MLL 100

Introduction to Materials Science and Engineering

Lecture-8 (January 19, 2022)

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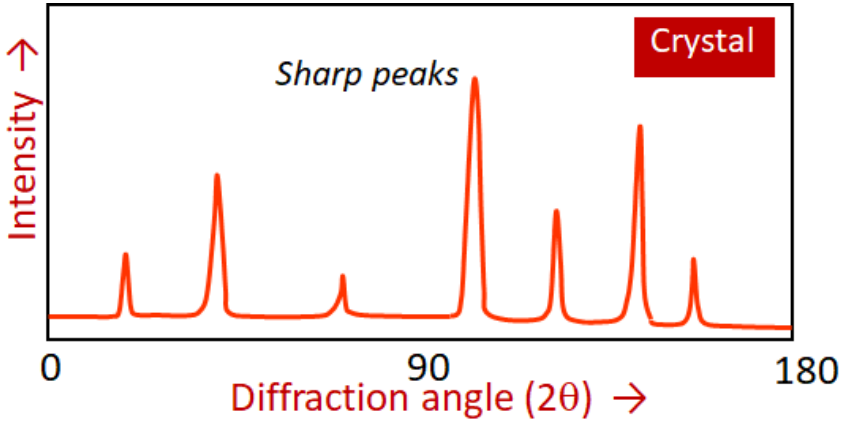
Topics covered

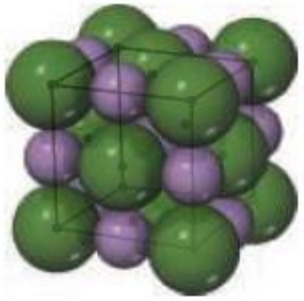
- X-ray diffraction

What is an XRD used for?

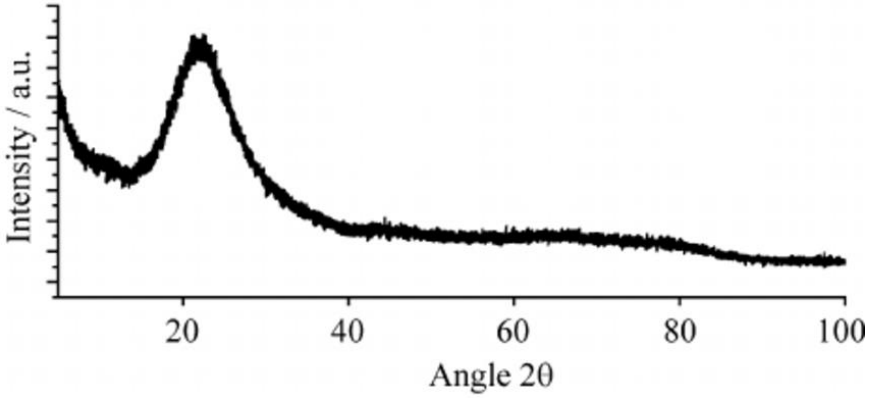
- Distinguishing between amorphous and crystalline solids

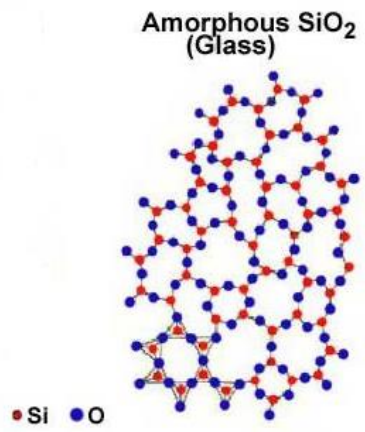
Crystalline



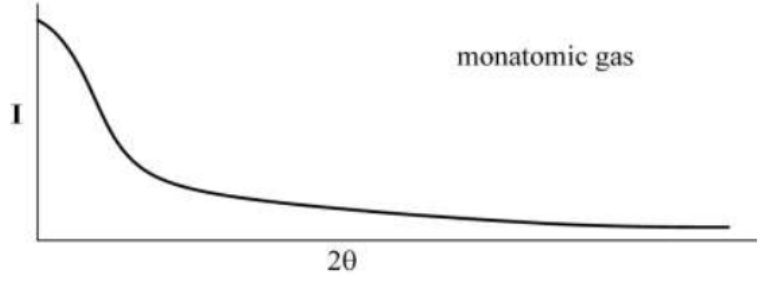


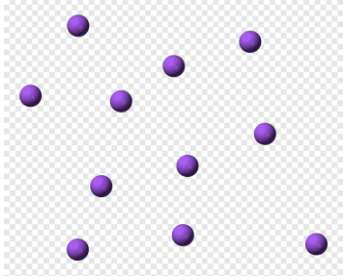
Amorphous





Monoatomic gas



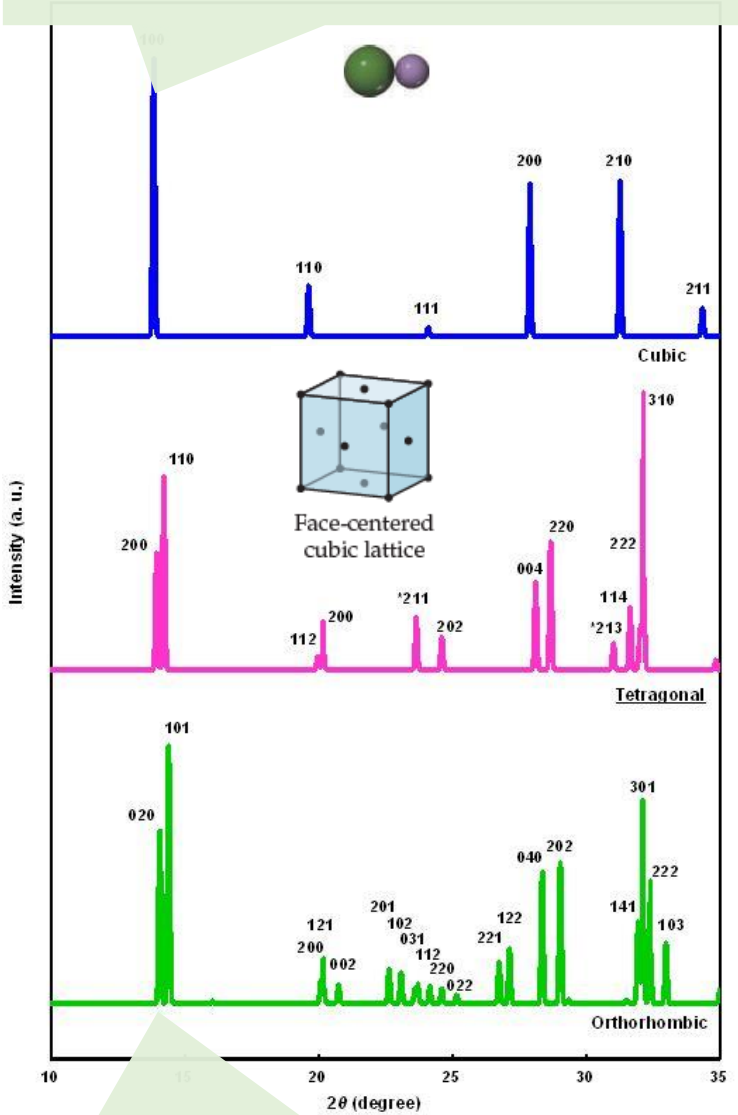


What is an XRD used for?

