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.

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.

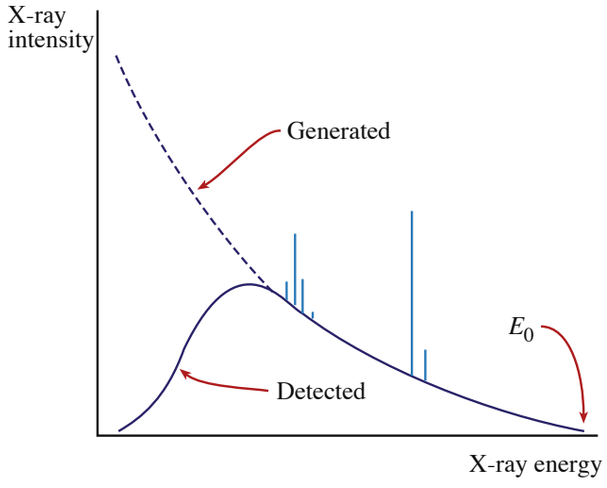


FIGURE 4.6. The bremsstrahlung X-ray intensity as a function of energy. The generated intensity increases rapidly with decreasing X-ray energy but at energies $<\sim 2$ keV the bremsstrahlung is absorbed in the specimen and in any detector being used so the observed intensity in the detected spectrum 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.

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 $<\sim 50$ 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.

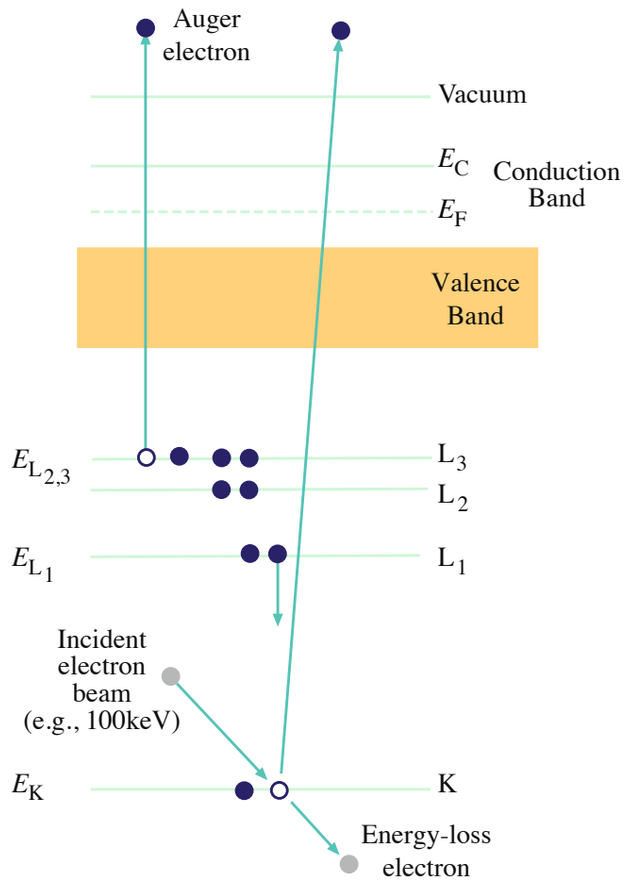


FIGURE 4.7. The process of inner (K) shell ionization and subsequent Auger-electron emission. The energy released when the L_1 electron fills the hole in the K shell is transferred to an electron in the $L_{2,3}$ shell which is ejected as a $KL_1L_{2,3}$ Auger electron.

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.

