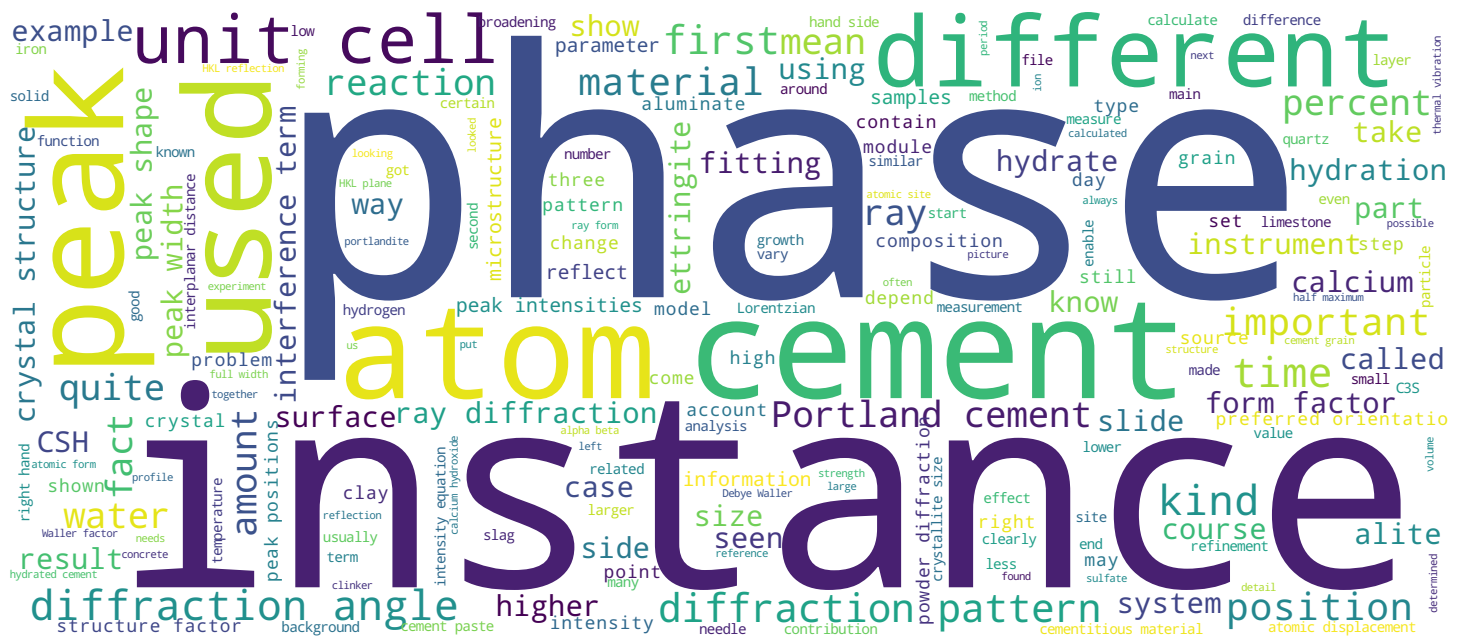
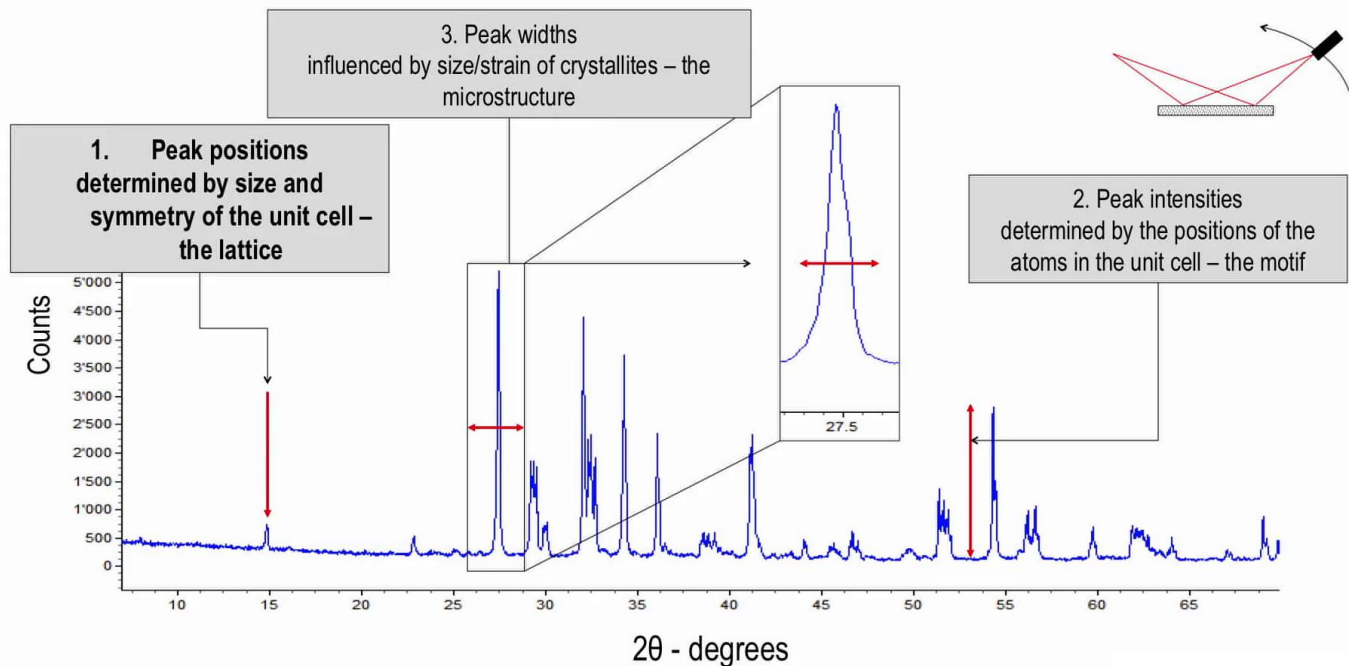


