Modern Crystallography II

Topics:

20.11.	**Crystalline state** definition, interaction types in crystalline materials lattice types, symmetry operations, reciprocal lattice
27.11.	**X-ray diffraction (kinematic theory)** Bragg equation, Laue equations, Ewald sphere, atomic form factor, structure factor, absorption
4.12	**experimental X-ray structure determination** experimental methods, phase problem, phase retrieval methods, structure refinement
11.12	**modern applications of crystallography** protein crystallography, powder diffraction, time-resolved crystallography (pump and probe)

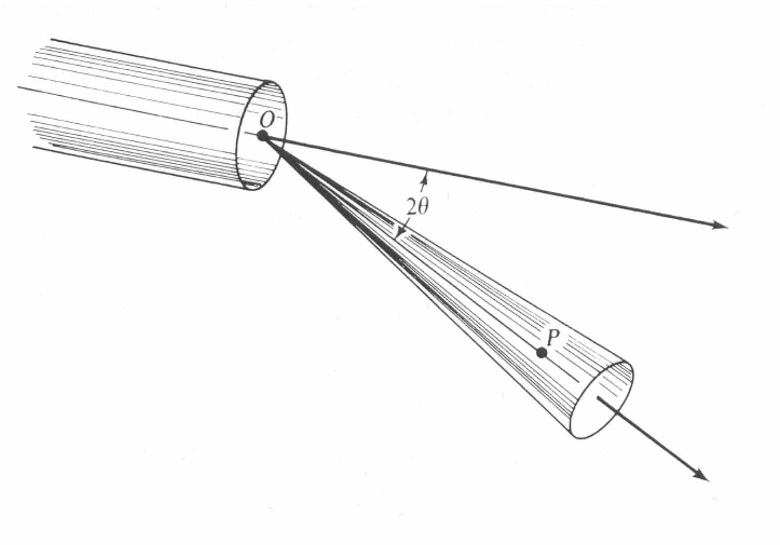
Recommended literature

Michael M. Woolfson: An introduction to X-ray crystallography
(Cambridge University Press)

C. Ciaccovazzo: Fundamentals of Crystallography
(International Union of Crystallography)

International Tables of Crystallography, Vol I
(International Union of Crystallography)

General description of a scattering process



general wave function:

$$y = A \cdot \cos(2\pi \nu t)$$

phase lag at P with respect to O:

$$\alpha_{OP} = 2\pi \overline{OP} / \lambda = 2\pi \nu \overline{OP} / c$$

scattering phase shift: α_s

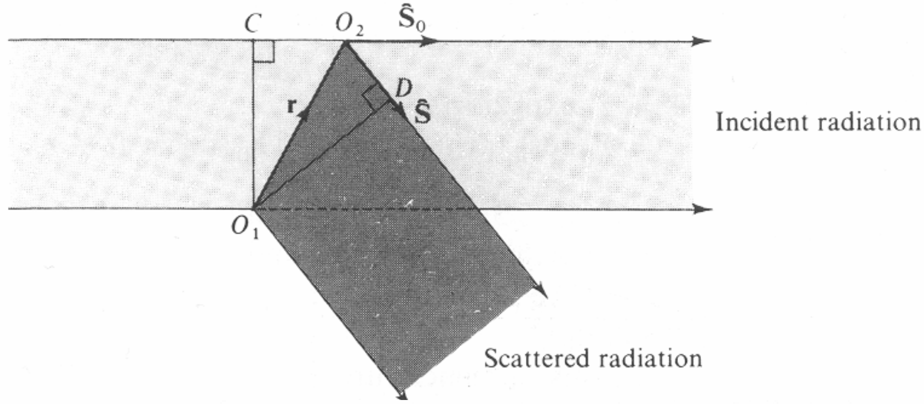
intensity fall off with distance r:

$$I \approx 1/r^2$$

displacement at P:

$$y(2\theta, D, t) = f_{2\theta} \frac{A}{D} \cos\left[2\pi\nu\left(t - \frac{D}{c}\right) - \alpha_s\right] \quad \text{or} \quad y(2\theta, D, t) = f_{2\theta} \frac{A}{D} \exp\left[2\pi i \nu\left(t - \frac{D}{c}\right) - \alpha_s\right]$$

