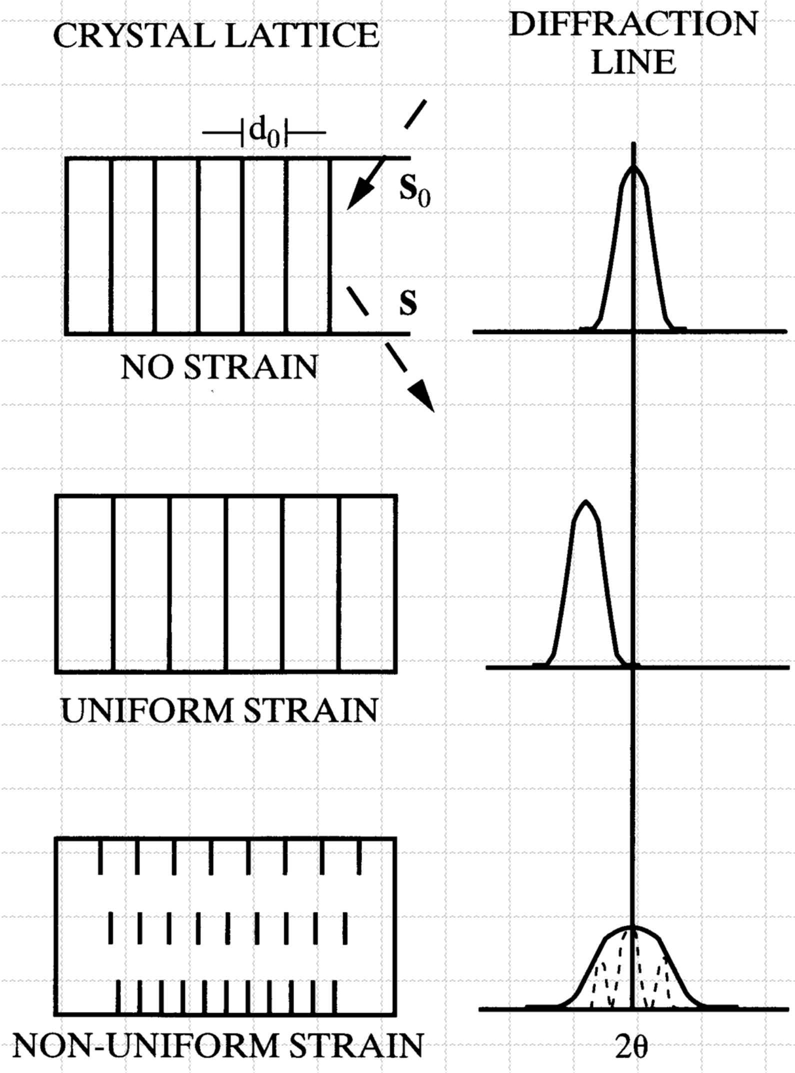
# Stress and Texture

# Strain

- Two types of stresses:
  - microstresses – vary from one grain to another on a microscopic scale.
  - macrostresses – stress is uniform over large distances.
- Usually:
  - macrostrain is uniform – produces peak shift
  - microstrain is nonuniform – produces peak broadening

$$b = \Delta 2\theta = -2\frac{\Delta d}{d}\tan\theta$$



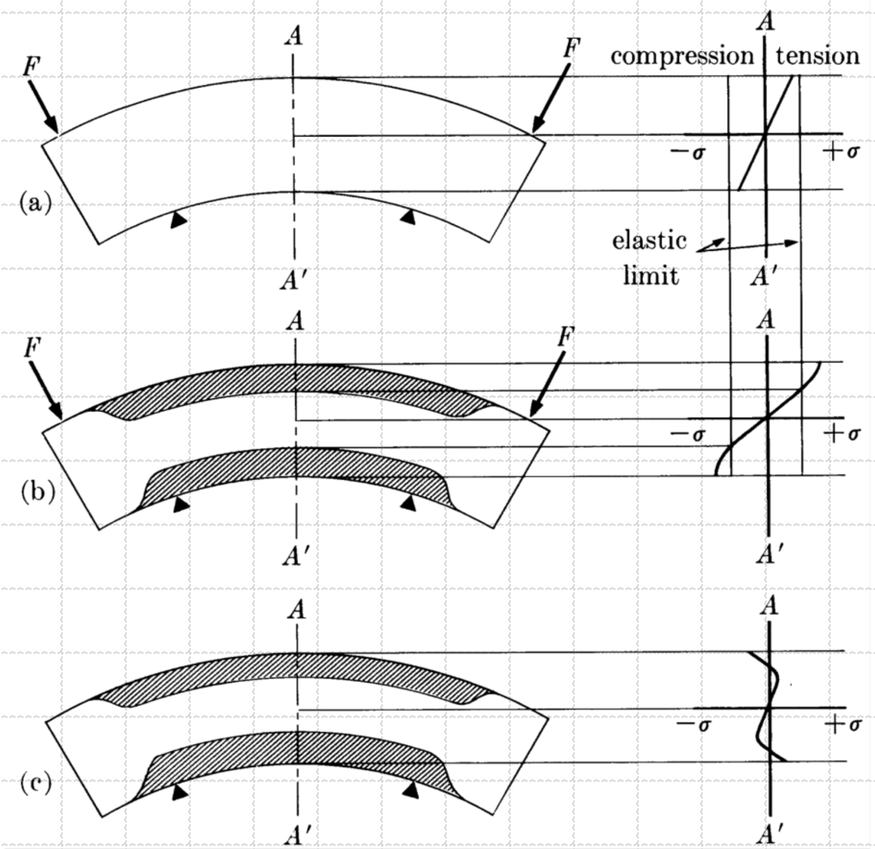
# Applied and Residual Stress

- Plastic flow can also set up residual stress.

Loaded below elastic limit

Loaded beyond elastic limit

Unloaded




Shaded areas show regions plastically strained

# Methods to Measure Residual Stress

- X-ray diffraction.
  - Nondestructive for the measurements near the surface: $t < 2\ \mu m$.
- Neutron diffraction.
  - Can be used to make measurements deeper in the material, but the minimum volume that can be examined is quite large (several $mm^3$) due to the low intensity of most neutron beams.
- Dissection (mechanical relaxation).
  - Destructive.

# General Principles

- Consider a rod of a cross-sectional area A stressed in tension by a force F.

Stress: $$\sigma_y = \frac{F}{A}, \; \sigma_x, \sigma_z = 0$$

Stress $\sigma_y$ produces strain $\varepsilon_y$:

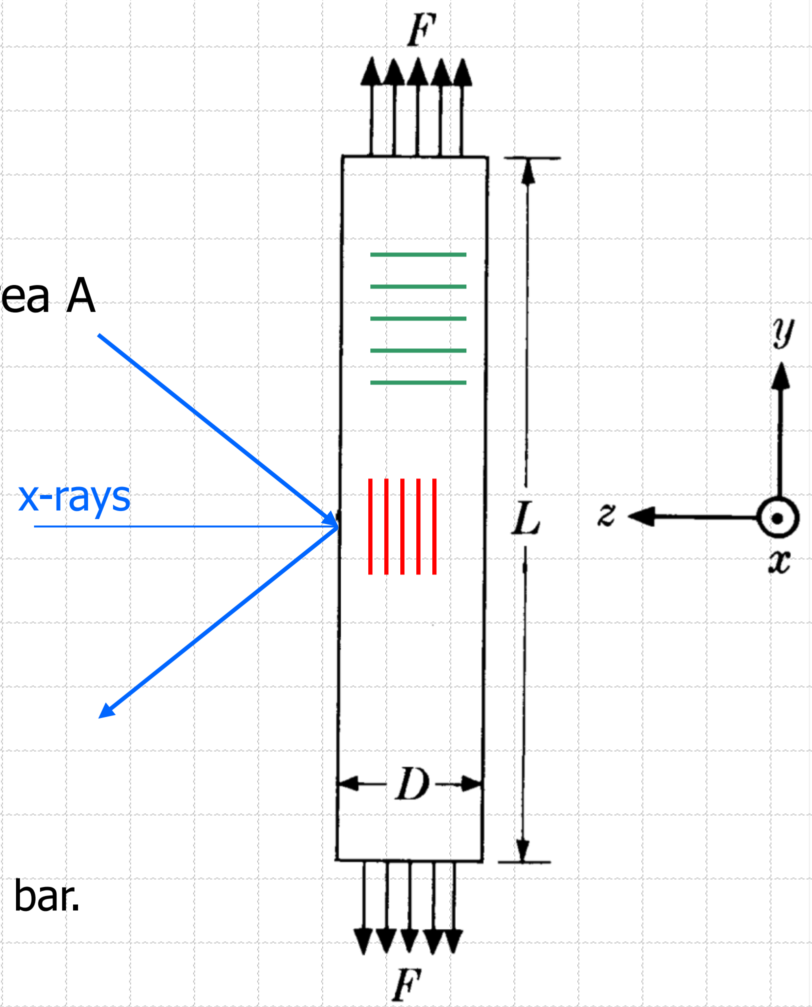
$$\varepsilon_y = \frac{\Delta L}{L} = \frac{L_f - L_0}{L_0}$$

$L_0$ and $L_f$ are the original and final lengths of the bar. The strain is related to stress as:

$$\sigma_y = E\varepsilon_y$$

L increases D decreases so:

$$\varepsilon_x = \varepsilon_z = \frac{\Delta D}{D} = \frac{D_f - D_0}{D_0}$$




$\varepsilon_x = \varepsilon_z = -\nu\varepsilon_y$ for isotropic material

$\nu$ – Poisson's ratio
usually $0.25 < \nu < 0.45$

# General Principles

- This provides measurement of the strain in the z direction since:

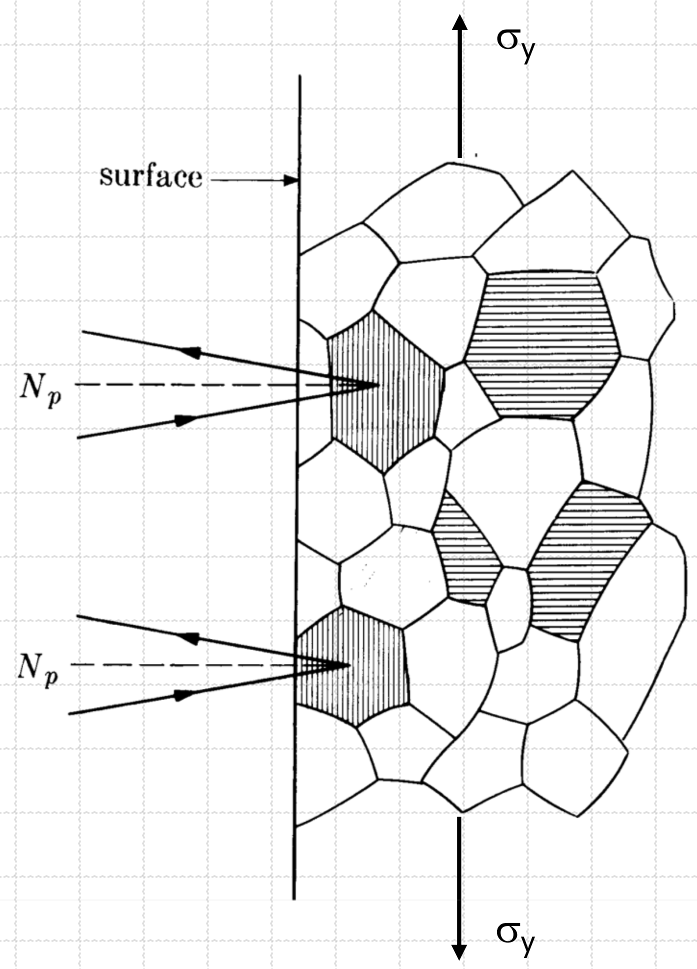
$$\varepsilon_z = \frac{d_n - d_0}{d_0}$$

Then the required stress will be:

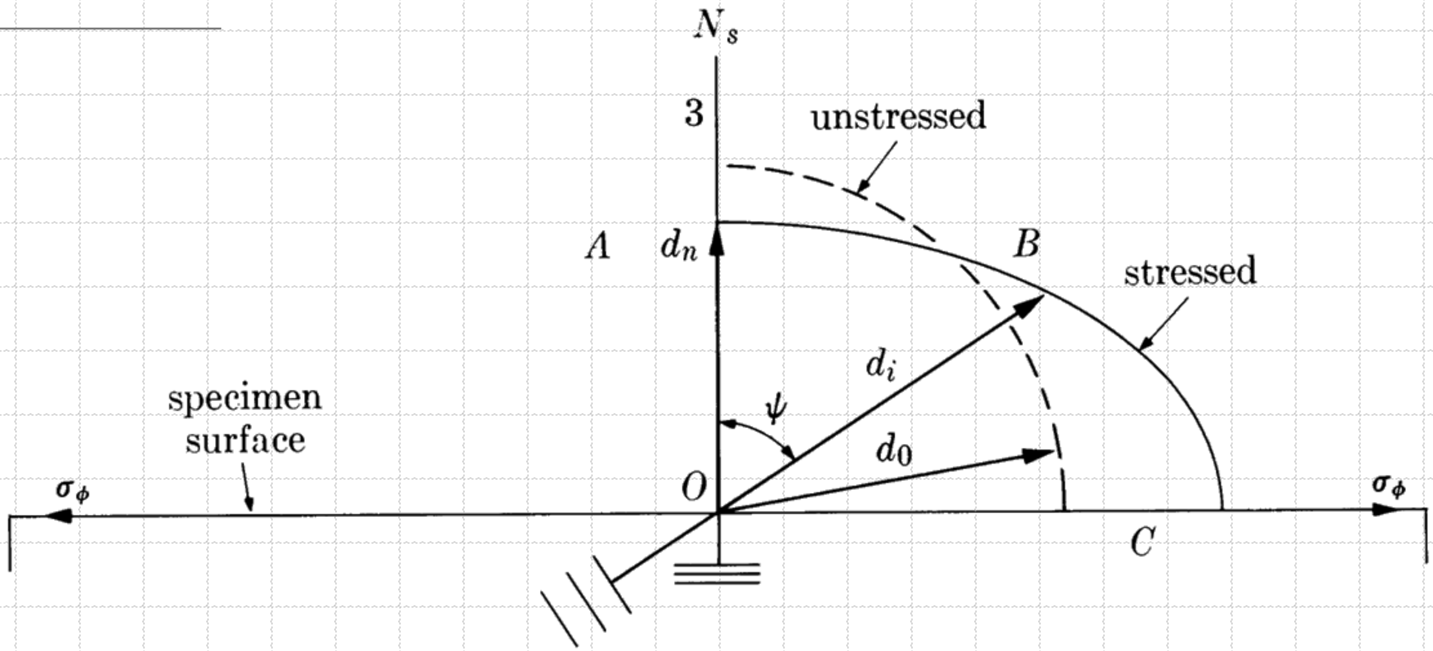
$$\sigma_y = -\frac{E}{\nu}\left(\frac{d_n - d_0}{d_0}\right)$$

**Diffraction techniques do not measure stresses in materials directly**

- Changes in d-spacing are measured to give strain
- Changes in line width are measured to give microstrain
- The lattice planes of the individual grains in the material act as strain gauges



# General Principles




Vector diagram of plane spacings $d$ for a tensile stress $\sigma_\phi$

$$\sigma_y = -\frac{E}{\nu}\left(\frac{d_n - d_0}{d_0}\right)$$

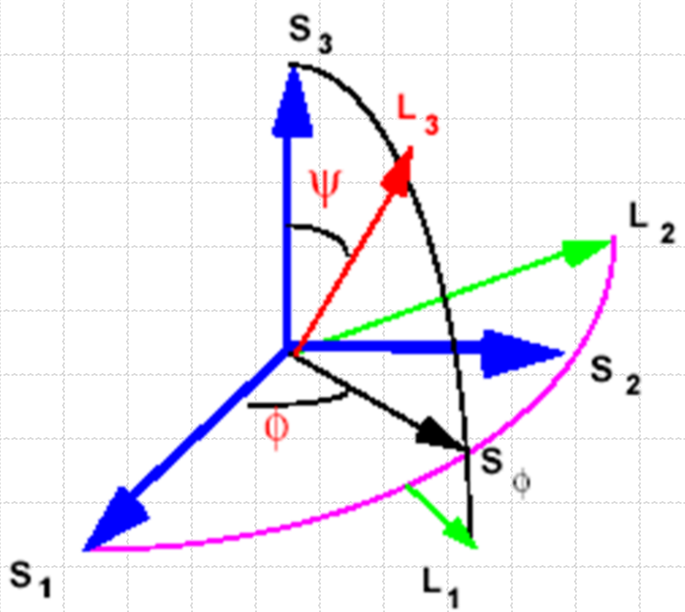
**we do not know $d_0$ !**

# Elasticity

- In general there are stress components in two or three directions at right angles to one another, forming biaxial or triaxial stress systems.
  - Stresses in a material can be related to the set of three principal stresses $\sigma_1$, $\sigma_2$ and $\sigma_3$.
- To properly describe the results of a diffraction stress measurement we introduce a coordinate systems for the instrument and the sample. These two coordinate systems are related by two rotation angles $\psi$ and $\phi$.

**$L_i$** – laboratory coordinate system
**$S_i$** – sample coordinate system

By convention the diffracting planes are normal to $L_3$



# Elasticity

- In an anisotropic elastic material stress tensor $\sigma_{ij}$ is related to the strain tensor $\varepsilon_{kl}$ as:

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$$

where $C_{ijkl}$ is elastic constants matrix.

Similarly:

$$\varepsilon_{ij} = S_{ijkl}\sigma_{kl}$$

where $S_{ijkl}$ is elastic compliance matrix.

