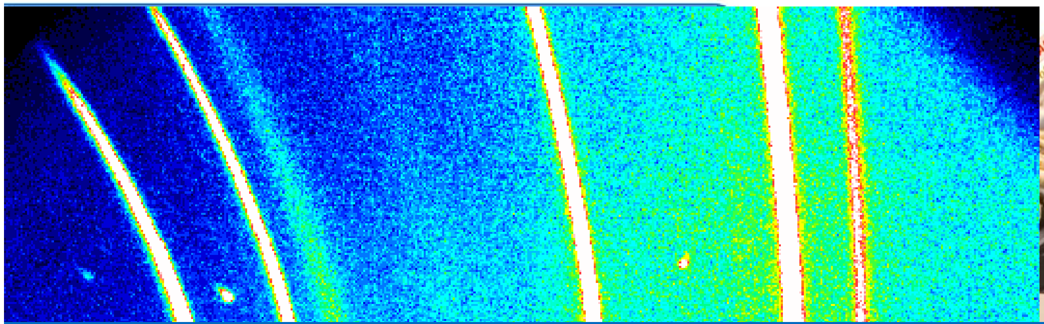
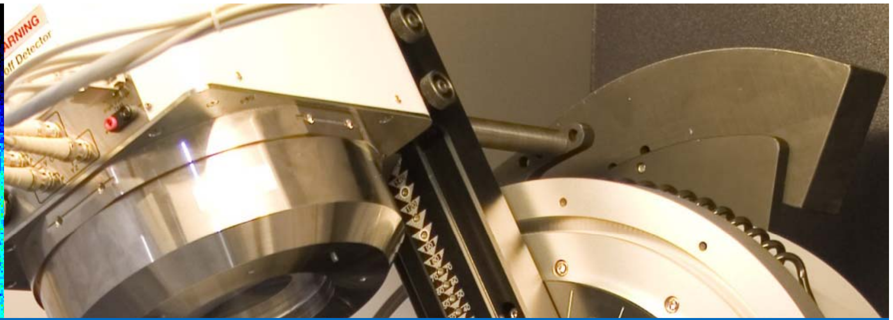
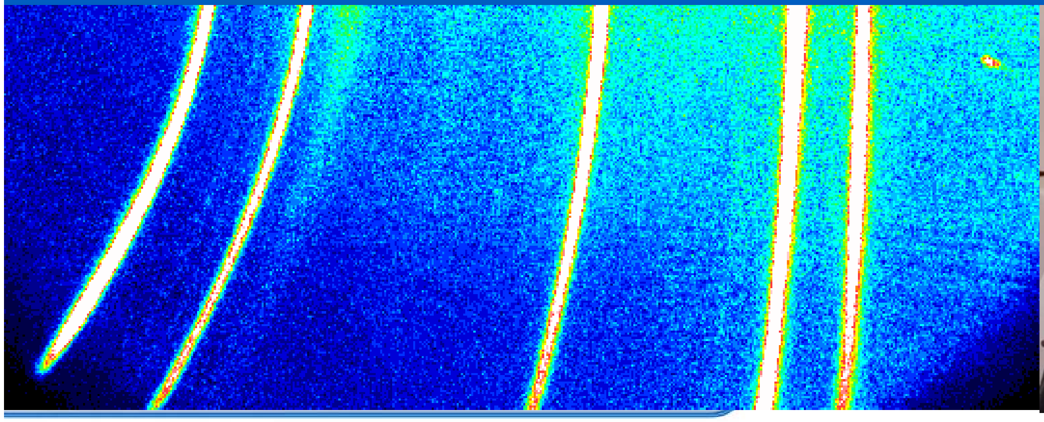
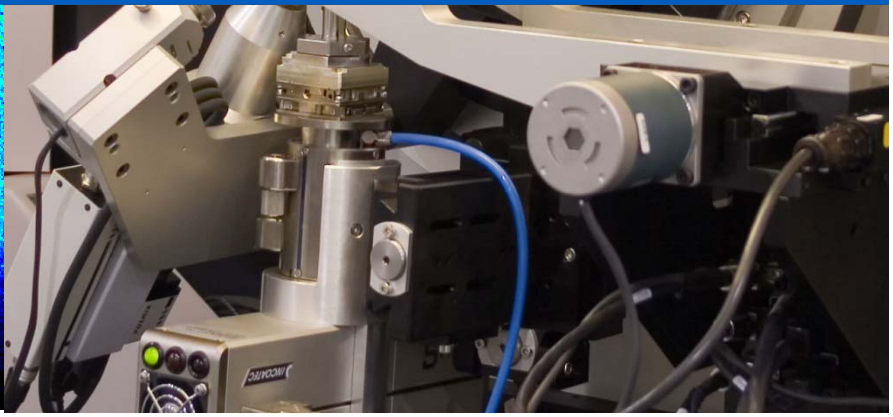



Geometry, Polarization and Absorption Corrections
for Two-dimensional X-ray Diffraction

Bob He Bruker AXS, Inc.

This document was presented at PPXRD - Pharmaceutical Powder X-ray Diffraction Symposium

Sponsored by The International Centre for Diffraction Data

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PPXRD Website – www.icdd.com/ppxrd ICDD Website - www.icdd.com

XRD²: What do we know about two-dimensional XRD?

Most recognized features of XRD² for pharmaceutical:

- High speed: 10^2 higher than XRD with a point detector
- Reliable info: Integration in γ (ring) direction
- Micro scale sample: Point beam and 2D pattern

Most concerns with XRD²:

- Resolution and geometry defocusing
- Relative intensity is different from Bragg-Brentano
- Higher instrument cost (but much higher productivity)

This presentation interprets the differences and suggests the best use of XRD² systems

X-ray Applications for typical pharmaceutical samples

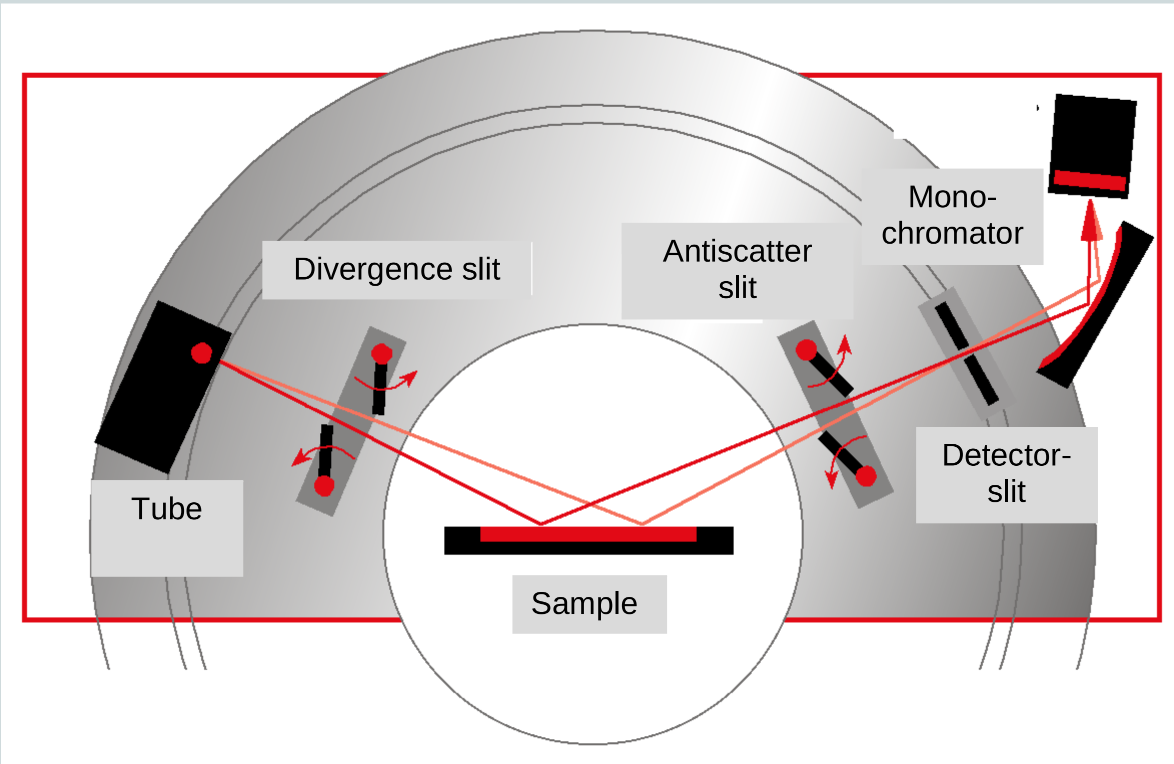
XRD & XRD^2	Single Crystal	Several Grains	Powder	Finished Product	Solutions
Qualitative Phase ID	✓Φ⊕	✓Φ⊕	✓Φ	✓Φ	✓Φ
Quantitative Rietveld analysis			✓		
Quantitative analysis with standards		✓	✓	✓	
X-ray movie, Non-Ambient	✓Φ	✓Φ	✓Φ	✓Φ	✓Φ
Structure solution, Indexing	✓Φ		✓		
Microdiffraction/ Mapping		✓Φ⊕	✓Φ⊕	✓Φ⊕	
Shape analysis			✓Φ	✓Φ	✓Φ
HTS	✓Φ⊕	✓Φ⊕	✓Φ⊕		
Grain-Size det.		✓Φ	✓Φ		
%Crystallinity		✓Φ⊕	✓Φ⊕	✓Φ⊕	✓Φ⊕

