Analytical Methods for Materials

Lesson 20

Components in an X-ray Diffractometer

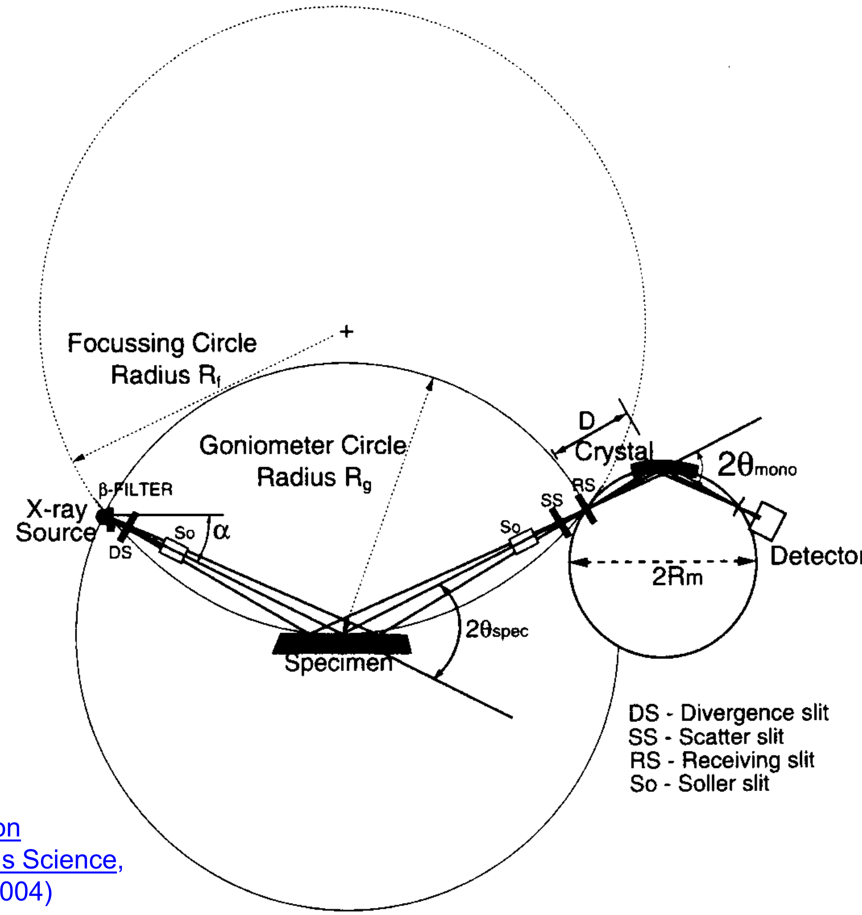
<u>Suggested Reading</u>

Chapter 6 in Cullity & Stock

Chapter 2 in Brandon & Kaplan

Geometry of the X-ray Diffractometer

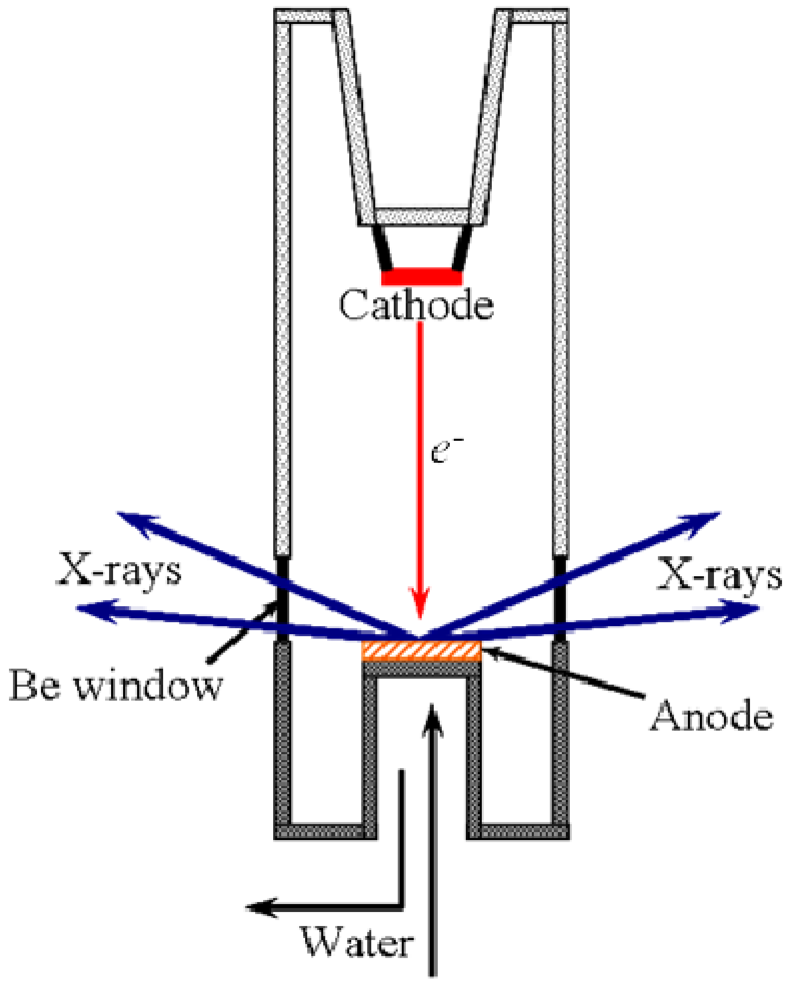
- Generically, diffractometers consist of:
  - X-ray source
  - X-ray detector
  - Specimen to be examined
  - Other things
    - Monochromators
    - Filters
    - Slits
    - Etc…



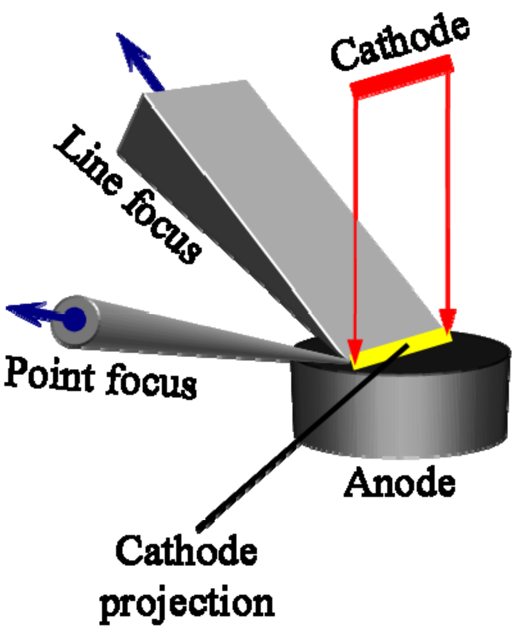
D.J. Dyson, X-ray and Electron Diffraction Studies in Materials Science, Maney Publishing, London (2004)

