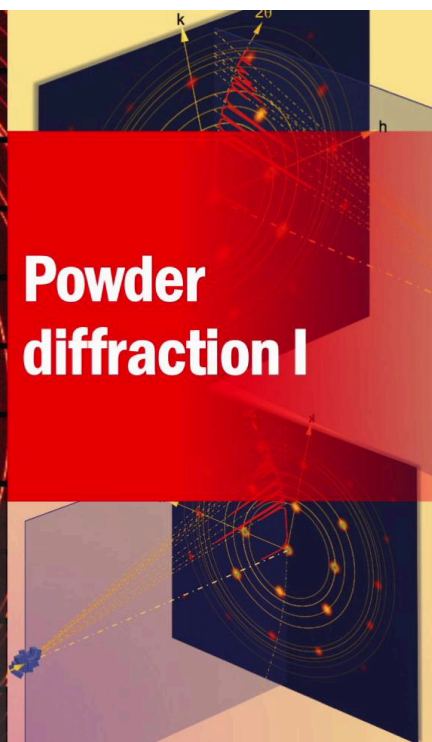
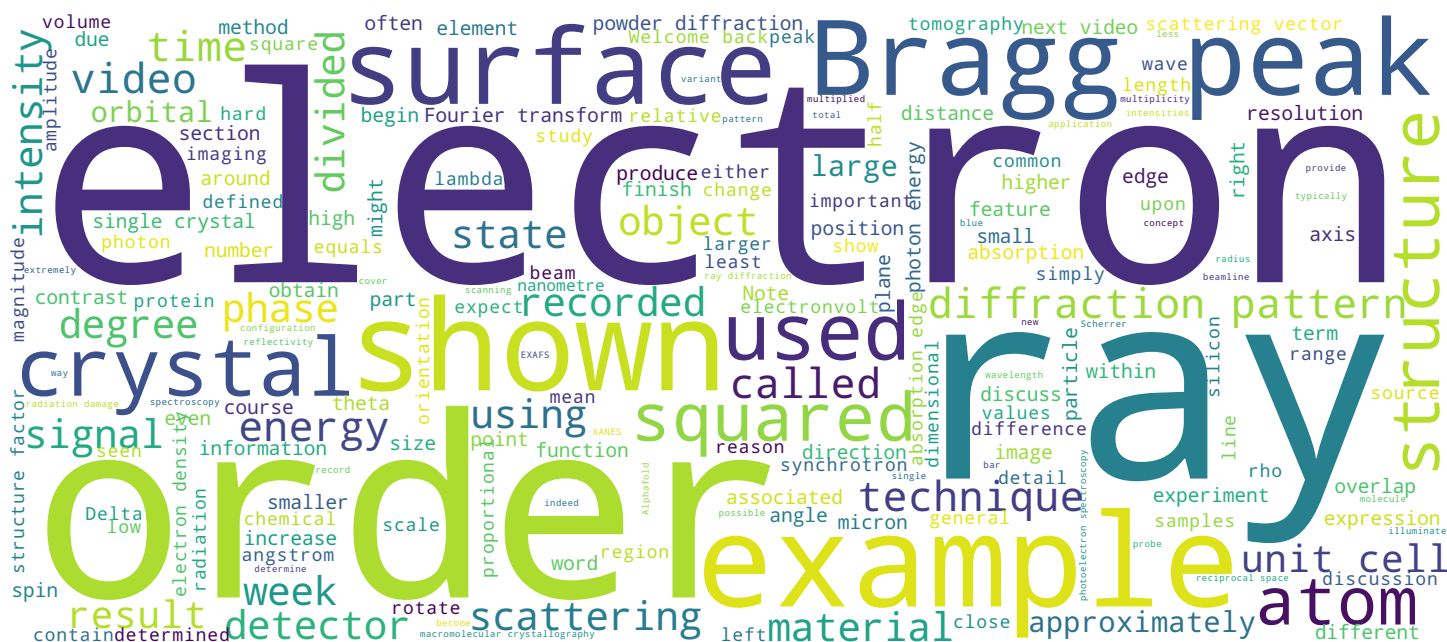


# Powder diffraction I

Synchrotrons and x-ray  
free-electron lasers  
Techniques and  
applications



Prof. Philip Willmott



Search MOOC



Video



# Contents and objectives of this video



- What is powder diffraction?
- Why powder diffraction?
- Features of powder diffraction
- Sample configurations
- The Scherrer equation

Hello again. In this, the first video of the second section of week 2, we are going to look at powder X-ray diffraction, what it is, why we might want to use it, its salient features and configurations, and because I work at his eponymous institute, a short summary of Paul Scherrer's equation.