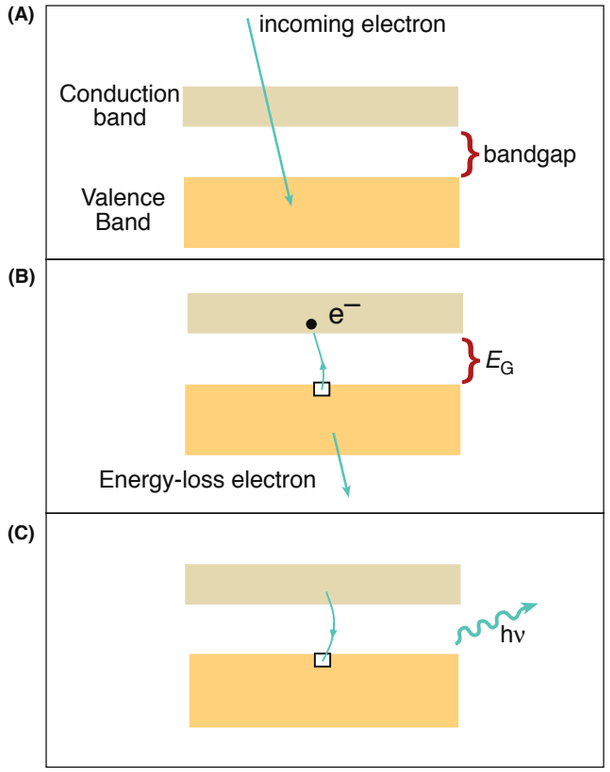


FIGURE 4.8. Schematic illustration of CL. (A) Initial state before a beam electron interacts with valence-band electrons. (B) A valence-band electron is excited across the gap into the conduction band, leaving a hole in the valence band. (C) The hole is filled by a conduction-band electron falling back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

