

# CHEM 30200 (Synthesis and Physical Methods in Inorganic Chemistry) Notes

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# Week 1

## Nanomaterials and Intro to XRD

### 1.1 Nanomaterials

- 1/3:
- Contact Dr. Shevchenko at eshevchenko@anl.gov or eshevchenko@uchicago.edu.
  - How to make nano.
    - Top-down approach: Start with large, end with nano. Includes nanofabrication.
    - Bottom-up approach: Solution-based approach.
      - Scalable and cheap.
      - Use an inorganic core with a coating.
  - What nanoparticles look like.
    - Differences in size, size distribution, shape, chemical composition, and structures.
    - Different sizes (like atoms) and different shapes (like bacteria and viri).
  - Ancient nanoscience.
    - The Lycurgus cup.
      - A 4th-century Roman glass cage cup.
      - Currently housed at the British Museum.
      - Contains  $\sim 70$  nm gold/silver nanoparticles.
      - When front-lit, it appears green (light is scattered by larger NPs).
      - When back-lit, it appears red (light is absorbed by NPs).
    - Hair dye.
      - 2000 years ago from Greco-Roman times.
      - Made of lead oxide ( $PbO$ ), slaked lime ( $Ca(OH)_2$ ), and water ( $H_2O$ ).
      - The lead oxide combines with sulfur-rich peptides in the hair to make  $\sim 5$  nm  $PbS$  NPs.
  - Applications of nanoparticles: Catalysis.
    - Refining of petroleum (transformation of crude oil into gasoline, jet fuel, diesel oil, and fuel oils).
    - Converter of automobile exhaust (reduction of nitrogen oxides [ $NO_x$ ] to  $N_2$  and  $O_2$ ; oxidation of  $CO$  to  $CO_2$ ; oxidation of unburnt hydrocarbons to  $CO_2 + H_2O$ ).
    - Hydrogenation of  $CO$  (synthesis of fuels such as methane or methanol).
    - Selective oxidation of hydrocarbons (synthetic fibers, plastics, and fine chemicals).
  - Methods of NP analysis: XRD, TEM, XANES, and XPS.

- Applications of nanoparticles: Displays.
  - Semiconductor nanoparticles (e.g., solutions of CdSe or InP nanoparticles) emit different colors.
  - Sony has announced that it will embed quantum dots in its latest flat-screen TV.
  - QLEDs can be made out of CdSe, CdS, InP coatings with silica, perovskite ( $\text{CsPbX}$  where  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), and cesium lead halide salts.
- Milestones in the synthesis of nanomaterials (a subjective and incomplete POV).
  - Alexei Ekimov (late 1970s-1981, USSR):  $\text{CuCl}_x$  and CdSe in molten glass matrix (fluorescence, gradient colors).
  - Alexander Afros (1982): Theoretical description of size effect.
  - Louis Brus (1983, Bell Labs, US): CdS in solution.
  - Paul Alivisatos (UChicago) and Moungi Bawendi (MIT).
  - Moungi Bawendi et al. (1993): Synthesis of monodisperse CdSe nanoparticles — a big one!
  - Philippe Guyot-Sionnest (1996): Synthesis of core/shell nanoparticles.
  - Paul Alivisatos (1997 and 2003): Synthesis of nanorods and tetrapods.
  - Chris Murray and Shouheng Sun (2000): Synthesis of magnetic FePt nanoparticles.
  - Benoit Dubert (2007, France): Synthesis of CdSe nanoplates (more stable, emission is polarized and directional).
  - Maksym Kovalenko (2015): Synthesis of perovskites.
  - Mostafe El-Sayed, Catherine Murphy, Peidong Yang, and Yunan Xia: Synthesis of Au and Ag nanoparticles.
- Synthesis of nanoparticles.
  - The 1993 Bawendi paper.
  - The innovation was the synthesis of NPs in organic solvents, still widely used today.
- LaMer model.
  - Precursors undergo nucleation, focusing, and “nano”-Ostwald ripening.
  - Key idea: Separation of nucleation and growth in time.
- Nanomaterials: State-of-the-art.
  - The chemistry behind QD synthesis is rather simple compared to what is used by organic or coordination chemists, but the field sometimes lacks depth and chemical understanding.
  - Indeed, only a fraction of reported results have been reproduced, and only a fraction of those have been understood and optimized.
  - This is a big problem for AI/ML approaches.
  - During the next 5-10 years, nanomaterials synthesis will progress mostly through systematic mechanistic studies.
- Synthesis of nanocrystals without Ostwald Ripening.
  - The nanocrystals form and grow during 0.1-1 minute after the start of the reaction.
  - Annealing at high temperatures (250-280 °C) is required to improve crystallinity.
  - No change in particle size takes place upon the annealing.
  - Tune particle size with nucleation, since growth proceeds until all monomer is consumed — fast nucleation leads to many particles, which can only grow so large; slow nucleation leads to a few particles which can grow very large (conservation of end volume).

- Synthesis with “artificial molecules.”
  - Rearrangement, addition, substitution, and elimination.
- Hollow nanocrystals: Kirkendal Effect at Nanoscale.
  - Uniform spherical cobalt nanocrystals can be synthesized by rapid pyrolysis of cobalt carbonyl in hot solvent.
  - Hollow nanocrystals form after sulfidation reaction.
- Kirkendal effect.

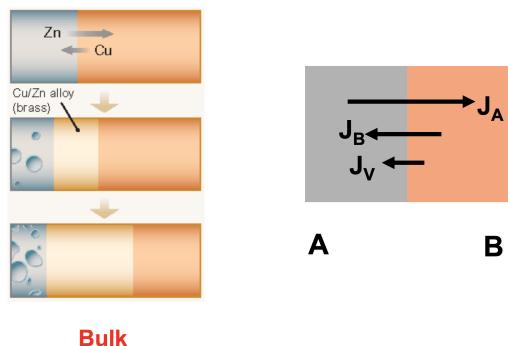
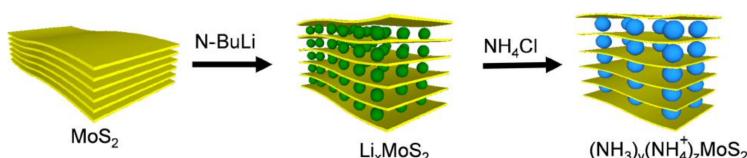


Figure 1.1: Kirkendal effect.

- Occurs when the diffusion rates of two species are different.
- When vacancies become supersaturated, they condense into voids in the fast diffusion species side.
- The Kirkendall voids result in weak bonding and lead to brittle fracture at the bonding interface.
- Top-down approaches for the synthesis of MoS<sub>2</sub>.

Figure 1.2: Top-down synthesis of MoS<sub>2</sub>.

- This is the synthesis of interlayer expanded (IE) MoS<sub>2</sub> through chemical intercalation of Li and the following exchange with NH<sub>3</sub> and NH<sub>4</sub>.
- Each MoS<sub>2</sub> layer is composed of an atomic layer of Mo sandwiched between atomic layers of S through strong ionic/covalent bonds. Weak van der Waals forces link individual MoS<sub>2</sub> layers with an interlayer spacing of 0.615 nm.
- Procedure.
  - Electron-donating species, e.g., alkali metals, Lewis bases, and organolithium compounds can intercalate between layers.
  - Alkali metals can after that be evaporated or react with water.
  - **Exfoliation** with ultrasound (mechanical exfoliation).
- Useful characterization methods: TEM, XRD, XPS.
- **Exfoliation:** The complete separation of the layers of a material.

- Bottom-up approaches for the synthesis of MoS<sub>2</sub>.
  - Chemical synthesis of interlayer expanded (IE) MoS<sub>2</sub>.
  - Chemical Vapor Deposition (CVD).
- MXene = 2D metal and surface chemistry.
  - Applications to supercapacitors, batteries, conductors, catalysts, and composites.
  - Most made out of Ti<sub>3</sub>AlC<sub>2</sub>.
- MXenes: Solution processed 2D transition metal carbides and nitrides.
  - Scanning electron microscopy (SEM) and HRTEM images shown.
  - Etching and delamination phases.
- MXenes: Variable termination groups.
  - Ask in OH??
- MXenes are solution processable 2D transition metal carbides and nitrides.
  - Lists various experimentally synthesized structures.
- What can and cannot be synthesized in solution?
  - Current solution synthesis methodology can be applied to materials that crystallize below 400 °C.  
Many materials that require higher temperatures to form, e.g., nitrides, carbides, GaAs.
  - Higher temperatures: Gas phase and solid state synthesis, as well as synthesis in molten salts.
- Nanocrystals in molten salts.
  - QDs are synthesized at high T in molten salts.
  - There is typically a postpreparative treatment phase still in molten salts.
- Nanoparticles as building blocks to make new materials.
  - The idea behind nanoparticles is encapsulated by the synthesis of NaCl from Na° and Cl<sub>2</sub>°: Two substances with certain properties combine to form a new material with very different properties.
  - Assembly of atoms leads to new materials and new properties!
- Self-assembly of nanoparticles.
  - Can be multilayered (up to five).
- Crystals of nanocrystals.
  - Example: 3D crystals (~ 30 µm) have been assembled from 3.3 nm CdSe nanocrystals.
  - Example: 3D crystals (~ 10 µm) have been assembled from 6 nm CoPt<sub>3</sub> nanocrystals.
  - More conventional example: Crystals of quartz (made by atoms).
- Binary nanoparticle superlattices.
  - Natural opal vs. synthetic opals (very similar appearance and properties).
  - Formation of binary superlattices depends on the ratio of nanoparticle radii ( $\gamma$ ), the concentration of nanoparticles, the size distribution of nanoparticles, the nature of the capping ligand, and the substrate.
  - Evaporating colloidal solutions of binary nanoparticle mixtures at 45 °C leads to the formation of binary nanoparticle superlattices.

- Periodic table of nanocrystals.
  - Different types of unit cells listed.
  - Examples include AlB<sub>2</sub>, MgZn<sub>2</sub>, Cu<sub>3</sub>Au, Fe<sub>4</sub>C, CaCu<sub>5</sub>, and CaB<sub>6</sub>.
- Directing of self-assembly of nanocrystals.
  - Various additives can be mixed in.
- Metal organic frameworks (MOFs).
  - MOFs (also called porous coordination polymers or PCPs) are two- or three-dimensional porous crystalline materials with infinite lattices synthesized from secondary building units (SBUs) — metal cations, salts, or clusters — and polydentate organic ligands with coordination type connections.
  - Common SBUs pictured.
  - From single-metal nodes to SBUs: More than 20,000 MOF structures have been reported so far.
  - Characterization methods: TEM, SEM, XRD, XANES, XPS, and electron paramagnetic resonance (EPR).
- Summary.
  - Structural information (XRD, ED).
  - Compositional information (XRD, ED, energy dispersive X-ray analysis [EDX], and X-ray fluorescence [XRF]).
  - Size and morphology of materials (TEM, SEM, and XRD).
  - Redox states of bulk and surface (XANES, XPS).
  - Important variables: Quality of synthesized materials, stability of materials during processes, and structure-property correlations.

