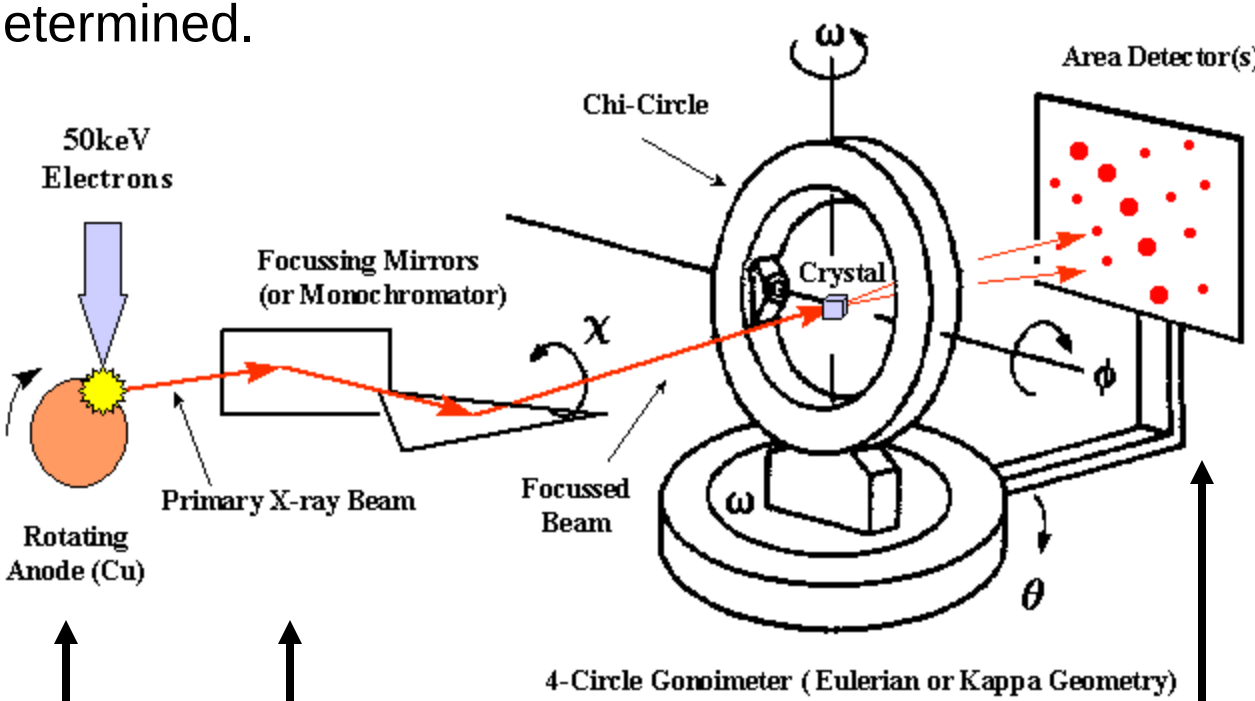
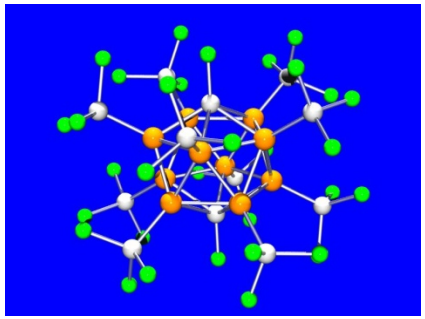
X-ray Crystallography

X-ray crystallography is an experimental technique that exploits the fact that X-rays are diffracted by the periodic electron density in crystals. Based on the diffraction pattern obtained from the periodic assembly of molecules or atoms in the crystal, the electron density can be reconstructed and thus the arrangement of the atoms can be determined.



