37

Electron Energy-Loss Spectrometers and Filters

CHAPTER PREVIEW

Electron energy-loss spectrometry (EELS) is the analysis of the energy distribution of electrons that have come through the specimen. These electrons may have lost no energy or may have suffered inelastic (usually electron-electron) collisions.

These energy-loss events tell us a tremendous amount about the chemistry and the electronic structure of the specimen atoms, which in turn reveals details of their bonding/valence state, the nearest-neighbor atomic structure, their dielectric response, the free-electron density, the band gap (if there is one), and the specimen thickness.

In order to examine the spectrum of electron energies, we invariably use a magnetic-prism spectrometer. As we saw with X-rays, it is now common to form images of the various EELS signals in addition to gathering spectra and to do this we use an energy filter, which is based on the same magnetic-prism concept. Energy-filtered TEM (EFTEM) is perhaps the most powerful AEM technique, as should become apparent. The magnetic prism/energy filter is a highly sensitive device with an energy resolution <1 eV, even when the electron-beam energy is as high as 300 keV.

In this chapter, we'll describe the operational principles of both the spectrometer and filter, how to focus and calibrate them, and how to determine the collection semi-angle (β). This angle affects the quality and interpretation of much of your experimental data. In subsequent chapters, we'll go on to look at the spectra and images in more detail and the information they contain.

The EELS technique is an excellent complement to, and is now more widely used than the somewhat simpler XEDS, since it offers substantially more information than mere elemental identification and is well suited to the detection of light elements, which are difficult to analyze with XEDS.

37.1 WHY DO EELS?

So why should we do EELS when XEDS can identify and quantify the presence of all elements above Li in the periodic table with a spatial resolution approaching a few atoms and analytical sensitivity close to the single-atom level? Well, in fact EELS does even more than XEDS in that it can detect and quantify *all* the elements in the periodic table and is especially good for analyzing the light elements. Furthermore, EELS offers even better spatial resolution and analytical sensitivity (both at the single-atom level) in addition to providing much more than just elemental identification as indicated in the preview. So the next question is, why bother with XEDS at all? The answer to this is that EELS, as you will see, can be a challenging experimental technique; it

requires very thin specimens to get the best information and understanding and processing the spectra and images requires somewhat more of a physics background than XEDS.

The main point that you need to understand is that XEDS and EELS are highly complementary techniques; most AEMs come equipped with both kinds of spectrometer.

37.1.A Pros and Cons of Inelastic Scattering

When a high-energy electron traverses a thin specimen it can either emerge unscathed or it loses energy by a variety of processes that we first discussed way back in Chapter 4. EELS separates these inelastically scattered electrons into a spectrum, which we can interpret and

quantify, form images or DPs from electrons of specific energy, and also combine the spectra and images via spectrum imaging, as we've already seen for XEDS (see Section 33.6.C). Throughout the book, we've already seen some contrasting aspects of inelastic scattering

- Kikuchi lines and HOLZ lines occur in DPs; the electrons in these lines are diffracted very close to the Bragg angle, and give us much more accurate crystallographic information than the SAD/CBED (spot/disk) pattern. In thick specimens, many of the electrons in these lines are inelastically scattered, so thicker specimens can be useful.
- Conversely, the background intensity that surrounds the direct beam in DPs, obscuring faint spots in SADPs and fine detail in CBDPs is due to inelastic scatter. So if you can remove (i.e., filter out) these electrons, you can considerably enhance the quality of your DPs.
- Chromatic aberration is due to energy-loss electrons following different paths through the objective lens and limits the image resolution in thick specimens. You can avoid this by using very thin specimens, but if you're stuck with a thick specimen then you can restore the quality of your images by filtering out inelastic electrons thus removing specimen-induced chromatic-aberration effects.
- Specimen damage, which is usually undesirable, is often caused by inelastic interactions and there isn't much you can do about this, as we discussed back in Chapter 4.
- In Chapter 4, we also discussed many of the other ways that electrons could lose energy going through the specimen, producing X-rays and other phenomena such as plasmons and phonons. These and other interactions produce energy-loss electrons, which contain useful information about the electronic structure and elemental makeup of your specimen.

In fact, if your AEM has an energy-loss spectrometer or filter, then inelastic scattering, in general, is something you should want to happen in your specimens because, if it didn't happen, TEM would be a much less useful technique and this book would be several chapters shorter (so we at least are happy).

The technique of EELS predates X-ray spectrometry. 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. If you want to read a brief history of the technique, see the classic book by Egerton. We'll refer to the second edition of Egerton's text on many occasions. In contrast to X-ray analysis, EELS was relatively slow to develop, but is now perhaps the dominant spectrometry technique on probe-forming TEMs for the reasons we gave at the start of the chapter.

Once you've finished this set of chapters, you should find Egerton's book to be highly informative and likewise, the multi-author text on energy-filtered imaging, edited by Reimer. Every 4 years since 1990, there has been an international, focused workshop on EELS and related techniques in the TEM (URL #1) and the proceedings have been published in special issues of various EM journals, as noted in the reference list.

37.1.B The Energy-Loss Spectrum

Let's start as we did for XEDS by looking at a typical spectrum such as Figure 37.1. We won't go into detail here but will save that for the subsequent chapters. For the time being, it's worth pointing out that we split up the spectrum into the low-loss and high-loss regions, with ~ 50 eV being the somewhat arbitrary break point. It isn't particularly apparent from the figure, but we'll see later that the low-loss region contains electronic information from the more weakly bound conduction and valence-band electrons, while the high-loss region contains primarily elemental information from the more tightly bound, core-shell electrons and also details about bonding and atomic distribution. For the time being, you should note that

- the zero-loss peak is very intense, which can be both an advantage and a hindrance
- the intensity range is enormous; this graph uses a logarithmic scale as the only way to display the whole spectrum
- the low-loss regime containing the plasmon peak (see Chapter 38) is relatively intense
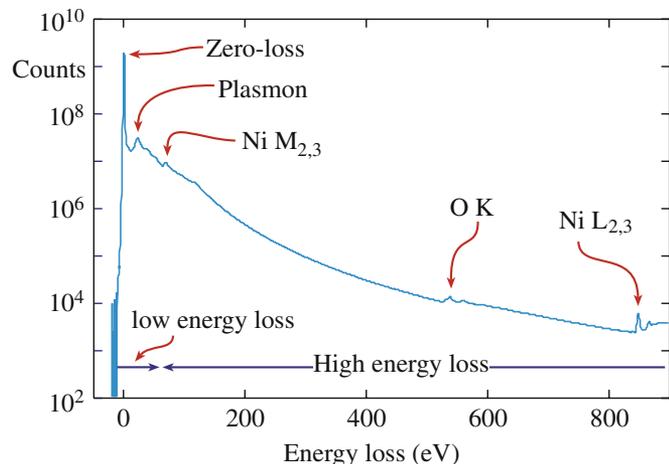

FIGURE 37.1. An EELS spectrum displayed in logarithmic intensity mode. The zero-loss peak is an order of magnitude more intense than the low energy-loss portion (characterized by the plasmon peak), which is many orders of magnitude more intense than the small ionization edges identified in the high energy-loss range. Note the relatively high (and rapidly changing) background.

