GCE2231
Materials Characterizations

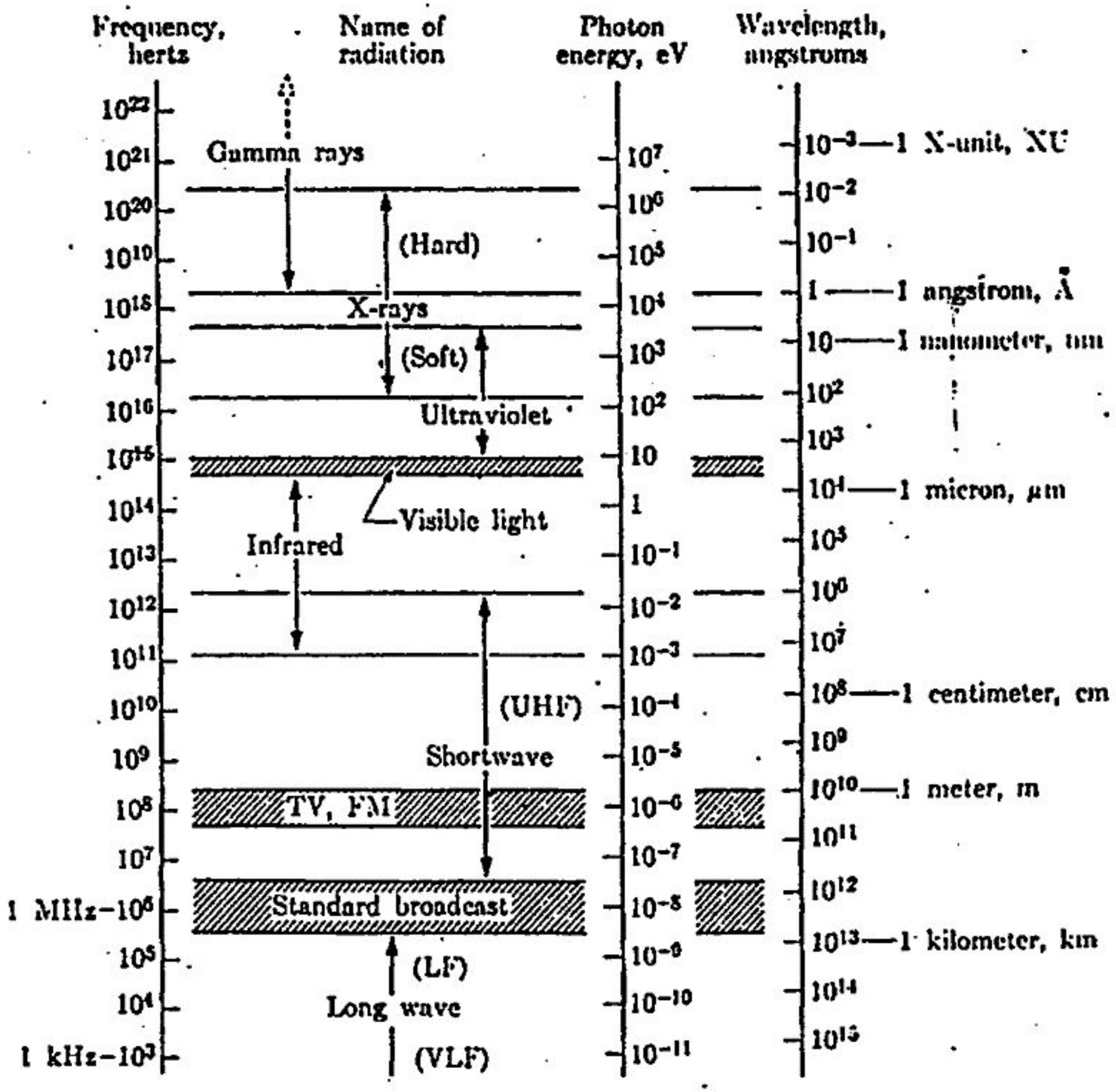
Mst. Esmotara Begum

Lecturer

GCE, RUET

X-Rays

- X-rays were discovered in 1895 by the German physicist Röntgen and were so named because their nature was unknown at the time.
- Diffraction of X-ray was discovered by W.H. Bragg and W.L. Bragg in 1912



Properties and Generation of X-Rays

- X-rays are electromagnetic radiation with very short wavelength (10^{-8} -10^{-12} m)
- The energy of the x-ray can be calculated with the equation $E = h\upsilon = hc/\lambda$; e.g. the x-ray photon with wavelength 1Å has energy 12.5 keV
- X-rays are produced whenever high-speed electrons collide with a metal target.
- Unlike ordinary light, these rays were invisible, but they traveled in straight lines and affected photographic film in the same way as light. On the other hand, they were much more penetrating than light and could easily pass through the human body, wood, quite thick pieces of metal, and other “opaque” objects. X-rays are a form of electromagnetic radiation (like light); they are of higher energy, however, and can penetrate the body to form an image on film.

- X-rays are produced when any electrically charged particle of sufficient kinetic energy rapidly decelerates. Electrons are usually used for this purpose, the radiation being produced in an x-ray tube which contains a source of electrons and two metal electrodes. The high voltage maintained across these electrodes, some tens of thousands of volts, rapidly draws the electrons to the anode, or target, which they strike with very high velocity. X-rays are produced at the point of impact and radiate in all directions. If e is the charge on the electron (1.60×10^{-19} coulomb) and V the voltage across the electrodes, then the kinetic energy (in joules) of the electrons on impact is given by the equation:

$$K.E = eV = \frac{1}{2} mV^2$$

- Where m is the mass of the electron (9.11×10^{-31} kg) and v its velocity in m/sec just before impact. At a tube voltage of 30,000 volts, this velocity is about one-third that of light. Most of the kinetic energy of the electrons striking the target is converted into heat, less than 1 percent being transformed into x-rays.

Production of X-rays

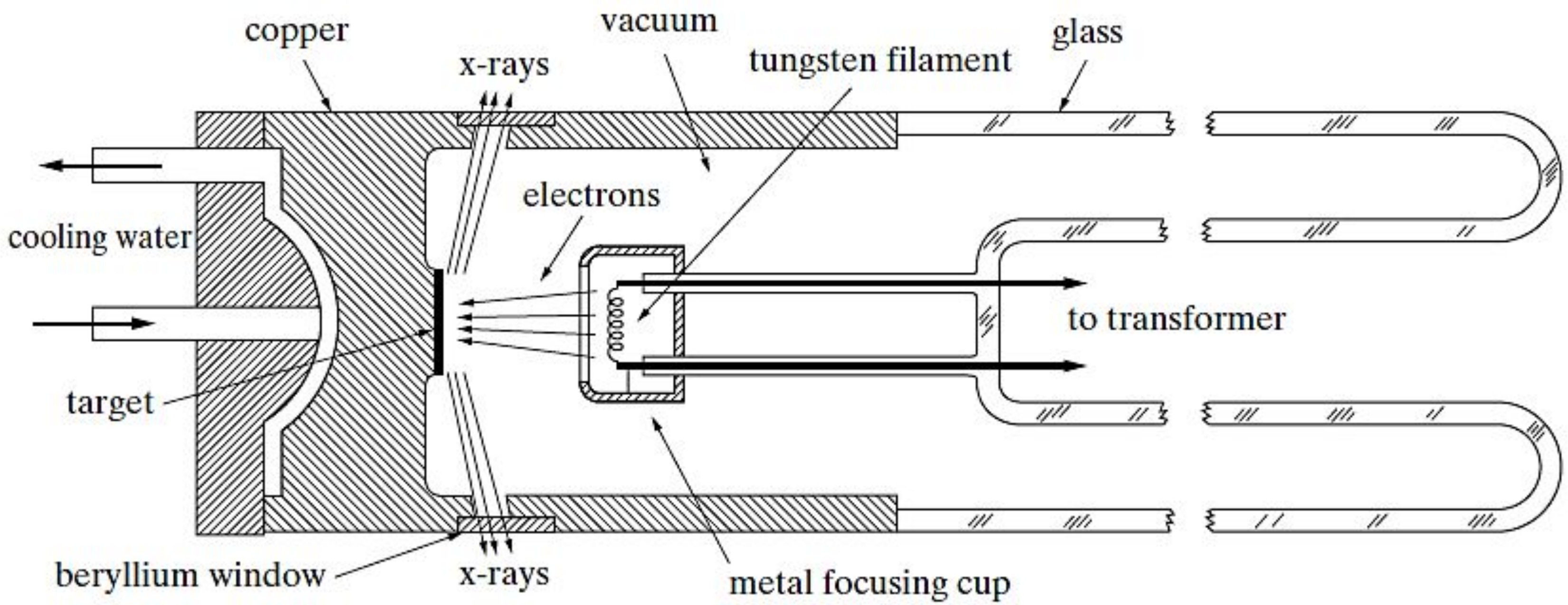
- X-rays can be generated by an X-ray tube, a vacuum tube that uses a high voltage to accelerate the electrons released by a hot cathode to a high velocity. The high velocity electrons collide with a metal target, the anode, creating the X-rays.
- As x-rays are produced whenever high-speed electrons collide with a metal target, any x-ray tube must contain
  1. **A source of electrons (hot W filament),**
  2. **A high accelerating voltage, and**
  3. **A metal target (Cu, Al, Mo,Mg)**
- Furthermore, since most of the kinetic energy of the electrons is converted into heat in the target, the latter is almost always **watercooled** to prevent its melting.

