X-ray Diffraction (XRD)

Q's

- Why do we (have to) use XRD?
- What is XRD? What is X-ray diffractometer?
- How to collect raw data of XRD?
- What kind of information can we get from XRD pattern?
- What kind of information can we get from θ-2θ XRD pattern? How?
- How can we get more accurate/precise results?

Elemental analysis vs. Phase analysis

- Elemental analysis
  - ✓ Optical spectroscopy
    - Probes the outer electronic structure of atoms
      - – Optical emission (e.g. ICP OES*)
      - – Atomic absorption spectrometry (AAS)
  - ✓ X-ray fluorescence spectroscopy (XRF)
    - Probes the inner electronic structure of atoms
- Phase analysis
  - ✓ X-ray diffraction (XRD)

- Qualitative analysis
- Quantitative analysis

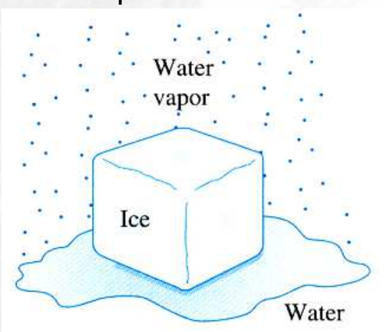
- Qualitative elemental analysis
- Quantitative elemental analysis
- Qualitative phase analysis
- Quantitative phase analysis

* inductively coupled plasma optical emission spectrometry

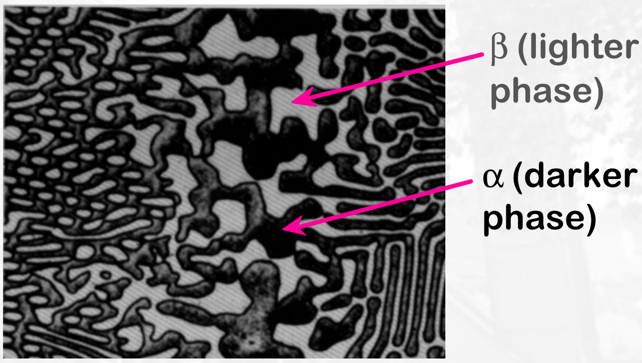
Phase

- a region of material that is chemically uniform, physically distinct, and (often) mechanically separable
- a chemically and structurally homogeneous region of material
- a physically and chemically distinct material region

1 component
3 phases

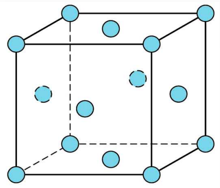


Aluminum-Copper Alloy

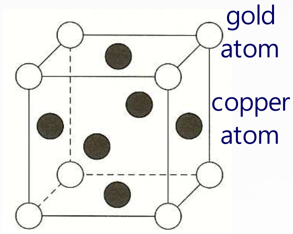


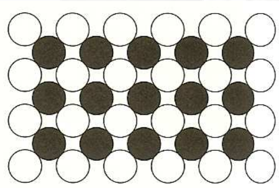
Examples

Crystal structure of Au & Cu



Crystal structure of $AuCu_3$





Portable XRF

Au, Cu

Au 30%, Cu 70%

Au, Cu

Au, $AuCu_3$

Cu, $AuCu_3$

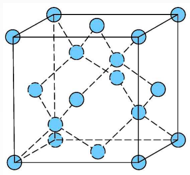
Au, Cu, $AuCu_3$

↑

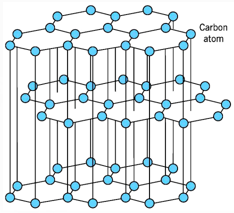
X-Ray Diffraction (XRD)

Structure of carbon

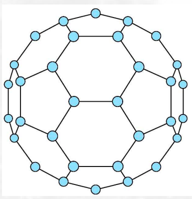
- Diamond (Si, Ge)



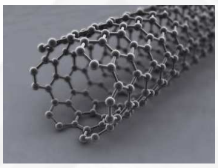
- Graphite (BN)



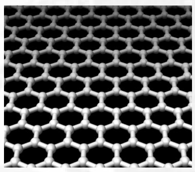
- Fullerene (buckyball)



- Carbon Nanotube



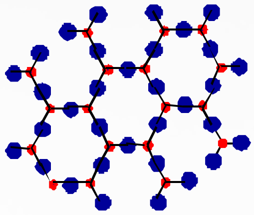
- Graphene



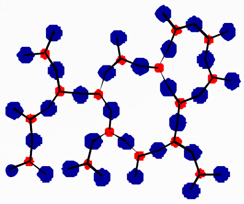
elemental analysis → carbon

phase analysis → diamond, graphite, CNT, graphene

Structure of SiO_2



crystalline SiO_2
quartz



noncrystalline SiO_2
fused silica

elemental analysis → Si & O

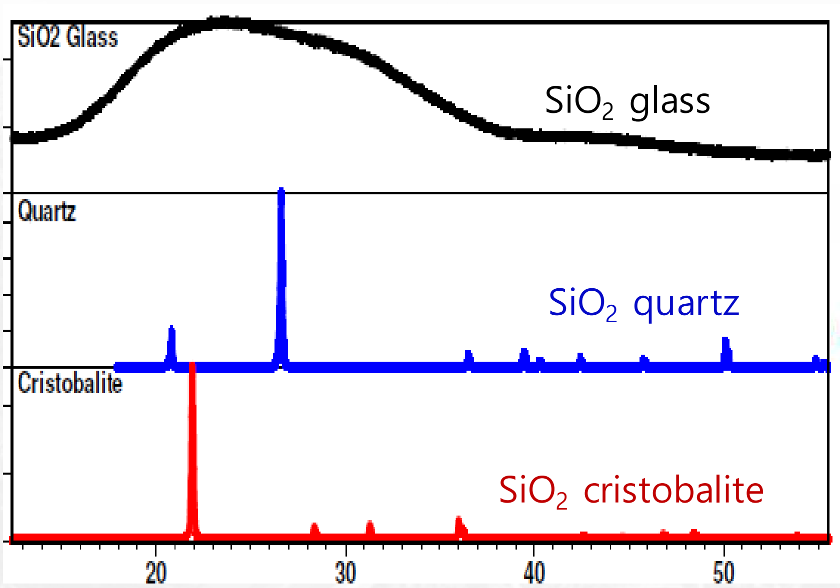
phase analysis → quartz, fused silica

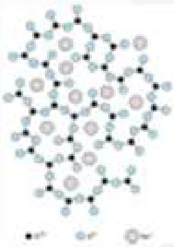
concentricusllc.com/event/crystalmining/2019-10-12/

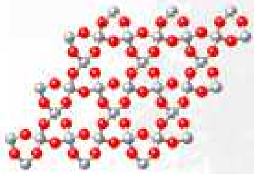
www.corning.com/kr/ko/products/advanced-optics/product-materials/semiconductor-laser-optic-components/high-purity-fused-silica.html

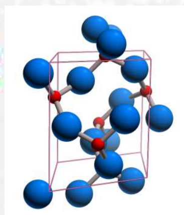
XRD Pattern vs Crystal Structure

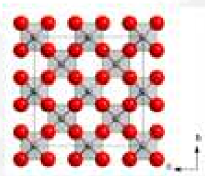
crystalline vs. non-crystalline (amorphous)

