

X-ray, Neutron and Electron Diffraction of Crystals

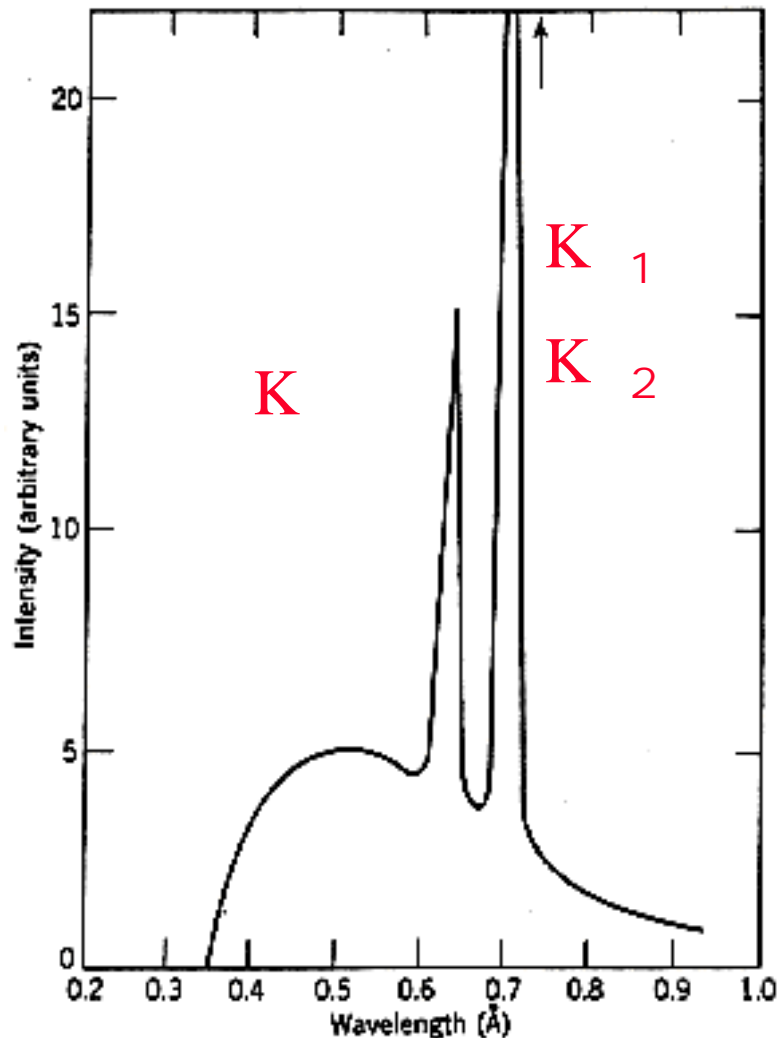
- Scope and Use of Diffraction Experiments in Materials Science
- X-ray Diffraction
 - X-ray Radiation
 - Electromagnetic Wave Theory
 - One-Electron Atom Scattering
 - Interference Between Waves
 - Atomic Scattering
 - Crystal Diffraction (Effect of Size, Defects, Orientation,..)
 - Experimental Techniques
- Neutron and Electron Diffraction
- General Scattering Concepts (extension to small angle X-ray or Neutron scattering and light scattering).

Scope and Use of Diffraction Experiments in Materials Science

- Crystal structure analysis
- Liquid, liquid-crystal structures
- Identification of crystal phases in polymorphic materials
- Degree of crystallinity in polymeric samples
- Crystal orientation (texture)
- Crystal or grain size
- Internal stresses and strains
- Crystal elastic constants
- Study of defects (dislocation, grain boundary, stacking fault, vacancy, etc. ...)

X-Ray Radiation

Discovered by:
W. Rontgen (1895)



- X-Ray radiation is produced when high energy electrons impinge on a metal target (the most useful of which for crystallography are iron, copper and molybdenum). As electrons decelerate, while they penetrate the metal target, they generate a radiation characterized by a broad band of continuously varying wavelength called “white light” or “Bremsstrahlung”. Superposed on the continuum are a few high intensity, sharp peaks, which arise from the collision of incoming electrons with inner shell electrons of the target metal. As the latter are expelled, higher energy orbital electrons fill the vacancies and emit the excess energy as an x-ray photon. $E = hc/$

X-Ray Radiation

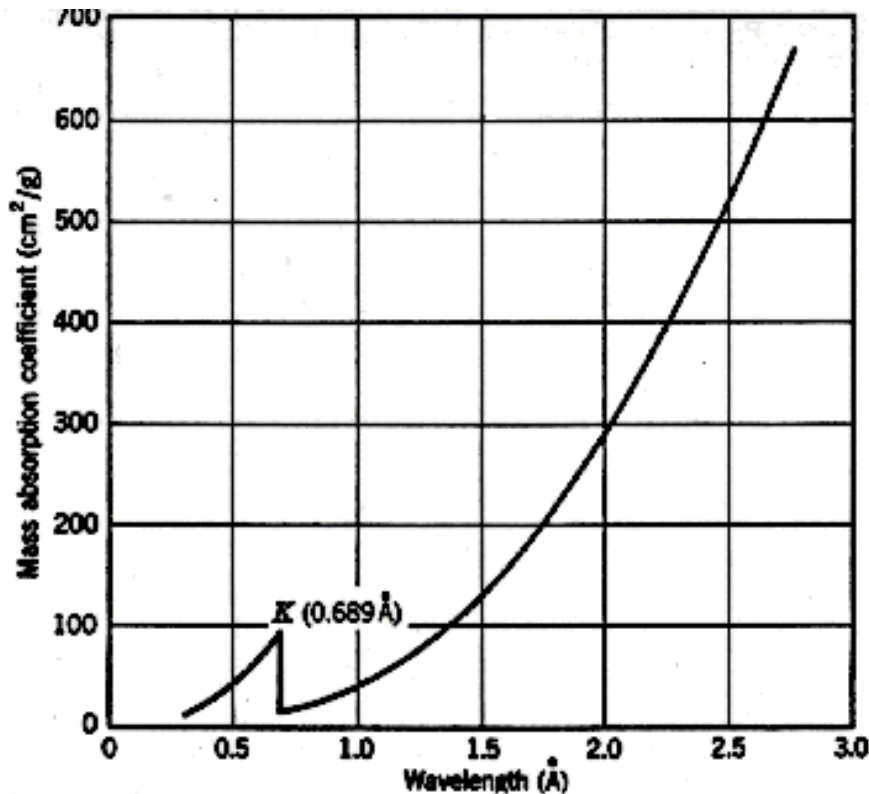
- X-rays are electromagnetic waves (i.e. waves described by **electric E** and **magnetic H fields** oscillating in planes at 90° from each other) and traveling in a direction defined by the **wave vector k** of magnitude $2\pi/\lambda$. Note that the **wavelength λ** is related to the **frequency ν** of the oscillating field by $\lambda = c/\nu$. (c is the speed of light in vacuum). X-ray wavelengths are intermediate between those of the ultraviolet and the gamma rays. For crystallographic purpose, λ ranges from 0.5 to 2.5 Å.
- **Electromagnetic Wave Theory:**

