Condensed Matter Physics I

Prof. Dr. Ir. Paul H.M. van Loosdrecht

II Physikalisches Institut, Room 312

E-mail: pvl@ph2.uni-koeln.de

Website: http:/www.loosdrecht.net/

Previously

- Crystal = Lattice + Basis
- Primitive unit cells
- Symmetry: Translations, Rotations
- Classification -> Bravais lattices

Today

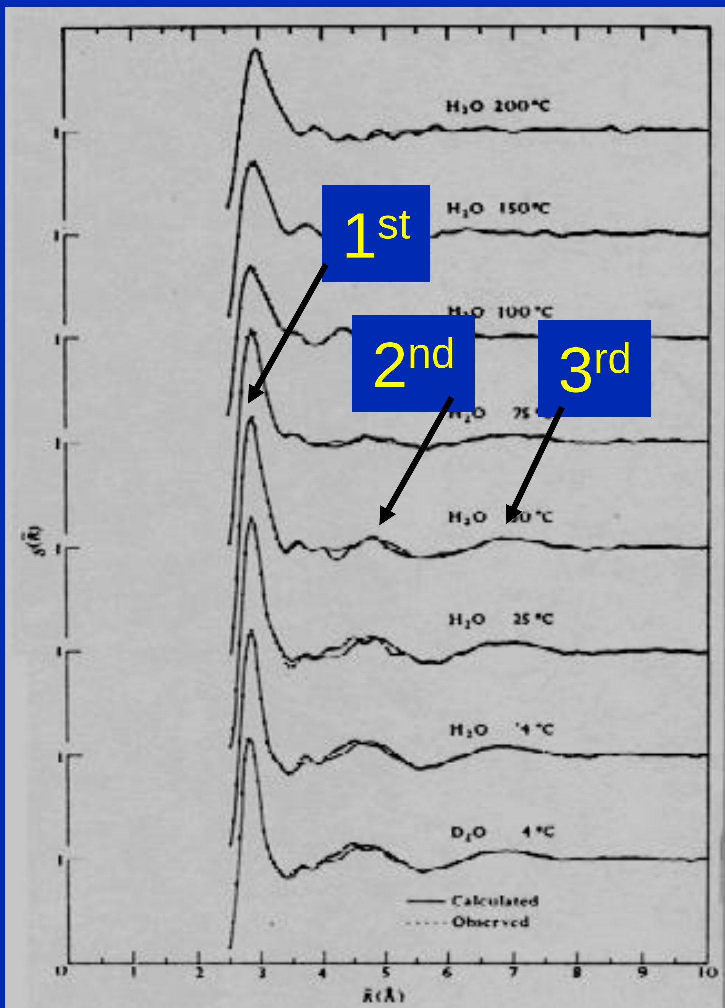
- Binding Attractive and repulsive potentials
- Lattice sums, cohesive energy, equilibrium structure

- Reciprocal space
- Diffraction

BINDING

Kittel Ch.3

Water



G(R)

R

- Kinetic energy
  vs Potential energy

- Density-density correlations

← Freezing point

Length scale atoms, orbitals, interatomic: $r \sim 1$ Å

Potential energy:

Coulomb

$$\boldsymbol{E} = \frac{\boldsymbol{q}^2}{\boldsymbol{r}}$$ ~ 14 eV (160.000 K)

Kinetic energy:

"Particle in a box":

$$\boldsymbol{E} = \frac{\hbar^2 \cdot (1/\boldsymbol{r})^2}{2 \cdot \boldsymbol{m}}$$ ~ 4 eV (45.000 K)

Ionic: Coulomb interaction

Metals: e^- - delocalization

Cohesive energy

- van der Waals: Induced dipole moments

  Heitler-London: Pauli repulsion

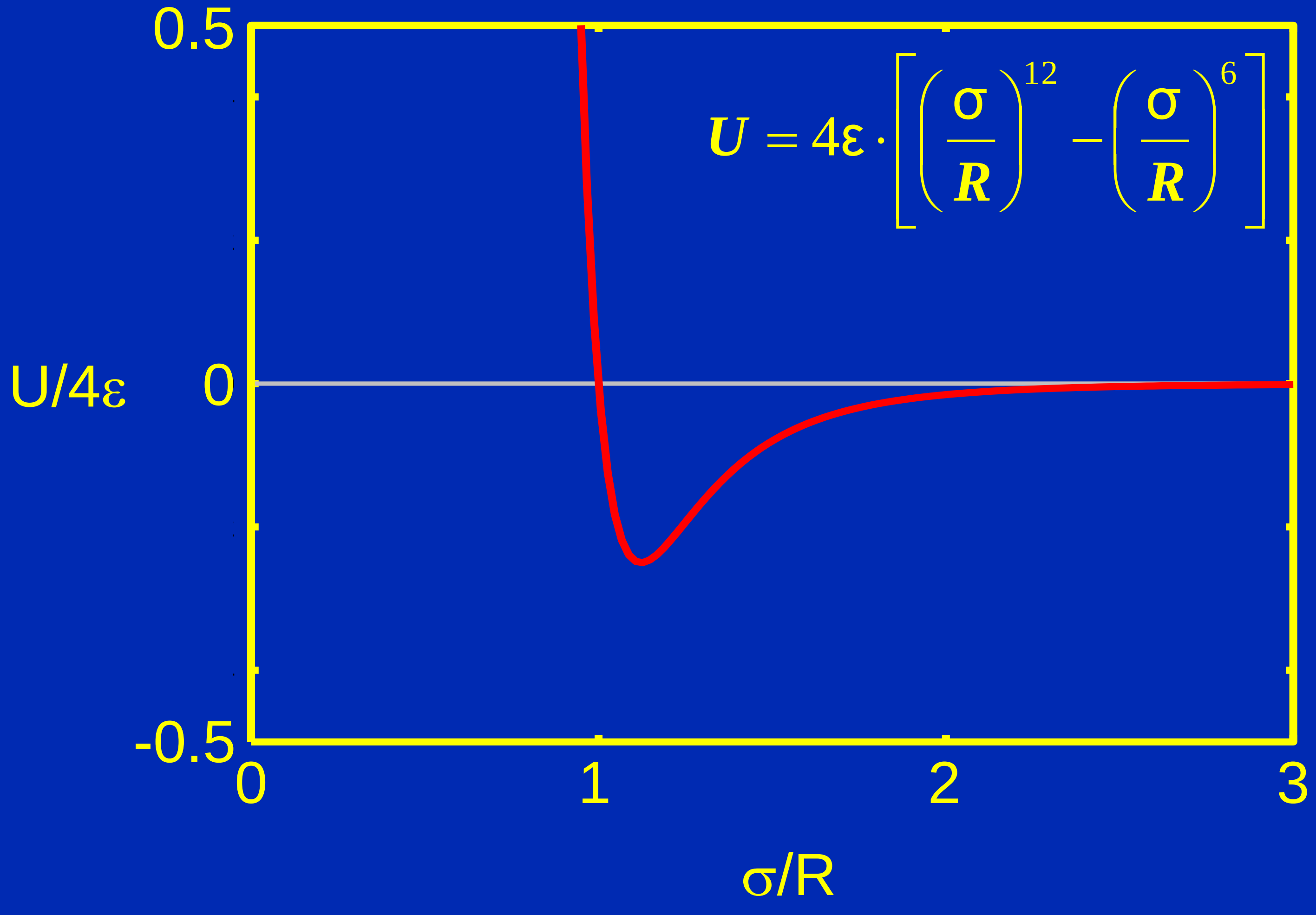
  Lennard-Jones: $$U = 4\varepsilon \cdot \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^{6} \right]$$

