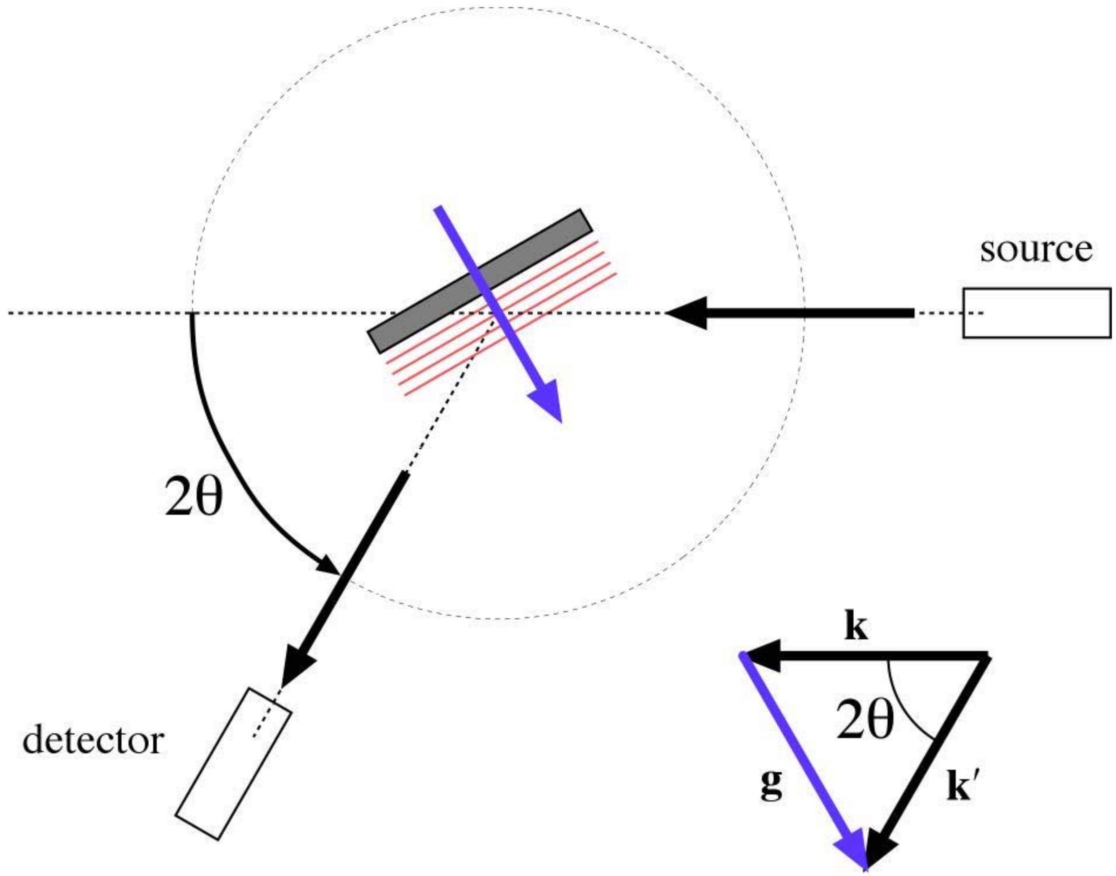
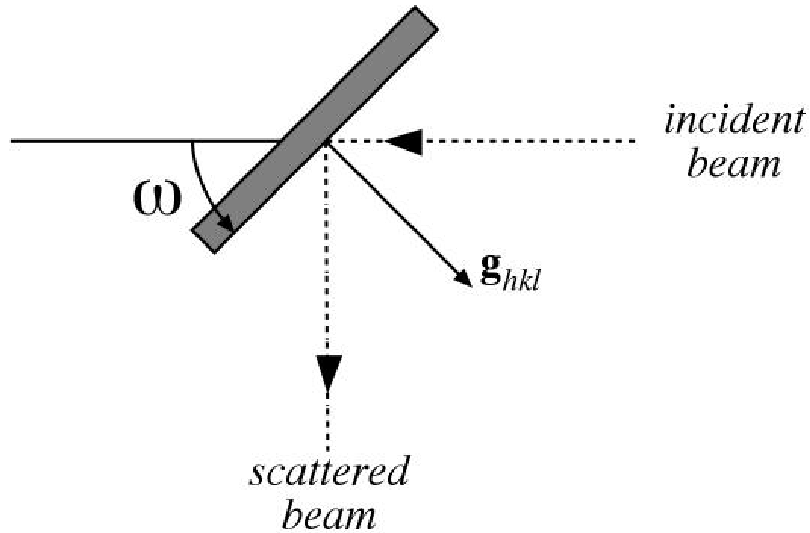
X-ray diffraction geometry



Setting ω



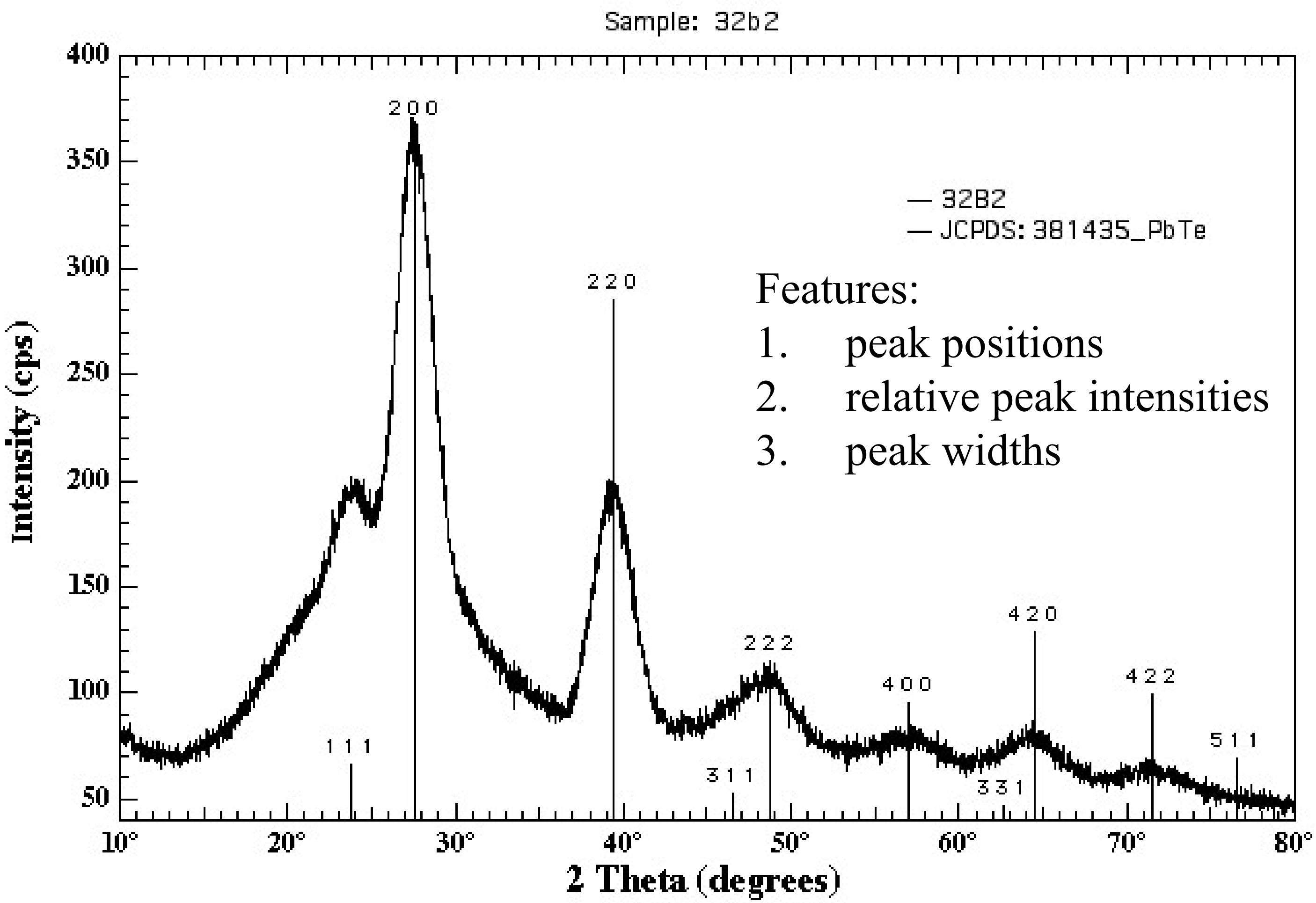
ω controls sample orientation in the diffraction plane.

• most important for single-crystal diffraction

For any poly- (or nano-) crystalline specimen, we usually set:

$$\omega = \frac{1}{2}(2\theta) = \theta$$

X-ray diffraction pattern from nanoparticles



Powder diffraction standards

PDF#00-029-1360: QM=Star(S); d=(Unknown); I=Diffractometer
Brookite
TiO2 Black
Radiation=CuKa1 Lambda=1.54056 Filter=Ni
Calibration= 2T=25.340-103.201 I/Ic(RIR)=
Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, v3 p57 (1964)

Orthorhombic - Powder Diffraction, Pcab (61) Z=8 mp=
CELL: 5.4558 x 9.1819 x 5.1429 <90.0 x 90.0 x 90.0> P.S=oP24 (O2 Ti)
Density(c)=4.120 Density(m)=4.140 Mwt=79.90 Vol=257.63 F(30)=57.8(.0115,45/0)
Ref: Ibid.

Strong Lines: 3.46/8 2.90/9 2.48/3 2.41/2 2.37/1
NOTE: To replace 00-016-0617 and validated by calculated pattern.
See ICSD 36408 (PDF 01-076-1934).
Specimen from Magnet Cove, Arkansas, USA (USNM 97661).
Spectrographic analysis: 0.1-1.0% Si; 0.01-0.1% each of Al, Fe, and V; 0.001-0.01% Mg.
Niobian brookite from Mozambique [Chemical analysis (wt.%): Ti O2 80.7, Nb2 O5 14.1, FeO 5.53];
Carvalho et al., Rev. Cien.Geol.Ser. A, 7 61 (1974) reports an identical pattern.
Pattern taken at 25 C.
Intensities verified by calculated pattern.

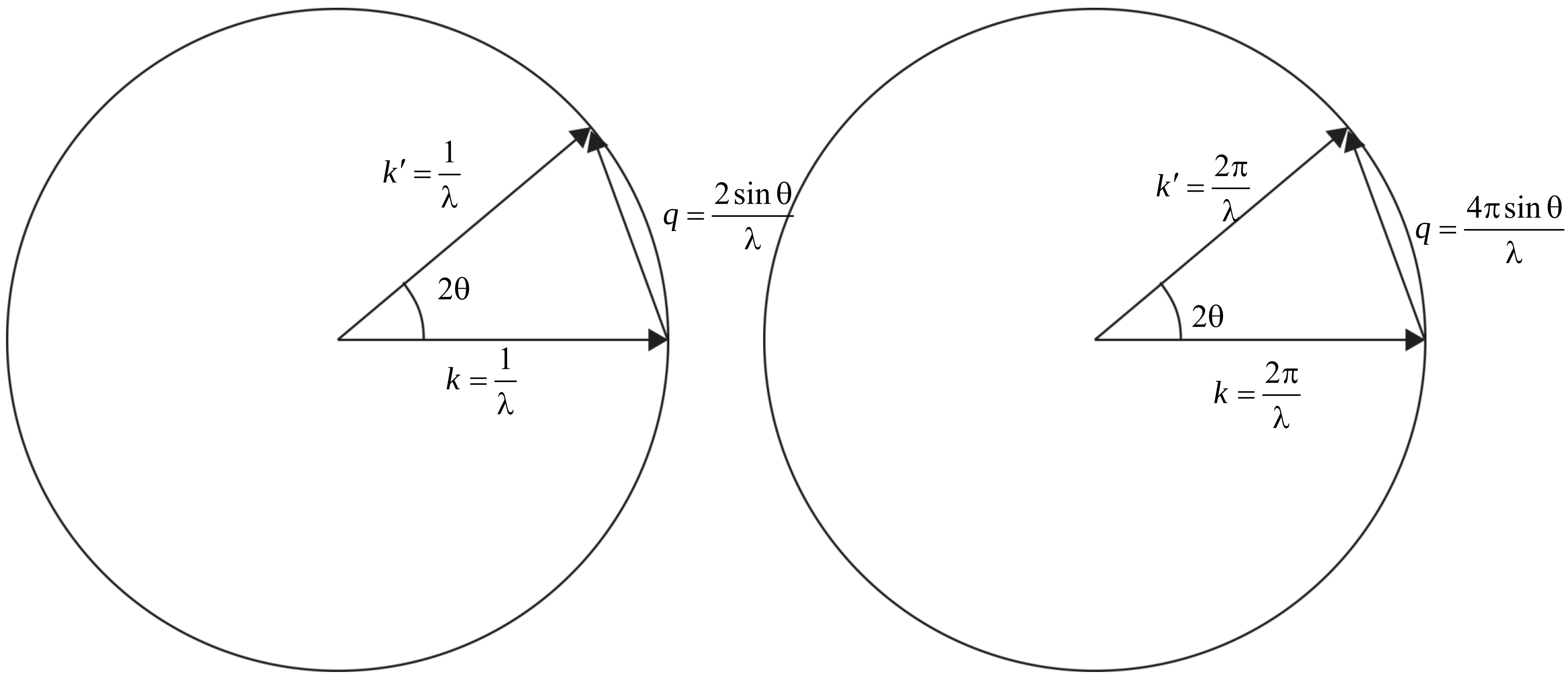
2-Theta	d(nm)	I(v)	(h k l)	Theta	1/(2d)	2pi/d	n^2
25.340	0.35120	92.0	(1 2 0)	12.670	0.01424	0.17891	
25.689	0.34650	74.0	(1 1 1)	12.845	0.01443	0.18133	
30.807	0.29000	100.0	(1 2 1)	15.404	0.01724	0.21666	
32.791	0.27290	5.0	(2 0 0)	16.395	0.01832	0.23024	
36.252	0.24760	33.0	(0 1 2)	18.126	0.02019	0.25376	
37.296	0.24090	24.0	(2 0 1)	18.648	0.02076	0.26082	
37.933	0.23700	8.0	(1 3 1)	18.967	0.02110	0.26511	
38.371	0.23440	5.0	(2 2 0)	19.185	0.02133	0.26805	
38.576	0.23320	6.0	(2 1 1)	19.288	0.02144	0.26943	
39.205	0.22960	7.0	(0 4 0)	19.603	0.02178	0.27366	
39.967	0.22540	11.0	(1 1 2)	19.983	0.02218	0.27876	
40.152	0.22440	26.0	(0 2 2)	20.076	0.02228	0.28000	
42.339	0.21330	24.0	(2 2 1)	21.170	0.02344	0.29457	
46.072	0.19685	26.0	(0 3 2)	23.036	0.02540	0.31919	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	

JCPDS: Joint Committee on Powder Diffraction Standards
PDF: Powder Diffraction File

Two conventions for scattering vector

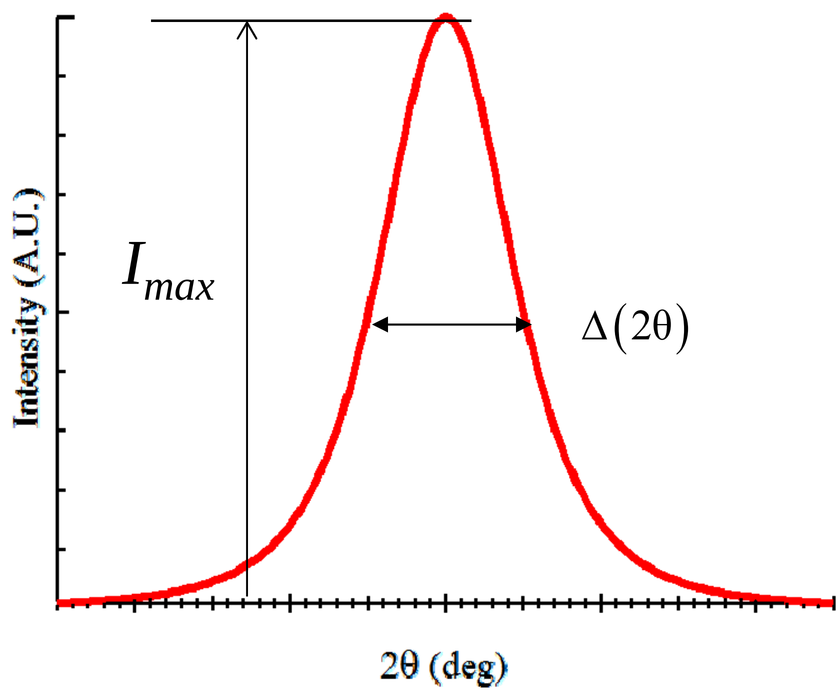
TEM: $q = \frac{1}{d} = \frac{2\sin\theta}{\lambda}$

