Inelastic Scattering and Beam Damage

4

CHAPTER PREVIEW

In the previous chapter, we discussed elastic scattering of the electron beam in which the incident electron lost no energy as it interacted with the specimen. Inelastic or energy-loss electrons are equally important and we'll discuss the processes here, but leave the applications till later. Why are we interested in inelastic scatter? Well, inelastic scattering generates a whole range of signals, each of which can tell us more about the specimen than we can find out from the elastic electrons. The most important signals are the X-rays, inelastic electrons, and secondary electrons, and so we'll emphasize how these signals arise. We will also discuss why these specific signals are useful to materials scientists.

So how do we use these other signals? First we have to detect the electrons and X-rays and we'll describe electron detection in Chapter 7. In Chapter 31 we will explain how we use some of the signals to form images of the specimen. We will discuss how to detect X-rays and get information from the spectra that are created in Chapters 32–36. Then in Chapters 37–40 we'll talk about detecting and analyzing the electrons that lose energy when they are scattered in the specimen. In all cases we get complementary information to that

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gained in conventional TEM images and diffraction patterns. Obviously then 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 the specimen which can damage beam-sensitive specimens. So we must also look at the down side of the signal-generating process and we end the chapter by discussing this problem under the general topic of beam damage or radiation damage.

A warning: This chapter contains some quite difficult theoretical concepts. However, it does form the basis of AEM, which is the topic of much of Part IV of the book. You can safely delay studying much of this material in detail until you reach Chapter 32.

Inelastic Scattering and Beam Damage

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4.1. WHICH INELASTIC PROCESSES OCCUR IN THE TEM?

Historically, the conventional TEM only used two *elastic* signals, namely, the direct beam and the diffracted beams. As we've seen, these signals constitute the diffraction pattern 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 those were shown back in Figure 1.3. These signals are sometimes sought 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 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 signal constitute analytical electron microscopy (AEM), which we discuss in detail in Part IV of this book. 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 analytical TEMs exist which, in one form or another, can detect all the signals shown in Figure 1.3. So in this chapter we'll cover all the signals that are detectable and what use (if any) they are to the materials scientist. We need to know:

- What are the inelastic scattering interactions?
- What is the energy loss associated with each process?
- What is the likelihood that each energy-loss process will occur?

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

A general rule of thumb: The deeper the electron penetrates into the atom, the higher 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.

We know the first two rather well, but the third is usually poorly defined. Figure 4.1 shows the cross sections for some of the more important inelastic processes that we'll talk about. 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 scatter in more detail as we describe each individual inelastic event.

4.2. X-RAY EMISSION

We'll consider X-ray emission first because it's the most important secondary signal generated in the specimen.

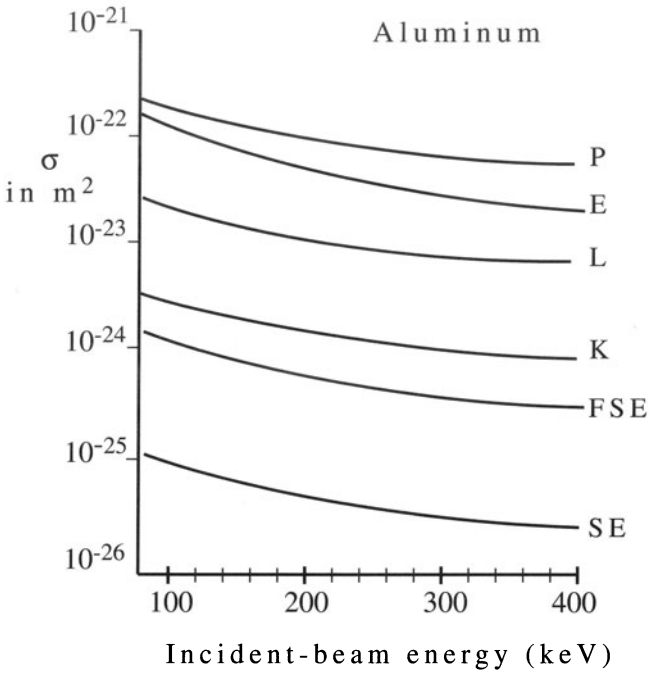

Figure 4.1. Cross sections for the various inelastic scattering processes in Al as a function of the incident electron energy, assuming a small angle of scatter ($\theta \sim 0°$); plasmon (P), K and L-shell ionization (K, L), fast and slow secondary electron generation (FSE, SE). For comparison purposes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

From X-rays we can find out easily 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 IV.) Two kinds of X-rays are produced:

- Characteristic X-rays which are useful to the materials scientist.
- Bremsstrahlung X-rays which are useful to the biologist but generally regarded as a nuisance by most materials scientists.

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 electron shells 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; that is, it escapes the attractive field of the nucleus, leaving a hole in the inner shell. When this happens the atom is left in an excited state because it has a higher 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 missing electron with one from the outer shells. It is this transition which is accompanied either by the emission of an X-ray or an Auger electron. This latter process was first described by the Frenchman Pierre Auger in 1925 and won him the Nobel Prize for Physics. Since the discoverer was French, we pronounce his name to sound like "Ogay" with a soft *g* as in "beige." In either case the energy of the emission is *characteristic* of the difference in energy of the two electron shells involved and so 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 4.7.

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 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 auger electron spectrometer (AES). More recently, however, we've found ways to detect the Auger signal in ultra-high vacuum (UHV) TEMs and so we'll discuss it in Section 4.3.C below.

You need to know several aspects of the ionization process to understand why the characteristic X-ray signal is so useful and what it takes to generate it:

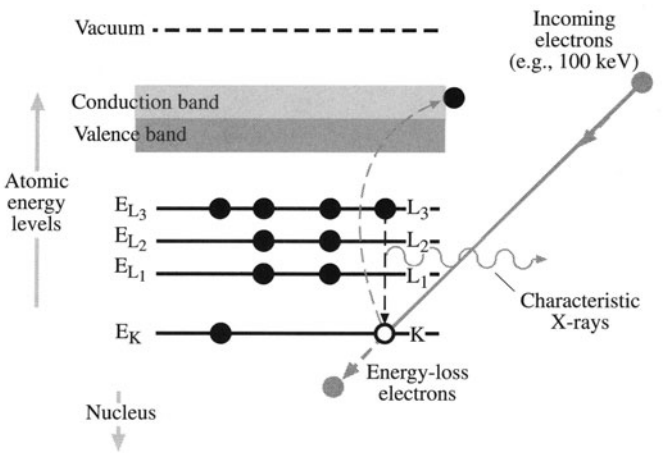

Figure 4.2. The ionization process. An inner (K) shell electron is ejected from the atom by a high-energy electron. When the hole in the K shell is filled by an electron from the L shell, characteristic K_α X-ray emission occurs. The beam electron loses energy but continues on through the specimen.

