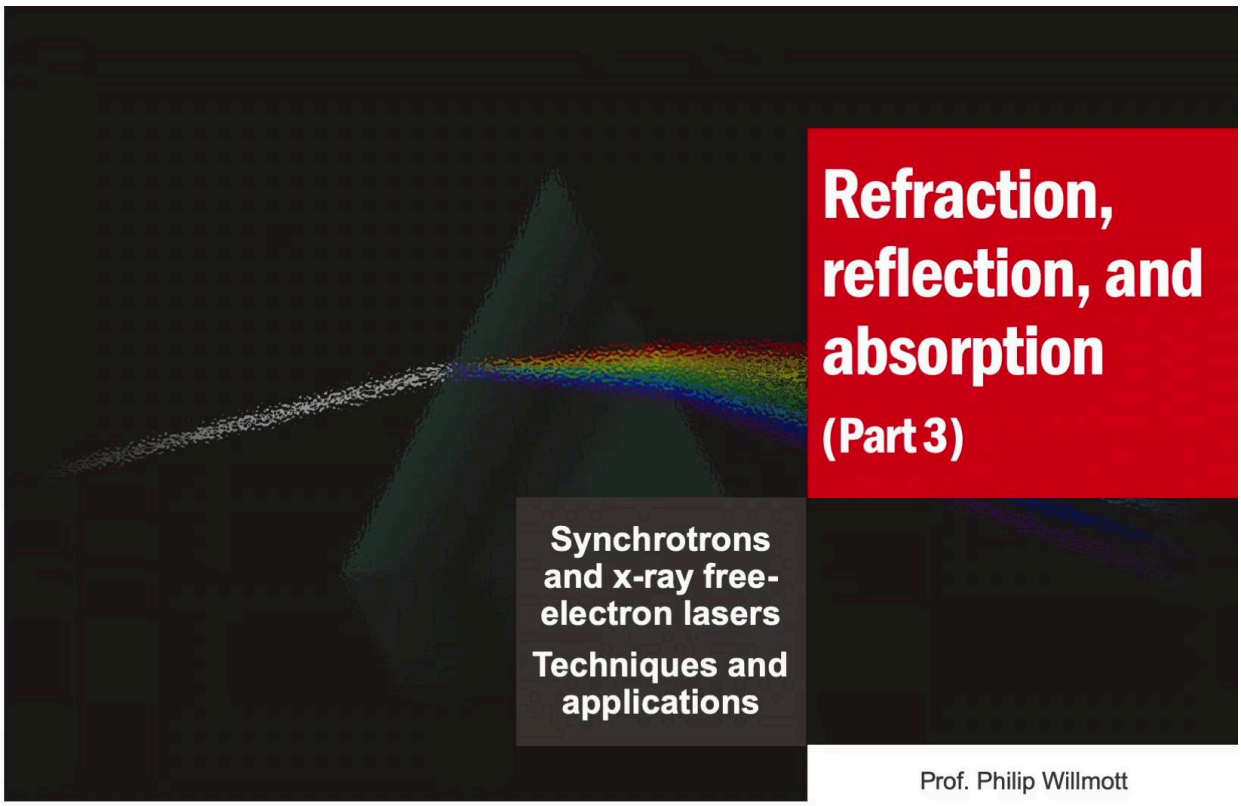


Refraction, reflection, and absorption

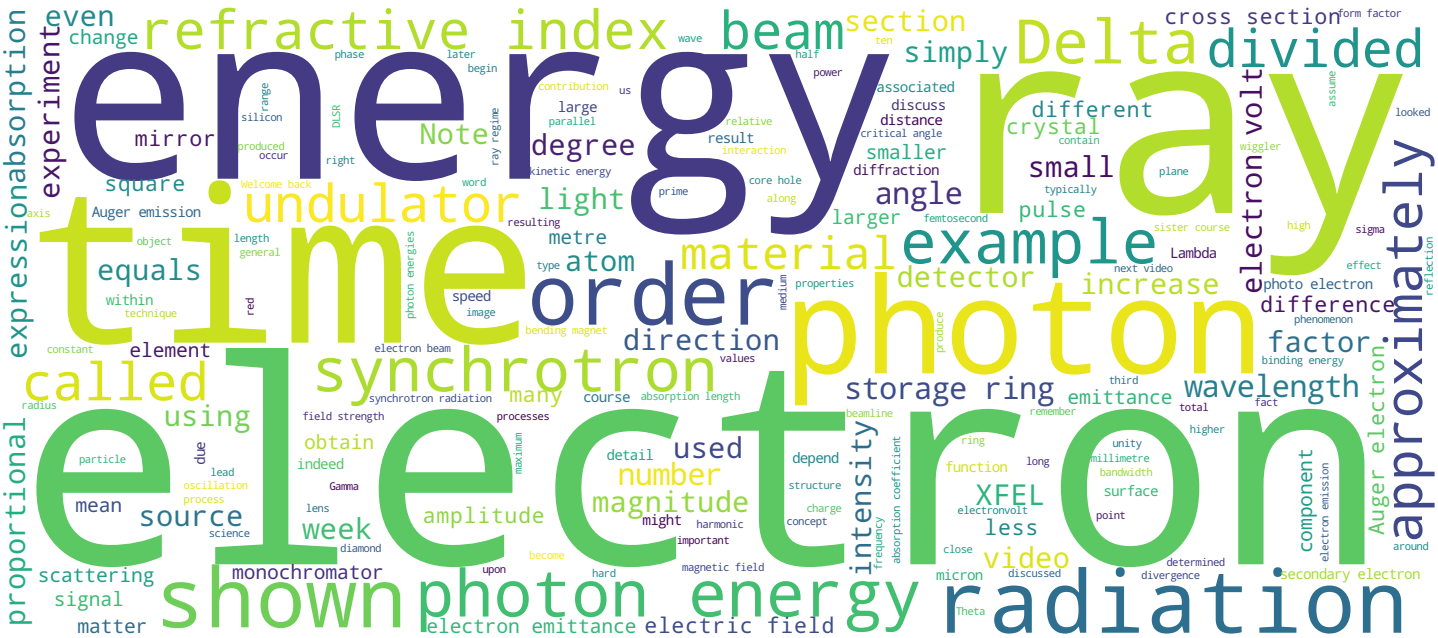
(Part 3)

