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"Crystal Structure Analysis"
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Chapter 5 Diffraction condition

In Chap. 4, it has been shown that the average structure factor of a crystal is given by the following expressions, even if the thermal vibration of atoms cannot be neglected.

$$\left\langle F_{\text{total}}(\vec{K})\right\rangle = G(\vec{K})F(\vec{K}) \quad \textbf{: average structure factor of a crystal}, \tag{5.1}$$

$$G(\vec{K}) \equiv \sum_{\xi,\eta,\zeta} \exp\left[2\pi \mathrm{i}\,\vec{K}\cdot\left(\xi\vec{a}+\eta\vec{b}+\varsigma\vec{c}\right)\right], \tag{5.2}$$

$$F(\vec{K}) = \sum_{j=1}^{M} f_j(\vec{K})T_j(\vec{K})\exp\left(2\pi \mathrm{i}\,\vec{K}\cdot\left\langle\vec{r}_j\right\rangle\right) \quad \textbf{: crystal structure factor}, \tag{5.3}$$

$$f_j(\vec{K}) \equiv \int_{\mathbf{R}^3} \rho_j(\vec{r})\exp\left(2\pi \mathrm{i}\,\vec{K}\cdot\vec{r}\right)\mathrm{d}v \quad \textbf{: atomic scattering factor}, \tag{5.4}$$

$$T_j(\vec{K}) \equiv \int_{\mathbf{R}^3} g_j(\vec{r})\exp\left(2\pi \mathrm{i}\,\vec{K}\cdot\vec{r}\right)\mathrm{d}v \textbf{: atomic displacement factor}, \tag{5.5}$$

where it is assumed that M atoms are included in a unit structure, and $\rho_j(\vec{r})$ is the electron density of the j-th atom, $g_j(\vec{r})$ is the probability density of the location of the j-th atom around the average position. Note that a simplified expression:

$$\int_{\mathbf{R}^3} \cdots \mathrm{d}v$$

is used instad of

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \cdots \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,,$$

in Eqs. (5.4) & (5.5). The symbol "$\mathbf{R}^3$" means that the function should be integrated over three dimensional real space, and $\mathrm{d}v = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$ means the volume element in the simplified expression.

In this chapter, the diffraction condition given by Eq. (5.2) is discussed. It will be shown that it is almost equivalent to the Bragg's law, though it may look quite different from the expression of the Bragg's equation: $n\lambda = 2d\sin\theta$.

5-1 Laue function & Laue condition

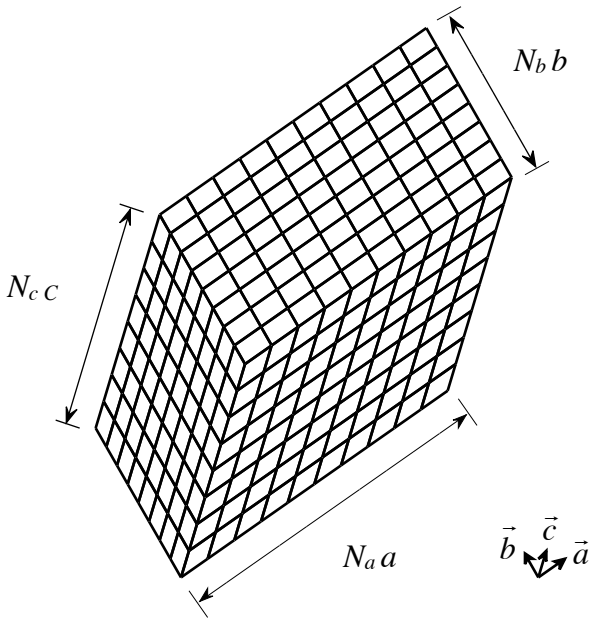

Fig. 5.1 A crystal with parallelepiped shape

Note that the expression of Eq. (5.2) does not fully determine the formula about the diffraction condition $G(\vec{K})$. The concrete formula of $G(\vec{K})$ should depend on the size and shape of the crystal, through the ranges of the subscripts ξ, η, ζ to locate each unit cell.

Assume that the shape of the crystal is parallelepiped with three edges given by the repetition numbers of N_a, N_b, N_c along the unit cell vectors $\vec{a}$, $\vec{b}$, $\vec{c}$, respectively. (It is known that a crystal of sodium chloride NaCl certainly tends to have cubic shape.) In this particular case, we can fully determine the formula of $G(\vec{K})$ by the following equation,

$$G(\vec{K}) = \sum_{\xi=0}^{N_a-1}\sum_{\eta=0}^{N_b-1}\sum_{\zeta=0}^{N_c-1}\exp\left[2\pi\mathrm{i}\,\vec{K}\cdot\left(\xi\vec{a}+\eta\vec{b}+\zeta\vec{c}\right)\right]$$

$$= \sum_{\xi=0}^{N_a-1}\exp\left(2\pi\mathrm{i}\xi\vec{K}\cdot\vec{a}\right)\sum_{\eta=0}^{N_b-1}\exp\left(2\pi\mathrm{i}\eta\vec{K}\cdot\vec{b}\right)\sum_{\zeta=0}^{N_c-1}\exp\left(2\pi\mathrm{i}\zeta\vec{K}\cdot\vec{c}\right). \tag{5.6}$$

It is not difficult to solve the above equation. For example, the sum :

$$\sum_{\xi=0}^{N_a-1}\exp\left(2\pi\mathrm{i}\xi\vec{K}\cdot\vec{a}\right) = 1+\exp\left(2\pi\mathrm{i}\vec{K}\cdot\vec{a}\right)+\exp\left(4\pi\mathrm{i}\vec{K}\cdot\vec{a}\right)+\cdots+\exp\left[2\left(N_a-1\right)\pi\mathrm{i}\vec{K}\cdot\vec{a}\right]$$

is nothing but the sum of a geometric progression with the first term of 1 and common ratio of $\exp\left(2\pi\mathrm{i}\vec{K}\cdot\vec{a}\right)$, and applying the formula :

$$\sum_{j=0}^{n-1}x^j = \frac{1-x^n}{1-x},$$

the solution is given by

$$\sum_{\xi=0}^{N_a-1}\exp\left(2\pi\mathrm{i}\xi\vec{K}\cdot\vec{a}\right) = \frac{\exp\left(2\pi\mathrm{i}N_a\vec{K}\cdot\vec{a}\right)-1}{\exp\left(2\pi\mathrm{i}\vec{K}\cdot\vec{a}\right)-1}. \tag{5.7}$$

As the energy of a wave is proportional to the squared amplitude, the intensity scattered by a crystal is proportional to

$$\left|\left\langle F_{\text{total}}(\vec{K})\right\rangle\right|^2 = \left|G(\vec{K})\right|^2 \left|F(\vec{K})\right|^2 . \tag{5.8}$$