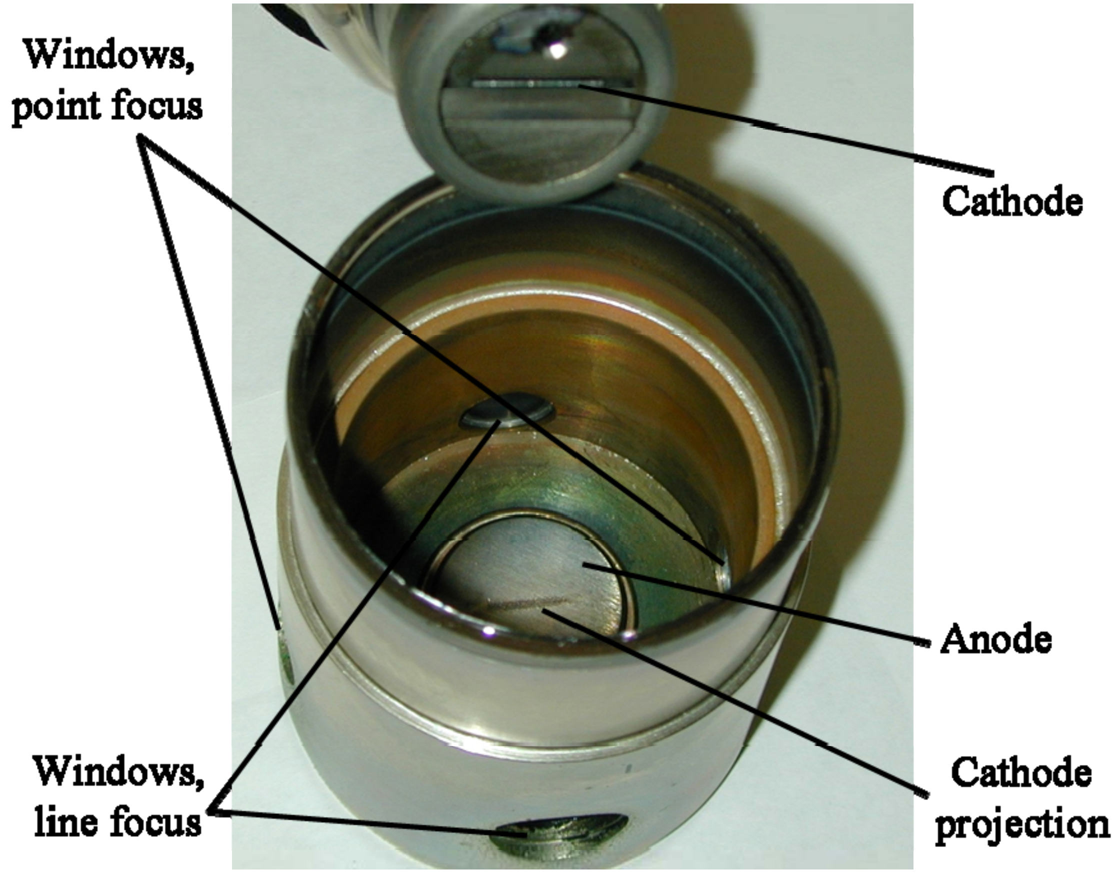
Fig. 5.5 The geometry of the diffractometer arrangement: DS is the divergence slit, SS is the scatter slit, RS is the receiving slit, So is the soller slit.

X-ray tube



Adapted from Vitalij K. Pecharsky and Peter Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, Kluwer Academic Publishers, 1999.





X-ray tubes will have line focus and point focus windows

Soller Slits

Divergence Slits

- Closely spaced parallel metal planes parallel to the plane of the diffractometer circle that collimate the incident beam. They are usually constructed of a high atomic number element to maximize absorption.

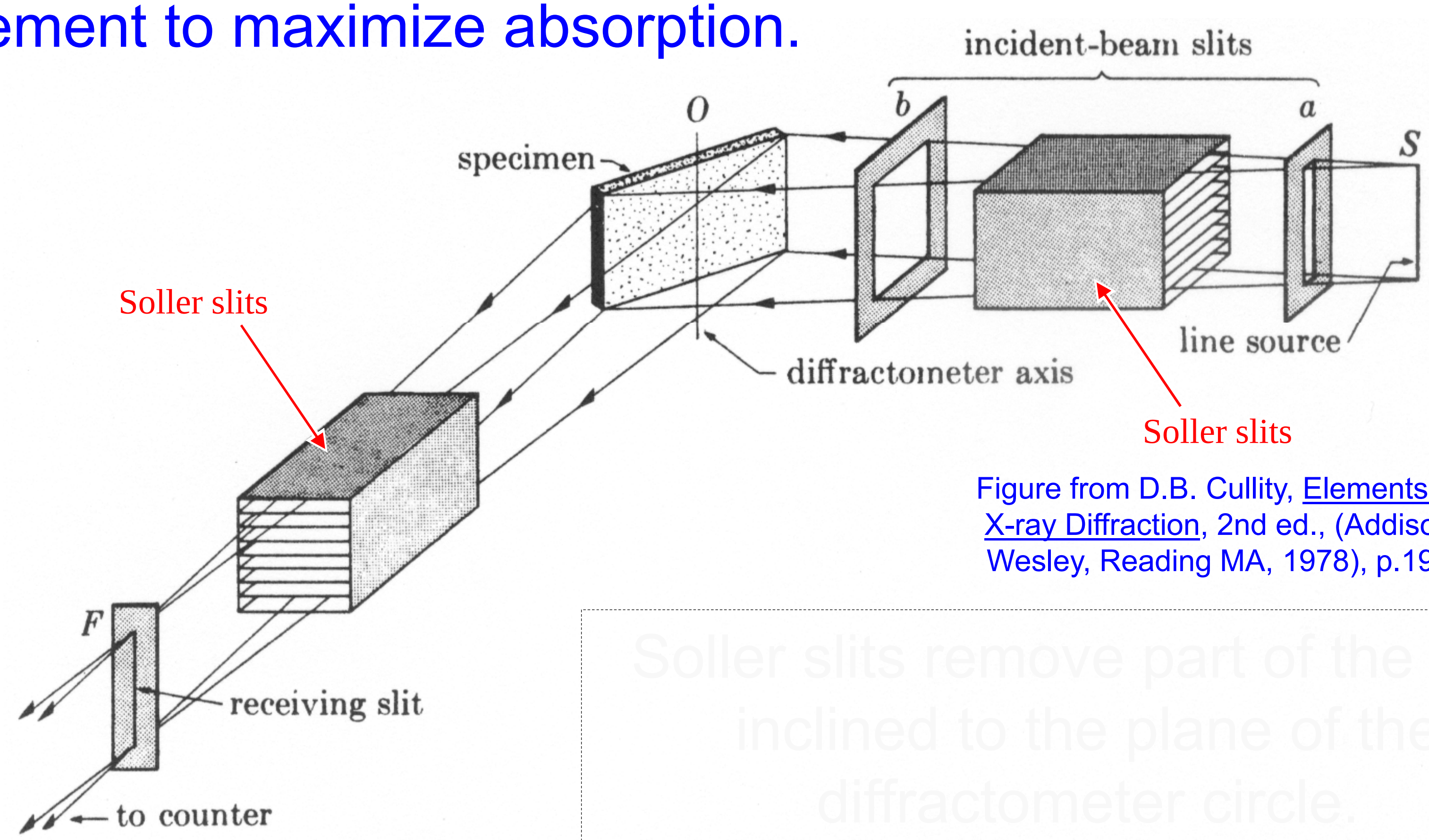
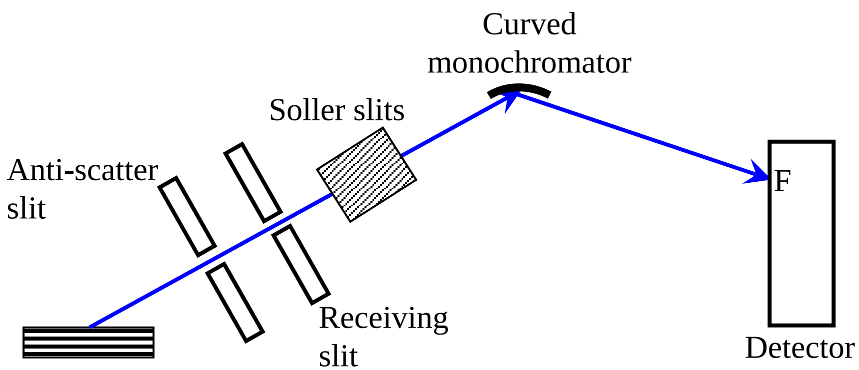


