

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 ~ 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 ~ 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 (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): 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.

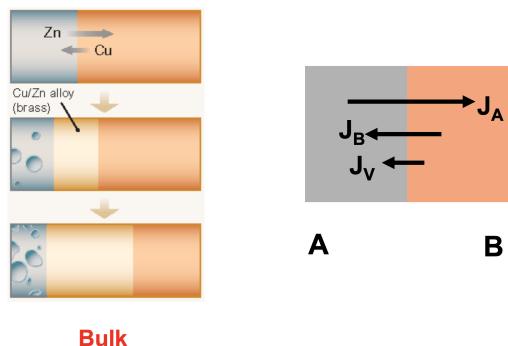
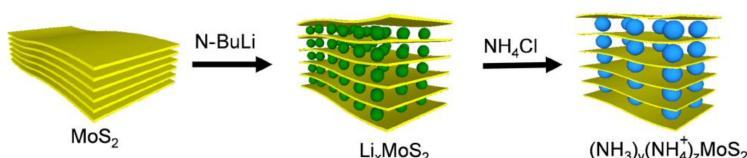


Figure 1.1: Kirkendal effect.

- 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 MoS₂.

Figure 1.2: Top-down synthesis of MoS₂.

- This is the synthesis of interlayer expanded (IE) MoS₂ through chemical intercalation of Li and the following exchange with NH₃ and NH₄.
- Each MoS₂ 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 MoS₂ 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 MoS₂.
 - Chemical synthesis of interlayer expanded (IE) MoS₂.
 - Chemical Vapor Deposition (CVD).
- MXene = 2D metal and surface chemistry.
 - Applications to supercapacitors, batteries, conductors, catalysts, and composites.
 - Most made out of Ti₃AlC₂.
- 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 Cl₂°: 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 CoPt₃ 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 (γ), 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 AlB₂, MgZn₂, Cu₃Au, Fe₄C, CaCu₅, and CaB₆.
- 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.

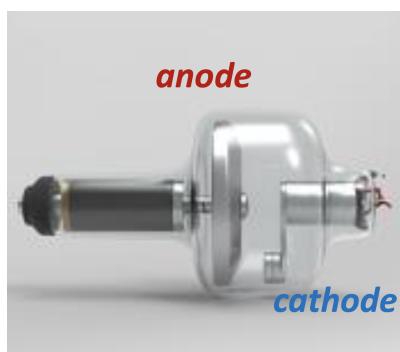
1.2 XRD Analysis

1/5:

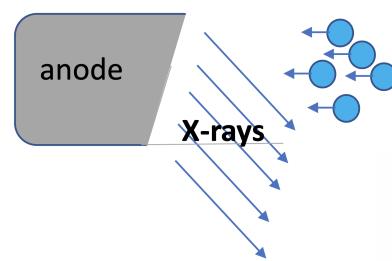
- Applications of X-ray diffraction.
 - Geology, environmental science, material science, engineering, biology.
 - Originally developed for analysis of minerals.
- What you can do with it.
 - Characterization of crystalline materials (structure, unit cell, etc.).
 - Identification of unknown/new crystalline 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} - 5×10^{-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°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.

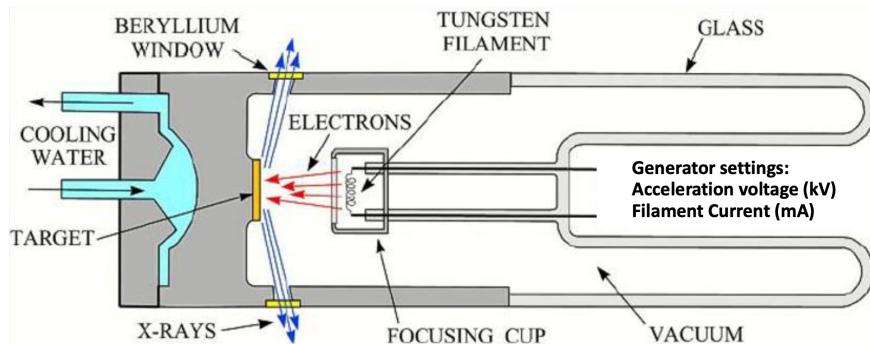


Figure 1.5: Schematic cross section of an X-ray tube.

- 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 ~ 2000 h (at ~ 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 ~ 20 kV and current of ~ 10 mA).