- Coulomb: $$U = \lambda \cdot e^{-r/\rho} \pm \frac{q^2}{r}$$

- Covalent: Homopolar bond

- Metals: Kinetic energy

Lennard-Jones potential



Molecular Hydrogen

General form wavefunction

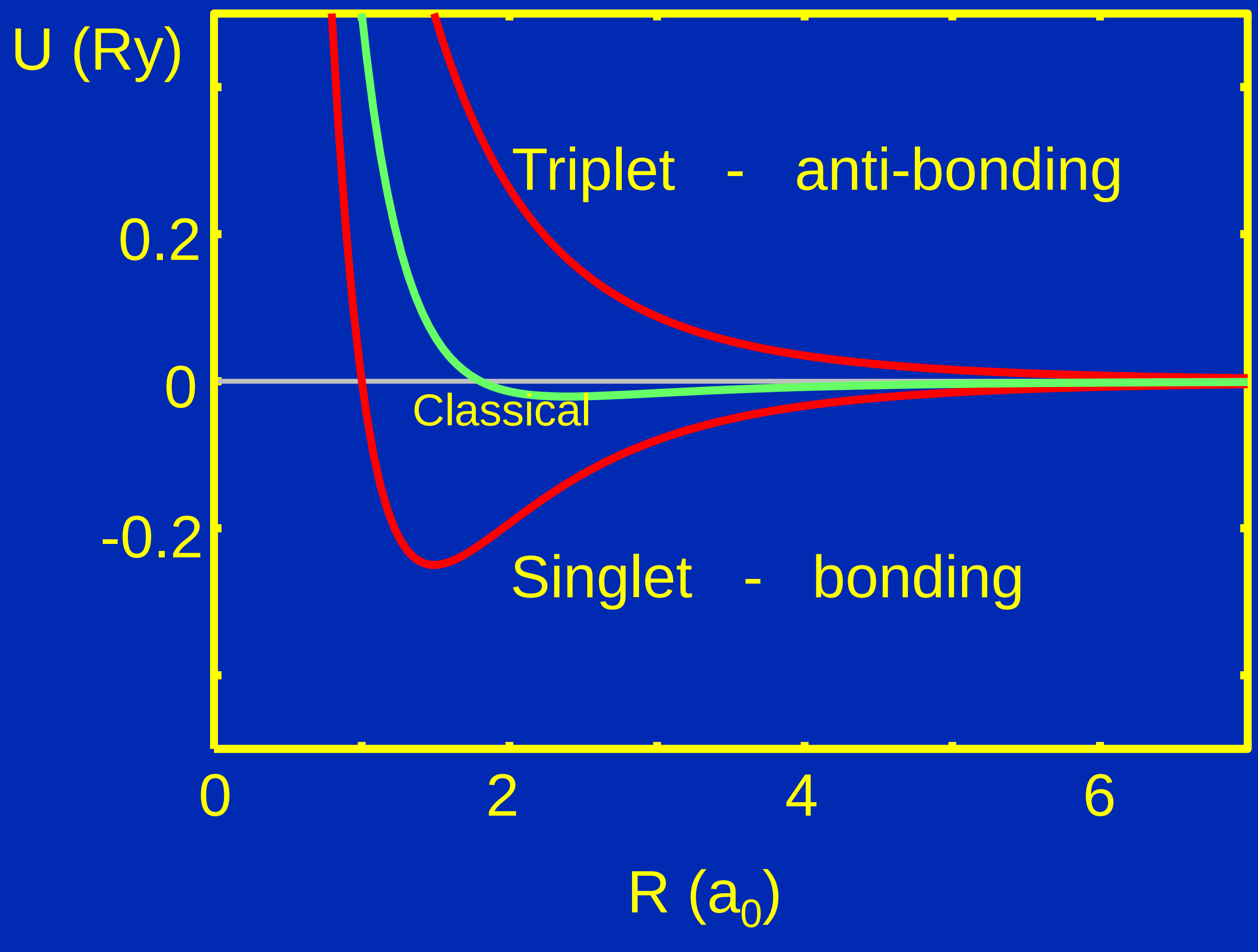
$$\Psi(\mathbf{r}_1,\sigma_1;\mathbf{r}_2,\sigma_2) = \psi(\mathbf{r}_1,\mathbf{r}_2)\cdot\chi(\sigma_1,\sigma_2)$$

