

# 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.

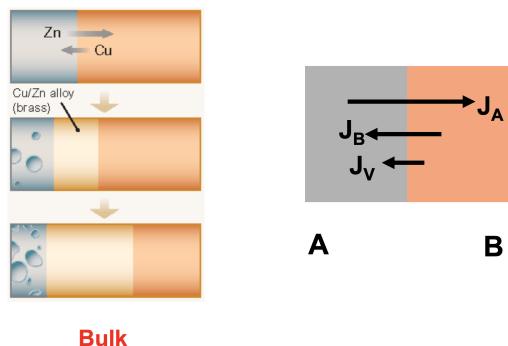
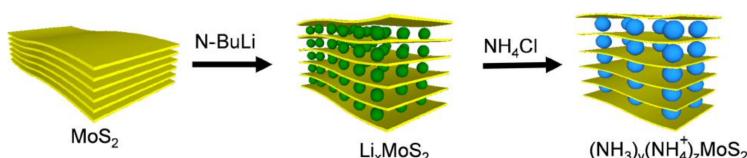


Figure 1.1: Kirkendal effect.

- 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  $\text{AlB}_2$ ,  $\text{MgZn}_2$ ,  $\text{Cu}_3\text{Au}$ ,  $\text{Fe}_4\text{C}$ ,  $\text{CaCu}_5$ , and  $\text{CaB}_6$ .
- 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.

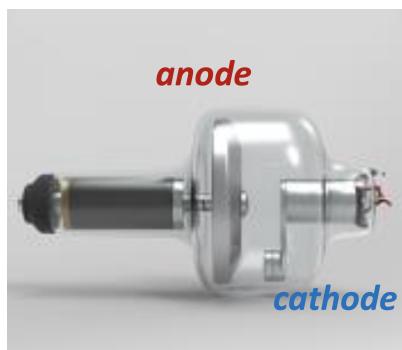
## 1.2 XRD Analysis 1

1/5:

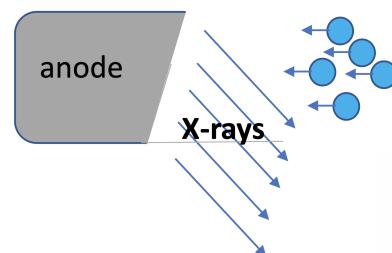
- Applications of X-ray diffraction.
  - Geology, environmental science, material science, engineering, biology.
  - Originally developed for analysis of minerals.
- What you can do with it.
  - Characterization of crystalline materials (structure, unit cell, etc.).
  - Identification of unknown/new 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.

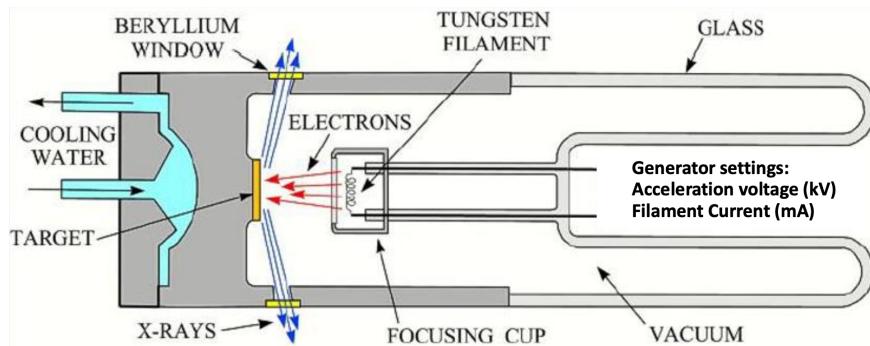


Figure 1.5: Schematic cross section of an X-ray tube.

- 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.

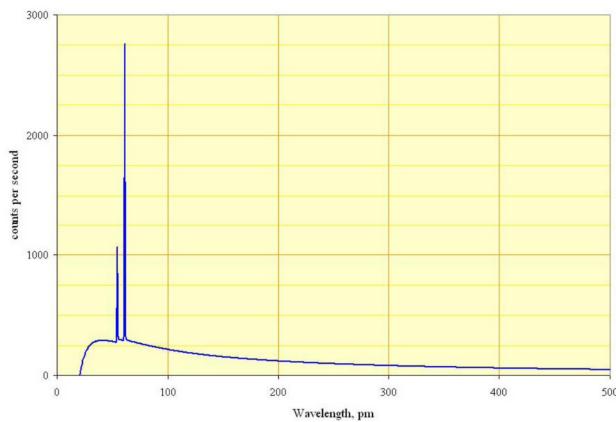


Figure 1.6: The spectrum of X-rays generated in an X-ray tube.

- 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.”

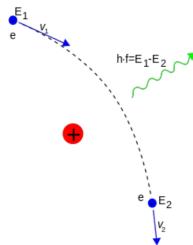


Figure 1.7: Generation mechanism for bremsstrahlung radiation.

- 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.

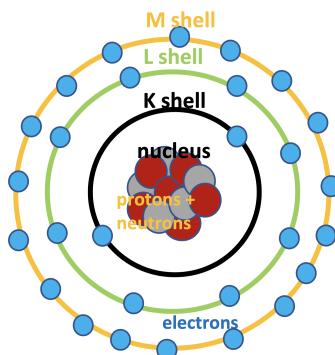


Figure 1.8: Energy levels in the Bohr model.

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

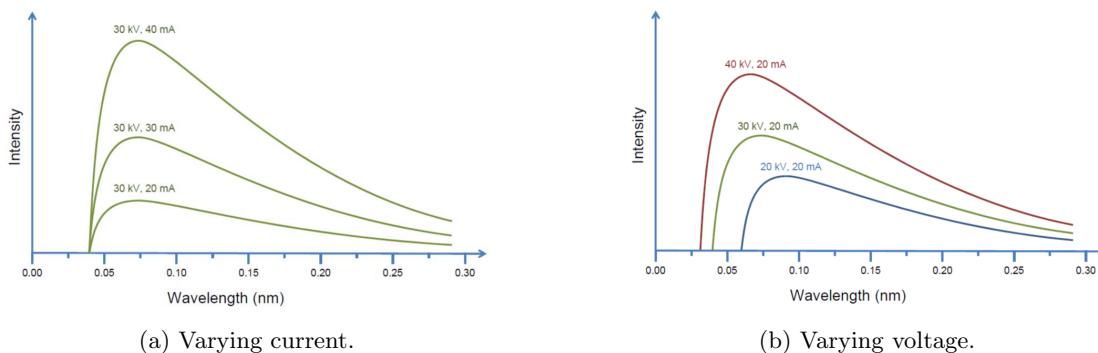


Figure 1.9: X-ray intensity vs. wavelength at different voltages and currents.

- The distribution of intensity (photon counts) against the wavelengths of the emitted radiation.
- Two settings you can change during the measurement: Current and voltage.
  - Current increase: Intensity increases (more electrons means more counts per second).
  - Voltage increase: Intensity increases and the max shifts to a higher frequency (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.
- Note also that the intensity of characteristic X-rays increases with increasing voltage, but their frequency never changes (since  $\nu$  is determined by  $\Delta E$  between atomic energy levels).
- **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.

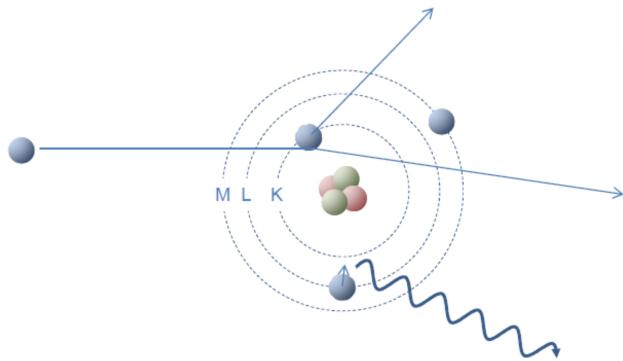


Figure 1.10: Generation mechanism for characteristic radiation.

- 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.

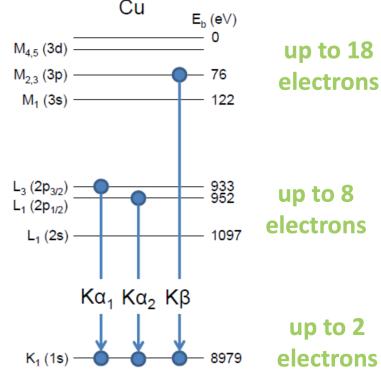


Figure 1.11: Copper spectral lines.

- 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.

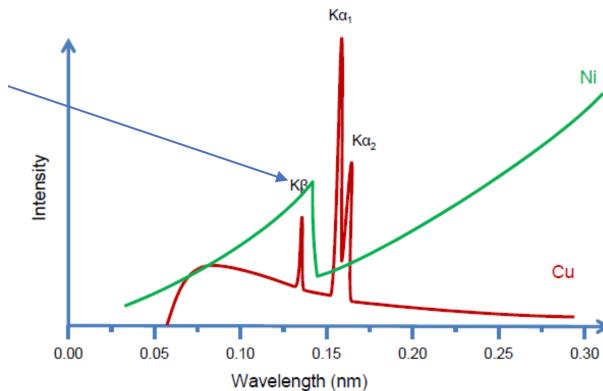


Figure 1.12: Nickel filter for a copper anode.

- 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  $1.488 \text{ \AA}$ . 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  $20 \mu\text{m}$  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. You 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 [1]) 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.

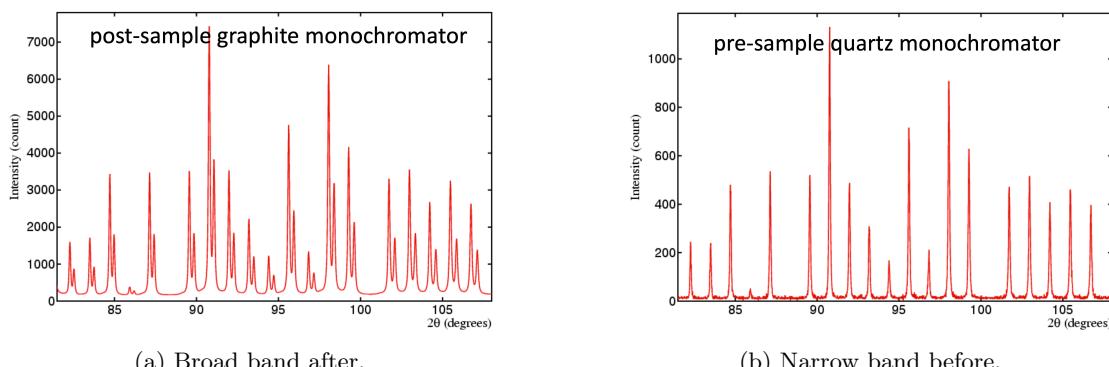


Figure 1.13: Effect of monochromator type and placement.

- 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
- 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  $K_{\alpha_2}$  wavelengths from a laboratory X-ray source??
- Is this all correct??
- Filters vs. monochromators.

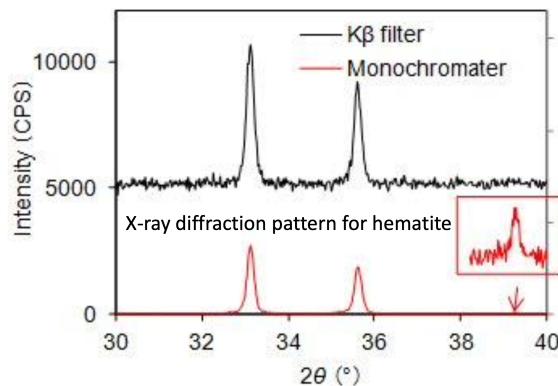


Figure 1.14: Filters vs. monochromators.

- 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.

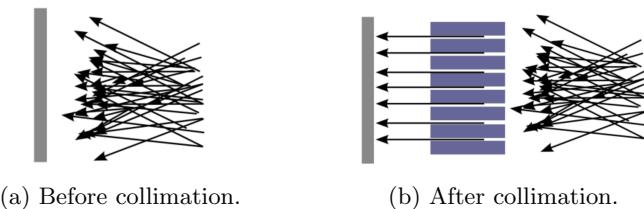


Figure 1.15: Collimator function.

- 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.

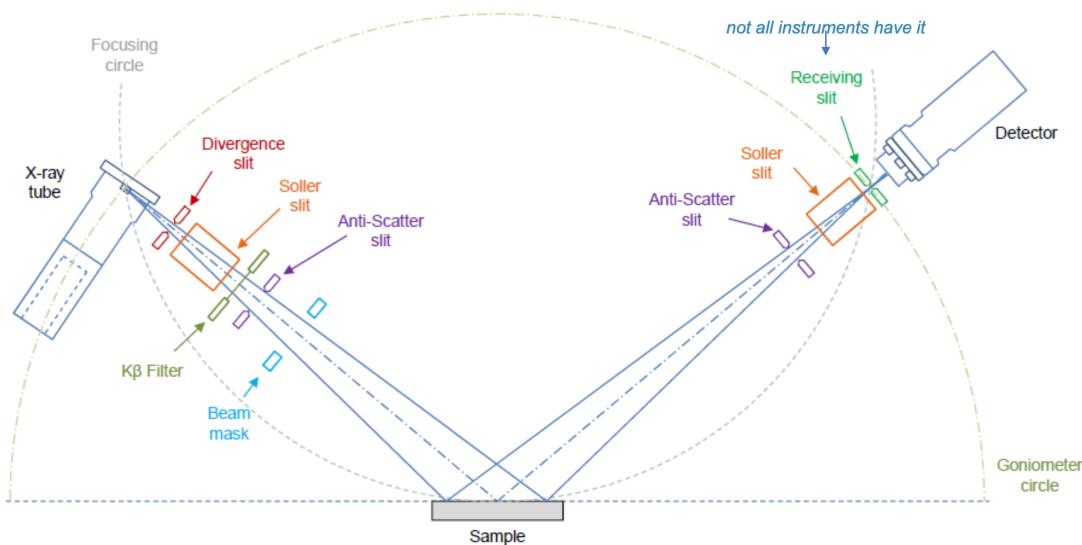


Figure 1.16: Typical diffractometer configuration.

- 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.

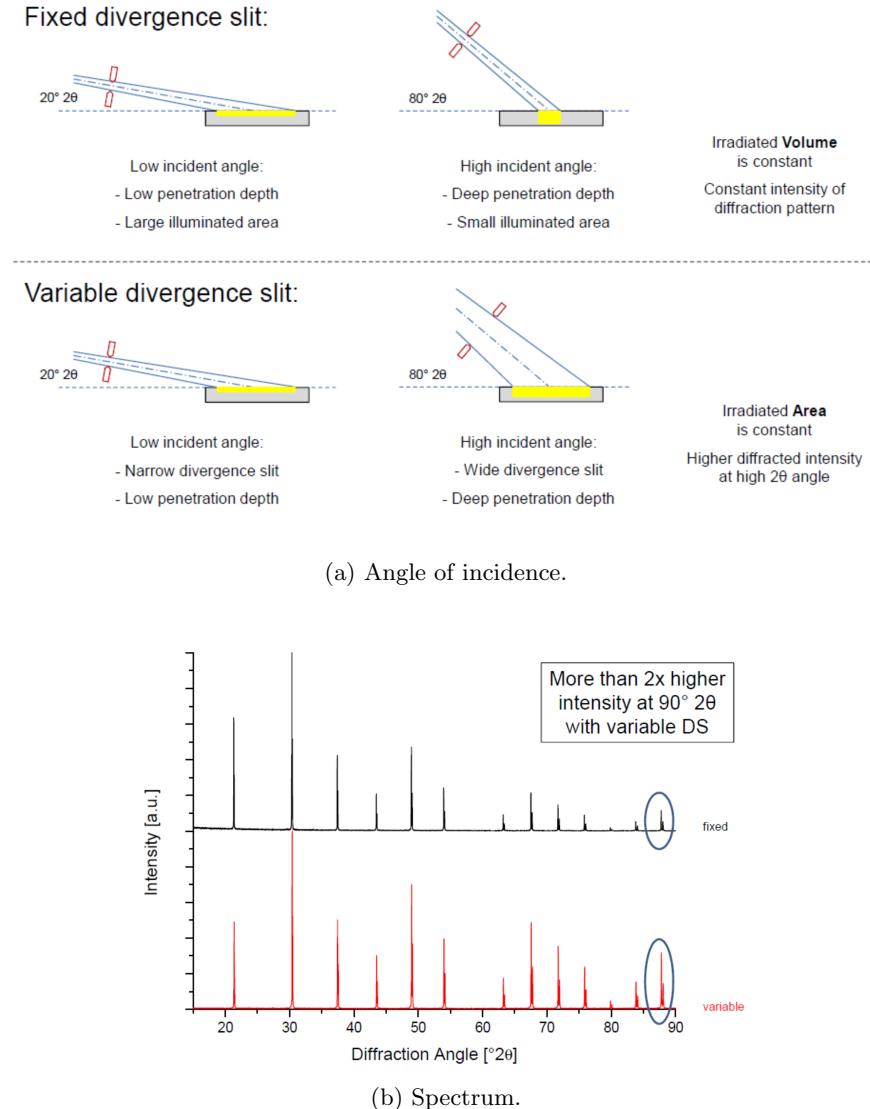


Figure 1.17: Fixed vs. variable divergence slits.

- 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.

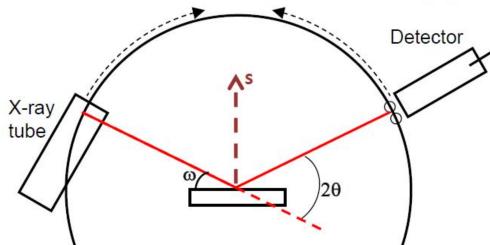


Figure 1.18: Bragg-Brentano geometry.

- 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.

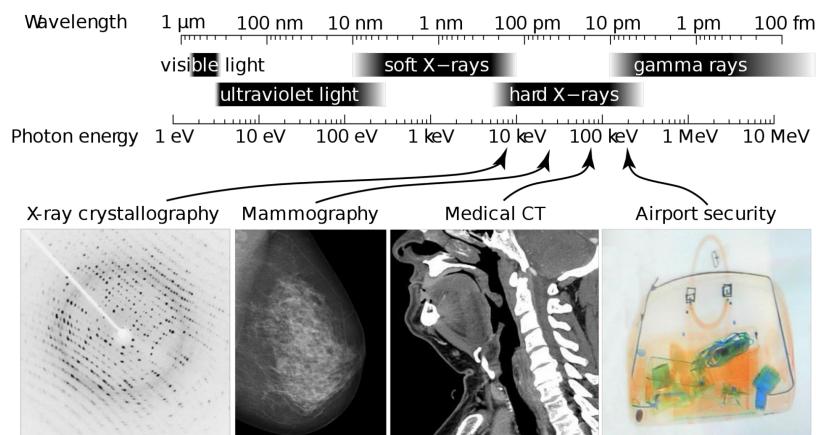


Figure 1.19: X-ray spectrum.

- 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.

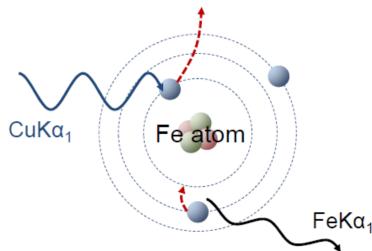


Figure 1.20: Absorption and fluorescence.

- **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?

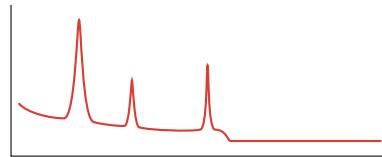


Figure 2.1: Enhancing XRD results.

– 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.

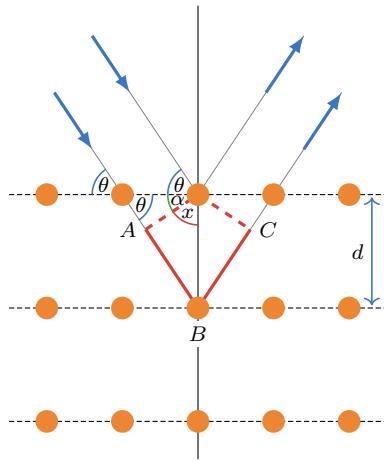


Figure 2.2: Bragg’s Law derivation.

- 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.

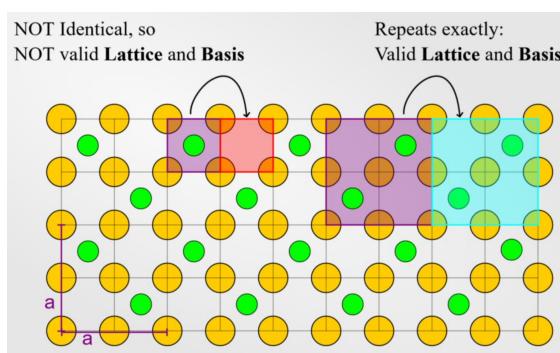


Figure 2.3: Decomposition of a crystal into its Bravais lattice.

- 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.

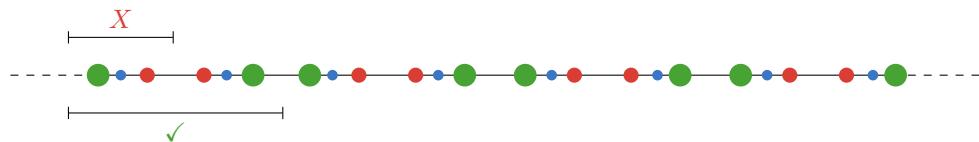


Figure 2.4: 1D Bravais lattices.

- 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.

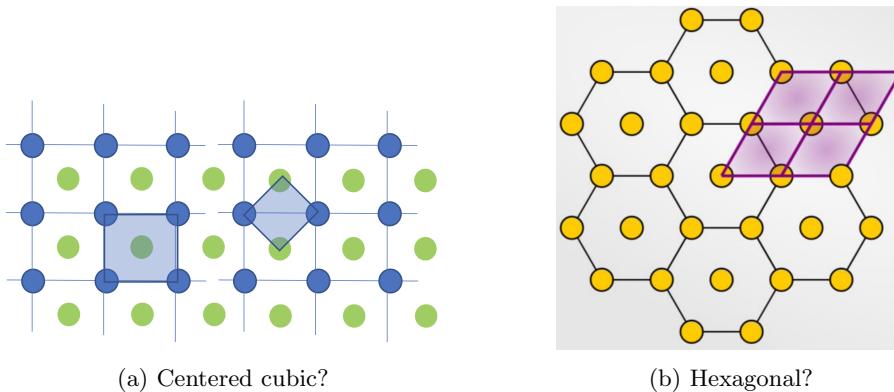


Figure 2.5: 2D Bravais lattices.

- 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 ( $a \neq b, \theta \neq 90^\circ$ ).
- Rhomboidal is also known as **oblique**.
- There does exist centered rectangular (a rectangular lattice with an additional vertex in the center of each rectangle), but there does not exist “centered cubic” because a smaller, rotated square can represent the entire lattice, so “centered cubic” is really just square. See Figure 2.5a.
- The “hexagonal” Bravais lattice can be simplified into a rhombus, but hexagon shows “true” symmetry (i.e., rotation, inversion, etc.). See Figure 2.5b.
- The honeycomb is not a Bravais lattice. Why??

- 3D Bravais lattice.

