

**Problems and solutions**  
**x-ray diffraction**  
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**1. Reciprocal lattice and Brillouin zone**

The primitive translation vectors of the hexagonal space lattice may be taken as

$$\mathbf{a}_1 = \frac{\sqrt{3}}{2} a \hat{x} + \frac{1}{2} a \hat{y}; \quad \mathbf{a}_2 = -\frac{\sqrt{3}}{2} a \hat{x} + \frac{1}{2} a \hat{y}, \quad \mathbf{a}_3 = c \hat{z},$$

where  $\hat{x}$ ,  $\hat{y}$ , and  $\hat{z}$  are unit vector in the Cartesian coordinate, and  $a$  and  $c$  are lattice constants.

- (a) Show that the volume of the primitive cell is  $\frac{\sqrt{3}}{2} a^2 c$ .
- (b) Show that the primitive translations of the reciprocal lattice are

$$\mathbf{b}_1 = \frac{2\pi}{\sqrt{3}a} \hat{x} + \frac{2\pi}{a} \hat{y}, \quad \mathbf{b}_2 = -\frac{2\pi}{\sqrt{3}a} \hat{x} + \frac{2\pi}{a} \hat{y}, \quad \mathbf{b}_3 = \frac{2\pi}{c} \hat{z},$$

so that the lattice is its own reciprocal, but with a rotation of axes.

- (c) Describe and sketch the first Brillouin zone of the hexagonal space lattice.

**((Solution))**

Hexagonal, space lattice

$$\mathbf{a}_1 = \frac{\sqrt{3}}{2} a \hat{x} + \frac{1}{2} a \hat{y}, \quad \mathbf{a}_2 = -\frac{\sqrt{3}}{2} a \hat{x} + \frac{1}{2} a \hat{y}, \quad \mathbf{a}_3 = c \hat{z}$$

- (a) The volume of the primitive cell is

$$V_c = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \begin{vmatrix} \frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \\ -\frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \\ 0 & 0 & c \end{vmatrix} = \frac{\sqrt{3}}{2} a^2 c$$

- (b)

$$\begin{aligned}
\mathbf{b}_1 &= \frac{2\pi}{V_c} (\mathbf{a}_2 \times \mathbf{a}_3) \\
&= \frac{2\pi}{\frac{\sqrt{3}}{2} a^2 c} \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \sqrt{3}a & a & 0 \\ 0 & 0 & c \end{vmatrix} \\
&= \frac{2\pi}{a} \left( \frac{1}{\sqrt{3}} \hat{x} + \hat{y} \right)
\end{aligned}$$

$$\begin{aligned}
\mathbf{b}_2 &= \frac{2\pi}{V_c} (\mathbf{a}_3 \times \mathbf{a}_1) \\
&= \frac{2\pi}{\frac{\sqrt{3}}{2} a^2 c} \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ 0 & 0 & c \\ \frac{\sqrt{3}a}{2} & \frac{a}{2} & 0 \end{vmatrix} \\
&= \frac{2\pi}{a} \left( -\frac{1}{\sqrt{3}} \hat{x} + \hat{y} \right)
\end{aligned}$$

$$\begin{aligned}
\mathbf{b}_3 &= \frac{2\pi}{V_c} (\mathbf{a}_1 \times \mathbf{a}_2) \\
&= \frac{2\pi}{\frac{\sqrt{3}}{2} a^2 c} \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \sqrt{3}a & a & 0 \\ \frac{2}{\sqrt{3}a} & \frac{a}{2} & 0 \end{vmatrix} \\
&= \frac{2\pi}{c} \hat{z}
\end{aligned}$$

## 2. x-ray diffraction (diamond)

The crystal structure of diamond is described in Fig.1. The basis consists of eight atoms if the cell is taken as the conventional cube. (a) Find the structure factor  $S$  of this basis, where the structure factor  $S$  is given by

$$S = \sum_j f_C \exp(-i\mathbf{G} \cdot \mathbf{R}_j).$$

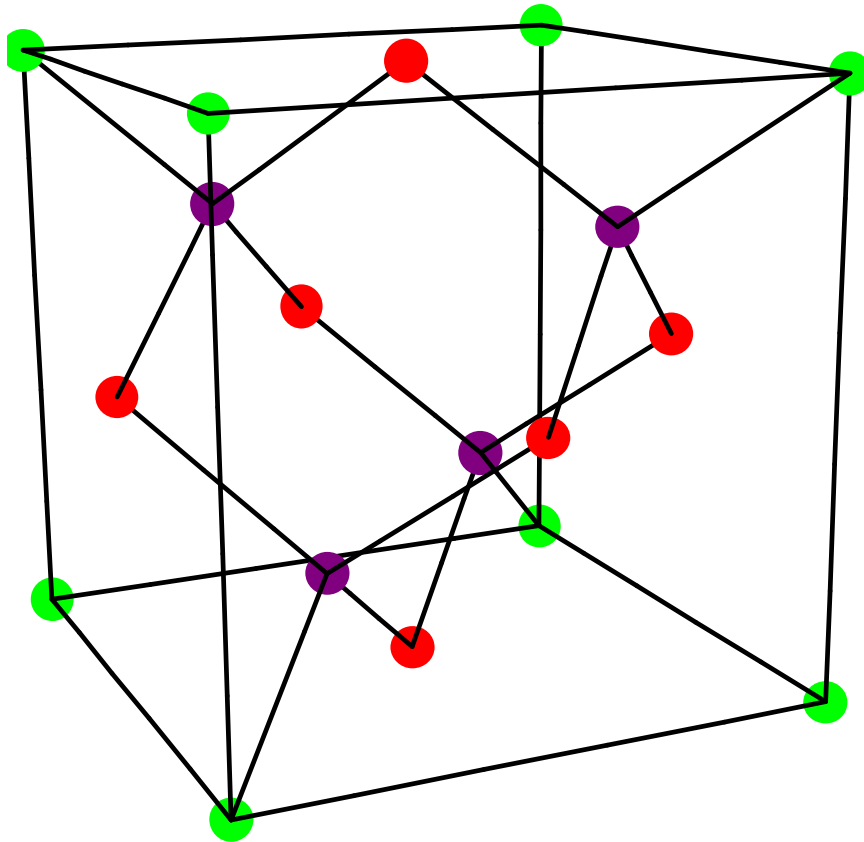
where  $f_C$  is the atomic form factor of C atom, and  $\mathbf{G}$  is the reciprocal lattice vector.

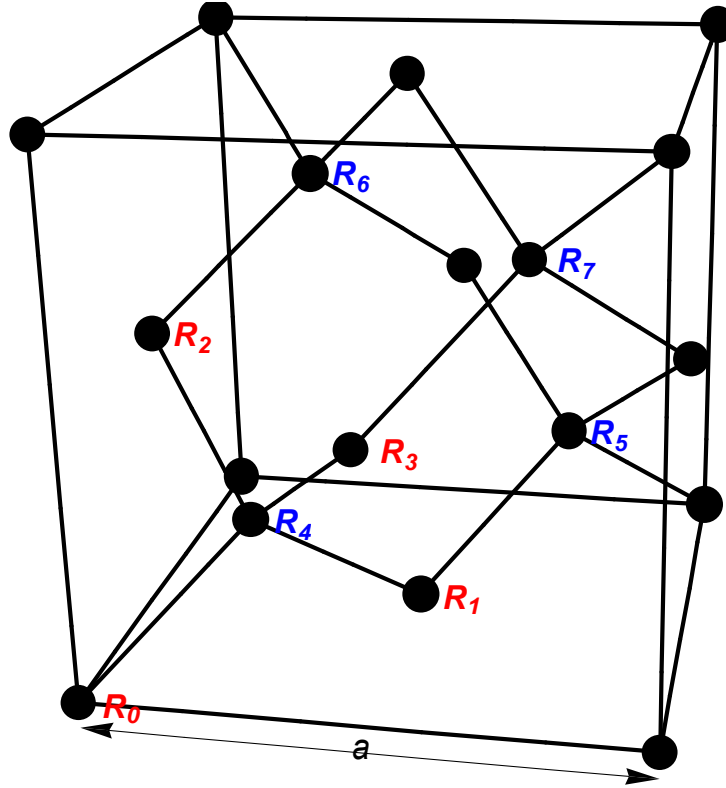
(b) Find the zeros of  $S$  and show that the allowed reflections of the diamond structure satisfy  $v_1 + v_2 + v_3 = 4n$ , where all indices are even ( $n$  is any integer), and satisfy  $v_1 + v_2 + v_3 = 4n \pm 1$ , where all indices are odd. (Notice that  $h, k, l$  may be written for  $v_1, v_2, v_3$  and this is often done.)

**Hint:** The reciprocal lattice for the conventional cubic cell is given by

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$$

with  $\mathbf{b}_1 = \frac{2\pi}{a} \mathbf{e}_x$ ,  $\mathbf{b}_2 = \frac{2\pi}{a} \mathbf{e}_y$ , and  $\mathbf{b}_3 = \frac{2\pi}{a} \mathbf{e}_z$ ,  $a$  is the lattice constant of the conventional cubic cell, and  $\mathbf{e}_x, \mathbf{e}_y$ , and  $\mathbf{e}_z$  are the unit vectors in the Cartesian co-ordinate.





