5. DIFFRACTION.

Aim: To give the basic knowledge necessary to extract structural data from diffraction measurements, in simple cases.

Crystal structures can be studied by diffraction techniques, using photons, electrons and neutrons as probes. In order to resolve the structure, the wavelength of the impinging radiation (or particle) must be less than the lattice constant, a. The directions of the beams diffracted by the lattice and basis give information on the structure. Essentially, diffraction methods probe the reciprocal lattice of the structure.

1. Experimental probes.

X-ray diffraction: The wavelength of a photon is given by:

$\lambda = hc/E = 12400/E(eV)$, if the wavelength is to be computed in Å units.

It is seen that X-ray photons with energies exceeding 10 keV are necessary for structural studies. It is the electrons that scatter the X-rays elastically, i.e. energy and wavelength does not change in the scattering process. The diffraction depends on the electron density $n(\mathbf{r})$.

X-ray diffraction is a standard laboratory tool for analysis of crystalline structures. In this lecture, we will primarily treat this method.

Electron diffraction: The de Broglie wavelength of the electron is:

$\lambda = (h^2/2mE)^{1/2} = 12 / (E(eV))^{1/2}$, with the wavelength in Å.

An energy that is larger than 150 eV is necessary to observe diffraction, but much higher energies are generally used, of the order of 100 keV, or larger. The electrons are then able to penetrate a thin film of the material. The electrons are scattered by the strong potential of the ion-electron system.

Electrons are very suitable for real space studies of structures. The electron microscope is a versatile research instrument with, under certain conditions, atomic resolution. Electron diffraction is used as a supplementary analysis technique in the electron microscope, but a quantitative interpretation of the data is more difficult than for X-rays.

Neutron diffraction: The de Broglie wavelength is in this case,

$\lambda (Å) = 0.28 / (E(eV))^{1/2}$.

In order to obtain diffraction neutrons of very low energy can be used (1 Å corresponds to an energy of 0.08 eV). Such thermal neutrons can penetrate cm's in a material. In non-magnetic substances, the neutrons interact only with the atomic nuclei. The technique can also be used to study magnetic structures, due to the spin of the neutron.

Thermal neutrons are produced in nuclear reactors. The research is concentrated to a small number of large facilities around research reactors.

2. Diffraction conditions (K p. 24-26, 30-33).

We assume that the incident radiation is specularly reflected from parallel planes of atoms in the crystal. A diffracted beam is obtained when the reflected waves interfere constructively. A simple geometrical construction (K p. 24) shows that constructive interference from adjacent planes occurs according to Bragg's law: $2d \sin \theta = n\lambda$. Here d is the interplanar distance, n is an integer and θ is measured from the plane.

A more rigorous derivation considers a plane incident wave scattered by two neighbouring atoms. The path length (and phase) difference and hence the condition for constructive interference can be seen from fig. 6, K p.30. The difference in wave vector, $\Delta\mathbf{k}$, between the scattered and incident rays is called the scattering vector. Note that the magnitude of the wave vector is equal for the incident and scattered rays.

We treat X-ray diffraction. Hence we have to integrate the phase factor over the electron distribution in the crystal. The resulting integral exhibits maxima when the scattering vector, $\Delta\mathbf{k}$, is equal to a reciprocal lattice vector $\mathbf{G}$. It can be shown to be negligible otherwise (see K p.44, Problem 4). This also means that the diffracted rays from a crystal can be labelled with the Miller indices (hkl) of the sets of planes giving rise to the diffraction.

The integer n in Bragg's law gives the order of the diffraction. Diffracted beams with n>1 correspond to reciprocal lattice vectors of the form (nh,nk,nl). These do not correspond to physical sets of planes in the lattice, but are necessary for the $\mathbf{G}$'s to form a lattice. Here we see that they have physical meaning.

3. Characterization of the basis (K p.39-42).

A basis associated with each lattice point will lead to further constraints on the diffraction than the condition above. The **structure factor**, S, is the integral of n($\mathbf{r}$) exp (-i$\mathbf{G}\cdot\mathbf{r}$) over a cell in the lattice. It may be a primitive cell or a crystallographic unit cell. The **atomic form factor** gives the contribution to the scattering amplitude from a single atom. Expressing the reciprocal lattice vectors in terms of Miller indices (hkl) and the basis in terms of the coordinates (x_j, y_j, z_j), we find:

$$S (hkl) = \sum f_j \exp [-2\pi i(hx_j + ky_j + lz_j)].$$

We now use this equation for the crystallographic unit cell of the cubic systems, in order to derive diffraction conditions, starting from the simple cubic lattice.

In the simple cubic lattice there is one atom per cubic unit cell and all reciprocal lattice vectors $\mathbf{G}$(hkl) give diffraction (i.e. h,k,l can be zero or any combination of integers). From Braggs law, the diffraction angle θ, can be obtained from,

$\sin^2 \theta = \lambda^2 / 4d^2$, where the interplanar distances in the cubic systems can be shown to be

$d^2_{hkl} = a^2 / (h^2 + k^2 + l^2)$, hence

$\sin^2 \theta = (\lambda^2 / 4a^2) (h^2 + k^2 + l^2)$

It is seen that the diffraction angles depend on $(h^2+k^2+l^2)$ for a certain substance and wavelength of the impinging radiation. Below we list the allowed diffractions for the cubic crystal structures in terms of $(h^2+k^2+l^2)$.

$(h^2+k^2+l^2)$	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
sc	x	x	x	x	x	x		x	x	x	x	x	x	x		x	x	x	x	x	x	x	
bcc		x		x		x		x		x		x		x		x		x		x		x	
fcc			x	x				x			x	x				x			x	x			
diamond cubic			x					x			x					x			x				

We can also treat the somewhat more complicated case of KBr and KCl, see figure 17 in K p. 42.

