Electron Energy-Loss Spectrometers

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CHAPTER PREVIEW

Electron energy-loss spectrometry (EELS) is the analysis of the energy distribution of electrons that have interacted inelastically with the specimen. These inelastic collisions tell us a tremendous amount about the electronic structure of the specimen atoms, which in turn reveals details of the nature of these atoms, their bonding and nearest-neighbor distributions, and their dielectric response. In order to examine the spectrum of electron energies we almost invariably use a magnetic prism spectrometer which, when interfaced to a TEM, creates another form of AEM. The magnetic prism is a simple, but highly sensitive, device with resolving power of approximately 1 eV even when the energy of the incident electron beam is up to 400 keV. Despite its simplicity the magnetic prism is operator-intensive and there is not yet the degree of software control to which we are accustomed with XEDS. In this chapter we'll describe the operational principles, how to focus and calibrate the spectrometer, and how to determine the collection semiangle (β). This angle is a most important parameter for interpreting your experimental data. In subsequent chapters we'll go on to look at the spectra, the information they contain, and how we extract quantitative data and images from them. As with XEDS there are standard tests to determine that the spectrometer is working correctly, and we'll describe these also.

D. B. Williams et al., *Transmission Electron Microscopy*

As a word of encouragement, or warning, you may get the impression from reviewing the older literature that EELS is the study of small blips which can only be seen by the "trained" eye. While the blips are still often small, we can now be very confident of our interpretation of these spectra. The EELS technique has come to be an excellent complement to the more widely used X-ray spectrometry, since it is well suited to the detection of light elements which are difficult to analyze with XEDS.

Electron Energy-Loss Spectrometers

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37.1. WHY DO ELECTRON ENERGY-LOSS SPECTROMETRY?

When the electron beam traverses a thin specimen, it loses energy by a variety of processes that we first discussed way back in Chapter 4. The reason we do EELS is so we can separate these inelastically scattered electrons and quantify the information they contain. We've already seen contrasting aspects of inelastic scattering in the TEM:

- Kikuchi lines occur in DPs; these electrons in Kikuchi lines are diffracted at precisely the Bragg angle, and give us much more accurate crystallographic information than the SAD pattern. In thick specimens, many of the electrons in Kikuchi lines are inelastically scattered.
- Chromatic aberration due to energy-loss electrons following different paths through the lenses limits the TEM image resolution, although you can avoid this by using very thin specimens, or STEM imaging. We'll see also, in Chapter 40, that EELS can filter out the chromatic aberration effect in TEM images.
- Specimen damage, which is of course undesirable, is often caused by inelastic interactions.

After reading the next three chapters you should agree that EELS is useful too. If you have an energy-loss spectrometer, it may be that inelastic scatter, in general, is something you would like to happen in your specimens.

The technique of EELS predates X-ray spectrometry; if you want to read a brief history of the technique see the book by Egerton (1996), which we will refer to on many occasions. In fact, the experimental pioneers of EELS, Hillier and Baker (1944), were the same two scientists who first proposed and patented the idea of X-ray spectrometry in an electron-beam instrument similar to the EPMA. In contrast to X-ray analysis, EELS has been very slow to develop and still remains firmly in research laboratories rather than applications laboratories. Since probe-forming AEMs became widespread, EELS has become more popular, primarily because it complements XEDS through better detection of the light elements. But as you'll see, we can extract a lot more from the spectra than merely elemental identification. When you have finished this set of chapters you will be ready to read Egerton's text and you will find the book edited by Disko *et al.* (1992) to be another excellent review. Two special issues of *Microscopy, Microanalysis, Microstructure* (Krivanek 1991, 1995a) and *Ultramicroscopy* (Krivanek 1995b) contain papers from EELS workshops.

Currently, there are only two major manufacturers of electron spectrometers for TEMs and they produce radically different instruments, designed for different purposes. We'll describe these two types of electron spectrometers in some detail.

> Two types of commercial spectrometers are presently manufactured: the magnetic prism spectrometer (Gatan) and the omega filter [Zeiss (now LEO)].

The magnetic prism is designed with energy spectrometry as its primary function; this application will constitute the bulk of this chapter. The omega filter is used mainly for energy-filtered imaging although spectra can be obtained; it is a specialized technique because this spectrometer has to be built into the microscope column rather than an optional addition (see later in Section 37.6). However, the Gatan Image Filter (GIF) may soon change this situation, particularly in the materials sciences, since the GIF combines both spectral and imaging capabilities. Magnetic electron spectrometers, along with electrostatic or combined electrostatic and magnetic systems, have been the subject of reviews by Metherell (1971) and Egerton (1996). If you're

an instrument enthusiast you should read these articles. Perhaps because there are so few manufacturers of the spectrometers, the competitively driven progress in user-friendly instrumentation and software control that has pushed X-ray spectrometry forward over the last two decades has been slow to occur in EELS; this lack of user friendliness, in part, accounts for the relatively small number of users of the technique.

> You should know also that there is another area of EELS research which uses electron spectrometers to measure exceedingly small (millivolt) energy losses in low-energy electron beams reflected from the surfaces of samples in UHV surface-chemistry instrumentation such as ESCA and Auger systems. We will ignore this type of EELS completely and deal only with transmission EELS studies of high-voltage electron beams.

There are two fundamentally different ways of detecting the spectrum generated by the magnetic prism spectrometer: either serially or, more efficiently, in parallel (see Section 37.3). Also, you can operate your TEM either in image mode or diffraction mode (see Section 37.4) and this choice has a major effect on the information that can be gathered. Before we look at these options, however, we need to look at the magnetic prism spectrometer itself.

37.2. THE MAGNETIC PRISM; A SPECTROMETER AND A LENS

We use a magnetic prism rather than one of the other kinds of spectrometer (e.g., electrostatic) for several reasons:

- It is compact, and therefore easily interfaced to the TEM. (Remember the WDS problem.)
- It offers sufficient energy resolution to distinguish all the elements in the periodic table and so is ideal for microanalysis.
- Electrons in the energy range 100–400 keV, typical of AEMs, can be dispersed sufficiently to detect the spectrum electronically, without limiting the energy resolution.

Schematic diagrams of the spectrometer optics are shown in Figures 37.1A and B. A picture of a Gatan spectrometer, which has to be installed beneath the camera system of a TEM or after the ADF detector in a DSTEM, is shown in Figure 37.2. Because these spectrometers are so widespread, many of the numerical values in this chapter are taken from the Gatan literature. For the details of operation you should, of course, read the instruction manual.

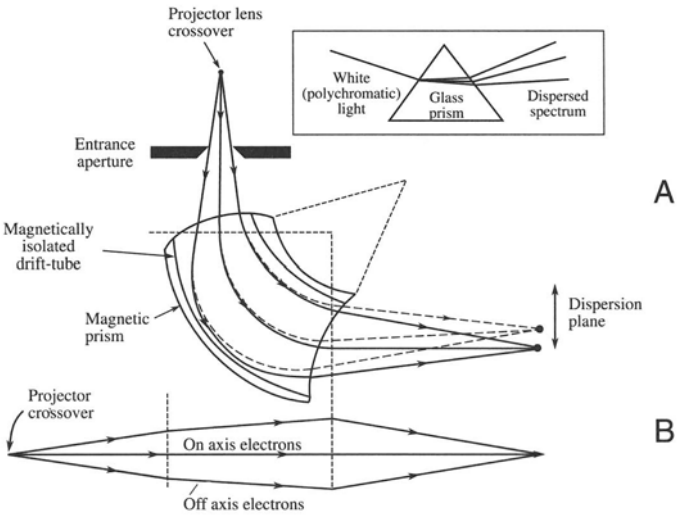

Figure 37.1. Ray paths through a magnetic prism spectrometer showing (A) dispersion and focusing of the electrons in the plane of the spectrometer and (B) the lens-focusing action in the plane normal to the spectrometer; compare the nonfocusing action of a glass prism on visible light (inset).

