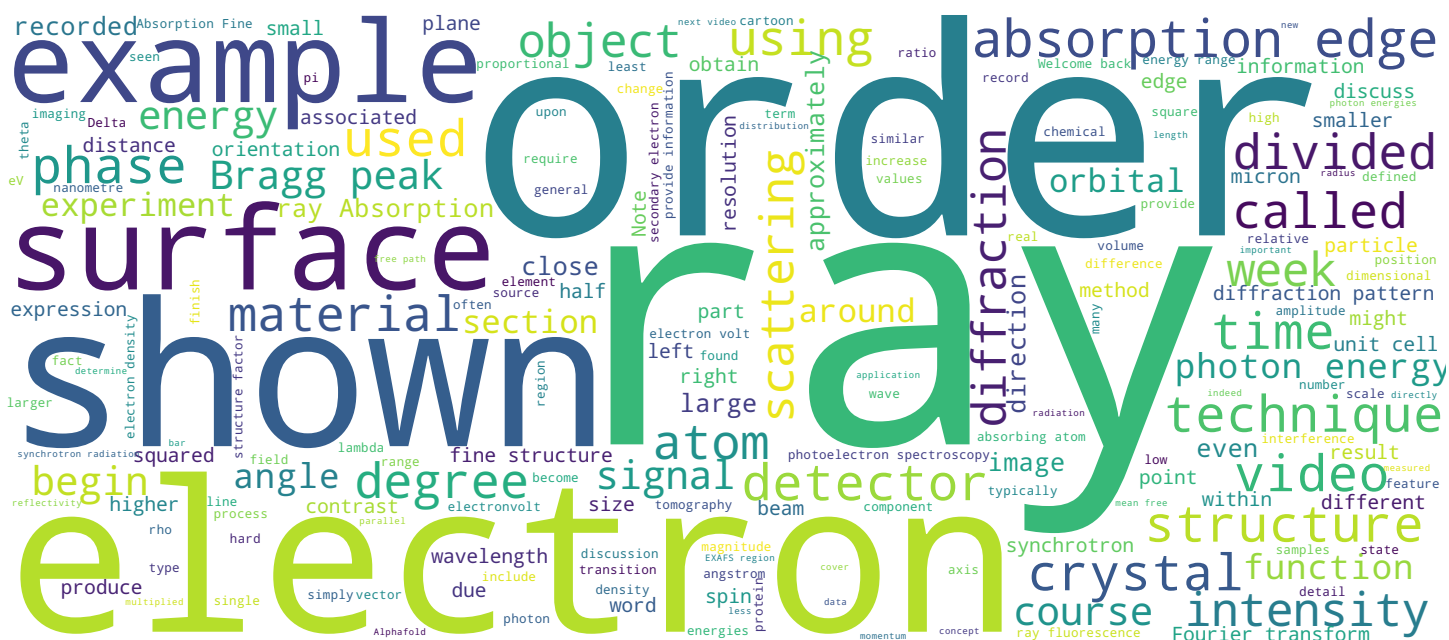


# X-ray absorption spectroscopies Introduction

Synchrotrons and x-ray  
free-electron lasers  
Techniques and  
applications

Prof. Philip Willmott



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Video



# Contents and objectives of this video



- Energy ranges in XAS
- Absorption fine structure
- Relationship between XAS, PES/Auger, and XRF
- Overview of absorption-spectroscopy approaches
- Some practical considerations

Welcome back to the third week of the second course on synchrotron radiation techniques. In this second section, we now begin to discuss X-ray Absorption Spectroscopies, or XAS, and the different variants of techniques which exploit this phenomenon. We begin in this video with an overview of the energy ranges in XAS relative to a given absorption edge, a quick description of absorption fine structure, and the relationship between XAS, photoelectron spectroscopies and Auger spectroscopies, and X-ray fluorescence. There are several ways in which the absorption of a sample can be measured, and the most common of these will be explained. We finish this video with some practical considerations, most importantly, the need to obtain high spectral resolution, and what one must do in order to achieve this.

