

An Introduction to Diffraction and Scattering

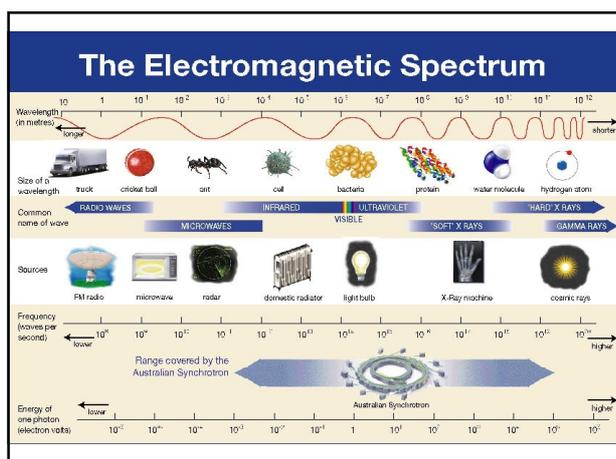
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Types of Forces

- 1) Strong forces
- 2) Weak forces
- 3) Electromagnetic forces
- 4) Gravity

Types of Matter

- 1) Atoms
- 2) Molecules
- 3) Crystals
- 4) Particles, Solids, Surfaces, Liquids, Glasses, Gases



Electromagnetic Radiation at a Synchrotron

Energy transmitted in the form of waves or particles

γ-rays X-rays UV Vis IR μ-waves

higher energy → lower energy

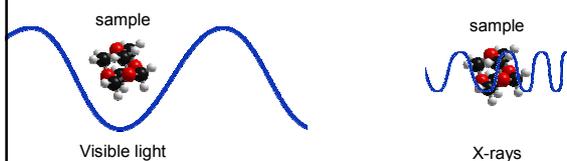
For particles:

de Broglie wavelength = Planck's const./momentum [$\lambda = h/p$]

For an electron accelerated through 100 Volts, $\lambda = 1.2 \text{ \AA}$,

Why is wavelength important?

To probe a sample you need radiation with a wavelength of similar, or smaller, magnitude to the size of the "object" under investigation.



To investigate atomic/molecular structure, we use X-rays, electrons, and neutrons, since they can have wavelengths about the sizes of atoms.

X-rays

- Hard X-ray wavelengths ~ 0.1 Å to 60 Å
- Soft X-ray wavelengths ~ 60 Å to 120 Å
- Interact weakly, ie. penetrating – therefore, can see inside of a structure, but most of the beam passes through, unperturbed.
- 10 x more photons are absorbed than scattered.
- X-rays scatter off of valence electrons (~ 1% off nuclei).

Interaction of X-rays and Matter



Scattering.

coherent, incoherent
elastic (Thomson), inelastic (Compton)

Absorption.

atoms: can then be emitted as fluorescence, photoelectrons, Auger electrons
molecules: can emit fluorescence, phosphorescence, transfer heat, (stimulated emission)

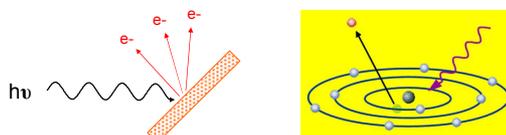
Diffraction. The bending of waves due to obstructions and small apertures, as with crystals.

Refraction. The bending of a wave as it passes from one medium to another

Reflection. Radiation bouncing back from one medium to the original medium, where the wavelength << size of the object.

Photoelectric Effect

Ionization occurs when a light has sufficient energy to eject an electron. The kinetic energy of the emitted electron is diagnostic of the orbital from which it was ejected. Allows Photoelectron spectroscopy.



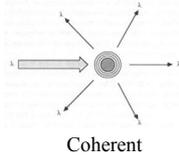
$$E_{h\nu} = \text{electron kinetic energy} + \text{electron binding energy}$$

Valence spectroscopy: information on bonding

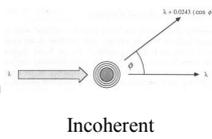
Core spectroscopy: qualitative and quantitative analysis, "chemical shift"

X-ray Scattering

Coherent scattering occurs when the X-ray particle collides with an atom and deviates without a loss in energy.



