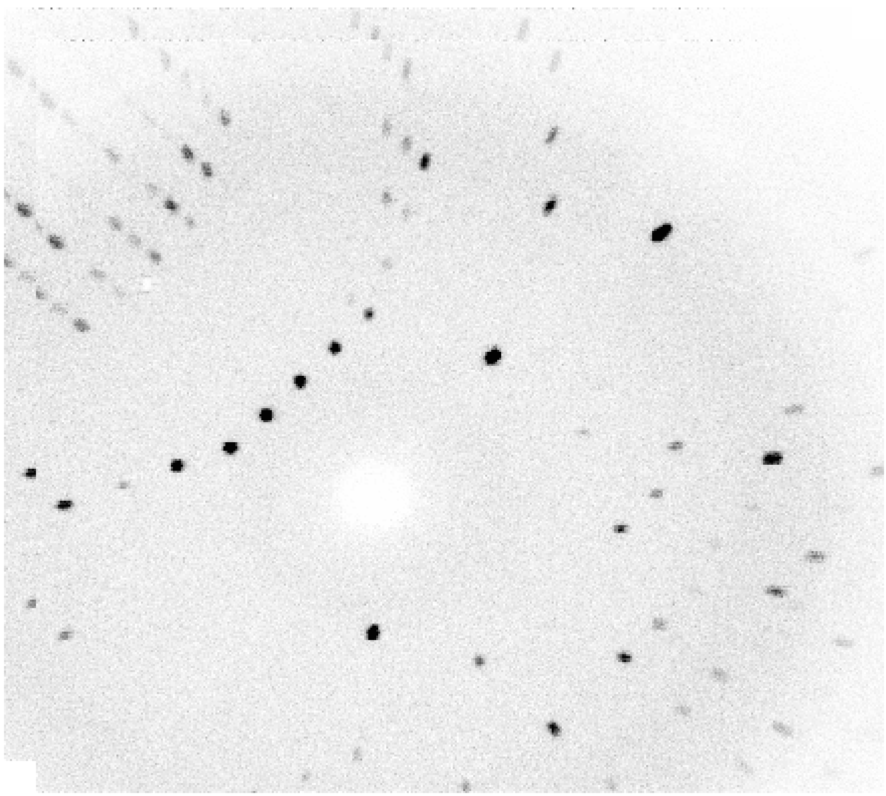
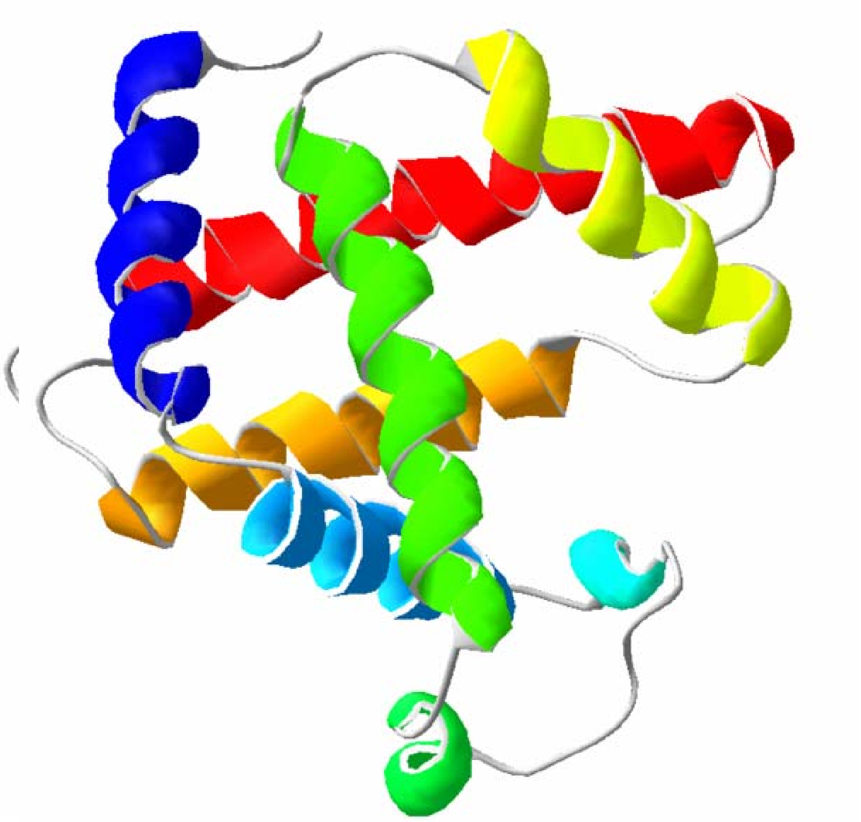
3.012 Fund of Mat Sci: Structure – Lecture 18

X-RAYS AT WORK



An X-ray diffraction image for the protein myoglobin. Source: Wikipedia.



