

Structure of Matter

The Solid State

WS 2013/14

Lectures (Tuesday & Friday)

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Last time:

Binding cont'd

Crystal structure

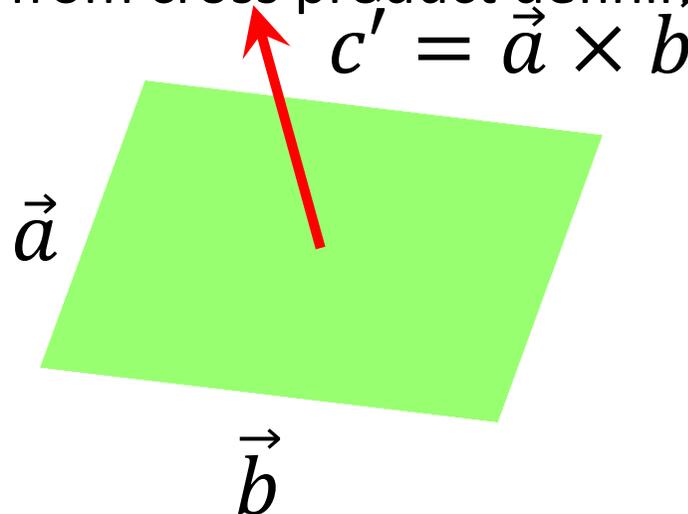
Start with reciprocal lattice

Today:

Reciprocal lattice and diffraction

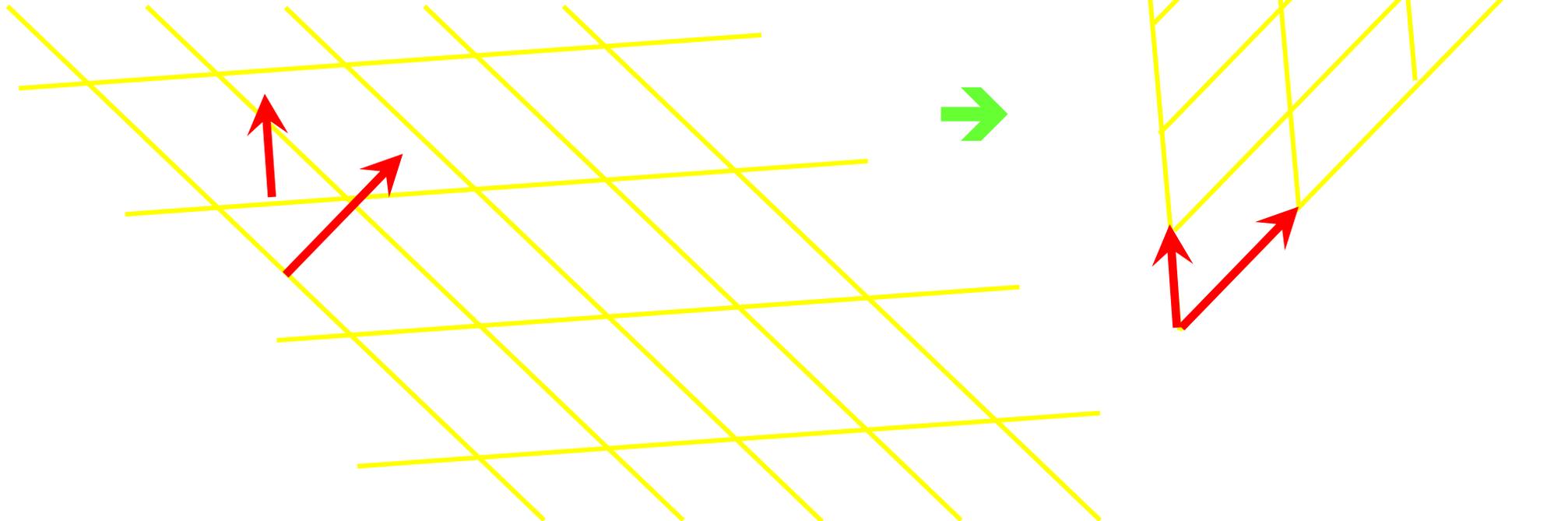
Miller indices

- Miller indices where derived as a set of reciprocal numbers defining lattice planes & directions
 - Set of planes is defined by
 - Direction hkl & spacing d between them
- direction from cross product defining vectors



New lattice derived from planes

- Take two sets of planes, e.g. $\{10\}$ and $\{01\}$
- Draw perpendicular directions
- Take length unit $1/\text{spacing}$ and construct new lattice



Fourier transform

- Reminder fourier transform:

$$F(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} f(t) dt$$

- We can do this with functions in space:

$$F(k) = \int_{-\infty}^{\infty} e^{-ikx} f(x) dx$$

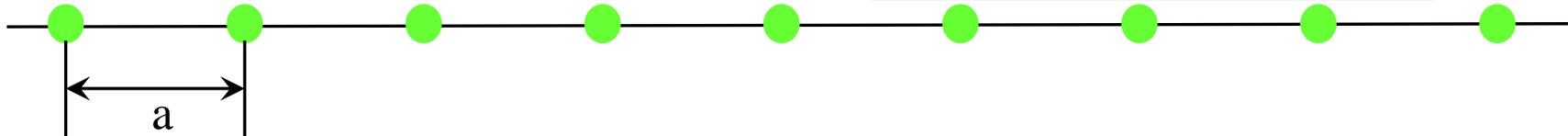
- Many interesting properties, for instance shift in space

$$F(k) = \int_{-\infty}^{\infty} e^{-ikx} f(x \pm a) dx = \int_{-\infty}^{\infty} e^{-ik(x' \mp a)} f(x') dx' = e^{\mp ika} \int_{-\infty}^{\infty} e^{-ikx} f(x) dx$$

