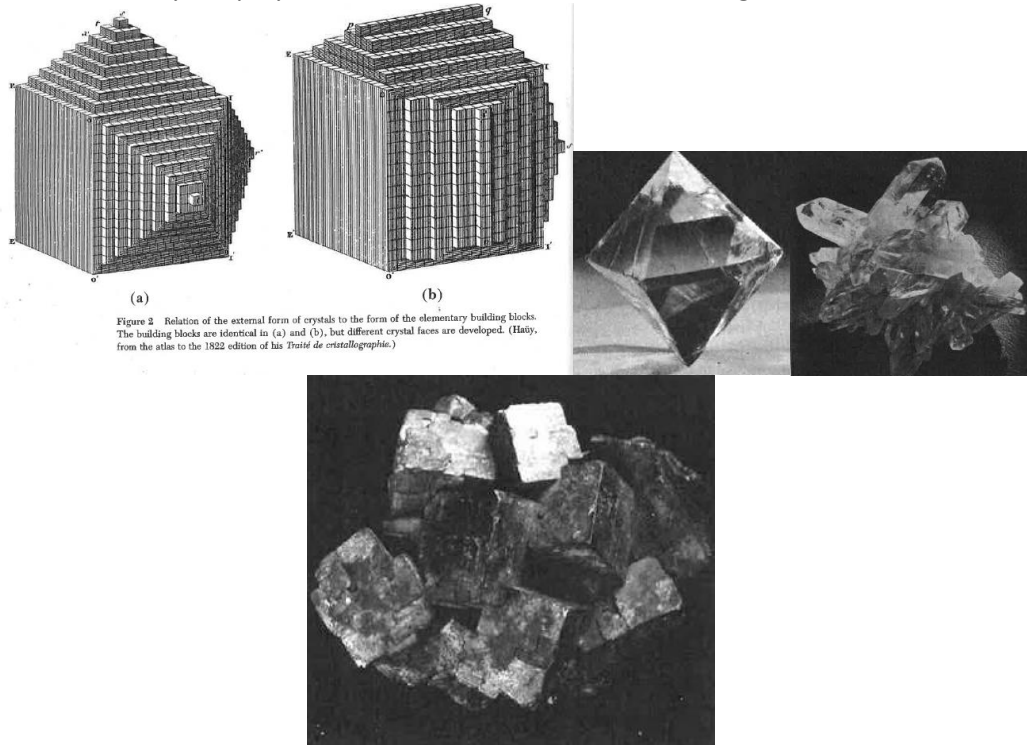


Chapter 2

Before a more quantitative and formal look at crystal structure and its description, let us have a more qualitative overview. The key interconnected concepts are order, structure, bonding and symmetry.

Seeing Crystalline order

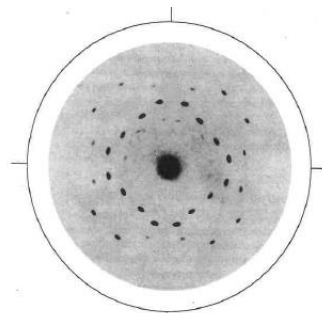
The order of a crystal is structural order. The atoms are located in definite positions relative to each other. This order is repetitive. This regularity accounts for the morphology (shape) of crystals when you look at them. They are polyhedral, with flat facets and distinct angles between the facets.



Crystalline structure is classified by the symmetry of the crystalline lattice. There are 14 Bravais lattices (Bravais 1848), 32 crystal classes (crystallographic point groups). When we add atoms to the lattice, we need 230 space groups for a complete classification (1891). You will probably be relieved to learn that this “zoology”, while important, will not be covered in the present course.

Rather we will focus on some common crystals structures, how they arise, and how they are described.

It is interesting that although the mathematical classification of lattices was fully developed in the 19th century, the crucial experimental demonstration of repetitive order in a crystalline solid was in 1912, with the demonstration by von Laue [Nobel Prize 1914] that x-rays are shone on a crystal they are diffracted by the regular crystal structure. The regularly spaced atoms scatter the “light” like the rulings of a diffraction grating.



