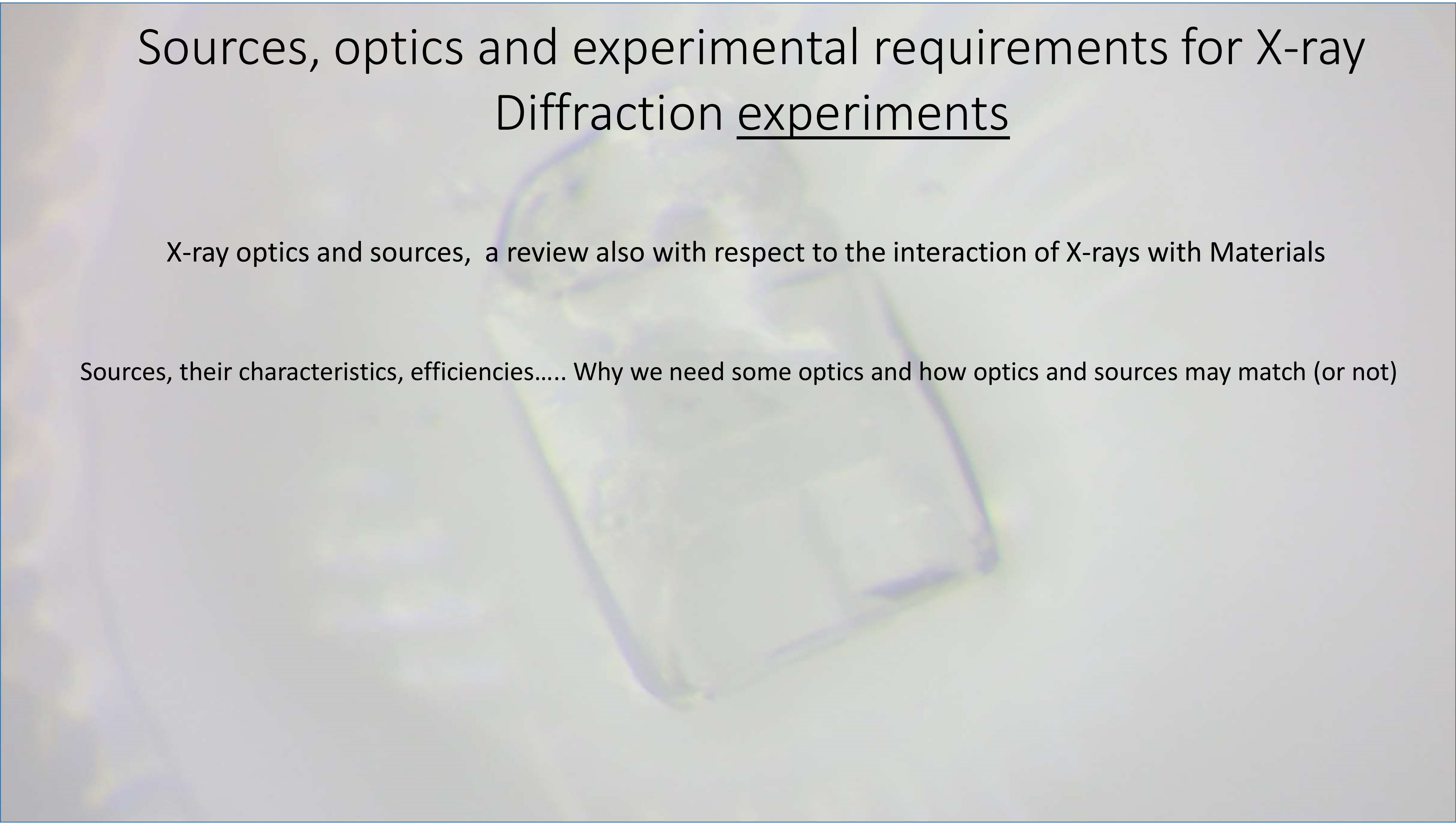
Sources, optics and experimental requirements for X-ray Diffraction experiments

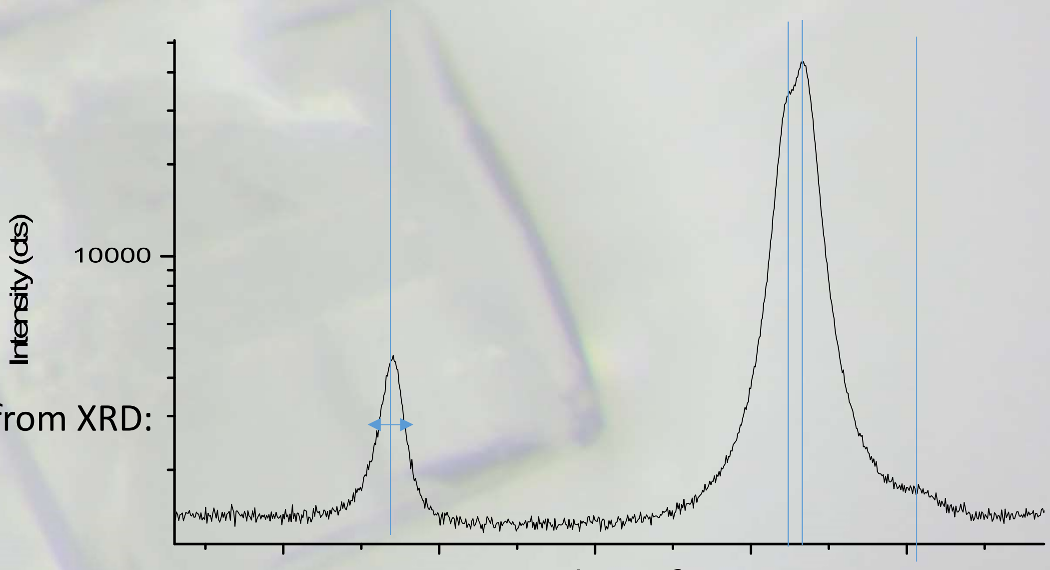


X-ray optics and sources, a review also with respect to the interaction of X-rays with Materials

Sources, their characteristics, efficiencies….. Why we need some optics and how optics and sources may match (or not)

Real X-ray experiments: the right “beam” for the right sample, Optics, sources and resolution

Preparation of the X-ray beam has significant influence on any experiment.
Crucial questions like Resolution vs statistics are of prime importance in XRD experiments



$$Q = \frac{4\pi sin\theta}{\lambda}$$

Review of the basic parameters to be extracted from XRD:

Peak *position* (Lattice parameter),

Peak *width* (crystal size and quality),

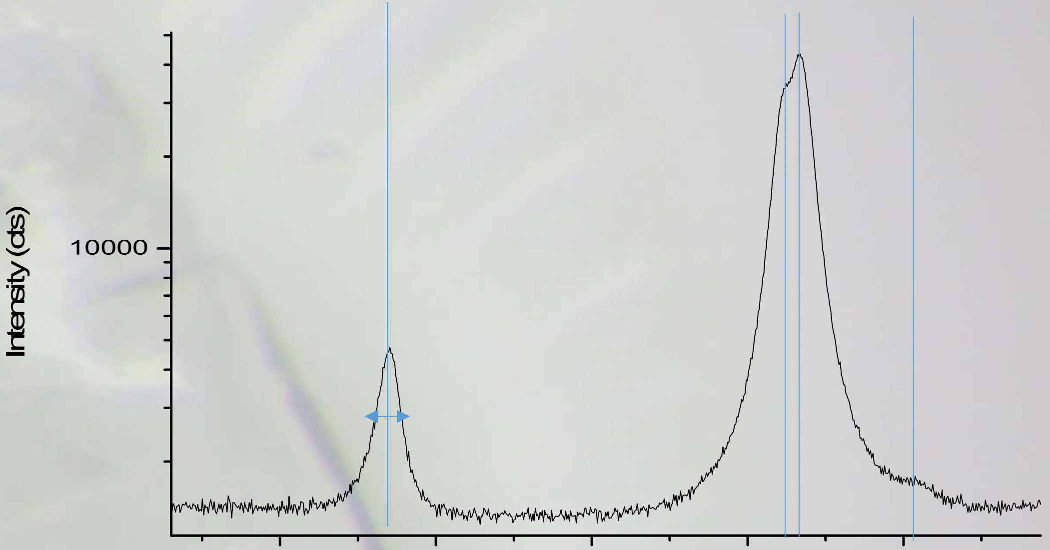
Peak *intensity* (integrated, of course -> structure factor, or quantification of a certain phase)

Peak width and instrumental influences

$$Q = \frac{4\pi sin\theta}{\lambda} \qquad \frac{dQ}{d\theta} = \frac{4\pi cos\theta}{\lambda}$$

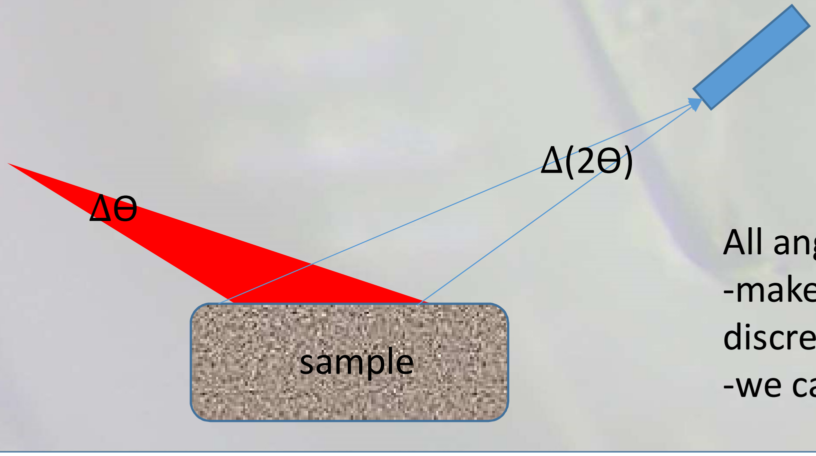
The precision we achieve in the determination of
Q(leading to lattice parameter),
ΔQ (crystal size, quality), ….

