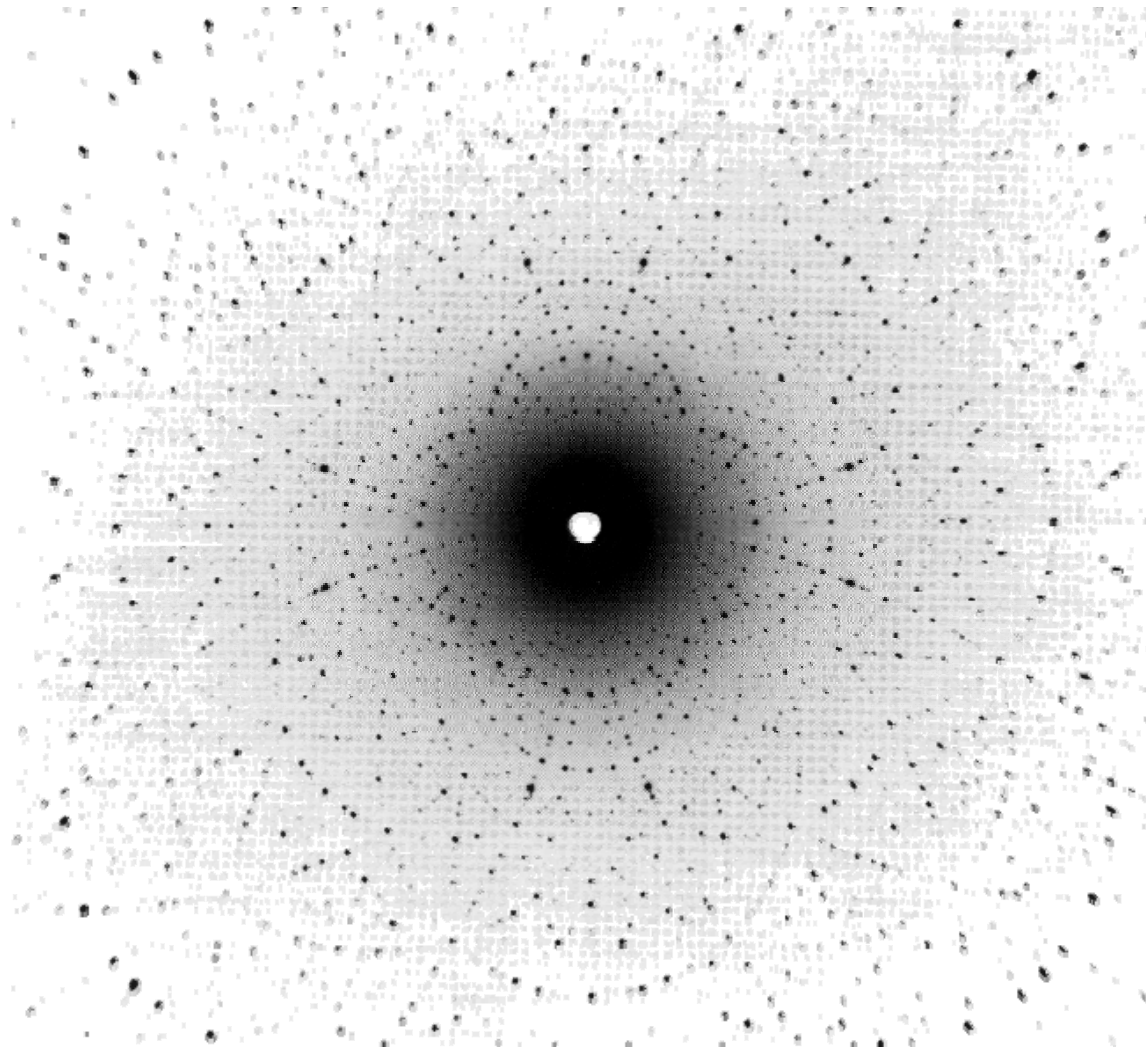# Chap 3 Scattering and structures

Dept of Phys

M.C. Chang

Von Laue was struck in 1912 by the intuition that X-ray might scatter off crystals in the way that ordinary light scatters off a diffraction grating.
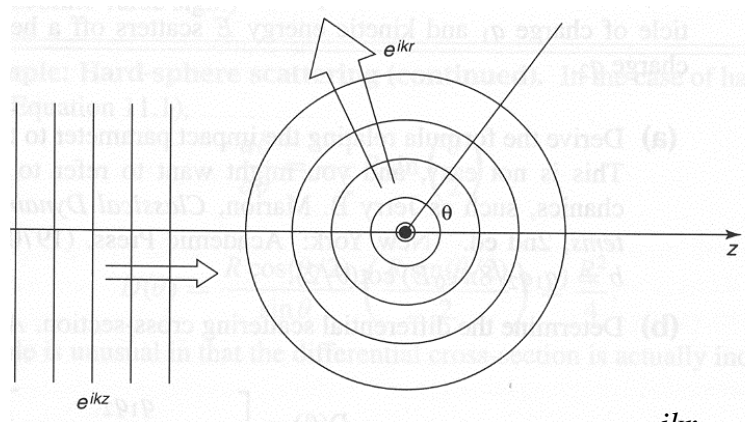
He discussed

his idea with colleagues Sommerfeld, Wien and others with the result of encountering a strong disbelief in a significant outcome of any diffraction experiment based upon the regularity of the internal structure of crystals. It was argued that the inevitable temperature motion of the atoms would impair the regularity of the grating to such an extent that no pronounced diffraction maxima could be expected.   —Ewald (1962), p. 42

• For example, For NaCl, the thermal fluctuation is expected to be $2 \cdot 10^{-9}$ cm ~ the wavelength of X-ray 10^{-9} cm (Marder, p.43)

• Now we know that thermal fluctuation would only broaden the diffraction peaks, but not distroy them.

• Laue did not actually do the experiment himself. Rather, he persuaded a couple of graduate students to do the experiment for him. Laue then set an example that has inspired PIs ever since – he was given all the credit!   https://wasatch.biochem.utah.edu/chris/teaching/2011/SM_3.pdf

Scattering from an array of atoms (Von Laue, 1912)

• The same analysis applies to EM wave, electron wave, neutron wave… etc.

Scattering off an atom at the origin:

$$\text{scattered wave } \psi(\vec{r}) \sim f_a(\theta)\frac{e^{ikr}}{r} \text{ for large } r$$

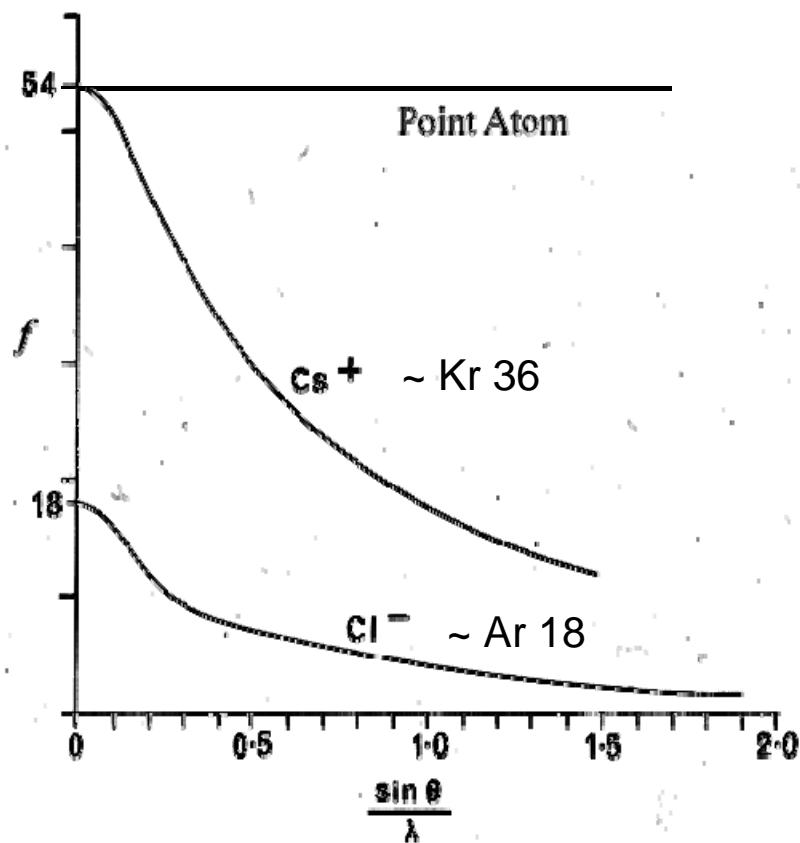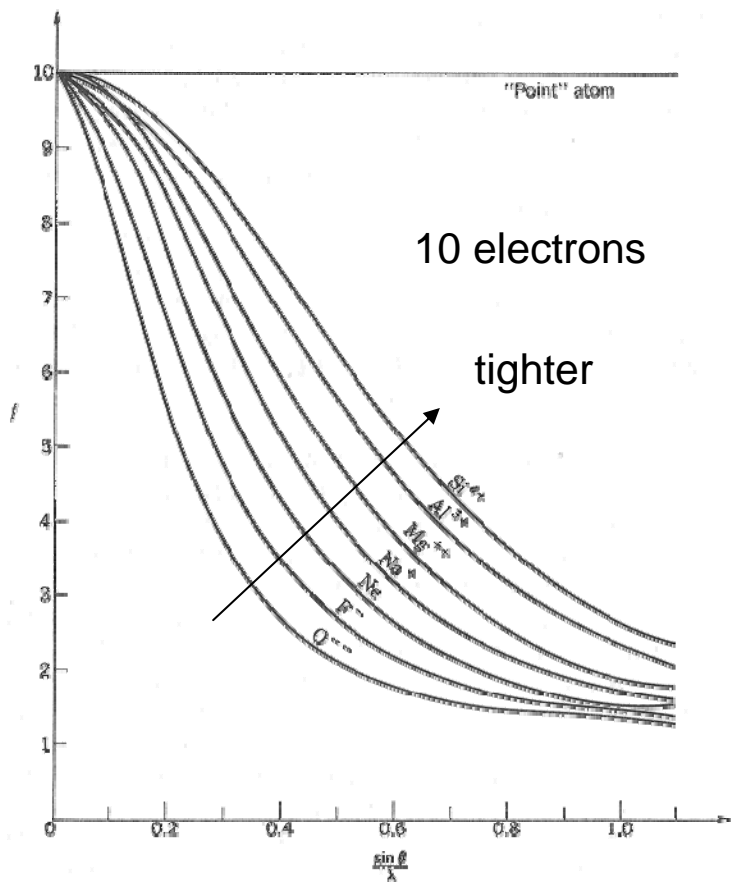• atomic form factor: Fourier transform of charge distribution $n(\rho)$

$$f_a(\Delta\vec{k}) = \int dV e^{-i\Delta\vec{k}\cdot\vec{\rho}} n(\vec{\rho}), \quad \Delta\vec{k} \equiv \vec{k}\,' - \vec{k}$$

