

## 7.1 General Description of X-Ray Scattering by Materials

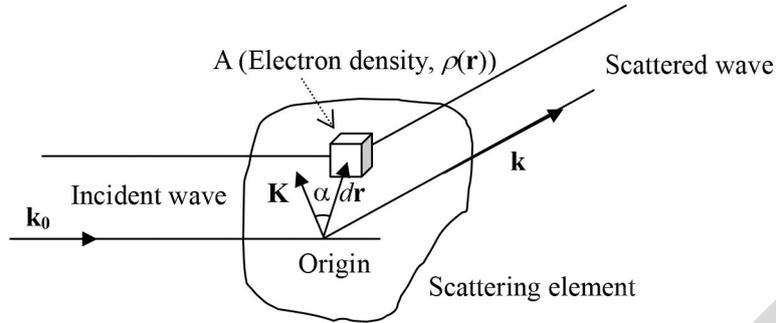


Fig. 7.1.2 X-ray scattering by scattering element

Here,  $I_0$  denotes the intensity of the incident wave. When  $I_e$  denotes the scattering intensity for a single electron, intensity can be rewritten, as follows:

$$I = I_e |A(\mathbf{K})|^2 = I_e \left| \int_{\text{scatterer}} \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d\mathbf{r} \right|^2 \quad \text{Formula 7.1.6}$$

This formula is a generic formula that applies whether the scattering element is a solid, liquid, or gas. It constitutes the foundation of the kinematical theory of diffraction.

## 7.2 X-Ray Scattering from Crystalline Material

At the beginning of Section 7.1.2, we stated that the electron density in a material is not uniform. The concentration and regularity in the electron density depends on the type of element constituting the material, the crystallinity, and the symmetry of the crystal. Next, we discuss scattering based on the type of element and the crystal system.

### 7.2.1 Atomic Scattering Factor and Crystal Structure Factor

The **atomic scattering factor** expresses the scattering intensity of the X-rays based on the electron density distribution of a single atom. The atomic scattering factor is obtained by applying the formula for the entire scattering element to a single atom as follows:

$$\int_{\text{atom}} \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} d\mathbf{r} \equiv f(\mathbf{K}) \quad \text{Formula 7.2.1}$$

$A(\mathbf{K})$  in Formula 1.2.11 is specifically expressed as  $f(\mathbf{K})$  when referring to a single atom.  $f(\mathbf{K})$  is a non-dimensional quantity and is a real number when the absorption by an atom is not considered. The amplitude of the scattering by an atom is  $-r_e f$ . The scattering intensity is given by the following formula:

$$I = I_e f^2 = I_0 \frac{r_e^2 f^2}{r^2} \quad \text{Formula 7.2.2}$$

We determine the expression for  $f$  by assuming a spherical symmetry in the electron density distribution of an atom. Electron density  $\rho(r)$  is a function of only  $r$ , which is the magnitude of  $r$ . When we take the direction of  $\mathbf{K}$  as the polar axis of the spherical coordinates  $(\rho, \alpha, \beta)$ ,  $f$  is given by the following formula:

$$f(K) = \int_0^\infty \int_0^\pi \int_0^{2\pi} \rho(r) \exp(-iKr \cos \alpha) r^2 \sin \alpha d\beta d\alpha dr$$

$$= \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin Kr}{Kr} dr$$

**Formula 7.2.3**

The atomic scattering factor  $f$  has the same value for different wavelengths of the X-rays if the magnitudes of the scattering vectors are the same.

The electron density distribution is calculated as the square of the wave function  $\psi(r)$  of an electron in the atom.

$$\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$$

**Formula 7.2.4**

The wave function  $\psi(r)$  is calculated by the Hartree-Fock method or the Thomas-Fermi method;  $f$  is calculated based on the results.

The atomic scattering factor  $f$  calculated as such depends on the atomic number and the scattering angle.