Data Processing

Structure Solution and Refinement



X-ray source

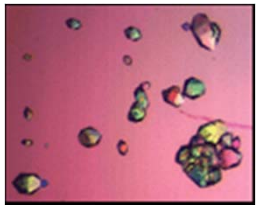
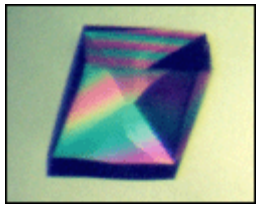
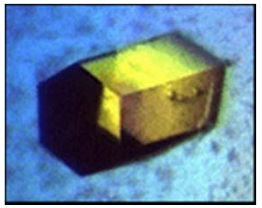
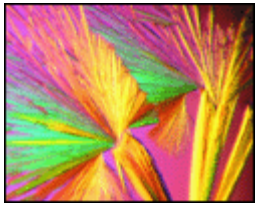
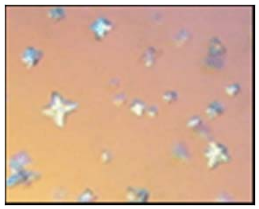
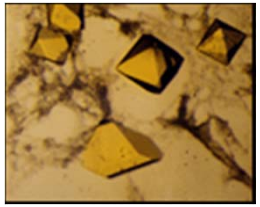
X-ray preparation

Diffraction

Detection

Crystal Growth

Whatever their external appearance, crystals are solids containing atoms arranged in a pattern that repeat periodically in 3 dimensions. Arguably the most difficult aspect of crystallography is obtaining crystals!


- Crystal growth methods

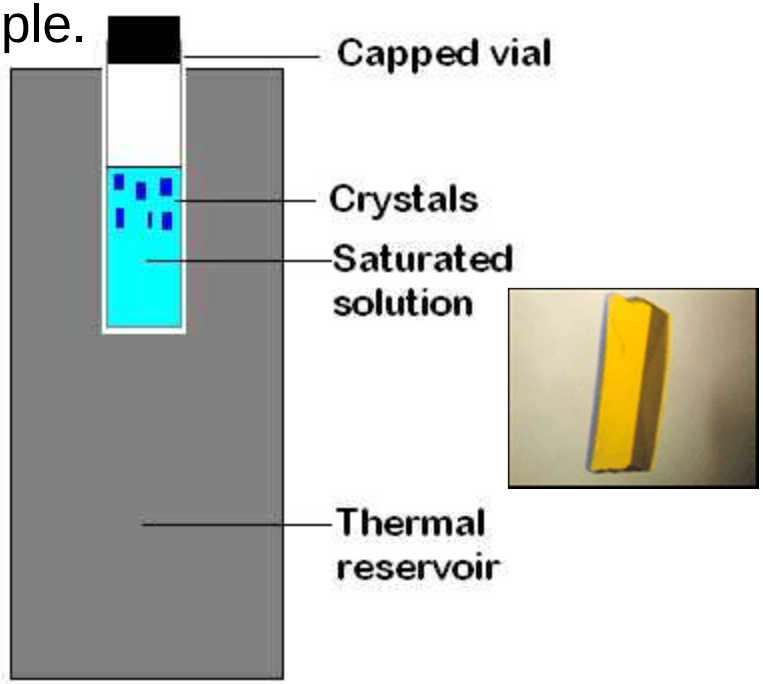
A.J. Blake: http://www.nott.ac.uk/~pczajb2/growcrys.htm#Introduction
P. D. Boyle: http://www.xray.ncsu.edu/GrowXtal.html

- Proteins and other large biomolecules etc. have a different set of techniques (see Hampton Research: http://www.hamptonresearch.com) their Photo Gallery is the source of the pictures above.

Crystal Growth

Crystallization is the process through which the atoms, molecules or ions arrange themselves in a repeating pattern. There are numerous methods to obtain crystals, any number of which may be applicable to a given compound. While sometimes it may seem that crystallization is more of an art than a science, there are several methods that generally produce crystals. For small molecules, these methods are typically based on reducing the solubility of the sample.

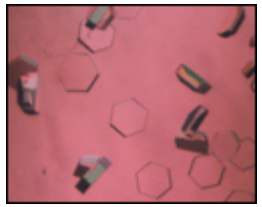
The solubility of most compounds decreases as the temperature is lowered thus the cooling of a saturated solution will often produce crystals. Since rapid cooling may cause the precipitation of amorphous solid or microscopic crystals, it is often wise to surround the flask with an insulating medium to slow the rate of cooling.



