Lecture II Reciprocal Lattice

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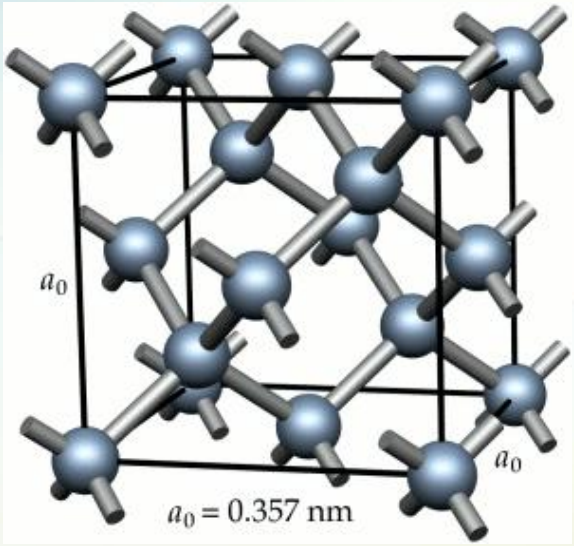
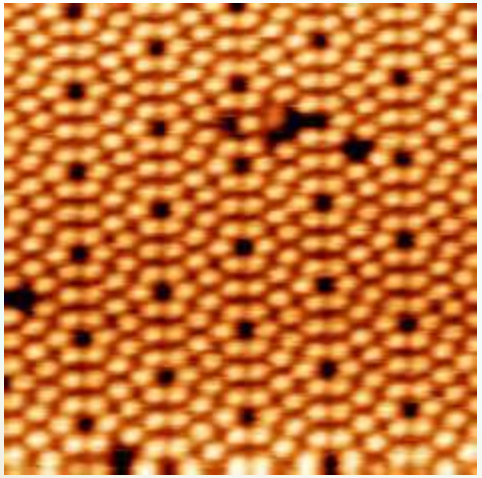


How do we learn about the structure of various crystals?

► Surface structure:

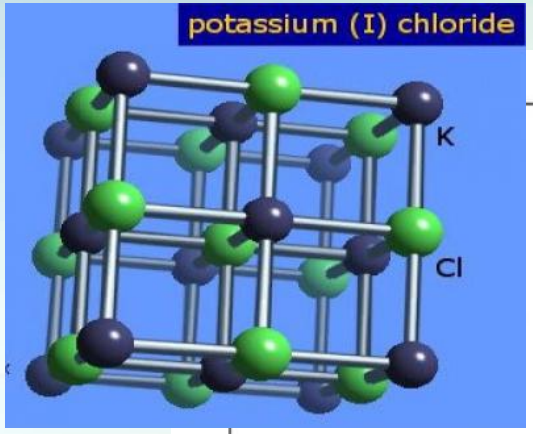
STM, AFM, SEM



Si(111)/STM

► Bulk structure:

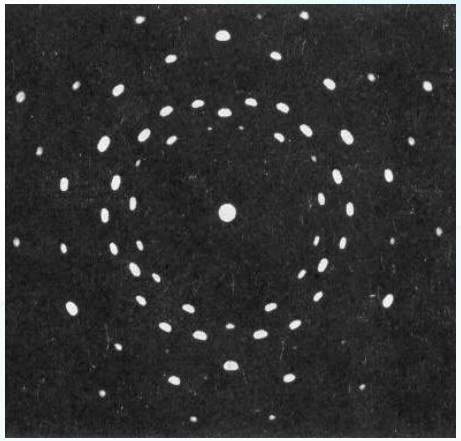
Diffraction by X-Ray, neutron, etc.



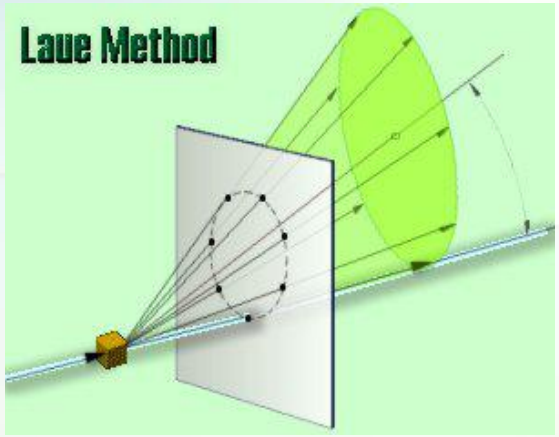
puzzle?

XRD

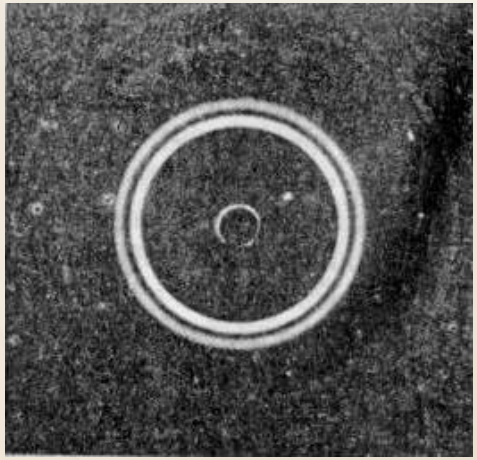
Laue method: with “white” X-ray and single crystals



Laue diffraction pattern of a single SiO_2 crystal

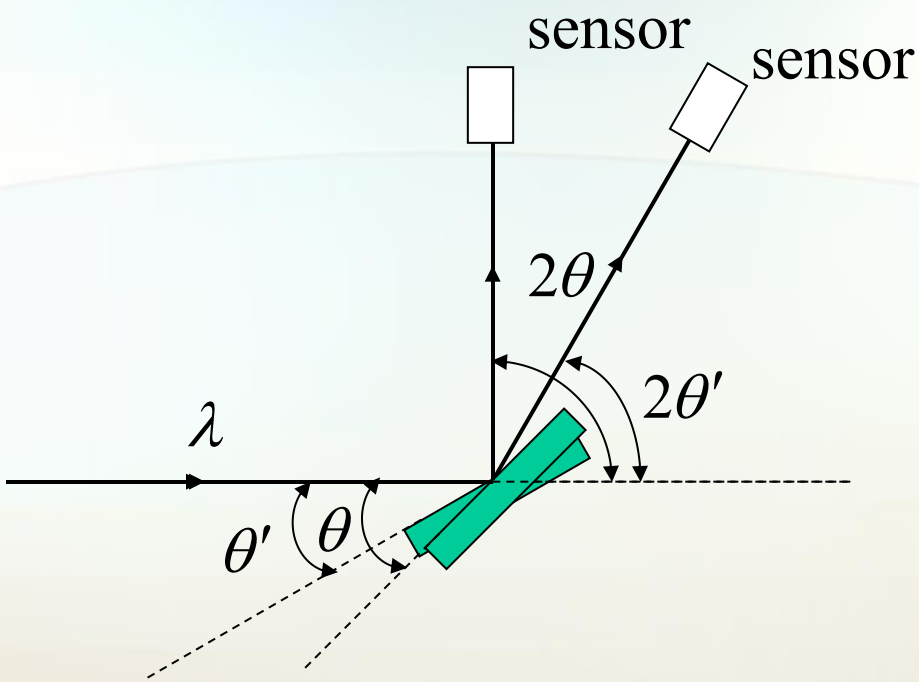


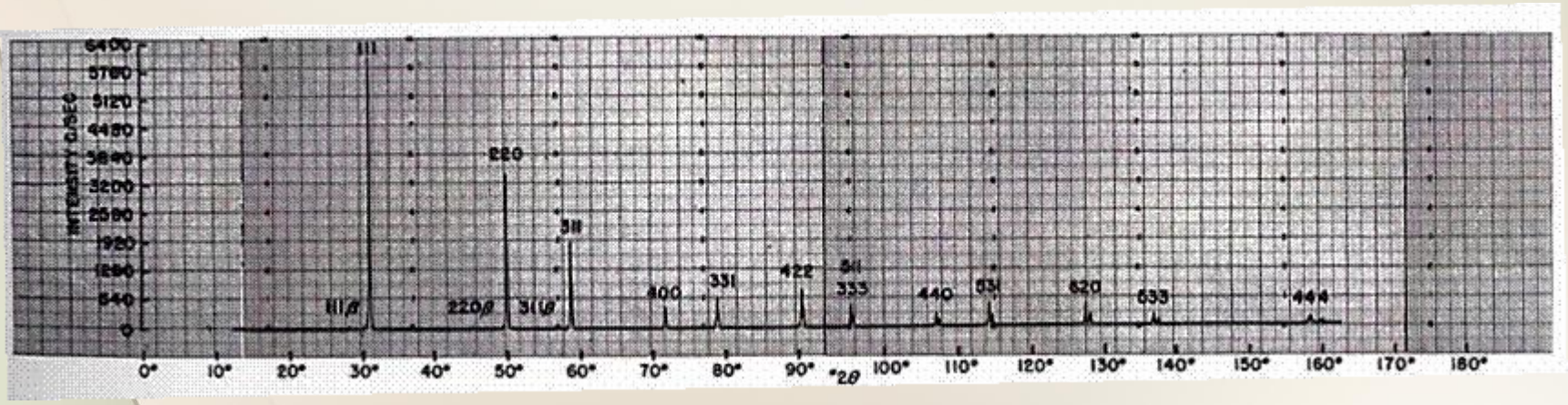
Debye method: with monochromatic X-ray and powder samples



Debye diffraction circles of Aluminum powders

X-ray diffractometer (monochromatic X-ray and scan θ)



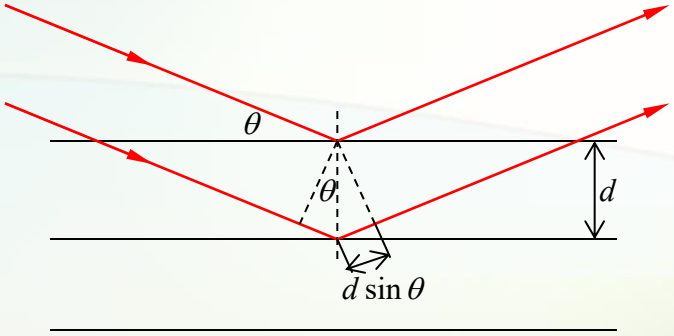


▶How the XRD peaks appear?

