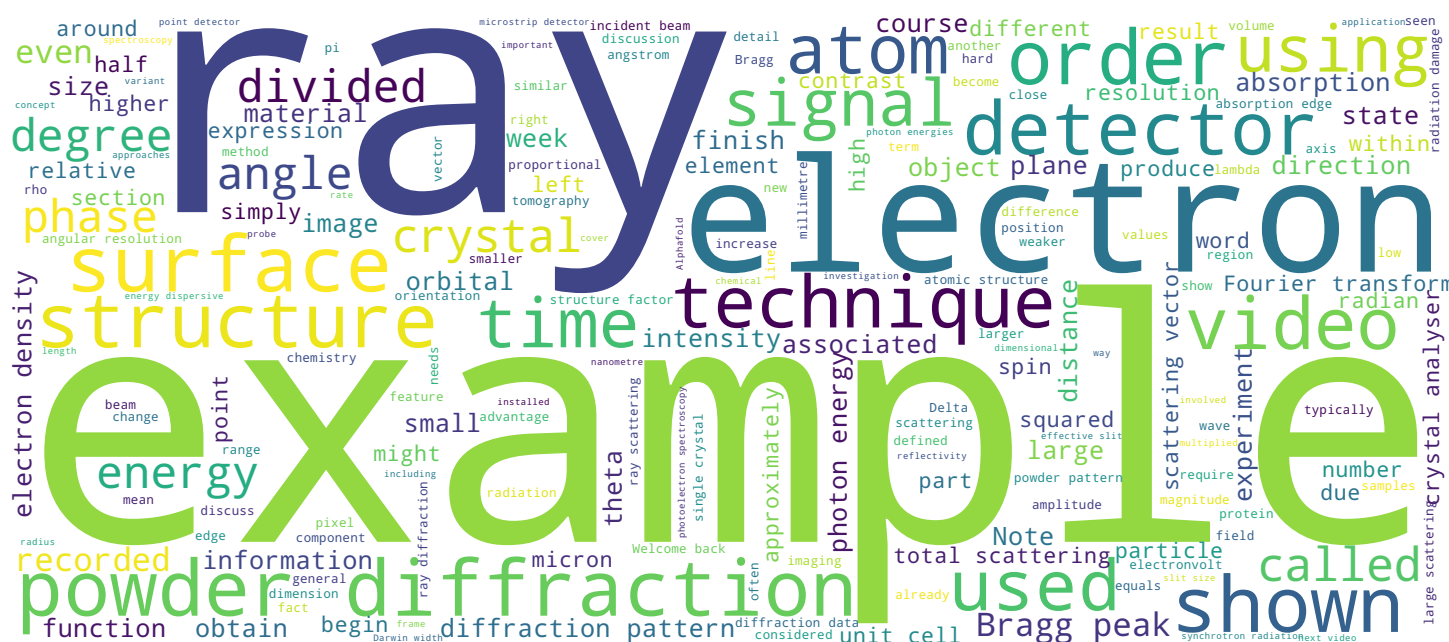


Prof. Philip Willmott



Search MOOC



Video



Contents and objectives of this video



- Angular resolution in PD
- Classic and modern PD setups and detector systems
- Solving structures from PD
- PD examples
- Energy-dispersive PD
- Total scattering

Welcome back. In the second video on powder diffraction, we begin by discussing the angular resolution and the progress from traditional set-ups to those used in modern synchrotron experiments. We touch on methods to solve structures from powder diffraction data, and then we'll show two examples: one regarding the necessity of using parallel data acquisition to obtaining meaningful results, the other demonstrating just how quickly diffraction data can nowadays be recorded and implemented to make dynamical studies on the microsecond timescale. We finish with a brief overview of energy-dispersive powder diffraction and total scattering, and particularly, the pair distribution function.

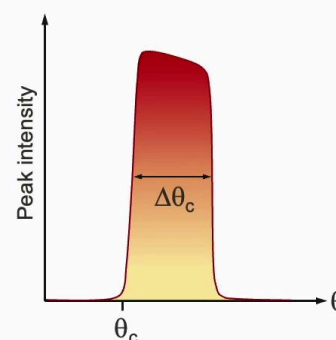
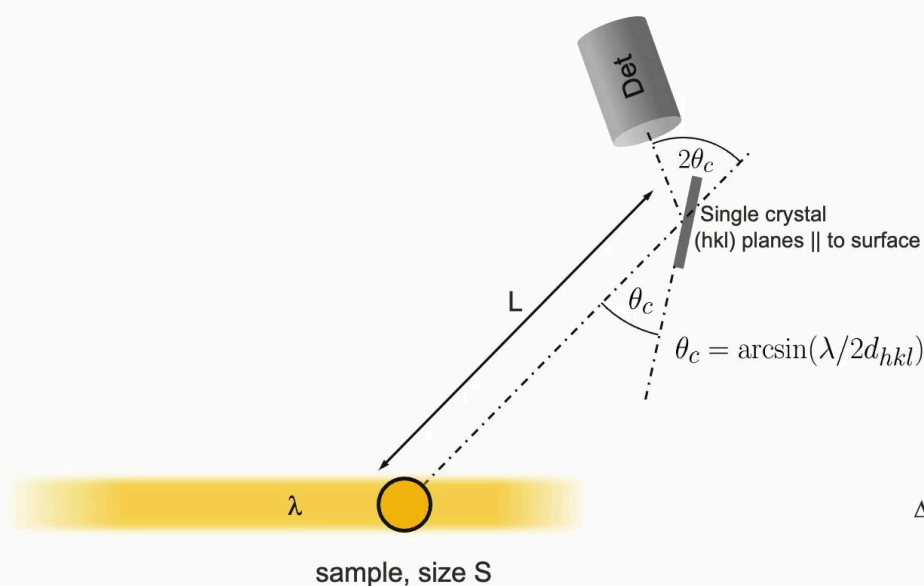
Notes

