POWDER DIFFRACTION

Principles

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DTU Chemistry

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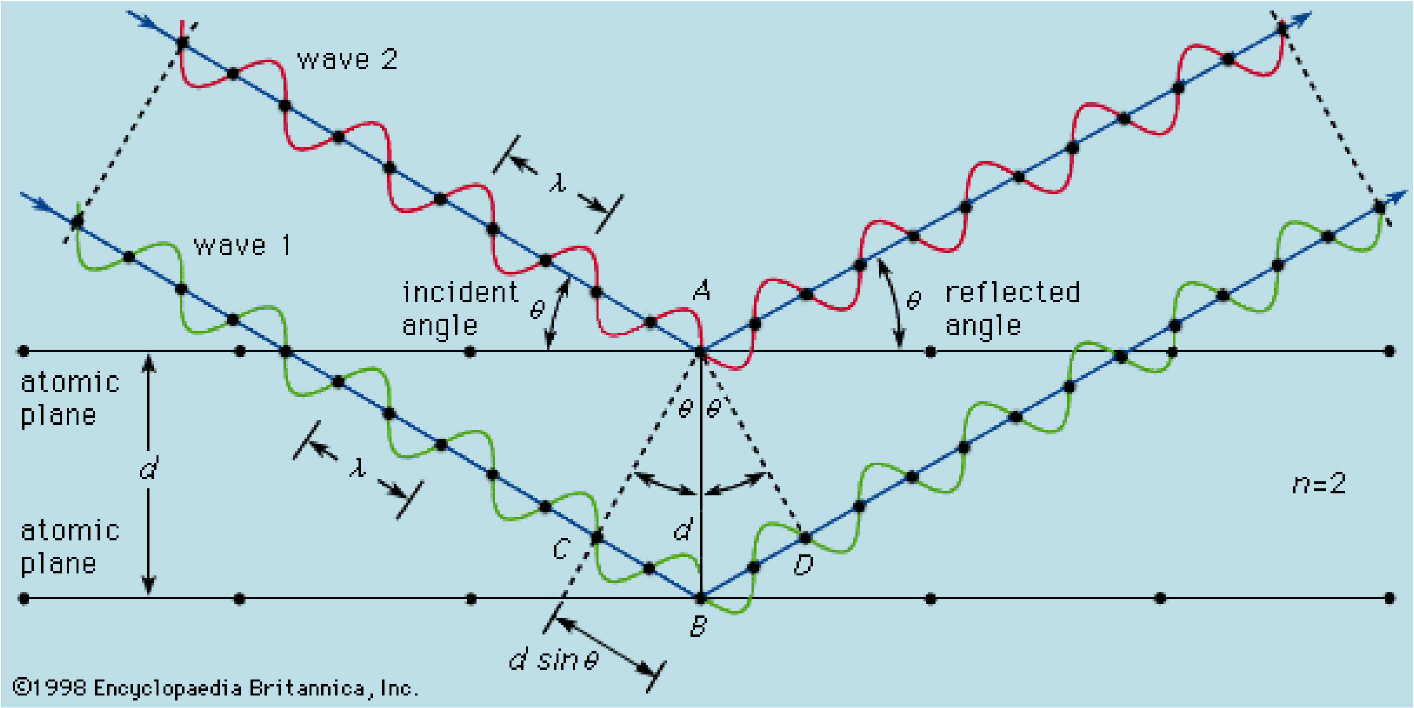
•Reciprocal space – reciprocal unit cell

•Ewald construction, monochromatic - single-crystal – powder

•Ewald construction, white/pink radiation – single-crystal – powder

•Reciprocal lattice points – the interference function

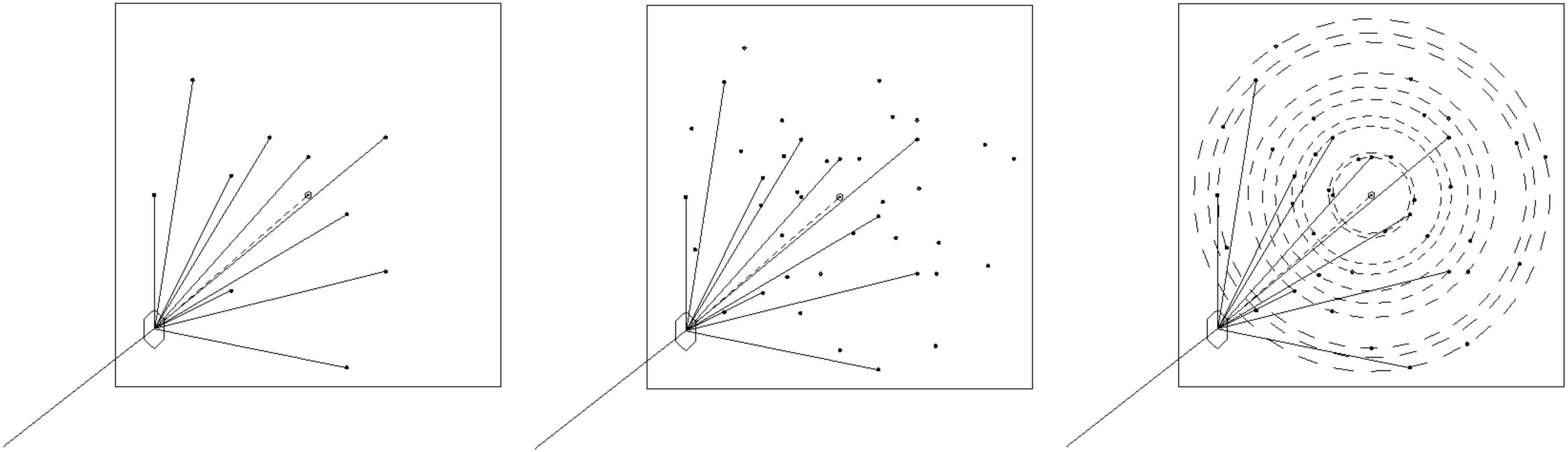
BRAGG'S LAW



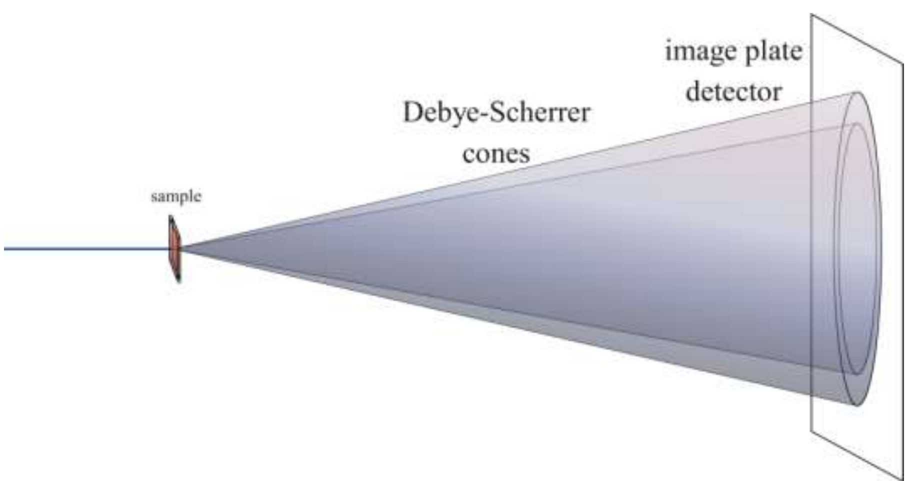
$$2\, d_{hkl} \sin \theta_{hkl} = n\, \lambda$$

(Geometric interpretation of diffraction)

