

#### **4. Inelastic Scattering**

##### **Some inelastic scattering processes**

A vast range of inelastic scattering processes can occur during illumination of a specimen with a high-energy electron beam. In principle, many of these do occur all the time, but their impact on our data collection, whether beneficial, deleterious, or insignificant is also widely varied. As stated in the previous chapter, TEM diffraction and imaging mostly rely on elastically scattered electrons. But inelastic scattering gives rise to a broader range of signals that we can potentially make use of to better characterize our material. The main categories of these processes and some examples are listed below:

1) Collective excitations: The transfer of energy from the beam to the sample, or even vice-versa, implies the generation or exchange of some type of excitation; a perturbation in the organization of constituent particles that make up a solid. When a single mode of excitation is involved, it can usually be identified as a discrete particle, in the quantum-mechanical sense. For example, a pure mode of oscillation in the electric field surrounding free electrons in a conductor is referred to as a “plasmon”. A small-amplitude vibration in the rigid lattice of a crystal can be identified as a “phonon”. The emission or absorption of these excitations in a material is sometimes detectable by slight shifts in energy or direction of the scattered beam, then related back to specimen properties.

2) X-ray emission: The detection of characteristic X rays emitted from materials during illumination with other X rays or high-energy electrons is one of the most popular and convenient ways to determine their composition. This occurs due to ionization of the specimen, followed by equilibration. X rays are also generated during illumination by high-energy electrons as a result of their acceleration called bremsstrahlung, or braking radiation.

3) Secondary-electron generation: Illumination of nearly any material with high-energy electrons ejects loosely bound electrons from the surface of the material into the vacuum. Many of these secondary electrons can be released for a single incident electron. Depending on their energies, they can be classified as either slow (< 50 eV) or fast (> 50 eV), and the abundant slow secondary electrons give the main contribution to most scanning electron microscopy images.

Instead of characteristic X-ray emission, ionization can also result on Auger electron emission. These electrons carry information about the valence electronic structure of materials. But their low yield make them difficult to detect usually requiring ultra-high vacuum conditions, and other stringent requirements make the Auger electron spectroscopy technique challenging.

4) Electron-hole-pair generation: Semiconductors are distinguished by an energy gap, which allows separate populations of electrons to coexist in different energy “bands”. Excitation by the electron beam excites carriers into the higher energy bands, which thermalize across the energy gap by emission of light, called luminescence, or cathodoluminescence, in this case. Spectroscopic study of this light is useful for characterizing these materials, but requires special optics fitted into the TEM column to detect the small amounts of light generated.

6) Beam damage: Any form of permanent alteration of a specimen by the incident beam comprises inelastic scattering. Radiolysis is the breaking or alteration of bonds within a specimen. Knock-on damage is the displacement of atoms from their original sites within a material, such as into interstitial sites.

##### **Head-on inelastic collision in 1-D**

We found the center-of-mass speed for a collision of a relatively light (mass  $m$ ) electron moving with initial speed  $v$  towards a heavy (mass  $M$ ) atom, which is free, but at rest. Momentum conservation requires the COM speed to be the same following the collision. If the electron becomes bound to the atom

(which is then an ion) in the collision, the ion must continue in the same direction as the initial electron motion with  $v_f = v_{COM}$ . So its kinetic energy is then given by

$$E_f = \left( \frac{m}{m+M} \right) \cdot E$$

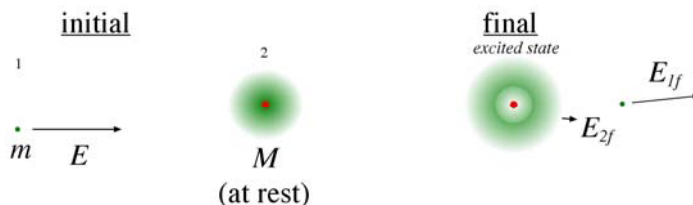
We can see that this final kinetic energy  $E_f$  is clearly less than the initial energy  $E$  (i.e.,  $E_f < E$ ), so there is no doubt that the collision is inelastic. Of course, the ion continues in the same direction as the initial electron motion. So, in a sense, the electron (which is now part of the ion) is forward scattered. This is a general quality of inelastic scattering: Compared to elastic scattering, inelastic scattering increases the probability that the incident particle is forward scattered, rather than back scattered.