How does a crystal scatter these X-rays to give a diffraction pattern? → Bragg's equation

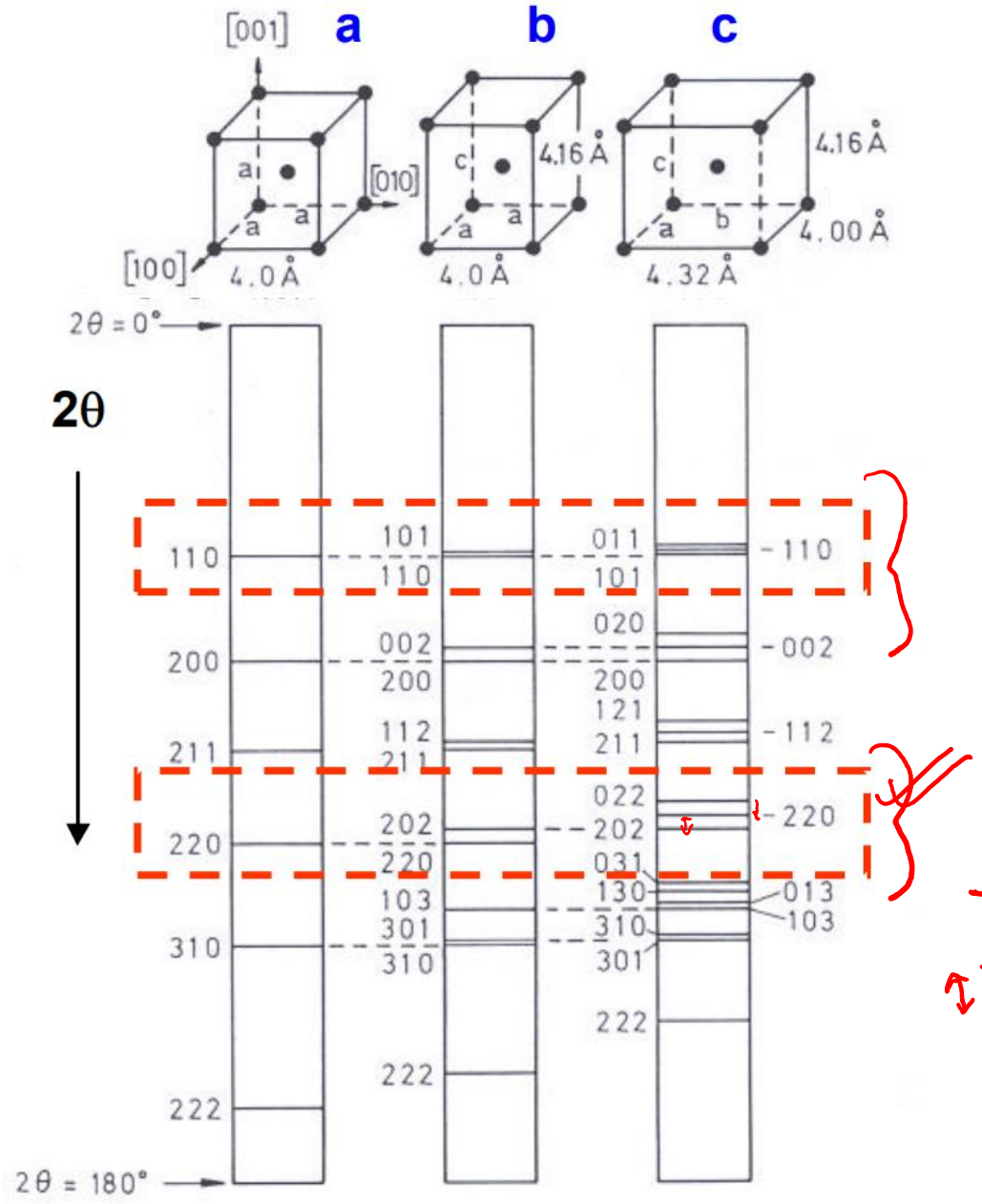
- ❑ Identification of crystalline materials
- ❑ Determination of the structure of crystalline solids
  - ▪ Determination of lattice parameter
  - ▪ Determination of Bravais lattice

What determines the intensity of the XRD peaks? → Motif (Many other factors also contribute to the intensity of a given peak)



What determines the position of the XRD peaks? → Characteristics of lattice.

Phase identification



What is the symmetry on XRD pattern?

- Cubic
  Lattice parameter = a (a = b = c)
- Tetragonal
  Lattice parameter: a and c (a = b ≠ c)
- Orthorhombic
  Lattice parameter: a, b, c (a ≠ b ≠ c)

