

Week 4

???

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).

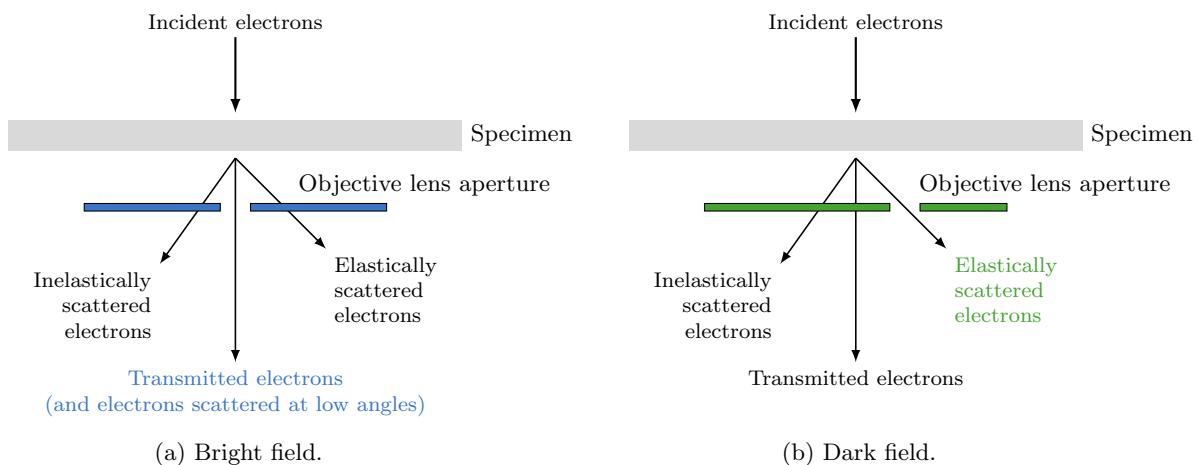


Figure 4.1: OL configuration in bright and dark field modes.

- 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.

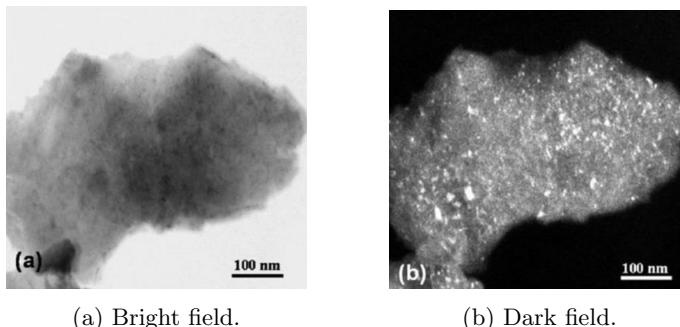


Figure 4.2: Bright field and dark field TEM micrographs.

- 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 Å (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.

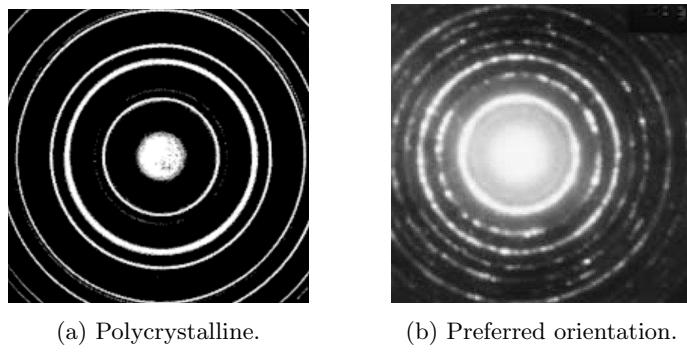


Figure 4.3: SAED images of polycrystalline vs. oriented materials.

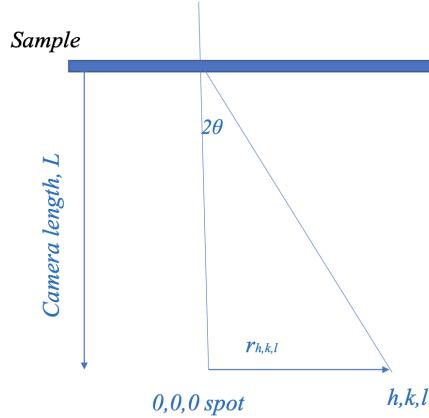


Figure 4.4: SAED condition derivation.

- 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 θ 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 Al₇₈Mn₂₂ 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/Fe₃O₄ 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.

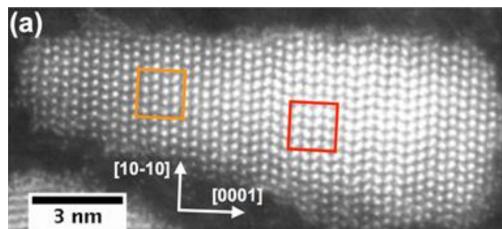


Figure 4.5: HAADF image of CdSe/CdS nanoparticles.

- “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^α , 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 MoS₂ 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.

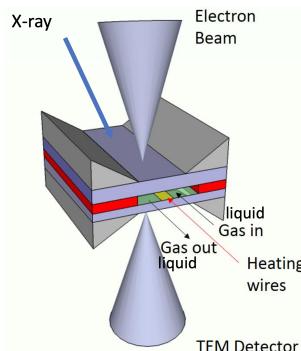


Figure 4.6: *In situ* TEM.

- 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.

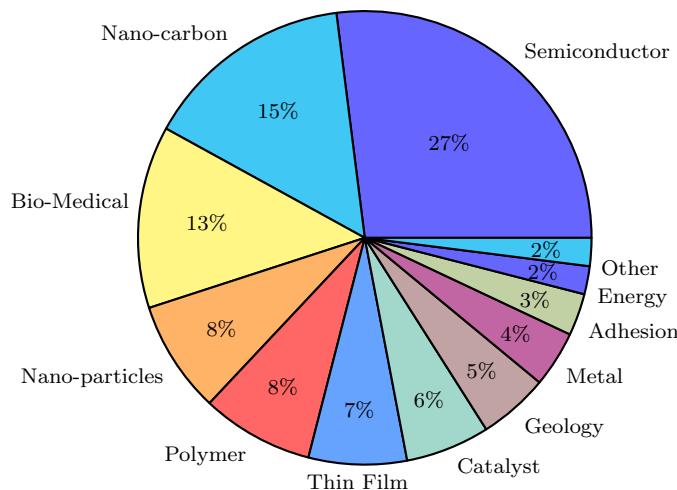


Figure 4.7: XPS in different fields.

- 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.

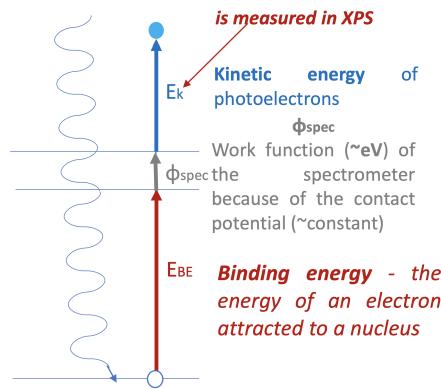


Figure 4.8: XPS equation visualization.

- In the domain of XPS, the following equation is very important, but we will not even touch it.

$$h\nu = E_{BE} + (E_k + \phi_{sp})$$
 - We want to find out the binding energy E_{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_{α_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_{α} and Mg K_{α} 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 σ .
 - 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^{II} species in Cu(OH)₂ 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 Δ_{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.