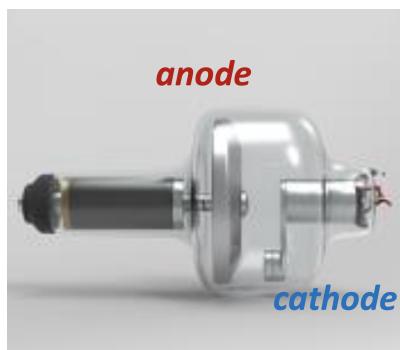
## 1.2 XRD Analysis 1

1/5:

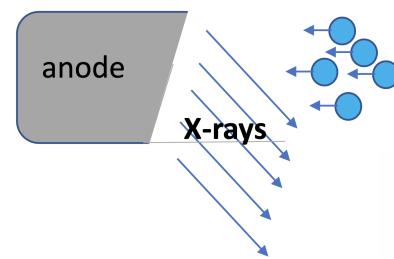
- Applications of X-ray diffraction.
  - Geology, environmental science, material science, engineering, biology.
  - Originally developed for analysis of minerals.
- What you can do with it.
  - Characterization of crystalline materials (structure, unit cell, etc.).
  - Identification of unknown/new crystalline materials (e.g., minerals, meteorites, etc.; rarely something on Earth since all of that has been extensively studied).
  - Evaluation of sample purity.
- XRD sample types: Can be used to characterize powders and thin films.
- Popular because...
  - It's relatively inexpensive.
    - There are benchtop instruments as well as larger ones.
  - It's relatively universal.
    - Standardized procedures.
  - It's nondestructive.

- Building blocks of X-ray diffractometers.
  - **X-ray tube**, sample, **backstop**, **goniometer**, **collimator**, **filter/monochromator**, **detector**, **shutter**, and **safety interlock**.
    - Basic definitions now; more on each of these devices later.
- **X-ray tube**: The shield around the X-ray tube.
- **Backstop**: The device located behind the sample that absorbs non-diffracted X-rays. *Also known as beam trap*.
- **Goniometer**: The mechanism that allows you to adjust the position of the sample relative to the incident X-ray beam.
- **Collimator**: The device that narrows the beam of X-rays.
- **Filter/monochromator**: The instrument that diffracts X-rays from a crystal to produce a beam comprising a narrow range of wavelengths.
- **Detector**: The device that measures diffraction patterns or energy spectra generated as a result of the interaction of X-rays with the sample.
- **Shutter**: The safety device (made of tungsten, tantalum, lead, etc.) inserted into the beam pass to stop all X-rays.
- **Safety interlock**: The device that stops the generation of X-rays when access to the interior part of the diffractometer is possible.
- How are X-rays generated?
  - Originally with a **Crookes tube**.
- **Crookes tube**: A type of discharge tube that facilitated the initial discovery of X-rays.
  - History.
    - Invented between 1869-1875 by William Crookes, who also discovered thallium.
    - Wilhelm Roentgen was responsible for the initial discover of X-rays — using a Crookes tube — in 1895.
  - Design.
    - Cold cathode vacuum tubes (no heated filament; these emit more electrons than can be supplied by thermionic emission alone).
    - Relies on electron emission induced by an electrostatic field or secondary electron emission.
    - Requires a small amount of gas (air) in them to function ( $10^{-6}$ - $5 \times 10^{-8}$  atm).
    - High voltage is applied to the tube.
    - Electric current causes the ionization of gas molecules: Electrons “knock off” electrons from other gas molecules forming positive ions and negative electrons (negative ions are also formed as a result of electron interactions with neutral gas molecules).
    - High velocity electrons hit the anode (metal) that creates the X-rays.
- The first images obtained using X-rays.
  - The first medical X-ray was by Röntgen (alternate spelling of Roentgen) of his wife in 1885.
    - It led Roentgen to win the first ever Nobel in physics in 1901.
  - People started making X-rays of their bones just for fun — like taking selfies — without realizing the harm of X-rays.
  - Some doctors notice improvement in cancer patients after X-ray exposure.

- X-rays were discovered accidentally.
  - A Crookes tube was wrapped in black cardboard to block the visible light.
  - A fluorescent screen painted with phosphor barium platinocyanide ( $\text{Ba}[\text{Pt}(\text{CN})_4]$ ) was  $\sim 1\text{ m}$  away.
  - When the tube was activated, the screen glowed green.
- Limitations of Crookes tubes.
  - X-rays originate from a rather large area. Thus, the resulting X-ray images lack contrast.
  - Low intensity of X-rays; necessitates long exposures of the object.
- Thus, Willian Coolidge develops the Coolidge tube in 1913.
  - This is a hot cathode tube.
  - It works with a much higher vacuum ( $\sim 10^{-9}\text{ atm}$ ).
  - Irving Langmuir designs an “extreme vacuum” with a new pump design (the Langmuir pump).
  - This enabled generation of an electron current using a hot thermionic filament as the cathode.
  - Other improvements.
    - Replaced Pt target with W.
    - Mo shield to focus the X-rays.
  - These improvements led to...
    - An X-ray source of remarkable brilliance and reliability;
    - Control over intensity and hence penetrating power.
  - Since then, basically nothing has changed, though we did start using rotating anodes (see below).
- Working principle of the X-ray tube.



(a) Overall design.



(b) Electrons to X-rays.

Figure 1.3: X-ray tube design.

- The **cathode** heats up and induces thermionic emission of a cloud of electrons.
- The **anode** attracts the electrons across the vacuum tube.
- The anode converts the energy of incident electrons into X-rays, dissipating heat as a byproduct.
- You rotate the anode very fast (up to 10 000 rpm) to prevent it from overheating (can get up to  $2000^\circ\text{C}$ ). This is why you often have a cooling system in high-power X-rays.
- The anode is a beveled disk (shaped to focus the X-rays).
- Most X-ray tubes have an **anode angle** of 12-15°.
  - A smaller angle results in a smaller effective **focal spot**.

- **Cathode:** The negatively charged filament.
- **Anode:** The positively charged disk. *Also known as anticathode.*
- **Anode angle:** The angle between the vertical and the target surface.
- **Focal spot:** The surface area on the anode over which X-rays are produced.



Figure 1.4: Anode focal spot.

- Naturally, increasing the angle will allow the electrons to spread out over more area.
- Design of the X-ray tube.

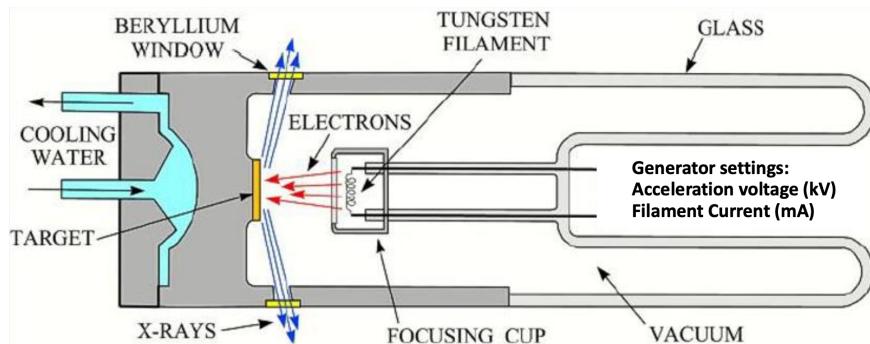


Figure 1.5: Schematic cross section of an X-ray tube.

- Beryllium is used as a window because it doesn't absorb X-rays, even though it's toxic.
- Beryllium has low X-ray absorbance because it is a very small atom. In technical terms, it has low **contact** (see below).
- A few practical comments on the anode (filament).
  - Lifetime of  $\sim 2000$  h (at  $\sim 50$  kV and 200 mA).
  - Reducing the tube current to 100 mA increases the lifetime by 50%.
    - Are there drawbacks to doing this?? Less intense X-rays, perhaps? Ask in OH.
  - The lifetime of the cathode depends on the number of times the X-ray source is turned on and off.
    - Turning the XRD system on and off stresses the filament as well as other components.
    - It is better to keep the XRD system on and in stand-by settings (power of  $\sim 20$  kV and current of  $\sim 10$  mA).

- The spectrum of X-rays generated in an X-ray tube.

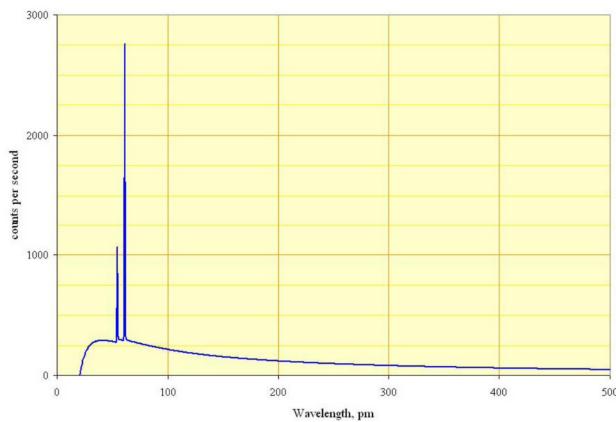


Figure 1.6: The spectrum of X-rays generated in an X-ray tube.

- The spectrum is a smooth, continuous curve with spikes.
- Implies two types of radiation: **Bremsstrahlung radiation** and **Characteristic radiation**.
- You want to get rid of the Bremsstrahlung radiation.
  - The ultimate goal is to get your X-ray tube to emit only a single wavelength at high intensity, and the natural choice is the highest characteristic peak. Thus, everything else must go.
- Bremsstrahlung radiation:** Electromagnetic radiation generated via deceleration of a charged particle when deflected by another charged particles (e.g., electrons by protons). *Also known as braking radiation, continuous X-radiation.* *Etymology* **bremsstrahlung** from German *bremsen* “to brake” and *strahlung* “radiation.”

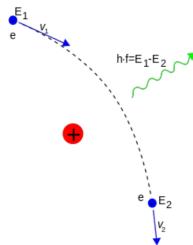


Figure 1.7: Generation mechanism for bremsstrahlung radiation.

- The charged particle loses kinetic energy via generation of photons (law of conservation of energy).
  - How is this “inelastic scattering??” What does that even mean? Ask in OH.
- If you work with high-Z (proton number) elements, these nuclei generate a rather strong electric fields.
- Strong electric fields scatter the electrons.
- The spectrum of these X-rays is continuous (hence the moniker “continuous X-rays”).
- The frequency of bremsstrahlung radiation is limited by the energy of incident electrons.
- Peak intensity shifts toward higher frequencies when the energy of the decelerated particle (particle to be decelerated) increases.
- Peak intensity increases when the energy of the decelerated particle increases.
  - Rationalizing these last two statements?? Ask in OH. Related to current and voltage below??

- X-ray notation for atomic energy levels.

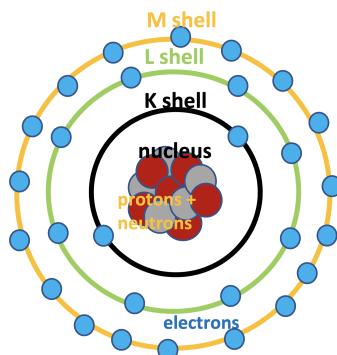


Figure 1.8: Energy levels in the Bohr model.

- The K, M, and L shells correspond to energy levels  $n = 1, 2, 3$ , respectively.
- Somewhat antiquated notation from the early days of X-ray invention when the Bohr model was still popular.
- Contribution of Bremsstrahlung.

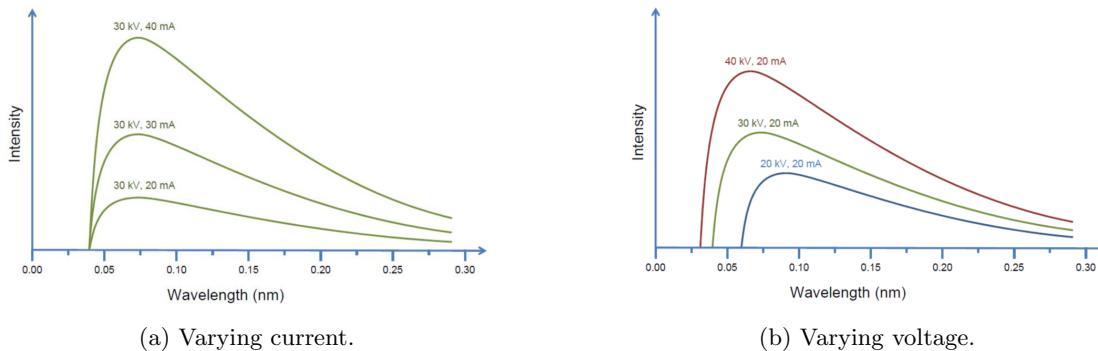


Figure 1.9: X-ray intensity vs. wavelength at different voltages and currents.

