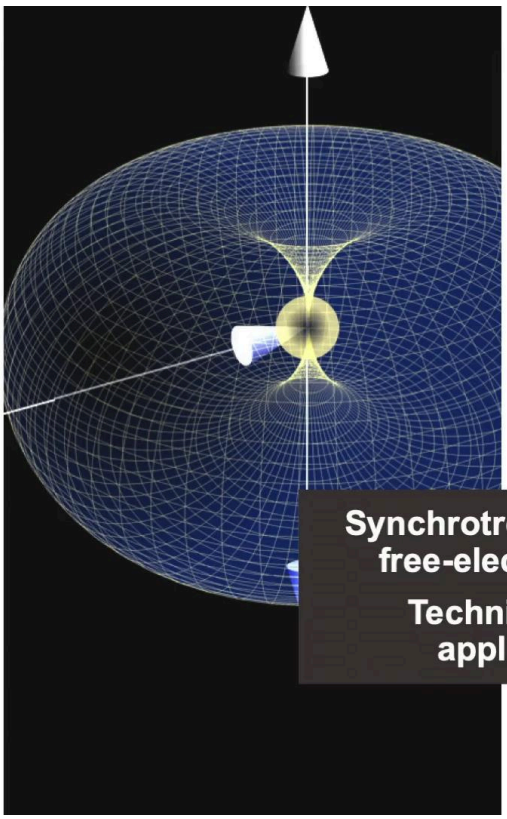


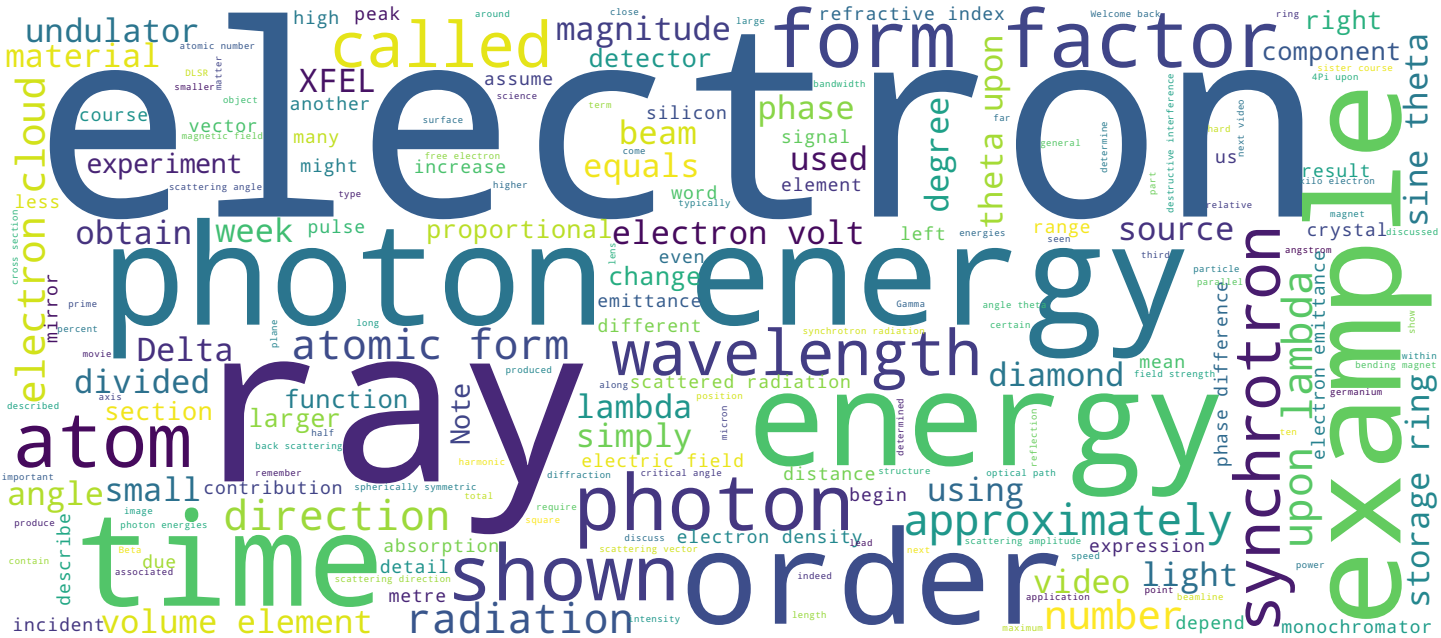
Thomson scattering
(Part 1)

Synchrotrons and x-ray free-electron lasers

Techniques and applications

École polytechnique fédérale de Lausanne

Prof. Philip Willmott



Search MOOC

Video

Contents and objectives of this video

- Elastic scattering of photons
- The Q-vector
- Elastic scattering from an atom
- Atomic scattering factors
- Sulfur – the movie!