Diffraction of waves by crystals

The Bragg law:

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



- elastic scattering
- periodic lattice
- does not refer to what kind of lattice
- does not refer to the detail of the basis
- no information of the intensity

▶How deep the X-Ray penetrates/diffracts?

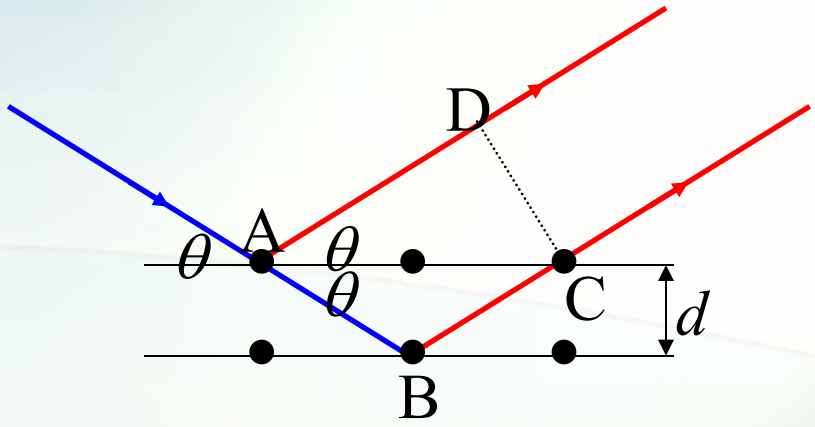
Each plane reflects 10^{-3} to 10^{-5} of the incident radiation.

Path difference for one incident beam

$$AB = BC = \frac{d}{\sin\theta}$$

$$AC = 2d\cot\theta$$

$$AD = AC\cos\theta = \frac{2d\cos^2\theta}{\sin\theta}$$

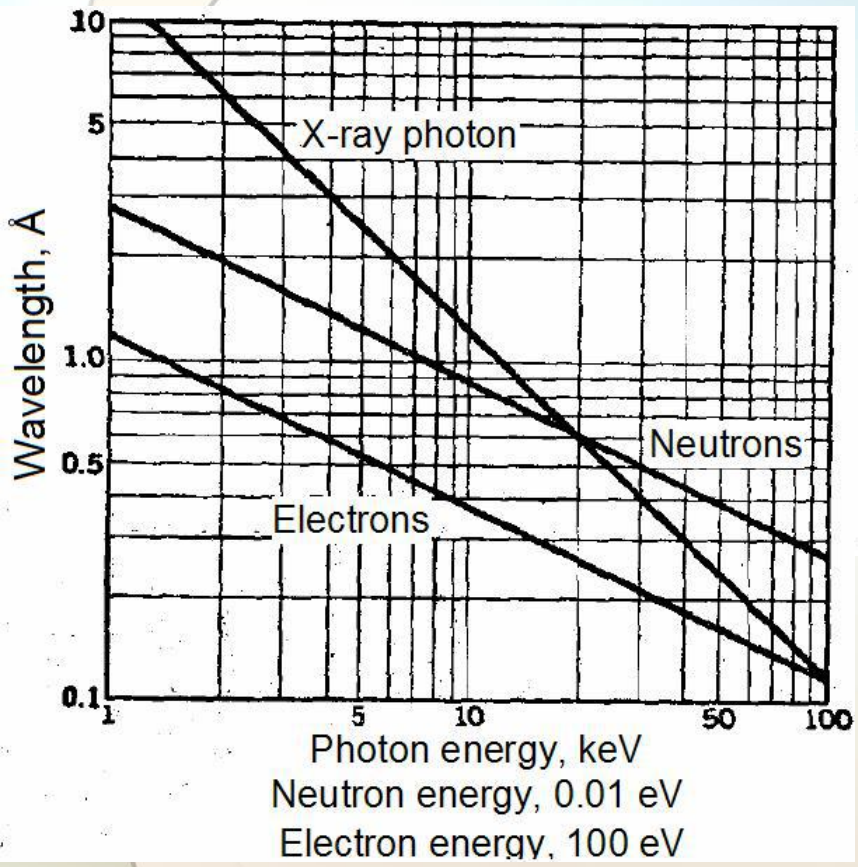


This path difference is:

$$AB + BC - AD = \frac{2d}{\sin\theta} - \frac{2d\cos^2\theta}{\sin\theta} = 2d\sin\theta$$

The condition of the constructive interference of the radiation is

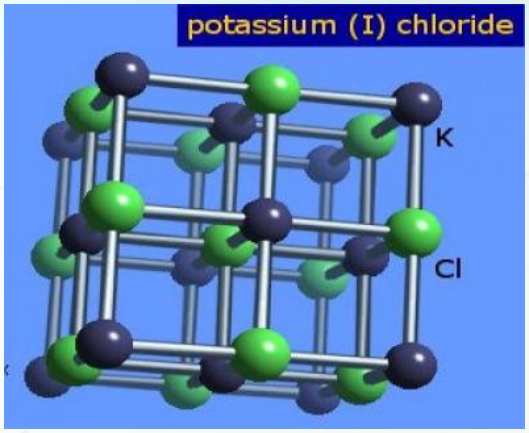
$$AB + BC - AD = 2d\sin\theta = n\lambda$$

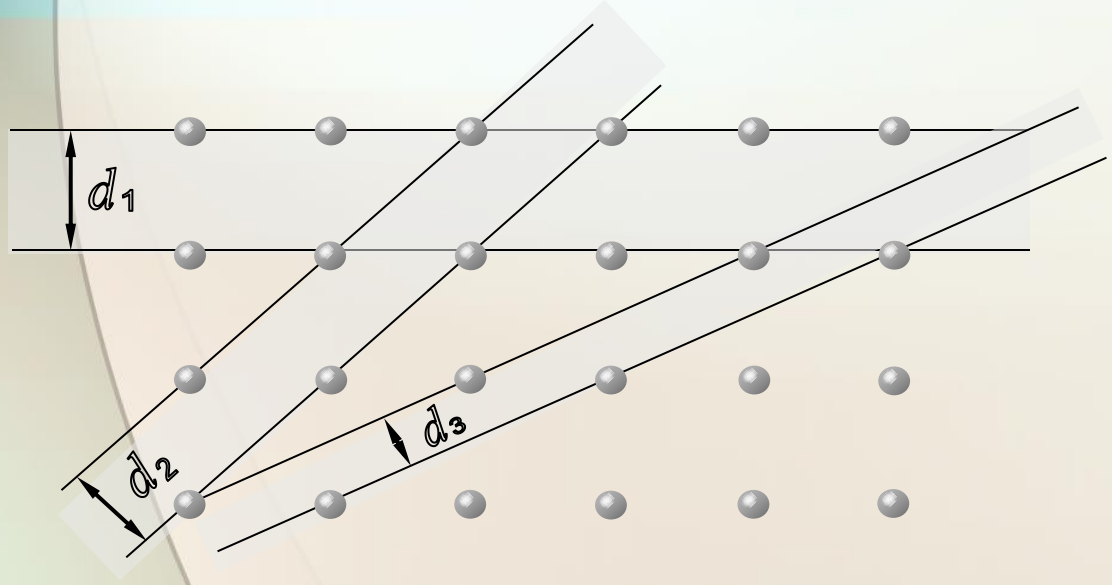


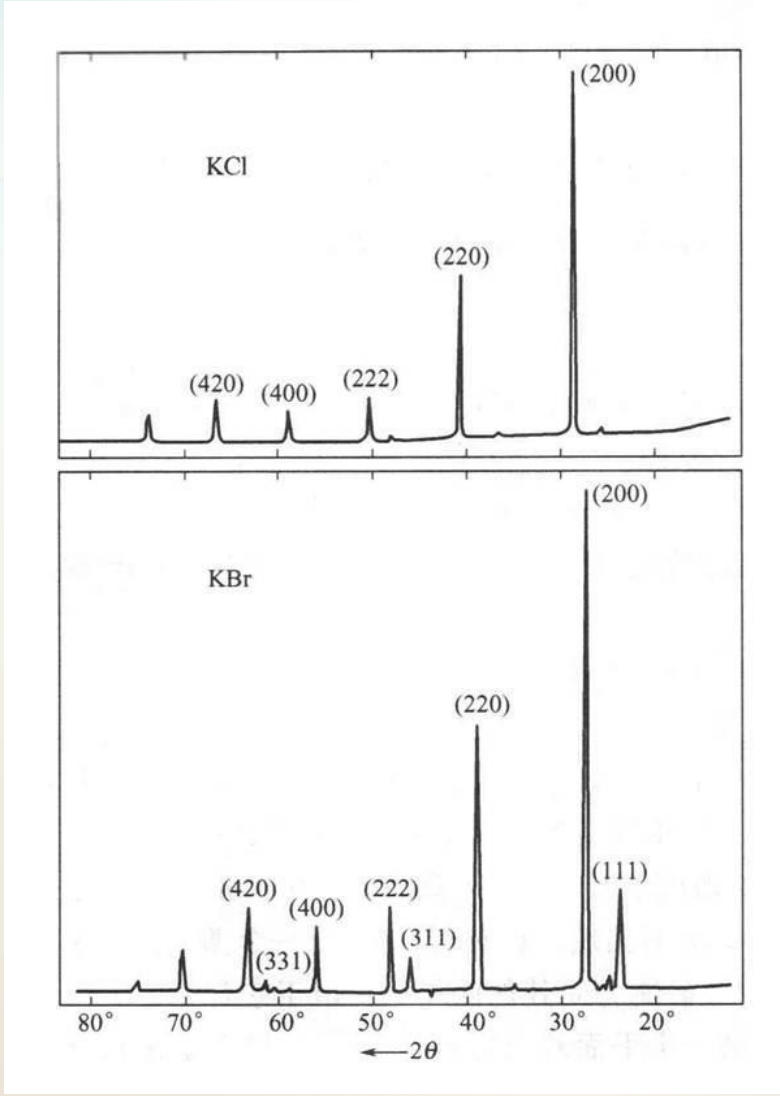
	X-rays	Neutrons	Electrons
Charge	0	0	$-e$
Mass	0	$1.67 \cdot 10^{-27}$ kg	$9.11 \cdot 10^{-31}$ kg
Typical energy	10 keV	0.03 eV	100 keV
Typical wavelength	1Å	1 Å	0.05Å
Typical attenuation length	100 μm	5 cm	1 μm
Typical atomic form factor, f	10^{-3} Å	10^{-4} Å	10 Å

Crystal structures are often studied through the diffraction of photons, neutrons, and electrons.

