

## X-RAY SPECTROSCOPY

### OBJECTIVES

To observe x-ray spectra from a wide variety of elements; to test whether Moseley's law is an adequate description of how x-ray wavelengths vary with atomic number; and to use x-ray spectroscopy as a non-destructive test to analyze the elemental composition of a sample.

### REFERENCES

See any modern physics textbook for Moseley's law; various *Table of Isotopes* books on the reference shelf; and the table of x-ray energies that will be provided with the experiment.

### INTRODUCTION

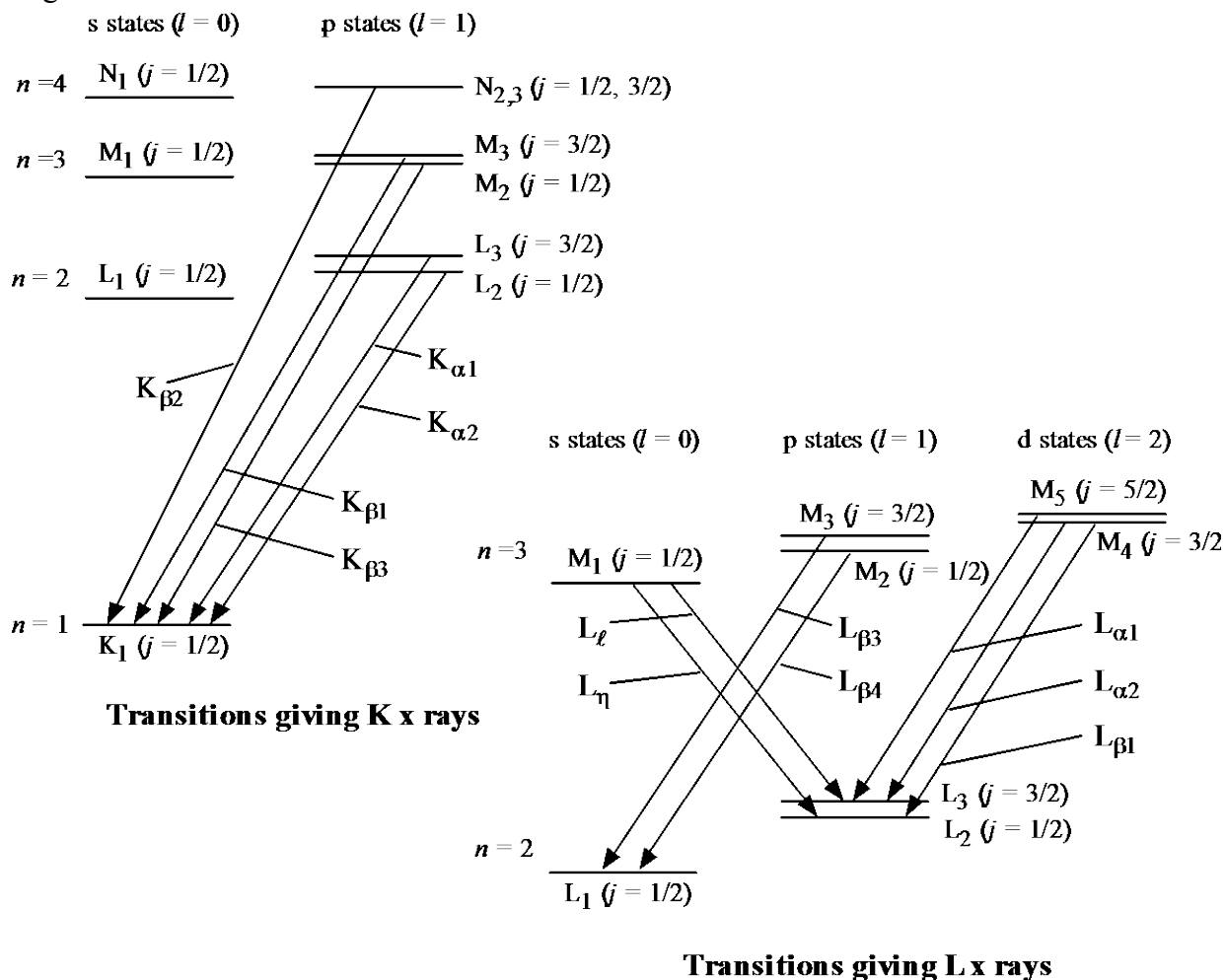
One of the ways to produce x-rays is to remove an inner-shell electron from an atom – usually through an electromagnetic or nuclear process. An electron from an outer shell then de-excites to the hole left in the inner shell, emitting a high-energy x-ray photon. Three major processes cause inner-shell vacancies:

1. A high-energy electron (many keV of kinetic energy) is incident on a target. This is what happens in an “x-ray tube” such as those used for medical and dental x-rays. We will not use that process in this experiment.
2. A high-energy photon (gamma ray) creates the inner-shell vacancy in a process called *photoionization*. In this case, the subsequent x-rays are called *fluorescent x rays*.
3. A nucleus in an excited nuclear state decays to a lower energy state by transferring its excess energy directly to an inner shell electron, giving the electron enough energy to kick it out of the atom. This process is called *internal conversion*.
4. In some proton rich nuclei, a proton will absorb the inner electron, becoming a neutron and emit an electron neutrino. Subsequent cascading into the new vacancy in the inner shell produces x-rays.