Basic operation of the TEM imaging system

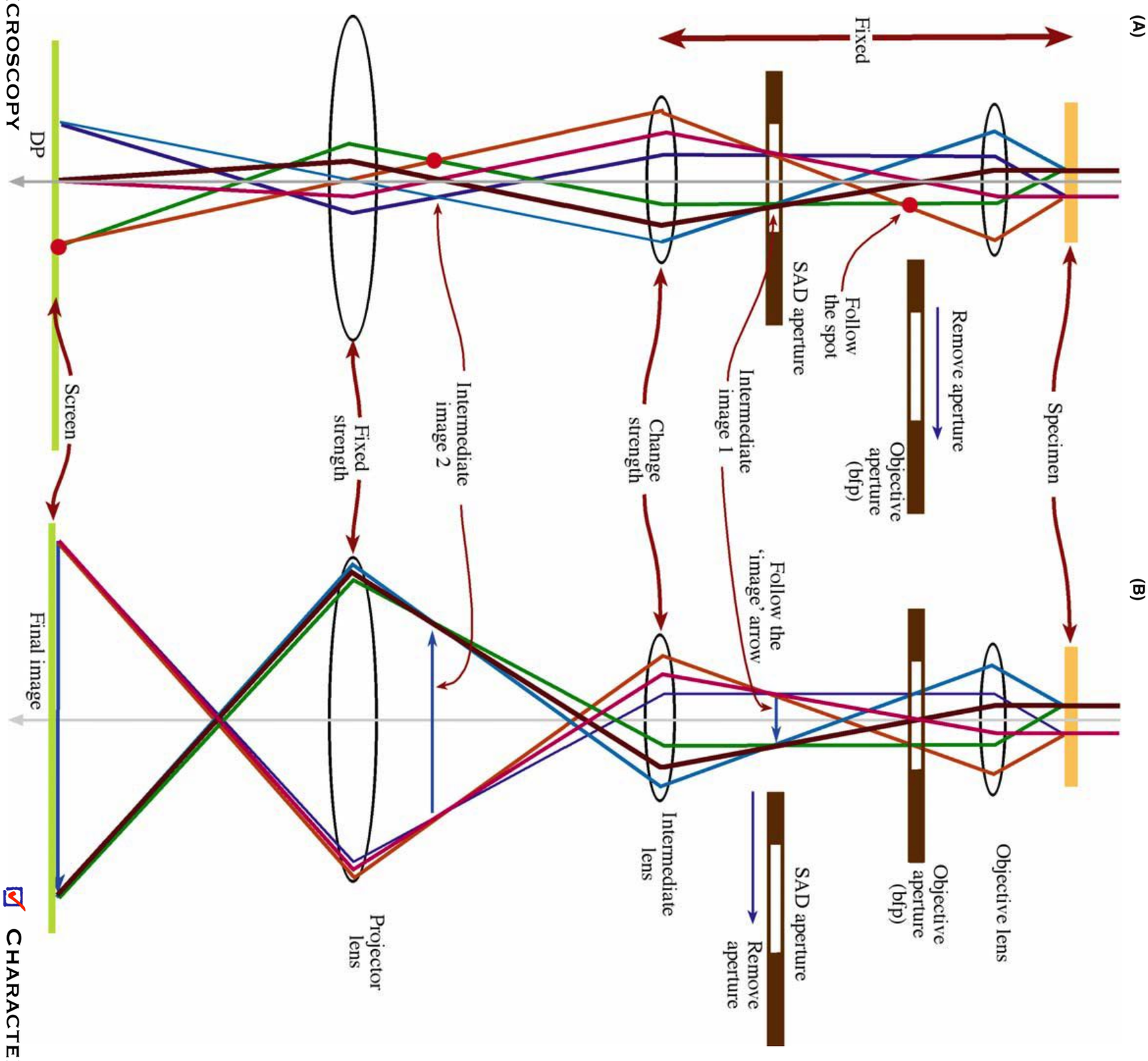
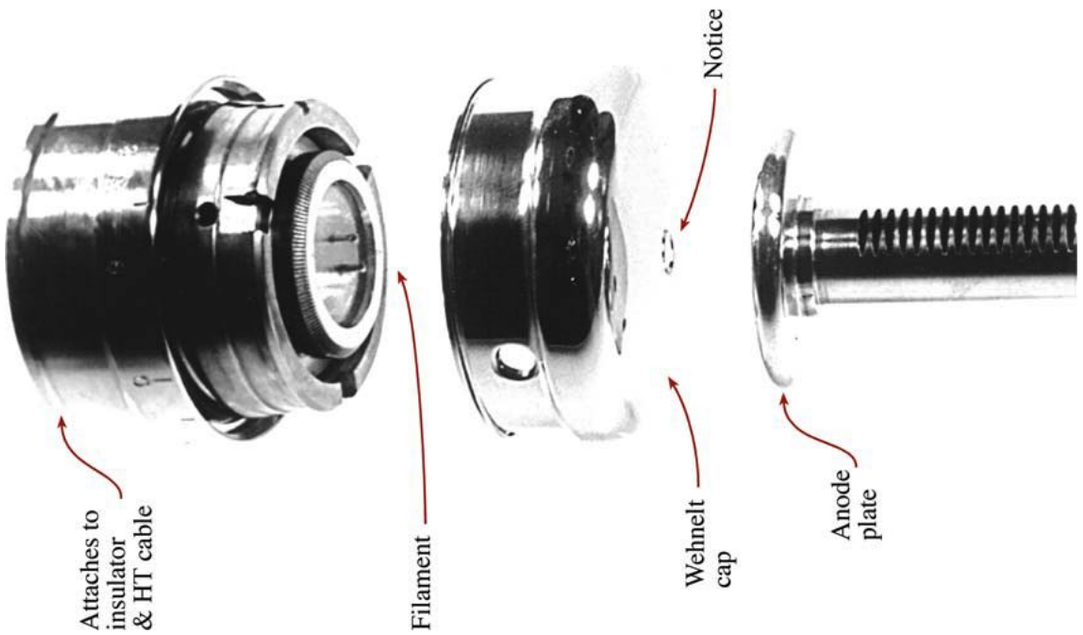


FIGURE 9.12. The two basic operations of the TEM imaging system involve (A) diffraction mode: projecting the DP onto the viewing screen and (B) image mode: projecting the image onto the screen. In each case the intermediate lens selects either the BFP (A) or the image plane (B) of the objective lens as its object. The imaging systems shown here are highly simplified. Most TEMs have many more imaging lenses, which give greater flexibility in terms of magnification and focusing range for both images and DPs. The SAD and objective diaphragms are also shown appropriately inserted or retracted. NOTE: This is a highly simplified diagram showing only three lenses. Modern TEM columns have many more lenses in their imaging systems.