Pauli exclusion principle: Heitler-London approach

$$\Psi_{\mathbf{s}}(1,2) = N_{\mathbf{s}}\left[\phi_{\mathbf{a}}(\mathbf{r}_1)\phi_{\mathbf{b}}(\mathbf{r}_2) + \phi_{\mathbf{b}}(\mathbf{r}_1)\phi_{\mathbf{a}}(\mathbf{r}_2)\right]\cdot\chi_{\mathbf{a}}(\sigma_1,\sigma_2)$$

$$\Psi_{\mathbf{t}}(1,2) = N_{\mathbf{t}}\left[\phi_{\mathbf{a}}(\mathbf{r}_1)\phi_{\mathbf{b}}(\mathbf{r}_2) - \phi_{\mathbf{b}}(\mathbf{r}_1)\phi_{\mathbf{a}}(\mathbf{r}_2)\right]\cdot\chi_{\mathbf{t}}(\sigma_1,\sigma_2)$$

Correlations: no two electrons on the same site


U (Ry)
0.2
0
-0.2
Triplet - anti-bonding
Classical
Singlet - bonding
0
2
4
6
R (a_0)

Lattice summations

$$U_{total} = \tfrac{1}{2} N \cdot \sum_j{}' \, U_{ij}$$

Lennard-Jones: $$U_{total} = \tfrac{1}{2} N \cdot 4\varepsilon \left\{ \sum_j{}' \left(\frac{\sigma}{p_{ij} R} \right)^{12} - \sum_j{}' \left(\frac{\sigma}{p_{ij} R} \right)^{6} \right\}$$

$\sum_j{}' \, P_{ij}^{-12}, \; \sum_j{}' \, P_{ij}^{-6}$ (FCC: 12.13; 14.45)

No net forces: $$\frac{\partial U_{total}}{\partial R} = 0 \quad \Rightarrow \quad R_0$$

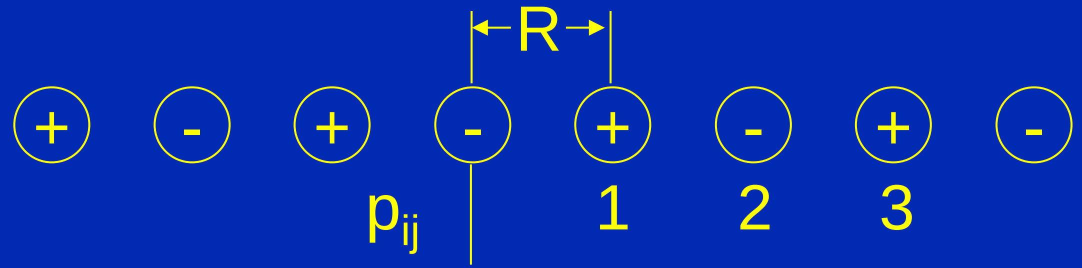
Cohesive energy: $U_{total}(R_0)$

Linear ionic crystal

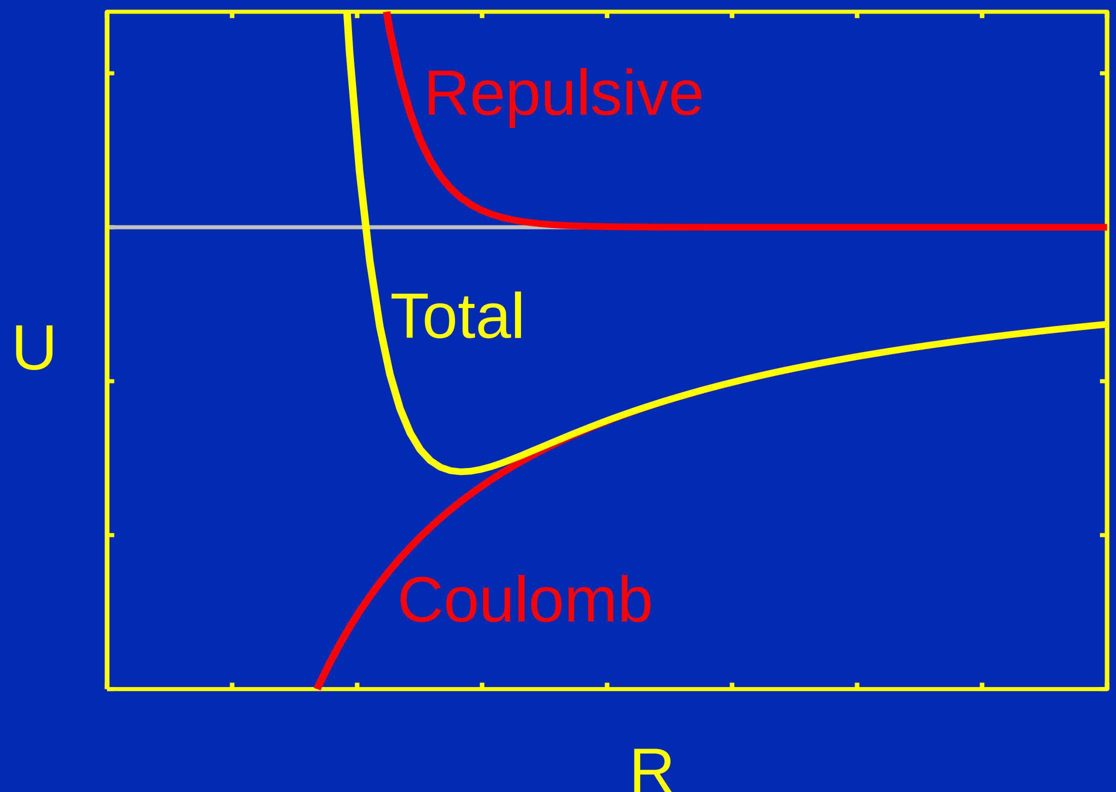
$$U_{ij} = \lambda \cdot e^{-\left(r_{ij}/\rho\right)} \pm \frac{q^2}{r_{ij}}$$

$$U_{total} = N \cdot \left(z\lambda e^{-(R/\rho)} - \sum_j{}' \frac{\pm q^2}{p_{ij} R} \right) = N \left(z\lambda e^{-(R/\rho)} - \alpha \frac{q^2}{R} \right)$$

$$\alpha = \sum_j{}' \frac{\pm 1}{p_{ij}}$$ Madelung constant



$$\alpha = \sum_j{}' \frac{\pm 1}{p_{ij}} = 2\cdot\left[1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}+\dots\right] = 2\cdot\ln(2)$$



