3.012 Fund of Mat Sci: Structure – Lecture 19

FROM DIFFRACTION TO STRUCTURE

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3-fold symmetry in silicon along the [111] direction.
Forward (left) and backward (right) scattering.

Homework for Mon Nov 28

- Study: 3.3 Allen-Thomas (Symmetry constraints)

- Read all of Chapter 1 Allen-Thomas

Last time:

1. Laue condition in 3 dimensions

2. Ewald construction

3. Bragg law, and equivalence to Laue condition

4. Powder diffraction, Debye-Scherrer
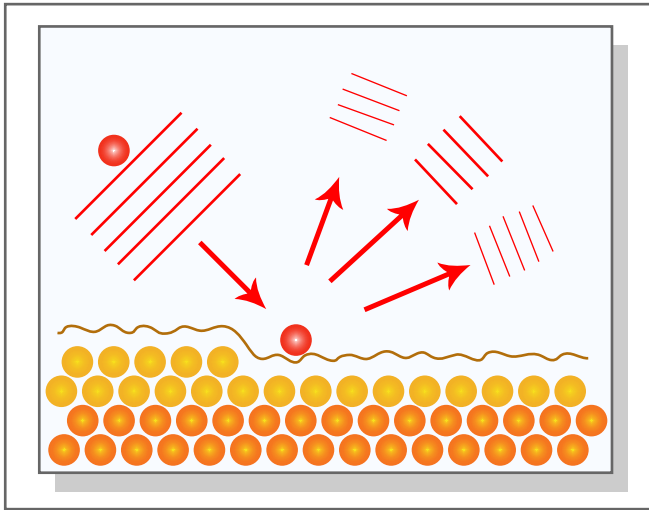
Atoms as spherical scatterers

Figure by MIT OCW.

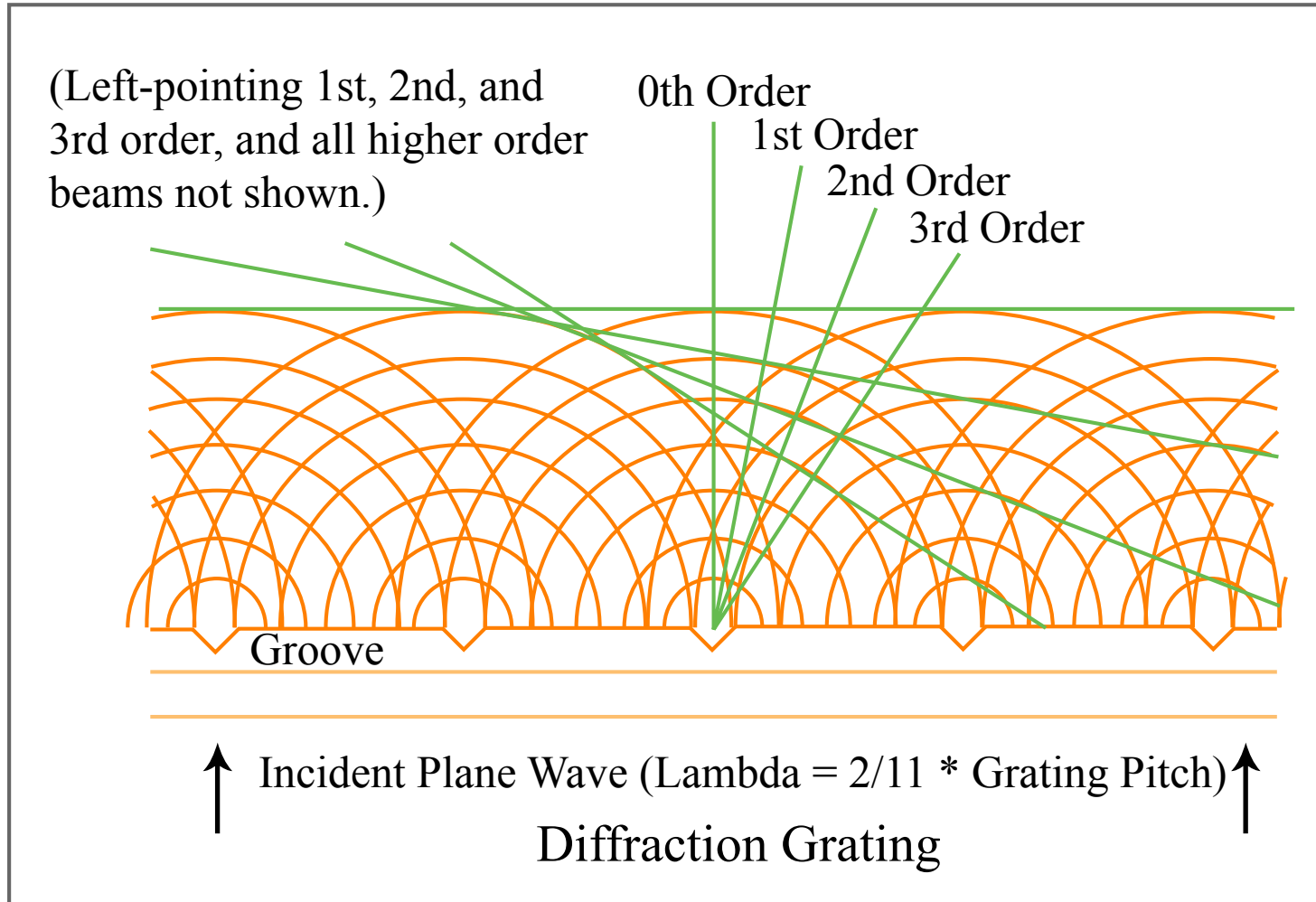Images removed for copyright reasons.

