Diffraction techniques
instrumental components

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X-rays in Materials - Dakar 2005

the target of the lecture is that by the end you should know:

1. what is an XRPD experiment ?
2. why should we do it ?
3. how can we perfom XRPD experiments ?

- ✓ try to focus on these main questions
- ✓ try to follow the details if you can, or ask
- ✓ or write down the questions for tomorrow’s exercise session

diffraction

- **elastic scattering**
- **kinematic approximation (theory of “ideally imperfect” crystal)**
- **geometrical interpretation by Bragg/Ewald/Laue**

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

- **direct space Û reciprocal space relationship**

$$F_{\infty}(\overrightarrow{r*}) = F_M(\overrightarrow{H}) \sum_{\substack{h,k,l \\ -\infty}}^{\infty} d(\overrightarrow{r*} - \overrightarrow{r_H*})$$

$$F_M(\overrightarrow{r*}) = \sum_{j=1}^{N} f_j(\overrightarrow{r*}) \exp(2pi\vec{r} \cdot \overrightarrow{r*})$$

XRPD experiment: what is it?

- we want to measure the intensity distribution in the reciprocal space
    - position of diffraction peaks (2θ, E, ToF $\Rightarrow d_{hkl}$)
    - intensity ($I_{hkl} \propto |F_{hkl}|^2$)
    - peak profile shape ($H(2\theta) = f(2\theta) \otimes g(2\theta)$)

- a correct experiment assumes:
    - the **homogeneous distribution** of crystallites in the sample
    - the **homogeneous probing** of the material by the beam
    - the **statistically correct** measurement of intensity

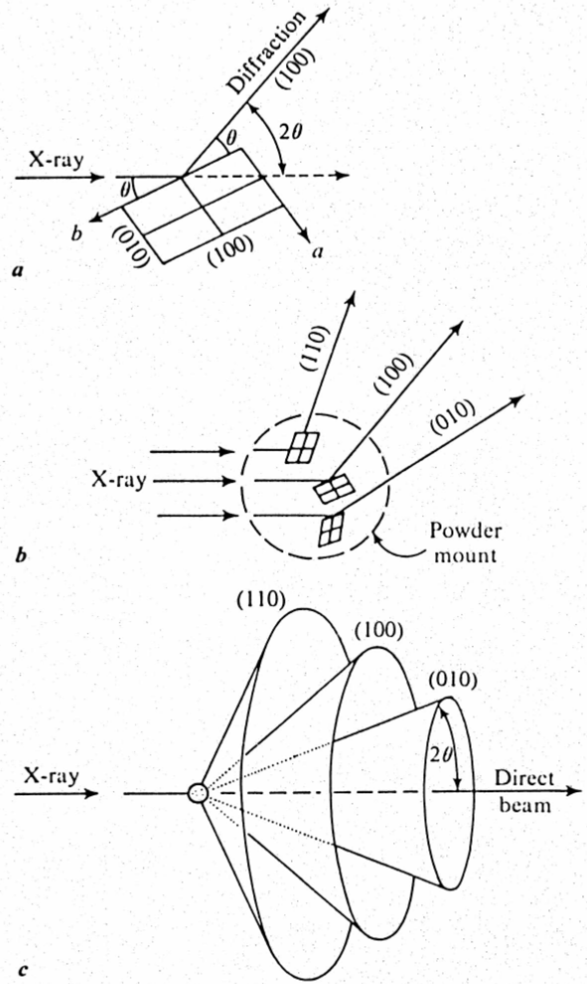
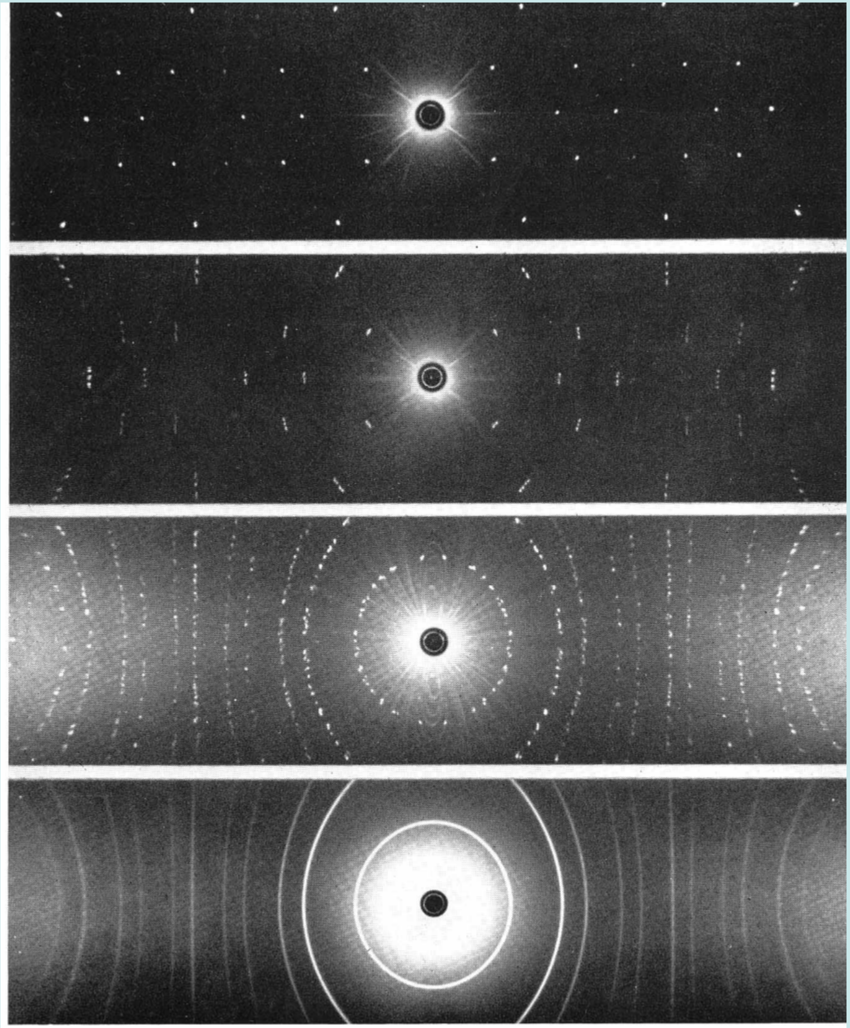
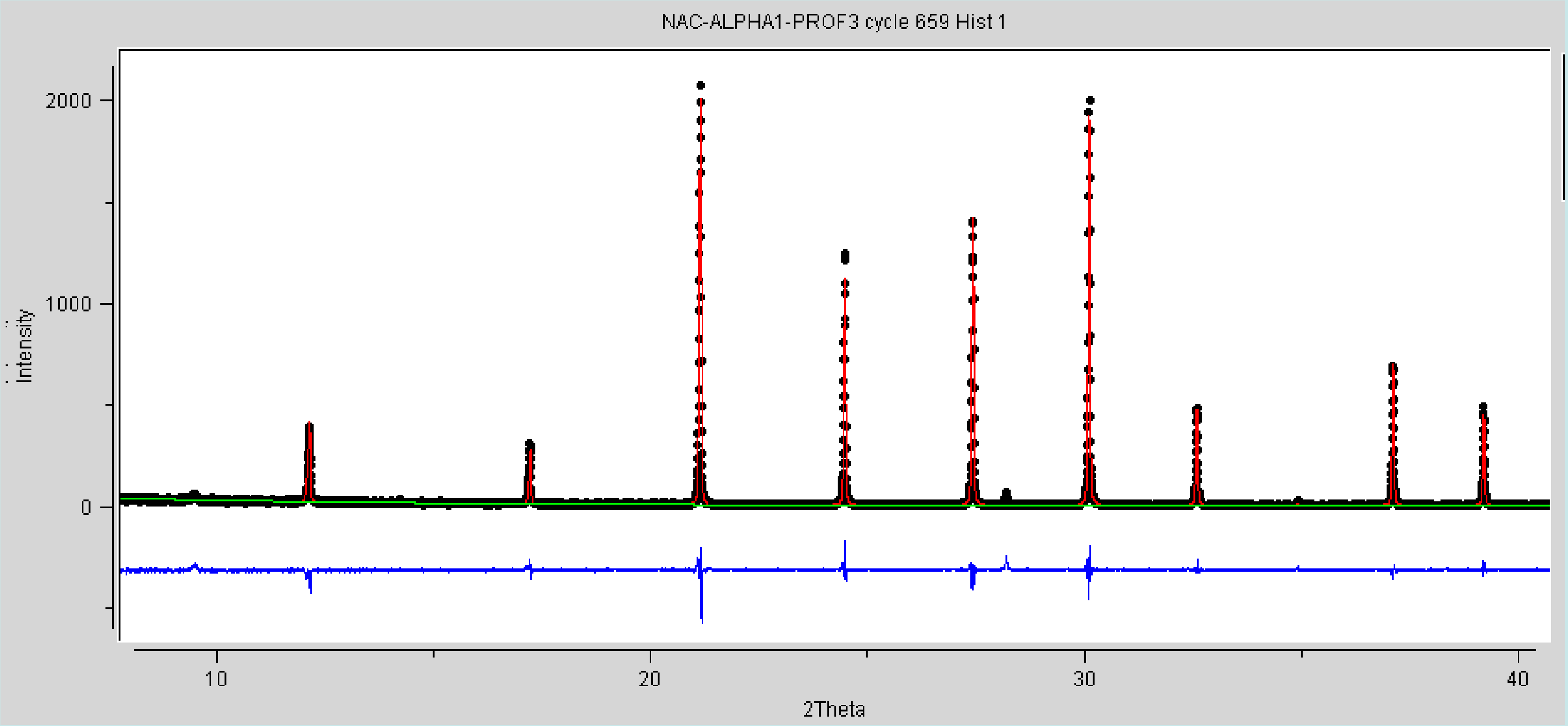


FIGURE 10.11 **Diffraction of monochromatic x-rays from (a) a single crystal and (b) an aggregate of small mineral fragments. (c) Diffraction cones produced by the powder method.**

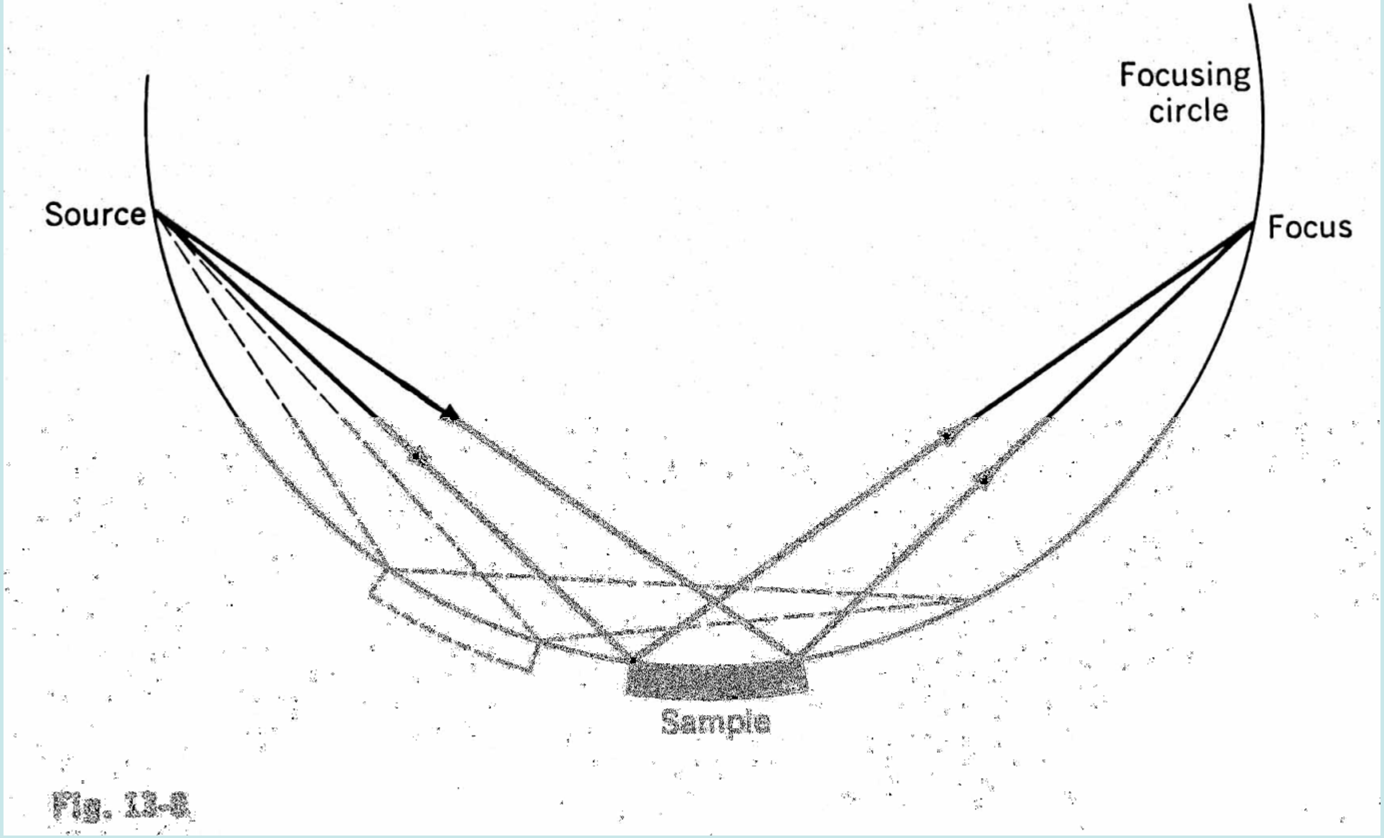


(*From top to bottom*). Fig. 197; Single-crystal rotation photograph of fluorite [100] vertical: Fig. 198; Single-crystal rotation photograph of fluorite [100] 2° to vertical: Fig. 199; X-ray photograph of five randomly oriented crystals of fluorite: Fig. 200; Powder photograph of fluorite.

XRPD experiment



focusing geometry



focusing geometry

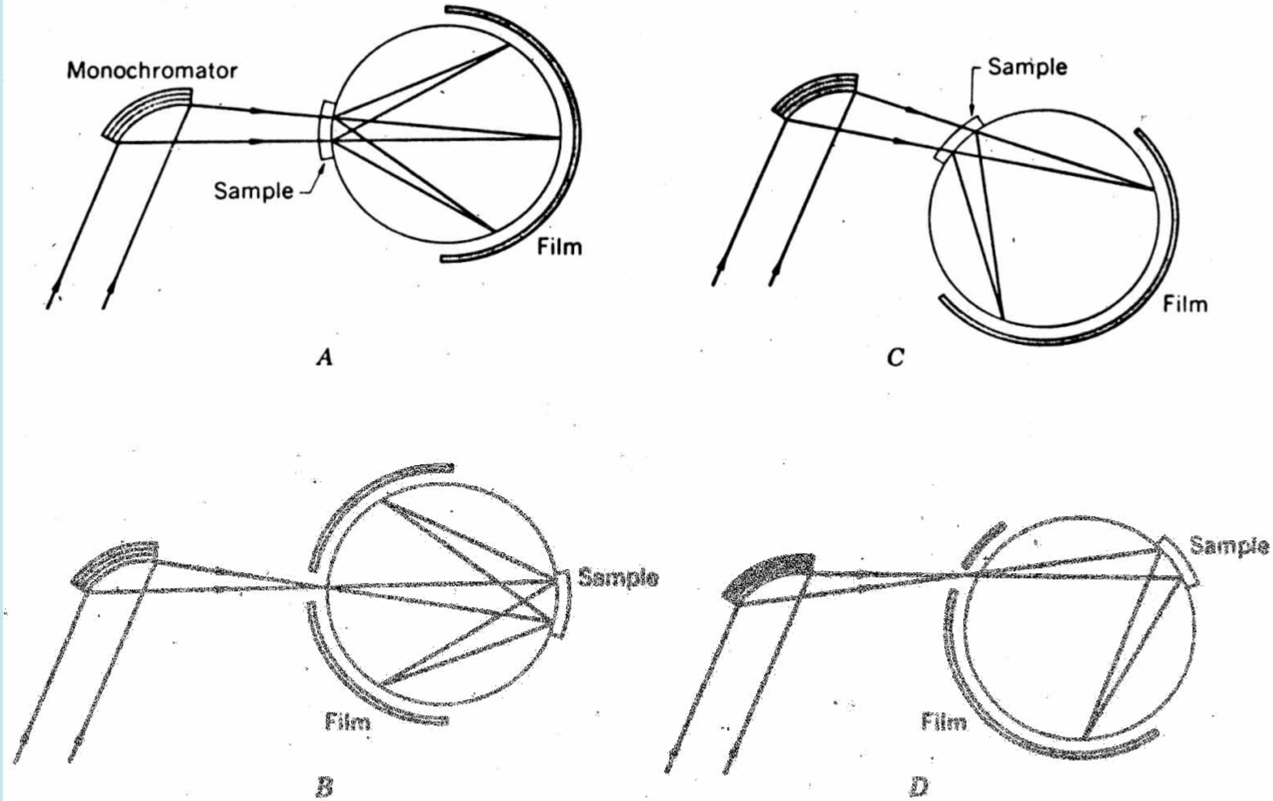
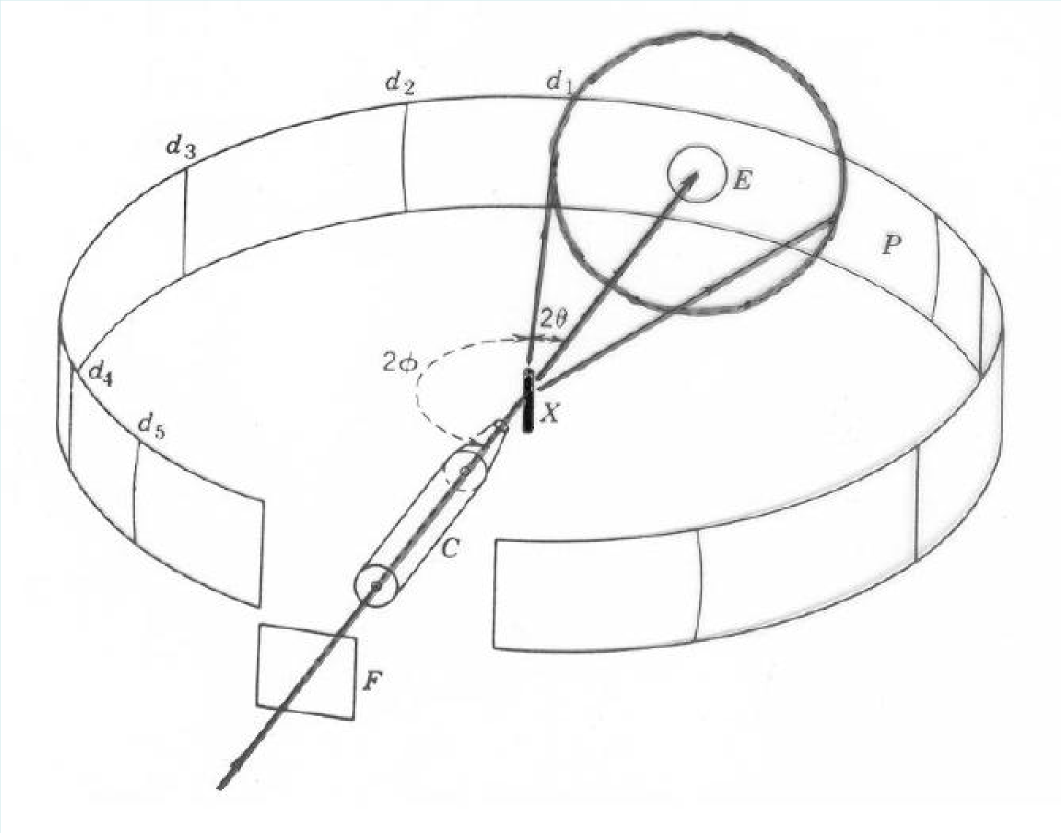


Fig. 17-12. Bent-crystal monochromators. (*A*) Symmetric transmission arrangement; (*B*) symmetric back-reflection arrangement; (*C*) Guinier asymmetric arrangement; (*D*) Seeman-Bohlin arrangement.

Debye-Scherrer geometry



parafocusing geometry

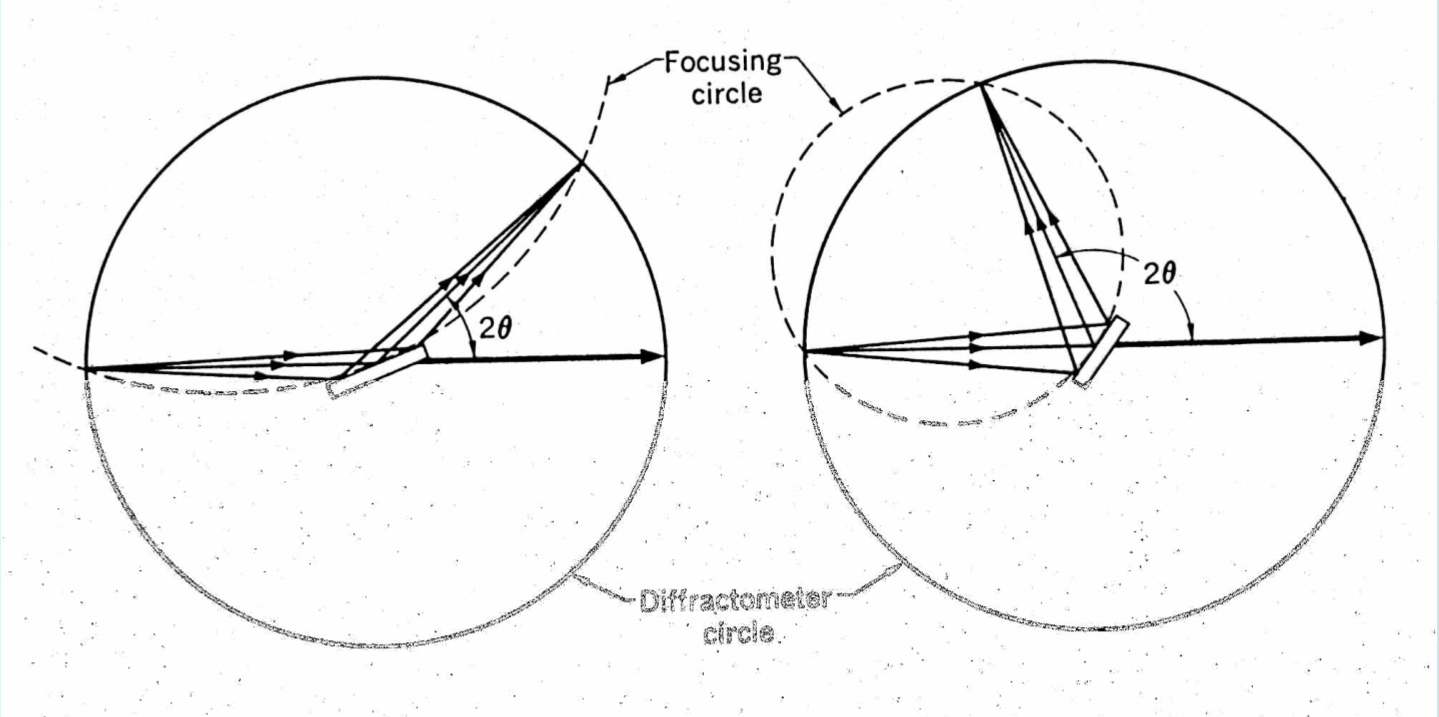


Fig. 13-9

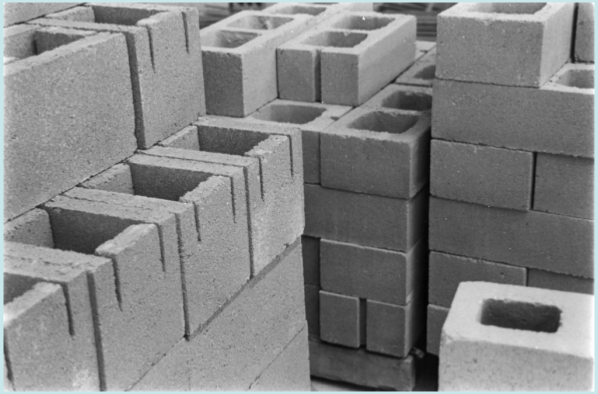
XRPD experiment: why?

to characterize materials

to characterize processes

can you make glass with this sand ?

