbf{G}/2$ the constant energy line will cross the two energy profiles at two different k-points. The correspondence between the two k-vectors at a constant energy is given in Fig. 2(b).

If the energy of an incoming wave lies in the gap of the energy solutions in the crystal, the reflection of the incoming wave will be very large. In this case the waves inside the crystal will be decaying with the distance from the surface of the film, since the Bloch waves cannot be matched to the wave outside the crystal. When the energy is in the middle of the gap, which occurs exactly at the Bragg angle of the incoming wave of θ_B, see Fig. 1, the reflection is complete. The range of the angles of the incident wave, θ, for which the transmission is unfavorable can be found easily:

$$\sin\theta = \left[\sin^2\theta_B \pm \frac{V_1}{2\hbar\omega_0}\right]^{1/2}. \tag{8}$$

On the other hand, when the experiment operates away from the Bragg condition, the matching of the incoming wave to the Bloch wave inside the crystal can be perfectly done, and, as a result, the amplitude of the reflected beam is very small.

3 Scattering of electrons in a crystal: general case

In this section we elaborate in more detail how the dynamical scattering can be studied in a way suggested in the previous section.

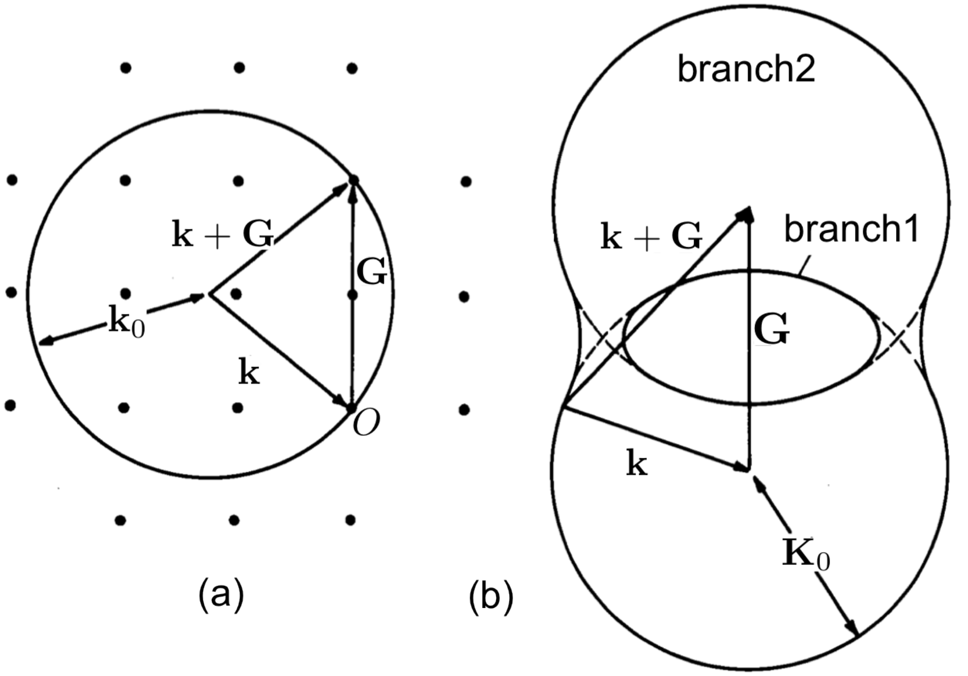

Fig. 3: *(a) Ewald sphere around the Bloch vector* $\mathbf{k}$ *of the radius corresponding to an incoming wave* $\mathbf{k}_0$*. The origin of the sphere is sometimes called the* Laue point*. (b) Dispersion surface for the two-beam case. Taken from [11].*

The motion of an electron in a solid is described by the Schrödinger equation Eq. (1):

$$H\psi = -\frac{\hbar^2}{2m}\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{9}$$

In an infinite periodic crystal the potential $V(\mathbf{r})$ is periodic with respect to translations by lattice vectors $\mathbf{R}$. The crystal potential can be split into contributions from different unit cells:

$$V(\mathbf{r}) = \sum_{\mathbf{R}} v(\mathbf{r}-\mathbf{R}) \tag{10}$$

where $v(\mathbf{r})$ is the potential of the Wigner-Seitz cell:

$$v(\mathbf{r}) = -\frac{Ze^2}{r} + \int_{V_C} d\mathbf{r}'\, \frac{e^2\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \tag{11}$$

Here, the first term represents the attractive interaction with the nucleus of charge $Z = \int_{V_C} d\mathbf{r}'\,\rho(\mathbf{r}')$, and the second one is the repulsive interaction with the electron density ρ in the unit cell of the volume V_C. The crystal potential can be decomposed into Fourier series:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}} \tag{12}$$

where the set $\{\mathbf{G}\}$ is the reciprocal lattice. The expression for the $\mathbf{G}$-components of V reads:

$$V_{\mathbf{G}} = \frac{1}{V_C}\int_{V_C} e^{-i\mathbf{G}\mathbf{r}} V(\mathbf{r})\, d\mathbf{r} = \frac{1}{V_C}\int_{\mathbb{R}^3} e^{-i\mathbf{G}\mathbf{r}} v(\mathbf{r})\, d\mathbf{r} \tag{13}$$

Using expression Eq. (11) we come to:

$$V_{\mathbf{G}} = -\frac{4\pi e^2}{V_C}\frac{Z - f_{\mathbf{G}}}{G^2} \tag{14}$$

with

$$f_{\mathbf{G}} = \int_{V_C} e^{-i\mathbf{Gr}}\rho(\mathbf{r})\,d\mathbf{r} \tag{15}$$

The quantity $f_{\mathbf{G}}$ is known as *atomic scattering factor*, and it is normally smaller or equal than Z, ensuring that all the Fourier components of the potential are negative. For small $\mathbf{G}$'s the $V_{\mathbf{G}}$'s approach a constant, while for higher harmonics the interaction with the nucleus becomes increasingly important.

According to the Bloch's theorem valid in periodic crystals, the solution of the Schrödinger equation with a wave vector $\mathbf{k}$ can be represented as:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{kr}}u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} A_{\mathbf{G}}(\mathbf{k})e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}, \tag{16}$$

where $u_{\mathbf{k}}(\mathbf{r})$ is a lattice-periodic function. The coefficients $A_{\mathbf{G}}(\mathbf{k})$ can be found by substituting the Bloch wave into the Schrödinger equation, leading thus to an infinite system of linear homogeneous equations:

$$\left\{E_{\mathbf{k}} - \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})\right\}A_{\mathbf{G}}(\mathbf{k}) = \sum_{\mathbf{G}'} V_{\mathbf{G}-\mathbf{G}'}A_{\mathbf{G}'}(\mathbf{k}) \tag{17}$$

By solving this system, for each $\mathbf{k}$ we can find a set of solutions $A_{\mathbf{G}}(\mathbf{k})$ which determine the Bloch wave, and the set of energies $E_{\mathbf{k}}$, with the latter one being commonly referred to as the *band structure*. This system has a solution only if the *dispersion equation* is satisfied:

$$\det\left[\left\{E_{\mathbf{k}} - \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G})\right\}\delta_{\mathbf{G},\mathbf{G}'} - V_{\mathbf{G}-\mathbf{G}'}\right] = 0 \tag{18}$$

The effect of the *absorption* for electrons in crystals can be phenomenologically included by considering complex potential $V(\mathbf{r})$, complex $\mathbf{k}$-vectors and complex energies $E_{\mathbf{k}}$.

As already mentioned, for electron and X-ray diffraction the calculation of the Bloch waves and the band structures can be very much simplified since the energy is much larger than the potential, and, analogously to the previous section, we can apply the perturbation theory. Assuming first that $V(\mathbf{r}) = 0$, we get the following system of equations:

$$\left\{\mathbf{k}_0^2 - (\mathbf{k}+\mathbf{G})^2\right\}A_{\mathbf{G}} = 0, \tag{19}$$

where the energy $E_{\mathbf{k}}$ is given by an incoming wave with $\mathbf{k}_0$: $E_{\mathbf{k}} = \frac{\hbar^2}{2m}\mathbf{k}_0^2$. For given energy and given $\mathbf{k}$ the expression in brackets will in general not vanish for all $\mathbf{G}$ and there are no allowed waves. Nevertheless, for a certain $\mathbf{k}$ it may happen that $\mathbf{k}_0^2 = (\mathbf{k}+\mathbf{G})^2$ for one $\mathbf{G}$, for example $\mathbf{G} = 0$. Then $A_{\mathbf{G}} = \delta_{\mathbf{G},0}$ and the wave $e^{i\mathbf{kr}}$ is allowed. For $V \neq 0$ the system of equations (18) comes to:

$$\left\{\mathbf{K}_0^2 - (\mathbf{k}+\mathbf{G})^2\right\}A_{\mathbf{G}} = \sum_{\mathbf{G}'\neq\mathbf{G}} v_{\mathbf{G}-\mathbf{G}'}A_{\mathbf{G}'}, \tag{20}$$