…directly depends on our resolution in θ and λ
Both certainly depend on our source qualities and our setup, eventually influenced by optics



$$Q = \frac{4\pi sin\theta}{\lambda}$$

Incoming beam with divergence ΔΘ (and eventually a band width Δλ)

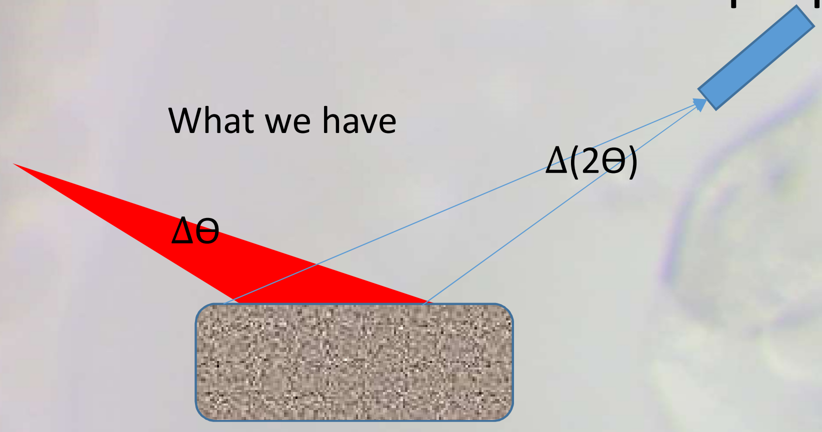


Spot size of X-ray beam on the sample leads to angular uncertainty on the detection side

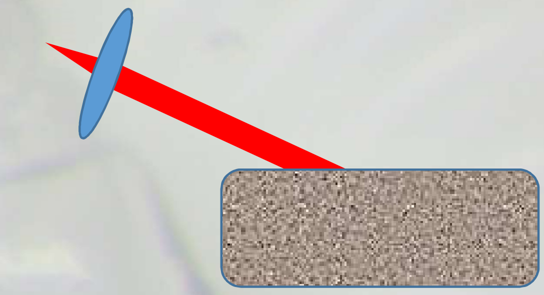
All angular uncertainties will lead to a broadening of the peaks and
-make peaks overlap (we cannot determine integrated intensity of discrete peaks anymore
-we cannot interpret the peak width

Beam preparation with X-ray optics

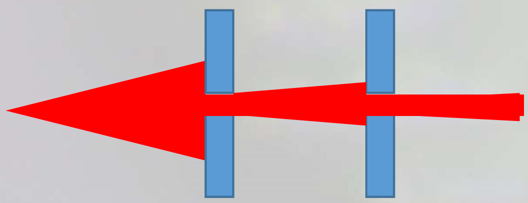
What we have



What we want



Simple form of beam preparation



If we want to preserve flux we need optics !

The dilemma of x-ray optics

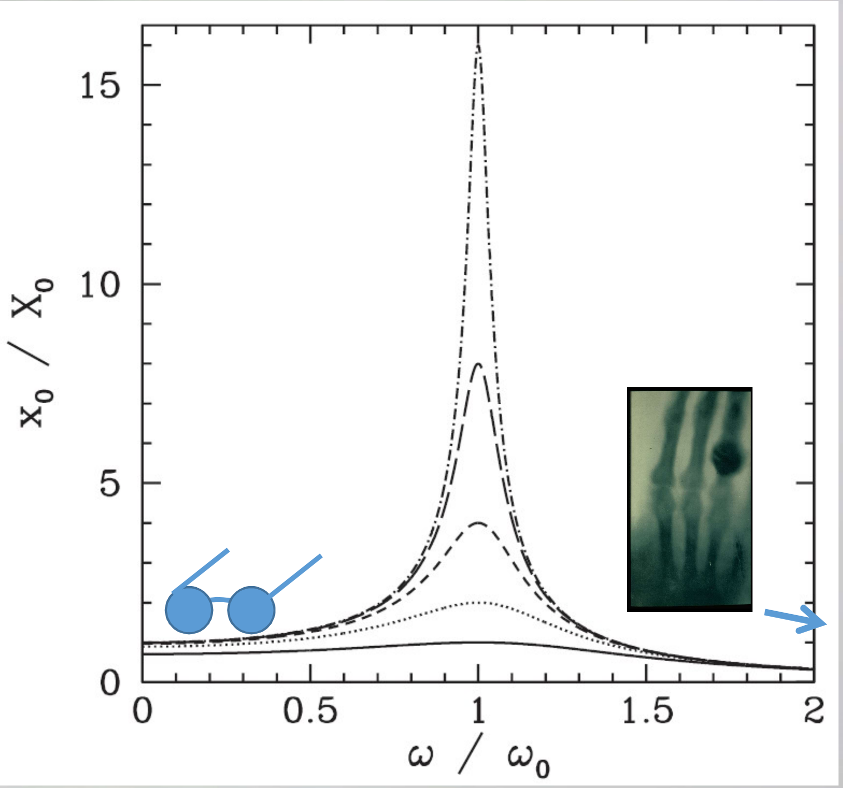
The refractive index is expressed as $n \approx \sqrt{1+\chi}$ χ=polarizability

Polarized electron clouds=driven harmonic oscillators

Polarization $P=\chi * E$ ~ equiv. mechanical Amplitude

Amplitude for a driven harmonic oscillator

$$X_0 \cong P \propto \frac{\omega_0^2}{\sqrt{(\omega_0^2-\omega^2)^2+\phi^2\omega^2}}$$



For $\omega \ll \omega_0$: P=const. (does hardly vary with ω)

eyeglasses work for all colours,
In this regime, refraction is almost achromatic

For $\omega \gg \omega_0$: $P \sim 1/\omega^2$, thus P-> 0

Refraction in the x-ray regime is very weak and highly chromatic!!,

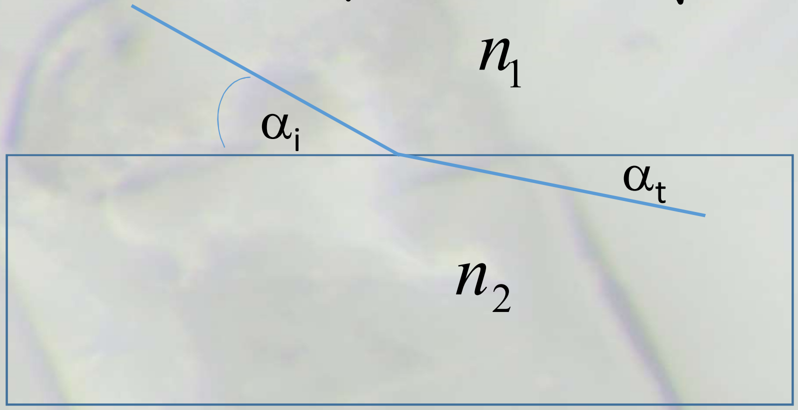
$n \approx 0.99999..$

The challenge of x-ray optics (reflection)

The refractive index is expressed as n=1- $\delta + i\beta = \sqrt{\varepsilon\mu} \approx \sqrt{\varepsilon} = \sqrt{\varepsilon_0(1+\chi)}$ ~0.9999 (typically)

1.00000(air) ↓ 0.9999(Matter) ↓

$$n_1 \cos\alpha_i = n_2 \cos\alpha_t$$



For $\alpha_i = 0.2^\circ$: total reflection ($\alpha_t = 0$)