Production of X-rays

- **X-ray tubes**

X-ray tubes may be divided into two basic types, according to the way in which electrons are provided: gas tubes, in which electrons are produced by the ionization of a small quantity of gas (residual air in a partly evacuated tube), and filament tubes, in which the source of electrons is a hot filament. But the gas tubes are now obsolete.

Production of X-rays: Filament Tube



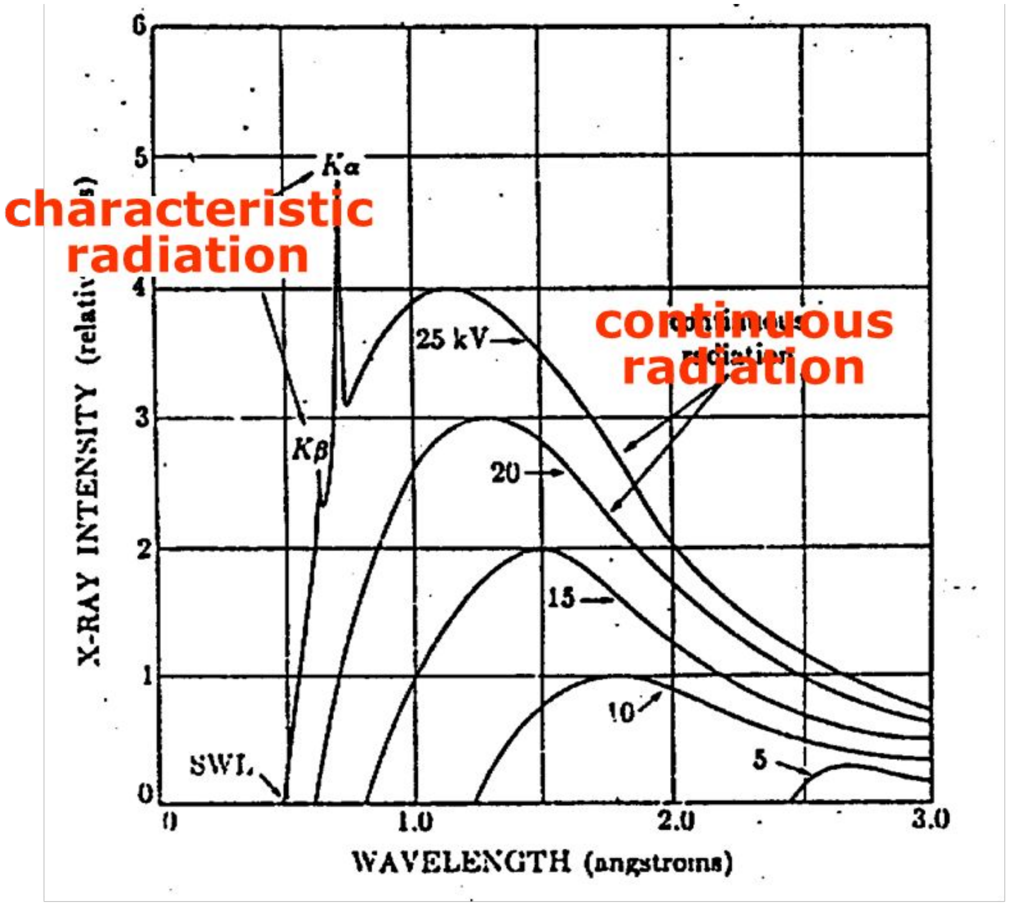
Cross section of sealed x-ray tube (schematic)

All X-ray tubes contain two electrodes, an anode (the metal target) and a cathode. In filament tubes, an evacuated glass envelope which insulates the anode at one end from the cathode at the other, the cathode being a tungsten filament and the anode a water-cooled block of copper containing the desired target metal as a small insert at one end. One lead of the high-voltage transformer is connected to the filament and the other to ground, the target being grounded by its own cooling-water connection. The filament is heated by a filament current of about 3 amp and emits electrons which are rapidly drawn to the target by the high voltage across the tube. Surrounding the filament is a small metal cup maintained at the same high (negative) voltage as the filament: it therefore repels the electrons and tends to focus them into a narrow region of the target, called the focal spot. X-rays are emitted from the focal spot in all directions and escape from the tube through two or more windows in the tube housing. Since these windows must be vacuum tight and yet highly transparent to x-rays, they are usually made of beryllium.

The target is always water-cooled to prevent its heating since most of the kinetic energy of the electrons is converted into heat in the target, less than 1 percent being transformed into x-rays. The filament is heated by a filament current of ~3 amp and emits electrons which are rapidly drawn to the target by the high negative voltage between the cathode and anode. A small metal cup maintained at the same negative voltage as the filament repels the electrons and tends to focus them into a narrow region of the target. X-rays are emitted from the focal spot in all directions and escape from the tube through windows in the tube housing.

X-ray Spectrum

- A spectrum of x-ray is produced as a result of the interaction between the incoming electrons and the inner shell electrons of the target element.
- Two components of the spectrum can be identified, namely, the continuous spectrum and the characteristic spectrum.



SWL - short-wavelength limit

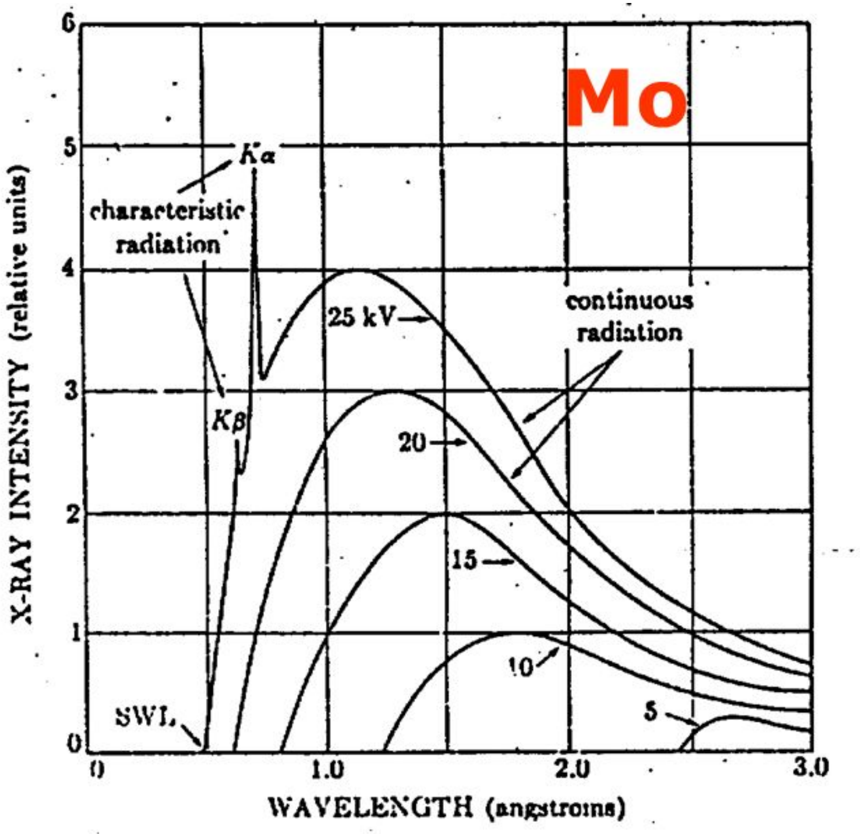
SWL - short-wavelength limit

The Continuous x-ray Spectra

- The electrons enter the target with kinetic energy equals to eV, where V is the accelerating voltage used. Fast moving e- will then be deflected or decelerated and EM radiation will be emitted.
- The energy of the radiation depends on the severity of the deceleration, which is more or less random, and thus has a continuous distribution.
- These radiation is called white radiation or bremsstrahlung (German word for ‘braking radiation’).

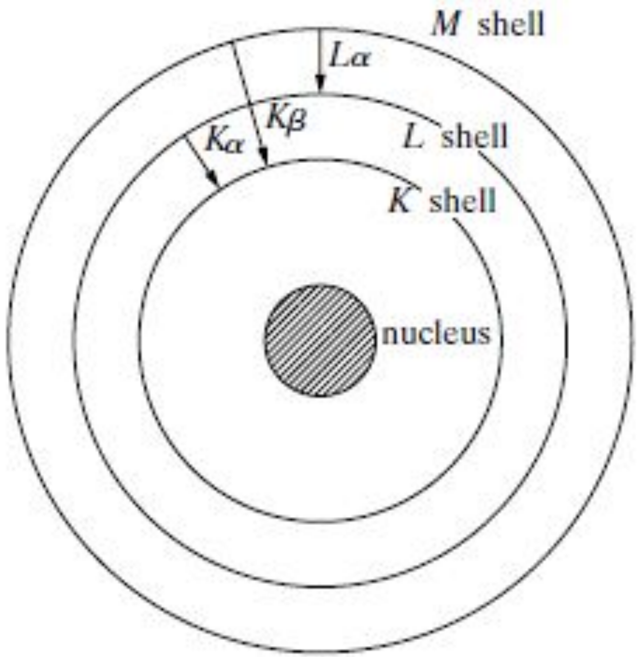
Characteristic x-ray Spectra

- Sharp peaks in the spectrum can be seen if the accelerating voltage is high (e.g. 25 kV for molybdenum target).
- These peaks fall into sets which are given the names, K, L, M…. lines with increasing wavelength



Characteristic x-ray Spectra

- If an incoming electron has sufficient kinetic energy for knocking out an electron of the K shell (the inner-most shell), it may excite the atom to an high-energy state (K state).
- One of the outer electron falls into the K-shell vacancy, emitting the excess energy as a x-ray photon.

