X-ray Spectroscopy

1. Introduction

X-rays are KeV photons. Atomic X-rays are emitted during electronic transitions to the inner shell states in atoms of modest atomic number. These X-rays have characteristic energies related to the atomic number, and each element therefore has a characteristic X-ray spectrum. In this experiment you will use a high resolution solid-state X-ray detector to record the characteristic spectra of several elements, repeat the pioneering work of Moseley relating X-ray energies to atomic number, and also explore the use of X-rays as a diagnostic tool for sample identification.
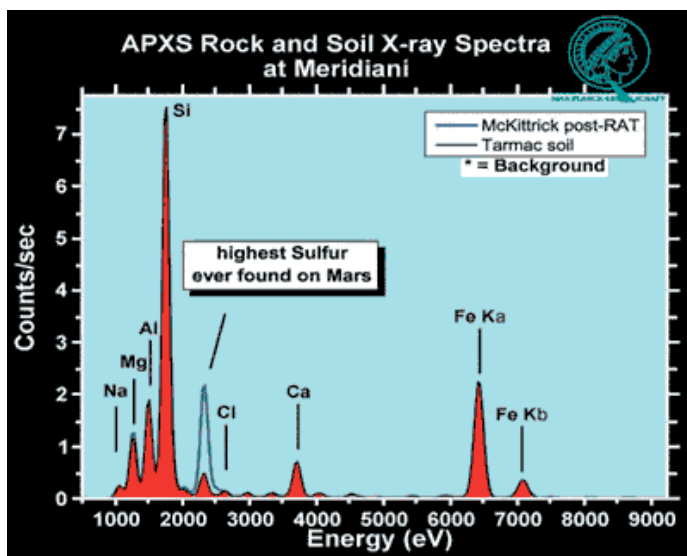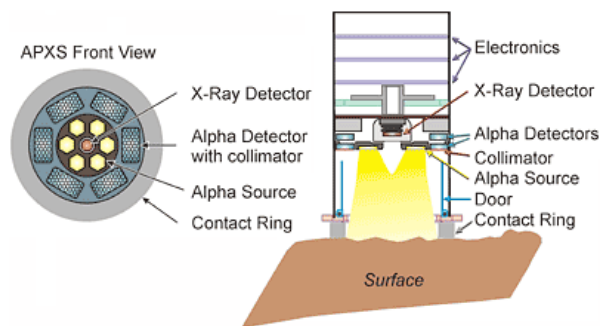

Fig. 1b – The Alpha Particle X-Ray spectrometer on the Mars Rover

Figure 1a – X-rays from Mars

2. X-Ray Spectra of the Elements

Required reading: Haken & Wolf, Chapter 18.
Recommended: Eisberg & Resnick 9.8; McGervey 4.1

2.1   Energetic electronic transitions

In the simplest model of electronic transitions in hydrogen-like atoms, an electron loses energy by moving between states with principle quantum numbers $n_{initial}$ and n_{final}, and a photon is emitted with energy

$$E_\gamma = E(n_i) - E(n_f) = \frac{me^4 Z^2}{2(4\pi\varepsilon_0)^2 \hbar^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = 13.6 \cdot Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) eV$$

In complex atoms, the inner shells remain hydrogen-like, so we may continue to use this formula as long as n_i and n_f are small. The single necessary correction is to account for the fact that electrons of a given n_i do not see the full charge of the nucleus because it is obscured by the electrons in lower lying shells. This reduces the Z by some effective *screening factor* s, thus:

$$E_\gamma = E(n_i) - E(n_f) = 13.6 \cdot (Z-s)^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) eV \tag{1}$$

If s is small and Z is greater than 10, the typical photon energy is of order 1 KeV, these are X-rays. There is also a well-defined relationship between the photon energy and the atomic number. As a specific example, for the transitions from $n_i = 2$ to $n_f = 1$ (which are otherwise known as the K_α transitions), we expect

$$\sqrt{E_\gamma} = \sqrt{\frac{3E_0}{4}} (Z-s); \quad E_0 = 13.6 \, eV \tag{1a}$$

Given measurements of the K_α X-ray energies for a series of elements, a plot of the square root of the energy *vs.* Z should be a straight line with slope that measures the ionization energy of hydrogen, and intercept which measures the screening factor for $2 \rightarrow 1$ transitions. Once the screening factor is known, the K_α X-ray energy can be used to calculate the Z of any unknown sample.

