X-ray production in the TEM

Lecture 18
What is an x-ray?

X-rays are electromagnetic radiation

- Can be considered as either photons or waves

Wavelengths between 100 nm (“soft”) and 100 pm (“hard”)

Like all photons:

\[ \lambda = \frac{hc}{eE} \]

\( \lambda \) = wavelength
\( h \) = Planck’s constant
\( c \) = speed of light
\( e \) = electron charge
\( E \) = energy
Bremsstrahlung X-ray emission

“Braking” radiation

Electron is decelerated by Coulomb (charge) field of the nucleus

Electromagnetic radiation (x-ray) is emitted

Can have any energy less than the incident energy
Bremsstrahlung X-ray emission

Resulting x-ray emission is forward peaked

- As incident electron energy goes up, the x-ray emission is more strongly forward peaked.

Angular distribution of Bremsstrahlung scatter
Bremsstrahlung X-ray emission

Results in a continuous background signal in an intensity vs. energy spectrum

Extends from low energies to up to the incident beam energy
Bremsstrahlung X-ray emission

Why do we care?

1. Forms a background signal under the signal of interest
   - Once a photon is created with a given energy, we cannot know what caused it
     - In other words, did the count in our spectrometer at a given energy come from a bremsstrahlung x-ray or a characteristic x-ray
   - Generally, this is nuisance in x-ray spectroscopy

2. But, carries information about the atomic number of the specimen
   - Can be useful in biological analyses
Reminder: quantum numbers

Atom composed of positively charged nucleus, surrounded by electrons

Each electrons has a given energy
- Described by quantum numbers
- These are the eigen-solutions to the Schrödinger Equation:
  \[ n = 1, 2, 3, \ldots \]
  \[ l = 0, 1, 2, \ldots, n-1 \]
  \[ j = l + s, \quad \text{where} \quad s = \pm \frac{1}{2} \]
  \[ m_j \leq |j| \]

Electrons subject to Pauli’s Exclusion Principle:
- No two electrons can have the exact same set of quantum numbers (and thus same energy)
Inner shell ionization

Incident electron imparts sufficient energy to an electron in an atom to remove it from its “shell”

Atom is left in an excited state

Atom relaxes to ground state through a limited set of transitions

http://www.matter.org.uk/tem/electron_atom_interaction/x-ray_and_auger.htm
Characteristic X-rays

One such transition is:

1. Incident electron ionizes atom
2. Electron from outer shell fills the hole left in the inner shell
3. Results in the emission of an x-ray

Importantly, the energy of the resultant x-ray is characteristic of the atom

- Energy levels are specific to each atom
- Thus difference between energy levels is also
Characteristic X-rays

Nomenclature used is ‘spectroscopic’

- K shell $\Theta \ n = 1$
- L shell $\Theta \ n = 2$
- M shell $\Theta \ n = 3$
- N shell $\Theta \ n = 4$
## Shells and Subshells of Atoms

<table>
<thead>
<tr>
<th>X-ray notation</th>
<th>Quantum numbers</th>
<th>Maximum electron population</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$n$</td>
<td>$l$</td>
</tr>
<tr>
<td>$K$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$L_{I}$</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>$L_{II}$</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>$L_{III}$</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>$M_{I}$</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>$M_{II}$</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>$M_{III}$</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>$M_{IV}$</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>$M_{V}$</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>$N_{I}$</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>$N_{II}$</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>$N_{III}$</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>$N_{IV}$</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$N_{V}$</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$N_{VI}$</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>$N_{VII}$</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>
Characteristic X-rays

X-rays, as EM radiation can be considered as either waves or photons.

Energy related to wavelength:

\[ E = h\nu = \frac{hc}{\lambda} \]

Each transition has a specific energy & wavelength associated with it \((E_K, E_L, E_M)\)

\[ E_K, E_L, E_M < E_c \]
Characteristic X-rays
Auger electron emission

Incident electron removes inner shell electron

Outer shell electron fills empty hole

Instead of x-ray emission, an electron from a higher shell is ejected

These electrons have a characteristic energy

- $E_C - E_{L2,3}$ in this case
- Favored in light atoms

Most Auger electrons are absorbed by the lattice

- Only those at the surface escape
- Auger spectroscopy (AES) requires UHV
"Coster-Kronig" transition

- Transitions of electrons from a higher states in a sub-shell to vacancies in a lower sub-shell
- Energy transferred to an electron near the Fermi Level
- Can be important when considering fluorescence quantitatively (SEM)
Characteristic X-rays

Ionization requires a critical energy $E_C$

- K shell ionization energy > L shell > M shell …
- Varies with element (makes sense!)
- Note: ionization energy does not equal energy of the emitted x-ray

Can describe a cross-section (probability that ionization will occur)

- Mathematical form not of interest here
- Two useful outcomes
  - The electron that caused the ionization undergoes a small angular deviation
  - The resultant characteristic x-ray is emitted uniformly over $4\pi$ steradian

### Critical Ionization Energies for Platinum

<table>
<thead>
<tr>
<th>Shell</th>
<th>Critical ionization energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>78.39</td>
</tr>
<tr>
<td>$L_1$</td>
<td>13.88</td>
</tr>
<tr>
<td>$L_{II}$</td>
<td>13.27</td>
</tr>
<tr>
<td>$L_{III}$</td>
<td>11.56</td>
</tr>
<tr>
<td>$M_1$</td>
<td>3.296</td>
</tr>
<tr>
<td>$M_{II}$</td>
<td>3.026</td>
</tr>
<tr>
<td>$M_{III}$</td>
<td>2.645</td>
</tr>
<tr>
<td>$M_{IV}$</td>
<td>2.202</td>
</tr>
<tr>
<td>$M_V$</td>
<td>2.122</td>
</tr>
</tbody>
</table>
Fluorescence yield

Partitioning between x-ray emission and Auger electron emission varies by element

Mathematically:

\[ \omega + a = 1 \]
Fluorescence yield

Strong atomic # dependence:

- One C $K_{\alpha}$ X-ray generated per 1000 ionization events
- One Ge $K_{\alpha}$ X-ray generated per 2 ionization events
You are only likely to see the $\alpha$ & $\beta$ lines of a given family
  - Unless you have very good signal and take a long acquisition

Note, you cannot compare across families
  - Relative probabilities between K, L, M & N vary with element

### Fluorescence yield

#### Approximate probability of occurrence

<table>
<thead>
<tr>
<th></th>
<th>$K_\alpha$</th>
<th>$K_\beta$</th>
<th>$L_\alpha, L_\beta$</th>
<th>$L_\gamma$</th>
<th>$L_\alpha, L_\gamma$</th>
<th>$L_\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_\alpha$</td>
<td>1</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L_\alpha, L_\beta$</td>
<td>1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.08</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>$M_\alpha$</td>
<td>1</td>
<td>0.6</td>
<td>0.05</td>
<td>0.08</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>
Characteristic X-rays
**Characteristic X-ray Energy**

**Moseley’s Law:**

\[
\lambda = \frac{B}{(Z - C)^2}
\]

B & C are element specific constants