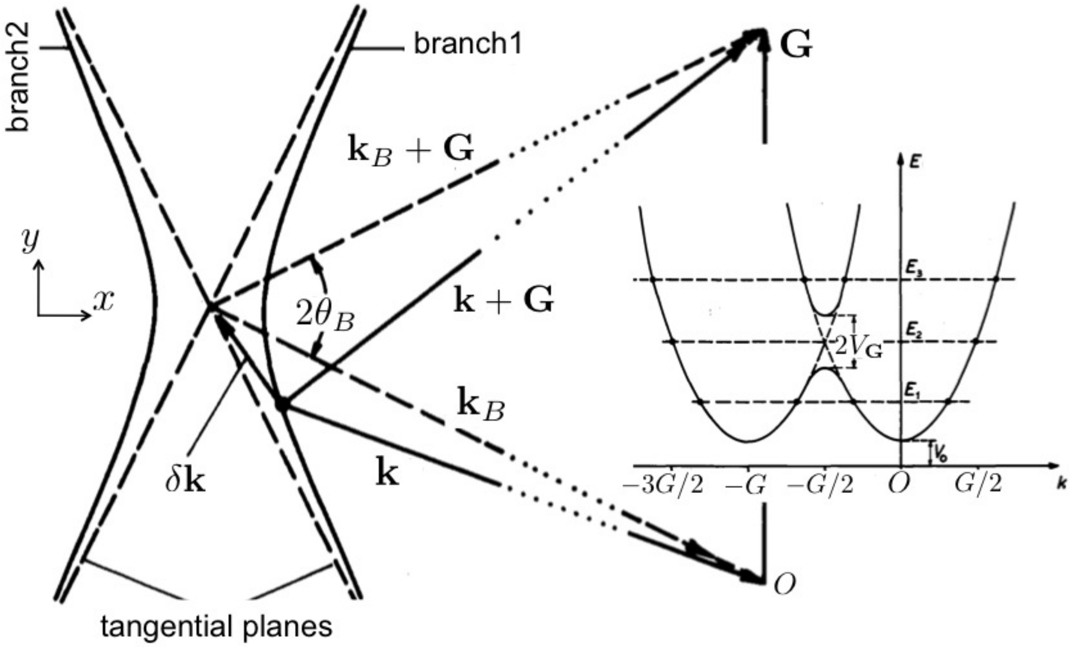

Fig. 4: *Left: Dispersion surface near the Bragg spot* $\mathbf{k}_B$*. Right: Bandstructure for the case on the right, for the direction of the Bloch vector along* y*. Taken from [11].*

with $v_\mathbf{G} = (2m/\hbar^2)V_\mathbf{G}$, and $\mathbf{K}_0^2 = \mathbf{k}_0^2 - v_0 = (2m/\hbar^2)(E_\mathbf{k} - V_0)$. It can be shown that for small $v_\mathbf{G}$ the secondary waves $A_\mathbf{G}$ for $\mathbf{G} \neq 0$ are small and we have only one strong beam $\psi = e^{i\mathbf{kr}}$ with a slightly renormalized $\mathbf{k}$-value.

However, if the condition $\mathbf{k}_0^2 \approx (\mathbf{k} + \mathbf{G})^2$ is fulfilled not only for the primary wave $\mathbf{G} = 0$ but also for other secondary waves $\mathbf{G} \neq 0$, then these waves may also become strong and the perturbation theory breaks down. This condition means that for certain $\mathbf{G}$ the vector $\mathbf{k} + \mathbf{G}$ lies near or at the so-called *Ewald sphere*, see Fig. 3. Because the energies $\frac{\hbar^2}{2m}\mathbf{k}^2$ and $\frac{\hbar^2}{2m}(\mathbf{k} + \mathbf{G})^2$ are close in this case, the degenerate perturbation theory has to be applied, which takes into account on an equal basis all the excited waves. Here, we restrict ourselves to the so-called *two-beam case*, for which only two waves are prominent in the crystal: at $\mathbf{k}$ and $\mathbf{k} + \mathbf{G}$. This approximation allows to obtain main conclusions of the dynamical scattering theory in a simple way, yet without loosing generality. We also used the two-beam approximation in the previous section. For two beams, the equations for the amplitudes of the waves read:

$$(\mathbf{K}_0^2 - \mathbf{k}^2)A_0 = v_{-\mathbf{G}}A_\mathbf{G}, \quad (\mathbf{K}_0^2 - (\mathbf{k} + \mathbf{G})^2)A_\mathbf{G} = v_\mathbf{G}A_0, \tag{21}$$

while the dispersion equation reads:

$$(\mathbf{K}_0^2 - \mathbf{k}^2) \cdot (\mathbf{K}_0^2 - (\mathbf{k} + \mathbf{G})^2) = v_\mathbf{G} \cdot v_{-\mathbf{G}}. \tag{22}$$

From the dispersion equation it is clear that in the absence of the crystal potential for a given by $\mathbf{K}_0^2$ energy the allowed $\mathbf{k}$-vectors lie on a *dispersion surface* consisting of two intersecting spheres centered around the origin, and $\mathbf{G}$, both with the radius $\mathbf{K}_0^2$, see Fig. 4. Non-zero $\mathbf{G}$-component of the potential, on the other hand, forces the intersection surface between the two spheres, at which the Bragg condition $\mathbf{k}^2 = (\mathbf{k} + \mathbf{G})^2$ is fulfilled, to split into two surfaces, of which the outer branch 2 completely surrounds the inner branch 1. While at the Bragg point

$\mathbf{k} = \mathbf{k}_B$, by setting $\mathbf{k} = \mathbf{k}_B + \delta\mathbf{k}$ around the intersection, we find:

$$4(\mathbf{k}_B \cdot \delta\mathbf{k})((\mathbf{k}_B + \mathbf{G}) \cdot \delta\mathbf{k}) = v_{\mathbf{G}} \cdot v_{-\mathbf{G}}, \tag{23}$$

if we neglect the 3rd and 4th orders in $\delta\mathbf{k}$. For convenience, we decompose the $\delta\mathbf{k}$ into x and y components, see Fig. 4. Using the condition that $K_0 \sin\theta_B = G/2$ we find:

$$\delta k_x^2 - \delta k_y^2 \tan^2\theta_B = \frac{|v_{\mathbf{G}}|^2}{4K_0^2\cos^2\theta_B}. \tag{24}$$

In this approximation, the dispersion surfaces are hyperbolas, the asymptotes of which are the tangential planes of the spheres, see Fig. 4. The smallest separation between the two branches is

$$\Delta k = \frac{|v_{\mathbf{G}}|}{K_0\cos\theta_B} \tag{25}$$

The distance $d_{ext} = \frac{2\pi}{\Delta k}$, over which the two Bloch waves from the opposite branches get a phase difference 2π, is called the *extinction length.*

From the dispersion equation we get the energy as a function of $\mathbf{k}$ as follows:

$$\frac{2m}{\hbar^2}E(\mathbf{k}) - v_0 = K_0^2 = \frac{1}{2}(\mathbf{k}^2 + (\mathbf{k}+\mathbf{G})^2 \pm \frac{1}{2}\sqrt{(\mathbf{k}^2 - (\mathbf{k}+\mathbf{G})^2)^2 + 4|v_{\mathbf{G}}|}, \tag{26}$$

showing that for $\mathbf{k}^2 = (\mathbf{k}+\mathbf{G})^2$ there is a band gap of the width $\Delta E = 2V_{\mathbf{G}}$, as in the previous section. We have plotted the bandstructure according to the relation above along the direction of $\mathbf{G}$ in Fig. 4. When the energy E_1 is below the gap, we get four allowed k-values. For the energy in the gap E_2 we obtain only two allowed k-values, while we restore the situation for E_1 when we go above the band gap (E_3).

From the previous formulas also the expressions for the amplitudes of the waves in the crystal can be derived:

$$A_0 = \frac{1}{\sqrt{2}}\sqrt{1 \mp \frac{W}{\sqrt{1+W^2}}}, \quad A_{\mathbf{G}} = \pm\mathrm{sign}(v_{\mathbf{G}})\frac{1}{\sqrt{2}}\sqrt{1 \pm \frac{W}{\sqrt{1+W^2}}}, \tag{27}$$

where an important parameter W, which measures the deviation from the Bragg angle, θ_B (see Fig. 4), is given by:

$$W = \frac{\delta\mathbf{k}\cdot\mathbf{G}}{|v_{\mathbf{G}}|}. \tag{28}$$

The limiting case of $|W| \to \infty$ corresponds to the situation away from the Bragg spot.