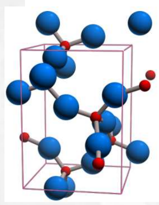






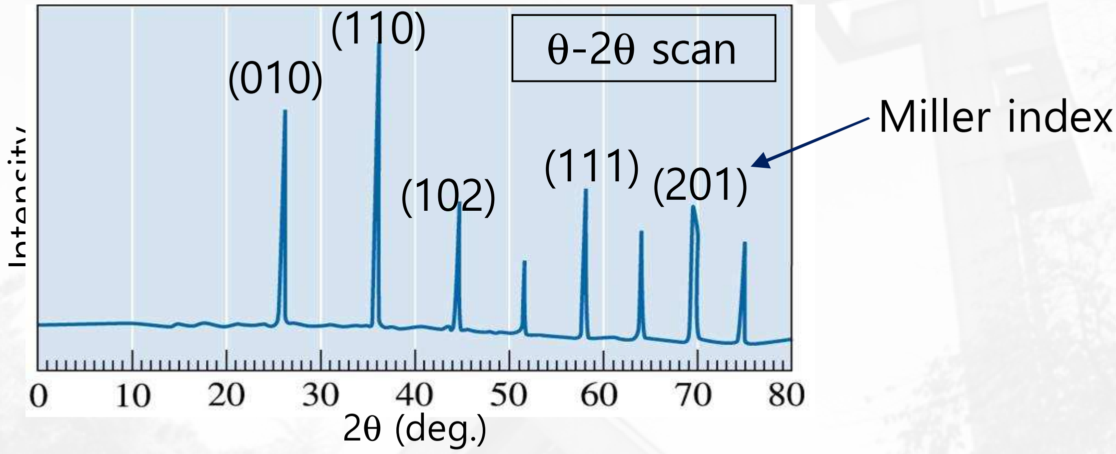


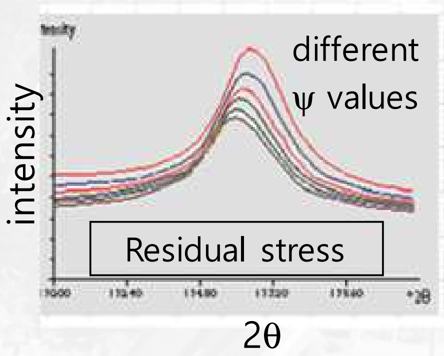


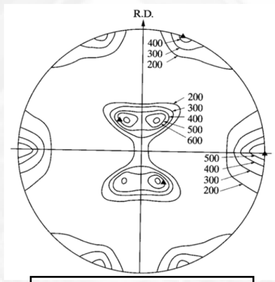


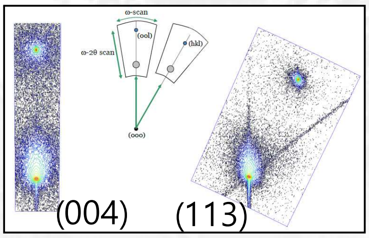
Scott Speakman

XRD Patterns





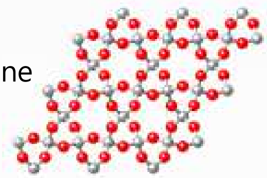


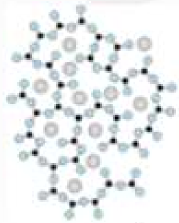


Crystal, Unit Cell, Crystal System, Lattice Parameter

- Crystal ; long-range, 3-dimensional, orderly periodic arrangements of atoms

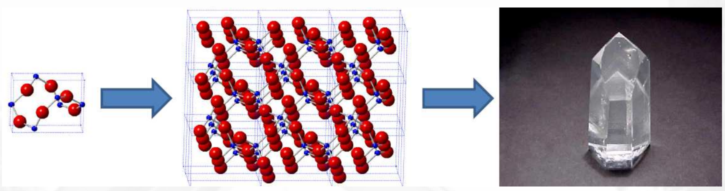
Crystalline solid



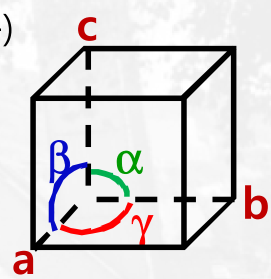


Non-crystalline solid

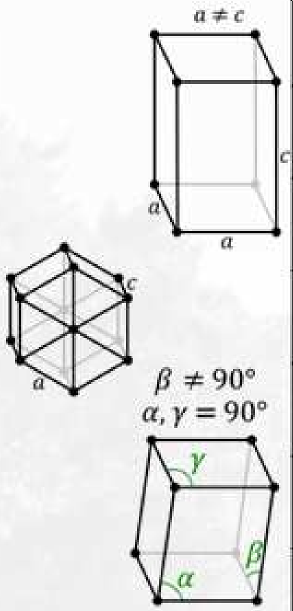
- Unit cell ; basic repeating unit that defines the crystal structure



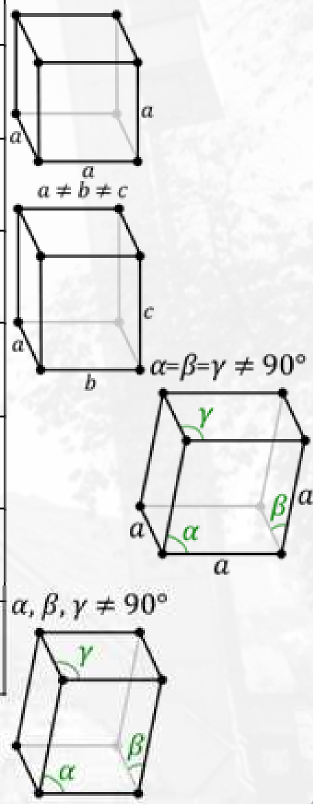
- **shape** of unit cell ← crystal system (cubic, tetragonal, ---)
- **size** of unit cell ← lattice parameter (a, b, c, α, β, γ)



Shape of Unit Cell ← 7 Crystal Systems



Crystal System	Axis System
Cubic	a=b=c, α=β=γ=90
Tetragonal	a=b≠c, α=β=γ=90
Orthorhombic	a≠b≠c, α=β=γ=90
Hexagonal	a=b≠c, α=β=90, γ=120
Rhombohedral	a=b=c, α=β=γ≠90
Monoclinic	a≠b≠c, α=γ=90, β≠90
Triclinic	a≠b≠c, α≠β≠γ≠90

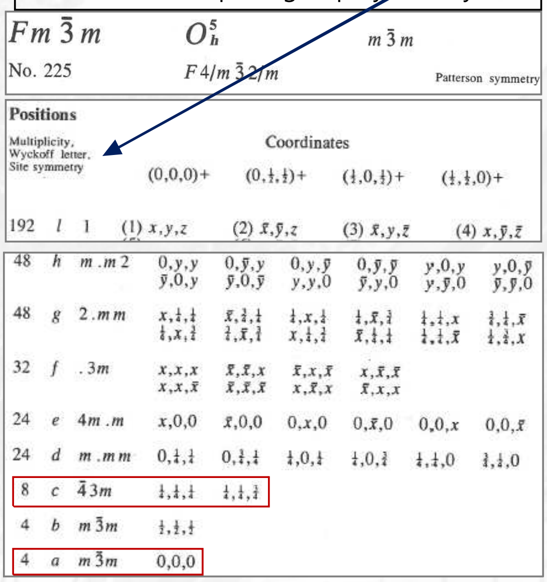


Crystal Structure of "cubic ZrO_2"

- **Space Group Fm$\bar{3}$m (225)**
  - **→ cubic**
- **Lattice Parameter a=5.11Å**

Atom	Wyckoff Site	x	y	z	B_{iso}	occupancy
Zr	4a	0	0	0	1.14	1
O	8c	0.25	0.25	0.25	2.4	1

International Tables for Crystallography, Volume A: Space-group symmetry


$Fm\bar{3}m$ O_h^5 $m\bar{3}m$
No. 225 $F4/m\,\bar{3}\,2/m$ Patterson symmetry

Positions
Multiplicity, Wyckoff letter, Site symmetry — Coordinates
(0,0,0)+ (0,½,½)+ (½,0,½)+ (½,½,0)+

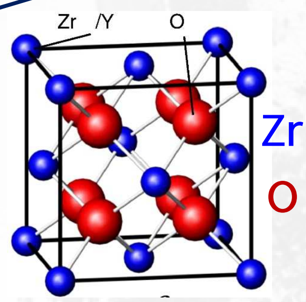
192 l 1 (1) x,y,z (2) x̄,ȳ,z (3) x̄,y,z̄ (4) x,ȳ,z̄