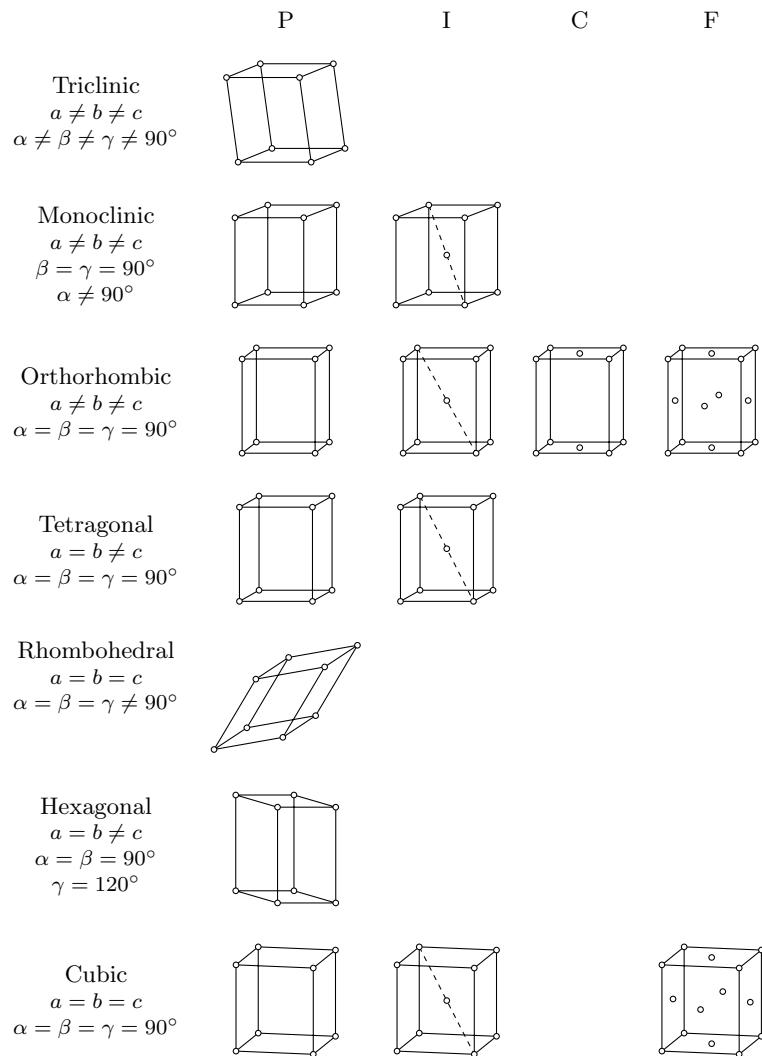


Table 2.1: Bravais lattices.

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

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

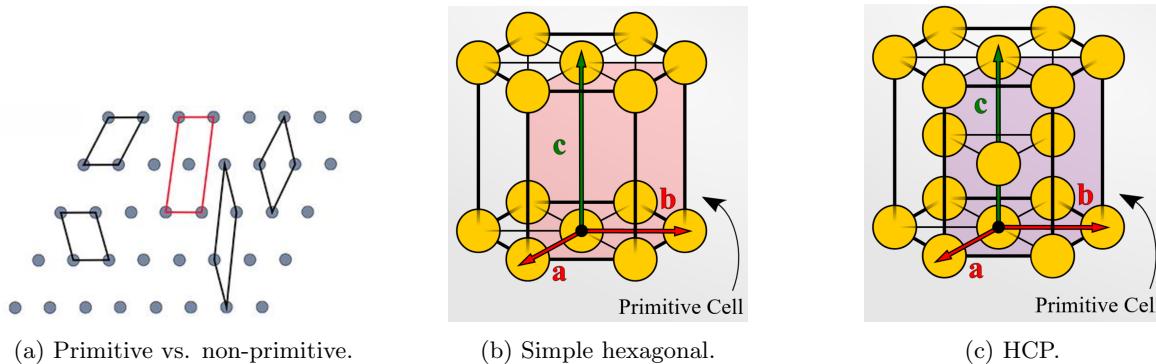


Figure 2.6: Conventional vs. primitive cells.

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

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

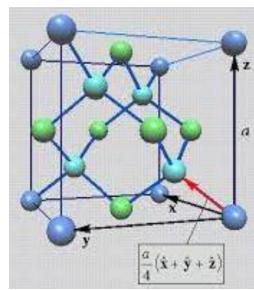


Figure 2.7: Diamond crystal structure.

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

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

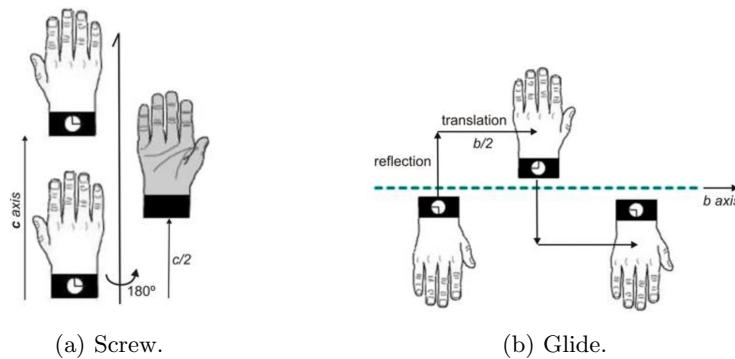


Figure 2.8: Screw and glide operations.

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

- Symmetry operator notation (Hermann-Mauguin).

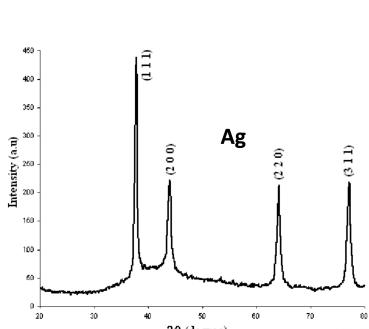
Type of symmetry element	Written symbol	Graphical symbol	
Centre of symmetry	$\bar{1}$		
Mirror plane	$m$	Perpendicular to paper	In plane of paper
Glide planes	$a\ b\ c$	glide in plane of paper	arrow shows glide direction
		glide out of plane of paper	
	$n$	.....	
Rotation	2 3 4 6		
Screw axes	$2_1$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

Table 2.2: Hermann-Mauguin notation.

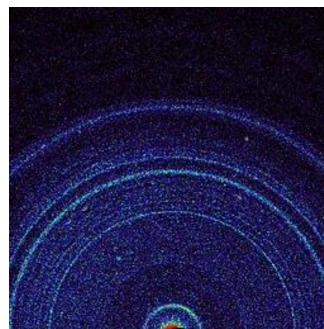
- Shevchenko won't go into too much depth; she doesn't even remember that much herself, but it's good to know how to read one.
- How to "read" space groups.
  - In the notation for a space group, the first letter is the Bravais lattice and then there are three symmetry elements with respect to 3 viewing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

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

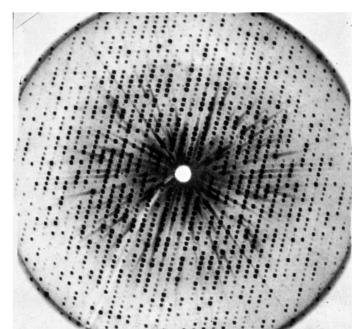
- Diffractograms.



(a) Peaks.



(b) 2D average.



(c) Dots (single crystal).

Figure 2.9: Diffractogram types.

- Our diffractograms will largely look like peaks (see Figure 2.9a).
- 2D detectors (as with synchrotrons) yield circular patterns or circular dot patterns.
- Dots (see Figure 2.9c) are generated by single crystals.
  - Myoglobin is a protein in muscles. It stores oxygen to bind and release oxygen depending on the oxygen concentrations in the cell, has functions in the hemostasis of nitric oxide and in the detoxification of reactive oxygen species. Myoglobin is the reason for the red color of the muscle of most vertebrates.
- Averaged rings (see Figure 2.9b) are generated by polycrystalline materials.
  - What is pictured is actually the first X-ray diffraction pattern of Martian soil (from the Curiosity rover at “Rocknest” on October 17, 2012).
  - **Feldspar**, **pyroxenes**, **olivine**, etc. were identified (this kind of identification and confirmation can take experts years since the data is so cluttered).
  - We read these with software in general. Calculate distances, work with the parameters of our instrument, etc.
    - 2D is better because gaps in the circles provide information, too??
    - Decades of experience and the help of your peers helps you decipher these images.
- Most of us will work with the APS at Argonne (shut down in April 2023 and will be back online a year later).
- **Feldspar**: Aluminum tectosilicate minerals, e.g.,  $KAlSi_3O_8$ ,  $NaAlSi_3O_8$ , and  $CaAl_2Si_2O_8$ .
- **Pyroxenes**: General form  $XY(Si, Al)_2O_6$ , where X can be Ca, Na, Fe<sup>II</sup>, 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.

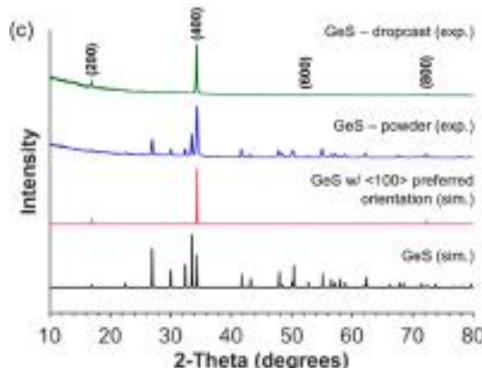


Figure 2.10: Preparation strategies vs. XRD clarity.

- 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.

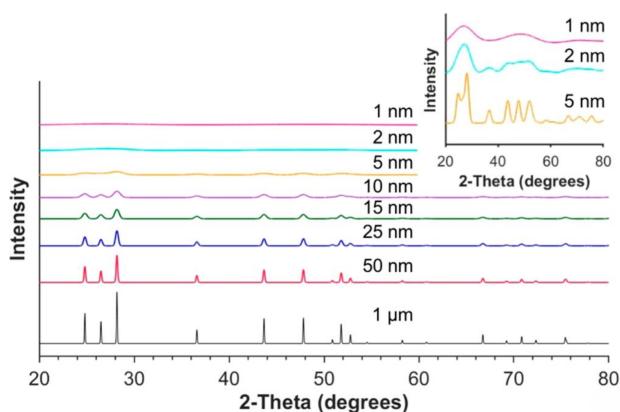
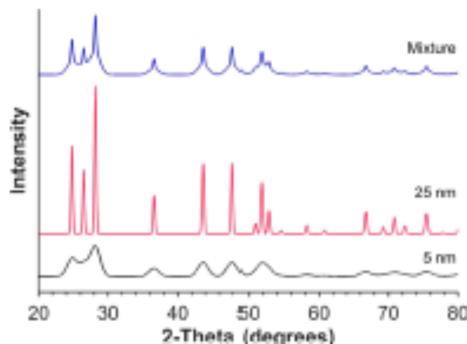


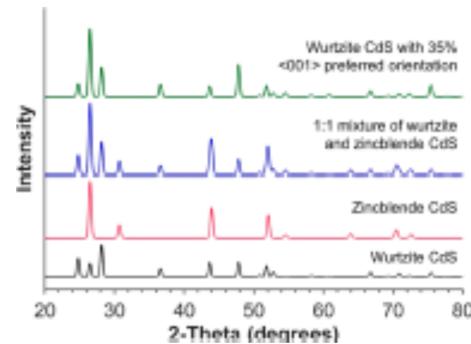
Figure 2.11: Resolution increases with larger crystal size.

- 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 **FHWM**, and  $\theta$  is the Bragg angle. *Given by*
- $$D = \frac{K\lambda}{B \cos \theta}$$
- Accurate size analysis requires correction for instrument broadening via
- $$B^2 = B_m^2 - B_{\text{ref}}^2$$
- where  $B_m$  is the measured FWHM and  $B_{\text{ref}}$  is the corresponding FWHM of the **bulk reference**.
- Readily applicable for crystal size of 2-100 nm.
    - Applicable up to 500 nm if a synchrotron light source is used.
  - **Bulk reference:** A reference crystalline material with large grain size ( $> 200$  nm).

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



(a) Mixture of sizes.



(b) Mixture of phases.

Figure 2.12: Mixtures of sizes and phases.

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

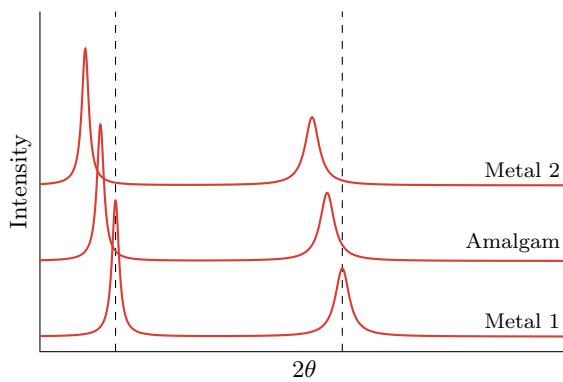


Figure 2.13: Vegard's law.

- Effect of strains.

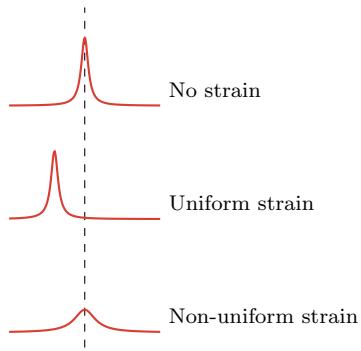


Figure 2.14: Strains.

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

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

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

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

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

Varies –  $d_1$  not constant

- Causes peak *broadening*.

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

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

- Therefore,

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

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

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

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

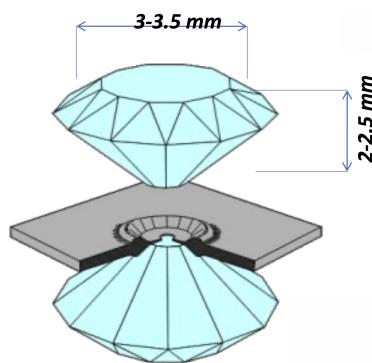


Figure 2.15: Diamond anvil cell.

- Working principle:

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

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

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

- Argonne's APS.

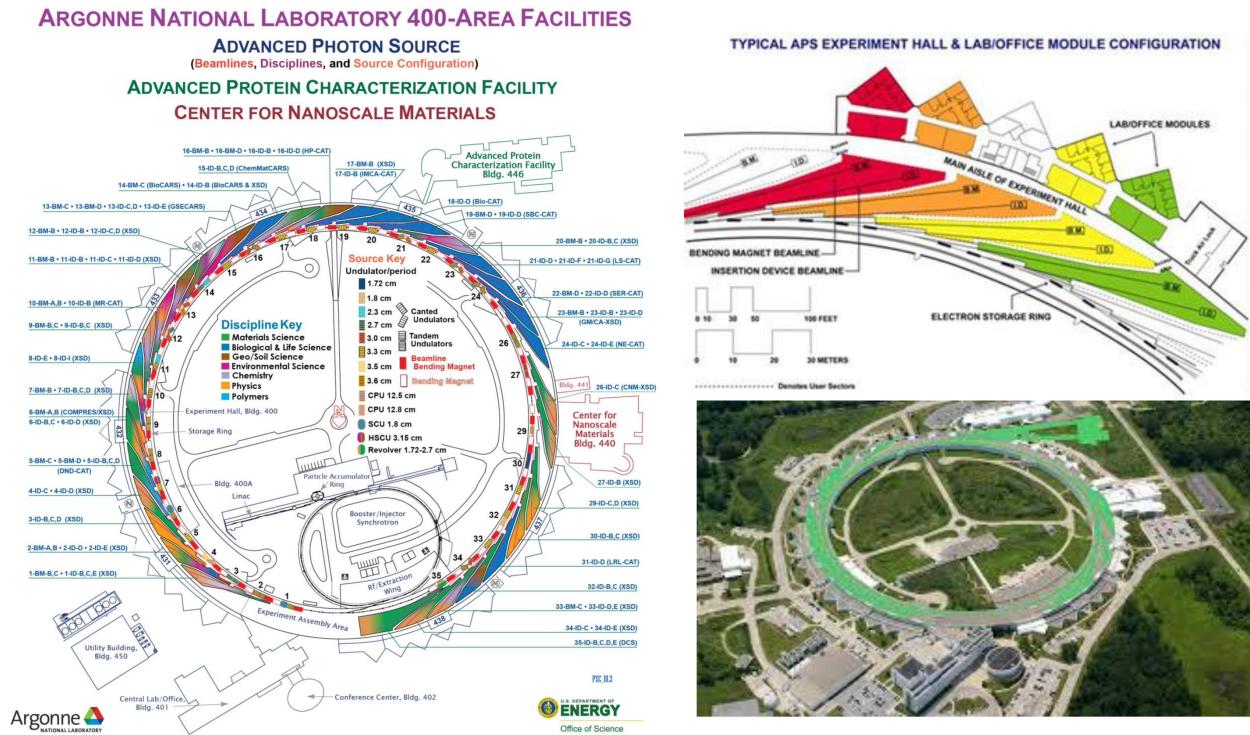


Figure 2.16: APS at Argonne.

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

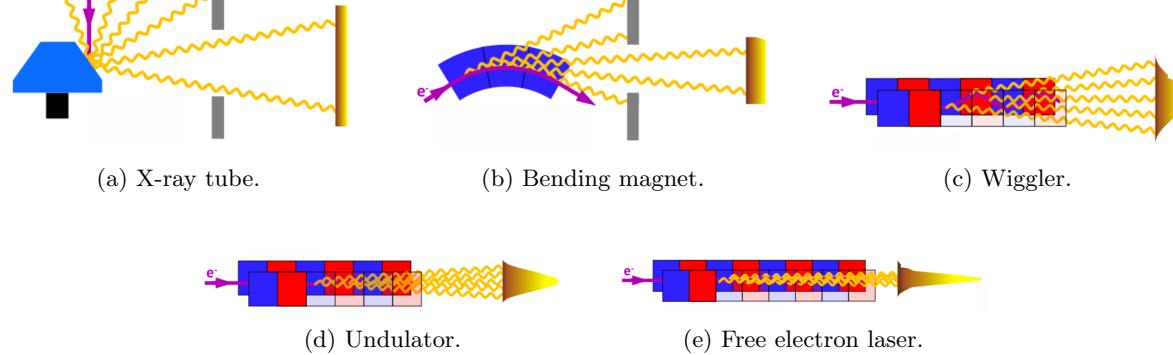


Figure 2.17: Making uniform X-rays.

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

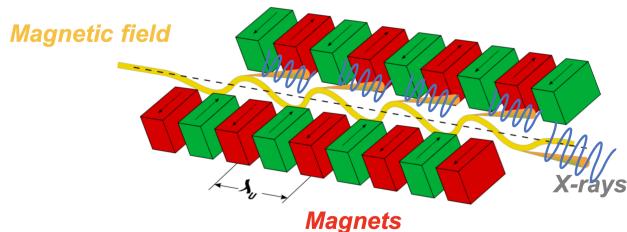


Figure 2.18: Undulator/wiggler structure.

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

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

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

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

### 2.3 Office Hours (Shevchenko)

1/13:

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

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

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

# Week 3

## Electron Microscopy

### 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. [2].

- 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  $\text{CoO}$  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 fragments 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?

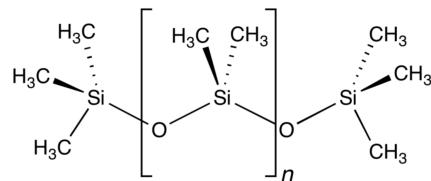


Figure 3.1: Polydimethylsiloxane silicone oil.

- 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.

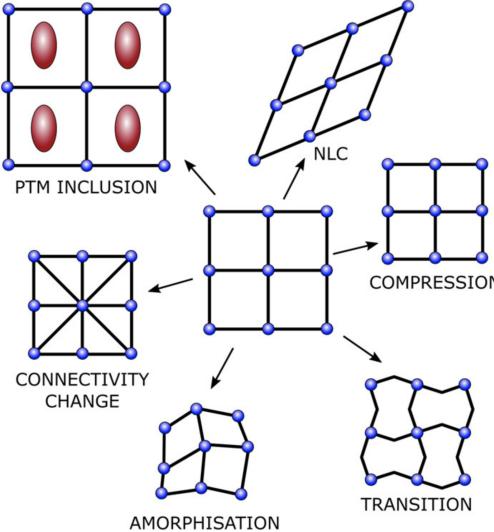


Figure 3.2: MOFs under extreme pressure.

- 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 concepts 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 23kV 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.

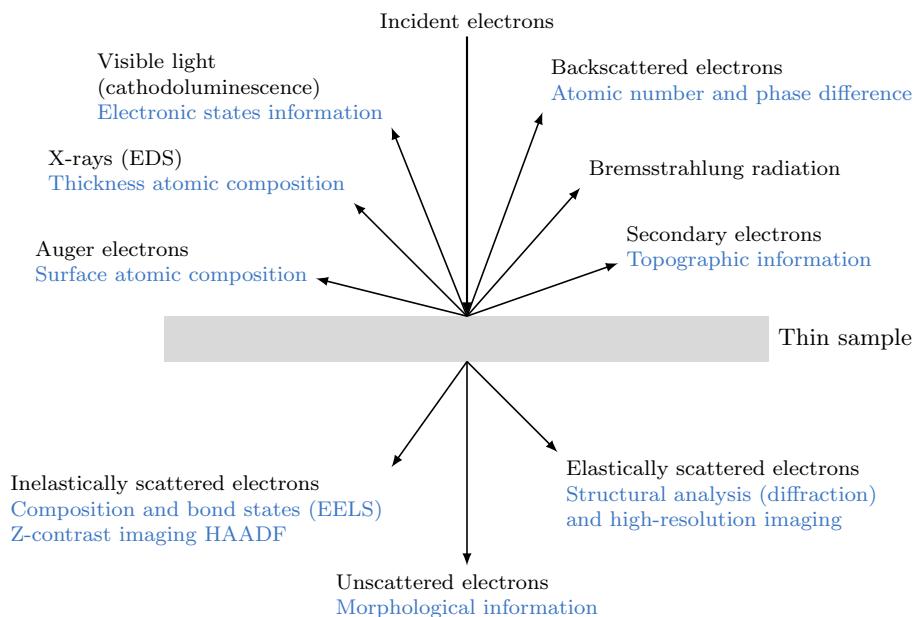


Figure 3.3: Interaction of electrons with matter.

- 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.*
  - Think “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.

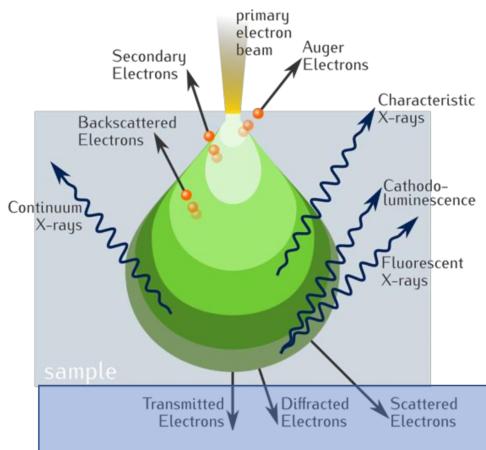


Figure 3.4: Electron interaction volume within a sample.

- **Auger electrons** are only generated at the very 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.

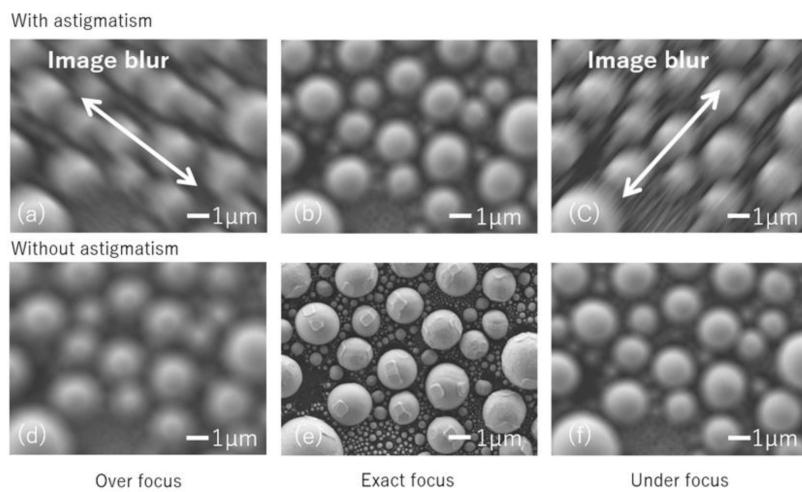


Figure 3.5: Correcting astigmatism.

- It is really important to have good focus.

## 3.2 Scanning and Transmission Electron Microscopy

1/19: • Image focusing.