Huygens construction

(Left-pointing 1st, 2nd, and 3rd order, and all higher order beams not shown.)

0th Order
1st Order
2nd Order
3rd Order

Groove

Incident Plane Wave (Lambda = 2/11 * Grating Pitch)

Diffraction Grating

Figure by MIT OCW.

All three Laue conditions

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

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

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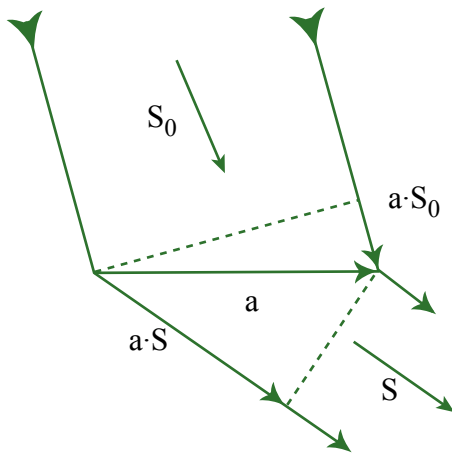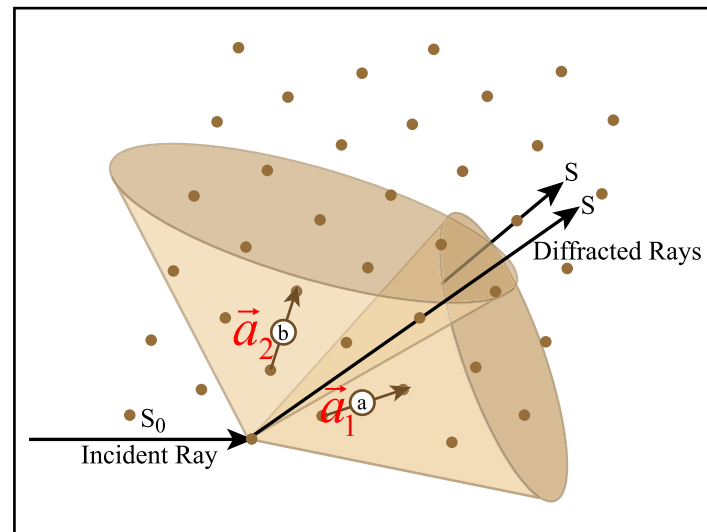