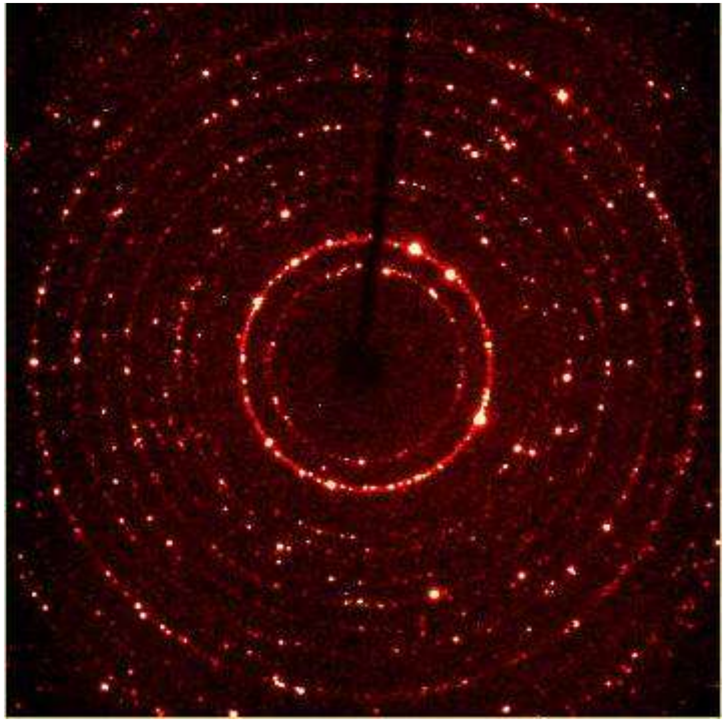
SINGLE- VS. MULTI-CRYSTAL DIFFACTION

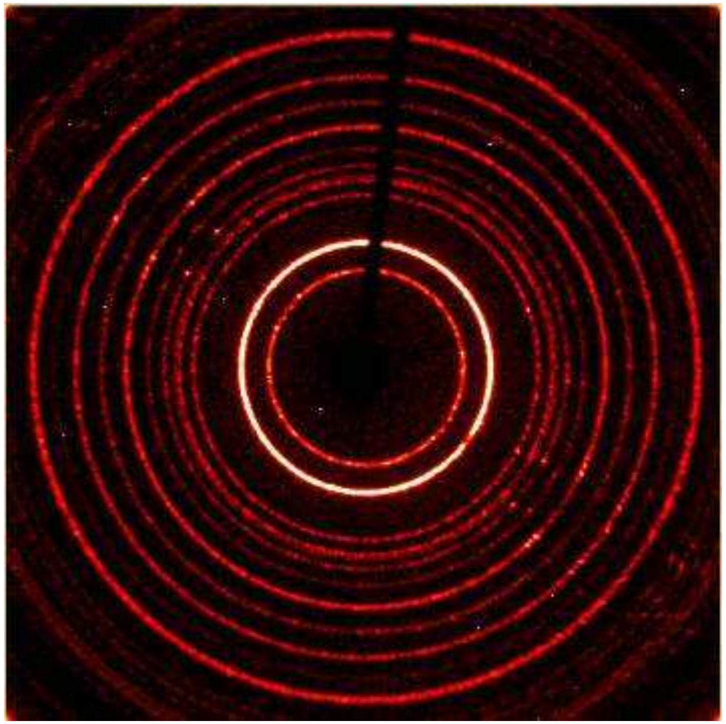


One crystal — Four crystals — Powder



POWDER DIFFRACTION





CRYSTAL PLANES – MILLER INDICES

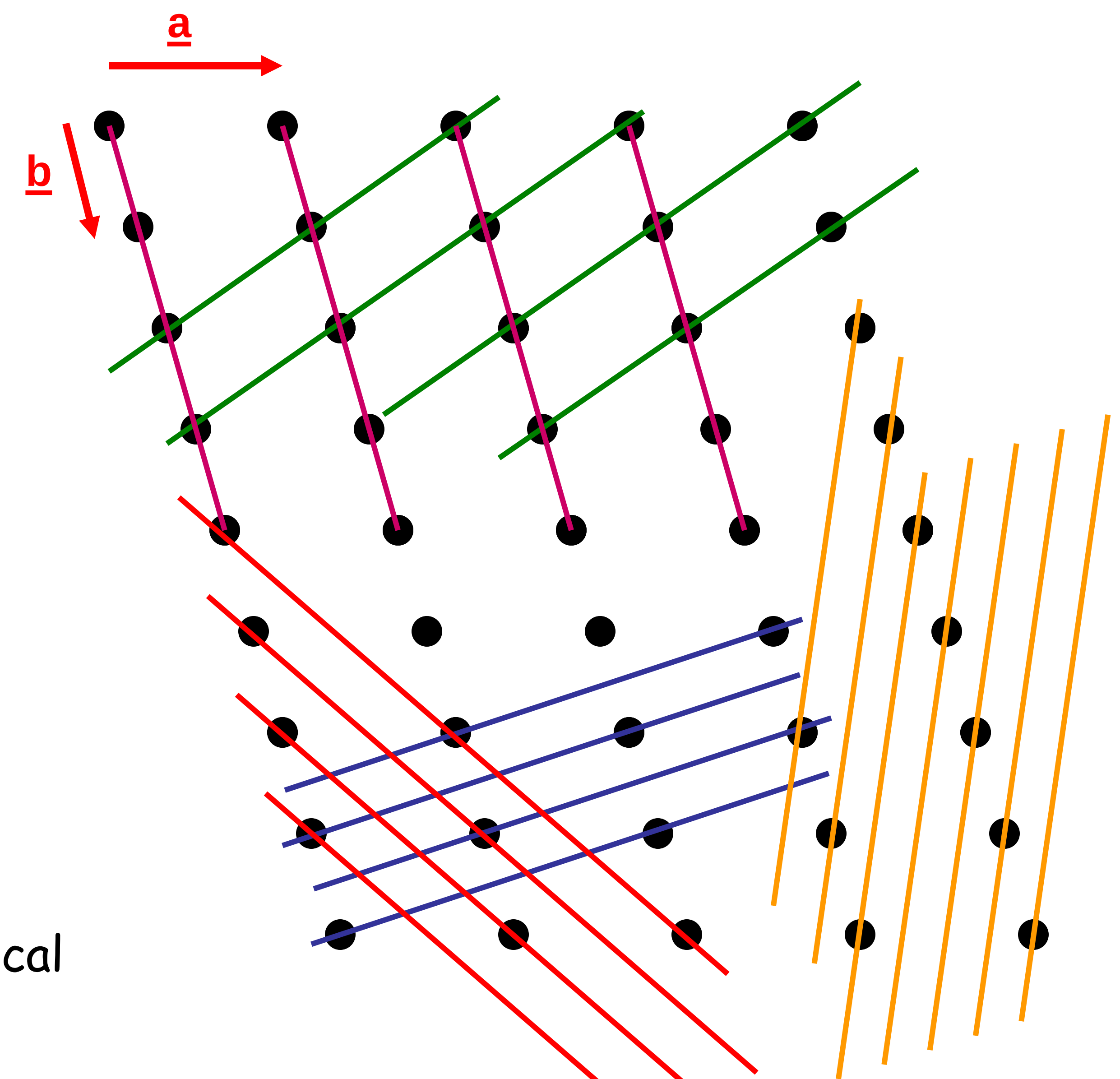
h=1, k=1

h=1, k=0

h=1, k=2

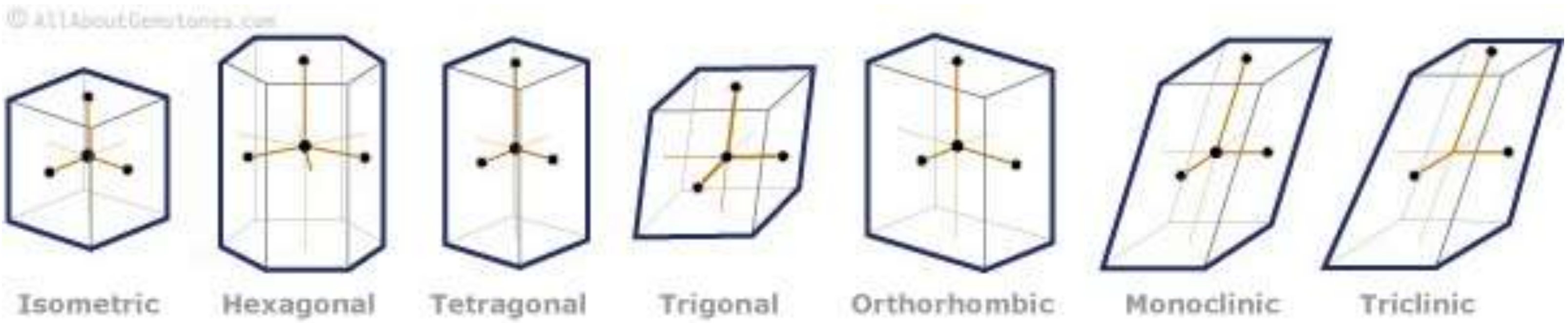
h=4, k=1

h=2, k=-1



Note that the 2, 2 and -2, -2 planes are identical

CRYSTAL PLANES – d-VALUES

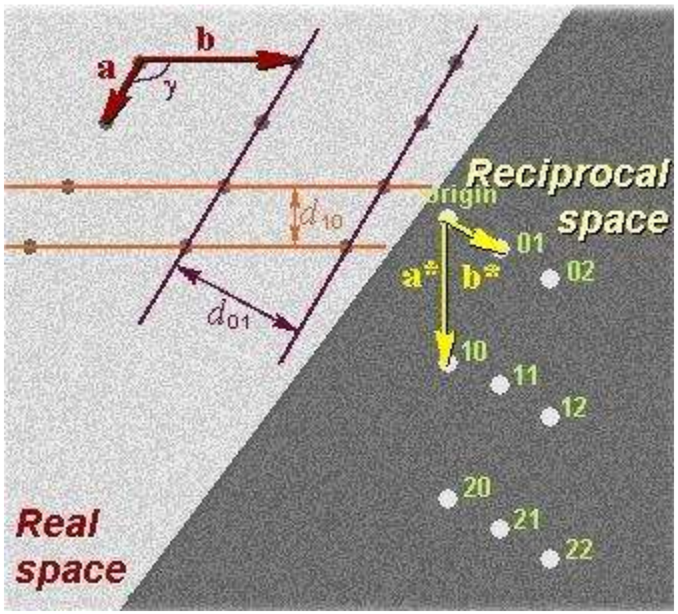


a b c (Å) α β γ (°)