Mult.	Letter	Site symmetry	Coordinates					
48	h	m.m2	0,y,y / ȳ,0,y	0,ȳ,y / ȳ,0,ȳ	0,y,ȳ / y,y,0	0,ȳ,ȳ / ȳ,y,0	y,0,y / y,ȳ,0	y,0,ȳ / ȳ,ȳ,0
48	g	2.mm	x,¼,¼ / ¼,x,¼	x̄,¾,¼ / ¼,x̄,¾	¼,x,¼ / x,¼,¾	¼,x̄,¾ / x̄,¼,¼	¼,¼,x / ¼,¼,x̄	¼,¾,x̄ / ¾,¼,x
32	f	.3m	x,x,x / x,x,x̄	x̄,x̄,x / x̄,x̄,x̄	x̄,x,x̄ / x,x̄,x	x,x̄,x̄ / x̄,x,x		
24	e	4m.m	x,0,0	x̄,0,0	0,x,0	0,x̄,0	0,0,x	0,0,x̄
24	d	m.mm	0,¼,¼	0,¾,¼	¼,0,¼	¼,0,¾	¼,¼,0	¾,¼,0
8	c	$\bar{4}$3m	¼,¼,¼	¼,¼,¾				
4	b	m$\bar{3}$m	½,½,½					
4	a	m$\bar{3}$m	0,0,0					

Temperature factor
B_{iso} U_{iso} B_{ij} U_{ij} β_{ij}

$$f = f_0 \exp\left[-\frac{B\sin^2\theta}{\lambda^2}\right]$$

$$B = 8\pi^2 U^2$$



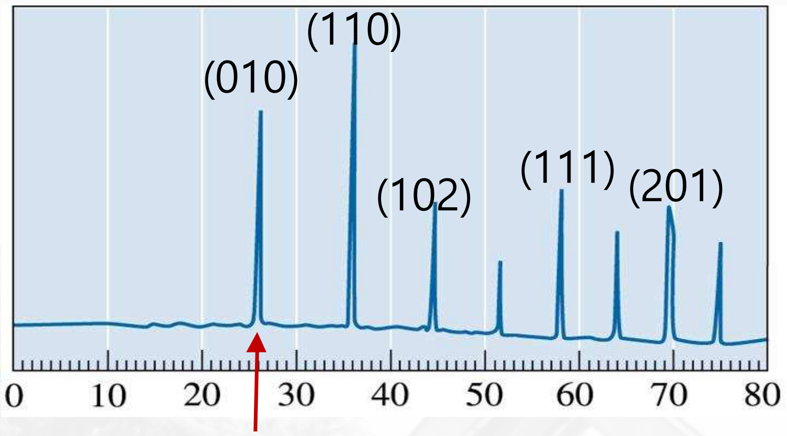
- Site occupancy = 1; every equivalent position of that site is occupied by that atom
- Site occupancy < 1; some of the sites are vacant
  - Site occupancy = 0.5; half of that site is occupied by the atom
- two atoms occupying the same site will each have a fractional site occupancy

Fake diamond

- Cubic zirconia (ZrO_2) - 8.5 on Mohs scale
- Moissanite (SiC) - 9.5 on Mohs scale, one of the best substitutes for diamond
- White sapphires (Al_2O_3) - 9 on Mohs scale
- Rutile (TiO_2) – 6 on Mohs scale
- White spinels - 8 on Mohs scale
- YAG (yttrium aluminium garnet), GGG (gadolinium gallium garnet) - 8 on Mohs scale
- Glass

Handheld XRF
X-ray fluorescence

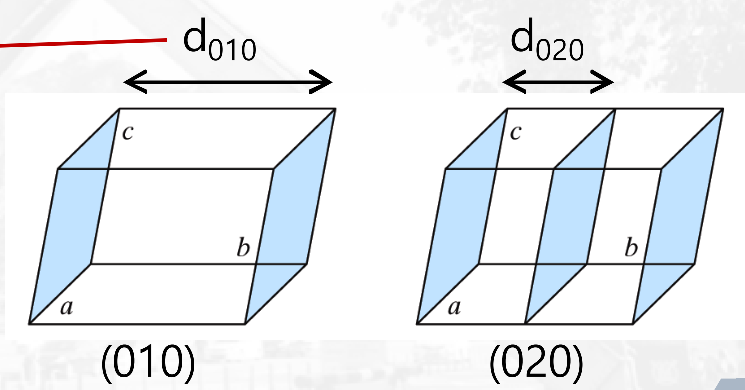
XRD Pattern vs Miller Index



- indexing

Peak position

d_{hkl}
Interplanar spacing
(면간 거리)



Interplanar Spacing (면간 거리) (d_{hkl})

	결정축계	$\frac{1}{d_{hkl}^2}$
Cubic	입 방	$\frac{1}{a^2}(h^2+k^2+l^2)$
tetragonal	정 방	$\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}$
orthorhombic	사 방	$\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}$
hexagonal	육 방	$\frac{4}{3a^2}(h^2+hk+k^2)+\frac{l^2}{c^2}$
rhombohedral	능 면	$\frac{1}{a^2}\frac{(h^2+k^2+l^2)\sin^2\alpha+2(hk+kl+lh)(\cos^2\alpha-\cos\alpha)}{1+2\cos^2\alpha-3\cos^2\alpha}$
monoclinic	단 사	$\frac{\frac{h^2}{a^2}+\frac{k^2}{b^2}-\frac{2kh\cos\gamma}{ab}}{\sin^2\gamma}+\frac{l^2}{c^2}$ (first setting)
		$\frac{\frac{h^2}{a^2}+\frac{l^2}{c^2}-\frac{2hl\cos\beta}{ac}}{\sin^2\beta}+\frac{k^2}{b^2}$ (second setting)
triclinic	삼 사	$\frac{\frac{h^2}{a^2}\sin^2\alpha+\frac{k^2}{b^2}\sin^2\beta+\frac{l^2}{c^2}\sin^2\gamma+\frac{2hk}{ab}(\cos\alpha\cos\beta-\cos\gamma)+\frac{2kl}{bc}(\cos\beta\cos\gamma-\cos\alpha)+\frac{2lh}{ca}(\cos\gamma\cos\alpha-\cos\beta)}{1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma}$

$$\frac{1}{d_{hkl}^2}$$

$$\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}$$

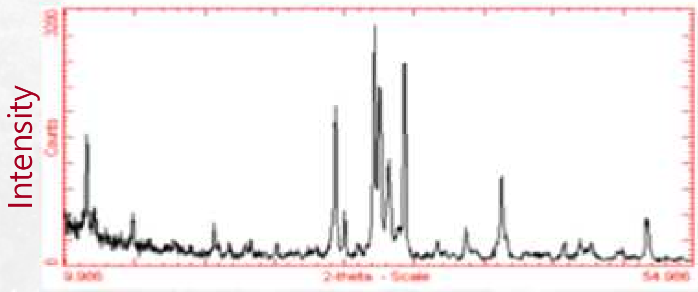
XRD-1
X-ray

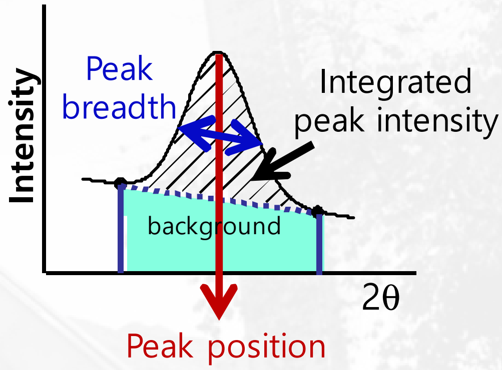
Read

Cullity Chapter 1-1~1-6

Periodic array causes ---

- Periodic array of **electrons** scatter **X-ray**
- Periodic array of **nuclei** scatter **neutron**
- Periodic array of scattering sites → specific directions of constructive interference