4.1.1 The electron gun

At the top of the instrument, about a metre above the seated operator's head, is the electron gun. The most common types of TEM have thermionic guns (section 2.3) capable of accelerating the electrons through a selected potential difference in the range 40–200 kV. The appropriate electron energy depends upon the nature of the specimen and the information required. For some applications, particularly if the specimen is relatively thick or very high resolution is required, it is an advantage to use much higher electron energies. A range of *medium voltage* (300–400 kV) and *high voltage* (600–3000 kV) microscopes have been developed for these purposes. The very high energy microscopes have become rarer as the resolution of lower energy microscopes has improved through better lens design and as specimen preparation techniques have developed. Furthermore, field emission guns have now developed to the point that very fine electron beams can be produced (of the order of 1 nm at the specimen) and they are becoming increasingly widespread.

4.1.2 The condenser system

Below the electron gun are two or more condenser lenses. Together, they demagnify the beam emitted by the gun and control its diameter as it hits the specimen (Figure 4.2). This enables the operator to control the area of the specimen which is hit by the beam and thus the intensity of illumination. An aperture is present between the condenser lenses (the *condenser aperture*) which can be used to control the convergence angle. At their simplest the condenser controls can be thought of as brightness controls but in fact they

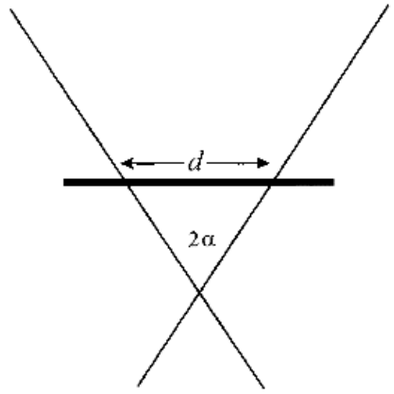


Figure 4.2 A beam coming to focus just after the specimen ('underfocused') illuminates an area of diameter *d*. The beam convergence is α.

permit a wide range of control over the region of specimen which is 'sampled' by the beam and over the type of diffraction pattern which is formed (section 3.4). It is useful to consider the widely used two-condenser illumination system in more detail. The first condenser lens (C1), often labelled *spot size*, sets the demagnification of the gun crossover (section 2.3). The second lens (C2, often *intensity*) provides control of the convergence angle of the beam leaving the condenser assembly, as Figure 4.3 shows. A parallel beam will illuminate a large area of the specimen (rays (i)); as the convergence angle is increased, the beam diameter at the specimen decreases until it reaches its minimum (rays (ii)), when the beam is focused on the specimen. As the convergence angle is increased still further, the beam focus is before the specimen and the illuminated area increases once more (rays (iii)).

The minimum possible illuminated area is controlled by the effective size of the source at the gun, the strength of C1 and the condenser aperture. It cannot of course be made any smaller than the limit imposed by diffraction at the condenser aperture and by aberrations in the condenser system.

When the beam is focused on the specimen, its convergence angle is controlled by the condenser aperture. The size of the condenser aperture also affects image quality, since the electrons which pass far from the optic axis will be strongly affected by spherical aberration (see Chapter 1). It also has a large effect on the intensity of the electron beam. The illumination provided by the condenser lens must be varied by the microscopist according to the kind of information he is trying to capture. As in most things, a balance must be sought to get the best result. Thus a diffraction contrast image is usually taken with a medium size condenser aperture, and fairly large spot size to maximize illumination (but not so large as to degrade image quality), and a close to parallel beam, to give even illumination and similar diffraction conditions (but sufficiently intense to avoid very long exposure times, which could cause problems due to specimen drift). Alternatively, a convergent beam

