

# Week 2

## X-Ray Diffraction

### 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?

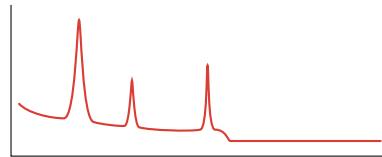


Figure 2.1: Enhancing XRD results.

– 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.

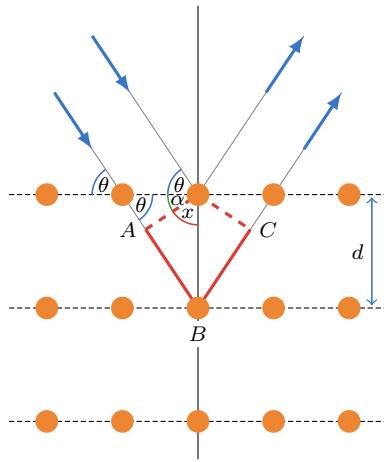


Figure 2.2: Bragg’s Law derivation.

- 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,  $\lambda$  is the wavelength of the X-rays,  $d$  is the spacing between the planes in the atomic lattice, and  $\theta$  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.

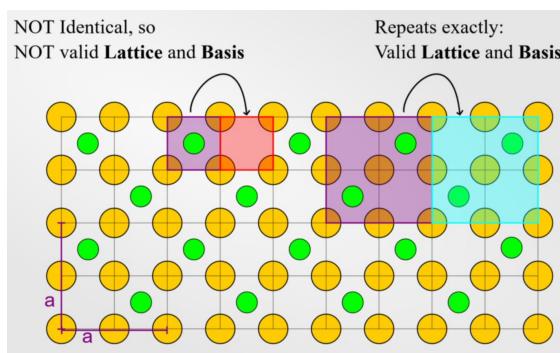


Figure 2.3: Decomposition of a crystal into its Bravais lattice.

- 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.

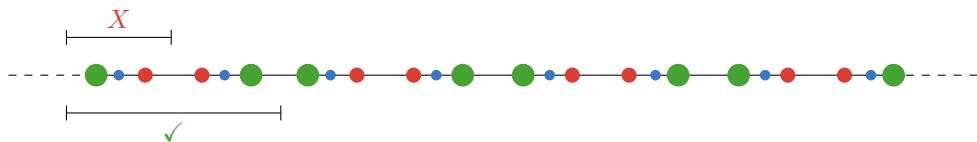


Figure 2.4: 1D Bravais lattices.

- 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.

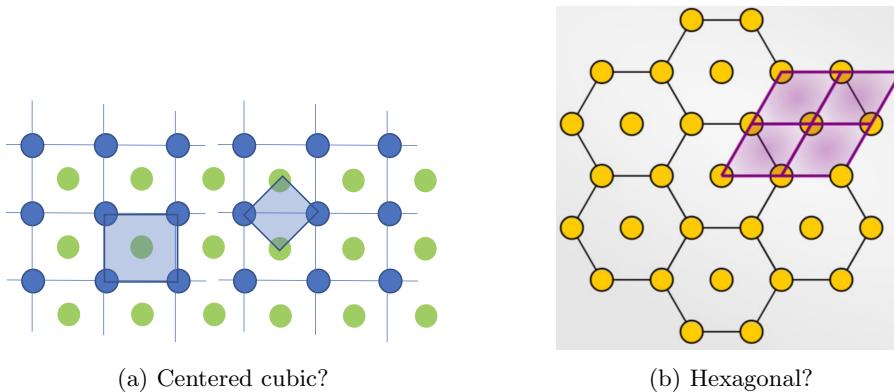


Figure 2.5: 2D Bravais lattices.

- 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 ( $a \neq b, \theta \neq 90^\circ$ ).
- Rhomboidal is also known as **oblique**.
- 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??

- 3D Bravais lattice.

