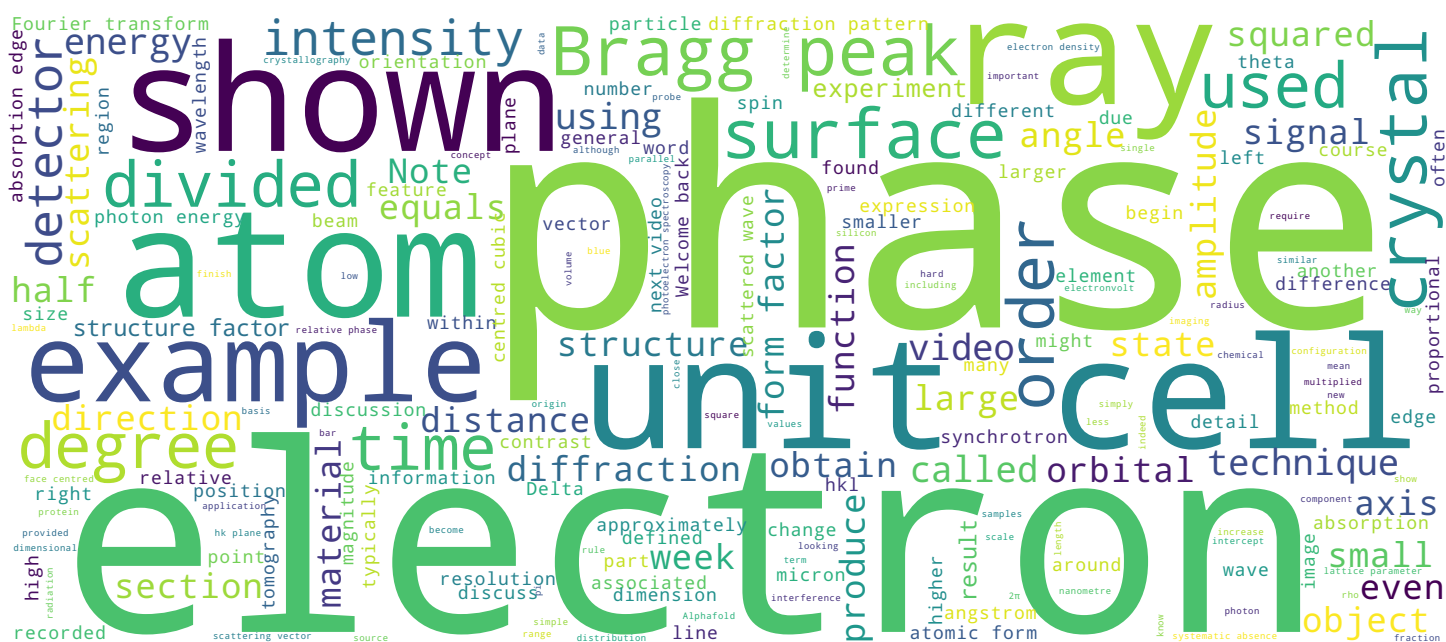


Synchrotrons and x-ray free-electron lasers

Techniques and applications

Prof. Philip Willmott



Search MOOC



Video



Contents and objectives of this video



- Scattering by atoms within a unit cell
- Determining the phases of the scattered waves
- The structure factor
- High-symmetry bases and “systematic absences”

Hello. Welcome back to this, the third section of this first week, which covers aspects of diffraction and crystallography. This section is actually quite long with seven videos. We will tackle the phase problem in crystallography in this section. In order to do this, we must first understand exactly what the problem is, which requires us to understand the influence of the basis, that is, the configuration of the atoms within the unit cell. This will lead us to the structure factor and how some high-symmetry bases produce so-called systematic absences.