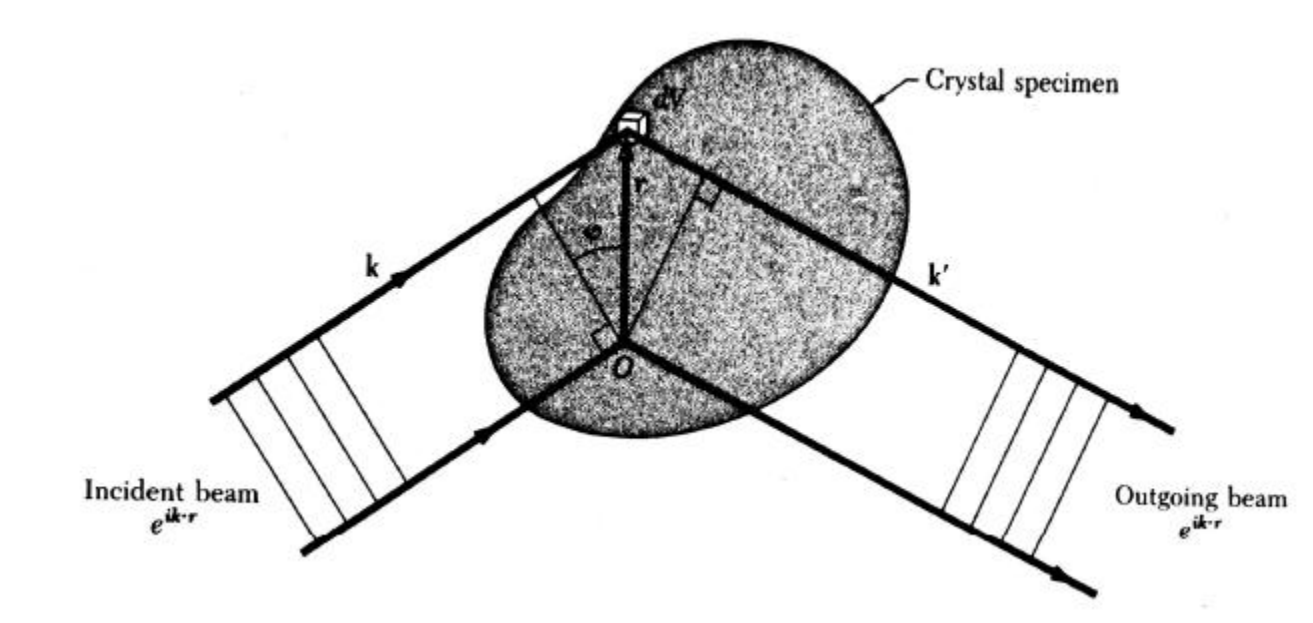
▶How to determine the structure from the peaks?







▶How to estimate the intensity of the peaks?



The transition rate between wave vector k and k′ is proportional to the square of the matrix element:

$$M_{\vec{k},\vec{k}'} = <\vec{k}\,|\,U\,|\,\vec{k}'> = \int d\vec{x}\,\exp(-i\vec{k}\cdot\vec{x})U(\vec{x})\exp(i\vec{k}'\cdot\vec{x})$$

$$U(\vec{x}) \sim \text{electron density } n(\vec{x}) \text{ for X-ray}$$

▶How to estimate the intensity of the peaks?

Scattered waves amplitude

Fourier analysis

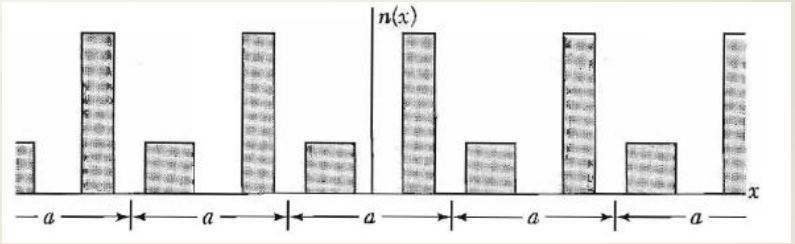
Periodic structure of crystal → The variance of the electrons density function

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

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

In one dimension, consider the wave function n(x) with period a in the direction x, the Fourier transformation of n(x) can be written as:

$$n(x) = \sum_p n_p \exp(i2\pi px/a)$$



where

$$n_p = a^{-1}\int_0^a dx\, n(x)\exp(-i2\pi px/a)$$

In three dimension, consider $n(x+a_1, y+a_2, z+a_3) = n(x, y, z)$, the Fourier transformation of $n(x)$ can be written as:

$$
\begin{aligned}
n(x,y,z) &= \sum_{p_1} n_x(y,z)\exp(i2\pi p_1 x/a_1) \\
&= \sum_{p_1,p_2} n_{xy}(z)\exp(i2\pi p_1 x/a_1)\exp(i2\pi p_2 y/a_2) \\
&= \sum_{p_1,p_2,p_3} n_{xyz}\exp(i2\pi p_1 x/a_1)\exp(i2\pi p_2 y/a_2)\exp(i2\pi p_3 z/a_3) \\
&= \sum_{p_1,p_2,p_3} n_{xyz}\exp[i(\frac{2\pi p_1}{a_1}x+\frac{2\pi p_2}{a_2}y+\frac{2\pi p_3}{a_3}z)] \\
&= \sum_{G} n_G \exp(i\vec{G}\cdot\vec{r})
\end{aligned}
$$

Here we define $\vec{G}=(p_1\frac{2\pi}{a_1}, p_2\frac{2\pi}{a_2}, p_3\frac{2\pi}{a_3})$ is the reciprocal lattice vector.

A short summary

Fourier transformation

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

The inversion of the Fourier series

$$n_G = V_C^{-1} \int_{cell} dV n(\vec{r}) \exp(-i\vec{G}\cdot\vec{r})$$

reciprocal lattice vector $\vec{G}=(p_1\frac{2\pi}{a_1}, p_2\frac{2\pi}{a_2}, p_3\frac{2\pi}{a_3})$

Reciprocal lattice (倒格子，倒易点阵) vectors

In general case, consider $n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r} + u_1\mathbf{a_1} + u_2\mathbf{a_2} + u_3\mathbf{a_3}) = n(\mathbf{r})$.
The Fourier transformation of $n(\mathbf{r})$ is

$$n(\vec{r}) = \sum_G n_G \exp(i\vec{G}\cdot\vec{r}).$$

The axis vectors $\mathbf{b_1}$, $\mathbf{b_2}$, $\mathbf{b_3}$ of the reciprocal lattice is:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{V_C}\vec{a}_2 \times \vec{a}_3;$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{V_C}\vec{a}_3 \times \vec{a}_1;$$

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

The reciprocal lattice vector

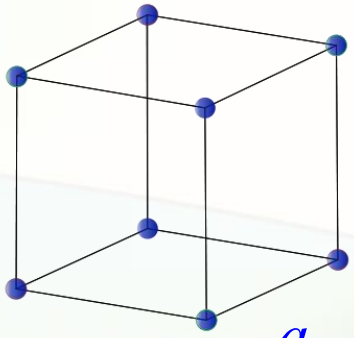
$$\vec{G} = v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3,$$

Reciprocal lattice to sc lattice

The primitive translation vectors of a sc lattice are

$$\vec{a}_1 = a\hat{x}; \qquad \vec{a}_2 = a\hat{y}; \qquad \vec{a}_3 = a\hat{z}.$$

The volume of the primitive cell is $V_C = a^3$.

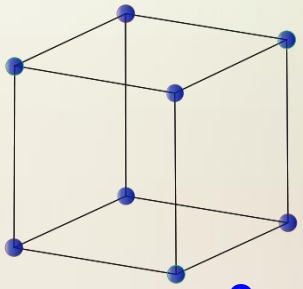


Then the primitive translation vectors of the reciprocal lattice are

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = 2\pi \frac{a^2 \hat{y} \times \hat{z}}{a^3 (\hat{x} \cdot \hat{y} \times \hat{z})} = \frac{2\pi}{a} \hat{x};$$

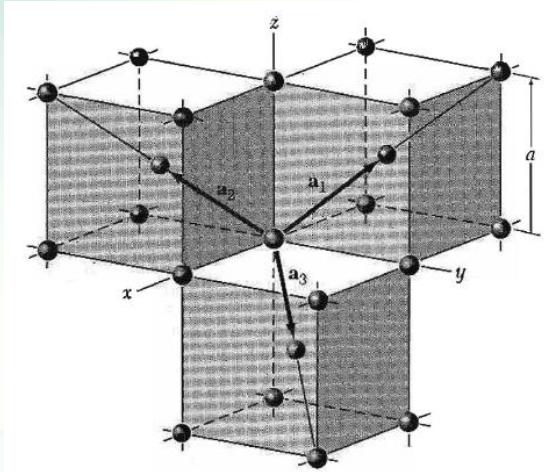
$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = 2\pi \frac{a^2 \hat{z} \times \hat{x}}{a^3 (\hat{x} \cdot \hat{y} \times \hat{z})} = \frac{2\pi}{a} \hat{y};$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = 2\pi \frac{a^2 \hat{x} \times \hat{y}}{a^3 (\hat{x} \cdot \hat{y} \times \hat{z})} = \frac{2\pi}{a} \hat{z}.$$



The reciprocal lattice of a sc lattice is a sc lattice with lattice constant $2\pi/a$.

Reciprocal lattice to bcc lattice



The primitive translation vectors of a bcc lattice are

$$\vec{a}_1 = \frac{a}{2}(-\hat{x}+\hat{y}+\hat{z}); \quad \vec{a}_2 = \frac{a}{2}(\hat{x}-\hat{y}+\hat{z}); \quad \vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z}).$$

The volume of the primitive cell is $V_C = a^3/2$.