- the element-characteristic features called ionization edges (see Chapter 39), are relatively low in intensity compared to the background
- the overall signal intensity drops rapidly with increasing energy loss, reaching negligible levels above ~2 keV, which really defines the energy limits of the technique (and this is about the energy when XEDS really comes into its own, emphasizing again their complementarity).

37.2 EELS INSTRUMENTATION

Throughout this and the subsequent chapters, we'll distinguish between spectrometers and energy filters (so called because they filter out electrons of specific energy). The former primarily produce spectra and are great for the dedicated spectroscopist. The latter can produce spectra but are designed to create images and so are more useful to microscopists who find spectra boring and who want filtered images and DPs to compare with standard ones produced by their TEM. There is only one kind of spectrometer commercially available, manufactured by Gatan, Inc. termed a parallel-collection EELS or PEELS. The PEELS is a magnetic-prism (sometimes called a magnetic-sector) system and is mounted on a TEM or STEM after the viewing screen or post-specimen detectors. There are two kinds of filters which result in radically different instruments which, nevertheless, perform similar functions. We'll describe these two types in some detail throughout the chapter.

The post-column Gatan Image Filter (GIF) is a development of their magnetic-prism PEELS. The in-column filter, a magnetic variant of the original Castaing-Henry magnetic prism/electrostatic mirror, is exemplified by the Omega (Ω) filter, pioneered by Zeiss and also now used by JEOL. The in-column filter, as the name implies, is integrated into the TEM and sits between the specimen and the viewing screen/detector (rather than being an optional addition, like the PEELS/GIF). Magnetic spectrometers, along with electrostatic or combined electrostatic/magnetic systems, have been the subject of serious reviews by Metherell and Egerton. If you're an instrument enthusiast, you should try to read these articles but if you just want a more concise summary, then try Egerton's chapter in Ahn's edited book.

ENERGY FILTERS

Two types of commercial filters are presently manufactured: the post-column filter and the in-column filter.

Surface scientists use electron spectrometers to measure exceedingly small (meV) energy losses in low-energy electron beams reflected from the surfaces of samples in UHV instrumentation, such as XPS and Auger systems. We will deal only with transmission EELS studies of high-voltage TEM beams. Recent advances in monochromators for electron guns, combined with spherical and chromatic aberration correction, mean that energy resolution <100 meV is now possible and in the near future this will open a whole new field of TEM-based EELS studies, complementing the established, surface-science techniques but with much better lateral resolution.

Whether you use a Gatan post-column PEELS, a GIF, or an Ω filter, the electron passes through one or more magnetic spectrometers, so we'll start by discussing the principles of this basic tool before moving on to the more complex filtering systems.

37.3 THE MAGNETIC PRISM: A SPECTROMETER AND A LENS

The magnetic prism spectrometer is preferred to an electrostatic or combined magnetic/electrostatic spectrometer, for several reasons

- It is compact and easily interfaced to the TEM. (Remember the WDS problem.)
- It offers sufficient energy resolution to distinguish spectra from all the elements in the periodic table and so is ideal for analysis.
- 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.

The basic PEELS-TEM interface and ray paths are shown in Figure 37.2 and a picture of a Gatan spectrometer (actually a combination imaging spectrometer), which would be installed beneath the camera system of a TEM, is shown in Figure 37.3. Because these spectrometers are so widespread, many of the numerical values in this chapter are taken from the Gatan literature (see URL #2). For the details of operation you should, of course, read the instruction manual and Brydson gives a concise summary of all the experimental steps.

From Figure 37.2B, you can see that electrons are selected by a variable entrance aperture (diameters: 1, 2, 3, or 5 mm in the Gatan system). (Obviously, you have to make sure the screen is raised and any on-axis detectors or cameras are removed in order to detect the spectrum.) The electrons travel down a 'drift tube' (Figure 37.2A) through the spectrometer and are deflected through $\geq 90°$ by the magnetic field. Electrons that have lost
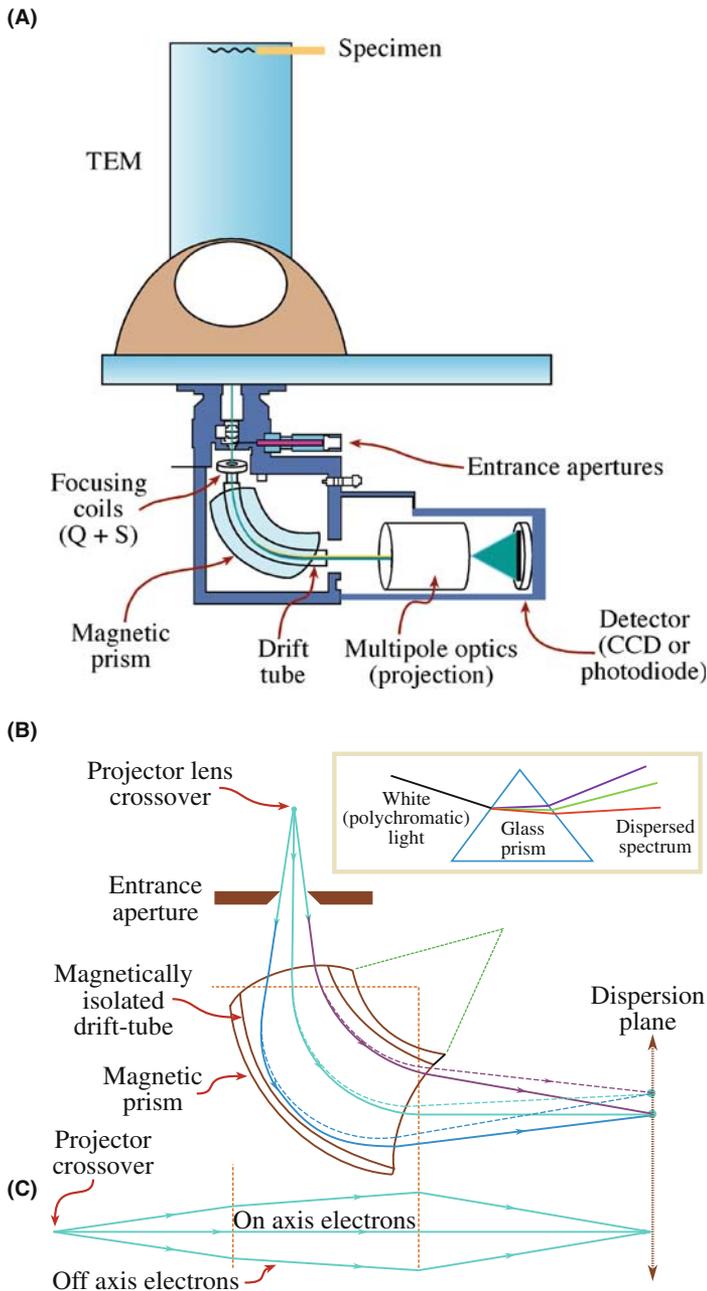
(A)

(B)

(C)

FIGURE 37.2. (A) Schematic diagram showing how a PEELS is interfaced below the viewing screen of a TEM and the position of the various components. (B) Ray paths through a magnetic prism spectrometer showing the different dispersion and focusing of the no-loss and energy-loss electrons in the image (dispersion) plane of the spectrometer. The inset shows the analogy with the dispersion of white light by a glass prism. (C) The lens focusing action in the plane normal to the spectrometer.

energy are deflected further than those suffering zero loss. A spectrum is thus formed in the dispersion plane, consisting of a distribution of electron intensity (I) versus energy loss ($\mathcal{E}$). You can see that this process is closely analogous to the dispersion of white light by a glass prism shown in the inset.