Fourier transform 1D lattice function

- Mass distribution 1D lattice

$$\rho(x) = \sum_n \delta(x + na)$$

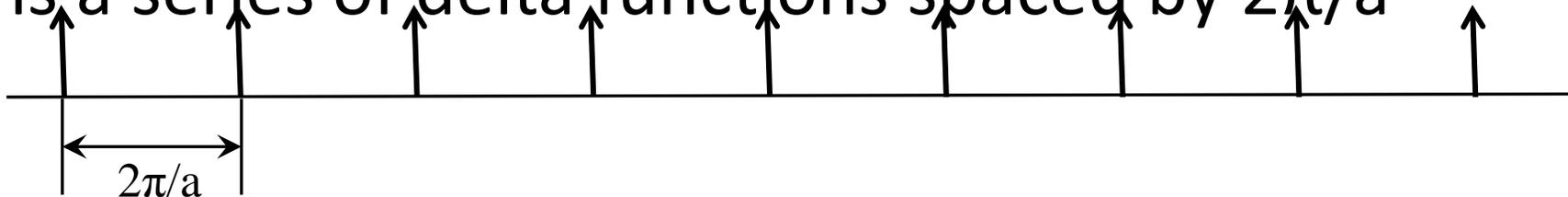


- Fourier transform

$$R(k) = \int_{-\infty}^{\infty} e^{-ikx} \rho(x) dx = \int_{-\infty}^{\infty} e^{-ikx} \sum_{n=-\infty}^{\infty} \delta(x - na) dx$$

$$= \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-ikx} \delta(x - na) dx = \frac{2\pi}{a} \sum_{n=-\infty}^{\infty} \delta(k - n \frac{2\pi}{a})$$

- is a series of delta functions spaced by $2\pi/a$



3D crystal structures

- More general: fourier transform of a translation symmetric function has discrete components spaced by $2\pi/\text{period}$
- Fourier transform 3D lattice:

$$R(\vec{k}) = \int_{-\infty}^{\infty} e^{-i\vec{k}\cdot\vec{r}} \rho(\vec{r}) d\vec{r} = \int_{-\infty}^{\infty} e^{-i\vec{k}\cdot\vec{r}} \sum_{p,q,s=-\infty}^{\infty} \delta(\vec{r} - p\vec{a} - q\vec{b} - s\vec{c}) d\vec{r}$$

Defines a lattice of allowed fourier components

Reciprocal lattice

$$1) \quad \vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}; \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1)}; \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)}$$

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

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

4) $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are primitive lattice vectors of an abstract lattice, conjugate to the lattice in direct space.

They span a Bravais lattice.

5) In general \mathbf{b}_j not easily scalable to \mathbf{a}_i and not parallel to them either

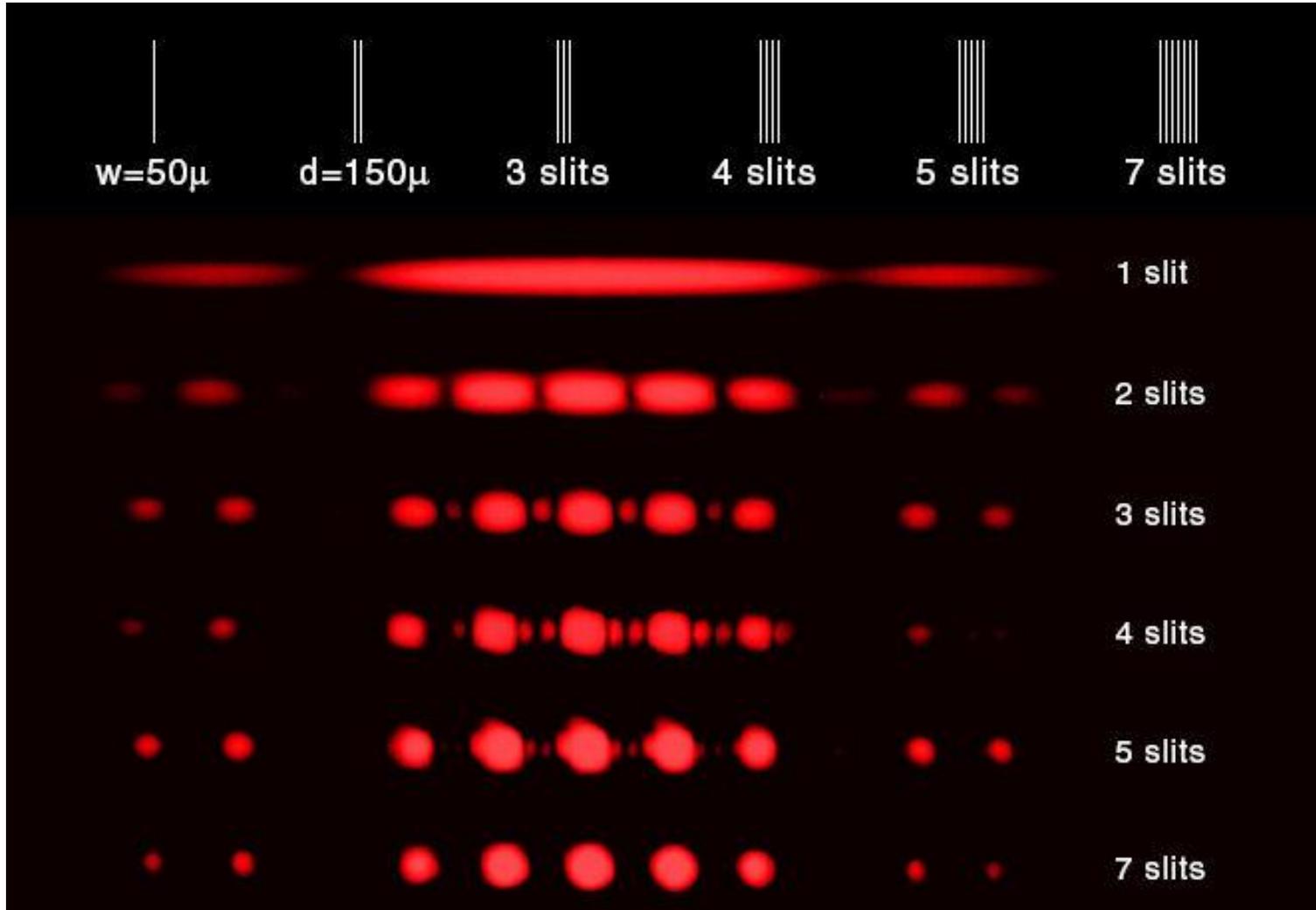
6) Reciprocal of reciprocal is real lattice again

