Crystallography course SCHEDULE

		Date		Topic
	1.	Wed	28.02.	Lec-1: Introduction
	2.	Mon	04.03.	Lec-2: Crystal Chemistry & Tolerance parameter
	3.	Mon	04.03.	EXERCISE 1
	4.	Wed	06.03.	Lec-3: Crystal Chemistry & BVS
	5.	Fri	08.03.	Lec-4: Symmetry & Point Groups
	6.	Mon	11.03.	EXERCISE 2
	7.	Wed	20.03.	Lec-5: Crystallography & Space Groups (Linda) Ke3
TODAY	8.	Fri	22.03.	Lec-6: XRD & Reciprocal lattice (Linda) Ke4
	9.	Mon	25.03.	EXERCISE 3 (Linda) Ke4
	10.	Thu	04.04.	Lec-7: Rietveld (Linda) 12:15-14, Ke3
	11.	Fri	05.04.	EXERCISE 4: Rietveld (Linda)
		Mon	08.04.	EXERCISE 4: Rietveld (Linda)
	12.	Thu	11.04.	Lec-8: ND & GI-XRD 12:15-14, Ke3
	13.	Fri	12.04.	Lec-9: XRR (Topias)
	14.	Mon	15.04.	EXERCISE 5: XRR (Topias)
		Wed	17.04.	EXERCISE 5: XRR (Topias)
	15.	Mon	22.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
	16.	Thu	25.04.	Mössbauer 12:15-14, Ke3
	17.	Fri	26.04.	EXERCISE 6
	18.	Mon	29.04.	Seminars:
	19.	Fri	03.05.	Seminars:
	20.	Mon	06.05.	ADDITIONAL DISCUSSION/QUESTION POSSIBILITY

LINDA'S LECTURES & EXERCISES

- 20.03. WEDNESDAY: 14.15 – 16 (Ke3)
- 22.03. FRIDAY: 12:15 – 14 (Ke3)
- 25.03. MONDAY: 14.15 – 16 (Ke4) *Exercise session*
    - *Exercise deadline 27.3 at 13:00*

Easter holidays break! ☺

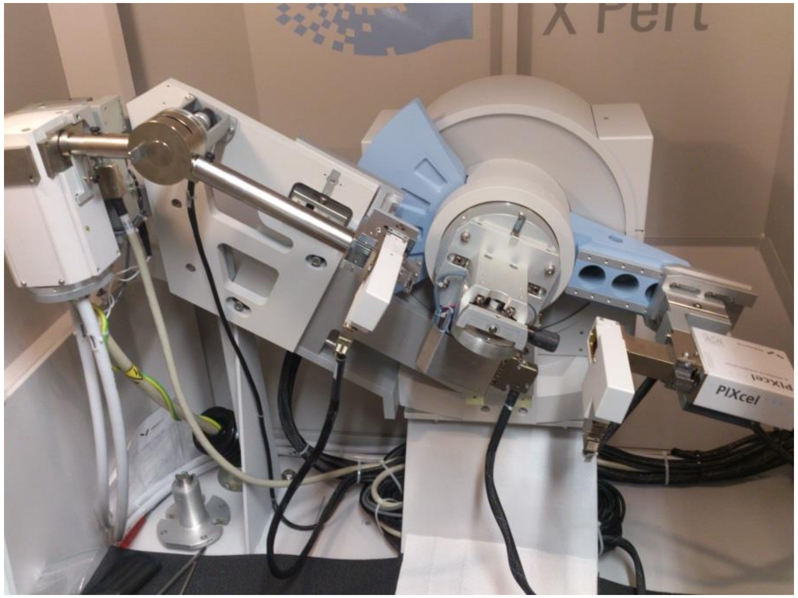
- 04.04. THURSDAY: 12:15 – 14 (Ke3)
- 05.04. FRIDAY: 12:15 – 14 (?) *Rietveld exercise 1*
    - *Getting started on FullProf*
- 08.04. MONDAY: 14:30 – 16 (?) *Rietveld exercise 2*
    - *Help with finishing the exercise*
    - *Exercise deadline on 10.4. at 13:00*

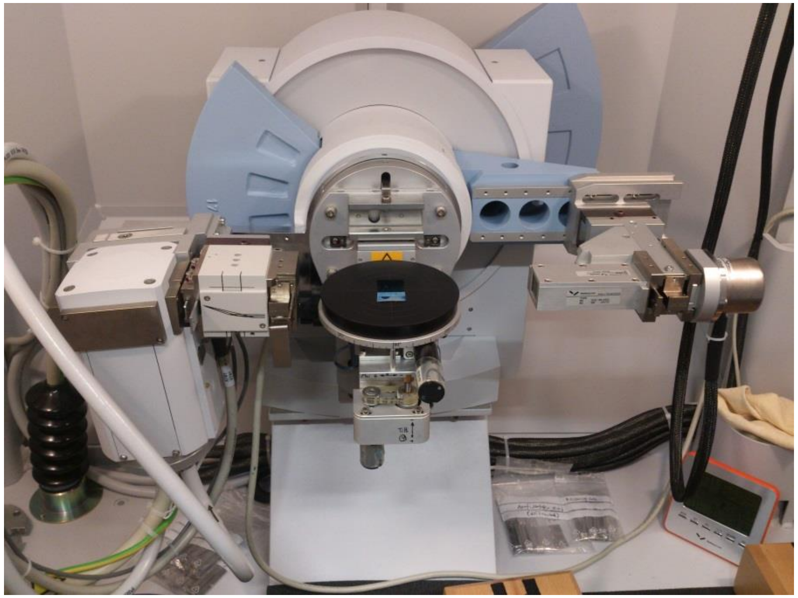
TODAY…

LECTURE 6: X-RAY (POWDER) DIFFRACTION

- History: X-ray sources and XRD equipment
- Bragg Equation (you have learned this earlier!)
- Mathematics of XRD
  - Reciprocal lattice, Brillouin zone, Ewald sphere
  - Allowed and forbidden reflections
- XRD pattern: Peak positions, peak intensities, peak shapes
  - Indexing (Miller indeces) & Lattice parameter determination
- Structure determination issues
  - Scattering factor, structure factor, phase problem
- *Rietveld refinement! (preview)*

Our X-ray diffractometers: you have already used them?





Powder XRD
PANalytical X'Pert PRO MPD Alpha1

- $\boxed{\theta/2\theta}$
- Johansson Ge monochromator
- Programmable slits
- Sample spinner
- PIXcel detector

Thin-film XRD
PANalytical X'Pert PRO MPD

- $\boxed{\omega/2\theta}$
- Cu mirror and collimator slit
- IR controlled sample stage
  - Height (z, 75 mm)
  - Rotation (φ, n*360°)
  - Tilt (ψ, 20°)

EARLY HISTORY OF X-RAY DIFFRACTION

1895	**Röntgen:** x-ray radiation
1912	Von Laue: diffraction of x-rays in crystalline solids (Nobel 1914)
1913	W.H. & W.L Bragg: **Bragg** equation (Nobel 1915)
1913	W.L. Bragg: first crystal structures: NaCl, KBr, ZnS, diamond
1923	First crystal structure determination of an organic compound
1924	Weissenberg: single-crystal camera
1934	Patterson: ”heavy-atom method”
1935	Le Galley: first powder diffractometer
1942	Buerger: precession camera
1947	**First commercial powder diffractometer (Philips)**
1948-	Development of ”direct methods” (H. Hauptman ja J. Karle, Nobel 1985)
1960	First crystal structure determination of protein
1962-	Development of automatic four-circle diffractometers
1969	**Rietveld:** “whole pattern analysis” (for neutron powder diffraction)

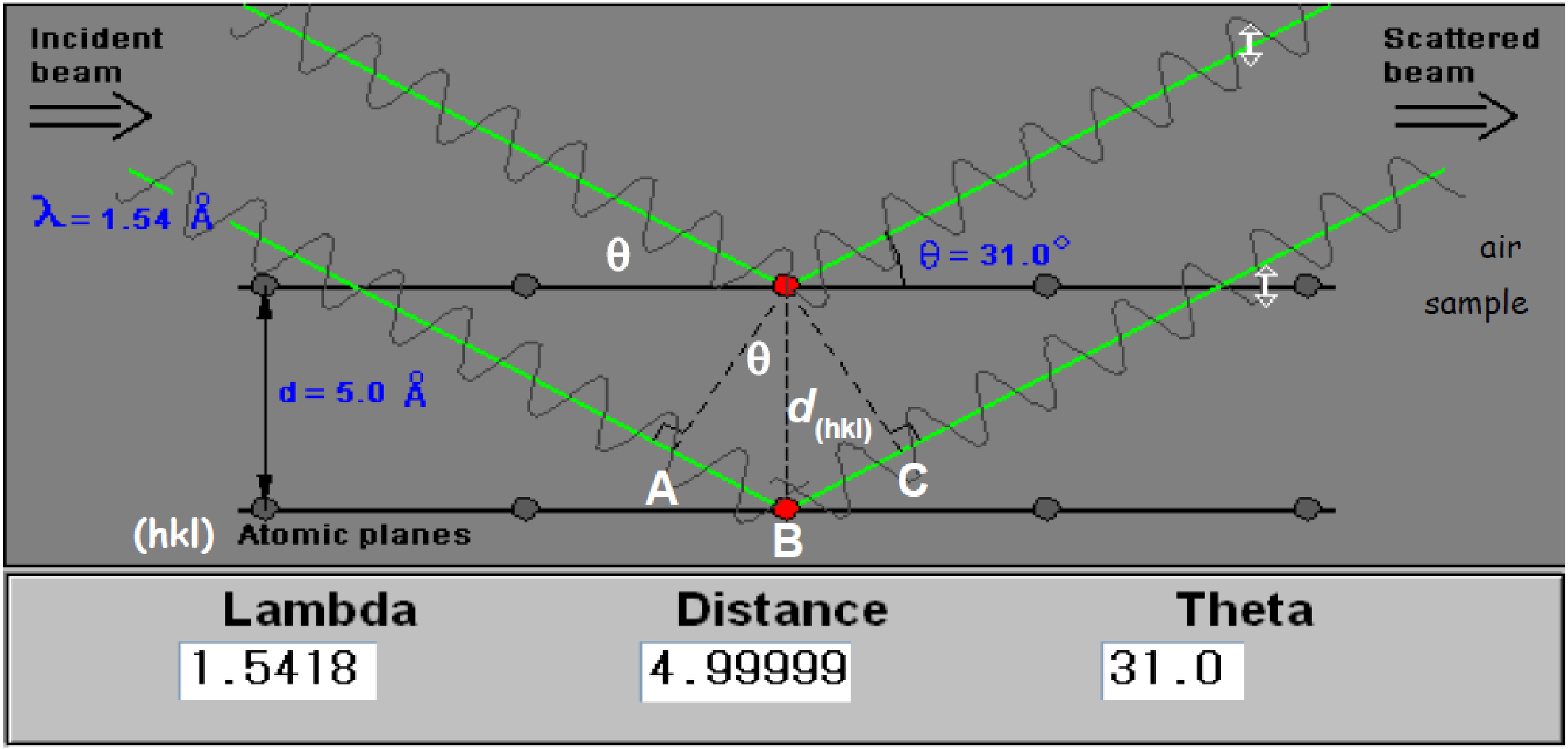
Our previous X-ray diffractometer: 1980s → 2013

Our previous XRD machine was a **Philips powder diffractiometer which we used from 1980 until 2013.** A really important cornerstone for our laboratory in both research and teaching, it was heavily used and very reliable. The reason for its retirement was that spare parts no longer were available.

Before throwing the old XRD out, we invited the people who originally purchased it to visit and say goodbye to the machine: professor emeritus Lauri Niinistö and senior laboratory engineer Lassi Hiltunen. They remembered to tell that the goniometer used for high-temperature measurements was actually taken from an even older XRD device, which had been in use already when TKK (Aalto predecessor) was housed in Hietalahti.

We decided to keep the old goniometer as a memory of our laboratory's very long history of X-ray crystallography expertise.