So the intensity should be proportional to the squared absolute value and the formula for intensity is given by

$$\begin{aligned}
&\left|\sum_{\xi=0}^{N_a-1} \exp\left(2\pi \mathrm{i}\,\xi \vec{K}\cdot\vec{a}\right)\right|^2 = \frac{\left|\exp\left(2\pi \mathrm{i}\, N_a \vec{K}\cdot\vec{a}\right)-1\right|^2}{\left|\exp\left(2\pi \mathrm{i}\, \vec{K}\cdot\vec{a}\right)-1\right|^2} \\
&= \frac{\left[\exp\left(-2\pi \mathrm{i}\, N_a \vec{K}\cdot\vec{a}\right)-1\right]\left[\exp\left(2\pi \mathrm{i}\, N_a \vec{K}\cdot\vec{a}\right)-1\right]}{\left[\exp\left(-2\pi \mathrm{i}\, \vec{K}\cdot\vec{a}\right)-1\right]\left[\exp\left(2\pi \mathrm{i}\, \vec{K}\cdot\vec{a}\right)-1\right]} \\
&= \frac{2-2\cos\left(2\pi N_a \vec{K}\cdot\vec{a}\right)}{2-2\cos\left(2\pi \vec{K}\cdot\vec{a}\right)} = \frac{1-\cos\left(2\pi N_a \vec{K}\cdot\vec{a}\right)}{1-\cos\left(2\pi \vec{K}\cdot\vec{a}\right)} = \frac{\sin^2\left(\pi N_a \vec{K}\cdot\vec{a}\right)}{\sin^2\left(\pi \vec{K}\cdot\vec{a}\right)},
\end{aligned} \tag{5.9}$$

for example. Finally, the following formula can be derived,

$$\left|G(\vec{K})\right|^2 = \frac{\sin^2\left(\pi N_a \vec{K}\cdot\vec{a}\right)}{\sin^2\left(\pi \vec{K}\cdot\vec{a}\right)} \frac{\sin^2\left(\pi N_b \vec{K}\cdot\vec{b}\right)}{\sin^2\left(\pi \vec{K}\cdot\vec{b}\right)} \frac{\sin^2\left(\pi N_c \vec{K}\cdot\vec{c}\right)}{\sin^2\left(\pi \vec{K}\cdot\vec{c}\right)} . \tag{5.10}$$

This function is called the **Laue function**.

The Laue function is defined as a three-dimensional function, but the main characteristics of the function can be understood through a one-dimensional part of the function.

What change is expected in the value of $\dfrac{\sin^2\left(\pi N_a \vec{K}\cdot\vec{a}\right)}{\sin^2\left(\pi \vec{K}\cdot\vec{a}\right)}$ on changing the length or direction of the scattering vector $\vec{K}$? The profile of the function is shown in Fig. 5.2, where $\vec{K}\cdot\vec{a}$ is taken as the horizontal axis. Main peak(s) of the function are located at $\vec{K}\cdot\vec{a} = h$ (h : integer), the intensity becomes zero at $\pm 1/N_a$, $\pm 2/N_a$, $\pm 3/N_a$, ..., and small sub-peaks are located between them. The height of the main peak is given by N_a^2 , that is,

$$\lim_{x\to 0} \frac{\sin^2\left(\pi N_a x\right)}{\sin^2\left(\pi x\right)} = N_a^2 \lim_{x\to 0}\left[\frac{\sin\left(\pi N_a x\right)}{\pi N_a x}\right]^2 \left[\frac{\pi x}{\sin\left(\pi x\right)}\right]^2 = N_a^2 \tag{5.11}$$

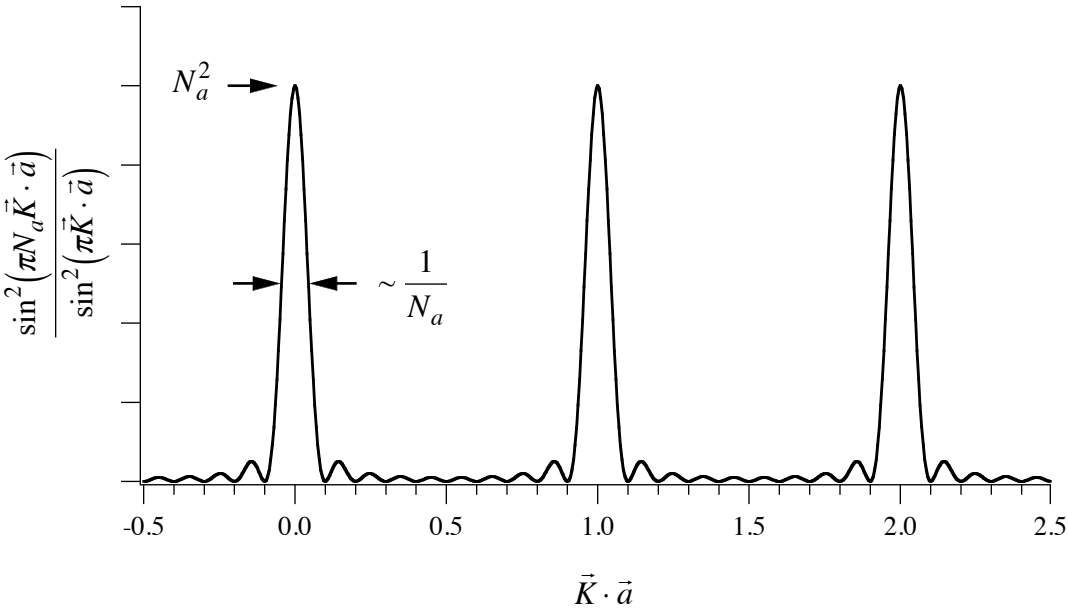

Fig. 5.2 Laue function $\dfrac{\sin^2\left(\pi N_a \vec{K}\cdot\vec{a}\right)}{\sin^2\left(\pi \vec{K}\cdot\vec{a}\right)}$ for the case $N_a = 10$

and the full width at the half maximum is about $1/N_a$. On increasing the value of N_a, the height of the main peak becomes higher, and the width becomes narrower. For the case of $N_a = 10$, the height of the main peak is $N_a^2 = 100$, while the height of the 1st sub-peak is about

$$\frac{\sin^2\left[\pi N_a\left(3/2N_a\right)\right]}{\sin^2\left[\pi\left(3/2N_a\right)\right]} = \frac{1}{\sin^2\left[\pi\left(3/2N_a\right)\right]} = 4.85\,,$$

and the height of the 2nd sub-peak is about

$$\frac{\sin^2\left[\pi N_a\left(5/2N_a\right)\right]}{\sin^2\left[\pi\left(5/2N_a\right)\right]} = \frac{1}{\sin^2\left[\pi\left(5/2N_a\right)\right]} = 2.00\,,$$