7) dimension $[\mathbf{b}_i] = \text{m}^{-1}$

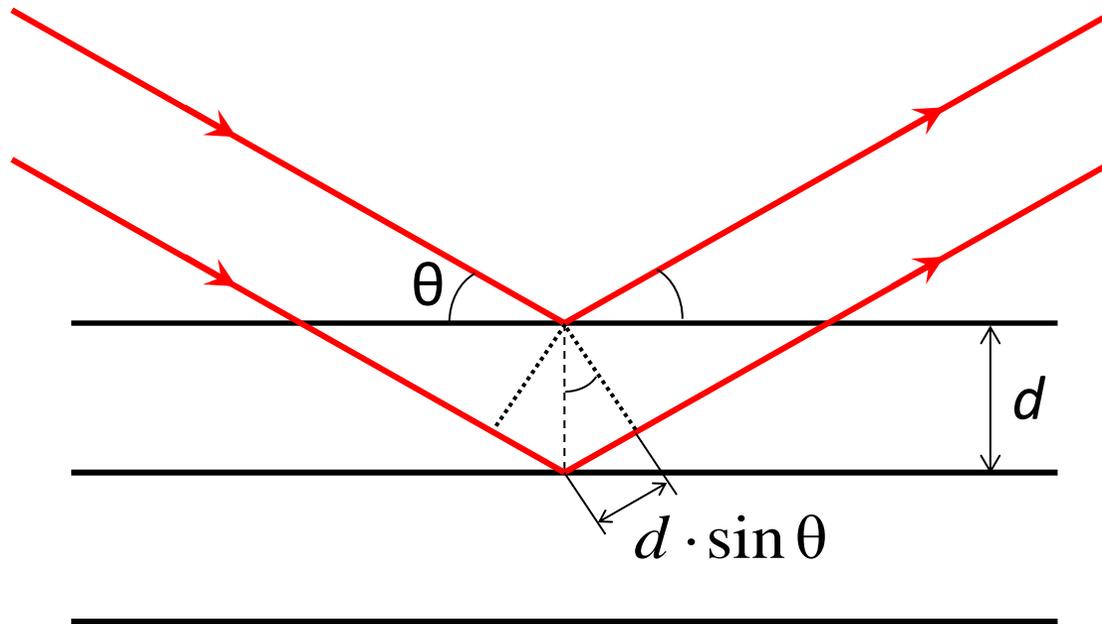
Reciprocal lattice

- Set of allowed Fourier components in FT from structure
- Set of directions in the real lattice
- Set of allowed diffraction directions
- Set describing allowed plane waves in periodic structures