XRD: $q = \frac{2\pi}{d} = \frac{4\pi\sin\theta}{\lambda}$



Integrated intensity factors for powder

- Structure factor squared $|F_{hk\ell}|^2$
- Multiplicity factor m (equivalent permutations of Miller indices)
- Lorentz polarization factor $L(\theta_B)$
- Debye-Waller (thermal) factors $M(\theta_B, T)$



If all peaks have the same shape:

$$I_{\text{int}} \propto I_{\text{max}} \cdot \Delta(2\theta)$$

Peak fitting

Gaussian:

$$f_{\{q_0,\Delta q\}}^{Gaussian}(q) = \exp\left\{-\ln(2)\left[\frac{q-q_0}{(\Delta q/2)}\right]^2\right\}$$

$$q = \frac{4\pi \sin\theta}{\lambda}$$

q_0 = centroid

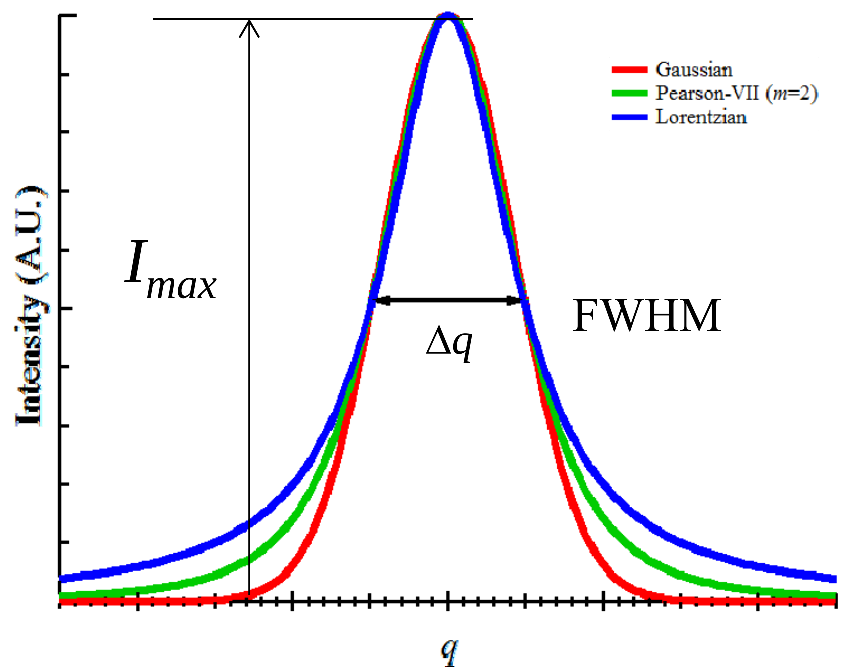
$\Delta q = FWHM$

Lorentzian:

$$f_{\{q_0,\Delta q\}}^{Lorentzian}(q) = \frac{1}{1+\left[\frac{q-q_0}{(\Delta q/2)}\right]^2}$$

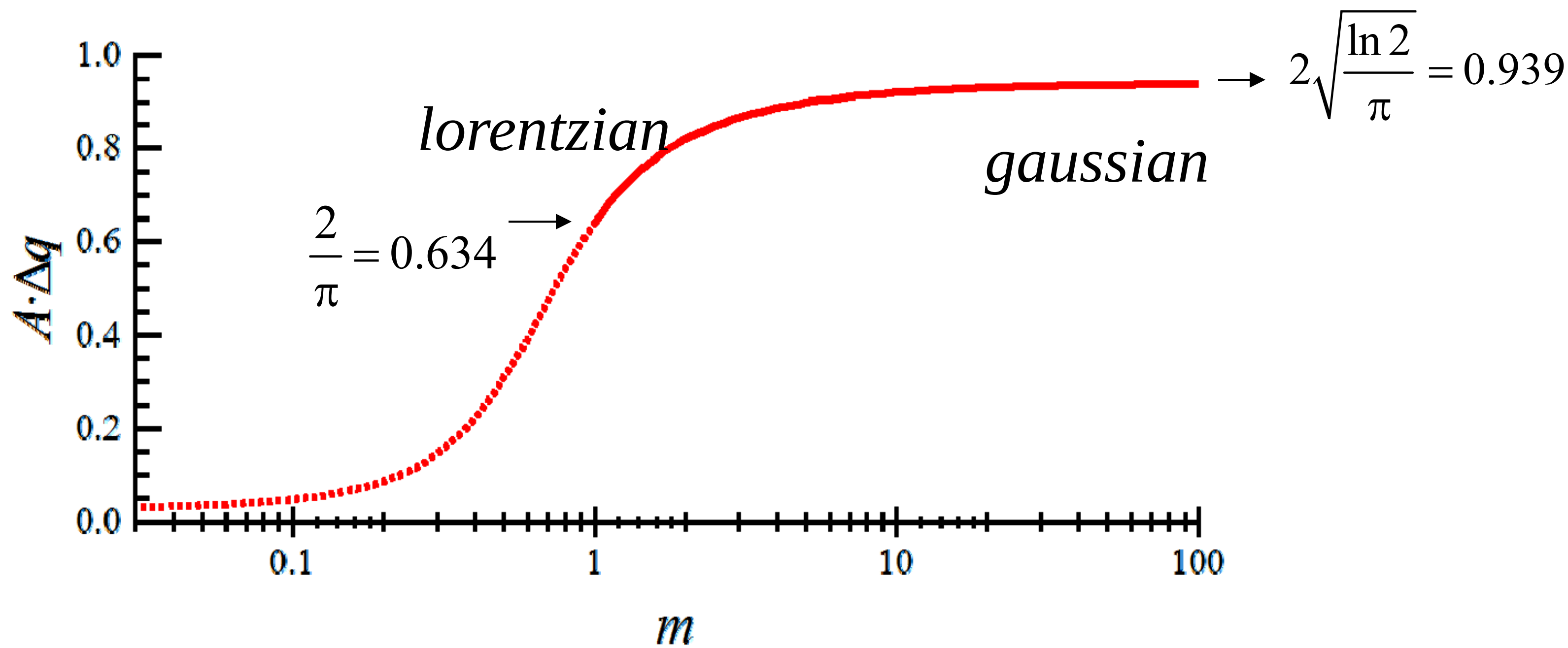
Pearson-7:

$$f_{\{q_0,\Delta q,m\}}^{Pearson-7}(q) = \frac{1}{\left[1+\left(2^{1/m}-1\right)\cdot\left[\frac{q-q_0}{(\Delta q/2)}\right]^2\right]^m}$$



Normalization

For comparison of integrated intensites, peaks need to be weighted properly:



Another important lineshape

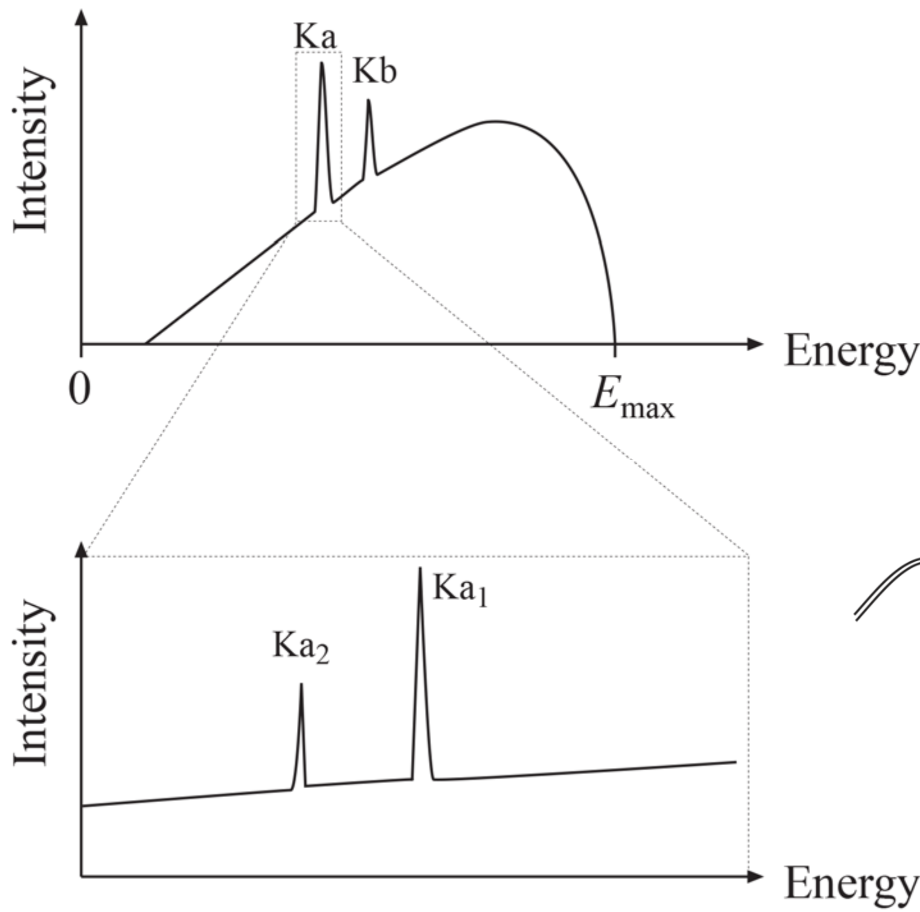
Voigt: Convolution of gaussian and lorentzian

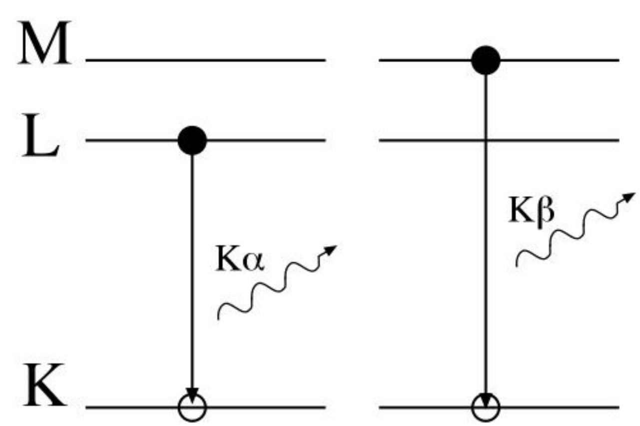
$$f^{Voigt}_{\{q_0,\Delta q\}}(q) = f^{Gaussian}_{\{q_0,\Delta q_1\}}(q) * f^{Lorentzian}_{\{q_0,\Delta q_2\}}(q)$$

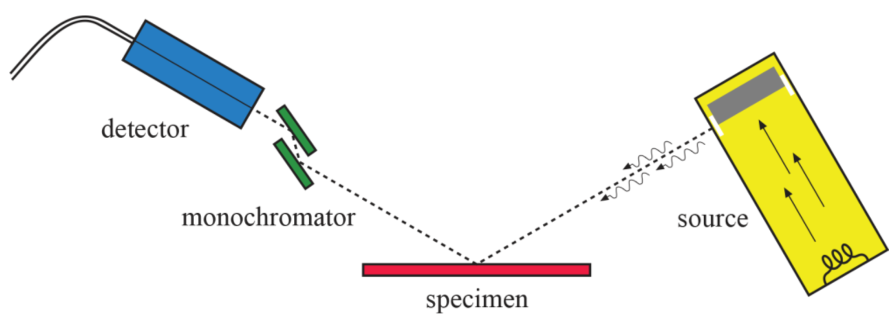
$$f_1(q) * f_2(q) = \int_{q'=-\infty}^{\infty} dq' \cdot f_1(q') \cdot f_2(q-q')$$

The convolution makes this difficult to use for computation.

X-ray sources







Bremstrahlung & characteristic X-rays

Usually use a monochromator or energy filter

Common X-ray sources

Cu-Kα:

Kα1	$2p_{3/2}$–>1s	8.048	0.15405	2.0
Kα2	$2p_{1/2}$–>1s	8.028	0.15443	1.0
			λ_{mean} (nm)	0.1542

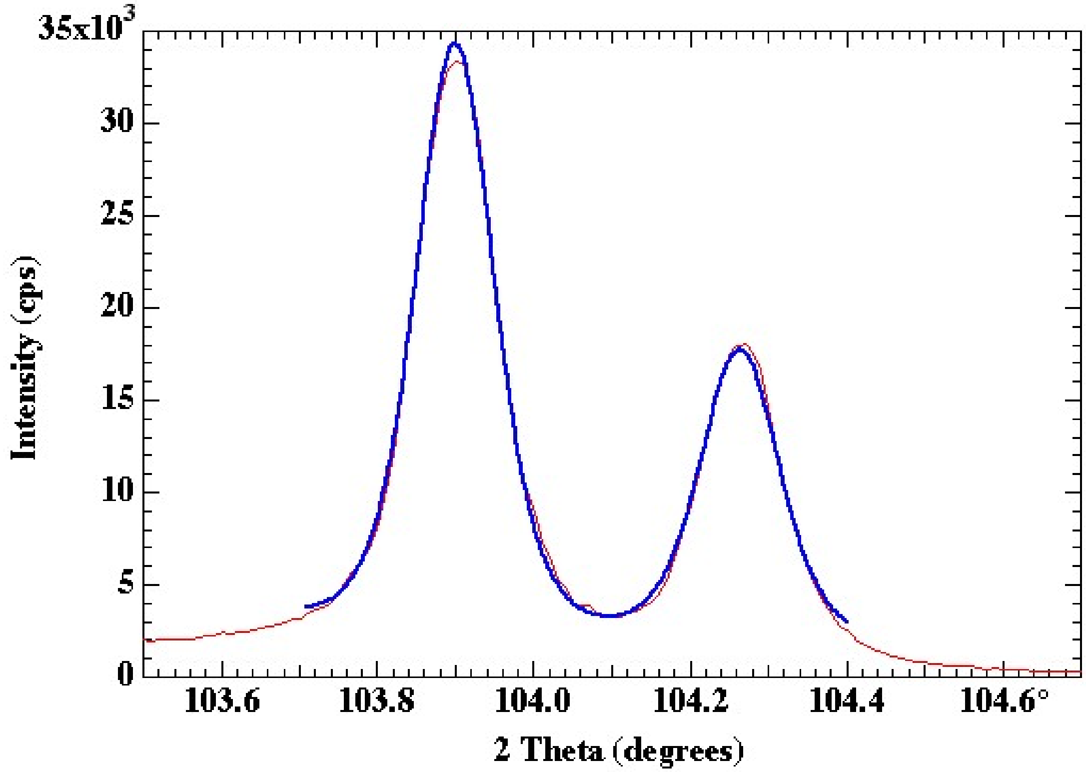
Mo-Kα:

label	transition	E(KeV)	λ (nm)	relative intensity
Kα1	$2p_{3/2}$–>1s	17.481	0.07093	2.0
Kα2	$2p_{1/2}$–>1s	17.376	0.07135	1.0
			λ_{mean} (nm)	0.07107

$$E = \frac{1240 \text{ eV} \cdot \text{nm}}{\lambda} = \frac{1.24 \text{ KeV} \cdot \text{nm}}{\lambda}$$

Co, Ag also used

Kα Peak Doublets



Two peaks corresponding to a single lattice spacing

$$q = \frac{2\pi}{d} = \frac{4\pi \sin\theta_1}{\lambda_1} = \frac{4\pi \sin\theta_2}{\lambda_2}$$

$$\frac{I_{K\alpha 1}}{I_{K\alpha 2}} \approx 2.0$$

Fitting the Kα Doublet

$$I(2\theta) = A_1 \cdot f_{\{q_0, \Delta q, \ldots\}}\left(\frac{2\sin\theta}{\lambda_1}\right)$$

$$+A_2 \cdot f_{\{q_0, \Delta q, \ldots\}}\left(\frac{2\sin\theta}{\lambda_2}\right)$$

$$+b_0 + b_1 \cdot (2\theta) + b_2 \cdot (2\theta)^2$$

$$q = \frac{2\sin\theta}{\lambda}$$

X-Ray Scattering by Charges

- An electric charge in an electric field experiences a force

$$\mathbf{F} = q\mathbf{E}$$

q: charge

- A mass subjected to a force accelerates:

$$\mathbf{a} = \mathbf{F}/m$$

m: mass

- An accelerating charge radiates:

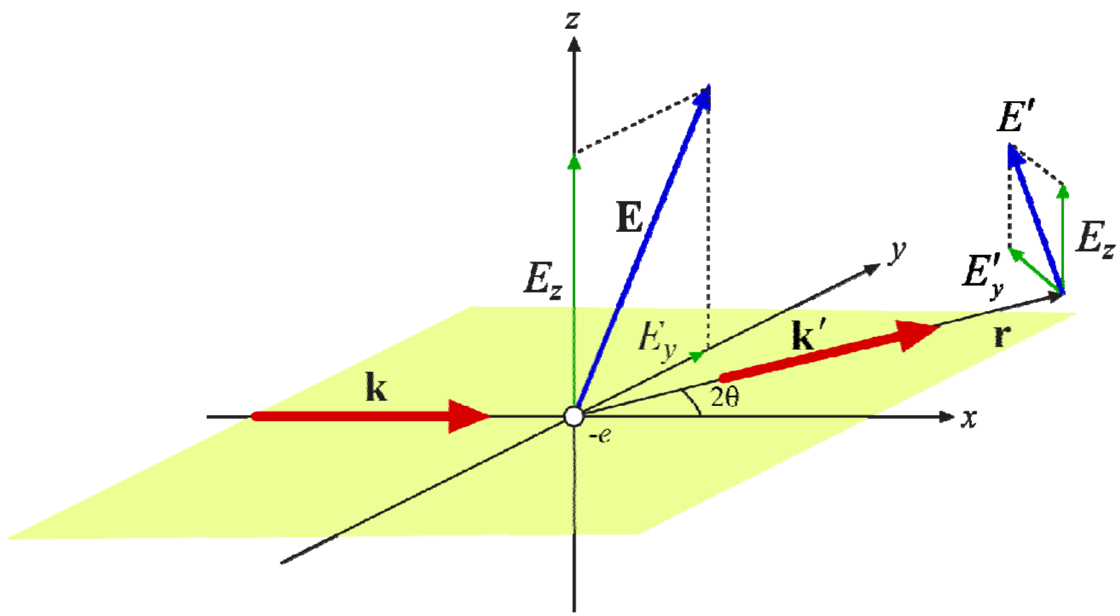
$$\mathbf{E}' = \frac{q}{c^2 r^3} \cdot \left[\mathbf{r} \times \left(\mathbf{r} \times \mathbf{a}\right)\right]$$

r points from charge to observation point

X-Ray Scattering from One Electron

$q = -e$

Scattering in *x*-*y* plane



$$E'_{y'} = \frac{e^2 E_y}{mc^2 r}\cos(2\theta)$$

$$E'_z = \frac{e^2 E_z}{mc^2 r}$$

$$I \propto |E|^2$$

$$|E|^2 = |E_{y'}|^2 + |E_z|^2$$

$$I' \propto |E'|^2$$

$$|E'|^2 = |E'_{y'}|^2 + |E'_z|^2 = \frac{e^4}{\left(mc^2\right)^2 r^2}\left(|E_y|^2 \cos^2(2\theta) + |E_z|^2\right)$$

Polarization Factor

Time averages: $$\left\langle |E|^2 \right\rangle = \left\langle |E_y|^2 \right\rangle + \left\langle |E_z|^2 \right\rangle$$

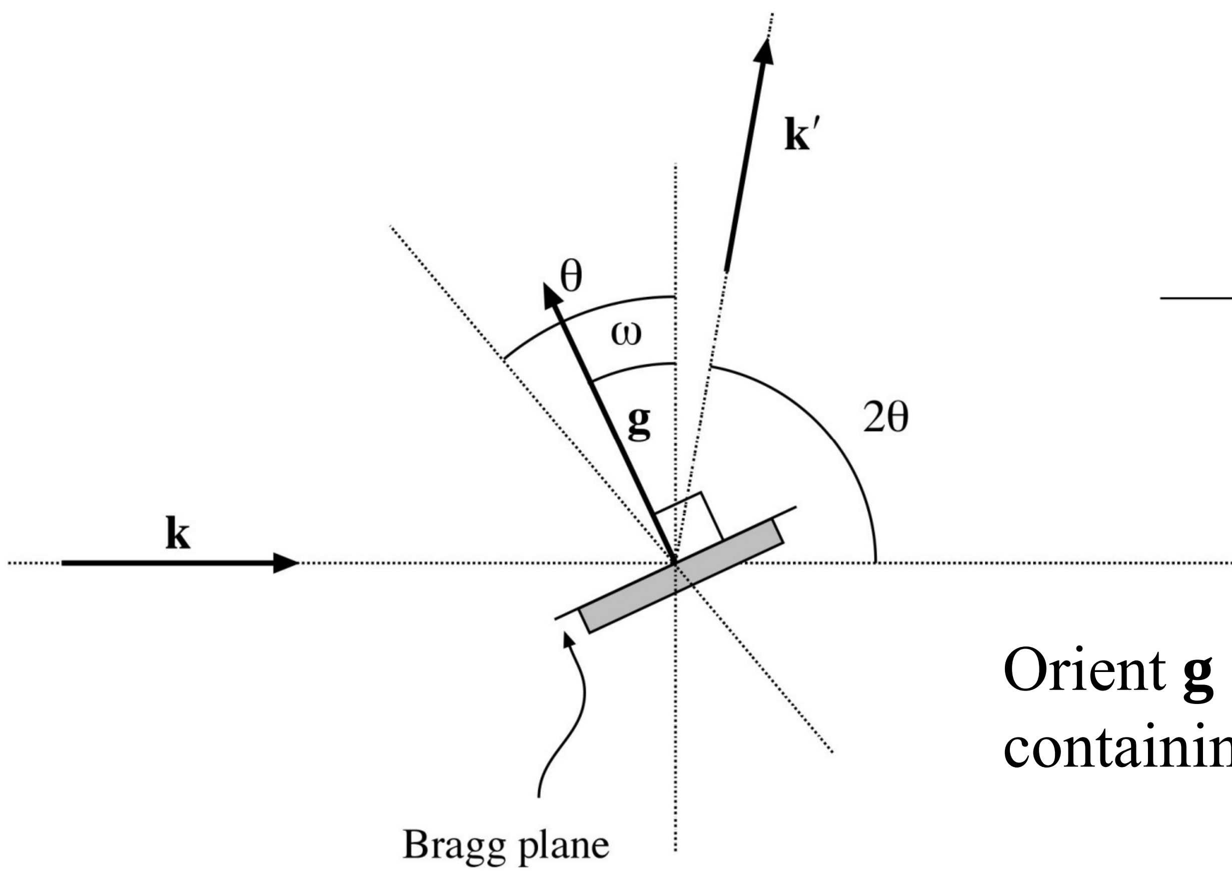
Incident beam unpolarized: $$\left\langle |E_y|^2 \right\rangle = \left\langle |E_z|^2 \right\rangle = \frac{1}{2}\left\langle |E|^2 \right\rangle$$

$$\langle I \rangle \propto \left\langle |E|^2 \right\rangle \to I \qquad \langle I' \rangle \propto \left\langle |E'|^2 \right\rangle \to I'$$

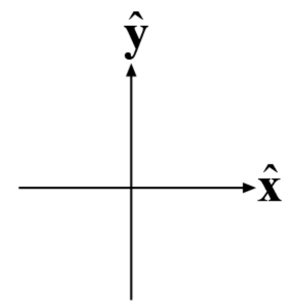
$$I' = I \cdot \frac{e^4}{\left(mc^2\right)^2 r^2} \underbrace{\left(\frac{1 + \cos^2(2\theta)}{2} \right)}_{\text{polarization factor}}$$

When the incident radiation is unpolarized, the polarization dependence of x-ray scattering causes the diffracted intensity to vary with scattering angle.

Diffraction Geometry



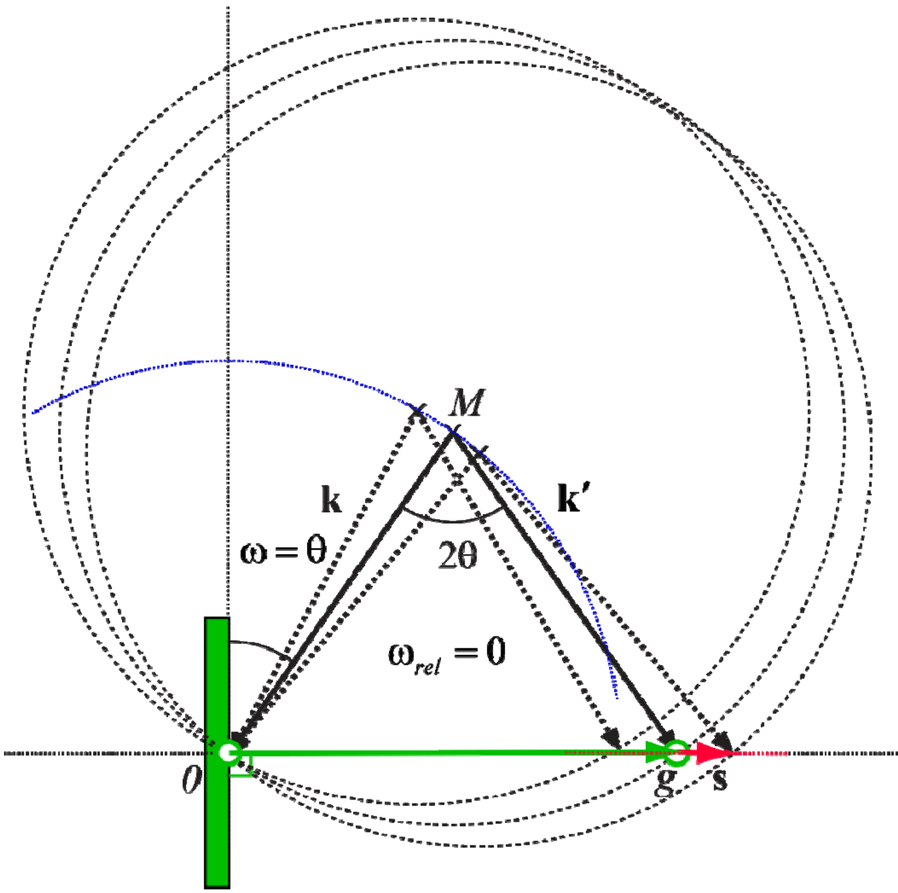
(Not pictured at Bragg condition.)

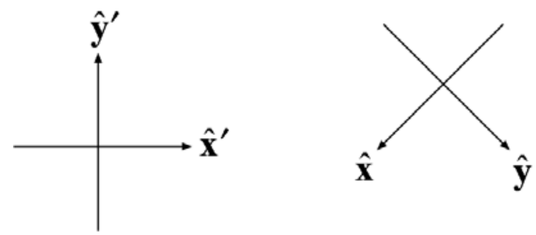


Orient **g** in the plane containing **k** and **k′**

Also assume $\mathbf{g} \perp \mathbf{k}$ when $\omega = 0$

Radial Scan (θ/2θ, or ω/2θ)



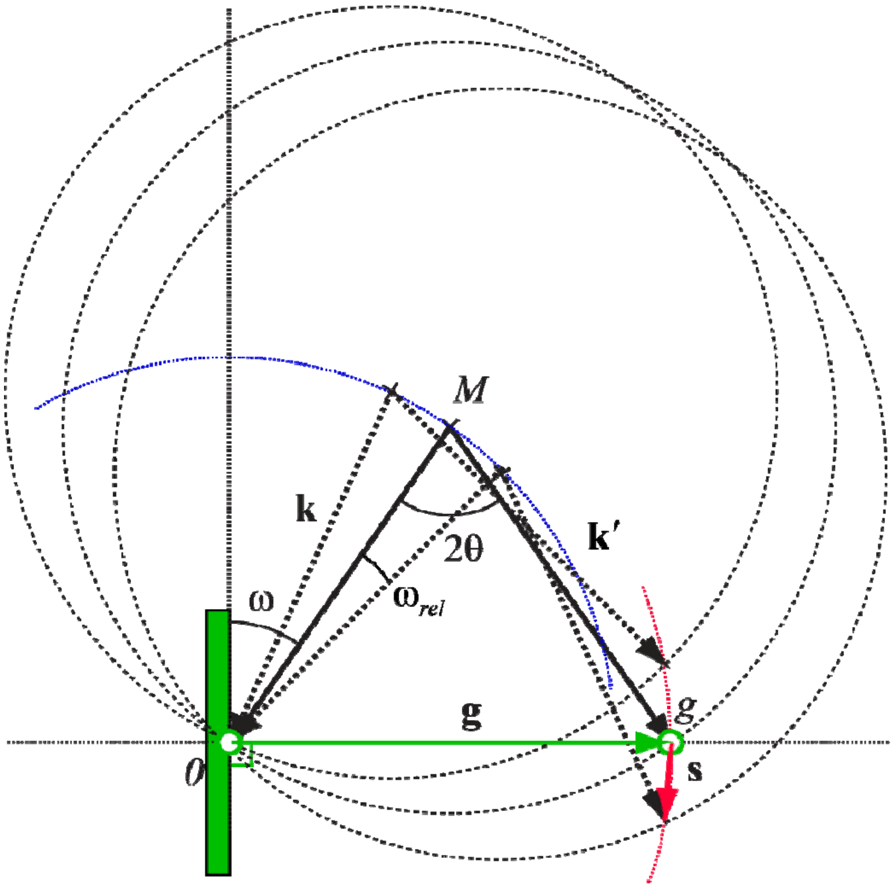


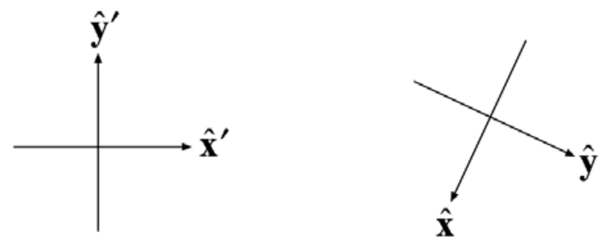
$$\sin\theta_B = \frac{g\lambda}{2}$$

$$\omega_{rel} \doteq \omega - \theta$$

- Vary 2θ and ω
- Maintain condition $\omega = \frac{1}{2}(2\theta)$
- Excitation point *M* orbits about *0*
- Excitation error **s** parallel to **g**

Rocking Curve (ω)





- 2θ fixed — usually set $2\theta = 2\theta_B$
- Vary ω — $\omega \neq \theta_B$
- *M* orbits about *0* — $\omega \neq \frac{1}{2}(2\theta)$
- **s** initially perpendicular to **g**

Excitation Error in XRD (I)

Excitation error: $\mathbf{s} = \mathbf{k}' - \mathbf{k} - \mathbf{g}$

From diffraction geometry:

2θ: detection angle

ω: sample rotation

$$\mathbf{k} = k\hat{\mathbf{x}}$$

$$\mathbf{k}' = k \cdot \left[\cos(2\theta)\hat{\mathbf{x}} + \sin(2\theta)\hat{\mathbf{y}}\right]$$

$$\mathbf{g} = g \cdot \left(-\sin\omega\hat{\mathbf{x}} + \cos\omega\hat{\mathbf{y}}\right)$$

Excitation Error in XRD (II)

$$\mathbf{k}' - \mathbf{k} = k\{[\cos(2\theta) - 1]\hat{\mathbf{x}} + \sin(2\theta)\hat{\mathbf{y}}\}$$

$$\mathbf{k}' - \mathbf{k} = 2k\sin(\theta)\cdot[-\sin(\theta)\hat{\mathbf{x}} + \cos(\theta)\hat{\mathbf{y}}]$$

Change Coordinates:

$$\hat{\mathbf{x}}' = -\sin\omega\hat{\mathbf{x}} + \cos\omega\hat{\mathbf{y}}$$

$$\hat{\mathbf{y}}' = -\cos\omega\hat{\mathbf{x}} - \sin\omega\hat{\mathbf{y}}$$

$$\hat{\mathbf{x}} = -\sin\omega\hat{\mathbf{x}}' - \cos\omega\hat{\mathbf{y}}'$$

$$\hat{\mathbf{y}} = \cos\omega\hat{\mathbf{x}}' - \sin\omega\hat{\mathbf{y}}'$$

$$\mathbf{k}' - \mathbf{k} = 2k\sin(\theta)\cdot\left[\cos\left(\theta - \omega\right)\mathbf{x}' + \sin\left(\theta - \omega\right)\hat{\mathbf{y}}'\right]$$

$$\mathbf{g} = g\mathbf{x}'$$

$$\mathbf{s} = 2k\sin(\theta)\cdot\left[\cos\left(\omega - \theta\right)\hat{\mathbf{x}}' - \sin\left(\omega - \theta\right)\hat{\mathbf{y}}'\right] - g\hat{\mathbf{x}}'$$

Excitation Error in XRD (III)

Define an angle that measures the deviation from the Bragg condition:

$$\omega_{rel} \doteq \omega - \theta$$

$$\mathbf{s} = 2k\sin\theta \cdot \left[\cos\left(\omega_{rel}\right)\hat{\mathbf{x}}' - \sin\left(\omega_{rel}\right)\hat{\mathbf{y}}'\right] - g\hat{\mathbf{x}}'$$

For a radial scan, $\omega_{rel} = 0$

$$\mathbf{s} = \left(2k\sin\theta - g\right)\cdot\hat{\mathbf{x}}'$$

Notice: $s = 0 \Rightarrow \sin\theta = \dfrac{g}{2k}$ $\rightarrow \theta = \theta_B$ (Bragg's Law)

Geometric Factor (Ia)

For a large crystal, the reciprocal lattice points are delta functions in reciprocal space.

$$I_{\text{int}}^{(s)} \propto \int_{s_x, s_y} S\left(s_x, s_y\right) \cdot ds_x \cdot ds_y \qquad \text{//reciprocal space}$$

Experimentally, we integrate intensity over an angular range.

$$I_{\text{int}}^{(\theta)} \propto \int_{\omega_{rel}, \theta} S\left(s_x, s_y\right) \cdot d\omega_{rel} \cdot d\theta \qquad \text{//angle space}$$

The integral over ω_{rel} occurs when a powder is used.

