Handout 8: Data Collection

Sources, detectors and methods

Chem 6850/8850

X-ray Crystallography

Department of Chemistry & Biochemistry

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Measurement of diffracted beams

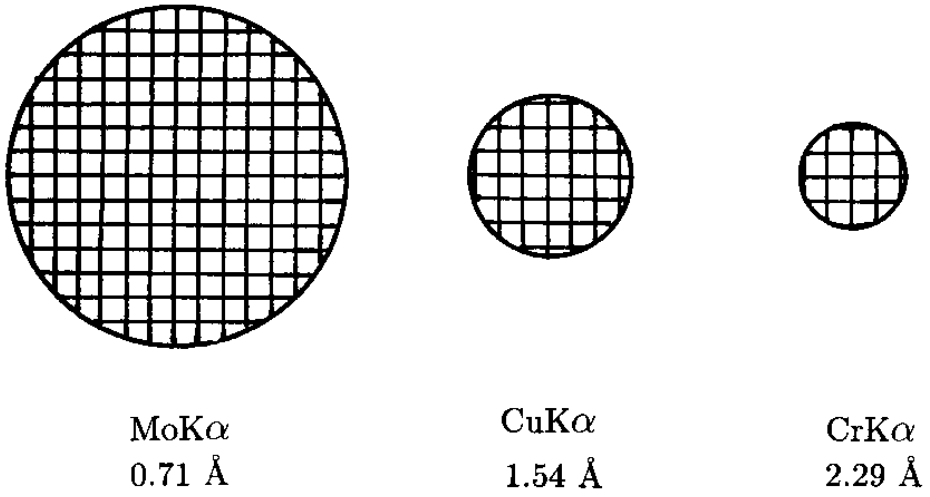
- **Position of diffracted beams gives information about unit cell dimensions and translational symmetry elements**
  - systematic absences
- **Intensity of beams arises from electron density distribution inside the unit cell**
  - type and position of atoms
- **There are many different ways of recording the diffracted beams**

Important parts of the experimental setup

- **Radiation source**
  - X-ray tubes, synchrotrons, neutrons
- **Specimen mount**
  - single crystal or powder
- **Detector setup**
  - film, image plate, point detector, area detector
- **Experimental method**
  - how do you sample reciprocal space, how much of it

How many reflections are needed?

- **For each parameter to be determined, you should measure ~10 reflections**
- **The number of reflections that can be measured depends on the X-ray wavelength**
  - $N = (4\pi/3)(8V/n\lambda^3)$
    - n = number of lattice points in the unit cell



"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

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Radiation sources

- **X-ray tube**
  - lab X-ray source
  - line source with white background
  - low flux
- **Synchrotron radiation**
  - high flux
  - white, tunable radiation
- **Neutrons from nuclear reactor or spallation source**
  - most expensive method
  - useful for light elements or distinction of elements that are close in Z

X-ray tubes

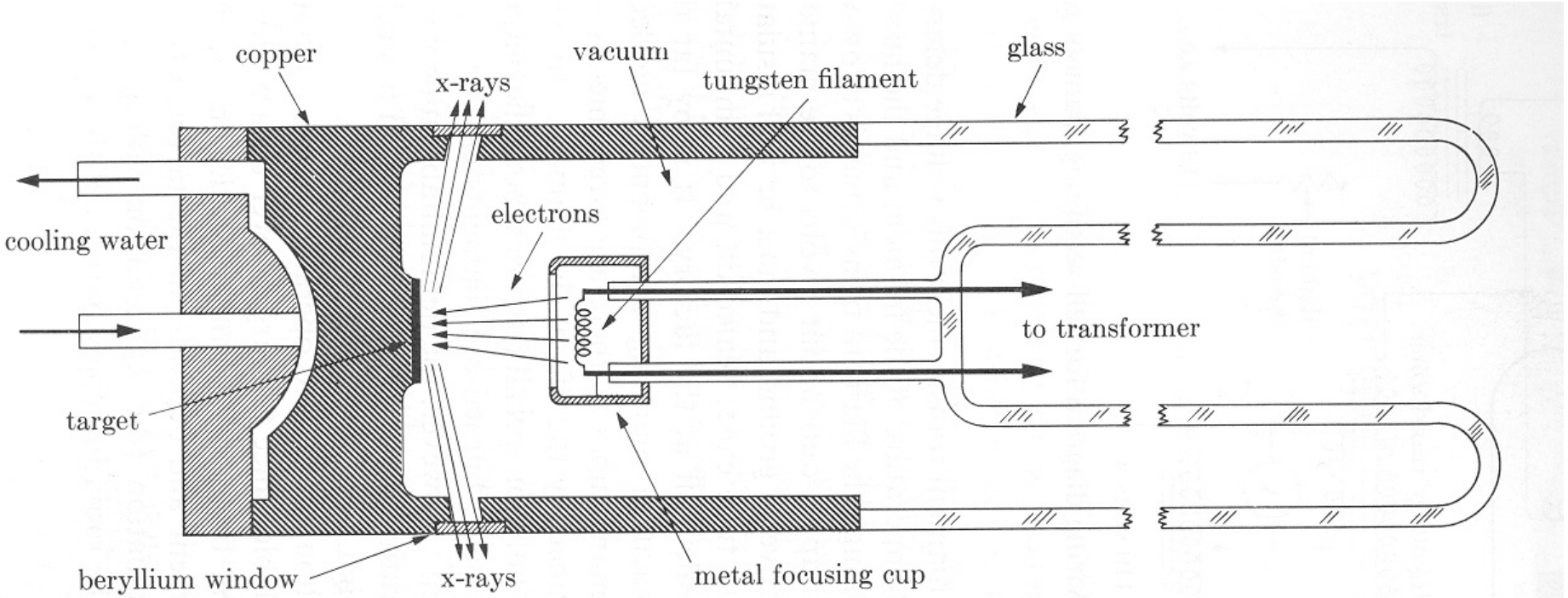

Fig. 1–15 Cross section of sealed-off filament x-ray tube (schematic).

"Elements of X-ray Diffraction", Cullity and Stock, Prentice Hall College Div., 3rd edition, 2001.

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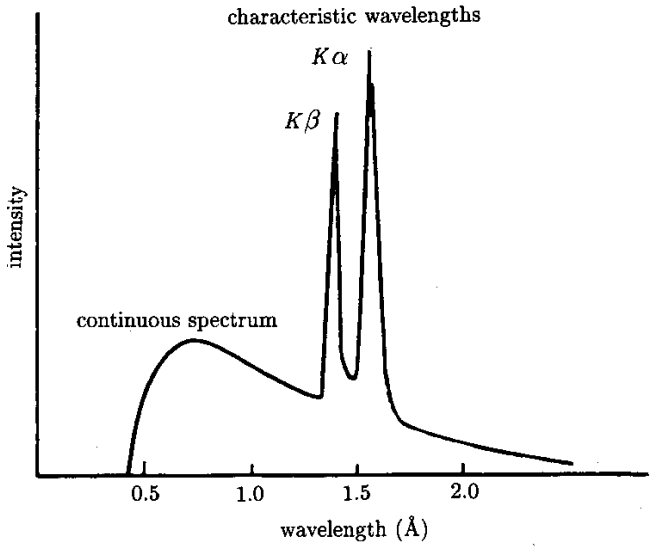
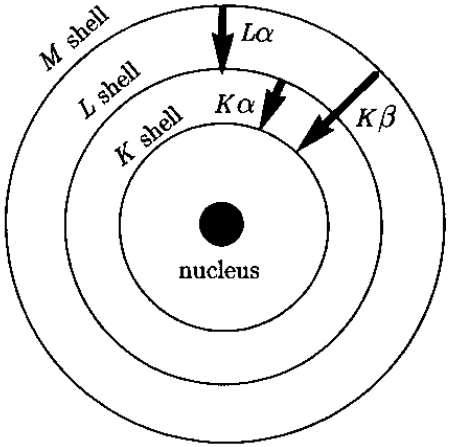
Radiation from X-ray tubes

- **X-rays are produced by hitting a metal target with an electron beam**
  - white radiation from deceleration of electrons in target, called *Bremsstrahlung*
  - characteristic radiation from electronic transitions after an inner shell electron is knocked out





"Elements of X-ray Diffraction", Cullity and Stock, Prentice Hall College Div., 3rd edition, 2001.

