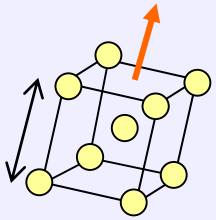
Thin films analysis

XRR
GIXRD
In-Plane diffraction
HR-XRD

What XRD reveals



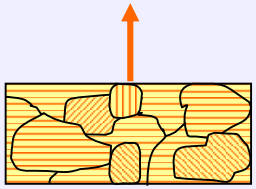
Position and coordinate

of reciprocal lattice points

lattice constant

crystal orientation

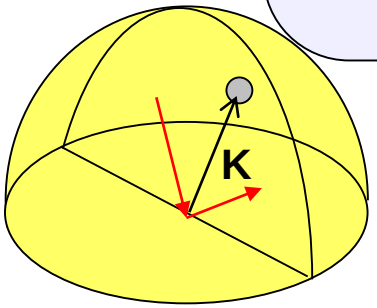
lattice distortion



spread of

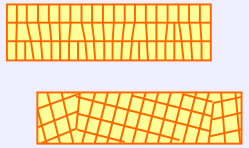
reciprocal lattice points

degree of preferred orientation



Shape of a reciprocal lattice distribution

crystal perfection,
Defects, mosaicity

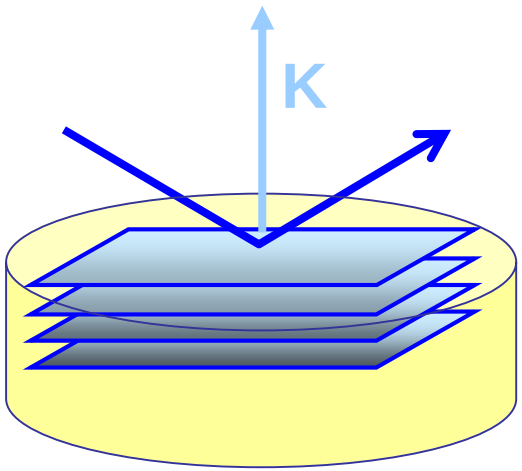


XRD scan modes

method	scan axes	purpose
Out-of-plane	$2\theta/\omega$	Qualitative analysis, crystal structure reflectivity
Thin film scan	2θ	Qualitative analysis, crystal structure
In-plane	$2\theta\chi/\phi$	Qualitative analysis, crystal structure
Pole figure	$\chi(\alpha)$, $\phi(\beta)$	Preferred orientation
Rocking curve	ω, χ, ϕ	Preferred orientation, crystal perfection
Rocking curve (high resolution)	$2\theta/\omega$	Crystal perfection, film thickness, composition rate
Reciprocal lattice map	$2\theta/\omega$, ω	Crystal perfection, epitaxial relationship analysis

Wide angle XRD

Out-of-plane

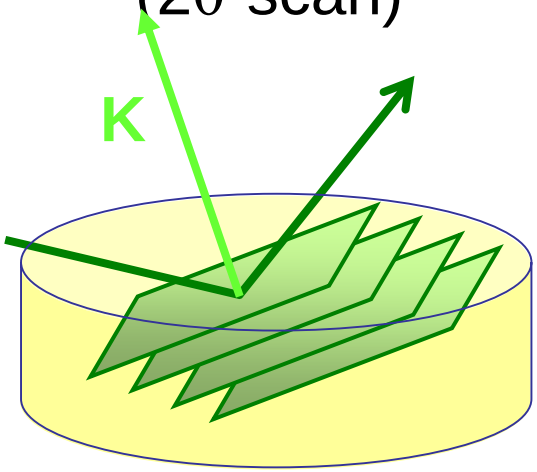


Observed plane is..

parallel to the surface

Thin film scan

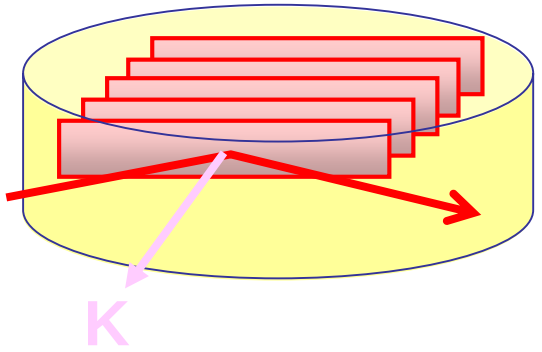
(2θ-scan)



tilting

(changing during a scan)

In-plane

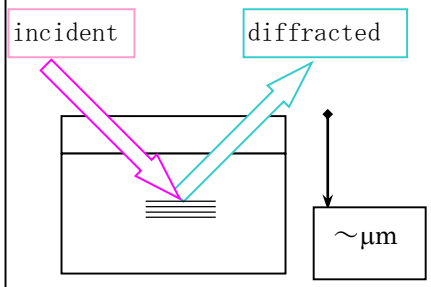


perpendicular

to the surface

XRD scan modes: Comparison

Conventional θ/2θ



Merit

・easy handling

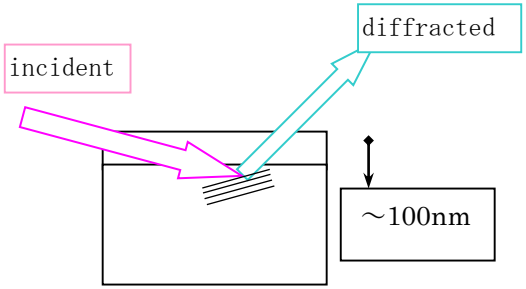
Demerit

・effective V small

・unidirectional information

・affected by substrate

θ-fixed; 2θ-scan



Merit

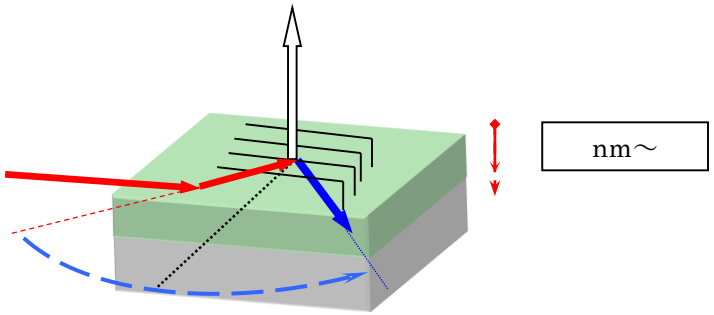
・relatively strong signals

Demerit

・orientation analysis

--- complicated

In-Plane Diffraction (2θχ/φ scan)



Merit

○surface sensitive！

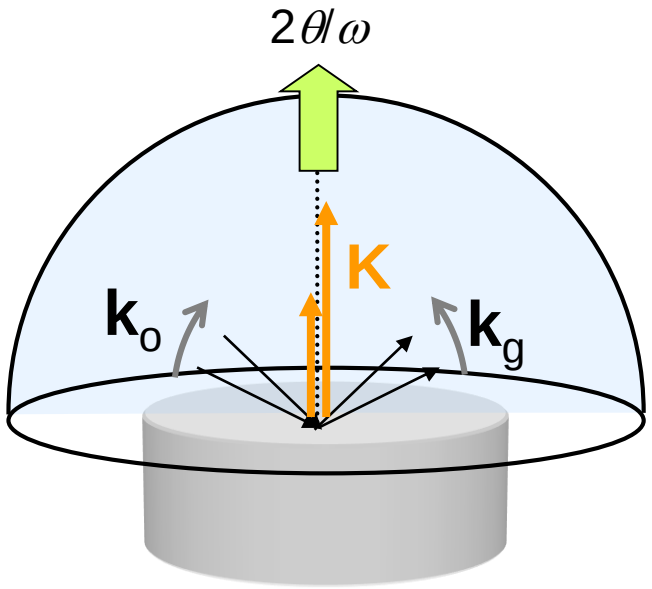
○depth analysis possible!

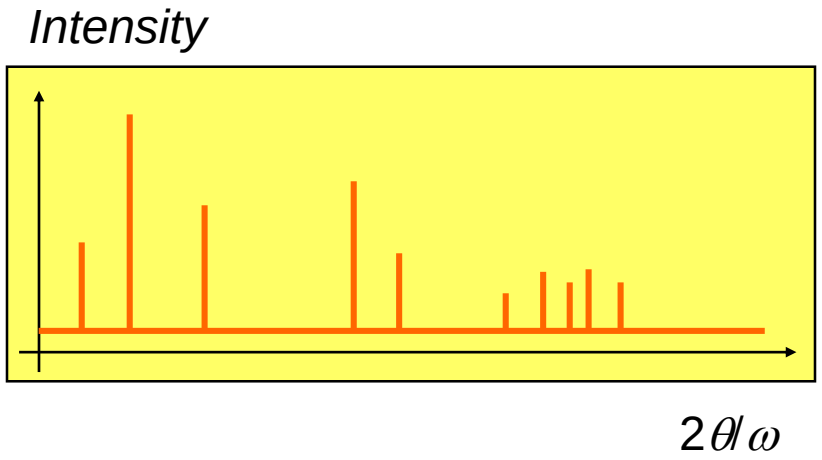
○avoiding signals from substrate！

○analysis of anisotropy in surface plane

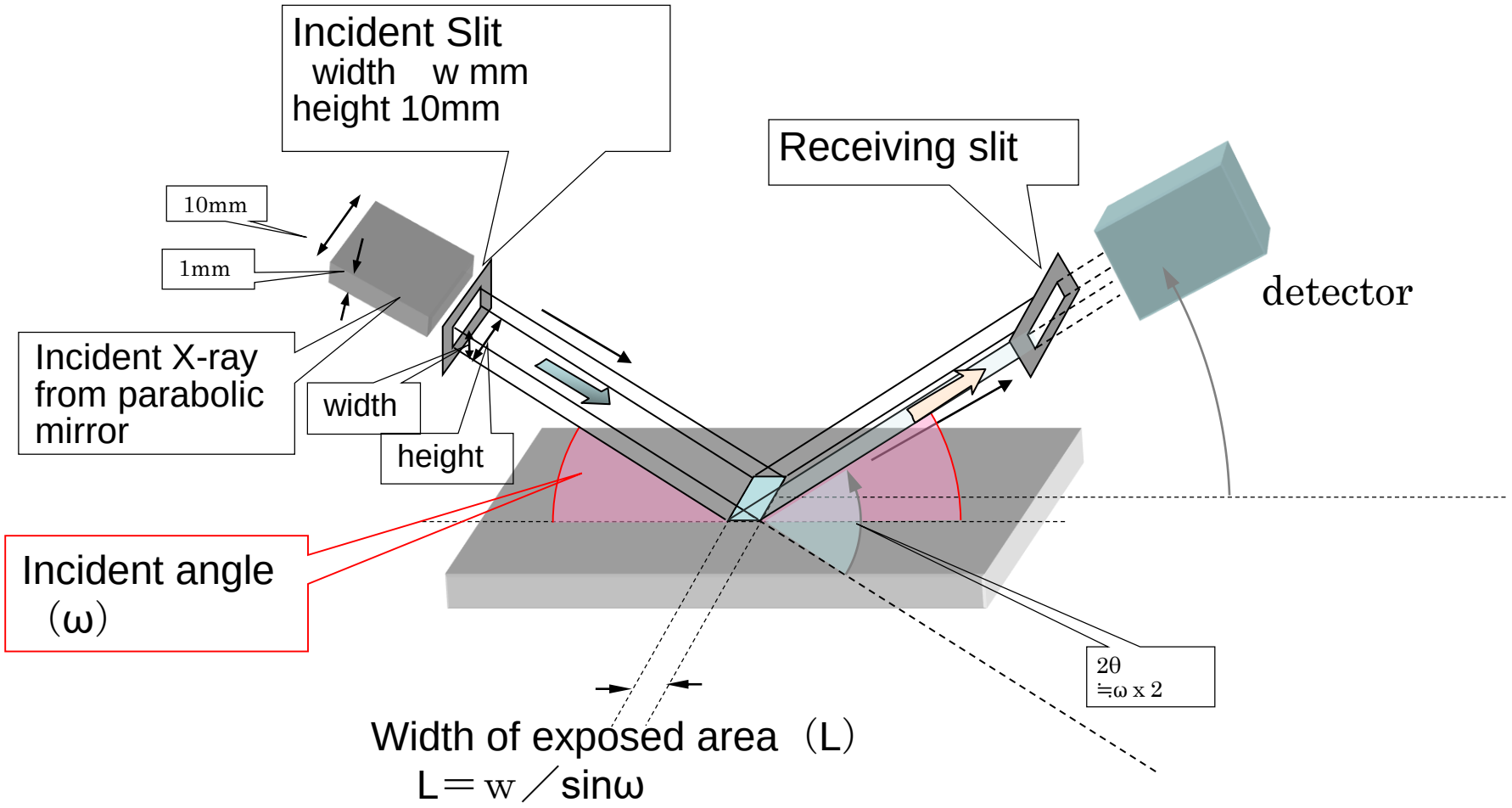
2θ/ω scan (out-of-plane)

