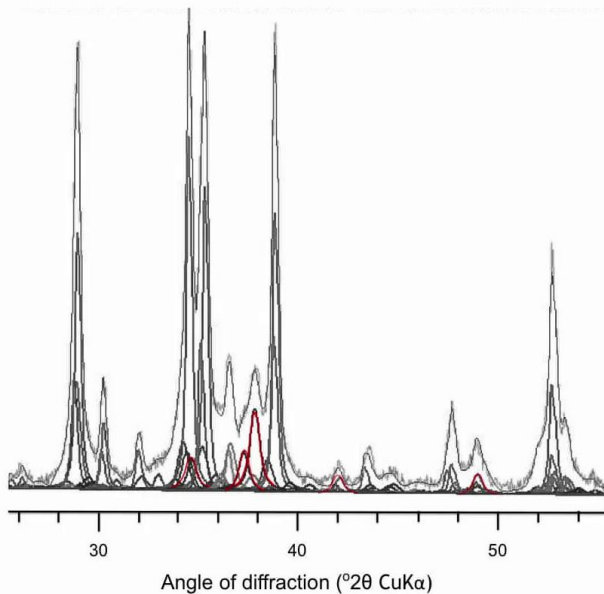


## Cement Chemistry and Sustainable Cementitious Materials

[illegible]

# Why use XRD to study cements?



- Alite ( $\text{Ca}_3\text{SiO}_5$ ) – 56 m%
- Belite ( $\text{Ca}_2\text{SiO}_4$ ) – 12 m%
- Aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ) – 6 m%
- Ferrite ( $\text{Ca}_4(\text{Al,Fe})_2\text{O}_{10}$ ) – 10 m%

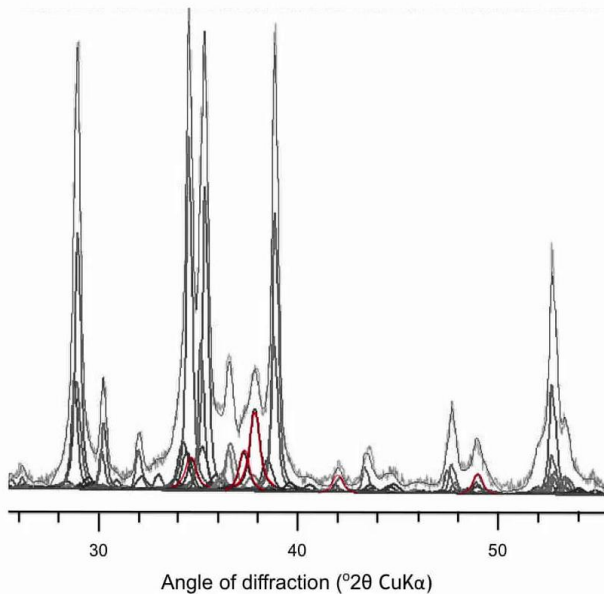
The aim of this session is to give a first introduction on the application of X-ray diffraction and to explain some of the basics underlying the diffraction of X-rays on crystalline materials. First we will illustrate how we can use X-rays to study cement and also we will show what are the main challenges to be met when applying this technique on cementitious materials. On the left side of the slide, you can see a typical example of part of an X-ray diffraction pattern of Portland cement. On the x-axis you can see the angle of diffraction and on the y-axis the intensity of the elastically scattered X-rays. The diffraction pattern itself looks a bit like an intricate landscape of peaks and valleys. As will be explained in more detail later in the course, characteristic series of peaks can be related to individual crystalline phases. The intensity of these sets of peaks scales with the concentration of the corresponding phases. The main phases present in the cement sample are alite, given in blue, belite, shown in purple, C3A or aluminate, in green, and ferrite, as shown in red here. Fitting of the intensity of these sets of peaks enables to extract the relative concentration of the different phases.

Notes

Summary



# Why use XRD to study cements?



- Alite ( $\text{Ca}_3\text{SiO}_5$ ) – 56 m%
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This, in this example, is done using a method called the Rietveld method and this method will be introduced later in this course as well. The results of the phase quantification are shown on the right hand side. Looking at the sets of peaks and how they overlap, it is very striking to see that there is really very much overlapping and this is a problem when we are treating the data and especially when looking at cements, this kind of problem of peak overlapping is one of the main challenges to obtain good quantification data.

