
The Solid State

WS 2013/14

Lectures (Tuesday & Friday)

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Last time:

Binding cont'd

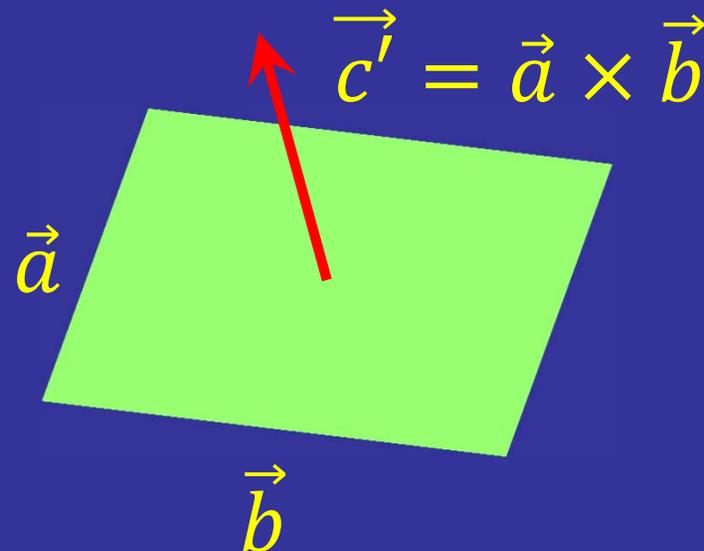
Crystal structure

Start with reciprocal lattice

Today:

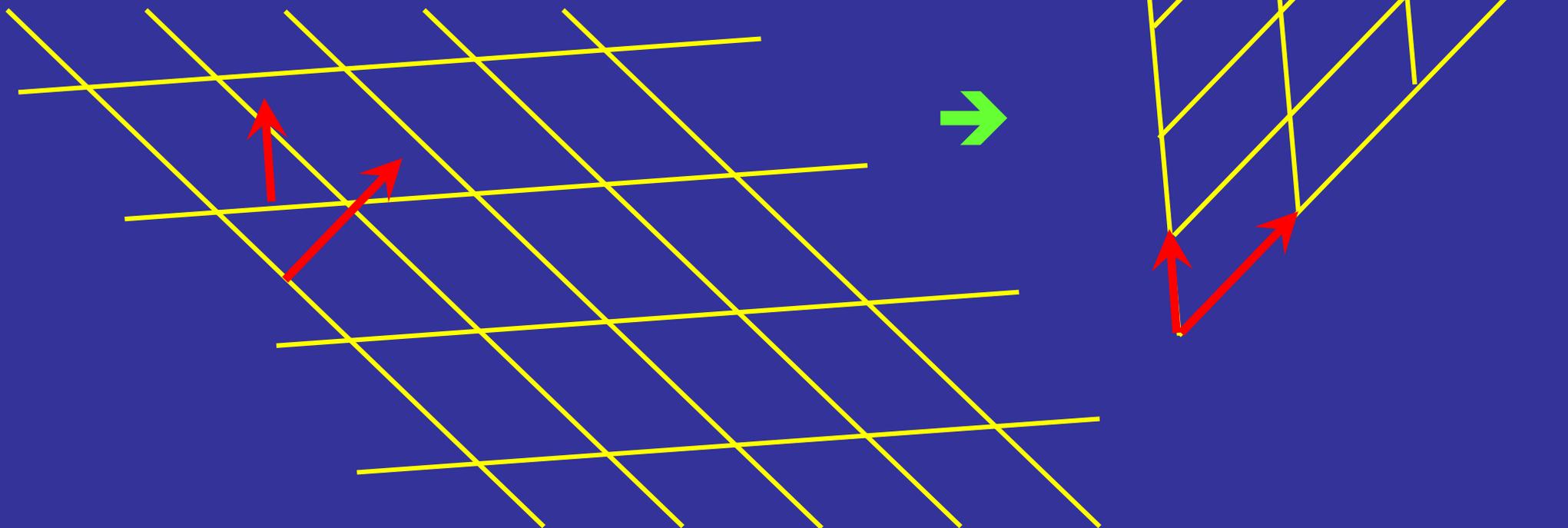
Reciprocal lattice and diffraction

- Miller indices 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:

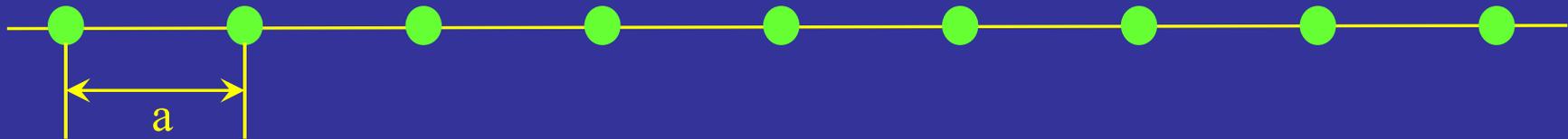
$$F(k) = \int_{-\infty}^{\infty} e^{-ikx} f(x) dx$$