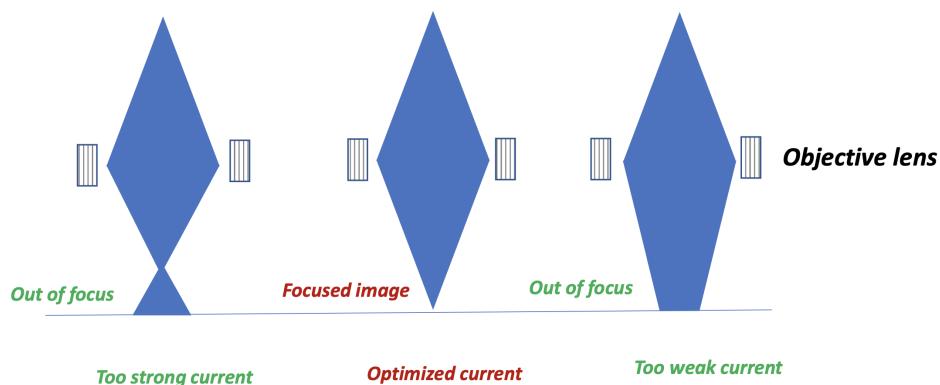


Figure 3.6: Image focusing.

- In optical microscopy, the focus is adjusted by moving the sample up and down.
- In SEM, we “move” the beam.
- In particular, we can adjust the magnetic field strength (and hence the focal length) of the OL by changing the current in it.
- SEM vs. TEM.
  - Example SEM vs. TEM images.
- Design of the SEM instruments.
  - Front-loading systems and sample transferring protocol.
- Low vacuum SEM.
  - Examples: Tabletop microscopes, environmental SEM.
  - The pressure can be adjusted in the sample chamber until the “electron charging” is removed from images.
  - Images without conductive coatings have lower resolutions.
  - Example problem you can address with LV-SEM: Whether face masks are effective in preventing the spread of COVID-19.
    - A 1 µm polymer was used to mimic the virus.
- **Cryo-SEM:** A special method using a deep-cooled stage that allows imaging of *hydrated* specimens by freezing the samples to very low temperatures (below  $-100^{\circ}\text{C}$ ) where solid water is stable even in vacuum.
  - Examples: Pictures of termites and collagen fibers.
- Is it possible to do imaging using SEM?
  - Yes??
- Review of Figure 3.4.
  - What was said here??

- We now move onto transmission electron microscopy (TEM).
- Early TEM.
  - In 1964, Dr. June Almeda took the first image of a coronavirus.
  - Dr. Almeda attempted to report particles like this before while investigating infectious bronchitis in chickens.
  - However, her paper was rejected because the reviewers said that the images could just be bad pictures of influenza virus particles.
  - More bio background on the development of TEM.
- Size comparison.
  - Light microscopes can resolve down to about 100 nm (about the size of the flu virus).
  - Electron microscopes can resolve from 1  $\mu\text{m}$  (about the size of a bacterium) down to about 0.5 nm (about the size of a buckyball).
  - Picture with more examples of objects in these size ranges.
- Discovery of electrons.
  - William Crookes of Crookes tubes returns!
  - In 1879, he found that **cathode rays** can be bent by a magnetic field and the direction of the deflection indicated that there were negatively charged particles (different metals or gases inside??).
    - However, these experiments did not settle the question of whether cathode rays were particles or radiation similar to light.
  - J. J. Thomson (1897): Studies cathode rays (in Crookes tubes with a good vacuum) between two parallel aluminum plates.
    - If the top Al electrode was negative, the rays moved down.
    - If the top Al electrode was positive, the rays moved up.
    - Furthermore, the deflection was proportional to the difference in potential between the plates.
  - These two sets of experiments established that cathode rays could be deflected, and that this deflection behavior could be induced by magnetic and electric fields.
  - Conclusion: Cathode rays have negatively charged particles (electrons).
  - Impact:
    - Shed light on the nature of electricity.
    - Determined the ratio of mass-to-charge for the electron (very small, explaining why electrons can “flow” through metals).
- Charge of the electron.

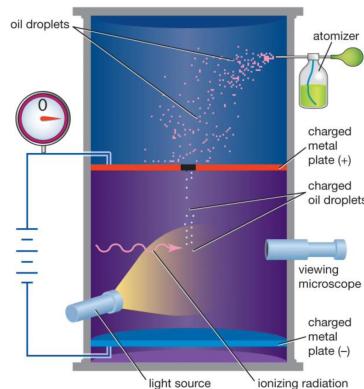
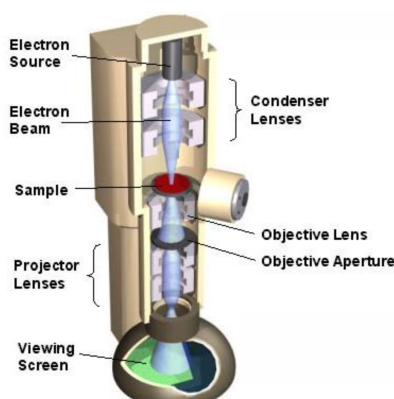
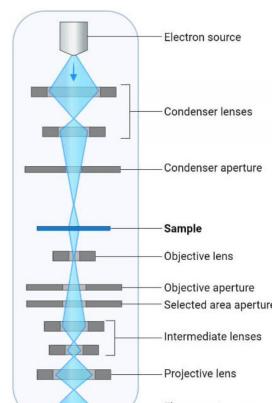


Figure 3.7: Oil-drop experiment.

- Robert Millikan (1910 at UChicago): Oil-drop experiment.
- X-rays interact with the oil and produce (a) charge(s) that is/are confined within a droplet.
- No charge applied: The fall of the droplet is determined by its mass and the medium's viscosity.
- Charge applied: The droplets stopped falling or even rose (depending on the number of charges).
- The position of droplets was dependent on the applied voltage.
- Millikan measured the electronic charge to two sig figs:  $1.6 \times 10^{-19}$  C.
- Electrons as waves.
  - Louis de Broglie (1924): Particles, such as electrons, could be described not only as particles but also as waves.
  - Derivation of the de Broglie wavelength  $\lambda_B$ :
$$\lambda_B = \frac{h}{p}$$
  - Photons always move at the same velocity (the speed of light).
  - Particles, on the other hand, have mass and momentum. If  $v \ll c$ , then
$$\lambda_B = \frac{h}{mv}$$
  - Keep in mind the difference between speed and velocity.
- Early days of TEM.
  - Max Knoll and Ernst Ruska (1931): The first transmission microscope.
    - Ruska won the 1986 Nobel prize in physics for his many achievements in electron optics.
  - 1939: First commercial TEM.
  - Working principle of TEM.
    - Similar to that of light microscopes: Light rays used to focus and produce an image vs. a beam of electrons used to focus on the sample to produce an image.
    - Electrons have much shorter wavelengths than light.
- Building blocks of the TEM.



(a) 3D picture.

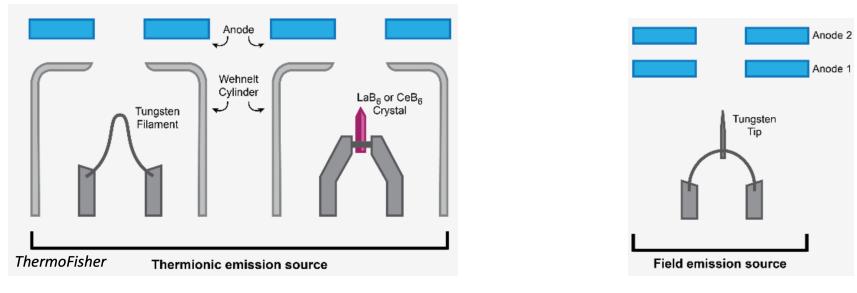


(b) 2D picture.

Figure 3.8: TEM building blocks.

- Electron source, electron beam, condenser lenses, sample, objective lens, objective aperture, projector lenses, viewing screen.

- Electron source.



(a) Thermionic source.

(b) Field Emission Gun.

Figure 3.9: TEM electron sources.

- **Thermionic source and field emission gun.**
- A high voltage ( $\sim 60 - 300$  kV) is applied.
- **Thermionic emission:** Emission of electrons into a vacuum achieved by applying a current (e.g., to single crystal of  $\text{LaB}_6$ ,  $\text{CeB}_6$ , or W) and heating.
  - W is cheap and easy to replace, but evaporates and breaks; lower brightness, broad beam, and hence reduced image resolution.
  - $\text{LaB}_6$  and  $\text{CeB}_6$ : Lower temperatures, lower beam spread, higher brightness, less volatile than tungsten (longer life time). But requires a higher vacuum (more expensive).
- **Field Emission Gun:** A strong electrostatic field is applied to a sharply pointed tip of W, leading to the release of high-energy electrons. *Also known as FEG.*
  - Developed by Albert Victor Crewe and Hittachi (1964 at UChicago).
  - The emission area is small and hence brightness is high; enhanced image quality (high spatial resolution and increased signal-to-noise ratio); last long; but expensive (require very high vacuum).
- **Schottky FEG:** A FEG that combines the thermionic and FEG sources (W coated with  $\text{ZrO}_2$ ).
- **Cold FEG:** Another type of FEG. *Also known as CFEG.*
  - Schottky FEGs have shorter lifetimes than CFEGs and worse image quality because of a larger energy spread, but better stability.
- Relativistic and non-relativistic electron KE vs. wavelength curves.
  - Also data on the accelerating voltage vs. frequency and wavelength.
  - Significance??
- Voltage:  $\lambda$  correlations.
  - Electrons are accelerated by the applied voltage  $V$  and thus gain kinetic energy  $mv^2/2$  (or, equivalently,  $eV$  where  $e$  is the charge of the electron).
  - Since  $\lambda_B = h/mv$ , increasing  $v = (eV/m)^{1/2}$  decreases the wavelength.
  - Combining these two equations and plugging in values for  $h, m, e$ , we learn that

$$\lambda_B = \frac{h}{(2meV)^{1/2}} = \frac{12.3}{V^{1/2}}$$

- The  $A$ ??

- **Condenser lens:** An electromagnetic or electrostatic lens that is used in an electron microscope to guide and focus the electrons.
  - The first lens through which the electrons pass (C1) determines the **spot size**.
  - The second lens through which the electrons pass (C2) varies the **brightness**.
- **Spot size:** The illumination spot on the sample.
- **Brightness:** The amount of illumination of the specimen.
- Aperture.
  - The origin of spherical aberration.
    - Electrons pass through the lens.
    - Those at the periphery of the lens are refracted more than those in the middle.
    - All the electrons will therefore not reach a common focal point.
  - Solution: An aperture is used to eliminate some of the peripheral electrons.
  - The aperture also helps control the amount of illumination reaching the specimen.
  - The origin of chromatic aberration.
    - High energy electrons get deflected more??
    - Ask more about this??
- Specimen area.

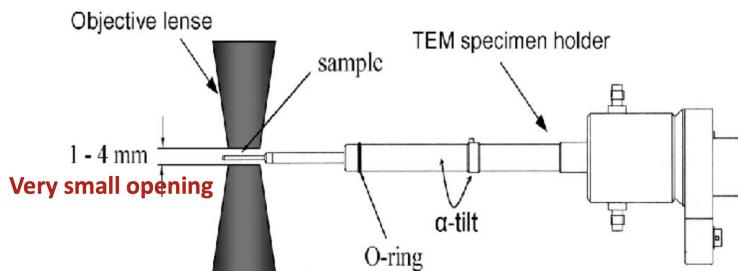


Figure 3.10: Sample holder for TEM.

- The sample is inserted using a sample holder.
  - Sample holders come in many shapes and sizes. There are regular **JEOLs**, JEOL high tilt retainers, multiple sample models, etc.
  - They can be further specialized for sample rotation (single tilt, double tilt, etc.), sample heating, or *in situ* experiments.
- The basic design is a long arm that extends to a gap between the objective lenses.
- Objective lenses.
  - **Objective lenses** and **objective apertures**.
- **Objective lens:** A lens that forms, magnifies, and focuses the first image. *Also known as OL.*
- **Objective aperture:** A lens that cuts off peripheral electrons to control contrast and spherical aberration. *Also known as OA.*
  - The OA consists of two **polepieces**, an upper and a lower one, surrounding the specimen holder from above and below. They are oppositely charged and create an appropriate field.

- Intermediate lenses.
  - These magnify the image from the OL and focus the diffraction pattern.
  - There is also an **intermediate aperture** that is a diffraction aperture responsible for choosing the diffracted area.
- Projective lenses.
  - Magnify the image/control magnification.
- Imaging systems.
  - A fluorescent screen or a **CCD (charge coupled device)** camera.
  - The CCD records in a digital format.
- Astigmatism.
  - Reviews astigmatism (see Figure 3.5 and the above discussion).
  - Stigmators are located in the condenser and objective lenses.
- Origin of image contrast in TEM.
  - Mass contrast: Absorption differences for different materials.
    - Dark contrast refers to the heavy element/large atom number/thick sample.
    - In other words, the darker regions of the image depict thicker or heavier samples.
  - Diffraction contrast: Contrast depends critically on diffraction conditions.
  - Phase contrast: Contrast that depends on the phase shift of electrons passing through the sample.
    - Lorentz microscopy and electron holography.
    - High-angle annular dark field (HAADF) imaging.
      - Also known as scanning TEM (STEM) contrast.
      - A function of atomic number.
- Mass contrast.
  - Same as above.
- Sample preparation.
  - We use special TEM grids.
  - There is often some polishing involved, also with polishing paper.
  - **Ion milling** can be used.
- **Ion milling:** Removal of the top layer of atoms.
  - A Ga ion source is often used.
  - This is composed of Ga in contact with a sharp W tip.
  - The electric field induces ionization and field emission of  $\text{Ga}^+$ .
  - Focusing is done by an electrostatic lens.
- Typical TEM images of nanoparticles and nanowires.
  - Many examples shown, including  $\text{CdSe}$ ,  $\text{CdS}$ ,  $\text{Fe}_x\text{O}_y$ , etc.
- Ag/AgCl dimer.
  - Mass contrast differentiates Ag and AgCl.

- Structural rearrangements in Au nanoparticles at high temperatures.
  - Beam heating, laser heating, and thermal heating (i.e., in a small furnace holder) can all be used to observe phase changes, structural changes, etc.
- TEM images of carbon nanomaterials.
  - Several examples.
- Dislocation upon nucleation (2D-to-3D transition).
  - Strained 2D layers become strain-free 3D islands.
  - Significance??
- Electronic devices with nanoparticle superstructures.
  - Pictures of computer-y stuff.
- More nanoparticle pictures.
  - Significance??

# Week 4

## Spectroscopy Wrap-Up

### 4.1 XPS and Misc. Spectroscopic Techniques

1/24:

- If it looks like there will be snow on exam day, we'll do a virtual exam.
- The exam is open notes, but we can do cameras on or something like that.
- Submit the HW any time before the exam to both Shevchenko's anl.gov and uchicago.edu addresses; put "Homework" in the subject line.
- We now start the lecture, picking up from last time on TEM.
- TEM back then.
  - High-voltage electron microscopy was developed in 1968, even though this is antiquated by today's standards.
  - The idea is that this high-voltage one (megavolt range) produced electron beams 10× as strong.
  - Check out *cite*; it was the state of the art back then.
  - Where has this slide gone??
- Interaction of electrons with matter.
  - Reviews Figure 3.3.
  - TEM utilizes the transmitted electrons (both elastically and inelastically scattered).
- Conventional TEM (CTEM).

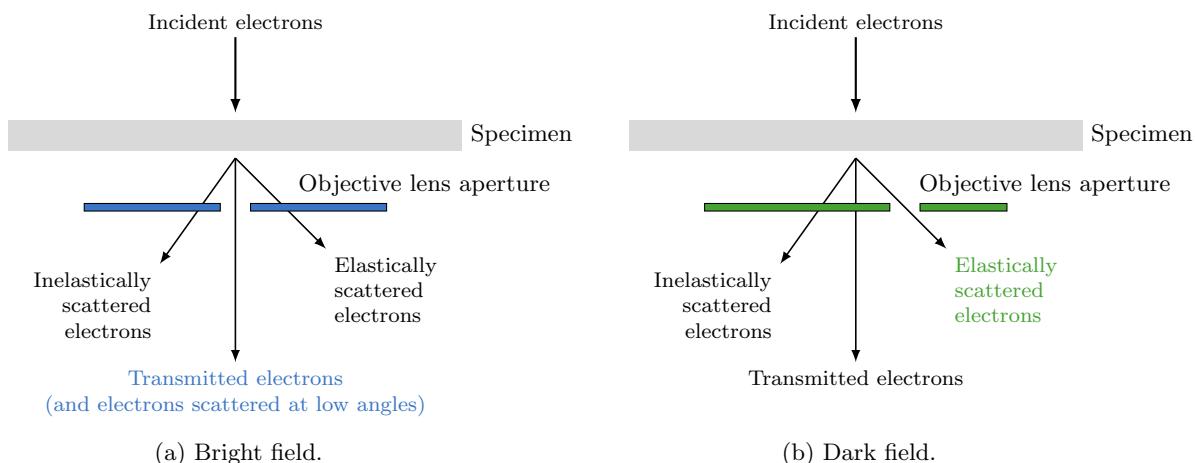


Figure 4.1: OL configuration in bright and dark field modes.

- You don't often see "CTEM" (usually just "TEM").
- The sample is illuminated with electrons.
  - Only the ones that pass through the specimen are used.
  - The direct image is formed by the objective lens and is recorded in the image plane.
  - Two modes: **Bright field** and **dark field**.
- **Bright field:** Some areas of the sample absorb electrons and appear darker, while other areas that transmit electrons appear brighter. The transmitted electron beam is selected with the aperture, and the scattered electrons are blocked.
- **Dark field:** The transmitted electrons are excluded from the aperture, and the scattered electrons are selected. The areas where there is no electron scattering (e.g., the areas around the sample) will be black.
  - The main difference between the two modes is which electron populations are used to construct the TEM image.
- Bright field and dark field TEM micrographs.

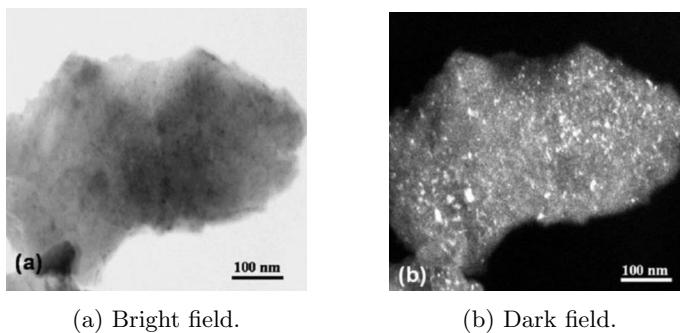
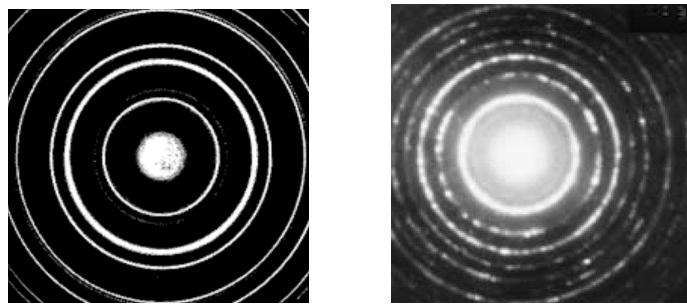


Figure 4.2: Bright field and dark field TEM micrographs.

- Can be used to study crystal lattices, crystal defects, stacking faults, dislocations, and particle/grain sizes.
- Basic observations.
  - Bright: Background is light.
  - Dark: Background is black.
- Specialties of each.
  - Bright: Conventional and sufficient for most applications.
    - Allows you to more easily see what's there and what's going on.
  - Dark: Highlights specific structures.
    - For example, crystalline domains in an amorphous material appear much more clearly in a dark field.
- Selected area electron diffraction (SAED).
  - Electrons passing through the thin sample easily "act" as waves with wavelength of about  $0.025\text{ \AA}$  (about 200 keV).
  - The spacing between atoms is about 100 times larger.
  - Electrons can diffract.
  - What is the significance of this??

- Indexing principles of ED.



(a) Polycrystalline.

(b) Preferred orientation.

Figure 4.3: SAED images of polycrystalline vs. oriented materials.

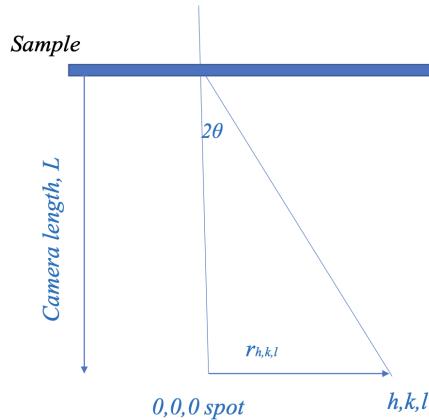


Figure 4.4: SAED condition derivation.

- A **polycrystalline** material gives perfect circles; each circle corresponds to an  $hkl$  plane.
  - When crystalline domains are in their preferred orientation, the rings appear as broken.
  - Same diffraction condition as with XRD.

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

- As before, we start with

$$\tan(2\theta) = \frac{r_{hkl}}{L}$$

See Figure 4.4.

- Moreover, since  $\theta$  is very small, we can invoke the SAA. This yields

$$\tan(2\theta) = 2\theta \quad \sin \theta = \theta$$

- Thus,  $2\theta = r_{hkl}/L$  and  $\lambda = 2d_{hkl}\theta$ , so

$$r_{hkl}d_{hkl} = \lambda L$$

- $L$  is the camera length.

- **Polycrystalline** (material): A material in which all possible orientations of the crystal domains are present.

- SAED example.
  - Measuring the distance between the center spot and other spots provides information about the ratios of  $d$  spacings.
  - Not much said on this — even Shevchenko doesn't know very much about how it works.
  - Dan Schechtman won the 2011 Nobel Prize in Chemistry for results based on this method that he struggled mightily to publish because the scientific community was so skeptical.
    - Essentially, he won for the discovery of icosahedral quasiperiodic structure.
    - The icosahedral symmetry, specifically, of the phase was revealed via SAED.
  - Outline of Schechtman's work.
    - Studied the rapid solidification of a melted metal.
      - Specifically, he studied the solidified Al-Mn alloys formed via rapid cooling.
    - Such cooling leads to the formation of *small-grain polycrystalline microstructures*. These are...
      - Structures with very small grain sizes;
      - Extremely difficult to study by X-ray diffraction;
      - Very suitable for TEM.
    - The slides have a picture of a series of SAD electron diffraction patterns obtained from the Al<sub>78</sub>Mn<sub>22</sub> rapidly solidified alloy by tilting a single grain. Based on these patterns, a unique non-crystallographic 10-fold axis and a one-dimensional periodicity of the decagonal phase were established.
      - For a long time, the community tried to explain away his results as coming from some defect.
      - Significance: This is the first known example of discovering a particular structure in a manmade material, and only later discovering it in natural materials.
- Au/Fe<sub>3</sub>O<sub>4</sub> nanoparticle superlattices.
  - Nanocrystals self-assemble to form a quasicrystal structure.
  - Image quality improvements are possible via post-processing with mathematical filters, e.g., FFT.
    - You have to be careful not to create artificial features in your image, though!
- Scanning transmission electron microscopy (STEM).
  - Picture of the setup (analogous to Figure 3.8b) present in slides.
    - In fact, the only major differences are the addition of deflection scan coils between the condenser aperture and the upper objective polepiece, and the addition of a STEM detector (back focal plane of objective lens) beneath the lower objective polepiece.
  - Unlike in CTEM, in STEM...
    - The electron beam is focused to a fine spot (approximate size: 0.05-0.2 nm).
    - The beam scans over the sample in a raster illumination system that is constructed so that the sample is illuminated at each point with the beam parallel to the optical axis.
  - STEM is great for analytical techniques such as Z-contrast annular dark-field imaging (which we'll talk about later), as well as spectroscopic mapping by energy dispersive X-ray (EDX) spectroscopy and/or electron energy loss spectroscopy (EELS).
  - A typical STEM is a CTEM plus additional scanning coils and detectors. However...
    - It can be very expensive to make these modifications, and it can't be done to every instrument.
  - Addition of an aberration corrector to STEMs enables electron probes to be focused to sub-Å diameters.
    - Images with sub-Å resolution (better than 1.36 Å) can be acquired.

- STEM vs. TEM.

- For STEM, there are special requirements for the housing room. To get atomic resolution images in STEM, the level of vibration, temperature fluctuations, electromagnetic waves, and acoustic waves must be limited.
- Thus, these machines are usually in a basement in a specially engineered room. Common features include a concrete layer, then some damping polymer, then another concrete layer.
- STEMs are also much more complicated-looking, clunky machines. No nice outer shell.
- CTEMs are usually built into a workstation with a computer and can be in most any room.
- Is this why GCIS has a sub-basement with all the spectroscopy stuff?