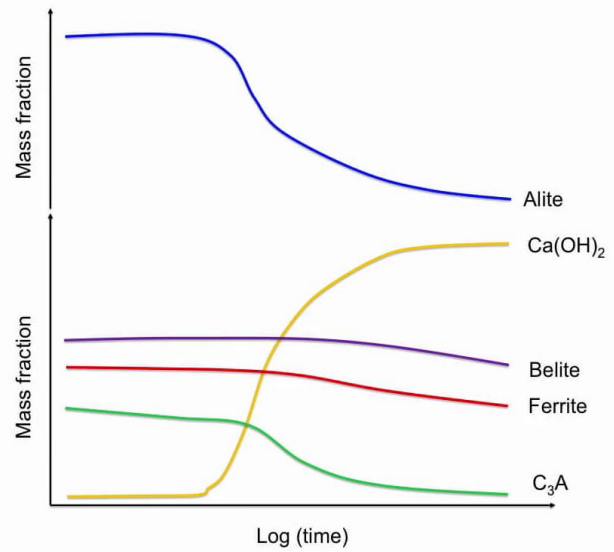
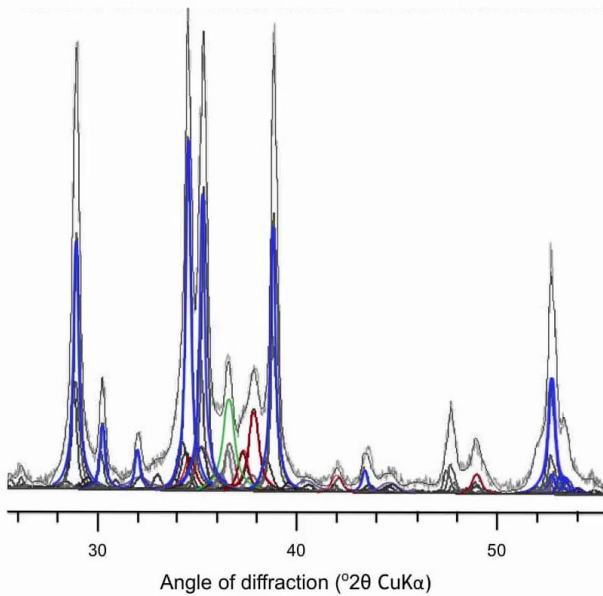
Notes

Summary



1m 31s

# Why use XRD to study cements?



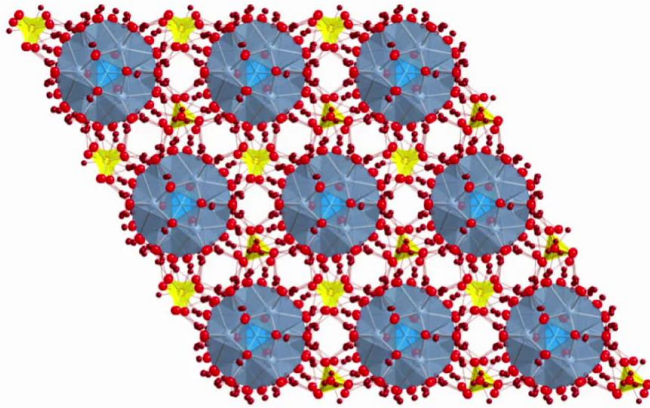
Performing this type of analysis on a time series of measurements enables you to study reaction kinetics and mechanisms in multi-phase mixtures such as hydrating cement. For instance the graph on the right side illustrates how clinker phases such as alite and belite get consumed over time during the hydration of the cement and how at the same time cement hydrates such as portlandite or calcium hydroxide or ettringite form. This type of information can for instance be used to unravel reaction mechanisms or to serve as an input for hydration models for a better understanding of the hydration of cement.