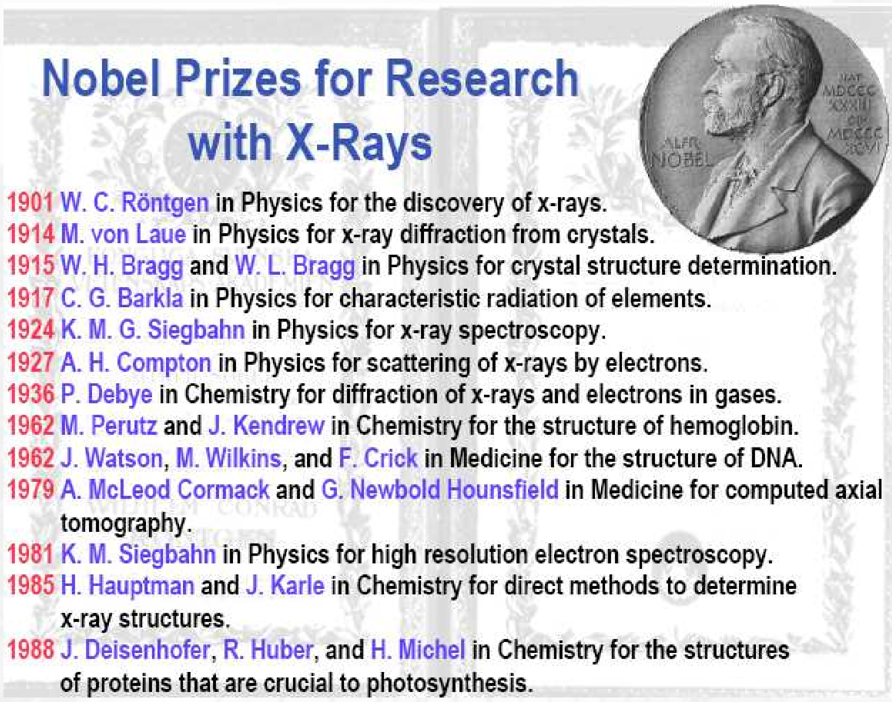




- Positions, intensities, shapes
  → crystal structure, physical state, etc.

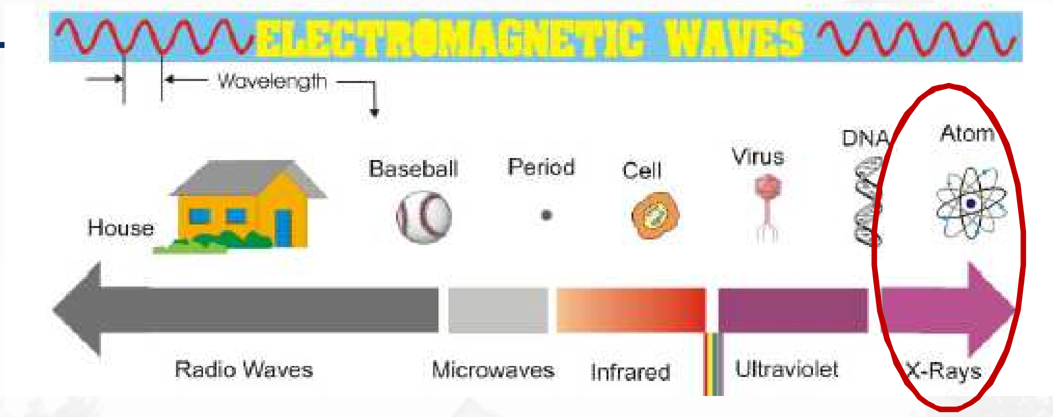
X-ray

- Wilhelm Conrad Röntgen discovered X-ray in 1895 (Wurzburg).
  - ✓ In 1901, he was honoured by the Noble prize for physics.
  - ✓ In 1995, German Post edited a stamp, dedicated to W.C. Röntgen.



Nobel Prizes for Research with X-Rays

1901 W. C. Röntgen in Physics for the discovery of x-rays.
1914 M. von Laue in Physics for x-ray diffraction from crystals.
1915 W. H. Bragg and W. L. Bragg in Physics for crystal structure determination.
1917 C. G. Barkla in Physics for characteristic radiation of elements.
1924 K. M. G. Siegbahn in Physics for x-ray spectroscopy.
1927 A. H. Compton in Physics for scattering of x-rays by electrons.
1936 P. Debye in Chemistry for diffraction of x-rays and electrons in gases.
1962 M. Perutz and J. Kendrew in Chemistry for the structure of hemoglobin.
1962 J. Watson, M. Wilkins, and F. Crick in Medicine for the structure of DNA.
1979 A. McLeod Cormack and G. Newbold Hounsfield in Medicine for computed axial tomography.
1981 K. M. Siegbahn in Physics for high resolution electron spectroscopy.
1985 H. Hauptman and J. Karle in Chemistry for direct methods to determine x-ray structures.
1988 J. Deisenhofer, R. Huber, and H. Michel in Chemistry for the structures of proteins that are crucial to photosynthesis.



- It is not always necessary to understand something in order to use it.
- Radiography

Diffraction – 1912 (Munchen)
Max v. Laue
hydrated copper sulfate
$CuSO_4 \bullet 5H_2O$

X-ray

- Electromagnetic wave; wavelength 0.3Å ~3 Å
- Detection
  - ✓ Photographic
  - ✓ Fluorescent (e.g. on ZnS, CdS, NaI, etc.)
  - ✓ Ionizing
- **Wavelength (0.3Å ~3 Å)~ atomic distance → can get info on the arrangement of atoms within the crystal by diffraction**
- Critical angle for total reflection ~ 1/6 to ½ degree
- Transmission → medical, nondestructive evaluation (NDE)