Synchrotrons and x-ray free-electron lasers

Techniques and applications

École polytechnique fédérale de Lausanne

Prof. Philip Willmott



Hello again. In this final video of the second week, we take a close look at photoabsorbtion and the processes that can occur thereafter, most notably fluorescence, Auger electron production, and the production of secondary electron cascades.

Notes

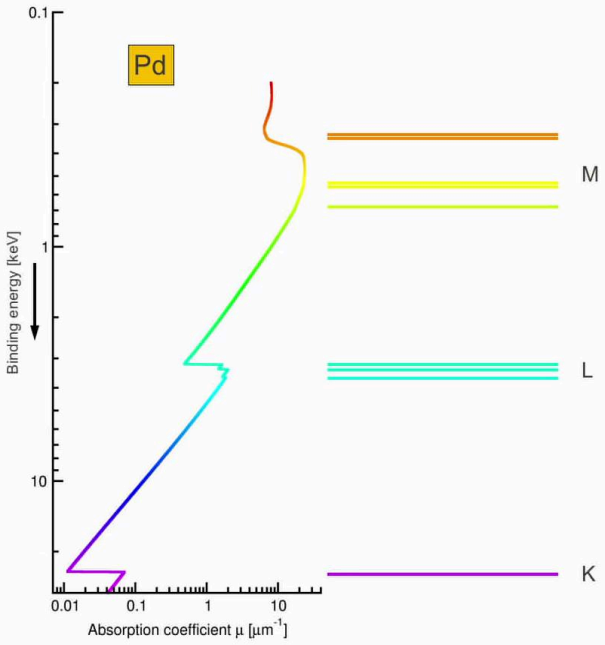
Summary

0m 05s

Photoabsorption

- Photon energy equal to the energy difference between an occupied bound state in the atom E_B and an unoccupied state or vacuum state (free electron) E_f

$$h\nu = E_f - E_B$$



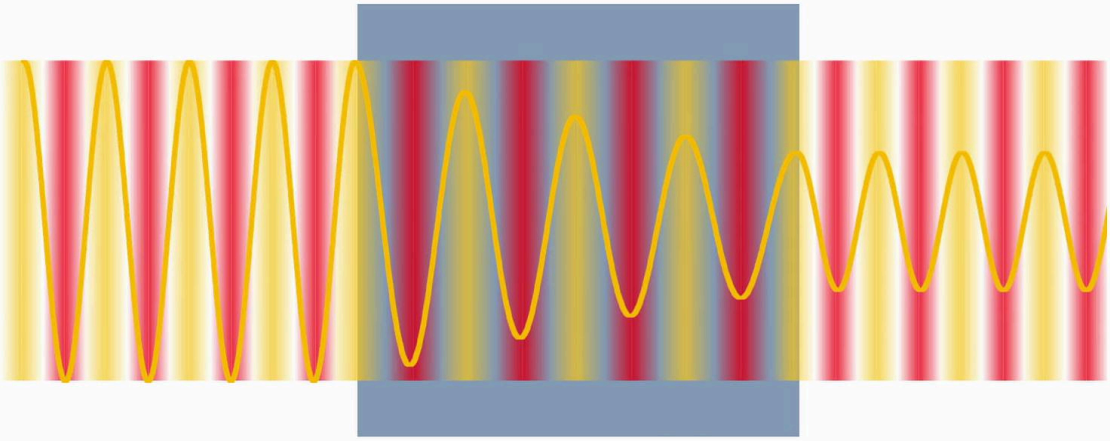
Photoabsorption can occur as a result of promoting an electron from where it resides in, by definition, an occupied state, to either an unoccupied but nonetheless bound state, normally an excited state, or indeed, into a so-called vacuum state for which the electron is completely free and has escaped the system. Photoelectron spectroscopy investigates the energy and momenta of such electrons. Conservation of energy dictates that the absorbed photon has an energy equal to the difference in energy between the final and initial states of the electron. The absorption coefficient as a function of binding energy is shown for Palladium for the most tightly bound 28 electrons with prime quantum numbers: n equals 1, 2, and 3 of the K, L, and M shells.