Summary



0m 05s

Crystal analyzers – getting the best angular resolution



$$\Delta\theta_c = (\Delta\lambda/\lambda) \tan \theta_c$$

$$\Delta\lambda/\lambda = \text{const} = 1.31 \times 10^{-4} \text{ for Si(111)}$$

$$\Delta\theta_c = 2.64 \times 10^{-5} \text{ rad @ 10 keV}$$

\equiv slit width of $18 \mu\text{m}$ for an infinitely small sample size S , and $L = 700 \text{ mm}$

See also: <https://www.chess.cornell.edu/users/calculators/x-ray-calculations-darwin-width>

Okay, let's consider a sample irradiated with X-rays so that it presents a size S in the direction of a detector, which is at a distance L from that sample. The acceptance width of the detector is either defined by the size of its sensitive area or by a pair of slits directly in front of it with a size W . Now, the resolution in 2θ given in radians is simply S plus W divided by L . If, for example, we take a capillary sample with an inner diameter of half a millimetre, and for the detector, a single element from a Mythen microstrip detector, and this has a width of 50 microns, and we place this 70 centimetres from the capillary, we obtain an angular resolution of approximately 8 times 10^{-4} radians or 0.045 degrees. Now, let's replace the slit detector system with a single crystal with a known hkl plane parallel to the surface. This, for example, could be a Si(111) or (001). We set this so-called analyser crystal at an angle θ_c , such that it satisfies the Bragg condition for the monochromatic radiation which is being used. The detector is also in the Bragg condition, in other words, at an angle of two θ_c relative to the diffracted beam.

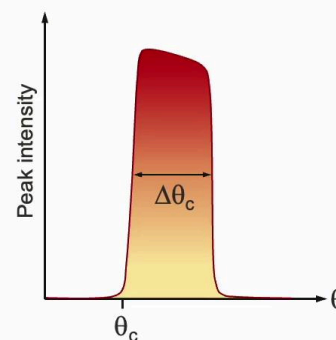
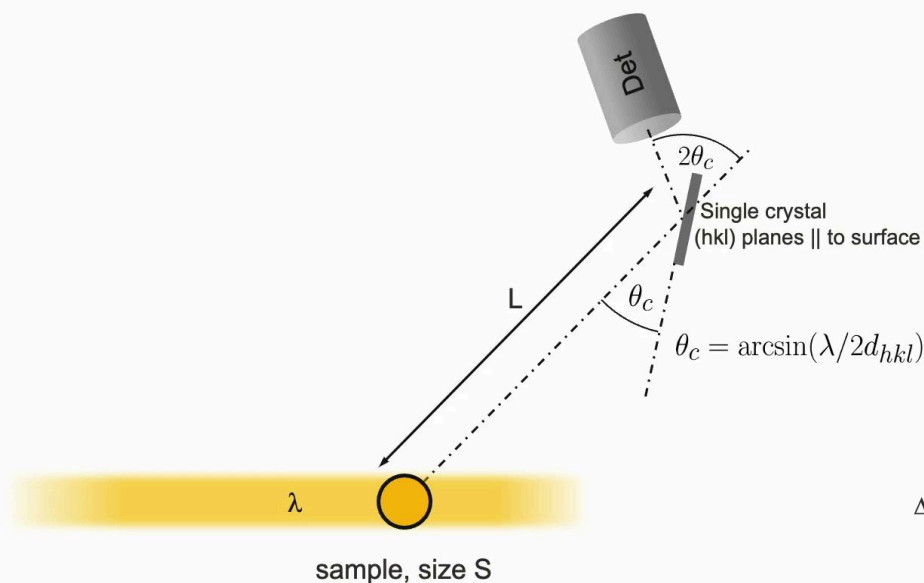
Notes

Summary



0m 51s

Crystal analyzers – getting the best angular resolution



$$\Delta\theta_c = (\Delta\lambda/\lambda) \tan \theta_c$$

$$\Delta\lambda/\lambda = \text{const} = 1.31 \times 10^{-4} \text{ for Si(111)}$$

$$\Delta\theta_c = 2.64 \times 10^{-5} \text{ rad @ 10 keV}$$

\equiv slit width of $18 \mu\text{m}$ for an infinitely small sample size S , and $L = 700 \text{ mm}$

See also: <https://www.chess.cornell.edu/users/calculators/x-ray-calculations-darwin-width>

Now, even a perfect single-crystal will have a range of angles within it which will diffract. This is because only a finite number of crystal planes are involved in the diffraction process, as each plane scatters a small fraction of the incoming radiation on it, meaning that asymptotically, the radiation will get weaker and weaker and weaker and be essentially entirely scattered after a certain depth, known as the extinction depth. Again, this isn't due to absorption, but simply because each atomic layer does scatter a small amount of the incident beam away. Because only a finite number of planes are involved in the diffraction process, this means that the diffraction maximum must have a finite width. It can't have zero width, can't be infinitely narrow. This is called the Darwin width. The expression for the Darwin width is given here. It turns out that, for example, at 10 keV, the intrinsic Darwin width of a Si(111) crystal is 2.64 times 10^{-5} radians. If one therefore assumes an infinitely small sample size S , the ultimate angular resolution is 2.64 times 10^{-5} radians or 1.5 millidegrees. This equates to an effective slit size W at 700 millimetres of only 18 microns.