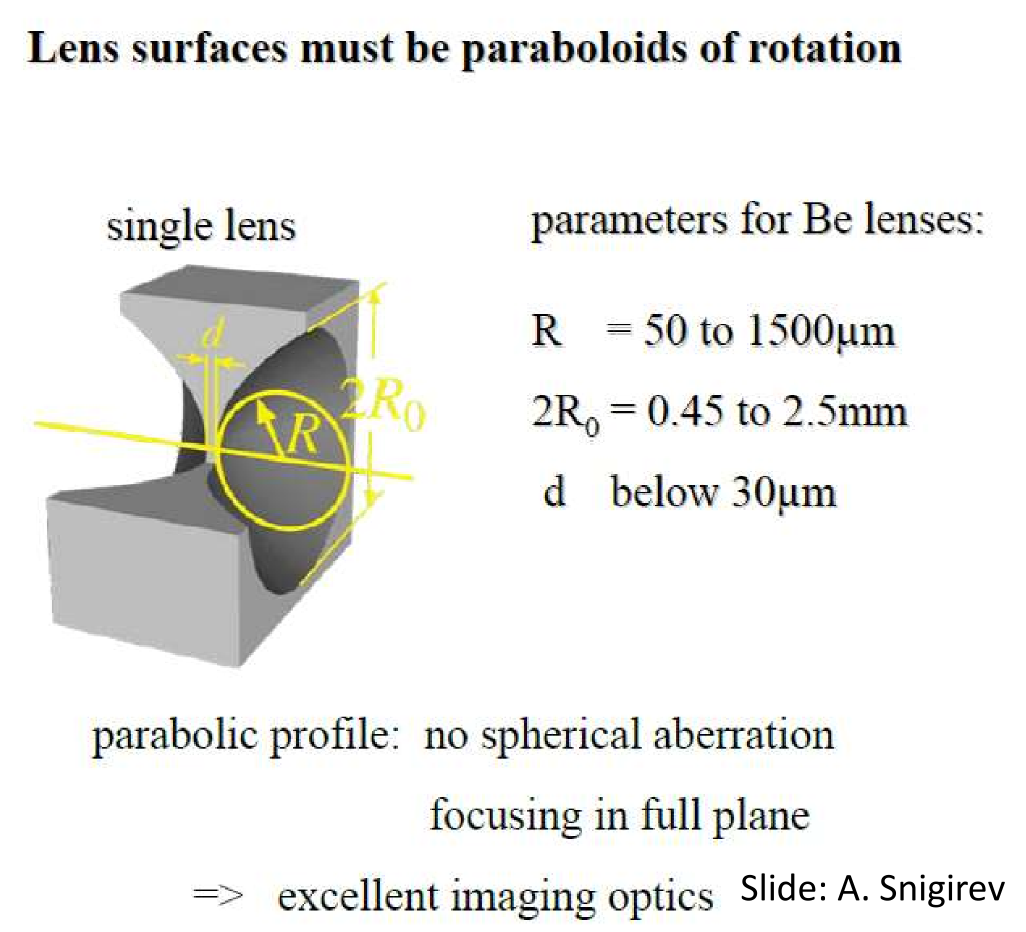
For $\alpha_i = 1^\circ$: $\alpha_t = 0.97^\circ$

For $\alpha_i = 3^\circ$: $\alpha_i = 2.99^\circ$

Refraction effects play a role only at grazing incidence (bad news for lenses)

Total reflection is only possible for grazing angles (bad news for dielectric mirrors)

Some X-ray lenses do exist , but…



Lens surfaces must be paraboloids of rotation

single lens

parameters for Be lenses:

$R = 50$ to $1500\mu m$

$2R_0 = 0.45$ to $2.5mm$

d below $30\mu m$

parabolic profile: no spherical aberration

focusing in full plane

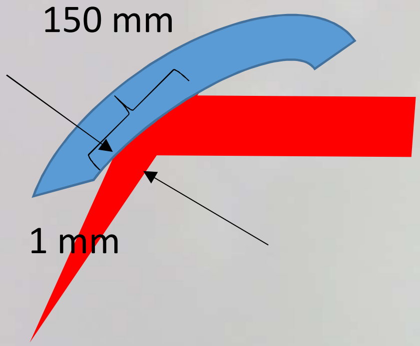
=> excellent imaging optics

Slide: A. Snigirev

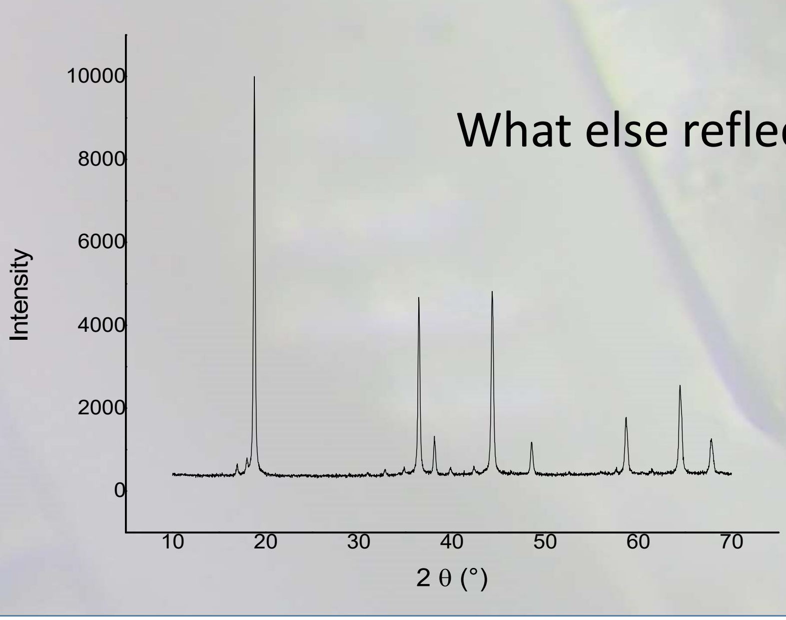
They need to be concave, with strong radius of curvature due to the weak refractive index,
They need to be made out of low Z materials as

Elastic interaction	absorption
$\sigma_c \sim \omega^{-2} Z^2$	$\sigma_a \sim \omega^{-3} Z^4$

Curved mirrors can make X-rays parallel (or even focus)



But: reflection only works at grazing angles (typically 0.4° for Au or Pt and 8 keV X-rays)
-> to “catch” a 1 mm big beam the mirror needs to be 150 mm long; for a very divergent beam such an optics cannot be “close to the source” due to its own size

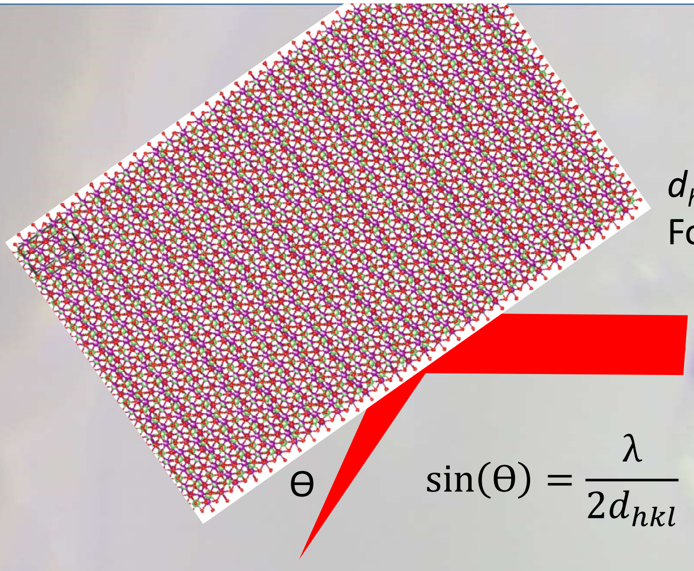


What else reflects X-rays ?

Diffraction from crystals is a good candidate

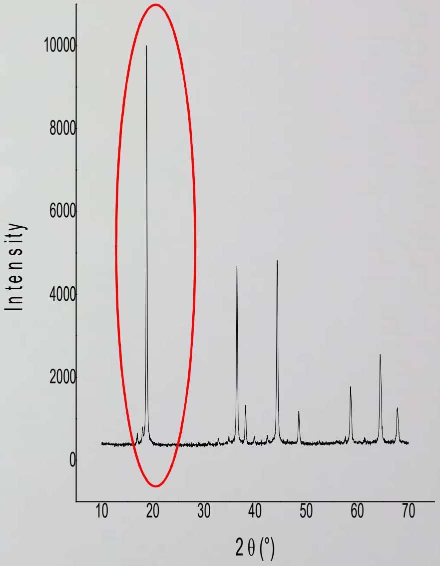
Crystals as X-ray optics

d_{hkl} depends on the cut of our monocrystal 3.136 for Si(111) or 4.2 % more for Ge(111),
For lab equipment Ge(220) is a common crystal monochromator.