Model of helical domains in myoglobin. Image courtesy of Magnus Manske

Homework for Wed Nov 23

- Prof Wuensch Lecture Notes
- http://capsicum.me.utexas.edu/ChE386K/ for many details (Lect 19 onwards, but note different 2π convention)
- Buy turkey

Last time:

1. X-rays generation: undulators and wigglers in synchrotrons, bremsstrahlung and core excitations (e.g. K_α) in X-ray tubes
2. Reciprocal lattice
3. Diffraction gratings – Huygens construction
4. Laue diffraction from periodic arrays in 1-d, 2-d, 3-d

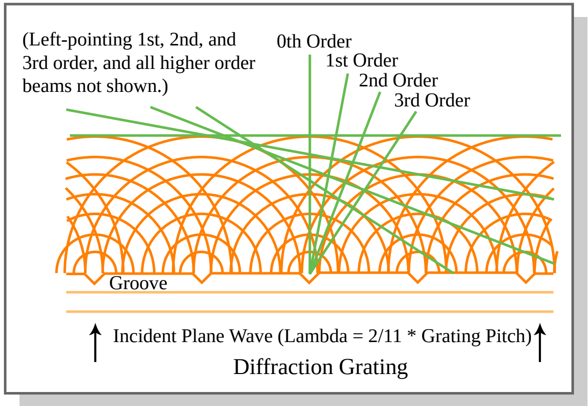


Figure by MIT OCW.

Reciprocal lattice (IV)

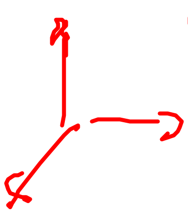
$\vec{G} = h\vec{b}_1 + i\vec{b}_2 + j\vec{b}_3$ with h, i, j integers,

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

$\vec{G} = (h, i, j)$ are the reciprocal-lattice vectors

d^*_{hkl} is distance between two planes of Miller indices h k l

in the reciprocal lattice $= \dfrac{2\pi}{d_{hkl}}$



$\vec{a}_1 = (a, 0, 0)$ $\quad \left(\frac{2\pi}{a}, 0, 0\right)$

$\vec{a}_2 = (0, a, 0)$ $\quad \left(0, \frac{2\pi}{a}, 0\right)$

$\vec{a}_3 = (0, 0, a)$ $\quad \left(0, 0, \frac{2\pi}{a}\right)$

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

$$e^{ik\vec{r}} \leftrightarrow e^{ik(\vec{r} + \vec{R})}$$

First and second Laue conditions

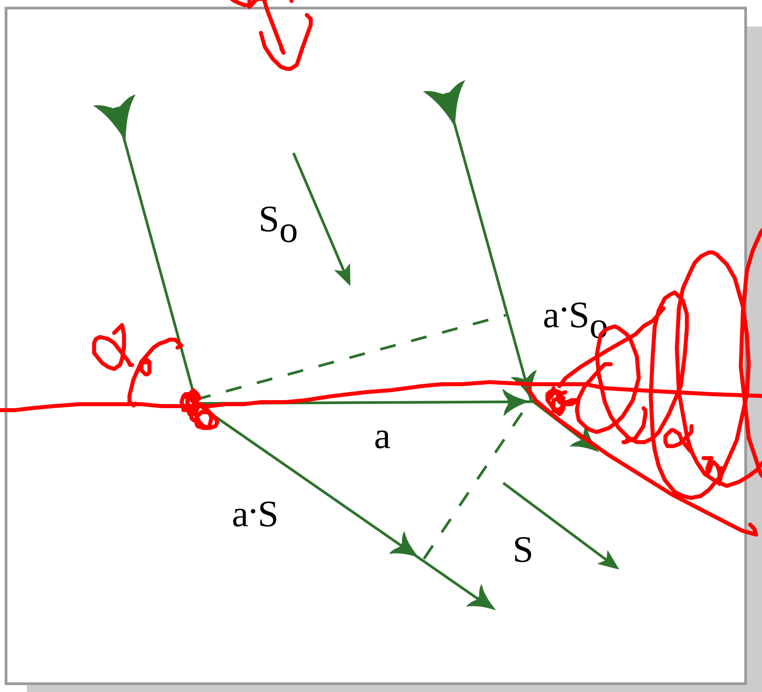


Figure by MIT OCW.

$$\vec{a}\cdot\vec{S} = a\cos\alpha_n$$

$$\vec{a}\cdot\vec{S}_0 = a\cos\alpha_0$$

$$a\left(\cos\alpha_n - \cos\alpha_0\right) = \vec{a}\cdot\left(\vec{S}-\vec{S}_0\right) = n_x\lambda$$