The logic of this regularity in the X-ray spectra was first laid out by H. G. Moseley in 1913, and he used it to establish the *existence* of the atomic numbers, resolve the inconsistencies in the placement of Co vs. Ni, and Ar vs. K in the periodic table (which, prior to this point, had been arranged by atomic *weight*), and predict the existence of new unseen elements at Z=43, 61, 72, and 75.

Moseley also discovered the expected arrangement of the X-ray lines into families reflecting the combinatorics in n_f and n_i. A chart of the K, L, and M families is shown at the top of the next page. The K X-rays are the various transitions to $n_f = 1$: K_α is the $2 \rightarrow 1$ transition, $K_{\beta 1}$ is the $3 \rightarrow 1$ transition, $K_{\beta 2}$ is the $4 \rightarrow 1$ transition. The L lines are transitions to $n_f = 2$, and the M lines are transitions to $n_f = 3$. Note that with very high resolution it is possible to see the spin-orbit splittings. For instance, as you can see in Fig. 2, with sufficiently precise detectors, the K_α line could be re-solved into the separate $K_{\alpha 1}$ and $K_{\alpha 2}$ lines, which measure the energy difference between the J = 3/2 and J=1/2 orbitals for n=2.

2.2 Induced X-ray Emissions

The energetic transitions described above will occur when a vacancy appears in an inner shell and an outer shell electron falls into the open state. The inner shell vacancy can be artificially induced in two ways:
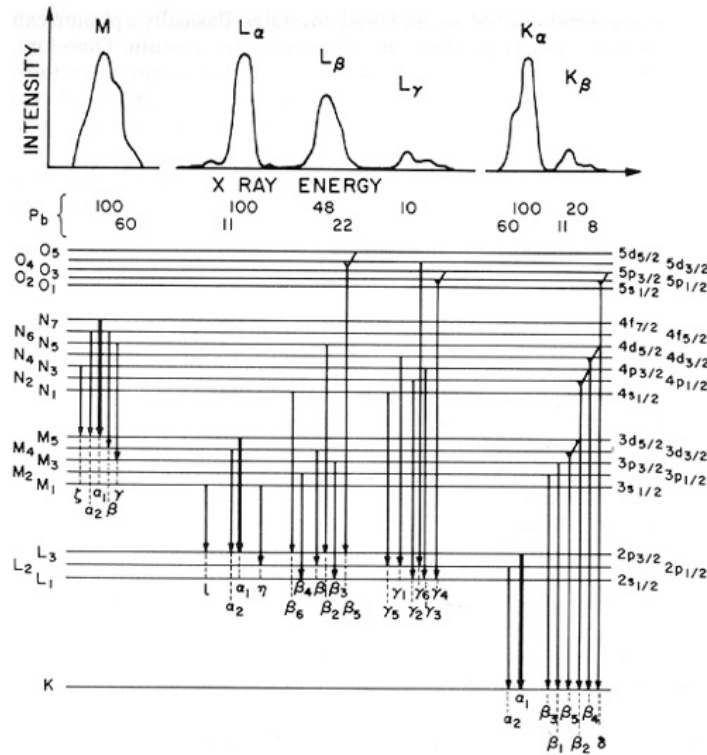
Figure 2 – X-ray Nomenclature (from Feldman & Mayer, Fundamentals of Surface and Thin Film Analysis)

a) The sample can be irradiated with some kind of high energy particles, which literally knock electrons from their orbitals, creating the vacancies, and allowing the processes above. This is called *Particle Induced X-ray Emission*, or PIXE. In this experiment, we will use a radioactive alpha source to provide the bombardment. Alpha-PIXE plus solid-state X-ray detection is one of the chemical analysis techniques used on the Mars Rover missions. See:

> http://athena.cornell.edu/the_mission/ins_apxs.html
> http://athena.cornell.edu/pdf/tb_apxs.pdf

b) Alternatively, if there is another source of X-rays, these can be used to irradiate a sample and provide the induced X-rays. This is called *X-ray fluorescence*.