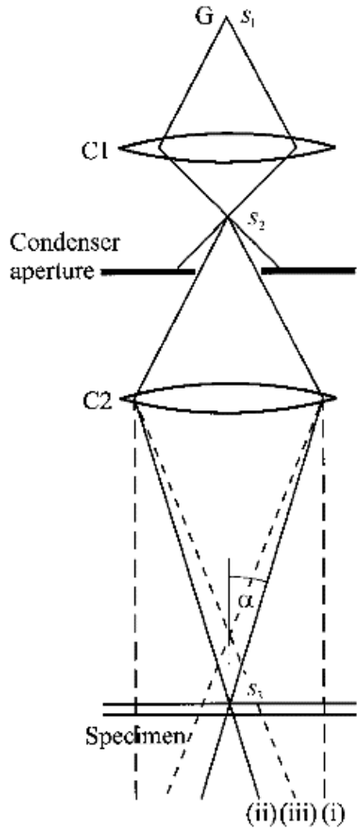


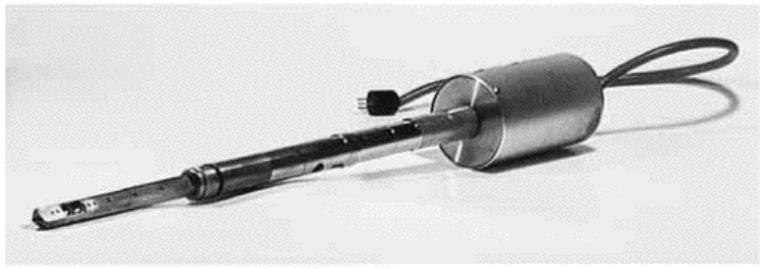
Figure 4.3 The two-lens condenser system. The spot of size s_1 at the gun crossover (G) is demagnified to s_2 by the first condenser lens C1. The second condenser lens C2 is used to focus the beam; it may also change the spot size to s_3. (i), (ii) and (iii) show underfocused, focused and overfocused beams respectively. The convergence angle α is controlled by the condenser aperture. An animated version of this diagram can be found in MATTER: Introduction to electron microscopes.

electron diffraction (CBED) pattern would need a small spot size (to reduce the effects of bending and defects in the sample), a large condenser aperture (to give a large disk in the CBED pattern) and the beam focused accurately onto the specimen using C2.

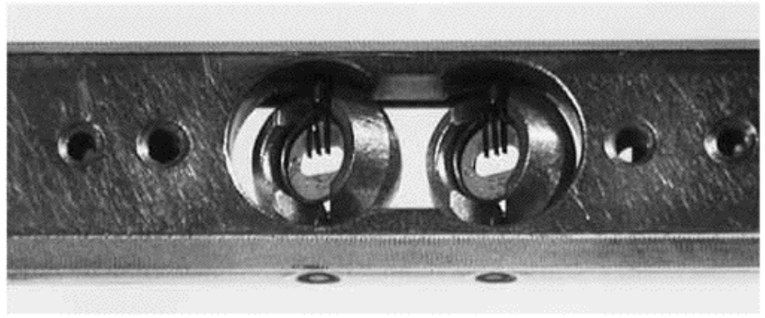
The MATTER software module 'The TEM' includes a model of a two-condenser system in which the strength of each lens can be varied independently and the effect on spot size and convergence can be observed.