Diffraction



Diffraction from crystals: Bragg's law



Constructive interference if

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

Crystal Structure

Lattice +

Basis

Fourier transform
periodic structure

Diffraction pattern

Diffraction intensity

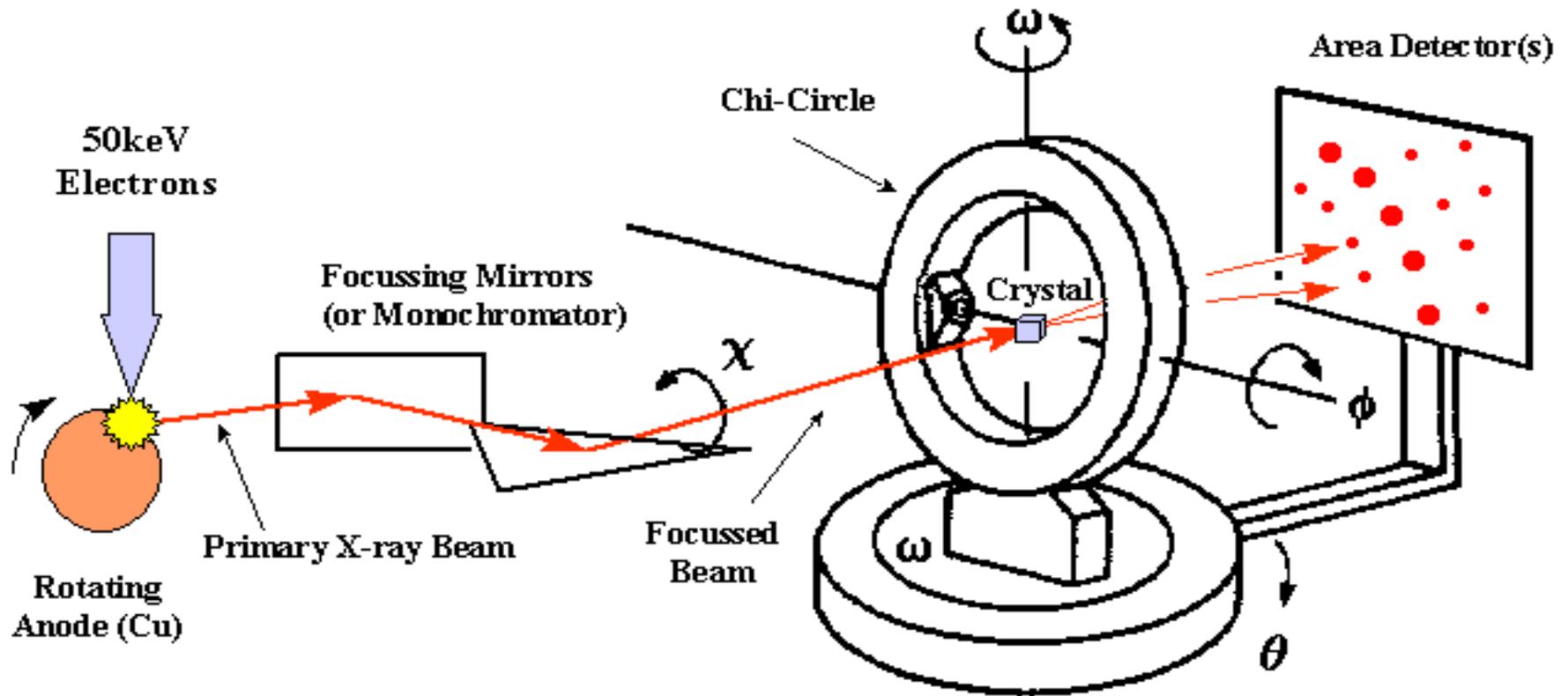
- Atomic form factor
- Structure factor

Reciprocal lattice

- Symmetry, Extinction conditions
- Primitive reciprocal lattice vectors
- Wigner Seitz cell, Brillouin zones
- Examples: SC, BCC, FCC lattices

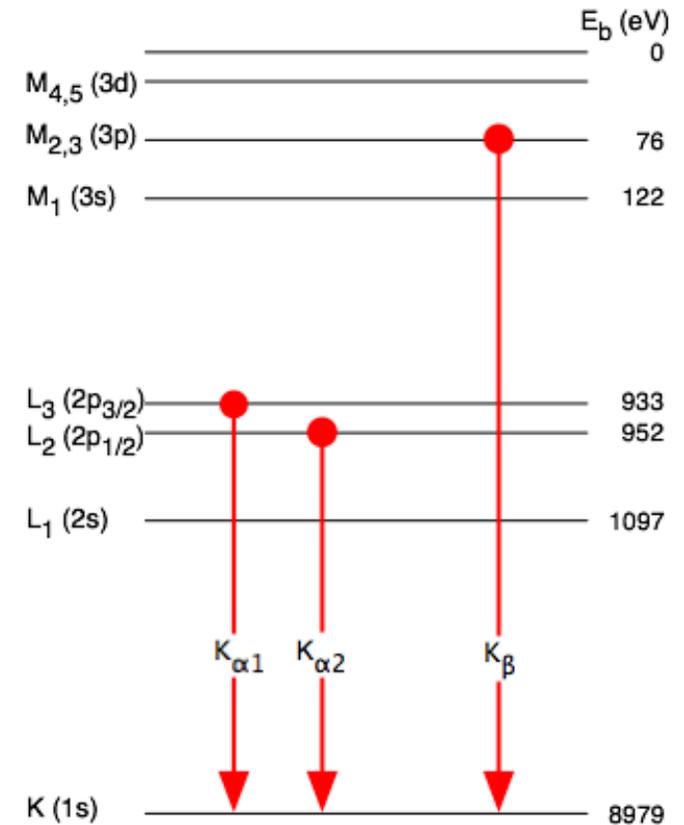
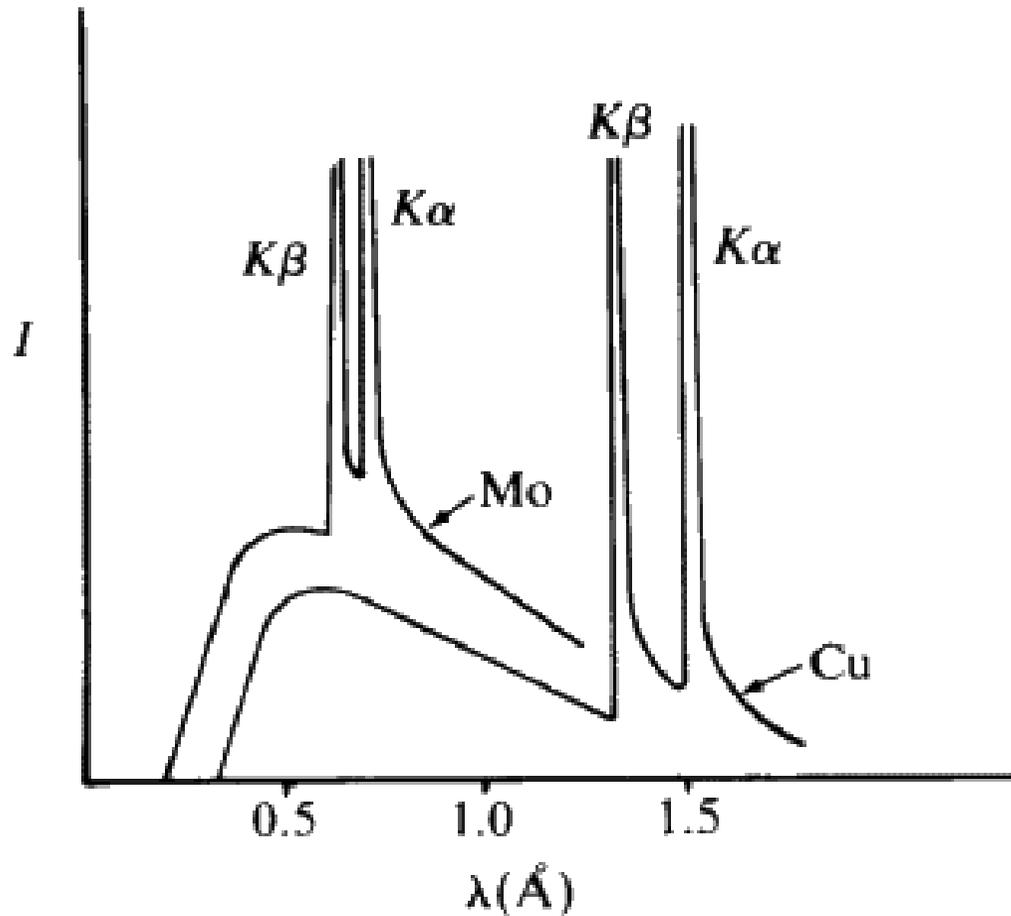
- Diffraction
- Lattice vibrations
- Electronic properties
- Bloch functions

