

Single Crystal X-ray Diffraction and Structure Analysis

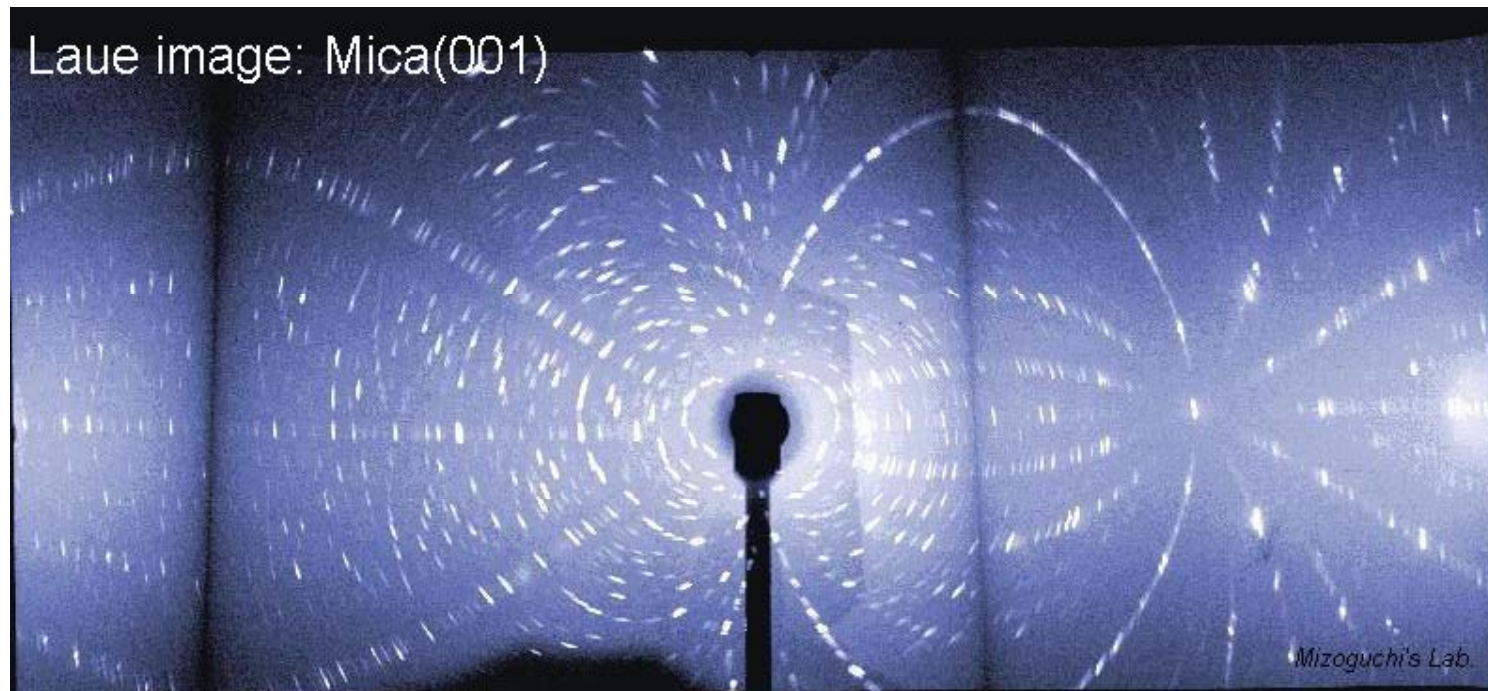
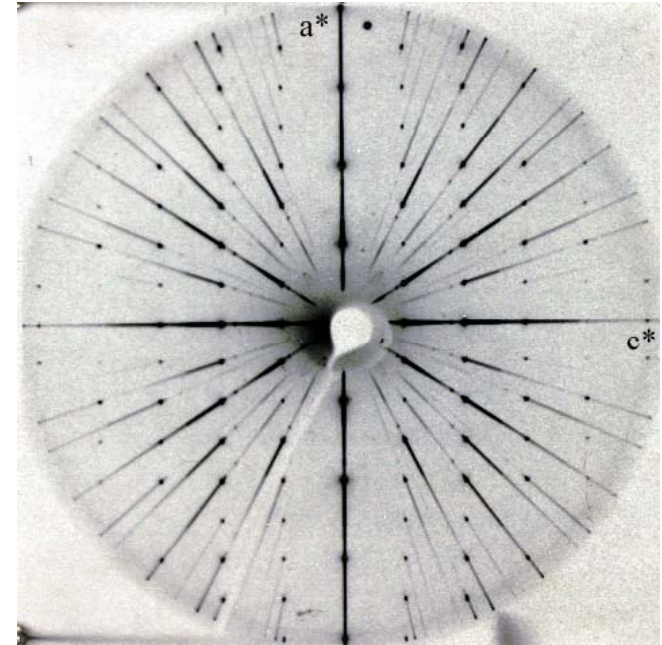
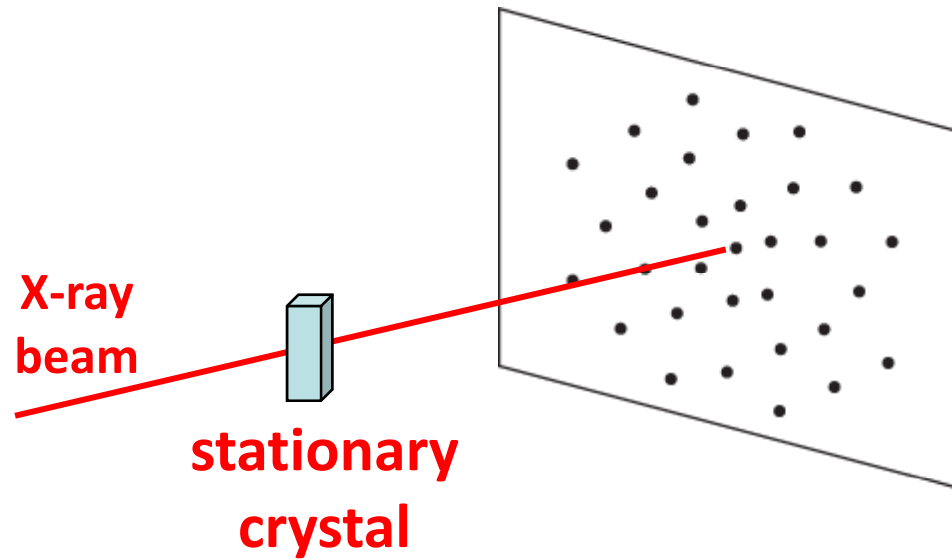
Modern diffractometry techniques employ electronic detectors, in either the first or second order.

