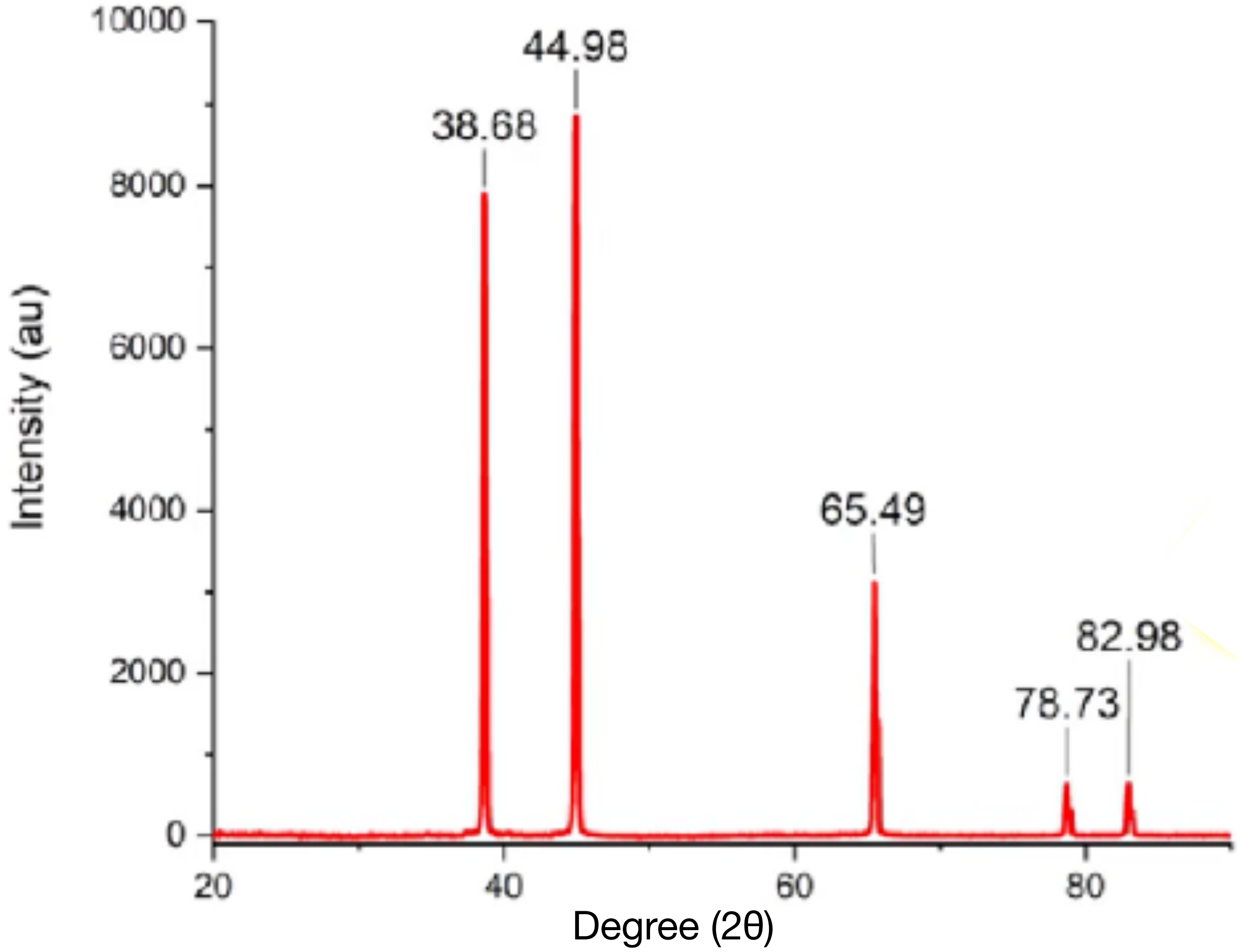