1914

The atom form factor $\qquad f_a(\vec{q}) = \int dV e^{-i\vec{q}\cdot\vec{\rho}} n(\vec{\rho})$
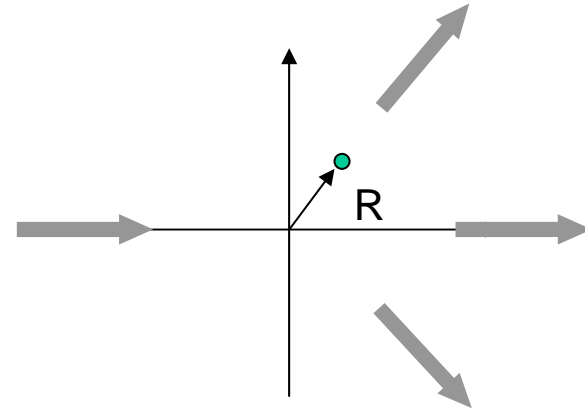

"Point" atom

10 electrons

tighter

Si^{4+}
Al^{3+}
Mg^{++}
Na^{+}
Ne
F^{-}
O^{--}

$\frac{\sin\theta}{\lambda}$

Point Atom

Cs^{+} ~ Kr 36

Cl^{-} ~ Ar 18

$\frac{\sin\theta}{\lambda}$

http://capsicum.me.utexas.edu/ChE386K/docs/29_electron_atomic_scattering.ppt

scattered wave $\psi(\vec{r}) \propto f_a(\Delta\vec{k}) \dfrac{e^{ik|\vec{r}-\vec{R}|}}{|\vec{r}-\vec{R}|} e^{i\vec{k}\cdot\vec{R}}$

$|\vec{r}-\vec{R}| \approx r - \hat{r}\cdot\vec{R}$

$\dfrac{1}{|\vec{r}-\vec{R}|} \approx \dfrac{1}{r} + O(r^{-2})$

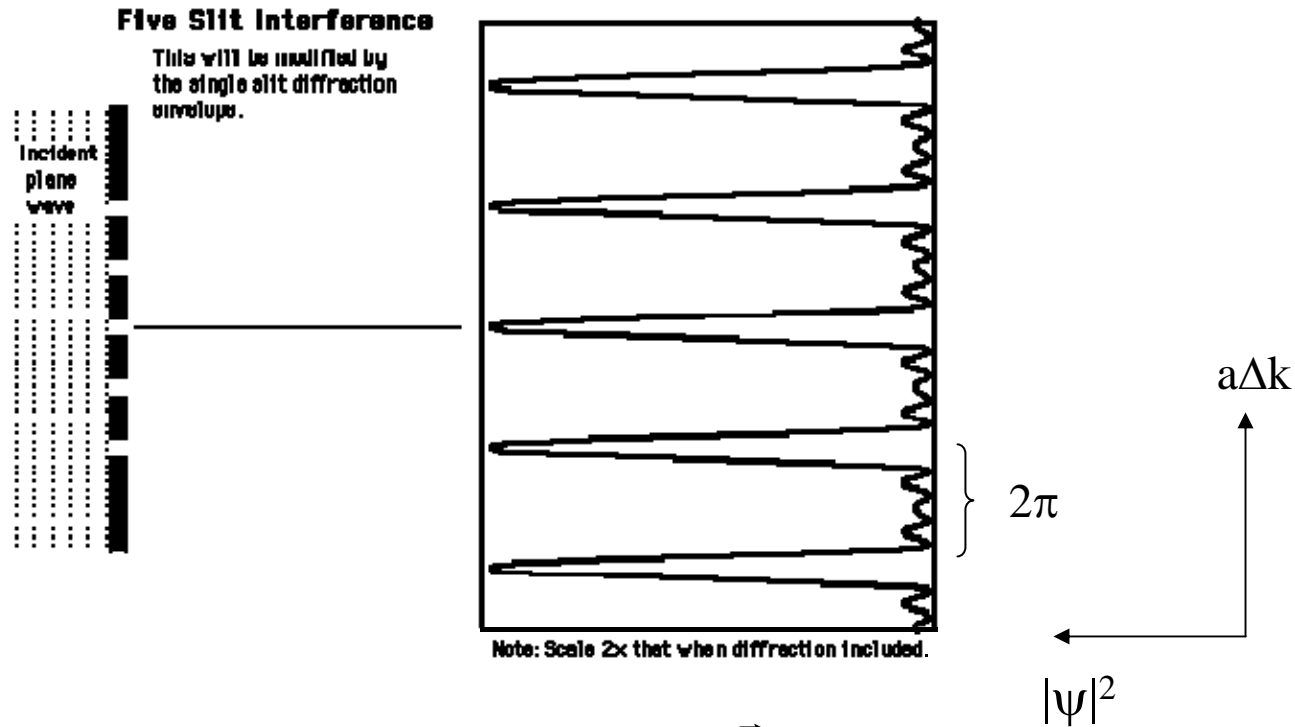$\therefore \psi(\vec{r}) \propto f_a(\Delta\vec{k}) \dfrac{e^{ikr}}{r} e^{-i\Delta\vec{k}\cdot\vec{R}}$

Two-atom scattering

$$\psi(\vec{r}) \propto f_a \dfrac{e^{ikr}}{r}\left(e^{-i\Delta\vec{k}\cdot\vec{R}_1} + e^{-i\Delta\vec{k}\cdot\vec{R}_2}\right)$$

N-atom scattering: one dimensional case

$$\psi \approx e^{-i\Delta k \cdot 0} + e^{-i\Delta k \cdot a} + e^{-i\Delta k \cdot 2a} + e^{-i\Delta k \cdot 3a} + e^{-i\Delta k \cdot 4a}$$

Five Slit Interference

This will be modified by the single slit diffraction envelope.

Incident plane wave

Note: Scale 2x that when diffraction included.

$a\Delta k$

2π

$|\psi|^2$

$$\psi \approx f_a \sum_{n=1}^{N} e^{-i\Delta \vec{k} \cdot n\vec{a}} = \frac{1 - \exp(-iN\Delta \vec{k} \cdot \vec{a})}{1 - \exp(-i\Delta \vec{k} \cdot \vec{a})}$$

For large N, ψ is nonzero only when

$$\Delta \vec{k} \cdot \vec{a} = 2\pi h \quad (h \text{ is an integer})$$

N-atom scattering (3D case, neglect multiple scatterings)

For a Bravais lattice

$$\psi(\vec{r}) \propto f_a \sum_{\vec{R}} e^{-i\Delta\vec{k}\cdot\vec{R}}, \quad \vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3.$$

The lattice-sum can be separated

$$\sum_{\vec{R}} e^{-i\Delta\vec{k}\cdot\vec{R}} = \left(\sum_{n_1} e^{-i\Delta\vec{k}\cdot n_1\vec{a}_1}\right)\left(\sum_{n_2} e^{-i\Delta\vec{k}\cdot n_2\vec{a}_2}\right)\left(\sum_{n_3} e^{-i\Delta\vec{k}\cdot n_3\vec{a}_3}\right)$$

$\neq 0$ only when

$$\begin{aligned}\Delta\vec{k}\cdot\vec{a}_1 &= 2\pi h,\\ \Delta\vec{k}\cdot\vec{a}_2 &= 2\pi k,\\ \Delta\vec{k}\cdot\vec{a}_3 &= 2\pi l.\end{aligned}$$

Laue's diffraction condition

$$\Rightarrow \sum_{\vec{R}} e^{-i\Delta\vec{k}\cdot\vec{R}} = N\delta_{\Delta\vec{k}\cdot\vec{a}_1,2\pi h}\delta_{\Delta\vec{k}\cdot\vec{a}_2,2\pi k}\delta_{\Delta\vec{k}\cdot\vec{a}_3,2\pi l} = N\delta_{\Delta\vec{k},\vec{G}_{hkl}}$$
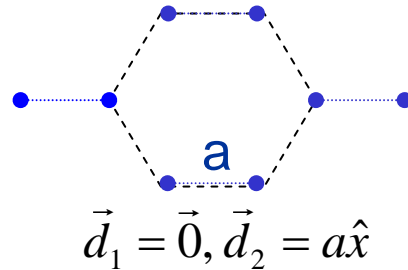
Number of atoms in the crystal