- The distribution of intensity (photon counts) against the wavelengths of the emitted radiation.
- Two settings you can change during the measurement: Current and voltage.
  - When you increase the current, the intensity increases (more electrons means more counts per second).
  - When you increase the voltage, the intensity increases and the peak shifts to higher frequencies (higher energy electrons means higher energy [resp. frequency] radiation).
- See **Kramer's law** and its consequence the **Duane-Hunt law** for more on the functional form of these curves. Note that these curves are different from the Planck blackbody distribution law, even though they look somewhat similar.
- **Kramer's law:** The law describing the spectral distribution of X-rays produced by electrons hitting a solid target. *Given by*

$$I(\lambda)d\lambda = K \left( \frac{\lambda}{\lambda_{\min}} - 1 \right) \cdot \frac{1}{\lambda^2} d\lambda$$

- The proportionality constant  $K$  is **contact**.
- $\lambda_{\min}$  is the  $x$ -intercept in Figure 1.9.

- **Contact:** A quantity proportional to the atomic number of the target element. *Denoted by  $K$ .*
- **Duane-Hunt law:** The relationship between the voltage  $V$  applied to an X-ray tube and the maximum frequency  $f$  of the  $x$ -rays emitted from the target. *Given by*

$$f = \frac{Ve}{h}$$

– Note:  $e = 1.602 \times 10^{-19} \text{ C}$  is the electron charge and  $h = 6.626 \times 10^{-34} \text{ Js}$  is Planck's constant.

- **Characteristic emission:** The emission of quantized photons with energy corresponding to the energy difference between higher and lower states in the target atoms.
- Mechanism of characteristic emission.

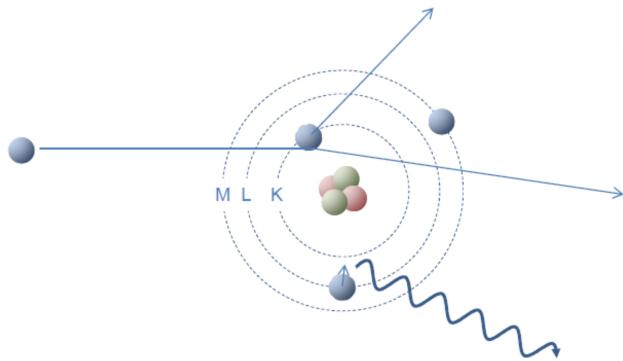


Figure 1.10: Generation mechanism for characteristic radiation.

- The target element is bombarded with high energy electrons.
- Incident electrons can knock orbital electrons out of the inner shell of the target atom.
- When this happens, the atom is left with a **core hole**.
- Outer shell electrons fill the vacancy, losing energy in the form of X-radiation to do so.
- Results in emissions characteristic of the target element (each element has unique energy levels).
- The maximum energy of the generated X-ray photon is limited by the energy of the incident electron, which is equal to the voltage on the tube times the electron charge.
- **Core hole:** A vacant energy level in the core electron shell.
- We often use copper as the target element.

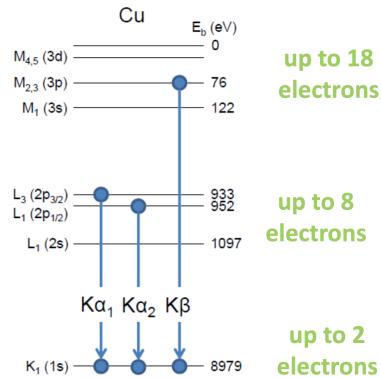


Figure 1.11: Copper spectral lines.

- The copper  $K_\alpha$  line has greater intensity than the  $K_\beta$  one and thus is more desirable in diffraction experiments.
- The same holds true in many elements, including the occasional alternative molybdenum.
- Achieving monochromatic emission.
  - The X-rays are released from the anode with a range of energies.
    - There are continuous X-rays produced by the X-ray tube,  $K_\beta$  rays, and fluorescent X-rays from the sample.
  - Applications require monochromatic X-rays, so all of these (except the desired  $K_\alpha$  ray) need to be filtered out.
  - X-rays of undesirable energies can be filtered using **filters** and **monochromators**.
  - You need filters to make the spectrum of X-rays really narrow??
- X-ray filters.

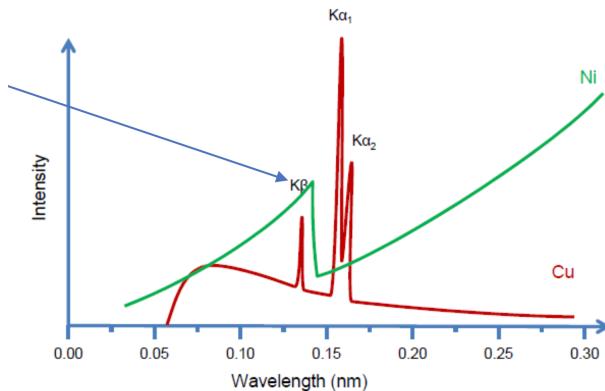


Figure 1.12: Nickel filter for a copper anode.

- The filter is usually made of a metal that has one proton less than the anode material (e.g., Ni filter for Cu anode and Nb filter for Mo anode).
- Main purpose: To filter the  $K_\beta$  line.
- The filtering of  $K_\beta$  line depends on the thickness of the filter material.
- Example: The absorption edge of nickel metal is at 1.488 Å. This is between the  $K_{\alpha_1}$  ( $\lambda = 1.542 \text{ \AA}$ ) and  $K_\beta$  ( $\lambda = 1.392 \text{ \AA}$ ) X-ray spectral lines of copper. Hence, nickel foil of an appropriate thickness can be used to reduce the intensity of the Cu  $K_\beta$  line.
  - In particular, nickel foil of thickness 20 μm is typically used. It reduces the  $K_\beta$  intensity by 99% and the  $K_\alpha$  intensity by only 58%.
- X-ray targets.
  - Most popular anode is Cu, but can be Co as well.
  - Fe, Cr, and Mn fluoresce under the incident Cu  $K_\alpha$  beam, resulting in polychromatic radiation and alteration of the XRD results (strange shapes and elevated background).
    - Implication: Be careful if you see something unusual in your spectra. We may not have won a Nobel prize for something novel; it could just be Fe, Cr, or Mn contamination of the sample.
  - In this case, seek out an instrument that doesn't use Cu or Co as the target element.
    - Or is it that we want to switch from Cu to Co in this case??

- Monochromators.
  - Main purpose: To remove all X-rays but the  $K_{\alpha}$  ones.
  - The monochromator is a crystal.
  - The monochromator works by reflecting wavelengths that obey Bragg's Law (see next lecture and Labalme (2022)) for the particular  $d$  spacings of the monochromator.
  - Desired characteristics.
    - The crystals should have suitable interplanar distances  $d$  so that the desired wavelength  $\lambda$  can be obtained.
    - The crystals must be mechanically strong and stable in the beam. This is why graphite and silicon are so popular.
    - Low absorbance of X-rays (we are interested in reflection).
    - Easy to grow single crystals at a reasonable cost.
  - Examples: pyrolytic graphite crystals, Si, Ge, LiF, and LiCl.
    - PG crystals and Si are particularly popular choices.
    - Graphite is a broad band monochromator: The variance around the allowed  $\lambda$  is relatively large due to its **mosaicity**.
    - In contrast, silicon is a narrow band monochromator.
  - With copper, the Bragg equation gives a very small difference in Bragg angle between  $K_{\alpha_1}$  and  $K_{\alpha_2}$ . Thus, we need a narrow band monochromator such as Si.
- **Mosaicity:** The spread of crystal plane orientations.
  - Essentially, less perfect crystals have planes that aren't perfectly aligned, creating spread.
- Effect of monochromators.

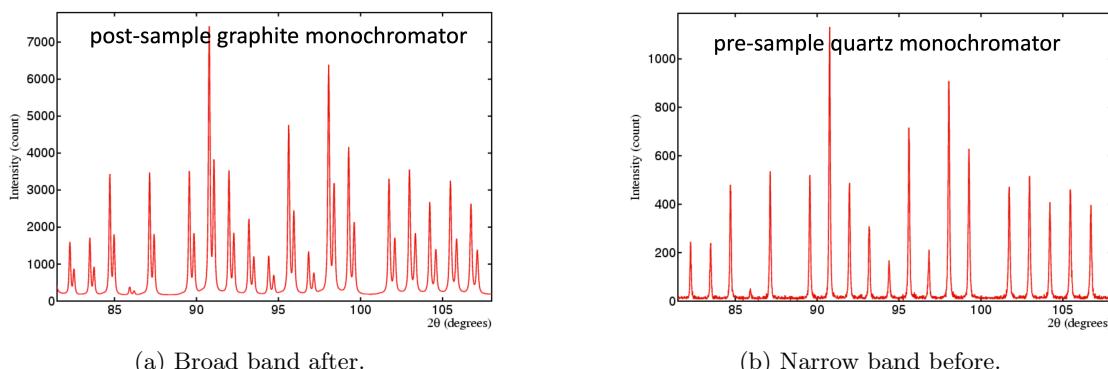


Figure 1.13: Effect of monochromator type and placement.

- Monochromators can be placed before or after the sample.
- Most instruments have both.
- The spectrum in Figure 1.13a was collected using a broad band monochromator after the sample.
  - Splitting of the diffraction peaks is due to the presence of both  $K_{\alpha_1}$  and  $K_{\alpha_2}$  radiation.
- The spectrum in Figure 1.13b was collected using a narrow band monochromator before the sample.
  - Benefit: The peaks due to  $K_{\alpha_2}$  radiation are removed.
  - Drawback: Diffraction intensity is decreased.

- Working principle of the monochromator.
  - Monochromators work based on Bragg's law ( $\lambda = 2d \sin \theta$ ) for the particular  $d$  spacings of the monochromator.
  - Let's investigate how a silicon monochromator can select for the  $K_{\alpha_1}$  line of copper.
    - Silicon has a cubic crystalline lattice with side length 0.543 nm.
    - Thus, the spacing of the 111 planes is

$$d_{111} = \sqrt{\frac{0.543^2}{1^2 + 1^2 + 1^2}} = 0.3135 \text{ nm}$$

- Using this value and the known wavelengths of the copper  $K_{\alpha_1}$  and  $K_{\alpha_2}$  lines (i.e.,  $\lambda = 154.051 \text{ pm}$ ,  $154.433 \text{ pm}$ , respectively), we can use Bragg's law to calculate the angle  $2\theta$  at which we should orient the silicon 111 planes relative to the incident X-rays in order to select for one line or the other. In particular, if we want to select for the copper  $K_{\alpha_1}$  line, we should use the angle of incidence

$$2\theta = 2 \sin^{-1} \left( \frac{\lambda}{2d} \right) = 2 \sin^{-1} \left( \frac{154.051 \text{ pm}}{2 \cdot 313.5 \text{ pm}} \right) \approx 28.442^\circ$$

- Owing to its high crystalline purity (low mosaicity), silicon at this angle can select for the desired wavelength.
- Graphite monochromators will pass both  $K_\alpha$  wavelengths, but not  $K_\beta$  for which the Bragg angle is considerably different.
- Silicon has a peak position at 28.46. This number is right between the copper peaks; thus, it can separate the  $K_{\alpha_1}$  and  $K_{\alpha_2}$  wavelenghts from a laboratory X-ray source??
- Is this all correct??