- Diffraction patterns contributed by the planes parallel to the sample surface are observed.
  - Qualitative analysis
  - Preferred orientation



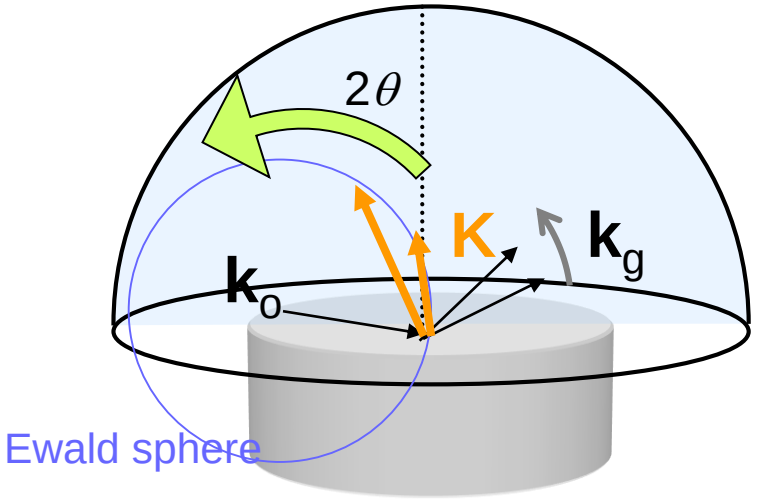


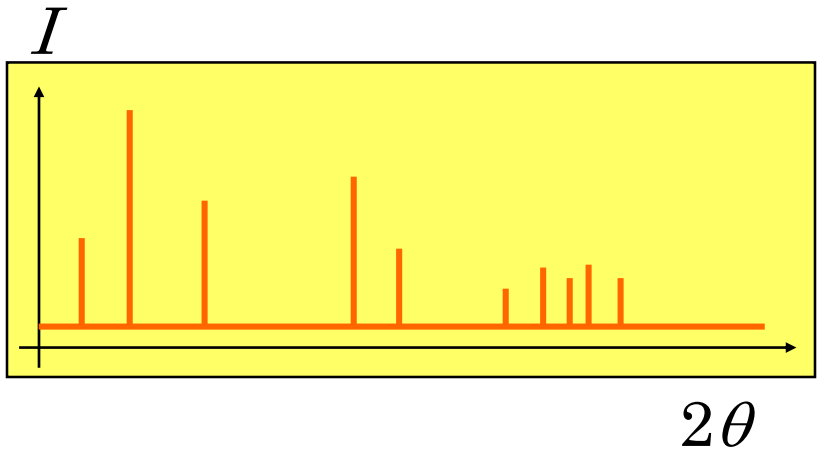
θ-2θ scan


Incident Slit
width w mm
height 10mm
Receiving slit
10mm
1mm
detector
Incident X-ray
from parabolic
mirror
width
height
Incident angle
（ω）
2θ
≒ω x 2
Width of exposed area（L）
L＝w／sinω

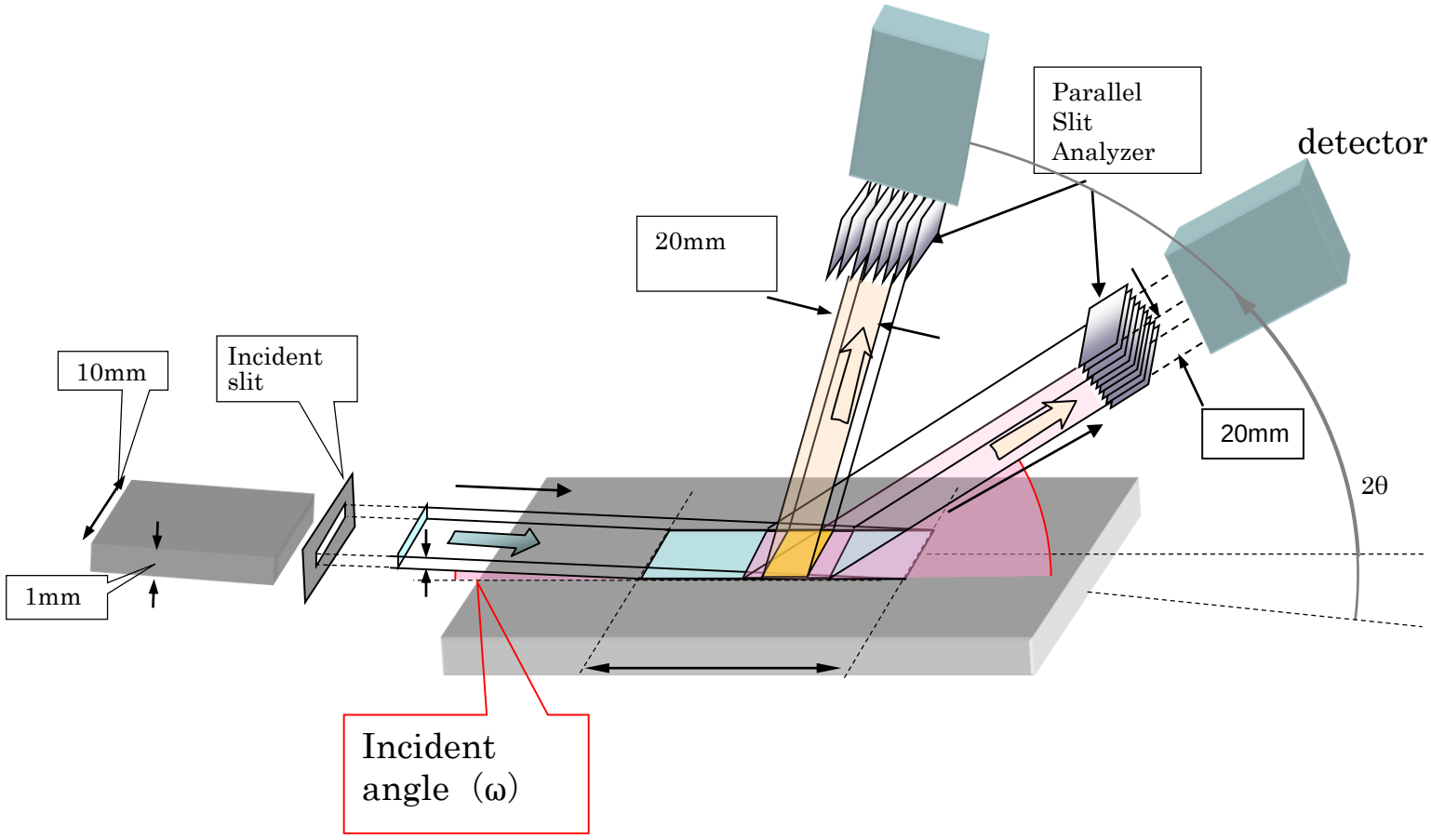
2θ scan (thin film XRD)

- XRD patterns from the sample surface layers are obtained.
  - Qualitative analysis for thin films (suitable for the case of random orientation)



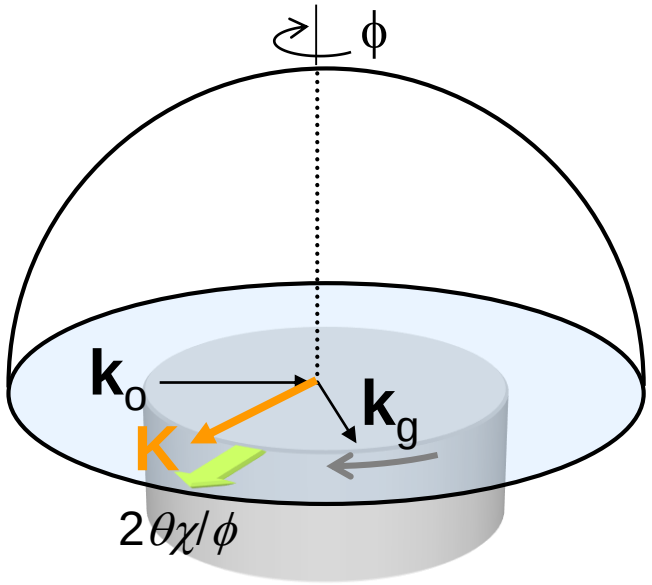


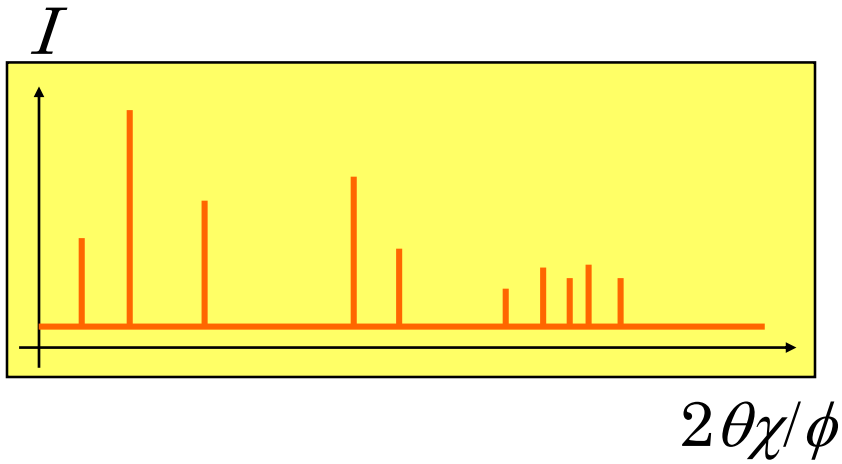
ω-fixed 2θ scan



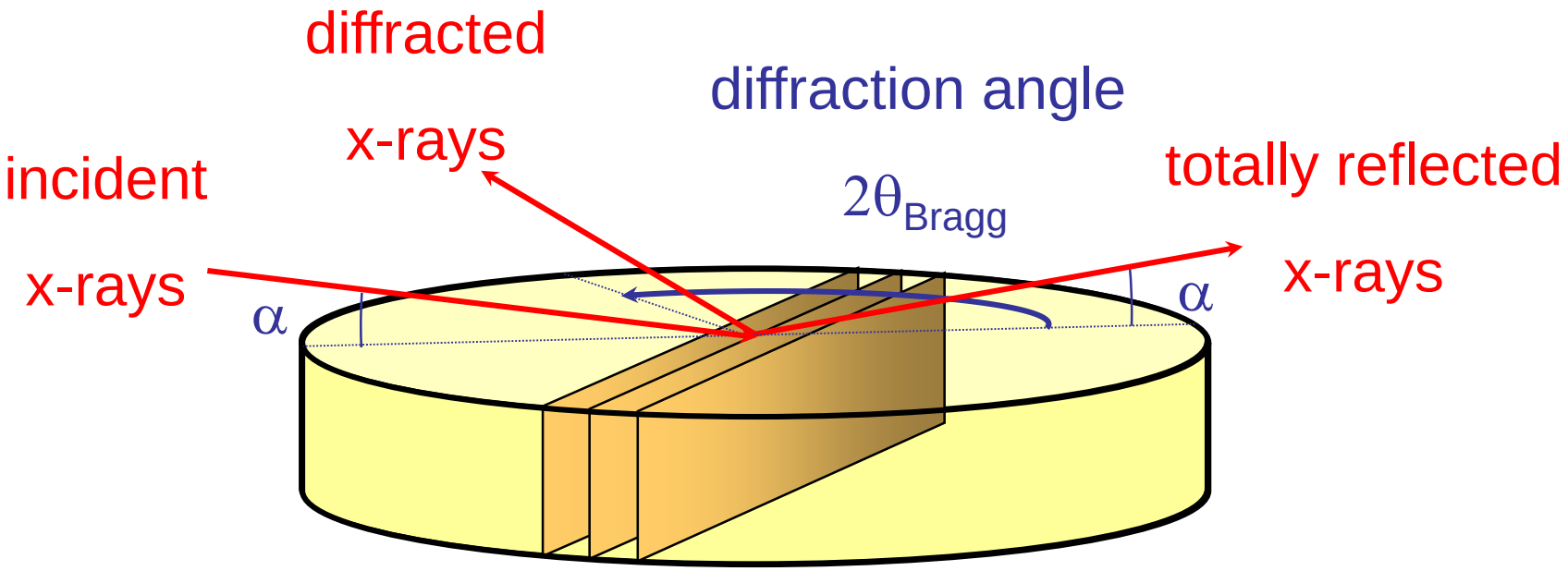
2θχ/ϕ scan (in-plane)