Notes

Summary

0m 21s

Relationship between refractive index and absorption



$$n = 1 - \delta + i\beta$$

- In matter: $E(z,t) = E_0 \underbrace{\exp(-\beta k_0 z)}_{\text{Exponential decay}} \exp\left[i \underbrace{(1-\delta)k_0}_{\text{Increased wavelength}} z - \omega t\right]$

Imagine now a plane wave of X-rays incident on an absorbing block of material with a refractive index: n equals 1 minus Delta plus iBeta. The refractive index causes the wavelength to increase by a factor of 1 divided by 1 minus Delta while travelling through the block. Moreover, the amplitude of the wave falls exponentially due to absorption. The rate of decay is determined by Beta. In vacuum, the time and space dependent electric field amplitude is given by: E equals E_0 times the exponent of I, k_0z minus Omega T. In the medium however, we need to include the refractive index in the spatial term. Obviously the temporal term Omega T is unaffected, as the frequency of the oscillations of the E field amplitude cannot change. Inserting the expression for the complex refractive index into the equation for propagation through matter, we arrive at an expression that contains a pre factor describing the exponential decay: E_minus B to K_0z, plus the oscillatory term, which the wave vector K decreases by a factor: 1 minus Delta, thus describing the increased wavelength in the medium.

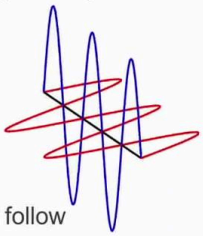
Notes

Summary

1m 19s

Electromagnetic fields – amplitude v intensity

- E- and B-fields: amplitudes E_0 and B_0



- What we (or detectors) "see"
  - Oscillations *much* too fast to follow
    - X-rays: $\nu \sim 10^{18}$ Hz
  - Lose phase information
  - Record intensity $\propto$ |amplitude|^2
- Absorption
  - Exponential decay of *amplitude*
    - $\exp(-\beta k_0 z)$
  - Exponential decay of measured *intensity*
    - $[\exp(-\beta k_0 z)]^2 = \exp(-2\beta k_0 z)$

So what do we actually detect when measuring X-rays? We can't follow the oscillations of the amplitude of the X radiation, which at approximately 10_18 Hertz, is many orders of magnitude too rapid to follow using even the fastest modern electronics. Instead, it's the intensity which is detected. This is proportional to the square of the magnitude of the amplitude. But we have just found out that the amplitude decays as E_minus Beta k_0Z, so the intensity will drop off as the square of this. In other words, iE_minus 2 Beta k_0z.