**Fig.** Crystal structure of diamond in the conventional cubic unit cell with the lattice constant  $a$ . There are 8 C atoms in this cell. The positions are given by

$$\mathbf{R}_0 = (0,0,0), \quad \mathbf{R}_1 = \left(\frac{1}{2}, \frac{1}{2}, 0\right), \quad \mathbf{R}_2 = \left(0, \frac{1}{2}, \frac{1}{2}\right), \quad \mathbf{R}_3 = \left(\frac{1}{2}, 0, \frac{1}{2}\right),$$

$$\mathbf{R}_4 = \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right), \quad \mathbf{R}_5 = \left(\frac{3}{4}, \frac{3}{4}, \frac{1}{4}\right) = \mathbf{R}_4 + \mathbf{R}_1, \quad \mathbf{R}_6 = \left(\frac{1}{4}, \frac{3}{4}, \frac{3}{4}\right) = \mathbf{R}_4 + \mathbf{R}_2$$

$$\mathbf{R}_7 = \left(\frac{3}{4}, \frac{1}{4}, \frac{3}{4}\right) = \mathbf{R}_4 + \mathbf{R}_3$$

**((Solution))**

The structure factor  $S$  is given by

$$S = f_C \sum_j \exp(-i\mathbf{G} \cdot \mathbf{R}_j),$$

where  $f_C$  is the atomic form factor of C atom.  $\mathbf{G}$  is the reciprocal lattice vector for the conventional cubic unit cell with side  $a$ ,

$$\mathbf{G} = \nu_1 \mathbf{b}_1 + \nu_2 \mathbf{b}_2 + \nu_3 \mathbf{b}_3 = \frac{2\pi}{a}(\nu_1, \nu_2, \nu_3),$$

with  $\mathbf{b}_1 = \frac{2\pi}{a} \mathbf{e}_x$ ,  $\mathbf{b}_2 = \frac{2\pi}{a} \mathbf{e}_y$ , and  $\mathbf{b}_3 = \frac{2\pi}{a} \mathbf{e}_z$ . In each cubic unit cell, there are 8 atoms

$$\mathbf{R}_0 = (0,0,0), \quad \mathbf{R}_1 = \left(\frac{1}{2}, \frac{1}{2}, 0\right), \quad \mathbf{R}_2 = \left(0, \frac{1}{2}, \frac{1}{2}\right), \quad \mathbf{R}_3 = \left(\frac{1}{2}, 0, \frac{1}{2}\right),$$

$$\mathbf{R}_4 = \left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right) = \mathbf{R}_1 + \mathbf{R}_0, \quad \mathbf{R}_5 = \left(\frac{3}{4}, \frac{3}{4}, \frac{1}{4}\right) = \mathbf{R}_1 + \mathbf{R}_2,$$

$$\mathbf{R}_6 = \left(\frac{1}{4}, \frac{3}{4}, \frac{3}{4}\right) = \mathbf{R}_1 + \mathbf{R}_2, \quad \mathbf{R}_7 = \left(\frac{3}{4}, \frac{1}{4}, \frac{3}{4}\right) = \mathbf{R}_1 + \mathbf{R}_3$$

in the units of  $a$ . Then we get the expression of  $S$  as

$$\begin{aligned} S &= [\exp(-i\mathbf{G} \cdot \mathbf{R}_0) + \exp(-i\mathbf{G} \cdot \mathbf{R}_1) + \exp(-i\mathbf{G} \cdot \mathbf{R}_2) + \exp(-i\mathbf{G} \cdot \mathbf{R}_3)] \\ &\quad + f_c [\exp(-i\mathbf{G} \cdot \mathbf{R}_0) + \exp(i\mathbf{G} \cdot \mathbf{R}_1) + \exp(-i\mathbf{G} \cdot \mathbf{R}_2) + \exp(-i\mathbf{G} \cdot \mathbf{R}_3)] \exp(-i\mathbf{G} \cdot \mathbf{R}_4) \\ &= f_c [1 + \exp(-i\mathbf{G} \cdot \mathbf{R}_4)] [\exp(-i\mathbf{G} \cdot \mathbf{R}_0) + \exp(-i\mathbf{G} \cdot \mathbf{R}_1) + \exp(-i\mathbf{G} \cdot \mathbf{R}_2) + \exp(-i\mathbf{G} \cdot \mathbf{R}_3)] \end{aligned}$$

The second term is the fcc structure factor.  $S$  can be rewritten as

$$\begin{aligned} S &= f_c \{1 + \exp[-i\frac{\pi}{2}(\nu_1 + \nu_2 + \nu_3)]\} \{1 + \exp[-i\pi(\nu_1 + \nu_2)] + \exp[-i\pi(\nu_2 + \nu_3)] \\ &\quad + \exp[-i\pi(\nu_3 + \nu_1)]\} \\ &= f_c S(\text{basis}) S(\text{fcc}) \end{aligned}$$

where

$$S(\text{basis}) = 1 + \exp[-i\frac{\pi}{2}(\nu_1 + \nu_2 + \nu_3)],$$

$$S(\text{fcc}) = 1 + \exp[-i\pi(\nu_1 + \nu_2)] + \exp[-i\pi(\nu_2 + \nu_3)] + \exp[-i\pi(\nu_3 + \nu_1)].$$

(b)

(i) Evaluation of  $S(\text{basis})$

$$S(\text{basis}) = 2 \quad \text{for} \quad \nu_1 + \nu_2 + \nu_3 = 4n.$$

$$S(\text{basis}) = 1 - i \quad \text{for} \quad v_1 + v_2 + v_3 = 4n + 1.$$

$$S(\text{basis}) = 0 \quad \text{for} \quad v_1 + v_2 + v_3 = 4n + 2.$$

$$S(\text{basis}) = 1 + i \quad \text{for} \quad v_1 + v_2 + v_3 = 4n - 1.$$

(ii) Product of  $S(\text{fcc})$  and  $S(\text{basis})$

If all indices are even,  $S(\text{fcc}) = 4$

$$v_1 + v_2 + v_3 = 4n \quad S(\text{basis}) = 2$$

$$v_1 + v_2 + v_3 = 4n + 2 \quad S(\text{basis}) = 0 \quad 5$$

If all indices are odd,  $S(\text{fcc}) = 4$

$$v_1 + v_2 + v_3 = 4n + 1, \quad S(\text{basis}) = 1 - i$$

$$v_1 + v_2 + v_3 = 4n - 1, \quad S(\text{basis}) = 1 + i$$

If one of indices is odd and the other two indices are even 5

$$S(\text{fcc}) = 0$$

If one of indices is even and other two indices are odd 5

$$S(\text{fcc}) = 0$$

The selection rule for diamond are compared with the data of neutron power diffraction