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

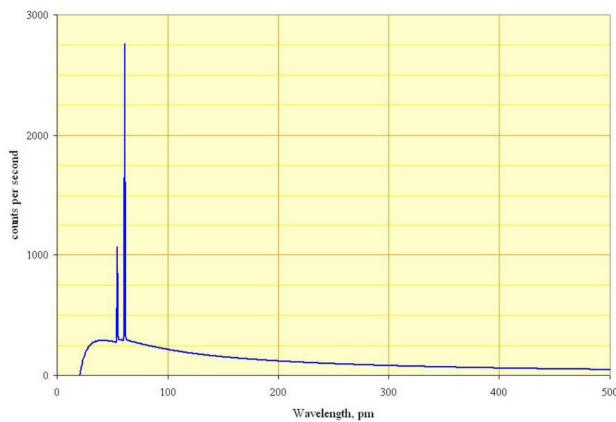


Figure 1.6: The spectrum of X-rays generated in an X-ray tube.

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

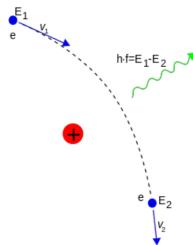


Figure 1.7: Generation mechanism for bremsstrahlung radiation.

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

- X-ray notation for atomic energy levels.

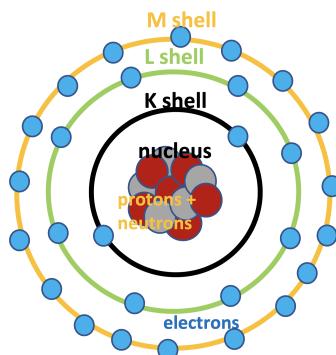


Figure 1.8: Energy levels in the Bohr model.

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

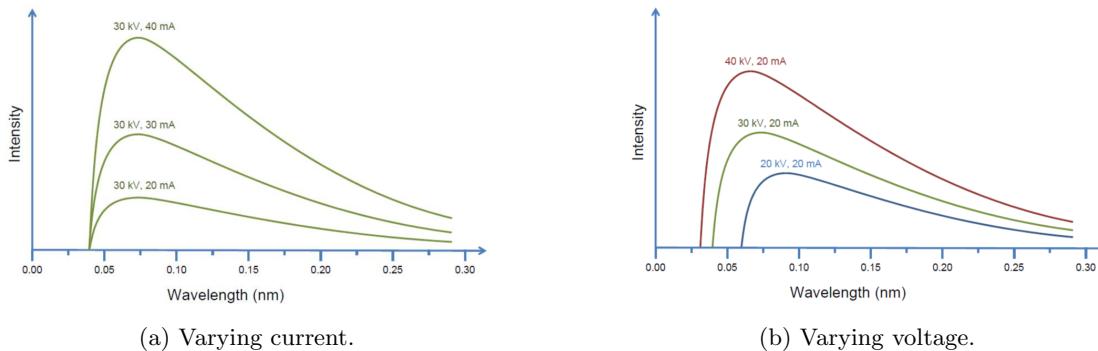


Figure 1.9: X-ray intensity vs. wavelength at different voltages and currents.

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

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

- The proportionality constant K is **contact**.
- λ_{\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.

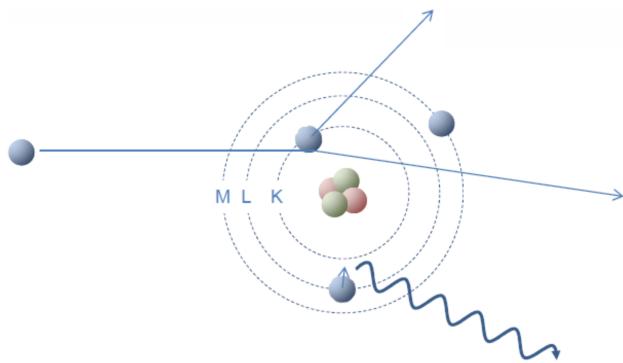


Figure 1.10: Generation mechanism for characteristic radiation.

- 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.

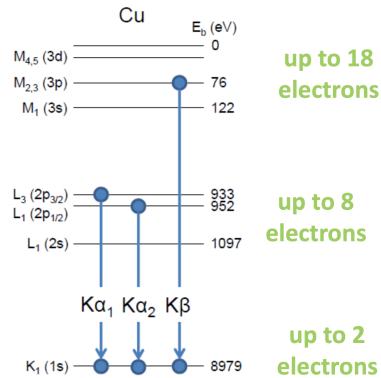


Figure 1.11: Copper spectral lines.

- The copper K_α line has greater intensity than the K_β 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_β rays, and fluorescent X-rays from the sample.
 - Applications require monochromatic X-rays, so all of these (except the desired K_α 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.

