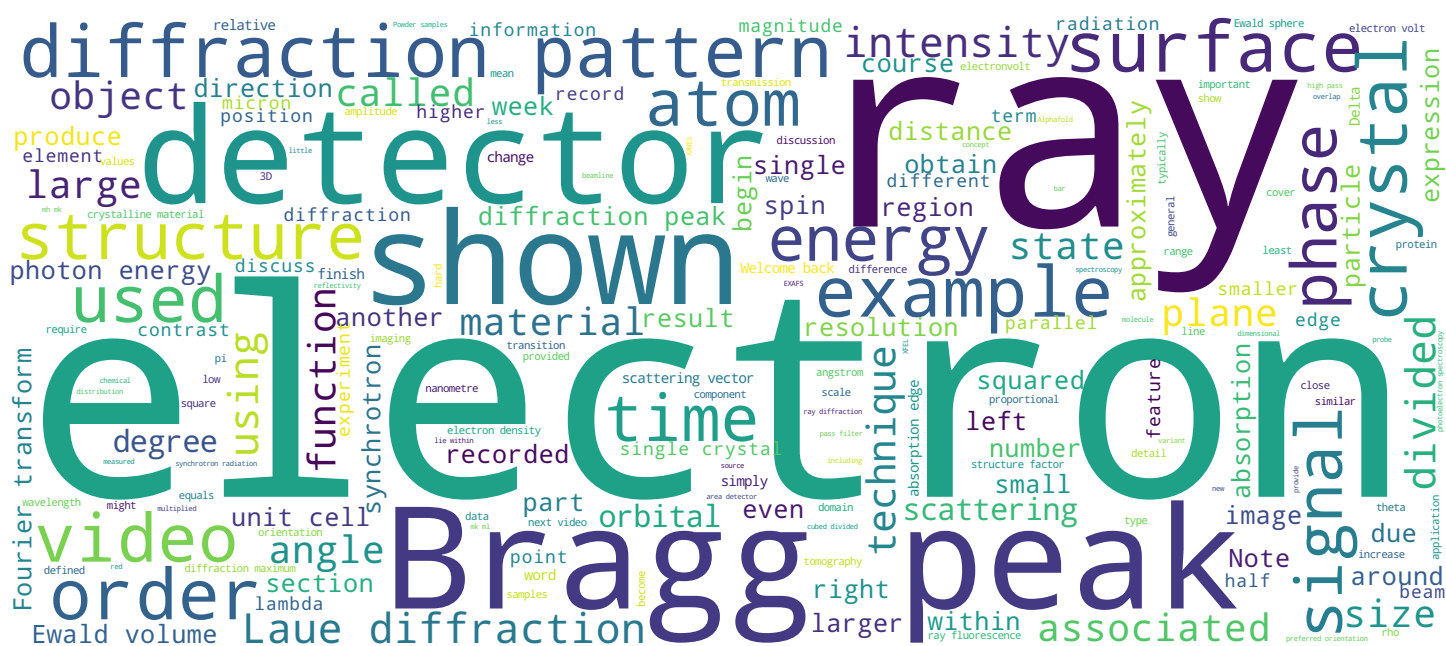


Synchrotrons and x-ray free-electron lasers

Techniques and applications

Prof. Philip Willmott



Search MOOC



Video



Contents and objectives of this video



- Types of crystalline samples
- Diffraction geometries
- Laue diffraction
 - Basic concepts
 - The overlap problem
 - Laue diffraction and modern detectors
 - Applications of Laue diffraction

Welcome back to the first video of week 2 of part 2 of the course. Introduction to Synchrotrons and XFELs. In this video, we will begin by considering different types of crystalline samples and diffraction geometries before discussing the first ever type of diffraction experiment, namely Laue diffraction. After discussing the basic concepts, we will see how traditionally Laue diffraction suffered from the so called overlap problem, and then how this can be overcome using modern area detectors. We finish this first video with two examples of applications of Laue diffraction.