The integral over θ occurs when scanning a range of 2θ.

$$S\left(s_x, s_y\right) = \int_{s'_x, s'_y} S\left(s_x - s'_x, s_y - s'_y\right) \cdot \Delta\left(s'_x\right) \cdot \Delta\left(s'_y\right) \cdot ds'_x \cdot ds'_y$$

↗ *scattering strength*

$$I_{\text{int}}^{(\theta)} \propto \int_{s'_x, s'_y} \left[\int_{\omega_{rel}, \theta} S\left(s_x - s'_x, s_y - s'_y\right) \cdot d\omega_{rel} \cdot d\theta \right] \cdot \Delta\left(s'_x\right) \cdot \Delta\left(s'_y\right) \cdot ds'_x \cdot ds'_y$$

Geometric Factor (Ib)

Related angle coordinates to reciprocal-space coordinates:

$$\frac{d\mathbf{s}}{d\omega_{rel}} = 2k\sin\theta \cdot \left[-\sin\left(\omega_{rel}\right)\hat{\mathbf{x}}' - \cos\left(\omega_{rel}\right)\hat{\mathbf{y}}'\right]$$

$$\frac{d\mathbf{s}}{d\theta} = 2k\cos\theta \cdot \left[\cos\left(\omega_{rel}\right)\hat{\mathbf{x}}' - \sin\left(\omega_{rel}\right)\hat{\mathbf{y}}'\right]$$

Near Bragg condition: $\omega_{rel} \approx 0$ $\theta \approx \theta_B$

$$\frac{d\mathbf{s}}{d\omega_{rel}} \approx -2k\sin\left(\theta_B\right)\hat{\mathbf{y}}', \qquad \frac{d\mathbf{s}}{d\theta} \approx 2k\cos\left(\theta_B\right)\hat{\mathbf{x}}'$$

$$d\omega_{rel} = -\frac{ds_y}{2k\sin\theta_B}, \qquad d\theta = \frac{ds_x}{2k\cos\theta_B}, \qquad d\omega_{rel}\cdot d\theta = -\frac{ds_x \cdot ds_y}{2k^2\sin\left(2\theta_B\right)},$$

Geometric Factor (Ic)

We can now perform the integral in reciprocal-space coordinates, weighted for angle coordinates:

$$I_{\text{int}}^{(\theta)} \propto \int\limits_{s'_x, s'_y} \left[\int\limits_{s_x, s_y} \frac{S\left(s_x - s'_x, s_y - s'_y\right) \cdot ds_x \cdot ds_y}{2k^2 \sin\left(2\theta_B\right)} \right] \cdot \Delta\left(s'_x\right) \cdot \Delta\left(s'_y\right) \cdot ds'_x \cdot ds'_y$$

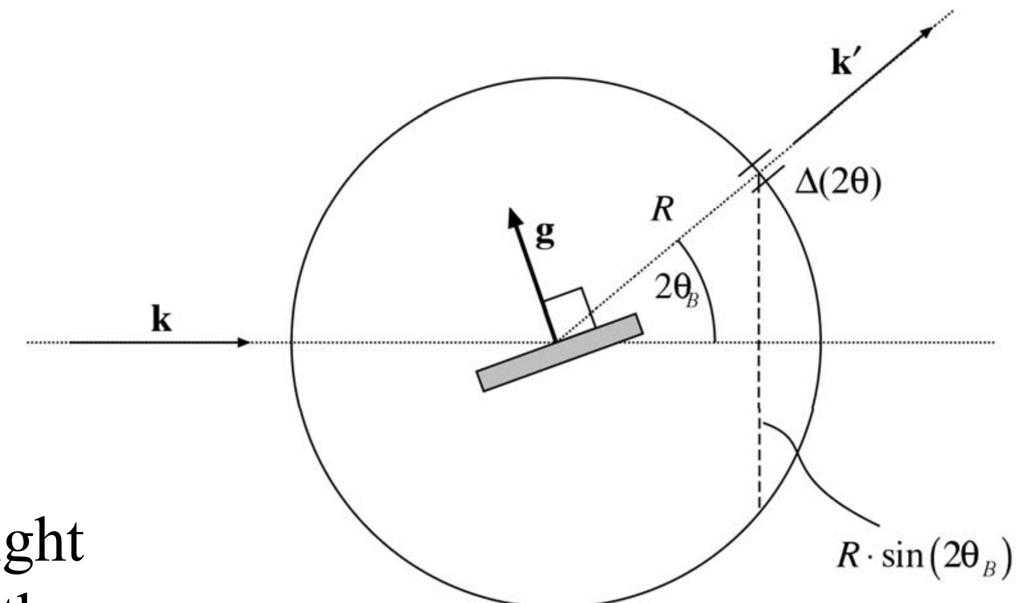
$$= \frac{1}{2k^2 \sin\left(2\theta_B\right)} \cdot I_{\text{int}}^{(s)}$$

So, the integrated intensity of a peak in a radial scan, summed over all sample orientations (e.g., a powder), depends on scattering angle.

$$I \propto \frac{1}{\sin\left(2\theta_B\right)}$$

Ring Circumference Factor

If a diffraction ring is sampled only along a short slit of fixed height,
the fraction of the ring contributing to the pattern depends on scattering angle.



Δh: slit height
L: arc length

$$\frac{\Delta L}{L_{tot}} = \frac{\Delta h}{2\pi R \sin(2\theta_B)} \propto \frac{1}{\sin(2\theta_B)}$$

$$I \propto \frac{\Delta L}{L_{tot}} \propto \frac{1}{\sin(2\theta_B)}$$

Grain Orientation Factor

For a randomly oriented powder, the fraction of grains oriented correctly for diffraction depends on scattering angle.

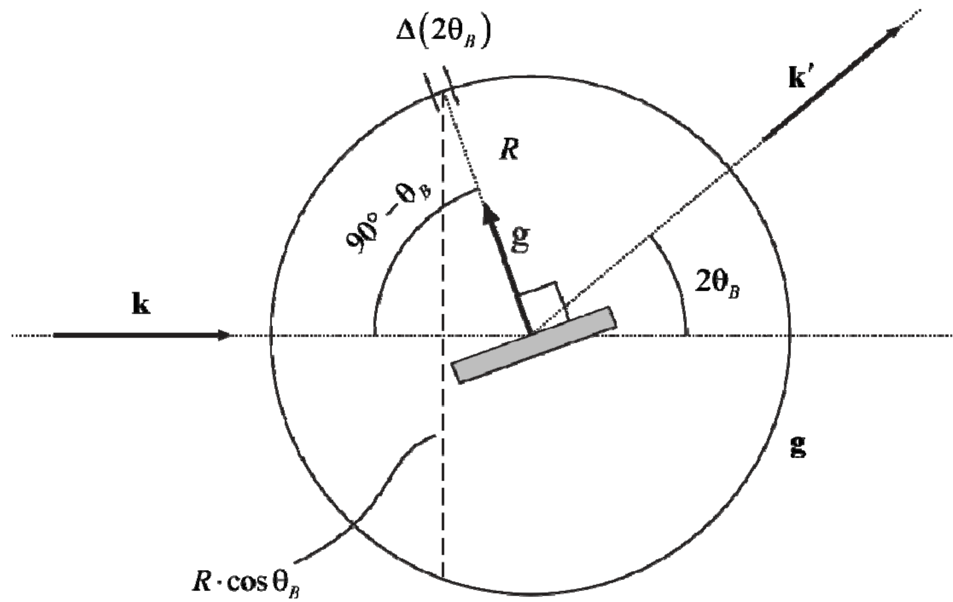
Total surface area of sphere, describing all possible grain orientations

$$A_{tot} = 4\pi R^2$$

Surface area of annular section of sphere, describing orientations of grains at Bragg condition

$$\Delta A = \left[2\pi R \sin\left(90° - \theta_B\right)\right] \cdot \left[R \cdot \Delta(2\theta)\right]$$

$$= 2\pi R^2 \cos\left(\theta_B\right) \cdot \Delta(2\theta)$$



$$\frac{\Delta A}{A_{tot}} = \frac{2\pi R^2 \cos\left(\theta_B\right) \cdot \Delta(2\theta)}{4\pi R^2} = \frac{1}{2}\cos\left(\theta_B\right) \cdot \Delta(2\theta)$$

$$I \propto \frac{\Delta A}{A_{tot}} \propto \cos\left(\theta_B\right)$$

Lorentz-Polarization Factor

Combine factors:

$$L(\theta_B) = \cos(\theta_B) \cdot \frac{1}{\sin(2\theta_B)} \cdot \frac{1}{\sin(2\theta_B)} \cdot \left[1 + \cos^2(2\theta_B)\right]$$

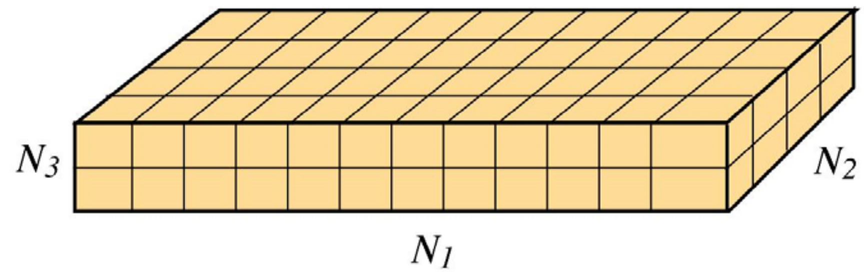
$$= \frac{1 + \cos^2(2\theta_B)}{\sin(\theta_B) \cdot \sin(2\theta_B)}$$

This factor is applied to the integrated intensities for powders in standard diffraction experiments.

$$I \propto m \cdot |F|^2 \cdot L(\theta_B) \cdot M(\theta_B, T)$$

Scattering from a Small Crystal

Assume a parallelepiped shape



$$E \propto F \sum_{n_1=0}^{N_1-1} \mathrm{e}^{2\pi i n_1 (\mathbf{k}'-\mathbf{k})\cdot\mathbf{a}_1} \cdot \sum_{n_2=0}^{N_2-1} \mathrm{e}^{2\pi i n_2 (\mathbf{k}'-\mathbf{k})\cdot\mathbf{a}_2} \cdot \sum_{n_3=0}^{N_3-1} \mathrm{e}^{2\pi i n_3 (\mathbf{k}'-\mathbf{k})\cdot\mathbf{a}_3}$$

$$S = \sum_{n=0}^{N-1} x^n = 1 + x^1 + x^2 + \ldots + x^{N-1}$$

$$xS = \sum_{n=0}^{N-1} x^{n+1} = x^1 + x^2 + \ldots + x^N$$

$$S = \frac{1 - x^N}{1 - x}$$

$$\sum_{n=0}^{N-1} \mathrm{e}^{2\pi i n (\mathbf{k}'-\mathbf{k})\cdot\mathbf{a}} = \frac{1 - \mathrm{e}^{2\pi i N (\mathbf{k}'-\mathbf{k})\cdot\mathbf{a}}}{1 - \mathrm{e}^{2\pi i (\mathbf{k}'-\mathbf{k})\cdot\mathbf{a}}}$$

$$\left| \frac{1 - \mathrm{e}^{2\pi i N (\mathbf{k}'-\mathbf{k})\cdot\mathbf{a}}}{1 - \mathrm{e}^{2\pi i (\mathbf{k}'-\mathbf{k})\cdot\mathbf{a}}} \right|^2 = \left\{ \frac{\sin\left[\pi N (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{a}\right]}{\sin\left[\pi (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{a}\right]} \right\}^2$$

$$I \propto |F|^2 \left\{ \frac{\sin\left[\pi N_1 (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{a}_1\right]}{\sin\left[\pi (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{a}_1\right]} \right\}^2 \cdot \left\{ \frac{\sin\left[\pi N_2 (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{a}_2\right]}{\sin\left[\pi (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{a}_2\right]} \right\}^2 \cdot \left\{ \frac{\sin\left[\pi N_3 (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{a}_3\right]}{\sin\left[\pi (\mathbf{k}' - \mathbf{k}) \cdot \mathbf{a}_3\right]} \right\}^2$$

Small Crystal $\Leftrightarrow$ Thin Foil

Small Crystal

$$I \propto |F|^2 \left\{ \frac{\sin[\pi N(\mathbf{k}' - \mathbf{k})\cdot\mathbf{a}]}{\sin[\pi(\mathbf{k}' - \mathbf{k})\cdot\mathbf{a}]} \right\}^2$$

$$= |F|^2 \left[\frac{\sin(\pi N \mathbf{s}\cdot\mathbf{a})}{\sin(\pi \mathbf{s}\cdot\mathbf{a})} \right]^2$$

$$\approx |F|^2 \left[\frac{\sin(\pi N \mathbf{s}\cdot\mathbf{a})}{\pi \mathbf{s}\cdot\mathbf{a}} \right]^2$$

$$= N^2 |F|^2 \operatorname{sinc}^2(\pi N \mathbf{s}\cdot\mathbf{a})$$

$$\mathbf{k}' = \mathbf{k} + \mathbf{g} + \mathbf{s}$$

$$\mathbf{g}\cdot\mathbf{a} = n \ \text{(integer)}$$

$$(\mathbf{k}' - \mathbf{k})\cdot\mathbf{a} = (\mathbf{g} + \mathbf{s})\cdot\mathbf{a} = n + \mathbf{s}\cdot\mathbf{a}$$

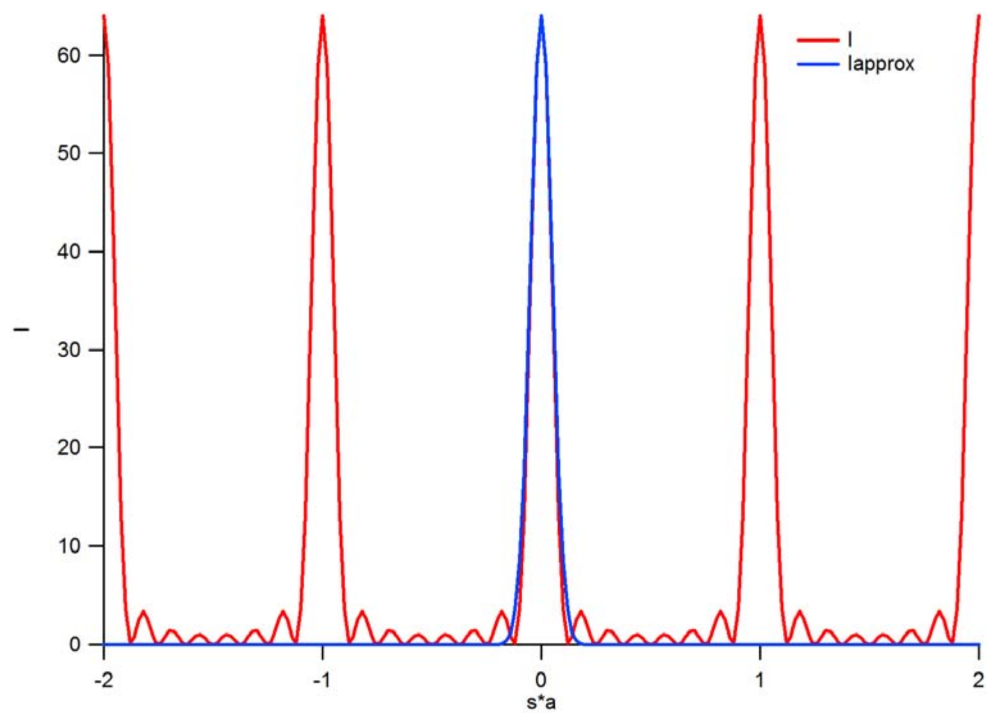
Thin Foil

$$I_{\mathbf{g}} = \left(\frac{\pi T}{\xi} \right)^2 \cdot \operatorname{sinc}^2(\pi s T)$$

Approximation

Near the Bragg condition:

$$\frac{\sin^2(\pi N \mathbf{s}\cdot\mathbf{a})}{\sin^2(\pi \mathbf{s}\cdot\mathbf{a})} \approx N^2 e^{-\pi(N\mathbf{s}\cdot\mathbf{a})^2} \longrightarrow I' \approx N^2 |F|^2 e^{-\pi(N\mathbf{s}\cdot\mathbf{a})^2}$$