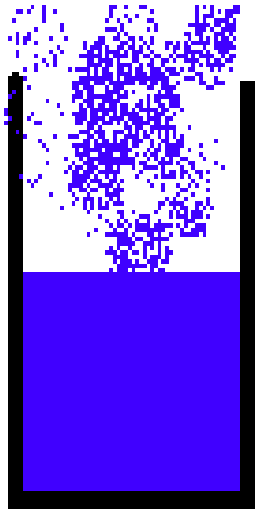
Crystal growth by controlled cooling

Controlled cooling

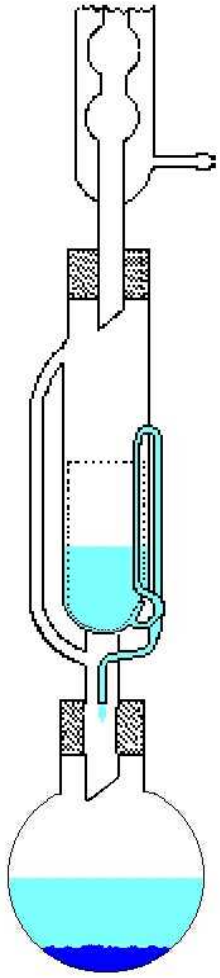
Crystal Growth



The slow concentration of dissolved samples is one of the most general ways of obtaining crystals – when the concentration exceeds the solubility, nucleation and crystallization/precipitation may follow. This can be done a variety of different ways such as evaporation of the solvent (in open or closed systems). For insoluble samples, Soxhlet extraction is often a particularly effective method of concentration.



