# X-ray Diffracrtometer

Pecharsky Chapter 6 Cullity Chapter 1 Krawitz Chapter 3 Jenkins & Snyder - Chapter 1, 4, 5, 6

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#### X-ray

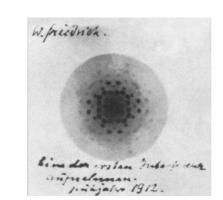
- ➤ W.C. Röntgen
  - ✓ 1895: Discovery of X-ray
  - ✓ 1901: First Nobel prize for Physics
- > M.T.F. von Laue
  - ✓ 1912: X-ray diffraction, in cooperation with Friedrich and Knipping
  - ✓ Laue equation, Laue reflections
  - ✓ 1914: Nobel prize for Physics
- > C.G. Darwin
  - ✓ 1912: Dynamical scattering theory
  - $\checkmark$  Darwin width
- > W.H. and W.L. Bragg
  - ✓ 1914: X-ray diffraction from powder samples
  - ✓ Bragg's equation, Bragg reflections
  - ✓ 1915: Nobel prize for Physics
- ≻ P.P. Ewald
  - ✓ 1916: Theoretical description of X-ray diffraction
  - ✓ Ewald construction, reciprocal space

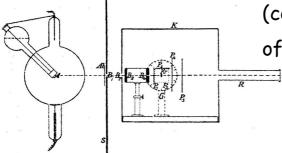












X-ray diffraction pattern of a single crystal of Zinc Blende (ZnS)

Friedrich, Knipping and von Laue, 1912, University of Munich

(confirmation of the wave character of x-rays)

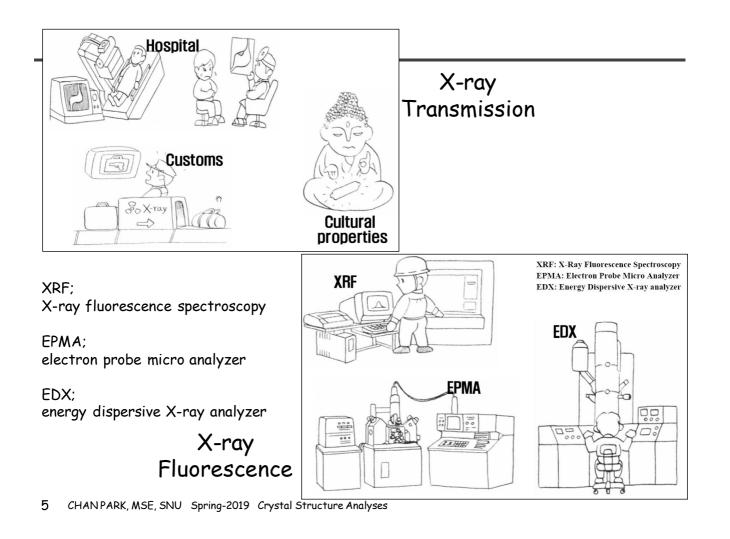
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# Nobel Prizes for Research with X-Rays

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.



# Characteristics of X-rays

- > Electromagnetic wave; wavelength 0.3Å ~3 Å
  - $\checkmark$  Strong penetration through matters
  - ✓ Invisible in air
  - $\checkmark$  No interaction with electric and magnetic field
- $\succ$  Photographic  $\rightarrow$  detection
- > Fluorescent (e.g. on ZnS, CdS, NaI, etc.)  $\rightarrow$  detection
- $\succ$  Ionizing  $\rightarrow$  detection
- $\succ$  Diffraction  $\leftarrow$  wavelength ~ atomic distance
- > Transmission  $\rightarrow$  medical, nondestructive evaluation (NDE)

Wavelength ≈ Object Size ≈ Angstroms

for Condensed Matter Research

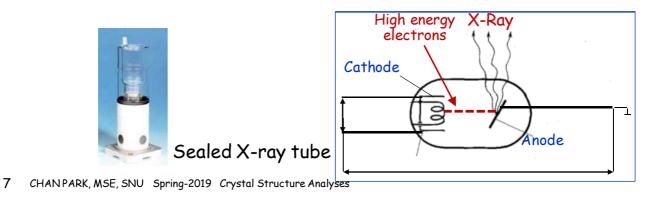
$$\lambda[\text{Å}] = \frac{12.398}{E_{\text{ph}}[\text{keV}]}$$

#### Generation of X-rays

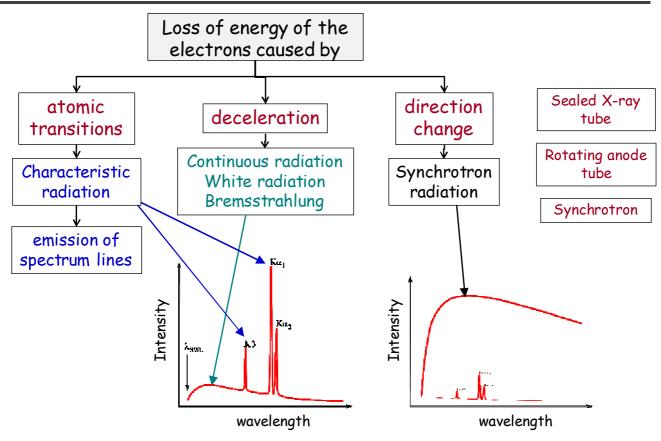
> X-rays are produced when any electrically charged particle of

sufficient kinetic energy rapidly decelerates

- $\checkmark$  change of speed of matter
- $\checkmark$  change of direction of movement
- > Bombardment of a target by electrons
- > Anode (Cu, Mo, W, Ag ..), Cathode (W, LaB6)
- $> 10^{-3} \sim 10^{-4}$  Torr chamber, high voltage (10  $\sim 50$ kV)

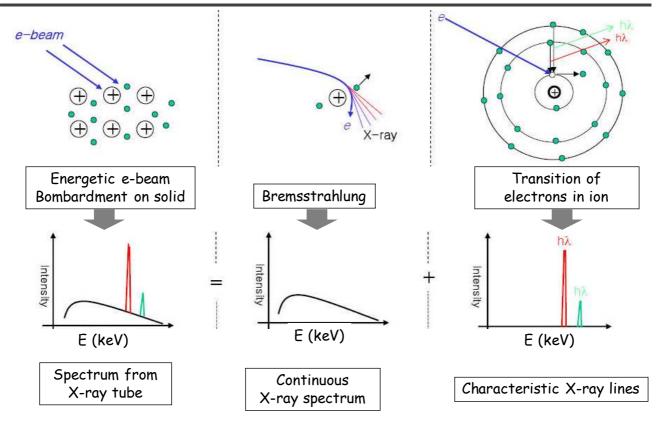


#### Generation of X-rays



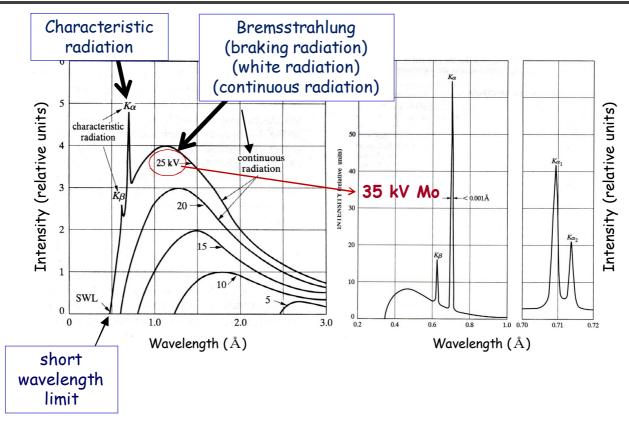


# Generation of X-rays

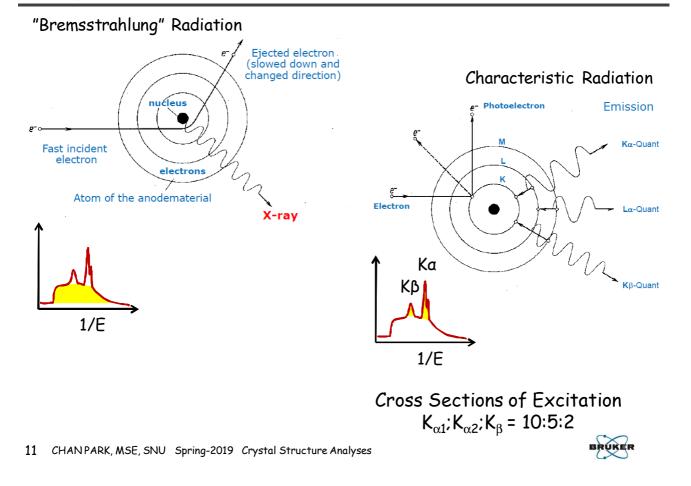


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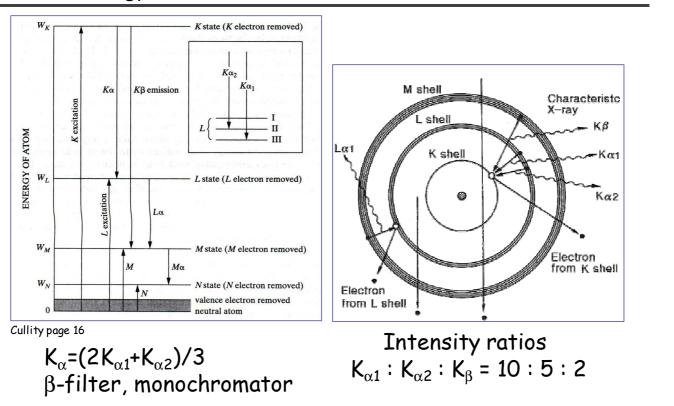
#### X-ray spectrum of molybdenum