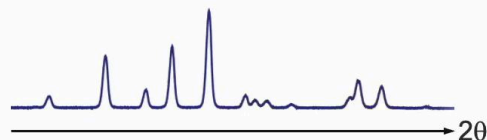
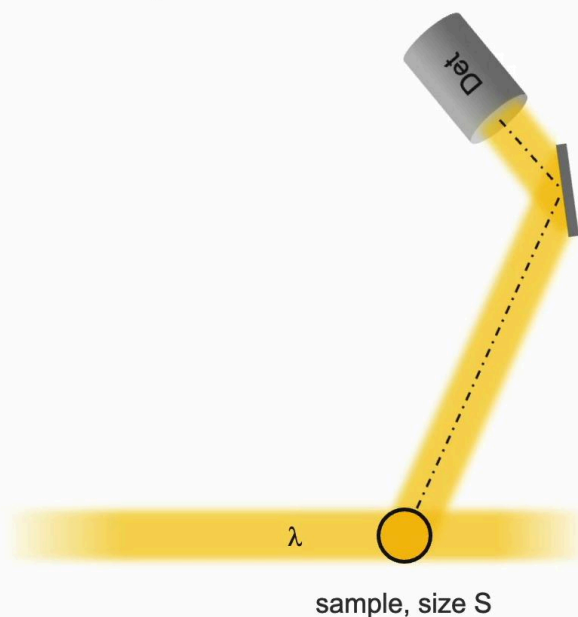
Notes

Summary



2m 28s

Crystal analyzers – nice but slow



Advantages

- Very high resolution, independent of sample size S
- Signal from entire illuminated part of sample
- Fluorescence suppressed through analyzer crystal

Disadvantages

- Very slow! Minutes to hours

What advantage does the use of this so-called crystal analyser system confer? The crystal acts as a virtual slit system, as we've just seen, normally with a very small effective slit size, depending on which crystal type is used. Hence, physical slits can be dispensed with, and the full width of the diffracted beam can be exploited, thus hugely increasing the signal intensity compared to a physical slit system that would have the same resolution. Using a crystal analyser can help in obtaining the very best angularly resolved powder patterns. Moreover, fluorescence is suppressed as it has longer wavelengths than the elastically scattered radiation, and hence it won't be selected by the crystal analyser. The major drawback of using crystal analysers and indeed, any kind of point detector, is that they are slow. The detector system needs to be rotated slowly, which typically requires recording times measured in minutes or actually, even hours in some cases.

Notes

Summary



4m 03s

Powder diffraction – 1-D and 2-D detectors

“Pilatus” 6M 2-D HPAD

2463 x 2527 pixels

172 μm pixel size

Best suited for ultrafast experiments

“Mythen” 1-D strip detector

30720 elements over 120°

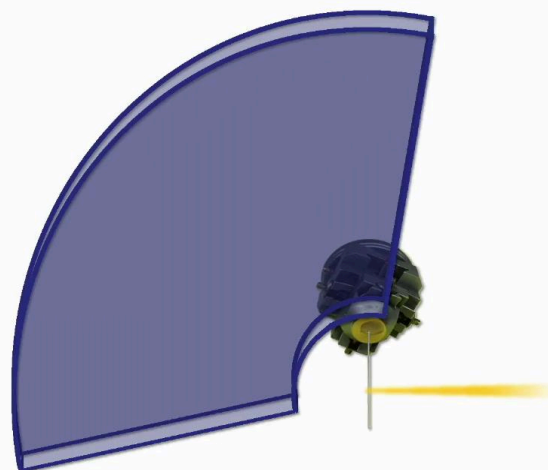
50 μm element width

Best suited for high-Q experiments



Materials Science beamline, SLS

See B. Schmitt *et al.*, [https://doi.org/10.1016/S0168-9002\(02\)02045-4](https://doi.org/10.1016/S0168-9002(02)02045-4)



Now, if your prime objective of a powder diffraction experiment is structure determination alone, one could argue that having the very best resolution is advantageous in order to resolve any closely lying peaks in the powder pattern that might be unresolved with a lower resolution. This was actually something of a mantra in the early 2000s. Anything less than the best resolution was considered to be just unserious. Nonetheless, if the effective slit size is small enough and the X-ray source powerful enough, as one might hope for synchrotron radiation and particularly DLSRs, there are many powder diffraction experiments, including those aiming simply at structure determination that can tolerate a more modest angular resolution. Indeed, many experiments are less interested in an ultra-precise determination of the atomic structure of a static system, but more so in changes due to chemistry or external physical influences, such as pressure or temperature, for example. In these instances, speed, more often than not, trumps angular resolution. Sorry for swearing. Advances in detector technology mean that parallel data acquisition using 1-D and/or 2-D detectors is now standard in synchrotron powder diffraction setups.

Notes

Summary



5m 12s

Powder diffraction – 1-D and 2-D detectors

"Pilatus" 6M 2-D HPAD

2463 x 2527 pixels

172 μm pixel size

Best suited for ultrafast experiments

"Mythen" 1-D strip detector

30720 elements over 120°

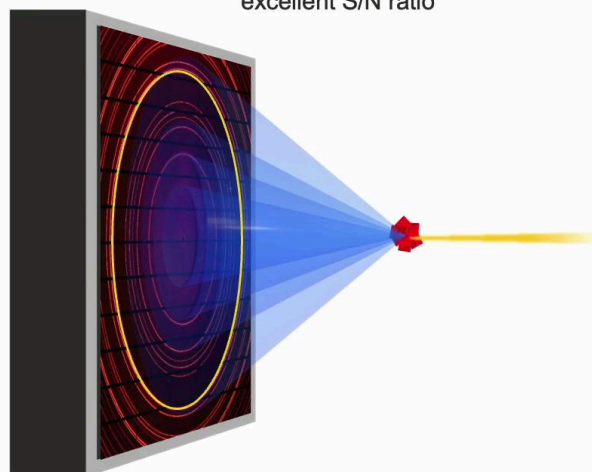
50 μm element width

Best suited for high-Q experiments



Materials Science beamline, SLS

Integrate along entire ring –
excellent S/N ratio



The first beamline worldwide to pursue this route was the Materials Science beamline at the Swiss Light Source. A photograph of it is shown here on the left. A 120-degree 1-D Mythen microstrip detector consisting of 30,720 elements was installed and commissioned in 2002, which allowed powder diffraction data to be recorded at unprecedented speeds, a capability which would prove not only to be advantageous but in fact, indispensable in some instances, as we will shortly see in our first example. The large subtended angle of two theta is equal to 120 degrees means that large scattering vectors, up to 30 reciprocal angstroms can be accessed, thus allowing resolutions as small as approximately 0.2 angstroms, an important capability for techniques such as total scattering, briefly discussed at the end of this video. More recently, a large "Pilatus" 6M detector was installed, while a smaller Eiger module was also made available. The large fraction of the Debye-Scherrer rings that can be captured and integrated, as we see here, using these area detectors provides an excellent signal-to-noise ratio, thus facilitating ultrafast powder experiments, as we will see in the second example shortly.