Bombardment of atoms by high-energy protons or alphas can also cause x rays, but the present experiment is limited to spectra arising from internal conversion and from fluorescence.

X-rays are understood by recalling the basic energy-level diagram of an atom. In order of increasing energy, the states of an atom are 1s, 2s, 2p, 3s, 3p 3d, and so on, where letter s represents orbital angular momentum quantum number  $l = 0$ , p is  $l = 1$ , and d is  $l = 2$ . All states with  $l > 0$  are split into two distinct energy levels by the spin-orbit interaction. The higher energy level has total angular momentum quantum number  $j = l + 1/2$ , the lower one  $j = l - 1/2$ .

The  $j$  value is often shown as a subscript on the s, p, d letter. This information is shown in the diagram below.



X-ray transitions must obey the same quantum mechanical selection rules as any other transition in an atom, namely  $\Delta l = \pm 1$  and  $\Delta j = \pm 1$ . These selection rules lead to the transitions shown.

Although x-ray transitions could be labeled something obvious, such as  $2p_{1/2} \rightarrow 1s$ , it turns out that x-ray spectroscopy, for various historical reasons, uses its own notation. To begin, the  $n = 1, 2, 3$  shells of the atom are called the K, L, and M shells. The energy levels in the figure have been labeled with this notation. To add further confusion, there are two common methods of labeling the transitions: The Siegbahn notation, shown on the figure, labels an x-ray first as to the energy level of the inner-shell vacancy (an x-ray filling a vacancy in the  $1s$  shell, or K shell, is called a “K x-ray”) and then with subscripts showing the energy level from which the quantum jump originated. Other x-ray spectroscopists label transitions explicitly with a notation such as K -  $L_3$ , but notice that the final state of the transition (i.e., the state which had the vacancy) is listed first.

The x-ray detector we will use, made by the AmpTek company, is a laboratory version of the x-ray spectrometer that has gone to Mars to study the composition of Martian soils and rocks. The heart of the detector is Li-drifted silicon diode that is cooled by a thermo-electric cooler to a temperature  $\approx -40^{\circ}\text{C}$ . An x-ray that is absorbed in the p-n junction liberates electron-hole pairs, creating a pulse whose height is directly proportional to the x-ray energy. The low temperature improves the energy resolution. Our detector has a nominal resolution of 200 eV when looking at x-rays with energies  $\approx 6\text{--}10\text{ keV}$ .

Fluorescent x-rays are created using a ring-shaped 100 mCi  $^{241}\text{Am}$  (atomic #95) source that emits 59.5 keV low-energy gamma rays. The gammas from this source are able to excite K x-rays from sample materials having atomic numbers up to  $Z \approx 70$ . (The 1s electrons in elements with  $Z > 70$  (such as the Americium itself) are too tightly bound to be photoionized by 59 keV photons.) However, the source can create L x-rays from all atoms in the periodic table. These gammas cause inner-shell photoionization of the sample. The fluorescent x-rays from the sample travel back through the collimator hole into the detector.

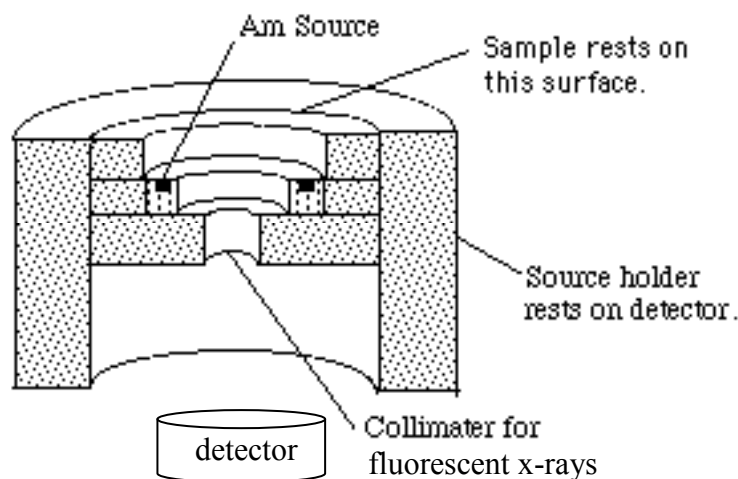


Figure 1. Fluorescent x-ray source assembly

## PROCEDURE

### >>> CAUTIONS <<<

- The source used in this experiment to produce fluorescent x-rays is 100 mCi of  $^{241}\text{Am}$ . This is a *very* strong source. It produces about 165 mrem/hr at 6" above the source when it is unshielded. **Only the instructor may place the source into position.** Use the Geiger Counter to convince yourself you are well shielded behind the lead shield with the sample Am on the detector. Should people stay away from the unshielded side? Be quantitative.