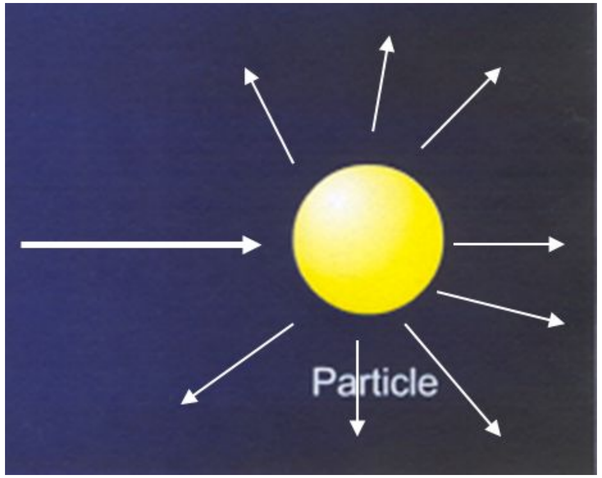


- Reference book

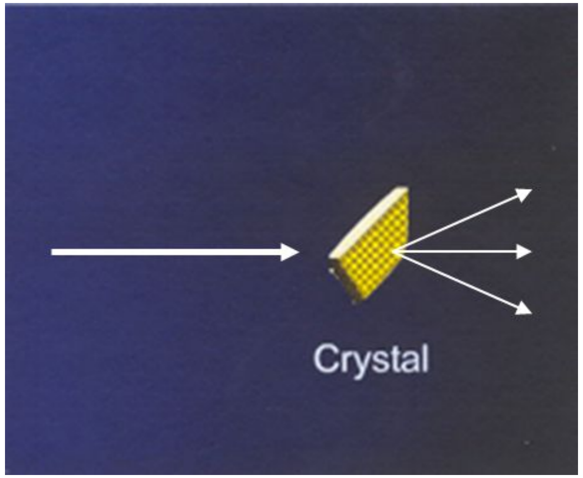
  -elements of x-ray diffraction (B.D. Cullity)

Diffraction

- Diffraction occurs when a wave encounters a series of regularly spaced obstacles that are capable of scattering the wave and have spacings that are comparable in magnitude to the wavelength.

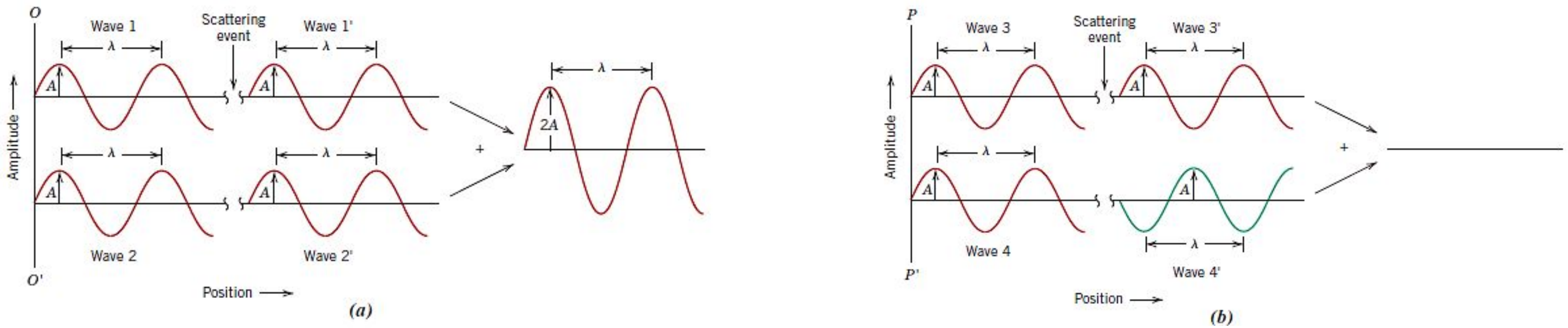


The particle scatters the incident beam uniformly in all directions.



The scattered beam may add together in a few directions and reinforce each other to give diffracted beams.

Constructive and Destructive Interference of Waves

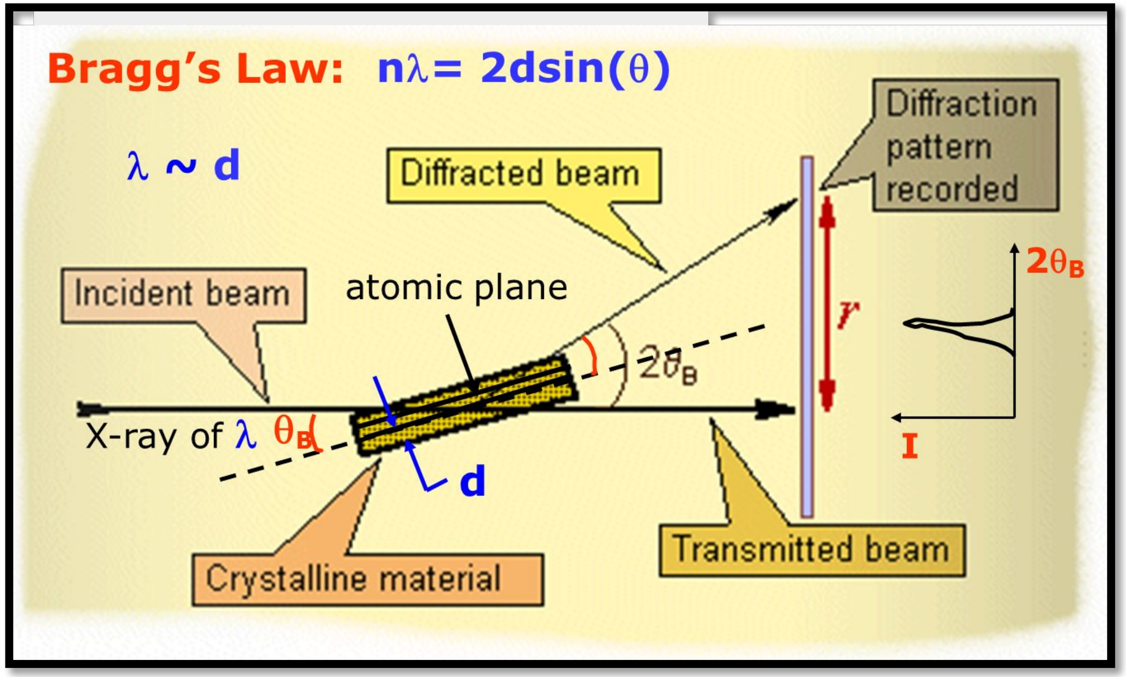


(a) Demonstration of how two waves (labeled 1 and 2) that have the same wavelength λ and remain in phase after a scattering event (waves 1’ and 2’) constructively interfere with one another. The amplitudes of the scattered waves add together in the resultant wave. (b) Demonstration of how two waves (labeled 3 and 4) that have the same wavelength and become out of phase after a scattering event (waves 3’ and 4’) destructively interfere with one another. The amplitudes of the two scattered waves cancel one another.

X-ray Diffraction (XRD)

X-ray Diffraction

- The atomic planes of a crystal cause an incident beam of x-rays (if wavelength is approximately the magnitude of the interatomic distance) to interfere with one another as they leave the crystal. The phenomenon is called x-ray diffraction.