DIFFRACTION
&
RECIPROCAL SPACE

(Kittel Ch. 2)

Crystal Structure

Lattice + Basis

Fourier Transform
periodic structure

Diffraction pattern

Diffraction intensity

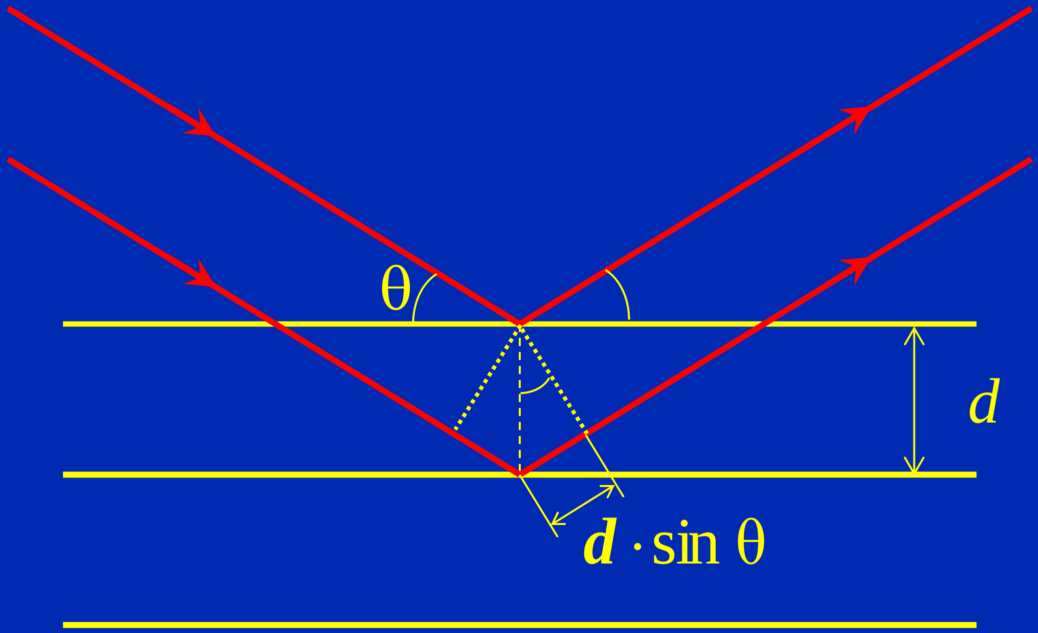
- Atomic form factor
- Structure factor

Reciprocal lattice

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

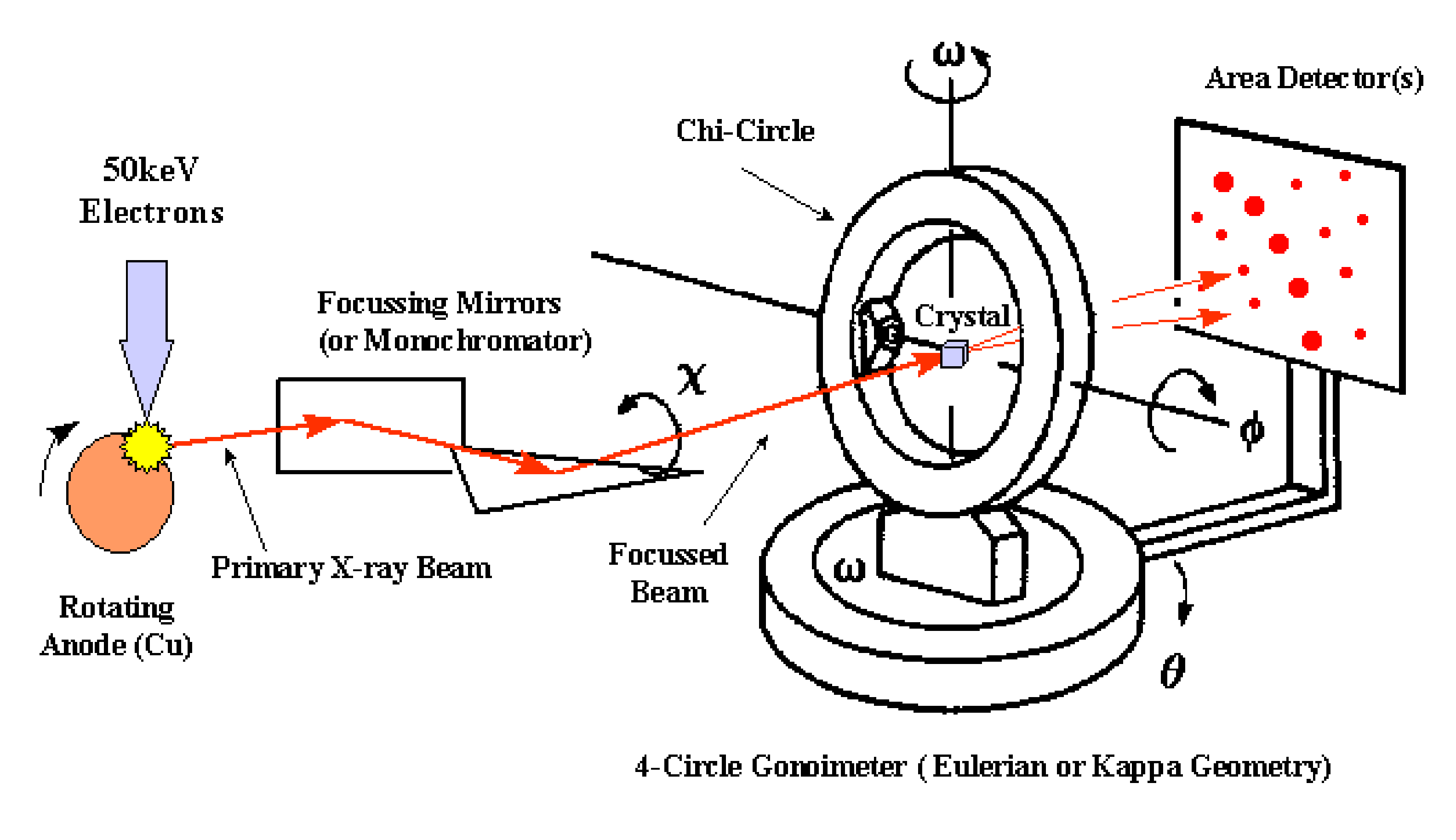
- Diffraction
- Lattice vibrations
- Electronic properties
- Bloch functions