... and so on, and we can expect all of the intensities of the small sub-peaks become negligible for large number of N_a, typically about $10^3 \sim 10^5$. In the case of an ordinary crystal, which has large values of N_a, N_b, N_c, the Laue function in Eq. (5.10) returns significant values, only when

$$\begin{cases} \vec{K}\cdot\vec{a} = h \\ \vec{K}\cdot\vec{b} = k \\ \vec{K}\cdot\vec{c} = l \end{cases} \qquad (h, k, l : \text{integer}) \tag{5.12}$$

and the maximum value should be given by

$$\left|G(\vec{K})\right|^2 \to \left(N_a N_b N_c\right)^2 = N^2 \tag{5.13}$$

The value $N_a N_b N_c = N$ is the total number of unit cells in the crystal. Since the width of the peak is proportional to $1/N$, the integrated intensity should be proportional to N, as expected. The condition given by Eq. (5.12) is called the **Laue condition**.

An approximate formula for the Laue function for the range near one of the maxima is given by

$$\left|G\left(K+\Delta K\right)\right|^2=\frac{\sin^2\left[\pi N_a\left(K+\Delta K\right)a\right]}{\sin^2\left[\pi\left(K+\Delta K\right)a\right]\left(\pi Ka\right)}=\frac{\sin^2\left(\pi N_a h+\pi N_a\Delta Ka\right)}{\sin^2\left(\pi h+\pi\Delta Ka\right)}$$

$$=\frac{\sin^2\left(\pi N_a\Delta Ka\right)}{\sin^2\left(\pi\Delta Ka\right)}=\frac{\sin^2\left(\pi\Delta KD\right)}{\sin^2\left(\pi\Delta KD/N_a\right)}\xrightarrow[N_a\to\infty]{}\frac{N_a^2\sin^2\left(\pi\Delta KD\right)}{\pi^2\left(\Delta K\right)^2D^2},$$

where $D=N_a a$ is the dimension of the crystal along the a-direction.

Another formula :

$$f_{Laue}\left(\Delta K\right)=\frac{\sin^2\left(\pi\Delta KD\right)}{\pi^2\left(\Delta K\right)^2D}, \tag{5.14}$$

satisfying the normalization condition:

$$\int_{-\infty}^{\infty}f_{Laue}\left(\Delta K\right)\mathrm{d}\left(\Delta K\right)=1,$$

may sometimes be more convenient. The peak-top value of the normalized formula is given by $\lim_{\Delta K\to 0}f_{Laue}\left(\Delta K\right)=D$.

The formula given by (5.14) is also called the Laue function. The relation between the scattering vector and scattering angle :

$$K=\frac{2\sin\theta}{\lambda}$$

leads the following relation

$$\Delta K=\frac{\left(\Delta 2\theta\right)\cos\theta}{\lambda},$$

which will be discussed again in Chap. 6.

5-2 Lattice vectors and reciprocal lattice vectors

The three vectors, $\vec{a}$, $\vec{b}$, $\vec{c}$, to represent the periodicity of the crystal are called the **lattice vectors** or the **unit translational vectors**. The three vectors, $\vec{a}^*$, $\vec{b}^*$, $\vec{c}^*$, defined by the following equations are called the **reciprocal lattice vectors**.

$$\begin{array}{lll}\vec{a}\cdot\vec{a}^*=1 & \vec{a}\cdot\vec{b}^*=0 & \vec{a}\cdot\vec{c}^*=0\\ \vec{b}\cdot\vec{a}^*=0 & \vec{b}\cdot\vec{b}^*=1 & \vec{b}\cdot\vec{c}^*=0\\ \vec{c}\cdot\vec{a}^*=0 & \vec{c}\cdot\vec{b}^*=0 & \vec{c}\cdot\vec{c}^*=1\end{array} \tag{5.15}$$

The vector $\vec{a}^*$ is perpendicular to $\vec{b}$ and $\vec{c}$, and the inner product with $\vec{a}$ is 1, for example. By using the reciprocal lattice vectors, the Laue condition defined by Eq. (5.12) is exactly equivalent to that the scattering vector $\vec{K}$ can be expressed by

$$\vec{K}=h\vec{a}^*+k\vec{b}^*+l\vec{c}^* \qquad (h,\ k,\ l:\text{integer}). \tag{5.16}$$

When we assume that the x, y, z components of the lattice vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ and the reciprocal lattice vectors $\vec{a}^*$, $\vec{b}^*$, $\vec{c}^*$ are given by

$$\vec{a}=\begin{pmatrix}a_x\\a_y\\a_z\end{pmatrix},\ \vec{b}=\begin{pmatrix}b_x\\b_y\\b_z\end{pmatrix},\ \vec{c}=\begin{pmatrix}c_x\\c_y\\c_z\end{pmatrix}, \tag{5.17}$$

$$\vec{a}^* = \begin{pmatrix} a_x^* \\ a_y^* \\ a_z^* \end{pmatrix},\ \vec{b}^* = \begin{pmatrix} b_x^* \\ b_y^* \\ b_z^* \end{pmatrix},\ \vec{c}^* = \begin{pmatrix} c_x^* \\ c_y^* \\ c_z^* \end{pmatrix}, \tag{5.18}$$

The relation given by Eq. (5.15) is equivalent with the following equation,

$$\begin{pmatrix} a_x^* & a_y^* & a_z^* \\ b_x^* & b_y^* & b_z^* \\ c_x^* & c_y^* & c_z^* \end{pmatrix}\begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{5.19}$$

which means the **inverse matrix** of the matrix defined by the reciprocal lattice vector $\begin{pmatrix} \vec{a} & \vec{b} & \vec{c} \end{pmatrix}$ is equivalent with the **transposed matrix** of the matrix defined by the lattice vectors $\begin{pmatrix} \vec{a}^* & \vec{b}^* & \vec{c}^* \end{pmatrix}$.