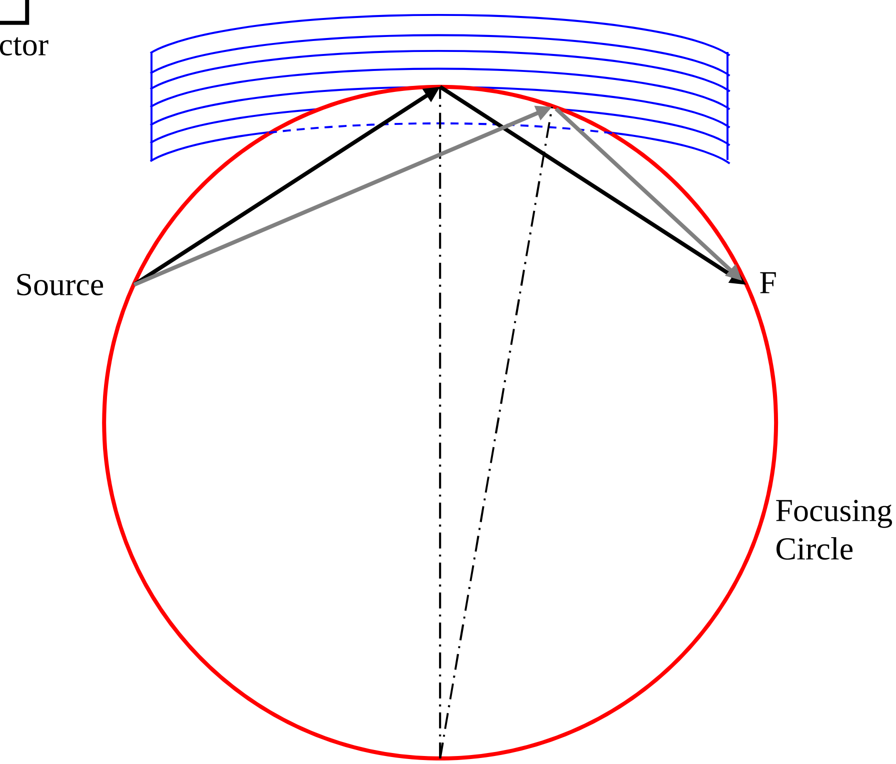
Figure from D.B. Cullity, Elements of X-ray Diffraction, 2nd ed., (Addison Wesley, Reading MA, 1978), p.199

Soller slits remove part of the rays inclined to the plane of the diffractometer circle.

Monochromator



A device in neutron and X-ray optics to select a defined wavelength of the radiation for further purpose



They re-focus the diffracted beam just as a parabolic mirror is used to focus light.

Eliminates Fluorescence!

X-ray Detectors

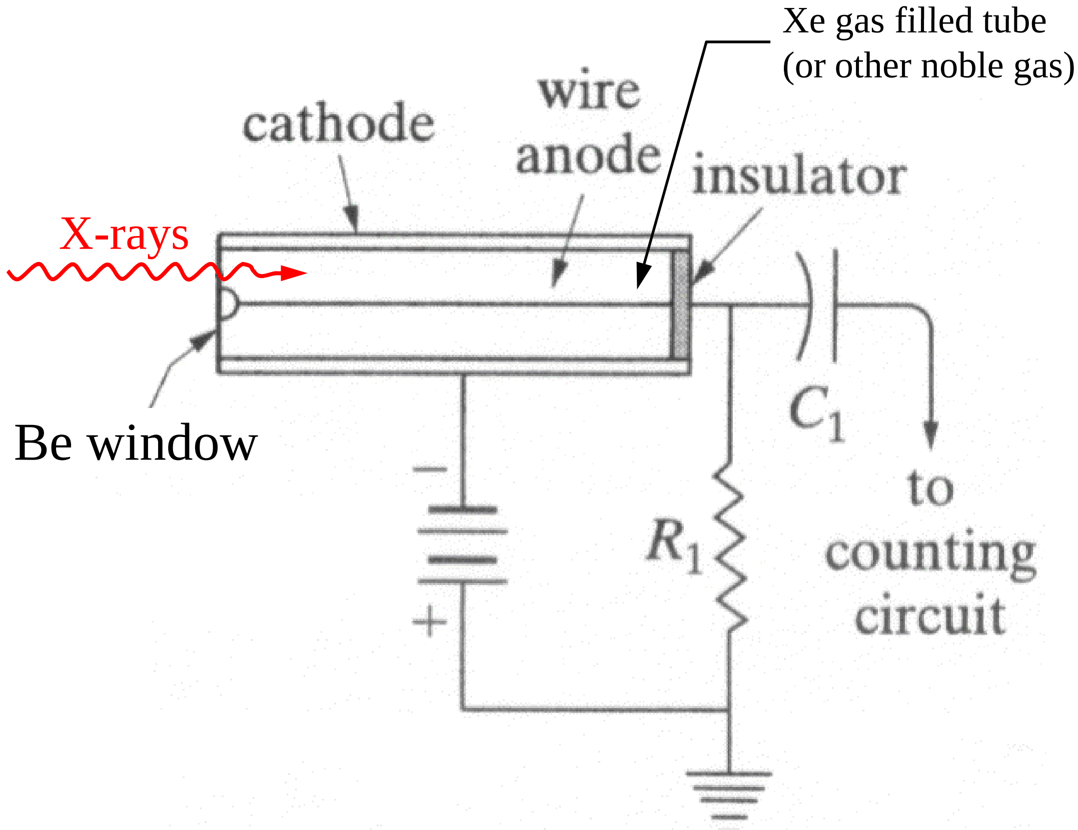
Table i7.1 Properties of different detector types.

	Proportional counter	**Scintillation counter**	**Solid-state detector**
Working principle	Electron–ion pair cascade	Conversion to light and electrons and electron multiplication	Generation and separation of electron–hole pairs
Transducing medium	Xe	NaI:Tl	Si, Ge
Noise rate (cps)	1	0.1–10	<0.1
Maximum count rate (cps)	10^5–10^6	10^5–10^6	10^4
Resolution $\Delta E/E$ (%)	18–20	40–50	depends on type
Costs	Low	Medium	High

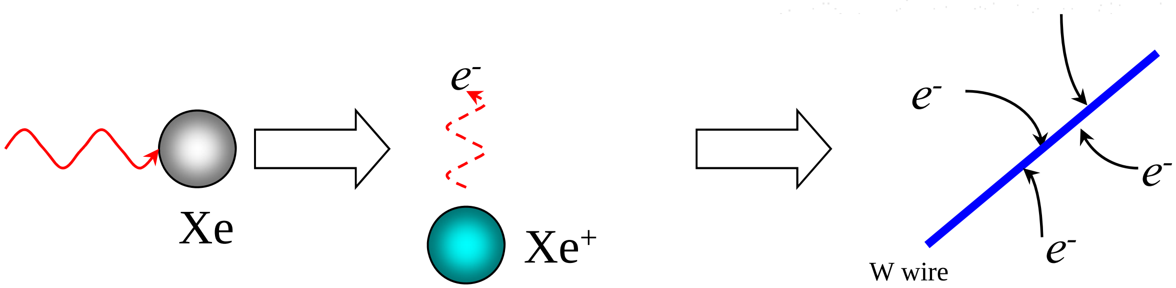
From M. Birkholz, Thin Film Analysis by X-ray Scattering, Wiley-VCH, Weinheim, 2006, p. 254

Proportional Detector

- Most common type of detector in powder diffraction.



Adapted from B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd Edition*, Prentice-Hall, Upper Saddle River, NJ (2001) page 203.



The way proportional detectors work

- X-rays enter the tube and are absorbed by gas atoms.
  - Results in the emission of a photoelectron (i.e., an electron produced by ionization of an atom by a photon).

- Released electrons are attracted to the W wire, resulting in a charge pulse.
  - The charge the collects on the W wire is “proportional” to the energy of the incident x-ray photon. This allows us to distinguish between photons with different E and λ.

Scintillation Detector

- Uses a NaI single crystal doped with Thallium ions (Tl^{+}) attached to a photocathode and photo-multiplier tube.