An element with a larger atomic number scatters X-rays more strongly, increasing the magnitude of  $f$ . The intensity of the scattered X-ray is proportional to the atomic number along the direction of X-ray propagation.

The intensity of the scattered X-rays is highest in the direction of the incident X-ray propagation and gradually decreases to the side and backwards. Along the direction of X-ray propagation, X-rays scattered by any electrons in the atom have the same phase, and the scattered X-rays interfere constructively. In the direction opposite the direction of X-ray propagation, the phase of the X-ray scattered by each electron differs depending on the position of the electron. The scattered X-rays interfere destructively, resulting in a low intensity.

Here, the curves differ depending on the elements because the orbitals of the electrons for each element and their spatial distribution differ. When the spread of the orbitals is small, X-rays scattered at any position have only small phase differences, since the distances between the scattering positions are small. When the spread of the orbitals is large, the phase difference may be large, depending on the positions at which the X-rays are scattered.

The atomic scattering factor basically does not depend on the wavelength of the X-rays. However, when X-rays have a wavelength extremely close to the absorption edge of the atom and demonstrate strong absorption, we observe the resonance effect and are compelled to consider anomalous scattering. The atomic scattering factor including **anomalous scattering** is given by the following formula:

$$f(\mathbf{K}) = f_0(\mathbf{K}) + \Delta f'(\mathbf{E}) + i\Delta f''(\mathbf{E})$$

**Formula 7.2.5**

Here,  $f_0(\mathbf{E})$  is the atomic scattering factor,  $f'(\mathbf{E})$  the real component of anomalous scattering, and  $f''(\mathbf{E})$  the imaginary component of the anomalous scattering. The parameters  $f'(\mathbf{E})$  and  $f''(\mathbf{E})$  depend on the element and wavelength of the X-rays and have been calculated based on theory.

## 7.2 X-Ray Scattering from Crystalline Material

The anomalous scattering occurs mainly due to the electrons in the K shell. Since the spatial spread of the K shell is small, the anomalous scattering terms of the atomic scattering factor lack strong scattering angle dependence. If we use X-rays with wavelengths a slight distance from the absorption edge, the anomalous scattering is small compared to  $f_0$  and can generally be ignored. However, it cannot be ignored for precise discussions of electron distribution. To perform analysis for a particular atom in a crystal, select a wavelength close to the absorption edge to use the anomalous scattering terms.

### 7.2.2 Crystal Structure Factor

A crystalline material is a three-dimensional regular structure of atoms or molecules. The **crystal structure factor** indicates the scattering caused by the entire material (in other words, the entire crystal) when atoms having atomic scattering factors characteristic to each element form a three-dimensional periodic structure in the crystal.

In a crystal, electron density distribution  $\rho(\mathbf{r})$  has a three-dimensional periodicity. Assume the origin (0, 0, 0) to be an arbitrary lattice point in the crystal and denote the fundamental vectors of the three-dimensional structure as  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ . If the coordinates of a lattice point are  $(p, q, r)$ , this lattice point is at position  $p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$  from the origin. When the distance to a point in the unit cell to which this lattice point belongs is denoted as  $\mathbf{r} = (p\mathbf{a} + q\mathbf{b} + r\mathbf{c}) + \mathbf{r}'$ ,  $\rho(\mathbf{r}) = \rho(\mathbf{r}')$  holds, since the crystal has a repeating structure.