Particle-size broadening

$$\mathbf{q} = \mathbf{k}' - \mathbf{k} = \mathbf{g} + \mathbf{s}$$

radial scan: $\mathbf{s} \parallel \mathbf{g} \parallel \mathbf{a}$

TEM convention: $q = \dfrac{2\sin\theta}{\lambda} \longrightarrow \dfrac{dq}{d\theta} = \dfrac{2\cos\theta}{\lambda} \longrightarrow s = \Delta q = \dfrac{2\cdot\Delta\theta\cdot\cos\theta}{\lambda}$

$$\mathbf{s}\cdot\mathbf{a} = s\cdot a = \frac{\Delta(2\theta)\cdot\cos\theta}{\lambda}\cdot a \qquad I' = I_{\max}\cdot e^{-\pi\left\{N\cdot\left[\frac{\Delta(2\theta)\cdot\cos\theta}{\lambda}\right]\cdot a\right\}^2}$$

Particle size: $L = Na$

FWHM: $\dfrac{1}{2}I_{\max} = I_{\max}\cdot e^{-\pi[L\cdot(\pm\Delta\theta)\cdot\cos\theta/\lambda]^2}$

Scherrer equation: $\Delta(2\theta) = 2\cdot(\Delta\theta) = \dfrac{2\sqrt{\dfrac{\ln 2}{\pi}}\cdot\lambda}{L\cdot\cos\theta} = \dfrac{(0.94)\lambda}{L\cdot\cos\theta}$ $\qquad K = 0.94$

Some Broadening Contributions to Δq

Influence of Δ(2θ) on Δq:

$$\frac{dq}{d\theta} = \frac{2\cos\theta}{\lambda}$$

$$\Delta q = \frac{2\cos\theta}{\lambda} \cdot \Delta\theta$$

$$\Delta q = \frac{\cos\theta}{\lambda} \cdot \Delta(2\theta)$$

Particle Size:

$$\Delta(2\theta)_L = \frac{K\lambda}{L\cos\theta} \qquad \Delta q_L = \frac{K}{L}$$

Spread in Wavelength:

$$\frac{dq}{d\lambda} = \frac{-2\sin\theta}{\lambda^2}$$

$$= -\frac{q}{\lambda}$$

$$\Delta q_\lambda = q \cdot \frac{\Delta\lambda}{\lambda}$$

More Broadening

"Microstrain":

$$q = \frac{1}{D}$$

$$\frac{dq}{dD} = -\frac{1}{D^2} = -\frac{q}{D}$$

$$D \propto a \qquad \frac{dD}{D} = \frac{da}{a}$$

$$\Delta q_a = q\left(\frac{\Delta a}{a}\right)$$

Optical Spread:

$$q = \frac{2\sin\theta}{\lambda}$$

$$\Delta q_\theta = \frac{2\cos\theta}{\lambda} \cdot \Delta\theta$$

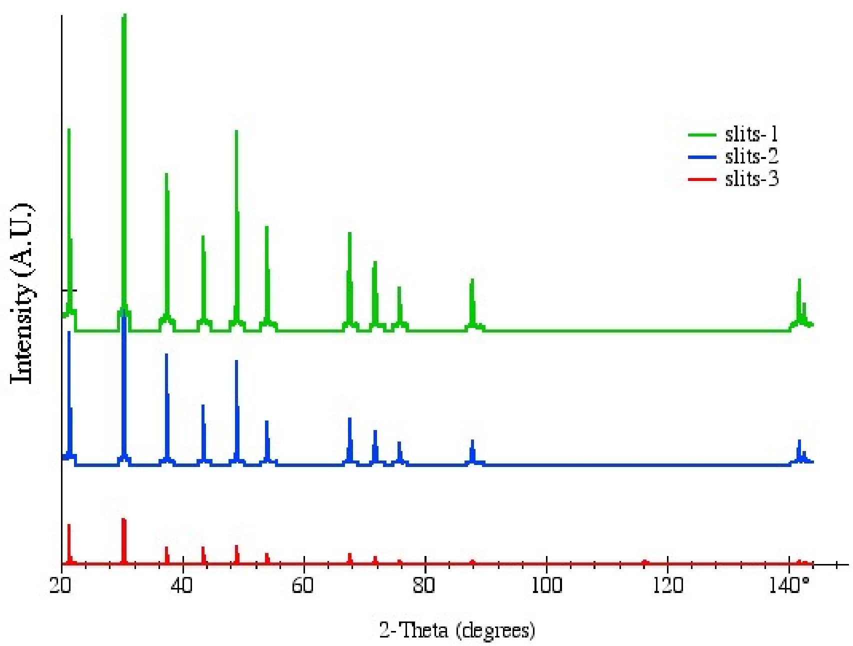
$$\Delta q_\theta = \sqrt{\left(\frac{2}{\lambda}\right)^2 - q^2} \cdot \Delta\theta$$

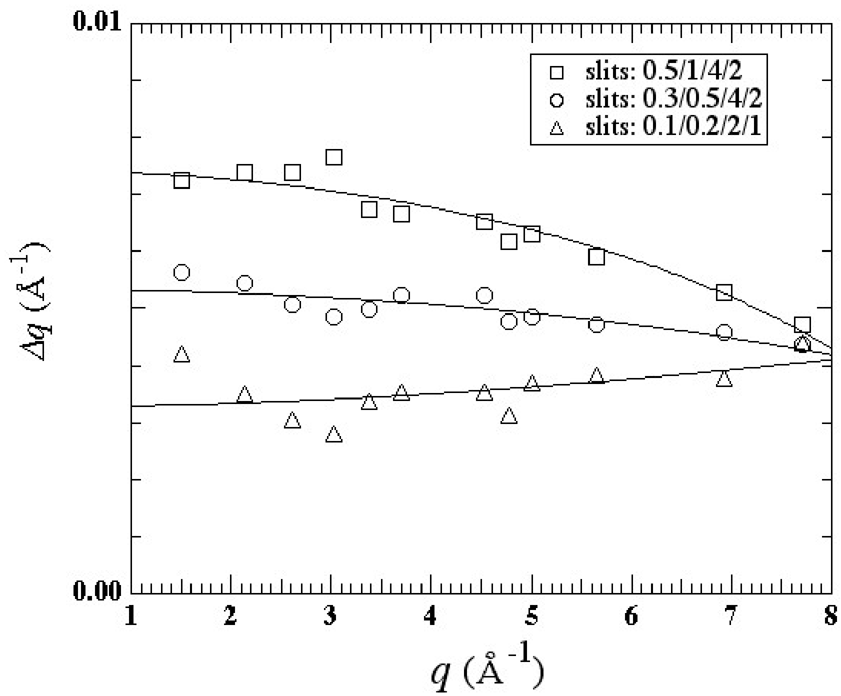
If errors are uncorrelated:

$$\Delta q = \sqrt{(\Delta q_1)^2 + (\Delta q_2)^2 + \ldots}$$

LaB_6 Standard

Measure Instrumental Broadening





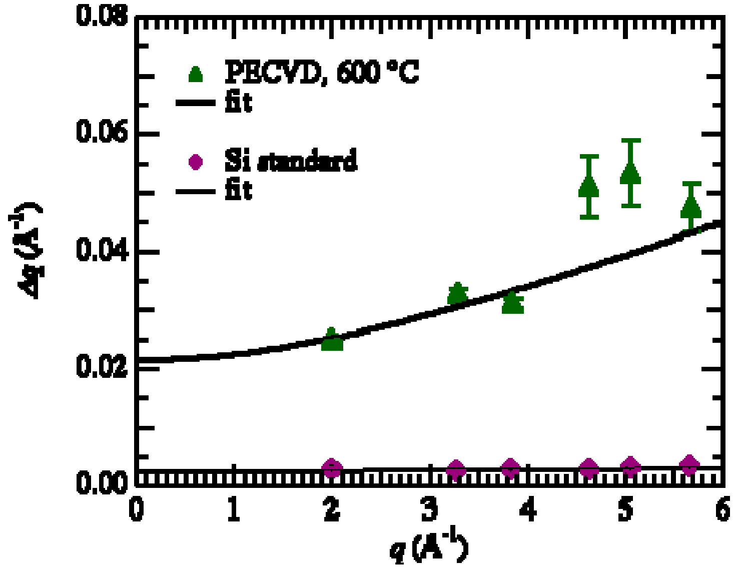
Example: Polycrystalline Si Films

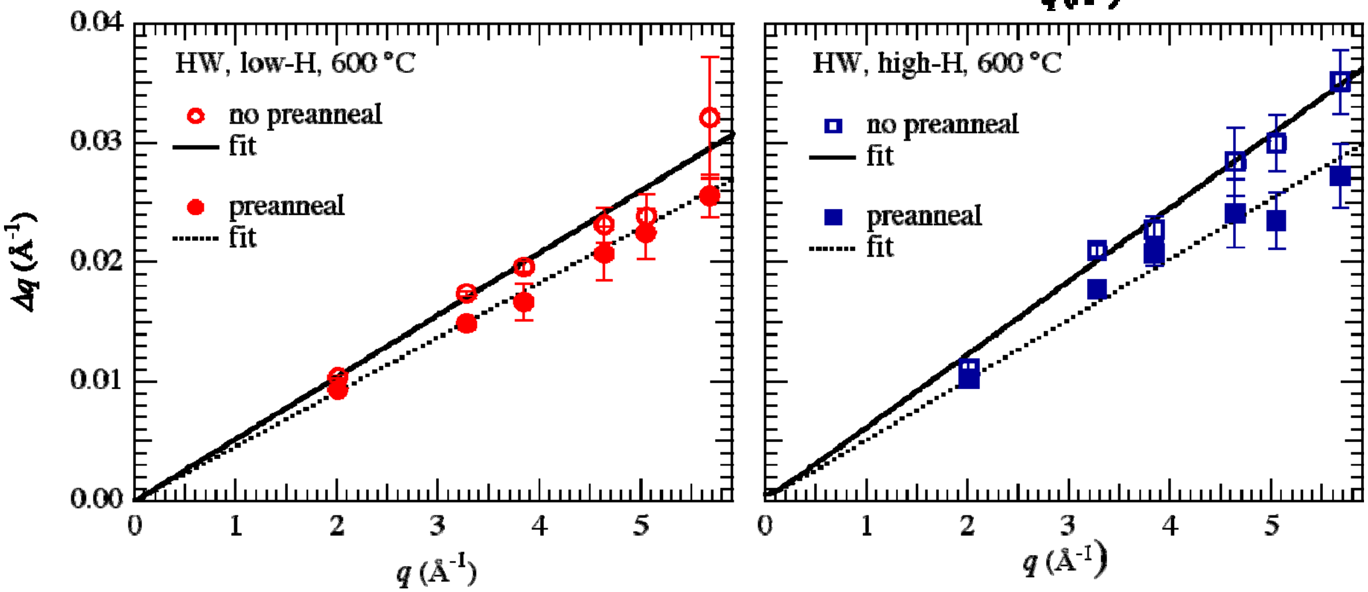
Sample type	HW, low-H	HW, high-H	PECVD
not preannealed:			
L (nm)	-	-	4.6±0.8
$\lvert\varepsilon\rvert$ (%)	0.520±0.004	0.614±0.011	0.70±0.03
preannealed:			
L (nm)	-	-	*no data*
$\lvert\varepsilon\rvert$ (%)	0.503±0.009	0.513±0.009	*no data*

plasma-enhanced CVD

vs.