Prior to 1970 almost all single crystal diffraction studies used film.

The crystal was mounted in the centre of the camera, the X-ray beam is focussed on it, creating diffracted X-rays.

Alternatively, the crystal can be rotated diffracting the X-rays from each of the atomic planes, onto a strip of film encompassing the crystal.

Laue method and precession method



The Laue Method – generally of historic value because it does not use filtered X-rays, however gives nice pictures where symmetry elements can be identified.

Other methods, the crystal is generally held stationary, and the film is rotated. In addition, the film is not often held flat, but placed in a cylinder giving an extra dimension of data acquisition.

Many of these techniques have been superseded with electronic detectors: either X-ray counters – direct measurement of X-rays – or optical detection of X-rays by CCD.

Improvements over film include greater accuracy of X-ray intensity and greater count rates.

Most common automated technique is the four-circle diffractometer. The name derives from the four arcs used to orient the crystal bringing the atomic planes into diffracting positions.

Atoms diffract x-rays by an incident beam that sets the atom(s) in motion and creates a ray to vibrate in an [infinite number of directions](#)

[Diffraction controls](#)

Both the [atom spacing](#) in the structure and the [wavelength of the incident beam](#) are a first order control on the diffracted rays produced

$$n\lambda = d_a (\cos \theta_d - \cos \theta_i)$$

The mathematical relationships between incident and diffracted x-rays are simplified in the Laue equation

d_a = spacing of atoms

λ = wavelength of radiation

θ = angle

[Path difference \$\lambda\$](#) , [Path difference \$2\lambda\$](#) , [Final equation graphically derived'](#)

Single crystal studies and identifying mineral structure.

The wealth of crystallographic information available, or derivable, from an unknown substance on the basis of X-rays is great.

**crystal system, space group, atom locations,
bond types, bond locations, bond angles,
chemical content of unit cell.**

Collecting this information is a combination of the logical and the iterative.

There is a relationship between many features of diffracted X-rays and the diffracting lattice planes.