From Figure 37.1A we can see that electrons are selected by a variable entrance aperture (diameters: 1, 2, 3, or 5 mm in the Gatan system). The electrons travel down a "drift tube" through the spectrometer and are deflected through $\geq 90°$ by the surrounding magnetic field. Electrons with greater energy loss (dashed line) are deflected further than those suffering zero loss (full line). A spectrum is thus formed in the dispersion plane which consists of a distribution of electron counts (again incorrectly referred to as intensity) (I) versus energy loss ($\mathcal{E}$). This process is exactly analogous to the dispersion of white light by a glass prism.

> Although we've consistently used the letter E for energy, energy loss should, therefore, be denoted by ΔE, since it's a change in energy. However, it is a convention in the EELS literature to use E interchangeably for both an energy loss (e.g., the plasmon loss E_p) and a specific energy (e.g., the critical ionization energy E_C). As a compromise we will use $\mathcal{E}$ (note the different font), but remember it really means a change in E.

Now if you look at Figure 37.1B, you'll see that electrons suffering the same energy loss but traveling in both on-axis and off-axis directions are also brought back to a focus in the dispersion plane of the spectrometer,

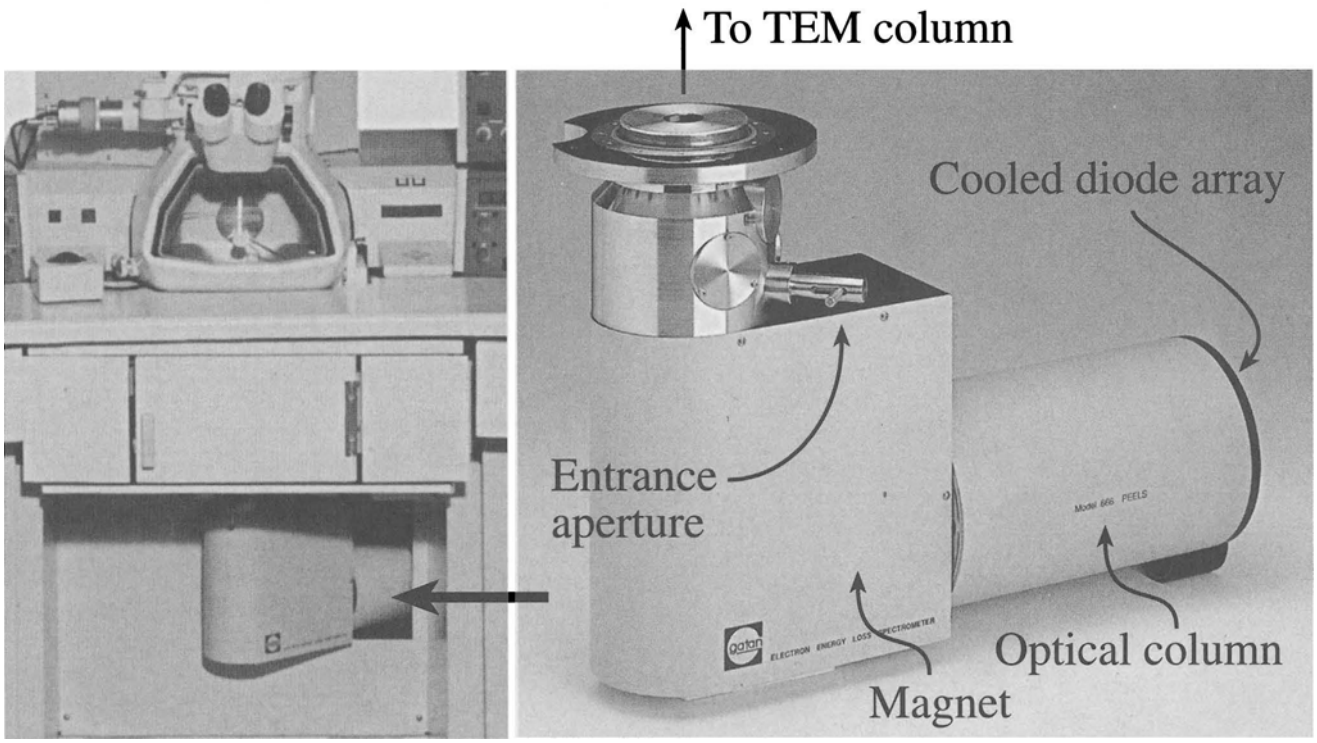

Figure 37.2. A Gatan parallel-collection magnetic prism spectrometer interfaced below the viewing screen of an AEM showing the shielded container for the magnet and the optical column and diode-array detection system.

which thus acts as a magnetic lens. The object plane of the spectrometer is usually set at the projector lens back focal plane, coincident with the differential pumping aperture. This focusing action is not seen in the otherwise analogous glass prism. Many examples of spectra will be given in the next two chapters.

37.2.A. Focusing the Spectrometer

Because the spectrometer is also a lens, you have to know how to focus it, and how to minimize the aberrations and astigmatism that are inherent in any magnetic lens. Correction of second-order aberrations and astigmatism are minor steps which we will not describe, but focusing is rather important.

The spectrometer has to focus the electrons because off-axis electrons experience a different magnetic field than on-axis electrons. The spectrometer is an axially *asymmetric* lens unlike the other TEM lenses. The path length of off-axis electrons through the magnet also varies, and the magnet has to be carefully constructed to ensure correct compensation for different electron paths so that focusing occurs. This correction is achieved by machining the entrance and exit faces of the spectrometer so they are not normal to the axial rays, as shown in Figure 37.1A. These nonnormal faces also act to ensure that electrons traveling out of the plane of the paper in Figure 37.1A are also focused in the dispersion plane, as shown in Figure 37.1B. Such a spectrometer is described as "double focusing." The faces are also curved to minimize aberrations.

As with any lens, the spectrometer takes electrons emanating from a point in an object plane and brings them back to a point in the image (dispersion) plane. Because the spectrometer is an asymmetric lens, we have to fix both the object distance and image distance if we want to keep the spectrum in focus. The object plane of the spectrometer depends on the TEM you are using.

> In a TEM/STEM, or a DSTEM with post-specimen lenses, the object plane is the back focal plane of the projector lens.
> In DSTEMs with no post-specimen lenses, the object plane is the plane of the specimen.

In the TEM the projector lens setting is usually fixed, and the manufacturer has already set this plane to coincide with the differential pumping aperture separating

the column from the viewing chamber. In some dedicated DSTEMs there are no post-specimen lenses, so the object plane of the spectrometer must be the plane of the specimen. In this case it is essential that you keep the specimen height constant.

Now in practice, the back focal plane of the projector does move a little as you change operating modes (for example, from TEM to STEM) and so you have to be able to adjust the spectrometer. You do this by looking at the electrons that come through the specimen without losing any energy. These electrons have a Gaussian-shaped intensity distribution which we call the "zero-loss peak"; we'll talk about this more in the next chapter. You can see the zero-loss peak on the CRT or computer display of the EELS system. You focus the peak by adjusting a pair of pre-spectrometer quadrupoles until it has a minimum width and maximum height. To correct second-order effects, a pair of sextupoles is also available. The actual method of focusing depends on the type of spectrometer. In a parallel-collection system, focusing is controlled directly by the quadrupoles. In a serial-collection system (see below), there is a slit in the dispersion plane. There are some rules to guide you when adjusting the slits:

- If the slit is too wide, then the zero-loss peak has a flat top and is very broad.
- If the slit is too narrow, you lose spectral intensity.
- If your spectrometer is not focused on the slit, the peak is also broad, but more Gaussian-shaped, as in Figure 37.3.