hot-wire CVD



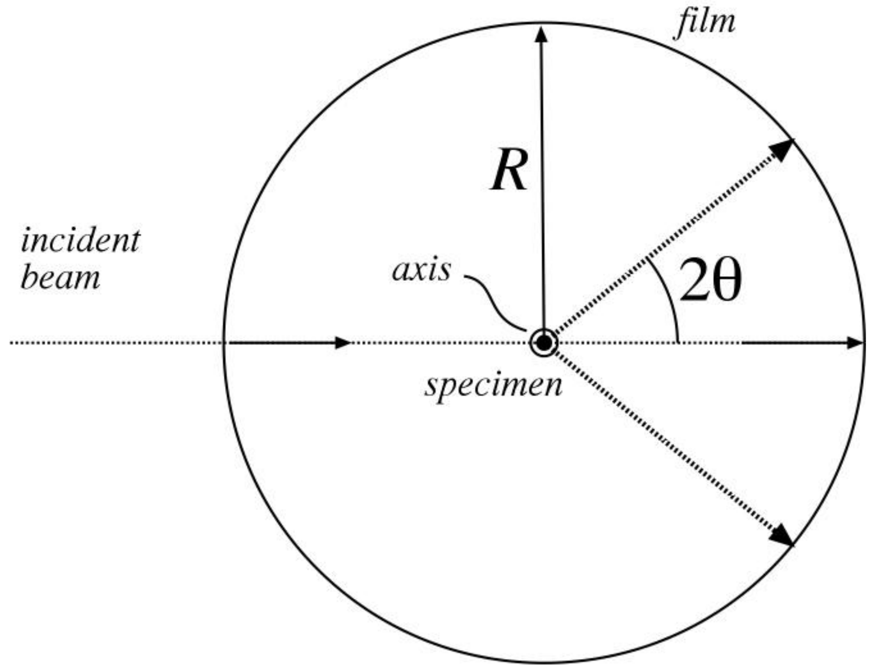


Debye-Scherrer Camera

Primarily a powder camera

Filtered or monochromatic radiation used

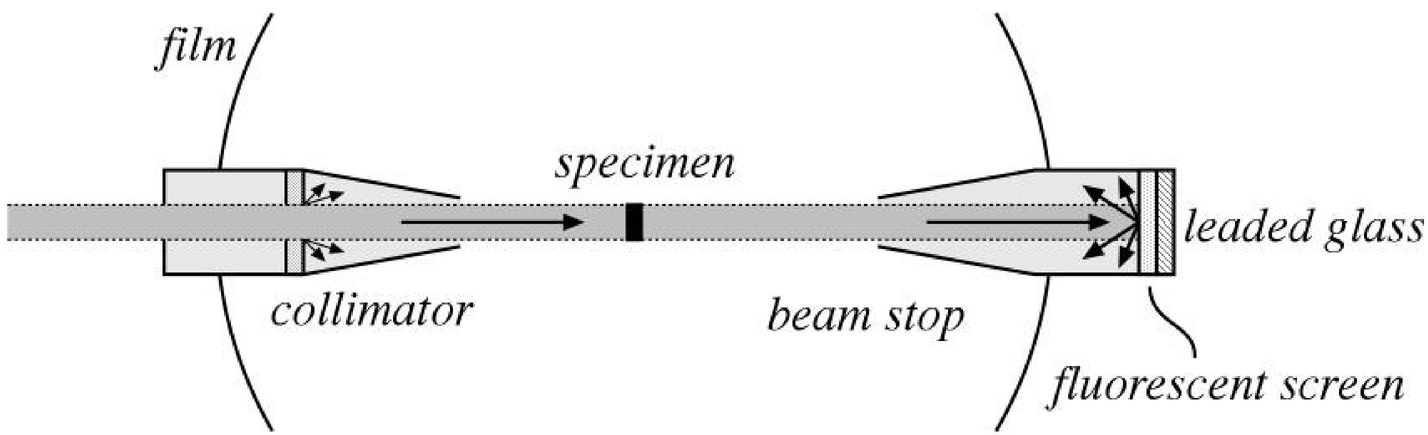
Debye-Scherrer Geometry



Sample is usually powder

Otherwise, rotate specimen about camera axis

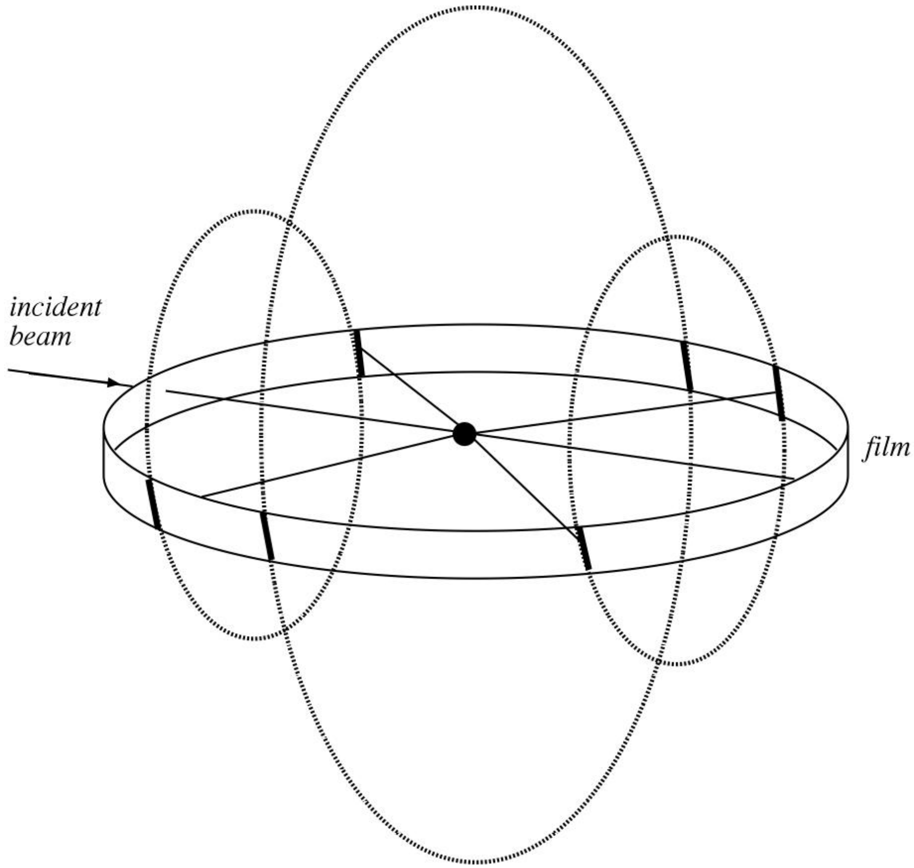
Debye-Scherrer Optics

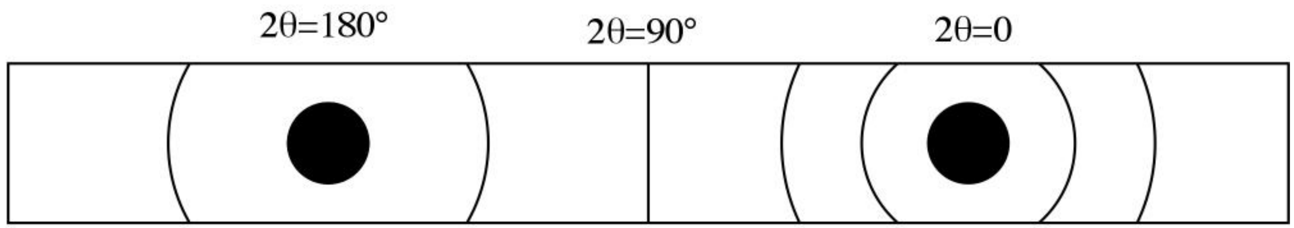


Collimator defines beam

Window used for alignment

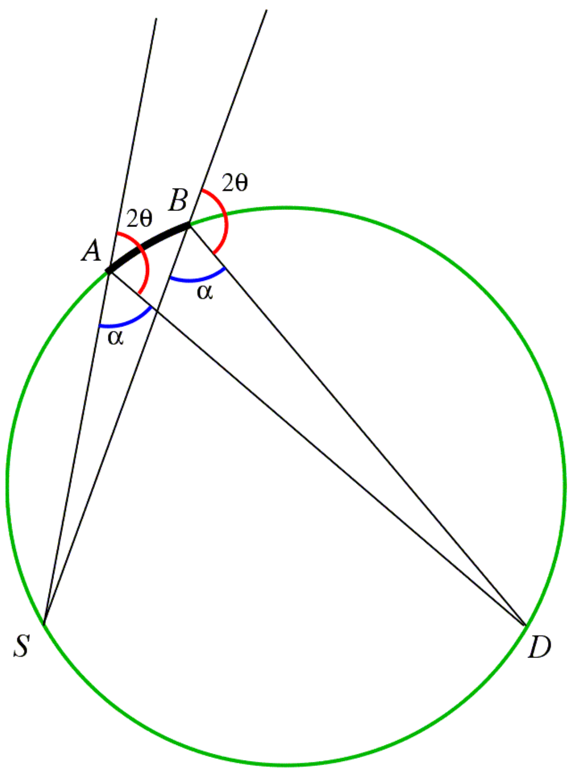
Debye-Scherrer Patterns

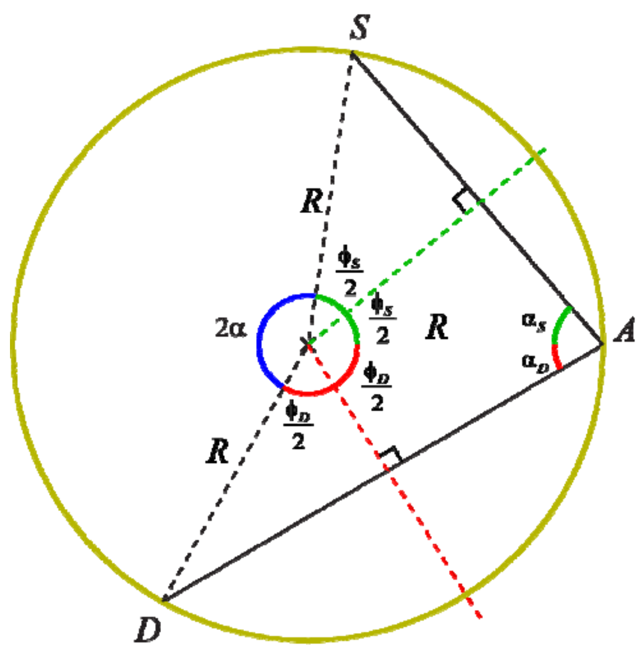




Bragg-Brentano Focusing (1)

If a point source (S), point detector (D) and all points on the sample (e.g., A) are on a circle, then the the angles between S and A is equal to that between D and A.



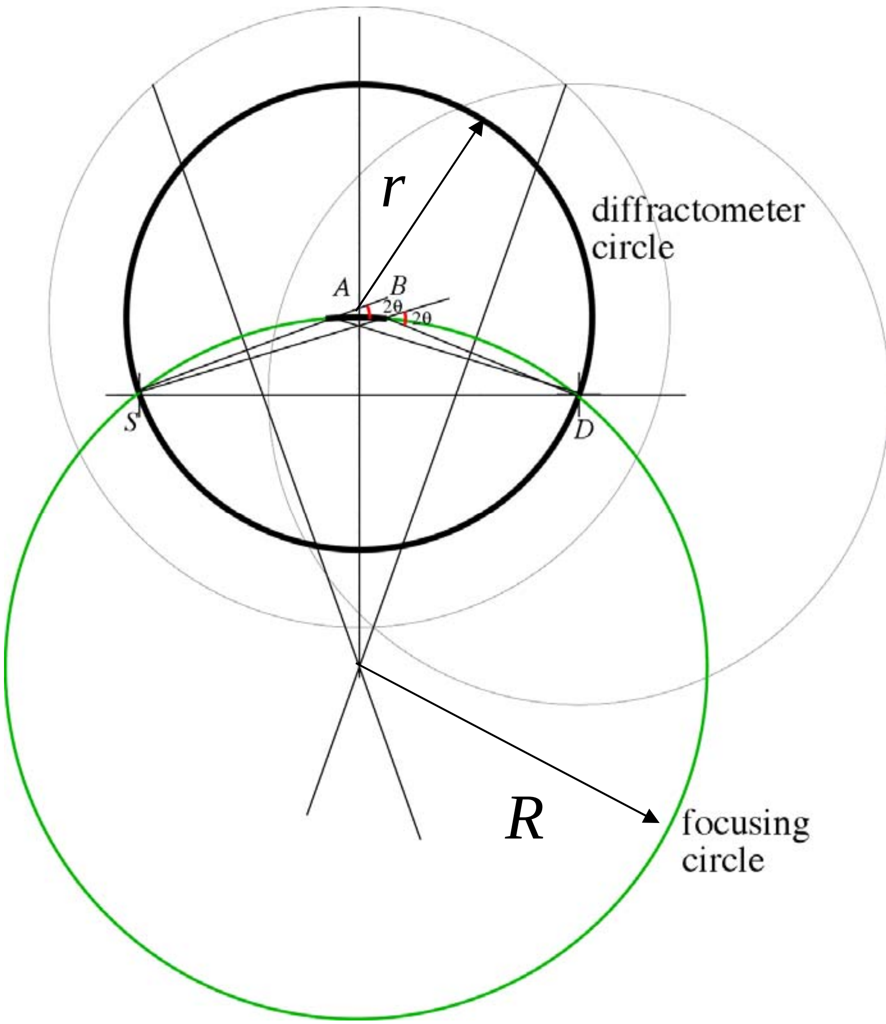


$$\alpha_S = 90° - \frac{\phi_S}{2} \qquad \phi_S = 180° - 2\alpha_S$$

$$\alpha_D = 90° - \frac{\phi_D}{2} \qquad \phi_D = 180° - 2\alpha_D$$

$$360° - \phi_S - \phi_D = 2\alpha_S + 2\alpha_D = 2\alpha$$

Bragg-Brentano Focusing (2)



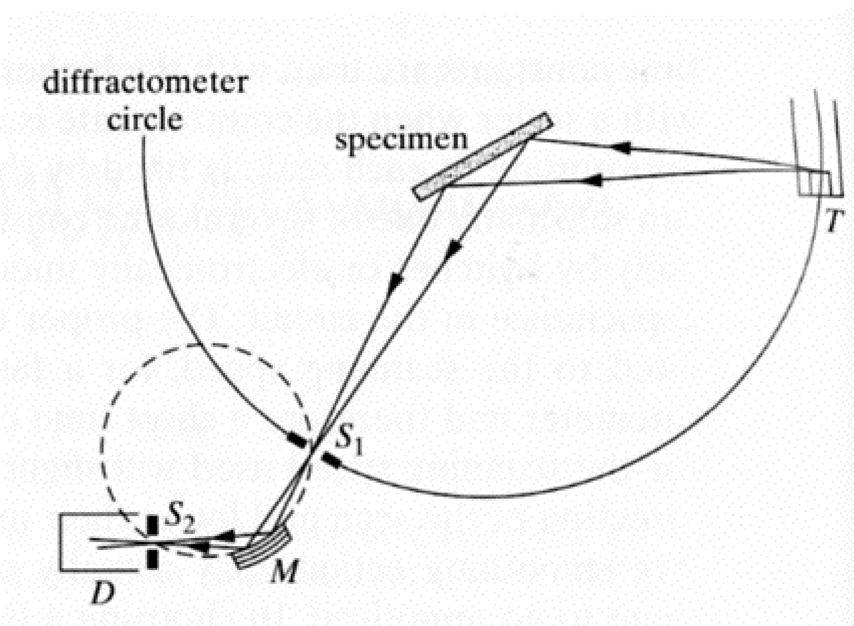
Fixed distances:

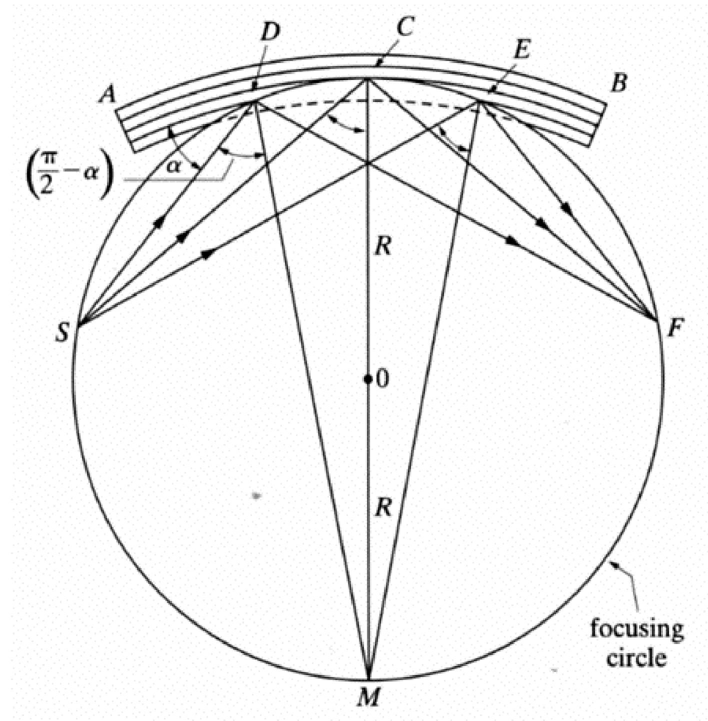
- source-sample
- sample-detector

Focusing circle radius changes with 2θ.

$$r = \frac{R}{2\sin\theta}$$

Cut and Bent Monochromator

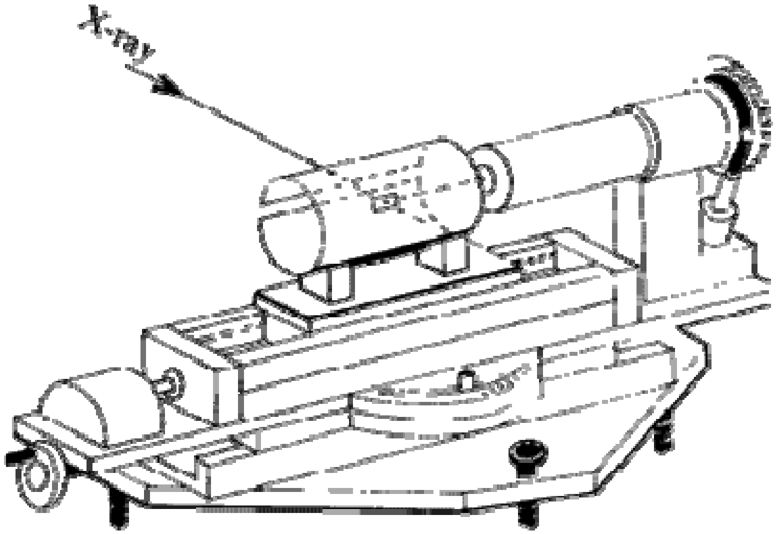


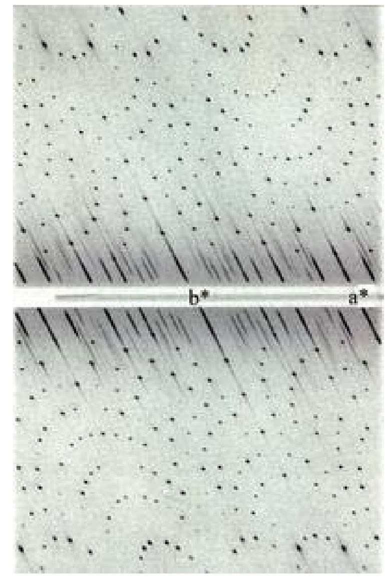


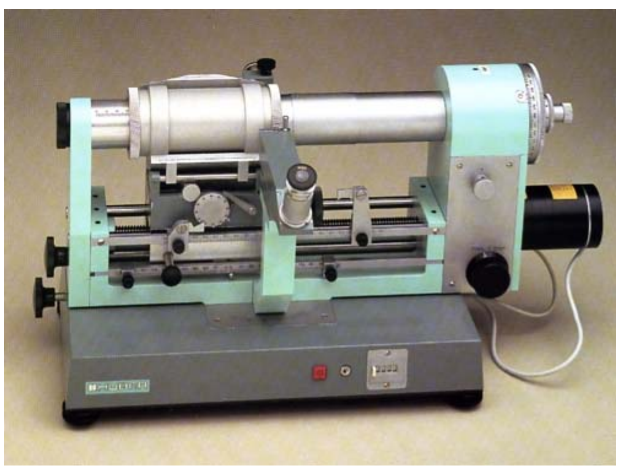
Laue Camera

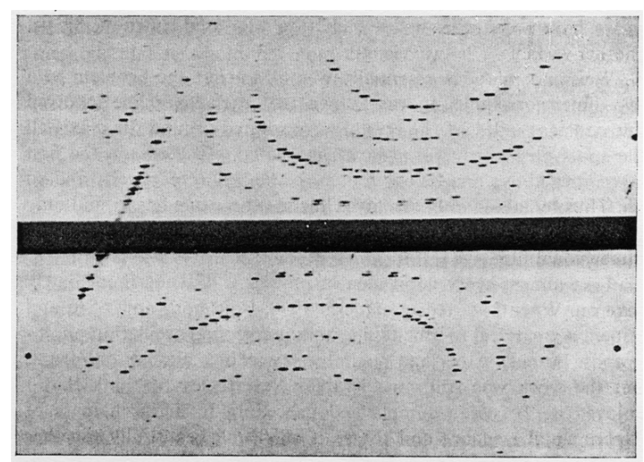
Back-Reflection Transmission

Moving Film Methods (I): Weissenberg Camera

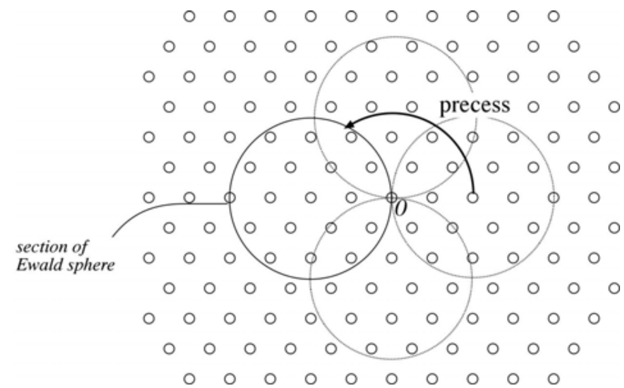


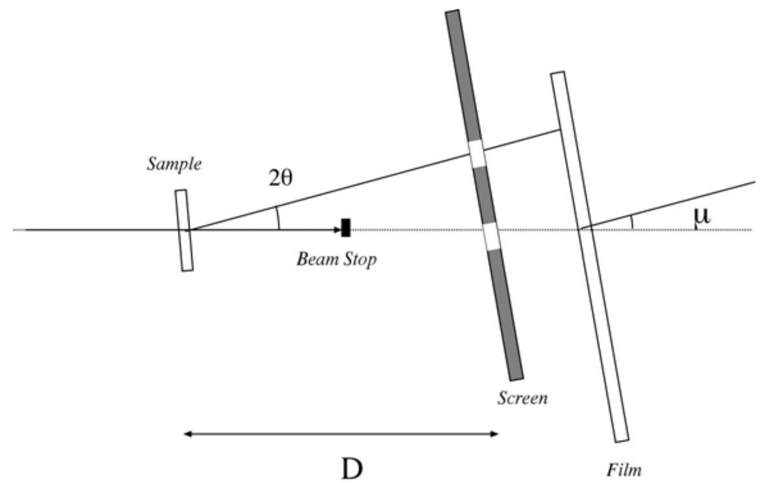






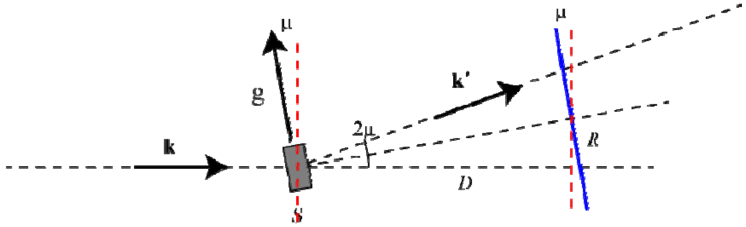
Moving Film Methods (II): Buerger Precession Camera