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Monochromatic X-rays

- **The majority of lab X-ray experiments requires monochromatic (single wavelength) radiation**
  - Exception: Laue patterns
- **X-ray tubes produce white and characteristic radiation**
  - White radiation has low intensity, but having more than one characteristic line would lead to superimposed patterns!
- **We need to monochromate the beam to get easily analyzable data**
  - Always done on incident beam for single crystal experiments
  - Incident beam, diffracted beam, and detector options are possible for powder setups
- **Generally, the Kα line is used (most intense)**

Making Radiation Monochromatic

- **Two common options:**
  - X-ray filters
  - Monochromators
- ***X-ray filters* absorb X-rays of unwanted wavelength**
  - Nickel filter for copper tubes, zirconium or niobium for molybdenum tubes
- ***Monochromators* diffract the desired wavelength**
  - Graphite 200 or others
  - Usually 2-bounce or 4-bounce setups
- **For powder experiments: Energy-sensitive detectors**
  - No monochromation necessary, only X-rays of the desired wavelength are counted
  - Very low background, very good intensity

X-ray Filters

- **X-ray filters absorb unwanted radiation**
- **Filters must be chosen to match the target**
  - Ni for Cu
  - Zr or Nb for Mo
- **Choose a filter with an absorption edge between the desired and all undesirable wavelengths**
  - Atomic number just below atomic number of the target element
- **A filter will not *eliminate*, but significantly reduce the intensity of unwanted wavelengths**
  - The thicker the filter, the more of the unwanted wavelengths is absorbed
  - But some Kα intensity is also absorbed → tradeoff

X-ray Filters

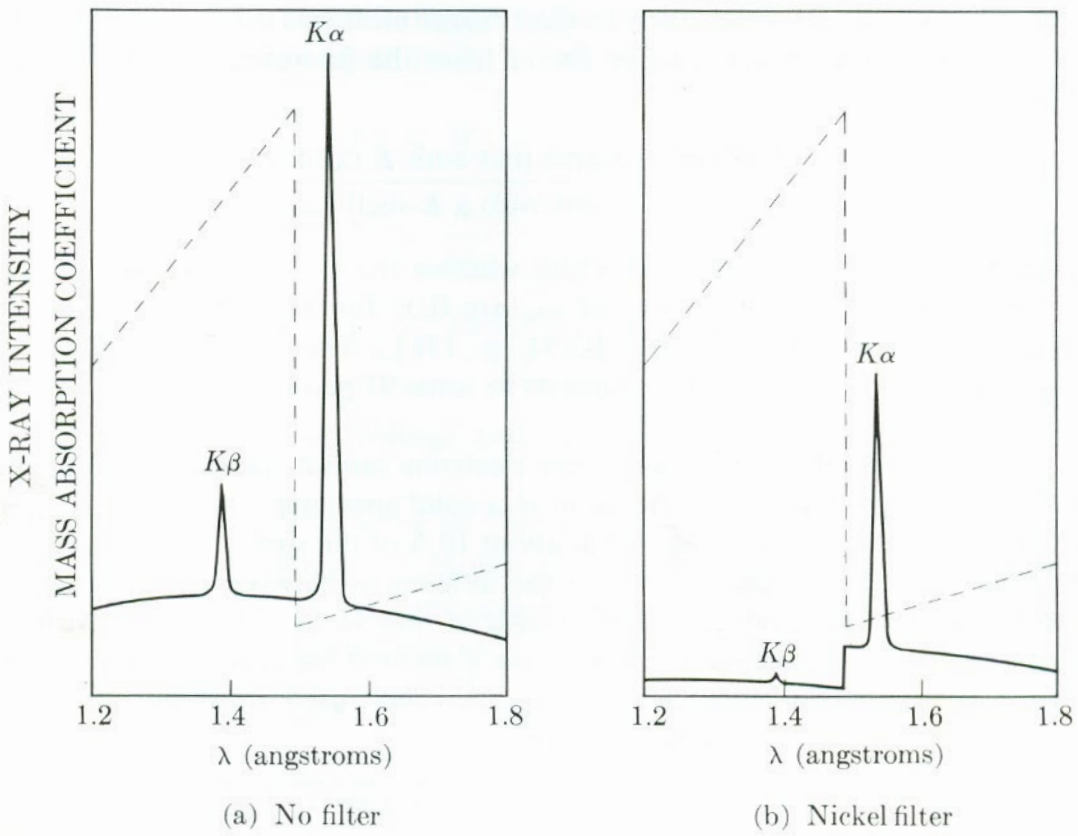

Fig. 1–13 Comparison of the spectra of copper radiation (a) before and (b) after passage through a nickel filter (schematic). The dashed line is the mass absorption coefficient of nickel.

Cullity; "Elements of X-ray Diffraction"

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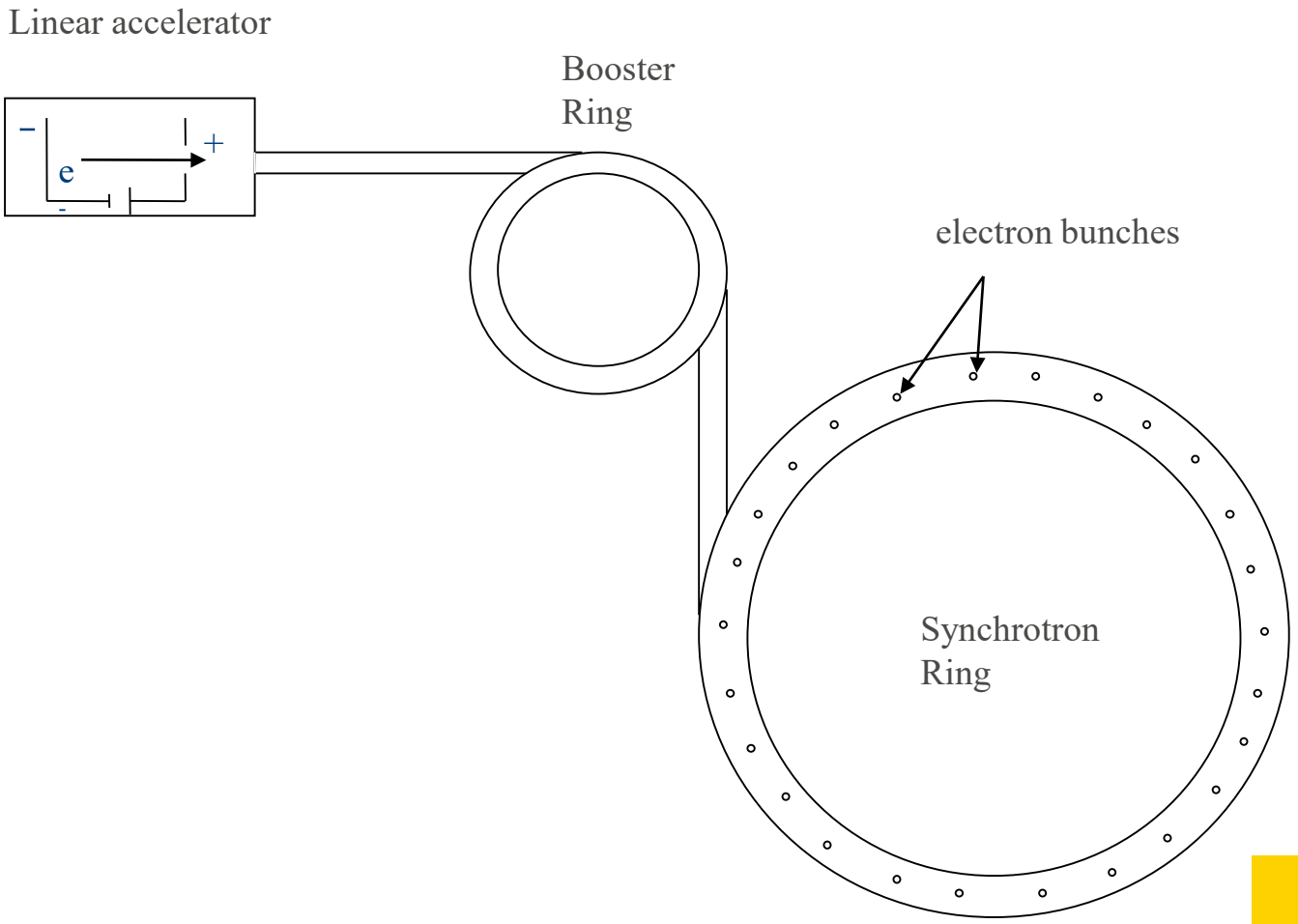
Synchrotron radiation



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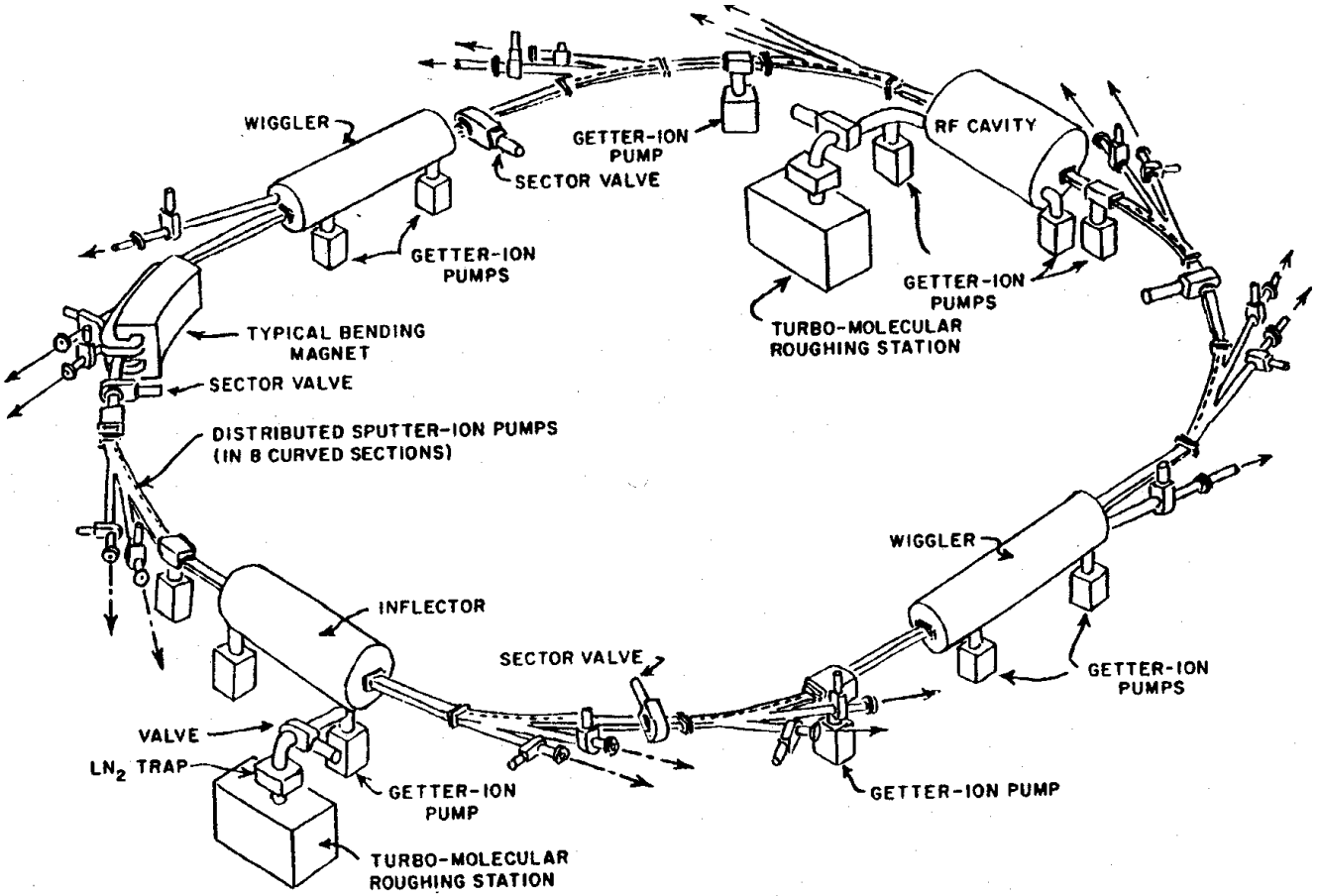
Producing Synchrotron Radiation