$$(111) \quad S_1 S_2 = 4(1 + i)$$

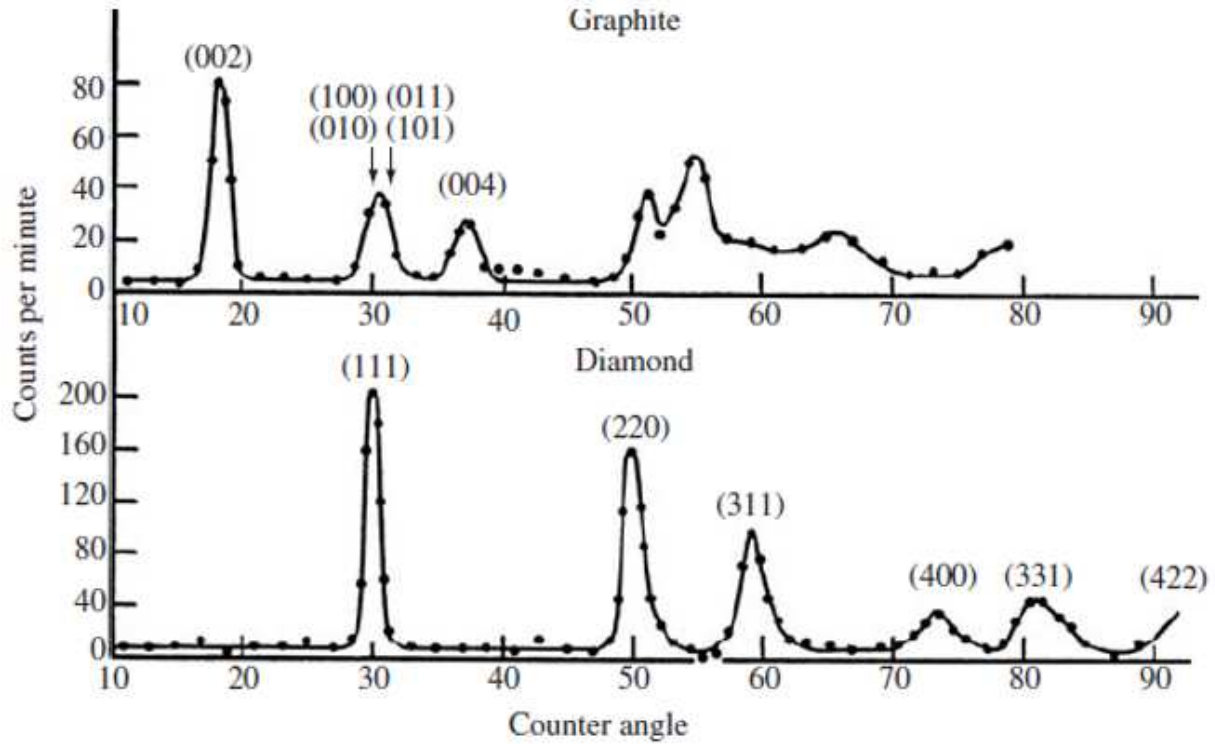
$$(220) \quad S_1 S_2 = 8$$

$$(311) \quad S_1 S_2 = 4(1 - i)$$

$$(400) \quad S_1 S_2 = 8$$

$$(331) \quad S_1 S_2 = 4(1 + i)$$

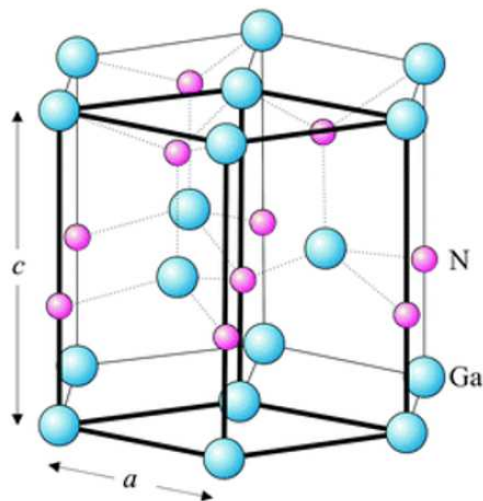
$$(422) \quad S_1 S_2 = 8$$



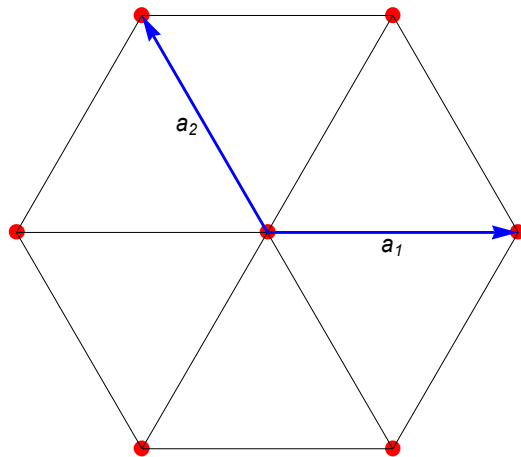
**Fig.** Neutron powder diffraction patterns recorded from powdered graphite and diamond (reproduced from Wollan and Shull, 1948)

### 3. Structure of GaN

A model of GaN crystal is given in the figure below. It has a hexagonal lattice with  $a_1 = a_2 = a$  and  $a_3 = c$ .



**Fig.** Crystal structure of GaN.



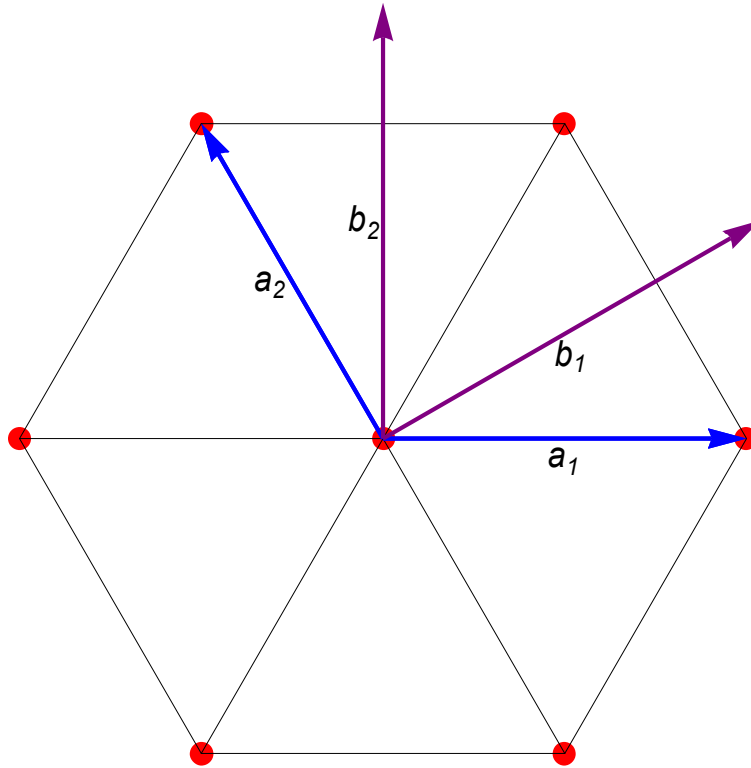
**Fig.** Hexagonal in-plane structure with the primitive lattice vectors  $a_1$  and  $a_2$ .

- (a) Write down the explicit expressions of a set of the basis vectors  $a_1$ ,  $a_2$ ,  $a_3$  in Cartesian co-ordinates, which form the unit cell of this crystal.
- (b) Write down the explicit expressions of a set of primitive reciprocal lattice vectors  $b_1$ ,  $b_2$ , and  $b_3$  in Cartesian co-ordinates (in terms of  $a$  and  $c$ ).
- (c) Draw the first Brillouin zone.
- (d) Find the volume of the first Brillouin zone in terms of  $a$  and  $c$ .
- (e) How many atoms of each kind are in the basis of this crystal structure?

**((Solution))**

- (a)





**Fig.** In-plane (hexagonal) structure of GaN.  $\mathbf{b}_1$  and  $\mathbf{b}_2$  are the reciprocal lattice vector.  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are the primitive lattice vector.

(a) In the above figure, we have  $\mathbf{a}_1 = a \mathbf{e}_x$ ,  $\mathbf{a}_2 = -\frac{1}{2}a \mathbf{e}_x + \frac{\sqrt{3}}{2}a \mathbf{e}_y$ ,

Since  $\mathbf{a}_1 \cdot \mathbf{b}_1 = \mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi$ , and  $\mathbf{a}_1 \cdot \mathbf{b}_2 = \mathbf{a}_2 \cdot \mathbf{b}_1 = 0$

$$\mathbf{a}_1 \cdot \mathbf{b}_1 = 2\pi \quad a_1 b_1 \cos(30^\circ) = 2\pi$$

leading to

$$b_1 = \frac{2\pi}{a_1 \cos(30^\circ)} = \frac{4\pi}{\sqrt{3}a}$$

$$\mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi \quad a_2 b_2 \cos(30^\circ) = 2\pi$$

leading to

$$b_2 = \frac{2\pi}{a_2 \cos(30^\circ)} = \frac{4\pi}{\sqrt{3}a}$$

Thus we have

$$\mathbf{b}_1 = \frac{4\pi}{\sqrt{3}a}(\cos 30^\circ, \sin 30^\circ, 0) = \frac{4\pi}{\sqrt{3}a}\left(\frac{\sqrt{3}}{2}, \frac{1}{2}, 0\right)$$

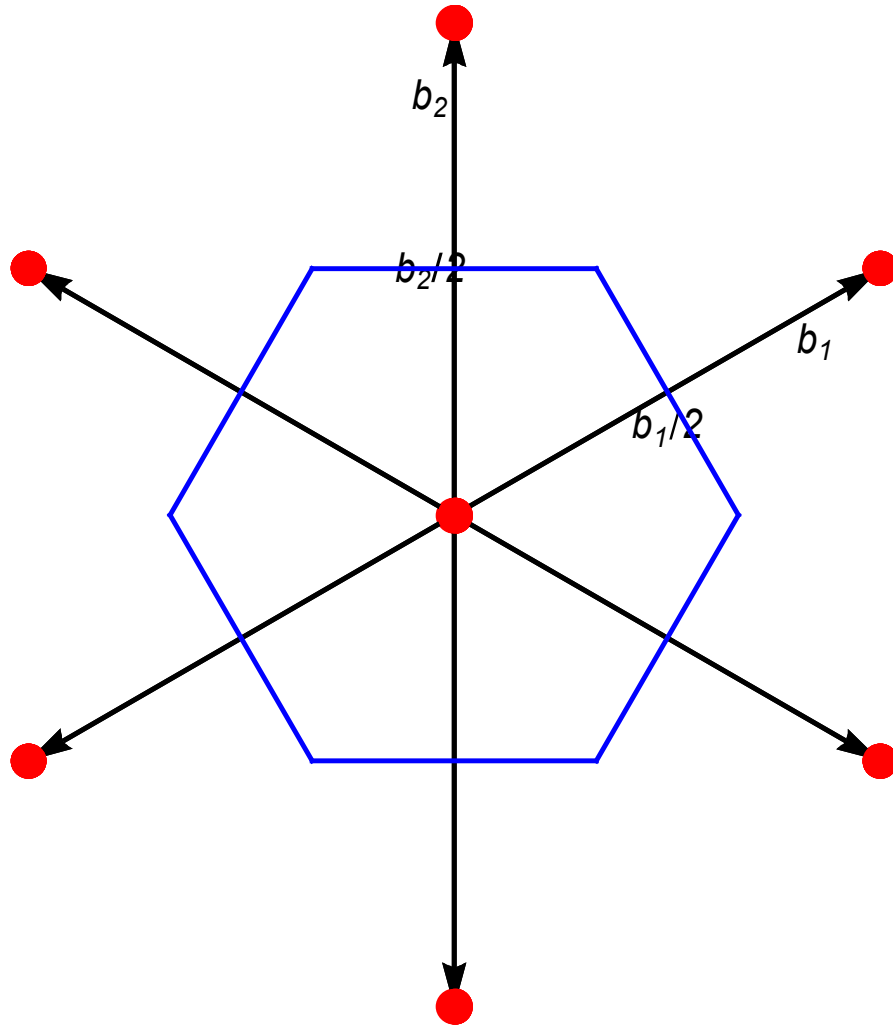
$$\mathbf{b}_2 = \frac{4\pi}{\sqrt{3}a}(\cos 90^\circ, \sin 90^\circ, 0) = \frac{4\pi}{\sqrt{3}a}(0, 1, 0)$$

Since  $\mathbf{a}_3 \cdot \mathbf{b}_3 = 2\pi$ , we have  $b_3 = \frac{2\pi}{c}$ , or

$$\mathbf{b}_3 = \left(0, 0, \frac{2\pi}{c}\right)$$

**(b) The first Brillouin zone**

The first Brillouin zone of the hexagonal lattice is also a hexagonal structure. The cross section of the Brillouin zone in  $(k_x, k_y)$  plane is illustrated by the shaded area in Fig. Sweep this shaded area along  $k_z$  axis from  $k_z = -\frac{\pi}{c}$  to  $k_z = \frac{\pi}{c}$ , we get the whole first Brillouin zone.