Figure by MIT OCW.
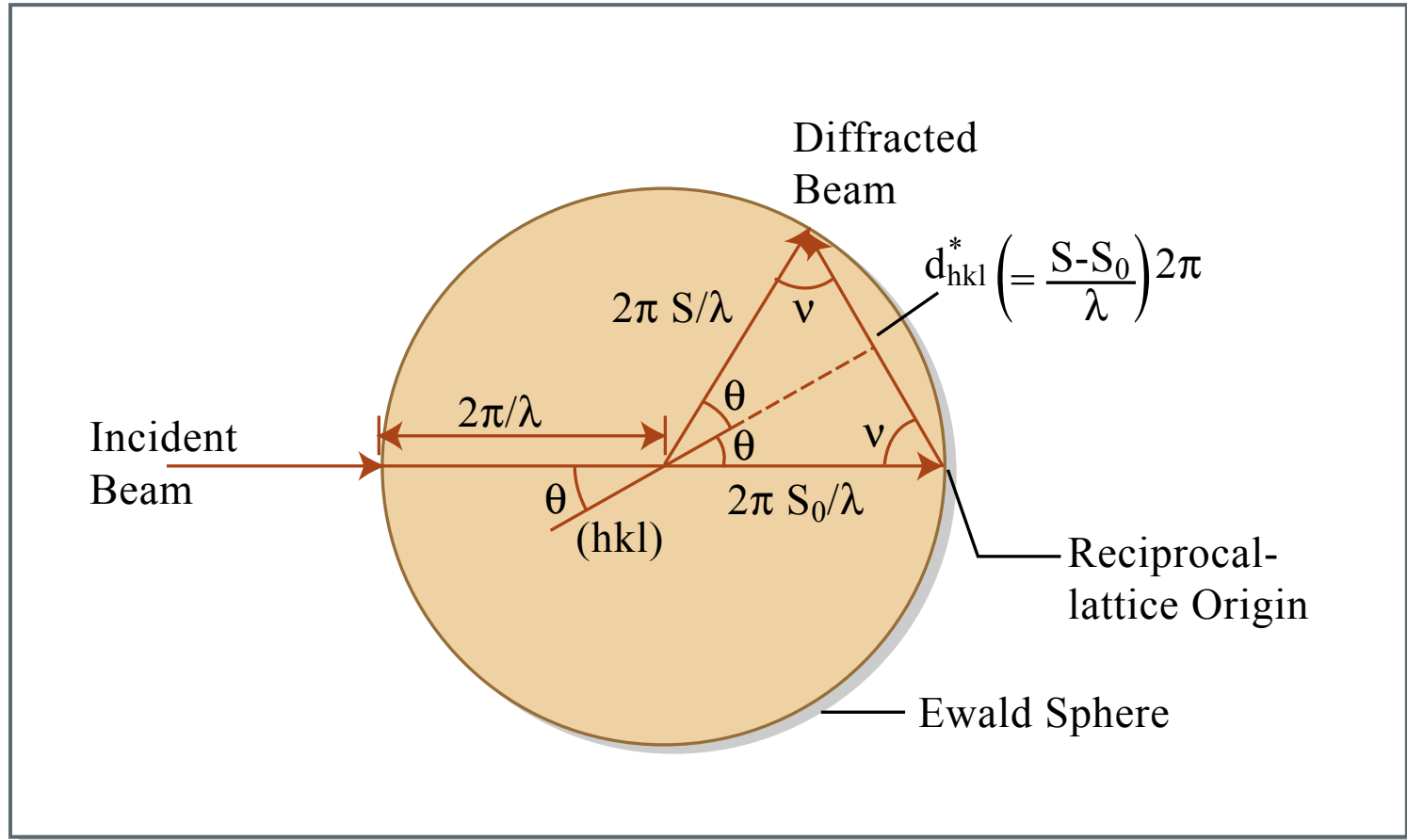

Figure by MIT OCW.

Ewald construction

Figure by MIT OCW.

Equivalence to Laue condition

$$\left(n\lambda = d_{hkl}\, 2\sin\theta \right)$$

Figure by MIT OCW.

