

Week 2

???

2.1 XRD Analysis 2

1/10: • Dealing with broadening of the XRD beam.

– Synchrotron radiation gets you better resolution.

• How do you get a cleaner spectra, given this one?

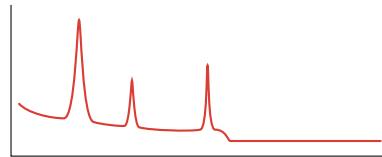


Figure 2.1: Enhancing XRD results.

– In general:

- You can change divergence slits, filter, and masks.
- You can't change the monochromator, however, because it's built into the machine.

– In this particular case:

- The issue is the high background which may be covering up smaller peaks.
- Solution: Use a smaller divergence slit and more masks.
- Another problem that could be causing high background is X-ray fluorescence, so check to make sure that your sample doesn't have iron or other similar things contaminating it.

• The principle of Bragg's law.

- The Braggs proposed that crystals can be described in terms of layers or planes of atoms.
- Their theoretical planes behave like **reflecting planes**.
- Strong “reflected” beams are produced when the path differences between reflections from successive planes in a family is equal to a whole number of wavelengths.
 - If we want to see something, neighboring planes' waves must be in phase, interfering constructively to amplify their intensity rather than dampening it with destructive interference.
- This approach is not correct in a physical sense — planes do not reflect X-rays. However, it is correct in a geometrical sense and provides us with a very simple expression for the analysis of crystal structure.

• **Reflecting plane:** A plane for which the angle of incidence equals the angle of reflection.

- Conditions that are necessary to make the phases of the beams coincide.
 - Refer to Figure 2.2 throughout the following.
 - The angles of the incident and “reflected” photons are equal.
 - The rays of the incident are always in phase and are parallel up to the point at which the top beam reaches the top layer at atom O .
 - The second beam continues to the next layer where it is scattered at atom B . If the two beams travel in adjacent and parallel fashion, the beam scattered at atom B travels an extra distance $AB + BC$. This extra distance should be equal to a whole number of wavelengths.
 - Again, a diffracted beam *looks* reflected, but what it really is is scattered radiation. Drill home that planes are not physically accurate!
- How to derive the Bragg's Law formula.

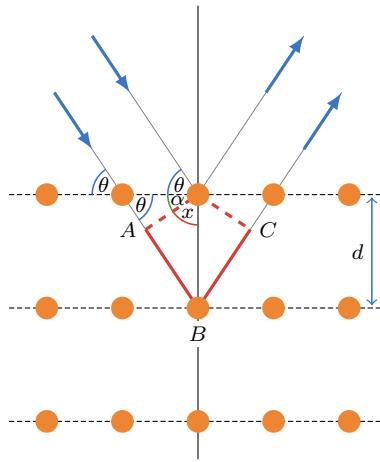


Figure 2.2: Bragg's Law derivation.

- Since $\theta + \alpha = 90^\circ$ and $\theta + x = 90^\circ$, we know that

$$x = \theta$$

- This combined with the observation that $\sin(x) = AB/d$ implies that

$$\begin{aligned} \sin \theta &= \frac{AB}{d} \\ AB &= d \sin \theta \end{aligned}$$

- Lastly, we may observe that $AB = BC$. Therefore, the total phase shift is

$$2AB = 2d \sin \theta$$

- Since we require that this is a whole number of wavelengths, our final condition is

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

where n is an integer determined by the order given, λ is the wavelength of the X-rays, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes.

- This condition is called **Bragg's Law**.
- Note that copper's $\lambda = 1.54 \text{ \AA}$ is the most common wavelength with which to work.