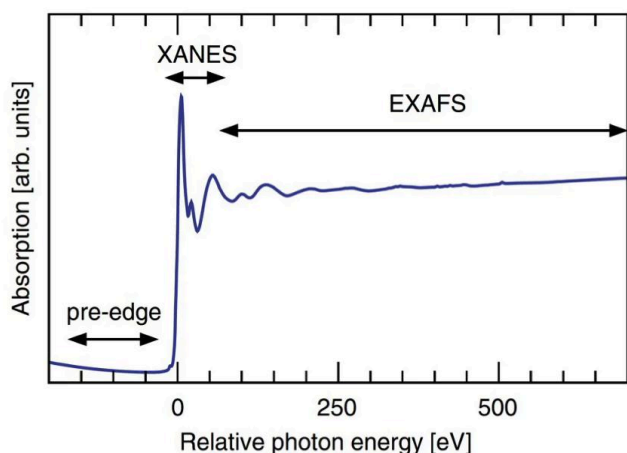
Notes

Summary



0m 05s

# Photon-energy ranges in XAS – XANES and EXAFS



- X-ray absorption fine structure, XAFS
  - Element specific
  - Requires tuneable radiation
  - Does not require crystallinity
    - Good for “real” and “dirty” samples
    - Liquids/solutions
    - Sensitivity down to ppm
- XAFS has two energy ranges
  - X-ray absorption near-edge spectroscopy XANES (alternatively, NEXAFS)
    - Pre-edge to ca. 50 eV above edge
    - De-Broglie wavelength  $\lambda_e \geq 2 \text{ \AA}$ , typically  $\approx 5 \text{ \AA}$
    - Probes extended neighbourhood of absorbing atom
  - Extended x-ray absorption spectroscopy EXAFS
    - ca. 50 – 1000 eV above edge
    - $\lambda_e < 2 \text{ \AA}$ , typically  $\approx 0.5 - 1 \text{ \AA}$
    - $\lambda_e < \text{interatomic distances}$

The first, perhaps obvious, but nonetheless important feature of absorption spectroscopy is that it is element-specific and requires tunable radiation, necessitating the use of synchrotron light. The sample need not be crystalline, making XAS a valuable technique for real and dirty systems, plus also liquids and solutions. In favourable cases, it is capable of detecting components down to parts per million, and with DLSRs potentially even further. XANES, or X-ray Absorption Near Edge Structure, and EXAFS, Extended X-ray Absorption Fine Structure are two complementary techniques used in X-ray spectroscopy to study the local electronic and structural properties of materials. XANES is sometimes referred to as NEXAFS, or Near Edge X-ray Absorption Fine Structure. I will avoid this moniker in this lecture course for the sake of consistency and the fact that, NEXAFS is, in any case for me, orthographically far too close for comfort to EXAFS. XANES measures the absorption of X-rays by a material as a function of the photon energy near the absorption edge of a particular element.