- Number of peaks
- Peak position
- Peak splitting

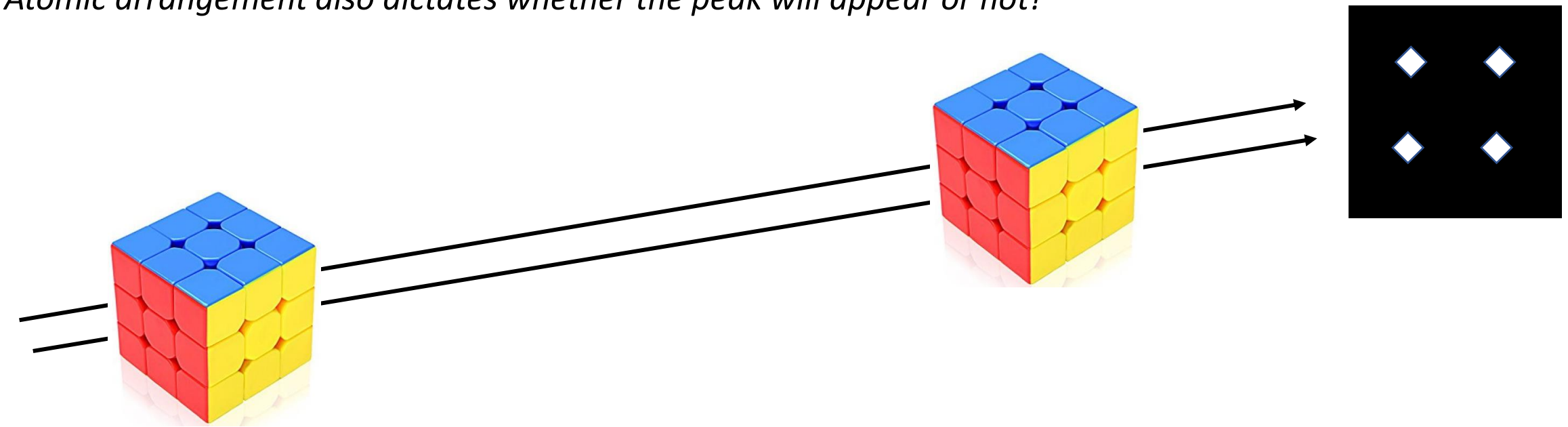
202
20$\bar{2}$

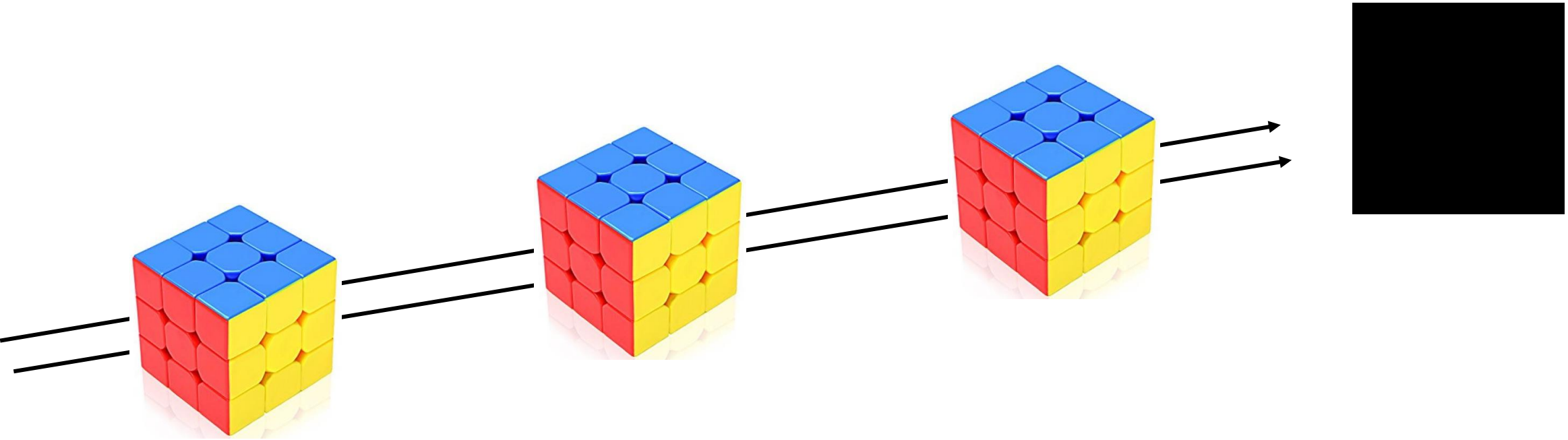
Triclinic
$\alpha \neq \beta \neq \gamma \neq 90$
$a \neq b \neq c$

{220} (202) (220) (02$\bar{2}$)

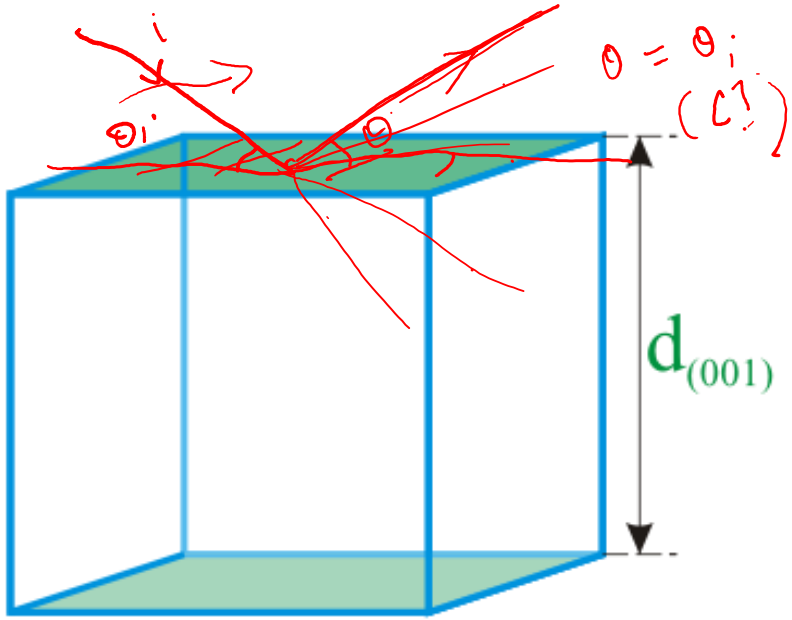
Which Bravais lattice may produce the first XRD peaks?

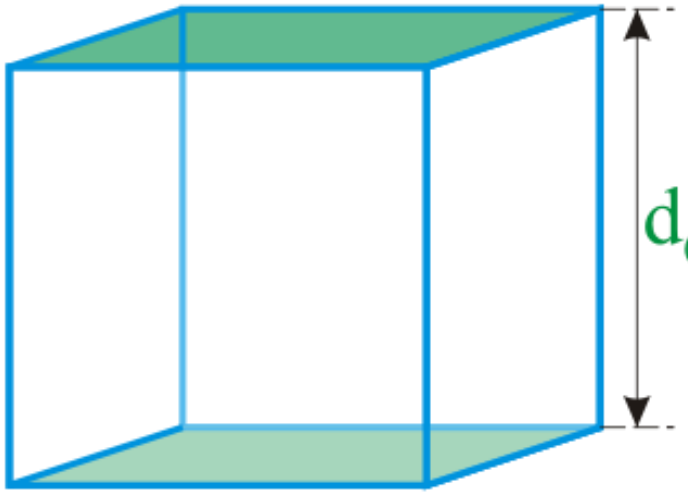
Atomic arrangement also dictates whether the peak will appear or not!