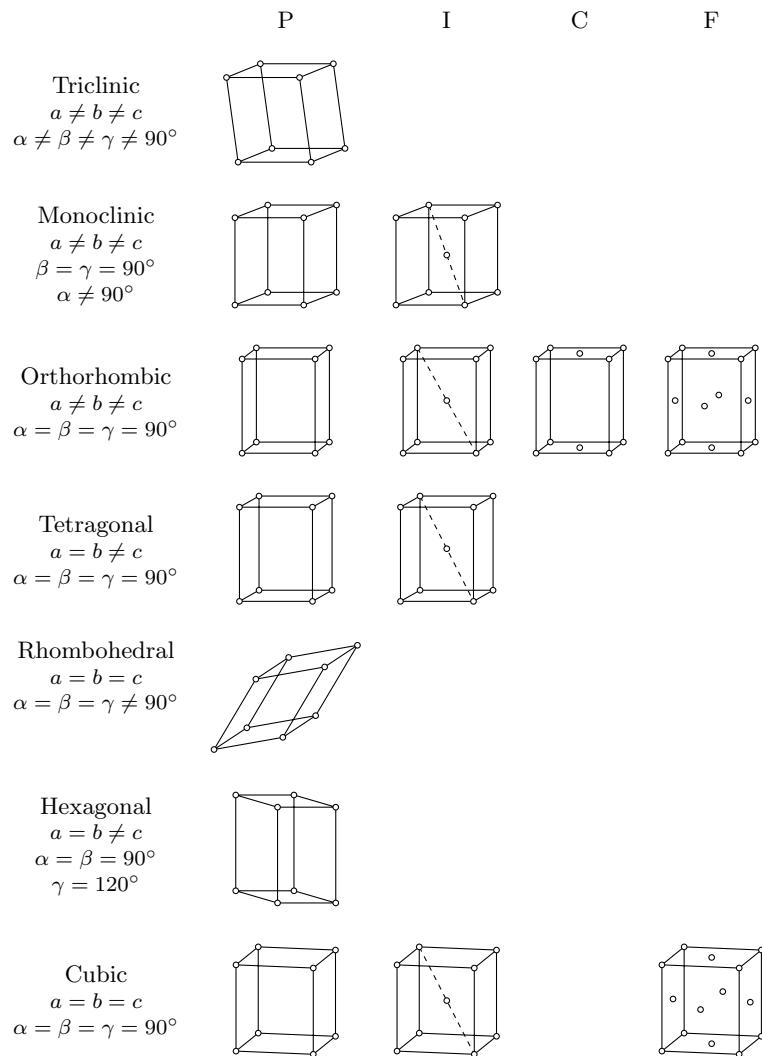


Table 2.1: Bravais lattices.

- 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.

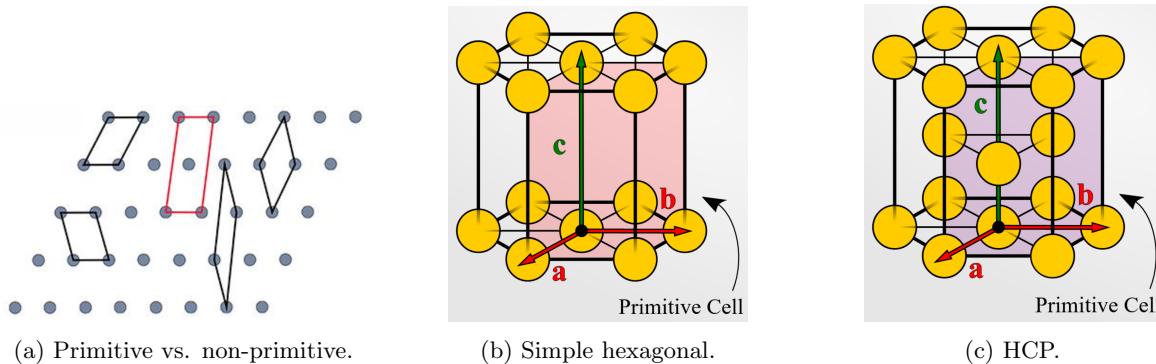


Figure 2.6: Conventional vs. primitive cells.

- 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 [1] 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.

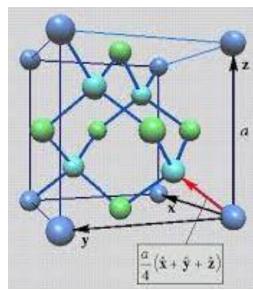


Figure 2.7: Diamond crystal structure.

- 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.

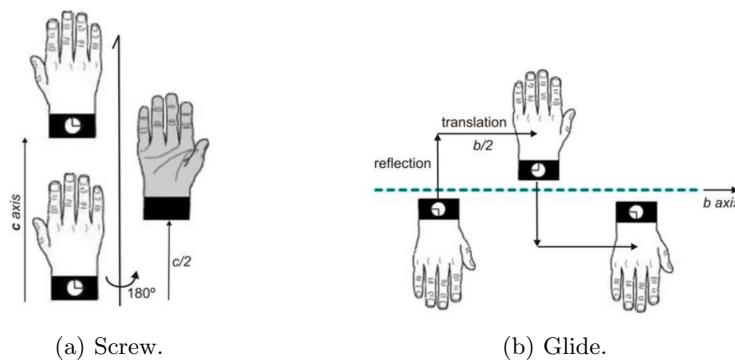


Figure 2.8: Screw and glide operations.

- 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	Written symbol	Graphical symbol	
Centre of symmetry	$\bar{1}$		
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.

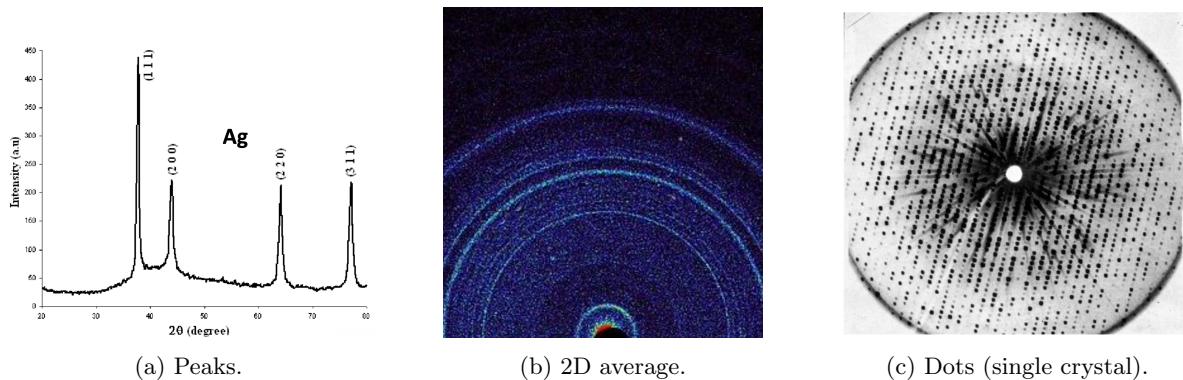


Figure 2.9: Diffractogram types.

- 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<sup>I</sup>I, 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.
  - You can just set them down, but more often than not you have to align them after the fact.
  - At 75% particle alignment, we're pretty good (fewer peaks; more emphasis on the actual peaks of importance).
  - 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.