Welcome back. We begin now the second section of week two of this course, Synchrotrons and X-ray Free Electron Lasers, Techniques, and Applications. In this video, we will describe the response of the cloud fo electrons that surround an atom to incoming electromagnetic radiation. This scenario differs in two important ways to the description of dipole radiation covered in the last video. Firstly, we can no longer in general consider the electron cloud to be a point source. Secondly, the electrons are no longer free, but are in fact bound to the atom by Coulomb attraction to the positively charged nuclear core. Moreover, we need to consider both the direction and wavelength of the scattered radiation encapsulated in the so-called Q vector. These considerations lead us to the atomic form factor. An example of which we look at in more detail for the case of sulphur.

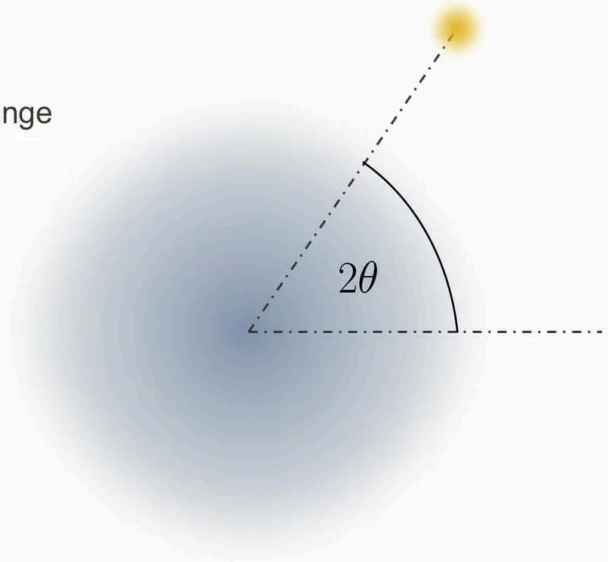
Notes

Summary

0m 05s

Elastic scattering of photons

- Elastic (Thomson) scattering of photons by electrons
  - $h\nu_{in} = h\nu_{out}$
- Direction (momentum) of photon can change thru' an angle 2θ
  - Wavevector $k = 2\pi/\lambda$
  - $E = hc/\lambda = \hbar ck$
  - Photon momentum $= h/\lambda = \hbar k$
  - $|k_{in}| = |k_{out}|$
  - $\overrightarrow{\Delta k} = \overrightarrow{Q} = \overrightarrow{k_{in}} - \overrightarrow{k_{out}}$
  - Q = "scattering vector"



We begin by considering elastic scattering by electrons that is with no loss in photon energy. This is referred to as Thompson scattering. Although the photon energy remains invariant, the direction or momentum of the photon can change. Don't forget, momentum is a vector. It has both a magnitude and a direction. First, we introduced the so-called k-vector or wavevector given by k is equal to 2Pi divided by lambda. Both the photon momentum and energy are proportional to k, as we see here. Let's consider scattering of a photon by a certain angle, which we call 2 theta as against simply theta for mathematical reasons that will shortly become apparent.

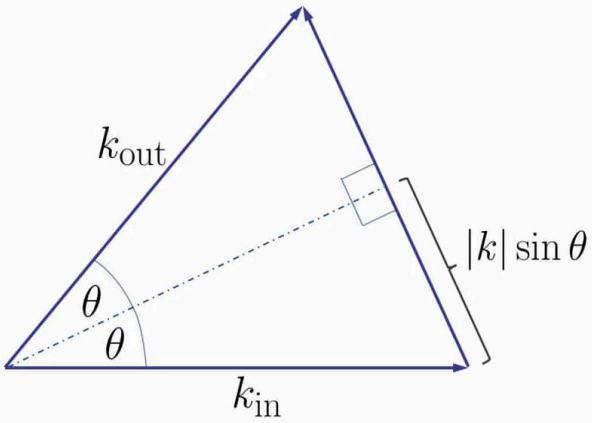
Notes

Summary

1m 14s

The Q-vector

- Elastic (Thomson) scattering of photons by electrons
  - $h\nu_{in} = h\nu_{out}$
- Direction (momentum) of photon can change thru' an angle 2θ
  - Wavevector $k = 2\pi/\lambda$
  - $E = \hbar ck$
  - Photon momentum $= h/\lambda = \hbar k$
  - $|k_{in}| = |k_{out}|$
  - $\overrightarrow{\Delta k} = \overrightarrow{Q} = \overrightarrow{k_{in}} - \overrightarrow{k_{out}}$
  - Q = "scattering vector"