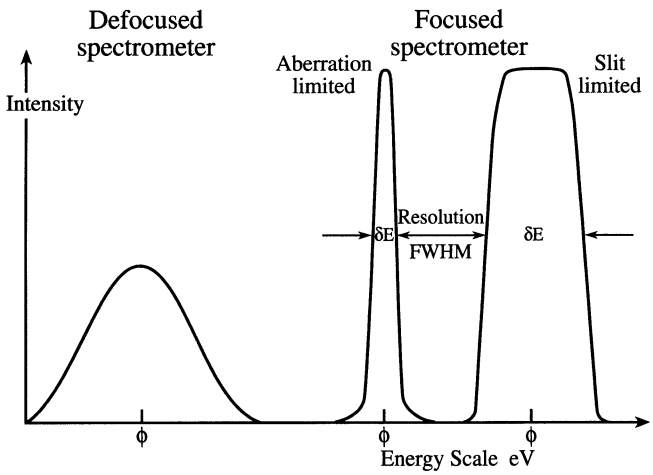

Figure 37.3. The zero-loss peak in a spectrum showing the effect of a defocused spectrometer, and the slit-limited condition, i.e., slits too wide (for serial collection only). In the usual focused condition, the resolution of the spectrometer is defined as the FWHM of the peak.

37.2.B. Calibrating the Spectrometer

We calibrate the spectrometer by placing an accurately known voltage on the drift tube. You will see this voltage displace the spectrum by a fixed amount. Alternatively, as in XEDS, you can look for features in a spectrum from a known specimen that occur at specific energies spanning the spectral display range, such as the zero-loss peak (at 0 eV) and the Ni L edge at 855 eV. (See Figure 37.4 and the next chapter for more details on the spectrum itself.) Modern electronics are reasonably stable and the calibration doesn't shift substantially, but you should check it regularly throughout an operating session since shifts of a few eV do occur and these are of the same order as the energy resolution of the spectrometer.

37.3. ACQUIRING A SPECTRUM

Figure 37.4A shows an EELS spectrum, which we'll describe in detail in the next chapter. For the time being note:

- The zero-loss peak is very intense.
- The intensity range is enormous; this graph uses a logarithmic scale.

There are two ways in which we acquire the spectrum. We either build up the spectrum one channel at a time, which is known as serial-acquisition EELS, or SEELS, or we acquire all the channels simultaneously, which is parallel-acquisition EELS, or PEELS (the word "acquisition" is often omitted when discussing the subject). The two modes are shown in the schematic spectra in Figure 37.4B and C . The intensity changes shown correspond to ionization "edges" and each element exhibits characteristic edges at specific values of $\mathcal{E}$. For example, the carbon K edge onset at 284 eV corresponds to the critical energy E_C required to eject the carbon K shell electron; more about this in Chapter 38.

37.3.A. Serial Collection

SEELS is the original, but least efficient, method of acquisition. No serial systems are now manufactured, but many remain in TEM labs. As shown in Figure 37.5A, the spectrometer system scans or "ramps" the spectrum across a slit in the dispersion plane, leaving the spectrum for a fixed "dwell time" (τ) at each energy loss. The collection and measurement is quite straightforward.

- Ramping is achieved magnetically by changing the current through a set of coils placed after the spectrometer magnet.

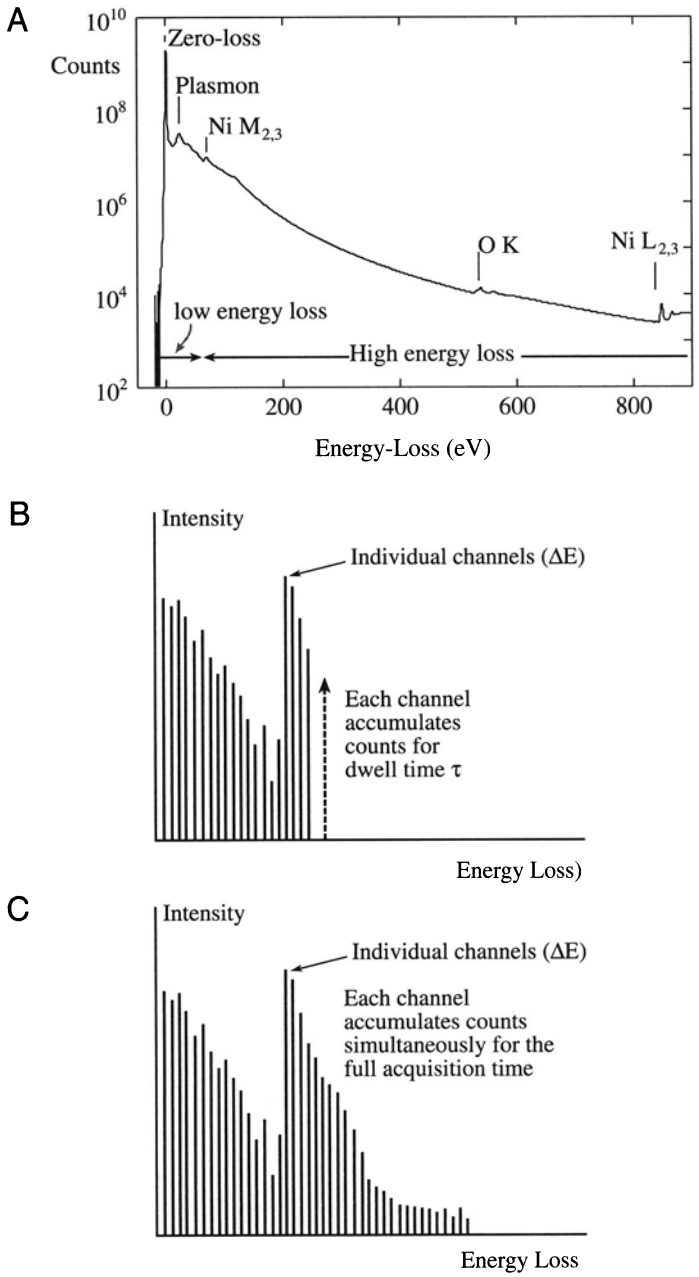

Figure 37.4. (A) An EELS spectrum displayed in logarithmic intensity mode. The zero loss is an order of magnitude more intense than the low-energy-loss portion, which is itself many orders of magnitude more intense than the small ionization edges, identified in the high-energy-loss range. The spectra can be acquired (B) serially or (C) in parallel. In serial collection, each of the energy channels accumulates counts for a given dwell time τ (typically 100 ms) before the next channel (energy range) is selected. In parallel collection, the complete spectrum is gathered simultaneously in all the available channels.

- A plastic scintillator located directly behind the slit receives an electron flux in time τ.
- The integrated electron current is converted to photons and amplified by a photomultiplier (PM) tube.
- After each dwell time, the total signal from the PM is then assigned to a channel corresponding to a specific energy loss, $\mathcal{E}$, in a multichannel analyzer (MCA).

We've already discussed scintillator-PM systems of the sort used for SE detection in the SEM or STEM, or direct beam (BF) detectors in the STEM (see Chapter 7).

- They have a tremendous gain and therefore can handle a large intensity range.
- They show a rapid response to intensity changes and exhibit both low noise and a high detective quantum efficiency, or DQE.

The DQE is close to 1 under ideal conditions, although the absolute DQE of SEELS is very low (≈0.001) since most of the electrons are wasted at any single acquisition time. These factors are particularly important in EELS, because the spectrum intensity can vary by many orders of magnitude. However, the susceptibility of scintillators to beam damage also means that the intense low-energy part of the EELS spectrum can be a health danger to the scintillator. The Gatan systems give an unmistakable audible warning when the electron flux is too great. Even with careful operation the plastic scintillator in your SEELS will become damaged and, as a wise precaution, you should replace it every few months.