Then the primitive translation vectors of the reciprocal lattice are

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

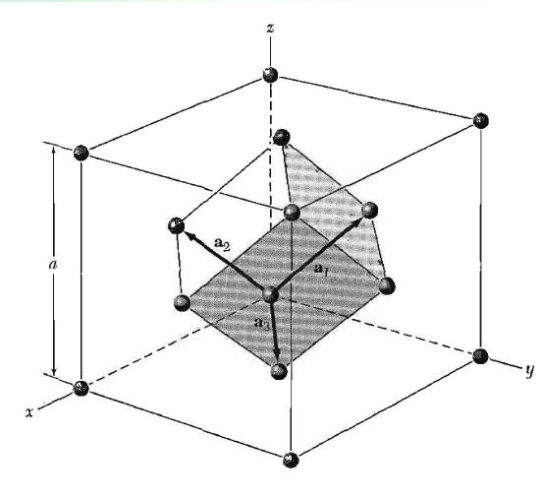
$$\vec{b}_2 = \frac{2\pi}{V_C}(\vec{a}_3 \times \vec{a}_1) = \frac{4\pi}{a^3}(\frac{a}{2})^2(\hat{x}+\hat{y}-\hat{z})\times(-\hat{x}+\hat{y}+\hat{z}) = \frac{2\pi}{a}(\hat{z}+\hat{x});$$

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

The reciprocal lattice of a bcc lattice is a fcc lattice with the lattice constant $4\pi/a$.

The volume of Brillouin cell is $(4\pi/a)^3/4 = 2(2\pi/a)^3$.

Reciprocal lattice to fcc lattice



The primitive translation vectors of a fcc lattice are

$$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z}); \quad \vec{a}_2 = \frac{a}{2}(\hat{z}+\hat{x}); \quad \vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y}).$$

The volume of the primitive cell is $V_C = a^3/4$.

Then the primitive translation vectors of the reciprocal lattice are

$$\vec{b}_1 = \frac{2\pi}{V_C}(\vec{a}_2 \times \vec{a}_3) = \frac{8\pi}{a^3}(\frac{a}{2})^2(\hat{z}+\hat{x})\times(\hat{x}+\hat{y}) = \frac{2\pi}{a}(-\hat{x}+\hat{y}+\hat{z});$$

$$\vec{b}_2 = \frac{2\pi}{V_C}(\vec{a}_3 \times \vec{a}_1) = \frac{8\pi}{a^3}(\frac{a}{2})^2(\hat{x}+\hat{y})\times(\hat{y}+\hat{z}) = \frac{2\pi}{a}(\hat{x}-\hat{y}+\hat{z});$$

$$\vec{b}_3 = \frac{2\pi}{V_C}(\vec{a}_1 \times \vec{a}_2) = \frac{8\pi}{a^3}(\frac{a}{2})^2(\hat{y}+\hat{z})\times(\hat{z}+\hat{x}) = \frac{2\pi}{a}(\hat{x}+\hat{y}-\hat{z}).$$

The reciprocal lattice of a fcc lattice is a bcc lattice with the lattice constant $4\pi/a$.

The volume of Brillouin cell is $(4\pi/a)^3/2 = 4(2\pi/a)^3$.

Property of the reciprocal lattice:

1. $\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij} = \begin{cases} 2\pi & (i = j) \\ 0 & (i \neq j) \end{cases}$

Note: $\boldsymbol{b}_\mathbf{i}$ is unnecessarily parallel to $\boldsymbol{a}_\mathbf{i}$.

2. $\vec{r} \cdot \vec{G} = 2\pi m$, where $\vec{r}$ is a lattice vector, $\vec{G}$ is a reciprocal lattice vector, and m is integer.

3. A reciprocal lattice vector $\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ is perpendicular to (hkl) plane in the crystal lattice.

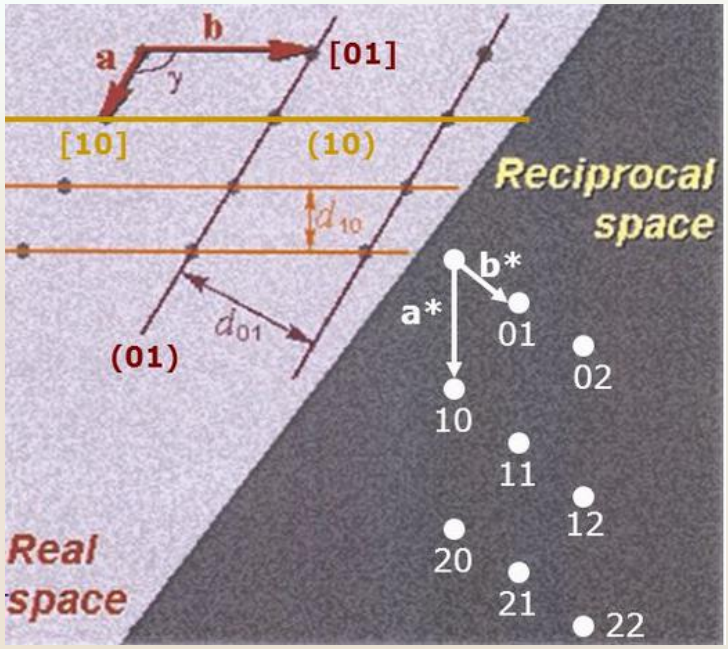
4. The volume of the primitive cell of the reciprocal lattice $V_C^* = (2\pi)^3 / V_C$, where V_C is the crystal primitive cell.

Every crystal structure has two lattices:

crystal lattice and reciprocal lattice

Microscope image
e.g. STM, AFM, TEM → Map of the crystal lattice

Diffraction pattern
e.g. XRD, neutron scattering → Map of the reciprocal lattice



NB:
2D reciprocal lattice

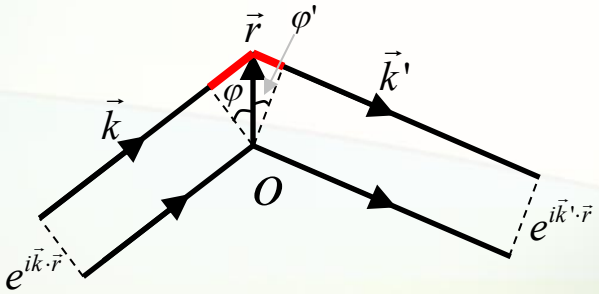
Diffraction conditions and Laue equations

Theorem: the set of reciprocal lattice vectors **G** determines the possible x-ray reflections.

For the incident wave **k**

The difference in path length: $r\sin\varphi$

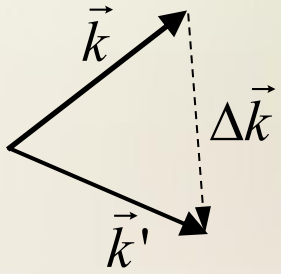
The difference in phase: $\frac{2\pi}{\lambda} r\sin\varphi = \vec{k}\cdot\vec{r}$



For the outgoing wave **k'**

The difference in path length: $r\sin\varphi'$

The difference in phase: $\frac{2\pi}{\lambda} r\sin\varphi' = -\vec{k}'\cdot\vec{r}$



The total difference in phase: $(\vec{k}-\vec{k}')\cdot\vec{r} = -\Delta\vec{k}\cdot\vec{r}$

The scattering amplitude:

$$F = \int dV\, n(\vec{r}) \exp(i\Delta\varphi) = \int dV\, n(\vec{r}) \exp(-i\Delta\vec{k}\cdot\vec{r})$$

Substitute $n(\vec{r}) = \sum_G n_G \exp(i\vec{G}\cdot\vec{r})$ in, we have

$$F = \sum_G \int dV\ n_G \exp[i(\vec{G} - \Delta\vec{k})\cdot\vec{r}]$$

The ***diffraction condition*** is: $\Delta\vec{k} = \vec{G}$

The amplitude is: $F \approx Vn_G$

For the elastic scattering, $|\mathbf{k}| = |\mathbf{k}'|$.

The diffraction condition is: $2\vec{k}\cdot\vec{G} + G^2 = 0$

or $2\vec{k}\cdot\vec{G} = G^2$

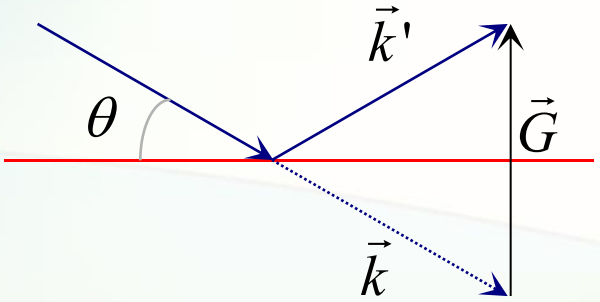
Project the diffraction condition to the crystal axes, we obtain the ***Laue equations***:

$$\vec{a}_1\cdot\Delta\vec{k} = 2\pi v_1; \qquad \vec{a}_2\cdot\Delta\vec{k} = 2\pi v_2; \qquad \vec{a}_3\cdot\Delta\vec{k} = 2\pi v_3$$

It can be proved that the condition for diffraction is another statement of the Bragg law.