4.1.3 The specimen chamber

Below the condenser lies the specimen chamber, which is one of the most crucial parts of the microscope. A very small specimen must be held in precisely the correct position inside the objective lens, but should also be



(*a*)



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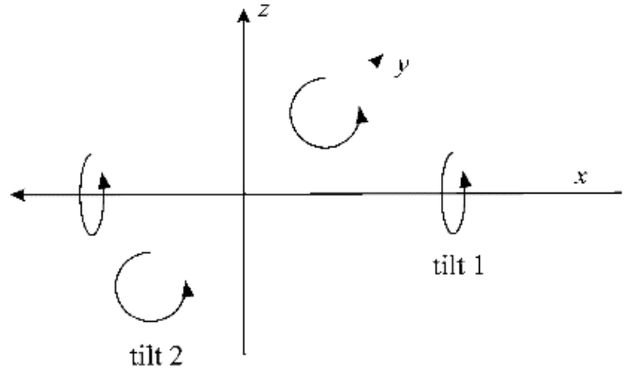

(*c*)

Figure 4.4 (*a*) A side entry double tilt holder. (*b*) A higher magnification view of the specimen cups. (*c*) The range of movements and tilts available with such a specimen holder. An animated diagram showing the effect of specimen tilt when the sample does not lie at the eucentric height is shown in MATTER: Introduction to electron microscopes.

capable of being moved several millimetres and tilted by large angles. Additionally, X-rays must be permitted to leave the area if the microscope is to be used in an analytical mode. These constraints are usually met by a side-entry specimen rod (e.g. Figure 4.4) which holds a 3 mm diameter specimen (or a smaller specimen on a 3 mm support grid) between the pole pieces of the

objective lens. The specimen rod enters the column through an airlock, and can usually be moved up to 2 mm in the x and y directions to locate the region of interest, and by a fraction of a millimetre in the z direction, in order to bring it to the object plane of the lens. It is quite easy to tilt the specimen about the long axis of the holder by up to 60 degrees by rotating the holder itself. Tilt about an axis perpendicular to this is also very desirable but is achieved with more difficulty. The mechanisms which provide all these movements and tilts must ensure that when the appropriate specimen position has been selected it does not move by more than about 0·1 nm or less while the micrograph is exposed (depending upon the magnification and type of image). A movement of 0·1 nm in 1 second is equivalent to 1 mm in four months – the specimen must clearly be extremely stable.

An important consideration is that the specimen does not move laterally when it is tilted. This can only be true if the axis of tilt accurately intercepts the optical axis of the microscope, along which the beam is travelling. It is possible to adjust most specimen holders so that one tilt is in this *eucentric* position, but normally it is not possible to also make the second axis of tilt eucentric. This means that it may be necessary to use considerable skill to set up some of the diffraction conditions described in Chapter 3 and later in this chapter.

4.1.4 The objective and intermediate lenses

The objective lens is so strong that the specimen sits within its pole pieces. The role of the objective lens is to form the first intermediate image and diffraction pattern, one or other of which is enlarged by the subsequent projector lenses and displayed on the viewing screen.

The optics of the objective lens are shown in Figure 4.5. As has been emphasized in Chapter 3, a diffraction pattern is inevitably formed in the back focal plane of the lens. The first projector lens (often called the intermediate or diffraction lens) can usually be switched between two settings, shown in Figure 4.5(a) and (b). In the *image* mode, it is focused on the image plane of the objective (Figure 4.5(a)). The magnification of the final image on the microscope screen is then controlled by the strength of the remaining projector lenses (not shown in Figure 4.5). In the *diffraction* mode the intermediate lens is focused on the back focal plane of the objective (Figure 4.5(b)) and the diffraction pattern is projected onto the viewing screen. The magnification of the diffraction pattern is controlled by the projector lenses and is usually described in terms of the effective *camera length* of the system.

An essential feature of the objective system is the aperture holder which enables any one of three or four small apertures to be inserted into the column in the back focal plane. The objective aperture clearly defines the angular range of scattered electrons which can travel further down the column and contribute to the image. Its diameter therefore controls the ultimate