Diffractometer

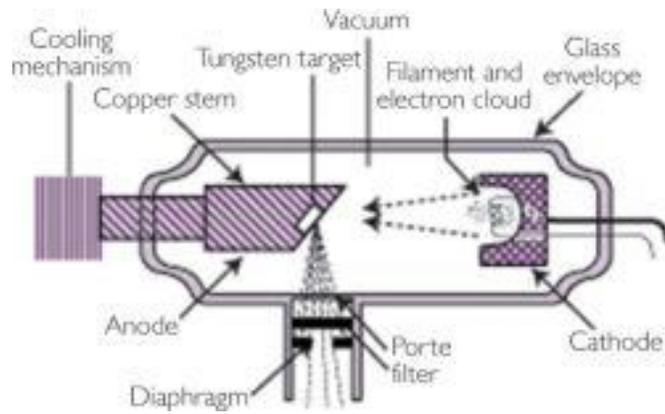


4-Circle Goniometer (Eulerian or Kappa Geometry)

Source: need wavelength \sim lattice spacing



X-ray sources



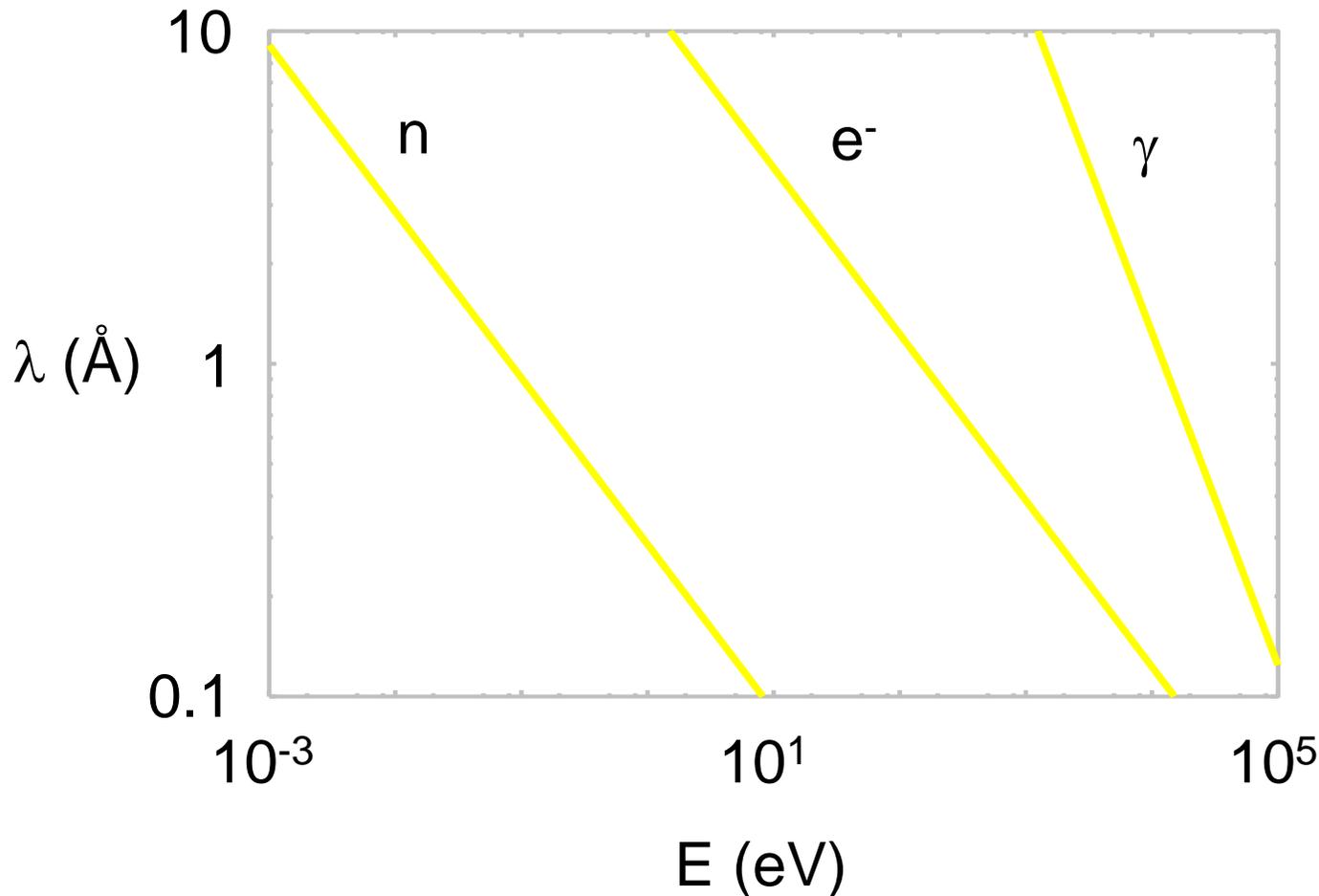
X-ray tube



Synchrotron (grenoble)