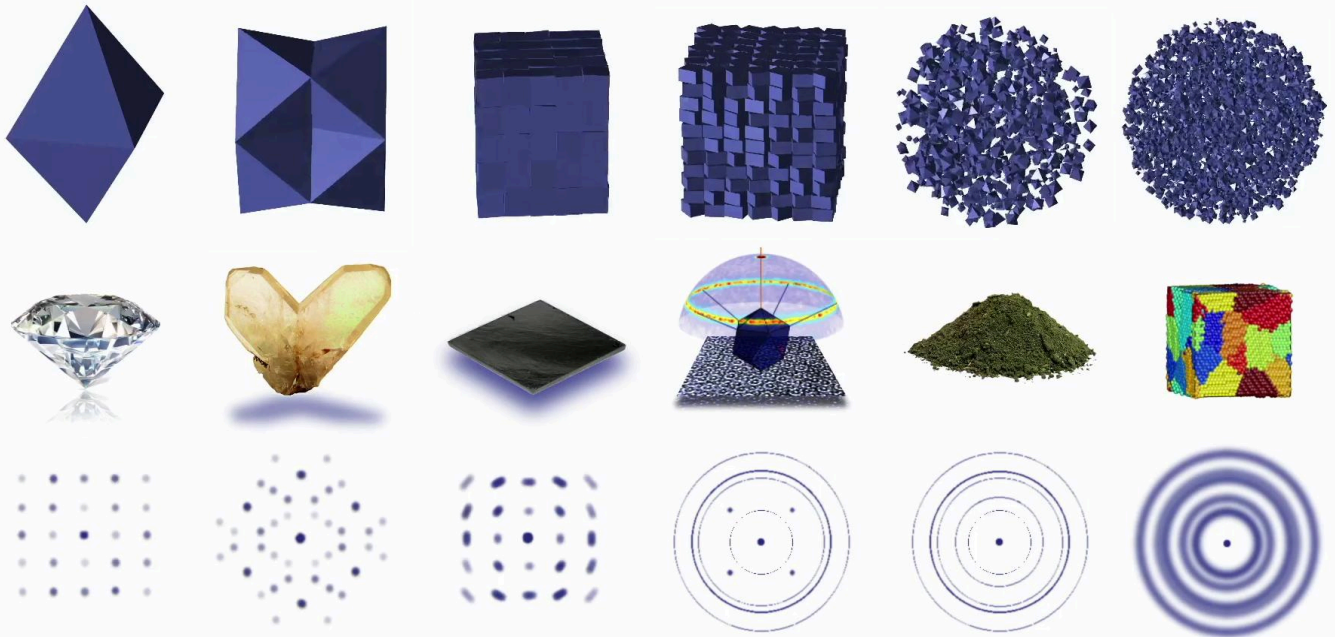
Notes

Summary



0m 05s

Types of crystalline samples



Images: Creative Commons

Crystalline material can come in many guises, depending on many parameters such as the degree of crystalline perfection and size. The simplest case is a single crystal with little or no macroscopic defects, such as a diamond or semiconductor-grade silicon wafers. Note that in reality, even these will have some crystalline defects such as interstitials, dislocations, and stacking faults. Twinned crystals are those that have two or more volumes with distinct crystallographic orientations, but they share a common so called twin plane, such as often seen in natural quartz crystals. The result is that a diffraction pattern recorded from a region that contains more than one twin will be more complex, consisting of one pattern rotated through some angle in 3D relative to another. A sample with mosaic spread is, as the name implies, close to being a single crystal, but consists of domains that are slightly misaligned relative to one another, causing a blurring of the diffraction pattern. Highly oriented pyrolytic graphite or HOPG is often used in X-ray monochromators to capture and use a larger fraction of the incident polychromatic radiation, than that which would be selected by a silicon crystal, for example.

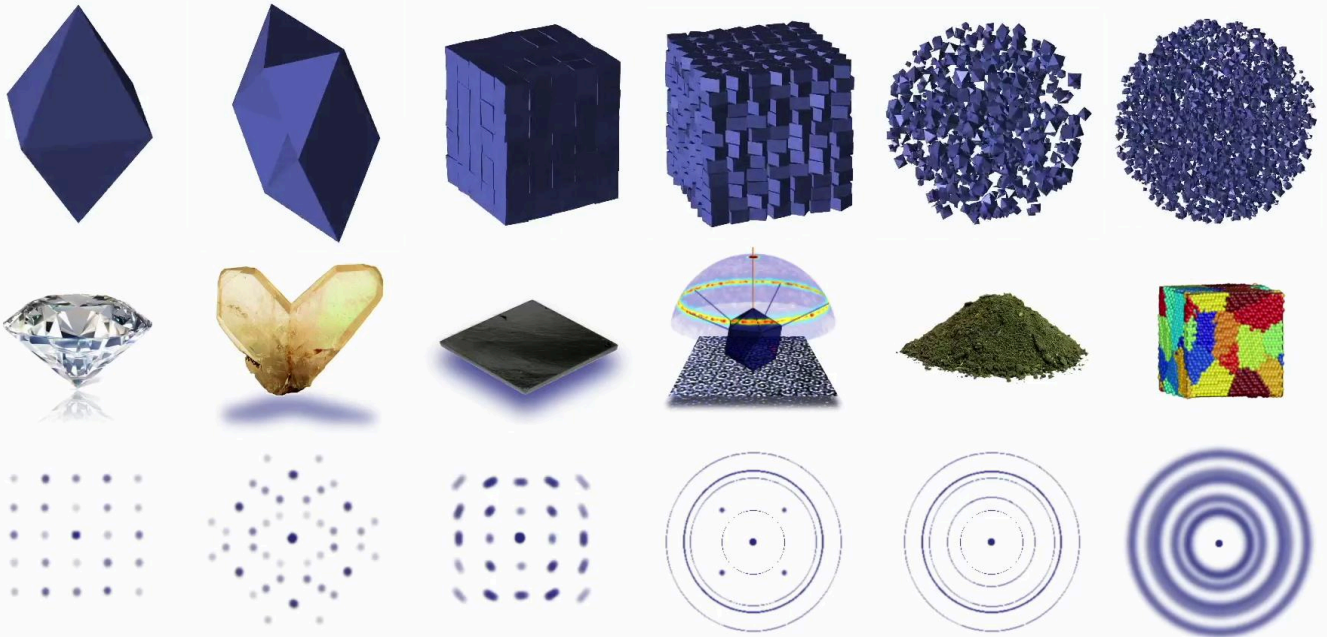
Notes

Summary



0m 44s

Types of crystalline samples



Images: Creative Commons

HOPG has a typical mosaic spread of approximately 1 degree. Textured or preferred orientation crystals have a preferred growth direction, but might have domains with random orientation perpendicular to this direction. Examples might include crystalline fibers, or, as shown here, the growth of a quasicrystal film on a crystalline surface, whereby the five-fold symmetry axis grows preferentially out of the film plane while in the plane the quasicrystal domains have no preferred orientation. The associated diffraction pattern of textured samples might exhibit one or two sharp diffraction maximum, and a set of rings associated with diffraction peaks that have a well defined angle relative to the growth direction but in any orientation in the plane perpendicular to that growth axis. Powder samples are simply an ensemble of small crystallites of the same material with no preferred orientation. The diffraction pattern consists of a set of rings centered around the incident beam axis. Nanocrystalline samples are simply powder samples in which the crystallite size is measured in nanometers and is thus only an order of magnitude also larger than the X-radiation wavelength.