For isotropic compound:

$$\varepsilon_{ij} = \frac{1+\nu}{E}\sigma_{ij} - \delta_{ij}\frac{\nu}{E}\sigma_{kk}$$

where $\delta_{ij}$ is Kroenecker's delta, "kk" indicates the summation $\sigma_{11} + \sigma_{22} + \sigma_{33}$

# Elasticity

- Or we can write it as:

$$\varepsilon_{11} = \frac{1}{E}\left[\sigma_{11} - \nu\left(\sigma_{22} + \sigma_{33}\right)\right],$$

$$\varepsilon_{22} = \frac{1}{E}\left[\sigma_{22} - \nu\left(\sigma_{11} + \sigma_{33}\right)\right],$$

$$\varepsilon_{33} = \frac{1}{E}\left[\sigma_{33} - \nu\left(\sigma_{11} + \sigma_{22}\right)\right],$$

$$\varepsilon_{23} = \frac{1}{2\mu}\sigma_{23},$$

$$\varepsilon_{31} = \frac{1}{2\mu}\sigma_{31},$$

$$\varepsilon_{12} = \frac{1}{2\mu}\sigma_{12}$$

where $\mu = \dfrac{E}{2\left(1+\nu\right)}$

shear modulus

# Elasticity

- Lets relate $\varepsilon_{mn}$ in one coordinate system to that in another system through transformation matrix:

$$\varepsilon_{mn}^{L} = M_{mi}^{SL} M_{nj}^{SL} \varepsilon_{ij}^{S}$$

The transformation matrix is:

$$M^{SL} = \begin{bmatrix} \cos\phi\cos\psi & -\sin\phi & \cos\phi\sin\psi \\ \sin\phi\cos\psi & \cos\phi & \sin\phi\sin\psi \\ -\sin\psi & 0 & \cos\psi \end{bmatrix}$$

so that we find

$$\begin{aligned} \left(\varepsilon_{33}^{L}\right)_{\phi\psi} &= M_{3i}^{SL} M_{3j}^{SL} \varepsilon_{ij}^{S} \\ &= \varepsilon_{11}^{S}\cos^2\phi\sin^2\psi + \varepsilon_{12}^{S}\sin 2\phi\sin^2\psi \\ &\quad + \varepsilon_{22}^{S}\sin^2\phi\sin^2\psi + \varepsilon_{33}^{S}\cos^2\psi \\ &\quad + \varepsilon_{13}^{S}\cos\phi\sin 2\psi + \varepsilon_{23}^{S}\sin\phi\sin 2\psi \end{aligned}$$

# Elasticity

- In terms of stresses:

$$\left(\varepsilon_{33}^{L}\right)_{\phi\psi} = \frac{1+\nu}{E}\left\{\sigma_{11}^{S}\cos^{2}\phi + \sigma_{12}^{S}\sin 2\phi + \sigma_{22}^{S}\sin^{2}\phi - \sigma_{33}^{S}\right\}\sin^{2}\psi + \frac{1+\nu}{E}\sigma_{33}^{S}$$
$$-\frac{\nu}{E}\left(\sigma_{11}^{S} + \sigma_{22}^{S} + \sigma_{33}^{S}\right) + \frac{1+\nu}{E}\left\{\sigma_{13}^{S}\cos\phi + \sigma_{23}^{S}\sin\phi\right\}\sin 2\psi$$
$$= \frac{d_{\phi\psi} - d_{0}}{d_{0}}$$

# Biaxial and Triaxial Stress Analysis

- Biaxial stress tensor is in the form:

$$\begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

since stress normal to a free surface must be zero: $\sigma_{ij}\mathbf{n}_j = 0$

For our tensor lets define:

$$\sigma_\phi^S = \sigma_{11}^S \cos^2\phi + \sigma_{22}^S \sin^2\phi$$

Then the equation for strain becomes:

$$\varepsilon_{\psi\phi}^L = \frac{d_{\phi\psi} - d_0}{d_0} = \frac{1+\nu}{E}\sigma_\phi^S \sin^2\psi - \frac{\nu}{E}\left(\sigma_{11}^S + \sigma_{22}^S\right)$$

# The $\sin^2\psi$ Method

- Stress $\sigma_{33}$ is zero, but strain $\varepsilon_{33}$ is not zero. It has finite value given by the Poisson contractions due to $\sigma_{11}$ and $\sigma_{22}$:

$$\varepsilon_{33}^{S} = -\nu\left(\varepsilon_{11}^{S} + \varepsilon_{22}^{S}\right) = -\frac{\nu}{E}\left(\sigma_{11}^{S} + \sigma_{22}^{S}\right)$$

Then strain equation can be written as:

$$\varepsilon_{\phi\psi}^{L} - \varepsilon_{33}^{S} = \frac{(1+\nu)\sigma_{\phi}^{S}}{E}\sin^2\psi$$

$$\varepsilon_{\phi\psi}^{L} - \varepsilon_{33}^{S} = \frac{d_{\phi\psi} - d_0}{d_0} - \frac{d_n - d_0}{d_0}$$

$$= \frac{d_{\phi\psi} - d_n}{d_0} = \frac{(1+\nu)\sigma_{\phi}^{S}}{E}\sin^2\psi$$

# The $\sin^2\psi$ Method

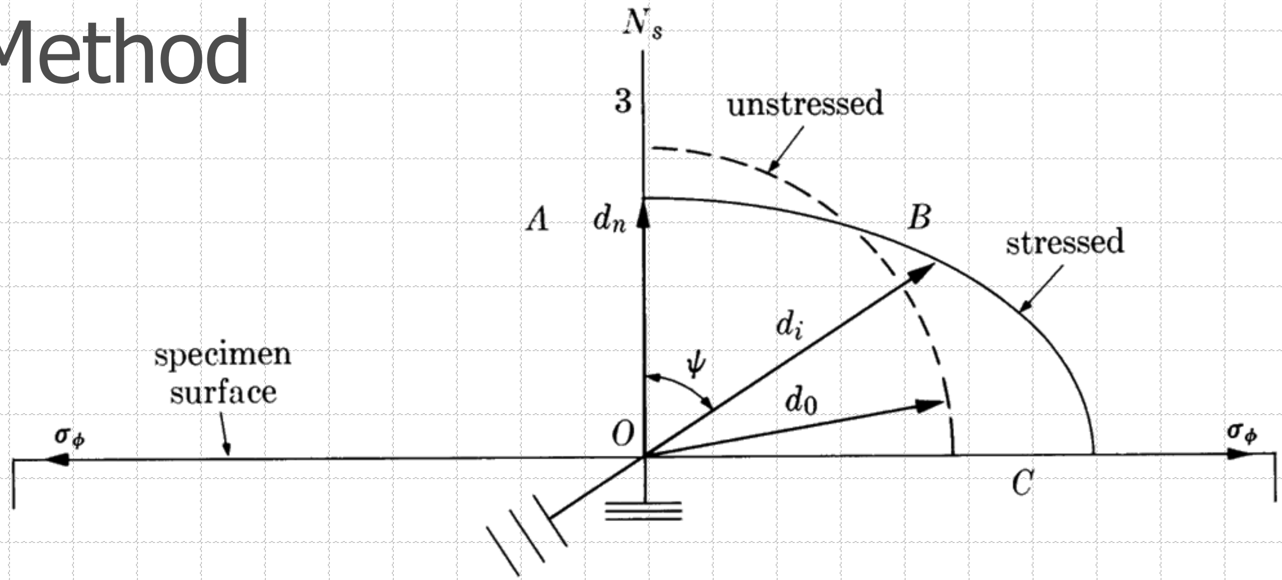
- We make ingenious approximation (by Glocker *et al*. in 1936):
  - $d_n$, $d_i$ and $d_0$ are very nearly equal to one another,
  - $(d_i - d_n)$ is small compared to $d_0$,
  - unknown $d_0$ is replaced by $d_i$ or $d_n$ with negligible error.

$$\boxed{\frac{d_{\phi\psi} - d_n}{d_n} = \frac{(1+\nu)\sigma_\phi}{E}\sin^2\psi}$$

$$\sigma_\phi = \frac{E}{(1+\nu)\sin^2\psi}\left(\frac{d_{\phi\psi} - d_n}{d_n}\right)$$

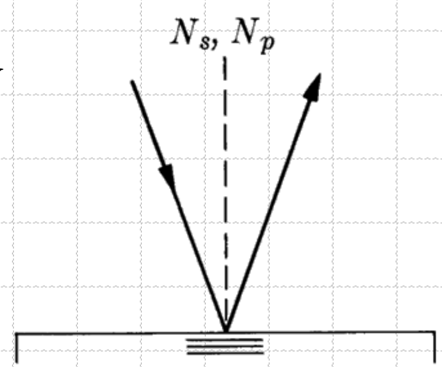
- The stress in a surface can be determined by measuring the *d*-spacing as a function of the angle $\psi$ between the surface normal and the diffracting plane normal
- Measurements are made in the back-reflection regime ($2\theta \rightarrow 180°$) to obtain maximum accuracy

# The $\sin^2\psi$ Method

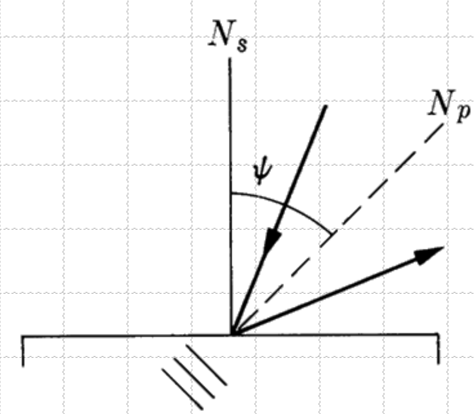



Vector diagram of plane spacings $d$ for a tensile stress $\sigma_\phi$

$$\frac{d_{\phi\psi} - d_n}{d_n} = \frac{(1+\nu)\sigma_\phi}{E}\sin^2\psi$$




Measurement of $d_n$




Measurement of $d_i$

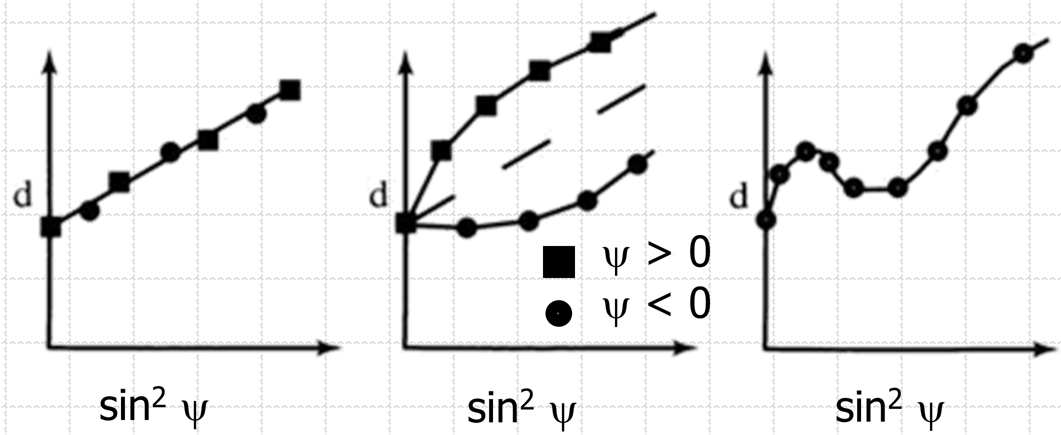
# The sin$^2\psi$ Method

- Lets assume that stresses in zx plane are equal. This is referred to as an equal-biaxial stress state. We can write sample frame stress as:

$$\begin{bmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

**No stress dependence on $\phi$**

$$\frac{d_\psi - d_n}{d_n} = \frac{(1+\nu)\sigma}{E}\sin^2\psi$$




Biaxial or uniaxial stress | Triaxial stresses present | Texture present

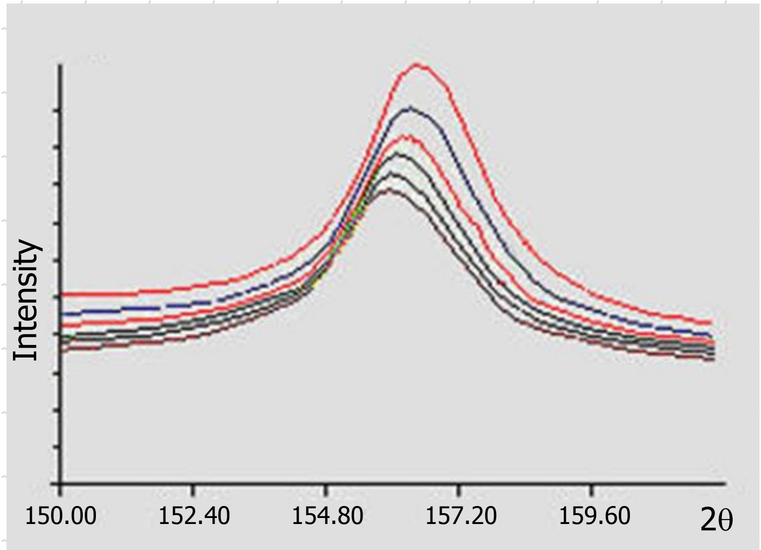
# The $\sin^2\psi$ Method

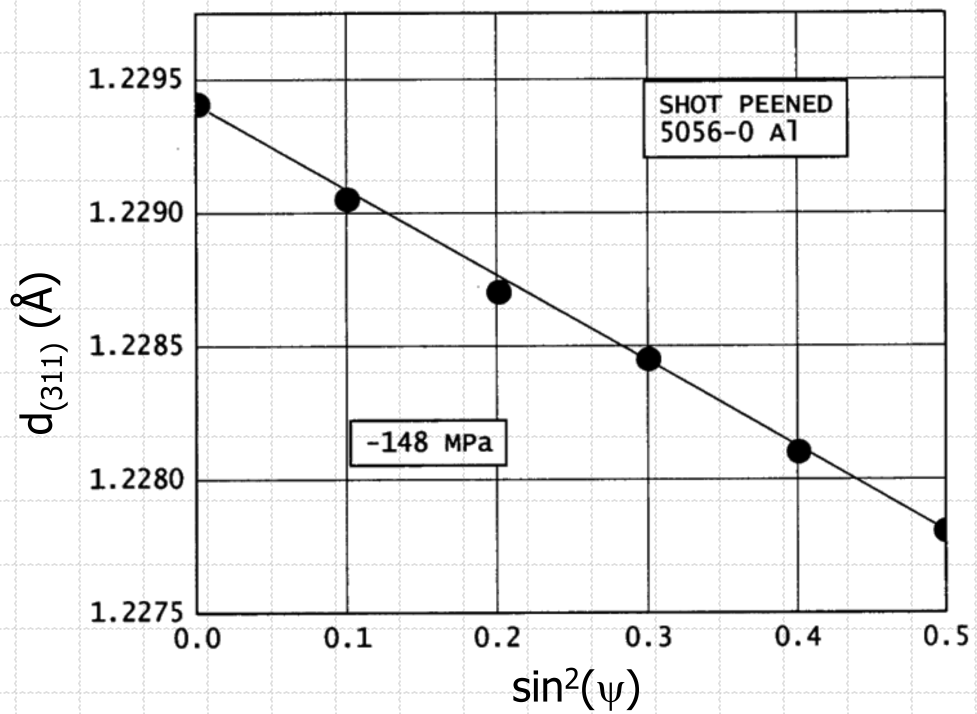
$$d_\psi = \frac{(1+\nu)\sigma}{E} d_n \sin^2\psi + d_n$$

Slope of the plot is:

$$\frac{\partial d_\psi}{\partial \sin^2\psi} = \frac{(1+\nu)}{E}\sigma d_n$$

Generally $\nu$ and E are well-known constants

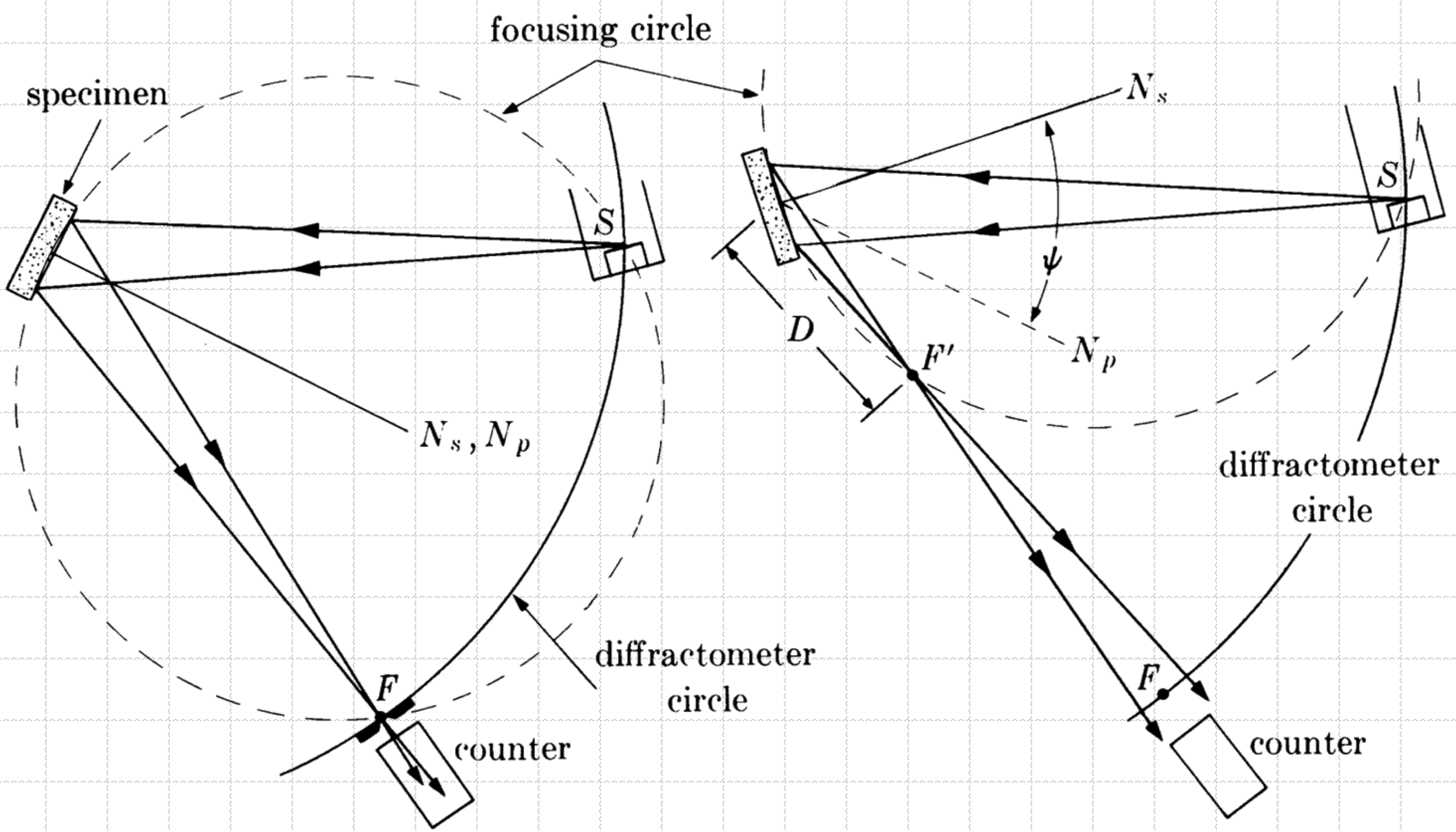



Linear dependence of d (311) upon $\mathrm{Sin}^2\psi$ for shot peened 5056-0 aluminum.