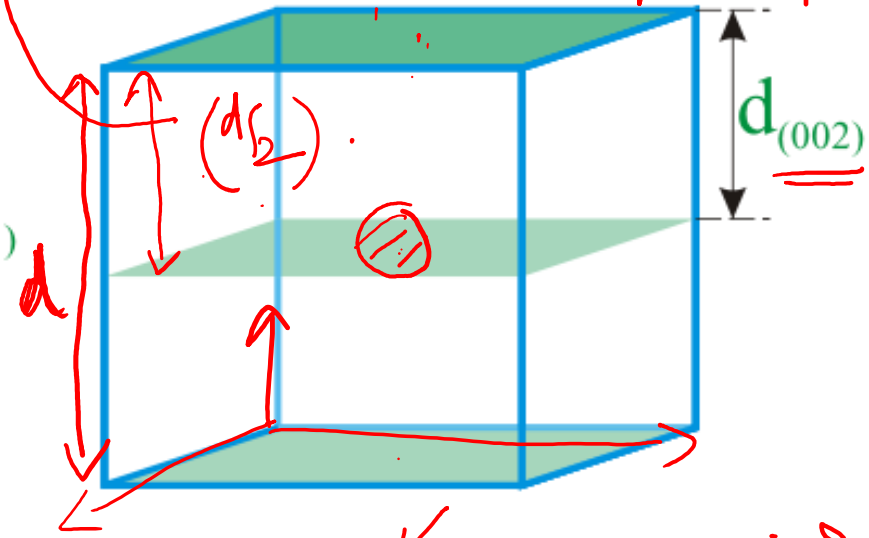


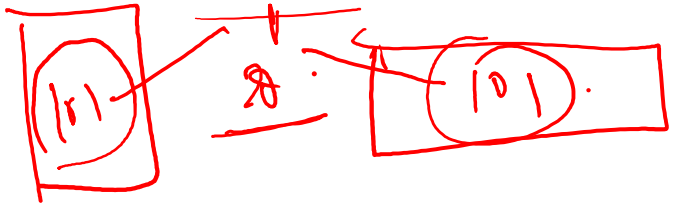


Systematic absence









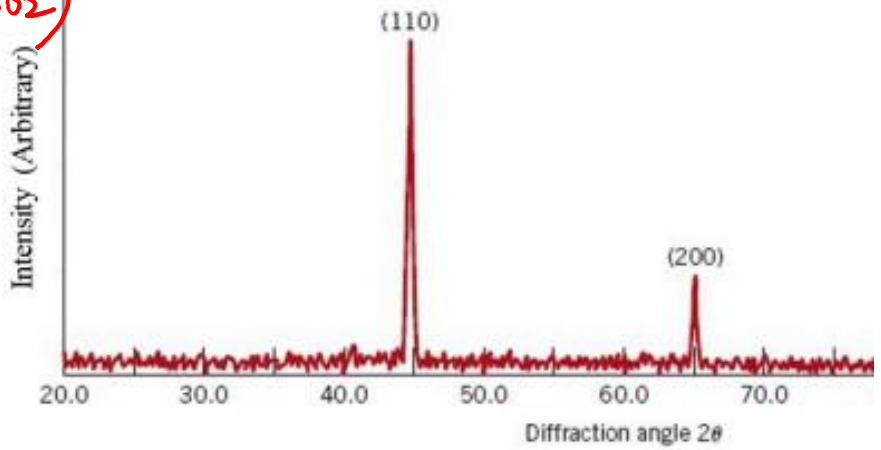
$$n\lambda = 2(d_{001})\sin\theta$$

$$n\lambda = 2(2 \cdot d_{002})\sin\theta$$

$$n\left(\frac{\lambda}{2}\right) = 2 \cdot d_{002}\sin\theta$$

- Simple cubic crystal, 100, 200, 300… are all allowed ‘reflections’ -----> no atoms in the planes lying *within* the unit cell.

- BCC: an atom is present also in the (0 0 2) plane.



Structure factor

$$F_{hkl} = \sum_{i=1}^{n} f^{i} . e^{2\pi i (hx_i + kx_i + lx_i)}$$

Electronic property of atom

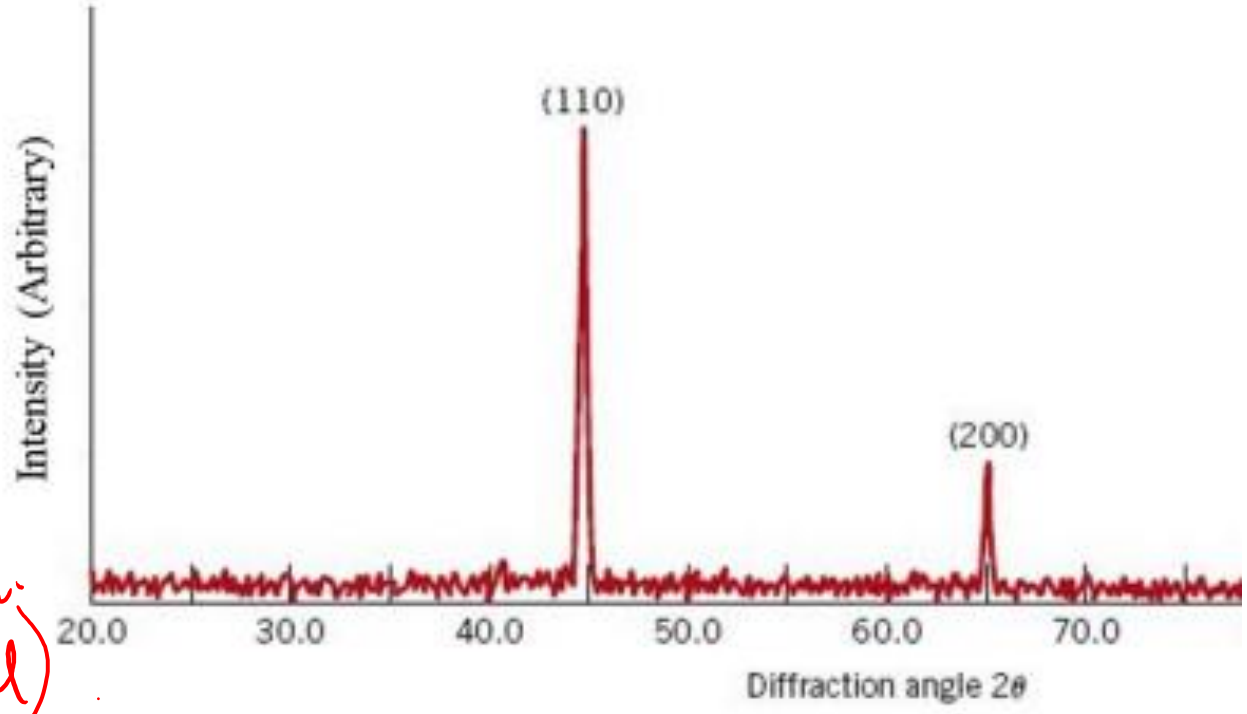
structural property of atom

BCC

M1

M2

d-spacing → e⁻ contribution (equipotential)



Systematic absences (Extinction rules)

- *Even if Bragg's equation is satisfied, 'reflections may go missing'*
  → this is due to the presence of additional atoms in the unit cell.

Bravais Lattice	Allowed reflections	Necessarily absent reflections
Simple	all	None
Body centred	(h + k + l) even	(h + k + l) odd
Face centred	h, k and l unmixed *(all even or all odd)*	h, k and l mixed
End centred (*C-centred*)	h and k unmixed	h and k mixed

Suppose an unknown sample is irradiated using the monochromatic X-ray produced from the Cu target ($\lambda_{Cu_{K_{\alpha_1}}}$ = 1.5418 Å)

- Determine the crystal structure.
- Determine the lattice parameter.