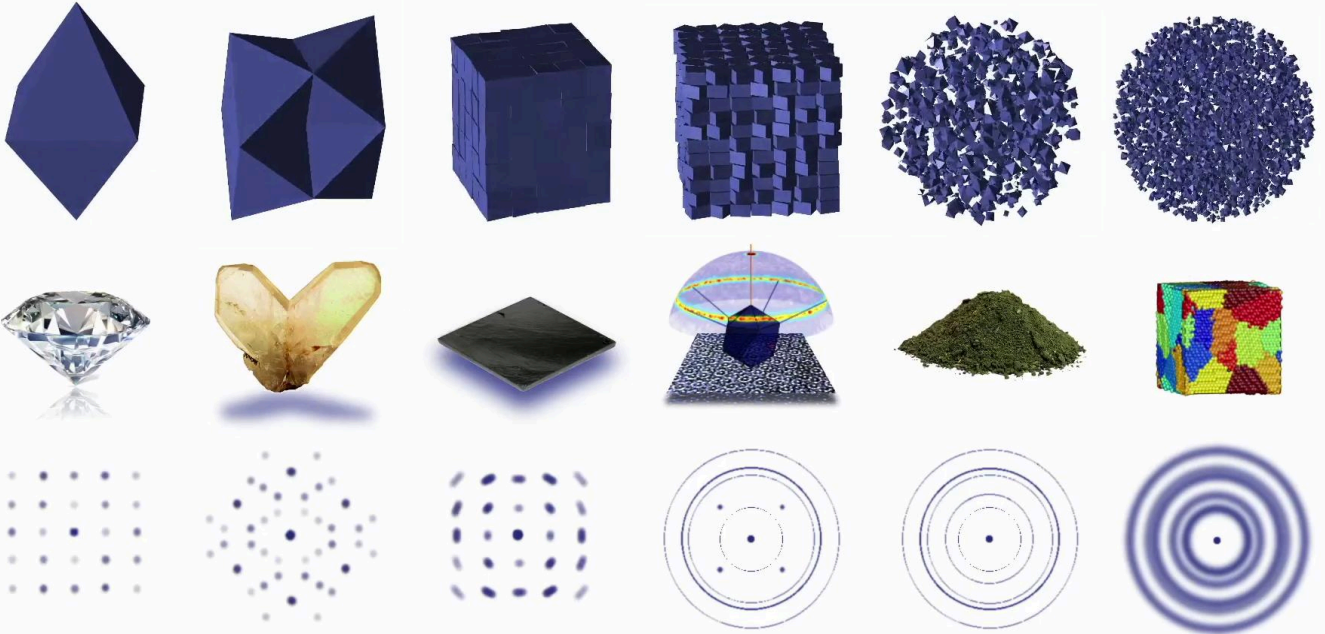
Notes

Summary



2m 15s

Types of crystalline samples



Images: Creative Commons

This means that the diffraction peaks are broader according to the Scherrer equation, which we will briefly visit later in this section. Note that in the above, I have assumed the samples are all chemically homogeneous, that is, any given sample we are looking at, has just one crystalline material. In many experiments, however, more than one crystalline material may be present, not least in the case of real samples, such as investigated in geology, soil science, cultural artefacts, or indeed many other disciplines.

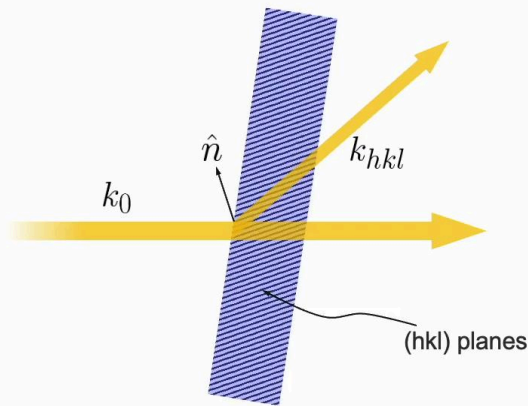
Notes

Summary

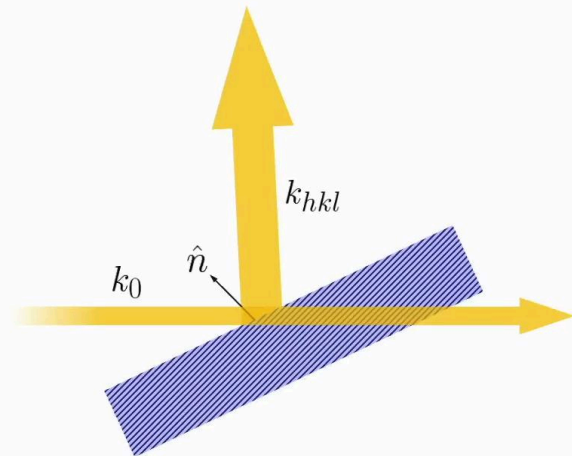


3m 49s

Laue and Bragg diffraction geometries



Laue (transmission) geometry



Bragg (reflection) geometry

(Bragg-Brentano geometry:
 \hat{n} perpendicular to sample surface)

In diffraction experiments, there are two general configurations. either the transmission or Laue geometry shown here on the left, or the reflection or Bragg geometry on the right. If the diffraction planes are parallel to the sample surface, one refers to it being the Bragg-Brentano geometry.