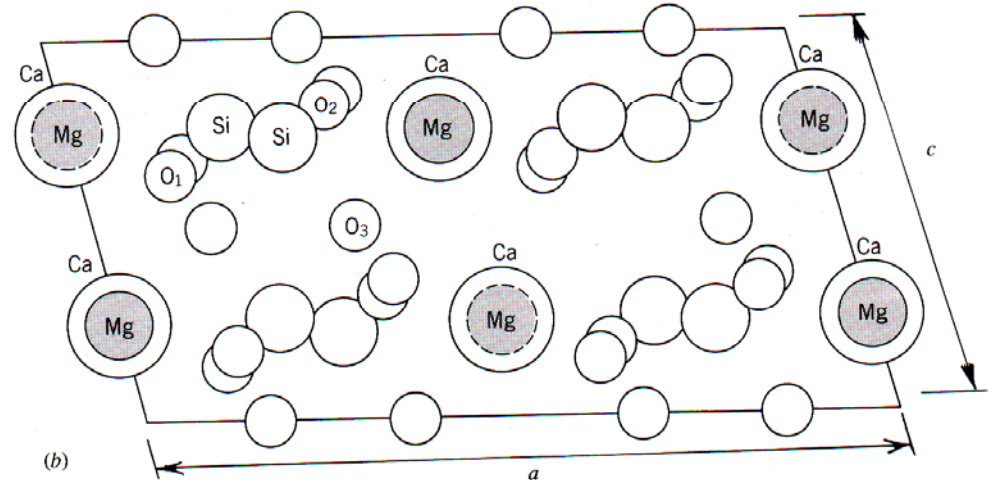
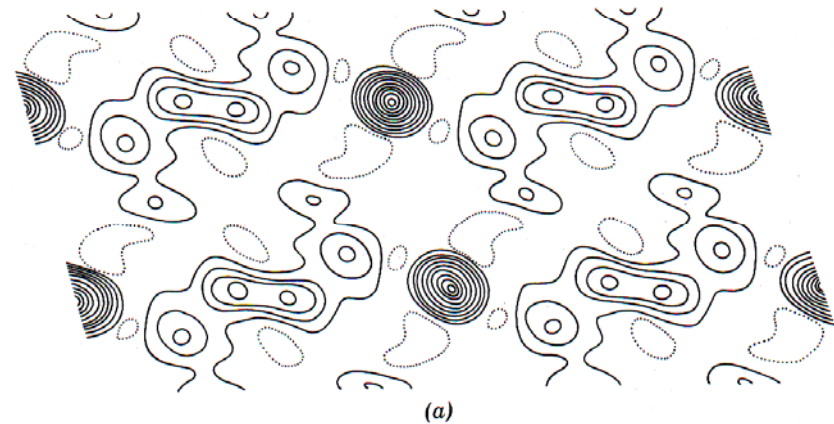
Interlinked features include intensity of diffracted beam for a given lattice plane.

This lattice plan has a Bragg diffraction indice (hkl).