Winick, Doniach; "Synchrotron Radiation Research"

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The Advanced Photon Source

http://www.aps.anl.gov/About/APS_Overview/

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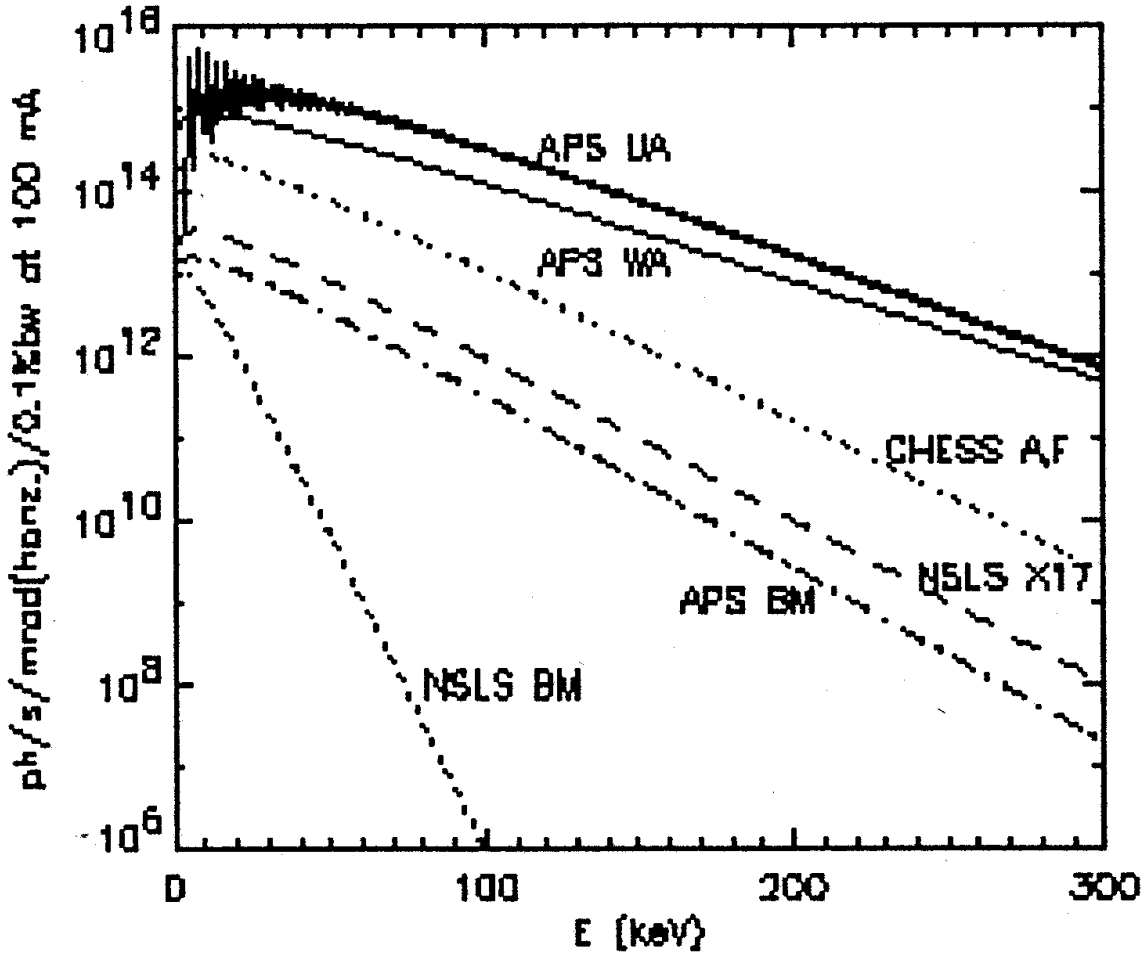
Energy spectrum of synchrotron radiation



- High intensity
- Plane polarized
- Intrinsically collimated
- White radiation
- Has time structure

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Neutron sources

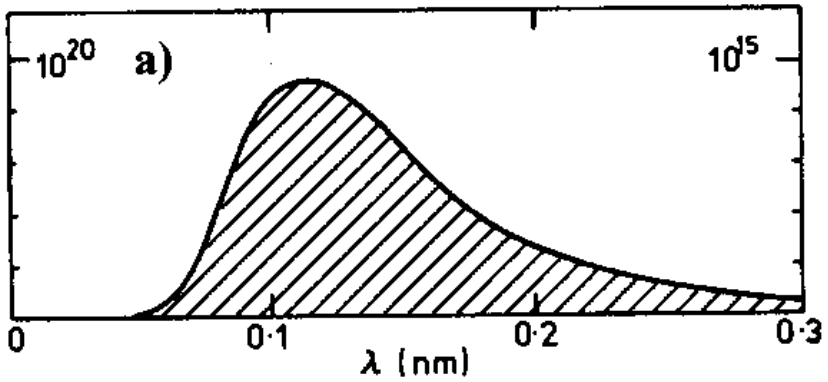
Reactor sources

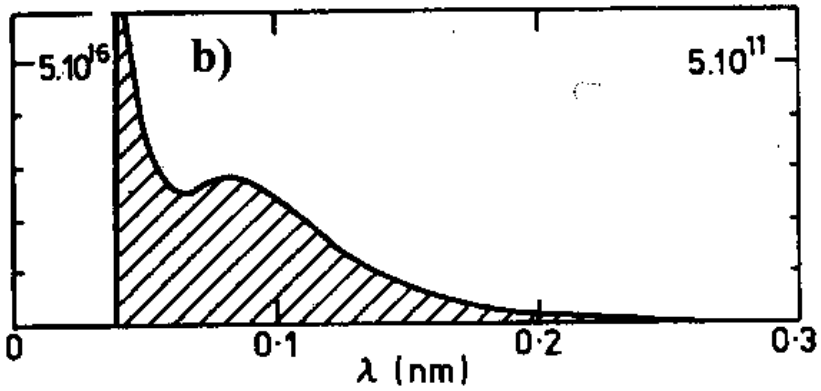
- Neutrons are produced by nuclear chain reaction
- Neutrons must be slowed down by moderator for use in diffraction
- Neutron wavelength distribution is thermal equilibrium distribution from moderator
- Monochromator needed => uses only small portions of the produced neutrons

Spallation sources

- Neutrons are produced by bombarding a metal target with protons
- Different wavelength distribution from reactor
- High peak flux, low average flux
- Due to time structure, all neutrons can be used

Windsor, C. G. *Pulsed Neutron Scattering*; Taylor & Francis Ltd.: London, 1981.





The Spallation Neutron Source at ORNL

(Image source: http://neutrons.ornl.gov)

Why neutrons?

- **Neutrons are scattered by nuclei, not by electrons**
  - form factor does not show rapid fall off at high angles
  - thermal motion of nuclei is much smaller than thermal motion of the electron cloud
- **Neutron form factors are not dependent on Z**
  - more sensitive to light elements than X-rays
  - isotopes or neighboring elements can often be distinguished
- **Neutrons interact with magnetic moments**
  - magnetic structure of materials can be determined by neutron diffraction
- **Most elements do not strongly absorb neutrons**

*Form factor/scattering lengths: Measure of how sensitive an element is to radiation, e.g., how strongly it scatters it (e.g., elements with more electrons scatter X-rays more)