$$Q = 2|k| \sin\theta = (4\pi/\lambda) \sin\theta$$

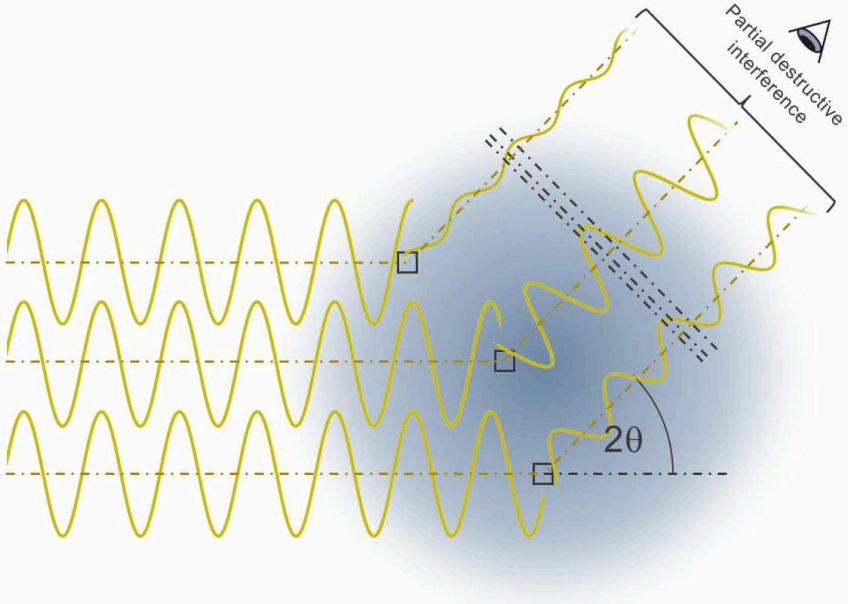
The vector difference between the incident and scattered photon wavevectors, which have the same magnitude but different directions, is equal to Q, which is referred to as the scattering vector. The magnitude of Q is easy to calculate as follows, half of Q is simply equal to k sine theta. As k equals 2Pi upon lambda, Q is therefore equal to 4Pi upon lambda sine theta.

Notes

Summary

2m 14s

Scattering from an atom



Scattering amplitude decreases with increasing angle 2θ!!

Now, let us consider a plane wave incident on a cloud of electrons with an electron density rho surrounding an atom, which is a function of the position in the cloud r. We make the somewhat dubious initial assumption that the electrons are unbound. We will correct for this later in our discussions. Now let us consider different volume elements, dV within the electron cloud, three of which are shown here. Each volume element will experience a different phase of the incident electromagnetic wave, which depends solely on their locations. The scattered radiation at an angle 2 theta from each volume element will have an amplitude that depends on the electron density at that element and the phase determined by the insurgent radiation and the angle 2 theta. This leads to partial destructive interference, which becomes more pronounced with increasing scattering angle.

Notes

Summary

2m 48s

Scattering between elements dV

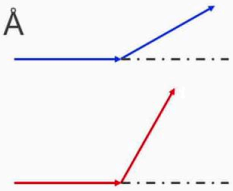
Optical path difference (OPD) between two volume elements dV separated by d

$$\mathrm{OPD} = 2d\sin\theta$$

$$\#\,\mathrm{wavelengths} = 2d\,\sin\theta/\lambda$$

$$\phi = 4\pi d\sin\theta/\lambda\; = Qd$$

- Example
  - θ = 14.48°, sin θ = 0.25. λ = 1 Å
    sin θ/λ = 0.25 Å^{-1}
  - θ = 30°, sin θ = 0.5. λ = 2 Å
    sin θ/λ = 0.25 Å^{-1}



- Interference effect (i.e., amplitude of scattered radiation @ 2θ) the same in both cases because sin θ/λ is the same

Let us now try to quantify the phase difference between scattered radiation from any two volume element dV separated by distance d. Once we have established this, we can integrate the contributions from all the volume elements and obtain the scattering amplitude of a given atom as a function of scattering angle and photon energy. We first identify the optical path difference between the scattered radiation from the two elements shown by the red line. Let's look at this in detail. The optical path difference, or OPD, is simply 2d sine theta. Hence, the number of wavelengths this corresponds to is the optical path difference divided by lambda. And therefore, the phase difference given in radians that is, is simply the number of wavelengths multiplied by 2PI. In other words, 4Pi d sine theta upon lambda. But hang on, Q is equal to 4Pi sine theta upon lambda, hence the phase difference is simply Q Times d. For a given separation d, a given sign theta upon lambda will result in the same interference. So if we consider the example of sine theta upon lambda is equal to 0.25 we would obtain the same phase difference fi, and therefore the same interference between two elements for the two cases shown here for 1 angstrom radiation scattered through 22.96 degrees and 2 angstrom radiation scattered through 60 degrees.