Dr. Ruben Snellings



Inside the powder diffraction pattern



In this session, we will have a closer look on what information is contained in the powder diffraction pattern. We will look at the properties of the diffraction peak or Bragg reflections, that make up the diffractogram. In brief we will introduce what material properties determine the position, intensity and width of the peaks in the powder pattern. We will need this as background knowledge to help us make the right decisions in data analysis and interpretation later. Now let's have a look at the X-ray powder diffraction pattern of a substance very well known in cements, this is part of diffraction pattern of alite for instance. In this part of the diffraction pattern we can see the appearance of a lot of peaks and these peaks appear at a certain position. And all the features of these peaks are OK, they don't only have a position, they also have a height and intensity. But that is also important to know as a characteristic. In what can peak differ as well? That is actually on the width of the peak. These are the three main properties of one peak but also of sets of peaks that actually contain the information that enables you to extract for instance crystallographic information but also phase compositional information in the end. Now let's have a closer look at what determines peak positions.

Notes

Summary



Inside the powder diffraction pattern

Peak positions

- Bragg's law

$$\lambda = 2d_{hkl} \sin\theta$$

- d-spacing formulae

- Cubic (a)

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Peak positions are determined by the size and the symmetry of the lattice or the unit cell. The unit cell is the basic building unit of your crystal. It has three dimensions typically called A, B and C if they are different in size and between these three dimensions we have angles: alpha, beta and gamma. Depending on the symmetry, whether your lattice is for instance cubic, or whether it is triclinic, one or more of these parameters can be identical. The other important part, you know, is OK one can have, and this is usually introduced in the crystallography course, it is what relates the distance between two planes in your crystal and the appearance of a certain reflection, HKL. The HKL plane with a certain interplanar distance d will diffract given a certain wavelength λ at a certain diffraction angle as is established in Bragg's law. That says the wavelength equals two times the interplanar distance times the sinus of the diffraction angle as seen in the previous session. Then, knowing for certain plane, HKL plane, what is the interplanar distance one can actually derive, what is the unit cell parameter of for instance a cubic lattice using the formula shown here?

Notes

Summary



1m 38s

Inside the powder diffraction pattern

Peak positions

- Bragg's law

$$\lambda = 2d_{hkl} \sin\theta$$

- d-spacing formulae

- Cubic (a)

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

- Triclinic (a, b, c, α , β , γ)

$$\begin{aligned} \frac{1}{d^2} = \frac{1}{V^2} [& h^2 b^2 c^2 \sin^2 \alpha + k^2 a^2 c^2 \sin^2 \beta + l^2 a^2 b^2 \sin^2 \gamma \\ & + 2hkabc^2 (\cos \alpha \cos \beta - \cos \gamma) + 2kla^2 bc (\cos \beta \cos \gamma - \cos \alpha) \\ & + 2hlab^2 c (\cos \alpha \cos \gamma - \cos \beta)] \end{aligned}$$