# Diffractometer Method

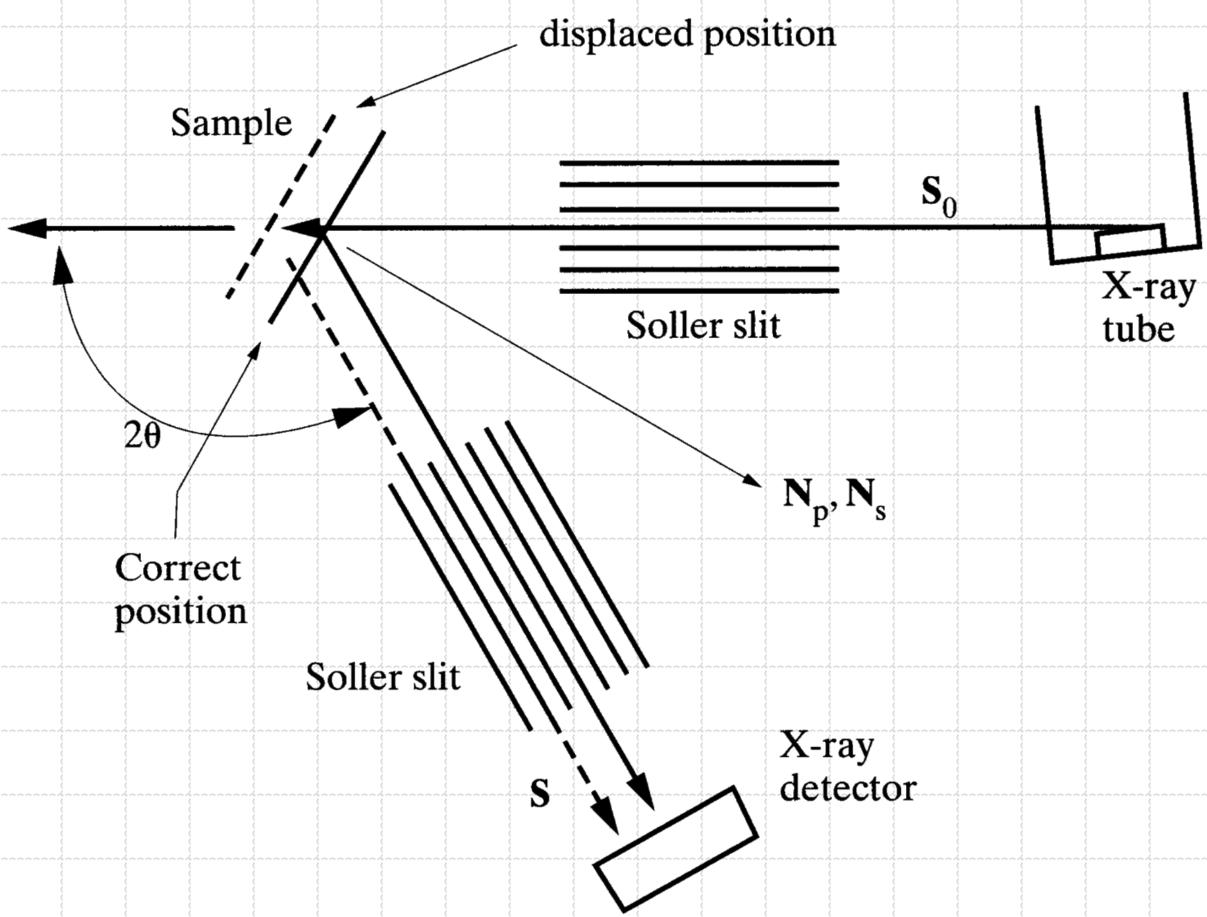
$$\frac{D}{R} = \frac{\sin(\theta-\psi)}{\sin(\theta-\psi)}$$




(a) $\psi = 0$ (b) $\psi = \psi$

# Diffractometer Method

- The effect of sample or $\psi$-axis displacement can be minimized if a parallel beam geometry is used instead of focused beam geometry.



# Measurement of Line Position

- Sample must remain on the diffractometer axis as $\psi$ is changed (even if the sample is large)
- Radial motion of the detector to achieve focussing must not change the measured $2\theta$
- L-P factor may vary significantly across a (broad) peak

$$\Rightarrow \; LPA = \left(\frac{1+\cos^2 2\theta}{\sin^2\theta}\right)(1-\tan\psi\cot\theta)$$

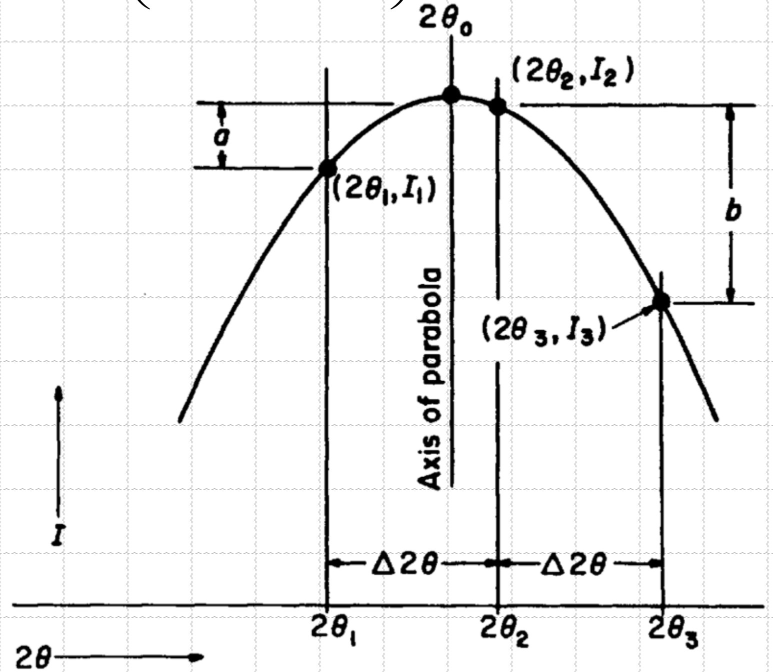
- Absorption will vary when $\Psi \neq 0$
- Measurement of peak position often requires fitting the peak with a parabola:

$$2\theta_0 = 2\theta_1 + \frac{\Delta 2\theta}{2}\left(\frac{3a+b}{a+b}\right)$$

$$a = I_2 - I_1$$

$$b = I_2 - I_3$$

$$\Delta 2\theta = 2\theta_2 - 2\theta_1 = 2\theta_3 - 2\theta_2$$



# Measurements of Stress in Thin Films

- Thin films are usually textured. No difficulty with moderate degree of preferred orientation.
- Sharp texture has the following effects:
  - Diffraction line strong at $\psi = 0$ and absent at $\psi = 45^o$.
  - If material anisotropic E will depend on direction in the specimen. Oscillations of d vs $\sin^2\psi$.

# Measurements of Stress in Thin Films

- In thin films we have a biaxial stress, so:

$$\frac{d_{\phi\psi} - d_n}{d_n} = \frac{(1+\nu)\sigma_\phi}{E}\sin^2\psi$$

If we have equal-biaxial stress then it is even simpler:

$$\frac{a_\psi - a_n}{a_n} = \frac{d_{hkl}^{\psi} - d_{hkl}^{n}}{d_{hkl}^{n}} = \frac{(1+\nu)\sigma}{E}\sin^2\psi$$

We can calculate $\psi$ for any unit cell and any orientation. For cubic:

$$\psi = a\cos\left(\frac{h_\perp h + k_\perp k + l_\perp l}{\sqrt{(h_\perp^2 + k_\perp^2 + l_\perp^2)(h^2 + k^2 + l^2)}}\right)$$

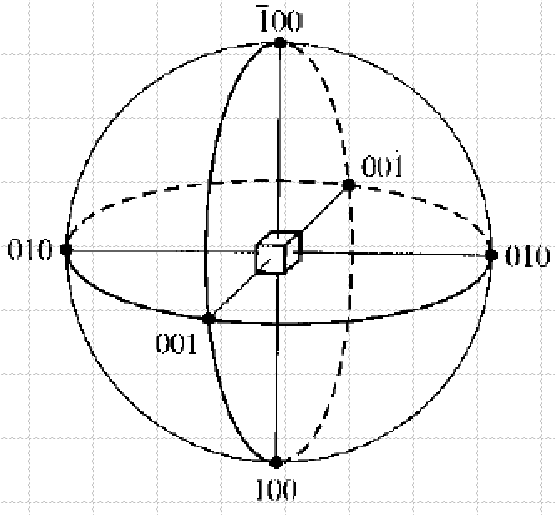
Symbols $h_\perp$, $k_\perp$ and $l_\perp$ define (hkl) - oriented film

# Texture Analysis

- The determination of the lattice preferred orientation of the crystallites in a polycrystalline aggregate is referred to as texture analysis.

- The term texture is used as a broad synonym for preferred crystallographic orientation in a polycrystalline material, normally a single phase.

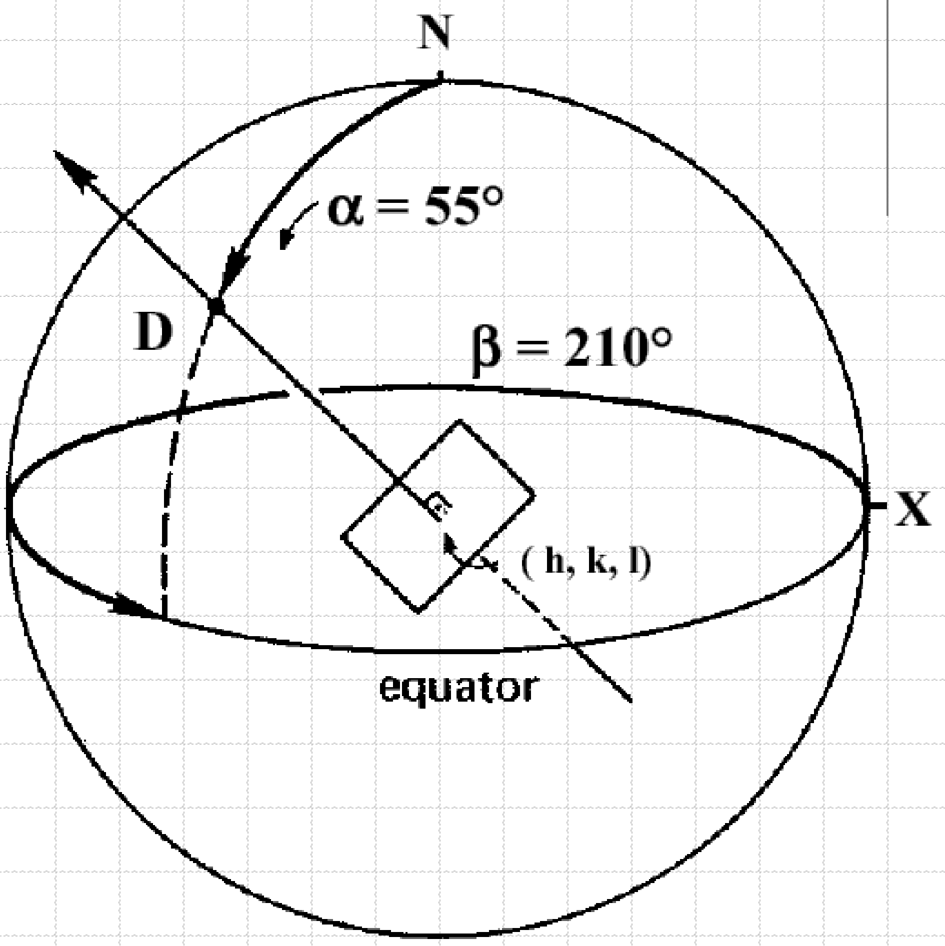
- The preferred orientation is usually described in terms of pole figures.




{100} poles of a cubic crystal

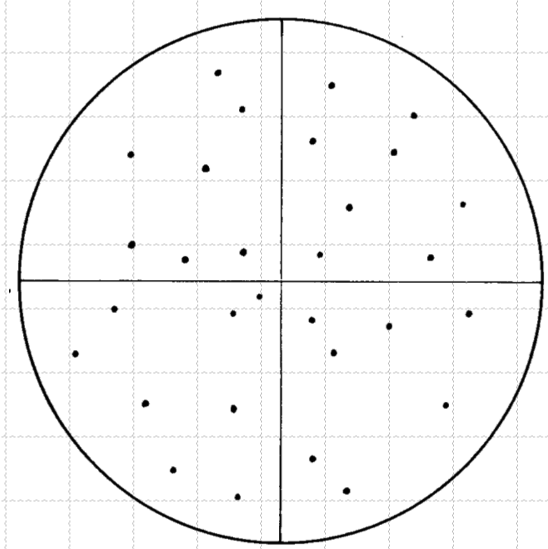
# The Pole Figures

- Let us consider the plane (h k l) in a given crystallite in a sample. The direction of the plane normal is projected onto the sphere around the crystallite.
- The point where the plane normal intersects the sphere is defined by two angles: pole distance $\alpha$ and an azimuth $\beta$.
- The azimuth angle is measured counter clock wise from the point X.

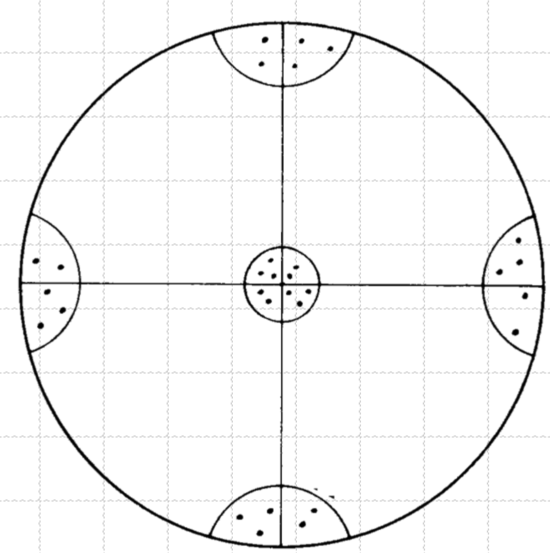


# The Pole Figures

- Let us now assume that we project the plane normals for the plane (h k l) from all the crystallites irradiated in the sample onto the sphere.
- Each plane normal intercepting the sphere represents a point on the sphere. These points in return represent the Poles for the planes (h k l) in the crystallites. The number of points per unit area of the sphere represents the pole density.