You have learned the Bragg's law: this is a good presentation to recall it



Lambda	Distance	Theta
1.5418	4.99999	31.0

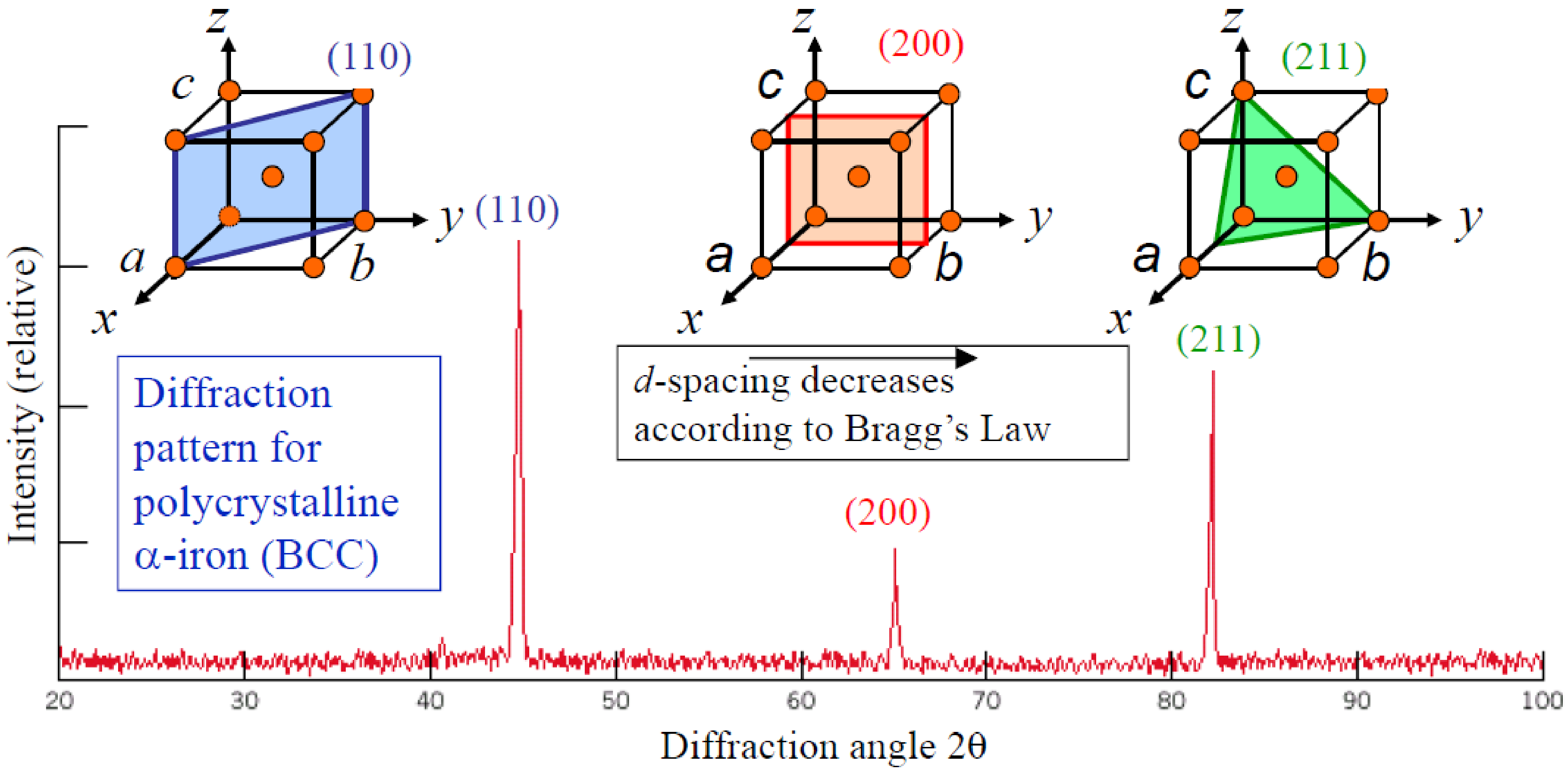
Figure from http://www.eserc.stonybrook.edu/ProjectJava/Bragg/

Bragg's law

Constructive interference

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

LATTICE PLANES → DIFFRACTION PATTERN

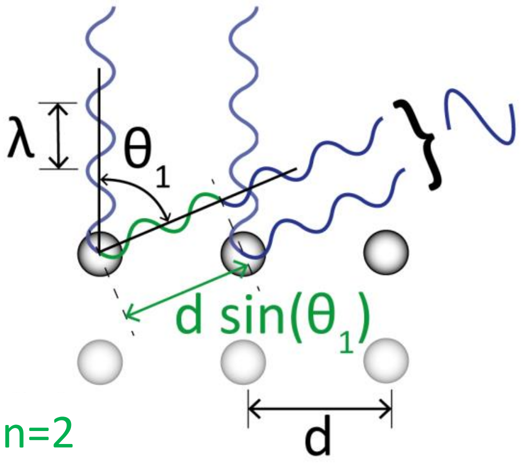


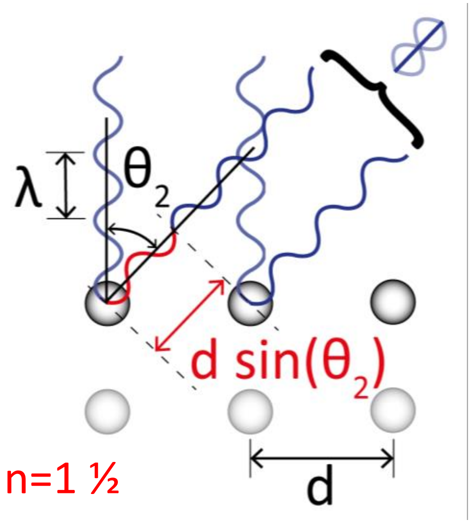
Only few peaks and at nearly same distance from each other → CUBIC

Can we see whether the lattice is primitive or not? … → YES (return to this later)

X-RAY DIFFRACTION

- X-ray range wavelengths are on the same size scale as lattice plane spacings
  - → part of the radiation is reflected from crystals (elastic scattering)
  - → diffraction can be utilized for crystal structure studies
- X-ray radiation is scattered from the **electron clouds of atoms**
- More electrons at the reflection plane (heavy atoms)
  - → high intensity of reflected radiation
- Less electrons at the reflection plane (light atoms)
  - → low intensity of reflected radiation





X-RAY DIFFRACTOMETER

- Production of x-ray radiation:

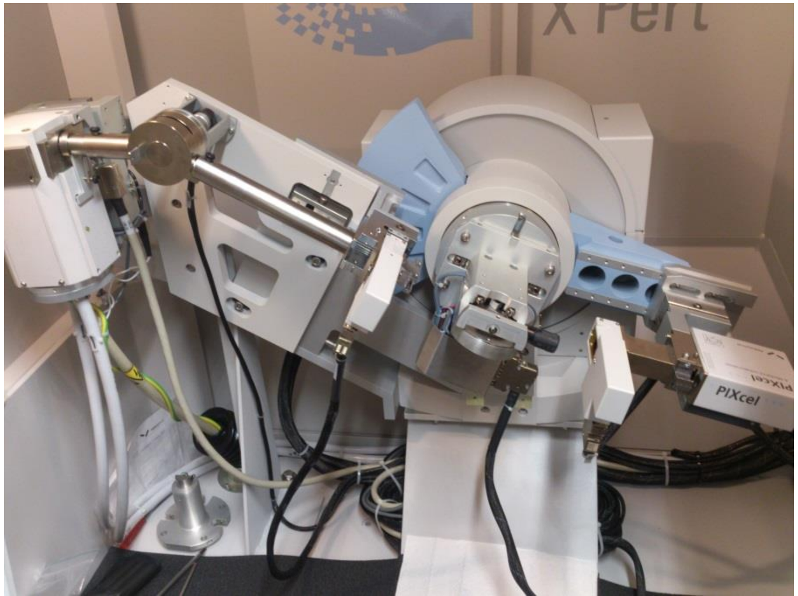
  (i) generator + x-ray tube (e.g. Cu-K_α 1.54 Å, Mo-K_α 0.71 Å)

  (ii) synchrotron (radiation with continuous wavelength)

- Recording of reflected radiation:

  (i) as pulses on counter (x-ray diffractometer)

  (ii) as black spots on film (x-ray camera; historical)

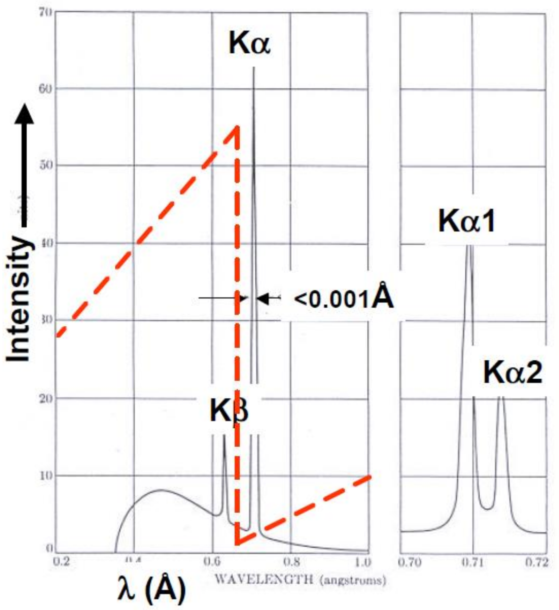


SOURCE →

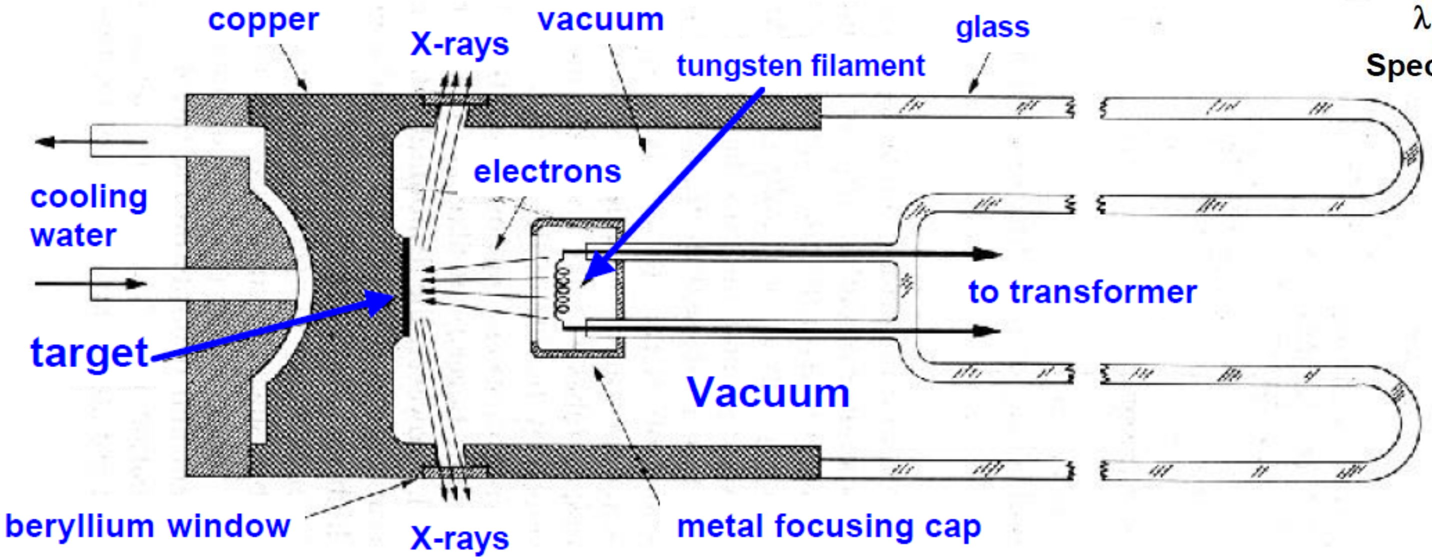
← DETECTOR

X-RAY TUBE: e.g. Cu

- Characteristic X-ray radiation:
  - Cu-K_{α} ($K\alpha_1 + K\alpha_2$) and Cu-K_{β}
- To get monochromatic radiation, Cu-K_{α} and Cu-K_{β} need to be separated (with a filter)



Spectrum of Mo at 35kV

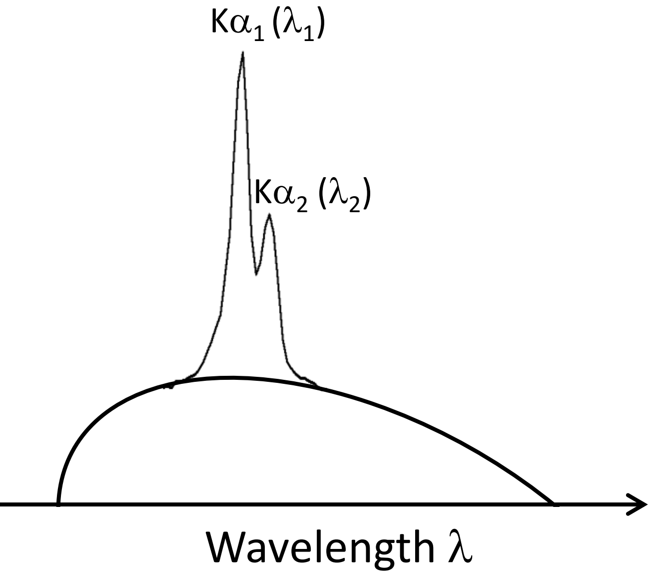


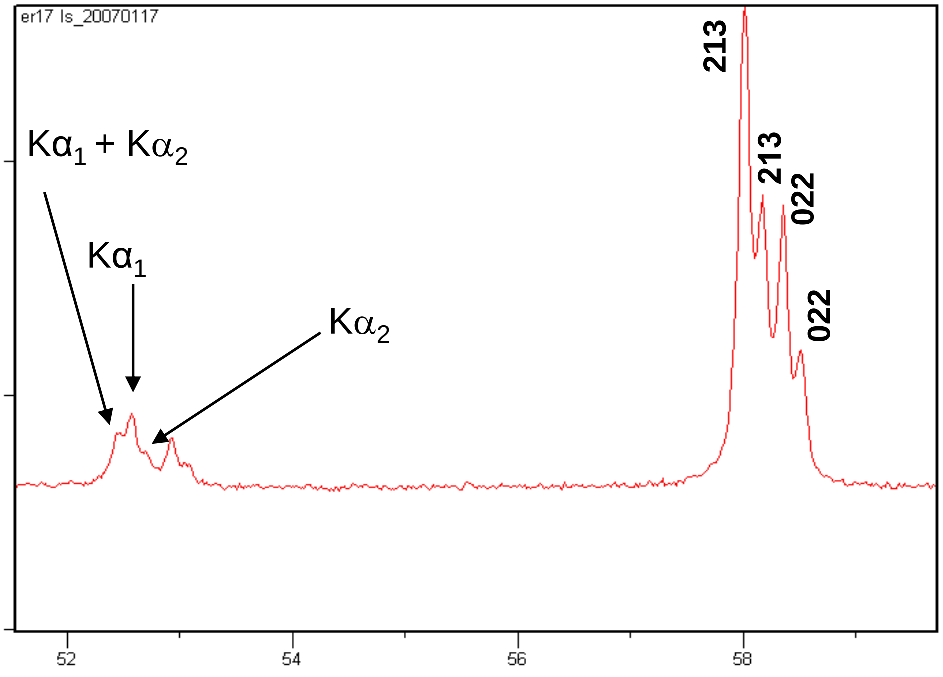
X-rays are produced whenever high-speed electrons collide with a metal target. A source of electrons – hot W filament, a high accelerating voltage between the cathode (W) and the anode and a metal target, *Cu*, Al, Mo, Mg. The anode is a water-cooled block of Cu containing desired target metal.