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

$$d_{(hkl)} = 2\pi/|G|$$



$$k = 2\pi/\lambda$$

$$2(2\pi/\lambda)\cdot(2\pi/d_{(hkl)})\cos(\pi/2-\theta) = (2\pi/d_{(hkl)})^2$$

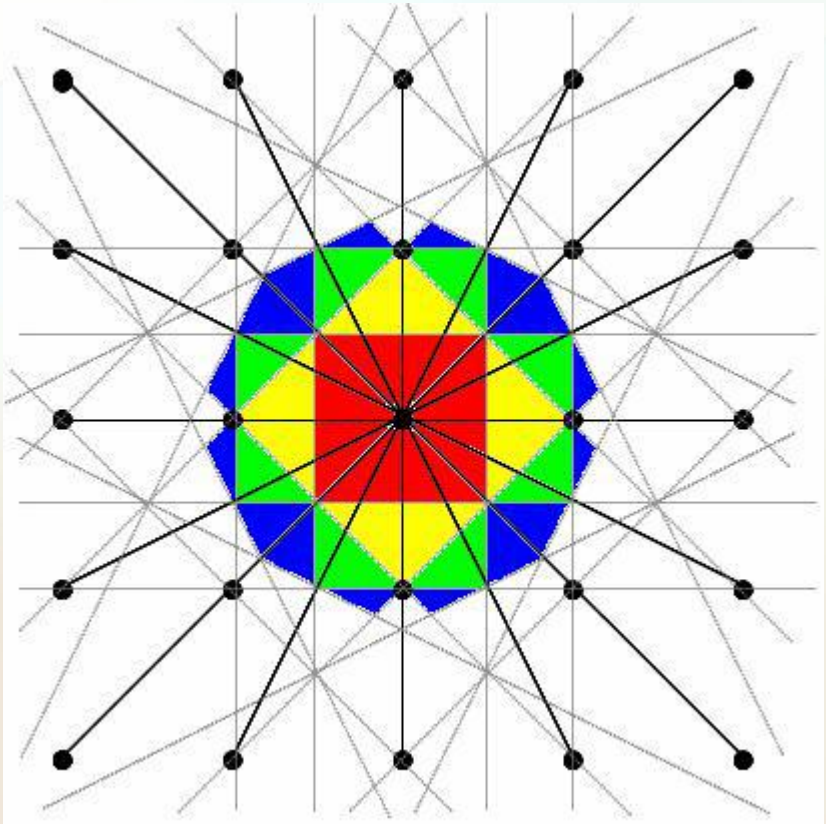
$$2d_{(hkl)}\cdot\sin\theta = \lambda$$

(hkl) may contain a common factor n.

$$2d_{(hkl)}\cdot\sin\theta = n\lambda$$

Brillouin zones

A Brillouin zone is defined as a Wigner-Seitz primitive cell in the reciprocal lattice.



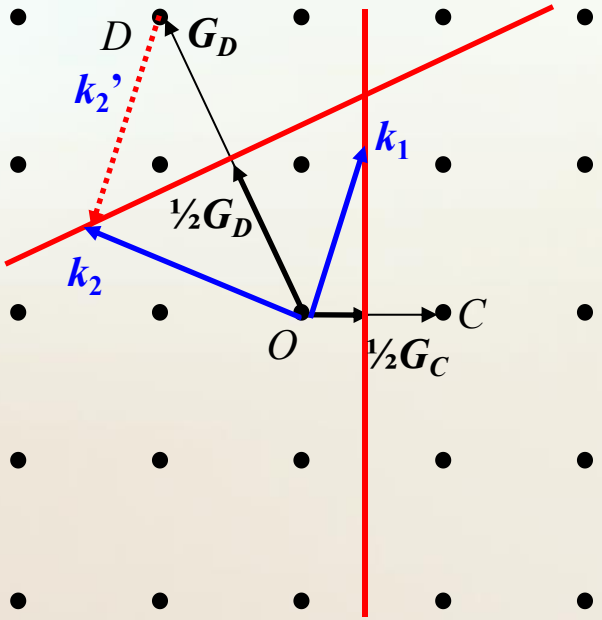
1st Brillouin zone
2nd Brillouin zone
3rd Brillouin zone
4th Brillouin zone

Q: Why do we define the Brillouin zones?

A wave whose wavevector drawn from the origin terminates on the Brillouin zone boundary will satisfy the condition for diffraction.

$$\vec{k} \cdot \left(\frac{\vec{G}}{2} \right) = \left(\frac{\vec{G}}{2} \right)^2$$

$$\vec{k}_2' - k_2 = -\vec{G}_D$$



Fourier analysis of the basis

Structure factor:

$$F_G = \int dV\ n(\vec{r}) \exp(-i\Delta\vec{k}\cdot\vec{r}) = \int dV\ n(\vec{r}) \exp(-i\vec{G}\cdot\vec{r})$$

$$= N \int_{cell} dV\ n(\vec{r}) \exp(-i\vec{G}\cdot\vec{r}) = NS_G$$

Defined the structure factor:

$$S_G \equiv \int_{cell} dV\ n(\vec{r}) \exp(-i\vec{G}\cdot\vec{r})$$

$$= \sum_j \int dV\ n_j(\vec{r}-\vec{r}_j) \exp(-i\vec{G}\cdot\vec{r})$$

$$= \sum_j \exp(-i\vec{G}\cdot\vec{r}_j) \int dV\ n_j(\vec{\rho}) \exp(-i\vec{G}\cdot\vec{\rho})$$

$$= \sum_j f_j \exp(-i\vec{G}\cdot\vec{r}_j)$$

Superposition of electron concentration functions

$$n(\vec{r}) = \sum_j^{cell} n_j(\vec{r}-\vec{r}_j)$$

$$\vec{\rho} \equiv \vec{r} - \vec{r}_j$$

Defined the atomic form factor:

$$f_j \equiv \int dV\ n_j(\vec{\rho}) \exp(-i\vec{G}\cdot\vec{\rho})$$

For the atom j

$$\vec{r}_j = x_j\vec{a}_1 + y_j\vec{a}_2 + z_j\vec{a}_3 \qquad 0 \le x_j, y_j, z_j < 1$$

For the reflection labeled by v_1, v_2, v_3

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

$$S_{(v_1v_2v_3)} = \sum_j f_j \exp[-i(v_1\vec{b}_1 + v_2\vec{b}_2 + v_3\vec{b}_3)\cdot(x_j\vec{a}_1 + y_j\vec{a}_2 + z_j\vec{a}_3)]$$

$$= \sum_j f_j \exp[-i2\pi(v_1x_j + v_2y_j + v_3z_j)]$$

If $S_G = 0$, the scattered density will be zero.

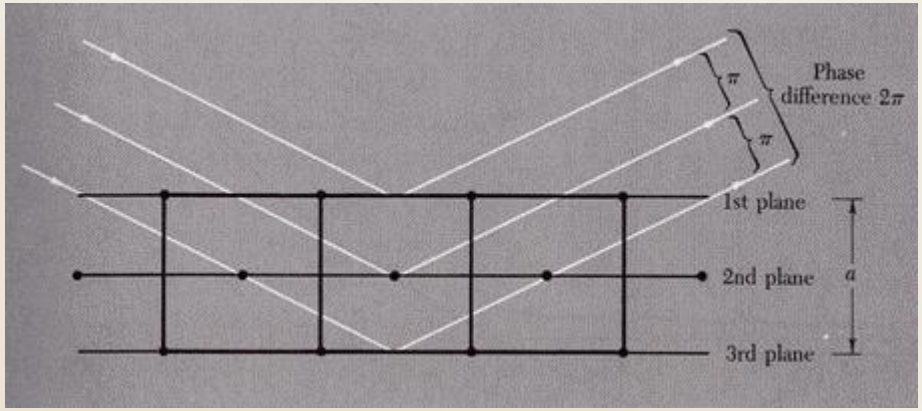
$$N_1(\text{cell})\times S_1(\text{basis}) = N_2(\text{cell})\times S_2(\text{basis})$$

Structure factor of the bcc lattice

Two identical atoms in the cubic cell

$$f_1 = f_2 = f,$$
$$x_1 = y_1 = z_1 = 0$$
$$x_2 = y_2 = z_2 = 1/2$$

$$S_{(\nu_1\nu_2\nu_3)} = f\{1+\exp[-i\pi(\nu_1+\nu_2+\nu_3)]\}$$
$$= \begin{cases} 0 & \text{when } \nu_1+\nu_2+\nu_3 = \text{odd} \\ 2f & \text{when } \nu_1+\nu_2+\nu_3 = \text{even} \end{cases}$$



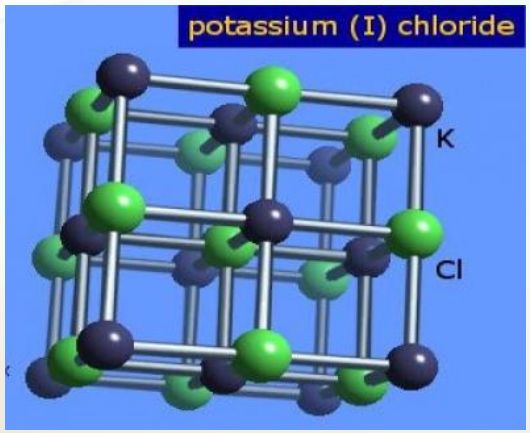
Structure factor of the fcc lattice

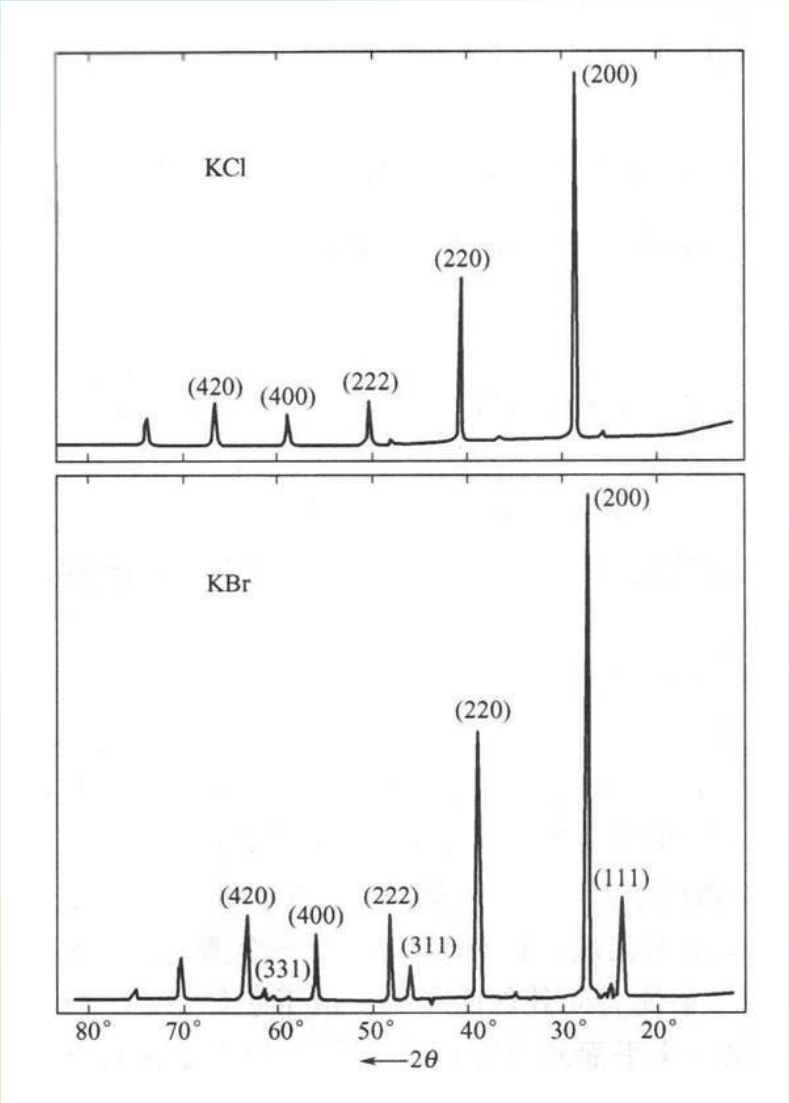
Four identical atoms in the cubic cell

$$f_1 = f_2 = f_3 = f_4 = f,$$
$$(x_1, y_1, z_1) = (0, 0, 0)$$
$$(x_2, y_2, z_2) = (0, 1/2, 1/2)$$
$$(x_3, y_3, z_3) = (1/2, 0, 1/2)$$
$$(x_4, y_4, z_4) = (1/2, 1/2, 0)$$