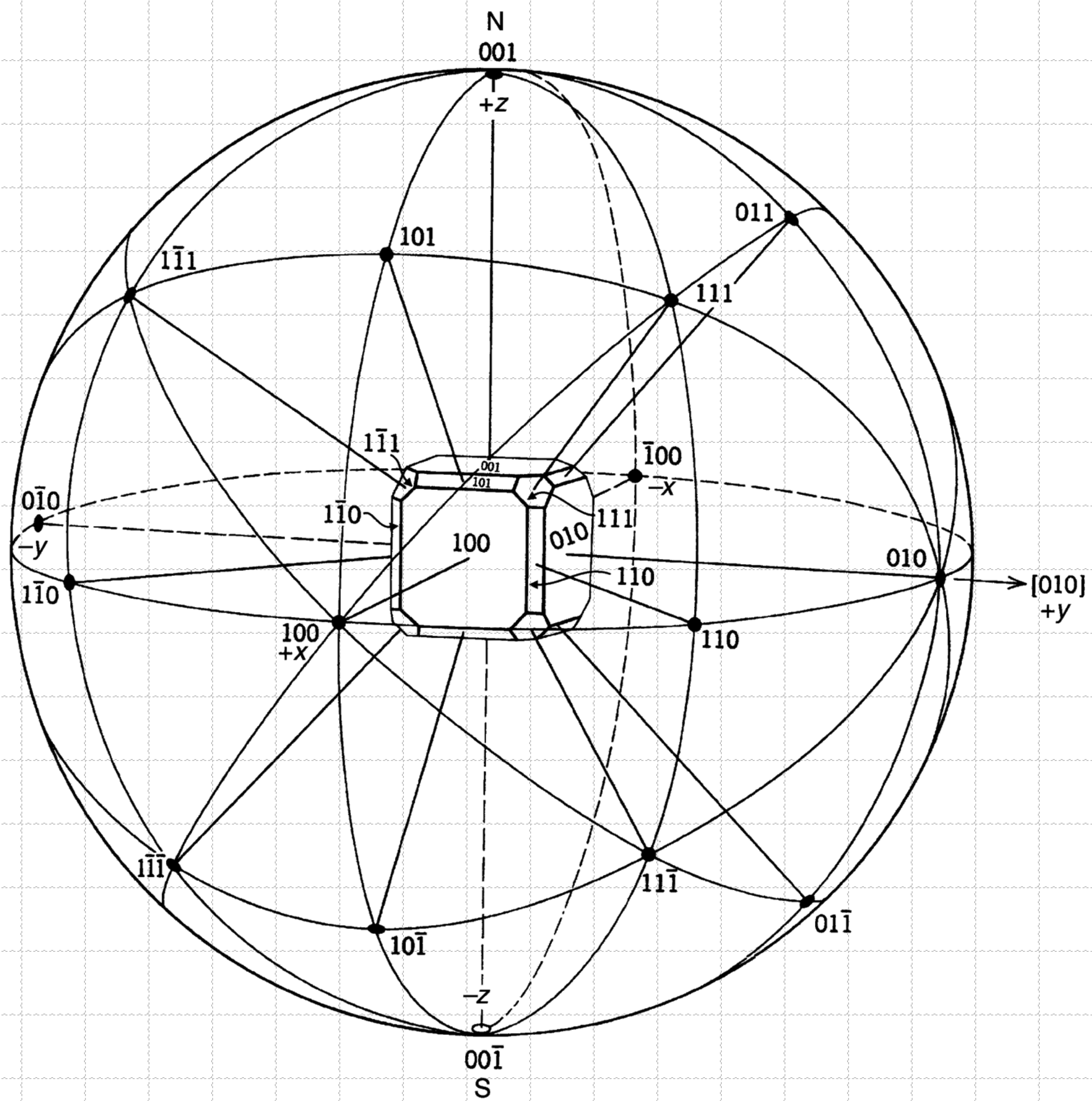


Random orientation

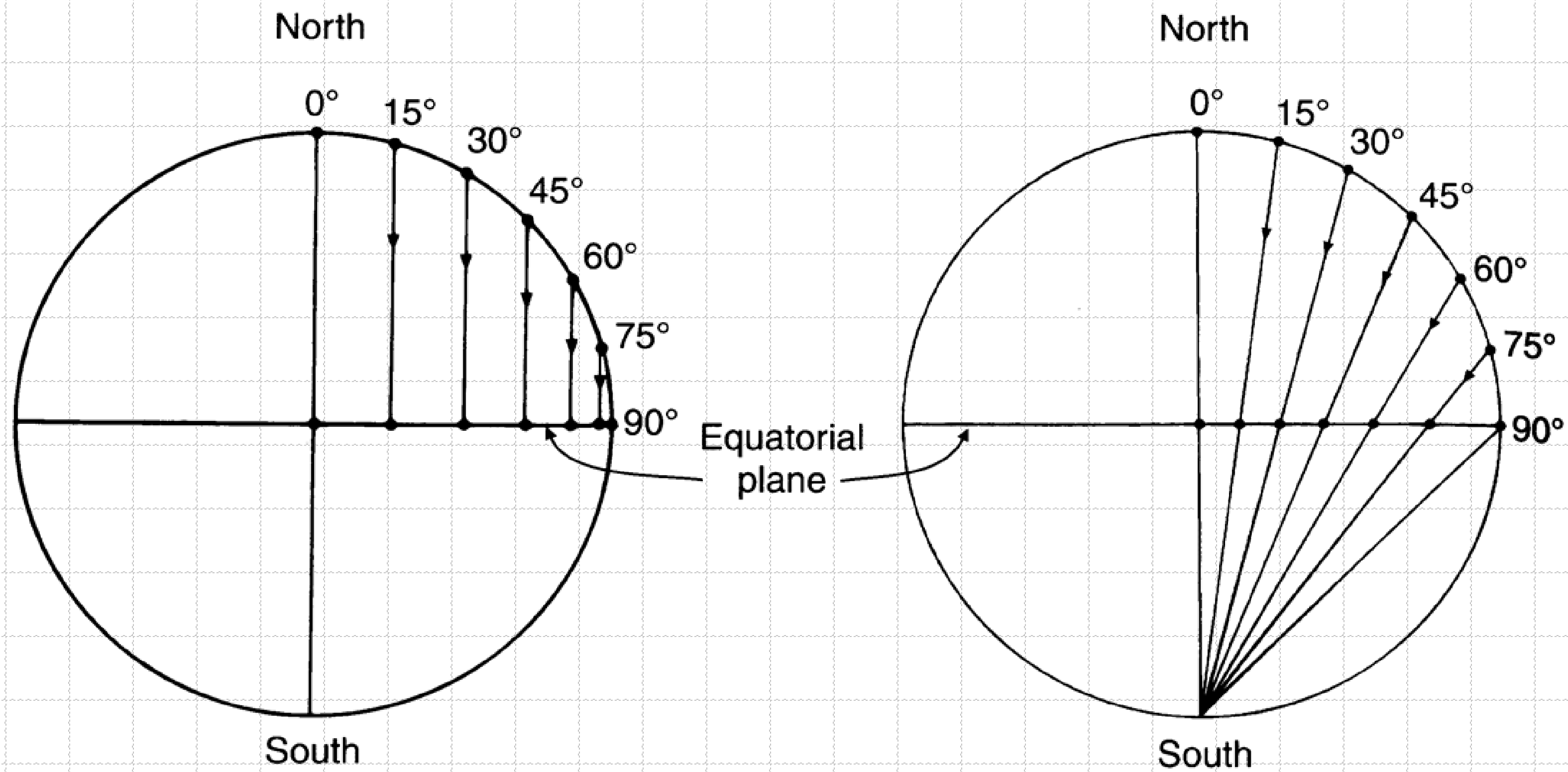


Preferred orientation

# The Pole Figures



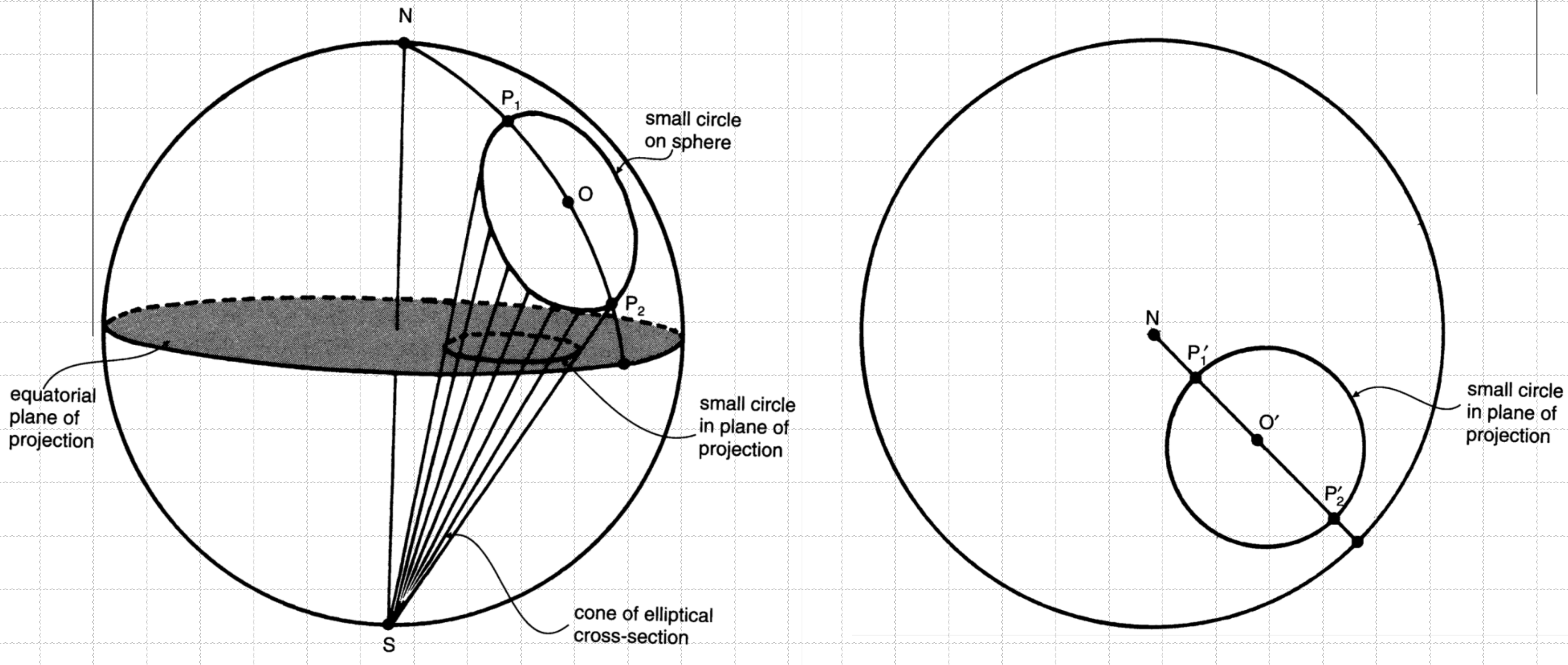
# The Stereographic Projection



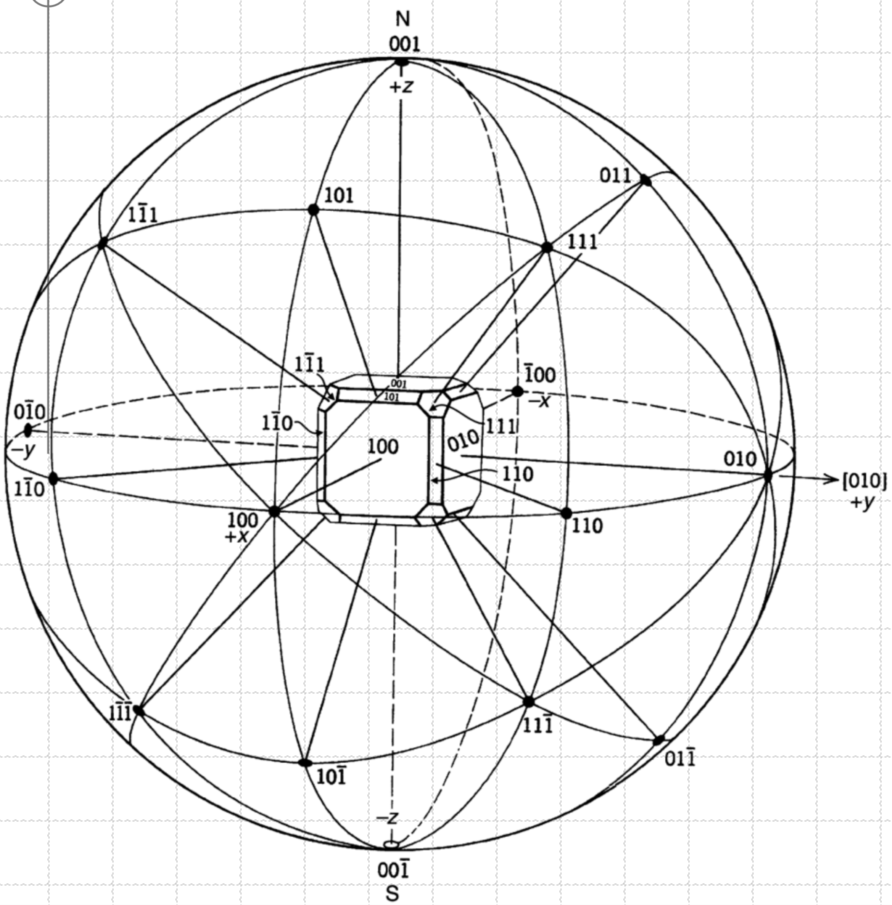

As we look down to the earth

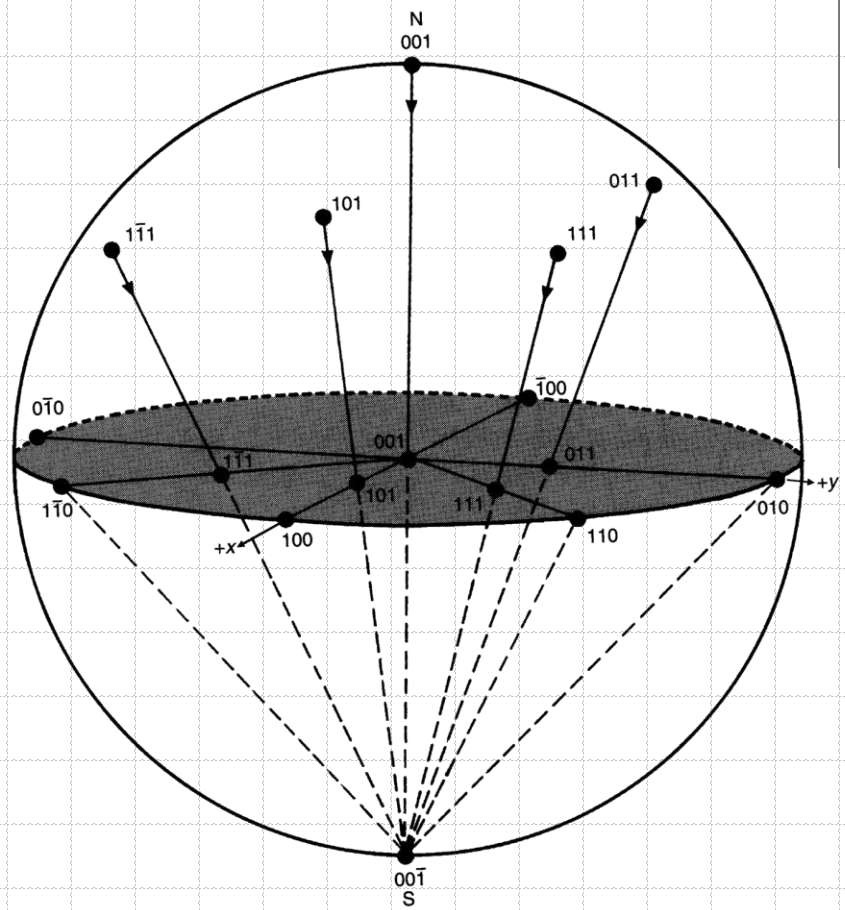
The stereographic projection

# The Stereographic Projection

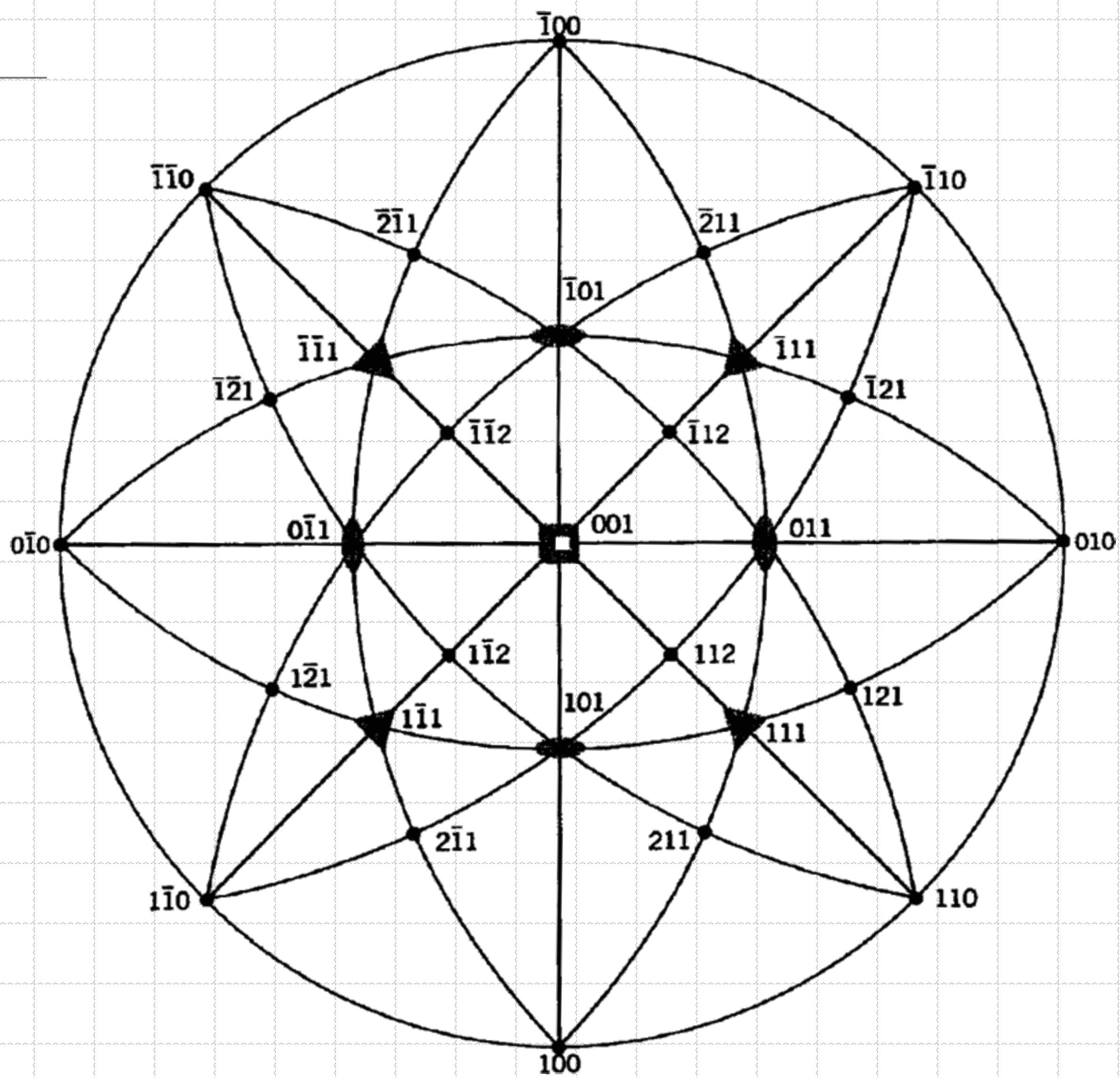


# The Pole Figures



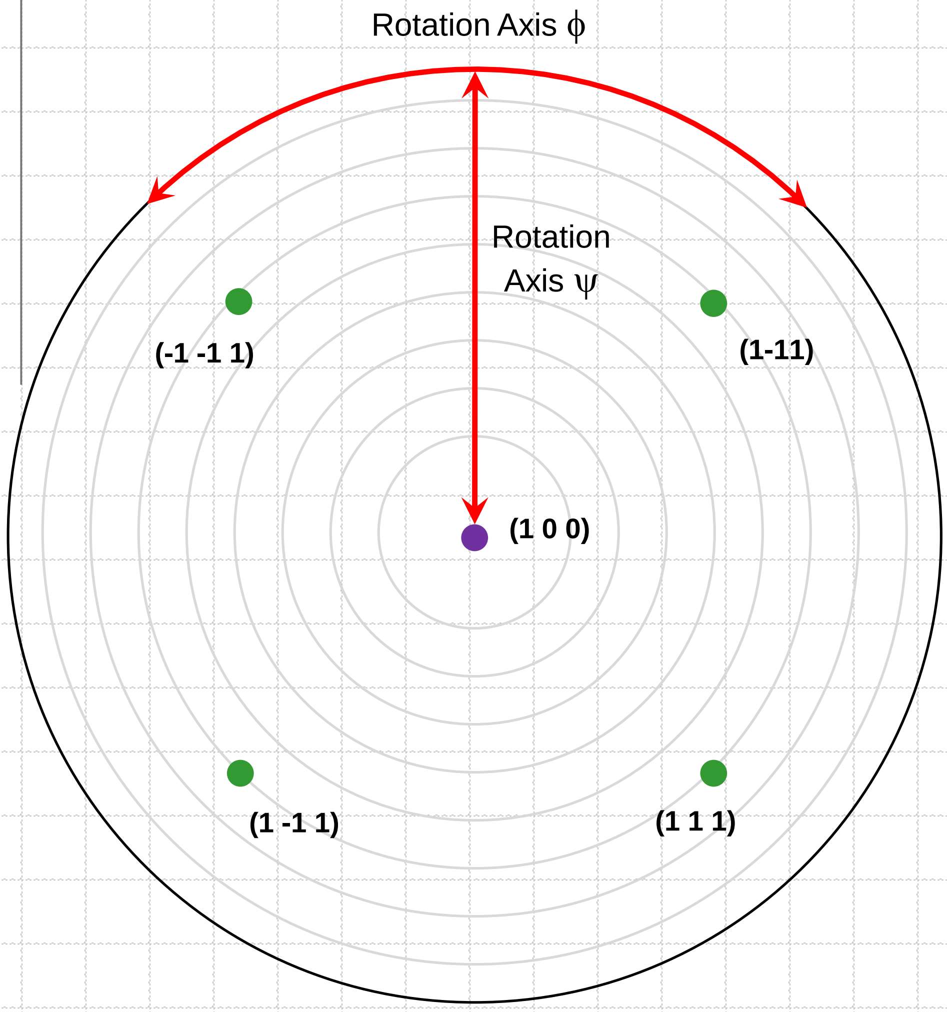
# The Pole Figures

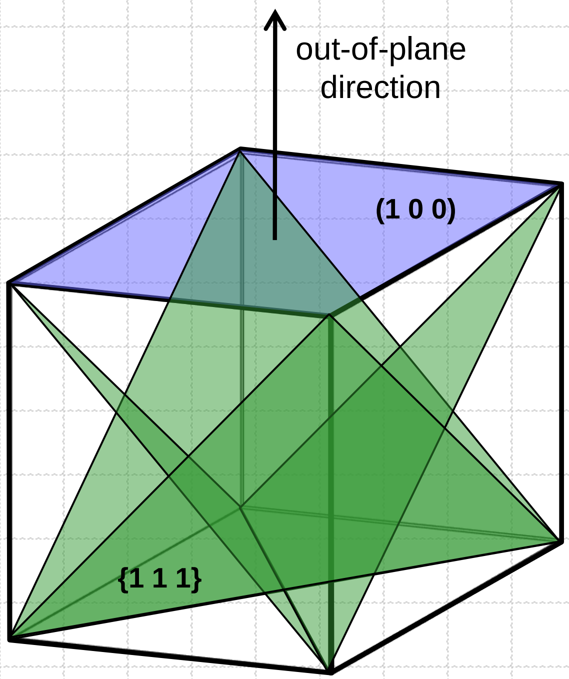


# The Pole Figures

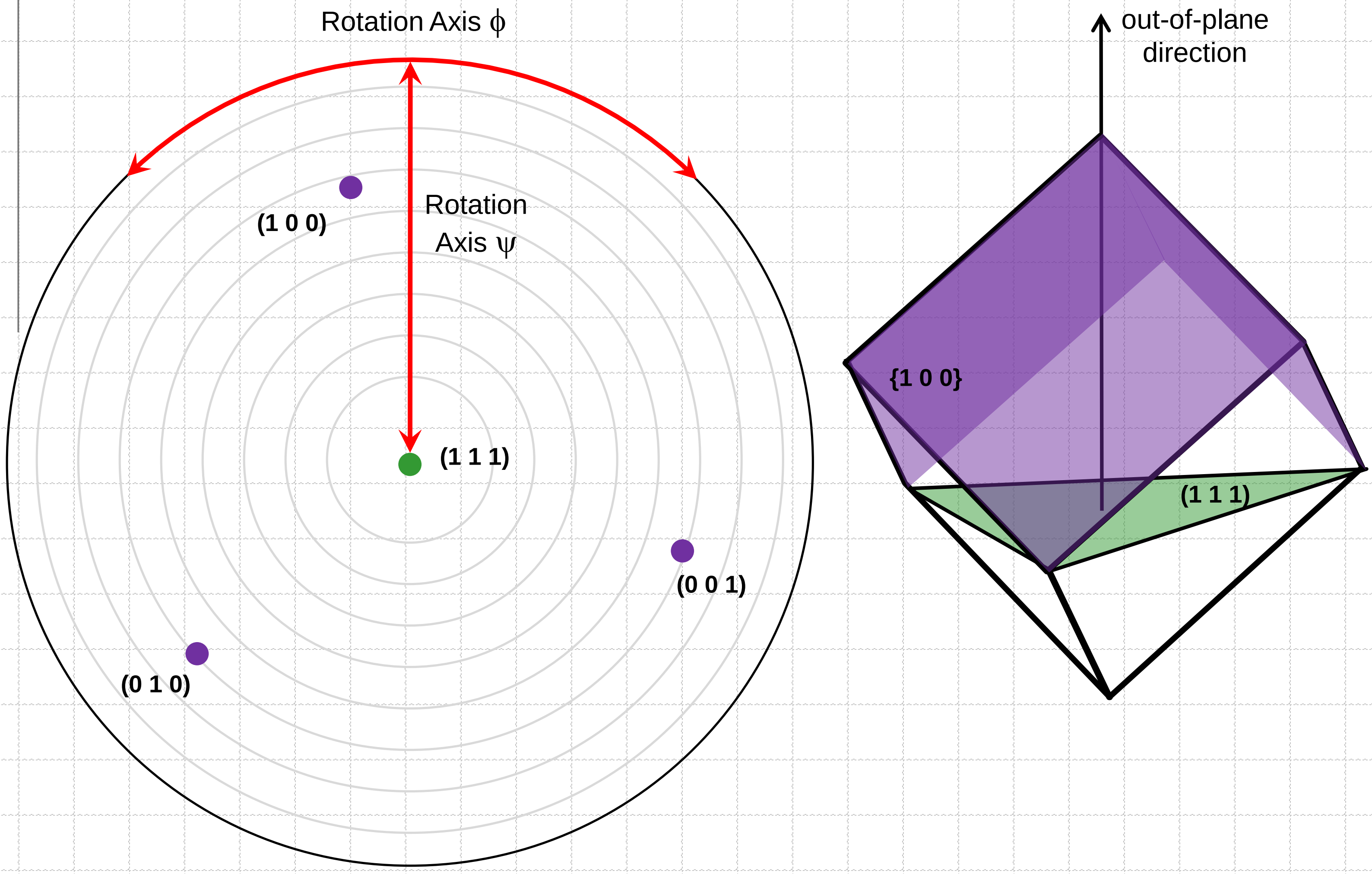
- We now project the sphere with its pole density onto a plane. This projection is called a pole figure.
  - A pole figure is scanned by measuring the diffraction intensity of a given reflection with constant $2\theta$ at a large number of different angular orientations of a sample.
  - A contour map of the intensity is then plotted as a function of the angular orientation of the specimen.
  - The intensity of a given reflection is proportional to the number of hkl planes in reflecting condition.
  - Hence, the pole figure gives the probability of finding a given (h k l) plane normal as a function of the specimen orientation.
  - If the crystallites in the sample have random orientation the contour map will have uniform intensity contours.

