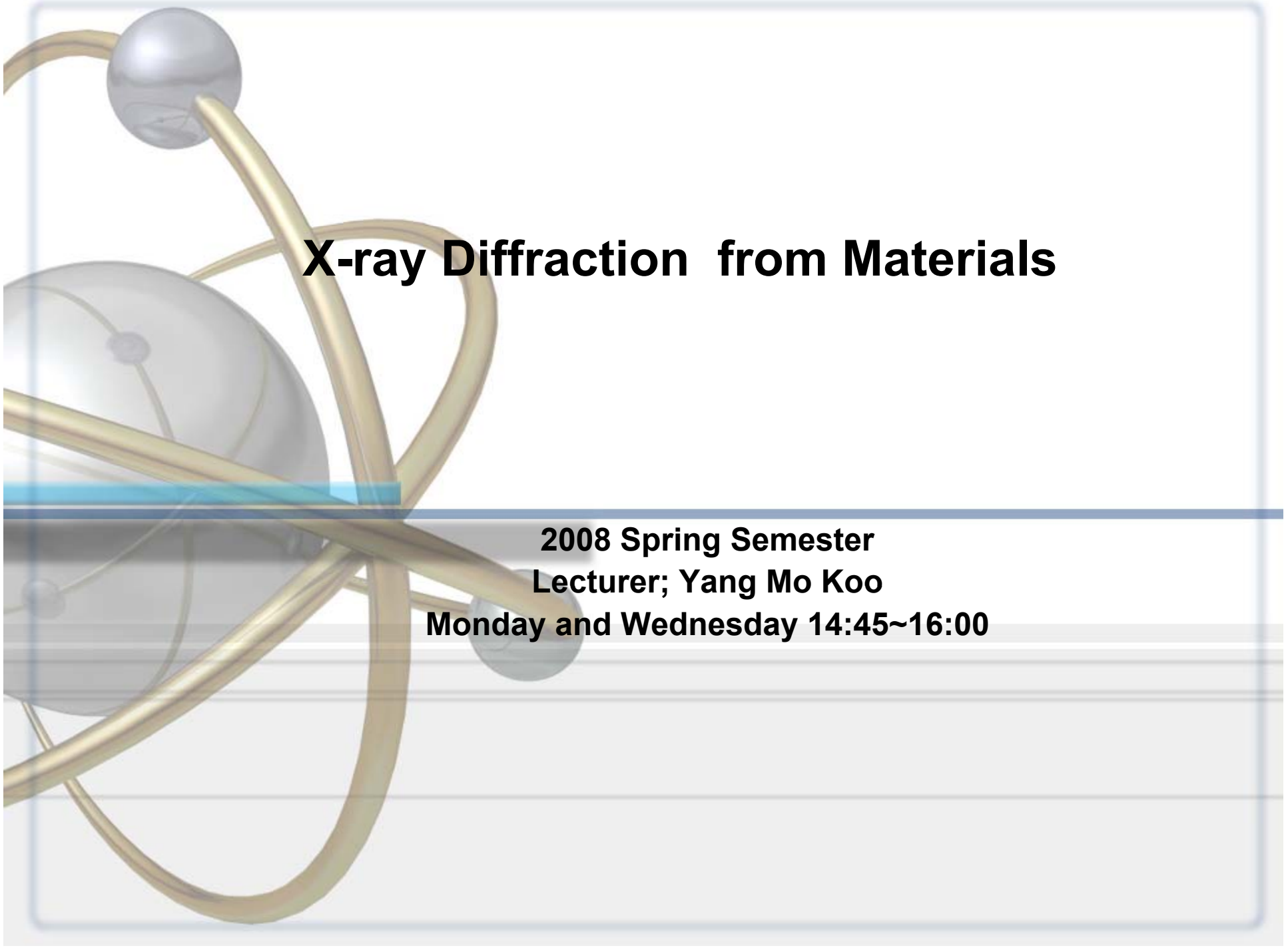


X-ray Diffraction from Materials

2008 Spring Semester

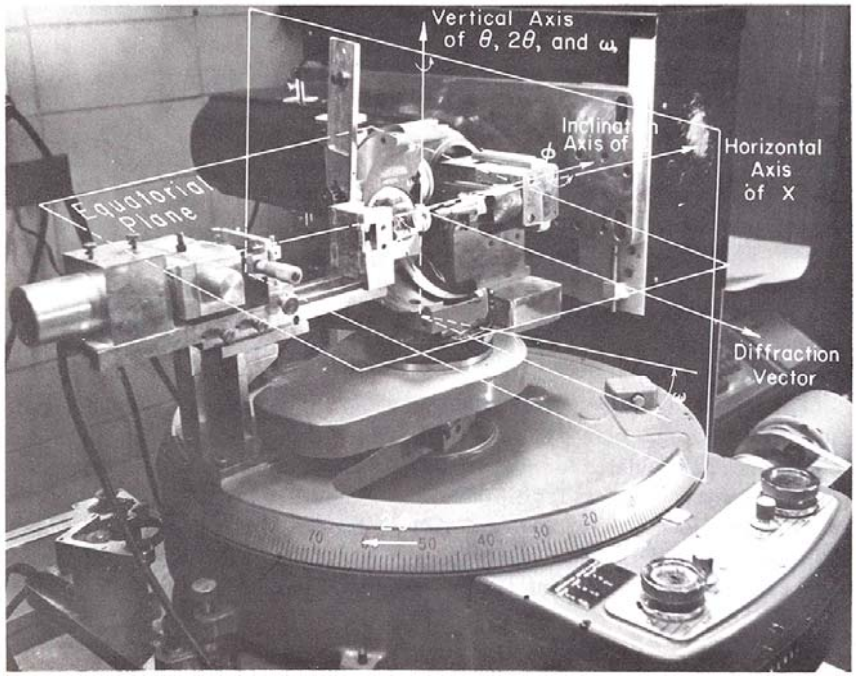
Lecturer; Yang Mo Koo

Monday and Wednesday 14:45~16:00

8.2 X-ray Diffractometers

Diffractometer: a measuring instrument for analyzing the structure of a usually crystalline substance from the scattering pattern produced when a beam of radiation or particles (as X rays or neutrons) interacts with it.

Goniometer: an instrument that either measures angle or allows an object to be rotated to a precise angular position.