Notes

Summary

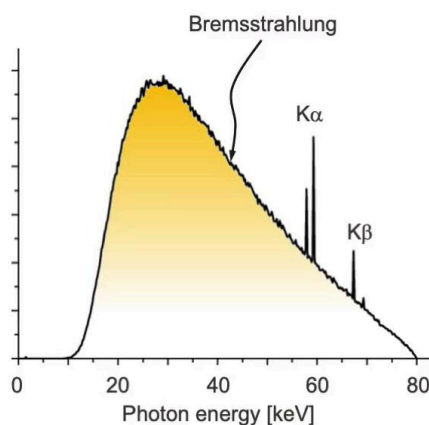


4m 25s

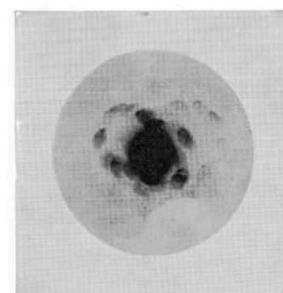
Laue diffraction



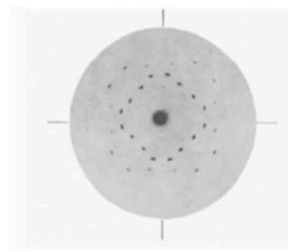
Max von Laue



Tungsten x-ray spectrum



copper sulfate pentahydrate



zinc sulfide

See also: https://www.iucr.org/_data/assets/pdf_file/0010/721/chap4.pdf
and <https://onlinelibrary.wiley.com/doi/epdf/10.1002/andp.19133461004>

The first ever recorded X-ray diffraction pattern was performed by Friedrich and Knipping, driven by the encouragement of Max Von Laue who posited that regular arrays of scatterers with characteristic repeat lengths similar in size to X-ray wavelengths such as crystals, should produce a diffraction pattern. The first result for a raw crystal of copper sulfate pentohydrate was no beauty, that's for sure. But the blobs of intensity were encouraging enough that when this sample was replaced with a more perfect platelet of zinc sulfide, the pattern was much more impressive. To record these patterns, Friedrich and Knipping used a broadband tungsten cathode ray tube with a high voltage set to 80 kiloelectronvolts. In addition to the broadband bremsstrahlung radiation, the spectrum contains sharp lines associated with X-ray fluorescence.

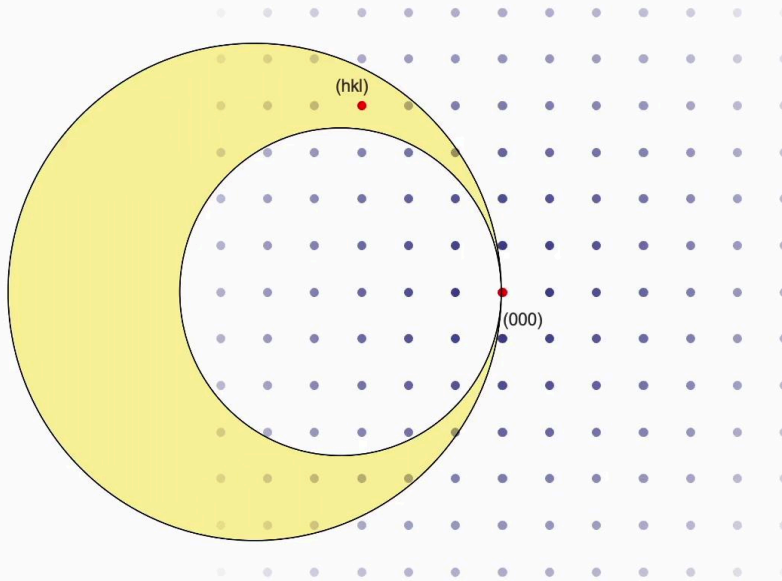
Notes

Summary



4m 48s

Laue diffraction



How does Laue diffraction actually work? Consider a set of diffraction maximum, which we show here only in 2D for the purposes of didactic simplicity. If we were to use a quasi monochromatic source, the Ewald sphere would be thin walled and be positioned so that its origin sits at a distance of k_{in} is equal to 2π divided by λ from the 000 direct beam diffraction peak. as we argued in last week's videos. If, however, one uses a broadband source, the Ewald sphere develops from being a 2 dimensional surface, or here in my 2D diffraction pattern example, it's actually just a hollow circle, with no width, to a 3D volume bounded by 2 spheres with radii which are inversely proportional to the wavelength limits of that broadband source. These spheres touch tangentially at the 000 peak. Any diffraction peak that lies within this volume, satisfies the Bragg condition and can be recorded using a detector at the right location. These are highlighted in red in this schematic. But what is that location? Let's consider just one of the Bragg peaks that lie within what I will now call the Ewald volume for Laue diffraction.