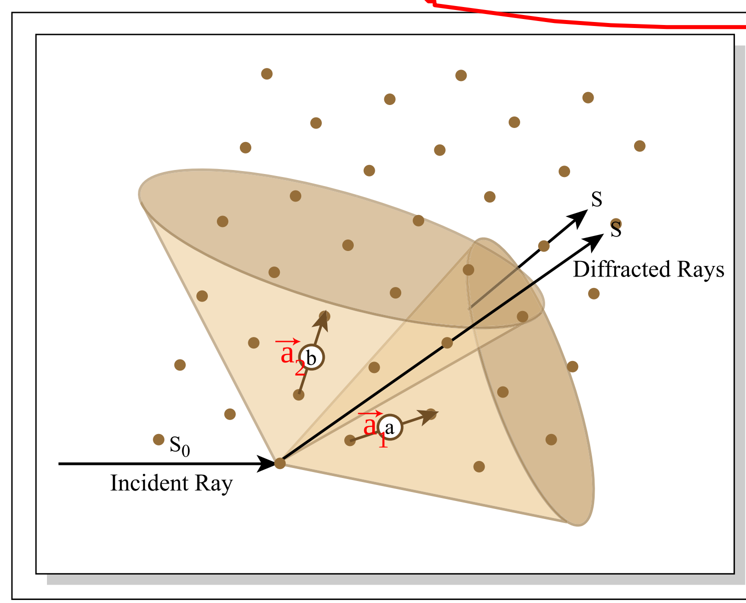


Figure by MIT OCW.

All three Laue conditions

$$\vec{a}_1 \cdot \left(\vec{S} - \vec{S}_0 \right) = \text{integer multiple of } \lambda$$

$$\vec{a}_2 \cdot \left(\vec{S} - \vec{S}_0 \right) = \text{integer multiple of } \lambda$$

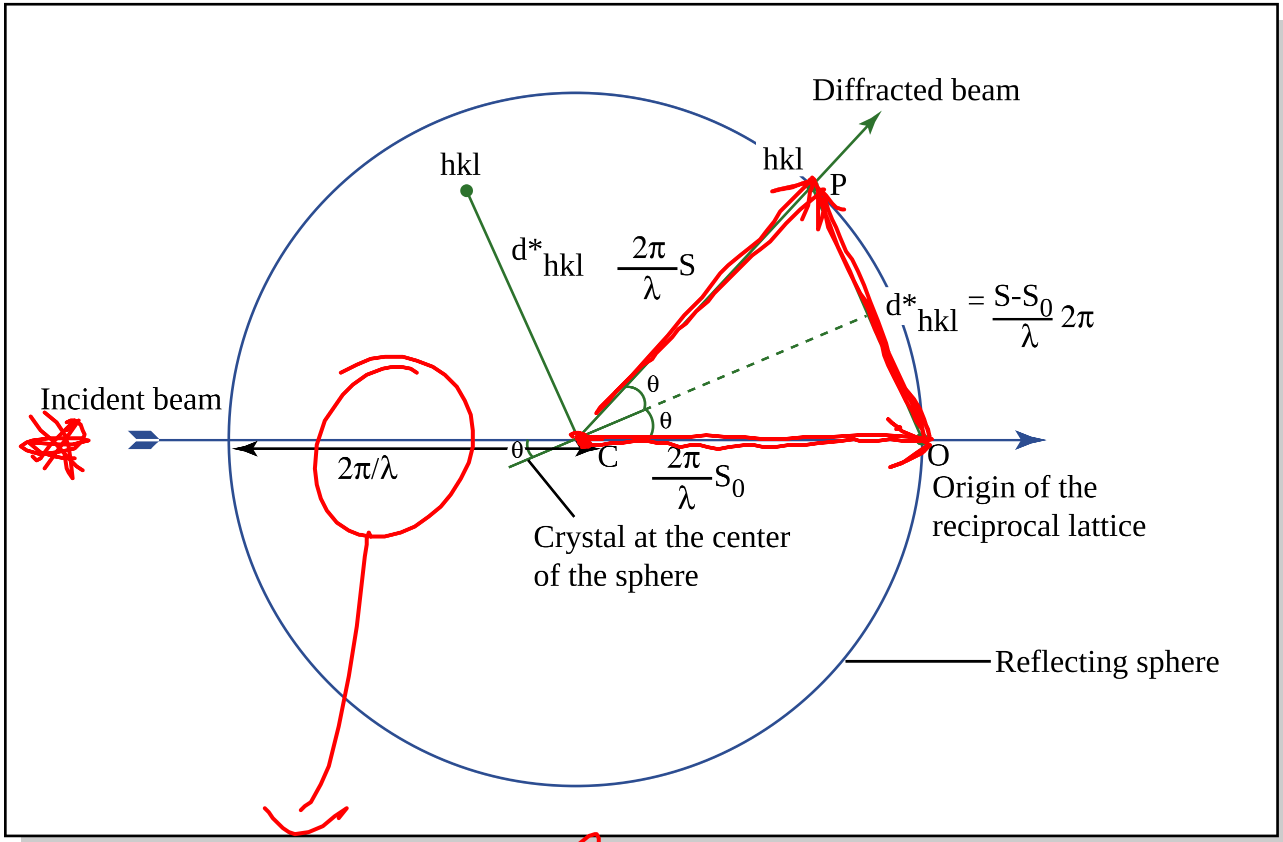
$$\vec{a}_3 \cdot \left(\vec{S} - \vec{S}_0 \right) = \text{integer multiple of } \lambda$$

$$\vec{a}_i \cdot \left(\frac{\Delta \vec{S}}{\lambda} 2\pi \right) = 2\pi \text{ INTEGER}$$

$$\frac{\Delta \vec{S}}{\lambda} 2\pi \in \text{RECIPROCAL LATTICE}$$

Ewald construction

$\frac{\Delta \vec{S}}{\lambda} 2\pi \in$ RECIP LATT.