- What are *electron shells?*
- 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, and so on; we used this terminology in Figure 4.2. All the shells (except the K shell) may themselves have subshells. We name the characteristic X-rays in terms of the shell being filled and the shell from which the electron comes. (The K, L, etc. terminology was first introduced by Charles Barkla, an early X-ray spectroscopist. 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 in 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 more complex because we differentiate the α X-rays in terms of α_1 and α_2, depending from which subshell of the outer shell the electron falls 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. But for X-ray detection in the TEM you don't need to worry about too many details because, as you'll see later, we 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 need to remember. Much more detail is given in books on X-rays and X-ray spectrometry, e.g., Williams (1990).

Not all electron transitions are equally probable and this is taken into account by the "weights" of the lines which are given in Table 4.1. These weights are only important within a given K, L, or M family and not between families, because experimental conditions affect each family differently. In microanalysis we only use the most intense lines, usually the α lines (or, if we can't resolve them, we use the α and β lines). This will become more obvious when you've learned about X-ray qualitative analysis in Chapter 34.

Critical ionization energy: The electron beam has to transfer an amount of energy greater than a critical value to the inner-shell electron to ionize the atom. This energy is called the critical ionization energy (E_c); if we're going to generate X-rays, then the beam energy E_0 must be greater than E_c. The value of E_c increases as the electrons are more tightly bound to the nucleus, so the innermost shell (K) has a higher E_c than the L shell, and so on. Atoms with higher Z have more protons and therefore have a higher E_c. You can see this effect if you go and look at Figure 1.4, 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. For a complete list you have to find a reference text such as Bearden's Tables (Bearden 1964). Such a list is also invaluable in EELS since the E_c values correspond to the positions of peaks in the energy-loss spectrum which, as we'll see in Chapter 38, can be used to identify uniquely the presence of a particular ionized atom in the specimen.

The cross section for ionization (σ) 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. What we have to take into account, however, is a parameter called the overvoltage, U, which is the ratio of the beam energy E_0 to E_c. The cross section varies with U as shown in Figure 4.4, and what this figure tells you is that if E_0 is close to E_c then there isn't much chance of ionization. Usually in the TEM, E_0 is ≥ 100 keV and E_c is < 20 keV, so U is greater than 5 and the ionization cross section is pretty constant. Despite this 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

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

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:

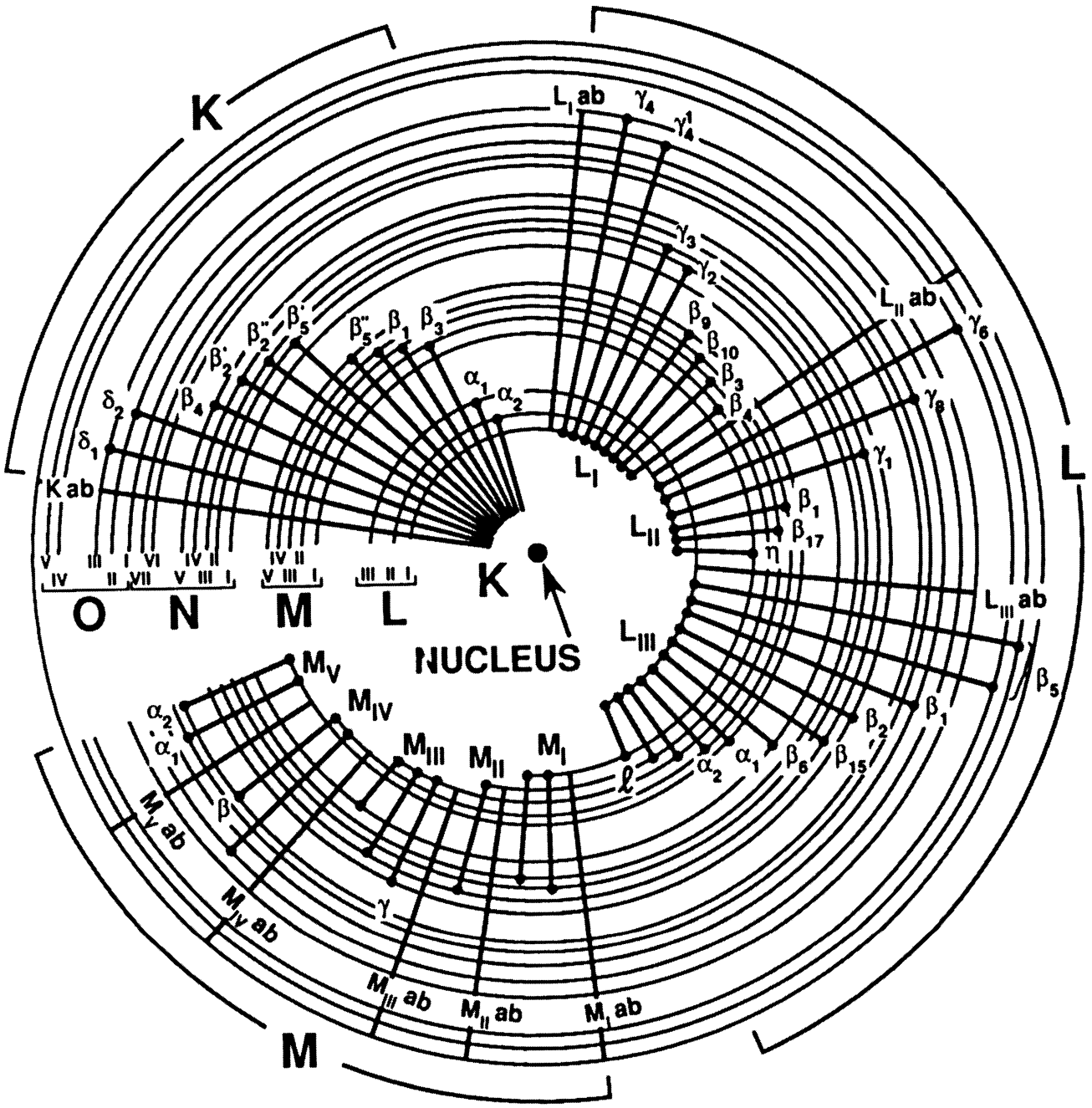

Figure 4.3. The complete range of possible electron transitions that give rise to K, L, and M characteristic X-rays. Not all these X-rays are detectable by EDS in the TEM.