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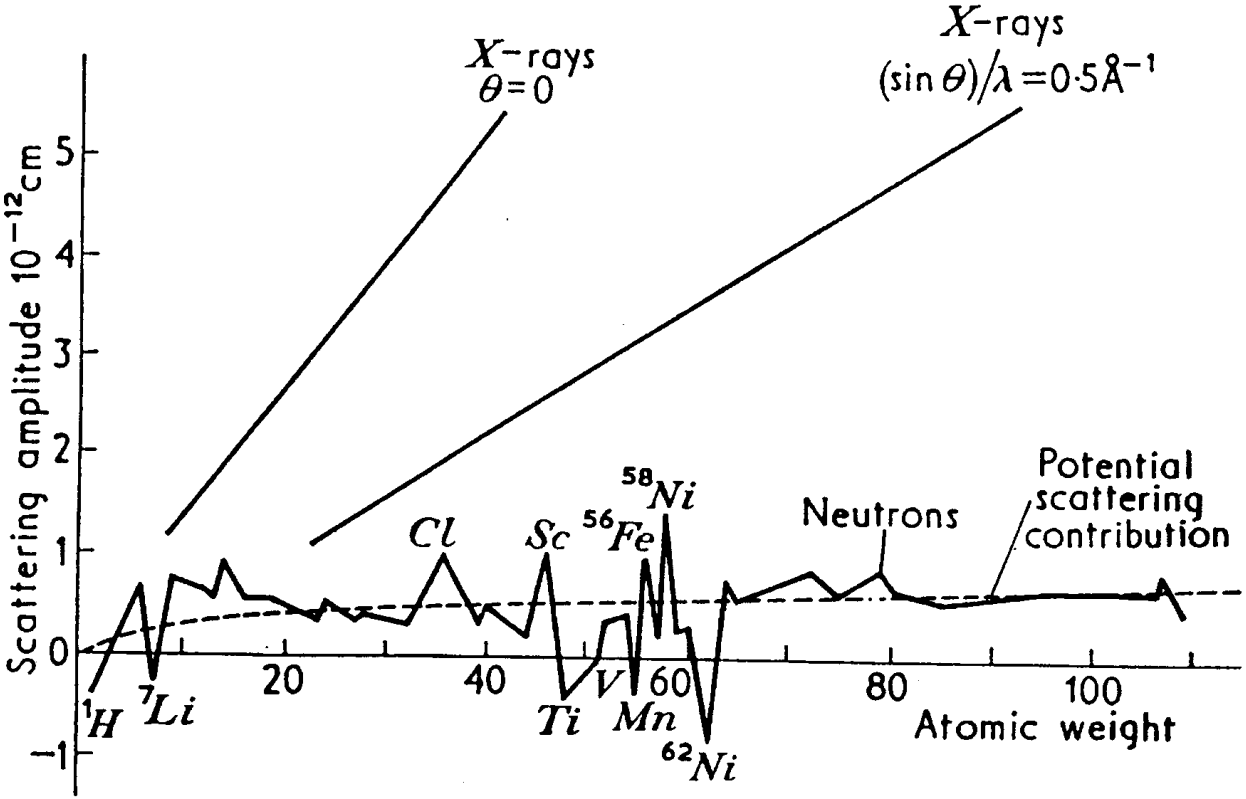
Neutron scattering lengths



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Specimen preparation - powder

- **A good powder sample should consist of fairly small particles**
  - should definitely be below 20 microns
  - ideal: 1-5 microns
  - usually achieved by grinding and passing through sieves
  - caution: do not overgrind your sample!
- **Sample morphology can be important**
  - e.g., rod like particles tend to result in preferred orientation
- **Most commonly used configurations: Flat plate samples or capillaries**
  - capillaries allow experiments with air sensitive samples or in a special environment (liquid, gas)
  - capillary size depends on absorption properties of the sample

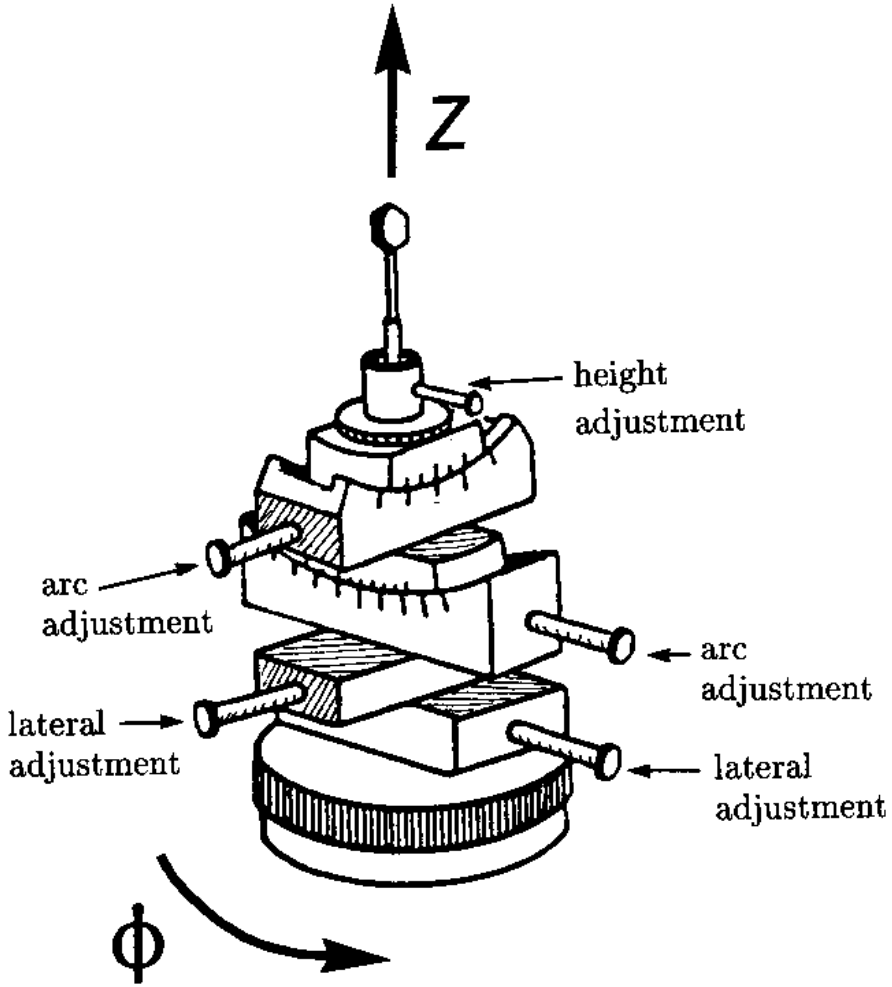
Specimen selection – single crystal

- **For lab experiments, crystals of ~50 to 200 micron size are generally needed**
  - exact size depends on scattering power
  - at a synchrotron, much smaller crystals might be sufficient
- **Quality is important**
  - only true single crystals will give a single diffraction pattern
  - use microscope and polarizers to make sure crystals are not split or twinned
- **If possible, crystals with approximately equal dimensions are chosen**
  - straightforward absorption correction

Specimen preparation – single crystal

- **Crystals can be attached to a glass fiber, a loop (common: MiTeGen loops), or sealed inside a capillary tube**
  - capillary protects air sensitive samples and could include mother liquor
- **Traditionally, crystals were glued to glass fibers with epoxy, but since the advent of low temperature methods, crystals are often mounted using grease or viscous oils**
  - the epoxy and the crystal will separate during cooling if their thermal expansion is considerably different
  - grease or oil will become rigid at low temperatures and immobilize the crystal
  - oil can often be used for slightly air sensitive crystals
- **The glass fiber or capillary are mounted on a goniometer head**

Goniometer heads



"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

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Detector options

- **Photographic film is darkened by X-rays**
  - oldest method
  - fairly sensitive, but difficult to get integrated intensities
  - small dynamic range
- **Image plates**
  - developed in the 1980's
  - very sensitive, wide dynamic range (six orders of magnitude)
  - can be read out by computer
  - reusable
  - photosensitive phosphor powder with organic binder
  - latent image of diffracted X-rays is stored and can be read out by scanning a laser across the image plate
    - photostimulated luminescence, detectable by a photomultiplier

Film

- Can be used for powder and single crystal methods

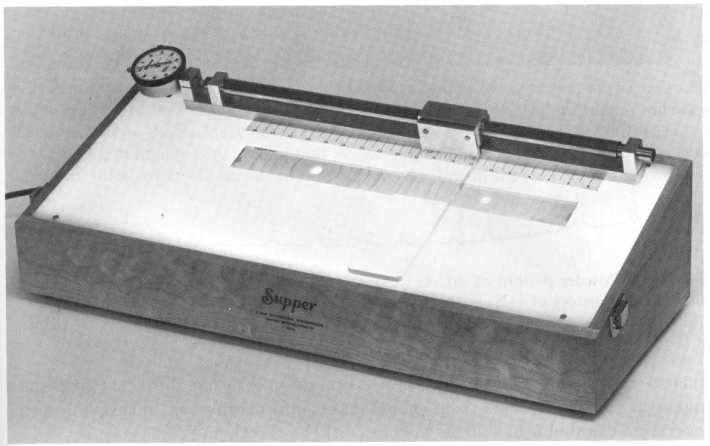

Fig. 6–18 Film-measuring device. (Courtesy of Charles Supper Company.)