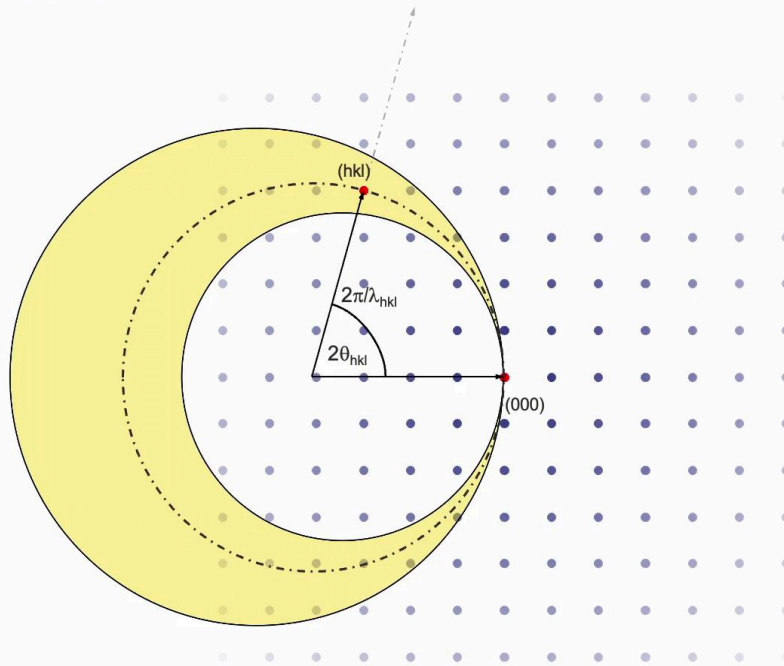
Notes

Summary

5m 51s



Laue diffraction



$$\lambda_{hkl} = 2d_{hkl} \sin \theta_{hkl}$$

This will be intercepted by a sphere with a unique radius k_{hkl} , which is equal to 2π divided by λ_{hkl} that must also tangentially pass through the 000 peak. The direction $2\theta_{hkl}$ of the scattered k vector, determines where the detector must be positioned. The relationship between θ_{hkl} and the wavelength λ_{hkl} follows Bragg's law, as always.

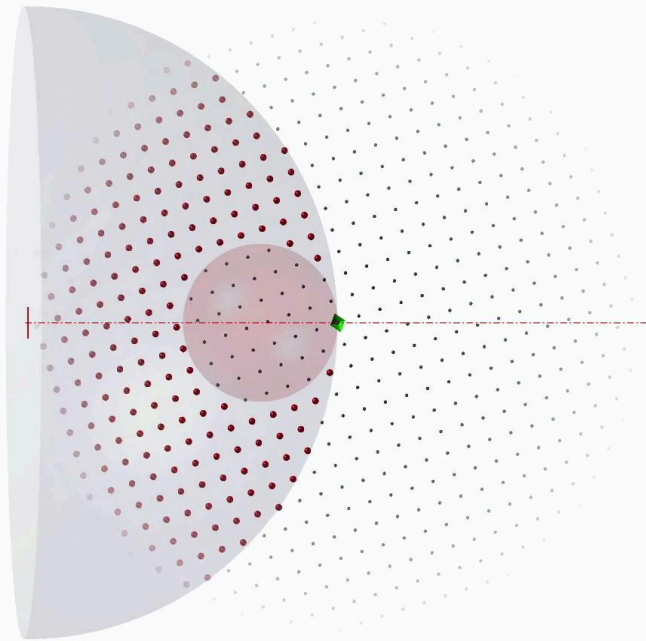
Notes

Summary



7m 19s

Laue diffraction



Hence, for a given crystal orientation, many Bragg peaks can be recorded simultaneously. assuming one has an area detector, by rotating the crystal. Still more diffraction peaks can be driven into the Ewald volume to obtain a more complete dataset. Note that here and in the next slide, I only drew half the outer Ewald volume boundary in order to save space. You should not interpret this as anything that is physically relevant.

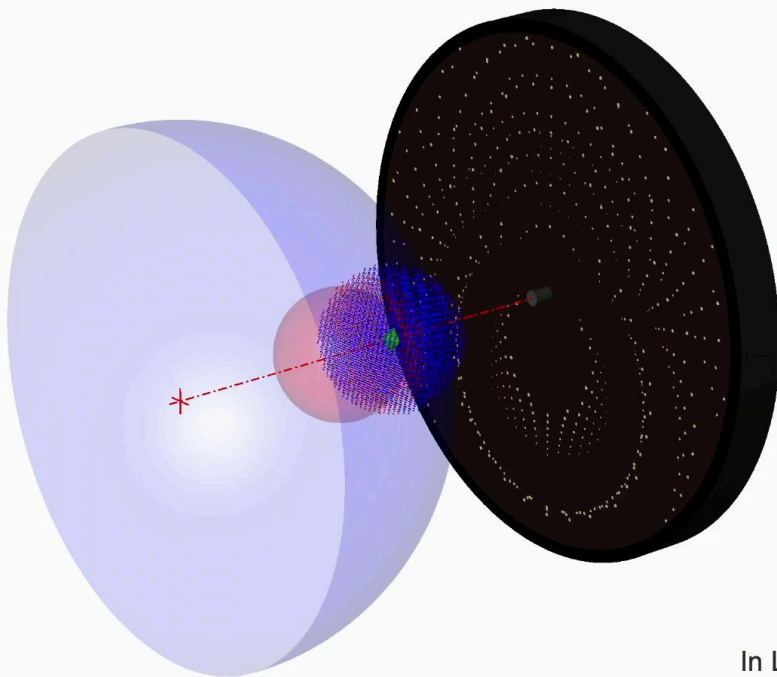
Notes

Summary



7m 53s

Laue diffraction in 3D



$$n_{\text{Laue}} = \frac{\frac{4}{3}\pi (k_{\text{max}}^3 - k_{\text{min}}^3)}{8\pi^3/V}$$