$$\sin(\Theta) = \frac{\lambda}{2d_{hkl}}$$

Perfect (=big) crystals make intense and sharp peaks

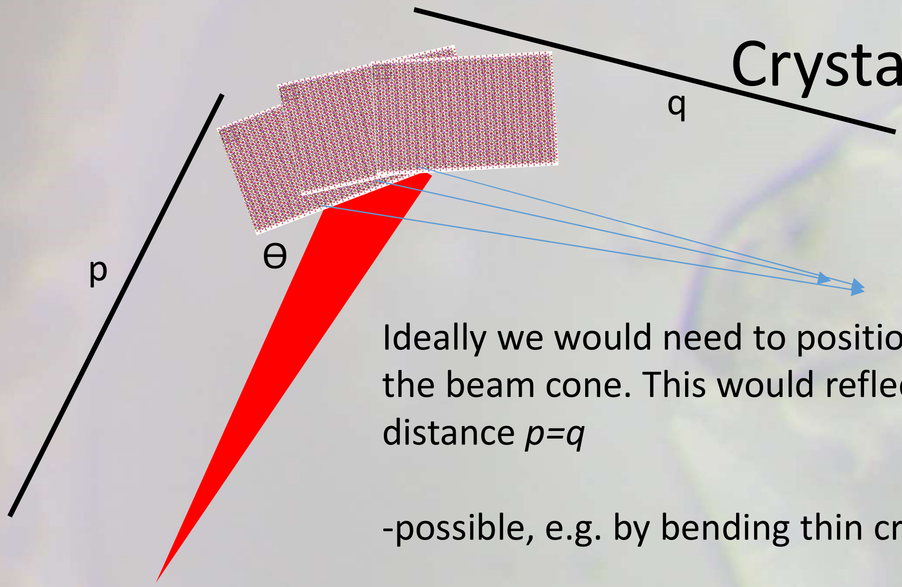


If our source emits only one wavelength λ, only one well defined Θ will be reflected !!,

This reduces our intensity but increases our resolution: we will get a very parallel and small beam

This compromise is sometimes difficult to accept…

Crystals as X-ray optics



$$\sin(\Theta) = \frac{\lambda}{2d_{hkl}}$$

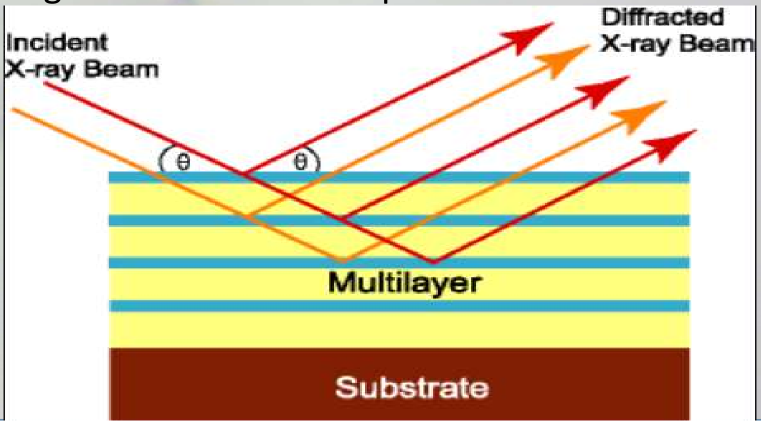
Ideally we would need to position a small crystal under slightly different angle at every position in the beam cone. This would reflect all rays of the primary beam and focus them into a spot at a distance *p=q*

-possible, e.g. by bending thin crystal sheets (done with graphite, Si, Ge)

But:
-> Cannot make the beam parallel, only refocus with 1:1 ratio
-> Not a good solution for most XRD applications as angular resolution is important

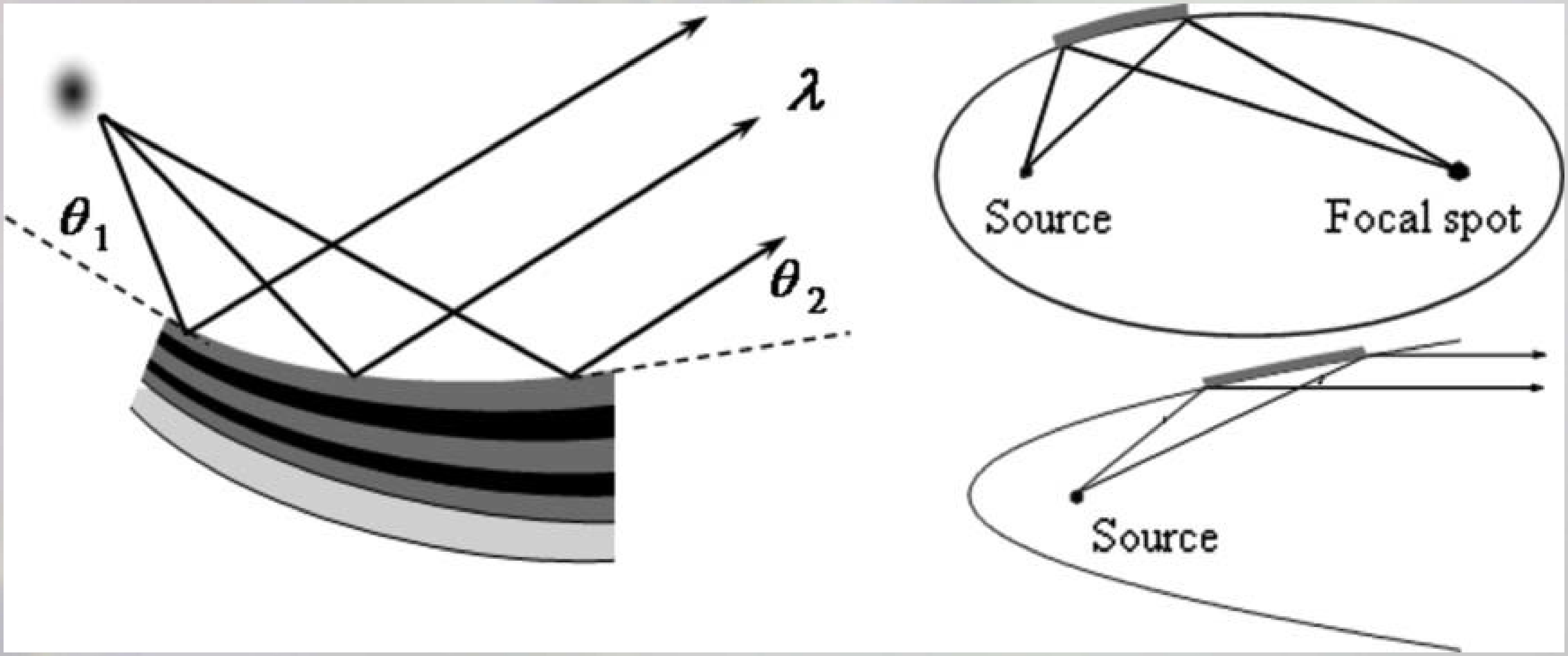
$$\sin(\Theta) = \frac{\lambda}{2d_{hkl}}$$

As every point at our reflector needs to satisfy the Bragg condition, we would need ideally to adapt d_{hkl} in every point in order to obtain another reflection angle for every position.
Multilayers as "artificial crystals" are a solution



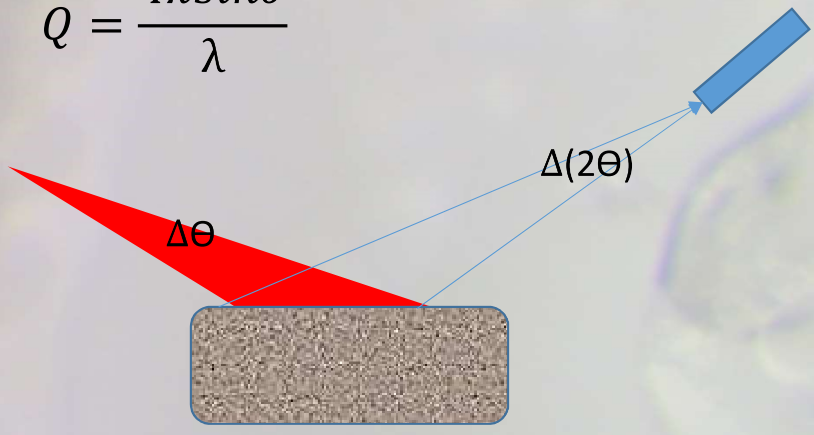
Multilayer optics

By choosing the d-spacing, every mirror shape can be realized and adapted to a certain wavelength;
Such a d-spacing will be bigger than the atomic d-spacing and the reflection angle will be low, typically 1-2 degrees.
-> still significantly bigger then the grazing angle of total external reflection -> moderately compact optics possible