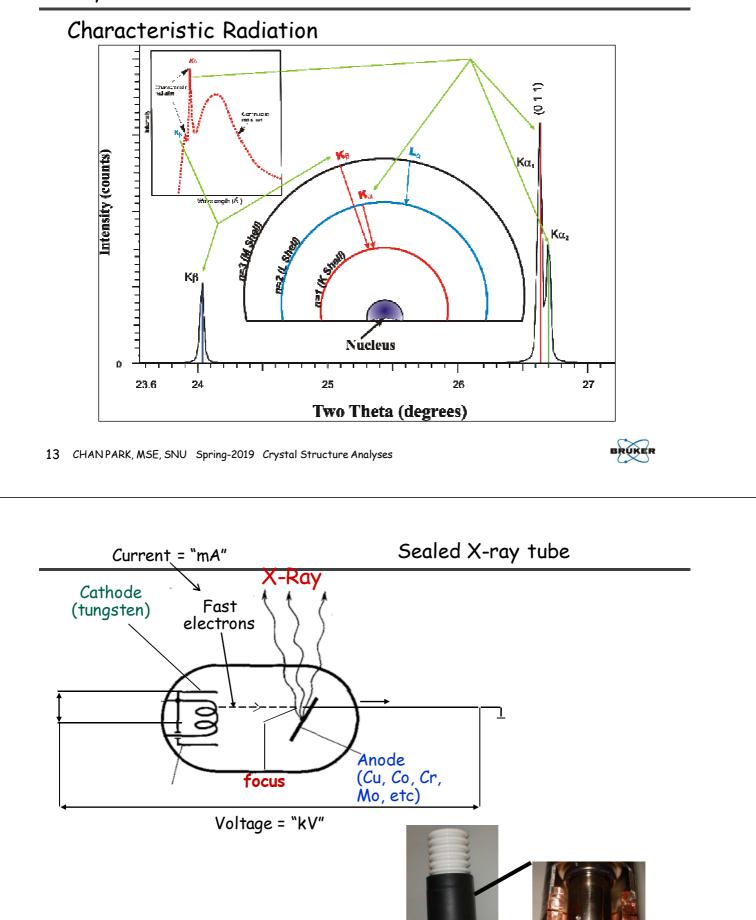
#### X-ray Generation



#### Atomic energy level



## X-ray Generation



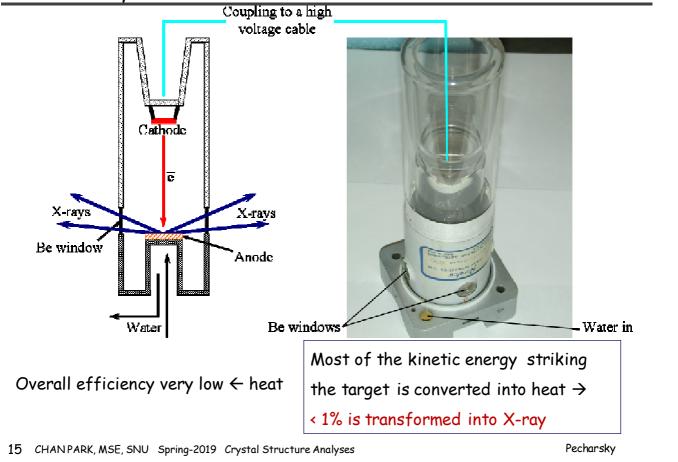
BRUKER

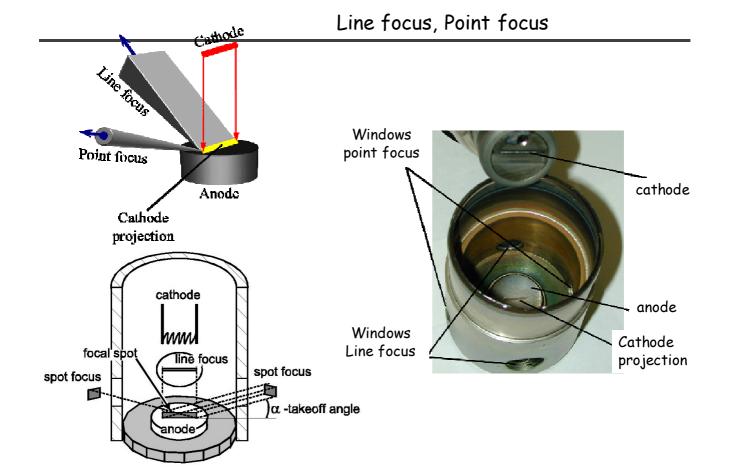
Filament

Anode (Cu)

Be windows

# Sealed X-ray tube



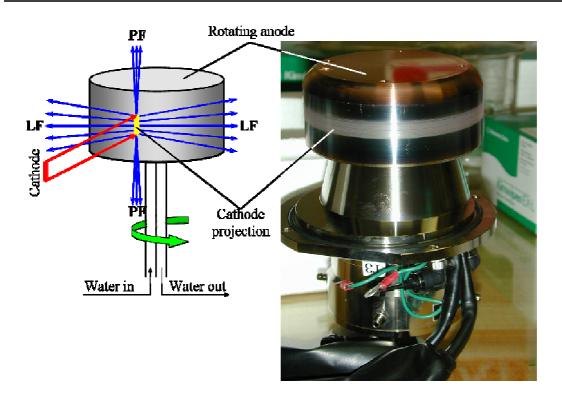


# X-ray from sealed tube

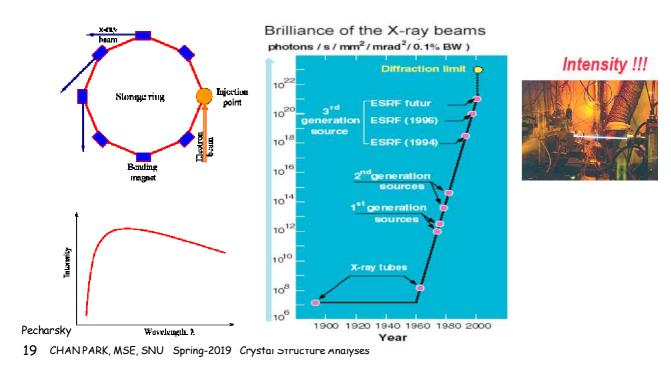
Anode	$\mathbf{K}\alpha_1(\mathbf{\mathring{A}})$	
Cu	1.54060	- Best for inorganics - Fe and Co fluorescence
Cr	2.28970	<ul> <li>High Resolution for large d-spacing</li> <li>High attenuation in air</li> </ul>
Fe	1.93604	<ul> <li>Used for ferrous alloys to reduce Fe fluorescence</li> <li>Causes Cr fluorescence</li> </ul>
Со	1.78897	- Used for ferrous alloys to reduce Fe fluorescence
Mo	0.70930	- Short wavelength used for small unit cells

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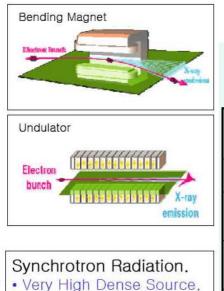
# Rotating anode X-ray source



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



# Synchrotron X-ray



- Very High Dense Source.
- Good Coherent Property.
- Continuous Spectrum.
- Huge Apparatus.

# Brightness & Fluxes for Neutron & X-Ray Sources

	Brightness $(s^{-1}m^{-2}ster^{-1})$	dE/E (%)	Divergence (mrad <sup>2</sup> )	Flux $(s^{-1}m^{-2})$	
Neutrons	10 <sup>15</sup>	2	$10 \times 10$	10 <sup>11</sup>	
Rotating Anode	10 <sup>20</sup>	0.02	0.5×10	5×10 <sup>14</sup>	
Bending Magnet	10 <sup>27</sup>	0.1	0.1×5	5×10 <sup>20</sup>	
Undulator (APS)	10 <sup>33</sup>	10	0.01×0.1	10 <sup>24</sup>	

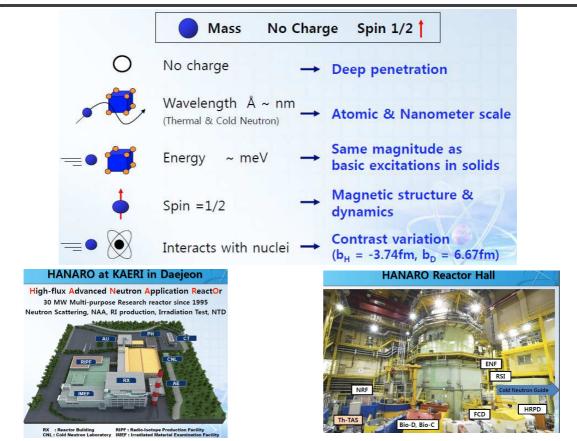
# Neutron diffraction

- > Produced in nuclear reactors, White spectrum
- > Scattered by nuclei (electron clouds in X-ray)
- > Scattering factor remains constant over the whole range of Bragg angles
- > Scattering factors not proportional to atomic number
- > 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