**Fig.** First Brillouin zone in the  $(k_x, k_y)$  plane.

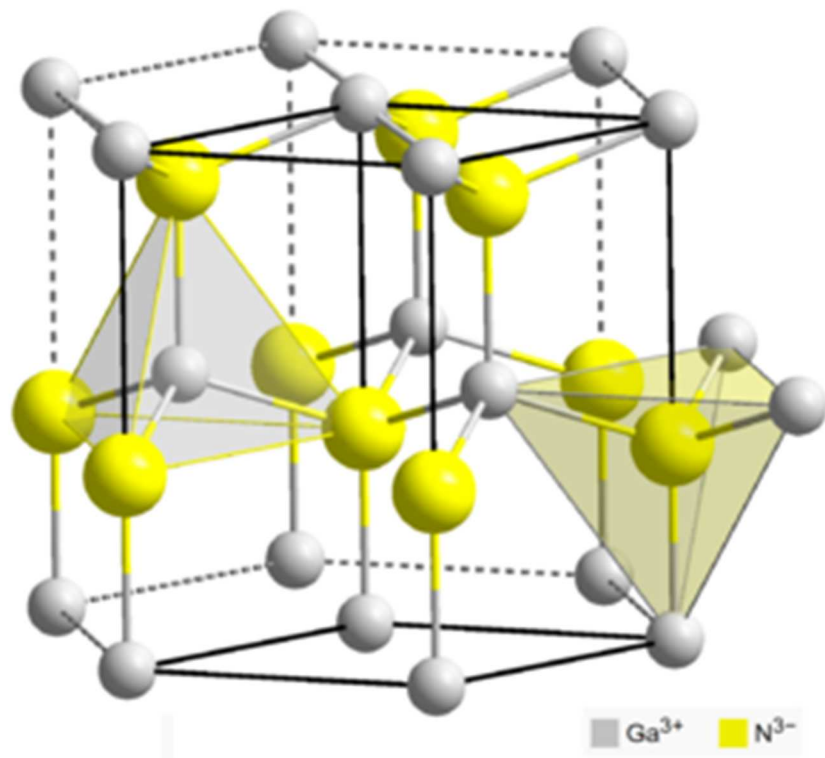
**(c) The volume of the first Brillouin zone**

$$\Omega = (|\mathbf{b}_1||\mathbf{b}_2|\sin 60^\circ)|\mathbf{b}_3| = \left(\frac{4\pi}{\sqrt{3}a}\right)^2 \frac{\sqrt{3}}{2} \frac{2\pi}{c} = \frac{(2\pi)^3}{a^2c} \frac{2\sqrt{3}}{3}$$

or

$$\Omega = (\mathbf{b}_1 \times \mathbf{b}_2) \cdot \mathbf{b}_3 = \begin{vmatrix} \frac{4\pi}{\sqrt{3}a} \left(\frac{\sqrt{3}}{2}\right) & \frac{4\pi}{\sqrt{3}a} \frac{1}{2} & 0 \\ 0 & \frac{4\pi}{\sqrt{3}a} & 0 \\ 0 & 0 & \frac{2\pi}{c} \end{vmatrix} = \frac{2\pi}{c} \left(\frac{4\pi}{\sqrt{3}a}\right)^2 \frac{\sqrt{3}}{2} = \frac{(2\pi)^3}{a^2 c} \frac{2\sqrt{3}}{3}$$

- (d) As shown in the figure below there are two 2 atoms of each kind per unit cell (denoted by black thick lines).



#### 4. X-ray powder diffraction of GaN)

In order to solve this problem, first you need to solve the **problem-2 (a)**.

- Calculate the primitive reciprocal lattice vectors  $\mathbf{b}_1$ ,  $\mathbf{b}_2$ , and  $\mathbf{b}_3$  in Cartesian coordinates (in terms of  $a$  and  $c$ ) for GaN structure.
- Suppose that we have a powdered x-ray diffraction of GaN. The reciprocal lattice vector  $\mathbf{G}$  is defined by

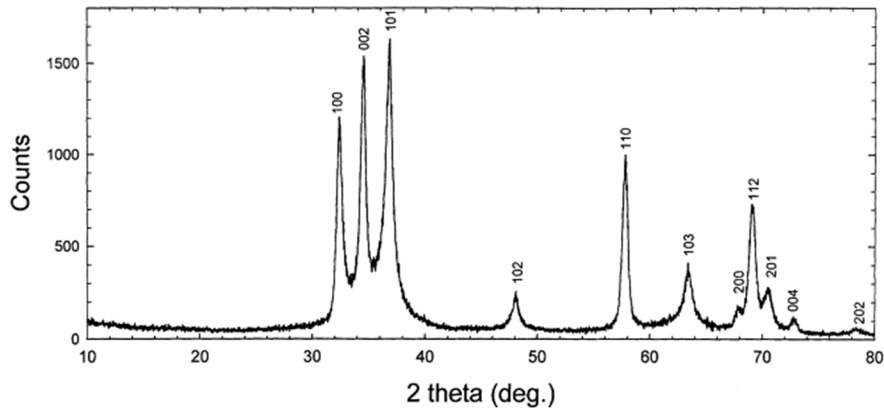
$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \quad (h, k, l: \text{integers}).$$

Calculate the magnitude  $|\mathbf{G}|$  in terms of  $h, k, l, a,$  and  $c$ .

(c) In the powder x-ray diffraction, the Bragg reflection occurs when the condition

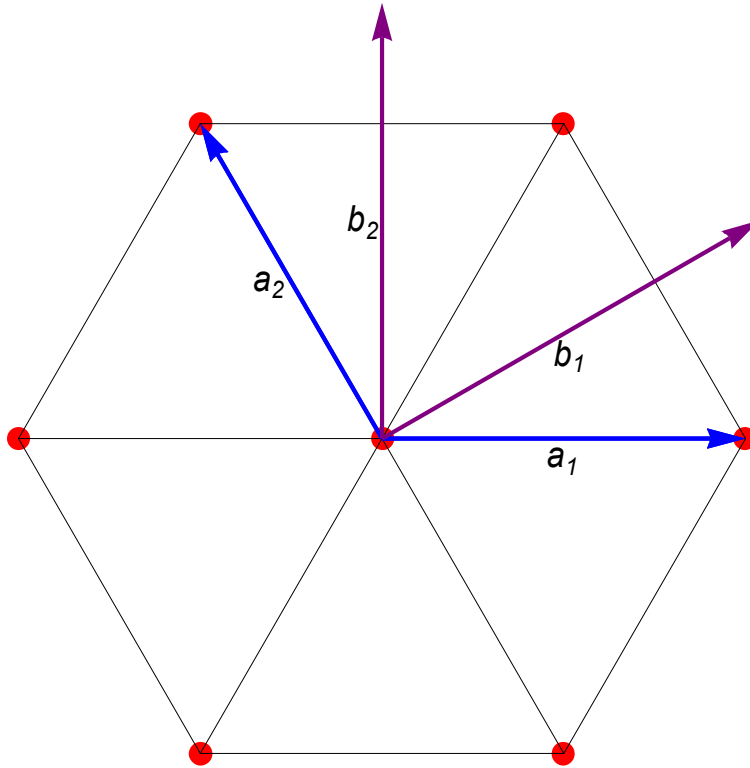
$$|\mathbf{Q}| = \frac{4\pi}{\lambda} \sin \theta = |\mathbf{G}|,$$

is satisfied, where  $\mathbf{Q}$  is the scattering vector,  $\lambda$  is the wave-length of x-ray (CuK $\alpha$  line, 1.54184Å). In GaN, we have  $a = 3.186 \text{ \AA}$  and  $c = 5.186 \text{ \AA}$ . Calculate the scattering angle ( $2\theta$ ) for typical indices ( $h, k, l$ ) and compare your result with the experimental result (powder x-ray diffraction of GaN with CuK $\alpha$ ) shown below.