- HAADF imaging.

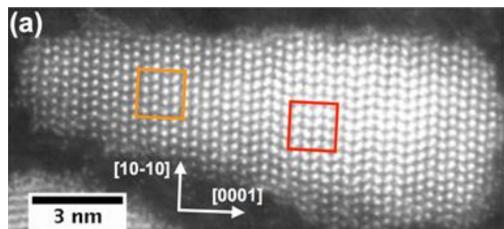


Figure 4.5: HAADF image of CdSe/CdS nanoparticles.

- “High angle annular dark field.”
- The scattering angle and extent of scattering of some electrons depends on  $Z$ .
- The central beam and all electrons scattered at very high semiangle are excluded from imaging.
- You block specific scattered electrons.
- The HAADF detector enables analysis of the crystals via  $Z$ -contrast imaging by capturing scattered electrons at specific angles.
- The intensity of the scattered electrons at the high angles is proportional to  $Z^\alpha$ , where  $Z$  is the atomic number and  $\alpha \in [1.6, 1.9]$  for most cases.
- Contrast variations in the atomic resolution images can thus be used to delineate the CdSe core structure embedded within the CdS shell, due to the weaker scattering cross-section of sulfur atoms compared to the selenium atoms.
- Orange box is CdS, and red is CdSe??
- Selenium is brighter, less contrast.
- Comparison of CTEM and HAADF.
- In HAADF, significant differences in  $Z$  lead to bright spots.
  - For example, single Pt atoms show up as white circles on an otherwise gray FeOx support.
  - Very much like in Figure 4.5 with Se vs. S.
- HAADF-STEM imaging is popular in the study of catalysts and electrocatalysts.
- CTEM images, on the other hand, just show broader shapes and outlines.

- Another HAADF example.

- We can get really high magnification here.
- Two layers of MoS<sub>2</sub> on top of each other.
- Commentary here on the applications of the FFT to spectroscopy.

- Electron energy loss spectroscopy (EELS).
  - Picture of the setup (analogous to Figure 3.8b) present in slides.
  - TEMs contain a great source of electrons for material interactions. However, we don't have to limit these sources to TEM alone. Indeed, we can repurpose them for other kinds of spectroscopy.
  - EELS allows you to study the phonons of individual atoms.
    - Can also measure oxidation states.
  - Working principle.
    - A sample is exposed to an electron beam with a very narrow energy distribution.
    - Some electrons undergo inelastic scattering (lose energy and pathways are deflected).
    - Inelastic interactions include photon excitations, inter- and intra-band transitions, plasmon excitations, ionization of the inner shell, etc.
    - The **inner-shell ionizations** are used to analyze the elemental components of a sample and oxidation state.
    - The amount of energy loss can be measured via an electron spectrometer.
  - Unless you specialize in microscopy, you won't need to know much about this technique.
- Electron tomography.
  - It is often the case that a two-dimensional view is not enough; three dimensions is better!
  - You use special holders that are much smaller and allow more tilting.
  - Collect images over a large range of tilt angles.
    - The more angles, the better the image.
  - Reconstruct using one of various methods to form a 3D image of the sample.
- A “reactor” in TEM: *In situ* TEM.

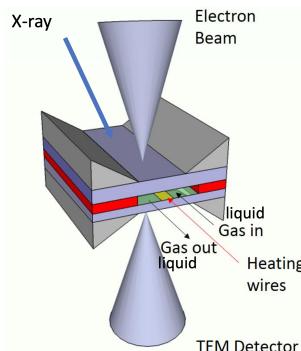


Figure 4.6: *In situ* TEM.

- There exist special liquid cells that allow you to observe reactions in progress.
- You have to be careful to make sure that the electron beam doesn't break the cell — it's very fragile.
- You can also study ion intercalation, which is important to the structural information of battery materials.
- Probe the dynamics at atomic scale.
  - The atoms at the surface of nanomaterials hop from one position to another based on the electrons.
  - You can observe atomic rearrangement and stuff like that.

- We now move on to X-ray photoelectron spectroscopy (XPS).
- XPS is a UHV (ultra-high vacuum) technique.
  - Some modifications can enable lower vacuums.
  - But in general, the higher the vacuum, the better the signal.
  - Topics of study: Clean surfaces, ambient reactions at surfaces, and controlled adsorption and reaction on clean surfaces, ranging from submonolayer through to situations that go deeper, such as the early stages of oxidation and corrosion.
- Contribution of XPS to different fields.

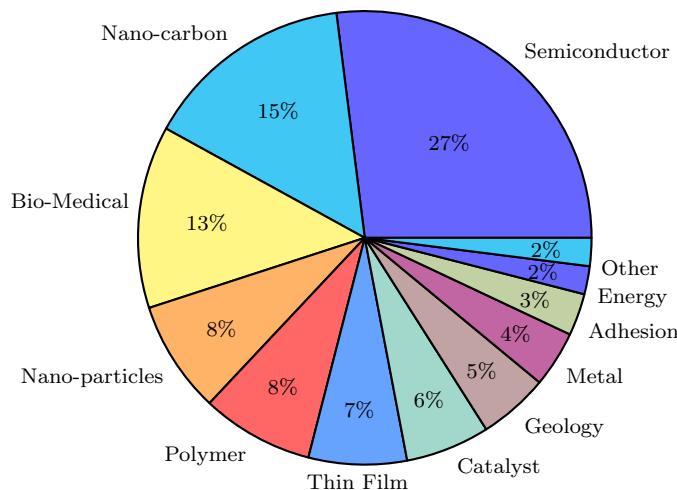


Figure 4.7: XPS in different fields.

- The applications are evidently broad.
- How do X-rays interact with matter?
  - See Lecture 1.2: Definitions of absorption, elastic scattering, and inelastic scattering.
- Photoelectric effect.
  - Recall the kinds of electrons that can be generated (Figure 3.3).
  - To stabilize the atom, an outer shell electron fills the vacancy in the inner shell.
  - We won't continue to talk about photoelectrons and auger electrons, but recall that the probability of the photoelectric effect is higher when...
    - The energy of the incident photon is greater than or equal to the binding energy of the electron in its shell;
    - The electron is tightly bound (e.g.,  $K$  shell).
  - Photoelectric absorption is proportional to

$$\frac{pZ^3}{E^3}$$

where  $p$  is the physical density of the attenuating medium,  $Z$  is the atomic number, and  $E$  is the energy of the incident photons.

- More on this equation??

- X-ray photoelectron spectroscopy.

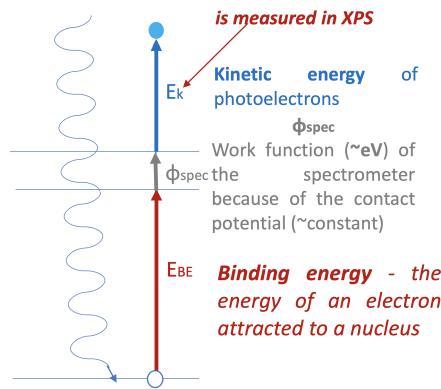


Figure 4.8: XPS equation visualization.

- In the domain of XPS, the following equation is very important, but we will not even touch it.
 
$$h\nu = E_{\text{BE}} + (E_k + \phi_{\text{sp}})$$
  - We want to find out the binding energy  $E_{\text{BE}}$ , so we measure  $E_k$ .
- The binding energy tells us how attracted an electron is to its nucleus. In particular, it tells us...
  - What element;
  - The valence state of the element;
  - The coordination environment (e.g., ligands).
- Binding energy reference.
  - A diagram of how the binding energy works.
  - Lots of interesting detail, but Shevchenko glossed over it.
- Early days of XPS.
  - Heinrich Hertz (1887): First experimental observation of the photoelectric effect.
  - Albert Einstein (1905): Explained the photoelectric effect.
  - Karl Manne Siegbahn (1924): XPS and Siegbahn notation ( $K_{\alpha_1}$ , etc.).
    - Siegbahn proposed **Siegbahn notation**; not in common use any more.
    - There is a chart on it in the slides, though.
  - Kai Siegbahn (1954): Significant improvements in the equipment; the first high-energy-resolution XPS spectrum of cleaved NaCl.
  - Kai Siegbahn (1967): XPS called Electron Spectroscopy for Chemical Analysis (ESCA).
  - Kai Siegbahn + Hewlett-Packard (1969): The first commercial monochromatic XPS instrument.
- XPS system.
  - Schematic of an XPS system (similar to Figure 3.8a, but a real pic).
  - Al  $K_{\alpha}$  and Mg  $K_{\alpha}$  provide soft X-rays of 1486.6 eV and 1254.4 eV, respectively.
  - Why do we need two X-ray sources?
    - To separate signals from Auger electrons and photoelectrons: The binding energy does not depend on the energy of the incoming X-rays, but the Augers will be affected.

- XPS is not destructive in a classical way; however, it can be coupled with an etching technique that removes the topic atomic layer.
  - Can induce possible artifacts (e.g., induced chemical changes, the preferential sputtering of elements, surface roughening, etc.).
- The largest size for a monochromatic beam of X-rays is 1-5 mm.
  - Non-monochromatic beam: 10-50 mm.
- XPS with synchrotron radiation: Down to  $\sim 200$  nm.
- Survey XPS spectra.
  - This is the first step; scan in a broad energy range. This will allow you to identify all elements present in the sample.
  - Drop and dry on a silicon wafer.
  - Wide-scan survey spectrum showing all elements present.
  - Then narrow the range for high-resolution XPS spectrum.
- XPS spectra: Example.
  - A series of oxide films of Ni-Cr-Mo alloys (corrosion resistant alloys in both oxidizing and reducing environments).
  - The spectra are usually presented from higher to lower counts; this is just canonical.
- Alex Filatov is a great resource for questions on XPS; Shevchenko only does it from time to time.
- Analysis.
  - Three main things.
    1. Peak position (along the  $x$ -axis, which is binding energy in eV): Indicates the elemental and chemical composition.
    2. Peak intensity ( $x$ -axis, total number of photoelectron counts per second): Indicates how much of a given element is present at a sample's surface.
    3. Overlapping peaks (complication; Sn and Pb can have interfering peaks).
  - XPSPEAK4.1 is an open-source peak fitting software that Shevchenko recommends.
    - CASA is a powerful, reliable, and broadly used software.
  - Make sure to check tables from multiple sources!
  - The number of peaks produced by a single element varies from 1 up to many.
- XPS signals.
  - Ideal case is no background.
    - All the intensity is from photoionizing a  $1s$  electron of Li and a  $1s$  electron from F.
    - No contribution of instrumental correction (work function).
    - Relative atomic concentrations: The measured intensities (the areas under the peaks) normalized by a partial photoionization cross section  $\sigma$ .
  - However, we often have some extrinsic background.
    - Formed from Auger electrons.
    - Peaks are formed by the intrinsic electrons ejected through the LiF matrix without energy loss (inelastic scattering). The inelastic mean free path length is very small, so the peaks originate from the surface.
    - The background is from photoelectrons that underwent inelastic collisions and lost energy on the way out (the extrinsic photoelectrons scattered once, twice, etc. times — energy contribution over a broad range — the background step extends 100s eV to lower KE).

- Probability of the electron transitions.

- Intensity ratio is given by

$$\frac{2j_- + 1}{2j_+ + 1}$$

- $j$  is the quantum number  $j = l + s$ .

- The relative photoelectron peak intensities are determined by the relative probability (partial photoionization cross sections) for each orbital level to undergo photoionization at given  $h\nu$ .

- These depend on the overlap between the X-ray wavefunction and the orbital wavefunction.

- Why can't H and He be detected by XPS?

- All electrons are used in chemical bonds; and the cross section is extremely low.

- Are bonding electrons generally harder to knock out than atomic ones??

- Example: U.

- A plot of the relative binding energies and ionization cross-section for uranium.

- **Spin orbital coupling:** The distance between the two peaks.

- The values of spin orbital splitting of a core level of an element in different compounds are nearly the same.
- The **peak area ratios** of a core level of an element in different compounds are also nearly the same.
- For  $p, d, f$  peaks, two peaks will be observed.

- **Chemical shift:** A slight change in the binding energy of a core electron due to major changes in the valence levels.

- Caused by bonding between atoms (chemistry — oxidation and coordination).
- Core binding energies of the electron depend on the electrostatic interaction between it and the nucleus.
- Core binding energies of the electron can be reduced by the electrostatic shielding of the nuclear charge from all other electrons in the atom, including valence electrons.
- Withdrawal of valence electrons (e.g., oxidation) leads to an increase in binding energy.
- Addition of valence electrons decrease the binding energy.
- Gold need not be 1 or 3; it can also be partially shifted.
- Binding energy in oxides is higher because electron density (e.g.,  $2s$ ) can be transferred to oxygen.

- Background.

- How do we edit out the background?

- Simplest method: Draw a straight line between the beginning and the end of the peak.

- The area under the peak is almost unaffected by small variations in where one picks the start and end.

- Good for qualitative analysis, not for quantitative analysis.

- Shirley background subtraction requires picking start and finish points, and the background goes up in proportion to the total number of photoelectrons below its binding energy position.

- Tougaard background subtraction is not entirely empirical, and attempts to calculate the actual inelastic scattering events used parameters derived from other experiments.

- There are also others.

- Ask Filatov if you're still curious; it's a good question for him.

- Satellite features.
  - Some of the photon energy can be used to excite the ion out of the zero loss state while at the same instant ejecting the photoelectron with the remaining photon energy. Example: Shake-up structure in the  $2p3/2$  spectrum for Cu<sup>II</sup> species in Cu(OH)<sub>2</sub> and CuO.
  - Shake-off events when more than one electron is ejected at the time of photoionization may lead to broadening of the core level peak.
- XPS on insulating materials.
  - Surface charge buildup: Positive charge at or near the sample surface is built up due to the emission of electrons. This charge build up can be non-uniform and can shift the energy of photoelectrons emitted from the sample, distorting the peak shape.
  - Siegbahn method relies on the use of C(1s) spectra of **adventitious** carbon present on all surfaces exposed to the ambient air (C–C/C–H component of the measured C(1s) spectrum has a binding energy in the range of 284.6–285.0 eV; the  $\Delta_{\text{corr}}$  is determined from the measured peak and applied as a constant shift to all peaks in the spectrum).
- No exam questions on any of the following.
- X-ray fluorescence (XRF).
  - XRF basics.
    - The energy of X-ray fluorescence photons is characteristic of each element.
    - XRF is quantitative, i.e., the number of XRF photons is directly related to the quantity of the element.
    - The photoelectric effect absorption crosssection is simple to calculate (use a monochromatic incident beam).
  - Spectroscopy that takes advantage of XRF: EDXRF.
    - Energy dispersive X-ray fluorescence (EDXRF) is a routinely used analytical technique for the qualitative and quantitative determination of major and minor atomic elements in a wide variety of sample types.
    - Rapid, non-destructive, multi-element analyses from low ppm levels to high weight percent (wt%) concentrations.
    - Non-destructive analysis of sodium to uranium in almost any matrix, from oils and liquids to solids, metals, polymers, powders, pastes, coatings, and thin films.
  - Applications.
    - Especially well-suited for semi-quantitative determination of elemental content in complete unknowns.
    - The instrument has variable spot size to collect information from different areas.
- X-ray fluorescence at a synchrotron.
  - We need: A coherent and monochromatic X-ray beam, optics, a sample mount, and a detector to read the spectrum.
  - Schematic of a hard X-ray microscope.
- XRF at APS.
  - A few sample mount options (described in the slides).
  - The beam size in Sector 2 is 450 nm and the step is 200 nm.
- Investigation of cartilage.
  - Pretty straightforward application ow what came before.

- Bench-top XRF instruments.
  - A 60 kV X-ray tube for wide elemental coverage (typically).
  - Automatic sample changers, sample spinner, and helium purge or vacuum atmosphere.
- Reading recommendation.
  - These provide great overviews of what we've talked out and what can be used to provide answers about various types of nanomaterials.
- Shevchenko will share last year's exam and this year's will be simpler; solve all questions.

## 4.2 Hands-On Class

- 1/26:
- XPS at this school never works.
  - Taught by Sophie Anferov (formerly Whitmeyer).
  - Sophie runs a lot of samples for a lot of people. Dong and Levin group have trained crystallographers, but most people go through her.
  - Sophie is a 4th year and will be thinking about passing the job along soon, so if we're interested, we should reach out.
  - If we ever have crystals (we're not organic, so probably not many of us), we can email Alex and CC her; they have a crystallography form that you can submit and then they'll schedule you.
  - First, we have to crystallize them.
    - Use a solvent that your substance isn't readily soluble in and pull your crystal out or add another solvent to kick it out; you want to promote slow growth.
  - Crystals are special because of their periodicity.
  - Most crystals are run cold ( $\sim 100\text{ K}$  here and in a  $\text{N}_2$  stream).
    - It shouldn't ice, but if you ever do see icing, let them know; it will affect your results since ice is a crystal, itself!
  - Crystals are run overnight (4PM-next morning) to get as much data as possible.
  - This instrument has a molybdenum source for most crystals (90% of the time; goes out further, better bond resolution, and bright enough) and a copper source for some (you need brighter, but will not "go out as far"). If you get a chiral space group, switching to copper may make sense.
  - This diffractometer model is 8-10 years old, but Sophie thinks its one of the best ones since some newer ones have problems.
  - The copper and molybdenum X-ray tubes are on the right.
  - This facility is mainly single crystal (the only one on campus), but can also do some PXRD.
  - The doors need to shut for the X-ray to turn on; make sure they're shut if you're having errors!
  - There is an emergency eject switch on the inside, but obviously don't get trapped inside.
  - Lights on the left side mean that both beams are ready to go.
  - **Twin spectra:** The dual spectra of two crystals overlaid on top of each other; complicates your results.
  - Crystals with lines in them are not good (inspect in dark mode on the microscope); this probably means they have a crack or an impurity.

- “It’s nice to have something you know diffracts in case something weird is happening.”
- We put the crystals in mineral oil to get them here, and then get them into the machine with a **crystal loop**.
  - Our loops are made of plastic (amorphous and thus don’t show up) and glass.
  - There’s a lot of loop history, but Sophie isn’t familiar.
- Your goal in mounting a crystal is to get the crystal onto the tip of the loop; it needs to be well-centered.
  - This is a bit of an acquired skill.
  - If you don’t center it properly, it may move out of the field during a rotation in the experiment.
  - The beam lies in the top-right quadrant, not the center, so you have to put it there.
- Make sure that the distance is about twice the length of your longest plane; if you have 10,10,20, then use 40??
- Mineral oil helps it adhere to the loop, helps with air sensitivity, and prevents things from skittering away if you...
- If your compound is soluble in Pet ether, it will probably dissolve in the mineral oil, in which case you need to use very small quantities of oil and move quickly. There aren’t really many alternatives to oil, so you just have to be fast.
- An intense ring indicates a powder structure; we need to watch out for this.
- You can take sample scans.
  - Here, our first step is determining the unit cell; this is an important check to make sure that our compound looks right. Prevents us from wasting our money and time on an XRD experiment.
  - This is not necessary at Argonne (or other synchrotrons), though.
- Most analysis is done on the new computer in the room.
  - Has a nice Cambridge database downloaded.
    - The CCDC.
    - Nicer than what you can get online.
  - Unit cell search to start.
  - It’s best policy to submit structure to the database before/after publishing. All of the information you need to upload should be in your crystal file. Questions? Ask Alex or Sophie.
- They *can* collect **connectivity structures** (lower res), but usually they only collect publication-quality structures.
  - Certain organic professors like publishing low-res structures, but this makes the department look bad.
  - You need to make sure that every frame in a rotation video has spots in it.
  - Sensitivity around 5 to collect lots of spots, but not spurious ones. Then click harvest. 51 distinct spots is usually enough to get a unit cell.
  - Some people don’t use least squares, but Sophie thinks its fine. Least squares and other mathematical techniques help you solve the structure.
  - Any time you see “rhombohedral” or “cubic,” you may well be running a salt.
    - They always run in triclinic.

- They charge for a more expensive first hour and much less expensive consecutive hours to encourage collecting good data.
- To confirm the unit cell, you want to make sure that the dots show up as a grid.
- The database allows us to make sure that our crystal isn't something common.
- We size the crystal from a video that we take.
  - Nice to take the video before collection in case something happens to your crystal during the experiment.
- Molybdenum's quality cutoff is  $0.84 \text{ \AA}$ ; if you have a lot of difficulties, you can sometimes get results up to  $0.9 \text{ \AA}$  published. Above that is a connectivity structure.
- Quick solve from connectivity data is about 100 frames; if it's not what you want, then adjust.
- There are a bunch of strategy parameters to adjust.
- Hang out for the first 10 frames and then leave, come back the next morning and do your data analysis.
- Data workup is done in Apex.
  - Sophie goes through a worked example.
- Any correlation above 0.5 is good, 0.3-0.4 may be solvable, below that leads to issues.
- Twin solves can be done, but it's a lot more work. You may not always be able to grow distinct crystals.
- Look for clean spots, no rings, and no twins.
- Scaling is different in different places (Argonne doesn't use an absorbance correction for instance).
- Cut the data around 30-50.
- After Apex, use Xprep.
- The software's suggestions are usually fine, even though we don't have to take them.
- Make sure your minimum  $I/\sigma$  stays above 2. Completion shouldn't go below 90% if you want to publish.
  - The worse your data is, the better your guess must be.
  - If fixing really isn't working, you may need to do *something more*.
  - “Never trust someone who says they know where protons are.”
    - They're too low  $Z$ .
- If your research ever really depends on an OH or NH, you need alternate data.
- $\text{CH}_3$ 's and  $\text{CF}_3$ 's have free rotation.
- Crystal data is almost always a solid-state analysis; we can't make claims about how our molecule behaves in solution based on the crystal data.
- A cool application of symmetry things from group theory, very puzzley, and you get to work with actual molecules instead of powders.

## Week 5

# Exam and Molecular Spectroscopy

### 5.1 Intro to Molecular Spectroscopy

2/2:

- First half of the course: Techniques that apply to materials.
- Second half of the course: Techniques that apply to molecular systems, specifically bioinorganic ones.
- Less structural information now; more **spectroscopy**.
- **Spectroscopy**: The study of the interaction of light with *molecular* systems.
- Today: Intro to spectroscopy (specifically vibrational) and group theory.
- Schedule after today:
  - Magnetism (doesn't really involve radiation, but whatever).
  - EPR, XAS, Mossbauer, elecrochemistry, NMR, and (time-permitting) some examples.
- The final: Tuesday, March 7 at the Registrar time (from 7:30am-9:30am).
  - We will probably start at 8:00am and just have a 1.5 h exam.
- Class will mainly be on the board.
  - If there's something that's completely illegible, please stop him and make him clarify it.
- Spectroscopy is the “eyes of the chemist.”
  - It's much more difficult to identify and characterize inorganic compounds vs. organic ones. We also tend to want a lot more information about inorganic systems.
- Flavors of spectroscopy (structure).
  - XRD: Solid-state structure.
    - May have very limited relevance to what's going on in solution.
  - NMR: Solution structure and dynamics.
    - Good for diamagnetic samples.
    - Can work for some paramagnets, but relaxation times keep it from working for many inorganic complexes.
  - EPR: Electron paramagnetic resonance. *Also known as* electron spin resonance (in older papers).
    - Good for paramagnetic samples.
    - Works both in solution and in the solid state.
    - Not good for bulk extended solids; you need isolated spin centers that won't couple.

