X-ray diffraction (XRD)

- SELECTION RULES
- INTERPRETING XRD SPECTRA

Selection rules

rewritten in terms of K_{SC}

$$\mathbf{K}_{SC} = \sum n_i \mathbf{b}_{i_{SC}} = \frac{2\pi}{a}(n_1, n_2, n_3) = \frac{2\pi}{a}(h,k,l) \quad \Rightarrow \quad \text{any } h,k,l$$

rewritten in terms of K_{SC}

$$\mathbf{K}_{BCC} = \sum n_i \mathbf{b}_{i_{BCC}} = \frac{2\pi}{a}(n_1+n_2, n_1+n_3, n_2+n_3) = \frac{2\pi}{a}(h,k,l)$$

$$\Rightarrow \quad h+k+l = 2(n_1+n_2+n_3) \;\Rightarrow\; h+k+l = \text{even number}$$

rewritten in terms of K_{SC}

$$\mathbf{K}_{FCC} = \sum n_i \mathbf{b}_{i_{FCC}} = \frac{2\pi}{a}(n_1+n_2-n_3, n_1-n_2+n_3, -n_1+n_2+n_3) = \frac{2\pi}{a}(h,k,l)$$

$$\Rightarrow \; h-k = 2(n_2-n_3); \quad h-l = 2(n_1-n_3); \quad k-l = 2(n_1-n_2)$$

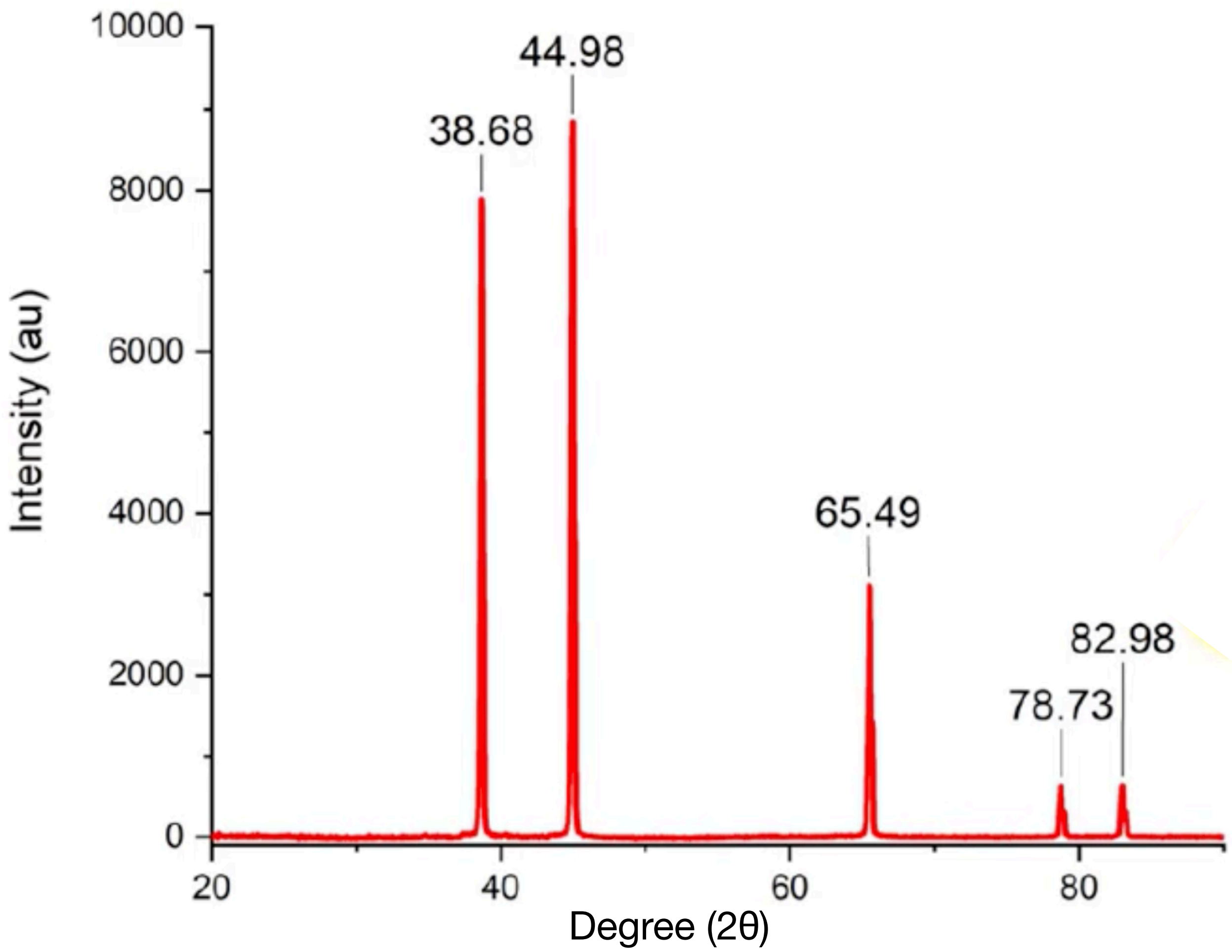
$\Rightarrow h,k,l$ differ one from each other by an even number
i.e. all even or all odd