The **outer product** $\vec{p}\times\vec{q}$ for arbitrary two three-dimensional vectors $\vec{p} = \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix},\ \vec{q} = \begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix}$ is defined by

$$\vec{p}\times\vec{q} \equiv \begin{pmatrix} p_y q_z - p_z q_y \\ p_z q_x - p_x q_z \\ p_x q_y - p_y q_x \end{pmatrix}. \tag{5.20}$$

From the definition, we obtain

$$\vec{p}\cdot\left(\vec{p}\times\vec{q}\right) = p_x\left(p_y q_z - p_z q_y\right) + p_y\left(p_z q_x - p_x q_z\right) + p_z\left(p_x q_y - p_y q_x\right) = 0, \tag{5.21}$$

$$\vec{q}\cdot\left(\vec{p}\times\vec{q}\right) = q_x\left(p_y q_z - p_z q_y\right) + q_y\left(p_z q_x - p_x q_z\right) + q_z\left(p_x q_y - p_y q_x\right) = 0, \tag{5.22}$$

and can confirm that the vector $\vec{p}\times\vec{q}$ is perpendicular to both $\vec{p}$ and $\vec{q}$. By comparing the following three equations,

$$\begin{aligned} &\left|\vec{p}\right|^2\left|\vec{q}\right|^2 = \left(p_x^2 + p_y^2 + p_z^2\right)\left(q_x^2 + q_y^2 + q_z^2\right) \\ &= p_x^2 q_x^2 + p_x^2 q_y^2 + p_x^2 q_z^2 + p_y^2 q_x^2 + p_y^2 q_y^2 + p_z^2 q_z^2 + p_z^2 q_x^2 + p_z^2 q_y^2 + p_z^2 q_z^2, \end{aligned} \tag{5.23}$$

$$\begin{aligned} &\left(\vec{p}\cdot\vec{q}\right)^2 = \left(p_x q_x + p_y q_y + p_z q_z\right)^2, \\ &= p_x^2 q_x^2 + p_y^2 q_y^2 + p_z^2 q_z^2 + 2p_x q_x p_y q_y + 2p_y q_y p_z q_z + 2p_z q_z p_x q_x \end{aligned} \tag{5.24}$$

$$\begin{aligned} &\left|\vec{p}\times\vec{q}\right|^2 = \left(p_y q_z - p_z q_y\right)^2 + \left(p_z q_x - p_x q_z\right)^2 + \left(p_x q_y - p_y q_x\right)^2 \\ &= p_y^2 q_z^2 + 2p_y q_z p_z q_y + p_z^2 q_y^2 + p_z^2 q_x^2 - 2p_z q_x p_x q_z + p_x^2 q_z^2 + p_x^2 q_y^2 - 2p_x q_y p_y q_x + p_y^2 q_x^2 \end{aligned} \tag{5.25}$$

we obtain

$$\left|\vec{p}\right|^2\left|\vec{q}\right|^2 = \left(\vec{p}\cdot\vec{q}\right)^2 + \left|\vec{p}\times\vec{q}\right|^2. \tag{5.26}$$

When the angle between the vectors $\vec{p}$ and $\vec{q}$ is θ, that is, $\vec{p}\cdot\vec{q} = \left|\vec{p}\right|\left|\vec{q}\right|\cos\theta$, the following relation is derived,

$$\left|\vec{p}\times\vec{q}\right| = \sqrt{\left|\vec{p}\right|^2\left|\vec{q}\right|^2 - \left|\vec{p}\right|^2\left|\vec{q}\right|^2\cos^2\theta} = \left|\vec{p}\right|\left|\vec{q}\right|\sin\theta\,, \tag{5.27}$$

that is, $\vec{p}\times\vec{q}$ is the vector perpendicular to $\vec{p}$ and $\vec{q}$ [Eq. (5.21), Eq. (5.22)] having the length of $\left|\vec{p}\right|\left|\vec{q}\right|\sin\theta$ [Eq. (5.27)].

The parallelepiped defined by the lattice vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ is traditionally called the **unit cell** in the field of crystallography.

The outer product $\vec{a}\times\vec{b}$ is the vector orthogonal to $\vec{a}$ and $\vec{b}$, having the length equal to the "area of the parallelogram" formed by $\vec{a}$ and $\vec{b}$. As $\dfrac{\vec{a}\times\vec{b}}{\left|\vec{a}\times\vec{b}\right|}$ is the vector perpendicular to $\vec{a}$ and $\vec{b}$, having the length of unity, $\dfrac{\left(\vec{a}\times\vec{b}\right)\cdot\vec{c}}{\left|\vec{a}\times\vec{b}\right|}$ is the length of projection of $\vec{c}$ on to the direction perpendicular to $\vec{a}$ and $\vec{b}$. The the unit cell volume is given by $V = \left(\vec{a}\times\vec{b}\right)\cdot\vec{c}$. Similar relations hold for the combination of ($\vec{b}$ and $\vec{c}$) and ($\vec{c}$ and $\vec{a}$), as summarized by

$$V = \left(\vec{a}\times\vec{b}\right)\cdot\vec{c} = \left(\vec{b}\times\vec{c}\right)\cdot\vec{a} = \left(\vec{c}\times\vec{a}\right)\cdot\vec{b}\,. \tag{5.28}$$

The following relations between the lattice vectors and the reciprocal lattice vectors are also satisfied,

$$\vec{a}^{\,*} = \frac{\vec{b}\times\vec{c}}{V}\,, \tag{5.29}$$

$$\vec{b}^{\,*} = \frac{\vec{c}\times\vec{a}}{V}\,, \tag{5.30}$$

$$\vec{c}^{\,*} = \frac{\vec{a}\times\vec{b}}{V}\,, \tag{5.31}$$

and the reciprocal lattice vector can be calculated from the lattice vectors by the above equations. It is not necessary to use the above formula on evaluation of the reciprocal lattice vectors. All we should do is evaluation of the 3-by-3 inverse matrix. But the coding (computer programming) based on Eqs. (5.29) - (5.31) is recommendable because of unambiguity and efficiency on realistic computing.

5-3 Lattice constants

The relations between the lattice constants a, b, c, α, β, γ and the lattice vectors $\vec{a}$, $\vec{b}$, $\vec{c}$ are following,

a : length of $\vec{a}$

b : length of $\vec{b}$

c : length of $\vec{c}$

α : angle between $\vec{b}$ and $\vec{c}$

β : angle between $\vec{c}$ and $\vec{a}$

γ : angle between $\vec{a}$ and $\vec{b}$

It is easy to evaluate the lattice constants $(a,b,c,\alpha,\beta,\gamma)$ from the components of the lattice vectors $(a_x,a_y,a_z,b_x,b_y,b_z,c_x,c_y,c_z)$,

$$a=|\vec{a}|=\sqrt{a_x^2+a_y^2+a_z^2}\ ,$$

$$\cos\alpha=\frac{\vec{b}\cdot\vec{c}}{bc}=\frac{b_xc_x+b_yc_y+b_zc_z}{\sqrt{\left(b_x^2+b_y^2+b_z^2\right)\left(c_x^2+c_y^2+c_z^2\right)}}$$

for example.

In contrast, it is a little complicated to evaluate the lattice vectors from the lattice constants, partly because of arbitrariness about the choice of direction of the coordinate system.

One unambiguous selection of the coordinate system is,

(i) assume $\vec{a}$ parallel to the X axis

(ii) assume $\vec{b}$ is on the upper XY plane (Y > 0).