For the case of exact Bragg condition $W = 0$ the two Bloch waves are:

$$\psi^I(\mathbf{r}) = \sqrt{2}e^{i(\mathbf{k}+\frac{\mathbf{G}}{2})\mathbf{r}} \cdot \cos\left(\frac{\mathbf{Gr}}{2}\right), \quad \psi^{II}(\mathbf{r}) = -i\sqrt{2}e^{i(\mathbf{k}+\frac{\mathbf{G}}{2})\mathbf{r}} \cdot \sin\left(\frac{\mathbf{Gr}}{2}\right) \tag{29}$$

In case of electron diffraction, the Fourier components of the potential are negative, and the ψ^I will be positioned on the outer branch, while ψ^{II} lies at the inner branch. This situation will be reversed for X-ray diffraction, in which case $v_{\mathbf{G}}$ is positive. Characteristic for both branches are the cosine and sine modulation functions. Owing to these modulation functions, ψ^I is always maximal at the atomic positions of the reflecting planes (situated along $\mathbf{G}$), while it is small in between the planes, see Fig. 5. The situation is reversed for ψ^{II}, which is maximal between the

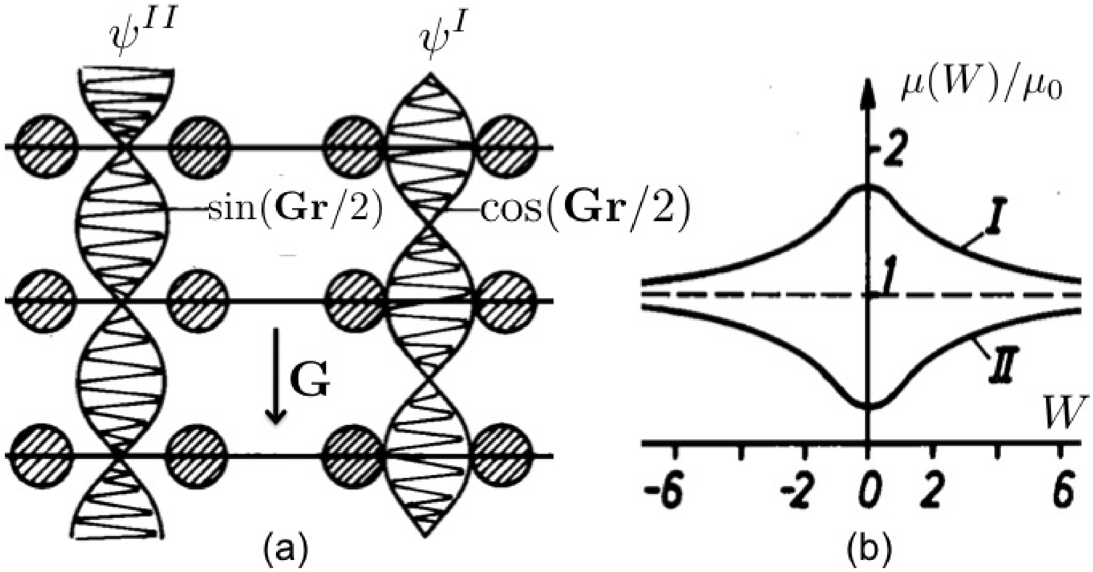

Fig. 5: *(a) Modulation factors of ψ^I and ψ^{II}. (b) Absorption for Bloch wave ψ^I and ψ^{II} at $\mu_G = 3/4\mu_0$. Taken from [11].*

atomic planes, while it almost does not interact with atomic potential. Both waves, of course, have the same energy, however, the Bloch vector of ψ^I is larger than that of ψ^{II}, since the solutions are positioned on different branches. This manifests the larger kinetic energy of the first wave, which is compensated by larger but negative energy coming from interaction with the atoms.

For an absorbing crystal it is clear that the absorption will be very much different for ψ^I and ψ^{II}. The absorption of wave ψ^I will be higher than normal since an electron in the Bloch wave spends more time on the atoms, while wave ψ^{II} manages to avoid the atoms and has therefore a smaller than average absorption, resulting in a so-called *anomalous transmission* (or *anomalous absorption*).

4 Transmission and reflection from crystal slabs

In order to find the intensities of the reflected and transmitted waves, we have to rigorously consider the scattering on the incident wave by a finite crystal of volume Ω. The potential in the whole space in a plausible approximation can be written as $V(\mathbf{r}) = \theta_\Omega(\mathbf{r})V_\infty(\mathbf{r})$, where $\theta_\Omega(\mathbf{r})$ is the step function equal to 1 in the crystal and 0 outside of it, while $V_\infty(\mathbf{r})$ is the potential of the infinite crystal. Since the solutions of the Schrödinger equation in the vacuum and in the crystal are plane waves and Bloch waves, respectively, the wavefunction in the vacuum can be represented as:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_0\mathbf{r}} + \sum_i R_i e^{i\mathbf{K}_i\mathbf{r}}, \tag{30}$$

while in the crystal

$$\psi(\mathbf{r}) = \sum_j P_j \psi_{\mathbf{k}_j}(\mathbf{r}), \tag{31}$$

with the energy $E = \frac{\hbar^2}{2m}\mathbf{k}_0^2 = \frac{\hbar^2}{2m}\mathbf{K}_i^2 = E(\mathbf{k}_j)$. How many waves in the vacuum and in the crystal are excited by an incident wave depends very much on the shape of the crystal, and the coefficients R_i and P_j have to be determined via imposing the boundary conditions. Namely, the wavefunction has to be continuous across the surface between the vacuum and the crystal, $\psi_{vac}(\mathbf{r}) = \psi_{crys}(\mathbf{r})$, and the same applies to the current through the surface, $\mathbf{n}(\mathbf{r})\frac{d\psi_{vac}(\mathbf{r})}{d\mathbf{r}} = \mathbf{n}(\mathbf{r})\frac{d\psi_{crys}(\mathbf{r})}{d\mathbf{r}}$, where $\mathbf{n}(\mathbf{r})$ is the surface normal. In order to take the evanescent states into consideration, we have to rely on the fact that the wave vectors in the vacuum and in the crystal can be in general complex.

The solution of the problem can be found by employing the integral equation for $\psi(\mathbf{r})$ in terms of the Green's function:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_0\mathbf{r}} + \int_{\mathbb{R}^3} d\mathbf{r}'\, G_0(\mathbf{r}-\mathbf{r}')V(\mathbf{r}')\psi(\mathbf{r}), \tag{32}$$

where $G_0(\mathbf{r}-\mathbf{r}')$ is the Green's function given by:

$$G_0(\mathbf{r}-\mathbf{r}') = -\frac{2m}{\hbar^2}\frac{e^{ik_0|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}. \tag{33}$$

Owing to the specific shape of our potential, as can be seen from (32) the wave in the vacuum consists of the incident wave and the sum of the spherical waves with the energy E, outgoing from the crystal. On the other hand, in the crystal, the spherical waves completely suppress the $e^{i\mathbf{k}_0\mathbf{r}}$ wave (so-called extinction theorem), while forming at the same time the Bloch solutions [11].

Equation (32) allows for a simple interpretation. The incident plane wave $e^{i\mathbf{k}_0\mathbf{r}}$ is compensated by spherical waves emitted from scattering at position $\mathbf{r}'$ in the crystal. The intensity of these scattered waves is proportional to the interaction potential $V(\mathbf{r}')$ and the amplitude of the total wave field $\psi(\mathbf{r}')$ at that point. Note that the wavefunction ψ appears both on the right and left hand side of Eq. (32). In *kinematical theory* of diffraction, the ψ on the right hand side of Eq. (32) is replaced by the incident wave $e^{i\mathbf{k}_0\mathbf{r}}$ itself, which corresponds to so-called *first Born approximation*. The physics behind the 1^{st} Born approximation is the assumption that the incoming wave scatters only *once* on the crystal potential before forming the scattered wave ψ^1. In most of the cases, especially for neutron scattering, the kinematic approximation works very well. On the other hand, for X-ray and especially electron scattering the kinematic theory very often does not provide good results. In this case using the theory which goes beyond the 1^{st} Born approximation, namely, *dynamical scattering theory*, is necessary. This can be done, for example, by iteratively using the solution of the $(n-1)^{st}$ Born approximation in order to construct the solution of the next interaction via solving Eq. (32). This procedure corresponds to converging the so-called *Born series*. For more details, see the manuscript of Prof. Stefan Blügel in this book [1].