Scattering from two identical point scatter centers

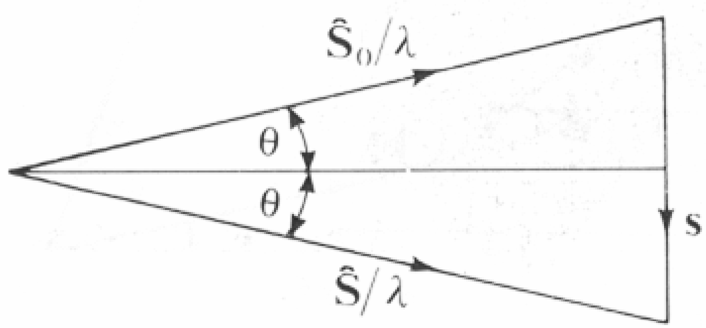


2 identical point scattering centers at O1 and O2

scattering phase shift α_s the same for both O1 and O2

Point P very far away compared to distance O1-O2

phase scattering shift α between waves scattered at O1 and O2:



$$\alpha_{O_1O_2} = -\frac{2\pi}{\lambda}\left(\overline{CO_2} + \overline{O_2D}\right)$$

$$\vec{s} = \frac{\vec{S} - \vec{S}_0}{\lambda}$$

$$\alpha_{O_1O_2} = 2\pi \cdot \vec{r}\left(\frac{\vec{S} - \vec{S}_0}{\lambda}\right) = 2\pi\vec{r} \cdot \vec{s}$$

Scattering from two identical point scatter centers (2)

scatterer O1 in origin, scatterer O2 at **r**:

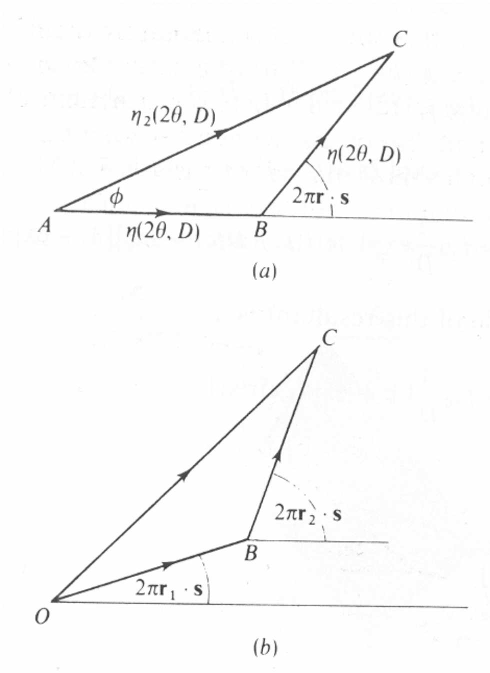
$$y(2\theta, D, t) = f_{2\theta}\frac{A}{D}\exp\left[2\pi i\,\nu\left(t-\frac{D}{c}\right)-\alpha_s\right]+\exp\left[2\pi i\,\nu\left(t-\frac{D}{c}\right)-\alpha_s+2\pi i\vec{r}\cdot\vec{s}\right]$$

