

## Chapter 6 Diffraction from small crystallites

In Chap. 5, it has been concluded that the diffraction condition should strictly be satisfied for the appearance of diffraction intensity, if a crystal is sufficiently large. In many cases, the size of crystals are certainly sufficiently large as compared with the size of atoms, even in the cases of crystallites included in polycrystalline materials, such as minerals, ceramics and alloys, and so on. On the other hand, it has also been shown in Chap. 5, that we can calculate the **diffraction peak profile** of a **finite-size crystal**, and the solution for the diffraction from the lattice planes parallel to a face of a parallelepiped crystal (that is,  $\vec{d}^* \parallel \vec{a}^*$ ,  $\vec{d}^* \parallel \vec{b}^*$  or  $\vec{d}^* \parallel \vec{c}^*$  for the parallelepiped crystal with the edges along  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$ ) should be the Laue function. We can expect that the width of an observed diffraction peak will be broadened for smaller size of a crystallite.

Broadening of X-ray diffraction peak profile is sometimes observed for very fine powder samples, and the effect of finite size of crystallites has experimentally been confirmed by comparisons with electron microscopy.

Of course, the size effect on the observed diffraction intensity profile cannot fully be understood by the Laue function. The first problem is that the shape of small crystallites is not usually parallelepiped. Very small crystallites tend to have nearly spherical shape to reduce the surface energy. Some materials tend to form needle-like crystallites, and other materials tend to form platy crystallites, depending on anisotropy in formation energy of crystal structure and possibly entropy caused by distribution of structural defects.

Another problem is that the application of the Laue function should be restricted to  $h00$ ,  $0k0$  and  $00l$  diffraction peaks, even in the case of really parallelepiped crystallites classified to orthogonal crystal system. The diffraction intensity profile of 111-diffraction peak for a cubic crystallite should be different from the Laue function, for example.

Is it possible to calculate the structure factor for arbitrary  $(hkl)$  lattice planes of a crystallite with arbitrary shape? On the assumption of the kinematical theory, the answer is YES. Just use the theory of Stokes and Wilson in Sec. 6-3 introduced in this chapter.

As described in Chap. 3, you (or a computer program you use for crystal structure analysis) don't have to calculate the Fourier transform in crystal structure analysis, because you can use the atomic scattering factors, which are the Fourier transforms of the atomic electron densities, someone has already calculated by a quantum mechanical method. But it is recommended to study fundamentals about Fourier transforms, if you feel difficulty to understand the Stokes-Wilson theory.

## 6-1 Mathematics about Fourier transformation

Fundamental mathematics about Fourier transform is briefly described in this section.

### 6-1-1 Definitions and expressions of Fourier transform

There is a variety of definitions and expressions about the Fourier transform. In this text, the Fourier transform  $F(k)$  of a one-dimensional function  $f(x)$  is defined by

$$F(k) = \int_{-\infty}^{\infty} f(x) \exp(2\pi i k x) dx, \quad (6.1)$$

and the inverse Fourier transform of the function  $F(k)$  is defined by

$$f(x) = \int_{-\infty}^{\infty} F(k) \exp(-2\pi i k x) dk. \quad (6.2)$$

The above relations are purely mathematical, but you may assume that the variable  $x$  corresponds to the position having the dimension of length with the unit of [m] (meter), and the variable  $k$  corresponds to the wavenumber having the dimension of reciprocal length with the unit of [m<sup>-1</sup>].

Three-dimensional Fourier transform  $F(k_x, k_y, k_z)$  of a three dimensional function  $f(x, y, z)$  is defined by

$$F(k_x, k_y, k_z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y, z) \exp[2\pi i (k_x x + k_y y + k_z z)] dx dy dz, \quad (6.3)$$

where you can assume  $x, y, z$  are the Cartesian coordinates of a position, and  $k_x, k_y, k_z$  are  $x, y, z$ -components of the diffraction vector. A simplified expression :

$$F(\vec{k}) = \int_{\mathbf{R}^3} f(\vec{r}) \exp(2\pi i \vec{k} \cdot \vec{r}) dv, \quad (6.4)$$

is used instead of Eq. (6.3), where

$$\vec{k} \equiv \begin{pmatrix} k_x \\ k_y \\ k_z \end{pmatrix}, \quad \vec{r} \equiv \begin{pmatrix} x \\ y \\ z \end{pmatrix},$$

and

$$\int_{\mathbf{R}^3} \cdots dv \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots dx dy dz.$$

The three-dimensional inverse Fourier transform is defined by

$$f(\vec{r}) = \int_{\mathbf{R}^3} F(\vec{k}) \exp(-2\pi i \vec{k} \cdot \vec{r}) dv^*, \quad (6.5)$$

where

$$\int_{\mathbf{R}^3} \cdots dv^* \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cdots dk_x dk_y dk_z.$$

## 6-1-2 Dirac's delta function and Fourier transform

The Dirac's delta function is widely used in the field of science and technology, because it often provides more simple or exact formulation for calculation.