## 2.2 XRD Analysis 3 + Diamond Anvil Cell

1/12: • HW will be posted today (mostly XRD questions).

- Today: Finishing up XRD and moving on to diamond anvil cells.
- We pick up from last time with texture/preferred orientations.
- Examples of effective preparation strategies.

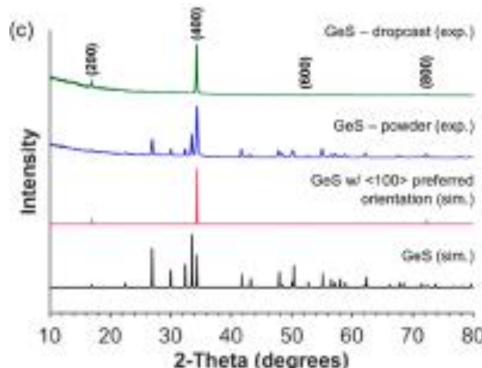


Figure 2.10: Preparation strategies vs. XRD clarity.

- Consider GeS NPs.
  - 2D semiconductor with 1.65 eV band gap in the bulk form.
  - They exhibit strong in-plane crystalline anisotropy.
- Effect of structure on properties: Highly anisotropic excitons, high carrier mobility channels, and thermal conduction pathways.
- If you look at the set X-ray diffractograms in Figure 2.10, you will see that certain synthetic techniques give better results.
  - Here, for instance, drop-cast is the best — PXRD shows a significant preferred orientation in the [100] direction when GeS nanosheets are drop-cast (green) and only minimal preferred orientation when prepared as a powder (blue).
- Sample height displacement.
  - Having to adjust the height of your sample.
    - This is not a super common issue, but it's more common than we'd like.
  - Many diffractometers (not synchrotron ones) have sample holders made of silicon or plastic with either no broad spectrum XRD peaks or one massive peak that can be used as a reference.
  - These sample holders have indentations made to be filled with powder. However, we need the powder surface to lie at the level of the sample holder, not above or below.
    - You can also fill the gap with silicon, place a drop of your sample, and then wait for it to dry, leaving behind a thin film.
  - Negative consequences of not correctly adjusting height.
    - $2\theta$  shift of the peaks (too low = shift to lower angles; too high = shift to higher angles).
    - Broader peaks.
    - Loss of intensity of the X-ray peaks.
    - Distorted peak profiles as a result of partial blocking of the beam.

- Rough sample surface.
  - Same negative consequences as with height displacement issues.
- Sample transparency.
  - Absorption of X-rays is unwanted.
  - Solution.
    - Use very thin samples.
    - Use a transmission Debye-Scherrer instrument with capillaries (instead of the Bragg-Brentano reflection geometry).
      - It's not very common to use this setup, but it does happen.
  - Similar negative consequences to the last two, except that loss of intensity is no longer an issue.
- The effect of the size of the crystalline domain.

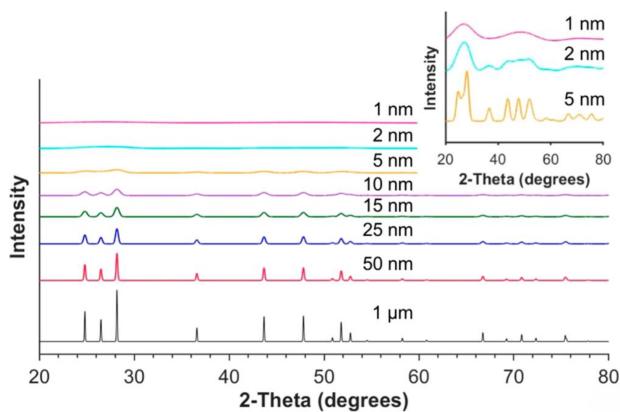
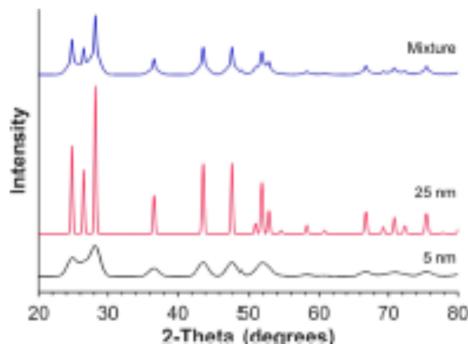


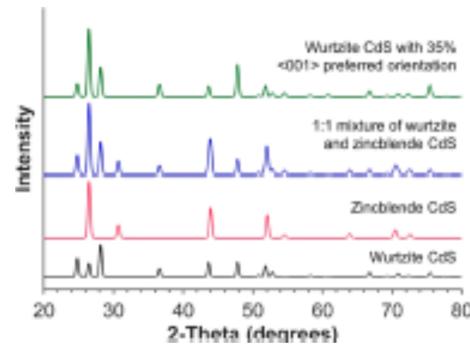
Figure 2.11: Resolution increases with larger crystal size.

- Increasing particle size leads to thinner, higher, and more well-defined peaks.
  - Blurring effects due to small particle size can also be observed in larger polycrystalline samples.
    - Indeed, SEM-observable micro-scale structures may not be single crystals; they may be polycrystalline, themselves.
  - The relation between particle size and peak broadening is formalized by the **Scherrer equation**.
  - **Scherrer equation:** The following equation, where  $D$  is the crystallite thickness / mean size of the ordered crystalline domains,  $\lambda$  is the X-ray wavelength,  $K$  is the shape factor ( $\sim 0.9$  for spherical grains),  $B$  is the **FWHM**, and  $\theta$  is the Bragg angle. *Given by*
- $$D = \frac{K\lambda}{B \cos \theta}$$
- Accurate size analysis requires correction for instrument broadening via
- $$B^2 = B_m^2 - B_{\text{ref}}^2$$
- where  $B_m$  is the measured FWHM and  $B_{\text{ref}}$  is the corresponding FWHM of the **bulk reference**.
- Readily applicable for crystal size of 2-100 nm.
    - Applicable up to 500 nm if a synchrotron light source is used.
  - **Bulk reference:** A reference crystalline material with large grain size ( $> 200$  nm).