- The electron that ionized the atom is deviated only through a small angle (<~10 mrads).
- The resultant characteristic X-ray is emitted uniformly over 4π sr.

As with the Rutherford cross section, the simple Bethe expression needs to be corrected for the effect of relativity at TEM electron energies, and this means substituting the term $m_0v^2/2$ for the beam energy and introducing a standard relativistic factor, β ($=v/c$)

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

Table 4.1. Weights of Lines (Approximate)[a]

K_α	(1)	K_β	(0.1)		
$L_{\alpha 1,2}$	(1)	$L_{\beta 1}$	(0.7)	$L_{\beta 2}$	(0.2)
$L_{\gamma 1}$	(0.08)	$L_{\gamma 3}$	(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)		

[a]The weights are given in parentheses.

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, and Powell (1976) gives a good review.

The X-ray energy/wavelength: X-rays are electromagnetic radiation and so we usually think of them 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 should 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; it 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 $h\nu$, where h is Planck's constant and ν is the frequency, and in order to express this energy in electron volts we equate it to E, where E is the X-ray energy.

Thus

$$E = h\nu = \frac{hc}{\lambda} \qquad [4.3]$$

Now since h and c are constants we can substitute, and we find that

$$\lambda = \frac{1.24}{E} \qquad [4.4]$$

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 in eV) that we derived back in Chapter 1 and you can easily confuse the two, so beware!

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. 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, H. Moseley (1914). 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

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

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 out in small "slide rules" by the manufacturers of X-ray spectrometers.

If you compare E_c and the X-ray energies you'll see that they are not identical. The X-ray energy E_K or E_L is invariably less than E_c. This is 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 shell. This hole must also be filled by another electron, and so on, until eventually a free electron from the conduction or valence band fills the last hole in one of the inner shells. So the atom returns to ground state by a cascade of transitions, depending on the complexity of the electronic structure of the atom.

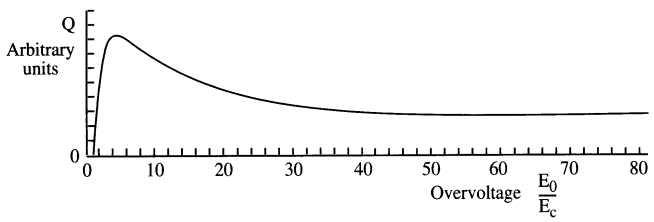

Figure 4.4. The variation of the ionization cross section with overvoltage. Ionization is most probable if the beam energy is ~5× the critical ionization energy. The cross section decreases, but not substantially, at higher overvoltages, typical of a TEM.

An example: A Cu K shell electron requires 8.98 keV of energy for ionization (E_c = 8.98 keV). One possible sequence by which this energy 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). The X-ray energies therefore total 8.978 keV and the remaining 2 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 a phonon (see below).

The possible variations are enormous and affected by such things 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 another atom, in which case the energy of the X-ray can be shifted slightly (<~5 eV). Such detail is well beyond what you need to know, but for any masochists among you the book by Dyson (1990) goes into the explicit details of this complicated subject (and our knowledge isn't complete by any means).

Fluorescence yield: Remember that an ionized atom does not have to lose energy by giving off a characteristic X-ray but can also emit an Auger electron. 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 approximate expression for ω gives

$$\omega = \frac{Z^4}{a + Z^4} \qquad [4.6]$$

where $a \approx 10^6$ for the K shell. This is only an approximation but is still a formidable dependence on Z. It predicts that, for carbon (Z = 6), ω is ~ 10^{-3} and, for Ge (Z = 32), ω is ~ 0.5. This means you have to ionize 1000 carbon atoms before you get a single C K_α X-ray generated but only 2 atoms for Ge. 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 detect light elements; you should use EELS (see Part IV).

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 is decelerated by the Coulomb (charge) field of the nucleus, it emits an X-ray. Since the electron can suffer any amount of deceleration depending on the strength of its interaction, then these X-rays can have any energy up to the beam energy. Such X-rays produced as the electron decelerates 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 (1923). This expression is often used for thin TEM specimens, although it was originally derived for bulk specimens. It is common to use the Kramers cross section to predict the bremsstrahlung production rather than the probability of interaction. Thus

$$N(E) = \frac{KZ(E_0 - E)}{E} \qquad [4.7]$$

where $N(E)$ is the number of bremsstrahlung photons of energy E, produced by electrons of energy E_0; K is the

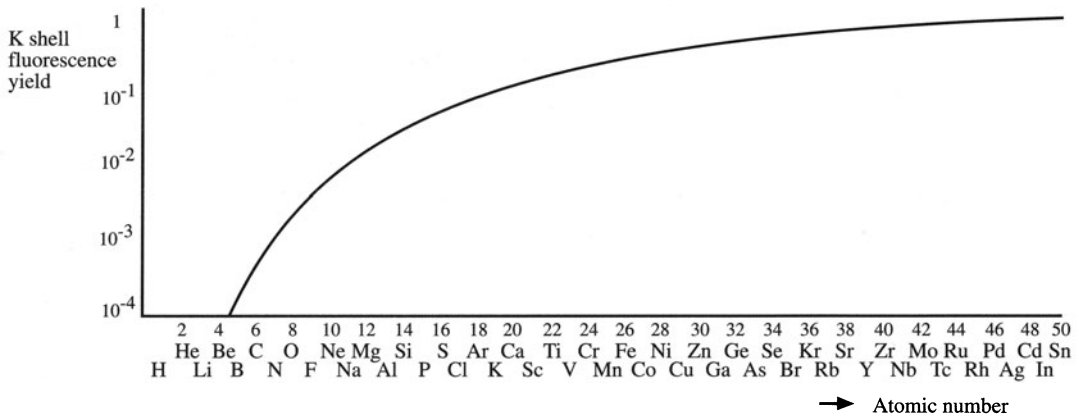

Figure 4.5. Fluorescence yield for K shell X-rays as a function of atomic number. Note the rapid decrease at low atomic numbers. X-rays from elements below Be are undetectable.