See 2 pages later

Scattering from a crystal with basis

d_j: location of the j-th atom in a unit cell

Eg.,

$$\vec{d}_1 = \vec{0}, \vec{d}_2 = a\hat{x}$$

atomic form factor
for the j-th atom

$$\psi(\vec{r}) \propto \sum_{\vec{R}} \left(\sum_{j=1}^{p} f_{aj} e^{-i\Delta\vec{k}\cdot(\vec{R}+\vec{d}_j)} \right)$$

$$= \left(\sum_{\vec{R}} e^{-i\Delta\vec{k}\cdot\vec{R}} \right) \left(\sum_{j=1}^{p} f_{aj} e^{-i\Delta\vec{k}\cdot\vec{d}_j} \right)$$

$$= N\delta_{\Delta\vec{k},\vec{G}_{hkl}} \cdot S(\Delta\vec{k})$$

structure factor

$$S(\Delta\vec{k}) = \sum_{j=1}^{p} f_{aj} e^{-i\Delta\vec{k}\cdot\vec{d}_j}$$

Laue's diffraction condition

$$\Delta \vec{k} \cdot \vec{a}_1 = 2\pi h,$$
$$\Delta \vec{k} \cdot \vec{a}_2 = 2\pi k,$$
$$\Delta \vec{k} \cdot \vec{a}_3 = 2\pi l.$$

What are the $\triangle$k's that satisfy this condition?

• Simplest case: h=1, k, l=0

$$\Delta \vec{k} \equiv \vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

• Similarly, for k=1 (the others 0), we have

$$\Delta \vec{k} \equiv \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

• for l=1 (the others 0), we have

$$\Delta \vec{k} \equiv \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

• In general, when h, k, l are nonzero,

$$\begin{cases} \Delta \vec{k} \cdot \vec{a}_1 = 2\pi h, \\ \Delta \vec{k} \cdot \vec{a}_2 = 2\pi k, \\ \Delta \vec{k} \cdot \vec{a}_3 = 2\pi l. \end{cases}$$
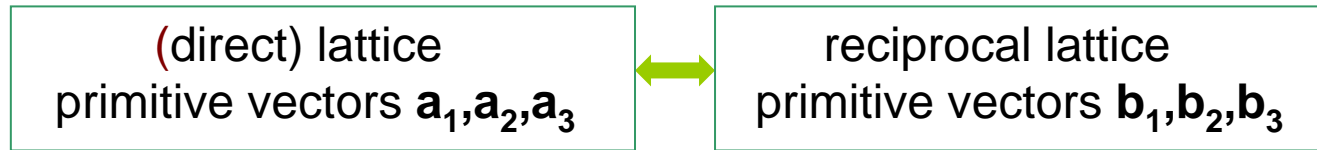
The soultion is just

$$\Delta \vec{k} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 \equiv \vec{G}_{hkl}$$

• That is, the set of solutions form a lattice with primitive vectors b_1, b_2, and b_3

(reciprocal lattice)

Reciprocal lattice (倒晶格)

| (direct) lattice primitive vectors $\mathbf{a_1, a_2, a_3}$ | ⟷ | reciprocal lattice primitive vectors $\mathbf{b_1, b_2, b_3}$ |

Def. 1

$$\vec{b}_1 \cdot \vec{a}_1 = 2\pi, \ \vec{b}_1 \cdot \vec{a}_2 = \vec{b}_1 \cdot \vec{a}_3 = 0,$$
$$\vec{b}_2 \cdot \vec{a}_2 = 2\pi, \ \vec{b}_2 \cdot \vec{a}_3 = \vec{b}_2 \cdot \vec{a}_1 = 0,$$
$$\vec{b}_3 \cdot \vec{a}_3 = 2\pi, \ \vec{b}_3 \cdot \vec{a}_1 = \vec{b}_3 \cdot \vec{a}_2 = 0.$$

$\vec{b}_1 \propto \vec{a}_2 \times \vec{a}_3$ because of orthogonality,

then use $\vec{b}_1 \cdot \vec{a}_1 = 2\pi$

to determine the constant.

Def. 2

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)},$$
$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)},$$
$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}.$$

• The reciprocal of a reciprocal lattice is the direct lattice (obvious from Def.1)

Ex: Simple cubic lattice
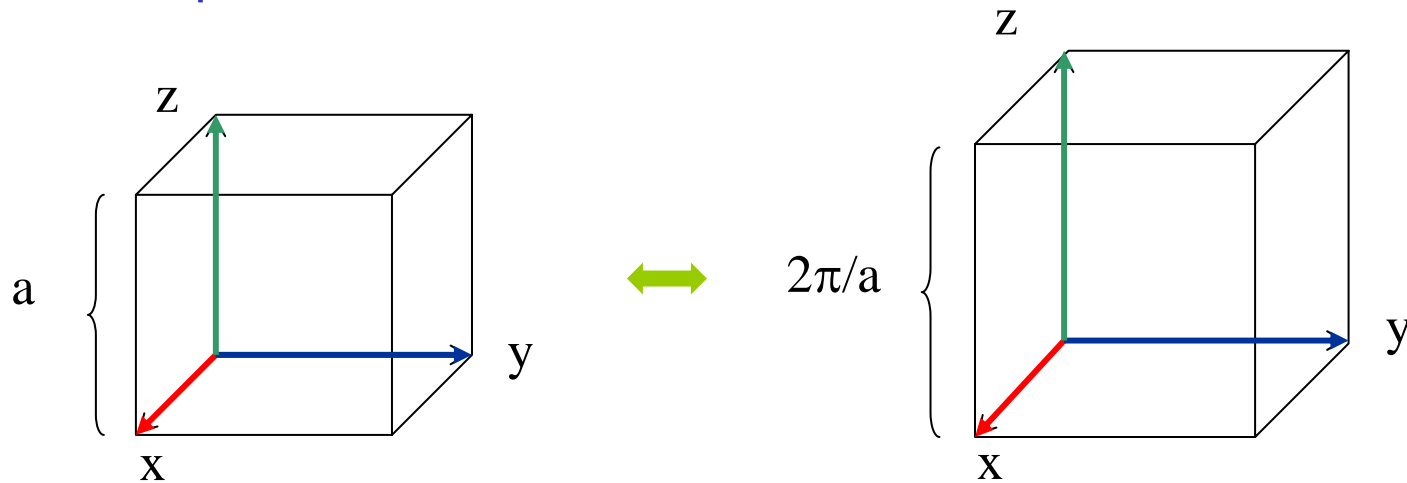
$$\vec{a}_1 = a\,\hat{x},$$
$$\vec{a}_2 = a\,\hat{y},$$
$$\vec{a}_3 = a\,\hat{z}.$$
$$\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = a^3$$

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{2\pi}{a}\,\hat{x},$$
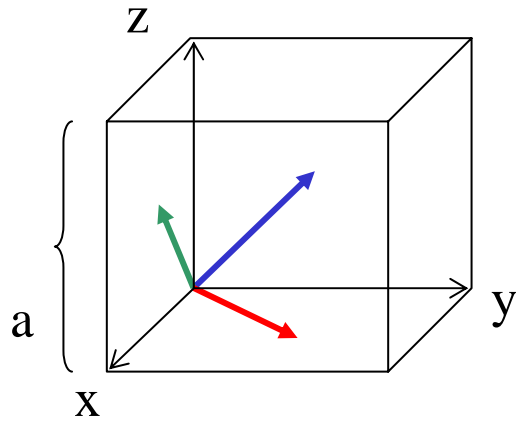
$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{2\pi}{a}\,\hat{y},$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{2\pi}{a}\,\hat{z}.$$

$$\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \left(\frac{2\pi}{a}\right)^3$$

• When the direct lattice rotates, its reciprocal lattice rotates the same amount as well.

FCC lattice

z

a

x

y

BCC lattice

$4\pi/a$

z

x

y

$$\vec{a}_1 = \frac{a}{2}(\hat{x} + \hat{y}),$$

$$\vec{a}_2 = \frac{a}{2}(\hat{y} + \hat{z}),$$

$$\vec{a}_3 = \frac{a}{2}(\hat{z} + \hat{x}).$$

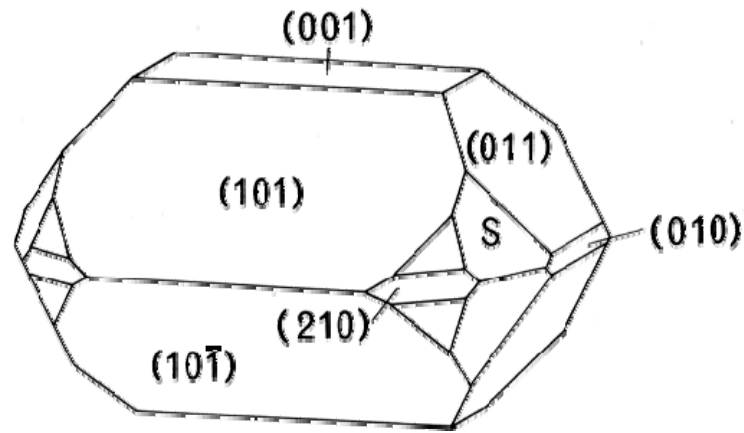$$\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = a^3 / 4$$
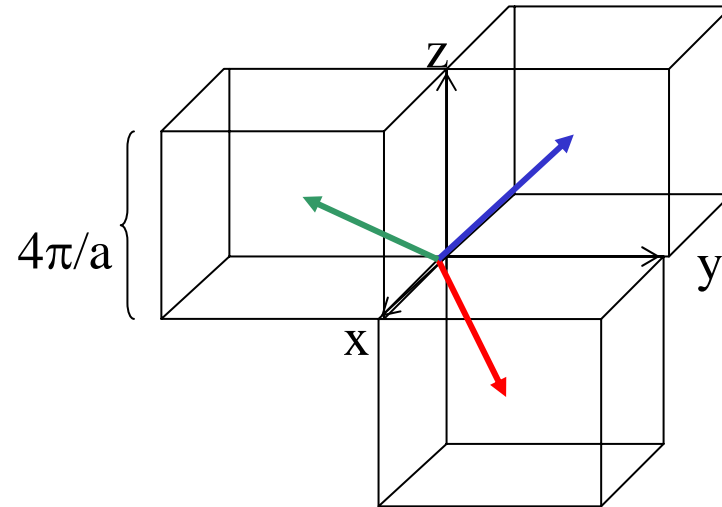
$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{4\pi}{a} \frac{1}{2} (\hat{x} + \hat{y} - \hat{z}),$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{4\pi}{a} \frac{1}{2} (-\hat{x} + \hat{y} + \hat{z}),$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} = \frac{4\pi}{a} \frac{1}{2} (\hat{x} - \hat{y} + \hat{z}).$$

$$\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{1}{2} \left(\frac{4\pi}{a} \right)^3$$