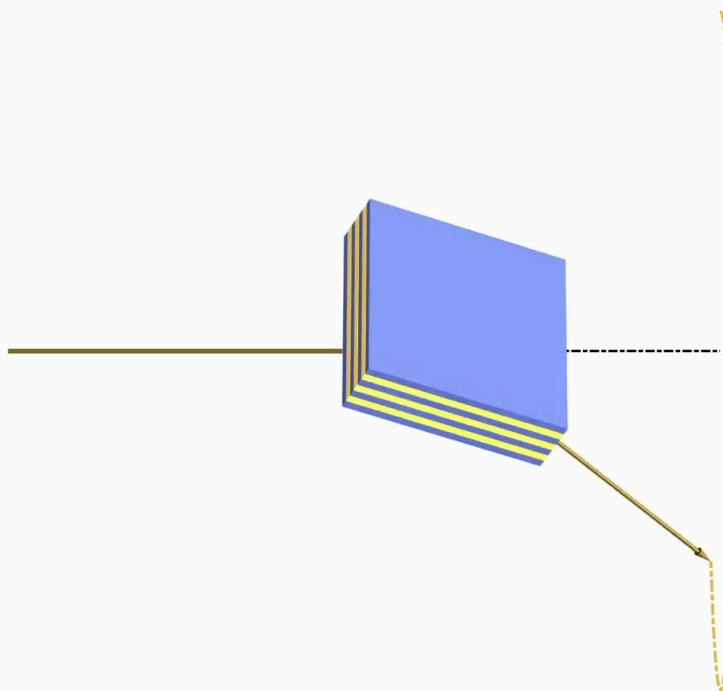
Notes

Summary



0m 05s

# Symmetry axis of the Bragg condition



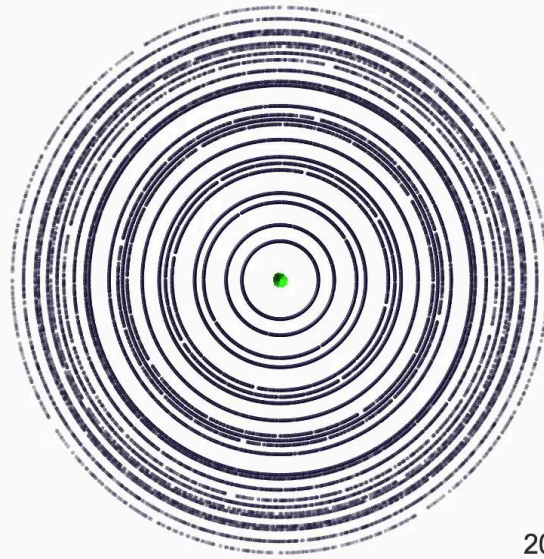
First, let's consider a simple experiment in which we have aligned a crystal so it satisfies the Bragg condition for a certain Bragg reflection. It should be clear to you that the Bragg condition is unaffected if we rotate the crystal around the normal to the pertinent  $hkl$  crystals. But not only that, what if we rotate the crystal about the axis of the incoming radiation?

Notes

Summary



# Generating Debye-Scherrer rings



200

The instant beam remains at an instant angle of  $\theta_{hkl}$  relative to the crystal planes. But the scattering plane contains  $k_{in}$ ,  $k_{out}$ , and the scattering vector  $Q$ , and this rotates in the same manner as the crystal. This means that the trace of the scattered radiation describes a conical surface. The incident beam axis is therefore an axis of cylindrical symmetry. If we look at a 2D diffraction pattern from the perspective of the incident radiation of a single crystal, we see something like this. If we add a second crystal at a random orientation relative to the first and illuminate both crystals simultaneously, we observe a second diffraction pattern at another rotation angle. Continuing this for ever more and more simultaneously illuminated and randomly orientated crystallites will result in a set of diffraction rings known as the Debye-Scherrer rings.

