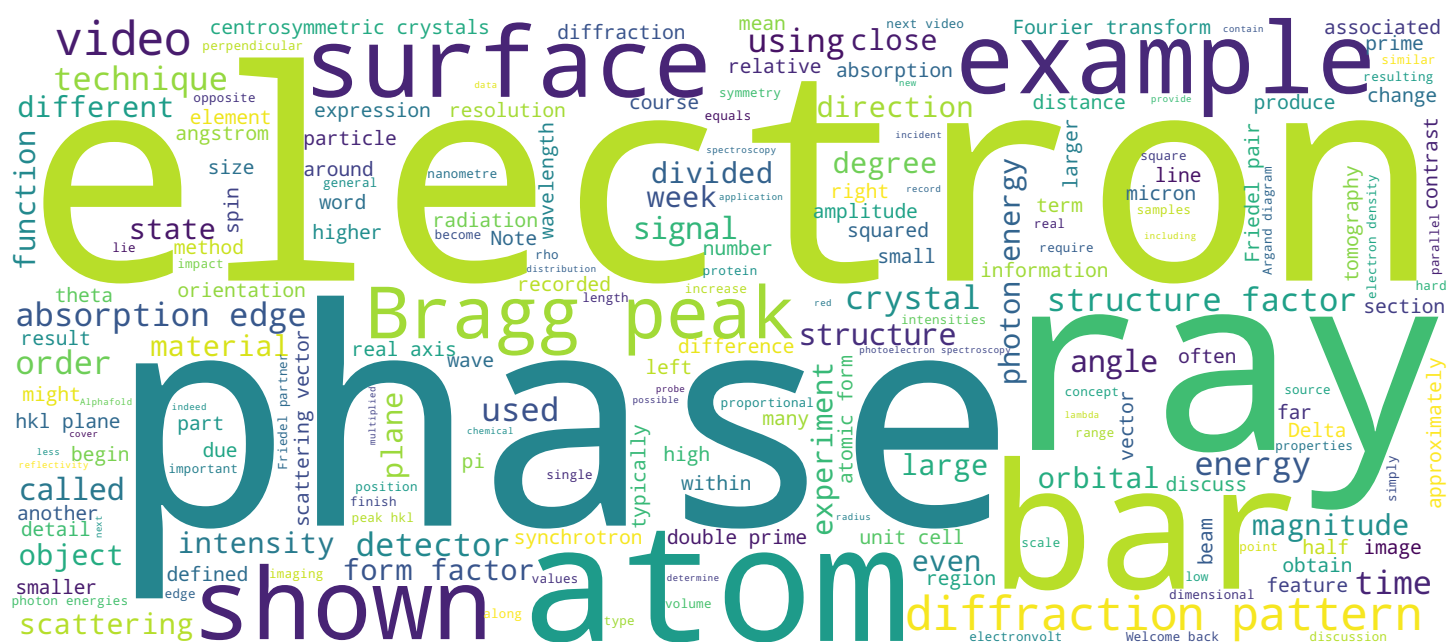


Synchrotrons and x-ray free-electron lasers

Techniques and applications

Prof. Philip Willmott



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Video



Contents and objectives of this video



- Friedel pairs
- Breaking Friedel's law
- Centrosymmetric crystals

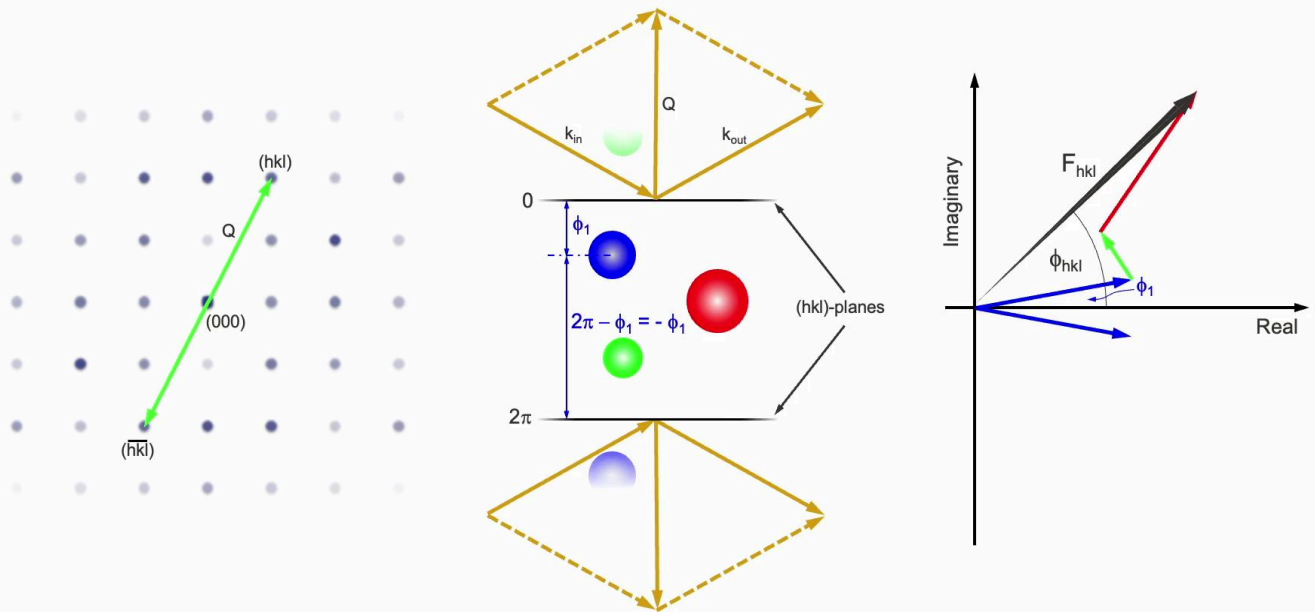
In this video, we take a short pause from discussing how to solve the phase problem to look at the symmetry expected in diffraction patterns and how this is broken when the X-rays have energies which are close to the absorption edges of one or more of the involved atoms. We begin by looking at the properties of diffraction peaks for a given Miller index set hkl compared to that for $\bar{h} \bar{k} \bar{l}$, or alternatively, $h \bar{k} l$, in so called Friedel pairs. We then see how this simple relationship is broken close to absorption edges and what we should expect for centrosymmetric crystals.

Notes

Summary



Friedel pairs



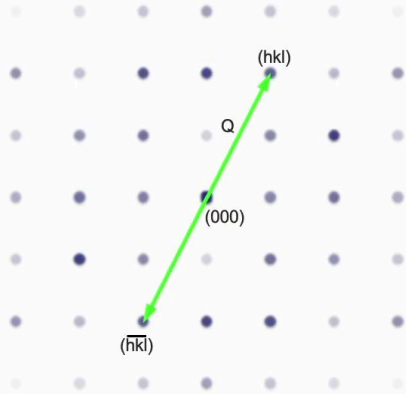
So let's begin by considering diffraction for a Bragg peak hkl . This has a scattering vector Q , connecting the forward direction 000 with the Bragg peak hkl . The Bragg peak found by point inversion through the 000 peak has Miller indices \bar{h} , \bar{k} , and \bar{l} , and a scattering vector equal in magnitude but opposite in direction. Together, these two Bragg peaks are a Friedel pair. So now let us consider the corresponding hkl planes which we have argued have a phase difference of two π . The incident and scattered wavevectors subtend the same angle to