✓- can be performed by either XRD or XRD^2

Φ – better with XRD^2

⊕ - accept performance and accurate results only with XRD^2

Bragg-Brentano-Geometry



Advantages

☑ Resolution

☑ Less expensive

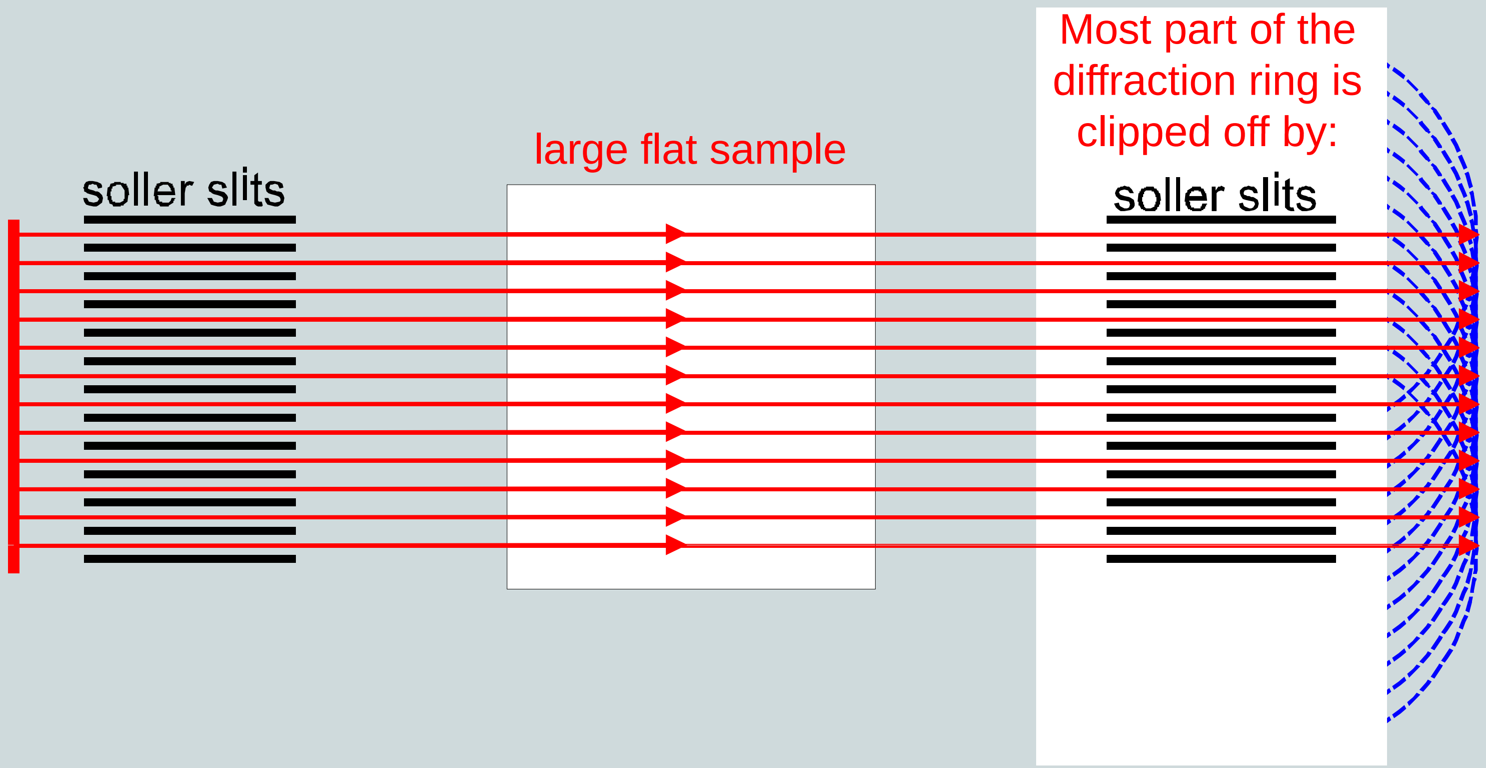
Disadvantages

☒ Requires flat sample surface

☒ Requires bulky powder sample

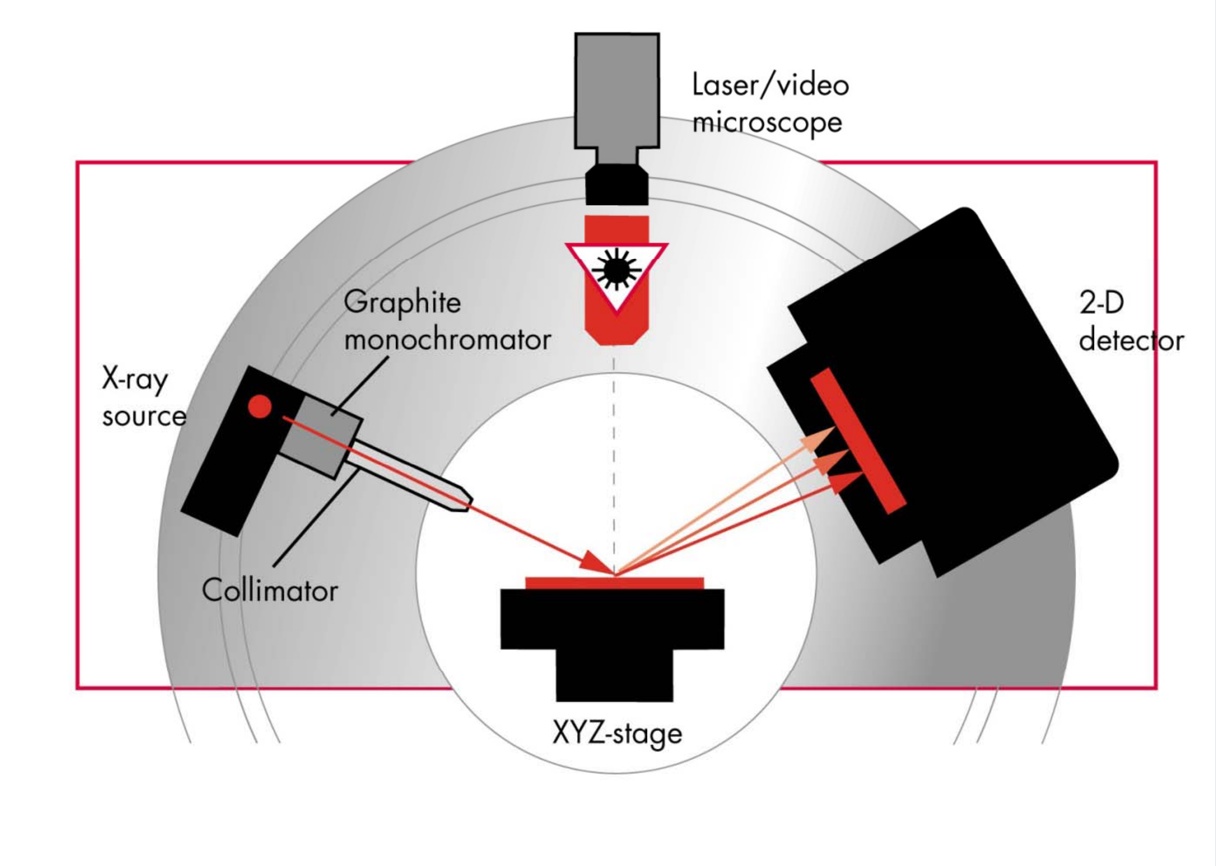
☒ Slow

Soller slits are used to control axial divergence



- In Bragg-Brentano geometry, the line focus beam can be considered as a superposition of point beams.
- All in parallel with the diffractometer plane and the same geometry condition separated by soller slit foils.

XRD²: Two-dimensional X-ray Diffraction



Advantages

☑ High speed

☑ Micro scale sample

☑ Virtual oscillation (large grain size & preferred orientation)

Disadvantages

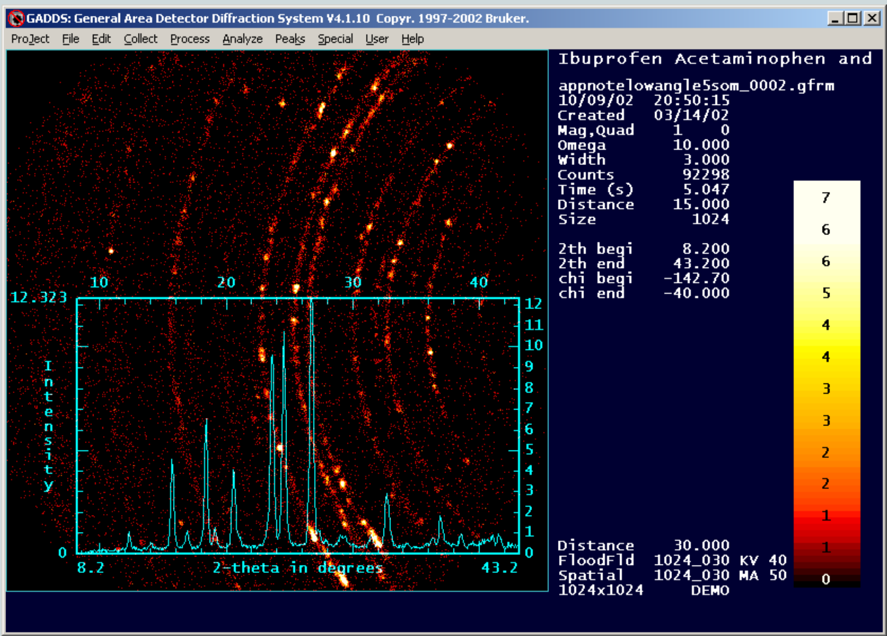
☒ Resolution is limited by the detector PSF

☒ Defocusing at low angle in reflection

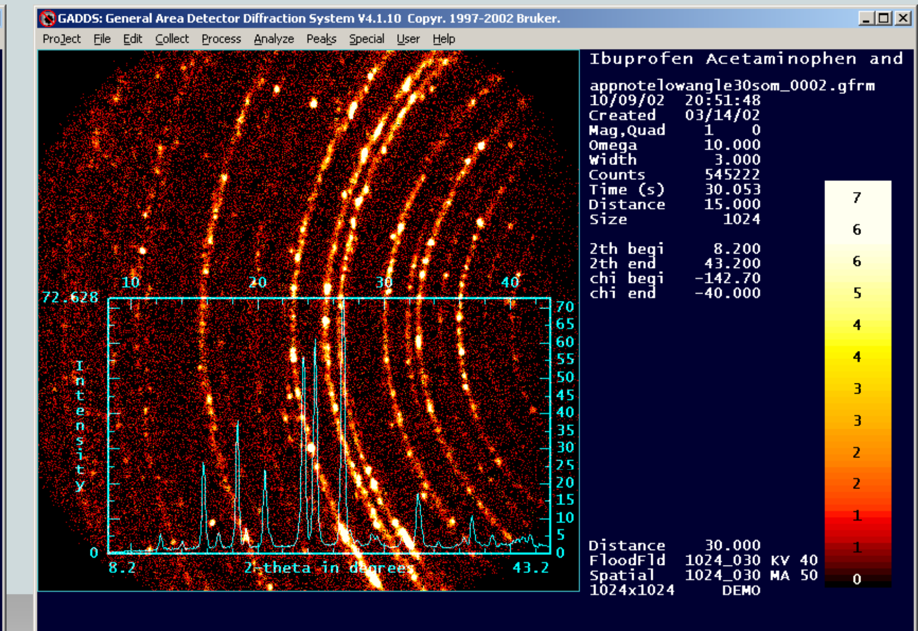
☒ Expensive

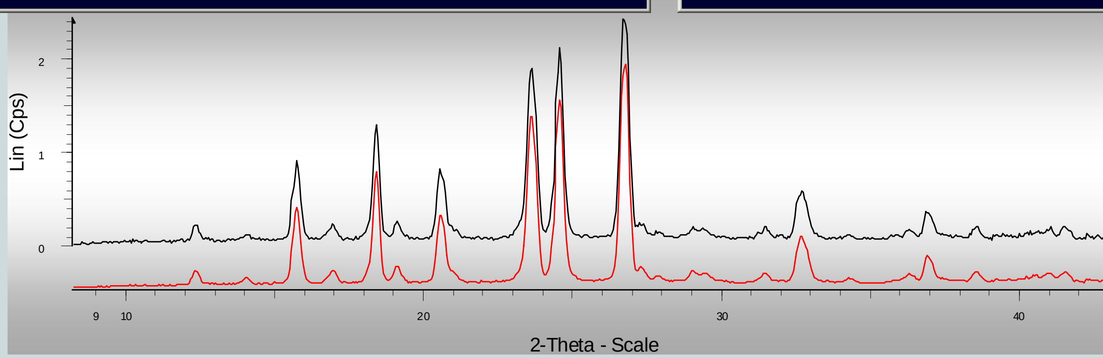
XRD^2: Data Collection:
Acetaminophen powder

5 second data collection



30 second data collection

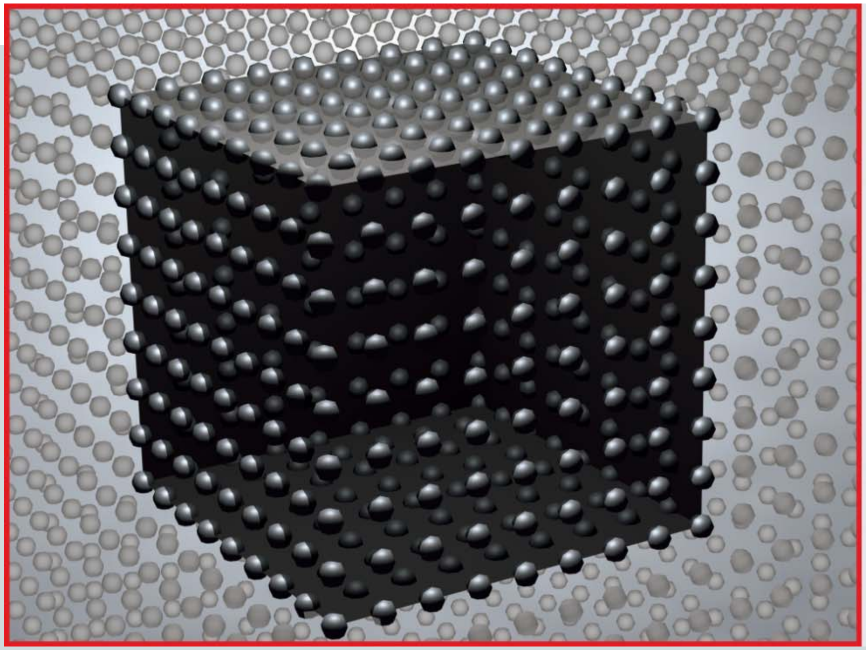


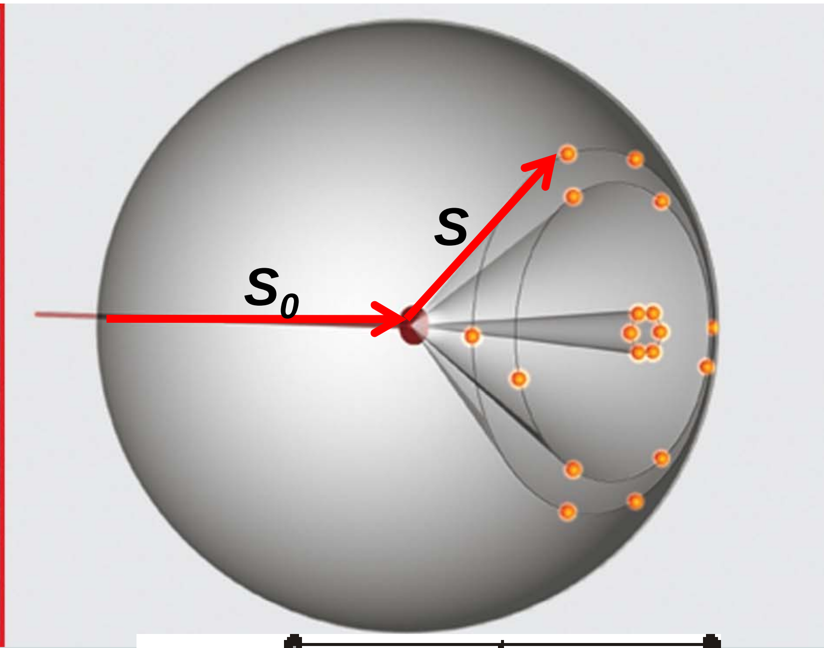


XRD^2: Diffraction vector approach

Applications	**Vector approaches**
Phase Identification:	Polarization and absorption correction
Texture Analysis:	Orientation mapping angles; Data collection strategy (scheme)
Stress Measurement:	Fundamental equation derived by second order tensor transformation; Data collection strategy (scheme)
Crystal Size Analysis:	Equations for the effective volume calculation at both reflection and transmission modes.