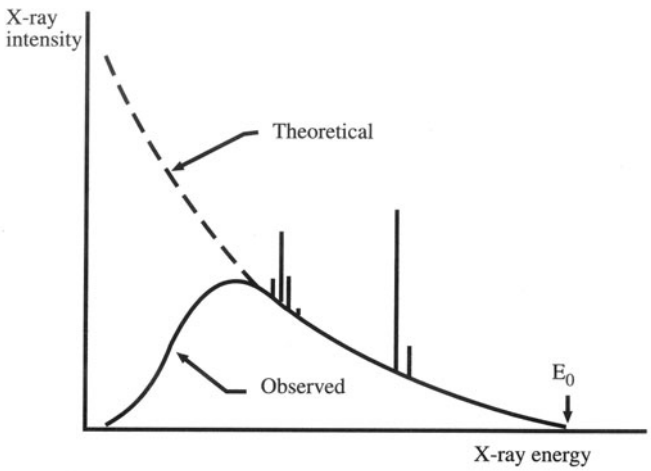

Figure 4.6. The bremsstrahlung X-ray intensity as a function of energy. The generated intensity increases rapidly at low energies but very low energy bremsstrahlung is absorbed in the specimen and the detector, so the observed intensity drops to zero. E_0 is the energy of the electrons that cause the X-ray emission. Two families of characteristic lines at specific energies are also shown superimposed on the bremsstrahlung.

Kramers constant and Z is the atomic number of the atom. This relationship predicts that it is far more likely that the braking event 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 is a function of energy as shown in Figure 4.6. In contrast to the isotropic emission of the characteristic X-rays, the bremsstrahlung is highly anisotropic, showing strong forward scatter which increases as E_0 increases.

The bremsstrahlung has a continuous energy spectrum on which the characteristic X-rays we just talked about are superimposed, as also shown schematically in Figure 4.6 and realistically in the experimental spectrum back in Figure 1.4. Since the characteristic X-rays have a narrow energy range, they appear as peaks in the spectrum at specific energies. The bremsstrahlung intensity depends on the average Z of the specimen and this is most useful to biologists who are interested in this aspect of their specimen. But materials scientists generally dismiss the bremsstrahlung as a useless background signal which only obscures characteristic lines. We'll come back to the X-ray spectrum in more detail in Chapter 32.

4.3. SECONDARY ELECTRON EMISSION

Secondary electrons (SEs) are electrons in the specimen that are ejected by the beam electron. They can be discussed as three distinct groups:

- If the electrons are in the conduction or valence bands then it doesn't take much energy to eject them, and they are called "slow SEs" with energies typically below about 50 eV.
- If the electrons are strongly bound inner-shell electrons they are less readily ejected, but when they are thrown out of their shells they can have a significant fraction (up to about 50%) of the beam energy, and they are then called "fast secondary electrons," or FSEs.
- If the electrons are ejected from an inner shell by the energy released when an ionized atom returns to ground state, then these secondary electrons are called Auger electrons. The process is often termed a "nonradiative transition" and energy undergoes "internal conversion" (which is not quite a religious experience).

Until quite recently SEs were only considered in relation to SEM, where they are used to form the images which are so sensitive to surface topography. We'll now discuss each of these signals and their relative importance in the TEM.

4.3.A. Slow Secondary Electrons

Slow 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. But 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 finding increasing use in STEMs, where they 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 31.

SE images in a STEM have much better resolution than SE images in low-kV SEMs.

We'll discuss several reasons for this in Chapter 31. Recent developments in high-resolution field emission gun (FEG) SEMs have produced SE image resolution better than 1 nm at 30 kV, and a STEM at 100 kV can offer simi-

lar or better resolution even without an FEG, so the slow SEs are very useful. (We discuss FEGs in Chapter 5.)

The number of slow SEs with energies >~50 eV is close to zero and rises to a maximum at about 5 eV. 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 SE 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 reflected light images we are accustomed to seeing with our eyes.

4.3.B. Fast Secondary Electrons

Fast secondary electrons (FSEs) are high-energy electrons which are generated in the specimen; they are high-energy because they receive a large fraction of the beam energy (Joy 1984). From the cross-section data in Figure 4.1 you can see that they should be an order of magnitude more probable than slow SEs. At the low beam energies we use in an SEM, FSEs aren't a problem, so nobody bothers about them. However, in a TEM, FSEs can have energies of ~50–200 keV, in which case they not only travel significant distances within the specimen, but they may also escape from deep within the specimen. As a result, FSEs degrade the spatial resolution of microanalysis in AEMs and they also generate significant numbers of X-rays which can cause problems in quantifying X-ray data, particularly at intermediate voltages. So FSEs aren't an image resolution problem, but rather a problem for chemical analysis.

> FSEs are generally both unavoidable and undesirable. We don't use them to form images or to give us spectroscopic data, but they may degrade the quality of the latter.

This phenomenon is only just beginning to be understood, but it may well turn out to be a major limitation of intermediate voltage microanalysis.