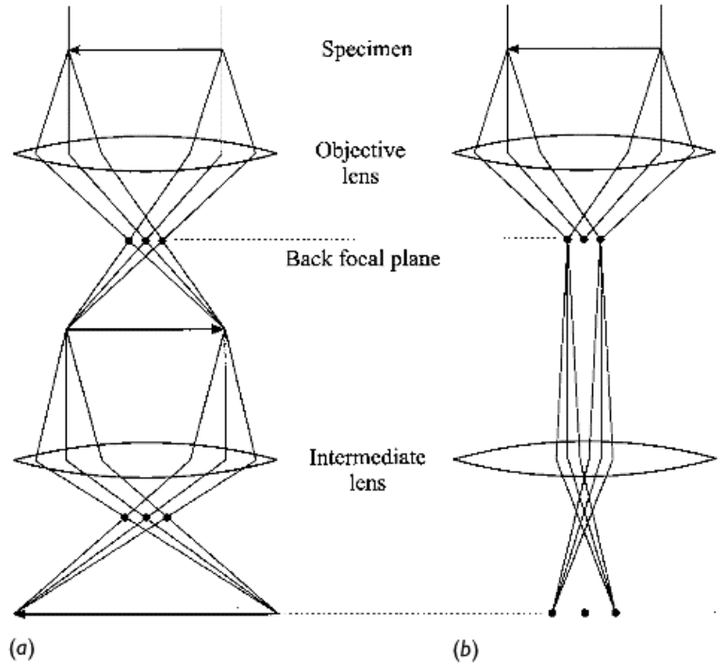

Figure 4.5 The objective and first intermediate lenses. The objective lens is focused on the specimen and forms an intermediate image as shown in (a). In imaging modes (a) the intermediate lens magnifies this image further and passes it to the projector lenses for display. In order to make the diffraction pattern visible (b), the intermediate lens is refocused on the back focal plane of the objective lens and the diffraction pattern is passed to the projector system. An animated version of this diagram together with a ray diagram can be found in MATTER: Introduction to electron microscopes.

resolution set by equation 1.7 and for high resolution a large aperture will be needed. A modern 200 kV microscope, with a spherical aberration coefficient C_s, of 1·2 mm, might show a resolution of 0·2 nm with an aperture of half-angle $4{\cdot}5 \times 10^{-3}$ radians (about a quarter of a degree).

However, for many purposes the highest resolution is not needed and the objective aperture serves a different function in controlling the contrast which will be seen in the image. In section 4.2 we consider the main contrast mechanisms available in a TEM.

4.1.5 The projector system – images

The first image produced by the objective lens usually has a magnification of 50–100 times. This is further magnified by a series of intermediate and *projector* lenses and is finally projected onto the fluorescent screen. By using three or four lenses, each providing a magnification of up to twenty times, a total magnification of up to one million is easily achieved. It is not necessary to

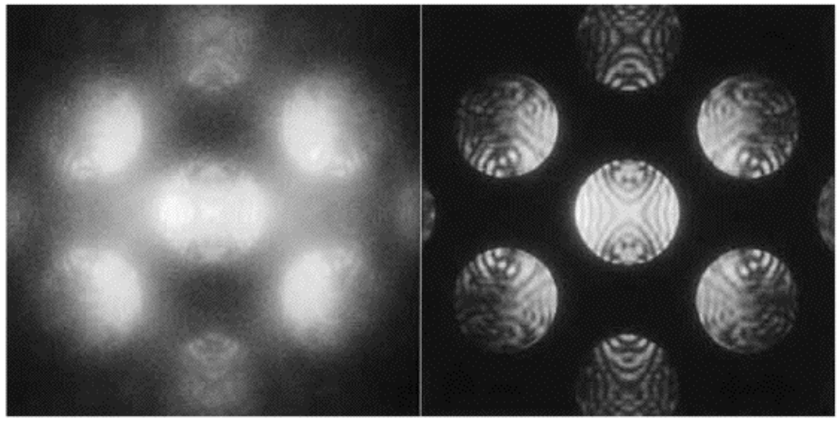

Figure 4.6 A convergent beam electron diffraction (CBED) pattern from relatively thick Si, taken with the incident beam along the [110] axis. Inelastic scattering gives a diffuse background and loss of contrast in the unfiltered image (left). An energy filter, tuned to accept only electrons which have been elastically scattered (zero energy loss electrons), removes this effect and gives a far clearer image (right). (Courtesy of C. B. Boothroyd, University of Cambridge)

use all the lenses to achieve a low magnification and in this case one or more projector lenses will be switched off.