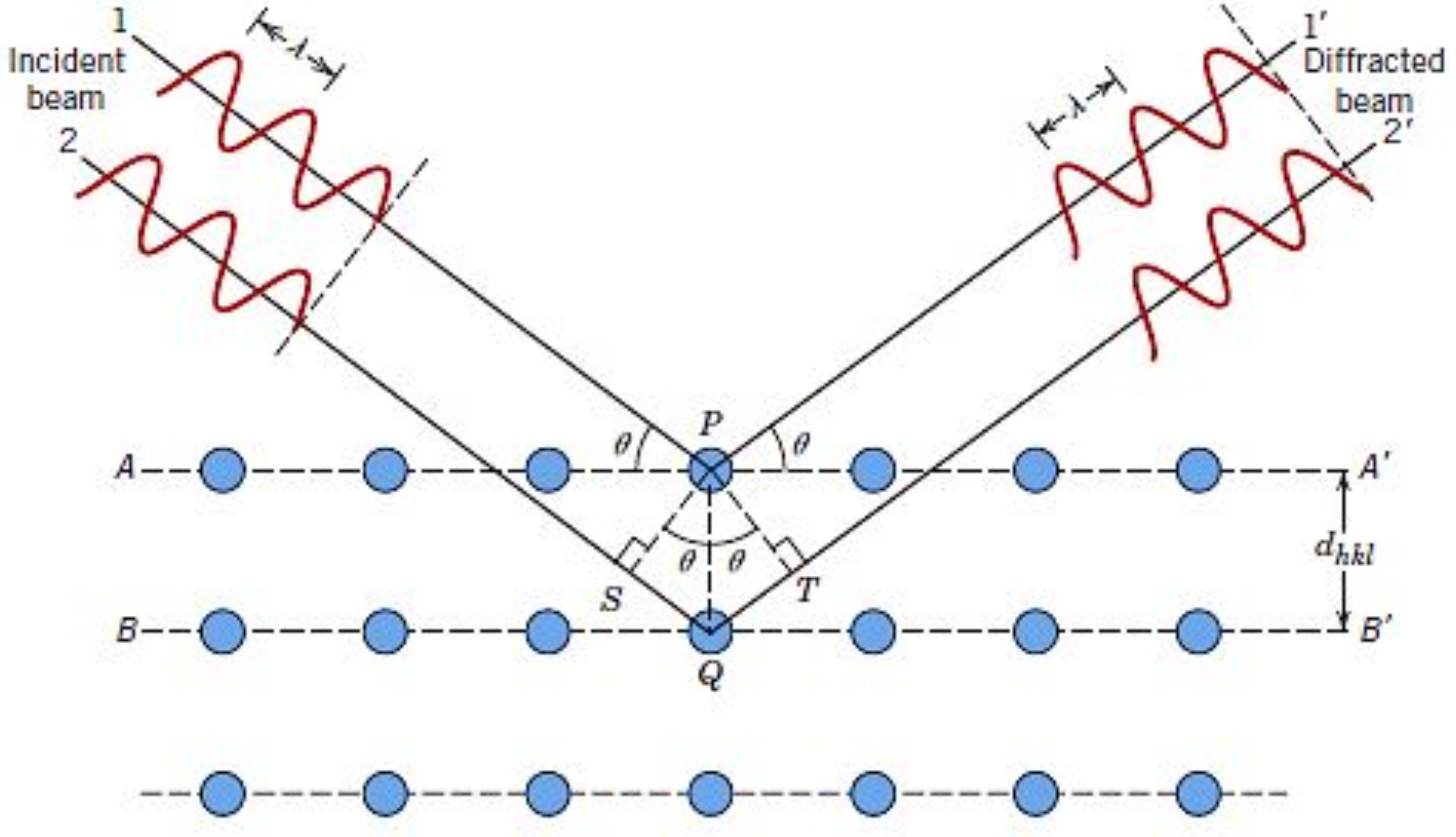


In XRD, X-rays with $\lambda \sim 0.5\text{-}2$Å, is incident on a specimen and is diffracted by crystalline phase in specimen according to Bragg's Law. The intensity of the diffracted X-ray is measured as a function of the diffraction angle and the specimen orientation.
XRD patterns will provide a lot of information about materials structure and properties.

Bragg's Law and X-ray Diffraction

- The incident waves are reflected specularly from parallel planes of atoms in the crystal.
- In specular (mirrorlike) reflection the angle of incidence is equal to the angle of reflection. The diffracted beams are found when the reflections from parallel planes of atoms interfere constructively.
- The energy of the x-ray is not changed on reflection _elastic scattering.

Bragg’s Law and X-ray Diffraction



Bragg's Law and X-ray Diffraction

$n\lambda = SQ + TQ$

$SQ = TQ$

$n\lambda = 2SQ$

$\sin\theta = SQ/d$

$SQ = d\sin\theta$

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

Condition for Bragg's law

- $n\lambda < 2d$

$$\boxed{\lambda = 2d_{hkl}\sin\theta_{hkl}}$$

n – integer, called the order of diffraction

- Diffraction occurs only when Bragg's Law is satisfied
- If Bragg's law is not satisfied, then the interference will be nonconstructive so as to yield a very low-intensity diffracted beam.

Bragg's Law and X-ray Diffraction

- The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS, and diamond.
- Limitations: It specifies when diffraction will occur for unit cells having atoms positioned only at cell corners. However, atoms situated at other sites (e.g., face and interior unit cell positions as with FCC and BCC) act as extra scattering centers, which can produce out-of-phase scattering at certain Bragg angles. The net result is the absence of some diffracted beams that should be present.