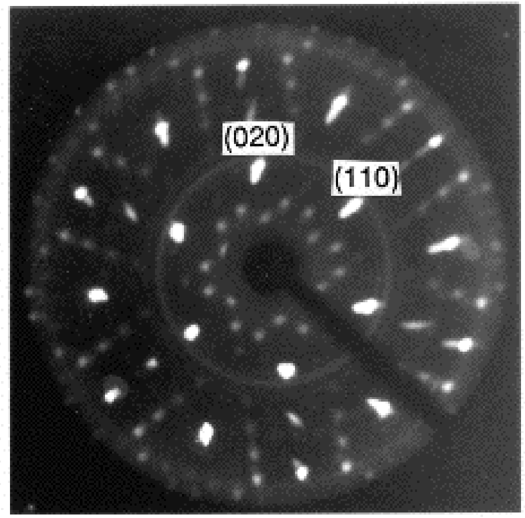


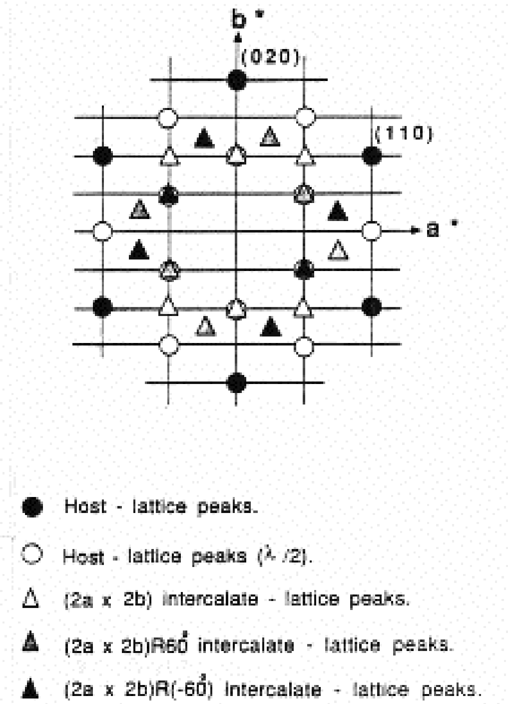


Sample diffraction only at intersection of ZOLZ with sphere

Precession Data

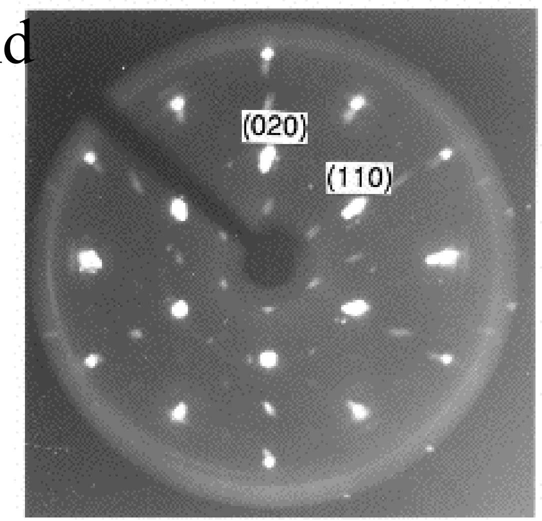




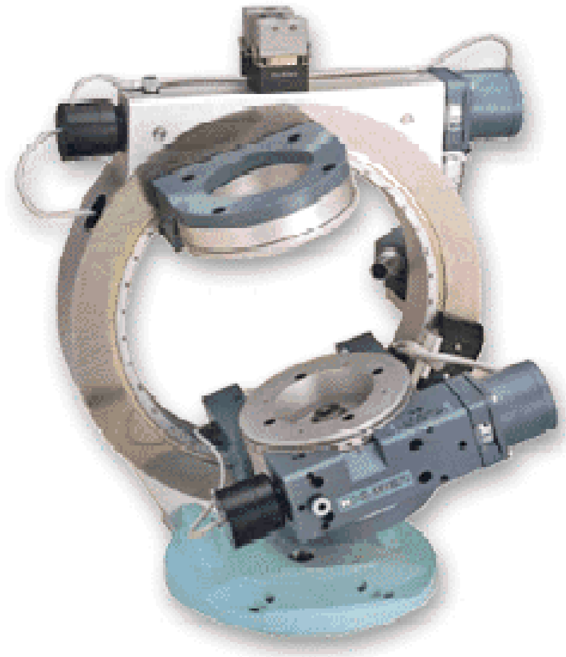


Screen radius, distance, and precession angle related:

$$\sin(\mu) = \frac{R}{D}$$

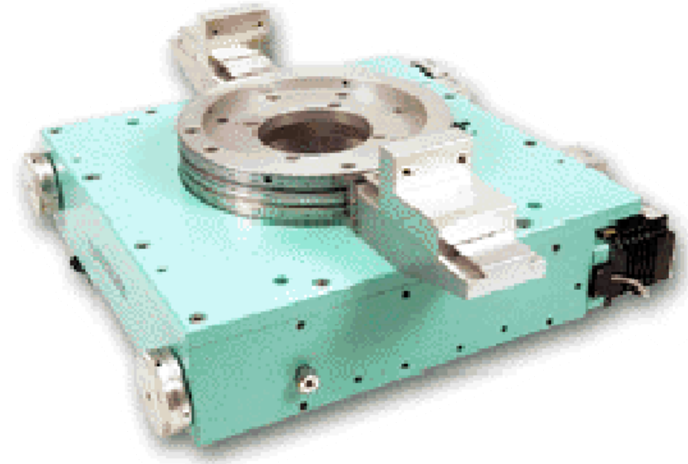


Single-Crystal Diffraction: Goniometers



Eulerian Cradle

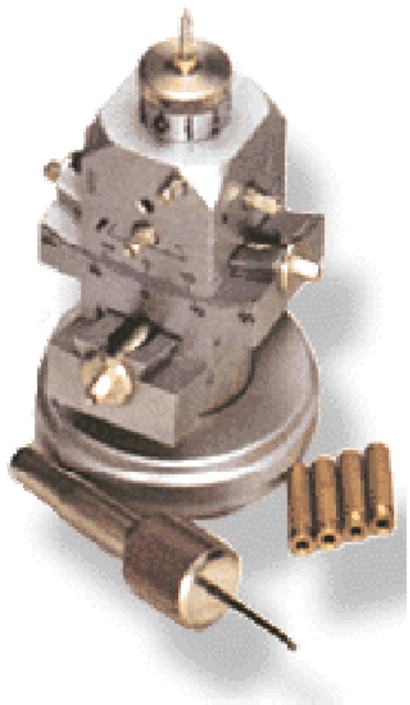
Phi/Chi

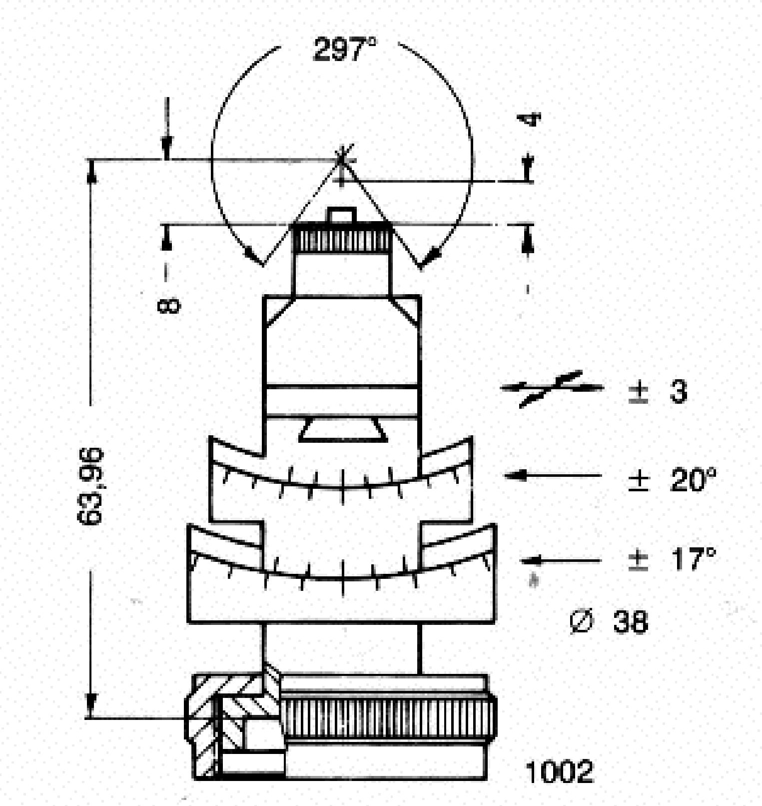


Two-Circle Goniometer

Omega/2-Theta

Goniometer Head





Sample usually mounted on glass fiber

Sample Orientation

$$M \cdot \begin{pmatrix} q \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} = U \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

Diffraction in x-y plane

$$M = \Phi \cdot \mathrm{X} \cdot \Omega$$

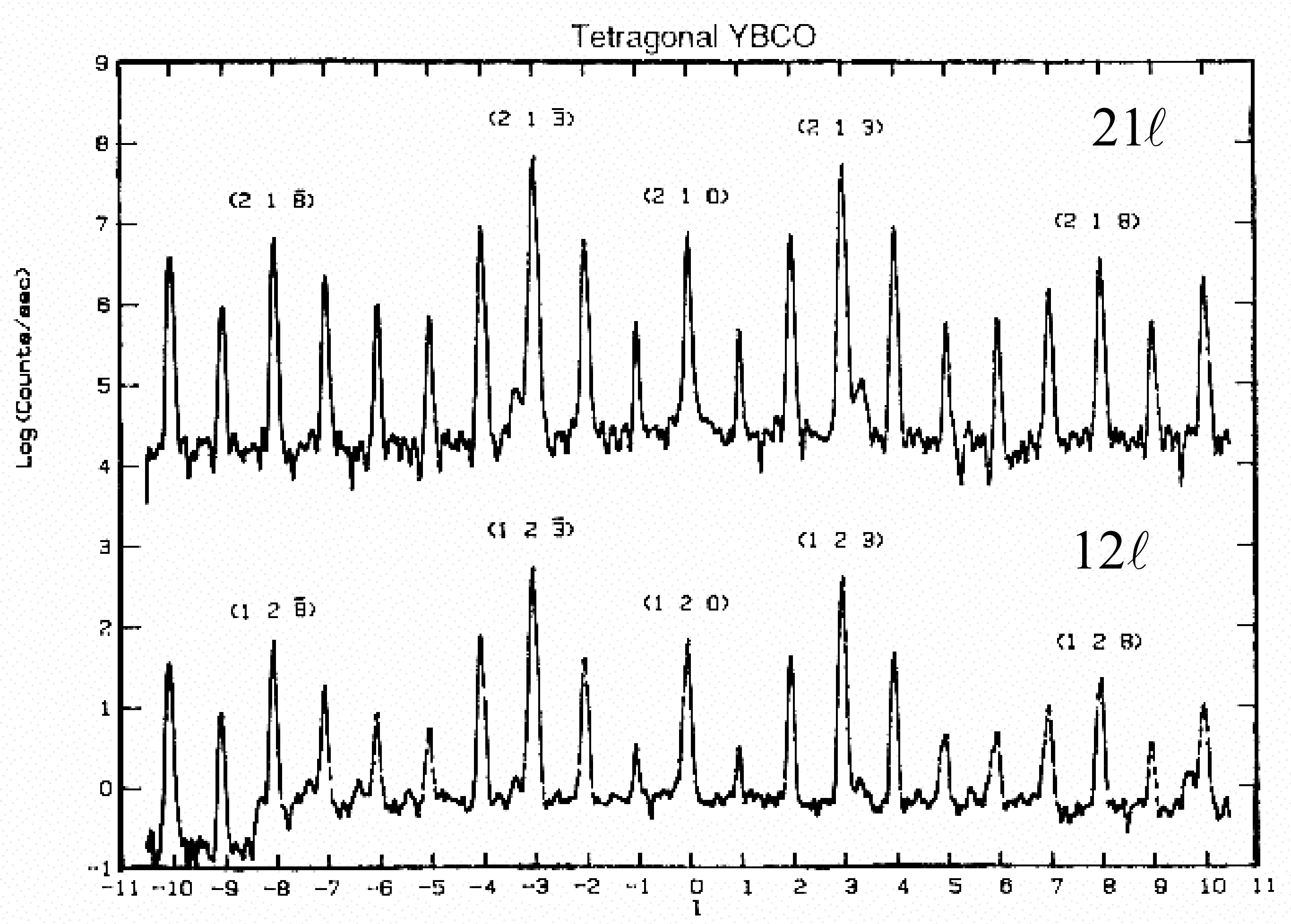
$$\Phi = \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \mathrm{X} = \begin{pmatrix} \cos\chi & 0 & -\sin\chi \\ 0 & 1 & 0 \\ \sin\chi & 0 & \cos\chi \end{pmatrix} \quad \Omega = \begin{pmatrix} \cos\omega & \sin\omega & 0 \\ -\sin\omega & \cos\omega & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Rotate by Bragg Angle

$$T = \begin{pmatrix} \cos(T/2) & \sin(T/2) & 0 \\ -\sin(T/2) & \cos(T/2) & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\begin{pmatrix} q_x \\ q_y \\ 0 \end{pmatrix} = T \begin{pmatrix} q \\ 0 \\ 0 \end{pmatrix}$$

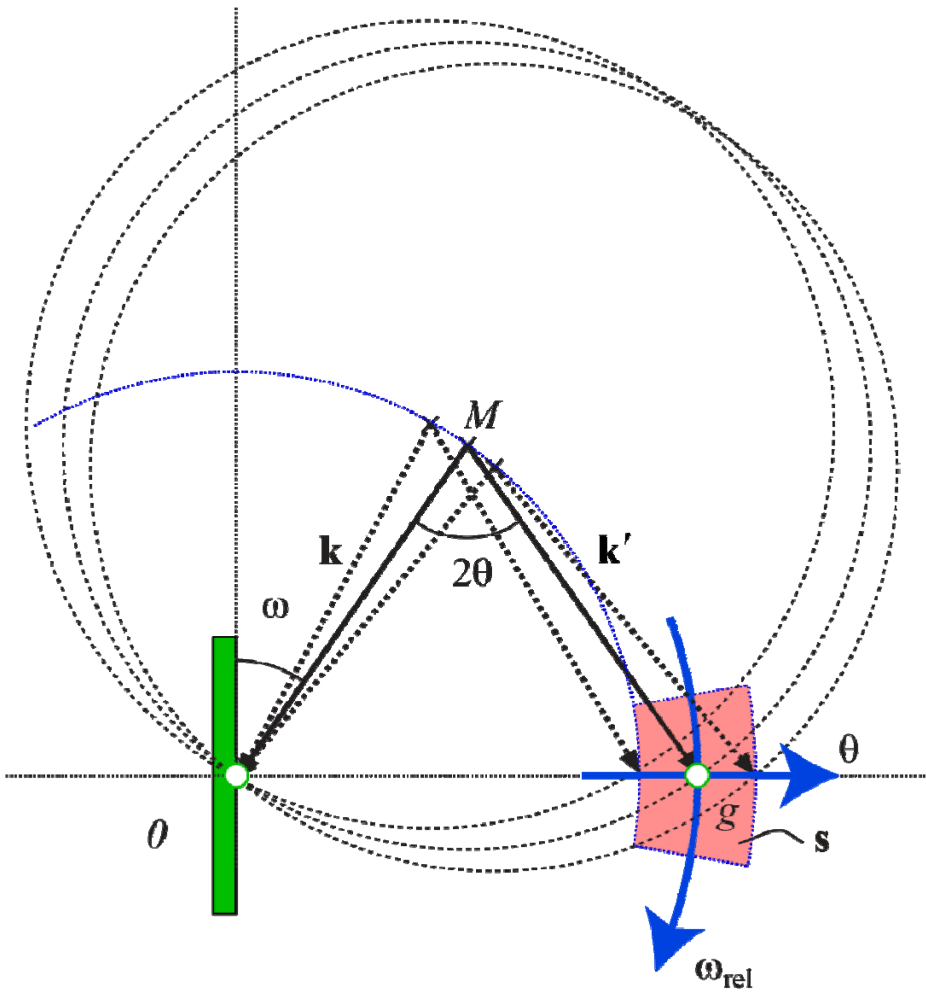
hkl Scans



Tetragonal YBCO
21ℓ
12ℓ
(2 1 $\bar{3}$)
(2 1 3)
(2 1 $\bar{8}$)
(2 1 0)
(2 1 8)
(1 2 $\bar{3}$)
(1 2 3)
(1 2 $\bar{8}$)
(1 2 0)
(1 2 8)
Log (Counts/sec)
l

Reciprocal-Space Mapping

Two-Dimensional Map: $I(\omega_{rel},\theta)$



Each θ scan performed with ω_{rel} fixed.