RADIUS $\frac{2\pi}{\lambda}$

Figure by MIT OCW.

Laue condition needs "white" spectrum

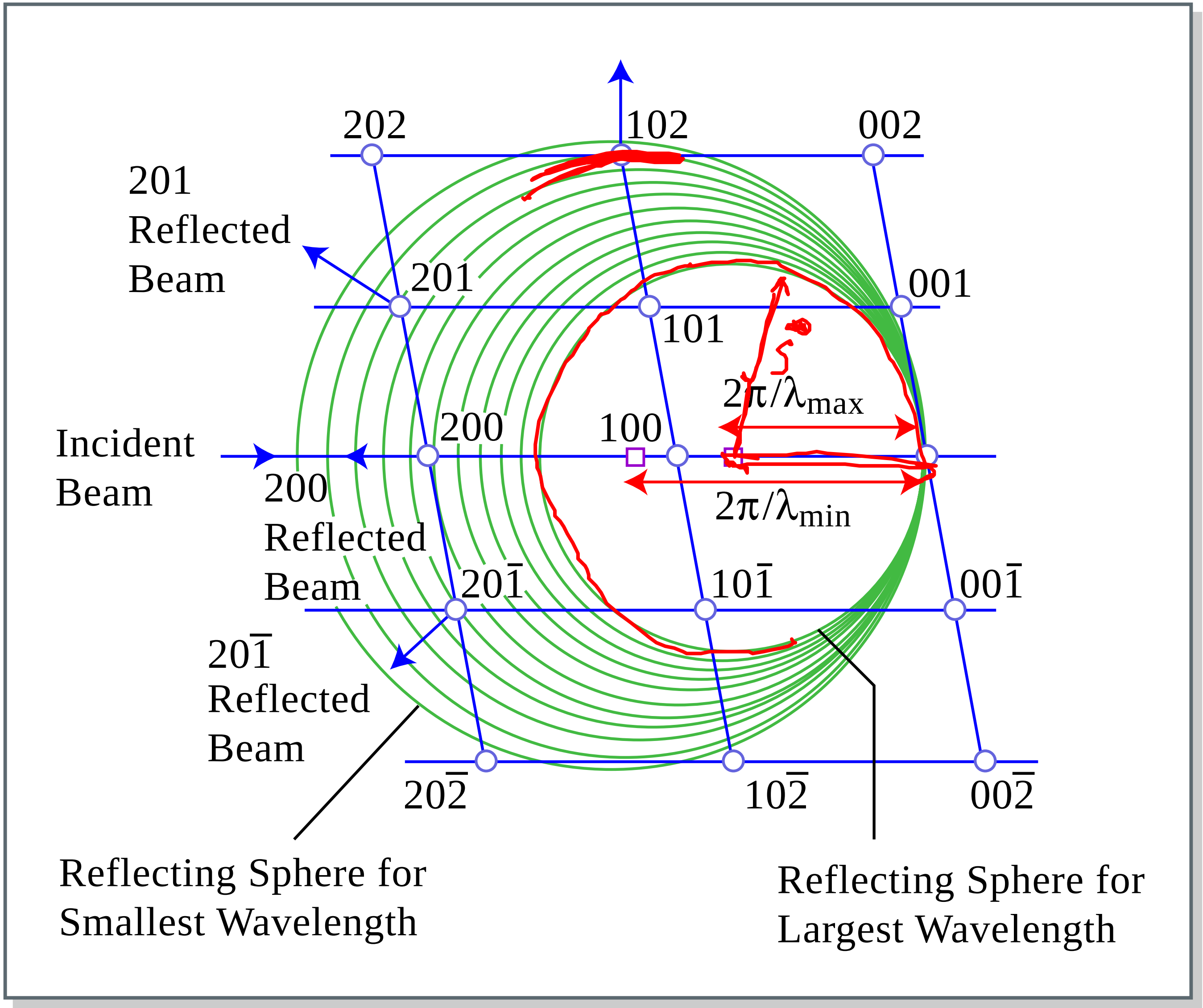


Figure by MIT OCW.

