Lecture Note on Solid State Physics

x-ray diffraction

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Abstract

This is a part of lecture notes on Solid State Physics (Phys 472/572). We discuss several important topics including Ewald sphere. This note may also be useful to the ongoing Senior Lab (Phys.427 and 429) and Graduate Lab (Phys.527).

One of the authors (M.S.) has been studying the structural and magnetic properties of quasi two-dimensional systems such as graphite intercalation compounds using x-ray and neutron scattering since 1978.

1. Introduction

1.1 X-ray source

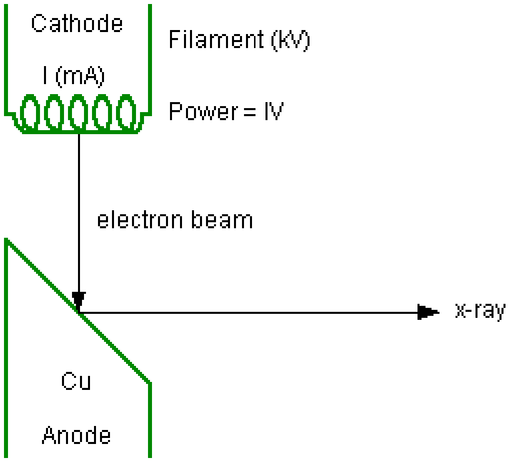


Fig.1 Schematic diagram for the generation of x-rays. Metal target (Cu or Mo) is bombarded by accelerating electrons. The power of the system is given by $P = I$(mA) V(keV), where I is the current of cathode and V is the voltage between the anode and cathode. Typically, we have I = 30 mA and V = 50 kV: P = 1.5 kW in our laboratory.

We use two kinds of targets to generate x-rays: Cu and Mo.
The wavelength of $\mathrm{CuK}_{\alpha 1}$, $\mathrm{CuK}_{\alpha 2}$ and CuK_{β} lines are given by

$$\lambda_{K\alpha 1} = 1.540562 \text{ Å}, \quad \lambda_{K\alpha 2} = 1.544390 \text{ Å}, \ \lambda_{K\beta} = 1.392218 \text{ Å}.$$

The intensity ratio of $\mathrm{CuK}_{\alpha 1}$ and $\mathrm{CuK}_{\alpha 2}$ lines is 2:1.

The weighed average wavelength $\lambda_{K\alpha}$ is calculated as

$$\lambda_{K\alpha} = \frac{2\lambda_{K\alpha 1} + \lambda_{K\alpha 2}}{3} = 1.54184 \text{ Å}.$$

((Note)) The wavelength of MoKα is $\lambda_{K\alpha}$ = 0.71073 Å. Figure shows the intensity versus wavelength distribution for x rays from a Mo target. The penetration depth of MoK_{α} line into samples is much longer than that of CuK_{α} line.

$$\lambda_{K\alpha 1} = 0.709300 \text{ Å}. \quad \lambda_{K\alpha 2} = 0.713590 \text{ Å}, \qquad \lambda_{K\beta} = 0.632 \text{ Å}$$

$$\lambda_{K\alpha} = \frac{2\lambda_{K\alpha 1} + \lambda_{K\alpha 2}}{3} = 0.71073 \text{ Å}.$$

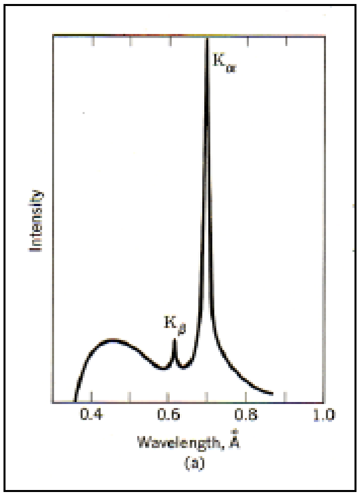


Fig.2 Intensitry vs wavelength distribution for x-rays from a Mo target bombarded by 30 keV electrons from C. Kittel, Introduction to Solid State Physics.

1.2 Principle of x-ray diffraction

x-ray (photon) behaves like both wave and particle. In a crystal, atoms are periodically located on the lattice. Each atom has a nucleus and electrons surrounding the nucleus. The electric field of the incident photon accelerates electrons. The electrons oscillate around a equilibrium position with the period of the electric field associated with incident photon. The nucleus does not oscillate because of the heavy mass.

Classical electrodynamics tells us that an accelerating charge radiates an electromagnetic field.

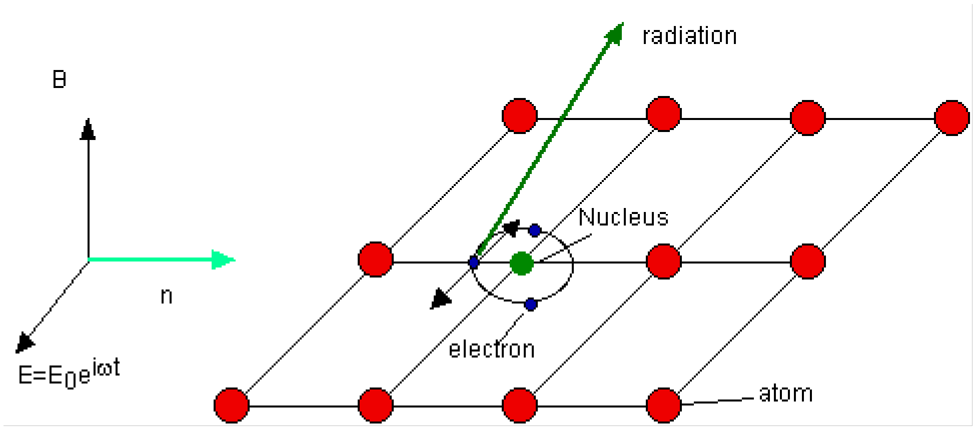


Fig.3 Schematic diagram for the interaction between an electromagnetic wave (x-ray) and electrons surrounding nucleus. The oscillatory electric field ($E = E_0 e^{i\omega t}$) of x-ray photon gives rise to the harmonic oscillation of the electrons along the electric field.

The instantaneous electromagnetic energy (radiation) flow is given by the pointing vector

$$\mathbf{S} \approx \frac{\dot{v}^2 \sin^2\theta}{R^2}\mathbf{n}$$

The direction of the velocity **v** (the direction of the oscillation) is along the *x* direction in Fig. 4. The direction of the photon radiation is in the (*x*, *y*) plane.

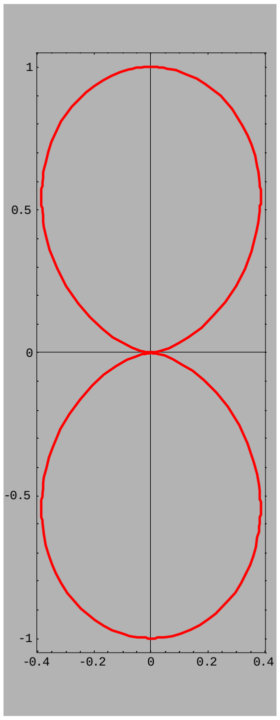


Fig.4 The distribution of instantaneous radiation energy due to the oscillation of electrons along the *x* direction. Thye Mathematica 5.2 (PolarPlot) is used.

1.3 Experimental configuration of x-ray scattering

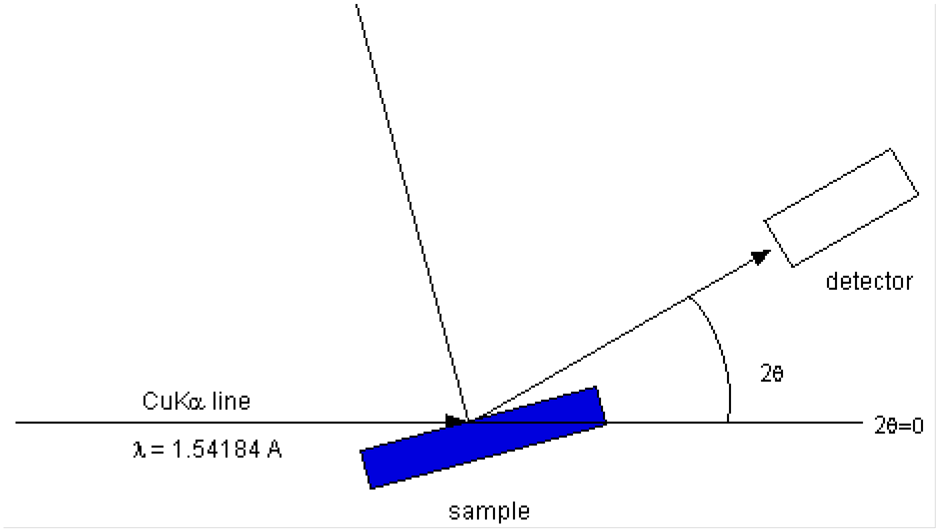


Fig.5 Example for the geometry of Ω (= θ) – 2θ scan for the (00*L*) x-ray diffraction. The Cu target is used. The direction of the incident x-ray beam is $2\theta = 0$. The angle between the detector and the direction of the incident x-ray beam is 2θ. Ω is the rotation angle of the sample.

((Example)) x-ray diffraction

We show two examples of the x-ray diffraction pattern whicha are obtained in my laboratory

(a) Stage- 3 $MoCl_5$ graphite intercalation compound (GIC). $MoCl_5$ are intercalated into empty graphite galleries. There are three graphene layers between adjacent MoCl5 intercalate layers.

(b) Ni vemiculte. Vermiculite is a layered silicate (a kind of clays). In the interlamellar space, Ni layer are sandwiched between two water layers.

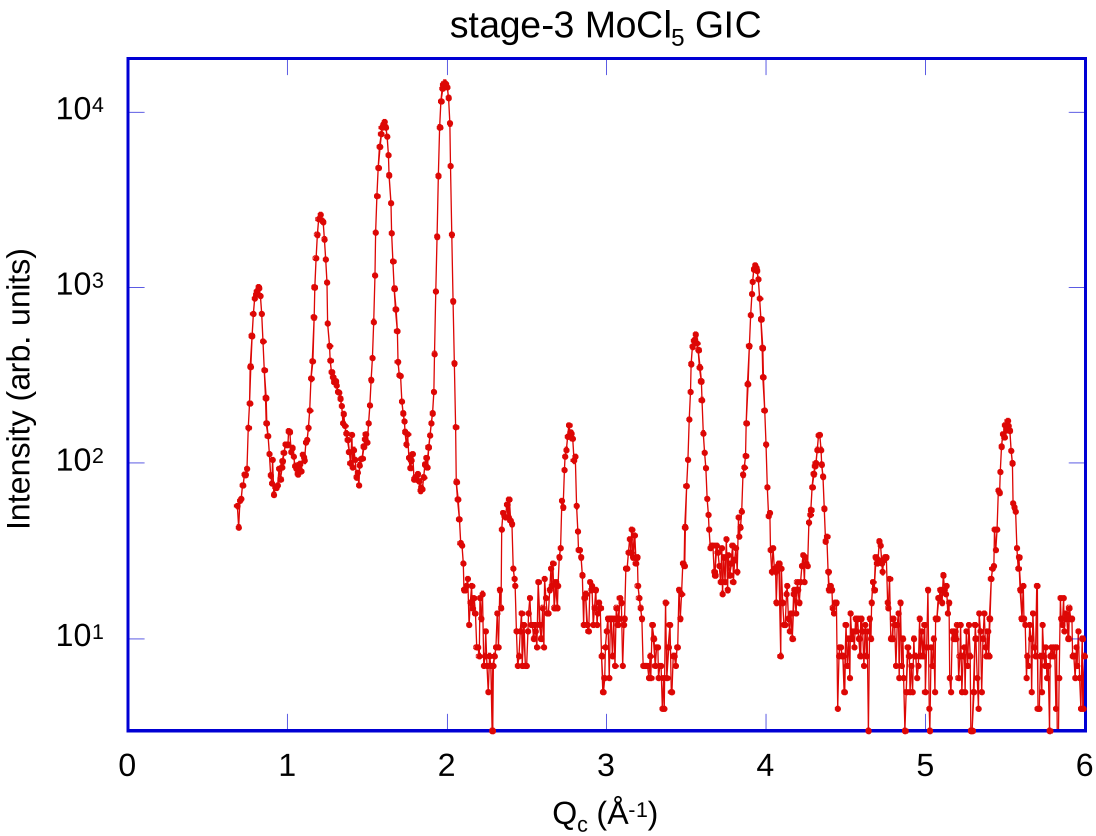


Fig.6 (00*L*) x-ray diffraction pattern of stage-3 $MoCl_5$ GIC. [M. Suzuki, C. Lee, I.S. Suzuki, K. Matsubara, and K. Sugihara, "c-axis resistivity of $MoCl_5$ graphite intercalation compounds," Phys. Rev. B **54**, 17128 (1996).]