Notes

Summary



6m 43s

Powder diffraction – 1-D and 2-D detectors

“Pilatus” 6M 2-D HPAD

2463 x 2527 pixels

172 μm pixel size

Best suited for ultrafast experiments

“Mythen” 1-D strip detector

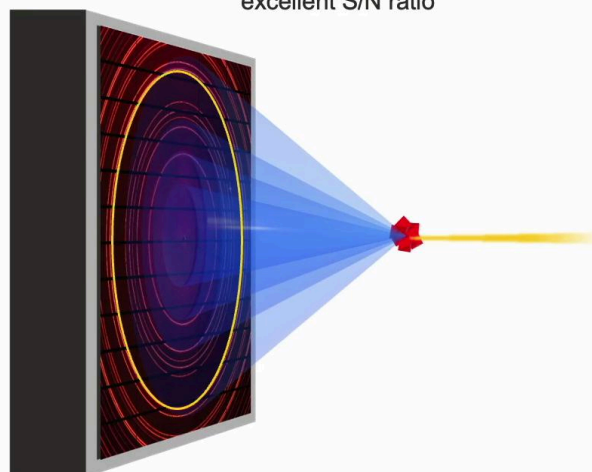
30720 elements over 120°

50 μm element width

Best suited for high-Q experiments



Materials Science beamline, SLS



Integrate along entire ring –
excellent S/N ratio

Note, by the way, that the five-fold crystal analyser system, which had been installed at the Materials Science beamline in the early days, was dismantled about a decade ago as it was simply just never used.

Notes

Summary



8m 14s

Solving the structure in PXRD – model building



- Indexing yields
 - Lattice constants
 - Space group symmetry
- Stoichiometry normally known
 - Apply constraint of physical bond lengths and volume typically occupied by an atom
- Other physical properties
 - e.g. piezoelectric \Rightarrow noncentrosymmetric
- Known motifs?
 - e.g. oxygen octahedra
 - Apply rigid-body translations and rotations
- Simulated annealing
- **Rietveld refinement**

Structural solutions in powder diffraction often follow model-building based on the space group symmetry revealed by indexing the Bragg peaks, stoichiometry, constraints of known physical bond lengths, and the volume occupied by an atom or ion, plus additional information like, for example, piezoelectricity, which implies non-centrosymmetry, or known quasi-rigid motifs, such as oxygen octahedra in perovskite structures. Techniques such as simulated annealing can also play an important role. Once the general structure is confidently known, further refinement using the Rietveld method is a standard approach to obtain an accurate atomic structure. The Rietveld method uses a least squares approach to refine a theoretical line profile until it matches the measured data. There are today many commercially available programmes for Rietveld refinement on the market.

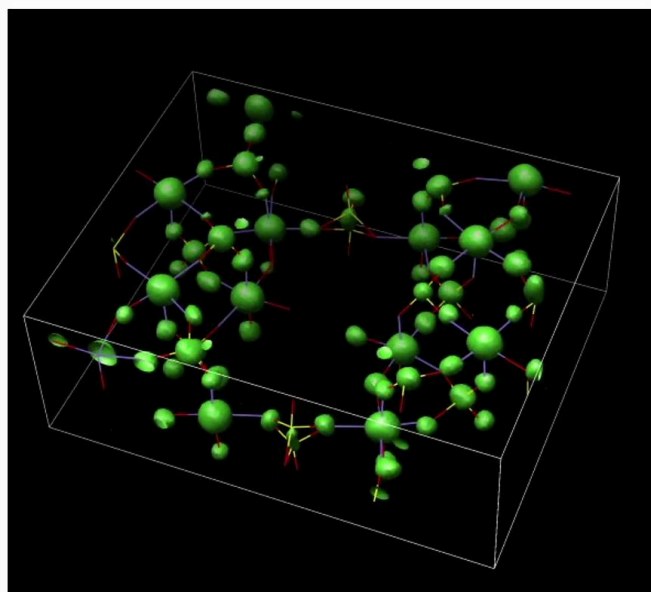
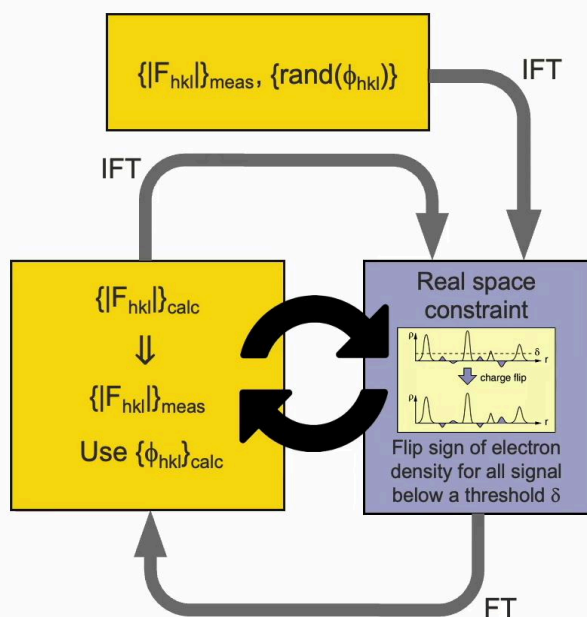
Notes

Summary



8m 27s

Charge flipping



See also: <http://www.crystal.mat.ethz.ch/research/ZeolitesPowderDiffraction/ChargeFlipping.html>