# The Pole Figures



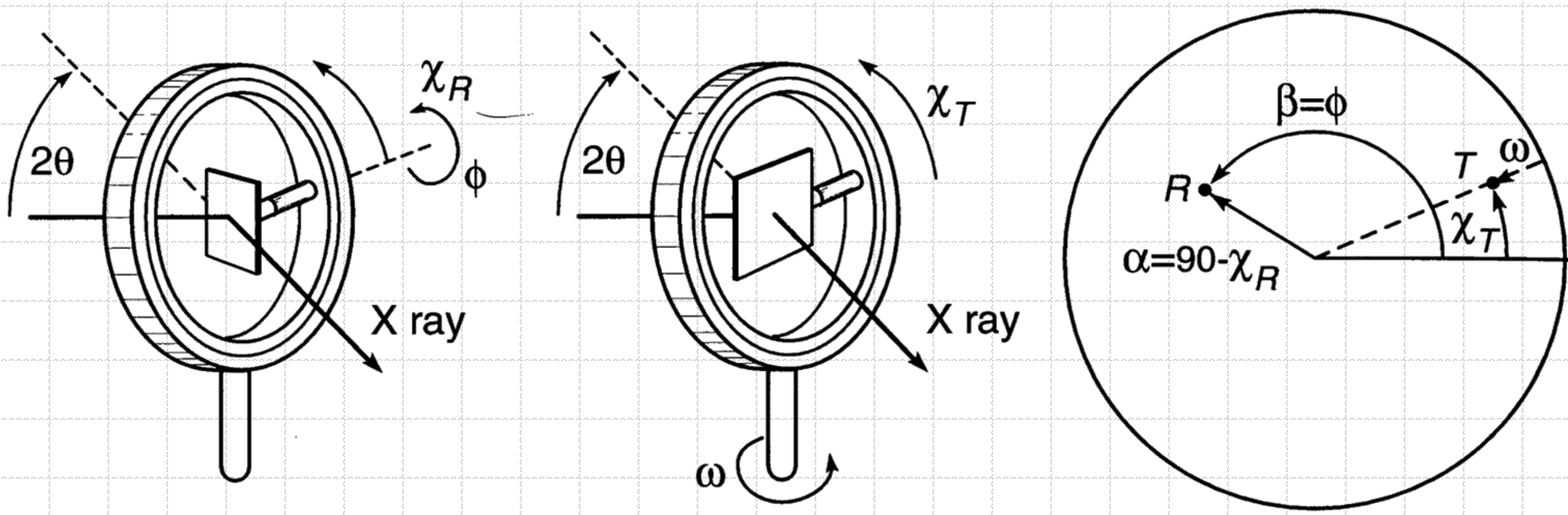



# The Pole Figures



# Texture Measurements

- Requires special sample holder which allows rotation of the specimen in its own plane about an axis normal to its surface, $\phi$, and about a horizontal axis, $\chi$.

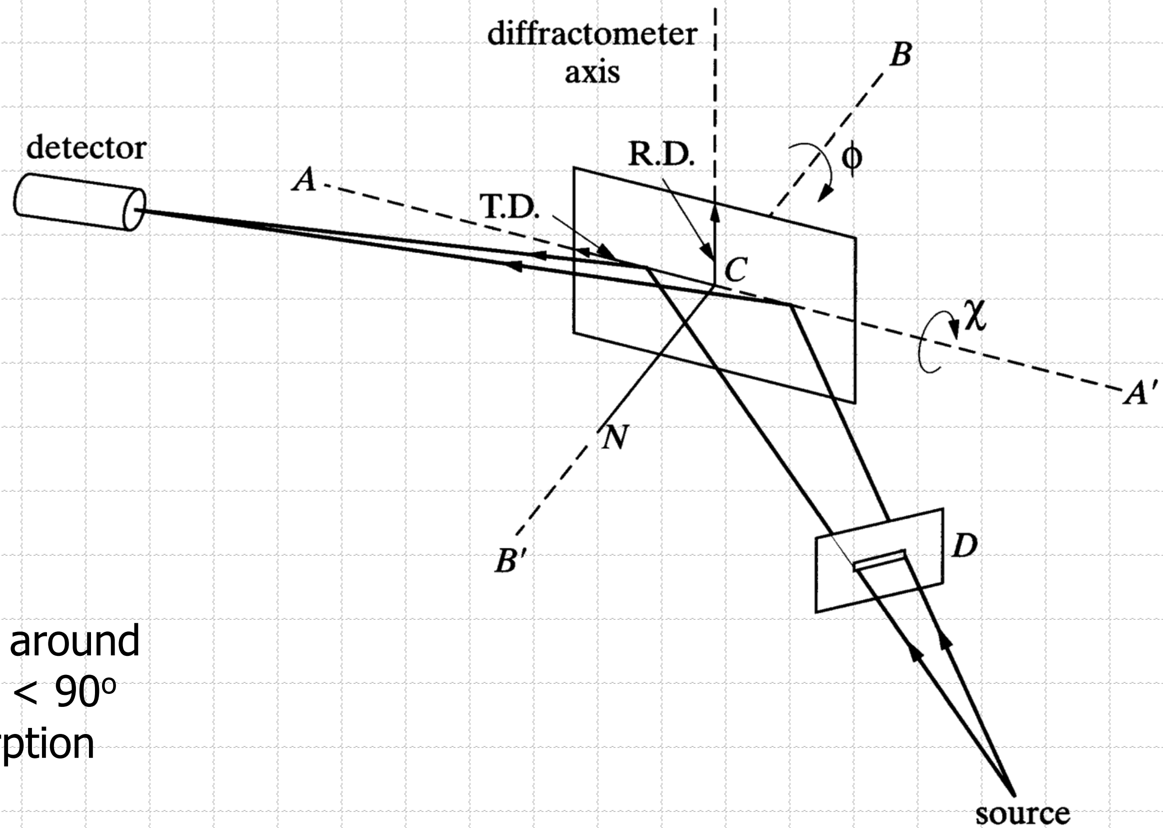



Reflection

Transmission

# Schulz Reflection Method

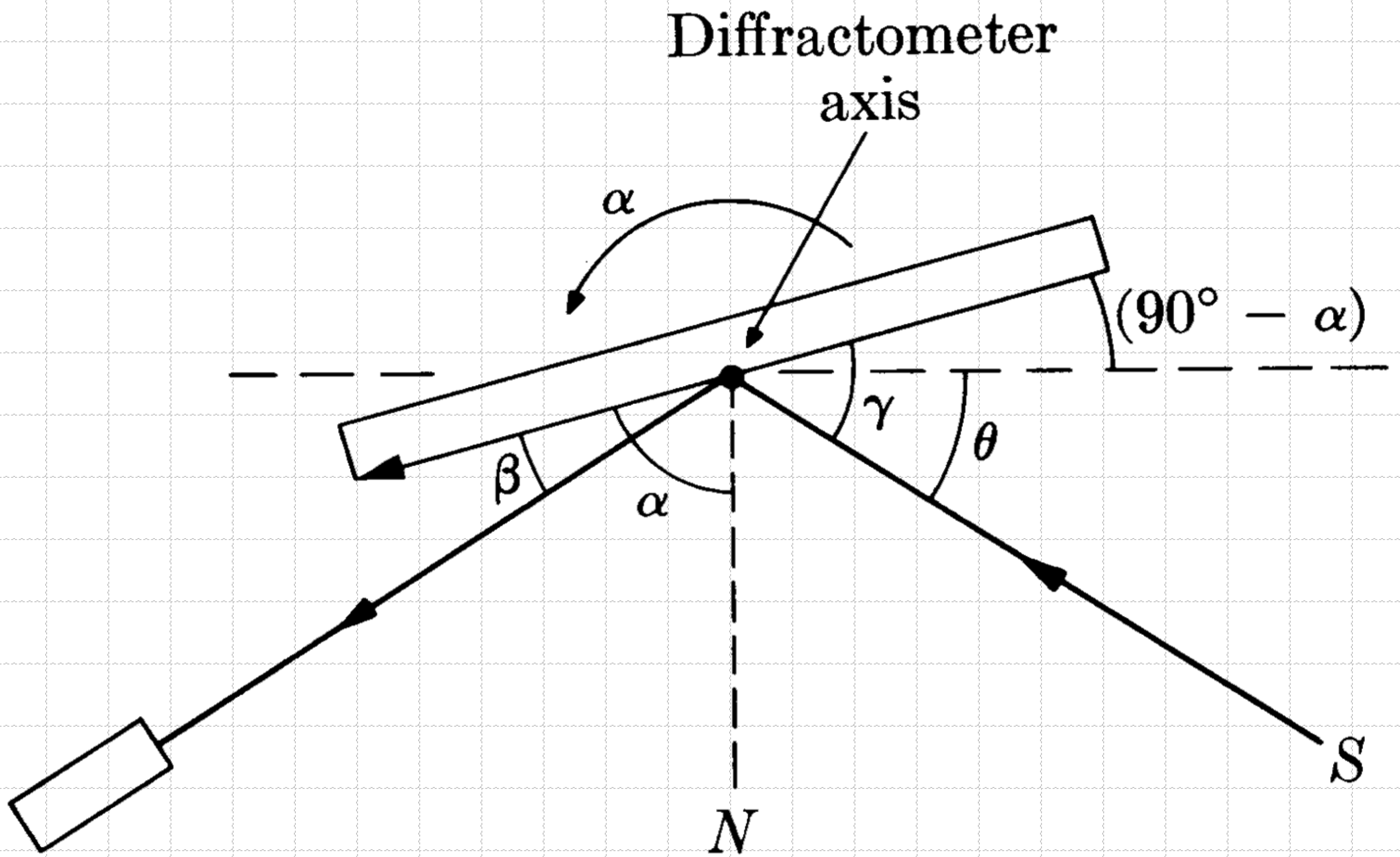
- In the Bragg-Brentano geometry a divergent x-ray beam is focused on the detector.
- This no longer applies when the sample is tilted about $\chi$.




Advantage: rotation in around $\chi$ in the range $40^o < \chi < 90^o$ does not require absorption correction.

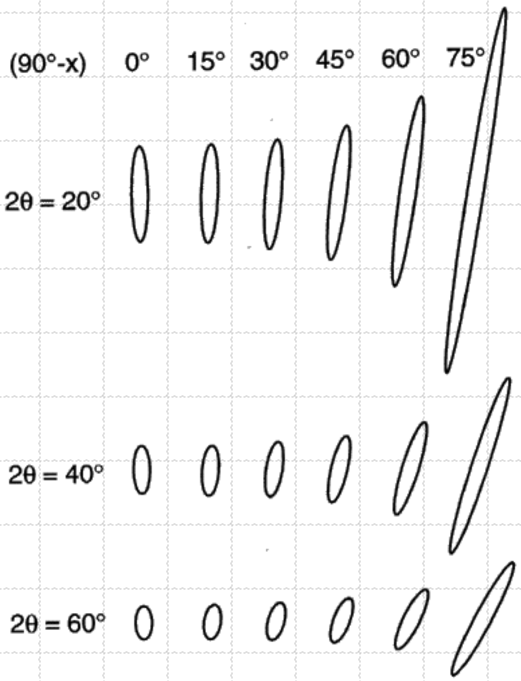
# Field and Merchant Reflection Method

- The method is designed for a parallel incident beam.

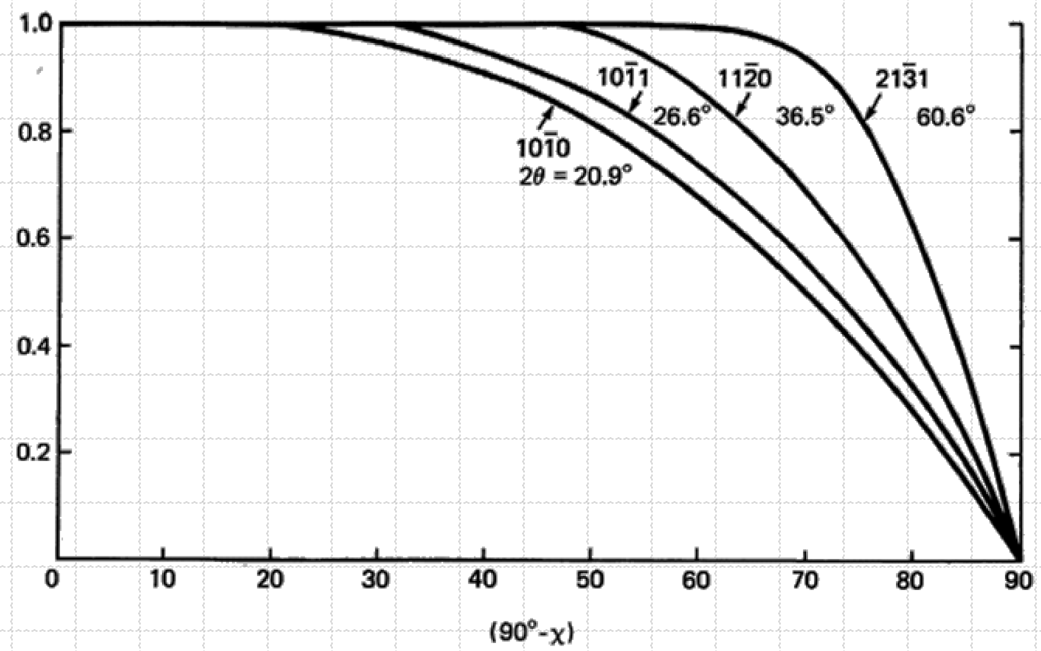


# Defocusing Correction

- As sample is tilted in $\chi$, the beam spreads out on a surface.
- At high $\chi$ values not all the beam enters the detector.
- Need for defocusing correction.




Change in shape and orientation of the irradiated spot on a sample surface for different sample inclinations as a function of tilt angle $\alpha$ and Bragg angle $2\theta$. The incident beam is cylindrical.




Intensity correction for x-ray pole figure determination in reflection geometry. Selected reflections for quartz.