Some specialized microscopes have an *energy filter* below the specimen, which can be tuned to allow the passage of only elastically scattered electrons or electrons which have suffered a particular energy loss. This has distinct advantages in, for example, high resolution electron microscopy (see section 4.2.4), since inelastic scattering degrades image quality. It is also useful in the quantitative interpretation of diffraction pattern intensities, since there is always a diffuse background of inelastically scattered electron intensity in an unfiltered diffraction pattern. Energy filters can also be deployed below the camera as part of an electron energy loss spectrometer. They can give dramatic improvements in the quality of images and diffraction patterns, especially from thick specimens where inelastic scattering effects are significant (Figure 4.6).

4.1.6 The projector system – diffraction patterns

It is often useful to examine or record the diffraction pattern from a selected area of the specimen. There are two fundamentally different ways of doing this. In the *selected area diffraction* technique, an area of specimen (usually circular) is selected, although a larger area is being illuminated. In the alternative *convergent beam diffraction* (also known as *microdiffraction*) technique the beam is condensed into a small spot so that the diffraction pattern comes from the whole of the (small) illuminated area.

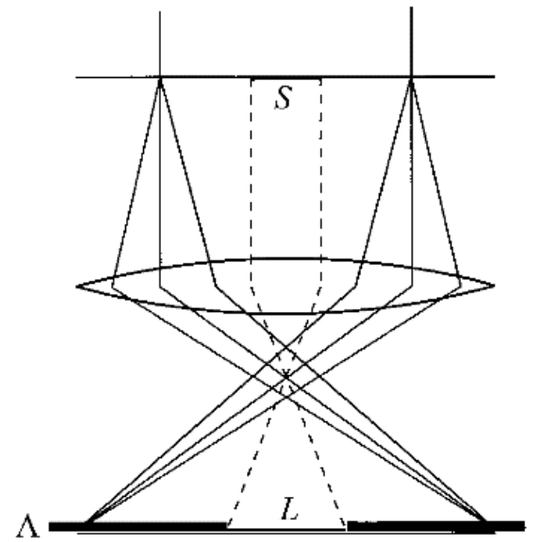

Figure 4.7 A selected area aperture A which selects a large area *L* in the intermediate image is optically equivalent to selecting the much smaller area *S* at the specimen.

Selected area diffraction could be achieved by inserting an aperture in the plane of either the specimen itself or the first image produced by the objective lens. The first of these is mechanically almost impossible while the second would require a very small aperture which is difficult to make, position and keep clean. The usual solution is to select the area using an aperture lower down the column, in the plane of the later intermediate images. In this way a much larger aperture can be used. For example if used in the plane of an intermediate image with magnification 200 ×, a 200 µm diameter aperture will select a region only 1 µm across. Figure 4.7 shows that selecting the area in an intermediate image is optically equivalent to selecting the smaller area at the specimen plane. The aperture used for this purpose is called the *selected area aperture*, or more loosely, the *diffraction aperture*. It is only useful to select an area 0·5–1 µm in diameter since one of the effects of spherical aberration is that electrons passing through the specimen as much as 1–4 µm outside the selected region may contribute to the diffraction pattern (depending upon the spherical aberration of the microscope). This is a small error if the selected region is 50 µm in diameter, but becomes the dominant feature if the selected area is only 1 µm in diameter.

The only way to obtain a good diffraction pattern from a region smaller than about 1 µm in diameter is to use the convergent beam diffraction technique (see section 3.4.2). In this case, the diameter selected is the same as the diameter of the beam at the specimen, which is controlled by the condenser lens system. In a modern microscope it may be possible to focus the electron beam (and hence selected areas) down to 1 or 2 nm in diameter, although in older instruments the limit may be as high as 100 nm.