Let us now consider the case of a finite crystal slab, which fills the space between $0 \leq z \leq d$, see Fig. 6 for setup. The potential in the crystal is thus periodic in the $x-y$ plane, with the reciprocal two-dimensional lattice $\{\mathtt{G}\}$. Correspondingly, each wavefunction in the crystal can be identified with a certain in-plane Bloch vector $\mathtt{k}$, and can be expanded in $\mathbb{R}^3$ as ($\mathtt{r}$ is the coordinate in-plane):

$$\psi_{\mathtt{k}}(\mathtt{r}, z) = \sum_{\mathtt{G}} \Gamma_{\mathtt{G}}(z) e^{i(\mathtt{k}+\mathtt{G})\mathtt{r}} \tag{34}$$

Owing to the boundary conditions, the Bloch vector is determined by the in-plane component of the incident wave $\mathbf{k}_0 = (\mathtt{k}, k_0^z)$ By substituting this equation into the Schrödinger equation

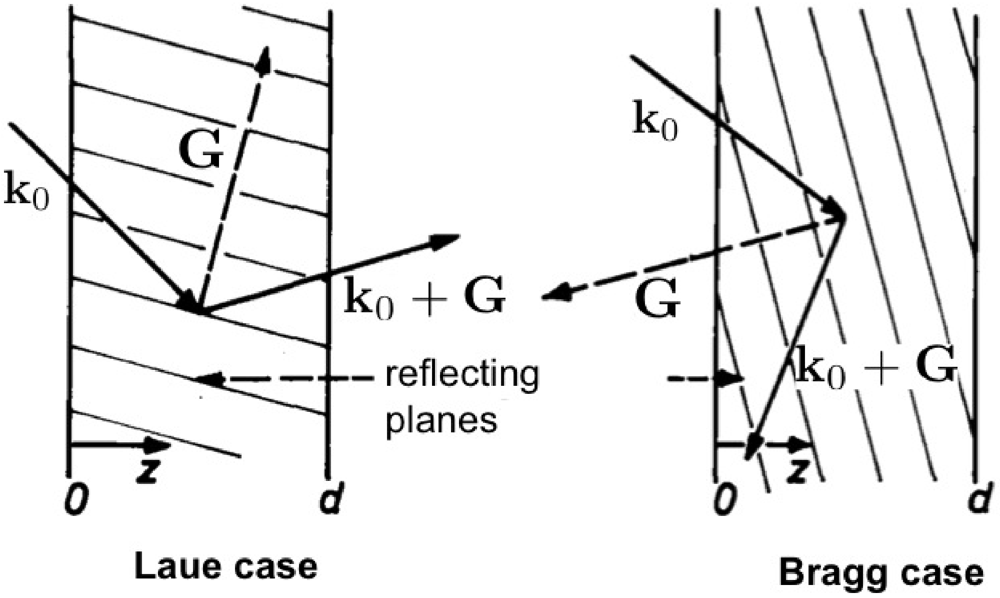

Fig. 6: *Incident wave* $\mathbf{k}_0$ *and reflected wave* $\mathbf{k}_0 + \mathbf{G}$ *for the Laue and Bragg case. Taken from [11].*

we obtain a set of equations for $\Gamma_{\mathtt{G}}(z)$:

$$\left[\partial_z^2 + (k_0^2 - (\mathtt{k}+\mathtt{G})^2)\right]\Gamma_{\mathtt{G}}(z) = \sum_{\mathtt{G}'} v_{\mathtt{G}-\mathtt{G}'}(z)\Gamma_{\mathtt{G}'}(z). \tag{35}$$

From this equation we can conclude that for each $\mathtt{G}$ the energy is split up into the energy for motion in-plane, $\frac{\hbar^2}{2m}(\mathtt{k}+\mathtt{G})^2$, and the remaining of the energy $\frac{\hbar^2}{2m}k_0^2$ for motion in the z-direction. Since $\mathtt{G}$ can be arbitrarily large, the energy along z can be negative, which corresponds to the bound modes decaying into the vacuum.

Equation (32) can be used to find the wavefunctions, and written for $\Gamma_{\mathtt{G}}(z)$ functions it reads:

$$\Gamma_{\mathtt{G}}(z) = \delta_{\mathtt{G},0}\, e^{izk_0^z} + \int dz'\, \frac{e^{iK_{\mathtt{G}}|z-z'|}}{2iK_{\mathtt{G}}} \sum_{\mathtt{G}'} v_{\mathtt{G}-\mathtt{G}'}(z')\Gamma_{\mathtt{G}'}(z'), \tag{36}$$

where

$$K_{\mathtt{G}} = \sqrt{k_0^2 - (\mathtt{k}+\mathtt{G})^2},\ \text{if } K_{\mathtt{G}}^2 > 0 \qquad K_{\mathtt{G}} = i\kappa_{\mathtt{G}},\ \kappa_{\mathtt{G}} > 0,\ \text{if } K_{\mathtt{G}}^2 < 0 \tag{37}$$

In the vacuum for $z < 0$ we get

$$\Gamma_{\mathtt{G}}(z) = \delta_{\mathtt{G},0}\, e^{izk_0^z} + R_{\mathtt{G}}\, e^{-izK_{\mathtt{G}}} \tag{38}$$

with

$$R_{\mathtt{G}} = \frac{1}{2iK_{\mathtt{G}}} \int_0^d dz'\, e^{+iK_{\mathtt{G}}z'} \sum_{\mathtt{G}'} v_{\mathtt{G}-\mathtt{G}'}(z')\Gamma_{\mathtt{G}'}(z'), \tag{39}$$

and analogously for $z > d$:

$$\Gamma_{\mathtt{G}}(z) = \delta_{\mathtt{G},0}\, e^{izk_0^z} + T_{\mathtt{G}}\, e^{+izK_{\mathtt{G}}} \tag{40}$$

with

$$T_{\mathtt{G}} = \frac{1}{2iK_{\mathtt{G}}} \int_0^d dz'\, e^{-iK_{\mathtt{G}}z'} \sum_{\mathtt{G}'} v_{\mathtt{G}-\mathtt{G}'}(z')\Gamma_{\mathtt{G}'}(z'). \tag{41}$$

Coefficients $R_{\mathtt{G}}$ and $T_{\mathtt{G}}$ are called the *reflection* and *transmission coefficients*, respectively. Only in the case when $K_{\mathtt{G}}^2 = k_0^2 - (\mathtt{k}+\mathtt{G})^2 > 0$ do we get a reflected plane wave with $\mathbf{K}_{\mathtt{G}}^- = (\mathtt{k}+\mathtt{G}, -K_{\mathtt{G}})$ and a transmitted plane wave $\mathbf{K}_{\mathtt{G}}^+ = (\mathtt{k}+\mathtt{G}, +K_{\mathtt{G}})$. The waves with complex $K_{\mathtt{G}}$ decrease exponentially into the vacuum. It is clear, that whereas we have only a finite number of reflected and transmitted waves, the number of decaying waves is infinite. A graphical construction of the waves $\mathbf{K}_{\mathtt{G}}^{\pm}$ is shown in Fig. 8, in which all vectors $\mathbf{K}_{\mathtt{G}}^{\pm}$ lie on the sphere of radius k_0. Assuming that the vector $\mathtt{G}$ lies in the plane of $\mathbf{k}_0$ and surface normal, the only four allowed real vectors $\mathbf{K}_{\mathtt{G}}^{\pm}$ and $\mathbf{K}_{2\mathtt{G}}^{\pm}$ are shown.

The kinematical scattering theory is constructed based on the substitution of $e^{iz'k_0^z}$ instead of $\Gamma_{\mathtt{G}'}(z')$ in the right hand side of Eq. (36). The intensities of the waves obtained within the kinematical theory can very much deviate from the predictions of the dynamical theory, especially for the case of Bragg reflection $k_0^z \pm K_{\mathtt{G}} + g = 0$, where g is the projection of $\mathbf{G}$ on the z-axis, see Fig. 6.

Inside the crystal, only those Bloch waves $\mathbf{k}_j$ with energy $E(\mathbf{k}_j) = \frac{\hbar^2}{2m}k_0^2$, are allowed. Moreover the in-plane component of the Bloch vector can differ from $\mathtt{k}$ only by an in-plane reciprocal vector $\mathtt{G}$. Since the energy of the Bloch states are periodic in reciprocal space, we can assume that $\mathbf{k}_j = (\mathtt{k}, k_{jz})$, where k_{jz} are determined from the energy conservation. The P_j coefficients in Eq. (31) can be also determined by matching the waves inside and outside the crystal at both vacuum boundaries.

4.1 Symmetric Laue case

Let us consider now the case when only one Bragg reflection $\mathbf{G}$ is excited, see Fig. 6. In this case we can apply the two-beam approximation. In principle, for an incident from $-\infty$ wave there are two situations to consider: when the crystal-reflected $\mathbf{k}_0 + \mathbf{G}$ wave propagates forward (*Laue case*) or backwards (*Bragg case*), see Fig. 6. In this subsection we discuss the so-called symmetric Laue case, for which $\mathbf{G}$ lies in-plane, and can be thus represented as $\mathbf{G} = (\mathtt{G}, 0)$. In this case the reflecting atomic planes are perpendicular to the surface of the slab.