Alternate geometrical view

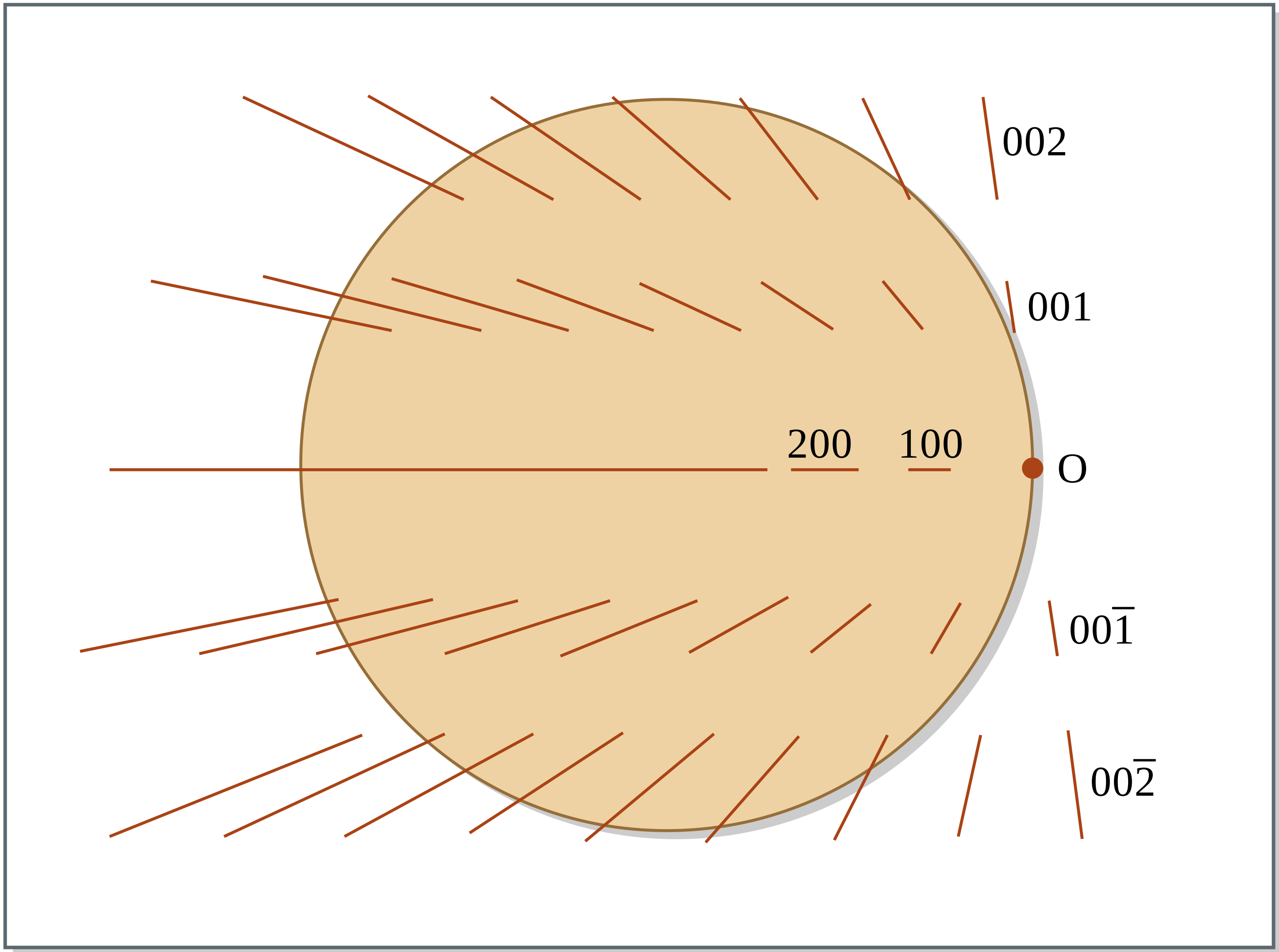


Figure by MIT OCW.