- **Full width at half maximum:** The width of a peak in an XRD spectrum at half of the maximum height. *Also known as FWHM.*
  - Normalize the baseline, then take the width of the peak at half of the maximum height.
  - Can be fit with Gaussian, Lorentzian, Gaussian-Lorentzian, etc.
  - Important for particle or grain size (as discussed above) and residual strain (discussed later).
- Mixture of sizes and phases.



(a) Mixture of sizes.



(b) Mixture of phases.

Figure 2.12: Mixtures of sizes and phases.

- Sizes: Leads to peak broadening at the bottom but not the peaks.
- Phases: Materials that have the same chemical composition can have different crystal structures (e.g., CdS can be both wurtzite and zinc blende).
  - The peak positions don't coincide, leading to both extra peaks than either individual spectrum would have and some loss of information.
  - Loss of information: When peaks coincide (see, for example, the second peak from the left in the bottom spectrum in Figure 2.12b, which adds into the one right above it), the two original peaks can no longer be separated.
  - Implication: When you analyze your data, you have to be aware that your material can exist in several forms.
  - This is especially important for those of us who work with MOFs; we need to check the database for all possible structures of what we might have!
- How do we know what the percent composition of our material is?
  - We have to play with conditions experimentally, get a bunch of spectrums, and then reverse engineer.
  - Check the database and if you see enhancement of a particular peak.
  - You can be like, “Yes it's wurtzite but there are other things I don't recognize; what's going on?”
- **Vegard's law:** Suggests a linear relationship between the lattice constants of an alloy and its composition. (See Figure 2.13, which is highly exaggerated and not to scale.)
  - An empirical observation (a useful estimate, but it is *not* a physical law).
  - If you have an alloy of silver and gold, your peak position will be somewhere in the middle; can help you determine the fractional composition of your alloy.
    - Could be another good midterm question.
  - The effect can be very small (e.g., gold and silver are very close, so the shift is pretty small).

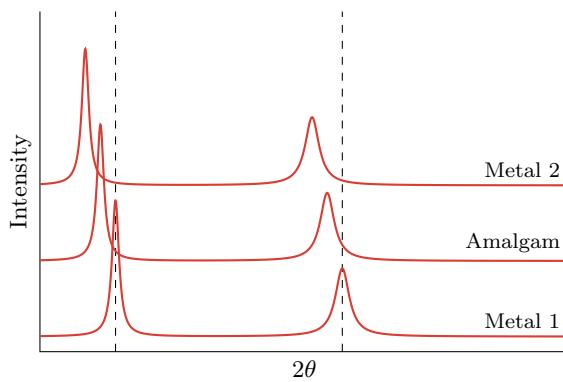


Figure 2.13: Vegard's law.

- Effect of strains.

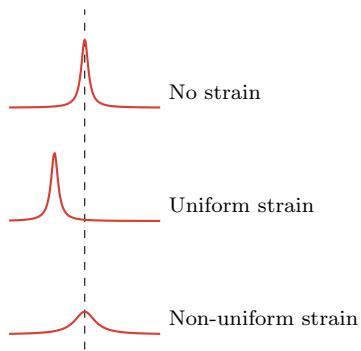


Figure 2.14: Strains.

- A common problem for those working in battery materials, and also NPs.
- **Strain:** The “amount” of deformation experienced by the material in the direction of force applied, divided by the initial dimension of the body. *Denoted by  $\varepsilon$ . Given by*

$$\varepsilon = \frac{\Delta L}{L} = \frac{\Delta d}{d}$$

- What is  $L$ ??
- **Uniform** (strain): Strain that affects lattice planes or all planes to the same extent.
- Example: Compressive strain.

$$\varepsilon = \frac{d_1 - d_0}{d_0}$$

- This is uniform strain along one Cartesian axis.
- Causes peak *shifts*. Peak shape is preserved.
- **Non-uniform** (strain): Strain that affects different parts of the sample to a different extent.
- Example: Bending a material such that the edges flex more than the middle.

Varies –  $d_1$  not constant

- Causes peak *broadening*.

- Strain comes from Bragg's law.
  - Throughout this derivation, we will assume uniform compressive strain.
  - Let  $\Delta d$  be the change in the interplanar distance  $d$  induced by the compression, and let  $\beta$  be the change in the Bragg angle.
    - Since  $\varepsilon = \Delta d/d$ ,  $\Delta d = \varepsilon d$ . Thus, the new interplanar distance is  $d - \varepsilon d$ .
    - Similarly, the new Bragg angle is  $\theta + \beta$ .
  - Thus, Bragg's law for the compressed system is

$$n\lambda = 2(d - \varepsilon d) \sin(\theta + \beta)$$

- Therefore,

$$\begin{aligned} n\lambda &= 2(d - \varepsilon d)(\sin \theta \cos \beta + \cos \theta \sin \beta) \\ &= (2d - 2\varepsilon d)(\sin \theta + \beta \cos \theta) \\ &= 2d \sin \theta - 2\varepsilon d \sin \theta + 2\beta d \cos \theta - 2\beta \varepsilon d \cos \theta \\ 0 &= -2\varepsilon d \sin \theta + 2\beta d \cos \theta - 2\beta \varepsilon d \cos \theta \\ &= -\varepsilon \sin \theta + \beta \cos \theta - \beta \varepsilon \cos \theta \\ &= -2\varepsilon \tan \theta + 2\beta - 2\beta \varepsilon \\ &= -2\varepsilon \tan \theta + 2\beta \\ \beta &= \varepsilon \tan \theta \end{aligned}$$