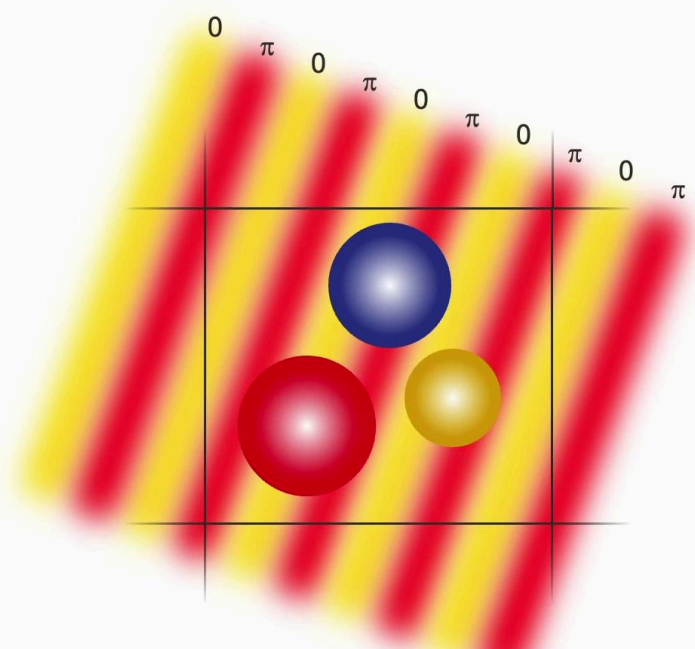
Notes

Summary



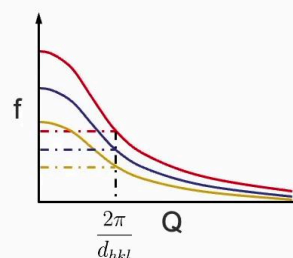
0m 05s

The wave and the cell



<http://lamp.tu-graz.ac.at/~hadley/ss1/crystaldiffraction/atomicformfactors/formfactors.php>

- Scattering atoms associated with basis in unit cell
- Phases of scattered waves
 - Depends on their location within the unit cell (next slide)
- Amplitudes of scattered waves
 - Given by atomic form factors for $Q = 4\pi/\lambda \sin \theta = 2\pi/d_{hkl}$



Let's consider a crystal within a unit cell, positioned so it meets the Bragg condition, that is, a diffraction maximum lies on the Ewald sphere. For this to be true, the positions of the peaks and troughs of the beam of X-rays incident on the unit cell must be invariant as one moves from one unit cell to another, as is the case here. We see that the corners of the unit cell, the phase is the same. It happens to be π radians, but it can be actually any value. The point is that it is the same for translation symmetry equivalent points. The atoms of the basis will experience different phases depending on their positions within the unit cell. The amplitude of the scattered radiation depends on their atomic form factors. The atomic form factors vary monotonically as a function of the scattering vector, Q , which itself is given by Q equals 4π divided by $\lambda \sin \theta$, or 2π divided by d_{hkl} , where θ is the angle of the incident wavevector k in relative to the hkl planes that produce the diffraction spot, and d_{hkl} is the interplanar separation of those planes. For those of you who would like to refresh your memories of the description of the atomic form factor in more detail, please refer to the sister course, Week Two, Section Two, Video One. An online calculator of the atomic form factors is provided in the link shown here.