$$= \frac{4\pi V}{3} \left(\frac{\lambda_{\text{max}}^3 - \lambda_{\text{min}}^3}{(\lambda_{\text{max}}\lambda_{\text{min}})^3} \right)$$

In Laue (forward-scattering) geometry

In 3D, the pattern can become very crowded. In principle, the number of data points that can be simultaneously recorded is equal to the volume of the Ewald volume, namely n_{Laue} is equal to $\frac{4}{3}\pi k_{\text{max}}^3$ minus k_{min}^3 , divided by the volume occupied by a single diffraction maximum, itself, equal to $8\pi^3$ divided by V_{uc} , where V_{uc} is the volume of the unit cell. By expressing the bounds in terms of wavelength rather than wavevector k , we obtain the expression that n_{Laue} is equal to $4\pi V$ divided by 3 times λ_{max}^3 minus λ_{min}^3 divided by $\lambda_{\text{max}}\lambda_{\text{min}}^3$. For example, the maximum number of recordable diffraction peaks from a cubic unit cell with a 4 angstrom lattice constant irradiated with 1 to 2 angstrom radiation is equal to approximately 230. But to simultaneously record all N Laue peaks, requires a detector that covers all angular space, that is, 4π steradians.

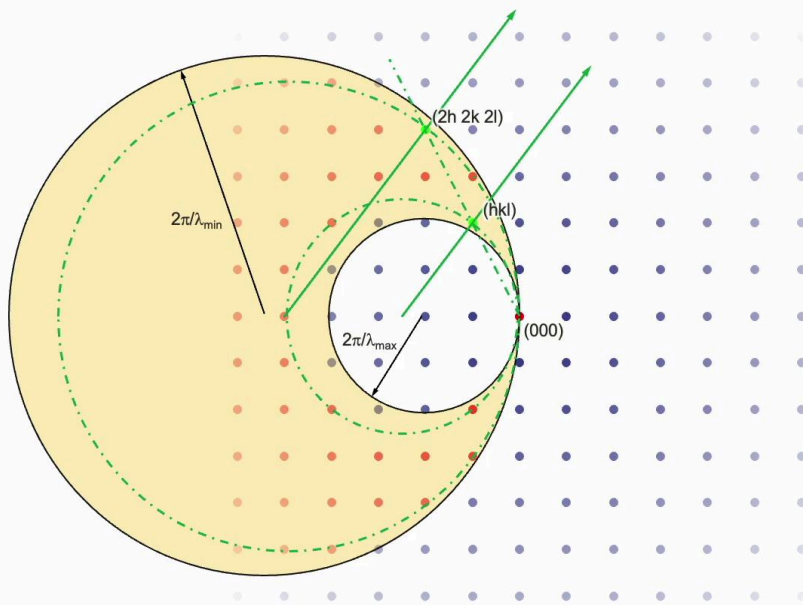
Notes

Summary



8m 26s

Laue diffraction and the overlap problem



$$\lambda_{hkl} = 2d_{hkl} \sin \theta_{hkl}$$

Families $(mh \ mk \ ml)$ for integral m that lie within the Ewald volume will precisely overlap on a detector

How does one extract their individual Bragg-peak intensities?

Now, a problem that's associated with Laue diffraction, is that due to the overlap of diffraction peaks. Let's consider two Bragg peaks with Miller indices hkl and $2h \ 2k \ 2l$. The former is associated with interplanar separations d_{hkl} , twice as large as those for the latter. We can directly determine the sizes and positions of the eval spheres associated with these two Bragg peaks and using very simple geometrical arguments, we see that the scattering vectors must be parallel to one another. From this, we can state that families of Braggs peaks, $mh \ mk \ ml$, for integral values of m that lie within the Ewald volume precisely overlap on the detector, which will thus record their summed intensities. This begs the question, how can we extract individual Bragg peak intensities from this overlapped data?