XRD^2 & Single Crystals



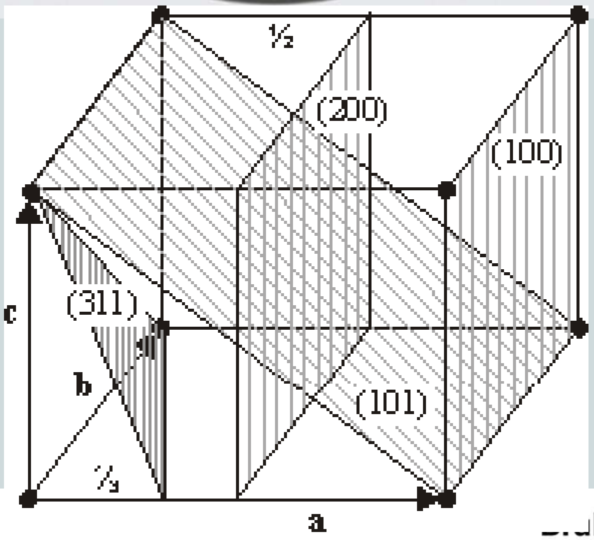


Laue equation

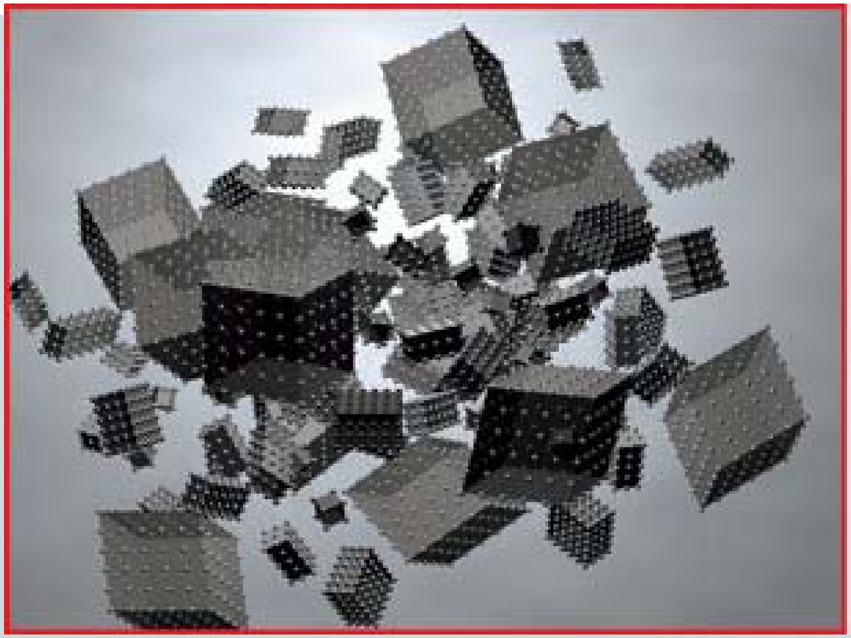
$$\boldsymbol{a}\cdot(\boldsymbol{s}-\boldsymbol{s}_0)=h\lambda$$

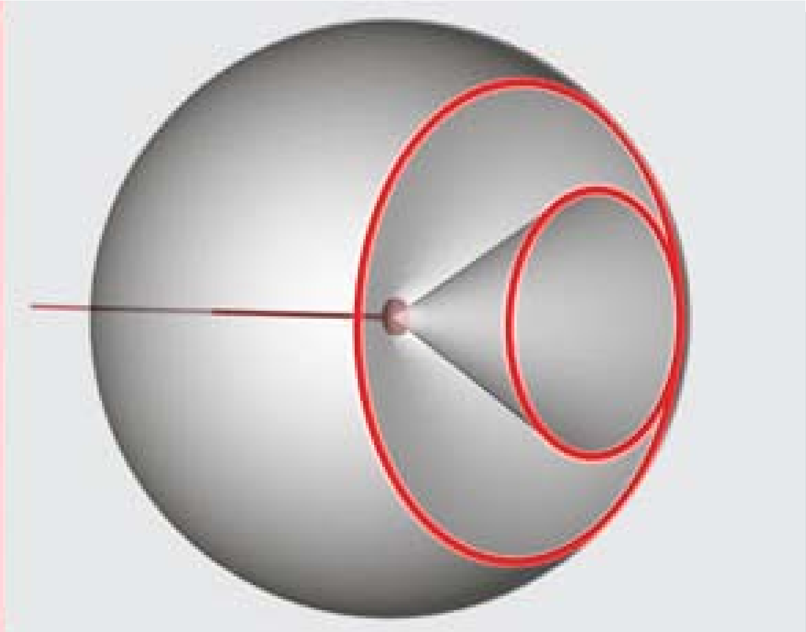
$$\boldsymbol{b}\cdot(\boldsymbol{s}-\boldsymbol{s}_0)=k\lambda$$