Diffraction: Bragg law

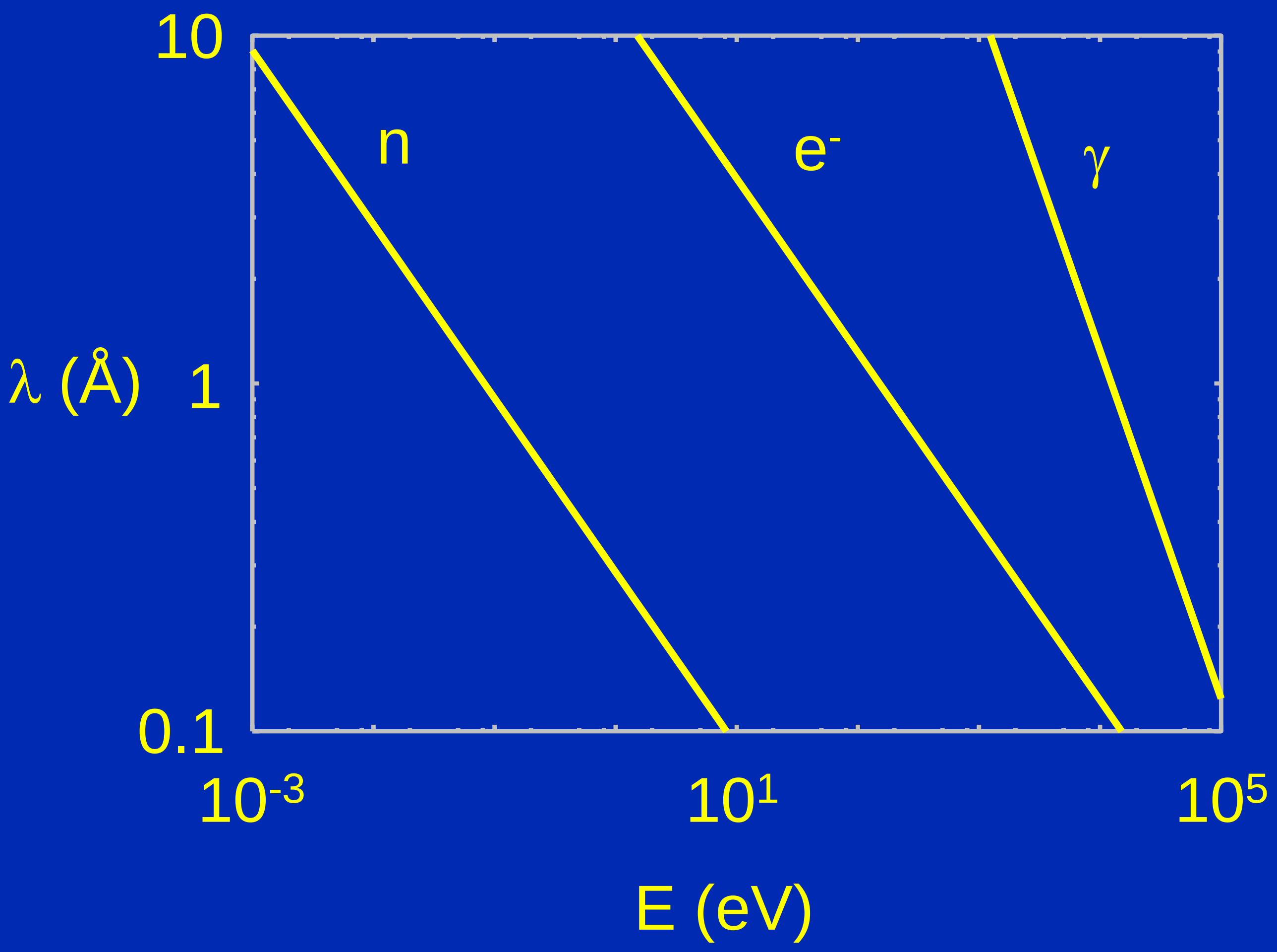


Constructive interference: $2 \cdot \boldsymbol{d} \cdot \sin\theta = \boldsymbol{n} \cdot \lambda$