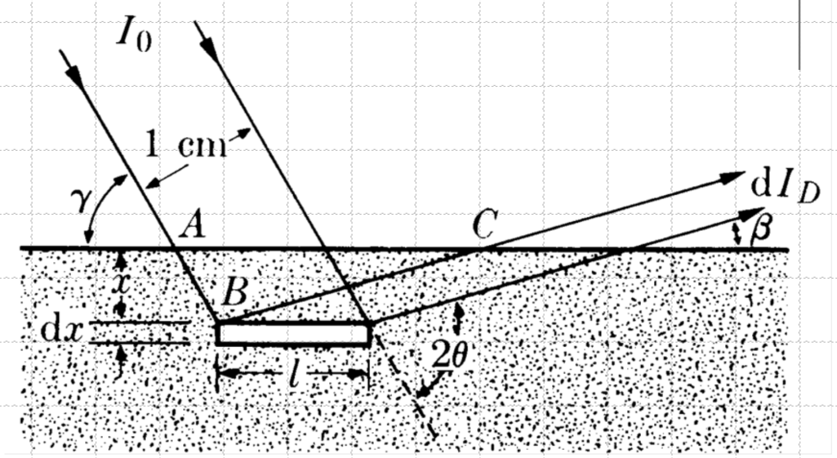
**U.F. Kocks, C.N. Tomé, and H.-R. Wenk, "Texture and Anisotropy" 2000.**

# Absorption Correction

- Diffracted intensities must be corrected for change in absorption due to change in $\alpha$.

$$dI_D = \frac{I_0 ab}{\sin\gamma} e^{-\mu x(1/\sin\gamma + 1/\sin\beta)} dx$$

*a* – volume fraction of a specimen containing particles having correct orientation for reflection of the incident beam.
*b* – fraction of the incident energy which is diffracted by unit volume




substitute

$$\gamma = \theta + (90^o - \alpha),\ \beta = \theta - (90^o - \alpha)$$

Integrate 0 < x < ∞

$$I_D = \frac{I_0 ab}{\mu\{1 - [\cos(\alpha-\theta)/\cos(\alpha+\theta)]\}}$$

We interested in the intensity at angle $\alpha$, relative to intensity at $\alpha$ = 90°:

$$S = \frac{I_D(\alpha = \alpha)}{I_D(\alpha = 90^o)} = 1 - \cot\alpha\cot\theta$$

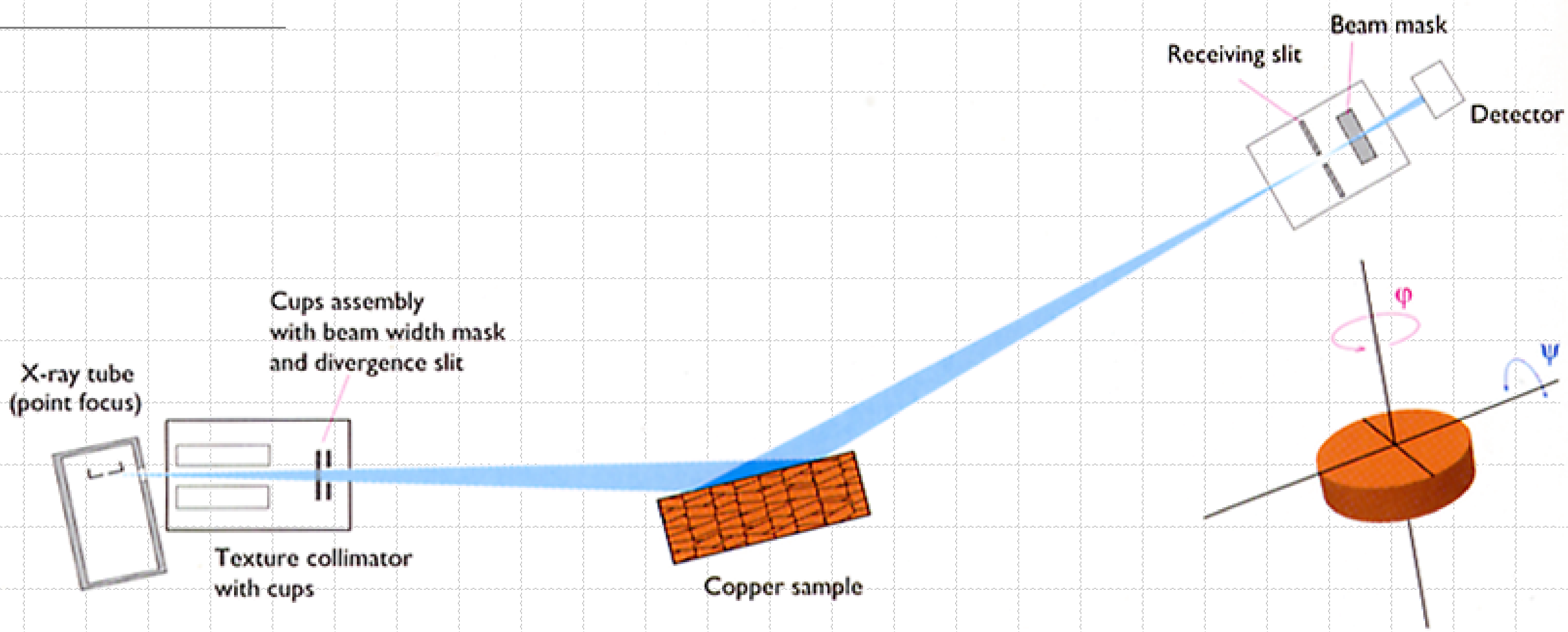
# Pole Figure Measurement

- Pole figure diffractometer consists of a four-axis single-crystal diffractometer.

Rotation axes:

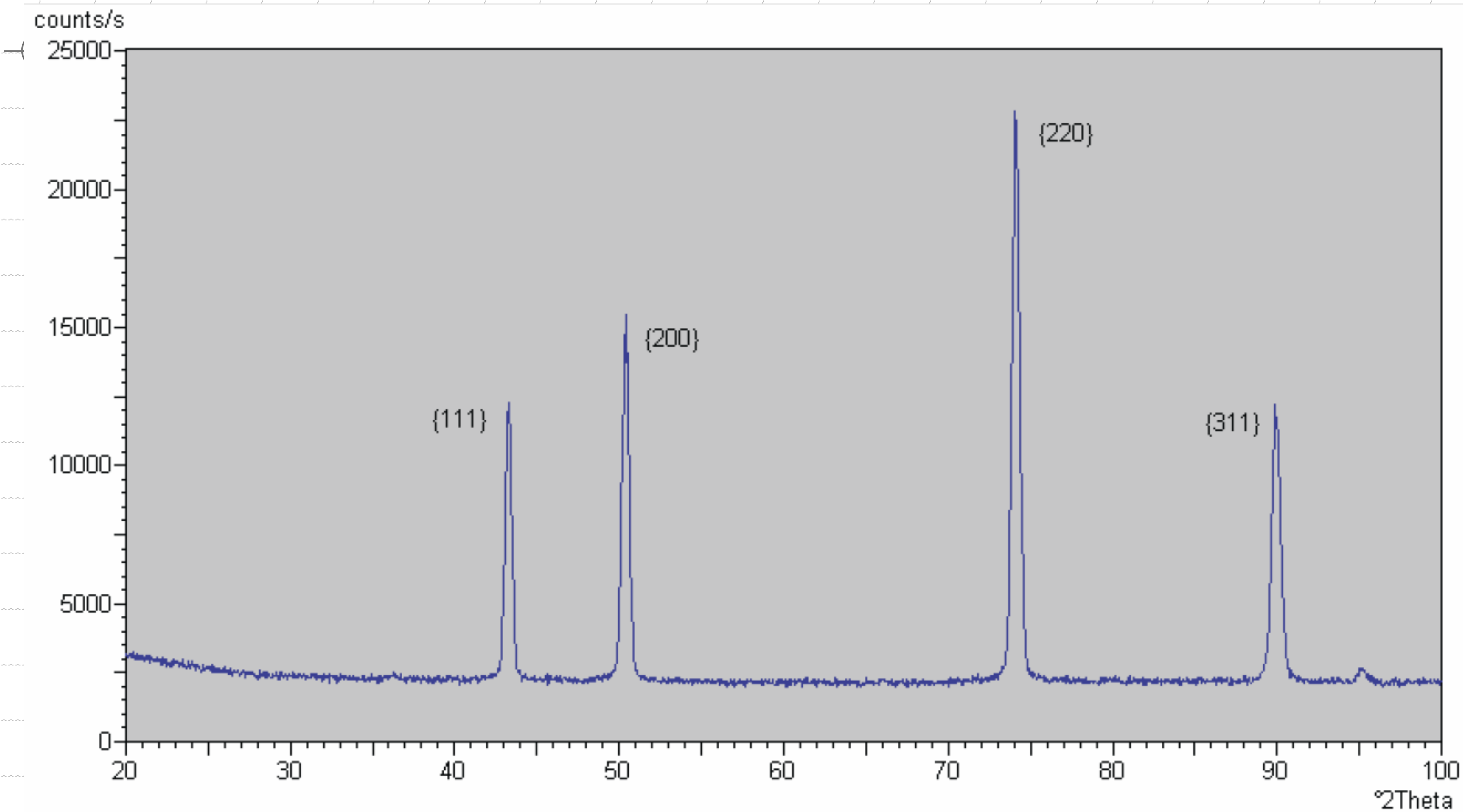
$\theta$, $\omega$, $\chi$, and $\phi$

# Example: Rolled Copper




- Texture measurements were performed on Cu disk Ø = 22 mm, t = 0.8 mm.
- Four pole figures (111), (200), (220) and (311) were collected using Schulz reflection method.
- Background intensities were measured next to diffraction peaks with offset $2\theta = \pm 4^{o}$.
- Defocusing effects were corrected using two methods:
    - measured texture free sample
    - calculated (FWHM of the peaks at $\psi = 0^{o}$ is required – obtained from $\theta$-$2\theta$ scan.
- X'Pert Texture program was used for quantitative analysis.

# Example: Rolled Copper

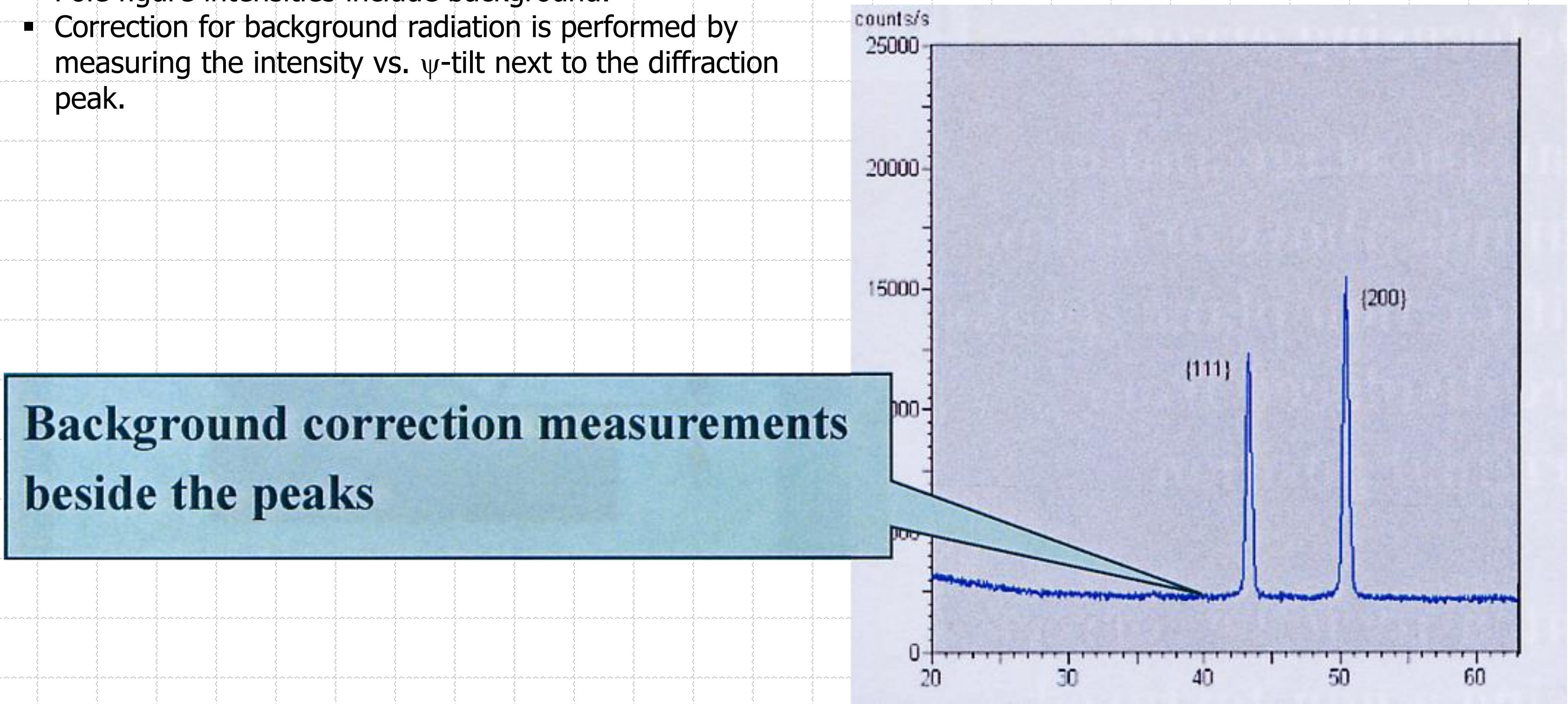



- Measure $\theta$-$2\theta$ scan in order to determine the reflections used for the pole figure measurements.
- Use FWHM of the peaks to calculate the defocusing curve.

# Example: Rolled Copper

## Background Correction

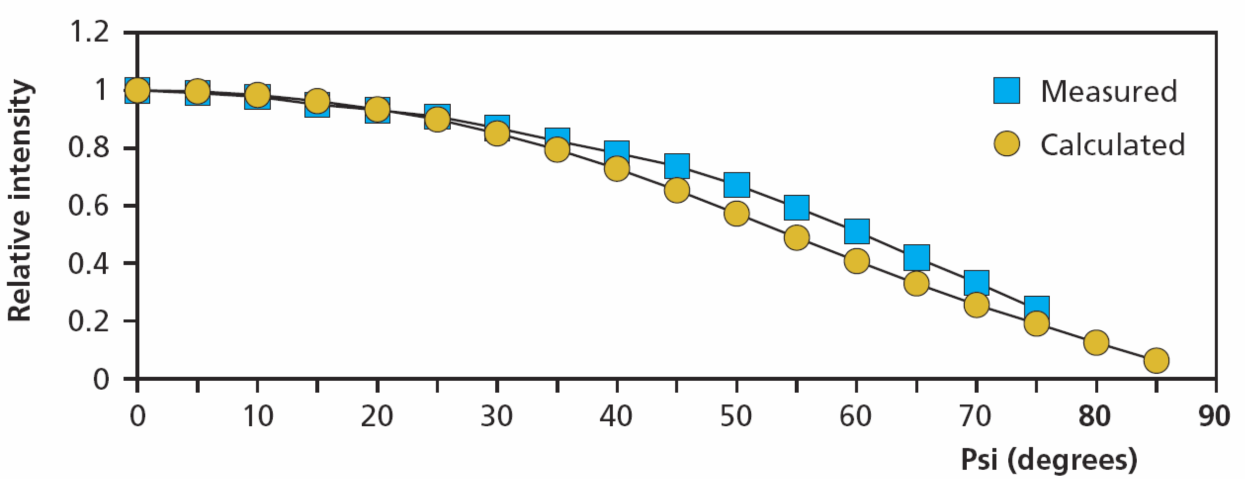
- Pole figure intensities include background.
- Correction for background radiation is performed by measuring the intensity vs. $\psi$-tilt next to the diffraction peak.



# Example: Rolled Copper

## Corrections

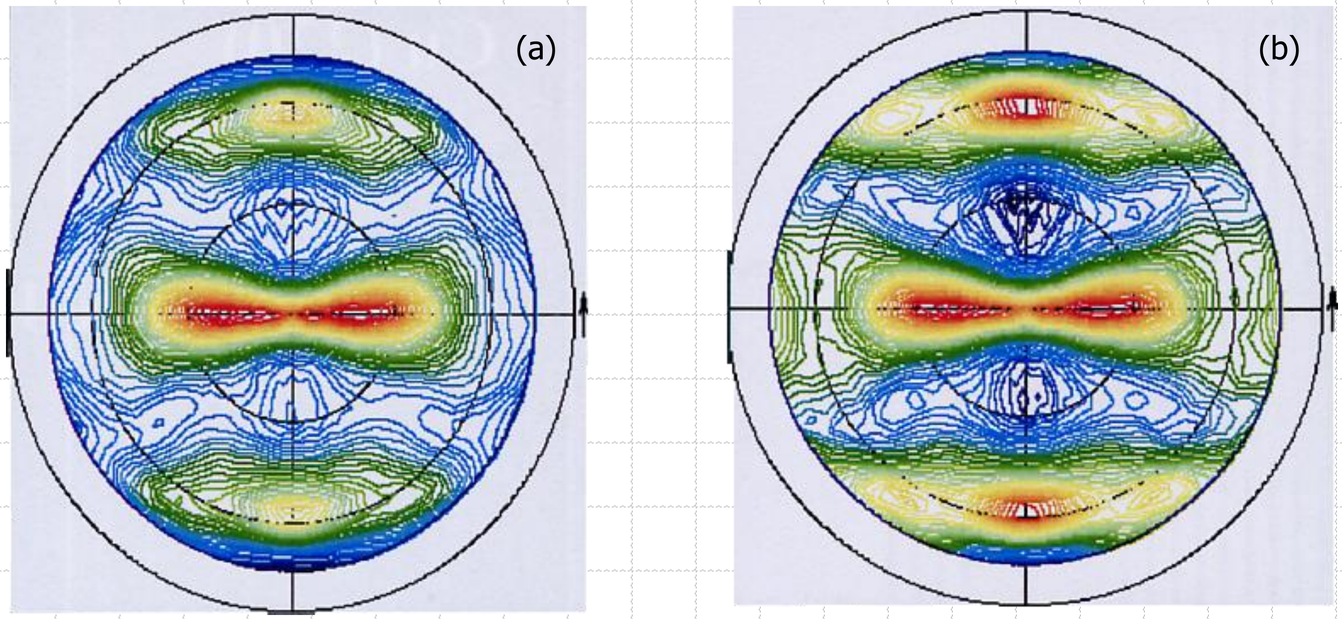
- Experimental pole figures are corrected for background intensities.
- Either experimental or theoretical defocusing correction curve is applied.