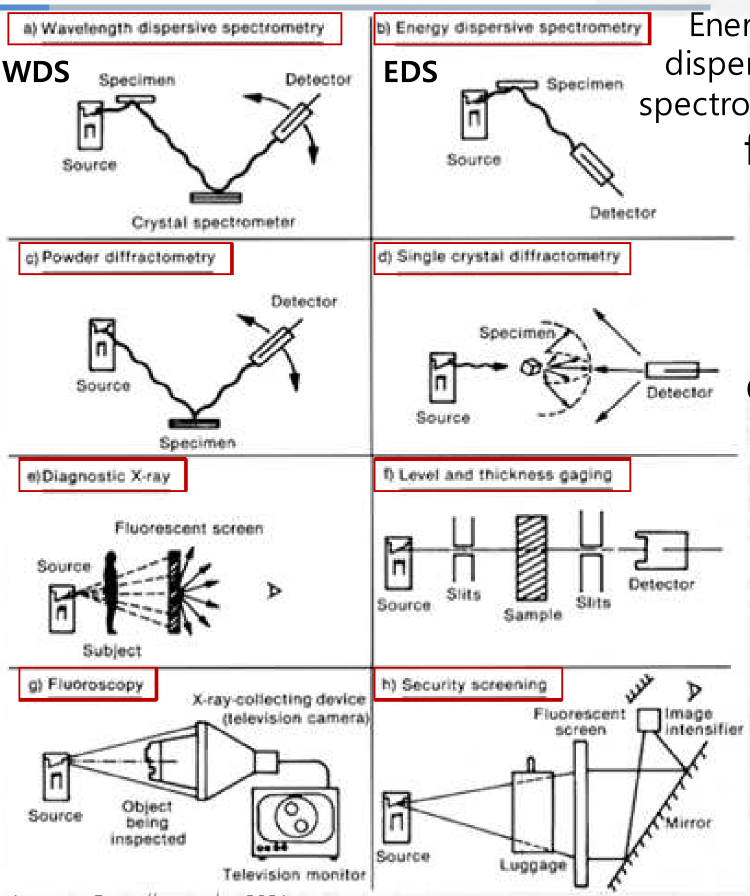
Generation
Detection

X-ray is used in ___

Wavelength dispersive spectrometry **WDS**

EDS Energy dispersive spectrometry

fluorescence

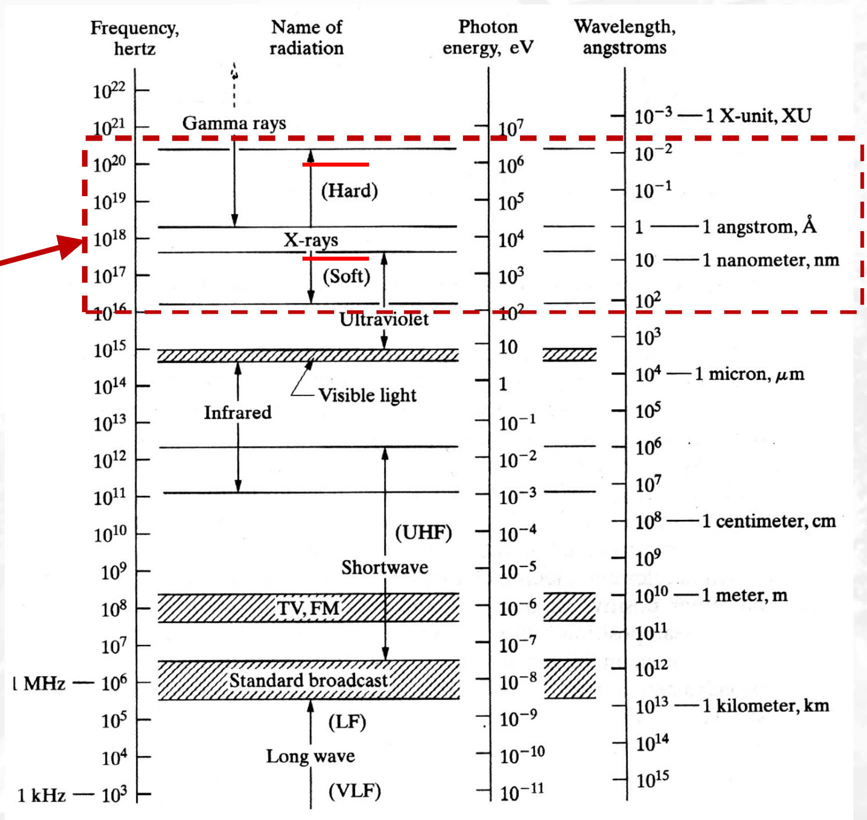


diffraction

absorption

Electromagnetic spectrum

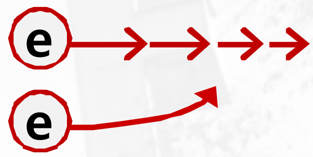
Wavelength ≈ Object Size ≈ Angstroms for Condensed Matter Research



Cullity page 3

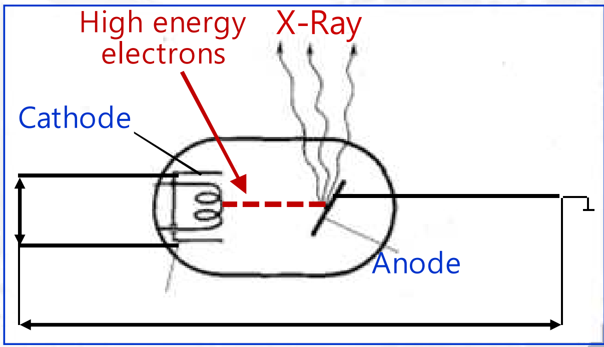
Generation of X-rays

- X-rays are produced <u>when any electrically charged particle of sufficient kinetic energy rapidly decelerates</u>
  - ✓ change of speed of matter
  - ✓ change of direction of movement



- Bombardment of a target by electrons
- Anode (Cu, Mo, W, Ag ..), Cathode (W, LaB_6)
- 10^{-3} ~ 10^{-4} Torr chamber, high voltage (10 ~ 50kV)

Sealed X-ray tube



Origin of X-rays

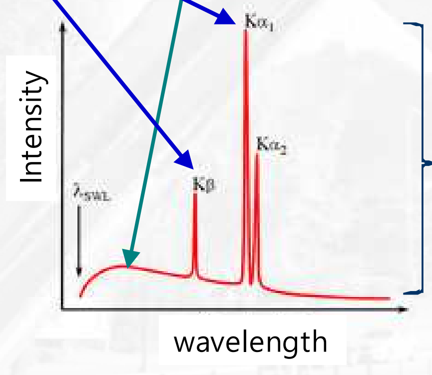
Loss of energy of electrons caused by

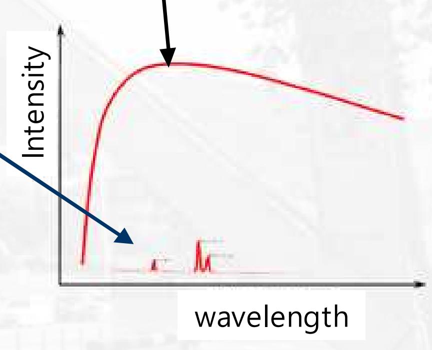
- atomic transitions → Characteristic radiation → emission of spectrum lines
- deceleration → Continuous radiation / White radiation / Bremsstrahlung
- direction change → Synchrotron radiation

Sealed X-ray tube

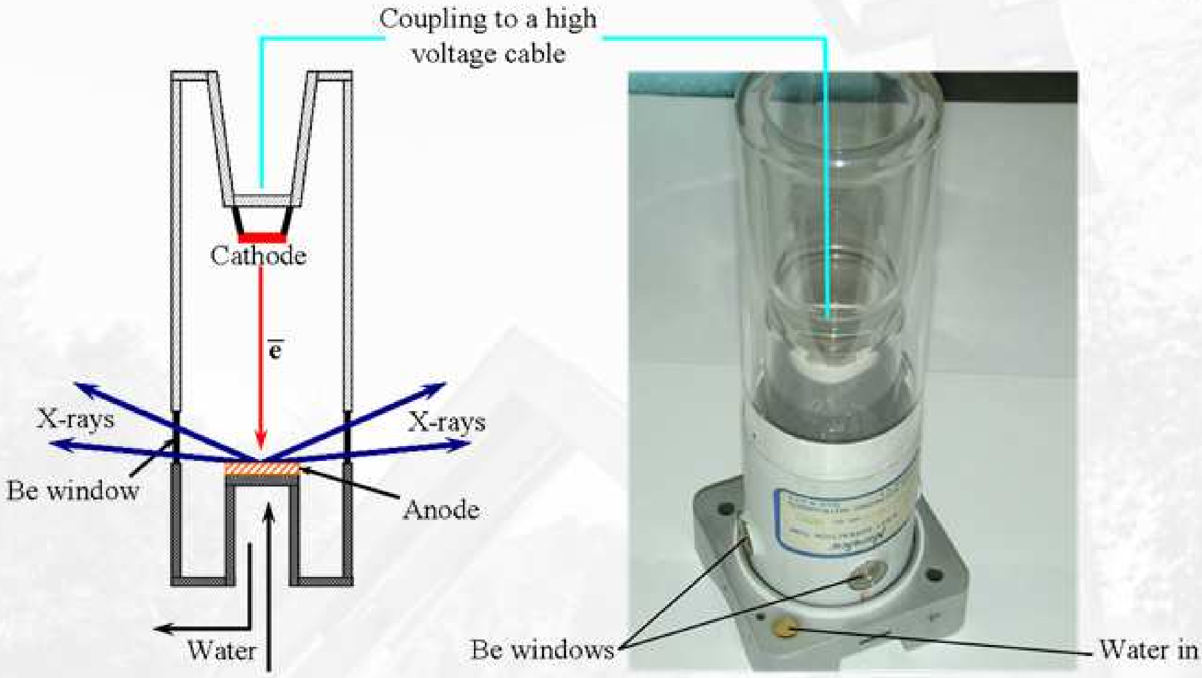
Rotating anode tube

Synchrotron





Sealed X-ray tube

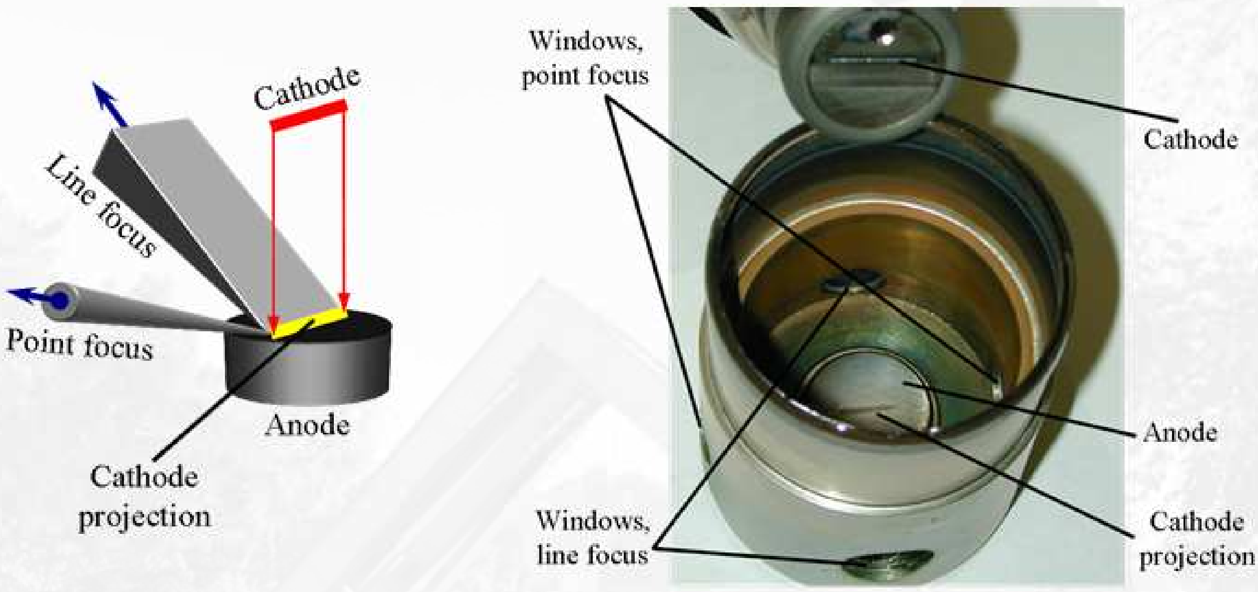


Overall efficiency very low
← heat

Most of the kinetic energy striking the target is converted into heat → < 1% is transformed into X-ray

