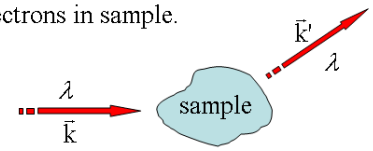
Appendix : X-ray diffraction

(I) *General*

X-ray diffraction process involves only ***elastic scattering*** of x-ray photons with electrons in sample.

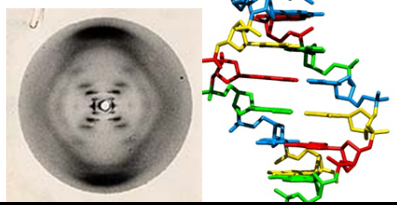
$$k = k' = \frac{2\pi}{\lambda}$$



- It is the most important tool to characterize the crystal structure of a sample, including
  1. type of crystal structure, location of atoms in unit cell, chemical phase
  2. microstructure (single crystal/polycrystalline/amorphous, grain size,…)
  3. strain,…

- Complicated crystal structure can be determined by x-ray diffraction.
  e.g. The double helix structure of DNA was studied in the beginning of the 1950s.

  See "The Discovery of the Molecular Structure of DNA – The Double Helix" at http://nobelprize.org/medicine/educational/dna_double_helix/readmore.html

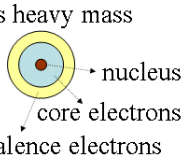


(II) *Principle*

(A) ***X-ray photon scattered by an electron*** (see Cullity, ch.3)
elastic scattering (first studied by J.J. Thomson)
(Note: Compton scattering is inelastic.)

(B) ***X-ray photon scattered by an atom***

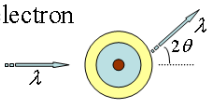
- not scattered by nucleus because of its heavy mass
- scattered elastically & coherently by all electrons



The scattering efficiency of an atom is measured by the ***atomic scattering factor***:

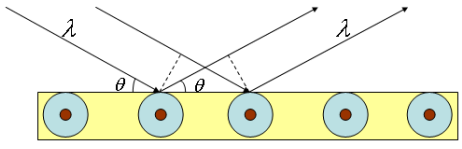
$$f = \frac{\text{amplitude of wave scattered by an atom}}{\text{amplitude of wave scattered by one electron}}$$

f depends on $\sin\theta/\lambda$



(f of different elements is tablulated:
http://www-structure.llnl.gov/xray/comp/scatfac.htm)

(C) *X-ray photon scattered by a plane of atoms in a lattice*

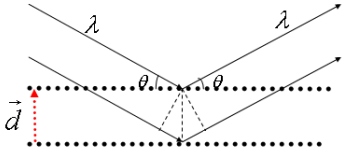


Just like a mirror, incident angle = reflection angle = θ
There is no path difference in the two rays. So the two rays have the same phase. The reflection (or ***diffraction***) intensity depends on the distribution of atoms in the plane and the atomic scattering factor(s) of the atom(s) and the angle θ.
The diffraction amplitude for an atomic plane

$$A \propto \sum_{\substack{i\text{-th atom in} \\ \text{one unit cell} \\ \text{in the plane}}} f_i \equiv F$$

planar structure factor

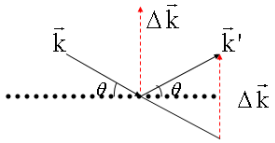
(D) *X-ray photon scattered by parallel planes of a crystal*



The two rays have a path difference = $2d\sin\theta$

Hence the phase difference ϕ: $\frac{\phi}{2\pi} = \frac{2d\sin\theta}{\lambda}$

or $\phi = 2k\,d\sin\theta = \Delta k\, d = \Delta\vec{k}\cdot\vec{d}$



$\vec{k} = \Delta\vec{k} + \vec{k}'$

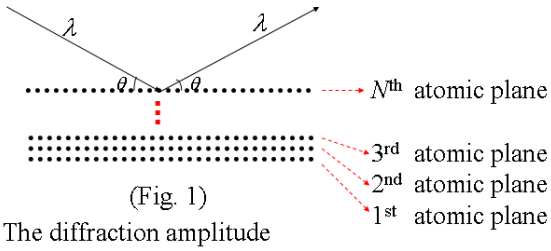
$(k = k' = \frac{2\pi}{\lambda})$

$\Delta k = 2k\sin\theta$

Note: $\Delta\vec{k}$ is normal to the planes.
Then the diffraction amplitude due to these two planes

$$\propto F_1 + F_2 e^{i\Delta k d}$$

For a crystal with N atomic planes:



(Fig. 1)

The diffraction amplitude

$$A \propto F_1 + F_2 e^{i\Delta k d} + F_3 e^{i\Delta k 2d} + \ldots + F_N e^{i\Delta k (N-1)d}$$

(Obviously, in general $A \propto \sum_{\substack{\text{all atoms} \\ \text{in sample}}} f_i e^{i\Delta\vec{k}\cdot\vec{R}_i}$.) ($\vec{R}_i$ = position of i^{th} atom)

Assume all planes are identical with planar structure factors:

$$F_1 = F_2 = \ldots = F_N \equiv F$$

Then

$$A \propto F\sum_{p=0}^{N-1} e^{ip\Delta k d} = F\frac{1-e^{iN\Delta k d}}{1-e^{i\Delta k d}} = F\frac{\sin(N\Delta k\, d/2)}{\sin(\Delta k\, d/2)} e^{i(N-1)\Delta k d/2}$$

The diffraction intensity

$$I \propto |A|^2$$
$$\propto |F|^2 \frac{\sin^2(N\Delta k\, d/2)}{\sin^2(\Delta k\, d/2)}$$

which is maximum ($= |F|^2 N^2$) if $\frac{\Delta k\, d}{2} = n\pi$

or $2d\sin\theta = n\lambda \quad n = 1, 2, \ldots$ ***Bragg equation*** of diffraction

This is the condition for observing a diffracted beam.

A sample (single phase) is characterized by
1. crystal type
2. lattice parameters: a b c and angles α β γ

Crystal planes can be labeled by (hkl).

Bragg equation for diffraction due to (hkl) crystal planes:

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

where d_{hkl} is the interplanar spacing (≡ the perpendicular separation between parallel (hkl) crystal planes.
d_{hkl} can be calculated with formulae tabulated in reference book. (e.g. B.D. Cullity, *Elements of x-ray diffraction*, 2/e, QC482.D5C84 1978).

The Bragg law can be rewritten as

$$\Delta k = \frac{2\pi}{d_{hkl}}$$

In general $\Delta\vec{k} = \vec{G}_{hkl}$

Here we use the reciprocal lattice vector $\vec{G}_{hkl} = h\vec{a}^* + k\vec{b}^* + \ell\vec{c}^*$

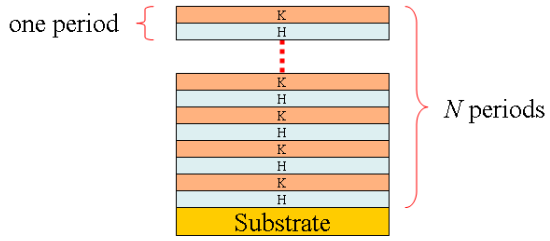
For a crystal lattice, the reciprocal lattice is constructed with fundamental vectors defined as:

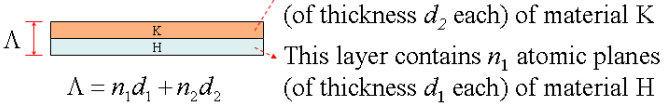
$$\vec{a}^* = \frac{2\pi\vec{b}\times\vec{c}}{\vec{a}\cdot\vec{b}\times\vec{c}} \quad \vec{b}^* = \frac{2\pi\vec{c}\times\vec{a}}{\vec{a}\cdot\vec{b}\times\vec{c}} \quad \vec{c}^* = \frac{2\pi\vec{a}\times\vec{b}}{\vec{a}\cdot\vec{b}\times\vec{c}}$$

To understand this principle, consider reciprocal lattice of cubic structure or 2D crystals*.
(* B.N. Narahari Achar, Am. J. Phys. **54**, 663 (1986))

(E) *X-ray diffraction of a superlattice*

Structure of a superlattice composed of two materials H & K:

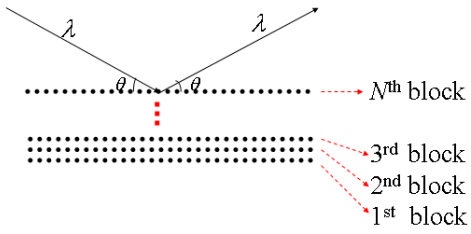




$\Lambda = n_1 d_1 + n_2 d_2$

We also call this sample a ***composition-modulated structure*** because its composition is "modulated" (i.e., changed periodically) in one dimension (usually normal to the substrate surface) and the superlattice period or modulation wavelength: $\Lambda = n_1 d_1 + n_2 d_2$

If we consider each period as a block and replace the N atomic planes in Fig. 1 by the N blocks, then



the diffraction amplitude

$$A \propto F_1' + F_2' e^{i\Delta k\Lambda} + F_3' e^{i\Delta k 2\Lambda} + \ldots + F_N' e^{i\Delta k(N-1)\Lambda}$$

All blocks are identical with block structure factors

$$F_1' = F_2' = \ldots = F_N' \equiv F'$$

Then $A \propto F' \sum_{p=0}^{N-1} e^{ip\Delta k\Lambda} = F' \dfrac{1-e^{iN\Delta k\Lambda}}{1-e^{i\Delta k\Lambda}}$

$$= F' \frac{\sin(N\Delta k\Lambda/2)}{\sin(\Delta k\Lambda/2)} e^{i(N-1)\Delta k\Lambda/2}$$

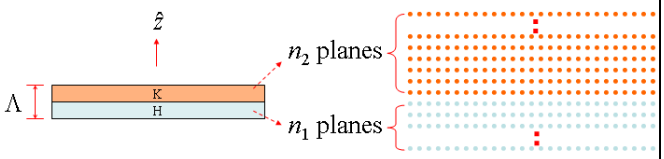
The diffraction intensity

$$I \propto |A|^2 \propto |F'|^2 \frac{\sin^2(N\Delta k\Lambda/2)}{\sin^2(\Delta k\Lambda/2)}$$

which is maximum ($=|F'|^2 N^2$) if $\dfrac{\Delta k\Lambda}{2} = n\pi$

or $2\Lambda\sin\theta = n\lambda \quad n = 1, 2, \ldots$

This diffraction condition can tell how we find the diffraction beams but their intensities are also determined by $|F'|^2$.



The first atomic plane of H is at $z = 0$ (assumed).
The first atomic plane of K is at $(n_1-1)d_1 + \frac{1}{2}(d_1+d_2)$
$= n_1 d_1 + \frac{1}{2}\Delta d$ $(\Delta d = d_2 - d_1)$

Then the structure factor of the block:

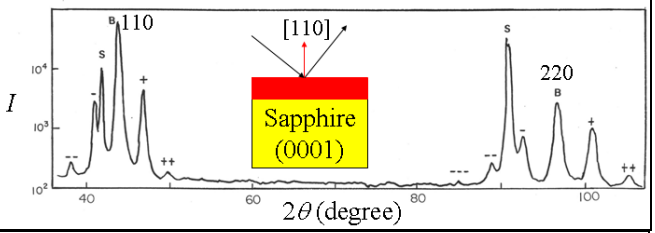
$$F' \propto F_1 + F_1 e^{i\Delta k d_1} + F_1 e^{i\Delta k 2d_1} + \ldots + F_1 e^{i\Delta k(n_1-1)d_1} + F_2 e^{i\Delta k(n_1 d_1 + \frac{1}{2}\Delta d)} + F_2 e^{i\Delta k(n_1 d_1 + \frac{1}{2}\Delta d + d_2)} + F_2 e^{i\Delta k(n_1 d_1 + \frac{1}{2}\Delta d + 2d_2)} + \ldots + F_2 e^{i\Delta k(n_1 d_1 + \frac{1}{2}\Delta d + (n_2-1)d_2)}$$

$$F' \propto F_1 \sum_{p=0}^{n_1-1} e^{ip\Delta k d_1} + F_2 e^{i\Delta k(n_1 d_1 + \frac{1}{2}\Delta d)} \sum_{p=0}^{n_2-1} e^{ip\Delta k d_2}$$

$$\frac{\sin(n_1\Delta k d_1/2)}{\sin(\Delta k d_1/2)} e^{i(n_1-1)\Delta k d_1/2} \qquad \frac{\sin(n_2\Delta k d_2/2)}{\sin(\Delta k d_2/2)} e^{i(n_2-1)\Delta k d_2/2}$$

$|F'|^2$ depends on $F_1 - F_2$ and Δd. See problem set 3.