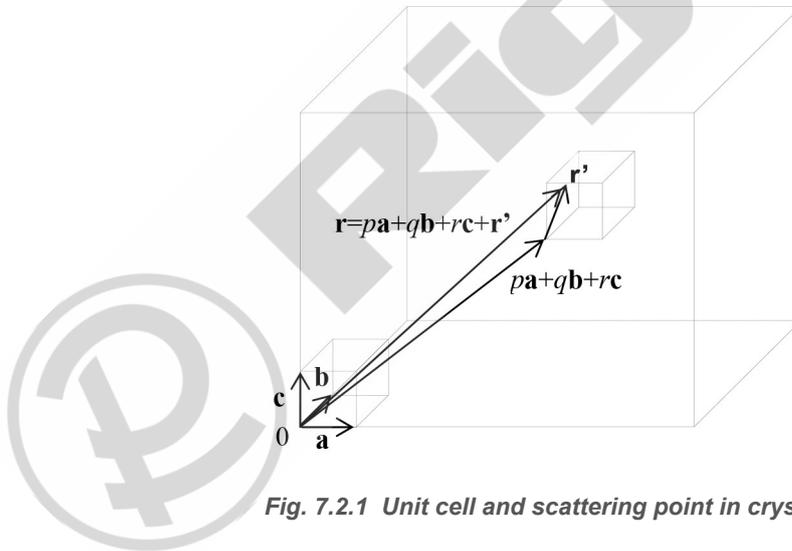


Fig. 7.2.1 Unit cell and scattering point in crystal

The amplitude of the scattered wave moving from the entire crystal is obtained by rewriting the formula expressing the amplitude of the scattered wave from an atom for the entire crystal. As the crystal has a regular structure, the formula can be transformed as follows:

$$A(\mathbf{K}) = \int_{\text{crystal}} \rho(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} d\mathbf{r} \quad \text{Formula 7.2.6}$$

$$= \sum_p \sum_q \sum_r \exp\{-i\mathbf{K} \cdot (p\mathbf{a} + q\mathbf{b} + r\mathbf{c})\} \int_{\text{unit lattice}} \rho(\mathbf{r}') \exp(-i\mathbf{K} \cdot \mathbf{r}') d\mathbf{r}' \quad \text{Formula 7.2.7}$$

Formula 1.3.9 shows that the scattering amplitude from the entire crystal is equivalent to the scattering amplitude calculated by assuming a scattering element at each lattice point with a proportional scattering amplitude, as expressed below:

$$F(\mathbf{K}) = \int_{\text{unit lattice}} \rho(\mathbf{r}) e^{-i\mathbf{K} \cdot \mathbf{r}} d\mathbf{r} \quad \text{Formula 7.2.8}$$

This  $F(\mathbf{K})$  is called the crystal structure factor and depends on the electron density in the unit cell or on the atomic arrangement.

We can express the electron distribution in the crystal as a superposition of the electron distribution of free electrons. Assume that the  $j$ -th atom in the unit cell is at position  $\mathbf{r}_j$  with respect to the origin of the unit cell and express the electron density distribution associated with this atom as  $\rho_j(\mathbf{r} - \mathbf{r}_j)$ . Then, the electron density distribution in the unit cell is given by the following formula:

$$\rho(\mathbf{r}) = \sum_j \rho_j(\mathbf{r} - \mathbf{r}_j) \quad \text{Formula 7.2.9}$$

Thus, the crystal structure factor is expressed as follows:

$$\begin{aligned} F(\mathbf{K}) &= \sum_j \int \rho_j(\mathbf{r} - \mathbf{r}_j) \exp(-i\mathbf{K} \cdot \mathbf{r}) d\mathbf{r} \\ &= \sum_j \exp(-i\mathbf{K} \cdot \mathbf{r}_j) \int \rho_j(\mathbf{r}') \exp(-i\mathbf{K} \cdot \mathbf{r}') d\mathbf{r}' \\ &= \sum_j f_j(\mathbf{K}) \exp(-i\mathbf{K} \cdot \mathbf{r}_j) \end{aligned} \quad \text{Formula 7.2.10}$$

Here, we used  $\mathbf{r} - \mathbf{r}_j = \mathbf{r}'$  and expressed the atomic scattering factor of the  $j$ -th atom as  $f_j(\mathbf{K})$ . The crystal structure factor is the sum of the atomic scattering factors of the atoms in the unit cell with the phase shift  $\mathbf{K} \cdot \mathbf{r}_j$  regarded to be the contribution from the atom at position  $\mathbf{r}_j$ .