- EXAFS/XAS: Extended X-ray Absorption Fine Structure, which is a type of X-ray Absorption Spectroscopy.
  - XAS looks at the *absorption* of X-rays by an atom, not just random scattering and diffraction.
  - Recall from the hands-on class that the first thing you do in XRD data analysis is apply an absorption correction; in XAS, that data is what you want.
  - Works in solution and solid. Allows you to measure bond distances and angles in the first shell.
  - EXAFS can be done on a solution or amorphous, disordered sample. This makes it extremely powerful, esp. relative to XRD.
  - Usually coordination and the first shell. You most commonly excite the K-edge ( $1s$ ) and then look at the electron wave's interactions with nearby nuclei.
  - There is a company that makes a benchtop “Easy EXAFS,” and Anderson is trying to get one on campus to help cope with the APS shutdown.
- Dynamics via spectroscopy.
  - Ask, “what is moving?”
  - Moving electrons? Probe with electrochemistry, EPR, optical spectroscopy (not covered much in this course), Mossbauer. We’re especially interested in *electron transfer*.
    - Will depend on the time scale of delocalization (this can be quite difficult to tease apart).
    - Electrons may be in stationary, static wavefunction states, but they can also move between locations as both a particle and a wave.
    - Not usually relevant to organic chemistry.
  - Moving nuclei? Probe with NMR, vibrational spectroscopy, kinetics.
    - Anderson would like to get a grad kinetics course.
    - The overall goal here is to obtain a “video” of the molecule.
- The difference between the techniques we’ve discussed thus far.
- Quick note: It follows from the definition of spectroscopy that XRD is *not* a spectroscopy.
  - This is because spectroscopy necessarily involves absorption of radiation, not diffraction.
- The main difference between different types of spectroscopy is energy regimes!
- Review: A bit of physics.
  - $E = h\nu = hc/\lambda$ . Thus,
$$\nu \text{ (s}^{-1}\text{)} = \frac{c \text{ (cm s}^{-1}\text{)}}{\lambda \text{ (cm)}}$$
  - We can define the wavenumber
$$\nu \text{ (cm}^{-1}\text{)} = \frac{1}{\lambda \text{ (cm)}}$$
- We now look at which energy regimes in the EM spectrum correspond to which types of spectroscopy.
  - $\lambda = 10^6 \text{ cm}$ : Radio frequency, NMR, nuclear spin flips.
  - $\lambda = 10^2 \text{ cm}$ : Microwave frequency, EPR, electron spin flip, rotations.
  - $\lambda = 10^{-2} \text{ cm}$ : Infrared frequency, IR and Raman spectroscopy, molecular vibrations.
  - $\lambda = 10^{-4} - 10^{-5} \text{ cm}$ : Visible, electronic transitions, orbital transitions, CD and MCD ([magnetic] circular dichroism, which we will not discuss).
  - $\lambda = 10^{-5} - 10^{-6} \text{ cm}$ : UV photoelectron spectroscopy (PES); won’t talk to much about this.
  - $\lambda = 10^{-6} - 10^{-9} \text{ cm}$ : X-rays, XRD and XAS.

- $\lambda = 10^{-10}$  cm: Gamma rays, Mossbauer (allows you to get very small peaks using very high energy radiation).
- Beyond gamma rays is electron beams.
- Now we have a bunch of different types of spectroscopy. The next logical question is, “what dynamic processes can be probed with each spectroscopy?”
  - To answer this question, we must consider the *timescales* on which dynamic processes occur.
  - Specifically, in order to relate processes to regions of the EM spectrum, we need to know the timescales as a function of the energies involved.
- Recall that
 
$$\frac{1}{t} = \nu = \frac{c}{\lambda}$$
  - $t$  is the maximum time resolution.
  - $\nu = 1/t$  follows from the Heisenberg uncertainty principle.
  - The above equation implies that
 
$$t = \frac{\lambda}{c}$$
- Example: For UV radiation at 300 nm, we have
 
$$t = \frac{3 \times 10^{-7} \text{ m}}{3 \times 10^8 \text{ m s}^{-1}} = 10^{-15} \text{ s} = 1 \text{ fs}$$
  - The period of a molecular vibration is on this order, so that's why UV/Vis is pretty good at resolving molecular vibrations.
- Time resolution ranges.
  - Electron diffraction:  $10^{-20}$  s.
  - Neutron diffraction:  $10^{-18}$  s.
  - XRD:  $10^{-18}$  s.
  - UV:  $10^{-15}$  s (per the above).
  - Vis:  $10^{-14}$  s.
  - IR/Raman:  $10^{-13}$  s.
  - EPR:  $10^{-4}$ - $10^{-8}$  s.
  - NMR:  $10^{-1}$ - $10^{-9}$  s.
  - Mossbauer:  $10^{-7}$  s.
  - Molecular beams:  $10^{-6}$  s.
  - Experimental isomer separation:  $10^2$  s.
  - For kinetics, about the fastest we can do is stop flow at  $10^{-3}$ - $10^{-5}$  s.
- A few misc. notes on time resolution follow.
- We cannot use XRD to resolve a molecular vibration (which happens much more slowly), or at least not easily.
  - This is because an XRD experiment collects many frames over 30-60 seconds and we average over all nuclear configurations that occur during that time.
  - It is this molecular vibration that makes our diffractograms not perfectly spherical but more ellipsoidal.
  - An individual X-ray pulse could resolve vibrations.

- Similarly, Mossbauer is relatively low time resolution even with gamma rays due to experimental limitations.
  - Units are  $\text{mm s}^{-1}$ .
- You need to think about what's going on physically in this course!
- Tangent on Lawrence Berkeley Laboratory (LBL) and determining the mechanism of water oxidation (which is only done by one natural system, chlorophyll photosystem II).
  - They use the FEL to get very good time resolution, growing thousands of crystals on a conveyor belt, dropping them in front of the laser, collecting one frame, and moving onto the next crystal. The random distribution of orientations (as opposed to rotating the goniometer) in the falling crystal leads to really good data.
- An example of where time resolution matters: Studying the Creutz-Taube ion.



Figure 5.1: The Creutz-Taube ion.

- History.
  - Henry Taube was a Nobel laureate and a physical inorganic chemist.
    - He did most of his work at Stanford and then UChicago lured him away and he's now proudly displayed on our website.
    - Anderson: This is a repeating pattern at UChicago.
  - Carol Creutz was his grad student (very brilliant). Anderson went to grad school with her nephew, who's now a professor in his own right.
- The ligand is most typically  $\text{NH}_3$ .
- A pertinent question: What is the oxidation state of Ru? Is it a fractional 2.5 oxidation state, or do we have one  $\text{Ru}^{\text{II}}$  and one  $\text{Ru}^{\text{III}}$ ?
  - Where time resolution comes in: The answer to the above question depends on which technique you use.
  - With good enough time resolution, the electron hopping rate is on the order of  $3 \times 10^8 \text{ s}^{-1}$ , so the lifetime  $1/\nu$  is on the order of  $3.3 \times 10^{-7} \text{ s}$ . Look for an IVCT (inter-valence charge transfer).
  - Visible and IR are the best techniques to use here. 1000-1600 nm is what you want to analyze these types of things.
- Misc. note: Be aware when you're doing UV/Vis! Make sure there's not something extra at the far end of the spectrum that might actually be important.
- Anderson is going to put all of his notes up on Canvas; make sure that we follow up if he forgets!
- Moving on: Vibrational spectroscopy now.
- IR is super boring and doesn't always tell you anything, but there are reasons to appreciate it.
  - Super fast time resolution.
  - Completely insensitive to the electronic structure of what you're looking at.
    - E.g., diamagnetic, paramagnetic, semiconductor, etc.
  - All that matters is the symmetry of the thing you're probing and certain selection rules.

- Very brief overview of group theory, character tables, and how they relate to spectroscopy.
  - Example: Water modes.
  - We can find nice GIFs of water vibrating by Googling “water vibration modes” (link).
  - Three modes: Symmetric stretch, asymmetric stretch, bending.
    - Called  $A_1, B_2, A_1$ .
  - $A_1, B_1, B_2$  are IR active via the character table (dipole must change, so  $x, y, z$  is important).
  - $A_1$  is Raman active via the character table (polarization must change, so  $x^2, y^2, z^2$  is important).
  - An IR-active stretch must not be centrosymmetric.
  - Prussian blues contain M–C≡N–M motifs; because the C≡N moieties are always polar, we get IR. If it’s M–N≡N–M instead, IR is forbidden, though we’ll still get Raman of course because *something* is changing in the molecules.
  - With Raman, you can see just about everything.
- IR has a pretty simple setup; Raman is much more complicated.

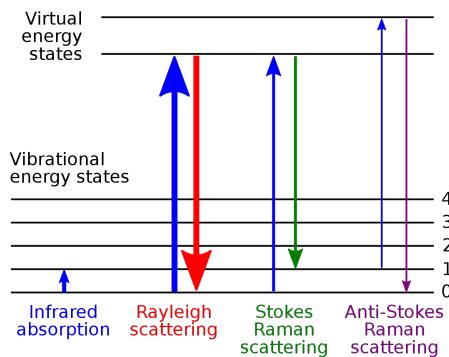


Figure 5.2: Raman spectroscopic mechanics.

- IR: Pump an electron up one vibrational mode. Sometimes multiple via overtones.
- Raman: Take your molecule, shoot a laser at the sample, and see what light scatters. You’re least interested in **Rayleigh scattering**. What you care about is different changes (**Stokes** and **Anti-Stokes Raman scattering**). Note that the latter will be far less intense than the former due to the differences in populations between the  $v = 0, 1$  states. We resolve vibrational energy levels by looking at differences between input and output frequency.
  - Indeed, in words: Rayleigh scattering is the most intense, Stokes is ok, and Anti-Stokes is poor.
- Populations are proportional to the sizes of the arrows in Figure 5.2.
- Raman is good for materials, not for molecules.
  - Great for MoS<sub>2</sub>, but for molecules, you need huge fluxes which tend to fry your sample.
- Anderson is not a huge fan of Raman spectroscopy.
- How Raman actually works: Your photon doesn’t so much get absorbed as it scatters off of the electron cloud by coupling with the polarization wavefunction.
- Rayleigh is elastic; Raman is inelastic scattering.
- Conjugated macrocycles (e.g., heme groups) are great, but most aren’t. Worth trying in the lab, but don’t get your hopes up.
- Resonance is when you have a specific optical bond being much more intense.

- To finish off our brief treatment of vibrational spectroscopy, we'll discuss isotope effects.
  - Many times we want to test whether an observed vibration corresponds to specific atoms. To do this, we want to do an isotopic substitution.
  - This can change the energy of a vibration by an amount that can be predicted by the simple harmonic oscillator approximation.
- Example: Consider  $^{16}\text{O}_2$  vs.  $^{18}\text{O}_2$ .
  - In Raman spectroscopy, we have  $\nu_{00} = 749 \text{ cm}^{-1}$  and  $\nu_{00} = 708 \text{ cm}^{-1}$ , respectively.
  - Recall that  $\nu = k\sqrt{F/\mu}$ , where

$$\frac{1}{\mu} = \frac{1}{^{16}\text{O}} + \frac{1}{^{16}\text{O}} = \frac{^{16}\text{O}^{16}\text{O}}{^{16}\text{O} + ^{16}\text{O}}$$

– Thus,

$$\mu_{16} = 0.125 \quad \mu_{18} = 0.111$$

– It follows that

$$\begin{aligned} \frac{\nu_{18}}{\nu_{16}} &= \frac{\sqrt{^{18}\text{O}_2}}{\sqrt{^{16}\text{O}_2}} \\ \nu_{18} &= \frac{\sqrt{0.111}}{\sqrt{0.125}} \cdot 749 \\ \nu_{18} &\approx 706 \text{ cm}^{-1} \end{aligned}$$

– We'll get to practice this on the HW.

- The HW will be due 1-2 weeks before the final.
- Further examples.
  1. Test if chlorophyll photosystem II is actively producing oxygen.
    - Air has regular ( $^{16}\text{O}_2$ ) oxygen, so we set the photosystem up with  $^{18}\text{OH}_2$  and use IR to hopefully detect  $^{18}\text{O}_2$  being generated.
  2. Test if a metal complex has a  $\text{M}\equiv\text{N}$  bond.
    - Synthesize your complex with both  $^{14}\text{N}$  and  $^{15}\text{N}$ .
    - Know that  $\text{M}\equiv^{14}\text{N}$  is approximately  $1000 \text{ cm}^{-1}$  and use the above to calculate that  $\text{M}\equiv^{15}\text{N}$  is about  $920 \text{ cm}^{-1}$ .
    - Take spectra of both complexes and then subtract the two to obtain a difference spectrum. If nitrogen is being incorporated, your difference spectrum should be flat except for two peaks (one positive and one negative) at  $1000 \text{ cm}^{-1}$  and  $920 \text{ cm}^{-1}$ .
- Last example from Anderson's written notes.
- **Nuclear resonance vibrational spectroscopy:** A type of vibrational spectroscopy that uses a synchrotron to induce a nuclear excitation. *Also known as NRVS.*
  - This excitation can then couple to vibrations of the excited nucleus.
  - Particularly relevant for Fe, the most common nucleon to study with NRVS.
  - Related to Mossbauer spectroscopy.

# Week 6

## Magnetochemistry

### 6.1 Magnetochemistry I

2/7:

- Extension from last time: Deriving the relationship between two simple harmonic oscillators' fundamental frequencies and reduced masses.
  - Suppose you have two homonuclear diatomic molecules A–A and B–B, and you wish to relate their vibrational frequencies.
  - Reduced masses of the molecules.

$$\mu_{AA} = \frac{m_A m_A}{m_A + m_B} \quad \mu_{BB} = \frac{m_B m_B}{m_B + m_B}$$

- Vibrational frequencies of the molecules in terms of the reduced masses.

$$\nu_{AA} = k \sqrt{\frac{F}{\mu_{AA}}} \quad \nu_{BB} = k \sqrt{\frac{F}{\mu_{BB}}}$$

- Take the ratio of the above two quantities to relate them.

$$\frac{\nu_{AA}}{\nu_{BB}} = \frac{k \sqrt{\frac{F}{\mu_{AA}}}}{k \sqrt{\frac{F}{\mu_{BB}}}} = \frac{\sqrt{\mu_{BB}}}{\sqrt{\mu_{AA}}}$$

- Today: Magnetochemistry.
  - 1-2 lectures on this.
  - Labalme [3] has a good write-up of the derivation at the beginning of today's lecture.
    - See Module 34: Magnetic Properties of Transition Metal Complexes.
  - Labalme [4] has more on the content at the end of the lecture.
    - See Lecture 3: TM Magnetism.
- Magnetism really is the province of inorganic chemistry since it's here that we find the compounds with unpaired electrons.
  - Organic compounds don't have these outside of free radicals.
- We begin with some terminology and relations.
- **Magnetic field.** Denoted by  $\mathbf{H}$ ,  $\vec{H}$ .
  - $H$  denotes the magnitude of  $\vec{H}$ .

- **Magnetization:** The response of the electrons in a material to a magnetic field. *Denoted by  $\mathbf{M}$ .*
  - Alternatively: The magnetic moment per unit volume.
  - Everything with electrons has *some* degree of a response to a magnetic field.
  - Depends on the strength of the field in which the material is placed.
- **Magnetic induction:** The density of magnetic field lines within a substance. *Denoted by  $\mathbf{B}$ . Units Teslas or Gauss. Given by*
  - $1 \text{ T} = 10000 \text{ G}$ .
  - The scale of these units.
    - The Earth's magnetic field is about  $3.1 \times 10^{-5} \text{ T}$ .
    - A 900 MHz NMR spectrometer is about 21 T.
    - An MRI is about 1.3-3 T.
- We now give a few relations between the above quantities.

- First, we have that

$$\mathbf{B} = \frac{\mathbf{F}}{Q\mathbf{v}}$$

where  $F$  is in Newtons,  $Q$  is in Coulombs, and  $v$  is in meters per second.

- Additionally, placing a sample with magnetization  $\mathbf{M}$  in a magnetic field  $\vec{H}$  alters the magnetic induction via

$$\mathbf{B} = \vec{H} + 4\pi\vec{M}$$

- Magnetically isotropic substances in a uniform magnetic field experience no force.
- In a region of nonhomogeneous field strength, a force is exerted along the axis of the field gradient as described by

$$\vec{f} = \vec{M} \cdot \frac{d\mathbf{H}}{dz}$$

- **Magnetic susceptibility:** *Denoted by  $\chi$ . Given by*

$$\chi = \frac{\vec{M}}{\vec{H}}$$

- A tensor of rank 2.
- It follows that  $\vec{M} = \chi \vec{H}$ .
- There are different types of  $\chi$ .
- **Volume susceptibility:** *Denoted by  $\chi_V$ . Units emu cm<sup>-3</sup>.*
  - This is a dimensionless quantity, but we still use the units listed above.
  - Note that an emu is an “electromagnetic unit.”

- **Gram susceptibility:** *Denoted by  $\chi_g$ . Units cm<sup>3</sup> g<sup>-1</sup>. Given by*

$$\chi_g = \frac{\chi_V}{d}$$

- **Molar susceptibility:** *Denoted by  $\chi_M$ . Units cm<sup>3</sup> mol<sup>-1</sup>. Given by*

$$\chi_m = \chi_g \cdot \text{MW}$$

- The sign of  $\chi$  (+/-) depends on the presence or absence of unpaired electrons. In particular...
  - $\chi > 0$  indicates unpaired electrons.
  - $\chi < 0$  indicates paired electrons.
- We now move on to diamagnetism.
- Most matter is diamagnetic.
- **Diamagnetic** (compound): A compound that has no unpaired electrons. *Also known as diamagnet.*
  - $S = 0$  for a diamagnet.
  - These materials are weakly repelled by magnetic fields.
  - The old-school way to measure this weak repulsion is with a **Gouy balance**.
- **Gouy balance:** An instrument that measures the change in mass of a sample as it is attracted or repelled by a powerful magnetic field.

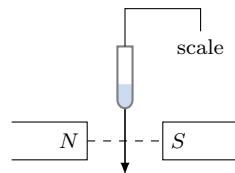


Figure 6.1: Gouy balance.

- Historically, varying a magnetic field precisely has been very difficult (we didn't always have electromagnets into which we could just dial any field).
  - In fact, even today, varying a magnetic field super precisely is difficult. This is why NMR machines vary the frequency domain over a constant magnetic field (as opposed to varying the magnetic domain over a constant frequency).
- Under a constant magnetic field, the sample (contained in an NMR tube) is linked to a scale. As the sample moves through that field, it experiences a changing magnetic field.
- The change in mass of the sample at different points in the field gives information on its magnetic susceptibility.
- Modern update to the Gouy balance: The superconducting quantum interference device, or SQUID.
  - We still measure the magnetic susceptibility essentially the same way, just with fancier toys.
  - Today, we move our sample through an electromagnet-generated magnetic field and then see what kind of current gets induced in a superconducting coil (recall that moving magnets induce currents).
  - The underlying physics is well beyond the scope of this course, but also fascinating. It involves **Josephson junctions**, etc.
- **Diamagnetic magnetic susceptibility.** Denoted by  $\chi_{\text{dia}}$ .
  - Since all electrons are *paired* in a diamagnetic compound, we have by the above that  $\chi_{\text{dia}} < 0$ .
  - Diamagnetic contributions can be calculated as follows.

$$\chi_{\text{dia}} = \sum \lambda + \sum n_i \chi_i$$

- $\lambda$  is a **constitutive correction** related to ring currents for bonds/ring delocalization.
- $n_i \chi_i$  is contributions from individual atoms.

- The values in the above equation can be looked up for a compound.
  - In particular, see Bain and Berry [5].
  - The paper has a nice introduction and does the derivation that Anderson just did, too.
  - Then it contains a bunch of tables of different corrections for various bond types.
  - These values are all pretty small, so it doesn't really matter if you just miss one or two things in ambiguous cases, but Anderson tries to sum over all of them.
  - You *do* need to do these corrections when you're doing a lot of these calculations.
    - The result will be on the order of  $10^{-6}$  emu, but that can be significant enough to effect your work.
  - These tables give both  $\lambda$  and  $\chi_i$  values; you need to sum over the individual atom  $\chi_i$  values and then constitutive corrections for groups. For example, for a Cp group, you have 5 carbons, 5 hydrogens, and a constitutive correction for the whole group (which should be equal to that of 5 carbons, 5 hydrogens, and 5 C=C double bonds??).
  - These values are field-independent and pretty constant.
- That's the contribution from paired electrons. What we really care about in general are the unpaired electrons, though.
- Paramagnetism.
- **Paramagnetic** (compound): A compound that has unpaired electrons. *Also known as paramagnet.*
  - Positive  $\chi$  values; thus, they get pulled into applied magnetic fields.
- Temperature dependence of  $\chi$ .
  - There is an inversely proportional relationship between  $\chi$  and  $T$ ; in other words, a plot of  $1/\chi$  vs.  $T$  is linear.
  - This notion is formalized by **Curie's law**.
- **Curie constant:** The following constant. *Denoted by  $C$ . Given by*
$$C = \frac{N_A g^2 \mu_B (S(S+1))}{3k_B (\text{in hertz}??)}$$
  - $g$  is the **gyromagnetic ratio**.
  - $\mu_B$  is the Bohr magneton.
  - $N_A$  is Avogadro's number.
  - $S$  is the spin quantum number.
- **Gyromagnetic ratio:** The quotient of the magnetic moment of an electron by its angular momentum. *Also known as magnetogyric ratio. Denoted by  $g$ .*
  - There are even more names that the gyromagnetic ratio is sometimes called, just for added complexity :)
  - Any fundamental particle can have one of these.
  - Nuclei have them, but we're only worried about electrons here.
  - Magnetic moment divided by angular momentum.
  - 2.011 for electrons.
  - More on this later.

- **Curie's law:** The relationship between  $\chi$  and  $T$ . Given by

$$\chi = \frac{C}{T}$$

- From the written notes: We have that

$$\mu_B = \frac{e\hbar}{2m_e} = 9.3 \times 10^{-24} \text{ J K}^{-1}$$

- We want to take the picture provided by Curie's law and simplify it down now.
- For the spin-only case (this restriction is very important), we can define the effective magnetic moment

$$\mu_{\text{eff}} = \sqrt{\frac{k_B}{N_A \mu_B^2}} \sqrt{\chi T} = 2.828 \sqrt{\chi T} = \sqrt{g^2(S(S+1))}$$

- What is the origin of the first equality??
  - We also frequently write
- $$\chi T = \frac{N_A g^2 \mu_B}{3k_B} (S(S+1)) = \frac{g^2}{8} (S(S+1))$$
- Magnetochemists almost exclusively use  $\chi T$ , but  $\mu_{\text{eff}}$  is oft reported for room temp characterizations.
  - Know the end results below: Very important for how stuff is computed and talked about in the lit.

$$\mu_{\text{eff}} = \sqrt{g^2(S(S+1))} \quad \chi T = \frac{g^2}{8} S(S+1)$$

- Approximating  $g \approx 2$ , we can rewrite the above as

$$\mu_{\text{eff}} = \sqrt{4(S(S+1))} \quad \chi T = \frac{1}{2} S(S+1)$$

- $g \not\approx 2$  always, though — take a look at the following examples.

- Elements and some paramagnetic parameters.

	$S$	$\mu_{\text{eff}}$	$\chi T_{SO}$	$\mu_{\text{exp}}$
$\text{Cu}^{2+}$	1/2	1.73	0.375	1.7-2.2
$\text{Ni}^{2+}$	1	2.83	1	2.8-3.5
$\text{Cr}^{3+}$	3/2	3.87	1.875	3.7-3.9
$\text{Fe}^{2+}$ HS	2	4.90	3	5.1-5.7
$\text{Fe}^{3+}$ HS	5/2	5.92	4.375	5.7-6

Table 6.1: Magnetic parameters for example elements.

- Notation: SO for spin only. HS for high spin. exp for experimental.
- To calculate the data in Table 6.1, find the number of unpaired electrons and go from there.
- Example:  $\text{Cu}^{2+}$ . From the periodic table,  $\text{Cu}^{2+}$  is  $d^9$ . Hence it has 1 unpaired electron. Thus...
  - $S = 1 \cdot 1/2 = 1/2$ .
  - $\mu_{\text{eff}} = \sqrt{4(S(S+1))} = \sqrt{4(1/2(1/2+1))} = \sqrt{3} = 1.73$ .
  - $\chi T_{SO} = 1/2 \cdot S(S+1) = 1/2 \cdot 1/2(1/2+1) = 3/8 = 0.375$ .
  - The calculated effective  $\mu$  often (not always) agrees with the experimental range.