One can also use electrons and neutrons

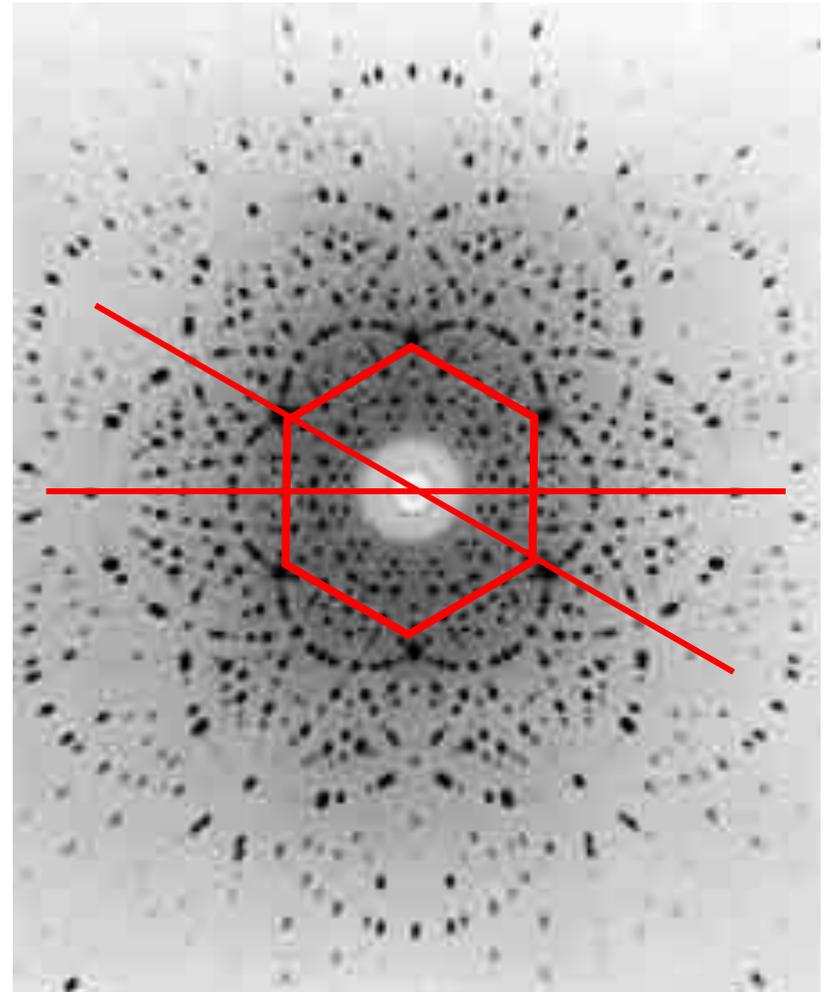


$$E_\gamma = \hbar\omega = \hbar ck = \frac{hc}{\lambda}$$

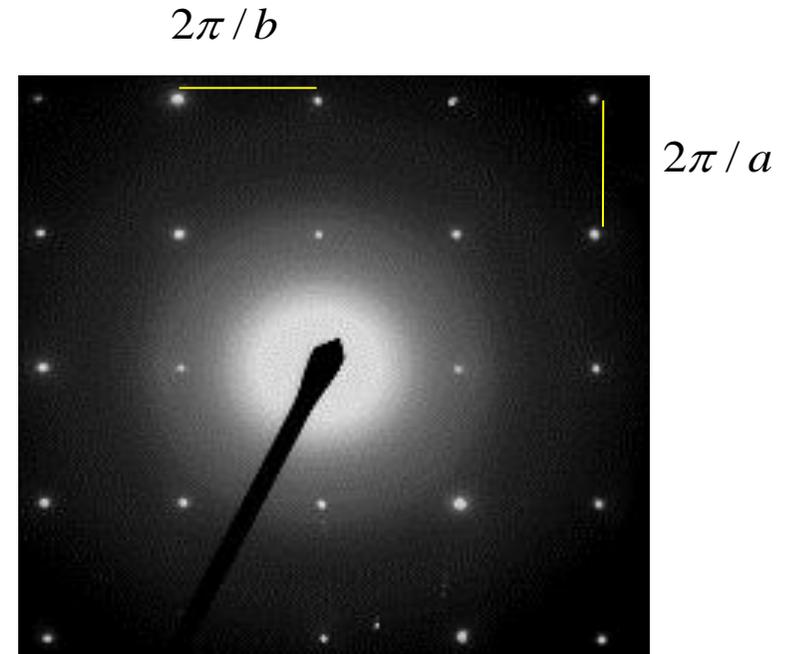
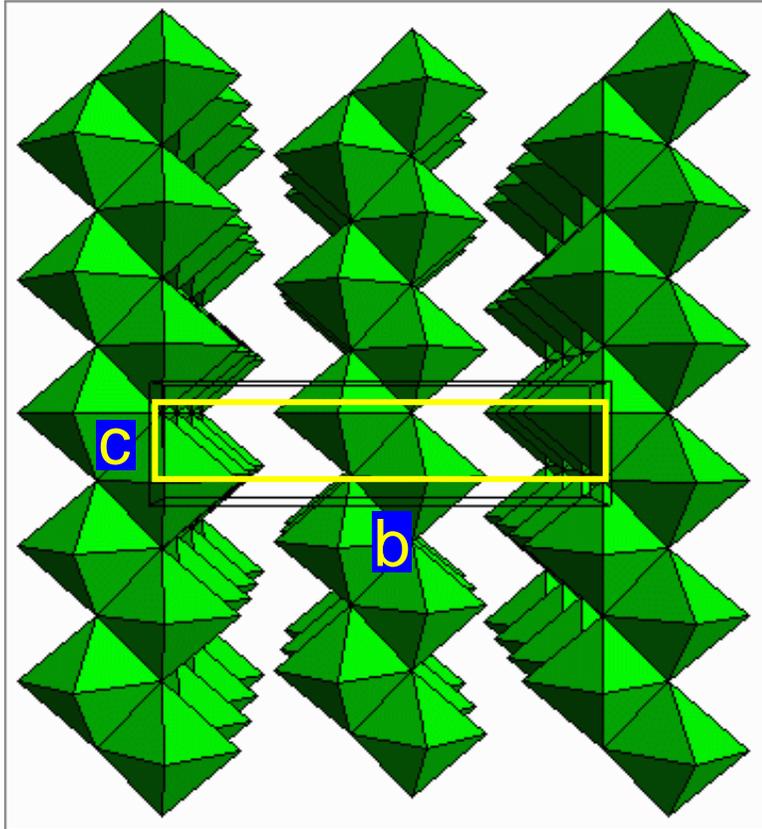
$$E_{e,n} = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$$