For symmetric Laue case the setup of the problem is presented in Fig. 7 in the reciprocal space. We have the following waves in the vacuum. For $z > d$: the transmitted wave $\mathbf{k}_0 = \mathbf{K}_0^+ = (\mathtt{k}, k_0^z)$ (given by vector AO) and the Bragg reflected wave $\mathbf{K}_{\mathtt{G}}^+ = (\mathtt{k}+\mathtt{G}, K_{\mathtt{G}})$ (given by vector BH). For $z < 0$ we have the incident wave $\mathbf{k}_0$, the surface reflected wave $\mathbf{K}_0^- = (\mathtt{k}, -k_0^z)$ (given by vector DO) and the surface reflected wave of the forward propagating $\mathbf{K}_{\mathtt{G}}^+$ wave, $\mathbf{K}_{\mathtt{G}}^- = (\mathtt{k}+\mathtt{G}, -K_{\mathtt{G}})$ (given by vector CH). In the crystal, we get four Bloch waves $\mathbf{k}_j = (\mathtt{k}, k_{jz})$, where the k_{jz} are determined from the dispersion relation:

$$(K_0^2 - \mathtt{k}^2 - k_{jz}^2)(K_0^2 - (\mathtt{k}+\mathtt{G})^2 - k_{jz}^2) = |v_{\mathtt{G}}|^2. \tag{42}$$

The dispersion surface in the vacuum (thin lines) and in the crystal (thick lines) is shown together with vectors $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4$ (numbers) in Fig. 7. Characteristically for electrons the radius $K_0 = \sqrt{k_0^2 - v_0}$ is larger than k_0 (opposite for X-rays). However, the difference $(K_0 - k_0)/k_0 \approx -v_0/(2k_0^2)$ is extremely small or high energy electrons. For example, if we have $E = 100$ eV and $-v_0 = 10$ eV one gets for the latter ratio a value of $5 \cdot 10^{-5}$. Therefore vectors $\mathbf{k}_0, \mathbf{k}_1, \mathbf{k}_2$ in Fig. 7 are basically the same.

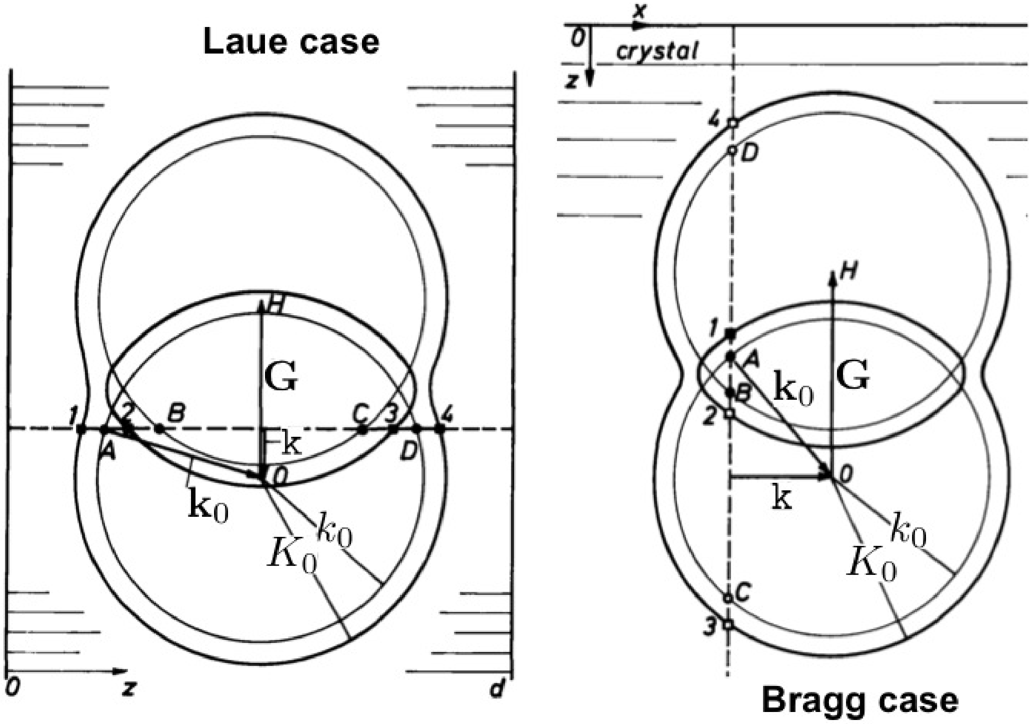

Fig. 7: *Dispersion surface in the crystal and in the vacuum for symmetric Laue case and symmetric Bragg case. Thin lines stand for the dispersion surface in the crystal, while thick lines stand for the dispersion surface in the crystal. Taken from [11].*

It can be shown by solving equations for transmission, reflection and R_j coefficients from the beginning of this section, that for the symmetric Laue case with a high degree of accuracy there are only two strong waves in the vacuum: $\mathbf{k}_0$ and $\mathbf{K}_{\mathsf{G}}^{+}$, while in the crystal the only two Bloch waves which can be considered are $\mathbf{k}_1$ and $\mathbf{k}_2$ (see Fig. 8(b)). The intensity of the transmitted waves can be calculated:

$$|T_0|^2 = \frac{W^2}{1+W^2} + \frac{1}{1+W^2}\cos^2\left(\frac{d\Delta k\sqrt{1+W^2}}{2}\right), \tag{43}$$

and

$$|T_{\mathsf{G}}|^2 = \frac{1}{1+W^2}\sin^2\left(\frac{d\Delta k\sqrt{1+W^2}}{2}\right), \tag{44}$$

where W and Δk are given by Eqs. (28) and (25). Exactly at the Bragg condition $W = 0$

$$|T_0|^2 = \cos^2\left(\frac{d\Delta k}{2}\right), \text{ and } \quad |T_{\mathsf{G}}|^2 = \sin^2\left(\frac{d\Delta k}{2}\right). \tag{45}$$

These are the so-called *Pendellösungen* (pendulum solutions), manifesting the exchange of intensity between the two transmitted beams as a function of the film thickness d, see Fig. 8. The period of this oscillation is the extinction length d_{ext}. By writing the wave field inside the crystal for the exact Bragg condition $\mathbf{k}_B = (\mathbf{k}_1 + \mathbf{k}_2)/2$:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_B\mathbf{r}}\cos\left(\frac{z\Delta k}{2}\right) + ie^{i(\mathbf{k}_B+\mathbf{G})\mathbf{r}}\sin\left(\frac{z\Delta k}{2}\right), \tag{46}$$

we observe again the pendulum solution with the thickness-dependent amplitude of the both waves which constitute the crystal wave field, see Fig. 8.

Effect of absorption. In case of a crystal with absorption it is important to realize the the Bloch waves $\mathbf{k}_1$ and $\mathbf{k}_2$ are absorbed differently, since they lie on different branches of the dispersion surface, as discussed in the previous section. It can be shown that as a function of W the absorption coefficient which describes the exponential decay of the intensity of the beam for both solutions is

$$\mu^{I,II}(W) = \mu_0 \pm \frac{1}{\sqrt{1+W^2}}\mu_{\mathtt{G}}, \tag{47}$$

where μ_0 and $\mu_{\mathtt{G}}$ are proportional to the corresponding parts of the Fourier components $\tilde{v}_0$ and $\tilde{v}_{\mathtt{G}}$ of the complex crystal potential which describes the absorption process. Clearly, μ_0 corresponds to the average strength of the absorption of a single plane wave by an "averaged" potential. An example of a behavior of the ratio $\mu^{I,II}(W)/\mu_0$ is given in Fig. 5(b). We can see that the difference in the absorption of the solutions on both branches is particularly strong in the vicinity of the Bragg condition. If the thickness of the crystal is rather large the wave lying on the 1^{st} branch will be therefore almost completely absorbed. Since the pendulum solutions arise due to the interference of the waves on both branches, in the limit of a semi-infinite crystal the oscillations in the intensity of two transmitted beams are diminished.