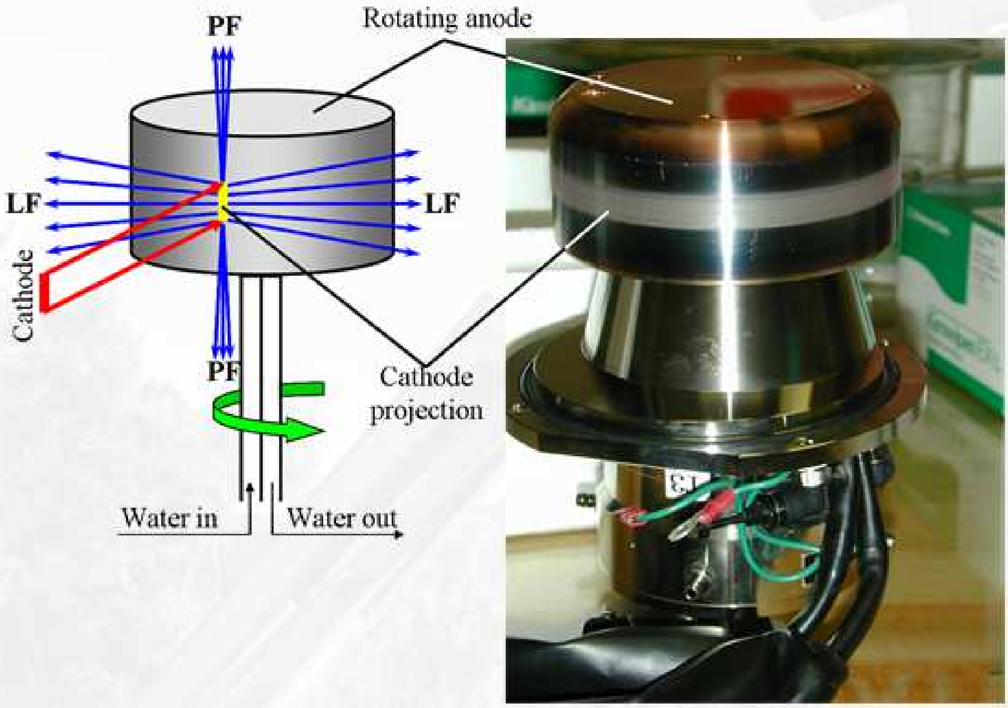
Pecharsky

Line focus, Point focus

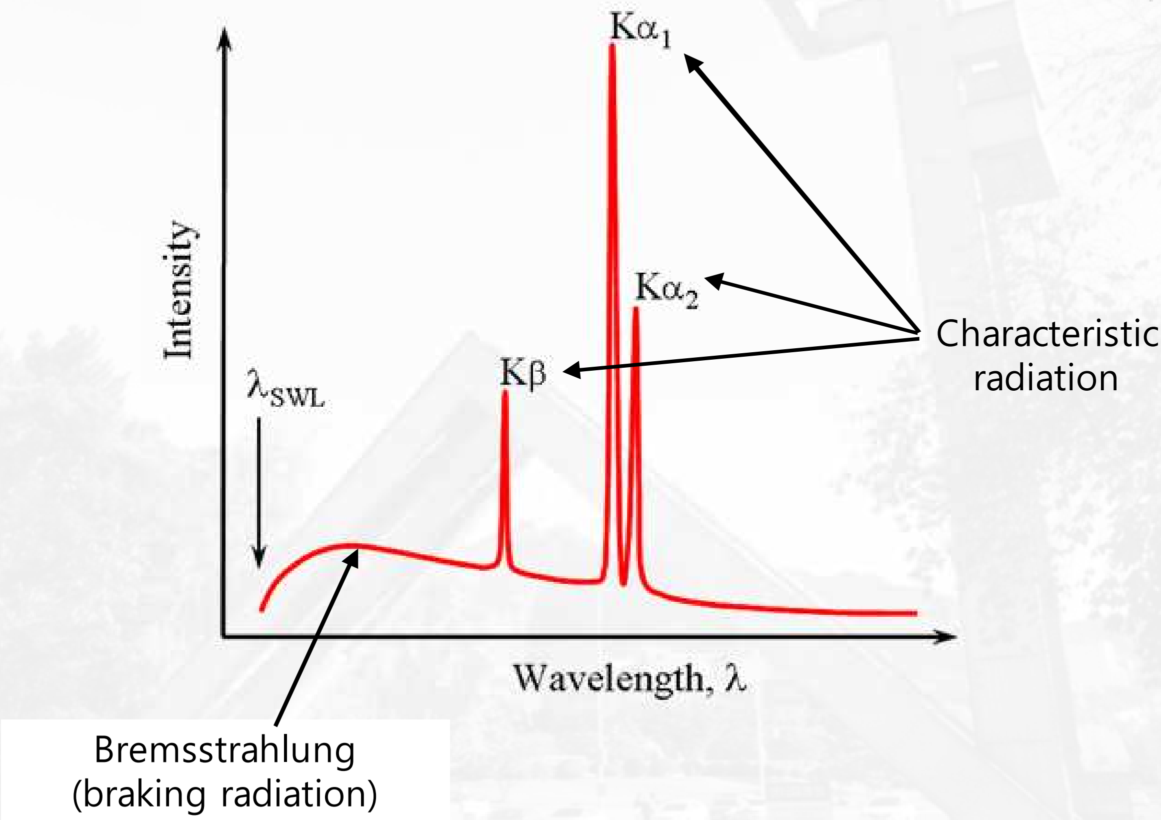


Pecharsky

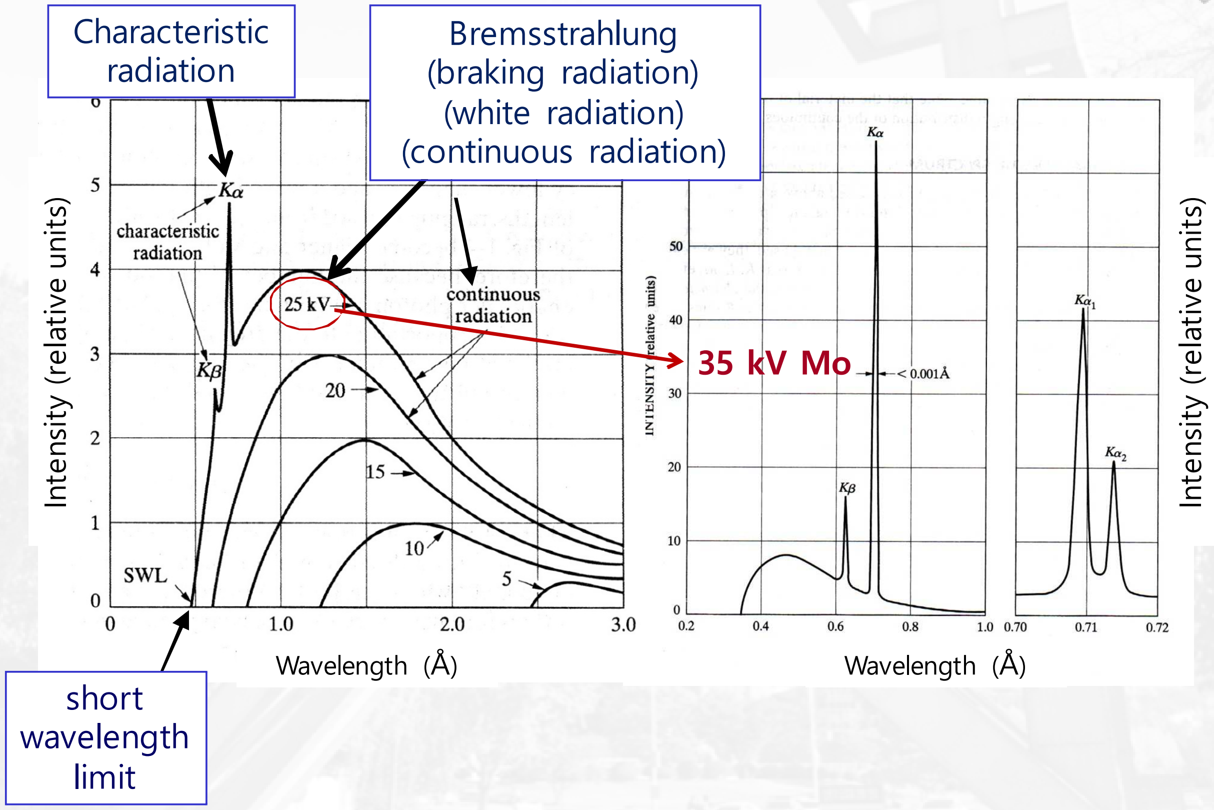
Rotating anode X-ray source



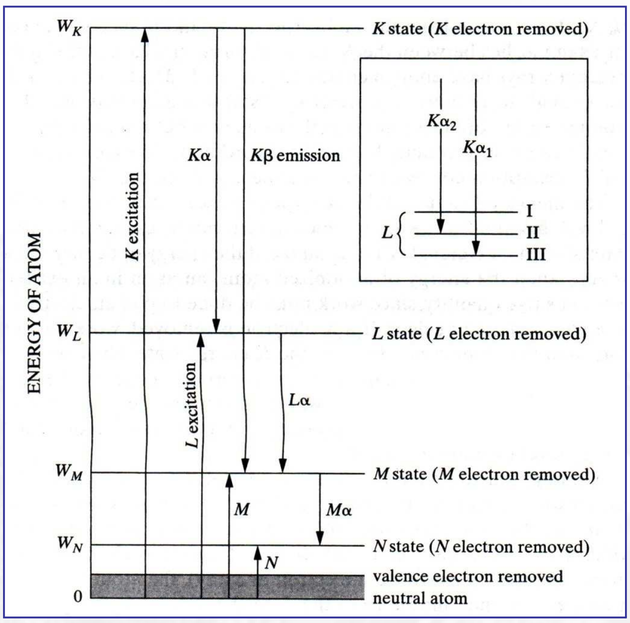
X-ray emission spectrum

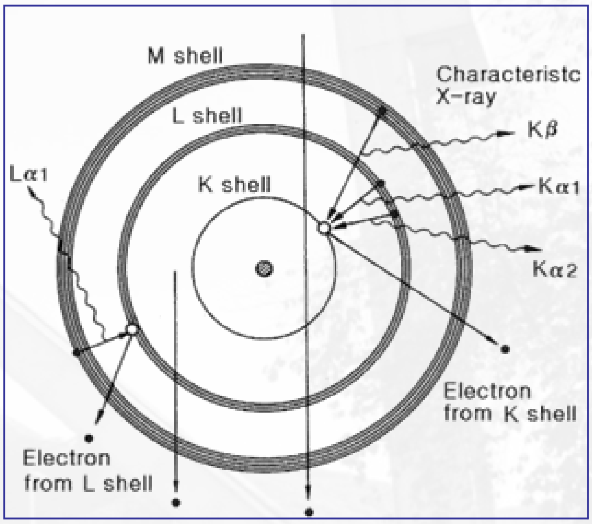


X-ray spectrum of molybdenum



Atomic energy level





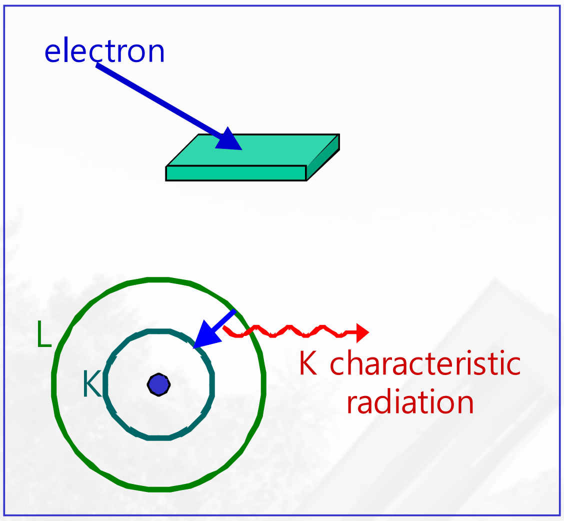
$K\alpha = (2K\alpha_1 + K\alpha_2)/3$