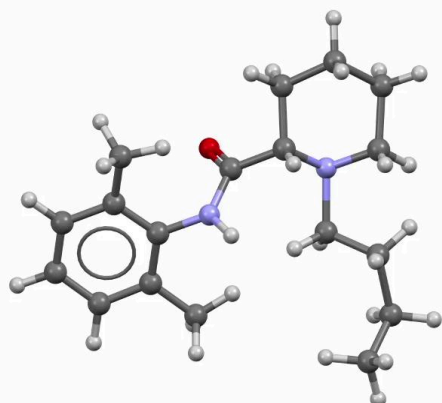
Now, another interesting approach to obtaining a structure from scratch is charge flipping. This is an iterative technique, as we have already encountered in week one of this course. In real space, it applies the action of flipping the sign of all electron density ρ that in a given iteration is below a set threshold. Not only from unphysical negative to physically reasonable positive, but perhaps, quite surprisingly, also vice versa. The justification for this is that if the algorithm has predicted a small positive peak with an associated electron density, which is below that of any atoms thought to be present in the structure, it sets this to the negative value, so that in the next iteration round, this is then probably cancelled out. From this statement, one should glean that the threshold is typically set to be a little smaller than the smallest expected electron density in the structure.

Notes

Summary

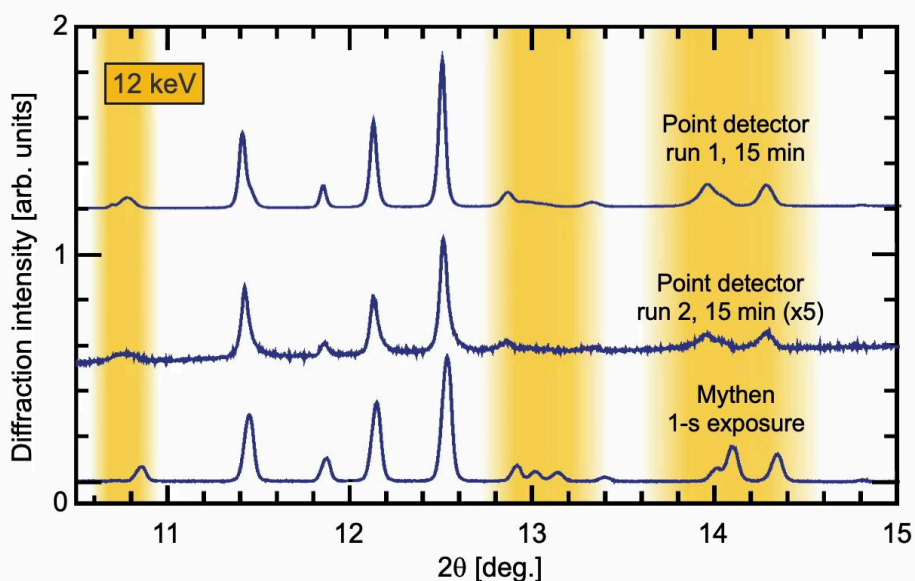


Example I – radiation damage testing pharmaceuticals



Bupivacaine – anaesthetic drug
R-enantiomer (chiral)
[S-enantiomer more vasoconstrictive]

(Courtesy Creative Commons)



See also: A. Bergamaschi *et al.*, <https://doi.org/10.1107/S0909049510026051>

We now look at two examples of modern powder diffraction. The first comes from quality assurance in the pharmaceutical sector. The local anaesthetic chiral drug, Bupivacaine, comes in two enantiomeric forms. The one under investigation is less vasoconstrictive than its enantiomer. Although pharmaceutical relevant, the point of this example is much more basic. An initial powder pattern of Bupivacaine was recorded between 10 and 15 degrees using a crystal analyser and point detector, a scan that took 15 minutes to complete. To make sure that the compound had not been radiation-damaged in the first run, a second identical scan was recorded. As you can see, this check was more than necessary. The pattern was much degraded. Note the five-time scaling factor in this second plot compared to the first, and the obvious increase in noise. A fresh sample was introduced and a diffraction pattern recorded in parallel with a one-second exposure using a microstrip detector. As can be seen in the regions highlighted here, this pattern differs significantly from even the first run, indicating that even towards the start of the first run, before the point detector had got to 11 degrees, radiation damage had already set in.

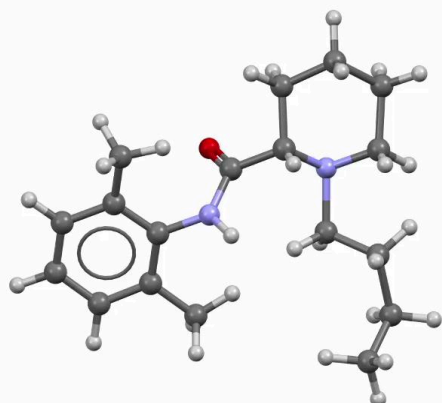
Notes

Summary



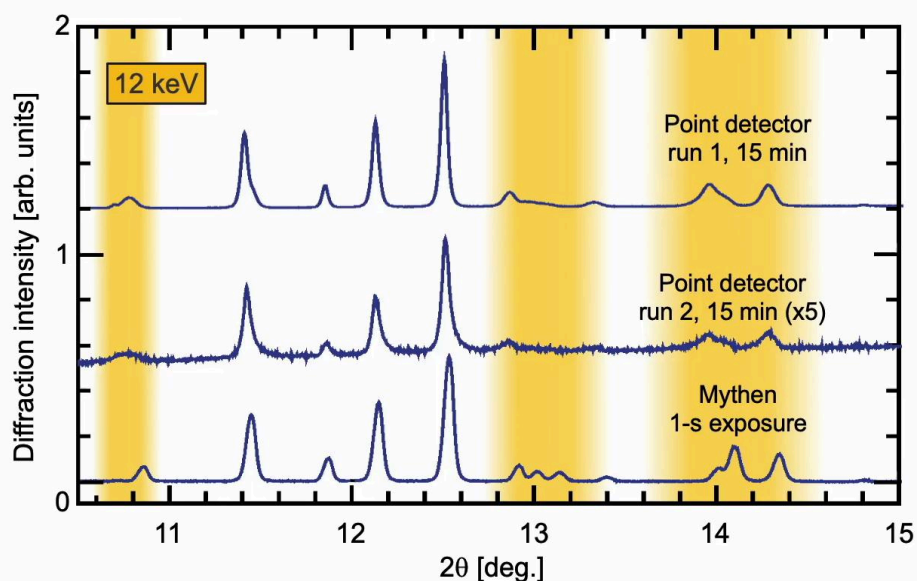
10m 31s

Example I – radiation damage testing pharmaceuticals



Bupivacaine – anaesthetic drug
R-enantiomer (chiral)
[S-enantiomer more vasoconstrictive]

