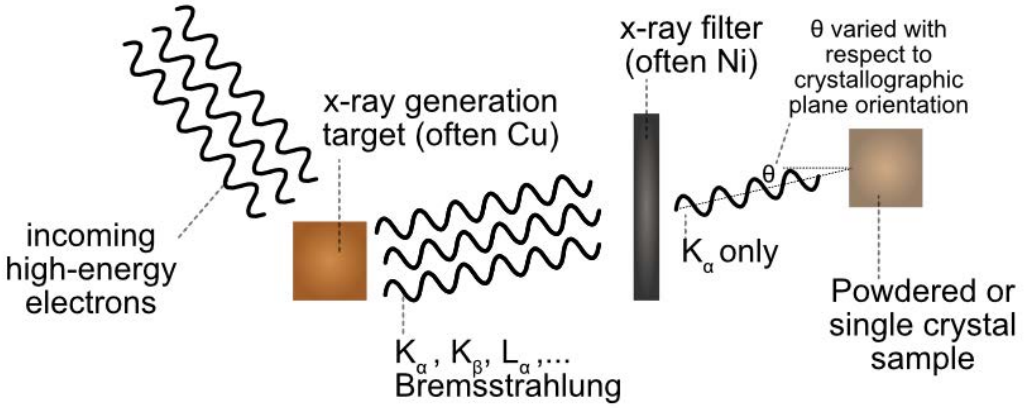
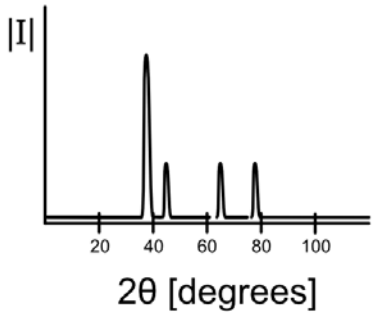
1 X-ray diffraction

Last time we discussed how to generate x-rays; now, let's talk about one application that plays a big role in materials characterization. X-ray diffraction is a tool that allows us to probe the crystal structure of a sample. Let's walk through the process:



First, we need to generate x-rays: this process is shown on the left. As we discussed, by shooting high energy electrons at a target made of heavy atoms (copper is a common choice), both characteristic x-rays and Bremsstrahlung are generated. Then, by bombarding an unknown sample with the x-rays, and measuring the scattered light as a function of incident angle, we can probe the interplanar spacing that exists within the crystal. However, recall that the Bragg condition is wavelength-dependent: to really do this effectively, we only want to keep a narrow band of wavelengths. This is accomplished by employing a filter, removing everything except the K_α x-rays, for example.

After all that, what is really measured in an XRD experiment is the intensity of scattered x-rays as a function of incident angle. A typical XRD spectrum looks something like this:



Plotted here is intensity/counts of x-rays on a detector as a function of 2θ, or twice the incident angle. It is helpful to utilize the following table to translate an XRD plot to a crystal structure/element:

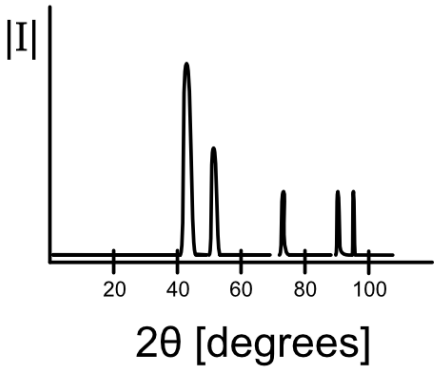
Peak #	2θ	θ	$sin^2\theta$	normalized	integer	plane
	from graph	$\leftarrow \times \frac{1}{2}$	calculator	divide all $\leftarrow$ by smallest of $\leftarrow$	multiply $\leftarrow$ by an integer (often 2 or 3)	$h^2 + k^2 + l^2 = \leftarrow$

2 Selection rules

As we discussed in lecture, we can apply selection rules to determine what kind of crystal structure a sample has. For each of the Bravais lattices, selection rules tell us which planes have coherent scattering and which do not:

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

Example: Use the following XRD spectrum to determine the element that was investigated. It is either BCC or FCC. Copper K_α radiation was used, which has a wavelength of 1.54 Angstroms.



Peak #	2θ
1	44.51
2	51.90
3	76.45
4	93.02
5	98.50

We are given a plot and the values of 2θ, so next let's construct the chart as described above. The first two columns are given, and we can quickly calculate the next two:

Peak #	2θ	θ	$sin^2\theta$	normalized	integer	plane
1	44.51	22.25	0.1434			
2	51.90	25.95	0.1915			
3	76.45	38.23	0.3829			
4	93.02	46.51	0.5263			
5	98.50	49.25	0.5739			

For the next column, normalized values, we simply divide all of the values in the $\sin^2\theta$ column by the *smallest* value in the $\sin^2\theta$ column, 0.1434.

Peak #	2θ	θ	$sin^2\theta$	normalized	integer	plane
1	44.51	22.25	0.1434	1		
2	51.90	25.95	0.1915	1.33		
3	76.45	38.23	0.3829	2.66		
4	93.02	46.51	0.5263	3.65		
5	98.50	49.25	0.5739	4		

Looking at the values in the normalized column, they seem to be approximately factors of $\frac{1}{3}$. To create integers, let's try multiplying each by 3.

Peak #	2θ	θ	$sin^2\theta$	normalized	integer	plane
1	44.51	22.25	0.1434	1	3	
2	51.90	25.95	0.1915	1.33	4	
3	76.45	38.23	0.3829	2.66	8	
4	93.02	46.51	0.5263	3.65	11	
5	98.50	49.25	0.5739	4	12	

Great, this created integers! The integers in this column should be the sum of h^2, k^2, and l^2 that form a particular plane. Let's try to match some planes:

Peak #	2θ	θ	$sin^2\theta$	normalized	integer	plane
1	44.51	22.25	0.1434	1	3	(111)
2	51.90	25.95	0.1915	1.33	4	(200)
3	76.45	38.23	0.3829	2.66	8	(220)
4	93.02	46.51	0.5263	3.65	11	(311)
5	98.50	49.25	0.5739	4	12	(222)

It takes a bit of time to develop intuition as to how to combine the squares of three numbers to form integers, but it comes with practice. For now, you can double check that these (hkl) planes really do generate the integers in the neighboring column. Also note that any member of a planar family could generate the integer in question: it's ok to choose any plane within that family! For example, the (200), (020), and (002) planes all satisfy $h^2 + k^2 + l^2 = 4$, so any would work there.

Next, we should check the selection rules. We see that for each of the planes, the values of h, k, and l are either all odd or all even. Further the (111) plane is forbidden for BCC crystals, since $1 + 1 + 1 = 3$, which is odd. We can conclude that this must be an FCC structure!

Finally, we need to figure out which FCC element it is. We can combine some old principles to figure this out. We know the Bragg condition is

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

where θ corresponds to one of the peaks above, which signify constructive interference. Recall also that the interplanar spacing is given by

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

By plugging in one of the entries from the table above, we can figure out what the lattice constant is. Let's use $\theta = 25.95$ degrees and the (200) plane:

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

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

$$a = \frac{1.54\mathring{A}}{2 * sin(25.95^o)}\sqrt{2^2 + 0^2 + 0^2} = 3.52\mathring{A}$$

Looking at the periodic table, an FCC element with lattice parameter around 3.52 $\mathring{A}$ is nickel!

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