In greater detail, if we consider the case of exact Bragg condition, $W = 0$, the intensities of the transmitted waves as a function of the thickness of the crystal d can be decomposed into "non-oscillating" (no) and "oscillating" (o) parts, which can be calculated to be:

$$|T_0|^2_{no} \sim e^{-(\mu_0+\mu_{\mathtt{G}})d} + e^{-(\mu_0-\mu_{\mathtt{G}})d}, \quad |T_0|^2_o \sim e^{-\mu_0 d}\cdot\cos^2\left(\frac{d\Delta k}{2}\right), \tag{48}$$

$$|T_{\mathtt{G}}|^2_{no} \sim e^{-(\mu_0+\mu_{\mathtt{G}})d} + e^{-(\mu_0-\mu_{\mathtt{G}})d}, \quad |T_{\mathtt{G}}|^2_o \sim e^{-\mu_0 d}\cdot\sin^2\left(\frac{d\Delta k}{2}\right). \tag{49}$$

Typical measured curves for the intensities look therefore similar to the case of X-ray scattering in silicon, see Fig. 10(a). What we observe from the above expressions is that on the non-oscillating background intensity which decays as $e^{-(\mu_0+\mu_{\mathtt{G}})d} + e^{-(\mu_0-\mu_{\mathtt{G}})d}$ with d, there is an oscillating term which decays proportionally to $e^{-\mu_0 d}$. It is important to realize that, away from the Bragg condition there is no interference of waves I and II, which leads to different absorption and oscillatory term in above expressions. Thus, away from the Bragg spot, the intensity of the transmitted waves is simply proportional to $e^{-\mu_0 d}$, owing to the "smearing" of the wave inside the crystal over the unit cell.

Imagine now a situation in which the angle of incidence is varied and the intensity of the transmitted beam (for certainty lets assume it is given by $|T_{\mathtt{G}}|^2$) is measured for a thick crystal with thickness d. Away from θ_B this intensity is proportional to $e^{-\mu_0 d}$, but once the angle of incidence approaches θ_B, the dominant contribution to intensity becomes proportional to $e^{-(\mu_0-\mu_{\mathtt{G}})d}$ (lets say $0 < \mu_{\mathtt{G}} < \mu_0$). Thus, experimentally, we see a peak in the measured intensity at the Bragg angle. This constitutes the essence of the *Borrmann effect*, observed first for X-rays. For X-rays, the absorption process in highly localized since it comes mostly from the excitations of electrons in inner atomic shells. Thus, the Fourier coefficients of the absorption function decay very slowly, and the value of $\mu_{\mathtt{G}}$ can be very close to μ_0, leading to a very pronounced peak in the measured intensity of the transmitted wave. For electrons the effect is more modest, since the absorption comes mostly from plasmon excitations.

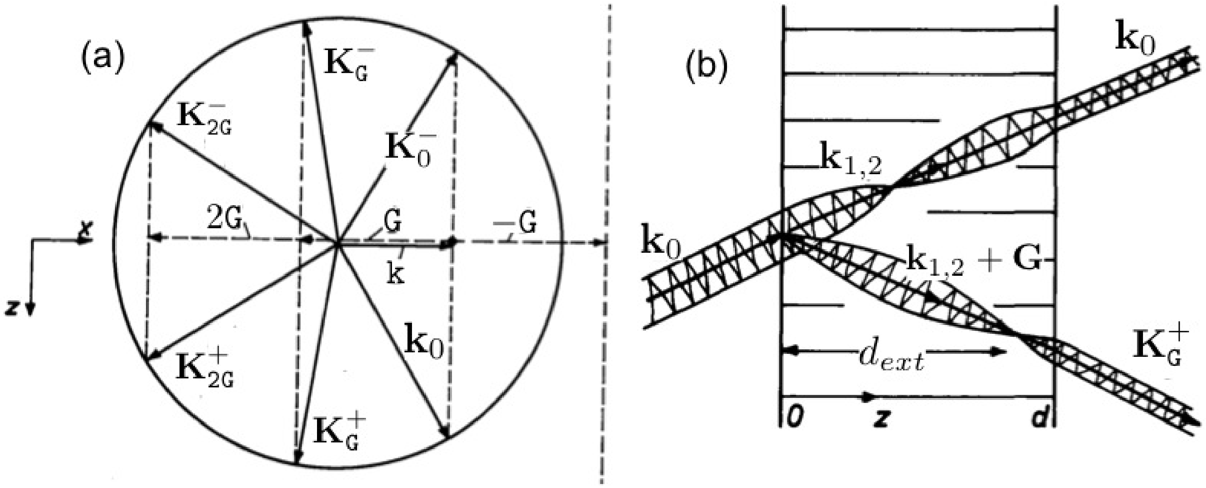

Fig. 8: *(a) Plane waves $\mathbf{K}_{\mathtt{G}}^{\pm}$ in the vacuum. (b) Wave fields in the symmetrical Laue case at exact Bragg condition ($W = 0$). Taken from [11].*

4.2 Symmetric Bragg case

In symmetric Bragg case the reflecting planes are parallel to the surface of the slab, i.e. $\mathbf{G} = (0, 0, -G)$, see Fig. 7. Here for simplicity we consider only the case of a semi-infinite crystal, which is exactly the case we considered in the first section.

The incident wave in the vacuum $\mathbf{k}_0 = (\mathtt{k}, k_0^z)$ is shown with vector AO in Fig. 7. All other allowed waves in the vacuum have to lie on one of the two spheres with radius k_0 and have the same in-plane component $\mathtt{k}$. The wave with vector DH is not a new wave since it is the same vector as AO. Since $BH = CO$ we have only one new wave in the vacuum, $\mathbf{K}_0^- = (\mathtt{k}, -k_0^z) = BH$. In the crystal we can in principle get four Bloch waves $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_3$ and $\mathbf{k}_4$, marked with corresponding numbers in Fig. 7. However, $\mathbf{k}_3$ and $\mathbf{k}_4$ do not lie in the first Brillouin zone, thus, they do not have to be considered. Moreover, it can be shown that only $\mathbf{k}_1$ has a positive group velocity and it is the only wave which should be considered in the crystal. In a slab of finite thickness both Bloch waves are allowed, leading to oscillations in the reflected intensity, analogously to the Laue case.

Upon decreasing the angle of incidence, or, equivalently, increasing the in-plane component $\mathtt{k}$ the vector $\mathbf{k}_1$ moves along the dispersion surface towards the neck between the two branches. When further increasing $\mathtt{k}$ the line of constant $\mathtt{k}$ enters the gap between the two branches before crossing the outer branch at the neck. Without absorption, the reflection coefficient can be calculated to be:

$$|R_0|^2 = \left| \frac{1}{-y \pm \sqrt{y^2 - 1}} \right|^2, \tag{50}$$

where

$$y = 2\frac{\delta k_x}{\Delta k} = \frac{2K_0 \cdot \cos\theta_B \cdot \delta k_x}{|v_{\mathbf{G}}|} \tag{51}$$

according to Eqs. (24) and (25). In the last equation sign ”−” refers to the inner branch while ”+” stands for the outer branch and the gap. For $|y| < 1$, i.e. inside the gap, the reflection coefficient $|R_0|^2 = 1$, while when the line $\mathtt{k} = \mathrm{const}$ deviates from the gap, the reflection coefficient decays very rapidly, see Fig. 9(a). The shape of R_0 as a function of the angle of

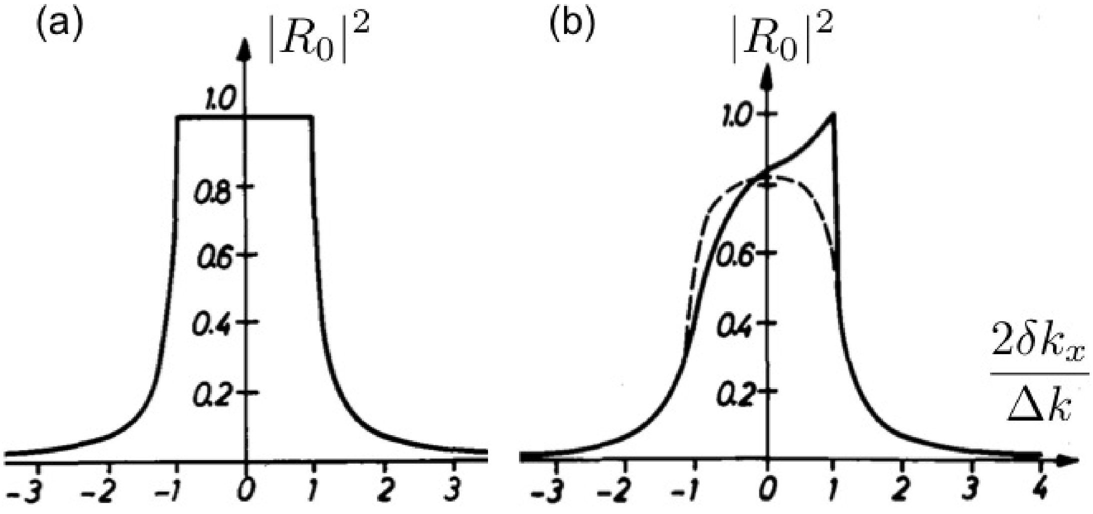

Fig. 9: *(a) Reflection coefficient $|R_0|^2$ in symmetric Bragg case without absorption. (b) Reflection coefficient $|R_0|^2$ in symmetric Bragg case with absorption with $\tilde{v}_0 = \tilde{v}_{\mathbf{G}}$ (solid line) and $\tilde{v}_{\mathbf{G}} = 0$ (dashed line). Taken from [11].*

incidence is known as the *Darwin profile*. The width of the gap where $|R_0|^2 = 1$, which is also called the *Darwin width*, exactly corresponds to the range of angle of incidence we derived in the first section, in which the perfect reflection is observed.