Notes

Summary

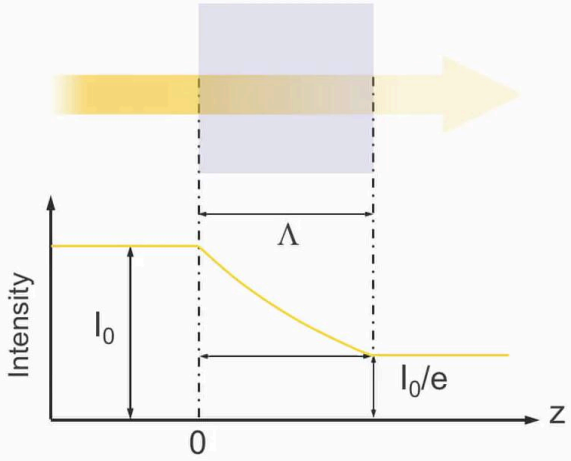
2m 54s

The absorption length and absorption coefficient

$$\exp(-z/\Lambda) = \exp(-2\beta k_0 z)$$

$$\Lambda = 1/(2\beta k_0) \qquad [\propto (h\nu)^3]$$

$$\boxed{\mu = 1/\Lambda = 2\beta k_0} \qquad [\propto (h\nu)^{-3}]$$

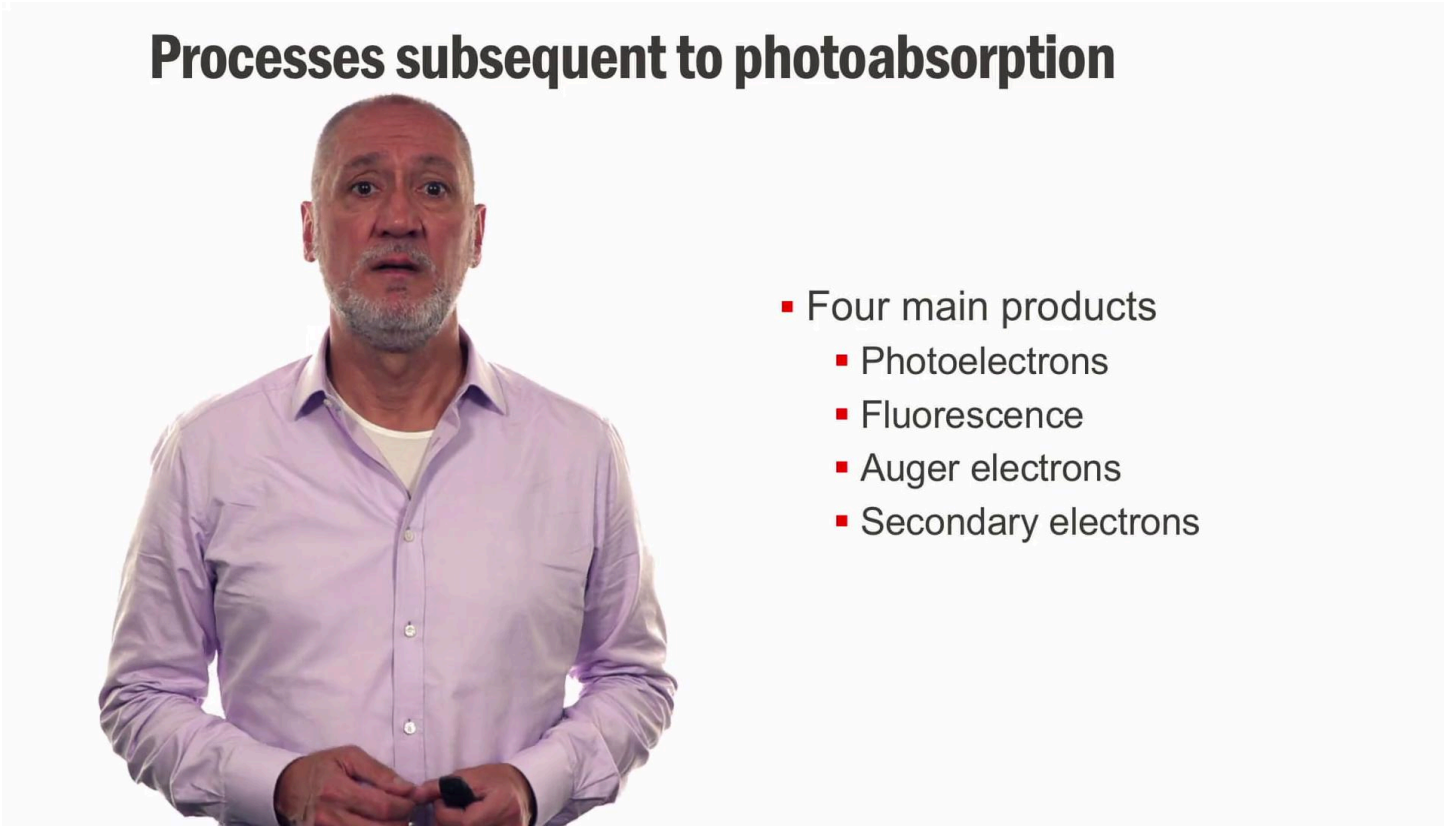


We can now equate the drop of intensity to a decay length or absorption length, which we call big Lambda, leading to: Lambda equals 1 upon 2 Beta k_0. We've already seen that Beta is itself inversely proportional to the fourth power of the photon energy, while K_0 is directly proportional to the photon energy. This therefore leads to an absorption length that is proportional to the cube of hMu. The absorption coefficient Mu, is simply the inverse of the absorption length, and is therefore proportional to the inverse cube of hMu. So, assuming that there are no absorption edges in between, the absorption length of a material will increase by a factor of 8, if the photon energy is doubled. High energy photons travel through material very easily.