X-ray Diffraction Methods

XRD Methods- Determination of crystal structure

Three X-Ray Diffraction Method

1. Laue Method
2. Powder Method
3. Rotating Crystal Method

Laue Method

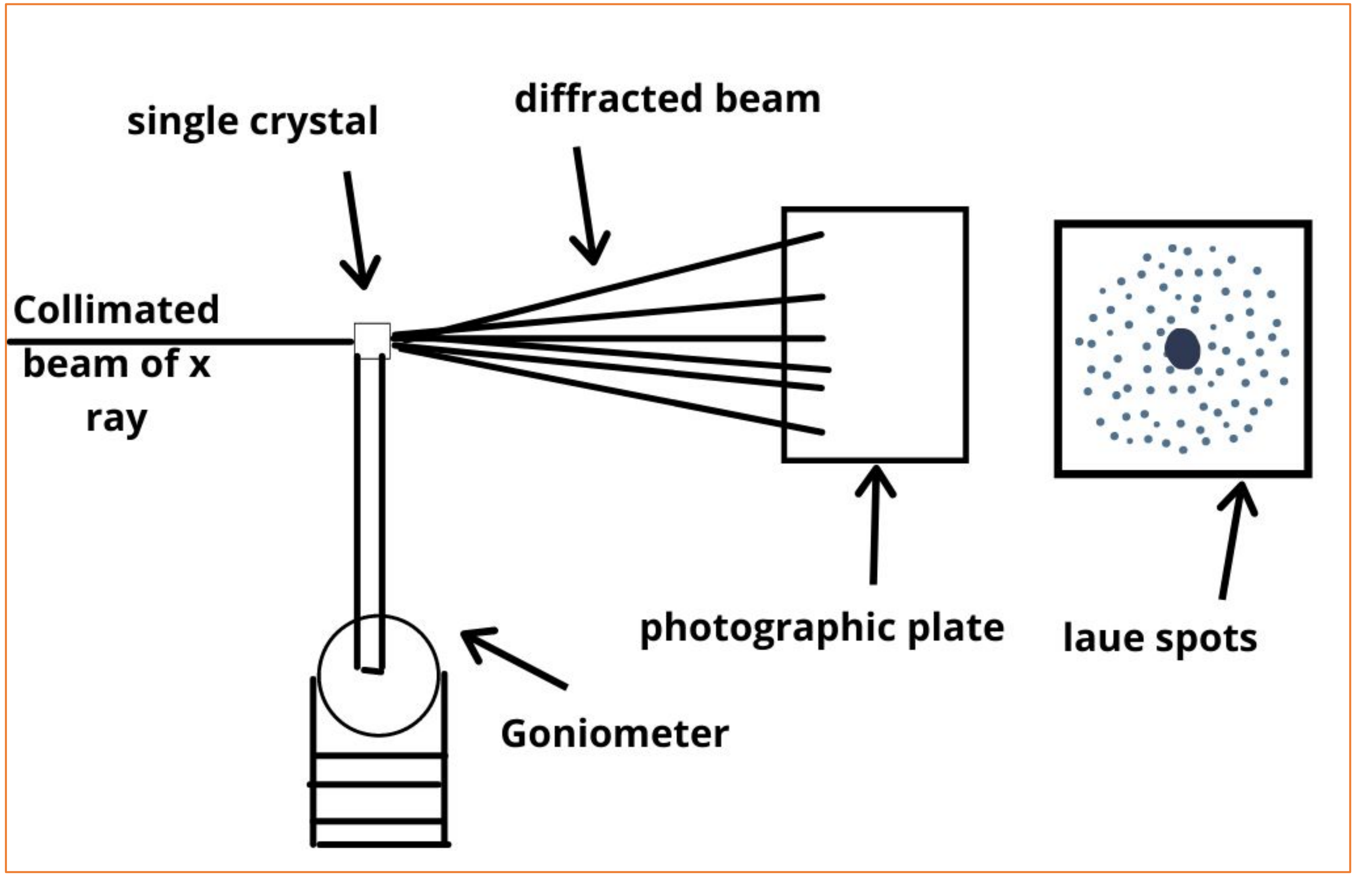
X-ray Source

Collimeter

Goniometer

Single Crystal

Photographic films



Laue Method

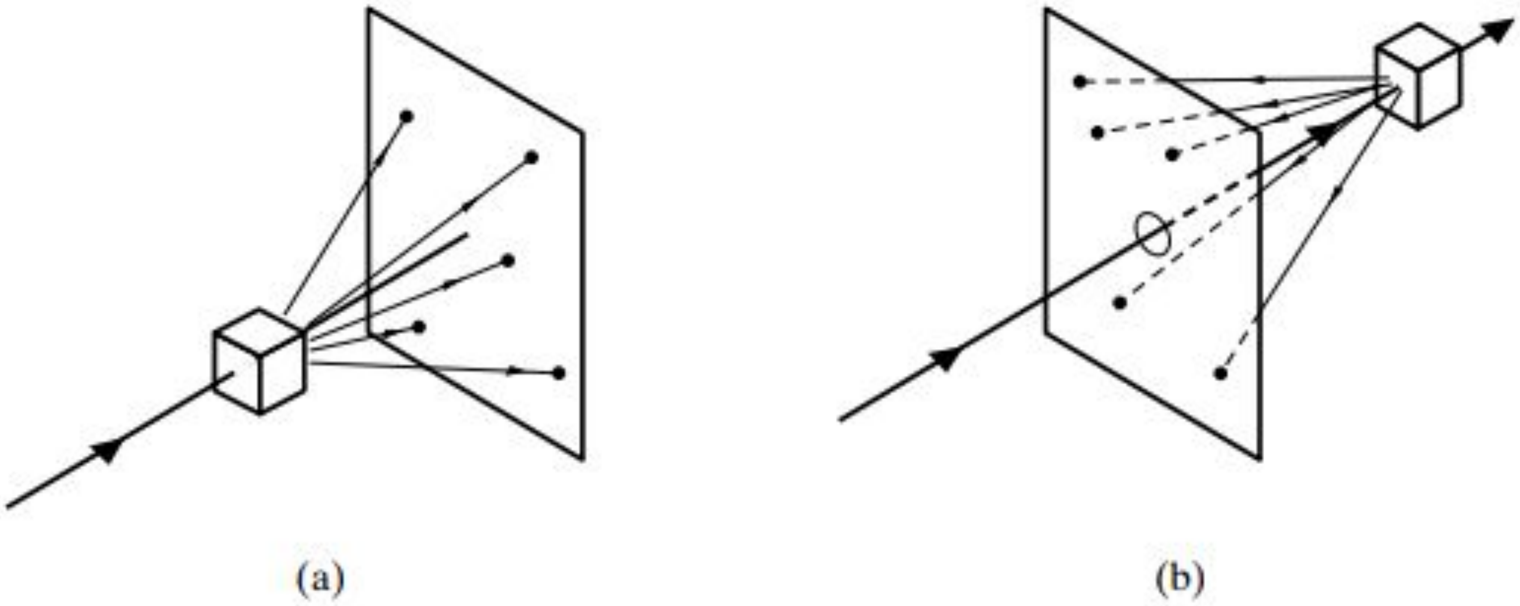
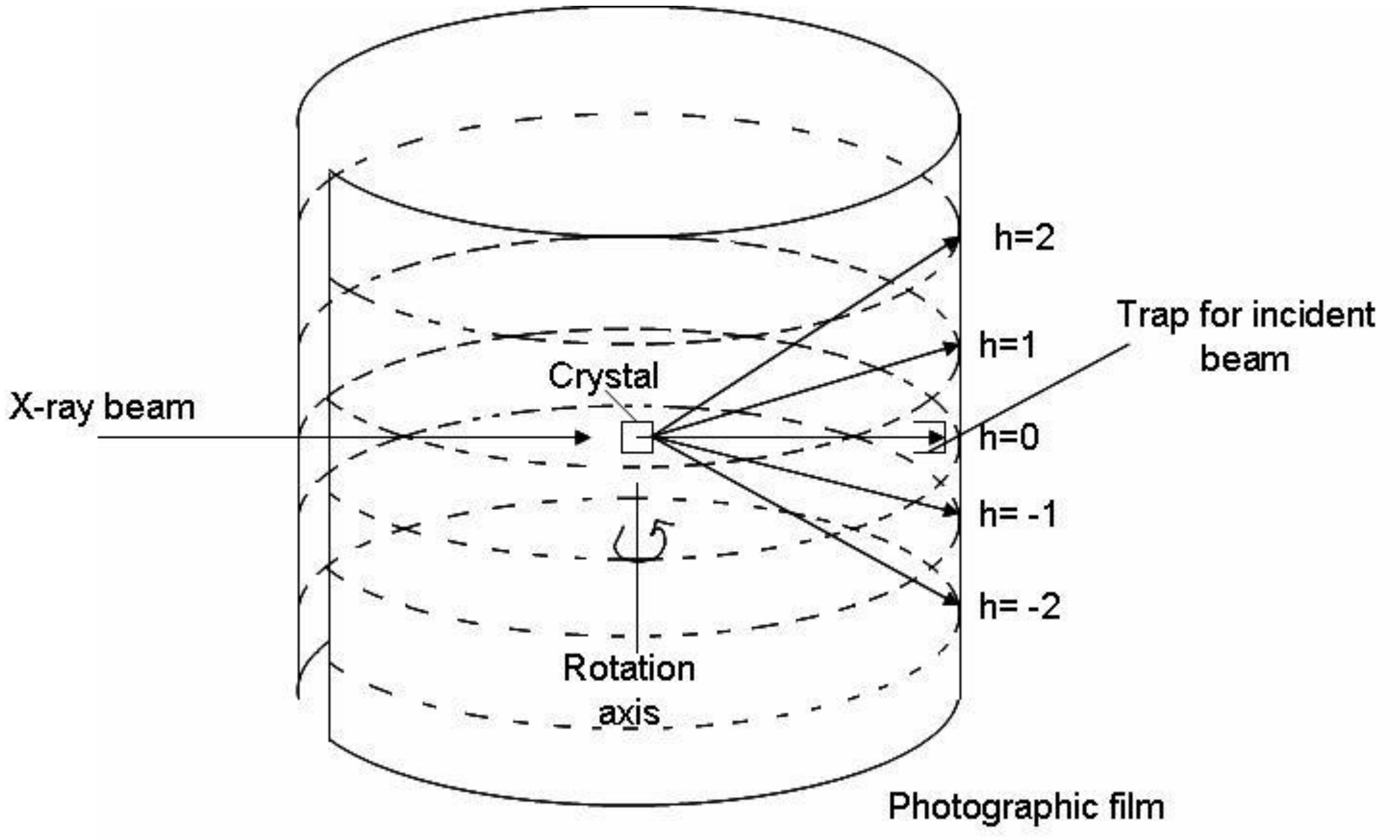
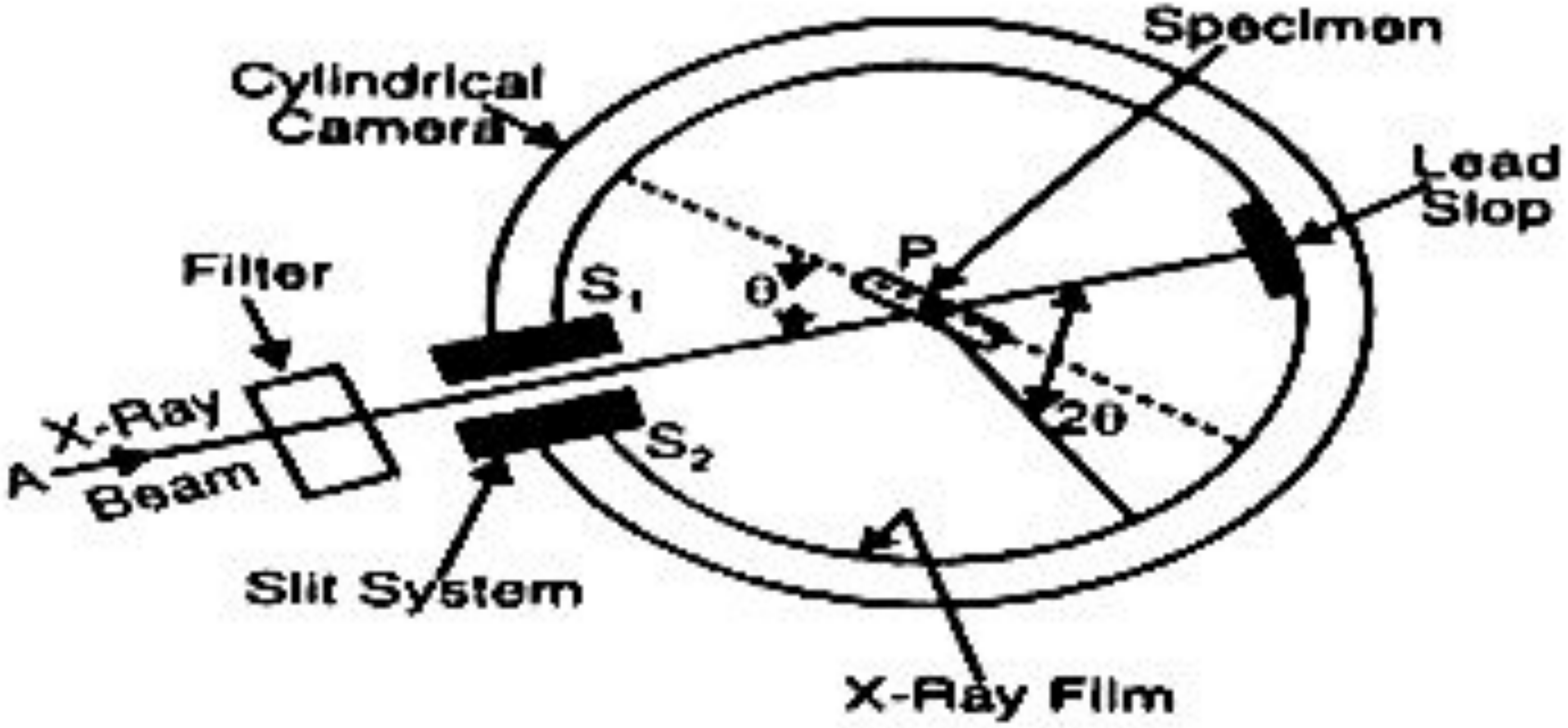


Figure 9 (a) Transmission and (b) back-reflection Laue methods.