Measured and calculated defocusing corrections for Cu(220) pole figure

# Example: Rolled Copper

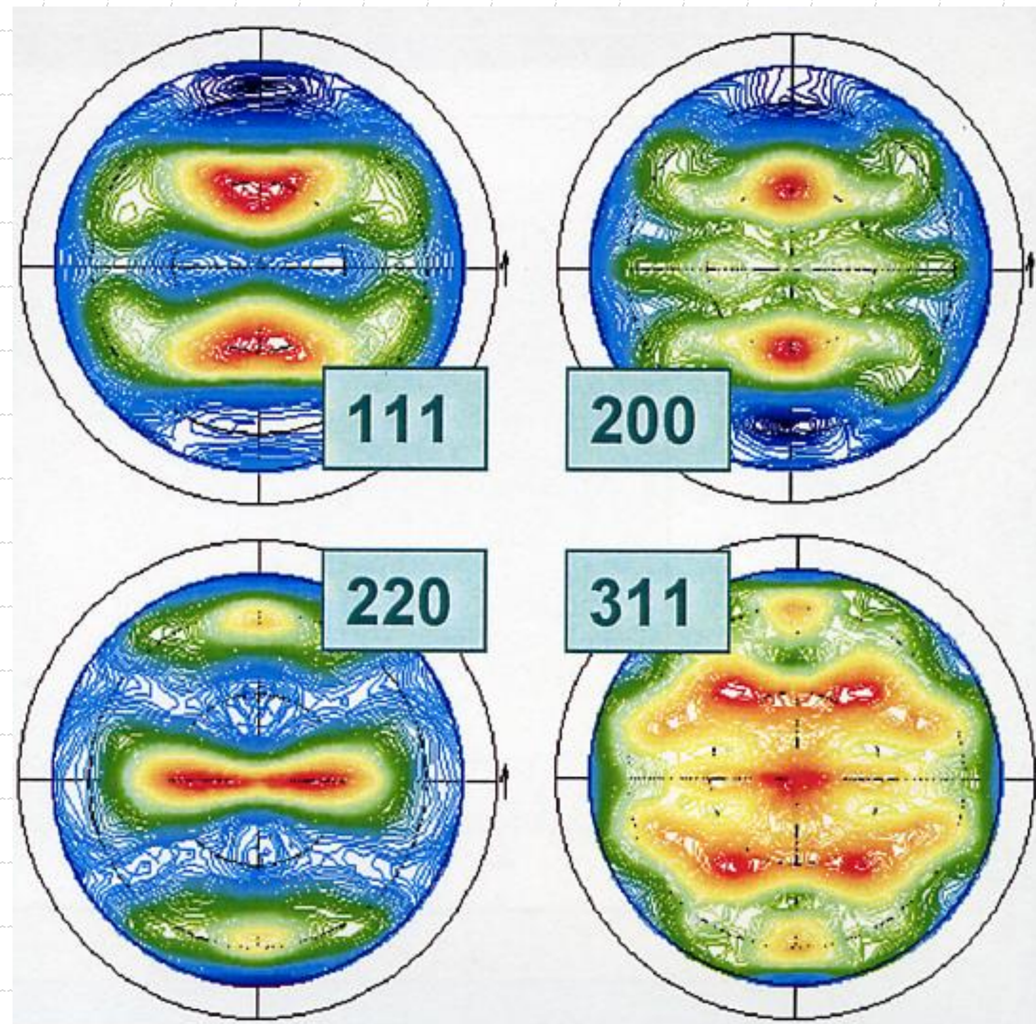
## Corrections




- 2D representation of Cu(220) pole figure as (a) measured and (b) corrected.
- The most noticeable effect is at higher $\psi$-tilt angles.

# Example: Rolled Copper

## Pole Figure Measurements

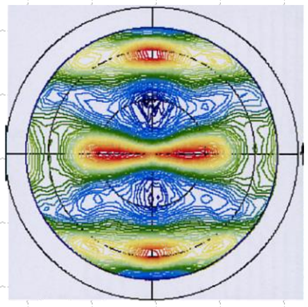


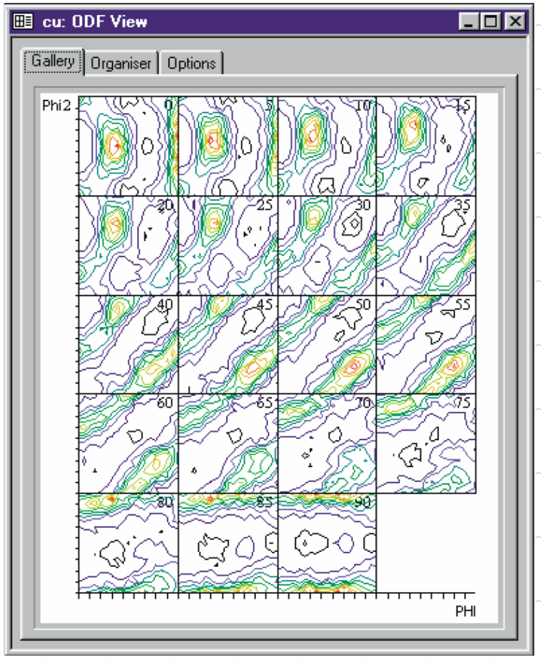

- Four pole figures have been measured.
- Symmetry of rolling process is obtained from the pole figures:
    - pole figure is symmetrical around $\phi = 0^o$ and $\phi = 90^o$.
- The symmetry is called orthorhombic sample symmetry.

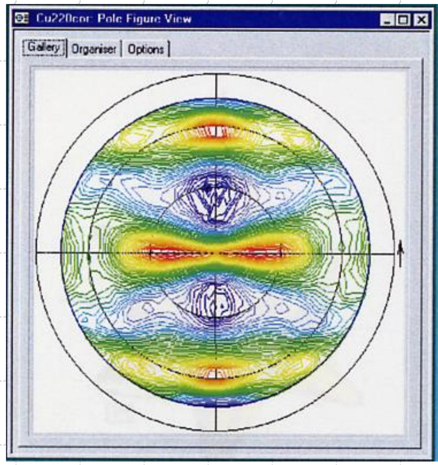
# Example: Rolled Copper

## Orientation Distribution Function Calculation

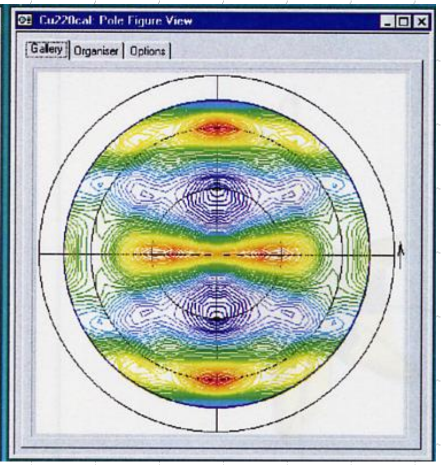
- X'Pert Texture calculates ODF
- When ODF is available X'Pert Texture can calculate pole figures and inverse pole figures for any set of (hkl).





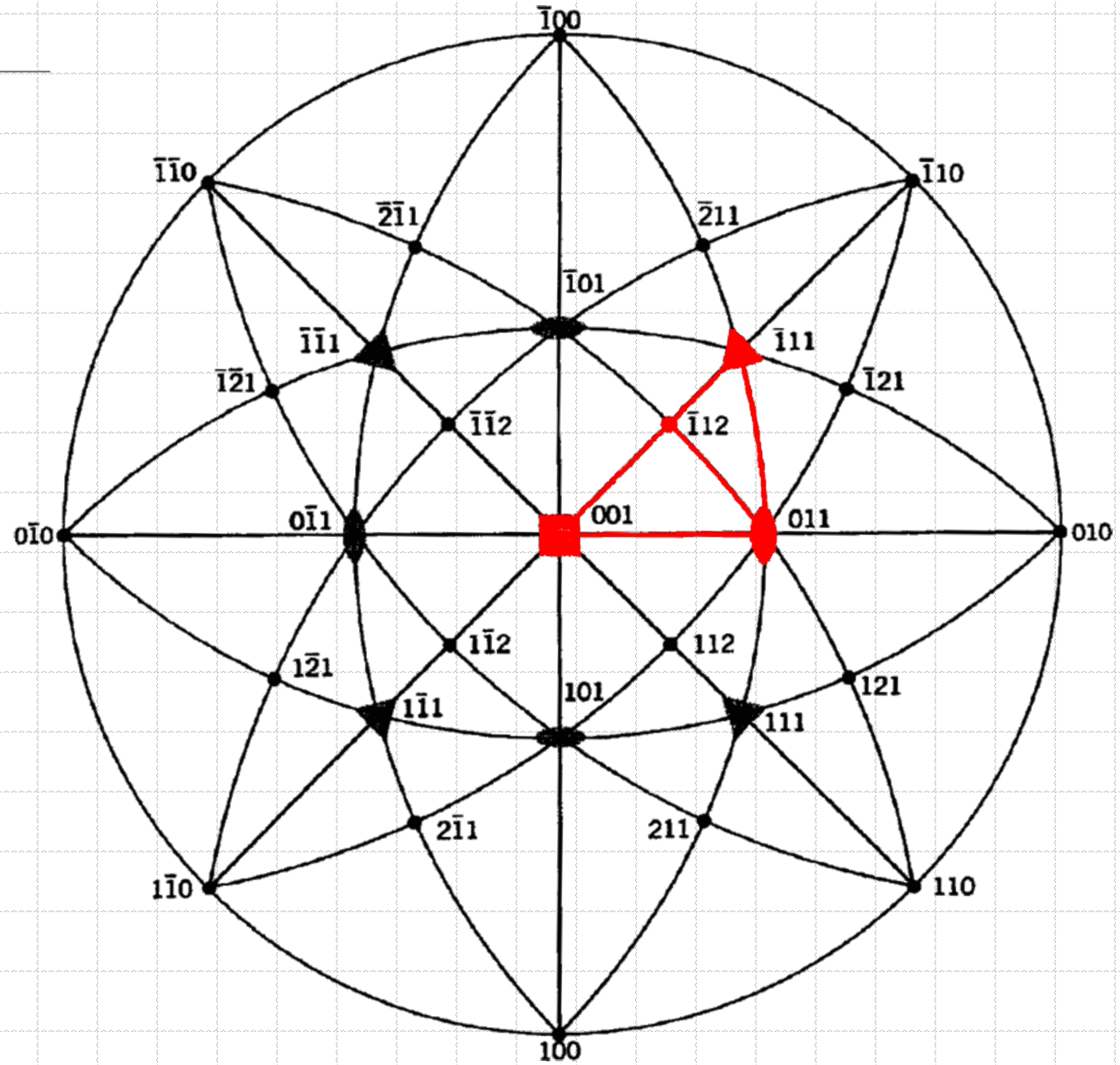




Measured

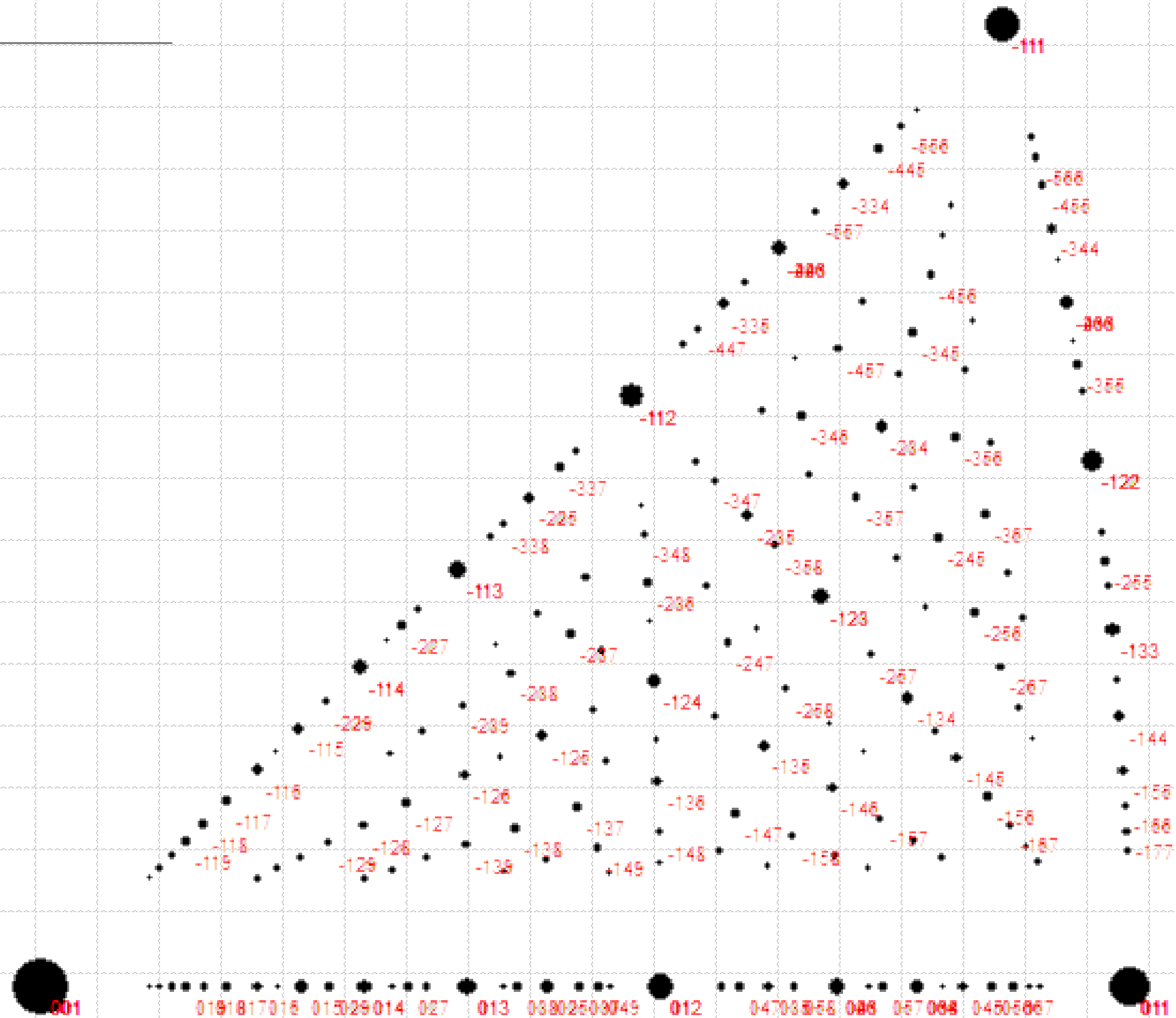



Calculated

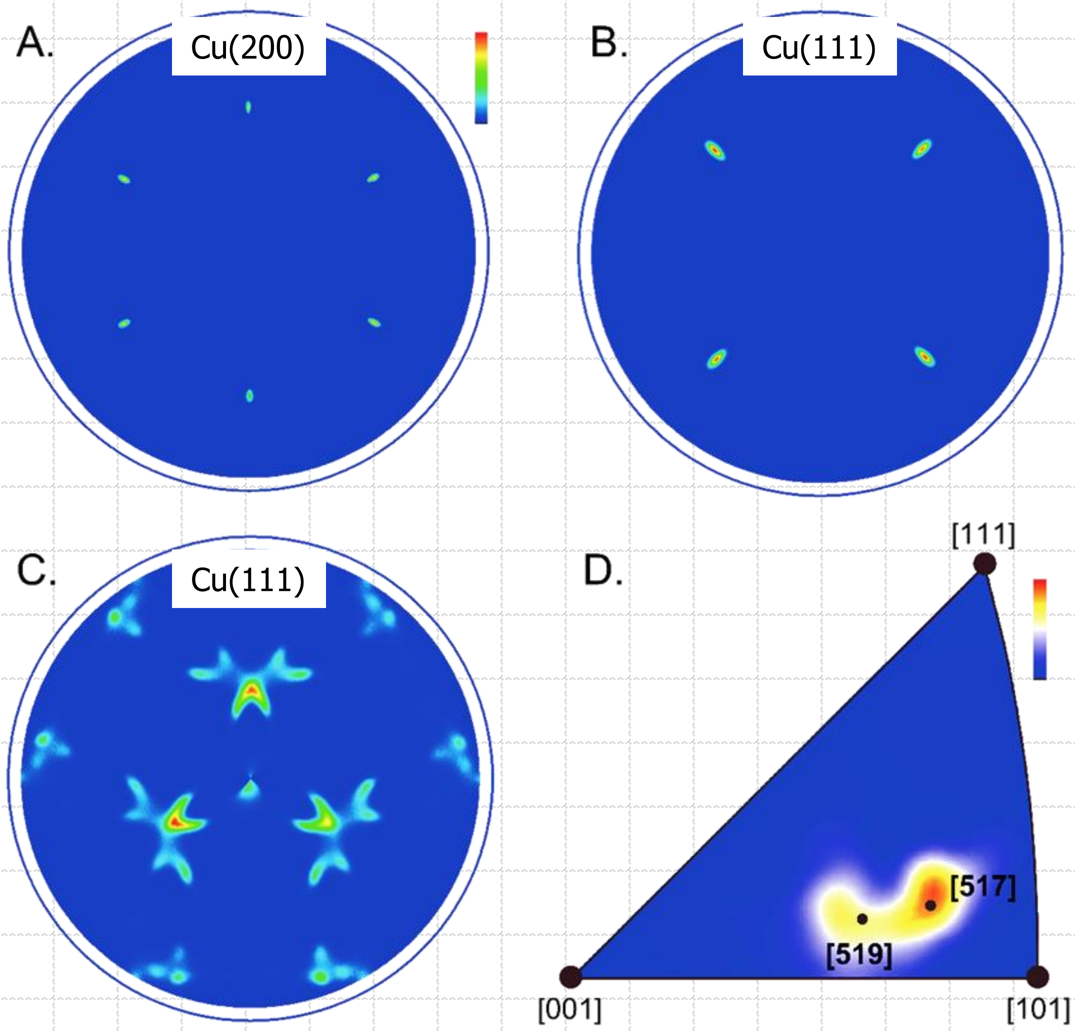
# Inverse Pole Figures



# Inverse Pole Figures



# Engineering Cu surfaces for the electrocatalytic conversion of $CO_2$




X-ray pole figures for:

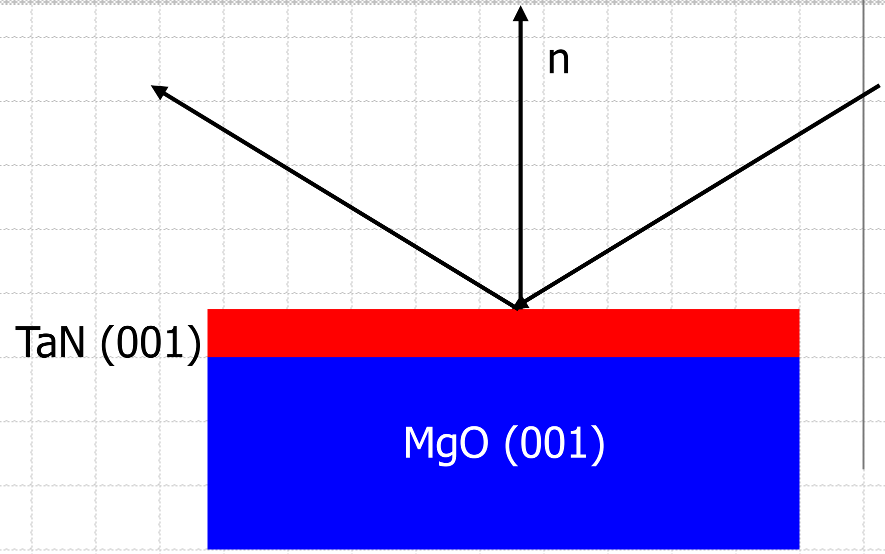
(A) Cu on $Al_2O_3(0001)$; Cu(200) intensities are shown.