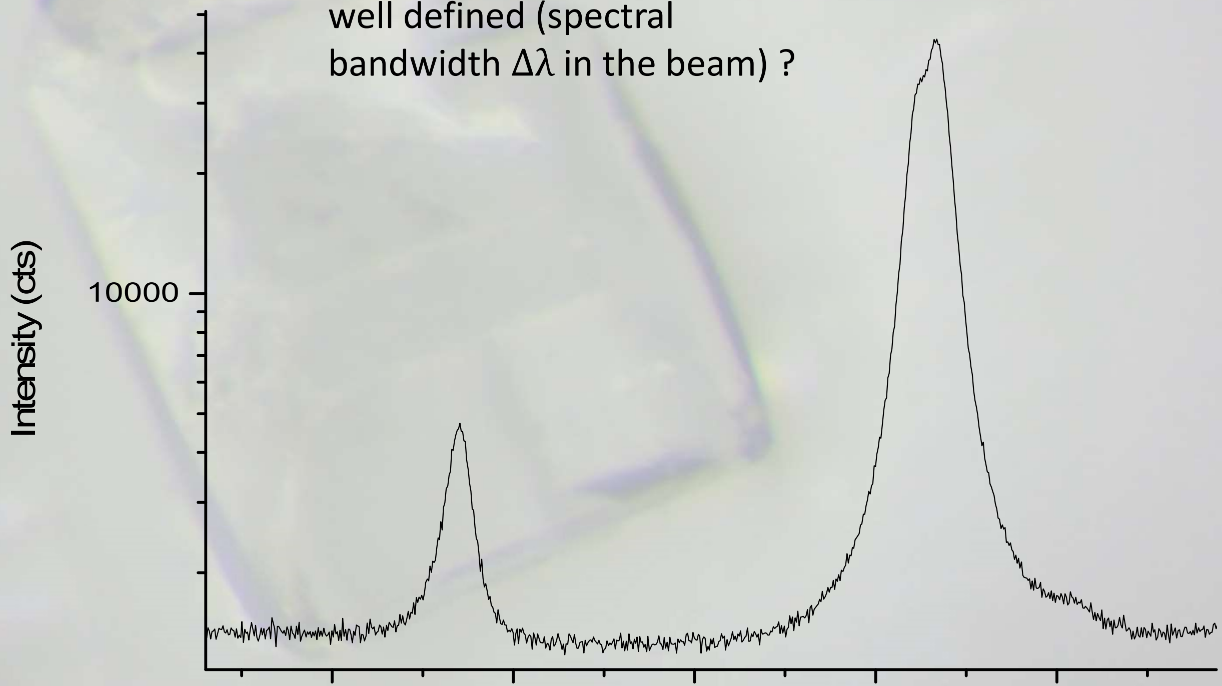
Optics and spectral purity

$$Q = \frac{4\pi sin\theta}{\lambda}$$



Beam divergence ΔΘ
leads to peak broadening,

What if our wavelength is not well defined (spectral bandwidth Δλ in the beam) ?

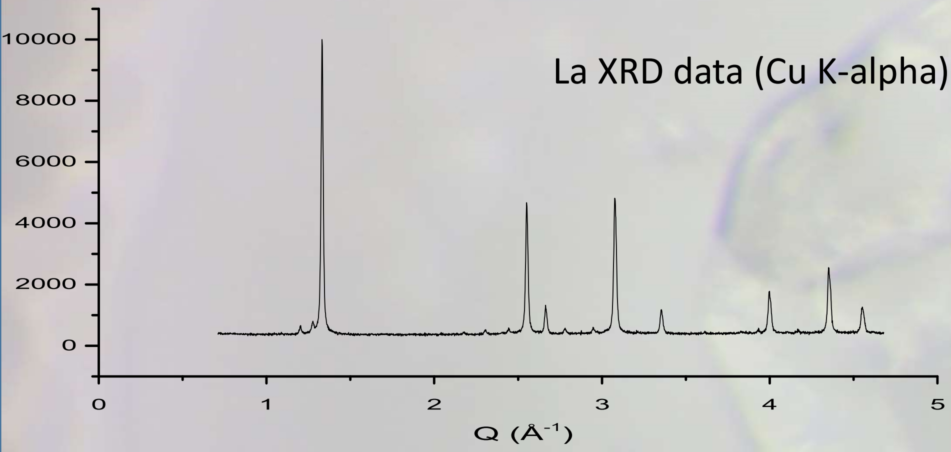


$$Q = \frac{4\pi sin\theta}{\lambda}$$

$$\frac{dQ}{d\lambda} = \frac{-4\pi sin\theta}{\lambda^2} = -\frac{Q}{\lambda}$$

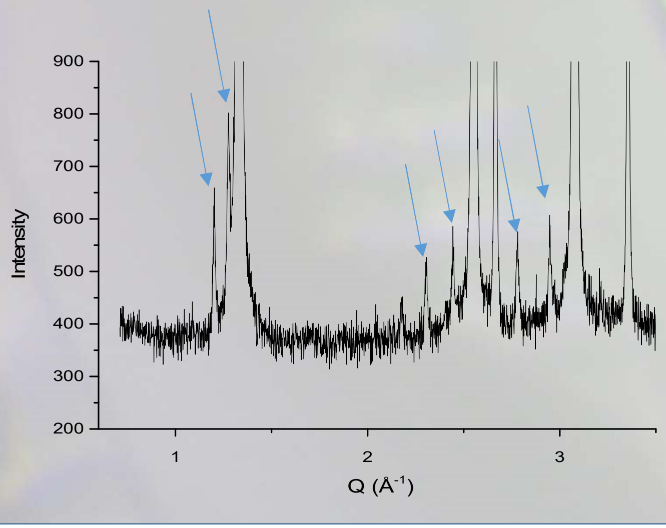
Of no importance for Q=0,
Getting worse for high Q

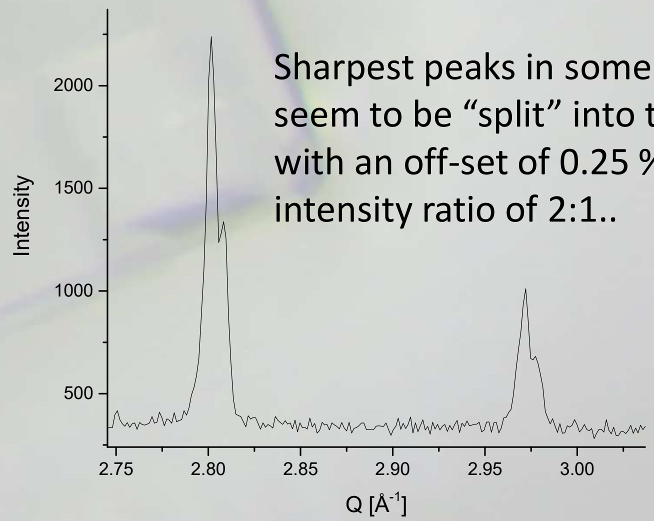
Optics and spectral purity, case for lab instruments



La XRD data (Cu K-alpha)

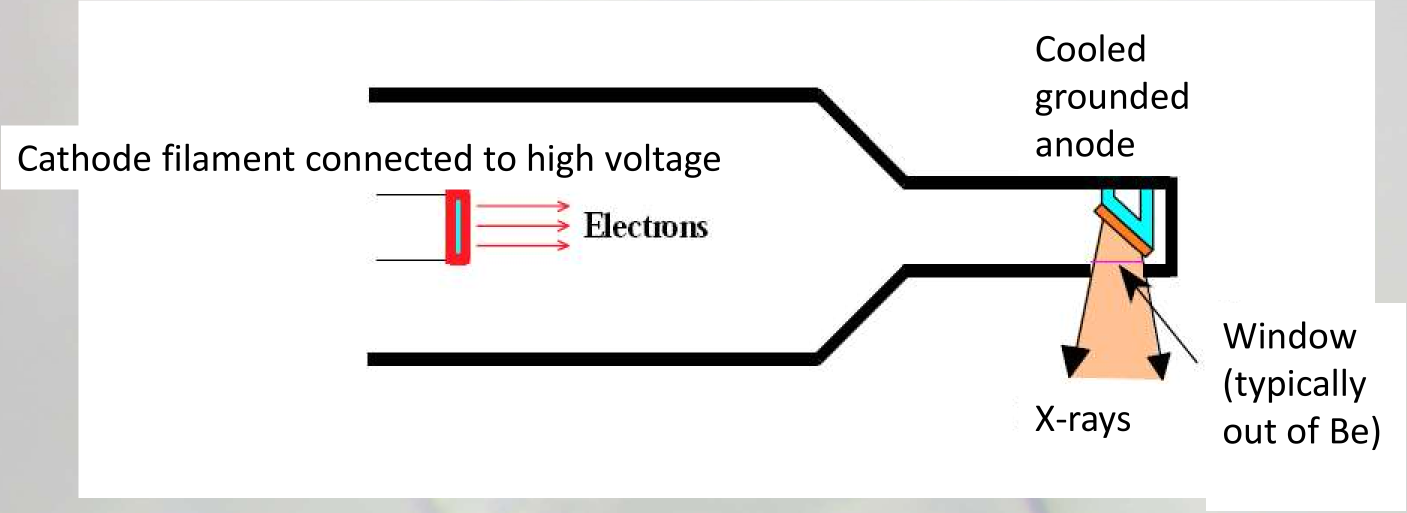
Satellite peaks, 4% and 10 % lower than the main peaks ?





Sharpest peaks in some samples seem to be “split” into two peaks with an off-set of 0.25 % and an intensity ratio of 2:1..

