4

Inelastic Scattering and Beam Damage

CHAPTER PREVIEW

In the previous chapter, we discussed elastic scattering of the electron beam in which the incident electrons lost no energy as they traversed the specimen. Inelastically scattered (often termed energy-loss) electrons are equally important and we'll discuss many of these processes here, but leave the applications till later. Why are we interested in inelastic scattering? Well, such scattering generates a whole range of signals, each of which can tell us more about the chemistry of the specimen than we can find out from the elastic electrons. In addition to the energy-loss electrons themselves, the most important signals are the characteristic X-rays, secondary electrons, and, occasionally, visible light (cathodoluminescence (CL)) and so we'll emphasize how these arise. We will also tell you why all these signals are useful, to varying degrees, to materials scientists, engineers, and nanotechnologists.

So how do we use these inelastic signals? First we have to detect them and we'll describe electron detection in general in Chapter 7 and the spectrometers that disperse electrons according to their energy in Chapter 37. Then in Chapters 38–40 we'll talk about analyzing these energy-loss electrons. We will discuss how to detect X-rays in Chapter 32 and how we get quantitative, elemental information from the spectra in Chapters 33–36. In all cases we get complementary information to that gained in TEM images and DPs. We'll briefly discuss CL images and spectra in Chapter 29. Obviously there's a lot of useful information in these signals and this is a major advantage to using ionizing radiation. However, the other side of the coin is that all the inelastic processes deposit energy in your specimen, which can be damaged if it is beam sensitive. So we must also look at the downside of the inelastic processes and we end the chapter by discussing this problem under the general topic of beam damage or radiation damage.

A warning: This chapter is based on some quite difficult theoretical, physical concepts. However, these concepts form the basis of AEM, which constitutes Part 4 of the book, so we have to address the material. You can safely delay studying much of this material in detail until you reach Chapter 32 and beyond.

- What you need to get out of this chapter is an appreciation that a modern TEM is primarily a signal-generating and detecting instrument, not just a tool for producing high-magnification images.

One redeeming feature is that in all these processes we can treat the electron as a particle. So this is (almost) a wave-free chapter, which generally means that it is more easily understandable unless you have an in-depth physics background.

4.1 WHICH INELASTIC PROCESSES OCCUR IN THE TEM?

Historically, the conventional TEM used only two *elastic* signals, namely, the direct beam and the diffracted beam(s). As we've seen, these signals constitute the DP and we'll see in due course how they can be used to produce images. In operating a TEM in this classical manner we are being extraordinarily inefficient; we throw away a vast amount of information about our specimen which is contained in the signals that result from *inelastic* scatter. Some of these signals are shown back in Figure 1.3 and are often used predominantly in related instruments such as the SEM and the Auger electron spectrometer (AES), but we can also use TEMs to detect many of these signals, thus allowing for a more complete characterization of the specimen.

Because some of the incident-beam electrons lose energy, all these signals are related to the general topic of electron energy-loss spectrometry (EELS). The EELS signals and the accompanying X-ray signals constitute analytical electron microscopy (AEM), which we cover in Part 4. In seeking to detect more signals from the specimen, we find that practically we cannot do everything at once, nor can we do it all with equal efficiency. Nevertheless, various kinds of analytical TEMs exist which, in one form or another, can detect all the signals shown in Figure 1.3. With the advent of aberration correction, the spatial resolution and the detection limits of the various techniques have reached or closely approach the single-atom level and so are very well suited to the characterization of nanostructured materials.

In this chapter we'll cover all the signals that are detectable and what use (if any) they are to the nanotechnologist. We need to know

- What are the inelastic-scattering interactions?
- What is the range of energy losses associated with each process?
- What is the likelihood that each energy-loss process will occur?
- What is the scattering angle for the various energy-loss electrons?

When a high-energy electron encounters an atom, it first penetrates the outer, loosely bound electron cloud, then it passes the more tightly bound inner (or core) shell electrons, and finally it may encounter the nucleus.

RULE OF THUMB

The deeper the electron penetrates into the atom, the greater the energy that may be lost. It is possible (but very rare) for the electron to lose all its energy in a single nuclear interaction.

This range of inelastic scattering produces a range of scattering angles, but there is no simple relationship between the energy lost and the scattering angle. We'll separate the inelastic processes into three components

- Processes that generate X-rays
- Processes that generate other (secondary) electrons
- Processes that result from collective interactions with many atoms or electrons

We know the first two rather well, but the third is usually poorly defined. Figure 4.1 shows the cross sections for the most important inelastic processes that we'll talk about. As you can see, the elastic and one of the inelastic (plasmon excitation) processes are by far the most likely events and together account for almost all of the *total scattering cross section* that we discussed back in Chapter 2 (with the caveat that the data in this figure are for small-angle scattering only). These cross sections vary over several orders of magnitude and this fact alone should give you some feel for the relative generation probability of each signal. We'll discuss the specific cross sections for inelastic scattering in more detail as we describe each individual scattering event.

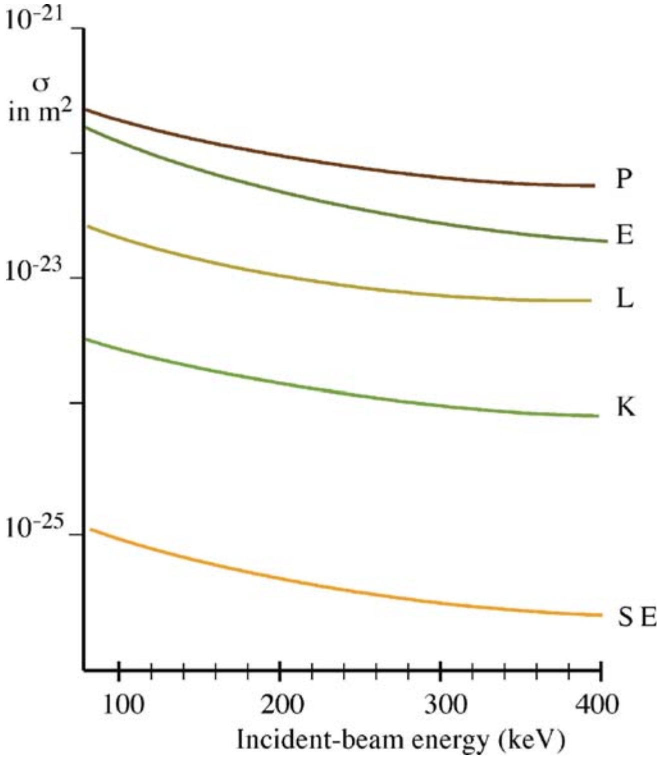

FIGURE 4.1. Cross sections for the various inelastic scattering processes in Al as a function of the incident electron energy, assuming a small angle of scattering ($\theta \sim 0°$); plasmon (P), K- and L-shell ionization (K,L), secondary-electron generation (SE). For comparison purposes the elastic cross section (E) is also included. The values are relatively insensitive to the beam energy.

We'll see throughout the book that energy-loss processes are both useful and damaging. For example, in Chapter 19 we describe how energy-loss electrons cause Kikuchi lines to arise in DPs and these are extraordinarily useful. In contrast, some of those same energy-loss electrons cause diffuse scatter that lowers the signal to background information in all DPs and images. If your specimen is thick enough, the energy-loss electrons hide all the useful contrast information, but we'll see in Part 4 how to use EELS to filter out those electrons from images and DPs. This filtering improves the quality of both image and DP and allows the study of much thicker specimens.

4.2 X-RAY EMISSION

We'll consider X-ray emission first because it's the most important secondary signal generated in the specimen. From X-rays we can quickly find out what elements constitute the part of the specimen interacting with the electron beam and we can also quantify the amount of each element in quite a straightforward manner. (The way to do all of this is described in Part 4.) Two kinds of X-rays are produced

- Characteristic X-rays; we'll see these are very useful for local elemental analysis of nano-structured materials and crystal defects.
- Bremsstrahlung X-rays, which are useful to the biologist, but generally regarded as a nuisance by most materials scientists (nano or otherwise).

4.2.A Characteristic X-rays

How do we produce characteristic X-rays and of what are they 'characteristic'? First of all, a high-energy beam electron must penetrate through the outer conduction/valence bands and interact with the inner-shell (or core) electrons. If more than a critical amount of energy is transferred to an inner-shell electron, that electron is ejected; i.e., it escapes the attractive field of the nucleus, leaving a hole in the inner shell. In an isolated atom, the electron is ejected into the vacuum while in a solid it escapes above the Fermi level into the unfilled states. The atom is then left in an excited state because it has more energy than it would like, and we describe it as ionized.

The ionized atom can return almost to its lowest energy (ground state) by filling in the hole with an electron from an outer shell. This transition is accompanied by the emission of either an X-ray or an Auger electron. This latter process was first described by Auger (1925) and won him the Nobel Prize for Physics. (Since the discoverer was French, we pronounce his name "Ozhay" with a soft *g* as in beige.) In both the X-ray and Auger cases, the energy of the emission is *characteristic* of the difference in energy between the two electron shells involved and this energy difference is unique to the atom. The process of X-ray emission is shown schematically in Figure 4.2. We'll cover Auger emission in Section 4.3.B

Note that characteristic X-rays can also be produced if an atom is ionized by a process other than electron irradiation. For example, ionization can occur as a result of X-ray bombardment also, in which case we use the term fluorescence. It is customary *not* to refer to electron-induced X-ray emission as fluorescence, although you may occasionally come across such usage in the literature.

We've been able to detect X-rays in electron microscopes for many years, but Auger electron detection is rather specialized and usually carried out in a dedicated AES. More recently, however, we've found ways to detect the Auger signal in ultrahigh vacuum (UHV) TEMs and so we'll discuss this in Section 4.3.B below.