- Mineralogy — Inspiration for crystallography.
 - Happened way before all of this math, when scientists had far fewer tools.
 - Researchers could only observe a crystal's **habit** and cleavage planes, and measure interfacial angles with a **goniometer**.
 - René Just Haüy postulates in 1801: Crystal structures are made up of orderly arrangements of integrant molecules in successive layers, according to geometrical laws of crystallization.
 - Haüy formulated the **theory of the rational indices** of the faces of a crystal, which is important for crystallographic calculations.
 - By 1792, he had identified several parallelepipeds to explain shapes of a few crystals.
 - This work, which may now seem elementary, is extremely impressive since he had so few tools.
- **Habit:** The tendency for specimens of a mineral to repeatedly grow into characteristic shapes.
- **Goniometer:** An instrument that either measures an angle or allows an object to be rotated to a precise angular position.
- **Theory of rational indices:** The theory that the intercepts of a crystal face with the crystallographic axes can be expressed as a/h , b/k , and c/l , where $1/h$, $1/k$, and $1/l$ are three simple rational numbers.
- Type of Lattice Systems.
 - Haüy (1784): The periodicity of crystalline materials involves the basic repetition of a basic unit called the **unit cell**.
 - Crystalline materials are formed by the repetition in (2D, 3D, etc.) space of cells (or **crystallites**).
 - In 3D space, cells are defined by three non-coplanar vectors (called **fundamental translations**).
 - There are 7 types of cells that together cover all possible point lattices.
 - Important: Crystal structures are defined by a **basis** and a **lattice**.
- **Basis:** *What* gets repeated in the crystal structure.
- **Lattice:** *How* it gets repeated.
- Bravais lattices.

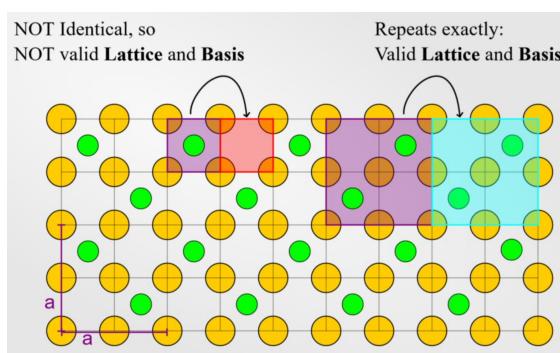


Figure 2.3: Decomposition of a crystal into its Bravais lattice.

- Auguste Bravais (1848) found mathematically that the number of crystalline lattices is finite.
- It is a fully geometrical concept and has nothing to do with atoms or crystalline planes.
- Bravais lattices are the basic lattice arrangements. All other lattices can simplify into one of the Bravais lattices. Bravais lattices move a *specific* basis by a translation.

- There are 14 3D Bravais lattices.
 - Bravais lattices only take into account *translational* symmetry (this is important!).
 - If you can exactly repeat the entire structure by a set of translations, that is the Bravais lattice.
 - Other symmetries, like reflection or inversion, are captured in point groups and space groups, not by Bravais lattices.
- 1D Bravais lattice.

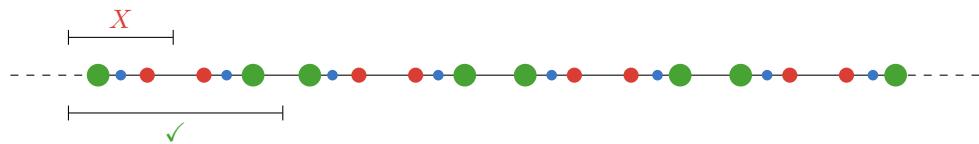


Figure 2.4: 1D Bravais lattices.

- Only one vector, hence only one possible Bravais lattice.
 - Bravais lattices do not allow mirror symmetry, only translation. Thus, we must choose as our basis the smallest structure that repeats *translationally*.
- 2D Bravais lattice.

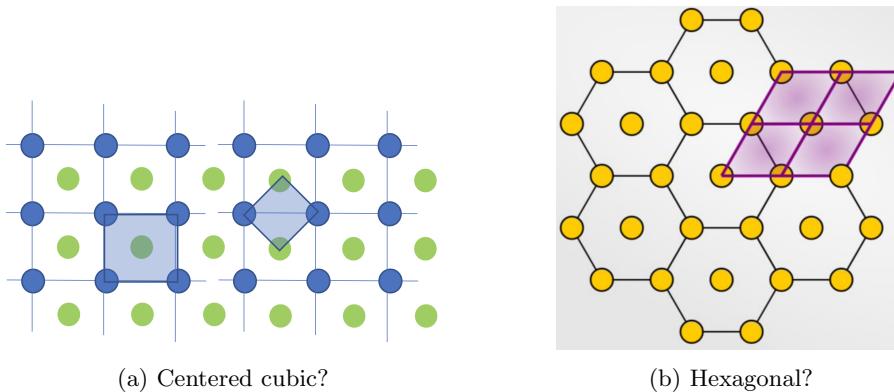


Figure 2.5: 2D Bravais lattices.