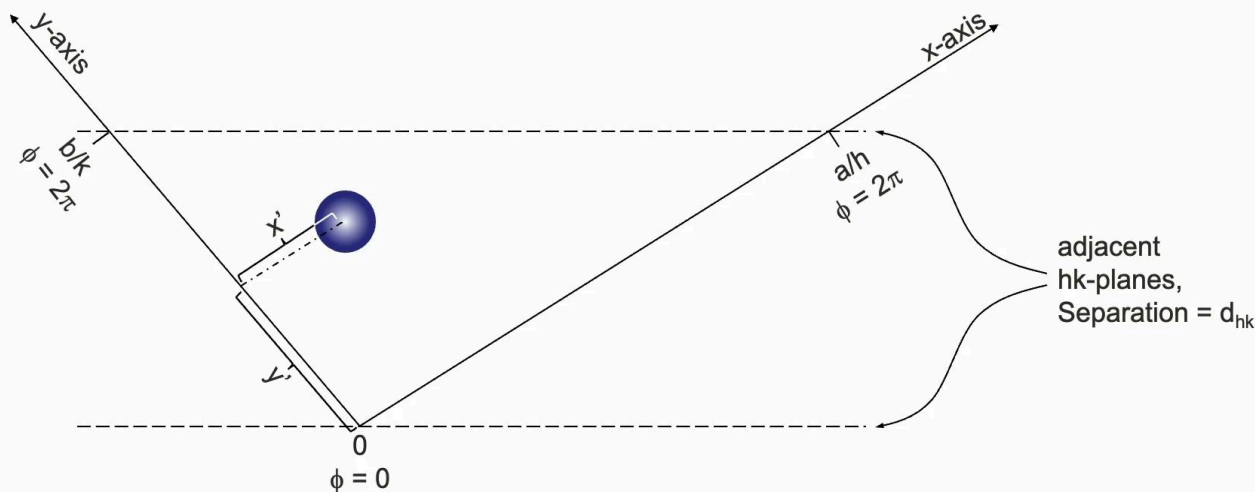
Notes

Summary



0m 42s

The phases of the atoms



How do we determine the relative phases of the atoms within the unit cell from their positions? Let's consider a general case in two dimensions with a unit cell having lattice parameters a and b . Extension of this to three dimensions is trivial. Because we're looking at the general case, the x - or a -axis and the y - or b -axis need not be horizontal or vertical, and their relative angle need not be 90 degrees. We consider two adjacent h - k planes separated by a distance, d_{hk} . As we're looking at relative phases, we can make the phase at the origin of the x - and y -axis any value we choose, and we choose this to be zero. From our discussion of crystallographic planes earlier this week, we can state that the intercept of the x -axis with the upper h - k plane will be at a distance a divided by h , and the phase there will have advanced by a whole wavelength, that is, 2π radians. This is also true for the intercept of the y -axis with the h - k plane. It has an intercept at b divided by k and also a phase of 2π . We now consider an atom within the unit cell. It has coordinates x' and y' relative to the x - and y -axis.