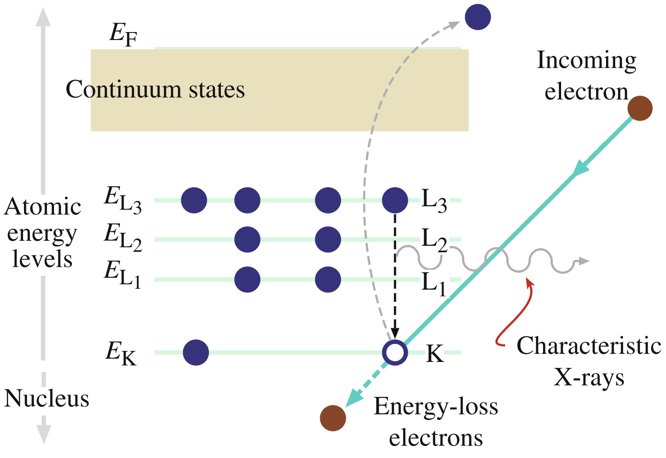

FIGURE 4.2. The ionization process. An inner (K) shell electron is ejected from the atom by a high-energy electron. When the hole in the K shell is filled by an electron from the L shell, characteristic (K_α) X-ray emission occurs. The beam electron loses energy but continues on through the specimen.

You need to know several aspects of the ionization process to understand why the characteristic X-rays are so useful and what it takes to generate them

- What are *electron shells*?
- Why do we use the terms X-ray *lines, families, and weights*?
- What is the *critical ionization energy* and the *ionization cross section*?
- What controls the *X-ray energy* and *wavelength*?
- What is the *fluorescence yield*?

Electron shells: We use a specific terminology to identify the different characteristic X-rays. To understand the terminology you must be familiar with the simple Bohr theory of atomic structure in which the electrons are circling the nucleus in specific shells. (The electrons stay in their shells rather than spiral into the nucleus because of the constraints imposed by quantum theory.)

> *Aside*: For historical reasons, the innermost electron shell is called the K shell and the next innermost is the L shell, the next the M, and so on, as used in Figure 4.2. All the shells (except the K shell) may themselves have subshells (e.g., L_1, L_2, etc.). We name the characteristic X-rays in terms of the shell being filled and the shell from which the electron comes. (The K, L, M, etc., terminology was first introduced by Charles Barkla, an early X-ray spectroscopist and has nothing to do with Royal

Dutch Airlines. The reason Barkla chose K as the first shell may have been because he wasn't sure if he'd need a J shell but knew he'd need an L shell!)

Remember that the difference between the two shell energies equals the energy of the characteristic X-ray. Thus, if we fill a K-shell hole from the L shell we get a K_α X-ray, but if we fill it from the M shell we get a K_β X-ray. If the hole is in the L shell and we fill it from the M shell we get an L_α X-ray, and if we fill it from the N shell we get an L_β X-ray. The notation is in fact much more complex because we differentiate the α X-rays in terms of α_1 and α_2 depending on which subshell of the outer shell the electron falls from to fill the hole. The α_1 X-ray is from the outermost subshell (e.g., the L_{III} or M_V), the α_2 from the next innermost (the L_{II} or M_{IV}). To make this a bit clearer you can look at the diagram in Figure 4.3, although it may in fact confuse you more since it's not at all obvious why, with all these possible electron transitions, only a small fraction generates sufficient X-rays for us to use. Suffice it to say that X-ray physics is an arcane discipline. Fortunately, for X-ray detection in the TEM

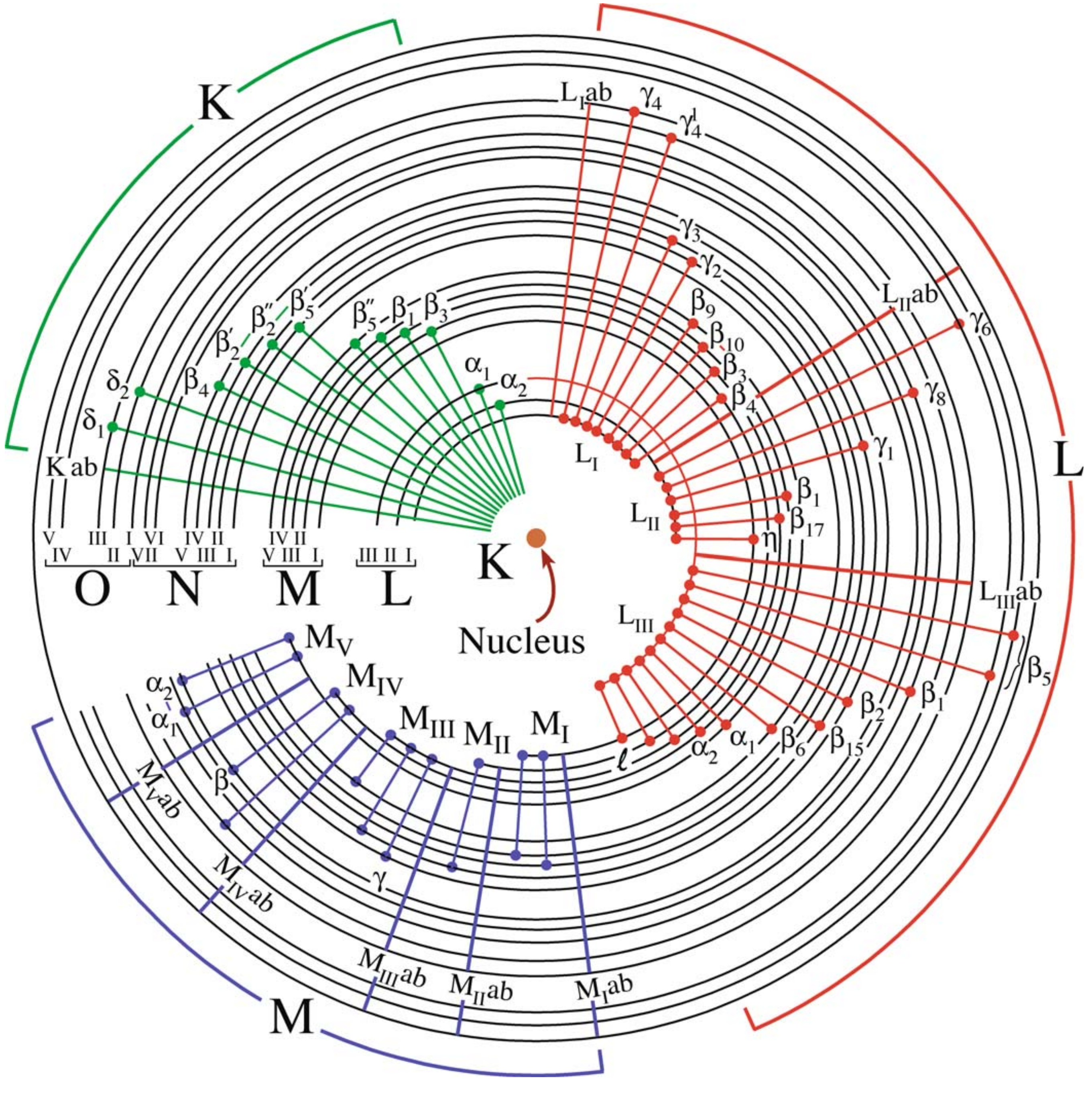

FIGURE 4.3. The complete range of possible electron transitions that give rise to K, L, and M characteristic X-rays. Not all these X-rays are detectable by the XEDS in the TEM.

you don't need to worry about such details because, as you'll see later, the detectors we use can't usually discriminate between the X-rays from different subshells, except at the highest X-ray energies, so K, L, and M and α and β are about all you'll need to remember.

X-ray lines, families, and weights: Often we refer to specific characteristic X-rays as 'lines' because they originally appeared as lines on photographic plates from early spectrometers. Each characteristic X-ray line has a specific wavelength or energy. Groups of lines that arise from transitions to a specific K, L, or M shell are often called 'families.' Much more detail can be found in books on X-rays and X-ray spectrometry, and we'll tell you more in Chapter 34.

Not all electron transitions are equally probable (think of those cross sections again) and this is taken into account by the different 'weights' (i.e., relative intensity compared with the most intense line) of the X-ray lines that are given in Table 4.1. These weights are only important within a given K, L, or M family and do not relate families (e.g., K to L), because experimental conditions affect X-ray generation in each family differently. In X-ray analysis in the TEM we only use the most intense lines, usually the α lines (or, if the spectrometer can't resolve them, both α and β lines). This will become more obvious when you've learned about X-ray qualitative analysis in Chapter 34.

K,L,M,. . .

A family is a group of X-ray lines and each member of the family has a different relative intensity, which unfortunately is called its weight.

Critical ionization energy: The electron beam has to transfer an amount of energy greater than a certain value to the inner-shell electron in order to ionize the atom. This energy is called the critical ionization energy (E_c). If we want to generate a useful number of X-rays, then the beam energy E_0 must be significantly greater than E_c. The value of E_c increases as the electrons are more tightly bound to the nucleus so, for a given element, the innermost shell (K) has a higher E_c than the next (L) shell, and so on. Atoms with higher Z have more protons binding the core electrons to the nucleus and, therefore, have a higher E_c. You can see this effect if you go and look at an X-ray spectrum, e.g., in Figure 1.4A (or one of many others throughout Part 4) in which the energy of the X-ray peaks increases with increasing atomic number. Since there's a lot of shells and a lot of atoms, the list of critical ionization energies is long, as you'll find out if you consult any X-ray textbook. A similar list is also invaluable in EELS since the E_c obviously corresponds to a critical amount of energy lost by a beam electron and thus gives rise to peaks (usually called edges) in the energy-loss spectrum. As we'll see in Chapter 39, EELS edges, like characteristic X-ray peaks, can also be used to identify uniquely the presence of a particular element in the specimen.