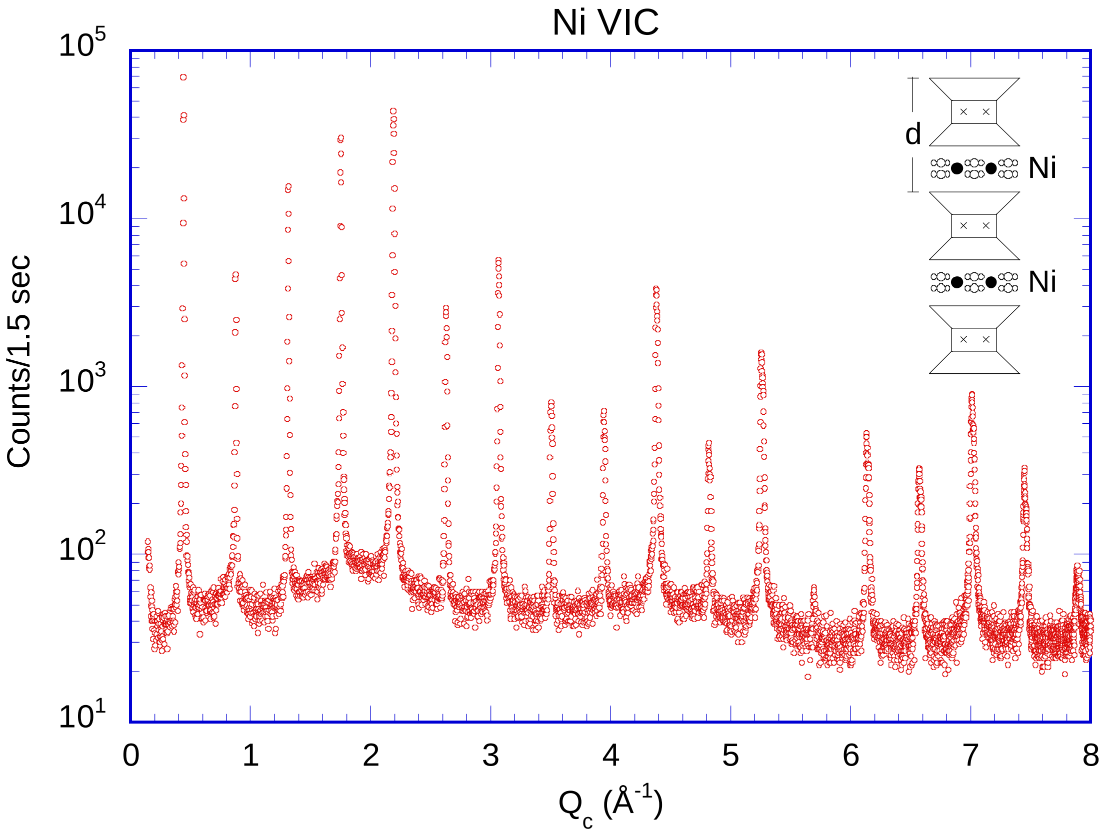


Fig.7 (00*L*) x-ray diffraction pattern of Ni-vermiculite with two water-layer hydration state. [M. Suzuki, I.S. Suzuki, N. Wada, and M.S. Whittingham, "Superparamagnetic behavior in Ni vermiculite intercalation compound," Phys. Rev. B 64, 104418 (2001)]

2. Bragg condition

2.1. Bragg law

The incident x-rays are reflected specularly from parallel planes of atoms in the crystal.

(a) The angle of incoming x-rays is equal to the angle of outgoing x-rays.
(b) The energy of x-rays is conserved on reflection (elastic scattering).

The path difference for x-rays reflected from adjacent planes is equal to $\Delta d = 2d\sin\theta$ (see Fig. 8). The corresponding phase difference is

$$\Delta\phi = k\Delta d = (2\pi/\lambda)2d\sin\theta .$$

where k is the wave number ($k = 2\pi/\lambda$) and λ is the wave length.

Constructive interference of the radiation from successive planes occurs when $\Delta\phi = 2l\pi$, where l is an integer (Bragg law).

$$2d \sin\theta = n\lambda$$

The Bragg reflection can occur only for $\lambda \leq 2d$.

The Bragg law is a consequence of the periodicity of the lattice. The Bragg law does not refer to the composition of the basis of atoms associated with every lattice point. The composition of the bases determines the relative intensity of the various orders of diffraction.

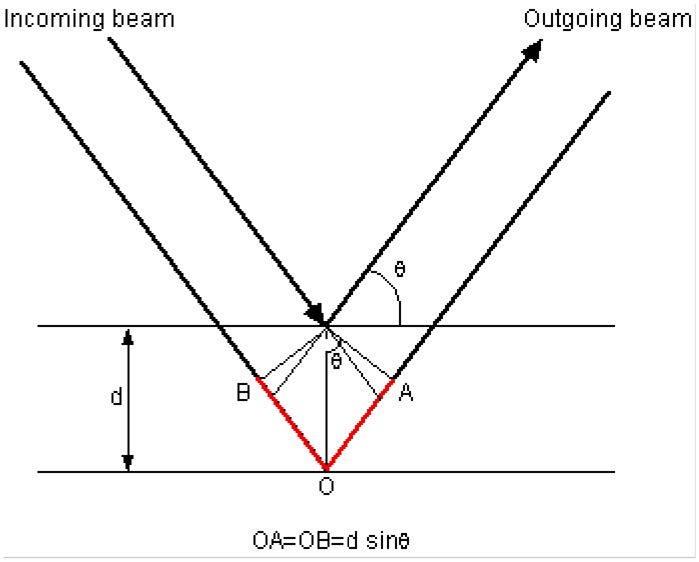


Fig.8 Geometry of the scattering of x-rays from planar arrays. The path difference between two rays reflected by planar arrays is OA + OB = $2d \sin\theta$.

2.2 Concept of Ewald sphere: introduction of reciprocal lattice

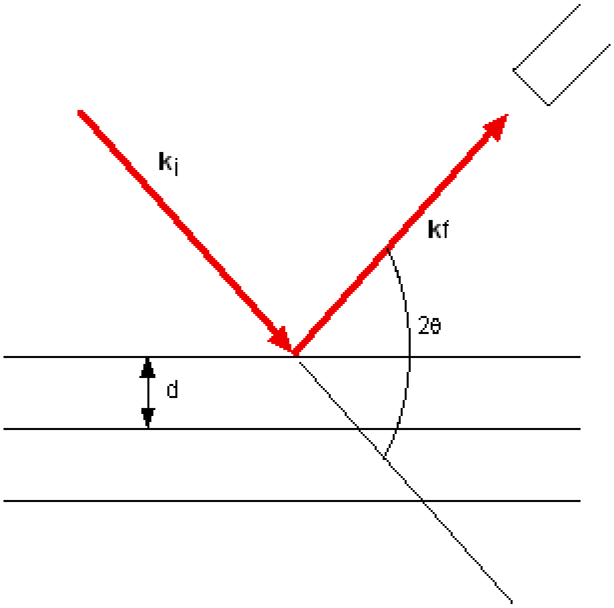


Fig.9 The geometry of the scattered x-ray beam. The incident x-ray has the wavevector $\mathbf{k}_i$ (= **k**), while the outgoing x-ray has the wavevector $\mathbf{k}_f$ (= **k'**). $|\mathbf{k}_i| = |\mathbf{k}_f| = 2\pi/\lambda$, where λ is the wavelength of x-ray. Note that $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$ is the scattering vector. **Q** is perpendicular to the plane of atoms.

Bragg law:

$$2d\sin\theta = l\lambda$$

$\mathbf{k}_i$ is incident wavevector.
$\mathbf{k}_f$ is the outgoing wavevector.

$$|\mathbf{k}_i| = |\mathbf{k}_f| = \frac{2\pi}{\lambda}$$

Q is the scattering vector:

$$\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f, \quad \text{or} \qquad \mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$$

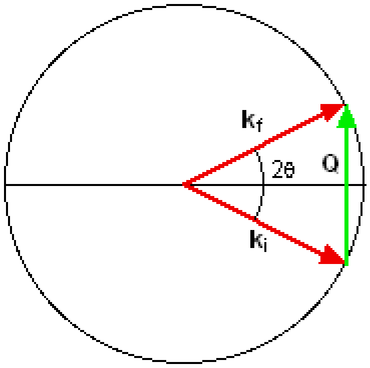


Fig.10 The geometry of Fig.9 using a circle with a radius k (= $2\pi/\lambda$). The scattering vector **Q** is defined by **Q** = $\mathbf{k}_f - \mathbf{k}_i$.

This is a part of the Ewald sphere. The detail of the Ewald sphere will be discussed later.

In the above configuration, **Q** is perpendicular to the surface of the system

$$|\mathbf{Q}| = 2|\mathbf{k}_i|\sin\theta = \frac{4\pi}{\lambda}\sin\theta = \frac{4\pi}{\lambda}\frac{l\lambda}{2d} = \frac{2\pi}{d}l \text{ (Bragg condition)}$$

which coincides with the reciprocal lattice point. In other words, the Bragg reflections occur, when **Q** is equal to the reciprocal lattice vectors.

3. Reciprocal lattice vector

3.1 Definition

Reciprocal lattice vector

$$\mathbf{G}\cdot\mathbf{T} = 2\pi$$

with

$$\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$$

We construct the axis vectors, $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ of the reciprocal lattice

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2\times\mathbf{a}_3}{[\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3]}, \quad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3\times\mathbf{a}_1}{[\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3]}, \quad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1\times\mathbf{a}_2}{[\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3]}$$

where

$$[\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3]=\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)=V_c \text{ = volume of unit cell}$$

$\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ are called the primitive vectors of the reciprocal lattice.

Note that

$$\mathbf{a}_1\cdot\mathbf{b}_1=2\pi,\quad \mathbf{a}_2\cdot\mathbf{b}_2=2\pi,\quad \mathbf{a}_3\cdot\mathbf{b}_3=2\pi$$

$\mathbf{b}_1$ is perpendicular to both $\mathbf{a}_2$ and $\mathbf{a}_3$.

$\mathbf{b}_2$ is perpendicular to both $\mathbf{a}_3$ and $\mathbf{a}_1$.

$\mathbf{b}_3$ is perpendicular to both $\mathbf{a}_1$ and $\mathbf{a}_2$.

The reciprocal lattice vector **G** is expressed by

$$\mathbf{G}=h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3.$$

Then we have

$$\mathbf{G}\cdot\mathbf{T}=(h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3)\cdot(u_1\mathbf{a}_1+u_2\mathbf{a}_2+u_3\mathbf{a}_3)=2\pi(hu_1+ku_2+lu_3)$$

3.2. Miller indices and reciprocal lattice vector

Index of planes

(*hkl*) plane

Consider the (*hkl*) plane.

(*hkl*) are the smallest three integers (Miller indices).

(1) The reciprocal lattice vector is defined by

$$\mathbf{G}=h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3.$$

G is perpendicular to the (*hkl*) plane.

((Proof))

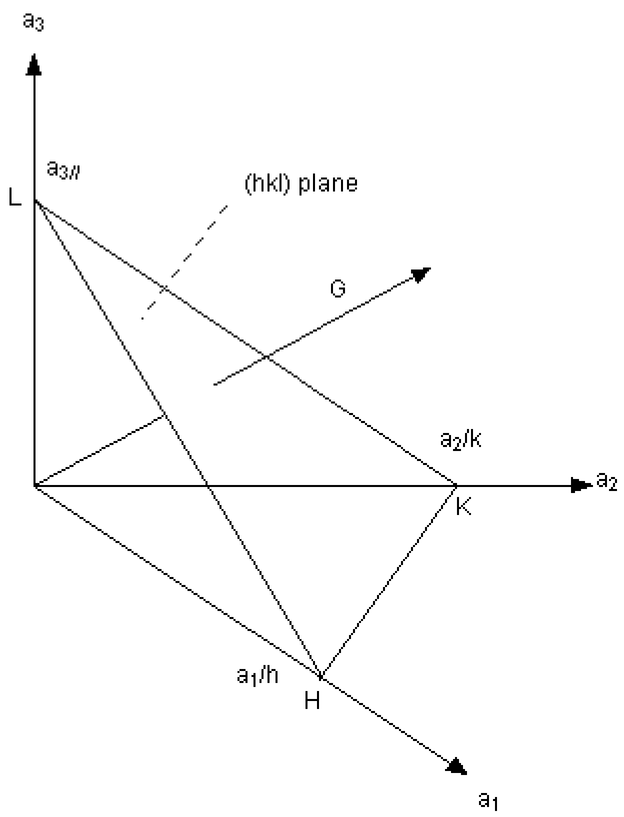


Fig.11 Definition of (*hkl*) plane where *h*, *k*, and *l* are the smallest three integers.

First we find the intercepts on the axes in terms of the lattice constants a_1, a_2, and a_3: a_1/h, a_2/k, a_3/l (see Fig. 11). We take the reciprocals of these numbers and then reduces to three integers having the same ratio, usually the smallest three integers: (*hkl*). These indices (*hkl*) may denote a single phase or a set of parallel planes. If a plane cuts an axis on the negative side of the origin, the corresponding index is negative, indicated by placing a minus sign above the index $(h\bar{k}l)$.

The vectors $\overrightarrow{HK}$ and $\overrightarrow{KL}$ are given by

$$\overrightarrow{HK} = \frac{\mathbf{a}_2}{k} - \frac{\mathbf{a}_1}{h}$$

$$\overrightarrow{KL} = \frac{\mathbf{a}_3}{l} - \frac{\mathbf{a}_2}{k}$$

These two vectors are perpendicular to **G**.

$$\overrightarrow{HK} \cdot \mathbf{G} = \left(\frac{\mathbf{a}_2}{k} - \frac{\mathbf{a}_1}{h} \right) \cdot (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) = 0$$

$$\overrightarrow{KL} \cdot \mathbf{G} = \left(\frac{\mathbf{a}_3}{l} - \frac{\mathbf{a}_2}{k} \right) \cdot (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) = 0$$

by using the relations

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij},$$

where $\delta_{ij} = 1$ for $i = j$, and 0 for $i \neq j$. Then the (*hkl*) plane is perpendicular to **G**.