4.3.C. 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 ground state. Figure 4.7 shows how an ionized atom ejects an outer-shell (Auger) electron, and it's instructive to compare with Figure 4.2 for

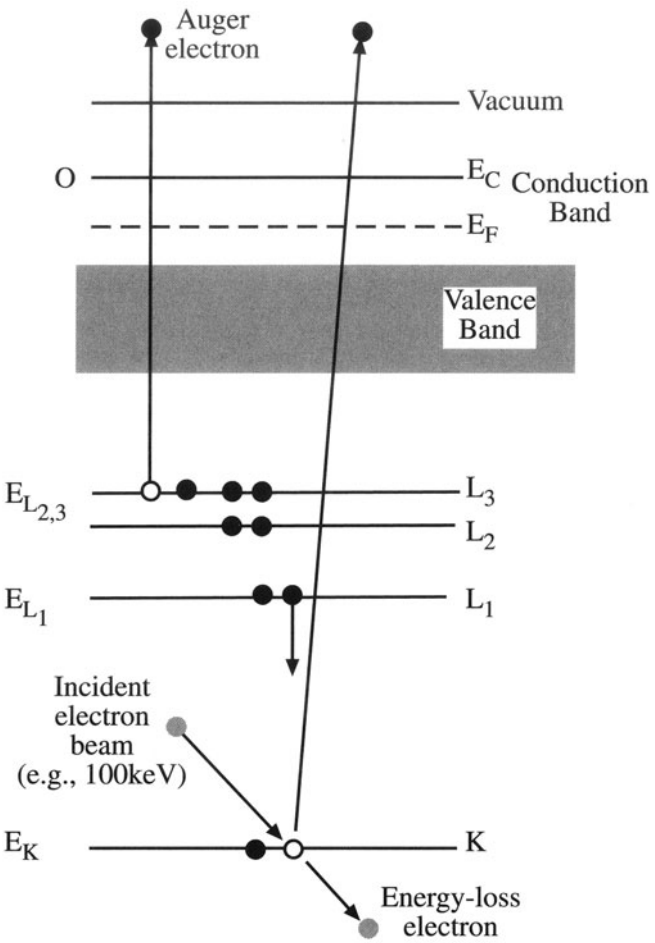

Figure 4.7. The process of inner (K) shell ionization and subsequent Auger electron emission. The energy released when the L_1 electron fills the hole in the K shell is transferred to an electron in the $L_{2,3}$ shell which is ejected as a $KL_1L_{2,3}$ Auger electron.

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. So the Auger electron has a characteristic energy which is dependent on the electronic structure of the ionized atom and is almost identical to the energy of the alternative characteristic X-ray.

> The Auger process is favored in atoms with a small binding energy, 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.

The Auger electrons that do escape come from very close to the surface. Consequently they contain surface chemical information and AES is a recognized surface

chemistry technique. Now you might ask why light-element X-ray analysis in the TEM is not just a surface technique, because of the similarity in energy between Auger electrons and characteristic X-rays. 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.

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 common, the Auger signal is of more interest and a few microscopists are reporting combined Auger/STEM results. However, since it is not simple to attach an Auger system to a STEM these instruments are still quite 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 which 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.

If you don't do anything, the electrons and holes will recombine, and in doing so give off light; this process is termed cathodoluminescence (CL).

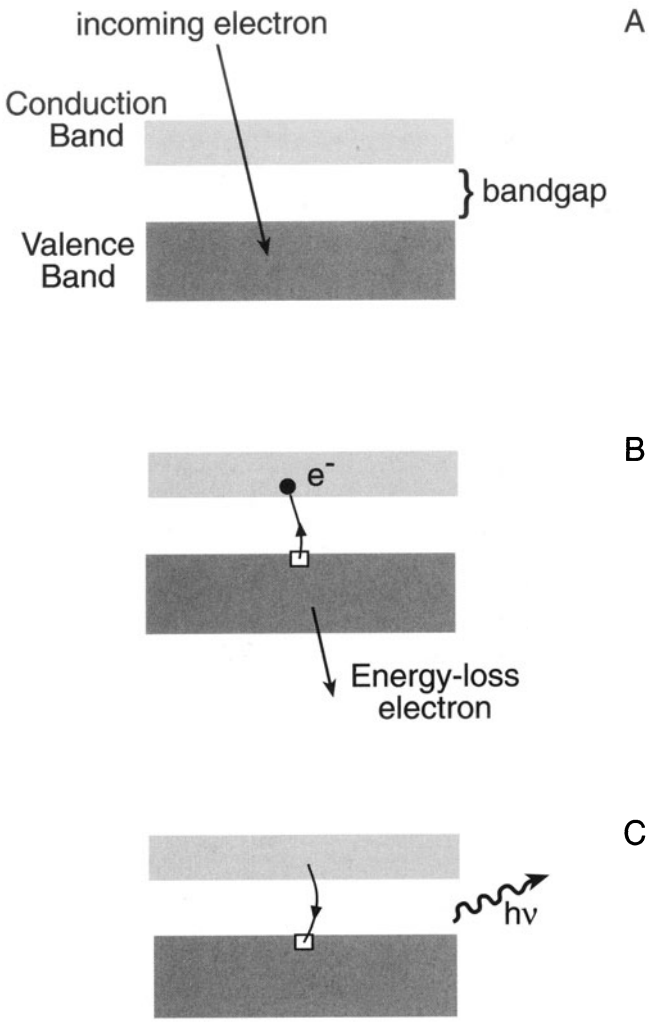

Figure 4.8. Schematic illustration of CL: (A) Initial state before a beam electron interacts with valence-band electrons. (B) A valence-band electron is excited across the gap into the conduction band, leaving a hole in the valence band. (C) The hole is filled by a conduction-band electron falling back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

The process is shown schematically in Figure 4.8. The photon has a frequency equal to the energy of the gap (E_G) divided by Planck's constant (h), and so if the band gap varies for some reason there will be a spectrum of light given off, or 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.

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 under the internal bias. You can pick up the signal if you ground the specimen through a picoammeter. In this situation, the specimen is acting as its own detector! The current you then detect is sometimes called the "electron beam induced current" or EBIC signal, and if you detect it and use it to form an image then you are doing "charge-collection microscopy" or 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, in general, all these imaging modes are rare and mainly limited to studies of semiconductors (although some minerals also exhibit CL). We'll describe CL detectors in Chapter 7 and the images in Chapter 31. Just remember that CL and CCM are powerful, but rather specialized techniques.

4.5. PLASMONS AND PHONONS

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

> Plasmons are collective oscillations of free electrons that occur when the beam electron passes through the free electron "gas."