Notes

Summary



# Why use XRD to study cements



- Follow individual phases
  - Changes in content
  - Changes in crystal structure – composition
- Assets
  - Identify and quantify cement composition – before and during hydration
  - Establish reaction mechanisms
  - Study kinetics of hydration or clinkering

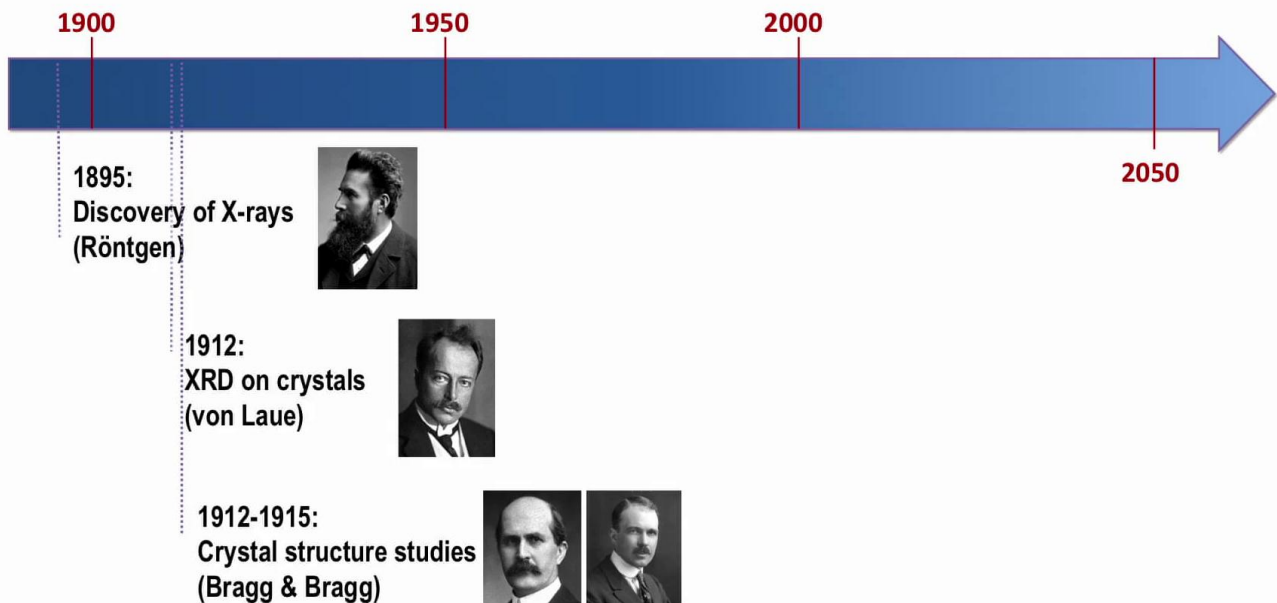
Not only changes in concentration of solids phases can be measured, also crystal structural changes can be tracked and related to external parameters such as changes in relative humidity or differences in temperature. XRD often delivers unique data compared to other common characterization techniques such as calorimetry, thermal analysis or electron microscopy. These complementary data can be used to unravel reaction mechanisms and, put all together, analyze the kinetics of hydration or the kinetics of clinkering.

Notes

Summary



# X-ray diffraction – background



Let's take a step back and have a historical look at the development of X-ray diffraction science. X-rays were first discovered by Wilhelm Röntgen in 1895. Doing electrical discharge experiments with cathode vacuum tubes, he noticed fluorescence occurring on a barium platinocyanide screen, even when the tubes were completely obscured by cardboard. This new type of electromagnetic radiation, called by Röntgen himself X-rays, has wavelengths that was significantly shorter than visible light, typically of the order of angstroms or a tenth of a nanometer. This discovery was first useful for medical purposes, for instance radiology. It was only later in 1912 that Max von Laue in Munich got the idea of positioning crystals in the X-ray beam in order to observe diffraction phenomena. The idea was quickly picked up by father and son Bragg to use the diffraction patterns to study crystal structures. All of these pioneers were actually awarded Nobel Prizes in physics for their contributions. Making a leap in time to 1969 Hugo Rietveld in the Netherlands developed a method to really calculate neutron powder diffraction patterns.