(Courtesy Creative Commons)



See also: A. Bergamaschi *et al.*, <https://doi.org/10.1107/S0909049510026051>

Further tests showed that radiation damage began after only about 5-10 seconds. Therefore, obtaining reliable data using conventional detectors for subsequent structural refinement is all but impossible for such sensitive organic crystals. The use of one-dimensional detectors for parallel acquisition is clearly indispensable.

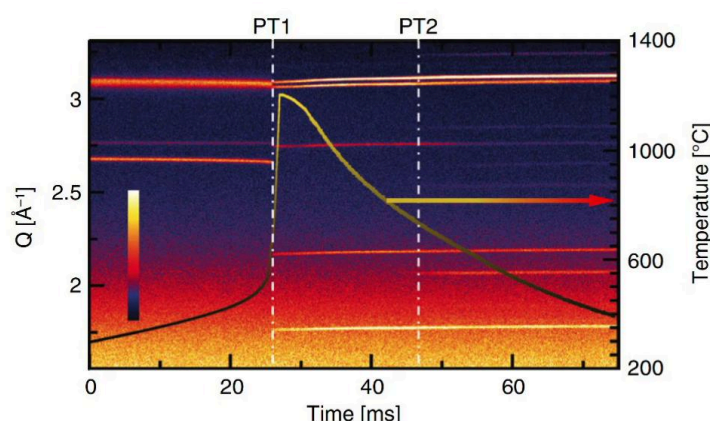
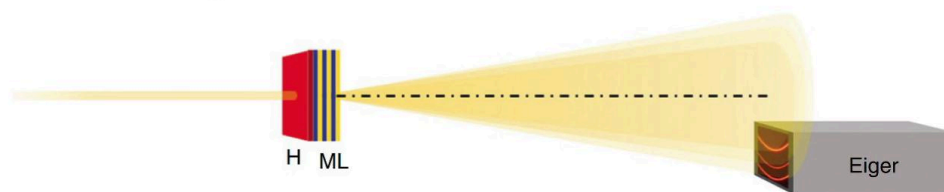
Notes

Summary



12m 08s

Example II – Ultrafast diffraction in real time



- Runaway exothermic alloying reaction in Al/Ni multilayers
 - H: 10'000 K/s heat rate up to 500°C
 - Ignition occurs @ ~ 400 – 500°C
 - Runaway reaction up to 10⁶ K/s takes over
 - Experiment ca. 0.1 s long!
- Eiger 500k detector
 - 4-bit/pixel ⇒ accelerated frame rate
 - 20 kHz frame rate (50 μs exposure – 4 μs dead time)
 - Max 2θ ≈ 30°
 - Integrate Debye-Scherrer ring signals azimuthally

See also: T. Neuhauser *et al.*, <https://doi.org/10.1016/j.actamat.2020.05.035>

The second example concerns the study of following the dynamics of a runaway exothermic alloying reaction, starting with a metallic multilayer of aluminium and nickel. A two-micron thick metallic multilayer was heated using a membrane-based heater, labelled H here, which was transparent to X-rays at 12.6 kiloelectronvolts. It heated at a rate of 4,000 Kelvin per second up to 500 degrees centigrade in order to initiate the alloying process. The powder pattern was recorded using an Eiger 500k detector running at 20 kilohertz and 4-bit operation, which had a dead time of four microseconds. The signal was integrated azimuthally along the powder rings. The temporal evolution of the powder pattern is shown, along with the measured temperature profile. Once alloying begins, a runaway reaction heats the sample rapidly from 500-1,200 degrees centigrade and drives forward the alloying formation. Two distinct phase transitions, PT1 and PT2 are observable, separated in time by only approximately 20 milliseconds. The colour scale bar spans 0.0-0.24 average counts per pixel per frame in the azimuthally integrated direction.

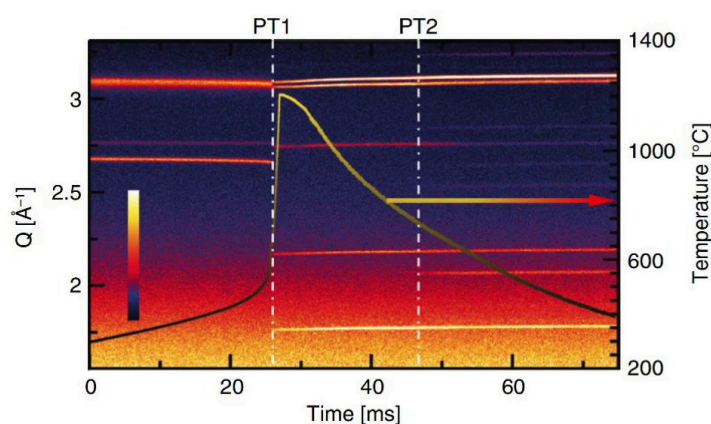
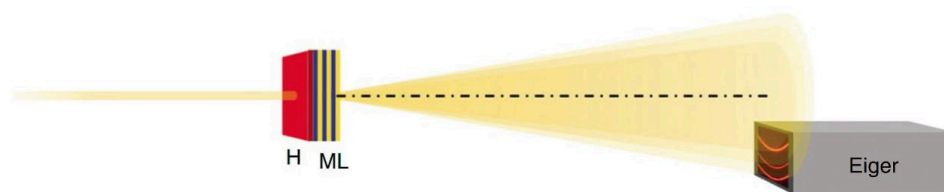
Notes

