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"Crystal Structure Analysis"
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Chapter 2 Kinematical theory of diffraction

There are two kinds of theories for diffraction; one is the **kinematical theory**, and another is the **dynamical theory**. The difference in the two theories is that the kinematical theory neglects the **multiple scattering**, but the dynamical theory takes multiple scattering into account. Multiple scattering means that X-ray (or quantum beam) scattered by a scatterer is scattered again, once or many times, by scatterers located at other positions.

This lecture will treat only the kinematical theory for diffraction hereafter, but note that multiple scattering should possibly occur, and the dynamical theory of diffraction will always be more correct than the kinematical theory. Most of diffraction data measured with X-ray or neutron beam are treated by the kinematical theory, partly because exact treatment of multiple scattering make the calculation quite more difficult. It is known that the dynamical theory of diffraction is necessary to treat diffraction data measured with electron beam, because the probability that the electron beam is scattered is much higher than X-ray or neutron beam. Dynamical theory is sometimes applied also to the X-ray diffraction at a crystal with high crystallinity.

Note that the Bragg's law in Chap. 1 is based on the kinematical theory of diffraction.

The two important points that are derived from the kinematical theory of diffraction are :

(1) The intensity of diffraction is proportional to the square of the absolute value of the structure factor

(2) The structure factor for X-ray diffraction is the Fourier transform of electron density (distribution)

Just the above two things are all you should know, and you don't have to know anything else about the kinematical theory.

Quiz: which is NOT connected with the above two statements :

A. X-ray is a kind of electromagnetic wave
B. An atom consists of nucleus and electron
C. Atoms are arranged periodically in a crystal
D. The energy of a wave is proportional to the squared amplitude

Assume the electron density in a material is given by $\rho(x,y,z)$. Note that the electron density is expressed by a function of the three-dimensional coordinate (x,y,z).

The structure factor is given by

$$F(k_x,k_y,k_z)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\rho(x,y,z)\mathrm{e}^{2\pi i(k_x x+k_y y+k_z z)}\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\ , \qquad (2.1)$$

or

$$F(k_x,k_y,k_z)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\rho(x,y,z)e^{-2\pi i(k_x x+k_y y+k_z z)}\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,. \tag{2.2}$$

2-1 X-ray as electromagnetic wave

X-ray is a kind of electromagnetic wave. Electromagnetic waves are called as various name, radio wave, microwave, far infrared ray, infrared ray, visible light, ultraviolet ray, vacuum ultraviolet ray (extreme ultraviolet ray), soft x-ray, (hard) x-ray, and so on, in the order of wavelength (or lower frequency).

Electromagnetic wave is oscillating electric and magnetic fields, which propagates at the speed of light. As the interaction of magnetic field with materials is not strong, we may think that **X-ray is an oscillating electric field**. A charged particle in electric field feels a force from the field. As the field oscillates, the charged particle also oscillates harmonically with the field.

A material consists of atoms, and an atom consists of nucleus and electrons. As the nucleus is positively charged and the electrons are negatively charged, the nucleus feels force along the direction of the electric field, and the electrons feel force against the direction of the electric field. As a result, the positions of the positive and negative charge are displaced to opposite directions, which leads electric polarization.

Although both nucleus and electrons should be displaced, the motion of nucleus is usually neglected, because a nucleus is much heavier than an electron. The mass of a proton, nucleus of a hydrogen atom, is $1.67262158(13)\times10^{-27}$ kg, which is heavier by about 1,800 times than the mass of an electron, $9.10938188(72)\times10^{-31}$ kg. So the motion of the nucleus is expected to be smaller by about 1,800 than that of electron in case of a hydrogen atom. As elements other than hydrogen has nucleus including neutron, the mass relative to the charge is generally larger than hydrogen atom, so the motion of nucleus is expected to be still smaller than that of hydrogen. That is the reason why the motion of the nucleus is neglected, and only the motion of electrons are taken into account in analyzing X-ray diffraction data.

2-2 Scattering of X-ray and structure factor

Electrons in a material are forced to oscillate, when irradiated by X-ray. And oscillating motion of charged particle causes emission of electromagnetic waves. That is the origin of scattering. If the oscillator is a **point charge**, the oscillating motion will cause radiation of electromagnetic wave, called **dipole radiation**. In case of dipole radiation, radiation is nondirectional about the polar axis. Since a scatterer has finite (non-zero) size, and the position of an electron has probability distribution, the intensity of the electromagnetic wave becomes varied on the propagating direction by the effect of interference.

First we assume that all the electrons in a material behave exactly in the same manner against the X-ray. It means neglect of different character of electrons, even though there should be a kind of difference in response of bound electrons. You may think even an electron bound to an atom appears similar to a free electron for X-ray, because the frequency of the oscillation is higher than

the natural frequency of a bound electron. More precisely, the difference of the response of bound electrons appears as dispersion effect, as will be discussed in Chap. 3.

It is not difficult to derive the formula of X-ray scattering. It is just the sum of the scattering at all the location on a scatterer (Fig. 2.1).