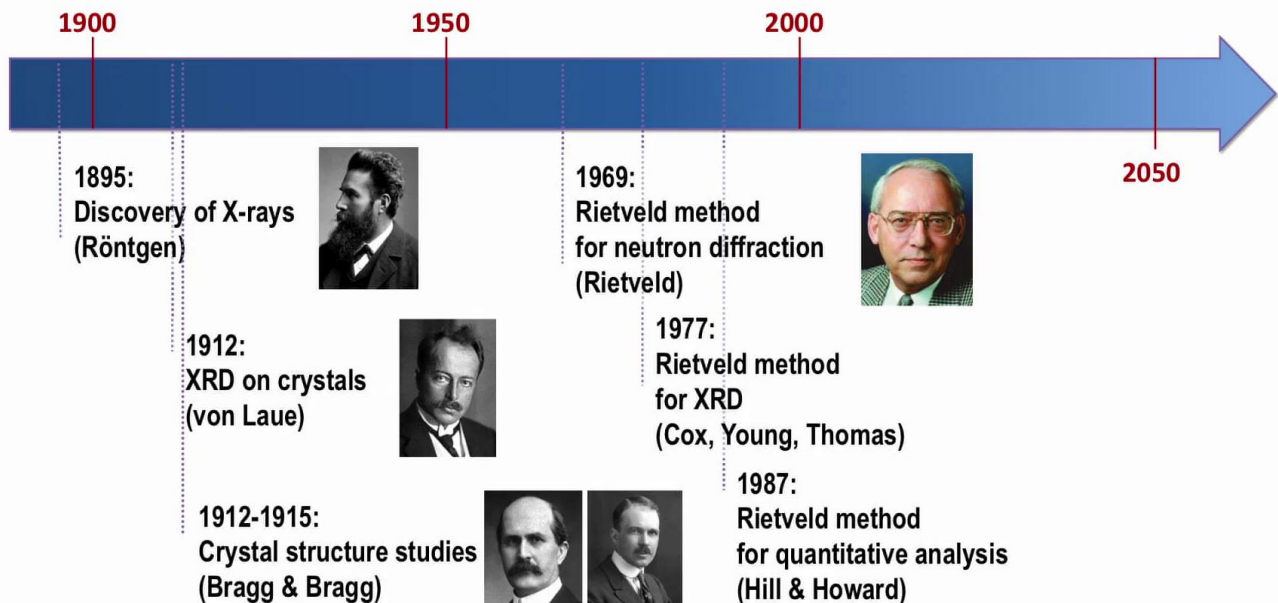
Notes

Summary



3m 30s

# X-ray diffraction – background



His calculation method is based on fundamental crystal structural parameters that, in the calculation process, can be adjusted or, as commonly called, refined to come to an optimal fit with an experimentally measured pattern. In the beginning this method was computationally quite expensive and it was also specifically developed for a special kind of diffraction, the neutron diffraction. So it took some time before the power of the method was realized by others in the fields and that it was adapted to X-rays which are the more common type of lab diffractometers. Even then after this extension was made it took more than 10 years before the method was adapted by Hill and Howard to enable measuring of mass based fractions in solids. Indeed it was the last extension that opened up a whole new field of quantitative phase analysis.

Notes

Summary





# X-ray diffraction – contributions to science



Linus Pauling (1901-1994)

- 2 time Nobel Prize winner
- X-ray diffraction as main tool
- Main achievements
  - “Crystal structures of minerals”
  - Pauling’s rules
  - Concept of electronegativity
  - “The nature of the chemical bond”

It is worth having a look at a few examples of major scientific achievements made using X-ray diffraction studies. One of the first chemists who mainly used X-ray diffractions to resolve the structure of crystals was Linus Pauling. Through systematically studying the structures of many minerals, he established a set of ground rules, the Pauling’s rules, that rationalized how atoms organize into crystals. He then proposed concepts such as electro negativity as a way to explain how outer shell like electrons of two given atoms would interact to form a chemical bond. Pauling then used these rules and concepts to resolve ever more complex structures going from simple inorganic structures to complex protein structures.