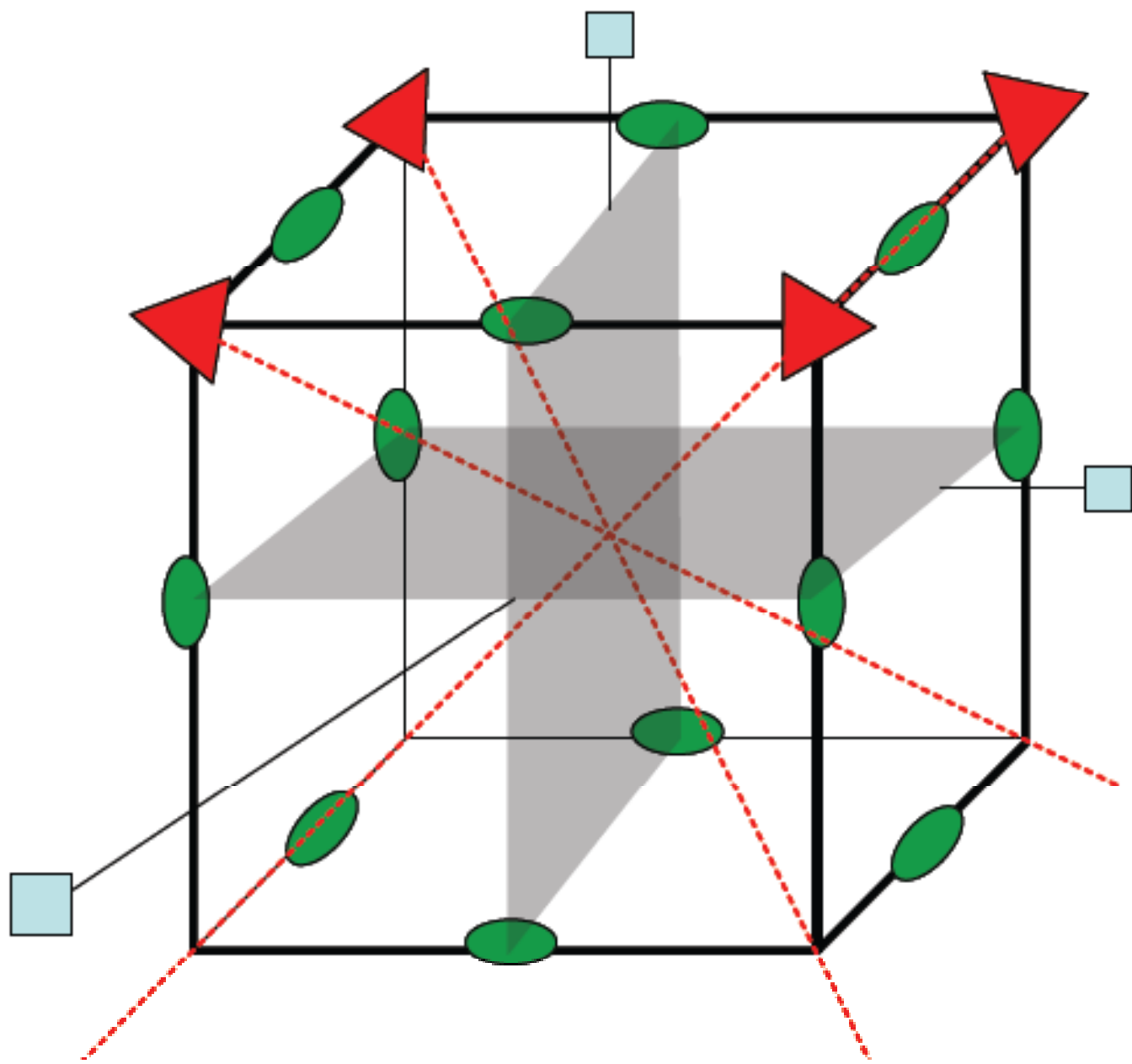
The lattice plane consists of atoms (j) with specific coordinates (x,y,z).

The electron cloud of each atom (j) has a scattering factor (f) which depends on its atomic number.

The properties can be used in an equation to generate the **structure factor**.



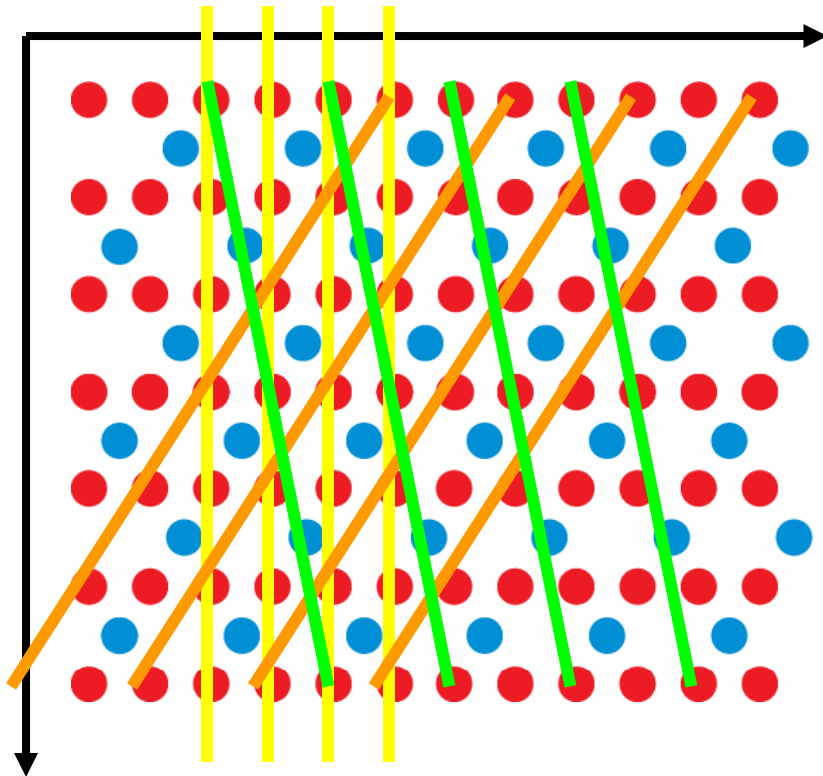
Fourier techniques are used to “map” atomic positions.