The spectrum display is built up in a serial manner, as we showed in Figure 37.4B. Typically, the MCA will have 1024 or 2048 channels. The display resolution can be selected from < 0.1 eV/channel to about 10 eV/channel, depending on how much of the spectrum you want to gather. For example, if you set the display resolution to 1 eV per channel, the entire EELS signal out to 1024 eV energy loss will be recorded. But even if you choose a short τ, e.g., 100 ms, it will still take you about 100 s to accumulate a full spectrum out to 1024 eV, and in 100 ms the total intensity in each channel is going to be small. In particular, the limited energy range that may be of interest to you will only have been sampled for a few seconds at best. So when you know what portion of the spectrum is of interest, you should restrict collection to fewer channels for a longer τ, or accumulate several spectra and add the intensities together in order to get satisfactory counting statistics across the full spectrum. We'll see later that you can influence the total intensity by your choice of operating mode.

During acquisition of a spectrum, the intensity changes by several orders of magnitude (see Figure 37.4A), and usually we are interested primarily in the low-intensity (high-energy-loss) part of the spectrum. Therefore, we have

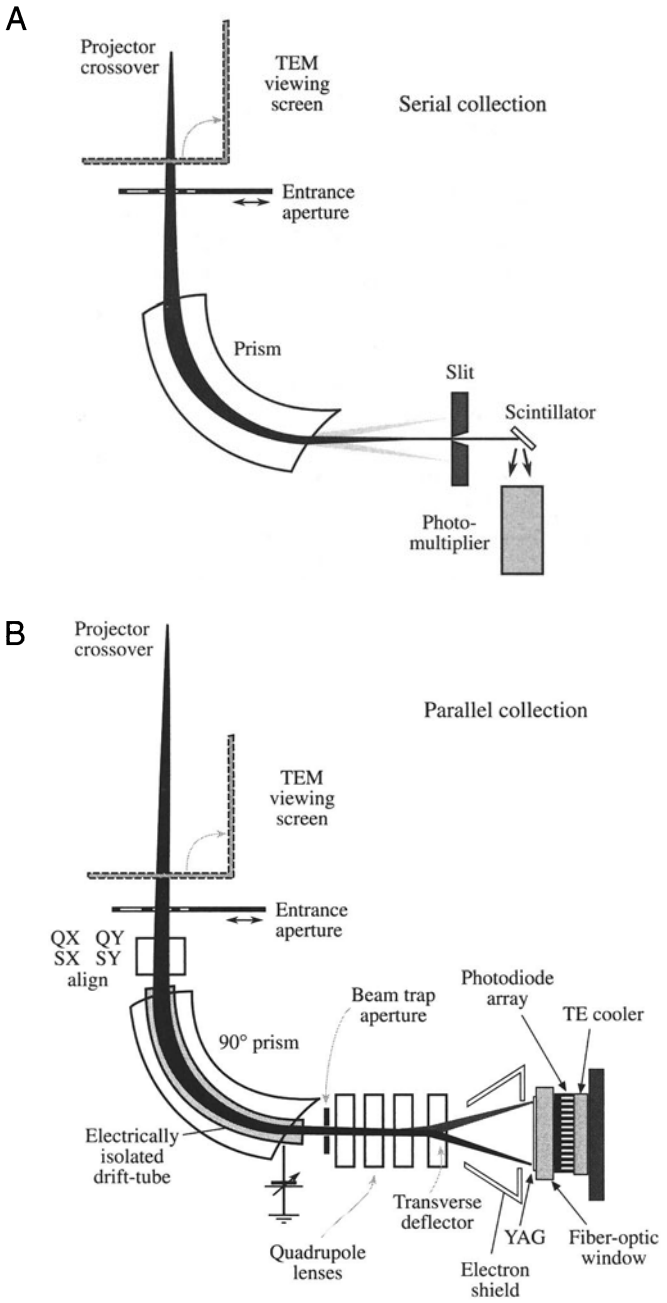

Figure 37.5. Comparison of EELS acquisition modes. (A) Serial collection of the spectrum through a slit onto a scintillator-PM system. (B) Parallel collection onto a YAG scintillator fiber-optically coupled to a thermoelectrically cooled (TE) semiconductor diode array. (Q = quadrupole, S = sextupole)

to change the display scale during SEELS spectrum collection in order to present a visible display of the low-intensity part of the spectrum. We can do this in one of two ways: either we increase τ by a factor of 10–100, or we electronically increase the gain of the scintillator-PM system by some orders of magnitude and operate it in two different modes, as explained below.

For very high electron fluxes encountered in the zero-loss and low-energy-loss portion of the spectrum, we use "analog collection." The total voltage generated at the exit of the PM can be related directly to the total electron current incident on the scintillator. Using a voltage-to-frequency (V/F) converter, this voltage is converted to a pulse that can be fed directly to the computer display. By changing the gain of the V/F converter we can handle electron fluxes in excess of 10^{10}/s (about 1 nA) with no problem. At this kind of incident current, the individual pulses overlap and are all integrated to give a continuous output. At the high-energy-loss end of the spectrum, where electron intensity is very low, the collection system can be changed to count the photon bursts generated by each electron, and this is termed "single-electron counting." You throw a switch on the SEELS electronics control panel to change the detection mode at a given point (energy loss) in the serial collection, or you can change modes under software control, usually at the same energy in the spectrum where the display gain change occurs.

We will see that it is sometimes essential to record the spectrum over a wide range, say from zero to several hundred eV loss. In this case, the intense low-loss region must be gathered and displayed in the same spectrum as the less-intense high-loss region. A potential problem in this situation is that, even if the intense low-loss region does not physically damage the detector, it may cause it to glow and the glow persists for some time after the electrons hit the scintillator. So it is possible that while you are gathering the low-intensity part of the spectrum, the afterglow will contribute unwanted noise.

> To avoid the afterglow, you should acquire all SEELS spectra in reverse-scan fashion. Start at the high loss, then go to the low-loss region, and finish at zero.

If the zero-loss peak is not required, then it is good practice to cease acquisition at about 5–10 eV to save the scintillator from the accumulated effects of high electron fluxes.

37.3.B. Parallel Collection

PEELS gathers the whole energy spectrum simultaneously and is much more efficient than SEELS. PEELS comprises a YAG scintillator coupled via fiber optics to a semiconductor photodiode array in the dispersion plane of the spectrometer, as shown in Figure 37.5B. The array consists of

1024 electrically isolated and thermoelectrically cooled silicon diodes, each about 25 μm across. These diode arrays show varying responses and exhibit specific artifacts, which we'll discuss in the next chapter.

The resultant spectrum accumulates across the whole energy range simultaneously, as we showed schematically back in Figure 37.4C. Rather than having a dwell time as in SEELS, we now have an integration time which can vary from a few msec to several hundred seconds. After integration, the whole spectrum is read out via an amplifier through an A/D converter and into an MCA system. Reasonable spectra can be acquired in a fraction of a second, making PEELS imaging a practical reality. We'll see more about this in Section 40.3.

The advantage of PEELS is that all regions of interest are gathered for the whole integration time, and not just some fraction of the acquisition time as in SEELS. Thus PEELS is much more efficient than SEELS, and its DQE is ~0.5.

A quick warning: you can damage the YAG scintillator, particularly in intermediate-voltage microscopes. Ways to avoid this problem, especially for the intense zero-loss beam, are still being developed. Currently, the zero-loss beam intensity is attenuated or deflected off the scintillator if it is not required, or if the beam current exceeds 0.5 nA. While the SEELS system can handle intense signals, the PEELS diode array saturates at signal intensities of about 16,000 counts.