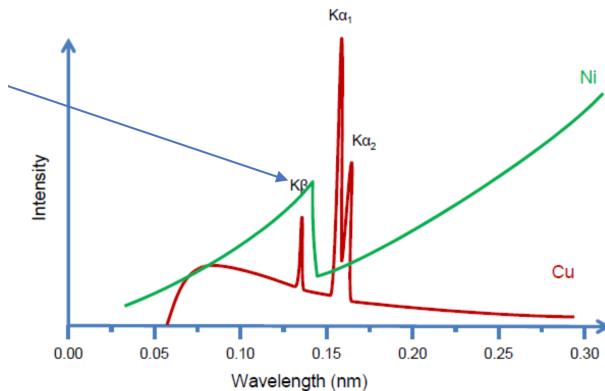


Figure 1.12: Nickel filter for a copper anode.

- 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_β line.
- The filtering of K_β line depends on the thickness of the filter material.
- Example: The absorption edge of nickel metal is at 1.488 Å. This is between the K_{α_1} ($\lambda = 1.542 \text{ \AA}$) and K_β ($\lambda = 1.392 \text{ \AA}$) X-ray spectral lines of copper. Hence, nickel foil of an appropriate thickness can be used to reduce the intensity of the Cu K_β line.
 - In particular, nickel foil of thickness 20 μm is typically used. It reduces the K_β intensity by 99% and the K_α 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_α beam, resulting in polychromatic radiation and alteration of the XRD results (strange shapes and elevated background).
 - Implication: Be careful if you see something unusual in your spectra. We may not have won a Nobel prize for something novel; it could just be Fe, Cr, or Mn contamination of the sample.
 - In this case, seek out an instrument that doesn't use Cu or Co as the target element.
 - Or is it that we want to switch from Cu to Co in this case??

- Monochromators.
 - Main purpose: To remove all X-rays but the K_{α} ones.
 - The monochromator is a crystal.
 - The monochromator works by reflecting wavelengths that obey Bragg's Law (see next lecture and Labalme (2022)) for the particular d spacings of the monochromator.
 - Desired characteristics.
 - The crystals should have suitable interplanar distances d so that the desired wavelength λ 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 λ 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_{α_1} and K_{α_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.

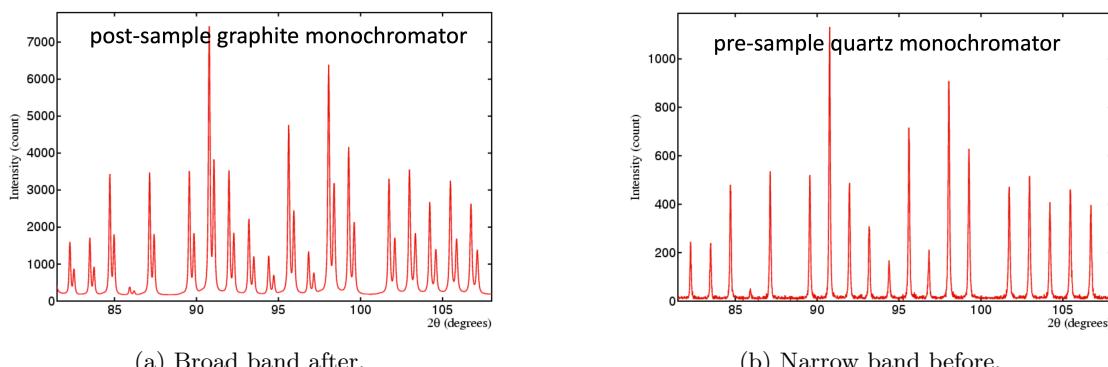


Figure 1.13: Effect of monochromator type and placement.

- 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_{α_1} and K_{α_2} radiation.
- The spectrum in Figure 1.13b was collected using a narrow band monochromator before the sample.
 - Benefit: The peaks due to K_{α_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_{α_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_{α_1} and K_{α_2} lines (i.e., $\lambda = 154.051 \text{ pm}$, 154.433 pm , respectively), we can use Bragg's law to calculate the angle 2θ 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_{α_1} line, we should use the angle of incidence

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

- Owing to its high crystalline purity (low mosaicity), silicon at this angle can select for the desired wavelength.
- Graphite monochromators will pass both K_α wavelengths, but not K_β 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_{α_1} and K_{α_2} wavelenghts from a laboratory X-ray source??
- Is this all correct??

- Filters vs. monochromators.