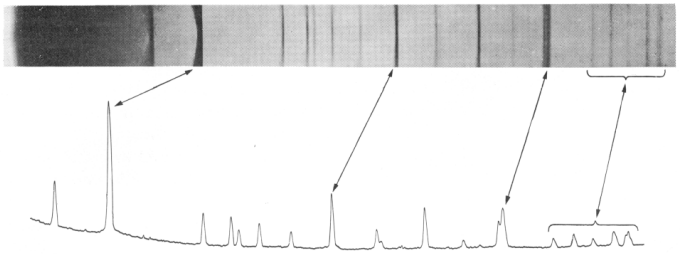

Fig. 6–19 Powder pattern of quartz (above) and corresponding microphotometer trace (below). (Courtesy of U.S. Bureau of Mines.) [6.7]

Cullity, "Elements of X-ray Diffraction"

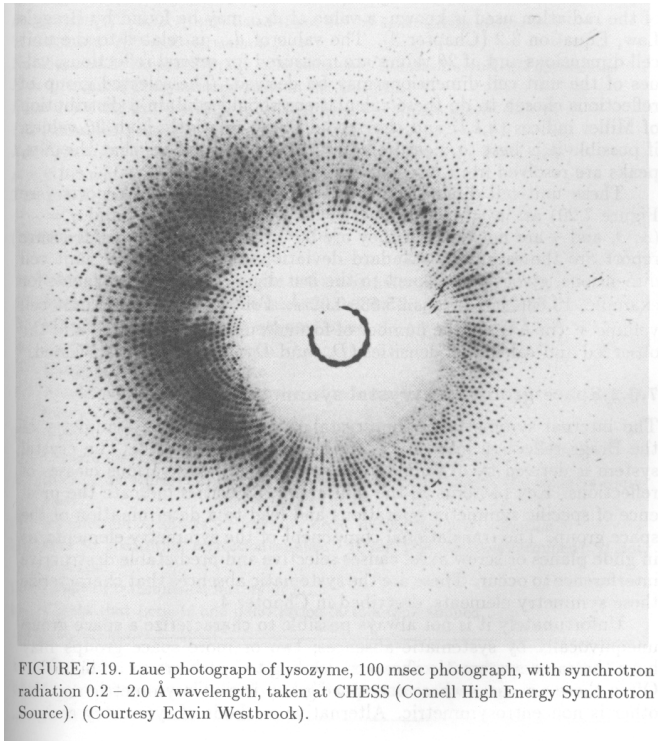

FIGURE 7.19. Laue photograph of lysozyme, 100 msec photograph, with synchrotron radiation 0.2 – 2.0 Å wavelength, taken at CHESS (Cornell High Energy Synchrotron Source). (Courtesy Edwin Westbrook).

"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

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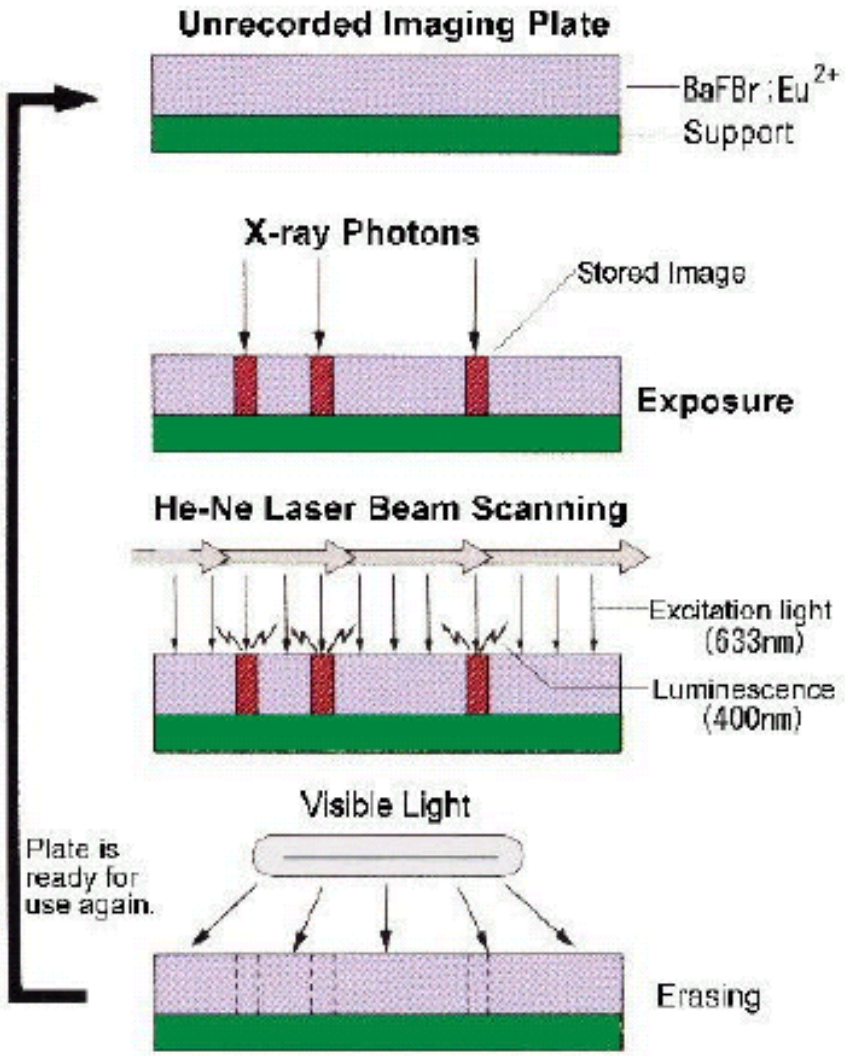
Image plates



http://xray0.princeton.edu/~phil/Facility/Guides/XrayDataCollection.html

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More detector options

- **Point detectors**
  - works well for powder samples
    - only 1D information collected anyway
  - rather slow for single crystal experiments
  - proportional, scintillation or solid-state counters
- **Area detectors**
  - collection of multiple spots at once
  - standard setup of most modern (small molecule) single crystal diffractometers
    - CCD detector = charge coupled device detectors
    - CMOS detector = Complementary Metal Oxide Semiconductor; also referred to as “active pixel detector”

Powder setups (1)

- **Oldest method: Debye-Scherrer camera**
  - capillary sample surrounded by cylindrical film
  - simple, cheap setup

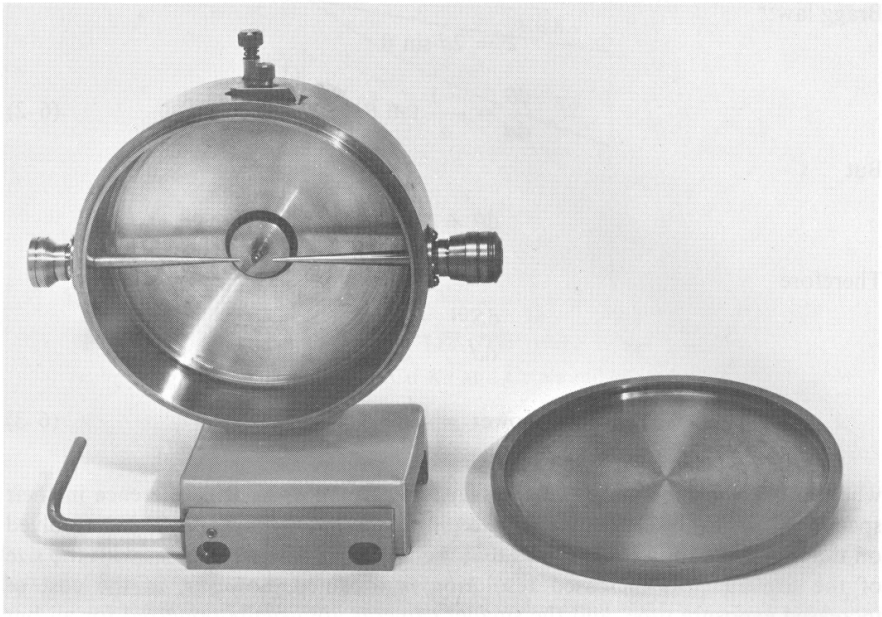

Fig. 6–1 Debye–Scherrer camera, with cover plate removed. (Courtesy of Philips Electronic Instruments, Inc.)

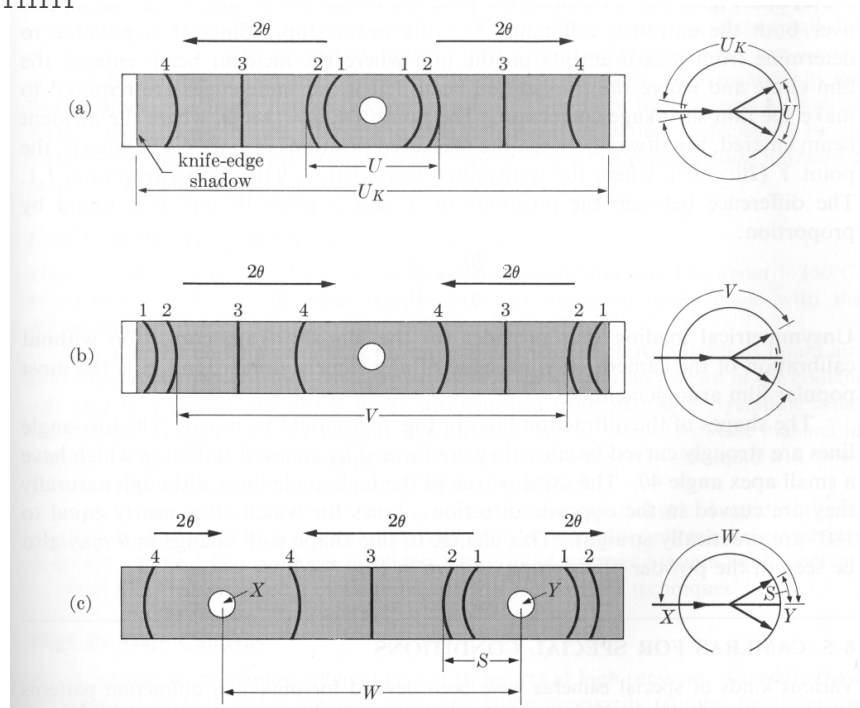

Fig. 6–5 Methods of film loading in Debye cameras. Corresponding lines have the same numbers in all films.