Diffractometer



X-rays, electrons, neutrons

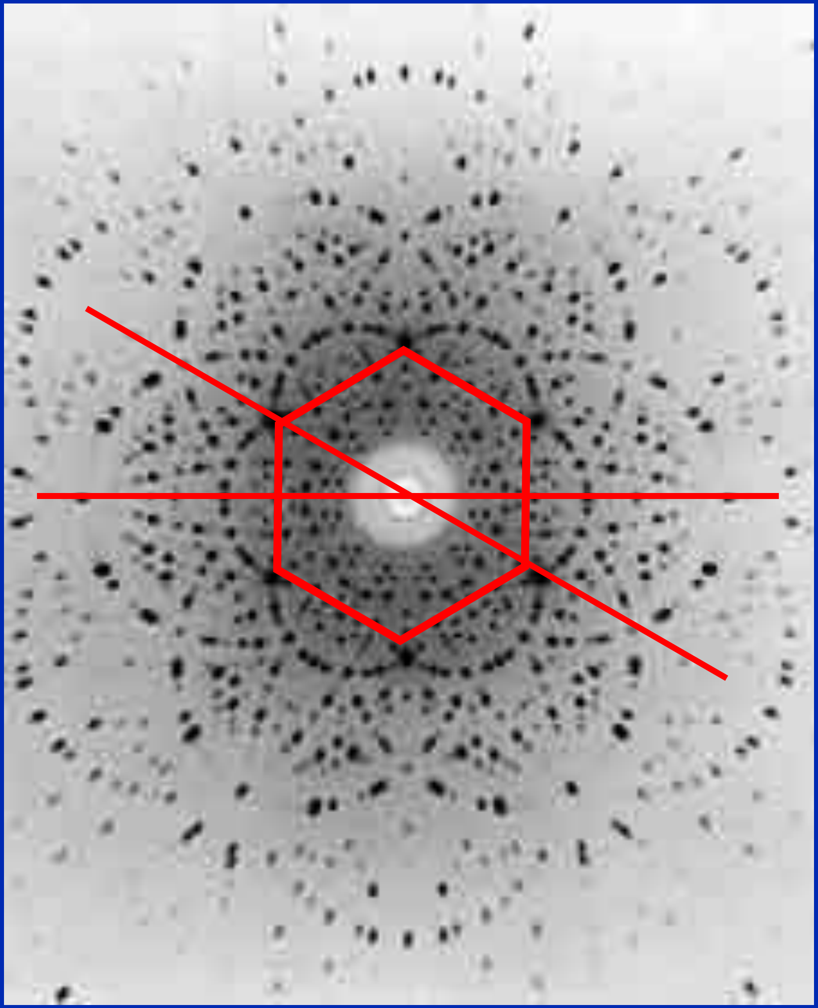


$$E = \hbar\omega = \hbar c k = \frac{hc}{\lambda}$$

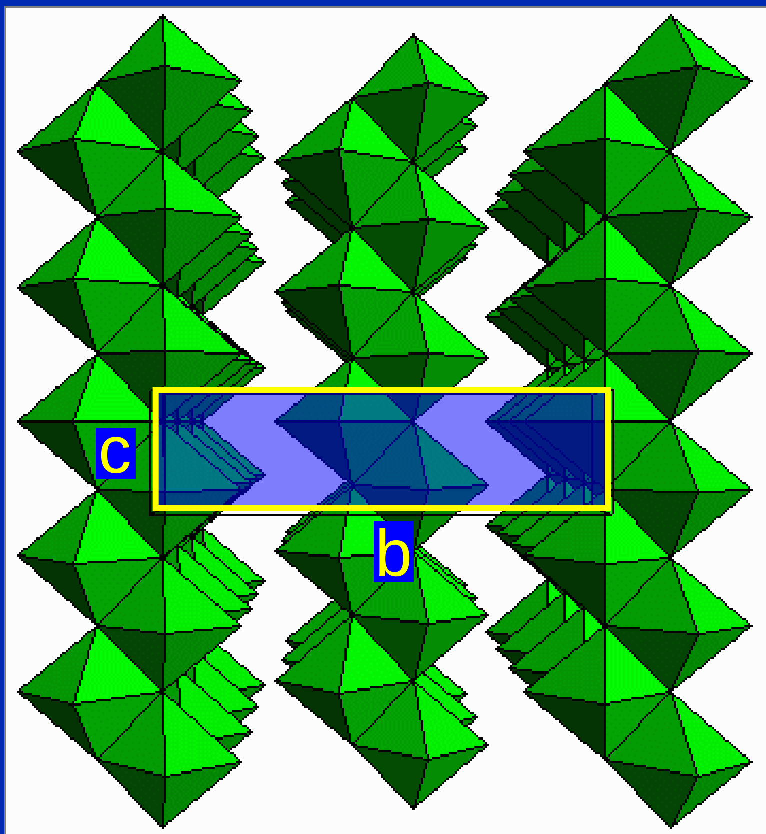
$$E = \frac{\hbar^2 k^2}{2m} = \frac{h^2}{2m\lambda^2}$$

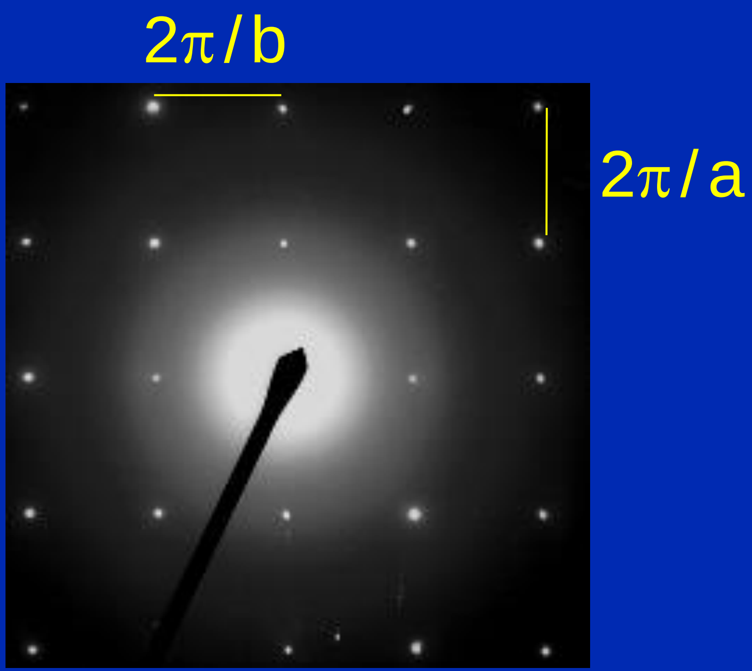
$$\frac{m_n}{m_e} \approx 1800$$

Beryl ($Be_3Al_2(SiO_3)_6$)