Notes

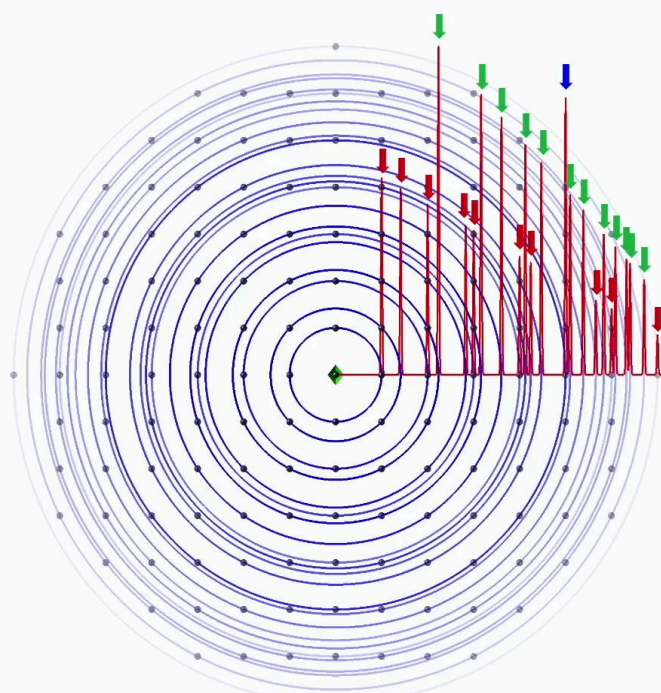
Summary



0m 51s



# Generating Debye-Scherrer rings



- $h$  or  $k = 0, h = k: M = 4$
- $h \neq k \neq 0: M = 8$
- $(hk) = (50)$  and  $(43)$  have same  $d_{hk} = d_{10}/5, M = 12$

Now, in danger of laboring a point, let's now, instead of adding individual diffraction sets at different angles, we simply rotate our single-crystal diffraction pattern through 360 degrees to obtain the same result. Now, one of the reasons I show this is that in high symmetry cases, some diffraction spots are symmetrically equivalent to others, hence their signals will overlap and increase the intensity. The number of equivalent spots for a given hkl is called the multiplicity of that reflection. Note for example this subset of maxima, which follow a more or less monotonic change in intensity and this, with yet another trend. Now there's one exception highlighted here in blue, and these can be understood in terms of their multiplicities. If either  $h$  or  $k$  is 0 or  $h$  is equal to  $k$ , the multiplicity is 4. For  $h$  not equal to  $k$  and not equal to 0, the multiplicity is 8. The special case highlighted with the blue arrow corresponds to an overlap of the 5 0 and 4 3 equivalent Bragg peaks as they have the same interplanar  $d$ -spacing of  $d_{10}/5$ . Now, why is that? Well it's because this is a square symmetry diffraction pattern, and from Pythagoras, 3 squared plus 4 squared is equal to 5 squared. Now, if we'd recorded out to  $h$  or  $k$  is equal to 13, we would, for the same reason, have seen a similar perfect overlap of non-equivalent Bragg peaks, the 13 0 with the 12 5 peaks.

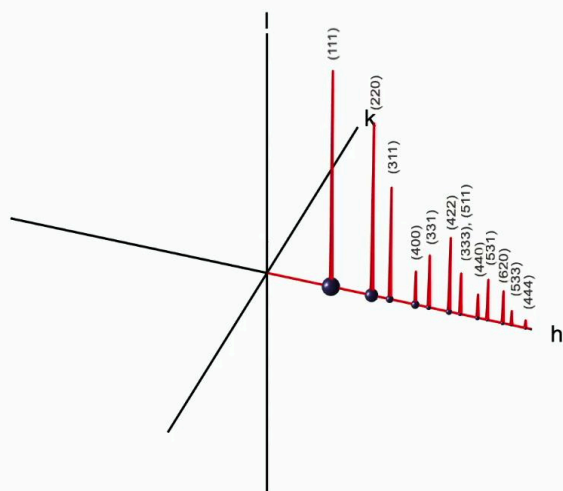
Notes

Summary



1m 56s

# Powder diffraction – the whys and wherefores



Silicon single crystal to powder pattern

- 3D information collapsed to 1D
  - e.g. silicon single crystal
    - $(h^2 + k^2 + l^2)^{1/2} \leq 7$   
246 Bragg peaks in 3D reduced to 12 in 1D
- Rapid data acquisition ✓
  - Time-resolved studies even down to  $\mu\text{s}$  regime
  - Reduced radiation damage
- Overlapping signal ✗
  - Density of peaks increases with decreasing symmetry (unit cell, basis)