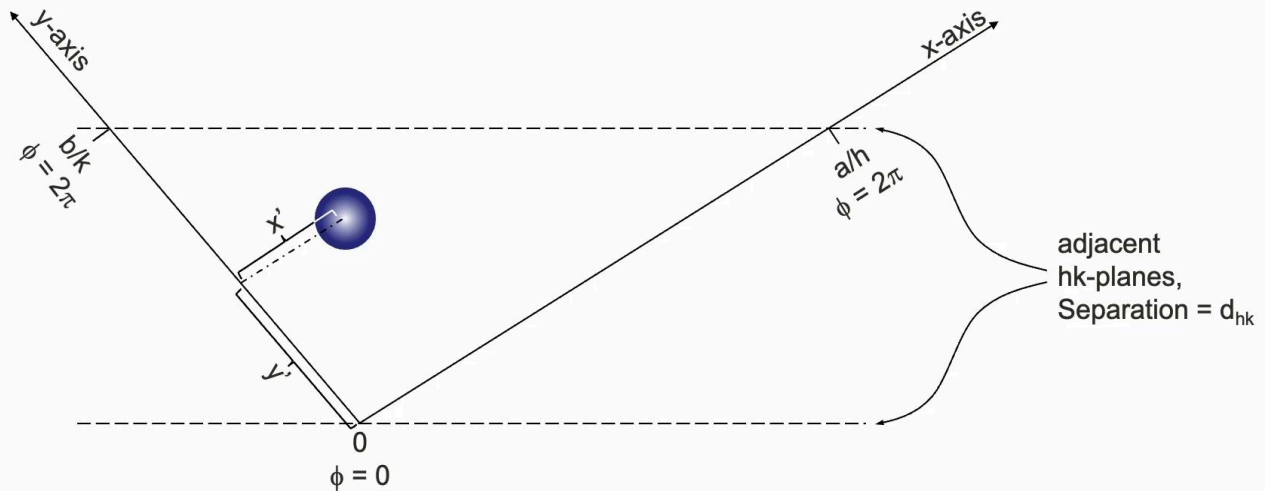
Notes

Summary



2m 30s

The phases of the atoms



$$\phi = 2\pi \left(\frac{x'}{a/h} + \frac{y'}{b/k} \right) \quad \text{or}$$

$$\phi = 2\pi (hx + ky) \quad \text{whereby} \\ x = x'/a, \quad y = y'/b$$

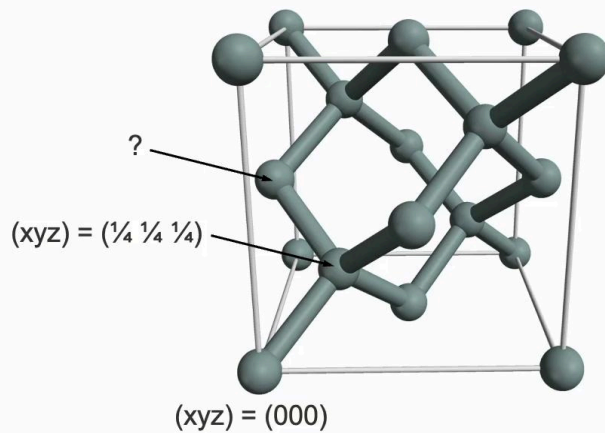
The phase will be the advance in the x direction given by $2\pi x$ prime divided by a over h , plus the advance in the y direction given by $2\pi y$ prime divided by b over k . For example, if x prime were half of the distance a divided by h , the phase advance due to the atom's position along the x -axis would be exactly π radians. We can reformulate this to ϕ is equal to $2\pi hx$ plus ky , where x is the fraction of the lattice parameter a and y equivalently the fraction of the lattice parameter b . x and y are therefore dimensionless.

Notes

Summary



The phases of the atoms



$$\phi = 2\pi(hx + ky + lz)$$

$$(hkl) = (220)$$

$$\begin{aligned}\phi &= 2\pi(2 \cdot \frac{1}{4} + 2 \cdot \frac{1}{4} + 0 \cdot \frac{1}{4}) \\ &= 2\pi\end{aligned}$$

In three dimensions, ϕ equals $2\pi hx$ plus ky plus lz . This is a very simple expression. For example, in the diamond-like unit cell of silicon, one of the eight atoms is positioned at x equals y equals z is equal to a quarter. In the case of, for instance, the 220 Bragg peak, that is h equals two, k equals two, l equals zero, we obtain a phase for this atom relative to the one at the origin of 2π times two times a quarter plus two times a quarter, which is equal to 2π . The phases of the atom at the origin and the one at a quarter, quarter, quarter are the same. Can you work out yourselves what you would expect the phase to be for this atom, also for the 220 Bragg peak?

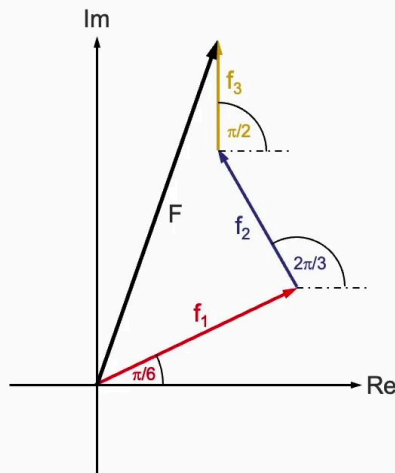
Notes

Summary



4m 58s

The structure factor, F



- F = vector sum of atomic form factors

$$F_{hkl} = \sum_j f_j \exp \left[-i2\pi \underbrace{(hx_j + ky_j + lz_j)}_{\phi_j} \right]$$

- Intensity of Bragg peak @ (hkl) is proportional to $|F_{hkl}|^2$
- All phase information ϕ_j is lost!
- This is the “phase problem”

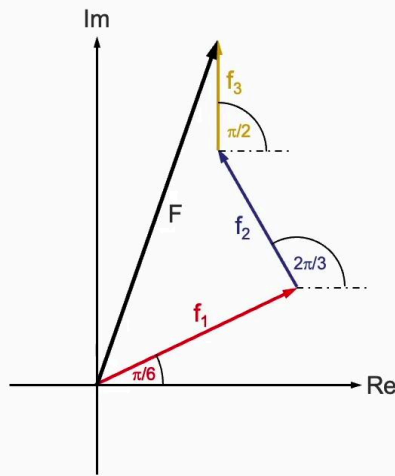
Armed with the phases for each atom, we can determine what the scattering amplitude will be for the entire unit cell for a given hkl. Each atom has its own phase, and its scattered wave will interfere with the others accordingly. We know the amplitude of each scattered wave from the respective atom's form factor value, small f , at the Q vector corresponding to the Bragg peak in question. For example, in the simple case of a unit cell containing three atoms, atom one, shown here in red, may be heavy and have a lot of electrons, meaning its scattered wave amplitude is large. It is in a position that results in a phase of π divided by six or 30 degrees. The second atom, shown here in blue, may have a phase of 2π divided by three or 120 degrees. The third golden atom, a phase of π divided by two or 90 degrees. We vectorially add up these three contributions in an Argand diagram to obtain the sum, large F , the so-called structure factor, which is nothing more than the total scattering amplitude of the atoms for that particular Bragg peak, hkl. We can express F mathematically as being equal to the expression shown here. Note that the expression for the phase of each atom is included in the exponent.