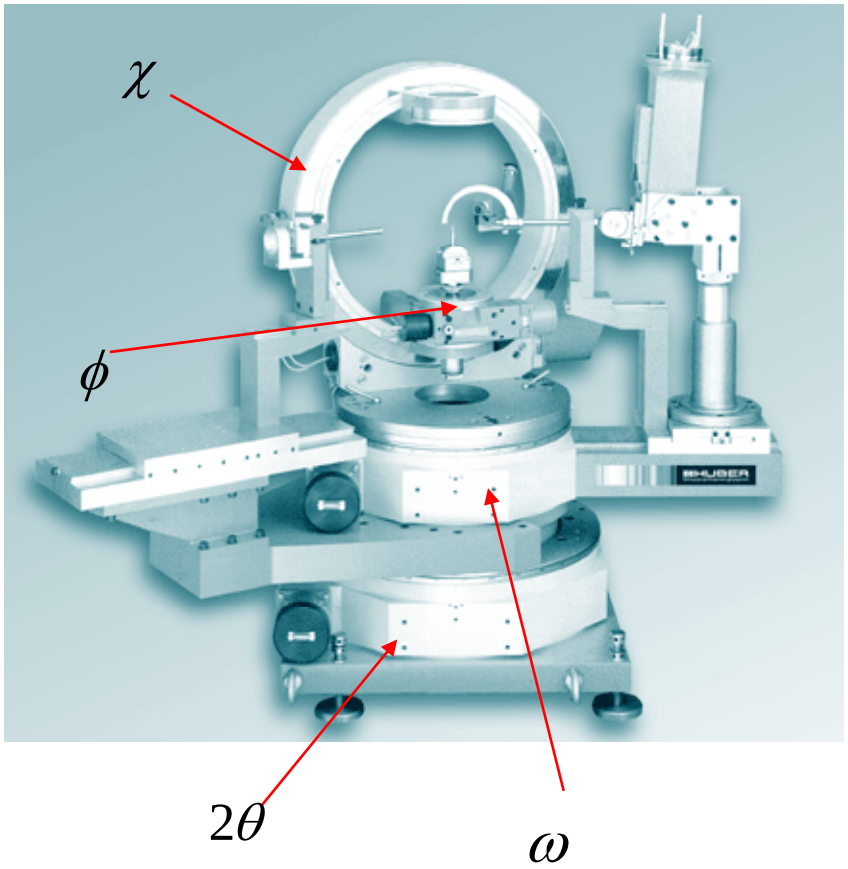


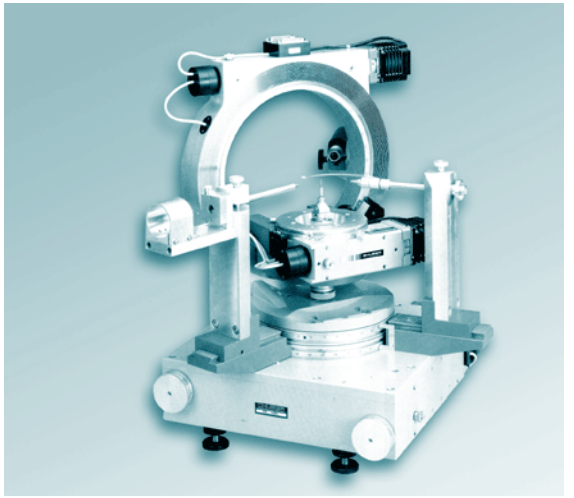
Diffractometer with 4-circle goniometer

Eulerian cradle (2-circle)

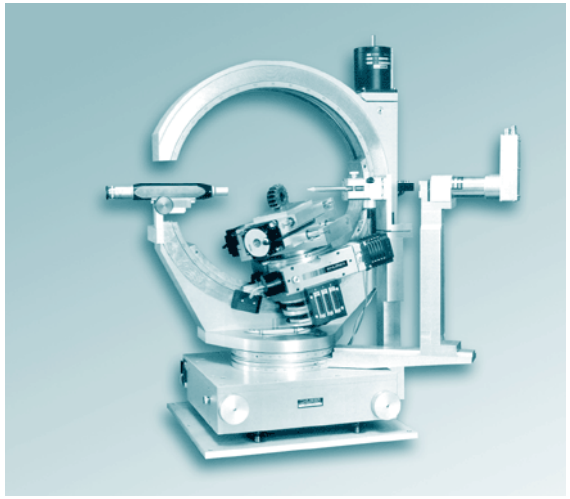
8.2 X-ray Diffractometers

4-circle goniometer





Full circle Eulerian cradle

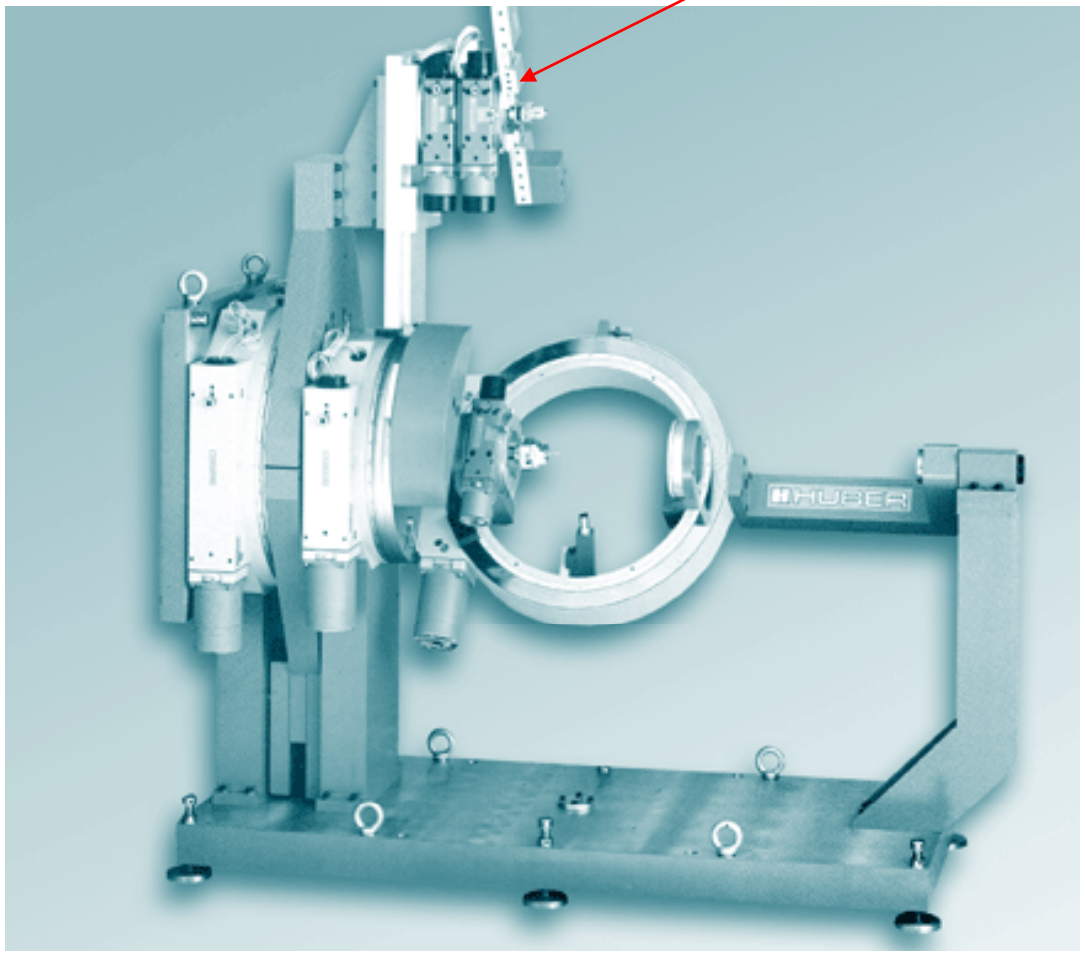


Eulerian cradle for texture measurement

8.2 X-ray Diffractometers

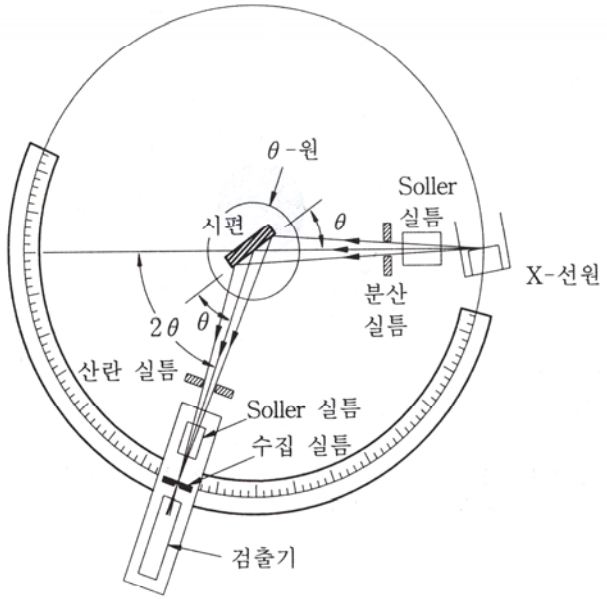
6-circle goniometer

Two circles (θ and 2θ) at detector side



8.2 X-ray Diffractometers

Diffractometer with 2-circle goniometer

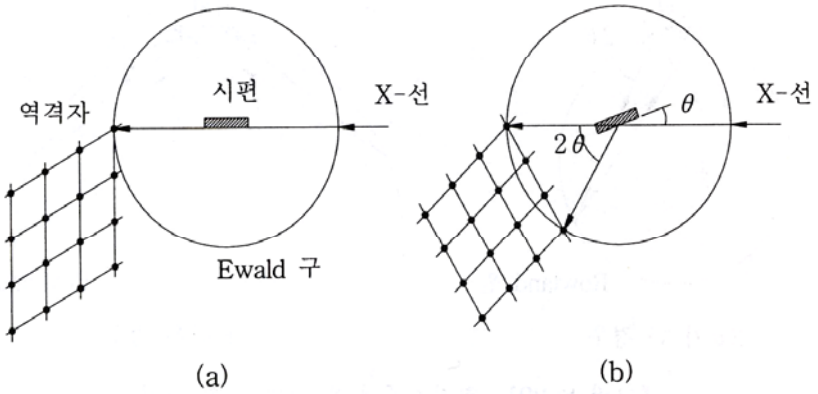


【그림 8-26】 2-회전축 측각기가 장착된 회절기의 개략도

Two rotation axes are **ω** and 2θ.
Focusing condition reflected beam from the sample: ω =θ.

