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FUNDAMENTALS OF STRUCTURAL CHARACTERIZATION BY DIFFRACTION TECHNIQUES



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МИНИСТЕРСТВО НАУКИ И ВЫСШЕГО ОБРАЗОВАНИЯ РОССИЙСКОЙ ФЕДЕРАЦИИ

УНИВЕРСИТЕТ ИТМО

Д.А. Кириленко FUNDAMENTALS OF STRUCTURAL CHARACTERIZATION BY DIFFRACTION TECHNIQUES

УЧЕБНО-МЕТОДИЧЕСКОЕ ПОСОБИЕ

РЕКОМЕНДОВАНО К ИСПОЛЬЗОВАНИЮ В УНИВЕРСИТЕТЕ ИТМО по направлению подготовки 16.04.01 Техническая физика в качестве Учебно-методического пособия для реализации основных профессиональных образовательных программ высшего образования магистратуры

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1. Diffraction methods of structural diagnostics

Diffraction is related to waves scattering on various objects, it may manifest violation of the geometric optics law. Diffraction is a visual reflection of the photons or particles wave nature. The phenomenon of diffraction strongly depends on the microstructure of the object, namely, on the distribution of tiny inhomogeneities, the size of which is of the order *of the wavelength*. Thus, diffraction is used to study such small details. For example, the diffraction of the room light on a CD surface, which is easily observed with the naked eye, makes it possible to deduce the period of tracks using only a ruler. On the other hand, the period can be directly obtained only using quite expensive microscopes, since the eye as an instrument does not allow these tracks to be evaluated directly due to their small size.



Figure 1.1 - Diffraction effects on a CD observed with the naked eye, and an image of CD surface structure obtained using a microscope.

This characteristic of diffraction effects has been actively applied in the studies of the atomic structure of various materials for more than 100 years. However, the wavelength of the radiation used for these purposes should be comparable with the interatomic distances or be even less, that is, make a few angstroms (1 Å = 0.1 nm) maximum.

The energy *E* of a photon with a wavelength of 1 Å is $E = \frac{hc}{\lambda} \approx 10,000 \text{ eV}$, that is, such radiation lies far beyond the visible light, in the so-called X-ray range. That is why X-ray diffraction is used for structural diagnostics.

The diffraction of various particles is also widely used, for example, that of electrons and neutrons, the wavelength of which is determined by de Broglie formula

 $\lambda = \frac{h}{p}$, where p is the momentum of the particle. Particles have a much greater momentum than photons at the same energies due to the presence of the rest mass. Thus, particles are characterized by much shorter wavelengths. For example, the electron wavelength at an energy of 10,000 eV will be less than 0.1 Å, and the neutron wavelength will be even 50 times smaller.

The following simple example allows to estimate the scale of the difference in the case of electrons. External electrons in atoms have the energy, the order of magnitude of which corresponds to Rydberg constant, that is, it is some eV. The wavelength of these electrons corresponds to the size of atoms, it has the order of Bohr radius (≈ 1 Å), since this radius is actually determined by the condition that the electron wavelength coincides with the length of its orbit.

In the above case, the wavelength of photons with an energy of the order of a few electron volts lies in the range of 100 nm–1 µm, that is, it is hundreds and thousands of times longer than the wavelength of the electrons with the same energies (≈ 1 Å). This difference is directly related to the so-called "fine structure constant" $\frac{e^2}{hc} \approx \frac{1}{137}$, and thus it is a fundamental characteristic of the photon emission when the electronic state changes.

It can be noted that the wavelength of photons that are emitted during the changes in the state of external electrons lies in the vicinity of the so-called. "visible range", that is, in the part of electromagnetic spectrum where the window of our eyes spectral sensitivity is located. The spectral sensitivity maximum of the human organs of vision is located approximately at a wavelength of 550 nm, in the green light area; the visible range itself represents the energies of 2-3 eV. This determines the ability to observe the typical flame colors, since it is the changes in the state of external electrons characterize the flame color. The chemical reactions, among them combustion as a special case, represent a change in the orbits of the external electrons of atoms with the formation of their new combinations, molecules. As a result of such a fusion, especially in the case of exogenous reactions, that is, those releasing heat, an electron, that was previously in the ground state in its atom, is often in the state from which a transition to a lower energy is possible within a molecule. This is accompanied by a release of energy, often by emission of an electromagnetic radiation quantum. In addition, the phenomenon of fluorescence, well known from practice, that is, in many cases observed with the naked eye, is related to a change in the state of external electrons.

(This is not a coincidence. More strictly speaking, it is by pure chance that the spectral sensitivity of our eyes appears to be in the region of the energy scale with the values typical for a change in the state of the external electrons. Our organs of vision are primarily tuned to the maximum of the Sun's spectrum, determined by its surface temperature. However, it is the favorable location of its spectrum in this region that results in the significant effect of solar radiation on terrestrial biological processes. For

example, photosynthesis in plants, which is essentially a chemical reaction induced by photons, as well as the fact that light detectors of the spectral range discussed can be built on the simple principle of changing the electronic state of a molecule. To give an example, this is implemented in our eyes, and therefore, the very fact of writing this book results from the transition energies of the external electrons lying in the vicinity of the photons energy in the visible range. Some electronic transitions are beyond this range, which leads to the emission of the so-called ultraviolet or infrared radiation, however, their energies are anyway of the order of Rydberg constant, that is, the binding energy of an electron in a hydrogen atom.)

An important effect is that our eye, as an instrument, is tuned to the wavelengths of hundreds to thousands ($\sim 2\pi \times 137$) times the size of atoms. This results in the fact that direct visual observation of the matter structure is impossible. For this reason, structural diagnostics involves using technically sophisticated approaches, with diffraction methods based on the use of radiation with a rather short wavelength among them.

2. Diffraction on three-dimensional objects

Let's consider a monochromatic wave with a complex amplitude $\psi_0(r) = exp(-2\pi i k_0 r)$. Here and below, we will rely on the definition of the wave vector length $|\mathbf{k}| = \frac{1}{\lambda}$, where λ is the wavelength. The coherently scattered wave $\psi(r)$ is described by the following integral equation:

$$\psi(\mathbf{r}) = \int \varphi(\mathbf{r}')(\psi_0(\mathbf{r}') + \psi(\mathbf{r}')) \frac{\exp\left(-2\pi i k_0 |\mathbf{r} - \mathbf{r}'|\right)}{4\pi |\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$
(2.1)

Where $\varphi(\mathbf{r})$ is the local scattering amplitude, a function describing the object. That is, each point of the object is a source of spherical waves with a wave vector $\mathbf{k}_0 = |\mathbf{k}_0|$ and the amplitude proportional to the amplitude of the propagating wave at a given point (taking into account the incident and the scattered waves) and to the scattering ability of the object.