TABLE 4.1 Relative Weights of X-ray Lines

K_{α} (1)	K_{β} (0.1)		
$L_{\alpha1,2}$ (1)	$L_{\beta1}$ (0.7)	$L_{\beta2}$ (0.2)	$L_{\gamma1}$ (0.08)
	$L_{\gamma3}$ (0.03)	L_{l} (0.04)	L_{η} (0.01)
M_{α} (1)	M_{β} (0.6)	M_{ζ} (0.06)	M_{γ} (0.05)
	$M_{II}N_{IV}$ (0.01)		

The cross section for ionization (σ): It is shown in Figure 4.1 for K- and L-shell electrons. It is not a strong function of energy and has a relatively large value, and so we expect to see X-rays generated in all TEMs. In low-voltage SEMs we have to worry about another parameter called the overvoltage, U, which is the ratio of the beam energy E_0 to the ionization energy E_c. The cross section varies with U as shown in Figure 4.4. What this figure tells you is that if E_0 is close to E_c then there isn't much chance of ionization occurring. However, in the TEM E_0 is $\geq$ 100 keV and E_c is generally $<$ 20 keV so U is usually $>$ 5. Therefore, X-ray generation is expected and the cross section is pretty constant with energy. Despite this relatively simple behavior, there is considerable uncertainty about the absolute value of the ionization cross sections because few reliable experimental measurements have been made at TEM voltages. Most models are variations on the original expression given by Bethe (1930) which describes the total (not the differential) ionization cross section as

$$\sigma_T = \left(\frac{\pi e^4 b_s n_s}{E_0 E_c}\right) \log\left(\frac{c_s E_0}{E_c}\right) \tag{4.1}$$

where the only new terms are n_s, which is the number of electrons in the ionized subshell, and b_s and c_s, which are constants for that shell. We are not particularly concerned with any angular variation in the ionization process. The differential form of the Bethe expression shows two features

- The electron that ionized the atom is deviated through a really small angle (<~10 mrads).

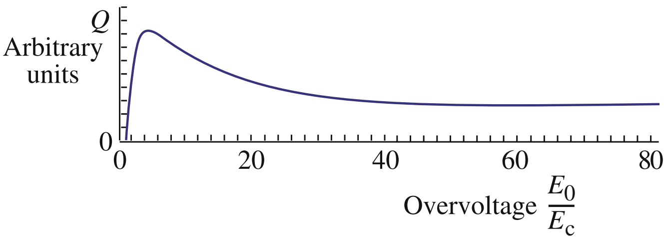

FIGURE 4.4. The variation of the ionization cross section with overvoltage. Ionization is most probable if the beam energy is ~5× the critical ionization energy. The cross section decreases, but not substantially, at higher overvoltages, typical of a TEM.

- The resultant characteristic X-ray is a spherical wave emitted uniformly over 4π sr.

Remember the Bethe expression is an *inelastic* cross section but, like the Rutherford (elastic) cross section, it also needs to be corrected for the effect of relativity at TEM beam energies. So we substitute the term $m_0v^2/2$ for the beam energy and introduce a standard relativistic factor, β (= v/c) (Williams 1933)

$$\sigma = \left(\frac{\pi e^4 b_s n_s}{\left(\frac{m_0 v^2}{2}\right) E_c}\right)\left[\log\left[c_s\left(\frac{m_0 v^2}{2E_c}\right)\right] - \log(1-\beta^2) - \beta^2\right] \tag{4.2}$$

This modified Bethe cross section can be manipulated to fit almost any X-ray data just by altering b_s and c_s, although such parameterization is not always justified. Several cross section models have been developed, all of which are modifications to Bethe's approach (e.g., Newbury 1986, Goldstein et al. 1986). A good source of cross section data can be found on the NIST Web site (URL #1).

The X-ray energy/wavelength: X-rays are electromagnetic radiation and so we usually think of them of as waves with a specific wavelength λ. But, just like electrons, X-rays can show particle-like characteristics and then we describe them as photons with a specific energy such as E_K or E_L, where the subscript refers to the shell from which the core electron was ejected.

There is a similar inverse relationship between the X-ray wavelength and its energy, as we saw for electrons back in Chapter 1. However, there are a couple of important differences which you *must* remember.

- An X-ray is a photon of electromagnetic energy, so the concepts of rest mass and momentum embodied in the electron energy are irrelevant; an X-ray has *no mass*.
- X-rays, like all electromagnetic radiation, travel at the speed of light (c) in vacuum and consequently we don't have to make increasing relativistic corrections as their energy increases. So the quantized X-ray energy is just hν where h is Planck's constant and ν is the frequency and in order to express this energy in eV we equate it to E, where E is the X-ray energy.

Thus

$$E = h\nu = \frac{hc}{\lambda} \tag{4.3}$$

Now since h and c are constants we can substitute values with appropriate units into the equation and find that the X-ray wavelength is given by

$$\lambda = \frac{1.24}{E} \tag{4.4}$$

where λ is in nm and E in keV. This expression is *very* similar to the expression for the uncorrected *electron* wavelength ($1.22/E^{1/2}$) where E is the electron energy in eV (not keV) that we gave back in Chapter 1. You can easily confuse the two, so beware!

SPEED

Don't confuse electromagnetic waves (e.g., X-rays), which always travel at the speed of light, with electron waves whose speed depends on their energy.

Because the X-ray energy depends on the difference in the inner-shell energies and these differences increase monotonically with Z, we can use the detection of a characteristic X-ray with a specific energy as an unambiguous sign of the presence of an element in the specimen (although it doesn't necessarily mean that that element is intrinsic to your specimen, as we'll see in Chapter 33). The concept of the atomic number (Z) of the specimen and its relationship to the X-ray energy/wavelength was reported by the brilliant young physicist, HGJ Moseley. Soon after his discovery, Moseley volunteered for the British army and, despite his talents, was dispatched to the trenches of Gallipoli in 1915 where he was promptly killed before he could be nominated for the Nobel Prize, which would undoubtedly have been his. He is remembered by Moseley's law which states

$$\lambda = \frac{B}{(Z-C)^2} \tag{4.5}$$

where B and C are constants. So we can also generate a list of X-ray energies which are associated with each atomic transition. As with E_c the complete list is enormous and given in Bearden's tables. More compact lists are given in the software attached to the XEDS system on your TEM or in handy 'slide rules' by the manufacturers of X-ray spectrometers, in textbooks, review articles, or on trusted Web sites such as NIST (URL #2) or NPL (URL #3).

If you compare the value of E_c and the relevant characteristic X-ray energy you'll see that they are not quite identical. The X-ray energy, E_K or E_L, is invariably less than E_c. Table 4.2 lists a comparison of critical ionization energies and corresponding X-ray energies for a range of elements. Note how the differences in energy increase with increasing Z. The differences arise because the atom doesn't return completely to ground state when the X-ray is emitted. If the electron that fills the hole in the ionized inner shell comes from an outer shell then this process will leave a hole in that outer shell.

TABLE 4.2 Difference Between E_c and E_K

Element	Critical ionization energy E_c (keV)	X-ray energy E_K (keV)
C	0.282	0.277
Al	1.562	1.487
Ca	4.034	3.692
Cu	8.993	8.048
Ag	25.531	22.163

Note that the energies may be affected by bonding states but shifts will only be a few eV.

This hole must also be filled by another electron with perhaps the emission of another X-ray (much more likely as Z increases) and so on until eventually a free electron from the conduction or valence band fills the last hole in the outermost core shell.

> **An example:** A Cu K-shell electron requires 8.993 keV of energy for ionization (E_c = 8.993 keV). One possible sequence by which this extra energy within the atom is lost is first by the creation of a Cu K_α X-ray (8.048 keV), then an L_α X-ray (0.930 keV). These X-ray energies total 8.978 keV and the remaining few eV could come from the hole in the M shell being filled from the conduction band with the emission of a photon or the generation of phonons (see below).

CASCADE TO GROUND

So the ionized atom returns to ground state not via a single event but by a cascade of transitions, depending on the complexity of the electronic structure of the atom.

The possible variations are enormous and affected by such events as Coster-Kronig transitions, in which the atomic shells rearrange their energies after the electron transition. The situation is further complicated if the ionized atom is bound to a different atom, in which case the energy of the X-ray can be shifted slightly ($<\sim 5$ eV). Such detail is well beyond what you need to know now but a textbook on X-ray spectrometry will give you more, if you so wish.

Fluorescence yield: Remember that an ionized atom does not have to lose energy by giving off a characteristic X-ray but can emit an Auger electron instead. The probability of X-ray versus Auger emission is described by the fluorescence yield, ω, which is the ratio of X-ray emissions to inner-shell ionizations. The fluorescence yield is a strong function of atomic number as shown in Figure 4.5, decreasing at a rate proportional to Z^4 as Z decreases. One common expression for ω gives

$$\omega = \frac{Z^4}{a + Z^4} \tag{4.6}$$

where $a \sim 10^6$ for the K shell. While an approximation, this equation still describes a formidable dependence on Z. For carbon ($Z = 6$), ω is $\sim 10^{-3}$ and for Ge ($Z = 32$), ω is $\sim$ 0.5. So you have to ionize 1000 carbon atoms before you get a single C K_α X-ray but only two ionizations are needed to produce a Ge X-ray. So if you ionize low-Z atoms, the chances are you won't see an X-ray and therefore XEDS is *not* the best way to analyze light elements; you should use EELS (see Part 4) because we can always detect the energy-loss electron whether or not it has generated an X-ray. If you want to know more about the chances of generating X-rays in your microscope then the database by Hubbell et al. is a good source.

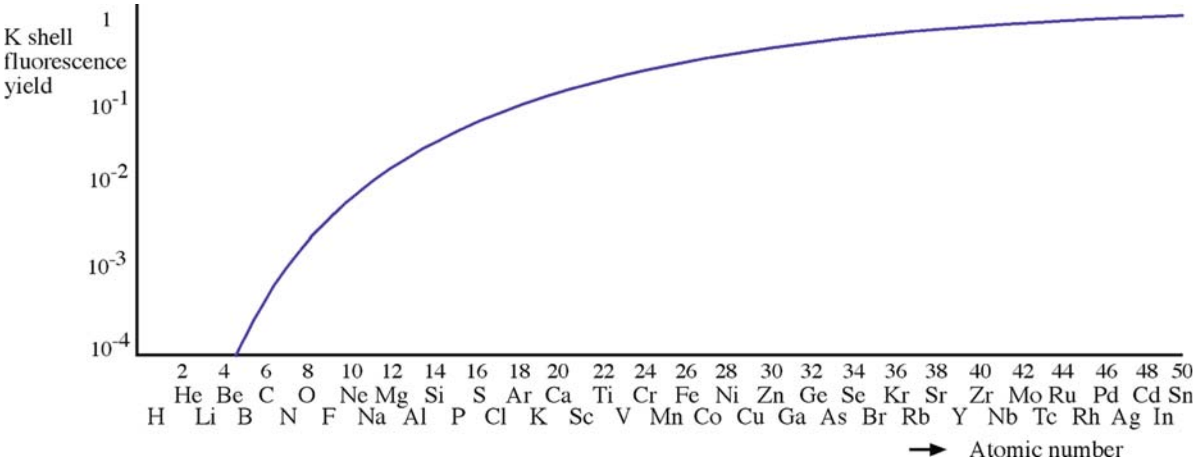

FIGURE 4.5. Fluorescence yield for K-shell X-rays as a function of atomic number. Note the rapid decrease at low atomic numbers. X-rays from elements below Be are not detectable.