# Electron diffraction

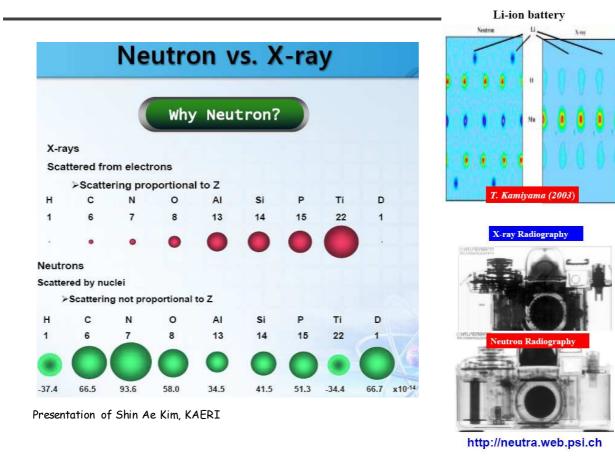
- > High vacuum is needed
- $\triangleright$  e's strongly interact with materials  $\rightarrow$  <u>dynamical theory</u> of diffraction
- Cost of equipment
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#### Properties of Neutron



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Presentation of Shin Ae Kim, KAERI



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## 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 $\lambda$ (Å)	0.5~2.5 (0.1~10)	~1	0.01~0.05	
l selection	fixed/variable	variable	variable	
Lattice image	recij	direct, reciprocal		
Direct structure image	no		yes	
Applicable theory of diffraction	kiner	natical	dynamical	

#### Safety (XRD) Beryllium - MSDS Electric shock Appearance: silvery solid or grey foil Melting point: 1278 C Boiling point: 2970 C > Radiation hazard Very toxic by inhalation - risk of serious damage to ✓ Burns health. May act as a human carcinogen for which there Radiation sickness is no safe exposure level. May act as a sensitizer. ✓ Genetic mutation Toxicity data IVN-RAT LD50 0.5 mg kg-1 > Be window Risk phrases R26 R27 R37 R39. $\geq$ **IVN** - intravenous LD50 - lethal dose 50% kill R26 - very toxic by inhalation R27 - very toxic in contact with skin R37 irritating to respiratory system > No special health risks R39 - danger of very serious irreversible effects with Be in solid form Skin Contact with Beryllium ✓ No effect on contact or temporary embedding. MATERION

- ✓ Solvents will not generate beryllium dust, but some acids will. Don't etch beryllium.
- $\checkmark$  Wear clean gloves to protect the skin and to protect the beryllium.

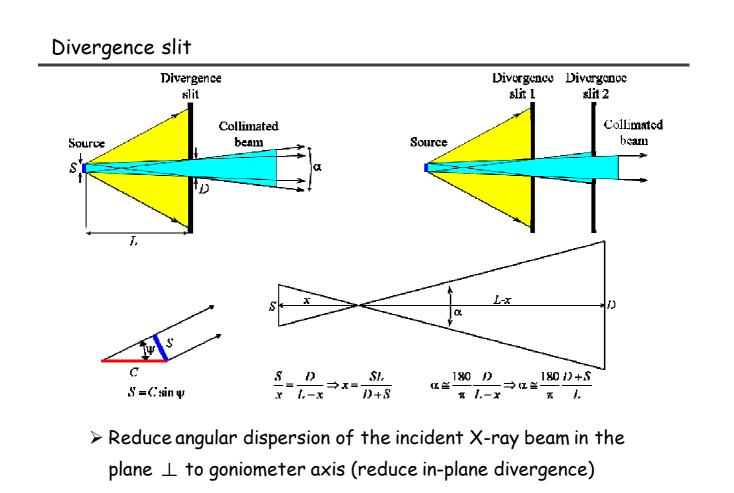
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# Collimation Monochromatization Diffractometer

#### Collimation & Monochromatization

- > Conventional X-ray (sealed tube, rotating anode tube) has
  - ✓ Polychromatic nature  $\rightarrow$  monochromatization
  - $\checkmark$  Angular divergence  $\rightarrow$  collimation
- 1. White radiation  $\rightarrow$  high background
- 2. Three intense characteristic lines  $(K_{\alpha 1}, K_{\alpha 2}, K_{\beta}) \rightarrow$  three Bragg peaks from each (hkl)
- 3. Angular divergence → broad & asymmetric Bragg peaks
- Incident X-ray beam needs to be conditioned to improve the quality of diffraction pattern
- > How to reduce both the angular & wavelength dispersion?
- How to reduce both with minimal loss of intensity of incident & diffracted beams?
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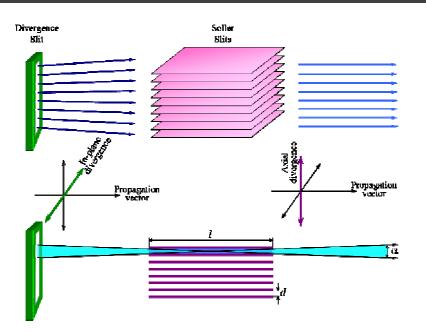
# Collimation slits



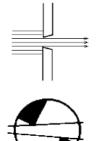
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Pecharsky

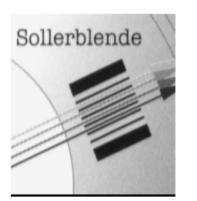
# Divergence slit & Soller slit

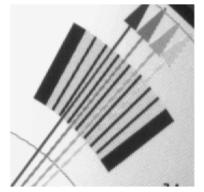


Soller slit - reduce angular divergence of the incident X-ray beam in the direction // to goniometer axis (reduce axial divergence)

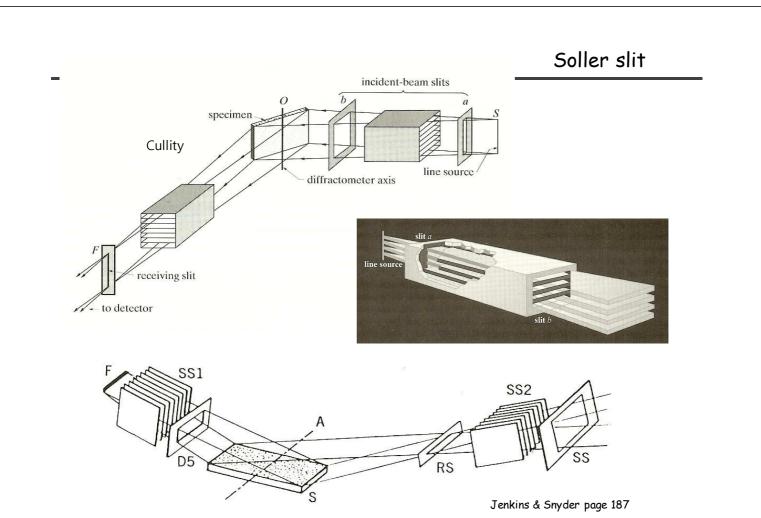


The normal slit consists of two blades, limiting the beam width. For automatic changing of the slit width, turnable edges are used.



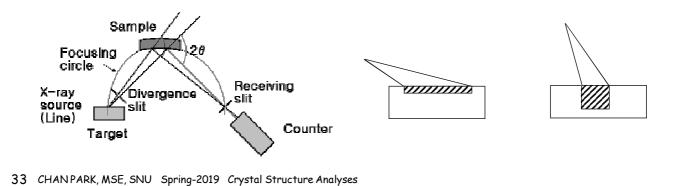


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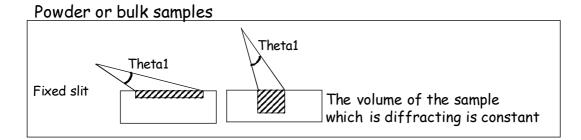


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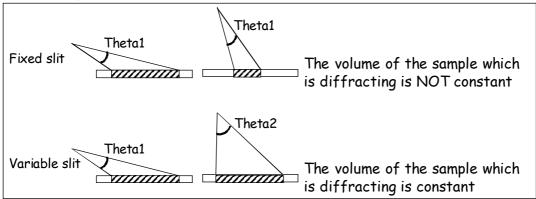
- In case the line intensities are to be compared over the whole range of 20, the same divergence must be used and specimen must be larger than the beam at <u>all angles</u>
- > <u>Variable divergence slit</u>  $\rightarrow$  irradiated area constant at all 20 angles
- > Fixed divergence slit  $\rightarrow$  irradiated volume constant at all 20 angles
- ➤ Receiving slit defines the width of beam admitted to the detector. Increase of receiving slit → increase of maximum intensity, loss of resolution