Notes

Summary

3m 38s

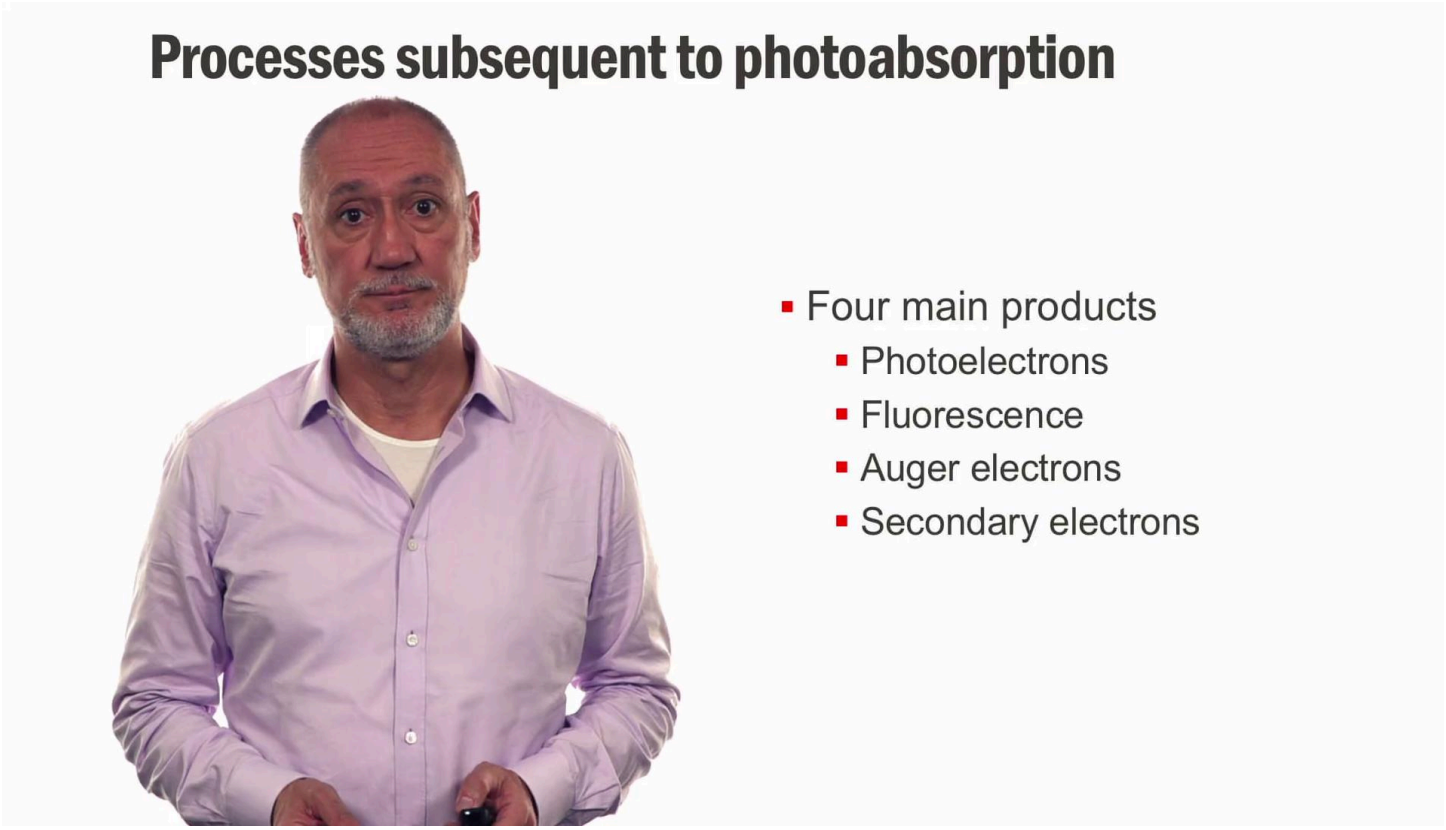


We now conclude this week's discussions of the interactions of X-rays with matter by considering the fate of electrons that have been excited through photoabsorption. The energy added to the system through absorption of a photon is initially channelled into the photo electron. This can in principle, relax again down to its initial state, resulting in the emission of a photon with an energy equal to that of the instant radiation. In many cases, however, the atom may subtly reconfigure during the time the electron is in the excited state, meaning that the state to which it then relaxes is not identical to the initial absorbing state, resulting in energy loss and inelastic scattering. This is the basis for the technique: Resonant Inelastic X-ray Scattering or RIXS, and will be discussed in more detail in the sister course. Anyway, let's assume here that the photoelectron is completely removed from the atom, leaving a core hole behind. Another electron can relax to this hole. The excess energy can be released either as a fluorescent photon or indeed through the ejection of yet another electron in a process called Auger emission.

Notes

Summary

4m 35s



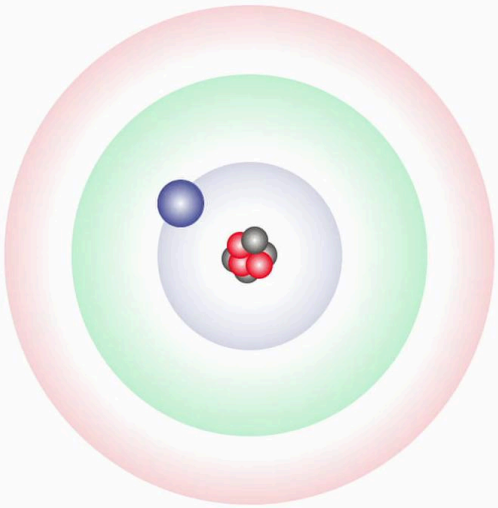
Finally, the ejected electrons can cause the ejection of electrons from outside the parent atom in an avalanche process, resulting in the formation of a secondary electron cascade characterised by their having low kinetic energies typically well under one electron volt.