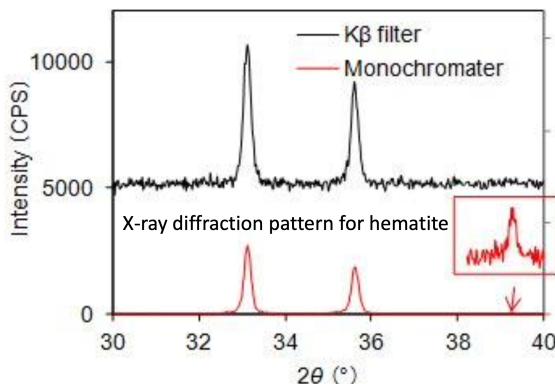


Figure 1.14: Filters vs. monochromators.

- Metal filter vs. a crystal monochromator.
- By using a monochromator, it is possible to obtain X-ray diffraction patterns with high signal-to-background ratios since the monochromator can remove interfering components such as continuous X-rays produced by the X-ray tube, K_β rays, and fluorescent X-rays from the sample.
- Notice the extra noise in the spectrum taken with a K_β 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.

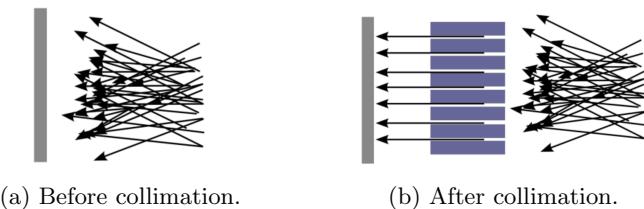


Figure 1.15: Collimator function.

- 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.

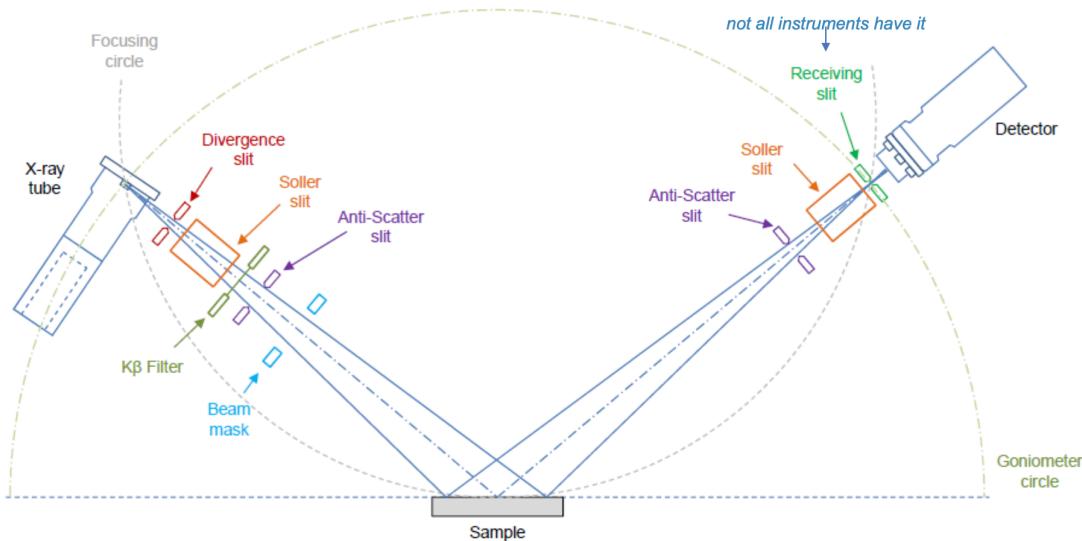


Figure 1.16: Typical diffractometer configuration.

- 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 2θ 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.

