Crystal Structure

CRYSTAL STRUCTURES

Lecture 4

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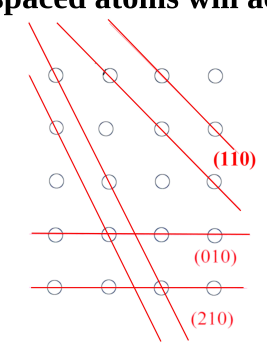
Structure & Diffraction

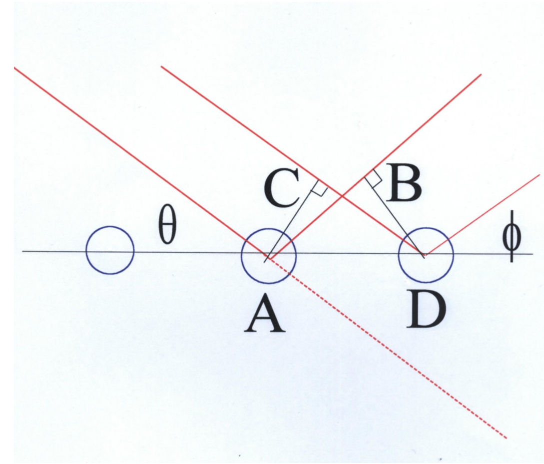
2 Crystal Diffraction

2.1 Bragg's Law

Any plane of regularly spaced atoms will act as a 'mirror':

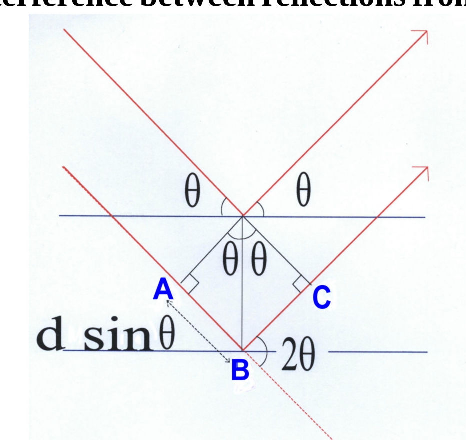


Any plane will do. The reflectivity will depend on the number of atoms per area in the plane.



The extra path travelled by the left-hand ray on the way out (AB) must equal the extra path travelled by the right-hand ray on the way in (CD), so $\theta = \phi$, a 'reflection' (corresponds to zeroth order from diffraction grating).

Now consider interference between reflections from successive planes:

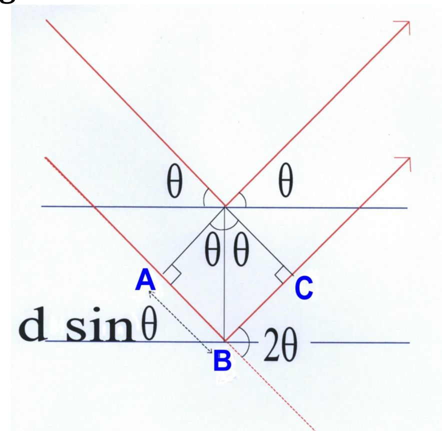


Constructive interference if the extra path $ABC = n\lambda$, or

$$2d \sin\theta = n\lambda,$$

Bragg's law.

Take care over angles:



- **The angle is between the ray and the plane – not the same convention as in optics**
- **If the Bragg angle is θ, the beam is deflected through 2θ.**

Notation:

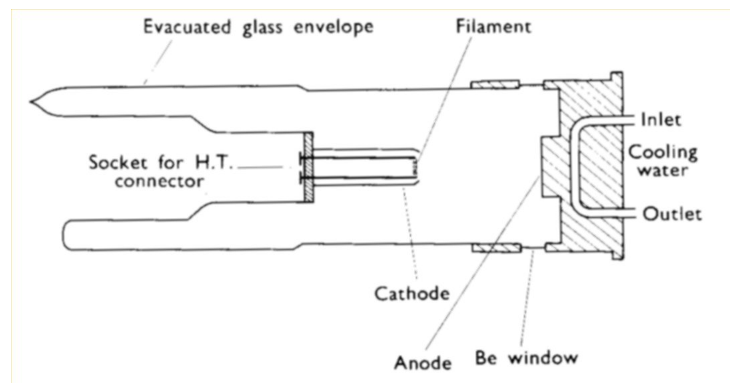
- **We refer to (hkl) reflections, according to the plane which is reflecting.**
- **The n in $2d\sin\theta = n\lambda$ is called the *order* of the reflection or of the diffraction.**
- **The terms nth order (hkl) reflection and $(nh\ \ nk\ \ nl)$ reflection are equivalent.**

2.2 Wavelengths and Energies

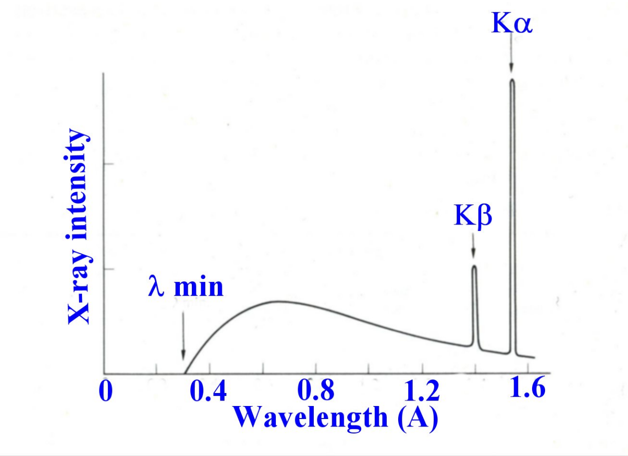
From Bragg's law $2d\sin\theta = n\lambda$ we must have $\lambda \leq 2d$, that is $\lambda \approx 1$ Å or 0.1 nm. We can use x-rays, neutrons (or electrons – but mainly for surfaces).