- Braggs equation: $\lambda = 2dSin\theta$

- Relation between interplanar distance and lattice parameter for a cubic crystal: $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

- Rearranging the terms: $\lambda^2 = \frac{4a^2 \sin^2 \theta}{h^2 + k^2 + l^2}$

- The LHS of the equation is a constant, and therefore, the RHS should also be a constant: $\frac{\lambda^2}{4a^2} = \frac{\sin^2 \theta}{h^2 + k^2 + l^2}$

You will get the 2θ values

Generate a set of $\sin^2\theta$ values

Normalize the $\sin^2\theta$ values by generating $\frac{sin^2\theta_2}{sin^2\theta_1}$

Clear fractions from normalized values

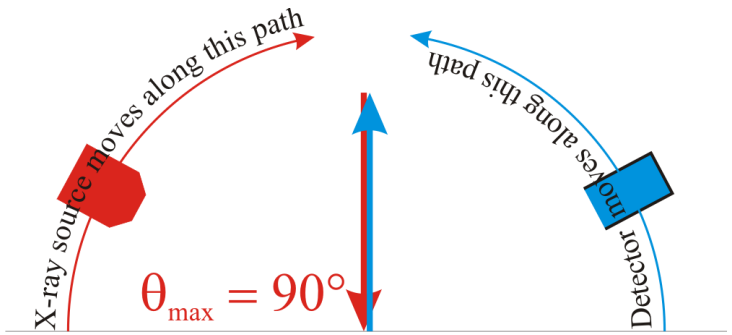
Speculate the h,k,l values such that $(h^2+k^2+l^2)$ = clear fraction column

2θ
44.48
51.83
76.35
92.9
98.4
121.87
144.54
155.51

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

$\lambda_{Cu_{K\alpha_1}}$ = 1.5418 Å

You will get the 2θ values	Generate a set of $\sin^2\theta$ values	Normalize the $\sin^2\theta$ values by generating $\frac{sin^2\theta_2}{sin^2\theta_1}$	Clear fractions from normalized values	Speculate the h,k,l values such that $(h^2+k^2+l^2)$ = clear fraction column	
2θ	**$\sin^2\theta$**	**$\frac{sin^2\theta_2}{sin^2\theta_1}$**	**$(h^2+k^2+l^2)$**	**(h k l)**	**$\frac{sin^2\theta}{(h^2+k^2+l^2)}$**
44.48	0.143	1	3	1 1 1	0.0477
51.83	0.191	1.34	4	2 0 0	0.0478
76.35	0.382	2.67	8	2 2 0	0.0477
92.9	0.525	3.67	11	3 1 1	0.0477
98.4	0.573	4.01	12	2 2 2	0.0477
121.87	0.764	5.34	16	4 0 0	0.0477
144.54	0.907	6.34	19	3 3 1	0.0477
155.51	0.955	6.68	20	4 2 0	0.0477