Coherent scattering implies the consistency of both the amplitude and phase of the emerging spherical wave with the scattering wave and, therefore, requires the equality of the frequencies of the scattered and the original waves, that is, the equality of the energies of quanta or particles before and after scattering. Thus, coherent scattering corresponds to *elastic scattering*.

In the general case, this integral equation (since $\psi(\mathbf{r})$ is both on the left side and under the integral sign) is rather challenging to solve. If we assume that the amplitude of the scattered wave is much smaller than the amplitude of the incident wave, that is, $|\psi(\mathbf{r})| \ll |\psi_0(\mathbf{r})|$, then equation (2.1) can be simplified to:

$$\psi(\mathbf{r}) = \int \varphi(\mathbf{r}')\psi_0(\mathbf{r}') \frac{\exp\left(-2\pi i k_0 |\mathbf{r} - \mathbf{r}'|\right)}{4\pi |\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$
(2.2)

In this case, $\psi(\mathbf{r})$ is calculated by simple integration. It can be noted that here we neglected the repeated scattering of the *scattered wave* $\psi(\mathbf{r})$, as if this wave, when propagating through the object, no longer creates the corresponding spherical waves. Thus, this approximation corresponds to single scattering of particles or quanta and is referred to as *the single scattering approximation* or, in quantum mechanics, *the first Born approximation*.

This approximation, under certain conditions, cannot accurately predict the intensities of diffraction maxima, when scattered by crystalline structures, but allows to accurately determine their location, that is, to reveal the typical *directions* of scattering. Therefore, the single scattering approximation in the perspective of diffraction theory is referred to as *kinematic approximation*.

In the cases where the kinematic approximation does describe the diffraction pattern quite well, we deal with *kinematic diffraction*, for example, if the object is thin enough and multiple scattering is unlikely. If a more accurate solution of equation (2.1) taking into account multiple scattering is required, we refer to *dynamic diffraction*. When there are significant deviations of the observed pattern from that described by the kinematic approximation, this is called *dynamic diffraction effects*.

In practice, the distance from the object to the scattered wave recorder is usually much larger than the size of the object itself, that is, in the integrand $|\mathbf{r}| \gg |\mathbf{r}'|$. This condition corresponds to the so-called *Fraunhofer diffraction* and allows to simplify formula (2.2) taking into account $\psi_0(\mathbf{r}) = exp(-2\pi i \mathbf{k}_0 \mathbf{r})$ to the following:

$$\psi(\mathbf{r}) = \frac{\exp(-2\pi i \mathbf{k}_0 \mathbf{r})}{4\pi r} \int \varphi(\mathbf{r}') \exp(-2\pi i \mathbf{g} \mathbf{r}') d\mathbf{r}'$$
(2.3)

Where $g = k_0 \frac{r}{r} - k_0 = k - k_0$, the change of the wave vector upon scattering in the direction r, is the so-called *diffraction vector*. Thus, the amplitude of the scattered wave at a large distance is determined by the Fourier transform of the spatial distribution of the object's scattering density. The Fourier image of the object lies in the *reciprocal space*, the diffraction vectors are vectors in reciprocal space as well as the wave vectors of the incident and scattered waves. The set of allowed diffraction vectors in the case of coherent scattering, since $|\mathbf{k}| = |\mathbf{k}_0| = k_0$, lies on a sphere, *the Ewald sphere* (Figure 2.1).

Taking into account the density distribution of the object in reciprocal space, the so-called *scattering amplitude* $-f(g) = \int \varphi(r)exp(-2\pi i g r) dr$, the shape of the diffraction pattern can be predicted, since the scattering amplitude in the direction *n* is proportional to $f(k_0n - k_0)$ within the kinematic approximation, which thus provides

a powerful tool for understanding the principles of formation of diffraction patterns from various materials and structures.



Figure 2.1 - Ewald sphere and the correspondence of the reciprocal space point to the scattering direction and, thus, to the point in the observed diffraction pattern.

3. Typical Properties of the Fourier Transform in the One-Dimensional Case

Understanding the basic properties of Fourier transform of various functions is necessary for realizing the relationship between structural features and observed diffraction patterns. Fourier transform $\mathcal{F}(\phi) = \tilde{\phi}(g)$ is:

$$\widetilde{\varphi}(\mathbf{g}) = \int \varphi(x) \mathrm{e}^{-2\pi i g x} \, dx$$
 (3.1)

It is important that Fourier transform is the *linear operation*, that is $\mathcal{F}(\alpha \varphi_1 + \beta \varphi_2) = \alpha \mathcal{F}(\varphi_1) + \beta \mathcal{F}(\varphi_2)$.

It is useful to perceive Fourier transform as a decomposition of the original function into a frequency spectrum. In the case of temporal signal transformation the function is decomposed by temporal frequencies, and in the case of spatial function transformation it is decomposed by *spatial frequencies*. Anyway, Fourier image shows how much of which frequency there is in the spectrum of our object.

The function $\varphi(x)$ can be restored from $\tilde{\varphi}(g)$ by inverse Fourier transform \mathcal{F}^{-1} :

$$\boldsymbol{\varphi}(\mathbf{x}) = \mathcal{F}^{-1}(\widetilde{\boldsymbol{\varphi}}) = \int \widetilde{\boldsymbol{\varphi}}(\boldsymbol{g}) \boldsymbol{e}^{+2\pi i \boldsymbol{g} \boldsymbol{x}} \, \boldsymbol{d} \boldsymbol{g} \tag{3.2}$$

Inverse Fourier transform is very close in its definition to the direct transform. In fact, if we apply the direct Fourier transform to $\tilde{\varphi}(g)$ instead of the inverse transform, then we get $\varphi(-x)$:

$$\mathcal{F}(\widetilde{\varphi}) = \mathcal{F}(\mathcal{F}(\varphi)) = \int \widetilde{\varphi}(g) e^{-2\pi i g x} dg = \int \widetilde{\varphi}(g) e^{+2\pi i g(-x)} dg = \varphi(-x)$$
(3.3)

Thus, direct and inverse transformations of an object are identical in their form. This plays a special role in the diffraction patterns. To give an example, if we know what Fourier image of an object looks like, then we immediately understand what Fourier image from Fourier image will look like – as the original object. Therefore, by defining Fourier transform of one function, we immediately solve two problems and we know at the same time Fourier transform of the function corresponding to the obtained Fourier image. Further, we will understand the comparison of an object with its Fourier image as a bidirectional relationship.