Cullity, "Elements of X-ray Diffraction"

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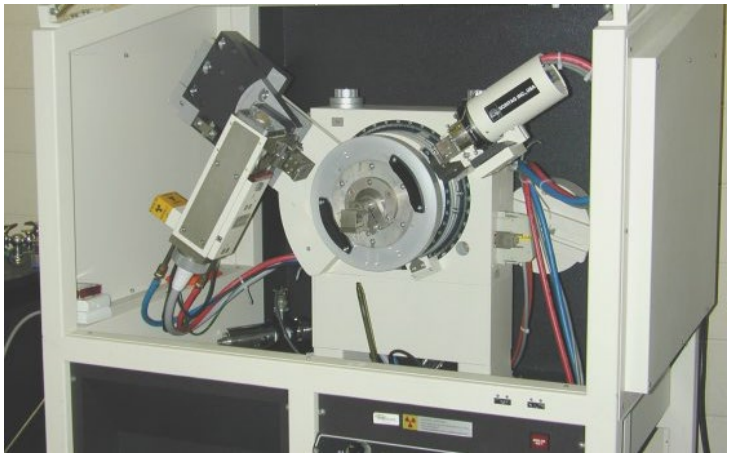
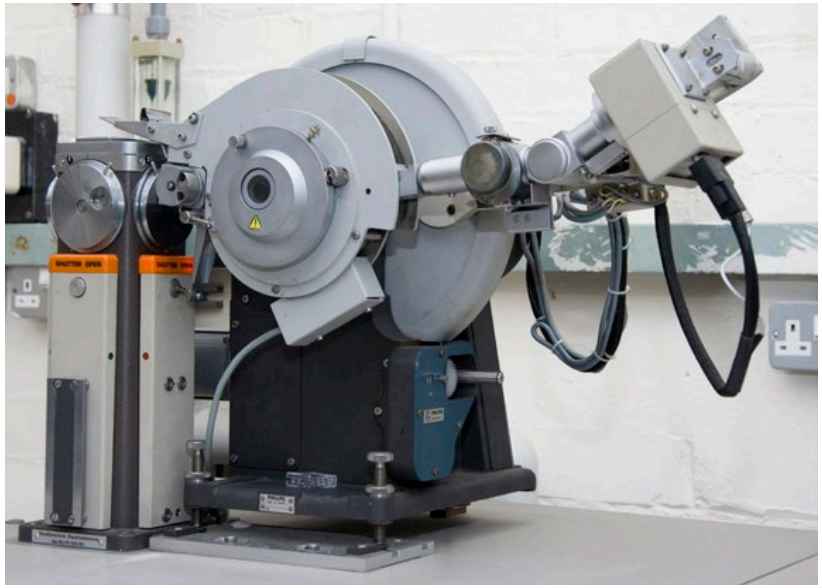
Powder setups (2)

- **Powder diffractometers**
  - theta-theta or theta-2theta
  - point or area detectors



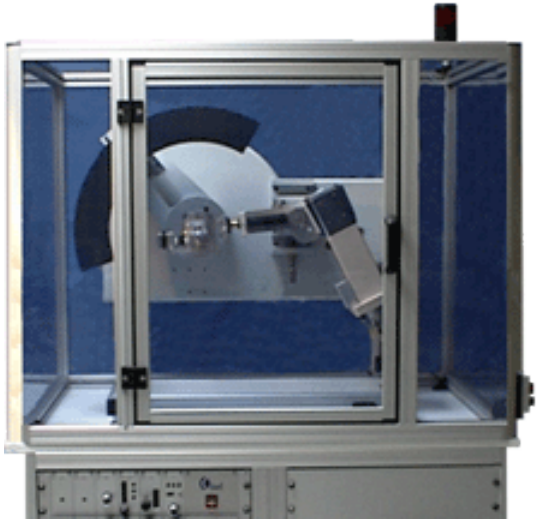
Scintag theta-theta diffractometer with Peltier cooled solid-state detector

http://www.msm.cam.ac.uk/xray/images/pdiff3.jpg



Philips PW1050 – first commercial diffractometer (1947)

www.inel.com



Inel diffractometer with 120° PSD (position sensitive detector)

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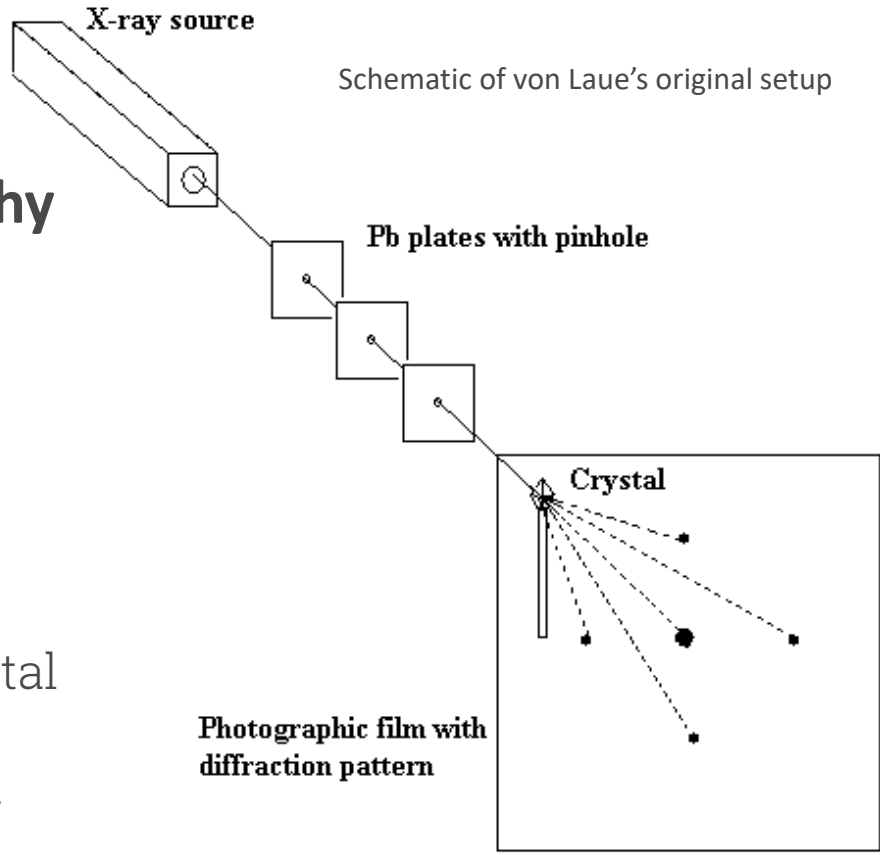
Single crystal setups: Historical methods

- **Oldest method: Laue photography**
  - still in use nowadays for determining orientation and indexing faces of crystals
- **Weissenberg, oscillation and precession methods**
  - used for a long time to check crystal quality before tying up diffractometer time (unnecessary with modern, fast instruments)



Schematic of von Laue's original setup

Oscillation and Weissenberg techniques

- **Use monochromatic radiation**
- **Crystal is rotated around the spindle axis by a few degree**
- **Spot patterns are recorded on film**
  - if a crystal axis is aligned with the rotation axis, the diffraction spots display a series of straight lines that are called *layer lines*
- **In the Weissenberg method, a metal screen allows selection of only one layer line**
  - oscillation is coupled to motion of film, which leads to better spot separation
- **Neither method gives a direct view of the reciprocal lattice!**
  - lattice spacings can be determined indirectly

Oscillation and Weissenberg techniques (2)

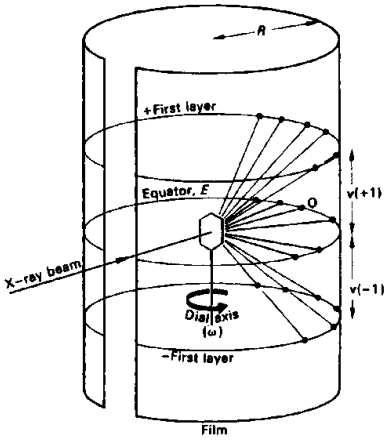


FIGURE 3.26. Basic geometry of the oscillation method, showing how diffraction spots are recorded on a cylindrical film placed around the crystal.

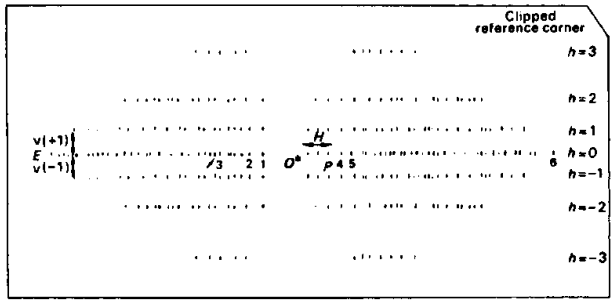


FIGURE 3.27 Sketch of a 15° oscillation photograph of an orthorhombic crystal mounted on the z axis (a = 6.167 Å); the camera radius R is 30.0 mm and λ (Cu $K\alpha$) = 1.2542 Å. The film is flattened out and the right-hand corner, looking toward the x-ray source, is clipped in order to provide a reference mark. P represents any equatorial reflection at a distance OP (= H mm) from the center O. Reflections numbered 1–6 on the zero level are indexed by the method given on page 156*ff*. The linear scale of the diagram is (1/1.78).

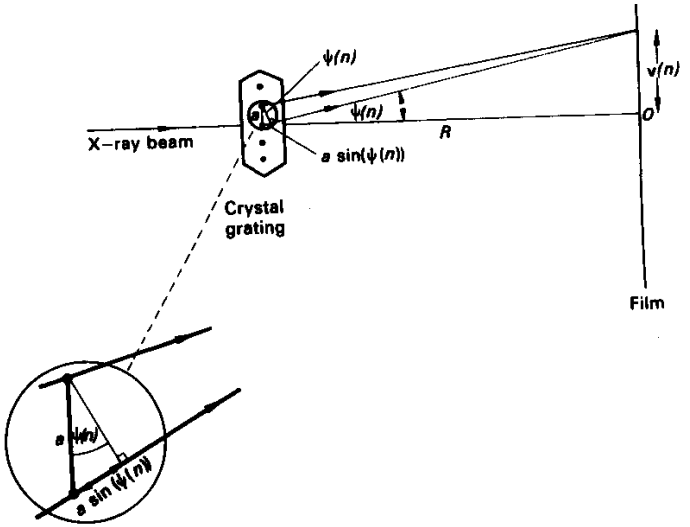


FIGURE 3.28. Diffraction-grating analogy explaining the layer-line spacings on oscillation photographs. Monochromatic x rays are incident normal to a (oscillation axis) in the crystal. The size of any spot at height such as $\nu(n)$ depends upon the experimental conditions.

$$a \cdot \sin\psi(n) = n\lambda \qquad \tan\psi(n) = \nu(n)/R$$

$$a = \frac{n\lambda}{\sin\left\{\tan^{-1}\left[\nu(n)/R\right]\right\}}$$

"Structure Determination by X-ray Crystallography", Ladd and Palmer, Plenum, 1994.