- Many interesting properties, for instance shift in space

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

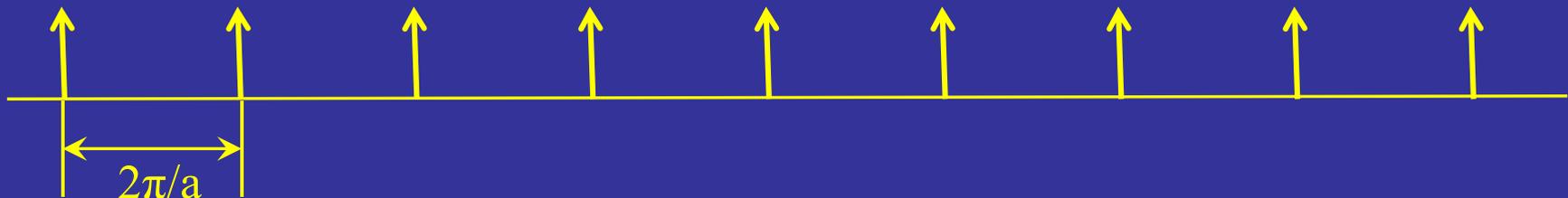
Fourier transform 1D lattice function

- 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

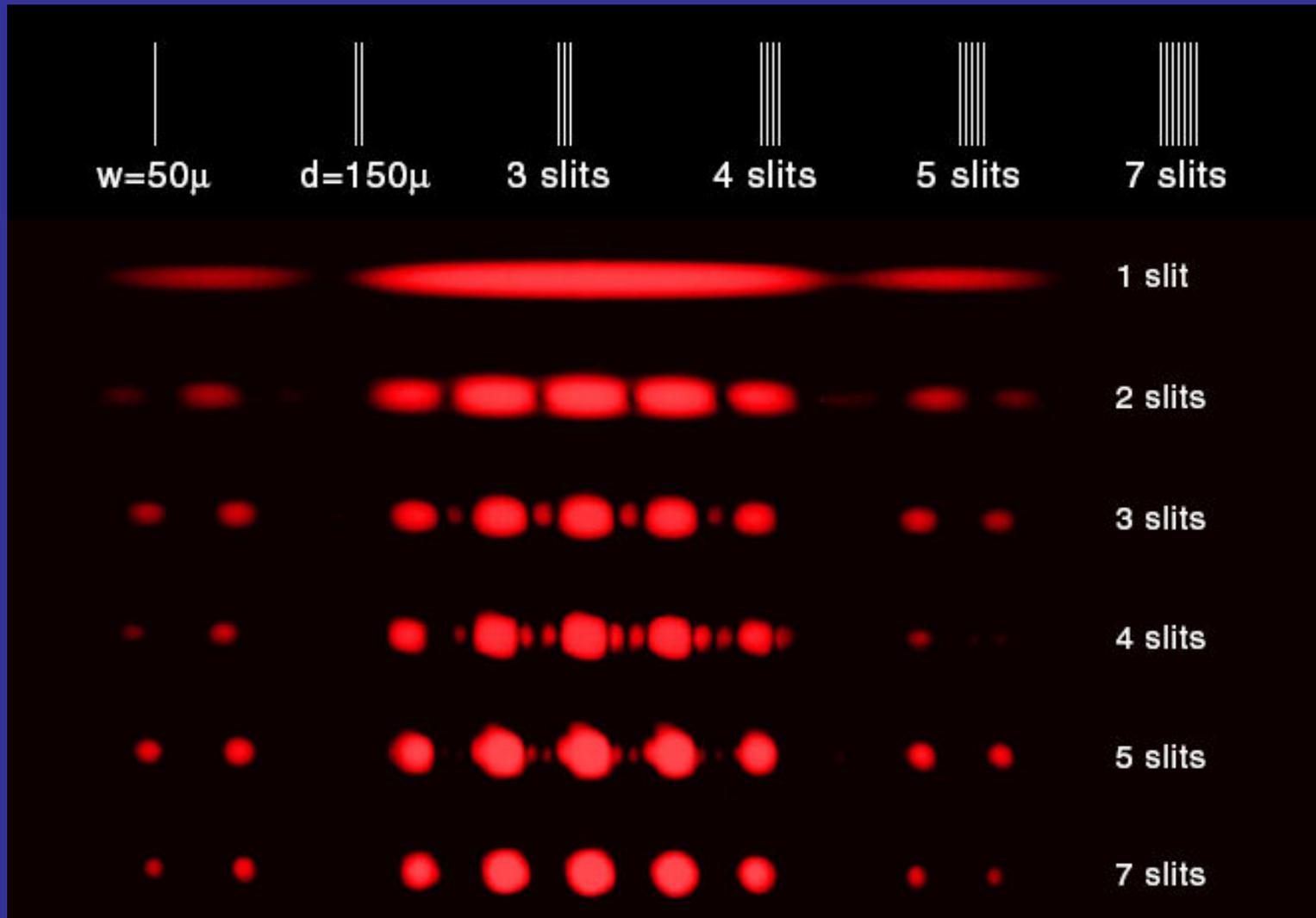
6) Reciprocal of reciprocal is real lattice again