$$1/d^2_{hkl} = [h^2\sin^2\alpha/ a^2 + k^2\sin^2\beta/ b^2 + l^2\sin^2\gamma/ c^2 + 2kl(\cos\beta\cos\gamma-\cos\alpha)/(bc) + 2hl(\cos\alpha\cos\gamma-\cos\beta)/(ac) + 2hk(\cos\alpha\cos\beta-\cos\gamma)/(ab)] / [1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma]$$

$$1/d^2_{hkl} = (h^2 + k^2 + l^2) / a^2$$

RECIPROCAL SPACE



$$a^* = b \text{ ¤ } c / V_{cell} \quad (= b\ c\ \sin\alpha / V_{cell})$$

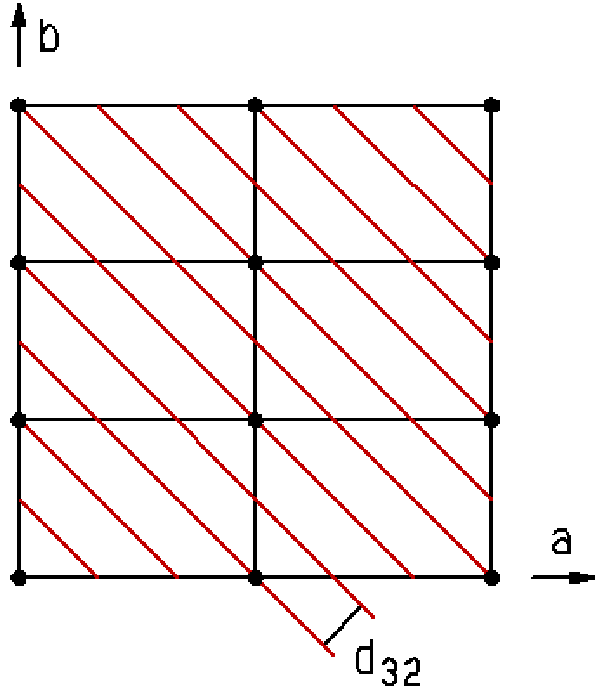
$$b^* = a \text{ ¤ } c / V_{cell} \quad (= a\ c\ \sin\beta / V_{cell})$$

$$c^* = a \text{ ¤ } b / V_{cell} \quad (= a\ b\ \sin\gamma / V_{cell})$$

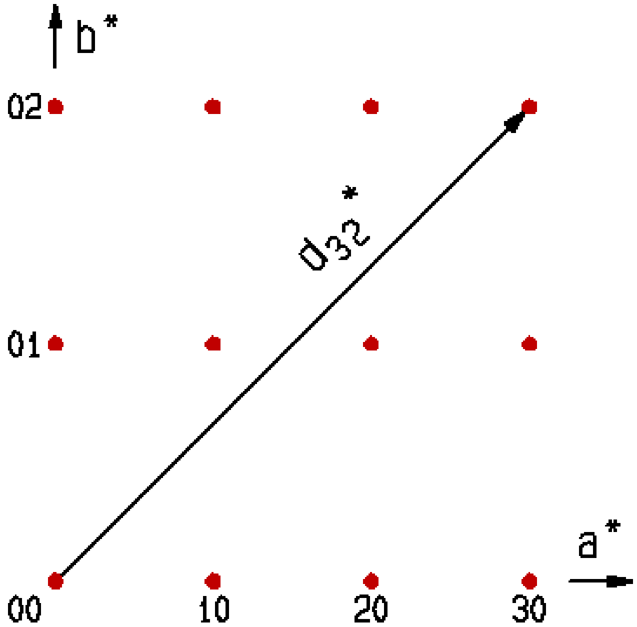
$$a \cdot a^* = 1 \qquad a \cdot b^* = 0$$

$$d_{hkl} = 1 / d_{hkl}^{\ *}$$

RECIPROCAL SPACE



Direct space

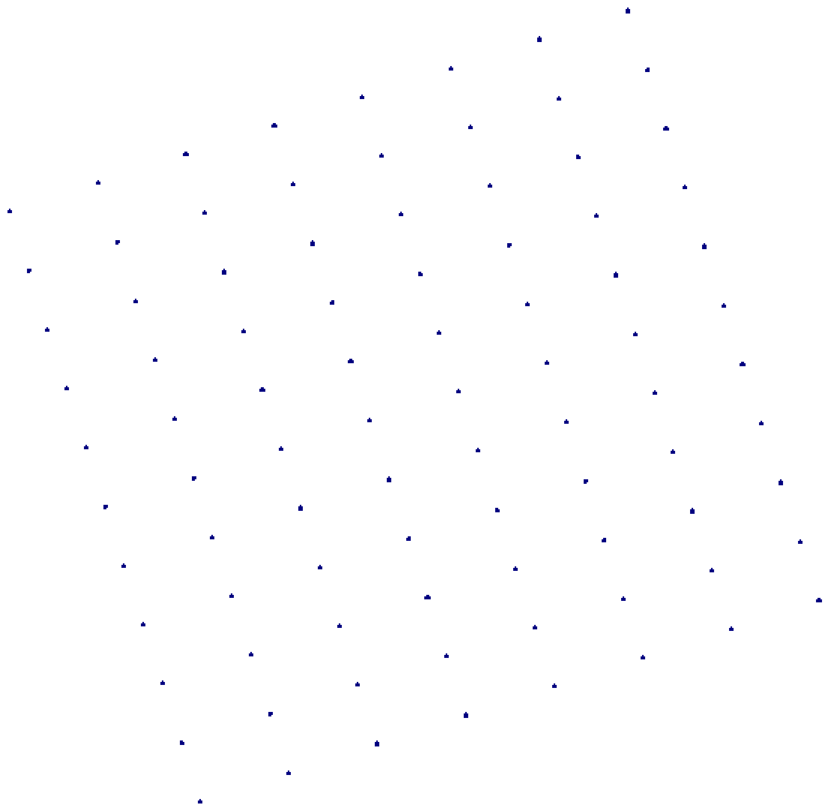


Reciprocal space

$$d_{32} = 1 / d_{32}^*$$

EWALD CONSTRUCTION

Single-crystal, monochromatic radiation



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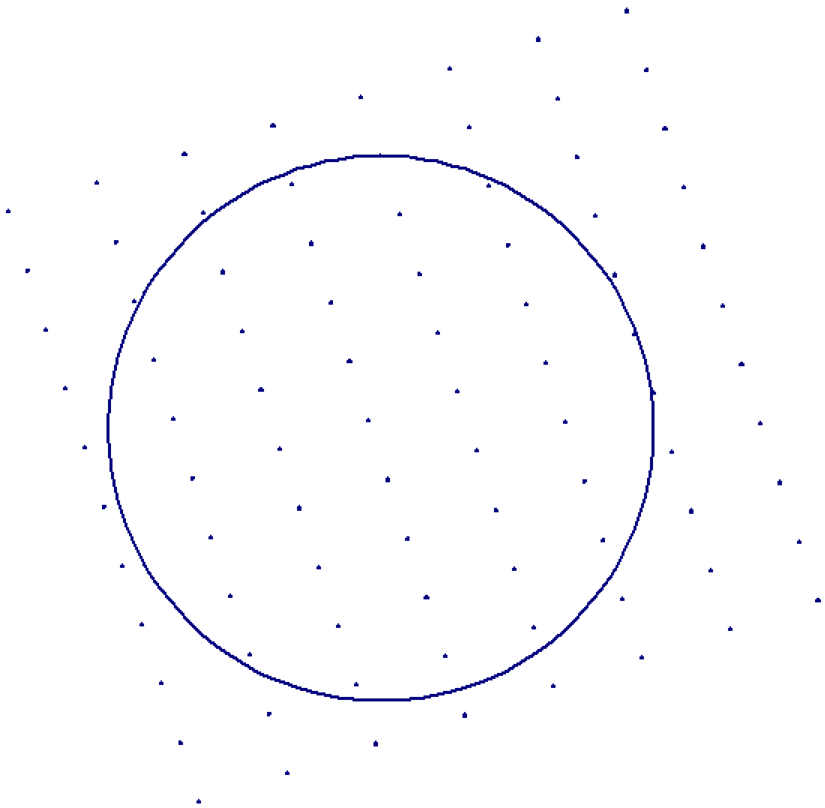