- Diffraction patterns contributed by the planes perpendicular to the sample surface are obtained.
  - Qualitative analysis for thin films
  - Preferred orientation

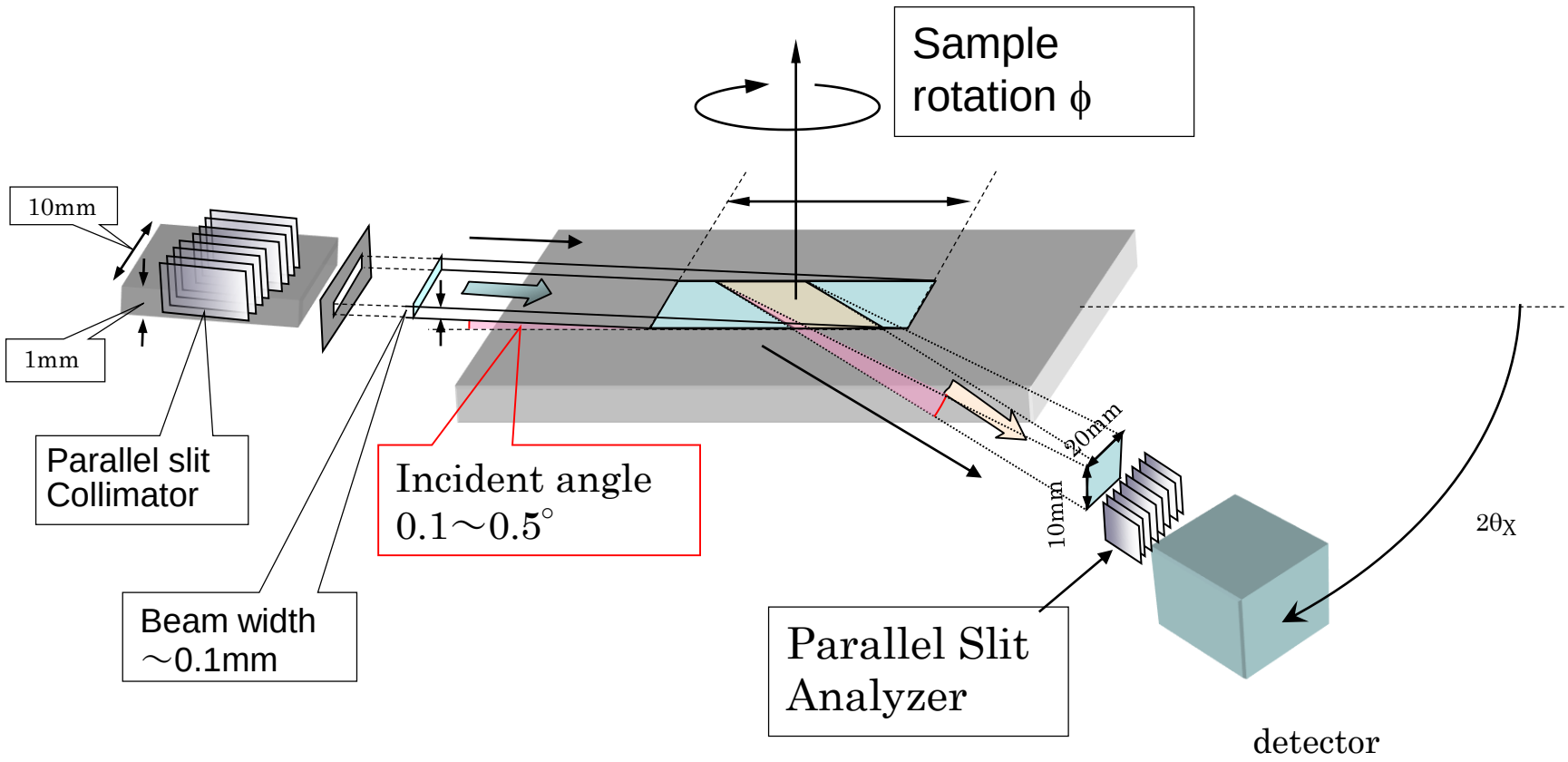




In-Plane measurement



In-Plane XRD



Sample is always mounted on horizontal plane

"3D"s for In-Plane diffraction

Direct observation of lattice planes normal to surface
utilizing total external reflection of X-rays

Depth analysis through small incident angle
non-destructive analysis of depth-variation
(d-values, crystallite-size, reaction layer, etc.)

Detection of minor phases
surface-sensitive
even weak signals can be effectively collected

Important point for In-Plane diffraction

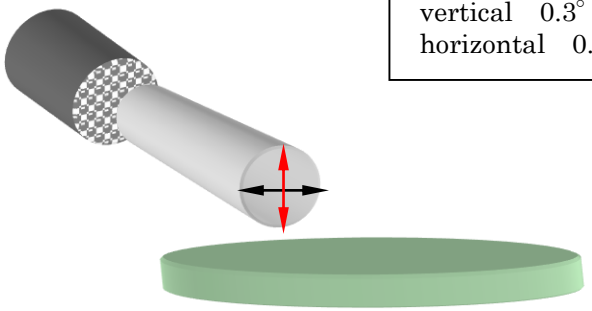
◎Divergence of Incident X-ray along surface normal direction

Polycapillary lenz

Without monochoromation
-> huge background noise
Impossible to select optical resolution

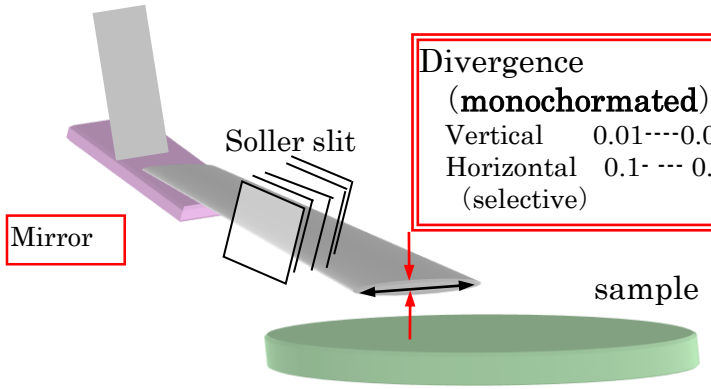
Polycap.

Div. (fixed)
vertical 0.3°
horizontal 0.3°



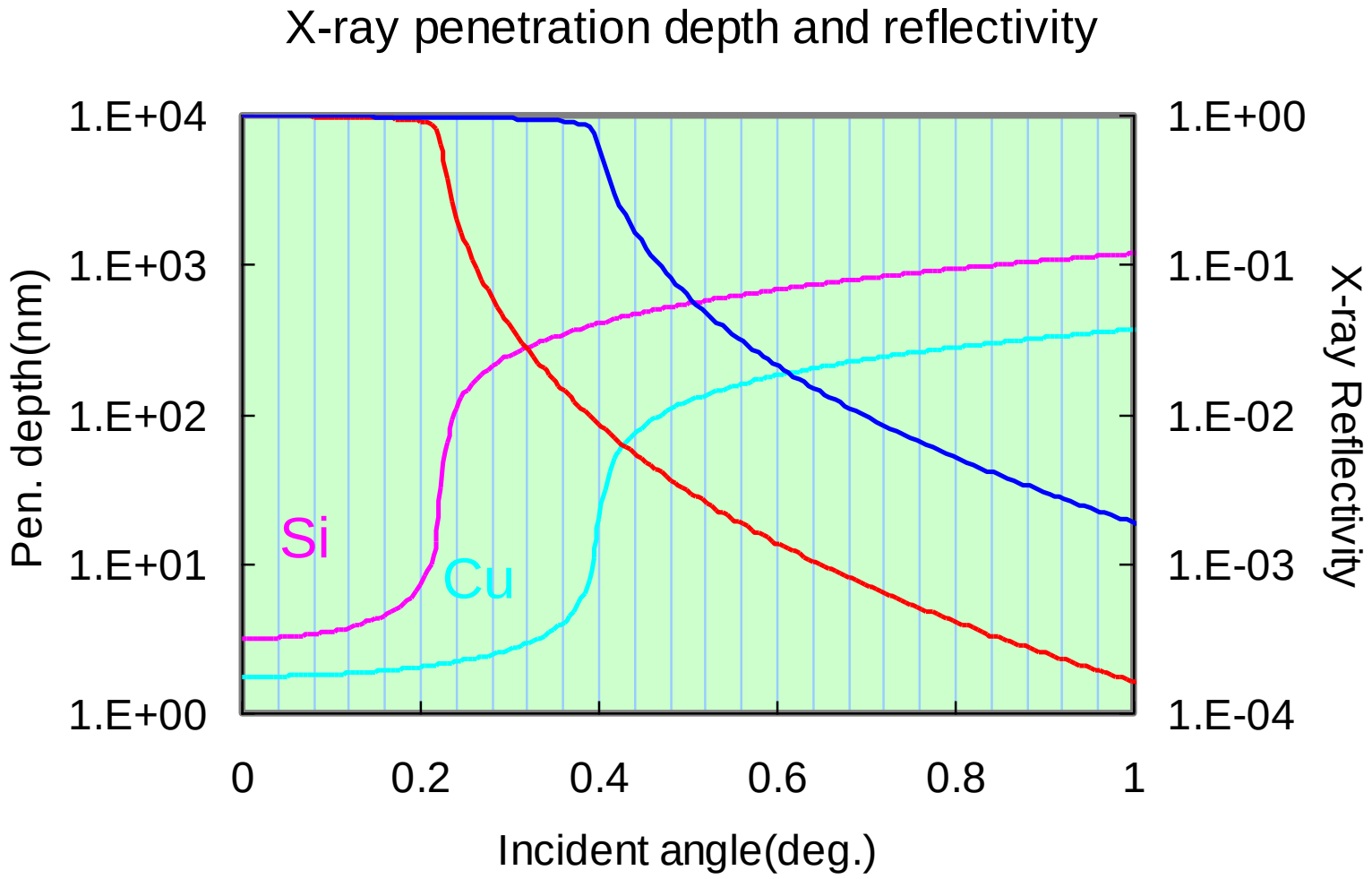
Parabolic mirror＋Soller slit

: monochromatic beam
: combination and selection of optical elements with adequate resolution necessary
: depth analysis ⇒controlled incident angle
→goniometric system and tilt-alignment



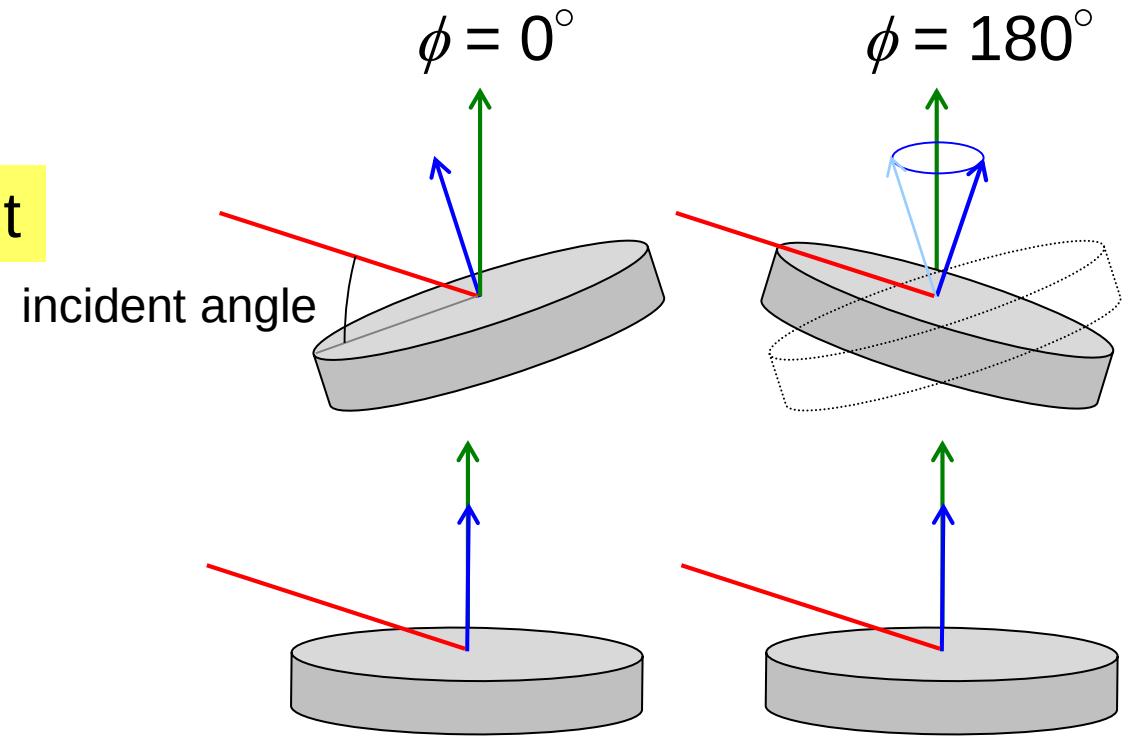
Divergence
(**monochormated**)
Vertical 0.01----0.04°
Horizontal 0.1- --- 0.5°
(selective)

incident angle vs penetration depth



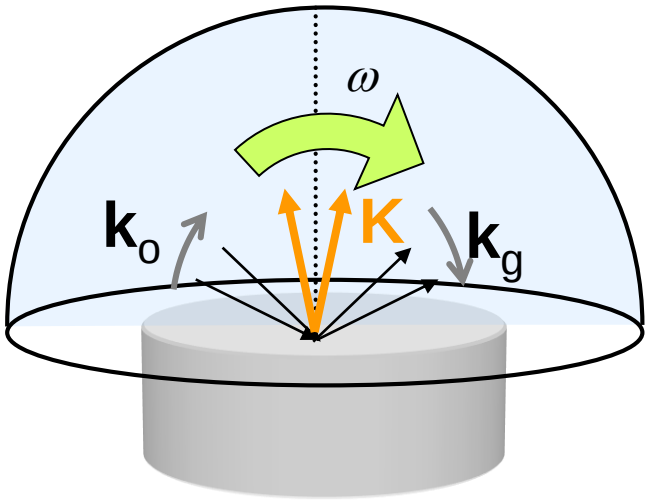
Sample alignment for In-plane measurement