$$\boldsymbol{c}\cdot(\boldsymbol{s}-\boldsymbol{s}_0)=l\lambda$$



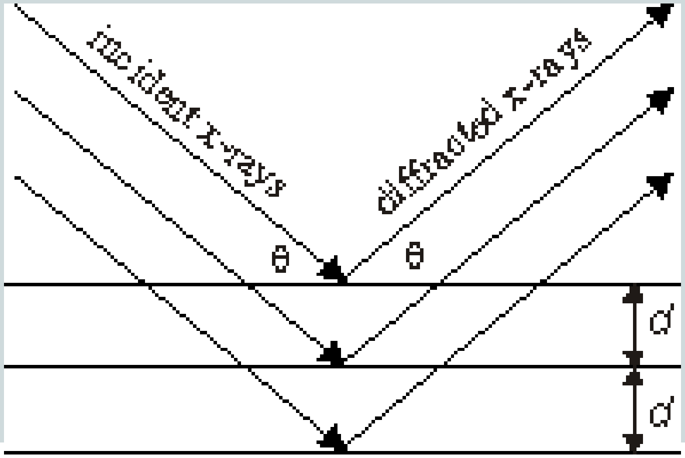
XRD² & Powders



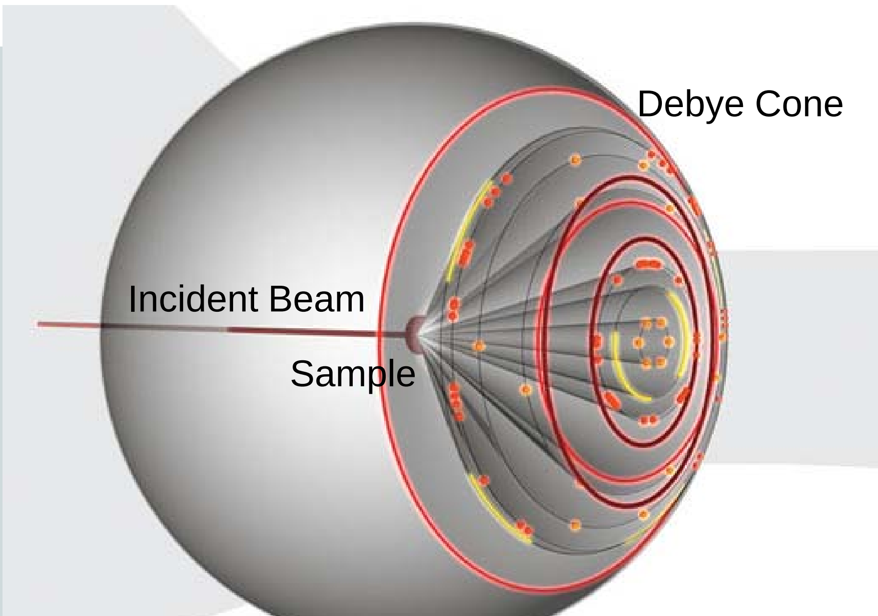


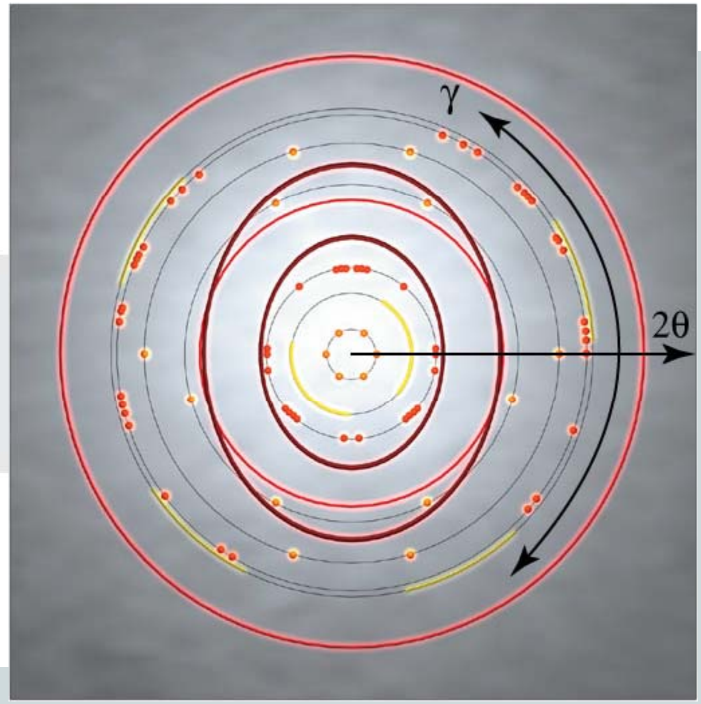
Bragg law

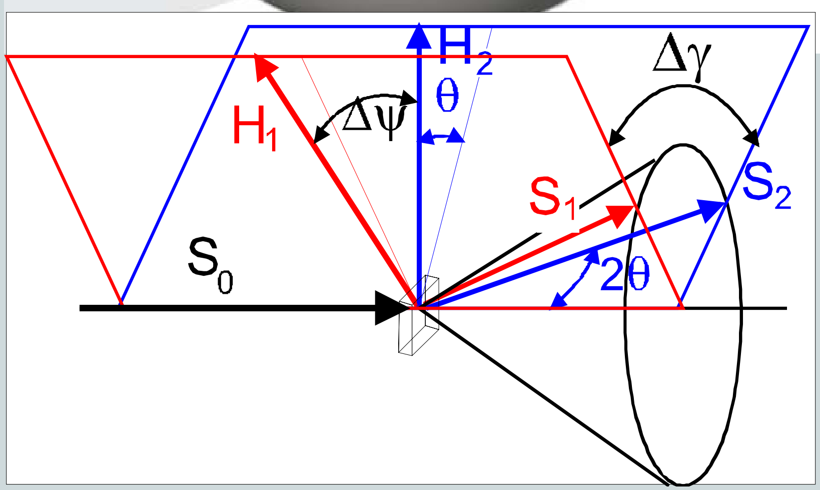
$$n\lambda = 2d \sin\theta$$



XRD[2]: Diffraction pattern with both γ and 2θ information



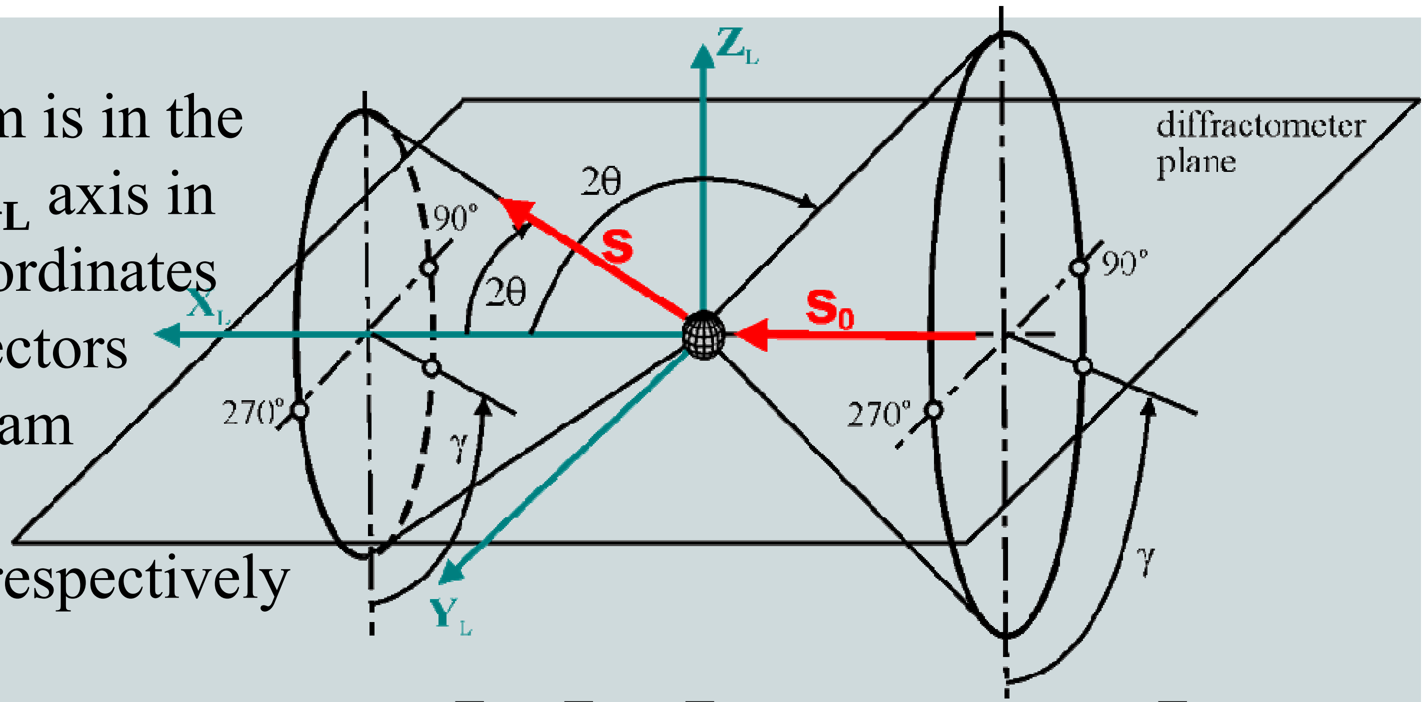




$$\boldsymbol{H} = \frac{\boldsymbol{s} - \boldsymbol{s}_0}{\lambda} = \frac{1}{\lambda}\begin{bmatrix} \cos 2\theta - 1 \\ -\sin 2\theta \sin \gamma \\ -\sin 2\theta \cos \gamma \end{bmatrix}$$

XRD²: Diffraction Space & Laboratory coordinators

The incident beam is in the direction of the $\mathbf{X_L}$ axis in the laboratory coordinates so that the unit vectors of the incident beam and diffracted beams are given respectively by:



$$\boldsymbol{s_0} = \begin{bmatrix} s_{0x} \\ s_{0y} \\ s_{0z} \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \qquad \boldsymbol{s} = \begin{bmatrix} s_x \\ s_y \\ s_z \end{bmatrix} = \begin{bmatrix} \cos 2\theta \\ -\sin 2\theta \sin\gamma \\ -\sin 2\theta \cos\gamma \end{bmatrix}$$

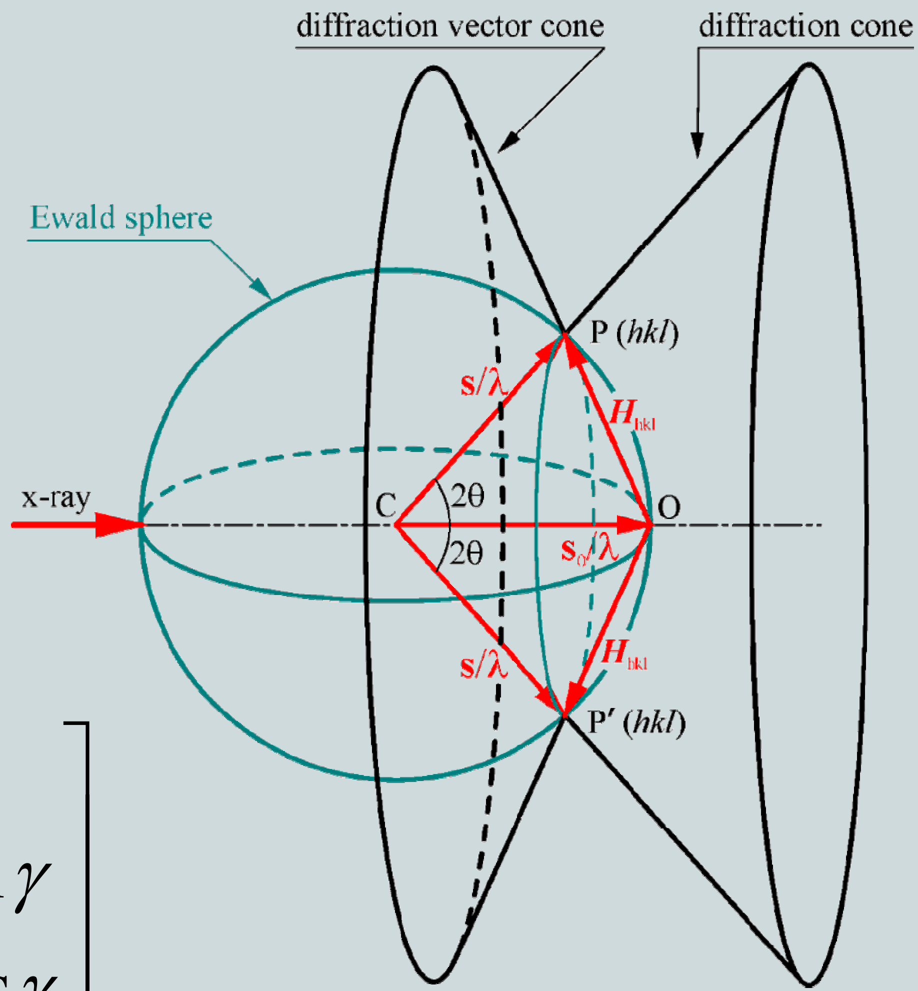
XRD^2: Diffraction Vector & Unit Diffraction Vector

The diffraction vector is given in laboratory coordinates by

$$\boldsymbol{H} = \frac{\boldsymbol{s} - \boldsymbol{s}_0}{\lambda} = \frac{1}{\lambda}\begin{bmatrix} s_x - s_{0x} \\ s_y - s_{0y} \\ s_z - s_{0z} \end{bmatrix} = \frac{1}{\lambda}\begin{bmatrix} \cos 2\theta - 1 \\ -\sin 2\theta \sin\gamma \\ -\sin 2\theta \cos\gamma \end{bmatrix}$$

The direction of each diffraction vector can be represented by its unit vector given by:

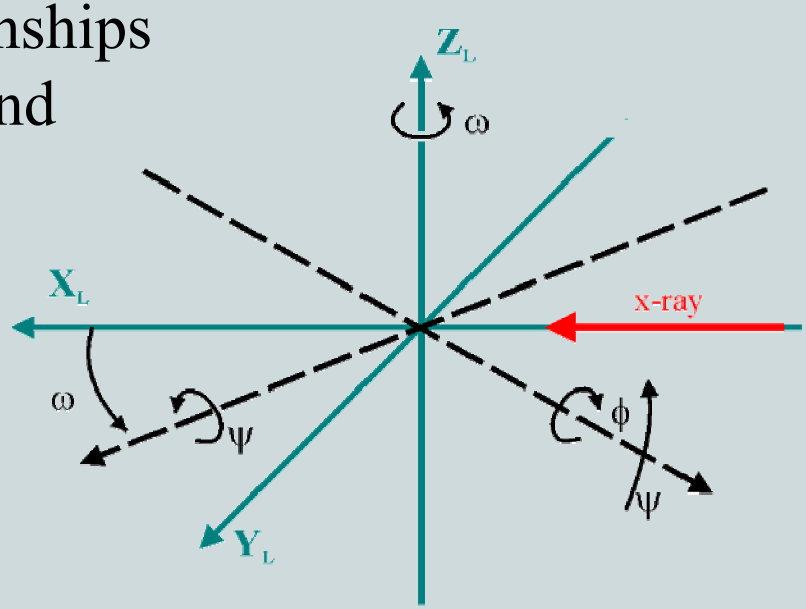
$$\boldsymbol{h}_L = \frac{\boldsymbol{H}}{|\boldsymbol{H}|} = \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix} = \begin{bmatrix} -\sin\theta \\ -\cos\theta \sin\gamma \\ -\cos\theta \cos\gamma \end{bmatrix}$$

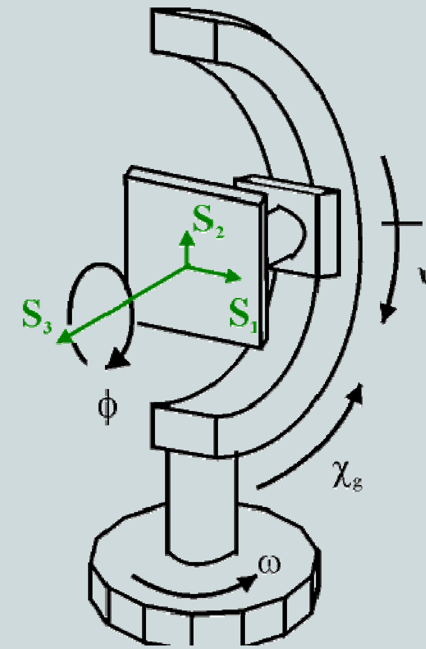


XRD^2: Sample Space & Eulerian Geometry

The angular relationships between $\mathbf{X_L Y_L Z_L}$ and $\mathbf{S_1 S_2 S_3}$ are:

	X_L	Y_L	Z_L
S_1	a_{11}	a_{12}	a_{13}
S_2	a_{21}	a_{22}	a_{23}
S_3	a_{31}	a_{32}	a_{33}





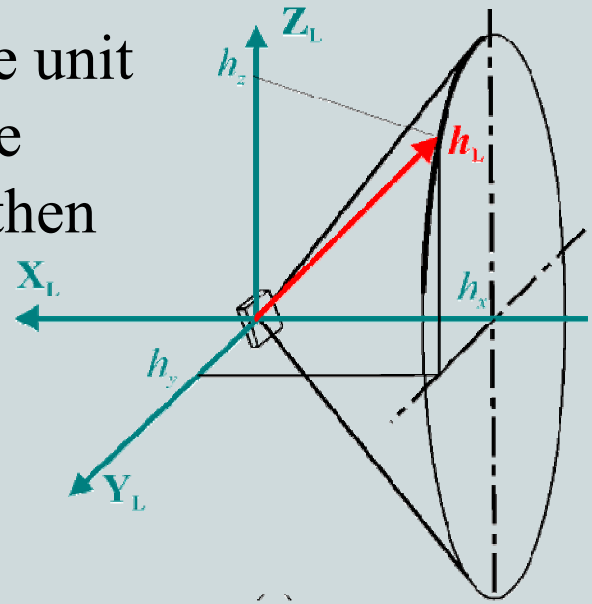
The transformation matrix from the diffraction space to the sample space is:

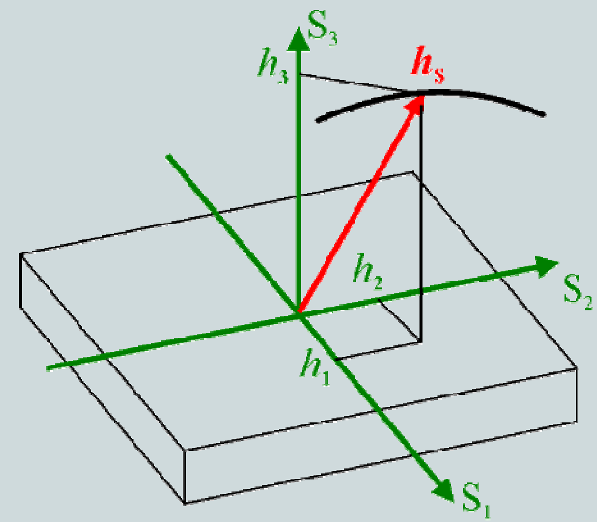
$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} = \begin{bmatrix} -\sin\omega\sin\psi\sin\phi - \cos\omega\cos\phi & \cos\omega\sin\psi\sin\phi - \sin\omega\cos\phi & -\cos\psi\sin\phi \\ \sin\omega\sin\psi\cos\phi - \cos\omega\sin\phi & -\cos\omega\sin\psi\cos\phi - \sin\omega\sin\phi & \cos\psi\cos\phi \\ -\sin\omega\cos\psi & \cos\omega\cos\psi & \sin\psi \end{bmatrix}$$

XRD^2: Sample Space & Unit Diffraction Vector

The components of the unit vector $\boldsymbol{h_S}$ in the sample coordinates $\mathbf{S_1S_2S_3}$ is then given by

$$\begin{bmatrix} h_1 \\ h_2 \\ h_3 \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix}$$



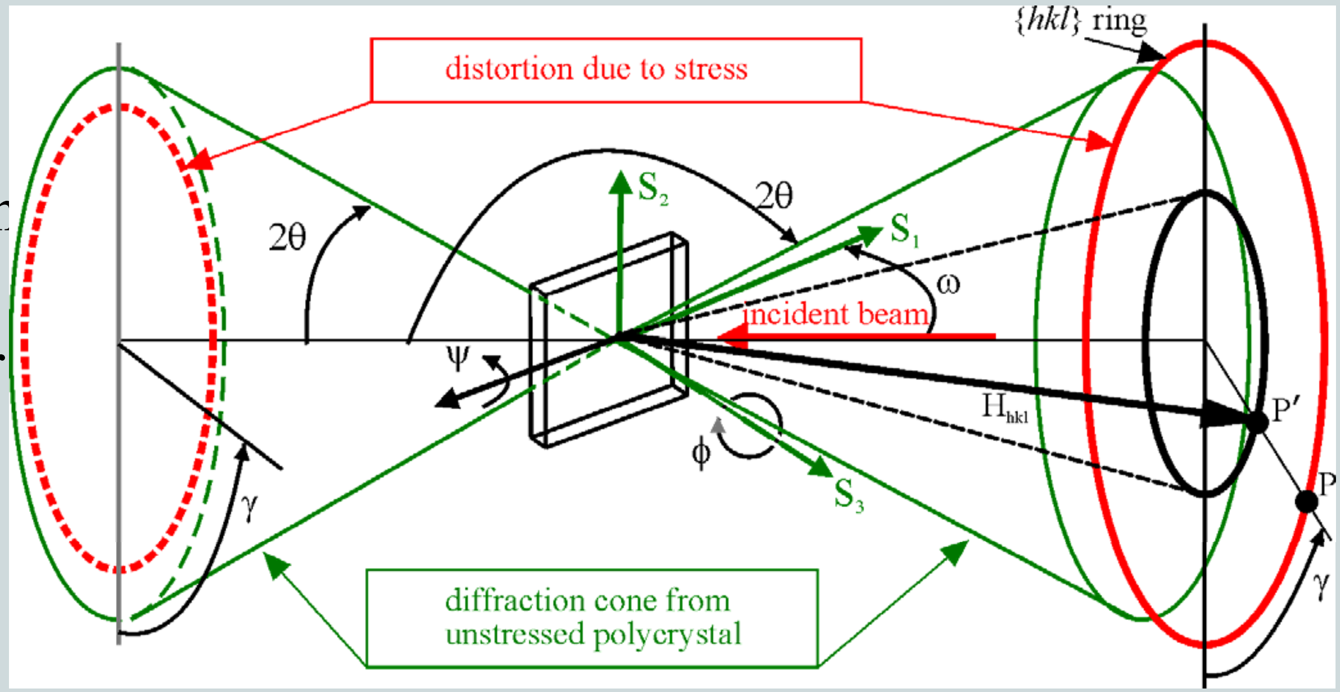


Or
in expanded form:

$$h_1 = \sin\theta(\sin\phi\sin\psi\sin\omega + \cos\phi\cos\omega) + \cos\theta\cos\gamma\sin\phi\cos\psi$$
$$-\cos\theta\sin\gamma(\sin\phi\sin\psi\cos\omega - \cos\phi\sin\omega)$$
$$h_2 = -\sin\theta(\cos\phi\sin\psi\sin\omega - \sin\phi\cos\omega) - \cos\theta\cos\gamma\cos\phi\cos\psi$$
$$+\cos\theta\sin\gamma(\cos\phi\sin\psi\cos\omega + \sin\phi\sin\omega)$$
$$h_3 = \sin\theta\cos\psi\sin\omega - \cos\theta\sin\gamma\cos\psi\cos\omega - \cos\theta\cos\gamma\sin\psi$$

XRD^2: Fundamental Equation for Stress Measurement

As a second order tensor, the relationship between measured strains and the strain tensor is given by:

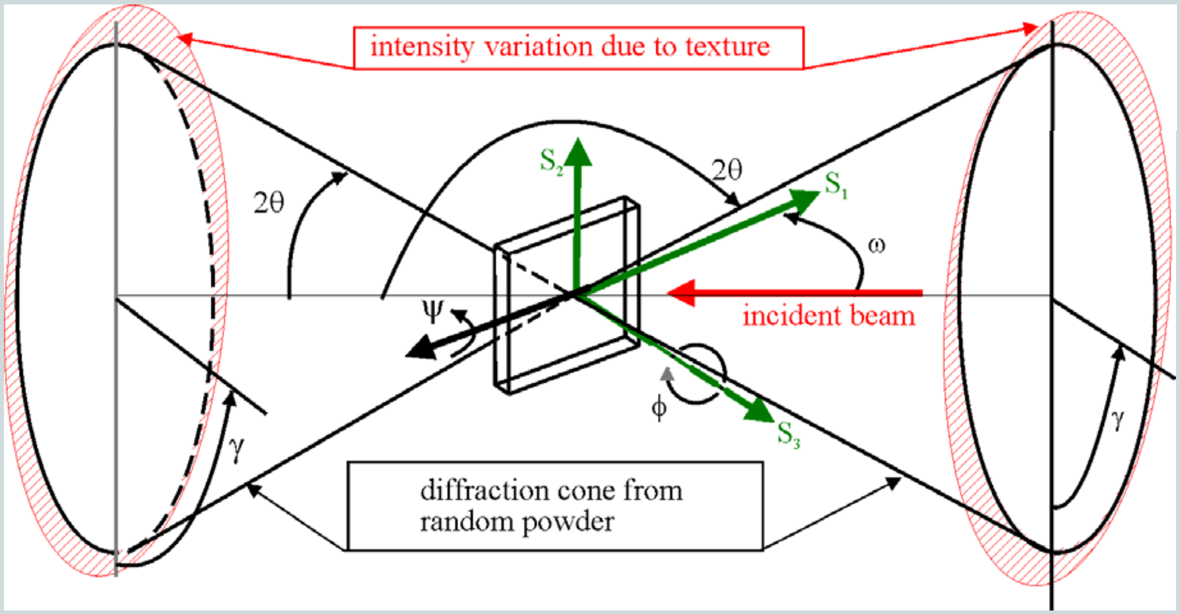


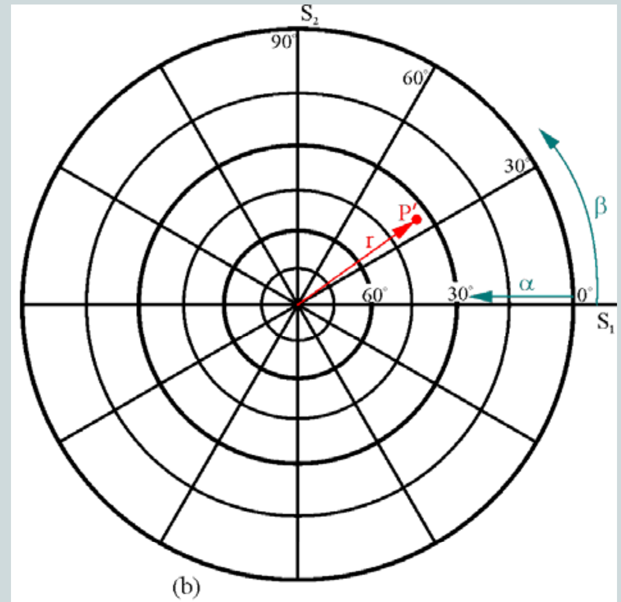
$$\varepsilon^{\{hkl\}}_{(\gamma,\omega,\psi,\phi)} = \varepsilon_{ij} \cdot h_i \cdot h_j$$

the fundamental equation for stress measurement in XRD^2:

$$S_1(\sigma_{11}+\sigma_{22}+\sigma_{33})+\tfrac{1}{2}S_2(\sigma_{11}h_1^2+\sigma_{22}h_2^2+\sigma_{33}h_3^2 + 2\sigma_{12}h_1h_2+2\sigma_{13}h_1h_3+2\sigma_{23}h_2h_3)=\ln\left(\frac{\sin\theta_0}{\sin\theta}\right)$$

XRD²: Fundamental Equation for Texture Analysis





The pole figure angles (α,β) can be calculated from the unit vector components by the pole mapping equations:

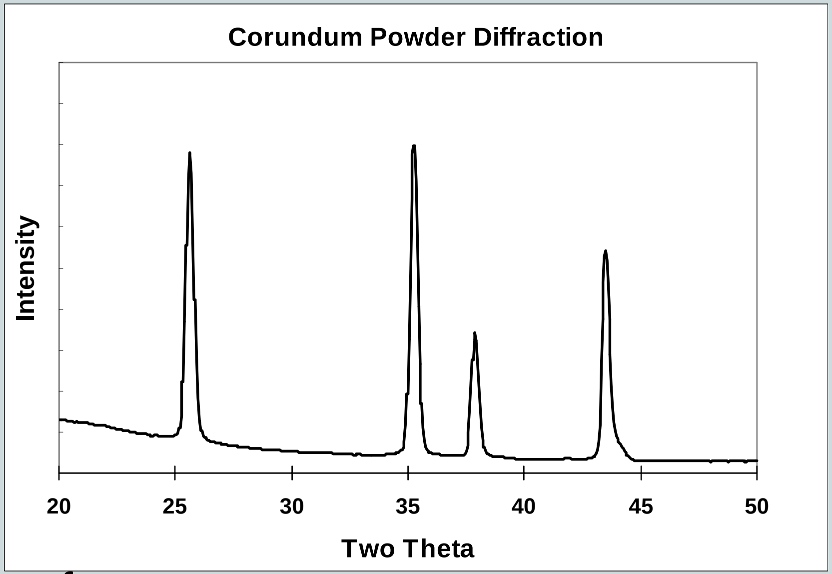
$$\alpha = \sin^{-1}|h_3| = \cos^{-1}\sqrt{h_1^2 + h_2^2}$$

$$\beta = \pm\cos^{-1}\frac{h_1}{\sqrt{h_1^2 + h_2^2}} \quad \begin{cases} \beta \geq 0° & if \quad h_2 \geq 0 \\ \beta < 0° & if \quad h_2 < 0 \end{cases}$$

XRD²: Relative Intensity of Powder Pattern

The integrated intensity diffracted from random polycrystalline materials is given by:

$$I_{hkl} = k_I \frac{p_{hkl}}{v^2}(LPA)\lambda^3 F_{hkl}^2 \exp(-2M_t - 2M_s)$$



where:

⊕ k_I - instrument constant;

p_{hkl} - the multiplicity of the planes;

v - the volume of the unit cell;

⊕ (LPA) - the Lorentz-polarization and absorption factors;

F_{hkl}^2 - the structure factor of the crystal plane (*hkl*) and

$\exp(-2M_t-2M_s)$ - the attenuation factor due to lattice thermal vibrations and weak static displacements.