- There are five 2D Bravais lattices.
 1. Square ($a = b, \theta = 90^\circ$).
 2. Hexagonal ($a = b, \theta = 120^\circ$).
 3. Rectangular ($a \neq b, \theta = 90^\circ$).
 4. Centered rectangular (see below).
 5. Rhomboidal ($a \neq b, \theta \neq 90^\circ$).
- There does exist centered rectangular (a rectangular lattice with an additional vertex in the center of each rectangle), but there does not exist “centered cubic” because a smaller, rotated square can represent the entire lattice, so “centered cubic” is really just square. See Figure 2.5a.
- The “hexagonal” Bravais lattice can be simplified into a rhombus, but hexagon shows “true” symmetry (i.e., rotation, inversion, etc.). See Figure 2.5b.
- The honeycomb is not a Bravais lattice. Why??

■ Ask in OH.

- 3D Bravais lattice.

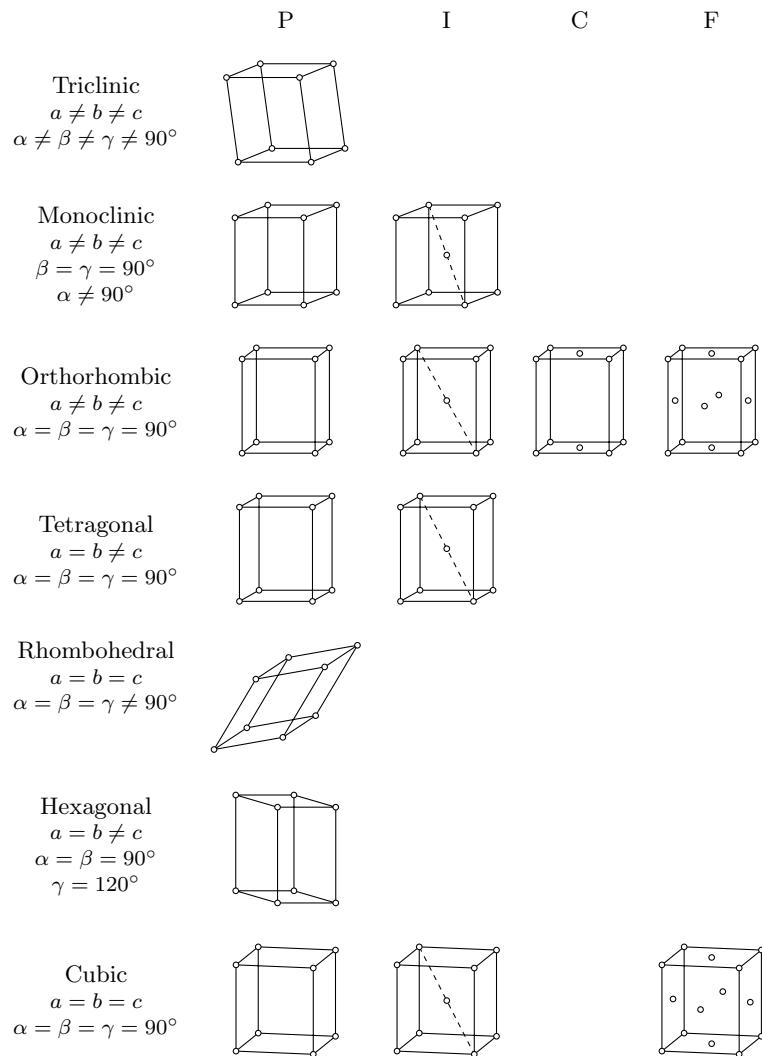


Table 2.1: Bravais lattices.

- Each lattice is a polyhedron.
 - The polyhedrons can be described using three different vectors.
- Some of the Bravais lattices can be expressed by other simple lattices: In 3D, the FCC lattice is also described by a rhombohedral lattice.
- There is no base-centered cubic Bravais lattice because what might be that is actually simple tetragonal.
- There are 4 types of Bravais lattices.
 - P - Primitive.
 - I - Body centered.
 - C - Base-centered.
 - F - Face centered.
 - More on these and how they correspond to space groups later.