Consider the Fourier transforms of some simple functions. The transformation of the Gaussian function will also be a Gaussian function:

$$F(e^{-x^2}) = \sqrt{\pi} e^{-g^2/16\pi^2}$$
(3.4)

Since the Fourier transform is a *linear transformation*, an increase in the amplitude of the original function leads to a proportional increase in the amplitude of the Fourier image.

There is another important property of the Fourier transform always holds: scaling the original function $\varphi(x) \rightarrow \varphi(ax)$ leads to the corresponding scaling of the Fourier transform, but in *the opposite* direction, $\tilde{\varphi}(g) \rightarrow \frac{1}{a} \tilde{\varphi}(\frac{g}{a})$. This directly follows from the definition:

$$\mathcal{F}(\varphi(ax)) = \int \varphi(ax) e^{-2\pi i gx} dx = \int \varphi(ax) e^{-2\pi i \frac{g}{a}(ax)} \frac{1}{a} dax = \frac{1}{a} \widetilde{\varphi}(\frac{g}{a})$$
(3.5)

So, shrinking of the original function leads the Fourier transform expansion and vice versa (Figure 3.1).



Figure 3.1 - Scaling Fourier image with scaling the original function.

This property can be regarded as an expression of a more general principle – more sharply / rapidly changing functions are characterized by larger amplitudes in the

region of the high spatial frequencies. As a detailed explanation, when stretched, the function becomes flatter, and its Fourier transform loses its amplitude at high spatial frequencies, which is manifested in the form of its compression, and vice versa.

Two important interrelated properties of the Fourier transform:

$$\mathcal{F}(\varphi') = 2\pi i g \mathcal{F}(\varphi) \qquad \mathcal{F}\left(\int \varphi dx\right) = \frac{1}{2\pi i g} \mathcal{F}(\varphi)$$
(3.6)

Thus, differentiation enhances high-frequency components, and integration, on the contrary, weakens. This is well known for everyone evolved in mathematical data processing.

Of particular importance is the following special case, the Fourier transform of Dirac delta function $\delta(x)$:

$$\mathcal{F}(\delta(\mathbf{x})) = \int \delta(x) e^{-2\pi i g x} dx = e^{-2\pi i g x}|_{x=0} = 1$$
(3.7)

That is, the transformation from a delta function is a constant, and vice versa, a transformation from a constant is a delta function at zero, $\mathcal{F}(1) = \delta(g)$. In other words, an infinitely short pulse contains all possible frequencies equally, and the constant is a function with single frequency – zero.

The antiderivative of the delta function is the Heaviside function $\theta(x)$, which is discontinuous at zero. According to (3.7) and (3.6) its Fourier image is equal to $\frac{1}{2\pi i g}$ (Figure 3.2).



Figure 3.2 - Fourier transform from the Heaviside function.

The antiderivative of the Heaviside function will actually be a function of |x|, it is continuous, but has a kink at zero, that is, a discontinuity in the first derivative. The Fourier image in this case will be described by the function $(\frac{1}{2\pi i q})^2$.

The next antiderivative will have a discontinuity only in the second derivative, its Fourier image is $(\frac{1}{2\pi i q})^3$.

It is important to note that the smoothness of a function is directly related to the rate of decrease in the amplitude of its Fourier transform at infinity, this is also a manifestation of the general principle mentioned above. Infinitely differentiable functions decrease faster than any power, like the Gaussian function whose Fourier transform decreases exponentially.

Moreover, due to the similarity of direct and inverse transformations, the following is also true: the slower the function decreases, the fewer continuous derivatives its Fourier image has.

A typical example is the Fourier transform of the Lorentz function:



Figure 3.3 – Lorentz function and its Fourier transform.

Lorentz function is infinitely differentiable, so its Fourier transform decreases exponentially. However, the function itself decays like $\frac{1}{x^2}$ and the second derivative of Fourier transform will contain a delta function, i.e. the first derivative will have a jump like Heaviside function, and Fourier transform itself will have a kink. Fourier transform of a function with a kink will not decrease faster than the second degree.

Thus, any breaks, discontinuities of the function, and the like lead to a much slower decrease in the Fourier transform, power-law instead of exponential. Again, the more abrupt changes / drops are present in the original function, the higher the amplitude of the high-frequency components of the spectrum.

The most obvious manifestation is the well-known difference between the sound of a harpsichord and a piano. The vibrations of a string can be represented as the sum of vibrations of its individual modes, the so-called "harmonics", each of them corresponding to the vibration of a wave, an integer number of half-periods of which fits the length of the string (Figure 3.4). The frequency of the harmonic is proportional to this number.



Figure 3.4 - String harmonics.

At the initial pull of the string, we set the initial amplitudes of various harmonics, which are defined as the spectrum of the string profile at t=0. The hammer in the piano is rounded, in the harpsichord the string is driven by a thin needle - a plectrum.



Figure 3.5 - The shapes of the percussion elements in the piano and harpsichord are significantly different.

The plectrum creates a sharper kink in the profile of a stretched string, which

results in a greater proportion of high frequencies in Fourier transform of its profile and a greater amplitude of high harmonics in its sound. This results in the typical "tinkling" sound of the harpsichord.

In structural diagnostics, this principle is manifested - heavier atoms, with a high charge, create sharper local changes in the potential or in the electron density, and therefore, scatter various types of radiation at larger angles.

Of particular interest is the case of periodic functions. The Fourier transform of the simplest periodic function – a constant – is a delta function concentrated at zero – $\delta(g)$. The Fourier transform of the function $e^{2\pi i \frac{x}{d}}$ will be a delta function concentrated at the point $g_0 = \frac{1}{d}$:

$$\mathcal{F}\left(e^{2\pi i\frac{x}{d}}\right) = \int e^{2\pi i\frac{x}{d}}e^{-2\pi igx} dx = \delta(g - \frac{1}{d})$$
(3.9)

Fourier transform of the harmonic functions with period d, for example, $\cos \frac{2\pi x}{d}$, due to the equality $\cos z = \frac{e^{iz} + e^{-iz}}{2}$, will be:

$$\mathcal{F}\left(\cos\frac{2\pi x}{d}\right) = \frac{1}{2}\delta\left(g - \frac{1}{d}\right) + \frac{1}{2}\delta\left(g + \frac{1}{d}\right)$$

$$2\pi x e^{2\pi i \frac{x}{d}} e^{-2\pi i \frac{x}{d}}$$
(3.10)

Fourier transform of $\sin \frac{2\pi x}{d} = \frac{e^{-a} - e^{-a}}{2i}$ will be:

$$\mathcal{F}\left(\sin\frac{2\pi x}{d}\right) = \frac{1}{2i}\delta\left(g - \frac{1}{d}\right) - \frac{1}{2i}\delta\left(g + \frac{1}{d}\right)$$
(3.11)

In diffraction patterns, especially in the case of radiation used in structural diagnostics, unfortunately, we register the signal intensity, that is, the square of the amplitude modulus, rather than the complex amplitude. Let us consider the two latter results as follows (Figure 3.6).