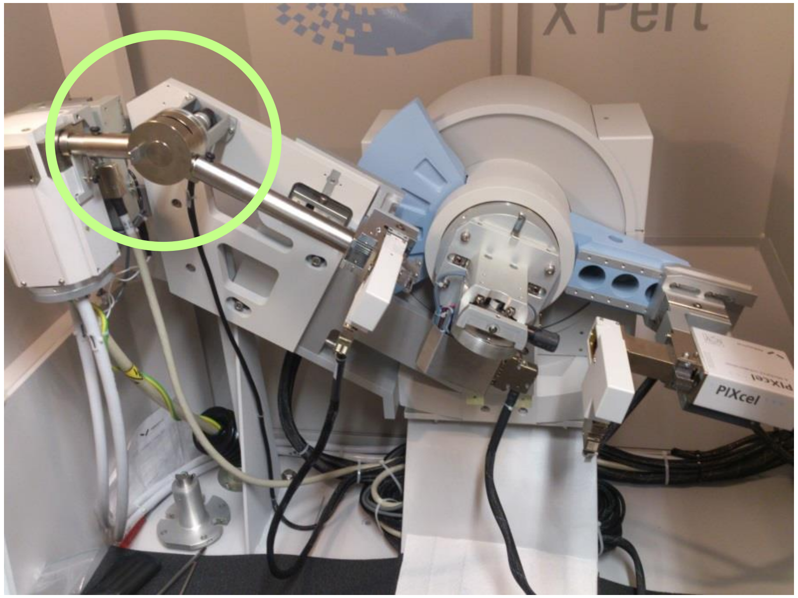
- Copper: $K\alpha_1$: $\lambda = 1.5406$ Å, $K\alpha_2$: $\lambda = 1.5444$ Å, K_β: $\lambda = 1.3923$ Å
- Typically: Cu-K_α and Cu-K_β are separated, but not $K\alpha_1$ and $K\alpha_2$

  (filters are expensive)
- If $K\alpha_2$ is removed, total intensity decreases
- Intensity ratio: $K\alpha_1 : K\alpha_2 = 2 : 1$
- $K\alpha_1$ and $K\alpha_2$ not separated → double reflections in the XRD pattern
- These are especially visible in the high 2θ range

  (Bragg law → resolution increases with increasing 2θ)

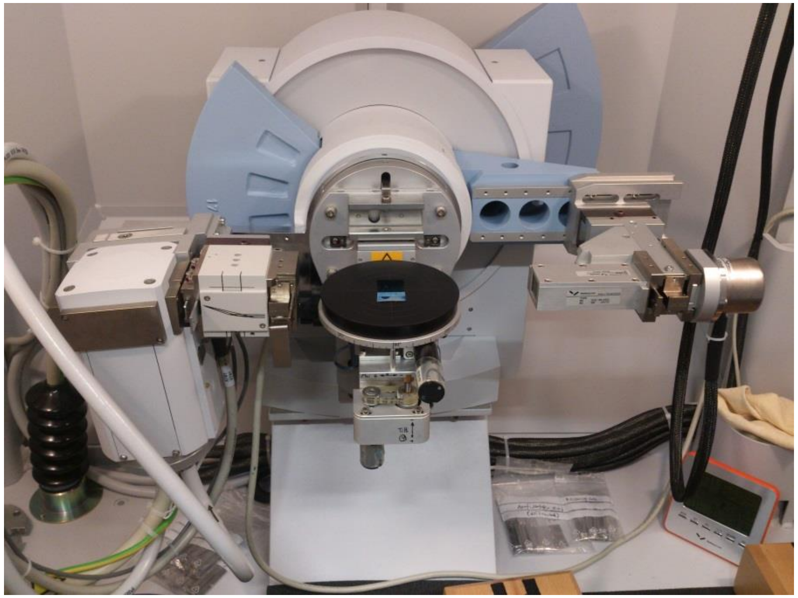






Powder XRD
PANalytical X’Pert PRO MPD Alpha1

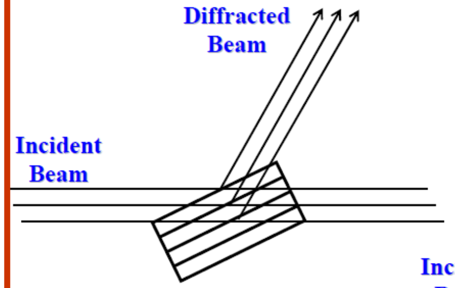
- θ/2θ
- **Johansson Ge monochromator (Kα$_2$ filter)**
- Programmable slits
- Sample spinner
- PIXcel detector



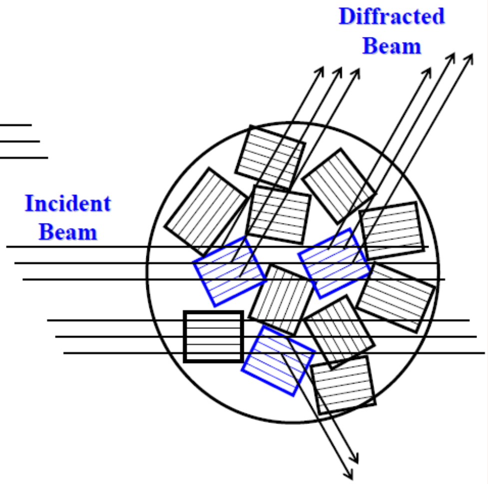
Thin-film XRD
PANalytical X’Pert PRO MPD

- ω/2θ
- Cu mirror and collimator slit
- IR controlled sample stage
  - Height (z, 75 mm)
  - Rotation (φ, n*360°)
  - Tilt (ψ, 20°)

Single Crystal Diffraction



Powder Diffraction



In powder diffraction only a small fraction of the crystals (shown in blue) are correctly oriented to diffract.

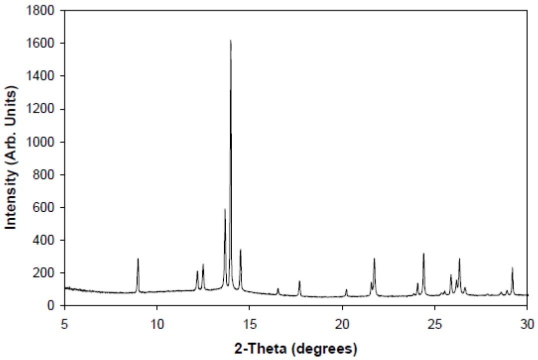
Single Crystal Diffractometer (4 circles)

Powder Diffractometer (2 circles)

https://chemistry.osu.edu/~woodward/

Single Crystal Diffraction (3D)

Powder Diffraction (1D)

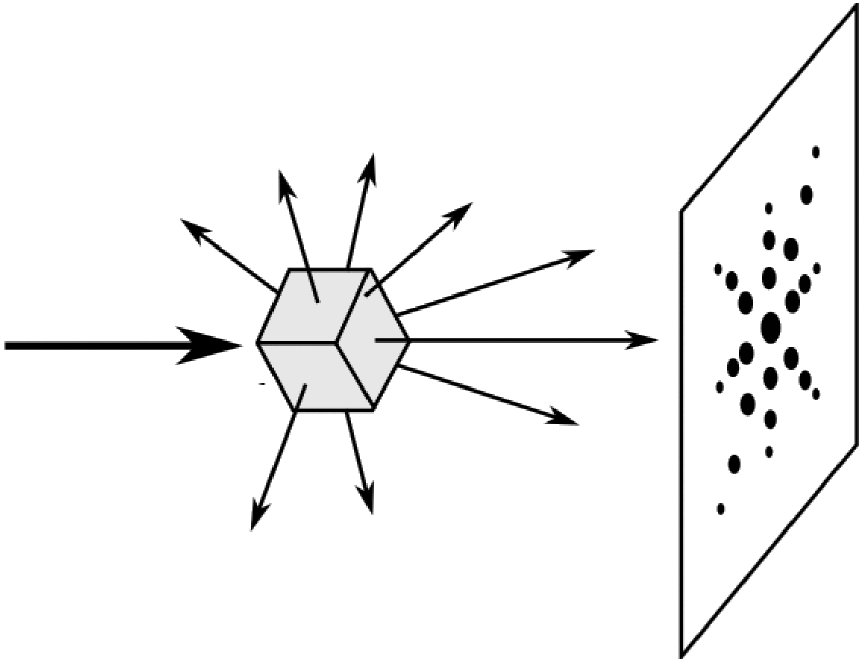


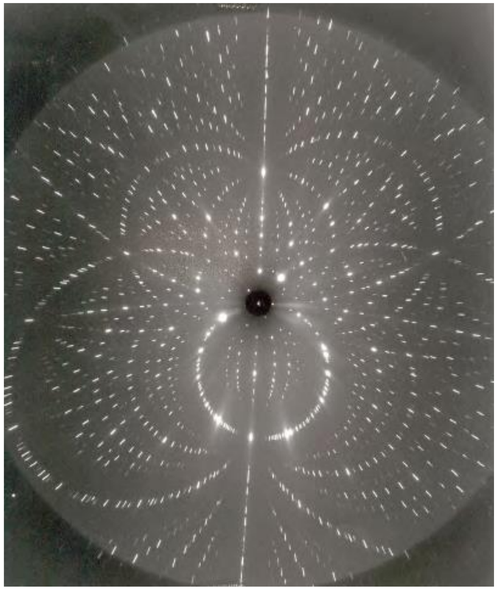
Information in a Diffraction Pattern

- Peak Positions
  - The peak positions tell you about the translational symmetry. Namely what is the size and shape of the unit cell.
- Peak Intensities
  - The peak intensities tell you about the electron density inside the unit cell. Namely where the atoms are located.
- Peak Shapes & Widths
  - The peak widths and shapes can give information on deviations from a perfect crystal. You can learn about the crystallite size if it is less than roughly 100 - 200 nm. You can also learn about extended defects and microstrain.