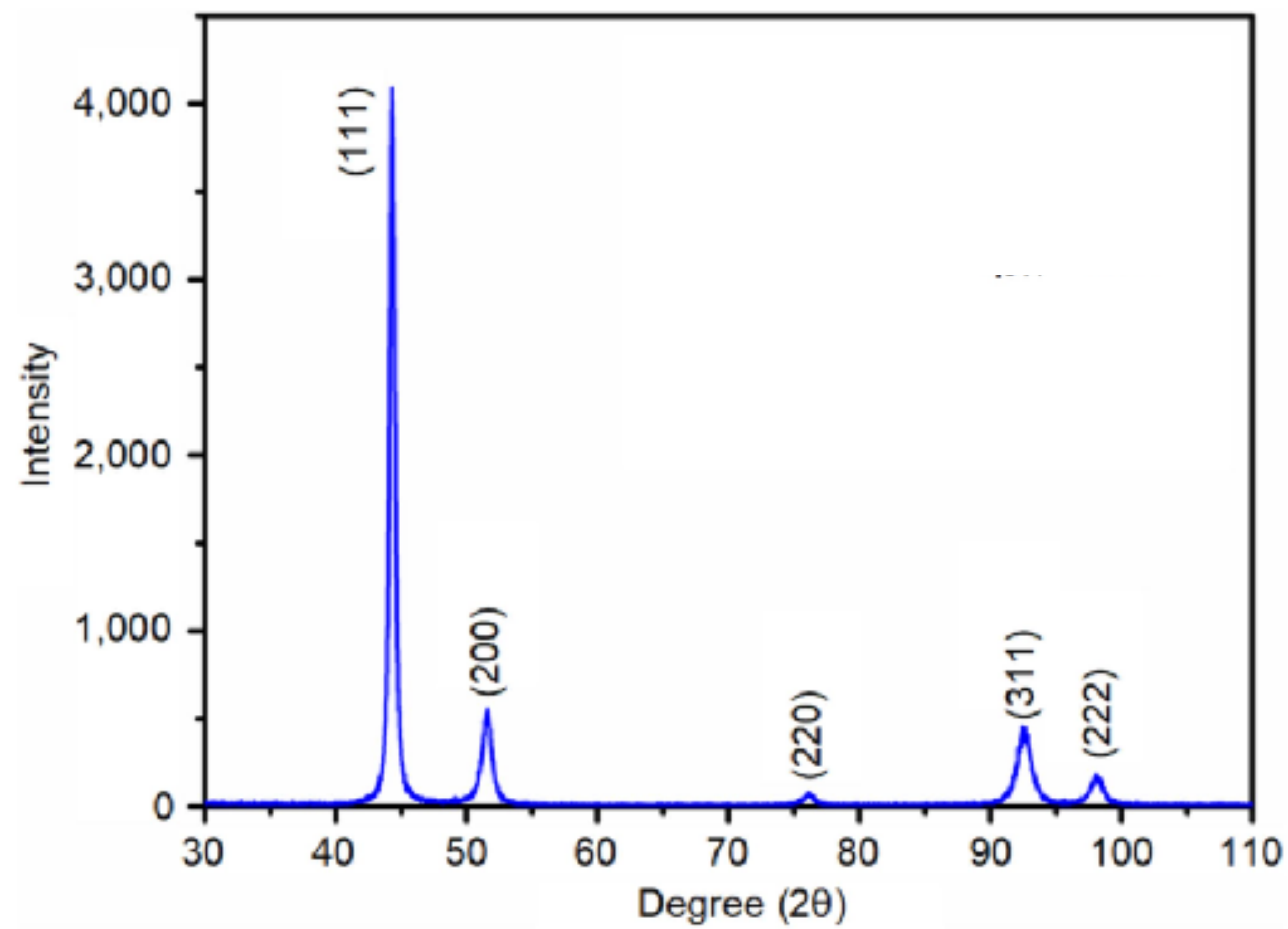
$$m^2(h^2+k^2+l^2)$$