# Variable slit vs. Fixed slit



#### Thin samples

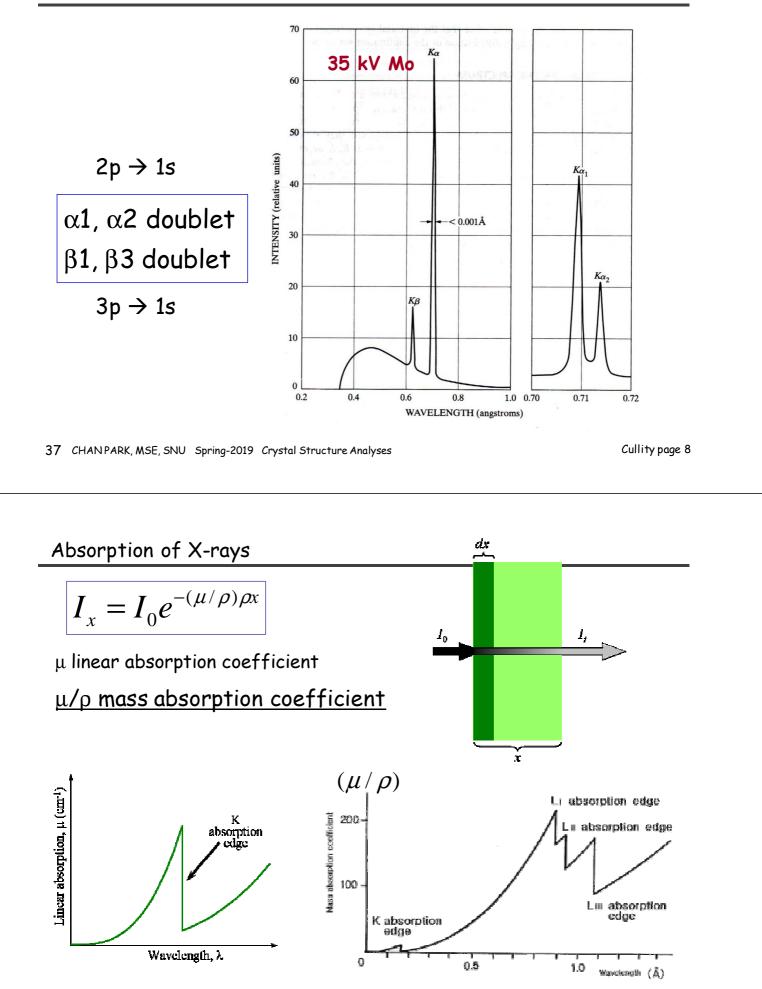


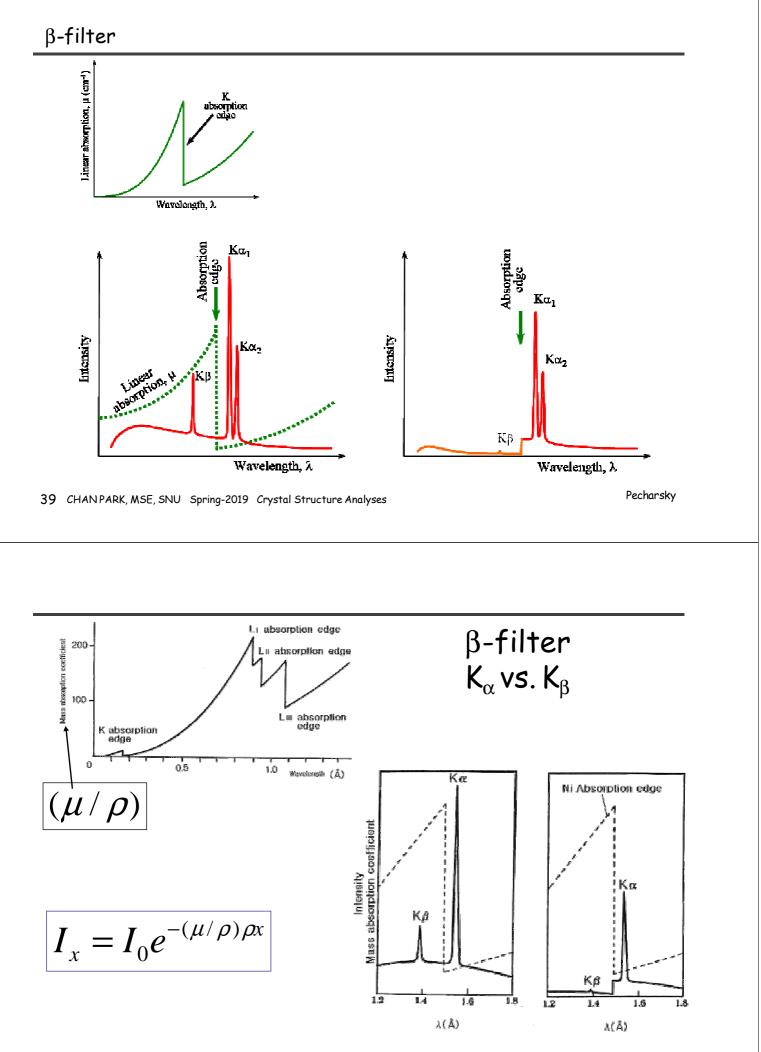
# Monochromators

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#### Monochromatic radiation

- Problems caused by polychromatic nature of diffracted beam & variability of angular dispersion
- ➤ XRD pattern from multiple wavelength, or that from unknown wavelength → difficulty in interpreting the pattern
- Why monochromatic beam is wanted? we want to obtain experimental pattern from a single wavelength
- Monochromatization by reducing the intensity of white radiation & by eliminating undesirable characteristic wavelengths from X-ray spectrum
  - ✓  $\beta$  filter
  - ✓ Diffracted beam monochromator
  - ✓ Primary beam monochromator
  - $\checkmark$  Pulse height selection using proportional counter
  - ✓ Use of solid state detector (high resolution energy resolving detector)



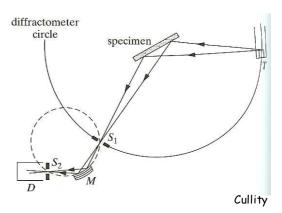


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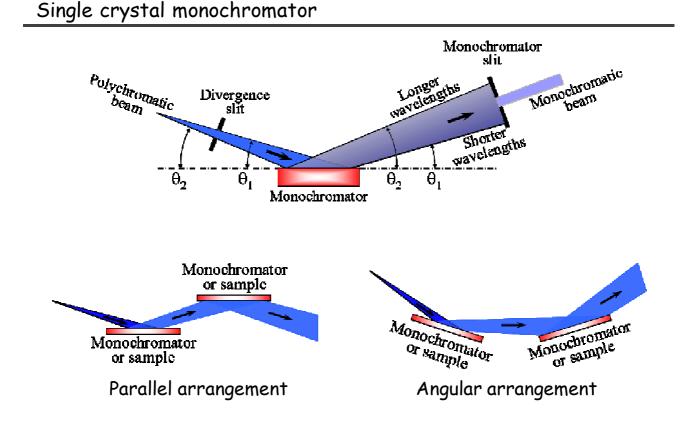
#### Monochromators

#### > Ways to reduce BKG

- ✓ Pulse-height analyser
- $\checkmark$  Diffracted beam monochromator  $\rightarrow$  suppress BKG radiation originating at the specimen (flourescent radiation, incoherent scattered radiation)
- ✓ Balanced filter
- Monochromator can be placed in diffracted beam in diffractometer (not in the area detector)
- ➤ Incident beam monochromator → Lp factor has to be changed (has to include contribution from the diffraction at the monochromator)
- LiF, graphite, Si, Ge, SiO<sub>2</sub> (quartz), etc

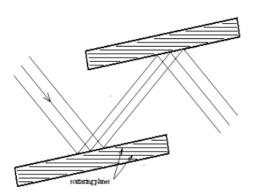


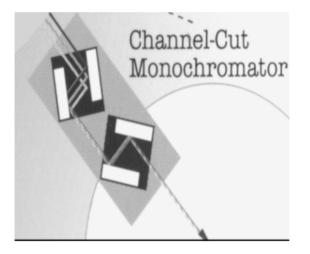
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# Multi bounce single crystal Monochromators

An arrangement of two or four plane crystals provides a beam with very low wavelength dispersion and divergence. Using special channel cut crystals, a high brilliance source is yielded.

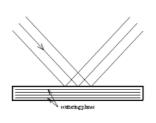


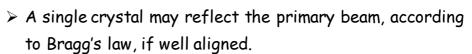


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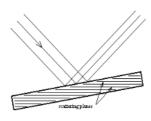


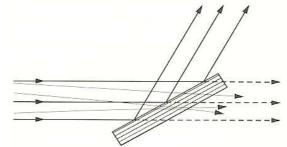
# Plane unbent crystal Monochromators

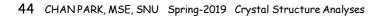




- ➤ It will reject radiation from the wrong direction or the wrong wavelength. → intensity low
- A perfect single crystal will show high resolution in angles or wavelength.
- > A poly-domain crystal will show low resolution.
- > The better the resolution, the more carefully it must be aligned.



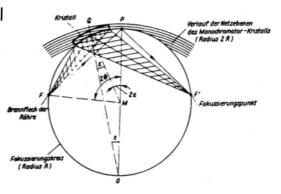


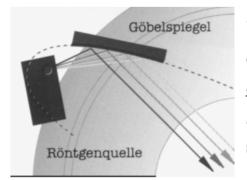




#### Bent crystal primary Monochromators

A <u>monochromator of type Johannson</u> is special cut and bent single crystal. It enables the focal spot or the divergent primary beam to be focused to a point again.