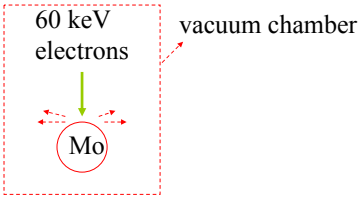
e.g. V_8Fe_8(110) superlattice on Al_2O_3(0001)



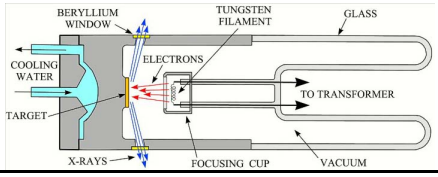
(III) *Equipment:*

(A) *X-ray sources*

- Synchrotron: very powerful (http://www-ssrl.slac.stanford.edu)
- Rotating anode (< 18 kW 60 kV)



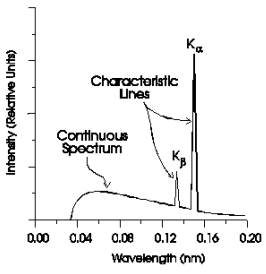
- X-ray tube (< 3 kW 60 kV)

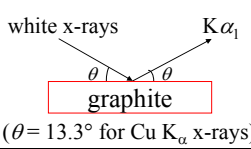


(B) *Monochromators*

The x-ray sources generate a white spectrum of x-rays. Monochromators are use to select only one wavelength for XRD experiment.

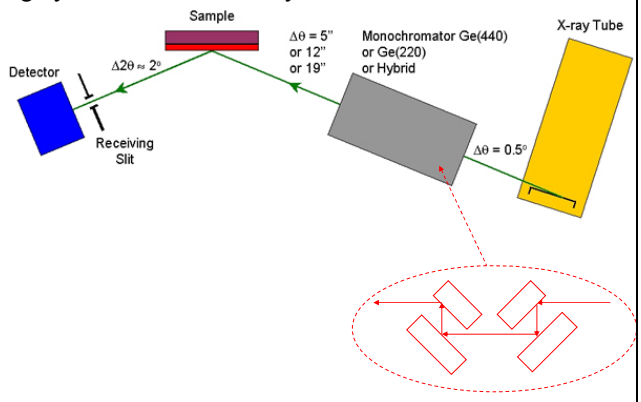
- Filter: e.g. a Ni foil can be used to roughly select Kα line of a Cu source.
- Single crystal monochromator: a graphite (or germanium, Ge) crystal can be used to select Kα_1 line of an x-ray source by means of diffraction effect. (Similar to using a grating to select monochromatic light for optical spectrometer.)





(θ = 13.3° for Cu K_α x-rays)

- 4 crystal monochromator to produce a parallel beam of highly monochromatic x-rays



(http://www-lam.stanford.edu/xlab/Main.htm)

(C) *x-ray detectors*

Simple detector: 1. gas proportional counter
2. scintillation counter

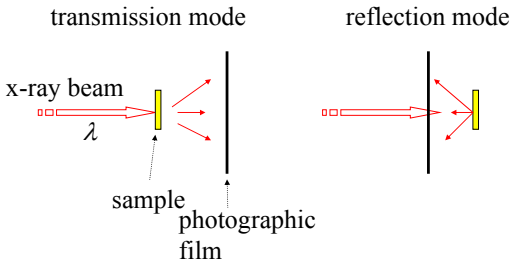
1D detector: curved position-sensitive detectors

2D detector: 1. multiwire proportional counter
2. CCD area detector

- For detail, refer to
  1. http://physics.web.cern.ch/Physics/ParticleDetector/BriefBook/
  2. http://www.shef.ac.uk/physics/teaching/phy311/