FIGURE 37.3. A Gatan Tridiem PEELS which interfaces below the viewing screen of an AEM.

NOTATION

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). So we will use $\mathcal{E}$ (note the different font) but remember, it really means a **change** in E.

Now if you look at Figure 37.2B, 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 (or image) plane of the spectrometer. So the prism also acts as a magnetic lens. This focusing action is not seen in the otherwise-analogous glass prism (if you recall your high-school physics lab, you had to use a post-prism convex lens to focus the spectrum and separate the individual colors (i.e., frequencies/energies)). We'll give many examples of EEL spectra in the subsequent chapters.

37.3.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. The latest spectrometers are fully corrected for third-order aberrations and the alignment, compensation for stray-AC fields, and focusing are all software controlled. So read the manual, because we will not reproduce it here, merely describe the principles.

The spectrometer has to focus the electrons because off-axis electrons experience a different magnetic field to 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 37.2B. These non-normal faces also act to ensure that electrons traveling out of the plane of the paper in Figure 37.2B are also focused in the dispersion plane, as shown in Figure 37.2C (because it focuses in two planes we call it 'double focusing'). The faces of the prism are curved to minimize aberrations and, like their counterparts within the TEM column, the spectrometer lenses continue to improve as higher-order aberrations are minimized. The many quadrupoles, sextupoles, and other focusing electronics and lenses are not shown, but the length of the spectrometer in Figure 37.3 (and looking ahead to Figure 37.15) gives you some idea of its complexity.

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 or filter depends on the detail of the machine you are using

- In DSTEMs with no post-specimen lenses the object plane for a post-column spectrometer is the plane of the specimen.
- In a TEM/STEM, or a DSTEM with post-specimen lenses, the object plane for a post-column spectrometer is the back-focal plane of the projector lens, which can contain either an image or a DP.
- In a TEM/STEM, or a DSTEM with post-specimen lenses, the object plane for an in-column filter is the back-focal plane of the first projector (or intermediate) lens, which can contain either an image or a DP.

In a TEM, the projector-lens setting is usually fixed, so the object plane is fixed and the manufacturer usually sets this plane to coincide with the differential pumping aperture separating the column from the viewing chamber. In some DSTEMs there are no post-specimen lenses so the object plane of the spectrometer is the plane of the specimen. In this case, it is essential that you keep your specimen height constant.

In practice, the back-focal plane of the projector may move slightly 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 called the zero-loss peak (ZLP), which we'll talk about more in the next chapter. You can see the ZLP on the computer display of the EELS system and the software focuses it by adjusting a pair of pre-spectrometer quadrupoles until it has a minimum width and maximum height.

The consistency of the information passed through the spectrometer is described by the transmissivity, which is the imaged area (object radius) as a function of the solid scattering angle for a given energy resolution. A perfect spectrometer would uniformly transmit electrons of a specific energy loss over the whole spectrum or, more importantly, over the whole image. If the ZLP is scanned across the spectrometer slit, then a uniform intensity should fall on the detector. Deviations from uniformity reflect the aberrations in the spectrometer; see the paper by Uhlemann and Rose for the details.

37.3.B Spectrometer Dispersion

We define the dispersion as the distance in the spectrum (dx) between electrons differing in energy by 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. For the Gatan magnet, the radius of curvature (R) of electrons traveling on axis is about 200 mm, and for 100-keV electrons dx/dE is ~ 2 μm/eV. For PEELS 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 $\sim 15\times$ before the spectrum can be detected with resolution closer to 1 eV. This magnification requires post-spectrometer lenses and four quadrupoles are used. The dispersion should be linear across the PDA (photo-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 different parts of the PDA.

37.3.C Spectrometer Resolution

We define the energy resolution of the spectrometer as the FWHM of the focused ZLP and, while it might seem trivial, you should remember to focus the spectrometer every time you acquire a spectrum or filtered image. The type of electron source determines the resolution. As we saw back in Chapter 5 (Table 5.1), at ~ 100 keV a W source has the worst energy resolution (~ 3 eV), a LaB_6 is slightly better at ~ 1.5 eV, a Schottky field emitter can give ~ 0.7 eV, and a cold FEG gives the best value of ~ 0.3 eV. These values will all get slightly worse at higher keV. Because of the high emission current from thermionic sources, the energy resolution is limited by electrostatic interactions between electrons at the filament crossover. This electron-electron interaction is called the Boersch effect. We can partially overcome this limit by undersaturating the filament and using only the electrons in the halo. Then a LaB_6 source can attain a resolution of ~ 1 eV but at the expense of a considerable loss of current, which we can compensate for by increasing the beam size and/or the C2 aperture. There are other ways you can improve the energy resolution, for example, dropping the kV and the probe current. Figure 37.4A shows data from a cold FEG operated at 200 keV delivering a FWHM of 370 meV (0.37 eV) which is about the best that can be obtained under standard operating conditions.
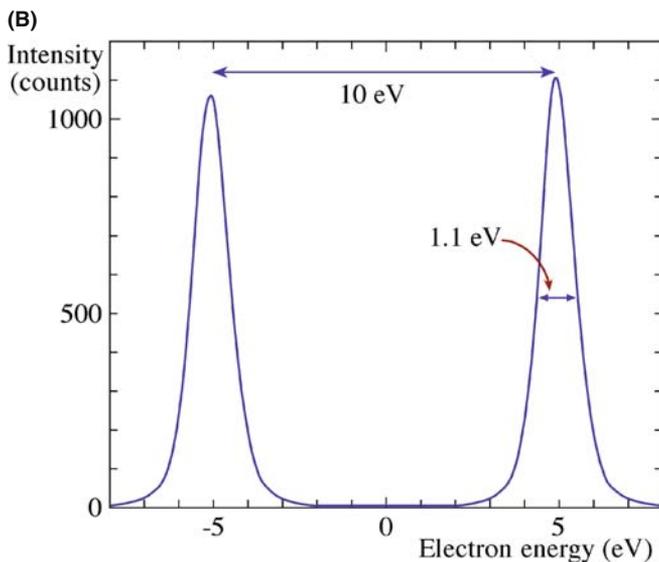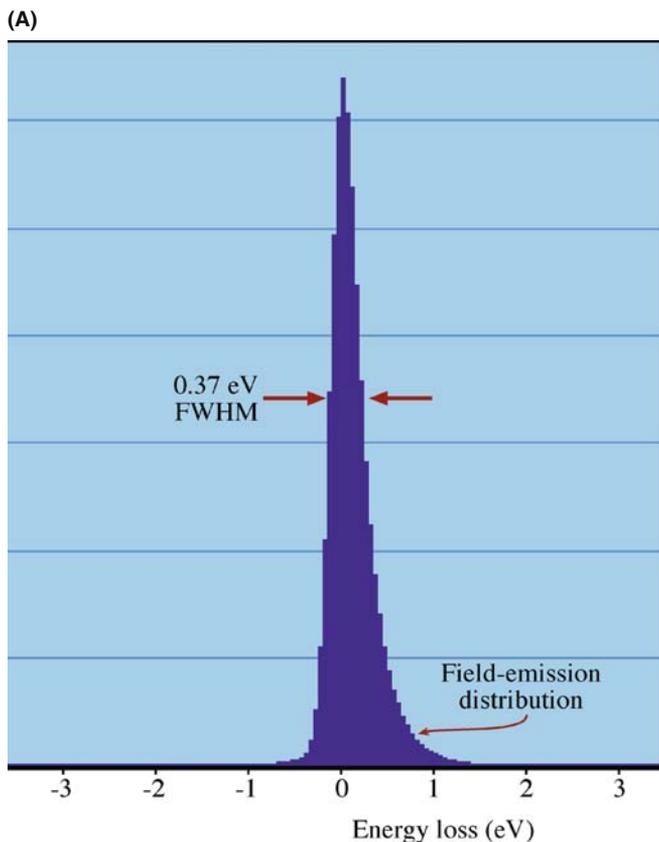
(A)