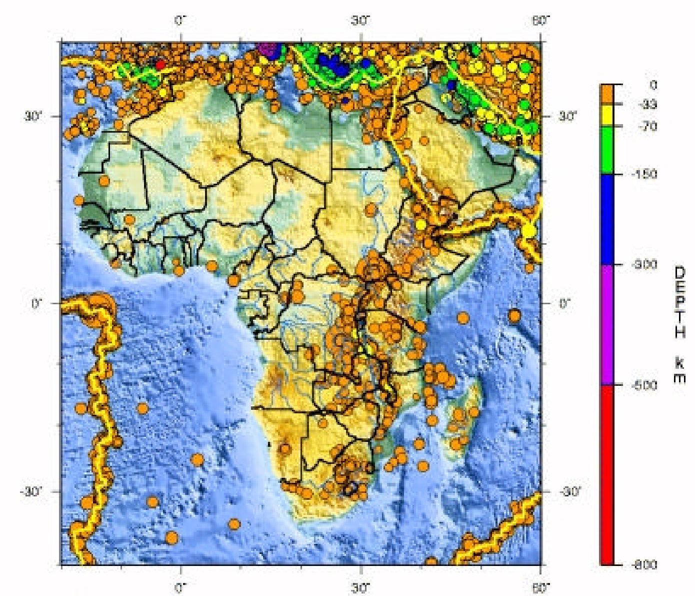
can you make bricks with this mud ?



Magnitude 6.8 - LAKE TANGANYIKA REGION, CONGO-TANZANIA
2005 December 5 12:19:57 UTC

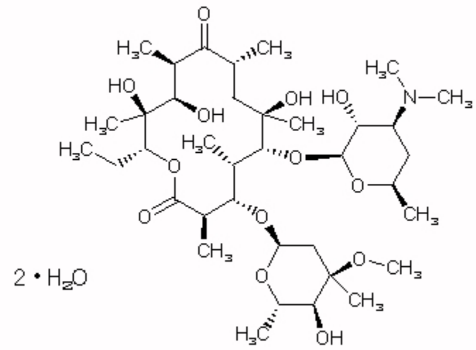
Preliminary Earthquake Report
U.S. Geological Survey, National Earthquake Information Center
World Data Center for Seismology, Denver

A strong earthquake occurred at 12:19:57 (UTC) on Monday, December 5, 2005. The magnitude 6.8 event has been located in the LAKE TANGANYIKA REGION, CONGO-TANZANIA. (This event has been reviewed by a seismologist.)

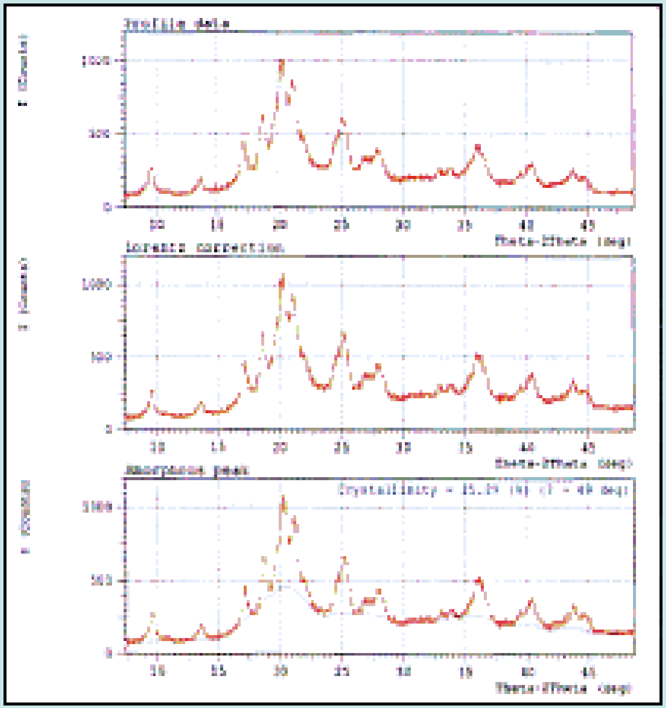


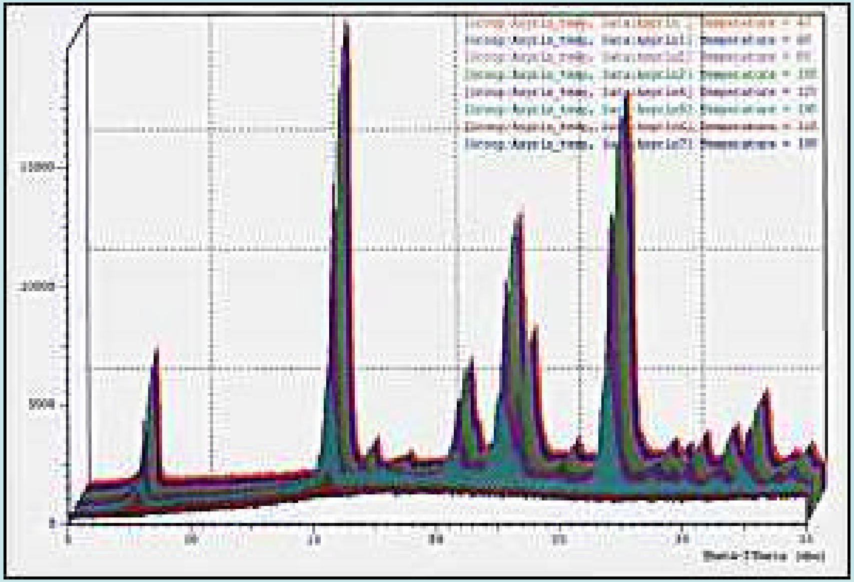
Seismicity of Africa, 1990 - 2000

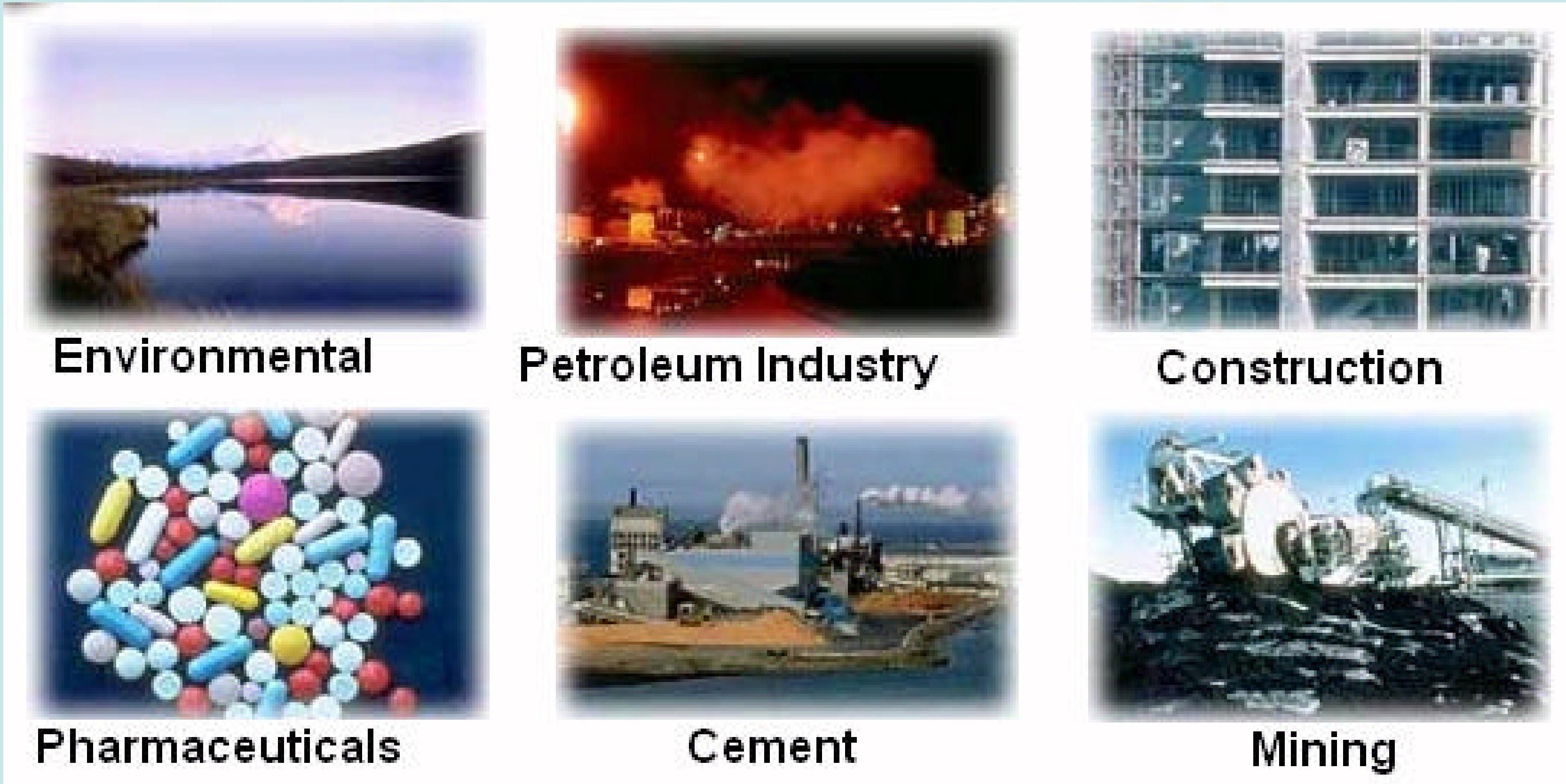
X-Ray Diffraction for Solid State Pharmaceutical Products.



Erythromycin A dihydrate






Environmental
Petroleum Industry
Construction
Pharmaceuticals
Cement
Mining

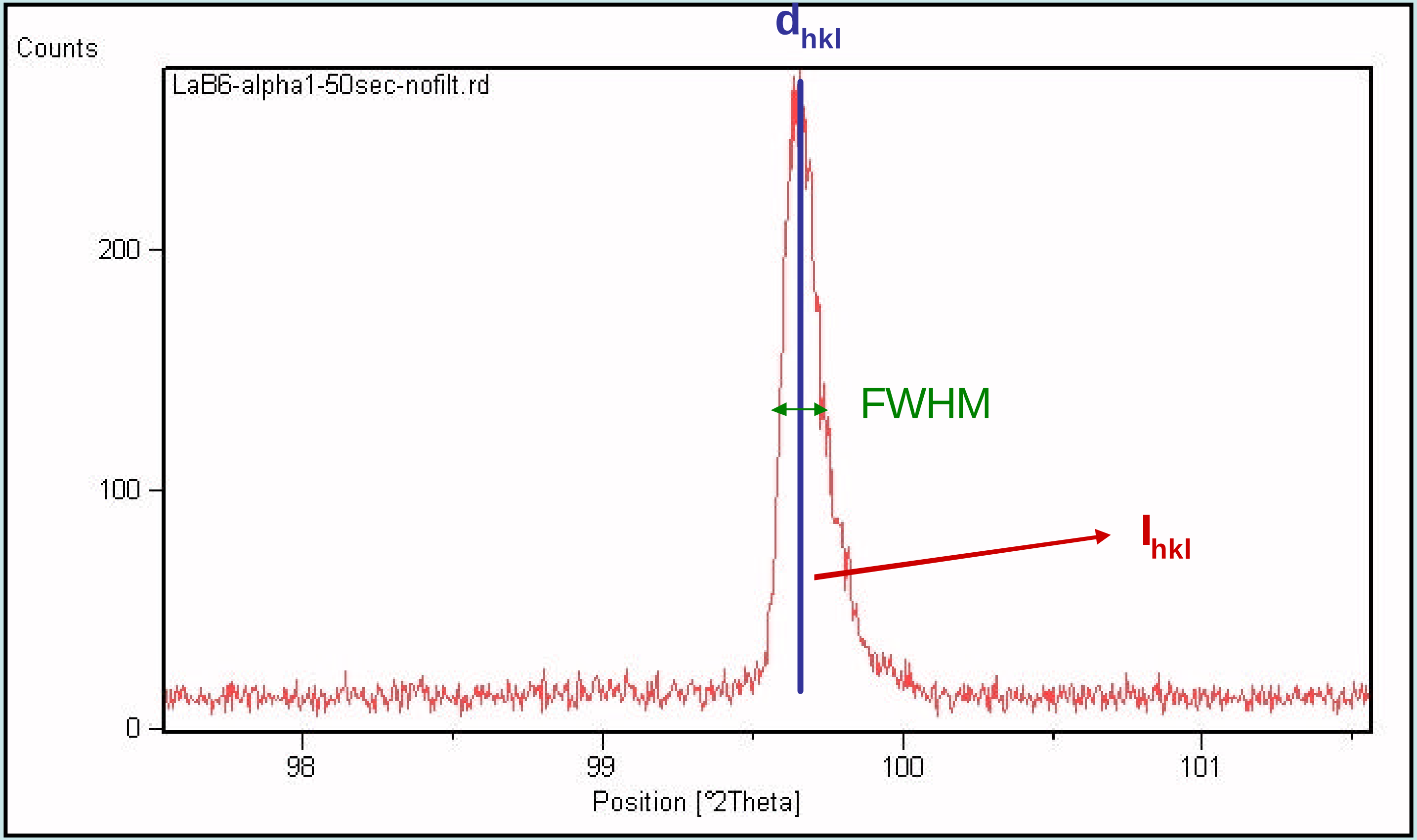
XRPD experiment: why?

XRD is used

- **to characterize the materials** (at equilibrium conditions)
  - *phase identification and quantification*
  - *crystal structure*
  - *crystal chemistry*
  - *structure dynamics (Debye-Waller factors)*

- **to characterize the processes** (kinetics, non-ambient)
  - *phase transformation*
  - *reaction kinetics*

XRPD experiment: what do we measure ?



measurements vs infos

	position d_{hkl}	shape $H(d_{hkl})$	intensity F_{hkl}
⇒ **phase identification**	x		(x)
⇒ **quantitative analysis**	x		x
⇒ **structure analysis**			x
⇒ **microstructure/texture**		x	(x)
⇒ **chemical reactions phase transformations kinetics**	x	(x)	x

FPPF = WPPF (Rietveld)

XRPD experiment: how ?

radiation source → sample (goniometer) (chamber) → detector

↓ optics (after radiation source) ↓ optics (after sample)

- *you need to configure your setup based on your needs*
- *in most cases a standard instruments satisfy primary needs for qualitative and quantitative analysis*
- *modern instrumentation allows easy change of the optics and the geometry by the use of modular components*

XRPD experiment: components

The choice of the components (of the data collection parameters, of the analytical strategies) depends on your target

$\Rightarrow$ ***phase qualitative analysis*** *(identification)*
$\Rightarrow$ ***phase quantitative analysis***
$\Rightarrow$ *structure analysis*
$\Rightarrow$ *microstructural analysis/texture*
$\Rightarrow$ *chemical reactions/phase transformation/kinetics*

XRPD experiment: ideal

- **source** ⇒ intense, well collimated, parallel beam
- l**,E** ⇒ optimal (bandpass, absorption, fluorescence, etc.)
- **side measurements** ⇒ primary beam attenuation, sample absorption, sample fluorescence
- **sample** ⇒ ideal shape and particles (strain-free, homogeneous particle size, no texture, no preferred orientation, etc.)
- **detector** ⇒ efficient, max coverage of reciprocal space
- **reciprocal space resolution** ⇒ max
- **instrumental aberrations** ⇒ min, ab initon modeling of the peak profile shape
- **experimental noise** ⇒ min
- **sample conditioning** ⇒ flexible

data quality

affected by

- Þ ***flux/quality of the source***
  - Þ ***quality/performance of the optics***
    - Þ ***amount/shape of the sample***
      - Þ ***type/efficiency of the detector***
        - Þ ***counting time***

source

synchrotron radiation

- bending magnets
- wigglers
- undulators

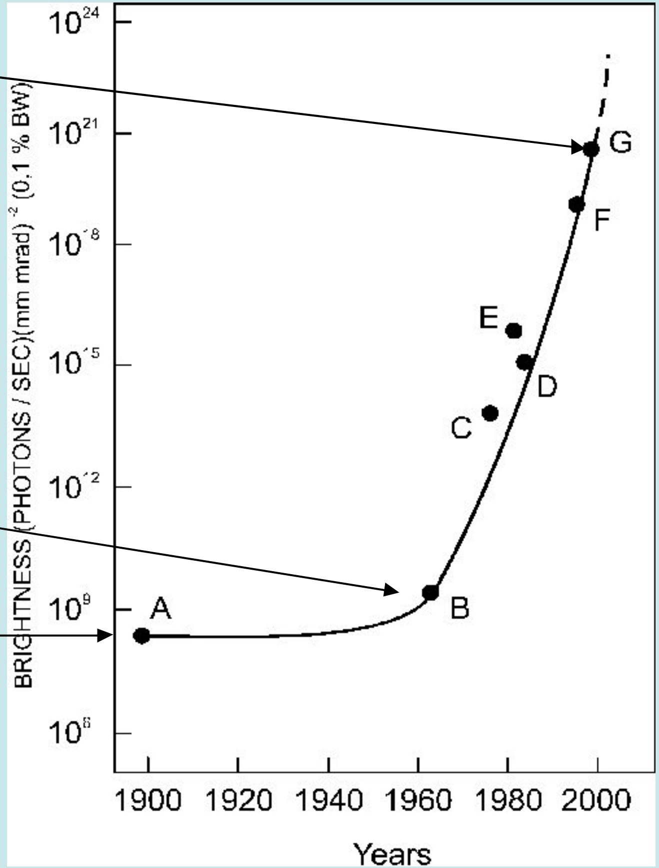
microsource

rotating anode

X-ray tube

– conventional

– ceramic



important source characteristics

- ⇒ ***total flux at the sample***
- ⇒ ***stability in time***
- ⇒ ***beam homogeneity***
- ⇒ ***divergence***
- ⇒ ***energy distribution***

source features

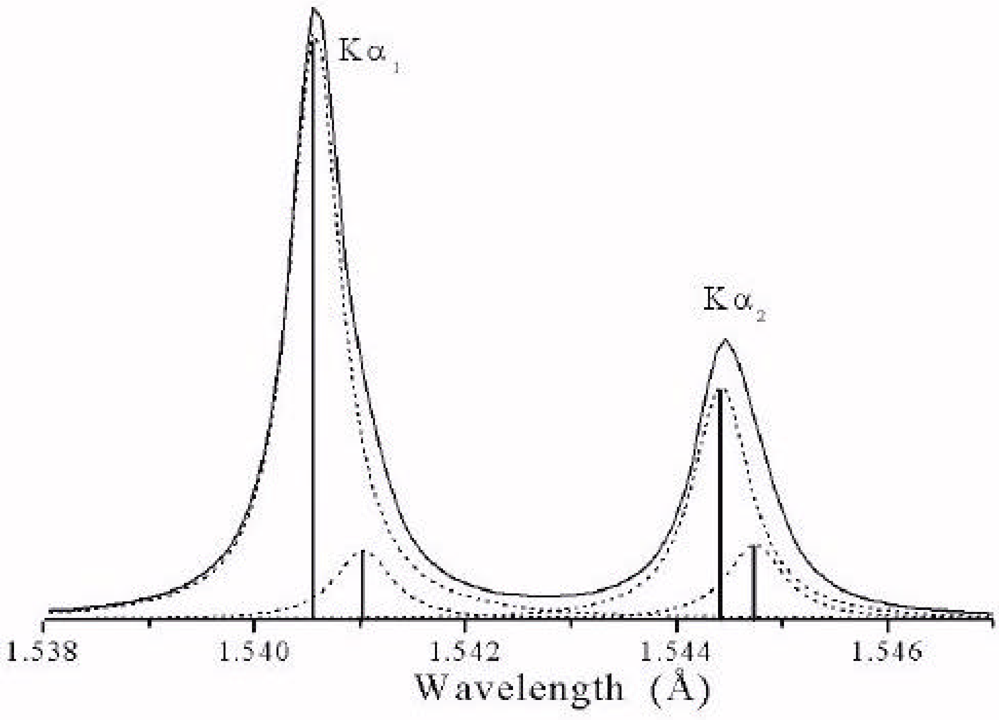


Fig. 2.2. Phenomenological representation of the Cu K_α emission profile based on four Lorentzians (from [19])

source features

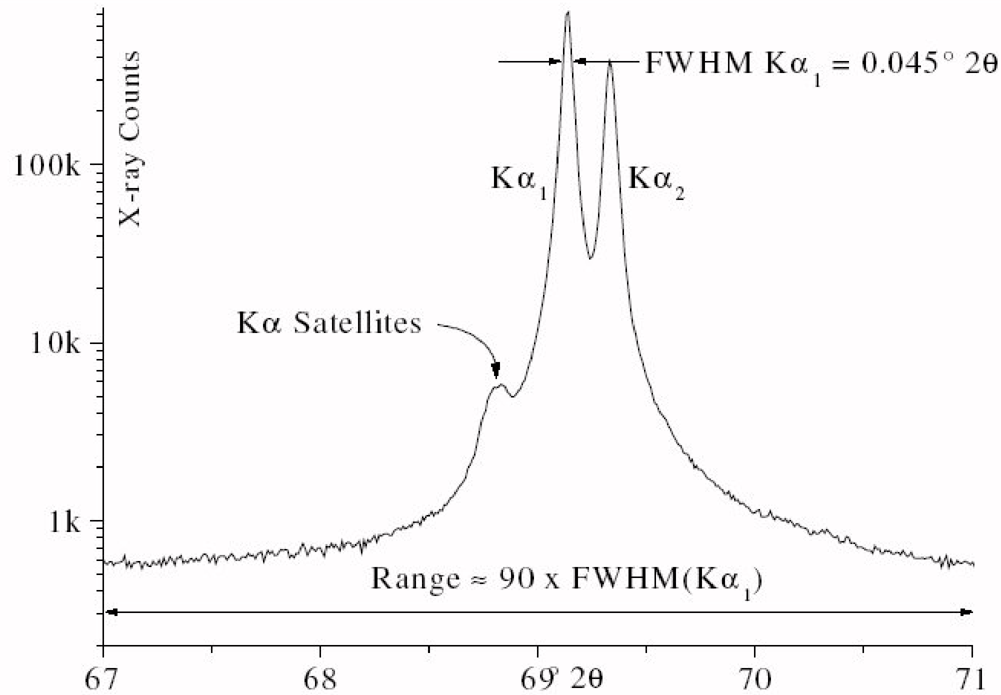
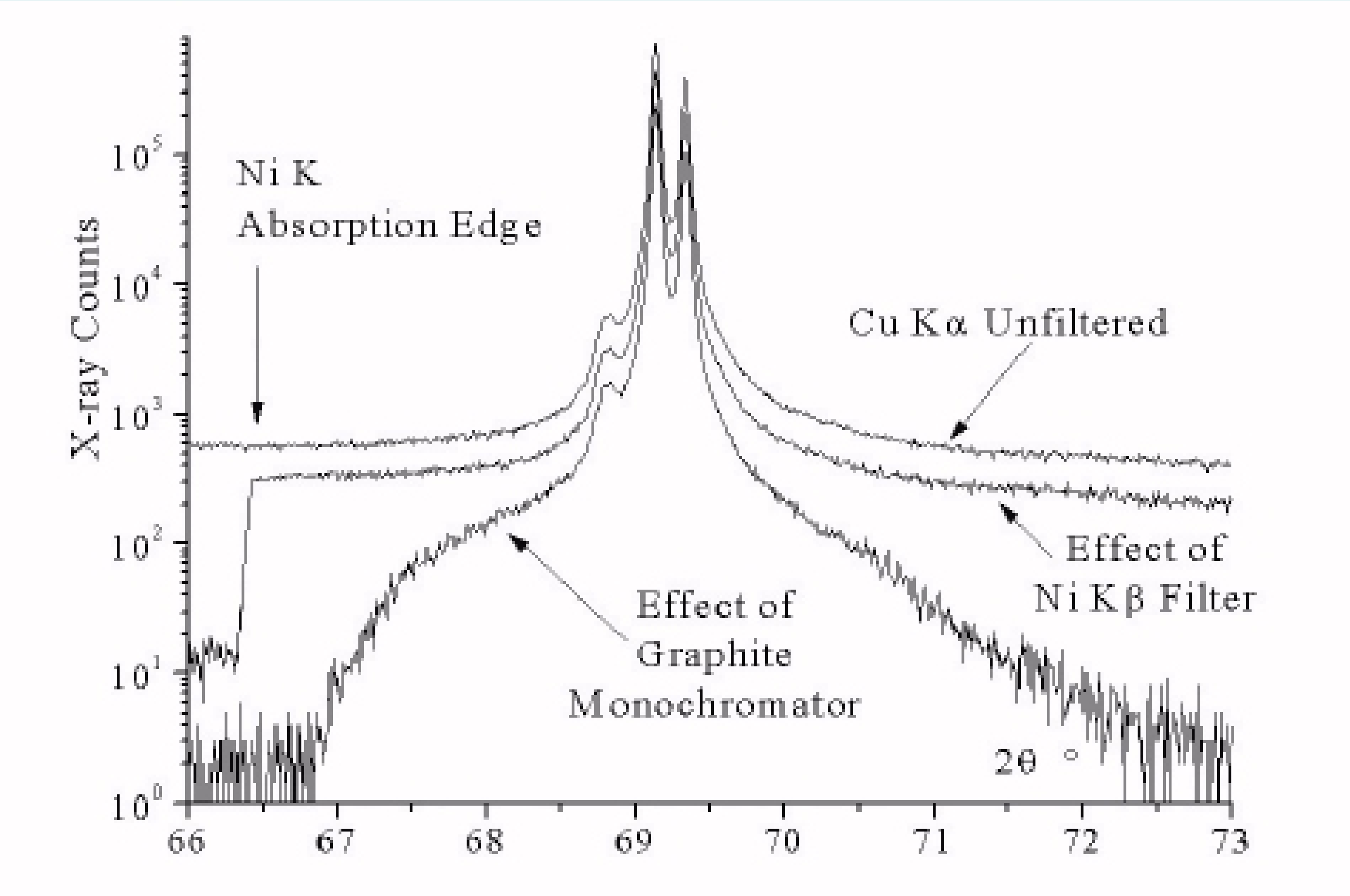