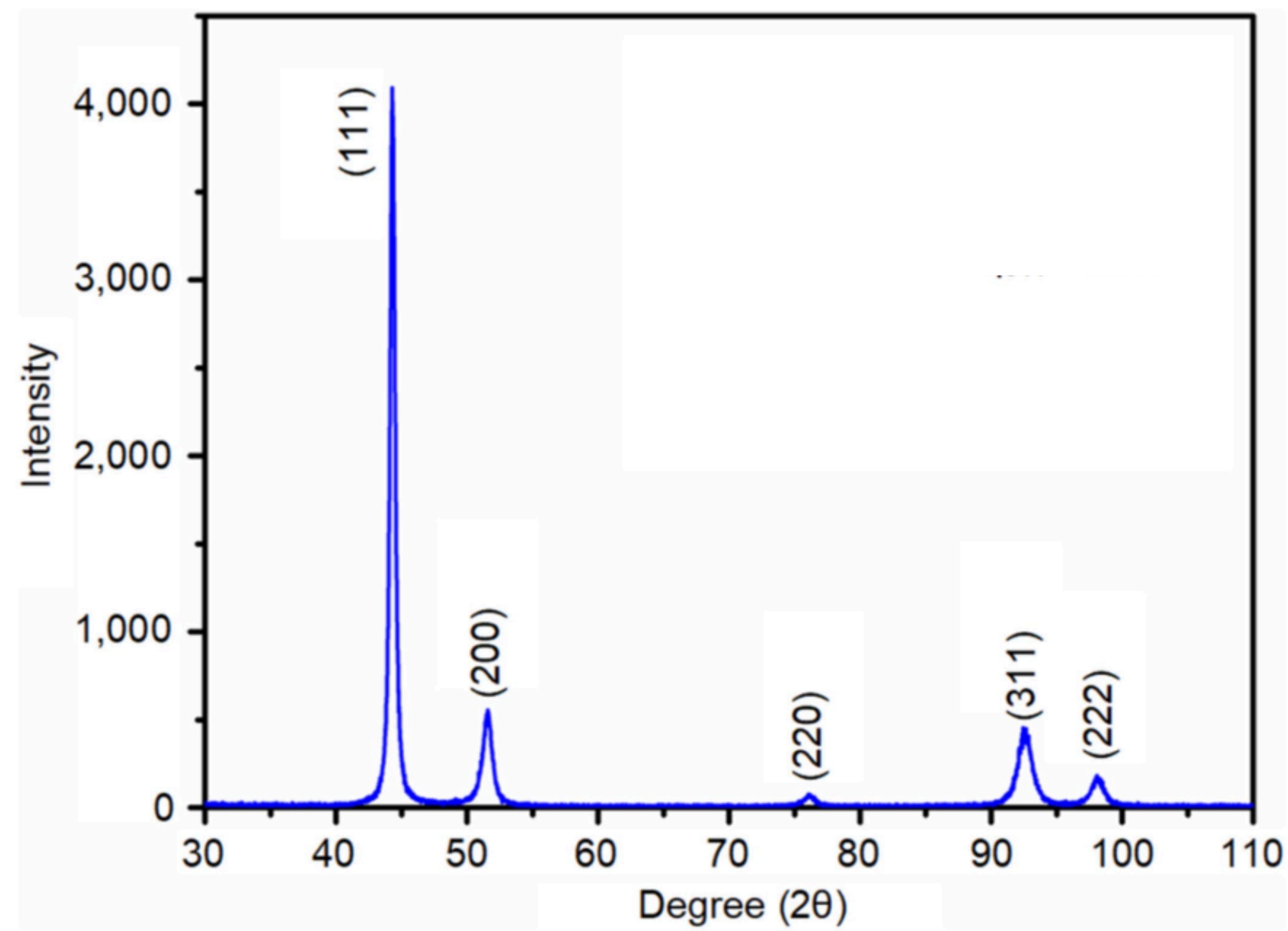
Cubic crystal	Allowed planes (hkl)	Forbidden planes(hkl)
SC	any h, k, l	none
BCC	h + k + l = even number	h + k + l = odd number
FCC	h, k, l all even h, k, l all odd	h, k, l mixed even and odd

X-Ray Diffraction

From XRD spectra to the crystalline (here: cubic only) structures

(i.e., from the angles to the Miller indices): how to?