RECIPROCAL LATTICE

- **Mathematical concept** that links the diffraction measurement data to the real lattice → abstract
- Diffraction from single crystal: the beam diffracted from a specific Miller plane will show up as a dot on the detector screen





Diffraction pattern of single crystal diffraction analysis

RECIPROCAL LATTICE

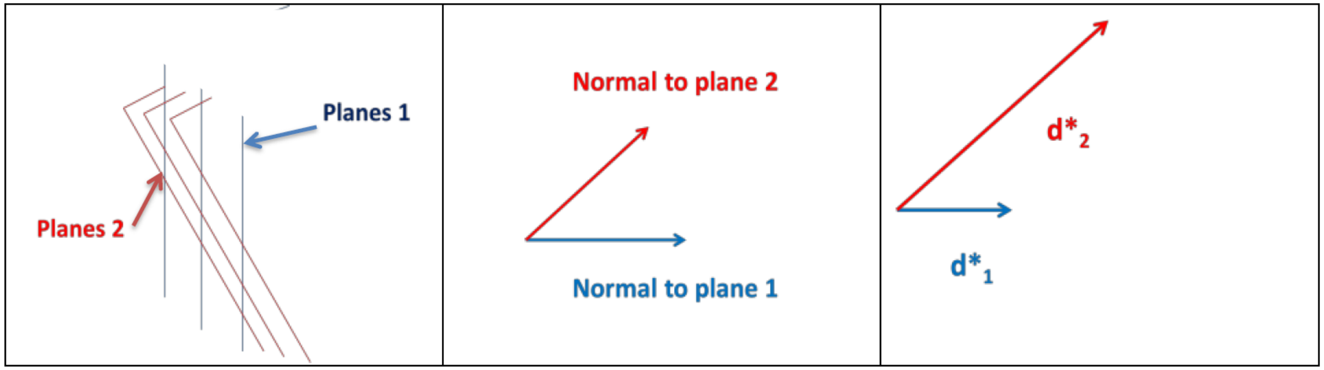
- **Direct lattice** = ”real” lattice
- **Reciprocal lattice:** (mathematically) Fourier transform of the direct lattice
  - Reciprocal space sometimes called momentum space or K-space
  - Fourier transformation equations are symmetrical: reciprocal lattice of the reciprocal lattice is equivalent to the original direct lattice
- Planes in real lattice are points in reciprocal lattice, and vice versa
- Length of reciprocal lattice vector is proportional to the reciprocal (inverse) of the length of direct lattice vectors →

  Big in real space is small in reciprocal space, and vice versa
- Reciprocal lattice has important role in diffraction theory:
  - **Diffraction pattern represents reciprocal lattice, not direct lattice**
  - From the diffraction pattern, the reciprocal vectors can be determined
- Brillouin Zone = ”Unit cell” in Reciprocal lattice

RECIPROCAL VECTORS

- Crystal planes all have a **normal vector: perpendicular** to the plane & the **length** is inversely proportional to the crystal plane spacing *d*

$$d^*_{hkl} = \frac{1}{d_{hkl}}$$



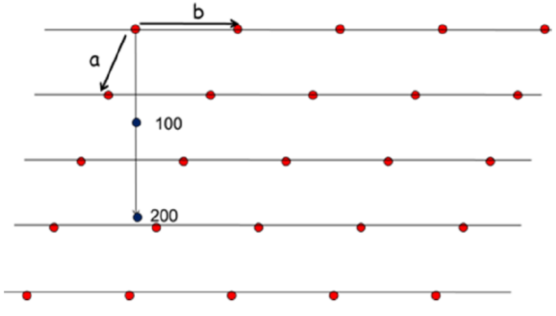
reciprocal lattice vectors have a dimension 1/length whereas direct lattice vectors have a dimension “length”.

- Each crystal plane set (defined by Miller index) gets its own vector
- These vectors exist in the reciprocal space

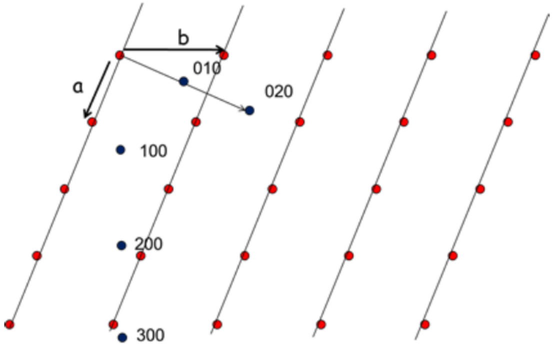
  (abstract space, mathematically constructed just like imaginary space)

DRAWING RECIPROCAL SPACE

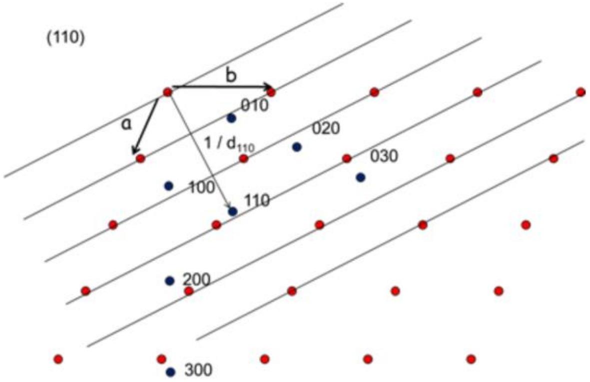
- The end points of the reciprocal lattice vectors form a grid and so can define a reciprocal lattice



[1 0 0] Miller plane series

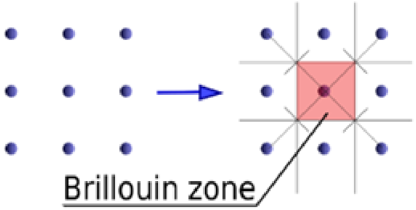


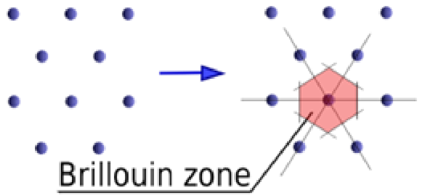
[0 1 0] Miller plane series



[1 1 0] Miller plane series

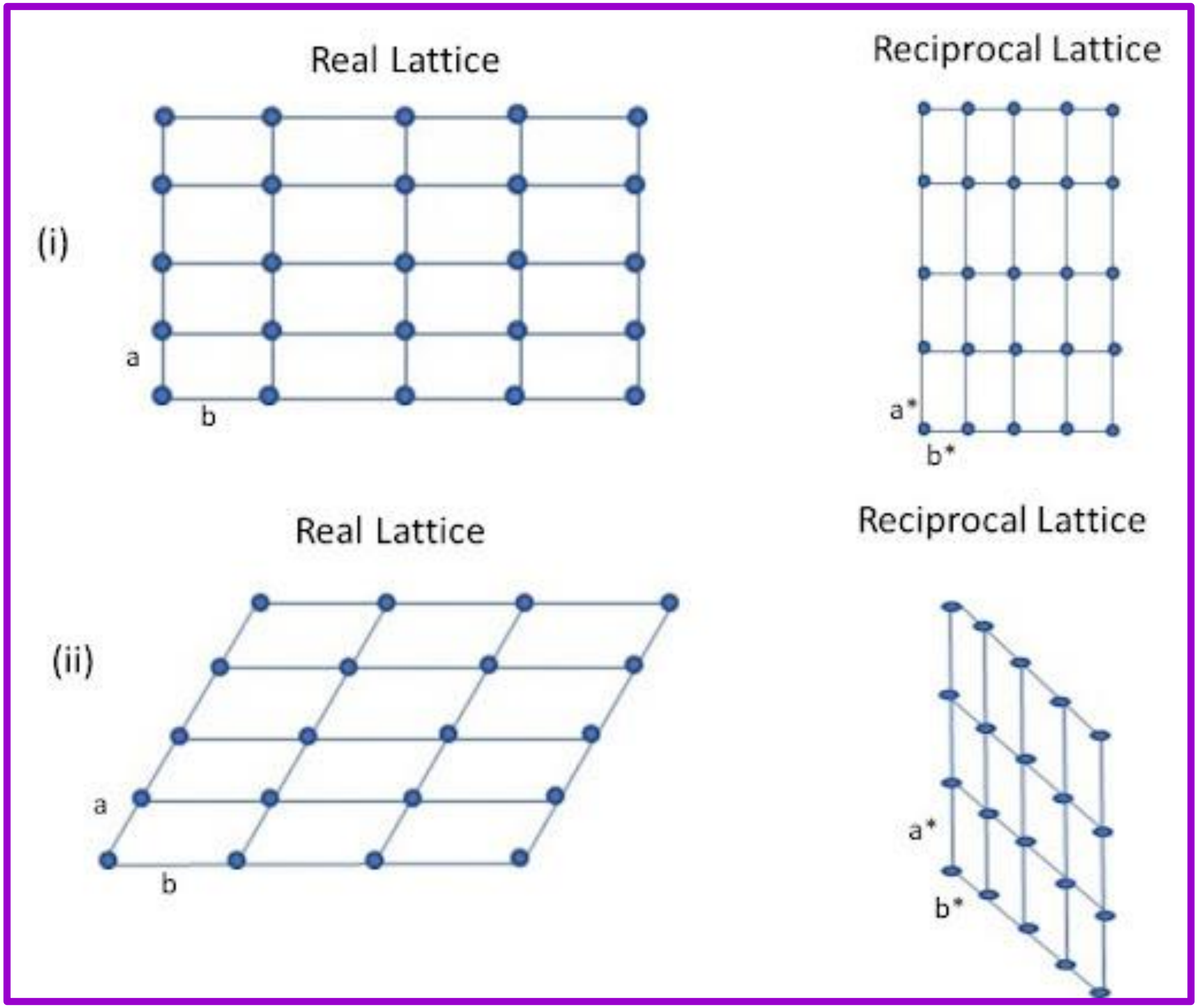
- The reciprocal “unit cell” is called Brillouin Zone
  - Defined by a*, b* and c* (α*, β*, & γ*)





a* =**d***100 with |**a***| = a*= 1/ d100
b* =**d***010 with |**b***| = b*= 1/ d010
c* =**d***001 with |**c***| = c*= 1/ d001

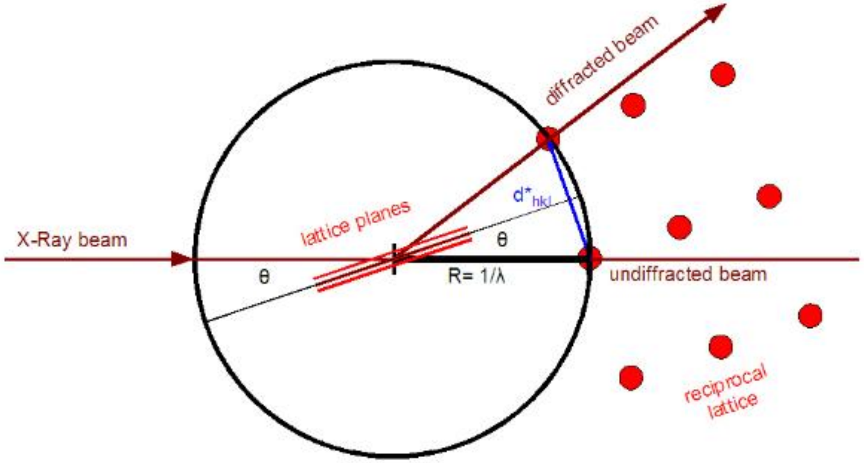
a* is perpendicular to b and c
b* is perpendicular to a and c
c* is perpendicular to a and b

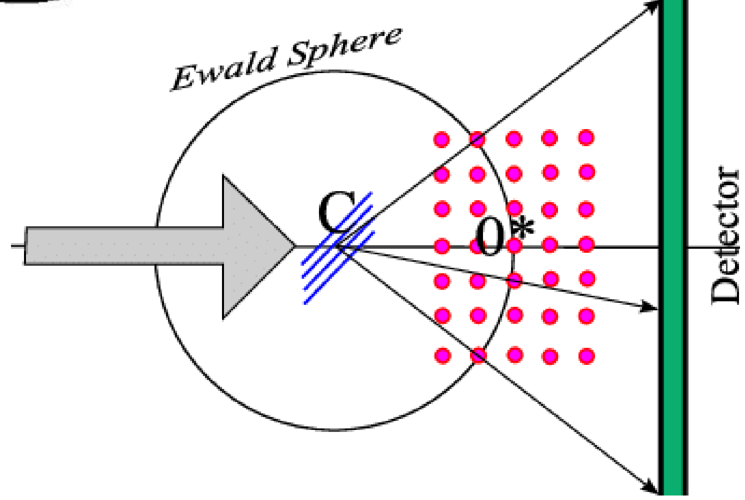

Real Lattice
Reciprocal Lattice
(i)
a
b
a*
b*
Real Lattice
Reciprocal Lattice
(ii)
a
b
a*
b*

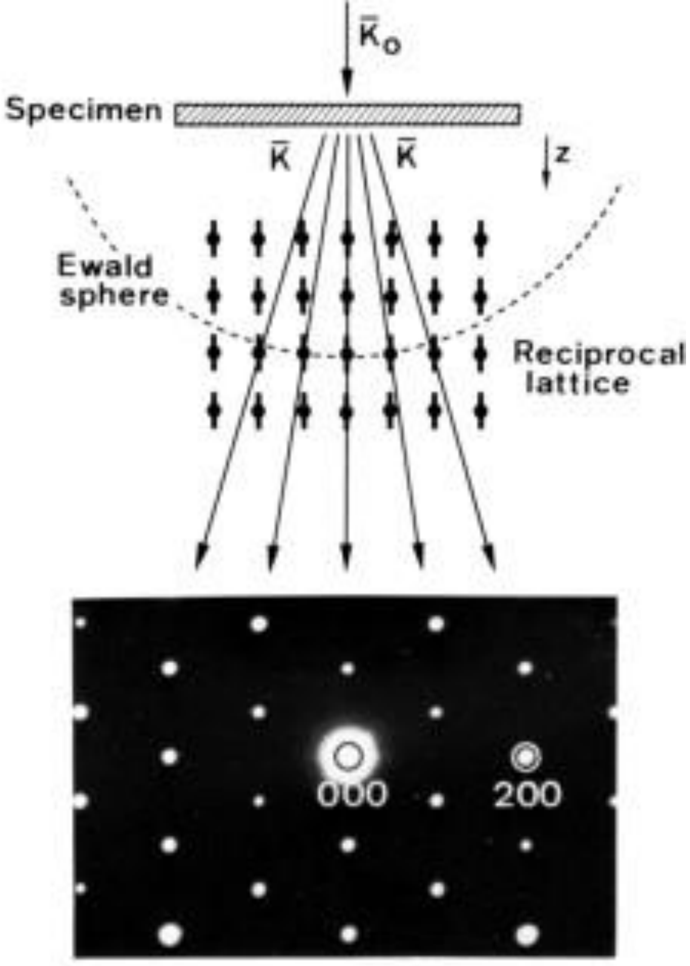
EWALD SPHERE: the reciprocal of the X-ray wavelength