We can consider plasmons as analogous to sound waves, since they are longitudinal oscillations 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 less than ten nanometers. If you go back to Figure 4.1 you'll see that the plasmon process has the largest cross section and it's by far the most common inelastic interaction occurring in materials. 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 thus a high free-electron density. The plasmon oscillation is quantized and the mean free path for plasmon excitation is of the order of 100 nm. As we'll see in Chapter 39, this makes the number of plasmon excitations a useful way to measure the specimen thickness. Also, the plasmon energy is a function of the free-electron density and this changes with composition, so the plasmon excitation process is chemically dependent, although we rarely use it for microanalysis.

A differential cross section for plasmon excitation was given by Ferrel (1956)

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

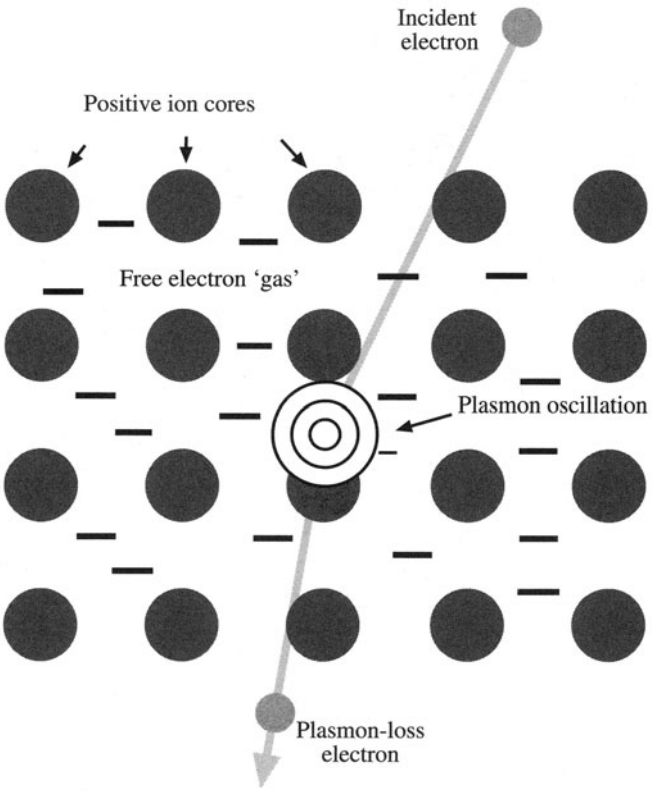

Figure 4.9. Schematic diagram of a high-energy beam electron exciting a plasmon oscillation in a free electron gas that permeates the ion cores in a metal.

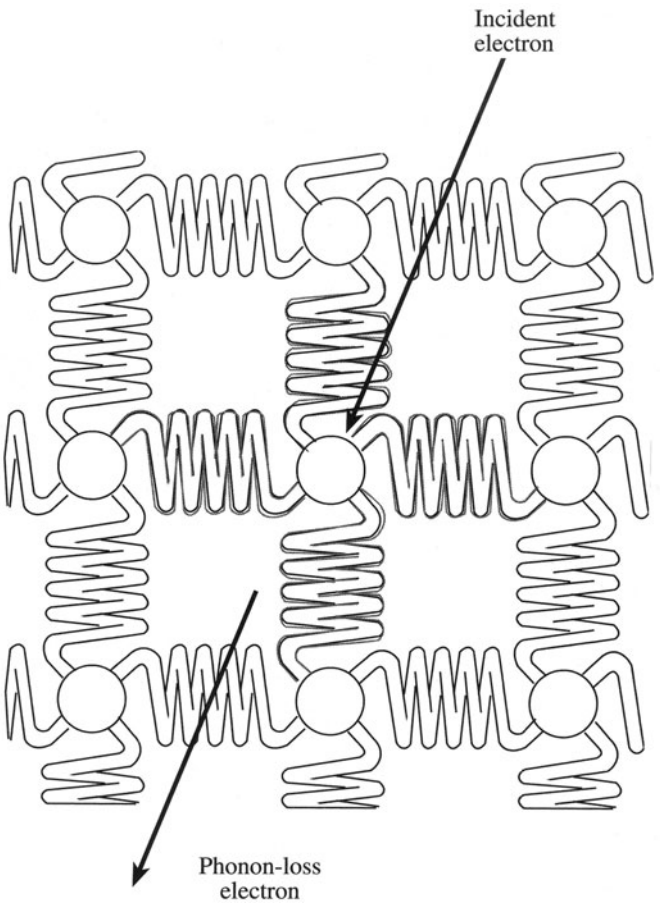

Figure 4.10. An illustration of the crystal lattice as a group of atoms linked elastically by springs. The bonds vibrate when struck by a high-energy electron creating lattice oscillations or phonons. The lattice absorbs heat by creating phonons, so phonon excitation is equivalent to heating the specimen.

where a_0 is the Bohr radius, θ is the scattering angle, and θ_E is the so-called "characteristic scattering angle" given by $E_P/2E_0$. 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 the 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, we can visualize the atoms as all linked 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 interband transitions 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 sample, even amorphous ones in which a crystal "structure" as such does not exist. Typically, a phonon vibration causes a very small energy loss of <0.1 eV but the phonon scattered electrons are scattered out to quite large angles (5–15 mrads), and these electrons account for the diffuse background intensity present between the Bragg spots in diffraction patterns. Phonon scattered electrons carry no useful microchemical information, nor do they carry contrast useful to the microscopist.

The phonon scattering cross section is not important to know exactly, but it is useful to remember that phonon scattering increases with Z with a dependence of approximately $Z^{3/2}$, which is rather less strong than for true elastic scattering. Also, because of the effect of temperature on atomic vibration, the phonon scatter is increased 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 clear diffraction patterns. The mean free path for phonon scatter 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 ~ 2–3×.

Phonons are oscillations where all the atoms in the crystal lattice vibrate collectively. Such vibrations of the atoms are equivalent to specimen heating. You can reduce the number of phonons by cooling the specimen.

We don't use either plasmons or phonons directly to form images, but we do detect the electrons that caused them, and we'll discuss the (rather limited) uses of plasmon energy-loss electrons in Chapter 40.