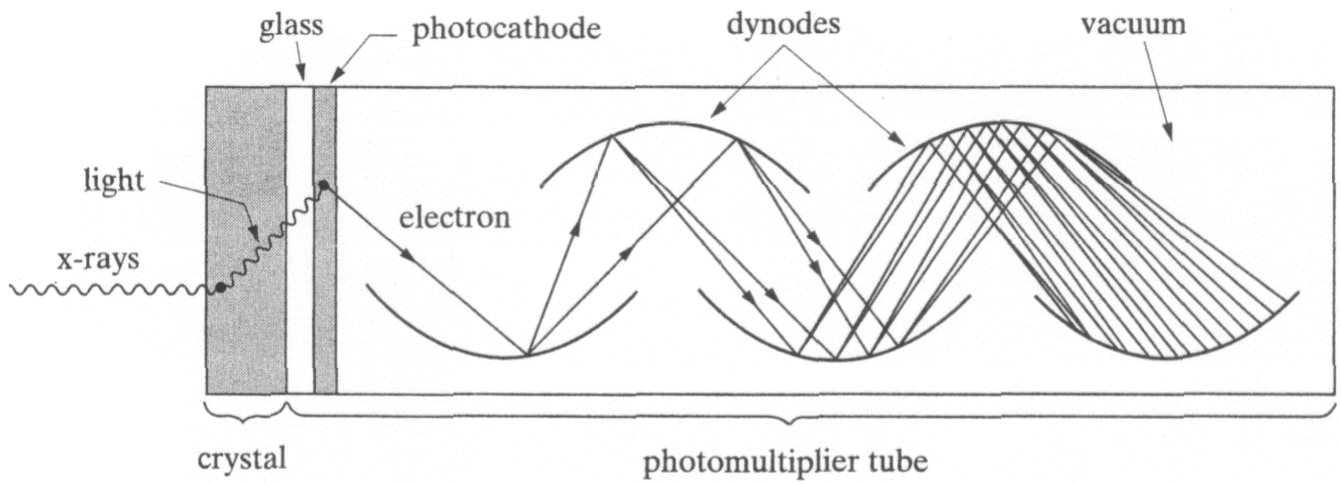
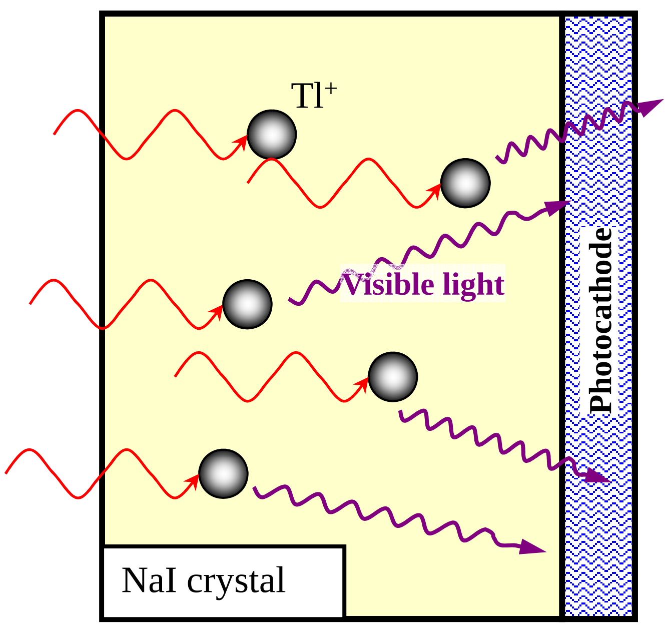


Figure 6-21 Scintillation detector (schematic). Electrical connections not shown.



Adapted from B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd Edition*, Prentice-Hall, Upper Saddle River, NJ (2001) page 207.

The way scintillation detectors work

1. Incident x-rays cause the crystal to fluoresce in the violet part of the EM spectrum.

2. A flash of light (*scintillation*) occurs for every X-ray photon absorbed.

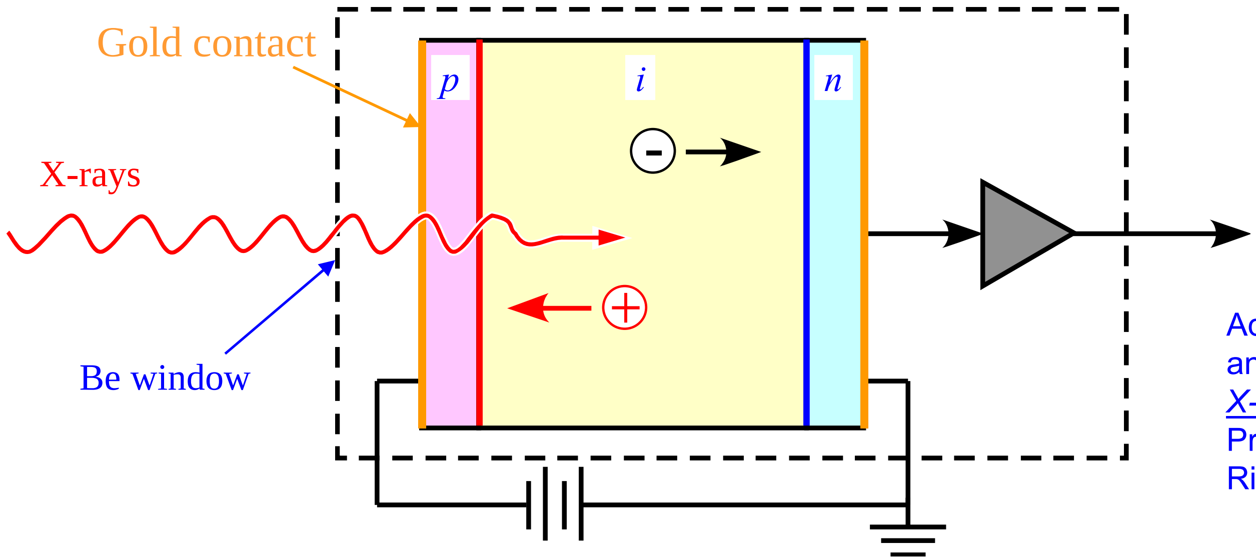
3. Light is measured with a photomultiplier attached to the photocathode.

4. Amount of light emitted is proportional to the X-ray intensity.

5. The magnitude of the light pulses is proportional to the energy of the X-rays.

Has lower resolution than proportional or solid state detectors.

Solid State Detector



Adapted from B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd Edition*, Prentice-Hall, Upper Saddle River, NJ (2001) page 210.

Schematic of a Si(Li) detector and a field effect transistor (FET) preamplifier. Both are in a cooled evacuated space. X-rays enter through a beryllium window. The detector is operated at around 1000 V.

- Based on the PIN diode
- Allows separation of CuK_α and CuK_β
- Eliminates the need for a β-filter or a monochromator to select K_α wavelengths.
- If it's advantageous one can record the XRD pattern using K_β radiation as opposed to K_α.
- Lower background signal which leads to improved signal to noise ratios.

The way solid state detectors work

- X-rays excite electrons from the valence band into the conduction band creating an electron hole pair.
- Application of a reverse bias potential causes the electrons and holes to separate, which allows a charge pulse of electrons to be measured.
- The number of electrons or holes is directly proportional to the energy of the x-ray photon.
- Solid state detectors offer the highest levels of efficiency and the highest resolution.