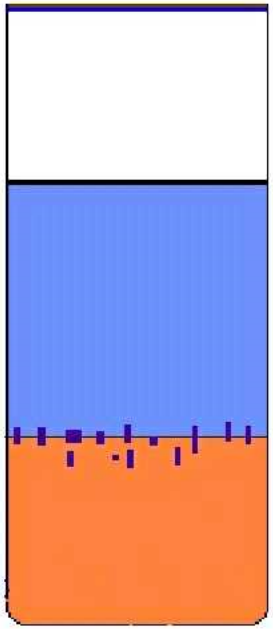
Evaporation



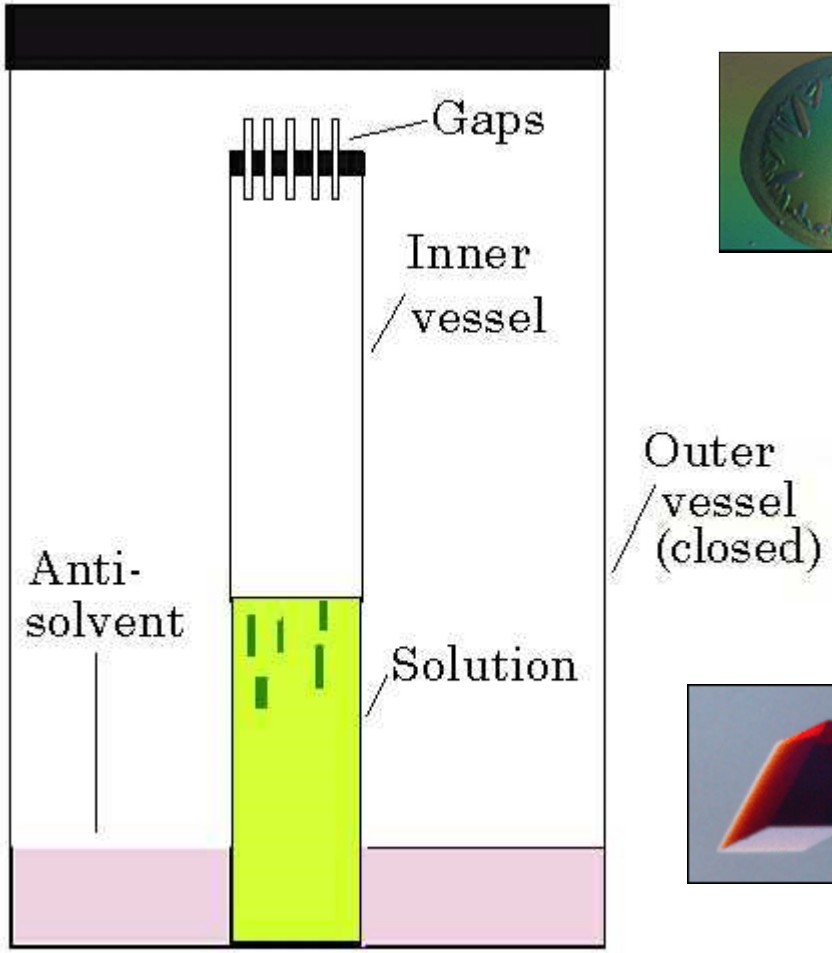
Soxhlet apparatus

Crystal Growth

The solubility of a compound in one solvent can be reduced through the slow introduction of another solvent in which the solute is not soluble (an anti-solvent). This can either be done by direct contact between the saturated solution and the anti-solvent ("layering") or by allowing the vapours of the anti-solvent to slowly diffuse into a saturated solution.

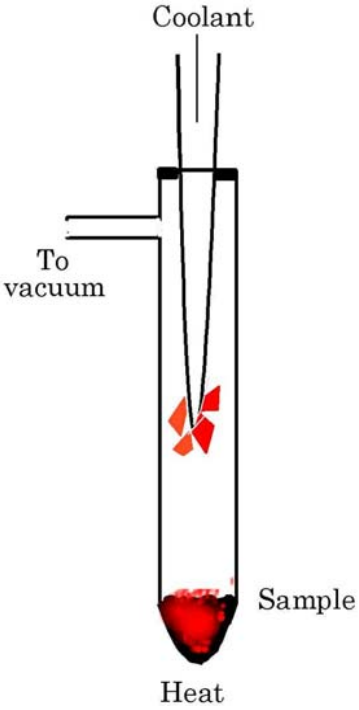


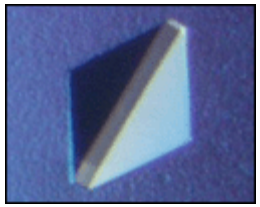
Solvent diffusion



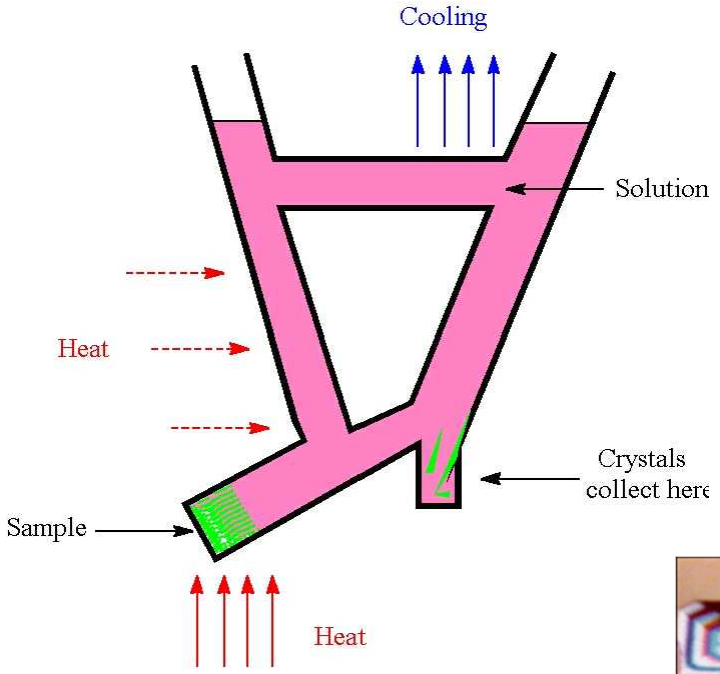
Crystal Growth

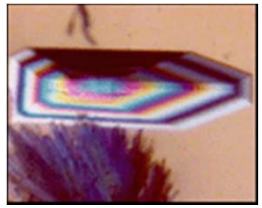
There are a large number of other methods for obtaining crystals of sufficient size and quality for X-ray diffraction experiments, including: sublimation, convection, the controlled cooling of melted solid, heating and cooling of micro-crystalline material, co-crystallization and many more. In practice, any method that produces adequate crystals is acceptable.