$R = 1 / \lambda$

EWALD CONSTRUCTION

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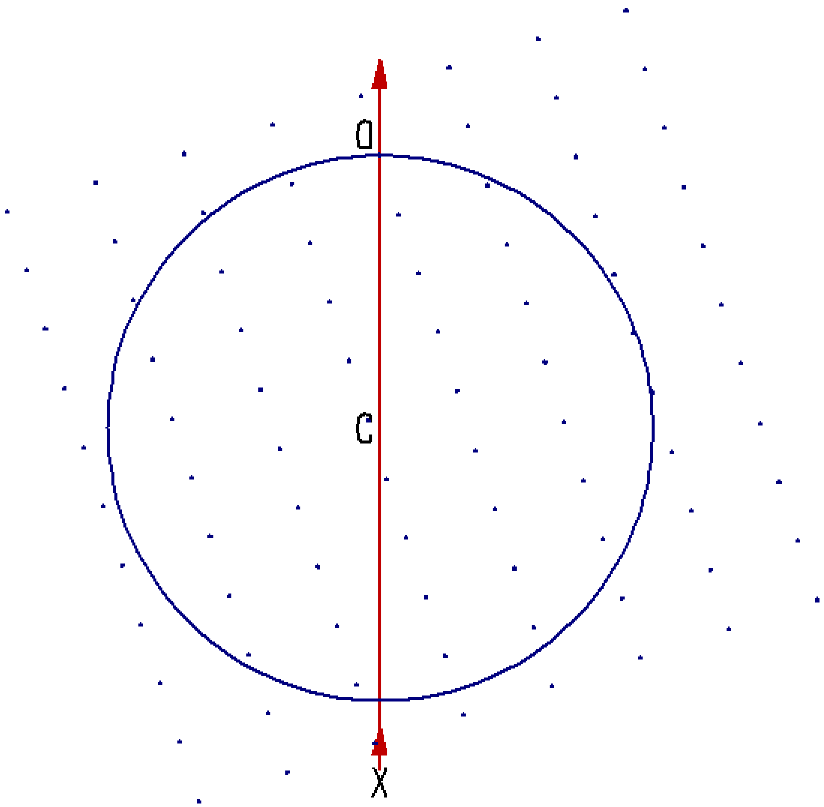

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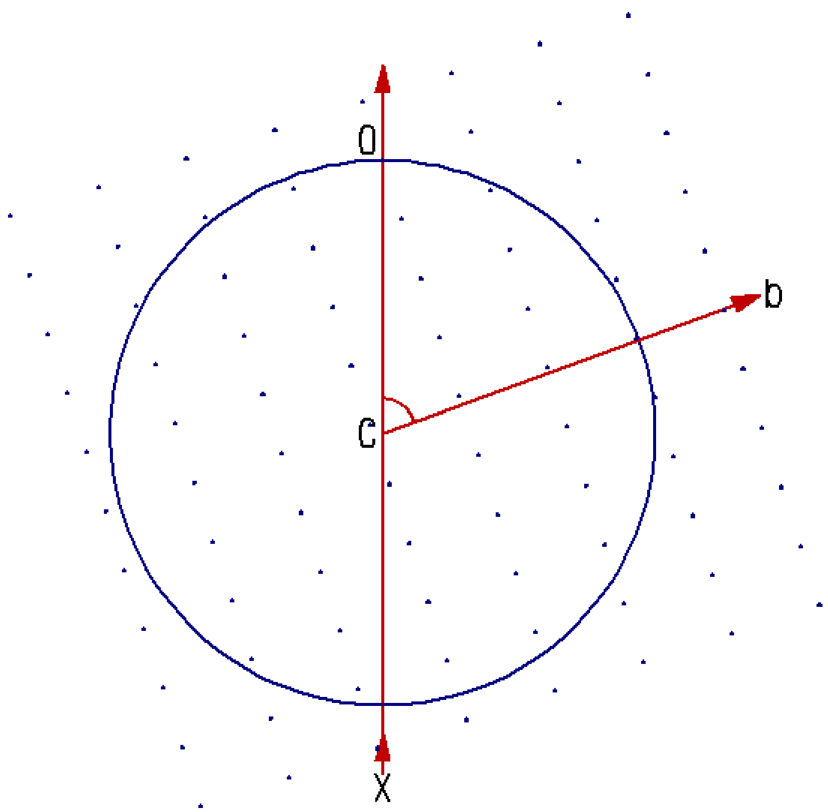
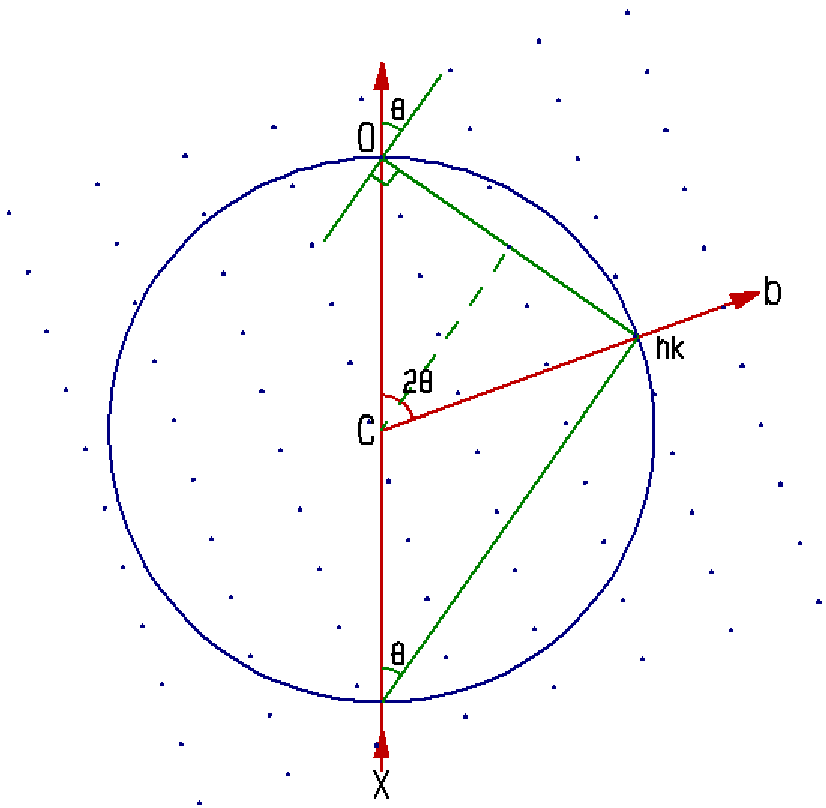