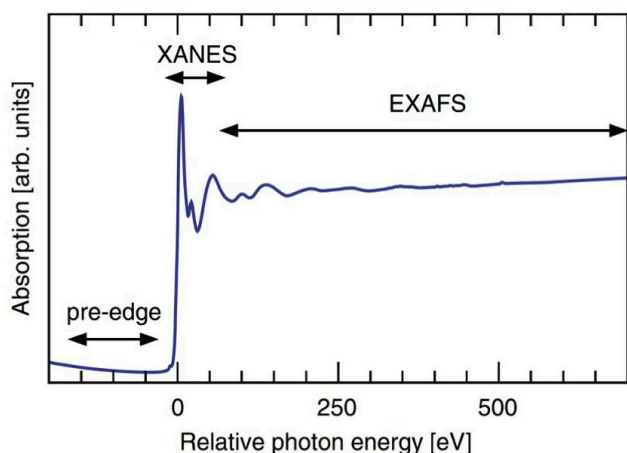
Notes

Summary



0m 57s

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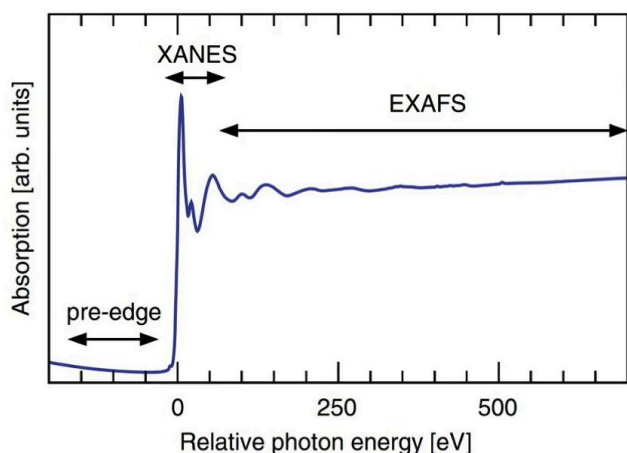
By analyzing the shape and intensity of the absorption spectrum, XANES can provide information about the electronic and chemical environment of the absorbing atom, including its oxidation state, coordination geometry, and bonding. EXAFS on the other hand, measures the oscillatory component of the X-ray absorption spectrum at energies above the absorption edge. By analyzing the fine structure of the spectrum, EXAFS can provide information about the local atomic structure including bond lengths, coordination numbers, and disorder in the material. What energy ranges are applied for XAS experiments? Most, if not all, such experiments are concerned with the response of a system close to an absorption edge of one of its component elements. As such, there are three regions of interest, a pre-edge region, which might contain information about surface absorbates, covering maybe one hundred electronvolts below the formal absorption edge; the XANES region, which includes the actual absorption edge in the first 50 to 100 eVs above that edge; and the EXAFS region that follows the XANES regime up to around a thousand electronvolts above the edge.

Notes

Summary



# Photon-energy ranges in XAS – XANES and EXAFS



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The relatively low energies of the electrons emitted in the XANES region means they have de-Broglie wavelengths of the order of five Å, meaning that XANES probes the extended neighbourhood of the absorbing atom. The word extended in Extended X-ray Absorption Fine Structure refers to the oscillations observed in the EXAFS region due to interference of photoelectron wavefunctions with themselves as a result of backscattering from other atoms in the immediate neighbourhood of the absorbing atom. Note that according to the expression we derived in the first section of this week, the energy range of EXAFS results in wavelengths for the electron waves between approximately a half and two Å. That is smaller than most interatomic distances.

Notes

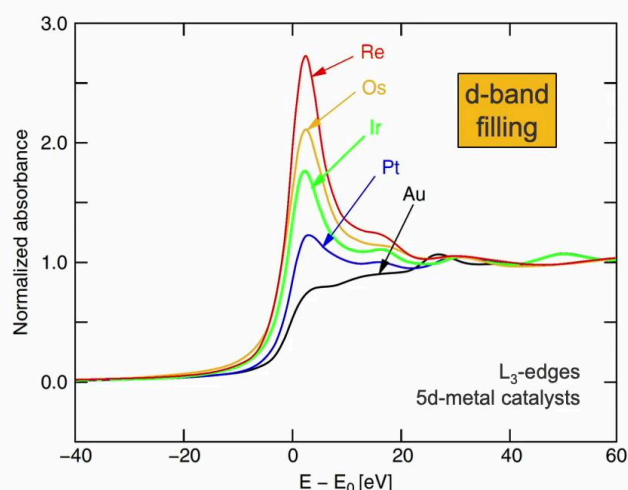
Summary



3m 45s



# The 'F' in XAFS



75 186.207 <b>Re</b> [Xe]4f <sup>14</sup> 5d <sup>5</sup> 6s <sup>2</sup>	76 190.23 <b>Os</b> [Xe]4f <sup>14</sup> 5d <sup>6</sup> 6s <sup>2</sup>	77 192.217 <b>Ir</b> [Xe]4f <sup>14</sup> 5d <sup>7</sup> 6s <sup>2</sup>	78 195.085 <b>Pt</b> [Xe]4f <sup>14</sup> 5d <sup>9</sup> 6s <sup>1</sup>	79 196.967 <b>Au</b> [Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>1</sup>
5	4			

G. Meitzner *et al.*, J. Phys. Chem., **96**, pp. 4960–4964 (1992)

- Fine structure
  - Modulation of an atom's x-ray absorption cross-section due to its chemical and physical state
- Sensitive to
  - Oxidation state
  - Distances, coordination number, species of the atoms surrounding the absorbing atom
  - Physi-/chemisorbed surface species
  - Coordination (metal-ligand) chemistry
  - Not normally surface sensitive (some exceptions)
- Fields of research
  - Catalysis
  - Biochemistry
  - Environmental sciences
  - Polymer sciences
  - Magnetism
  - Cultural heritage
  - ...