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Precession method

- **Uses monochromatic radiation**
- **Crystal axis precesses about the X-ray beam**
- **Film is always kept perpendicular to the crystal axis**
  - very complex mechanical setup!
- **Spot patterns are recorded on film**
  - gives true picture of reciprocal lattice
  - useful for lattice and space group determination
  - no longer used since advent of fast diffractometers

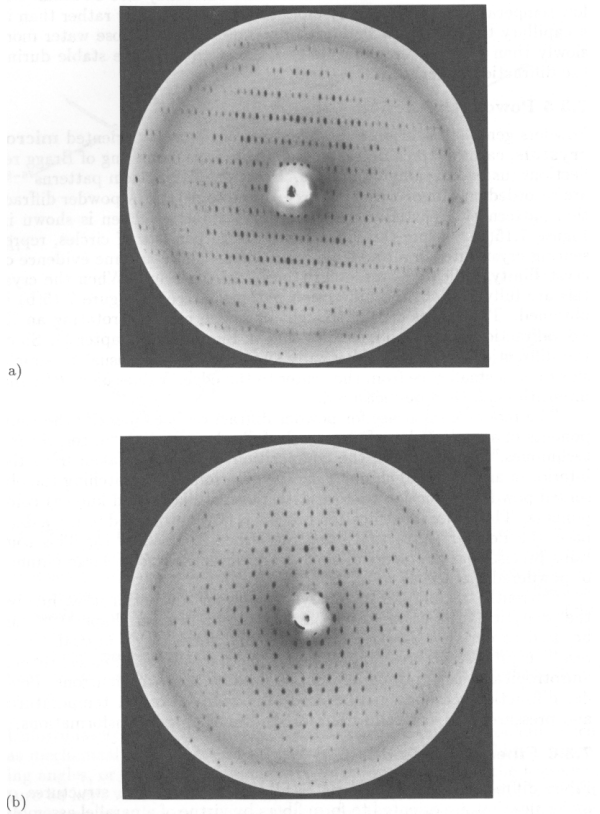

FIGURE 7.14. Two precession photographs of a protein crystal (lac repressor). (a) $0kl$ photograph. (b) $hk0$ photograph. The $hk0$ photograph was also shown in Figure 3.15 (Chapter 3).

"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

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Laue method

- **Uses white radiation**
- **Stationary crystal**
  - Fulfillment of Bragg condition is achieved by varying the wavelength
- **Spot patterns are recorded on film**
  - still in use for determining crystal orientations
  - useful for determining Laue groups from pattern symmetry

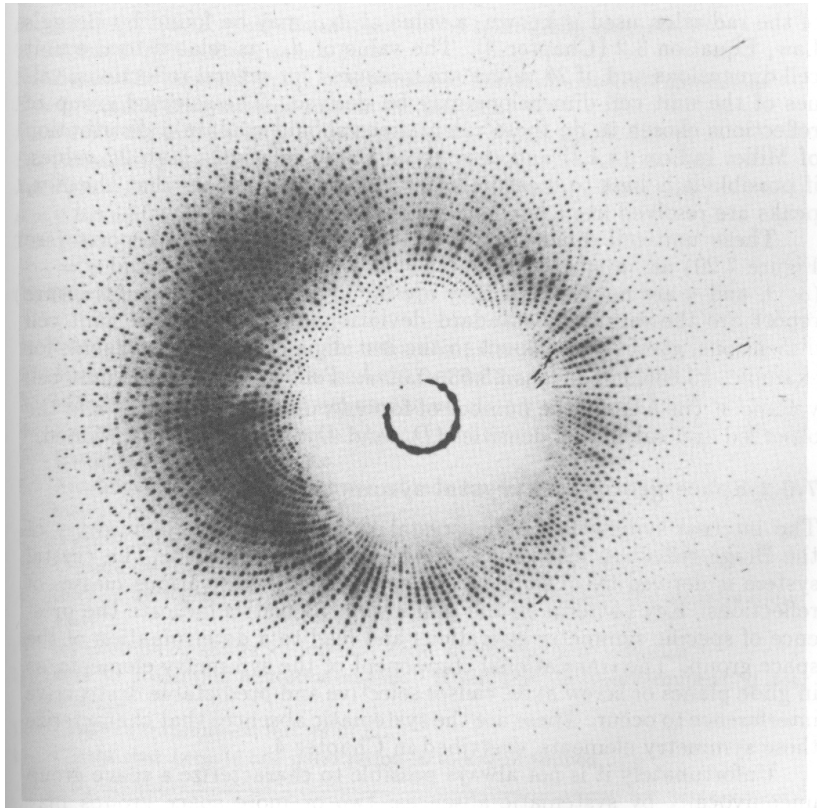

FIGURE 7.19. Laue photograph of lysozyme, 100 msec photograph, with synchrotron radiation 0.2 – 2.0 Å wavelength, taken at CHESS (Cornell High Energy Synchrotron Source). (Courtesy Edwin Westbrook).

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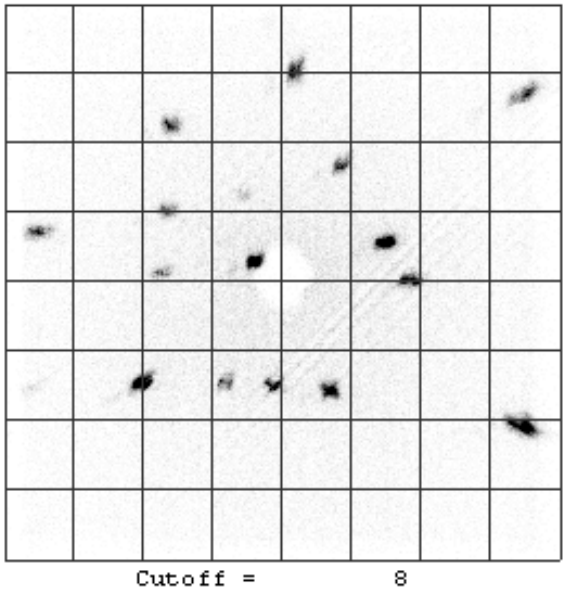
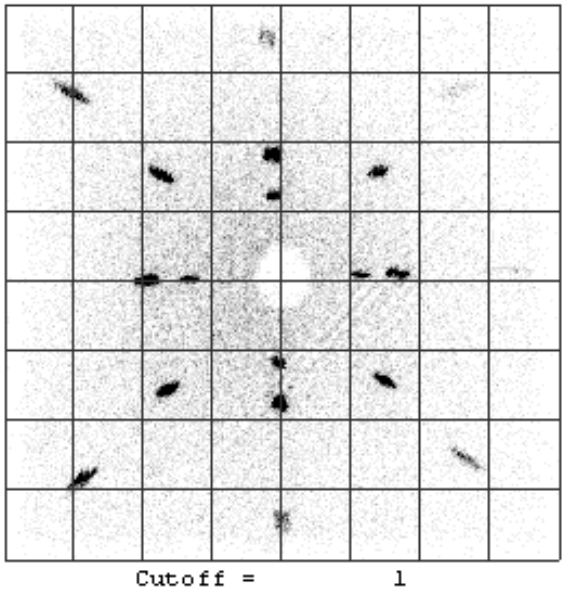
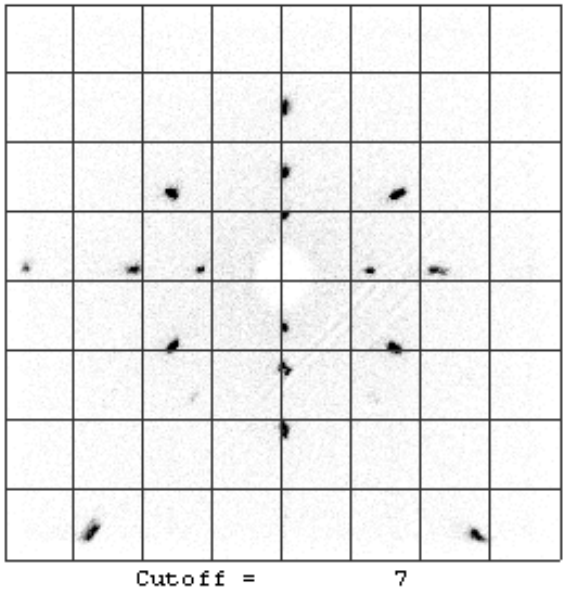
Laue photographs







PbF_2 Laue photographs: a) unoriented, b) 100, c) 110.

Courtesy of Jonathan P. Wrubel

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Laue groups

- **The symmetry in Laue patterns allows to determine the *Laue group* of a crystal**
  - can be very useful for narrowing down possible space groups!