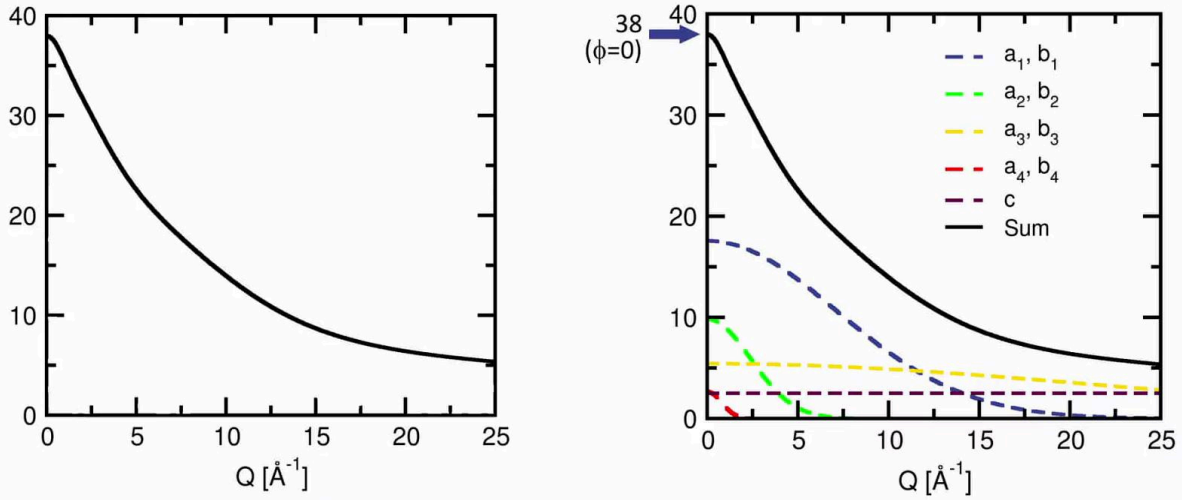
Notes

Summary

3m 56s

f - The atomic scattering factor

- Example: strontium (Z = 38)



f describes the spatial distribution of elastic scattering by an atom relative to the direction of the incident photon

The total scattering amplitude as a function of sine theta upon lambda, or more commonly Q, which is proportional to sine theta upon lambda, can thus be calculated by integrating scattering from all the infinitesimal volume elements dV over the entire electron density cloud surrounding the atom. This integrated value is called the atomic scattering factor or the atomic form factor. And as we have already said, it describes the angular distribution of elastic scattering by an atom relative to the direction of the incident being of known photon energy. For the more mathematically inclined view, the atomic form factor is in fact simply the Fourier transform of the electron density cloud rho r. An example is shown here for strontium, which has the atomic number 38. It can be described as the sum of 4 Gaussians, plus a constant, which we can see component for component here. Note that the value of F at Q equals 0 is simply Z, the atomic number. This is because if Q is equal to 0, then scattering is in the forward direction for which theta is equal to 0. All the scattered radiation remains in phase because fi is always 0 for all the volume elements, and hence integration is simply the summation of the electron density of the atom, which is equal to the number of electrons Z at least the neutral atoms.

Notes

Summary

5m 54s

Database for atomic scattering factors

- Also called “atomic form factors”
- Fit to four Gaussians + constant

$$f^0(\sin\,\theta/\lambda) = \sum_{i=1}^{4} a_i \exp(-b_i \sin^2\theta/\lambda^2) + c$$

International Tables for Crystallography

See also:
http://it.iucr.org/Cb/ch6o1v0001/
http://lamp.tu-graz.ac.at/~hadley/ss1/crystaldiffraction/atomicformfactors/formfactors.php

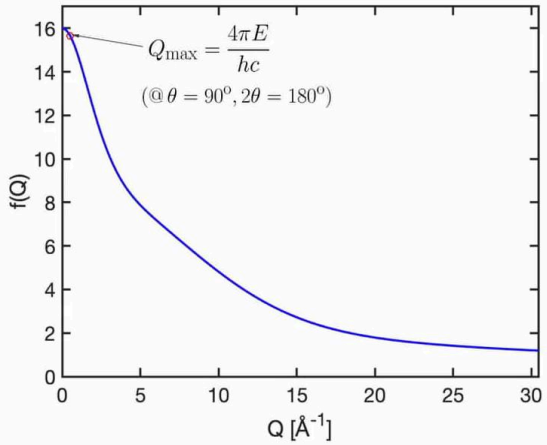
The nine constants, a1 to a4, b1 to b4 and c require to generate the elemental atomic form factors can be found in the international tables for crystallography or, for example, at the two websites given here.