So why powder diffraction? Now, let's consider the simulated 3D diffraction pattern of silicon shown here. There are a total of 246 Bragg peaks with a scattering vector less than or equal to 7 times the reciprocal lattice constant  $2\pi$  divided by a silicon, not including the 0 0 0 direct beam, by the way. If we collapse this first azimuthally, then in the polar direction, this reduces to just 12 peaks in 1D. This means diffraction data can be recorded much more quickly, especially as the powder peaks can be recorded in parallel using a 1D or 2D detector. This opens up the possibility of performing time-resolved studies even down to the microsecond regime, and without the need for stroboscopic approaches such as used in serial macromolecular crystallography. Moreover, parallel data acquisition, as we will see in an example in the next video, reduces the problem of radiation damage. On the negative side, overlapping signal becomes an issue, especially for crystals with low symmetry and/or large unit cell sizes. Note for example, the overlap of the 3 3 3 with the 5 1 1 peaks, again because of Pythagoras, 3 squared, plus 3 squared, plus 3 squared is equal to five squared, plus one squared, plus one squared. In many cases, overlaps are coincidental and not necessarily mathematically exact, but just sufficiently close that they cannot be distinguished.

Notes

Summary



3m 46s

# Powder diffraction – the whys and wherefores



- Materials that only produce micro- or nanocrystals of sufficient quality – PXRD!
- Identification of composite parts in multicomponent mixtures – PXRD!
  - Pharmaceuticals, earth sciences, minerology, archaeology, catalysis...
- Extreme environmental studies, phase changes as function of temperature and/or pressure – PXRD!
  - Information often only extractable from powder samples
    - Microcrystallites' large surface area-to-volume ratio accommodates phase changes by relaxation and propagation of crystallographic faults to surface

The advantages of powder diffraction extend beyond rapid data acquisition. Some materials only produce micron or even nano-sized crystals of sufficient quality, precluding them from single-crystal studies. Moreover, powder diffraction allows composite parts of multi-component mixtures to be quantitatively identified, something that is very important in the pharmaceutical industry where trace amounts of some other compound might have a catastrophic impact. Many scientific disciplines deal with real systems that include many different components, such as in the earth sciences, archaeology, catalysis, and so on and so forth. Powder samples are often also preferred in extreme environmental studies where, for example, exerted pressures or elevated temperatures can induce wholesale changes in the chemical and crystallographic structure. Such wholesale changes cannot be accommodated in a large single crystal. It would just break up into small pieces. However, the small size of the micron-sized crystals typically found in powder diffraction studies have got a large surface area to volume ratio, and this can accommodate phase changes by relaxation and propagation of crystallographic faults towards the surface.