Miller indices

An Indexed PbSO$_4$ Crystal
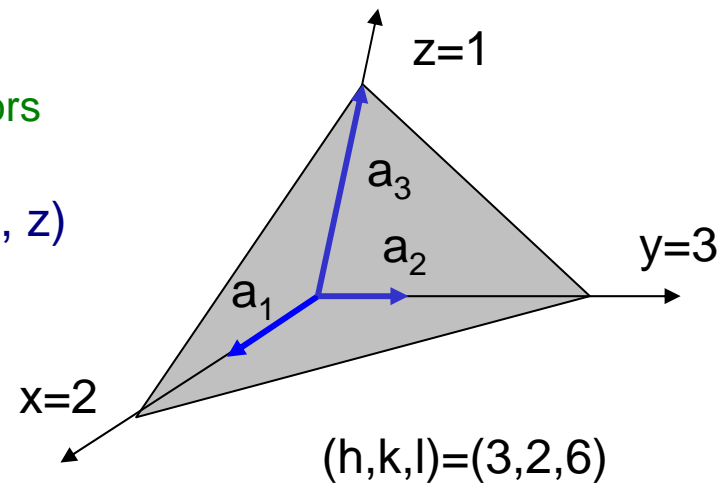
The Miller indices (h,k,l) for a crystal plane

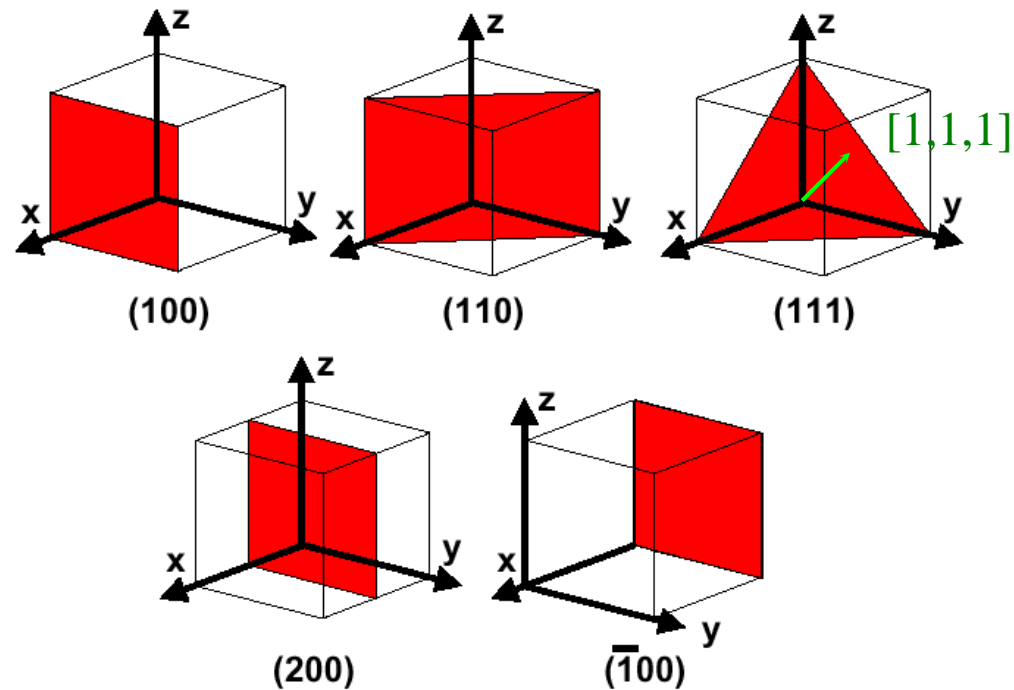rules:

no need to be primitive vectors

1. 取截距 (以**a**$_1$, **a**$_2$, **a**$_3$爲單位) 得 (x, y, z)

2. 取倒數 (1/x,1/y,1/z)

3. 通分成互質整數 (h,k,l)

z=1

a$_3$

a$_2$

y=3

a$_1$

x=2

(h,k,l)=(3,2,6)

Cubic crystals (including bcc, fcc… etc)

(100) (110) (111) [1,1,1]

(200) ($\bar{1}$00)

- Square bracket [h,k,l] refers to the "direction" $h\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3$, instead of a crystal plane.

- For cubic crystals, [h,k,l] direction $\perp$ (h,k,l) planes

Diamond structure (eg. C, Si or Ge)

Termination of 3 low-index surfaces:

<111>   <100> highest density   <110>
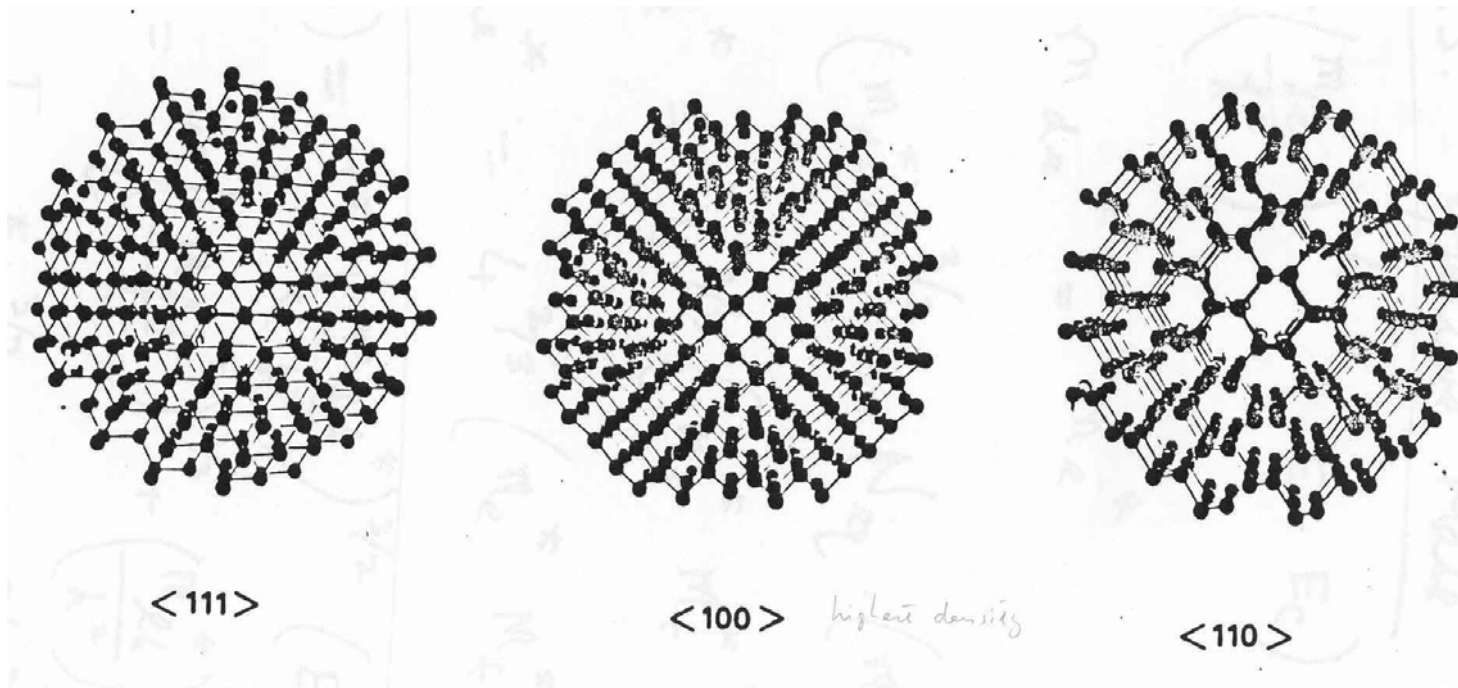
- {h,k,l} = (h,k,l)-plane + those equivalent to it by crystal symmetry
- <h,k,l>= [h,k,l]-direction + those equivalent to it by crystal symmetry

Miller Indices for hexagonal lattice (i, j, k, l)

