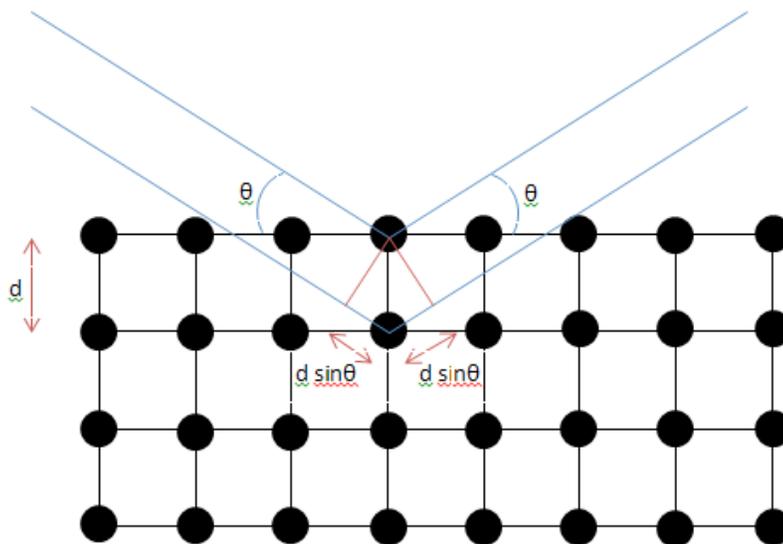


## Powder X-Ray Diffraction (Powder XRD) [6.3.2]

### *Introduction to Powder XRD*

- Powder X-Ray Diffraction was developed as a technique that could be applied where traditional single-crystal diffraction cannot be performed. This includes cases where the sample cannot be prepared as a single crystal of sufficient size and quality. Powder samples are easier to prepare, and is especially useful for pharmaceuticals research.
- Diffraction occurs when a wave meets a set of regularly spaced scattering objects, and its wavelength of the distance between the scattering objects is of the same order of magnitude. This makes X-rays suitable for crystallography, as its wavelength and crystal lattice parameters are both in the dimension of angstroms.
- Crystal diffraction can be described by the Bragg diffraction equation:
- $\lambda = 2d \sin \theta$
- Where  $\lambda$  is the wavelength of the incident monochromatic X-ray,  $d$  is the distance between parallel crystal planes, and  $\theta$  the angle between the beam and the plane.
- For constructive interference to occur between two waves, the path length difference between the waves must be an integral multiple of their wavelength. This path length difference is represented by  $2d \sin \theta$ .
- Because  $\sin \theta$  cannot be greater than 1, the wavelength of the X-ray limits the number of diffraction peaks that can appear.



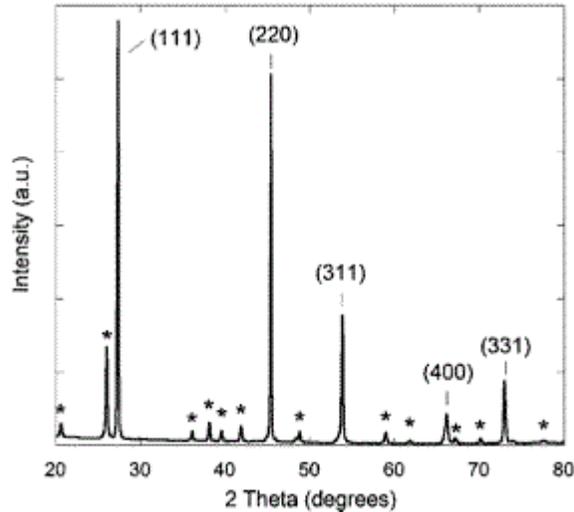
• **Figure 6.xx:** Bragg diffraction.

## ***Production and detection of X-rays***

- Most diffractometers use copper as an X-ray source, and specifically the  $K\alpha$  radiation of 1.54 Å. A stream of electrons is accelerated towards the metal target anode from a tungsten cathode, with a potential difference of about 30-50 kV. As this generates a lot of heat, the target anode must be cooled to prevent melting.
- Detection of the diffracted beam can be done in many ways, and one common system is the Gas Proportional Counter (GPC). The detector is filled with an inert gas such as argon, and electron-ion pairs are created when X-rays pass through it. An applied potential difference separates the pairs and generates secondary ionizations through an avalanche effect. The amplification of the signal is necessary as the intensity of the diffracted beam is very low compared to the incident beam. The current detected is then proportional to the intensity of the diffracted beam.
- A GPC has a very low noise background, which makes it widely used in labs.