- Radius: λ* = 1/λ (λ = wavelength of incident beam)
- Illustrates which reciprocal lattice points result in diffraction signal

  (reciprocal points that touch the sphere)
- Connected to mathematical description of Bragg’s law in reciprocal space



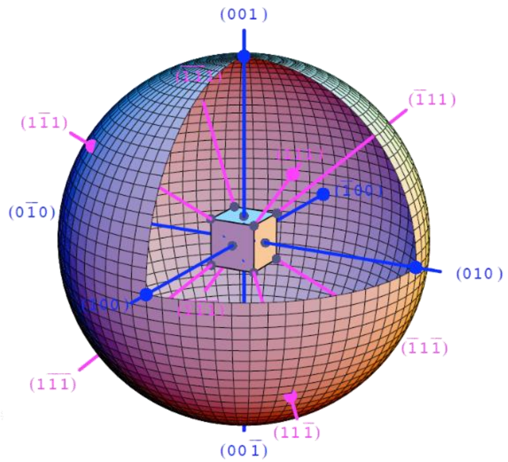


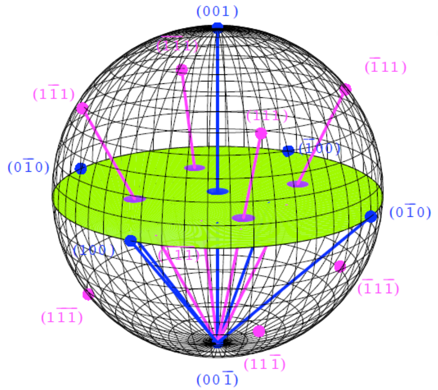


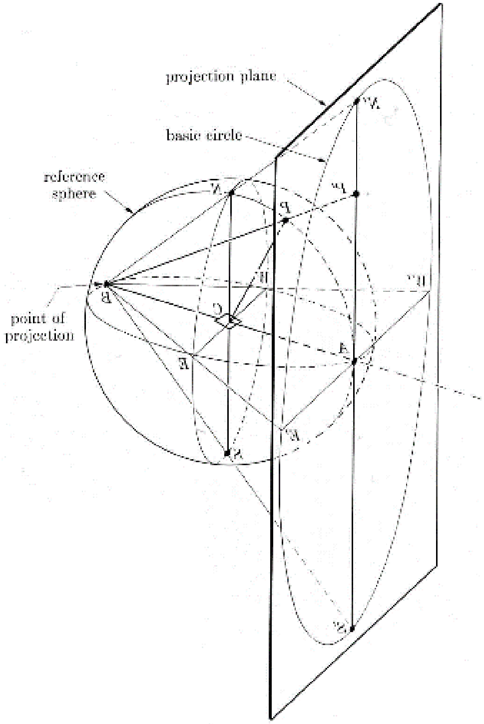
SINGLE-CRYSTAL DIFFRACTION and SYMMETRY GROUP SYMBOLS

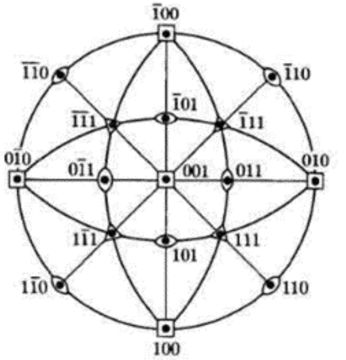
Via the Ewald sphere, we can connect together

- The real crystal to
- The single-crystal diffraction pattern to
- The point group of the point seen by the beam to
- The crystal system and space group

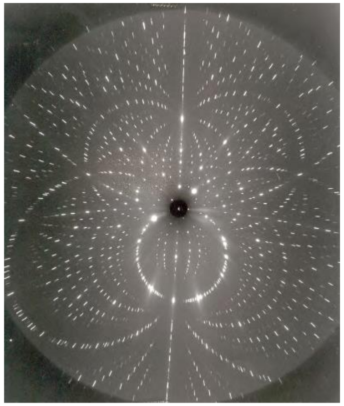






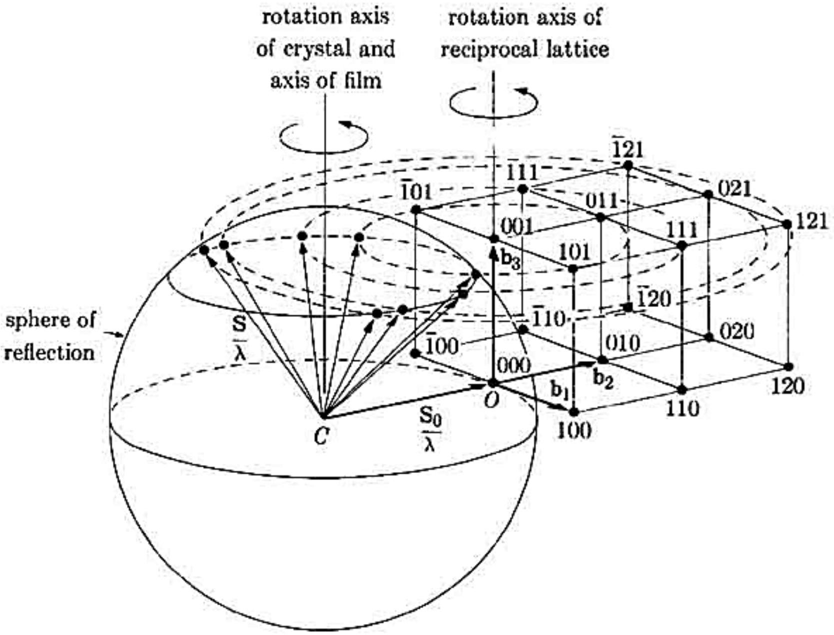


$\bar{4}3m$ point group
→ cubic crystal



POWDER XRD PATTERN

- Classic Bragg-Bentano setup: symmetric movement of beaM source and detector to scan a range of angles
    - capture all the diffracted beams = plane distancings
- In mathematical language: spin the Ewald sphere and the reciprocal lattice around an origo → dots become circles which becomes peaks on a x-y-plot



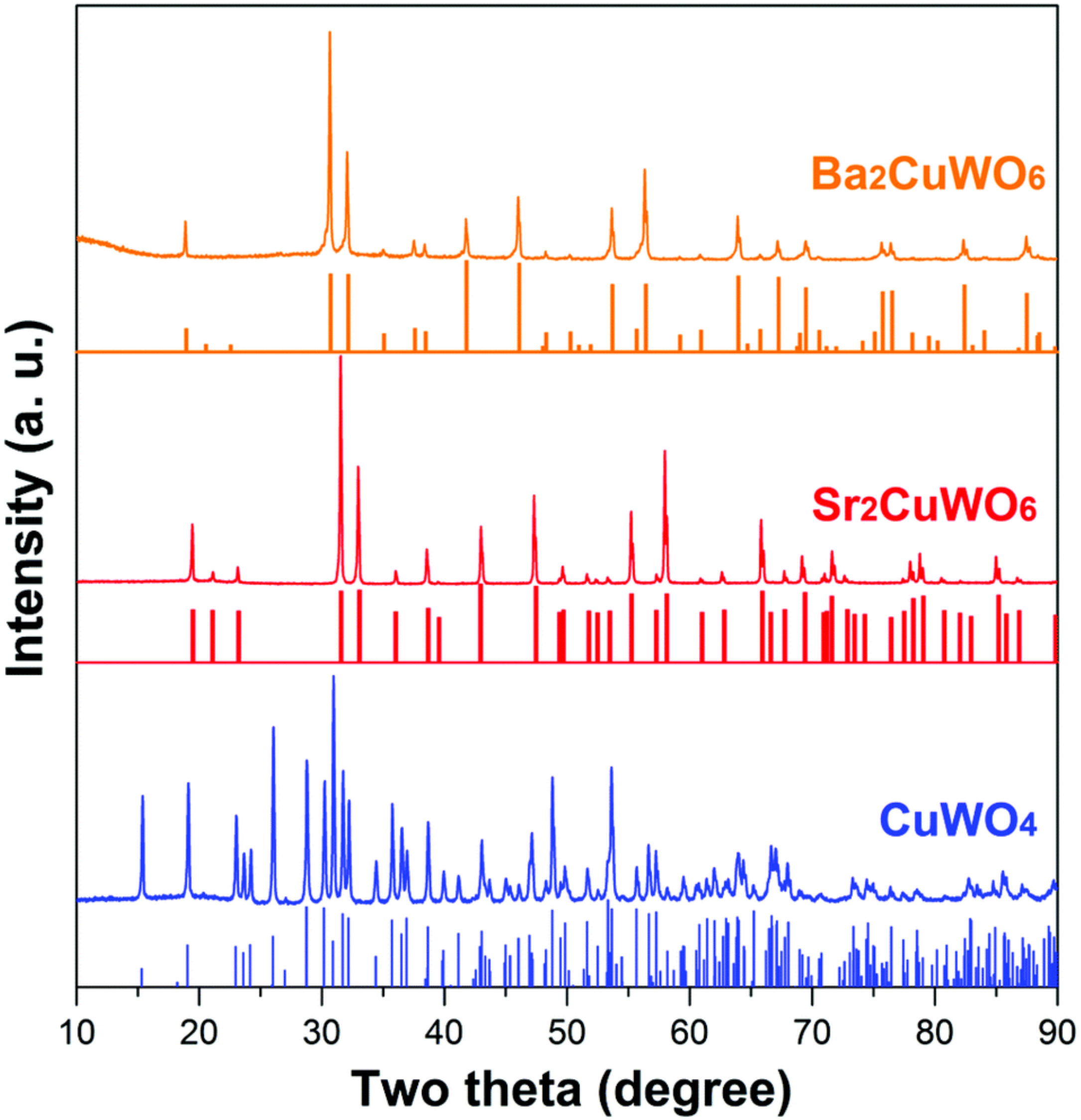
Every reciprocal lattice point
= a specific lattice plane set
(with specific distancing)
↓↓
How many of the reciprocal lattice
points fit inside the Ewalds sphere
= how many peaks can be seen in the
XRD pattern (at most)

EXAMPLES OF XRD PATTERNS

Experimental patterns (on the top) and JSPDS card data (below) for some (double) perovskite samples.

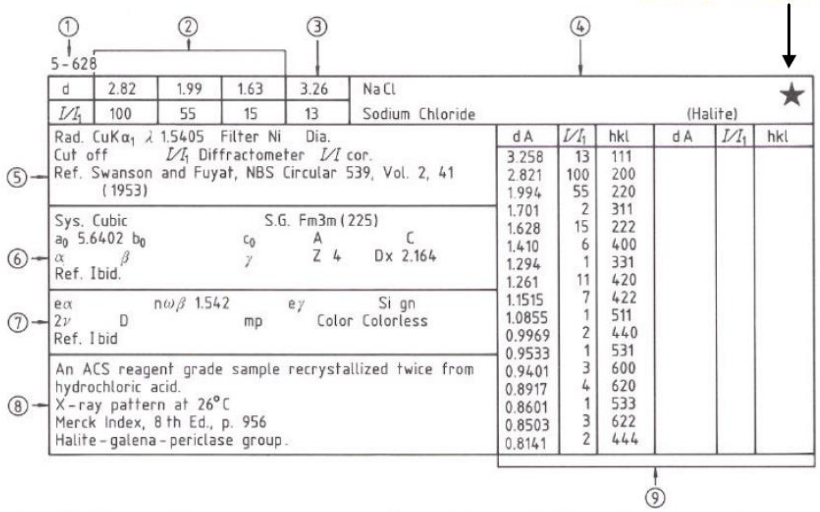
The JSPDS data are kind of ”diffractogram lines” showing the peak positions and intensities, but not the shapes).

CuWO4 (JSPDS: 01-070-1732)
Sr_2CuWO_6 (JSPDS: 01-076-0086)
Ba_2CuWO_6 (JSPDS: 01-076-0084)



DOI: 10.1039/C9QI00675C (Research Article) Inorg. Chem. Front. (2019) **6**, 2096.