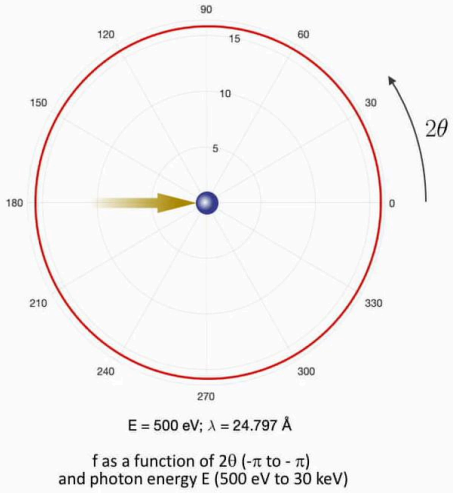
Notes

Summary

7m 34s

Scattering from a sulfur atom – The movie!





$$Q = \frac{4\pi}{\lambda}\sin\theta = \frac{4\pi E}{hc}\sin\theta$$

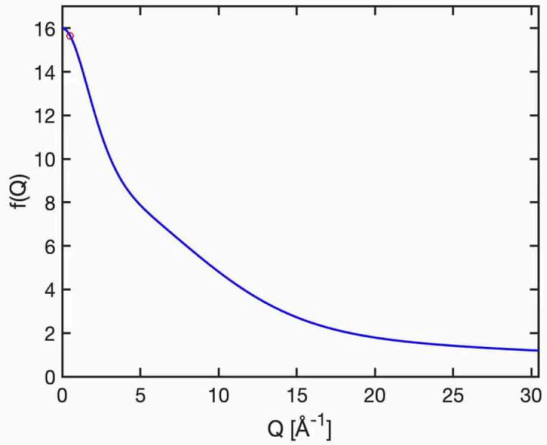
As we have already found out, although the atomic form factor for a given element is determined by Q, or sine theta upon lambda, the angular dependence changes with photon energy. We show this now for the element sulphur. Plotted on the left is the atomic form factor of sulphur as a function of Q. On the right is a movie that I will shortly play showing how the angular dependence changes with photon energy. The range of the atomic form factor curve on the left that can be accessed depends on the photon energy or wavelength. The maximal accessible Q value is for when theta is equal to 90 degrees or 2 theta equals 180 degrees, in other words, exactly in the count of propagating or back scattering direction. In this case, Q is equal to 4Pi upon lambda or 4Pi E divided by hc. The movie begins at E is equal to 500 electron volts, for which lambda is equal to 24.8 angstroms. So the maximum Q value that can be accessed at this energy is 4Pi upon lambda, which is approximately equal to 4PI upon 25, which is approximately equal to 0.5 reciprocal angstroms. This value for Q is shown in the form factor curve with the small red circle.

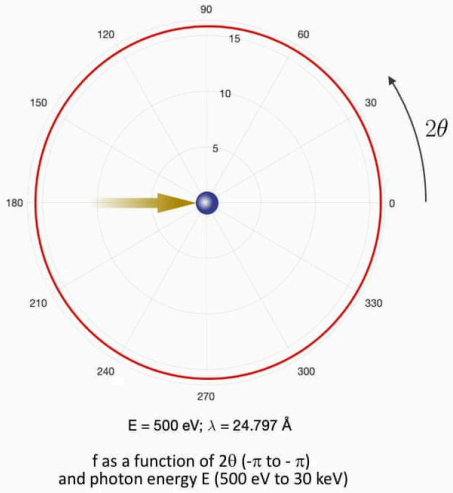
Notes

Summary

7m 52s

Scattering from a sulfur atom – The movie!





$$Q = \frac{4\pi}{\lambda}\sin\theta = \frac{4\pi E}{hc}\sin\theta$$

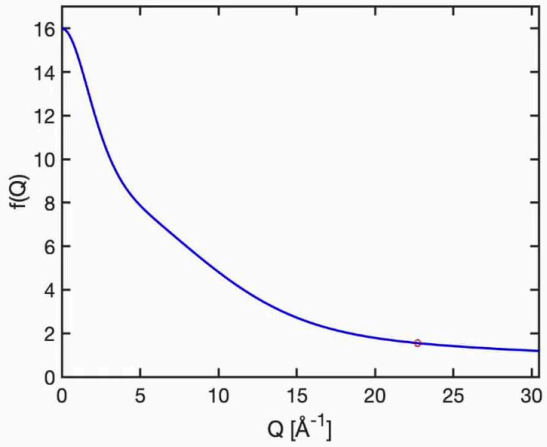
Note that this form factor value F at 2 theta is equal to 180 degrees is only marginally smaller than the value of F equals 16 for Q equals 0. And indeed, the angular distribution at 500 eV shown on the right only very slightly deviates from a circle. Scattering at all angles is almost the same. Now, if we think about it, this should come as no surprise. The wavelength of nearly 25 angstroms is much larger than the diameter of sulphur. Its covalent radius is about 1 angstrom, and therefore, its diameter is approximately 12 times smaller than the wavelength of a 500 electron volt photon. So the phase differences between the different volume elements of the electron cloud of sulphur must all be less than approximately 30 degrees. And for the large majority of the electron cloud, substantially smaller than this, meaning that destructive interference between the volume elements must be small and scattering in all directions is close to being fully constructive for the sulphur atom at 500 eVs, therefore, it must appear to the x-rays to be like a point source. We now start the movie, which runs from a photon energy of 500 electron volts up to 30 kilo electron volts.