In this case, it is easy to find that the lattice vector $\vec{a}$ should be

$$\vec{a}=\begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix} \tag{5.32}$$

and the lattice vector $\vec{b}$ should be given by

$$\vec{b}=\begin{pmatrix} b\cos\gamma \\ b\sin\gamma \\ 0 \end{pmatrix}. \tag{5.33}$$

It is assumed that the lattice vector $\vec{c}$ is given by

$$\vec{c}=\begin{pmatrix} c_x \\ c_y \\ c_z \end{pmatrix}. \tag{5.34}$$

The condition : "the angle between $\vec{c}$ and $\vec{a}$ is β" is expressed by

$$\vec{c}\cdot\vec{a}=ca\cos\beta\ , \tag{5.35}$$

and the following relation is derived from Eqs. (5.32) and (5.34),

$$\vec{c}\cdot\vec{a}=c_xa+c_y0+c_z0=c_xa\ . \tag{5.36}$$

Then, from Eq. (5.35), the *x*-component of the lattice vector $\vec{c}$ is determined by

$$c_x=c\cos\beta\ . \tag{5.37}$$

Next, the relation : "the angle between $\vec{b}$ and $\vec{c}$ is α" gives

$$\vec{b}\cdot\vec{c}=bc\cos\alpha\ , \tag{5.38}$$

and from Eqs. (5.33) and (5.34) ,

$$\vec{b}\cdot\vec{c}=bc_x\cos\gamma+bc_y\sin\gamma$$

$$=b\left(c\cos\beta\cos\gamma+c_y\sin\gamma\right), \tag{5.39}$$

and then

$$c_y = \frac{c\left(\cos\alpha - \cos\beta\cos\gamma\right)}{\sin\gamma}. \tag{5.40}$$

Finally, the condition : "the length of $\vec{c}$ is c" determines the z-component c_z of the lattice vector $\vec{c}$ by

$$c_z = \sqrt{c^2 - c_x^2 - c_y^2} \tag{5.41}$$

The coordinates derived by this method belongs to the "right-handed system".

The unit cell volume V can be calculated from the components of the lattice vectors determined in the above way, simply by

$$V = a_x b_y c_z \tag{5.42}$$

The components of the reciprocal lattice vectors can be calculated by

$$\vec{a}^* = \begin{pmatrix} a_x^* \\ a_y^* \\ a_z^* \end{pmatrix} = \frac{\vec{b}\times\vec{c}}{V} = \frac{1}{V}\begin{pmatrix} b_y c_z - b_z c_y \\ b_z c_x - b_x c_z \\ b_x c_y - b_y c_x \end{pmatrix},$$

and so on.

5-4 Lattice plane

The Laue condition restricts the appearance of sharp diffraction peaks for the scattering (diffraction) vector $\vec{K}$ to satisfy $\vec{K} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$ (h, k, l : integer). On the other hand, the vector defined by

$$\vec{d}_{hkl}^* \equiv h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \tag{5.43}$$

means the vector with the length of reciprocal interplanar spacing along the direction orthogonal to the lattice plane indexed by h, k, l (hkl-plane). The index hkl is called **Miller index**.

The orthogonal direction and interplanar spacing of the hkl-plane are equivalent with the orthogonal direction of a flat plane passing through the three points defined by the three vectors $\frac{\vec{a}}{h}$, $\frac{\vec{b}}{k}$, $\frac{\vec{c}}{l}$ (for $h \neq 0$, $k \neq 0$, $l \neq 0$), and the distance of the plane from the origin, respectively. The vector $\vec{p}$ locating an arbitrary point on this plane is expressed by

$$\vec{p} = \frac{\vec{a}}{h} + x\left(\frac{\vec{b}}{k} - \frac{\vec{a}}{h}\right) + y\left(\frac{\vec{c}}{l} - \frac{\vec{a}}{h}\right) \qquad (x, y : \text{arbitrary real number}), \tag{5.44}$$

and the plane that is parallel to the above plane and passes through the origin should be expressed by

$$\vec{p}_0 = x_0\left(\frac{\vec{b}}{k} - \frac{\vec{a}}{h}\right) + y_0\left(\frac{\vec{c}}{l} - \frac{\vec{a}}{h}\right) \qquad (x_0, y_0 : \text{arbitrary real number}). \tag{5.45}$$

Examine the inner product of the vectors $\vec{p}_0$ and $\vec{d}_{hkl}^*$, defined by Eq. (5.45) and Eq. (5.43). You will find that the relation: $\vec{p}_0 \cdot \vec{d}_{hkl}^* = 0$ is always satisfied for any x_0, y_0. It means that the vector

$\vec{d}^*_{hkl}$ is directed along the orthogonal direction of the (hkl) plane. The interplanar spacing should be given by the inner product of $\vec{p}$ and $\frac{\vec{d}^*_{hkl}}{\left|\vec{d}^*_{hkl}\right|}$. As the relation: $\vec{p}\cdot\vec{d}^*_{hkl}=1$ holds for any x and y, we can conclude that the interplanar spacing is equivalent to $\frac{1}{\left|\vec{d}^*_{hkl}\right|}$.

Next, let us examine the case of $l=0$. The $hk0$ -plane means that it passes through the two points $\frac{\vec{a}}{h}$ and $\frac{\vec{b}}{k}$, and is parallel to $\vec{c}$. The vector $\vec{p}$ to express this plane is given by

$$\vec{p}=\frac{\vec{a}}{h}+x\left(\frac{\vec{b}}{k}-\frac{\vec{a}}{h}\right)+y\vec{c} \qquad (x, y : \text{arbitrary real number}) \tag{5.46}$$

and the plane that is parallel to the above and passes through the origin is given by

$$\vec{p}_0=x_0\left(\frac{\vec{b}}{k}-\frac{\vec{a}}{h}\right)+y_0\vec{c} \qquad (x_0, y_0 : \text{arbitrary real number}), \tag{5.47}$$

and the relations : $\vec{p}_0\cdot\vec{d}^*_{hkl}=0$ and $\vec{p}\cdot\vec{d}^*_{hkl}=1$ are satisfied. The situation will exactly be same for the case of $k=0$ or $h=0$.

Finally, examine the case of $k=l=0$. The $h00$ -plane passes through $\frac{\vec{a}}{h}$, and is parallel to both $\vec{b}$ and $\vec{c}$. The vector $\vec{p}$ to express this plane is given by

$$\vec{p}=\frac{\vec{a}}{h}+x\vec{b}+y\vec{c} \qquad (x, y : \text{arbitrary real number}), \tag{5.48}$$

and the parallel plane passing through the origin is given by

$$\vec{p}_0=x_0\vec{b}+y_0\vec{c} \qquad (x_0, y_0 : \text{arbitrary real number}), \tag{5.49}$$

and you will find the relations $\vec{p}_0\cdot\vec{d}^*_{hkl}=0$ and $\vec{p}\cdot\vec{d}^*_{hkl}=1$ again. Of course, the situation about the case of $h=l=0$ or $h=k=0$ will be similar.