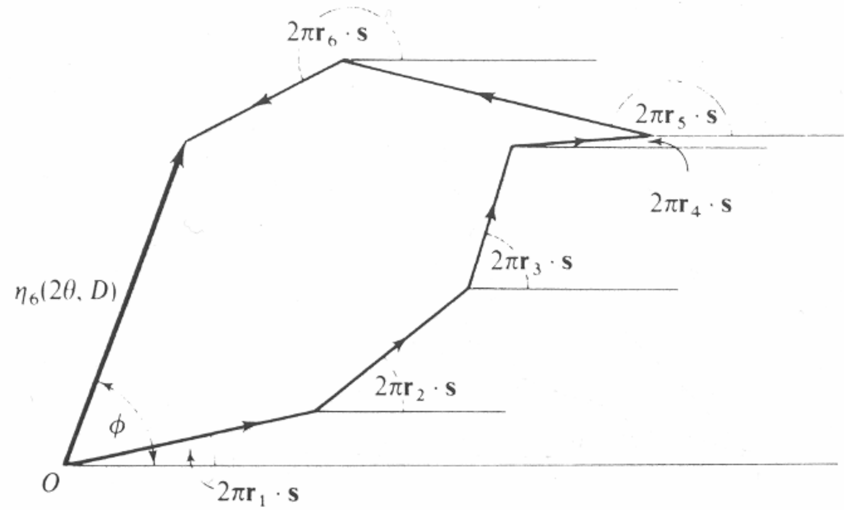
$$= f_{2\theta}\frac{A}{D}\exp\left[2\pi i\,\nu\left(t-\frac{D}{c}\right)-\alpha_s\right]\left[1+\exp(2\pi i\vec{r}\cdot\vec{s})\right]$$

resultant amplitude:

$$\eta(2\theta, D) = f_{2\theta}\frac{A}{D}\left[1+\exp\left(2\pi i\vec{r}\cdot\vec{s}\right)\right]$$

Scattering from a general distribution of point scatterers





n identical point scatterers:

$$\eta_n(2\theta, D) = \sum_{j=1}^{n} \left[n(2\theta, d)\right]_j \exp(2\pi i \vec{r}_j \cdot \vec{s})$$

n different point scatterers:

$$\eta_n(2\theta, D) = \eta(2\theta, D) \sum_{j=1}^{n} \exp(2\pi i \vec{r}_j \cdot \vec{s})$$

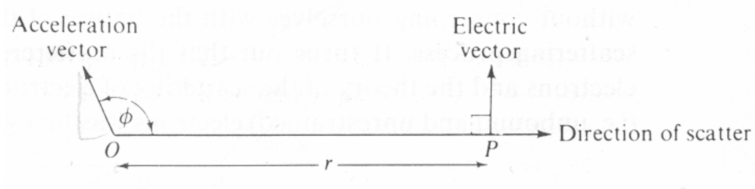
Thomson scattering I

alternating electromagnetic field of incident radiation leads to alternating acceleration of the electron – harmonic motion

can be envisaged as absorption and re-emission of radiation

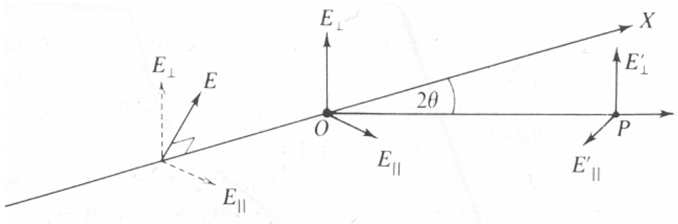
Assumption: electron in origin 0, charge e, mass m, acceleration with amplitude a, results in an electric vector of amplitude at point P:

$$E = \frac{ea\sin\varphi}{4\pi\varepsilon_0 rc^2}$$



Amplitudes a:

$$a_\perp = \frac{e}{m}E_\perp \qquad a_\parallel = \frac{e}{m}E_\parallel$$

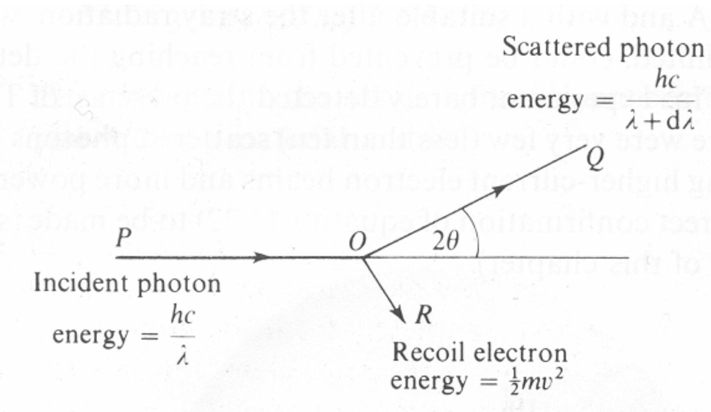


$$E'_\perp = \frac{e^2}{4\pi\varepsilon_0 rc^2 m}E_\perp \qquad E'_\parallel = \frac{e^2\cos 2\theta}{4\pi\varepsilon_0 rc^2 m}E_\parallel$$