Incoherent scattering is where the incident X-ray loses some of its energy to the scattering electron. As total momentum is preserved, the wavelength of the scattered photon is increased.



Compton Scattering

Compton scattering occurs when the incident x-ray photon is deflected from its original path by an interaction with an electron. The electron is ejected from its orbital position and the x-ray photon loses energy because of the interaction but continues to travel through the material along an altered path. Energy and momentum are conserved in this process. The energy shift depends on the angle of scattering and not on the nature of the scattering medium.

$$\lambda_{scattered} - \lambda_{initial} = \left[\frac{h}{m_e c} \right] (1 - \cos \theta)$$

where h is Planck's constant; m_e the mass of the electron; c the speed of light; and θ the angle the photon is deflected by.

Since the scattered x-ray photon has less energy, it has a longer wavelength and less penetrating than the incident photon.

Thompson Scattering

- An electron will oscillate in phase with an x-ray beam according to the following equation:

$$I = \frac{I_0}{r^2} \left[\frac{e^2}{m_e c^2} \right]^2 \frac{1 + \cos^2(2\theta)}{2}$$

where I_0 is the intensity of the incident beam; e the charge on the electron; m_e the mass of the electron; c the speed of light; and r the distance from the scattering electron to the detector.

Clearly (by the second term) the scattered energy from a single electron is quite low. Third term, involving the cosine function, is called the *polarisation factor* because it indicates that the incoming non-polarised x-ray is polarised by the scattering process, resulting in a directional variation in the scattered intensity.

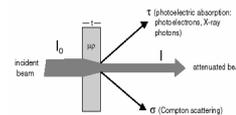
Absorption

When X-rays pass through a material, the intensity is attenuated (decreased) through absorption by the elements in the material.

Attenuation is due to two effects:

Compton scattering (σ) of the beam, which diverts photons in directions different from the primary beam:

Photoelectric absorption (τ), which produces fluorescence or Auger electrons.



Absorption

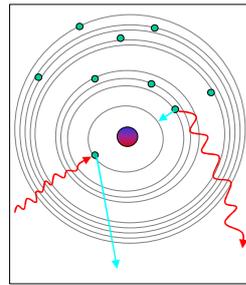
These two effects may be combined into a single bulk mass absorption coefficient (μ). This coefficient is different for each element and wavelength and is defined as the sum of photoelectric and Compton scattering:

$$\mu = \tau + \sigma$$

Where τ = photoelectric absorption coefficient and σ is the Compton Scattering coefficient

In many materials photoelectric absorption accounts for about 95 percent of the absorption and Compton scattering can be ignored. Further, Compton scattering is not important at wavelengths less than 1 Å.

Fluorescence



If an X-ray photon of sufficiently high energy strikes an inner shell electron the electron can be ejected from the atom.

Higher energy electrons cascade to fill vacancy, giving off characteristic fluorescent X-rays.

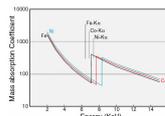
Higher energy electrons cascade to fill vacancy, giving off characteristic fluorescent X-rays.

Secondary Fluorescence

The absorption of an incident X-ray to produce another X-ray produces an effect termed secondary fluorescence. Secondary fluorescence produces an excess intensity. Some elements undergo self-absorption: K-line X-rays may be absorbed by other atoms of same element to produce L-line X-rays. For a given element of interest, any X-rays of energy higher than E_c produced from other elements can cause fluorescence. The energy at which the mass absorption coefficient increases abruptly is the absorption edge and corresponds to E_c exactly.

For example, consider a material composed of 1/3 Fe, 1/3 Ni, and 1/3 Co. One would expect about 33.3% of the total X-rays observed to be produced by each element, but instead we see 40% Fe, 28% Ni, and 32% Co. The Fe in the material is fluoresced by Ni-K α producing Fe-K α X-rays and absorbing Ni-K α .