Diffracted Beam

$2\pi\, S/\lambda$

ν

$d_{hkl}^{*}\left(= \dfrac{S\text{-}S_0}{\lambda} \right) 2\pi$

$2\pi/\lambda$

θ

Incident Beam

θ

ν

θ

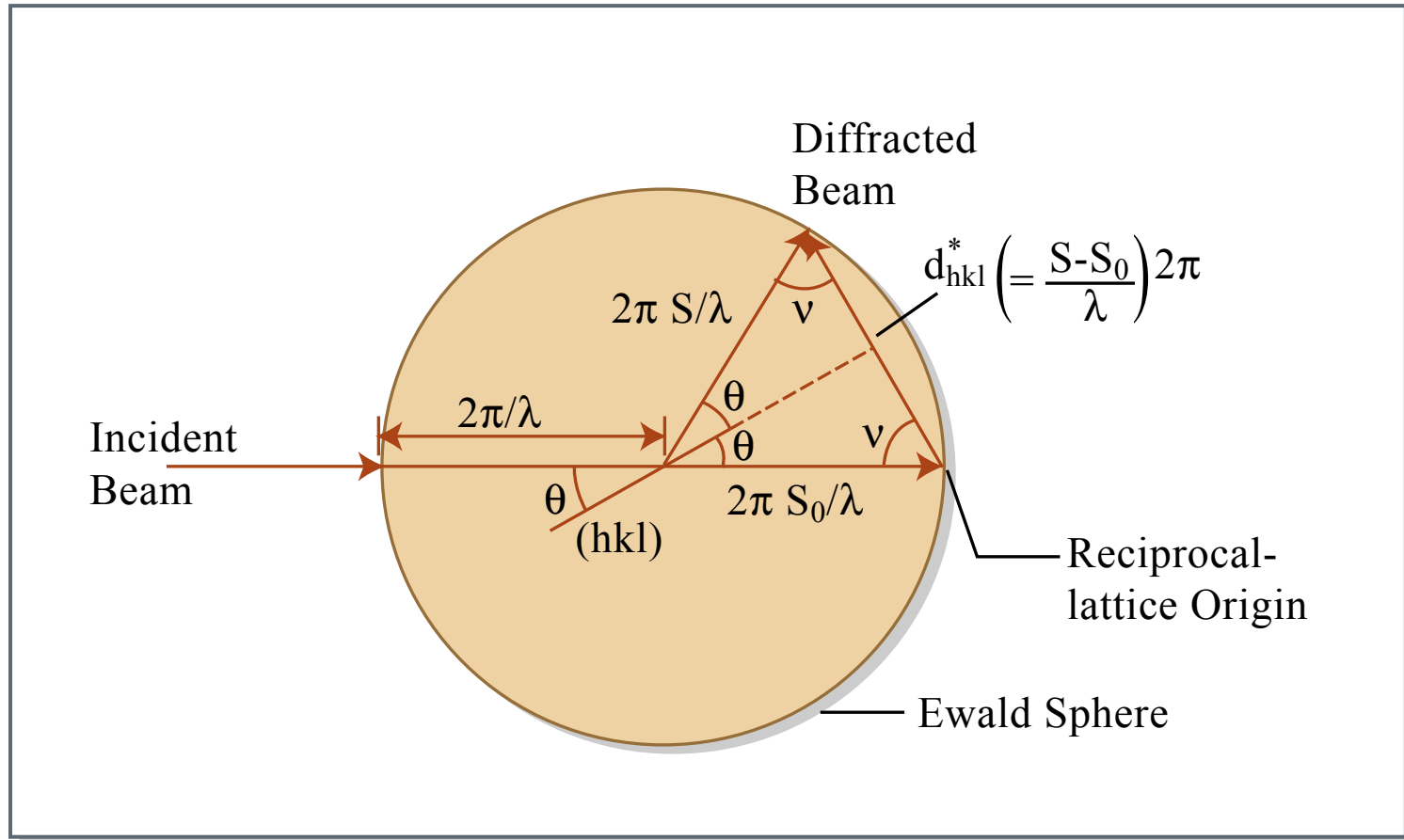$2\pi\, S_0/\lambda$

θ

(hkl)