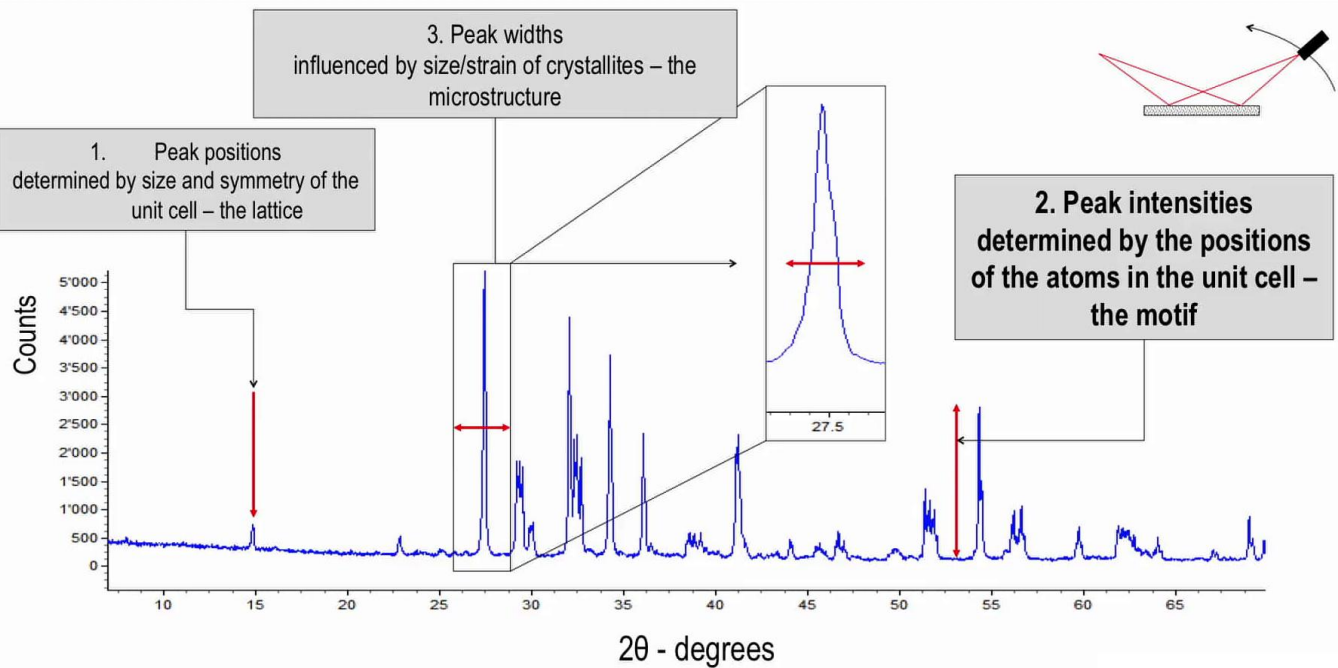
One can also derive the lattice parameters of much more complicated symmetries, for instance a triclinic symmetry in which we have A, B C, alpha, beta and gamma which are all different values. And then one would need to use this kind of formula. Of course there this gets to be a system of equations where for a whole set of HKL planes and their distances and diffraction angles connected - and one can actually computationally easily solve these kinds of equations once one knows whether the crystal investigation is of cubic, triclinic or other symmetry. That is about peak positions.

Notes

Summary



Inside the powder diffraction pattern



Now let's have a look at peak intensities. Peak intensities are determined by the positions of the atom in the unit cell, so this is really where your crystal structure information is used.

Notes

Summary

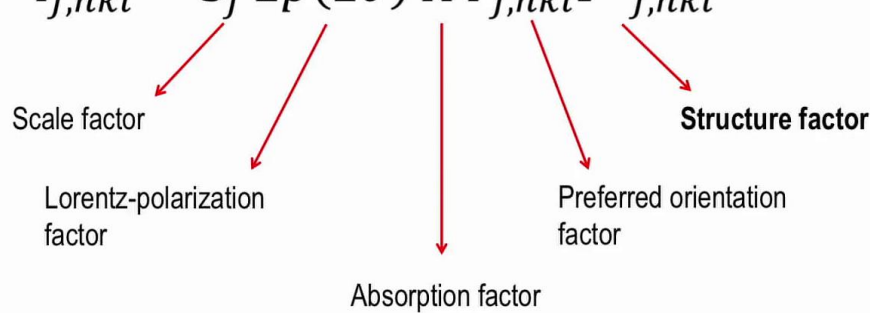


4m 20s

Inside the powder diffraction pattern

Peak intensities

- For a crystalline phase j in a powder sample:

$$I_{j,hkl} = S_j Lp(2\theta) A P_{j,hkl} F_{j,hkl}^2$$


Scale factor

Lorentz-polarization factor

Absorption factor

Preferred orientation factor

Structure factor

For the crystalline phase, in a multiphase powder sample for instance, one can actually have this kind of intensity equation for each HKL reflection of that phase. This intensity equation consists of different factors, most of which are not related to the sample crystal structure but rather to the set up of your instruments or the composition of your sample or for instance whether there is some preferred orientation of particles in your sample or not. So there is a general scale factor, I mentioned this, there is a Lorentz-polarization factor which mostly depends of how the diffraction takes place in your instrument. There is the absorption factor, which takes into account how much of the incoming radiation is absorbed by the sample. And there is a preferred orientation factor that takes into account whether some HKL reflections are over or under represented because of the effect that for instance some crystallite that have a non-uniform dimension for instance platelets or needles, they can actually be solicited more than other kind of reflections. Finally, and most importantly, there is the structure factor.

Notes

Summary



Inside the powder diffraction pattern

Peak intensities

- Structure factors

$$I_{hkl} \approx |F|_{hkl}^2$$

$$F_{hkl} = \sum_n f_n o_n \exp(2\pi i\{hx + ky + lz\}) \exp(-W_n)$$

- Vector quantity (magnitude F and phase φ)
- Summation over all atoms n in unit cell
 - X-ray form factor $f_n(2\theta)$
 - Site occupation o_n
 - Interference term: $\exp(2\pi i\{hx + ky + lz\})$
 - Debye-Waller factor W_n

Looking a bit closer into the structure factor we see where actually all the crystal structural information is situated. So as seen in the previous formula, the intensity of a certain reflection is proportional to the square of the structure factor. Structure factor itself, for a certain HKL reflection is actually the sum over all atoms n in a unit cell and it takes into account for each atomic site, for each atom in the unit cell, the atomic form factor, the occupation of the site by that atom, for instance it can vary between 0 and 1. Let's say if you have a solid solution series where you have 50 percent of the time iron and 50 percent of the time aluminum at that site, then the occupation site, the number can actually distinguish between for instance the scattering of aluminum and that of iron. The important thing is the interference term. This term takes into account the atomic coordinates. So where are these atoms located in your unit cell? And finally there is a Debye-Waller factor or the atomic displacement factor that takes into account thermal displacements of your atoms that can actually kind of reduce the intensities of your structure factor.