R = 1 / λ

EWALD CONSTRUCTION

Single-crystal, monochromatic radiation



$R = 1 / \lambda$

$R * \sin\theta = r_{hk} / 2$

$r_{hk} = d_{hk}^* = 1 / d_{hk}$

$2\, d_{hk} \sin \theta_{hk} = \lambda$

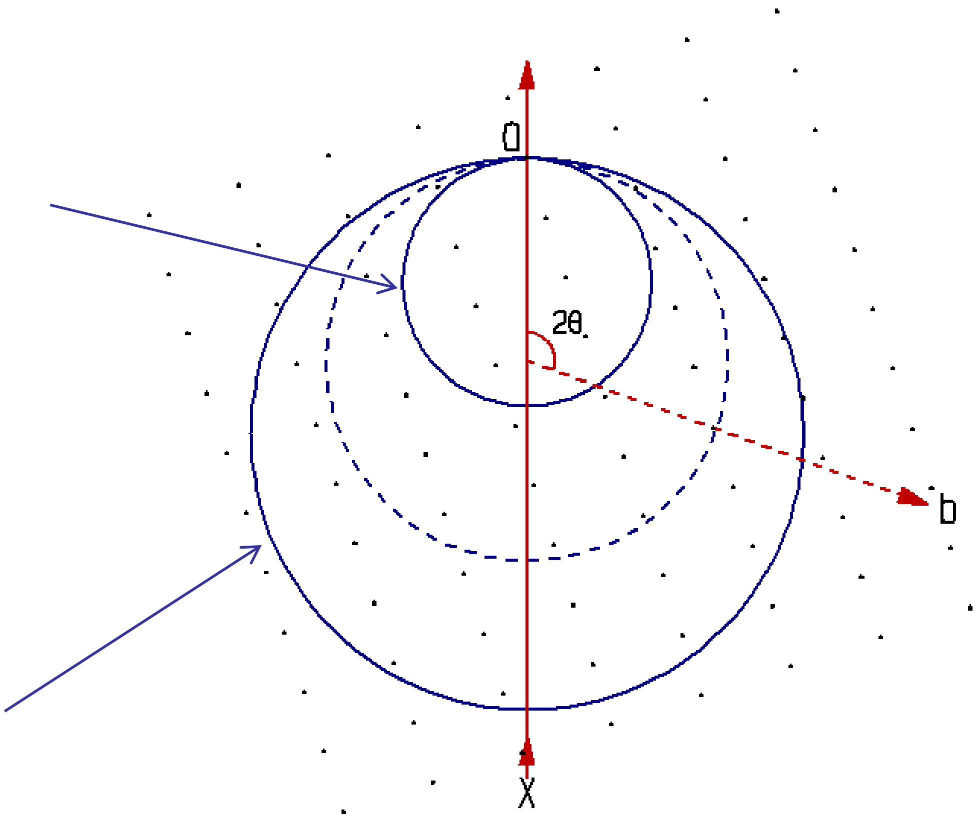
Reflections within a radius of 2R can be observed

http://www.doitpoms.ac.uk/tlplib/reciprocal_lattice/ewald.php

SINGLE-CRYSTAL LAUE DIFFRACTION

Single-crystal, white or ”pink” radiation

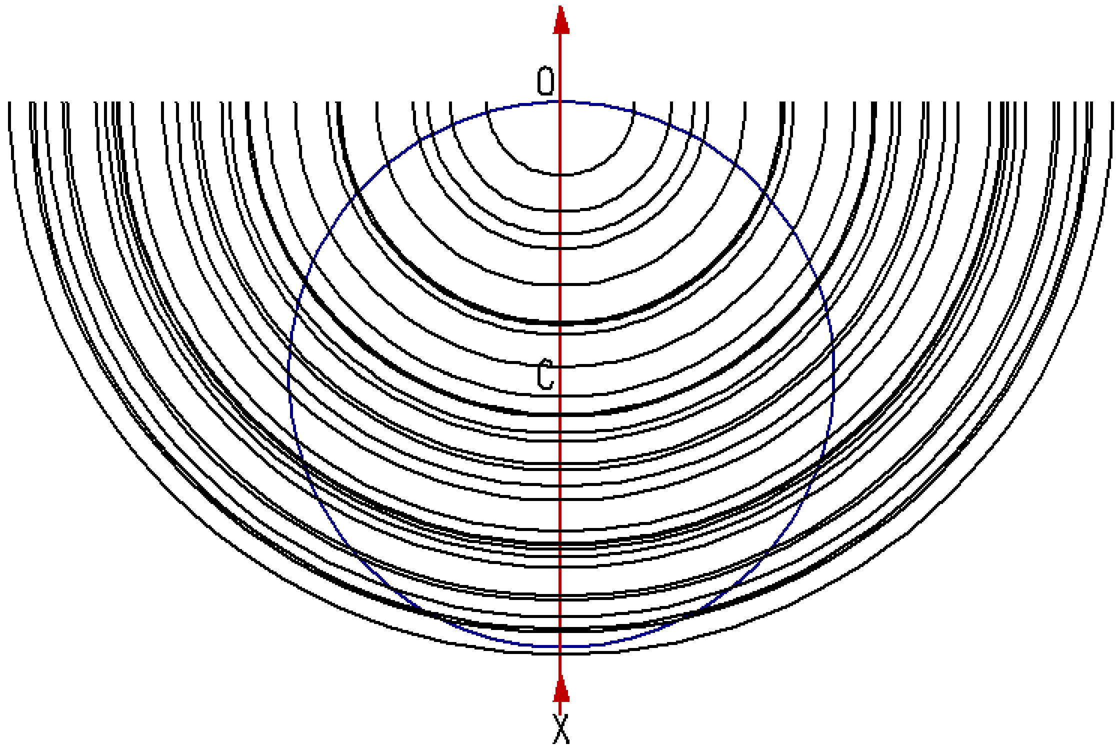
Max. wavelength
Min. energy

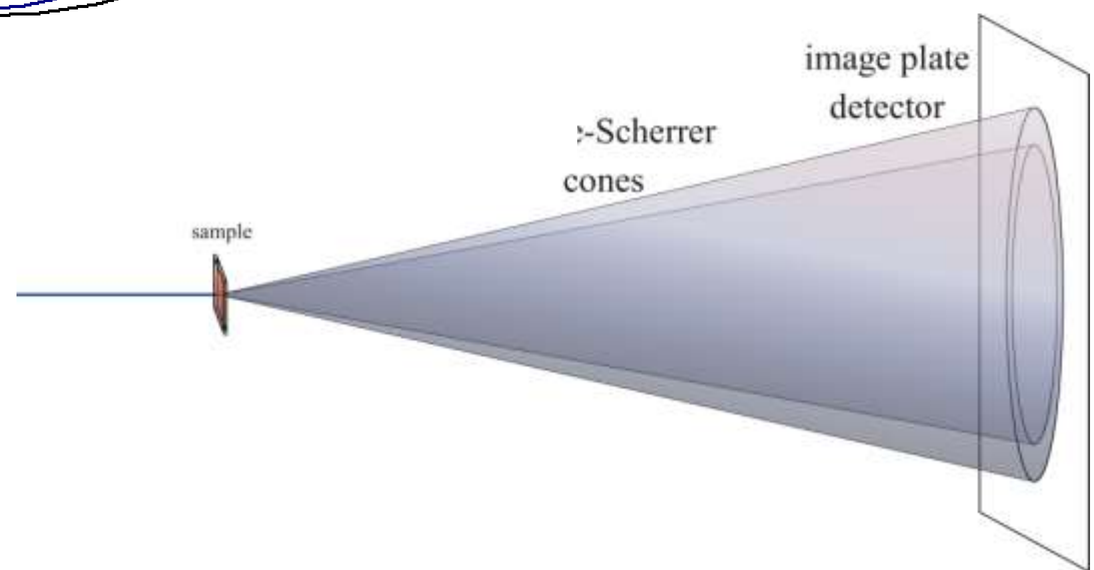


Min. Wavelength
Max. energy

All reflections between the two Ewald spheres can be observed.