2.3 Other X-ray sources

A number of radioactive nuclei are fortuitous X-ray sources. Co-57 decays to Fe-57 by inverse beta-decay, capturing an electron from an inner orbital. The new Fe nucleus finds itself in an unstable spin state and decays electromagnetically to lower energy states, emitting 122 KeV and 14 KeV photons (see decay scheme on next page). In addition, since it was born via electron capture, the new Fe atom is missing an inner shell electron, and thus will also emit characteristic Fe X-rays, such as the prominent K_α line at 6.4 KeV. Cd-109 is a similar electron capture source,
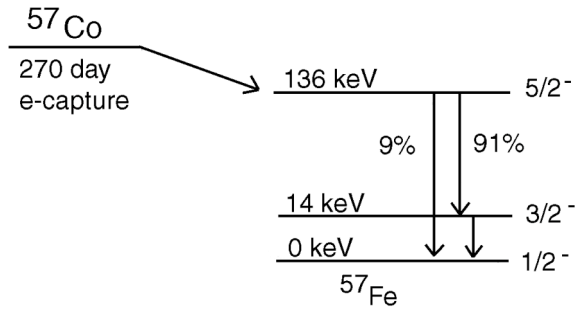
Figure 3 – Co-57 Decay Scheme

emitting an 88 KeV photon from the nuclear excitation in addition to Ag X-rays. Fe-55 is also a familiar X-ray source, which also decays by electron capture, and emits Mn X-rays. Note that it is more usual to find radioactive nuclei that emit gamma rays (*MeV* photons) rather than X-rays.

Finally, note that X-rays can be easily created by boiling electron off of a filament, accelerating them across a gap of a few KeV, and stopping them with a target, where the rapid deceleration causes stopping radiation or *bremsstrahlung* in the X-ray region. The typical energy spectrum of these X-rays is a continuum, with an upper cutoff at the incident electron energy, superposed on with the characteristic spectrum of the materials in the target. See Fig. 4. This technique allows for large intensities and is the means employed in commercial X-ray tubes, e.g. in the dentists office. We have such a device in the Advanced Lab, and it can be used for high intensity studies of Bragg scattering, and X-ray fluorescence and transmission.

3. Experimental Set-up

Required reading: Melissinos 3.5, 8.2.1-8.2.2, 8.2.5, 8.5.1-8.5.2
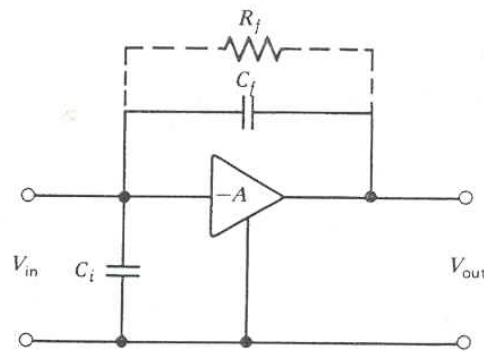**Recommended: Knoll, Chapters 2 and 11, Leo 10.1-10.5**

You will measure X-ray energies using detector and electronics from Amptek. Much detail on silicon detectors and readout electronics can be found in the references and the Amptek website, which you should consult. A detector similar to ours is described at http://amptek.com/pdf/xr100cr.pdf.
We offer here just a brief review.