The fine structure in XAFS is found in both the XANES and EXAFS region, and is due to the sample's chemical and physical state. It can reflect oxidation states, neighbour distances, and coordination number, provide information on the orientation, and physisorption characteristics of surface species, and yield insights into the coordination chemistry of metal ligands. A didactic and illustrative example is shown here on the left of the absorption edges of different 5d-metals. The intensity of transitions to excited bound state but unoccupied orbitals can be high depending on their density and selection rules. In early experiments, for which the spectra were recorded on photographic strips, These bound excited state features were easily identifiable as sharp and strong white lines on the photographic paper. This is how they were subsequently named in XANES spectra. The spectra shown here of the five 5d-metals, rhenium, osmium, iridium, platinum, and gold reveal their electronic configuration. The ground state electronic configuration of rhenium is Xenon 4f<sup>14</sup> 5d<sup>5</sup> 6s<sup>2</sup>. As one moves to the right in the periodic table from rhenium, the remaining five available 5d states are gradually filled.

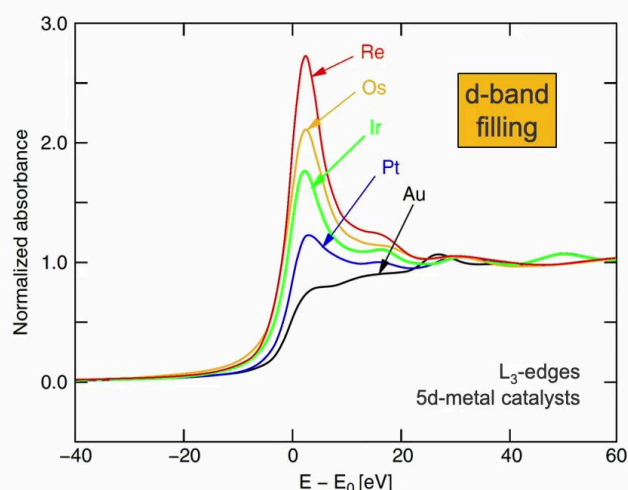
Notes

Summary



4m 37s

# The 'F' in XAFS



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5	4	3	1	0

G. Meitzner *et al.*, J. Phys. Chem., **96**, pp. 4960–4964 (1992)

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  - ...

In gold, these states are all occupied and a transition to here from the 2p electrons associated with the L-edge is excluded in contrast to the elements rhenium to platinum, for which bound, but unoccupied 5d states, which are below the ionization threshold, are seen as intense white lines. As gold has no such unoccupied states, excitation is directly into the unbound continuum. XAS in general is used in very many different disciplines, such as catalysis and energy research, biochemistry, the environmental sciences, polymer sciences, magnetism, and cultural heritage to name just those fields which we will touch on in this course.

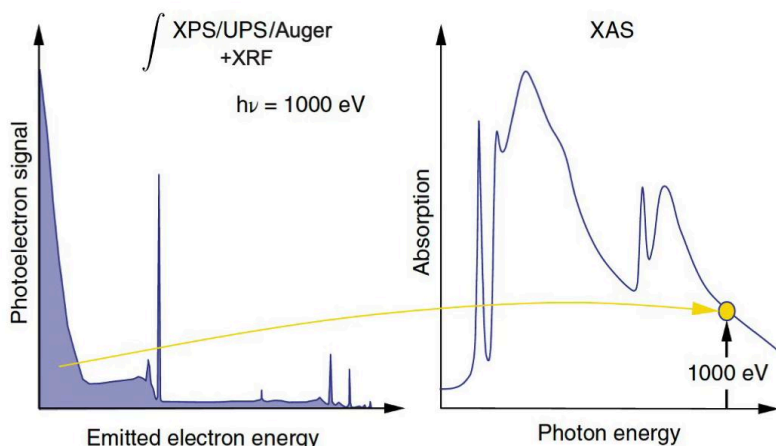
Notes

Summary



6m 18s

# Relationship between XAS, XRF, and PES/Auger



- Sum of fluorescence, Auger electrons, and directly emitted photoelectrons
- XAS measures the total density of states of the **initial core level** with all possible final states, consistent with conservation and selection rules
- Note: In contrast, photoelectron spectroscopy probes the final (free-electron) state only
- Depending on conditions, one process subsequent to absorption may dominate...

Each point in a XAS spectrum includes all the possible processes occurring subsequent to absorption of a photon of energy,  $h\nu$  and can thus be thought of as the energy-integrated signal from photoelectron spectroscopy, Auger spectroscopy, and fluorescence for the photon energy of interest. XAS probes the total density of states of the initial core level via all possible final states that are consistent with conservation of energy and momentum. In contrast, photoelectron spectroscopy probes only the final free electron state. Depending on the conditions, such as incident photon energy, polarization, et cetera, the process that dominates after absorption can vary significantly.