• corresponding to the I, J, K, L axes below
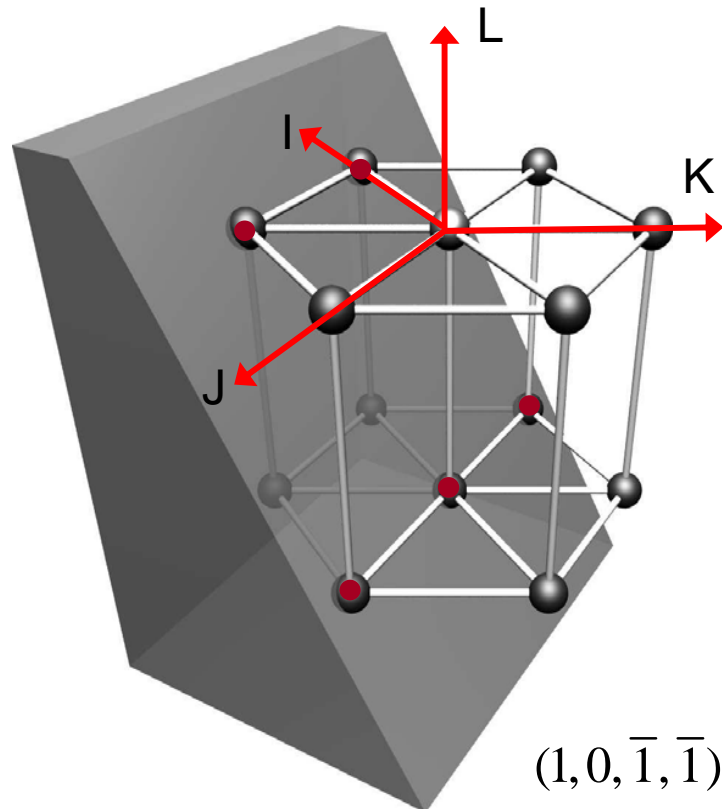
$(1, 0, \bar{1}, \bar{1})$

advantage?

[Courtesy of M.F.Yang at Tunhai Univ.]

1.
(1 0 0) plane <-> (1 0 -1 0)
[2 1 0] vector <-> [1 0 -1 0]
[2 1 0] vector ⊥ (1 0 0) plane,
or we can say
[1 0 -1 0] vector ⊥ (1 0 -1 0) plane.

2.
For two side faces, they can be
(1 0 0)、(-1 1 0), or
(1 0 -1 0)、(-1 1 0 0),
which belong to the same {-1 1 0 0}

• k = - (i+j)

Geometrical relation between G_{hkl} vector and (hkl) planes

$$(h,k,l) \text{ planes} \perp \vec{G}_{hkl} \equiv h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

Pf:

$$\begin{cases} \vec{v}_1 = \dfrac{m}{h}\vec{a}_1 - \dfrac{m}{l}\vec{a}_3 \\[2mm] \vec{v}_2 = \dfrac{m}{k}\vec{a}_2 - \dfrac{m}{l}\vec{a}_3 \end{cases}$$

$$\Rightarrow \quad \begin{array}{l} \vec{G}_{hkl} \cdot \vec{v}_1 = 0 \\[2mm] \vec{G}_{hkl} \cdot \vec{v}_2 = 0 \end{array}$$

$$\therefore \ \vec{G}_{hkl} \perp (h,k,l)\text{-plane}$$

Inter-plane distance

(*hkl*) lattice
planes
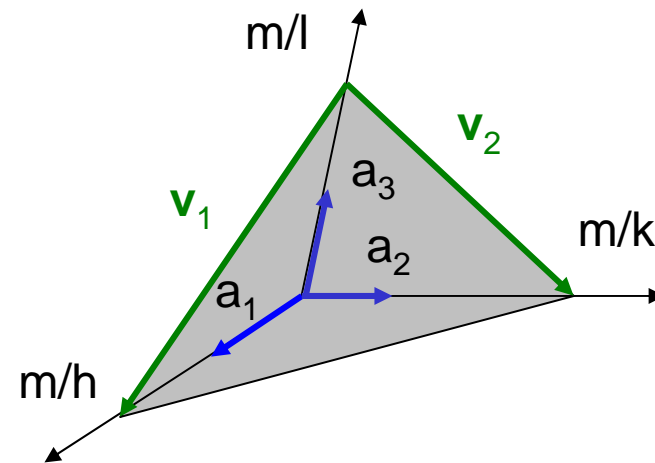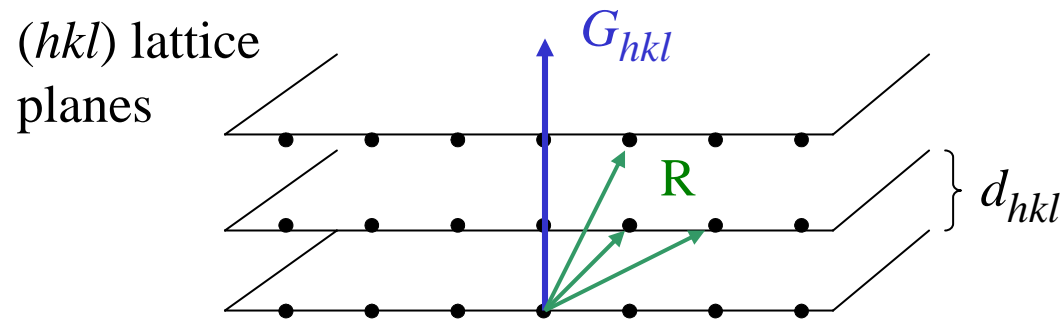
$$\vec{G}_{hkl} \cdot \vec{R} = 2\pi n \quad (n \in Z)$$

$$\Rightarrow \quad \hat{G}_{hkl} \cdot \vec{R} = 2\pi n / | \vec{G}_{hkl} |$$

$$\therefore \text{ inter-plane distance } d_{hkl} = 2\pi / | \vec{G}_{hkl} |$$

For a cubic lattice

$$\vec{G}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

$$= \frac{2\pi}{a} \left(h\hat{x} + k\hat{y} + l\hat{z} \right)$$

$$\therefore \quad d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

• In general, planes with higher index have smaller inter-plane distance

Laue's diffraction condition

$$\mathbf{k'} = \mathbf{k} + \mathbf{G}_{hkl}$$

• Given an incident **k**, want to find a **k'** that satisfies this condition

(under the constraint $|\mathbf{k'}|=|\mathbf{k}|$)

• One problem: there are infinitely many $\mathbf{G}_{hkl}$'s.

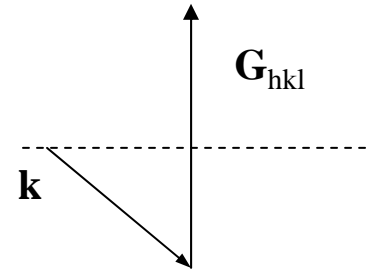• It's convenient to solve it graphically using the Ewald construction

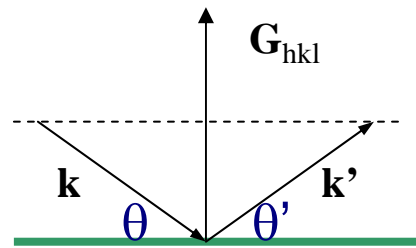(Ewald 構圖法)
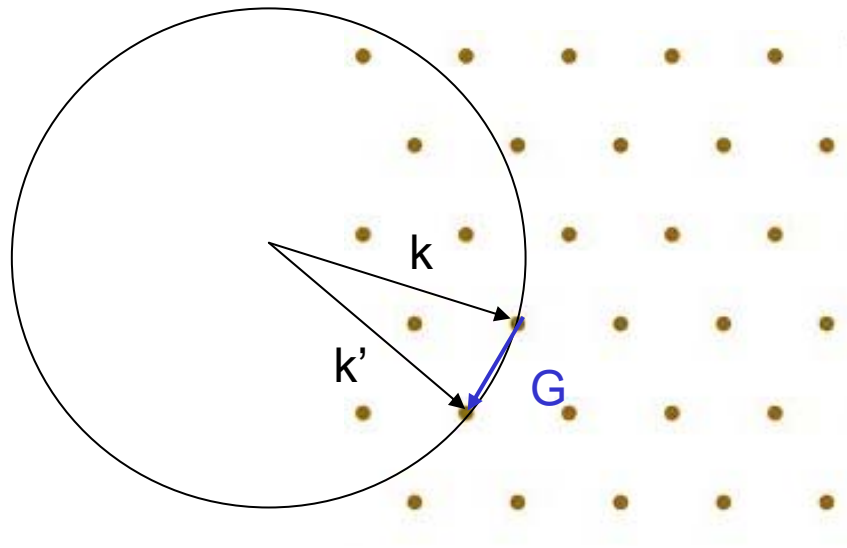
More than one (or none) solutions may be found.

Laue's condition = Braggs' condition

• From the Laue condition, we have

$$\vec{k} \cdot \hat{G}_{hkl} = -\frac{G_{hkl}}{2}$$

• Given k and $\mathbf{G}_{hkl}$, we can find the diffracted wave vector $\mathbf{k}$'

(**k** vector points to the plane bi-secting the $\mathbf{G}_{hkl}$ vector)

a (*hkl*)-lattice plane

• It's easy to see that $\theta = \theta$' because $|\mathbf{k}| = |\mathbf{k}'|$.

By using $\quad 2k \sin \theta = G_{hkl} = \dfrac{2\pi n}{d_{hkl}}$

and $\qquad k = \dfrac{2\pi}{\lambda}$,

$\Rightarrow \boxed{2d_{hkl} \sin \theta = n\lambda.}$ Bragg's diffraction condition

Braggs' view of the diffraction (1912, father and son)

You can view the same phenomena from 2 (or more) different angles, and each can get you a Nobel prize!