The X-rays **detector** is a reverse biased PiN diode. The X-ray is photoelectrically absorbed and the liberated electron loses energy in the silicon by creating electron-hole pairs @ 3.6 eV per pair. Recall that in a p-n junction the majority carriers diffuse across the interface creating an electric field that sweeps any excess charge out of the *depletion zone*. The trick for using this as a detector is to make the depletion zone thick enough to collect all the ionization. In a PiN diode, a layer of **i**ntrinsic silicon is placed between the p and n (thus p-i-n), which creates a large depletion zone if the detector can be reverse biased to sufficiently high voltage. This typically creates a significant reverse (or "dark") current, which complicates the readout and also introduces *shot-noise*. The dark current can be eliminated by running at lower temperatures, which is done here by mounting the detector on a thermoelectric cooler based on the Peltier junction. The PiN diode then offers a detector that is thick enough to stop X-rays, and produces a charge signal that is proportional to the X-ray energy.

The charge q is converted into a voltage in the **pre-amplifier** stage. The pre-amplifier is usually the most critical part of any experimental electronics, as it must solve the practical laboratory version of Heisenberg's conundrum: measure a system without disturbing it. Operational amplifiers, with their huge input impedances, are naturals. (Why is that?), but there can still be complications.

Say we use a voltage amplifier, as in Melissinos Sec. 3.5. The input voltage is derived from the charge signal and the input capacitance $V_{in} = q / C_{in}$. The detector capacitance is related to the geometry of the depletion region, the size of the reverse bias, and perhaps the temperature and X-ray rate. It is small, of order pF, and will appear in combination with stray capacitances from connections and cables. The calibration of voltage to charge cannot be known to any better than the total uncertainty in this messy combined C_{in}.

 A better scheme is to use a charge sensitive preamplifier:

Figure 4 – A charge integrating amplifier (Knoll).

Use a treatment similar to that in Melissinos Sec. 3.5 to show that for large open-loop gain (A or α) the output voltage in this configuration is simply related to the feedback capacitance $V_{out} = -q / C_f$. In this case, the input capacitance effectively disappears from the problem, the output is related to the charge signal in a controlled way.

This voltage signal is then sent to a **linear amplifier** for pulse shaping: the signal is differentiated to remove baseline shifts, and then integrated to remove high frequency noise. The time-constant of this circuit is called the "shaping time", and sets the ability of the apparatus to resolve pulses close together in time. The overall amplification allows increased resolution in the electronics for small energy differences but is still completely linear: the peak voltage is proportional to the charge collected in the detector. The Amptek device also performs a correction called Rise Time Discrimination (RTD), which corrects for a shaping distortion that occurs when ionization is collected near the edges of the detector. This helps reject small pulses that would otherwise confuse the spectrum.

Finally, the amplifier output is sent to an **analog-to-digital converter (ADC)** in the small black box, which converts the height of the voltage pulse to a number and sends the number over the serial bus to the computer, which runs software with the plotting, histogram, and analysis package. The ADC value is a number between 0 and some power of 2, and is called the channel number. For instance, a typical setting is that the pulse height varies from 0-5 V, and is converted to a number between 0 and 512. In this case, the full dynamic range is split over 512 bins, with each representing

a voltage interval of 5/512 ~ 0.01V. The histogram has 512 bins or *channels*, and the height in each channel is the number of times there was a pulse in that particular voltage bin. If your resolutions warrants, you can go to a finer binning by using 1024 or 2048 channels: this is good because you will have more bins in each peak, and more resolution on measuring the peak resolution. But it's bad because you have to count longer to populate the individual channels with good statistics. The best practice uses the minimum number of channels to put 5-6 channels in each peak.

In the end it is a histogram recording the frequency of pulse-heights, thus a pulse-height- analysis or PHA. In the pre-computer days, the histogram function was done in hardware with a special pur-pose instrument like a big oscilloscope, which could record data in many channels (remarkable at the time), and hence was called a Multi-Channel-Analyzer. The jargon MCA has stuck, and that's why our device is called "Pocket-MCA".