(B)

FIGURE 37.4. (A) The energy resolution (0.37 eV) of a cold FEG at 200 keV with 150 pA of current determined from the FWHM of the ZLP. The peak is not symmetrical because of electrons tunneling out from the tip with a slight (< 1 eV) loss of energy. (B) The intensity profile across the ZLP exposed on a CCD camera, then displaced by 10 eV and re-exposed. The resolution, defined by the FWHM, in this case is 1.1 eV and if the number of channels between the peak centroids is counted (e.g., 100 channels) then the dispersion (0.1 eV/channel) is easy to calculate.

The energy resolution decreases slightly as the energy loss increases, but it should be no worse than ~1.5× the ZLP width up to 1000 eV energy loss.

If you operate at a higher voltage you should also expect a degradation of energy resolution as the kV increases, approximately tripling from 100 to 400 kV.

Because the magnetic prism is so sensitive, external magnetic fields in the microscope room may limit the resolution. If you have an older PEELS, you may see a disturbance to your spectrum if you sit in a metal chair and move around or if you open metal doors into the TEM room, so fine, hand-carved chairs are *de rigeur* for old EELS operators.

ENERGY RESOLUTION

For comparison: for XEDS it's >100 eV; for EELS it's <1 eV.

The best energy resolution requires a small projector crossover and a small (1 or 2 mm) entrance aperture giving a collection semi-angle of ~ 10 mrads (see Section 37.4.B below). A larger entrance aperture degrades the resolution because the off-axis beams suffer aberrations. The resolution may change as you deflect the ZLP onto different regions of the PDA, although this should not happen if your spectrometer is properly aligned.

37.3.D Calibrating the Spectrometer

We can calibrate the spectrometer (in terms of eV/channel, just like an XEDS) by placing an accurately known voltage on the drift tube, or changing the accelerating voltage slightly, both of which displace the spectrum by a known, fixed amount. Figure 37.4B shows images of the ZLP displaced by a known amount, thus defining both the resolution and the dispersion of the spectrometer at the same time. Usually, calibration is automatically handled by the software but, if you have a really early system, you can (as in XEDS) look for features in a spectrum from a known specimen that occur at specific energies, such as the ZLP at 0 eV and the Ni L$_3$ ionization edge at 855 eV. Modern electronics are reasonably stable and the calibration doesn't shift substantially but, unless you have the PEELS, which automatically compensates for energy and current drift, you have to check these regularly throughout an operating session since, if shifts of even a few eV occur, they are of the same order as the energy resolution of the spectrometer.

37.4 ACQUIRING A SPECTRUM

To gather a spectrum, such as shown in Figure 37.1, we need a recording device in the dispersion plane of the spectrometer. Historically this was photographic film and early commercial PEELS had a semiconductor PDA but now a CCD is used, in common with both

GIFs and Ω filters (we talked about CCDs in Chapter 7). CCDs show lower gain variation, ~30× better sensitivity, higher dynamic range, and improved energy resolution compared with PDAs. It's worth a brief aside to mention serial EELS or SEELS which was the first commercial method of recording spectra around 1980. While it offered some advantages, SEELS was slow and tedious since each energy loss channel was recorded sequentially and it was rapidly superseded by PEELS which gathers the whole energy range simultaneously. The Gatan PEELS uses a YAG scintillator coupled via fiber optics to a PDA or CCD in the dispersion plane of the spectrometer, as shown in Figure 37.5. Since many PDA-PEELS systems are still in use, it is worth describing its operation and limitations, The PDA consists of 1024 electrically isolated and thermoelectrically cooled Si diodes, each ~25 μm across. The integration time to gather a spectrum can vary from a few msec to several hundred seconds depending on the intensity of the signal. Because each diode saturates at ~16,000 counts you have to select an integration time that avoids saturation during any single acquisition, and you can then sum as many individual integration times as you need to give a spectrum of the desired quality. The CCD detector is 100 × 1340 array of 20 μm pixels and does not saturate rapidly like the PDA so acquisition is much more straightforward. After

integration, the whole spectrum is read out via an amplifier through an A/D converter and into the computer display system. The Gatan software offers a variety of standard acquisition conditions suited to different types of spectra.