XRD Patterns

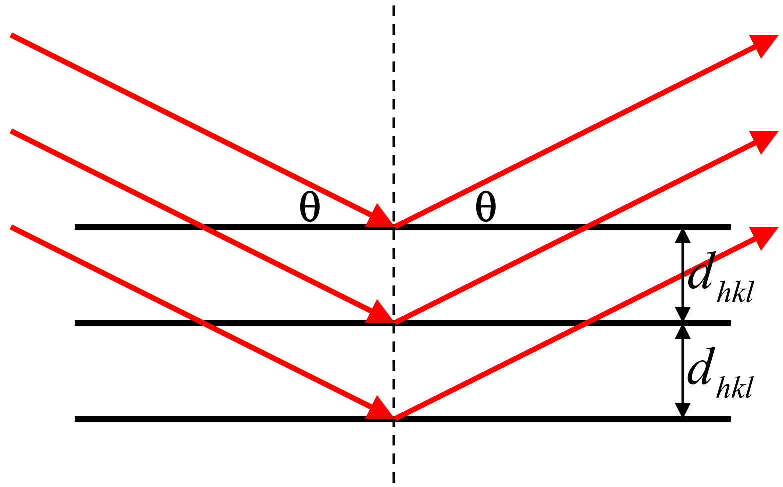
- Peak positions depend upon:
  - X-ray wavelength λ
  - Crystal structure
  - Crystal Size

- Long wavelengths spread the pattern over a wider 2θ range (yields fewer reflections).

- Short wavelengths result in more reflections.

Bragg's law tells what conditions are required for diffraction.

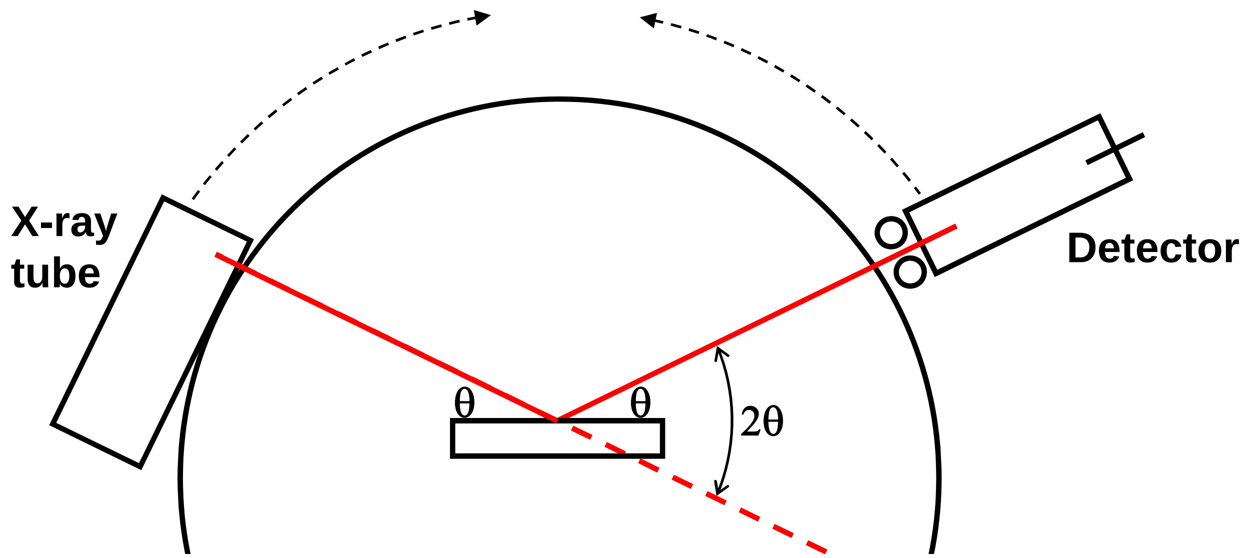
$$\lambda = 2d_{hkl} \sin\theta$$



- For parallel planes of atoms, with a space d_{hkl} between the planes, constructive interference only occurs when Bragg's law is satisfied.
  - A family of planes will produce a diffraction peak only at a specific angle θ.
  - Plane normal must be parallel to the diffraction vector
- **The space between diffracting planes of atoms determines peak positions.**
- **The peak intensity is determined by what atoms are in the diffracting plane.**

Adapted from the notes of Dr. Scott Speakman, MIT Center for Materials Science and Engineering, http://prism.mit.edu/xray

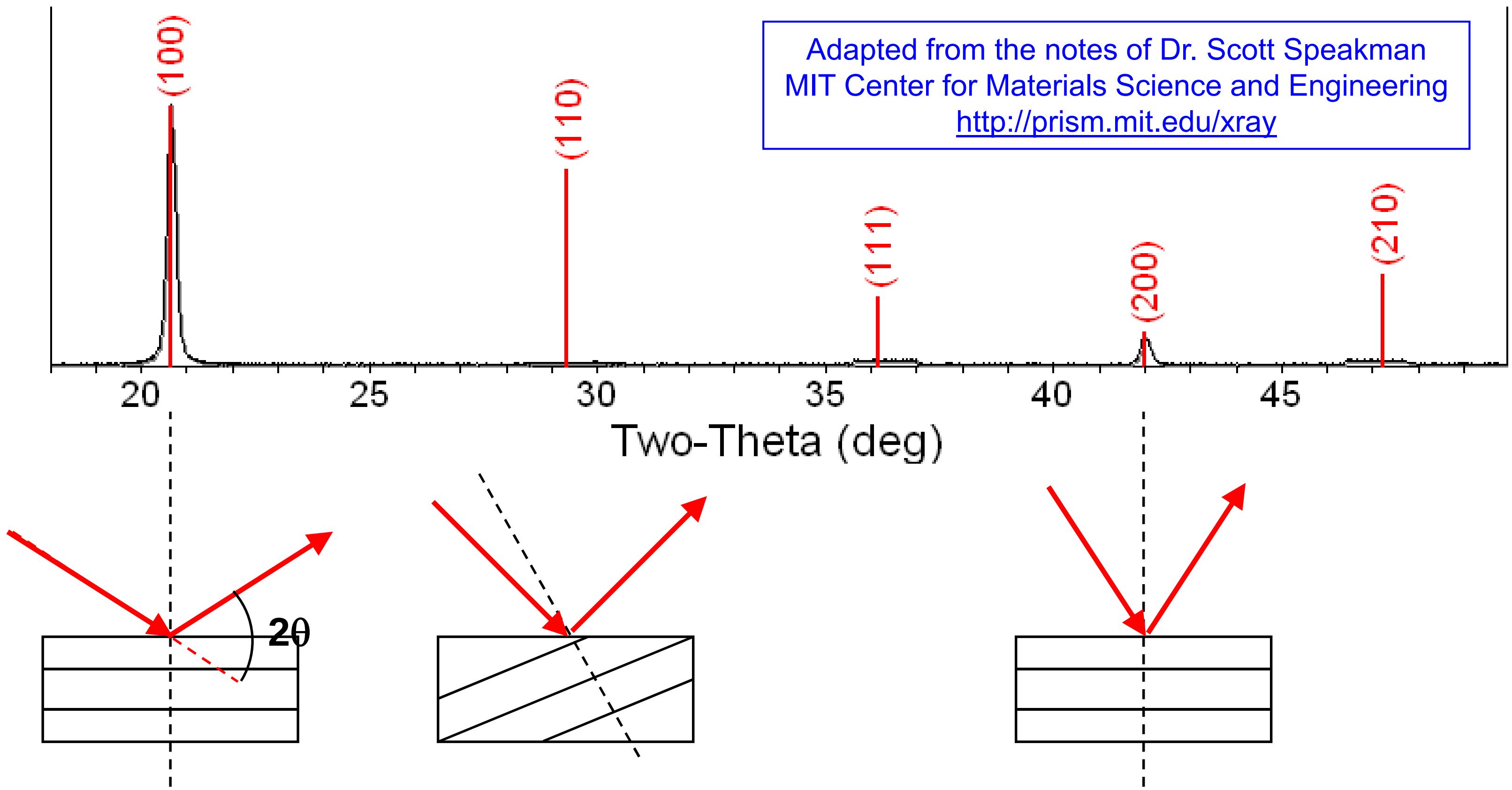
Our diffractometers use the Bragg-Brentano geometry.