Reciprocal-lattice Origin

Ewald Sphere

$$2\pi\left(\frac{\vec{S} - \vec{S}_0}{\lambda} \right) = \frac{2\pi}{\lambda}\cos\nu = d_{hkl}^{*} = \frac{2\pi}{d_{hkl}} = \frac{2\pi}{\lambda}\, 2\sin\theta$$
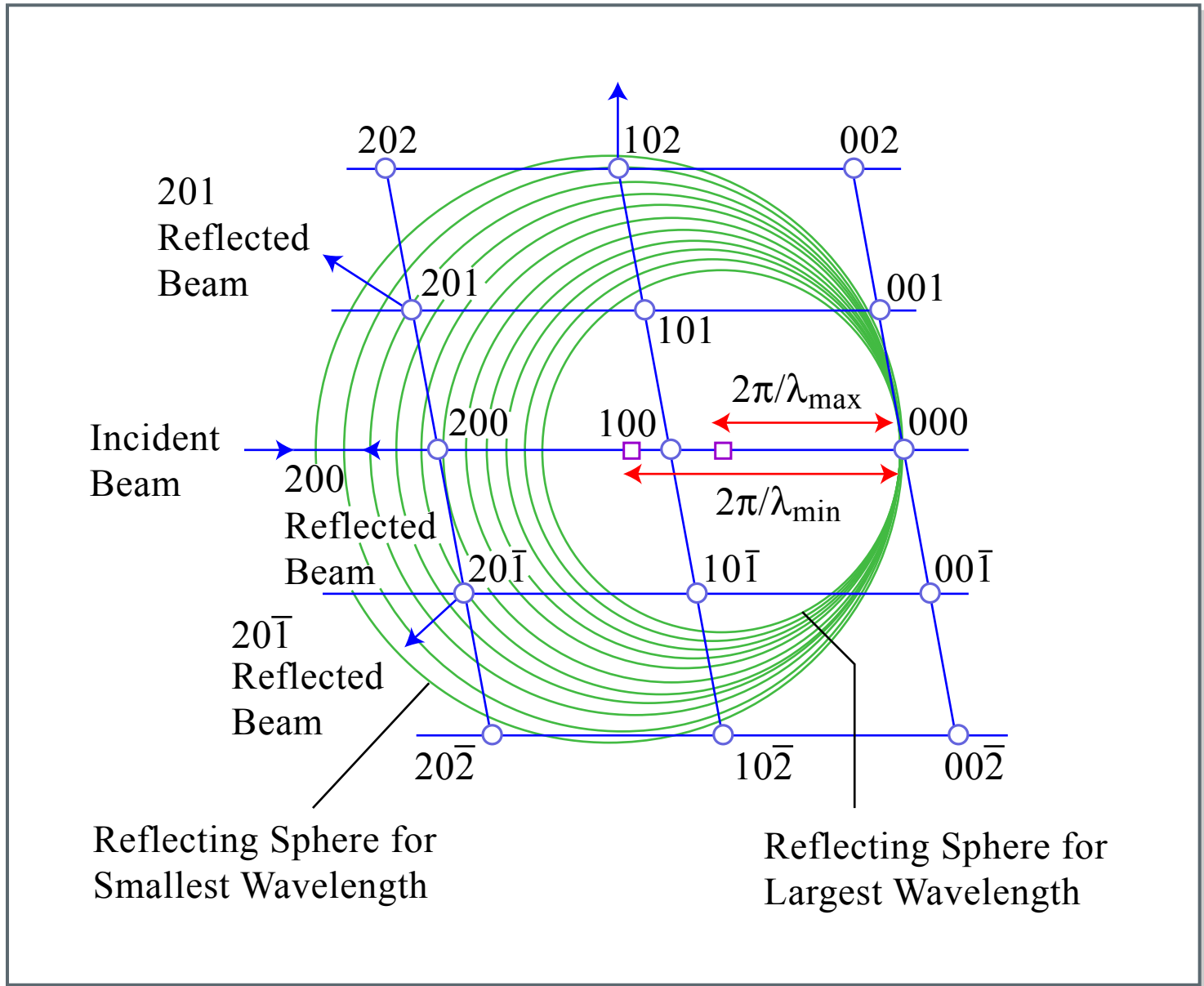
Laue condition needs "white" spectrum

Figure by MIT OCW.