4.2.B Bremsstrahlung X-rays

If the electrons in the beam penetrate completely through the electron shells they can interact inelastically with the nucleus. If the electron interacts with the Coulomb (charge) field of the nucleus, it can suffer a substantial change in momentum and during this process it may emit an X-ray. Since the electron can suffer any amount of energy loss, depending on the strength of its interaction, then these X-rays can have any energy up to the beam energy. Such X-rays are known by their original German name of *bremsstrahlung* which can be translated as 'braking radiation.'

The likelihood of bremsstrahlung creation is usually described by the cross section derived by Kramers. This expression is often used for thin TEM specimens, although it was originally derived for bulk samples. It is common to use the Kramers cross section to predict the bremsstrahlung production rather than the probability of interaction. The approximate expression used is

$$N(E) = \frac{KZ(E_0 - E)}{E} \tag{4.7}$$

where $N(E)$ is the number of bremsstrahlung photons of energy E (i.e., the intensity) produced by electrons of energy E_0, K is Kramers' constant, and Z is the atomic number of the ionized atom. This relationship predicts that it is far more likely that the interaction causes a small loss of energy and exceedingly rare that the electron loses all its energy in one deceleration at the nucleus. So the bremsstrahlung intensity as a function of energy is shown in Figure 4.6. In contrast to the isotropic emission of the characteristic X-rays, the bremsstrahlung is highly anisotropic, showing strong forward scattering which increases as E_0 increases. This anisotropy is very useful since it allows us to design spectrometers that collect many more useful characteristic X-rays than relatively useless bremsstrahlung X-rays.

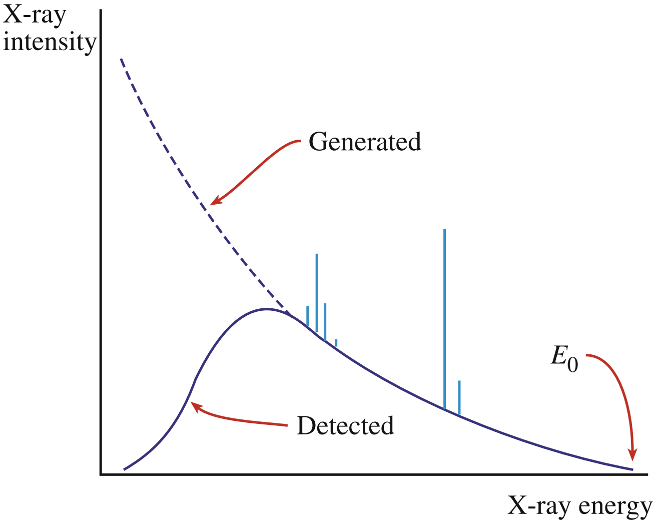

FIGURE 4.6. The bremsstrahlung X-ray intensity as a function of energy. The generated intensity increases rapidly with decreasing X-ray energy but at energies <~ 2 keV the bremsstrahlung is absorbed in the specimen and in any detector being used so the observed intensity in the detected spectrum drops rapidly to zero. E_0 is the energy of the electrons that cause the X-ray emission. Two families of characteristic lines at specific energies are also shown superimposed on the bremsstrahlung.

The bremsstrahlung has a continuous energy spectrum on which the characteristic X-rays that we just talked about are superimposed, as also shown schematically in Figure 4.6 and experimentally in the spectrum back in Figure 1.4. Since the characteristic X-rays have a narrow energy range, they appear as sharp peaks in the spectrum centered at specific energies, indicated by computer-generated lines on the display (now another reason to call them 'lines'). The bremsstrahlung intensity depends on the average Z of the specimen and this is useful to biologists or polymer scientists who are interested in this aspect of their specimens. But materials scientists generally dismiss the bremsstrahlung as a signal, which only succeeds in obscuring characteristic lines. We'll come back to the X-ray spectrum in more detail in Chapters 32–36.

4.3 SECONDARY-ELECTRON EMISSION

Secondary electrons (SEs) are electrons within the specimen that are ejected by the beam electron.

- If the electrons are in the conduction or valence bands then it doesn't take much energy to eject them and they typically have energies <~ 50 eV.
- If the electrons are ejected from an inner shell by the energy released when an ionized atom returns to the ground state, then these SEs are called Auger electrons. The process is often termed a non-radiative transition (since no X-ray emerges from the atom) and the energy undergoes an 'internal conversion' (which is not quite a religious experience).

Historically, SEs were usually considered only in relation to the SEM where they are used to form (often stunning) images which are sensitive to surface topology. We'll now discuss each of these SE signals and their relative importance in the TEM.

4.3.A Secondary Electrons

SEs are ejected from the conduction or valence bands of the atoms in the specimen. The actual emission process can be quite complex and no simple cross section model covers all production mechanisms. The data in Figure 4.1 indicate that SE emission is a far less likely process than all the other inelastic processes we've discussed, but enough are generated for them to be useful in the TEM.

Usually, SEs are assumed to be free electrons, i.e., they are not associated with a specific atom and so they contain no specific elemental information. Because SEs are weak they can only escape if they are near the specimen surface. So we use them in SEMs for forming images of the specimen surface. While SEs are the standard signal used in SEMs, they are also used in STEMs where they can provide very high resolution, topographic images of the specimen surface. We'll discuss ways to detect SEs in Chapter 7 and we'll talk about the images themselves in Chapter 29.

We'll discuss several reasons for the improved (SE) resolution in STEM in Chapter 29. However, recent developments in high-resolution field-emission gun (FEG) SEMs have produced SE image resolution <0.5 nm (close to surface atom resolution) at 30 kV. (We discuss FEGs in the next chapter.) A STEM at 100 kV can offer similar or better resolution even without an FEG, so the SEs are very useful. Aberration correction in STEM naturally brings about even higher-resolution SE images, close to the atomic level.

SE RESOLUTION

SE images in a STEM have much better resolution than SE images in the (relatively) low-kV SEMs.

The number of SEs does depend on energy; it rises to a maximum at about 5 eV and drops close to zero with energies >~50 eV. (You should know that, on rare occasions, strongly bound inner-shell electrons can be ejected with energies up to about 50% of the beam energy. Such fast SEs are generally ignored because they do not seem to limit the resolution of XEDS in the TEM.) The SE yield (number of SEs/incident-beam electron) is generally regarded as being independent of E_0; if there is any Z dependence (which is still a matter of some debate) then it is very small. The angular distribution of emitted SEs is not important since the detector uses a strong field to gather SEs emerging from the surface at any angle. But the *number* of SEs increases with specimen tilt because SEs escape more easily as the surface is tilted parallel to the beam. This behavior is a critical aspect of SE emission because it mimics Lambert's cosine law of visible-light reflection, accounting for the great similarity between SE images of rough specimens and the everyday, reflected-light images we are accustomed to seeing with our eyes.

4.3.B Auger Electrons

Remember we said at the start of this chapter that the emission of Auger electrons is an alternative to X-ray emission as an ionized atom returns to its ground state.

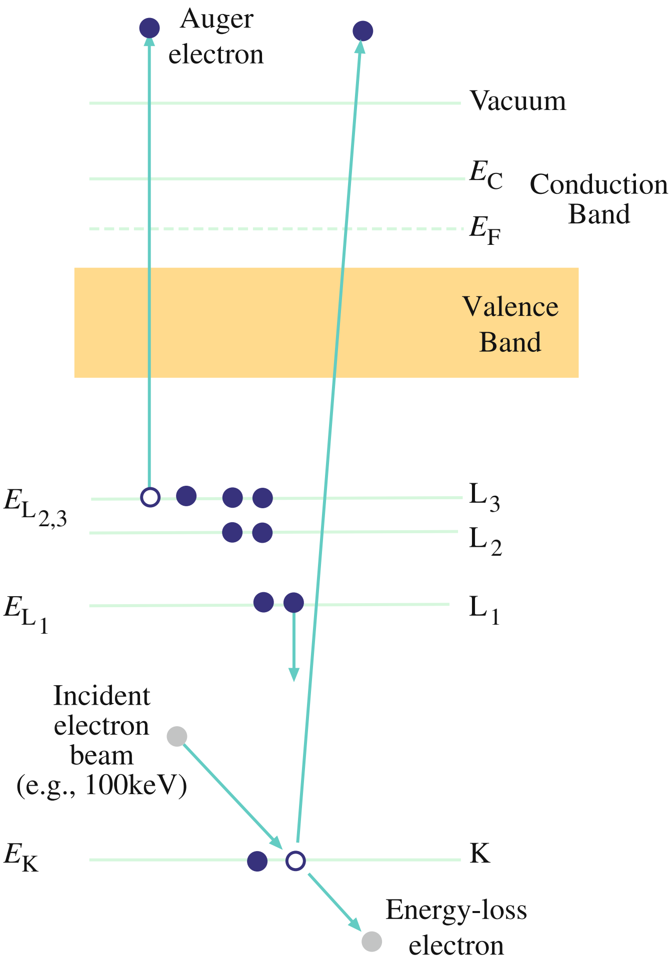

FIGURE 4.7. The process of inner (K) shell ionization and subsequent Auger-electron emission. The energy released when the L_1 electron fills the hole in the K shell is transferred to an electron in the $L_{2,3}$ shell which is ejected as a $KL_1L_{2,3}$ Auger electron.

Figure 4.7 shows how such an atom ejects an outer-shell (Auger) electron; it's instructive to compare with Figure 4.2 for X-ray emission. The ejected electron has an energy given by the difference between the original excitation energy (E_c) and the binding energy of the outer shell from which the electron was ejected. This explains the rather complex nomenclature used to describe each Auger electron (see the caption to Figure 4.7). So the Auger electron has a characteristic energy that is dependent on the electronic structure of the ionized atom and is almost identical to the energy of the alternative, characteristic X-ray.