Figure 3.6 - Fourier transform from harmonic functions. In the first case $\tilde{\varphi}(g)$ a purely imaginary function, in the second one it is real, while the squares of the moduli of each of them coincide.

The sine and cosine graphs differ from each other only by a shift along the x. If we shift some function along the axis by a certain amount $\varphi(x) \rightarrow \varphi(x - x_0)$, then its Fourier transform will change simply by the phase factor $\tilde{\varphi}(g) \rightarrow e^{2\pi i g x_0} \tilde{\varphi}(g)$, and the modulus of this complex function will not change which is what the figure shows. Also, the diffraction pattern will not change if the object is slightly moved.

In addition, it can be noted that the Fourier transform of real functions is always somewhat symmetric, more precisely Hermitian, since in this case $\varphi(x) = \overline{\varphi(x)}$, where the bar over the expression means complex conjugation. It can be expressed by the following:

$$\tilde{\varphi}(-g) = \int \varphi(x) e^{-2\pi i (-g)x} dx = \int \overline{\varphi(x)} e^{-2\pi i gx} dx = \overline{\tilde{\varphi}(g)}$$
(3.12)

Thus, the modulus of the Fourier transform of real functions is strictly symmetric $|\tilde{\varphi}(-g)| = |\tilde{\varphi}(g)|$, as well as the density distribution in the reciprocal space of any physical object.

Consider the Fourier transform of other periodic functions. For example, $(1 + \cos \frac{2\pi x}{d})^2$ and $(1 + \cos \frac{2\pi x}{d})^4$. It is easy to show that: $\left(1 + \cos \frac{2\pi x}{d}\right)^2 = \frac{3}{2} + 2\cos \frac{2\pi x}{d} + \frac{1}{2}\cos 2\frac{2\pi x}{d}$ (2.12)

$$\left(1 + \cos\frac{2\pi x}{d}\right)^4 = \frac{35}{8} + 7\cos\frac{2\pi x}{d} + \frac{7}{2}\cos2\frac{2\pi x}{d} + \cos3\frac{2\pi x}{d} + \frac{1}{8}\cos4\frac{2\pi x}{d}$$
(3.13)

With successive exponentiation, our periodic function becomes a sequence of increasingly sharp impulses. This corresponds to the ever higher frequencies emerging in its composition, which is manifested in the shape of Fourier transform (Figure 3.7).



Figure 3.7 - Fourier transforms from $(1 + \cos \frac{2\pi x}{d})^2$ and $(1 + \cos \frac{2\pi x}{d})^4$.

The spectrum of a periodic function always consists of a set of delta functions concentrated at frequencies that are multiples of $\frac{1}{d}$, that is, it consists of "harmonics". The amplitude of these "harmonics", that is, the coefficients at the corresponding delta functions, correspond to the coefficients of the Fourier series of the given periodic function.

Figure 3.7 illustrates the fundamental idea that periodic objects in reciprocal space are represented as an ordered set of points where density is concentrated, and that the diffraction pattern from periodic objects consists of bright spots, in the ideal case corresponding to a delta function.

Of particular importance is the Fourier transform of a periodic function in the form of an infinite sequence of delta functions with period d, $\varphi(x) = \sum_{n=-\infty}^{+\infty} \delta(x - nd)$, which is also an infinite sequence of delta functions with period 1/d:

$$\mathcal{F}\left(\sum_{n=-\infty}^{+\infty}\delta(x-nd)\right) = \sum_{n=-\infty}^{+\infty}e^{-2\pi i g n d} = \sum_{m=-\infty}^{+\infty}\delta\left(g-\frac{m}{d}\right)$$
(3.14)

This is not an obvious result, but it is in full agreement with the characteristic features of the Fourier transform. First, as the period of the original sequence changes, the Fourier transform will rescale itself accordingly in the opposite direction. Secondly, any delta function essentially contains all kinds of frequencies, and the amplitude of the Fourier transform does not tend to zero at infinity. Thirdly, the resulting Fourier transform does not contain frequencies other than multiples of the frequency of the original periodic function (Figure 3.8).



Figure 3.8 - Fourier transform from a periodic sequence of delta functions.

Consider an important property of the Fourier transform in relation to the convolution operation. The convolution of two functions $\varphi_1(x)$ and $\varphi_2(x)$ is the following function of x:

$$\varphi_1 * \varphi_2 = \int \varphi_1(t)\varphi_2(x-t)dt \qquad (3.15)$$

It is easy to show that the Fourier transform of the convolution of two functions is the *product* of the corresponding Fourier transforms:

$$\mathcal{F}(\varphi_1 * \varphi_2) = \mathcal{F}(\varphi_1) \cdot \mathcal{F}(\varphi_2) \tag{3.16}$$

And, by the way, on the contrary, the Fourier transform of the product of two functions is the convolution of the corresponding Fourier images.

The convolution of any function with a delta function concentrated at zero will equal the original function:

$$\varphi * \delta(x) = \int \varphi(t)\delta(x-t)dt = \varphi(t)|_{x-t=0} = \varphi(x)$$
(3.17)

The convolution of the function $\varphi(x)$ with the delta function shifted to the point x_0 , that is, with $\delta(x - x_0)$, will be the function φ shifted exactly the same, that is, $\varphi(x - x_0)$:

$$\varphi * \delta(x - x_0) = \int \varphi(t) \delta(x - t - x_0) dt = \varphi(t)|_{x - t - x_0 = 0} = \varphi(x - x_0)$$
(3.18)

Moreover, the convolution operation is linear, that is $\psi * (\varphi_1 + \varphi_2) = \psi * \varphi_1 + \psi * \varphi_2$.