(2) The distance between two parallel adjacent (*hkl*) planes is

$$d(hkl) = \frac{2\pi}{|\mathbf{G}|} \text{ (nearest neighbor distance)}$$

where (*hkl*) indices are the smallest integers.

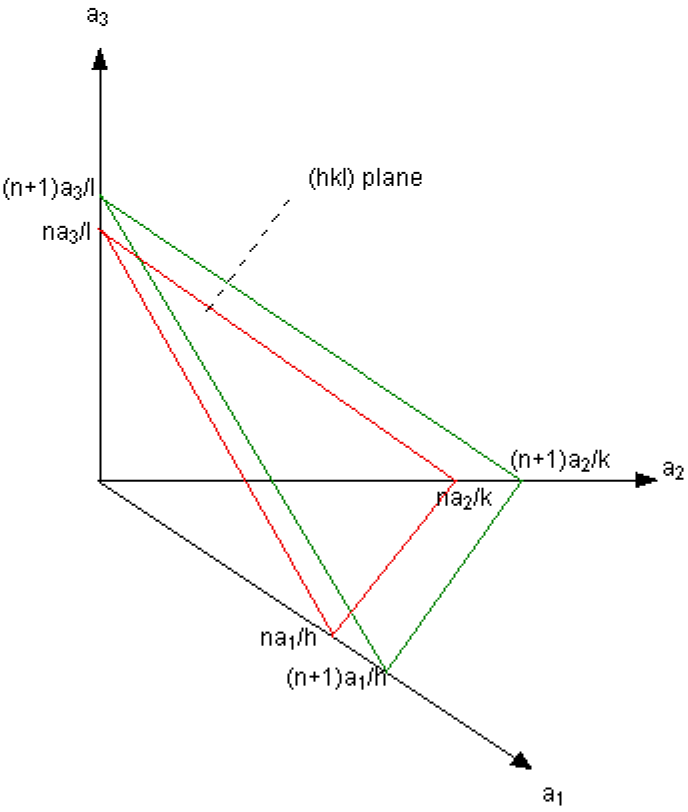


Fig.12 Adjacent (*hkl*) planes.

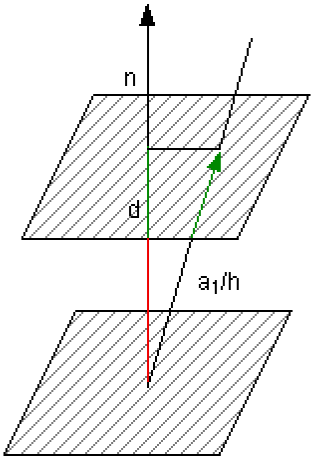


Fig.13 The nearest neighbor distance between the adjacent (*hkl*) planes.

n (*hkl*) plane

$$\frac{1}{\frac{n}{h}} : \frac{1}{\frac{n}{k}} : \frac{1}{\frac{n}{l}} = \frac{h}{n} : \frac{k}{n} : \frac{l}{n}$$

adjacent (*n*+1) (*hkl*) plane

$$\frac{1}{\frac{n+1}{h}} : \frac{1}{\frac{n+1}{k}} : \frac{1}{\frac{n+1}{l}} = \frac{h}{n+1} : \frac{k}{n+1} : \frac{l}{n+1}$$

$$\mathbf{n} = \frac{\mathbf{G}}{G}$$

Since (*hkl*) plane is perpendicular to ***G***,

$$d(hkl) = \frac{1}{h}\mathbf{a}_1 \cdot \mathbf{n} = \frac{1}{h}\mathbf{a}_1 \cdot \frac{\mathbf{G}}{G} = \frac{2\pi}{G}$$

or

$$d(hkl) = \frac{2\pi}{G}$$

What is the separation distance between the *n*(*hkl*) plane and (*n*+*m*) (*hkl*) plane?

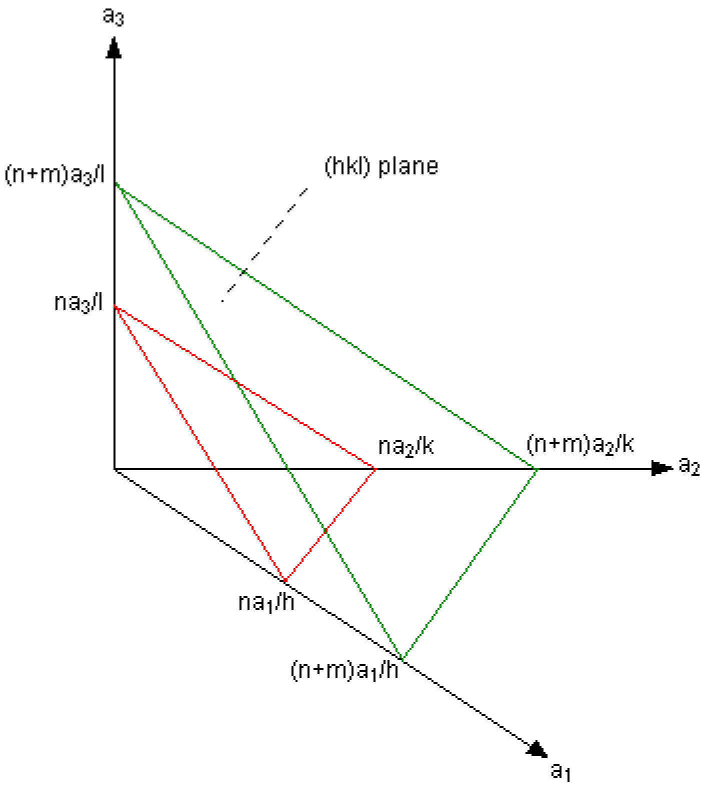


Fig.14 Two (*hkl*) planes.

$$d_m = \frac{1}{h} m\mathbf{a}_1 \cdot \mathbf{n} = \frac{1}{h} m\mathbf{a}_1 \cdot \frac{\mathbf{G}}{G} = \frac{2\pi m}{G} = md(hkl).$$

3.3 Reciprocal lattice vector

A different pattern of a crystal is a map of the reciprocal lattice of the crystal.

(a) Square lattice

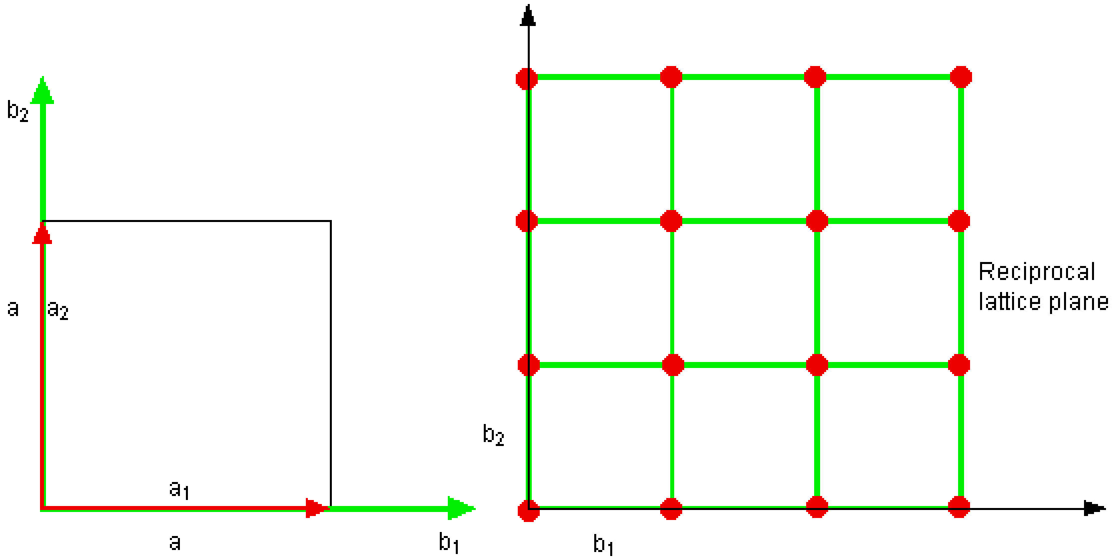


Fig.15 Real space for the square lattice and the corresponding reciprocal lattice plane

a$_1$ and **a**$_2$ are the lattice vectors, and **b**$_1$ and **b**$_2$ are the reciprocal lattice vectors. The direction of **b**$_1$ (**b**$_2$) is the same as that of **a**$_1$ (**a**$_2$).

$$\mathbf{a}_1 \cdot \mathbf{b}_1 = \mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi$$

$$a_1 b_1 = 2\pi, \qquad \text{or} \qquad b_1 = \frac{2\pi}{a_1}$$

$$a_2 b_2 = 2\pi, \qquad \text{or} \qquad b_2 = \frac{2\pi}{a_2}$$

(b) Hexagonal lattice (or triangular lattice)

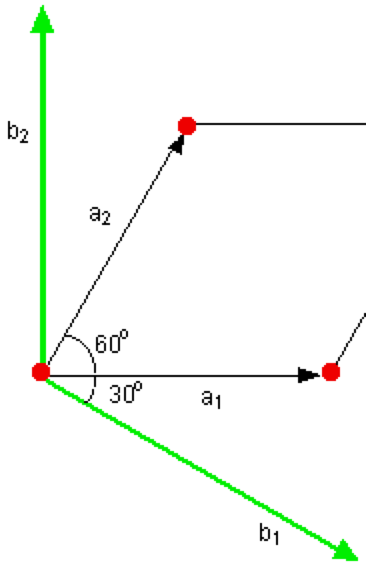


Fig.16 Real space for the hexagonal (triangular) lattice and the corresponding reciprocal lattice plane

a$_2$ is perpendicular to **b**$_1$.
a$_1$ is perpendicular to **b**$_2$.

$$\mathbf{a}_1 \cdot \mathbf{b}_1 = \mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi$$

$$a_1 b_1 \cos(30^\circ) = 2\pi, \quad \text{or} \quad b_1 = \frac{4\pi}{\sqrt{3}a_1}$$

$$a_2 b_2 \cos(30^\circ) = 2\pi, \quad \text{or} \quad b_2 = \frac{4\pi}{\sqrt{3}a_2}$$

$$\mathbf{b}_1 = \frac{2\pi}{\sqrt{3}a_1}(\sqrt{3},-1) \quad \text{and} \quad \mathbf{b}_2 = \frac{4\pi}{\sqrt{3}a_1}(0,-1)$$

The angle between **a**$_1$ and **b**$_1$ is 30º. The angle between **a**$_2$ and **b**$_2$ is 30º.

(c) Graphite 2D lattice (honeycomb)

There are two atoms per cell. The lattice constant a is equal to 2.46 Å.

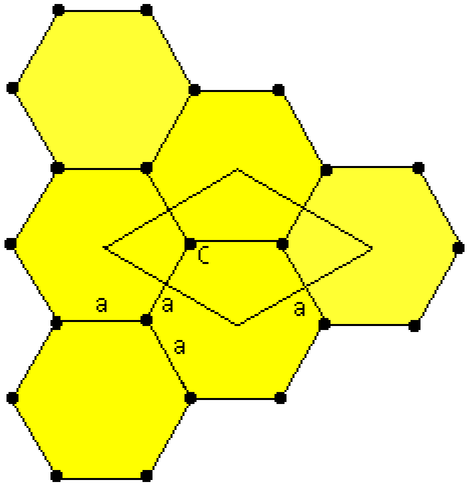


Fig.17 Two dimensional lattice for graphite layer (honeycomb). There are two carbon C atoms per unit cell.

The lattice constant of graphite is a = 2.46 Å. The graphite has a A-B stacking sequence along the c axis. We now consider the reciprocal lattice plane of the graphite lattice. The vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are the in-plane lattice vectors. The vectors $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ are the reciprocal lattice vectors. Note that $\mathbf{a}_1 \cdot \mathbf{b}_2 = 0$ and $\mathbf{a}_2 \cdot \mathbf{b}_1 = 0$. The angle between $\boldsymbol{a}_1$ and $\boldsymbol{b}_1$ is 30º.

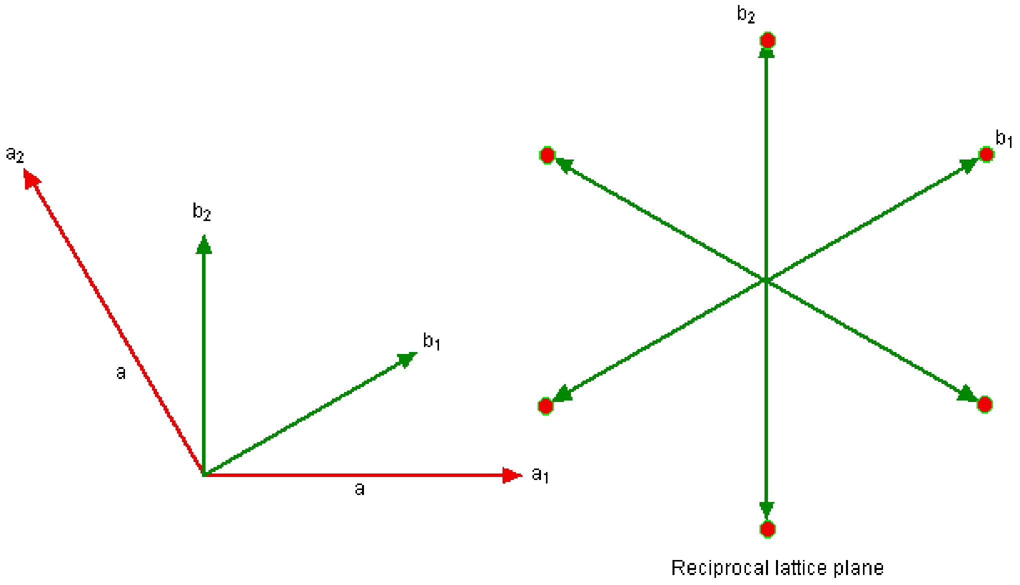


Fig.18 In-plane structure and the corresponding reciprocal lattice of the graphite lattice. a_1 = 2.46 Å. $b_1 = 4\pi/(\sqrt{3}a_1)$ = 2.95 Å^{-1}.

$$\mathbf{a}_1 \cdot \mathbf{b}_1 = \mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi$$

$$a_1 b_1 \cos(30^\circ) = 2\pi, \quad \text{or} \quad b_1 = \frac{4\pi}{\sqrt{3}a_1} = 2.95\ \text{Å}^{-1}.$$

$$a_2 b_2 \cos(30^\circ) = 2\pi, \quad \text{or} \quad b_2 = \frac{4\pi}{\sqrt{3}a_2} = 2.95\ \text{Å}^{-1}.$$

4. Electron density

4.1 Fourier analysis

A crystal is invariant under any translation of the form

$$\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$$

where u_1, u_2, u_3 are integers and $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the periods along the crystal axes.