37.4.A Image and Diffraction Modes

When using any spectrometer or filter in a TEM/STEM, we can operate in one of two modes, and the terminology for this is confusing. If we 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, which the post-column spectrometer uses as its object. From the spectroscopist's viewpoint, therefore, this is termed 'diffraction mode' or 'diffraction coupling,' but from the microscopist's viewpoint, it is more natural to call this 'image mode' since we 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 (post-column) spectrometer/GIF object plane contains an image, and the terminology is reversed. Likewise, as we'll see for an in-column filter, the back-focal plane of the intermediate lens on which the filter is focused can contain either an image (diffraction mode; there's a DP on the TEM screen) or a DP (image mode; there's an image on the TEM screen).
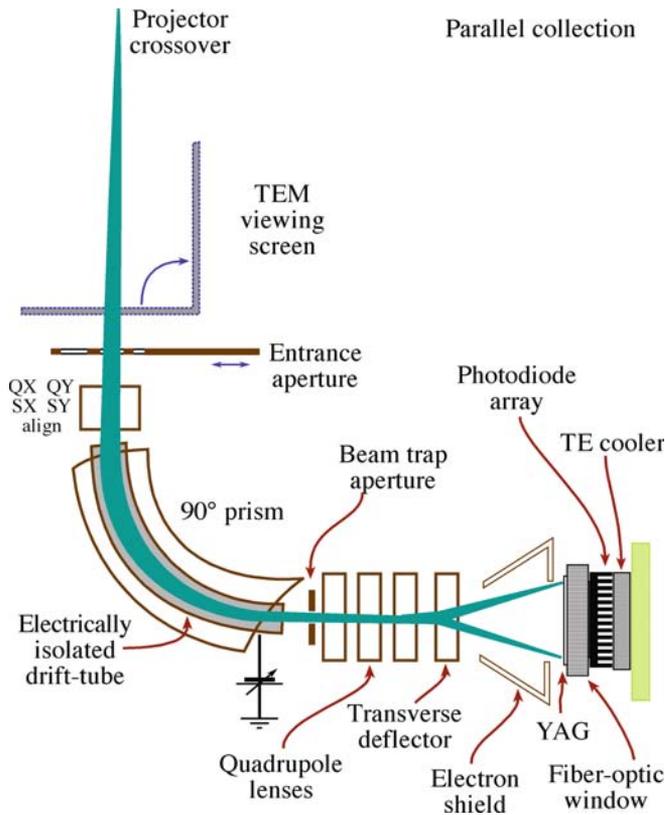
- The spectroscopist uses the term *image coupling* and the microscopist says *diffraction mode*.
- In this text, *image mode* means an image is present on the TEM screen; naturally, we use the microscopists' terminology. You should *not* use this mode for any spectroscopy, only for EFTEM imaging.
- You should use *diffraction (or STEM) mode* for all spectroscopy and imaging, except for EFTEM imaging.
- Both sets of terms appear in the earlier literature, often without precise definition, so it can be rather confusing, but the microscopists have generally won this conflict.

37.4.B Spectrometer-Collection Angle

The collection angle (as before, we really mean semi-angle) of the spectrometer (β) is a most important variable in several aspects of EELS, so you should know β for all your usual operating modes. If you do gather spectra with different β it is difficult to make sensible comparisons without considerable post-acquisition processing. Poor control of the collection angle is the most common error in quantification, although it is less important the higher the value of β that you use. The detailed intensity variations in the spectrum depend on the range of electron-scattering angles gathered by the spectrometer. Under certain circumstances, the effective value of β can be modified if the beam-convergence

FIGURE 37.5. Schematic diagram of parallel collection of the energy-loss spectrum onto a YAG scintillator fiber-optically coupled to a semiconductor PDA.

angle α is $> \beta$, but we'll discuss that when we talk about quantification of ionization edges in Chapter 39. Likewise, we'll see that there is a characteristic or most-probable scattering angle for specific loss processes and typically, β should be $2-3\times$ that angle. So, if in doubt, make β larger. The value of β is affected by your choice of operating mode, and so we will describe how to measure β under different conditions that you may encounter and, while the Gatan software can calculate the value for you, it's good to know the principles behind the black box. Let's start by considering the most simple definition for β, as illustrated in Figure 37.6.

> ### SEMI-ANGLE β
> β is the semi-angle subtended at the specimen by the entrance aperture to the spectrometer or filter.

Dedicated STEMs. In a basic DSTEM the situation is straightforward if there are no post-specimen lenses because, as shown in Figure 37.6, β 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
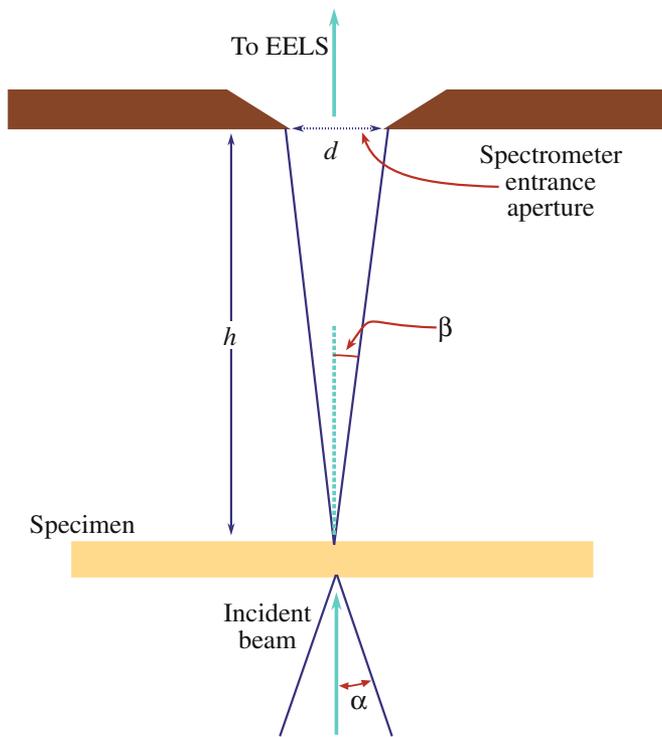
$$\beta \approx \frac{d}{2h} \qquad (37.1)$$

FIGURE 37.6. Schematic diagram showing the definition of β in a DSTEM in which no lenses exist between the specimen and the spectrometer entrance aperture.

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 the spectrometer apertures. Therefore, if h is $\sim$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 we discuss below.

TEM-image mode. Remember that, in image mode, a magnified image of the specimen is present on the viewing screen or detector. 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 we control the angular distribution of electrons contributing to any TEM image by the size of the objective aperture in the back-focal plane of the objective lens. If we don't use an objective aperture then the collection angle is very large ($>\sim$100 mrads) and need not be calculated accurately because we'll see that small differences in a large β 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). As you will recall, this magnification is controlled by 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$\times$ then L is 0.05 mm. Thus we can show