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

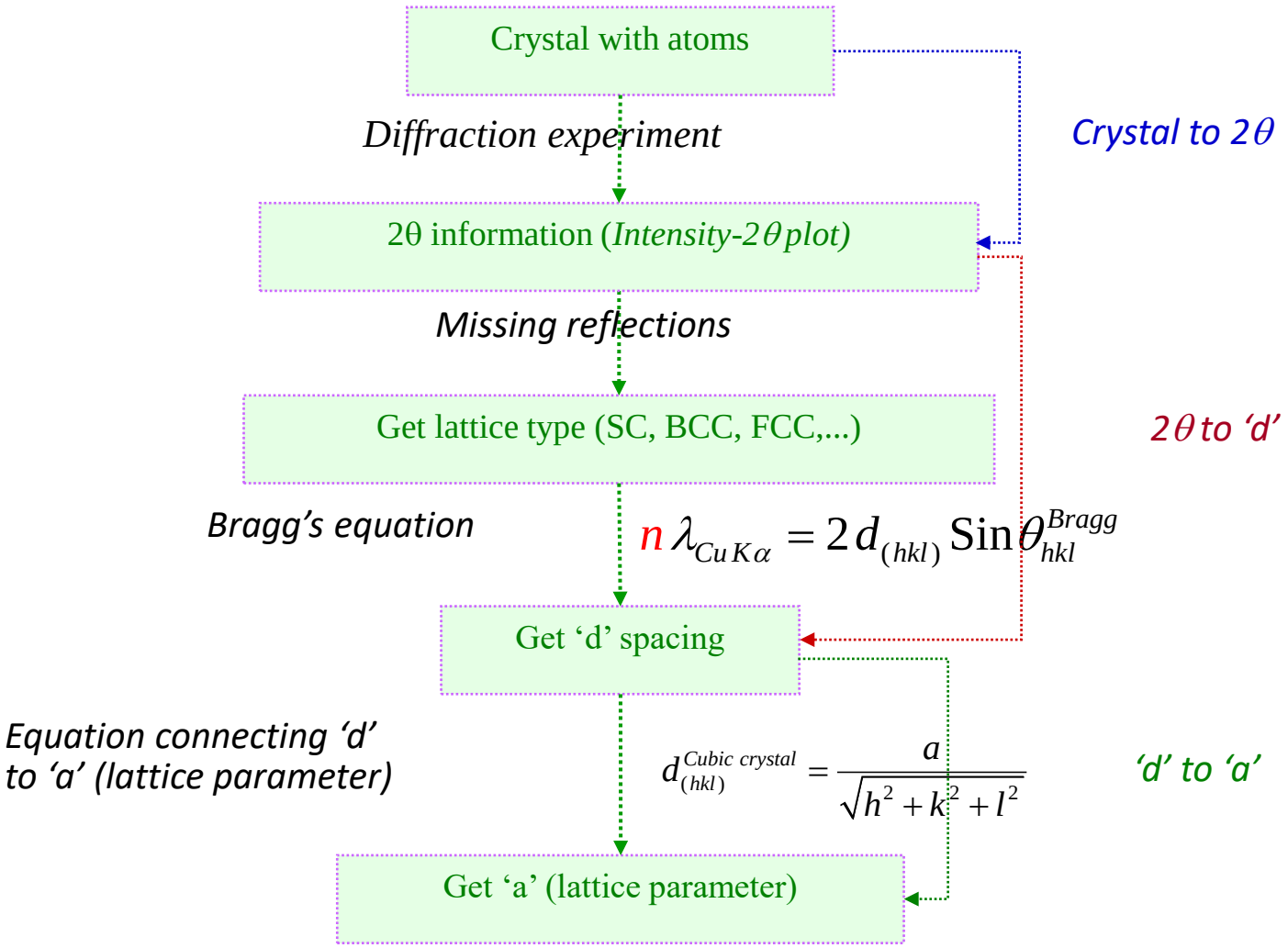
$\lambda_{Cu_{K\alpha_1}}$ = 1.5418 Å

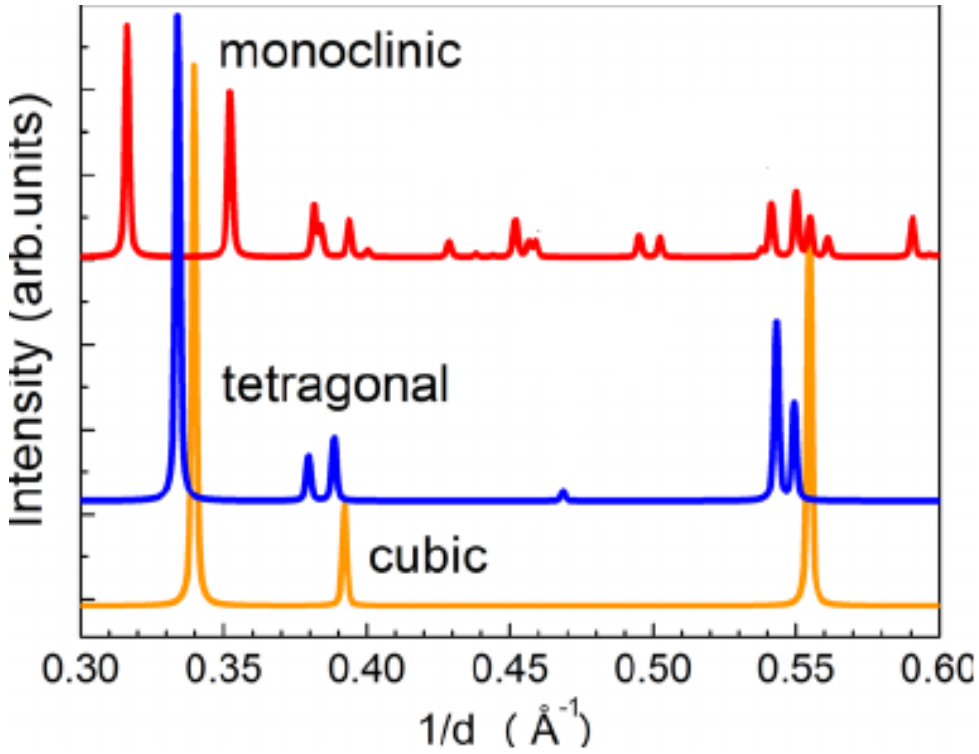
Allowed reflections in SC, BCC, FCC and DC crystals

Cannot be expressed as $(h^2+k^2+l^2)$

$h^2 + k^2 + l^2$	SC	FCC	BCC	DC
1	100			
2	110		110	
3	111	111		111
4	200	200	200	
5	210			
6	211		211	
7				
8	220	220	220	220
9	300, 221			
10	310		310	
11	311	311		311
12	222	222	222	
13	320			
14	321		321	
15				
16	400	400	400	400
17	410, 322			
18	411, 330		411, 330	
19	331	331		331

Determination of lattice parameter of a crystal





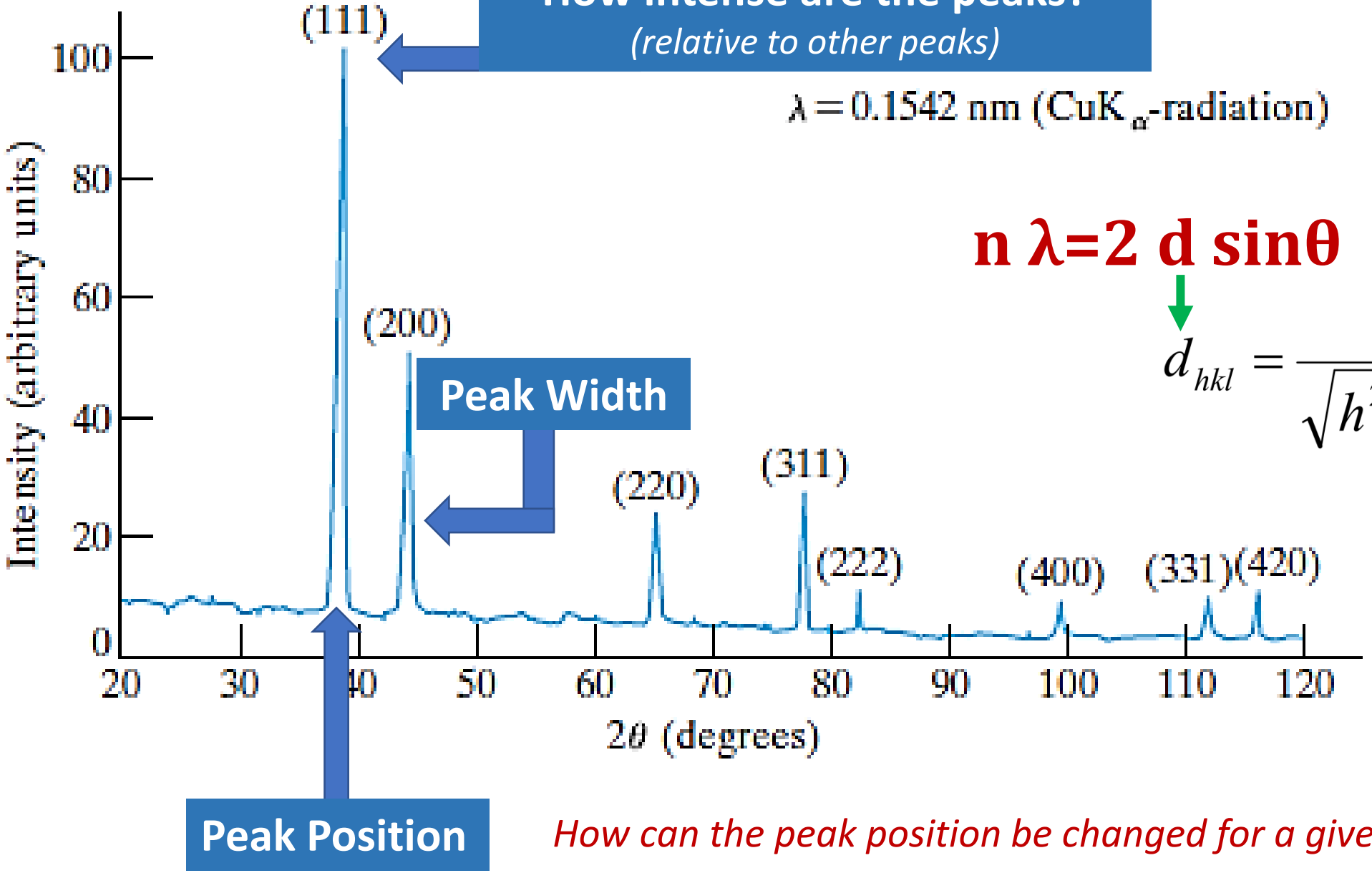
- Lower the symmetry of the crystal, more the number of peaks (e.g., in tetragonal crystal the 100 peak will lie at a different 2θ as compared to the 001 peak).