**Fig.** Powder x-ray diffraction of GaN. The x-ray intensity vs the scattering angle  $2\theta$ .

**((Solution))**



**Fig.** The relation between the reciprocal lattice vectors and lattice vectors.

$$a = 3.186 \text{ \AA}, \quad c = 5.186 \text{ \AA}, \quad \lambda = 1.54184 \text{ \AA} \text{ (CuK}\alpha \text{ line)}$$

**(a)**

$$\mathbf{a}_1 \cdot \mathbf{b}_1 = 2\pi \quad a_1 b_1 \cos(30^\circ) = 2\pi$$

leading to

$$b_1 = \frac{2\pi}{a_1 \cos(30^\circ)} = \frac{4\pi}{\sqrt{3}a}$$

$$\mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi \quad a_2 b_2 \cos(30^\circ) = 2\pi$$

leading to

$$b_2 = \frac{2\pi}{a_2 \cos(30^\circ)} = \frac{4\pi}{\sqrt{3}a}$$

Thus we have

$$\mathbf{b}_1 = \frac{4\pi}{\sqrt{3}a}(\cos 30^\circ, \sin 30^\circ) = \frac{4\pi}{\sqrt{3}a}\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)$$

$$\mathbf{b}_2 = \frac{4\pi}{\sqrt{3}a}(\cos 90^\circ, \sin 90^\circ) = \frac{4\pi}{\sqrt{3}a}(0, 1)$$

(b)

The reciprocal lattice vector:

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

where  $h$ ,  $k$ , and  $l$  are integers. We note that

$$\mathbf{b}_1 \cdot \mathbf{b}_3 = 0, \quad \mathbf{b}_2 \cdot \mathbf{b}_3 = 0, \quad b_3 = \frac{2\pi}{c}$$

$$\mathbf{b}_1 \cdot \mathbf{b}_2 = b_1^2 \cos(60^\circ) = \frac{1}{2}b_1^2$$

Then we have

$$\begin{aligned} |\mathbf{G}|^2 &= (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \cdot (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \\ &= h^2 b_1^2 + 2hk\mathbf{b}_1 \cdot \mathbf{b}_2 + k^2 b_2^2 + l^2 b_3^2 \\ &= (h^2 + hk + k^2)b_1^2 + l^2 b_3^2 \\ &= (h^2 + hk + k^2)\left(\frac{4\pi}{\sqrt{3}a}\right)^2 + l^2\left(\frac{2\pi}{c}\right)^2 \end{aligned}$$

or

$$|\mathbf{G}| = \sqrt{(h^2 + hk + k^2)\left(\frac{4\pi}{\sqrt{3}a}\right)^2 + l^2\left(\frac{2\pi}{c}\right)^2}$$

(c)

The Bragg condition:

$$|\mathbf{Q}| = \frac{4\pi}{\lambda} \sin \theta = |\mathbf{G}| = \sqrt{(h^2 + hk + k^2) \left(\frac{4\pi}{\sqrt{3}a}\right)^2 + l^2 \left(\frac{2\pi}{c}\right)^2}$$

The scattering angle ( $2\theta$ ) is obtained as

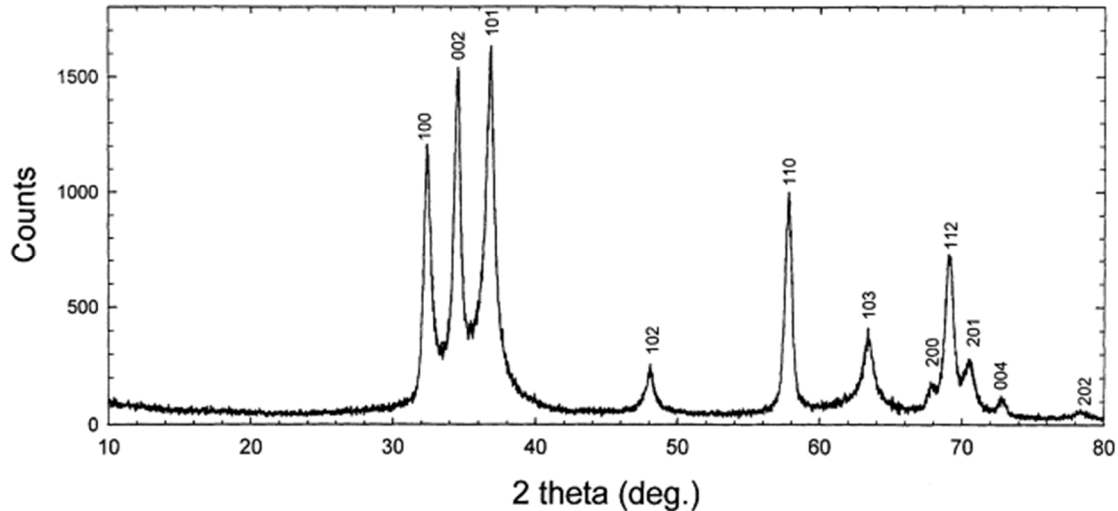
$$2\theta = 2 \arcsin\left(\frac{\lambda}{4\pi} \sqrt{(h^2 + hk + k^2) \left(\frac{4\pi}{\sqrt{3}a}\right)^2 + l^2 \left(\frac{2\pi}{c}\right)^2}\right)$$

Using Mathematica we calculate  $2\theta$  (degrees) as a function of the index ( $h, k, l$ ).

$(h, k, l)$	$2\theta$
(1,0,0)	32.4493°
(0,0,2)	34.592°
(1,0,1)	36.9013°
(1,0,2)	48.1577°
(1,1,0)	57.8864°
(1,0,3)	63.5061°
(2,0,0)	67.9469°
(1,1,2)	69.2179°
(2,0,1)	70.6541°
(0,0,4)	72.9706°
(2,0,2)	78.5401°

The experimental values of the scattering angle  $2\theta$  for each ( $h, k, l$ ) for GaN can be well explained by the above calculations.





**Fig.** Power x-ray diffraction of GaN. The x-ray intensity vs the scattering angle  $2\theta$ .  $a = 3.186 \text{ \AA}$ ,  $c = 5.186 \text{ \AA}$ ,  $\lambda = 1.54184 \text{ \AA}$  (CuK $\alpha$  line)

### 5. x-ray powder diffraction (Debye-Scherrer)

Describe Ewald's construction for X-ray diffraction. In a Debye-Scherrer experiment the following values of  $\sin^2 \theta$  were obtained with Fe  $K\alpha$  radiation:

0.1843	0.6707
0.2450	0.6719
0.4887	0.7314
	0.7345
	0.9739
	0.9777

Fe  $K\alpha_1$ , 1.932  $\text{\AA}$ ; Fe  $K\alpha_2$ , 1.936  $\text{\AA}$ . Determine the crystal structure and lattice parameter of the substance under study.

- (a) What is the wavelength of the FeK $\alpha$ ?
- (b) What is the Bragg condition for the conventional cubic cell? Show that the values of  $h^2 + k^2 + l^2$  is equal to 3, 4, 8, 10, 12, ... for fcc ?
- (c) Determine the structure of the system. What is the lattice constant  $a$  for the conventional cubic cell? Assume that there is only one kind of atom.
- (d) Suppose that the mass of each atom is  $m = 26.9815 \text{ amu}$ , what is the density of the system? 1 atomic mass unit (amu) =  $1.660538782 \times 10^{-24} \text{ g}$ .

**((Solution))**

(a), (b) (c)

$$\lambda = \frac{2\lambda(K_{\alpha 1}) + \lambda(K_{\alpha 2})}{3} = 1.933\text{\AA}^{-1}$$

In a Debye-Scherrer experiment, we have the Bragg condition,

$$Q = 2k \sin \theta = \frac{4\pi}{\lambda} \sin \theta = G = \frac{2\pi}{a} \sqrt{h^2 + k^2 + l^2}$$

or

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

Experimentally we have

$$\begin{aligned} \sin^2 \theta &= 0.1843 = 0.0607 \times 3 \\ &= 0.2459 = 0.0607 \times 4 \\ &= 0.4887 = 0.0607 \times 8 \\ &= 0.6707 = 0.0607 \times 11 \\ &= 0.7314 = 0.0607 \times 12 \\ &= 0.9739 = 0.0607 \times 16 \end{aligned}$$

Thus

$$h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16 \quad (\text{fcc structure})$$

$$\frac{\lambda^2}{4a} = 0.0607$$

leading to

$$a = 3.92 \text{\AA} \quad (\text{fcc lattice})$$

There are four atoms in conventional unit cell for the fcc structure. The density is

$$\rho = \frac{4m}{a^3}$$

where

$$m = 26.9815 \text{ amu, with 1 atomic mass unit (amu) = } 1.660538782 \times 10^{-24} \text{ g.}$$

$$\rho = 2.976 \text{ g/cm}^3$$

### 6. x-ray scattering intensity

Calculate the scattered intensity from a linear chain of atoms with ordered domains of  $N$  atoms. Assume that there is no phase correlation between atoms in different domains.

Hint: Consider a domain where there are  $N$  atoms. Hint: discuss the structure factor.