## ***Performing diffraction***

- The particle size distribution should be even to ensure that the diffraction pattern is not dominated by a few large particles near the surface. This can be done by grinding the sample to reduce the average particle size to  $<10\mu\text{m}$ . However, if particle sizes are too small, this can lead to broadening of peaks. This is due to both lattice damage and the reduction of planes that cause destructive interference.
- The diffraction pattern is actually made up of angles that did not suffer from destructive interference due to their special relationship described by the Bragg Law. If destructive interference is reduced close to these special angles, the peak is broadened and becomes less distinct.
- Some crystals such as gypsum and calcite have preferred orientations and will change their orientation when pressure is applied. This leads to differences in the diffraction pattern of 'loose' and pressed samples. Thus, it is important to avoid even touching 'loose' powders to prevent errors when collecting data.
- The sample powder is loaded onto a sample dish for mounting in the diffractometer, where rotating arms containing the X-ray source and detector scan the sample at different incident angles. The sample dish is rotated horizontally during scanning to ensure that the powder is exposed evenly to the X-rays.
- A sample X-ray diffraction spectrum of germanium is shown below, with peaks identified by the planes that caused that diffraction. Germanium has a diamond cubic crystal lattice, named after the crystal structure of Diamond. The crystal structure determines what crystal planes cause diffraction and the angles at which they occur. The angles are shown in  $2\theta$  as that is the angle measured between the two arms of the diffractometer.



**Figure 6.xx:** Powder XRD spectra of Germanium, adapted from Phase Changes in Ge Nanoparticles by Hsiang Wei Chiu, Christopher N. Chervin, and Susan M. Kauzlarich.

### ***Determining crystal structure for cubic lattices***

- There are three basic cubic crystal lattices, and they are the Simple Cubic (SC), Body-Centered Cubic (BCC) and the Face-Centered Cubic (FCC). These structures are simple enough to have their diffraction spectra analyzed without the aid of software.
- Each of these structures has specific rules on which of their planes can produce diffraction, based on their Miller indices (hkl).
- SC lattices show diffraction for all values of (hkl), e.g. (100), (110), (111), ...
- BCC lattices show diffraction when the sum of h+k+l is even, e.g. (110), (200), (211), ...
- FCC lattices show diffraction when the values of (hkl) are either all even or all odd, e.g. (111), (200), (220), ...
- Diamond Cubic lattices like Ge show diffraction when the values of (hkl) are all odd or all even and the sum h+k+l is a multiple of 4, e.g. (111), (220), (311), ...
- The order in which these peaks appear depends on the sum of  $h^2 + k^2 + l^2$ . These are shown in a table as follows:
- 

(hkl)	$h^2 + k^2 + l^2$	BCC	FCC
100	1		
110	2	√	
111	3		√
200	4	√	√
210	5		

211	6	√	
220	8	√	√
300, 221	9		
310	10	√	
311	11		√
222	12	√	√
320	13		
321	14	√	
400	16	√	√
410, 322	17		
411, 330	18	√	
331	19		√
420	20	√	√
421	21		

- **Table 6.xx:** List of planes and the corresponding  $h^2 + k^2 + l^2$  value.
- The value of  $d$  for each of these planes can be calculated using the equation:
- $1/d^2 = (h^2 + k^2 + l^2)/a^2$
- Where  $a$  is the lattice parameter of the crystal.
- A worked example for sample diffraction of NaCl with Cu  $K\alpha$  radiation is shown below. Given the values of  $2\theta$  that result in diffraction, a table can be constructed.

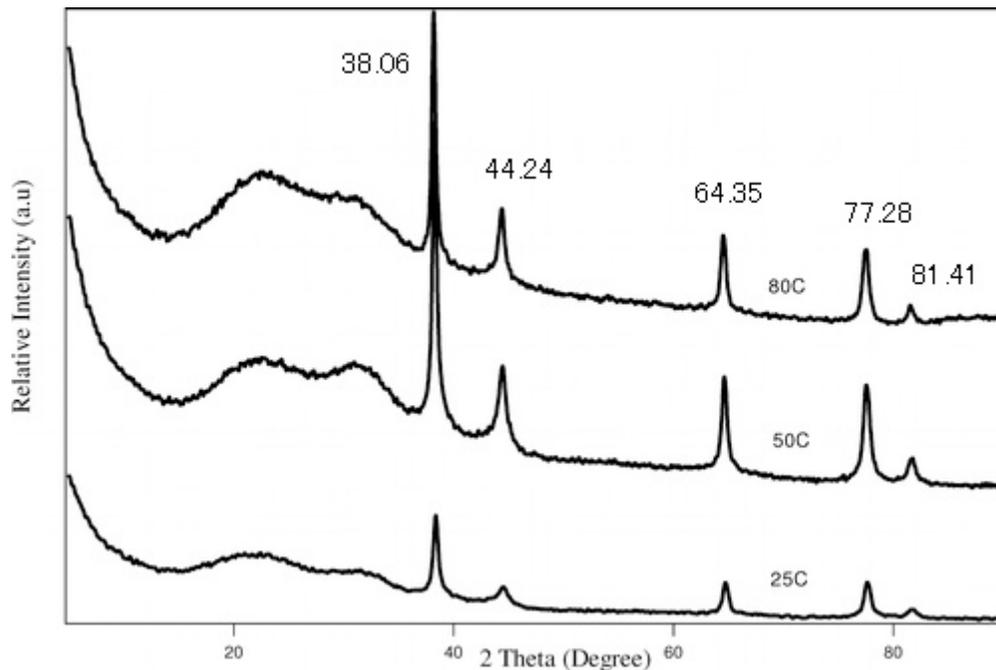
$2\theta$	$\theta$	$\sin \theta$	$\sin^2 \theta$
27.36	13.68	0.24	0.0559
31.69	15.85	0.27	0.0746
45.43	22.72	0.39	0.1491
53.85	26.92	0.45	0.2050
56.45	28.23	0.47	0.2237
66.20	33.10	0.55	0.2982
73.04	36.52	0.60	0.3541
75.26	37.63	0.61	0.3728