Any local physical property of the crystal is invariant under $\boldsymbol{T}$: charge concentration, electron number, magnetic moment density.

Electron number density $n(\boldsymbol{r})$ is a periodic function of $\boldsymbol{r}$, with periods $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ in the directions of the three axes.

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$$

We consider the Fourier series

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_G \exp(i\mathbf{G} \cdot \mathbf{r})$$

$$n(\mathbf{r} + \mathbf{T}) = \sum_{\mathbf{G}} n_G \exp[i\mathbf{G} \cdot (\mathbf{r} + \mathbf{T})] = \exp[i\mathbf{G} \cdot \mathbf{T})]\sum_{\mathbf{G}} n_G \exp(i\mathbf{G} \cdot \mathbf{r}) = n(\mathbf{r})$$

or

$$\mathbf{G} \cdot \mathbf{T} = 2\pi l$$

where l is an integer.

The extension of the Fourier analysis to periodic function $n(\boldsymbol{r})$ in the 3D is given by

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_G \exp(i\mathbf{G} \cdot \mathbf{r})$$

where $\mathbf{G}$ is the reciprocal lattice vector, and $n_{\mathbf{G}}$ determines the x-ray scattering amplitude.

Derivation of the Fourier component n_G:

$$\int_V n(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}d\mathbf{r} = \int_V \sum_{\mathbf{G}'} n_{\mathbf{G}'}e^{i\mathbf{G}'\cdot\mathbf{r}}e^{-i\mathbf{G}\cdot\mathbf{r}}d\mathbf{r} = \sum_{\mathbf{G}'} n_{\mathbf{G}'}\int e^{i(\mathbf{G}'-\mathbf{G})\cdot\mathbf{r}}Vd\mathbf{r} = n_{\mathbf{G}}V$$

or

$$n_{\mathbf{G}} = \frac{1}{V}\int_V n(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}d\mathbf{r}$$

where $V = N\, V_{\text{cell}}$

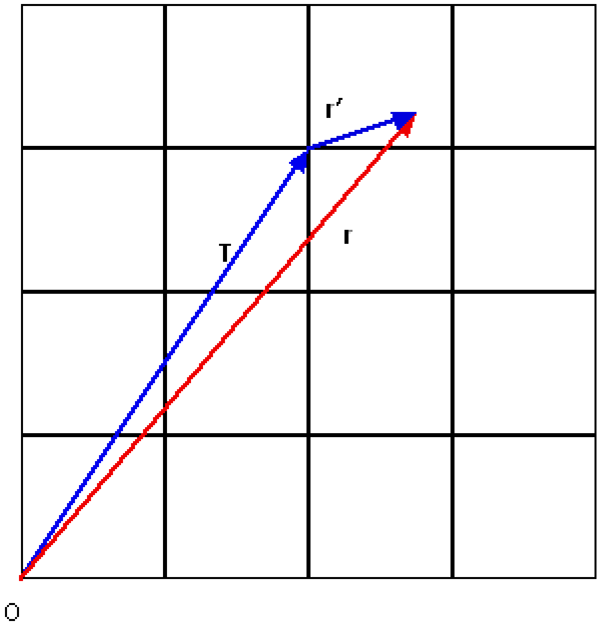


Fig.19 Systsm consisting of periodic cells. **T** is the translation vector.

$$\mathbf{r} = \mathbf{T} + \mathbf{r}'$$

$$n(\mathbf{r}) = n(\mathbf{T} + \mathbf{r}') = n(\mathbf{r}')$$

$$e^{-i\mathbf{G}\cdot\mathbf{r}} = e^{-i\mathbf{G}\cdot(\mathbf{r}'+\mathbf{T})} = e^{-i\mathbf{G}\cdot\mathbf{r}'}$$

Then we have

$$n_{\mathbf{G}} = \frac{1}{NV_{cell}}[N\int_{V_{cell}} n(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}d\mathbf{r}] = \frac{1}{V_{cell}}\int_{V_{cell}} n(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}d\mathbf{r}$$

Here we define the structure factor as

$$S_{\mathbf{G}} = \int_{V_{cell}} n(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} d\mathbf{r}$$

or

$$n_{\mathbf{G}} = \frac{1}{V_{cell}} S_{\mathbf{G}}$$

4.2 One dimensional case

For simplicity, we consider a function $n(x)$ with a period a in the x direction (one dimensional case).

$$n(x) = n(x+a)$$

Suppose that $n(x)$ may be expressed by

$$n(x) = \sum_g n_g \exp(igx)$$

$$n(x+a) = \sum_g n_g \exp[ig(x+a)] = \exp(iga)\sum_g n_g \exp(igx) = \exp(iga) n(x) = n(x)$$

In other words

$$\exp(iga) = 1$$

or

$$g = \frac{2\pi}{a} l$$

Thus we have

$$n(x) = \sum_g n_g \exp(igx)$$

$$n_g = \frac{1}{a}\int_0^a dx n(x) e^{-igx}$$

((Example)) What is the value of n_g? We consider the simplest case.

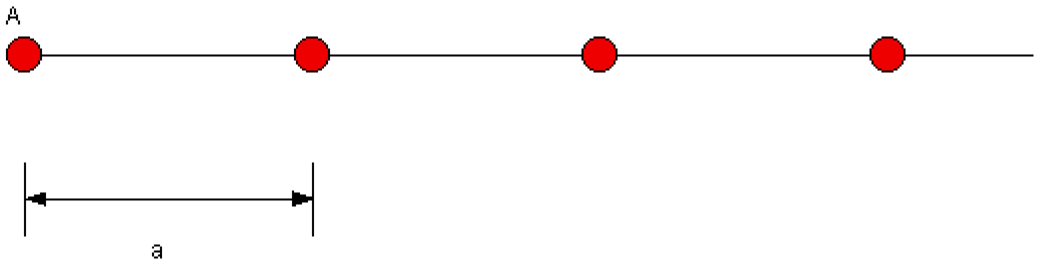


Fig.20 A simple one dimensional array with a lattice constant *a*.

$$n_g = \frac{1}{a}\int_0^a \delta(x)edx = \frac{1}{a}$$

with $g = \frac{2\pi}{a} l$

where $\delta(x)$ is the Dirac delta function.

((Example 2))
There are two atoms in each unit cell with the lattice constant *a*.

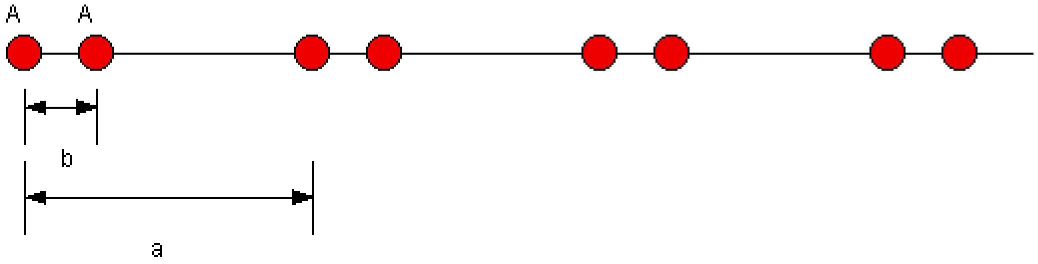


Fig.21 One dimensional array with to atoms per unit cell with a lattice constant *a*.

$$n_g = \frac{1}{a}\int_0^a [\delta(x) + \delta(x-b)]e^{-igx}dx = \frac{1}{a}(1+e^{-igb})$$

$$|n_g|^2 = n_g n_g^* = \frac{(1+e^{-igb})(1+e^{igb})}{a^2} = \frac{4}{a^2}\cos^2(\frac{gb}{2})$$

with $g = \frac{2\pi}{a} l$

((Mathematica 5.2)): $|n_g|^2$ vs l where a = 1 and b = 0.3.

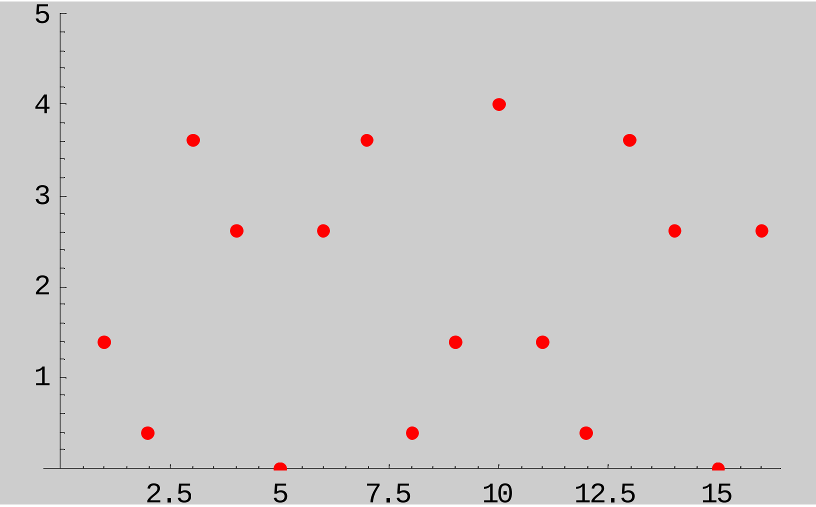
$$\mathbf{f} = \frac{4}{a^2}\,\mathrm{Cos}\left[\frac{\pi\, b\, L}{a}\right]^2$$

$$\frac{4\,\mathrm{Cos}\left[\frac{b\,L\,\pi}{a}\right]^2}{a^2}$$

```
f1=f/.{a→1, b→0.3}
```

$$4\,\mathrm{Cos}[0.942478\ L]^2$$

```
ListPlot[Table[f1,{L,1,16}],PlotRange→{0,5},
PlotStyle→Hue[0],                    Prolog→AbsolutePointSize[5],
Background→GrayLevel[0.8]]
```



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-Graphics-
```

Fig.22 Intensity $|n_g|^2$ vs Bragg index l for the 1D system shown in Fig.21.

This figure shows the intensity vs the Bragg index l (integers).

4.3 Two dimensional case

We calculate the electron density of the triangular lattice using Mathematica 5.2. Note that the reciprocal lattice vectors of the system is discussed before.

((Mathematica 5.2))
In-plane density contour plot of $n(\boldsymbol{r})$ for the triangular lattice

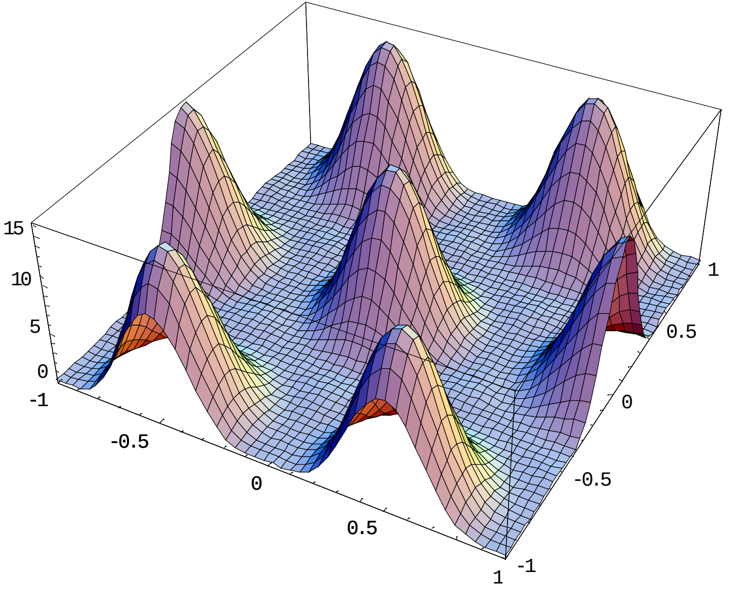
```
(*example of n(r), triangular lattice*)
```

f =

$$\left(1+\mathrm{Cos}\left[\frac{4\pi}{\sqrt{3}\,a}\,\mathrm{Cos}[30\,°]\,x+\frac{4\pi}{\sqrt{3}\,a}\,\mathrm{Sin}[30\,°]\,y\right]+\mathrm{Cos}\left[\frac{4\pi}{\sqrt{3}\,a}\,\mathrm{Cos}[150\,°]\,x+\frac{4\pi}{\sqrt{3}\,a}\,\mathrm{Sin}[150\,°]\,y\right]+\mathrm{Cos}\left[\frac{4\pi}{\sqrt{3}\,a}\,\mathrm{Cos}[270\,°]\,x+\frac{4\pi}{\sqrt{3}\,a}\,\mathrm{Sin}[270\,°]\,y\right]\right)\ /.\ a\to 1$$

$$1+\mathrm{Cos}\left[\frac{4\pi y}{\sqrt{3}}\right]+\mathrm{Cos}\left[2\pi x-\frac{2\pi y}{\sqrt{3}}\right]+\mathrm{Cos}\left[2\pi x+\frac{2\pi y}{\sqrt{3}}\right]$$

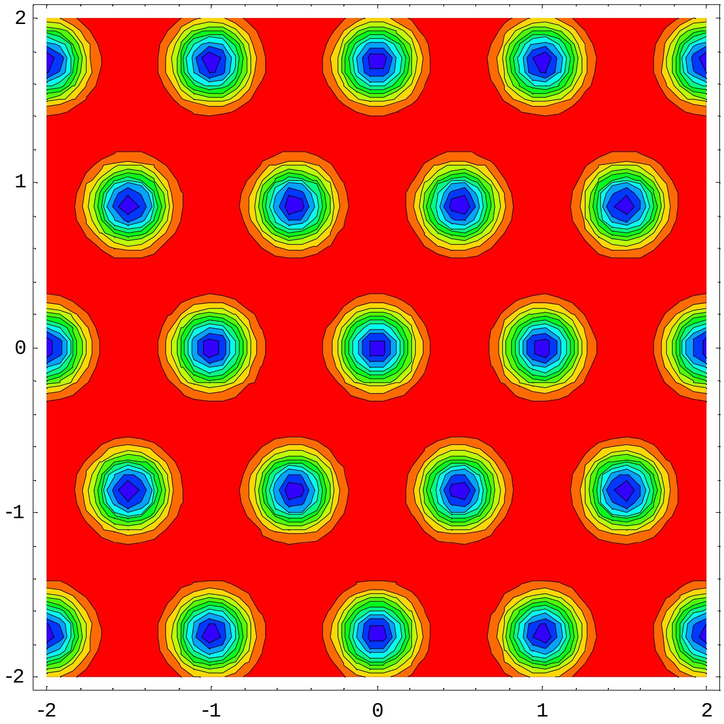
```
Plot3D[f^2, {x, -1, 1}, {y, -1, 1}, PlotPoints → 50]
```