Notes

Summary

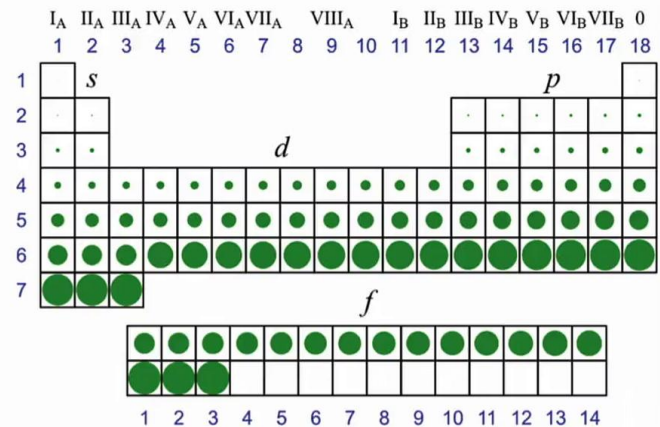


6m 04s

Inside the powder diffraction pattern

Peak intensities

- X-ray form factors $f_n(2\theta)$: the **nature** of the atoms
 - X-rays interact with atomic electron cloud
 - The higher Z, the higher f_n



Looking at the first of the parameters that is in the intensity equation we have the X-ray form factors that actually reflect the nature of the atom itself. X-rays in fact interact with the atomic electron cloud. The higher the number of electrons in this cloud or the higher the atomic number z , the higher the X-ray form factor will be. This is why is reflected in the slides on the right hand side where you can see the periodic table and in the periodic table the size of the spheres actually reflects the value of the atomic form factor. So it also means that phases, minerals that contain atoms with a higher atomic number, will reflect X-rays more efficiently or light phases will typically have lower X-ray intensities than phases that are typically heavier.

Notes

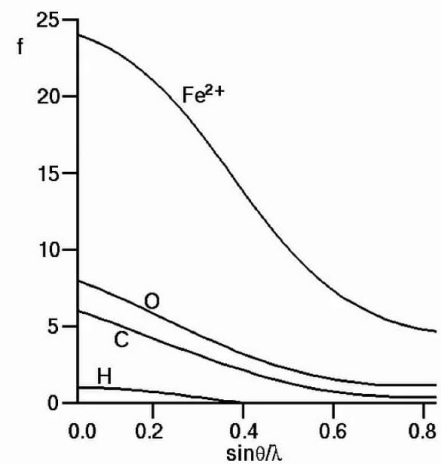
Summary



Inside the powder diffraction pattern

Peak intensities

- X-ray form factors $f_n(2\theta)$: the **nature** of the atoms
 - X-rays interact with atomic electron cloud
 - The higher Z , the higher f_n
 - The higher θ , the lower f_n



The X-ray form factor does not only depend on the nature of the atom but also on the diffraction angle. This can be clearly seen on the right hand side of the slide, where we have a comparison between the form factors iron, oxygen, carbon and hydrogen as a function of the diffraction angle, here normalized by the wavelength to give a more general treatment of the matter. One can directly see that these form factors really decrease sharply with diffraction angles. This in fact also explains why when we look at diffraction patterns for X-rays, intensities tend to be higher at the low angle site than the high angle site. This is simply because the atoms will reflect the X-rays more efficiently at the lower diffraction angles.

Notes

Summary



Inside the powder diffraction pattern

Peak intensities

- Interference term: the **position** of the atoms

$$\exp(2\pi i\{hx + ky + lz\})$$

- Reflects atomic structure
- Vector dot product between the position of the atom n (\mathbf{r}_n) in the unit cell and the scattering vector (\mathbf{Q}_{hkl}):

$$\mathbf{r}_n = x_n \mathbf{a} + y_n \mathbf{b} + z_n \mathbf{c}$$

$$\mathbf{Q}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

- Not a smooth function of 2θ
- Reflections with similar d spacings may have large or small interference terms

The other part of the intensity equation is basically governed by the interference term. This interference term is actually reflecting the position of the atoms in the unit cell. One can see the positions of the atoms reflected in this first formula where we see the fractional coordinates X , Y and Z appearing. These are the fractional coordinates of the atom in the unit cell. This interference term does reflect the underlying atomic structure in the unit cell, also called the motive. In fact the interference term is a vector dot product between the position of the atom $n(\mathbf{r}_n)$, as one can see here, and the scattering vector \mathbf{Q} , hkl , in which hkl is a reflection plane. It is important to realize that this interference term is not a smooth function of 2θ and that thus reflections with similar d spacings may really have larger or similar interference terms. This really depends on the positions of the atoms in the unit cell and the interference with the scattering vector.

Notes

Summary



Inside the powder diffraction pattern

Peak intensities: the structure model

- Contains lattice parameters (a, b, c, alpha, beta, gamma)
- Symmetry group, space group
- Asymmetric unit: atomic coordinates, occupancy, etc.