A convolution, for example, of a Gaussian function $e^{-\frac{x^2}{a^2}}$ with a periodic sequence of delta functions $\sum_{n=-\infty}^{+\infty} \delta(x-nd)$ will therefore be a periodic sequence of Gaussian functions:

$$e^{-\frac{x^2}{a^2}} * \sum_{n=-\infty}^{+\infty} \delta(x - nd) = \sum_{n=-\infty}^{+\infty} e^{-\frac{(x - nd)^2}{a^2}}$$
(3.19)

The Fourier transform of such a periodic function will be equal to the product of the Fourier transforms of the original convolution components, that is:

$$\mathcal{F}\left(\sum_{n=-\infty}^{+\infty} e^{-\frac{(x-nd)^2}{a^2}}\right) = \mathcal{F}\left(e^{-\frac{x^2}{a^2}}\right) \mathcal{F}\left(\sum_{n=-\infty}^{+\infty} \delta(x-nd)\right) = A e^{-\frac{(ag)^2}{16\pi^2}} \sum_{m=-\infty}^{+\infty} \delta\left(g-\frac{m}{d}\right)$$

$$= A \sum_{m=-\infty}^{+\infty} e^{-\frac{(am)^2}{16\pi^2 d^2}} \delta\left(g-\frac{m}{d}\right)$$
(3.20)

Where the coefficient A is a value of the order of unity, in the context of the analysis of diffraction patterns it does not affect their appearance. Thus, the amplitude of the original delta functions in the Fourier transform is modulated accordingly to the Fourier transform of the Gaussian function. Moreover, it can be noted that if a < d, that is, the width of the Gaussian function is less than the period, then the changes in the resulting Fourier transform are less significant than in the case of a > d, when almost all components are significantly weakened, except for the corresponding zero frequency, which happens as a result of the overlap of adjacent Gaussian functions (Figure 3.9).



Figure 3.9 - Fourier transform from periodic functions.

Thus, the amplitude of Fourier components of a periodic function is determined by Fourier transform of the profile of one period. In diffraction patterns, the intensity ratio of different diffraction reflections is determined by the scattering density profile within the unit cell.

In the case of a period profile described by a Gaussian function, the amplitude of the Fourier components decays exponentially. Let's consider other periodic functions. Of particular interest is the case of a piecewise constant function, which can be obtained as a convolution with a meander. The Fourier transform of the meander is a function of the form $\frac{\sin g}{g}$, which is of great importance in structural diagnostics. More precisely, for a symmetrical meander with height 1 and width *D*:

$$\mathcal{F}(\Pi) = \int_{-D/2}^{+D/2} 1 \cdot e^{-2\pi i g x} \, dx = \frac{e^{-2\pi i g x} |_{x=-D/2}^{x=D/2}}{-2\pi i g} = \frac{\sin \pi D g}{\pi g}$$
(3.21)

The amplitudes of the spectrum component are modulated accordingly (Figure 3.10).



Figure 3.10 - Fourier transform of a periodic piecewise linear function.

The smaller the width of the meander, the wider the modulating function, and the closer the form of the Fourier transform will be to the original one. If the width of the meander *D* equals the period *d*, then the individual meanders will merge into a solid line, and the resulting function will turn into a constant. This corresponds to the case when at the locations of the harmonics in the region of spatial frequencies turn out to be exclusively the zeros of the function $\frac{\sin \pi Dg}{\pi g}$ and only the component corresponding to the zero frequency is preserved.

It can be noted that a piecewise linear function contains a series of discontinuities, for this reason the amplitude of its Fourier transform decreases as $\frac{1}{g}$ in

strict accordance with the previously stated representations. If the shape of the peaks is slightly smoother, for example, in the form of a meander smoothed by convolution with a Gaussian function, then the Fourier transform is also modulated by the Gaussian transform, and the amplitude of the oscillations will decrease faster.

Thus, the Fourier transform of periodic functions is easily estimated if one imagines what the transformation of one period looks like. Another approach to the analysis of the form of Fourier transforms is also important. Let us determine the Fourier transform shape of a periodic function confined along x axis. It can be done by multiplication of the original periodic function by a meander of a sufficiently large width. The Fourier transform from multiplication will be the convolution of the corresponding Fourier transforms, and since the spectrum of a periodic function is a sequence of delta functions, the resulting spectrum will be a sequence of Fourier transforms from a meander (Figure 3.11):

$$\mathcal{F}\left(\prod \cdot \sum_{n=-\infty}^{+\infty} \delta(x-nd)\right) = \frac{\sin \pi Dg}{\pi g} * \sum_{m=-\infty}^{+\infty} \delta\left(g - \frac{m}{d}\right) = \sum_{m=-\infty}^{+\infty} \frac{\sin \pi D\left(g - \frac{m}{d}\right)}{\pi \left(g - \frac{m}{d}\right)}$$



Figure 3.11 - Fourier transform from a finite set of peaks.

The following is important: the trimming of the periodic function leads to a modification of the peaks shape in the reciprocal space, the delta functions are broadened, turning into Fourier transforms from the trimming profile. In this case, the width of the peaks in the reciprocal space obviously corresponds to the width of the remaining portion of the original periodic function. A simple rule is that the peak in the reciprocal space is as many times narrower than the distance between the peaks does not change and corresponds to the period. The diffraction peaks from crystals of finite size behave similarly: the smaller the crystallite, the more the diffraction reflections are broadened. This peak broadening effect is called *shape effect*, as it is related to the shape of the crystallite. The most important point is the following – the shape effect is the same for all peaks in the reciprocal space since it is the result of convolution.

Before proceeding to the features of Fourier transform from three-dimensional objects, including from three-dimensional lattices, we can summarize the above using the example of flat optical diffraction gratings:

- 1. The intensity ratio for different diffraction orders is determined by the reflectance profile of the diffraction grating period. If the edges of the diffraction grating line are sharp enough, then the amplitude decreases inversely with the order of reflection, and the intensity decreases inversely with the square of the order. If the reflectivity varies sinusoidally, there will only be first-order reflections.
- 2. The angular divergence of the reflection is inversely proportional to the number of lines in the grating, which thus determines its resolution.
- 3. A small shift of the diffraction grating only changes the phase in the reflections without changing the appearance of the final diffraction pattern.

These conclusions, which are well-known facts from the physics of diffraction gratings, are presented here to emphasize the importance of being familiar with the properties of Fourier transform.

4. Fourier transform of 3D objects

Fourier transform of 3D scattering density distribution $\varphi(\mathbf{r})$ is a 3D complex function $\widetilde{\varphi}(\mathbf{g})$:

$$\widetilde{\varphi}(\mathbf{g}) = \int \varphi(\mathbf{r}) \mathrm{e}^{-2\pi i \mathbf{g} \mathbf{r}} \, d\mathbf{r} = \iiint \varphi(x, y, z) \mathrm{e}^{-2\pi i (\xi x + \eta y + \zeta z)} \, dx dy dz \tag{4.1}$$

Consider Fourier transforms, that is, representations in reciprocal space, of the simplest three-dimensional objects. A rectangular parallelepiped can be defined as the product of three meanders of different widths D_x , D_y and D_z in mutually normal directions. Thus, in the space limited by the parallelepiped the density will be 1 and it will be zero outside it:



Figure 4.1 – Mathematical description of a rectangular parallelepiped.