In case with absorption, it can be shown, that absorption is especially effective at the edges of the two branches, as can be seen from Fig. 9(b). Overall, the deviation of $|R_0|^2$ from one is inversely proportional to $\sqrt{v'_{\mathbf{G}}}$, where $v_{\mathbf{G}} = v'_{\mathbf{G}} + i\tilde{v}_{\mathbf{G}}$ is the Fourier component of the complex crystal potential. It is clear that while the absorbing potential is uniform, that is, it is given only by $\tilde{v}_0$, the waves on both dispersion branches are absorbed equivalently, as can be seen in Fig. 9(b) (dashed line). On the other hand, when the absorbing potential assumes the crystal structure, e.g. for $\tilde{v}_{\mathbf{G}} = \tilde{v}_0$, the waves I and II which have different distribution with respect to positions of the atoms, are absorbed differently, and an asymmetry in the reflection coefficient as a function of δk_x, or, equivalently, the angle of incidence, is evident, see Fig. 9(b) (solid line). An experimental example of such behavior can be clearly seen for instance in case of X-ray scattering in GaAs, for which the *rocking curve* (reflected intensity as a function of the angle of incidence) is shown in Fig. 10(b).

Physically, perfect reflection as that one in Fig. 9(a) is observed for neutrons scattered by thick slabs, since for neutrons the absorption is negligible. For X-rays the photoelectric absorption is concentrated mainly at the inner dispersion branch which results in anomalous transmission effect, and asymmetrical curves of Fig. 9(b) can be seen experimentally.

5 X-ray scattering

The theory of X-ray diffraction is quite analogous to the theory of electron diffraction with the exception that the wave fields are vector fields in nature (see Fig. 1). The interaction of X-rays with the medium arises via excitation of atomic electrons. The frequencies of motion of electrons are of the order of $\omega_0 \approx v_e/a_B$, where v_e is the velocity of electron motion around

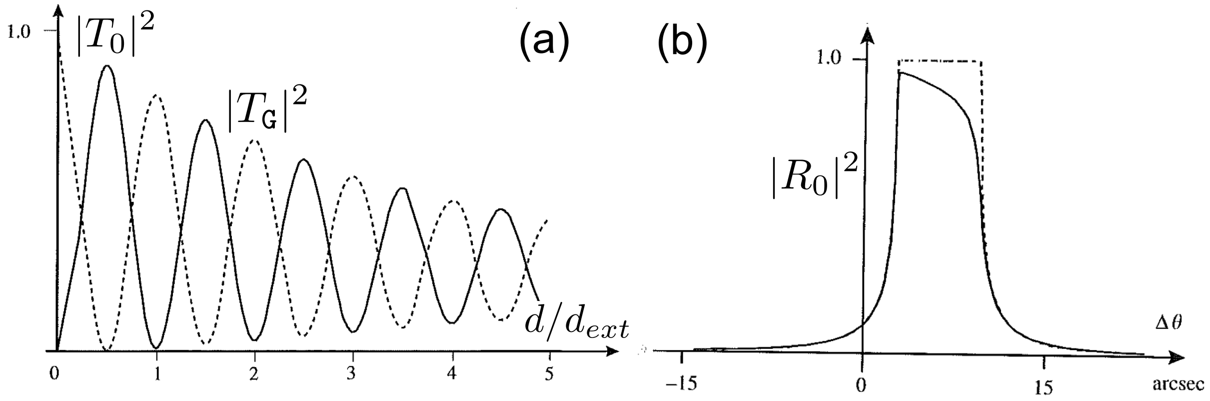

Fig. 10: *(a) Intensities of transmitted beams as a function of crystal thickness for 220 reflection of silicon with CuK*$_\alpha$ *radiation,* $d_{ext} = 15.26$ *μm. (b) Rocking curve (reflected intensity) for a thick crystal of 400 reflection of GaAs with CuK*$_\alpha$ *radiation (solid curve) compared to a theoretical calculation without absorption. Darwin width is 7.54 arcsec. Taken from [8].*

the atom, and a_B is Bohr's radius. The wavelength of X-rays is comparable to a_B while their frequencies are of the order of $2\pi c/\lambda$ with c as the speed of light, that is, much higher than those of the electrons. Thus, electrons can be treated as free. This simplification leads to the following formulation of the Maxwell's equations, which have to be solved instead of the Schrödinger equation for electrons (assuming harmonic time-dependence of the X-ray field with the frequency ω):

$$\nabla \times \mathbf{E} = i\frac{\omega}{c}\mathbf{H}, \quad \nabla \times \mathbf{H} = -i\frac{\omega}{c}\mathbf{D}, \tag{52}$$

where the electric displacement field $\mathbf{D} = \varepsilon\mathbf{E}$ and ε is the dielectric function of the medium:

$$\varepsilon(\mathbf{r},\omega) = 1 - \frac{4\pi e^2}{m\omega^2}\rho(\mathbf{r}), \tag{53}$$

with $\rho(\mathbf{r})$ as the electronic density. Additionally,

$$\nabla \cdot \mathbf{D} = \nabla \cdot \mathbf{H} = 0, \quad \nabla \times \nabla \times \mathbf{E} = (\omega/c)^2\mathbf{D}. \tag{54}$$

Deviation of ε from unity is actually very small for X-rays and the quantity $\chi = \varepsilon - 1$ normally varies between 10^{-6} and 10^{-4}. Thus, we can write that

$$\mathbf{E} = \frac{1}{\varepsilon}\mathbf{D} \approx \mathbf{D} - \chi\mathbf{D}. \tag{55}$$

This equation is a great simplification, which, substituted into previous equations leads to an equation for $\mathbf{D}$ alone:

$$(\nabla^2 + k_0^2)\mathbf{D}(\mathbf{r}) = -\nabla \times \nabla \times [\chi(\mathbf{r})\mathbf{D}(\mathbf{r})] \tag{56}$$

In an infinite periodic crystal the charge density as well as the dielectric function are periodic and can be expanded in terms of the Fourier series in analogy to the potential for electrons Eq. (12). Analogously to electrons, the solution to Eq. (56) can be sought in the shape of a Bloch wave:

$$\mathbf{D}_\mathbf{k}(\mathbf{r}) = \sum_\mathbf{G} \mathbf{D}_\mathbf{G} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}. \tag{57}$$

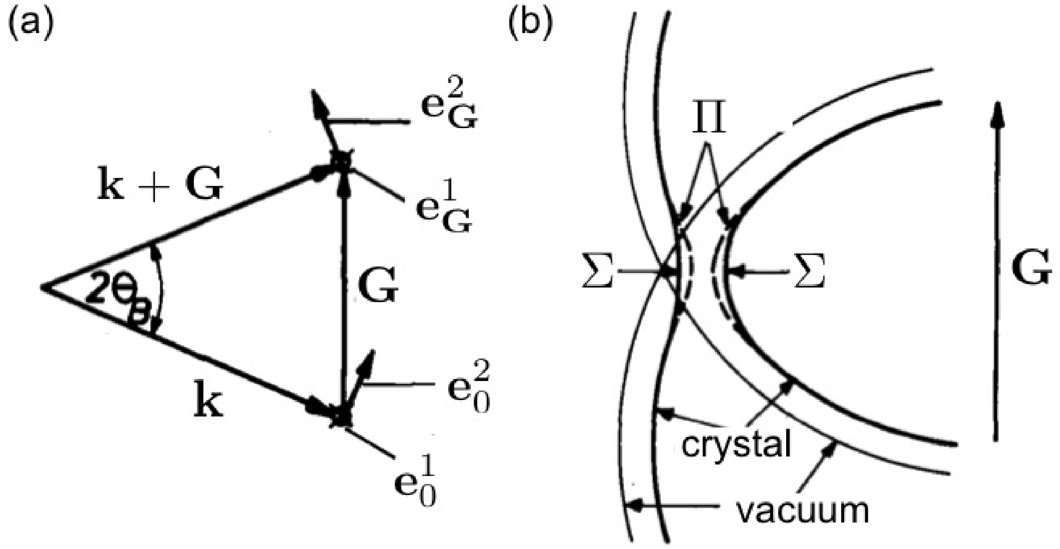

Fig. 11: *(a) Direction of polarization vectors. Vectors* $\mathbf{e}_0^1 = \mathbf{e}_\mathbf{G}^1$ *are normal to the plane of the plot. (b) Dispersion surface for* Σ *and* Π *polarizations. Taken from [11].*

Since $\nabla \cdot \mathbf{D} = 0$ the vectors $\mathbf{D}_\mathbf{G}$ are orthogonal to $\mathbf{k}+\mathbf{G}$: $\mathbf{D}_\mathbf{G} \cdot (\mathbf{k}+\mathbf{G}) = 0$. It can be shown that the corresponding component $\mathbf{H}_\mathbf{G}$ is orthogonal both to $\mathbf{k}+\mathbf{G}$ and $\mathbf{D}_\mathbf{G}$, while $\mathbf{E}_\mathbf{G}$ lies in the plane of $\mathbf{D}_\mathbf{G}$ and $\mathbf{k}+\mathbf{G}$, but the difference between $\mathbf{E}_\mathbf{G}$ and $\mathbf{D}_\mathbf{G}$ is very small owing to the smallness of χ.