$$\beta \approx \frac{r_0}{L} \qquad (37.3)$$

where r_0 is the maximum radius of the DP in the focal plane of the spectrometer. Typically, r_0 is $\sim$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 $\beta = 100$ mrads, any calculation or quantification you do will be effectively 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, β is the objective-aperture diameter divided by twice the focal length of the objective lens, as shown in Figure 37.7. For example, with a focal length of 3 mm and a 30 μm diameter aperture, β is $\sim$ 5 mrads, which is good if you need high-energy resolution.
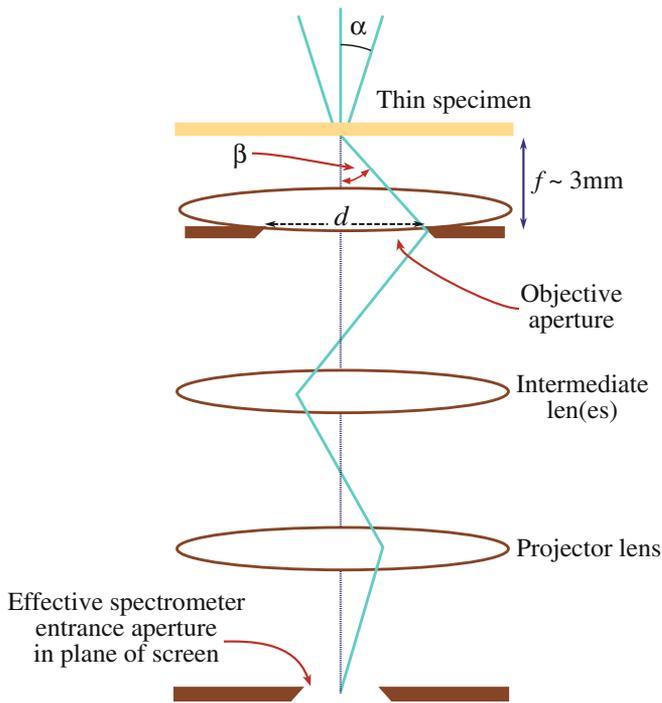
FIGURE 37.7. The value of β in TEM image mode is governed by the dimensions of the objective aperture in the BFP of the objective lens.
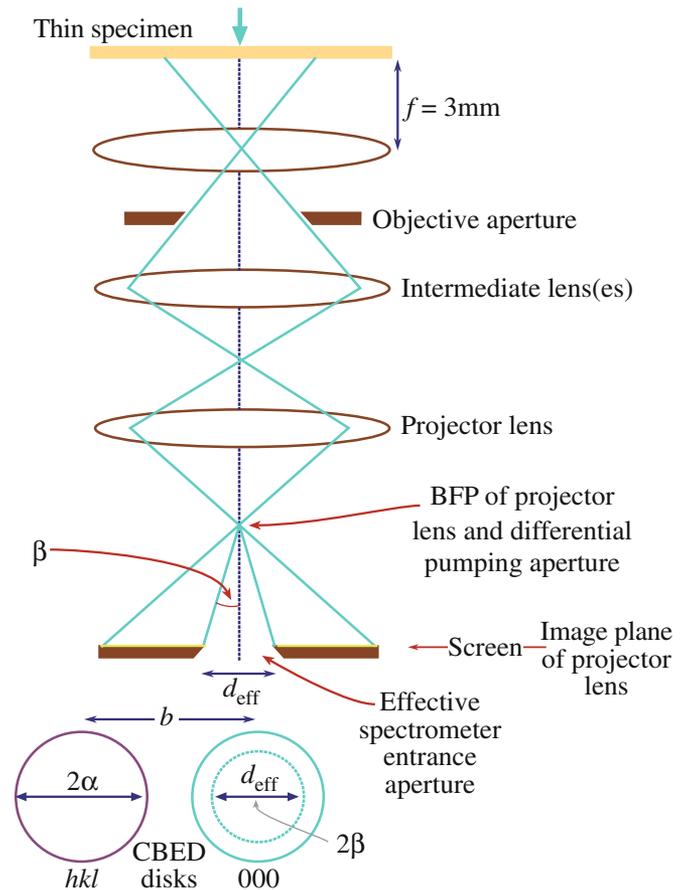

FIGURE 37.8. The value of β in TEM/STEM diffraction mode is determined by the dimensions of the spectrometer entrance aperture, projected into the plane of the DP. The dimensions can be calibrated by reference to a known DP.

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 to the area of the image that sits directly above the spectrometer-entrance aperture. However, as we'll see in Section 37.4.C, there is some considerable error (~ 100 nm) due to chromatic aberration. We will return to this point in Section 39.10 when we discuss the spatial resolution. Remember also that with the objective aperture inserted, you cannot do XEDS, so 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. We focus the spectrometer on an image of the specimen; so we see a DP on the screen and also in the plane of the spectrometer-entrance aperture. Under these circumstances, you control β by your choice of the spectrometer-entrance 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 shown in Figure 37.8. Knowing the size of the spectrometer-entrance aperture, the value of β can be calibrated because the distance (b) that separates the 000 spot and a known hkl maximum is twice the Bragg angle, $2\theta_B$. If the effective aperture diameter in the recording plane (equivalent to the

STEM detector collection angle back in Section 22.6) is d_{eff} and $b = 2\theta$ then

$$\beta = \frac{d_{eff}}{2}\frac{2\theta_B}{b} \qquad (37.4)$$

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

$$d_{eff} = \frac{d\,D}{D_A} \qquad (37.5)$$

where D is the distance from the projector crossover to the recording plane and D_A is the distance between the crossover and the 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 Gatan PEELS systems but D varies depending on the TEM; you have control over d and L. For example, if D is 500 mm and L is 800 mm then for a 5 mm diameter aperture, β is ~ 5 mrads.

If we 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, we have moved the specimen to the focal plane of the spectrometer. This special value of L is equal to D, which you should know for your own microscope. Then β is simply the entrance aperture diameter divided by D_A (610 mm).

In summary, the collection angle is a crucial factor in EELS and the spectrometer/filter software should calculate the values of β in the various operating conditions that you'll encounter.

- Generally, large collection angles will give high intensity but poor energy resolution.
- If you collect your spectrum in image mode without an objective aperture then you won't compromise your energy resolution but spatial resolution is poor, as we'll see below.
- If you're in diffraction mode and you control β with the entrance aperture, then a large aperture (high intensity, high β) will lower the resolution and vice versa.
- Generally, smaller collection angles also give a higher signal-to-noise ratio in the spectrum.

37.4.C 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, we position the area to be analyzed on the optic axis, above the 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 analysis 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

$$\Delta f = C_c \frac{\mathcal{E}}{E_0} \qquad (37.8)$$

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 E_0 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 very large compared to the value of 10 nm, which we calculated without considering chromatic-aberration effects.

In TEM diffraction mode, you select the area of the specimen contributing to the DP in the usual way. You can use either 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 EELS, just as for XEDS analysis. But rather than just selecting a single point, it is much better to keep the beam scanning and gather a spectrum at every point (i.e., spectrum imaging; see Section 37.8). This conclusion is true for both in-column and post-column filtering.

> **THE PRICE**
> While TEM-image mode might be good for gathering spectra with a large β and high-energy resolution, the price you pay is much poorer spatial resolution, so we don't recommend it.

37.5 PROBLEMS WITH PEELS

There are several standard tests you need to perform to determine that all is well with the PEELS PDA and electronics, just as we described for XEDS back in Chapters 32 and 33.