Molybdenum oxide MoO_3





Orthorhombic MoO_3

Reciprocal Space

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

Reciprocal lattice

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

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

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

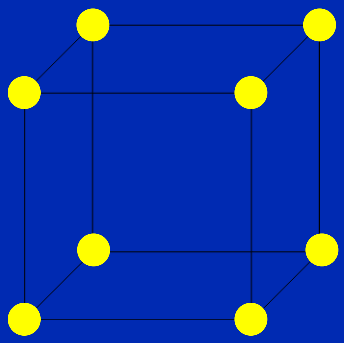
4) $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are primitive lattice vectors of an abstract lattice, conjugate to the lattice in direct space.
They span a Bravais lattice.

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

6) Reciprocal of reciprocal is real lattice again

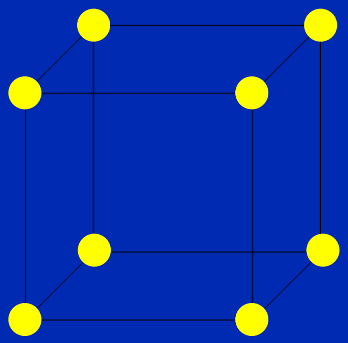
7) dimension $[\mathbf{b}_i] = m^{-1}$

Reciprocal lattice of SC



$$\vec{a}_1 = a \cdot \vec{e}_x$$
$$\vec{a}_2 = a \cdot \vec{e}_y$$
$$\vec{a}_3 = a \cdot \vec{e}_z$$

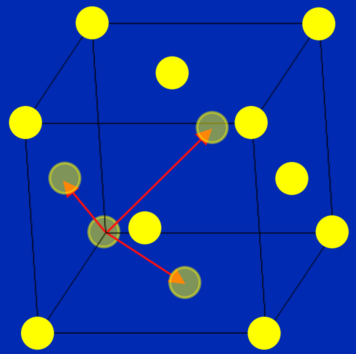
$V=a^3$



$$\vec{b}_1 = \left(2\pi / a\right) \cdot \vec{e}_x$$
$$\vec{b}_2 = \left(2\pi / a\right) \cdot \vec{e}_y$$
$$\vec{b}_3 = \left(2\pi / a\right) \cdot \vec{e}_z$$

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

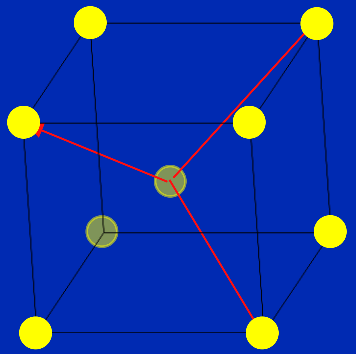
Reciprocal lattice of FCC



a

$$\vec{a}_1 = a/2 \cdot \left(\vec{e}_y + \vec{e}_z\right)$$
$$\vec{a}_2 = a/2 \cdot \left(\vec{e}_x + \vec{e}_z\right)$$
$$\vec{a}_3 = a/2 \cdot \left(\vec{e}_x + \vec{e}_y\right)$$

$V = a^3/4$



$4\pi/a$

$$\vec{b}_1 = (2\pi/a) \cdot \left(-\vec{e}_x + \vec{e}_y + \vec{e}_z\right)$$
$$\vec{b}_2 = (2\pi/a) \cdot \left(\vec{e}_x - \vec{e}_y + \vec{e}_z\right)$$
$$\vec{b}_3 = (2\pi/a) \cdot \left(\vec{e}_x + \vec{e}_y - \vec{e}_z\right)$$

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

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

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

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

Crystal Structure

Lattice + Basis

Fourier Transform
periodic structure

Diffraction pattern → Reciprocal lattice

Diffraction intensity → 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

Theorem: 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) => $\Delta\vec{k} = \vec{G}$

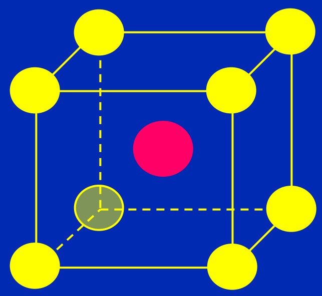
Laue condition

Ewald construction

Brillouin construction

CsCl, exponential charge distributions

$$n(\vec{r}) = \sum_{\vec{T}} \left[\frac{A}{\pi \rho_A^3} e^{-2\frac{\left|\vec{r}-\vec{T}\right|}{\rho_A}} + \frac{B}{\pi \rho_B^3} e^{-2\frac{\left|\vec{r}-\vec{T}-\vec{r}_{AB}\right|}{\rho_A}} \right]$$



$$\vec{T} = a(m\vec{e}_x + n\vec{e}_y + p\vec{e}_z)$$

$$\vec{r}_{AB} = \frac{a}{2}(\vec{e}_x + \vec{e}_y + \vec{e}_z)$$

Atomic form factors: $f_j = \int d^3\vec{r} e^{-i\vec{G}\cdot\vec{r}} n_j(\vec{r})$

$$f_A\left(\vec{G}\right) = \frac{16A}{4 + \left|\vec{G}\right|^2 \rho_A^2} \qquad f_B\left(\vec{G}\right) = \frac{16B}{4 + \left|\vec{G}\right|^2 \rho_B^2}$$