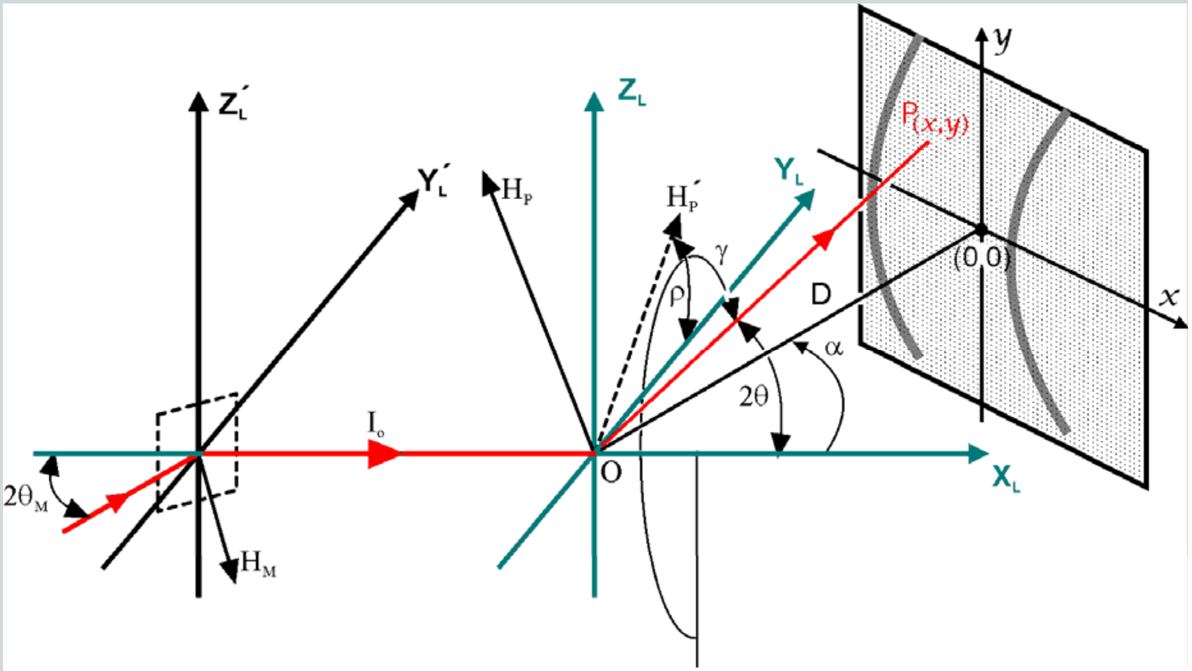
⊕ Denotes the factors which are different between Bragg-Brentano geometry and XRD² geometry. k_I is determined by the source, optics and detector (PPXRD-7) (LPA) will be given in this presentation.

XRD^2: Polarization Correction

The polarization factor for Bragg-Brentano geometry with incident beam monochromator is:

$$P_I = \frac{1+\cos^2 2\theta_M \cos^2 2\theta}{1+\cos^2 2\theta_M}$$

where $2\theta_M$ is the Bragg angle of the monochromator.



Geometric relationship between the monochromator and detector in laboratory coordinates.

The general polarization factor for the diffracted beam to point P is:

$$P_G = \frac{(\cos^2 2\theta \cos^2 \rho + \sin^2 \rho)\cos^2 2\theta_M + \cos^2 2\theta \sin^2 \rho + \cos^2 \rho}{1+\cos^2 2\theta_M}$$

XRD²: Polarization Correction

The unit vector of the diffraction vector $\mathbf{H_P}$ and its projection on Y_L-Z_L plane, $\mathbf{H'_P}$, in the laboratory system are given respectively as:

$$\boldsymbol{h}_\mathrm{L} = \begin{bmatrix} h_x \\ h_y \\ h_z \end{bmatrix} = \begin{bmatrix} -\sin\theta \\ -\cos\theta\sin\gamma \\ -\cos\theta\cos\gamma \end{bmatrix} \qquad \boldsymbol{h}'_\mathrm{L} = \begin{bmatrix} 0 \\ h'_y \\ h'_z \end{bmatrix} = \begin{bmatrix} 0 \\ -\sin\gamma \\ -\cos\gamma \end{bmatrix}$$

The unit vector of Y_L is $\mathbf{y_L}$=[0,1,0], then:

$$\cos\rho = \cos(\boldsymbol{h}'_L, y_\mathrm{L}) = \boldsymbol{h}_L \bullet y_\mathrm{L} = -\sin\gamma$$

Therefore, $\cos^2\rho = \sin^2\gamma$ and $\sin^2\rho = \cos^2\gamma$

The polarization factor for XRD² can then be given as a function of both θ and γ:

$$P(\theta,\gamma) = \frac{(1+\cos^2 2\theta_M \cos^2 2\theta)\sin^2\gamma + (\cos^2 2\theta_M + \cos^2 2\theta)\cos^2\gamma}{1+\cos^2 2\theta_M}$$

XRD^2: Sample Absorption Correction

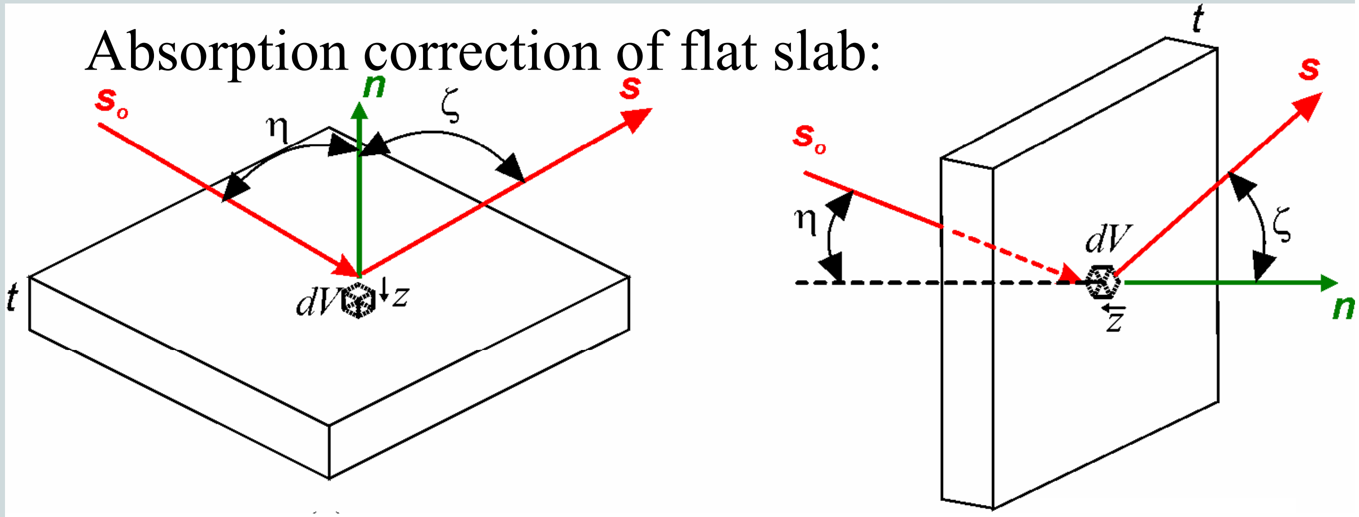
The absorption can be measured by the transmission coefficient:

$$A = \frac{1}{V}\int_V e^{-\mu\tau} dV$$

where τ is the total beam path and *A* is the average over all the element *dV*. For Bragg-Brentano geometry, we have:

$A_{BB} = 1/(2\mu)$

Absorption correction of flat slab:

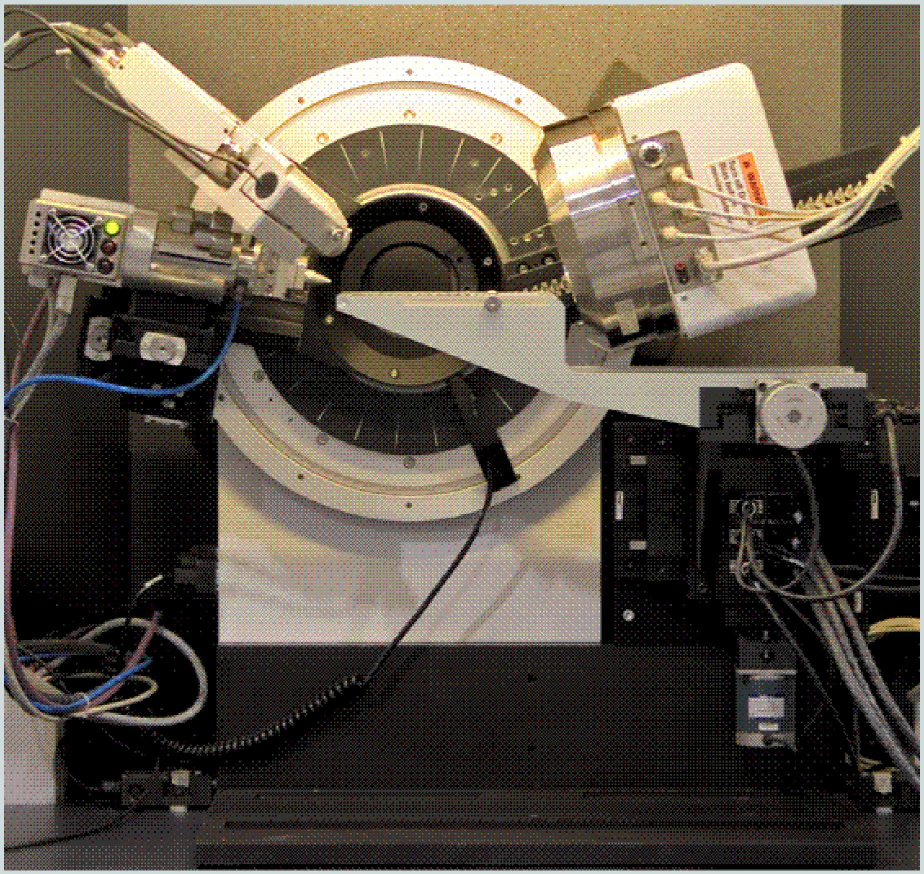


(a) reflection (b) transmission.

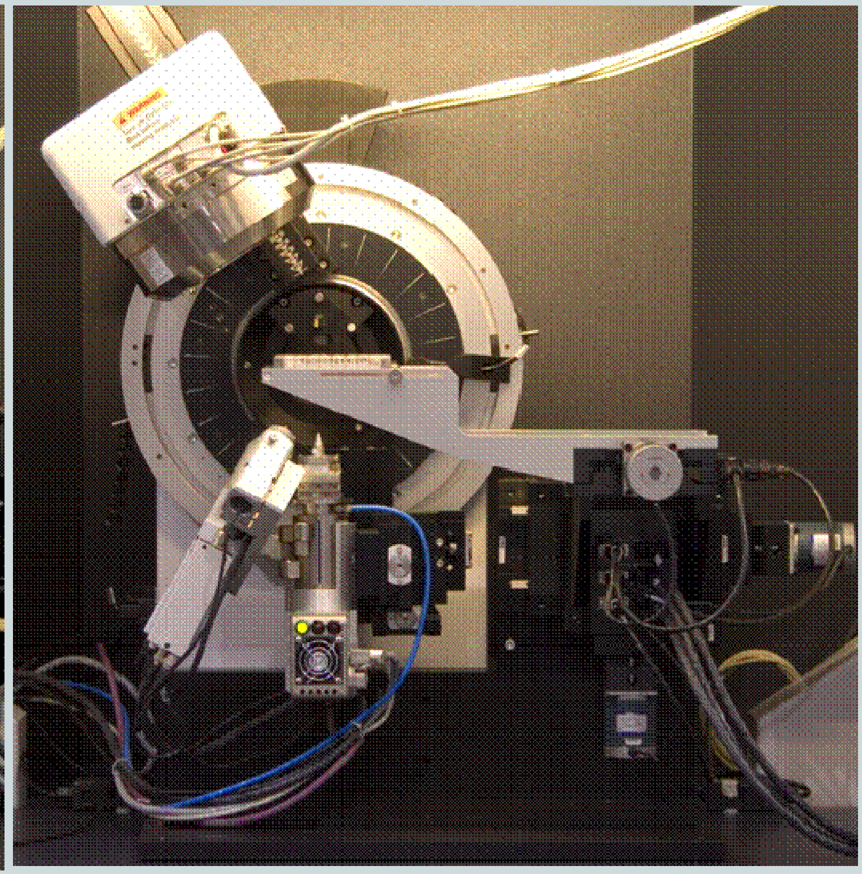
To make the relative intensity comparable to Bragg-Brentano geometry, we introduce a normalized transmission coefficient *T*:

$$T = A/A_{BB} = 2\mu A$$

D8 DISCOVER with GADDS HTS (IµS):
Reflection & Transmission (Pharmaceutical Delight)