Fig. 2.3. Cu$K\alpha$ emission profile showing the satellite group of lines and the extent of the tails from the $K\alpha 1$ and $K\alpha 2$ emission lines. This profile was recorded using the 400 line from a silicon single crystal wafer (from [19])

source features



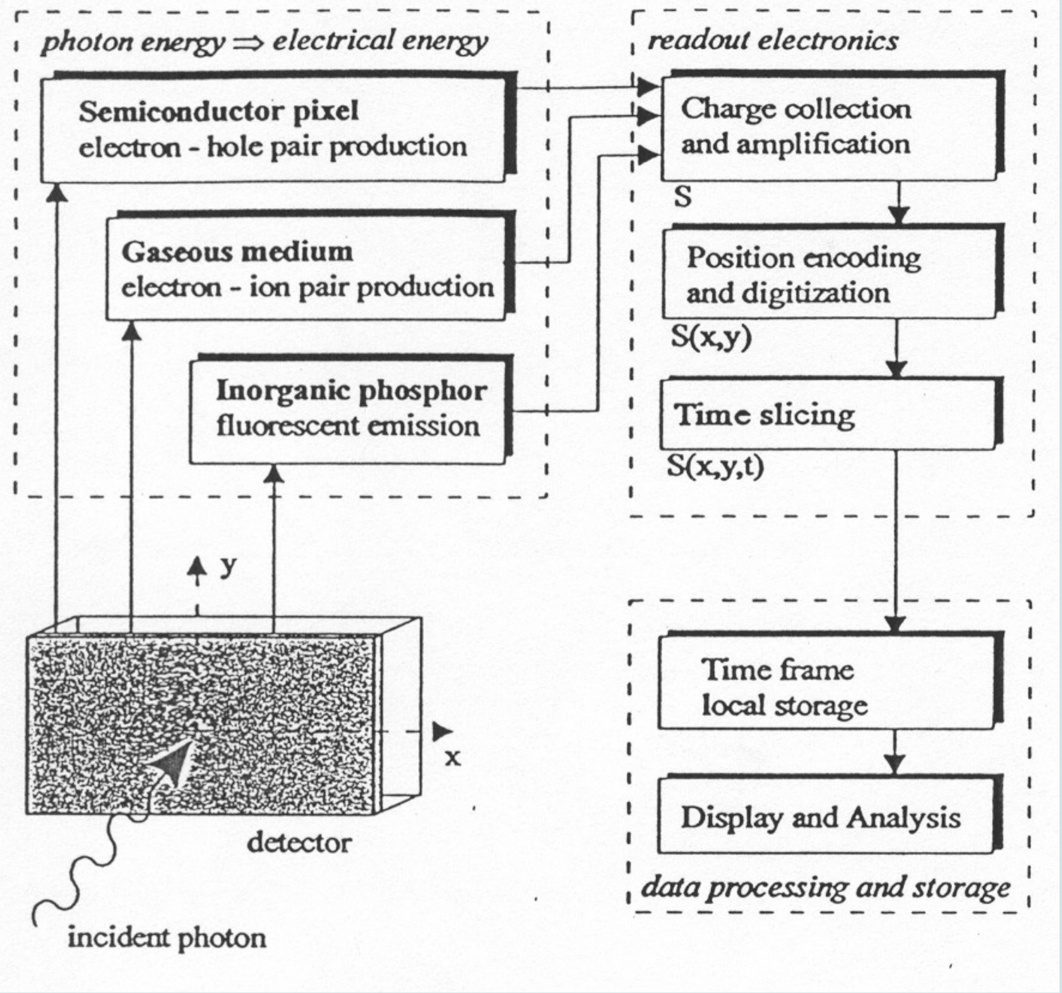
sample geometry

- flat
  - reflection
    - “infinitely” thick sample
    - transparent sample / thin films
    - diluted samples / precipitates / aerodispersed filters
  - transmission
- cylindrical
  - air sensitive sample
- irregular-rough
  - art / archaeological samples
  - industrial / mechanical components

detector characteristics

- **detective quantum efficiency**
  - (**DQE=N_d/N_i**) ratio between detected photons N_d and incoming photons N_i
- **dynamic range**
  - (**DR = I_{max}/I_{min}**) ratio between maximum and minimum detectable signal
  - the maximum detectable signal I_{max} is limited by linearity
  - the minimum detectable signal I_{min} depends on the intrinsic noise of the system
- **count rate linearity**
  - is referred to the linearity of the **DQE** with respect to the incident flux
  - the secondary signal produced by each photon must be constant in the whole dynamic range (**DR**)
- **sensitivity**
  - (**S = dI/dj**) current variation dI produced by a variation dj of the incident photon flux
  - it determines the minimum number of photons detectable per unit time
- **energy** resolution/proportionality/sensitivity
- **spatial** resolution/uniformity (active area)
- **data acquisition rate** (dead time, time stability)

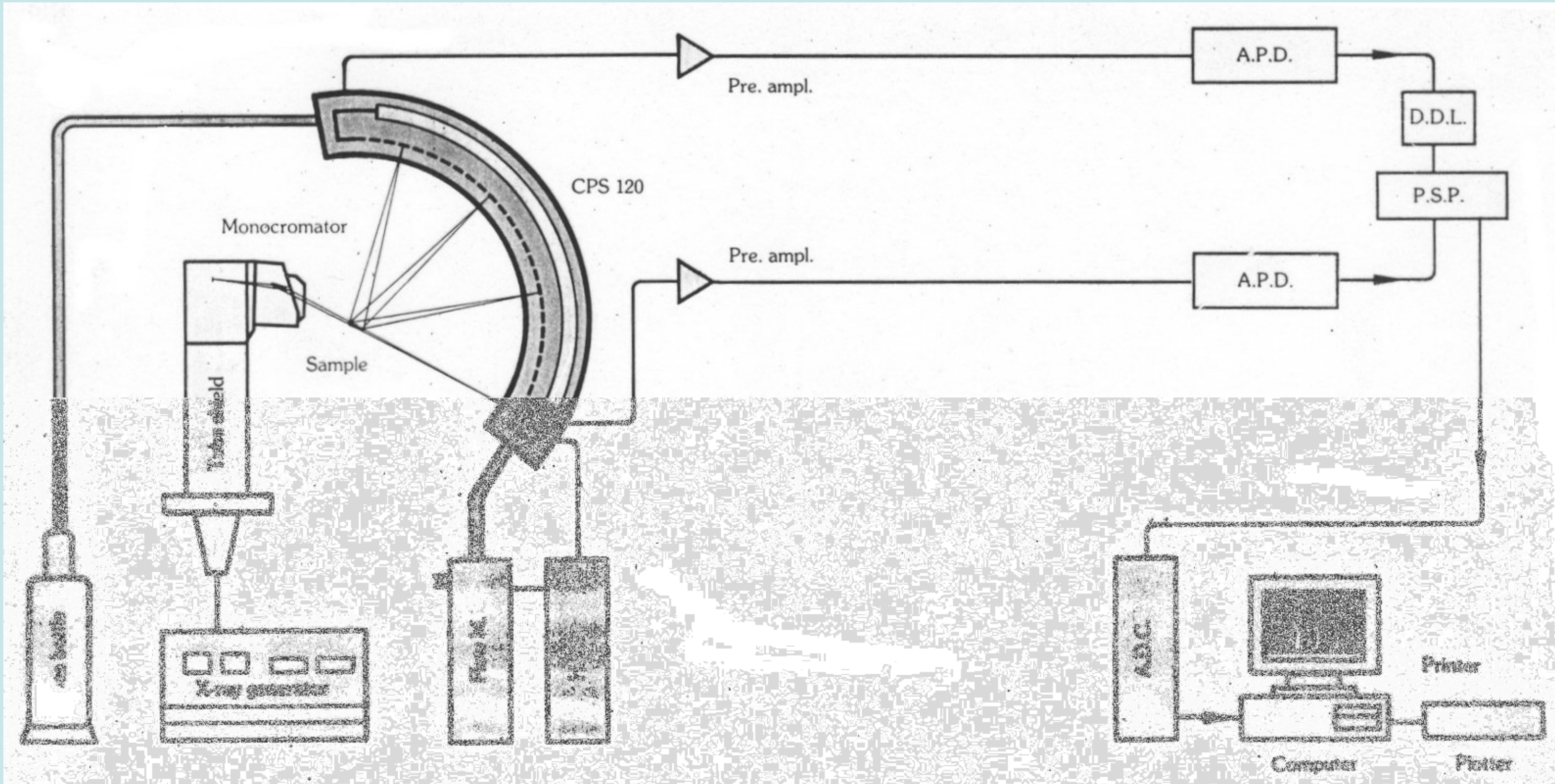
X-ray detectors



X-ray detectors

	gas ionization	*phosphors*	*semi-conductors*	*other*
spot *0-D*	**proportional counters**	**scintillators**	**solid state Si(Li), Ge(Li)**	
linear *1-D*	**gas linear PSD**		**photo-diode arrays**	
area *2-D*	**multiwires**	**phosphors IP**	**CCD**	**films**

X-ray detectors: gas



X-ray detectors: gas

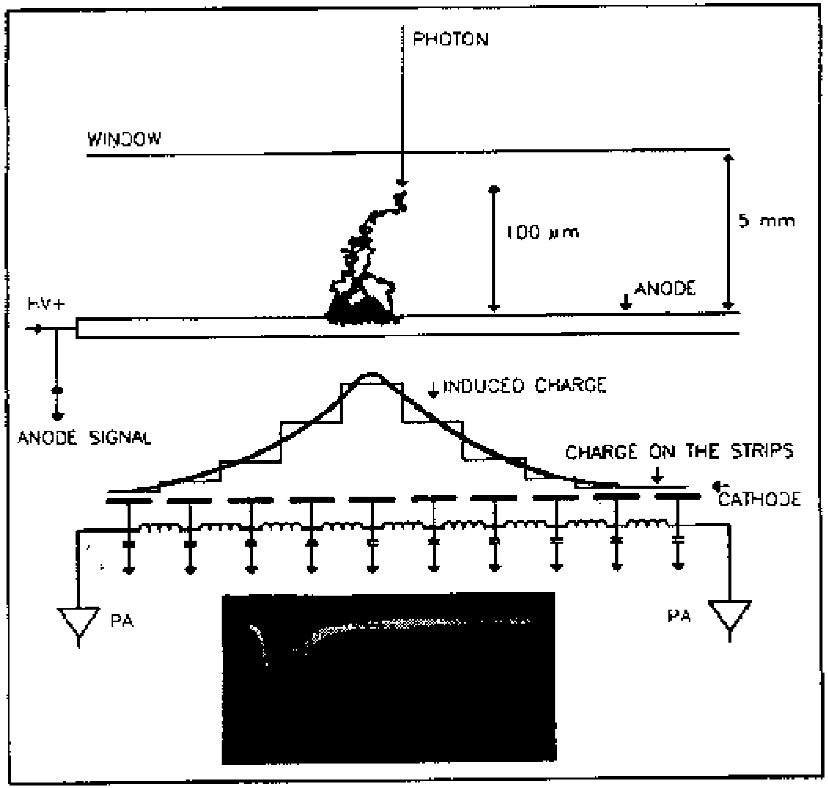
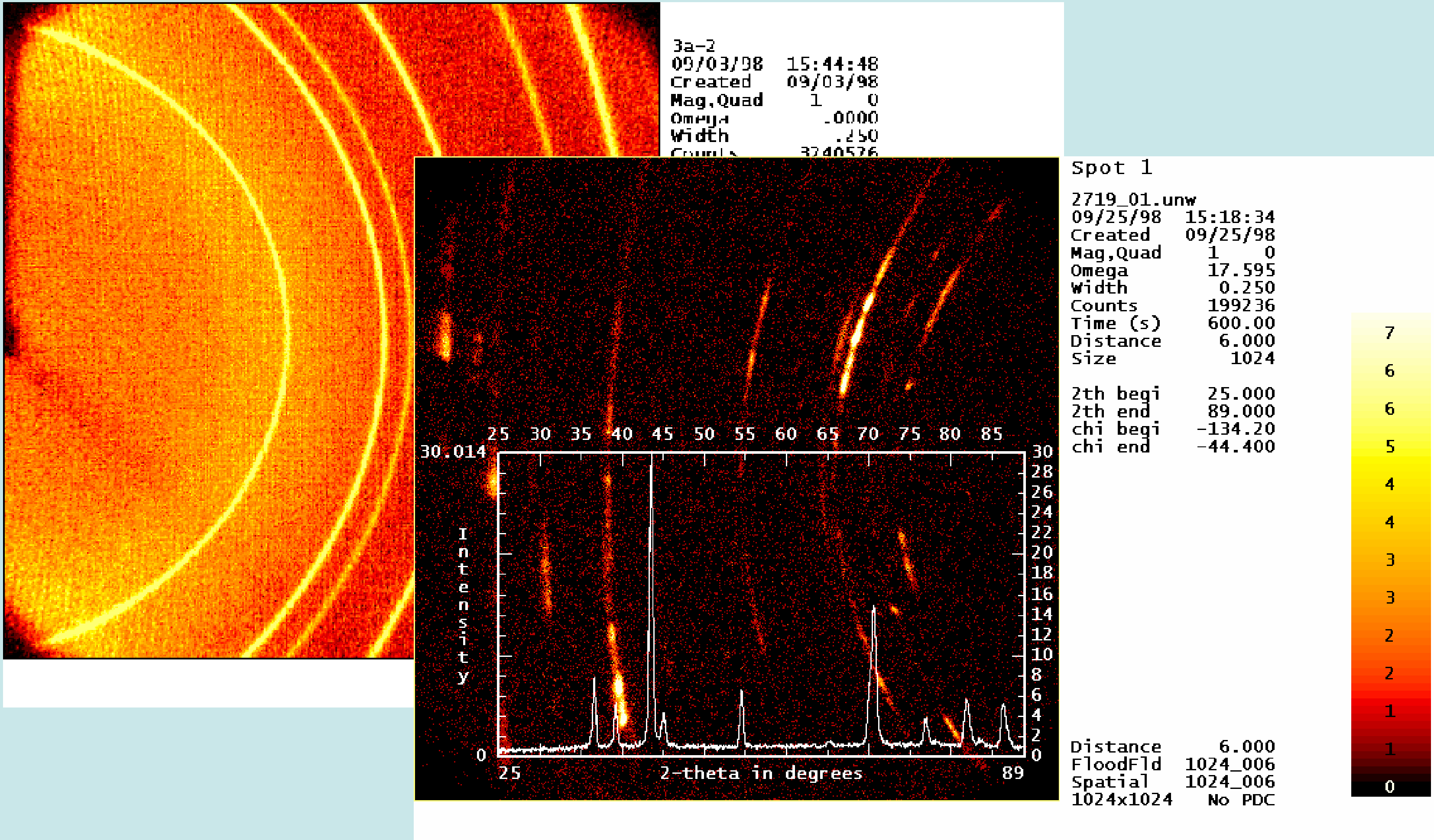


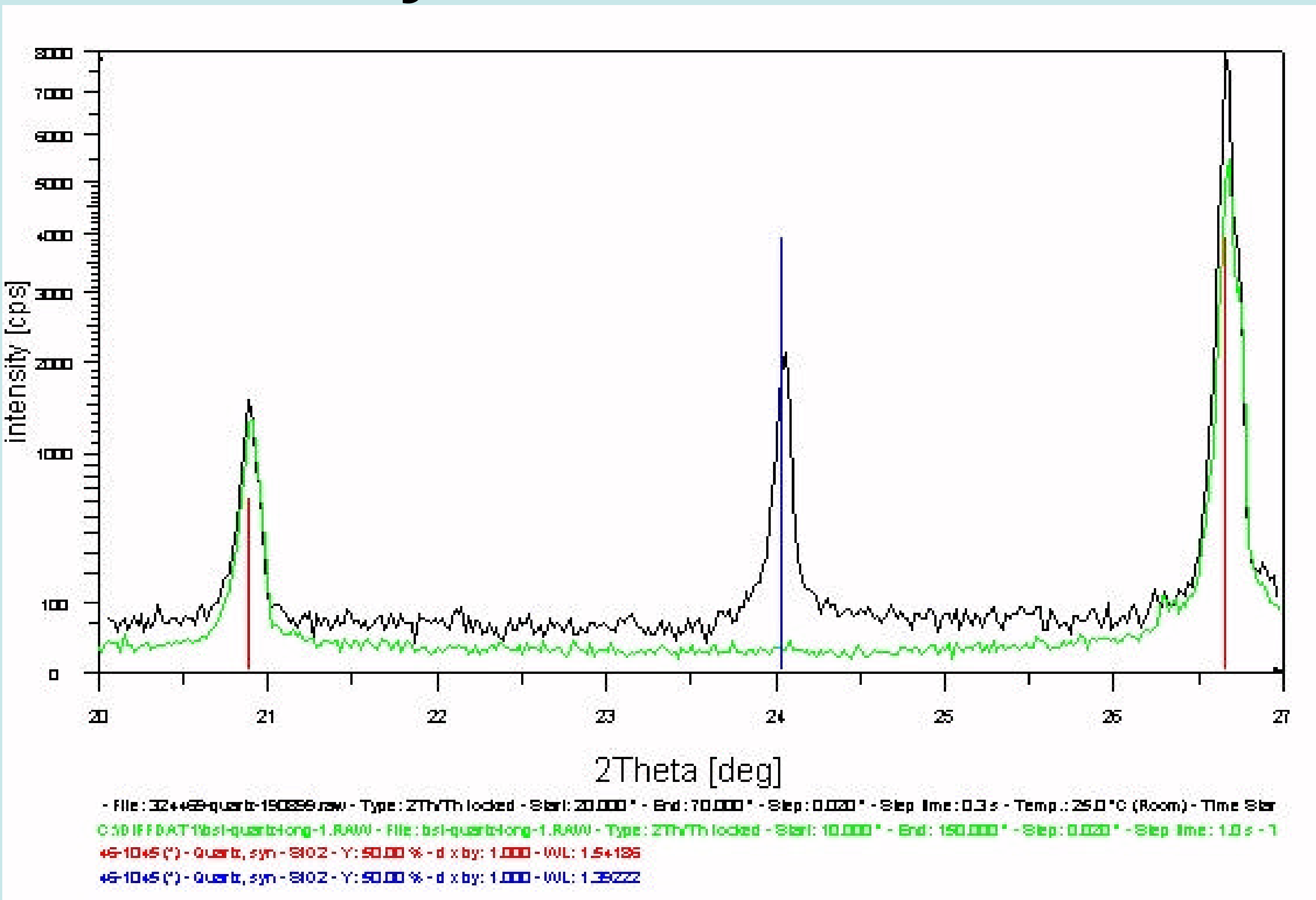
FIG. 2. Schematic of the formation of an avalanche after absorption of an x-ray photon in a proportional detector (modified from Ref. 6; shape of the avalanche obtained by simulation [10]). The insert displays the output signal of the cathode preamplifiers (PA). The scale of the insert corresponds to 250 mV vertically and 470 ns horizontally.