1915

Treat the lattice as a stack of lattice planes
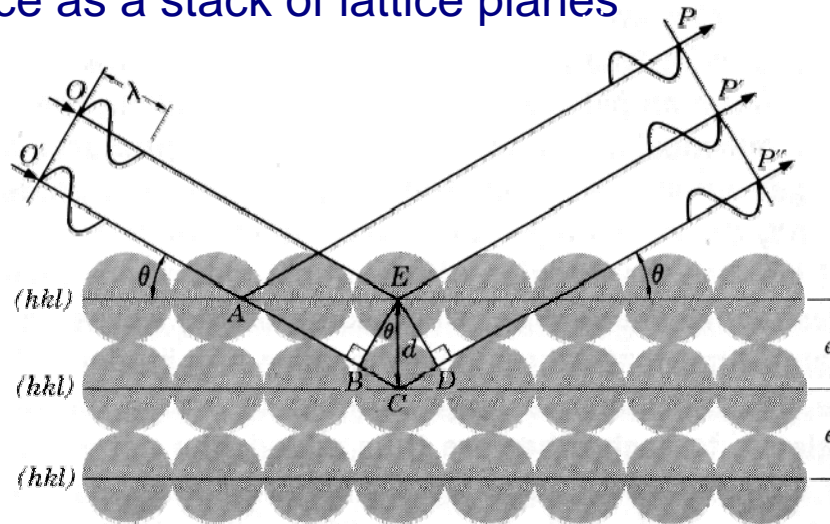
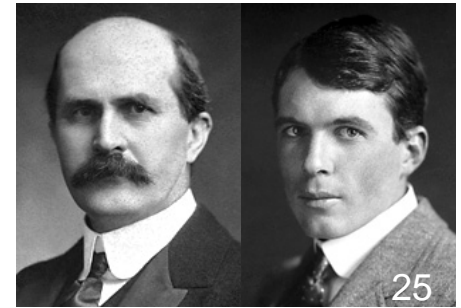- mirror-like reflection from crystal planes when

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

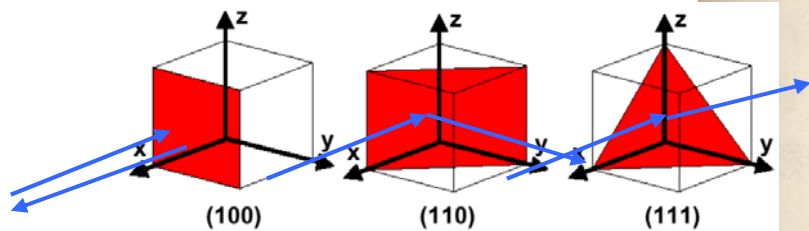- Difference from the usual mirror reflection:
  λ > 2d, no reflection
  λ < 2d, reflection only at certain angles

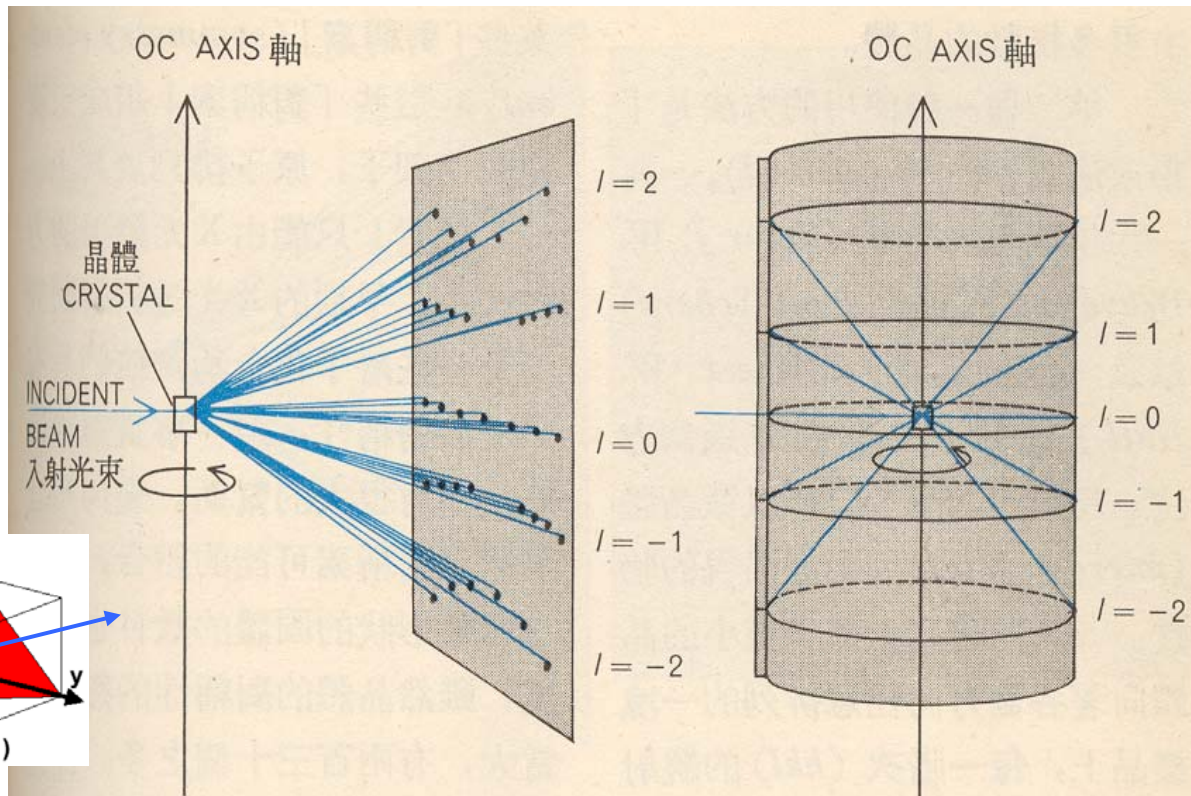- Measure λ, θ → get distance between crystal planes d

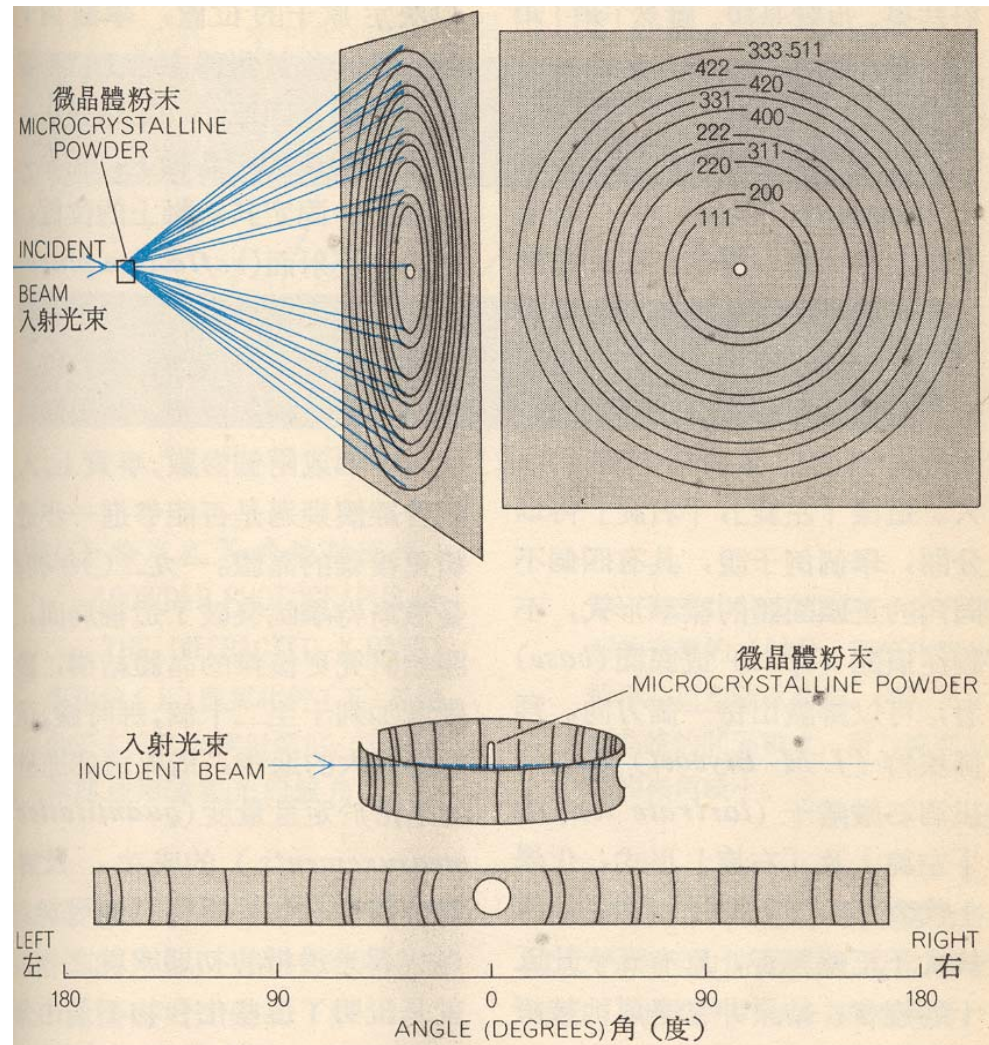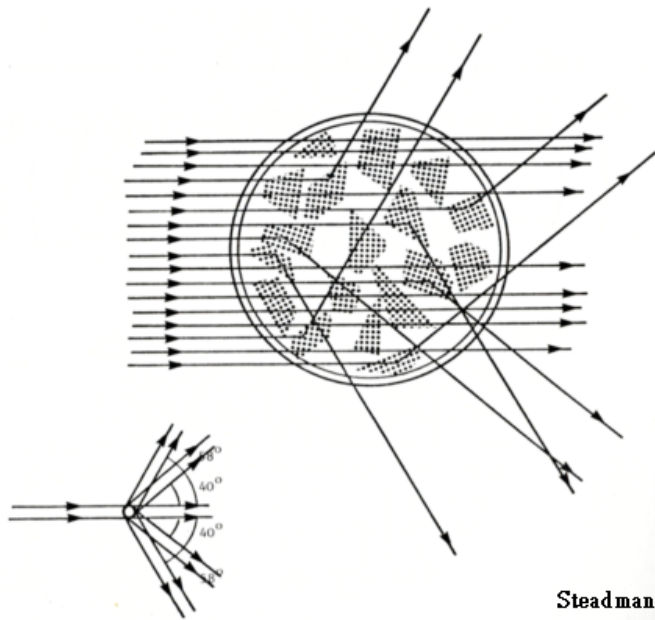# Rotating crystal method