Physical origin of x-rays from a sealed tube



Cathode filament connected to high voltage

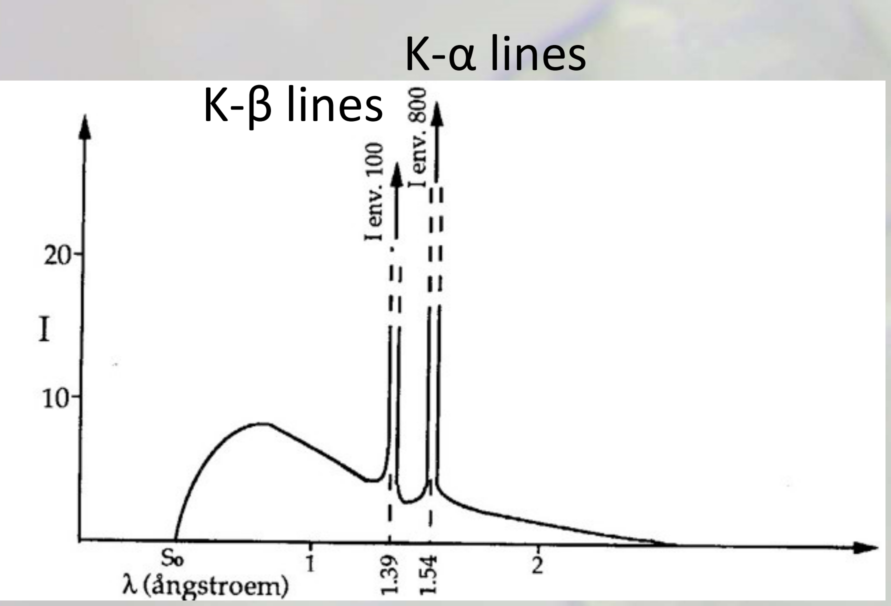
Cooled
grounded
anode

Window
(typically
out of Be)

X-rays

Accelerated electrons (typically30-60 keV hit the anode, get slowed down and emit **Bremsstrahlung**. The Anode Material is subject to multiple electronic excitations leading to **characteristic radiation**. Most of the electrons’ energy is converted into **heat** however. In general the Anode is water-cooled.

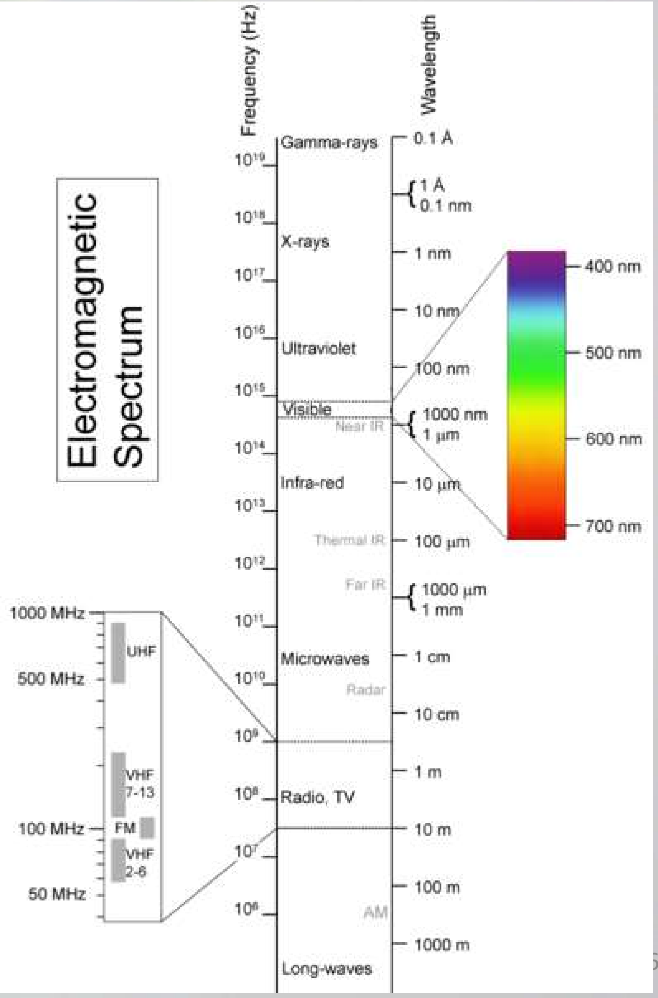
Spectrum of an x-ray tube, example of Cu