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

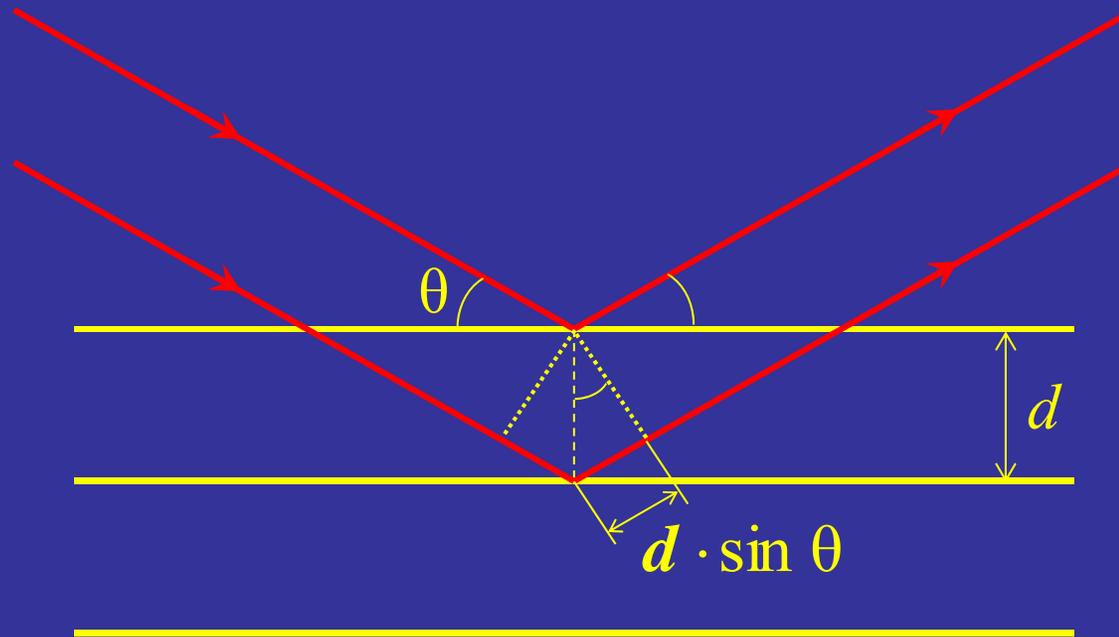
Reciprocal lattice

- 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

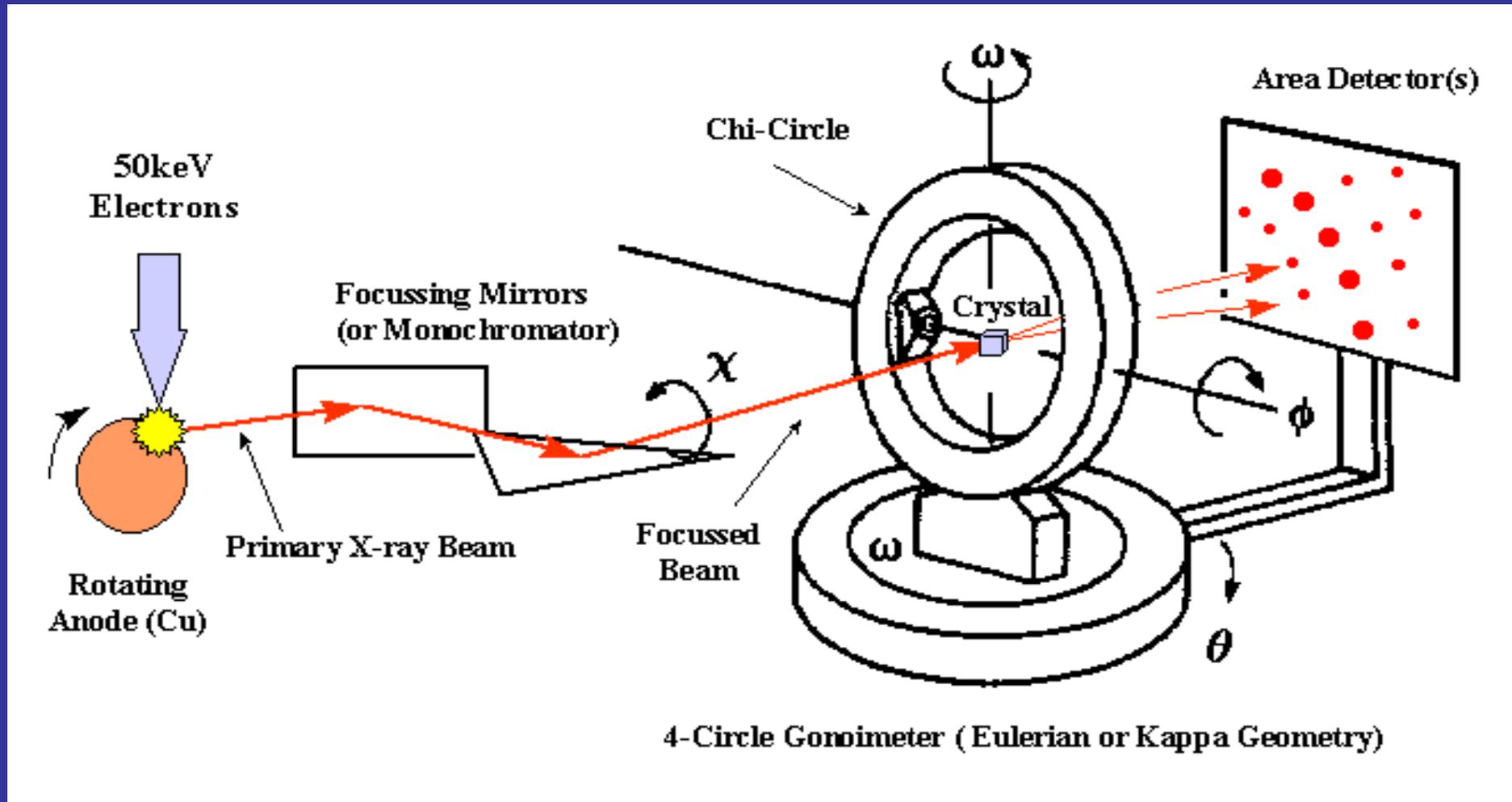
- Atomic form factor
- Structure factor