Notes

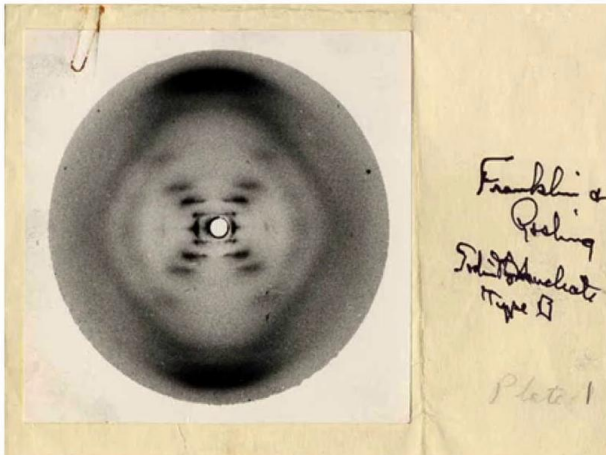
Summary



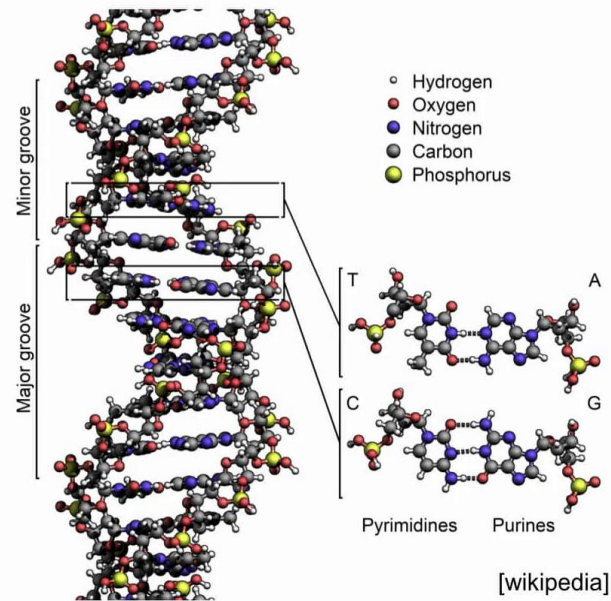
5m 56s



# X-ray diffraction – contributions to science



[X-ray diffraction image of DNA by Rosalind Franklin]



This went so far that by 1952 Pauling was also engaged in the race to be first to resolve the structure of the carrier of the human genome, DNA. Unfortunately for him he came too late. It was the rather obscure diffraction pattern of the complex DNA molecule, made by Rosalind Franklin, that formed an important part of the evidence that underpinned the double helix model that was first proposed by James Watson and Francis Crick the same year.