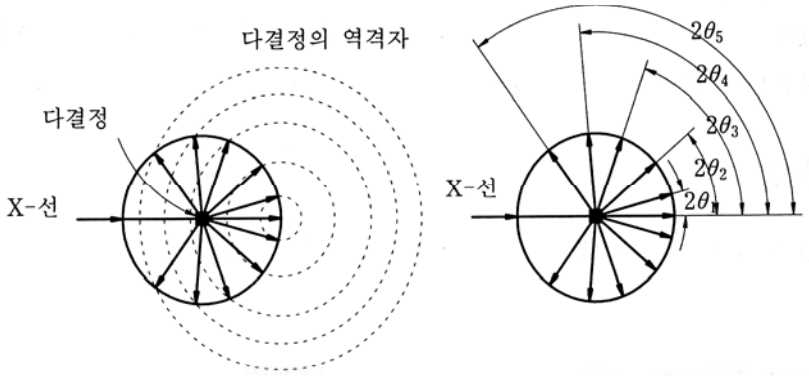
8.2 X-ray Diffractometers

Diffraction condition for a single crystal



【그림 8-27】 2-회전축 측각기에서 단결정의 회절 조건

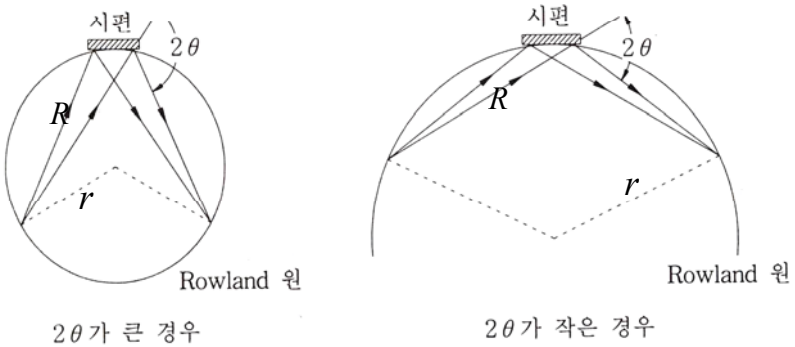
Diffraction condition for poly-crystal or powder sample



【그림 8-28】 2-회전축 측각기에서 다결정의 회절 조건과 역격자

8.2 X-ray Diffractometers

Focusing condition of reflected beam from sample surface

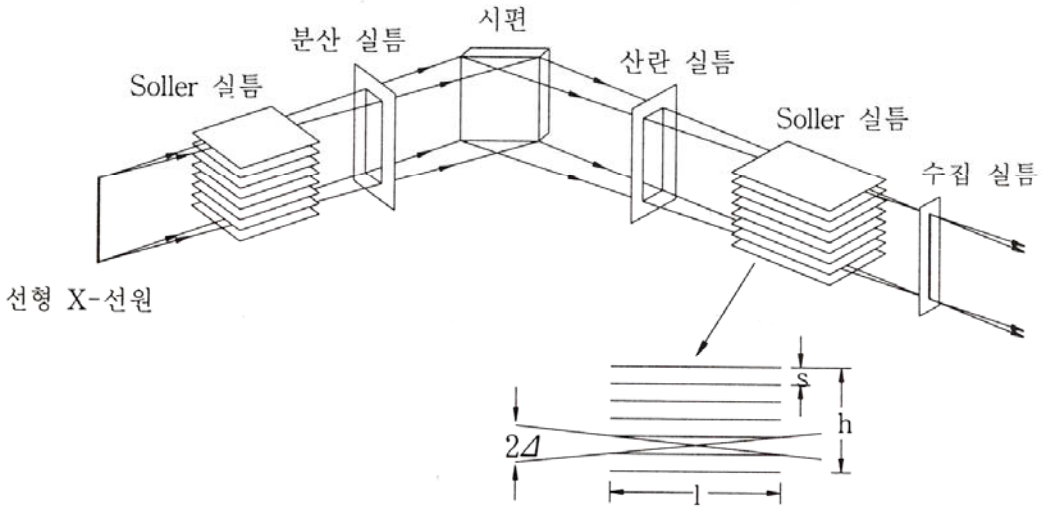


【그림 8-29】 회절기에서 X-선의 집속 조건

$$r = R / 2\sin\theta$$

8.2 X-ray Diffractometers

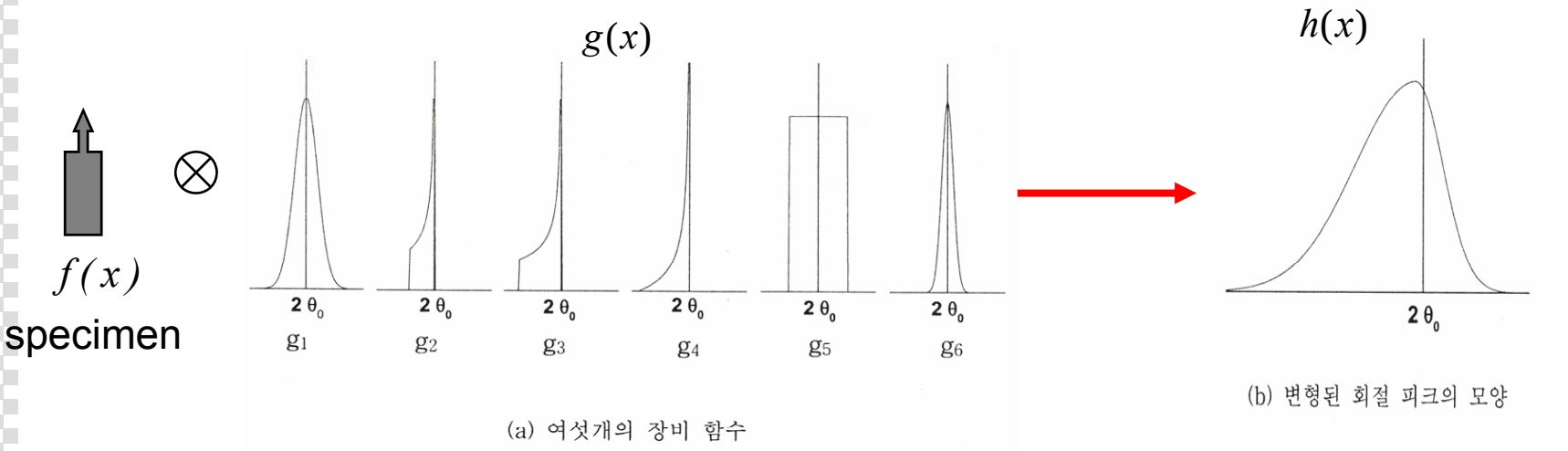
Slit system of powder diffractometer



【그림 8-30】 2-회전축 측각기에서 부품들의 위치

8.2 X-ray Diffractometers

Elements effecting diffraction peak shape



$$h(x) = f(x) \otimes g(x)$$

where $g(x) = g_1(x) \otimes g_2(x) \otimes g_3(x) \otimes g_4(x) \otimes g_5(x) \otimes g_6(x)$

$g_1(x)$: x-ray source

$g_2(x)$: flat surface of specimen

$g_3(x)$: vertical divergence of x-ray beam

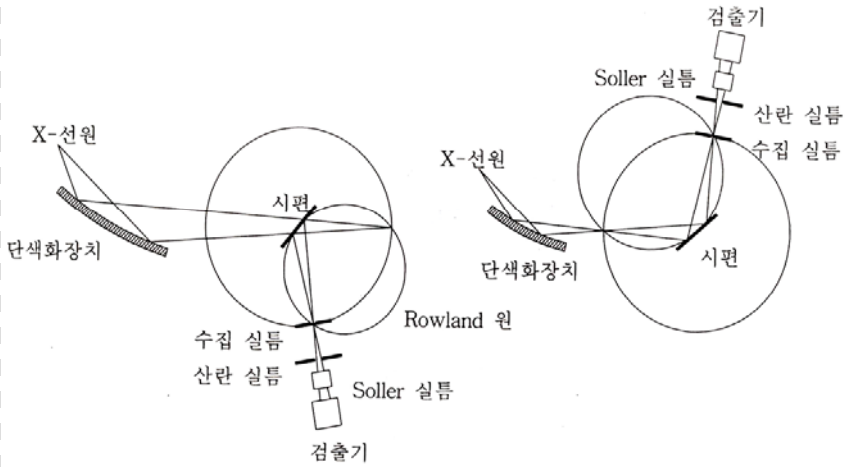
$g_4(x)$: transparency of x-ray in the specimen