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, that of 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 mainly on the beam energy. Certain materials are more susceptible than others, but in the end, you can damage virtually anything that you put into the TEM. 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 our specimen changes it. Once the structure or the chemistry is changed, the specimen is not representative of the parent material and interpreting TEM images, diffraction patterns, and spectra becomes more difficult and eventually impossible. 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 use electron damage to emulate other forms of radiation damage. Generally, however, beam damage is undesirable.

Damage takes one of two principal forms:

- *Radiolysis:* Inelastic scattering (mainly ionization) breaks the chemical bonds of certain materials such as polymers and alkali halides.
- *Knock-on damage:* Direct displacement of atoms from the crystal lattice creates point defects.

We will see that, paradoxically, the former is reduced at higher beam energies while the latter is increased, so there is sometimes no way around the problem.

Phonons represent heat in the specimen and heat is a major source of damage to polymers. Electron–electron interactions can give rise to chemical bonding changes through *radiolysis;* this process is common in polymers and alkali halides. Atomic displacement is termed "knock-on damage" within the specimen or "sputtering" if it occurs at the surface of the thin foil, and these processes are ubiquitous if E_0 is high enough. 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 is describe the fundamental processes in different materials, explain how you can determine if your specimen is being damaged, and how you can minimize or eliminate the problem. First, however, we need to know the terms we use to measure beam damage.

4.6.A. Electron Dose

In the TEM we define the electron dose as the charge density (Cm^{-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 dose is defined by the Gray (Gy), which is the absorption of 1 joule 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 in the TEM are well above lethal doses for human tissue. While this is another warning about the dangers inherent in the 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 experimental variables that can affect the result, such as the thermal conductivity, thickness, and surface condition of the specimen and the beam size, energy, and current. Hobbs (1979) 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.

In addition to these practical steps, beam heating is 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.

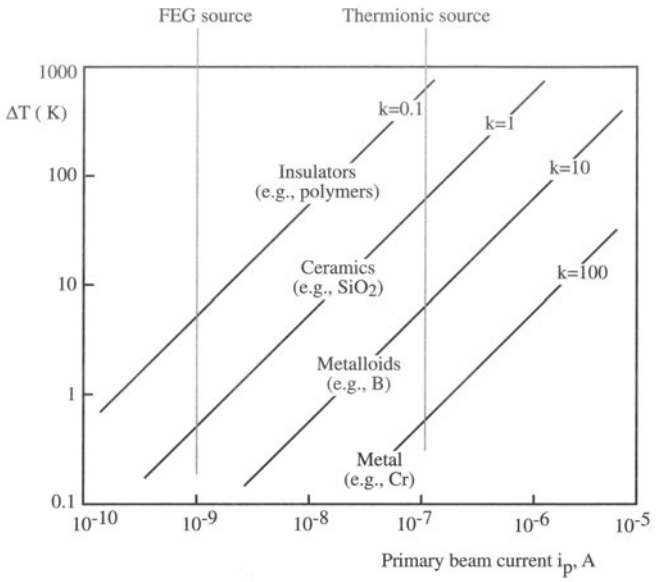

Figure 4.11. The increase in specimen temperature as a function of the beam current and the thermal conductivity k, in $Wm^{-1}K^{-1}$ of the specimen. Typical materials are noted, but should not be considered representative, since k varies substantially in any class of materials.

Beam heating for metals is negligible under standard TEM conditions, but if thermal conduction is poor, then heating can be quite substantial. Small ceramic particles may be heated by the beam to temperatures of ~1700°C.

4.6.C. Beam Damage in Polymers

Polymers are most sensitive to the electron–electron interactions which, by one means or another, generate phonons or lattice vibrations. These phonons heat the specimen and break the bonds, creating new structures. This process is called 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 cross link to form a new structure.

A break formed this way in the polymer chain is known as scission. Generally, polymers show a tendency either to break down or to cross link. In the former case the polymer will continue to lose mass under irradiation, while in the latter the polymer eventually becomes mainly a mass of carbon. Mass loss can sometimes be measured directly in the TEM by electron spectrometry, and it can also manifest itself as major dimensional changes in the specimen.

Mass loss ultimately results in a hole forming in the illuminated area of the specimen; the image contrast will usually change before the hole appears!

If the polymer was crystalline originally, then radiation damage results in a loss of crystallinity, and you can measure this quantitatively either from the loss of diffraction contrast in the image or the loss of intensity in the diffraction pattern and the gradual appearance of an amorphous pattern. Sometimes the crystal structure can be preserved by staining. However, whenever you stain a specimen you affect its structure and mask the chemistry, so this isn't ideal.

There are several methods you can use to minimize beam damage in polymers (Sawyer and Grubb 1987):

- Use low-dose imaging techniques (see Chapter 30).
- Operate at the highest kV.
- Cool the specimen to liquid-N_2 temperatures or lower.
- Coat the specimen with a conducting metal film.
- Use STEM imaging (Section 22.3).
- Do all of the above if necessary.

4.6.D. Beam Damage in Covalent and Ionic Crystals

In covalent and ionic materials such as ceramics and minerals, radiolysis can occur which changes the specimen chemistry and possibly the structure through a series of reactions driven by the electron beam. The major inelastic interaction is that of interband transitions similar to those responsible for CL. The interband 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, can create an anion vacancy and a cation interstitial. In a similar process crystalline quartz can be amorphized. Often the process can result in the formation of new compounds which can be identified by electron diffraction and AEM. The formation of Ag from Ag halides in the photographic plate is an example of radiolysis.

We can't stop radiolysis simply by cooling or coating the specimen, since it isn't affected by heat transfer considerations. We can use higher voltages to lower the cross section for the electron–electron interactions. The best way is to use both higher voltages and thin specimens. Nevertheless, radiolysis remains a major limitation when looking at certain ceramics and minerals, and many polymers in the TEM.

4.6.E. Beam Damage in Metals

The primary way that metals are affected is by knock-on or displacement 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).

Knock-on damage is directly related to the beam energy.