$$S_{(\nu_1\nu_2\nu_3)} = f\{1 + \exp[-i\pi(\nu_2 + \nu_3)] + \exp[-i\pi(\nu_1 + \nu_3)] + \exp[-i\pi(\nu_1 + \nu_2)]\}$$
$$= \begin{cases} 4f & \text{when } \nu_1, \nu_2, \nu_3 \text{ are all odd or all even} \\ 0 & \text{else} \end{cases}$$

The comparison of XRD patterns between KCl and KBr





solving the puzzle

Atomic form factor:

f_i is a measure of the scattering power of the jth atom in the unit cell.

In X-ray diffraction, the value of f_i involves the number and the distribution of atomic electrons, and the wavelength and the angle of scattering of the radiation.

$$f_j \equiv \int dV\, n_j(\vec{r}) \exp(-i\vec{G}\cdot\vec{r})$$

spherically symmetric approximate

$$= \int r^2 \sin\alpha\, dr d\varphi d\alpha\, n_j(r) \exp(-iGr\cos\alpha)$$

$$= 2\pi \int dr\, r^2 n_j(r) \int d(\cos\alpha) \exp(-iGr\cos\alpha)$$

$$= 4\pi \int dr\, n_j(r) r^2 \frac{\sin(Gr)}{Gr}$$

If $n_j(r) = z\delta(r)$, or $G = 0$

$$f_j = 4\pi \int dr\, n_j(r) r^2 = z$$

Experimental atomic scattering factors

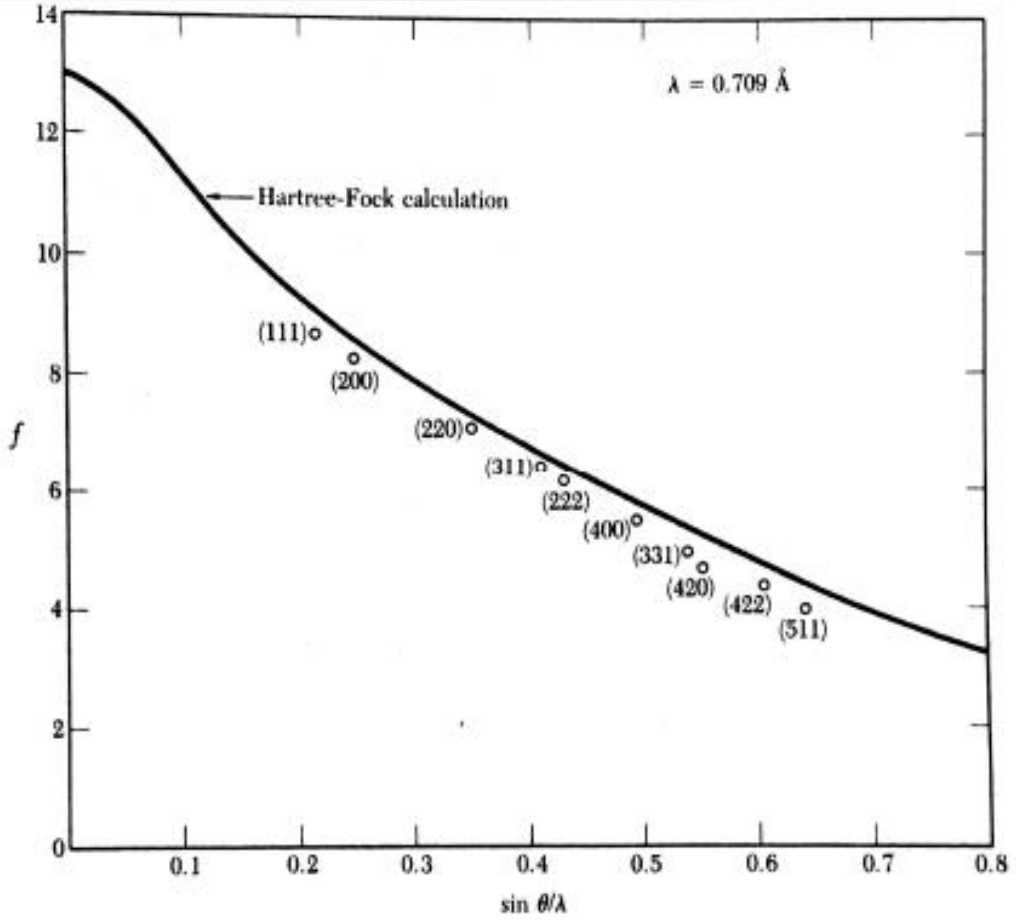
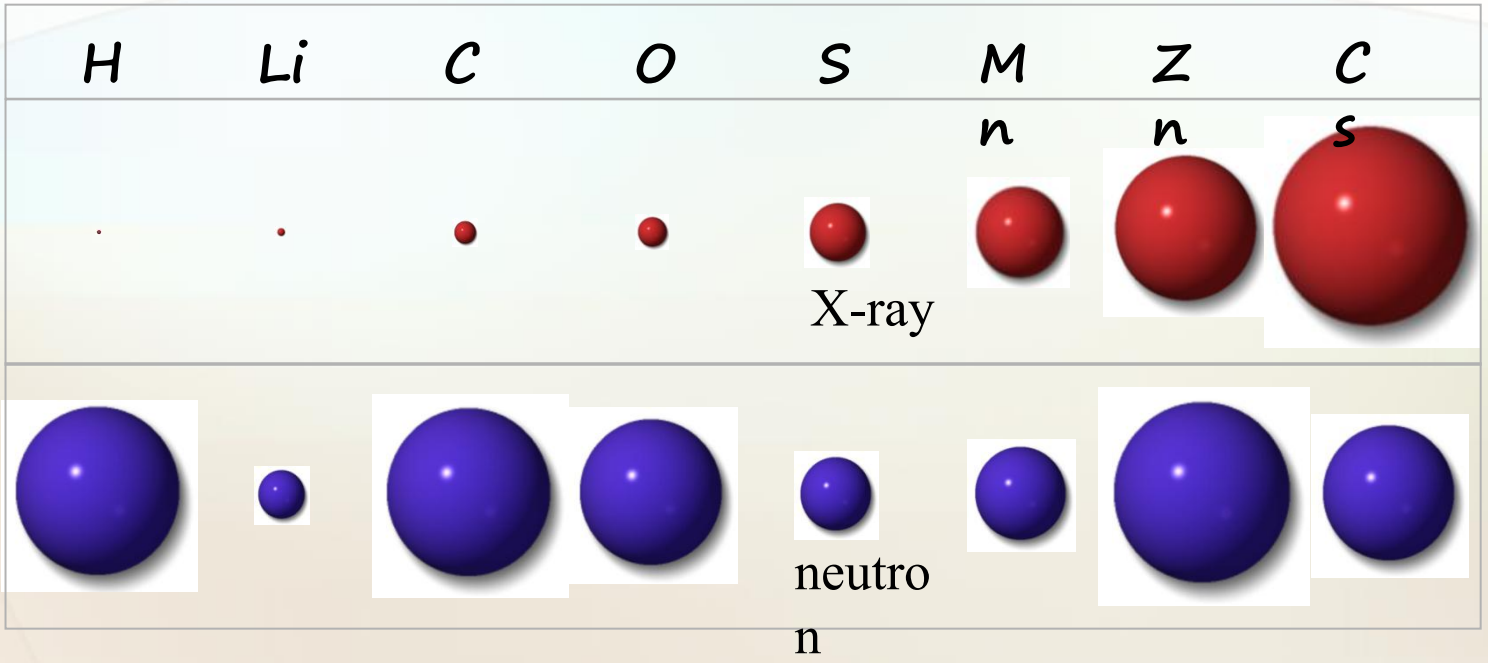


Figure 18 Absolute experimental atomic scattering factors for metallic aluminum, after Batterman, Chipman, and DeMarco. Each observed reflection is labeled. No reflections occur for indices partly even and partly odd, as predicted for an fcc crystal.

For neutron scattering, f_j relates not only to the electrons but also to the core.