- We now move on to spin-orbit coupling.
- Spin-orbit coupling:  $g > 0$  for a more-than-half-filled shell;  $g < 0$  for a less-than-half-filled shell.
- Consider a generic metal M with  $S = 1/2$  and another with  $S = 1/2$  and a bridging ligand L between them.
  - Three possibilities to determine magnetism: The spins can be coupled antiferromagnetically (opposite directions) so  $S = 0$ , coupled ferromagnetically so  $S = 1$ , or uncoupled so both behave as their own spin center but are chemically/mechanically linked within the molecule.
- Now for a specific example of metal centers with different spins: Consider Cu–L–Mn, which has  $S = 1/2$  and  $S = 5/2$ . Then

$$\langle \mu \rangle = \sqrt{\mu_{\text{Cu}}^2 + \mu_{\text{Mn}}^2} = \sqrt{3 + 35} = 6.16 \mu_B$$

- How does this work?? What is  $\langle \mu \rangle$ ?
  - Alternatively,  $\chi T$  can be calculated (this is easier??).
  - A brief note about temperature-independent paramagnetism.
    - If we measure Cu<sup>II</sup> and Co<sup>II</sup>, we get  $60 \times 10^{-6}$  emu and  $400 \times 10^{-6}$  emu.
      - These come from excited state mixing: These excited states are not thermally populated, but they are a quantum mechanically admixed state (what does this mean??).
      - What are these values??
  - Note: Curie's law doesn't always hold. In cases where it doesn't, we can correct it to the **Curie-Weiss law**.
  - **Weiss constant:** A constant describing certain magnetic interactions. *Denoted by  $\theta$ .*
    - $\theta = 0$  for a pure paramagnet.
    - $\theta \neq 0$  for a long range magnetic interaction in a solid sample.
  - **Curie-Weiss law:** The following relation, where  $C$  is the Curie constant,  $T$  is temperature, and  $\theta$  is the Weiss constant. *Given by*
- $$\chi = \frac{C}{T - \theta}$$
- Don't rush to use the Curie-Weiss law if your data isn't fitting to Curie's law, though: Magnetic measurements are very sensitive and 90% of the time you're data isn't fitting, it's because your sample isn't clean.
  - We now return to the question of when  $g$  deviates from 2: Indeed, this only happens when there is a substantial magnetic contribution from the orbital angular momentum.
  - $S$  is our spin angular momentum quantum number, and  $L$  is our orbital angular momentum quantum number.
    - If spin and orbital angular momenta couple, then  $S, L$  are no longer good quantum numbers.
    - To fix this problem, we define a new one:  $J$ .
  - We define  $J = L + S$  to characterize coupling.
    - $J$  is very important with the lanthanides where our coupling is extremely large.
      - In fact, in the lanthanides, coupling is so strong that you have to start with only a  $J$  quantum number.
      - For first-row transition metals, we treat  $J$  just as a perturbation.

- We know that

$$L = \sum_i \ell_i \quad S = \sum_i s_i$$

- Thus, our Hamiltonian is

$$H = \hat{H}_0 + \hat{H}_{\text{elec}} + \hat{H}_{\text{SO}}$$

– SO denotes spin-orbit

– We have that

$$\hat{H}_{\text{SO}} = \lambda \hat{L} \cdot \hat{S} + \beta (\hat{L} + g_e \hat{S}) - H$$

where  $\lambda$  is the SOC constant.

– The energy that we get out of this Hamiltonian is

$$E_n = E_n^0 + H E_n^1 + H^2 E_n^2$$

■ The first-order correction is **Zeeman**; the second-order is **2nd order Zeeman**.

- An intuitive mental picture of SOC.

– Consider a perfectly octahedral  $d^1$  complex.

– The electron can migrate through a degenerate set of orbitals, inducing a ring current.

– This is a useful classical analogy with predictive power.

■ However, it is not quantum mechanically accurate at all.

- In a nutshell, we expect to see SO-coupling when we have unequally occupied degenerate orbitals.

– Consider  $\text{Ni}^{2+}$ . It can be  $O_h$  or  $T_d$ . It's tetrahedral because  $\text{Ni}^{2+}$  is  $d^8$  and thus if you draw out the orbital diagram, we'll have one excess electron in the upper triply degenerate orbital. This unequal occupation will lead to a Jahn-Teller distortion, though.

- Aside on free atom configurations.

– These are not a real thing; in this class, we'll always assume that transition metals are realistic, i.e., elemental, in a compound, etc., and thus any higher-level  $s$  electrons fall down to  $d$  electrons.

- Lanthanides' bonding orbitals are too deeply buried.

- **Zero-field splitting:** The removal of spin degeneracy in the absence of an applied magnetic field. *Denoted by  $D$ .*

– Important for Qbits or more exotic materials.

– Look at graphs of energy as a function of applied magnetic field  $H$  (see Figure 6.2).

– We get Zeeman splitting as we increase the magnetic field. In the  $D = 0$  case, our splitting begins from a single point as in Figures 6.2a-6.2b.

– In Figure 6.2c, however, we can observe splitting even at  $H = 0$ .

–  $D$  is on the order of single wavenumbers.

– Affects what EPR values you can excite and other important things. The  $M_s = 0$  state is still a triplet with parallel or antiparallel spins.

– In the  $S = 3/2$  case, we have multibranched splitting??

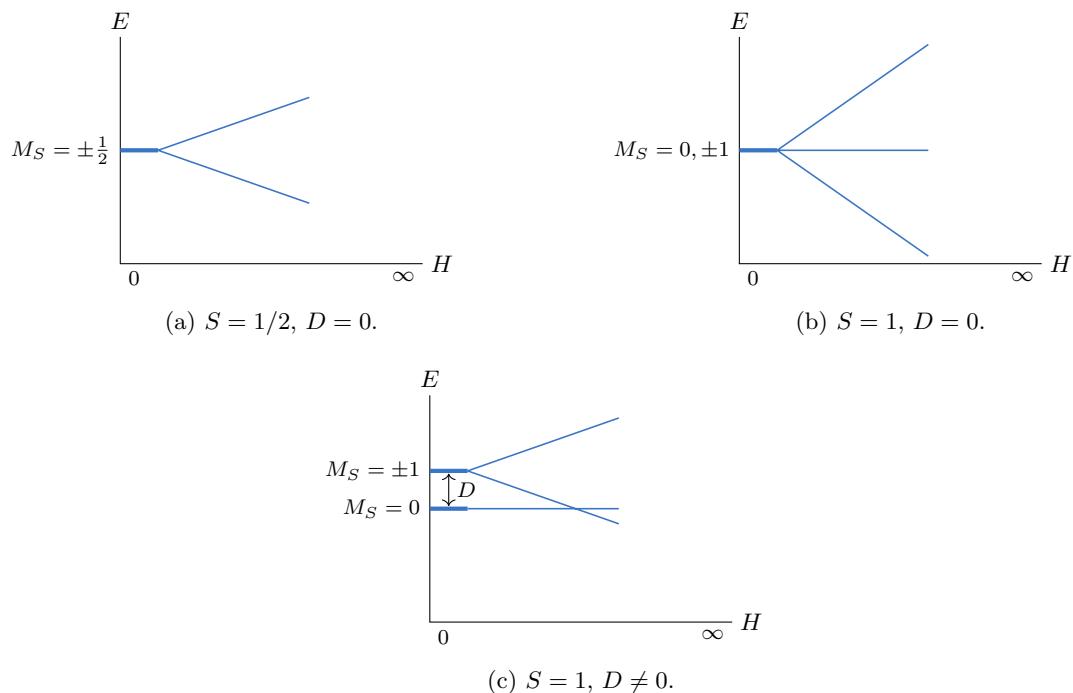


Figure 6.2: Zero field splitting.

## 6.2 Magnetochemistry II

2/9:

- Today: Materials magnetism.
  - We finish up last time's material first, and then head into new content.
- Classical example of zero-field splitting for an  $S = 1$  compound (see Figure 6.2c).
  - The magnitude of spin-orbit coupling determines zero-field splitting.
  - $D$  can be both positive and negative, so it can vary whether the higher state goes up or the lower state goes down. The short answer is just that splitting occurs.
  - Recent example from the literature (unpublished): An aryl-bismuth compound with  $S = 1$  and massive  $D \approx 500 \text{ cm}^{-1}$ . Another one is  $\text{Bi-Bi}^{2-}$ .
- Coupling.
  - Electrons can couple parallel (FM — ferromagnetic) or antiparallel (AF — antiferromagnetic).
    - AF is more common.
    - Relevant Hamiltonian: The **Heisenberg-Dirac-Vleck Hamiltonian**.
  - We measure coupling by measuring  $\chi$  vs.  $T$ .
    - FM systems: As temperature decreases,  $\chi$  slightly increases until the **Curie/critical temperature**  $T_C$ . At this point, the curve turns upwards sharply. For a bulk compound, the curve peaks at  $T_C$  and then goes down.
    - AF systems: As temperature decreases, there is a similar rise to a peak (this time at the **Neel temperature**  $T_N$ ) and drop.
    - As  $J$  gets larger, the FM curve increases (i.e.,  $\chi$  increases). On the other hand, the AF curve decreases and flattens.
    - See Figure 1.13 of Labalme [4] and the picture from class.

- **Heisenberg-Dirac-Van Vleck (Hamiltonian):** The Hamiltonian defined as follows. *Given by*

$$\hat{H}_{\text{HDVV}} = -2J \cdot \vec{S}_1 \cdot \vec{S}_2$$

- $J$  is the coupling constant in  $\text{cm}^{-1}$ .
- $J < 0$  for AF;  $J > 0$  for FM.

- **Bleaney-Bowers equation:** The equation describing the shape of the  $\chi$  vs.  $T$  plot for two spin centers of  $S = 1/2$ . *Given by*

$$\chi = \frac{N\beta^2 g^2}{3k_B T} \cdot \frac{3}{3 + e^{2J/k_B T}} + P \cdot \frac{C}{T}$$

- Fitting data to this functional form allows you to pull out a value of  $J$ .
- Works best for two spin centers of  $S = 1/2$ .
- $P$  is the percentage of paramagnetic impurities.
- If  $S > 1/2$ , the functional form becomes much more complicated and we need softwares to do the fitting.
  - One example is Dave (contact Anderson if you need it).
- Which of the previously discussed plots (FM/AM and bulk/molecular) can we fit with this equation?? Also check the functional form — 2 in the numerator and negative sign in the exponent?

- Orbital interactions for coupling.

- The goal here is to use our understanding of bonding and MO theory to predict magnetic coupling interactions.
- It is a challenging question, but also quite fundamental.
- Example question in this field: If two electrons couple antiferromagnetically, at what point does a strong antiferromagnetic interaction become a bond?
  - Depends on orientation and orbital overlap.
- There are many approaches, but we shoot for a general qualitative picture, only good enough to help us predict the sign and magnitude of coupling in a given system.

- First system to analyze: Picture two spin centers A, B coupled with some diamagnetic bridging ligand X such that we have A–X–B.

- There are two possible ground states:  $S = 0$  (singlet) and  $S = 1$  (triplet).
- Relevant quantitative parameter: the **singlet-triplet gap**.
- The only structure we assert is an orbital  $\phi_A$  on A and likewise on X and B.
- These three orbitals mix to create a bonding, nonbonding, and antibonding set with zero nodes, one node, and two nodes, respectively. We call these  $\phi_0, \phi_1, \phi_2$ , respectively. As LCAOs:

$$\phi_0 = \phi_X + \epsilon(\phi_A + \phi_B) \quad \phi_1 = \phi_A - \phi_B \quad \phi_2 = (\phi_A + \phi_B) - \epsilon\phi_X$$

- $\epsilon$  is an overlap parameter dictated by both spatial and energetic overlap.
  - Specifically,  $\epsilon$  quantifies overlap with X by A and B.
  - In general TM chemistry, X will be more electronegative than A,B. Since it is lower in energy, this will lead to lesser splitting.
  - Thus, more electropositive X have greater coupling, splitting, and singlet ground states.

- **Singlet-triplet gap:** The splitting between the ground states  $S = 0$  and  $S = 1$  in a  $2 \times S = 1/2$  setup. *Denoted by  $J$ .*

- This  $J$  is identical to the exchange coupling constant between A and B.

- Quantifying FM and AF contributions: The total coupling constant is given by

$$J_{\text{tot}} = 2K + 4\beta S - 2S^2(2\alpha + J)$$

- $S$  is the overlap integral and hence kind of replaces  $\varepsilon$ .
- The second order term is usually negligible.
- $2K$  is  $J_{\text{FM}}$ .
  - Notice that  $J_{\text{FM}}$  is only related to distance.
  - What does  $K$  denote?? What are its units?
- $4\beta S$  is  $J_{\text{AF}}$ .
- To maximize FM, we want a short distance and no overlap; to maximize AF, we want a long distance and big overlap.
  - How does this make sense?? Don't short distances and big overlaps already correlate?
  - Takeaway: This allows us to use our chemical intuition of orbital interactions to predict AF vs. FM interactions, and their rough magnitude.

- Examples.
- Example: There's a lot of data on compounds like di-copper compounds with bridging ligands.

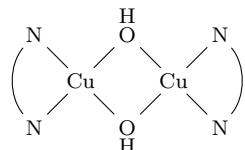
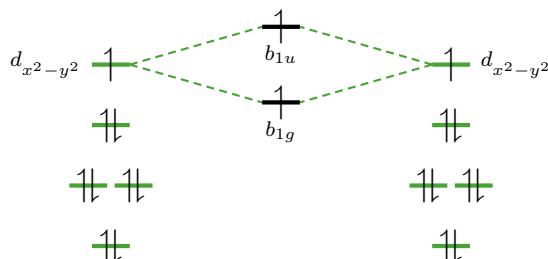


Figure 6.3: A di-copper compound with bridging ligands.

- See Kahn [6].
  - Anderson presents data showing that  $J$  varies quite a bit as a function of the Cu–O–Cu angle.
    - The exact data can be found in the notes.
  - As the bond becomes more linear,  $J$  gets more negative.
  - Performing a linear fit on Anderson's data yields
- $$J = -74 \cdot \text{angle} + 7270 \text{ cm}^{-1}$$
- It follows by comparison to the  $J_{\text{tot}}$  equation that  $2K = 7270$  and  $4\beta S = -74 \cdot \text{angle}$ .
  - The above comparison suggests that  $J_{\text{FM}}$  is constant. Is this a good or a bad approximation?
    - Changing the angles changes the distance, so assuming  $J_{\text{FM}}$  is constant is a *bad* approximation.
    - Indeed, the linear fit is not at all fundamentally correct. However, it's not bad as a first approximation, which is remarkable in its own right.
  - Example (continued): Two copper orbitals combining.



(a) MO diagram.

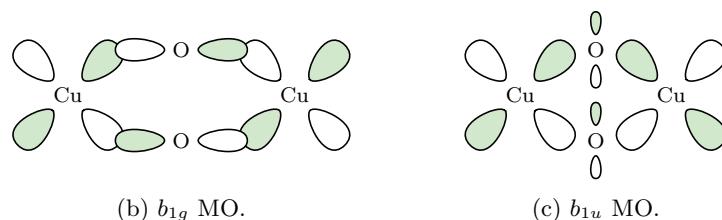


Figure 6.4: Molecular orbitals in a di-copper compound.

- Recall that each copper center will have the orbital structure depicted in Figure 6.4a due to the extreme Jahn-Teller distortions associated with the square planar geometry.
- The  $d_{x^2+y^2}$  orbitals are singly occupied. Thus, they couple and split.
  - The magnitude of the splitting is that of your AF coupling.
  - Are you sure you don't mean the  $d_{xy}$  orbitals?? That's what it looks like you've drawn.
- The  $b_{1g}$  orbital (Figure 6.4b) is antibonding.
- The  $b_{1u}$  orbital (Figure 6.4c) is nonbonding.
- As we linearize,  $b_{1g}$  will be stabilized (better overlap) and  $b_{1u}$  will be destabilized (less overlap).
  - This increases splitting and favors a lower spin state.
  - Thus, as we linearize, eventually the electrons (which have been coupled ferromagnetically in different orbitals) will pair (antiferromagnetically) in the same orbital. This is also the point at which the data anderson presents flips signs from positive  $J_{\text{tot}}$  (FM dominates) to negative  $J_{\text{tot}}$  (AF dominates).
- Three open-shell states corresponding to  $M_s$  values all get rolled into one closed shell state??
- Another example: Goodenough-Kanamori rules.
  - Started out very empirically (experimental work by John Goodenough) and then grew into a more robust theory (theoretical work by Junjiro Kanamori) as our understanding of orbitals grew.
  - John Goodenough won the Nobel prize for lithium ion batteries, made foundational contributions to metal oxides, and was a UChicago physics PhD.
    - “These people that are super important somewhere tend to crop up everywhere” - Anderson.
  - Consider a generic metal with an unpaired electron in the  $d_{z^2}$  orbital. Connect two of these with the  $p$ -orbital of a bridging oxygen.
    - The singly occupied states ( $d_{z^2}$  orbitals) will mix and split.
    - The splitting determines  $S = 0$  and  $S = 1$ .
    - **Superexchange, direct exchange, and double exchange** can take place.
  - Rule 1: Linearity maximizes AF exchange.
    - To obtain molecules of this type, we build in symmetry, linearity, etc. via ligands, etc.
  - Rule 2:  $90^\circ$  maximizes FM exchange.
    - To obtain molecules of this type, we build in orbital orthogonality by design.
  - In between  $90$  and  $180$  isn't readily experimentally accessible.
  - What is all of this??
- **Superexchange:** Coupling/virtual electron transfers between atoms with a net spin through a diamagnetic linker.
- **Direct exchange:** The electrons of magnetic atoms interact with their nearest neighbors.
- **Double exchange:** A magnetic exchange that arises between ions in different oxidation states.

- Getting a large FM interaction: An example of orthogonality by design.

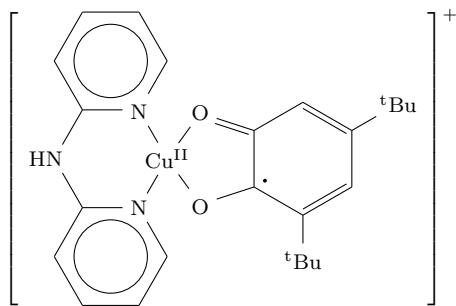


Figure 6.5: Designing a compound with orthogonal electrons.

- A dipyridyl and semiquinoid ligand on copper. This is overall a monocation.
- We search for compounds like this (high FM) when we want to make magnetic materials.
- Key: The unpaired electron on the semiquinoid is rigorously orthogonal to the copper one since they are in  $d_{x^2-y^2}$  vs.  $p_z$  orbitals.
  - Moreover, the Cu electron has  $\sigma$  symmetry, while the C electron has  $\pi$  symmetry. This is further evidence of rigorous orthogonality.
  - Recall that we are (simplistically) looking to bring spins as close together as possible while having no orbital overlap: In addition to the rigorous orthogonality here, spacing is 2-3 Å.
- $J > 200 \text{ cm}^{-1}$  here.
- $\chi T$  vs. temperature.
  - Our emphasis on FM coupling means that spins certainly couple parallel here, making  $S = 1/2 + 1/2 = 1$ . This means that we have a triplet ( $2S + 1 = 3$ ) ground state.
  - We see a triplet ground state at super low temperatures.
  - The slope fits the Boltzmann population of the spin manifold.
  - Thermal energy can break the triplet and populate some singlet states, as observed in the variable temperature susceptibility??
- General structure of Prussian blue analogs.

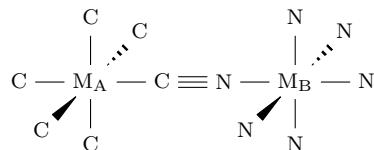


Figure 6.6: Prussian blue analogs.

- Metals with ligands linked by a tightly bound cyanide.
- Gadet et al. [7] recognized that if  $M_A = \text{Ni}^{\text{II}}$  and  $M_B = \text{Cr}^{\text{III}}$ , then  $M_A$  is  $d^8$  and  $M_B$  is  $d^3$ . Thus, the two metals are rigorously orthogonal.
  - What we mean by this is that drawing out the  $d$ -orbital MO diagrams ( $t_{2g}$  and  $e_g$  sets), we see that  $\text{Ni}^{\text{II}}$  has 2 unpaired electrons in the  $e_g$  set, and  $\text{Cr}^{\text{III}}$  has 3 unpaired electrons in the  $t_{2g}$  set. Thus, the molecule overall has five unpaired electrons in MOs.
- This is one of the highest ordering magnetic materials known.
  - FM coupling is still not great, though, due to the long distance.
- This material can be extended into a 3D crystal.

- Prediction of the nature of interaction between differently occupied orbitals table.

	$d^3$	$d^4$ elongated	$d^5$	$d^8$	$d^9$ elongated
$d^3$	AF $\leftarrow$ AF	AF	AF	F	F
$d^4$ elongated	AF	AF $\leftarrow$ AF	F	F	F
$d^5$			AF (or F) $\rightarrow$ AF	F $\rightarrow$ AF	F $\rightarrow$ AF
$d^8$				F $\rightarrow$ AF	F $\rightarrow$ AF
$d^9$ elongated				F $\rightarrow$ AF	

Table 6.2: Predicting the nature of magnetic orbital interactions.

- Reading the table.
  - F: Ferromagnetic.
  - AF: Antiferromagnetic.
  - $\rightarrow$ : The interaction is expected to be more antiferromagnetic when the bridging angle *increases* from 90°.
  - $\leftarrow$ : The interaction is expected to be more antiferromagnetic when the bridging angle *decreases* toward 90°.
- Don't memorize the table!
  - In many cases, it's just better to draw our your  $d$ -orbital diagrams.
  - I am including it solely for practice checking my predictions.
- General rules:
  - Certain compounds will have rigorous orthogonality.
  - In general, though, we'll have a mix of FM and AF interactions.
  - In these cases, we have to carefully consider the strength and orthogonality of all possible magnetic orbital interactions (that is, all possible interactions between singly occupied orbitals).
  - Rough guess: AF interactions typically win out.
- We *now* start materials.
- Summary of bulk coupling in materials.

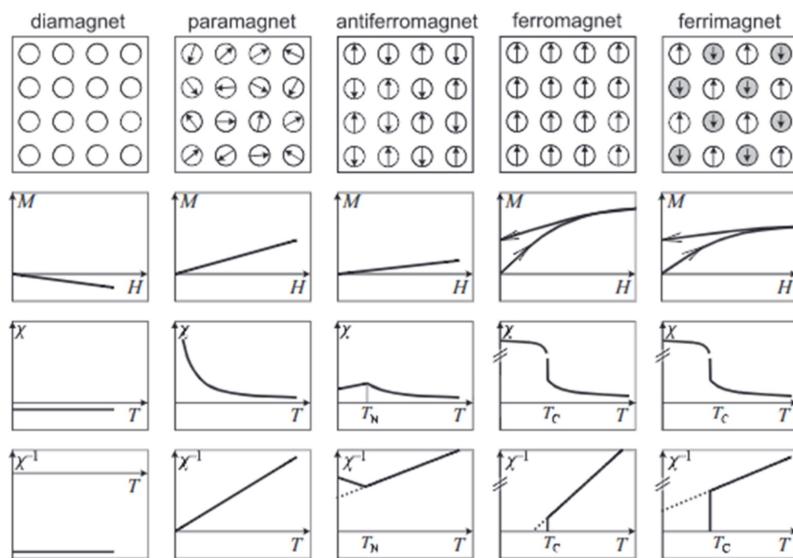


Table 6.3: Bulk magnetic coupling.

- Paramagnets have a bunch of spins with no preference for alignment. Note that  $1/\chi$  is linear as discussed last lecture!
- Ferromagnet: We would need thermal energy to break the paired spins. This is an unstable equilibrium.
- Ferrimagnet: Closer to an antiferromagnet theoretically. Treats alloys where we have oppositely aligned differing spin populations. Behavior is almost exactly ferromagnetic.
- Bulk behavior is dictated by nearest neighbor interactions.

- One exception is as follows, where the delocalized electron cloud can be polarized by a magnetic field.
- **Pauli paramagnetism:** A metal that's a pool of electrons which are sloshing around in a band structure. Pool of positive and negative spins. Treat it as an electron gas. Applying a magnetic field changes the relative energies of the pool of electrons.

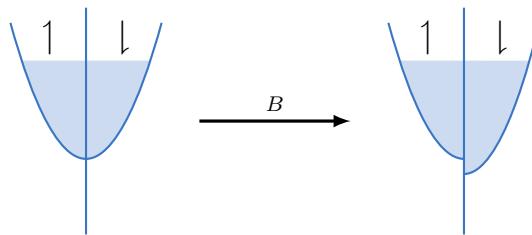


Figure 6.7: Pauli paramagnetism.