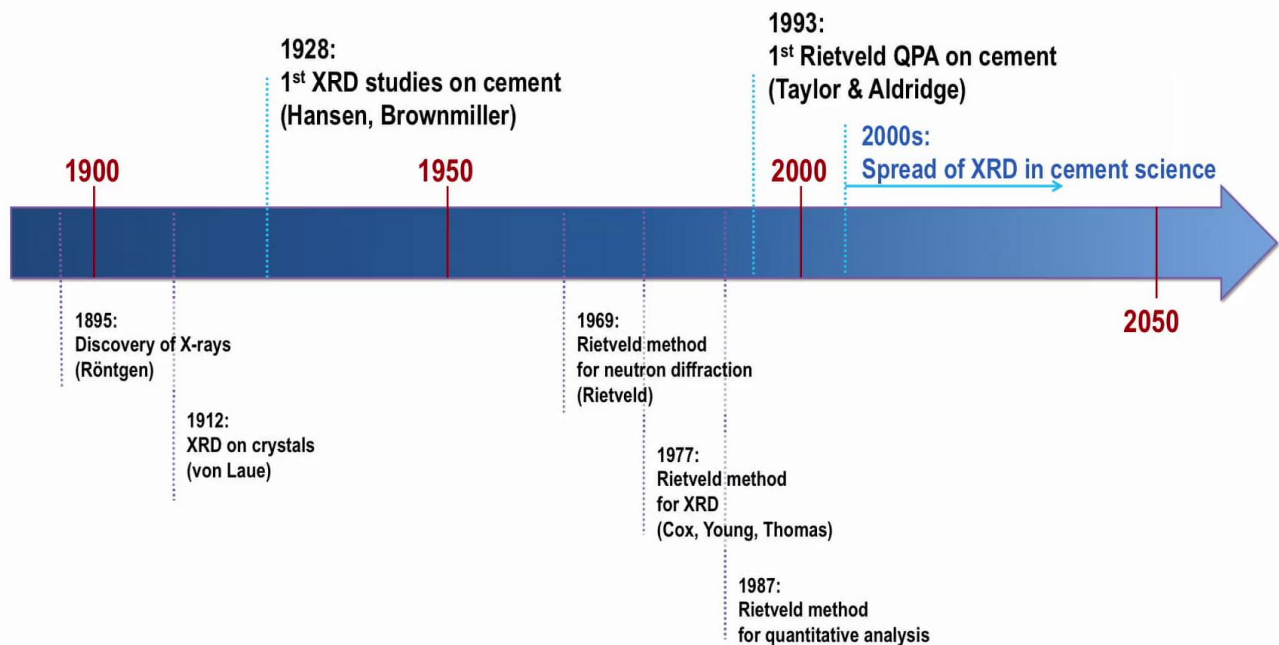
Notes

Summary



6m 47s

# X-ray diffraction and cement - history



Simultaneously to these great accomplishments made in other parts of material science, X-ray diffraction was also applied to study cements and in particular at first the crystal structure of the phases present in the cement. One of the first studies on the matter was published in 1928 by Hansen and Brownmiller. Over the years the structures of most phases present in the cement were reported. But even up to now the structure of some complex hydrate phases are not yet fully solved. In terms of studying the relative concentrations of these phases in cement, it was only in 1993 that Taylor and Aldridge first applied the Rietveld method to cement. Compared to previous methods for phase quantification, the Rietveld method considered the whole experimental profile for fitting and thus enabled to mitigate the effects of peak overlap. This really opened up X-ray diffraction for cement science.

Notes

Summary



7m 14s

# X-ray diffraction: intro and basics



Introduction and history of X-ray diffraction

Diffraction basics

Now let's have a look at some basic concepts of X-ray diffraction and scattering.

Notes

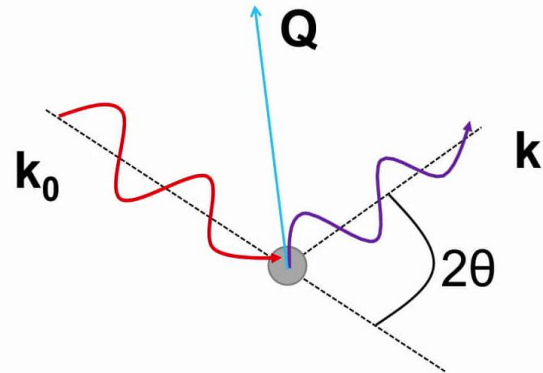
Summary

8m 11s



# X-ray diffraction: intro and basics

- **Elastic scattering conserves wave energy**
- Incident radiation  
Wave vector:  $\mathbf{k}_0$   
 $|\mathbf{k}_0| = 2\pi/\lambda$
- Scattered radiation  
Wave vector:  $\mathbf{k}$   
 $|\mathbf{k}| = 2\pi/\lambda$
- Momentum transfer  
 $\mathbf{Q} = \mathbf{k} - \mathbf{k}_0$   
 $\mathbf{Q}$  is related to the scattering angle  $2\theta$   
 $Q = 4\pi \sin(\theta)/\lambda$



X-ray diffraction is actually based on elastic scattering of incoming radiation by a scatterer, usually an atom or a plane of atoms. In elastic scattering, it is important to remember that wave energy is conserved. This means that the energy or also called the wavelength of the incoming radiation is equal to that of the scattered radiation. So the scattering only changes the direction of the wave. This change in direction, or the scattering angle, is often expressed as  $Q$ , the momentum transfer. While the scattering angle changes depending on the wavelength of the radiation,  $Q$  is actually independent of this and directly related to crystal structures.  $Q$  can also be used to compare experiments that were done by different wavelengths.