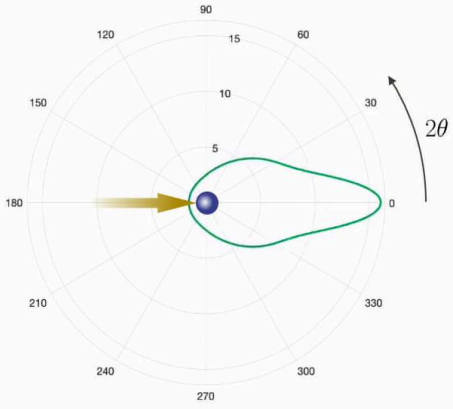
Notes

Summary

9m 29s

Scattering from a sulfur atom – The movie!





E = 22200 eV; λ = 0.558 Å

f as a function of 2θ (-π to - π)
and photon energy E (500 eV to 30 keV)

$$Q = \frac{4\pi}{\lambda}\sin\theta = \frac{4\pi E}{hc}\sin\theta$$

The maximal accessible Q value is tracked by the red circle on the left and to repeat is equal to the form factor in the back scattering direction at 180 degrees in the movie on the right. Okay. So let's begin. Note that as the photon energy increases, so does the maximum accessible Q vector in the back scattering direction, for which the form factor decreases and decreases. As a result, the polar plot of the atomic form factor on the right becomes less and less round and more pronounced in the forward direction. I suggest you rewind this part of the video as many times as you need until you fully understand it, because it is very important, particularly for scattering experiments, which we described in the sister course.

Notes

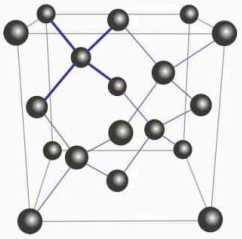
Summary

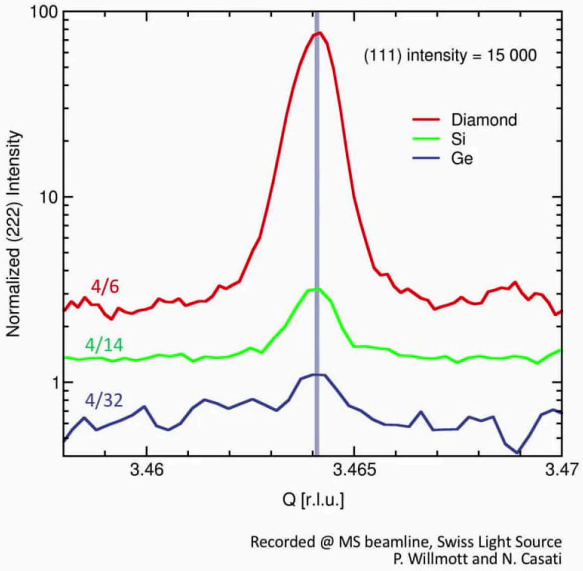
11m 01s

Spatial (in)dependence of f

- Spherical symmetry of electron cloud around atom assumed
- Not always a good approximation!
- e.g. carbon in diamond
  - Six electrons in total
    - Two core 1s electrons
    - One 2s electrons
    - Three 2p electrons

  } four sp^3 hybrid orbitals tetrahedral symmetry





Before we finish this video by summarising our understanding of the atomic form factor, so far, a brief word of warning. Although the data you can obtain from the International Tables of Crystallography and other sources provide atomic form factors that vary with Q, the scattering vector away from the instant beam, they assume that the electron cloud around the atom itself is spherically symmetric. In other words, it ignores the spatial heterogeneity of the electron orbitals. Now, this is often a good simplification, especially for atoms with large atomic numbers, and thus a large number of electrons. But for some atoms, perhaps most relevantly, carbon, this is not a very good approximation. Let's consider diamond, for example, each carbon atom in diamond is covalently bound to four neighbouring carbon atoms in a tetrahedral configuration. In order to achieve this structure, the outer for electrons in the N equals 2 shell combine to form tetrahedral, so-called sp3 hybrid orbitals with the necessary symmetry to form the diamond structure. But carbon only contains a total of 6 electrons, so 4 out of the 6, two-thirds of these form an electron cloud that is most certainly not spherically symmetric.