Summary

12m 32s



Example II – Ultrafast diffraction in real time



- Runaway exothermic alloying reaction in Al/Ni multilayers
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See also: T. Neuhauser *et al.*, <https://doi.org/10.1016/j.actamat.2020.05.035>

This experiment was made possible by running the small 500k-pixel Eiger detector with a dynamic range of only four bits, which equates to a maximum of eight counts, which allowed this frame rate of 20 kilohertz. Now, although the recorded maximum photon counts per pixel per frame were only of the order of one quarter, integration along the Debye-Scherrer rings provided a much more than sufficient signal-to-noise ratio. Such experiments would have been wholly unthinkable even five years earlier, and are excellent examples of how advances along the technological chain in synchrotron science here in the field of X-ray detectors can open up new and exciting scientific vistas.

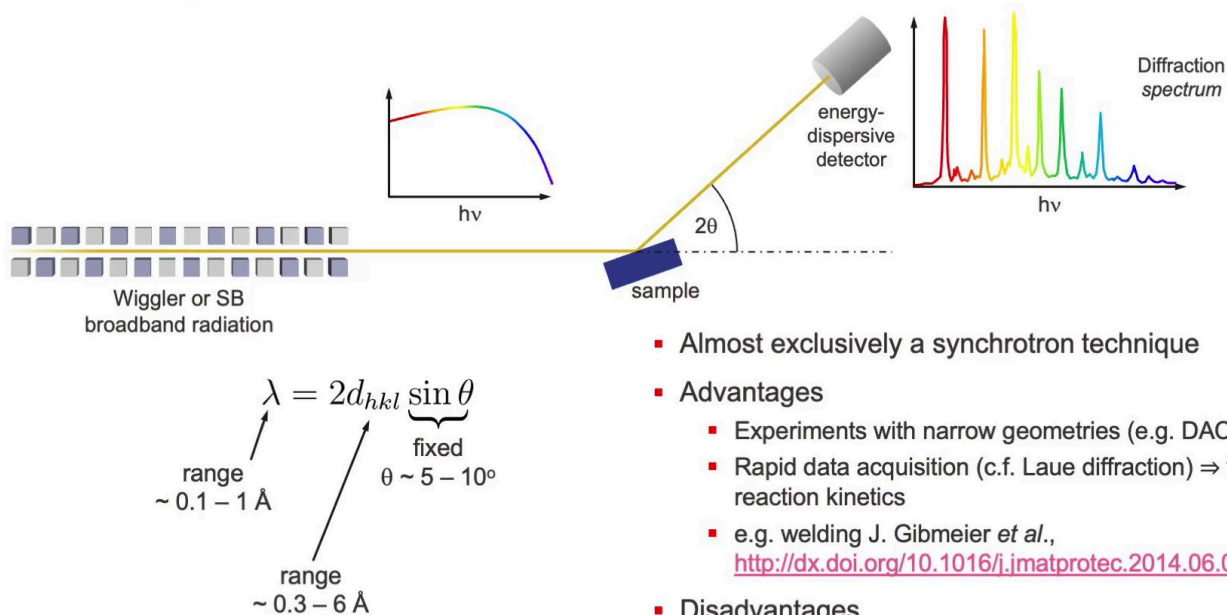
Notes

Summary

14m 03s



Energy-dispersive powder diffraction



- Almost exclusively a synchrotron technique
- Advantages
 - Experiments with narrow geometries (e.g. DAC)
 - Rapid data acquisition (c.f. Laue diffraction) \Rightarrow follow reaction kinetics
 - e.g. welding J. Gibmeier *et al.*, <http://dx.doi.org/10.1016/j.jmatprotec.2014.06.008>
- Disadvantages
 - Radiation damage due to intense beam
 - Poor resolution compared to angle-dispersed methods

See e.g. Ch. Genzel *et al.*, <https://doi.org/10.1016/j.nima.2007.05.209>

We finish this video with two techniques related to standard powder diffraction. The first of these is energy-dispersive powder X-ray diffraction or EDPXT. Simply stated, in contrast to standard powder diffraction, in which the monochromatic radiation is dispersed angularly, in this technique, one varies λ , the photon wavelength and keeps the detector angle constant. This thus requires the broadband radiation offered by wiggler, superbends, or bending magnets. The selected wavelengths, according to Bragg's law, are detected using an energy-dispersive detector and a diffraction spectrum is recorded. EDPXD might be preferred for experiments with very narrow geometries, such as when using a diamond anvil cell. The detector records all the photon energy simultaneously, hence, EDXPD can be fast, as in Laue diffraction, and reaction kinetics can be followed. Disadvantages include the high doses and potential radiation damage associated with the broadband incident beam and all the technical challenges of handling such high-power sources and the fact that the peaks in the spectra are intrinsically broad, making overlap of signal a serious issue.