$g_5(x)$: size of reciving slit

$g_6(x)$: misalignment

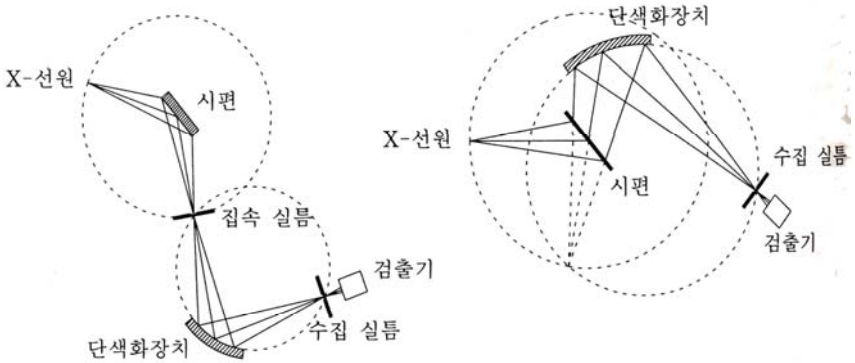
8.2 X-ray Diffractometers

Monochromator



투과 시편 - 반사 단색화장치　　반사 시편 - 반사 단색화장치

【그림 8-33】 단색화장치가 X-선원 쪽에 설치된 경우의 집속 조건

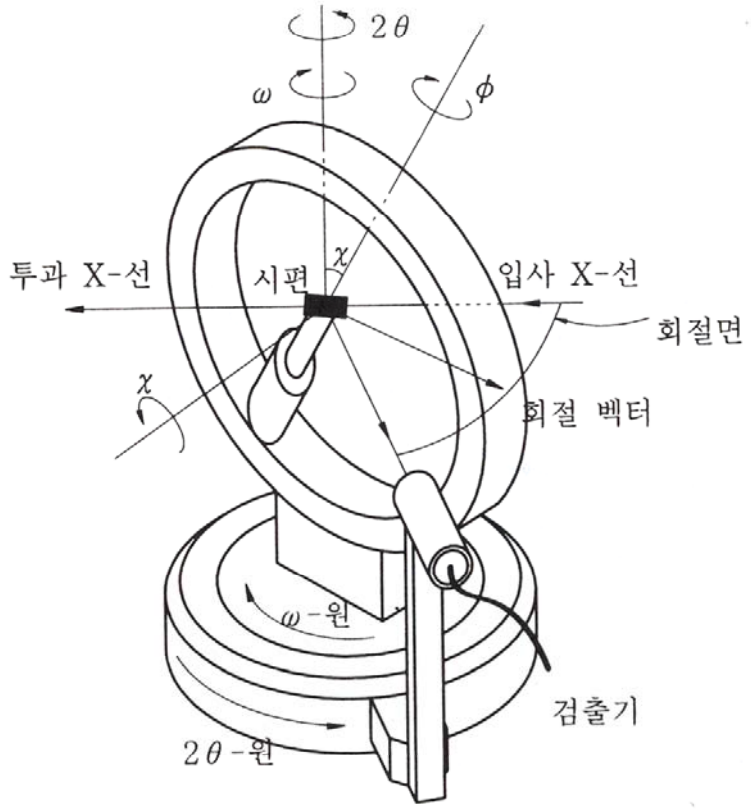


반사 시편 - 반사 단색화장치　　투과 시편 - 반사 단색화장치

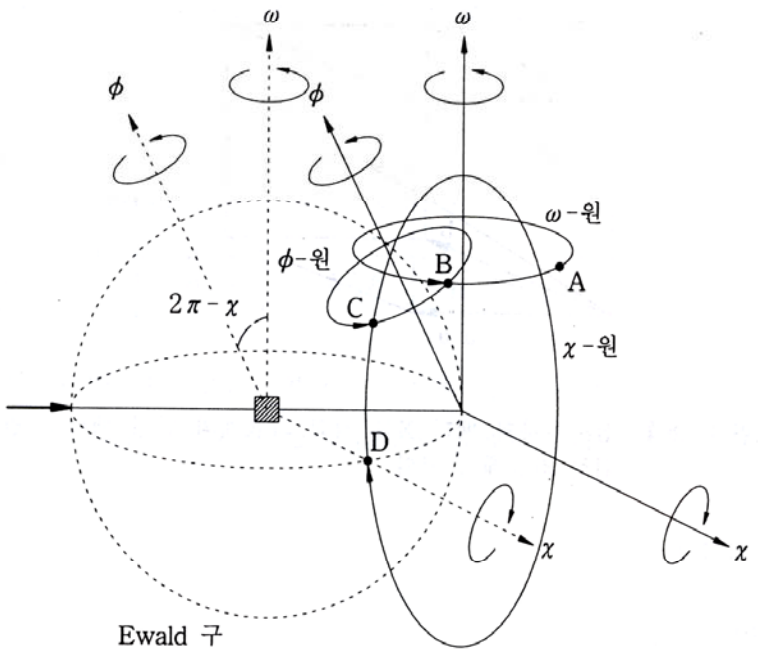
【그림 8-32】 단색화장치가 검출기 쪽에 설치된 경우의 집속 조건

8.2 X-ray Diffractometers

Diffractometer with 4-circle goniometer



【그림 8-34】 4-회전축 측각기의 회전축과 회전 방향



【그림 8-35】 ω, φ, χ 축을 차례로 회전시켜 A점의 역격자점을 회절면 위의 점 D로 이동시키는 순서

8.2 X-ray Diffractometers

Diffraction condition for 4-circle goniometer

In order to get diffraction peak of hkl, one can move reciprocal point to diffraction plane by rotating a combination of **ω**, φ, and χ. Any diffraction pot can be moved by rotating two different angles such as ω and φ, φ and χ, and ω and χ. However, rotations of all three angles are used for real experiment because of geometric restriction of the diffractometer. 2θ circle is used for moving detector to the reflected x-ray beam position. The angle, ω set θ for keeping focusing condition of reflected beam, and φ, and χ are adjusted to move reciprocal lattice point on the diffraction plane.

The coordinates system in 4-circle goiniometer

(I) the coordinates system of diffractormeter : an orthonormal system related to diffractometer.

$$\mathbf{A}_D = \begin{pmatrix} \mathbf{a}_D \\ \mathbf{b}_D \\ \mathbf{c}_D \end{pmatrix}$$

where

b_D is parallel to the diffraction vector for positive 2θ and always bisects the angle $(2\pi - 2\theta)$

$\mathbf{a}_D$ is in the diffraction plane, perpendiculart o b_D is directed toward the x – ray source when $2\theta = 0$.

$\mathbf{c}_D$ is coincident with the main axis of the instrument.

(II) the coordinate system of specimen : an orthonormal system

$$\mathbf{A}_C = \begin{pmatrix} \mathbf{a}_C \\ \mathbf{b}_C \\ \mathbf{c}_C \end{pmatrix}$$

$\mathbf{A}_C$ fixed in the specimen. The axes are defined such that

$\mathbf{A}_C$ is coincident with A_D when $\omega = \phi = \chi = 0$.

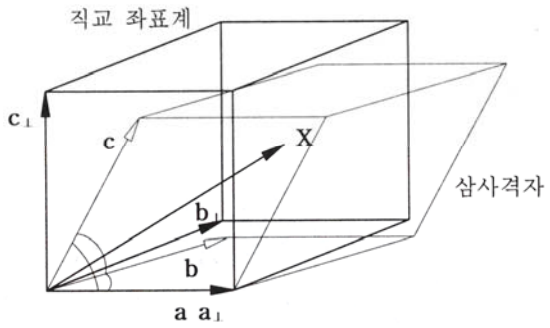
$\mathbf{c}_C$ is always coincident with the ϕ axis.