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

〔圖七〕 旋轉式攝影 (ROTATION PHOTOGRAPHS)

作旋轉式攝影時，將 X 光對準一小塊晶體，這塊晶體繞著與一主晶軸平行之軸旋轉，繞射光束可由一平的感光板（左）或圓柱形的感光片（右）記錄，所有反射光束的像都排在層線上，本圖之晶軸沿 OC，層線對應於 $l=0$, $l=1$, $l=2$；所有的點對應於全部不同的 h 及 k。

Powder method

Steadman

【圖八】 粉末式攝影 (POWDER PHOTOGRAPHS)

作粉末式照像時,X光照射在一塊許多向任意方向排列的小晶體上,每一階次 (*hkl*) 的繞光束組成一圓椎體,如以垂直於入射光之平面感光板記錄,每一階次以圍繞中心的圓環狀出現;(上)

本圖的這些環的位置是面心正方晶格的典型式。爲了比較方便,經常使用圓柱形底片;其軸垂直於入射光(下)圓椎體與圓柱相交照出的弧線,差不多可以包括所有的角度直至 180°;底片可打開成條形。

The structure factor for a crystal with basis:

$$S(h,k,l) \equiv \sum_{j=1}^{p} f_{aj} e^{-i\vec{G}_{hkl} \cdot \vec{d}_j}$$

f_a is the atomic form factor

Example:

fcc lattice = cubic lattice with a 4-point basis
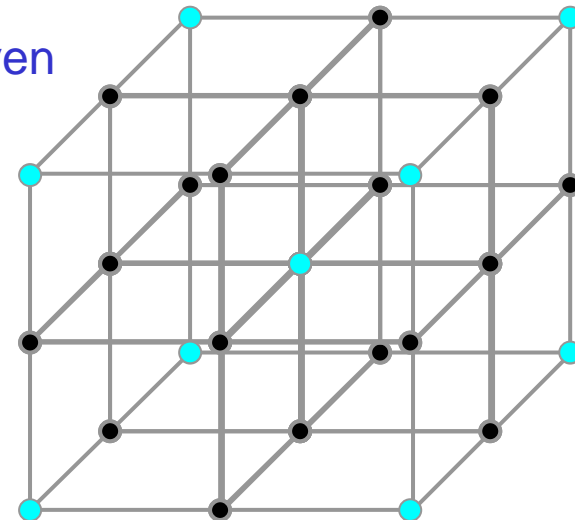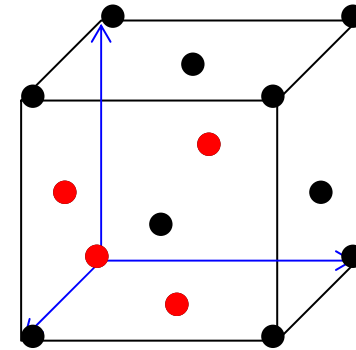
$$\vec{d}_1 = \vec{0},$$

$$\vec{d}_2 = \frac{\vec{a}_1}{2} + \frac{\vec{a}_2}{2}, \vec{d}_3 = \frac{\vec{a}_2}{2} + \frac{\vec{a}_3}{2}, \vec{d}_4 = \frac{\vec{a}_3}{2} + \frac{\vec{a}_1}{2}$$

$$\vec{G}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

$$S(h,k,l) = f_a \left[1 + e^{-i\pi(h+k)} + e^{-i\pi(k+l)} + e^{-i\pi(l+h)} \right]$$

$\begin{cases} = 4f_a \text{ when } h,k,l \text{ are all odd or all even} \\ = 0 \text{ otherwise} \end{cases}$

Eliminates all the points in the reciprocal cubic lattice with S=0. The result is a bcc lattice, as it should be!

$h^2 + l^2 + k^2$ 0 1 2 3 4 5 6 ● 8 9 10 11 12 13 14 ● 16 17 18 19 20 21 22 ● 24
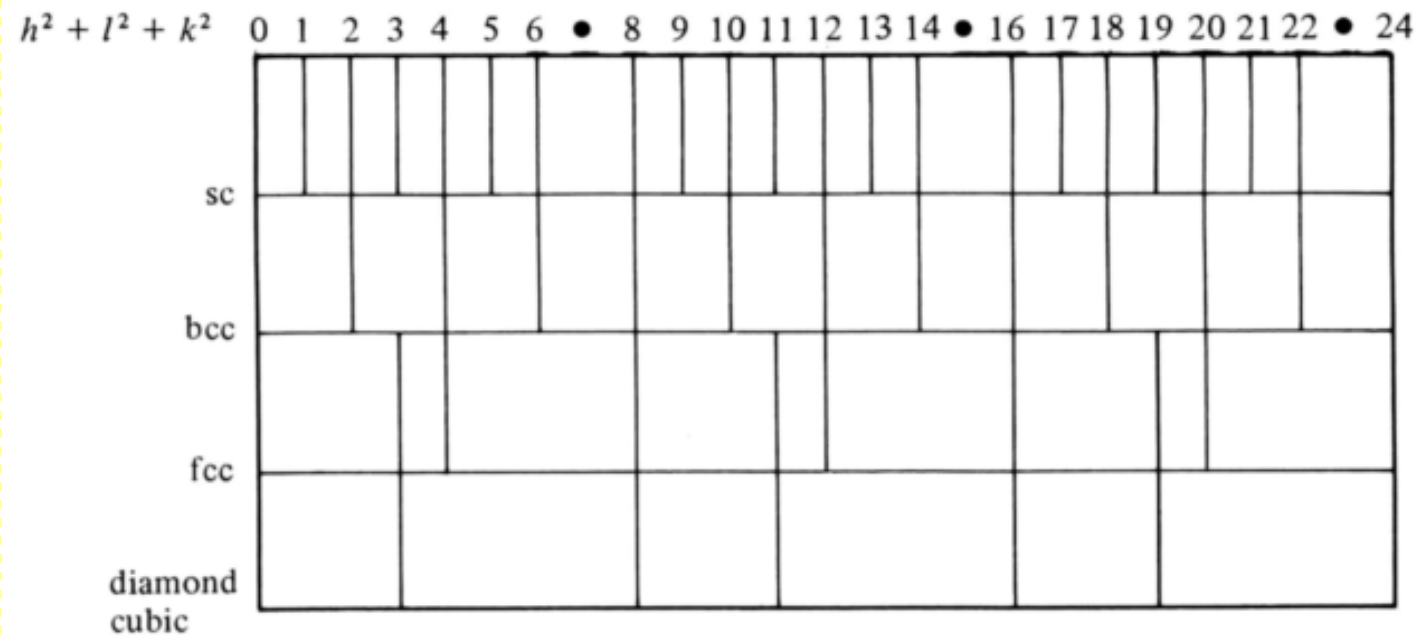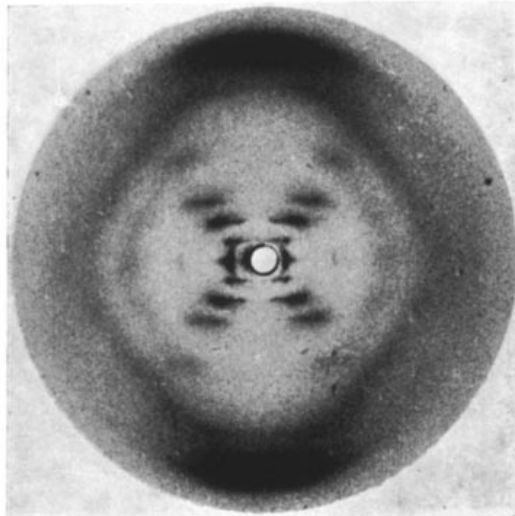
sc

bcc

fcc

diamond
cubic

Fig. 3.4 Permitted diffracted beams in cubic systems are characterized by the values of $h^2 + k^2 + l^2$. The figure shows how the addition of a basis to the simple cubic primitive cell reduces the number of allowed beams, increasingly the more atoms in the basis. Note the regular sequence of each pattern. The correct angular separations are not reproduced in this diagram.   *Myers*