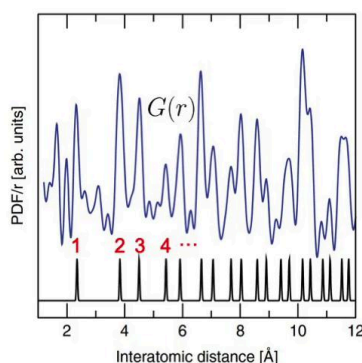
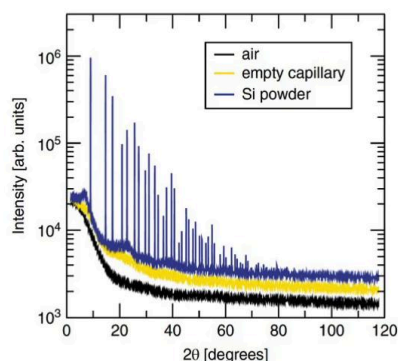
Notes

Summary



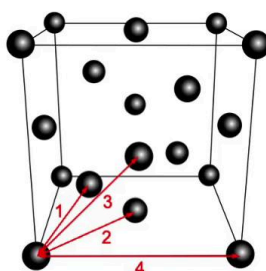
14m 50s

Scattering techniques for disordered systems



$$S(Q) = \text{signal} - \text{capillary} - \text{air}$$

$$G(r) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} Q [S(Q) - 1] \sin Qr dr$$



■ Total scattering

- Diffuse and Bragg scattering
- Up to large Q-values ($\sim 40 \text{ \AA}^{-1} \equiv 0.15 \text{ \AA}$)
 - Small $\lambda \Rightarrow$ reduced elastic scattering
 - Large $\theta \Rightarrow$ drop-off in $f(Q)$
 - e.g. Fe @ $Q = 35 \text{ \AA}^{-1} = 1.72$
 - Extremely photon hungry, almost exclusively synchrotron-based

■ "Real" materials

- Point, extended defects
- Surface reconstructions and adsorbates
- Nanoscale morphology
- ...

■ 1D weighted Patterson function

- Yields interatomic distances but no angles
- **Pair-distribution function PDF(Q)**
- Complementary to EXAFS(k_e)

See also: S.J.L. Billinge, <http://dx.doi.org/10.1098/rsta.2018.0413>

We finish this video with total scattering, a technique used for disordered systems. It's related to small and wide-angle X-ray scattering and requires one to record signal at large scattering vectors or up to large scattering vectors. Because this normally means one has to have high photon energies or small X-ray wavelengths and large scattering angles, the atomic form factor here can be very small indeed, making total scattering a very photon-hungry technique that is almost exclusively synchrotron-based. For example, iron with a scattering amplitude of 26 in the forward direction, has only a value of 1.72 at 35 reciprocal angstroms. Total scattering is a powerful technique in the investigation of real materials, which deviate significantly from semi-perfect model systems and might include different types of crystalline defects, adsorbates, and unusual nanoscale morphologies. It's normally based on the so-called pair distribution function, which yields interatomic distances but not angles. In this sense, it's mathematically similar to a 1D weighted Patterson function and can be thought of as being complementary to EXAFS which exploits interference between scattered electron waves. We'll discuss EXAFS next week.

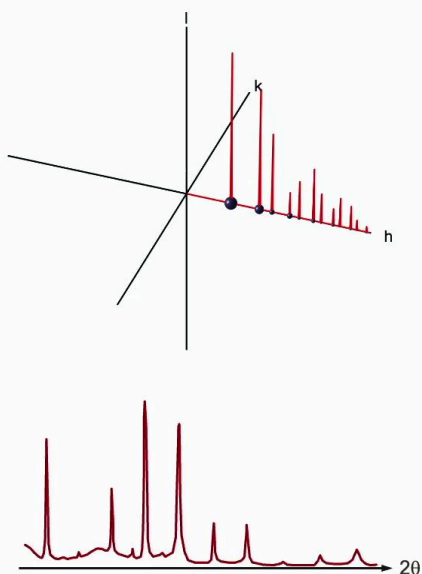
Notes

Summary



16m 16s

Summary of this section



Summarising this two-video section on powder diffraction, we considered what advantages and problems are associated with collapsing a 3D diffraction pattern into one dimension.

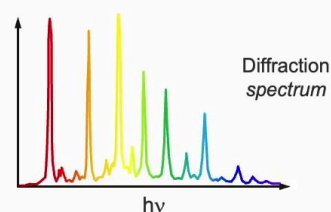
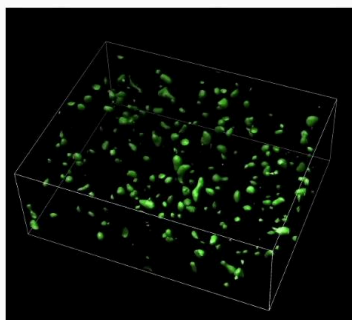
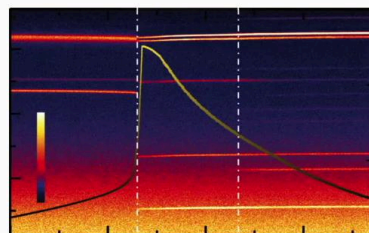
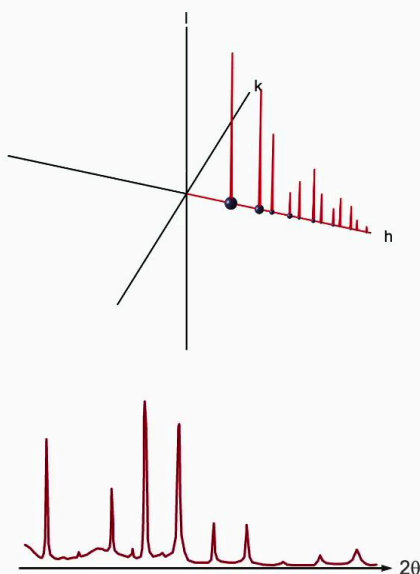
Notes

Summary

17m 47s



Summary of this section



We discovered what information can be typically extracted from powder-fraction data and how modern synchrotron powder stations have profited from developments in detector technology. We also looked at approaches to determining atomic structures from powder diffraction data and looked at two examples of the kind of science modern powder diffraction stations are capable of. We finished with a brief overview of the related techniques of energy-dispersed powder diffraction and total scattering.

Notes

Summary

18m 04s



In the next section...



In the next section, we will take a look at surface X-ray diffraction, a photon-hungry technique that probes crystalline surfaces and interfaces, regions that are becoming increasingly important to understand as material science shrinks ever more in the nanometre regime, especially in the world of novel electronic materials.

Notes

Summary

18m 33s