- **Unit cell:** The smallest group of atoms which has the overall symmetry of a crystal.
 - Can be used to build the entire lattice by repetition in three dimensions.
 - A 3D structure.
- **Primitive cell:** The smallest possible element of a lattice.
 - May or may not include all symmetry elements.
 - Can have 2D or 3D structure.
- Conventional and primitive cells.

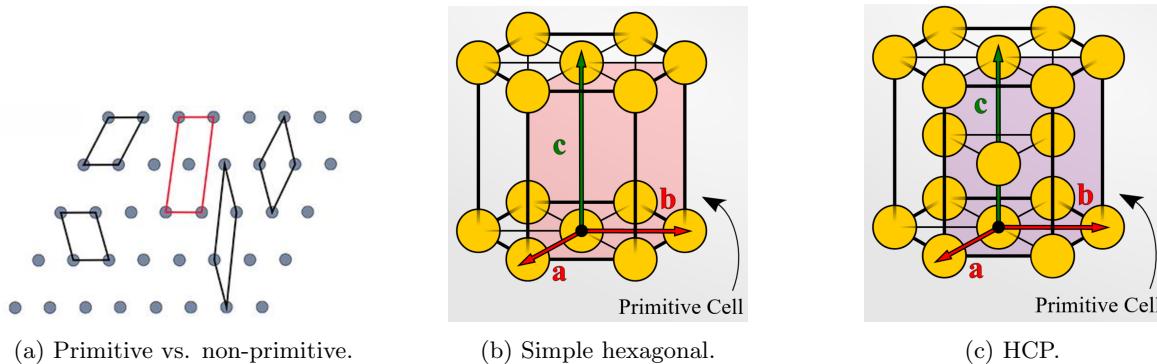


Figure 2.6: Conventional vs. primitive cells.

- The hexagonal 2D Bravais lattice (the conventional cell) might also be described as rhombic (the primitive cell). See Figure 2.5b.
- The hexagonal 3D Bravais lattice is a hexagonal prism that can also be constructed from a primitive cell which is a parallelepiped.
- Know simple hexagonal vs. hexagonal close-packed (HCP). See Figures 2.6b-2.6c.
- Clarification on primitive vs. non-primitive?? See Figure 2.6a.
- What is a lattice point??
- Miller indices.
 - In 1839, the British mineralogist William H. Miller used *reciprocal quantities* — namely, the integer numbers h, k, l — to describe crystal faces.
 - Miller indices are used to specify directions and planes.
 - These directions and planes could be in lattices or in crystals.
 - Notation (important information!):
 - (h, k, l) represents a **point** (commas are used).
 - $[hkl]$ represents a **direction**.
 - $< hkl >$ represents a **family of directions**.
 - (hkl) represents a **plane**.
 - $\{hkl\}$ represents a **family of planes**.
 - Be careful when writing/reading research literature to use/interpret the write notation.
 - Negative numbers and directions are depicted with a bar on top of the number.
- Miller indices for directions.
 - Let's consider a 2D lattice with Miller indices $(4, -2)$.

- Defines a vector pointing in the direction $4\vec{a} - 2\vec{b}$. It is parallel to many other vectors.
- The index $(4, -2)$ [notational issue here??] represents the set of all such parallel vectors.
- The number of indices matches the dimension of lattice (e.g., 1D lattice has 1 Miller index, 2D lattice has 2 Miller indices, etc.).
- Fractions in $(r_1 r_2 r_3)$ are eliminated by multiplying all components by their common denominator. Example: $(1, 3/4, 1/2)$ will be expressed as $(4, 3, 2)$.
- Miller indices: hkl review.
 - See Labalme (2022) for more.
 - You just have to remember that Miller indices represent the reciprocals of the fractional intercepts which the plane makes with crystallographic axes.
 - Notice how (421) [i.e., parentheses] is used to denote a plane!
- How to find Miller indices for planes.
 - Great slide in the slideshow; one stop shop for Miller indices.
 - The planes we will most commonly study are (100) , (001) , and (010) planes.
 - Algorithm.
 - Identity the plane intercepts on the x -, y -, and z -axes.
 - Define intercepts in fractional coordinates.
 - Take the reciprocals of the fractional intercepts.
- Miller indices.
 - Continuation of the previous slide but for slanted planes.
 - Keep in mind that different planes have different chemical distributions. One plane in an oxide may be mostly oxygen; another may be mostly copper.
- Crystal structure, lattice, etc.
 - Crystal structure combines **lattice** with the **basis** again.
 - A lattice is not a crystal. However, if the basis consists of one atom, crystal structures look exactly like the Bravais lattice.
 - Common metallic crystal structures: BCC, FCC, hexagonal close-packed (HCP).
- Example 1: Diamond.