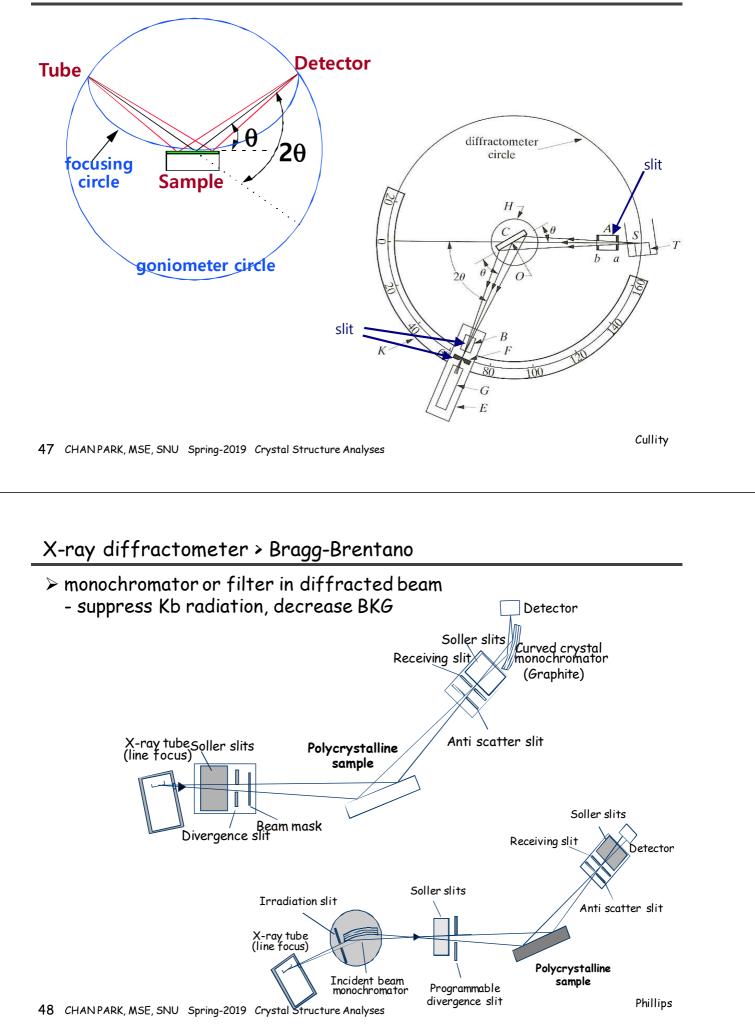
The <u>Göbel Mirror</u> is bent like a parabola. The divergent beam emitted by the X-ray tube is <u>converted into a parallel one</u> illuminating the sample. Mounted in the diffracted beam, the beam off the mirror is reflected into the receiving slit.

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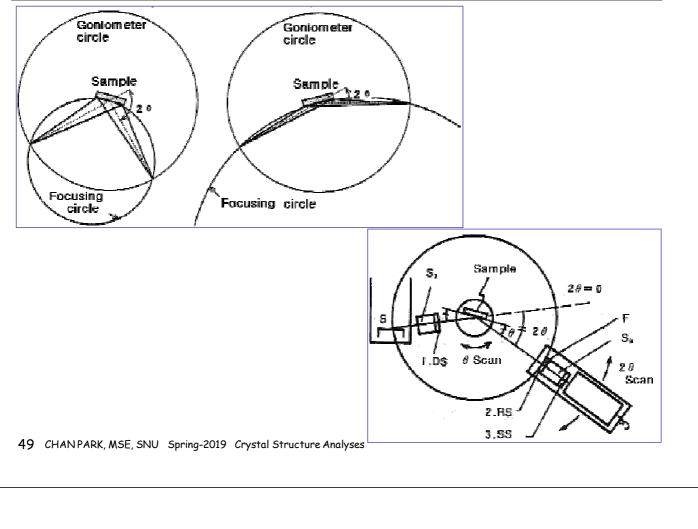


# X-ray Diffractometer

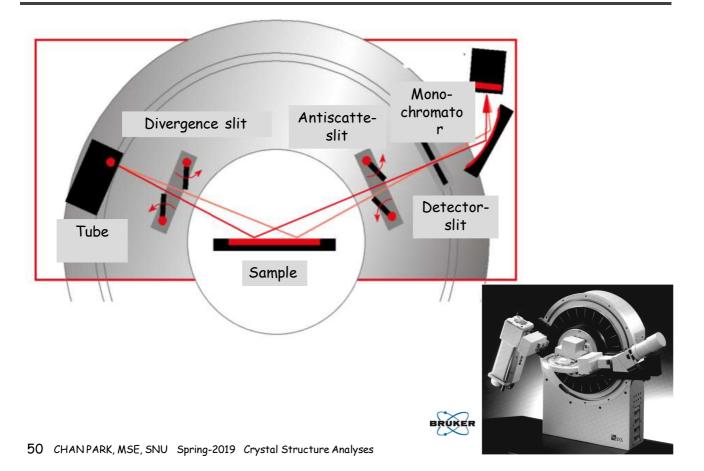
# Bragg-Brentano geometry (parafocusing geometry)

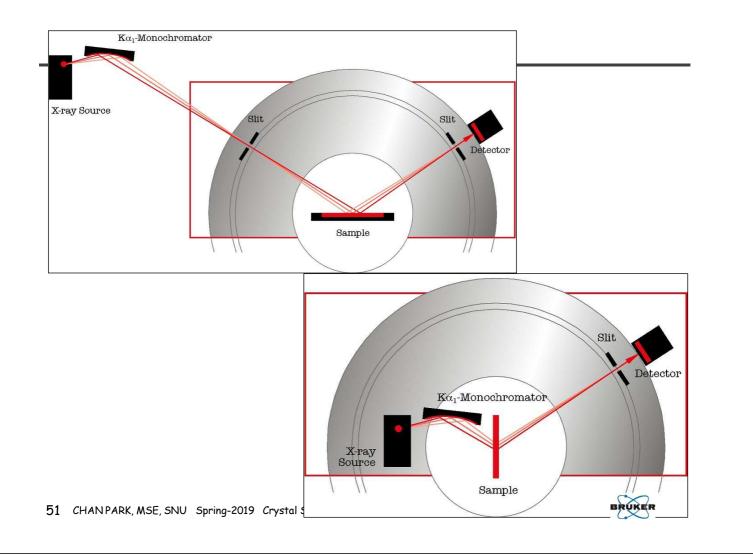


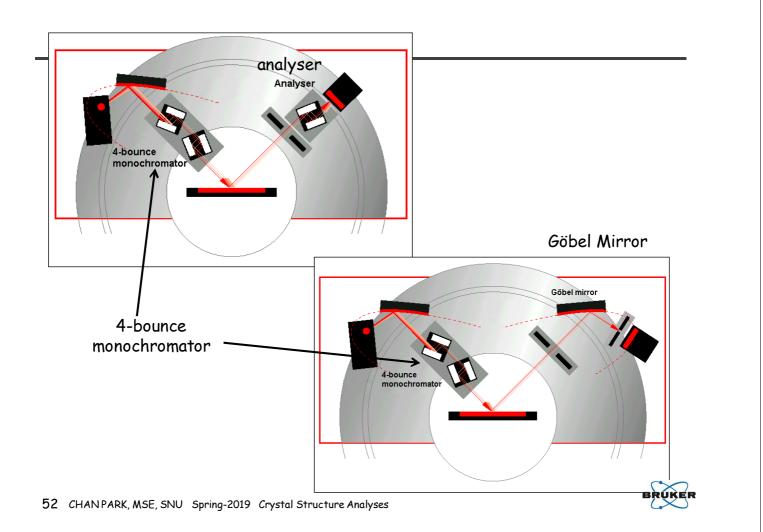
# Bragg-Brentano Geometry (parafocusing geometry)