Sublimation





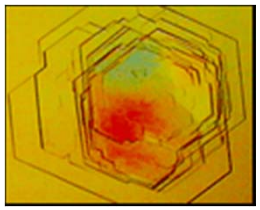
Convection

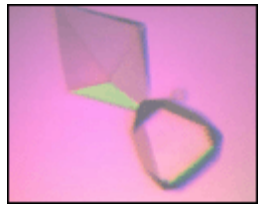
Crystal Selection and Mounting

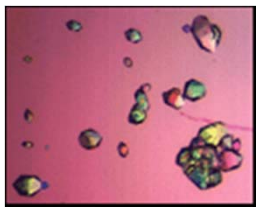
Size
- between around 0.01 – 0.5 mm

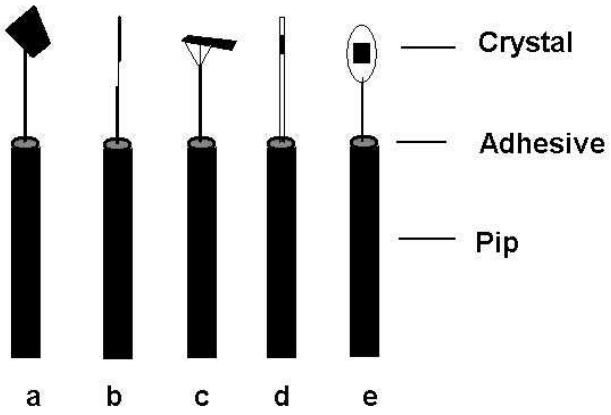
Shape
- must be a single crystal
- the closer to spherical, the better

Mosaicity

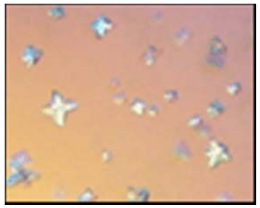


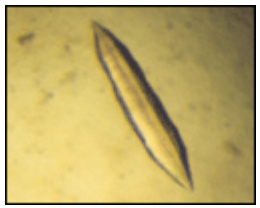






Some ways to mount crystals: a) on a glass fibre; b) on a "two-stage" fibre; c) on a fibre topped with several lengths of glass wool; d) within a capillary tube; e) in a solvent loop.





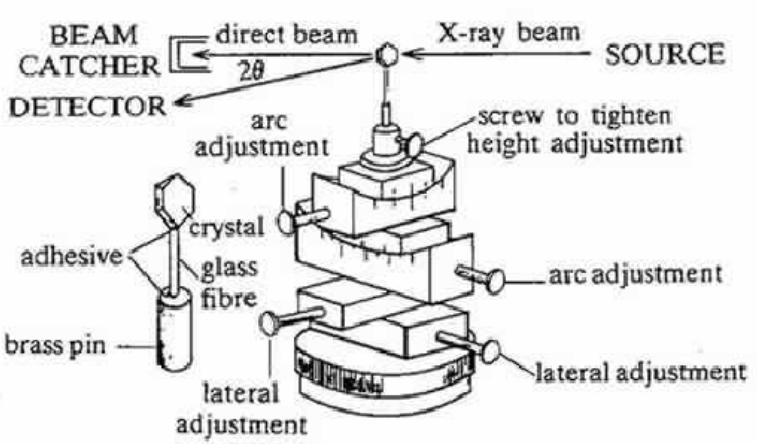
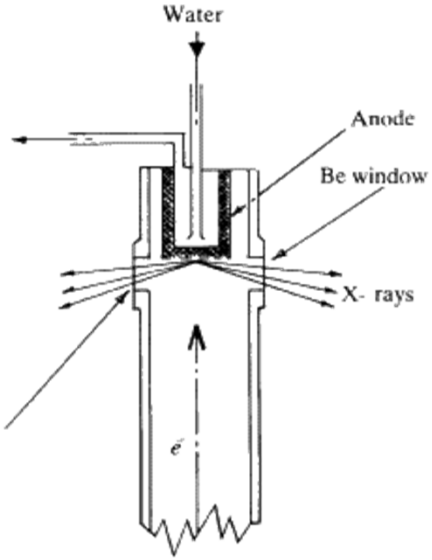