- To keep the incident angle constant during a scan
  - ϕ rotation axis and sample surface normal should be parallel to each other! (in-plane alignment)

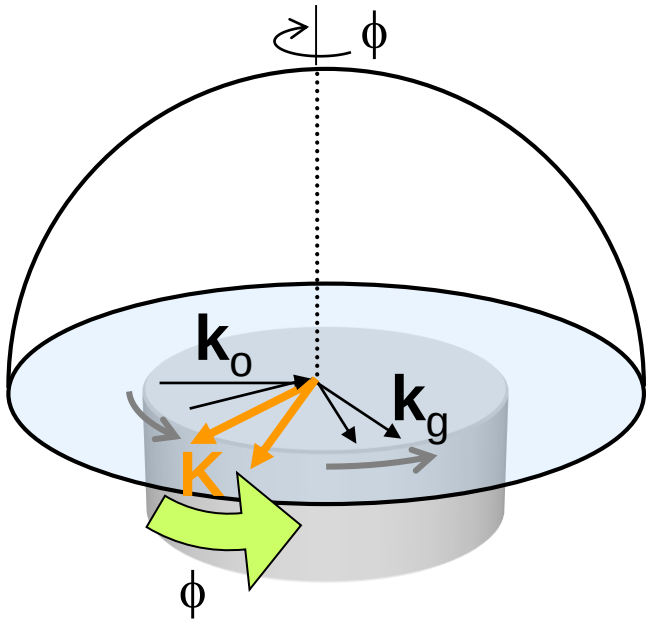


Rocking curve measurement

- tilting : ω scan with fixed 2θ. (Out-of-plane)
- twisting : ϕ scan with fixed $2\theta\chi$. (In-plane)



tilting



twisting

X-ray Residual Stress Measurement

What is Residual Stress

- **Residual stresses** are internal stresses remaining in materials after the external force is removed. The residual stress plays important role in the processes of elastic and plastic deformations, material hardness and plasticity, material damages and other processes related to physical and mechanical properties of solid state
- In the equilibrium condition, the **sum of residual stresses** in the sample must be equal zero
- There are negative (**compressive**) and positive (**tensile**) stresses
- The residual stresses are observed in **polycrystalline** materials and **single crystals**
- In single crystals or epitaxial films, usually the “language of **strains**” is used instead of “**stress**”
- In polycrystals, the residual stress exists in most of solid state samples
- Stress is related to strain via **Hook’s law**

Origin of stress

- Inhomogeneous plastic deformations: rolling, grinding, polishing
- Microscopic transformations: dislocations, stacking faults, defects, twins
- Thermal incompatibility
- Phase transitions
- Hardening processes (quenching, laser treatment, thermal heating)
- Implantations, for example ion-implanted semiconductors
- Deformation
- Recrystallization
- Film synthesis with plasma, laser and ion beams
- Crystallization to boundary surfaces
- …and many others

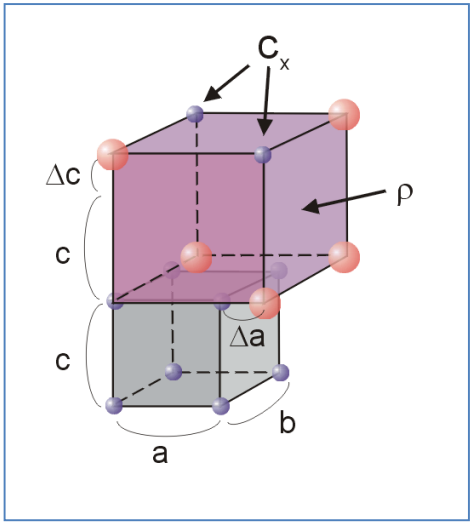
Strain

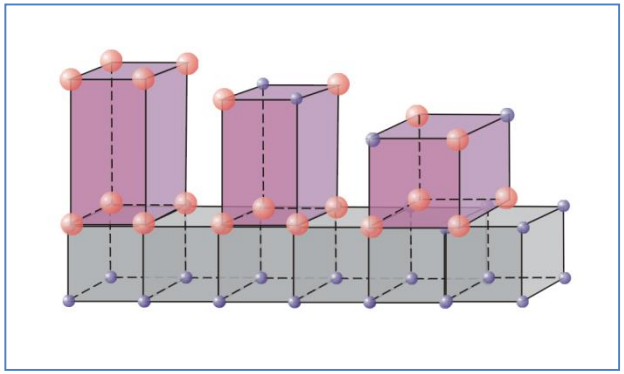
Strain is a measure of the resulting deformation of a solid body caused by stress. Strain is calculated from the change in the size and shape of the deformed solid due to stress.

For crystalline or polycrystalline materials possessing crystallographic lattice *(a, b, c),* the strain in the selected direction *a* is defined:

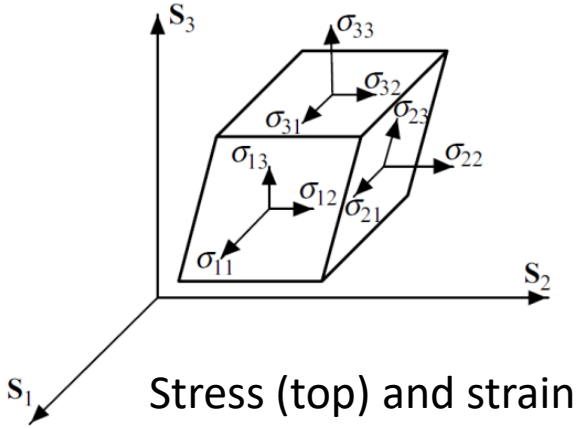
$$\varepsilon_a = \frac{a - a_0}{a_0}$$

Strain is a measure of displacement of crystallographic lattice and reflects the stress status of the lattice. In coherent structures (perfect crystals, epitaxy), the strain is also related to lattice **mismatch**

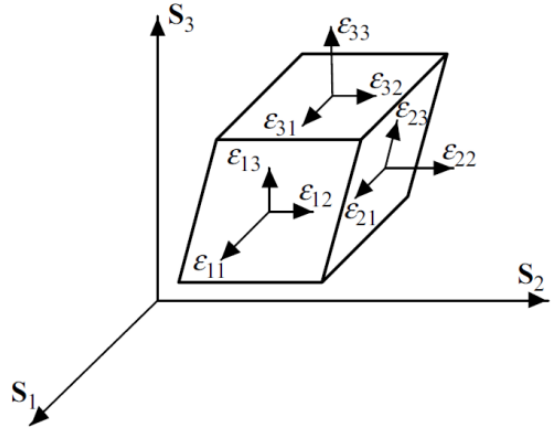




Strain&Stress&Units



Stress (top) and strain (bottom) components in a volume of the sample



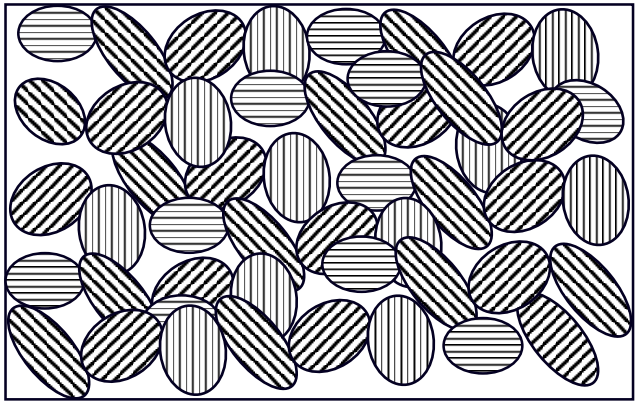
Unit for stress: **Pa** (Pascal; measure of force per unit area, N/m^2).

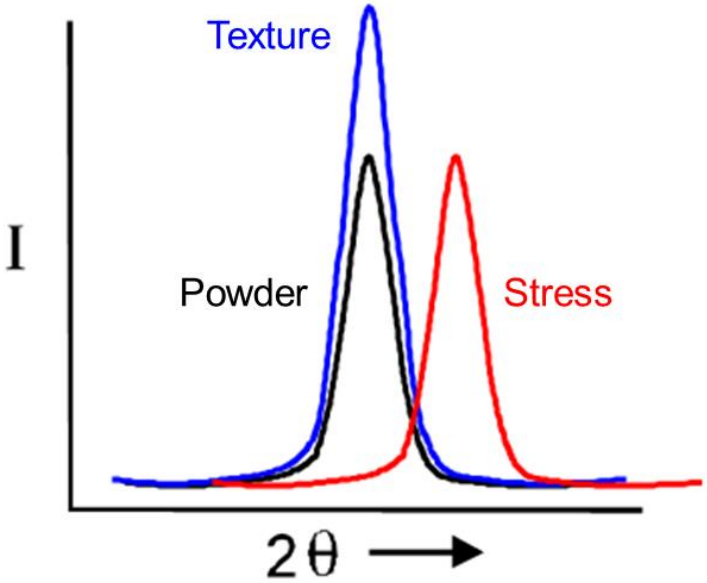
For most metals, stress is normally given in MPa, which is defined as MN/m^2 (million Newtons per square meters) or equivalently N/mm^2 (newton per square millimeter). Other units:

1 GPa = 1000 MPa
1 ksi (1000 lb/in^2) = 6.895 MPa
1 kg/mm^2 = 9.807 MPa

Randomly Oriented Crystal Grains

Polycrystalline materials are composed of millions of crystal grains. Residual stress induced in materials with randomly oriented crystal grains only is treated here.



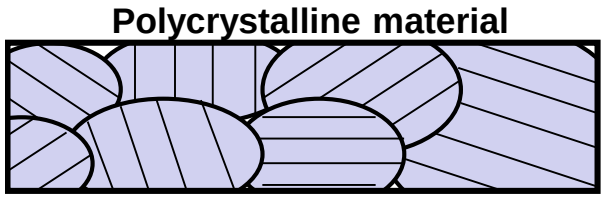


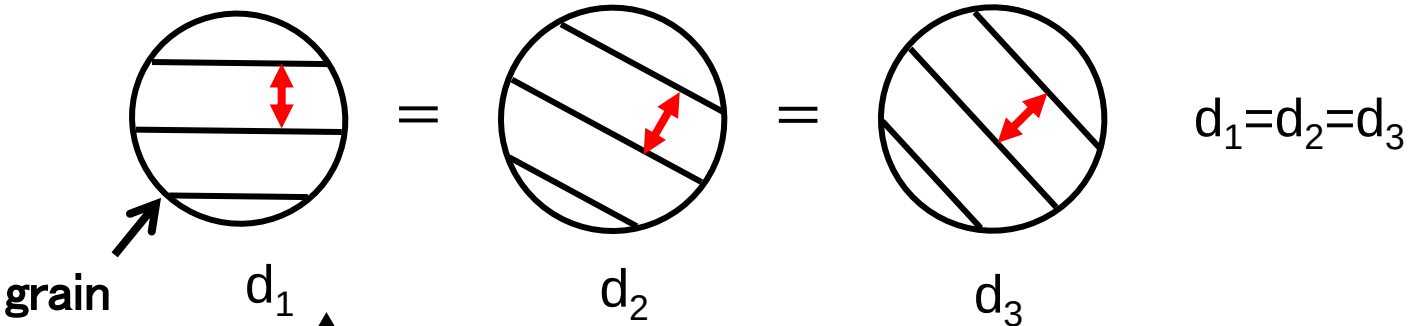
X-ray diffraction measures the real lattice constants of crystallographic lattice in crystallites which compose polycrystalline sample. If the lattice is deformed (strained), the Bragg peak is shifted from the position corresponding to relaxed lattice. Thus X-ray Bragg diffraction measures the **lattice strain.**

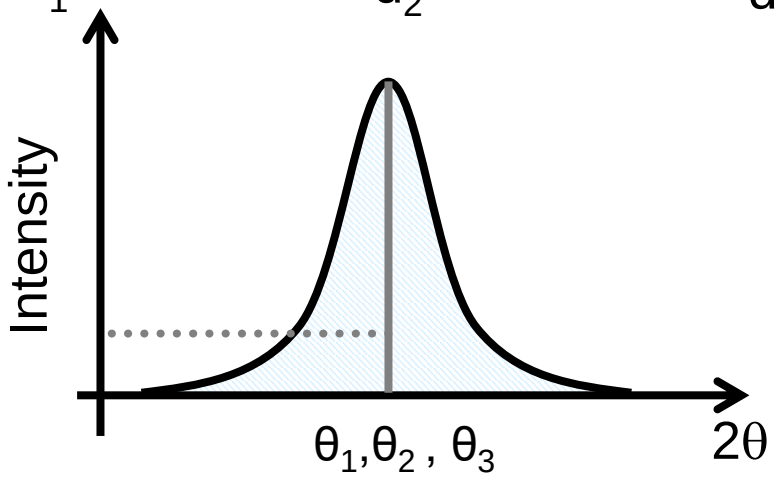
The isotropic distribution of crystallites causes the scattered X-ray intensity is distributed in **Debye rings**, in the same way as in powder diffraction. However, due to the strain, the rings are **deformed** in different way depending on stress status.