```
-SurfaceGraphics-
```

Fig.23 Plot3D of electron density of the 2D triangular lattice. We assume $n_g = 1$ for simplicity. We use Mathematica 5.2.

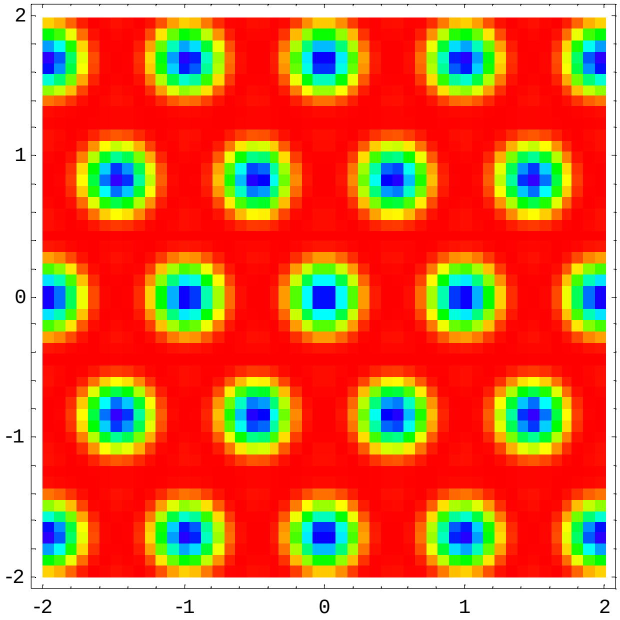
```
ContourPlot[f^2, {x, -2, 2}, {y, -2, 2}, PlotPoints → 50, ColorFunction → (Hue[0.7 #] &)]
```



```
-ContourGraphics-
```

Fig.24 The corresponding Contour plot.

```
DensityPlot[f^2, {x, -2, 2}, {y, -2, 2}, PlotPoints→50, Mesh→False, ColorFunction→(Hue[0.7 #] &)]
```