### Inelastic scattering in 2-D

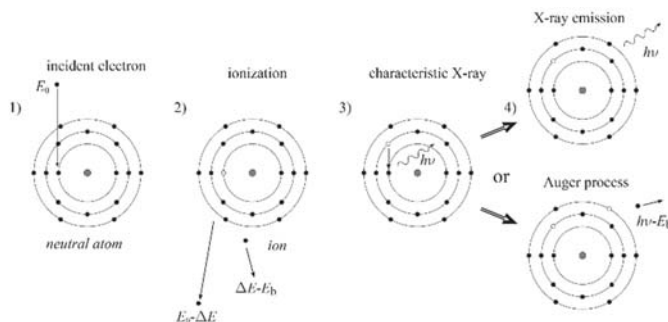
In a more realistic, 2-D inelastic scattering event, the electron may remain free after scattering, but the atom will likely end up in some excited state. This excitation takes up part of the initial kinetic energy, so  $E > E_{1f} + E_{2f}$ . Thus, the scattered electron wave will be incoherent with respect to the incident wave.

Moreover, from the previous discussion in 1-D, we can say that the scattering is likely to be in the forward direction.



### X-ray generation by ionization

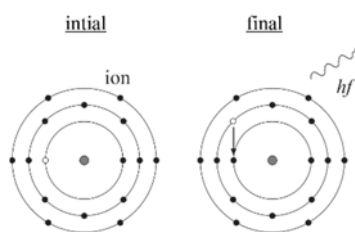
The ionization of atoms in a specimen - or even elsewhere within the TEM column - is a frequent result of electron irradiation. Given an electron beam of sufficiently high energy, it is likely that the incident beam will penetrate well into an atom and eject an orbital electrons from a core level, leaving the atom in an ionized state. The ejected electron will have received some energy from the beam, so it will escape with that energy, less the binding energy. The beam electron will have a corresponding reduction in its energy in this inelastic scattering process. Usually, these two electrons just contribute to diffuse background in an electron image and it may even be desirable to eliminate their contributions with an energy filter.



Meanwhile, an electron from a higher-energy level may fall into the vacated core level of the ion, releasing an X-ray photon. This X ray is likely to escape the specimen and can be detected to identify the element. These core transitions are relatively insensitive to the chemical environment of the atom, so characteristic X rays are very useful for elemental assay. Alternatively, the X ray could get absorbed by the specimen, ejecting a higher-energy electron, typically a valence electron. This is called an Auger process and the ejected electron is an Auger electron. Their spectra contain detailed information about chemical environments, but their detection is quite challenging, requiring ultra-high vacuum.

### Characteristic X-rays: Moseley's law

Moseley realized that the characteristic X rays energies were excellent for identifying all of the different elements on the periodic table (except H). The energies even fall into very nice patterns that indicate the proper order in which the elements should be sorted by atomic number  $Z$ . The basic trends can be explained with a simple model.



Assuming H-like energy shells, the energies of an electron state can be written:

$$E_i \approx -\frac{(Z - Z_{i,enc})^2}{n_i^2} \cdot E_R,$$

Imagining spherical orbits, we have  $Z_{i,enc}$  electrons enclosed within the orbit of a level, which screen the electric charge of the nucleus. As in the Bohr model, the principal quantum number is  $n_i$  and the energy  $E_R = 13.6$  eV is called a Rydberg. For transitions between closely spaced levels  $i$  and  $j$ , in elements with relatively large  $Z$ , we assume  $Z_{i,enc} \approx Z_{j,enc} = Z_{enc}$ . So the transition energy is:

$$h\nu \approx (Z - Z_{enc})^2 \cdot E_R \cdot \left( \frac{1}{n_i^2} - \frac{1}{n_j^2} \right)$$

Changing to X-ray wavelength ( $\lambda = c/f$ ) we sometimes see this written:

$$\lambda \approx \frac{hc}{(Z - Z_{enc})^2 \left( \frac{1}{n_i^2} - \frac{1}{n_j^2} \right) \cdot E_R} = \frac{B}{(Z - C)^2}$$

where  $B$  and  $C$  are constants. The precise transition energies and wavelengths are extensively tabulated (cf., <http://physics.nist.gov/PhysRefData/XrayTrans/Html/search.html>).