Because they have such low energies, the Auger electrons that do escape come from very close to the specimen surface. They contain chemical information and consequently AES is a recognized surface-chemistry technique. Because of the similarity in energy between Auger electrons and characteristic X-rays, you might ask, why is light-element X-ray analysis in the TEM not just a surface technique? What you have to remember is that characteristic X-rays are much less strongly absorbed in the specimen than electrons of similar energy. So most X-rays generated in a thin TEM specimen can escape and be detected. (So it's all to do with the cross sections for interaction in the first place.)

AUGER

The Auger process is favored in atoms having small binding energies, i.e., the lighter elements. Typical Auger electron energies are in the range of a few hundred eV to a few keV and are strongly absorbed within the specimen.

Because Auger emission is a surface phenomenon, the state of the specimen surface is paramount. Oxidation or contamination will prevent interpretable Auger analysis of the true surface chemistry and so we only carry out AES in a UHV system. As a result, the Auger signal has traditionally been ignored by electron microscopists and confined to the realm of surface chemistry, along with such techniques as ESCA and SIMS. However, as TEMs are being built with better vacuums and UHV STEMs become more common, the Auger signal may receive more interest. Unfortunately, it is not simple to attach an Auger system to a STEM unless you build a dedicated instrument in which routine AEM is difficult, so such studies are still very rare.

4.4 ELECTRON-HOLE PAIRS AND CATHODOLUMINESCENCE (CL)

These two signals are closely related. We'll see in Chapter 7 that one way to detect electrons is to use a semiconductor that creates electron-hole pairs when hit by high-energy electrons. So if your specimen happens to be a direct-gap semiconductor then electron-hole pairs will be generated inside it.

Cathodoluminescence is explained schematically in Figure 4.8. The emitted photon has a frequency (i.e., color) equal to the energy of the gap (E_G) divided by Planck's constant (h). If the band gap varies for some reason, there will be a spectrum of light given off or the color of the light will vary depending on what part of the specimen is being observed. So CL spectroscopy has applications in the study of semiconductors and impurity effects therein. While the spatial resolution of CL is not down to the nanometer level like X-rays or secondary electrons, it is still well within the nano-scale range, typically defined as <100 nm.

CATHODOLUMINESCENCE

Electrons and holes will recombine and in doing so give off light; this process is referred to as CL.

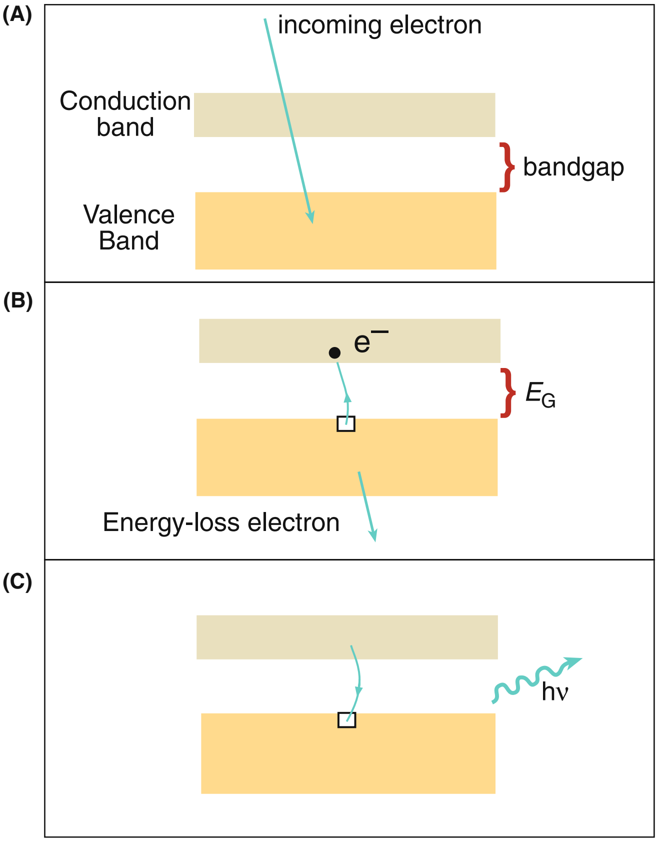

FIGURE 4.8. Schematic illustration of CL. (A) Initial state before a beam electron interacts with valence-band electrons. (B) A valence-band electron is excited across the gap into the conduction band, leaving a hole in the valence band. (C) The hole is filled by a conduction-band electron falling back into the valence-band hole. Upon recombination a photon of light is emitted with a frequency determined by the band gap.

Now if you apply a bias to your specimen or if it happens to be a p-n junction or a Schottky-barrier diode, then the electrons and holes can be separated by the internal bias. You can pick up this charge if you ground the specimen through a picoammeter. In this situation, your specimen is acting as its own detector! The current you then detect is sometimes called the electron-beam-induced current (EBIC) signal. If you detect this signal and use it to form an image then you are doing charge-collection microscopy (CCM).

The CL and CCM modes of operation are standard methods of characterizing bulk samples in the SEM. In principle, there is nothing to prevent us doing the same in a STEM, and a few people have built dedicated instruments, but generally the space available in the TEM stage limits the efficiency of signal collection. This may improve with C_s correction, but, in general, these two techniques are rare and mainly limited to studies of semiconductors (e.g., Boyall et al.) although some minerals also exhibit CL. We'll describe

CL detectors in Chapter 7 and show you an image in Chapter 29. Just remember that CL and CCM are potentially powerful, but highly specialized, techniques.

4.5 PLASMONS AND PHONONS

We can link these two phenomena because they are both examples of what we call collective oscillations.

We can consider plasmons as analogous to sound waves, since they are longitudinal oscillations of the free-electron gas, which create regions of varying electron density as shown schematically in Figure 4.9. These oscillations are damped out in less than a femtosecond and the wave is localized to <10 nm. If you go back to Figure 4.1, you'll see that the plasmon process has the largest cross section so it's by far the most common inelastic interaction occurring in materials and, as we'll see in Chapter 38, plasmon peaks are strong features of EEL spectra. Plasmons can occur in any material with weakly bound or free electrons, but they occur predominantly in metals, particularly ones like aluminum which have a large Fermi surface and, therefore, a high free-electron density. The plasmon oscillation is quantized and the mean free path for plasmon excitation is ~100 nm. As we'll also see in Section 38.3.C this quantization makes the number of plasmon excitations a useful way to measure your specimen thickness. Also, the plasmon energy is a function of the free-electron density and this changes with composition (see Chapter 38 also), so the plasmon excitation is chemically dependent, although we rarely use it for elemental analysis.

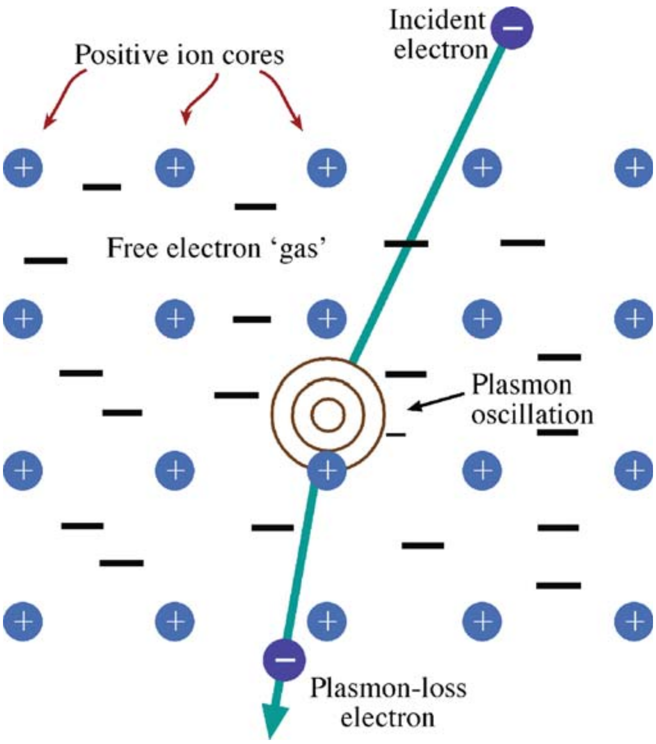

FIGURE 4.9. Schematic diagram of a high-energy beam electron exciting a plasmon oscillation in a free-electron gas that permeates the ion cores in a metal.

PLASMONS AND PHONONS

Plasmons are collective oscillations of free electrons that occur when a beam electron interacts with the free electron 'gas.'

Phonons are collective oscillations of atoms in a solid that arise when the atomic lattice is struck by a beam electron.

The differential cross section for plasmon excitation has a general Lorenztian form

$$\frac{d\sigma_\theta}{d\Omega} = \frac{1}{2\pi a_0}\left(\frac{\theta_E}{\theta^2+\theta_E^2}\right) \tag{4.8}$$

where a_0 is the Bohr radius, θ is the scattering angle, and θ_E is the so-called characteristic scattering angle given by $E_P/2E_0$ (which is always going to be small given the large value of E_0 in TEMs). Since E_P, the plasmon energy, is almost fixed (~15–25 eV), the cross section is a strong function of θ, dropping rapidly to zero at values much above 10 mrads, indicating once again the strong forward scattering of such energy-loss electrons.

When a high-energy electron strikes an atom in the specimen, the lattice shakes, just like hitting a chain-link fence with a stick. This process occurs because, as shown in Figure 4.10, all the atoms are linked together elastically. Phonons can also be generated by other inelastic processes occurring within the atom; for example, the energy of Auger or X-ray emission or an interband transition is sometimes converted internally to lattice vibrations. Any shaking of the atoms is equivalent to heating up the specimen and the net result of all phonons is that the specimen gets warmer. As we will see, this is particularly damaging to some specimens.

The incident electron can generate phonons in any solid specimen, even amorphous ones in which there is no periodic crystal structure. Typically, a phonon vibration causes a very small energy loss of < 0.1 eV but the phonon-loss electrons are scattered out to quite large angles (5–15 mrads), and these electrons account for the diffuse background intensity present between the Bragg intensity maxima in DPs. Phonon-scattered electrons carry no useful chemical information nor do they carry contrast useful to the microscopist.