The Dirac's delta function  $\delta(x)$  is such a function as is

(1) the value at the origin  $x = 0$  is infinity, and the value at locations  $x \neq 0$  is zero,

$$\delta(x) = \begin{cases} +\infty & [x = 0] \\ 0 & [x \neq 0] \end{cases},$$

(2) and the area (integration from  $-\infty$  to  $+\infty$ ) is equal to unity.

$$\int_{-\infty}^{\infty} \delta(x) dx = 1$$

The delta function can be defined by the limit  $\gamma \rightarrow 0$  of the following rectangular function,

$$g_R(x) = \begin{cases} \frac{1}{\gamma} & \text{for } -\frac{\gamma}{2} < x < \frac{\gamma}{2} \\ 0 & \text{for } x \leq -\frac{\gamma}{2} \quad \text{or} \quad \frac{\gamma}{2} \leq x \end{cases}, \quad (6.6)$$

$$\delta(x) = \lim_{\gamma \rightarrow 0} g_R(x) \quad (6.7)$$

One of the most important properties of the delta function is that the following equation

$$\int_{-\infty}^{\infty} f(x) \delta(x) dx = f(0) \quad (6.8)$$

is satisfied for any function  $f(x)$ . The relation can be derived from the definition by Eqs. (6.6) and (6.7) as follows,

$$\int_{-\infty}^{\infty} f(x) \delta(x) dx = \lim_{\gamma \rightarrow 0} \frac{1}{\gamma} \int_{-\gamma/2}^{\gamma/2} f(x) dx = f(0). \quad (6.9)$$

As a result, the Fourier transform or the inverse Fourier transform of the delta function (the Fourier transform and the inverse Fourier transform of symmetric function are equivalent) is given by

$$\int_{-\infty}^{\infty} \delta(x) e^{\pm 2\pi i k x} dx = 1, \quad (6.10)$$

and the Fourier (or inverse Fourier) transform of  $f(x) = 1$  is the delta function, that is,

$$\int_{-\infty}^{\infty} e^{\pm 2\pi i k x} dk = \delta(x) \quad (6.11)$$

It is easy to extend the one-dimensional delta function to three-dimensional delta function. The three-dimensional delta function is simply defined by  $\delta^3(\vec{r}) = \delta(x)\delta(y)\delta(z)$ , and the following equations are satisfied,

$$\int_{\mathbf{R}^3} \delta^3(\vec{r}) d\mathbf{v} = 1, \quad (6.12)$$

$$\int_{\mathbf{R}^3} f(\vec{r}) \delta^3(\vec{r}) d\mathbf{v} = f(\vec{0}), \quad (6.13)$$

where

$$\vec{0} \equiv \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}.$$

### 6-1-3 Convolution and correlation

The **convolution** of two functions  $f(x)$  and  $g(x)$  are defined by

$$h(x) = \int_{-\infty}^{\infty} f(x-y)g(y)dy . \quad (6.14)$$

Another formula for definition of the convolution is

$$h(x) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \delta(x-y-z)f(y)g(z)dydz . \quad (6.15)$$

The above relations are usually written by

$$h(x) = f(x) * g(x) , \quad (6.16)$$

or

$$h(x) = f(x) \otimes g(x) . \quad (6.17)$$

The Fourier transform of the convolution is equivalent to the product of the Fourier transforms of the component functions, that is,

$$H(k) = F(k)G(k) , \quad (6.18)$$

for

$$H(k) = \int_{-\infty}^{\infty} f(x)e^{2\pi kx} dx , F(k) = \int_{-\infty}^{\infty} f(x)e^{2\pi kx} dx , G(k) = \int_{-\infty}^{\infty} g(x)e^{2\pi kx} dx , \quad (6.19)$$

The above equivalency is called the **convolution theorem**.

It is not difficult to extend the one-dimensional convolution to three dimensions. The three-dimensional convolution can be defined by

$$h(\vec{r}) = \int_{\mathbf{R}^3} f(\vec{r} - \vec{r}')g(\vec{r}')d\mathbf{v}' . \quad (6.20)$$

The **correlation** of functions  $f(x)$  and  $g(x)$  is defined by

$$\text{Corr}[f(x),g(x)] = \int_{-\infty}^{\infty} f(x+y)g(y)dy , \quad (6.21)$$

and it is equivalent to the convolution of  $f(x)$  and  $g(-x)$ . When the function  $g(x)$  is a real function (function that returns a real value), “the Fourier transform of  $\text{Corr}[f(x),g(x)]$ ” is equal to the product of “the Fourier transform of  $f(x)$ ” and “the complex conjugate of the Fourier transform of  $g(x)$ ”, that is,

$$\int_{-\infty}^{\infty} \text{Corr}[f(x),g(x)]e^{2\pi ikx} dx = \int_{-\infty}^{\infty} f(x)e^{2\pi ikx} dx \left[ \int_{-\infty}^{\infty} g(y)e^{2\pi iky} dy \right]^* \quad (6.22)$$

This relation is called the **correlation theorem**.

In a particular case of  $g(x) = f(x)$ , the correlation

$$\text{Corr}[f(x),f(x)] = \int_{-\infty}^{\infty} f(x+y)f(y)dy \quad (6.23)$$

is called the **autocorrelation**. “the Fourier transform of the autocorrelation” is equivalent to “the square of the absolute value of the Fourier transform”,

$$\int_{-\infty}^{\infty} \text{Corr}[f(x), f(x)] e^{2\pi i k x} dx = \left| \int_{-\infty}^{\infty} f(x) e^{2\pi i k x} dx \right|^2. \quad (6.24)$$

## 6-2 Dependence of diffraction intensity from a small crystallite upon diffraction vector

Let us consider the function to define the three dimensional shape of a crystal, which the author likes to call the **volume function**. The volume function returns 1 for the position inside of the body and returns 0 for the position outside of the body.