```
-DensityGraphics-
```

Fig.25 The corresponding Density plot.

5. Structure factor

5.1 Fourier analysis of the basis

S_G is called the structural factor and defined as an integral over a single cell.

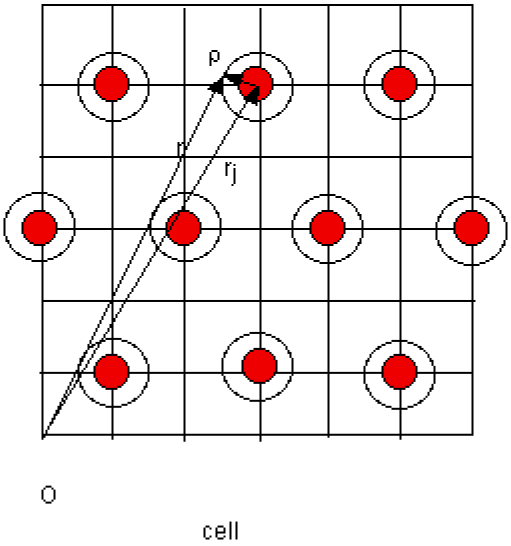


Fig.26 Unit cell having more than two atoms

Let $n_j(\boldsymbol{r}-\boldsymbol{r}_j)$ be defined by the contribution of atom j to the electron concentration.

$$n(r) = \sum_{j=1}^{s} n_j(\mathbf{r} - r_j)$$

over the *s* atoms of the basis.

Then we have

$$S_{\mathbf{G}} = \sum_j \int_{V_{cell}} n_j(\mathbf{r} - \mathbf{r}_j) e^{-i\mathbf{G}\cdot\mathbf{r}} d\mathbf{r}$$

$$S_{\mathbf{G}} = \sum_j e^{-i\mathbf{G}\cdot\mathbf{r}_j} \int_{V_{cell}} n_j(\boldsymbol{\rho}) e^{-i\mathbf{G}\cdot\boldsymbol{\rho}} d\boldsymbol{\rho}$$

We now define the atomic form factor as

$$f_j = \int_{V_{cell}} n_j(\boldsymbol{\rho}) e^{-i\mathbf{G}\cdot\boldsymbol{\rho}} d\boldsymbol{\rho}$$

The atomic form factor is a measure of the scattering power of the *j*-th atom in the unit cell. The value of *f* involves the number and distribution of atomic electrons.

Then S_G is given by the form

$$S_{\mathbf{G}} = \sum_j f_j e^{-i\mathbf{G}\cdot\mathbf{r}_j}$$

The structure factor S_G need not to be real because the scattering intensity will involve

$$S_{\mathbf{G}} * S_{\mathbf{G}} = |S_{\mathbf{G}}|^2$$

5.2 Atomic form factor

When $\boldsymbol{G} = 0$, f_j is equal to the total number of electrons around the nucleus (Z)

$$f_j = \int_{V_{cell}} n_j(\boldsymbol{\rho}) d\boldsymbol{\rho} = Z$$

The value of *f* for atoms may be found in the international tables for x-ray crystallography.

Suppose that the electron distribution is spherically symmetric about the origin:

$$n_j(\boldsymbol{\rho}) = n_j(\rho)$$

$$f_j = 4\pi \int d\rho \rho^2 n_j(\rho) \frac{\sin(G\rho)}{G\rho}$$

We now calculate the form factor of atomic hydrogen in the ground state. The number density is given by

$$n(\rho) = \frac{1}{\pi a_0^3} e^{-2r/a_0}$$

where a_0 is the Bohr radius (a_0 = 0.53 Å)

$$f_G = \frac{16}{(4 + G^2 a_0{}^2)^2}$$

((Mathematica 5.2))

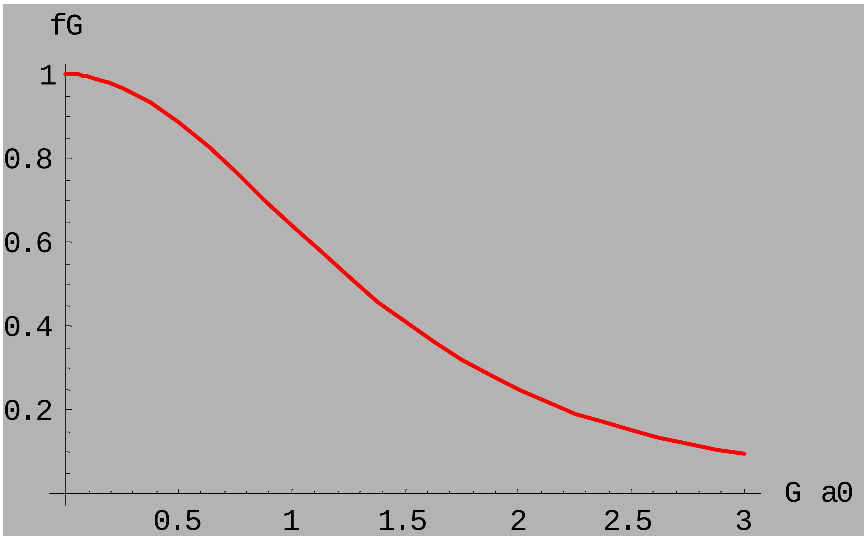


Fig.27 The atomic form factor of hydrogen in the ground state. Note that $f_G = 1$ at $G = 0$.

5.3 The structure factor for 1D, 2D and 3D systems

5.3.1 One dimensional case

The structure factor for the 1D case is given by

$$S_G = \int n(x) e^{-iG_x x} dx$$

S_G depends only on G_x, which leads to the Bragg plane.

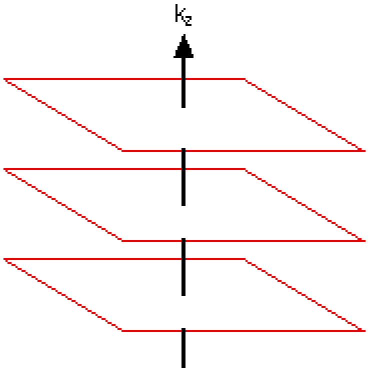


Fig.28 Bragg plane ($k_z = (2\pi l/a$, l: integer) in the reciprocal lattice space, which is a significant feature common to the 1D system where atoms are arranged along the z axis with a lattice constant a.

5.3.2 Two dimensional case

The structure factor S_G for the 2D case is given by

$$S_\mathbf{G} = \int n(x,y) e^{-i(G_x x + G_y y)} dxdy$$

S_G depends only on G_x and G_y, which leads to the Bragg ridge (or Bragg rod).

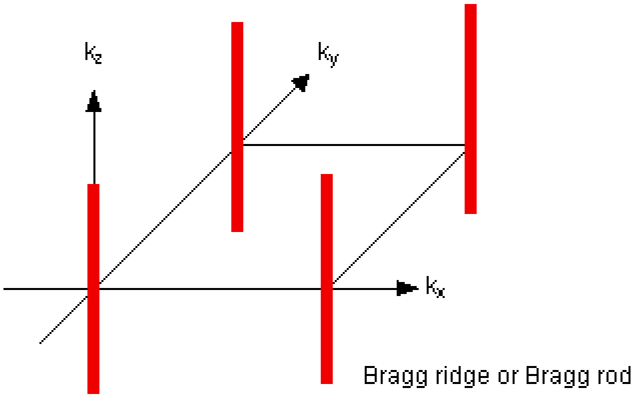


Fig.29 Bragg ridge (or rod) in the reciprocal lattice space (in the case of square lattice), which is a significant feature common to the 2D system.

5.3.3 Three dimensional case

The structure factor S_G for the 3D case is given by

$$S_\mathbf{G} = \int n(x,y,z) e^{-i(G_x x + G_y y + G_z z)} dxdydz$$

S_G depends only on G_x, G_y, and G_z, which leads to the Bragg point.

6. Diffraction conditions

6.1 Scattering amplitude

The set of reciprocal lattice vectors determines the possible x-ray reflections.

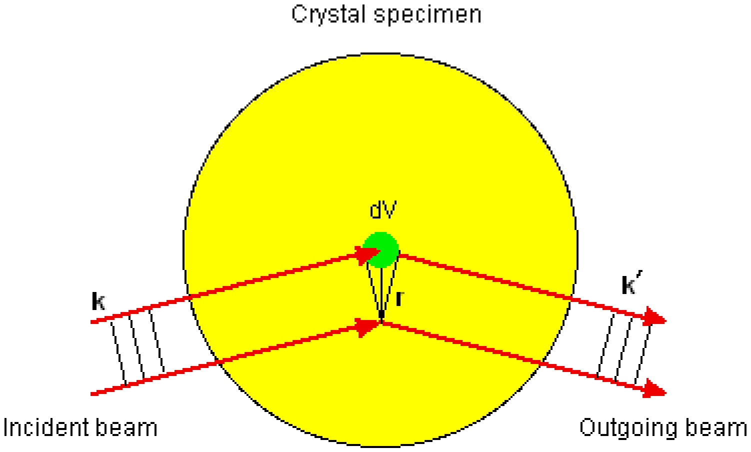


Fig.30 Geometry of the x-ray scattering.

$\mathbf{k}_i = \mathbf{k}$ is the incident wavevector.
$\mathbf{k}_f = \mathbf{k}'$ is the outgoing wavevector.

The difference in phase factor is $\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}]$ between beams scattered from volume elements **r** apart. The amplitude of the wave scattered from a volume element is proportional to the local electron concentration $n(\mathbf{r})$.

The scattering amplitude F is

$$F = \int dv n(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} = \int dv e^{-i\mathbf{Q}\cdot\mathbf{r}} \sum_{\mathbf{G}} n_G e^{i\mathbf{G}\cdot\mathbf{r}}$$

where ***Q*** is the scattering vector

$$\mathbf{Q} = \mathbf{k}' - \mathbf{k}$$

Then F is rewritten as

$$F = \sum_{\mathbf{G}} n_G \int dv e^{i(\mathbf{G}-\mathbf{Q})\cdot\mathbf{r}}$$

$F = n_G V$ for $\mathbf{Q} = \mathbf{k}' - \mathbf{k} = \mathbf{G}$, and $F = 0$ otherwise. This is the Bragg law.