- The detector has a *very thin* beryllium window (to permit the low-energy x-rays to enter). It can easily be broken, destroying the detector. Be *very careful* when placing samples over the detector.

### Calibration

1. Set the conversion gain of the MCA to 512 channels. Turn on the x-ray spectrometer and give it about 5 minutes for the detector to cool down. Make sure the Am source is installed. If it's not, have your instructor install it.

2. Place an iron foil over the source and record the fluorescent x-ray spectrum of iron. Doing so only takes  $\approx 10$  second! The two peaks you see are the  $K_\alpha$  and  $K_\beta$  lines. Each peak is actually a blend of two lines ( $K_{\alpha 1} + K_{\alpha 2}$  and  $K_{\beta 1} + K_{\beta 2}$ ) that are much too close together to resolve.

**NOTE:** Some peaks may span two channels – say 66 and 67 – with nearly equal counts. In that case, you can improve your accuracy by assigning the peak to a fractional channel – 66.5 in this example.

- Measure the FWHM of the  $K_\alpha$  line in channels.
- Look up the energies of the  $K_\alpha$  and  $K_\beta$  lines in the x-ray data tables that are available.

**NOTE:** The energies in the x-ray data tables are in keV. The second line of each entry is intensity, but these are *very approximate* since they are measured using electron bombardment rather than x-ray fluorescence. Don't take them overly seriously, but they will indicate which lines you should expect to see (intensity values  $> 1$ ) and lines you probably won't see (intensity values  $\ll 1$ ).

- Use the energy separation between the lines to determine the FWHM in eV. This is the energy resolution of your system. **Do this calculation now, because knowing the resolution will help you figure out what you're looking at as you go along.** How does your result compare to the nominal 200 eV specified by the manufacturer?
3. Record the peak channels of the  $K_\alpha$  and  $K_\beta$  lines for Cu, Ni, and (if available) Zn. Look up the energies. The  $K_{\alpha 1}$  and  $K_{\alpha 2}$  lines will remain blended, but the two energies will start getting farther apart as the atomic number increases. Using an average  $K_{\alpha 1}/K_{\alpha 2}$  energy is appropriate. Then perform an energy-versus-channel number linear regression to get a preliminary calibration equation. **Do this now.**
4. Record the spectra of Zr, Mo, and Rh. As you start getting to heavier elements, you'll find that there are weak, spurious peaks in your spectra due to the reflection of Np x-rays from the source. Use your preliminary calibration equation and the looked-up energies for these elements to positively identify the real peaks. Now, with 6 more peaks and 6 more energies, re-do the calibration with all the data you have to this point. Do this **now**, before continuing

with the experiment, since you'll want to determine energies as you go along. Your data points should fall *perfectly* along a straight line. Even the slightest deviation indicates that you incorrectly measured a point or used the wrong energy.

### Moseley's law

Appendix A describes Moseley's law for x-rays. Use your  $K_{\alpha}$  x-rays to test Moseley's law by fitting  $E^{1/2}$  to  $a(Z-b)$ . How do  $a$  and  $b$  compare to the values predicted by Moseley's law? Be sure to use a program that will give you *uncertainties* in your fitting parameters (Graphical Analysis, Matlab, Python, etc.). **Do this at the end of lab, if there's time, or later so as to finish the experiment in one day.**

### Other samples

**Caution:** As noted above, heavier elements tend to reflect some x-rays from the source, and this can be confusing. However, the reflections tend to be *broad*, noisy peaks between roughly 10 keV and 25 keV. Notice the widths of the lines you've been measuring. You should continue looking for lines with similar, fairly narrow widths while ignoring lines that are much broader.

As you take data, use your calibration equation to immediately turn channels into energies and try to figure out what you're looking at. (You may want to put the calibration equation onto the computer or your calculator so that you can easily and quickly use it.) You're unlikely to get good results if you simply collect spectra without thinking about what they are, hoping to analyze them all later.