From Maxwell's theory we know that the amplitude E of the X-ray wave must satisfy the relation:

$$\nabla^2 E - \frac{\epsilon\mu}{c^2} \ddot{E} = 0 \quad \text{where } \mu \text{ and } \epsilon \text{ are the magnetic permeability and dielectric permittivity, respectively.}$$

- A solution to the Maxwell equations is:
 $E = E_0 \exp[i(\mathbf{k} \cdot \mathbf{r} + \omega t)]$ (plane transverse electromagnetic wave)
 where: $k = 2\pi / \lambda$ and $\omega = 2\pi \nu = 2\pi c / \lambda$
 \mathbf{r} is a vector characterizing the position, t is the time
- As an electromagnetic wave interacts with matter, a number of events can occur:
 - **elastic scattering** by electrons in atoms (photon's trajectory is deviated but its energy is conserved).
 (this is where we obtain the structural information).
 - **inelastic scattering**: slight loss of energy (increase in wavelength) for the photons as they interact with free or loosely bound electrons. There is no phase relationship between incident and scattered rays. Compton or incoherent scattering.
 - **absorption** by atoms (photoelectric effect) leads to either the Auger Effect (loss of another electron) or Fluorescence (X-photon emission).

Absorption Behavior of x-rays



K absorption edge of zirconium

On traversing matter, x-rays are absorbed to an extent given by their linear absorption coefficient μ at the specific wavelength of the radiation:

$$I = I_0 \exp(-\mu t)$$

The mass absorption coefficient μ/ρ is independent of the physical and chemical states of matter. Except for pronounced discontinuities (absorption edge), the mass absorption coefficient of any substance increases with the wavelength of the x-rays. For

$\lambda < \lambda_{\text{crit}}$, the radiation has sufficient energy to eject an electron. Thus μ/ρ increases dramatically in the region of the edge (Zr used as β -filter for K Mo and Ni is used as β -filter for K Cu). More monochromatic radiation can be obtained with crystal monochromators.

One-Electron Atom Scattering

- As an atom, having a single electron, interacts with an electromagnetic wave of electric field \mathbf{E} , the field exerts a force $\mathbf{F} = q\mathbf{E}$ on the electron. If the electron is at the origin when the field is off, then when the field is on, the electron position is \mathbf{X} :

- $m_e (d^2\mathbf{X}/dt^2) + \gamma (d\mathbf{X}/dt) + k\mathbf{X} = e E_0 \exp(i\omega t)$ the solution of which is:

$$\mathbf{X} = e E_0 \exp(i\omega t) [(k - m_e \omega^2)^2 - \gamma^2]^{-1/2} / [(k - m_e \omega^2)^2 + (\gamma/2)^2]^{-1/2}$$

$$\mathbf{X} = X_0 \cos(\omega t - \phi) = (a - ib)(\cos(\omega t) + i \sin(\omega t))$$

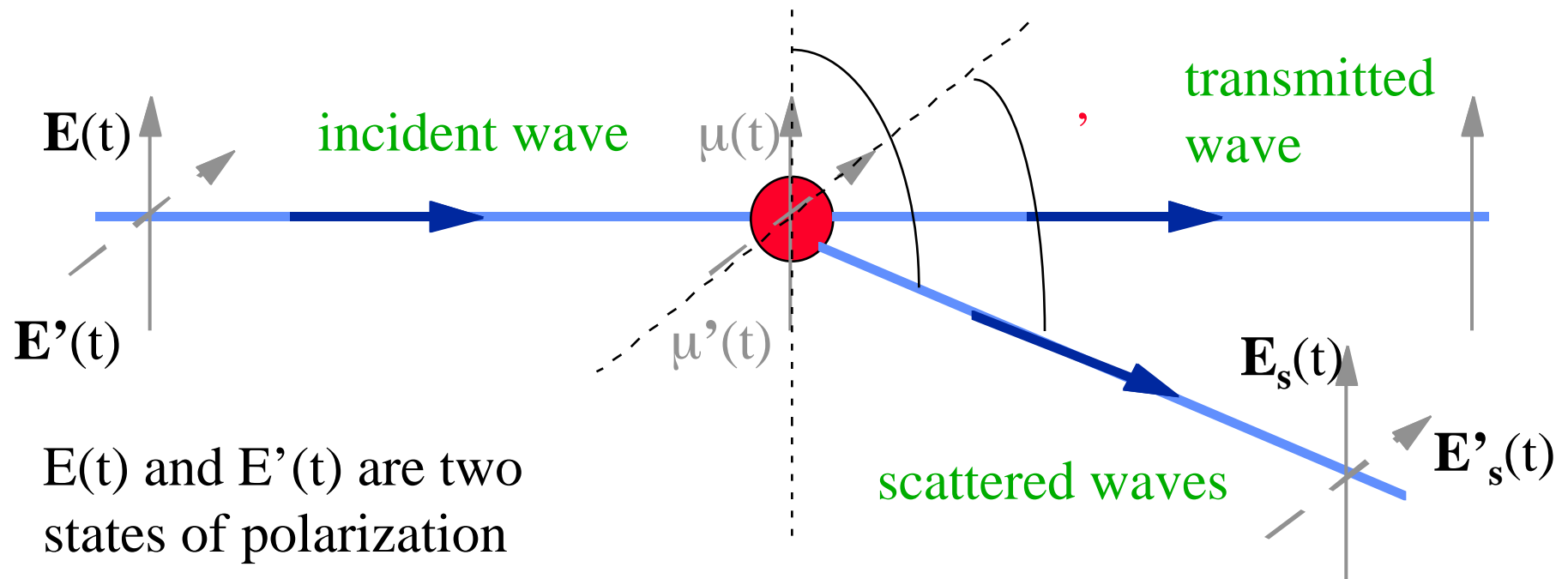
$$X_0^2 = a^2 + b^2 = (e E_0 / [(k - m_e \omega^2)^2 + (\gamma/2)^2]^{1/2})^2$$