4. Experimental Procedure

You are going to calibrate the set-up, then use alpha ray PIXE to verify Moseley's Law in the first row of the transition elements, and to measure the composition of an unknown sample.

4a. Set-up

Connect things up according to the circuit block diagram in the Appendix. Notice there is a Gate connection between the shaping amp and the MCA that can throttle the input to the MCA when it is busy. Record the detector temperature by using a DVM in ammeter mode. The Amptek docu-mentation claims 1 deg K per micro-amp. Set RTD on. Set the gain knob on the linear amplifier to 2.5 for starters. Set the "ADC Gain" to 2048 in the MCA setup, so that the full scale on the MCA is 2048 counts. The ADC threshold sets the minimum channel to be recorded; 30 channels or so is reasonable to suppress noise.

Place the Co-57 source in front of the detector. Start the MCA software. Tell it to connect to an MCA. On the pull down menu under "MCA", pick "Start Acquisition". You should see the Co-57 peaks begin to accumulate. Familiarize yourself with the system. Note the information in the sidebar that tells you the total number of counts, as well as the count rate. Use the help menu and manual to learn how to fit regions-of-interest and find peaks. Try varying the linear amplifier gain. See what happens if you turn off RTD. Note that it is not always obvious which is the "front" side of the button sources, so try putting both sides against the detector. The side that gives the higher count-ing rate is the front side.   Note also that the detector is quite small, ~3 mm diameter (take a look at the "business end" of the detector), so you will need to carefully align the source on the detector.

Our detector is not sensitive to X-rays with energies above about 20 keV, so you will <u>not</u> be able to see the 122 and 136 keV lines (Fig. 3).   You should be able to see the 14 keV line, and the Fe-57 K-lines. (Why?) In the calibration, you will want to set the amplifier gain so that full scale is about 20 keV. Once you are able to recognize the 14 keV line, you can set the gain so it is about 70% of full scale.

4b. Calibration

The first order of business is to calibrate the energy scale of the MCA. This can be done using "known" lines.   Since, in principle, all the X-ray lines you will be dealing with are known, the choice

of lines to use for calibration is somewhat arbitrary. First try various γ sources and various samples with the alpha source until you are confident that you can recognize the lines. Then choose several lines between ~2 keV and ~20 keV to use as your "knowns".   Once this is done, consider all other lines as unknowns that you can compare to published values. [Consult the Amptek chart of K_α energies at http://www.amptek.com/xray_chart.html. There are many other tables on the Internet.]

It is best to set up two calibrations, one for lines up to 20 keV and one for lines up to say 5 keV, so that you can get more accurate energies for lines below 5 keV. This will require two gain settings on the amplifier. To make things simpler, choose calibration samples that are all one element, not a composite. Good possibilities for calibration lines are the K-lines of silicon, aluminum, and silver and the L-lines of lead. Fig. 1a and the lead fluorescence spectrum from Cd-109 shown on the right may provide some ideas.
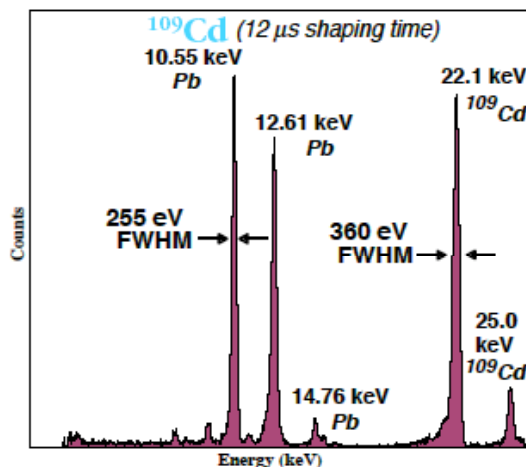

Figure 10. Lead (Pb) Fluorescence from ^{109}Cd

Once you have settled on a strategy, accumulate peaks from the samples. Fit all the peaks (there is a function which can find many automatically). Use the software calibration feature to fit the relationship between channel number and energy. Also make plots of energy *vs*. MCA channel for both calibration settings. Note that there is likely to be an offset so that zero energy does not correspond to channel = zero.
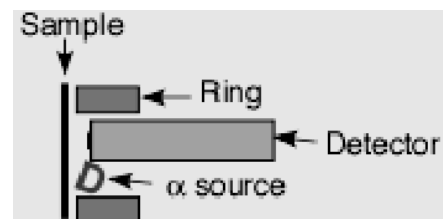
You now have a calibrated device. Be sure to understand the precision and uncertainty in your calibration.