Homework: Find out the structure factor of the honeycomb structure, then draw its reciprocal structure. Different points in the reciprocal structure may have different structure factors. Draw a larger dots if the associated $|S|^2$ is larger.
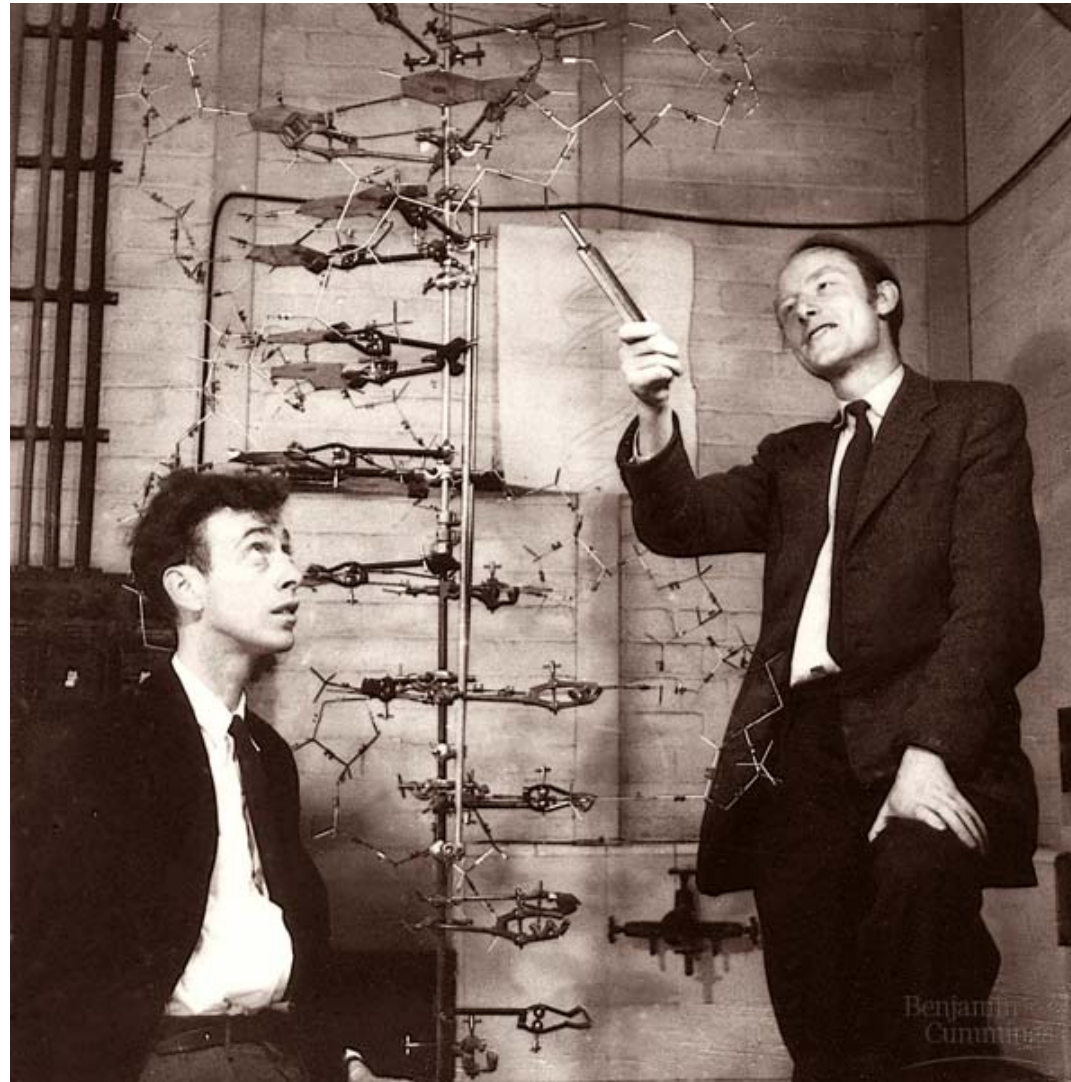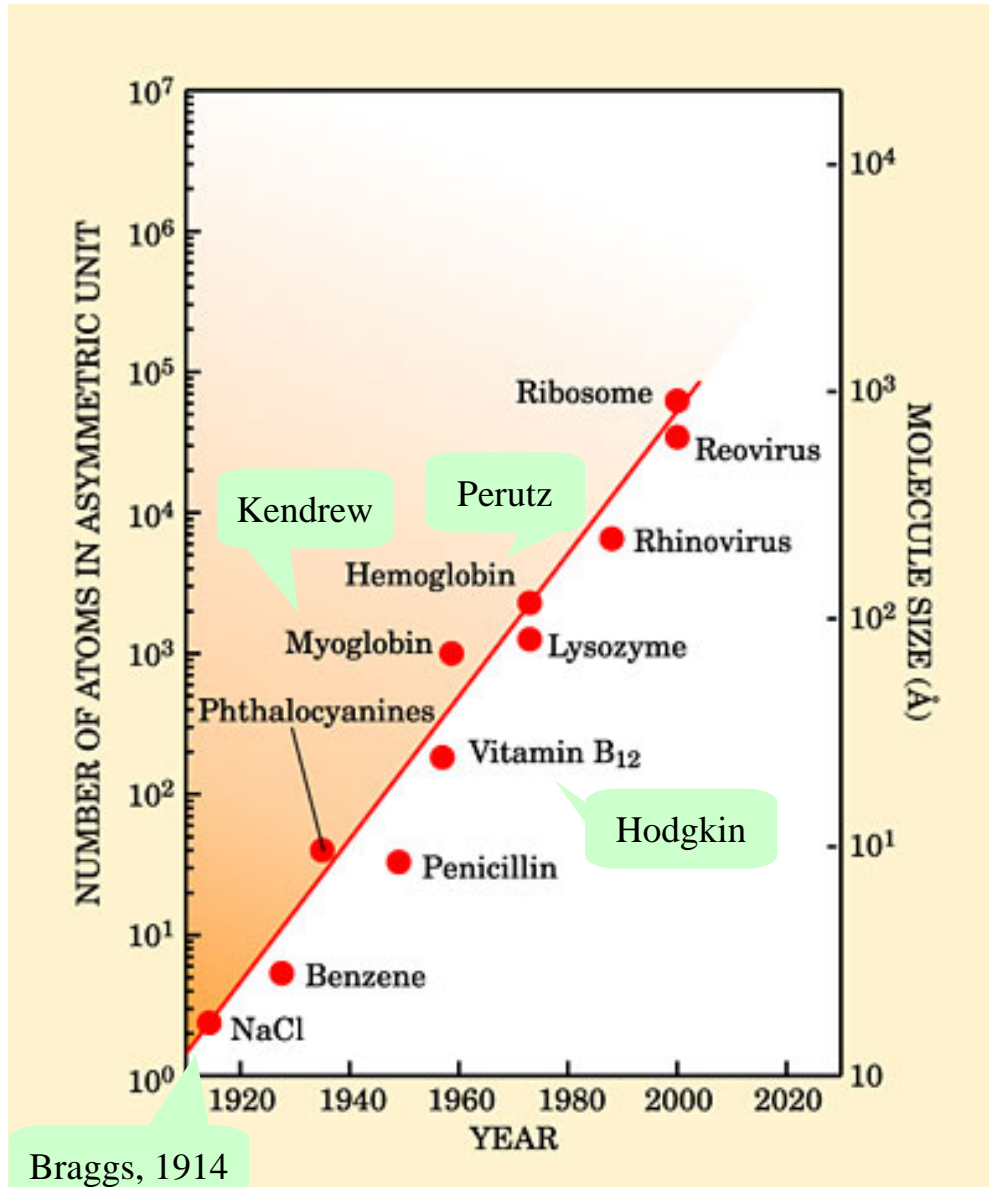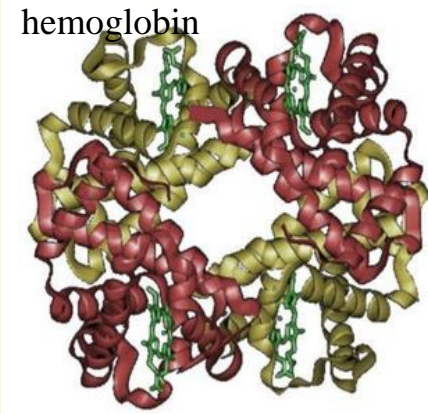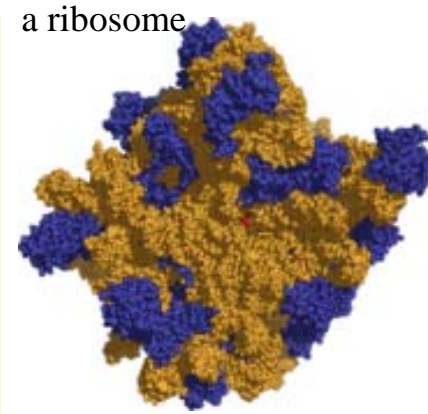
Franklin and Gosling, 1953

Watson and Crick, 1953

(See *Double helix*, highly recommended)

a ribosome

hemoglobin

NUMBER OF ATOMS IN ASYMMETRIC UNIT

MOLECULE SIZE (Å)

Ribosome
Reovirus
Kendrew
Perutz
Rhinovirus
Hemoglobin
Myoglobin
Lysozyme
Phthalocyanines
Vitamin B$_{12}$
Hodgkin
Penicillin
Benzene
NaCl
Braggs, 1914

YEAR

DOROTHY HODGKIN 20

Shen et al, Phys Today Mar, 2006

3.4.6 Accuracy of Structure Determinations

Catalogs of crystal structures must always be employed with the possibility in mind that published results are inaccurate or incorrect. Abrahams et al. (1967) describe an effort to determine how big these errors might be, by taking a carefully prepared crystal to multiple research groups and asking them to measure Bragg peak intensities independently. Although each group claimed accuracy in determining structures of around 1%, discrepancies between different groups were typically on the order of 5%–6%, and measurements of the intensity of the (1 1 1) reflection varied by 50%. In revisiting the results of this experiment, Mackenzie and Maslen (1968) call the results "grossly discordant." An example of an incorrect structure determination is provided by the high-cristobalite structure of SiO_2, on page 318 of