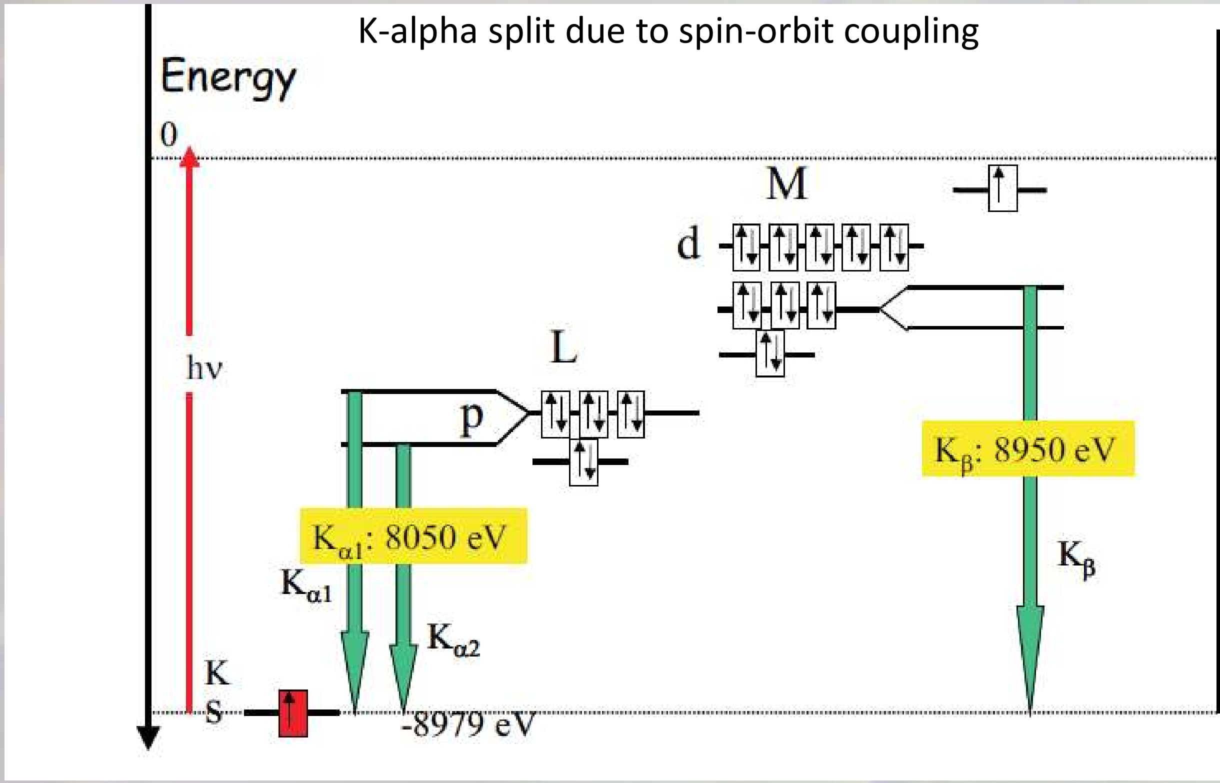
$\lambda=c/\nu$

$E_{ph}=h*c/\lambda$

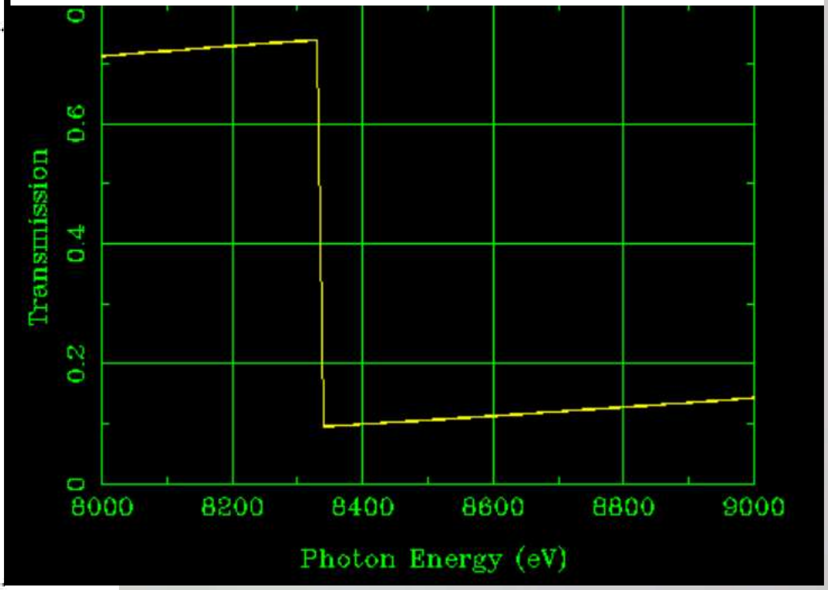
$E_{ph}(keV)=12.399/\lambda(Å)$



X-ray spectrum, example of Cu


K-alpha split due to spin-orbit coupling

8 micrometer Ni: ~70 % transmission at 8048 eV
~ 10 % transmission at 8950 eV



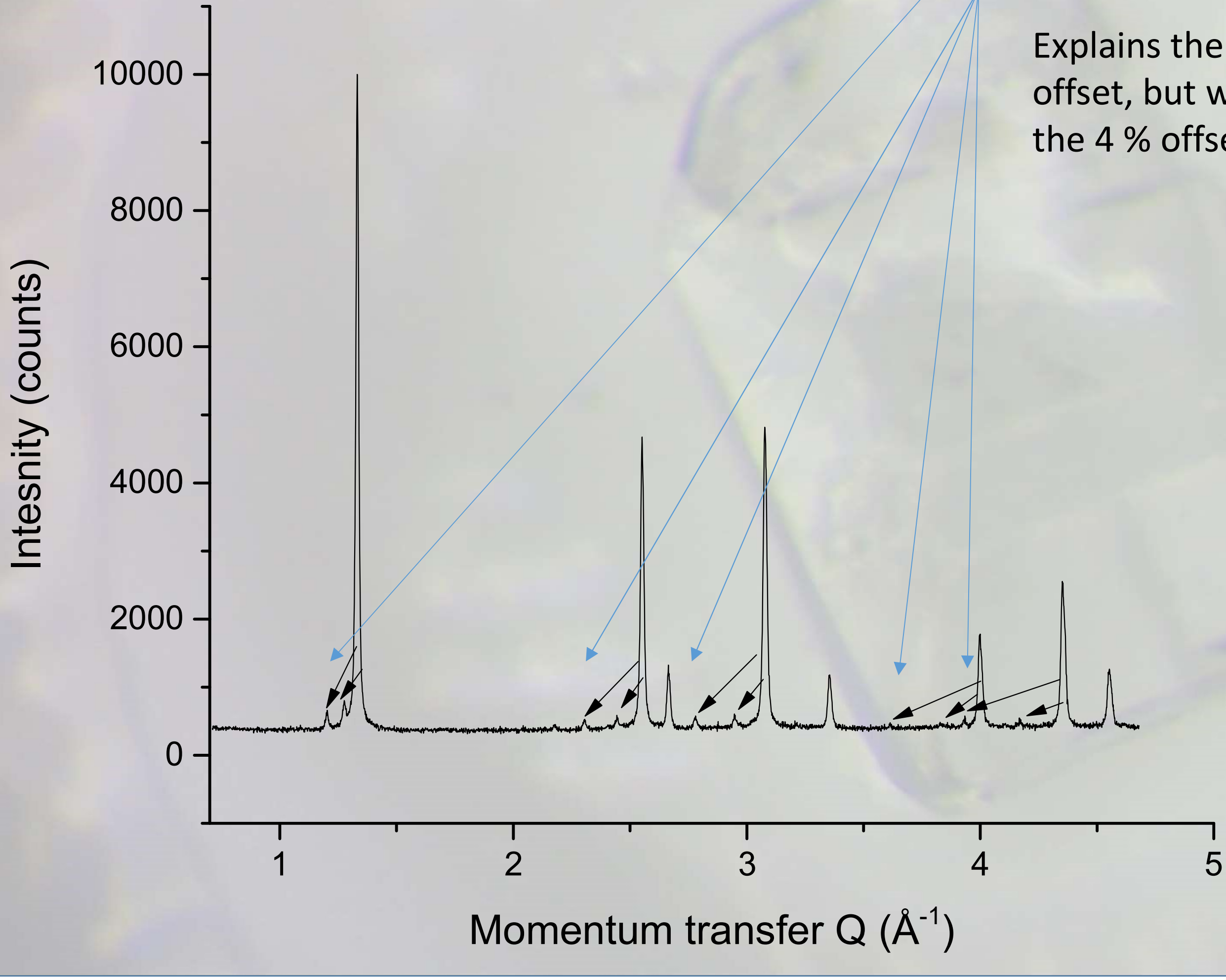
Rule of thumb 1: K-alpha is about 10 % below ionization level K-beta less then 1 % below Ionization level

Rule of thumb 2: The Ionization Level of element Z-1 lies in between K-alpha and K-beta of element Z

Cu K-beta filter: a piece of Nickel-foil !

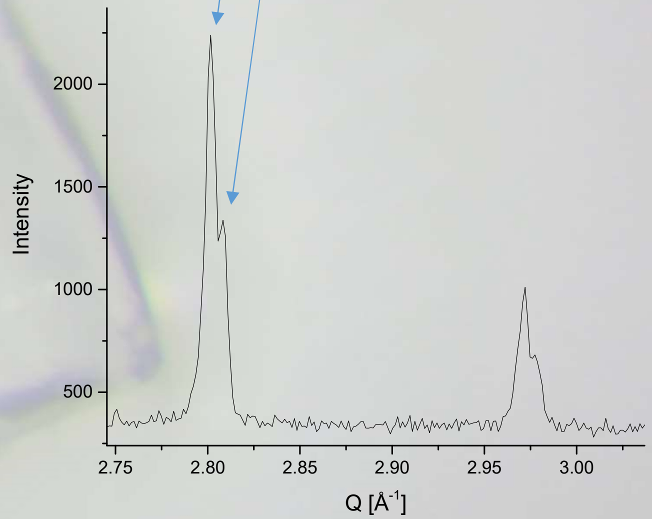
Spectral impurities and extra peaks

Radiation: Cu K$\alpha_{1\&2}$: 8.04 keV some Cu Kβ: 8.905 keV (=1.107*kα)



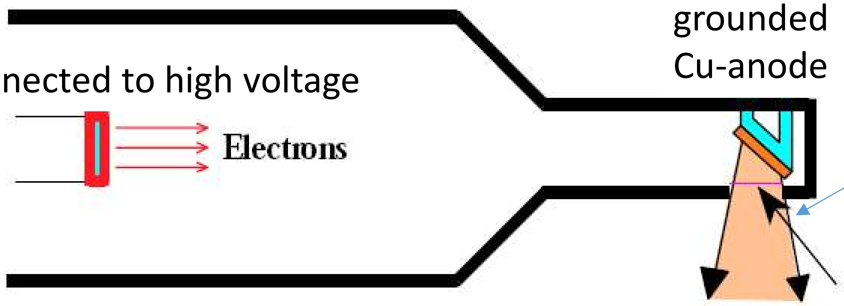
Explains the lines at 10 % offset, but what about the 4 % offset ones ?

K-α_1 : 8.048 keV (1.5406 Å)
K-α_2 : 8.028 keV (1.5444 Å)



Sharpest peaks in the sample seem to be “split” into two peaks with an off-set of 0.3 % and an intensity ratio of 2:1..

Spectral emission lines from a Cu-anode



Cathode filament connected to high voltage

Cooled grounded Cu-anode

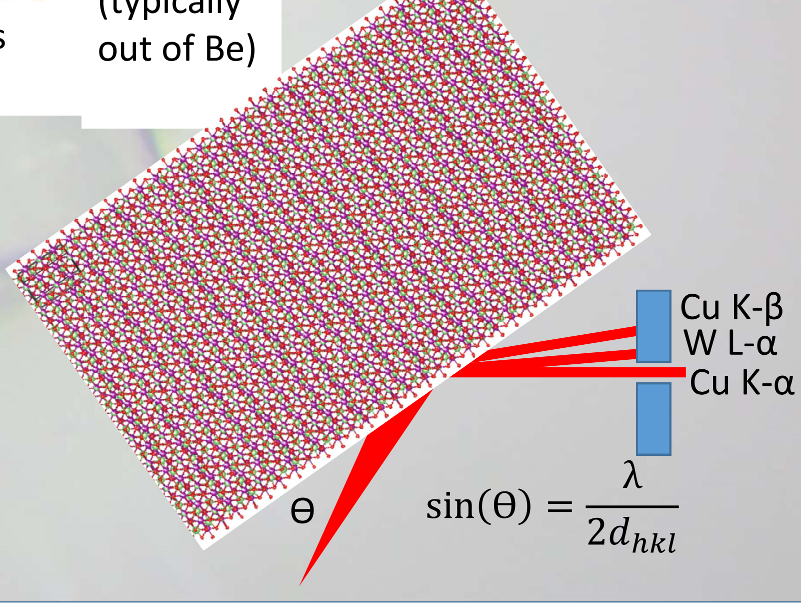
Contains the characteristic lines of the Cu spectrum, K-α, K-β…

Window (typically out of Be)

X-rays

Hot filament out of W, leads to W-evaporation and deposition and a W-contamination of the anode. W being a lot heavier (K-edge at 69 keV), it's L- α emission line lies at 8.4 ke V, 4 % higher than Cu k-α….