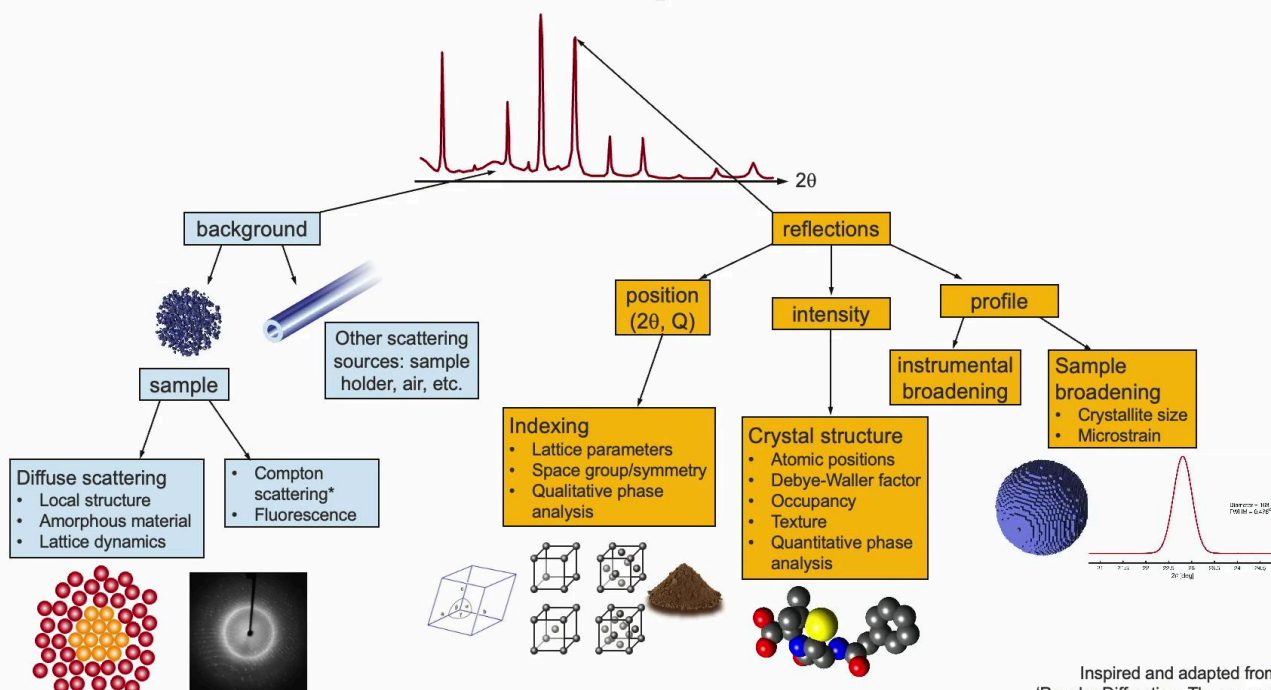
Notes

Summary



5m 32s

# Information content from powder diffraction data



\* See Part 1, Week 2, Section 2, Video 3

Inspired and adapted from figure in  
'Powder Diffraction: Theory and Practice'  
Eds. R.E. Dinnebier & S.J.L. Billinge (RSC, 2008)

Okay. What information content can we hope to extract from powder patterns? Let's first deal with any background signal we might have. This can have its origins in scattering from other sources, such as a capillary tube used to hold the powder, or from the sample itself due to diffuse scattering from local structure or scattering from truly amorphous material such as the well-known water ring in protein crystallography, for example. Physical phenomena such as fluorescence or Compton scattering can also contribute. The reflections provide their positions in reciprocal space, which lead to a determination of the lattice parameters and space group symmetry. The intensities allow one to determine the basis, in other words, the atomic positions, the degree of the disorder, including occupancy, texture, etc. The width and shape of the Bragg peak profiles may be largely determined by instrumental broadening, but might also be due to finite size effects as in the Scherrer equation or microstrain, resulting in the determination of strain tensors, etc.

Notes

Summary





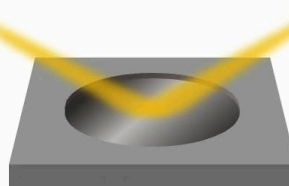
# Common sample configurations

## Capillary



- Transmission (Debye-Scherrer) geometry
- Diameter typically between 0.2 and 1 mm
- Requires good transmission
- Quartz, sapphire capillaries
- Normally true powder/randomly oriented crystallites
- Option to spin capillary

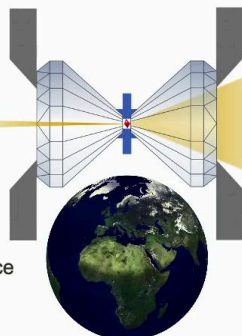
## Flat plate



- Reflection geometry
- Often Bragg-Brentano geometry ( $\theta$ - $2\theta$ )
- Often high-Z materials
- Thin heteroepitaxial films
- Often textured sample
- Option to spin plate around sample normal

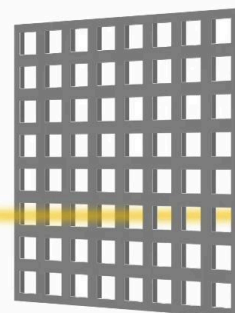
## Diamond anvil cell

- High-pressure experiments up to 200 GPa (2 million atmospheres)
- Insert small ruby crystal to calibrate pressure via its fluorescence lines
- Geology/deep-earth simulations
  - Up to 600 GPa, 5000 K
  - Inner core conditions
  - See e.g. S. Anzellini *et al.*, Science DOI: [10.1126/science.1233514](https://doi.org/10.1126/science.1233514)



## Multisample plate

- Survey experiments
- Rapid exchange of samples via rastering of plate in x- and y-directions
- 100s of samples/plate possible



Powder samples can vary according to the application. Shown here are just four common examples. The use of capillaries is common in synchrotron powder experiments. Such a sample configuration requires good transmission and low scattering of the capillary material such as by fused silica quarts. A flat plate geometry is more common in experiments using lab-based sources and reflection geometry or for the study of thin heteroepitaxial films on substrates. Diamond anvil cells are used in high-pressure experiments up to two million atmospheres similar to pressures exerted on material deep within the earth's core. Some experiments require the study of many similar samples, in which case multi-sample plates can be employed in which the openings are moved in a raster-like manner, left and right and up and down.