8.2 X-ray Diffractometers

(III) Crystal axes of unit cell

$$\mathbf{A} = \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}$$

where $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are lattice parameters of unit cell



【그림 8-36】 삼사격자의 벡터 X를 직교 좌표계의 단위 벡터로 변환하기 위한 좌표계의 정의

Orthogonal axes system

$$\mathbf{X}_\perp = \mathbf{T}\mathbf{X}$$

$$where\ \ \mathsf{T} = \begin{pmatrix} \mathsf{a} & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & c(\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma \\ 0 & 0 & c(1-\sin^2\alpha+\cos^2\beta-2\cos\alpha\cos\beta\cos\gamma)^{1/2}/\sin\gamma \end{pmatrix}$$

This matrix often used for calculating |**X**|

$$|\mathbf{X}| = |\mathbf{X}_\perp| = \left(\mathbf{X}_\perp^T \mathbf{X}_\perp\right)^{1/2}$$

Therefore

$$|\mathbf{X}_\perp| = \{(\mathbf{TX})^T(\mathbf{TX})\}^{1/2} = \{\mathbf{X}^T\mathbf{T}^T\mathbf{TX}\}^{1/2} = \{\mathbf{X}^T(\mathbf{T}^T\mathbf{T})\mathbf{X}\}^{1/2} = \{\mathbf{X}^T\mathbf{GX}\}^{1/2}$$

G is called metric tensor

$$\mathbf{G} = \mathbf{T}^T\mathbf{T} = \begin{pmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ca\cos\beta & bc\cos\alpha & c^2 \end{pmatrix}$$

$$= \begin{pmatrix} \mathbf{a}\cdot\mathbf{a} & \mathbf{a}\cdot\mathbf{b} & \mathbf{a}\cdot\mathbf{c} \\ \mathbf{b}\cdot\mathbf{a} & \mathbf{b}\cdot\mathbf{b} & \mathbf{b}\cdot\mathbf{c} \\ \mathbf{c}\cdot\mathbf{a} & \mathbf{c}\cdot\mathbf{b} & \mathbf{c}\cdot\mathbf{c} \end{pmatrix} = \mathbf{A}^T\mathbf{A}$$

If axes system is orthogonal, metric tensor become unit matrix;

$$\mathbf{G} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \mathbf{I}$$

8.2 X-ray Diffractometers

(IV) Reciprocal crystal axes

$$\mathbf{A}^* = \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}^* \\ \mathbf{c}^* \end{pmatrix}$$

where $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ are reciprocal unit vectors

The magnitude of reciprocal vector can be estimated by metric tensor

$$\left|\mathbf{X}^*\right| = \left\{\mathbf{X}^{*T}\mathbf{G}^*\mathbf{X}^*\right\}^{1/2}$$

and

$$\mathbf{G}^* = \begin{pmatrix} \mathbf{a}^*\cdot\mathbf{a}^* & \mathbf{a}^*\cdot\mathbf{b}^* & \mathbf{a}^*\cdot\mathbf{c}^* \\ \mathbf{b}^*\cdot\mathbf{a}^* & \mathbf{b}^*\cdot\mathbf{b}^* & \mathbf{b}^*\cdot\mathbf{c}^* \\ \mathbf{c}^*\cdot\mathbf{a}^* & \mathbf{c}^*\cdot\mathbf{b}^* & \mathbf{c}^*\cdot\mathbf{c}^* \end{pmatrix} = \mathbf{A}^{*T}\mathbf{A}^*$$

8.2 X-ray Diffractometers

(V) Coordinates of a reciprocal vector

The coordinates of a vector in reciprocal space in the $\mathbf{A}_C$, $\mathbf{A}_D$, and $\mathbf{A}^*$ system

$$\mathbf{H}_C \equiv (x_C, y_C, z_C)$$
$$\mathbf{H}_D \equiv (x_D, y_D, z_D)$$
$$\mathbf{H} \equiv (h, k, l)$$

such that a reciprocal vector $\mathbf{h}$ may be written

$$\mathbf{h} = \mathbf{H}\mathbf{A}^* = h\mathbf{a}^* + h\mathbf{b}^* + l\mathbf{c}^*$$
$$= \mathbf{H}_D\mathbf{A}_D = x_D\mathbf{a}_D + y_D\mathbf{b}_D + z_D\mathbf{c}_D$$
$$= \mathbf{H}_C\mathbf{A}_C = x_C\mathbf{a}_C + y_C\mathbf{b}_C + z_C\mathbf{c}_C$$

The relationship between $\mathbf{A}_C$ and $\mathbf{A}_D$ after rotation of specimen ω, χ, and ϕ

$$\mathbf{A}_C = \mathbf{F}\mathbf{A}_D$$

where transformation matrix $\mathbf{F}$ is defined by

8.2 X-ray Diffractometers

$$\mathbf{F} = \mathbf{R}(\phi)\mathbf{R}(\chi)\mathbf{R}(\omega)$$

$$= \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\chi & sin\chi \\ 0 & -\sin\chi & \cos\chi \end{pmatrix} \begin{pmatrix} \cos\omega & sin\omega & 0 \\ -\sin\omega & \cos\omega & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} \cos\phi\cos\omega - sin\phi sin\omega\cos\chi & \cos\phi sin\omega + sin\phi\cos\omega\cos\chi & sin\phi sin\chi \\ -sin\phi\cos\omega - \cos\phi sin\omega\cos\chi & -\sin\phi sin\omega + \cos\phi\cos\omega\cos\chi & \cos\phi sin\chi \\ sin\chi sin\omega & -\sin\chi\cos\omega & \cos\chi \end{pmatrix}$$

It follows that

$$\mathbf{X}_C = \mathbf{X}_D\mathbf{F}^{-1} \text{ or } \mathbf{X}_C^T = \mathbf{F}\mathbf{X}_D^T$$

since F is unitary matrix and thus

$$\mathbf{F}^{-1} = \mathbf{F}^T$$

8.2 X-ray Diffractometers

(VII) The orientation matrix

It is convinient to introduce an orientation matrix U such that

$$\mathbf{A}^{*} = \mathbf{U}\mathbf{A}_{C}$$

The matrix U (which is in general not symmetric) has nine independent elements which are related to the six sell constants and three angles describing the specimen oreientation. The cell constants may be obtained, independent of the orientation, by forming the product of A^{*} and its transposeA^{*T}.

$$\mathbf{G}^{-1} = \mathbf{A}^{*}\mathbf{A}^{*T} = \mathbf{U}\mathbf{A}_{C}\mathbf{A}_{C}^{T}\mathbf{U}^{T}$$

from which we obtain, since $\mathbf{A}_{C}\mathbf{A}_{C}^{T} = \mathbf{I}$

$$\mathbf{G}^{-1} = \mathbf{U}\mathbf{U}^{T}$$

Thus, by forming the product $\mathbf{U}\mathbf{U}^{T}$, the reciprocal cell constants and hence the unit cell constant of the crystal may be obtained.

8.2 X-ray Diffractometers

Calculation of setting angles at 4-circle goiniometer

If ω, χ, φ are such that the diffraction conditions are met, then

$$\mathbf{H}_D = (0, d^*, 0)$$

where $d^* = |\mathbf{h}|$

Thus it follows, using rotational transformation matrix, F

$$\mathbf{H}_C^T = d^* \begin{pmatrix} \cos\phi\sin\omega + \sin\phi\cos\chi\cos\omega \\ -\sin\phi\sin\omega + \cos\phi\cos\chi\cos\omega \\ -\sin\chi\cos\omega \end{pmatrix}$$

Since

$$\mathbf{HA}^* = \mathbf{HUA}_C \quad \text{and} \quad \mathbf{HA}^* = \mathbf{H}_C\mathbf{A}_C$$

we have

$$\mathbf{HU} = \mathbf{H}_C$$

Knowing H and U, we can calculate the components of H_C and hence the setting angles by solution of equation $\mathbf{H}_C^T$.

Determination of the orientation matrix

Determination of U from three reflections:
At any value of ω, measurement of χ, φ, and d* for reflection h is a measurement of three independent quantities which may be used in the determination of U.