- The incident angle, θ, is defined between the X-ray source and the sample.
- The diffracted angle, 2θ, is defined between the incident beam and the detector angle.
- The incident angle θ is always ½ of the detector angle 2θ .
- In our θ:2θ instrument (e.g. Philips 3720), the tube is fixed, the sample rotates at θ °/min and the detector rotates at 2θ °/min.
- In a θ:θ instrument (e.g. Bruker D8 Discover with GADDS), the sample is fixed and the tube rotates at a rate -θ °/min and the detector rotates at a rate of θ °/min.

Adapted from the notes of Dr. Scott Speakman, MIT Center for Materials Science and Engineering, http://prism.mit.edu/xray

A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.

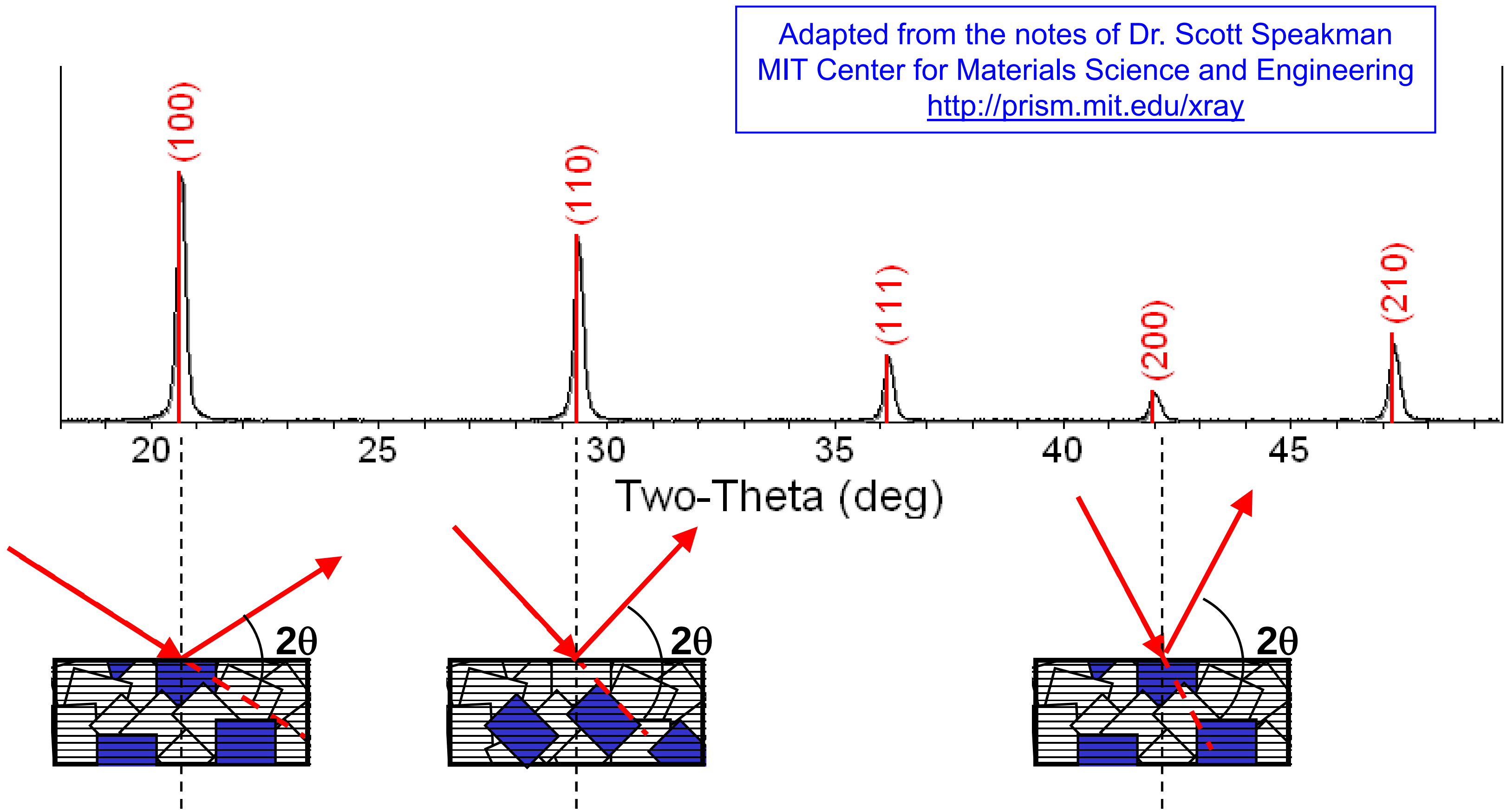


At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.

The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.

The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.



- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

← **Type of Radiation**

Reflection (peak)

2θ	MoKα (0.709 Å)	CuKα (1.541 Å)	CrKα (2.291 Å)
(110)	17.54	38.67	58.96
(200)	24.90	55.84	88.21
(211)	30.62	69.99	116.94
(220)	35.50	82.94	159.62
(310)	39.86	95.53	>180.00
(222)	43.85	108.46	
(321)	47.57	122.33	
(400)	51.69	138.95	4 Reflections
(411)	54.43	166.75	
(420)	57.64	>180.00	

D.J. Dyson, X-ray and Electron Diffraction Studies in Materials Science, Maney Publishing, London (2004)