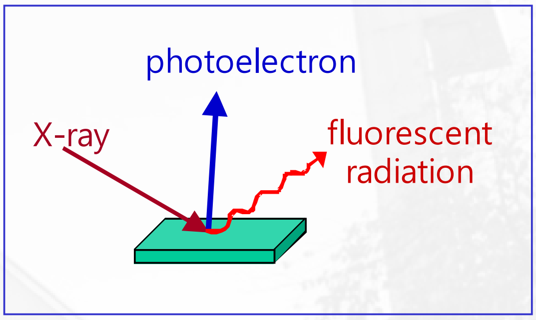
β-filter, monochromator

Intensity ratios

$K\alpha_1 : K\alpha_2 : K\beta = 10 : 5 : 2$

X-ray vs. photoelectron

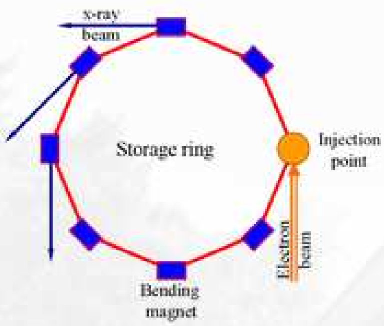


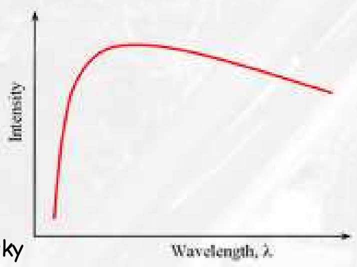


Auger electron, see Cullity page 17

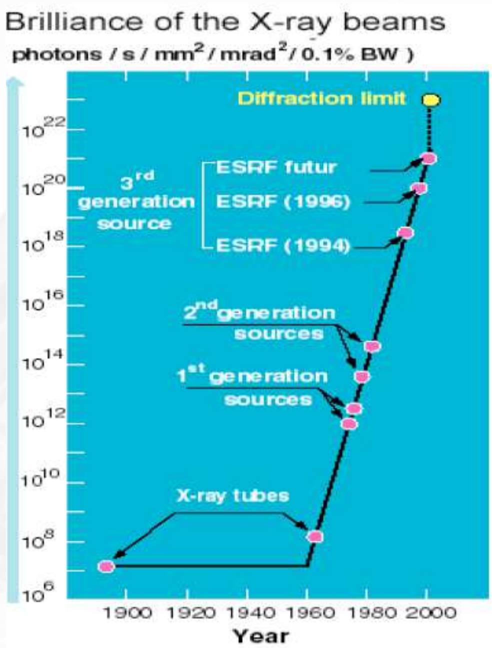
Synchrotron X-ray

- Most powerful X-ray radiation source
- High brilliance X-ray beam
- Distribution of beam intensity as a function of wavelength