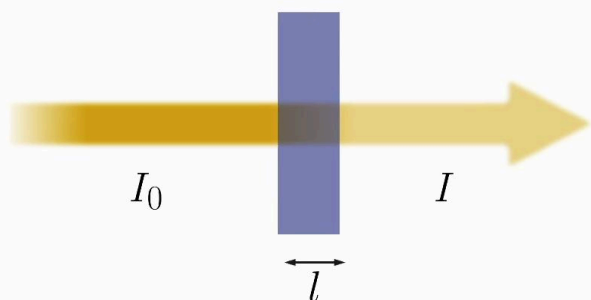
Notes

Summary



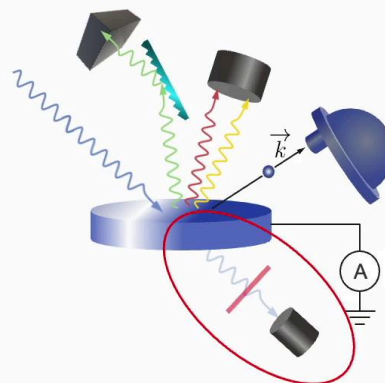


# Methods of ascertaining the degree of absorption



$$I = I_0 e^{-\mu l}$$

- Transmission
  - $l$  neither
    - too thin (too little absorption) nor
    - too thick (insufficient transmission)
- In some experimental configurations, measuring transmission behind sample is impractical



What methods are at hand to determine the degree of absorption? The most obvious is simply the degree of transmission. Depending on the sensitivity of the detector and the incident intensity, this approach will have a limited range, whereby the ratio of  $I$  divided by  $I_0$  is neither too close to zero or too close to unity, that is, the sample thickness is neither too thin nor too thick. Moreover, in some experiments, measuring transmission behind a sample might be impractical, for example, the samples which are heated by a back plate.

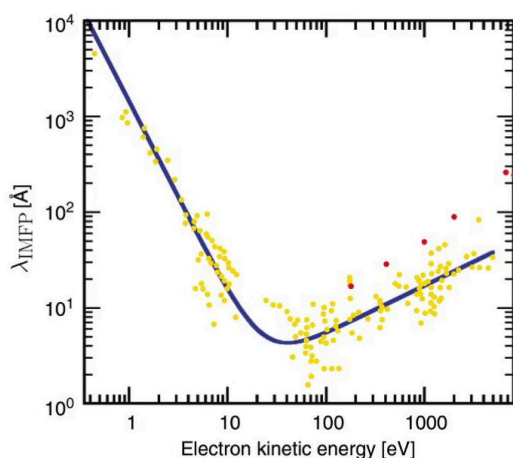
Notes

Summary



8m 02s

# Methods of ascertaining the degree of absorption



- Photoabsorption attenuation lengths for most elements (even at absorption edges) > 100 nm, often several microns
  - i.e. larger than  $\lambda_{\text{IMFP}}$  for all photoelectrons above ca. 1 – 5 eV
  - Only electrons within  $\sim \lambda_{\text{IMFP}}$  of surface can escape without being inelastically scattered
  - Large majority of produced photoelectrons undergo multiple collisions and produce a cascade of increasingly thermalized “secondary electrons” with kinetic energies  $\sim 0.1 - 5$  eV
  - Secondary electrons have  $\lambda_{\text{IMFP}} \sim$  microns
  - Record secondary-electron current as measure of degree of photoabsorption

Another approach is to record the so-called secondary electron current. The photoabsorption depth of most materials, even at their absorption edges, are greater than a hundred nanometers and can often be several microns or even several tens of microns. The lengths are significantly larger than the inelastic mean free path of electrons at least for electron kinetic energies above about one eV or thereabouts. Hence, only electrons with very low kinetic energies of around an eV will escape the material. Almost all photoelectrons are eventually converted into low-energy secondary electrons. Recording the drainage current associated with these electrons is thus an accurate measure of photoabsorption.