- Justifications of some of the above equalities.
  - Second equality: Note that  $\beta$  is very small, hence  $\cos \beta \approx 1$  and  $\sin \beta \approx \beta$ .
  - Fourth equality: Originally,  $n\lambda = 2d \sin \theta$ .
  - Seventh equality:  $\beta$  is very small permits neglecting the  $-2\beta \varepsilon$  term in the sixth line.
- Origin of strains in materials.
  - Dislocations, stacking faults, long range stresses, grain boundaries, sub-boundaries, internal stresses, chemical heterogeneities, etc.
  - Some are natural (those at the beginning??), some are induced (those at the end??).
- Phase identification.
  - Symmetry has an effect on the XRD pattern.
  - In particular, structures with higher symmetries have fewer peaks.
  - The fundamentals of this were covered in a different class.
    - How much do I need to know about these fundamentals??
- **Isomorphism:** Property of some substances which have different chemical composition but crystallize with a similar external shape because of their similar crystal structure.
- **Polymorphism:** Property of certain substances with the same chemical composition but different external shapes because they can crystallize with more than one crystal structure.
- **Allotropism:** The property of some chemical elements to exist in two or more different forms in the same physical state.
  - Relevance to crystallography: Allotropic crystals, when heated, can expand unequally in the direction of dissimilar axes.
- **Allotrope:** One of the forms defined by allotropism.

- We now move on to diamond anvil cell (DAC) experiments.
  - You're not limited only to XRD here, but this is a common application.
  - Shevchenko chose to present this because there's a lot of expertise on the technique at UChicago and especially at the APS.
- Advanced synchrotron for characterization and synthesis of materials.
  - Questions about this or want to do it? Contact Vitali Prakapenka at APS, Sector 13.
  - This can be high pressure, or really really high pressure.
  - Most of what we know about the structure of the Earth's deep interior comes from the study of seismic wave velocities.
  - In order to interpret such measurements in terms of mineralogical/compositional models of the Earth's interior, data on the physical and chemical properties of minerals at high pressures and temperatures are essential.
  - Knowledge of thermodynamics, phase equilibria, crystal chemistry, crystallography, rheology, diffusion, and heat transport are required to characterize the structure and dynamics of the Earth's deep interior.
- Understanding the universe.
  - What certain planets' cores are made of. Dependence on temperature, presence of oxygen, etc.
  - We hypothesize about other planets' cores by studying Earth's.
    - Recall the first X-ray diffraction pattern of Martian soil (Figure 2.9b). Based on what happens on Earth, we can make assumptions about what happens elsewhere.
  - Research on what's underground on Earth is done with things like the Kola Superdeep Borehole (just 9 inches in diameter, but at 12,000+ meters; half the distance or less to the mantle). Operational between 1970-1989; close to Shevchenko's birthplace (Belarus).
  - Bertha Rogers hole in Washita county, Oklahoma (9,000+ meters).
  - May 2008: Curved borehole BD-04A in the Al Shaheen Oil Field of Qatar is being actively investigated.

- **Diamond anvil cell. Also known as DAC.**

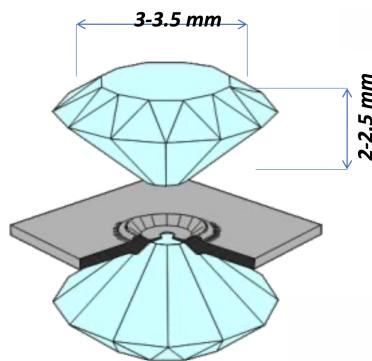


Figure 2.15: Diamond anvil cell.

- Working principle:

$$P = \frac{F}{A}$$

- Thus, if we want to achieve high pressure, one way to do this is to decrease the surface area.

- Sample placed on the **cullets** of the diamond.
- Reasons to use diamond.
  - It's a very hard material (rated 10/10 on the Mohs scale of mineral hardness).
  - It is also a transparent perfect crystal, so we can do spectroscopic studies (in the case of XRD, we get one characteristic peak).
  - There is no phase transition upon compression.
  - High thermal stability.
- One problem: Crushing of diamonds.
- **Cullet:** The surface area at the top of the diamond.
  - 2-500  $\mu\text{m}$  in size, depending on the type of DAC.
- Ultra-high-pressure experiments to beyond 1 TPa.
  - We can be smart and load another smaller diamond into onto the cullet.
  - Beamline 30 is the world's best source for this stuff.
  - It is common to study the different phases of water.
- Types of diamond anvil cells.
  - Many pictures of real-life ones plus a GIF of the different components (see Excess Class Pictures).
  - Change the pressure via the screws, which determine how close the diamonds are.
  - The cell casing is usually made of materials that are functional at extremely high and extremely low temperatures because these are often conditions of interest.
  - Contains a **gasket**.
  - The **pressure medium** transmits force to your material.
  - We monitor the pressure using spectroscopy.
    - Typically either ruby balls or gold flakes are included in the pressure medium.
    - Ruby balls are good; gold flakes can be monitored using XRD.
    - Gold is superior because it does not have any phase transitions and all lattices move, i.e., are isotropically contracted. In fact, it is required at very high pressure.
  - Important parameters.
    - Size of the cullet. If larger, you need more pressure, but at too high pressure, you get some cracks. Usually around 200-250  $\mu\text{m}$ ??
    - Beam size.
    - One or many samples. If many, consider movement of the samples upon compression and pressure release.
    - Pressure medium (isotropic/anisotropic).
  - You need to make sure that no part of your sample is too close to the edge.
  - You can get help with sample loading at a beamline.
- **Gasket:** The wedge that encloses the pressure-transmitting medium.
- Pressure transmitting medium.
  - Gas, solid, or liquid.
  - Gas is great because it applies the same pressure in every direction (it is isotropic).
  - He and Ne are the best gases; lightweight, very small, not high-Z enough to interfere with XRD.
  - If you study the same sample but use different pressure transmitting media, the result can be totally different.