**((Solution))**

In a linear crystal there are identical point scattering centers at every lattice point  $\rho_m = ma$ , where  $m$  is an integer. The total amplitude is proportional to  $F$ ;

$$F(Q) = \sum_{m=0}^{N-1} \exp(-i \rho_m Q) = \sum_{m=0}^{N-1} \exp(-imaQ)$$

or

$$F(Q) = 1 + \exp(-iaQ) + \exp(-i2aQ) + \dots + \exp[-i(N-1)aQ]$$

or

$$F(Q) = \frac{1 - \exp(-iNaQ)}{1 - \exp(-iaQ)}$$

$$F(Q) = \frac{\exp\left(-i\frac{NaQ}{2}\right) \left[\exp\left(i\frac{NaQ}{2}\right) - \exp\left(-i\frac{NaQ}{2}\right)\right]}{\exp\left(-i\frac{aQ}{2}\right) \left[\exp\left(i\frac{aQ}{2}\right) - \exp\left(-i\frac{aQ}{2}\right)\right]}$$

or

$$F(Q) = \frac{\exp\left(-i\frac{NaQ}{2}\right) \sin\left(\frac{NaQ}{2}\right)}{\exp\left(-i\frac{aQ}{2}\right) \sin\left(\frac{aQ}{2}\right)}$$

The intensity is

$$I(Q) = [F(Q)]^2 = \frac{\sin^2(\frac{NaQ}{2})}{\sin^2(\frac{aQ}{2})} \quad (4)$$

Suppose that

$$Q = n \frac{2\pi}{a} + \varepsilon \quad (4)$$

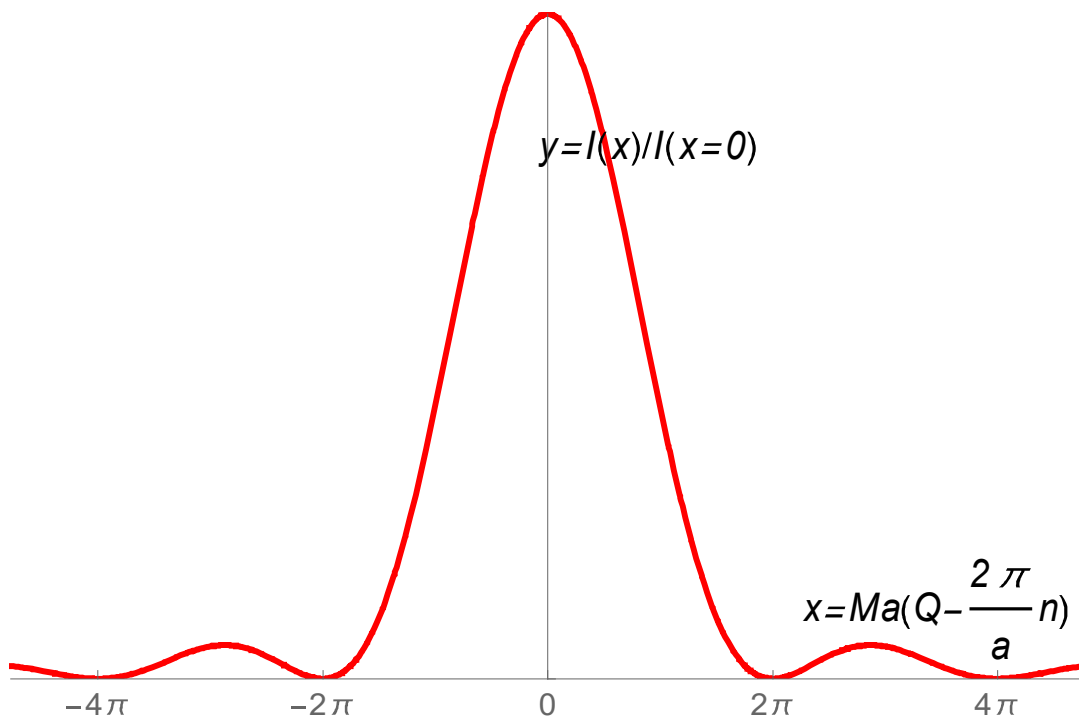
or

$$aQ = 2n\pi + a\varepsilon$$

leading to

$$I(Q) = [F(Q)]^2 = \frac{\sin^2(\frac{Na\varepsilon}{2})}{\sin^2(\frac{a\varepsilon}{2})} \quad (4)$$

- (a) When  $\varepsilon \rightarrow 0$ ,  $I(Q)$  tends to  $N^2$ , where  $Q = n \frac{2\pi}{a}$  (Bragg point). (3)
- (b)  $I(Q)$  becomes zero at  $x = Na\varepsilon = 2\pi m$  or  $\varepsilon = \frac{2\pi}{Na} m$



**Fig.**  $Q = \frac{2\pi}{a}n + \varepsilon$ .  $x = Na\varepsilon = Na(Q - \frac{2\pi}{a}n)$ . The normalized intensity shows a peak at  $x = 0$  (Bragg point;  $Q = \frac{2\pi}{a}n$ ). Note that  $N = M$  in this Fig. (5)

The Bragg peak appears at  $Q = \frac{2\pi}{a}n$ . The width of the Bragg peak is

$$Na\Delta\varepsilon = 2\pi$$

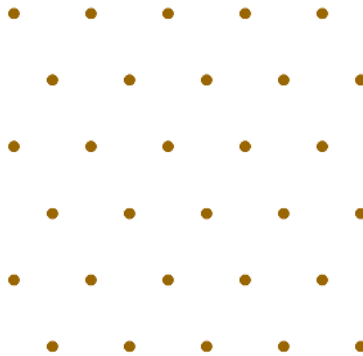
or

$$\Delta\varepsilon = \Delta Q = \frac{2\pi}{Na} \quad (5)$$

When  $N$  becomes large, the width of the Bragg peak becomes sharper.

## 7. **Triangular lattice**

The figure below shows a triangular lattice in two dimensions, where  $a$  is the distance between the atoms.

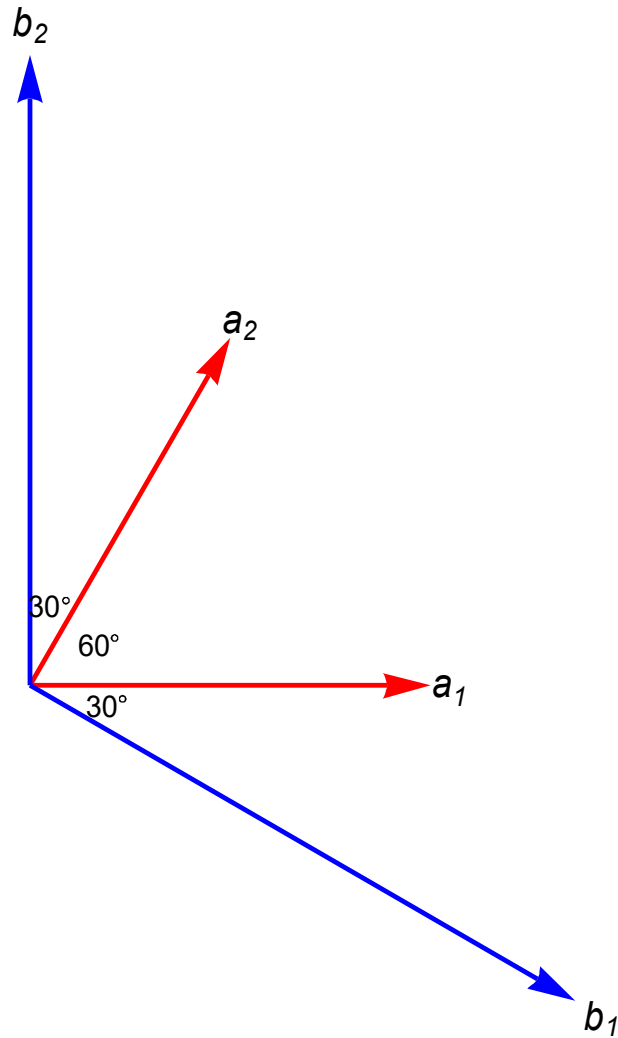


- Determine the primitive lattice vectors appropriate to this lattice and calculate the area of the unit cell.
- Determine the reciprocal lattice vectors appropriate to this lattice and draw the first Brillouin zone.
- Derive the equation for the phonon modes using the first nearest-neighbor approximation.
- Calculate the phonon frequency at  $\Gamma$ , M, and K points in the Brillouin zone (BZ) ( $\Gamma$  is the center of the BZ, M is the center of any edge of the BZ, and K is any corner of the BZ).

---

**((Solution))**

(a)



The primitive lattice vectors:

$$\mathbf{a}_1 = a(\cos(0^\circ), \sin(0^\circ), 0) = a(1, 0, 0),$$

$$\mathbf{a}_2 = a(\cos(60^\circ), \sin(60^\circ), 0) = a\left(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right),$$

$$\mathbf{a}_3 = (0, 0, 1) \quad (\text{this primitive vector is used only for the calculation of } \mathbf{b}_1 \text{ and } \mathbf{b}_2).$$

Area  $A$  is given by

$$A = |\mathbf{a}_1 \times \mathbf{a}_2| = |\mathbf{a}_1| |\mathbf{a}_2| \sin 60^\circ = a^2 \frac{\sqrt{3}}{2} =$$

The reciprocal lattice vectors;  $\mathbf{b}_1, \mathbf{b}_2$

(b)

We note that

$$\mathbf{a}_1 \cdot \mathbf{b}_1 = \mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi, \quad \mathbf{a}_1 \cdot \mathbf{b}_2 = \mathbf{a}_2 \cdot \mathbf{b}_1 = 0$$

Then we have

$$\mathbf{a}_1 \cdot \mathbf{b}_1 = a_1 b_1 \cos 30^\circ = 2\pi \quad b_1 = \frac{4\pi}{\sqrt{3}a},$$

$$\mathbf{a}_2 \cdot \mathbf{b}_2 = a_2 b_2 \cos 30^\circ = 2\pi \quad b_2 = \frac{4\pi}{\sqrt{3}a}.$$

The reciprocal lattice vector  $\mathbf{b}_2$  is perpendicular to  $\mathbf{a}_1$  and  $\mathbf{b}_1$  is perpendicular to  $\mathbf{a}_2$ .