Rotating Crystal Method



Powder Method



Summary of the XRD Methods

Methods	**Source**	**Specimen**	**λ**	**θ**
Laue	White X-ray	Single Crystal	Variable	Fixed
Powder	Monochromatic	Powder	Fixed	Variable
Rotating Crystal	Monochromatic	Single Crystal	Fixed	Variable (in part)

X-ray Diffraction Data

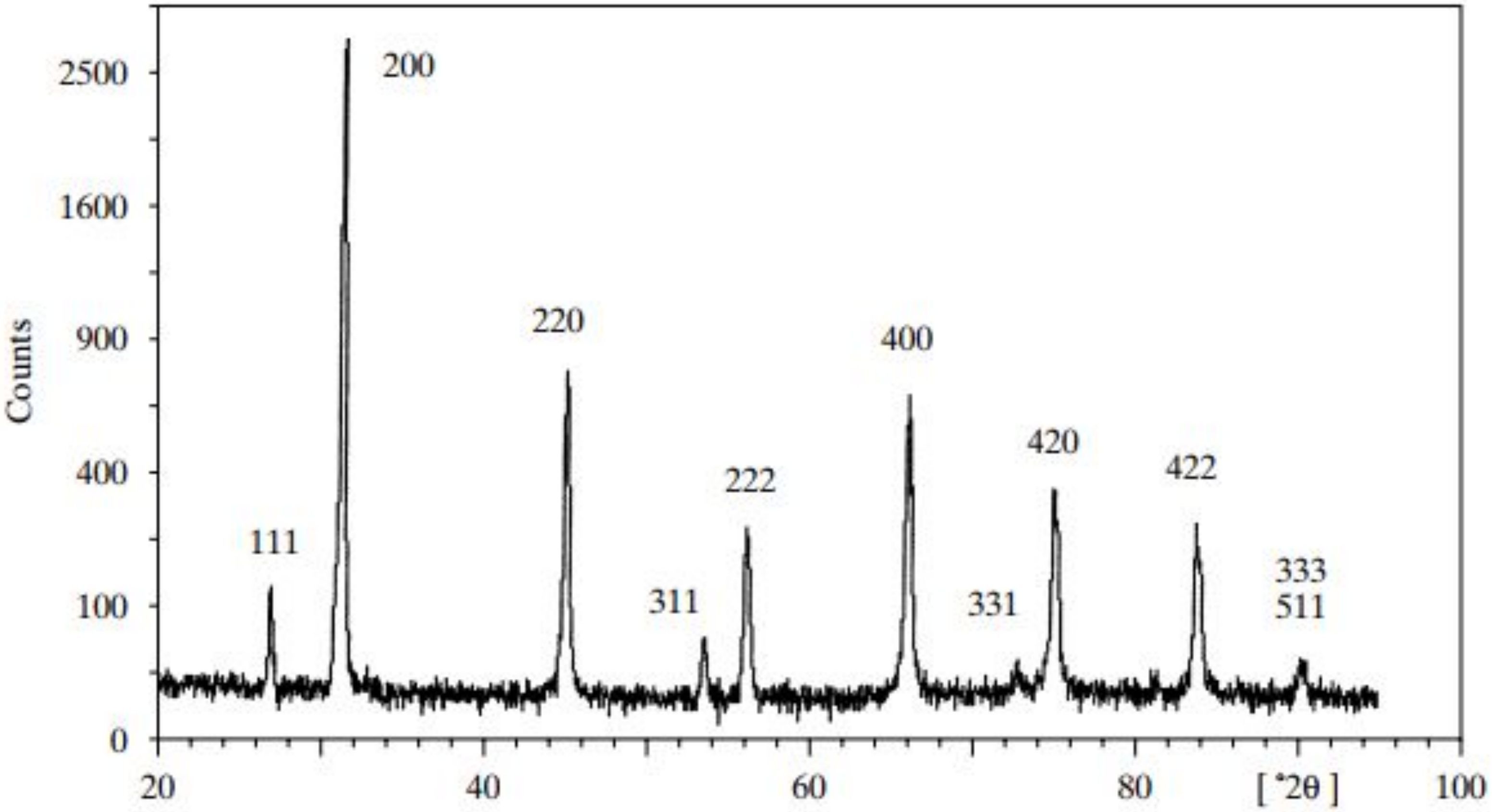


Figure 5 Diffraction pattern of NaCl powder. Copper Kα radiation, monochromator, variable divergence slit diffractometer. About one-half of the entire range of 2θ is shown here. The vertical axis shows the square root of the number of counts.

X-ray Diffraction Data

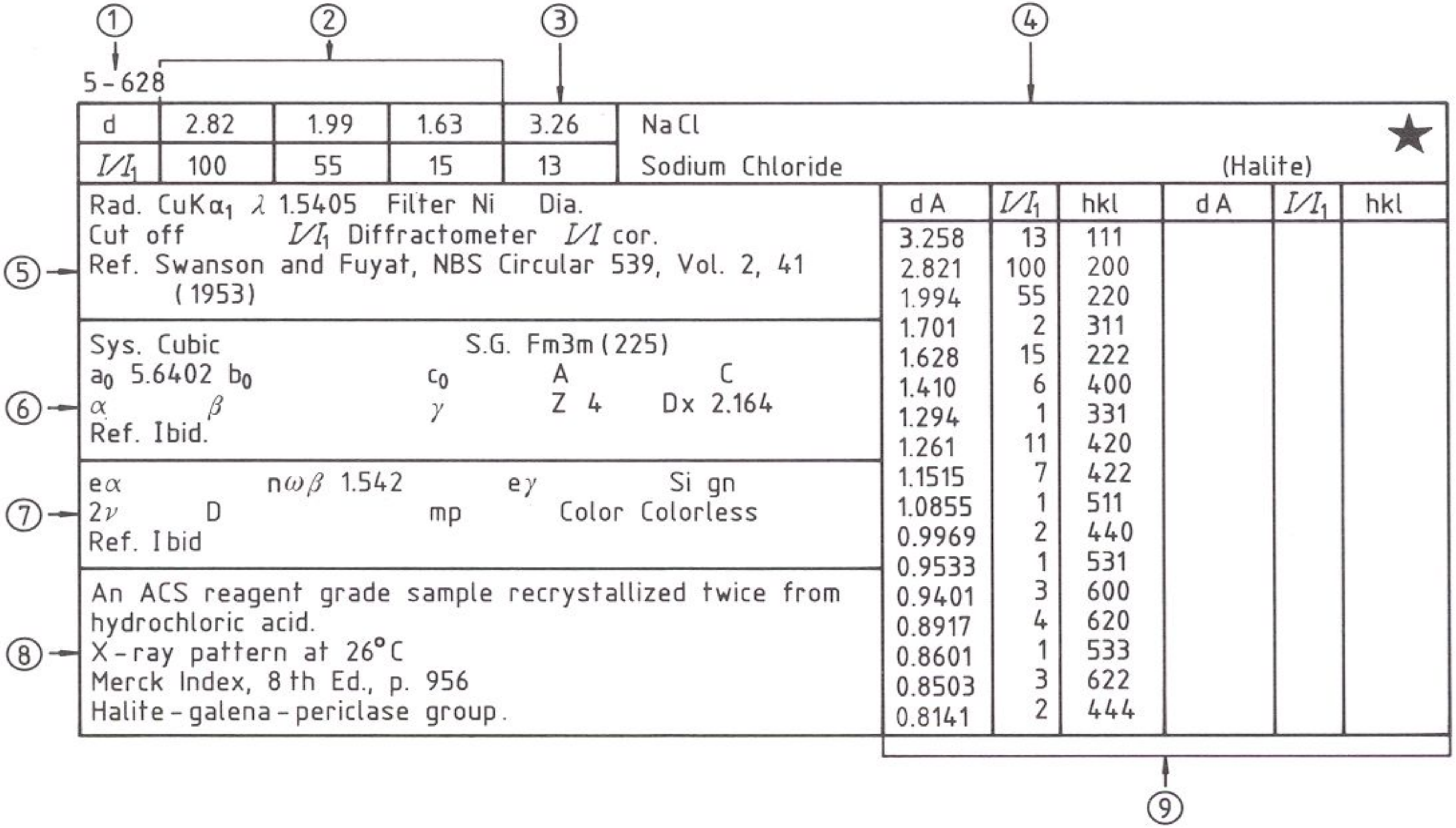
A diffractometer records changes of diffraction intensity with 2θ. The diffractometer records the diffraction intensity starting from a low 2θ and ending at a high 2θ. A number of intensity peaks located at different 2θ provide a ‘‘fingerprint’’ for a crystalline solid of each individual. Each peak represents diffraction from a certain crystallographic plane. Matching an obtained peak spectrum with a standard
spectrum enables us to identify the crystalline substances in a specimen. Spectrum matching is determined by the positions of the diffraction peak maxima and the relative peak intensities among diffraction peaks. In a modern diffractometer, data acquisition and treatment are mainly done by computer.