Reciprocal lattice

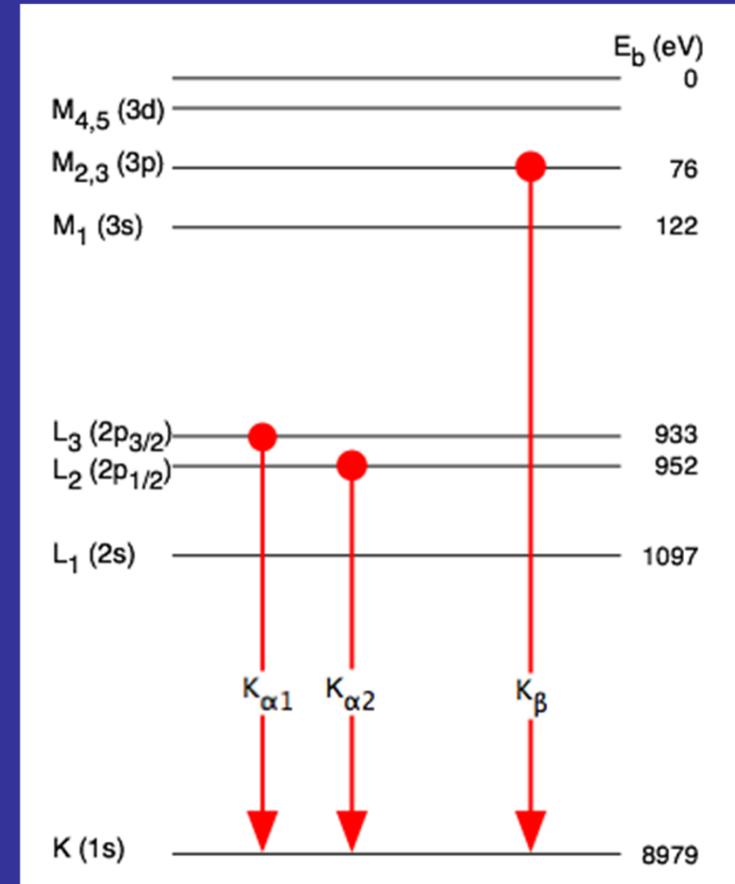
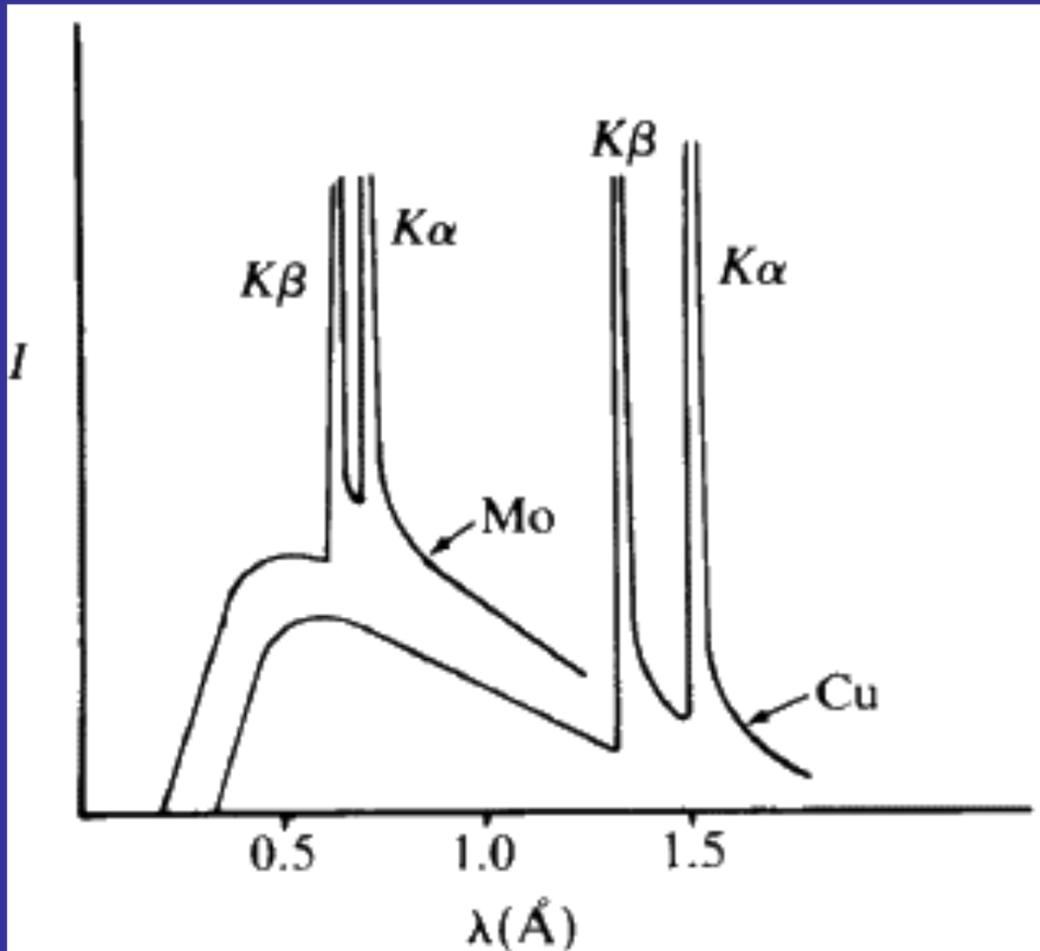
- Symmetry, Extinction conditions
- Primitive reciprocal lattice vectors
- Wigner Seitz cell, Brillouin zones
- Examples: SC, BCC, FCC lattices