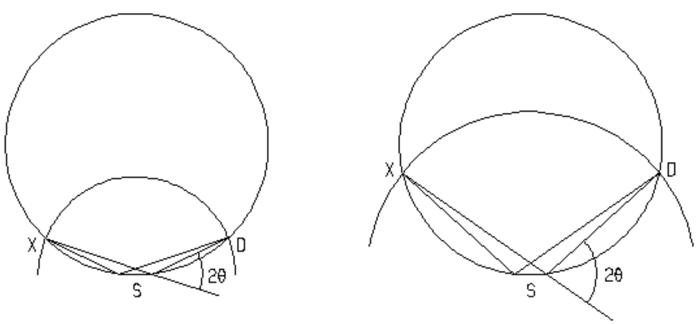
POWDER DIFFRACTION



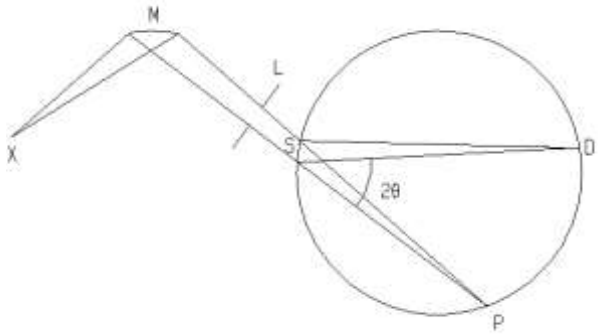


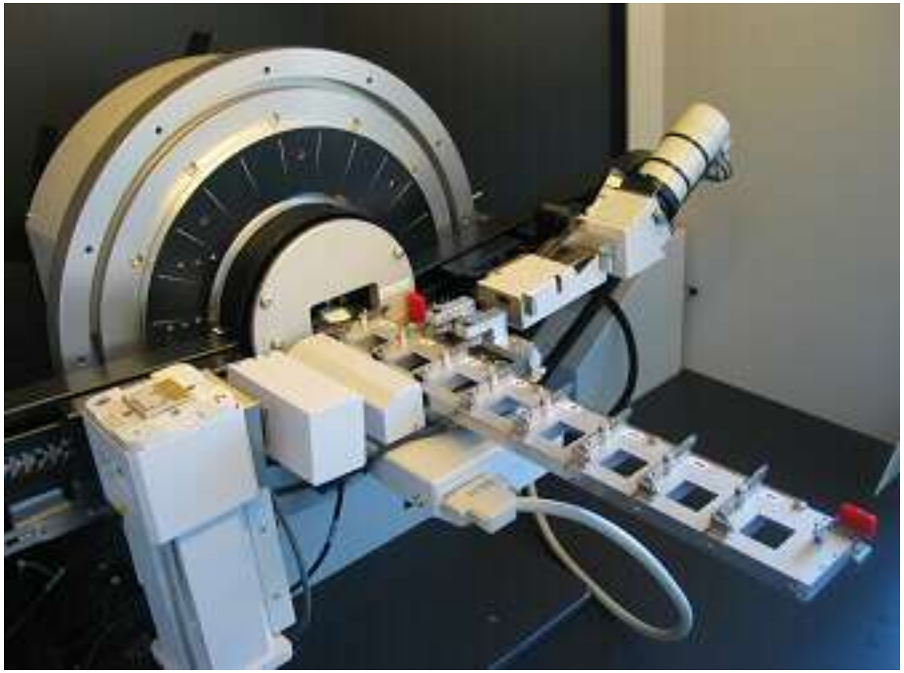
POWDER DATA COLLECTION

Bragg-Brentano (reflection mode)

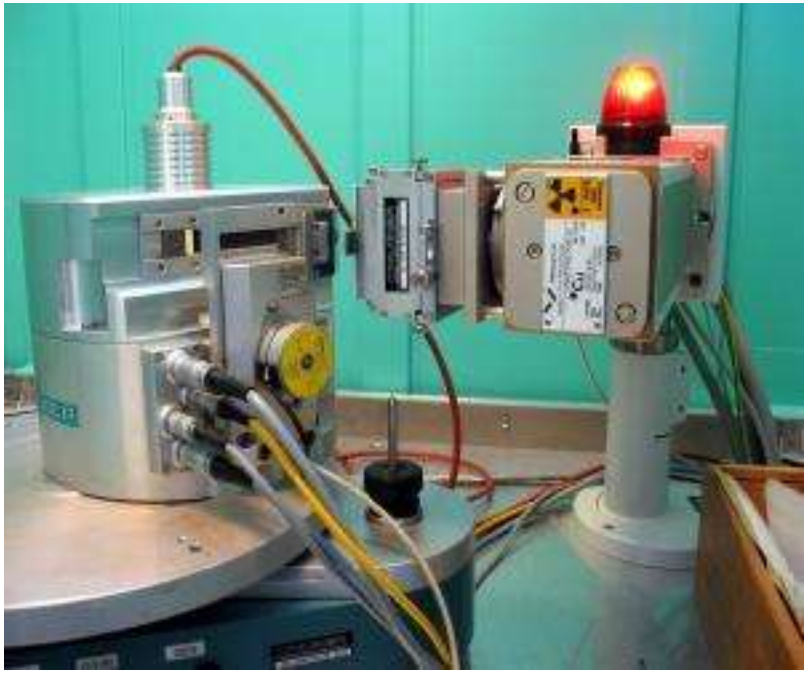


Guinier (transmission mode)





Bruker D8 Advance

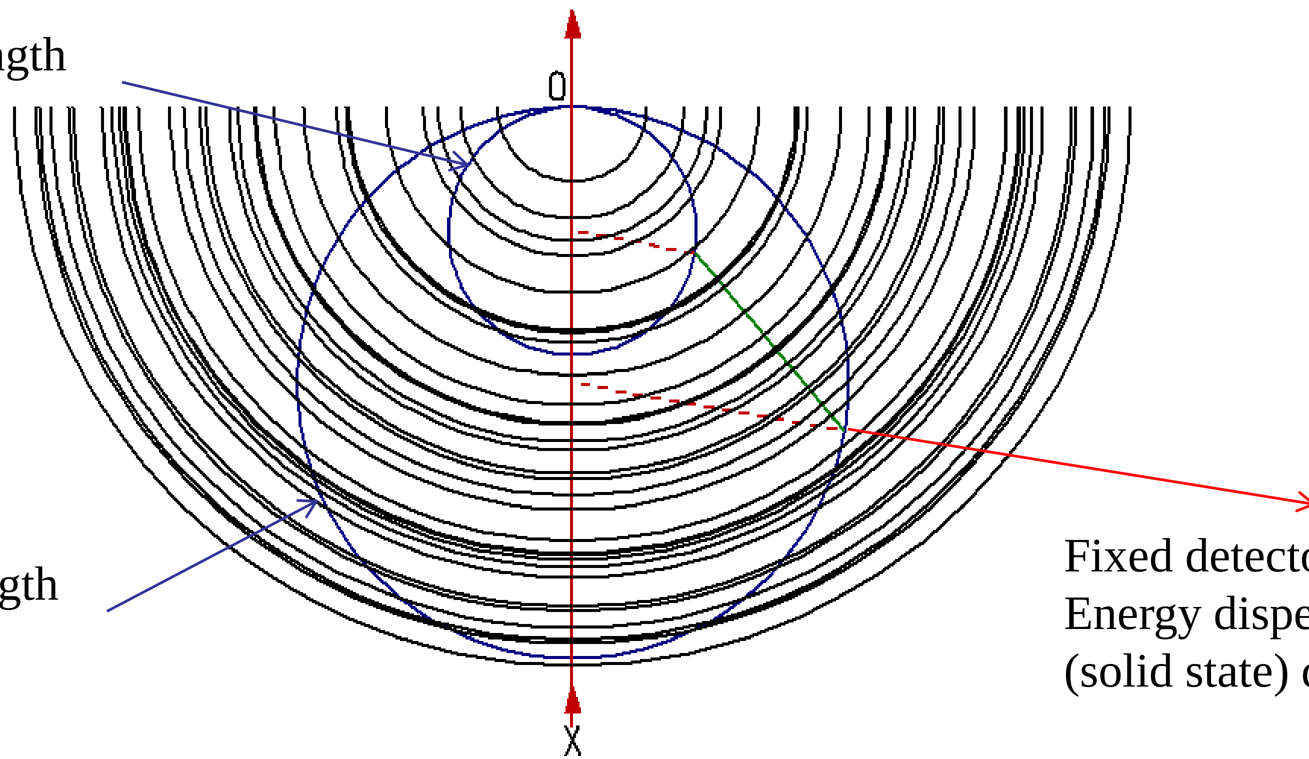


Huber G670

ENERGY DISPERSIVE POWDER DIFFRACTION

Powder, white or ”pink” radiation

Max. wavelength
Min. energy



Min. wavelength
Max. energy

Fixed detector angle
Energy dispersive
(solid state) detector

Reflections crossing the green line can be observed

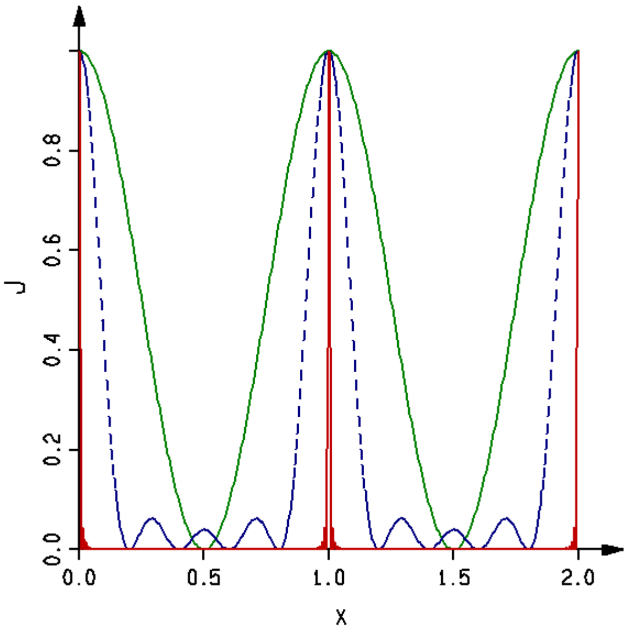
INTERFERNCE FUNCTION

$$\mathbf{f}_j = f_j \exp\{2\pi i(\mathbf{r} + \mathbf{v}) \cdot \mathbf{r^*}\}$$