It is not important to know the phonon-scattering cross section exactly, but it is useful to remember that

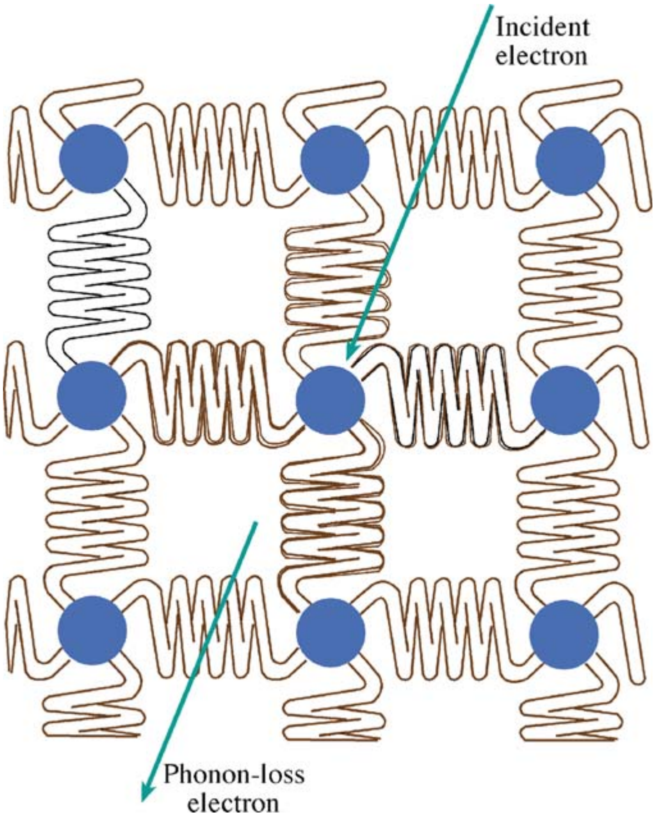

FIGURE 4.10. An illustration of the crystal lattice as a group of atoms linked elastically by springs. The bonds vibrate when struck by a high-energy electron creating lattice oscillations or phonons and these vibrations are equivalent to heating the specimen.

phonon scattering increases with Z with a dependence $\sim Z^{3/2}$, which is a somewhat weaker dependence than for true elastic scattering. Also, because of the effect of temperature on atomic vibration, phonon scattering increases as the temperature rises. This accounts for the increase in thermal-diffuse scattering with temperature and is the major reason why we cool specimens if we want to obtain good, sharp DPs. The mean free path for phonon scattering at room temperature varies from a couple of nm for Au up to about 350 nm for Al, and at liquid-He temperatures these values increase ~ 2–3X.

We don't use either plasmons or phonons directly to form images (although in principle this is possible), but we do detect the electrons that caused them, and we'll discuss the (rather limited) uses of plasmon energy-loss electrons in Chapter 38.

PHONONS

These oscillations involve all the atoms in the crystal lattice vibrating collectively. Such vibrations are equivalent to specimen heating. You can reduce the number of phonons by cooling your specimen.

There are other inelastic processes that can occur as the beam electron traverses the specimen, such as inter-band and intra-band transitions within the valence or conduction bands. The bonding between the atoms and local atomic arrangements within the specimen can also affect many of the inelastic events that we have described in ways that we can both predict and discern. Other electronic features such as the band gap can affect the possibility of certain inelastic interactions occurring. In principle, any atomic or electronic characteristic of your particular specimen that reduces the energy of a beam electron during its passage through the specimen can be detected, measured, and perhaps quantified and simulated. These signals can all be used to form images containing information which complements that contained in the elastic-electron (mainly diffraction-contrast) images that constitute traditional TEM studies of materials. We'll give you plenty of examples of such inelastic images in Part 4.

4.6 BEAM DAMAGE

The inelastic collisions that give us all the useful signals we've just discussed bring with them an unfortunate side effect, electron-beam damage. We are often less precise and call this phenomenon radiation damage. The damage, which affects the structure and/or the chemistry of the specimen, depends, in some form or other, on the incident-beam energy. Certain materials are more susceptible than others but, in the end, you can damage virtually anything that you put into the TEM, particularly now that aberration correction permits even more electron current to be focused into even smaller beams. Therefore, damage represents a real physical limit on what the TEM can do and may be regarded as the microscopists' analog of the Heisenberg uncertainty principle in that the very act of observing your specimen can change it.

DAMAGE

Once its structure or chemistry is changed, your thin specimen is not representative of its parent material and interpreting any of your TEM images, DPs or spectra becomes more difficult.

On the other hand, we can sometimes use beam damage to aid certain in-situ transformations that are speeded up by the damage process or we can use electron damage to emulate other forms of radiation damage. Generally, however, beam damage must be considered undesirable.

Damage takes one of three principal forms

- *Radiolysis:* Inelastic scattering (mainly electron-electron interactions such as ionization) breaks the chemical bonds of certain materials such as polymers and alkali halides.

- *Knock-on damage or sputtering:* Knock-on damage is the displacement of atoms from the crystal lattice and creates point defects. If atoms are ejected from the specimen surface we call it sputtering. These processes are ubiquitous if the beam energy (E_0) is high enough.
- *Heating:* Phonons heat your specimen and heat is a major source of damage to polymers and biological tissue.

We will see that, paradoxically, radiolysis is reduced at higher E_0 while knock-on damage is increased; so there is sometimes no way around the damage problem; you can get it at all energies. Cooling your specimen can obviously help if it is likely to be damaged by heating.

All these processes occur in the voltage range available in commercial TEMs and so you must be aware of the dangers. The actual processes can be very complicated and are also specimen-specific, so we could get bogged down in an enormous amount of detail. What we'll do, however, is describe the fundamental processes in different materials, explain how you can determine if your specimen is being damaged and describe how you can minimize or eliminate the problem.

If you find you need to know more about radiation damage, the text by Jenkins and Kirk is the place to start. But we should also note upfront that whole areas of TEM such as in-situ studies and environmental TEM actually take advantage of radiation damage to enhance particular reactions.

We'll start our brief overview of damage in different kinds of TEM specimens by explaining the terms we use to measure damage.

4.6.A Electron Dose

In the TEM we define the electron dose as the charge density (C/m^2) hitting the specimen. It is easy to convert this to the number of electrons/unit area (usually e/nm^2) knowing that $e = 1.6 \times 10^{-19}$ C. This term is *not* the same as for radiation effects on the human body, for which we define dose as the energy absorbed per unit volume. This human dose is defined by the Gray (Gy) which is the absorption of 1 J of ionizing radiation/kg of material and 1 Gy = 100 rads (in pre-SI units). If we convert the incident electron dose to an absorbed dose it can easily be shown that typical electron exposures inside the TEM are well above the lethal limit for human tissue and early microscopists occasionally found this out to their cost (although we hasten to add that, to our knowledge, while no deaths occurred, digits were apparently lost). While this fact is another warning about the dangers inherent in TEM it is more pertinent as a reminder to you that we put an enormous amount of energy into our specimens. This latter point is well illustrated if you calculate the total power input into the specimen, as we do in the next chapter. Fortunately, such a small fraction of the beam energy is transferred to a thin specimen that most specimens survive this, otherwise hostile, environment.

4.6.B Specimen Heating

Specimen heating is difficult to measure experimentally because of the many variables that can affect the result, such as the thermal conductivity, thickness, and surface condition of the specimen as well as the beam size, energy, and current. Hobbs has calculated the effects of beam current and thermal conductivity on the specimen temperature, as shown in Figure 4.11. From these results we can say that, as a rule for metals and other good conductors, beam heating is negligible under standard TEM conditions but, for insulators, it can be quite substantial. To minimize heating, follow the instructions given at the end of the next section.

You will often hear questions about beam heating from people who don't use TEM.

- If thermal conduction is very high, heating is negligible.
- If thermal conduction is poor, heating can be quite substantial.

So, beam heating for metals is usually minimal but small ceramic particles may be heated by the beam to temperatures of ~1700°C. If a good thermal conductor is thermally insulated from its surroundings, considerable

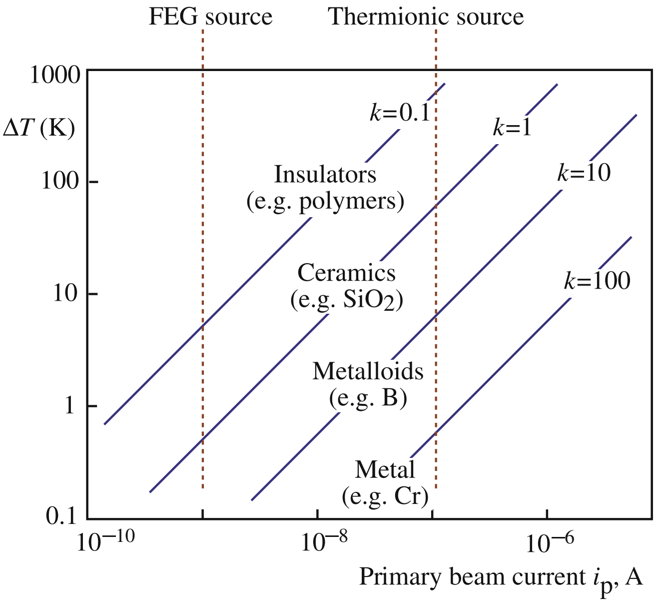

FIGURE 4.11. The increase in specimen temperature as a function of the beam current and the thermal conductivity of the specimen (k, in W/m K). Typical materials are noted, but should not be considered representative, since k varies substantially in any class of materials.

beam heating can occur. Most electrons go through a thin specimen and lose very little energy, as we'll see in our discussion of EELS.

4.6.C Beam Damage in Polymers

Polymers are particularly sensitive to the electron-electron interactions since these can break chemical bonds creating new structures; we call this process radiolysis.

- Electrons can cause the main polymer chain to break, thus changing its basic structure.
- Electrons can cause side groups to break off, leaving reactive free radicals which may crosslink to form a new structure.

Breaking a polymer chain this way is known as scission. Generally, polymers show a tendency either to break down or to crosslink under electron irradiation. In the former case, the polymer will continue to lose mass while, in the latter, the polymer eventually becomes mainly carbon. Mass loss can sometimes be measured directly by EELS in the TEM and it can also manifest itself as a major dimensional change in your specimen because, ultimately, a hole appears in the damaged area; if you're watching carefully you'll see that the image contrast will usually change before the hole appears!