For example, the volume function for a spherical crystallite with the radius of  $R$  is given by

$$V(\vec{r}) = \begin{cases} 1 & [|\vec{r}| \leq R] \\ 0 & [|\vec{r}| > R] \end{cases}, \quad (6.25)$$

or

$$V(x, y, z) = \begin{cases} 1 & [x^2 + y^2 + z^2 \leq R^2] \\ 0 & [x^2 + y^2 + z^2 > R^2] \end{cases}. \quad (6.26)$$

The volume function for a crystal of orthogonal shape with the edge lengths of  $A, B, C$ , growing along the lattice vectors  $\vec{a}, \vec{b}, \vec{c}$  is given by

$$V(x, y, z) = \begin{cases} 1 & \left[ |x| \leq \frac{A}{2} \quad \text{and} \quad |y| \leq \frac{B}{2} \quad \text{and} \quad |z| \leq \frac{C}{2} \right] \\ 0 & \left[ |x| > \frac{A}{2} \quad \text{or} \quad |y| > \frac{B}{2} \quad \text{or} \quad |z| > \frac{C}{2} \right] \end{cases}, \quad (6.27)$$

When the crystal structure factor  $F(\vec{K})$  and the volume function  $V(\vec{r})$  are given, the total structure factor of the crystal with arbitrary shape can be determined by

$$F_{\text{total}}(\vec{K}) = G(\vec{K})F(\vec{K}) \quad (6.28)$$

where

$$\begin{aligned} G(\vec{K}) &= \sum_{\xi, \eta, \zeta} \exp[2\pi i \vec{K} \cdot (\xi \vec{a} + \eta \vec{b} + \zeta \vec{c})] \\ &= \sum_{\xi=-\infty}^{\infty} \sum_{\eta=-\infty}^{\infty} \sum_{\zeta=-\infty}^{\infty} V(\xi \vec{a} + \eta \vec{b} + \zeta \vec{c}) \exp[2\pi i \vec{K} \cdot (\xi \vec{a} + \eta \vec{b} + \zeta \vec{c})]. \end{aligned} \quad (6.29)$$

Note that the shape and size of the crystallite is fully determined without loss of generality in the expression on the right side of the second equivalency of Eq. (6.29) by introducing the volume function  $V(\vec{r})$ . The function  $G(\vec{K})$  can be expressed by the Fourier-transform of a function,

$$G(\vec{K}) = \int_{\mathbf{R}^3} \sum_{\xi=-\infty}^{\infty} \sum_{\eta=-\infty}^{\infty} \sum_{\zeta=-\infty}^{\infty} V(\vec{r}) \delta(\vec{r} - \xi \vec{a} - \eta \vec{b} - \zeta \vec{c}) \exp(2\pi i \vec{K} \cdot \vec{r}) d\mathbf{v} \quad (6.30)$$

which can be derived from Eq. (6.29) by applying a property of the delta function given by Eq. (6.13). Here we define a function  $\sigma_{\infty}(\vec{r})$  by

$$\sigma_{\infty}(\vec{r}) \equiv \sum_{\xi=-\infty}^{\infty} \sum_{\eta=-\infty}^{\infty} \sum_{\zeta=-\infty}^{\infty} \delta(\vec{r} - \xi \vec{a} - \eta \vec{b} - \zeta \vec{c}), \quad (6.31)$$

and the function  $G(\vec{K})$  is now expressed as the Fourier transform of “the product of  $V(\vec{r})$  and  $\sigma_{\infty}(\vec{r})$ ” as follows,

$$G(\vec{K}) = \int_{R^3} V(\vec{r}) \sigma_{\infty}(\vec{r}) \exp(2\pi i \vec{K} \cdot \vec{r}) d\mathbf{v} \quad (6.32)$$

Applying the correlation theorem, the function  $G(\vec{K})$  is equivalent to the convolution of “the inverse Fourier transform of  $V(\vec{r})$ ” and “the inverse Fourier transform of  $\sigma_{\infty}(\vec{r})$ ”.

Now, what is “the inverse Fourier transform of  $\sigma_{\infty}(\vec{r})$ ”? We can derive the solution :

$$\begin{aligned} \int_{-\infty}^{\infty} \sigma_{\infty}(\vec{r}) \exp(-2\pi i \vec{k} \cdot \vec{r}) d\mathbf{v} &= \sum_{\xi=-\infty}^{\infty} \sum_{\eta=-\infty}^{\infty} \sum_{\zeta=-\infty}^{\infty} \int \delta(\vec{r} - \xi \vec{a} - \eta \vec{b} - \zeta \vec{c}) \exp(-2\pi i \vec{k} \cdot \vec{r}) d\mathbf{v} \\ &= \sum_{\xi=-\infty}^{\infty} \sum_{\eta=-\infty}^{\infty} \sum_{\zeta=-\infty}^{\infty} \exp[-2\pi i \vec{k} \cdot (\xi \vec{a} + \eta \vec{b} + \zeta \vec{c})], \end{aligned} \quad (6.33)$$

and find that it is nothing but the amplitude of the Laue function in Chap. 5, for “an infinitely large crystal”. It means that the function returns non-zero values only for the diffraction vector satisfying

$\vec{k} = \vec{d}_{hkl}^* = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$  ( $h, k, l$ : integer), and returns zero otherwise. In other words, “the

inverse Fourier transform of  $\sigma_{\infty}(\vec{r})$ ” is equivalent to the sum of the delta functions located at

$\vec{d}_{hkl}^* = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$  for all the Miller’s indices  $h, k, l$ . As we are interested in the diffraction

peak profile around one of the peak locations, what we should consider is the dependence of the

structure factor  $G(\vec{d}_{hkl}^* + \Delta\vec{k})$  for small deviation of the diffraction vector  $\Delta\vec{k}$  from the peak

location  $\vec{d}_{hkl}^* = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$ , which can be approximated by the convolution of “the Fourier

transform of the volume function  $V(\vec{r})$ ” with “the three-dimensional delta function  $\delta^3(\vec{r})$ ”. As the

convolution with the delta function is an identity operation (similar to “multiplication by 1” or

“addition of 0”), we can conclude that “the diffraction peak profile of the structure factor is

equivalent to the Fourier transform of the volume function  $V(\vec{r})$ ”.