37.5.A Point-Spread Function

In a PEELS, you can reduce the magnification of your spectrum so that the ZLP occupies a single PDA channel or pixel on the CCD. Any intensity registered outside that channel is an artifact of the system and is called the point-spread function (PSF). This function acts to degrade the inherent resolution of the magnetic spectrometer. The ZLP may spread on its way through the YAG scintillator and the fiber optics before hitting the PDA or CCD. Figure 37.9A shows the PSF of a PEELS and clearly there is intensity well outside a single channel, although a CCD offers considerably better PSF performance than the PDA. The PSF broadens features in your spectrum such as ionization edges, but you need to remove its effect by deconvolution (see Section 39.6) thus restoring the resolution of the spectrum to that inherent in the beam, in the same way we described for X-ray spectra in Section 34.4, except that the commercial software is available and it makes sense to deconvolute the PSF from any spectrum that you gather. The concept is essentially the same as the point-spread function we
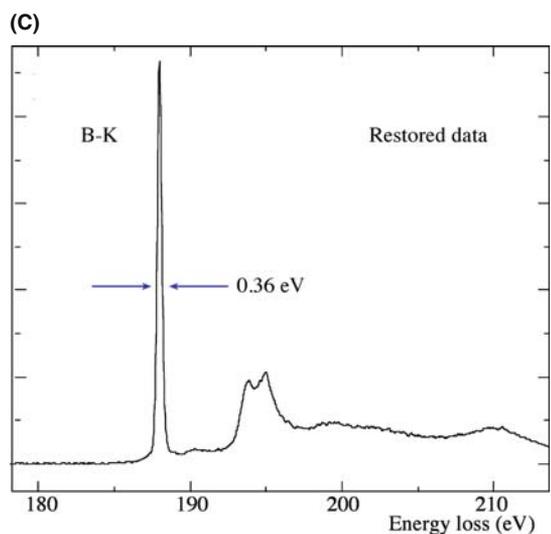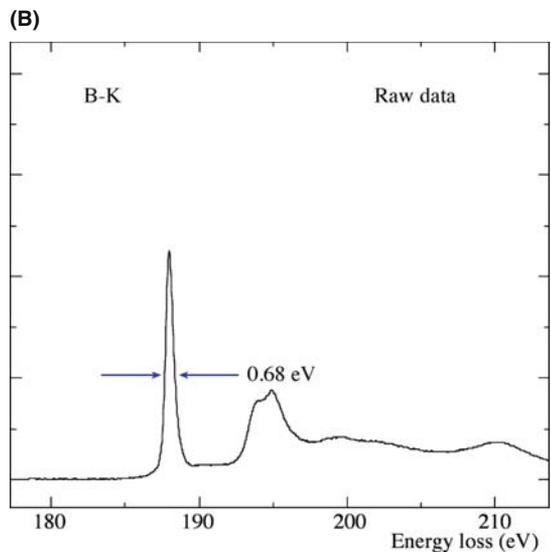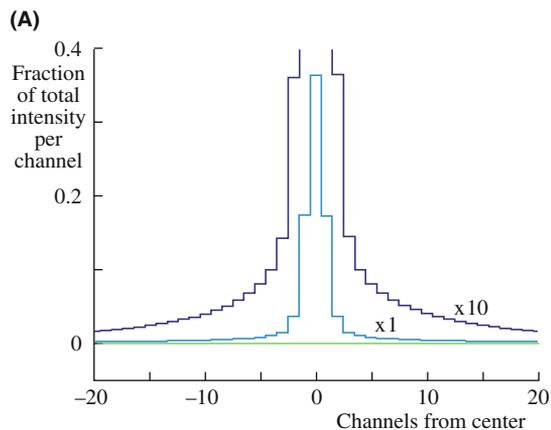
(A)

(B)

(C)

FIGURE 37.9. (A) The point-spread function showing the degradation of the intense well-defined ZLP through spreading of the signal as it is transferred from the scintillator via the fiber optic coupling to the PDA or CCD. The peak should occupy a single channel but is spread across several channels. (B, C) The improvement in energy resolution in the boron K edge from a BN nanotube as a result of ZLP deconvolution. The raw data (B) indicate a resolution of 0.68 eV for the B-K edge and this is improved (C) to 0.36 eV after deconvoluting the point-spread function.

discussed for HRTEM. Figure 37.9B and C demonstrates that such energy deconvolution can produce a significant sharpening of the spectrum and, just as in XEDS, there is no reason not to run a ZLP deconvolution routinely to get the best resolution in your spectrum, so long as you are confident (e.g., by testing the software on spectra from known specimens (see Section 39.6)) that such processing does not introduce its own artifacts; which is a good segue into the next section.

37.5.B PEELS Artifacts

Almost all the artifacts in a PEELS system are a consequence of the PDA, which is why CCD detectors have been introduced. If you have a PDA system, then the individual diodes will differ slightly in their response to the incident electron beam and therefore, there will be a channel-to-channel gain variation in intensity. If you spread the beam uniformly over the array using at least the 3 mm aperture and looking at the diode readouts, you can see any variation, as shown in Figure 37.10. You have to divide your experimental spectrum by this response spectrum to remove any gain variation. Alternatively, and this is recommended, you can gather two spectra with slight energy shifts ($\sim$1–2 eV) or spatial shifts between them and superimpose them electronically. Using a 2-D CCD array, as in the GIF, also removes this problem.

If you gather many spectra and superimpose them to avoid saturation of the PDA, you'll generate readout noise. Random readout noise or shot noise from the electronics chain is minimized by taking fewer readouts, and by thermoelectric cooling of the PDA. Individual diodes may fail and give high leakage currents which appear as spikes in the spectrum. The fixed-pattern noise is a function of the three-phase readout circuitry. All these effects will appear when there is no current falling on the diodes and together they constitute the dark current (see Figure 37.11). The dark current is
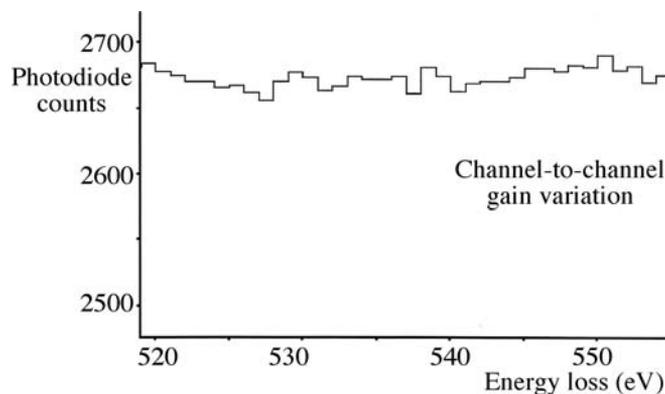

FIGURE 37.10. The variation in the response of individual diodes in the PEELS detection system to a constant incident electron intensity. The channel-to-channel gain variation is clear and each detector array has its own characteristic response function.
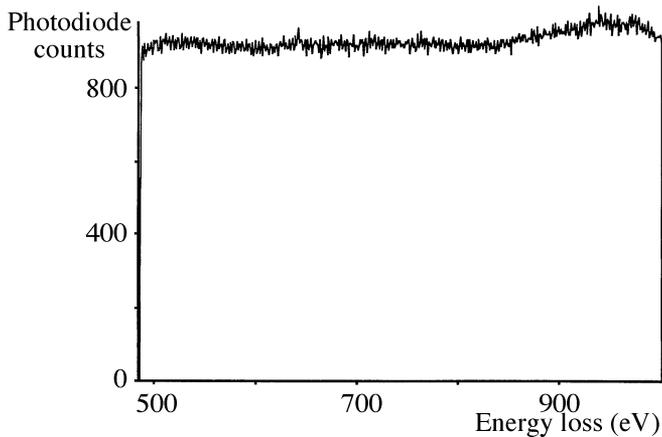
FIGURE 37.11. The intensity of the dark current which flows from the PDA when no electron beam is present.

small unless you have a bad diode and it is only a problem when there are very few counts in your spectrum or you have added together multiple (e.g., 10 or more) spectra. A CCD detector has a higher dark current than a cooled PDA. Figure 37.12 shows some of these effects and how to remove them.