$$\frac{m_n}{m_e} \approx 1800$$

Beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$)

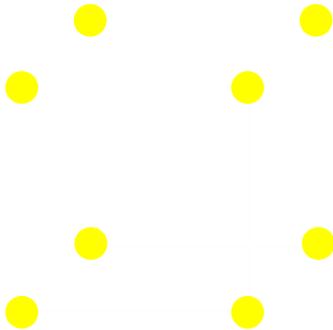


Molybdenum oxide MoO_3



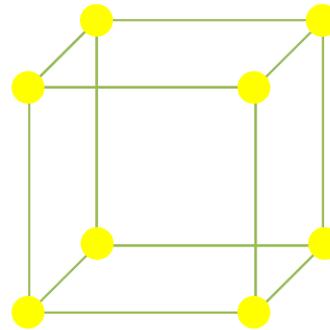
Orthorhombic MoO_3

Reciprocal lattice of SC



$$V = a^3$$

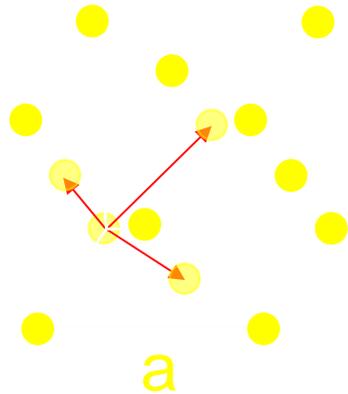
$$\begin{aligned}\vec{a}_1 &= a \cdot \vec{e}_x \\ \vec{a}_2 &= a \cdot \vec{e}_y \\ \vec{a}_3 &= a \cdot \vec{e}_z\end{aligned}$$



$$V = (2\pi/a)^3$$

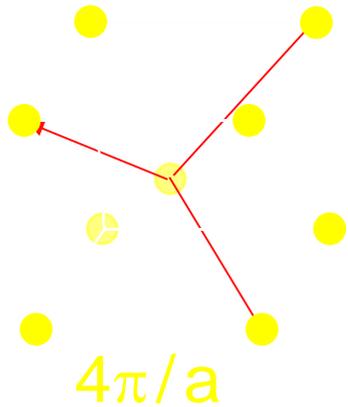
$$\begin{aligned}\vec{b}_1 &= (2\pi/a) \cdot \vec{e}_x \\ \vec{b}_2 &= (2\pi/a) \cdot \vec{e}_y \\ \vec{b}_3 &= (2\pi/a) \cdot \vec{e}_z\end{aligned}$$

Reciprocal lattice of FCC



$$\begin{aligned}\vec{a}_1 &= a/2 \cdot (\vec{e}_y + \vec{e}_z) \\ \vec{a}_2 &= a/2 \cdot (\vec{e}_x + \vec{e}_z) \\ \vec{a}_3 &= a/2 \cdot (\vec{e}_x + \vec{e}_y)\end{aligned}$$

$$V = a^3/4$$



$$\begin{aligned}\vec{b}_1 &= (2\pi/a) \cdot (-\vec{e}_x + \vec{e}_y + \vec{e}_z) \\ \vec{b}_2 &= (2\pi/a) \cdot (\vec{e}_x - \vec{e}_y + \vec{e}_z) \\ \vec{b}_3 &= (2\pi/a) \cdot (\vec{e}_x + \vec{e}_y - \vec{e}_z)\end{aligned}$$

This is BCC !