You must select an integration time that won't saturate the detector and then collect as many consecutive integrations as you need.

One other advantage of the PEELS system is that the scintillator shield is designed to act as a Faraday cup, and so you can use it to measure the total beam current. Usually, the beam is moved onto the shield whenever acquisition ceases, so a constant record of the beam current is available.

To summarize:

- SEELS detects one channel at a time; the detector is easy to optimize and simple to operate.
- PEELS detects the whole spectrum at one time, but the diode array is hard to optimize.
- PEELS exhibits artifacts, and has more complex electron optics, but is 2–3 orders of magnitude more efficient than SEELS with a relatively high DQE.

37.3.C. Spectrometer Dispersion

We define the dispersion as the distance in the spectrum (dx) between the positions of electrons differing by energy dE. It is a function of the strength of the magnetic field (which is governed by the strength (i.e., size) of the spectrometer magnet) and the energy of the incident beam, E_0. In the commercial serial spectrometers, the radius of curvature (R) of electrons traveling on axis is about 200 mm, and for 100-keV electrons dx/dE is about 2 μm/eV. This dispersion, while small, is sufficiently large so as not to limit the energy resolution (see below). A serial-detection system can process the spectrum without any post-spectrometer magnifying lenses. For parallel collection this dispersion value is inadequate, and typically electrons with an energy range of about 15 eV would fall on each 25-μm-wide diode. Therefore, the dispersion plane has to be magnified ~15× before the spectrum can be detected with resolution closer to 1eV. This magnification requires post-spectrometer lenses; 4 quadrupoles are used in the Gatan system. The dispersion should be linear across the diode array; you can check this by measuring the separation of a known pair of spectral features (e.g., zero loss and C K edge) as you displace the spectrum across the diode array.

You may wonder why we don't record the spectrum on film rather than collect it electronically. In fact, this was the first method used to detect electron spectra, but it is an analog method and photographic film does not have a linear response over the usual range of spectral intensities. Furthermore, the grain size of the photographic emulsion (10–20 μm) would limit energy resolution to about 5 eV unless the dispersion were increased, so photographic recording is no longer used.

37.3.D. Spectrometer Resolution

We define the energy resolution of the spectrometer as the FWHM of the zero-loss peak (see back in Figure 37.3). If you don't focus your spectrometer as we just described, then you won't get the best resolution. The best resolution you can get is determined by the type of electron source. As we discussed back in Chapter 5 (see Table 5.1), at ~100 keV a W source has the worst energy resolution (2.5 eV), and a LaB_6 is slightly better than W at 1.5 eV while a cold FEG gives the best value (0.3 eV). Because of the high emission current from thermionic sources, the energy resolution is in fact limited by electrostatic interactions between electrons at the filament crossover. This electron–electron interaction is called the Boersch effect. You can partially overcome this by undersaturating the filament and using only the electrons in the halo. Under these circumstances a LaB_6 source can attain a resolution below

1 eV, but at the expense of a considerable loss of signal, for which you can compensate by increasing the beam size and/or the C2 aperture.

> The energy resolution decreases slightly as the energy loss increases, but it should be no worse than ~1.5 times the zero-loss peak width up to 1000-eV energy loss.
> If you operate at higher voltage, you should also expect a degradation of energy resolution as the kV increases, approximately tripling from 100 kV to 400 kV.

Because the magnetic prism is so extremely sensitive, external magnetic fields in the microscope room may limit the resolution. You may see a disturbance to the spectrum directly if you sit in a metal chair and move around, or if you open metal doors into the TEM room. Remember, for comparison, that the energy resolution of XEDS is >100 eV.

For different EELS operations, different factors affect the resolution. In a SEELS system the resolution is most easily changed by adjusting the slit width. A larger slit width results in poorer energy resolution, but has the advantage of increasing the total current into the detection system. In a PEELS system optimum resolution requires a small projector crossover and a small (1 mm or 2 mm) entrance aperture. The resolution is degraded by choosing a larger entrance aperture because of off-axis beams; i.e., degradation is caused by a C_s effect for the lenses in the energy analyzing spectrometer. Similarly, the resolution may change as you deflect the zero-loss peak onto different regions of the photodiode, although this should not happen if the spectrometer optics are properly aligned.

37.3.E. Point-Spread Function

In a PEELS, you can reduce the magnification of your spectrum so that the zero-loss peak occupies only a single photodiode channel. Any intensity registered outside that single channel is an artifact of the detector system array and is called the point-spread function. This function acts to degrade the inherent resolution of the magnetic spectrometer. The zero-loss peak may spread on its way through the YAG scintillator and the fiber optics before hitting the photodiode. Figure 37.6 shows the point-spread function of a PEELS and clearly there is intensity well outside a single channel. This is important because this spreading broadens features in your spectrum, such as fine structure in ionization edges, and you need to remove it by deconvolution (see Section 39.6). The concept is essentially the same as the point-spread function we discussed for HRTEM.

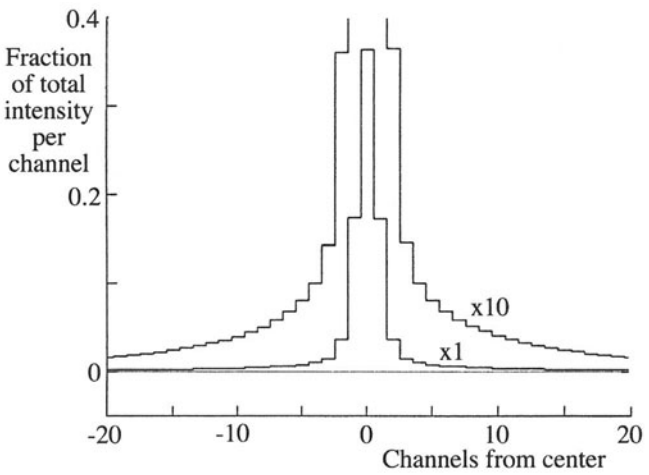

Figure 37.6. The point-spread function, showing the degradation of the intense well-defined zero-loss peak through spreading of the signal as it is transferred from the scintillator via the fiber-optic coupling to the photodiodes. The peak should occupy a single channel but is spread across several channels.

37.4. IMAGE AND DIFFRACTION MODES

When performing EELS in a TEM/STEM, you can operate in either of two modes, and the terminology for this is confusing. If you operate the TEM such that an image is present on the viewing screen, then the back focal plane of the projector lens contains a DP, and the spectrometer uses this pattern as its object. From the spectroscopists' viewpoint, therefore, this is termed "diffraction mode" or "diffraction coupling," but from the microscopists' viewpoint it is more natural to call this "image mode" since you are looking at an image on the screen. Conversely, if you adjust the microscope so a DP is projected onto the screen (which includes STEM mode in a TEM/STEM), then the spectrometer object plane contains an image, and the terminology is reversed.

> The spectroscopist uses the term "image mode" or "image coupling" and the microscopist says "diffraction mode."

Both sets of terms appear in the literature, often without precise definition, so it can be rather confusing.

> In this text "image mode" means an image is present on the TEM screen; i.e., we use the microscopists' terminology.

So your first step is to ensure that a focused image or DP is present on your TEM screen, and then the spectrum can be focused onto the dispersion plane.

37.4.A. Spectrometer Collection Angle

The collection semiangle of the spectrometer (β) is the most important variable in quantification, so you should know β for all your standard operating situations. If you do gather spectra with different β, it is difficult to make sensible comparisons without considerable post-acquisition processing. The detailed intensity variations in the spectrum depend on the range of electron scattering angles which are gathered by the spectrometer. Under certain circumstances, the effective value of β can be modified by the beam-convergence semiangle, α, but we'll discuss that when we talk about quantification in Chapter 39.