X-ray Diffraction Data

- Crystal-Phase Identification-One of the most important uses of XRD

  - Obtain XRD pattern
  - Measure d-spacings
  - Obtain integrated intensities
  - Compare data with known standards in the JCPDS file, which are for random orientations (there are more than 50,000 JCPDS cards of inorganic materials).
  - Compare data with known standards in the ICSD data file

JCPDS Card



5-628

d	2.82	1.99	1.63	3.26	NaCl ★
I/I_1	100	55	15	13	Sodium Chloride (Halite)

Rad. $CuK\alpha_1$ λ 1.5405 Filter Ni Dia.
Cut off I/I_1 Diffractometer I/I cor.
Ref. Swanson and Fuyat, NBS Circular 539, Vol. 2, 41 (1953)

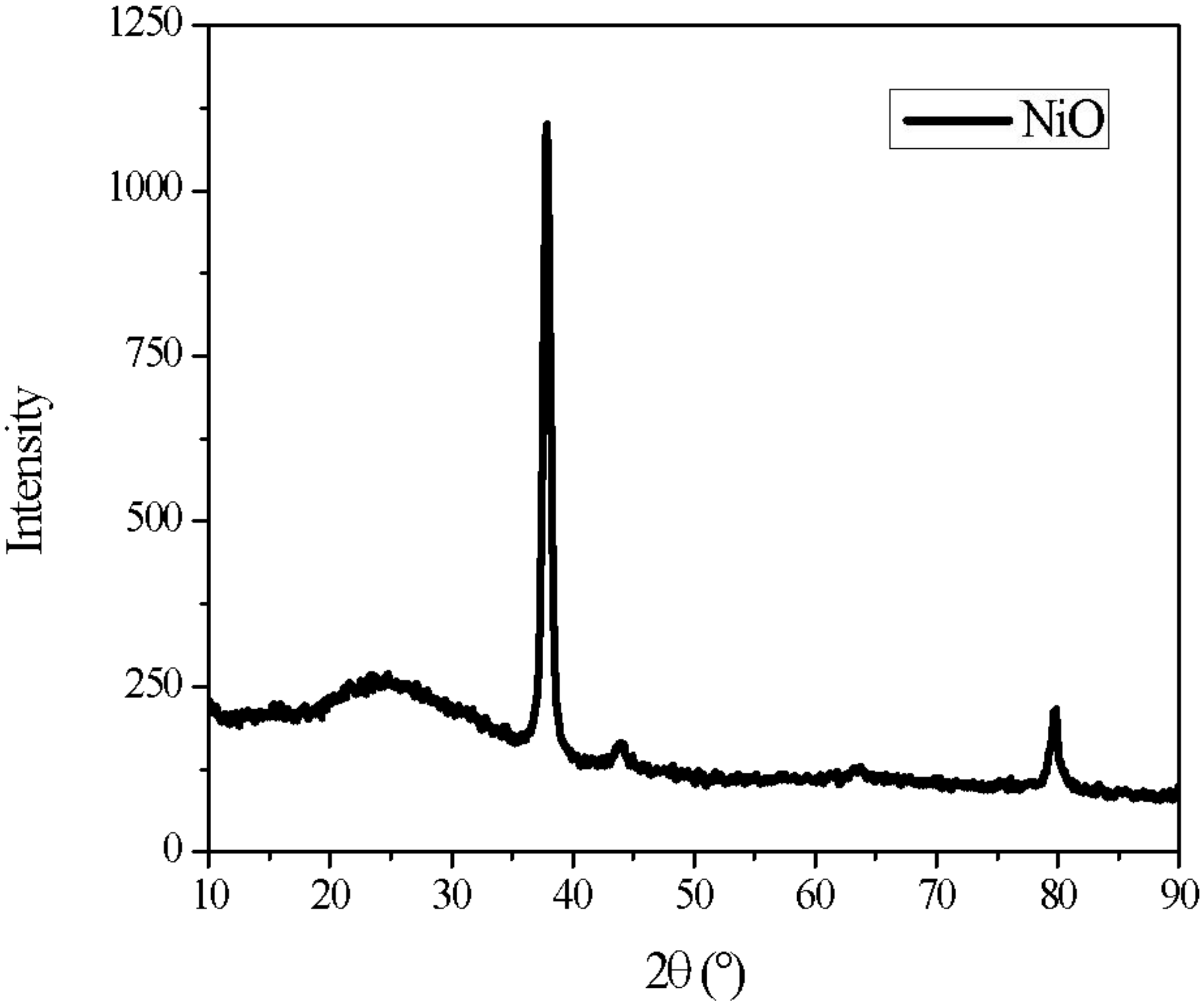
Sys. Cubic S.G. Fm3m (225)
a_0 5.6402 b_0 c_0 A C
α β γ Z 4 Dx 2.164
Ref. Ibid.

$\epsilon\alpha$ $n\omega\beta$ 1.542 $\epsilon\gamma$ Si gn
$2V$ D mp Color Colorless
Ref. Ibid

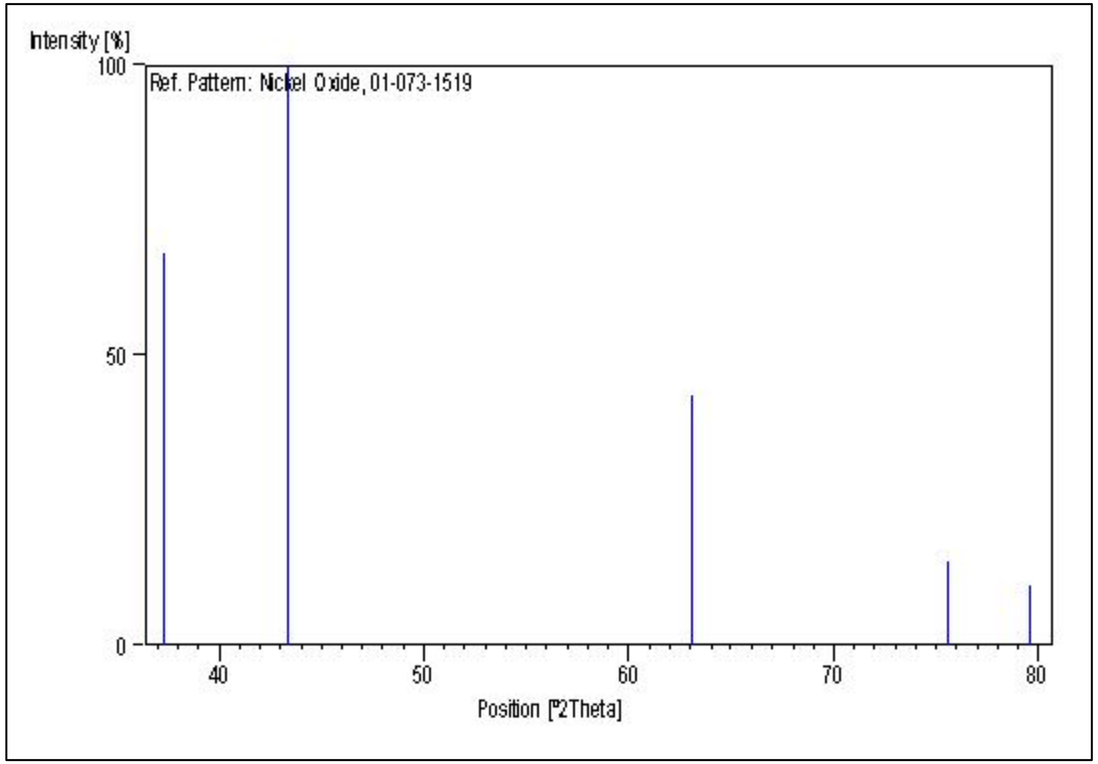
An ACS reagent grade sample recrystallized twice from hydrochloric acid.
X-ray pattern at 26°C
Merck Index, 8 th Ed., p. 956
Halite-galena-periclase group.

d A	I/I_1	hkl	d A	I/I_1	hkl
3.258	13	111			
2.821	100	200			
1.994	55	220			
1.701	2	311			
1.628	15	222			
1.410	6	400			
1.294	1	331			
1.261	11	420			
1.1515	7	422			
1.0855	1	511			
0.9969	2	440			
0.9533	1	531			
0.9401	3	600			
0.8917	4	620			
0.8601	1	533			
0.8503	3	622			
0.8141	2	444			

1.file number 2.three strongest lines 3.lowest-angle line 4.chemical formula and name 5.data on diffraction method used 6.crystallographic data 7.optical and other data 8.data on specimen 9.data on diffraction pattern.



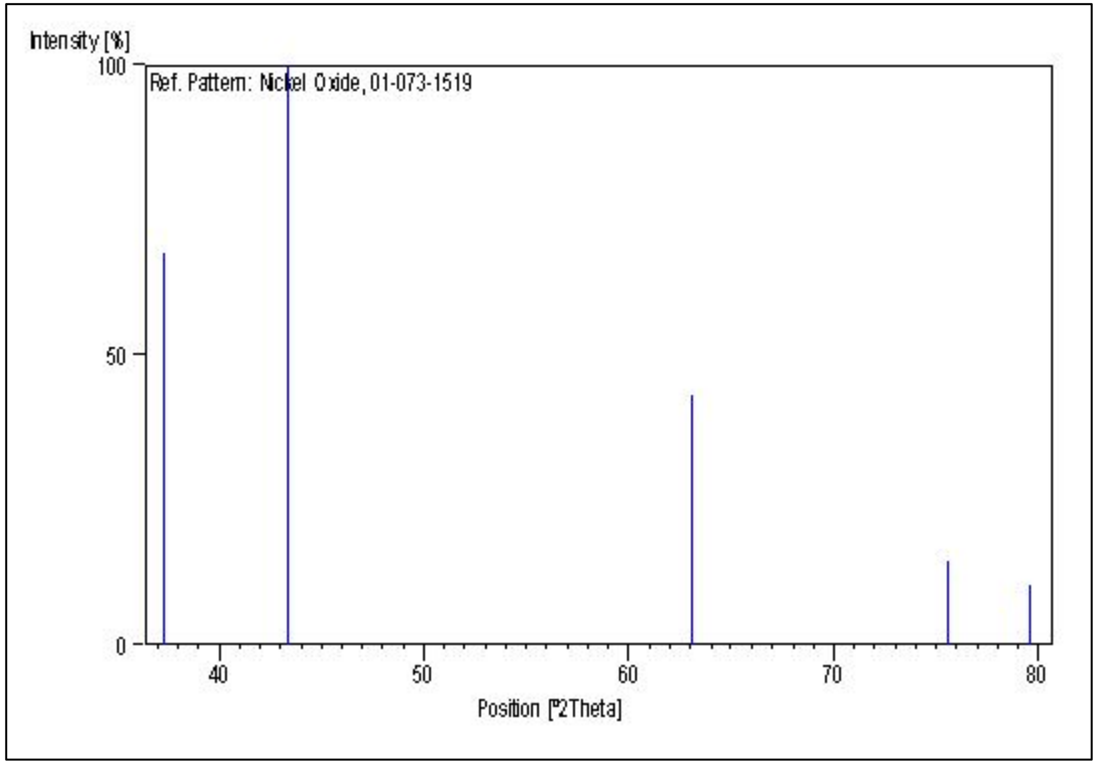
XRD pattern of NiO (experimental)