- Filters vs. monochromators.

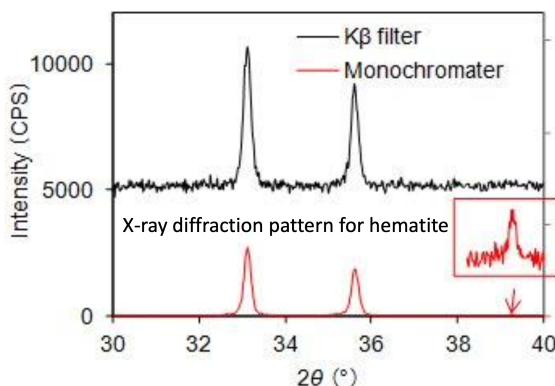


Figure 1.14: Filters vs. monochromators.

- Metal filter vs. a crystal monochromator.
- By using a monochromator, it is possible to obtain X-ray diffraction patterns with high signal-to-background ratios since the monochromator can remove interfering components such as continuous X-rays produced by the X-ray tube,  $K_\beta$  rays, and fluorescent X-rays from the sample.
- Notice the extra noise in the spectrum taken with a  $K_\beta$  filter in Figure 1.14.
- One nice thing about using a filter, though, is that you preserve more intensity (monochromators rely on relatively low-probability reflection events as opposed to high probability transmission events).

- Beam divergence.

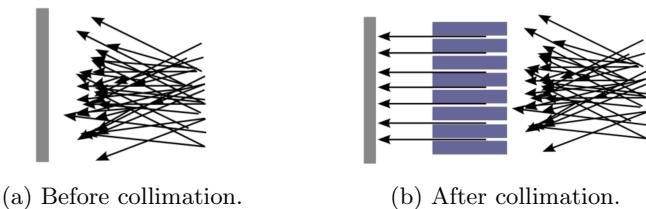


Figure 1.15: Collimator function.

- A generated X-ray beam is far from perfect; the X-rays go in many directions.
  - Solution: Use a collimator.
    - Typically lead, but can be tungsten, molybdenum, tin, bismuth, high density plastics, etc.
      - Lead is preferred because of its high density and low cost.
    - Mechanism: Most X-rays get absorbed; the right ones (straight forward ones) pass through.
  - How a diffractometer is made.

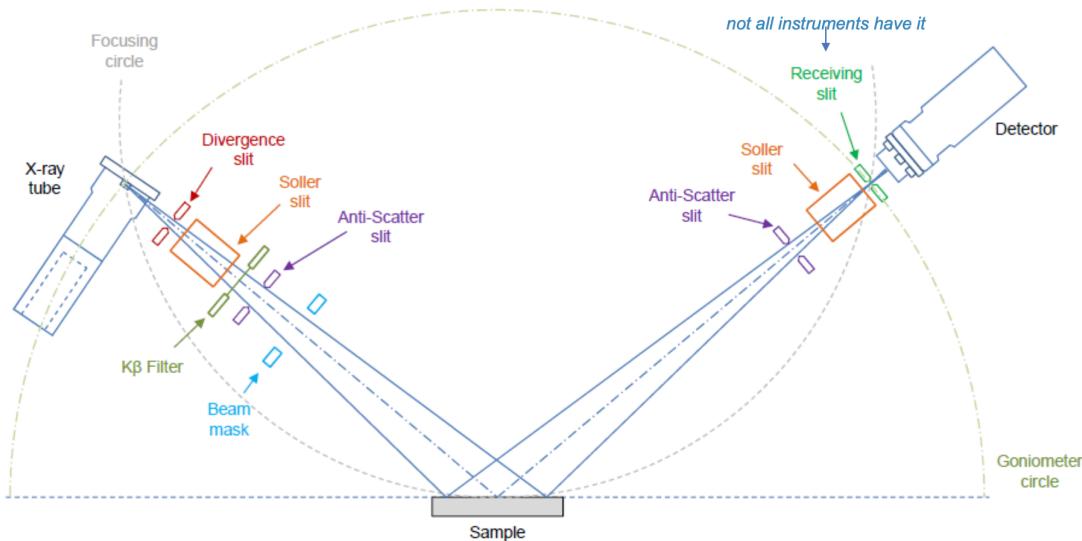


Figure 1.16: Typical diffractometer configuration.

- X-rays are generated and emitted by an X-ray source.
  - Next, they pass through a **divergence slit**, which limits the total irradiation area of the sample.
    - At higher  $2\theta$  angles, less area is irradiated, which decreases diffraction intensity. The depth of penetration of the beam becomes commensurably deeper with higher angles.
  - Then its into the sample chamber.
  - After that, they pass through **scatter slits**, which address the scattering because of “too thick” samples, rough samples, scattering from the substrate or material matrix, etc.
  - Another round of slits is the **Soller slits**.
  - The final “filter” is a monochromator, which removes 75% of the unwanted wavelengths.
  - Finally, the X-rays arrive at the detector.

- There is another diffractometer schematic and a labeled picture of an actual one in the slides.
- Examples of slits and masks.
  - **Divergence slits, beam masks, programmable divergence slits**, and Soller slits.
- **Divergence slit:** A piece of metal with an opening of a certain width.
- Fixed vs. variable divergence slits.

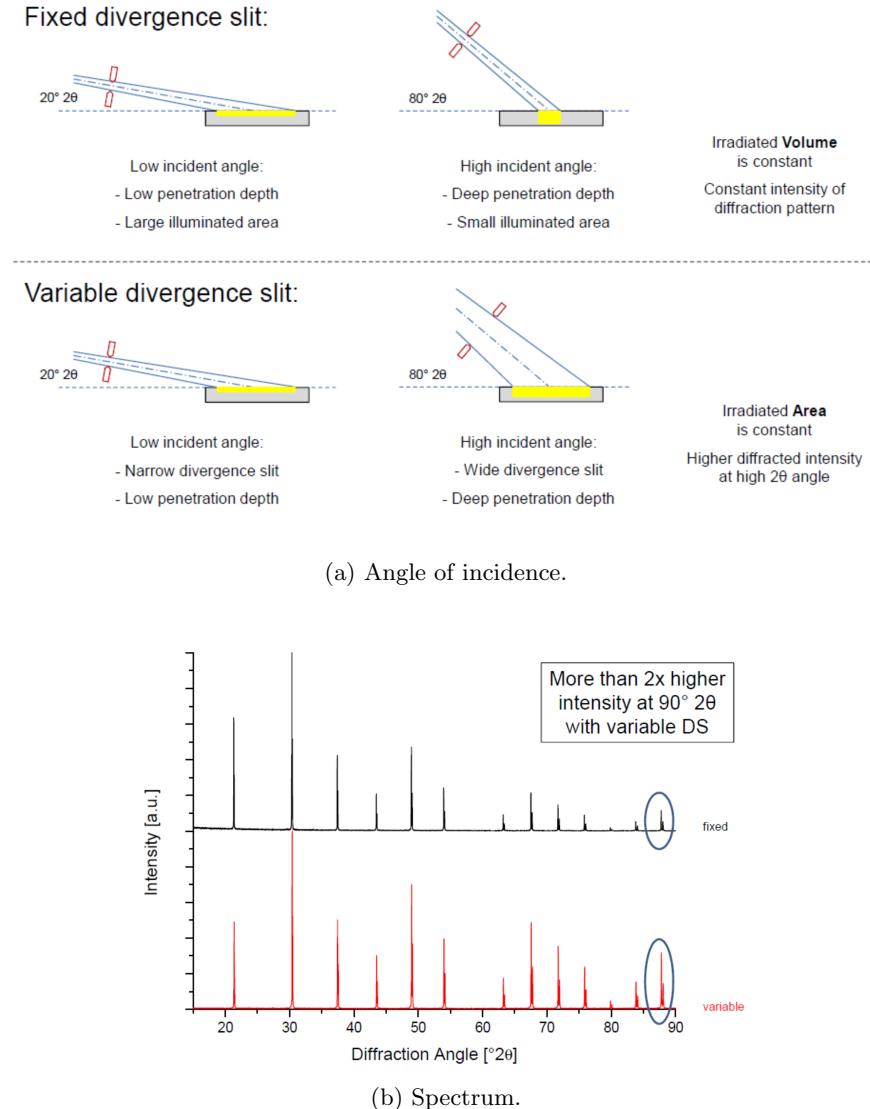


Figure 1.17: Fixed vs. variable divergence slits.

- Fixed divergence slit: As the angle changes, the amount of surface area illuminated decreases.
- With a variable divergence slit, we can solve this issue.
- Signals are the same at low  $2\theta$ ; signals differ in intensity at high  $2\theta$ .
- **Beam mask:** Similar to a divergence slit.
- **Programmable divergence slit:** A divergence slit with slots for a beam mask, Soller slits, and attenuation foil or a  $\beta$ -filter.

- **Soller slits:** A stack of metal films that enable removal of  $\sim 99\%$  of the unwanted wavelengths of radiation from the beam. *Also known as receiving slits, RSm slits.*
  - These are a part of the instrument and you cannot touch them.
  - Not all instruments have these.
- Most common targets for X-ray tubes.
  - Usually copper, especially for crystallography.
  - Medical X-ray tubes use tungsten.
  - Softer X-rays are needed for mammography, so molybdenum is used.
- Detectors.
  - For lab experiments, the characteristic emission lines of metal targets such as Cr, Cu, Co, and Mo are used in X-ray tubes.
  - Therefore, the detector should detect X-ray photons with energies in the range of 5-20 keV. The background bremsstrahlung photons (an unwanted byproduct) have energies up to 55 keV.
  - There are two types of detectors.
    - (i) **Photon counting** detectors.
    - (ii) **Integrating** detectors.
- **Photon counting** (detector): A detector that, during a measurement, converts the energy of each individual photon into a charge and registers the charge package. *Also known as digital.*
- **Integrating** (detector): A detector that integrates (or “adds up”) the charge that is generated due to the conversion of the photon’s energy into electric charge. *Also known as analog.*
  - The energy information of the photons that are detected is lost and cannot be recovered.
- Types of the detectors.
  - **Point, linear, and area** detectors.
  - These are 0D, 1D, and 2D, respectively.
  - What are these??
  - Typical brands listed.
- **Point** (detector): A detector in which the receiving slit determines the active height.
- **Linear** (detector): A detector comprised of a linear array of solid state detectors.
- **Area** (detector): A detector comprised of a 2D array of solid state detectors.
- What regimes are used in different instruments?
  - Powder sample?
    - The scanner moves along a line.
  - Other important takeaways here??
- Examples of detectors.
  - Bruker uses a 1D detector and a Ni filter.
  - Certain Panalytical machines also use a 1D detector and a Ni filter.
  - Another type of Panalytical machine uses a 0D detector and a graphite filter.
  - We can’t change the detectors.

- Bragg-Brentano geometry.

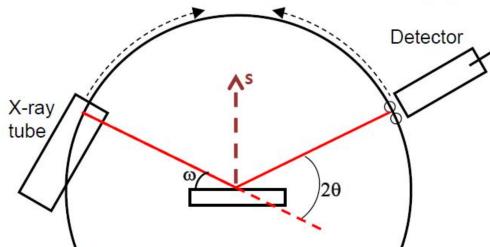


Figure 1.18: Bragg-Brentano geometry.