(D) *Photographic techniques:*

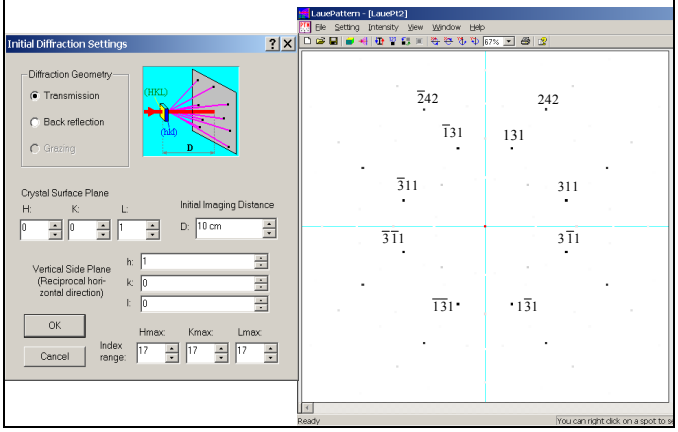
Laue diffraction:



For polycrystalline sample, monochromatic x-rays are used.
For single crystal sample, white x-rays are used.
Main features: very cheap and useful

A transmission Laue picture calculated by LauePattern

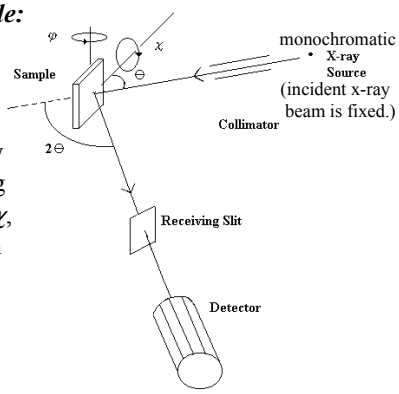
(http://ccp14.minerals.csiro.au/ccp/web-mirrors/xianrong-huang/)



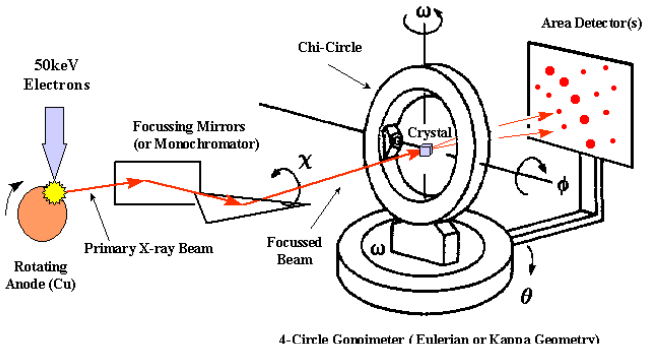
(E) *Diffractometer techniques*

4 circle x-ray diffractometer with a simple detector for single crystal sample:

Look for all possible diffractions (that satisfy Bragg law) by adjusting sample orientation (φ, χ, θ) and detector position (2θ). Based on these recorded (φ, χ, θ, 2θ) data, the crystal structure of the sample can be determined.



4 circle x-ray diffractometer with an area detector for single crystal sample:

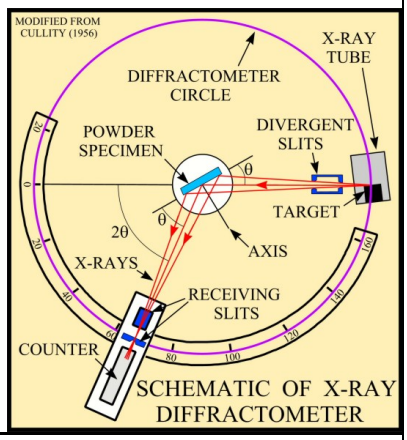


(http://www-structure.llnl.gov/Xray/101index.html)

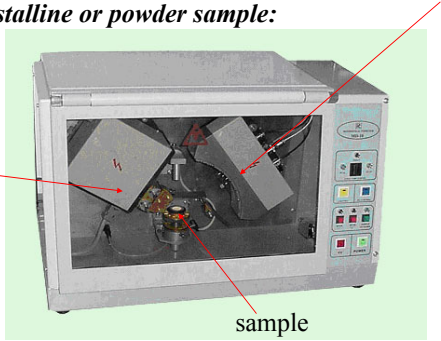
2 circle diffractometer with a simple detector for polycrystalline (or powder) sample:

Incident x-ray beam is fixed and monochromatic (produced by a filter or crystal monochromator).