Notes

Summary



8m 16s

# Typical sample sizes



- u.c. linear dimensions  $\sim 10 \text{ \AA}$
- $1000 \text{ u.c./}\mu\text{m}$ ;  $10^9/\mu\text{m}^3$ 
  - SR @ DLSRs:  $\ell_c^{(l)} \sim 10 \mu\text{m}$ ,  $\ell_c^{(t)} \sim 100 \mu\text{m}$
  - $\Rightarrow$  linear crystallite size  $\sim 5 \mu\text{m}$  should be coherently illuminated  $\equiv 10^{11} \text{ u.c.}$
- Take  $0.5\text{-mm } \phi$  ID capillary, illuminate  $2\text{-mm}$  length
  - $\sim 10^6$  crystallites illuminated
  - Spin sample to get larger fraction of these in Bragg condition
    - Factor  $= 2\pi/(\text{BP width}) \sim 2 \times 10^4$
- Radiation damage?
  - Shift capillary along its own axis

Now, how large should a sample be? Each individual crystallite might be of the order of a cubic micron in size and contain a billion unit cells. As a longitudinal coherent length is also of the order of a micron for monochromatic synchrotron hard X-rays, and the transverse coherent lengths are at least an order of magnitude larger, one can expect such particles to be fully coherently illuminated and contain of the order of 10 to the 11 unit cells, depending on the exact details of the crystallite dimensions. If one illuminates a  $0.5\text{-millimetre}$  diameter capillary along  $2 \text{ millimetres}$  of its length, one can expect to illuminate about 10 to the 6, 1 million crystallites. If one spins the capillary around its own cylindrical axis, one will bring a larger fraction of these into the Bragg condition by a factor which is approximately equal to  $2 \text{ Pi}$  radians divided by the Bragg peak width. If radiation damage becomes an issue, the capillary can also be shifted along its own axis to expose fresh material.

Notes

Summary

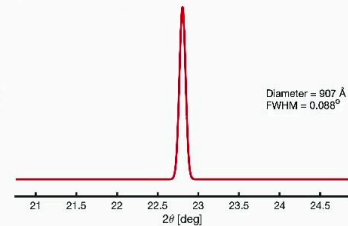
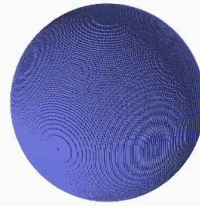


# The Scherrer equation

$$\tau = \frac{K \lambda}{\beta \cos \theta}$$

- $\tau$  = crystallite size (same units as  $\lambda$ )
- $K$  = form factor  $\approx$  unity
- $\lambda$  = x-ray wavelength
- $\beta$  =  $2\theta$ -FWHM of Bragg peak in radians
- $\theta$  = Bragg angle

- Only valid if crystallite size < coherence volume  $\ell_c^{(l)} \cdot \ell_c^{(t,x)} \cdot \ell_c^{(t,y)}$  and quasi monodisperse
- 3<sup>rd</sup> generation: crystallites  $\sim 0.1 \mu\text{m}$ 
  - Scherrer eqn. unsuitable for single-crystal diffraction
- DLSRs: 1 – 5  $\mu\text{m}$



Intrinsic Si(111) peak @ 10 keV for spherical crystallites between 9 and 201 unit-cell diameter



See also e.g.: <http://prism.mit.edu/XRAY/oldsite/CrystalSizeAnalysis.pdf>

Now we're going to finish this, the first of two videos of powder diffraction, with a précis of the Scherrer equation. This states that the characteristic crystallite size can be determined by the equation given by  $K \lambda$  divided by  $\beta \cos \theta$ , where  $K$  is a constant which is close to unity,  $\lambda$  is the X-ray wavelength,  $\beta$  is the full-width half maximum of the Bragg peaks in radians, and  $\theta$  is a Bragg angle. Now, in my experience, the Scherrer equation is overused and the limitations of its validity are often not fully understood. The most important of these is that it's only valid if the crystallite can fit within the coherence volume of the X-rays defined through the two transverse and one longitudinal coherence lengths. The smallest of these is of the order of a micron or two. Hence, this represents the upper limit of validity. Another important consideration is that the equation assumes a monodisperse ensemble, that is, an ensemble in which all of the crystallites are approximately of the same size. Note also that if some crystallites are strained and others aren't, or if the strain is not homogeneous, which is a likely scenario actually, then the result through the Scherrer equation will deliver a size that is smaller than in reality.

Notes

Summary



10m 26s

## In the next video...



In the next video, we look at practical aspects of powder diffraction, including detector schemes, phase retrieval algorithms, and two recent examples. We will finish with a very brief description of the pair distribution function, a technique used primarily for highly disordered and nano-scaled systems.

Notes

Summary



11m 57s