Beam	Scattered from	Energy for $\lambda = 1$ Å	General (λ in Å and E in eV)
x-ray	electrons	12 keV	$\lambda = \frac{12399}{E}$
neutron	nuclei	0.08 eV	$\lambda = \frac{0.2862}{\sqrt{E}}$
electron	electrons	150 eV	$\lambda = \frac{12.264}{\sqrt{E}}$

2.2.1 X-ray sources

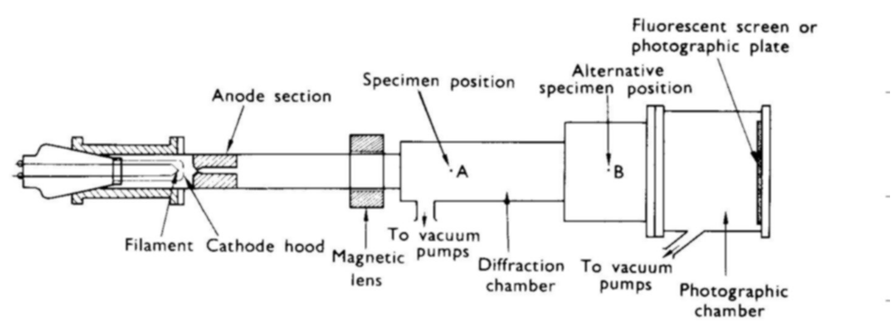


Kilovolt electrons impinge on target.



Continuum background plus sharp lines from intra-atomic transitions.

2.2.2 Electron sources



Schematic diagram of an electron diffraction apparatus.

Hot cathode – electrons accelerated by electric field, focussed with magnetic field. Low penetration – study thin films or surfaces.

2.2.3 Neutron sources

Reactor:

- **thermal neutrons (energy about k_BT) – need moderator to slow neutrons**
- **Boltzmann velocity distribution**
- **collimate beam**

Use broad range of wavelengths, or put through monochromator

- **mechanical chopper – time taken to traverse known distance gives velocity**
- **Bragg's law 'in reverse' – use crystal of known plane spacing, so know wavelength if know θ**

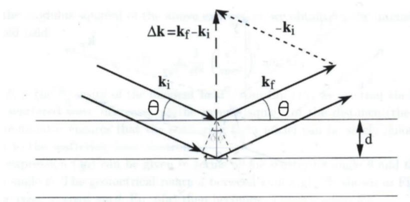
Spallation source

- **accelerate protons and fire at heavy nuclei**
- **neutrons thrown off**

Intense,usually pulsed, source.

2.3 Elastic Scattering

Energy of waves is conserved – exit wavelength equal to incident wavelength.



$$\lambda_i = \lambda_f,$$

so

$$|\mathbf{k}_i| = |\mathbf{k}_f|.$$

$$|\Delta k| = 2|\mathbf{k}_i|\sin\theta = 2\frac{2\pi}{\lambda}\sin\theta = n\frac{2\pi}{d},$$

from Bragg's law.

Special relationship between Δk and the planes:

- **Δk is perpendicular to the scattering planes,**
- **length of Δk is integer multiple of 2π divided by the plane spacing.**

2.3.1 Example

X-ray scattering from $\mathrm{NaClO_3}$. Cu K_α radiation, $\lambda = 1.54\ \mathring{A}$.

θ°	$\sin\theta$	$\sin^2\theta$	N	(hkl)	a
9.544	**0.1658**	**0.0275**	**2**	**(110)**	**6.568**
11.720	**0.2031**	**0.0413**	**3**	**(111)**	**6.567**
13.561	**0.2345**	**0.0550**	**4**	**(200)**	**6.567**
15.201	**0.2622**	**0.0688**	**5**	**(210)**	**6.567**
16.701	**0.2874**	**0.0826**	**6**	**(211)**	**6.563**
19.374	**0.3317**	**0.1100**	**8**	**(220)**	**6.566**
20.597	**0.3518**	**0.1238**	**9**	**(221)(300)**	**6.566**
21.771	**0.3709**	**0.1376**	**10**	**(310)**	**6.565**

- **tabulate $\sin\theta$ (remember to check whether θ or 2θ is given)**
- **tabulate $\sin^2\theta$**
- **take out common factor (remember the (100) reflection is not always there)**
- **from integers $N = h^2 + k^2 + l^2$ identify reflections (remember N cannot equal 7)**
- **then use $a = \sqrt{N}\lambda/(2\sin\theta)$.**