$$\mathbf{v} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$$

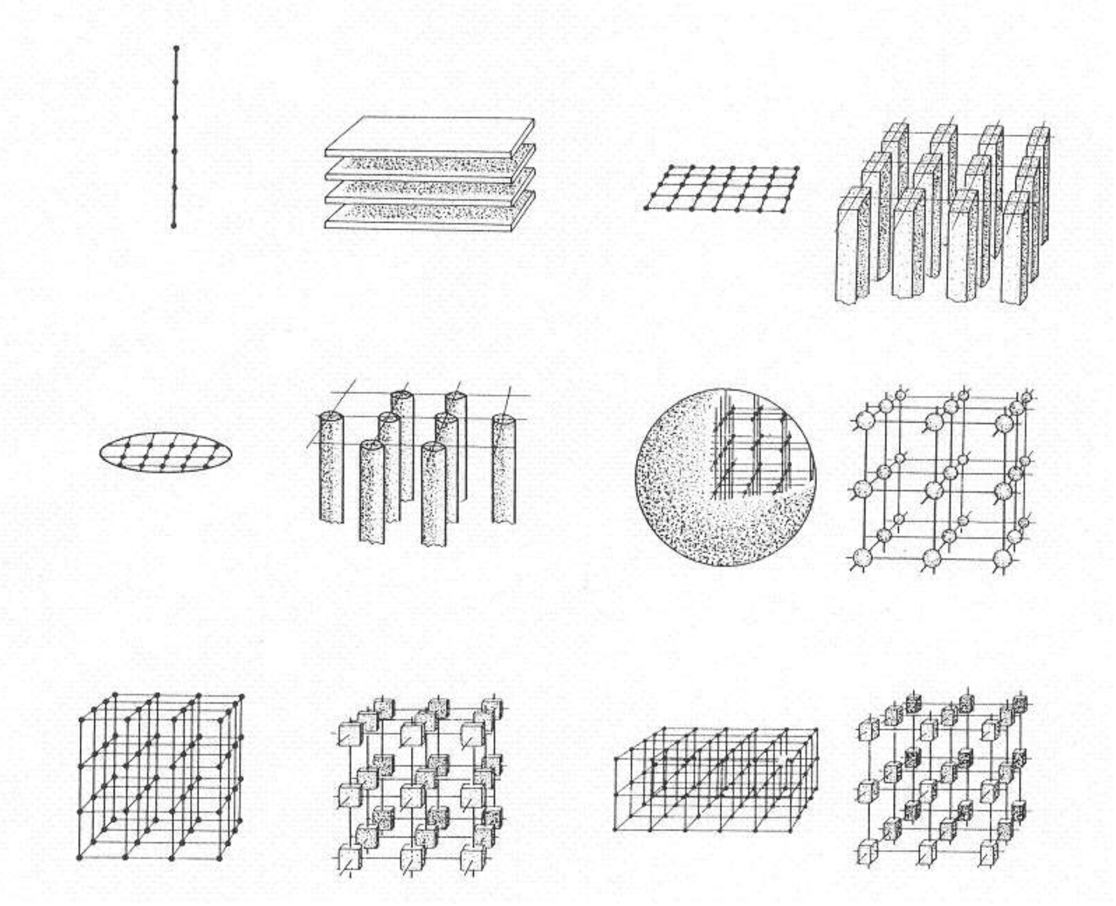
$$\mathbf{F}_{cryst} = \Sigma_{cryst}\exp\{2\pi i\ \mathbf{v} \cdot \mathbf{r^*}\} \cdot \mathbf{F}_{hkl} = J(\mathbf{r^*}) \cdot \mathbf{F}_{hkl}$$

$$\Sigma_{N1} \exp\{2\pi i\ n_1\mathbf{a} \cdot \mathbf{r^*}\} = (1 - \exp\{2\pi i\ N_1\mathbf{a} \cdot \mathbf{r^*}\}) / (1 - \exp\{2\pi i\ \mathbf{a} \cdot \mathbf{r^*}\}) = \sin\{\pi\ N_1\mathbf{a} \cdot \mathbf{r^*}\} / \sin\{\pi\ \mathbf{a} \cdot \mathbf{r^*}\}$$



$$\sin^2\{\pi\ N_1x\} / \sin^2\{\pi\ x\}$$

INTERFERENCE FUNCTION



PARTICLE SIZE - STRESS / STRAIN (DEFECTS)

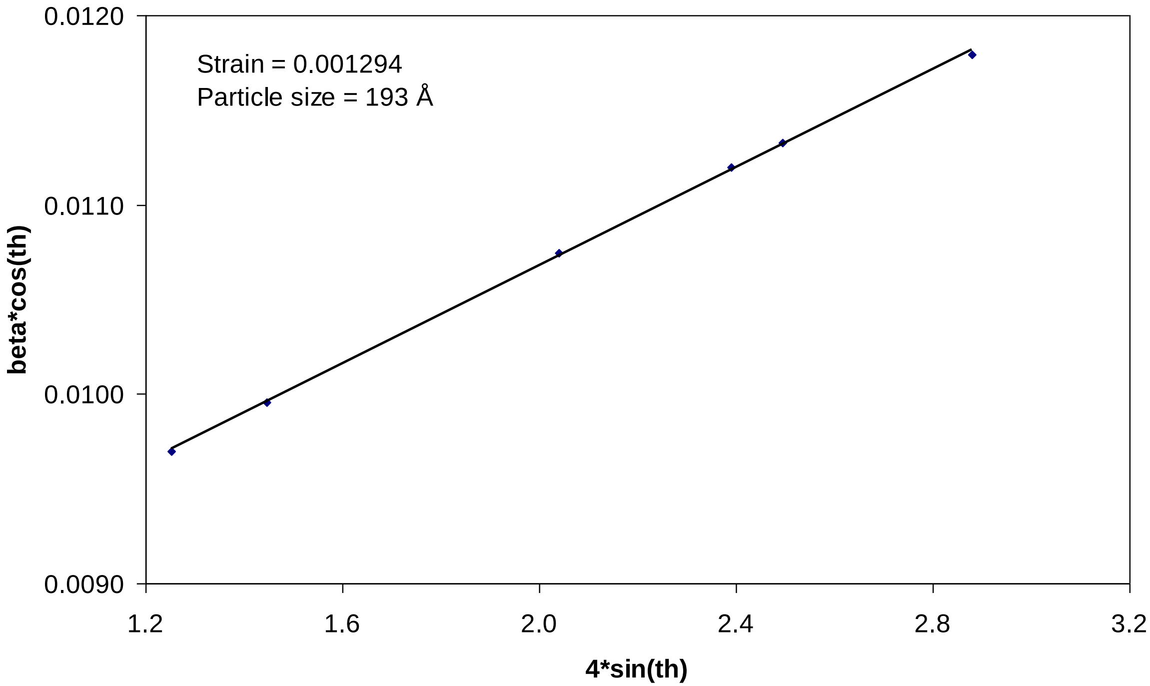
Size (τ) (Sherrer) : $\beta = k\,\lambda / \tau \cos(\theta)$

$\beta^2 = FWHM_{obs}^2 - FWHM_{ref}^2$ (rad)

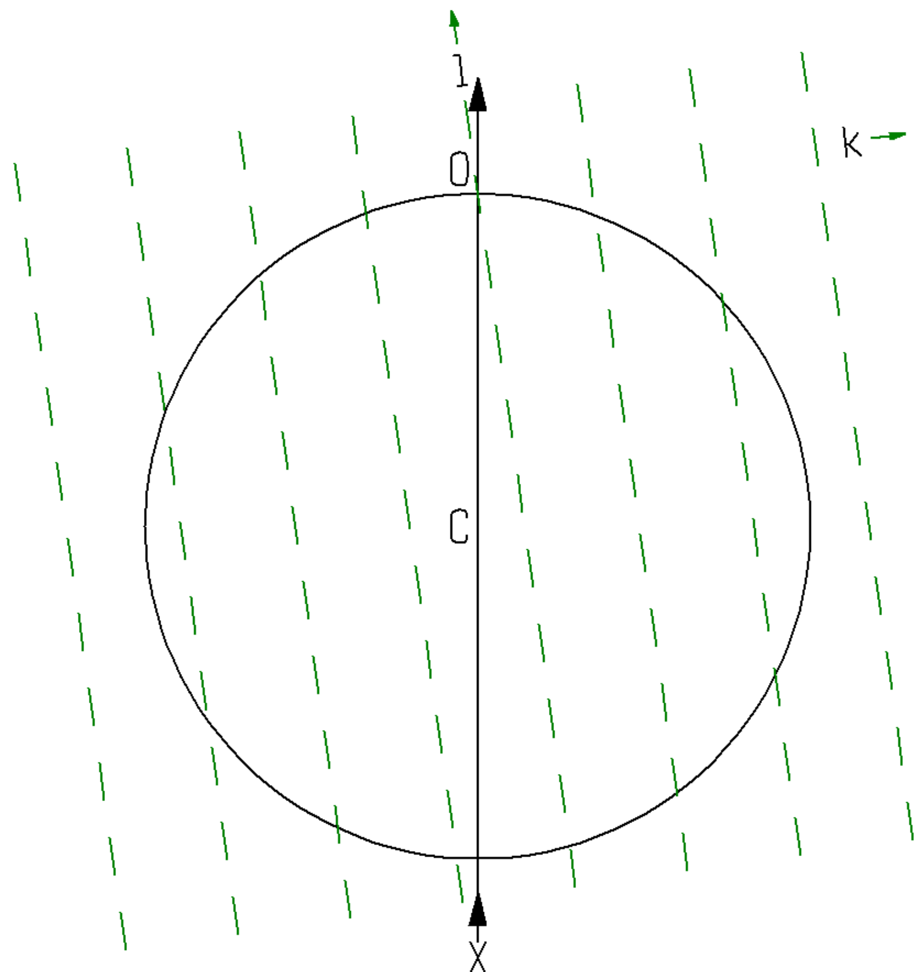
Stress/strain (ε): $\beta = 4\,\varepsilon \tan(\theta)$