- We now have more spin down, creating a net magnetic field that will be very small. *This is Pauli paramagnetism.*
- Ferromagnets.
  - Most applications for magnets are with ferromagnetic materials.
  - NdFeB is the strongest **hard** ferromagnet.
  - The most classic case of a ferrimagnet is magnetite (mixed  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ).
- Ferromagnets ideally have only one magnetic domain.

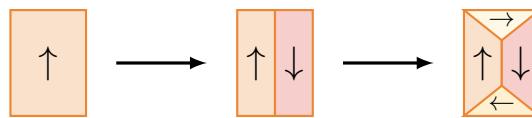


Figure 6.8: Ferromagnetic domains.

- Over time, different magnetic fields fracture domains. The products may align antiparallel.
- Applying a strong external magnetic field can anneal the domain walls and get you back to a single domain.
- **Saturation magnetization:** The maximal magnetization of a material. *Denoted by  $M_{\text{sat}}$ .*
- **Remnant magnetization:** The magnetization of a magnetized material after the external field is dialed back. *Denoted by  $M_{\text{rem}}$ .*
- **Coercive field:** The amount of external field required to flip a magnet. *Denoted by  $H_C$ .*

- Visualizing  $M_{\text{sat}}$ ,  $M_{\text{rem}}$ , and  $H_C$ .

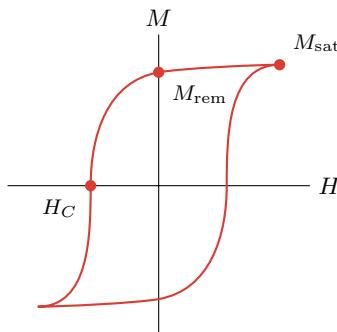


Figure 6.9: Hysteresis loop.

- A hysteresis loop characterizes the energy penalty to homogenize away domain boundaries and then flip the spin of a bulk domain; this quantity is what gives ferromagnets their useful properties.
- $H_C \propto \text{SOC}$ , i.e., spin-orbit coupling.
- Things like  $\text{Fe}^{3+}$  HS  $d^5$  with equally (singly) occupied  $d$  orbitals have no preferred orientation.
  - $\text{Ti}^{3+}$  with  $d^1$  can generate “ring currents,” giving it a preferred orientation.
- The wider the curve, the **harder** the ferromagnet.
- **Soft** is much skinnier (good for things like transformers that you want to be able to switch).
- To mediate coupling between  $f$  orbitals in lanthanides, we mix in a bit of iron to use its free electrons.
- Exotic things just to be aware of.
  - Ferrometals: Iron is an example.
    - Metallic band structure even in the absence of a magnetic field.
  - Ferro half metal.
    - Charge carriers are spin-polarized.
    - Important in spin-tronic type applications, P/N junctions, etc.
    - Example:  $\text{CrO}_2$ .
  - Metals have a continuous set of bands at the Fermi level regardless.
  - Ferro insulator.
    - Filled band with no density of states. A magnet that is not conductive, essentially.
    - Example:  $\text{EuO}$ .
  - Weak coupling or frustration. AF exchange with spins that get frozen in. Frustration: Triangular lattice with up/down/what's the third.
  - Spin glass: Freeze-in spin orientations such that when you get back to a certain magnetization, you auto-drop.
- Magnetic properties of some anonymized commercial polycrystalline hard magnets.
- Do we have to learn the stuff at the end of the notes on exotic materials, ferrimagnetism, and commercial magnets??
- Next week: EPR.

# Week 7

## EPR and XAS

### 7.1 EPR Spectroscopy

2/14:

- Today: EPR Spectroscopy.
- Thursday: XAS and EXAFS (guest lecturer with great experience in the field).
- As an official policy and a cautionary note, don't use ChatGPT to solve this course's homework.
- Benefits of EPR.
  - Allows you to look at electronic spin flips.
  - Allows you to look at paramagnetic complexes (the class complementary to those you can observe with NMR).
- Most of today: Doublets.
- Electron spin.
  - An electron can be either spin up or spin down.
  - These states are degenerate in the absence of a magnetic field.
  - However, a magnetic field induces a Zeeman<sup>1</sup> splitting described as follows.
- The intrinsic electron spin has a magnetic moment defined as

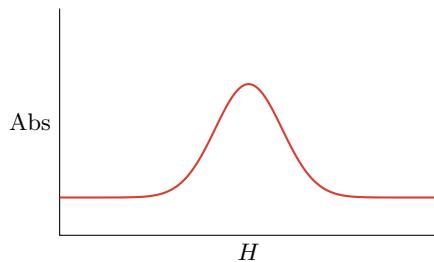
$$\mu_z = g\beta M_s$$

- $g$  is the gyromagnetic ratio for an *electron* ( $= 2.0023219278$ ; we usually just treat it as 2; can deviate depending on SOC).
- $M_s = \pm 1/2$  is our spin quantum number.
- $\beta = e\hbar/2m_e$  is our Bohr magneton.
- It follows that
$$E = -\mu \cdot \vec{H} = -\mu H \cos(\vec{\mu} \cdot \vec{H}) = -\mu_z H = g\beta H M_s = \pm \frac{1}{2} g\beta H$$
  - This Zeeman splitting is pretty easy to visualize (see Figure 6.2a).
  - Thus, the energy to flip an electron is going to be  $g\beta H$ .
    - This is also known as the **resonance condition**.
- Aside: Be familiar with ENDOR spectroscopy, a combination of nuclear and electronic.

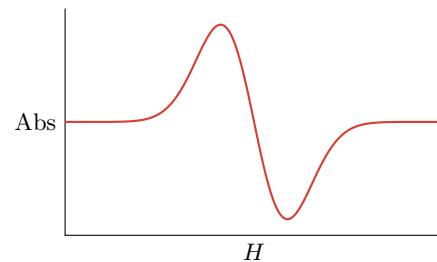
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<sup>1</sup>ZAY-mon.

- In an EPR experiment, we apply radiation to stimulate a spin flip.
  - $E = h\nu = g\beta H$ .
  - This energy is in the microwave region.
  - Microwaves are much higher in energy than radio waves, thus are more difficult to handle for technical reasons.
  - Thus, we cannot run complex, pulsed experiments analogous to in NMR; we just run more simple scans.
  - Indeed, herein we *fix* the microwave frequency and vary the magnetic domain.
  - Takeaway: EPR is much cruder than NMR in many ways (for technical reasons).
- The frequency domain  $\nu$  can vary based on the spectrometer from 1-285 GHz.
  - X-band (9.6 GHz) spectrometers are the most common.
  - More rarely, Q-band (35 GHz) and W-band (95 GHz) are used.
  - Milwaukee has an S-band EPR at 2 GHz.
  - High frequencies give you worse splitting (opposite of NMR) but better signal-to-noise.
- **Continuous wave EPR:** EPR experiments run under a fixed frequency domain and variable magnetic domain. *Also known as CW EPR.*
  - All of the setups described above constitute CW EPR.
- We scan across our magnetic field and observe (fairly broad) Gaussian lineshapes. Thus, we usually plot the first derivative.



(a) Gaussian lineshape.



(b) First derivative.

Figure 7.1: EPR spectra are plotted as the first derivative.

- There are two main types of EPR line broadening.
  1. **Secular broadening.** This comes from processes that vary the local magnetic field. Two subclasses.
    - (a) *Dynamic broadening.* A homogeneous broadening obtained by adding a paramagnetic ion to a solution of a free radical. This gives Lorentzian lineshapes.
    - (b) *Static broadening.* This is effectively the same, but induced by frozen solution and hence no longer homogeneous. This gives Gaussian lineshapes.

**2. Lifetime broadening.** This occurs when the excited state lifetime is too short. It mathematically originates from the Heisenberg uncertainty principle. In particular, we have that

$$\begin{aligned}\Delta E \Delta t &= \frac{\hbar}{2\pi} & \Delta h\nu = \Delta E = g\beta H = g\beta \Delta H \\ \Delta h\nu \Delta t &= \frac{\hbar}{2\pi} & \Delta\nu = \frac{g\beta}{h} \Delta H \\ \Delta\nu &= \frac{1}{2\pi \Delta t} & \Delta H = \frac{h}{g\beta} \Delta\nu\end{aligned}$$

so, combining the above two expressions, the FWHM  $\Delta H$  is given by

$$\Delta H = \frac{\hbar}{2\pi} \frac{1}{g\beta \Delta t}$$

Essentially, as  $\Delta t$  gets really small, everything else starts to blow up since its in the denominator in the last term.

- We typically do EPR experiments in a frozen solution.
- Two flavors of EPR we really care about.
- **Spin-lattice relaxation:** The interaction of spin with the surroundings. *Denoted by  $T_1$ . Given by*

$$\Delta H = \frac{\hbar}{g\beta} \frac{1}{2T_1}$$

– In other words, if some spin is oriented away from  $H$ , how much time does it take to “reparallelize?”

- **Spin-spin relaxation.** *Denoted by  $T_2$ . Given by*

$$\Delta H = \frac{\hbar}{g\beta} \frac{1}{T_2}$$

- Combining the two gives the total homogeneous line width  $T'_2$ :

$$\frac{1}{T_2} = \frac{1}{T_2} + \frac{1}{2T_1}$$

- Result: We need to go to low temperatures for EPR spectroscopy both for the lifetime reason and for technical reasons.
  - We need to go to helium temperatures in many cases.
  - Low spins may be observable at “high” temperatures like 77 K or even room temperature in some cases.
- $g$ -values.
  - The  $g$ -value is sort of like a ppm shift value for the EPR signal.
  - Recall that  $g$  is determined by the resonant frequency  $H_r$  at which we observe the excitation.

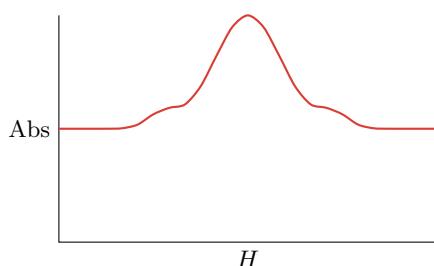
$$\Delta E = \Delta E$$

$$g\beta H_r = h\nu$$

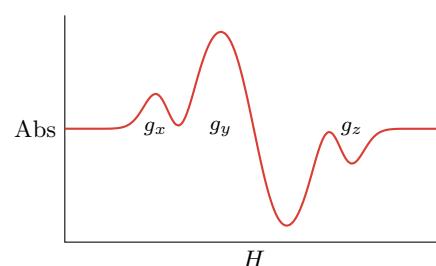
$$g = \frac{h\nu}{\beta H_r}$$

– Organic radicals almost always exist at  $g = 2$  and are isotropic. Deviation might be 1/10,000. This is because organic compounds are composed of light atoms that just don't have much SOC.

- For TM's (and lanthanides),  $g$  varies widely. Fortunately, it varies in a way that we can understand with orbitals.
  - Again, we visualize “ring currents.”
  - One that opposes the magnetic field induces  $g < 2$ .
    - Think of a lone electron in a set of 5 degenerate  $d$ -orbitals.
  - If a hole “hops” through and generates a ring current as in  $d^9 \text{ Cu}^{2+}$ , we have a ring current that reinforces the magnetic field and hence  $g > 2$ .
  - Essentially, there are three scenarios that determine the value of  $g$ .
    - If the  $d$ -orbitals are less than 1/2 filled,  $g < 2$ .
    - If > half filled,  $g > 2$ .
    - At a perfectly half-filled shell, we should have  $g \approx 2$ .
  - This gives us sign. For magnitude...
    - The magnitude of the deviation is related to the magnitude of the SOC.
    - To a first approximation, this will relate to symmetry and the degeneracy of orbitals.
  - Trust the half-filled value, not the hole: When you have  $d^2$  in an octahedral field, for instance, the  $t_{2g}$  set is less than half-filled, so  $g < 2$ ; it's not that you have one hole rotating so  $g > 2$ .
  - It is the possibility of orbital angular momentum coupling with the spin angular momentum that allows  $g$  to change.
- Anisotropy: Thus far, we've only considered the effect of isotropic transitions. But both the magnetic field and spin are tensors with  $x, y, z$ -components.
  - An isotropic magnetic field is described by
 
$$\hat{H}_{\text{iso}} = g\beta\hat{H} \cdot \hat{S}$$
  - You spin your samples to try to average this out in solid-state NMR, but it's not perfect so you do need to take axes into account.
  - An anisotropic magnetic field is described by
 
$$\hat{H}_{\text{aniso}} = \beta\hat{H} \cdot \hat{g} \cdot \hat{S} = \beta(H_x, H_y, H_z) \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} = \beta H_x g_x S_x + \beta H_y g_y S_y + \beta H_z g_z S_z$$
  - If a molecule has very high symmetry (e.g.,  $T_d$ ,  $O$ ,  $I_h$ , etc.), then  $g_x = g_y = g_z$ . In this case, we get back to our nice isotropic, one peak picture (Figure 7.1a).
  - Molecular geometry is *related* to  $g$  variations, but they're not the same thing. Don't make the mistake of looking at a highly symmetric molecule and thinking you know what the EPR spectra should be! You have to consider orbitals.
  - EPR is often done on frozen solutions (sometimes powders) so that we don't have rapid solution-phase tumbling to average out the  $g$ -values but have everything stuck in some orientation. In particular,  $g$ -values will be inequivalent in frozen solutions!
- Anisotropic spectra.



(a) Gaussian lineshape.



(b) First derivative.

Figure 7.2: Rhombic anisotropic EPR spectra.

- Note that we don't know anything about Cartesian coordinates from the spectrum, so Anderson prefers  $g_1, g_2, g_3$ .
- This is a rhombic spectrum, meaning that  $g_x \neq g_y \neq g_z$ .
- Axial spectra are often referred to as  $g_{\parallel}$  and  $g_{\perp}$ . This corresponds to  $g_x \approx g_y \neq g_z$ .
  - We typically have a small  $g_{\parallel}$  peak downfield of a big  $g_{\perp}$  peak (picture in notes).
  - You see spectra like this for when your molecules have a clear symmetry axis; decreasing the symmetry further will tend to introduce some more rhombicity.
- Anisotropy only occurs via coupling into orbital angular momentum. Thus, it is observed for TMs but typically not for organic radicals.
- We now discuss fine structure for a while.
- Fine structure basics.
  - The electron spin can also interact with nuclear spin in **hyperfine interactions** and **superhyperfine interactions**.
    - These lead to additional signals and structure.
    - Be aware of the differences between hyperfine and superhyperfine, but only hyperfine interactions will be analyzed for the remainder of the time.
  - The quantum-mechanical basis for fine structure involves the following Hamiltonian.

$$\hat{H} = g\beta\vec{H} \cdot \hat{\vec{S}} + a\hat{\vec{I}} \cdot \hat{\vec{S}} = g\beta H \cdot \hat{S}_z + a\hat{I}_z \cdot \hat{S}_z$$

- $\hat{I}$  is the nuclear spin operator.
- $\hat{S}$  is the electron spin operator.
- $z$  is the component along  $H$ .
- $a$  is the hyperfine coupling constant.

- Energies: Found by calculating eigenvalues.

$$E = \pm \frac{1}{2}g\beta H + \frac{a}{4} = \frac{1}{2}g\beta H \pm \frac{a}{4}$$

- **Hyperfine interaction:** An interaction with the direct nucleus which bears the radical.
- **Superhyperfine interaction:** An interaction involving additional coupling to other nuclei via delocalization.
- Hyperfine Zeeman splitting diagram.

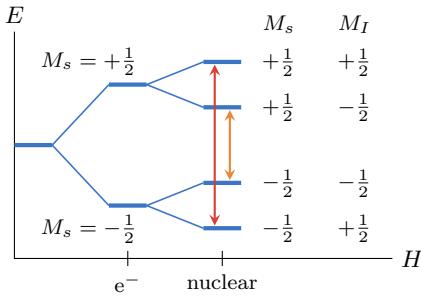


Figure 7.3: Hyperfine splitting.

- We first have our electron splitting.
- Then if we turn on nuclear splitting, that happens next, yielding four distinct states.

- Hyperfine election rules.
  - Thus far, we have implicitly used  $\Delta M_s = \pm 1$ .
  - We must have  $\Delta M_I = 0$  as well! We can have an electron spin flip, but we can't do a nuclear spin flip at the same time, which may make some intuitive sense as well since the probability that these two unlikely events would happen simultaneously is very low.
  - Thus, we have two allowed transitions in Figure 7.3.
- Hyperfine EPR spectrum.
  - The peak splitting is  $A$ , which is related to the actual hyperfine coupling constant  $a$  as we'll talk about shortly.
  - A lot of the time, you don't see  $y$ -axis labels in EPR spectra because "the first derivative of absorbance" is not a particularly helpful unit.
- A few final notes on hyperfine coupling.
  1. The hyperfine coupling constant  $a$  is field independent.
    - Zeeman splitting is the only thing that is field dependent.
  2.  $a$  is a scalar HF constant and
 
$$a = g\beta A$$
    - $A$  is measured in Gauss; it is the *experimental* HF constant.
  3.  $a$  can also be anisotropic.
    - Each of the values  $g_x, g_y, g_z$  can have an  $a$ .
    - $a$  can be 0 for some  $g_i$  and not others.
  4.  $M_I$  can have many values.
    - Just like with NMR, a nuclear spin with  $M_I > 1/2$  can give multiline patterns.
    - Examples.
      - $^{14}\text{N}$  has  $M_I > 1/2$ .
      - TMs can go up to  $7/2$  or  $9/2$ , leading to very complicated multiline coupling patterns very quickly.
  5.  $M_I$  sums the contribution from other neighboring nuclei.
    - Multiple nuclei can also give multiline patterns, notably with  $2nI + 1$  lines.
  6. If a spin active nucleus is not 100% abundant, we get a superposition.
    - Cool example:  $\text{Mo}(\text{CN})_8^{3-}$ .
      - This is a  $d^1$   $S = 1/2$  compound.
      - $I = 0$  is 75% abundant, but  $^{97}\text{Mo}$  is 25% abundant with  $I = 5/2$ .
      - Thus, an amount of intensity equivalent to  $1/3$  of the central signal gets divided among 6 smaller neighboring peaks that are all evenly spaced apart (see notes for image).
  - We now get move on to higher spin species.
    - This is a further level of complication.
    - However, these species may have more accessible EPR transitions.
    - We usually have larger splitting for higher  $M_s$  values.
  - **Kramer's theorem:** Ions with an odd number of electrons will always have as their lowest energy level at least a doublet that will split in an applied magnetic field and give rise to an EPR signal.
  - **Kramer's doublet:** The doublet predicted by Kramer's theorem.

- Example: Transitions predicted to be visible for a quartet ( $S = 3/2$ ).

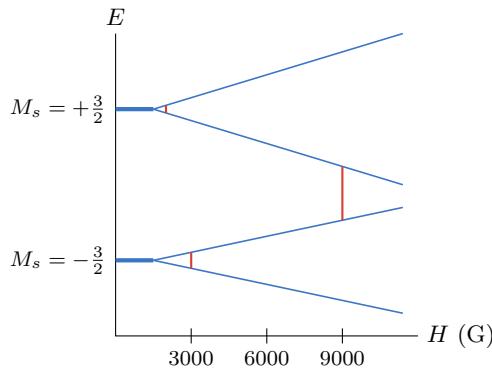


Figure 7.4: Quartet EPR signals.

- Something lower around 2000 G, higher around 3000 G and, if our spectrometer is powerful enough, something around 9000 G.
- Recall  $\Delta M_s = \pm 1$ .
- Example: Transitions predicted to be visible for a triplet ( $S = 1$ ).
  - Triplets are very difficult to see because the lower state takes a long time to drop low enough to see the ground state.
  - Treating spin-orbit coupling.
    - We have that  $\vec{\mu} = g\beta\vec{J}$ .
    - It follows that
 
$$g = \frac{J(J+1) \cdot S(S+1) - L(L+1)}{2J(J+1)} + 1$$
    - What people tend to do is look at the spectrum.
  - That's it for higher spin species.
  - A few practical points on EPR spectroscopy.
    1. Use a microwave cavity, a fixed frequency, and vary the field.
    2. Avoid solvents that strongly absorb microwaves (e.g., water, other polar solvents). This can sometimes be ok if the sample is frozen.
    3. Usually quote  $g$ -values.
      - Do we report values as  $H$  or  $g$ ??
    4. You can double integrate vs. a standard to quantity  $\pm 20\%$ .
  - We now move on to advanced EPR techniques.
    - These are analogous to some of the fancy things you can do with NMR.
    - Essentially, they are alternate ways of getting data out of an EPR machine besides straight-up absorption spectra.
  - In particular, we will focus on **ENDOR** and **ESEEM** spectroscopy.
  - **Electron spin echo envelope modulation** (spectroscopy). *Also known as ESEEM.*
  - **Electron nuclear double resonance** (spectroscopy). *Also known as ENDOR.*

- Background.
  - Most EPR spectroscopy compared to NMR is pretty rudimentary.
    - In NMR, every carbon spectrum you take is proton-decoupled (we'll talk about this later).
    - Radiofrequency is really nice to control.
  - However, these are both 2D experiments between EPR and NMR.
    - They allow us to see spin-active nuclei that are close to the paramagnetic center.
    - 2D EPR can give you a ton of information about paramagnetic compounds; the most useful are those that couple electron transitions with nuclear transitions.
  - These are super powerful techniques.
- ENDOR spectroscopy.

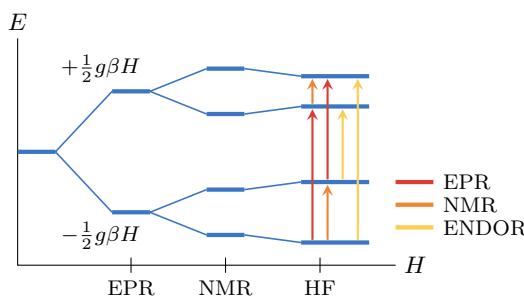


Figure 7.5: ENDOR splitting.

- The quantum-mechanical basis for ENDOR involves the following Hamiltonian.
$$\hat{H} = \underbrace{g\beta\hat{H} \cdot \hat{S}}_{\text{EPR}} - \underbrace{g_N\beta_N\hat{H} \cdot \hat{I}}_{\text{NMR}} + \underbrace{\hbar\alpha\hat{I} \cdot \hat{S}}_{\text{HF}}$$
- Three levels of splitting: EPR, NMR, and HF.
  - The last one doesn't actually induce splitting; it's just coupling between the first two that affects energy levels.
- EPR has  $\Delta M_s = \pm 1$ ,  $\Delta M_I = 0$ .
- Here, we turn on semi-forbidden transitions, i.e., those with  $\Delta M_s = \pm 1$  and  $\Delta M_I = \pm 1$ .
- $1 \rightarrow 3$  and  $2 \rightarrow 4$  are EPR allowed.
- $1 \rightarrow 2$  and  $3 \rightarrow 4$  are NMR allowed.
- ENDOR transitions (which we're turning on in this experiment) are  $2 \rightarrow 3$  and  $1 \rightarrow 4$ .
- ENDOR spectra tend to look like a big messy hunk corresponding to the nucleus, and then distinct ones further out which correspond to the NMR transitions.
- Possibly a bit more ENDOR on Friday.
- We now move on to ESEEM.
  - Do we need to know this??

## 7.2 X-ray Absorption Spectroscopy

- 2/16:
- The pic that Anderson drew wasn't great; you can also find bootleg copies of Drago [8].
  - Patrick (or Pat): Guest lecturer on XAS, which he used a lot in his PhD.
    - He's currently a post-doc in Anderson's group.
    - Studied a lot of high-valent iron complexes.
  - We now begin the lecture.
  - X-ray absorption spectroscopy:** A range of techniques which are all based on the absorption of X-rays by a nucleus of choice. *Also known as XAS.*

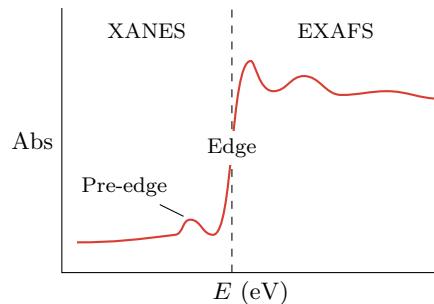


Figure 7.6: An X-ray absorption spectrum.