X-ray detectors: gas

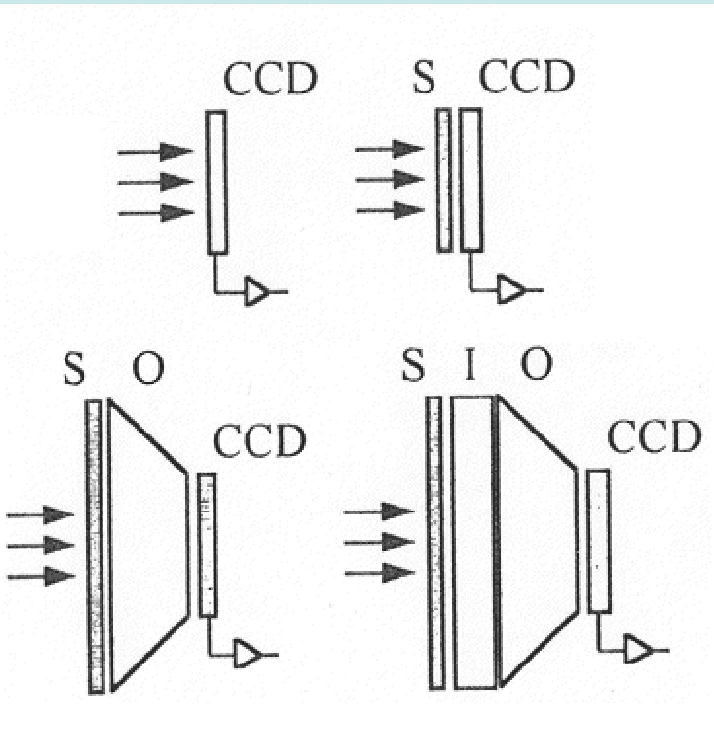


X-ray detectors: SSD

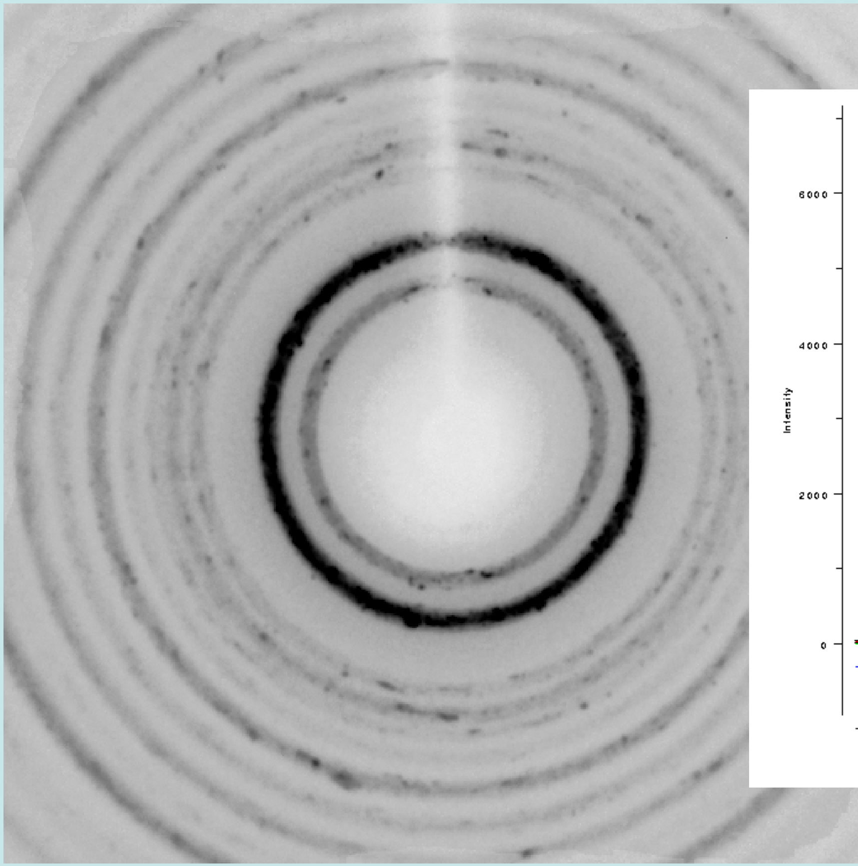
X-ray detectors: SSD

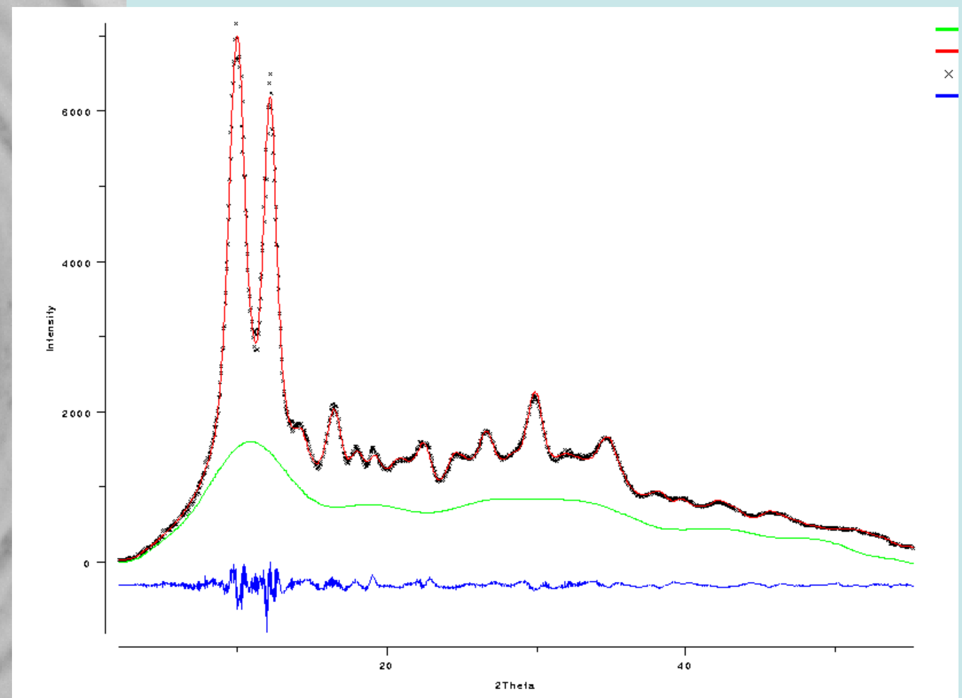


X-ray detectors: CCD



X-ray detectors: CCD





X-ray detectors: CCD

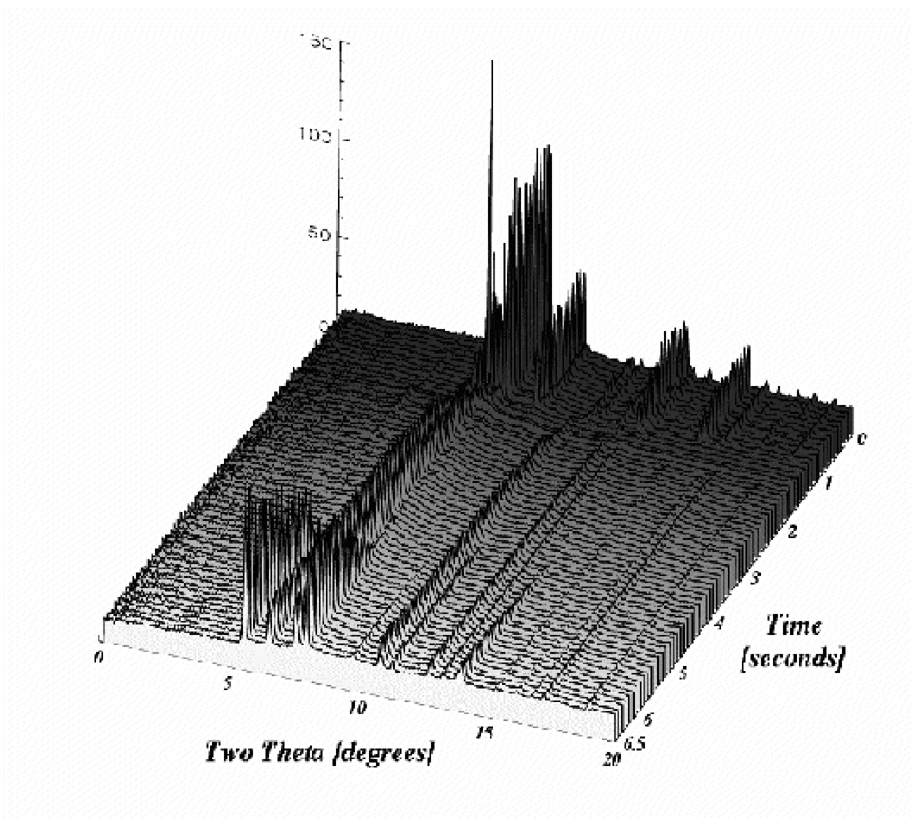
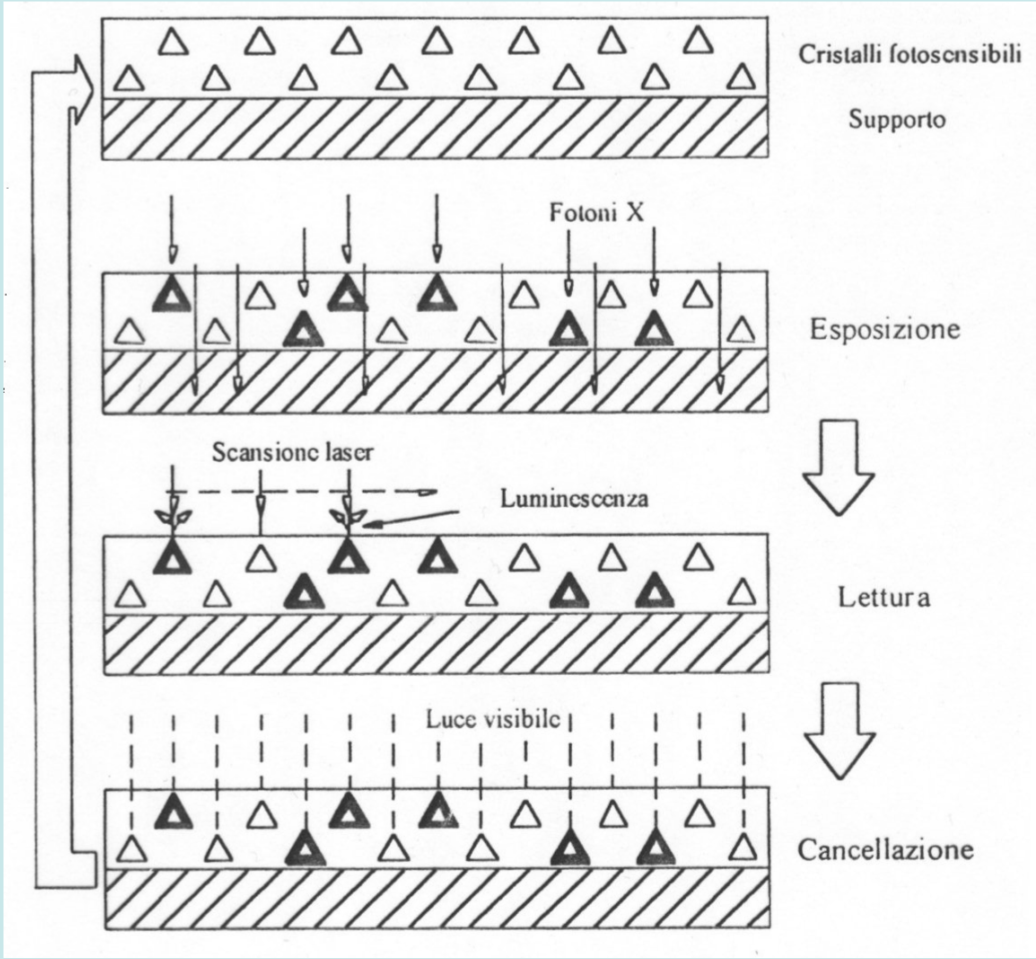
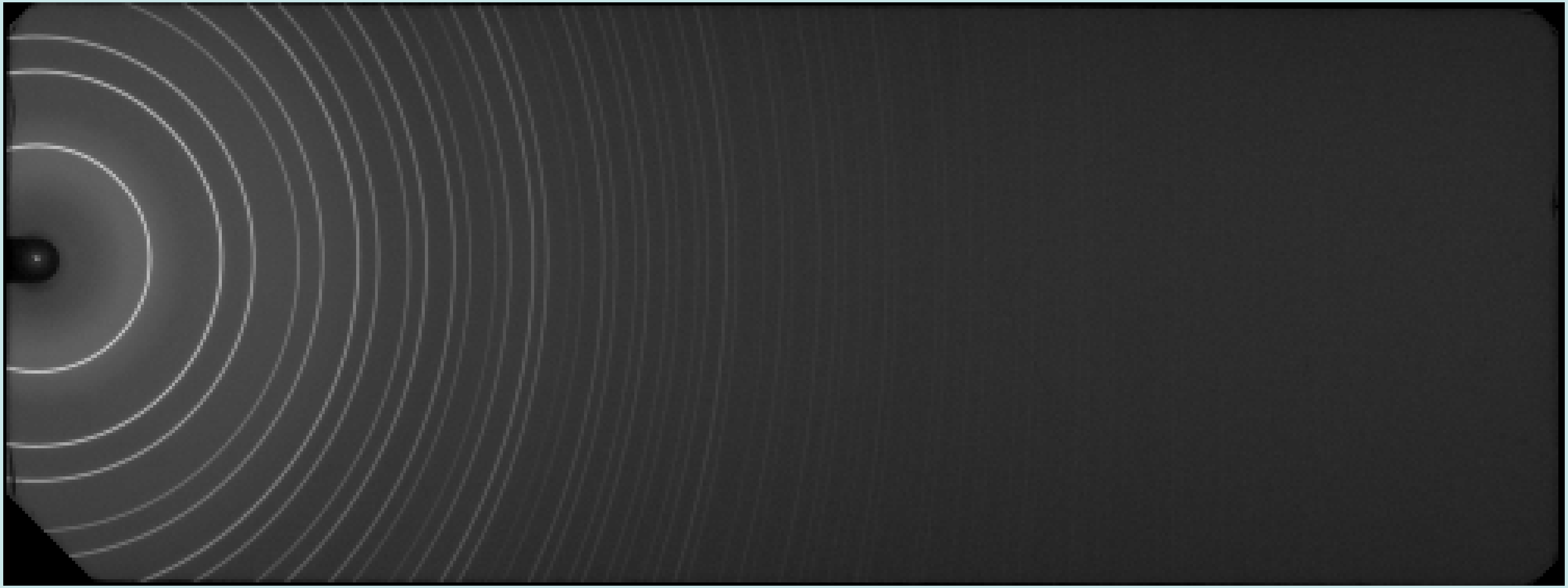


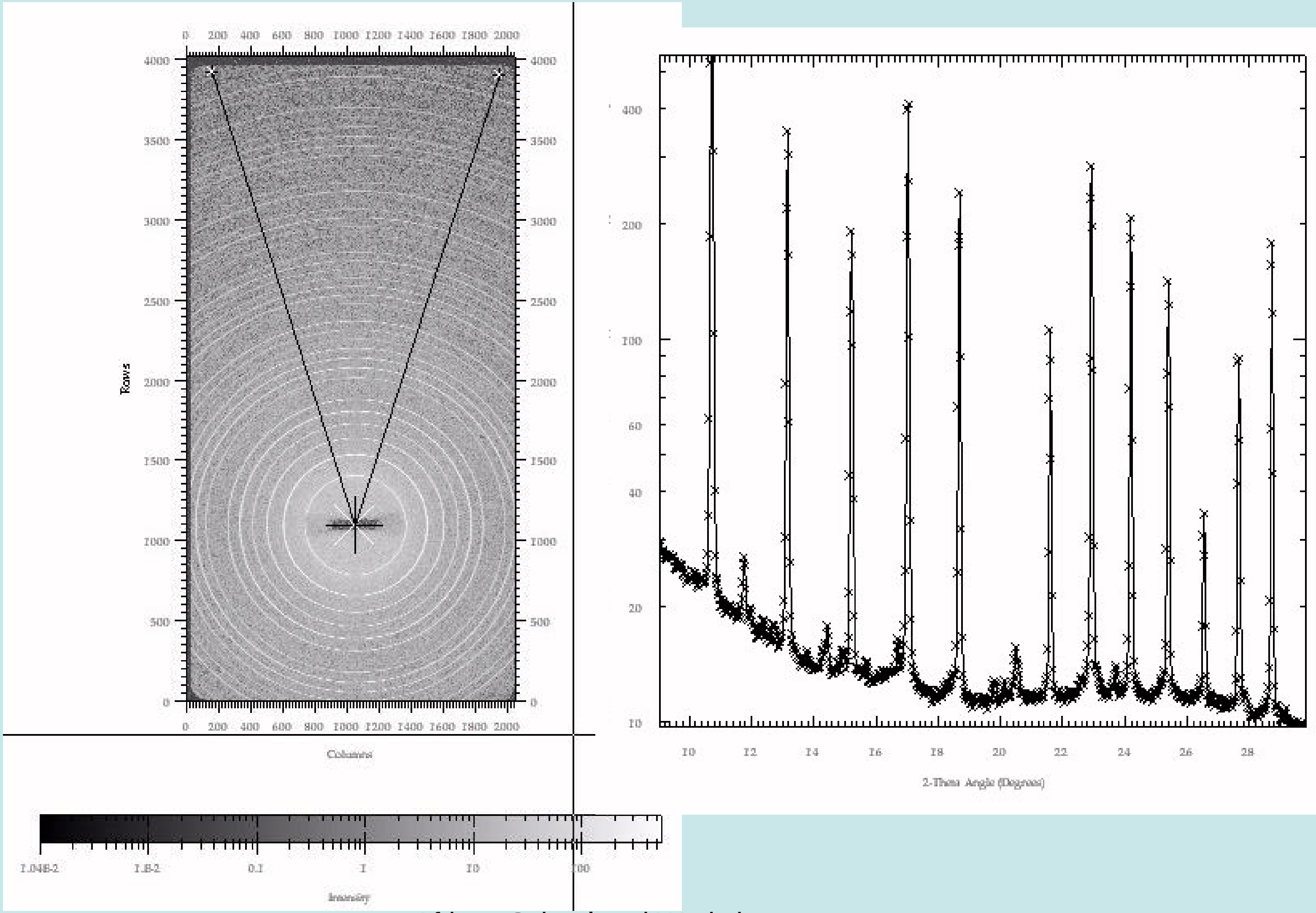
Figure 3: Time-resolved evolution of a fast reaction studied by in situ synchrotron powder diffractometry. Each spectrum was collected at ESRF ID11 beamline for about 20 ms, using a CCD Frelon camera.

X-ray detectors: IP



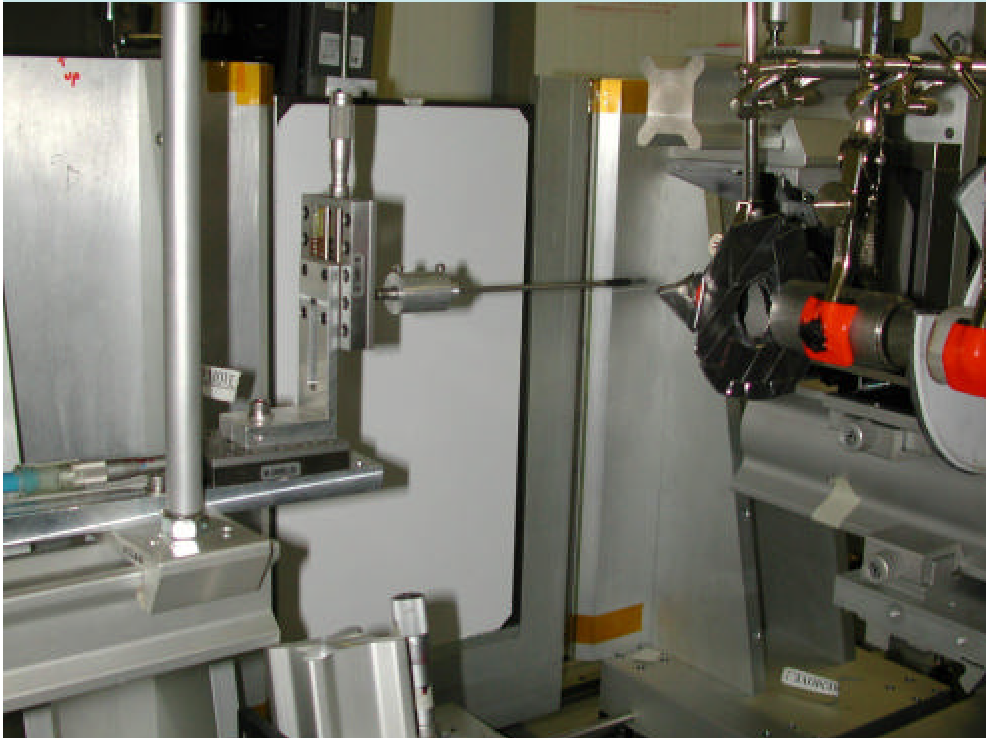
X-ray detectors: IP

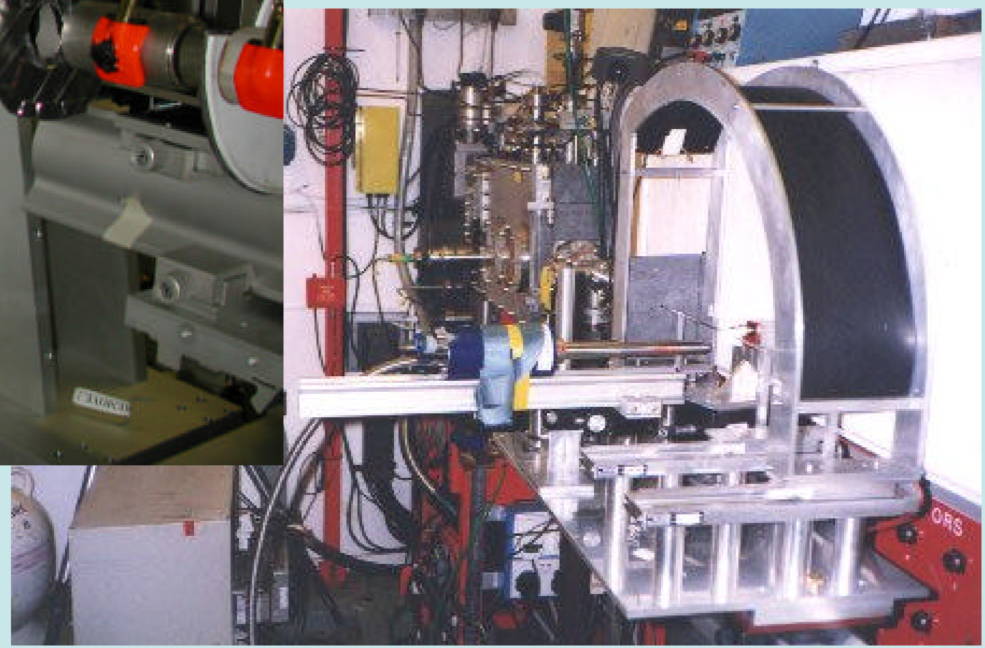




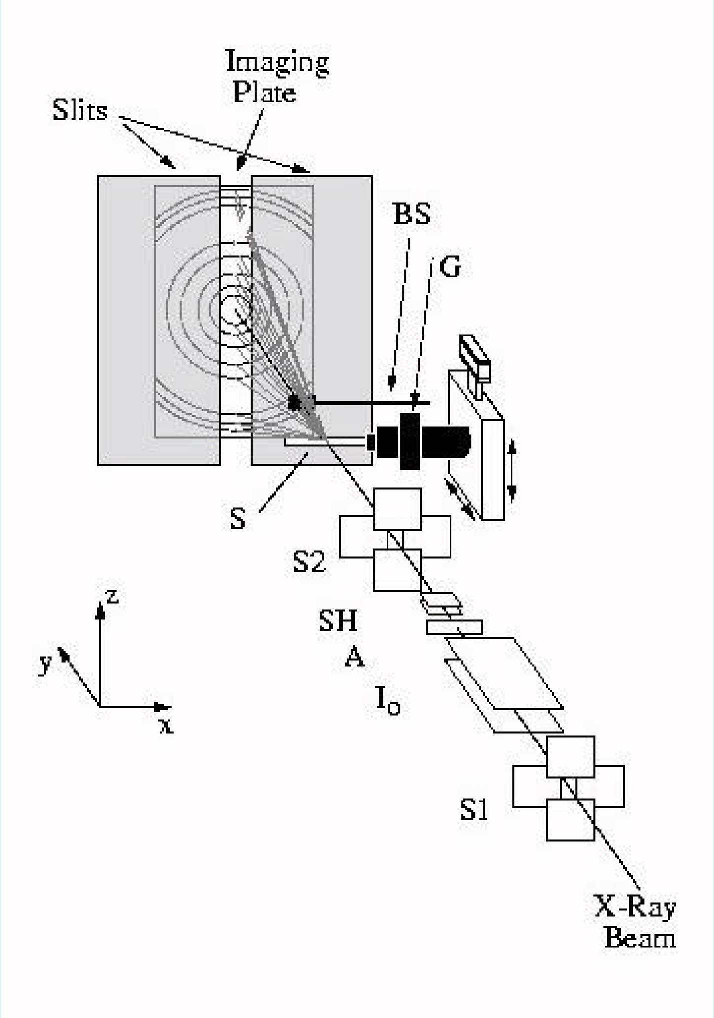
Rows
Columns
Intensity
2-Theta Angle (Degrees)