- Diffraction
- Lattice vibrations
- Electronic properties
- Bloch functions

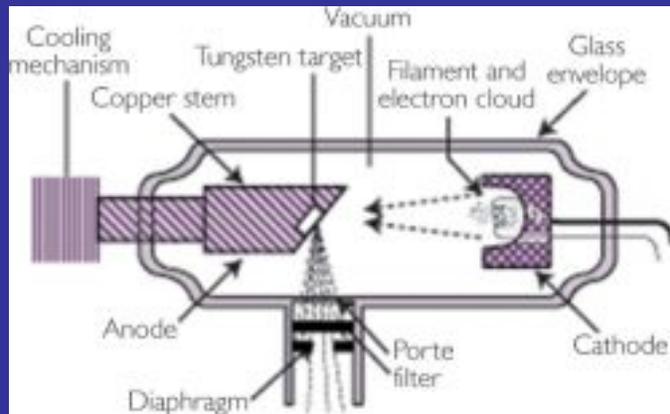
Diffractometer



Source: need wavelength \sim lattice spacing



X-ray sources



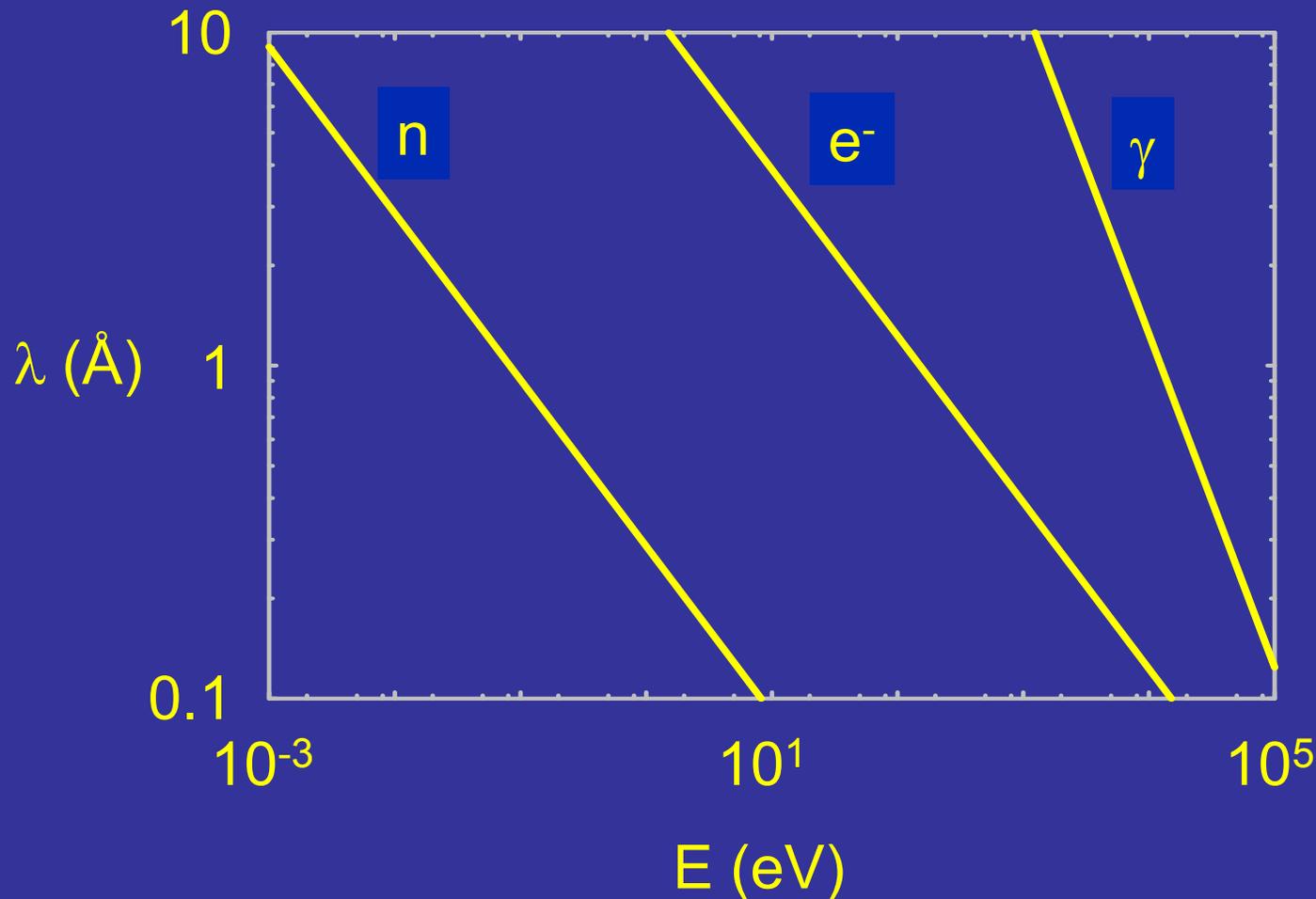
X-ray tube



Synchrotron (grenoble)