The Fourier transform of such a figure is calculated quite easily, since our function $\varphi(\mathbf{r})$ in this case is factorized, that is, it is presented as a product of functions of independent variables. In general, if $\varphi(\mathbf{r}) = \varphi(x) \cdot \varphi(y) \cdot \varphi(z)$, then Fourier transform from it will be the product of the three corresponding one-dimensional transformations:

$$\mathcal{F}(\varphi(x)\varphi(y)\varphi(z)) = \iiint \varphi(x)\varphi(y)\varphi(z)e^{-2\pi i (\xi x + \eta y + \zeta z)} dxdydz$$

$$= \int \varphi(x)e^{-2\pi i \xi x} dx \int \varphi(y)e^{-2\pi i \eta y} dy \int \varphi(z)e^{-2\pi i \zeta z} dz$$
(4.2)

Thus, a rectangular parallelepiped with dimensions $D_x \times D_y \times D_z$ in reciprocal space will be have the following density distribution:

$$\mathcal{F}\left(\square\right) = \frac{\sin \pi D_x \xi}{\pi \xi} \frac{\sin \pi D_y \eta}{\pi \eta} \frac{\sin \pi D_z \zeta}{\pi \zeta}$$
(4.3)

It is important that the scale of this object along any of the axes will be inversely proportional to the original dimensions, that is, a thin plate will be represented by a rod, and vice versa, the rod will be represented in reciprocal space by a thin plate. In this case, there will be density oscillations in the directions normal to the original faces (Figure 4.2).



Figure 4.2 - Fourier transform of a parallelepiped, section in the plane (ξ, η) parallel to the plane (x, y).

Similarly, Fourier transform from an ellipsoid will be characterized by the radial oscillations due to the abrupt limits of the figure, while the proportions of the figure will be inverse to the original proportions (Figure 4.3).



Figure 4.3 - Fourier transform from the disks and the rod.

If the dimensions of a disk/plate tend to infinity, then the rod in reciprocal space will become infinitely thin. If, in this case, the thickness of the disk tends to zero, then the length of the rod tends to infinity. In other words, Fourier transform of a plane is a straight line normal to the given plane. Indeed, if the density of the original object is concentrated in the XY plane and distributed uniformly there, that is, it exists only at z= 0 and is equal to zero in the rest of the space, it can be described by the function $\delta(z)$, more precisely, by the function $1(x) \cdot 1(y) \cdot \delta(z)$, since we mean a three-dimensional function. In this case, the three-dimensional Fourier transform will be:

$$\mathcal{F}(\delta(z)) = \iiint \delta(z) e^{-2\pi i (\xi x + \eta y + \zeta z)} dx dy dz = \iint e^{-2\pi i (\xi x + \eta y)} dx dy (\not = . \oint (\xi) \cdot \delta(\eta)$$

Thus, the density will be concentrated on the straight line $\xi = \eta = 0$, that is, the axis ζ parallel to the *z* and normal to the XY plane, and will be zero in all other space.

Similarly, Fourier transform of a line is the plane normal to the given line (Figure 4.4).



Figure 4.4 - Fourier transform from a plane and a straight line.

Consider a periodic sequence of planes with the period *d*. It is described by an infinite sum $\sum_{n=-\infty}^{+\infty} \delta(z - nd)$ like a periodic sequence of delta functions in the one-dimensional case, with the only difference that here we mean a three-dimensional function that is constant on *x* and *y*, that is, it just describes continuous planes at *z*=*nd*. Fourier transform will be:

$$\mathcal{F}\left(\sum_{n=-\infty}^{+\infty}\delta(z-nd)\right) = \iiint \sum_{n=-\infty}^{+\infty}\delta(z-nd) e^{-2\pi i(\xi x+\eta y+\zeta z)} dxdydz$$

=
$$\iint e^{-2\pi i(\xi x+\eta y)} dxdy \sum_{n=-\infty}^{+\infty} e^{-2\pi i\zeta nd} = \delta(\xi) \cdot \delta(\eta) \cdot \sum_{m=-\infty}^{+\infty} \delta\left(\zeta - \frac{m}{d}\right)$$
(4.5)

The result is a line $\delta(\xi) \cdot \delta(\eta)$ axis *z*, whose density is 0 everywhere except for a series of points $\zeta = \frac{m}{d}$ (Figure 4.5).

Thus, a periodic system of planes in reciprocal space corresponds to a chain of point nodes in the direction normal to these planes, the so-called *systematic row*.

Let us multiply the two systems of planes, for example, parallel to the XY plane and the XZ plane $-\sum_{n=-\infty}^{+\infty} \delta(y - nd_1) \times \sum_{m=-\infty}^{+\infty} \delta(z - md_2)$, the density distribution will be a grid of lines $y = nd_1, z = md_2$, i.e., parallel to the *x*. Fourier transform in this case will also represent the product:



Figure 4.5 - Fourier transform from a system of planes.

In fact, it will also be a grid of lines parallel to the axis ξ or x, however, multiplying by $\delta(\xi)$ will leave only the points in the plane $\xi = 0$, that is, parallel to the YZ plane. Thus, Fourier transform from a regular grid of lines is a flat grid of point nodes, which can also be represented as a convolution of a systematic series of one system of planes with the systematic series of the second system of planes (Figure 4.6).



Figure 4.6 - Fourier transform from a grid of lines.

If this construction is multiplied by a system of planes going in the third direction, then it is rows of point nodes that will remain from the straight lines, that is, we will get a three-dimensional lattice. At each node of the flat grid of Fourier transform, a systematic series will appear in the direction normal to the grid plane, which is also a three-dimensional grid. Thus, a three-dimensional lattice in reciprocal

space is represented by a three-dimensional lattice, the so-called *reciprocal lattice*. However, the nodal rows of the reciprocal lattice run normal to the planes of the original one, while the period of the nodal rows is inversely proportional to the period of the planes.

If the initial lattice is specified using the crystallographic basis **a**, **b**, **c**, then the reciprocal lattice will be described using the following basis:

$$\boldsymbol{a}^* = \frac{\boldsymbol{b} \times \boldsymbol{c}}{\boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c}}; \ \boldsymbol{b}^* = \frac{\boldsymbol{c} \times \boldsymbol{a}}{\boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c}}; \ \boldsymbol{c}^* = \frac{\boldsymbol{a} \times \boldsymbol{b}}{\boldsymbol{a} \cdot \boldsymbol{b} \times \boldsymbol{c}}$$
(4.7)

The vectors of a given basis, as is shown, are normal to the planes of the original lattice, the period of any systematic series that can be built in such a basis is inversely proportional to the period of the corresponding planes (Figure 1.1).



Figure 4.7 - Direct and reciprocal lattices, the third axis is normal to the plane of the figure.