Residual Stress and Lattice Spacings for Grains without Strain

- Crystal grains without strain.
  Every crystal grain forms the same lattice spacing d.







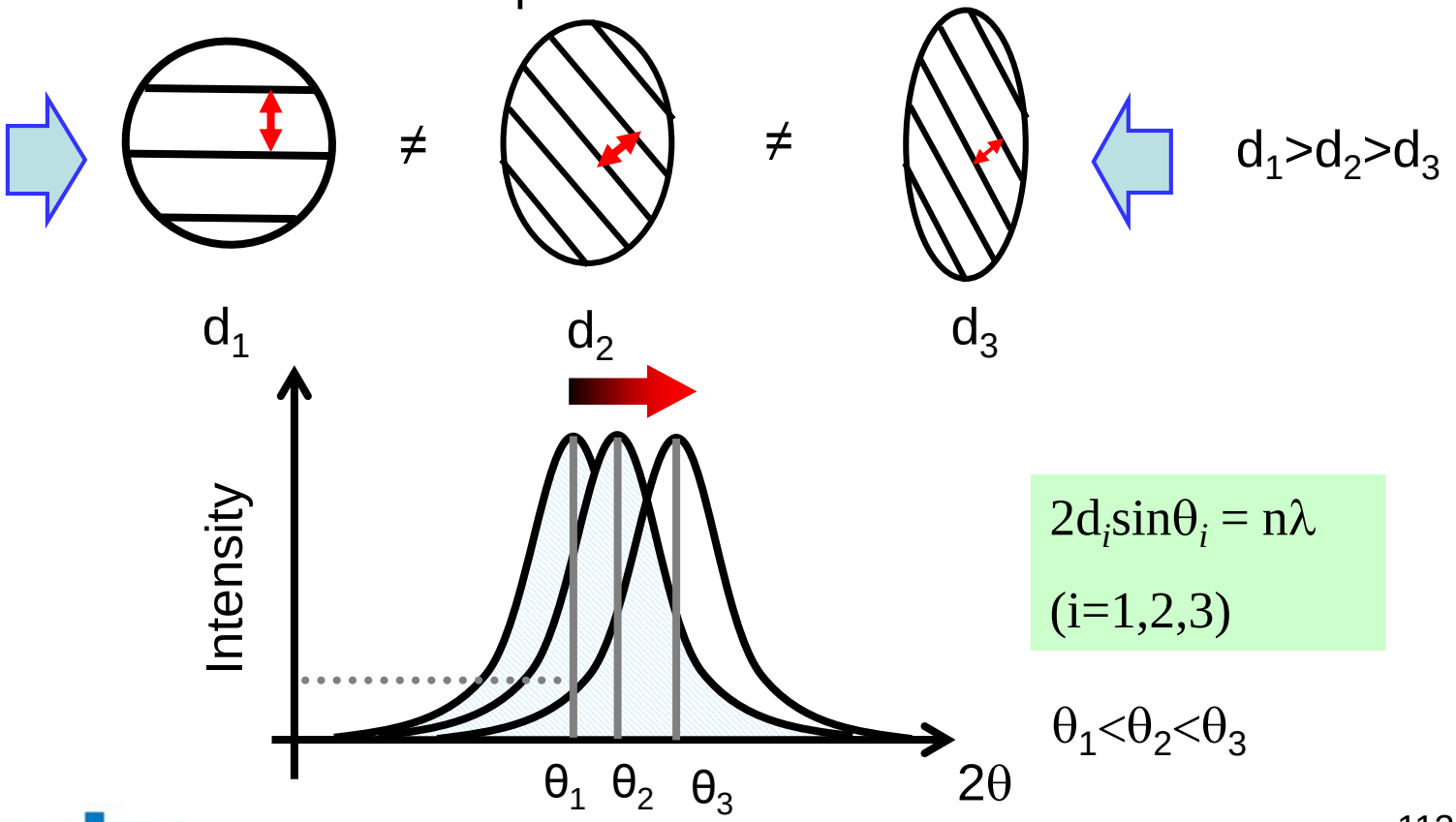
$2d_i \sin\theta_i = n\lambda$

$(i=1,2,3)$

$\theta_1=\theta_2=\theta_3$

Residual Stress and Lattice Spacings for Grains with Compressive Strain

- Compressive stress applied
- The lattice spacing d decreases as the normal of lattice planes tilts from the normal of the sample surface.

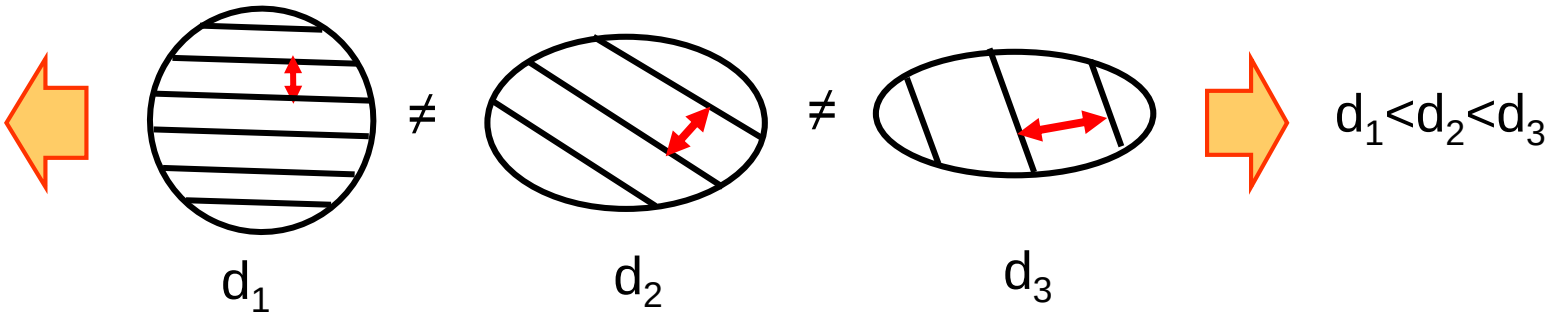


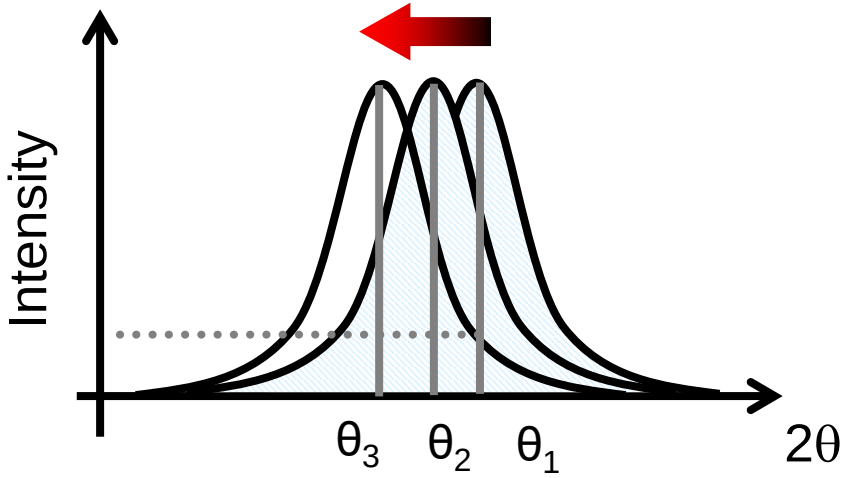
$2d_i \sin\theta_i = n\lambda$

$(i=1,2,3)$

$\theta_1 < \theta_2 < \theta_3$

Residual Stress and Lattice Spacings for Grains with Tensile Strain



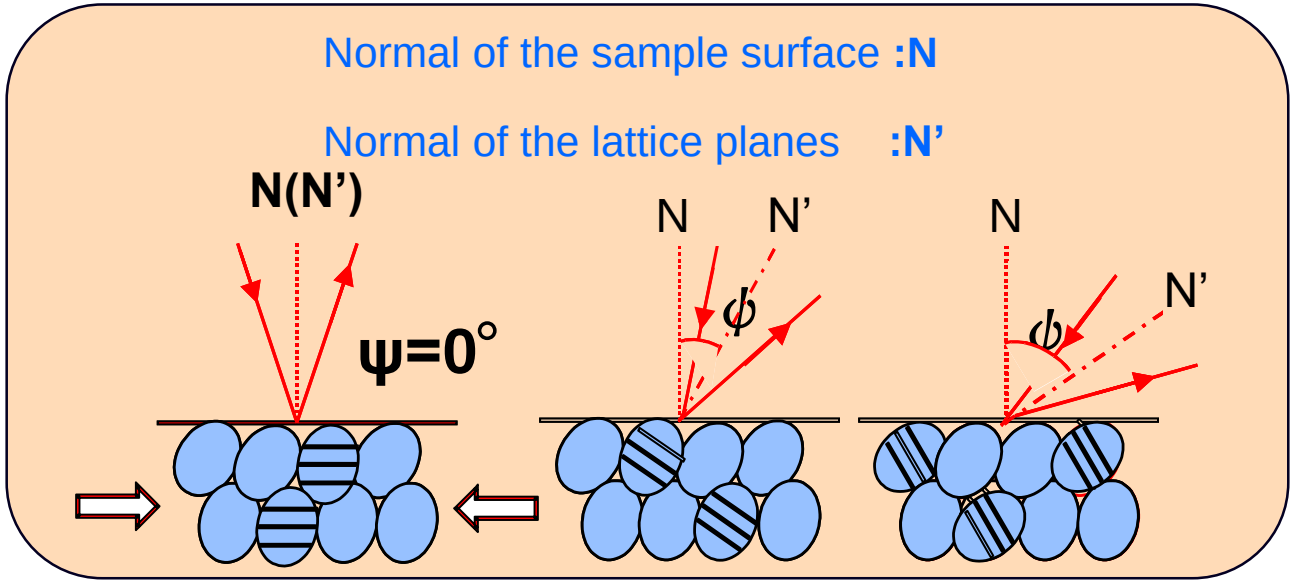


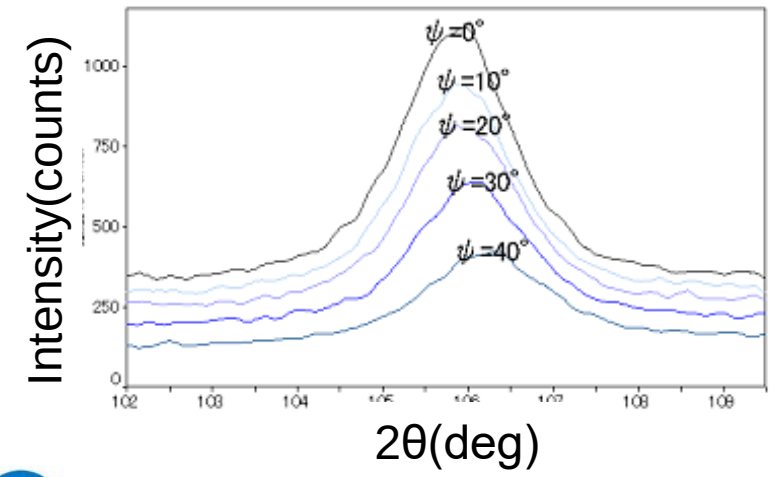
$2d_i\sin\theta_i = n\lambda$

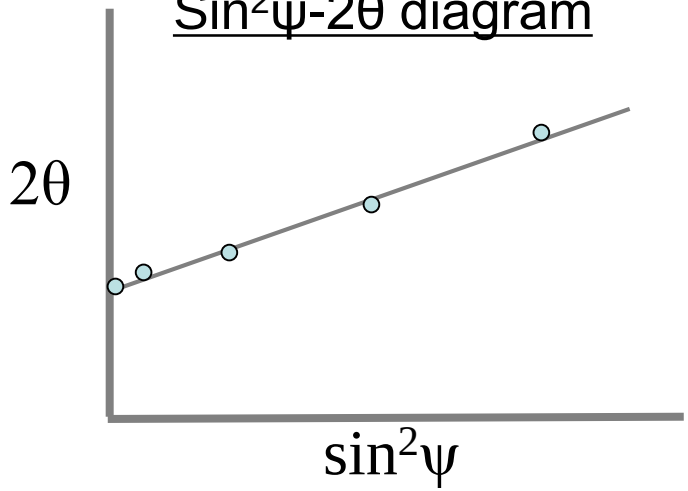
$(i=1,2,3)$

$\theta_1>\theta_2>\theta_3$

Sin²ψ method







$Sin^2\psi$ method — uni-axial stress measurement method

(1) Measurement conditions of $Sin^2\psi$ method

① A sufficient number of crystallites exists in the area irradiated by X-rays.