One can also use electrons and neutrons

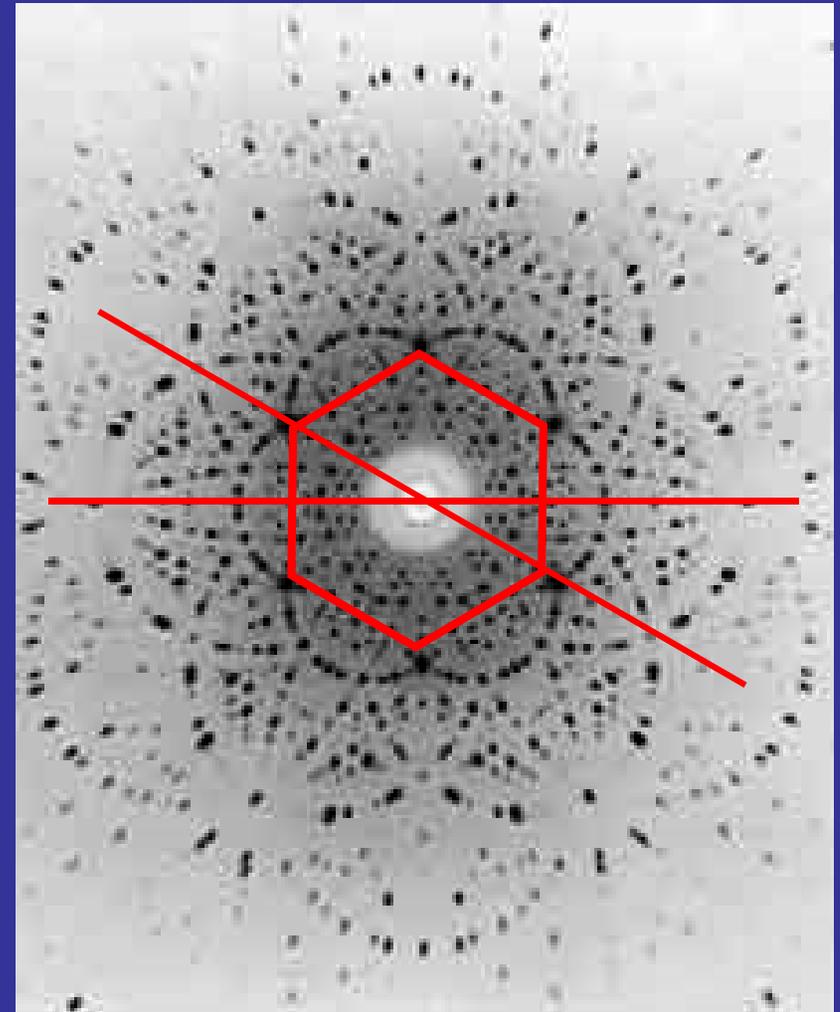


$$E_\gamma = \hbar\omega = \hbar ck = \frac{hc}{\lambda}$$

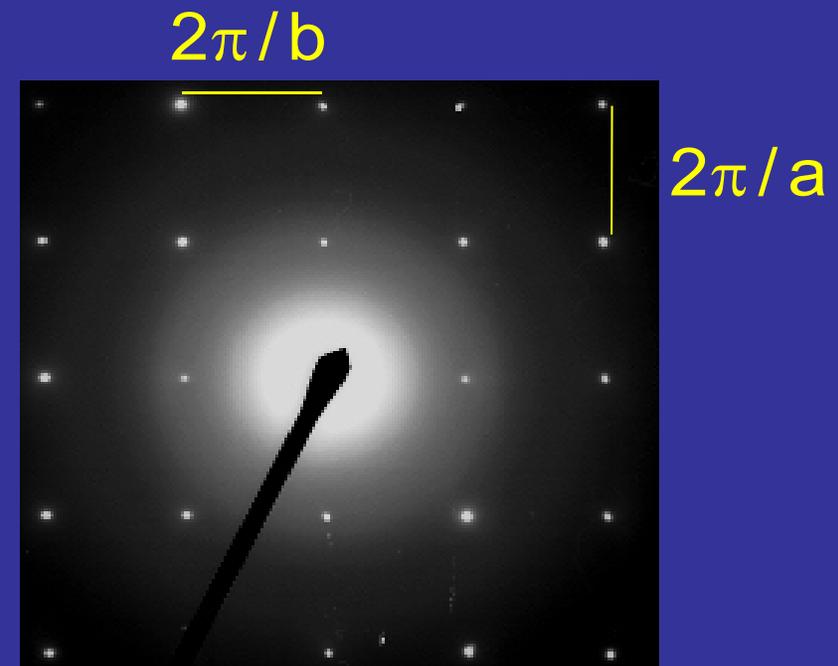
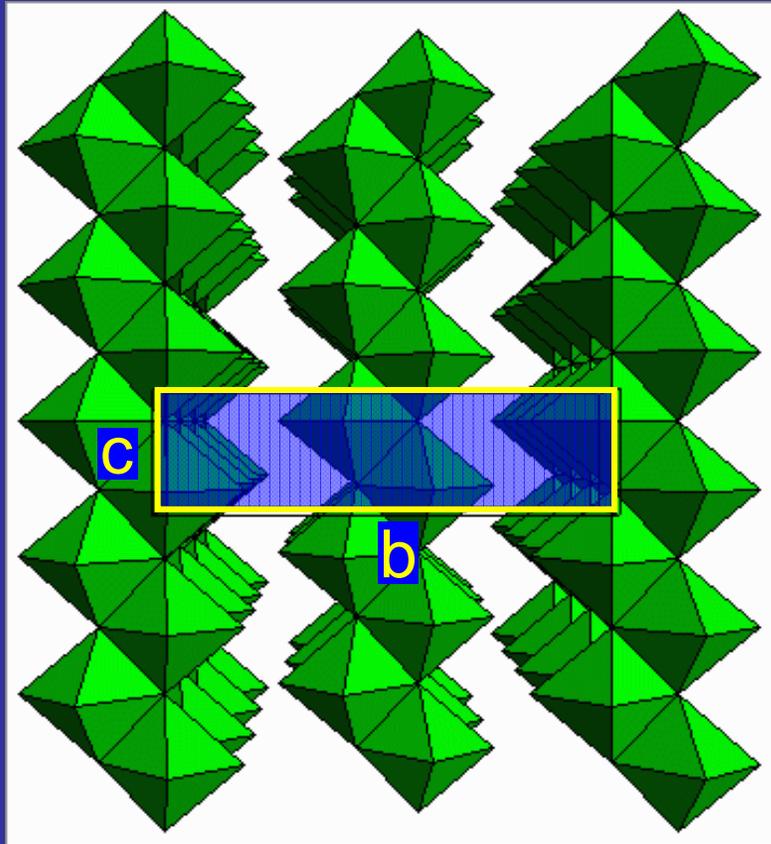
$$E_{e,n} = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$$

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

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