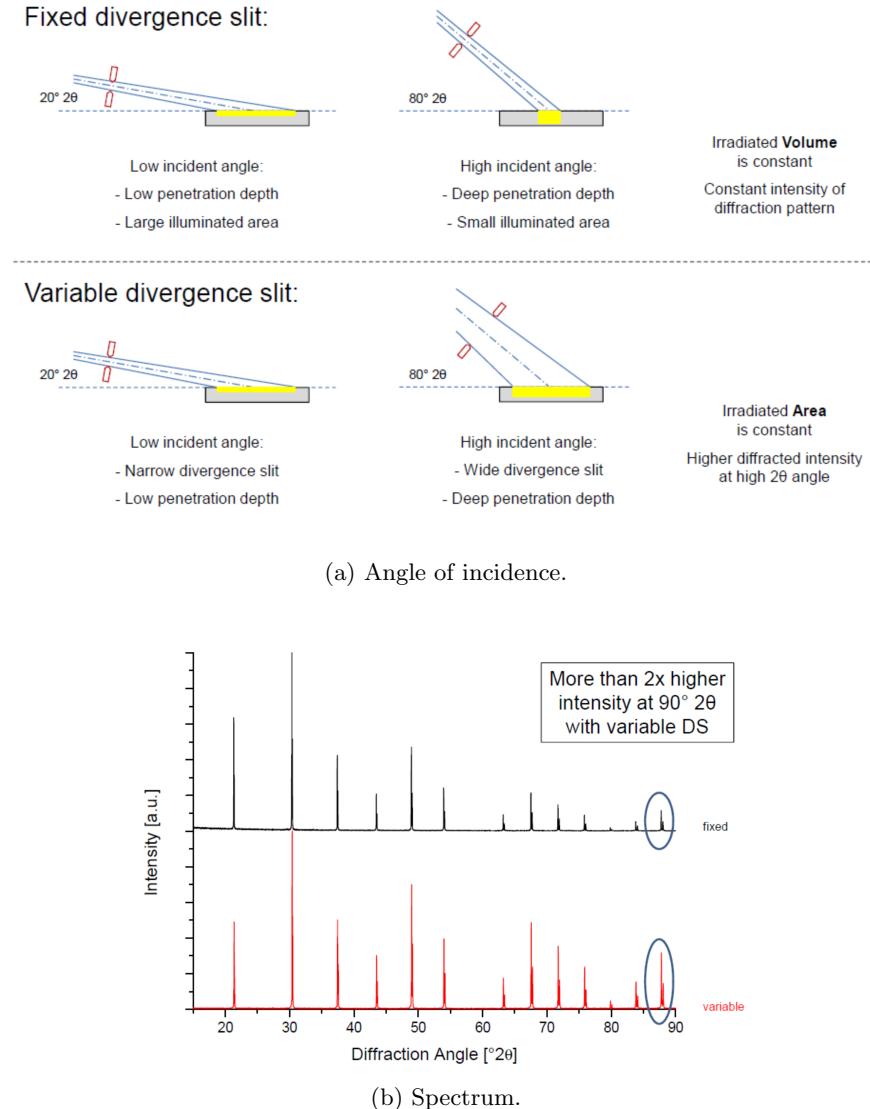


Figure 1.17: Fixed vs. variable divergence slits.

- 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 2θ ; signals differ in intensity at high 2θ .
- **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 β -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.

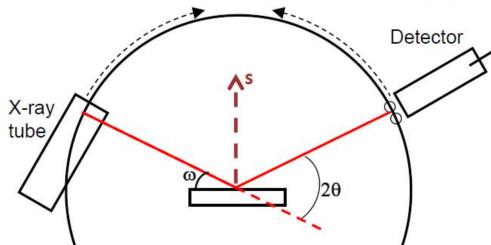


Figure 1.18: Bragg-Brentano geometry.

- 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 ω between X-ray source and the sample is always half of the detector angle 2θ .
- Two types of setups.
 1. Fixed X-ray tube: The sample rotates at θ/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 θ/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.

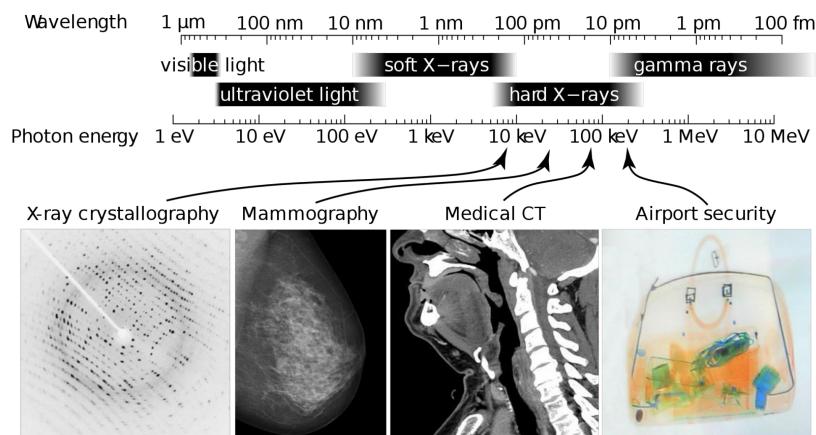


Figure 1.19: X-ray spectrum.

- 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.

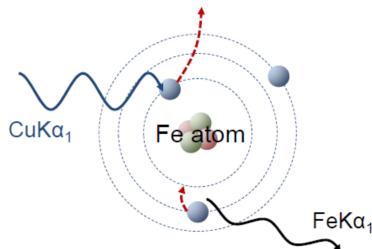


Figure 1.20: Absorption and fluorescence.

- **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 λ .

- 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!

Bibliography

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