- Argonne's APS.

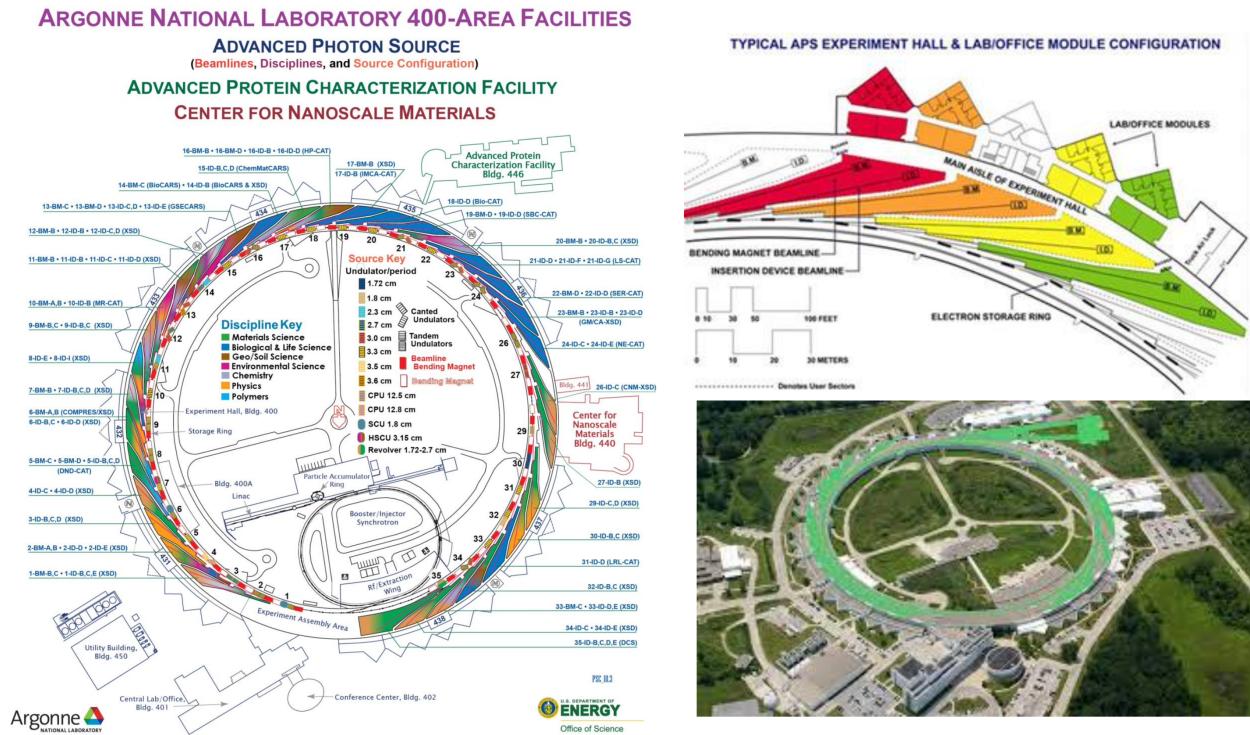


Figure 2.16: APS at Argonne.

- It's a relatively large circular building.
- Different numbers correspond to the sectors; each sector has different beamlines.
- Along the ring, electrons are traveling.
- Electrons are generated in the same way that they're generated in electron microscopes. Then there is an inner circle in which they are traveling. Then they are extracted using magnets and go to the larger circle.
- The quality of synchrotron facilities is determined by a few parameters. One of them is the uniformity of the X-rays.
- Uniformity of the X-rays.

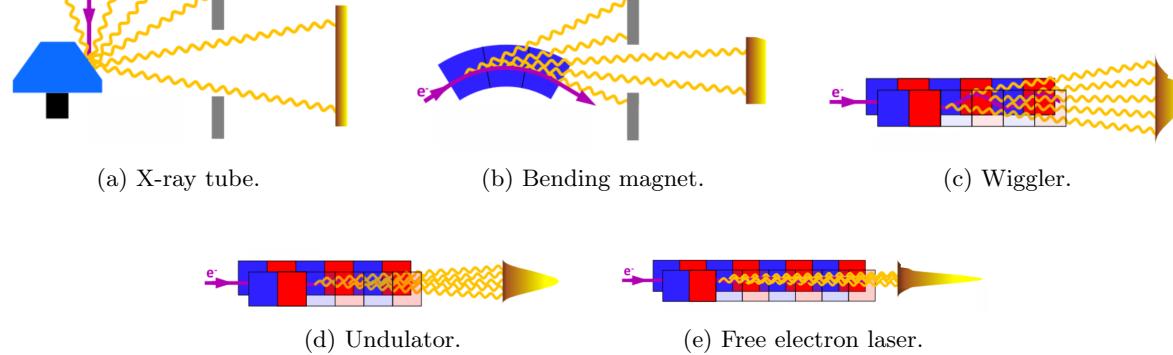


Figure 2.17: Making uniform X-rays.