X-ray detectors: translating IP

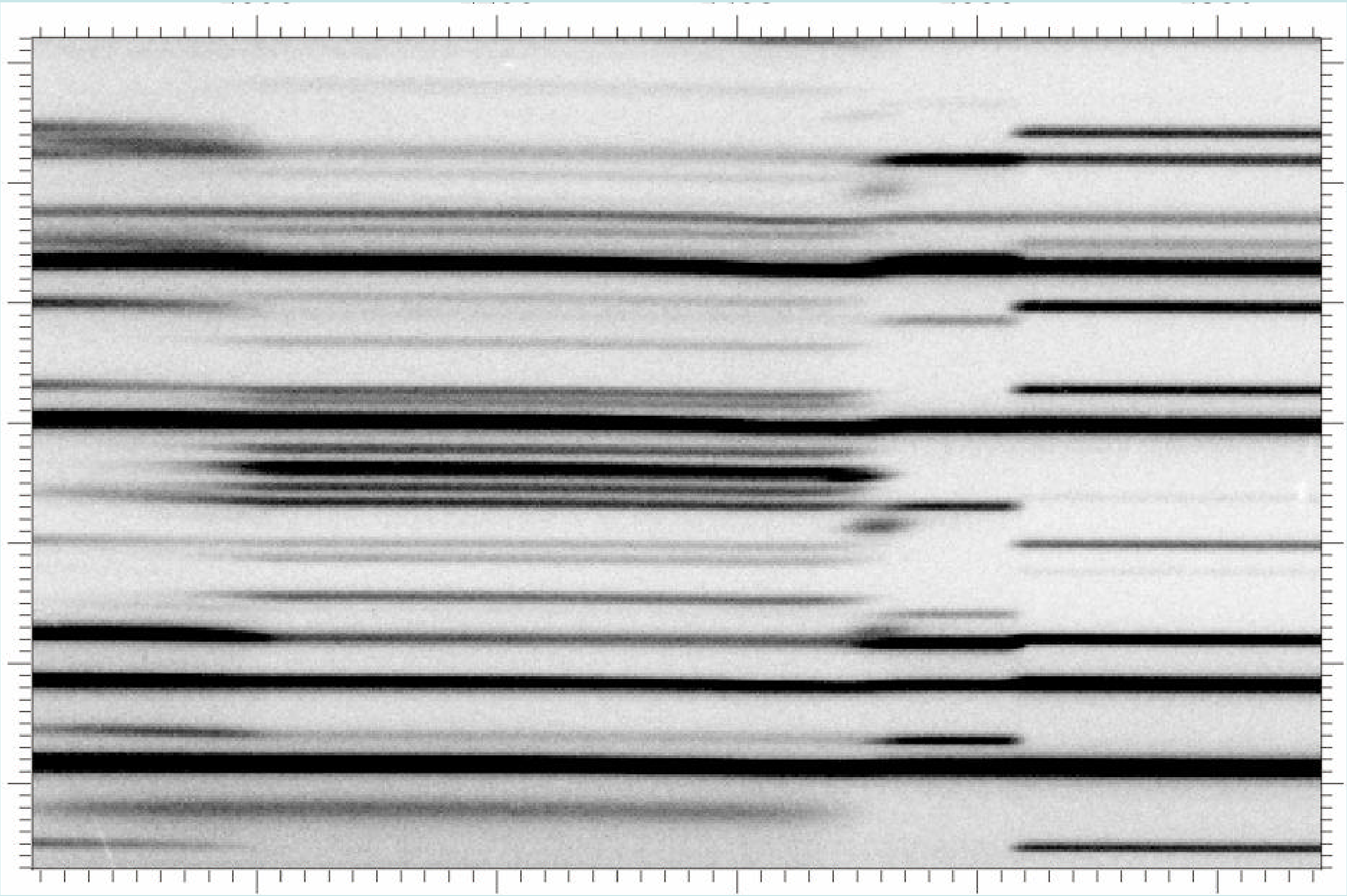




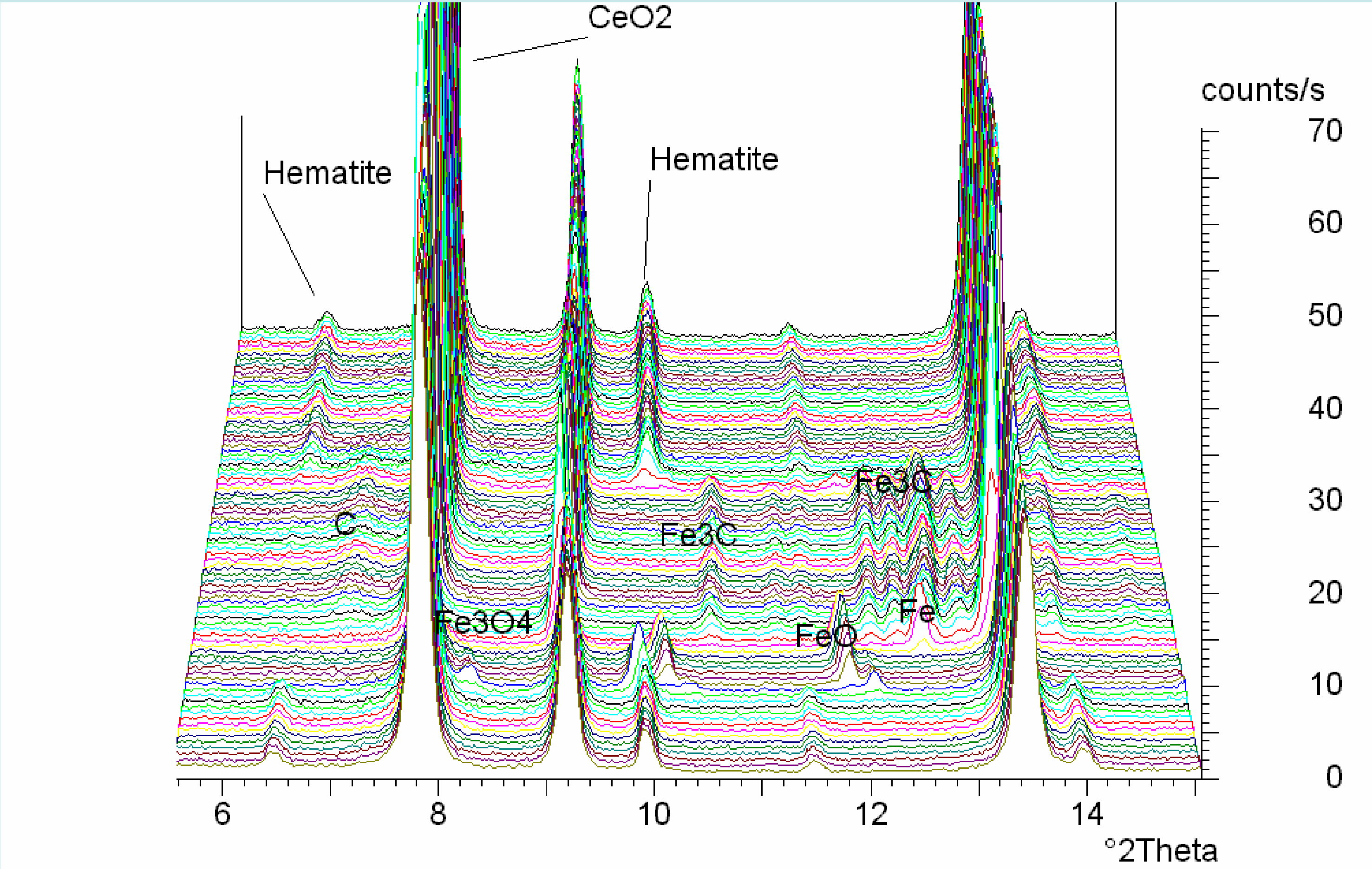
X-ray detectors: translating IP



X-ray detectors: translating IP



X-ray detectors: translating IP

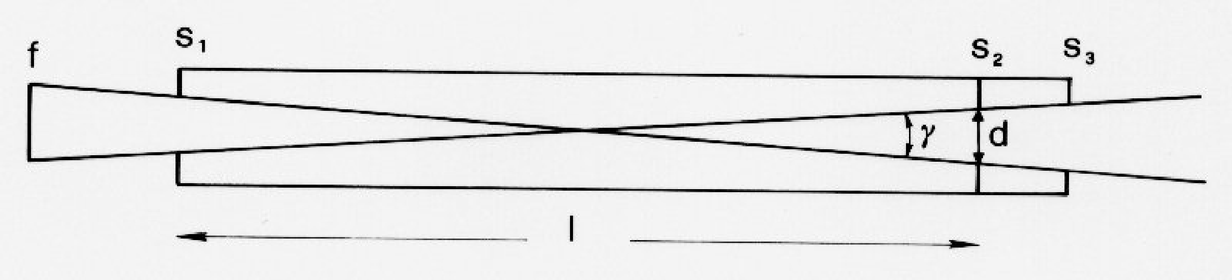


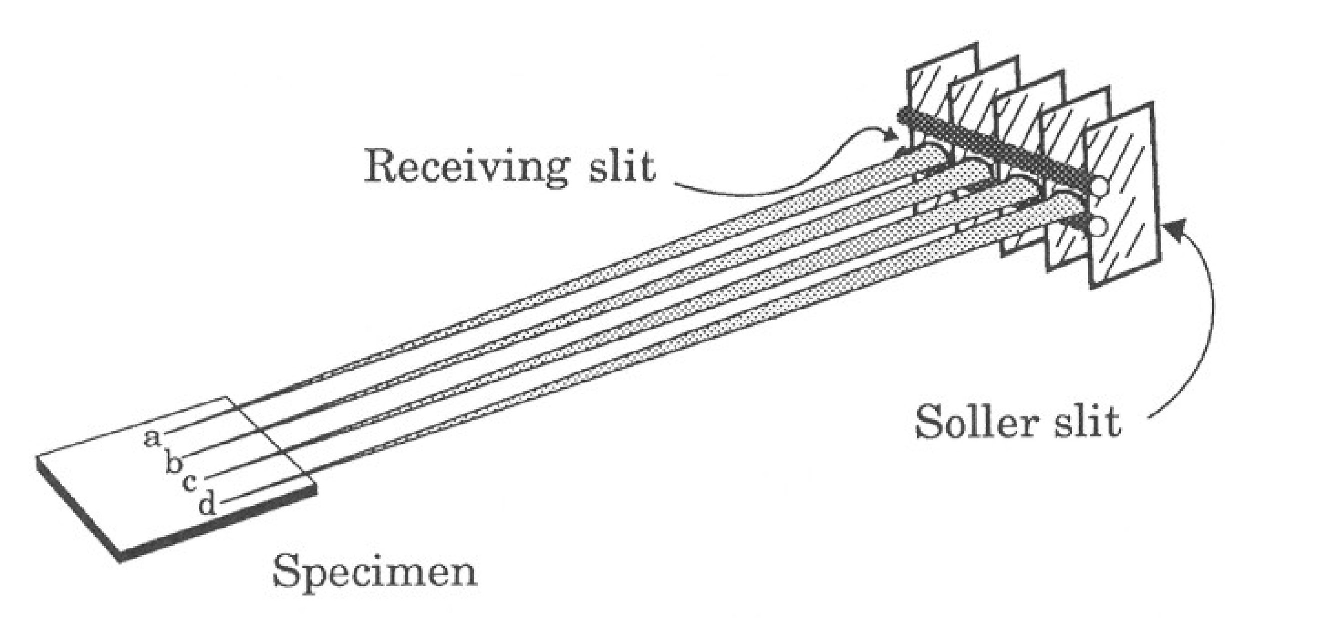
optics

- collimators / fenditures
  - *they define the shape of the beam incident on the sample*
  - *they limit the angular divergence of the beam*
- mirrors
  - *they modify the direction/focusing/divergence of the beam*
- monochromators
  - *they modify the energy distribution of the beam*

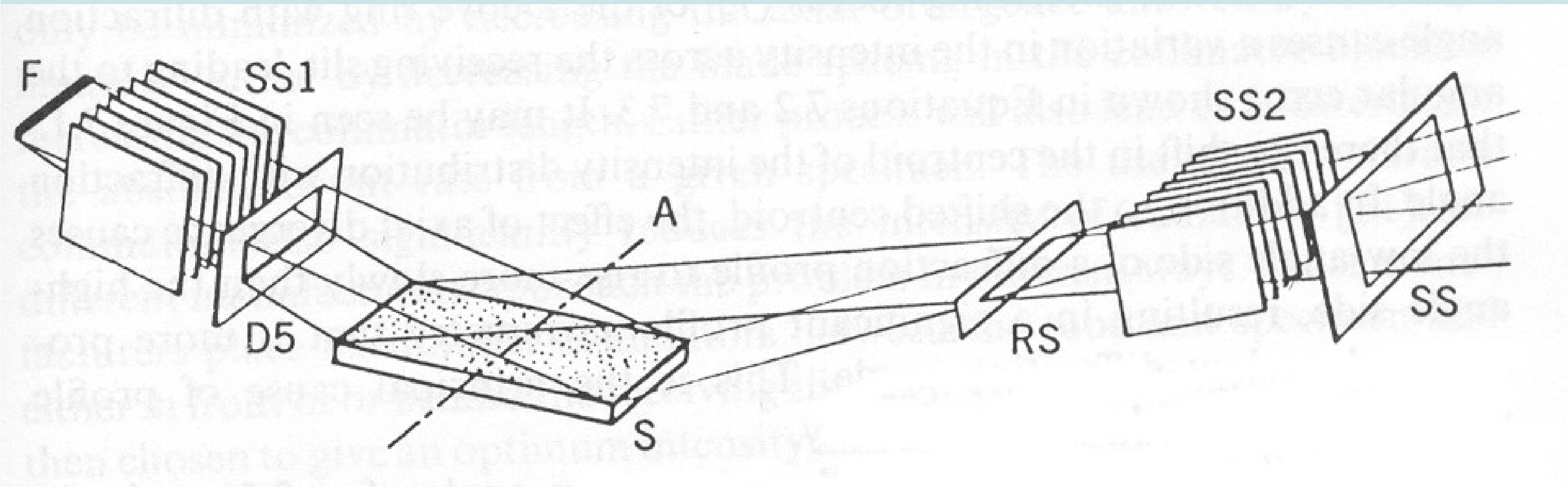
nowadays there are a number of
hybrid / multifunctional optical elements

collimators / fenditures

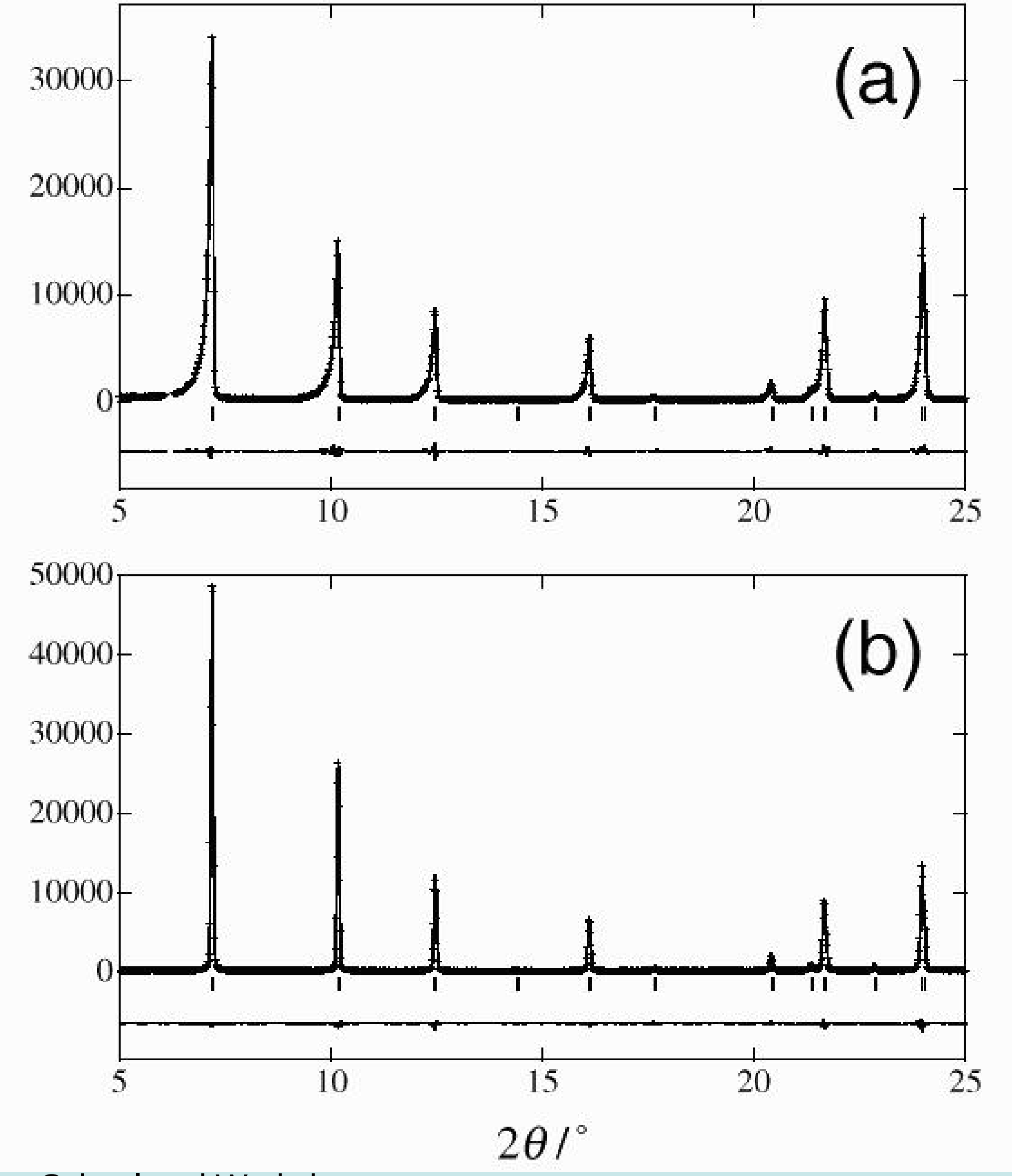




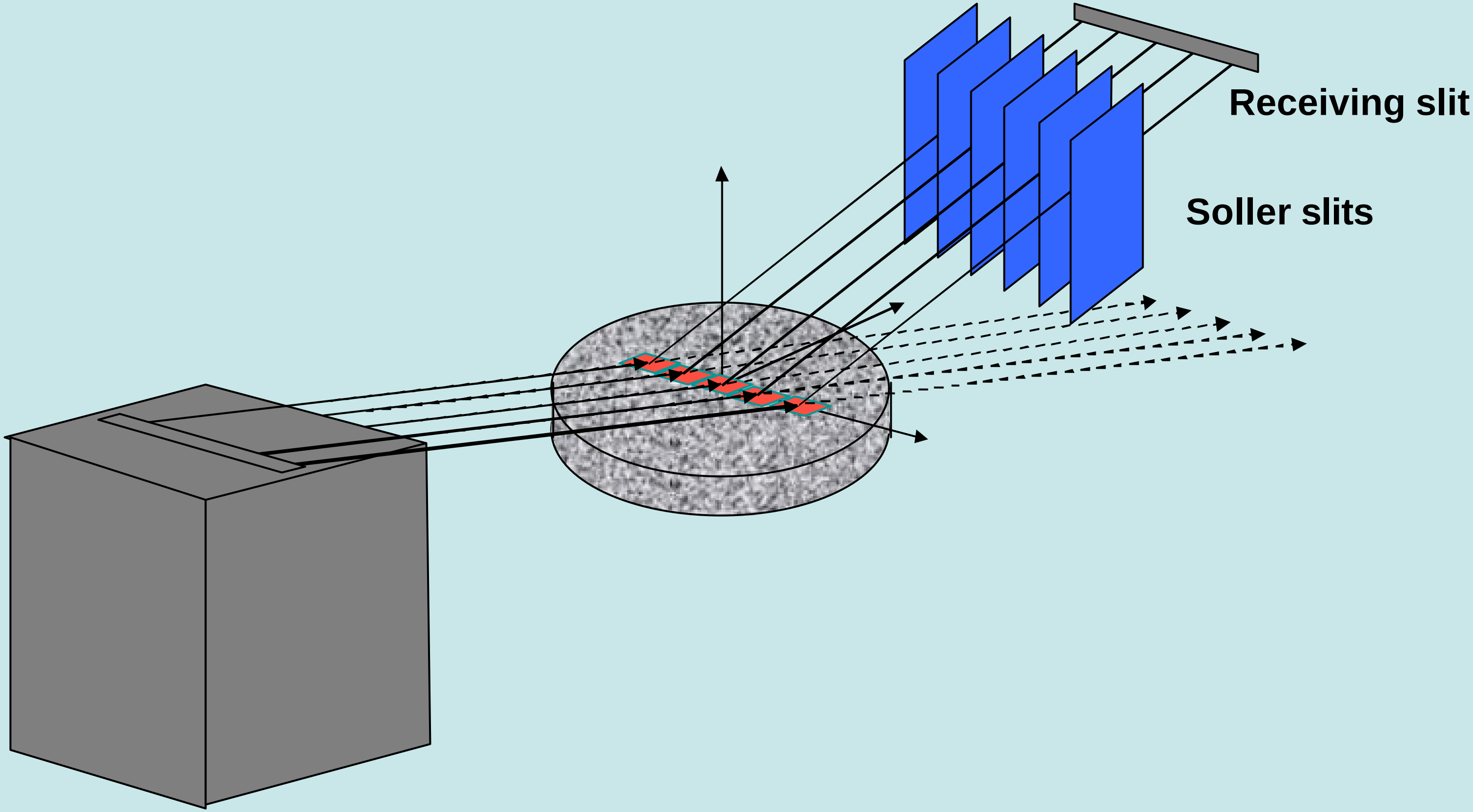
fenditures



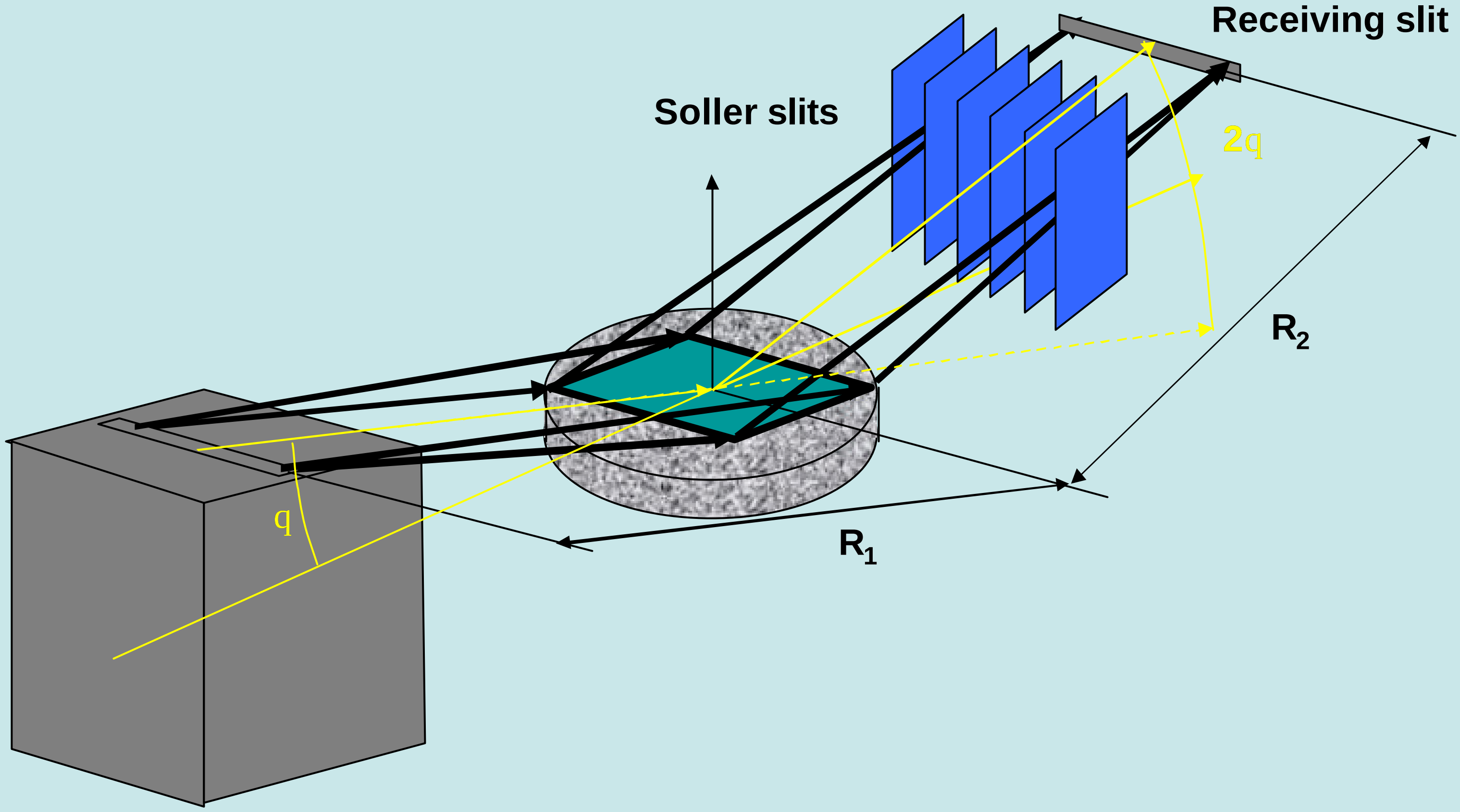
fenditures


(a)
30000
20000
10000
0
5
10
15
20
25
(b)
50000
40000
30000
20000
10000
0
5
10
15
20
25
2θ / °