Bragg Law

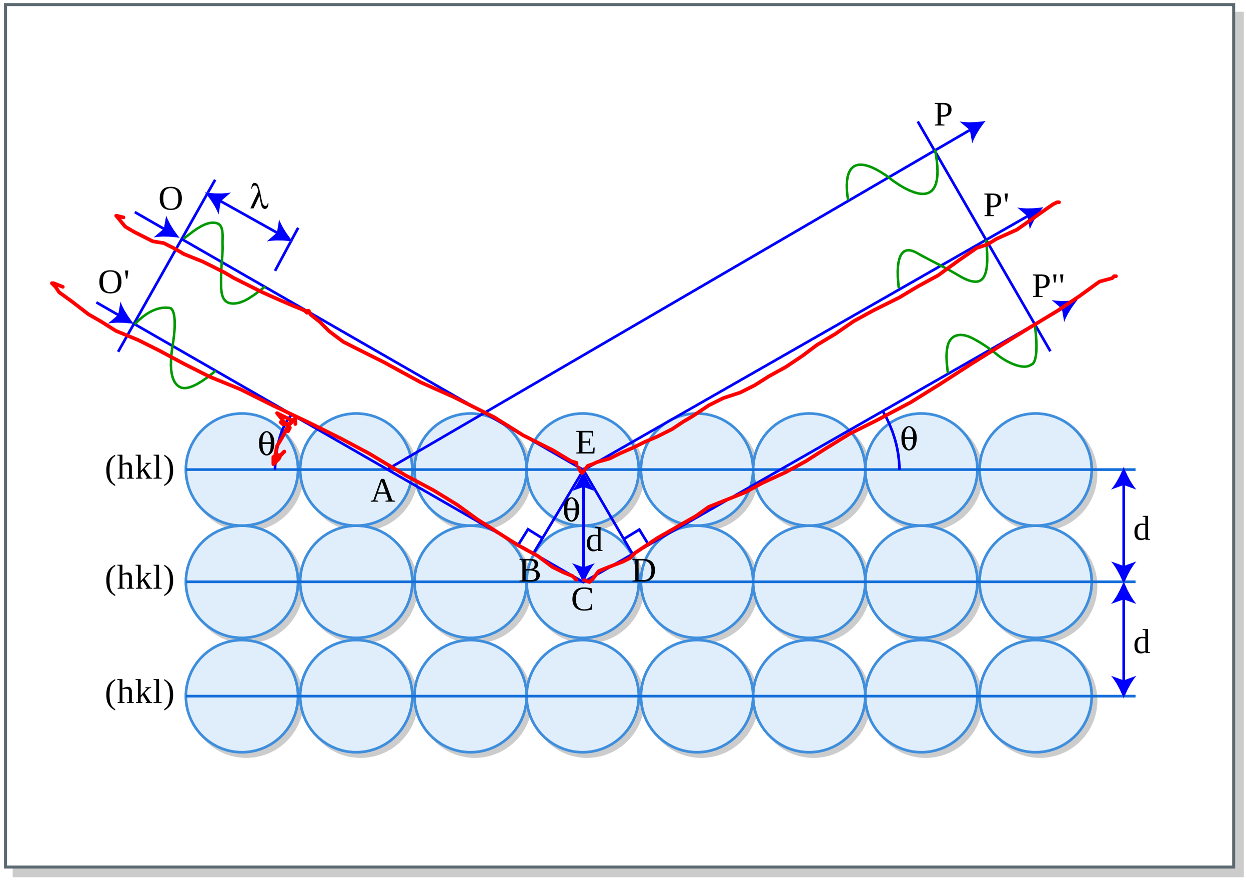


Figure by MIT OCW.

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

Equivalence to Laue condition

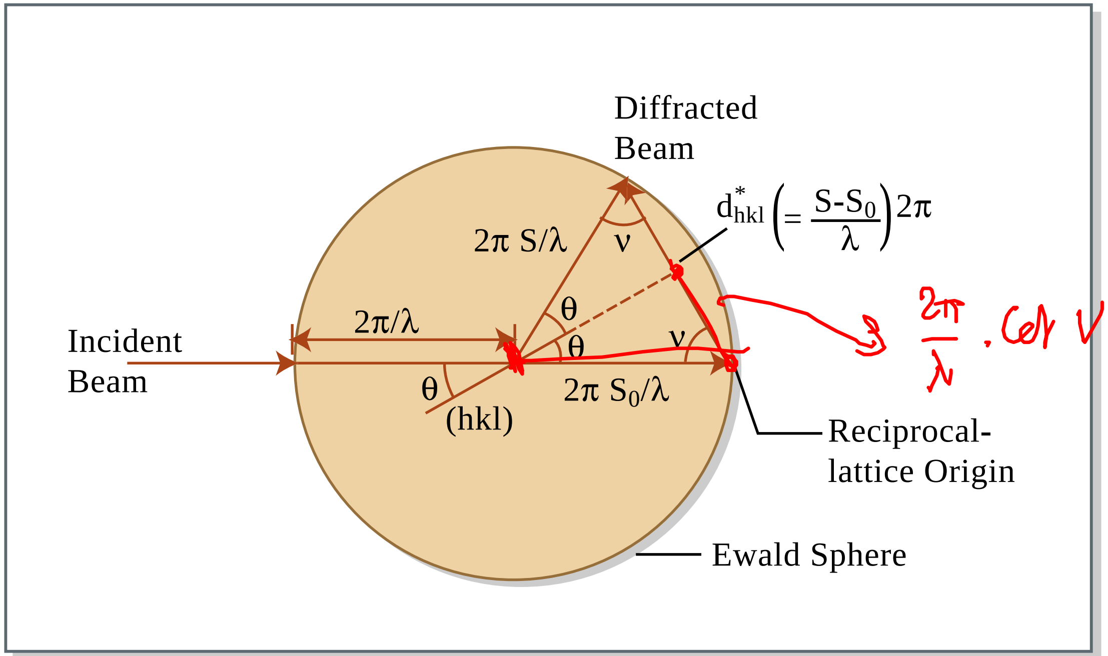


Figure by MIT OCW.

$$2\pi\left(\frac{\vec{S}-\vec{S}_0}{\lambda}\right) = \frac{2\pi}{\lambda}\cos\nu = d^*_{hkl} = \frac{2\pi}{d_{hkl}} = \frac{2\pi}{\lambda}2\sin\theta$$

Powder diffraction (I)