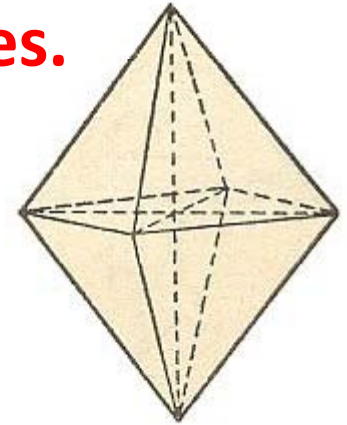
Regularly spaced parallel planes of atoms.

What does each peak represent?

How are such planes of atoms expressed in an actual crystal?



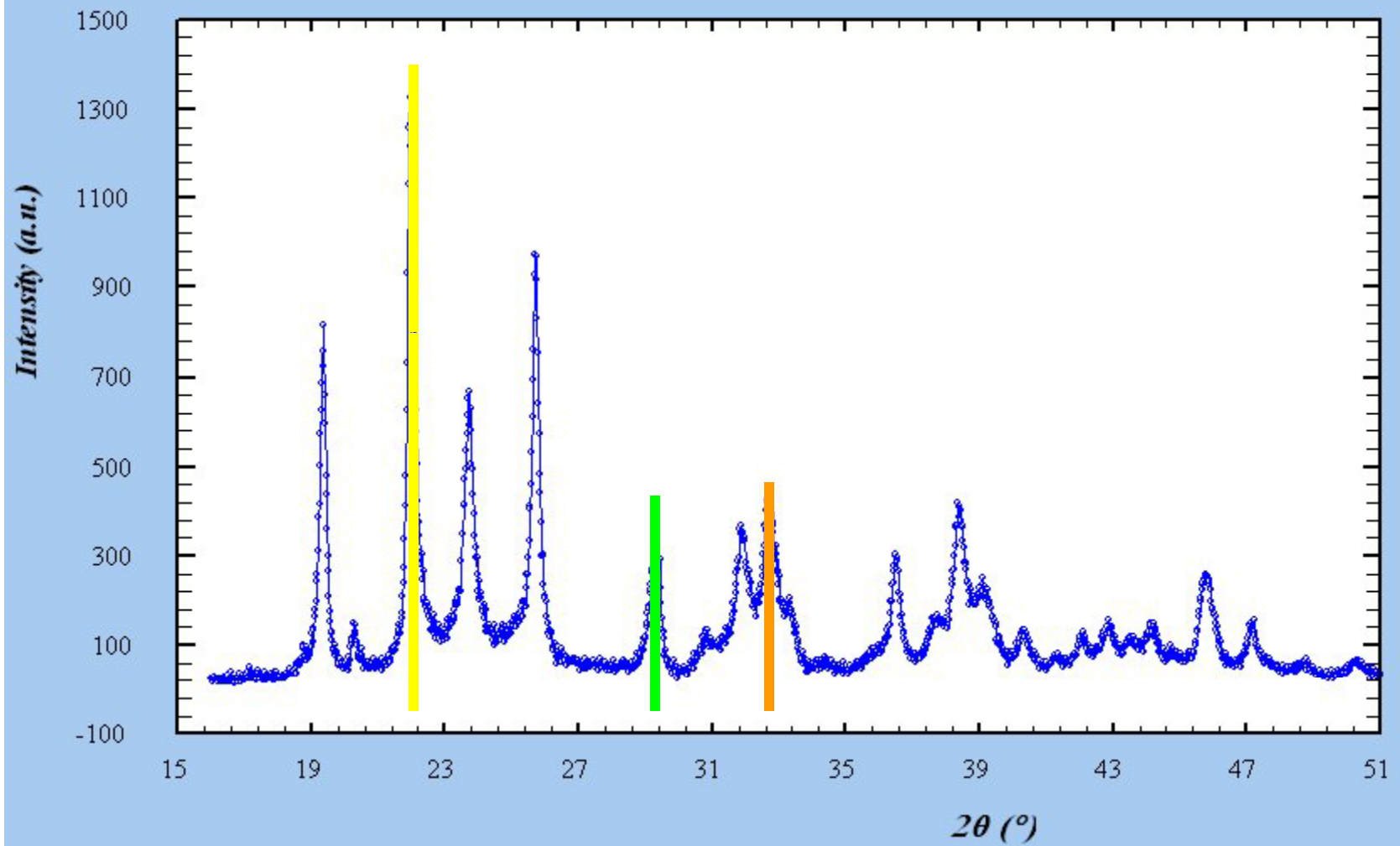
As crystal faces.