In elastic scattering (energy is conserved), $|\mathbf{k}'| = |\mathbf{k}|$

Then we have

$$\mathbf{k}'^2 = (\mathbf{k}+\mathbf{G})^2 = \mathbf{k}^2 + \mathbf{G}^2 + 2\mathbf{k}\cdot\mathbf{G}$$

or

$$2\mathbf{k}\cdot\mathbf{G} = -\mathbf{G}^2, \qquad \text{or} \qquad (\mathbf{k}+\frac{\mathbf{G}}{2})\cdot\frac{\mathbf{G}}{2} = 0$$

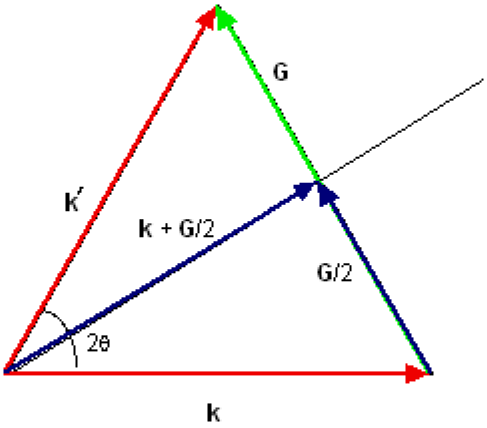


Fig.31 Geometry of **k**, **k′**, and reciprocal lattice vector **G**.

The vector (**k**+**G**/2) is always perpendicular to the vector **G**/2.

6.2 Brillouin zone

If **G** is a reciprocal lattice vector, so is –**G**. With this substitution, we have

$$\mathbf{k} - \mathbf{k}' = \mathbf{G}$$

and

$$(\mathbf{k} - \mathbf{G}/2)\cdot\mathbf{G}/2 = 0.$$

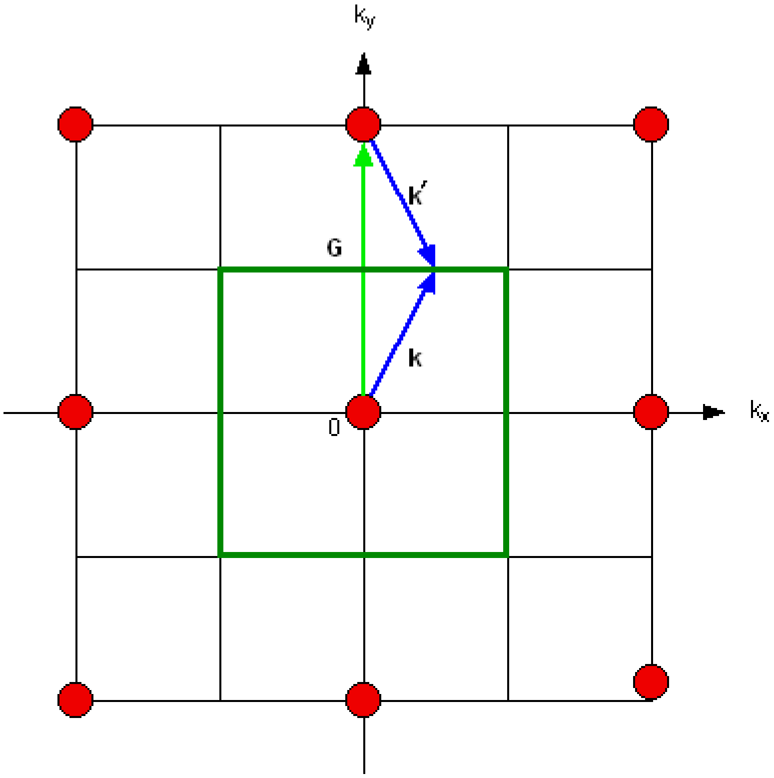


Fig.32 Condition for the Bragg reflection. It is required that the wavevector **k** is located at the zone boundary of the first Brillouin zone in the reciprocal lattice plane. When ***k*** is not on the zone boundary, no Bragg reflection occurs.

We construct a plane normal to **G** at its midpoint. This plane forms a part of the zone boundary. A x-ray beam will be diffracted if its wavevector **k** has the magnitude and direction required by

$$2\mathbf{k}\cdot\mathbf{G}=\mathbf{G}^2$$

The diffracted beam will then be in the direction **k'** = **k** – **G**.

The set of planes that are the perpendicular bisectors of **G** is of general importance in the theory of wave propagation in crystals. The first Brillouin zone is the smallest volume entirely enclosed by planes that are perpendicular bisectors of the reciprocal lattice vectors drawn from the origin.

A wave whose wavevector drawn from the origin terminates on any of these planes will satisfy the condition of diffraction: x-ray, phonon, magnon, and electron.

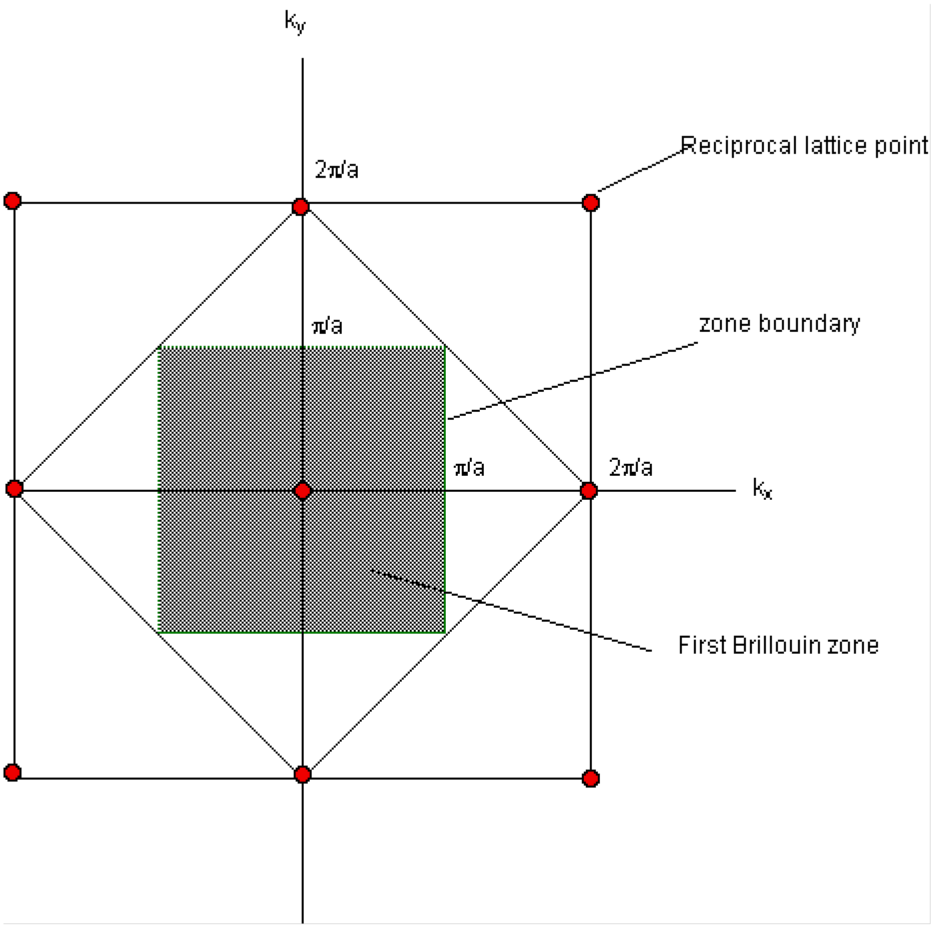
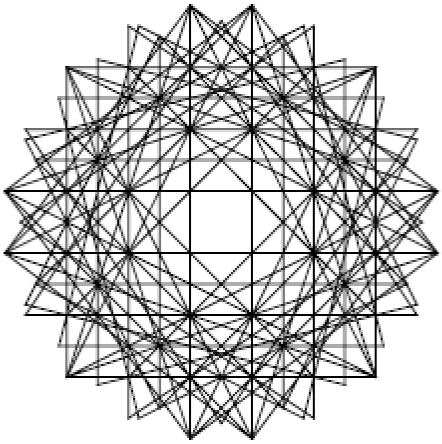


Fig.33 First Brillouin zone for the 2D square lattice (lattice constant *a*).

(a)

Brilloun zone for square lattice with the unit cell of *a* x *a* (by M. Trott)



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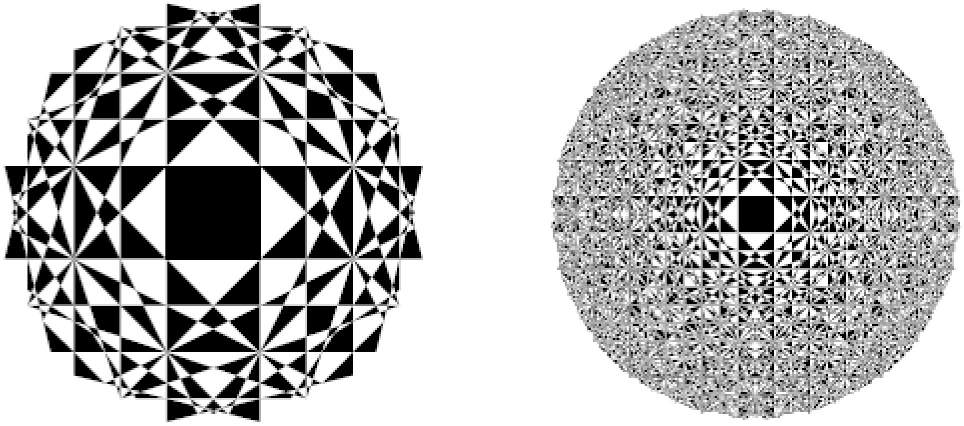
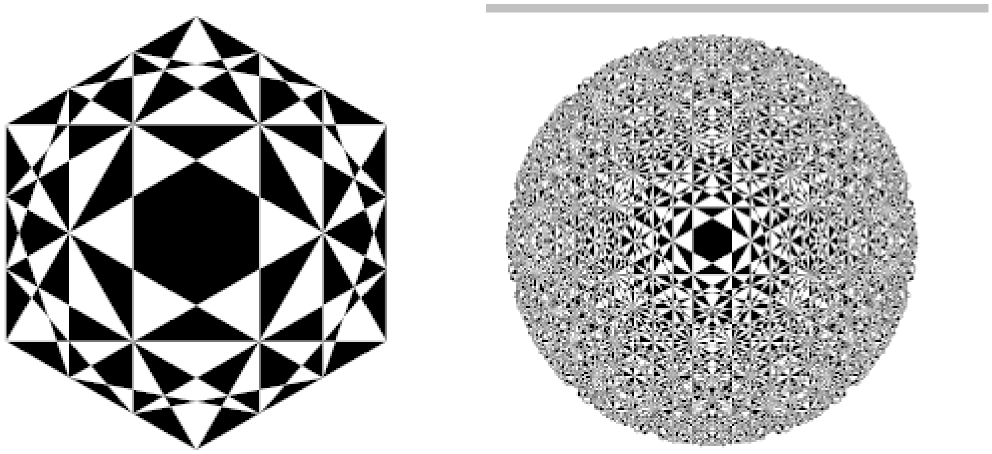


Fig.34, 35, 36
The lines of Fig.34 are perpendicular bisectors (so called bisector lines) of the reciprocal lattice vectors. The first and higher Brillouin zone for the square lattice. See the book of M. Trott, Mathematica Guide Book, Springer 2006) for the detail how to draw them.

(b)

Brillouin zone for the triangular lattice (by M/ Trott).



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[29]=  - Graphics -
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Fig.37, 38
The first and higher Brillouin zone for the triangular (hexagonal) lattice. See the book of M. Trott, Mathematica Guide Book, Springer 2006) for the detail how to draw them.

(c) One dimensional case

We now consider the 1D case of the Brillouin zone

The Bragg condition occurs when $k - k' = 2\pi/a$.

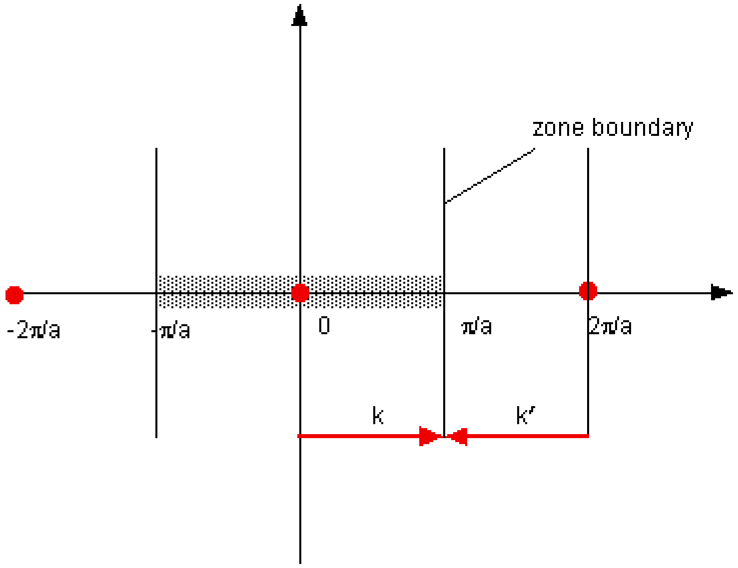


Fig.39 First Brillouin zone for the 1D system with a lattice constant a. Bragg reflection occurs only at $k = \pi/a$.

7. Ewald sphere and scattering

7.1 Construction of Ewald sphere

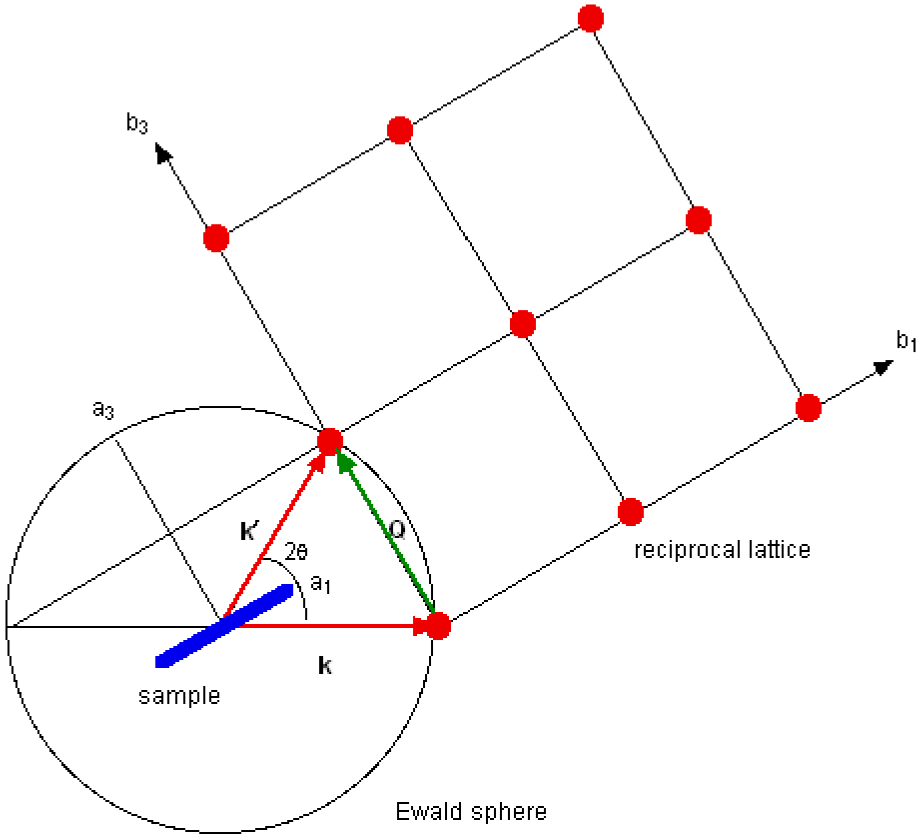


Fig.40 Ewald sphere. The origin of the reciprocal lattice is located at the end of the wavevector **k** of the incident beam.

We draw a sphere of radius $k=2\pi/\lambda$ about the starting point of **k**. The origin of the reciprocal lattice plane corresponding to the real space of the sample is at the end point of **k**. A diffracted beam will be formed if this sphere intersects any other point in the reciprocal lattice. The Ewald sphere intercepts a point connected with the end of **k** by a reciprocal lattice vector **G**. This construction is due to Paul Peter Ewald.

Paul Peter Ewald: He was born in Berlin, Germany on January 23, 1888. He was a U.S. (German-born) crystallographer and physicist. He was a pioneer of the x-ray diffraction methods. He was also the eponym of Ewald construction and the Ewald sphere. He was a Professor of Physics Department, Brooklyn Polytechnic Institute (1949 – 1959), New York. He was the father-in-law of Prof. Hans Bethe (the late). He died at Ithaca, New York on August 22, 1985. He was awarded the Max Planck medal in 1978.

7.2 Experimental configuration

Ω is the angle of sample and 2θ is the angle between the direction of the incident x-ray and the outgoing x-ray.

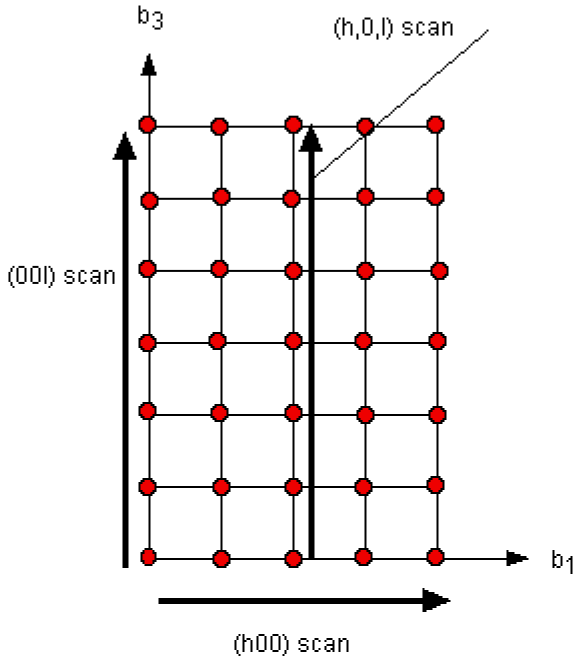