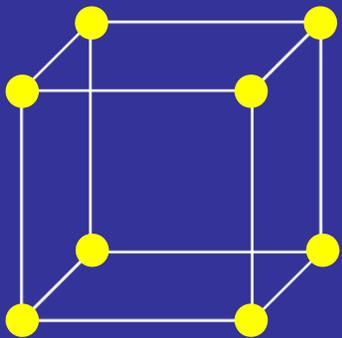


Molybdenum oxide MoO_3



Orthorhombic MoO_3

Reciprocal lattice of SC

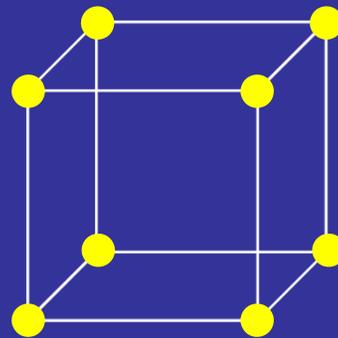


$$\vec{a}_1 = a \cdot \vec{e}_x$$

$$\vec{a}_2 = a \cdot \vec{e}_y$$

$$\vec{a}_3 = a \cdot \vec{e}_z$$

$$V = a^3$$



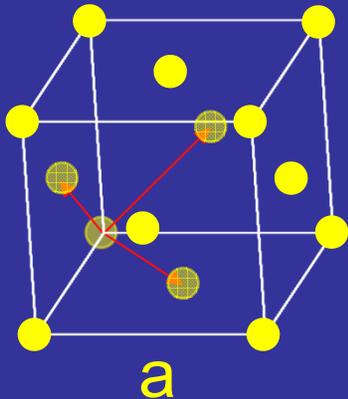
$$\vec{b}_1 = (2\pi/a) \cdot \vec{e}_x$$