X-rays are high frequency/small wavelength electromagnetic radiation, “light”. The key point is that the wavelength of x-rays [Röntgen Nobel Prize 1901] is comparable to the separation of atom (spacing

of rulings of “grating”), which is a requirement for diffraction. Typical wavelength of x-rays is 0.1nm, much smaller than visible light (400-600nm).

Production of x-rays. Electrons are accelerated through voltage V (typically tens of kV) to energy eV and hit a metal anode target. The deceleration of the electrons leads to a continuous spectrum of electromagnetic radiation (x-rays) up to a minimum wavelength determined by $h\nu = hc / \lambda \leq eV$. In addition there is emission of x-rays at specific wavelengths arising from atomic transitions in the anode material. For example if an electron is kicked out of an inner 1s level of a copper atom, an electron can make a transition from a 2p state emitting an x-ray with wavelength 0.154 nm. [This line is split into because transitions can occur from 2p ($j=3/2$) or 2p ($j=1/2$); these are the $K_{\alpha 1}$, $K_{\alpha 2}$ lines.

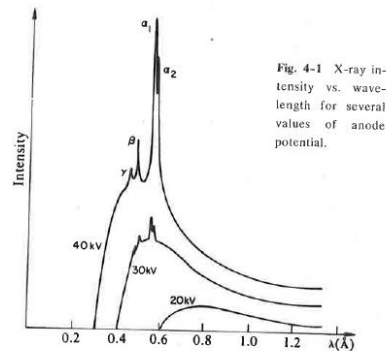
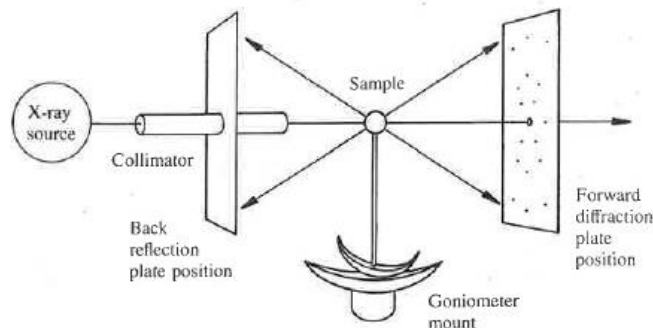
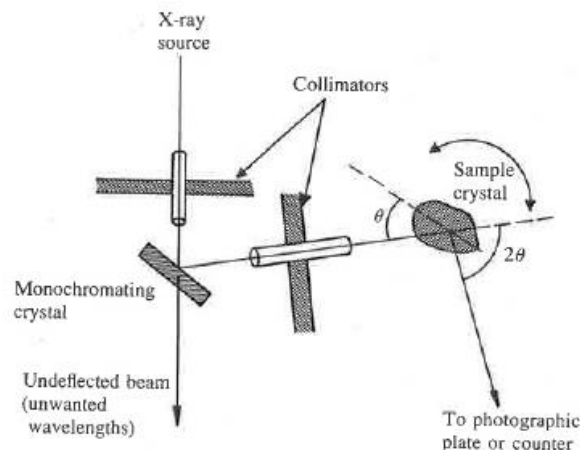


Fig. 4-1 X-ray intensity vs. wavelength for several values of anode potential.

The Laue diffraction pattern is generated using a continuous spectrum of x-rays, with a single crystal sample like this. Each set of crystal planes satisfies the Bragg condition for one wavelength, diffracts to produce a spot. The symmetry of the array of spots reflects the crystal symmetry in the direction of the incident beam, so the crystal orientation is adjusted (using the goniometer) so that a crystal symmetry axis is oriented along the incident beam direction. Mostly just used to orient crystals and determine their symmetry.



The rotating crystal, first selects monochromatic x-rays, then rotates the crystal to satisfy the diffraction condition, like this.



The Debye-Scherrer method is used with a so called powder sample i.e. one containing many small crystallites, randomly oriented. All possible planes may be seen in one go. It relies on a monochromatic

x-ray beam. Those crystallites in the distribution oriented in such a way that a given set of planes makes glancing angle θ to the incident beam give diffracted beams which lie in some orientation on the cone of half angle 2θ shown.