Quasicrystal --Beyond the periodical crystal

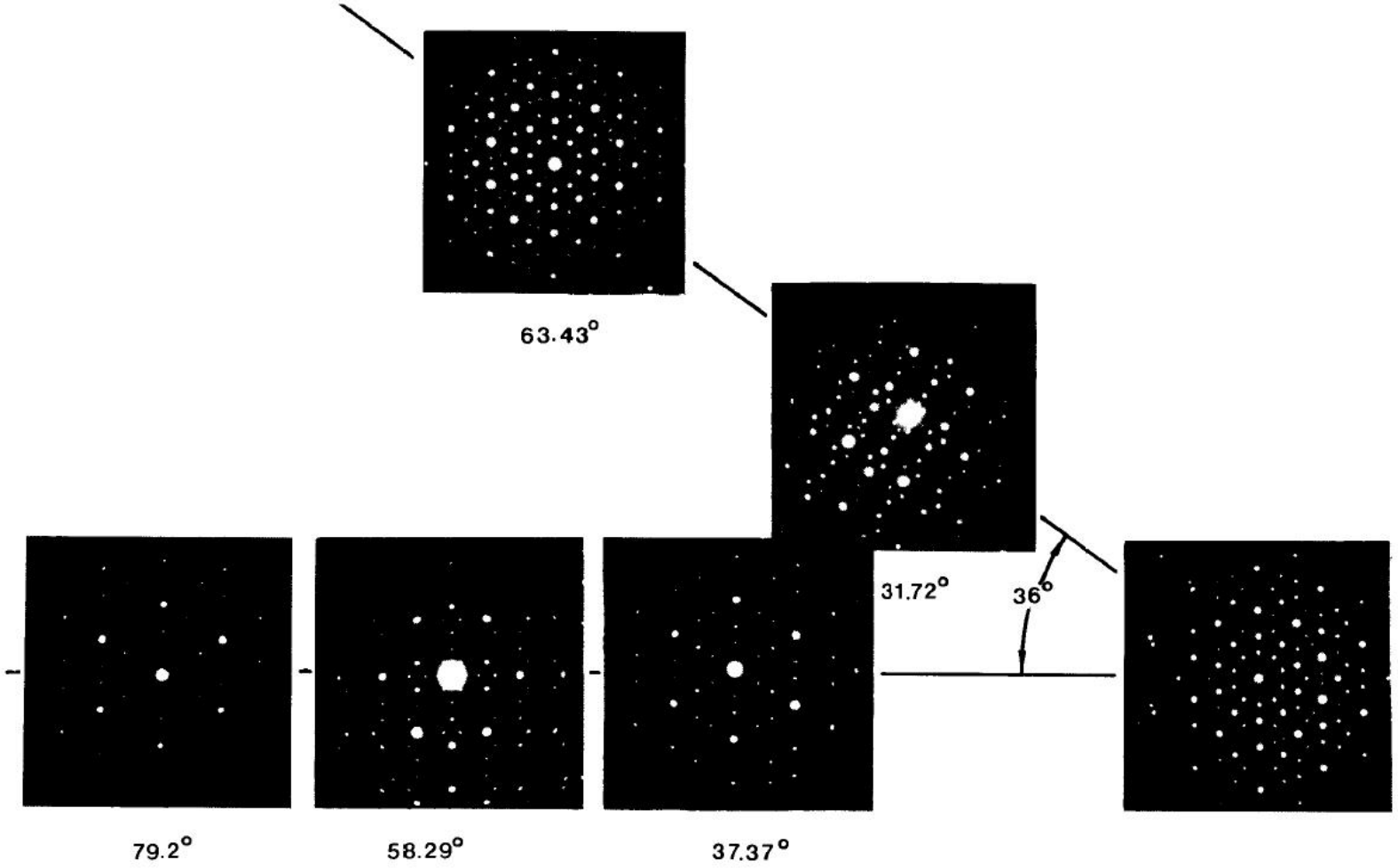
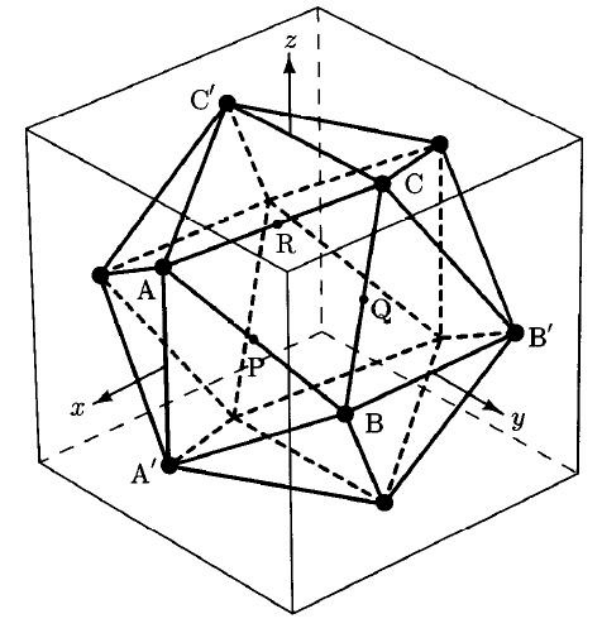
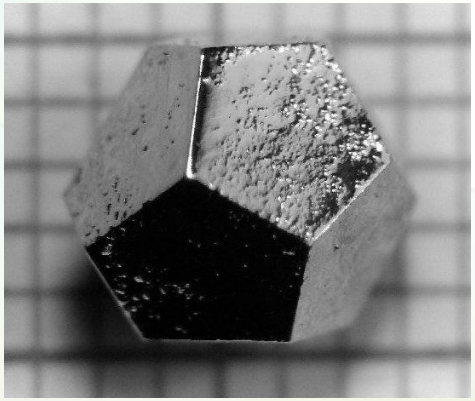


Fig. 2.10.2. Experimental diffraction from icosahedral $AlMn_6$ [D.S. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, *Phys. Rev. Lett.* **53**, 1951 (1984)].

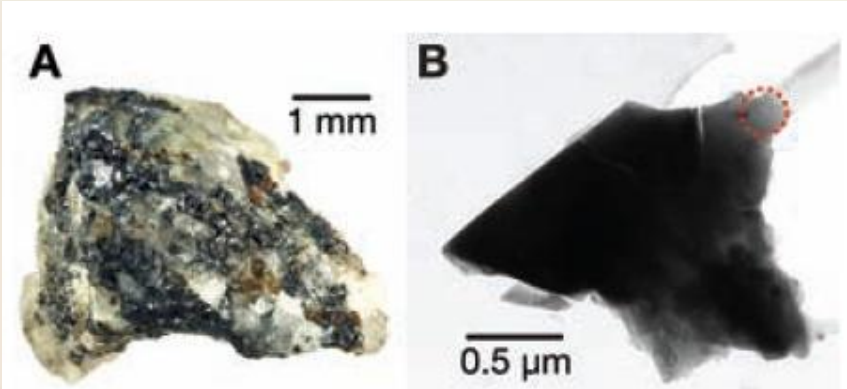
$AlMn_6$

Quasicrystal --Beyond the periodical crystal





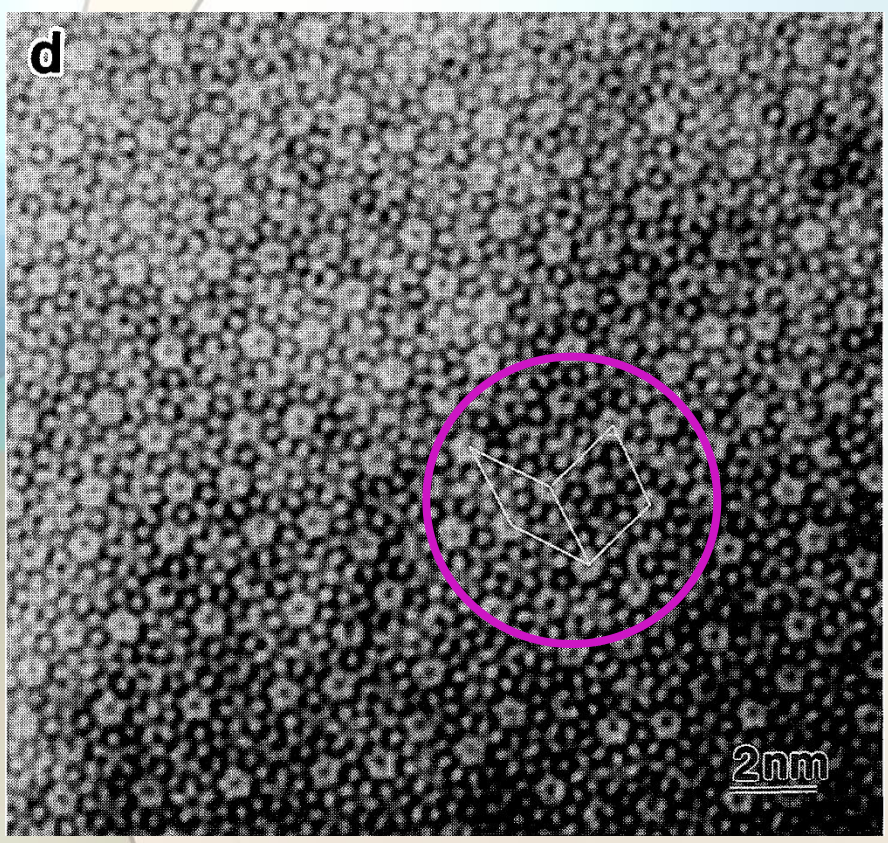
2008 Natural quasicrystals discovered



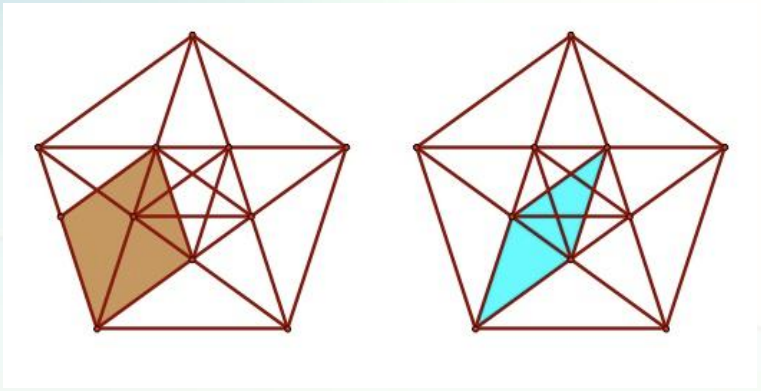
$Al_{63}Cu_{24}Fe_{13}$

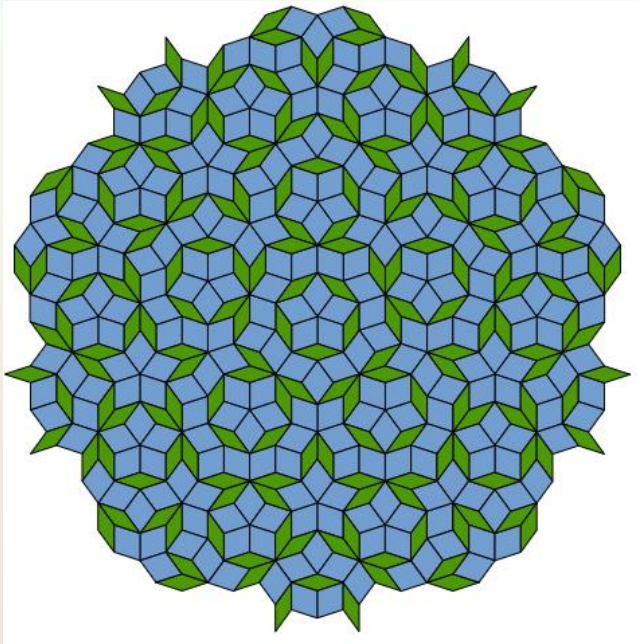
Confirmed as a 4.5 billion years old meteorite