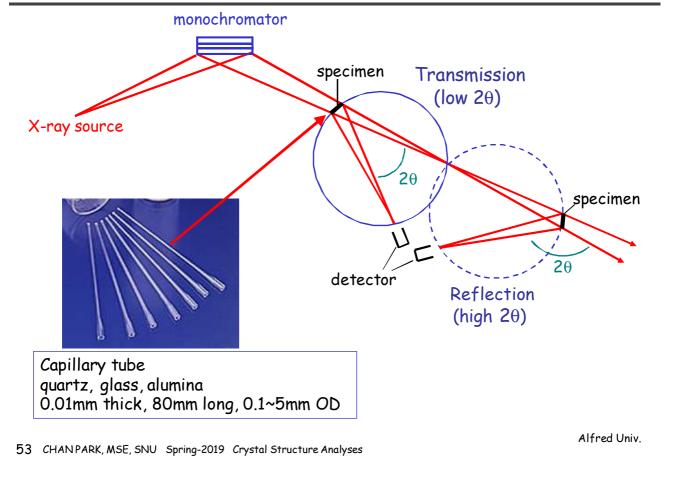
# The Bragg-Brentano Geometry



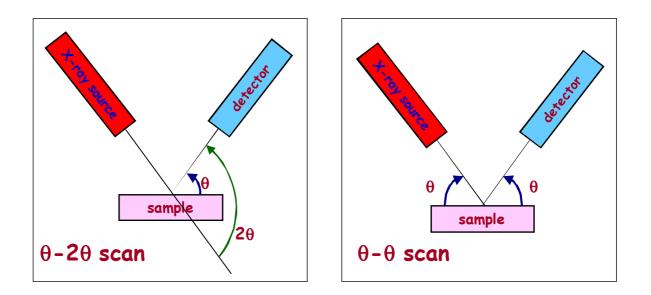




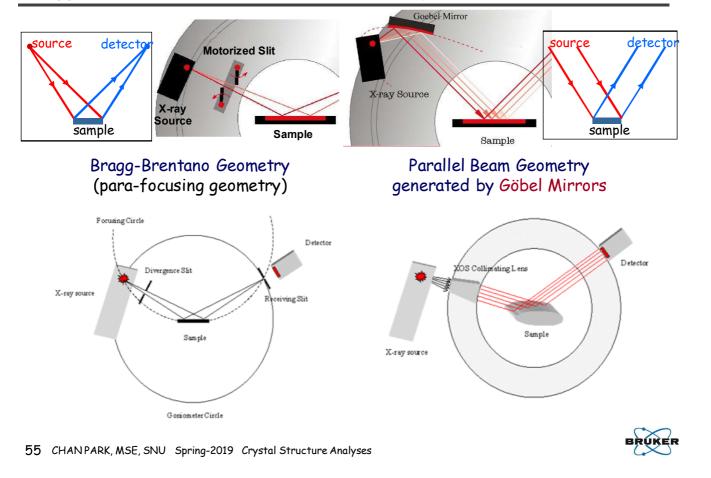
# Guinier Diffractometer



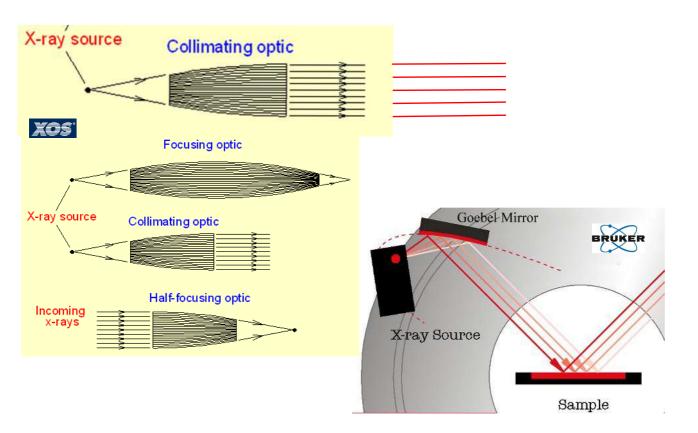
#### $\theta\text{-}2\theta$ scan vs. $\theta\text{-}\theta$ scan

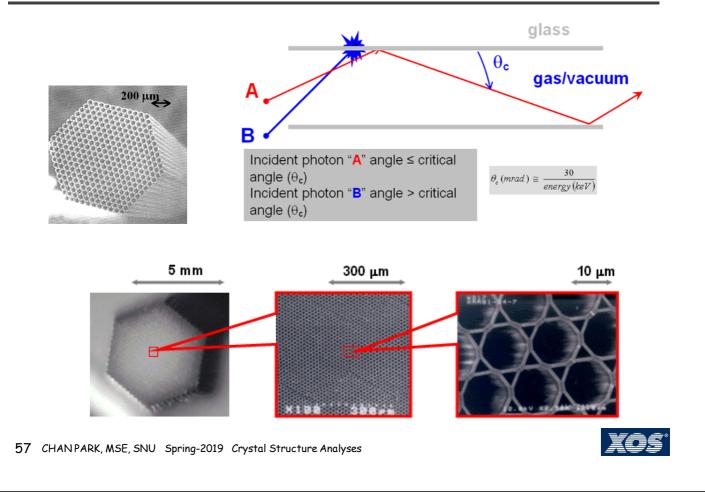


# Bragg-Brentano vs. Parallel Beam Geometry



# Parallel beam optics $\rightarrow$ no sample displacement error





# Parallel beam geometry can be used for

- > analysis of samples with <u>non-flat surfaces</u>, e.g. corrosion on pipes
- samples you would prefer not to grind to a powder, e.g. jewelry, archaeology or forensic samples



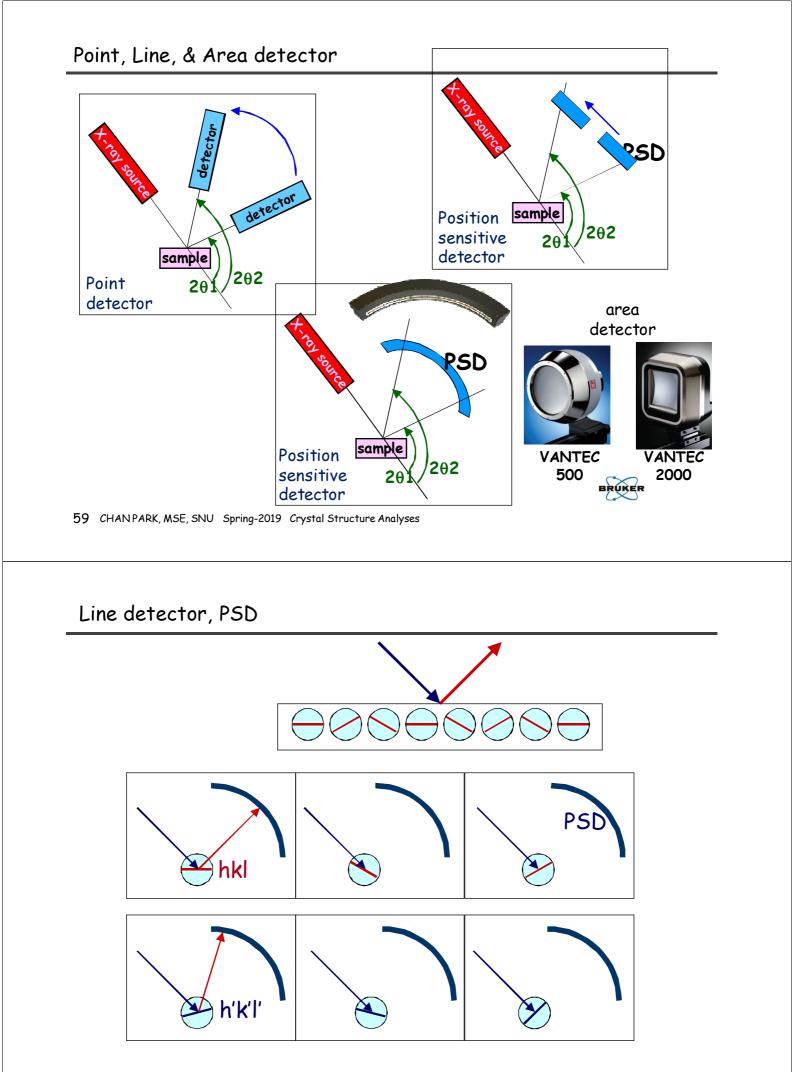
Sodalite Bracelet



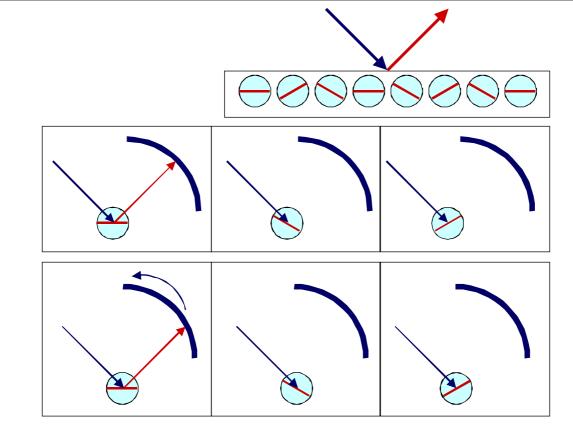
Vesuvianite Pebble

- > measure <u>thermal expansion and contraction</u> when using the heating/cooling stage
- > grazing incidence diffraction (GID) of layers on substrates
- > reflectometry for thin film thickness and roughness