We can conclude that the length of the vector $\vec{d}^*_{hkl}$ is always equal to the reciprocal of the interplanar spacing of the hkl -plane.

If all the components $(a^*_x, a^*_y, a^*_z, b^*_x, b^*_y, b^*_z, c^*_x, c^*_y, c^*_z)$ of the reciprocal lattice vectors $\vec{a}^*$, $\vec{b}^*$, $\vec{c}^*$ are given, the reciprocal interplanar distance of the hkl -plane can be calculated by

$$d^*_{hkl}=\left|\vec{d}^*_{hkl}\right|=\sqrt{\left(ha^*_x+kb^*_x+lc^*_x\right)^2+\left(ha^*_y+kb^*_y+lc^*_y\right)^2+\left(ha^*_z+kb^*_z+lc^*_z\right)^2}\,. \tag{5.50}$$

Note that the interplanar distance d_{hkl} of the lattice plane in the Bragg's law is generally calculated as the " reciprocal of the 'reciprocal interplanar distance d^*_{hkl}' ".

5-5 Crystal structure factor and Miller indices

The average position of the j-th atom in the unit cell $\left\langle\vec{r}_j\right\rangle$ is expressed by

$$\left\langle\vec{r}_j\right\rangle=x_j\vec{a}+y_j\vec{b}+z_j\vec{c} \tag{5.51}$$

where x_j , y_j , z_j are the **fractional coordinate** having values from 0 to 1. As the diffraction peak only appears when the scattering vector $\vec{K}$ is given by $\vec{K} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$ (h, k, l : integer), the crystal structure factor denoted by $F(\vec{K})$ so far, can be expressed by

$$F_{hkl} = \sum_{j=1}^{M} f_j\left(\vec{d}^*_{hkl}\right) T_j\left(\vec{d}^*_{hkl}\right) \exp\left[2\pi \mathrm{i}\left(hx_j + ky_j + lz_j\right)\right] \tag{5.52}$$

where

$\vec{d}^*_{hkl} \equiv h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$.

Here $f_j\left(\vec{d}^*_{hkl}\right)$ is the atomic scattering factor, and it depends only on the interplanar distance $d_{hkl} = \dfrac{1}{\left|\vec{d}^*_{hkl}\right|}$, when the electron density distribution of the atom is assumed to have spherical symmetry. The atomic scattering factor can be expressed by $f_j\left(\dfrac{\sin\theta_{hkl}}{\lambda}\right)$, using the Bragg angle θ_{hkl} satisfying the Bragg's equation, $\lambda = 2d_{hkl}\sin\theta_{hkl}$.

And $T_j\left(\vec{d}^*_{hkl}\right)$ is the atomic displacement factor, generally representing anisotropic displacement of an atom from the average position.

5-6 Anisotropic atomic displacement factor

The probability density function about the displacement of an atom from the average position can be modeled by

$$g_j(\vec{r}) = \frac{1}{(2\pi)^{3/2} U_1^{1/2} U_2^{1/2} U_3^{1/2}} \exp\left(-\frac{X^2}{2U_1} - \frac{Y^2}{2U_2} - \frac{Z^2}{2U_3}\right), \tag{5.53}$$

where it is assumed that the displacement of the atom is expressed by the anisotropic (ellipsoidal) Gaussian function, and the vector locating the atomic position $\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$ is expressed by

$$\vec{r} = X\vec{p}_X + Y\vec{p}_Y + Z\vec{p}_Z \,, \tag{5.54}$$

using the unit vectors along the three principal axes of the ellipsoid,

$$\vec{p}_X = \begin{pmatrix} p_{Xx} \\ p_{Xy} \\ p_{Xz} \end{pmatrix},\ \vec{p}_Y = \begin{pmatrix} p_{Yx} \\ p_{Yy} \\ p_{Yz} \end{pmatrix},\ \vec{p}_Z = \begin{pmatrix} p_{Zx} \\ p_{Zy} \\ p_{Zz} \end{pmatrix}.$$

The probability density function about the atomic displacement given by Eq. (5.53) corresponds to the modeling of thermal vibration of atoms by independent harmonic oscillators. The relation given by Eq. (5.54) is rewritten by using a matrix

$$\mathbf{P} = \begin{pmatrix} \vec{p}_X & \vec{p}_Y & \vec{p}_Z \end{pmatrix} = \begin{pmatrix} p_{Xx} & p_{Yx} & p_{Zx} \\ p_{Xy} & p_{Yy} & p_{Zy} \\ p_{Xz} & p_{Yz} & p_{Zz} \end{pmatrix}, \tag{5.55}$$

as

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \mathbf{P}\begin{pmatrix} X \\ Y \\ Z \end{pmatrix}. \tag{5.56}$$

The matrix $\mathbf{P}$ is an **orthogonal matrix**, the **transpose matrix** of which is equivalent to the **inverse matrix**, that is,

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \mathbf{P}^{-1}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \mathbf{P}^{t}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} P_{Xx} & P_{Xy} & P_{Xz} \\ P_{Yx} & P_{Yy} & P_{Yz} \\ P_{Zx} & P_{Zy} & P_{Zz} \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{5.57}$$

The atomic displacement factor based on the probability distribution of atomic displacement shown in Eq. (5.53) is given by

$$\begin{aligned} T_j(\vec{K}) &= \int_{R^3} g_j(\vec{r})\exp\left(2\pi \mathrm{i}\,\vec{K}\cdot\vec{r}\right)\mathrm{d}v \\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} g_j(\vec{r})\exp\left(2\pi \mathrm{i}\,\vec{K}\cdot\vec{r}\right)\mathrm{d}X\,\mathrm{d}Y\,\mathrm{d}Z \\ &= \frac{1}{(2\pi)^{3/2}U_1^{1/2}U_2^{1/2}U_3^{1/2}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left(-\frac{X^2}{2U_1}-\frac{Y^2}{2U_2}-\frac{Z^2}{2U_3}\right)\exp\left[2\pi \mathrm{i}\left(K_X X + K_Y Y + K_z Z\right)\right] \\ &\qquad \times \mathrm{d}X\,\mathrm{d}Y\,\mathrm{d}Z \\ &= \exp\left[-2\pi^2\left(K_X^2 U_1 + K_Y^2 U_2 + K_Z^2 U_3\right)\right] \\ &= \exp\left[-2\pi^2\begin{pmatrix} K_X & K_Y & K_Z \end{pmatrix}\begin{pmatrix} U_1 & 0 & 0 \\ 0 & U_2 & 0 \\ 0 & 0 & U_3 \end{pmatrix}\begin{pmatrix} K_X \\ K_Y \\ K_Z \end{pmatrix}\right] \\ &= \exp\left[-2\pi^2\begin{pmatrix} K_x & K_y & K_z \end{pmatrix}\mathbf{P}\begin{pmatrix} U_1 & 0 & 0 \\ 0 & U_2 & 0 \\ 0 & 0 & U_3 \end{pmatrix}\mathbf{P}^{t}\begin{pmatrix} K_x \\ K_y \\ K_z \end{pmatrix}\right]. \end{aligned}$$