Connection of Quasicrystal with special tiling

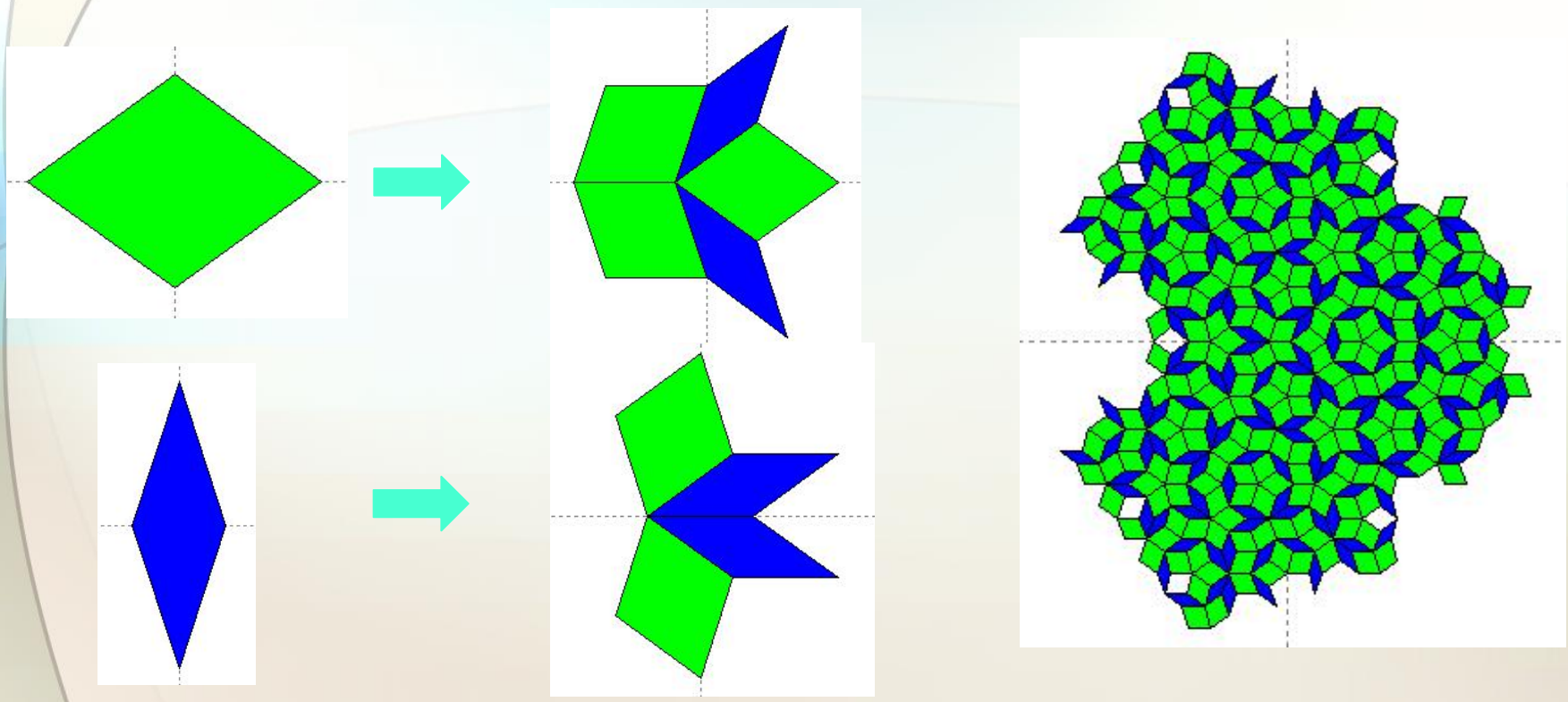


HAADF-STEM image of d-Al-Co-Ni
(only Co, Ni can be seen)





Deflation rule of Penrose tiling



...

Quasicrystal --Beyond the periodical crystal

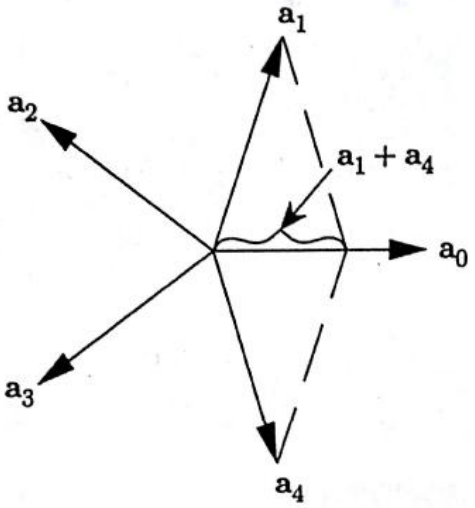


Fig. 2.6.2. The five vectors $\mathbf{a}_n = [\cos(2\pi n/5), \sin(2\pi n/5)]$ generated by applying five-fold symmetry operations to the vector $\mathbf{a}_0$. The vector $\mathbf{a}_1 + \mathbf{a}_4$ is parallel to and shorter than the vector $\mathbf{a}_0$.

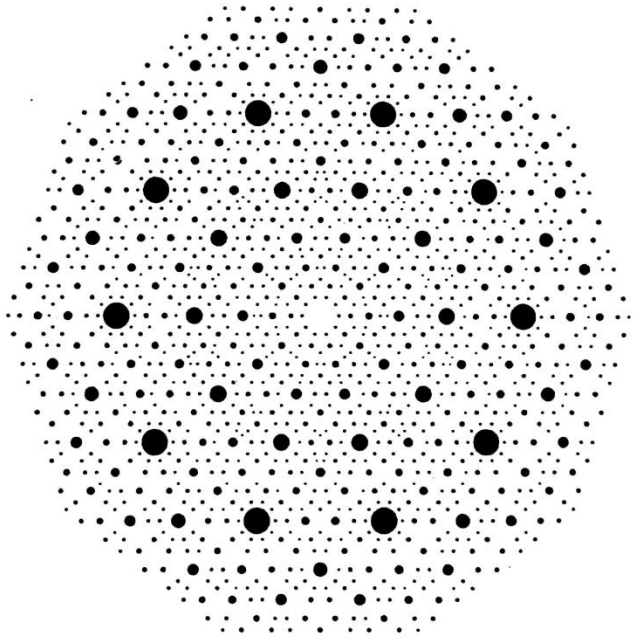
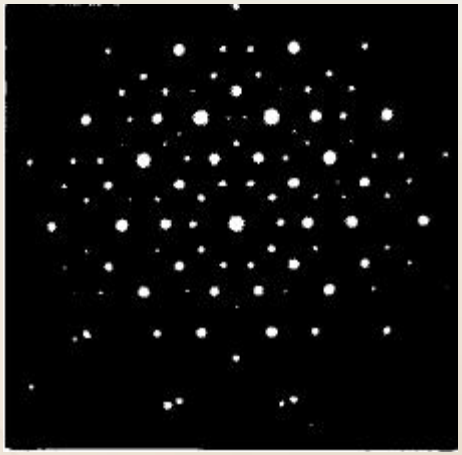


Fig. 2.10.3. Points **G** in a reciprocal lattice with ten-fold symmetry (the presence of the negative of vectors converts five-fold to ten-fold symmetry) generated by $\sum A_n \mathbf{a}_n$ with $A_n = 0, \pm 1, \pm 2$ with $|\mathbf{G}|/|\mathbf{a}_0| \leq 4$.



Homework

1. Problem 2.1 of textbook.
2. Problem 2.2 of textbook.
3. Problem 2.4 of textbook.
4. Problem 2.5 of textbook.
5. see next page. **Q1-4 waived**.

Please send your homework in a week to
840629016@qq.com

PROBLEMS

1. Powder specimens of three different monatomic cubic crystals are analyzed with a Debye-Scherrer camera. It is known that one sample is face-centered cubic, one is body-centered cubic, and one has the diamond structure. The approximate positions of the first four diffraction rings in each case are (see Figure 6.13):

VALUES OF ϕ FOR SAMPLES

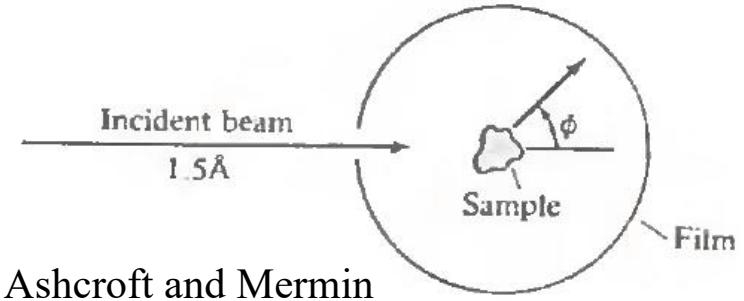
A	*B*	*C*
42.2°	28.8°	42.8°
49.2	41.0	73.2
72.0	50.8	89.0
87.3	59.6	115.0

(a) Identify the crystal structures of *A*, *B*, and *C*.

(b) If the wavelength of the incident X-ray beam is 1.5 Å, what is the length of the side of the conventional cubic cell in each case?

(c) If the diamond structure were replaced by a zincblende structure with a cubic unit cell of the same side, at what angles would the first four rings now occur?

Figure 6.13
Schematic view of a Debye-Scherrer camera. Diffraction peaks are recorded on the film strip.



Solid State Physics, Ashcroft and Mermin