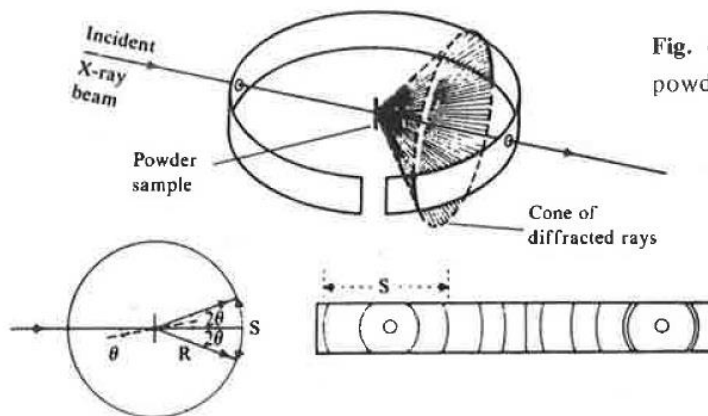
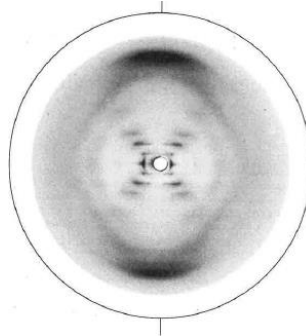


Fig. 4-6 The Debye-Scherrer powder diffraction technique.

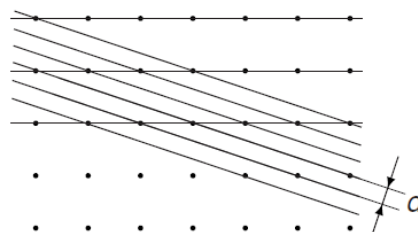
The impact of x-ray diffraction in determining structure has been immense. For example haemoglobin and DNA. Below is Rosalind Franklin's x-ray diffraction obtained from firing an x-ray beam normal to a fibre containing approximately aligned strands of DNA. This experimental evidence informed Watson and Crick's structural model of the double helix structure of DNA.



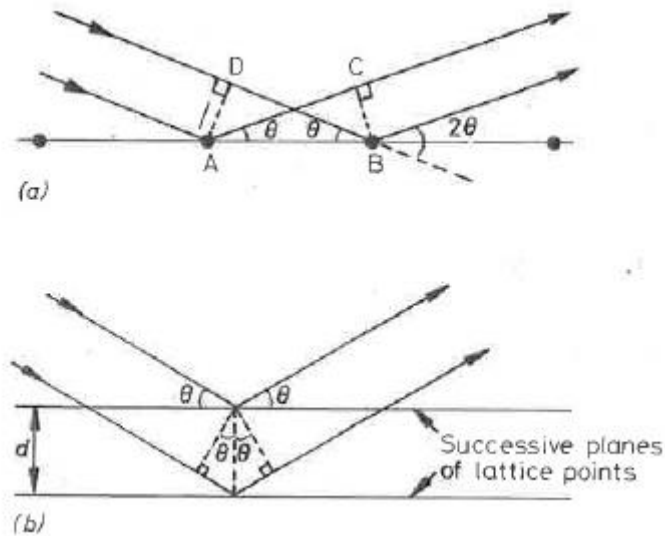
Bragg's law $2d \sin \theta = n\lambda$

It was WL Bragg and WL Bragg [Nobel Prize 1915], father and son, who came up with a simple intuitive understanding of x-ray diffraction, that enabled them to quantitatively determine crystal structure.

A crystal is a regular structure of atoms. Think of it rather (and equivalently) as a set of planes. You can allocate atoms to different sets of parallel planes. For each set there is a particular spacing between the planes. This cartoon in two dimensions gives you the idea.



Consider a beam of x-rays incident on one of these planes. Some part of the beam will pass straight through. The remainder will be reflected, as from a mirror. This is because the light scattered by adjacent atoms is in phase in this case. So you end up with a coherent reflected wavefront. The path length of each ray is the same. This is true for any angle of incidence. [Note that conventionally in x-ray diffraction angles are defined between ray and plane (rather to surface normal as usual in optics).