How do we represent crystal faces?

Miller indices.

So, Miller Indices also provide information about the internal structure of a mineral.



X-ray Powder Diffraction

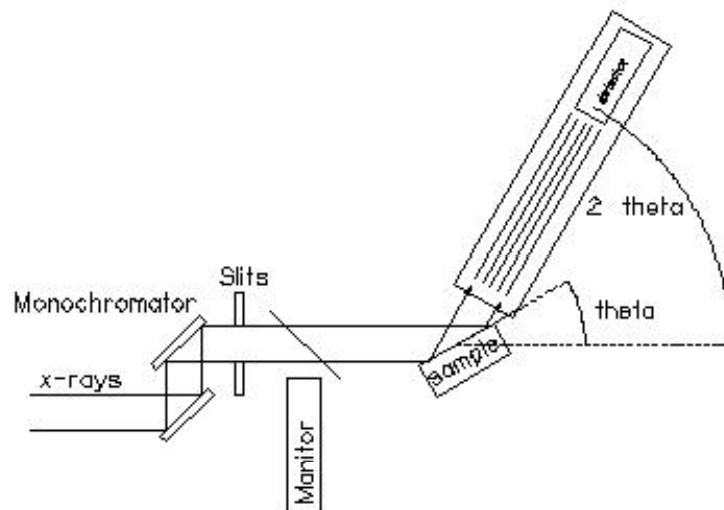
Single crystal material is complicated, time consuming, and requires a high degree of homogeneity to the selected crystal.

So, while ideal (and necessary) for the identification of new mineral species, is not user friendly for those wishing to identify the constituents of a rocks.

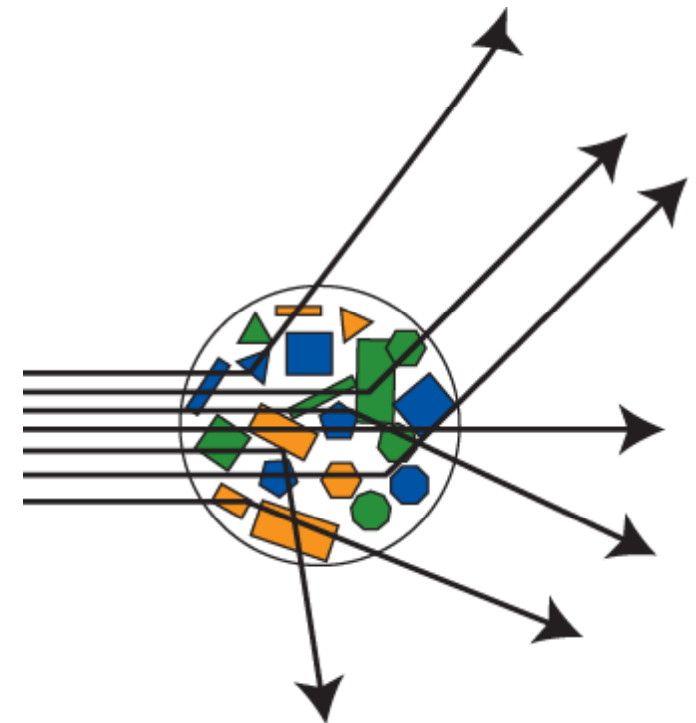
To overcome such hurdles, most diagnostic mineral diffractometry is completed on powdered samples.

A powder mount is prepared: Very fine grained particles are mounted so as to approach ideal randomness of orientation.