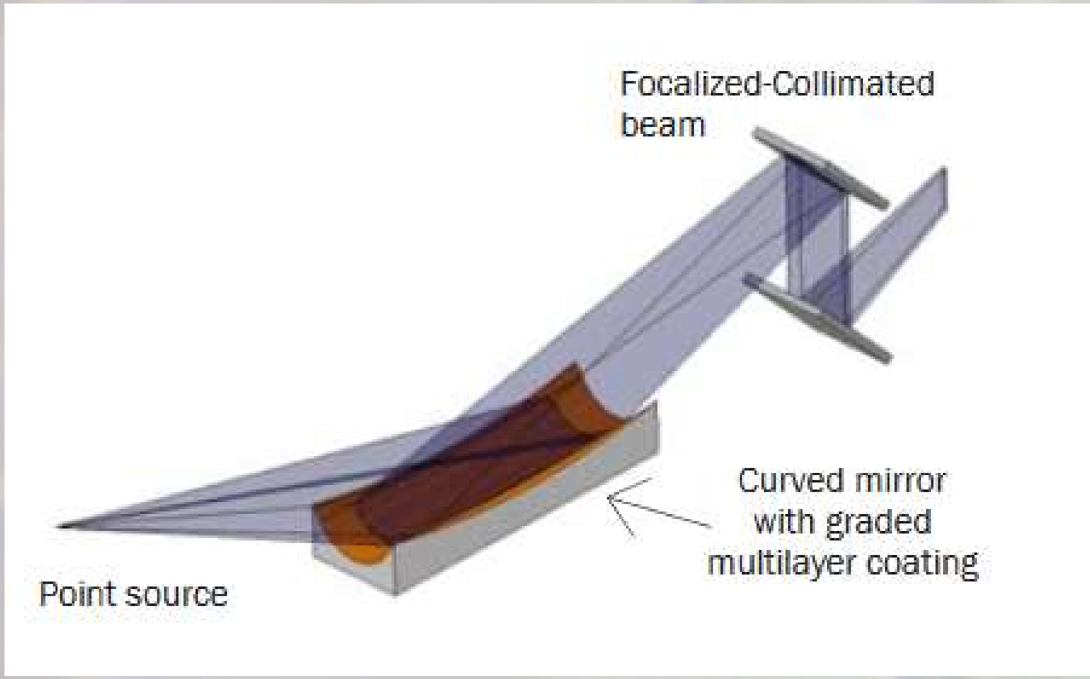
To filter out these different contributions, crystal monochromators are the method of choice; as they are very selective in the angular regime as well they "kill a lot of intensity



$$\sin(\Theta) = \frac{\lambda}{2d_{hkl}}$$

Combined mirror-crystal optics

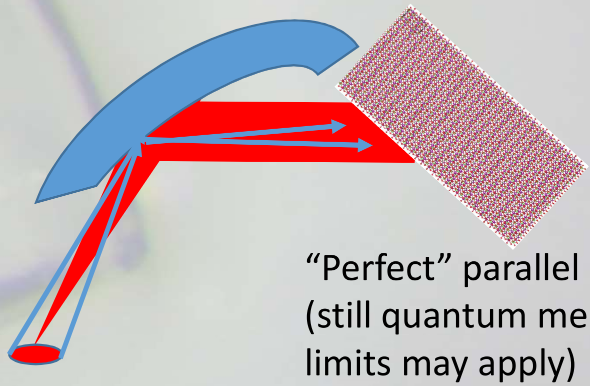
Making the beam “parallel” with a (multilayer) mirror, and selecting thr right wavelength (K-α) is eventually a good (though expensive and alignment intense) compromise. Mirror development over the last decades has improved to reject efficiently a large fraction of parasitic lines.



Good source: as small as possible,
Emitting a beam as parallel as possible

These optics have also limits, depending on the source itself

$$\sin(\theta) = \frac{\lambda}{2d_{hkl}}$$



“Perfect” parallel beam (still quantum mechanical limits may apply)

“Perfect point source”

Extended source: every point on the mirror sees radiation from different angles. This is reproduced as a finite beam divergence after the mirror

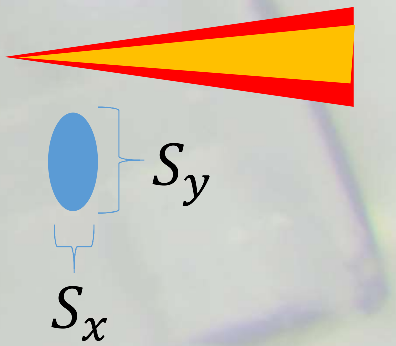
Definition of a good source

Small, low divergence, monochromatic, emitting lots of photons/second

Brilliance of a source: $B = {}^{photons}/_{s}\ \dfrac{1}{0.1\ \%\ Bandwidth}\ \dfrac{1}{\theta_x \theta_y S_x S_y}$

Divergences $\theta_x \theta_y$

Source size $S_x S_y$



Technical limits for classic X-ray tubes: melting of anode material by energy density of the electron beam

Efficiency of a lab X-ray tube.

At 60 KV acceleration Voltage, approx. 0.5 % of the electron energy is converted into radiation (rest: heat).

Most of this radiation goes “the wrong way” (in all spatial directions… 4 π). And most of the photons are not in the spectral range we are interested in (For ex. Cu K-alpha).

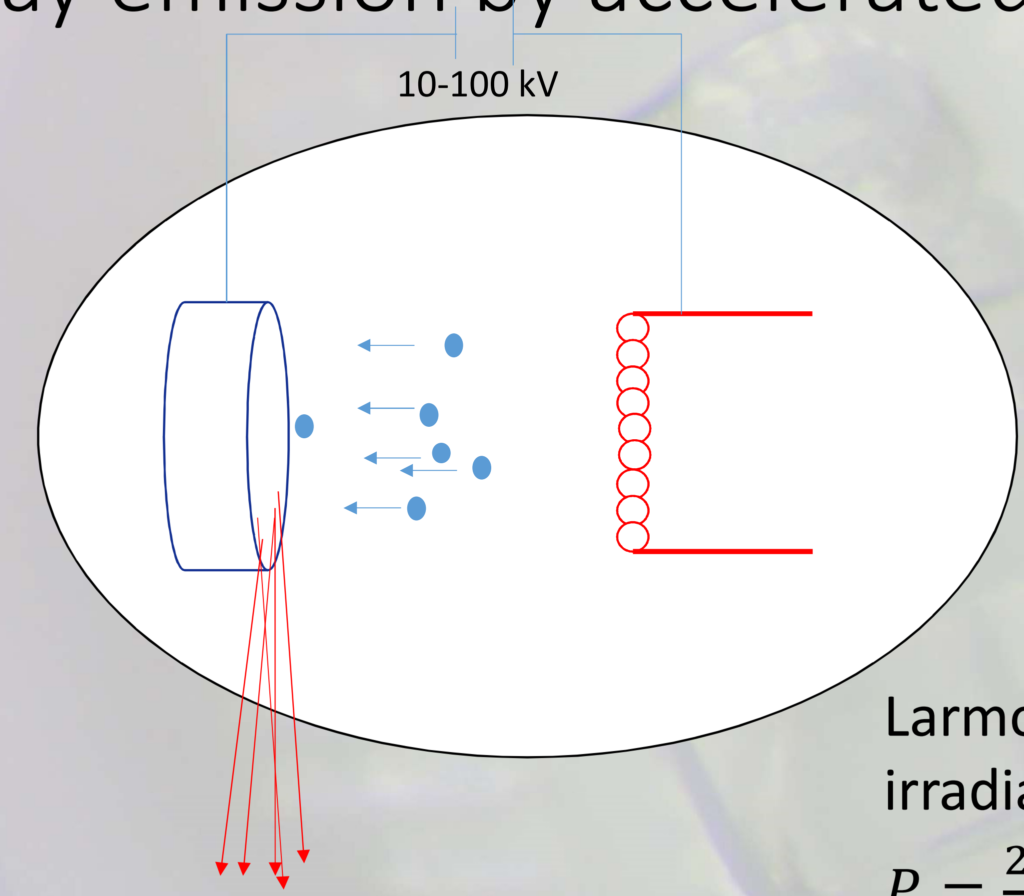
Example: 3 kW point focus monocrystal diffraction apparatus, with typical collection optics at the anode exit accepting 150 mrad x150 mrad of radiation: 2.25 exp-4 of the emitted angular range of radtiation can be collected by the optics (that has an efficiency of about 50 % .

Thus the estimated efficiency is

$$\underbrace{0.5*10^{-2}*2.25*10^{-4}*0.5*}_{5.5*10^{-7}}\text{(spectral fraction of K-alpha line)}$$

Simpler: measure the amount of photons/sec on the sample of such an apparatus ~ few 10^{-9} ph/s This corresponds to about~10^{-6} W of beampower for a photon energy of 8 keV. At an input powder of a few kW this yields a total efficiency of 10^{-9}

X-ray emission by accelerated charges: X-ray tube



X-rays (Bremsstrahlung)

Larmors formula (19th century):
irradiated power by accelerated charges:

$$P = \frac{2}{3}\frac{e^2}{c^3}\left|\dot{\vec{v}}\right|^2$$

Discovery of Synchrotron Radiation

1947
First observation of synchrotron radiation
70 MeV
GE, Schenectady, NY