When we define a matrix,

$$\mathbf{U} = \begin{pmatrix} U_{xx} & U_{xy} & U_{xz} \\ U_{yx} & U_{yy} & U_{yz} \\ U_{zx} & U_{zy} & U_{zz} \end{pmatrix} \equiv \mathbf{P}\begin{pmatrix} U_1 & 0 & 0 \\ 0 & U_2 & 0 \\ 0 & 0 & U_3 \end{pmatrix}\mathbf{P}^{t},$$

the atomic displacement factor of the *j*-th atom is given by

$$\begin{aligned} T_j(\vec{K}) &= \exp\left[-2\pi^2\begin{pmatrix} K_x & K_y & K_z \end{pmatrix}\mathbf{U}_j\begin{pmatrix} K_x \\ K_y \\ K_z \end{pmatrix}\right] \\ &= \exp\left(-2\pi^2\vec{K}^{t}\mathbf{U}_j\vec{K}\right), \end{aligned} \tag{5.58}$$

and the expansion results in the following formula,

$$T_j(\vec{K}) = \exp\left[-2\pi^2 \begin{pmatrix} K_x & K_y & K_z \end{pmatrix} \begin{pmatrix} (U_{xx})_j & (U_{xy})_j & (U_{zx})_j \\ (U_{xy})_j & (U_{yy})_j & (U_{yz})_j \\ (U_{zx})_j & (U_{yz})_j & (U_{zz})_j \end{pmatrix} \begin{pmatrix} K_x \\ K_y \\ K_z \end{pmatrix}\right]$$

$$= \exp\left\{-2\pi^2 \left[\left((U_{xx})_j K_x^2 + (U_{yy})_j K_y^2 + (U_{zz})_j K_z^2 \right.\right.\right.$$

$$\left.\left.\left. +2(U_{xy})_j K_x K_y + 2(U_{yz})_j K_y K_z + 2(U_{zx})_j K_z K_x \right]\right\}. \qquad (5.59)$$

Define the matrix

$$\begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{12} & U_{22} & U_{23} \\ U_{13} & U_{23} & U_{33} \end{pmatrix}$$

$$= \begin{pmatrix} a_x^*/a^* & a_y^*/a^* & a_z^*/a^* \\ b_x^*/b^* & b_y^*/b^* & b_z^*/b^* \\ c_x^*/c^* & c_y^*/c^* & c_z^*/c^* \end{pmatrix} \begin{pmatrix} U_{xx} & U_{xy} & U_{zx} \\ U_{xy} & U_{yy} & U_{yz} \\ U_{zx} & U_{yz} & U_{zz} \end{pmatrix} \begin{pmatrix} a_x^*/a^* & b_x^*/b^* & c_x^*/c^* \\ a_y^*/a^* & b_y^*/b^* & c_y^*/c^* \\ a_z^*/a^* & b_z^*/b^* & c_z^*/c^* \end{pmatrix}$$

$$= \begin{pmatrix} \frac{1}{a^*} & 0 & 0 \\ 0 & \frac{1}{b^*} & 0 \\ 0 & 0 & \frac{1}{c^*} \end{pmatrix} \begin{pmatrix} a_x^* & a_y^* & a_z^* \\ b_x^* & b_y^* & b_z^* \\ c_x^* & c_y^* & c_z^* \end{pmatrix} \begin{pmatrix} U_{xx} & U_{xy} & U_{zx} \\ U_{xy} & U_{yy} & U_{yz} \\ U_{zx} & U_{yz} & U_{zz} \end{pmatrix} \begin{pmatrix} a_x^* & b_x^* & c_x^* \\ a_y^* & b_y^* & c_y^* \\ a_z^* & b_z^* & c_z^* \end{pmatrix} \begin{pmatrix} \frac{1}{a^*} & 0 & 0 \\ 0 & \frac{1}{b^*} & 0 \\ 0 & 0 & \frac{1}{c^*} \end{pmatrix}, \qquad (5.60)$$

and the following relation will be derived,

$$\begin{pmatrix} U_{xx} & U_{xy} & U_{zx} \\ U_{xy} & U_{yy} & U_{yz} \\ U_{zx} & U_{yz} & U_{zz} \end{pmatrix}$$

$$= \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix} \begin{pmatrix} a^* & 0 & 0 \\ 0 & b^* & 0 \\ 0 & 0 & c^* \end{pmatrix} \begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{12} & U_{22} & U_{23} \\ U_{13} & U_{23} & U_{33} \end{pmatrix} \begin{pmatrix} a^* & 0 & 0 \\ 0 & b^* & 0 \\ 0 & 0 & c^* \end{pmatrix} \begin{pmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{pmatrix}$$

$$= \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix} \begin{pmatrix} U_{11}a^{*2} & U_{12}a^*b^* & U_{13}a^*c^* \\ U_{12}a^*b^* & U_{22}b^{*2} & U_{23}b^*c^* \\ U_{13}a^*c^* & U_{23}b^*c^* & U_{33}c^{*2} \end{pmatrix} \begin{pmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{pmatrix}, \qquad (5.61)$$

which leads the formula of the atomic displacement factor for the scattering vector $\vec{K} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$,

$$T_j(\vec{K}) = \exp\left[-2\pi^2 \left((U_{11})_j h^2 a^{*2} + (U_{22})_j k^2 b^{*2} + (U_{33})_j l^2 c^{*2} \right.\right.$$

$$\left.\left. +2(U_{12})_j hka^*b^* + 2(U_{13})_j hla^*c^* + 2(U_{23})_j klb^*c^* \right)\right]. \qquad (5.62)$$