Compton scattering (incoherent)

Thomson scattering is elastic - Compton scattering is **inelastic**
scattered radiation of longer wavelength than incident radiation

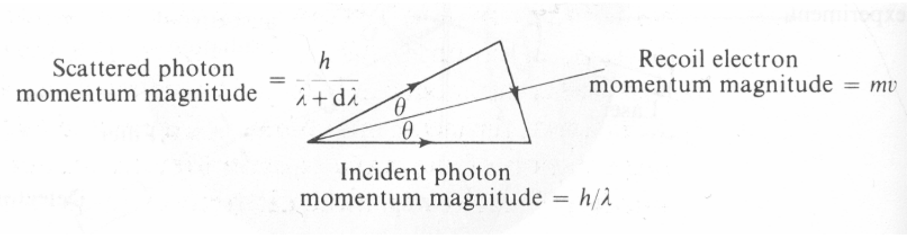
conversation of energy:



$$\frac{hc}{\lambda} = \frac{hc}{\lambda + d\lambda} + \frac{mv^2}{2} \qquad \frac{hc}{\lambda^2} d\lambda = \frac{mv^2}{2}$$

momentum conversation:

$$\frac{mv}{2} = \frac{h}{\lambda} \sin\theta$$

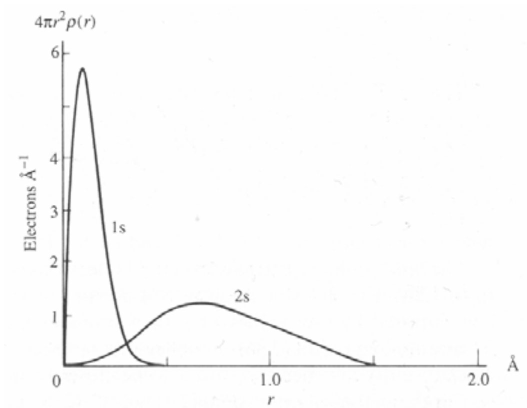


$$d\lambda = \frac{2h}{mc} \sin^2\theta = \frac{h}{mc}(1 - \cos 2\theta)$$

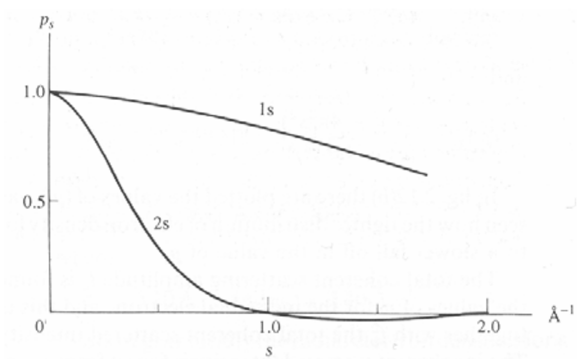
Maximum possible wavelength
change for backscattering $2\theta = \pi$

scattering of X-rays by atoms

Assumption: spherically symmetric electron density ρ(r)