4. Experimental techniques.

The Laue conditions for diffraction are very special and it is very difficult to find diffracted beams for a general combination of wavelength of, and crystal orientation relative to, the incident radiation. This is illustrated by the Ewald sphere (K p.32-33). The vector **k** is drawn in the direction of the incident beam and the origin (C) is chosen so that it terminates on a reciprocal lattice point. Only if the sphere with radius $k=2\pi/\lambda$ around the origin intersects another lattice point will diffraction take place. The figure below illustrates the Ewald sphere for incident radiation with a single wavelength and a range of wavelengths.

Ewald sphere
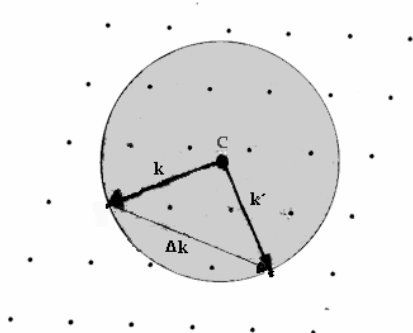
Laue method
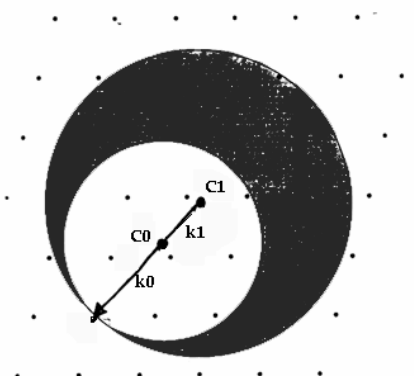
a) Laue method.

It is seen that using a range of X-ray wavelengths, all reciprocal lattice points falling between the two Ewald spheres of minimum and maximum radii, k_0 and k_1, respectively, give rise to diffraction. By using a broad wavelength interval one can be certain of observing a number of diffracted beams.

In this method the sample is a stationary single crystal. The diffracted beams are seen as a point pattern, either in transmission (for thin samples) or in back-reflection. The method is used for determination of the orientation and symmetry of a crystal and for quick orientation of crystals.

Many modern instruments use a constant wavelength and a rotating (around three axes) crystal in order to observe the diffracted beams.

b) Debye-Scherrer method.

Monochromatic X-ray radiation is used. The sample is in powder form, which means that it consists of crystallites with different orientations. All diffracted beams are seen since Bragg's law is fulfilled for at least some crystals in the sample. The angle between the incoming and diffracted beams is 2θ. Each diffracted beam is then a cone with this apex angle. When mapped onto a photographic film it becomes a concentric ring. The diffraction angles can be measured directly. Since the observable angles, θ, must be less than 90 deg., there is a limit to the magnitude of $(h^2+k^2+l^2)$ that can be observed.
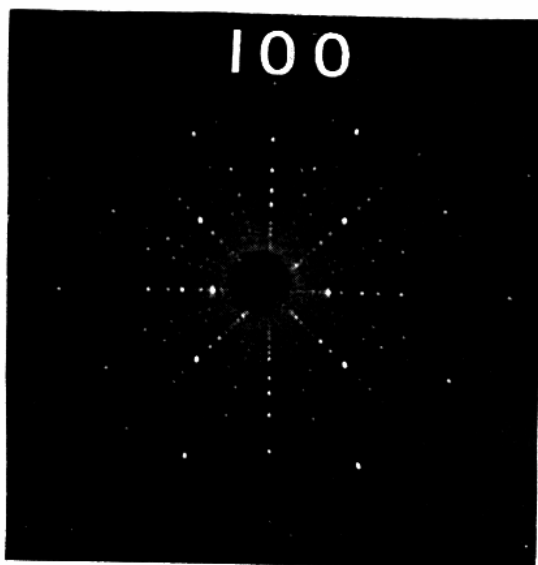
The figure below shows a schematic picture of the method.
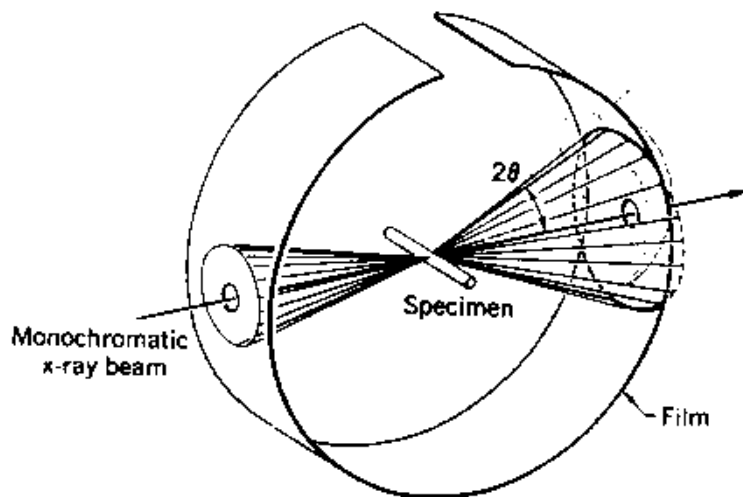
The method is a standard tool for determining the structure and lattice constant of polycrystalline samples by both X-ray and electron diffraction. For electron diffraction complete rings can usually be seen. The method also enables different phases in a composite sample to be identified.

Below are shown examples of diffraction patterns from (top) a single crystal-Laue method, (middle) a polycrystalline sample-electron diffraction and (bottom) Debye-Scherrer method.

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Laue