② Stress induced in the specimen is bi-axial ($\sigma_{33}=\sigma_{23}=\sigma_{13}=0$).

③ No stress distribution does exist within the X-ray penetration depth.

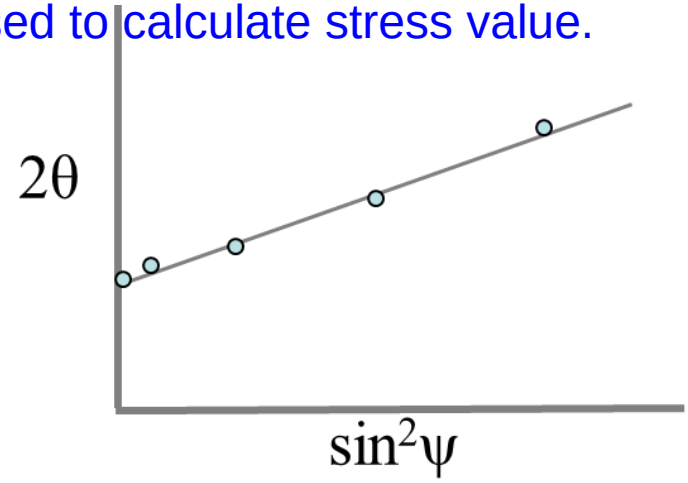
④ No strong texture does exist in the specimen.

⑤ The dependence of the 2θ on $\sin^2\psi$ is defined by a straight line.

The inclination angle of the line is used to calculate stress value.

(2) Advantage of the $\sin^2\psi$ method

Residual stress can be obtained **without using the accurate diffraction angle $2\theta_0$** of undistorted lattice planes !



Sin²ψ method (II)

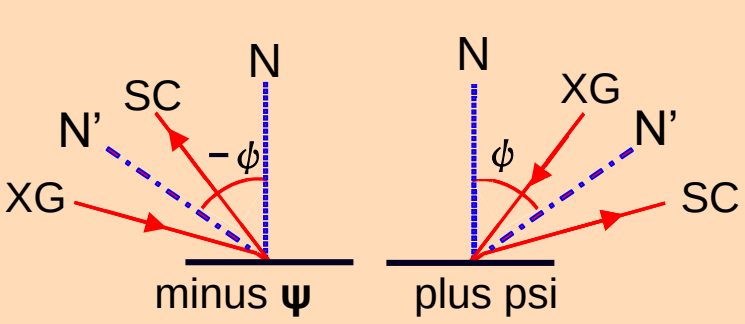
Stress: σ = K·M

- ***Bragg's law : λ= 2 d sinθ***
- ***Hooke's law : ε= σ/E***

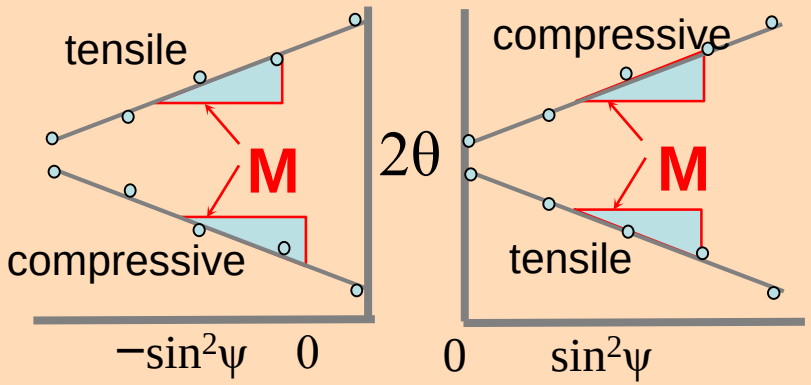
Stress constant : **K** = $\dfrac{-E}{2(1+\nu)} \cdot \cos\theta_0 \cdot \dfrac{\pi}{180}$

Tilt of diagram : **M** = $\dfrac{\Delta 2\theta}{\Delta \sin^2\psi}$

E: Young's modulus,
ν: Poisson's ratio,
θ_0: Bragg angle without strain



Iso-inclination method(Fixed **ψ**)



Stress Sensitivity

The following equation is derived from the derivative of the Bragg's equation ($\lambda=2d\sin\theta$). When the **strain ε** is constant, the **larger θ** gives the **larger Δθ**, which is half of the peak shift caused by the residual stress. Thus, reflections in the high diffraction angles 2θ are very sensitive to stress!

$$\varepsilon = -\Delta\theta \cot\theta$$

ε : strain $(=(d-d_0)/d_0)^*$

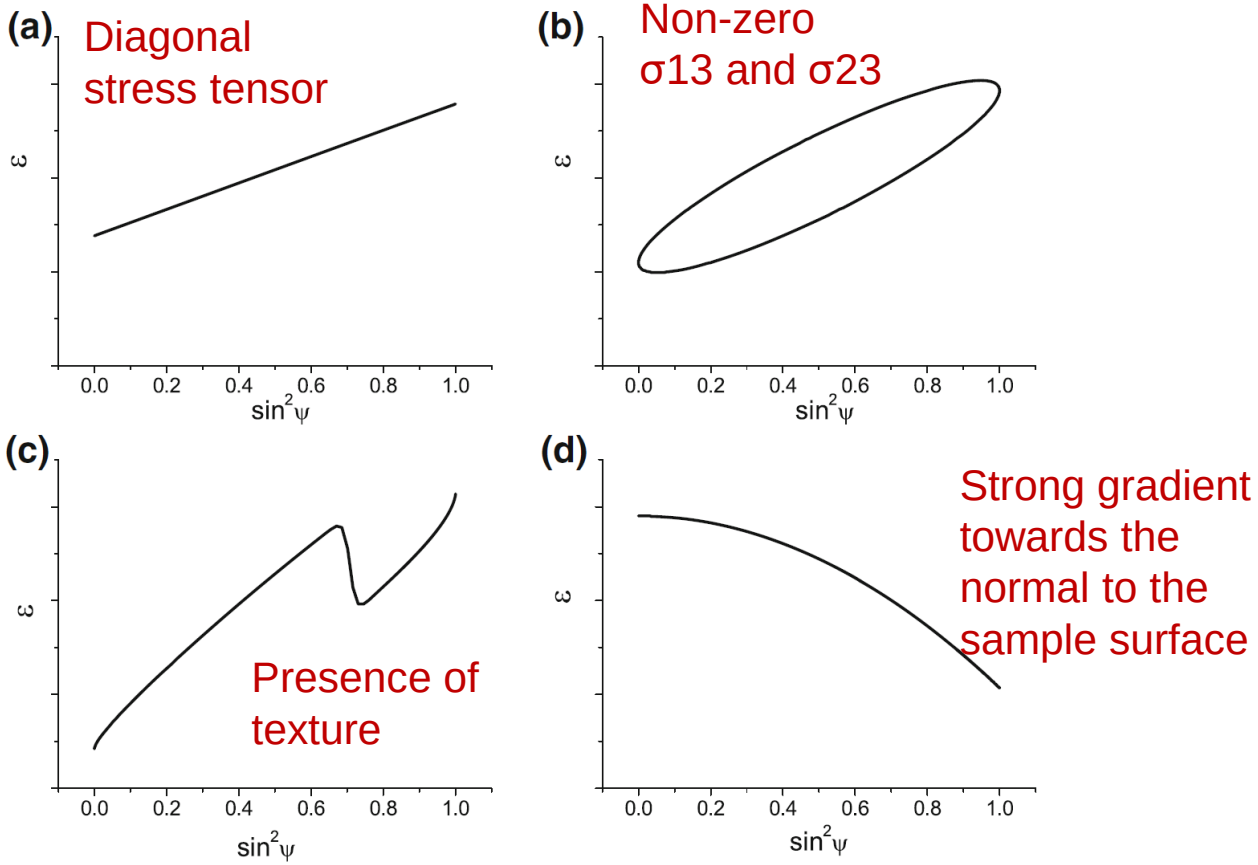
* d and d_0 are the lattice spacings with and without strain, respectively.

2θ : Diffraction angle

Lattice Planes Used for Residual Stress Measurement

Sample	Lattice constant (Å)	Characteristic X-ray	Lattice plane	Diffraction angle (°)
α-Fe (Ferrite、Martensit)	2.8664	CrKα	(211)	156.08
		CoKα	(310)	161.35
γ-Fe (Austenite)	3.656	CrKβ	(311)	149.6
		CrKα	(220)	128.9
Al and allays	4.049	CrKα	(222)	156.7
		CoKα	(420)	162.1
		CoKα	(331)	148.7
		CuKα	(333)	164.0
Cu	3.6153	CrKβ	(311)	146.5
		CoKα	(400)	163.5
		CuKα	(420)	144.7
WC	2.9062	CoKα	(211)	165.8
	2.8378	CuKα	(301)	146.76
Ti	2.950	CoKα	(114)	154.6
	4.686	CoKα	(211)	142.3
		CuKα	(302)	148.7
Ni	3.5238	CrKβ	(311)	157.7
		CuKβ	(420)	155.6
Cr	2.8845	CrKα	(211)	153.0
		CoKα	(310)	157.5

Non-linearity of $\sin^2\psi$-2θ diagram

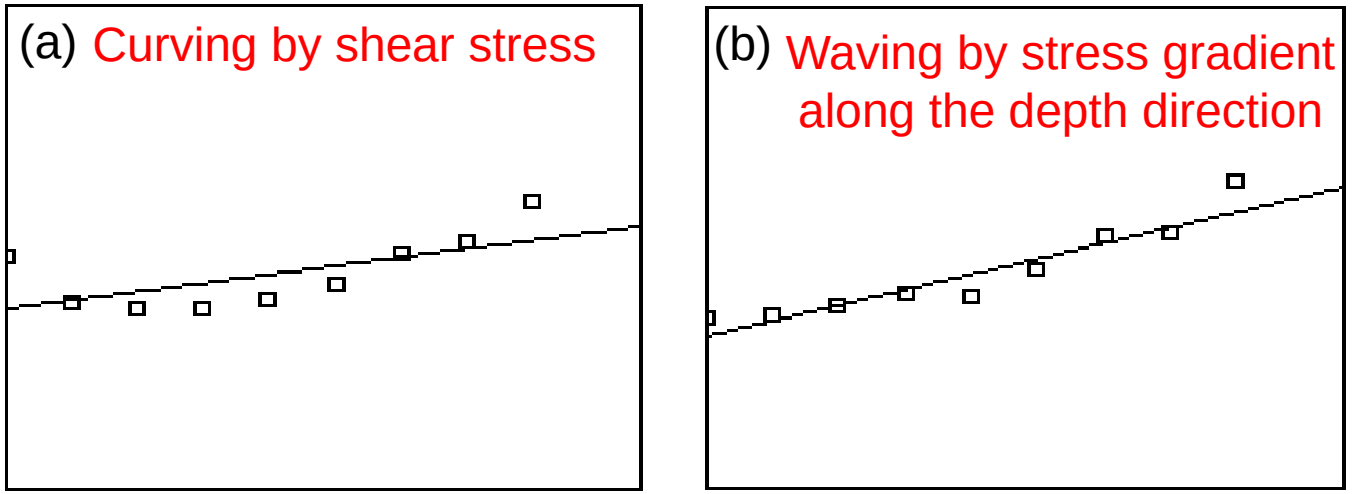


Typical shapes of $\sin^2\psi$-ε diagrams

For anisotropic and non-uniform polycrystals, the $\sin^2\psi$ method does not permit to calculate the components of the stress tensor, however, the curves $\varepsilon^{hkl}{}_{\psi\varphi}(\sin^2\psi)$ are helpful to investigate qualitatively the distribution of the stresses in the sample, for example, presence of stress gradient or texture

Non-linearity of $\sin^2\psi$-2θ diagram

Non-linearity of $\sin^2\psi$-2θ diagrams can be complemented by increasing number of **ψ** points, where the non-linearity is caused by texture, stress gradient along the depth direction and shear stress components σ_{13} and σ_{23}.