Powder diffractometer schematic

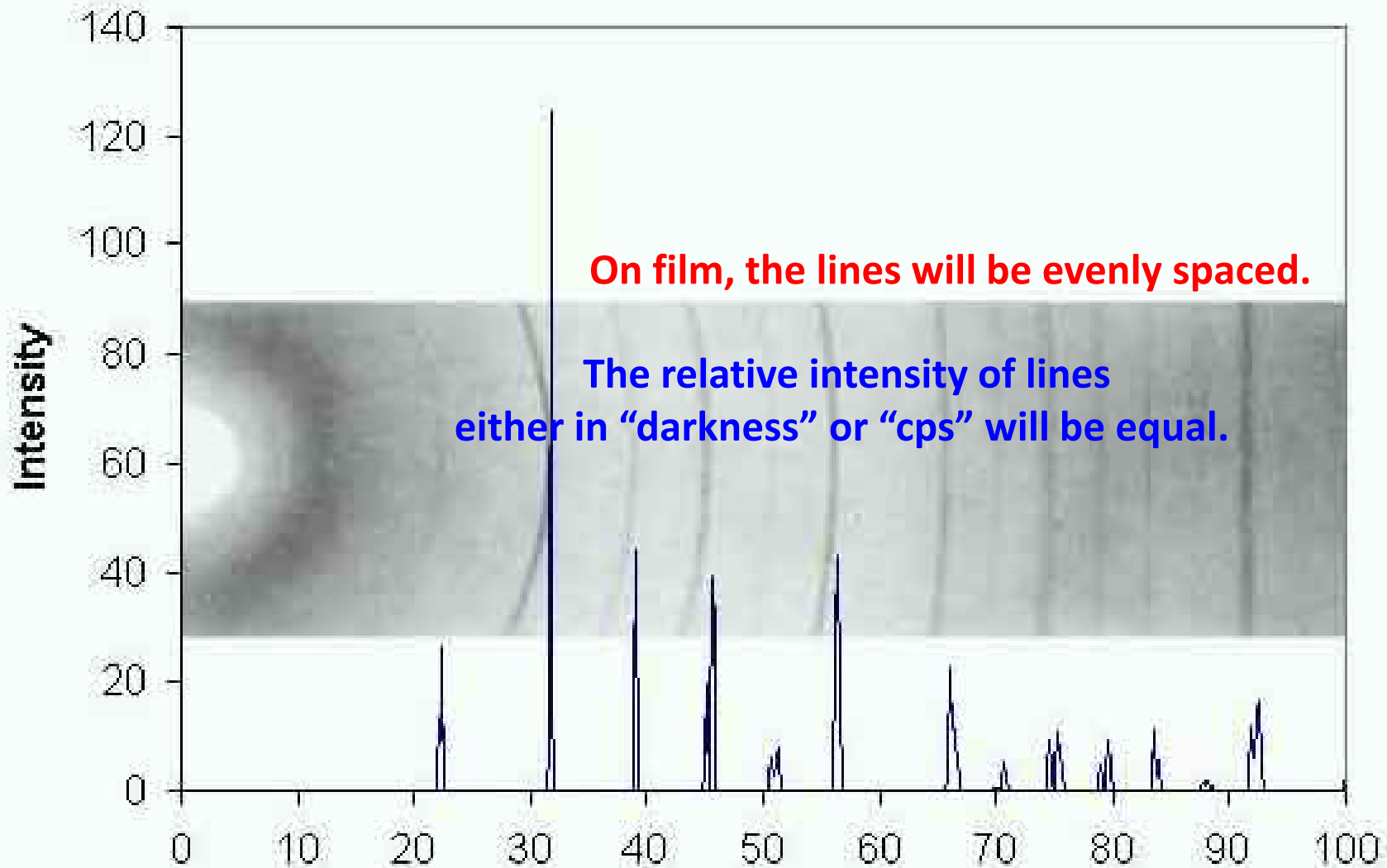


Depending on the method, the sample is mounted on a simple geometry.



In many cases, the sample is rotated, while the either/or/both source and detector are moved on a continuous arc.

A powder pattern of identical minerals will result in identical patterns.



On film, the lines will be evenly spaced.

**The relative intensity of lines
either in "darkness" or "cps" will be equal.**

Peaks will occur at the same 2θ values.