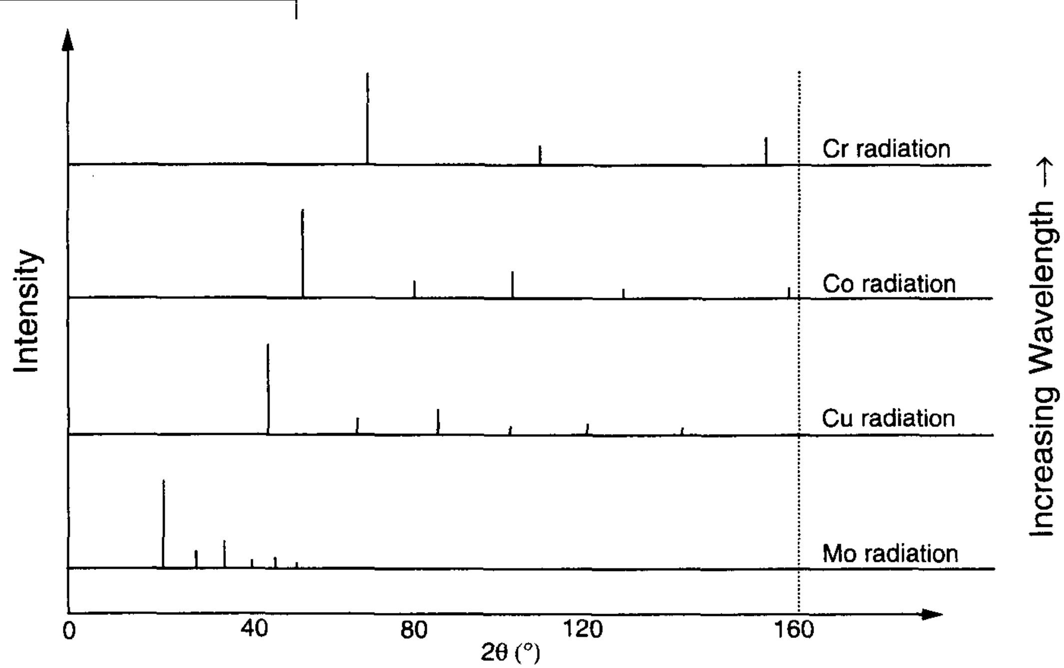
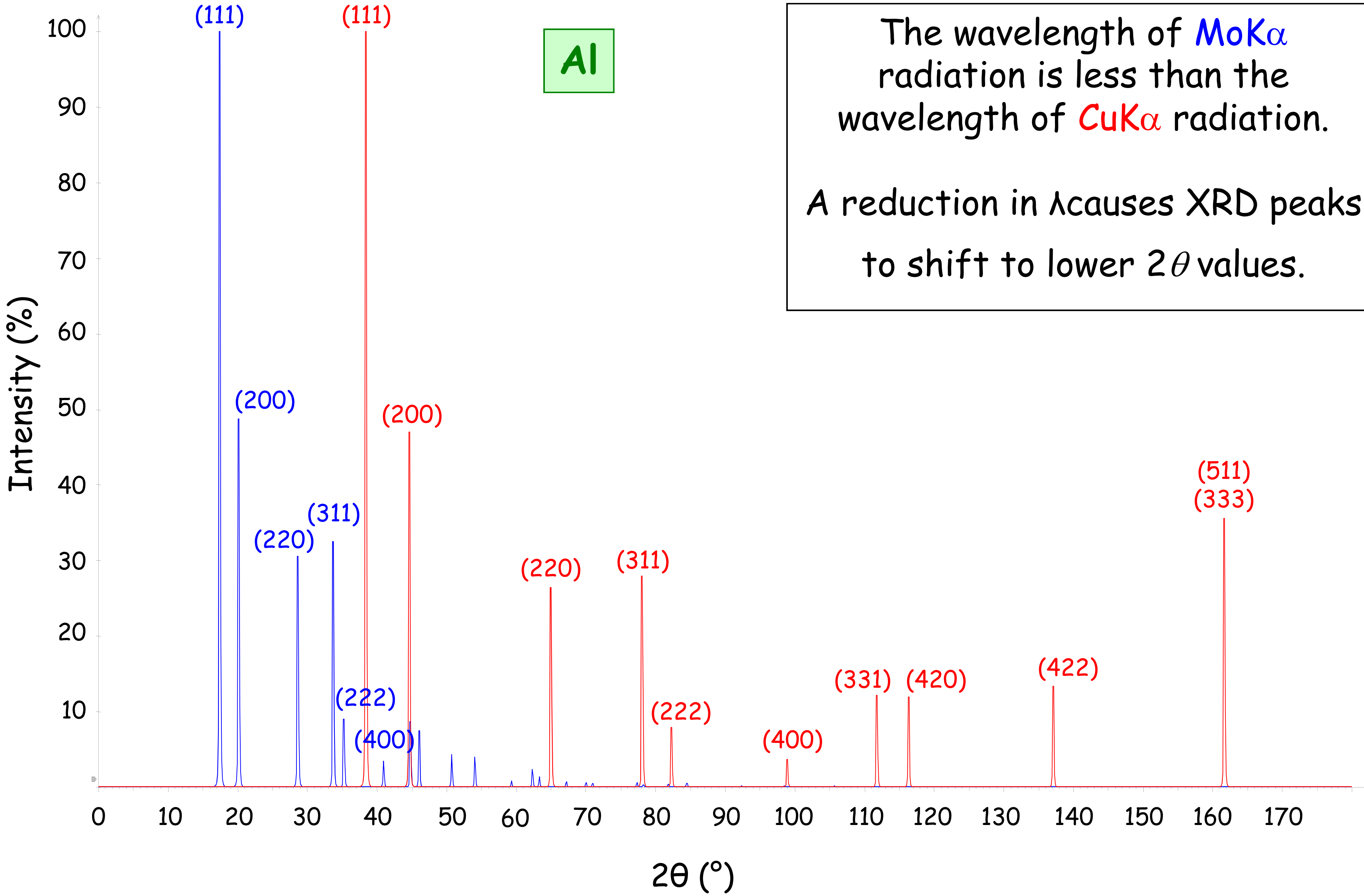


Fig. 5.1 Dispersion: the effect of the wavelength of the radiation.



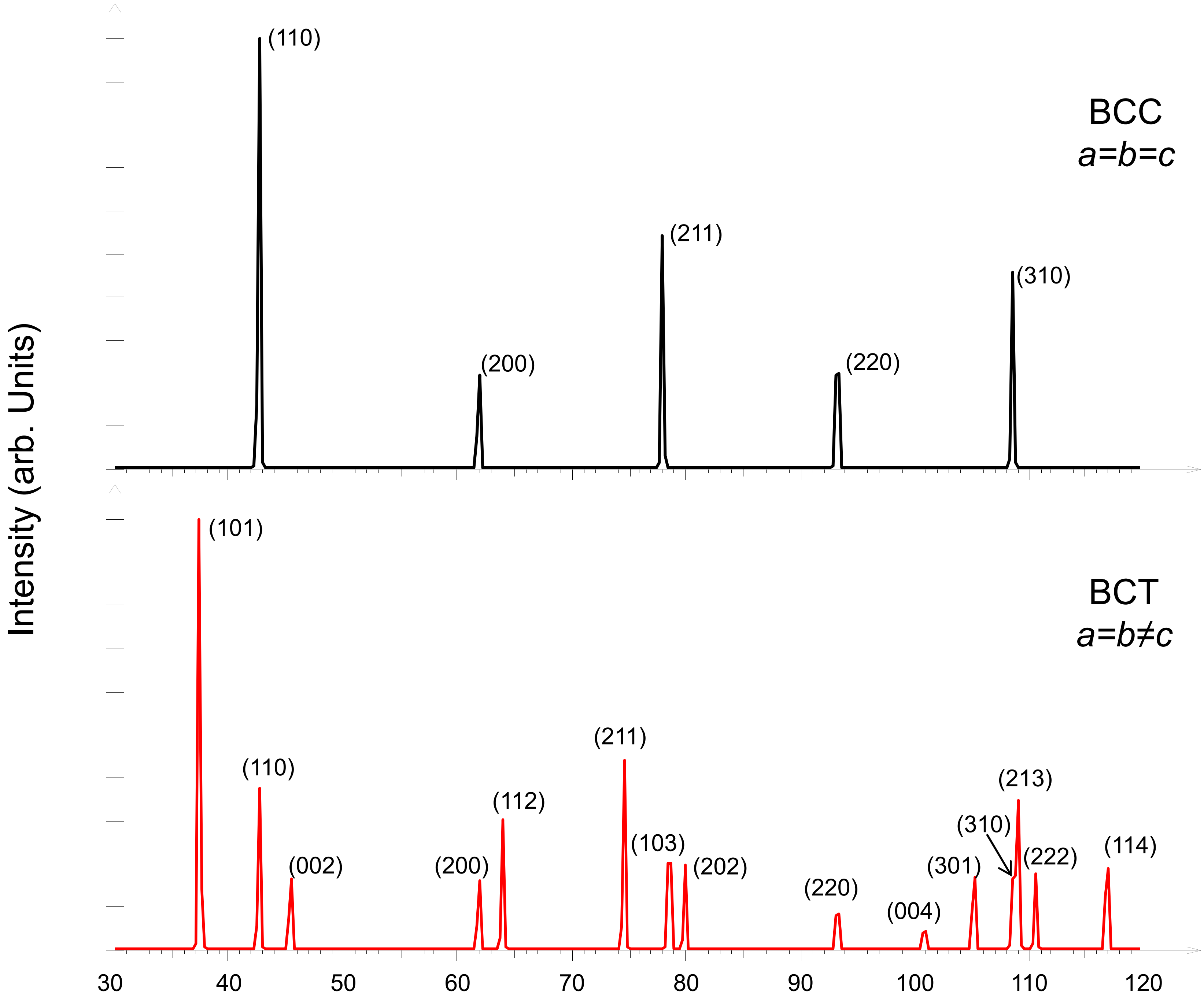
The wavelength of MoKα radiation is less than the wavelength of CuKα radiation.

A reduction in λ causes XRD peaks to shift to lower 2θ values.

Influence of Symmetry

- As crystal symmetry decreases, the number of diffraction peaks increases.