For PbF2: Reflection conditions are

- hkl: h+k, h+l, k+l
- 0kl: k, l
- hhl: h+l
- 00l: l

CUBIC, Laue classes $m\bar{3}$ and $m\bar{3}m$

Reflection conditions (Indices are permutable, apart from space group No. 205)†				Extinction symbol	Laue class				
					$m\bar{3}$ (2/m $\bar{3}$)		$m\bar{3}m$ (4/m $\bar{3}$ 2/m)		
					Point group				
hkl	0*kl*	*hhl*	00*l*		23	$m\bar{3}$	432	$\bar{4}3m$	$m\bar{3}m$
				P---	$P23$ (195)	$Pm\bar{3}$ (200)	$P432$ (207)	$P\bar{4}3m$ (215)	$Pm\bar{3}m$ (221)
			l	$P2_1$-- $P4_2$--	$P2_13$ (198)				
							$P4_232$ (208)		
			$l = 4n$	$P4_1$--			$P4_132$ (213) $P4_332$ (212)		
		l	l	P--n				$P\bar{4}3n$ (218)	$Pm\bar{3}n$ (223)
	k†		l	Pa--		$Pa\bar{3}$ (205)			
	$k + l$		l	Pn--		$Pn\bar{3}$ (201)			$Pn\bar{3}m$ (224)
	$k + l$	l	l	Pn-n					$Pn\bar{3}n$ (222)
$h + k + l$	$k + l$	l	l	I---	$I23$ (197) $I2_13$ (199)	$Im\bar{3}$ (204)	$I432$ (211)	$I\bar{4}3m$ (217)	$Im\bar{3}m$ (229)
$h + k + l$	$k + l$	l	$l = 4n$	$I4_1$--			$I4_132$ (214)		
$h + k + l$	$k + l$	$2h + l = 4n, l$	$l = 4n$	I--d				$I\bar{4}3d$ (220)	
$h + k + l$	k, l	l	l	Ia--		$Ia\bar{3}$ (206)			
$h + k + l$	k, l	$2h + l = 4n, l$	$l = 4n$	Ia-d					$Ia\bar{3}d$ (230)
$h + k, h + l, k + l$	k, l	$h + l$	l	F---	$F23$ (196)	$Fm\bar{3}$ (202)	$F432$ (209)	$F\bar{4}3m$ (216)	$Fm\bar{3}m$ (225)
$h + k, h + l, k + l$	k, l	$h + l$	$l = 4n$	$F4_1$--			$F4_132$ (210)		
$h + k, h + l, k + l$	k, l	h, l	l	F--c				$F\bar{4}3c$ (219)	$Fm\bar{3}c$ (226)
$h + k, h + l, k + l$	$k + l = 4n, k, l$	$h + l$	$l = 4n$	Fd--		$Fd\bar{3}$(203)			$Fd\bar{3}m$ (227)
$h + k, h + l, k + l$	$k + l = 4n, k, l$	h, l	$l = 4n$	Fd-c					$Fd\bar{3}c$(228)

† For No. 205 only cyclic permutations permitted. Conditions are $0kl$: $k = 2n$; $h0l$: $l = 2n$; $hk0$: $h = 2n$.

"International Tables for Crystallography, Vol. A", Kluwer, 1993.

Single crystal diffractometers

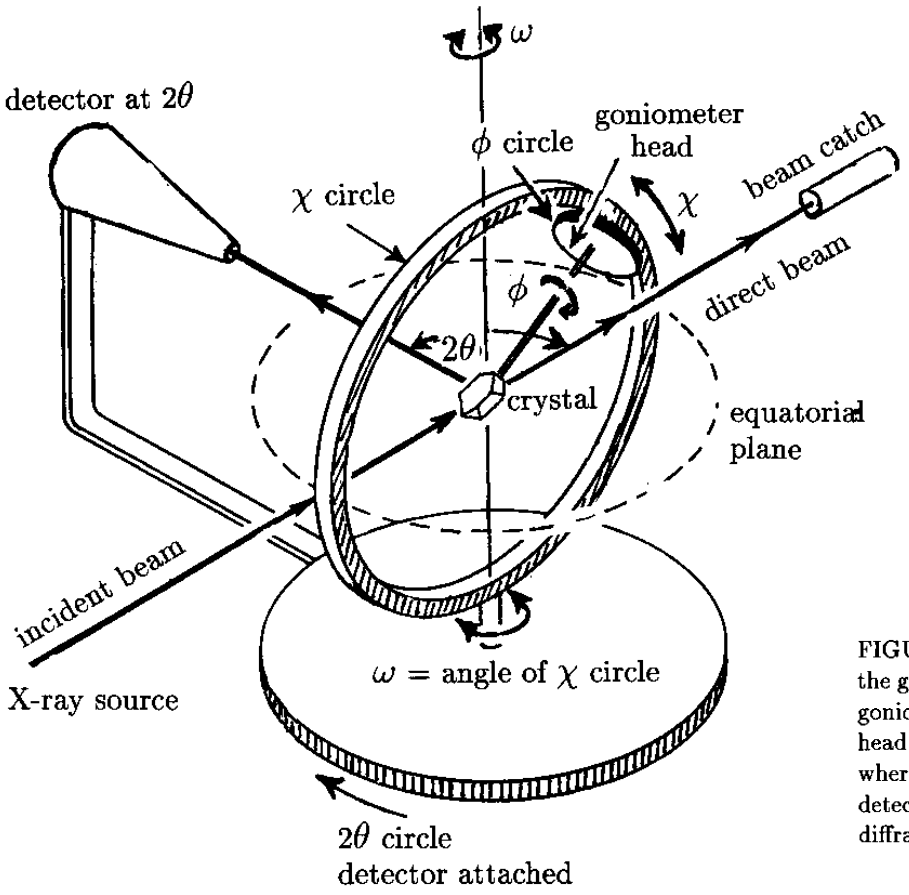

FIGURE 7.16. Diagram of an automatic diffractometer. The crystal is mounted on the goniometer head, which is attached, in turn, to the χ circle. The spindle axis of the goniometer head is ϕ. The angle χ is the angle between the ϕ axis of the goniometer head and the base of the diffractometer. The χ circle can be rotated about the ω axis, where ω is the angle between the diffraction vector and the plane of the χ circle. The detector is moved on the 2θ circle, where 2θ is the angle between the incident and diffracted beams.

"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

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Single crystal diffractometry

- **Uses monochromatic radiation**
  - Mo tube for small molecule crystallography; Cu is useful for absolute structure
  - Nowadays: Mainly Cu for macromolecules
- **Normal approach: Collect a rotation matrix**
  - a series of 60-90 frames that the program will try to index
  - if you cannot index the matrix, the crystal is probably not worth collecting on!
- **Check spot quality**
  - should be single, spherical spots
  - streaky spots or shoulders usually point to low crystal quality, defects, twinning…
- **If everything looks good: Collect a full data set!**
  - normal exposure times: 10 to 60s
  - number of frames depends on crystal symmetry

Judging spot quality

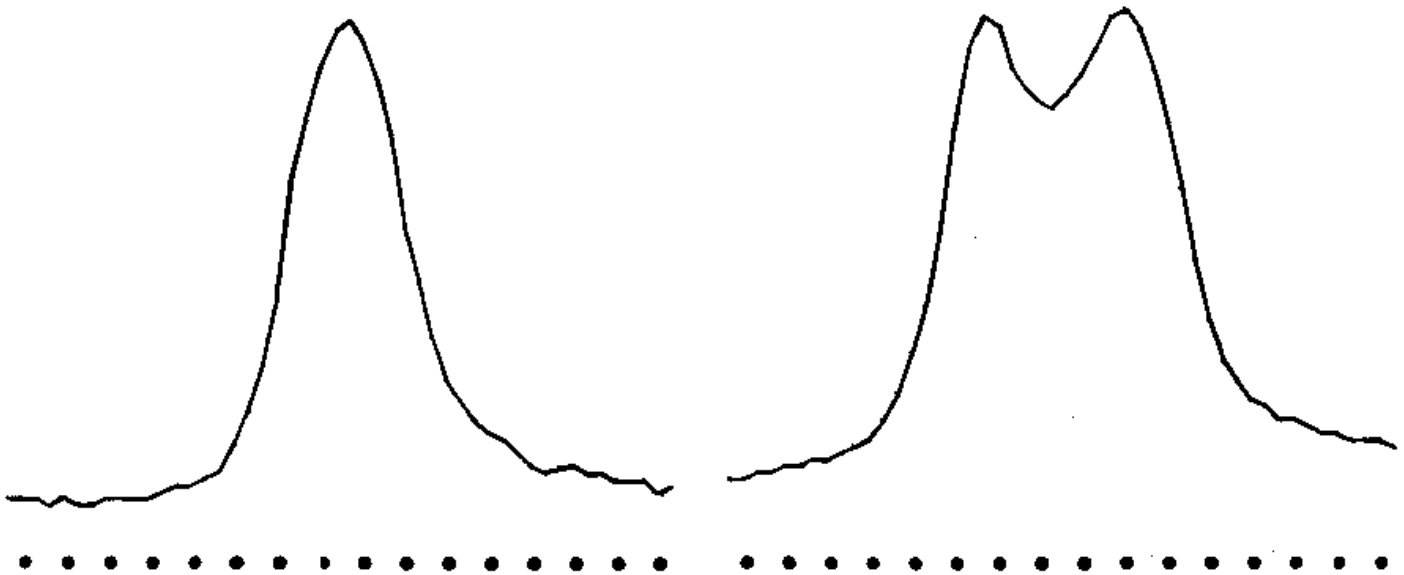

FIGURE 7.18. (a) A good and (b) a bad peak profile.

"Crystal Structure Analysis for Chemists and Biologists", Glusker, Lewis and Rossi, VCH, 1994.

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