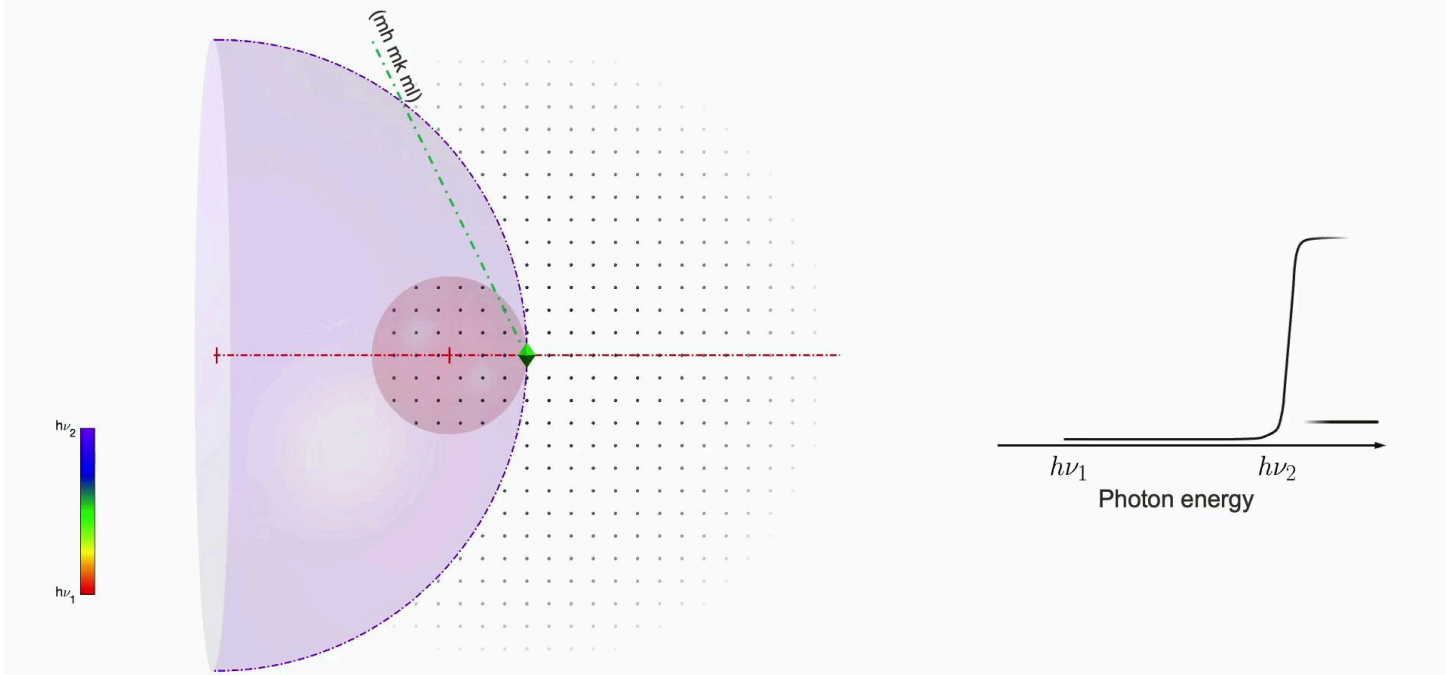
Notes

Summary



9m 46s

Laue diffraction and modern detectors



Now, let's consider again our cartoon of Laue diffraction in 3D. Here, I have color coded the Bragg peaks that lie within the Ewald volume according to their associated photon energy that will select them, see the color bar on the left. A set of 4 Bragg peaks from the same $mh\ mk\ nl$ family are highlighted along with their outgoing scattered vectors shown as color coded, dotted arrows. Now imagine that our detector has a facility to vary the threshold of an internal high pass filter. Now, a high pass filter is, as its name implies, actually, one that allows high energy signal to pass but which suppresses signal below a set threshold photon energy. The transition between full and no signal is typically measured in a few 100 electron volts for hard X-ray detectors. We begin to scan the threshold energy of the detector's high pass filter and observe that once it reaches the lowest energy $h\nu_1$ of the broadband radiation, the effective inner bound of the Ewald volume expands and Bragg peaks become undetectable. Hence, one by one, the Bragg peaks within our highlighted $mh\ mk\ nl$ family disappear, changing the intensity in the associated scattering vector direction. Each step drop in the intensity corresponds to the intensity of the filtered away Bragg peak.

Notes

Summary

10m 50s



Applications of Laue diffraction

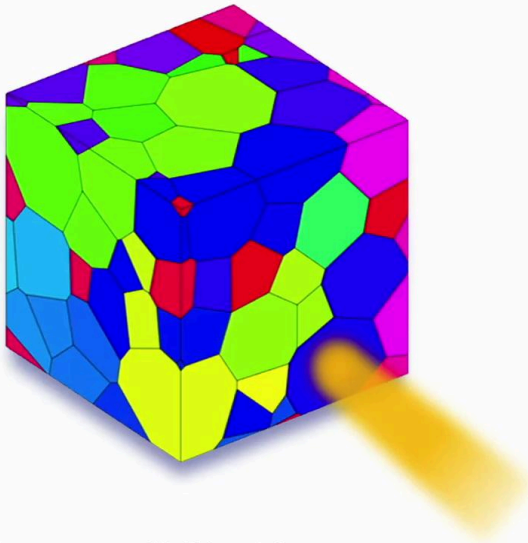


Image courtesy of S. Falco *et al.*,
Comp. Mat. Sci. **136** 20-28 (2017)

- Laue diffraction traditionally for single crystals, unsuitable for powder samples
 - Many randomly oriented crystallites simultaneously illuminated \Rightarrow extremely dense ring pattern: unsolvable
- DLSRs: focus can be made to be smaller than crystallites (limit ~ 100 nm)
 - Scan and rotate sample \Rightarrow diffraction tomogram “ μ Laue diffraction tomography”, e.g. @ BM32 beamline, ESRF

<https://www.esrf.fr/UsersAndScience/Experiments/CRG/BM32/Microdiffraction>
<http://scripts.iucr.org/cgi-bin/paper?S1600576715002447>

Now, traditionally, Laue diffraction was only applicable to single crystal samples, or at least samples with only minor twinning or mosaicity. Powder samples which contain many randomly oriented crystallites will produce an extremely dense ring pattern making analysis completely impossible. However, with the advent of extremely tight focusing, well below a micron, but with a high degree of collimation maintained at DLSRs, one can select individual crystallites or a line of crystallites in a novel technique called micro Laue diffraction tomography, in which both different crystalline materials and their orientations can be extracted. Early successes are provided in the 2 links given here.