**Close, reliable
starting models necessary!**

```
_cell_length_b      14.61(2)
_cell_length_c      5.380(5)
_cell_angle_alpha   90.
_cell_angle_beta    90.
_cell_angle_gamma   90.
_cell_volume        439.23
_cell_formula_units_Z 4
_symmetry_space_group_name_H-M 'I b m 2'
_symmetry_Int_Tables_number 46
_refine_ls_R_factor_all 0.029
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1      'x, y-1/2, z'
2      'x, -y-1/2, z'
3      '-x, -y, z'
4      '-x, y, z'
5      '-x-1/2, y, z-1/2'
6      'x-1/2, -y, z-1/2'
7      '-x-1/2, -y-1/2, z-1/2'
8      'x-1/2, y-1/2, z-1/2'
```

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_atom_type_oxidation_number
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Ca2+ 2
Fe3+ 3
O2- -2
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_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_attached_hydrogens
Ca1 Ca2+ 8 c 0.0270(1) 0.1084(1) 0.4910(3) 1. 0
Fe1 Fe3+ 4 a 0 0 0 0.85 0
Al1 Al3+ 4 a 0 0 0 0.15 0
Fe2 Fe3+ 4 b 0.9293(2) 0.25 0.9516(4) 0.55 0
Al2 Al3+ 4 b 0.9293(2) 0.25 0.9516(4) 0.45 0
O1 O2- 8 c 0.2533(8) 0.9856(2) 0.2520(8) 1. 0
O2 O2- 8 c 0.0687(6) 0.1429(2) 0.0269(8) 1. 0
O3 O2- 4 b 0.8668(8) 0.25 0.6147(9) 1. 0
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```

Most of the information in fact that is used to calculate the diffraction pattern of a certain mineral or phase is written down in databases and saved for instance under a format like crystallographic information files. One can see an example of this at the bottom side of this slide. These files, they contain lattice of parameters such as cell lengths A, B, C or cell angles, alpha, beta and gamma, they contain symmetry groups, space groups and they contain also for each atomic site, the type of atom which is positioned at that site, for instance calcium, diffraction coordinates X, Y, Z and the atomic sites of occupancy. For the calcium sites there is always a calcium atom sitting in that position. For other sites, for instance the iron aluminum position, they have the same atomic coordinates. However, 85 percent of the time this site is occupied by iron and only 50 percent of the time it is occupied by aluminum. All this information is needed to calculate on this side the position of the reflections and usually more on that side the intensity of the reflections. When we want to do a proper fitting of a diffraction pattern it is very important that we have close reliable starting models.

Notes

Summary



11m 09s

Inside the powder diffraction pattern

Peak intensities: the structure model

- Contains lattice parameters
(a, b, c, alpha, beta, gamma)
- Symmetry group, space group
- Asymmetric unit: atomic coordinates, occupancy, etc.

**Close, reliable
starting models necessary!**

```
_cell_length_b      14.61(2)
_cell_length_c      5.380(5)
_cell_angle_alpha    90.
_cell_angle_beta     90.
_cell_angle_gamma    90.
_cell_volume         439.23
_cell_formula_units_Z 4
_symmetry_space_group_name_H-M 'I b m 2'
_symmetry_Int_Tables_number 46
_refine_ls_R_factor_all 0.029
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1      '-x, y-1/2, z'
2      'x, -y-1/2, z'
3      '-x, -y, z'
4      'x, y, z'
5      '-x-1/2, y, z-1/2'
6      'x-1/2, -y, z-1/2'
7      '-x-1/2, -y-1/2, z-1/2'
8      'x-1/2, y-1/2, z-1/2'
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Ca2+ 2
Fe3+ 3
O2- -2
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_atom_site_symmetry_multiplicity
_atom_site_wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_attached_hydrogens
Ca1 Ca2+ 8 c 0.0270(1) 0.1084(1) 0.4910(3) 1. 0
Fe1 Fe3+ 4 a 0 0 0 0.85 0
Al1 Al3+ 4 a 0 0 0 0.15 0
Fe2 Fe3+ 4 b 0.9293(2) 0.25 0.9516(4) 0.55 0
Al2 Al3+ 4 b 0.9293(2) 0.25 0.9516(4) 0.45 0
O1 O2- 8 c 0.2533(8) 0.9856(2) 0.2520(8) 1. 0
O2 O2- 8 c 0.0687(6) 0.1429(2) 0.0269(8) 1. 0
O3 O2- 4 b 0.8668(8) 0.25 0.6147(9) 1. 0
#End of data_2841-IC5D
```

If for instance we have a bad starting model, then the calculation routine, the fitting routine will have a very hard time in finding the correct refined fitted parameters in your X-ray diffraction experiments.