- Many diffractometers use this parafocusing geometry.
  - Most common; can be used in all types of analysis.
  - Efficiency is not that great for thin films, though.
- The incident- and diffracted-beam slits move on a circle that is centered at the sample. X-rays from the source hit the sample at different points on its surface. During the diffraction process, the X-rays are refocused on the detector slit.
- The incident angle  $\omega$  between X-ray source and the sample is always half of the detector angle  $2\theta$ .
- Two types of setups.
  1. Fixed X-ray tube: The sample rotates at  $\theta/\text{min}$  and the detector is always at  $2\theta/\text{min}$ .
  2. Fixed sample: The tube rotates at the same rate as the detector at  $\theta/\text{min}$ .
- Sample surface is kept on the tangent plane of the **focusing circle**.
- **Focusing circle:** The circle lying in the unique plane containing the sample, X-ray source, and receiving slit.
- Grazing incidence XRD.
  - Helps with thin films.
  - Other takeaways??
- The X-ray spectrum.

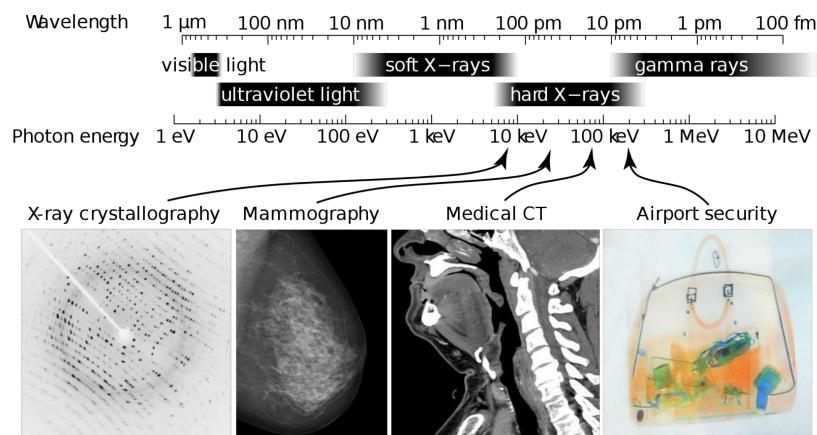


Figure 1.19: X-ray spectrum.

- Airport (1000 keV), medical (100 keV), mammography (10 keV), X-ray crystallography (8 keV).

- Applications of X-ray diffraction.
  - Same slide as at the beginning.
  - Shevchenko is really good at circling back to things over and over again so they stick!
- Diffraction basics.
  - X-rays interact with matter, resulting in **absorption**, **elastic scattering**, and **inelastic scattering**.
- **Absorption:** The energy of the incident photon has to be larger than the **ionization energy threshold** of an atom or molecule, or the **work function** of a metal.
  - Results in the photoelectric effect, which in turn leads to **fluorescence**.
  - Extremely beneficial for elemental analysis.
  - Absorption is not something we want to see in XRD.
    - See earlier discussion of fluorescence.
- **Fluorescence:** The two step process consisting of (1) absorption of radiation by an atom and ionization and (2) relaxation and emission of characteristic radiation.

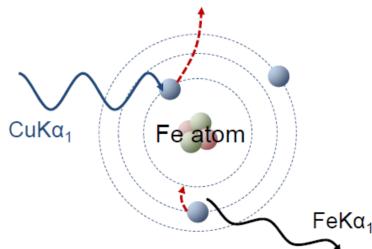


Figure 1.20: Absorption and fluorescence.

- **Elastic scattering:** Only the *direction* of the scattered photon changes, without changing its initial energy. *Also known as Thomson scattering.*
  - The scattering of optical light from electrons was first observed in 1906 by J. J. Thomson.
  - X-rays are scattered at the electrons of the atomic shell.
  - X-ray diffraction is a special case of elastic scattering.
- **Inelastic scattering:** The interaction of X-ray photons with a charged particle (electron) resulting in a decrease in energy of the photon. *Also known as Compton scattering.*
  - First observed by Arthur Compton in 1923.
  - The frequency shift has been explained by the momentum transfer of light quanta to the electrons of the material. This provided direct evidence for the quantum nature of light.
  - Initial energy of the photon is *changing*.
- Why X-rays?
  - X-ray scattering experiments have played a central role in nearly all areas of physics, chemistry, and material science to study microscopic structure and the state of matter.
  - We use X-rays because the interatomic distances in crystals are between 0.15-0.4 nm and X-ray wavelengths span this range. Thus, the match is perfect for structure determination.
  - Indeed, interference phenomena are possible only for features of about  $\lambda$ .

- The first use of X-rays to study crystal structure.
  - Reported by Max von Laue (Nobel Prize 1914).
  - Laue considered crystals in terms of a 3D network of rows of atoms. His analysis is based on the notion that crystals are like 3D diffraction gratings.
  - Laue utilized white X-radiation (broad spectrum, unfiltered).
  - The diffraction spots that surrounded the central spot of the primary beam could be explained as an interference pattern due to the crystal's space lattice. Each spot was caused by X-rays that corresponded to a certain lattice constant and wavelength.
- Bragg's law.
  - Obtained as a result of experiments by William Lawrence Bragg and his father, Sir William Henry Bragg in 1912.
  - Nobel Prize (1915) for their work determining the crystal structures of NaCl, ZnS, and diamond, and for "their services in the analysis of crystal structure by means of X-rays."
  - The Bragg spectrometer had an X-ray tube, filters, collimators, a crystal sample, and a detector.
- The principle of Bragg's law.
  - We'll start here next class.
- Write out ppt. notes ahead of time next time!

# 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?

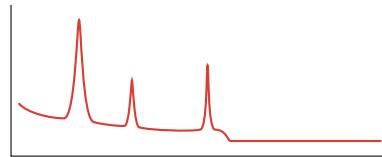


Figure 2.1: Enhancing XRD results.

– 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.

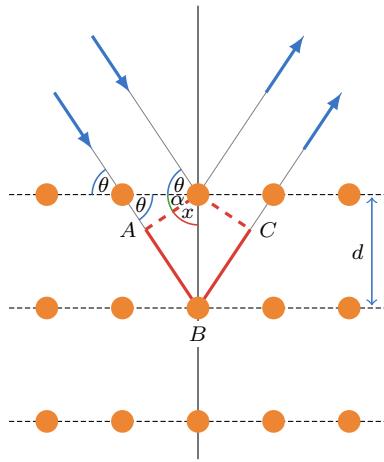


Figure 2.2: Bragg’s Law derivation.

- 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.

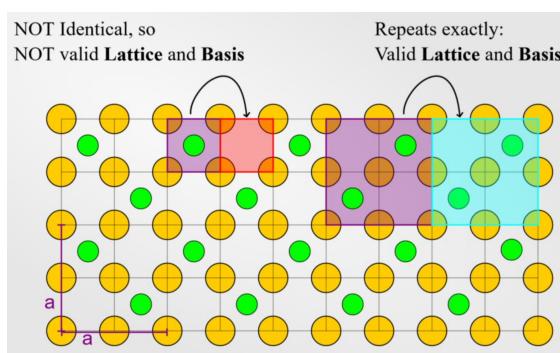


Figure 2.3: Decomposition of a crystal into its Bravais lattice.

- 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.

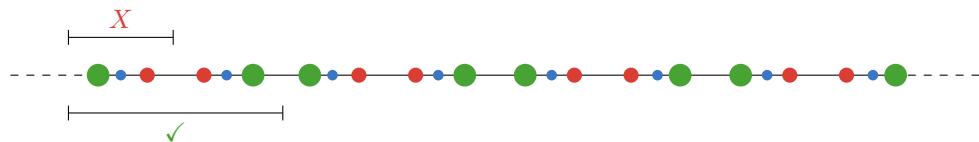


Figure 2.4: 1D Bravais lattices.

- 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.

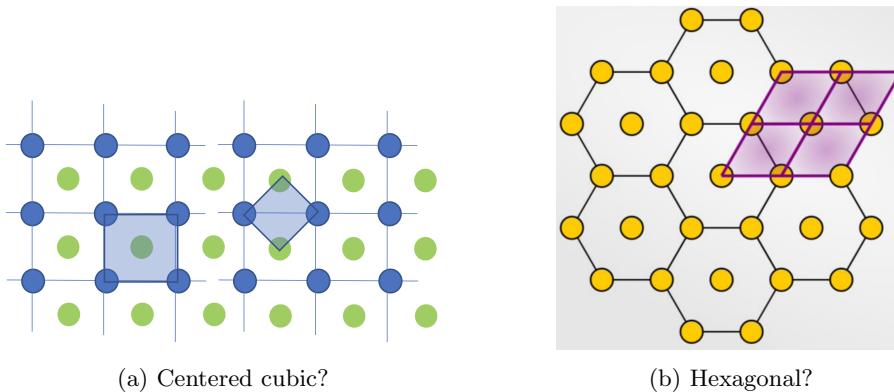


Figure 2.5: 2D Bravais lattices.

- 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 ( $a \neq b, \theta \neq 90^\circ$ ).
- 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.

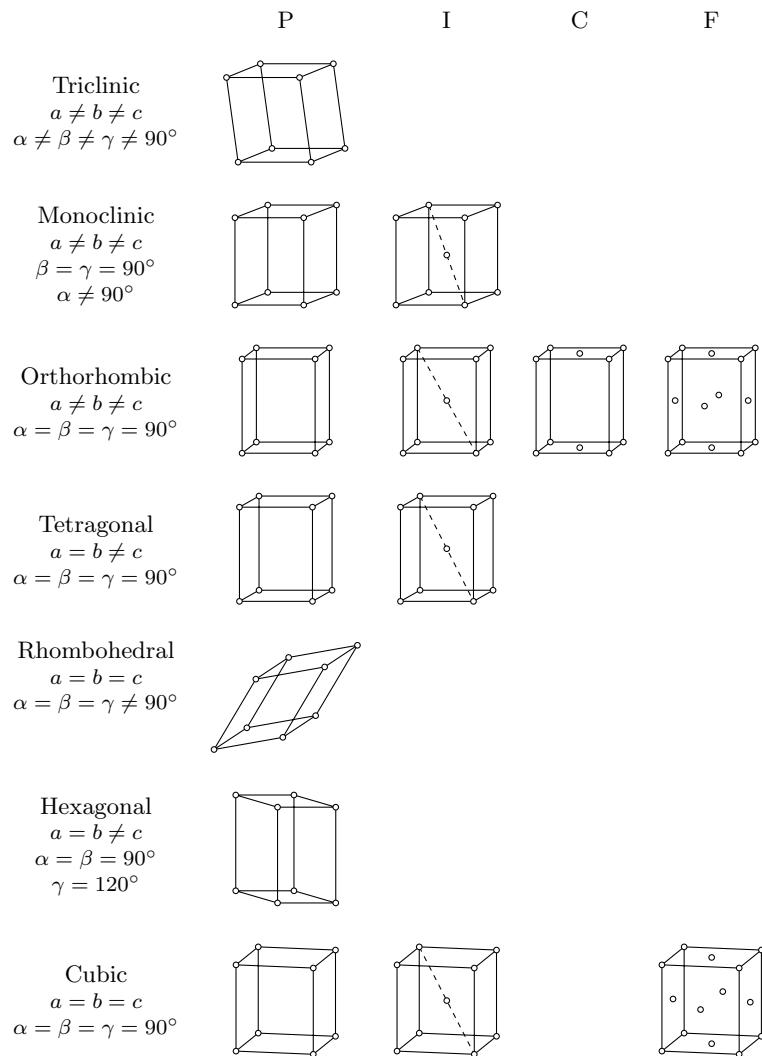


Table 2.1: Bravais lattices.

- 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.