Notes

Summary



The structure factor, F



- F = vector sum of atomic form factors

$$F_{hkl} = \sum_j f_j \exp \left[-i2\pi \underbrace{(hx_j + ky_j + lz_j)}_{\phi_j} \right]$$

- Intensity of Bragg peak @ (hkl) is proportional to $|F_{hkl}|^2$
- All phase information ϕ_j is lost!
- This is the “phase problem”

The factor i , the square root of minus one, means that the exponential term is circular. In other words, it codes for the phase angle ϕ_j . But what we measure is the intensity of the wave, not its amplitude. As we have stated several times already, the intensity is proportional to the absolute square of the amplitude, hence, all the phase information is lost to these ϕ_j s. We only know a priori the magnitude of the structure factor F , but we know nothing about its phase or indeed the relative phases of the vector amplitudes for the atomic form factor contributions that produce it. This is the phase problem.

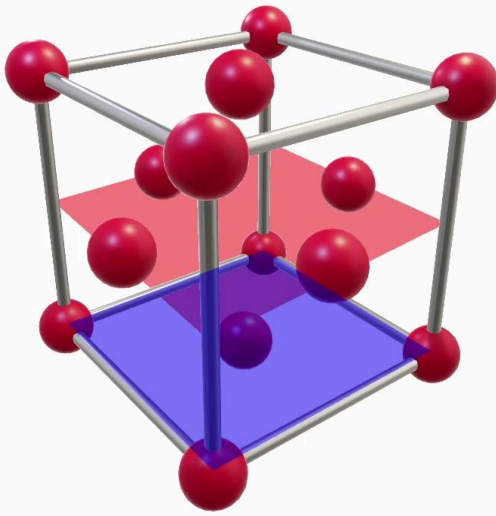
Notes

Summary



7m 34s

The structure factor for some high-symmetry examples



See also Supplementary material "Systematic absences"

- Face-centered cubic (fcc): 4 identical atoms/unit cell
- x_j, y_j, z_j
 - 0, 0, 0 (corner)
 - $\frac{1}{2} \frac{1}{2} 0$ (face centre)
 - $\frac{1}{2} 0 \frac{1}{2}$ (face centre)
 - $0 \frac{1}{2} \frac{1}{2}$ (face centre)
- F_{001} ?
- $F_{001} = f_{\text{atom}} [\exp(0) + \exp(0) + \exp(-i\pi) + \exp(-i\pi)]$
 $= f_{\text{atom}} [1 + 1 - 1 - 1] = 0!!$

$\Delta\phi = \pi$
- Bragg's law tells you that you will see a Bragg peak at $(hkl) = (001)$
- But structure factor here = 0... **"systematic absence"**
- General rule for fcc crystals: only BP intensity if h,k,l all odd, or h,k,l all even

Before we discuss the phase problem in more detail, let's consider some special cases of unit cells that have got a high degree of internal symmetry regarding their atomic positions. We take as an example, a face-centred cubic unit cell consisting of four identical atoms with positions at zero, zero, zero, a half, half, zero, a half, zero, half, and zero, a half, a half. Note, by the way, that although we show here a total of 14 atoms in this figure, there are only four non-equivalent positions. All the others are equivalent atoms in neighbouring unit cells. Using our expression for the phases of each atom, let's calculate the intensity of the 1, 0, 0 Bragg peak. It turns out, and you can do the math yourself if you like, that the two inequivalent atoms in the lower plane, shown here in blue, each have a phase of zero, while the other two in the central plane halfway up the unit cell, shown here in red, have phases of π . If we add these together, this results in a total structure factor of zero. This is called a systematic absence. Systematic absences occur when interference between all the individual scattered waves from the unit cell's atoms result in them cancelling out.

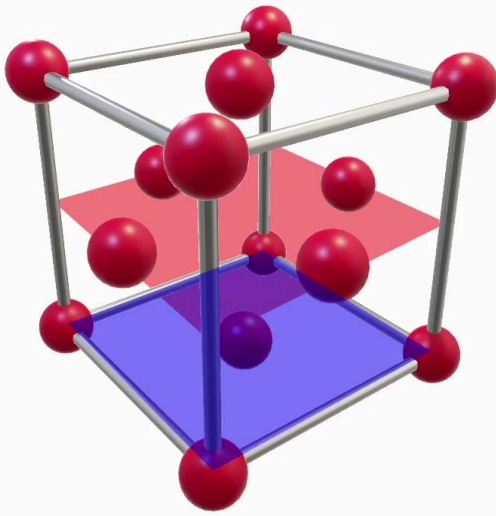
Notes

Summary



8m 23s

The structure factor for some high-symmetry examples



See also Supplementary material "Systematic absences"