Plot of the X-ray absorption curves for Fe (black), Co (red), and Ni (blue), showing the K α absorption edges. The locations of the K α lines for these elements is also shown. Note that Ni-K α x-rays have sufficient energy to fluoresce Fe-K α x-rays.



Scattering and Diffraction Techniques

- 3-Dimensional X-ray crystallography
- Phasing methods
- 2-Dimensional Grazing incidence diffraction
- Low-angle scatter
- Dynamics
 - Equilibrium: B factors, diffuse scatter
 - Non-equilibrium: Laue method

Other Synchrotron Techniques

Scattering:

- Raman (inelastic, due to vibrations)
- visible Rayleigh (elastic, information on particle size and dynamics)

Absorption and related techniques:

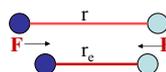
EXAFS (measure fluorescence in an excitation spectrum)

UV, vis, IR (electronic, vibrations)

- absorption (CD, linear, time-resolved)
- fluorescence
- phosphorescence (luminescence)

Infra-red Spectroscopy

Displacement of atoms during vibration lead to distortion of electrical charge distribution of the molecule.



atoms (mass) are connected with bonding electrons. r_e is the equilibrium distance and F : force to restore equilibrium.

$$\omega_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{\mu_i}}$$

$F(x) = -kx$ where X is displacement from equilibrium k_i is the force constant and μ_i is reduce mass of a particular motion.

Molecular vibration lead to oscillation of electric charge governed by vibration frequencies of the system.

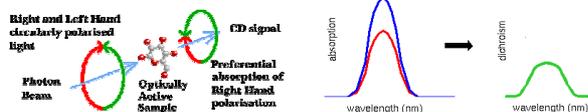
Oscillating molecular dipole can interact directly with oscillating electric vector of electromagnetic radiation of the same frequency

$$h\nu = h\omega$$

Energy is quantized and vibrations are in the range 10^{11} to 10^{13} Hz
=> 30 - 3,000 cm^{-1}

Circular Dichroism

- CD measures the difference between the absorption of left and right handed circularly-polarized light by a chiral chromophore.



- This difference is measured as a function of wavelength, and is always very small ($\ll 1/10000$ of total). Therefore CD spectroscopy requires a high flux source that provides stable linear polarization over and extended wavelength range (VUV-Near IR)

X-ray Scattering by an Atom

- Scattering by an atom is essentially the sum of the scattering of the electron "cloud" around the nucleus.

- Scattering from each electron follows the Thompson equation. Because of the distance between electrons scattering within the atom and the fact that the x-ray wavelength is of the same order as the atomic dimensions, there will be path differences between the scattered waves. These differences will always be less than one wavelength, so the interference will always be partially destructive.

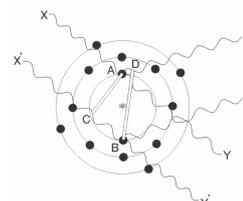


Figure 3.12. The scattering of X-rays from a real atom extended in space.

- This phenomenon is called the *atomic scattering factor*, described by the quantity f_s . This function is normalized in units of the amount of scattering occurring from a single electron in the Thompson equation. At zero degrees, f_s will be equal to the number of electrons surrounding the atom or ion. At higher scattering angles, the factor will be less.

Intensity

- The intensity of the diffracted beam can be given by:

$$I = SLP|F_{hkl}|^2$$

- S is a scale factor that is dependent on the intensity of the source and the detector efficiency.
- LP is a combination of the Lorentz and polarisation factors which for a non-polarised X-ray beam is given by:

$$LP = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta}$$

The Structure Factor F_{hkl}

- For a reflection from a plane hkl . The structure factor F_{hkl} is:

$$F_{hkl} = \sum_{i=1}^{\text{unit-cell}} f_i \cdot \exp\left[-B_i \frac{\sin^2 \theta_{hkl}}{\lambda^2}\right] \cdot \exp[2\pi i hkl \cdot x_i]$$

- $x_i = (x_i, y_i, z_i)$ are the fractional coordinates for atom i in the cell
- hkl are the Miller indices for the reflection
- B_i is the Debye-Waller displacement (thermal) factor for atom (in \AA^2)
- f_i is the scattering factor.