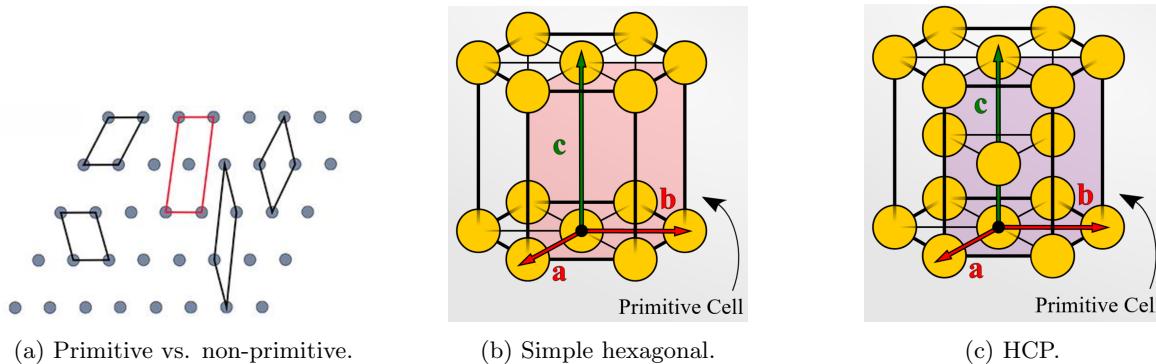


Figure 2.6: Conventional vs. primitive cells.

- 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.

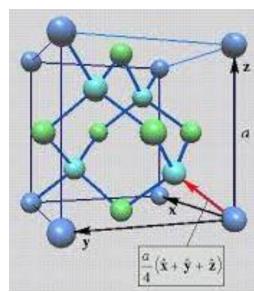


Figure 2.7: Diamond crystal structure.

- 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.

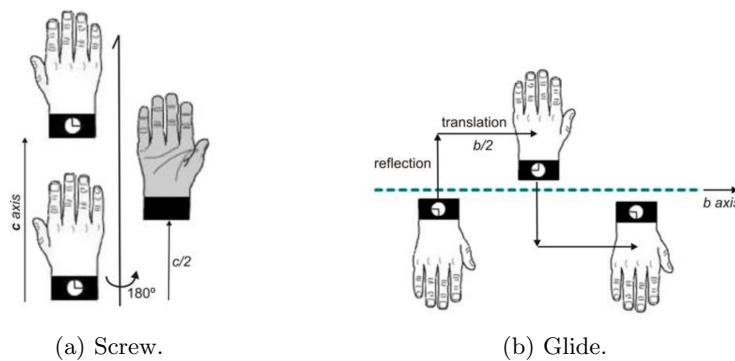


Figure 2.8: Screw and glide operations.

- 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	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.

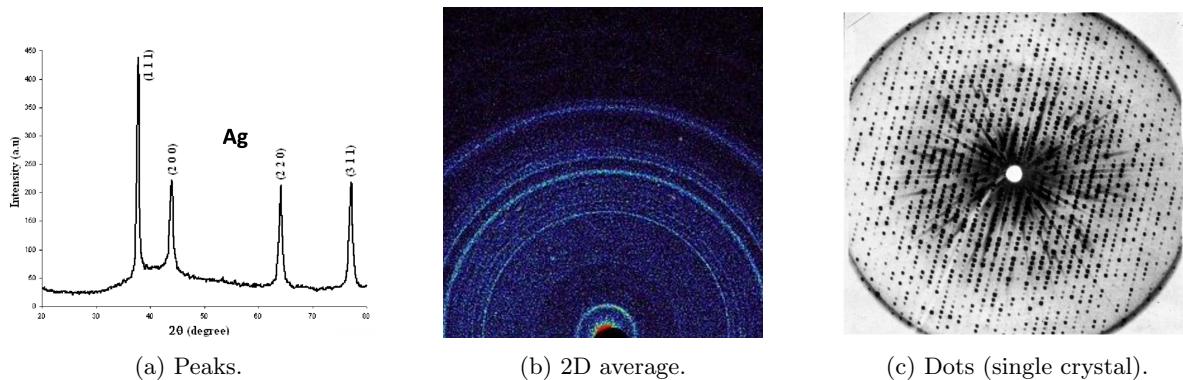


Figure 2.9: Diffractogram types.

- 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.

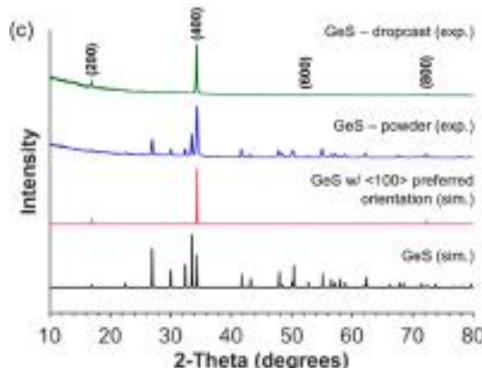


Figure 2.10: Preparation strategies vs. XRD clarity.

- 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.

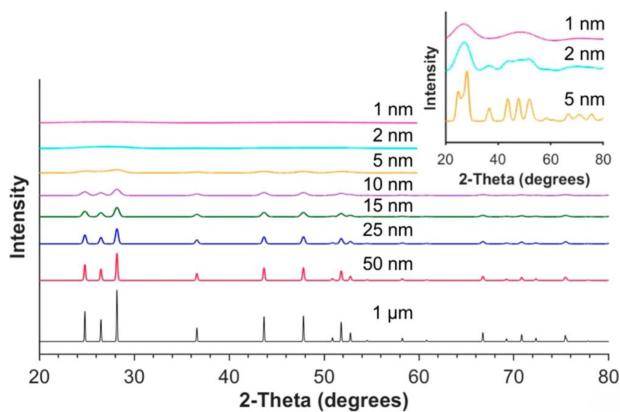
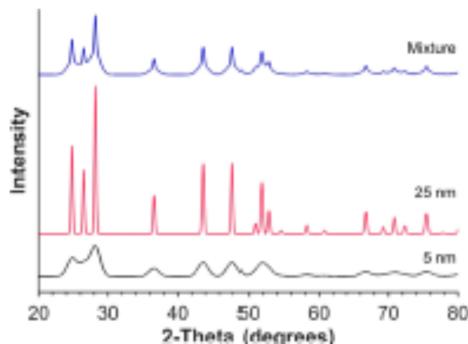


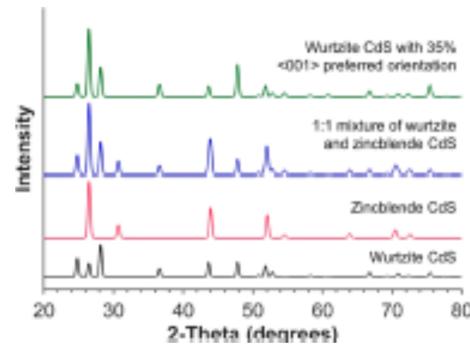
Figure 2.11: Resolution increases with larger crystal size.

- 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).

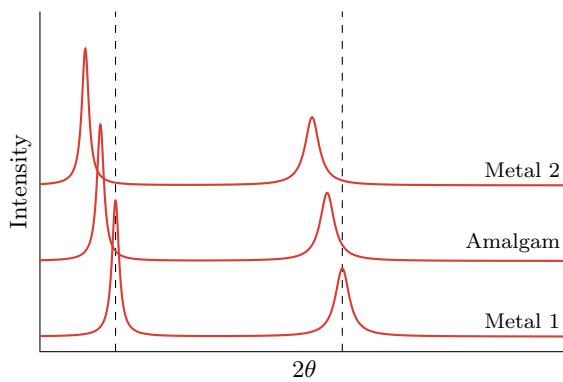


Figure 2.13: Vegard's law.

- Effect of strains.

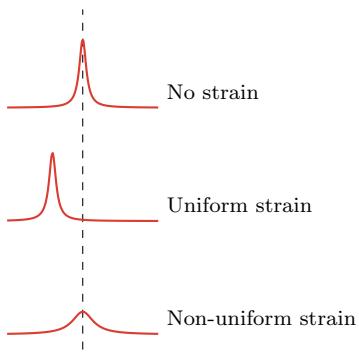


Figure 2.14: Strains.

- 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.**

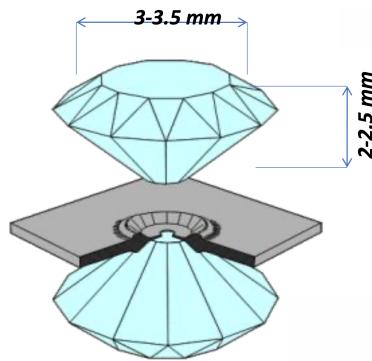


Figure 2.15: Diamond anvil cell.

- 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.

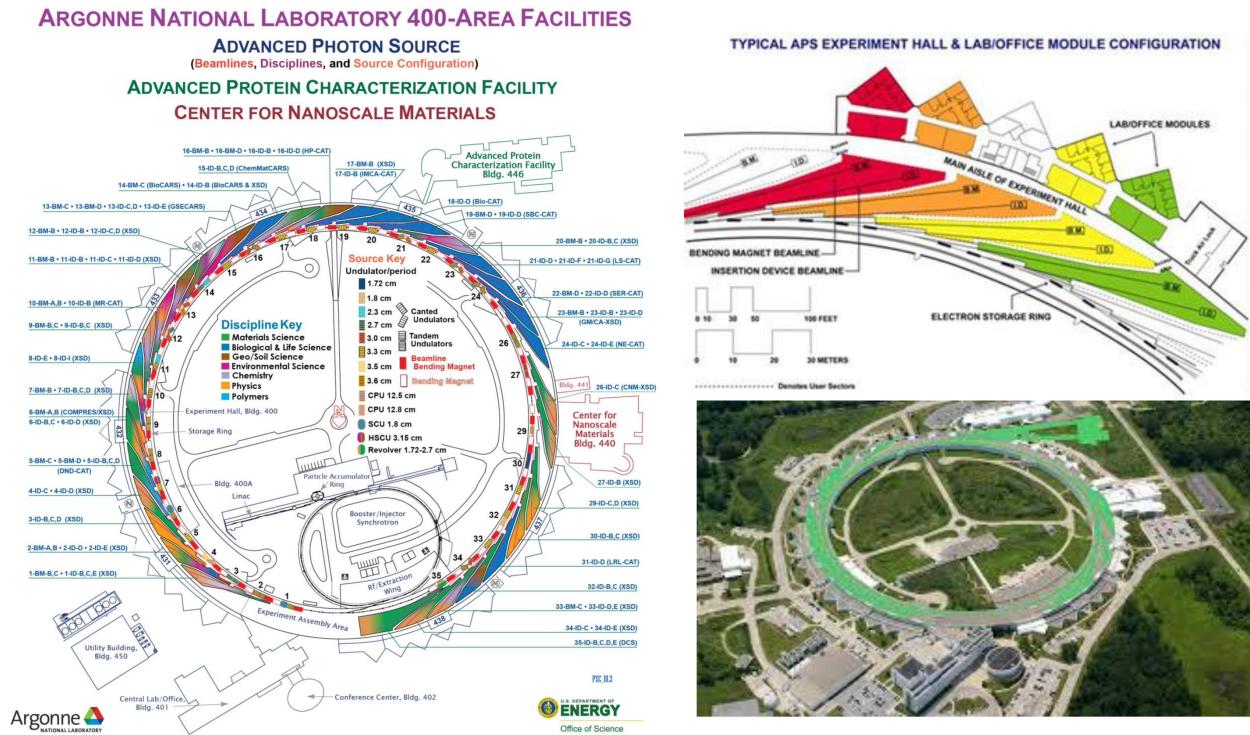


Figure 2.16: APS at Argonne.

- 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.