Non-linearity of $\sin^2\psi$-2θ diagrams

Strain and Stress tensors: Hook's law

Strains and stresses both form 2nd rank tensors, each having 9 components. Due to the symmetry, $s_{ij} = s_{ji}$ and $e_{ij} = e_{ji}$:

$$\sigma = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix} \qquad \varepsilon = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{pmatrix}$$

Generalized Hook's low connects strain and stress tensors via 4-rank stiffness tensor c_{ijkl} or compliance tensor s_{ijkl}, each with 81 components (36 independent due to symmetry)

$$\sigma_{ij} = c_{ijkl}\varepsilon_{kl} \qquad \varepsilon_{ij} = s_{ijkl}\sigma_{kl}$$

For materials with isotropic elastic properties, the Young modulus E and Poisson ratio ν connect stress and strain:

$$\sigma_{11} = E\varepsilon_{11} + \nu(\sigma_{22} + \sigma_{33}) \qquad \sigma_{12} = {E\varepsilon_{12}}/{(1+\nu)}$$

$$\sigma_{22} = E\varepsilon_{22} + \nu(\sigma_{11} + \sigma_{33}) \qquad \sigma_{13} = {E\varepsilon_{13}}/{(1+\nu)}$$

$$\sigma_{33} = E\varepsilon_{33} + \nu(\sigma_{22} + \sigma_{11}) \qquad \sigma_{23} = {E\varepsilon_{23}}/{(1+\nu)}$$

Stress states

Uniaxial: all except one diagonal components are zero:

$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ or } \sigma_{ij} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ or } \sigma_{ij} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$

Biaxial: all non-zero components are located at single plane:

$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Biaxial with shear: except ε_{33} all components are non-zero:

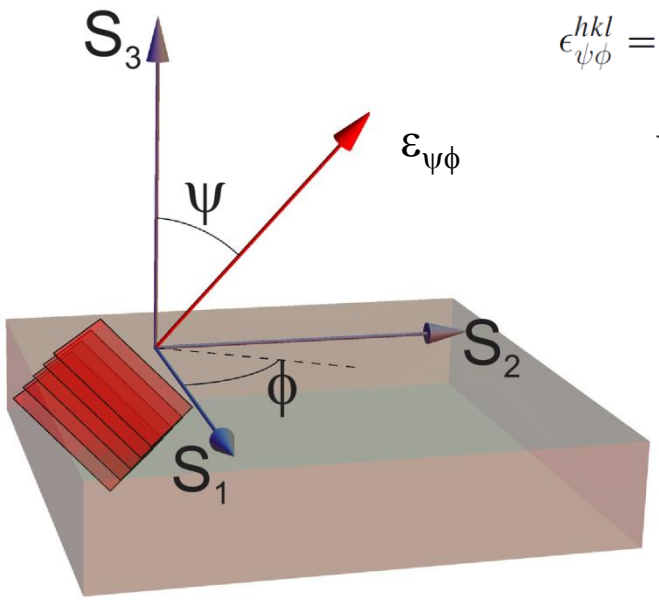
$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & 0 \end{bmatrix}$$

Triaxial: all components are non-zero

$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix}$$

Fundamental equation

Using the Hook's law, the measured strain $\varepsilon_{\psi\phi}$ at Bragg reflection *hkl* is connected to stress via so-called **fundament equation** for residual stress (isotropic case)



$$\epsilon_{\psi\phi}^{hkl} = \frac{1}{2}S_2 \sin^2\psi[\sigma_{11}\cos^2\phi + \sigma_{12}\sin 2\phi + \sigma_{22}\sin^2\phi - \sigma_{33}]$$
$$+ \frac{1}{2}S_2 \sin 2\psi[\sigma_{13}\cos\phi + \sigma_{23}\sin\phi] + S_1(\sigma_{11}+\sigma_{22}) + \sigma_{33}(\frac{1}{2}S_2 + S_1).$$

where **X-ray Elastic Constants** (XEC):

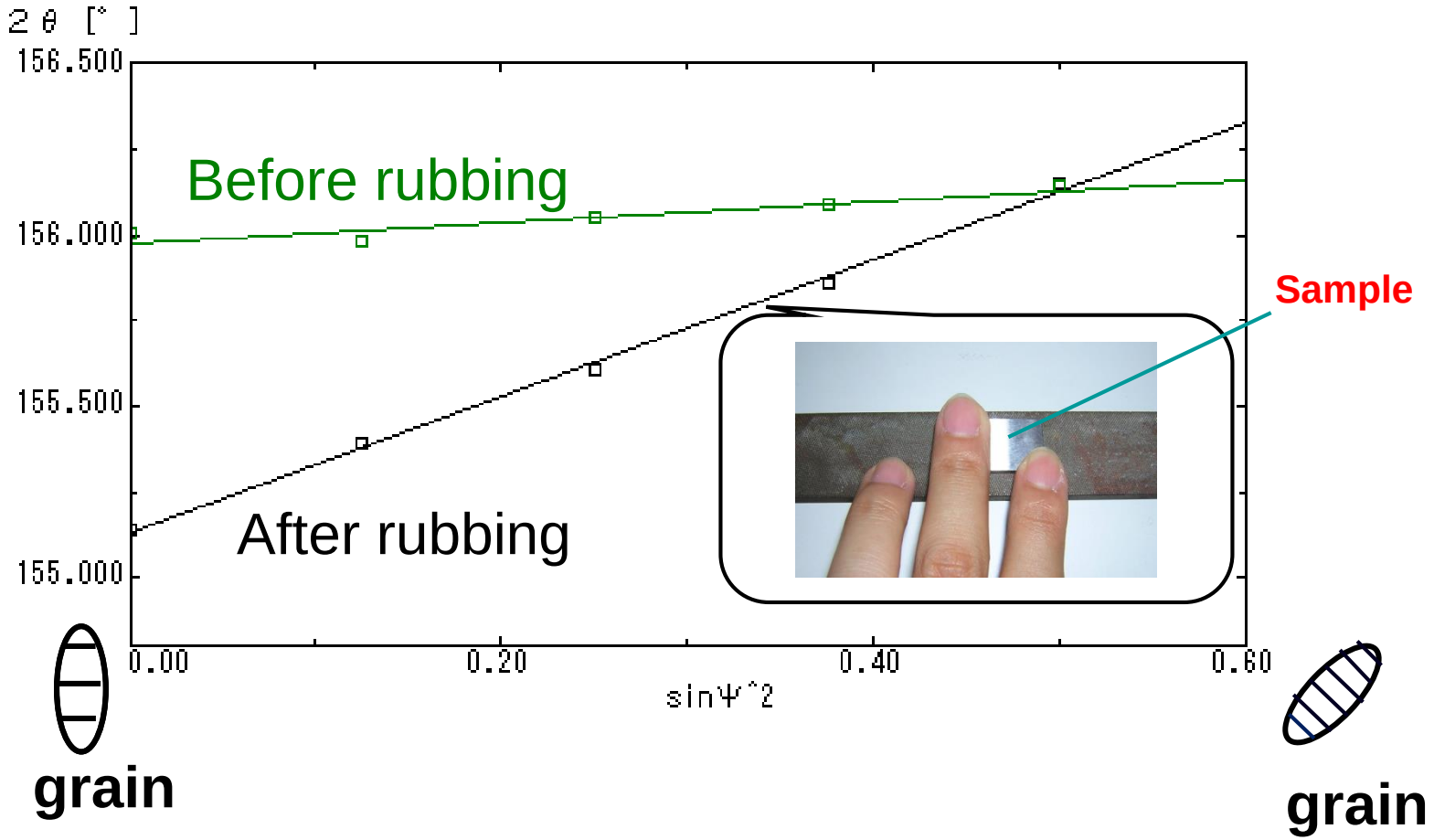
$$S_1 = -\frac{\nu}{E}; \quad \frac{1}{2}S_2 = \frac{1+\nu}{E}.$$

Fundamental equation contains 6 unknown stress tensor components. They can be found as a solution of the system of linear equations obtained from the measurement of strain at 6 different angles ψ and φ.

The values of the diagonal and non-diagonal components of the strain tensor may differ essentially, and thus even small errors in the measured positions of the diffraction peaks make the analysis unstable. Therefore, the analytical $\sin^2\psi$ method is used.

Inducing Residual Stress in a Sample

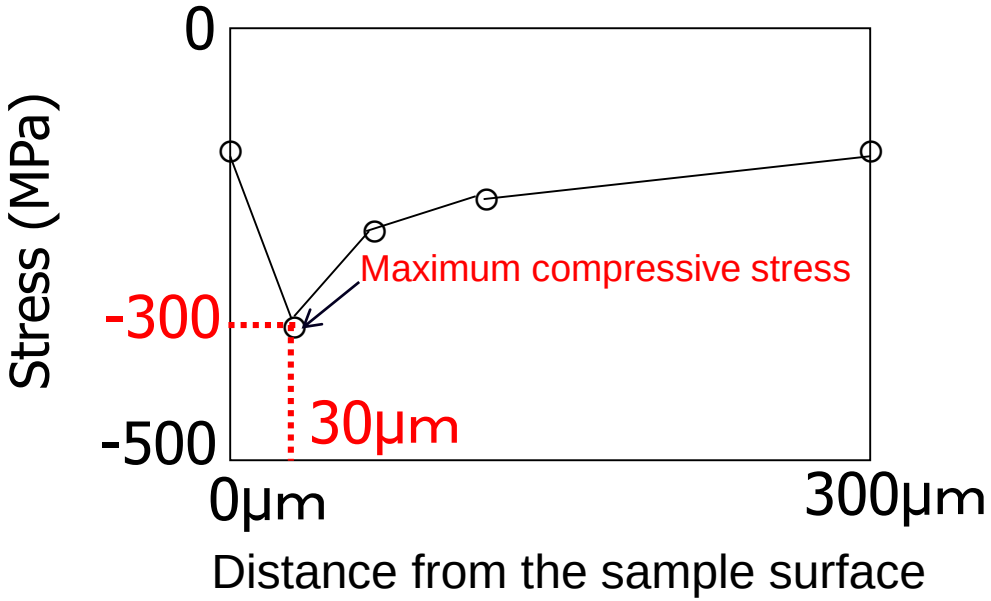
- Iron plate (Sample)

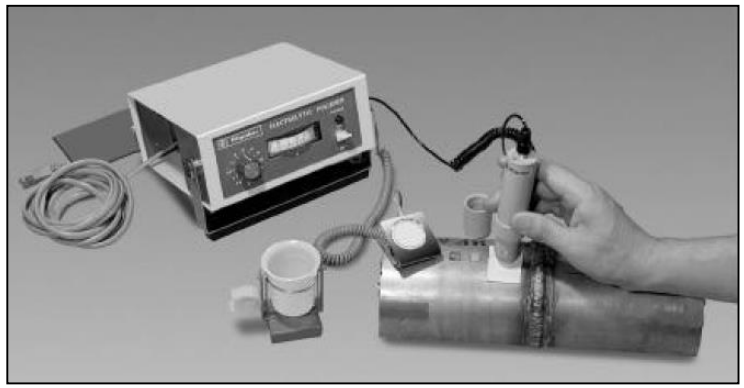


Analysis of stress distribution along the depth direction

Electrical polishing allows us to observe the residual stress along the depth direction.