JCPDS Card



Quality of data

5-628

d	2.82	1.99	1.63	3.26	NaCl
I/I_1	100	55	15	13	Sodium Chloride (Halite) ★

Rad. CuKα_1 λ 1.5405 Filter Ni Dia.
Cut off I/I_1 Diffractometer I/I cor.
Ref. Swanson and Fuyat, NBS Circular 539, Vol. 2, 41 (1953)

Sys. Cubic S.G. Fm3m (225)
a_0 5.6402 b_0 c_0 A C
α β γ Z 4 Dx 2.164
Ref. Ibid.

$\varepsilon\alpha$ $n\omega\beta$ 1.542 $\varepsilon\gamma$ Si gn
2V D mp Color Colorless
Ref. Ibid

An ACS reagent grade sample recrystallized twice from hydrochloric acid.
X-ray pattern at 26°C
Merck Index, 8th Ed., p. 956
Halite-galena-periclase group.

d A	I/I_1	hkl	d A	I/I_1	hkl
3.258	13	111			
2.821	100	200			
1.994	55	220			
1.701	2	311			
1.628	15	222			
1.410	6	400			
1.294	1	331			
1.261	11	420			
1.1515	7	422			
1.0855	1	511			
0.9969	2	440			
0.9533	1	531			
0.9401	3	600			
0.8917	4	620			
0.8601	1	533			
0.8503	3	622			
0.8141	2	444			

1.file number 2.three strongest lines 3.lowest-angle line 4.chemical formula and name 5.data on diffraction method used 6.crystallographic data 7.optical and other data 8.data on specimen 9.data on diffraction pattern.

Joint Committee on Powder Diffraction Standards, JCPDS (1969)
Replaced by International Centre for Diffraction Data ICDD (1978)

Qualitative Analysis
Searching with the ICDD

Once you have a powder pattern you can use it like a fingerprint to see if it matches the powder pattern of an already known compound. Nowadays this is usually done with the help of a computer.

The International Centre for Diffraction Data (ICDD) maintains a database of known powder diffraction patterns (www.icdd.com)

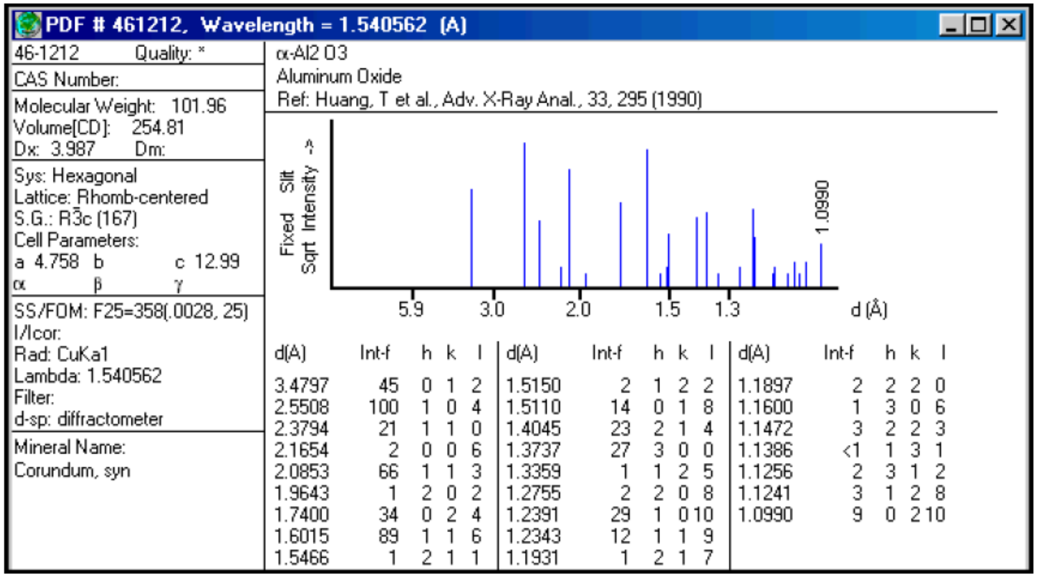
- 115,000 patterns (not all unique)
- 95,000 Inorganic compounds
- 20,000 Organic compounds

"FINGERPRINT" APPROACH

Phase recognition + Impurity phases

I believe you have done this in some lab works already?

ICDD "Card"



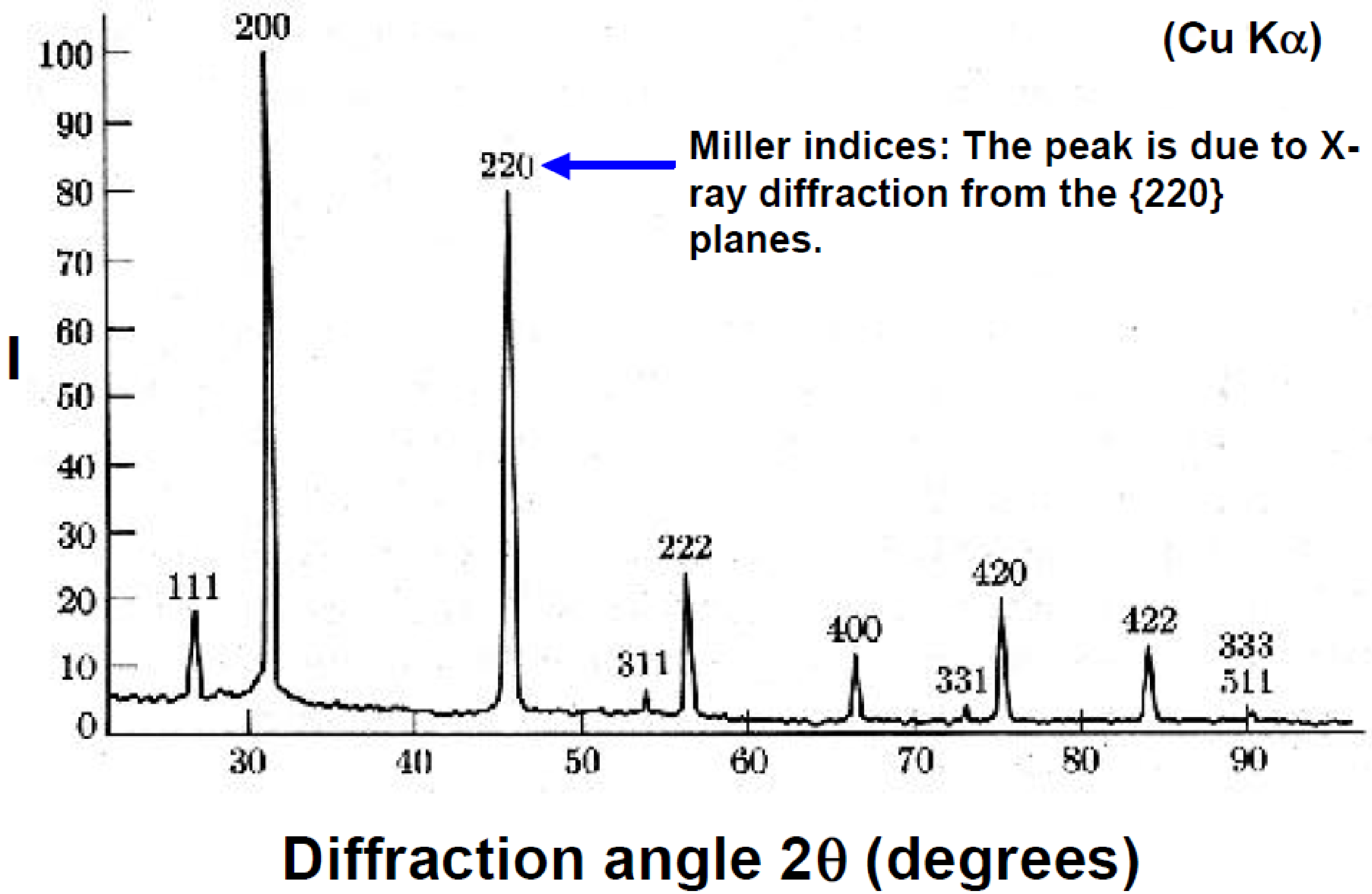
PDF # 461212, Wavelength = 1.540562 (A)

46-1212 Quality: *
CAS Number:
Molecular Weight: 101.96
Volume[CD]: 254.81
Dx: 3.987 Dm:
Sys: Hexagonal
Lattice: Rhomb-centered
S.G.: R$\bar{3}$c (167)
Cell Parameters:
a 4.758 b c 12.99
α β γ
SS/FOM: F25=358(.0028, 25)
I/Icor:
Rad: CuKa1
Lambda: 1.540562
Filter:
d-sp: diffractometer
Mineral Name:
Corundum, syn

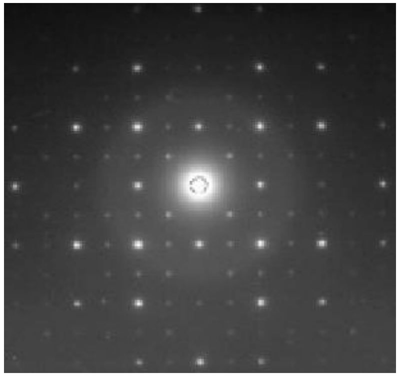
α-Al2 O3
Aluminum Oxide
Ref: Huang, T et al., Adv. X-Ray Anal., 33, 295 (1990)

d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l	d(A)	Int-f	h	k	l
3.4797	45	0	1	2	1.5150	2	1	2	2	1.1897	2	2	2	0
2.5508	100	1	0	4	1.5110	14	0	1	8	1.1600	1	3	0	6
2.3794	21	1	1	0	1.4045	23	2	1	4	1.1472	3	2	2	3
2.1654	2	0	0	6	1.3737	27	3	0	0	1.1386	<1	1	3	1
2.0853	66	1	1	3	1.3359	1	1	2	5	1.1256	2	3	1	2
1.9643	1	2	0	2	1.2755	2	2	0	8	1.1241	3	1	2	8
1.7400	34	0	2	4	1.2391	29	1	0	10	1.0990	9	0	2	10
1.6015	89	1	1	6	1.2343	12	1	1	9					
1.5466	1	2	1	1	1.1931	1	2	1	7					

XRD Pattern of NaCl Powder



Miller indices: The peak is due to X-ray diffraction from the {220} planes.



Single crystal pattern

As you are going to see soon, not only the peak positions and intensities but also the peak shapes carry information; Hence, the correct terminology is "pattern", not diffracto"gram"

More on Bragg's Law

- Bragg's Law is a necessary but insufficient condition for diffraction.
- It only defines the diffraction condition for *primitive unit cells*, e.g. P cubic, P tetragonal, etc., where atoms are only at unit cell corners.
- Crystal structures with non-primitive unit cells have atoms at additional lattice (basis) sites.
- These extra scattering centers can cause out-of-phase scattering to occur at certain Bragg angles.
- The net result is that some of the diffraction predicted by Bragg's Law (eq. 1) does not occur, i.e. certain sets of planes do not exist (forbidden reflections).
- **Selection (or Reflection) rules**:

Bravais Lattice	Example Compounds	Allowed Reflections	Forbidden Reflections
Primitive Cubic	Simple Cubic (α-Po)	Any h,k,l	None
Body-Centered Cubic	Body-Centered Cubic metal	h+k+l even	h+k+l odd
Face-Centered Cubic	Face-Centered Cubic metal	h,k,l all odd or all even	h,k,l mixed odd or even
Face-Centered Cubic	NaCl-rocksalt, ZnS-zincblende	h,k,l all odd or all even	h,k,l mixed odd or even
Face-Centered Cubic	Si, Ge - Diamond cubic	As FCC, but if all even and $h+k+l \neq 4n$, then absent (n is integer)	h,k,l mixed odd or even and if all even and $h+k+l \neq 4n$
Primitive Hexagonal	Hexagonal closed packed metal	All other cases	h+2k=3n, l odd

In the example on the previous page, only 110, 200 and 211 peaks seen, while 100 and 210 are missing → Body-centered cubic

Selection Rules for Cubic Crystals

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{S}}$$

where "*S*" is reflection or line #,
e.g. (100) is 1st order reflection and (200) is 4th order reflection.