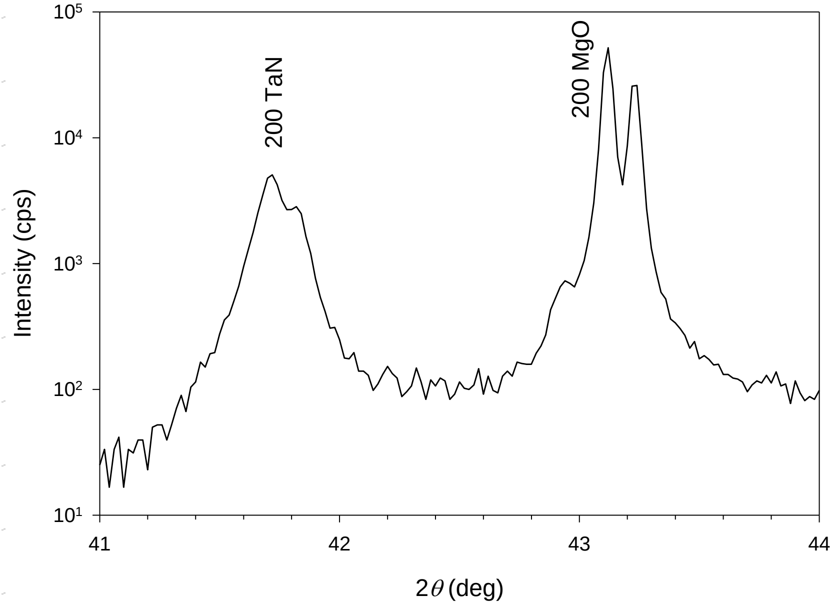
(B) Cu on Si(100); Cu(111) intensities are shown.

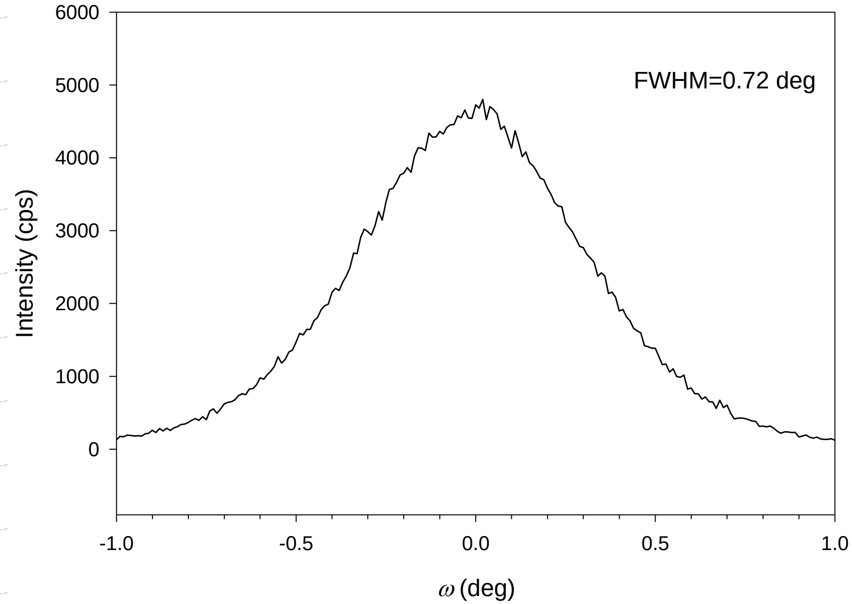
(C) Cu on Si(111); Cu(111) intensities are shown.

(D) Inverse pole figure shows highest intensities for the (751) plane, indicating that Cu on Si(111) is predominantly oriented in the [517] direction out-of-plane.

# TaN Thin Film

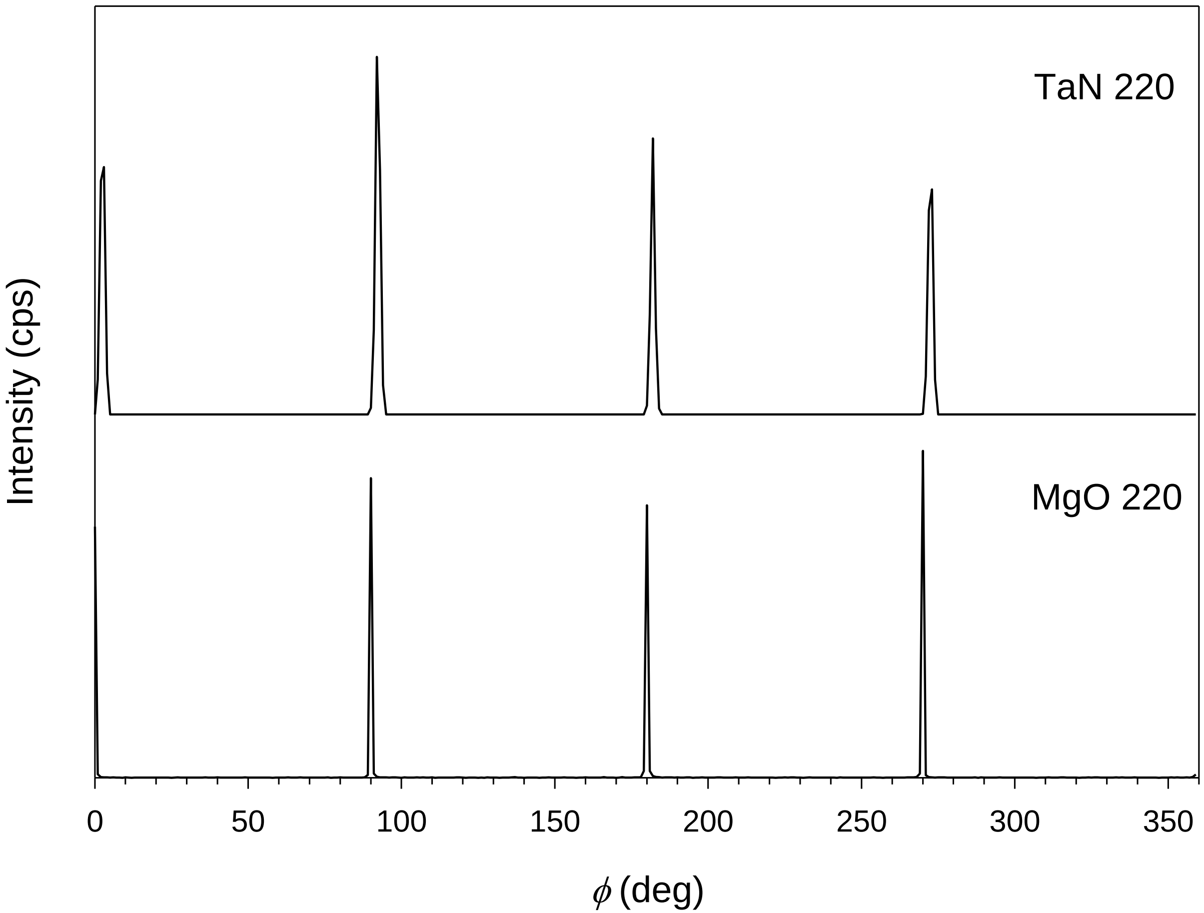


# TaN Thin Film

- ϕ-scan of TaN (202) and MgO (202) reflections.



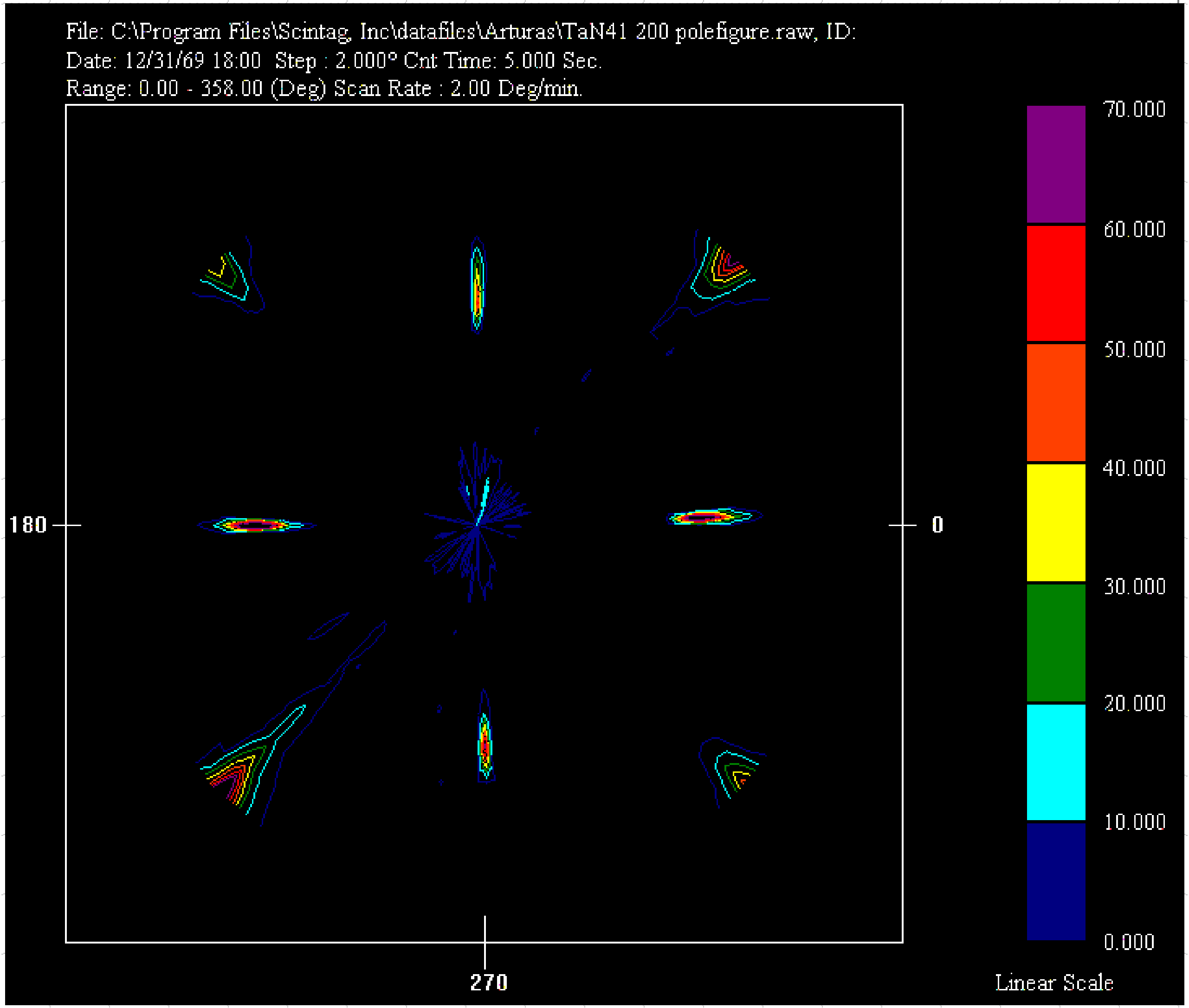
# TaN Thin Film

- TEM reveals additional structure.

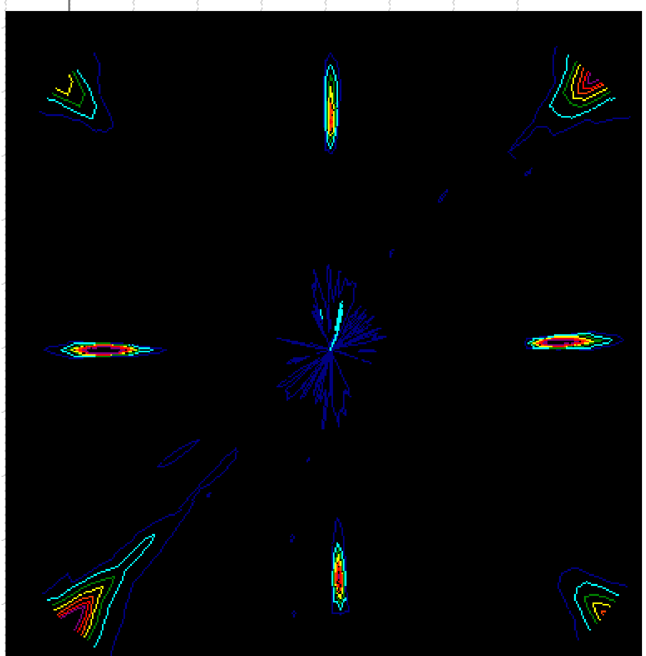
TaN23

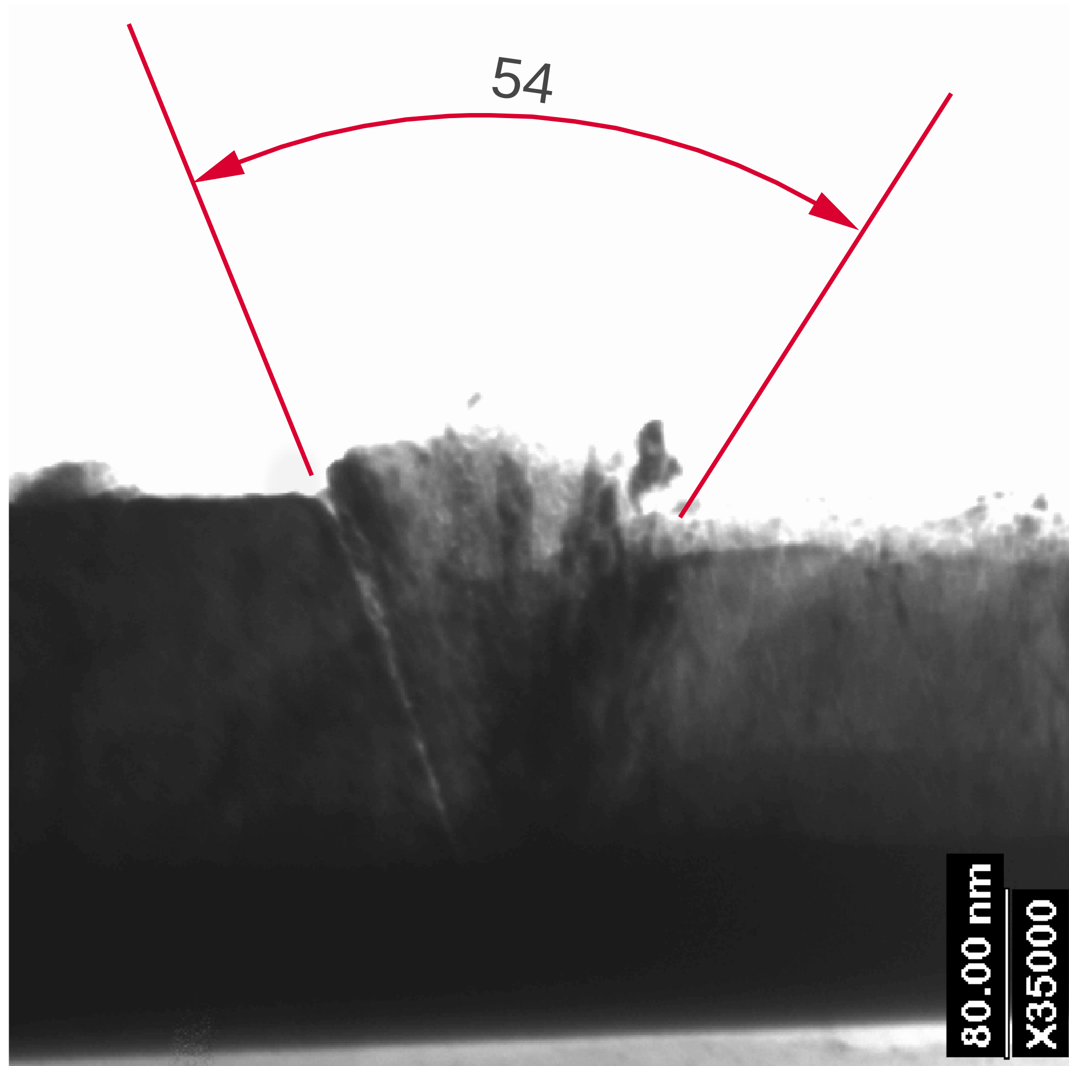
# TaN Thin Film

- XRD 002 pole figure of TaN film



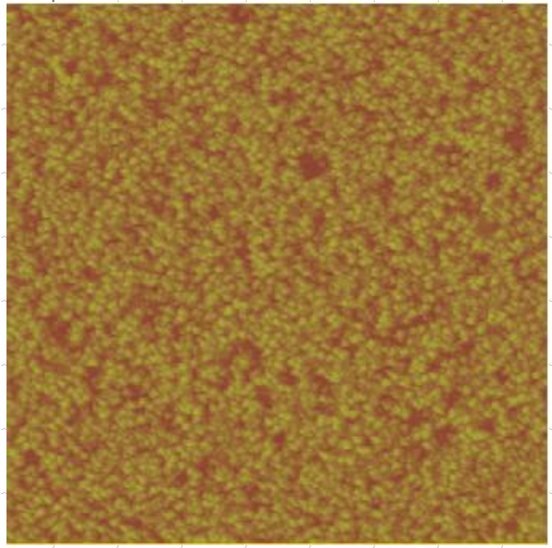
# TaN Thin Film



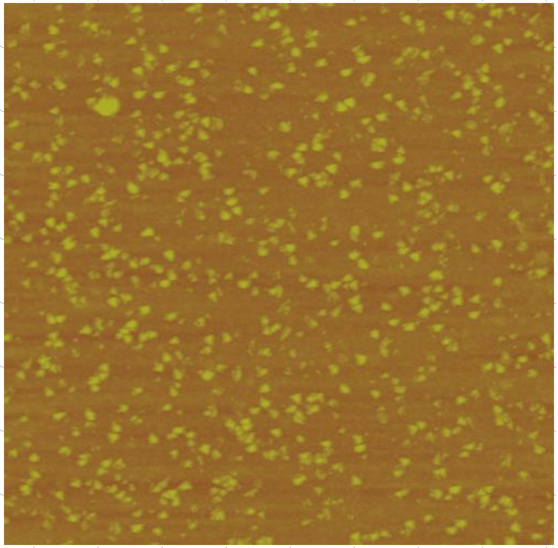


# TaN Thin Film

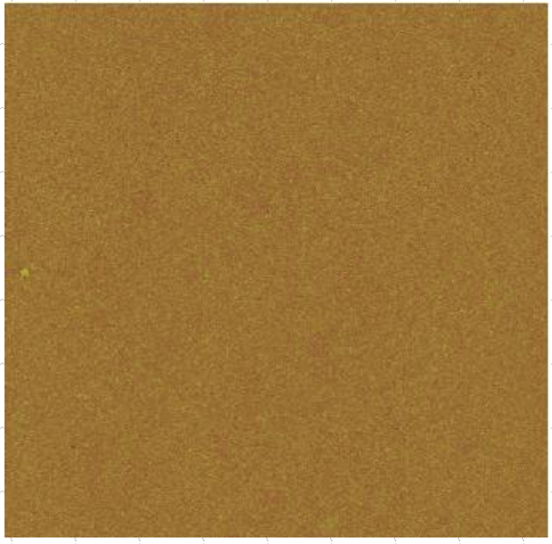
- Atomic Force Microscopy images of TaN films prepared under different $N_2$ partial pressure



$p_N$=2 mTorr



$p_N$=2.5 mTorr



$p_N$=4 mTorr