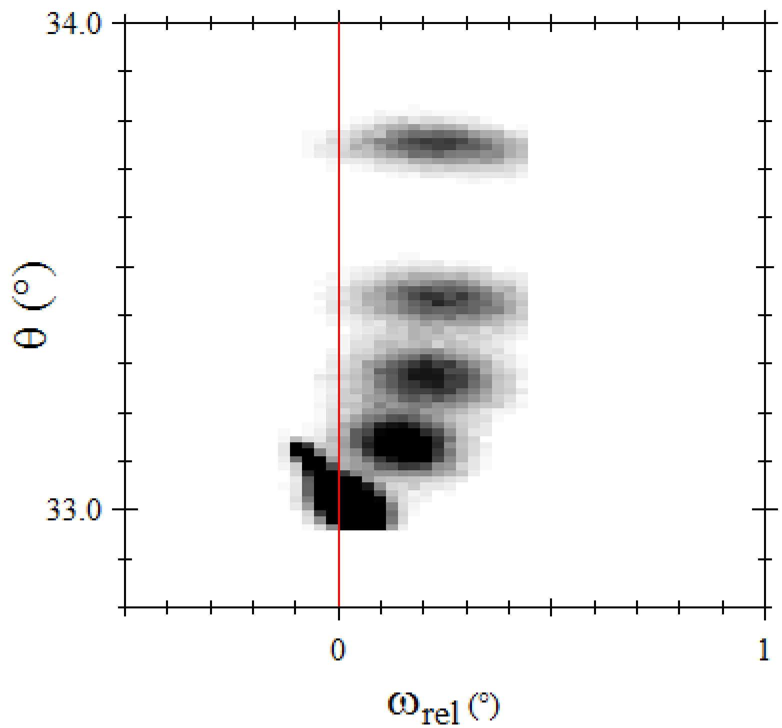
Intensity measured at each point (ω_{rel}, θ).

The two directions of scanning are perpendicular.

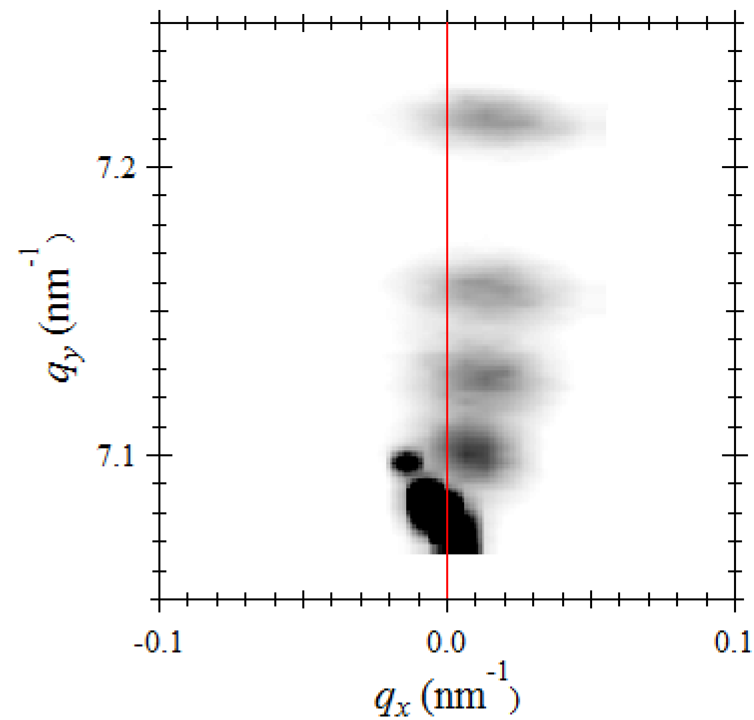
Example

Ga(As,P) on GaAs

004 map



004 RSM

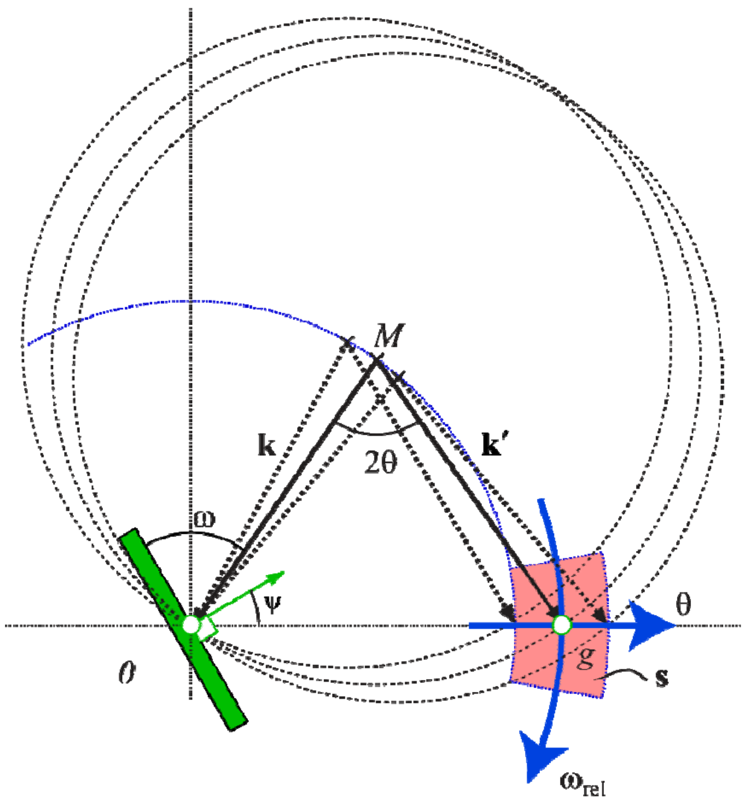


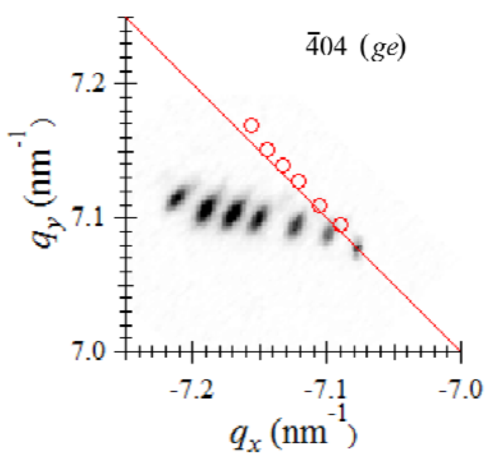
The data are transformed into reciprocal space (i.e., **q**)

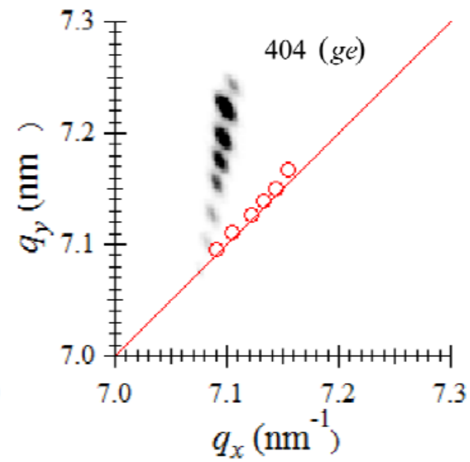
Asymmetric Reflections

$$q_x = 2k\sin\theta\cos(\omega_{rel} \pm \psi)$$
$$q_y = -2k\sin\theta\sin(\omega_{rel} \pm \psi)$$

(-) grazing incidence
(+) grazing exit







Influence of Strain

strain tensor:

$$\tilde{\varepsilon} = \begin{pmatrix} \varepsilon_x & 0 & 0 \\ 0 & \varepsilon_y & 0 \\ 0 & 0 & \varepsilon_z \end{pmatrix}$$

unstrained:

$$\mathbf{g}_0 = \tilde{B}_0 \cdot \begin{pmatrix} h \\ k \\ \ell \end{pmatrix}$$

$$\tilde{B}_0 = \left(\tilde{A}_0^{-1}\right)^T$$

strained:

$$\tilde{A} = \left(\tilde{1} + \tilde{\varepsilon}\right) \cdot \tilde{A}_0$$

$$\tilde{B} = \left(\tilde{A}^{-1}\right)^T = \left(\tilde{1} - \tilde{\varepsilon}\right) \cdot \tilde{B}_0$$

$$\mathbf{g} = \tilde{B} \cdot \begin{pmatrix} h \\ k \\ \ell \end{pmatrix} = \left(\tilde{1} - \tilde{\varepsilon}\right) \cdot \mathbf{g}_0$$

Measuring Strain

$$\mathbf{g}_0 = g_0 \begin{pmatrix} \cos\phi \cdot \sin\psi \\ \sin\phi \cdot \sin\psi \\ \cos\psi \end{pmatrix}$$

$$g_0 = \frac{\sqrt{h^2 + k^2 + \ell^2}}{a_0}$$

$$\mathbf{g} = (1 - \tilde{\varepsilon}) \cdot \mathbf{g}_0 = g_0 \begin{pmatrix} (1-\varepsilon_x) \cdot \cos\phi \cdot \sin\psi \\ (1-\varepsilon_y) \cdot \sin\phi \cdot \sin\psi \\ (1-\varepsilon_z) \cdot \cos\psi \end{pmatrix}$$

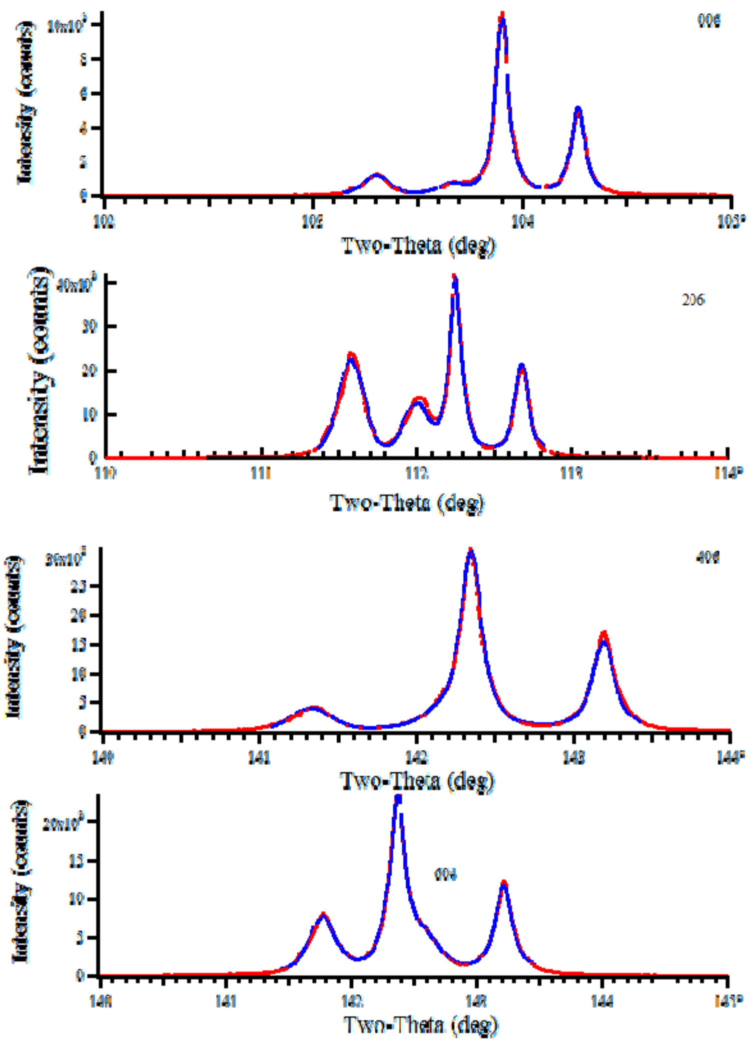
$$g \approx g_0 \left[1 - \left(\varepsilon_x \cdot \cos^2\phi + \varepsilon_y \cdot \sin^2\phi \right) \cdot \sin^2\psi - \varepsilon_z \cdot \cos^2\psi \right] = \frac{\sqrt{h^2 + k^2 + \ell^2}}{a(\phi, \psi)}$$

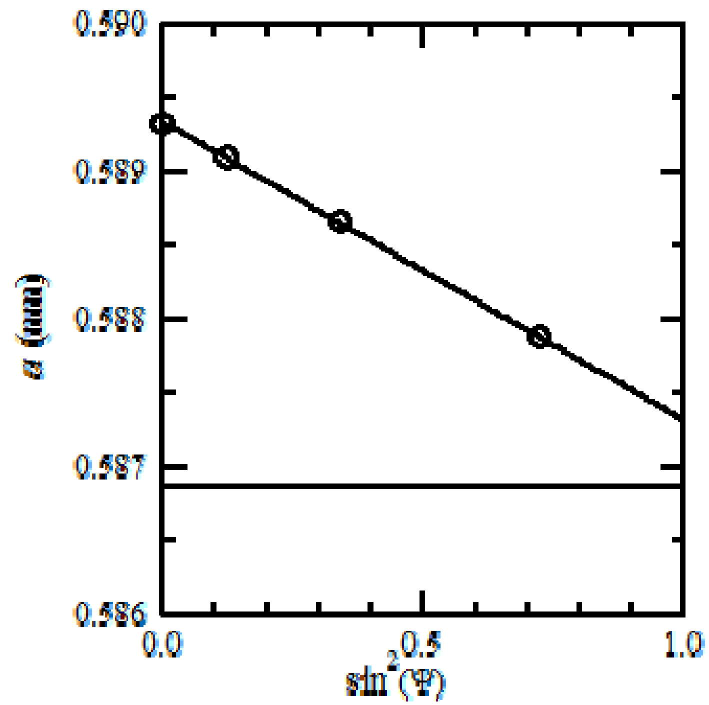
For a particular ϕ:

$$g = g_0 \left[1 - \varepsilon_{\parallel} \cdot \sin^2\psi - \varepsilon_{\perp} \cdot \cos^2\psi \right] = \frac{\sqrt{h^2 + k^2 + \ell^2}}{a(\psi)}$$

$$a(\psi) = a_{\parallel} \cdot \sin^2\psi + a_{\perp} \cdot \cos^2\psi = a_{\perp} + \left(a_{\parallel} - a_{\perp} \right) \cdot \sin^2\psi$$

Fitting Data





1-921: GaInPAs

apara =0.58732 nm
aperp=0.589337 nm

Single-Crystal Substrate Restrictions

(001) orientation

$(h0\ell)$ plane

Ewald Sphere

$$h_{\max} = \left(\frac{2a}{\lambda}\right)\cdot \sin\Psi$$

$$\ell_{\max} = \left(\frac{2a}{\lambda}\right)\cdot \cos\Psi$$

$$0 \le \Psi < 90^\circ$$

$$\sin\theta_B = \frac{\lambda}{2d}$$

$$\cos\Psi = \frac{\ell}{\sqrt{h^2+\ell^2}}$$

$$\sin\Psi = \frac{h}{\sqrt{h^2+\ell^2}}$$

$$\Psi + \theta_B < 90^\circ$$

Unobstructed

$$d_{\min} = \frac{\lambda}{2}$$

$$d_{\min} = \frac{a}{\sqrt{h_{\max}^2+\ell_{\max}^2}}$$

$$\sqrt{h_{\max}^2+\ell_{\max}^2} = \frac{2a}{\lambda}$$

$$h_{\max} = x\cdot\left(\frac{2a}{\lambda}\right)$$

$$\ell_{\max} = \sqrt{1-x^2}\cdot\left(\frac{2a}{\lambda}\right)$$

$$0 \le x < 1$$