http://www.csec.ed.ac.uk/Instruments/D8\_diffractometer/D8\_parallel-beam.html

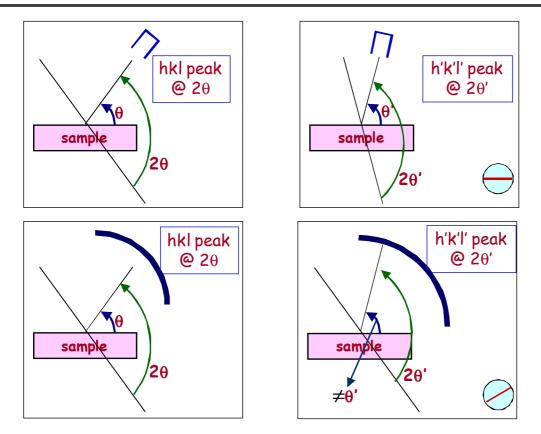


Line detector, PSD

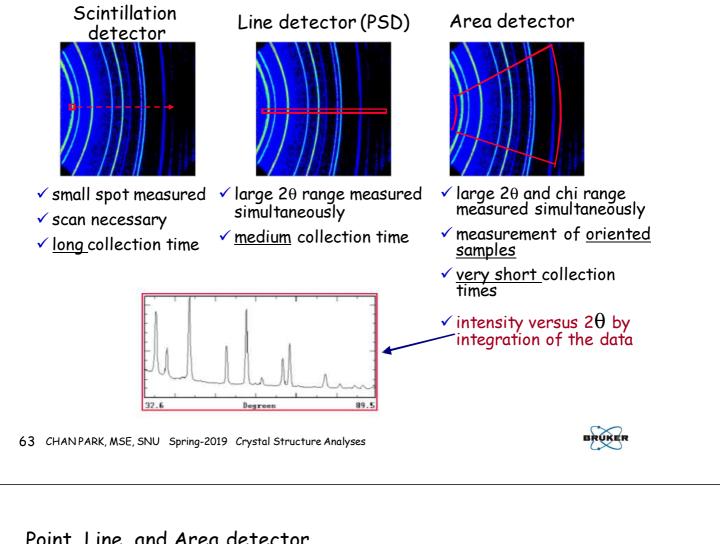


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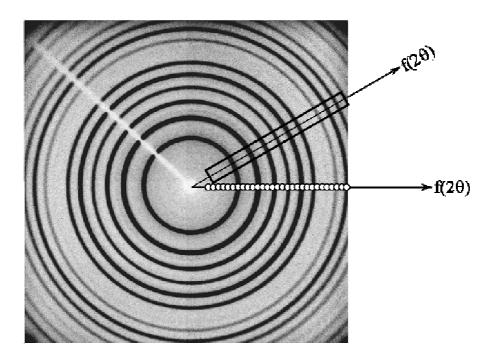
# Point detector vs. Line detector



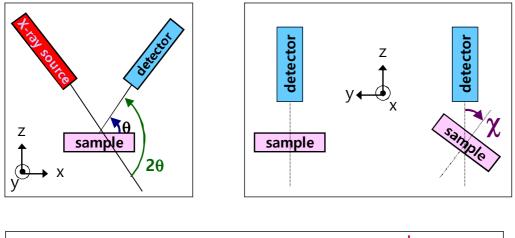
# Point, Line, and Area detector

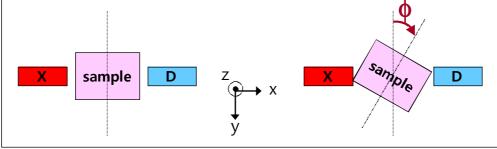


# Point, Line, and Area detector

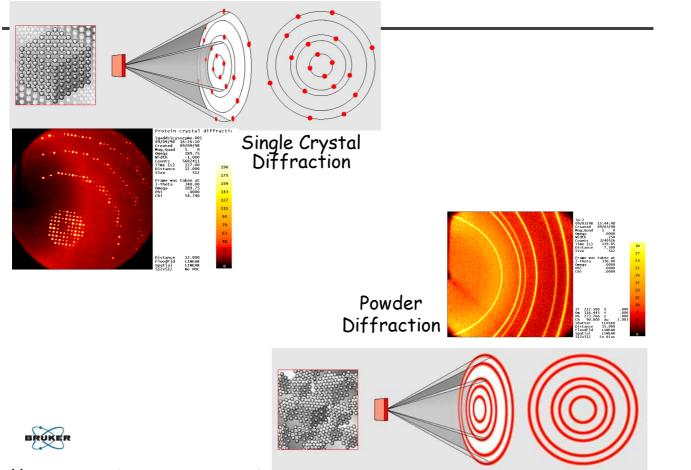


Angles -  $\theta(\omega)$ ,  $2\theta$ ,  $\phi$ ,  $\chi$ 



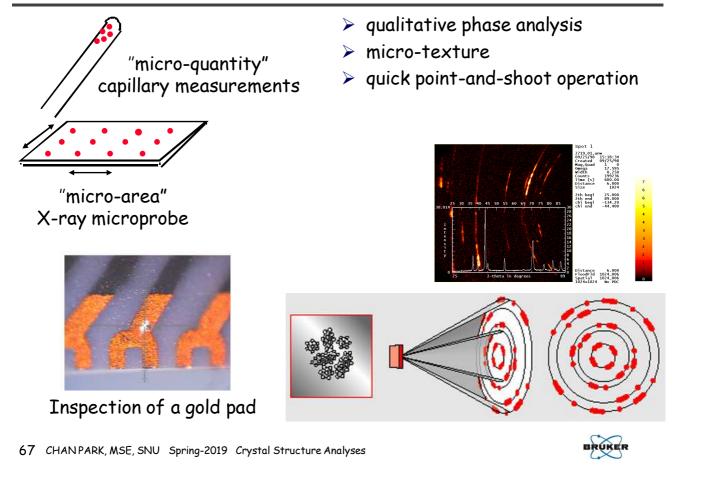


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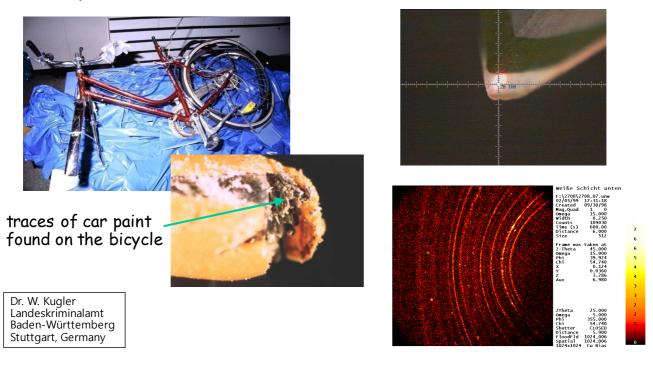
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# Microdiffraction



## Forensic Application

#### Fatal Bicycle Accident Collection of Evidence





# Detector

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#### Detectors

- > X-ray detector = transducer + pulse formation circuit
- > Transducer convert the energies of X-ray photons to electric currents
- Pulse formation circuit convert current into voltage pulses that are counted/integrated by counting equipment
- Transducer = detector or counter
- > Gas proportional counter, scintillation counter, Si(Li) detector, intrinsic germanium detector  $\rightarrow$  all use the ability of X-rays to ionize matter

#### ➢ Quantum efficiency

 How efficiently it collects x-ray photons and then converts them into a measurable signal

#### ➤ Linearity

- ✓ Linear when there is a linear dependence between the photon flux and the rate of signals generated by the detector per second
- ✓ Dead time

#### > Proportionality

 ✓ How the size of the generated voltage pulse is related to the energy of the x-ray photon

#### $\succ$ Resolution

✓ Ability to resolve x-ray photons of different energy and wavelength

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Scintillation			Xe Sealed Gas			Si(Li)		
Cr	Cu	Mo	Cr	Cu	Mo	Cr	Cu	Mo
60	98	100	90	90	75	90	95	80
Less than 1%			Up to 5%			Up to 50%		
Very stable			Pulse shift at high c/s			Pileup, etc., at moderate c/s		
55	45	31	17	14	10	3	2	1
	Cr 60 Les Vo	Cr Cu 60 98 Less than Very stal	Cr Cu Mo 60 98 100 Less than 1% Very stable	Cr       Cu       Mo       Cr         60       98       100       90         Less than 1%       L         Very stable       P         a       a	Cr       Cu       Mo       Cr       Cu         60       98       100       90       90         Less than 1%       Up to 5         Very stable       Pulse sh at high	Cr       Cu       Mo       Cr       Cu       Mo         60       98       100       90       90       75         Less than 1%       Up to 5%         Very stable       Pulse shift at high c/s	Cr       Cu       Mo       Cr       Cu       Mo       Cr         60       98       100       90       90       75       90         Less than 1%       Up to 5%       U         Very stable       Pulse shift       Pileup at high c/s	CrCuMoCrCuMoCrCu60981009090759095Less than 1%Up to 5%Up to 5Very stablePulse shift at high c/sPileup, etc., a moderate

#### Table 5.3. Properties of Common X-ray Detectors

#### Photographic film

- > Silver halide  $\rightarrow$  metallic silver, when exposed to x-ray photons
- Once developed (darkened), further incoming X-rays can change nothing
   → loss of information (dead time in electronic counters)
- Film darkening is proportional to the intensity of exposing X-rays over LINEAR RANGE of the film
- > When measuring intense sources
  - ✓ (1) Have to reduce X-ray intensity with filters or reduce incident beam flux
  - $\checkmark$  (2) extend linear range of the film
- > Low proportionality range, limited spatial & energy resolution

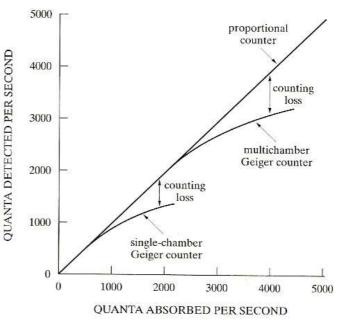
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#### Detector