- Lattice type ➢ in SC we will get more peaks as compared to (say) FCC

- Smaller the wavelength of the X-rays, more will be the number of peaks possible.

Peak characteristics in XRD

How intense are the peaks?
(relative to other peaks)

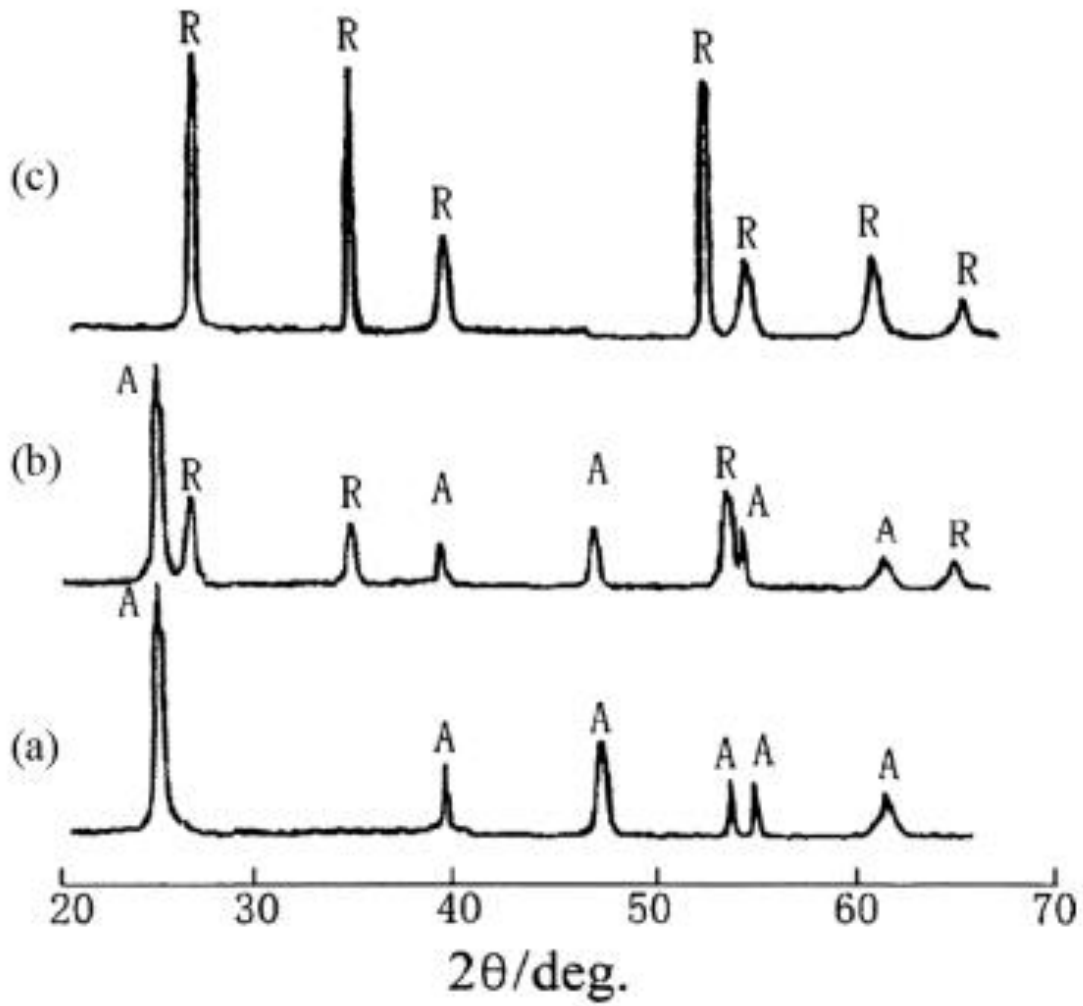


$$n\lambda = 2\,d\sin\theta$$

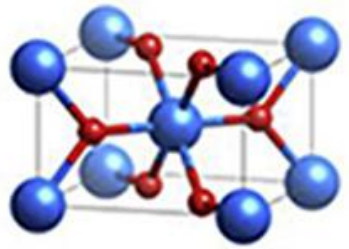
$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

How can the peak position be changed for a given material?