If your polymer specimen was originally crystalline, then radiation damage results in a loss of crystallinity, which you can measure quantitatively from the loss of diffraction contrast in the image or the loss of sharp peaks in the DP (which are gradually replaced with diffuse scattered intensity characteristic of amorphous structures (go back and look at Figure 2.13A). Sometimes you can preserve the crystal structure by staining with a heavy metal such as Pb or U. However, whenever you stain your specimen you affect its structure and change the chemistry, so this isn't ideal.

There are several methods you can use to minimize beam damage in polymers

- Use low-dose imaging techniques (see Chapter 31).
- Cool the specimen to liquid N_2 temperatures or lower T, if possible.
- Coat the specimen with a conducting metal film.
- Use STEM imaging (Section 22.3).
- Do all of the above, if necessary.

In addition to these practical steps, any contribution to damage from beam heating is generally minimized by reducing the cross section for inelastic scatter, i.e., by using the highest available voltage. So HVEMs are better for the study of heat-sensitive materials. If the specimen is thinner than the mean free path for inelastic interaction then less energy is transferred to the specimen and the result is less damage due to heating effects.

4.6.D Beam Damage in Covalent and Ionic Crystals

In covalent and ionic materials such as ceramics and minerals, radiolysis can change the specimen chemistry and possibly its structure through a series of reactions driven by the electron beam. The inelastic interaction primarily responsible for radiolysis is the interband transition, similar to that which causes CL. The transition of a mobile, valence-band electron to the conduction band leaves a hole in the original energy level. Rather than emitting a photon, the electrons and holes may partially recombine via an intermediate, metastable state called an exciton which, through a rather complicated sequence of events, can create an anion vacancy and a cation interstitial. Crystalline quartz (although a very hard material) can be amorphized by a similar process. Often radiolysis can result in the formation of new compounds, which can be identified *in situ* as they form, by electron diffraction and AEM. The formation of Ag from Ag halides in a photographic emulsion is a (rare) example of useful radiolysis. So, somewhat paradoxically, if we use photographic film we depend on radiation damage to record the information we generate in our TEMs (more about this in Chapter 7).

We can't stop radiolysis simply by cooling or coating our specimen, since it isn't affected by heat-transfer considerations. The best way is to lower the cross section for the initiating electron-electron interactions and we can do this by using higher voltages and thinner specimens (thinner is better again). Nevertheless, radiolysis remains a major limitation in the TEM when looking at certain ceramics and minerals and most polymers.

4.6.E Beam Damage in Metals

The primary way that metals are damaged is by knock-on or displacement/sputtering damage. This process occurs by the direct transfer of the beam energy to atoms in the solid, knocking them out of their atomic site and creating a combination vacancy and interstitial (or Frenkel pair). For an atom to be kicked out of its very comfortable and stable crystal lattice site, the beam electron has to penetrate close to the nucleus and be effectively stopped in its tracks by the Coulombic attraction, thus transferring most, if not all, of its energy to the atom.

KNOCK-ON DAMAGE

It is directly related to the incident beam energy.

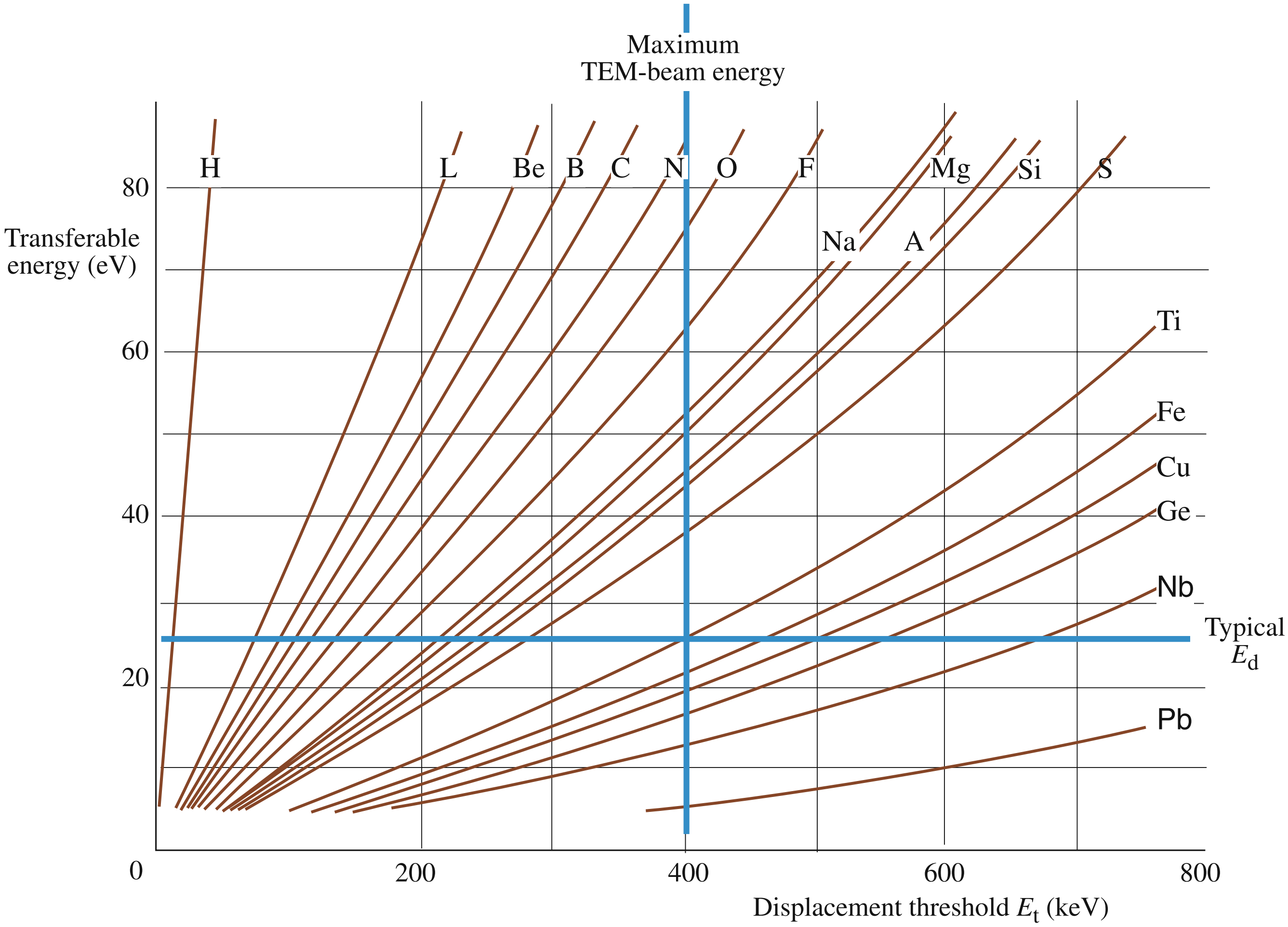

FIGURE 4.12. The maximum transferable energy for a range of atoms as a function of the displacement-threshold energy. A maximum IVEM beam energy is indicated (400 keV) and a typical E_d is shown as ~25 eV, but it can vary substantially with bond strength in different materials. In regions of the graph above 400 keV and below E_d, damage will not occur.

How strongly the atoms are bonded to their neighbors will also be a factor. A simple expression given by Hobbs for the displacement energy E_d allows us to determine the threshold energy (E_t) for displacement of atoms of atomic weight A

$$E_t = \frac{\left(\frac{100 + AE_d}{5}\right)^{1/2} - 10}{20} \qquad (4.9)$$

where E_t is in MeV and E_d is in eV. E_d is typically in the range from 5 to 50 eV, but varies with bonding type. If you can transfer more than the threshold energy to an atom then you will displace it from its site. This concept is summarized in Figure 4.12. So, for example, at 400 keV, $>$ 80 eV can be transferred to a carbon atom, about 45 eV can be transferred to an Al atom, and about 25 eV to a Ti atom. If we assume an average displacement energy of ~ 25 eV then it is quite evident that if you have a 400-kV intermediate voltage TEM, you can displace any atom with an atomic weight below about Ti (unless it happens to be bonded so that E_d is much greater than the typical value in Figure 4.12). If you're using an HVEM with beam energies of 1 MeV or more you will *invariably* cause displacement damage, except perhaps in the heaviest elements. The only way to avoid displacement damage is to operate below threshold and you should determine this energy experimentally given the very approximate nature of Figure 4.12.

How can you identify displacement damage? The only sure way is to record images of the same area before and after radiation and compare the contrast under the same imaging conditions. Knock-on damage often manifests itself as small vacancy clusters which appear as black-white lobe contrast or dot contrast, as we showed back in Figure 1.8. Sometimes damage is discernible as dislocation loops and stacking fault tetrahedra caused by the agglomeration of vacancies. Such crystal defects could of course be easily confused with defects that are intrinsic to the material rather than introduced by the act of observing the materials in the TEM. Displacement damage can also occur in polymers and minerals, of course. The problem here is that we just suggested going to higher voltages as one way of minimizing thermal effects and radiolysis and in doing so, we may well induce knock-on damage. So depending on your material, there may in fact be no way to avoid damaging your specimen in one way or another except, perhaps, by becoming a metallurgist.

Perhaps the only bright side to displacement damage is that we can study it for its own sake. It can be argued, though by no means conclusively, that electron-beam damage in materials can be equivalent to neutron damage, such as that occurring in nuclear reactors. A general rule of thumb is that a few minutes' exposure in an HVEM is equivalent in terms of damage to many years in a nuclear reactor and so accelerated studies of materials degradation in reactor environments were possible. With this justification, an enormous amount of work was carried out in the 1960s when nuclear power was in vogue. Three Mile Island and Chernobyl seriously reduced the number of such studies but there are many reviews extant in the older literature and an occasional more modern reference. Given that the current political climate (!) is more favorable toward nuclear energy than for some decades, it is not unreasonable to suspect that beam damage might see a resurgence in importance. So, if you haven't settled on a career yet, you may wish to spend a little time studying this field because all known radiation-damage microscopists have retired or are close, and the hard-earned knowledge from the early halcyon years is in danger of being forgotten!