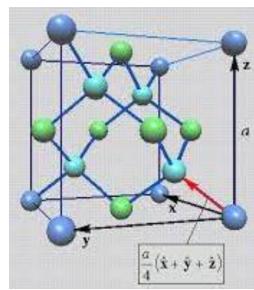


Figure 2.7: Diamond crystal structure.

- Bravais lattice: FCC with a two-atom basis.
- Crystal structure: Cubic diamond.
- Two atom basis at $(0, 0, 0)$ and $(1/4, 1/4, 1/4)$.

- Example 2: NaCl.
 - Bravais lattice: FCC.
 - Crystal structure: FCC.
 - Both atoms make FCC lattices and you get the overall structure by inserting one lattice into the other.
- Example 3: Primitive cubic substances.
 - Examples: Fe, CsCl, and NiAl.
 - Bravais lattice: Primitive cubic with a two-atom basis (Cs at $(0, 0, 0)$ and Cl at $(1/2, 1/2, 1/2)$).
 - Crystal structure: Primitive.
- From Bravais lattices to a full description of crystalline structure.
 - Bravais lattices: There are 14 and they account for translational symmetry. But there are also additional symmetry elements (rotation, inversion, reflection).
 - We discount additional potential translation symmetry operations for now.
 - If you apply all of these other operations to the Bravais lattices, you get 32 crystal classes/point groups.
 - If you add in **screw** and **glide** operations, you get 230 total space groups. This number does depend on the dimension of the space, though, i.e., fewer space groups exist in 2D (to a significant extent).
- **Screw:** Rotation followed by a translation.
- **Glide:** Reflection followed by a translation.
- Screw and glide operations.

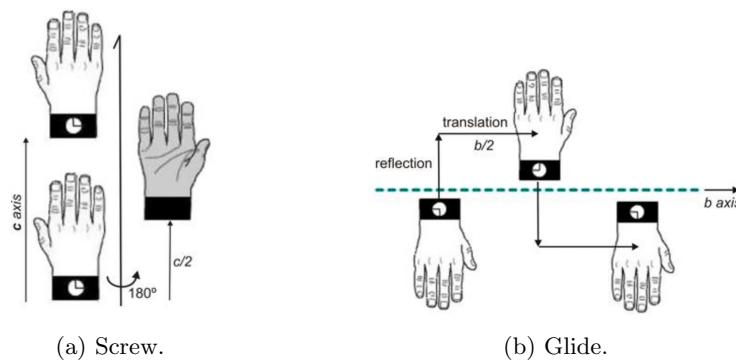


Figure 2.8: Screw and glide operations.

- These are essentially just combinations of the rotation axes and the mirror planes with the characteristic translations of the crystals.
- Discovery of the space groups.
 - Retrat de Arthur Schoenflies (Germany) and Evgraf Fedorov (Russia) proposed space groups while in correspondence via mail.
 - The triumph of their studies was only after the discovery of the utilization of X-rays in structural studies of minerals.
 - Developed 1890-92.

- Symmetry operator notation (Hermann-Mauguin).