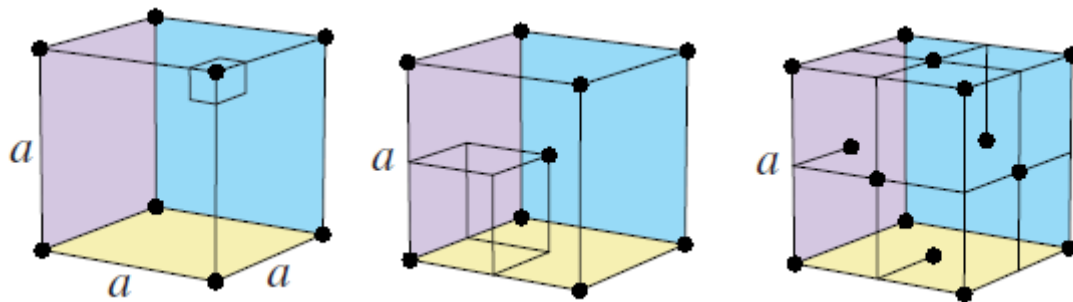
Now consider the interference between rays of a given wavelength, at angle θ as shown, scattered from adjacent planes. The path difference for the two rays shown is $2d \sin \theta$. The condition for constructive interference is

$$2d \sin \theta = n\lambda \quad (0.1)$$

This equation is a milestone in crystallography [www.nature.com/milestones/crystallography].

Lattices with cubic symmetry

Of the 14 Bravais lattices there are three of cubic symmetry. Shown below. They are called: simple cubic (sc); body centred cubic (bcc); face centred cubic (fcc). Relative to sc the bcc lattice has a point at the centre of the cube. Relative to sc the fcc lattice has a point at the centre of each cube face. For the simplest crystal you just put an atom on each lattice point. Repeating this unit cell defines the crystal.

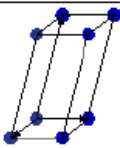
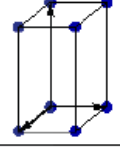
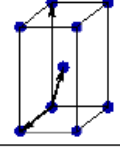
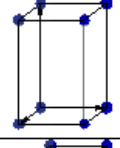
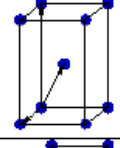
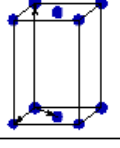
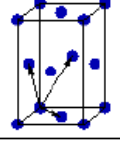
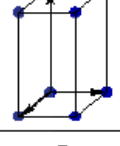
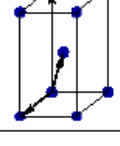
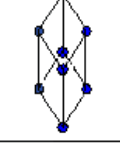
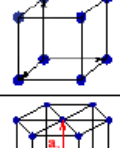
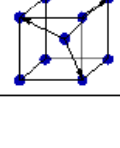
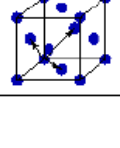
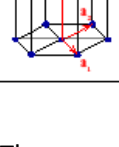


For a given size of cubic unit cell (denoted by symbol a), bcc and fcc have extra planes of atoms. Bragg realised that these different varieties of cubic lattice could be distinguished from one another in x-ray diffraction, because for certain orders, diffraction from the extra planes is out of phase, so these are missing from the pattern if the crystal is bcc or fcc. In his earliest studies of crystal structure he was able to determine the structure of ZnS and NaCl, KCl.

We will discuss further after having introduced the important concept of the reciprocal lattice in a later lecture.

The 14 Bravais lattices

For completeness, here they are:

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^\circ$ $\alpha_{12} \neq 90^\circ$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^\circ$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^\circ$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^\circ$ $\alpha_{23} = \alpha_{31} = 90^\circ$				

Symmetry in a nutshell, roughly speaking. The seven crystal systems (above) are distinguished by their different symmetry. Carry out one of a number of possible symmetry operations, and ask which leaves the lattice invariant i.e. the lattice looks the same before and after the operation. The point symmetry operations are as follows:

Identity (do nothing)

Inversion: define an origin and for each lattice point take \underline{r} to $-\underline{r}$.

Rotation: find the axes about which you can rotate by $2\pi/n$.

Reflection: find the planes about which you can reflect.

Improper rotation: rotation followed by a reflection.

As we said there are 32 possible crystallographic point groups which apply to the 14 Bravais lattices [denoted by either the Schoenflies or International Crystallographic convention].