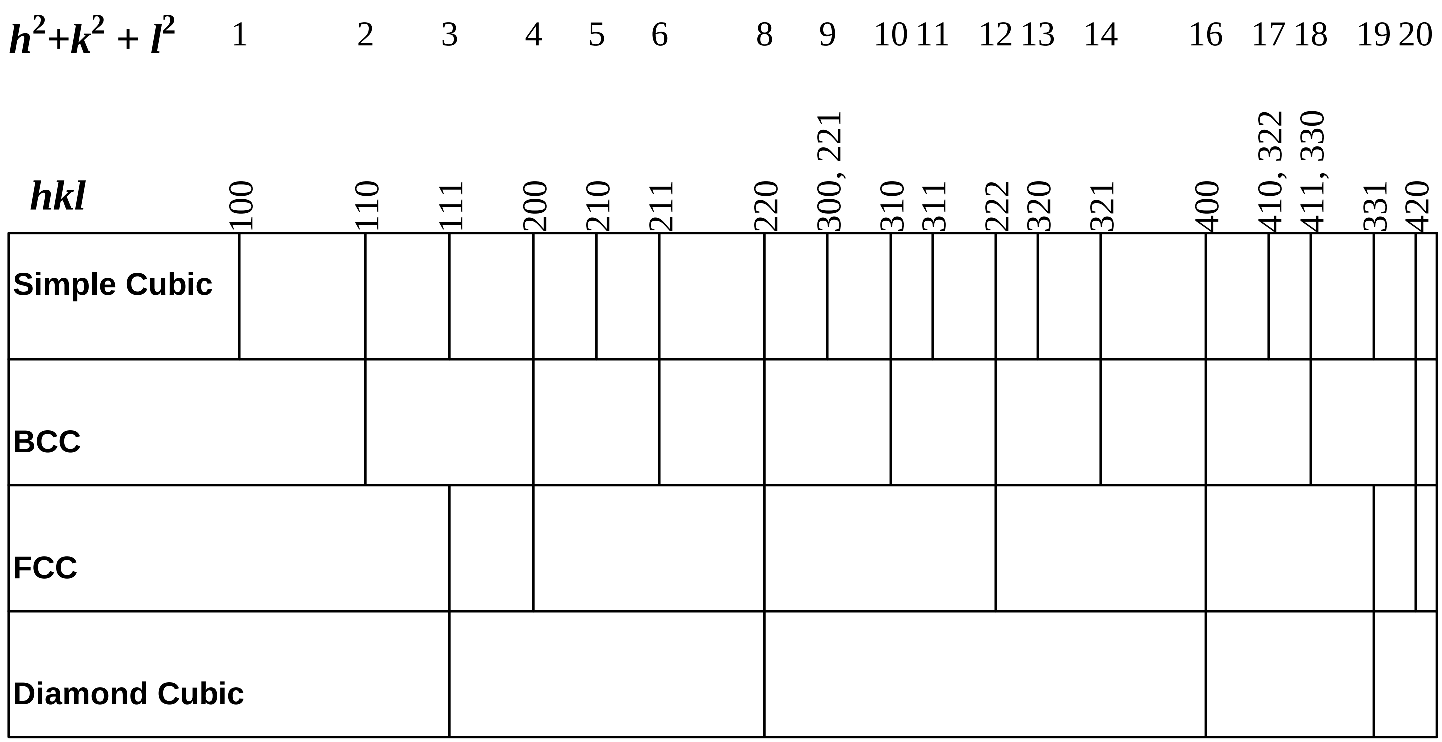
- Examples:
  - Cubic crystals – relatively high symmetry – few peaks (exception is simple cubic, which shows all reflections)
  - Tetragonal crystal – lower symmetry than cubic – a few more reflections.
  - Hexagonal crystals – low symmetry – large number of peaks.
  - WHY?



Intensity (arb. Units)
BCC
a=b=c
(110)
(200)
(211)
(220)
(310)
BCT
a=b≠c
(101)
(110)
(002)
(200)
(112)
(211)
(103)
(202)
(220)
(004)
(301)
(310)
(213)
(222)
(114)
30
40
50
60
70
80
90
100
110
120

For Cubic Systems

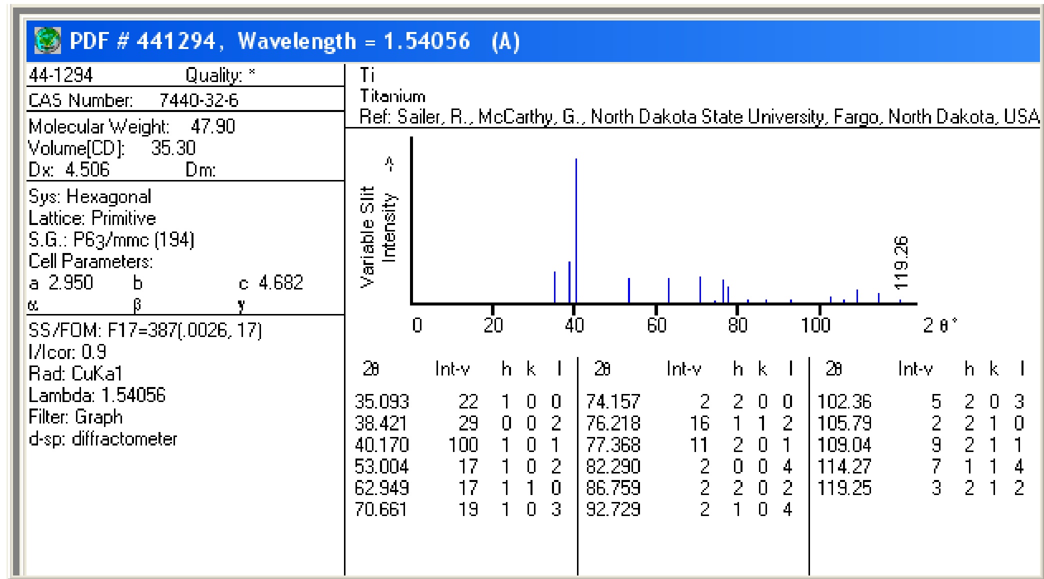
- For cubic structures it is often possible to distinguish crystal structures by considering the periodicity of the observed reflections.



Schematic comparison of XRD results from materials with differing CUBIC crystal structures

Powder Diffraction Files

- Collections of single-phase powder diffraction patterns in the form of tables of interplanar spacing *d* and corresponding relative intensities.
- Compiled by the International Centre for Diffraction Data (ICDD).
- Formerly known as the Joint Committee on Powder Diffraction Standards (JCPDS).



2θ	Int-v	h	k	l	2θ	Int-v	h	k	l	2θ	Int-v	h	k	l
35.093	22	1	0	0	74.157	2	2	0	0	102.36	5	2	0	3
38.421	29	0	0	2	76.218	16	1	1	2	105.79	2	2	1	0
40.170	100	1	0	1	77.368	11	2	0	1	109.04	9	2	1	1
53.004	17	1	0	2	82.290	2	0	0	4	114.27	7	1	1	4
62.949	17	1	1	0	86.759	2	2	0	2	119.25	3	2	1	2
70.661	19	1	0	3	92.729	2	1	0	4					

- A typical ICDD card is reproduced above. This card was retrieved from the 1999 release of the ICDD card file using the PCPDF-Win program.

XRD Patterns

- Consists of a series of sharp peaks (reflections)
- Each peak corresponds to x-rays diffracted from a specific family of planes.
- We usually report an integrated (relative) intensity rather than the absolute intensity.
- Intensity of the reflections depends on:
  - Structure factors
  - Slit widths
  - Voltage and current of x-ray source

Collection of XRD Patterns

- Continuously scanning $\Rightarrow$ (good **qualitative or quantitative** information)

- Step scanning $\Rightarrow$ (good **quantitative** information)

- With more modern machines, all results tend to be more quantitative. On our instrument continuous scanning is just as accurate as step scanning.

- Scan rate, step size, and count time control peak-to-background ratio (i.e., noise).

Collection of XRD Patterns

- Influences resolution (ability to find “small” peaks).
- Typical scan rates: 1-2° 2θ/min
- Typical step sizes: 0.02° 2θ steps (2 sec/step)
- Each experiment is different. You must use your common sense to determine which conditions are best for your application.