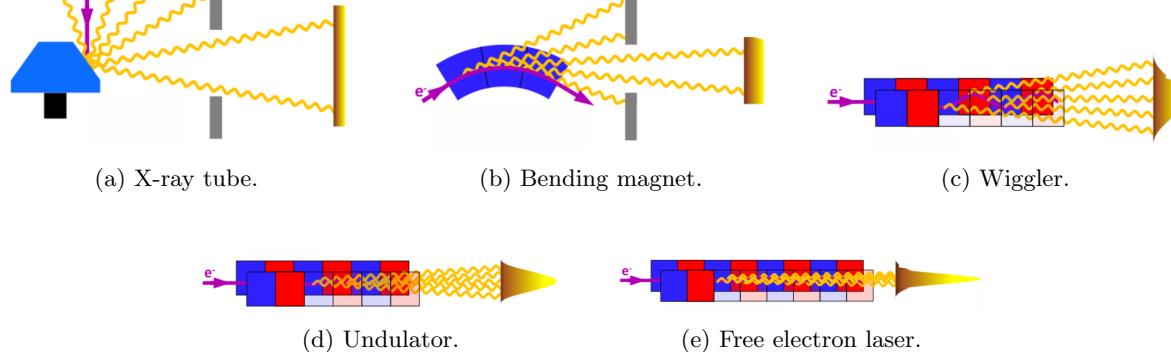


Figure 2.17: Making uniform X-rays.

- Methods of achieving uniform, collimated X-rays.
  - Bending magnets (BMs).
    - Aren't super precise.
  - Insertion devices (IDs).
    - E.g., **wigglers** 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.

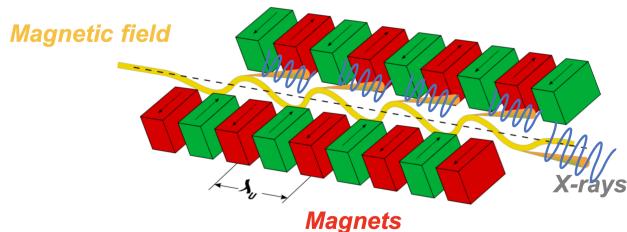


Figure 2.18: Undulator/wiggler structure.

- 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 basic 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 rn. 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.

# Week 3

???

## 3.1 Diamond Anvil Cell + Scanning Electron Microscopy

1/17:

- There will be a demonstration class with Dr. Filatov some afternoon. He will show us how to run some experiments, both sample-wise and data-wise.
- Review of DAC content from last class.
- Diamond anvil cell program and GSECARRs.
  - UChicago's dedicated beamline is Sector 13.
  - It pulls electrons out of the storage ring using IDs or BMs.
  - “S” on this slide stands for single-crystal.
  - DACs are now automated to a very large extent; no more manual screw adjustment.
- An example experiment: Phase relations of iron carbides at high temperatures and pressures.
  - You don't need to remember this; it's just to give you a flavor of what can be done.
  - These compounds are applicable to geology since they're often far in the ground.
  - DACs and laser heating replicate the heat and pressure present deep in the earth.
  - The researchers built a phase diagram from the XRD spectra of both solid and liquid phases.
  - Main takeaway: You can study more than crystalline phase transitions; indeed, even solid-to-liquid transitions are on the table.
- Another example experiment: Magnesium peroxide formation.
  - Magnesium peroxide is present in some geological objects.
  - In these experiments, researchers recreated the conditions that can cause the geological formation of  $MgO_2$  over  $MgO$  to observe how it happens.
- One more example experiment: NaCl stoichiometry
  - Published in Science: You'd think it'd be hard to be surprised by a result about NaCl at this point, but these scientists proved the existence of  $Na_3Cl$  and  $NaCl_3$  at high pressures.
  - $Na_3Cl$  is composed of layers of pure sodium and layers of NaCl.
  - These new “isomers” have special properties, e.g., the pure sodium layer in  $Na_3Cl$  conducts electricity in two-dimensions, and the surrounding NaCl layers act as insulators.
  - Good follow-up question: What is the charge? Could  $Na_3Cl$ , for instance, still be neutral?
  - Shevchenko recommends we check out the paper: Zhang et al. (2013).

- Challenges for DAC studies.
  - Chemical reaction of sample/medium with diamond.
    - Especially prevalent with alkali metals and hydrogen.
  - Any imperfections in the diamond anvil culet surface cause them to easily crack.
    - Cracking the diamond forces you not just to get new diamonds (expensive), but to have to restart your experiment (costly in terms of time).
  - Hydrogen penetrates the metal gasket and diamond anvils easily at higher temperatures and pressures.
  - Solution: Use cryogenic temperatures (just slow down the process).
    - Even in this case, you can still do heating experiments; you just have to *locally* heat your sample.
- Synthesis of new materials.
  - Procedure: Synthesize a material, create possible models of it, calculate the predicted XRD pattern, test alignment with the actual XRD pattern.
  - Example:  $\text{NaH}_3$  with elongated molecules of  $\text{H}_2$  incorporated into the crystal lattice.
- First DAC experiments on nanomaterials.
  - First conducted by Sarah H. Tolbert (now a UCLA prof) and A. P. Alivisatos in 1995.
  - Examined pressure-induced structural transformations in semiconductor nanocrystals.
  - Observed elevation in solid-solid structural transformation pressure as crystallite size decreases.
  - Example: CdSe nanocrystals.
    - The CdSe nanocrystals undergo a wurtzite to rock salt transition (similar to bulk CdSe).
    - The nanocrystal phase transition pressures varied from 3.6-4.9 GPa for crystallites ranging from 21-10 Å in radius (bulk CdSe: 2.0 GPa).
    - Demonstrated that the transition only nucleates once in each nanocrystal.
- Probing of mechanical properties using DAC.
  - DACs are often used to probe nanoparticle assemblies.
  - NPs can be assembled into periodic structures (recall the first class).
  - Compress a ruby and PbS up to 50 GPa.
  - Can you bring NPs close enough together to observe collective properties? At close enough distances, the organic strings around them intercalate. Can you push them even closer?
  - The computer simulations of this took much longer than the actual DAC experiment.
  - Removing pressure allows elastic recovery.
  - Conclusions: In this case, we could not bring particles close enough together to observe collected properties. Not conclusive though; maybe other ligands, more pressure would work.
- High-pressure structural stability and elasticity.
  - Many cases of using DACs to study structures made out of gold or CoO particles.
  - Recall that NPs are often single crystals.
  - NPs can have a preferred orientation when we compress them.
- Mechanical stability of crystals assembled from  $\text{Fe}_x\text{O}_y$  NPs.
  - Vacant, polycrystalline shells should implode/explode upon isotropic compression, but instead they are very stable (maybe something to do with the spherical shape).

- How “hollow” are hollow  $\text{Fe}_x\text{O}_y$  NPs?
  - Alivisatos is often mentioned in this course because he did actually play a very big role in the development of nanoscience.
  - This example is from Shevchenko’s own work.
  - At high temperatures, NPs start to seed; you end up with large blobs. Thus, reactivity goes down (if you’ve got catalysts mounted on their surface).
  - The shell is not penetrable to gases.
    - Pores (defects) can allow gases to enter in theory, though.
  - Inside the shell, there are tiny fragment of Fe or  $\text{Fe}_x\text{O}_y$ .
  - These particles are hoped to be able to deliver drugs since they have pores.
  - If He or Ne diffuses into the NPs, we know that Ne crystallizes upon compression, so if it goes into the NPs, then you start to see broader peaks (relation to Figure 2.14??).
  - This was not observed, so Shevchenko concluded that  $\text{Fe}_x\text{O}_y$  shells do not allow the transport of atoms in and out.
- Pressure-mediated doping in graphene.
  - Alcohol was used as a pressure transmitting media.
  - Raman spectroscopy monitored the transition in graphene.
  - Conclusion: Alcohol can dope graphene upon compression.
  - No doping is observed when Ar is used as a pressure transmitting medium.
  - First reported in 2011 (when graphene was exploding); mechanism in 2017.
  - Conclusion: Electron charge injection is through the  $\text{SiO}_2$  substrate.
  - The formation of silanol groups ( $\text{Si}–\text{O}–\text{H}$ ) on the surface of oxidized silicon substrates (similar to CNTs) — origin of doping in graphene.
- Pressure studies on MOFs.
  - Since MOFs are promising for separation (which requires compression at some point), researchers wanted to know how they behave under compression.
  - Different behavior under pressure? And can liquid get inside MOF shells under pressure?
  - Pressure-transmitting medium 1 was NaCl: Irreversible amorphization (collapsing) of the empty structure occurs at about 0.4 GPa.
  - Pressure-transmitting medium 2 was oil: Slight lattice expansion and a strong modification of the peak frequency and shape of the MOF hydroxyl vibration below 0.1 GPa.
  - Pressure-transmitting medium 3 was high-viscosity polydimethylsiloxane silicone oil: Framework stability is enhanced under pressure with the amorphization onset shifted to about 7 GPa.
- Why were the media from previous selected?

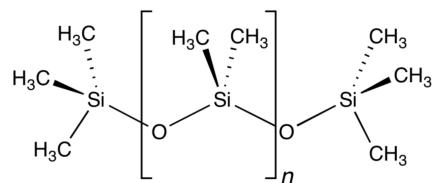


Figure 3.1: Polydimethylsiloxane silicone oil.

- NaCl: Optically transparent in the study areas, so minimal background interference.
- Nujol: An inert mineral oil used in infrared spectroscopy. It has a relatively simple IR spectrum.
- Polydimethylsiloxane silicone oil: Inert and optically transparent.
- You have to be sure that your medium does not overlap with your sample.
- Pressure-mediated changes in MOFs.

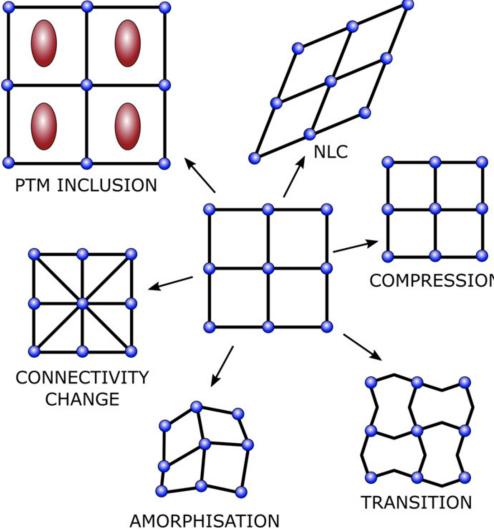


Figure 3.2: MOFs under extreme pressure.

- Negative linear compressibility (NLC).
  - Either causes expansion or net zero compressibility (compressibility along one or two axes, expansion along two or one).
- Compression.
- Transition.
- Amorphisation.
  - Note that transition preserves crystallinity in some form, while amorphisation does away with it entirely.
- Connectivity change.
- Pressure-transmitting medium (PTM) inclusion.
- Summary of DAC studies.
  - Use them to...
    - Study phase transformation;
    - Study the synthesis of novel materials;
    - Understand the universe/the formation of extant Earthbound or extraterrestrial minerals.
- We now move on to scanning electron microscopy.
- Examples of SEM images.
  - Pollen from different plants, the eye of a fruit fly, and opal.
    - Note that opal is made of (possible fused) silicon beads of either uniform or different sizes.
  - False color: Allows you to highlight certain features.

- First SEM.
  - The concept was first proposed in 1935 by Max Knoll.
  - At the time, researchers were actively working on using electrons for imaging but were focusing on transmission.
  - Manfred von Ardenne designed the first scanning transmission electron microscope (STEM) in 1937-38 by adding scan coils to a transmission electron microscope to surpass its resolution.
  - The first STEM micrograph depicts ZnO crystals imaged at an operating voltage of 23 kV at a magnification of 8000 times, and a spatial resolution between 50-100 nm.
    - Nowadays, the resolution is about 1.5 nm.
  - Keep in mind that SEM and STEM are different.

- Interactions of electrons with matter.