For three reflections $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$ we have

$$\mathbf{H}_1\mathbf{A}^* = \mathbf{H}_{C_1}\mathbf{A}_C$$

$$\mathbf{H}_2\mathbf{A}^* = \mathbf{H}_{C_2}\mathbf{A}_C$$

$$\mathbf{H}_2\mathbf{A}^* = \mathbf{H}_{C_2}\mathbf{A}_C$$

Let us define the following matrices

$$\mathbf{H}_{\text{Reflection}} = \begin{pmatrix} \mathbf{H}_1 \\ \mathbf{H}_2 \\ \mathbf{H}_3 \end{pmatrix} = \begin{pmatrix} h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \\ h_3 & k_3 & l_3 \end{pmatrix} \quad \text{and} \quad \mathbf{H}_{\text{Specimen}} = \begin{pmatrix} \mathbf{H}_{C_1} \\ \mathbf{H}_{C_2} \\ \mathbf{H}_{C_2} \end{pmatrix} = \begin{pmatrix} x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \\ h_3 & y_3 & z_3 \end{pmatrix}$$

Then

$$\mathbf{H}_{\mathrm{Re}\,flection}\mathbf{A}^{*} = \mathbf{H}_{Specimen}\mathbf{A}_{C}$$

$$\mathbf{A}^{*} = \mathbf{H}^{-1}_{\mathrm{Re}\,flection}\mathbf{H}_{Specimen}\mathbf{A}_{C}$$

But since

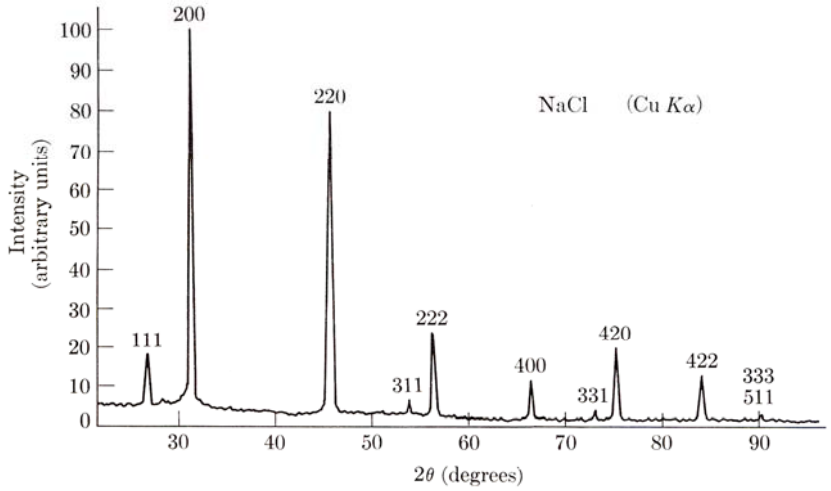
$$\mathbf{A}^{*} = \mathbf{U}\mathbf{A}_{C}$$

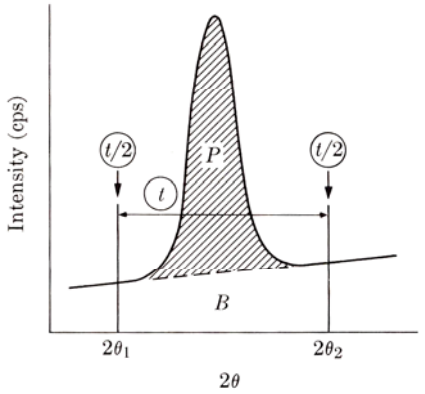
we have

$$\mathbf{U} = \mathbf{H}^{-1}_{\mathrm{Re}\,flection}\mathbf{H}_{Specimen}$$

The matrix $\mathbf{H}_{\mathrm{Specimen}}$ depends only on ω, χ, φ, and d* for three reflections. The matrix $\mathbf{H}_{\mathrm{specimen}}$ depends only on the indices. Hence we may solve for U.

8.3 The Integrated X-ray Intensity of a Diffraction Peak





Integrated intensity: the shade area of the diffraction peak.

1. Direct x-ray beam power: $A_0 I_0$
2. Structure factor
3. the number of family planes
4. Temperature factor
5. X-ray absorption by specimen
6. Lorentz factor (geometric factor)
7. Exposure time to detector
8. Polarization of x-ray

8.3 The Integrated X-ray Intensity of a Diffraction Peak

Diffraction from a small crystal

Small crystal: $N_1N_2N_3$

$$I_P = I_e |F|^2 \frac{\sin^2 N_1 \pi \mathbf{s}\cdot\mathbf{a}}{\sin^2 \pi \mathbf{s}\cdot\mathbf{a}} \frac{\sin^2 N_1 \pi \mathbf{s}\cdot\mathbf{b}}{\sin^2 \pi \mathbf{s}\cdot\mathbf{b}} \frac{\sin^2 N_1 \pi \mathbf{s}\cdot\mathbf{c}}{\sin^2 \pi \mathbf{s}\cdot\mathbf{c}}$$

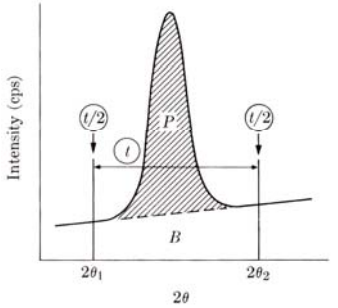
where N_1, N_2, N_3 are the number of unit cell with respect to $\mathbf{a}, \mathbf{b}, \mathbf{c}$.

Ideal diffraction experimental case, the maximum intensity becomes

$$I_{P,\max} = I_e |F|^2 N_1^2 N_2^2 N_3^2$$

Real case, the shape of diffraction peak
- divergence of x-ray beam
- defect of crystal
- misalignment
- other instrumental factor

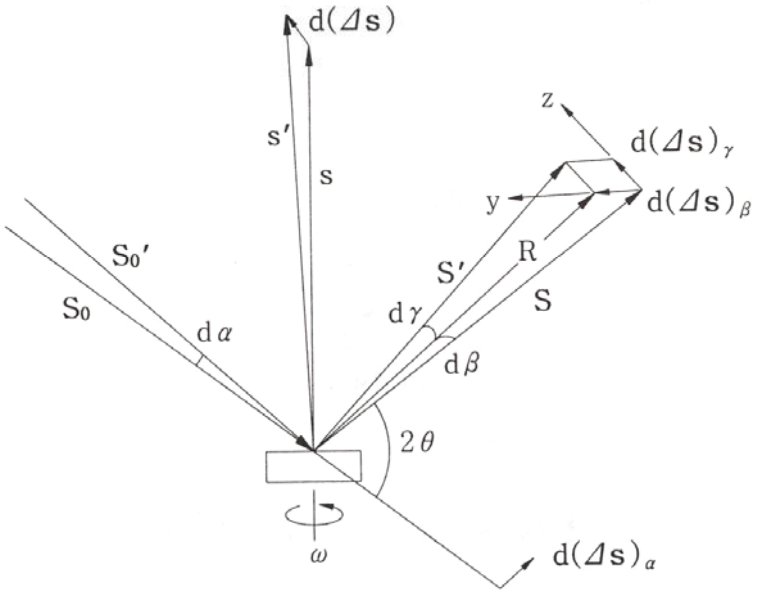
Measure
Integrated intensity



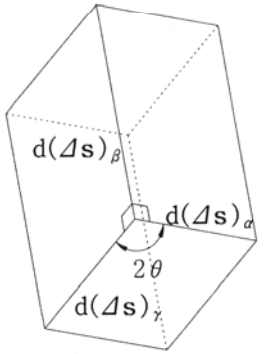
8.3 The Integrated X-ray Intensity of a Diffraction Peak

Integrated intensity for hkl peak

- ω is angular velocity of rotating (hkl), and ω axis is parallel to (hkl)
- reflected x-ray radiates into a solid angle dβdγ for S_0.
- S_0' can be reflected by (hkl) because divergence of incident x-ray beam



【그림 8-37】 작은 결정에서 회절 가능한 각의 범위



【그림 8-38】 d(Δs)가 차지하는 부피

8.3 The Integrated X-ray Intensity of a Diffraction Peak

Integrated intensity of small volume of reciprocal

$$I = \iint I_P dt dA$$

where $dt = d\alpha/\omega$, and detecting area $dA = R^2 d\beta d\gamma$

$$I = \iiint \frac{I_P}{\omega} R^2 d\alpha d\beta d\gamma$$

In order to integrate this equation, let us change dαdβdγ to reciprocal space unit as Δs.

$$\Delta \mathbf{s} = p_1 \mathbf{a}^* + p_2 \mathbf{b}^* + p_3 \mathbf{c}^*$$

where p_1, p_1, p_1 are very small. Then

$$\left|\Delta \mathbf{s}_\alpha\right| = \left|\mathbf{S}_0\right| d\alpha, \quad \left|\Delta \mathbf{s}_\beta\right| = \left|\mathbf{S}\right| d\alpha, \text{ and } \quad \left|\Delta \mathbf{s}_\gamma\right| = \left|\mathbf{S}\right| d\alpha,$$