Bragg law: $2d\sin\theta = m\lambda$

and: $d = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$

$\Big\}$ => $\boxed{\sin^2\theta = m^2(h^2+k^2+l^2)\dfrac{\lambda^2}{4a^2}}$

If there is one peak for *m*=1, all the others should be its multiple according to *m^2(h^2+k^2+l^2)*

X-Ray Diffraction

From XRD spectra to the crystalline (here: cubic only) structures

(i.e., from the angles to the Miller indices): how to?

Bragg law: $2d \sin\theta = m\lambda$

and: $d = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

$$\left.\begin{aligned} 2d \sin\theta &= m\lambda \\ d &= \frac{a}{\sqrt{h^2+k^2+l^2}} \end{aligned}\right\} \Rightarrow \boxed{\sin^2\theta = m^2(h^2 + k^2 + l^2)\frac{\lambda^2}{4a^2}}$$

If there is one peak for *m*=1, all the others should be its multiple according to *m^2(h^2+k^2+l^2)*

in other words:

$$\frac{\sin^2\theta}{m^2(h^2 + k^2 + l^2)} = \frac{\lambda^2}{4a^2} = constant\ for\ a\ given\ \lambda$$

therefore there must be a set of integers *(hkl)* for which

$$\frac{\sin^2\theta}{m^2(h^2 + k^2 + l^2)}$$

gives a constant quotient

1) from 2θ to sin^2(θ)

The smallest θ (smallest $sin^2\theta$) is the peak with the smallest $m^2(h^2+k^2+l^2)$

we fix it as our reference, since the others $sin^2\theta$ should be its multiple by $m^2(h^2+k^2+l^2)$

(here other data, not those from previous slides)

A	B	C	D	E	F
	2θ (degrees)	θ (radians)	sin θ	sin^2(θ)	sin^2(θ) /peak 1
1	38,46	0,335627	0,3294	0,1085	1
2	55,54				
3	69,58				
4	82,46				
5	94,94				
6	107,64				
7	121,36				

2) calculate the ratios of the others sin^2(θ) w.r.t. the first peak

Do the numbers (~integers!) obtained correspond to $m^2(h^2 + k^2 + l^2)$?

(with proper choice of the indices, but ALL must be obtained in that way)

A	B	C	D	E	F
	2θ (degrees)	θ (radians)	sin θ	sin^2(θ)	sin^2(θ) /peak 1
1	38,46	0,335627	0,3294	0,1085	1,00
2	55,54	0,484678	0,4659	0,2171	2,00
3	69,58	0,6072	0,5706	0,3256	3,00
4	82,46	0,719599	0,6591	0,4344	4,00
5	94,94	0,828508	0,7369	0,5431	5,01
6	107,64	0,939336	0,8072	0,6515	6,01
7	121,36	1,059066	0,8719	0,7602	7,01

3) We make the hypothesis that the first peak (m=1) corresponds to the shortest $\mathbf{K}_{SC}$, i.e. $\mathbf{K}=2\pi/a(100)$, i.e. h^2+k^2+l^2=1.

Can we find in the XRD spectrum ALL the other peaks? i.e., can we obtain ALL the numbers 2, 3,…7, 8, 9… from m^2(h^2+k^2+l^2) ?

We can try with the smaller Miller indices (permutations do not matter) and starting with m=1

A	B	C	D
h	k	l	h^2+k^2+l^2
1	0	0	1
1	1	0	2
1	1	1	3
2	0	0	4
2	1	0	5
2	1	1	6
2	2	0	8

=> 7 CANNOT be obtained

4) may be the peak 1 does not correspond to (hkl)=(100); could be (110)?

i.e., h^2+k^2+l^2=2, and hence multiply everything by 2

A	B	C	D	E	F	G
	2θ (degrees)	θ (radians)	sin θ	sin^2(θ)	sin^2(θ) /peak 1	x 2
1	38,46	0,335627	0,3294	0,1085	1,00	2
2	55,54	0,484678	0,4659	0,2171	2,00	4
3	69,58	0,6072	0,5706	0,3256	3,00	6
4	82,46	0,719599	0,6591	0,4344	4,00	8
5	94,94	0,828508	0,7369	0,5431	5,01	10
6	107,64	0,939336	0,8072	0,6515	6,01	12
7	121,36	1,059066	0,8719	0,7602	7,01	14

5) can we obtain ALL the even numbers 2, 4,…14 from $m^2(h^2+k^2+l^2)$? (with m=1)

Let's continue filling our table…

h	k	l	h^2+k^2+l^2
1	0	0	1
1	1	0	2
1	1	1	3
2	0	0	4
2	1	0	5
2	1	1	6
2	2	0	8
2	2	1	9
3	0	0	9
3	1	0	10
3	1	1	11
2	2	2	12
3	2	0	13
3	2	1	14

OK!!!!   But which lattice does correspond to that list of Miller indices?