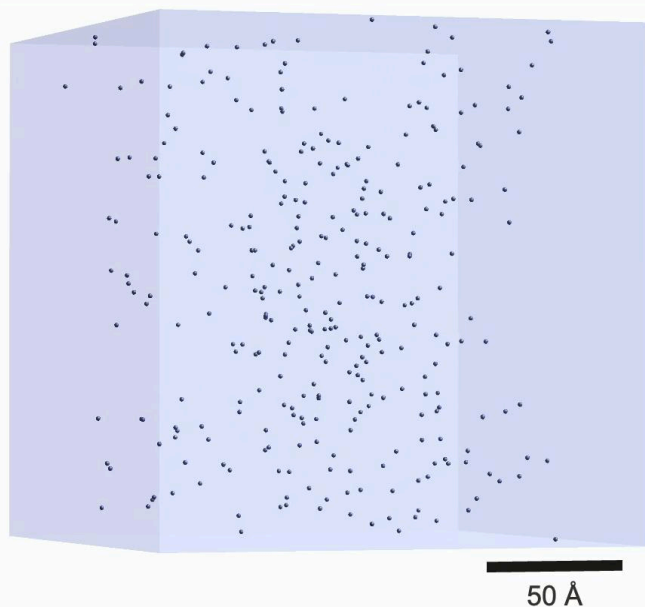
Notes

Summary

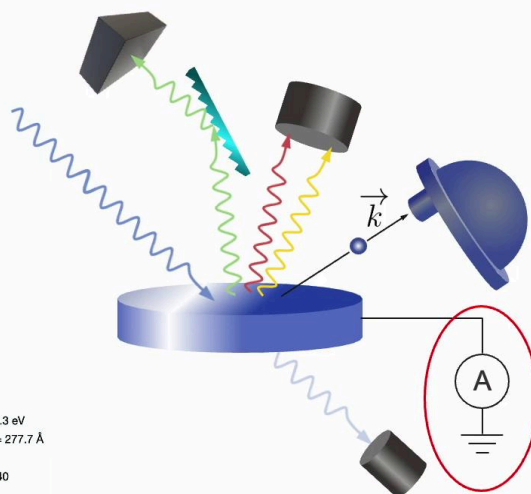


8m 41s

# Methods of ascertaining the degree of absorption



Average KE = 2.3 eV  
Average IMFP = 277.7 Å  
 $t = 13.7922$  fs  
# electrons = 440



Shown here is a cartoon of the generation of secondary electrons. The cartoon is only semi-physical, insofar it conserves energy. However, it does ignore binding energies, which is semi-valid for the higher electron energies to begin with, but is certainly not so for the lower ones. It assumes that each inelastic collision divides the energy of the incoming electron equally between it and the single electron it releases. The semitransparent cube has an edge that are 180 Å in length. Measuring the total electron yield is a common approach for thick or embedded samples.

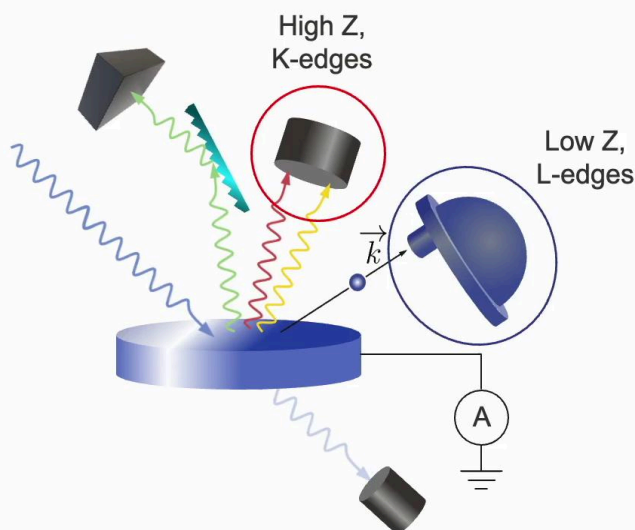
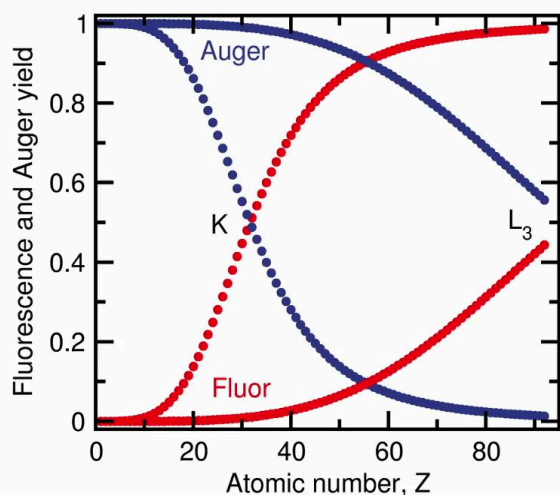
Notes

Summary



9m 31s

# Methods of ascertaining the degree of absorption



N.B. Detection via Auger-electron yield provides high surface sensitivity!!