The sample is rotated by θ and detector is rotated by 2θ. Diffraction beams are observed whenever Bragg law is satisfied.



2 circle x-ray diffractometer with a position-sensitive detector for polycrystalline or powder sample:

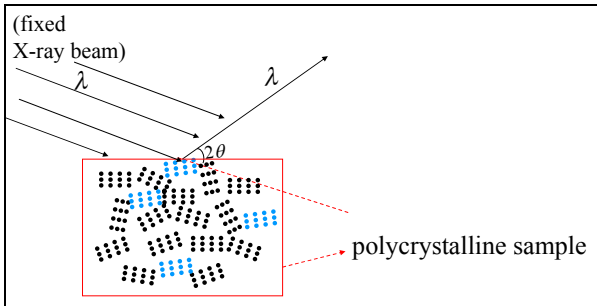


incident (fixed) x-ray beam

diffraction beams

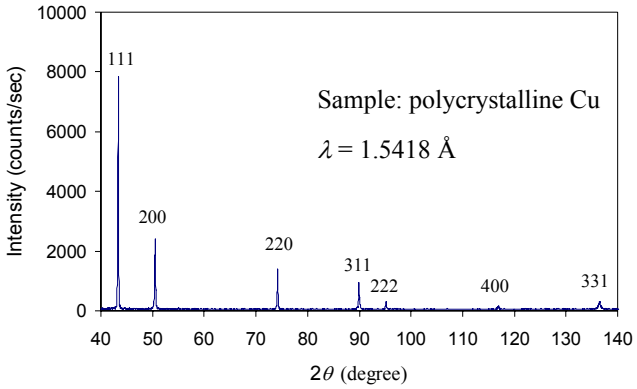
sample

(http://www.radicon.xraysite.com/index.html)



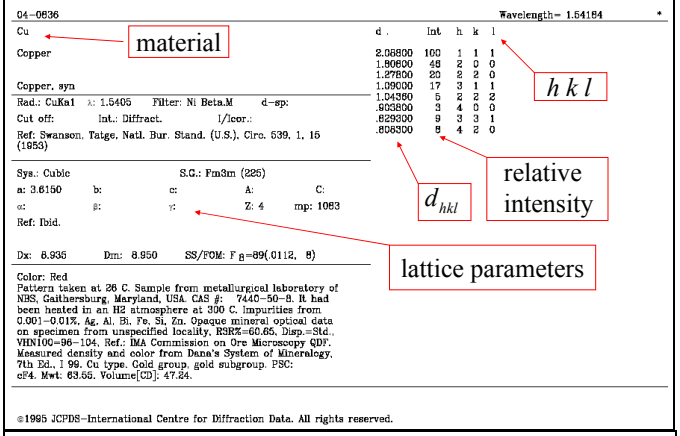
For a given material, the 2θ angles that satisfy Bragg equation are known or fixed (see example on next two pages). Only those grains in the sample with the right orientation can diffract the x-ray beam.

XRD pattern:



Crystal structure and the unit cell content can be determined using careful analysis of the "powder XRD spectrum".

ICDD tabulated possible diffractions for many materials: (http://www.icdd.com/)



(IV) ***Useful resources in internet***

Basic:

(1) Ron *Jenkins,* "X-ray Techniques: Overview" in *Encyclopedia of Analytical Chemistry,* ed. by R.A. Meyers, pp. 13269–13288 (Wiley 2000)

(2) **x-ray data booklet** (for x-ray data) (http://xdb.lbl.gov/)

Tutorial:

(1) Teaching guide X-Ray and neutron diffraction (http://www.kri.physik.uni-muenchen.de/geo/crystal/teaching/content.html)

(2) http://www.matscieng.sunysb.edu/esm512/webers-calcs/

(3) http://www.mrl.ucsb.edu/mrl/centralfacilities/xray/xray-basics/Xray-basics.html