Here we define “the Fourier transform of  $V(\vec{r})$ ” as  $H(\vec{k})$ , that is,

$$H(\vec{k}) \equiv \int_{R^3} V(\vec{r}) \exp(2\pi i \vec{k} \cdot \vec{r}) d\mathbf{v}. \quad (6.34)$$

The diffraction peak profile for small deviation of the diffraction (scattering) vector  $\Delta\vec{k}$  from the peak position  $\vec{d}_{hkl}^*$  should be determined by

$$G(\vec{d}_{hkl}^* + \Delta\vec{k}) \sim H(\Delta\vec{k}). \quad (6.35)$$

The distribution of the diffraction intensity should be proportional to  $|H(\Delta\vec{k})|^2$ . The correlation

theorem predicts that  $|H(\vec{k})|^2$  should be proportional to “the autocorrelation of the volume function  $V(\vec{r})$ ”, that is,

$$|H(\vec{k})|^2 = \int_{R^3} \int_{R^3} V(\vec{r} + \vec{r}') V(\vec{r}') d\mathbf{v}' \exp(2\pi i \vec{k} \cdot \vec{r}) d\mathbf{v}. \quad (6.36)$$

### 6-3 Powder diffraction measurement

It is often technically difficult to detect the small change in diffraction peak profile caused by the effect of finite crystal size. But the size effect on the diffraction peak profile is sometimes observed

in **powder diffraction measurement**, where fine powder or polycrystalline samples are used for the measurement.

In analysis of powder diffraction data, it is usually assumed that the small crystallites in the specimen are randomly oriented. The diffracted beam should run on a cone, because the angle between the directions of the incident and diffracted beams is restricted to be  $2\Theta$ . This is what is called the “diffraction cone” or “Debye-Scherrer cone”.

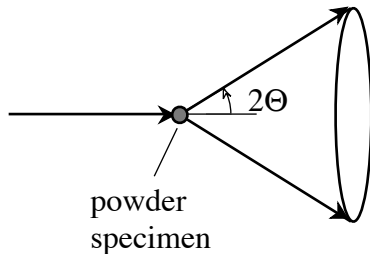


Fig. 6.1 The diffraction condition of powder diffraction measurement.  
The diffracted beam runs on a side face of the “diffraction cone”.

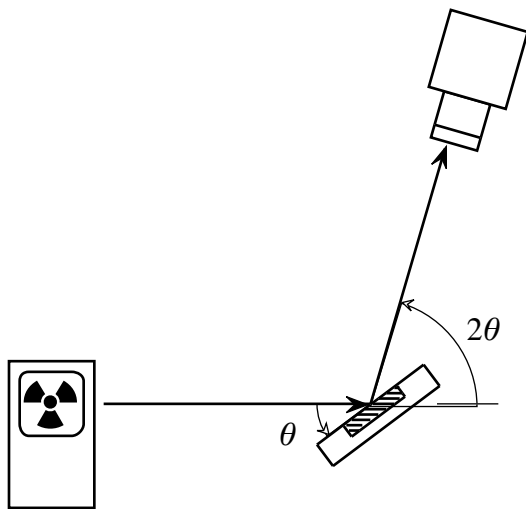


Fig. 6.2 Schematic illustration of a “vertical-type” diffractometer

In use of a powder diffractometer attached with an X-ray detector, the detector is moved as it vertically crosses the diffraction cone. The design of a vertical-type diffractometer shown in Fig. 6.2 is most commonly used in powder diffraction measurement, where the X-ray source is fixed, and the specimen and the detector are moved associatively. There is another type of the powder diffractometer, as shown in Fig. 6.3, where the orientation of the specimen face is always fixed horizontally, and the X-ray source and detector are moved symmetrically. It will be easier to understand what is observed, by imagining the horizontal-specimen type diffractometer in Fig. 6.3, because the scattering vector is always directed upright in this motion.

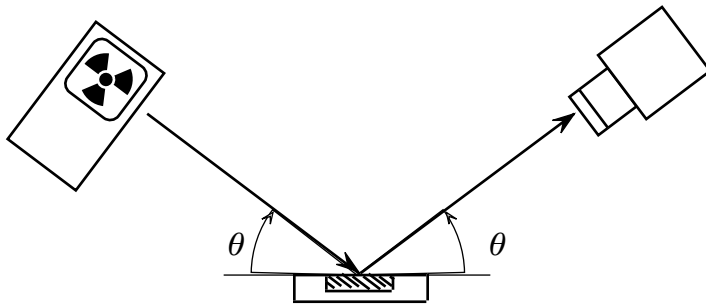


Fig. 6.3 Schematic illustration of a “horizontal-specimen type” diffractometer

What the horizontal-specimen type diffractometer does in its motion is extension and reduction of the scattering vector, keeping the direction unchanged (Fig. 6.4).

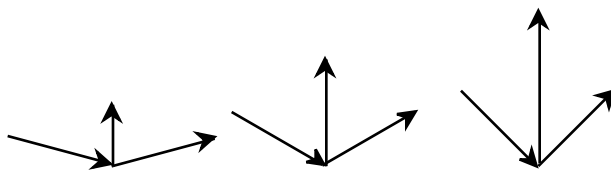


Fig. 6.4 The change of diffraction vector in a “horizontal-specimen type” diffractometer.

The dependence of the diffraction intensity of a crystallite on the scattering vector should be expressed as spots arranged in a three dimensional reciprocal space. And the diffraction intensity should appear, only when the orientation of a lattice plane satisfies the diffraction condition, that is, the crystal or lattice planes should be oriented to the direction specified by the diffraction condition. When the crystal is continuously rotated about a direction, one of the lattice planes may satisfy the diffraction condition just for a moment during the rotation, and the spot of the diffracted beam will be recorded on an X-ray film.

In contrast, the diffraction condition of a powder specimen should be the trace of the diffraction spots for a crystallite by three-dimensional rotation, and it will look like an onion shell (Fig. 6.5).