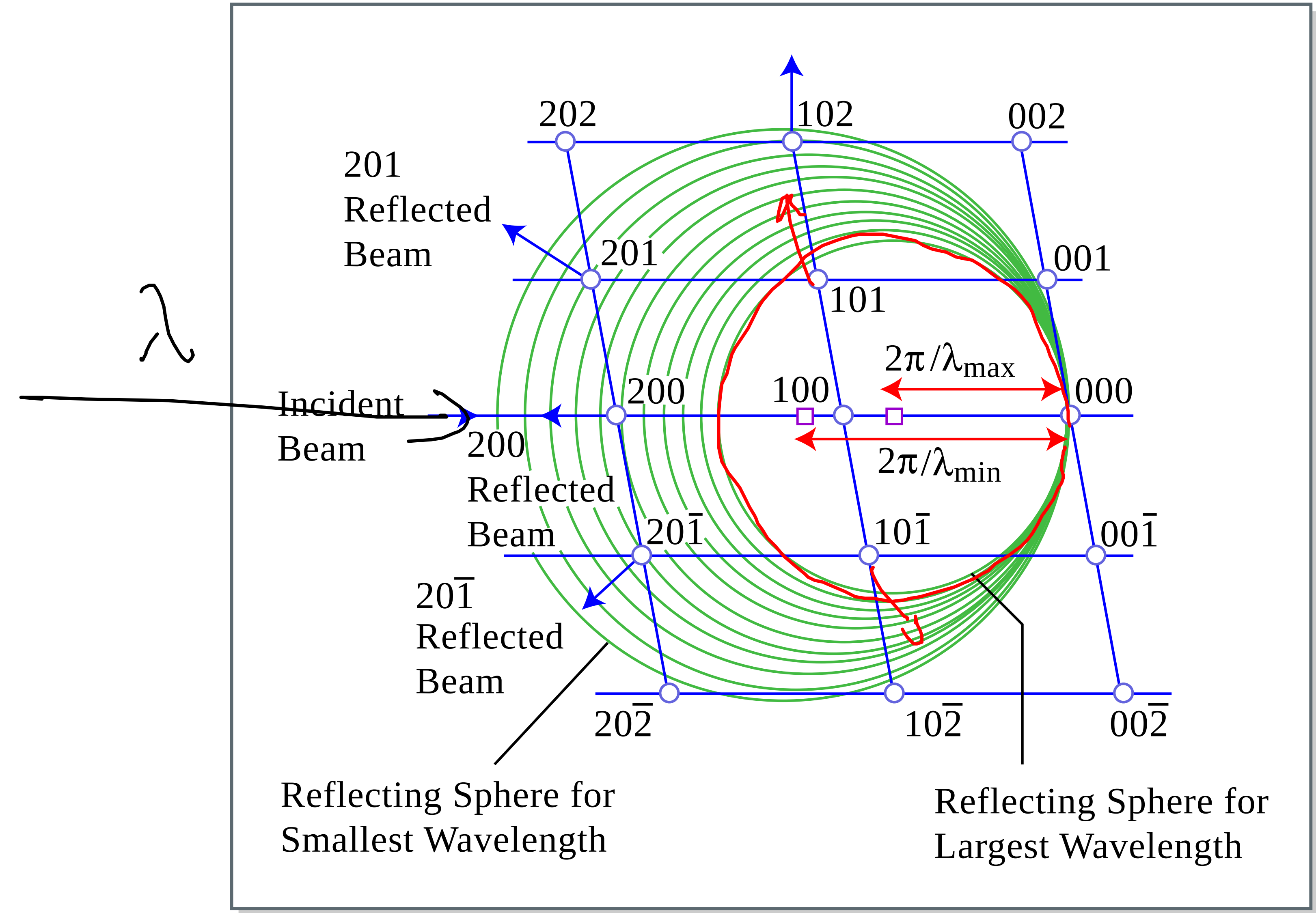


Figure by MIT OCW.

Powder diffraction (II)

Image removed for copyright reasons. Please see the diagram at http://capsicum.me.utexas.edu/ChE386K/html/powder_diffraction_3.htm.

Powder diffraction (III)

Diagrams of the Powder Method removed for copyright reasons.

See the images at http://www.matter.org.uk/diffraction/x-ray/powder_method.htm

X-ray filters

Image removed for copyright reasons.
Please see the graph at http://capsicum.me.utexas.edu/ChE386K/html/absorption_edge.htm.

Image removed for copyright reasons.
Please see the diagrams at http://capsicum.me.utexas.edu/ChE386K/html/filter.htm.

Debye-Scherrer camera

Photographs of a Debye-Scherrer camera removed for copyright reasons.