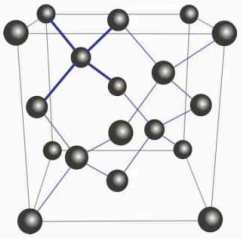
Notes

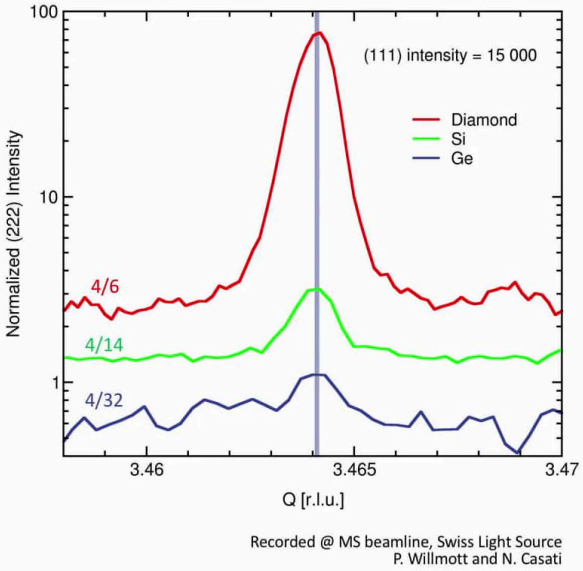
Summary

11m 59s

Spatial (in)dependence of f

- Spherical symmetry of electron cloud around atom assumed
- Not always a good approximation!
- e.g. carbon in diamond
  - Six electrons in total
    - Two core 1s electrons
    - One 2s electrons } four sp^3 hybrid orbitals
    - Three 2p electrons } tetrahedral symmetry





Recorded @ MS beamline, Swiss Light Source
P. Willmott and N. Casati

Now, there are certain diffraction peaks in diamond-like structures, which include diamond itself, silicon, and germanium that are curiously missing in their diffraction patterns. One of these is the so-called 222 diffraction peak. We will look into diffraction and the nomenclature used in it in the sister course. Suffice it to say here that such missing peaks or so-called systematic absences are only predicted to have a mathematically 0 intensity by diffraction theory when one assumes that the electron cloud is spherically symmetric. Shown here on the right of the three diffraction peaks for the 222 reflection of diamond and also silicon and germanium, all of which, as I have said, have a diamond-like structure shown at the bottom. Their intensities have been normalised to the allowed 111 peak for each element. The diamond 222 peak is clearly detectable, even if its intensity is only about 0.5 percent of the 111 peak. Like I just said, for the six electrons in diamonds are certainly not spherically symmetric. For silicon, on the other hand, only four of the 14 electrons are involved in tetrahedral bonding. And as a consequence, the 222 peak is now approximately one 10,000 that of the 111 peak.

Notes

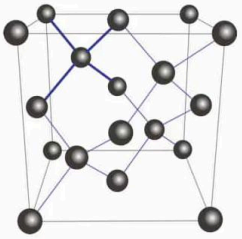
Summary

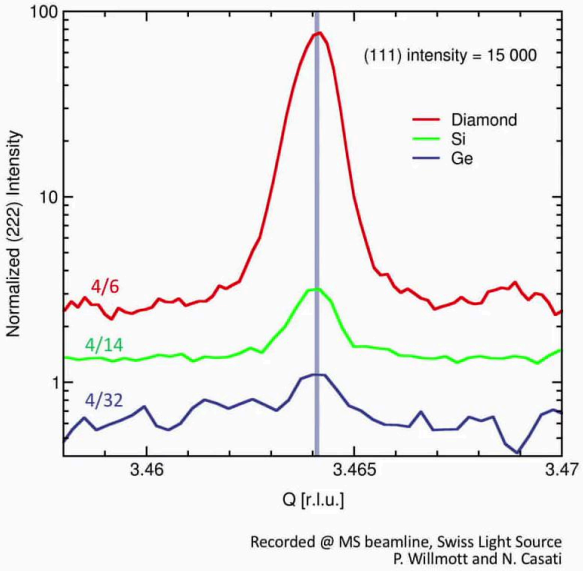
13m 32s

Spatial (in)dependence of f

- Spherical symmetry of electron cloud around atom assumed
- Not always a good approximation!
- e.g. carbon in diamond
  - Six electrons in total
    - Two core 1s electrons
    - One 2s electrons
    - Three 2p electrons

  } four sp^3 hybrid orbitals tetrahedral symmetry





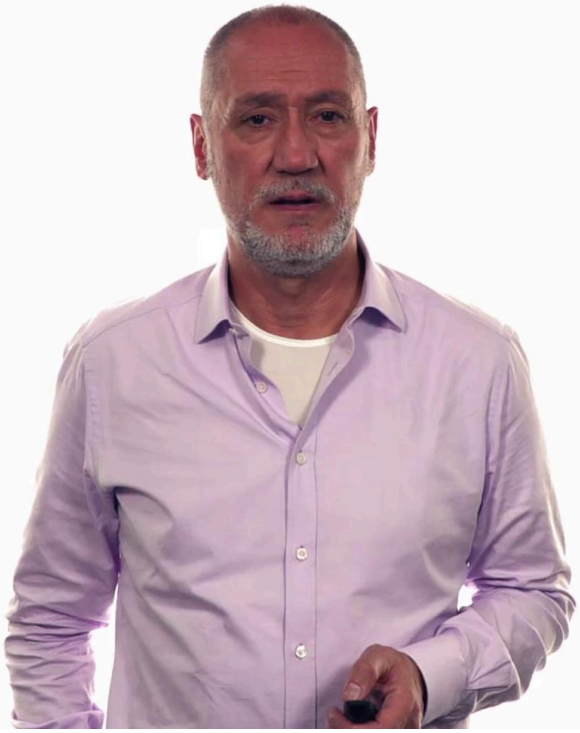
In the case of germanium, for which only four of its 32 electrons are involved in bonding, it's difficult to say for certain that the small feature seen here is real or just part of the noise. Well, for the purposes of our discussion from here on in, however, we can assume that the approximation of spherically symmetric electron clouds is more or less valid. Only in very special circumstances, mainly outside the brief of this course, do we need to question its validity. The one case in which this will come up again in this course is in considering the intensities of harmonic energies in crystal monochromators that use silicon, germanium, or diamond. We discussed this in week five.