- Example of a sample with shot-peening process

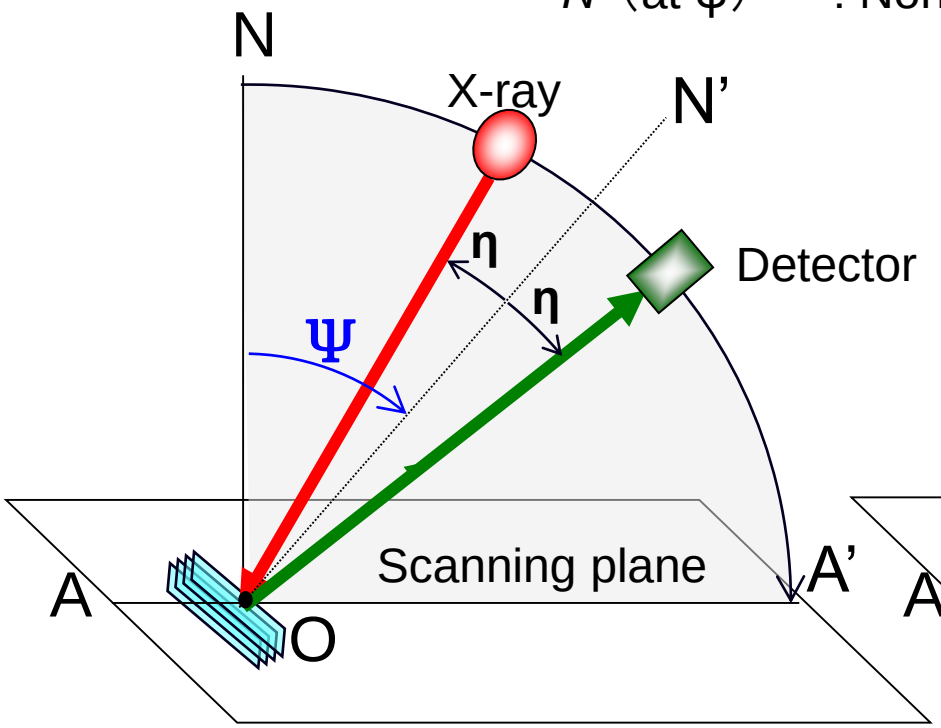




Iso-inclination method and Side-inclination method

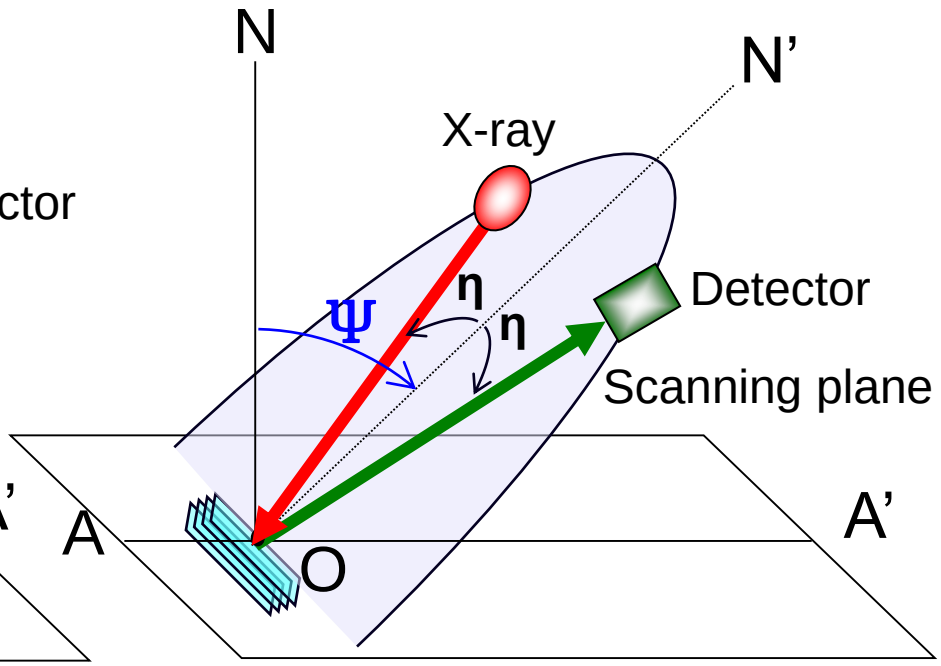
N (at ψ=0º) : Normal of the sample surface

N' (at ψ) : Normal of the lattice planes



Iso-inclination

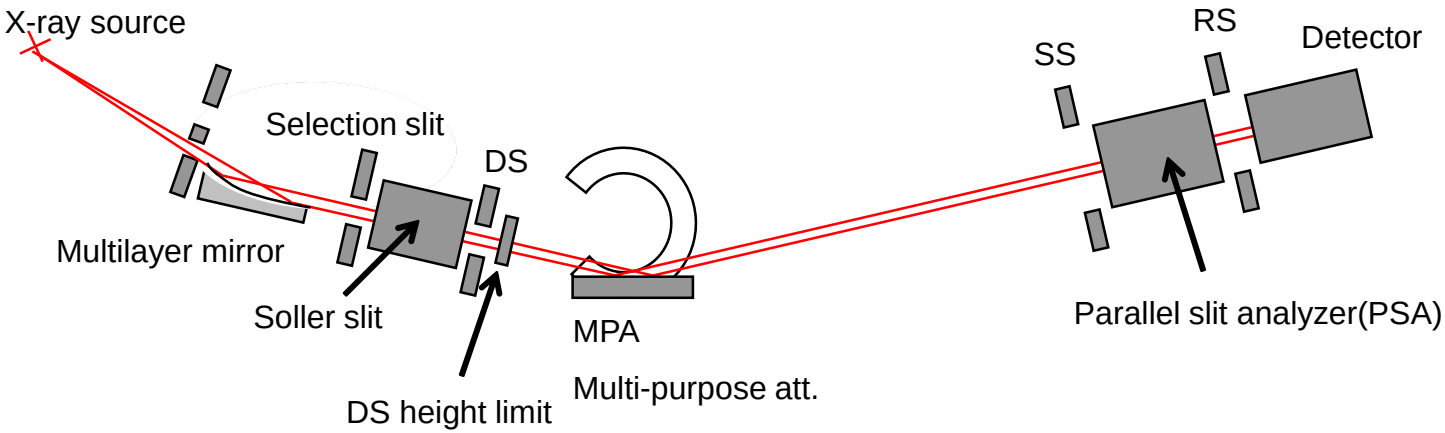
The scanning plane is parallel to the N-A-A' plane.

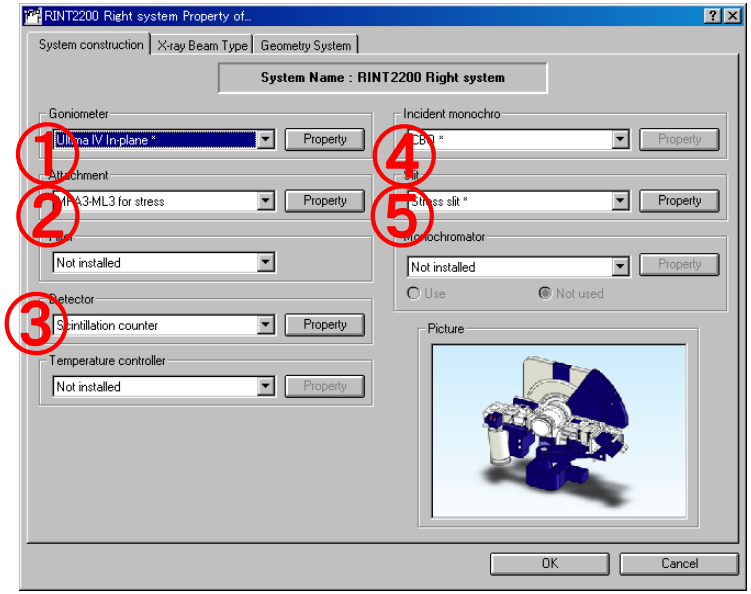


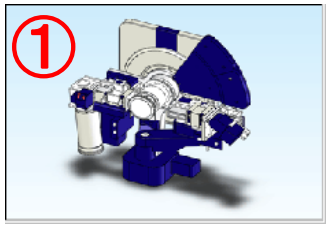
Side-inclination

The scanning plane is perpendicular to the N-A-A' plane

Optical System of Stress Measurement





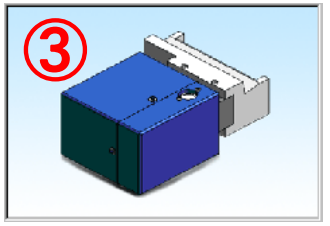


Goniometer:

Ultima IV In-plane

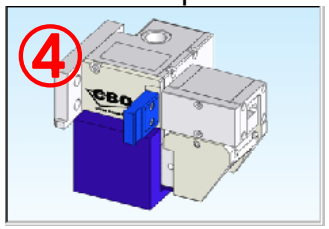
Attachment:

Multi Purpose Attachment



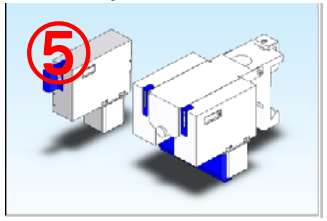
Detector:

Scintillation Counter



Incident monochrometor:

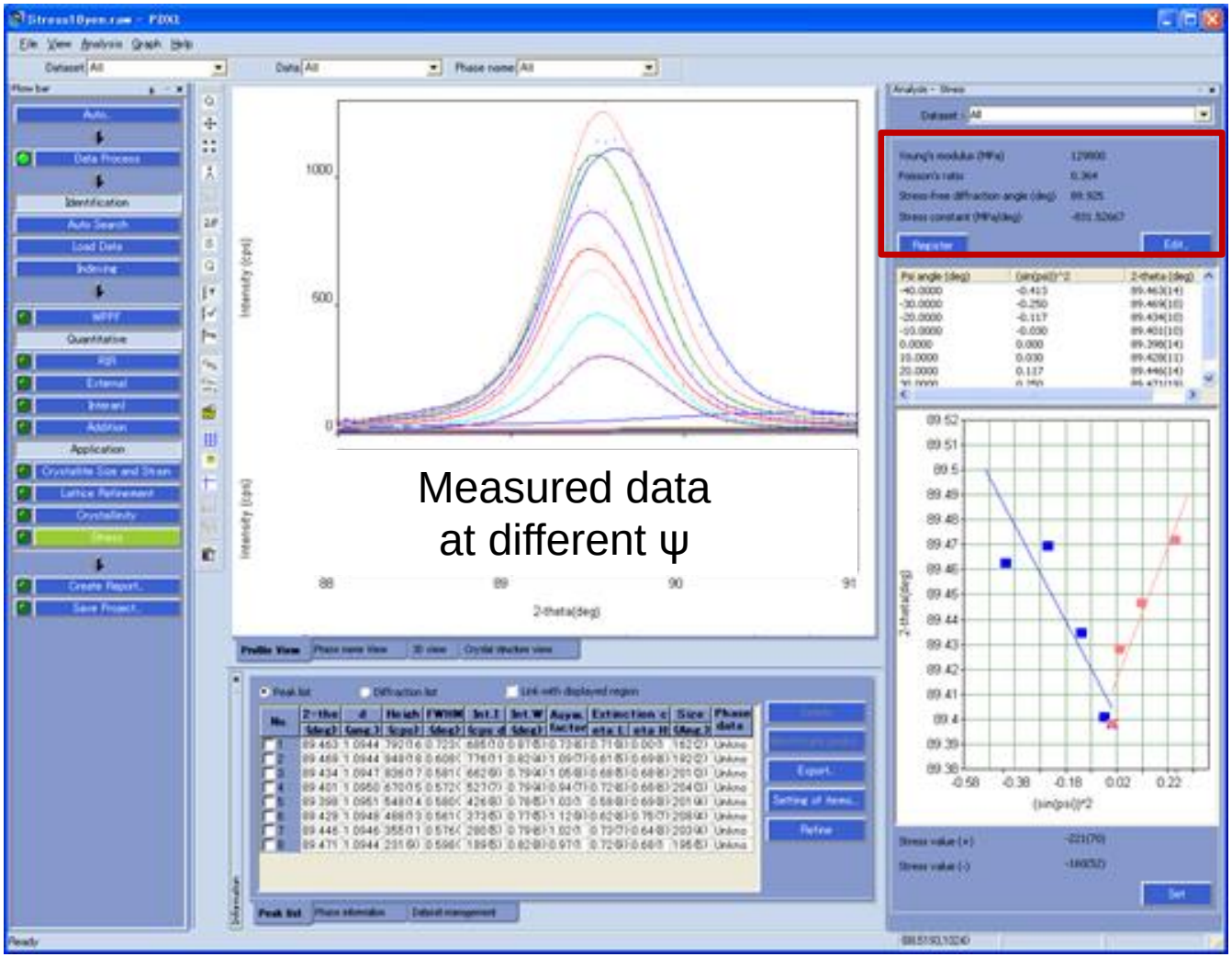
Cross Beam Optic



Slit:

Stress slit

PDXL software: Stress



Young's modulus (MPa),
Poisson's ratio,
Stress-free 2theta angle (deg.),
Stress constant (MPa/deg.)