- Reflection mode



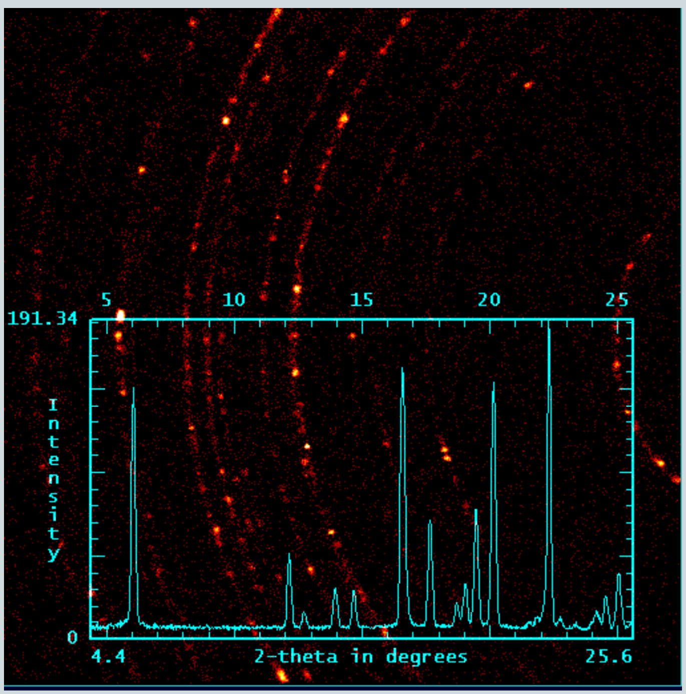
- Transmission mode

Comparison: Ibuprofen
IµS & VÅNTEC-2000 vs. Clasical set-up

Sealed Tube

- **0.3 mm collimator**
- **Sample-Detector distance 29 cm**

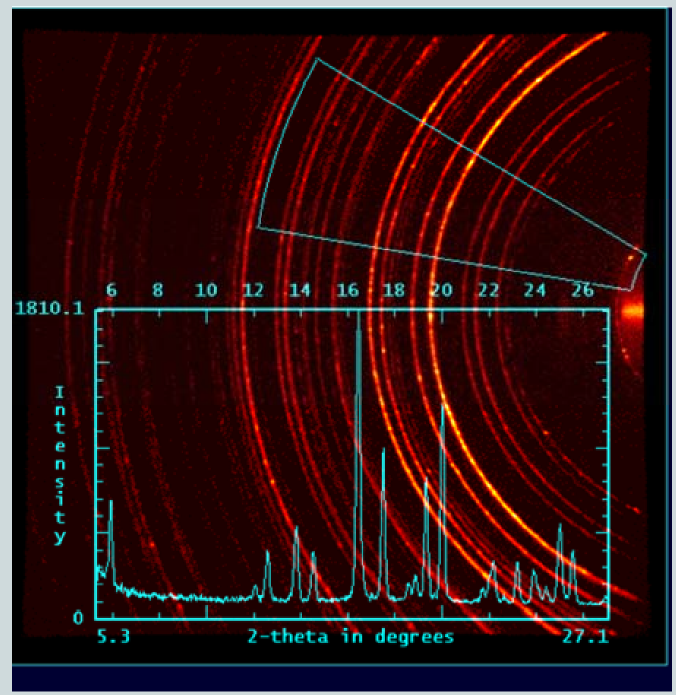
120 sec collection time



IµS – XRD² – focus

- **2mmX2mm on sample, and 200um spot focused on detector**
- **small slice for integration to obtain better resolution**

15 sec collection time



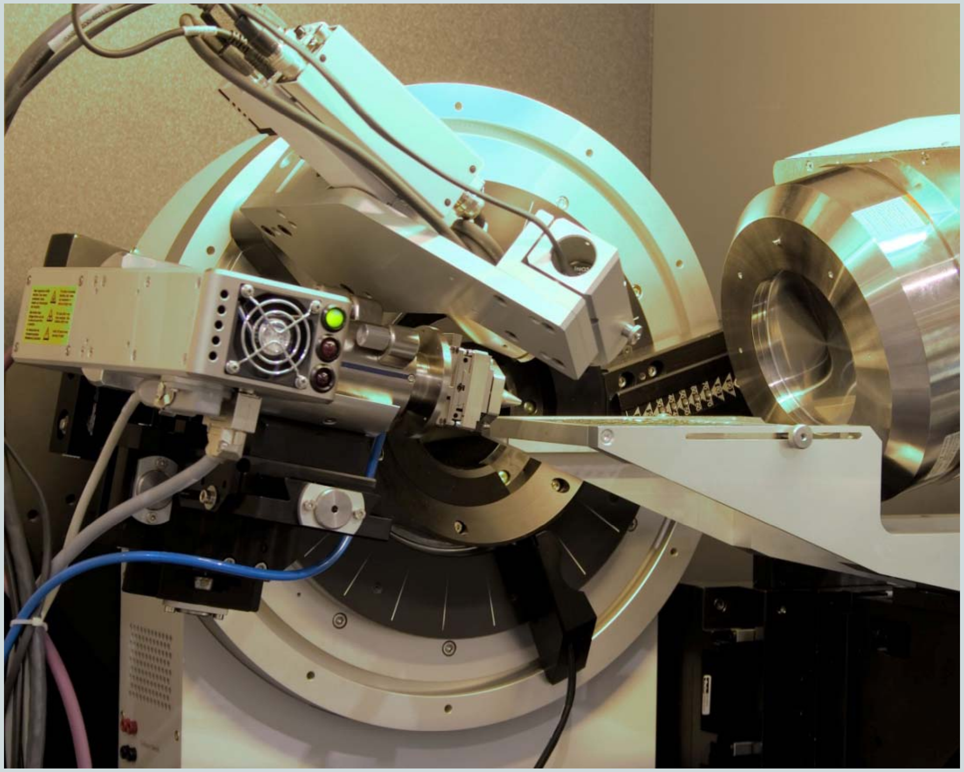
XRD²: Sample Absorption Correction

For reflection mode diffraction with a thick plate:

$$\boldsymbol{s_o} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \qquad \boldsymbol{s} = \begin{bmatrix} \cos 2\theta \\ -\sin 2\theta \sin\gamma \\ -\sin 2\theta \cos\gamma \end{bmatrix}$$

and

$$\boldsymbol{n} = \begin{bmatrix} -\sin\omega\cos\psi \\ \cos\omega\cos\psi \\ \sin\psi \end{bmatrix}$$



The normalized transmission coefficient:

$$T = \frac{2\cos\eta}{(\cos\eta + \cos\zeta)} \quad \text{with} \quad \begin{aligned} \cos\eta &= -\boldsymbol{s_o} \cdot \boldsymbol{n} = \sin\omega\cos\psi \\ \cos\zeta &= \boldsymbol{s} \cdot \boldsymbol{n} = -\cos 2\theta \sin\omega\cos\psi \\ &\quad -\sin 2\theta \sin\gamma \cos\omega\cos\psi - \sin 2\theta \cos\gamma \sin\psi \end{aligned}$$

XRD²: Sample Absorption Correction

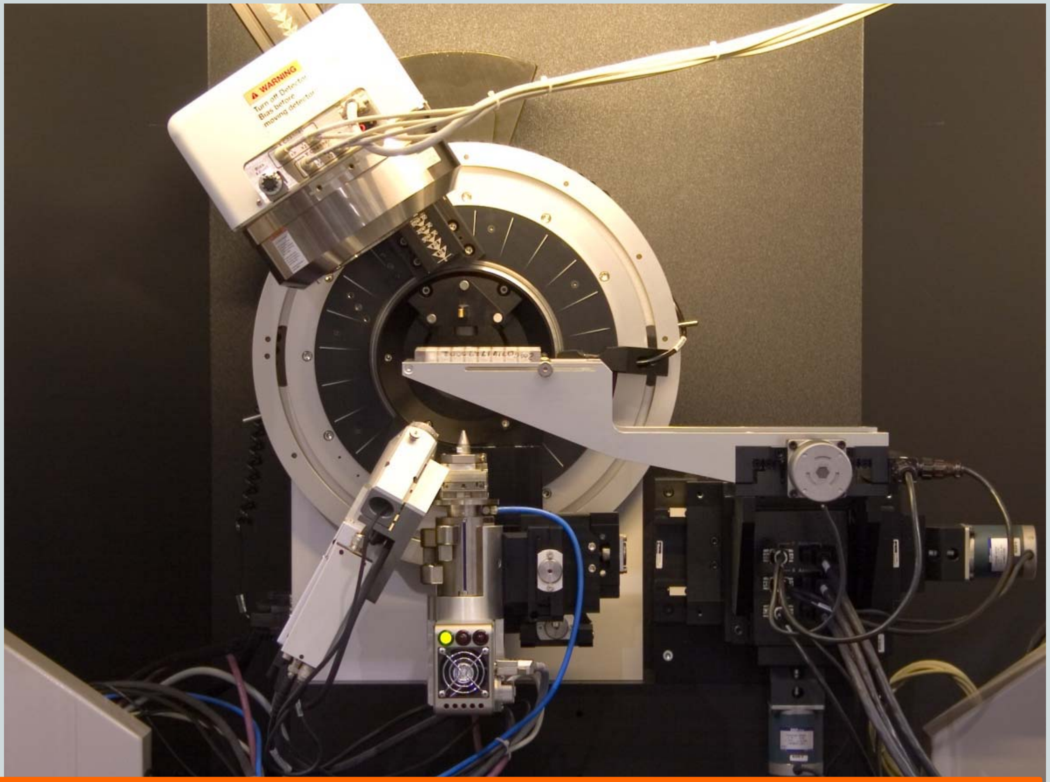
For transmission mode:

$$\boldsymbol{s_o} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \qquad \boldsymbol{s} = \begin{bmatrix} \cos 2\theta \\ -\sin 2\theta \sin\gamma \\ -\sin 2\theta \cos\gamma \end{bmatrix}$$

and

$$\boldsymbol{n} = \begin{bmatrix} \sin\omega \sin\psi \sin\phi + \cos\omega \cos\phi \\ -\cos\omega \sin\psi \sin\phi + \sin\omega \cos\phi \\ \cos\psi \sin\phi \end{bmatrix}$$

The normalized transmission coefficient :



$$T = \frac{2\sec\eta[\exp(-\mu t \sec\eta) - \exp(-\mu t \sec\zeta)]}{\sec\zeta - \sec\eta}$$

$$\cos\eta = \boldsymbol{s_o} \cdot \boldsymbol{n} = \sin\omega \sin\psi \sin\phi + \cos\omega \cos\phi$$

$$\begin{aligned} \cos\zeta = \boldsymbol{s} \cdot \boldsymbol{n} = & (\sin\omega \sin\psi \sin\phi + \cos\omega \cos\phi) \cos 2\theta \\ & + (\cos\omega \sin\psi \sin\phi - \sin\omega \cos\phi) \sin 2\theta \sin\gamma \\ & - \cos\psi \sin\phi \sin 2\theta \cos\gamma \end{aligned}$$

XRD²: Texture Effect and Correction

The integrated intensity with texture is:

$$\boldsymbol{I}_{hkl} = k_I \frac{p_{hkl}}{v^2}(LPA)\lambda^3 F_{hkl}^2 g_{hkl}(\alpha,\beta)\exp\left(-2M_t - 2M_s\right)$$

where *g()* is the normalized pole density function.