the hkl planes, and the Q vector is perpendicular to them. In this example, each of the three atoms will have a certain phase which determine how their individual form factors add up together to produce the structure factor F_{hkl} . The Bragg peak \bar{h} , \bar{k} , \bar{l} is generated by approaching the hkl planes from the opposite side. Now, if, for example, the blue atom has a phase ϕ_1 for the Bragg peak hkl , it will have a phase $2\pi - \phi_1$ for the Friedel partner, \bar{h} , \bar{k} , \bar{l} , which is equivalent to a phase of $-\phi_1$ and its form factor in the Argand diagram on the right will be a mirror image across the real axis of the form factor for hkl .

Notes

Summary



Friedel pairs and Friedel's law



$$|F_{hkl}|^2 = |F_{\bar{h}\bar{k}\bar{l}}|^2$$

$$\phi_{hkl} = -\phi_{\bar{h}\bar{k}\bar{l}}$$

Diffraction patterns are centrosymmetric...

... as long as $h\nu$ is far from absorption edges

Now, using the same arguments for the other two atoms, or however many atoms the unit cell actually may have, it becomes clear that the vectors involved in generating F_{hkl} will all be mirrored across the real axis, and the phase of the \bar{h} , \bar{k} , \bar{l} structure factor will be the negative of that for hkl . Friedel's law therefore states that the magnitude of the structure factor of Friedel pairs are equal and their phases equal but opposite. From this, we can conclude that diffraction patterns are centrosymmetric, although this is predicated on the assumption as we will see in just a moment, that the used photon energy is far from any absorption edge.