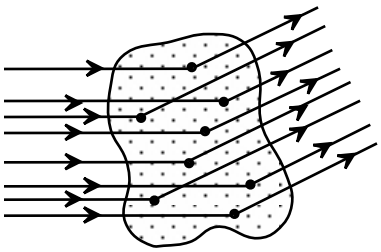

Fig. 2.1 Just calculate the sum of amplitudes of beam scattered at all the location, to derive the formula for the scattering intensity by an arbitrary scatter.

More concretely, (i) evaluate the path difference of each scattered wave, and (ii) calculate the amplitude of the superimposed waves as the sum of the waves with the phase shift given by the path difference.

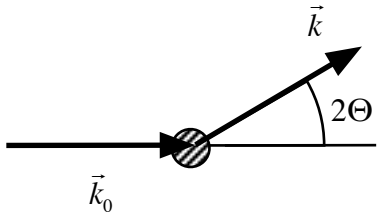

Fig. 2.2 Scattering of X-ray. $\vec{k}_0$ and $\vec{k}$ are the wavenumber vectors of the incident wave and scattered wave.

As shown in Fig. 2.2, let

$\vec{k}_0$: wavenumber vector of incident wave,

$\vec{k}$ ：wavenumber vector of scattered wave.

Wavenumber vector is the vector having the direction of propagation of the wave, and the length of reciprocal wavelength, that is,

$$\left|\vec{k}_0\right| = \left|\vec{k}\right| = k = \frac{1}{\lambda} \tag{2.3}$$

for the wavelength λ. The scattering angle is expressed by 2Θ. The scattering vector $\vec{K}$ is defined by $\vec{K} \equiv \vec{k} - \vec{k}_0$ as shown in the left side of the figure below.

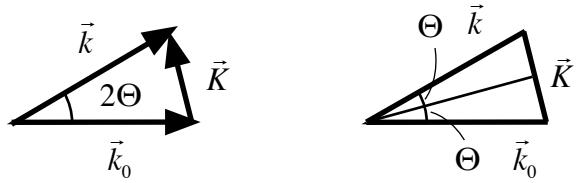

Fig. 2.3 Definition of the scattering vector $\vec{K}$ (left).
The length of the scattering vector K is equal to the length of the base of an isosceles triangle (right).

From the illustration on the right side of Fig. 2.3, it is easy to find the relation :

$$K = \left|\vec{K}\right| = 2k\sin\Theta = \frac{2\sin\Theta}{\lambda}. \tag{2.4}$$

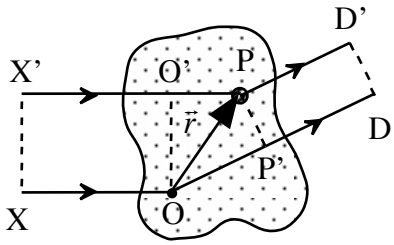

Fig. 2.4 What is the path difference of the scattering at an arbitrary position P from the scattering at the origin O ?

Consider the path difference of the scattering at the position P displaced by $\vec{r}$ from the origin O. When the scattering at the origin O is treated as the reference, the path difference is given by $\overline{O'P} - \overline{OP'}$. The question is how the length $\overline{O'P} - \overline{OP'}$ is expressed by $\vec{r}$, $\vec{k}_0$ and $\vec{k}$.

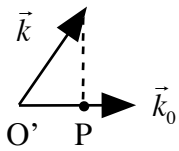

Fig. 2.5 What is the length O'P ?

As shown in Fig. 2.5, the length $\overline{O'P}$ is given by

$$\overline{O'P} = \frac{\vec{k}_0 \cdot \vec{r}}{\left|\vec{k}_0\right|} = \frac{\vec{k}_0 \cdot \vec{r}}{k}, \tag{2.5}$$

and similarly, the length $\overline{OP'}$ is given by

$$\overline{OP'} = \frac{\vec{k} \cdot \vec{r}}{\left|\vec{k}\right|} = \frac{\vec{k} \cdot \vec{r}}{k}. \tag{2.6}$$

Then the path difference $\overline{O'P} - \overline{OP'}$ is given by

$$\overline{O'P} - \overline{OP'} = \frac{\left(\vec{k}_0 - \vec{k}\right) \cdot \vec{r}}{k} = -\frac{\vec{K} \cdot \vec{r}}{k} = -\lambda \vec{K} \cdot \vec{r}, \tag{2.7}$$

and the phase shift should be given by

$$\frac{2\pi}{\lambda}\left(-\lambda\vec{K}\cdot\vec{r}\right)=-2\pi\vec{K}\cdot\vec{r}\ . \tag{2.8}$$

The theory of diffraction is based on the **principle of superposition**. It means that displacement (positional deviation, polarization etc) at a location should be the sum of the displacements caused by different waves. This relation may not be obvious. It requires at least the displacement is proportional (linear) to the strength of waves scattered at different positions. In general, nonlinearity may appear on extremely large displacement, even if it is practically not observed in X-ray diffraction measurements.