Williamson-Hall: $\beta = k\,\lambda / \tau \cos(\theta) + 4\,\varepsilon \tan(\theta)$

$\beta \cos(\theta) = k\,\lambda / \tau + 4\,\varepsilon \sin(\theta)$



ANISOTROPIC SIZE EFFECTS



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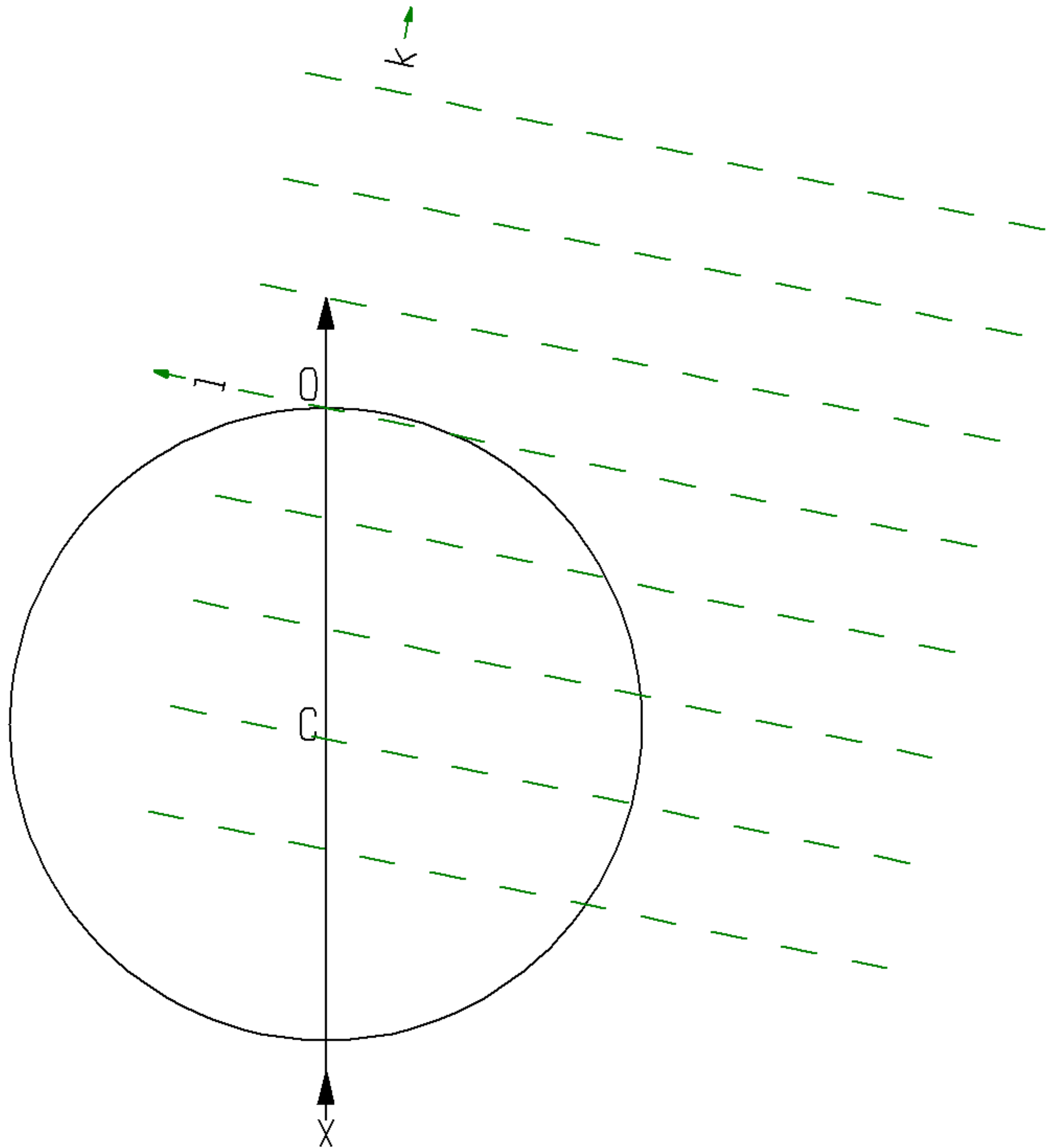

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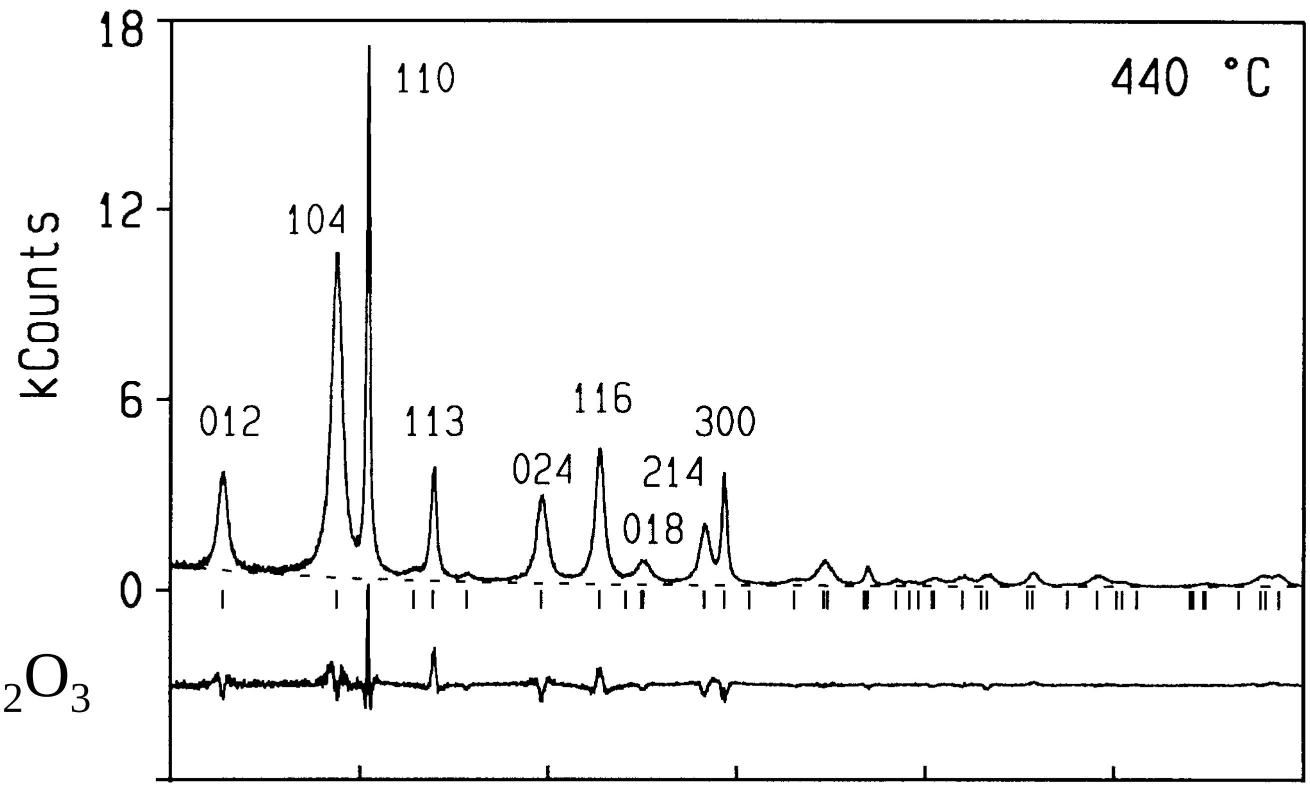

Fe_2O_3

a = 5.0364(8), c = 13.750(2) Å   D(a) = 399(3) Å, D(c) = 87(2) Å