Vacancies caused by displacement damage can enhance diffusion processes which, in turn, can speed diffusional transformations when they're being studied in situ in the IVEM/HVEM. There are many other problems that can arise during in-situ observations, so interpretation isn't always straightforward. The book by Butler and Hale is recommended for more facts, practical hints, and many beautiful images of reactions occurring, in real time, in thin foils. More recently, Gai has edited a volume of contributed chapters on in-situ TEM and there is much excitement in the field about the possibilities for growth of this important area due (not surprisingly) to the advent of C_s correction bringing about TEM stages with larger pole-piece gaps, thus permitting easier insertion of gas-reaction stages.

4.6.F Sputtering

The displacement of surface atoms, or sputtering, occurs in the TEM at voltages which are $<0.5E_t$. If your specimen is quite thick then this problem is minor since the average, through-thickness, characteristics of the specimen are not changed significantly by any changes on the surface. But, as we've already noted many times, your specimen should really be very thin (thinner is better yet again) if you want to get the best images and the best analytical information. In these specimens, modifications of the surface structure and chemistry may be sufficient to affect the image interpretation and/or change the average through-thickness composition enough to affect the accuracy of any quantitative analysis. Table 4.3 lists typical sputtering threshold energies (E_s) compared with displacement thresholds (E_d) and their relative values compared to how much energy can be transferred by electrons of different energies. As you can see, there is cause for concern even with 100-keV beams. A STEM can easily drill a hole through MgO.

TABLE 4.3 Comparison of Maximum Transferable Kinetic Energy (T) at 100, 200, 300 and 400 keV with Displacement (E_d) and Sputtering (E_s) Energies

Element	T (eV)				E_d (eV)	E_s (eV)
	100 keV	200 keV	300 keV	400 keV		
Al	8.93	19.5	31.6	45.3	16	4–8
Ti	5.00	11.0	17.8	25.5	15	4–8
V	4.73	10.3	16.72	24.0	29	7–14
Cr	4.63	10.1	16.38	23.5	22	5–11
Fe	4.31	9.40	15.25	21.8	16	4–8
Co	4.08	8.91	14.45	20.7	23	5–12
Ni	4.10	8.94	14.5	20.8	22	6–11
Cu	3.79	8.26	13.4	19.2	18	4–9
Zn	3.69	8.03	13.03	18.7	16	4–8
Nb	2.59	5.65	9.17	13.2	24	6–12
Mo	2.51	5.47	8.88	12.7	27	7–14
Ag	2.23	4.87	7.90	11.3	28	7–14
Cd	2.14	4.67	7.58	10.9	20	5–10
Ta	1.33	2.90	4.71	6.75	33	8–16
Pl	1.23	2.69	4.37	6.26	33	8–16
Au	1.22	2.67	4.32	6.2	36	9–18

CHAPTER SUMMARY

Inelastic scattering transfers energy to your specimen, generating a lot of useful signals with which we can form different images or get spectroscopic information about the chemistry and electronic structure of the specimen. Much of this information is localized at the nanometer level or below.

- The generation of many different characteristic signals all localized with nanometer-scale (or below) spatial resolution is a most powerful aspect of TEM.

- Unfortunately, these same inelastic processes create beam damage and heat which can be disastrous under certain conditions for all kinds of TEM specimens. To minimize heat transfer, cool your specimen and use higher voltages and thinner specimens but beware:
- If the accelerating voltage is high enough, knock-on and sputtering damage will occur in all materials, creating non-characteristic crystal defects and changing the surface chemistry.

On the brighter side, beam damage can be a positive help in the simulation of nuclear-radiation effects and can also enhance in-situ transformation studies and environmental TEM.

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Hobbs, LW 1979 in *Introduction to Analytical Electron Microscopy* Eds. JJ Hren, JI Goldstein and DC Joy Plenum Press New York p437 gives calculations of beam heating.

Jenkins, ML and Kirk, MA 2000 *Characterization of Radiation Damage by Transmission Electron Microscopy* Institute of Physics Bristol and Philadelphia. The only text on this topic; helpful reading if specimen damage affects your work. Includes discussion of knock-on damage.

Sawyer, LC, Grubb, DT and Meyers, GF 2008 *Polymer Microscopy* 3rd Ed. Springer New York. For polymers, of course.

SPECIAL TECHNIQUES

Boyall, NM, Durose, K and Watson IM 2003 *A Method of Normalizing Cathodoluminescence Images of Electron Transparent Foils for Thickness Contrast Applied to InGaN Quantum Wells* J. Microsc. **209** 41–46.

Goldstein, JI, Williams DB and Cliff, G 1986 *Quantitative X-ray Analysis* in *Introduction to Analytical Electron Microscopy* Eds. JJ Hren, JI Goldstein and DC Joy p 155 Plenum Press New York.

Hubbell, JH, Trehan, PN, Singh, N, Chand, B, Mehta, D, Garg, ML, Garg, RR, Singh, S and Puri, S 1994 *A Review, Bibliography and Tabulation of K, L and Higher Atomic Shell X-ray Fluorescence Yields.* J. Phys. Chem. Ref. Data **23** 339–364.

Markowicz, AM and van Grieken, RE 2002 *Handbook of X-ray Spectrometry* Marcel Dekker New York. Excellent text for when you really need more detail on topics such as families of X-rays.

Newbury, DE 1986 in *Introduction to Analytical Electron Microscopy* Eds JJ Hren, JI Goldstein and DC Joy p 6 Plenum Press New York.

Venables, JA, Hembree, GG, Drucker, J, Crozier PA and Scheinfein MR 2005 *The MIDAS Project at ASU: John Cowley's Vision and Practical Results* J. Electr. Microsc. **54** 151–162. Rare example of attaching an Auger system to a STEM.

URLs

1. www.physics.nist.gov/PhysRefData/Ionization/Xsection.html
2. www.physics.nist.gov/PhysRefData/XrayTrans/index.html

SELF-ASSESSMENT QUESTIONS

Q4.1 Distinguish background, continuum and bremsstrahlung X-rays.
Q4.2 'Characteristic' X-rays are characteristic of what?
Q4.3 Why shouldn't we refer to an 'ionized' electron?
Q4.4 Approximately how large is an electron shell relative to an electron?
Q4.5 What is the critical ionization energy?
Q4.6 What is the ionization cross section?
Q4.7 What controls the energy and wavelength of the characteristic X-ray?
Q4.8 What is the fluorescence yield?
Q4.9 What do we mean by the term 'weight of an X-ray line'?
Q4.10 What is overvoltage?
Q4.11 What is the difference in the angular distribution of the ionizing electrons and the emitted X-rays?
Q4.12 Does an X-ray have kinetic energy like an electron?
Q4.13 Why is all the energy transferred to the atom during ionization (E_c) not recovered by the emission of the characteristic X-ray(s)?
Q4.14 How is energy conserved in the overall electron-atom interaction?
Q4.15 Why should you be concerned about fast secondary electrons in TEM?
Q4.16 What is cathodoluminescence?
Q4.17 How can you minimize electron-beam damage to your specimen?
Q4.18 Why does sputtering of atoms from the surface of the specimen take less energy than displacing atoms in the interior?
Q4.19 What is radiolysis?
Q4.20 What's the best reason for using an HVEM to intentionally displace atoms in a specimen?

TEXT-SPECIFIC QUESTIONS

T4.1 Look at Figure 4.1 and explain why
  A. We need to be concerned about plasmon energy losses whenever inelastic scatter compromises the operation of the TEM.
  B. All scattering processes show approximately the same dependence on beam energy.
T4.2 What does Figure 4.1 tell us about the advantages and disadvantages of operating at 400 kV rather than 100 kV?
T4.3 From Figure 4.2
  A. Explain what kind of characteristic X-ray has actually been emitted. (Hint: go to Figure 4.3.)
  B. What happens to the hole left by the electron falling out of the L_3 energy level?
  C. Under what conditions is the presence of the vacuum energy level expected?
T4.4 If, as stated in the text, K-shell X-rays have higher energy than L-shell X-rays and so on, why does the Ag L line (2.3keV) have a higher energy than the Al K line (1.5keV)?
T4.5 Use equation 4.6 to determine the relative fluorescence yields of (a) Be and N and (b) Si and Ag. Cross-check your answer with Figure 4.5. Use your answers to explain why X-ray analysis is challenging at lower atomic numbers and quantification is relatively straightforward for higher atomic numbers. Do Auger electrons have an equivalent 'yield'? If so, derive the approximate dependence on Z.
T4.6 Can you explain why we talk about 'braking' radiation when the nucleus and the electron have opposite charges that one might expect to attract one another very strongly?
T4.7 Looking at Figure 4.6, the generated bremsstrahlung intensity increases for lower X-ray energies, but we have just learned that the characteristic X-ray intensity decreases at lower energies (from lower atomic number elements). Explain this difference.
T4.8 Why are the conduction and valence bands shown separately in Figure 4.8 but not in Figure 4.2?
T4.9 Calculate the electron dose in a 1-nm electron probe containing 1 nA of current.
T4.10 Using Equation 4.9, compare the displacement threshold energies for Li, Al, Cu and Au and estimate the sputtering energies. Compare your answers where possible with the data in Table 4.3 and Figure 4.12.

T4.11 Inelastic scattering ultimately limits the information we can obtain from the TEM because the transfer of energy to the specimen can change its structure or chemistry (the two characteristics that the TEM is best at discerning) either temporarily or permanently. So, why do we take great pains to both maximize the generation and detection of inelastic scattering?

T4.12 Relate the amount of energy lost by the electron to the typical potential-well model of the atom.

T4.13 If you look at Table 4.1 you'll see that the cross sections are smaller for interactions that result in larger energy transfer. Why is this a good thing for TEM operators?

T4.14 Why don't we routinely try to use Auger electrons for surface analysis in the TEM?

T4.15 Based on Figures 4.1, 4.4 and 4.5 explain the most likely signal(s) generated when (a) a 100-kV electron beam strikes specimens of Be and Si and (b) when a 300-kV beam does the same.

T4.16 Compare and contrast plasmons and phonons. (Hint: consider their generation processes, energies, scattering angles, cross sections, range, effects on the specimen.) From your answer discuss their relative importance to the TEM user in terms of the information they contain or destroy.

T4.17 (Extra challenge) If the electron beam sputters Au from the surfaces of a thin film, which surface is affected most?