illuminated area vs detector

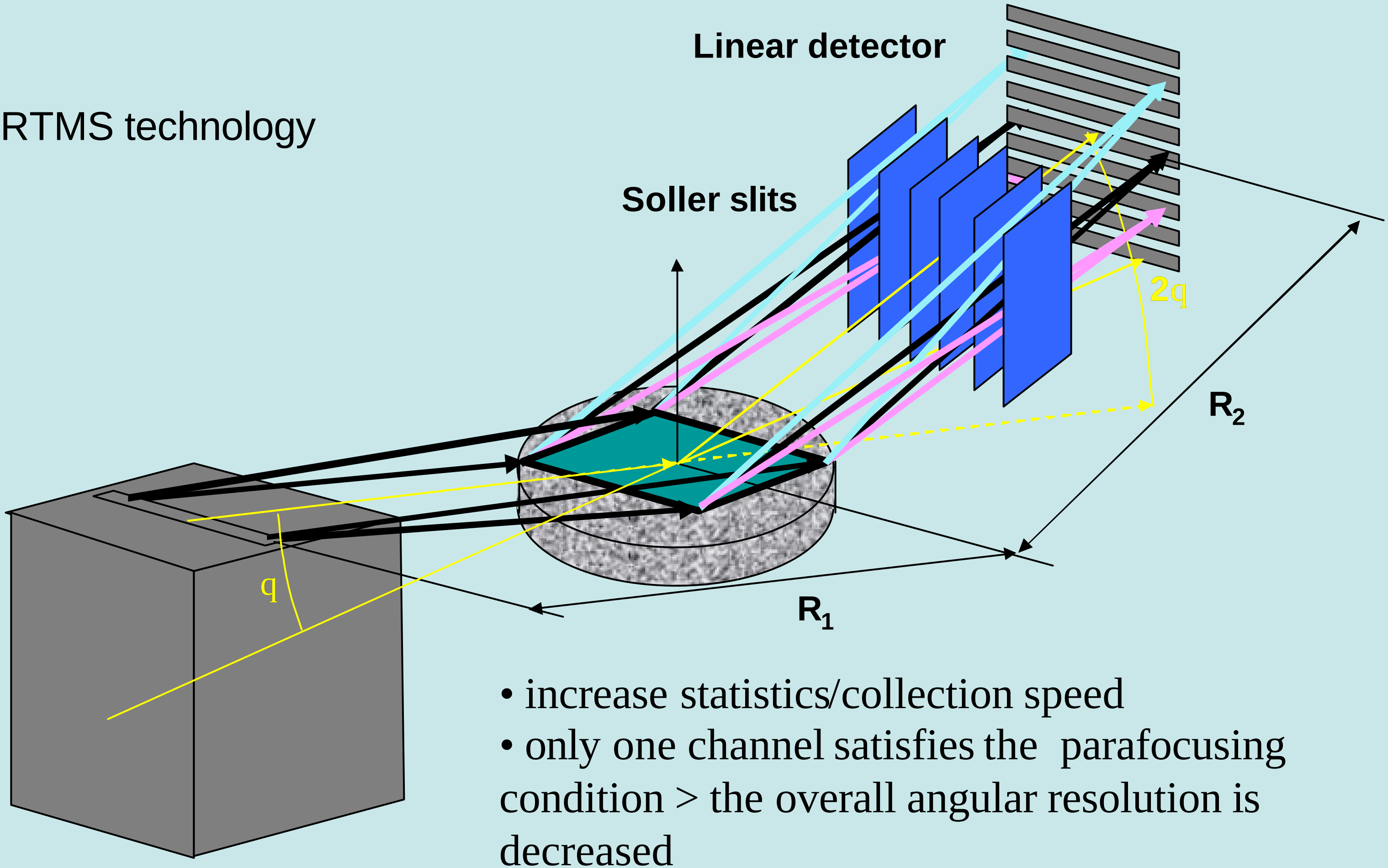


illuminated area vs detector



illuminated area vs detector

RTMS technology



• increase statistics/collection speed

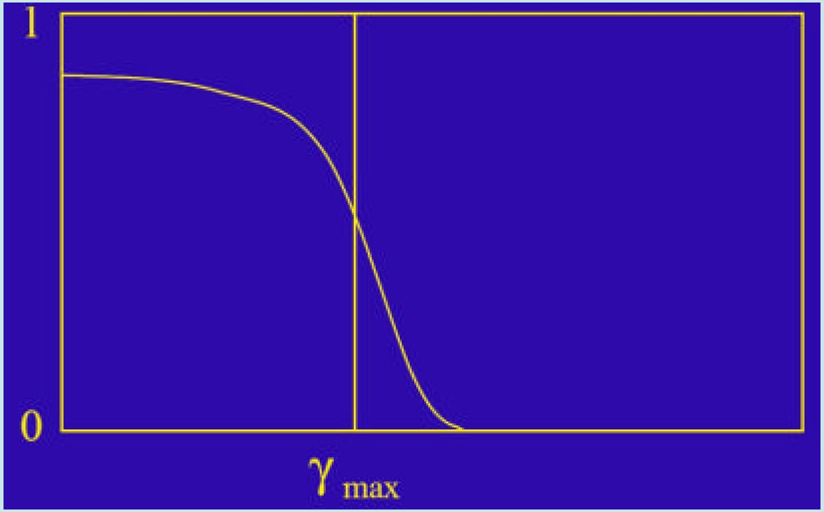
• only one channel satisfies the parafocusing condition > the overall angular resolution is decreased

mirrors

• the ***true mirrors*** are based on the principle of **total reflection**, occurring at incident angles smaller than the critical angle γ

• they are made by coatings of materials with different Z, typically W, Pt, Au on Si

$n = 1 - \delta - i\mu \quad \Rightarrow \quad \gamma = (2\delta)^{1/2} = [1°@1\text{keV}] = [0.1°@45\text{keV}]$

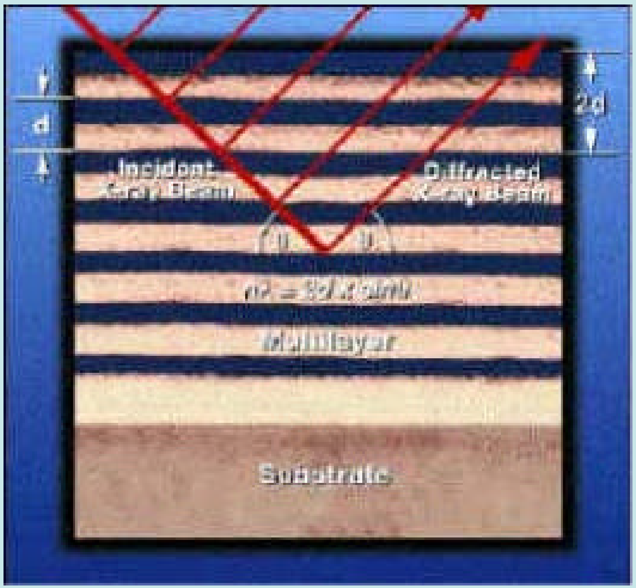


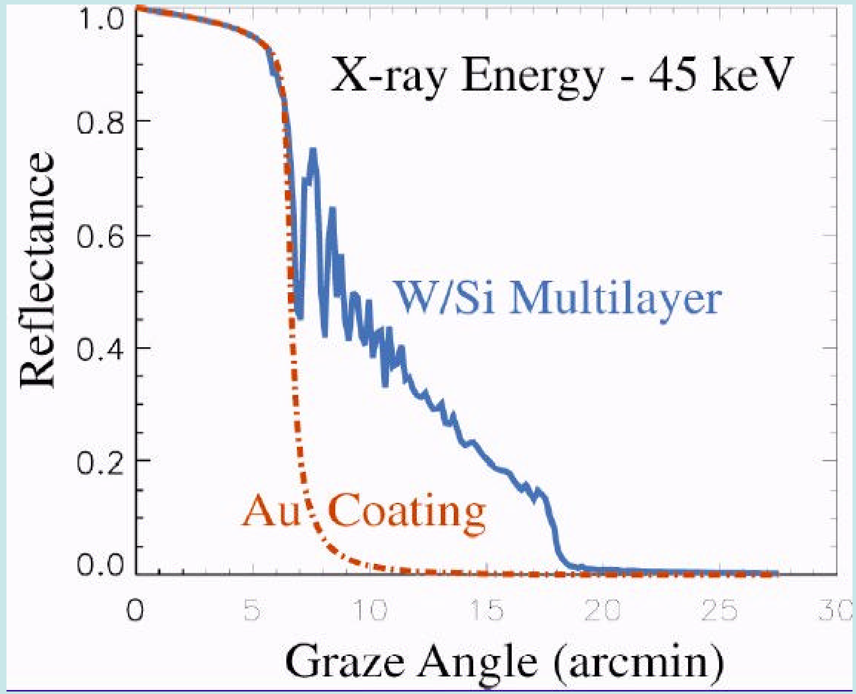
multilayers

• the ***multilayers*** are based on diffraction, that is **Bragg's Law** at incident angles lower than the critical angle γ

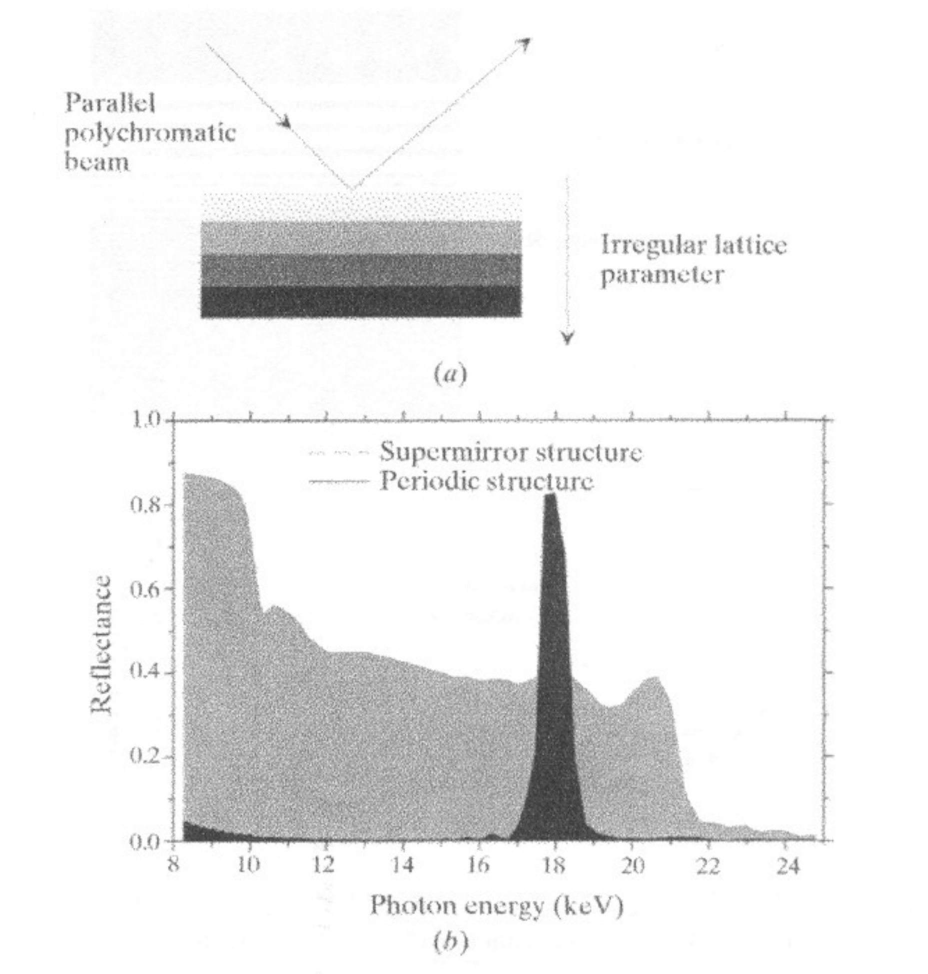
• they are made by alternating layers with high and low Z

• they extend the mirror reflectivity

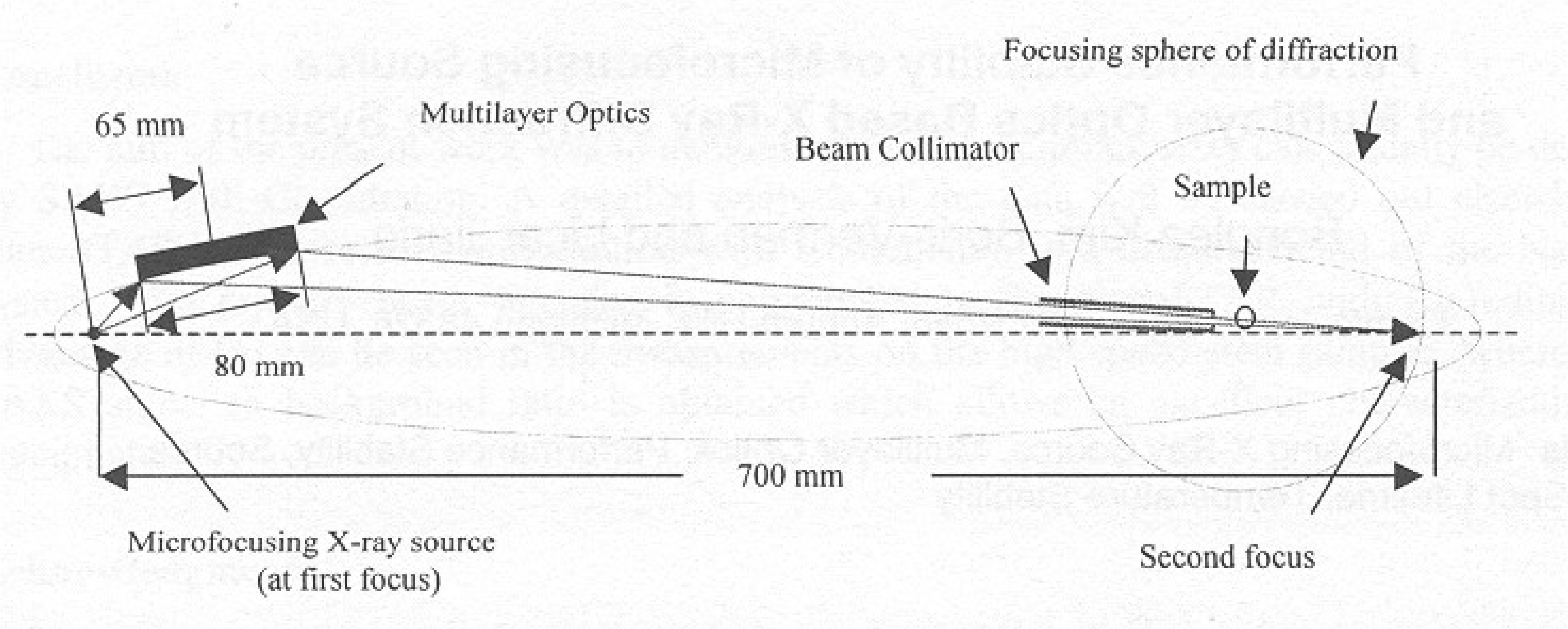




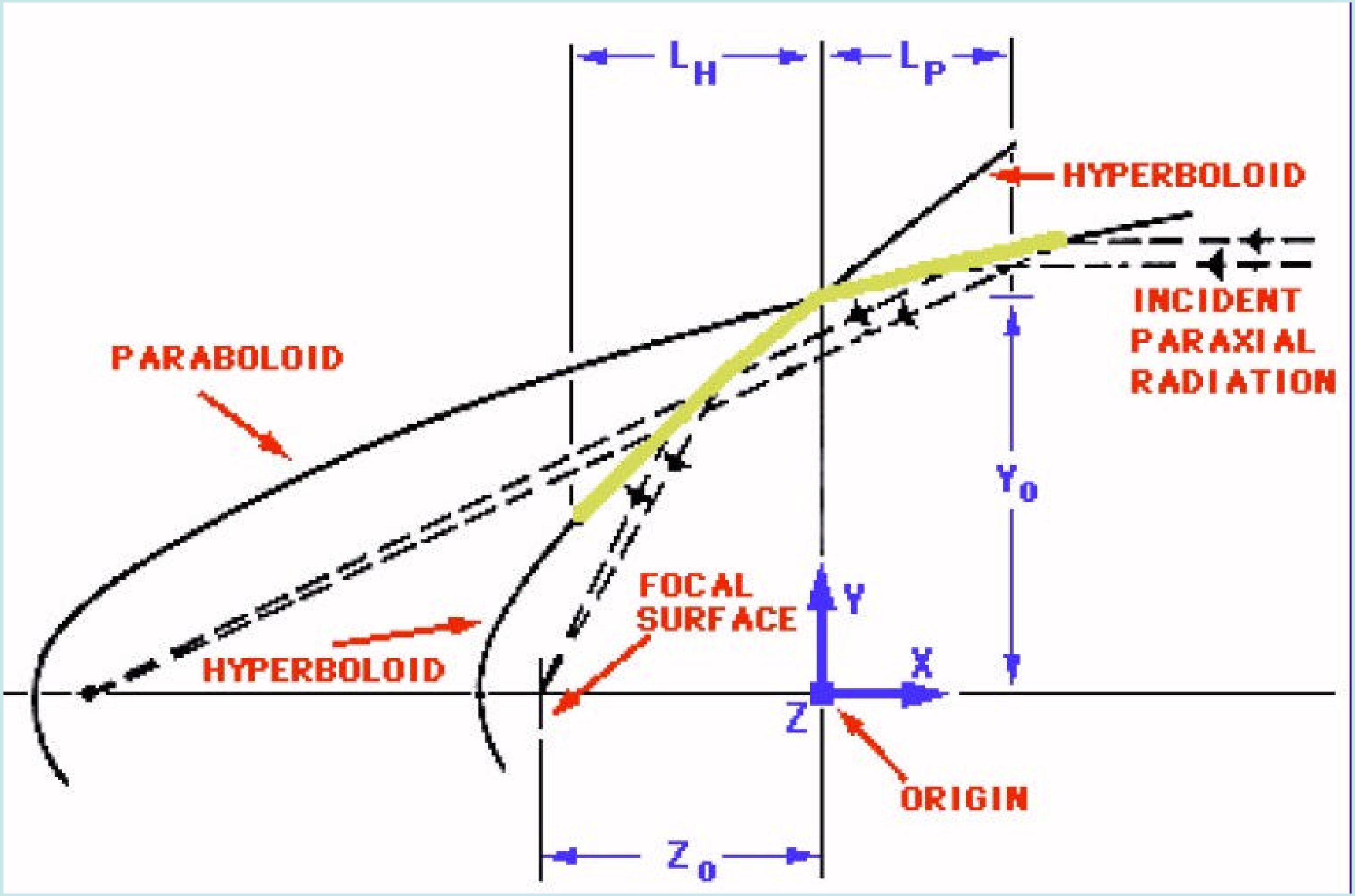
multilayers reflectivity/focusing



multilayers reflectivity/focusing

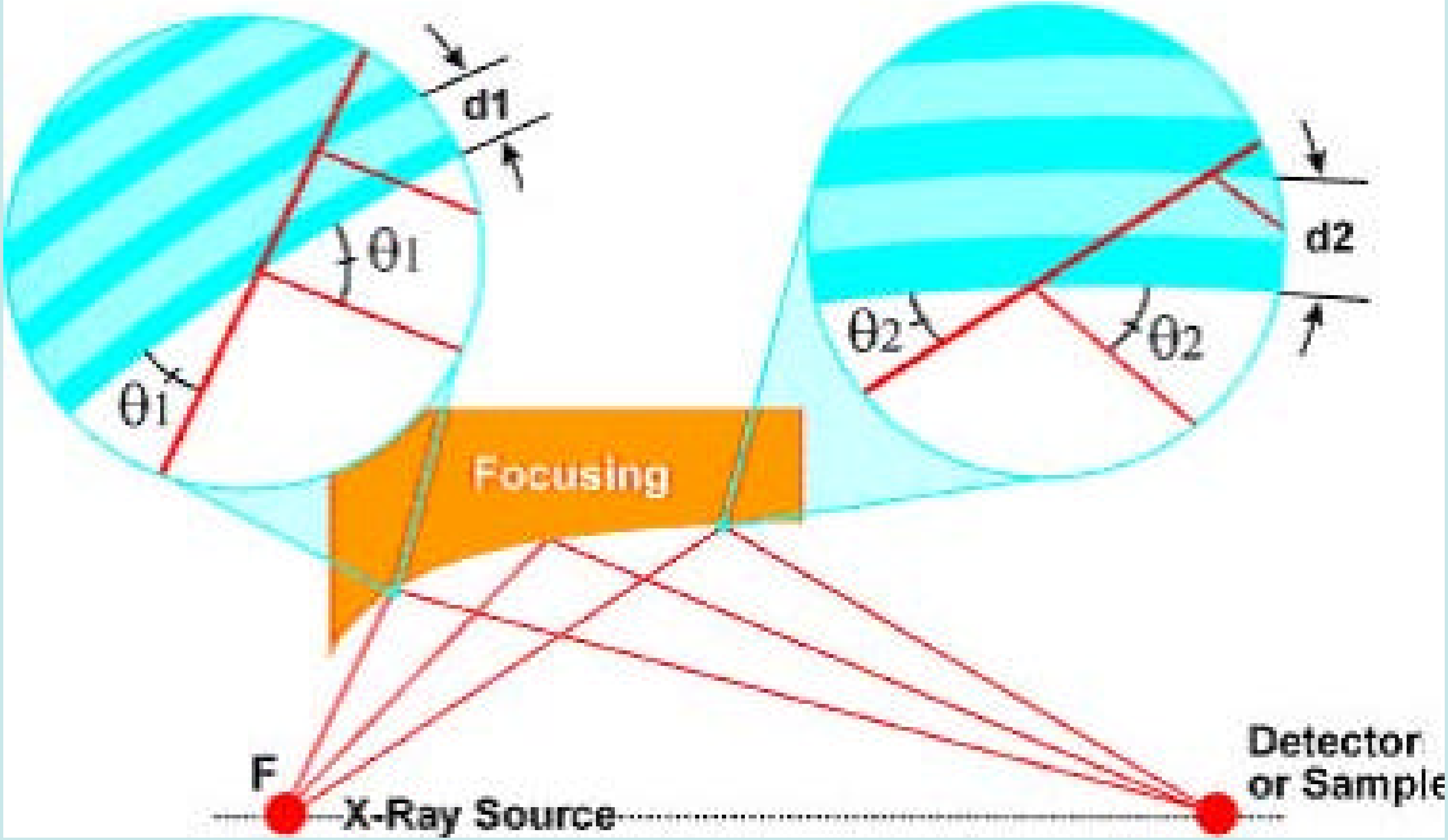


focusing

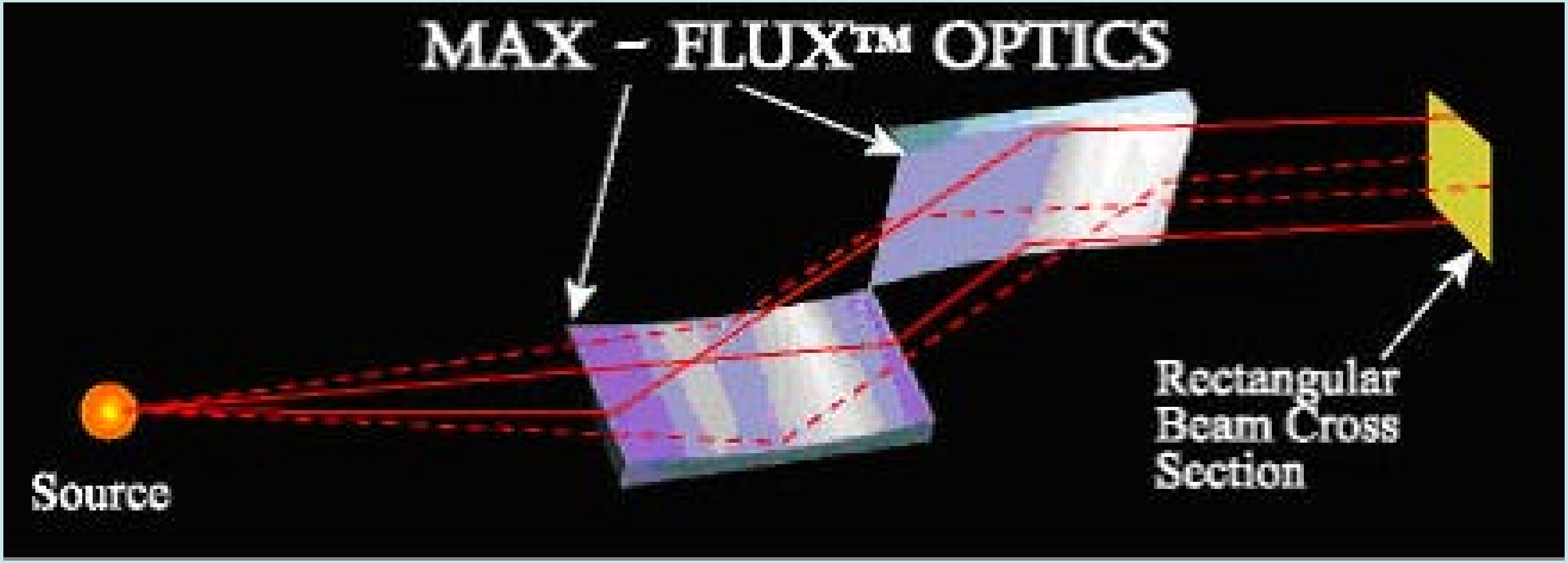


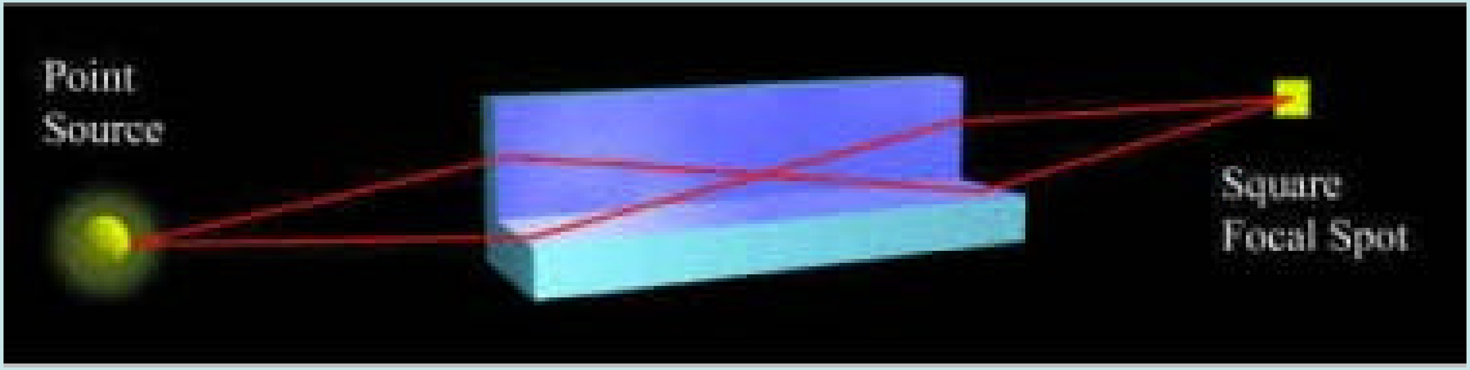
L_H
L_P
HYPERBOLOID
INCIDENT
PARAXIAL
RADIATION
PARABOLOID
Y_0
FOCAL
SURFACE
Y
HYPERBOLOID
X
Z
ORIGIN
Z_0