Notes

Summary



13m 00s

Inside the powder diffraction pattern

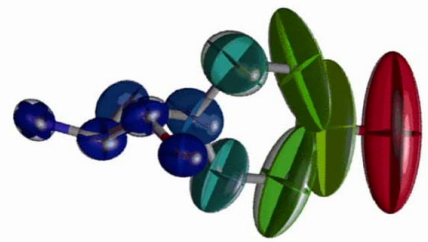
Peak intensities

- Debye-Waller factors (W_n) or atomic displacement (ADP) factors
- Thermal vibrations
 - atomic position is not frozen
 - time and space average of atoms is larger
 - leads to destructive interference
 - reduction of peak intensities

$$\exp(-W_n) = \exp\left(-\frac{B_n \sin^2 \theta}{\lambda^2}\right) = \exp\left(-\frac{B_n}{4d^2}\right)$$

$$= \exp\left(-\frac{2\pi^2 U_n}{d^2}\right)$$

- U_n is mean-square atomic displacement
- B_n often preferred since values are around 1
- The lighter the atom the larger the ADP



The last parameter in the intensity creation is the Debye-Waller factors also called the atomic displacement factors. This factor in fact reflects the thermal vibrations of the atoms in their positions. They are not frozen, they vibrate around the position which means that actually the size of the atoms, time and space average is larger than they actually are. This actually leads to destructive interference when your X-rays are being diffracted and thus leads to a reduction of the peak intensities. Expressions for this effect can be found here, one of which uses the Debye-Waller factor as such, but other expressions exist as well, for instance one which is more directly related to the mean-square atomic displacement and B which is often preferred since it has values around 1 and is thus easier to judge. Typically when looking at atoms and thermal vibrations, the general rule is that the lighter the atom is, the larger the atomic displacement will be. Heavy atoms like iron will barely move, smaller atoms like hydrogen will move a lot and spread out their electron density or electron cloud. This again adds up with the fact for instance that for hydrogen we have a very low atomic form factor together with a large thermal displacement, a thermal vibration.

Notes

Summary



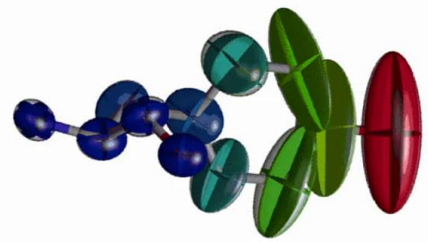
Inside the powder diffraction pattern

Peak intensities

- Debye-Waller factors (W_n) or atomic displacement (ADP) factors
- Thermal vibrations
 - atomic position is not frozen
 - time and space average of atoms is larger
 - leads to destructive interference
 - reduction of peak intensities

$$\exp(-W_n) = \exp\left(-\frac{B_n \sin^2 \theta}{\lambda^2}\right) = \exp\left(-\frac{B_n}{4d^2}\right) \\ = \exp\left(-\frac{2\pi^2 U_n}{d^2}\right)$$

- U_n is mean-square atomic displacement
- B_n often preferred since values are around 1
- The lighter the atom the larger the ADP



It makes it very hard for X-ray diffraction experiments to actually see hydrogen atoms, their impact on the diffraction pattern will be very low.

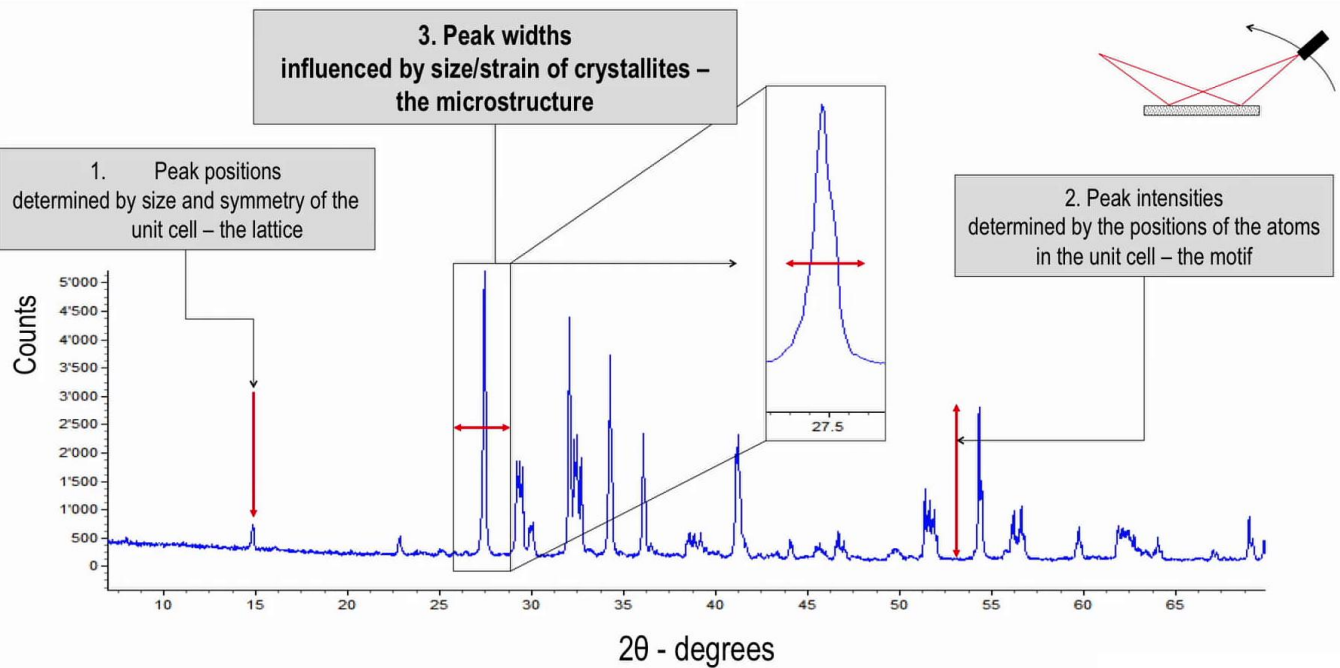
Notes

Summary



15m 07s

Inside the powder diffraction pattern



The last property that we need to look at is the peak width. The peak width actually tells you more about the microstructure of your sample, not the crystal structure, the microstructure. Typically the size of the crystallites that are diffracting or the lattice string in these crystallites can be extracted from an analysis of peak width.