Mathematically,

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{[\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]} = \frac{4\pi}{\sqrt{3}a} \left( \frac{\sqrt{3}}{2}, -\frac{1}{2}, 0 \right),$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{[\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3]} = \frac{4\pi}{\sqrt{3}a} (0, 1, 0).$$

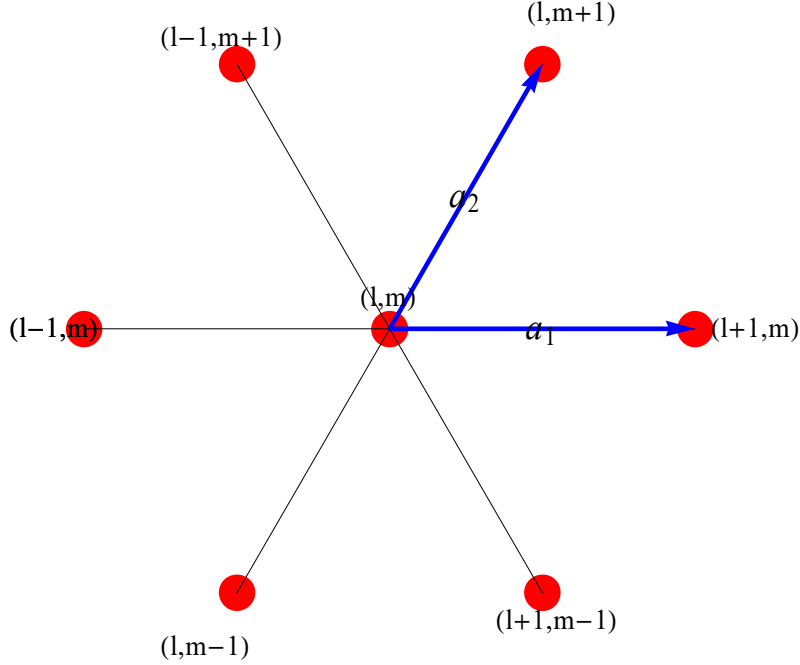
or more conveniently, we use

$$\mathbf{b}_1 = \frac{4\pi}{\sqrt{3}a} \left( \frac{\sqrt{3}}{2}, -\frac{1}{2} \right), \quad \mathbf{b}_2 = \frac{4\pi}{\sqrt{3}a} (0, 1)$$

for the 2D reciprocal lattice vectors.

(c)

Consider the following two-dimensional close-packed lattice and its unit cell:



**Fig.** Real space for the 2D triangular lattice.

Primitive cell vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are shown. Determine the first Brillouin zone appropriate to this lattice. Arrange that the reciprocal lattice vectors  $\mathbf{b}_1$  and  $\mathbf{b}_2$  are correctly oriented. Then, using the nearest-neighbor approximation for a vibrating net of point masses, determine the dispersion equation [let the central mass points have coordinates  $(l\mathbf{a}_1, m\mathbf{a}_2)$ ]. Calculate the frequency at two non-equivalent symmetry points on the zone boundary.

We set up the equation of the motion for the atom at the center. There are nearest neighbor interactions from atoms surrounding the atom at the center.

$$M\ddot{\mathbf{u}}(l, m) = C[\mathbf{u}(l+1, m) + \mathbf{u}(l, m+1) + \mathbf{u}(l-1, m+1) + \mathbf{u}(l-1, m) + \mathbf{u}(l, m-1) + \mathbf{u}(l+1, m-1) - 6\mathbf{u}(l, m)] \quad (1)$$

where  $M$  is the mass of atom,  $C$  is the spring constant, and  $\mathbf{u}_{l+1, m}$  is the displacement vector for the atom at the position  $(l\mathbf{a}_1, m\mathbf{a}_2)$ . We assume the solution of the form as

$$\mathbf{u}(l, m) = \mathbf{u}(0) \exp[i\mathbf{k} \cdot (l\mathbf{a}_1 + m\mathbf{a}_2) - \omega t].$$

with

$$\mathbf{u}(l \pm 1, m) = \exp(\pm i\mathbf{k} \cdot \mathbf{a}_1) \mathbf{u}_{l, m},$$



$$\mathbf{u}(l, m \pm 1) = \exp(\pm i\mathbf{k} \cdot \mathbf{a}_2) \mathbf{u}_{l,m}.$$

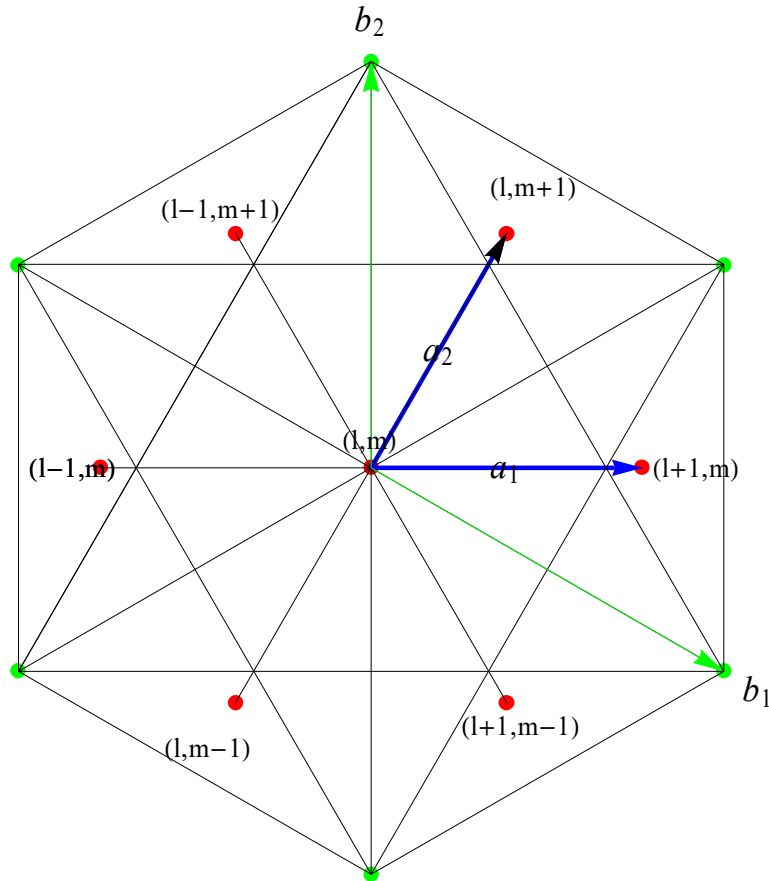
Substituting these into Eq.(1), we get

$$\begin{aligned} -M\omega^2 \mathbf{u}(l, m) = C[ & \exp(i\mathbf{k} \cdot \mathbf{a}_1) + \exp(i\mathbf{k} \cdot \mathbf{a}_2) + \exp[i(-\mathbf{k} \cdot \mathbf{a}_1 + \mathbf{k} \cdot \mathbf{a}_2) \\ & + \exp(-i\mathbf{k} \cdot \mathbf{a}_1) + \exp(-i\mathbf{k} \cdot \mathbf{a}_2) + \exp[i(\mathbf{k} \cdot \mathbf{a}_1 - \mathbf{k} \cdot \mathbf{a}_2) - 6] \mathbf{u}(l, m) \end{aligned}$$

Then we have the dispersion relation of  $\omega$  vs  $\mathbf{k}$  as

$$\frac{M\omega^2}{2C} = [3 - \cos(\mathbf{k} \cdot \mathbf{a}_1) - \cos(\mathbf{k} \cdot \mathbf{a}_2) - \cos(\mathbf{k} \cdot \mathbf{a}_1 - \mathbf{k} \cdot \mathbf{a}_2)]$$

The Brillouin zone for the triangular lattice is shown below.



**Fig.** Relation between the real space (lattice vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$ ) and the reciprocal lattice ( $\mathbf{b}_1$  and  $\mathbf{b}_2$ ). The magnitude of  $\mathbf{a}_1$  and  $\mathbf{b}_1$  are chosen appropriately.

(d) At the middle of a Brillouin zone (zone boundary)

At the  $\Gamma$  point,  $k = 0$ .

$$\omega = 0.$$

At the M point

$$\mathbf{k} = \frac{\mathbf{b}_1 + \mathbf{b}_2}{2}.$$

$$\mathbf{k} \cdot \mathbf{a}_1 = \frac{1}{2} \mathbf{a}_1 \cdot \mathbf{b}_1 = \pi, \quad \mathbf{k} \cdot \mathbf{a}_2 = \frac{1}{2} \mathbf{a}_2 \cdot \mathbf{b}_2 = \pi.$$