The six independent elements of the matrix, $\{U_{11},U_{22},U_{33},U_{12},U_{13},U_{23}\}$, is called **anisotropic atomic displacement parameters**. When we define another matrix

$$\begin{pmatrix} B_{11} & B_{12} & B_{13} \\ B_{12} & B_{22} & B_{23} \\ B_{13} & B_{23} & B_{33} \end{pmatrix} = 2\pi^2 \begin{pmatrix} a_x^* & a_y^* & a_z^* \\ b_x^* & b_y^* & b_z^* \\ c_x^* & c_y^* & c_z^* \end{pmatrix} \begin{pmatrix} U_{xx} & U_{xy} & U_{zx} \\ U_{xy} & U_{yy} & U_{yz} \\ U_{zx} & U_{yz} & U_{zz} \end{pmatrix} \begin{pmatrix} a_x^* & b_x^* & c_x^* \\ a_y^* & b_y^* & c_y^* \\ a_z^* & b_z^* & c_z^* \end{pmatrix}, \tag{5.63}$$

the following relation is derived,

$$\begin{pmatrix} U_{xx} & U_{xy} & U_{zx} \\ U_{xy} & U_{yy} & U_{yz} \\ U_{zx} & U_{yz} & U_{zz} \end{pmatrix} = \frac{1}{2\pi^2} \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix} \begin{pmatrix} B_{11} & B_{12} & B_{13} \\ B_{12} & B_{22} & B_{23} \\ B_{13} & B_{23} & B_{33} \end{pmatrix} \begin{pmatrix} a_x & a_y & a_z \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{pmatrix}, \tag{5.64}$$

and the formula of atomic displacement factor for the scattering vector $\vec{K} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^*$ should be

$$T(\vec{K}) = \exp\left\{-\left[\left(B_{11}\right)_j h^2 + \left(B_{22}\right)_j k^2 + \left(B_{33}\right)_j l^2 + 2\left(B_{12}\right)_j hk + 2\left(B_{13}\right)_j hl + 2\left(B_{23}\right)_j kl\right]\right\}. \tag{5.65}$$

The formula given by Eq. (5.65) is a little more convenient for calculation than the formula given by Eq. (5.62). The six independent elements of the matrix $\{B_{11},B_{22},B_{33},B_{12},B_{13},B_{23}\}$ is also called anisotropic atomic displacement parameters. The anisotropic *U* parameters and anisotropic *B* parameters are related by the following equations,

$$B_{11} = 2\pi^2 a^{*2} U_{11},\ B_{22} = 2\pi^2 b^{*2} U_{22},\ B_{33} = 2\pi^2 c^{*2} U_{33},$$
$$B_{12} = 2\pi^2 a^* b^* U_{12},\ B_{13} = 2\pi^2 a^* c^* U_{13},\ B_{23} = 2\pi^2 b^* c^* U_{23}. \tag{5.65}$$

Note that the above relations between the anisotropic *B* and *U* parameters are different from the relation between the isotropic displacement parameters *B* and *U*,

$$B = 8\pi^2 U,$$

as shown in Chap. 4.

It is difficult to find what anisotropy is expected from the value of anisotropic *B* parameters, while the parameter U_{11} has the meaning of "mean square atomic displacement along $\vec{a}^*$", U_{22} is the "mean square atomic displacement along $\vec{b}^*$", and U_{33} is the "mean square atomic displacement along $\vec{c}^*$". As the definition of *B* parameters may be introduced just for slight convenience on calculation, .

The values of anisotropic displacement parameters are sometimes restricted by the symmetry of the atomic positions. Let us examine the restriction by symmetry of a crystal structure belonging to hexagonal system, as an example.

In a hexagonal crystal system, the c axis is traditionally taken to be parallel to the six-fold rotation axis. If an atom is located on the six-fold rotation axis, one of the principal axes of the ellipsoidal atomic displacement is uniquely assigned to the *c*-axis (*z*-axis). There remains arbitrariness in the selection of the direction of *a* and *b* axes, or the other two principal axes of the ellipsoid, but we can assume that the *a*-axis (*x*-axis) is parallel to one of the principal axes, and the last principal axis is on the *ab*-plane and orthogonal to the *a*-axis, which means that the last

principal axis can be taken parallel to the *y*-axis. Then, we should assume $U_{xx} = U_{yy} = U_1$, $U_{zz} = U_3$, $U_{xy} = U_{xz} = U_{yz} = 0$. When we apply the three lattice vectors as

$$\vec{a} = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix}, \vec{b} = \begin{pmatrix} -a/2 \\ \sqrt{3}a/2 \\ 0 \end{pmatrix}, \vec{c} = \begin{pmatrix} 0 \\ 0 \\ c \end{pmatrix},$$

we find the reciprocal lattice vectors,

$$\vec{a}^* = \begin{pmatrix} 1/a \\ 1/\sqrt{3}a \\ 0 \end{pmatrix}, \vec{b}^* = \begin{pmatrix} 0 \\ 2/\sqrt{3}a \\ 0 \end{pmatrix}, \vec{c}^* = \begin{pmatrix} 0 \\ 0 \\ 1/c \end{pmatrix}$$

and the unit vectors along the direction parallel to the reciprocal lattice vectors

$$\frac{\vec{a}^*}{a^*} = \begin{pmatrix} \sqrt{3}/2 \\ 1/2 \\ 0 \end{pmatrix}, \frac{\vec{b}^*}{b^*} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \frac{\vec{c}^*}{c^*} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$$

and then we have the formula for the anisotropic displacement for the atom,

$$\begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{12} & U_{22} & U_{23} \\ U_{13} & U_{23} & U_{33} \end{pmatrix} = \begin{pmatrix} \sqrt{3}/2 & 1/2 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} U_1 & 0 & 0 \\ 0 & U_1 & 0 \\ 0 & 0 & U_3 \end{pmatrix} \begin{pmatrix} \sqrt{3}/2 & 0 & 0 \\ 1/2 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} \sqrt{3}/2 & 1/2 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \sqrt{3}U_1/2 & 0 & 0 \\ U_1/2 & U_1 & 0 \\ 0 & 0 & U_3 \end{pmatrix} = \begin{pmatrix} U_1 & U_1/2 & 0 \\ U_1/2 & U_1 & 0 \\ 0 & 0 & U_3 \end{pmatrix},$$

which implies the restrictions: $U_{22} = U_{11}$, $U_{12} = U_{12}/2$ and $U_{13} = U_{23} = 0$.

Exercise

Assume the lattice constants $a = 6.000$ Å, $b = 5.000$ Å, $c = 4.000$ Å, $\alpha = 120.0°$, $\beta = 110.0°$, $\gamma = 100.0°$. Evaluate all the components of the lattice vectors

$$\vec{a} = \begin{pmatrix} a_x \\ 0 \\ 0 \end{pmatrix}, \vec{b} = \begin{pmatrix} b_x \\ b_y \\ 0 \end{pmatrix}, \vec{c} = \begin{pmatrix} c_x \\ c_y \\ c_z \end{pmatrix},$$

and also the components of the corresponding reciprocal lattice vectors. Next, calculate the interplanar distance of the 123-plane (the lattice plane with $h = 1$, $k = 2$ and $l = 3$)