As we will determine later when we calculate the structure factors, these selection rules also hold for other Bravais lattices, *e.g.*
I-tetragonal,
F-orthorhombic, *etc.*

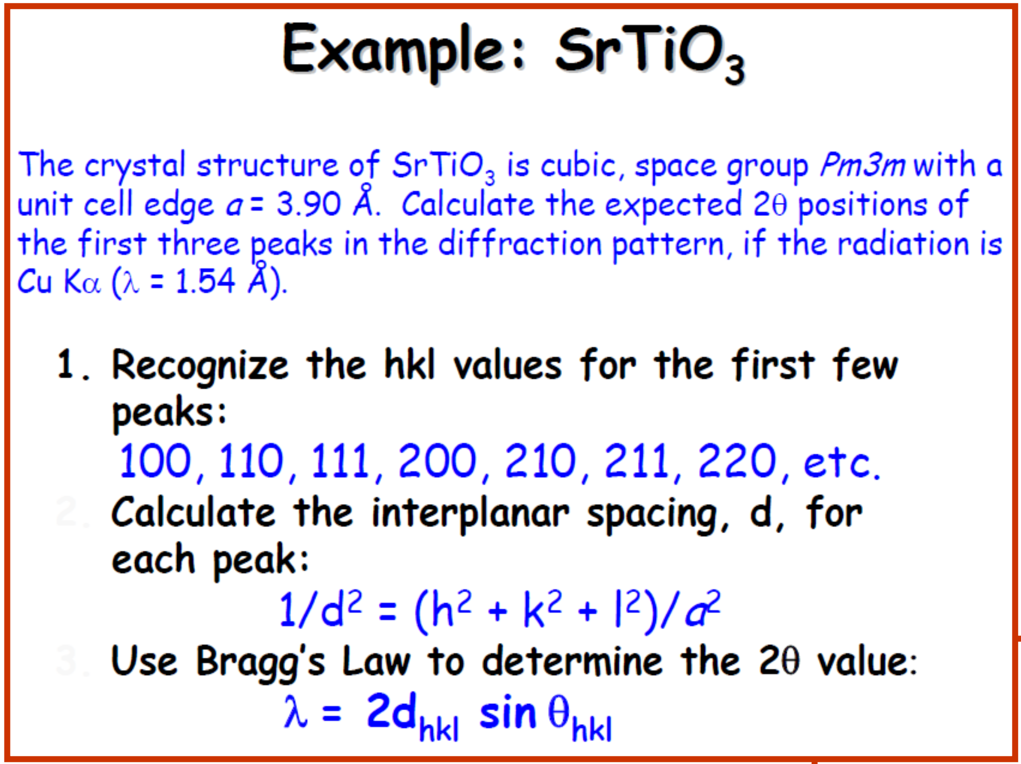
P		I		F		
S	(hkl)	S	(hkl)	S	(hkl)	
1	100	-	-	-	-	→ Odd+even
2	110	2	110	-	-	→ Odd+even
3	111	-		3	111	→ All odd
4	200	4	200	4	200	→ All even
5	210	-	-	-	-	→ Odd+even
6	211	6	211	-	-	→ Odd+even
7	-	-	-	-	-	
8	220	8	220	8	220	→ All even
9	221,300	-	-			→ Odd+even
10	310	10	310			→ Odd+even
11	311	-	-	11	311	→ All odd
12	222	12	222	12	222	→ All even

Type equation here.

Primitive *Body-centered* *Face centered*

↑

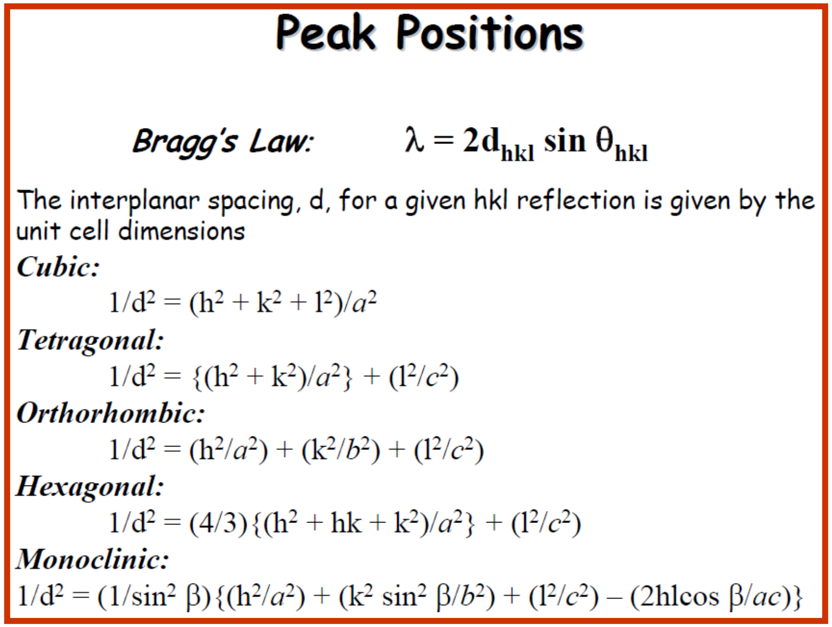
$S = h^2 + k^2 + l^2$



Example: $SrTiO_3$

The crystal structure of $SrTiO_3$ is cubic, space group *Pm3m* with a unit cell edge *a* = 3.90 Å. Calculate the expected 2θ positions of the first three peaks in the diffraction pattern, if the radiation is Cu Kα (λ = 1.54 Å).

1. Recognize the hkl values for the first few peaks:
   100, 110, 111, 200, 210, 211, 220, etc.
2. Calculate the interplanar spacing, d, for each peak:
   $$1/d^2 = (h^2 + k^2 + l^2)/a^2$$
3. Use Bragg's Law to determine the 2θ value:
   $$\lambda = 2d_{hkl} \sin \theta_{hkl}$$



Peak Positions

Bragg's Law: $\lambda = 2d_{hkl} \sin \theta_{hkl}$

The interplanar spacing, d, for a given hkl reflection is given by the unit cell dimensions

Cubic:

$$1/d^2 = (h^2 + k^2 + l^2)/a^2$$

Tetragonal:

$$1/d^2 = \{(h^2 + k^2)/a^2\} + (l^2/c^2)$$

Orthorhombic:

$$1/d^2 = (h^2/a^2) + (k^2/b^2) + (l^2/c^2)$$

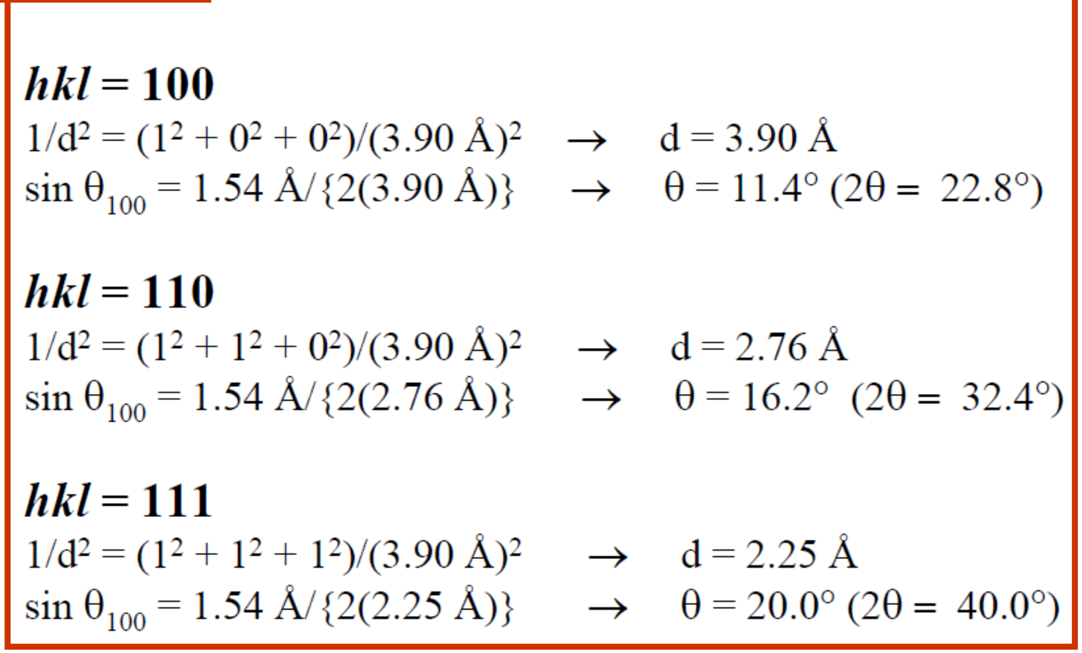
Hexagonal:

$$1/d^2 = (4/3)\{(h^2 + hk + k^2)/a^2\} + (l^2/c^2)$$

Monoclinic:

$$1/d^2 = (1/\sin^2 \beta)\{(h^2/a^2) + (k^2 \sin^2 \beta/b^2) + (l^2/c^2) - (2hl\cos \beta/ac)\}$$

Example: $SrTiO_3$



***hkl* = 100**

$$1/d^2 = (1^2 + 0^2 + 0^2)/(3.90\ \text{Å})^2 \quad \rightarrow \quad d = 3.90\ \text{Å}$$

$$\sin \theta_{100} = 1.54\ \text{Å}/\{2(3.90\ \text{Å})\} \quad \rightarrow \quad \theta = 11.4^\circ\ (2\theta = 22.8^\circ)$$

***hkl* = 110**

$$1/d^2 = (1^2 + 1^2 + 0^2)/(3.90\ \text{Å})^2 \quad \rightarrow \quad d = 2.76\ \text{Å}$$

$$\sin \theta_{100} = 1.54\ \text{Å}/\{2(2.76\ \text{Å})\} \quad \rightarrow \quad \theta = 16.2^\circ\ (2\theta = 32.4^\circ)$$

***hkl* = 111**

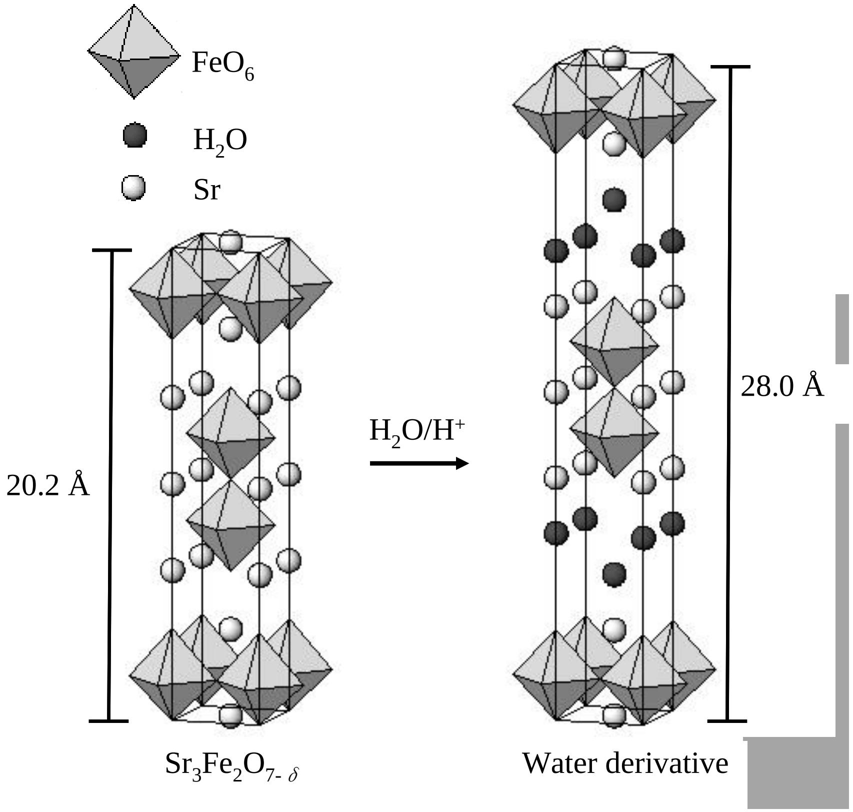
$$1/d^2 = (1^2 + 1^2 + 1^2)/(3.90\ \text{Å})^2 \quad \rightarrow \quad d = 2.25\ \text{Å}$$

$$\sin \theta_{100} = 1.54\ \text{Å}/\{2(2.25\ \text{Å})\} \quad \rightarrow \quad \theta = 20.0^\circ\ (2\theta = 40.0^\circ)$$

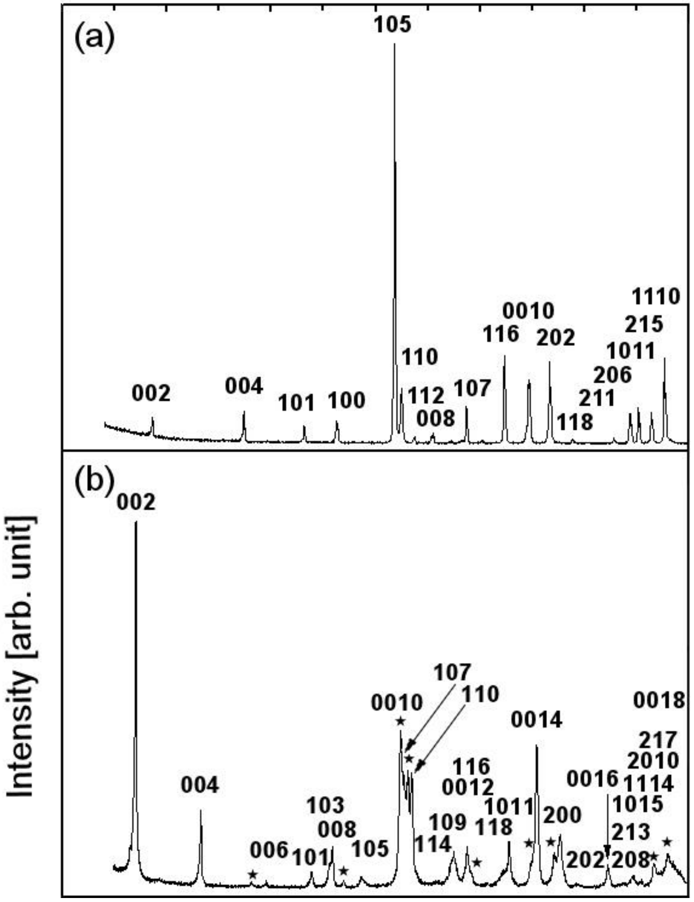
How to calculate lattice parameters if we know the structure type and Miller indices