Powder diffraction

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Please see the diagram at http://capsicum.me.utexas.edu/ChE386K/html/powder_diffraction_3.htm.

Interplanar spacings

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

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

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

Rhombohedral:

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

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

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

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

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: $d^2_{hkl} = \dfrac{a^2}{h^2 + k^2 + l^2}$ $\left(d^*_{hkl} = \dfrac{2\pi}{d_{hkl}} \right)$
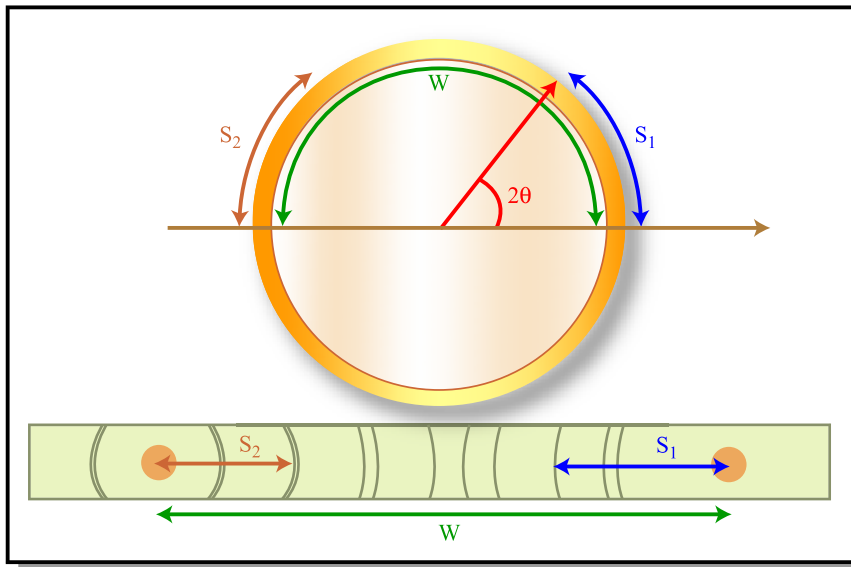
Debye-Scherrer camera

Figure by MIT OCW.

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

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

$$h^2 + k^2 + l^2 = a^2\left(\frac{2\sin\theta}{n\lambda}\right)^2$$

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

Systematic absences

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

Effects of symmetry on diffraction

Images removed for copyright reasons.
Please see the images at http://capsicum.me.utexas.edu/ChE386K/html/diffraction_symmetry1.htm.

Structure Factor

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

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

Friedel's law

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

Point symmetry + inversion = Laue
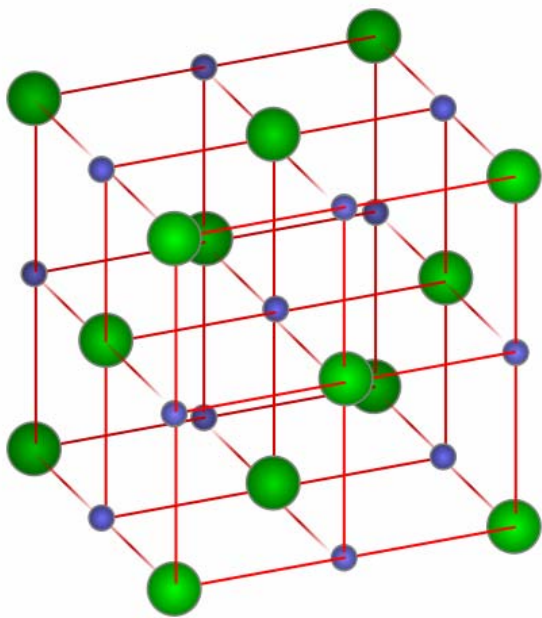
Image removed for copyright reasons.
Please see the table at http://capsicum.me.utexas.edu/ChE386K/html/diffraction_symmetry2.htm.