Notes

Summary

15m 03s

Summary – elastic scattering... so far



- Forward scattering
  - $\theta = 0$; $Q = 0$
  - All volume elements dV scatter in phase: $\phi = 0$
  - Integral of $\rho(r)$ is therefore simply Z, the number of electrons in the atom (assuming no ionicity)
  - $f(Q = 0) = f(0) = Z$
- As θ increases
  - Increasing "scrambling" and destructive interference between scattering from different volume elements dV
  - $f(\sin\theta/\lambda)$ [or f(Q)] decreases quasi-monotonically (sum of four Gaussians + constant)
  - Maximum accessible Q-value increases with photon energy

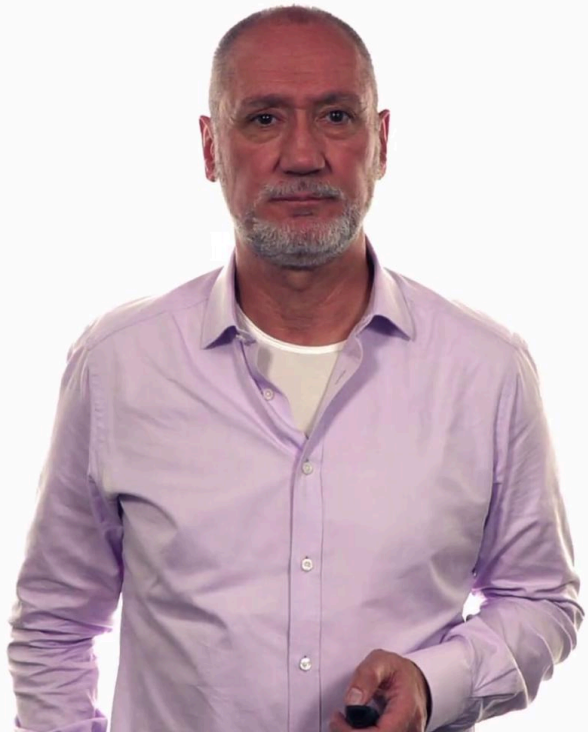
Let's summarise our understanding of Thomson scattering and the atomic scattering factor so far. Because the electron cloud around an atom is not a point scatterer, in order to determine the scattering amplitude for a given scattering angle and wavelength of radiation, we need to integrate the contributions over the entire electron cloud, taking into account the phase of the scatted wavelets from each volume element dV. We have seen that these phases, which determine the amount of destructive interference and hence the scattering amplitude depend on sine theta upon lambda, which itself is proportional to Q scattering vector. This is the vector that describes the difference in the incident in scattered way vectors. In the forward scattering direction, that is for theta equals 0, and so Q equals 0, all the volume elements scatter in phase with one another and interfere purely constructively. Integrating this over the entire electron cloud, therefore yields the number of electrons in the atom, which, if assumed to be neutral and not an ion, is equal to Z, the atomic number. As the scattering angle increases, partial destructive interference occurs, resulting in a reduction of the atomic scattering factor.

Notes

Summary

15m 51s

Summary – elastic scattering... so far



- Forward scattering
  - $\theta = 0$; $Q = 0$
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  - $f(Q = 0) = f(0) = Z$
- As θ increases
  - Increasing “scrambling” and destructive interference between scattering from different volume elements dV
  - $f(\sin \theta/\lambda)$ [or $f(Q)$] decreases quasi-monotonically (sum of four Gaussians + constant)
  - Maximum accessible Q-value increases with photon energy

This can be described as a sum of 4 Gaussians plus a constant. Note also that the maximum theoretically accessible Q value in the exact back scattering direction for two theta is equal to 180 degrees increases with photon energy. In the next video, we take into account that the electrons are bound to the nuclear core of the atom, which leads the correction terms, to F, the atomic form factor, which depend on the photon energy. In other words, they're dispersive. This prepares us for the third section of this week in which we describe the complex refractive index from which phenomena of refraction, reflection, and absorption can be quantitatively described.

Notes

Summary

17m 27s