For each Fourier component we can introduce two polarization vectors $\mathbf{e}_\mathbf{G}^\sigma \cdot (\mathbf{k}+\mathbf{G}) = 0$ and $\mathbf{e}_\mathbf{G}^\sigma \cdot \mathbf{e}_\mathbf{G}^{\sigma'} = \delta_{\sigma,\sigma'}$, where σ and σ' are either "1" or "2". Thus, we can write that $\mathbf{D}_\mathbf{G} = \sum_\sigma D_\mathbf{G}^\sigma \mathbf{e}_\mathbf{G}^\sigma$. Since χ is very small, we can significantly simplify Eq. (56), arriving at the following system of equations for the scalar Fourier components of $\mathbf{D}$:

$$\left(k_0^2 - (\mathbf{k}+\mathbf{G})^2\right) D_\mathbf{G}^\sigma = \sum_{\mathbf{G}',\sigma'} \varkappa_{\mathbf{G}-\mathbf{G}'} \left(\mathbf{e}_\mathbf{G}^\sigma \cdot \mathbf{e}_{\mathbf{G}'}^{\sigma'}\right) D_{\mathbf{G}'}^{\sigma'}, \tag{58}$$

where

$$\varkappa_{\mathbf{G}-\mathbf{G}'} = -k_0^2 \chi_{\mathbf{G}-\mathbf{G}'} = \frac{4\pi r_e}{V_C} f_{\mathbf{G}-\mathbf{G}'} \tag{59}$$

with $f_\mathbf{G}$ as the atomic scattering factor, Eq. (15), and r_e as the classical electron radius of 2.82×10^{-13} cm. Note that since $\mathbf{e}_\mathbf{G}^\sigma \cdot \mathbf{e}_{\mathbf{G}'}^{\sigma'}$ is in general non-zero because $\mathbf{G} \neq \mathbf{G}'$, the latter equations couple both polarizations. Also note complete similarity between Eq. (58) and Eqs. (17) and (20) derived previously for the case of electron scattering in a crystal. Thus, $\varkappa_{\mathbf{G}-\mathbf{G}'}$ is analogous to the corresponding component of the crystal potential for electrons. The eigenenergies, or, bands $\omega_\mathbf{k}$ of X-ray Bloch states in a crystal are determined from the secular equation which is very much the same as Eq. (18). Analogously to the case of electrons the effect of absorption lies in complexity of the k-vectors, eigenenergies and Fourier components of the crystal "potential" $\varkappa$.

For scattering of X-rays from a finite crystal, the boundary conditions have to be formulated. Owing to the nature of Maxwell's equations given in the beginning of the section, and smallness of χ, the boundary conditions are very simple: both normal and tangential components of $\mathbf{D}$ have to be continuous across the boundary between the crystal and the vacuum. In general one writes the fields in the vacuum before the slab (see Fig. 6) as:

$$\mathbf{D}(\mathbf{r}) = \hat{\mathbf{D}}e^{i\mathbf{k}_0\mathbf{r}} + \sum_{\mathtt{G}} \mathbf{R}_{\mathtt{G}} e^{i\mathbf{K}^{-}_{\mathtt{G}}\mathbf{r}}, \quad z < 0, \tag{60}$$

and after the slab:

$$\mathbf{D}(\mathbf{r}) = \sum_{\mathtt{G}} \mathbf{T}_{\mathtt{G}} e^{i\mathbf{K}^{+}_{\mathtt{G}}\mathbf{r}}, \quad z > d, \tag{61}$$

while in the crystal we seek the solution in terms of Bloch waves:

$$\mathbf{D}(\mathbf{r}) = \sum_{j} P_j \mathbf{D}_{\mathbf{k}_j}(\mathbf{r}), \tag{62}$$

where all the reflection ($\mathbf{R}_{\mathtt{G}}$), transmission ($\mathbf{T}_{\mathtt{G}}$) and P_j coefficients are found by satisfying the boundary conditions. It is noteworthy to remark, that, in analogy to electrons, the kinematic and dynamical theory of X-ray scattering can be also developed starting from the integral equation for the $\mathbf{D}$-field, analogous to Eq. (32):

$$\mathbf{D}(\mathbf{r}) = \hat{\mathbf{D}}e^{i\mathbf{k}_0\mathbf{r}} + \nabla \times \nabla \times \int d\mathbf{r}' \frac{e^{i\mathbf{k}_0|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}\chi(\mathbf{r}')\mathbf{D}(\mathbf{r}'). \tag{63}$$

In analogy to electrons, if the scattering occurs away from Bragg condition, we have only one strong beam. If the Bragg reflection is excited, we have two strong beams $\mathbf{k}$ and $\mathbf{k}+\mathbf{G}$. In this case there is a natural choice for polarization vectors: (i) Σ-polarization for $\sigma = 1$: $\mathbf{e}^1_0 = \mathbf{e}^1_{\mathbf{G}}$ perpendicular to both $\mathbf{k}$ and $\mathbf{k}+\mathbf{G}$, and (ii) Π-polarization for $\sigma = 2$: $\mathbf{e}^2_0 = \mathbf{e}^2_{\mathbf{G}}$ in the plane of $\mathbf{k}$ and $\mathbf{k}+\mathbf{G}$, see Fig. 11. Via this particular choice of polarization vectors we can decouple the equations (58) for Σ and Π waves:

$$(k_0^2 - \varkappa_0 - k^2)D^{\sigma}_0 = \varkappa_{\mathbf{G}} P_{\sigma} D^{\sigma}_{\mathbf{G}}, \tag{64}$$

$$(k_0^2 - \varkappa_0 - (\mathbf{k}+\mathbf{G})^2)D^{\sigma}_{\mathbf{G}} = \varkappa_{\mathbf{G}} P_{\sigma} D^{\sigma}_0, \tag{65}$$

where polarization factor $P_{\sigma} = \mathbf{e}^{\sigma}_0 \cdot \mathbf{e}^{\sigma}_{\mathbf{G}}$ equals one for Σ-polarization, and $\cos 2\theta_B$ for Π-polarization. For each polarization the allowed k-vectors lie on the dispersion surface given by:

$$(k_0^2 - \varkappa_0 - k^2)(k_0^2 - \varkappa_0 - (\mathbf{k}+\mathbf{G})^2) = P_{\sigma}^2|\varkappa_{\mathbf{G}}|^2. \tag{66}$$

As we can see, far away from the Bragg condition the dispersion surfaces are spheres around $\mathbf{k} = 0$ and $\mathbf{k} = \mathbf{G}$ with the radius $\sqrt{k_0^2 - \varkappa_0}$ for both polarizations. Near the Bragg condition the degeneracy between both polarizations is lifted and the smallest separation between the outer and inner branches becomes polarization-dependent:

$$\Delta k_{\sigma} = \frac{2\pi}{d_{ext}} = \frac{P_{\sigma}\varkappa_{\mathbf{G}}}{k_0 \cos\theta_B}, \tag{67}$$

see Figure 10. In this figure the dispersion surface in the vacuum, degenerate for both polarizations, is shown with thin lines, while the dispersion surface in the crystal is shown with thicker lines. The expressions for the coefficients D^{σ}_0 and $D^{\sigma}_{\mathbf{G}}$ are exactly the same as those in Eq. (27), with $v_{\mathbf{G}}$ replaced by $P_{\sigma}\varkappa_{\mathbf{G}}$. The resulting Σ-fields are identical to those given by the Bloch waves ψ^I and ψ^{II} from the previous section. However, for Π-polarization we do not get pure sine and cosine waves but only a combination of both, since $\mathbf{e}^2_0 \neq \mathbf{e}^2_{\mathbf{G}}$. Correspondingly, only Σ-waves show an anomalous transmission effect, while Π-waves never vanish at the atomic positions completely. Interestingly, for multi-beam cases, important for X-ray diffraction, the situation complicates significantly, since both polarizations cannot be anymore decoupled.

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