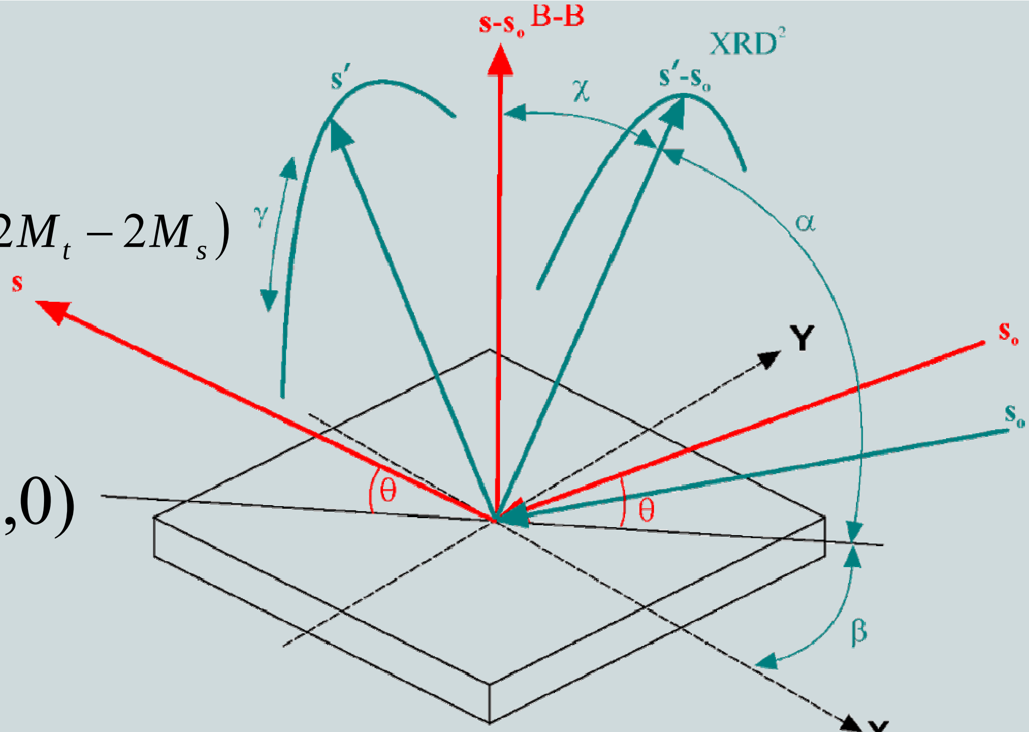
For the BB geometry, $g_{hkl}(\frac{\pi}{2},0)$

The texture effect for XRD²:

$$\boldsymbol{I}_{hkl}^{c} = \frac{\boldsymbol{I}_{hkl}^{m}}{\left\langle g_{hkl}(\Delta\gamma)\right\rangle}$$

Correct to the B-B equivalent with a texture effect:

$$\boldsymbol{I}_{hkl}^{BB} = \frac{g_{hkl}(\frac{\pi}{2},0)\boldsymbol{I}_{hkl}^{m}}{\left\langle g_{hkl}(\Delta\gamma)\right\rangle}$$



For fiber texture:

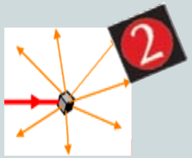
$$\left\langle g_{hkl}(\Delta\gamma)\right\rangle = \frac{\int_{\gamma_1}^{\gamma_2} g_{hkl}[\chi(\gamma)]\gamma d\gamma}{\gamma_2 - \gamma_1}$$

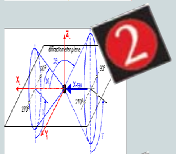
and $\chi = \cos^{-1}\left|h_3\right|$

XRD^2: Summary and Suggestions

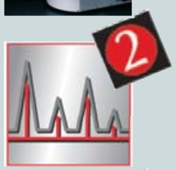
- Two-dimensional X-ray diffraction has many advantages over the conventional diffraction (speed, completeness and accuracy, micro-sample volume).
- The discrepancy between XRD^2 and Bragg-Brentano in geometry, polarization, absorption and preferred orientation can be interpreted and corrected.
- Fortunately, most of the discrepancies can be ignored without affecting the specific application.
- Or the corrections are already built in the software, so users do have to work on the correction details.

XRD²: Theory, System and Applications


X-ray Diffraction (XRD)

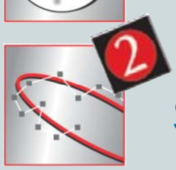

Geometry Conventions

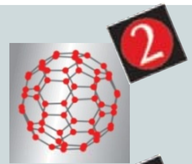

System and Configuration


Phase Identification


Quantitative Analysis

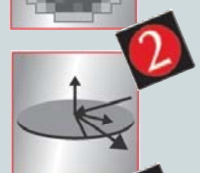

Texture


Stress

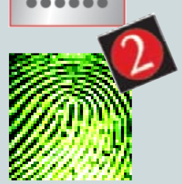

Small Angle X-ray Scattering

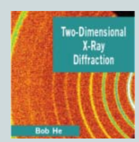

Micro Diffraction


Mapping


Thin Films

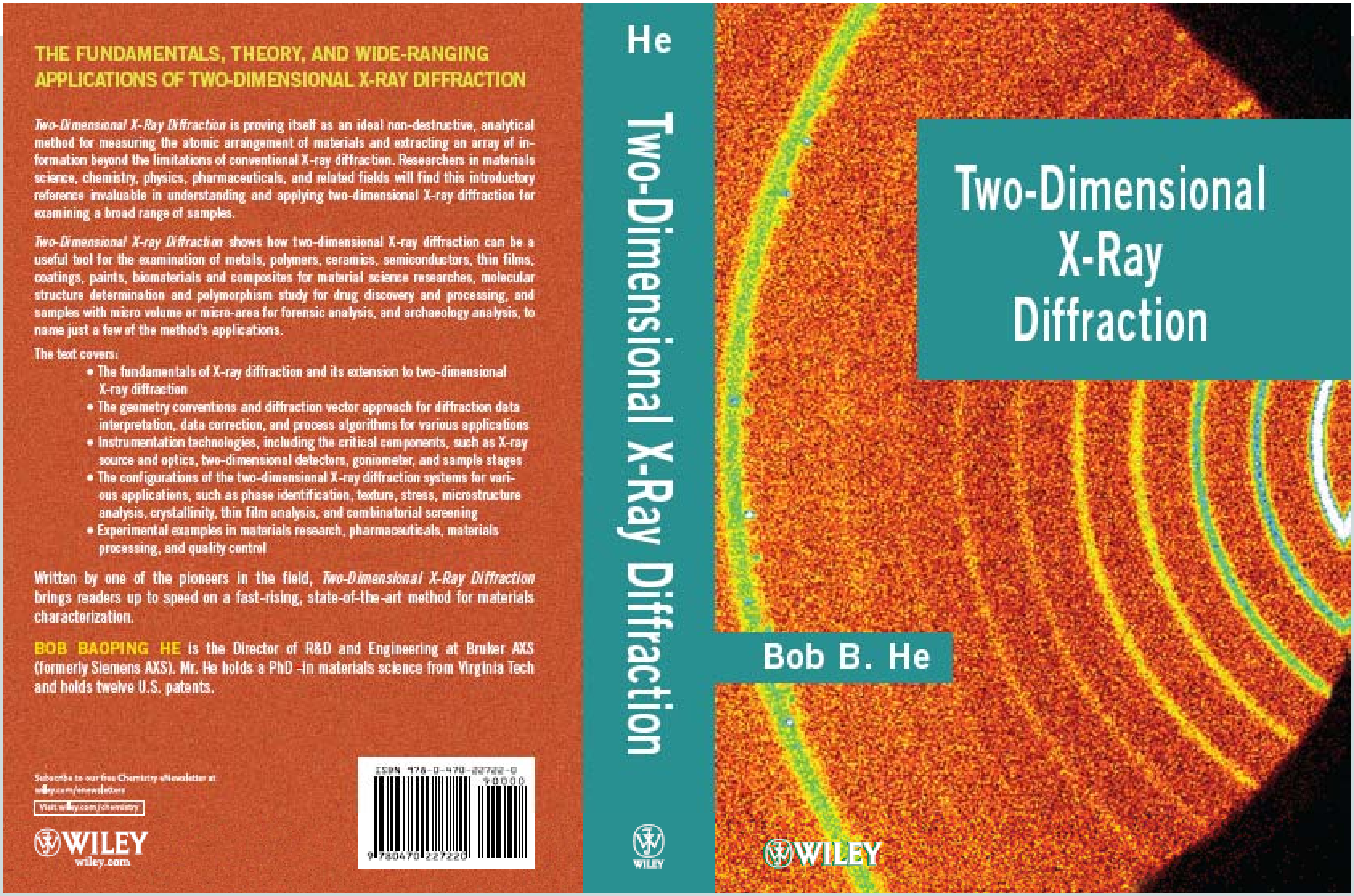

High-Throughput Screening


Forensics and Archaeology



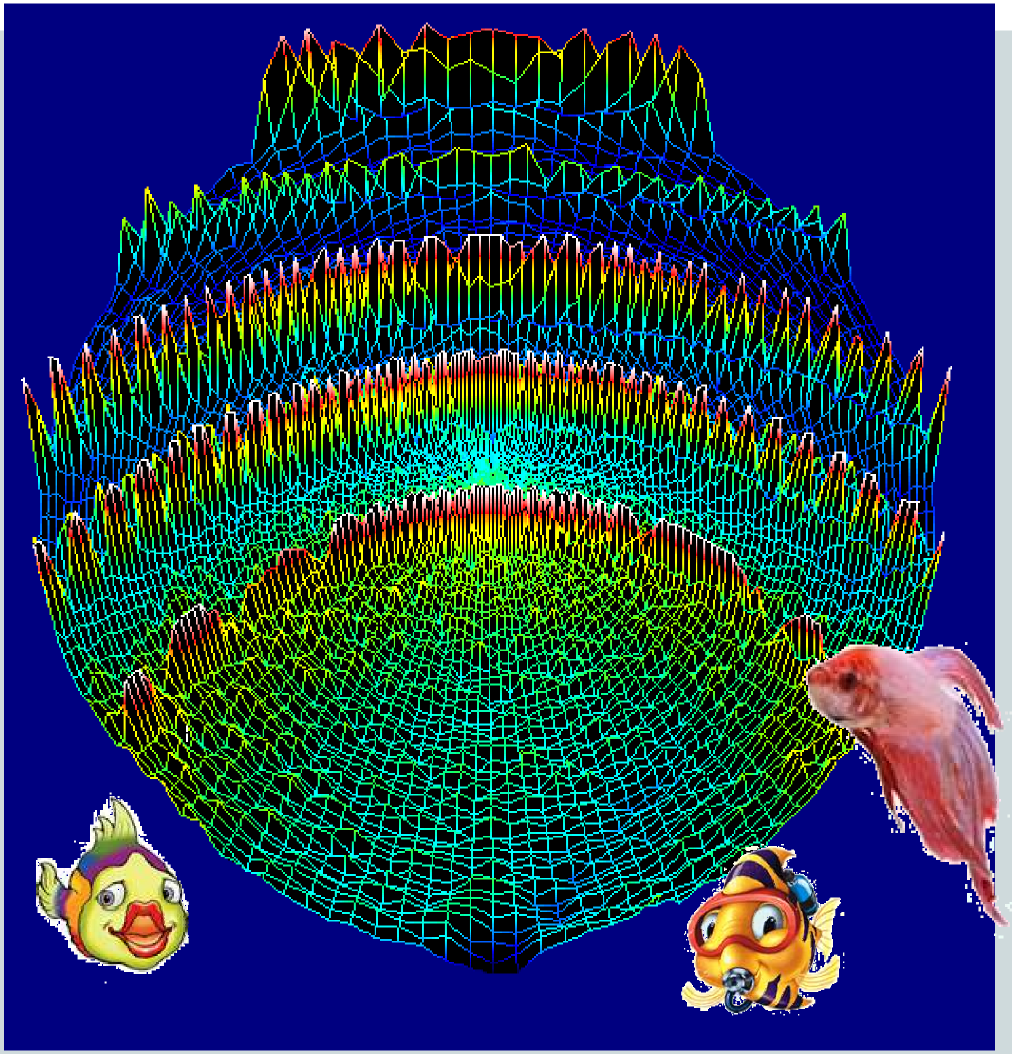
Reference

XRD^2: Fundamentals, theory and applications



Bruker AXS

Finalist of MRS "Science as Art" competition:
3D View of Corundum Powder Pattern



Thank You for Your Attention