- Face-centered cubic (fcc): 4 identical atoms/unit cell
- x_j, y_j, z_j
 - 0, 0, 0 (corner)
 - $\frac{1}{2} \frac{1}{2} 0$ (face centre)
 - $\frac{1}{2} 0 \frac{1}{2}$ (face centre)
 - $0 \frac{1}{2} \frac{1}{2}$ (face centre)
- F_{001} ?
- $F_{001} = f_{\text{atom}} [\exp(0) + \exp(0) + \exp(-i\pi) + \exp(-i\pi)]$
 $= f_{\text{atom}} [1 + 1 - 1 - 1] = 0!!$

$\Delta\phi = \pi$
- Bragg's law tells you that you will see a Bragg peak at $(hkl) = (001)$
- But structure factor here = 0... **"systematic absence"**
- General rule for fcc crystals: only BP intensity if h, k, l all odd, or h, k, l all even

It can be shown that for face-centred cubic crystals, there is a general rule that Bragg peaks will only have non-zero intensity if all the Miller indices are odd or all the Miller indices are even. See the supplementary material systematic absences for a derivation of this rule and those for other high-symmetry structures.

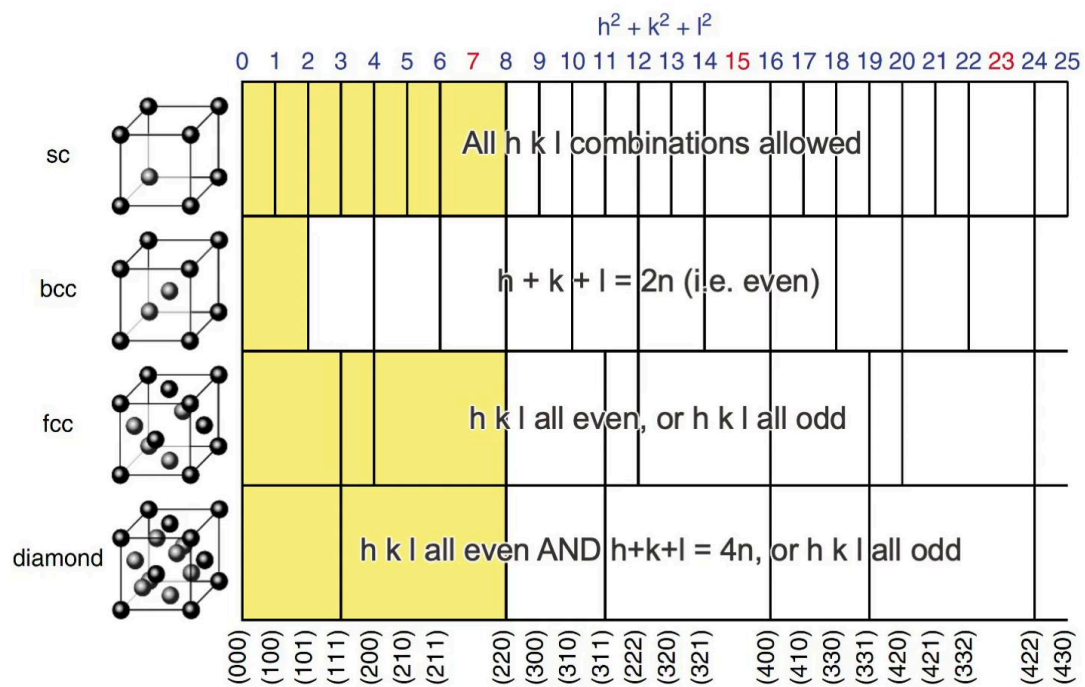
Notes

Summary



10m 01s

The structure factor for some high-symmetry examples



Shown here are the Bragg peaks that exist and are found for the cases of simple cubic, body-centred cubic, face-centred cubic, and diamond-like crystals, plus the rules that determine whether they are found or not for different values of $h^2 + k^2 + l^2$.

Notes

Summary

10m 26s



In the next video...



In the next video, we will dive deeper into the phase problem and some approaches used to solve it.

Notes

Summary



10m 49s