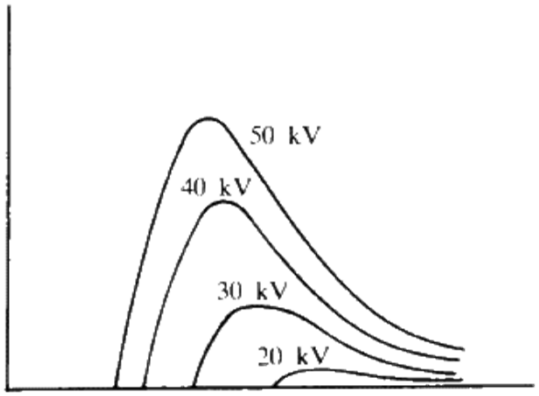
Fig. 23.

The goniometer head allows the crystal to remain in the X-ray beam in every orientation

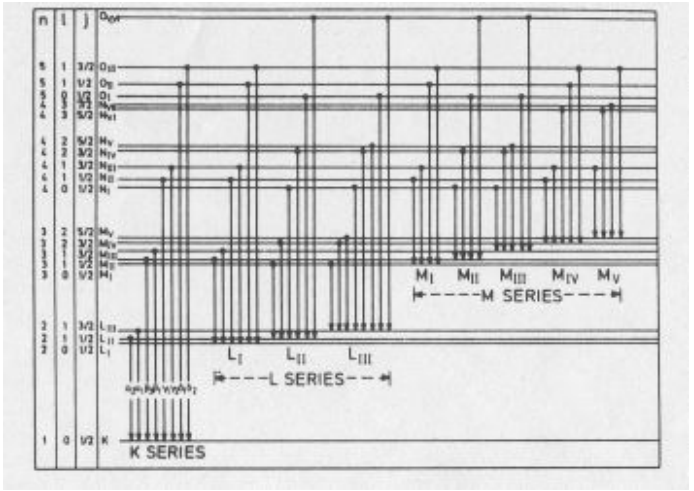
X-ray sources

X-rays have the proper wavelength (in the Ångström range, ~10^{-10} m) to be scattered by the electron cloud of an atom of comparable size (we will look at this in much more detail later).