The displacement *y* at the position *x* and the time *t* for the wave of frequency ν, wavelength λ and amplitude *A* can be expressed by a trigonometric function,

$$y=A\cos\left[2\pi\left(\nu t-\frac{x}{\lambda}\right)\right] \tag{2.9}$$

and applying the Euler's equation,

$$e^{i\theta}=\cos\theta+i\sin\theta\ ,$$

we will have the formula

$$y=A\,\mathrm{Re}\left\{\exp\left[2\pi i\left(\nu t-\frac{x}{\lambda}\right)\right]\right\}, \tag{2.10}$$

where $\mathrm{Re}\{\cdots\}$ means to take the real part of a complex number. Be sure that the relation

$$\cos(2\pi\phi)=\mathrm{Re}\left[\exp(2\pi i\phi)\right] \tag{2.11}$$

always holds. Generally, it is more convenient to use the formula $e^{2\pi i\phi}$ to treat waves, not only for the theory for diffraction.

We often need to calculate the superposition of waves with identical frequency, but different amplitudes and phases. What is the amplitude of a wave given by

$$y=A_1\cos\left[2\pi(\nu t+\phi_1)\right]+A_2\cos\left[2\pi(\nu t+\phi_2)\right]+\cdots, \tag{2.12}$$

as expressed by trigonometric functions ? By applying the exponential formula ,

$$\begin{aligned} y&=A_1\,\mathrm{Re}\left\{\exp\left[2\pi i(\nu t+\phi_1)\right]\right\}+A_2\,\mathrm{Re}\left\{\exp\left[2\pi i(\nu t+\phi_2)\right]\right\}+\cdots \\ &=\mathrm{Re}\left\{\exp(2\pi i\nu t)\left[A_1\exp(2\pi i\varphi_1)+A_2\exp(2\pi i\varphi_2)+\cdots\right]\right\} \end{aligned} \tag{2.13}$$

and let the content of the second equation [ ] be expressed by $A\exp(2\pi i\phi)$, then

$$A=\left|A_1\exp(2\pi i\phi_1)+A_2\exp(2\pi i\phi_2)+\cdots\right| \tag{2.14}$$

$$y=A\,\mathrm{Re}\left\{\exp\left[2\pi i(\nu t+\phi)\right]\right\} \tag{2.15}$$

wehre *A* is just the amplitude of the synthesized wave.

The amplitude of the scattered X-ray should be proportional to the density $\rho(\vec{r})$ of the scatterer at the point $\vec{r}$. When the wave scattered at the origin has amplitude of $A\rho(0)$, the amplitude of the wave scattered at the point $\vec{r}$ will be given by $A\rho(\vec{r})\mathrm{e}^{-2\pi \mathrm{i}\vec{K}\cdot\vec{r}}$. Just by adding all the scattered wave from everywhere in the scatterer, the amplitude of the scattered wave should be proportional to

$$F(\vec{K}) = \int_V \rho(\vec{r})\mathrm{e}^{-2\pi \mathrm{i}\vec{K}\cdot\vec{r}}\,\mathrm{d}v \tag{2.16}$$

where $\int_V \cdots \mathrm{d}v$ menas the integration over whole the volume of the scatterer. Even if the scatterer may have finite volume, the integral can be extended to infinite range, by assuming that the value of the density function is zero ($\rho(\vec{r}) = 0$) outside of the scatterer. In this case, we can use the expression :

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \rho(x,y,z)\cdots \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z \tag{2.17}$$

instead of

$$\int_V \rho(\vec{r})\cdots \mathrm{d}v\,. \tag{2.18}$$

So the amplitude of the scattered wave should be proportional to

$$F(K_x,K_y,K_z) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \rho(x,y,z)\mathrm{e}^{-2\pi \mathrm{i}(K_x x+K_y y+K_z z)}\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,. \tag{2.19}$$

The factor $F(\vec{K}) = F(K_x,K_y,K_z)$ is called **structure factor**. As the scatterer for X-ray is an electron, the assumed density of the scatterer $\rho(\vec{r}) = \rho(x,y,z)$ is nothing but **electron density.** The above equation is expressed by the statement : "**structure factor is the Fourier transform of electron density**". As the intensity of the wave is proportional to the squared amplitude, the intensity of scattered X-ray should be proportional to the squared absolute value of structure factor, $\left|F(\vec{K})\right|^2$.

2-3 Structure factor

If you have an experience of crystal structure analysis, you may remember the "crystal structure factor" F_{hkl} defined by three integer suffix h, k, l. Be sure that we do not restrict the scatterer to be a crystal in this chapter, and the structure factor should be given as a function of diffraction vector $\vec{K}$. The discussion in this chapter can straightforwardly be applied to the structure factor of an atom, a molecule or an amorphous material.

Since even one atom has distribution of electron density, the intensity of the X-ray scattered by the atom varies depending on the direction of the scattered beam. This effect is usually called

atomic scattering factor, but sometimes called atomic form factor or atomic structure factor. All of them mean the Fourier transform of the electron density.

When the X-ray is scattered by a crystal, diffraction intensity will be observed only for the special directions determined by discrete suffix *hkl*, and this relation is naturally derived just as the Fourier transform of periodic electron density. The structure factor of a crystal is called crystal structure factor.

Atomic scattering factor will be discussed in Chap. 3, and crystal structure factor will be discussed in Chap. 4 of this lecture.