$$\tan(\phi) = b/a = \gamma / (k - m_e \omega^2)$$

- The maximum in the energy dissipation can be calculated through: $dW = \mathbf{F} \cdot d\mathbf{X}$ by integrating between $t = 0$ and $2\pi/\omega$. It is found that the resonance (energy absorption) occurs at ω_R
- Different electrons have different force constants k , and will show resonance at different frequencies.

- First: $\mu(t) = \epsilon_0 \chi E(t)$ (dipole moment induced by the field)
 Second, since the field varies periodically with time, then the dipole varies also periodically in time. The dipole motion is equivalent to the motion of a charge which is equivalent to a time dependent electrical current. From Maxwell's equation, we know that a time dependent current can produce an electromagnetic field.

$$E_s(t) = (d^2\mu/dt^2) \sin(\theta) / (c^2 r)$$



Since $\mu = \nabla \cdot \mathbf{E}$ and $\mathbf{E} = \mathbf{E}_0 \exp(i \mathbf{k} \cdot \mathbf{r} - \omega t)$ then:

$\mathbf{E}_s(\mathbf{r}, t) = -\frac{1}{c^2} \nabla \times (\nabla \times \mathbf{E}_0 \exp(i \mathbf{k} \cdot \mathbf{r} - \omega t)) / r$ and the wave intensity is:

$$I_s = (c/4\pi) \mathbf{E}_s \cdot \mathbf{E}_s^* = (c/4\pi) \frac{E_0^2 \sin^2(\theta)}{r^2} / (c^4 r^2)$$

If we have a non-colored system, for which $\lambda \ll R$, then

$\mathbf{X} = e \mathbf{E}_0 \exp(i \mathbf{k} \cdot \mathbf{r} - \omega t) / k$ and $\mu = \nabla \cdot \mathbf{X} = e^2 \mathbf{E} / k$. Thus $\mu = e^2 / k$

This is what one calls Rayleigh Scattering (scattering of visible light)

If $\lambda \gg R$, then $\mathbf{X}_0 = e \mathbf{E}_0 / [(k - m_e c^2)^2 + (\hbar \omega)^2]^{1/2}$ or

$\mathbf{X}_0 = e \mathbf{E}_0 / [m_e c^2]$ and $\mu = \nabla \cdot \mathbf{X} = e^2 \mathbf{E} / m_e c^2$

Therefore $\mu = e^2 / m_e c^2$ which leads to:

$I_s = I_0 (\sin^2(\theta) / r^2) (e^2 / m_e c^2)^2$ where the term $(e^2 / m_e c^2)$ is the classical electron radius.

- For an X-ray beam polarized vertically ($\mathbf{E}(t)$), the scattered intensity measured with a vertical detector located in the horizontal plane is $I_V = r_e^2 I_0 / r^2$ where r_e the classical radius of the electron (2.818×10^{-15} m).
- If we now assume that the X-ray beam is polarized horizontally ($\mathbf{E}'(t)$), the scattered intensity measured with a horizontal detector located in the horizontal plane is:

$$I_H = r_e^2 \sin^2(\theta) I_0 / r^2$$

- For a beam of unspecified polarization, the calculation is made by decomposing the beam into two separate beams whose electric vectors are respectively perpendicular and parallel to the plane of the incident and scattered rays and in proportions k and k' . Then if the beam is unpolarized, $k = k' = 1/2$. If we define 2θ as the scattering angle (angle between incident and scattered rays):

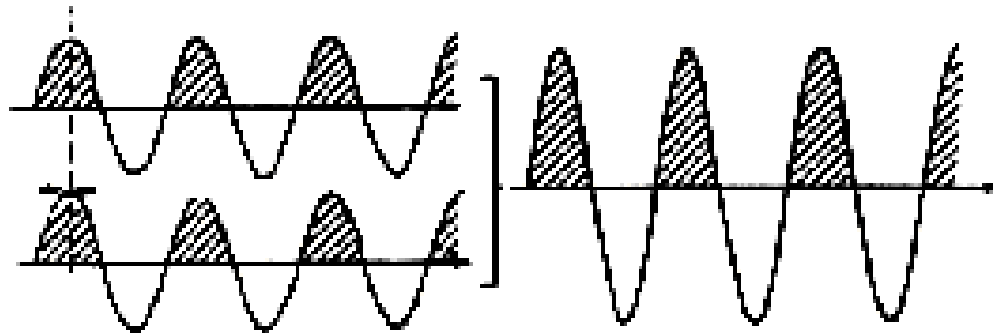
$$I_e = r_e^2 (\sin^2(\theta) + 1) I_0 / r^2 = (1 + \cos^2(2\theta)) r_e^2 I_0 / r^2$$

This is the **Thomson Formula**.