Notes

Summary



Inside the powder diffraction pattern

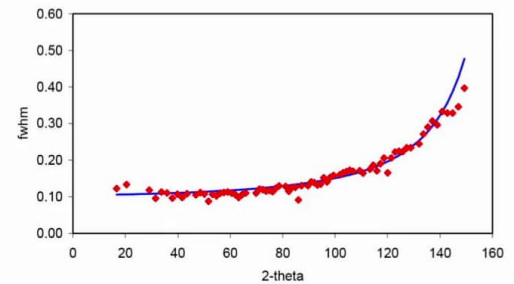
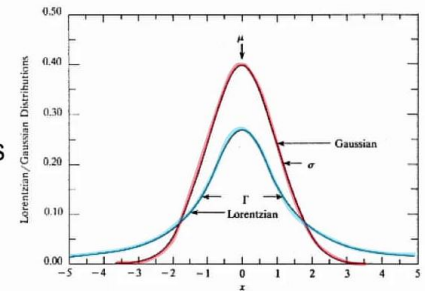
Peak widths and shapes

- Depend on source, instrument and sample
- 1. Peak description by analytical functions
 - Gaussian, Lorentzian, or mixed (Pseudo-Voigt)- symmetric functions
 - Extended versions (TCHZ, Pearson VII,...)
 - *fwhm* dependence on 2θ

$$\text{Gauss: } fwhm = (U \tan^2 \theta + V \tan \theta + W)^{1/2}$$

$$\text{Lorentz: } fwhm = \frac{X}{\cos \theta} + Y \tan \theta$$

Caglioti et al. (1958)



Peak width and peak shape really depends on the source of your X-rays, the instrument, the optics of the instrument you are using and also your sample itself. The classical way of treating peak shapes and calculating and fitting powder diffraction files is by using analytical functions. Typically, Gaussians and Lorentzians are mixed pseudo-Voigt functions and are used to model the peak shape. So this did not really represent well asymmetric properties of X-ray diffraction peak shapes. There are extended versions like the TCHZ or the Pearson VII that can take into account some measures of asymmetry of the peak. On the right hand side we can see for instance what is the difference between a typical Gaussian and a typical Lorentzian. A Gaussian actually has very short tails while a Lorentzian has typically quite long tails to both sides from the maximum. Mixing those can give you a good representation of your peak shape by X-ray diffraction. Actually peak shapes also really depend on the diffraction angle. Typically they get wider, the higher the diffraction angle is. So for both Gaussian and Lorentzian peak shape functions one needs to include a dependence on the diffraction angle.

Notes

Summary



15m 42s

Inside the powder diffraction pattern

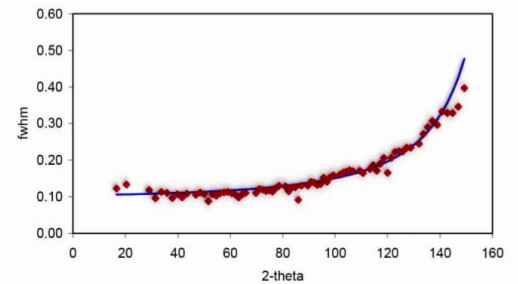
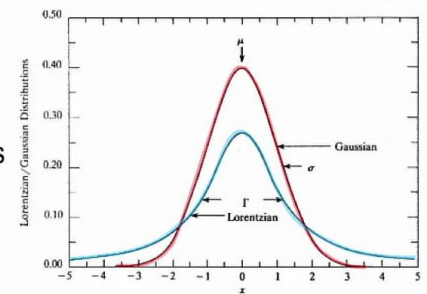
Peak widths and shapes

- Depend on source, instrument and sample
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 - *fwhm* dependence on 2θ

$$\text{Gauss: } fwhm = (U \tan^2 \theta + V \tan \theta + W)^{1/2}$$

$$\text{Lorentz: } fwhm = \frac{X}{\cos \theta} + Y \tan \theta$$

Caglioti et al. (1958)



The classical approach to this was made or developed by Caglioti et al. in 1958. And he used for instance for the Gaussian dependence three parameters that can be fitted: U, V and W. For the Lorentzian he used two factors X and Y and fitting those to the experimental data enabled to obtain a good fit between the full width of half maximum at lower angles and that at higher angles as well.