XRD pattern of NiO (Standard ICSD)

XRD pattern of NiO (Standard ICSD)

According to ICSD data
Reference code: 01-073-1519



Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	1	1	1	2.40663	37.335	67.7
2	2	0	0	2.08420	43.381	100.0
3	2	2	0	1.47375	63.024	43.1
4	3	1	1	1.25682	75.598	14.3
5	2	2	2	1.20331	79.606	10.3

X-ray Diffraction Data

- Significance of Peak Shape in XRD
  - Peak position
  - Peak width
  - Peak intensity

X-ray Diffraction Data

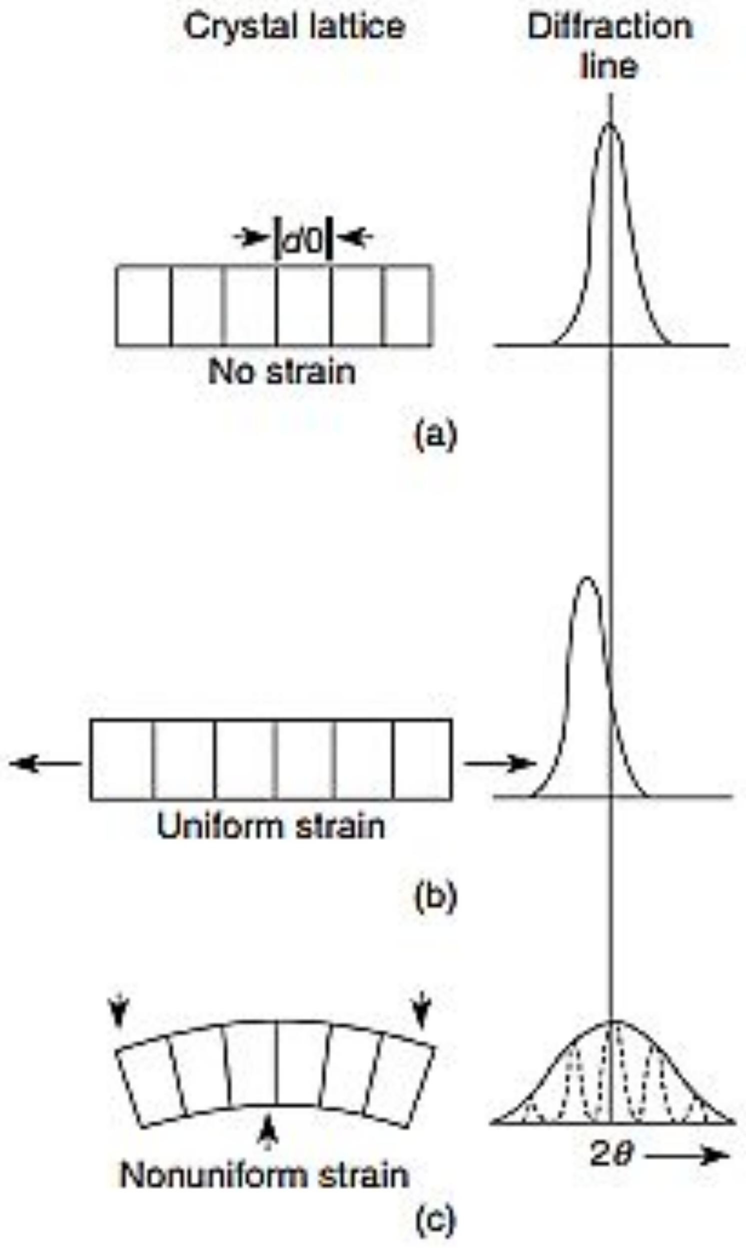
Peak Position

Effects of residual stress and strain on diffraction peak position and shape:

(a) No strain;

(b) Uniform strain;

(c) Nonuniform strain.



The tensile stress of increasing the spacing shifts a peak to lower 2θ, while the compression stress of decreasing the spacing shifts a peak to higher 2θ in the spectrum.

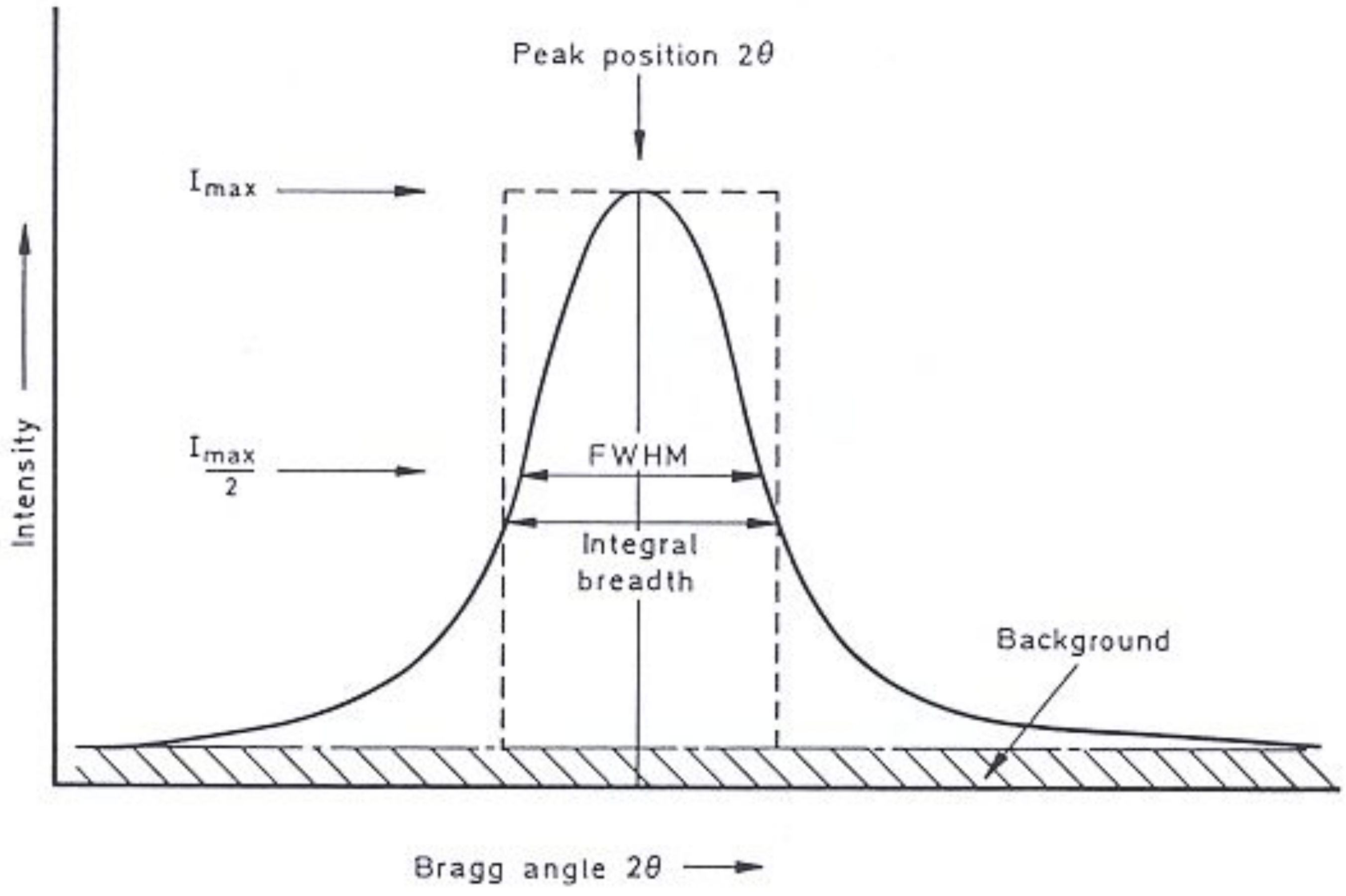
X-ray Diffraction Data

Peak Width-Full Width at Half Maximum (FWHM)

1. Crystallite Size
2. Residual strain

Scherer's formula

$$D = \frac{k\lambda}{FWHMcos\theta}$$



X-ray Diffraction Data

Peak Intensity

1. Preferential Orientation