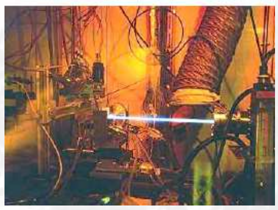




Pecharsky



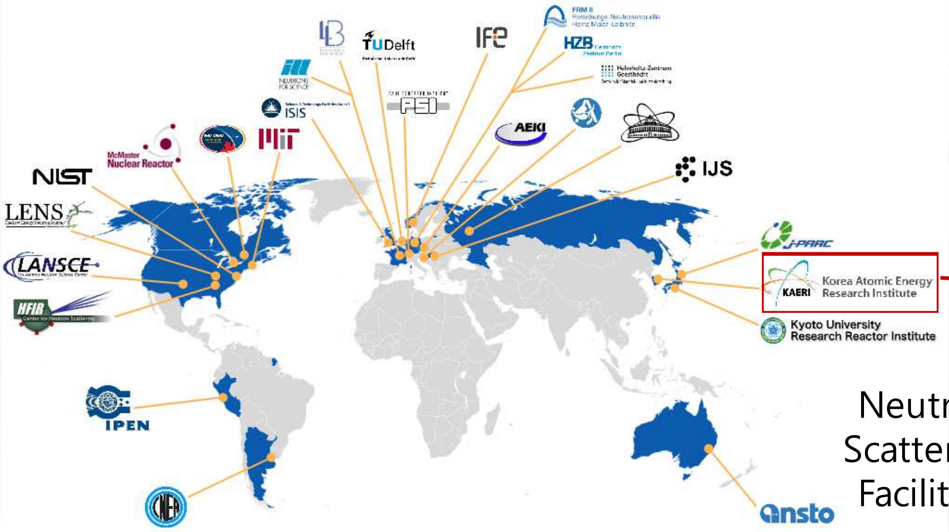
Intensity !!!



Synchrotron, Neutron

Synchrotron Radiation Facilities

PAL



Hanaro

Neutron Scattering Facilities

www.veqter.co.uk/images/content-images/neutron-diffraction/map-of-world-neutron.png

Neutron source

HANARO at KAERI in Daejeon

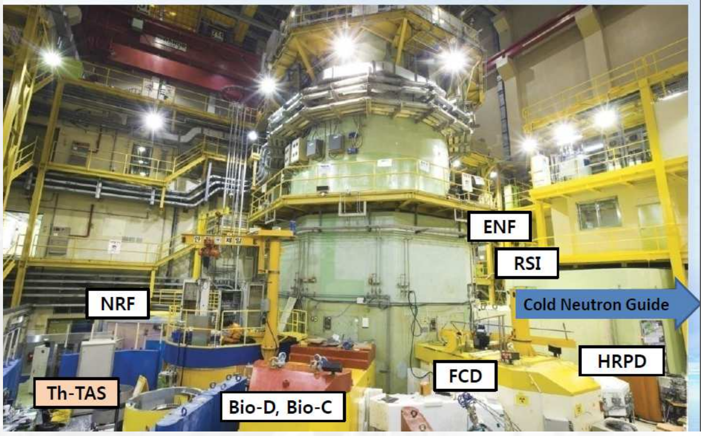
High-flux Advanced Neutron Application ReactOr

30 MW Multi-purpose Research reactor since 1995

Neutron Scattering, NAA, RI production, Irradiation Test, NTD

RX : Reactor Building
CNL : Cold Neutron Laboratory
RIPF : Radio-Isotope Production Facility
IMEF : Irradiated Material Examination Facility

HANARO Reactor Hall



Presentation of Shin Ae Kim, KAERI

Properties of Neutron

Mass	No Charge	Spin 1/2 ↑

- No charge → **Deep penetration**
- Wavelength Å ~ nm (Thermal & Cold Neutron) → **Atomic & Nanometer scale**
- Energy ~ meV → **Same magnitude as basic excitations in solids**
- Spin =1/2 → **Magnetic structure & dynamics**
- Interacts with nuclei → **Contrast variation (b_H = -3.74fm, b_D = 6.67fm)**

Neutron vs. X-ray

Why Neutron?

X-rays

Scattered from electrons

➢Scattering proportional to Z

H	C	N	O	Al	Si	P	Ti	D
1	6	7	8	13	14	15	22	1

Neutrons

Scattered by nuclei

➢Scattering not proportional to Z

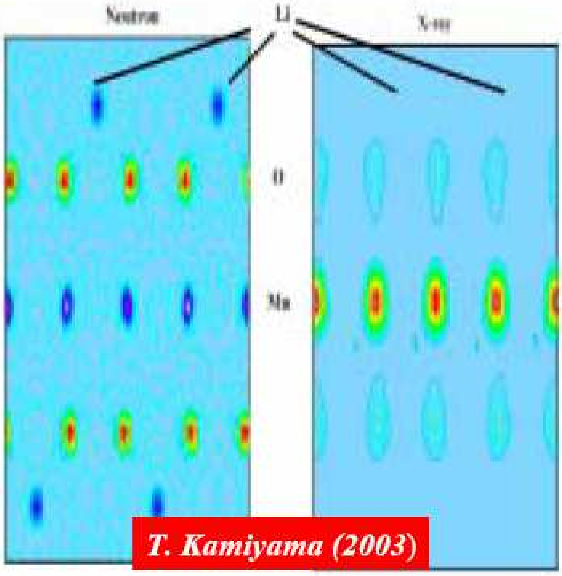
H	C	N	O	Al	Si	P	Ti	D	
1	6	7	8	13	14	15	22	1	
-37.4	66.5	93.6	58.0	34.5	41.5	51.3	-34.4	66.7	$\times 10^{-14}$

Neutron vs. X-ray

ntroduction

Neutron vs. X-ray

neutron **Li-ion battery** X-ray



X-ray Radiography

http://neutra.web.psi.ch

Electron diffraction, Neutron diffraction

- Electron diffraction
  - ✓ High vacuum is needed, Cost of equipment
  - ✓ **e's strongly interact with materials → dynamical theory of diffraction**

- Neutron diffraction
  - ✓ **Neutrons generated in nuclear reactors**
  - ✓ White spectrum
  - ✓ **<u>Scattered by nuclei (X-ray is scattered by electron)</u>**
  - ✓ Scattering factor remains constant over the whole range of Bragg angles
  - ✓ **<u>Scattering factors not proportional to atomic number</u>**
  - ✓ Scattering factors are different for different isotopes of the same element
  - ✓ Neutrons have spins → interact with unpaired e' spins (magnetic moments), can be used to determine ordered magnetic structures

X-ray, neutron, & electron

	X-ray (conv/sync)	Neutron	Electron
nature	wave	particle	particle
medium	atmosphere	atmosphere	high vacuum
scattering by	**e' density**	**nuclei, magnetic spins of e's**	**electrostatic potential**
range of λ (A)	0.5~2.5 (0.1~10)	~1	0.01~0.05
selection of λ	fixed/variable	variable	variable
focusing	none		magnetic lenses
lattice image	**reciprocal**		**direct, reciprocal**
direct structure image	no		yes
applicable theory of diffraction	**kinematical**		**dynamical**

Safety (XRD)

- Electric shock
- Radiation hazard
  - ✓ Burns
  - ✓ Radiation sickness
  - ✓ Genetic mutation
- Be window

Beryllium - MSDS

- Appearance: silvery solid or grey foil
  Melting point: 1278 C Boiling point: 2970 C
- Very toxic by inhalation - risk of serious damage to health. May act as a human carcinogen for which there is no safe exposure level. May act as a sensitizer.
- Toxicity data IVN-RAT LD50 0.5 mg kg-1
- Risk phrases R26 R27 R37 R39.

IVN – intravenous
LD50 – lethal dose 50% kill
R26 – very toxic by inhalation
R27 – very toxic in contact with skin
R37 irritating to respiratory system
R39 – danger of very serious irreversible effects

- No special health risks with Be in solid form
- Skin Contact with Beryllium
  - ✓ No effect on contact or temporary embedding.
  - ✓ Solvents will not generate beryllium dust, but some acids will. Don't etch beryllium.
  - ✓ Wear clean gloves to protect the skin and to protect the beryllium.

todos

- XRD-1, Read
  - ✓ Cullity Chapter 1-1~1-6
- XRD-1 Homework (due in 1 week)
  - ✓ Cullity 1-1, 1-2, 1-16