Then we get

$$\frac{M\omega^2}{2C} = 3 - \cos(\pi) - \cos(\pi) - \cos(\pi - \pi) = 4$$

or

$$\omega^2 = \frac{8C}{M}$$

At the K point

$$\mathbf{k} = \frac{\mathbf{b}_1 + 2\mathbf{b}_2}{3}$$

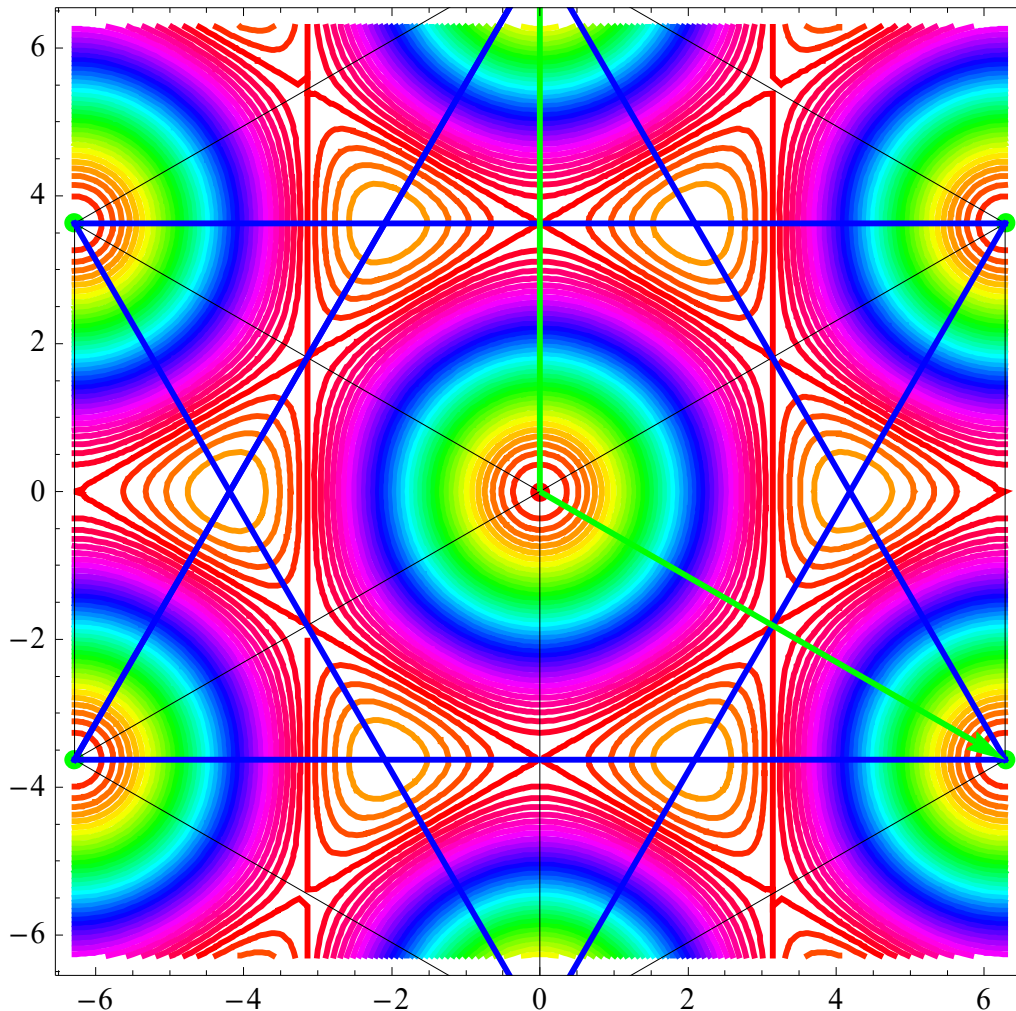
$$\mathbf{k} \cdot \mathbf{a}_1 = \frac{1}{3} \mathbf{a}_1 \cdot \mathbf{b}_1 = \frac{2\pi}{3}, \quad \mathbf{k} \cdot \mathbf{a}_2 = \frac{2}{3} \mathbf{a}_2 \cdot \mathbf{b}_2 = \frac{4\pi}{3}$$

Then we get

$$\frac{M\omega^2}{2C} = 3 - \cos\left(\frac{2\pi}{3}\right) - \cos\left(\frac{4\pi}{3}\right) - \cos\left(-\frac{2\pi}{3}\right) = \frac{9}{2}$$

or

$$\omega^2 = \frac{9C}{M}$$



**Fig.** Contour plot of constant energy in the reciprocal lattice plane. The first Brillouin zone is shown by the blue solid line. The energy of the point K (the corner of the first Brillouin zone) is higher than that of the point M (the middle of the zone boundary).

### 9. x-ray powder diffraction (Aluminium)

In a Debye-Scherrer diffractogram, we obtain a measure of the Bragg angles  $\theta$ . In a particular experiment with Al (Aluminium) powder, the following  $\theta$  data were obtained when  $\text{CuK}\alpha$  radiation (the wavelength  $\lambda = 1.54184 \text{ \AA}$ ) was used:

19.48°, 22.64°, 33.00°, 39.68°, 41.83°, 50.35°, 57.05°, 59.42°.

Aluminium has atomic weight 27 g/mol and density 2.7 g/cm<sup>3</sup>. (c) Show that Al has a fcc (face centered cubic) structure, where  $h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32, 35, 40, 36, 43, 44, 48$ . (d) What is the lattice parameter of Al of the conventional cubic unit cell? (e) Calculate the Avogadro's number.

**Hint:** The basis consists of four lattice points if the cell is taken as the conventional cube for fcc.

$$\frac{4\pi}{\lambda} \sin \theta = \frac{2\pi}{a} \sqrt{h^2 + k^2 + l^2} .$$

**((Solution))**

We use the Bragg condition given by

$$\frac{4\pi}{\lambda} \sin \theta = \frac{2\pi}{a} \sqrt{h^2 + k^2 + l^2}$$

where  $h, k, l$  are the integers,  $a$  is the lattice constant of the conventional cubic lattice.  $\lambda = 1.54184$  Å for CuK $\alpha$ . This formula can be rewritten as

$$a \frac{2}{\lambda} \sin \theta = \sqrt{h^2 + k^2 + l^2}$$

Suppose that Al has a fcc structure. In this case, it is expected that

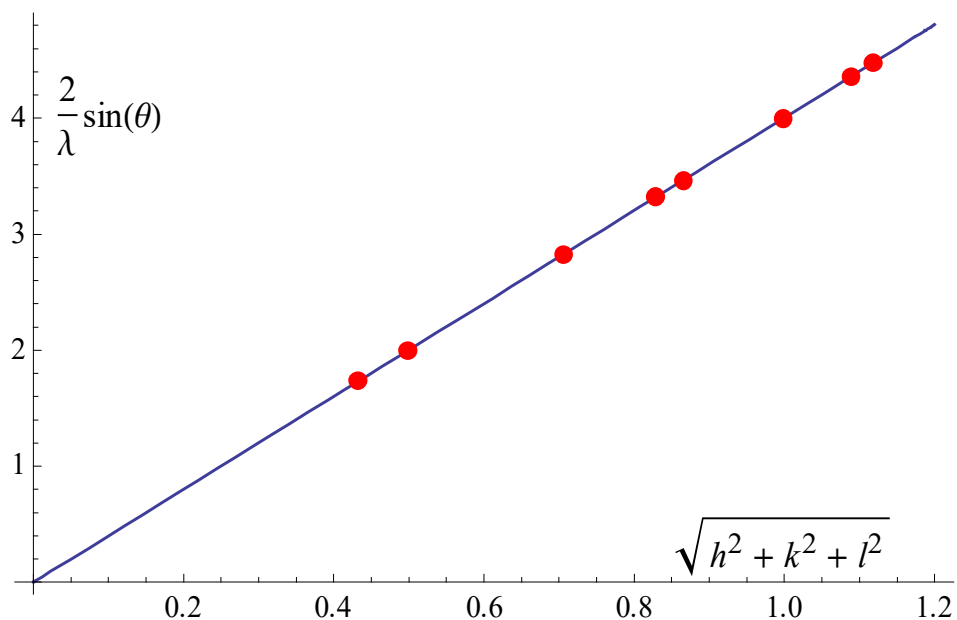
$$h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32, \dots$$

We make a plot of the date of  $\frac{2}{\lambda} \sin \theta$  as a function of  $\sqrt{h^2 + k^2 + l^2}$  .

$\theta = 19.48^\circ,$	$\sqrt{h^2 + k^2 + l^2} = \sqrt{3}$
$\theta = 22.64^\circ,$	$\sqrt{h^2 + k^2 + l^2} = \sqrt{4}$
$\theta = 33.00^\circ,$	$\sqrt{h^2 + k^2 + l^2} = \sqrt{8}$
$\theta = 39.68^\circ,$	$\sqrt{h^2 + k^2 + l^2} = \sqrt{11}$
$\theta = 41.83$	$\sqrt{h^2 + k^2 + l^2} = \sqrt{12}$
$\theta = 50.35^\circ,$	$\sqrt{h^2 + k^2 + l^2} = \sqrt{16}$
$\theta = 57.05^\circ,$	$\sqrt{h^2 + k^2 + l^2} = \sqrt{19}$

$$\theta = 59.42^\circ.$$

$$\sqrt{h^2 + k^2 + l^2} = \sqrt{20}$$



The least-squares fit of the data yield the lattice constant  $a$  as  $a = 4.0045 \text{ \AA}$ .

The Avogadro number can be evaluated as follows, based on the lattice constant  $a$ . In Al (fcc), there are 4 Al atoms in the conventional cubic lattice.

The volume for Al 1 mol is

$$V_A = \frac{M}{\rho} = \frac{27}{2.7} = 10$$

where  $M = 27 \text{ g/mol}$  and  $\rho = 2.7 \text{ g/cm}^3$ . There are  $N_A$  (Al atoms) in this volume  $V_A$ . Then we have

$$\frac{V_A}{N_A} = \frac{a^3}{4}$$

The Avogadro number is evaluated as

$$N_A = \frac{4V_A}{a^3} = 6.229 \times 10^{23}$$

Note that the correct value is  $6.023 \times 10^{23}$ .