1. Record the x-ray spectrum for tin (Sn). This spectrum is a little more complex than those you've seen so far. Make sure you can identify **every peak**.
2. Record the x-ray spectrum of lead.
  - Why is the lead spectrum very different from the other spectra? Explain.
  - Try to identify *every peak* in the lead spectrum. There are a lot. Some are easy to identify, others take more effort to understand the energy-level structure of lead and require using data tables. Since most of this lab is pretty easy, a substantial part of the lab grading will be based on how much effort you've made to understand the lead spectrum.
3. Brass and stainless steel are alloys, made from more than one element. Record the x-ray spectra of brass and stainless steel, then figure out what they're made from.
4. Find out what "galvanized steel" is.

5. You have two “unknowns,” labeled K1 and K2. The unknowns are thin foils sandwiched in mylar. It’s the mylar you’re seeing, so visual appearances don’t tell you anything about K1 and K2. Identify K1 and K2 from their x-ray spectra. Both will require you to distinguish real peaks from background, so see the Caution above.

### Other samples

One of the major uses of x-ray spectroscopy is to determine the elemental composition of samples. The x-ray spectrometers on Mars help identify the composition of rocks. Study the composition of at least 3 samples of your choosing. Feel free to do more than 3 since taking spectra is quick and easy. Note the following:

- The lower atomic limit of the spectrometer is sulfur ( $Z = 16$ ), a limit set by the transmission of the beryllium window. Don’t expect to see any signal from plastic (hydrocarbons), glass, or other materials made entirely of low- $Z$  elements.
- The sample box contains a variety of rocks, shells, and other samples that you can use. Or you can bring your own. Note that very small samples will not fit over the source – nor should you try, since they could fall through and break the window.
- As noted above, some samples seem to reflect Np (atomic #93) x-rays from the source back into the detector. **If you see rather broad peaks in the range roughly 10–25 keV, these are likely Np peaks.** Your identifications can be grossly incorrect if you’re not aware of this.
- Many interesting samples consist mostly of low- $Z$  elements with just a very small percent of heavier elements – although it may be the heavier elements that make the sample interesting. Because the heavier elements are now much less concentrated than in the pure element metals you’ve been observing, the photon count rate will be *much less* and you’ll need to be patient while waiting long enough – up to 10 minutes or more – to get a good spectrum.
- Full credit for this part of the experiment requires more than simply recording spectra. You must (1) find interesting objects to study, (2) analyze the spectra carefully, including weak lines, to determine the elemental composition, and (3) draw conclusions.

### Report

The procedure steps have already indicated the major items that should be included in your report. Ingenuity in finding samples to analyze will be rewarded.

## Appendix A: Moseley's Law

W. Moseley was the first to show that the energy of atomic x-rays varies systematically with atomic number  $Z$  according to the law

$$E(K_\alpha) = C^2 (Z - S)^2 \quad (1)$$

where  $E(K_\alpha)$  is the energy (in keV) of the  $K_\alpha$  x-ray of the element with atomic number  $Z$ .

According to the Bohr model, the energy of an electron in state  $n$  of a hydrogenic ion with atomic number  $Z$  is given by

$$E_n = -13.6 Z^2/n^2 \text{ eV} = -0.0136 Z^2/n^2 \text{ keV} \quad (2)$$

A  $K_\alpha$  x-ray is emitted in a  $2 \rightarrow 1$  transition, so the x-ray photon energy is

$$E(K_\alpha) = E_2 - E_1 = 0.0136 Z^2(1 - 1/4) \text{ keV} = 0.0102 Z^2 \text{ keV} \quad (3)$$

Equation 3 must be modified for a multi-electron atom. A  $K_\alpha$  x-ray occurs when there is a 1s vacancy, but a multi-electron atom has a second 1s electron. The electron remaining in the 1s shell tends to screen (i.e., reduce) the nuclear charge seen by electrons in the higher shells. This results in an *effective nuclear charge*  $Z - S$ , where  $S$  is a constant. Although all the other electrons contribute to the screening, the electron remaining in the K-shell will make the largest contribution and thus we expect  $S$  to be *roughly* 1. Hence the  $K_\alpha$  x-ray energy becomes

$$E(K_\alpha) = E_2 - E_1 = C^2 (Z - S)^2 \text{ keV} \quad (4)$$

Taking the square root of both sides gives

$$[E(K_\alpha)]^{1/2} = 0.101 (Z - S) \quad (5)$$

where Moseley's theory predicts  $C = 0.101 \text{ keV}^{1/2}$  and  $S$  is *roughly* 1. (The actual value of  $S$  tells you how much the nuclear charge is screened by inner electrons.) A plot of  $[E(K_\alpha)]^{1/2}$  as a function of  $Z$ , with  $E$  in keV, will allow you to determine  $C$  and  $S$  experimentally.