The point nodes, that is, those described by delta functions are observed only when the original object is of infinite sizes. A finite object can be obtained by multiplying an infinite object by the function of a sufficiently large box. As a result of this multiplication, Fourier image of the finite fragment of the lattice will be described by a convolution with Fourier transform of the cutting function. Thus, each node of the reciprocal lattice will turn into Fourier image of the parallelepiped (Figure 4.8). With a high aspect ratio of the shape of our crystal, for example, a disk or a rod, the nodes of the reciprocal lattice will take the form of a rod or disk, respectively, normal to the original ones. In general, any abrupt edges of a crystal will correspond to oscillating streaks of the nodes in reciprocal space.



Figure 4.8 - Reciprocal lattice nodes of the finite crystal.

5. Kinematic diffraction on crystalline structures

Diffraction patterns produce an image of radiation scattering. In kinematic approximation, that is, in the approximation of single scattering, this pattern is determined by the cross section of crystal Fourier image by the Ewald's sphere. Crystalline bodies are represented in reciprocal space in the form of the so-called reciprocal lattice, a three-dimensional grid of regularly spaced nodes. Therefore, bright narrow diffracted beams, the so-called, *diffraction reflections* are typical for diffraction by crystals (Figure 5.1). Each diffraction reflection corresponds to a specific reciprocal lattice node.

If radiation is monochromatic, that is, it has a strictly defined wavelength and, thus, the strictly defined modulus of the wave vector, then the thickness of the Ewald sphere is zero. In this case, diffraction reflections appear only for a strictly limited orientation of the lattice with respect to the direction of the incident beam. This fundamentally differs diffraction on three-dimensional gratings from that on twodimensional or one-dimensional ones, in the latter case, many diffraction reflections are observed simultaneously for a plane monochromatic wave.

In the case of a non-monochromatic particle/quantum beam, there will be multiple Ewald spheres of various radii in reciprocal space (Figure 5.2).

In this case, multiple diffraction reflections will be simultaneously observed for any orientation of the lattice. However, each reflection will correspond to the intersection of a certain node by an Ewald sphere of a certain radius, and, therefore, in each reflection the beam will have a certain wavelength. It is in this way that crystals, like any three-dimensional gratings, can be used to monochromatize radiation.



Figure 5.1 - Ewald sphere and reciprocal crystal lattice.



Figure 5.2 - A non-monochromatic beam corresponds to a finite volume covered by Ewald spheres of various radii.

From the above analysis, it follows that to obtain diffraction reflection, it is essential that the corresponding node of the reciprocal lattice is not removed from the origin of coordinates by more than the diameter of Ewald sphere, that is, $2|\mathbf{k}| > |\mathbf{g}|$, where \mathbf{g} is the reciprocal lattice vector, the allowed diffraction vector on the lattice.

This condition can be expressed as follows $-\lambda < 2d$, where *d* is the period of the planes corresponding to a given node of the reciprocal lattice. In other words, to obtain diffraction on a crystal structure, the radiation wavelength must be sufficiently small, no more than twice the lattice period.

For a detailed study of the reciprocal space structure, in particular, the shape of the reciprocal lattice nodes, only monochromatic radiation is used, corresponding to an almost ideally thin Ewald sphere. In this case, to obtain some information about the density distribution in the reciprocal space, as mentioned above, it is necessary to consistently tilt the sample by measuring the intensity of the scattered radiation. It is possible to obtain a density scan in the region limited by the diameter of the sphere, which is determined by the wavelength of the radiation used.

A bright diffraction reflection occurs when Ewald sphere crosses any node of the reciprocal lattice. Let the vector connecting the origin in reciprocal space to this node, the diffraction vector in this case, be equal to \boldsymbol{g} . The wave vector of the diffraction reflection will be $\boldsymbol{k}^* = \boldsymbol{k} + \boldsymbol{g}$, where \boldsymbol{k} is the wave vector of the incident radiation. Then the half angle between \boldsymbol{k} and \boldsymbol{k}^* will be determined by the following relationship $-2\sin\theta |\boldsymbol{k}| = |\boldsymbol{g}|$, otherwise, taking into account $|\boldsymbol{k}| = \frac{1}{\lambda}$ and $|\boldsymbol{g}| = \frac{1}{d}$, where d is the period of the planes corresponding to the node \boldsymbol{g} , we get $2d\sin\theta = \lambda$. However, any system of planes corresponds to a systematic row of reciprocal lattice nodes for which $|\boldsymbol{g}| = \frac{n}{d}$, where n is any integer. Thus, it is possible to obtain an expression for the possible scattering angles on a certain system of planes of the period d:

$$2d\sin\theta = n\lambda\tag{4.7}$$

This expression is called *Wulf-Bragg formula*. Since the system of planes itself is normal to the vector g, the formula describes the incidence angles at which intense diffraction reflections emerges, the so-called, *Bragg angles*.

Bragg angle depends on the wavelength; the shorter the wavelength, the smaller the angle, which generally corresponds to a decrease in the scattering angle with increasing particle energy. Thus, when using particles with a shorter wavelength, the diffraction pattern narrows, however, the dimensions of the reciprocal lattice remain unchanged, since they are related solely to the geometry of the object. That is, the analysis of diffraction patterns is based on independent determination of the shape of an object in reciprocal space and the scheme of a diffraction experiment that allows scanning the density distribution in reciprocal space.



Figure 5.3 - Determination of Bragg angle.

In view of the above, it is interesting to consider the features of diffraction by low-dimensional objects. For example, according to the analysis described earlier (Figure 4.6), the 3D Fourier transform of a 2D crystal will be a regular grid of rods. Indeed, a two-dimensional crystal is ultra-thin three-dimensional. With a decrease in the thickness of the crystal the nodes of the reciprocal lattice are extended until they merge into solid straight lines when one atomic layer is the only thing that remains from the crystal (Figure 5.4).

In this case, almost regardless of the orientation of the crystal, the diffraction pattern will contain many diffraction reflections, since Ewald sphere in any case crosses the rods that are not too far from the center. This essentially differs diffraction by two-dimensional crystals from that by three-dimensional crystals.

It is also interesting to evaluate the form of the reciprocal lattice of a crystal in which only two atomic layers remain. The easiest way to do this is to add Fourier transforms from the first and second layers taking into account the shift between them.

$$\mathcal{F}_{1} + \mathcal{F}_{2} = \mathcal{F}_{1} + \mathcal{F}_{1} e^{2\pi i \zeta d_{2}} = \mathcal{F}_{1} e^{\pi i \zeta d_{2}} 2 \cos \pi \zeta d_{3}$$
(4.6)

Thus, the presence of two identical layers leads to the appearance of a periodic density modulation along the third axis. The more layers, the sharper the modulation data will be, most pronounced in the case of a bulk crystal, when diffraction reflection occurs only at strictly defined angles of incidence.

