X-RAY FLUORESCENCE

George Brown
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LABORATORY OBJECTIVES

The objective of this laboratory is to understand the phenomenon of x-ray fluorescence, and to understand methods of generating and detecting x-rays.

INTRODUCTION

Fluorescence is the general property of atoms and molecules to emit light subsequent to excitation by light, by electrons, or by other projectiles. Fluorescence is commonly observed at visible wavelengths; it is the workhorse of fluorescent light bulbs. It is also a common property of atoms at x-ray wavelengths.

Moseley was able to subject 21 elements to an x-ray beam, creating single K-shell vacancies, and study the fluorescence resulting from the transition of an L-shell electron into the K vacancy. An amazing regularity was discovered, which settled once and for all the atomic number assignments of the elements.[1] Sadly, Moseley was killed in the collective madness known as World War I, vividly described in a book by Paul Fussel.[2]

X-ray fluorescence is a common and powerful analytical technique for measuring impurity concentrations in materials.

PHYSICS

Both fast electrons and x-rays can create inner atomic vacancies in atoms. (Fast electrons may also create x-rays by colliding with the nuclei of atoms, resulting in continuum x-radiation, known as *bremsstrahlung* or braking radiation). The correspondence between the x-ray notation for the inner shells, and the atomic spectroscopic notation, is given below. We include the binding energies for metallic copper, for reference.

K	1s	8978.9 eV
L_I	2s	1096.9 eV
L_{II}	$2p_{1/2}$	951.0 eV
L_{III}	$2p_{3/2}$	931.1 eV
M_I	3s	119.8 eV
M_{II}	$3p_{1/2}$	73.6 eV
M_{III}	$3p_{3/2}$	73.6 eV
M_{IV}	$3d_{3/2}$	1.6 eV
M_V	$3d_{5/2}$	1.6 eV

Table 1. The binding energies of electrons for metallic copper.

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[1] H. G. J. Moseley, *Phil. Mag*. **26,** 1024 (1913) and **27**, 703, (1914).

[2] Paul Fussel, **The Great War and Modern Memory**.

Furthermore, there is a notation for the transitions allowed for filling a K-vacancy. In the following table, we give the energies for the strongest K-vacancy transitions in metallic copper, which are computed from the level diagram above:

$K\alpha_2$	$2p_{1/2}\rightarrow 1s$	8027.9 eV
$K\alpha_1$	$2p_{3/2}\rightarrow 1s$	8047.8 eV
$K\beta_1$	$3p_{1/2}\rightarrow 1s$	8905.3 eV

Table 2. K-shell X-ray fluorescence lines from metallic copper

You may ask, what happens when the incident projectile ejects an L or shallower electron? From the tables above for metallic copper, one sees that the resulting vacancy will be filled by even shallower lines, accompanied by the emission of x-rays with energy of order 1,000 eV or less. However, since photons with energies between about 3 eV and 3,000 eV are readily absorbed by materials, including air, observing them requires emitters and detectors in a vacuum. The lower energy end of this range is accordingly called the vacuum ultraviolet (VUV), and the upper end of the range is called the soft x-ray range.

For heavier elements, such as lead, L-vacancies lead to transitions in the x-ray region. The nomenclature for most x-ray transitions is shown in the table below.

		VACANCY→	K	L_1	L_2	L_3	M_5
			1s	2s	$2p_{1/2}$	$2p_{3/2}$	$3d_{5/2}$
DONOR							
L_1	2s						
L_2	$2p_{1/2}$		$K\alpha_2$				
L_3	$2p_{3/2}$		$K\alpha_1$				
M_1	3s					L*l*	
M_2	$3p_{1/2}$		$K\beta_3$				
M_3	$3p_{3/2}$		$K\beta_1$				
M_4	$3d_{3/2}$				$L\beta_1$	$L\alpha_2$	
M_5	$3d_{5/2}$					$L\alpha_1$	
N_1	4s						
N_2	$4p_{1/2}$		$K\beta_2$				
N_3	$4p_{3/2}$		$K\beta_2$				
N_4	$4d_{3/2}$				$L\gamma_1$		
N_5	$4d_{5/2}$				$L\beta_2$		
N_6	$4f_{5/2}$						
N_7	$4f_{7/2}$						$M\ \alpha_1$

Table 3. Nomenclature for X-ray fluorescence transitions.

The strongest x-ray emission lines resulting from the bombardment of a material with energetic x-rays or electrons are the Kα_1 and Kα_2 lines, which are so close together that they can only be resolved with a crystal analyzer. If we suppose that the K and L energies are approximated with an atomic hydrogen model with energies $E_n = -R_y Z_{eff}^2 / n^2$, we get

$$\begin{aligned} &E_K = -R_y(Z-\sigma_K)^2 \quad E_L = -\frac{1}{4}R_y(Z-\sigma_K)^2 \\ &E_L - E_K \approx \frac{3}{4}A(Z-\sigma_K)^2 \end{aligned} \tag{1}$$

Where we have introduced the empirical parameters A and σ to account for the screening. The result gives a surprisingly good fit to the data.

EXPERIMENTAL METHOD

In our experiment, continuum bremsstrahlung x-rays are generated by bombarding a tungsten anode with electrons in vacuum. The resulting x-rays then emerge through a beryllium window into air, and proceed to excite target atoms of our choice.

The detector is a single crystal of highly purified silicon (sometimes called intrinsic silicon) which has a high voltage impressed across it. An incident x-ray deposits all of its energy in the crystal, resulting in a pulse whose integrated charge is proportional to the x-ray energy. The pulse is registered by a multichannel analyzer, which records the distribution of pulse amplitudes.

PROCEDURE

For at least six known samples record either the K or L emission spectra. It is best to run the x-ray generator a few keV above the K or L line of interest. You may calibrate the multichannel analyzer for each run by noting where the bremsstrahlung emission line cuts off.

For at least three unknown samples, record the K or L emission spectra.

ANALYSIS

1. Compare the observed x-ray lines of the known samples with the tabulated values.

2. Identify three unknown samples, using the fluorescence lines

FURTHER QUESTIONS

1. Plot the K-shell energies taken from the tables for all of the elements for $Z > 1$ as a function of Z, and fit to the function $E(Z)=A(Z-\sigma)^2$. Is it a reasonable fit? Determine the constant A and the effective screening charge σ. Interpret your results.

REFERENCES

1. The Lawrence Berkeley National Laboratory x-ray data booklet, http://xdb.lbl.gov
2. **Handbook of Chemistry and Physics**. CRC Publishing Company.
3. J. A. Bearden, *Rev. Mod. Phys.* 39, 78 (1967).