Notes

Summary

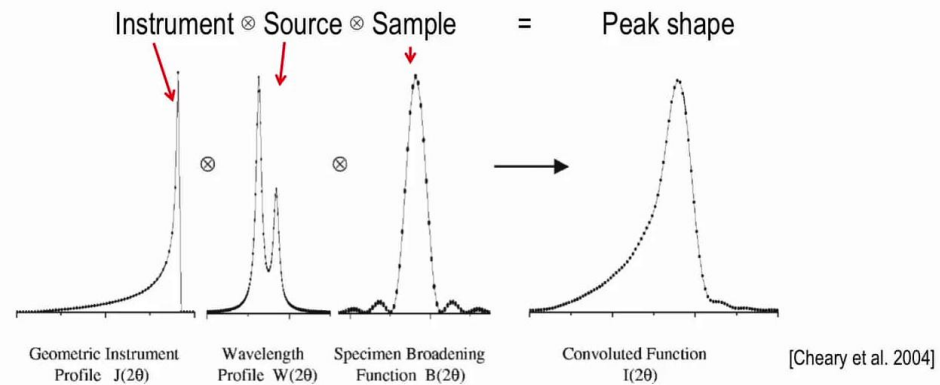


17m 26s

Inside the powder diffraction pattern

Peak widths and shapes

- Depend on source, instrument and sample
- 2. Peak description by separating contributions from source and instrument to that of sample (**fundamental parameters approach**)



Using analytical functions is one way of coping with the problem of fitting and modeling experimental diffraction data. Another way is the fundamental parameters approach. Here, one actually starts from the assumption that yes we can separate the instrumental, the source and the sample contributions from each other. To do this one needs to know what is the source profile and what is the instrument profile. The instrument profile can be calculated from optical parameters. And they are actually established by typical physical equations. The source profile is also usually known for commercial sources so one can easily fix those and then just retain the contribution by the sample, the sample broadening.

Notes

Summary



18m 01s

Inside the powder diffraction pattern

Peak widths and shapes

- Depend on source, instrument and sample
- 2. Peak description by separating contributions from source and instrument to that of sample (fundamental parameters approach)
 - Allows analysis of sample texture (crystallite size, strain)
 - Size contribution

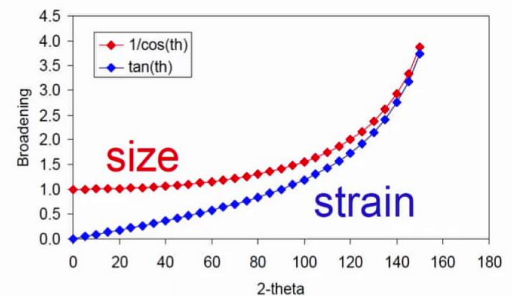
$$fwhm = k\lambda/D_{Vol}\cos\theta \quad (\text{Scherrer formula})$$

↓
Volume weighted mean crystallite size

- Strain contribution

$$fwhm = 4\varepsilon_0\tan\theta$$

↓
 $\varepsilon_0 = \Delta d/d$ or mean strain



So if we can separate contributions from the source, the instruments and that of the sample in the fundamental parameters approach, one can actually analyze a sample texture, one can obtain information on what is the crystallite size and what is the strain on the lattice for certain materials. This can be very important for instance in deformation studies of metals. Scientists can be assessed through the Scherrer formula. This formula uses the dependence of the full width of half maximum, the width of the peak as a function of the diffraction angle and enables you to extract a volume weighted mean crystallite size. Another formula can be used to extract information on strain. In this respect the full width of half maximum has a tangential dependence on the diffraction angle. Having a look at how both vary over wider range and diffraction angles can enable one to separate strain and size contributions to the broadening of your peaks. However this is only possible for pure or very simple metals for instance or powders. When we look at complex mixtures of powder such as a Portland cement, typically the separation between size and strain becomes impossible for a certain phase and we usually use an apparent crystallite size to model the broadening as a function of 2θ.

Notes

Summary



18m 55s

Inside the powder diffraction pattern

Peak widths and shapes

- Depend on source, instrument and sample
- 2. Peak description by separating contributions from source and instrument to that of sample (fundamental parameters approach)
 - Allows analysis of sample texture (crystallite size, strain)
 - Size contribution

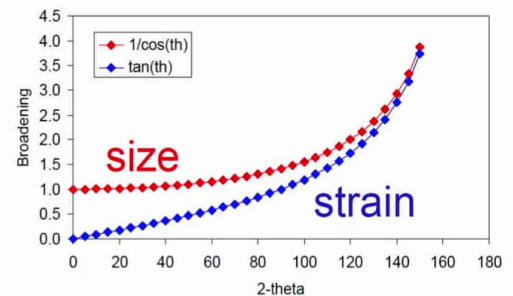
$$fwhm = k\lambda/D_{Vol}\cos\theta \quad (\text{Scherrer formula})$$

↓
Volume weighted mean crystallite size

- Strain contribution

$$fwhm = 4\varepsilon_0\tan\theta$$

↓
 $\varepsilon_0 = \Delta d/d$ or mean strain



Peak intensities and peak width - these are the main properties that can be used or looked at in part of diffraction patterns to retrieve information on materials. Peak positions relates to the unit cell dimensions and symmetry, peak intensities relate back to what type of atoms are contained in your unit cell and what their positions really are and peak width goes back to what is the microstructure, the microtexture of your sample, how large are actually these crystallites in your sample or what is their deformation. The relationship between these analytical properties of your diffraction pattern and the material properties have been used in a very wide array of applications. In the next session we will actually look at how we can best measure an X-ray diffraction pattern and then specifically apply it to cement. We will look at the diffraction geometry, the instruments and then we will look at what are the best settings of your instruments to measure a Portland cement sample for instance. Also we will look at what is the best sample preparation procedure for your problem.

Notes

Summary



20m 30s