CsCl, diffraction conditions

Structure factor: $S_{\vec{G}} = \sum_j f_j \exp\left\{-i\vec{G}\cdot\vec{r}_j\right\}$

$$S_{\vec{G}} = f_A\left(\vec{G}\right) + f_B\left(\vec{G}\right)e^{-i\vec{G}\cdot\vec{r}_{AB}} = f_A\left(\vec{G}\right) + f_B\left(\vec{G}\right)e^{-i\left[G_x + G_y + G_z\right]a/2}$$

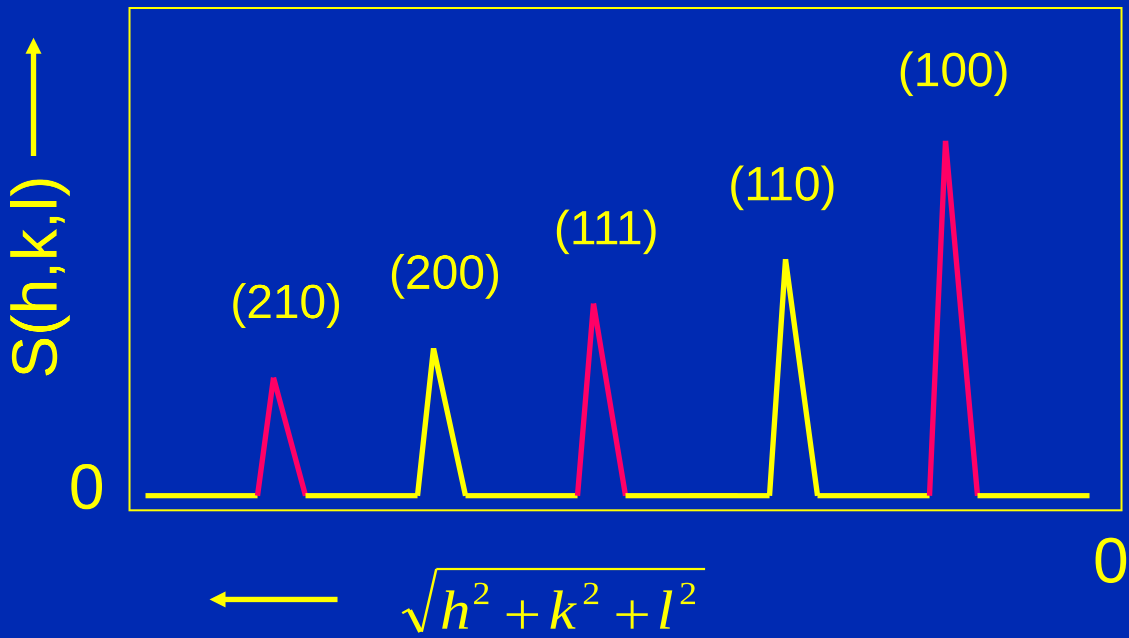
Simple cubic lattice, Bragg condition: $\vec{G} = \frac{2\pi}{a}\left\{h\hat{x} + k\hat{y} + l\hat{z}\right\}$

$$S(h,k,l) = f_A + f_B e^{-i\pi\left(h+k+l\right)} =$$

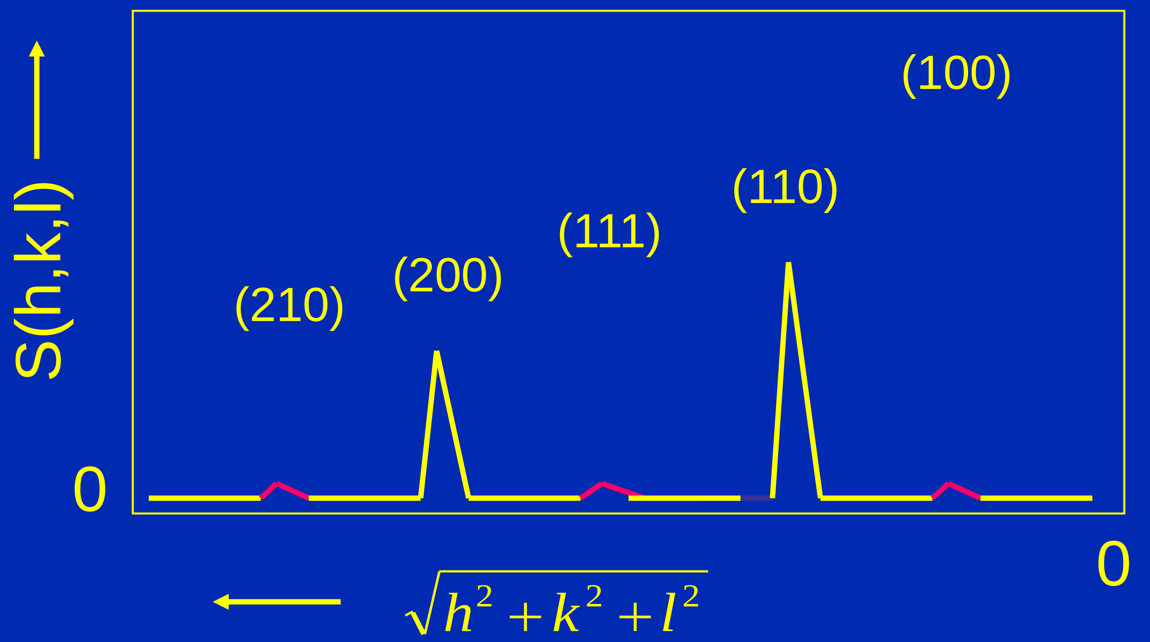
$= f_A + f_B$ h+k+l even

$= f_A - f_B$ h+k+l odd

Case I: $f_A >> f_B$



Case II: $f_A = f_B$



Pseudo-bcc

Diffraction for $\vec{G} = \frac{2\pi}{a}\left\{h\hat{x}+k\hat{y}+l\hat{z}\right\}$

with $h + k + l$ even ($f_A = f_B$) : '*pseudo-bcc*'