### Characteristic X rays: notation

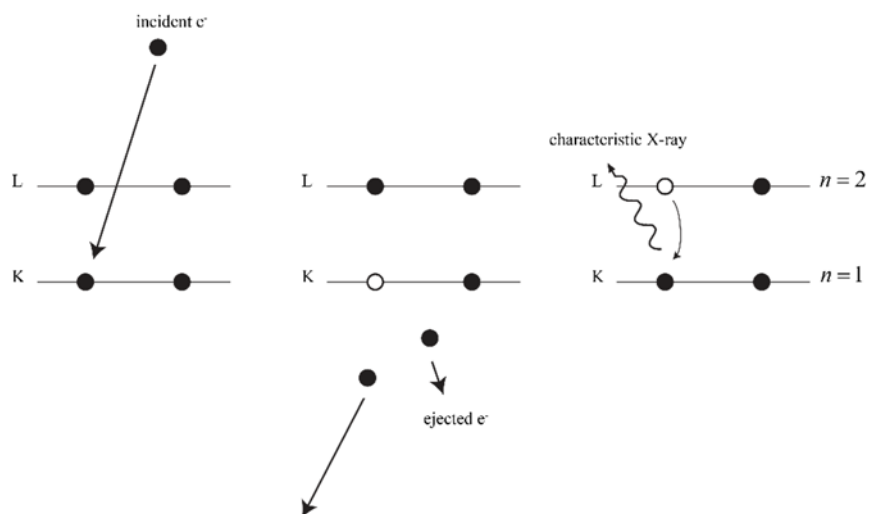
Speaking of characteristic X rays, let's look at the naming convention to distinguish the different transitions. Mathematically, core shells arise from principle quantum numbers but these have been assigned letters, as follows:

$n$	letter
1	K
2	L
3	M

The letter corresponds to the lower energy state, into which an electron falls. The number of shells the transition spans,  $\Delta n = n_j - n_i$ , is given a Greek character, which is listed after the letter above:

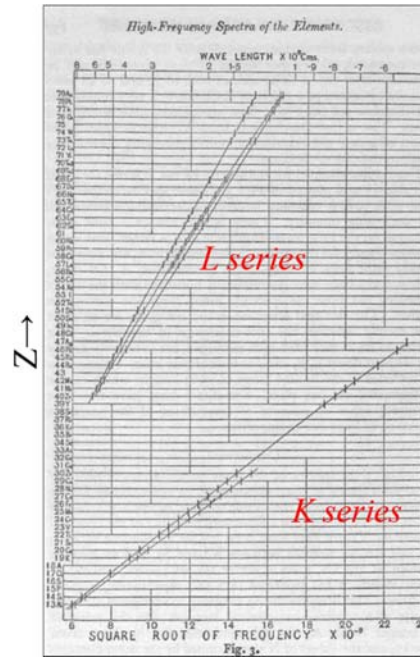
$\Delta n$	character
1	$\alpha$
2	$\beta$
3	$\gamma$

So a L→K transition emits a K $\alpha$  X ray; an M→K transition emits a K $\beta$  X ray, an M→L transition emits a K $\gamma$  X ray, and so on...



### Moseley's Law

Moseley demonstrated this trend very clearly [H. G. J. Moseley, *Phil. Mag.* (1913), p. 1024], plotting  $Z$  vs.  $\sqrt{f}$  for dozens of elements and fitting to a straight line (i.e.,  $Z \propto \sqrt{f} + C$ )