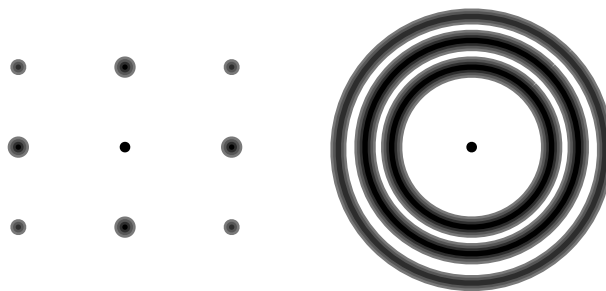


Fig. 6.5 Diffraction patterns of a uniaxially rotated crystallite (left) and a powder specimen (right).

So the distribution of the powder diffraction intensity should be given by

$$I_{\text{PD}}(K) \sim \int_0^{2\pi} \int_0^{\pi} \langle |F_{\text{cryst}}(\vec{K})|^2 \rangle \sin \theta_K \, d\theta_K \, d\phi_K, \quad (6.37)$$

where

$$K = |\vec{K}| \quad (6.38)$$



$$\vec{K} = \begin{pmatrix} K_x \\ K_y \\ K_z \end{pmatrix} = \begin{pmatrix} K \sin \theta_K \cos \phi_K \\ K \sin \theta_K \sin \phi_K \\ K \cos \theta_K \end{pmatrix}. \quad (6.39)$$

We may approximate the diffraction condition given by the spherical plane by the flat plane that touches the spherical face (Fig. 6.6), when the diffraction vector is sufficiently longer than the size of the diffraction spots.



Fig. 6.6 The spherical plane for the diffraction condition (left) is approximated by a flat plane (right).

We may use the following equation

$$I_{\text{PD}}(K) \sim \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left\langle \left| F_{\text{cryst}}(\vec{K}) \right|^2 \right\rangle dK_x dK_y \quad (6.40)$$

instead of Eq. (6.31). The distribution of the diffraction beam intensity should be proportional to  $|H(\vec{k})|^2$ . The diffraction peak profile is then given by

$$\begin{aligned} p_{\text{PD}}(k) &\sim \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |H(\vec{k})|^2 dk_x dk_y \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{R^3} \int_{R^3} V(\vec{r} + \vec{r}') V(\vec{r}') d\mathbf{v}' e^{2\pi i \vec{k} \cdot \vec{r}} d\mathbf{v} dk_x dk_y \\ &= \int_{R^3} \int_{R^3} V(\vec{r} + \vec{r}') V(\vec{r}') d\mathbf{v}' e^{2\pi i(k_x x + k_y y + k_z z)} \delta(x) \delta(y) d\mathbf{v} \\ &= \int_{R^3} \int_{-\infty}^{\infty} V(z\vec{e}_z + \vec{r}') V(\vec{r}') e^{2\pi i k_z z} dz d\mathbf{v}' \\ &= \int_{-\infty}^{\infty} \left[ \int_{R^3} V(\vec{r}) V(\vec{r} + z\vec{e}_z) d\mathbf{v} \right] e^{2\pi i k_z z} dz, \end{aligned} \quad (6.41)$$

where  $\vec{e}_z$  is the unit vector along the  $z$ -direction.

The above formula means that the diffraction peak profile is given by “the one-dimensional Fourier transform of  $\int_{R^3} V(\vec{r}) V(\vec{r} + z\vec{e}_z) d\mathbf{v}$ ”. And  $\int_{R^3} V(\vec{r}) V(\vec{r} + z\vec{e}_z) d\mathbf{v}$  is the common volume of “the crystal shape” and “the phantom body of the crystal shape shifted by  $z$  along the  $z$ -direction” (Fig. 6.7).

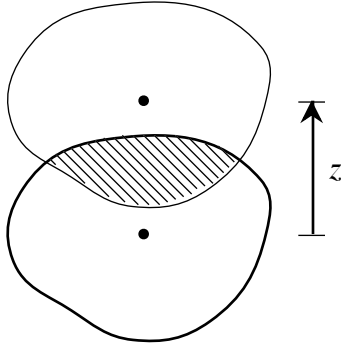


Fig. 6.7 What the formula  $\int_{R^3} V(\vec{r})V(\vec{r} + z\vec{e}_z)dv$  means is the volume of the common region as shown as shaded area in the above illustration.

The above relation provides a method to predict the powder diffraction peak profile affected by the finite size of a crystallite with any shape. What is described in this section is known as the **Stokes-Wilson theory**.

#### 6-4 Powder diffraction peak profile from a small spherical crystallite

In this section, we will restrict our attention to the powder diffraction peak profile of a spherical crystallite. Common volume with the body shifted by  $z$  exists only in the case of  $-D < z < D$  for a spherical crystallite with the diameter of  $D$ . The shape of the common part for the spherical body is same as a “biconvex lens”, as shown as hatched area in Fig. 6.8.

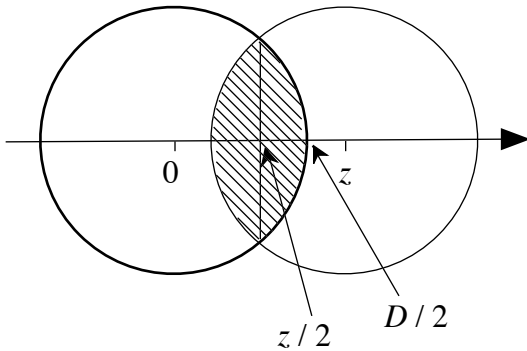


Fig. 6.8 Common part (hatched) of a sphere and a shifted body.