Notes

Summary

5m 56s

Auger electrons



Auger-electron
KE independent of hν

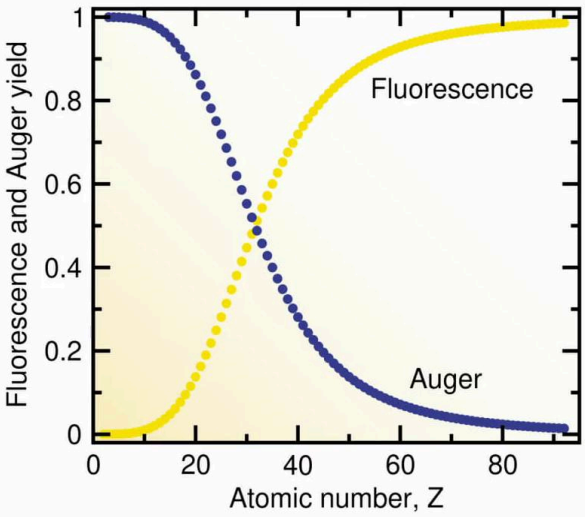
Photoelectrons, fluorescence, and Auger emission are closely interrelated. A photon is absorbed in parting enough kinetic energy to the core electron that it is fully ejected from the atom. This is a photoelectron. The core hole left behind can be filled by an electron from a shell further out, resulting in the emission of a photon with an energy equal to the difference in energy between that of the relaxing electron and the core level. This will be lower in energy than the instant radiation. Auger emission is a three electron process. As in fluorescence, a photo electron is ejected and an outer electron relaxes to fill the resulting core hole. Now, the difference here is the energy gained by relaxation of the second electron isn't expended in fluorescence, but instead in the ejection of a third electron from another orbital. Note that the kinetic energy of this Auger electron is simply the relaxation energy of the second electron, minus the binding energy of the Auger electron itself, and is therefore independent of the instant photon energy, unlike the case of the directly ejected photo electron.

Notes

Summary

6m 17s

Fluorescence or Auger?



$$p_{\text{fl}} \propto (h\nu)^3$$

$$Y_K = \frac{Z^4}{10^6 + Z^4}$$

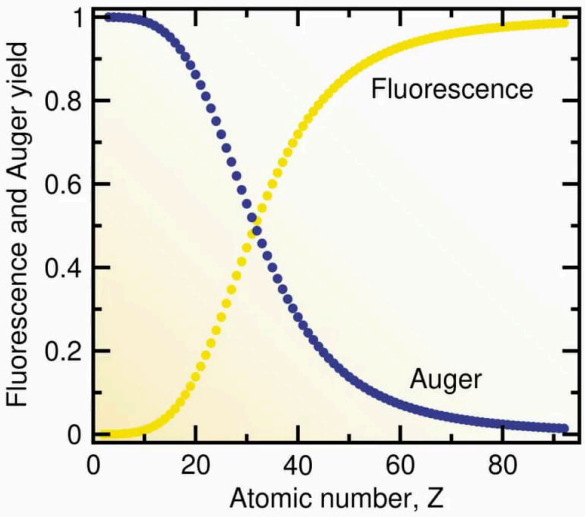
So, which process is more likely to occur? Fluorescence, or Auger electron emission? Clearly, Auger electron emission and X-ray fluorescence are competitive processes. The probability of spontaneous emission of radiation through electronic relaxation was shown by Einstein in 1916 to be proportional to the cube of the relaxation energy. Hence, for a given there atom type, the filling in of a one S hole is more probable than that for a two S hole, for example. Moreover, heavier atoms for which the relaxation back down to a core level is associated with a larger energy drop due to the Coulomb attraction of the nucleus with charge: plus ZE will have a higher fluorescence probability. The empirical expression for the yield for K shell fluorescence is: Y_K is equal to Z_4, divided by 10_6 plus Z_4, plotted here. The probability for Auger emission is simply 1 minus that full fluorescence. The relatively high yield for Auger emission in light atoms has deleterious consequences in macro molecular crystallography. The dominant mechanism resulting in radiation damage of protein crystals is the secondary ionisation of atoms by Auger electrons, which have a significantly larger cross-section than the initial photoelectrons.