Tetragonal $Sr_3Fe_2O_7$

- **Ruddlesden-Popper structure; consists of layers: SrO-SrO-FeO_2-SrO-FeO_2**
- **Absorbs easily water molecules in between SrO-SrO layers**
- **c-parameter increases while a- and b-parameters remain nearly the same**
- **How can you see this from the XRD patterns: (a) $Sr_3Fe_2O_7$, (b) $Sr_3Fe_2O_7$ + water**



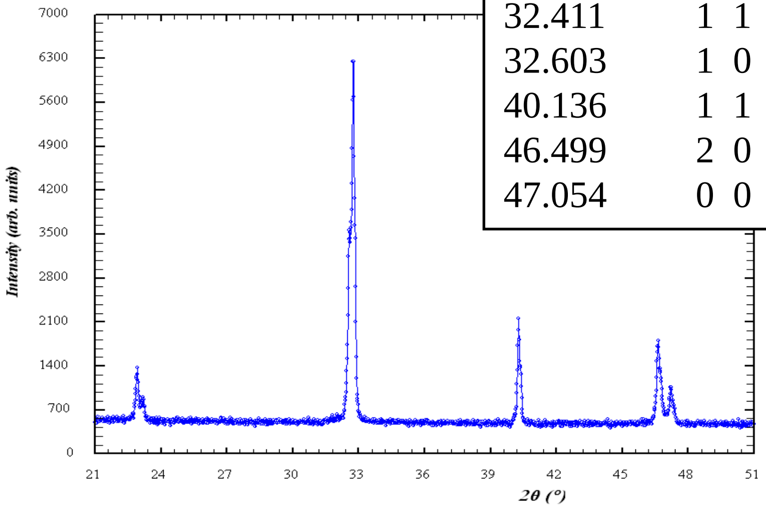
Lehtimäki, Hirasa, Matvejeff, Yamauchi & Karppinen, *J. Solid State Chem.* **180**, 3247 (2007).



EXAMPLE: DETERMINATION OF LATTICE PARAMETERS

Calculate the lattice parameters based on the following data for the seven first Bragg reflections:
tetragonal *P*4/*mmm*; $\text{CuK}_\alpha = 1.5406$ Å.

2θ	*hkl*
22.766	1 0 0
23.026	0 0 2
32.411	1 1 0
32.603	1 0 2
40.136	1 1 2
46.499	2 0 0
47.054	0 0 4



ANSWER:

$$\sin^2\theta = (h^2 + k^2)\cdot\frac{\lambda^2}{4a^2} + l^2\cdot\frac{\lambda^2}{4c^2}$$

Miller	2θ	sinθ	$\sin^2\theta$	Parameter (Å)
002	23.03	0.1996	0.0398	7.724
004	47.05	0.3991	0.1593	7.725
100	22.77	0.1947	0.0390	3.905
200	46.50	0.3947	0.1558	3.906

→ c

→ a = b

RECOMMENDATION: Take an average of the two values; Also, you could verify the numbers by using the 110, 102 and 112 reflections.

FURTHER ANALYSIS OF DIFFRACTION PATTERN

- **First step: Indexing → find the Miller indices for the reflections**
- **This allows the determination of the lattice parameters**
- **This is relatively easy for high-symmetry structures**

Indexing

- Indexing is the process of determining the unit cell dimensions from the peak positions. To index a powder diffraction pattern it is necessary to **assign Miller indices, *hkl*, to each peak**.
- A diffraction pattern cannot be analyzed until it has been indexed. **It is always the first step in analysis.**
- Unfortunately it is not just the simple reverse of calculating peak positions from the unit cell dimensions and wavelength.
- We will show how one can manually index diffraction patterns of high symmetry structures. For lower symmetry structures (orthorhombic, monoclinic, triclinic) it is usually necessary to use a computer algorithm. **This is called Autoindexing**.

Indexing a Cubic Pattern

Bragg's Law tells us the location of a peak with indices hkl, θ_{hkl}, is related to the interplanar spacing, d, as follows:

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

$$1/d = 2 \sin \theta / \lambda$$

$$1/d^2 = 4 \sin^2 \theta / \lambda^2$$

Earlier we saw that for a cubic phase the d-values can be calculated from the Miller indices (hkl)

$$1/d^2 = (h^2 + k^2 + l^2)/a^2$$

Combining these two equations we get the following relationship

$$\sin^2 \theta / (h^2 + k^2 + l^2) = \lambda^2 / 4a^2$$

Need to find values of h,k,l for that give a constant when divided by each $\sin^2 \theta$.

Cubic Example

2-Theta	1000 $\sin^2\theta$	1000 $\sin^2\theta$ /CF	hkl
22.21	37.1		
31.61	74.2		
38.97	111		
45.31	148		
51.01	185		
56.29	222		
66.00	297		
70.58	334		
75.03	371		
79.39	408		

We need to find a common factor, CF, that can be divided into each of the values in the second column to give an integer = $h^2+k^2+l^2$

CF = (37.1/1000) = $\lambda^2 / 4a^2 \rightarrow$ (a = 4.00 A)

2-Theta	1000 $\sin^2\theta$	1000 $\sin^2\theta$ /CF	hkl
22.21	37.1	1.00	1 0 0
31.61	74.2	2.00	1 1 0
38.97	111	2.99	1 1 1
45.31	148	3.99	2 0 0
51.01	185	4.99	2 1 0
56.29	222	5.98	2 1 1
66.00	297	8.01	2 2 0
70.58	334	9.00	300/221
75.03	371	10.00	3 1 0
79.39	408	11.00	3 1 1

INDEXING EXAMPLE

XRD pattern measured for a sample of cubic unit cell using Cu-K$_\alpha$ (λ = 1.5418 Å) radiation shows peaks at 2θ values listed in the table below. Index the reflections.

What is the Bravais lattice type?

Answer:

1. First, we calculate $\sin^2\theta$ values, and multiply them by 10^6 just for convenience.
2. To find the "constant value" A, we calculate the differences between consecutive $\sin^2\theta$ values; from this list we can "see" that ca. 19355 is included as a term in all these difference numbers, hence, it could be our "A". Then we notice that $h^2+k^2+l^2 = (10^6 \times \sin^2\theta) / A$.
3. Finally, the hkl combinations can be easily derived from these numbers.
4. From the resultant list of reflections (S=3,4,8,11,12,…), we identify the systematic absences as typical for FCC and conclude that the lattice type is face-centered cubic.

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

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

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} = \frac{4\sin^2\theta}{\lambda^2}$$

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)(h^2+k^2+l^2)$$

$$\left(\frac{\lambda^2}{4a^2}\right) \text{ is constant}$$

$S = h^2 + k^2 + l^2$

↓

2θ	$sin^2\theta \cdot 10^6$	Difference	Constant	$\frac{sin^2\theta \cdot 10^6}{A}$	hkl
27,88	58036			2,999	111
32,3	77369	19334	19355 (ka.)	3,997	200
46,32	154685	77316		7,992	220
54,92	212640	57955		10,986	311
57,6	232087	19446		11,991	222
67,6	309465	77378		15,989	400
74,62	367390	57925		18,982	331
76,9	386674	19284		19,978	420
85,88	464077	77403		23,977	422
92,54	522158	58081		26,978	511; 333

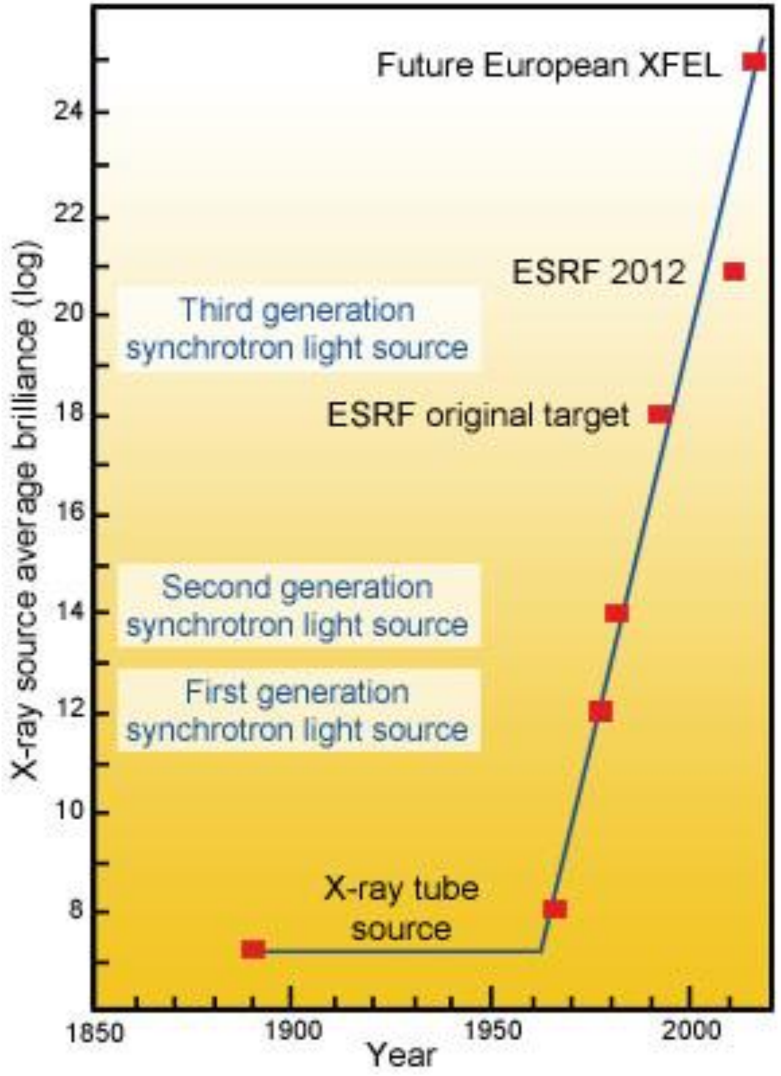
SYNCHROTRON RADIATION

- **Very bright/intense** x-ray radiation
- Used for x-ray diffraction in case of demanding samples (e.g. light elements)
- **Continuous spectrum**
  (c.f. the characteristic peaks from x-ray tube)
- We will discuss synchrotron radiation in detail in the context of EXAFS and XANES

$$\text{brilliance} = \frac{\text{photons}}{\text{second} \cdot \text{mrad}^2 \cdot \text{mm}^2 \cdot 0.1\%\ \text{BW}}$$

Divergence **Beam area**

Wavelength spread



NEUTRON AND ELECTRON DIFFRACTION

- **Particles have wave nature:**
  → Moving particles have wavelength

- Particles with proper mass/energy ratio can be utilized for diffraction
  → **neutron** diffraction and **electron** diffraction

EQUATIONS

UNIT CELL VOLUMES

- The equations for unit cell volume:

Cubic: $V = a^3$

Tetragonal: $V = a^2c$

Orthorhombic: $V = abc$

Hexagonal: $V = 0.866\ a^2c$

Rhombohedral: $V = a^3\sqrt{1 - 3cos^2\alpha + 2cos^3\alpha}$

Monoclinic: $V = abc\sin\beta$

Triclinic: $V = abc\left((1 - cos^2\alpha - cos^2\beta - cos^2\gamma) + \sqrt{\cos\alpha\ \cos\beta\ \cos\gamma}\right)$

LATTICE PLANE SPACING *d*

- For a given set of lattice plane Miller indices, the d-spacing can be calculated:

Cubic:

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

Tetragonal:

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

Orthorhombic:

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

Hexagonal:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Rhombohedral:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)sin^2\alpha + 2(hk + kl + hl)cos^2\alpha - cos\,\alpha}{a^2(1 - 3cos^2\alpha + 2cos^3\alpha)}$$

Monoclinic:

$$\frac{1}{d^2} = \frac{1}{sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2 sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\,cos\,\beta}{ac}\right)$$

Triclinic:

$$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

$$V = abc\left((1 - cos^2\alpha - cos^2\beta - cos^2\gamma) + \sqrt{\cos\alpha\ \cos\beta\ \cos\gamma}\right)$$

$$S_{11} = b^2c^2sin^2\alpha \qquad S_{12} = abc^2(\cos\alpha\ \cos\beta - \cos\gamma)$$

$$S_{22} = a^2c^2sin^2\beta \qquad S_{23} = a^2bc(\cos\beta\ \cos\gamma - \cos\alpha)$$

$$S_{33} = a^2b^2sin^2\gamma \qquad S_{13} = ab^2c(\cos\gamma\ \cos\alpha - \cos\beta)$$