$$\vec{b}_2 = (2\pi/a) \cdot \vec{e}_y$$

$$\vec{b}_3 = (2\pi/a) \cdot \vec{e}_z$$

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

Reciprocal lattice of FCC

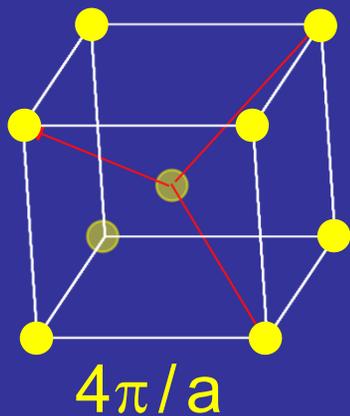


$$\vec{a}_1 = a/2 \cdot (\vec{e}_y + \vec{e}_z)$$

$$V = a^3/4$$

$$\vec{a}_2 = a/2 \cdot (\vec{e}_x + \vec{e}_z)$$

$$\vec{a}_3 = a/2 \cdot (\vec{e}_x + \vec{e}_y)$$



$$\vec{b}_1 = (2\pi/a) \cdot (-\vec{e}_x + \vec{e}_y + \vec{e}_z)$$

$$\vec{b}_2 = (2\pi/a) \cdot (\vec{e}_x - \vec{e}_y + \vec{e}_z)$$

$$\vec{b}_3 = (2\pi/a) \cdot (\vec{e}_x + \vec{e}_y - \vec{e}_z)$$

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

FT

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

Structure factor:

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

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

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

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 $n(\mathbf{r})$

Scattering amplitude:

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

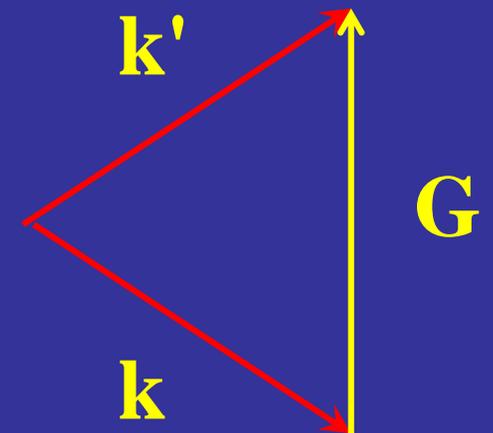
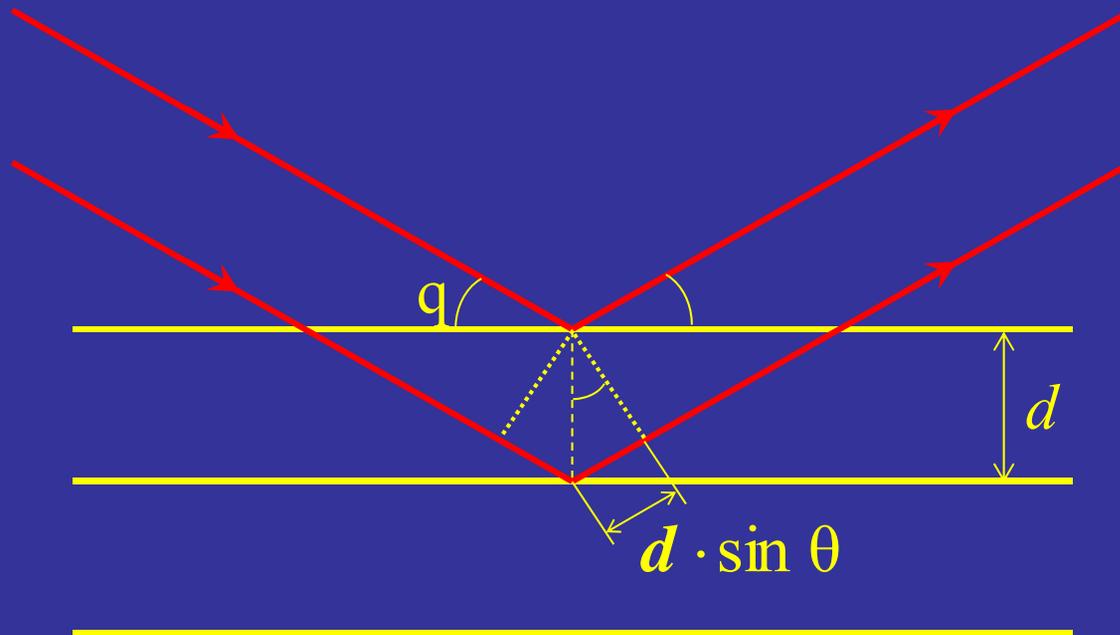
Periodicity $n(\mathbf{r}) \Rightarrow \Delta\vec{k} = \vec{G}$

Bragg again

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

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

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



Bragg's law

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

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

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

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

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

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

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