Yet another approach and one that is often used for insulating materials is X-ray fluorescence, in which the entire fluorescence spectrum is integrated, in other words, the fluorescent signal is not dispersed. For absorption of low Z materials or for lower energy absorption edges, the Auger electron yield can provide the necessary signal including element and surface sensitivity.

Notes

Summary

10m 14s



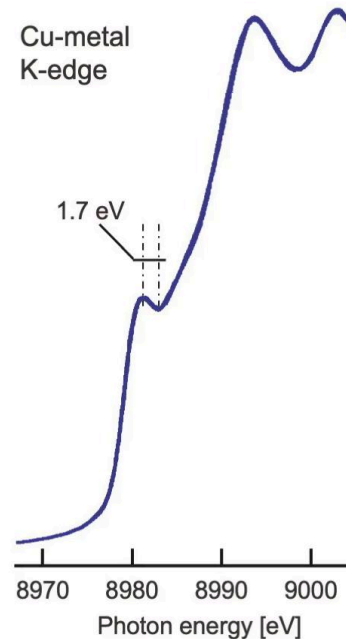
# Other experimental considerations

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

$$E = \frac{hc}{\lambda}$$

$$\Rightarrow d\theta = \tan \theta \frac{dE}{E}$$

- e.g. Pre-edge Cu-metal
  - Si(111) mono: pk-valley = 1.7 eV
  - $\theta = 12.718^\circ$
  - Require  $< 0.85$  eV resolution
- $\Rightarrow d\theta < 20 \mu\text{rad}$
- But natural opening angle =  $1/\gamma \sim 200 \mu\text{rad}$ 
  - $\Rightarrow$  Need to collimate polychromatic radiation before mono using bent mirror



An important requirement in many spectroscopic techniques is good spectral resolution. The monochromator will select a band of photon energies or wavelengths according to Bragg's law  $\lambda$  equals  $2d \sin \theta$ . It is a simple exercise to demonstrate that if the incident angle  $\theta$  has a range of values,  $d\theta$ , then the relative energy bandwidth,  $dE$  upon  $E$ , is equal to  $d\theta$  divided by  $\tan \theta$ . For example, measuring the pre-edge of copper using a silicon 111 crystal monochromator requires a divergence of the beam that is smaller than  $20 \mu\text{rad}$  in order to resolve the small feature shown here at 8980 electron volts.

Notes

Summary





# Other experimental considerations

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$$\Rightarrow d\theta = \tan \theta \frac{dE}{E}$$

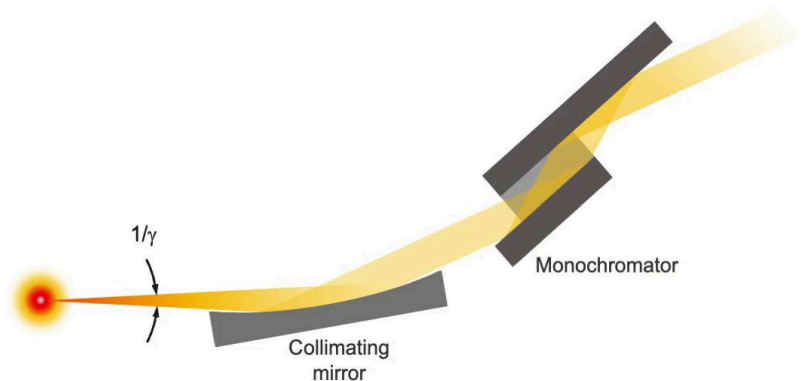
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But the natural opening angle of synchrotron radiation is  $1/\gamma$ , where  $\gamma$  is the ratio of the storage ring, electron beam energy, to the electron rest-mass energy. This is of the order of  $200 \mu\text{rad}$ , depending, of course, on the facility's storage ring energy. Hence, for those beamlines concerned with high-resolution spectroscopy, the beam needs to be collimated by a bent mirror in the plane containing the diffracted beam.

Notes

Summary



## In the next video...



In the following video, we begin to look at specific absorption techniques by considering XANES, which probes absorption features in the immediate energy regime around the absorption edge.

Notes

Summary



12m 04s