X-ray powder diffraction images removed for copyright reasons.

- X-ray powder diffraction for silver, aluminum, gold, and copper

X-ray powder diffraction images removed for copyright reasons.

- Detail, back-scattering direction, showing the line splitting that takes place due to the presence of the K-alpha-1 and K-alpha-2 lines of the copper spectrum which the x-ray machine produced. Measurements of the diffraction angles for these lines can yield very accurate values for the crystal unit cell size.

Source: Wikipedia

Rocksalt

X-ray powder diffraction images removed for copyright reasons.

- Detail of the small-angle end of the film, showing that the NaCl and KCl patterns do not look the same, and that the crystal sizes are different. The KCl appears almost exactly as if it were a simple cubic, due to the fact that the K and Cl ions, very close to each other on the periodic table, are almost exactly alike. The Na and Cl ions are not so close on the periodic table, thus their ions are not the same, thus the powder diffraction pattern does not look like the pattern from a simple cubic crystal.

Physical properties and their relation to symmetry

- Density (mass, from a certain volume)

- Pyroelectricity (polarization from temperature)

- Conductivity (current, from electric field)

- Piezoelectricity (polarization, from stress)

- Stiffness (strain, from stress)

Scalar, vector, tensor properties
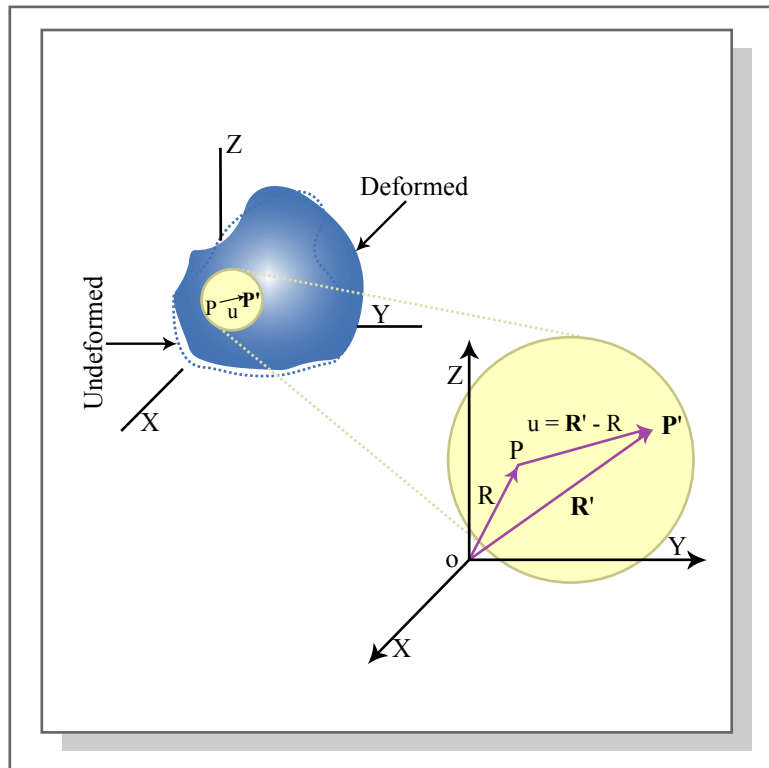
- Mass (0), polarization (1), strain (2)

Figure by MIT OCW.

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$$

Transformation of a vector

Orthogonal Matrices

Transformation of a tensor

Neumann's principle

- *the symmetry elements of any physical property of a crystal must include all the symmetry elements of the point group of the crystal*

Tensor properties of materials

Symmetry constraints

Curie's Principle

- *a crystal under an external influence will exhibit only those symmetry elements that are common to the crystal without the influence and the influence without the crystal*