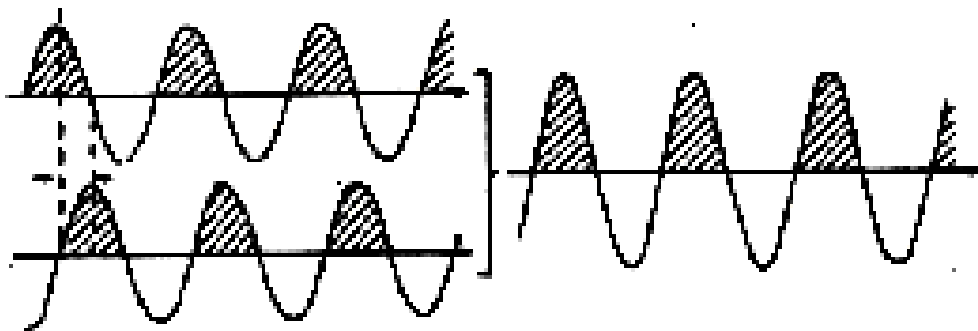
- Since we can only measure the intensity I of an electromagnetic wave $I = E^2$ in a given direction and at a given distance from the center of scattering (sample), then we do not need to worry about the time dependence of the scattering process. The intensity is actually measured by averaging the flux of photons over some period of time (scattering is a stochastic process I is proportional to the square root of the number of photons hitting the detector).
- Also note that in all previous calculations, we have clearly neglected the motion of the nucleus, which in principle also contributes to the scattering. However, $I \propto m^{-2}$ and the protons weigh ca. 1900 times more than the electrons....
- The index of refraction associated with X-rays is given by:

$$n = 1 - 2.72 \times 10^{-6} \frac{Z}{M} \frac{1}{\lambda^2}$$
where M is the atomic mass, Z is the atomic number, ρ is the density and λ the wavelength (Å). $1-n$ is at most 10^{-4} and most often 10^{-5}

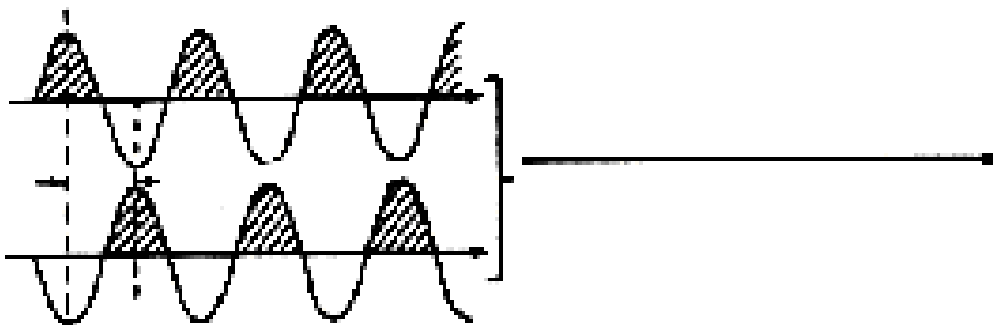
Interference Between Waves



Zero Phase Diff.,
 $A = 2, I = 4$



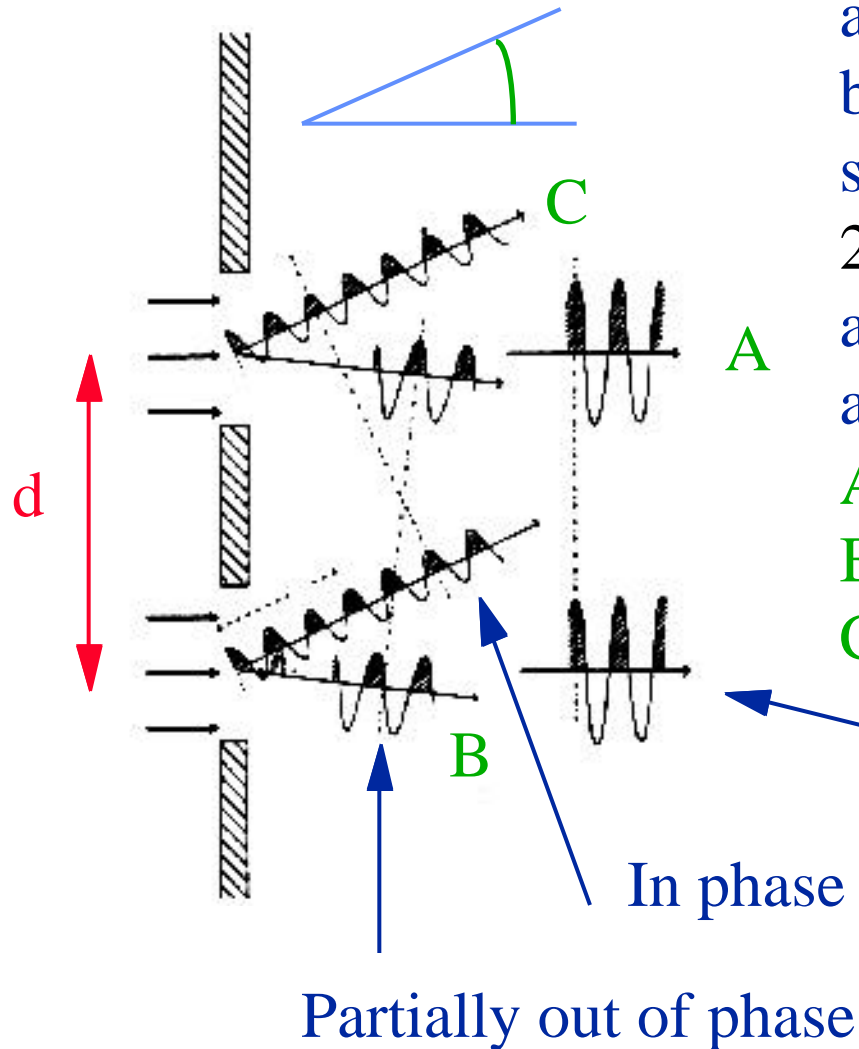
$\pi/4, \pi/2$ Phase Diff.,
 $A = 1.4, I = 2$



$\pi/2$, Phase Diff.,
Out of Phase
 $A = 0, I = 0$

When diffraction occurs from two slits, two effects need to be noted:

1. The variation in intensity with angle as a result of interference between waves generated within each slit separately (see previous figure)
2. The interference of scattered waves at a given angle with those at the same angle from the adjacent slit.