The cross section at the position  $z'$  should be circular, and the area of the circle is given by  $\pi[(D/2)^2 - z'^2]$  in the range  $z/2 < z' < D/2$ . Then the common volume for  $z > 0$  should be

$$\begin{aligned}
 2 \int_{z/2}^{D/2} \pi \left[ \left( \frac{D}{2} \right)^2 - z'^2 \right] dz' &= 2\pi \left[ \frac{D^2 z'}{4} - \frac{z'^3}{3} \right]_{z/2}^{D/2} = 2\pi \left[ \left( \frac{D^3}{8} - \frac{D^2 z}{8} \right) - \left( \frac{D^3}{24} - \frac{z^3}{24} \right) \right] \\
 &= \frac{\pi}{6} \left( D^3 - \frac{3D^2 z}{2} + \frac{z^3}{2} \right) \tag{6.42}
 \end{aligned}$$

and the case of  $z < 0$  can also be included in the following expression,

$$\int_{R^3} V(\vec{r})V(\vec{r} + z\vec{e}_z) d\mathbf{v} = \begin{cases} \frac{\pi}{6} \left( D^3 - \frac{3D^2|z|}{2} + \frac{|z|^3}{2} \right) & [|z| < D] \\ 0 & [|z| \geq D] \end{cases} \quad (6.43)$$

The profile of the above function is shown in Fig. 6.9.

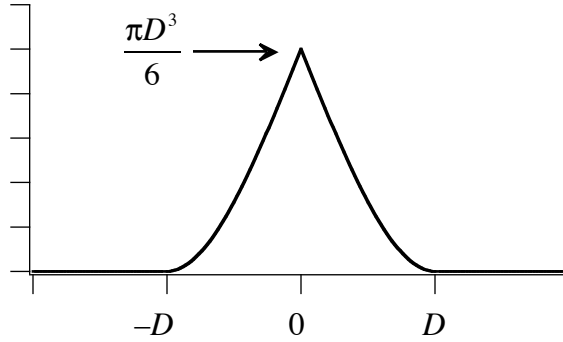


Fig. 6.9 The profile of the function given by Eq. (6.43).

The diffraction peak profile is then given by

$$\begin{aligned} p_{\text{PD}}(k) &\sim \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |H(\vec{k})|^2 dk_x dk_y = \int_{-\infty}^{\infty} \left[ \int_{R^3} V(\vec{r})V(\vec{r} + z\vec{e}_z) d\mathbf{v} \right] e^{2\pi i k z} dz \\ &\stackrel{\text{Eq. (6.37)}}{=} \int_{-D}^D \frac{\pi}{6} \left( D^3 - \frac{3D^2|z|}{2} + \frac{|z|^3}{2} \right) e^{2\pi i k z} dz \\ &\stackrel{\text{symmetry}}{=} \frac{\pi}{3} \int_0^D \left( D^3 - \frac{3D^2z}{2} + \frac{z^3}{2} \right) \cos(2\pi k z) dz \\ &\stackrel{\text{partial integration}}{=} \frac{\pi}{3} \left\{ \left[ \left( D^3 - \frac{3D^2z}{2} + \frac{z^3}{2} \right) \frac{\sin(2\pi k z)}{2\pi k} \right]_0^D - \frac{3}{4\pi k} \int_0^D (-D^2 + z^2) \sin(2\pi k z) dz \right\} \\ &\stackrel{\text{partial integration}}{=} \frac{1}{4k} \left\{ \left[ -(D^2 - z^2) \frac{\cos(2\pi k z)}{2\pi k} \right]_0^D - \frac{1}{\pi k} \int_0^D z \cos(2\pi k z) dz \right\} \\ &\stackrel{\text{partial integration}}{=} \frac{D^2}{8\pi k^2} - \frac{1}{4\pi k^2} \left\{ \left[ \frac{z \sin(2\pi k z)}{2\pi k} \right]_0^D - \frac{1}{2\pi k} \int_0^D \sin(2\pi k z) dz \right\} \\ &= \frac{D^2}{8\pi k^2} - \frac{1}{4\pi k^2} \left\{ \frac{D \sin(2\pi k D)}{2\pi k} - \frac{1}{2\pi k} \left[ -\frac{\cos(2\pi k z)}{2\pi k} \right]_0^D \right\} \\ &= \frac{D^2}{8\pi k^2} - \frac{1}{4\pi k^2} \left[ \frac{D \sin(2\pi k D)}{2\pi k} + \frac{\cos(2\pi k D) - 1}{4\pi^2 k^2} \right] \\ &= \frac{D^2}{8\pi k^2} - \frac{1}{4\pi k^2} \left[ \frac{D \sin(2\pi k D)}{2\pi k} - \frac{\sin^2(\pi k D)}{2\pi^2 k^2} \right] \end{aligned}$$

$$\begin{aligned}
&= \frac{D^2}{8\pi k^2} \left[ 1 - \frac{\sin(2\pi kD)}{\pi kD} + \frac{\sin^2(\pi kD)}{\pi^2 k^2 D^2} \right] \\
&\stackrel{\substack{\uparrow \\ s=2\pi kD}}{=} \frac{\pi D^4}{2s^2} \left[ 1 - \frac{2\sin s}{s} + \frac{4\sin^2(s/2)}{s^2} \right] \tag{6.44}
\end{aligned}$$

where  $s \equiv 2\pi kD$ . In the limit of  $s \rightarrow 0$ , the value of the function should approach to

$$\begin{aligned}
&\frac{\pi D^4}{2s^2} \left[ 1 - \frac{2\sin s}{s} + \frac{4\sin^2(s/2)}{s^2} \right] \\
&= \frac{\pi D^4}{2s^2} \left[ 1 - \frac{2\left(s - s^3/6 + s^5/120 - \dots\right)}{s} + 4\left(\frac{s/2 - s^3/48 + s^5/3840 - \dots}{s}\right)^2 \right] \\
&= \frac{\pi D^4}{2s^2} \left[ 1 - 2\left(1 - \frac{s^2}{6} + \frac{s^4}{120} - \dots\right) + \left(1 - \frac{s^2}{24} + \frac{s^4}{1920} - \dots\right)^2 \right] \\
&= \frac{\pi D^4}{2s^2} \left( 1 - 2 + \frac{s^2}{3} - \frac{s^4}{60} + \dots + 1 + \frac{s^4}{576} + \dots - \frac{s^2}{12} + \frac{s^4}{960} - \dots \right) \\
&= \frac{\pi D^4}{2s^2} \left( \frac{s^2}{4} - \frac{s^4}{72} + \dots \right) \rightarrow \frac{\pi D^4}{8}. \tag{6.45}
\end{aligned}$$