The volume of the small reciprocal space associated with Δs.

$$\Delta V^* = \Delta \mathbf{s}_\alpha \times \Delta \mathbf{s}_\gamma \cdot \Delta \mathbf{s}_\beta = \frac{\sin 2\theta}{\lambda^3} d\alpha d\beta d\gamma$$

ΔV^* can also be written in reciprocal unit vector

$$\Delta V^* = dp_1 \mathbf{a}^* \times dp_2 \mathbf{b}^* \cdot dp_3 \mathbf{c}^* = \frac{1}{V_{unit\ cell}} dp_1 dp_2 dp_3$$

8.3 The Integrated X-ray Intensity of a Diffraction Peak

therefore

$$\mathrm{d}\alpha\mathrm{d}\beta\mathrm{d}\gamma = \frac{\lambda^3}{V_{unit\ cell}\ sin\,2\theta} dp_1 dp_2 dp_3$$

The intgrated intensity becomes

$$\mathrm{I} = \frac{\mathrm{R}^2}{\omega}\frac{\lambda^3}{V_{unit\ cell}\ sin\,2\theta}\iiint I_p dp_1 dp_2 dp_3$$

The triple integral becomes

$$\iiint I_p dp_1 dp_2 dp_3 = I_e |F|^2 \iiint \frac{sin^2 N_1\pi(\mathbf{s}+\Delta\mathbf{s})\cdot\mathbf{a}}{sin^2 \pi(\mathbf{s}+\Delta\mathbf{s})\cdot\mathbf{a}}$$

$$\times \frac{sin^2 N_2\pi(\mathbf{s}+\Delta\mathbf{s})\cdot\mathbf{b}}{sin^2 \pi(\mathbf{s}+\Delta\mathbf{s})\cdot\mathbf{b}} \frac{sin^2 N_3\pi(\mathbf{s}+\Delta\mathbf{s})\cdot\mathbf{c}}{sin^2 \pi(\mathbf{s}+\Delta\mathbf{s})\cdot\mathbf{c}} dp_1 dp_2 dp_3$$

$$= I_e |F|^2 \iiint \frac{sin^2 N_1\pi p_1}{sin^2 \pi p_1} \frac{sin^2 N_2\pi p_2}{sin^2 \pi p_2} \frac{sin^2 N_3\pi p_3}{sin^2 \pi p_3} dp_1 dp_2 dp_3$$

Since the above equation exist only vicinity of Bragg peak, p_1, p_2, p_3 are very small values. Hence $\sin\pi p_1 \approx \pi p_1$.

8.3 The Integrated X-ray Intensity of a Diffraction Peak

With this approximatin and using the result of integral from integration table;

$$\int_{-\infty}^{\infty} \frac{\sin^2 Nx}{x^2} = N$$

We have

$$\mathrm{I} = \frac{I_e R^2 \lambda^3 |F|^2}{\omega V_{unit\ cell} \sin 2\theta} N_1 N_2 N_3$$

Let us change $N_1N_2N_3$ to more practical parameters. If the volume of small crystal δV, $\delta V = V_{unit\ cell} N_1 N_2 N_3$.

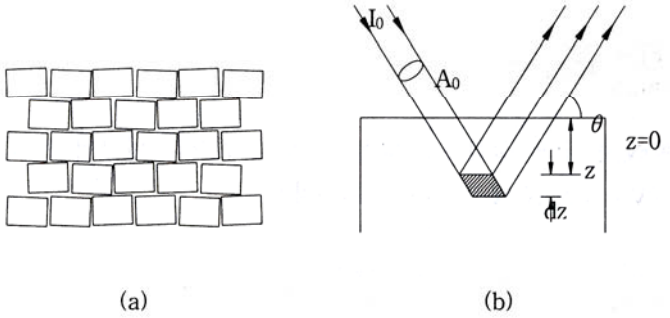
$$\mathrm{I} = \frac{I_0}{\omega} \frac{e^4}{4\pi\varepsilon_0 m_e^2 c^4} |F|^2 \lambda^3 \frac{\delta V}{V_{unit\ cell}} \left(\frac{1+\cos^2 2\theta}{2} \right) \left(\frac{1}{\sin 2\theta} \right)$$

(1/sin2θ) is called Lorentz factor which was driven from geometry of diffractometer. Lorentz-polarization factor is the combination of Lorentz factor and polarization factor.

8.3 The Integrated X-ray Intensity of a Diffraction Peak

Diffraction from mosaic crystal

A crystal with mosaic structure does not have its atoms arranged on a perfectly regular lattice extending from one side of crystal to the other; instead, the lattice is broken up into a number of tiny small crystal, each slightly disoriented one from another. The size of these crystal is order of 100nm, while the maximum angle of disorientation between them may vary from a very small value to as much as one degree, depending on the crystal.



【그림 8-39】 (a) 단결정의 모자이크 구조와 (b) X-선이 결정 내부의 dz에서 회절되는 모양

Integrated intensity from mosaic crystal can be calculated with help of the figure;

$$I = \frac{I_0}{\omega}\frac{e^4}{4\pi\varepsilon_0 m_e^2 c^4}|F|^2\lambda^3\frac{\delta V}{V_{unit\ cell}^2}\left(\frac{1+\cos^2 2\theta}{2\sin 2\theta}\right)\int_{z=0}^{\infty} e^{-2\mu z/\sin\theta}\frac{A_0 dz}{\delta V}$$

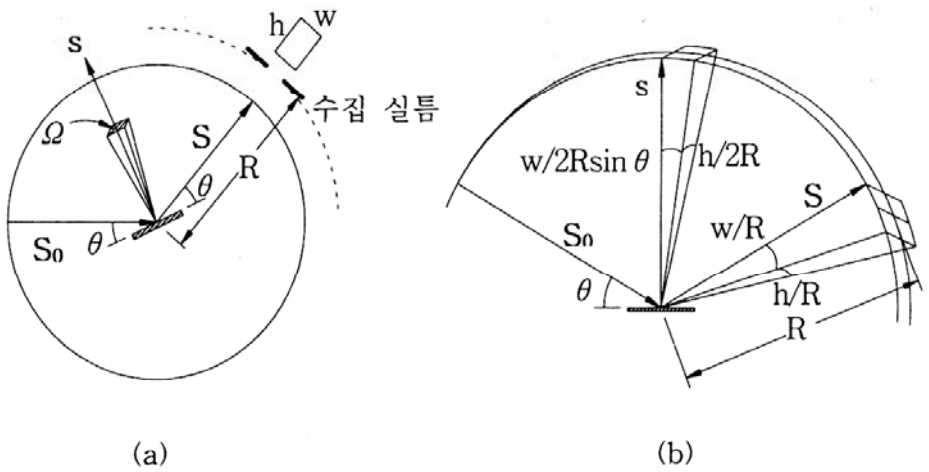
$$= \frac{I_0 A_0}{\omega}\frac{e^4}{4\pi\varepsilon_0 m_e^2 c^4}\frac{|F|^2\lambda^3}{2\mu V_{unit\ cell}^2}\left(\frac{1+\cos^2 2\theta}{2\sin 2\theta}\right)$$

where A_0 is cross sectional area of incident beam,

μ is linear absorption coefficient of mosaic crystal.