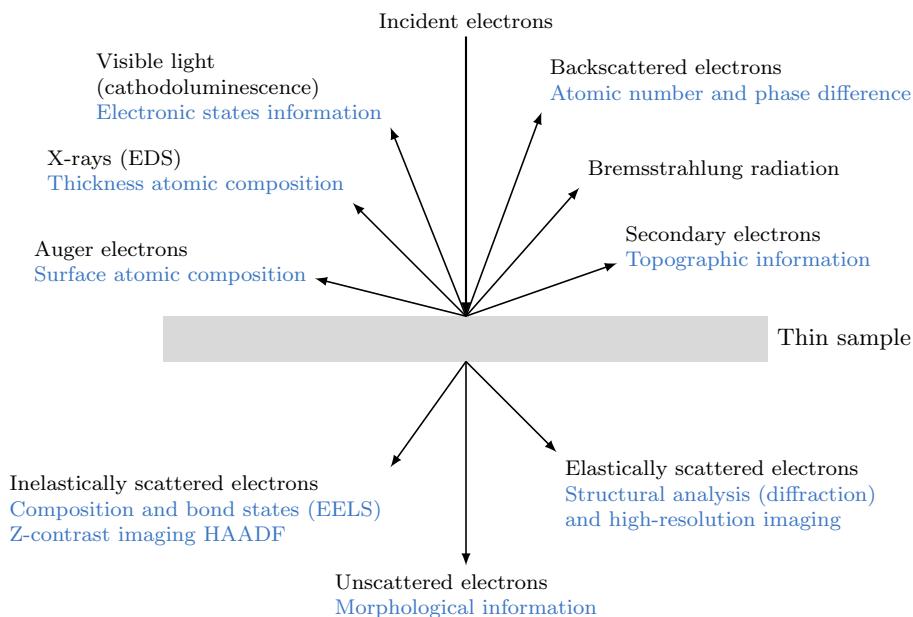


Figure 3.3: Interaction of electrons with matter.

- Consider a thin sample.
- We can cause a whole bunch of changes in our material with incoming electrons.
- We will talk about all of these eventually.
- SEM uses **backscattered electrons** and **secondary electrons**.
- **Secondary electron:** An electron knocked out of a substance by a separate incident electron. *Also known as SE.*
- **Backscattered electron:** An incident electron that gets rerouted back in the original direction via a close encounter with the nucleus. *Also known as BSE.*
  - Thing “gravitational assist” from rocketry.
- Bohr atomic model.
  - Very simplistic, but says what we need. Shevchenko reviews Figure 1.8.
  - Generation of characteristic X-rays, depth profiles, and other phenomena.

- Electron interaction volume within a sample.

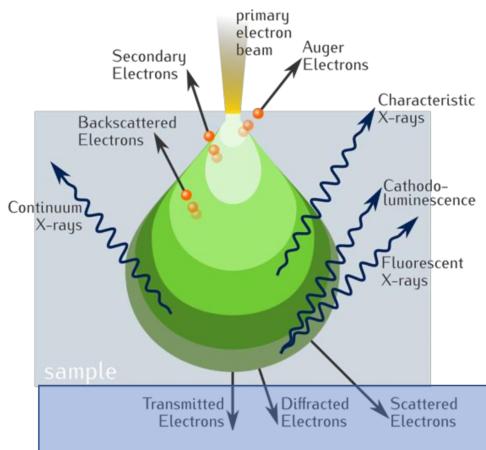


Figure 3.4: Electron interaction volume within a sample.

- **Auger electrons** are only generated at the very very top of the sample.
- The beam electron may be scattered inelastically by the Coulomb field of an atomic nucleus, losing some of its energy in the process as Bremsstrahlung radiation.
- The beam electrons can give up any amount of energy, so the energy distribution of the emitted X-rays is continuous up to the beam energy.
- **Auger electron:** An electron that escapes its atom via the following process. *Also known as AE.*
  1. Incident electrons heat the atom.
  2. A core electron gets removed.
  3. A higher energy electron falls down, releasing energy as it does so.
  4. This energy is not released in the form of light, but is transferred to the electron of interest and used to escape.
- Example: Nickel.
  - Conditions.
    - Sample is predominantly  $Z = 28$ .
    - Accelerating voltage is 20 kV.
    - $0^\circ$  tilt, i.e., incident beam is normal to specimen surface.
  - Penetrations.
    - Augers: Only 10-30 Å.
    - Secondaries: Up to 100 Å.
    - Backscattered:  $< 1 - 2 \mu\text{m}$ .
    - Range of electron penetration: About 5  $\mu\text{m}$  in total.
- Secondary electrons.
  - Often perform the SEM imaging.
  - The electrons, once ionized, often leave the atom with a very small kinetic energy ( $\sim 5 \text{ eV}$ ).
  - There is only a slight energy loss and trajectory change in the incident electron; thus, each incident electron can produce several secondary electrons.
  - Collection of these electrons is aided by using a **collector** in conjunction with the SE detector.

- **Collector:** A grid or mesh with a 100 V potential applied to it which is placed in front of the detector, attracting the negatively charged secondary electrons to it which then pass through the grid holes and into the detector to be counted.
- Secondary electrons for imaging.
  - Mostly effective up to 5 nm in the material.
  - Indeed, secondary electrons provide **surface topology imaging**.
    - Due to their low energy, only SEs that are close to the surface can exit the sample.
    - This small distance enables fine resolution in the SEM.
  - However, secondary electrons provide little-to-no information about elemental contribution.
  - How does a detector tell electrons from the sample vs. the beam?
    - We arrange the detector so that it only picks up electrons from one specific direction, and we control the direction to choose only electrons that are coming up at a particular angle.
    - Lighter elements have greater penetration depths.
    - Secondary electrons are basically ionized electrons.
- Imaging with secondary electrons.
  - Extremely popular with nanofabrication.
- Backscattered electrons (BSE).
  - Elastic scattering happens with little loss of energy.
  - BSEs provide elemental information since the number of BSEs produced is proportional to the atomic number of the elements within the specimen.
    - Higher-atomic number elements “produce” more backscattered electrons and appear brighter than lower atomic number elements.
    - This interaction is utilized to differentiate parts of the specimen that have different average atomic number.
  - Very popular for imaging metal alloys.
- Imaging with backscattered electrons.
  - We don’t know flat vs. texture, but we can still see contrast in the images.
  - In the picture in the slides, we can make out pores, as well as differentiate Mo-rich (lighter colored) regions from Si-rich (darker colored) regions.
    - Since Mo is higher- $Z$  than Si, it makes sense that it should be lighter.
- Backscattered electrons vs. secondary electrons.
  - Comparison of images for different alloys.
  - SEs provide more information on the topology of the material.
    - This information *can* coincide with elemental information, but it does not have to.
- Characteristic X-rays.
  - Utilized for elemental analysis since they’re *characteristic*.
  - We have already discussed how these are generated.
  - When electrons are not from the inner shell, an electron drops down, releasing energy in the form of photons in the process.
  - Not relevant to SEM imaging; just elemental analysis.

- Analytical use of characteristic X-rays.
  - EDS=EDX: Energy dispersive spectroscopy and energy dispersive X-ray.
  - Qualitative and quantitative analysis.
  - EDS systems: X-ray detector plus software to collect and analyze energy spectra.
    - Use Si-Li detectors, aka “silicon drift” detectors.
    - Sometimes, such detectors need cooling systems. These are annoying to deal with, and thus are not present in more expensive models that use better, more idealized materials instead.
  - Working principle of the detector: The X-ray absorption converts the energy of individual X-rays into electrical voltages of proportional size.
    - Incoming photons ionize the detector material, yielding free electrons in the crystal.
    - The crystal becomes conductive and produces an electrical charge bias.
    - The electrical pulses correspond to the characteristic X-rays of the element.
- Chemical information (EDS).
  - Spectra, elemental mapping, and line scans.
- Bremsstrahlung.
  - Review of Figures 1.6-1.7.
- Auger electrons (AE).
  - Auger spectroscopy (AES) is liked by some researchers and is rapidly evolving right now.
    - Carries information about the surface of the specimen (the first few atomic layers).
  - Since orbital energies are unique to an atom of a specific element, ejected electrons carry specific chemical information about the surface.
- Building blocks of SEM.
  - Electron source.
  - Limiting apertures surround...
  - Condenser lenses 1-2.
    - These lenses focus them on a spot.
  - Then scanning coils.
  - Lastly, an objective lens focuses everything downward.
  - Three detectors.
    - The BSE detector: A ring surrounding the point at which the incident electrons enter.
    - The SE detector.
    - The EDS detector.
  - These machines are big.
  - The BSE detector is positioned as such so that it can catch backscattered electrons that circle around the nucleus and return close to their original trajectory.
  - The apparatus doesn’t move, but the beam does.
  - The detectors stay where they are; you just change the beam position.
  - By varying the current passing through the coils with the time, the position of the beam can be shifted (rastered).
  - Many elements are similar to those in CTEM, but SEM images are not obtained all at once; rather, they are created in a rastering mode.

- SEM resolution.
  - High-Z materials have less penetration.
  - More KE leads to a deeper penetration.
  - Condenser lenses (1-2) focus the beam to a spot of  $\sim 0.4 - 5$  nm, and they determine the focus of the instrument.
  - Resolution can be limited by the interactions of electrons and materials.
    - Dirty samples deposit carbon inside the instrument, spoiling the vacuum and harming the machine.
    - Always be careful! Dirty samples are the product of lazy scientists.
  - Interaction volume depends on material: High-Z materials have smaller interaction volumes.
  - Interaction volume also depends on voltage.
    - More voltage means a higher depth profile (may not be a good thing; for topology, you only want to study only the top surface).
- Astigmatism of your images.
  - Takes place when a lens field is not symmetrical in strength (weaker in one place than in another).
  - Origins of astigmatism.
    - Imperfect polepiece boring.
    - Nonhomogeneous blending of polepiece materials.
    - Dirt on the polepieces, apertures, and/or specimen holders (most common).
  - Solution: A stigmator can be used to selectively correct the field.
    - Stigmators produce weak fields compared to the electromagnetic lenses they correct.
- Detection of astigmatism.
  - Underfocusing the objective lens: Image details line up with the beam shape at that focus.
  - Overfocusing: Image details line up along a direction orthogonal to the underfocused image.
  - At exact focus: Image is OK-ish, but not really as sharp as it could be because the probe size (e.g., condensor) is larger than it should be.
  - Essentially, turn the nob different ways until you get exact focus.
- The last slide on astigmatism.

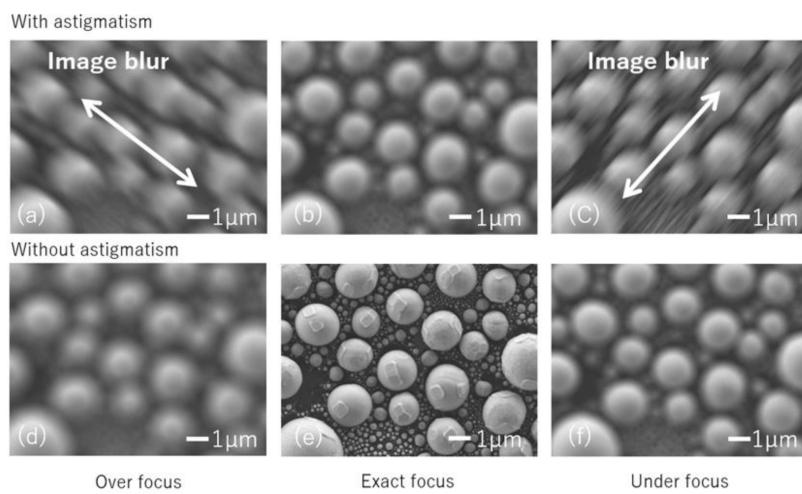


Figure 3.5: Correcting astigmatism.

- It is really important to have good focus.

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