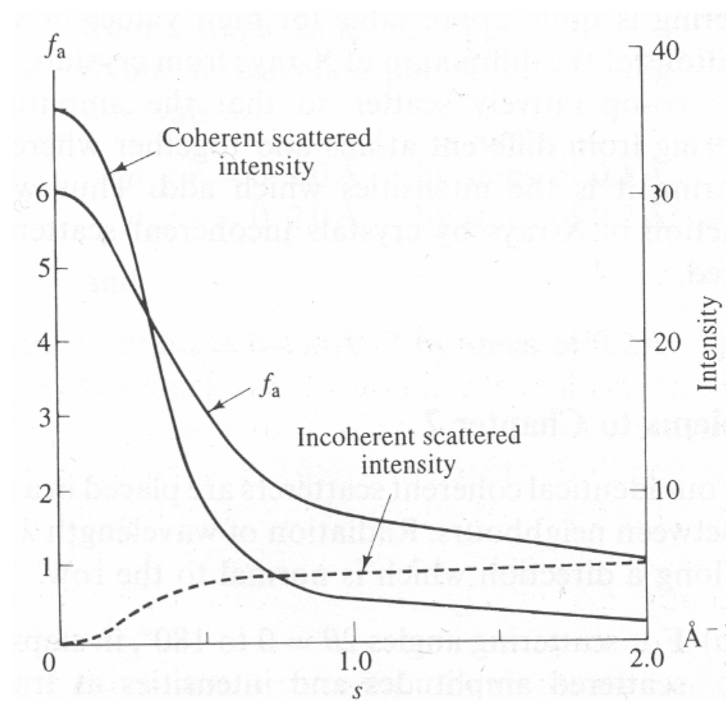
Contributions from 1s and 2s electrons to the atomic form factor



atomic form factor f_a:

$$f_a = 4\pi \int_0^\infty \rho_a(r) r^2 \frac{\sin(2\pi rs)}{2\pi rs} dr$$

tabulated in International Tables for X-ray Crystallography (Vol. III)

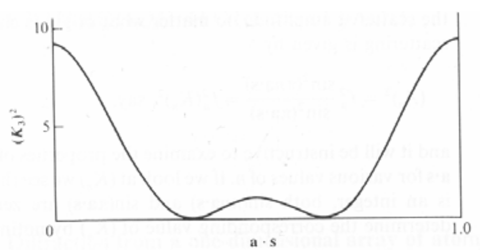


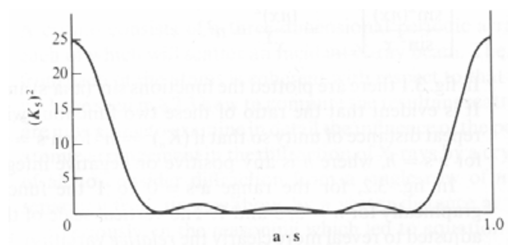
diffraction from a one-dimensional array of atoms

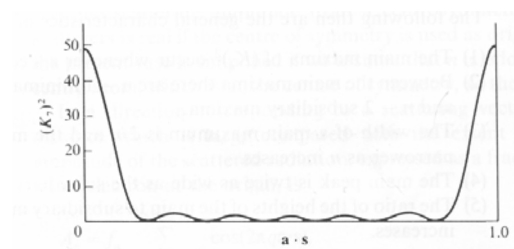
scattering amplitude for a single row of n atoms
n=odd, one atom in origin, translation vector **a**:

$$A_n = f_a \sum_{q=-\frac{1}{2}(n-1)}^{\frac{1}{2}(n-1)} \cos(2\pi q \vec{a}\cdot\vec{s}) = \frac{f_a}{2\sin(2\pi\vec{a}\cdot\vec{s})} \sum_{q=-\frac{1}{2}(n-1)}^{\frac{1}{2}(n-1)} 2\cos(2\pi q \vec{a}\cdot\vec{s})\sin(2\pi\vec{a}\cdot\vec{s})$$

$$A_n = f_a \frac{\sin(\pi n \vec{a}\cdot\vec{s})}{\sin(\pi\vec{a}\cdot\vec{s})} \qquad \left(A_n\right)^2 = f_a^2 \frac{\sin^2(\pi n\vec{a}\cdot\vec{s})}{\sin^2(\pi\vec{a}\cdot\vec{s})} = f_a^2 (K_n)^2$$







main maxima at **a**·**s** = integer
intensity at the maxima increase with increasing n
intensity between the main maxima vanishes with increasing n

Laue equations – diffraction from a three dimensional array of atoms

diffraction maxima for (h,k,l = integer):

$$\vec{a}\cdot\vec{s}=h$$
$$\vec{b}\cdot\vec{s}=k \qquad (1)$$
$$\vec{c}\cdot\vec{s}=l$$

definition of reciprocal lattice:

$$\begin{array}{lll} a\cdot a^*=1 & b\cdot a^*=0 & c\cdot a^*=0 \\ b\cdot a^*=0 & b\cdot b^*=1 & c\cdot b^*=0 \\ c\cdot a^*=0 & c\cdot b^*=0 & c\cdot c^*=1 \end{array} \qquad (2)$$

reciprocal lattice vector:

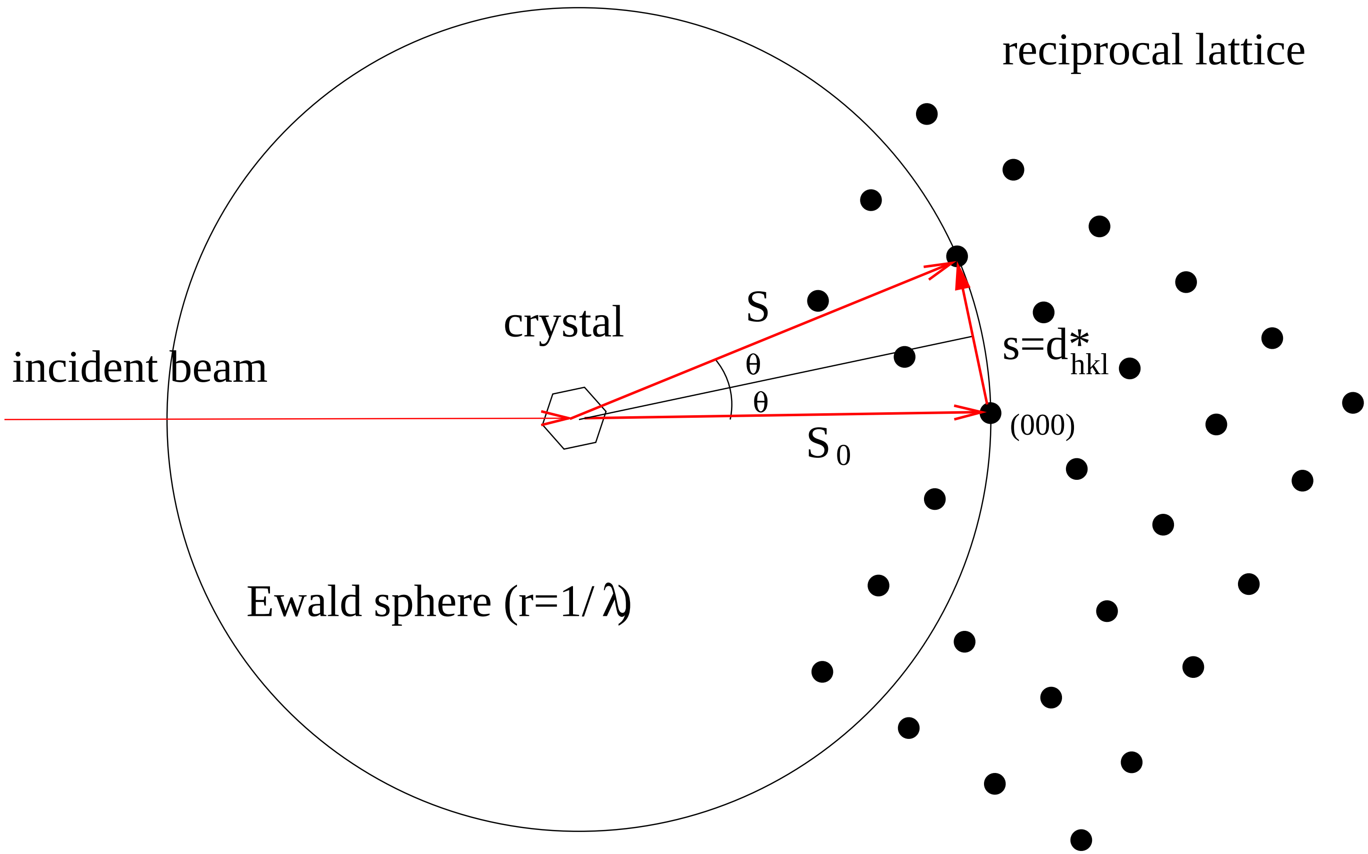
$$\vec{d}^*_{hkl}=h\cdot\vec{a}*+k\cdot\vec{b}*+l\cdot\vec{c}* \qquad (3)$$

combination of (1), (2), and (3):