> β is the semiangle subtended at the specimen by the entrance aperture to the spectrometer.

This definition is illustrated in Figure 37.7. The value of β is affected by the mode of microscope operation, and so we will describe how to measure β under different conditions that may be encountered.

Dedicated STEMs. In a basic DSTEM the situation is straightforward if there are no post-specimen lenses because, as shown in Figure 37.7, the collection angle can be calculated from simple geometry. Depending on the diameter (d) of the spectrometer entrance aperture and the distance from the specimen to the aperture (h), β (in radians) is given by

$$\beta \approx \frac{d}{2h} \qquad [37.1]$$

This value is approximate and assumes β is small. Since h is not a variable, the range of β is controlled by the number and size of available apertures. Therefore, if h is ~100 mm, then for a 1-mm-diameter aperture, β is 5 mrads. If there are post-specimen lenses and apertures, the situation is similar to that in a TEM/STEM, as discussed below.

TEM-image mode. Remember that in image mode, a magnified image of the specimen is present on the viewing screen and the spectrometer object plane contains a DP. In contrast to what we just described for a dedicated STEM, the angular distribution of electrons entering the spectrometer aperture below the center of the TEM screen is *independent* of the entrance aperture size. This is because you can control the angular distribution of electrons contributing to any TEM image by the size of the objective aperture in the DP in the back focal plane of the objective lens. If you don't use an objective aperture, then the collection semiangle is very

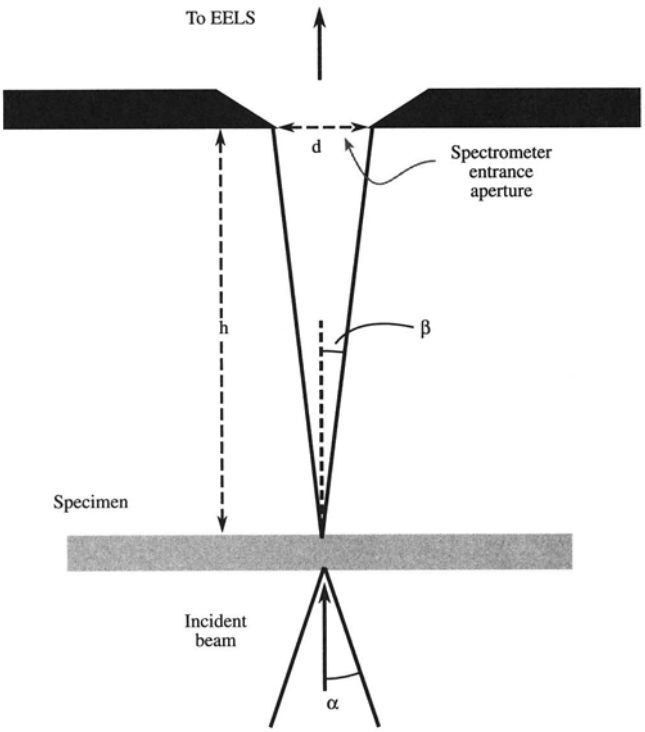

Figure 37.7. Schematic diagram showing the definition of β in a DSTEM in which no lenses exist between the specimen and the spectrometer entrance aperture.

large (>~100 mrads) and need not be calculated accurately, because we'll see that small differences in a large β value do not affect the spectrum or subsequent quantification.

If, for some reason, you do wish to calculate β in image mode with no aperture inserted, you need to know the magnification of the DP in the back focal plane of the projector lens (which is the front focal plane of the spectrometer). This magnification may be described in terms of the camera length L of the DP, and this is given by

$$L \approx \frac{D}{M} \qquad [37.2]$$

where D is the distance from the projector crossover to the recording plane and M is the magnification of the image in that plane. So if D is about 500 mm and the screen magnification is 10,000×, then L is 0.05 mm. Thus we can show that

$$\beta \approx \frac{r_0}{L} \qquad [37.3]$$

where r_0 is the maximum radius of the DP in the focal plane of the spectrometer. Typically, r_0 is approximately 5 μm, and so β is 0.1 rads or 100 mrad which, as we just said, is so large that we rarely need to know it accurately. In fact, in TEM-image mode without an objective aperture,

if you just assume β = 100 mrad any calculation or quantification you do will be independent of β.

If you insert an objective aperture and you know its size and the focal length of the objective lens, then β can easily be calculated geometrically. To a first approximation, in a similar manner to equation 37.1 above, β is the objective aperture diameter divided by twice the focal length of the objective lens, as shown in Figure 37.8. For example, with a focal length of 3 mm and a 30-μm aperture, β is about 5 mrad.

If you insert an objective aperture, a normal BF image can be seen on the TEM screen and the information in the spectrum is related (with some considerable error) to the area of the image that sits directly above the spectrometer entrance aperture. We will return to this point in more detail in Section 37.4 when we discuss the spatial resolution of microanalysis. Remember also that with the objective aperture in, you cannot do XEDS. Therefore, simultaneous EELS and XEDS is not possible in this mode.

TEM/STEM diffraction mode. In diffraction (also STEM) mode, the situation is a little more complicated. Remember, the object plane of the spectrometer (the projector lens BFP) contains a low-magnification image of the specimen; so you see a DP on the screen and the same DP is in the plane of the spectrometer entrance aperture. Under these circumstances we control β by our choice of the spectrometer entrance aperture, as shown in Figure 37.9.

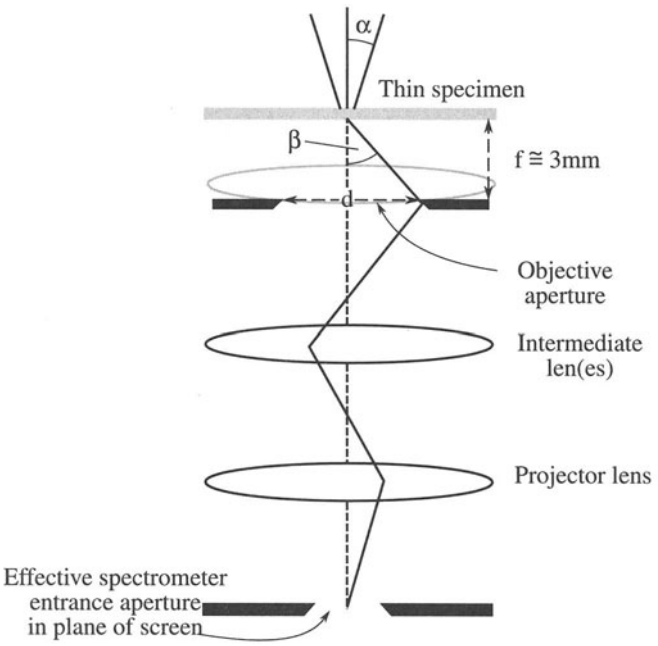

Figure 37.8. The value of β in TEM-image mode is governed by the dimensions of the objective aperture.

If a small objective aperture is inserted, it is possible that it may limit β; the effective value of β at the back focal plane of the projector lens is β/*M*, where *M* is the magnification of the image in the back focal plane of the projector lens.