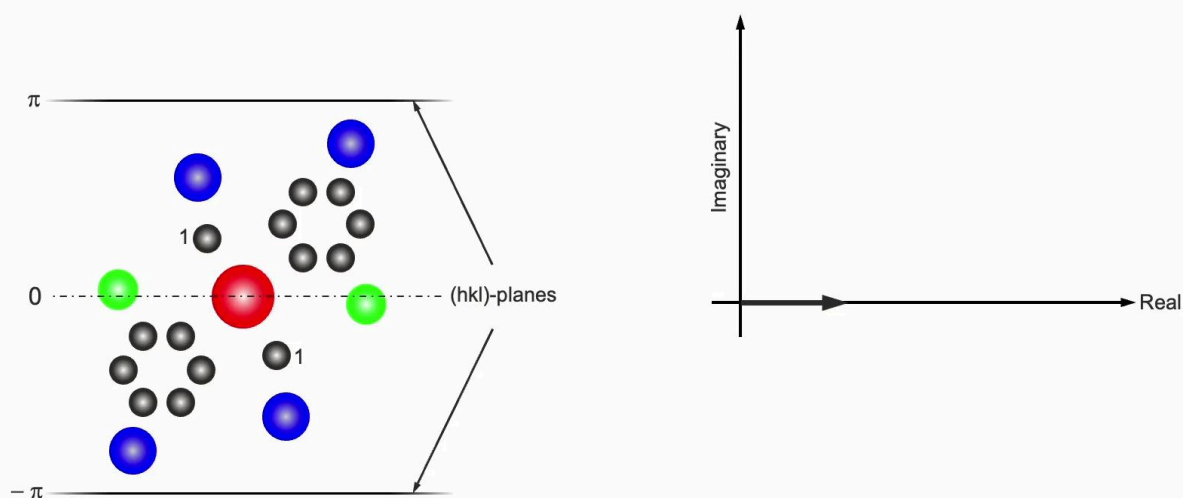
Notes

Summary



2m 41s

Centrosymmetric crystals



Before we look at how things change if we are close to an absorption edge due to the correction dispersion terms f' and f'' , we first make some predictions about the phases of structure factors associated with centrosymmetric crystals. Please don't mix up the concepts of centrosymmetric diffraction patterns and centrosymmetric crystals. As I said just now, all diffraction patterns for all types of crystals are centrosymmetric, not just for centrosymmetric crystals, for photon energies far from absorption edges. So anyway, let's look at this schematic of a centrosymmetric basis set of atoms. We can set the zero for the phase at any arbitrary position as long as the difference in phase between adjacent hkl planes is 2π . So we set the 0 phase to be in the plane that contains the inversion point of the centrosymmetric arrangement. The two hkl planes are therefore at plus and minus π . We want to see how the atomic form factors add up in an Argand diagram. We consider first these two equivalent atoms, which I've labelled 1. The phase of one is the negative of the phase of the other, which means that their sum, their vector sum, is along the real axis, as the imaginary components cancel one another out.

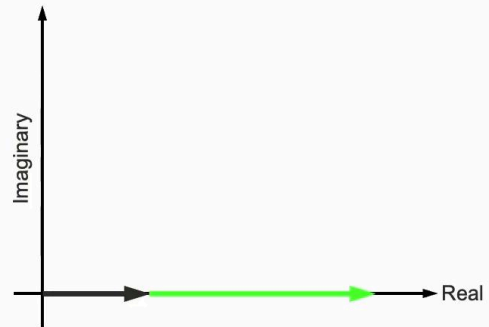
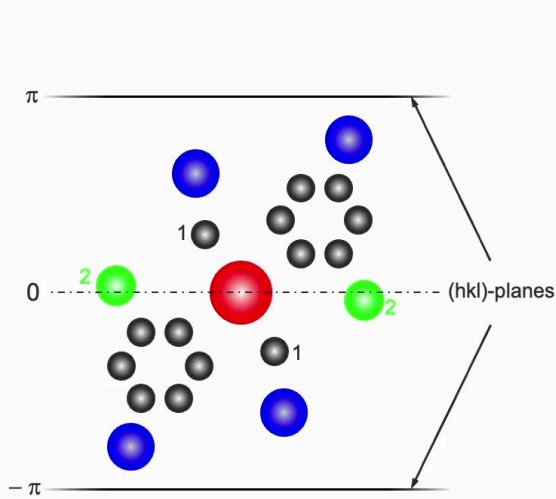
Notes

Summary



3m 39s

Centrosymmetric crystals



Structure factors of centrosymmetric crystals are real ($\phi_{hkl} = 0$ or π)...