Notes

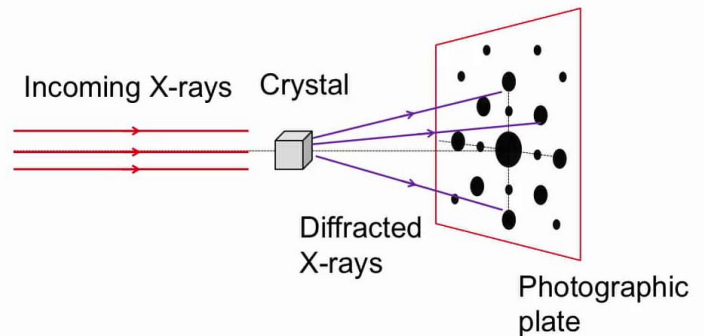
Summary



# X-ray diffraction: intro and basics



## Laue experiment (1912)



For an incident beam to be diffracted by a crystal, its wavelength must be of the same order of magnitude as the interatomic distances (a few angströms)

It is important to remember that for diffraction phenomena to occur, the wavelength of the incoming wave needs to be of the same order of magnitude as the size of the grid. Similarly, crystals can be seen as three-dimensional arrays of plates, or a lattice, and this lattice can produce diffraction if a wave of the appropriate wavelength is used. This was exactly what the Max von Laue thought of designing when he was designing his experiment in 1912. He correctly assumed that the X-rays produced by a cathode tube would be of the same order of magnitude as the interatomic distances in crystals and indeed, when placing a crystal in the incoming X-ray beam, clearly a diffraction pattern appeared on the photographic plate placed behind the crystal.

Notes

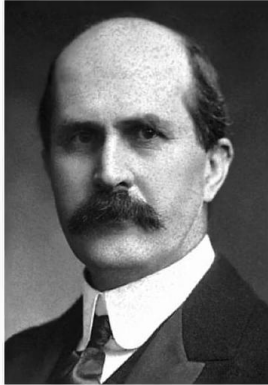
Summary



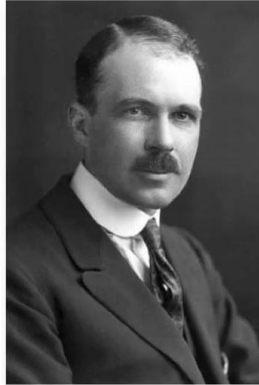
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# X-ray diffraction: intro and basics

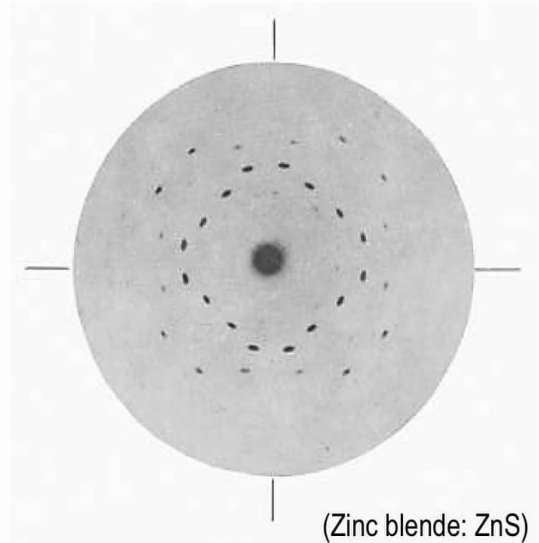
- How to interpret the diffraction patterns?



W. H. Bragg



W. L. Bragg



(Zinc blende: ZnS)

This discovery was quickly picked up by father and son Bragg who immediately applied this to the structure of crystals and common minerals. On the right side you can see an example of zinc blend or the diffraction pattern of zinc blend.