- Another table can then be constructed using various ratios of  $\sin^2 \theta$  compared to the smallest value of  $\sin^2 \theta$ .

$\sin^2 \theta$	$\sin^2 \theta / \sin^2 \theta$	$2 * \sin^2 \theta / \sin^2 \theta$	$3 * \sin^2 \theta / \sin^2 \theta$
0.0559	1.00	2.00	3.00
0.0746	1.33	2.67	4.00
0.1491	2.67	5.33	8.00
0.2050	3.67	7.34	11.00
0.2237	4.00	8.00	12.00
0.2982	5.33	10.67	16.00
0.3541	6.34	12.67	19.01

0.3728	6.67	13.34	20.01
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- The values of these ratios can then be inspected to see if they corresponding to an expected series of hkl values. In this case, the last column gives a list of integers which corresponds to the  $h^2 + k^2 + l^2$  values of the FCC lattice diffraction. Hence, NaCl has a FCC structure.
- The lattice parameter of NaCl can now be worked out from this data. The first peak occurs at  $\theta = 13.68^\circ$ . Given that the wavelength of the Cu  $K\alpha$  radiation is  $1.54 \text{ \AA}$ , the Bragg Equation can be applied as follows:
  - $\lambda = 2d \sin \theta$
  - $1.54 = 2d \sin 13.68$
  - $d = 3.26 \text{ \AA}$
  - Since the first peak corresponds to the (111) plane, the distance between two parallel (111) planes is  $3.26 \text{ \AA}$ .
  - The lattice parameter can now be worked out using the equation
  - $1/d^2 = (h^2 + k^2 + l^2)/a^2$
  - $1/3.26^2 = (1^2 + 1^2 + 1^2)/a^2$
  - $a = 5.65 \text{ \AA}$
- **Practice:** Below is a powder XRD spectrum of Ag nanoparticles, also imaged with Cu  $K\alpha$  radiation of  $1.54 \text{ \AA}$ . Determine its crystal structure and lattice parameter using the labeled peaks.
- **Answer:** FCC,  $4.09 \text{ \AA}$ .



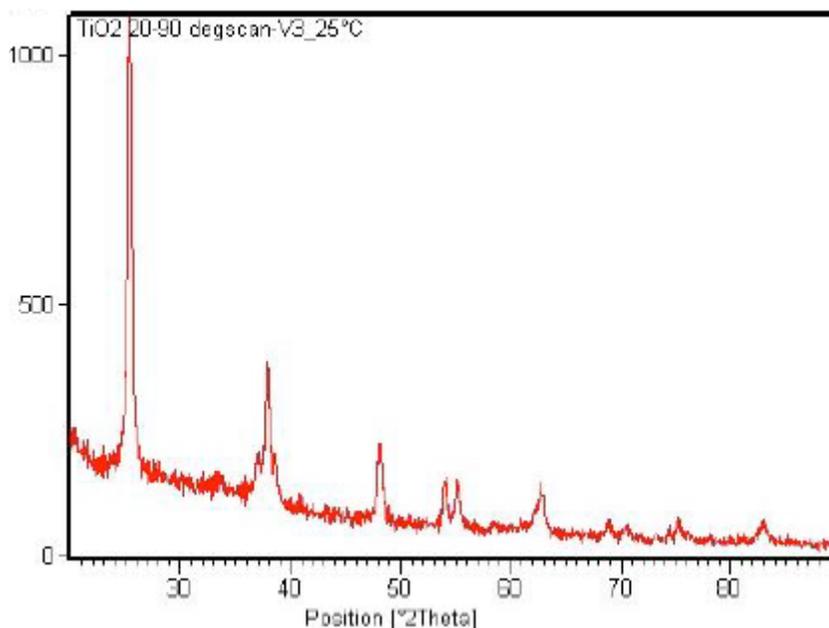
**Figure 6.xx:** Powder XRD spectra of Ag, adapted from Biosynthesis of Iron and Silver Nanoparticles at Room Temperature Using Aqueous Sorghum Bran Extracts by Eric C. Njagi, Hui Huang, Lisa Stafford, Homer Genuino, Hugo M. Galindo, John B. Collins, George E. Hoag, and Steven L. Suib.