Focusing Multilayer Optic

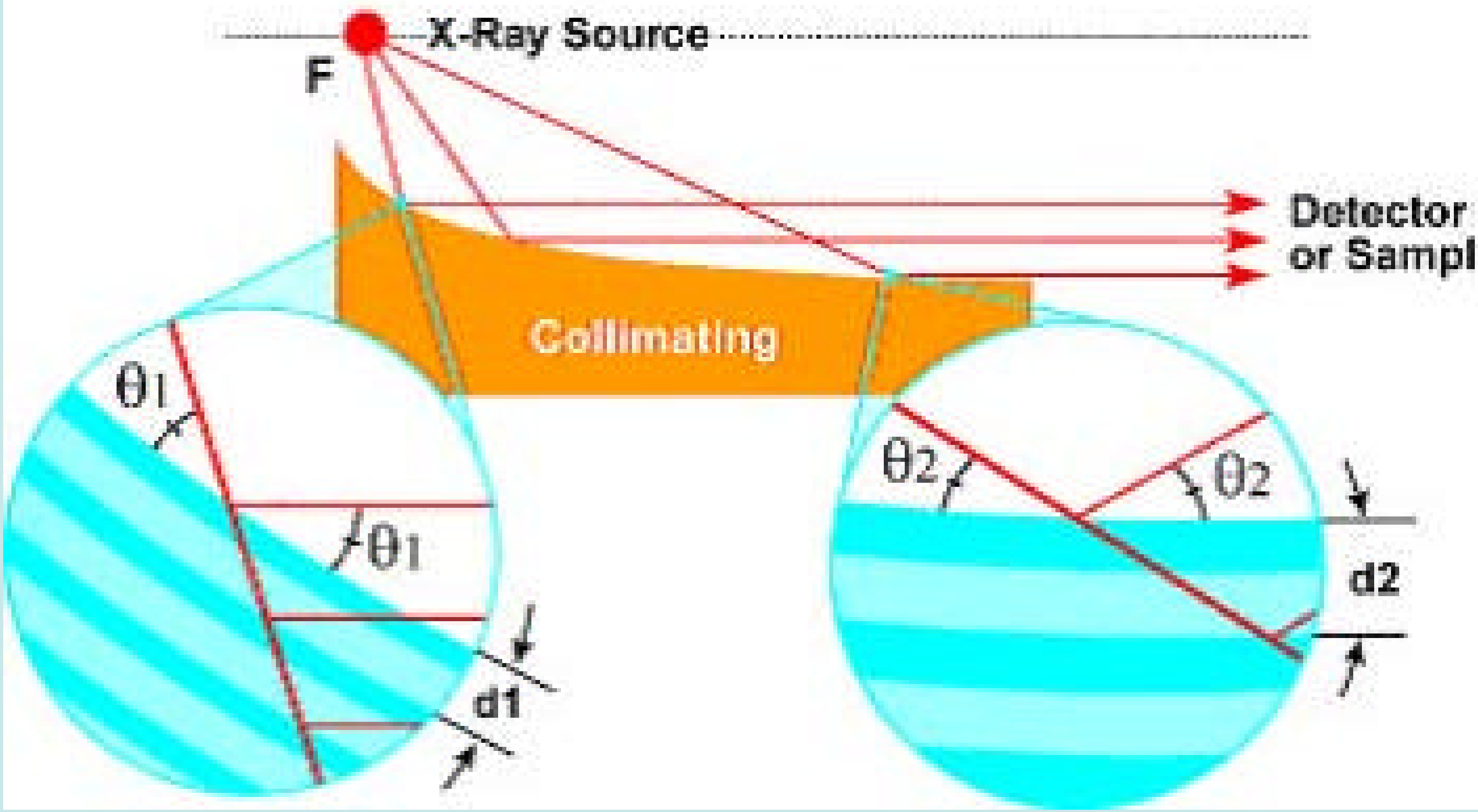


focusing

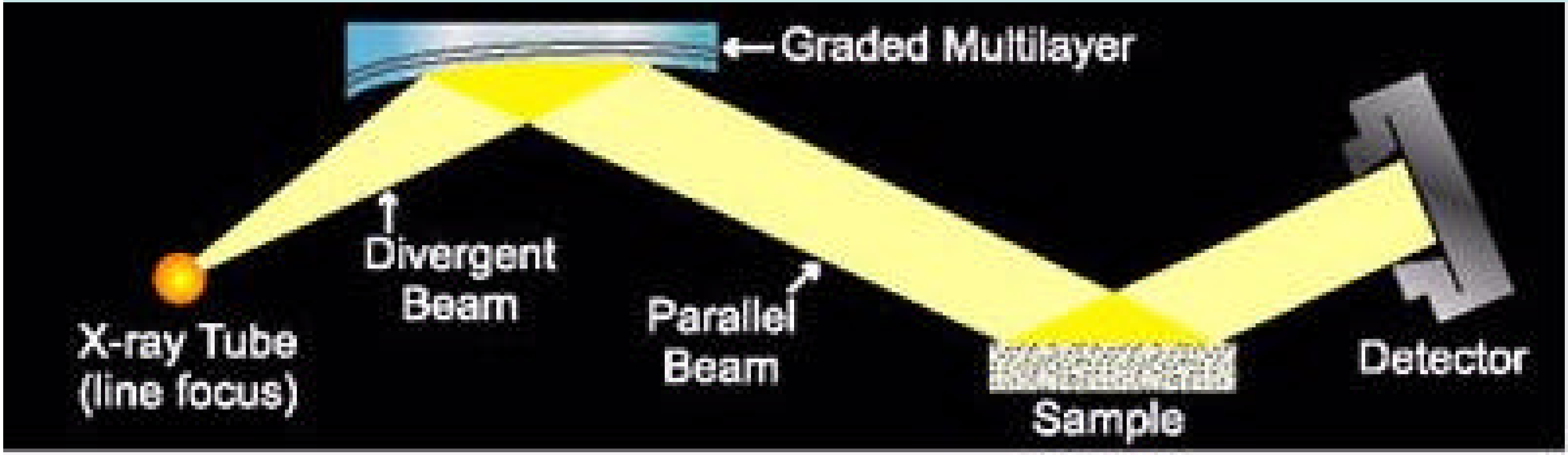

MAX - FLUX™ OPTICS
Rectangular
Beam Cross
Section
Source


Point
Source
Square
Focal Spot

Collimating Multilayer Optic



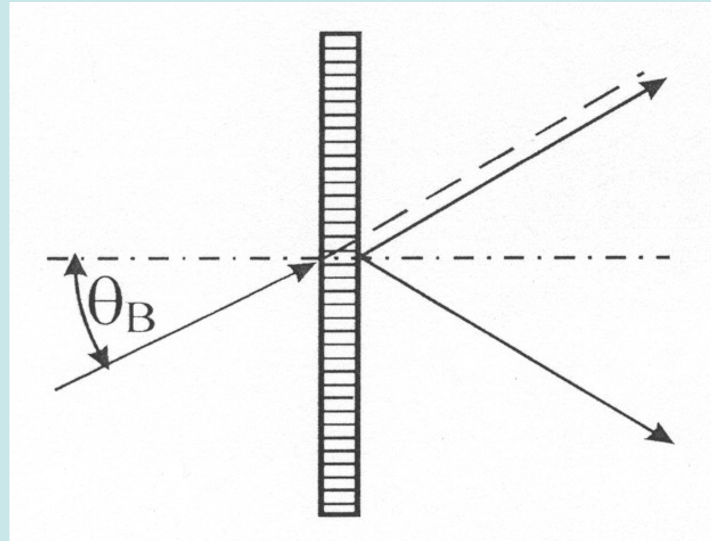
parallel beam

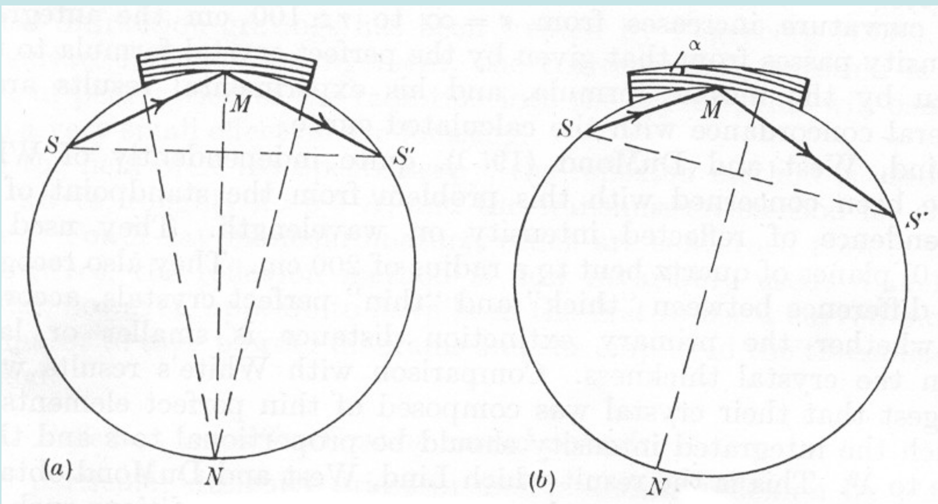


parallel beam

monochromators

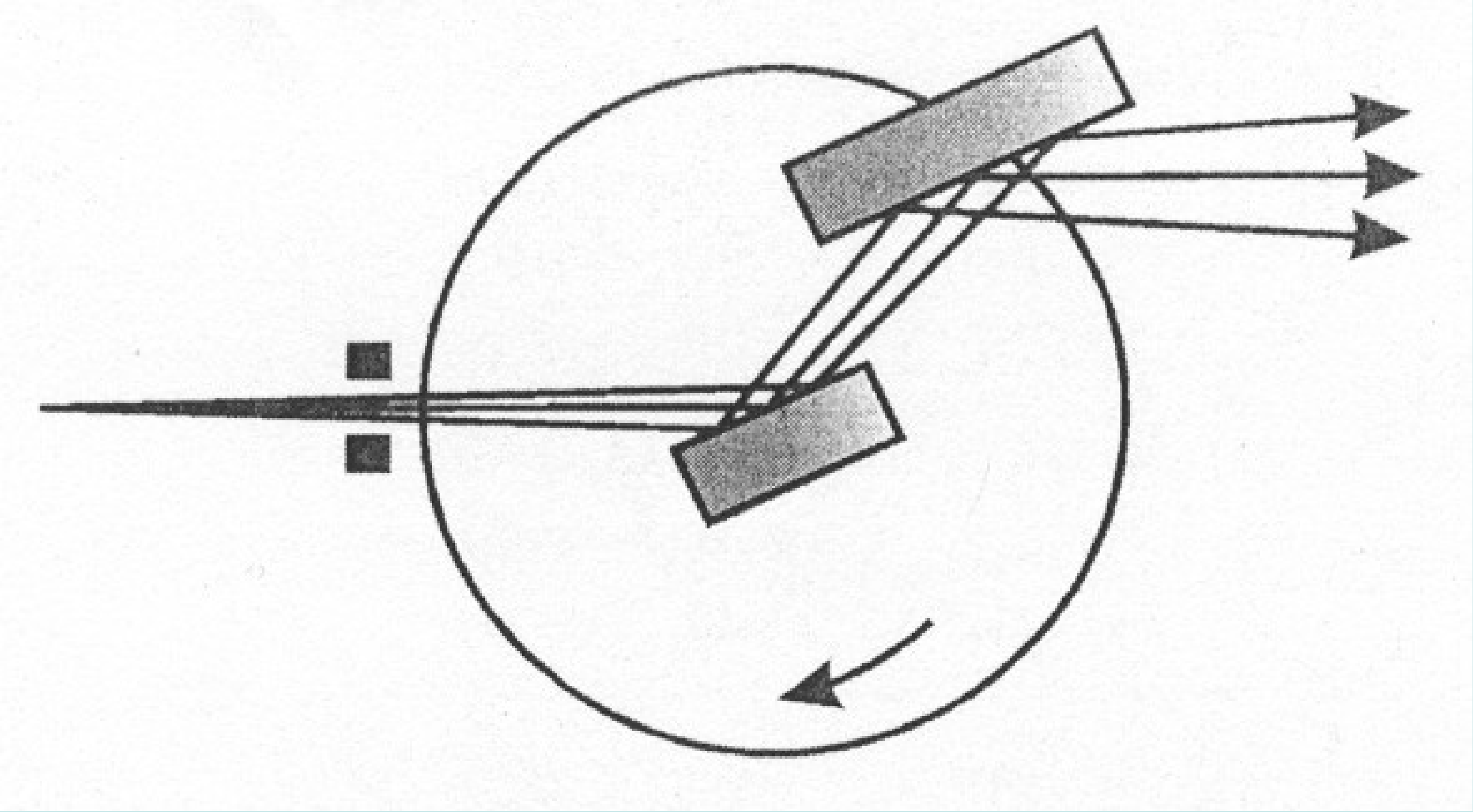
- filters
- flat crystals
- curved crystals





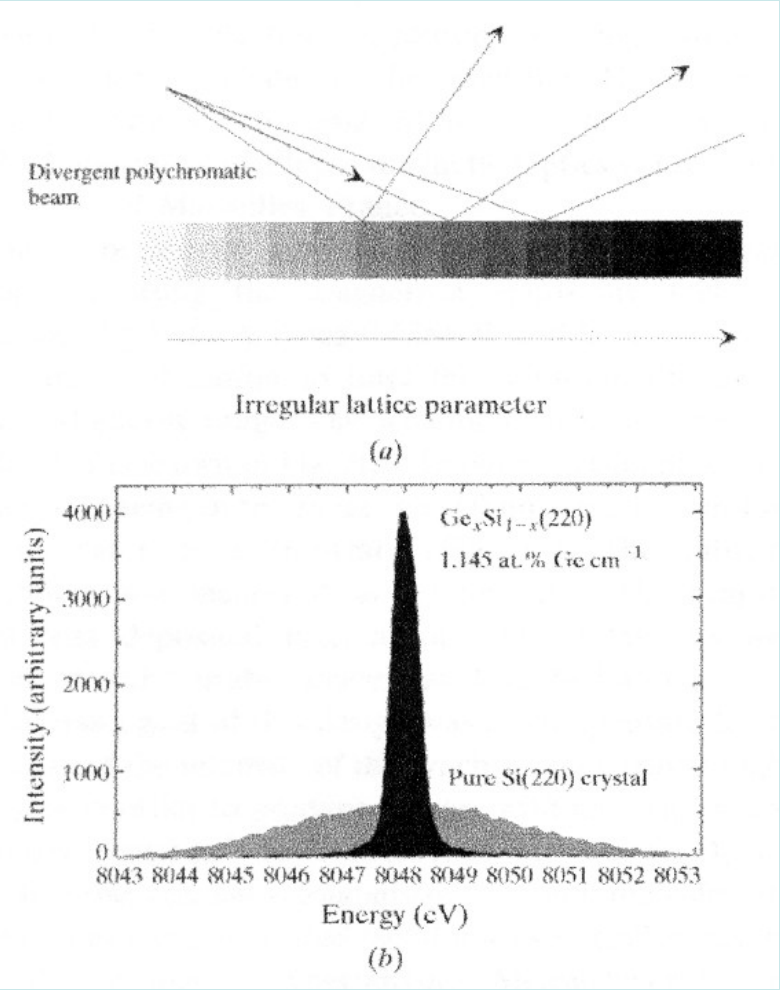
monochromators

- double crystal / channel cut



monochromators

- multilayers
- diffraction grating



monochromators / focusing

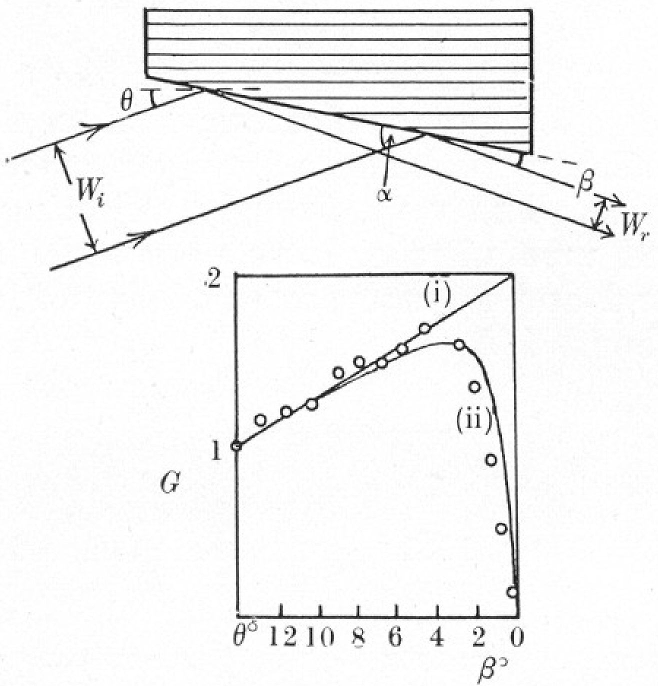


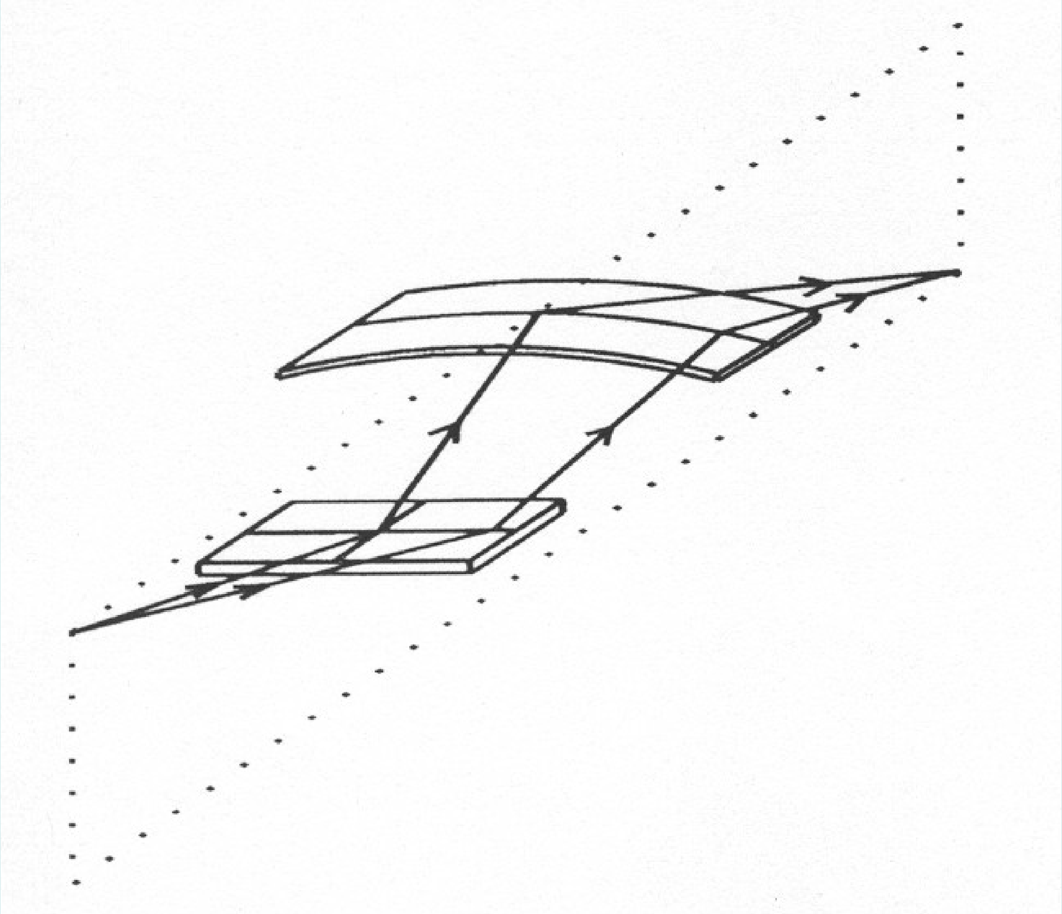
Fig. 42. Plane-concentrating monochromator. Variation of G, ratio of intrinsic intensities from concentrating monochromator and from symmetrical monochromator, with angle β° (after Evans, Hirsch and Kellar, 1948).

(i) Theoretical variation taking account of absorption in the crystal.

(ii) Theoretical variation taking account of absorption in the crystal and in a non-reflecting surface layer.