X-ray Diffraction

- In X-ray diffraction f_i is given by:

$$f_i^2 = (f_0 + \Delta f')^2 + (\Delta f'')^2$$

- $\Delta f'$ and $\Delta f''$ are the real and anomalous dispersion terms.
- The first term f_0 depends on the diffraction angle 2θ .

Anomalous X-ray Scattering

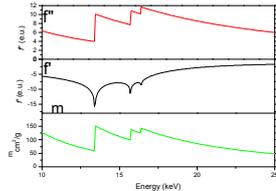
$$f_i^2 = (f_0 + \Delta f')^2 + (\Delta f'')^2$$

- Anomalous scattering* or *anomalous dispersion* occurs when the incident X-ray energy is sufficient to cause photoelectric x-ray production in a target atom. The process is called fluorescence. This phenomenon is responsible for "absorption edge" observed when certain elements interacting with particular wavelength x-rays. In this process a characteristic X-ray photon is produced in the target; subsequent interaction produces coherent X-rays which are slightly out of phase with other coherently scattered X-rays. The net result is a reduction of the scattered intensity from the element.

Bi Wavelength Dependence

Just as the absorption coefficient shows large jumps at “edges” the scattering power of elements shows rapid changes near edges.

- Minimum absorption is obtained near 13.31 eV (0.93 Å)
- Maximum Δf is ca 8 electrons by measuring at 13.3 and 13.5 eV.



Dynamics

Equilibrium

- B factors
- Diffuse scatter

Non-equilibrium

- Laue crystallography
- Rapid Mixing and Small angle scattering

The temperature (B) factor

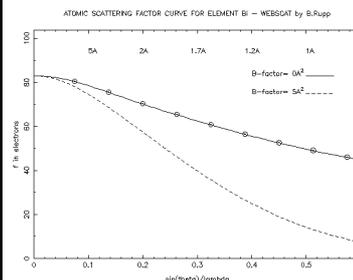
- Atoms are not located at fixed points - undergo vibrations about their mean positions.
- The amplitude of these vibrations increase as the temperature increases.
- Due to such motion, the scattering factor falls off exponentially. The greatest reduction in intensity is at high angles (low d-values).

$$f_B = f \cdot e^{-B(\sin \theta / \lambda)^2}$$

Debye-Waller temperature factor $B = 8\pi^2 \langle u^2 \rangle$

Where $\langle u^2 \rangle$ is mean-square amplitude of atomic vibration. This is directional and can be anisotropic

The temperature (B) factor

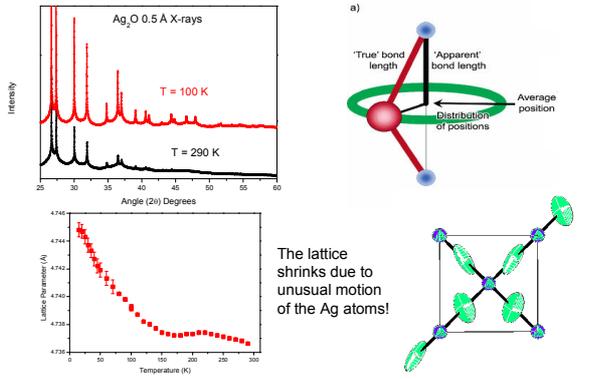


Increasing motion of an atom induces an angular dependent reduction in intensity. The greatest reduction is at high angles (low d-values).

$$f_B = f \cdot e^{-B(\sin \theta / \lambda)^2}$$

Debye-Waller temperature factor $B = 8\pi^2 \langle u^2 \rangle$

Effect of Temperature Ag₂O



Diffuse Scatter

- Diffuse Scatter is the scatter that is not in the Bragg reflections. Every crystal has it.
- Diffuse scatter can arise from:
 - Thermal displacement
 - Occupational disorder
 - Displacive Disorder
 - Short Range Order
 - Stacking Faults