A will give a bright central spot

B will give very little diffraction

C will give a diffraction maximum

Direct beam (in phase)

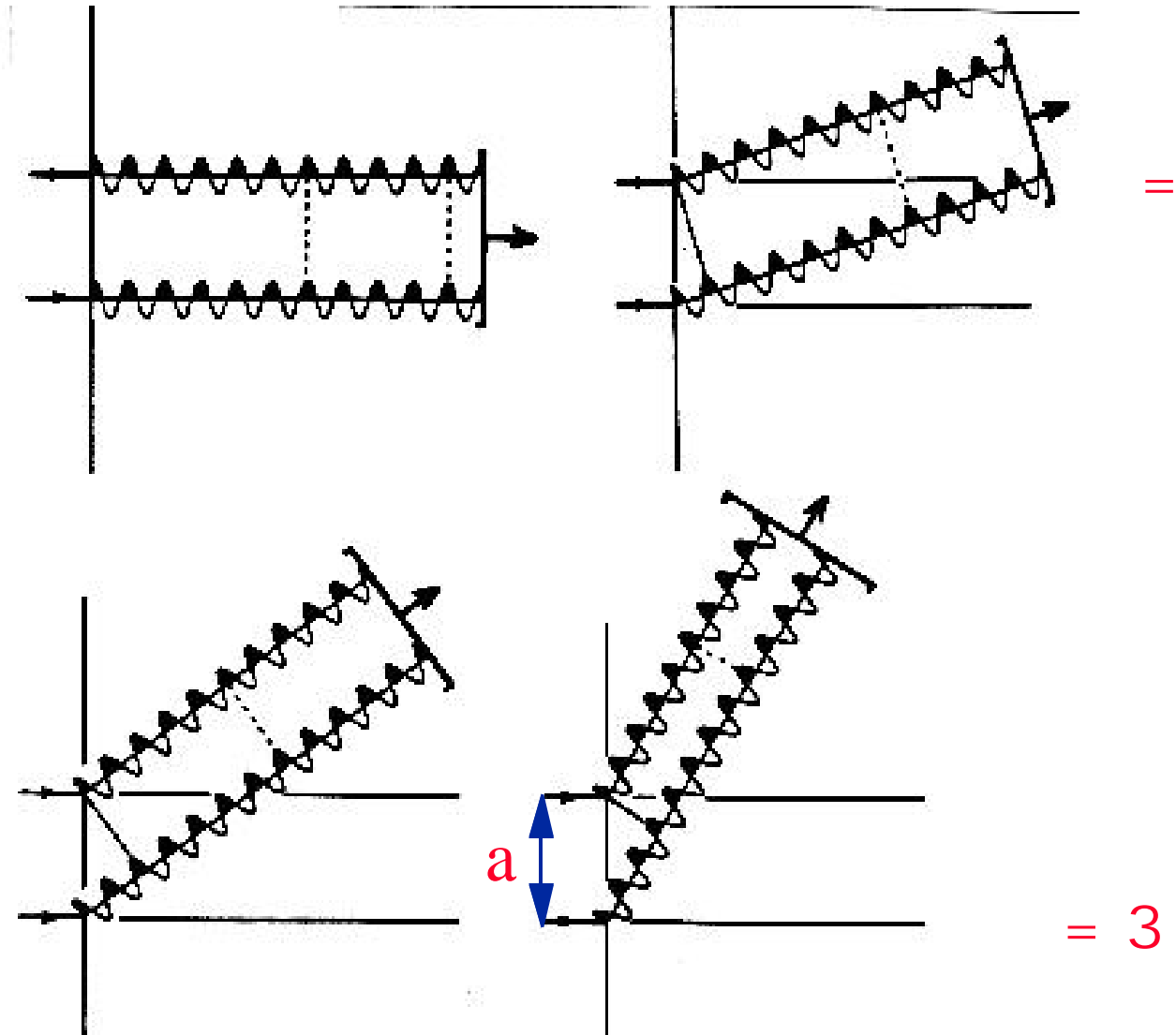
In phase (third order) $d \sin(\theta) = 3\lambda$

Partially out of phase

Scattering Order and the Path Difference

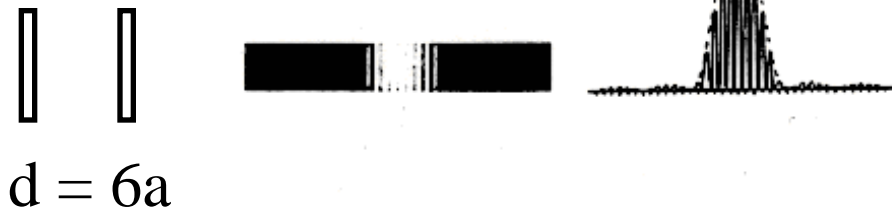
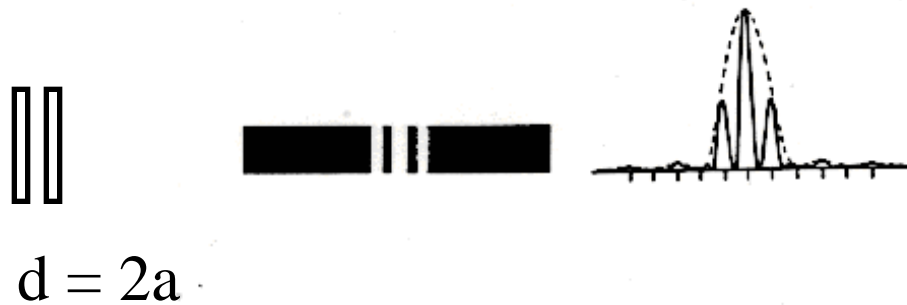
First, second, third and higher orders of diffraction are obtained when waves differ by one, two, three and more wavelengths. Think about the effect of changing **a**