Notes

Summary

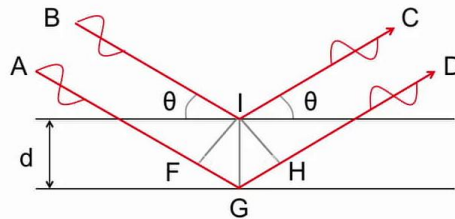
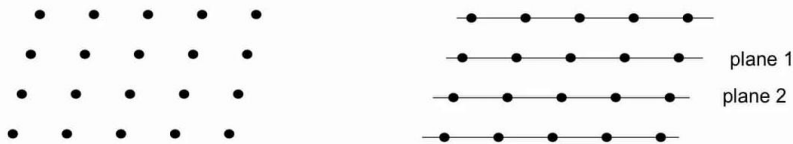


10m 00s



# X-ray diffraction: intro and basics

- Bragg's law: condition for constructive interference



The beams IC and GD scattered by 2 adjacent planes must be in phase to get constructive interference

$$FG + GH = n\lambda$$

with  $FG = GH = d \cdot \sin\theta$



$$n\lambda = 2d \sin\theta$$

**Bragg's law**

Father and son Bragg derived a law that stated the condition for constructive interference on a set of planes having an interplanar distance  $d$ . Using simple geometry, one can derive that in order for X-rays to be reflected on a set of planes, they need to be in phase. This means that the path difference on the graph on the lower side between ray AD and ray BC, or in effect the distance  $FG + GH$ , should be an integer value of  $\lambda$ , the wavelength. With both  $FG$  and  $GH$  equal to the interplanar distance  $d$  times the diffraction angle, then the Bragg condition really reduces down to  $n\lambda = 2d \sin\theta$ . And this is the famous Bragg law. This relationship can be used to determine the geometry of a crystal lattice and, given some additional data such as the density of the material and chemical composition, it can be used to solve simple crystal structures such as rock salt, zinc blends or diamonds.

Notes

Summary

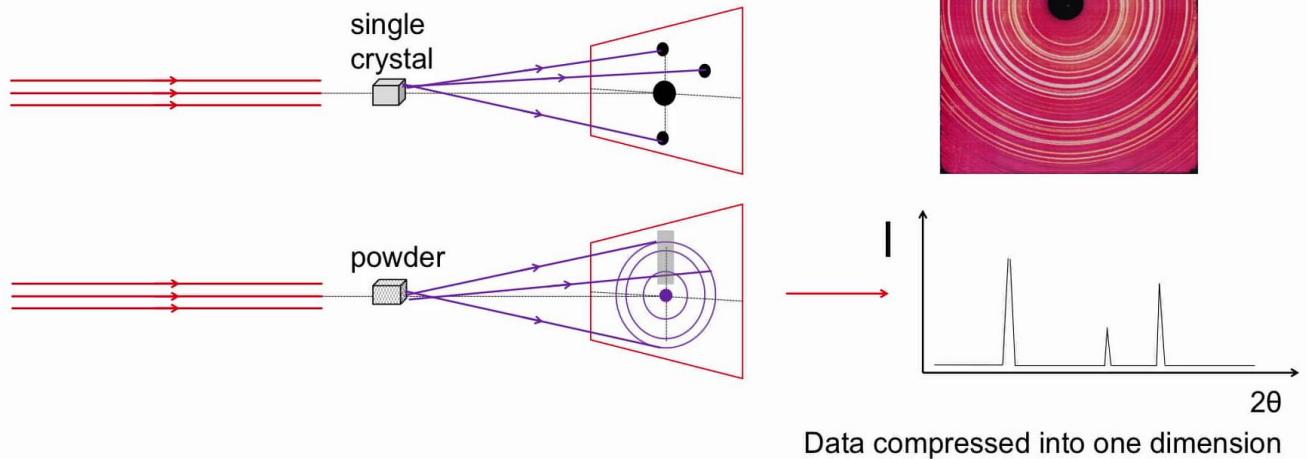


10m 17s



# X-ray diffraction: intro and basics

- From single crystal to powder



When doing X-ray diffraction experiments on fine powders rather than on single crystals, the spots originally seen on the screen become concentric rings. This is because the powder now consists of a very large number of randomly oriented crystals that effectively diffract in all directions. As long of course as the Bragg condition is obeyed. When we now take the camera image on the right upper hand side and record the intensity of the scattered radiation as a function of the distance from the center point or equivalently as a function of the diffraction angle, then we end up with the conventional representation of X-ray powder diffraction data as shown on the lower right. In the next session we will have a closer look at how we can read and extract information from these kind of diffraction data.

Notes

Summary



11m 28s