### Bremsstrahlung spectra

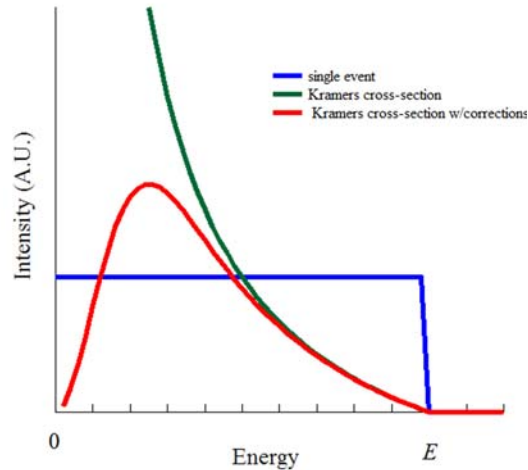
Bremsstrahlung X rays are emitted throughout the TEM column, because electrons “brake” whenever they interact with any part of the instrument or the specimen. In principle, the actual spectrum is fairly simple, as explained by Kramers. For an electron of any initial energy  $E$ , subjected to acceleration, there is an equal probability per unit energy of emission of a photon of any energy from 0 to  $E$ . That is, the number of X-rays per unit energy is a boxcar function:

$$\frac{dN}{d(h\nu)} = \begin{cases} \text{constant,} & 0 < h\nu \leq E \\ 0, & E < h\nu \end{cases}$$

After emitting an X ray, the electron’s energy has dropped, so the spectrum for a subsequent emission is shifted to a corresponding lower energy. Thus, multiple scattering events shift the spectra to lower energies, whereas the amount of braking increases with  $Z$  of the target, so that:

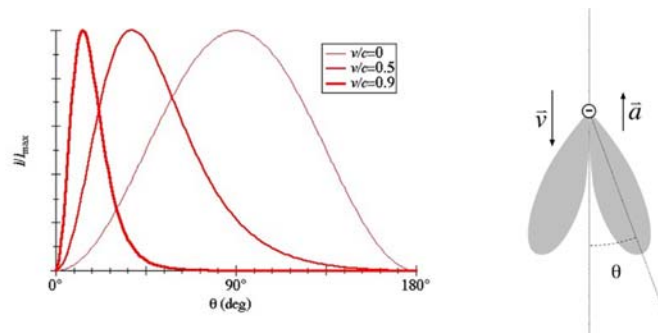
$$I(h\nu) \propto Z \cdot \left( \frac{E}{h\nu} - 1 \right)$$

This would seem to blow up at low energies, but the lower-energy X rays are more easily absorbed by matter, so the intensity instead fades to zero at low energies, leaving a maximum bump somewhere in the middle of the spectrum. In an arbitrary system, the precise shape of this spectrum depends on several factors, so, if it is not of critical interest, it is often just modeled with a simple function and subtracted off.



### Bremsstrahlung X rays: Direction of emission

Electromagnetic theory provides a very accurate description of the directions in which braking radiation is emitted. The mechanism for radiation is the acceleration of charge, and at the high energies associated with X rays (tens of KeV), we should include relativity. Although the intensity is proportional to the magnitude of the acceleration  $a$  squared, the direction is distributed in all directions, but is concentrated in a conical plume extending in the direction of the velocity  $\vec{v}$  with an interior semi-angle  $\theta$ .



### Bremsstrahlung: Angular distribution

Let's use  $\beta = v/c$  to specify the electron speed. The intensity varies with angle as

$$I(\theta) \propto \frac{a^2 \cdot \sin^2 \theta}{(1 - \beta \cdot \cos \theta)^5}$$

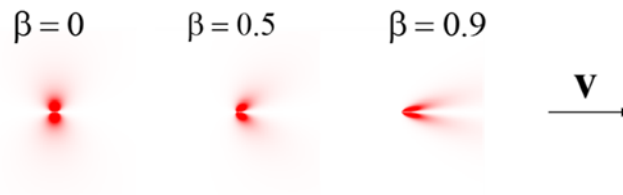
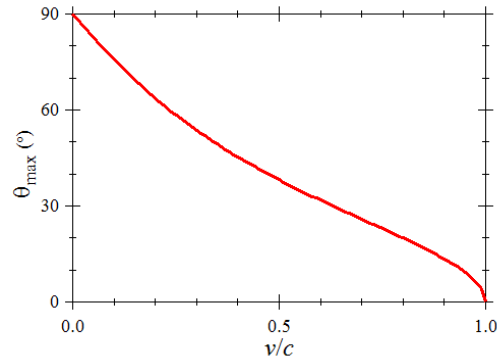
So, at what angle from the direction of motion is the maximum intensity? Take

$$\left. \frac{dI}{d\theta} \right|_{\theta_{\max}} = 0$$

We find:

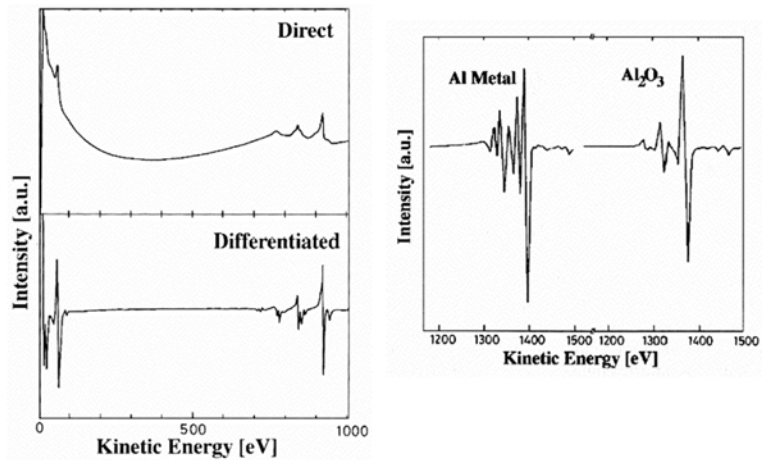
$$\theta_{\max} = \cos^{-1} \left[ \frac{1}{3\beta} (\sqrt{1 + 15\beta^2} - 1) \right]$$

The radiation becomes more concentrated in the forward direction as the velocity increases.



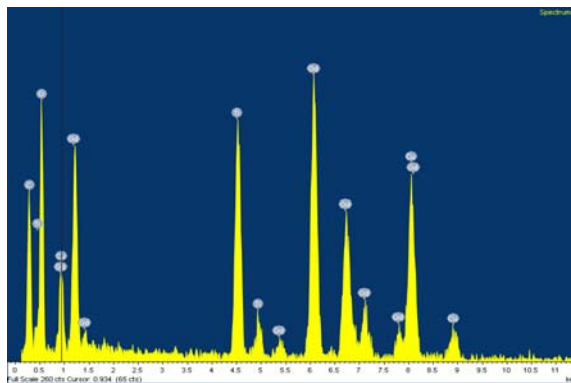
### Auger spectra

The analysis of Auger electrons requires very clean specimen surfaces and excellent vacuum conditions. The spectra do not have simple peaks from which we can read off energies and intensities. Instead, the features are usually brought out by differentiation.



### Characteristic X-ray spectra

In comparison, characteristic X-ray spectra are extremely simple. The peaks are often clearly defined and extremely sharp; their widths are almost always limited by our detection method, rather than complexities of the emission process. As stated before, the precise energies are quite well known. Even relative intensities for peaks from a single element are reasonably well known. Comparing the relative intensities among different elements is a tractable problem that will be discussed later in the course.



### Minimizing beam damage

Inelastic scattering almost always gives rise to some amount of beam damage. The question is whether that amount is tolerable. How can we minimize the damage?:

First and foremost, minimize the beam dose. The dose can be measured in various units, such as  $C/m^2$  or  $e^-/nm^2$ . We can keep track of the relative beam current using the “current density” indicator on most TEM models, then multiply by the exposure time. To minimize the dose, we should divert the beam from the region of interest when we are not acquiring data. This is often a built-in feature of TEM instruments, sometimes called “low-dose mode”, which allows the user to focus on one region, then shifts the beam to the region of interest to expose a film plate. It can be argued that scanning TEM reduces beam damage, because it acquires images in a serial, rather than parallel, fashion. So each point on the sample is only irradiated briefly during acquisition. On the other hand, the irradiation is quite intense at the scanned point, so the advantage is debatable.

In some cases, operating at a higher KV reduces specimen heating, because less beam energy is transferred to the specimen, since most of the electrons are transmitted. On the other hand, operating at lower KV reduces local damage, such as knock-on damage, which can alter the atomic structure of a specimen.

Cooling the specimen should reduce thermal effects, and also limits the desorption of volatile constituents. Coating the specimen with a conducting film, such as gold or amorphous carbon, prevents charging, by allowing a conducting path to reduce the accumulation of charge.