### ***Determining composition***

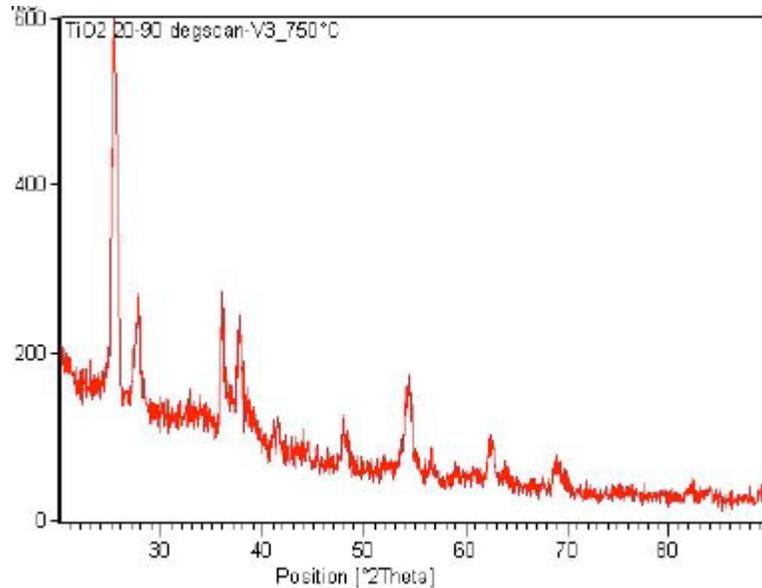
As seen above, each crystal will give a pattern of diffraction peaks based on its lattice type and parameter. These fingerprint patterns are compiled into databases such as the one by the Joint Committee on Powder Diffraction Standard (JCPDS). Thus, the XRD spectra of samples can be matched with those stored in the database to determine its composition easily and rapidly.

### ***Conclusion***

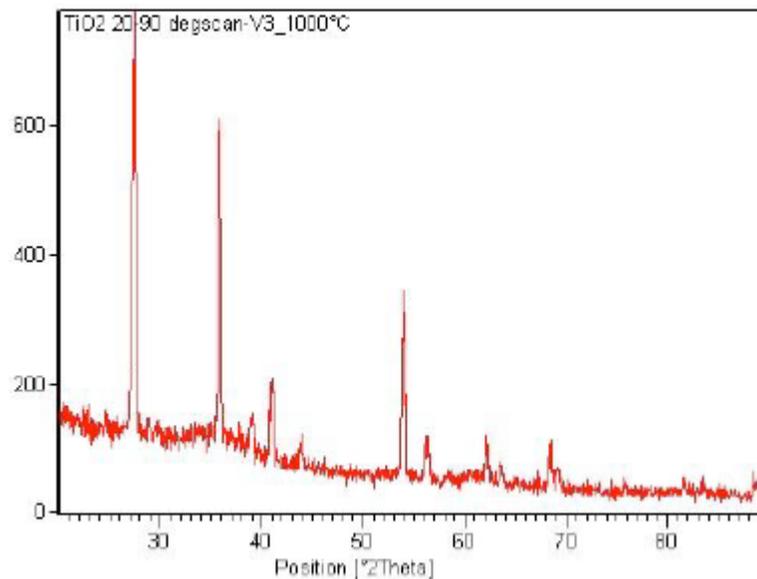
- XRD can allow for quick composition determination of unknown samples, and give information on crystal structure.
- Powder XRD is a useful application of X-ray diffraction, due to the ease of sample preparation compared to single-crystal diffraction.
- Powder XRD is also able to perform analysis like solid state reaction monitoring, such as the TiO<sub>2</sub> anatase to rutile transition. A diffractometer equipped with a sample chamber that can be heated can take diffractograms at different temperatures to see how the reaction progresses. Spectra of the change in diffraction peaks during this transition is shown below:



- **Figure 6.xx:** Powder XRD spectra of TiO<sub>2</sub> at 25°C, courtesy of Jeremy Lee



- **Figure 6.xx:** Powder XRD spectra of TiO<sub>2</sub> at 750°C, courtesy of Jeremy Lee



- **Figure 6.xx:** Powder XRD spectra of TiO<sub>2</sub> at 1000°C, courtesy of Jeremy Lee

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