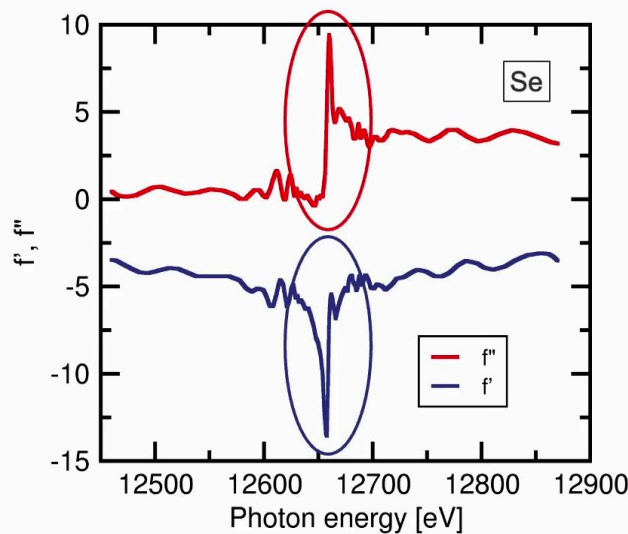
We proceed to the next pair of atoms to obtain the next combined pair of form factors that add up to have only a real component as well. This leads us to the conclusion that the structure factors of centrosymmetric crystals are real with a phase of 0 or π radians, provided that the photon energy is far from any absorption edge of the involved atoms.

Notes

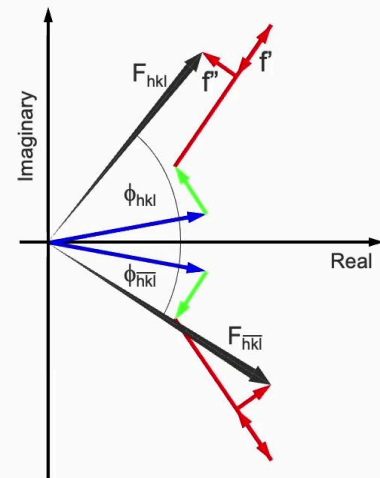
Summary



Including dispersion terms f' and f''



Close to an absorption edge



$$f(\hbar\omega, Q) = f^0(Q) + f'(\hbar\omega) + i f''(\hbar\omega) \quad |F_{hkl}|^2 \neq |F_{\bar{h}\bar{k}\bar{l}}|^2 \quad \phi_{hkl} \neq -\phi_{\bar{h}\bar{k}\bar{l}}$$

We now consider how the amplitudes and phases of Friedel pairs are affected by the photon energy being close to an absorption edge. Here we have the additional dispersive correction terms f' and f'' to the atomic form factor. Let's assume that the photon energy has been tuned so it is close to an absorption edge of the atom, with the atomic form factor shown in red in the Argand diagram on the right. The term f' is generally negative, thus shortening the magnitude of f , while the term f'' is perpendicular to f , resulting in this value for the structure factor F_{hkl} . Now, for the Friedel partner, the reduction of the magnitude of f due to f' is the same if mirrored as before. But crucially, the sense of the rotation by 90 degrees of f'' is invariant, meaning it's not a mirror image of its Friedel partner. The resulting structure factor $F_{\bar{h}\bar{k}\bar{l}}$ is therefore different in magnitude and does not have an equal but opposite phase. The diffraction pattern therefore loses its centrosymmetry. This extra information can be exploited in phasing techniques of macromolecular crystals.

Notes

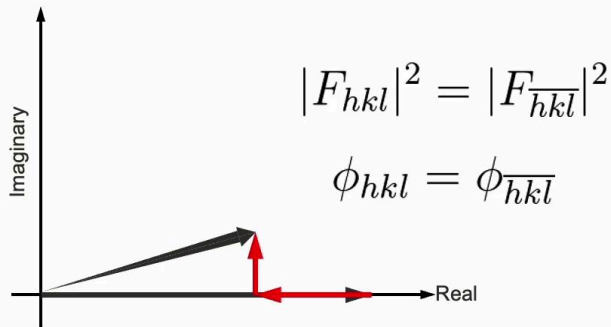
Summary



5m 53s

Impact of f' and f'' on centrosymmetric crystals

- SFs without dispersion terms are real
($\phi = 0$ or $\pi \Rightarrow$ no imaginary component)
- Adding f' and f'' changes the SFs identically for hkl and $\bar{h}\bar{k}\bar{l}$



One last point, centrosymmetric crystals are a special case regarding the impact of absorption on their structure factors. We have argued earlier in this video that far from absorption edges, the structure factors lie on the real axis. The sum of all the f' terms must therefore also lie on the real axis, and the sum of the imaginary terms f'' is perpendicular to this, that is, parallel to the imaginary axis, resulting in this total structure F_{hkl} . This is true for both Friedel partners and hence they have equal magnitudes and phases. Thus centrosymmetric crystals always have centrosymmetric diffraction patterns, even for photon energies near absorption edges.

Notes

Summary



7m 26s

In the next video...



Now, we've covered the impact of absorption of x-rays on the symmetry and intensities of diffraction patterns, we return in the next two videos to phasing techniques for macromolecules that exploit this phenomenon and the related effect of substituting one or more atoms with chemically similar but heavier other atom types.

Notes

Summary



8m 25s