And the area of the peak profile is given by

$$\int_{-\infty}^{\infty} p_{PD}(k) dk \sim \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |H(\vec{k})|^2 dk_x dk_y dk_z = \int_{R^3} V(\vec{r})V(\vec{r}) d\mathbf{v} = \int_{R^3} V(\vec{r}) d\mathbf{v} = \frac{\pi D^3}{6}. \tag{6.46}$$

The diffraction peak profile given by Eq. (6.44) is shown in Fig. 6.10.

The **integral breadth** is defined for an arbitrary peak profile as the width of the rectangle that has the common values of both the height and area of the original peak profile. The integral breadth of the diffraction peak profile caused by the finite size of the crystallite with the diameter of

$D$  is given by  $\frac{\pi D^3/6}{\pi D^4/8} = \frac{4}{3D}$ .

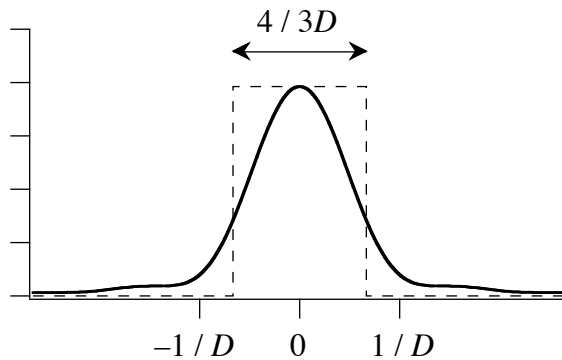


Fig. 6.10 Diffraction peak profile from a spherical crystallite with the diameter of  $D$  (solid line).

The broken line shows the rectangle with the same area and height, the width of which  $4/3D$  is the integral breadth of the peak profile.

## 6-5 Effect of size distribution

The method to derive the powder diffraction peak profile of a collection of crystallites with the common shape and size may have already been described so far. However, the shape and size of crystallites in a realistic powder or polycrystalline sample should always have statistical distribution. And there is no doubt that the realistic powder diffraction peak profile should be affected by the statistical distribution of crystallite size.

Let us assume that the density function of the **size distribution** is expressed by  $f_{SD}(D)$ . As an example, the density function of the “log-normal distribution” is given by

$$f_{SD}(D; m, \omega) = \frac{1}{\sqrt{2\pi\omega D}} \exp\left\{-\frac{[\ln(D/m)]^2}{2\omega^2}\right\}, \quad (6.47)$$

where  $m$  is the median diameter, and  $\omega$  is the logarithmic standard deviation.

The integrated intensity of a diffraction peak from a crystallite is proportional to the volume or  $D^3$ , and the peak-height is proportional to  $D^4$  (because the width is proportional to  $1/D$ ). When we assume the diameter of the  $j$ -th crystallite among  $N$  crystallites to be  $D_j$ , The total diffraction intensity should be proportional to  $\langle D^3 \rangle = \frac{1}{N} \sum_{j=1}^N D_j^3$ , and the peak height should be proportional to

$$\langle D^4 \rangle = \frac{1}{N} \sum_{j=1}^N D_j^4. \quad \text{The diffraction peak profile from a collection of small crystallites should be}$$

varied on the size distribution, but the integral breadth defined as the ratio of the integrated intensity to the peak intensity is still determined by  $\langle D^4 \rangle / \langle D^3 \rangle$ , independent of the size distribution. The ratio of the average of the fourth power of the diameter to the average cubic diameter is called the **volume weighted average diameter**, and defined by the following equation,

$$\langle D \rangle_V \equiv \langle D^4 \rangle / \langle D^3 \rangle. \quad (6.48)$$

When we assume the shape of the crystallites to be spherical, the integral breadth  $B$  on the horizontal scale of the length of the scattering vector  $K$  is given by

$$B = \frac{4}{3\langle D \rangle_V} \quad (6.49)$$

For the wavelength of  $\lambda$  and the diffraction angle  $2\theta$ , the relation :

$$K = \frac{2\sin\theta}{\lambda} \quad (6.50)$$

will give the formula :

$$\Delta K = \frac{2\cos\theta}{\lambda} \Delta\theta = \frac{(\Delta 2\theta)\cos\theta}{\lambda} = \frac{B\cos\theta}{\lambda}, \quad (6.51)$$

and a formula :

$$\langle D \rangle_V = \frac{4\lambda}{3B\cos\theta} \quad (6.52)$$

is derived, where  $B$  is the integral breadth (in rad. unit) on horizontal scale of the diffraction angle  $2\theta$ . We can evaluate the “volume weighted average diameter” from the integral breadth by Eq. (6.52). This equation is the **Scherrer’s equation** for spherical crystallites. In general, the

proportionality factor depends on the shape of the crystallite, though the volume weighted average diameter  $\langle D \rangle_v$  is still proportional to  $\frac{\lambda}{B \cos \theta}$ .

## 6-6 Scherrer's equation

A formula of the Scherrer's equation given by

$$D = \frac{K\lambda}{(\Delta 2\theta)\cos\theta}, \quad (6.53)$$

is often used for evaluation of crystallite size by diffraction line broadening analysis. The proportionality factor  $K$  is called the **Scherrer's constant**, the value of which is often assumed to be  $K = 0.94, 0.89$  or  $0.9$ , and the full-width at half maximum (FWHM) is used instead of the integral breadth. In this text, the value  $K = 0.94$  is referred as the Scherrer's constant and the value  $K = 0.89$  is referred as the Bragg's constant.