= 2

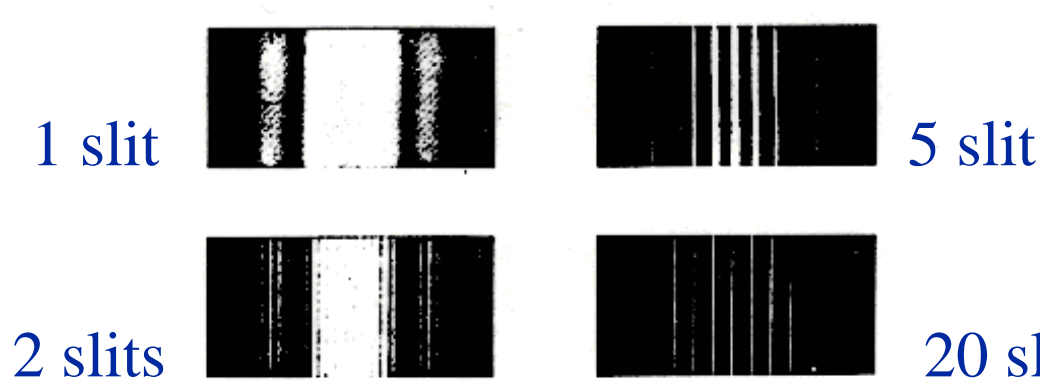


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Diffraction Patterns from Equidistant Parallel Slits



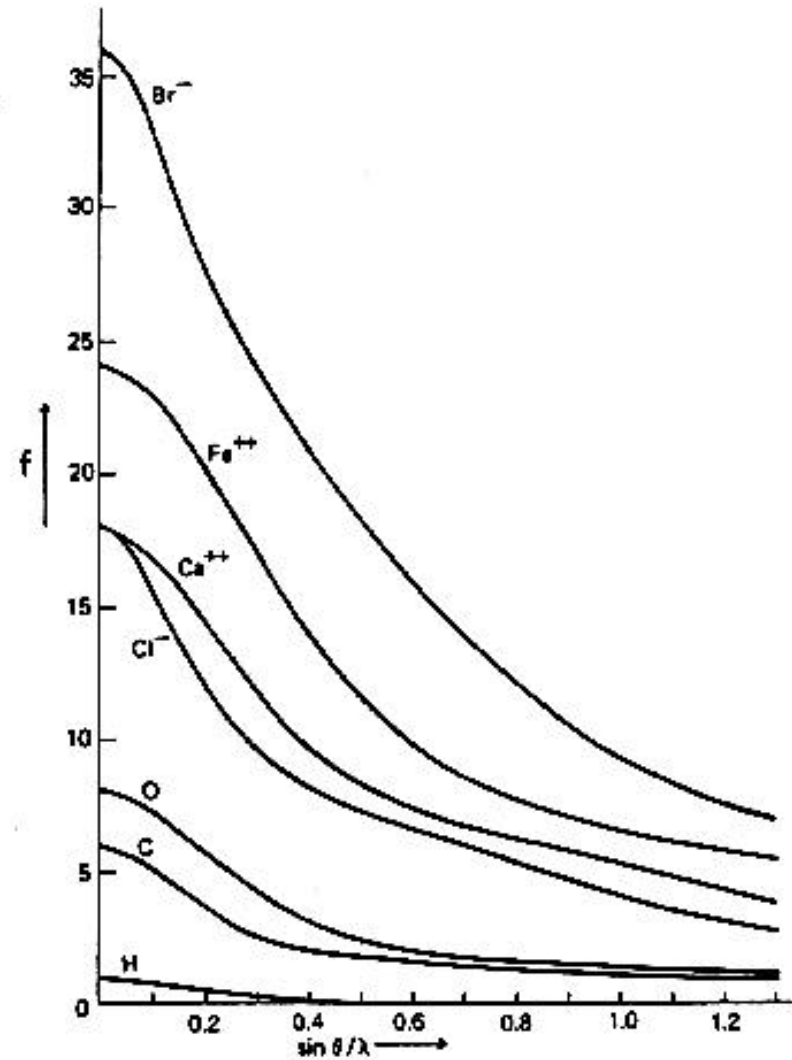
The effect of varying the distance between the slits narrow spacing between slits, wide spacing between sampling region and vice versa.