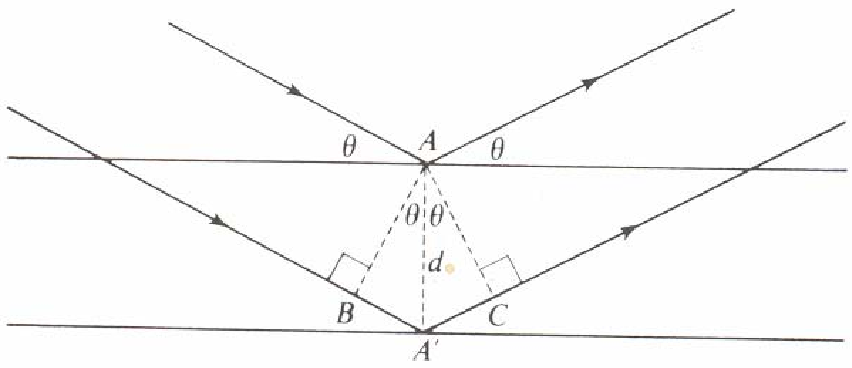
$$\left(h\vec{a}^*+k\vec{b}^*+l\vec{c}^*\right)\cdot\vec{a}=h$$
$$\left(h\vec{a}^*+k\vec{b}^*+l\vec{c}^*\right)\cdot\vec{b}=k \qquad (4)$$
$$\left(h\vec{a}^*+k\vec{b}^*+l\vec{c}^*\right)\cdot\vec{c}=l$$

- diffraction maxima from crystals occur if scattering vector **s** equals a reciprocal lattice vector $\mathbf{d}^*_{hkl}$
- crystal orientation to observe a diffraction maxima can be calculated by applying eq. (4)

Ewald sphere



Bragg's law



phase difference for wave scattered at A and A':

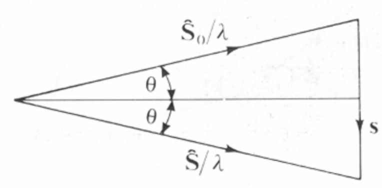
$$\overline{BA'} + \overline{A'C} = d \cdot \sin\theta + d \cdot \sin\theta = 2d\sin\theta$$

constructive interference of waves scattered at A and A' for:

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

remember from Laue equations:

$$\left| d^*_{hkl} \right| = 1/d_{hkl}$$



Structure factor

summation over all n atoms in unit cell:

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp\left(2\pi i \vec{r}_j \cdot \vec{s}\right)$$

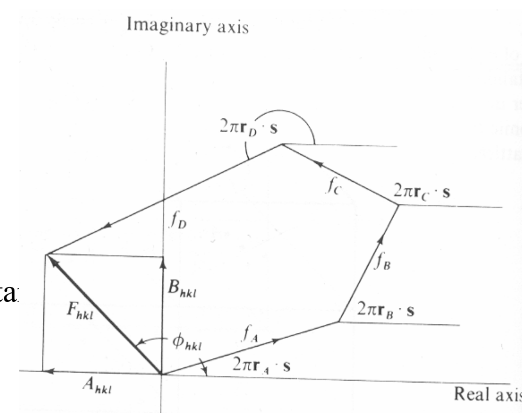
h,k,l reflection indices

$$F_{hkl} = A_{hkl} + iB_{hkl}$$

$$A_{hkl} = \sum_{j=1}^{N} f_j \cos\left(2\pi \vec{r}_j \cdot \vec{s}\right) \qquad B_{hkl} = \sum_{j=1}^{N} f_j \sin\left(2\pi \vec{r}_j \cdot \vec{s}\right)$$

$$I = \left|F_{hkl}\right| = A_{hkl}^2 + B_{hkl}^2$$

ta



for a centrosymmetric structure:

$$F_{hkl} = \sum_{j=1}^{N} f_j (\cos 2\pi \vec{r}_j \cdot \vec{s})$$

scattering amplitude is real