Notes

Summary

7m 43s

Fluorescence or Auger?



$$p_{\text{fl}} \propto (h\nu)^3$$

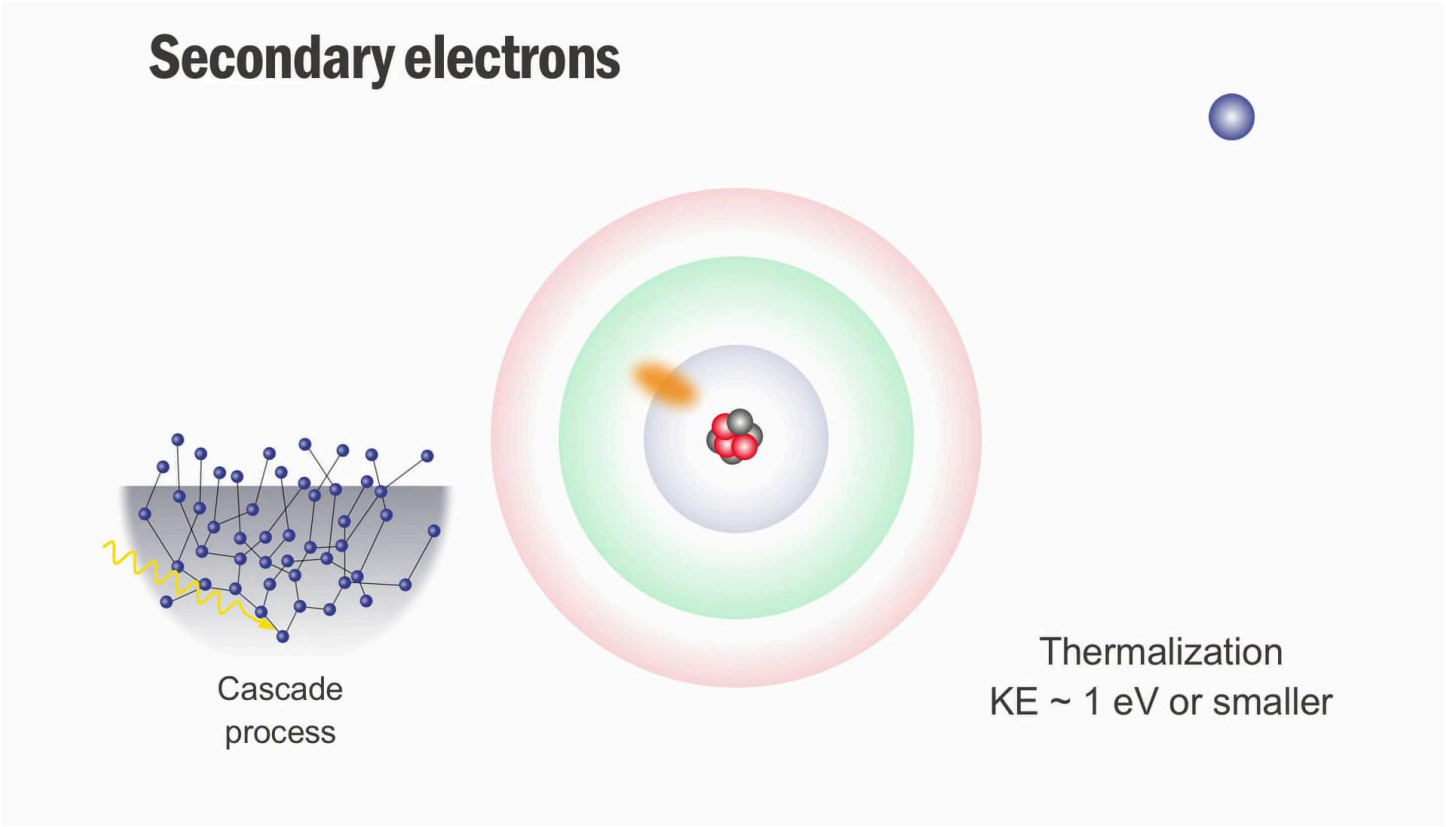
$$Y_K = \frac{Z^4}{10^6 + Z^4}$$

The number of secondary electrons generated can exceed the number of photoionisation events by well over an order of magnitude, leading to radical formation and the breaking of bonds.

Notes

Summary

9m 19s



These secondary electrons partake in an avalanche-like process until the electrons become almost fully thermalized, and the cross section for further capture and electron ejection becomes so small, that the mechanism just shuts down. Because so many more electrons can be released than the initial photo electron, the resulting current is often used as a sensitive probe for absorption processes, such as in many variants of X-ray absorption spectroscopy. Indeed, spatial variation in the amount of secondary electron emission across an irradiated sample can even be imaged using an electron microscope in techniques like Photoemission Electron Microscopy.

Notes

Summary

9m 32s

Summary of important relationships

Summary of the dependence of some basic material properties as a function of photon energy E and atom type Z.

	f''	δ	β	σ_a	σ_T	α_c	μ
E	E^{-2}	E^{-2}	E^{-4} †	E^{-3} ‡	E^0 ($E \lessapprox 1$ keV), E^{-2} ($E \gtrapprox 5$ keV)	E^{-1}	E^{-3}
Z	Z^4	Z^{1} *	Z^4 *	Z^4	Z^2	$Z^{-1/2}$ *	Z^4