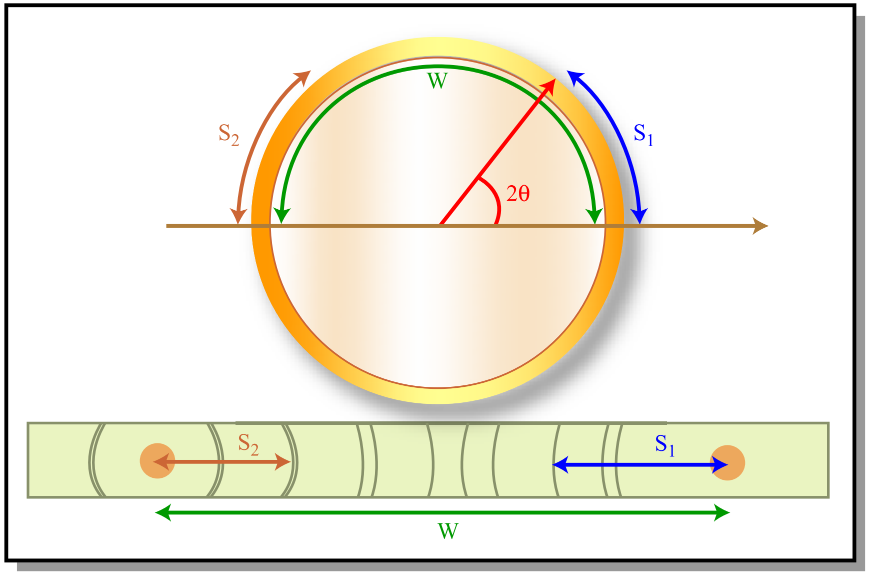


Figure by MIT OCW.

Interplanar spacings

Cubic: $$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal: $$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal: $$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Rhombohedral:
$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

Orthorhombic: $$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Monoclinic: $$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic: $$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

In the equation for triclinic crystals

$$V = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$$

$$S_{11} = b^2c^2\sin^2\alpha,$$
$$S_{22} = a^2c^2\sin^2\beta,$$
$$S_{33} = a^2b^2\sin^2\gamma,$$
$$S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma),$$
$$S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha),$$
$$S_{13} = ab^2c(\cos\gamma\cos\alpha - \cos\beta).$$

Cubic: $$d_{hkl}^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

Debye-Scherrer camera

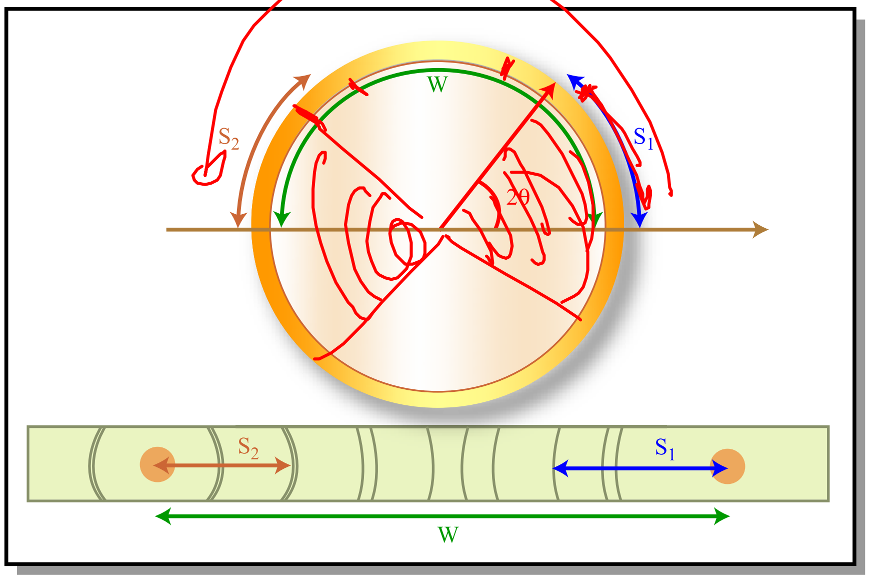


Figure by MIT OCW.

$$\lambda = d_{hkl} 2 \sin\theta$$

$$\text{Cubic: } d_{hkl}^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

$$\sin\theta = \frac{\lambda}{2 d_{hkl}}$$

$$2\vartheta = \frac{S_1}{2W} \text{ RADIANS}$$

$$\sin^2\vartheta = \frac{\lambda^2}{4} \frac{h^2 + k^2 + l^2}{a^2}$$

Tables removed for copyright reasons. See http://www.matter.org.uk/diffraction/x-ray/indexing_powder_pattern.htm

PLANES PRESENT IN CRYSTAL

Systematic absences

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Please see the table at http://capsicum.me.utexas.edu/ChE386K/html/systematic_absences.htm.

Effects of symmetry on diffraction

Please see the images at http://capsicum.me.utexas.edu/ChE386K/html/diffraction_symmetry1.htm.

Structure Factor

STRUCTURE FACTOR

$$\mathbf{F}(hkl) = \sum_{n=1}^{N} f_n e^{2\pi i (hx_n + ky_n + lz_n)}$$

SUM ATOMS

$\| F \|^2$ = INTENSITY

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Please see the graph at http://capsicum.me.utexas.edu/ChE386K/html/scattering_factor_curve.htm.

Friedel's law

$$F(hkl) = F^*(-h,-k,-l)$$

$$\|F(hkl)\|^2 = \|F^*(-h,-k,-l)\|^2$$

- The diffraction pattern is always centrosymmetric, even if the crystal is not centrosymmetric

Point symmetry + inversion = Laue

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Please see the table at http://capsicum.me.utexas.edu/ChE386K/html/diffraction_symmetry2.htm.

Back-reflection and transmission Laue

Diagrams of the Laue Method removed for copyright reasons.
See the images at http://www.matter.org.uk/diffraction/x-ray/laue_method.htm.