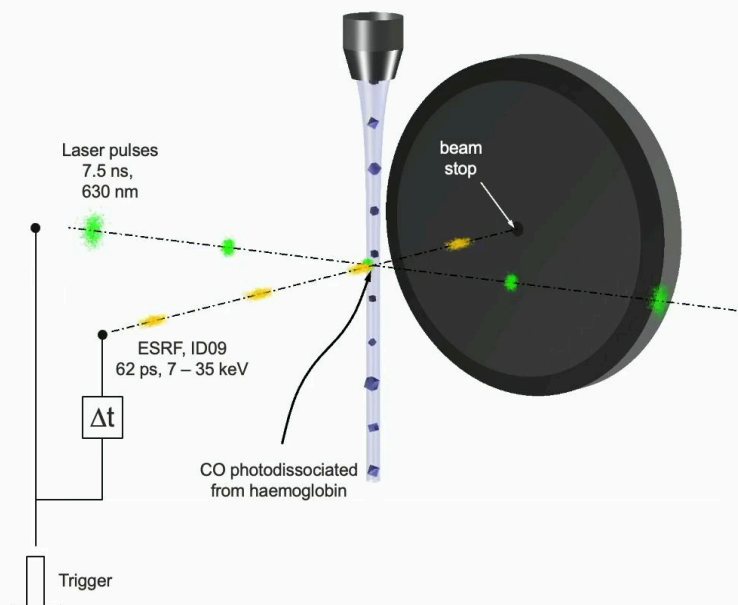
Notes

Summary

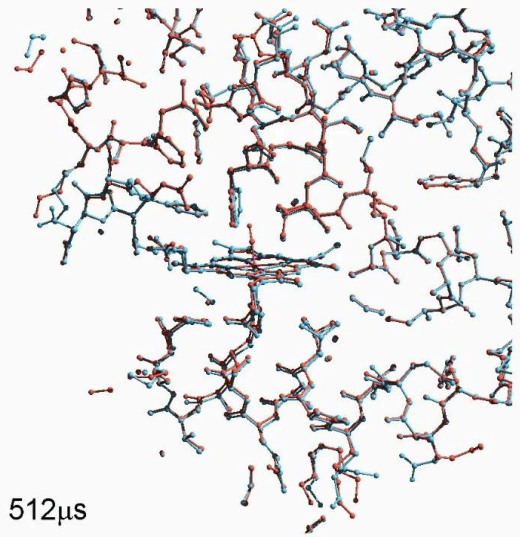


12m 31s

Applications of Laue diffraction



Time-Resolved Photolysis of CO-Haemoglobin
[V. Šrajer et al., Biochemistry 40 13802 \(2001\)](#)



Courtesy American Chemical Society

Laue diffraction is an interesting technique in reversible biochemical reactions, often photo induced, as large fractions of the dataset can be recorded in a single sample orientation. By recording the diffraction pattern as a function of delay, between an excitation source, such as a laser and the synchrotron radiation peaks, temporal resolution to below one nanosecond is possible. Serial crystallography for crystallites in a stream, provides a larger data set and improved signal to noise ratio.

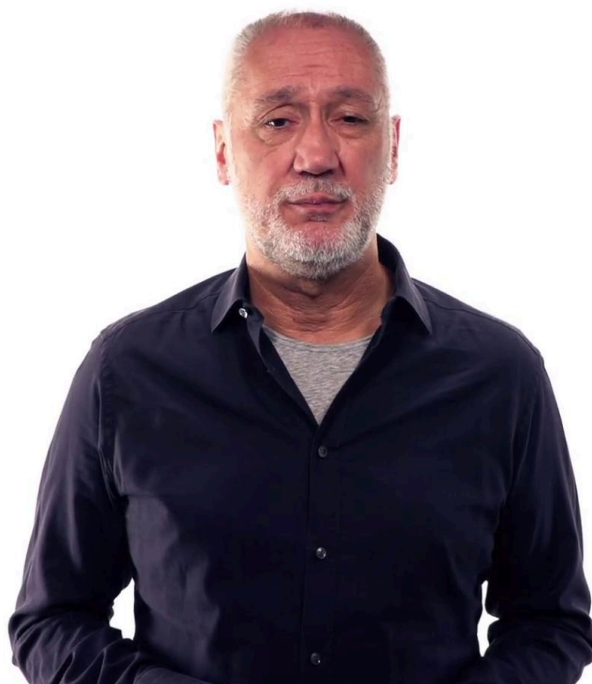
Notes

Summary



13m 20s

In the next video...



In the next video, we continue our discussion of single crystal diffraction but we now turn to the use of monochromatic X-rays in the rotation method, serial synchrotron diffraction, and the selected Bragg peak method.

Notes

Summary

13m 58s