4.c. Induced X-rays and Moseley's Law

You will use a 1 millicurie Cm-244 source to provide 5 MeV alpha rays for PIXE. The source is in a circular plastic holder which accepts disk shaped samples.
When using the α source, place it as close as possible to the sample. Point it generally at the sample as shown, and place the detector as close as possible to the sample to maximize the counting rate. If the sample is mounted in a metal holder, try to illuminate the sample itself, rather than the holder in order to minimize the X-rays from the holder. [See also Fig. 1b.] Don't forget that α's have a very short range so you will only see X-rays from a thin surface layer.

We have samples of the first row transition elements V through Zn. A few of these are discs that fit into the source holder, but most of the samples are smaller disks mounted in square metal sheets. For the latter you will need to tape the source holder over the sample.   The YBCO superconducting disks used in the High T_c superconductivity experiment contain yttrium, which is an interesting element.   Try to do the largest possible range of Z's

Alpha rays have very short range in air (~3 cm), so this is not an intrinsically dangerous environment, but you should try to minimize the amount of handling, keep the source pointed into the plastic when it is not in use, and by all means avoid touching the source material which is mounted on a very fragile foil.

The induced X-ray spectra will include characteristic X-rays from the samples, from the metal sheet surrounding the samples, from the source itself, and from material in the source holder. You can minimize the backgrounds by illuminating only the sample itself with α's. You can learn to distinguish the contributions by taking spectra with no sample and spectra from the material surrounding the samples.

Accumulate spectra for as many samples as possible. Fit peaks and record widths. Your lab report should contain representative spectra with all notable features clearly labeled as in Fig. 1. Make a table of X-ray energies $vs.$ Z for K_α and K_β lines and L_α and L_β lines wherever possible. Plot $\sqrt{E_\gamma}$ $vs.$ Z as in Eq. 1. Fit for the slopes and intercepts for each family. From these data, determine the screening factor s for each family and E_0.

4.d. X-ray Forensics

Find some samples that are known alloys, and try to do a quantitative analysis of the compositions. Pick an interesting unknown sample and perform PIXE analysis of its composition. U.S. coinage is interesting, especially if you have some older coins to compare to newer coins. Or perhaps you can pick some interesting minerals, and compare to results coming back from the Mars Rovers. Ask the instructor for an unknown and determine its composition.

5. Questions

(1) Ideally the width of the peaks should be determined by the statistical fluctuations in the number of electron-hole pairs formed in the silicon. Assume it takes 1.6 eV per pair and calculate the expected width for a few energies. Compare these with measured widths.

(2) Compare your measured widths with those in the detector specifications at http://amptek.com/pdf/xr100cr.pdf.

(3) Compare your screening constants and E_0 with expected values. Discuss any discrepancies.

(4) Do your data agree with Moseley's law? Discuss.

(5) What did you find for the composition of the unknown?

References:

Amptek Website: www.amptek.com.
Eisberg, R. and Resnick, R., Quantum Physics of Atoms, Molecules, Solids, Nuclei,
          and Particles, 2nd Edition
Knoll, G., Radiation Detection and Measurement, 3rd Edition
McGervey, J.D., Introduction to Modern Physics
Melissinos, A. and Napolitano, J., Experiments in Modern Physics, 2nd Edition

Appendix 1: Electronics Block Diagram

Connection Diagram for the XR-100CR to the PX2CR and MCA8000A