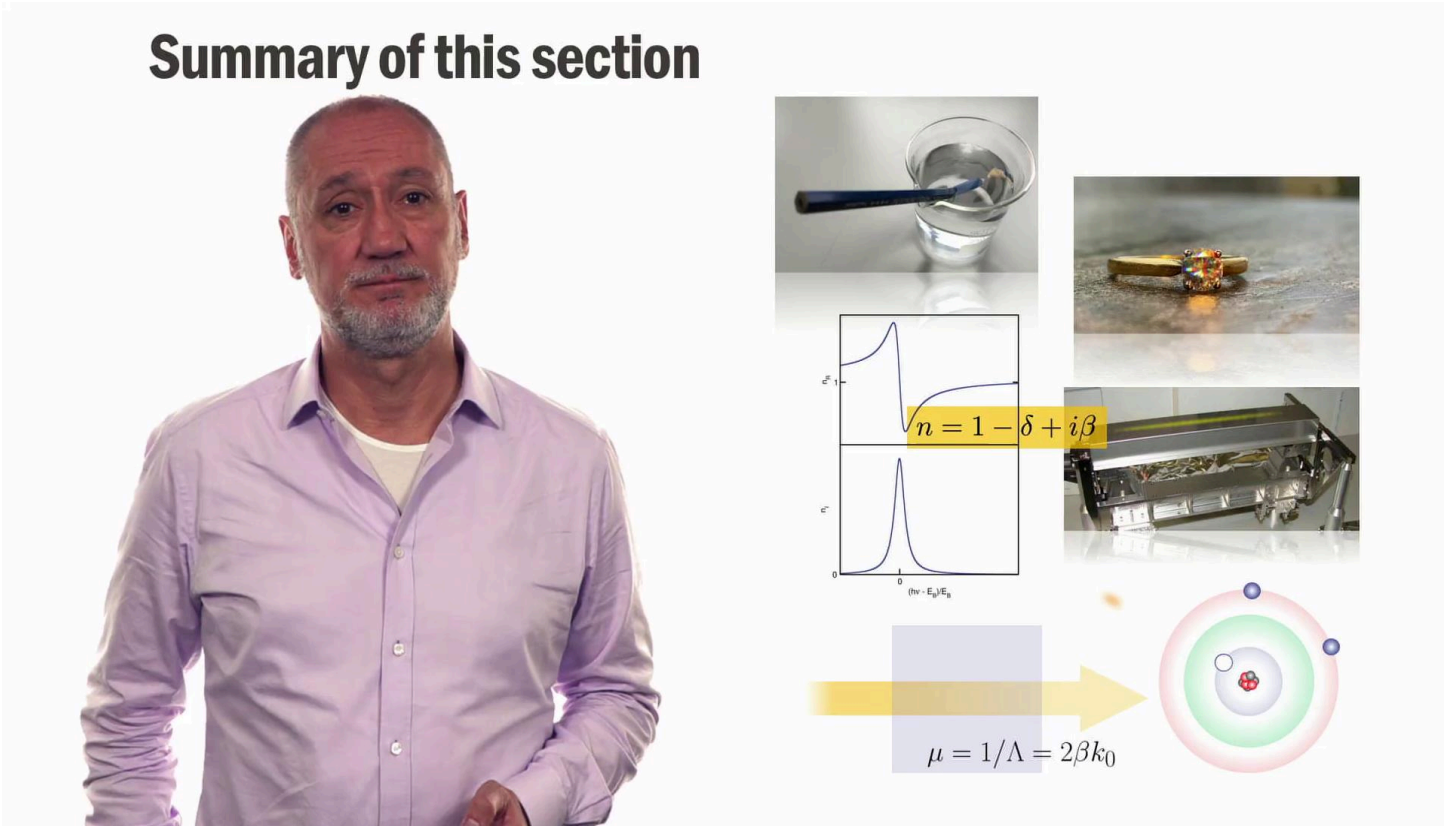
*: Approximate.
† Changes to E^{-2} at high photon energies.
‡ Changes to E^{-1} at high photon energies.

It's worth summarising some important relationships that we have encountered in this week's videos, particularly as a function of the photon energy and the atomic number Z. You might even like to take a screenshot of this to use as a crib sheet for later in this course, and additionally, as a reference in the sister course on synchrotron techniques.

Notes

Summary

10m 19s



To summarise the last section of Week Two, we looked at the phenomenon of refraction and dispersion of different components of the refractive index, which led us to a formal description of the refractive index in the X-ray regime, in which the two parameters of the refractive index decrement, or Delta, and the absorption index, Beta, were introduced and shown to be much smaller than unity. The fact, however, that the real part of the refractive index is less than unity in the X-ray regime led directly to the phenomenon of total external reflection of x rays below a certain critical incident angle that depends on the value of Delta. Finally, we looked more closely at absorption, and the absorption coefficient, Mu, plus processes that can occur subsequent to photoabsorption. Next week, we move on to the basics of machine physics, revisiting electron and the magnetic forces before embarking on a brief discussion of special relativity in the context of synchrotron radiation. We then discuss the properties of synchrotron light that define a facility. We finish by looking at the components of the so-called magnet lattice that make up the essential components of a synchrotron facility.

Notes

Summary

10m 41s