You have to calibrate β from the DP of a known crystalline specimen, as also shown in Figure 37.9. Knowing the size of the spectrometer entrance aperture, the value of β can be calibrated by twice the Bragg angle, $2\theta_B$, that separates the 000 spot and a known *hkℓ*, disk. If the effective aperture diameter in the recording plane is d_{eff} and the distance b is related to the angle $2\theta_B$, as shown in Figure 5.8, so

$$\beta \approx \frac{d_{eff}}{2}\frac{2\theta_B}{b} \qquad [37.4]$$

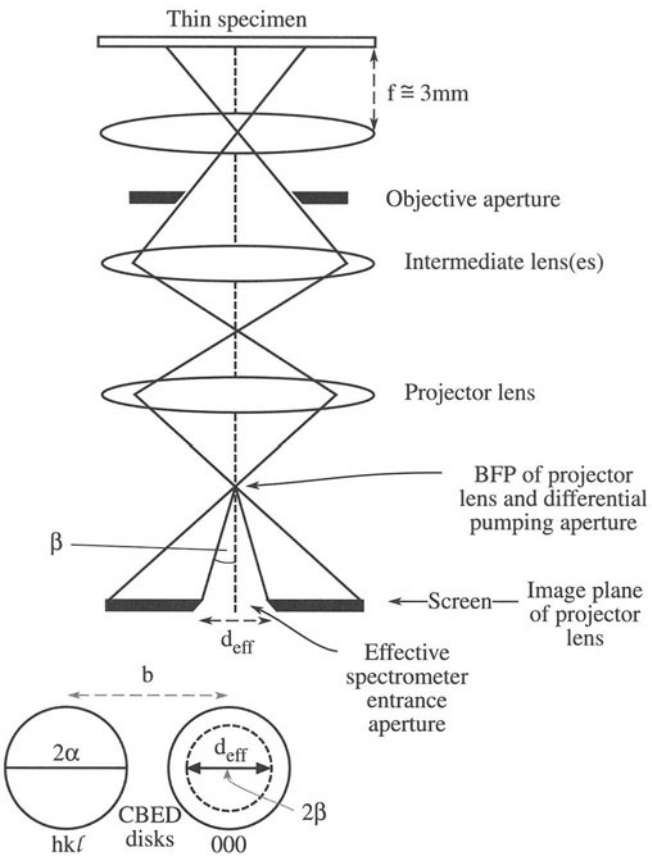

Figure 37.9. The value of β in TEM/STEM diffraction mode is determined by the effective diameter of the spectrometer entrance aperture (d_{eff}), projected into the plane of the diffraction pattern. The value of the d_{eff} can be calibrated by reference to a known diffraction pattern (below) in which d_{eff} can be related to $2\theta_B$.

The effective entrance aperture diameter d_{eff} at the recording plane is related to the actual diameter d by

$$d_{\text{eff}} = \frac{d\,D}{D_A} \qquad [37.5]$$

where D is the distance from the projector crossover to the recording plane (remember, the film is not at the same height as the screen); D_A is the distance between the crossover and the actual entrance aperture. Alternatively, β can be determined directly if the camera length on the recording plane (L) is known, since

$$\beta = \frac{D}{D_A}\frac{d}{L} \qquad [37.6]$$

D_A is typically 610 mm for most Gatan PEELS systems, but D varies from microscope to microscope; you have control over d and L. For example, if D is 500 mm and L is 800 mm, then for the 5-mm entrance aperture, β is ~5 mrads.

If you choose a camera length such that the image of the specimen in the back focal plane of the spectrometer is at a magnification of 1×, then, in effect, you have moved the specimen to the object plane of the spectrometer. This special value of L is equal to the D, which you should know for your own microscope. Then β is simply the entrance aperture diameter divided by D_A (610 mm). Life will be much easier when all these calculations are incorporated in ELP (see Section 1.5).

In summary, the collection angle is a crucial factor in EELS. Large collection angles will give high intensity in the spectrum. If you collect your spectrum in image mode without an objective aperture, then you don't compromise your energy resolution. If you're in diffraction mode and you control β with the entrance aperture, then a large aperture (high intensity, large β) will degrade the energy resolution.

37.4.B. Spatial Selection

Depending on whether you're operating in image or diffraction mode, you obtain your spectrum from different regions of the specimen. In TEM-image mode, you position the area to be analyzed on the optic axis, above the spectrometer entrance aperture. The area selected is a function of the aperture size demagnified back to the plane of the specimen. For example, if the image magnification is 100,000× at the recording plane and the *effective* entrance aperture size at the recording plane is 1 mm, then the area contributing to the spectrum is 10 nm. So, you might think that you can do high-spatial-resolution microanalysis without a probe-forming STEM. However, if you're analyzing electrons that have suffered a significant energy loss, they may have come from areas of the specimen well away from the area you selected, because of chromatic aberration. This displacement d is given by

$$d = \theta\,\Delta f \qquad [37.7]$$

where θ is the angle of scatter, typically <10 mrads, and Δf is the defocus error due to chromatic aberration given by

$$\Delta f = C_c\frac{E}{E_0} \qquad [37.8]$$

where C_c is the chromatic aberration coefficient. So if we take a typical energy loss $\mathcal{E}$ of 284 eV (the energy required to eject a carbon K shell electron) and we have a beam energy of 100 keV, then the defocus due to chromatic aberration (with C_c = 3 mm) will be close to 10 μm, which gives an actual displacement, d, of 10^{-4} mm, or 100 nm. This figure is large compared to the value of 10 nm which we calculated without considering chromatic aberration effects.

> While TEM-image mode is good for gathering spectra with a large β and high-energy resolution, the price you pay is poorer spatial resolution.

In TEM diffraction mode, you select the area of the specimen contributing to the DP in the usual way. You can either use the SAD aperture, which has a lower limit of about 5 μm, or you can form a fine beam as in STEM, so that a CBED pattern appears on the screen. In the latter case, the area you select is a function of the beam size and the beam spreading, but is generally < 50 nm wide. Therefore, this method is best for high-spatial-resolution microanalysis; just as for XEDS microanalysis, STEM operating mode is recommended for EELS microanalysis.

- Form an image in STEM mode.
- Stop the probe from scanning.
- Position it on the area to be analyzed.
- Switch on the EELS; in a TEM/STEM you have to lift up the TEM viewing screen also!

37.5. WHAT YOU NEED TO KNOW ABOUT YOUR PEELS

As with XEDS, where there are several standard tests you need to perform to determine that all is well with the detector and the electronics, there are similar tests for the PEELS diode array and electronics. Some of these are described in the Gatan handbook and others have been proposed by Egerton *et al.* (1993). We'll discuss specific artifacts visible in the spectrum in the next chapter.

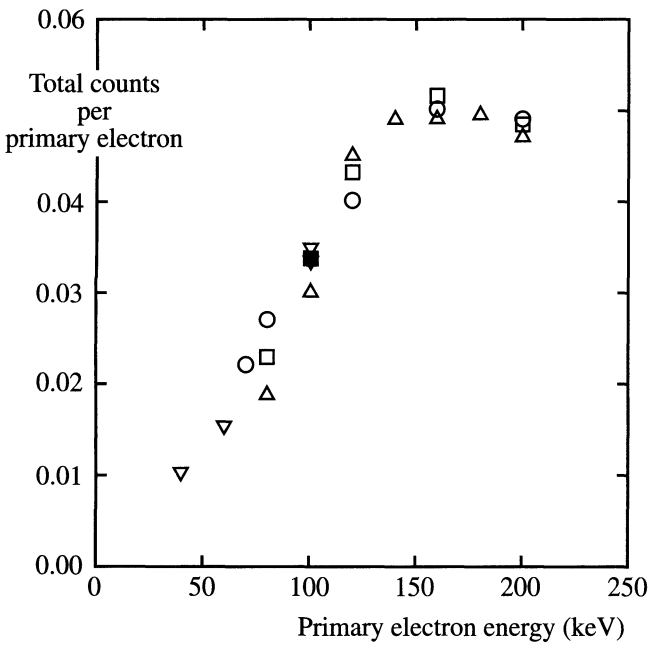

Figure 37.10. Nonlinear response of the diode array as a function of the beam energy. The response saturates at ~150 keV. Different symbols represent different dispersion settings.