- Methods of achieving uniform, collimated X-rays.
  - Bending magnets (BMs).
    - Aren't super precise.
  - Insertion devices (IDs).
    - E.g., **wiggler**s and **undulators**.
  - Free electron lasers.
  - See Figure 2.17 for schematics of all of these.
- Look for BMs and IDs in Figure 2.16.
- Dipole magnets are used to get **bends** in the **design trajectory** (or **orbit**) of the particles.
  - This is what the APS currently uses.
- The wavelength of the radiation emitted can be readily tuned by adjusting the energy of the electron beam or the magnetic-field strength.
- Undulator/Wiggler I.

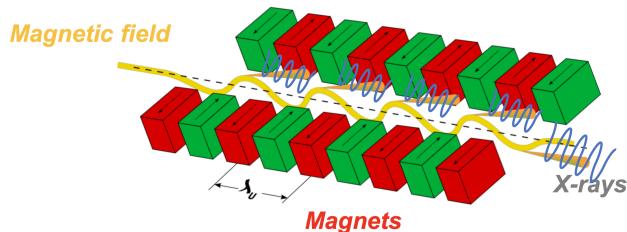


Figure 2.18: Undulator/wiggler structure.

- Undulators/wigglers are insertion devices consisting of a periodic structure of dipole magnets.
- History.
  - Vitali Ginsburg (1947): Theoretical prediction of undulators.
  - Hans Motz (Stanford, 1952): First experimental use to get coherent radiation (IR waves).
- The magnets can be permanent or superconducting.
  - Synchrotrons use the latter.
- The static magnetic field alternates along the length of the undulator with a wavelength  $\lambda_u$ .
  - So we use super small magnets?? How do we get significant enough changes in the magnetic field??
  - Electrons going through the periodic magnet structure are forced to oscillate, emitting radiation.
  - The direction of the beam is called the **longitudinal direction**.
  - The direction of the beam path is called **transverse**.
  - Electromagnetic Lorentz force from the magnetic field causes the electrons in the beam to wiggle transversely.
- Undulator/Wiggler II.
- Undulator and wiggler are similar (can be the same device): By increasing or decreasing magnetic field strength or moving permanent magnets closer or farther apart, the device can be setup as a wiggler or undulator.
- Determining if a device is an undulator or a wiggler:

$$K = \frac{eB\lambda_u}{2\pi m_e c}$$

- Variable definitions.
  - $K$  is an undulator strength parameter (characterizes the nature of electron motion).
  - $e$  is the electron charge.
  - $B$  is the magnetic field.
  - $\lambda_u$  is the spatial period of the undulator magnets.
  - $m_e$  is the electron rest mass.
  - $c$  is the speed of light.
- We cannot change  $e, m_e, c$ .
- If  $K \leq 1$ , the oscillation amplitude of the electron motion is small and we get a narrow energy distribution of X-rays.
  - The radiation produced is very intense, concentrated in narrow energy bands in the spectrum, and collimated.
  - This yields an undulator.
- If  $K \geq 1$ , then the oscillation amplitude of the electron motion is big.
  - The radiation produced lies in a broad energy distribution of X-rays.
  - This yields a wiggler.
- APS.
  - 35 sectors with 68 beamlines (22 BM and 46 undulators; no FEL).
- APS upgrade timeline.
  - Starts April 17, 2023.
  - Ends April 2024.
    - A similar upgrade at the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory is scheduled to begin in 2025.
  - Shevchenko predicts most of us will get a chance to experience it before it closes.
    - I should ask Yingjie about this!
- APS upgrade details.
  - Upgrade of the storage ring to a Multi-Bend Achromat (MBA) lattice (APS-U).
    - Will lead to dramatic improvements in the brightness of the X-rays in both ID and BM beamlines at the APS.
  - More on the major changes to the storage ring.
    - The number of photons will remain the same, but electrons will be really concentrated.
    - The energy of the electrons will be lowered from 7 to 6 GeV.
  - Don't just memorize this info, but also think about why these changes are needed.
    - For example, lowering the energy is necessary because it easier to keep the electrons in the ring (think  $mv^2/r$ ); if we didn't lower energy, we'd need either a whole new facility with a larger radius or stronger magnets (but neither of these are really reasonable).
  - Major changes to the beamlines.
    - New optimized undulators for all the beamlines (ID lines) since the energy of the electrons is changing.
    - Possibly some BM upgrades?
  - Reduction of the horizontal emittance of the machine by a factor of about 40 (the number may actually be much higher).
    - Leads to a much smaller electron beam source size.

- Free-electron laser.
  - The principle is the same as for the undulator/wiggler: Indeed, the beam passes through a periodic arrangement of magnets with alternating poles across the beam pass.
    - However, the beam of electrons (a lot of them) is accelerated to almost the speed of light (thus, these facilities are huge).
  - The released photons from an undulator are monochromatic but still incoherent because the electromagnetic waves from randomly distributed electrons can interfere constructively and destructively.
    - To solve this problem, FELs send electrons in a bunch — the radiation emitted by the bunched electrons can be in phase and hence is coherent.
    - Implies great time resolution (useful for studying CdSe, etc. by sending pulses).
  - The credit for these machines should be given to John Madley (Stanford, 1971). He built on Motz's work on the undulator.
  - The released photons are captured by mirrors in the laser cavity, inducing more electrons to emit light, resulting in amplification of the light.
  - It is very difficult to get time at these facilities.
- We now talk about some examples of high-pressure studies at APS.
- Diamond anvil cell program at GSECARRs (Sector 13).
  - Raman, infrared, visible, XRD, heat, etc. All kinds!
  - If you're planning an experiment, talk to someone at the beamline.
  - I should read that XAFS basics book more!
- A few examples will be wrapped up next time.