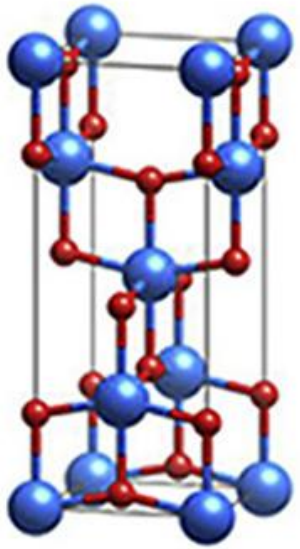
Polymorphism



rutile

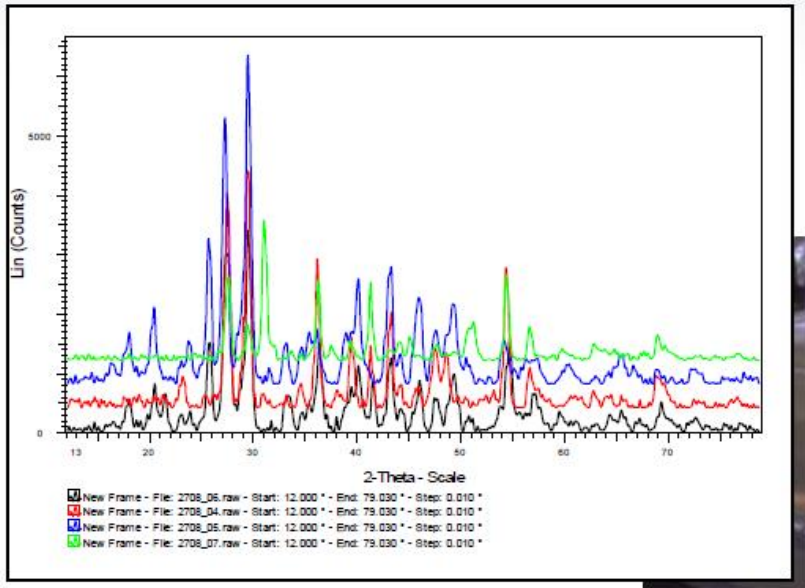


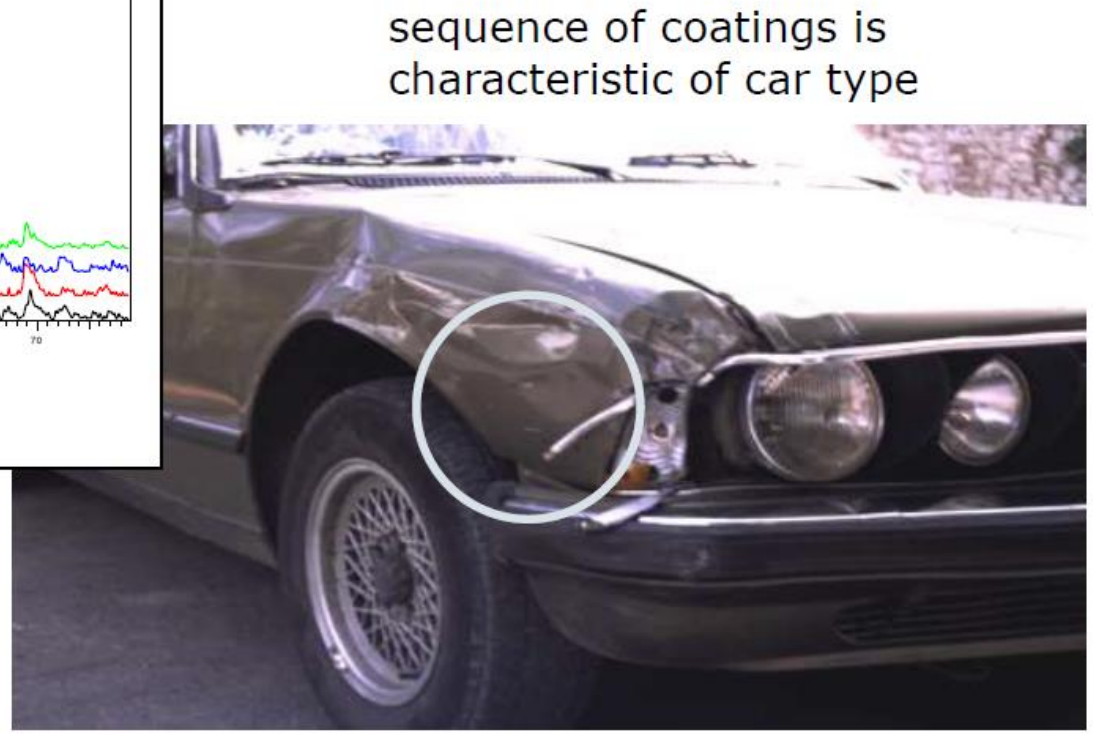
anatase



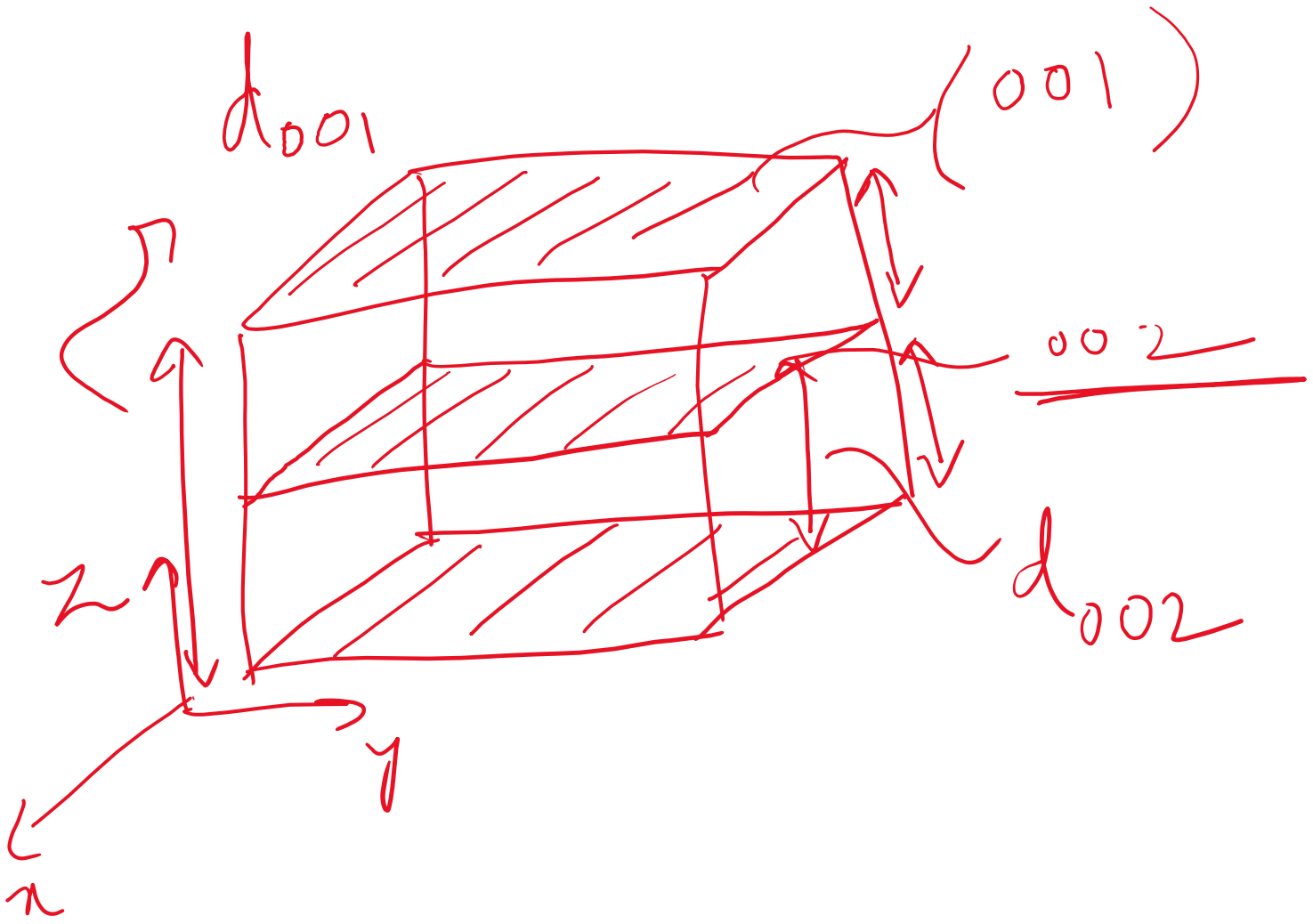
H. Ijadpanah-Saravy , M. Safari , A. Khodadadi-Darban & A. Rezaei (2014) Synthesis of Titanium Dioxide Nanoparticles for Photocatalytic Degradation of Cyanide in Wastewater, Analytical Letters, 47:10, 1772-1782

Forensic Sciences





- Paint chips are transferred in car accidents, either from one car to another or, in the case of a hit-and-run, from the car to the victim.
- Chemical identity of the various layers of the paints


d_{001}
(001)
002
d_{002}
z
y
x