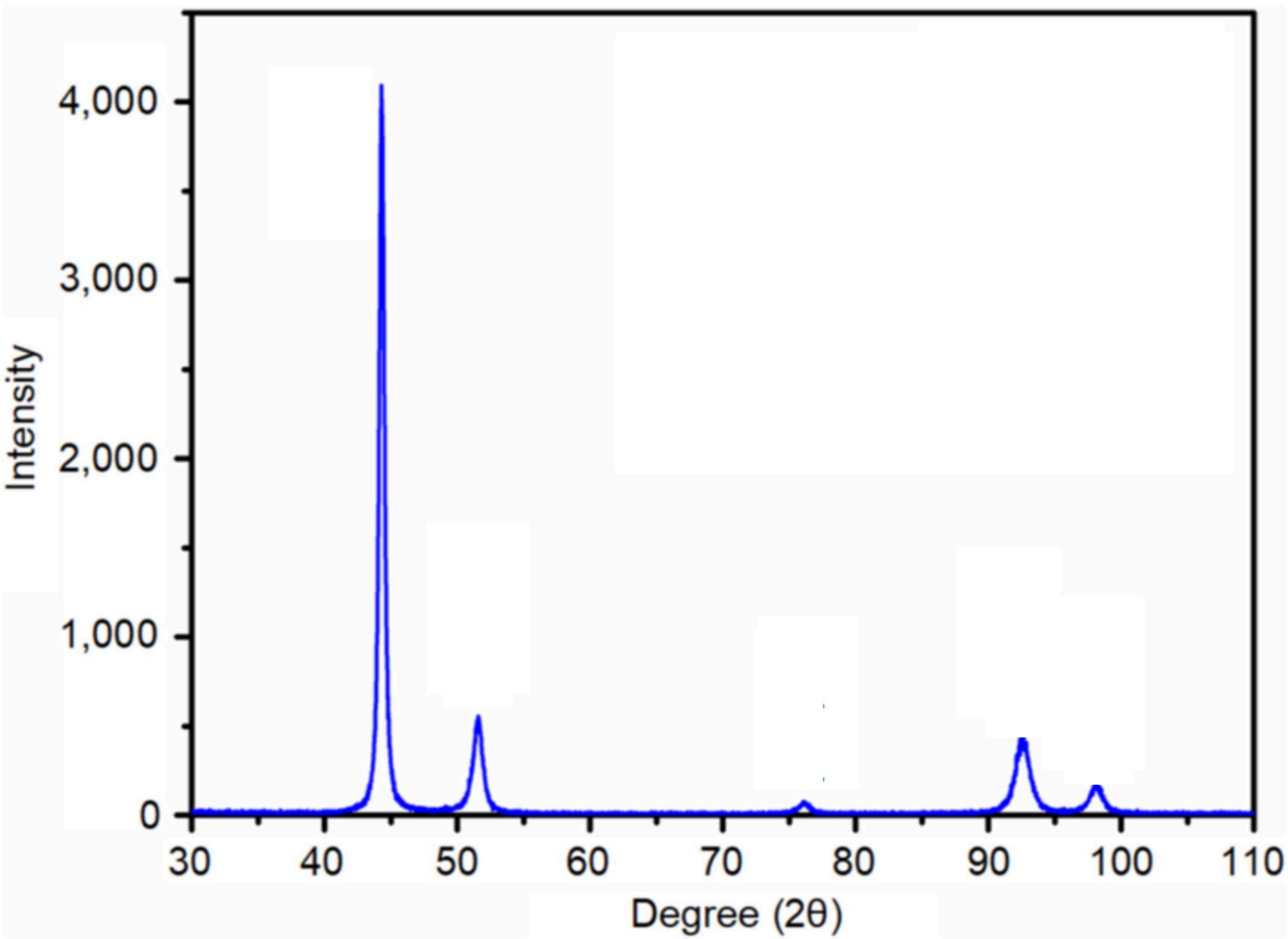
6) check…

A	B	C	D	E
h	k	l	h^2+k^2+l^2	h+k+l
1	0	0	1	1
1	1	0	2	2
1	1	1	3	3
2	0	0	4	2
2	1	0	5	3
2	1	1	6	4
2	2	0	8	4
2	2	1	9	5
3	0	0	9	3
3	1	0	10	4
3	1	1	11	5
2	2	2	12	6
3	2	0	13	5
3	2	1	14	6

SC: no, since some combinations of Miller indices do not appear
BCC: could be! h+k+l are all even
FCC: no, since for instance in (211), h and k do not differ by an even number

=> BCC!!!

and this?



4,000
3,000
2,000
1,000
0
Intensity
30
40
50
60
70
80
90
100
110
Degree (2θ)

https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Introduction_to_Solid_State_Chemistry/06%3A_Recitations/6.16%3A_X-ray_Diffraction_and_Selection_Rules