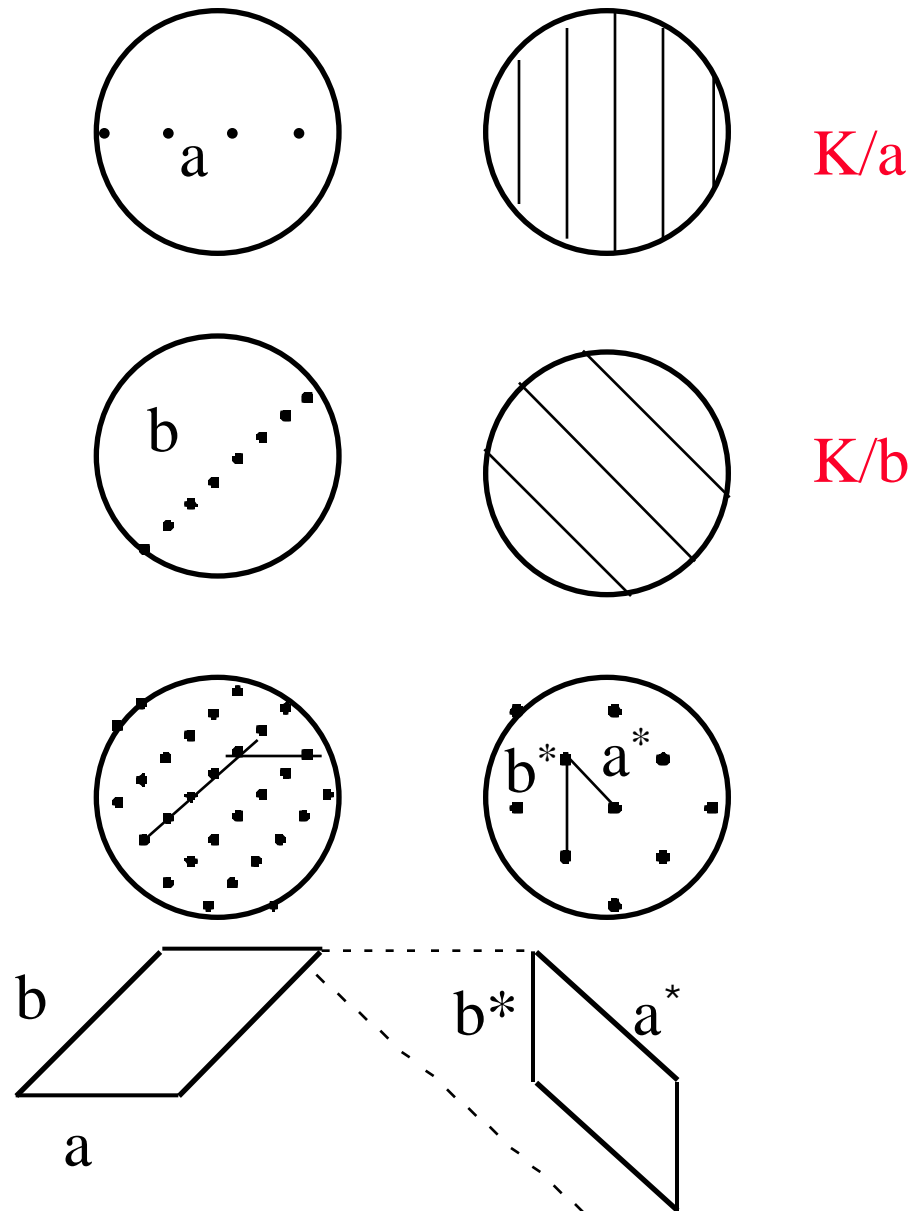
When increasing the number of equidistant slits, the radiation is concentrated in increasingly narrower regions

Atomic and Ionic Scattering Factors

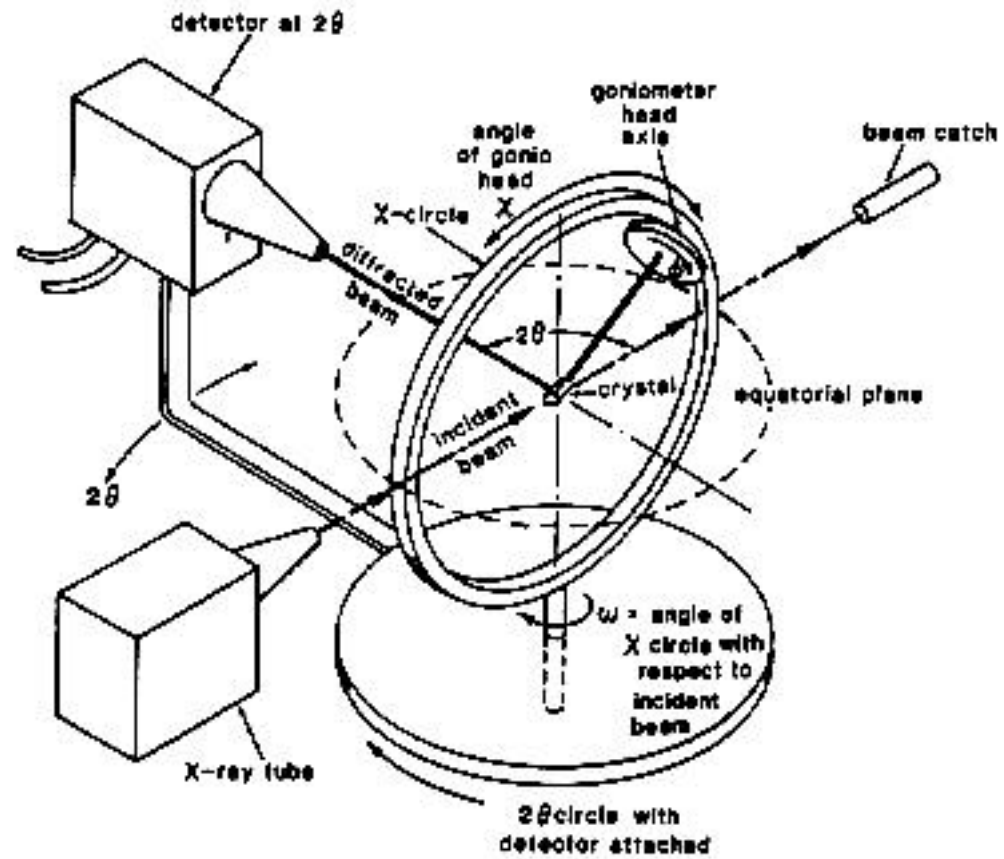
The atomic form or scattering factors account for the interferences between waves scattered by different electrons in the atom or ion. All scattered rays are in phase for $\theta = 0$ and destructive interferences occur at all non-zero angles. These are available in the [International Tables](#) and have been computed on the basis of quantum mechanical data on atomic orbitals.