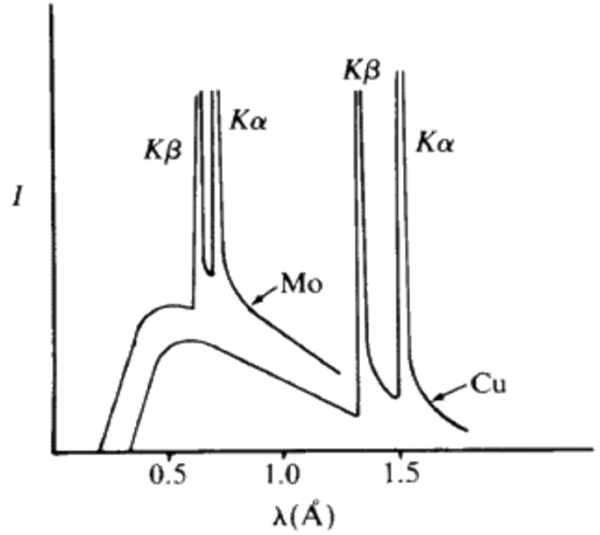




White radiation



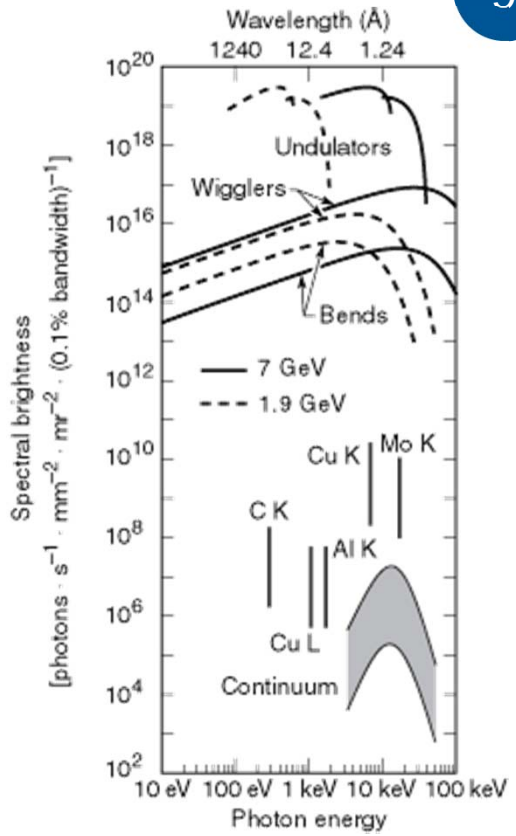
X-rays are produced by accelerating electrons into a metal target. This produces mostly heat (cooling is essential) and "white" radiation (*Bremsstrahlung*). If enough energy is provided, some of the incoming electrons will collide with and eject core (K shell, 1s) electrons. Higher energy electrons release energy characteristic of the target to fill the hole – if $\Delta n = 1$, the transition is called α, if $\Delta n = 2$, the transition is called β.



X-ray sources

Selected X-Ray Wavelengths and Excitation Potentials.

	Cr	Fe	Cu	Mo
Z	24	26	29	42
***K*α$_1$, Å**	2.28962	1.93597	1.54051	0.70932
***K*α$_2$, Å**	2.29351	1.93991	1.54433	0.71354
***K*α$_{ave}$, Å**	2.29092	1.93728	1.54178	0.71073
***K*β, Å**	2.08480	1.75653	1.39217	0.63225
β filter	Ti	Cr	Ni	Nb
Resolution, Å	1.15	0.95	0.75	0.35
Excit. Pot. (kV)	5.99	7.11	8.98	20.0

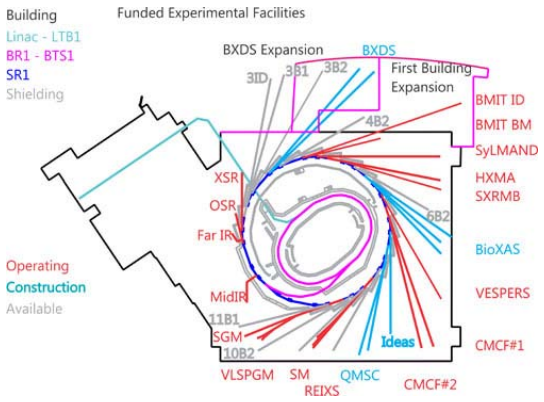


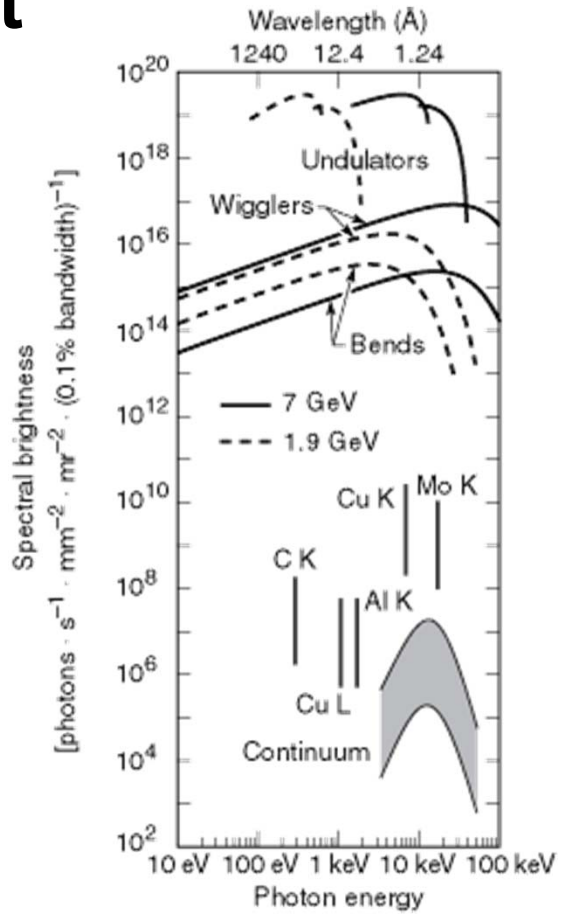
There are several other sources of X-rays, such some radioactive materials and synchrotrons. Synchrotrons produce a significantly higher flux (particles area^{-1} time^{-1}) of X-rays and the wavelength of the radiation may changed, as necessary. A high-flux source offers many advantages including reduced experimental time and smaller allowable crystal sizes.