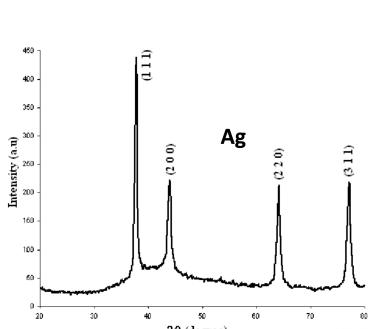
Type of symmetry element Centre of symmetry	Written symbol	Graphical symbol	
	$\bar{1}$	\bullet	
Mirror plane	m	Perpendicular to paper	In plane of paper
Glide planes	$a\ b\ c$	glide in plane of paper	arrow shows glide direction
		glide out of plane of paper	
	n		
Rotation	2 3 4 6	● ▲ ◆ ◆	→
Screw axes	2_1 $3_1, 3_2$ $4_1, 4_2, 4_3$ $6_1, 6_2, 6_3, 6_4, 6_5$	● ▲▲ ◆◆◆ ◆◆◆◆◆◆	→
Inversion axes	$\bar{3}$ $\bar{4}$ $\bar{6}$	△ ◊ ◊	

Table 2.2: Hermann-Mauguin notation.

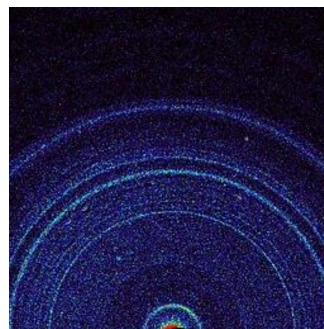
- Shevchenko won't go into too much depth; she doesn't even remember that much herself, but it's good to know how to read one.
- How to "read" space groups.
 - In the notation for a space group, the first letter is the Bravais lattice and then there are three symmetry elements with respect to 3 viewing directions.
 - Example: NiAsS is orthorhombic with space group $Pca2_1$.
 - P refers to the Bravais lattice.
 - c refers to a glide plane $c \perp a$.
 - a refers to a glide plane $a \perp b$. What do these mean??
 - 2_1 refers to a screw axis parallel to c .
 - In screw axis notation, "the big number is how many stops you make???"
 - Can 3 symmetry elements describe the full symmetry?
 - There are structures with more symmetry elements (e.g., 8, 16, etc.).
 - Their symmetries can be derived from generators, though. So yes??
- **Space group:** The symmetry group of an object in space.
 - Alternate definition: A set of symmetry elements and respective operations that completely describes the spatial arrangements of a given 3D periodic system.
 - In crystals, space is three dimensional.

- Viewing directions.
 - The position of the symmetry element depends on the type of lattice.
 - If it is triclinic, the symmetry elements are always “around” the center of inversion.
 - If it’s monoclinic, there is one viewing direction besides the inversion center (mathematicians have arbitrarily chosen b to be said direction).
 - Shevchenko doesn’t think many people memorize this unless they’re really into it, but it’s worth understanding once. How much do we need to know??
 - Consider building models.
- XRD databases.
 - This is probably the most important/relevant information in this lecture for our research.
 - In the 1940s, the best crystallographers in the world analyzed a bunch of materials and started to build a database.
 - Started by Hanawalt and associates while he was at Dow chemicals. They built a database and used it for chemical analogies.
 - The principal of the analysis is based on the d spacings of the strongest reflections.
 - \$50 per set was very expensive at the time, but worth it because it saved so much work.
 - In 1941, the JCPDS (Joint Committee on Powder Diffraction Standards) was founded.
 - 1978: Became the ICDD (International Center for Diffraction Data).
 - Still have a ton of scientists working on diffraction analysis (around 300 in 1978).
- Data analysis.
 - The slides list databases that contain powder diffraction data (line positions and their intensities).
 - We have access as UChicago students.
 - Different databases have different specialties.
 - Programs for search and match are available, too.
 - Website for visualization, coordinates, and finding primitive and basis vectors ([link](#))
- XRD analysis can help you with...
 - Phase identification;
 - Crystallite size measurements.
 - Texture analysis.
 - Etc.
 - We can also study processes (this is very useful).
 - Examples:
 - Phase transitions.
 - Crystallite growth.
 - Thermal expansion.
 - Ion intercalation.
 - Decomposition.
 - Oxidation.
 - We can observe a flattening/broadening of curves. The oxidized material may be crystalline, but it may well be amorphous, too, leading to said broadening.
 - Stability of the catalysts.