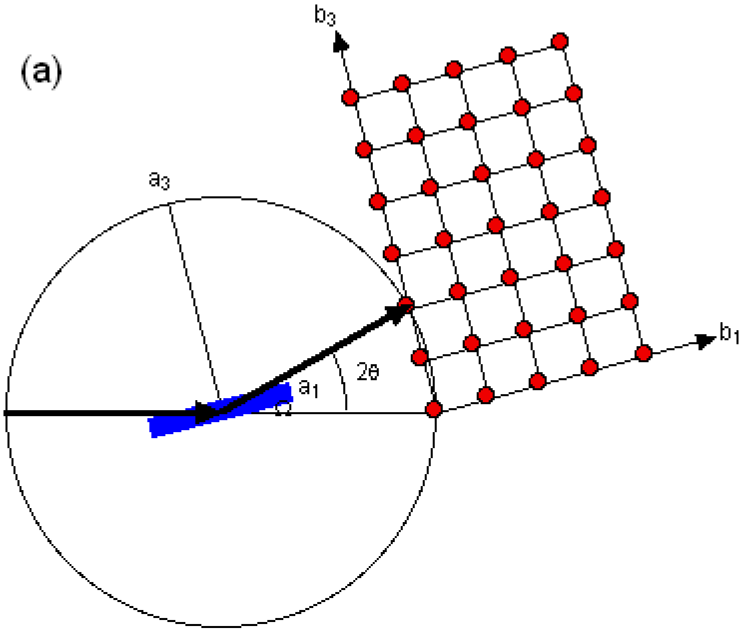


Fig.41 Schematic diagram of (*hkl*) scan for the x-ray scattering experiment.

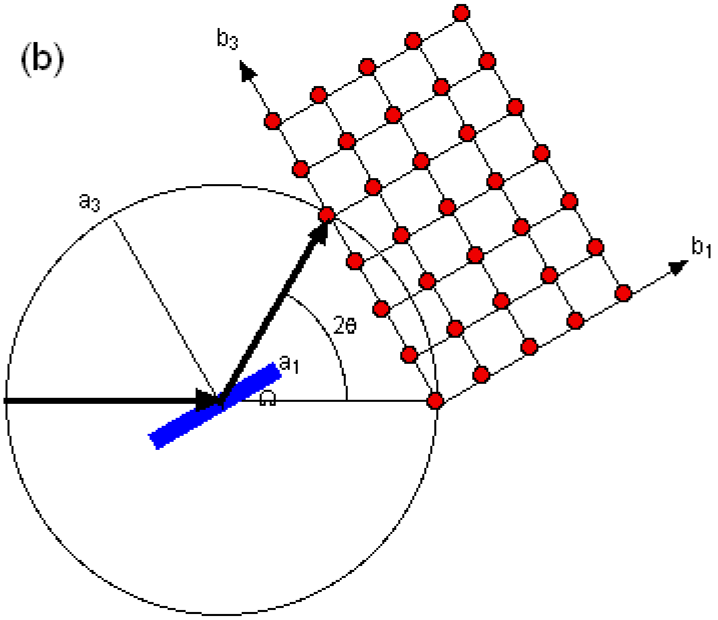
7.2.1. (00*l*) scattering

Ω (= θ) -2θ scan

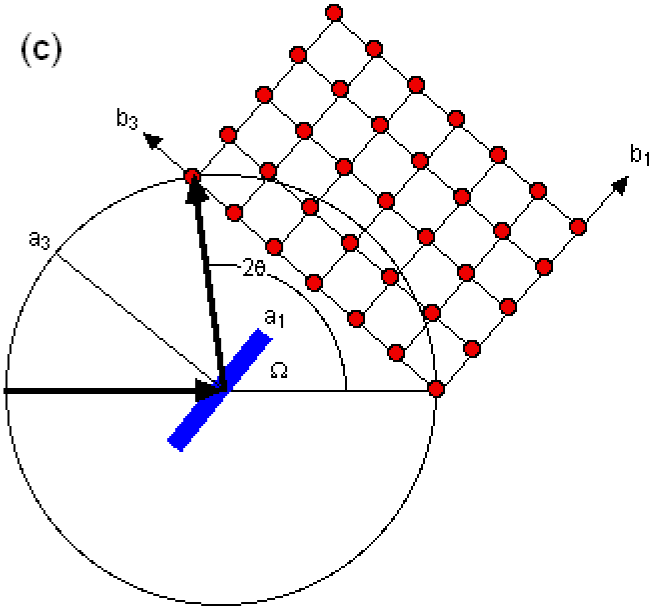
Ewald sphere-1 (θ-2θ scan)



Ewald sphere-2 (θ-2θ scan)



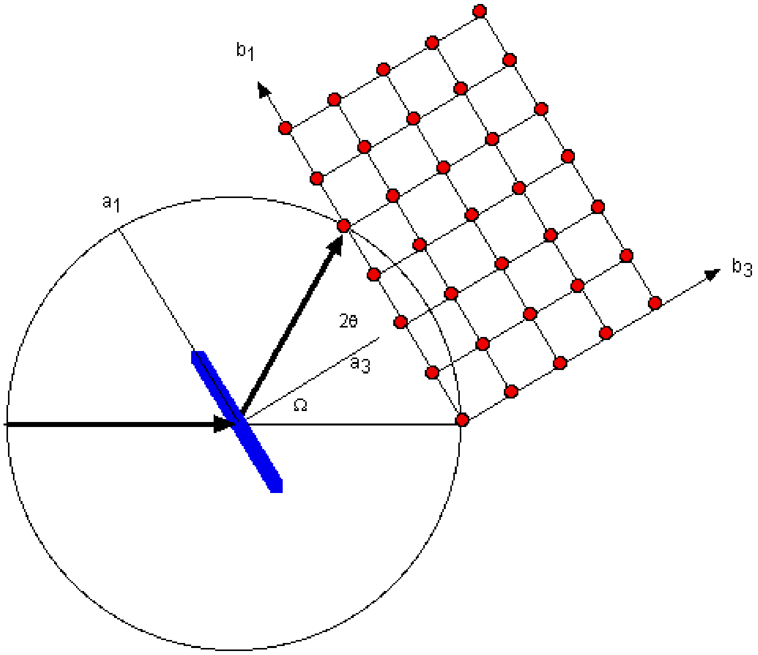
Ewald sphere-3 (θ-2θ scan)



Figs.42 Examples for the Ewald construction for the (00*l*) x-ray diffraction. Ω (= θ) – 2θ scan.

7.2.2 In-plane (*h*, *k*,0) scattering

Ω=(90° +θ) - 2θ scan



Figs.43 Example for the Ewald construction for the (*H*00) x-ray diffraction. Ω (= θ +90°) – 2θ scan.

7.2.3 Rocking curve around (00*l*) Bragg point.

2θ is fixed, while Ω is rotated.

Note that $Q = \frac{4\pi}{\lambda} \sin\theta = const$

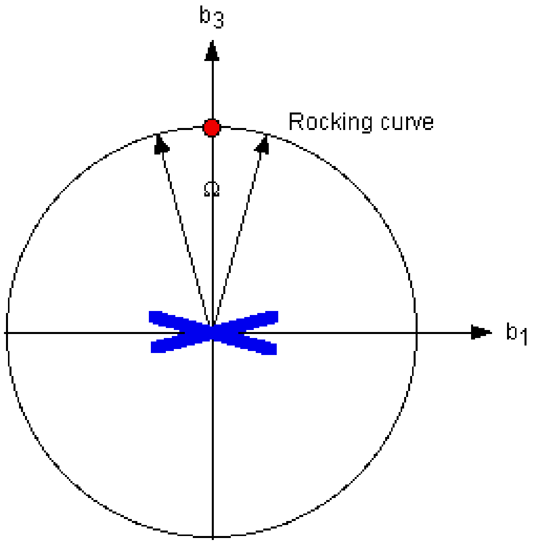


Fig.44 Schematic diagram of the reciprocal plane for the rocking curve experiment.

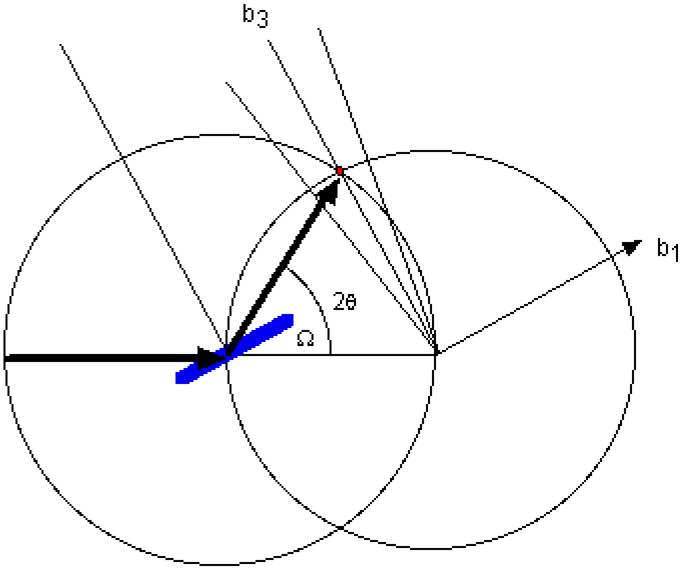


Fig.45 Example for the Ewald construction for the rocking curve where 2θ = fixed. Ω is rotated.

Using this curve, one can estimate the mosaic spread of the sample.

8. X-ray diffraction in Low dimensional systems

8.1 One dimensional system

For the one dimensional system with the lattice constant d, there exist Bragg planes with $k_z = (2\pi/d_c)l$. The Bragg reflections occur on the surface of Ewald sphere where the Bragg planes intersect with the sphere. The incident beam of x-ray is perpendicular to the line of atoms.

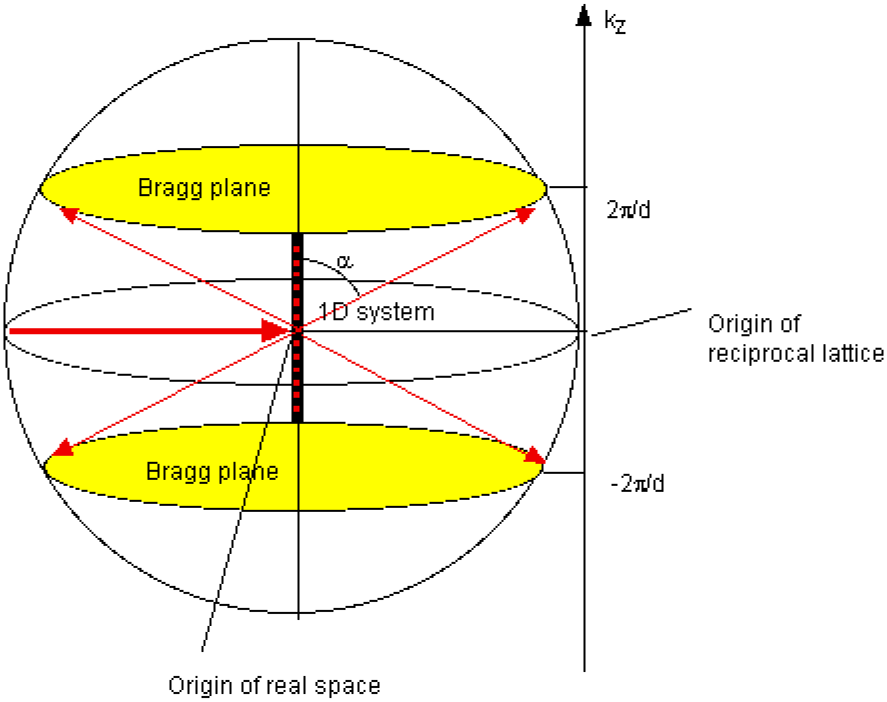


Fig.46 Schematic diagram of the Ewald construction. Because of the 1D chain, there are Bragg planes in the reciprocal lattice plane. The direction of 1D chain is the same as the direction of incident beam.

The interference condition is

$$k\cos\alpha = (2\pi/d)l\,.$$

Since $k = 2\pi/\lambda$, this is rewritten as $(2\pi/\lambda)\cos\alpha = (2\pi/d)l$. or $d\cos\alpha = l\lambda$, where d is the lattice constant of the 1D system, l is an integer, and α is the angle between the diffracted beam and the line of atoms.

We also consider the case when the incident beam of x-ray is parallel to the line of atoms. We note that a 1D system has Bragg planes in the reciprocal lattice. The direction of diffracted beam is determined using the Ewald sphere.

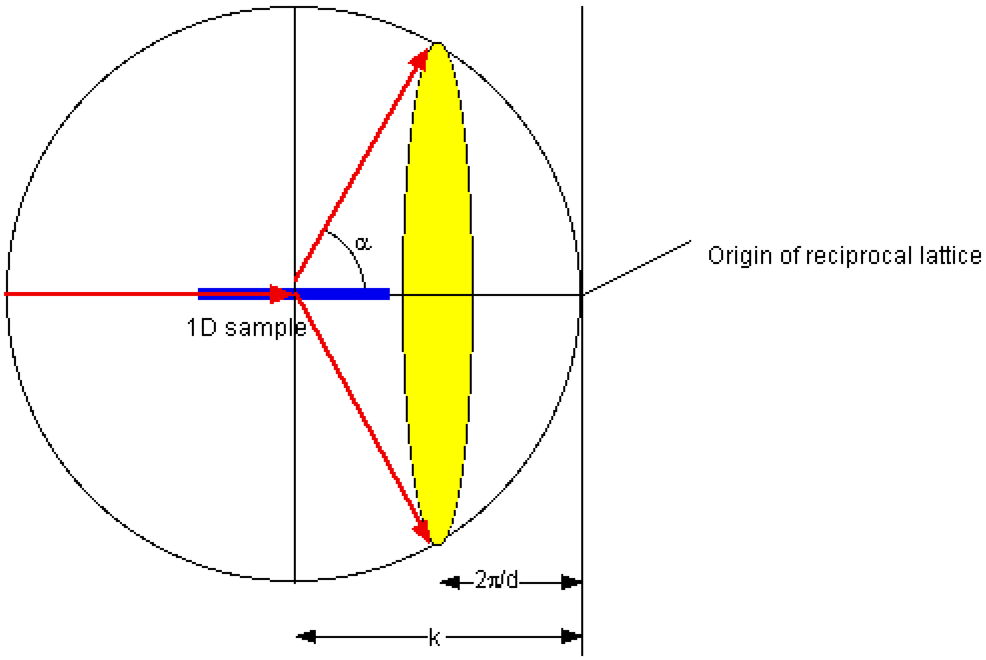


Fig.47 Schematic diagram of the Ewald construction. Because of the 1D chain, there are Bragg planes in the reciprocal lattice plane. The direction of 1D chain is perpendicular to the direction of incident beam.

The interference condition is

$$k(1-\cos\alpha) = (2\pi/d)l.$$

Since $k = 2\pi/\lambda$, this is rewritten as $(2\pi/\lambda)\, 2\sin^2\alpha = (2\pi/a)l$.

or $$2\sin^2\alpha = \frac{\lambda}{d}l,$$

where α is the angle between the diffracted beam and the line of atoms.

8.2 Two dimensional system

A single plane of atoms form a square lattice of lattice constant *a*. The plane is normal to the incident beam. There exist Bragg rods (Bragg ridge). The Bragg reflections occur on the surface of Ewald sphere where the Bragg rods intersect with the sphere.

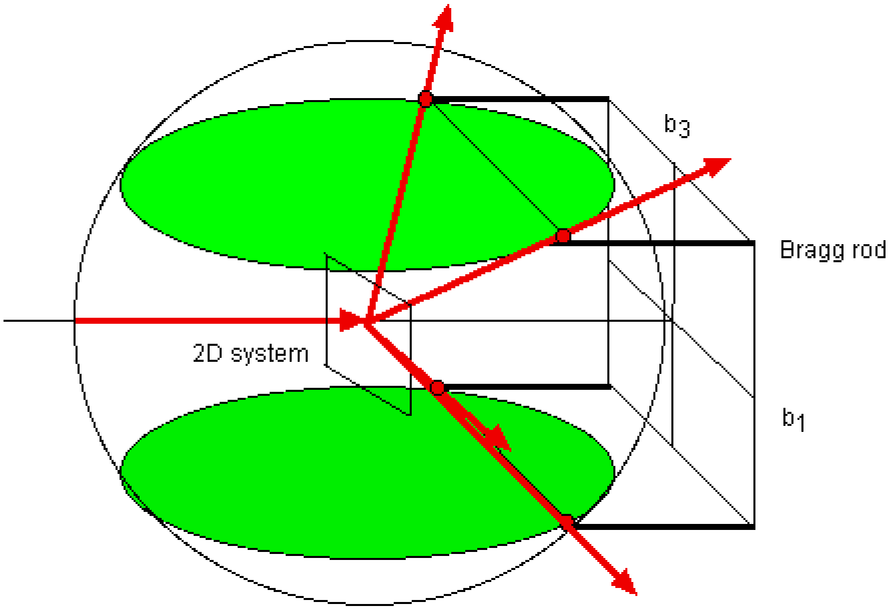


Fig.48 Schematic diagram of the Ewald construction. Because of the 2D system, there are Bragg rods (ridges) in the reciprocal lattice space. The direction of 2D plane is perpendicular to the direction of incident beam.

8.3 Relation between the lattice and reciprocal lattice for the 2D square and hexagonal lattice

For the square lattice, the shape of the lattice and the reciprocal lattice is the same. The rotation angle between these two lattices is equal to 0º.

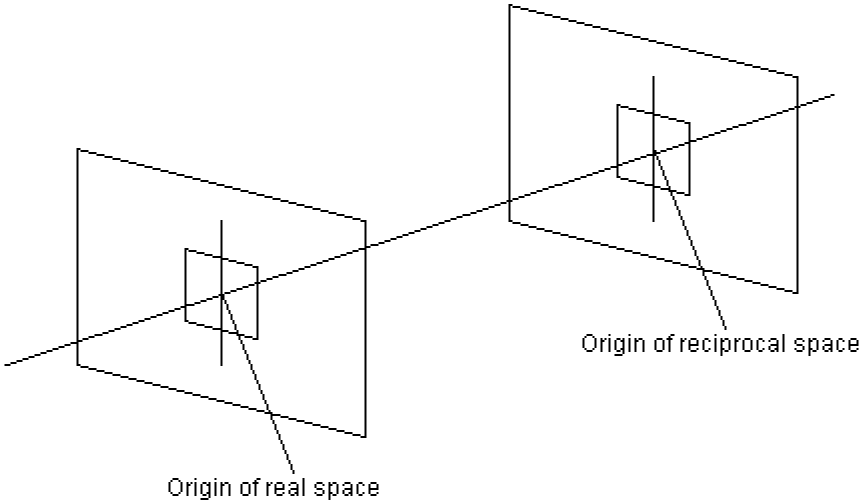


Fig.49 A part of the Ewald sphere diagram. Relation of the real space and the reciprocal space for the 2D square lattice. The rotation angle between the $\mathbf{a}_1$ axis and $\mathbf{b}_1$ axis is 0º.

For the hexadonal lattice, the shape of the lattice and the reciprocal lattice is the same. The rotation angle between these two lattices is equal to 30º.

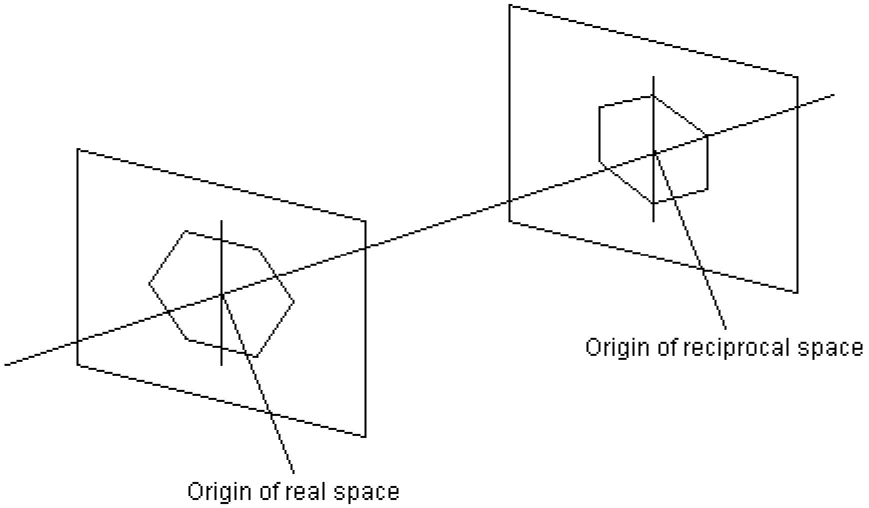


Fig.50 A part of the Ewald sphere diagram. Relation of the real space and the reciprocal space for the 2D triangular (hexagonal) lattice. The rotation angle between the $\mathbf{a}_1$ axis and $\mathbf{b}_1$ axis is 30º.

REFRENCES

1. C. Kittel, Introduction to Solid State Physics, Fourth Edition (John Wiledy & Sons, New York 1971).
2. M. Trott, Matheamtica Guided Book, vol 1 – 4 (Programming, Graphics, Numerics, and Symmbols (Springer Verlag, 2005-2006, New York).