Obviously, based on Figure 4.5, we can say that the diffraction pattern from a one-dimensional crystal will be a series of concentric circles.

To summarize, the diffraction pattern is described by the intersection of Ewald sphere with the reciprocal lattice of the crystal. The position of Ewald sphere in the reciprocal space is determined by the radiation wavelength and the orientation of the beam towards to the crystal. The reciprocal lattice consists of nodes, the shape of which is determined by the shape of the crystal, and their location in space is determined by the lattice of the crystal. The weight of each node is determined by the distribution of the scattering density within the unit cell of the crystal, that is, its structure, as well as by the type of scattering radiation.



Figure 5.4 - Reciprocal lattice of single-layer and two-layer twodimensional crystals.

The most significant difference in the diffraction of electrons, X-rays and neutrons is that different types of radiation are scattered by different entities that make up the object. Roughly, electrons scatter on electric potential, X-ray quanta on electron density, and neutrons scatter only on atomic nuclei. Thus, the scattering density profile for these types of radiation will be somewhat different, that is, the ratio of the intensity of various reflections will be different, too.

The scale of the diffraction pattern or, in other words, the characteristic scattering angles, also depends on the wavelength. The radiation normally used is that whose wavelength is close to interatomic distances (X-ray quanta ≈ 10 keV, that is, ≈ 1 Å, or thermal neutrons), so that the characteristic scattering angles are of the order of 1 rad. The maximum angles minimize the relative error in measuring their magnitude. Significantly smaller scattering angles, about 10^{-2} rad, are usually typical for electron diffraction, since it is high-energy electrons (≈ 100 keV) with a wavelength of ≈ 3 pm are mainly used due to the strong absorption of charged particles by matter. This increases their penetration depth at least up to $\approx 1 \,\mu$ m, but reduces the accuracy of diffraction data measurements.

X-ray diffraction is perhaps the most widely used method of structural diagnostics and is known to have the highest accuracy in determining the lattice parameters. Electron diffraction, on the other hand, makes it possible to obtain diffraction patterns from individual nanovolumes of a material, resulting, among other things, from the presence of a charge and, thus, high cross sections of various interaction processes with a substance. Neutron diffraction, despite the difficulties and limitations due to using the corresponding sources, has a significant advantage. The neutron scattering cross section for various elements does not depend much on the atomic number $\propto Z^{1/3}$ in comparison with the dependence, for example, on $\propto Z^2$ for electrons, or a similar strong dependence for X-ray quanta. For this reason, the

influence of light elements, especially hydrogen, on X-ray or electron diffraction patterns is insignificant or even practically immeasurable, while neutron diffraction provides much more information about their location in the structure.

6. Dynamic Diffraction

Kinematic approach provides a basis for the analysis of diffraction patterns, however, multiple scattering can lead to special effects that also need to be considered. As mentioned above, equation (2.1) cannot be solved in a general case, nevertheless, in particular cases, a fairly informative analysis can be carried out.

Dynamic diffraction, that is, diffraction considering two-, three-, etc. multiple scattering from crystalline materials is described as follows. Single scattering in this case creates a discrete set of diffraction reflections, then, each of the reflections is also scattered into a similar series of reflections when propagating through the object, and so on. The most typical case, when using highly coherent radiation, is the occurrence of only one diffraction reflection, then, due to the geometry of the process, the secondary reflection is codirectional with the primary beam. Thus, the assumption that only one reflection exists is called *the two-beam approximation*. If we neglect the absorption and assume the strict Bragg conditions, the amplitude variations of the primary beam and the diffracted beam are described by the following equations:

$$\frac{d\varphi_g}{dx} = \frac{i\pi}{\xi_g} \varphi_0$$

$$\frac{d\varphi_0}{dx} = \frac{i\pi}{\xi_g} \varphi_g$$
4.6

The equations describe continuous transition of the amplitude of the primary beam φ_0 to the diffracted beam φ_g and a similar transition of the diffraction reflection to the primary beam. The parameter ξ_g determines the growth rate of the reflection amplitude, that is, the scattered wave, is directly related to the scattering cross section by the angle 2θ and is an analog to the refractive index.

The solution to this equation implies functions oscillating with a period of $2\xi_g$, which under the initial conditions $\varphi_0(0) = 1$ and $\varphi_q(0) = 0$ gives:

$$\varphi_0 = \cos \frac{\pi x}{\xi_g}$$

$$\varphi_g = \sin \frac{\pi x}{\xi_g}$$
(4.6)

In practice, this leads to intensity oscillations of both the transmitted and the reflected beams with the thickness of the sample, which manifests itself in the form *of thickness contours* on images of the wedge-shaped edges of the crystals:



Figure 6.1 - Thickness contours on the images of wedge-shaped fragments of crystals in an electron microscope and in X-ray topography.

When the thickness of the crystal equals ξ_g , the intensity of the primary beam becomes equal to 0, that is, it is completely extinguished, so the value ξ_g is referred to as *extinction length*. Electrons extinction length for various reflections in various materials is about 10-100 nm, for X-ray quanta it is several orders of magnitude larger, and even more for neutrons, which is an additional advantage of using the latter, since this simplifies the analysis of diffraction data. On the other hand, it can be noted that for all types of radiation at sufficiently small thicknesses, the amplitude of diffraction reflection grows proportionally to the thickness. Significant deviations from kinematic approximation arise only at the thicknesses when the amplitude of the scattered wave becomes comparable with the amplitude of the primary beam.

In the case of excitation of several diffraction reflections, the change in their amplitude is described by a more sophisticated system of differential equations, the solutions of which also vary nonmonotonically with the thickness. The most prominent feature in this case may be the occurrence of reflections that are not observed in the kinematic approximation as a result of *double diffraction*, that is, the diffraction of a diffracted beam.

Coherent scattering on crystalline structures creates a discrete set of beams diffraction reflections. Incoherent scattering, for example, due to inelastic processes, localizes a quantum, which leads to the formation of a wave that spreads from a given point of the sample and does not interfere with other waves. Incoherent scattering thus creates a continuous, *diffused*, background in diffraction patterns. However, in the case of subsequent coherent scattering of this wave there are features appearing in the diffuse background associated with the crystalline structure of the substance, the socalled *Kikuchi lines*. Since a sufficiently large thickness is required to observe the effects of double scattering, the Kikuchi lines are more typical for electron diffraction, since the extinction lengths in this case are relatively small. Кириленко Демид Александрович

Fundamentals of Structural Characterization by Diffraction Techniques

Учебно-методическое пособие

В авторской редакции Редакционно-издательский отдел Университета ИТМО Зав. РИО Н.Ф. Гусарова Подписано к печати Заказ № Тираж Отпечатано на ризографе

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