8.3 The Integrated X-ray Intensity of a Diffraction Peak

Diffraction from polycrystal



【그림 8-40】 회절기의 수집 실틈의 크기가 h×w 일 때 이에 해당하는 회절 벡터의 입체각

If the reflected intensity is measured by the receiving slit of which size is (h x w), solid angle, Ω along scattering vector corresponding to slit size becomes

$$\Omega = \frac{hw}{4R^2 \sin\theta}$$

8.3 The Integrated X-ray Intensity of a Diffraction Peak

When the number of grains (mosaic crystals) irradiated by x-ray is N, the probability of (hkl) reflection solid angle, Ω may be $(\Omega/4\pi)m_{hkl}$. Intensity reflected from (hkl) becomes

$$I = I_{mosaic}\left(\frac{\Omega}{4\pi}\right)m_{hkl} = I_{mosaic}\left(\frac{hw}{4R^2\sin\theta}\right)\left(\frac{1}{4\pi}\right)m_{hkl}$$

$$= \frac{I_0 A_0}{\omega}\frac{e^4}{4\pi\varepsilon_0 m_e^2 c^4}\frac{|F|^2\lambda^3}{\mu V_{unit\ cell}^2}\frac{m_{hkl}}{64\pi R^2}\left(\frac{1+\cos^2 2\theta}{\sin\theta\sin 2\theta}\right)$$

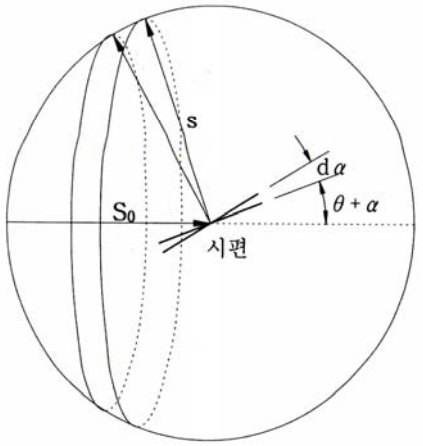
8.3 The Integrated X-ray Intensity of a Diffraction Peak

Diffraction from powder sample

The number of powder which is diffracted because of angular divergence of incident x-ray

$$dN = \frac{Nm_{hkl} 2\pi R^2 \cos(\theta + \alpha) d\alpha}{4\pi A R^2}$$

$$\approx \frac{Nm_{hkl}}{2} \cos\theta d\alpha \qquad \text{for small } \alpha$$



【그림 8-41】 $\theta+\alpha$와 $\theta+\alpha+d\alpha$ 사이의 방위를 갖는 결정면

Irradiated area of reflected beam may be written by angular divergence dβdγ;

$$dA = R^2 d\beta d\gamma$$

Integrated intensity reflected by (hkl) becomes

$$I = \iiint I_P \frac{Nm_{hkl}}{2} R^2 \cos\theta d\alpha d\beta d\gamma$$

8.3 The Integrated X-ray Intensity of a Diffraction Peak

When the reflected x-ray is detected using the size of (h x w) receiving slit,

$$I = \iiint I_P \frac{N m_{hkl}}{2} R^2 \cos\theta \frac{h}{2\pi R 2\sin 2\theta} d\alpha d\beta d\gamma$$

Comparing the other equations

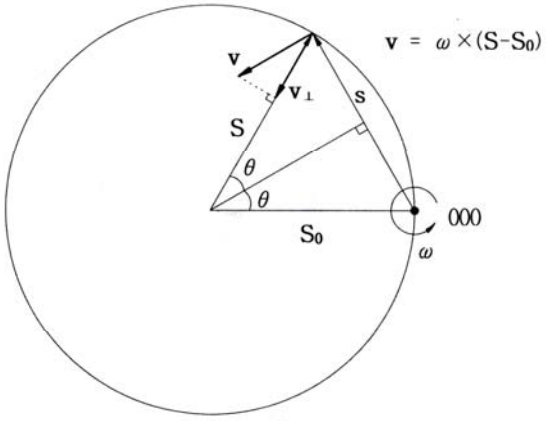
$$I = \frac{I_0 A_0}{16\pi R} \frac{e^4}{4\pi\varepsilon_0 m_e^2 c^4} \frac{|F|^2 \lambda^3 m_{hkl} h}{2\mu V_{unit\ cell}^2} \left(\frac{1+\cos^2 2\theta}{\sin\theta \sin 2\theta} \right)$$

where $(1/\sin\theta \sin 2\theta)$ is Lorentz factor for powder diffraction.

8.3 The Integrated X-ray Intensity of a Diffraction Peak

Lorentz factor

Lorentz factor is related to the time it takes a point in the reciprocal to move through the Ewald sphere.



【그림 8-42】 회전하는 작은 결정에 의해 회절 벡터와 Ewald 구가 만나는 모양

If a crystal is rotating at angular velocity ω about 000, the velocity of diffracting point is ω|S-S0|, and the component of velocity normal to the sphere ($v_\perp$), is ω|S-S0|cosθ

The time (t) for a point to pass through
The reflecting position is proportional to 1/ $v_\perp$.

$$t = \frac{1}{v_\perp} = \frac{1}{\omega|S - S_0|\cos\theta} = \frac{1}{\omega 2\sin\theta\cos\theta}$$

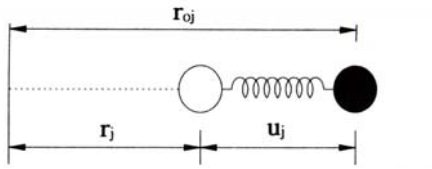
$$= \frac{1}{\omega\sin 2\theta} = \frac{L}{\omega}$$

$$where \;\; L = 1/\sin 2\theta; \;\; Lorentz \;\; facor$$

8.3 The Integrated X-ray Intensity of a Diffraction Peak

Effect of temperature

Assume that atomic bonding motion is harmonic oscillator. The structure factor of the crystal becomes



【그림 8-43】 온도에 의한 원자의 조화운동

$$F(s)=\sum_{j=1}^{N} f_j e^{2\pi i\mathbf{s}\cdot\mathbf{r}_j}=\sum_{j=1}^{N} f_j e^{2\pi i\mathbf{s}\cdot(\mathbf{r}_{0,j}+\mathbf{u}_j)}=\sum_{j=1}^{N} f_j e^{2\pi i\mathbf{s}\cdot\mathbf{r}_{0,j}} e^{2\pi i\mathbf{s}\cdot\mathbf{u}_j}$$

Since u_j changes with temperature, and is small values, the exponential term of u_j can be approximated

$$e^{2\pi i\mathbf{s}\cdot\mathbf{u}_j}=1+2\pi i\mathbf{s}\cdot\mathbf{u}_j-2\pi^2(\mathbf{s}\cdot\mathbf{u}_j)^2+\ldots$$

Time average of this equation becomes

$$e^{\overline{2\pi i\mathbf{s}\cdot\mathbf{u}_j}}=1-2\pi^2\overline{(\mathbf{s}\cdot\mathbf{u}_j)^2}+\frac{2\pi^4}{3}\overline{(\mathbf{s}\cdot\mathbf{u}_j)^4}-\ldots$$

$$\approx e^{-2\pi^2\overline{(\mathbf{s}\cdot\mathbf{u}_j)^2}}$$

If u_j does not have directionality, then we have

$$\overline{(\mathbf{s}\cdot\mathbf{u}_j)^2}=\overline{s^2u_j^2\cos\phi}=\frac{1}{3}\overline{s^2u_j^2}$$

8.3 The Integrated X-ray Intensity of a Diffraction Peak

If u_j does not have directionality, then we have

$$\overline{(\mathbf{s}\cdot\mathbf{u}_j)^2} = \overline{s^2u_j^2\cos\phi} = \frac{1}{3}\overline{s^2u_j^2}$$

Therefore, the time average structure factor affecting temperature can be written

$$\overline{f}_{j,T} = f_j e^{\overline{2\pi i\mathbf{s}\cdot\mathbf{u}_j}} = f_j e^{-\frac{2\pi^2}{3}\overline{(s^2u_j^2)}} = f_j e^{-\frac{8\pi^2}{3}\frac{\sin^2\theta}{\lambda^2}\overline{u_j^2}}$$

$$= f_j e^{-8\pi^2\frac{\sin^2\theta}{\lambda^2}\overline{u_{j,s}^2}} = f_j e^{-B_j\frac{\sin^2\theta}{\lambda^2}}$$

where $B_j = 8\pi^2\overline{u_{j,s}^2}$ (temperature factor),

and $u_{j,s}$ the component of $u_{j,s}$ along $\mathbf{s}$ direction

Since the diffraction peak intensity is proportional to the square of structure factor, thermal motion of atom reduces the diffraction intensity by a factor of

$e^{-\left(2B\sin^2\theta/\lambda^2\right)}$ *Debye-Waller factor*

8.3 The Integrated X-ray Intensity of a Diffraction Peak

Debye developed the temperature factor, B as follows;

$$B = \frac{6h^2}{mk_B\Theta}\left\{\frac{\phi(x)}{x} + \frac{1}{4}\right\}$$

where h is Plank constant, K_B Boltzmann constant, m mass of atom,

Θ Debye temperture of atom, and $x = \Theta/T$. And $\phi(x)$ is given by

$$\phi(x) = \frac{1}{x}\int_0^x \frac{\xi}{e^{\xi} - 1} d\xi$$

8. Experimental X-ray Diffraction Procedures

Homework

Due date: April 21, 2008

Solve the problems; 8.1, 8.4

If possible, please solve 8.7 (Extra points)