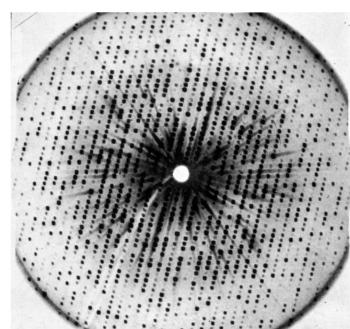
- Diffractograms.



(a) Peaks.



(b) 2D average.



(c) Dots (single crystal).

Figure 2.9: Diffractogram types.

- Our diffractograms will largely look like peaks (see Figure 2.9a).
- 2D detectors (as with synchrotrons) yield circular patterns or circular dot patterns.
- Dots (see Figure 2.9c) are generated by single crystals.
 - Myoglobin is a protein in muscles. It stores oxygen to bind and release oxygen depending on the oxygen concentrations in the cell, has functions in the hemostasis of nitric oxide and in the detoxification of reactive oxygen species. Myoglobin is the reason for the red color of the muscle of most vertebrates.
- Averaged rings (see Figure 2.9b) are generated by polycrystalline materials.
 - What is pictured is actually the first X-ray diffraction pattern of Martian soil (from the Curiosity rover at “Rocknest” on October 17, 2012).
 - **Feldspar**, **pyroxenes**, **olivine**, etc. were identified (this kind of identification and confirmation can take experts years since the data is so cluttered).
 - We read these with software in general. Calculate distances, work with the parameters of our instrument, etc.
 - 2D is better because gaps in the circles provide information, too??
 - Decades of experience and the help of your peers helps you decipher these images.
- Most of us will work with the APS at Argonne (shut down in April 2023 and will be back online a year later).
- **Feldspar**: Aluminum tectosilicate minerals, e.g., $KAlSi_3O_8$, $NaAlSi_3O_8$, and $CaAl_2Si_2O_8$.
- **Pyroxenes**: General form $XY(Si, Al)_2O_6$, where X can be Ca, Na, Fe^II, Mg, etc. and Y can be Cr, Al, Mg, Co, Mn, Sc, V, etc.
- **Olivine**: General form $(Mg^{2+}, Fe^{2+})_2SiO_4$.
- Sample preparation.
 - Methods:
 - Drop and dry: Make a suspension of nanoparticles or a colloidal solution, drop it onto the plate, and wait for it to dry.
 - Grinding: Powder gets grinded and then compacted.
 - Crystallization: Proteins get crystallized, for example.
 - Diffractogram depends on:
 - Graininess.

- Micro-absorption.
 - Texture.
 - Sample height displacement/adjustments.
 - Surface roughness.
 - Sample transparency.
- Diffractograms.
 - Peak positions are determined by the size and shape of the unit cell.
 - Peak intensities are determined by the atomic number and position of the various atoms within the unit cell.
 - Peak widths determined by instrument parameters (and other factors, discussed later).
 - Temperature, crystal size, strain, and other imperfections in the material.
 - Sample's graininess.
 - Single crystals should generate "spotty diffracted rays." Powder samples should generate continuous rings.
 - Grainy samples lead to variation in the intensity of the peaks, missing peaks, etc.
 - If you work with grainy samples, grind first and adjust the divergence slits second. You can also spin the sample and/or open the divergence slits to increase the probability of something getting hit.
 - Micro-absorption.
 - There are materials and elements with high and low absorption of X-rays. Your spectrum will depend on the high absorption ones??
 - In XRD, we don't care about elements, but we do care about their Z-number.
 - CsCl and CsI are interesting examples. They have the same structure but different numbers of lines in the X-ray pattern.
 - Cs and Cl are not isoelectronic but Cs and I are. X-rays are scattered by electrons, so to X-rays, these atoms look the same. Leads to systematic peak absences.
 - Size-effect.
 - Thicker films have more peaks in general.
 - Texture/preferred orientation.
 - Nanoparticles vs. short rods vs. long rods.
 - It looks a lot better when you have more nanoparticles aligned in particular directions.
 - At 75%, we're pretty good.
 - Same story with the types of rods.
 - There are various creative solutions found on the internet (including Vaseline, hair spray, etc.) to get the particles to line up the way you want.
 - The underlying tactic is always providing some medium in which the particles can interact/rearrange.