It should be noted that the observed peak width is affected by the **instrumental broadening** as well as the broadening caused by the size effect (**size broadening**). It is also often assumed that the size broadening  $B$ , instrumental broadening  $b$  and observed width  $B_{\text{obs}}$  are related by

$$B_{\text{obs}} = B + b, \quad (6.54)$$

even though it is not fully consistent with the assumption about  $K = 0.94$  or  $0.89$ .

Both Scherrer and Bragg have assumed a cubic shape of a crystallite with the edge length of  $D$ , and the diffraction vector directed orthogonal to one of the face of the cube, that is,  $h00, 0k0$  or  $00l$  diffraction peak is assumed. Then the theoretical diffraction peak profile should be the the Laue function given by

$$f_{\text{Laue}}(\Delta k; B) = \frac{\sin^2(\pi\Delta k / B)}{\pi^2(\Delta k)^2 / B}, \quad (6.55)$$

$$\Delta k = \frac{(\Delta 2\theta)\cos\theta}{\lambda}, \quad (6.56)$$

where  $B$  is the integral breadth of the diffraction peak, and it can be related to the edge length of the cube  $D$ , simply by

$$B = \frac{1}{D} \quad (6.57)$$

Note that there is no fractional constants in the above equations. The values of the Scherrer's constant  $K = 0.94$  and Bragg's constant  $K = 0.89$  are both intended to use the FWHM instead of the integral breadth. We can imagine that it was (or may still be) technically easier to evaluate the FWHM than the integral breadth from the observed diffraction peak profile. In the following sections, it will be shown how the values of  $K = 0.94$  and  $K = 0.89$  are derived.

### 6-6-1 Scherrer's constant, $K = 0.94$

Scherrer (1918) approximated the Laue function by the Gaussian function with the equivalent integral breadth, which is given by

$$f_{\text{Gauss}}(k; B) = \frac{1}{B} \exp\left(-\frac{\pi k^2}{B^2}\right) \quad (6.58)$$

As shown in Fig. 6.11, the Laue and Gaussian functions with the common integral breadth certainly show similar profile.

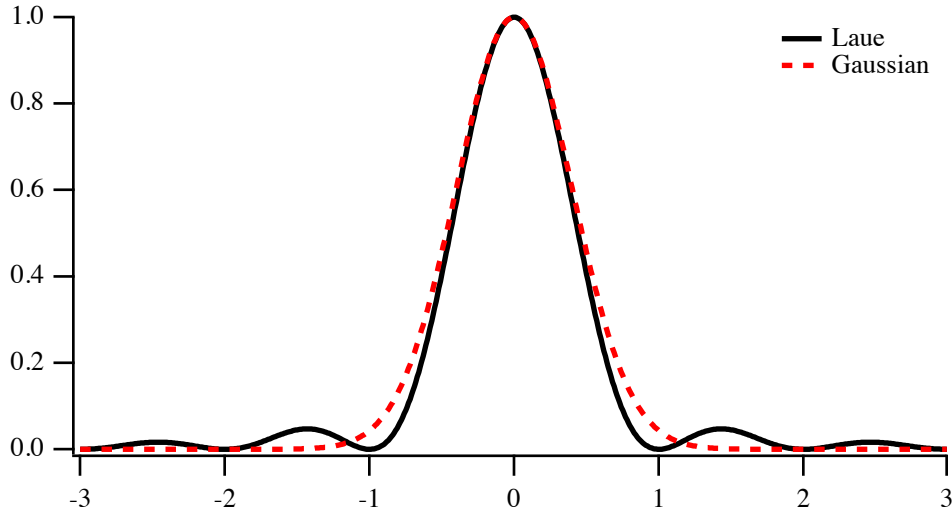


Fig. 6.11 The Laue and Gaussian functions

The FWHM,  $W$ , of the Gaussian function with the integral breadth of  $B$  is exactly given by

$$W = \sqrt{\frac{\ln 2}{\pi}} B, \quad (6.59)$$

while the analytical formula for the FWHM of Laue function is not available. The Gaussian approximation gives the following formula,

$$W = \frac{K\lambda}{D \cos \theta}, \quad (6.60)$$

$$K = 2\sqrt{\frac{\ln 2}{\pi}} = 0.939437\dots \quad (6.61)$$

So the use of the value  $K = 0.94$  implies such assumptions as (i) cubic crystallite shape, (ii)  $h00$ ,  $0k0$  or  $00l$ -reflection, (iii) use of FWHM instead of the integral breadth, and (iv) the Laue function can be approximated by the Gaussian function.

#### 6-6-2 Bragg's constant, $K = 0.89$

Bragg & Bosanquet (1921a, 1921b) have also assumed the Laue function, but derived the solution about the ratio of the FWHM,  $W$ , of the Laue function to the integral breadth  $B$  by numerical calculation,

$$\frac{1}{\sqrt{2}} = \frac{\sin(\pi W / 2B)}{\pi W / 2B} \Leftrightarrow \frac{W}{B} = 0.885892\dots \quad (6.56)$$

So the use of the value  $K = 0.89$  also implies the assumptions: (i) cubic crystallite shape, (ii)  $h00$ ,  $0k0$  or  $00l$ -reflection, and (iii) use of FWHM instead of the integral breadth, but the Laue function is not approximated by the Gaussian function.

The value  $K = 0.9$  has also been used as the Scherrer's constant, probably because it is consistent with both Scherrer's and Bragg's constants within the significant figures. However, it is generally recommended to use the integral breadth of the size broadening extracted from the observed diffraction peak profile.

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