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

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

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)*

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 $m^2(h^2+k^2+l^2)$

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) can we obtain ALL the numbers 1, 2, 3,…7 from m^2(h^2+k^2+l^2) ?

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

=> NO!!! 7 CANNOT be obtained

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

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

consider its value as 2, and hence mutiply 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 $m^2(h^2+k^2+l^2)$?

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?

Selection rules

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

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

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

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

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

$$\Rightarrow h, k, l \text{ differ one from each other by an even number}$$

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

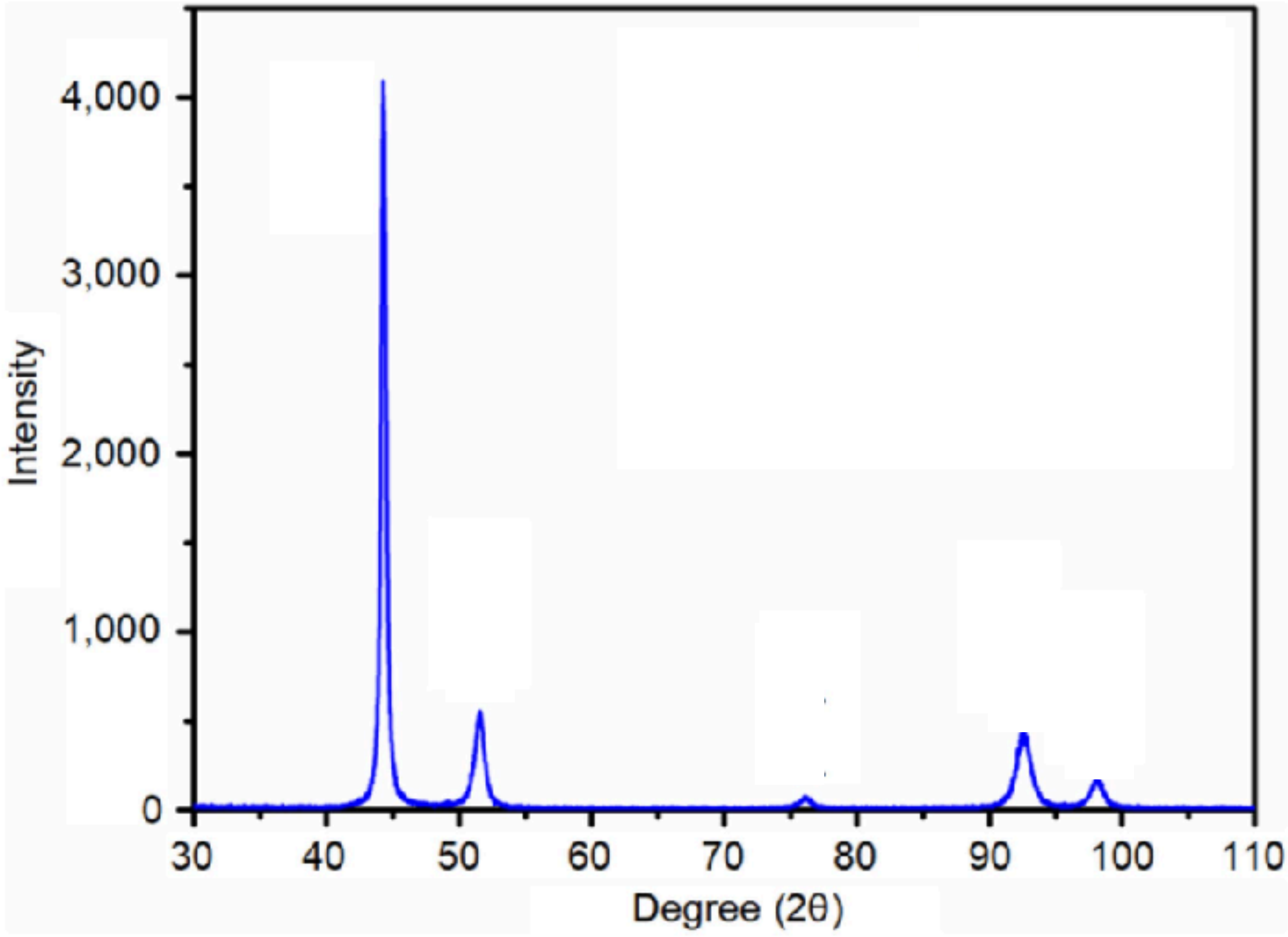
6) check…

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

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
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

Comparing eq. 2 and 3

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

1. As s must be an integer and $\frac{\lambda^2}{4a^2}$ is constant for a given pattern
2. There is a set of integers for which $\frac{\sin^2\theta}{s}$ yields a constant quotient
3. Fixed number of possible reflections for each crystal structure

Each crystal structure has a fixed
number of possible reflections

Based on the atomic scattering factors (f) and structure factors (F), the sets of integers for s (allowed reflections), corresponding to different crystal lattice types are as follows;

1. **Simple cubic:** Any h, k, l
   1, 2, 3, 4, 5, 6, 7, 8, 9, 10, ...
2. **Body-centered cubic:** h+k+l even
   2, 4, 6, 8, 10, 12, 14, ...
3. **Face-centered cubic:** h+k+l all odd or all even
   3, 4, 8, 11, 12, 16, ...
4. **Diamond cubic:** As FCC, if all even, then h+k+l=4n
   3, 8, 11, 16, ...

h+k+l is a multiple of 4. That is,