Fourier analysis

FT
$$\tilde{n}(\vec{k}) = \frac{1}{V} \int d^3r n(\vec{r}) \cdot e^{i\vec{k}\cdot\vec{r}}$$

Back
$$n(\vec{r}) = \frac{V}{(2\pi)^3} \int d^3k \tilde{n}(\vec{k}) \cdot e^{-i\vec{k}\cdot\vec{r}}$$

Translational invariance:
$$n(\vec{r}) = n(\vec{r} + \vec{T})$$

Each unit cell is the same \rightarrow split FT in lattice and basis

Fourier analysis

FT

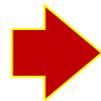
$$\tilde{n}(\vec{k}) = \sum_{\vec{T}} S_{\vec{k}} \cdot e^{i\vec{k} \cdot \vec{T}}$$

Structure factor:

$$S_{\vec{k}} = \frac{1}{V_{u.c.}} \int_{u.c.} d^3r n(\vec{r}) \cdot e^{i\vec{k} \cdot \vec{r}}$$

Direct space periodicity:

$$\tilde{n}(\vec{k}) = e^{i\vec{k} \cdot \vec{T}} \cdot \tilde{n}(\vec{k})$$



$$\vec{k} \cdot \vec{T} = 2\pi s$$

$$\vec{k} \in \vec{G} = h \cdot \vec{b}_1 + k \cdot \vec{b}_2 + l \cdot \vec{b}_3$$

Crystal Structure

Lattice + Basis

Fourier Transform
periodic structure

Diffraction pattern

Diffraction intensity

Reciprocal lattice

Structure factor
Atomic form factor

Atomic form factor

Structure factor:

$$S_{\vec{G}} = \frac{1}{V_{u.c.}} \int_{u.c.} d^3r n(\vec{r}) \cdot e^{i\vec{G}\cdot\vec{r}}$$

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

e.g. $n(\vec{\rho}) = A e^{-\frac{|\vec{\rho}|}{\rho_A}}$
 $\vec{\rho} = \vec{r} - \vec{r}_j$

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

Atomic form factor:

$$f_j = \int d^3\rho n_j(\vec{\rho}) e^{i\vec{G}\cdot\vec{\rho}}$$

Diffraction conditions

The set of reciprocal vectors \vec{G}
determines the possible x-ray reflections

Scattering from k to k' is proportional to $n(r)$

Scattering amplitude:

$$F = \int d^3r n(\vec{r}) e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}} = S_{\Delta\vec{k}} = \sum_{\vec{G}} \int d^3r n_{\vec{G}} e^{-i(\vec{G}-\Delta\vec{k})\cdot\vec{r}}$$

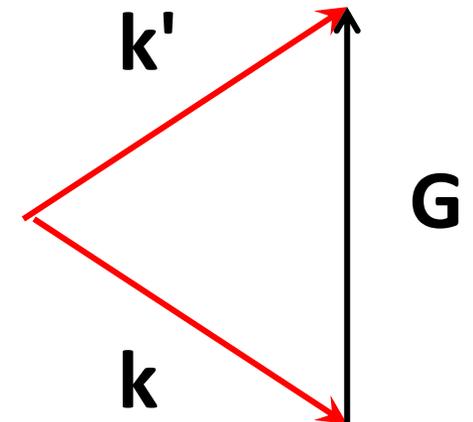
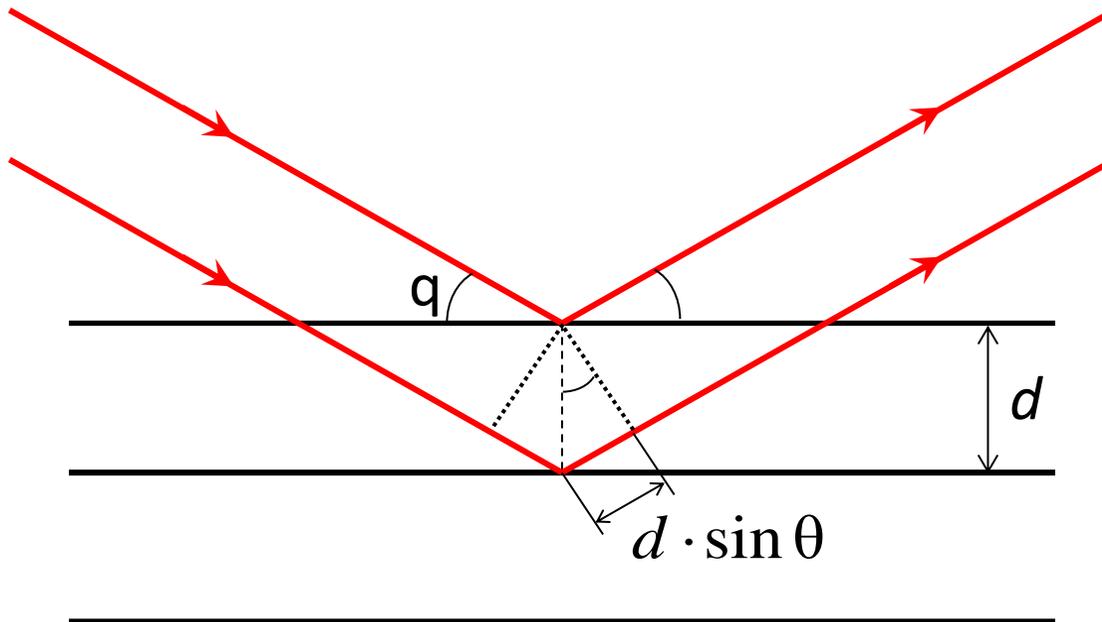
Periodicity $n(r) \Rightarrow \Delta\vec{k} = \vec{G}$

Bragg again

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

$$\Delta \vec{k} = \vec{G}$$

$$G = 2k \sin(\theta)$$



Bragg's law

$$\Delta \vec{k} = \vec{G}$$

$$\vec{k} + \vec{G} = \vec{k}' \Rightarrow |\vec{k} + \vec{G}|^2 = k^2 \Rightarrow 2\vec{k} \cdot \vec{G} + G^2 = 0$$

$$G = 2k \sin(\theta)$$

$$d = \frac{2\pi n}{G};$$

$$k = \frac{2\pi}{\lambda}$$

$$\frac{2\pi n}{d} = \frac{4\pi}{\lambda} \sin(\theta)$$

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