- > all use the ability of X-rays to ionize matter
  - $\checkmark$  Matter = gas  $\rightarrow$  Proportional, Geiger
  - $\checkmark$  Matter = solid  $\rightarrow$  Scintillation, semiconductor
- > Proportional
- > Geiger
- Scintillation
- > Semiconductor

# Counting loss

- > When time interval between pulses is very small, adjacent pulses may not be counted as separate pulses
   → counting loss begins
- Resolving time (t<sub>s</sub>)- minimum time
   between two resolvable pulses

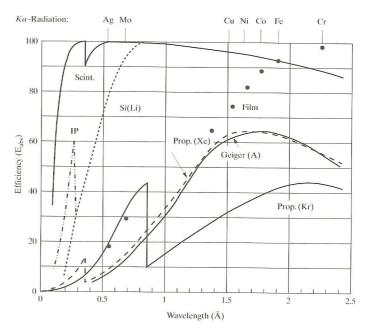


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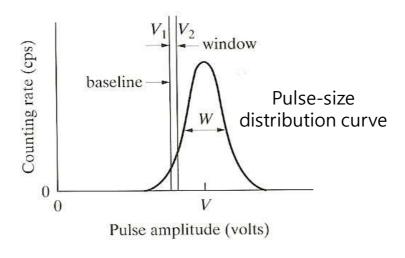
#### Counting efficiency

- > Efficiency of detector in collecting radiation incident upon it
- Most detectors designed for XRD are optimized for the measurement of Cu Ka radiation. Loss of efficiency can result when different I is used.



Resolution

- > A measure of detector's ability to resolve two X-ray photons of different energy
- Size of voltage pulses produced by detectors are proportional to the energy of the x-ray quantum absorbed
- $\succ$  Resolution R = W/V

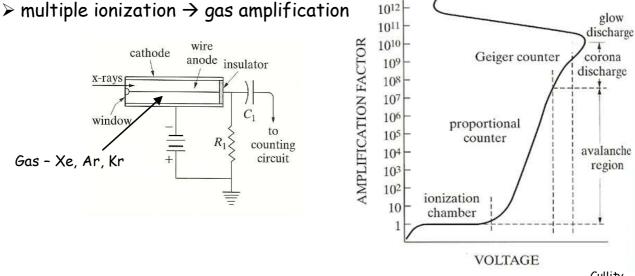


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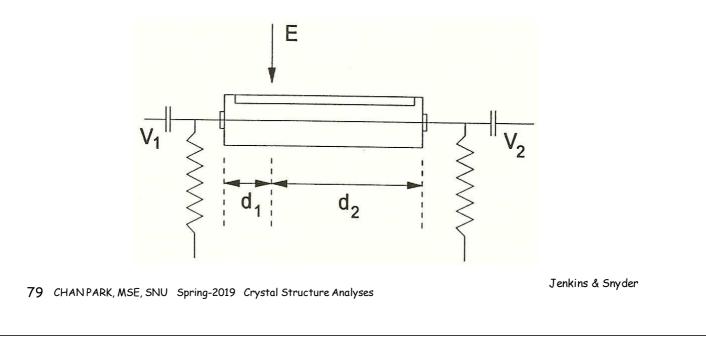
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#### Proportional counters

- > Size of pulse ∞ energy of X-ray quantum absorbed → X-ray quanta of different energies can be distinguished
- > Gas is ionized by incoming X-ray
- ightarrow e' ightarrow anode, positive ion ightarrow cathode (cylindrical metal shell)



- > Increased speed of data acquisition
- ➤ Measure "rise time" (rate at which a pulse develops) at each end of the wire → detect position can be located
- > Angular resolution not very high

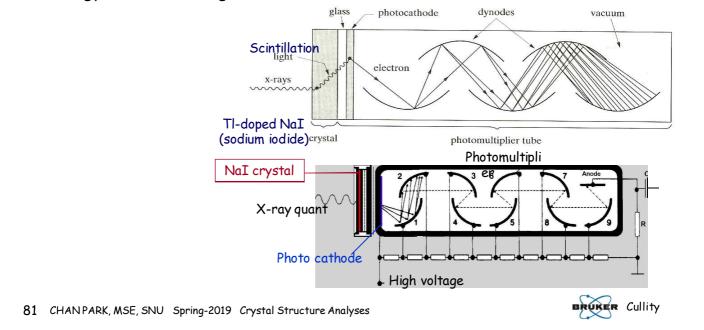


# Geiger counter

- > Very high voltage in a proportional counter  $\rightarrow$  Geiger counter
- Gas amplification factor much larger than proportional counter
- All pulses have the same size, regardless of the energy of Xray quanta
- ➤ Cannot count at high rates without losses → seldom used in diffractometry

Scintillation detector

- > X-ray can cause certain substances to fluoresce visible light
- > Amount of light  $\propto$  emitted X-ray intensity
- > Pulses produced ~ energy of X-ray quanta
- ➤ Difficult to discriminate between X-ray quanta of different energies → energy resolution not great

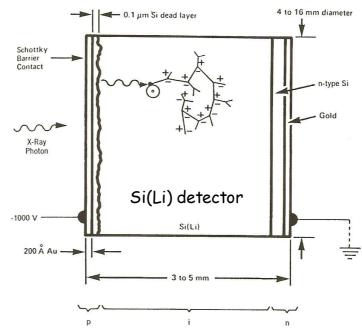


#### Semiconductor detector

- Best energy resolution
  - ✓ Produces pulses proportional to the absorbed X-ray energy with better energy resolution than any other detector

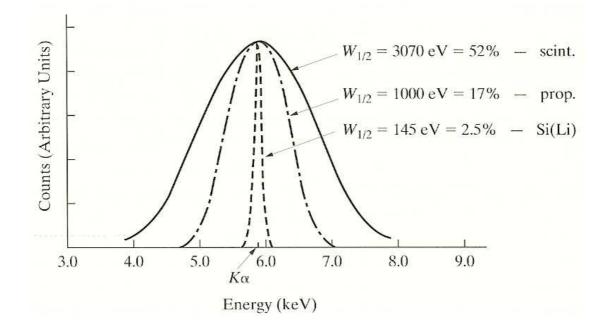
#### ➤ Si(Li), Ge(Li), HPGe

➢ Need LN2 cooling



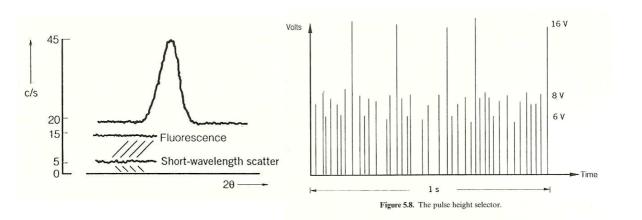
Jenkins & Snyder

#### Pulse-height distribution curves

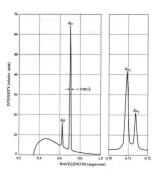


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# Pulse height selection (PHS)



- ➤ Different energy → different size of voltage pulse → can be electronically discriminated --- PHS, pulse height analyzer (PHA)
- Can remove such effects as sample fluorescence & BKG that may arise from short wavelength X-rays from X-ray tube continuum that pass the b filter



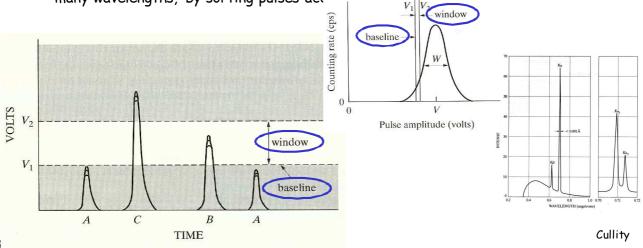
Jenkins & Snyder

- Proportional, scintillation semiconductor detectors "proportional"; they produce pulses having a size proportional to the energy of the incident X-rays
- If pulses of different size can be distinguished, X-rays of different energies can be distinguished
- > Pulse-height discriminator
- > Single-channel pulse-height analyzer
- > Multi-channel pulse-height analyzer (MCA)

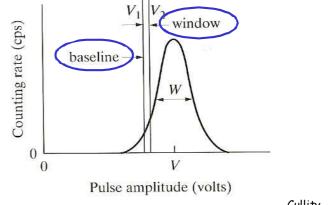
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# Pulse height analysis

- Pulse-height discriminator
  - $\checkmark\,$  Reject any pulses smaller than V $_1$
- > Single-channel pulse-height analyzer
  - $\checkmark\,$  Only pulses having sizes between  $V_1\,\&\,V_2$  can pass
  - $\checkmark$  Can reduce BKG of diffraction pattern by excluding short I white radiation
- > Multi-channel pulse-height analyzer (MCA)
  - ✓ Can separate pulses from a detector that is receiving incident radiation of many wavelengths, by sorting pulses acc



- Pulse-height discriminator
- > Single-channel pulse-height analyzer
  - ✓ Entire energy range is scanned serially in time by moving channel
- > Multi-channel pulse-height analyzer (MCA)
  - $\checkmark$  A large number of fixed channels cover the entire range
  - ✓ All channels simultaneously receive the count-rate information appropriate to each channel  $V_1 ||_{V_1}$



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