- In a basic experiment, the absorption of X-rays is directly measured.
- An X-ray with sufficient energy can eject an electron from a core orbital.
  - The ejected electron (**photoelectron**) dissociates at the **edge energy**.
- Photoelectron:** An electron ejected from a core orbital by an X-ray.
- Edge energy:** The energy needed to take the photoelectron to the infinite energy level.
- Different edges give different information.
- The **K**- and **L**-edges give the most important information.
  - Pat uses the **L<sub>III</sub>** edge most commonly.
  - It corresponds to a  $2p \rightarrow 3d$  excitation.
- K-edge:** The excitation of a core **1s** electron from an element.
  - The edge that can give you oxidation, symmetry, and structural information based on the photo-electron's environment.
  - The **K**-edge energy roughly correlates with  $Z$ .
  - Serena DeBeer does a lot on **K**-edge spectroscopy.
- L-edge:** The excitation of a core **2s** or **2p** electron.
  - The edge that can give you bonding and molecular orbital information.
  - Nothing more on this today; look up Kyle Lancaster's work if you're curious.
- Benefits of XAS.
  - You don't need a crystal.

- Allows you to study transient intermediates, esp. in biochemistry; freeze-quench a reaction and get structural info about active states.
  - Better local picture than XRD.
  - Sensitive to local geometric structure of an absorber, i.e., ligation, oxidation state, spin state, symmetry.
  - Lower X-ray dose needed than in crystallography; more control of photoreduction.
  - XAS is *element specific* and can be applied to almost any system — biochemistry, synthetic inorganic chemistry, materials chemistry, etc.
  - Can be measured at multiple edges.
  - Tolerates less concentrated samples.
- All XAS uses the same fundamental principle, but there are many detection methods to get a lot of information.
    - Beamline scientists love to geek out about this.
    - Transition mode vs. fluorescence mode.
  - **Transition mode:** Measure the difference between incident and final intensity.
    - Better for solid samples than frozen solutions, esp. close-packed ones.
  - Frozen solutions with an X-ray-transparent window: Collect in fluorescence mode.
  - To freeze: Submerge in a liquid nitrogen or isopropanol bath.
  - K-Edge spectra.
    - Two main regions: XANES (X-ray absorption near edge structure) which includes the pre-edge (symmetry information) and the *K*-edge (oxidation state info).
    - The *K*-edge is the energy at which you actually eject the electron into the continuum.
      - This energy will change with oxidation state: As you probe something that's more oxidized, you know that its electrons will be held more tightly due to decreased repulsions, so the *K*-edge will increase.
    - The pre-edge consists of a  $1s \rightarrow 3d$  transition.
      - While the edge energy is the energy required to eject an electron into the continuum, the pre-edge features correspond to excitation into valence orbitals.
  - Pre-edge.
    - In *K*-edge XAS, the pre-edge feature is primarily the  $1s \rightarrow 3d$  transition (electron-dipole forbidden, electric-quadrupole allowed). Thus, as symmetry decreases and we get more coupling, this increases.
    - The pre-edge area is indicative of deviation from centrosymmetry and  $3d/4p$  mixing.
      - High symmetry molecules will give *d-p* mixing/hybridization and thus have more intense pre-edge features.
    - Selection rule:  $\Delta e = \pm 1$ , so technically  $s \rightarrow p$  is allowed and  $s \rightarrow d$  is not.
  - Example of XANES: Fe<sup>V</sup> vs. Fe<sup>VI</sup>.
    - The pre-edge tends to get over-interpreted.
    - A pure metal foil is often used as a standard; there is some debate about what a pure-metal *K*-edge is, though. Make sure you know what the standard is when you read literature!

- $K$ -edge XANES may be the best technique we have to measure oxidation state, even though oxidation state doesn't really exist. Perhaps better for seeing that an electron was removed; much better in a comparative/relative sense than in an absolute sense.
- Pre-edge area is sensitive to the oxidation state.
  - This is because we often lose symmetry as we go to higher oxidation states.
  - Even just shortening the axial ligand in a square pyramidal complex can have a drastic effect.
  - Less symmetry  $\Rightarrow$  greater peak area.
  - You measure the area with any peak-fitting program (e.g., Fit It).
    - There's a paper by Ed Solomon in the 1990s that describes fitting in greater detail; a lot of the best practices are included.
    - You fit with a pseudo-Gaussian that's 50% Gaussian and 50% Voight. Sometimes it's hard to distinguish between two close peaks because there can be substantial overlap.
  - Metal-ligand bonding can turn on more pre-edge area; metal-ligand interactions shouldn't be too important; multiply bonded ligands with shorter oxidation states help more.
- Mossbauer in theory predicts bond lengths. You get a much better correlation with bond states when...
- Case study: Determining  $\Delta$  from the pre-edge region.
  - High-spin Fe<sup>III</sup> should give two distinct  $1s \rightarrow 3d$  transitions; the splitting between them is  $\Delta$ .
- If you have a metal in different oxidation states, XANES is probably what you want.
  - We use a metal standard because it's somewhat stable and...
  - When you use foil, that's your  $x$ -axis calibration standard.
  - Some compounds don't have a pre-edge.
  - To fit our pre-edge, fit...
- People in the XAS community are usually willing to discuss, share, and argue about their XAS fitting.
  - Parameters varied: Computer program, function or algorithm, procedure.
- Beamline scientists hate giving tutorials on how to do something or how to fix something, but they like looking at data and science.
- A short EXAFS primer.
  - Pat's favorite part.
  - Includes the wavy features after the edge.
  - Mechanism: Ionizing radiation hits an absorber atom, ejecting the  $1s$  electron which leaves the **absorber** atom. Then the surrounding atoms send the waves back, leading to constructive and destructive interference.
  - You can also get multiple scattering (photoelectron may be scattered by more than one atom before returning to the center).
- Equations and quantities relevant to EXAFS.
  - Let  $R_j$  be the distance between the absorber and back scatterer  $j$ .
  - Recall that  $I = I_0 e^{-\mu t}$ , where  $I_0$  is the incident irradiation,  $\mu$  is the linear absorption coefficient, and  $t$  is the thickness.
  - The signal can be modeled with the **EXAFS equation**.
  - We have that  $\chi = (\mu - \mu_s)/\mu_0$ , where  $\mu_s$  is with a smooth background and  $\mu_0$  normalizes for free atoms.

- How we get information from EXAFS: Use the EXAFS equation.

$$\chi(k) = \sum_i \frac{(N_i S_0^2) F_i(k)}{k R_i^2} \cdot \sin(2kR_i + \delta_i(k)) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)}$$

- The XAS spectrum is the sum of multiple sines.
- The sine wave overlies the fluorescence decay, which can also be important.
- $\chi(k)$  depends on a number of things, but for a shell made of the same scattering atoms, the variables we control are  $N_i$  — the number of equivalent scatterers.
- $R_i$  is the distance between your absorber and your scatterer.
- $f_j$  is the electron backscattering amplitude of the scatterer.
  - It depends on  $Z$ .
  - $\sigma_i$  is the root mean square variation in  $R_j$ .
  - $\delta_i$  is the scatterer phase shift from the theory or model.
  - Together  $\sigma_i$  and  $\delta_i$  make up the **Debye-Waller factor**, which accounts for disorder.
  - $k$  is the photoelectron vector.
  - It is given by

$$k = \sqrt{\frac{2m_e}{\hbar^2}(E - E_0)}$$

where  $E_0$  is the threshold energy for electron ejection.

- To accurately describe these variables, a lot of information is needed about the system...
- We  $k$ -weight our spectrum to account for differences between heavy and light elements.
- We FT our spectrum to transform it to space data.

- **Debye-Waller factor:** Equivalent to thermal ellipsoids in crystallography. If it's negative, it's fake; if it's too big, it's fake. *Given by*

$$e^{-2\sigma_i^2 k^2}$$

- You get transitions in the edge in some specific compounds.
- Principles to guide data analysis.
  - You can fit anything if you try hard enough. Use your chemical intuition. Does a fit make sense?
  - Error in EXAFS is typically  $\pm 0.02 \text{ \AA}$ , but the shell resolution is usually much larger (equal to  $\pi/(2\Delta K)$ ). Don't give things within a shell-resolution of each other!
  - EXAFS is very much a "helper" spectroscopy.
    - XAS should be the last step of any project you perform. Just to fill in the gaps; you need chemical intuition to make sense of your data.
- Information we can get out of our data: A good fit tells us...
  1. The number, type, and distance of scatterers.
    - This can inform on the immediate coordination sphere of a metal center.
    - Heavier atoms scatter more, and shorter distances scatter more.
    - From XAFS, you can get the number of scatterers  $\pm 1$ .
  2. You can pull out angular information if the data is really good and the geometry is right.
    - Pat thinks this is fake, though.
  3. You can do it in solution phase and with amorphous materials.
    - You can also pull out EXAFS data for 6-8  $\text{\AA}$  in certain solids.

- Case study: Oxygen activation at a diiron site.
  - Can't do Mossbauer with iron, so even if it's not giving you approximate...
  - Typically, you want to aim for  $R(\text{\AA}) < 6$ .
  - Both irons will be oxidized...
  - Data can be decomposed with a linear combination analysis.
- Data fitting is not always so easy.
  - Mössbauer...
  - This is the decay of 3.
  - Thermal decay: The things we don't want to see is...
  - Took 11 attempts to fit (that's a lot for Pat).
- Big picture for the diiron system.
  - Getting more and more rigid.
- Not a lot of people use this technique, so a lot of labs publish bad data, but reach out to them if you're confused! They'll usually be willing to work with you.
- Ask for slides!
- Review **XAFS for Everyone!**
- Return to ENDOR spectroscopy.
  - The energy level diagram we want is the one in the picture.
- Experimental considerations.
  - You need a high energy, intense X-ray beam (typically a synchrotron).
    - The closest synchrotron to us is the APS at Argonne.
    - We can also run at the SLAC at Stanford, and there are others elsewhere, too.
  - Data workup is involved and needs to be done carefully.
    - The relevant software suite is called Demeter and published by Bruce Ravel; it is all free.
- A note on the data.
  - After treatment, the data is typically plotted as a Fourier transform.
  - Note: The “distance”  $R$  in an FT plot is often not true distance; true distance is usually  $R$  plus approximately 0.4 Å.
- Next Tuesday: Mossbauer.

# Week 8

## Mossbauer and EChem

### 8.1 Mossbauer Spectroscopy

- 2/21:
- HW will be posted tonight. Due on 3/2.
  - Final is still on the same date.
  - Mossbauer is pretty short, so we may start on NMR today, too. NMR will be at least 2 lectures.
  - Mossbauer was discovered by Rudolf Mossbauer in 1958 when he was 29. He won the Nobel for it in 1961 at age 32.
  - Basic principle: Involves the resonant nuclear absorption of a gamma rays.
    - We use these rays to excite spin flips.
  - Generating gamma rays: A source nuclei A in an excited state decays, emitting a gamma ray with energy  $E_\gamma$  which will excite our resonant absorption nucleus B and raise it up in energy by  $E_r$ .
  - Common source nuclei to use.

Common Nuclei	$E_\gamma$ (keV)	Precursor Nucleus	$T_{1/2}$	Abundance
$^{57}\text{Fe}$	14.4	$^{57}\text{Co}$	267 d	2.2%
$^{124}\text{I}$	26.8	$^{125}\text{Te}$	33 d	0.63%
$^{119}\text{Sn}$	23.9	$^{119m}\text{Sn}$	245 d	8.6%
$^{195}\text{Pt}$	99	$^{195}\text{Au}$	192 d	33.8%
$^{61}\text{Ni}$	67.4	$^{61}\text{Co}$	1.65 h	1.2%

Table 8.1: Typical Mossbauer gamma ray source nuclei.

- 90% or more of Mossbauer is done with  $^{57}\text{Fe}$ .
  - At 14.4 keV, it's a pretty hot but not super hot  $\gamma$  ray.
  - The cobalt precursor nucleus comes from Russia, so a lot of Mossbauer spectroscopists are probably looking at very lean times right now.
- $^{119}\text{Sn}$  is also pretty common.
  - With respect to the precursor nucleus, 119m means a **metastable** state of tin.
- There are a few synchrotrons in the world that are set up to do Mossbauer as well. Argonne is one of them! Even with a synchrotron source, though, not all nuclei are good; you need a long-ish life time, or your peak is just gonna be way too broad.

- The most common equation in Mossbauer.

$$E_\gamma = E_R + D - R$$

- $R$  is the recoil energy.
  - Gamma rays are so powerful that when one is emitted, there is literally a shotgun-style recoil of the emitting nucleus.
  - If you lose too much energy to recoil KE, your gamma rays may not match the target source.
  - Thus, you try to hold your atoms very stable, usually by embedding them in a solid lattice.
- $D$  is the doppler energy.
  - A Doppler shift is relevant to the experimental setup of Mossbauer.
  - Essentially, you literally hook up your emitter to a speaker and vibrate it at a hertz frequency to add or subtract a tiny bit of energy to/from the gamma rays.
  - This setup allows you to get resolution in a very small window around a certain excitation energy of your nucleus.
  - It also leads to the common unit of mm/s.
- **Recoil free fraction:** The fraction of atoms of the source material that are held still enough that  $R$  is minimized.
- Mossbauer is one of the only techniques that provides direct information about nuclei.
- Three main factors that influence the energy of a Mossbauer transition (i.e., quantities you can pull out of the data).
  1. Electron density at the nucleus.
    - Usually measured by the **isomer shift**  $\delta$  (think ppm from NMR).
    - Correlated with oxidation state in theory, but more accurately with bond length.
  2. Electronic symmetry at the metal center.
    - Measured by the quadrupole splitting  $\Delta E_Q$ .
    - If the charge distribution around the nucleus is totally symmetric, this splitting goes away. But because this is almost never the case, you can get info on SOC, etc.
    - Low spin iron shows up more here because of the anisotropy in the  $d$ -orbital splitting diagram (not all orbitals are occupied here, and ring currents may be induced).
      - In general, the electronic symmetry is affected by the  $d$ -count or configuration.
      - You can also see enormous quadrupole splitting with very electron dense and short ligands.
  3. Magnetic interactions.
    - In an applied field, the nuclear levels split.
- Typically, the isomer shift spans  $\delta = -1$  to  $\delta = 3$ .
- Where do typical oxidation states of Fe lie along this band?
  - $\text{Fe}^{\text{IV}}$ :  $-0.4$  to  $-0.1$ .
  - $\text{Fe}^{\text{III}}$ :  $0.0$  to  $0.6$ .
    - Per quadrupole splitting??
  - $\text{Fe}^{\text{II}}$ :  $0.0$  to  $1.0$ .
  - $\text{Fe}^{\text{I}}/\text{Fe}^{\text{0}}$ :  $1.1$  to  $2.0$ .
  - Cautionary note: These numbers hold in general for iron hemes (because all of this was first applied in bioinorganic chemistry), but can vary quite a bit.
  - Like TMS defines the 0 of chemical shift, stainless steel is the standard for the Mossbauer 0.

- What do the spectra look like?
    - It's a percent absorption spectrum plotted against the Doppler shift.
      - See Figure 8.1b for an example.
    - An  $I = 1/2 \rightarrow 3/2$  transition, for instance, induces a single peak.
  - Mossbauer spectra of iron compounds.

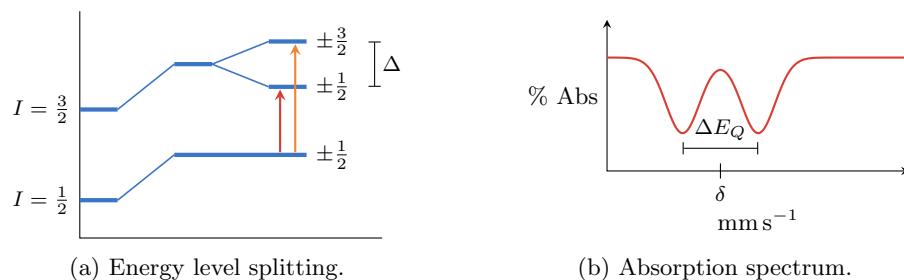


Figure 8.1: The Mossbauer “vampire fangs” spectrum.

- Most iron compounds have two transitions, one into each  $M_I$  state.
    - These are known as the “vampire fangs” (see Figure 8.1b).
  - Recall that  $I = 3/2$  is equivalent to  $M_I = -3/2, -1/2, 1/2, 3/2$  and  $I = 1/2$  is equivalent to  $M_I = \pm 1/2$ .
  - $\delta$  is the center of the quadrupole doublet.
  - $\Delta E_Q$  is the splitting between the peaks.
  - The world record for splitting is 6-7 mm/s, for those nitride compounds with massive charge density and very short bonds.
  - Selection rule:  $\Delta M_I = 0, \pm 1$ .
  - The splitting  $\Delta$  (see Figure 8.1a) between the upper  $M_I$  states is proportional to  $e^2 q Q$ .
    - $e$  is the electric charge.
    - $q$  is the electronic field gradient.
    - $Q$  is the nuclear quadrupole moment.

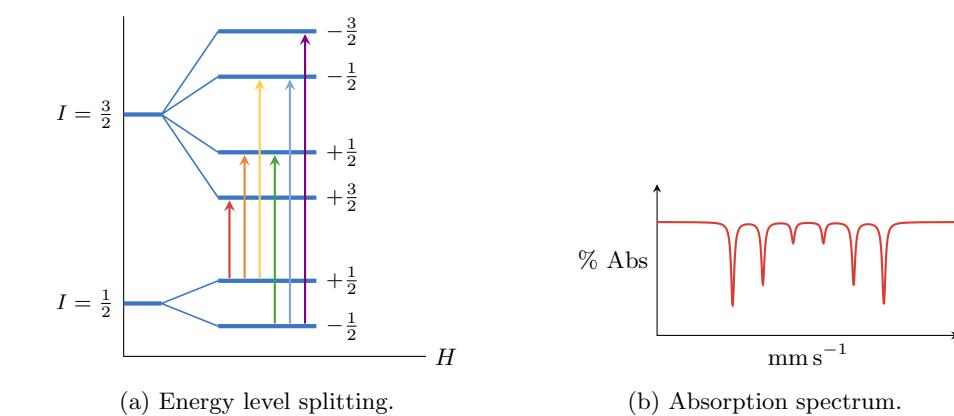


Figure 8.2: Mossbauer spectroscopy under an applied magnetic field.

- Apply  $H$  either parallel or perpendicular to the axis of the radiation.
- All states visible in Figure 8.1a break degeneracy under a magnetic field, yielding Figure 8.2a.
- We'll assume zero quadrupole splitting for simplicity.
- We get six total allowed transitions.
  - This is what you see in fact for Fe metal.
  - You can only obtain this splitting at helium temperatures.
- Takeaway: Huge, clean splitting is obtainable at low temps (low  $T$  minimizes recoil).
- There will be a slight asymmetry due to quadrupole splitting. This allows you to pull out the internal magnetic field of the compound.
- This concludes Mossbauer.
- With the remaining time today, we'll start on electrochemistry.
- Anderson: Professor Wuttig should really be giving this lecture!
- The website “standard operating procedures for cyclic voltammetry,” aka, SOP4CV ([link](#)) has a lot of good resources.
- Introduction.
  - Enables direct probing of electron transfer events, as well as physical properties such as capacitance and conductivity.
  - Our focus: Solution electrochemistry.
  - Solid state EChem is probably more important, though (think of batteries).
- A typical electrolytic cell.
  - The basis is an electrolyte solution in some container.
  - There is a **reference electrode**.
  - You then typically apply a voltage across the reference and **working electrode**. The working electrode is where you do your measurement. The electrons flow out of our working electrode and into the **auxiliary electrode**.
- **Reference electrode:** An electrode with a fritted filter at the bottom and some electrolyte like saturated AgCl in there.
  - The potential is extremely well defined, which gives you a good reference.
  - Ag/AgCl is very common. Another one is SCE using Hg/HgCl, but mercury so people try to avoid this.
- Aside: A current hot topic in EChem is organic electrosynthesis. But Anderson has doubts.
  - Constant current electrolysis pumps a lot of electrons into solution, but no one knows into what! There's a lot of black boxes here.
  - A Cornell scientist is working on this.
- Common electrodes materials.
  - Working electrode: Pt, HOPG carbon, glassy carbon (GC), gold, etc. You can also use very specialized, designer electrodes such as nanomaterial-based ones.
  - Auxiliary electrode: Pt wire/mass.
- Aqueous media is common, but nonaqueous solvents include MeCN, THF, DCM, DMF, DMSO; one of Anderson's faves is 1,2-dichlorobenzene (1,2-DCB) since it is very inert.

- The electrolyte added to solution.
  - Aqueous media: You usually throw in  $\text{Na}_3\text{PO}_4$ .
  - Nonpolar media: TBA,  $\text{PF}_6^-$ ,  $\text{BAr}^{\text{F}}$  (but expensive).
- **Nernst equation:** The applied potential  $E_{\text{app}}$  equals

$$E_{\text{app}} = E + iR_s = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

where  $F$  is Faraday's constant and  $n$  is the number of electrons you transfer during the process.

- $iR_s$  is the current times some internal resistance from the system.
- The Nernst equation is only valid for relatively simple electron transfers. Systems that obey the Nernst equation are referred to as **Nernstian**.
- Intro to CV.
  - You typically scan one way and then scan the other way.
  - The midpoint between the peaks is  $E^\circ$ .
  - Peak to peak separation is 57 mV for  $n = 1$ , and then it shrinks as  $n$  increases.
  - Electrochemists call the shape on a CV diagram a "duck."

## 8.2 Electrochemistry

2/23:

- Electrochemical data is recorded on current vs. potential axes.
  - The applied potential in volts, both positive and negative, makes up the  $x$ -axis.
    - Negative potentials are to the right, and positive ones are to the left.
  - Current makes up the  $y$ -axis, with  $I_{\text{cathode}}$  being positive and  $I_{\text{anode}}$  being negative.
- We now discuss the electrode surface in solution under an applied potential.
- **Electrochemical double layer:** The complex, multilayered structure that forms near the surface of an electrode under an applied potential.

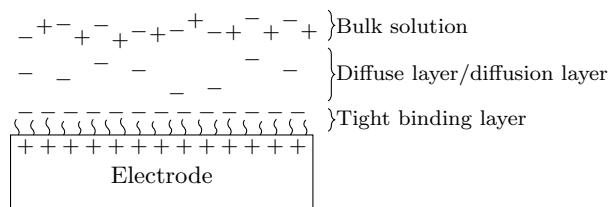


Figure 8.3: Electrochemical double layer.

- Charge transfer to the analyte occurs through this double layer.
- Cyclic voltammetry.
  - One of the most common experiments in electrochem.
  - You sweep between two potentials linearly, plotting the current that flows vs. the potential applied.
  - The anode oxidizes and the cathode gets reduced during the course of the reaction.

- A *reversible* electrochemical reaction appears at a certain potential as a “duck.”
  - Here, the maximum current ( $I_{P_c}$ ; the peak of the duck) and minimum current ( $I_{P_a}$ ; the belly of the duck) should have the same magnitude.
- An *irreversible* electrochemical reaction appears at a certain potential as a one-sided hump or dip.
- As stated last time, the peak-to-peak separation should be about 59 mV, but it almost never is.
  - 57 mV or 59 mV??
  - This is the origin of the following equation (possibly related to the SHE vs. pH one from Labalme [9]?).

$$E_{P_c} - E_{P_a} = \frac{0.059 \text{ V}}{n}$$

- There is also a scan-rate dependence on peak separation given by

$$i_P = 2.99 \times 10^{-5} \cdot n(\alpha n)^{1/2} AC_0^* D^{1/2} V^{1/2}$$

- $n$  is the number of electrons.
- $\alpha$  is the transfer coefficient.
- $A$  is the area of the electrode.
- $C_0^*$  is the concentration.
- $D$  is the diffusion coefficient.
- $V$  is the sweep voltage.
- Differential pulse voltammetry.
  - This is another technique that allows better resolution than CV for closely spaced features.
  - More??
- Rotating disk or ring electrodes.
  - Diffusion is difficult to account for in electrochemistry.
  - With rotation, we can eliminate diffusion.
  - We can also add an outside ring around the active electrode to further characterize any compound generated.
  - If the electrode is rotating, the diffusion path of particles in solution is to move toward the center of the working electrode from underneath and then be spun out to the sides.
- Anything else I missed in this lecture??

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