How strongly the atoms are bonded to their neighbors will also be a factor. A simple expression given by Hobbs (1979) 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 5–50 eV, but varies with bonding type. If we assume that a typical value of E_d is ~25 eV, we can determine the threshold potentials for a range of elements from Figure 4.12. From this figure it is quite evident that if you have a 400-kV intermediate voltage TEM, you can displace atoms with atomic weight below about Ti. 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, or those with particularly strong covalent bonds such as diamond. The only way to avoid displacement damage is to operate below threshold.

How can you identify displacement damage? It usually manifests itself as small vacancy clusters which appear as black-white lobe contrast or dot contrast as we showed back in Figure 1.8, or sometimes damage is discernible as dislocation loops. 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. So depending on your specimen there may in fact be no way to avoid damage of one form or another in the TEM.

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

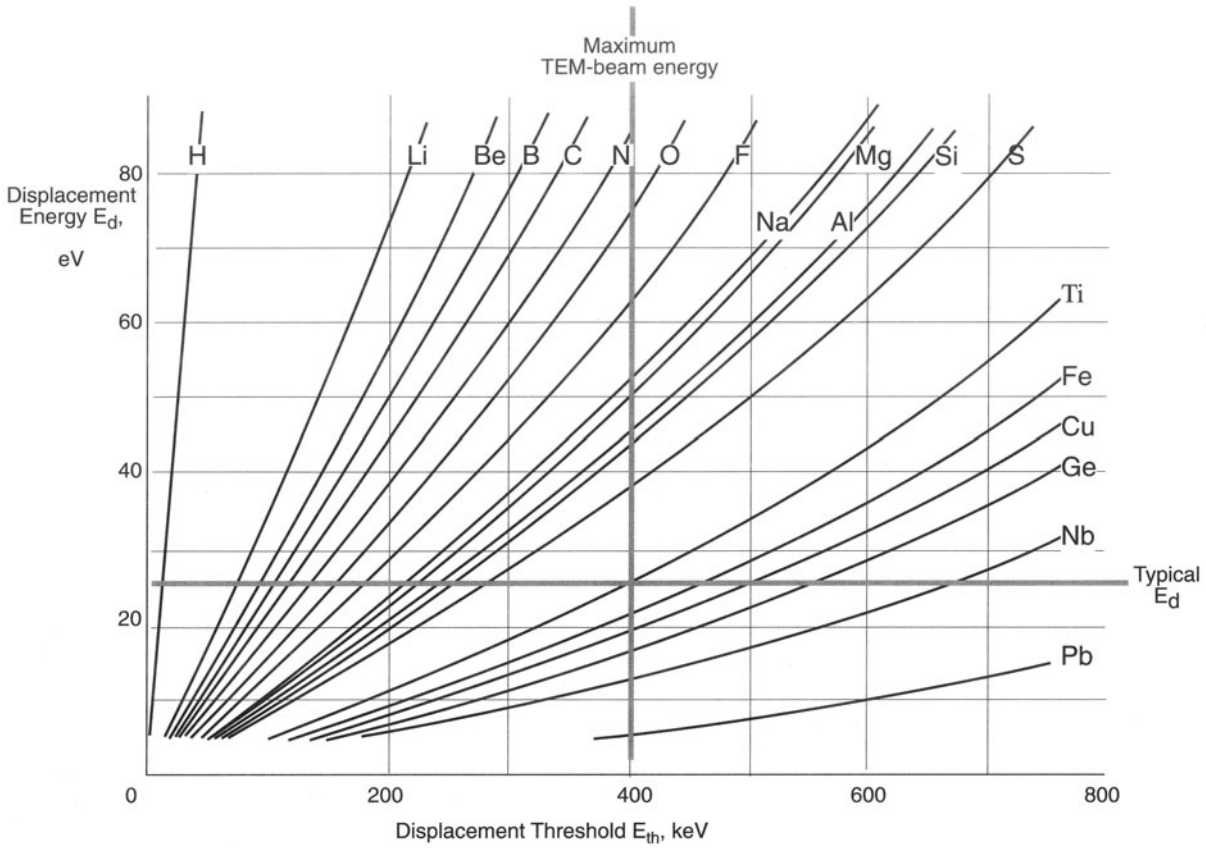

Figure 4.12. The displacement energy for a range of atoms as a function of the threshold energy (i.e., the beam energy) required for displacement damage. In a typical material E_d is ~15–25 eV, but it can vary substantially with bond strength.

Table 4.2. Comparison of Maximum Transferable Kinetic Energy (T) with Displacement and Sputtering Energies at 100, 200, 300, and 400 kV (from Zaluzec and Mansfield 1987)

	T (eV)				E_d (eV)	E_s (eV)
Element	100 kV	200 kV	300 kV	400 kV		
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
Pt	1.23	2.69	4.37	6.26	33	8–16
Au	1.22	2.67	4.32	6.2	36	9–18

occurring in nuclear reactors. A general rule of thumb was that a few minutes' exposure in an HVEM was equivalent to many years in a nuclear reactor and so accelerated studies of materials degradation 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 have seriously reduced the number of such studies, but if you want to find out about it there are reviews in the literature, such as Laidler and Mastel (1975).

Vacancies caused by displacement damage can enhance diffusion processes, and this in turn can speed diffusional transformations when they're being studied *in situ* in the HVEM. There are many other problems that can arise when doing this, and other *in situ* observations, so interpretation isn't always straightforward. The book by Butler and Hale (1981) is recommended for more facts.

4.6.F. Sputtering

The displacement of surface atoms, or sputtering, occurs in the TEM, at voltages which are about 50% less than knock-on thresholds. If your specimen is quite thick then this problem is minor, but often the specimen has to be very thin if you want the best images and the best microanalytical resolution. In these circumstances sputtering may substantially change the surface chemistry of the specimen and affect quantitative microanalysis. Table 4.2 lists typical sputtering threshold energies (E_s) compared with displacement thresholds (E_d(eV)) and, as you can see, there is cause for concern even at 100 kV.

CHAPTER SUMMARY

Inelastic scatter transfers energy to the specimen, generating a lot of useful signals which we can use to form different images of the specimen or get spectroscopic information about its chemistry and electronic structure. Unfortunately, the same processes transfer heat to the specimen which can be disastrous for certain materials such as polymers. To minimize heat transfer, higher voltages should be used, but eventually knock-on and sputtering damage occur which create defects and change the surface chemistry of all materials.

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