An excellent site for information about X-rays and Synchrotrons: http://xdb.lbl.gov/
For X-ray transitions see: http://www.nist.gov/pml/data/xraytrans/index.cfm

Synchrotron Radiation Sources: The Future is Bright

Canadian Centre canadien Light de rayonnement Source synchrotron

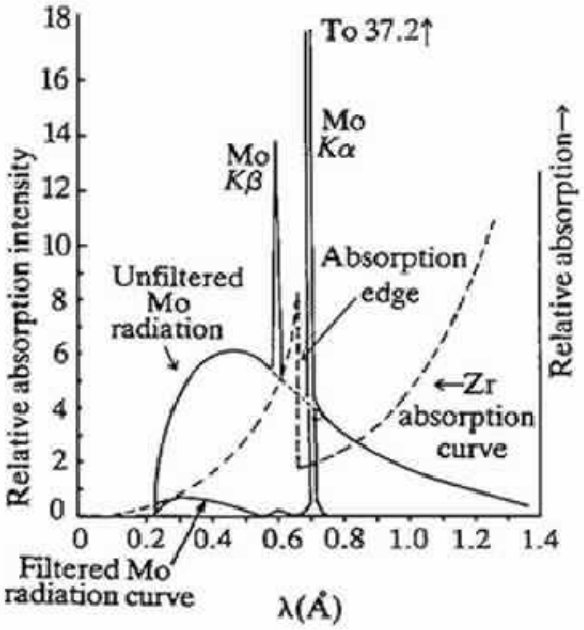




Much more intensity!

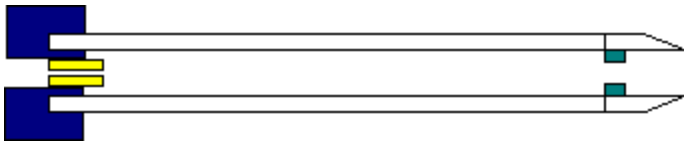
Filters, Monochromators and Collimators

To obtain the best results, the X-ray beam used in the diffraction experiment should all be of a single wavelength and they should be as parallel as possible. To accomplish this in practice, we use filters, monochromators and collimators.



The filter is a material that begins to absorb X-rays strongly between the α and β. This allows us to obtain only the α band.

A monochromator is a very stable single crystal that acts like a diffraction grating (much more on diffraction later) that further filters the radiation to make it as monochromatic as possible.



A collimator is a tube containing smaller tubes (ca. 0.5 mm) that attempts to reduce the dispersion of the X-ray beam and limits the diameter of the beam.

More information can be found at:
http://xrayweb.chem.ou.edu/notes/xray.html

X-ray detectors

X-rays may be detected by a variety of different devices, some of which are listed in the handout from the X-ray data booklet (http://xdb.lbl.gov/). While there are differences in the allowed X-ray energies, sensitivities, resolution etc., for most purposes, the major distinction between detectors is in the number of reflections they are able to collect at a single time.

Point detectors can only collect a single reflection at a given time and, because of this deficit, are not as useful for routine crystallography. This limitation can require collection times of several days to weeks, which can also be detrimental to the crystal and the instrument.

Area detectors can collect many reflections simultaneously and are thus preferred for routine data collection. Examples of such detectors include CMOS detectors, photon counters, CCD cameras, Image Plates, multi-wire detectors and even X-ray film (in the past).