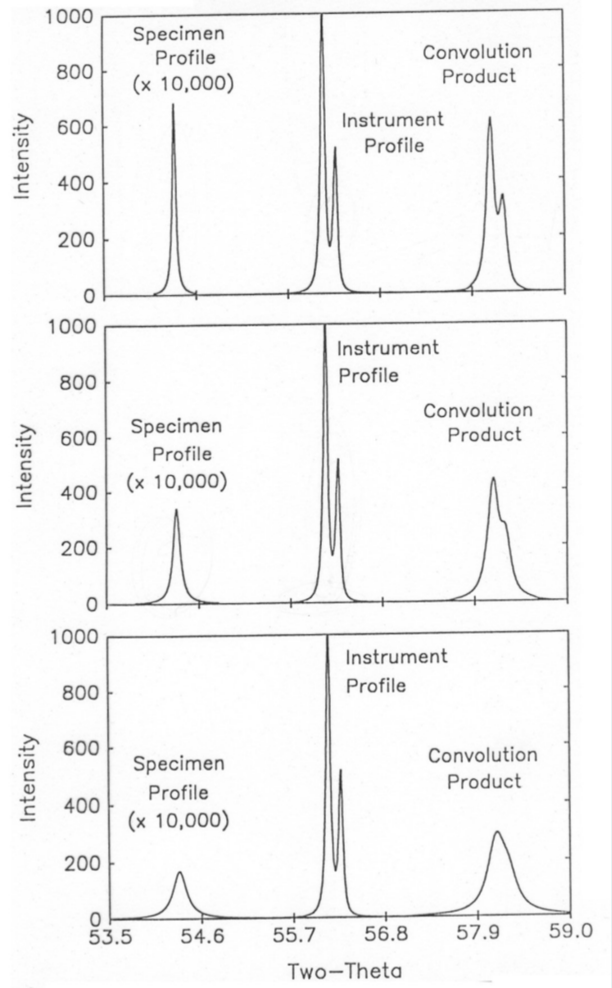
Circles represent experimental values for a calcite crystal.

monochromators / focusing



the exp peak profile shape

- the measured peak profile is the convolution of all **instrumental** and **sample** parameters



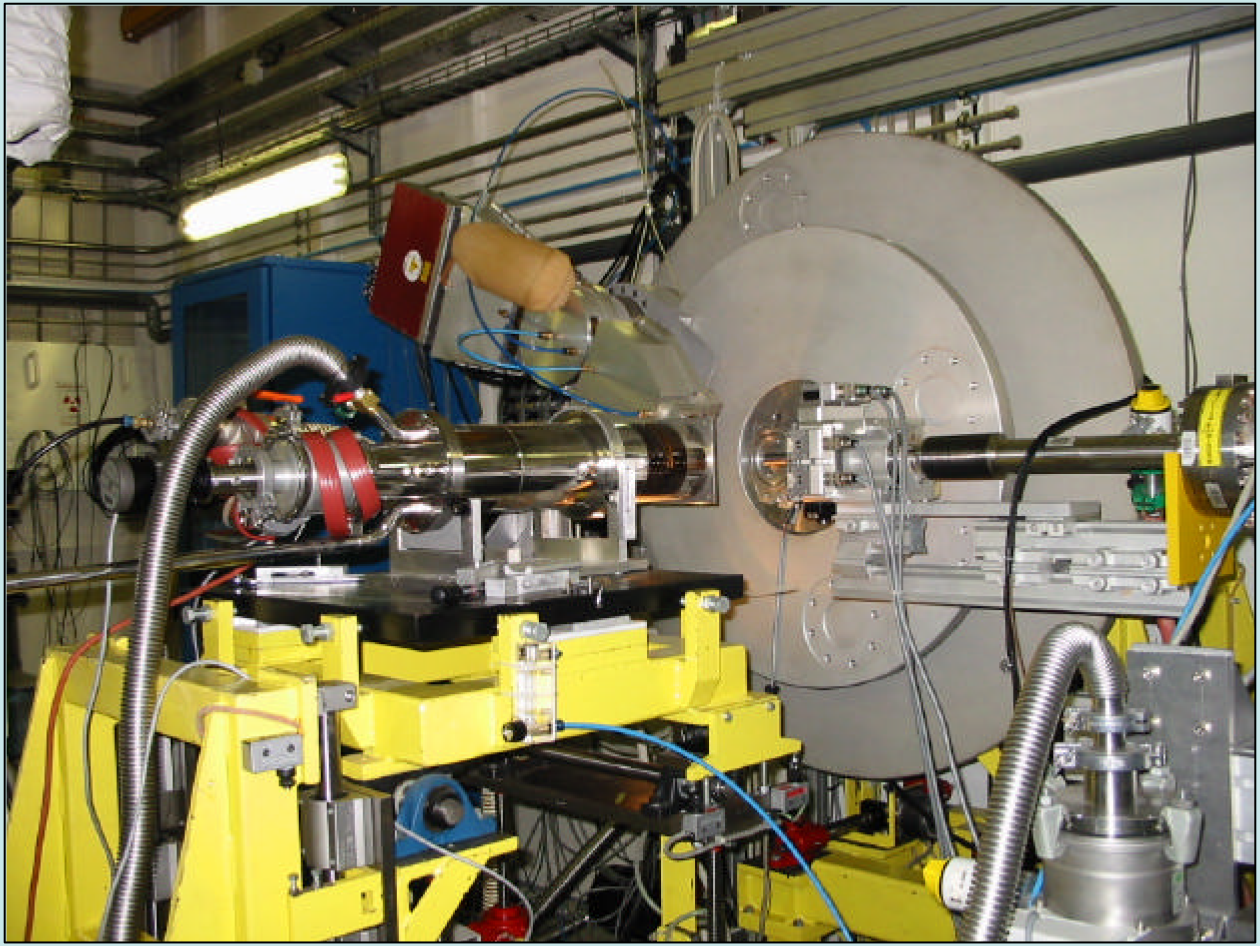
- common exp aberrations:
  - *axial divergence*
  - *sample shift*
  - *asymmetry*
  - *absorption/transparency*

ideal peak profile shape

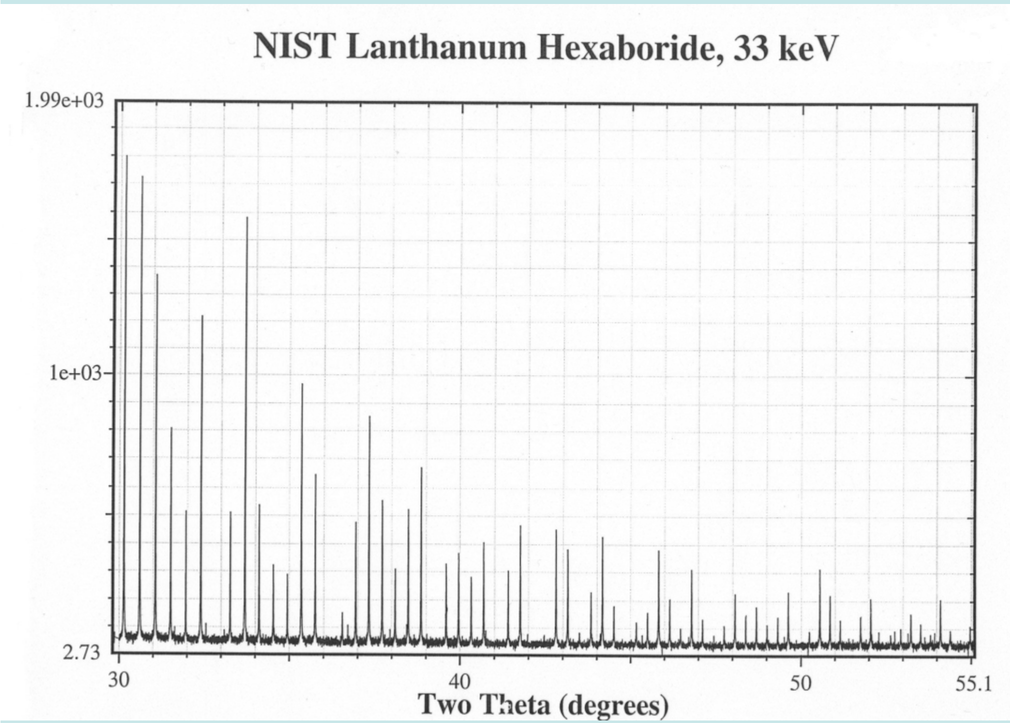
- ID31-ESRF is the closest we get to ideal:
  - incident flux from undulator
  - monochromator band pass: $\Delta\lambda/\lambda=10^{-4}$
  - collection time: minutes
  - optimal signal/noise ratio
  - instrumental peak broadening: FWHM<0.001 °

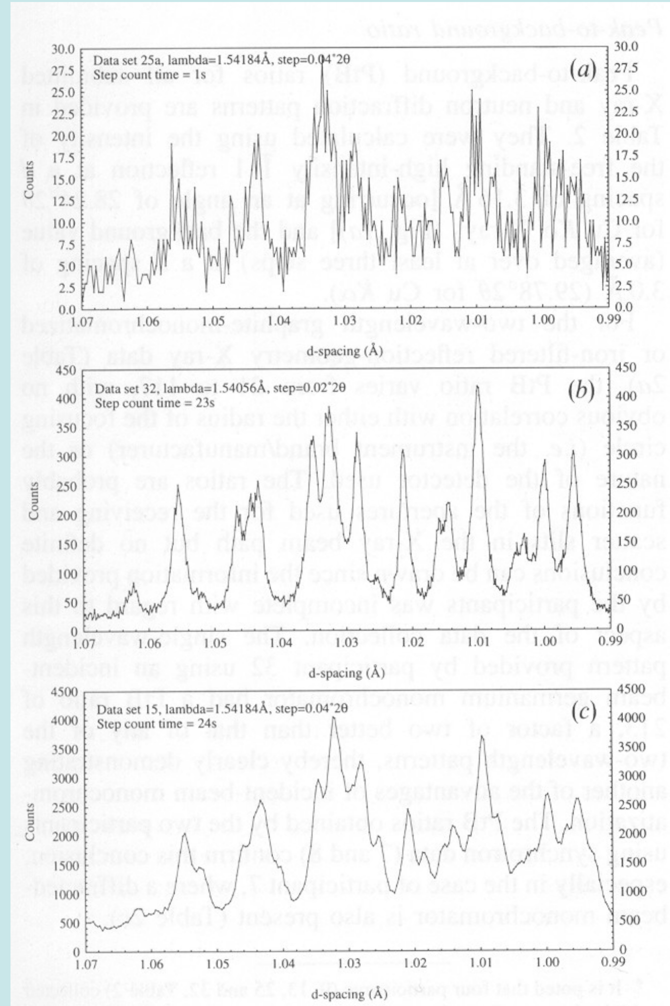
➢ how does it compare to laboratory data ?

Debye geometry at ESRF: ID31

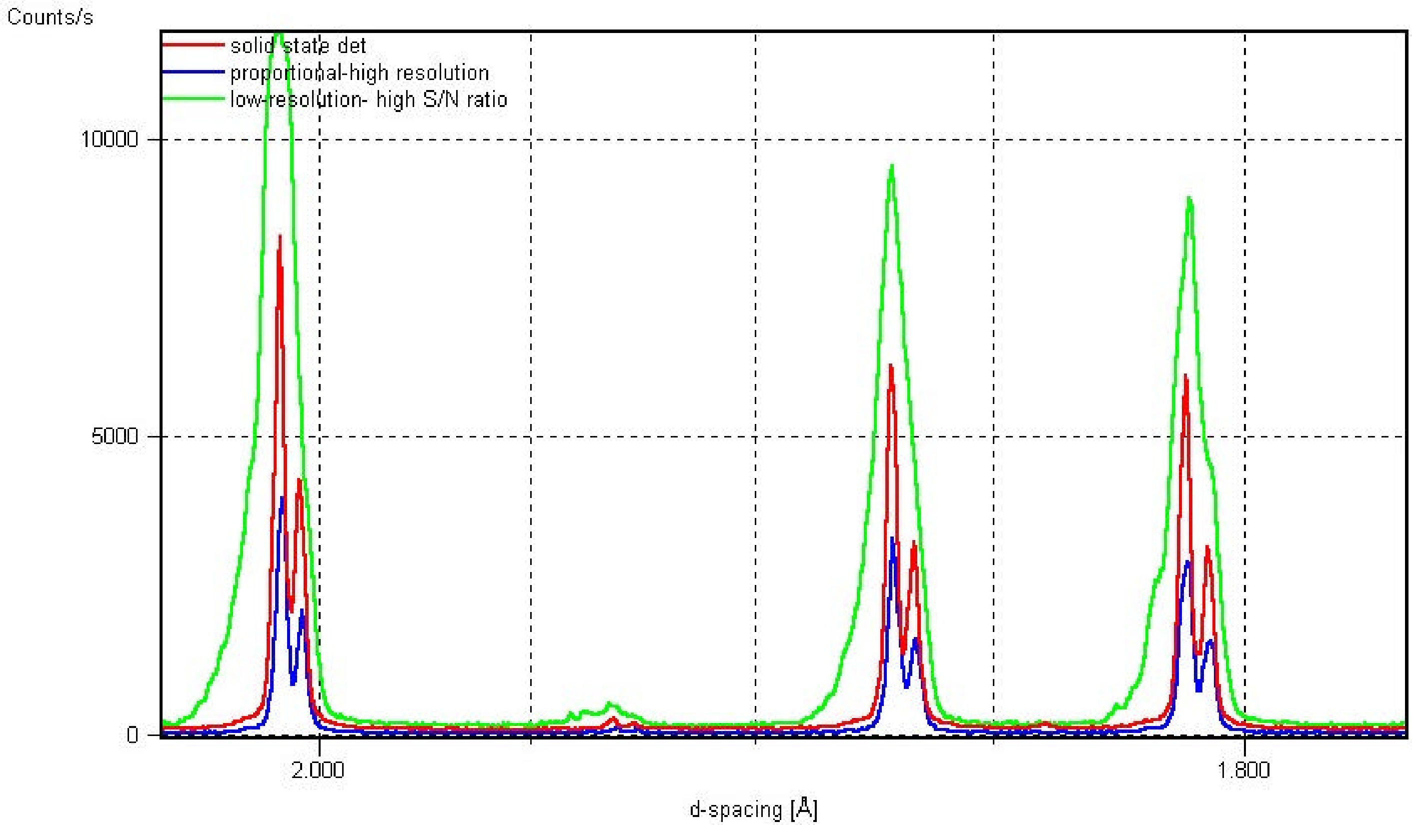


ideal vs real data

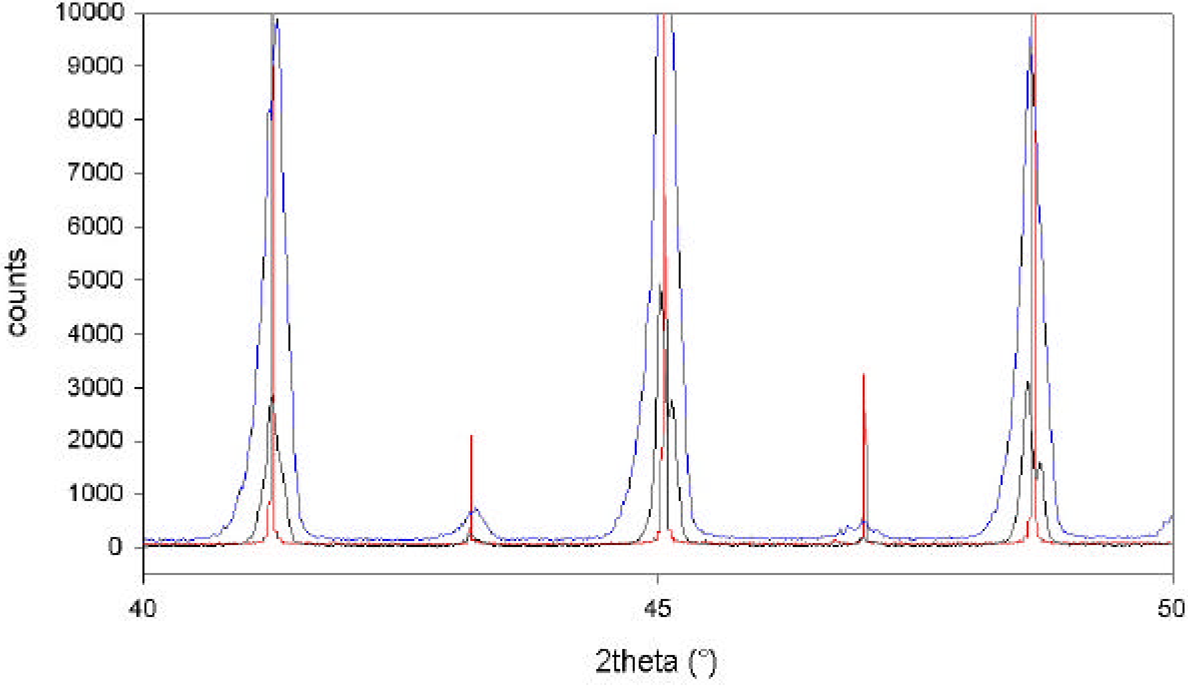




real data


Counts/s
solid state det
proportional-high resolution
low-resolution- high S/N ratio
10000
5000
0
2.000
1.800
d-spacing [Å]

real data



10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
counts
40
45
50
2theta (°)

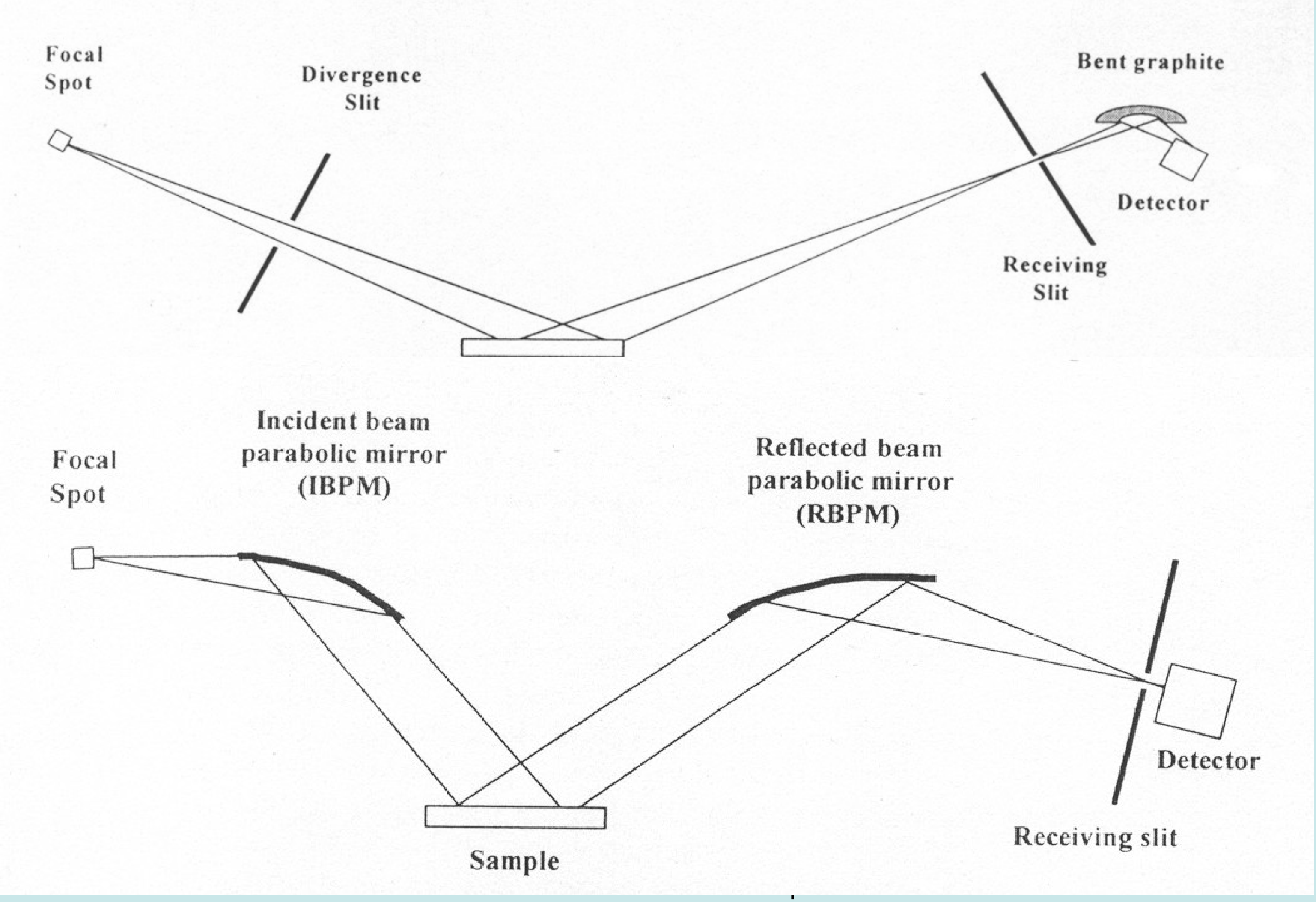
standard configurations

geometry	*goniometer*	*detector*
diverging beam flat sample (**parafocusing**)	Bragg-Brentano (θ-θ or θ-2θ)	proportional cnt scintillator SSD
convergent beam capillary sample (**Debye**)	capillary	gas linear PSD image plate
parallel beam (**mirrors**)	capillary irregular sample	proportional cnt scintillator SSD

Bragg-Brentano upgrades

- **SSD**
  - » it eliminates the fluorescence noise from the sample
  - » it has a good dynamic range
  - » it improves detection efficiency and counting statistics
- **primary monochromators**
  - » it eliminates Kβ lines
  - » it decreases the instrumental broadening
- **focusing/parallel beam mirrors**
  - » capillary sample
  - » sample with irregular surface
- **long Soller slits on the diffracted beam**
  - » they improve the instrumental resolution
  - » they improve the peak/noise ratio

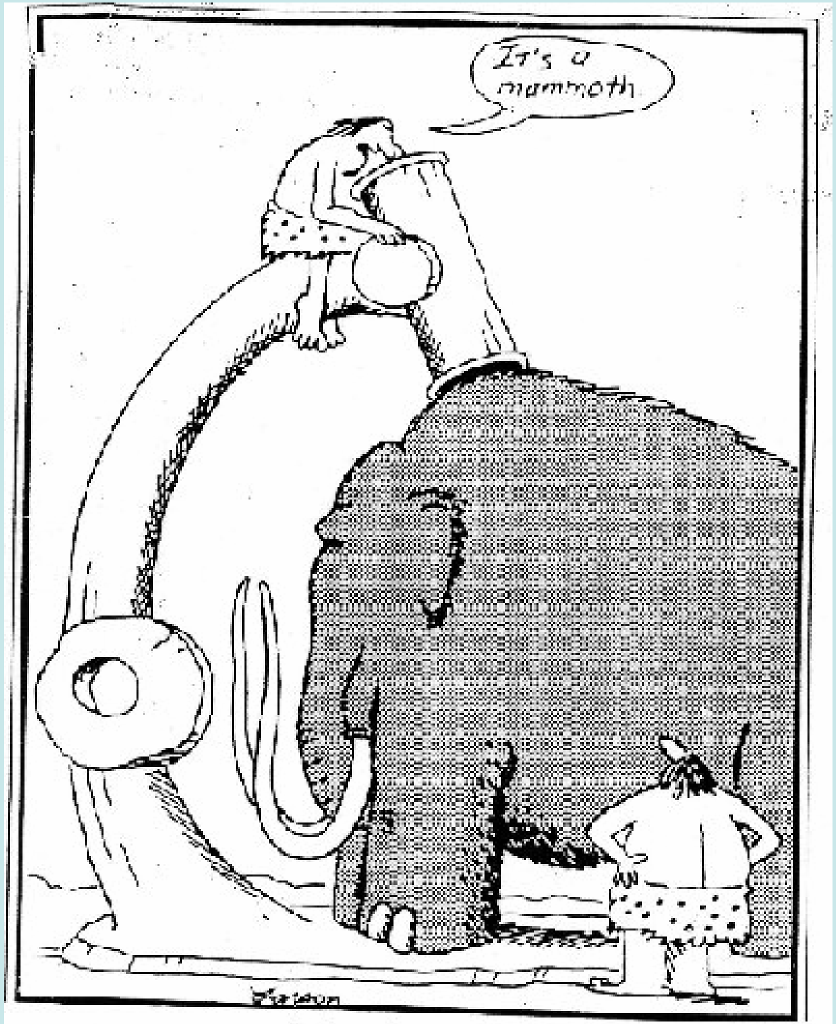
Bragg-Brentano upgrades



instrumental optimization

- we always have to face the compromise between
  - **intensity** (short collection time – good counting statistics – acceptable peak/noise ratio)
  - **resolution** (peak broadening – peak shape)

scientific problems → instrumental configuration → data collection strategy



Early microscope