Since increasing the keV means more electrons are generated in the scintillator, the sensitivity of the diode array should be linearly related to the electron energy. Egerton *et al.* (1993) have shown (see Figure 37.10) that, in fact, the Gatan diode-array response saturates at ~150 keV because of electron penetration. This nonlinearity doesn't affect quantification, since we typically make measurements over a very small energy range (<1 keV), but it means that there is no gain in count rate by operating >~150 keV. More important is the need for the YAG to respond linearly to different intensities incident on it; you should check that this is so by comparing the zero-loss intensity measured in a single 1-s readout with that recorded, say, in 40 readouts each of 0.025 s. In each case, you have to subtract the dark current (see Section 38.5). Obviously, the ratio of these two intensities should be unity for all levels of signal falling on the YAG. If it is not so, then you should consult the manufacturer.

37.6. IMAGING SPECTROMETERS

Two types of electron spectrometers are designed for energy-filtered imaging:

- In-column spectrometers on Zeiss 902 and LEO 912 series TEMs for "electron-spectroscopic imaging" (ESI).
- The Gatan Imaging Filter (GIF), which is a variation of the magnetic prism spectrometer.

Zeiss first used a mirror-prism system originally devised by Castaing and Henry (1962) and described by Zanchi *et al.* (1982). The drawback to the mirror-prism is the need to split the high-tension supply and raise the mirror to the same voltage as the gun. So LEO now use a magnetic omega (Ω) filter (Lanio *et al.* 1986). The Ω filter disperses the electrons in the column, as shown in Figure 37.11A. The spectrometer is placed in the TEM column between the intermediate and the projector lenses. Usually, you project an image into the prism, which is focused on a DP in the back focal plane of the intermediate lens. Therefore, the entrance aperture to the spectrometer selects an area of the specimen and the angle of collection is governed by the objective aperture (i.e., the same as image mode for the magnetic prism spectrometer). Electrons following a particular path through the spectrometer can be selected by the post-spectrometer slit. Thus only electrons of a given energy range, determined by the slit width, are used to form the image projected onto the TEM screen. ESI has several advantages over conventional TEM images, as we'll see in Section 40.3. We will also see then that the magnetic prism, which is primarily used for spectrometry, can also be used in a STEM to form energy-filtered images.

You can also change the microscope optics and project a DP into the prism, thus producing an energy-filtered DP on the TEM screen. Then, if you use the slit to select a portion of the DP, you get an energy-loss spectrum showing not only the intensity distribution as a function of energy but also the angular distribution of the electrons.

The GIF (Krivanek *et al.* 1992) shown in Figure 37.11B is basically a PEELS with an energy-selecting slit after the magnet and a two-dimensional slow scan CCD array detector rather than a single line of diodes. There are also more quadrupoles and sextupoles in the optics of the GIF. The first two quadrupoles before the slit increase the dispersion of the spectrometer onto the slit and the quadrupoles after the slit have two functions. Either they project an image of the spectrum at the slit onto the CCD, or they compensate for the energy dispersion of the magnet and project a magnified image of the specimen onto the CCD (which has advantages over the diode array in a conventional PEELS). In the first mode, the system is operating like a standard PEELS; in the second, it produces images (or DPs) containing electrons of a specific energy selected by the slit. Obviously, such a large number of variable sextupoles and quadrupoles could be a nightmare to operate without appropriate computer control, and this is built into the system. We'll describe energy filtering with the GIF in Section 40.3.

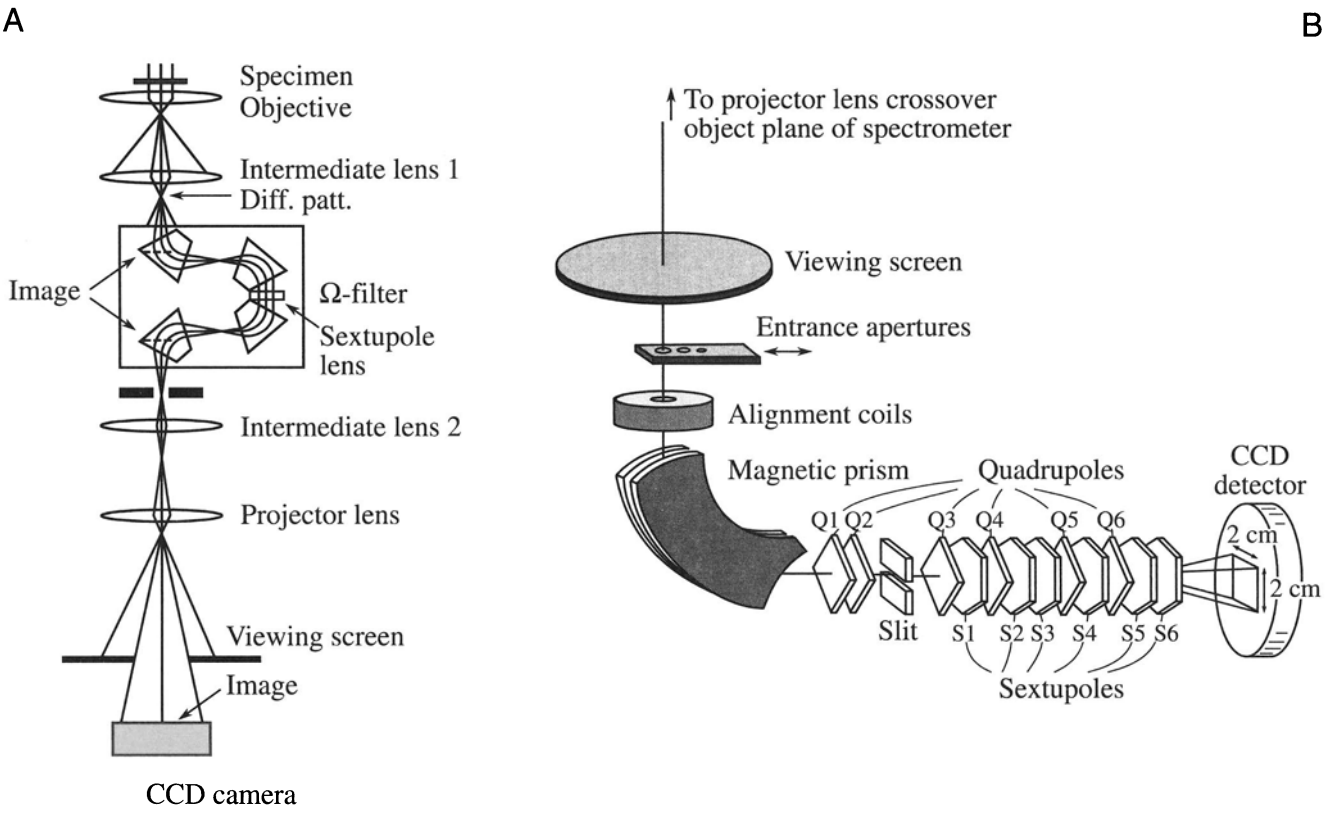

Figure 37.11. (A) Ray paths through the Ω filter system inserted in the imaging lens system of the LEO TEM. (B) The Gatan Imaging Filter attached to the TEM column after the imaging lenses, in the same position as a PEELS.

CHAPTER SUMMARY

We generally use a magnetic prism spectrometer for EELS. It is a simple device and very sensitive, but requires careful operation and an understanding of how it functions in combination with different TEM modes. PEELS is the preferred type of spectrometer, and it is best operated with the TEM in diffraction or STEM mode, or with a DSTEM. You have to know how to focus and calibrate it and how to determine the collection semi-angle, β. Once you can do this you're in a position to analyze energy-loss spectra, so in the next chapter we'll tell you what these spectra look like and what information they contain. If you have an Ω filter, or GIF, you can routinely form images or DPs with electrons of specific $\mathcal{E}$.

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