### 2.3 Office Hours (Shevchenko)

1/13:

- What do you want us to know about MXenes, esp. concerning variable termination groups?
  - There may be questions about these on the exams.
  - Very popular; worth Googling. One of the hottest materials in material science right now. Used for everything.
  - You take a MAX phase and etch aluminum out of it.
  - Termination: You start with a MAX phase, then using HF or some other mixture that generates it (e.g., LiF, HCl), you will etch aluminum and get these.
  - You can use molten salts for synthesis and termination of MXenes.
  - Worth introducing these materials as examples of things we can characterize.
  - Suppose we study these with XRD; how will certain peaks change/disappear?
  - Metal, carbon, aluminum. You remove the aluminum.
  - MAX phase (metal, aluminum, X for something else [carbon or nitride]).
  - A bunch of layers that are glued together with aluminum; you remove the aluminum with acid etching, yielding free-standing layers that are several atoms thick. T stands for termination. Either OH or =O groups.
  - Synthesis can be scaled up; this is why they're popular.
  - Solution at the bottom shows that you can scale it up.
  - The layers can interact via van der Waals interactions and stay together. When you do microscopy, the samples can be oriented differently.

- Lithium can intercalate into these materials.
  - As MXenes separate, fewer peaks in the small  $2\theta$  area (corresponding to big interplanar distances).
  - Don't need to know anything about the synthesis of the MAX phase; just assume it exists.
  - Different functional capping groups are useful when you want to change the functionality. OH is hard to replace; others may be easier to substitute out.
  - You can use molten salts to do etching in addition to acid; hot metal ions diffuse into the layers and remove aluminum.
  - Talapin and another guy at Drexel are very strong in MXenes. Even as a generic chemist, I will probably overlap with this type of material at some point!
- With respect to an X-ray tube, you said that reducing the tube current to 100 mA from 200 mA increases the lifetime by 50%. Are there drawbacks to doing this or any real reason not to?
    - Not information worth remembering.
    - Instruments are built to only last so long so companies don't have to do back compatibility.
  - Bremsstrahlung radiation: You called it "inelastic scattering." How? Because energy is lost to radiation?
  - Bremsstrahlung radiation: How does an increase in peak intensity result from an increase in energy of the particle to be decelerated? Is it because these higher energy particles more readily give off energy?
  - Fe, Cr, and Mn fluoresce under the Cu  $K_{\alpha}$  beam. To mitigate this effect, is it that we want to switch to an instrument that doesn't use Cu or Co, or switch from one that uses Cu to one that uses Co.
    - Switching to cobalt can work. You just have to make sure that the concerning elements don't fluoresce under the new radiation. Unless you're in a specialized lab, though, you won't have both a copper and cobalt instrument in the same lab. Cobalt is mainly used in older instruments. Best solution: Use a synchrotron, because there you can adjust the energy of electrons.
  - Working principle of a monochromator: Can't we just orient it at the angle we need to select for the wavelength we want for any suitably crystalline material? Check the derivation.
    - We do have to align the monochromator correctly.
  - Divergence slits vs. beam masks?
    - Divergence slits and masks refine the beam in different ways (vertical vs. horizontal).
    - Controls what's illuminated.
    - Shevchenko is not quite sure why we would want to do this.
    - Better than a hole just because it's easier to control.
    - You can insert these things partially.
  - What are 0D, 1D, and 2D detectors?
    - Signals get generated in every direction when your beam impinges on the sample; this just determines how many points you observe.
    - For APS, 0D and 1D are functionally the same.
    - 2D allows you to get the whole picture right away.
    - Allows us to improve the resolution of the signal if we have higher dimensions.
    - There may not be much difference though.
    - Important because companies always specify which they're machines are, so it's good to understand it.

- Detector type may not be tied to geometry.
- Takeaways from your discussion of grazing incidence XRD?
  - The two detectors move at the same pace in both, but there is a fixed offset angle.
  - Think about the surface of a thin film.
  - Initial angle is closest to your surface. At smaller angles, you have a higher chance of interacting with the thin film. Side of a piece of paper visual.
  - We don't go to all the angles, just the low ones.
  - Read more about this online.
  - We use this to study the surface.
- Clarification on primitive vs. non-primitive unit cells?
- Notation: Set of all parallel vectors pointing in the direction  $(4, -2)$  should be denoted  $\langle 4\bar{2} \rangle$ ?
- Reading space groups: Glide planes?
- To confirm, in a space group, three symmetry elements can describe the full symmetry?
- Space groups: Viewing directions for different Bravais lattices. What do we need to know?
  - We don't need to pay much attention to space groups.
  - Important for very careful analyses, new materials that need proper characterization, etc. But not important for common use.
  - Very simple questions about this only, needing common knowledge
- What is  $L$ ?
  - Just generic.
- How much do you expect we know about XRD coming in?
  - Closer to the exam, Shevchenko will say which questions on the midterm will cover which topics (this, that, or that)?
  - This is a grad-student course, so you know symmetry groups and stuff but not much about XRD.
  - One explanation will give you full credit for things when multiple factors could be relevant.
    - For example, if you observe a shift in peak positions, you could talk about compression for instance.
    - As long as you're close enough, full credit.
    - What kind of media do we use for higher compression in DACs, or what is the best pressure-transmitting medium?
  - It will be open note.
  - Last time, one student did fantastic, most did very well, and 2 struggled.