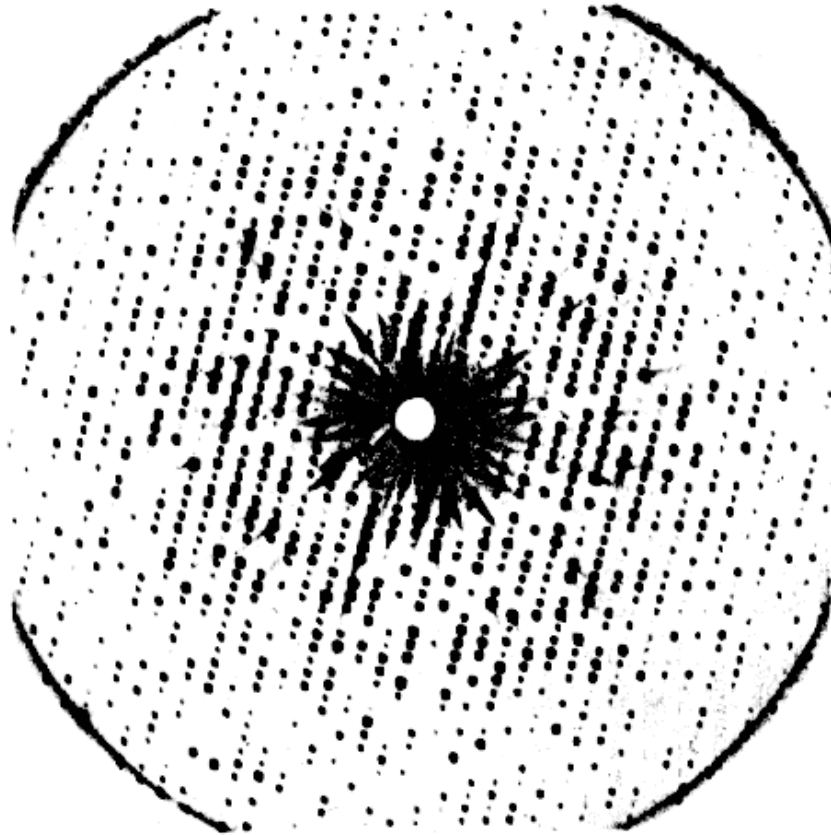
Diffraction Pattern From One and Two-Dimensional Arrays



Diffraction Set-up

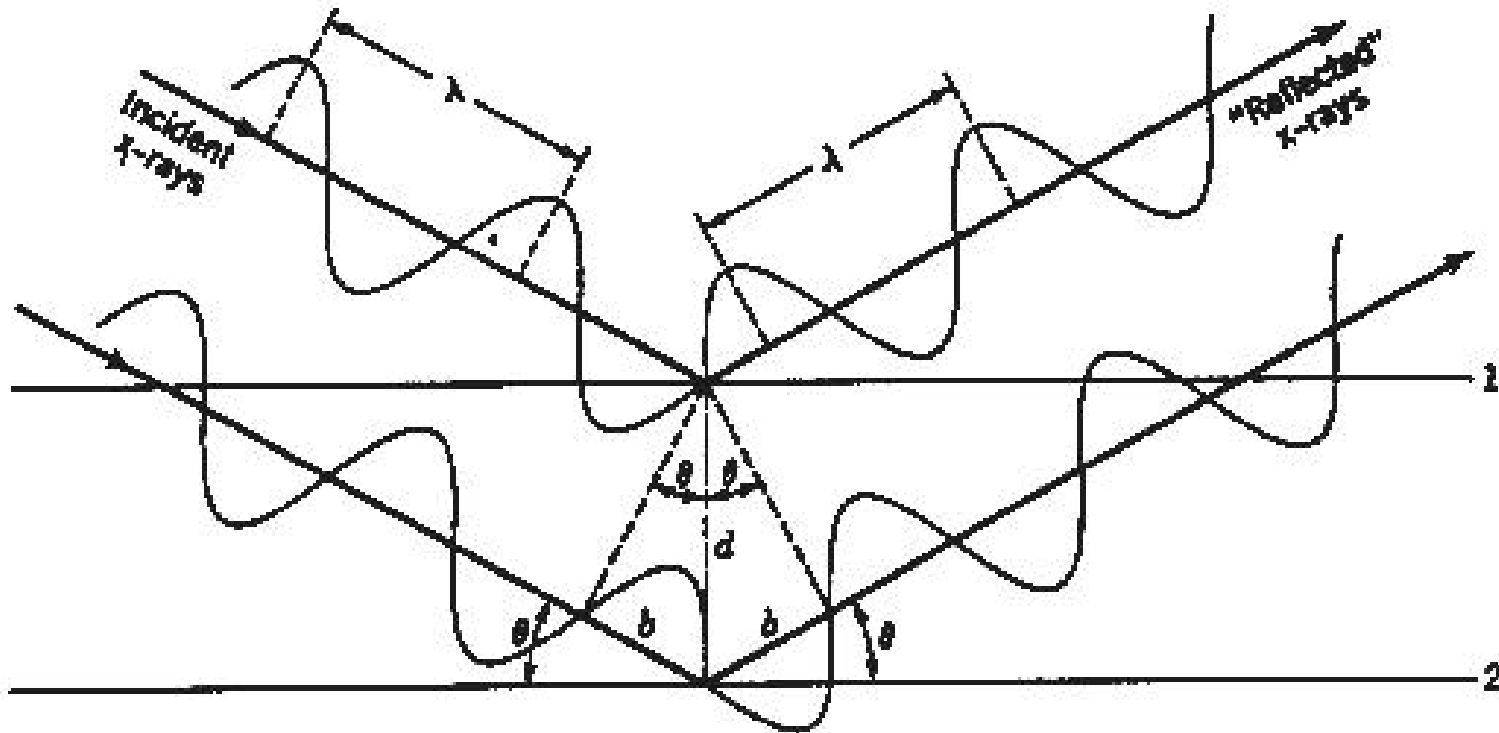


X-Ray Diffraction Photograph taken by the Precession Method



Streaks
Spot position
Spot intensity

Diffraction and the Bragg Equation



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

Bragg Relationship (1913) describes the path difference between waves scattered from adjacent lattice planes with equivalent indices.

It is derived by considering that the diffracted beams behave as if they were reflected from planes passing through points of the lattice