When the diodes are cooled, only ~95% of the signal is read out in the first integration, ~4.5% on the second, ~0.25% on the third, and so on. This incomplete readout can introduce an artifact if you saturated the diodes with an intense signal like the ZLP. This residual peak then shows up as a ghost peak in the next readout and decays slowly over several readouts. So, if a ghost peak appears, just run several readouts and it will disappear; this way you'll never confuse a ghost with a genuine ionization edge or other spectral feature. You can also get a ghost peak on a CCD detector if you overexpose the scintillator.

Increasing the keV means more electrons are generated in the scintillator and the sensitivity should be linearly related to the electron energy. If you're doing quantitative analysis, check that the YAG responds linearly to different intensities 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, subtract the dark current. Obviously the ratio of these two intensities should be unity, for all levels of signal falling on the YAG. If you're more intent on low-loss spectrometry or fine-structure studies, this non-linearity is not important.

USING A CCD

If you use a PEELS, GIF, or another filter with a CCD detector, all these artifacts are absent, except the ghost peak and dark current.

We can summarize the PDA artifacts and how we eliminate them in Table 37.1.
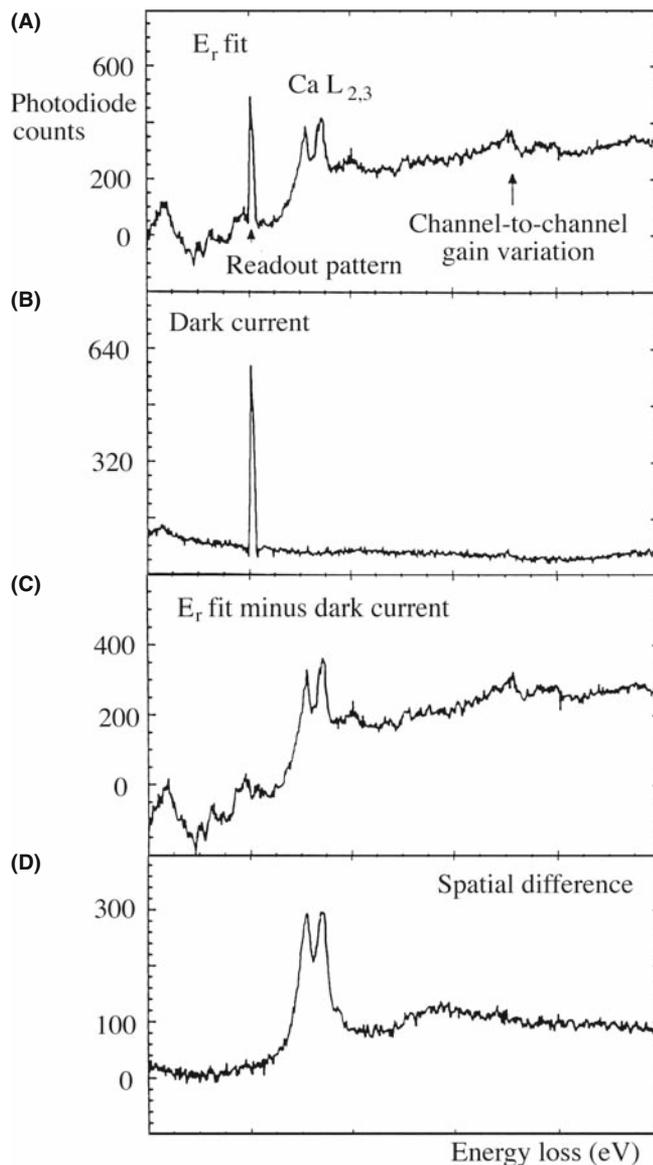

FIGURE 37.12. (A) A Ca $L_{2,3}$ edge spectrum showing both channel to channel gain variation and a faulty diode with a high leakage current which appears as a spike in the spectrum. The spike is referred to as the readout pattern and is present in every recorded spectrum. Subtracting the dark current (shown in (B)) removes the spike (C) and a difference spectrum (D) removes the gain variation, leaving the desired edge spectrum.

37.6 IMAGING FILTERS

Energy-filtered TEM (EFTEM) is sometimes termed energy-filtered imaging (EFI) or electron-spectroscopic imaging (ESI) and is perhaps the most powerful AEM technique, as will become apparent. To perform EFTEM, you basically select (or filter out) electrons of a specific energy coming through the spectrometer and form either an image or a DP. Doing EFTEM is perfectly acceptable in TEM image mode (unlike spectroscopy) so long as you keep the energy slit small to minimize chromatic aberration and, to select the

TABLE 37.1 PEELS Artifacts and How to Eliminate Them

Artifact	Source	Elimination
High leakage current (spike)	Bad diodes	Subtract dark current
Channel to channel gain variation	Different diode responses	Gather spectra on different portions of array and superimpose
Internal scanning noise	Electronics readout	Adjust the electronics and subtract the dark count
Ghost peak	Saturation of diode	Run several readouts
Non-linear response	YAG scintillator is damaged	Zero-loss intensity from different readout numbers with same total integrated time should be identical; if not, replace scintillator

electrons with a specific energy, you change the gun voltage slightly such that those electrons come on-axis and you don't need to keep re-focusing the objective lens.

At the start of the chapter, we noted that there are two types of energy filters: the in-column (Ω) filter and the post-column GIF and both produce EFTEM images. In-column filters are placed in the heart of the TEM imaging system, between the intermediate and projector lenses such that the recording CCD detector only receives electrons that have come through the filter. So all images/DPs consist of electrons of a specific selected energy. (You can, of course, turn off the filter and use the microscope like a normal TEM, but since there are so many advantages to filtered imaging, your reasons for doing this would be questioned.) You can also record a spectrum as we'll show, but the in-column filters are primarily imaging tools and it is both feasible and desirable to operate all the time in filtered mode.

The post-column GIF is added below the TEM viewing screen, just like a PEELS and therefore you can choose to use it or not. The GIF can be seen as either a more flexible instrument or one that limits you to having to decide whether or not to filter your images. Such differences, while perhaps pedantic, have been known to lead to fights in bars at M&M conferences. The best solution, of course, is to have one of each type of filter in your laboratory, but this takes some of the fun out of going to bars at M&M. Let's examine each type of filter in more detail.

37.6.A The Omega Filter

Zeiss first used a mirror-prism system originally devised by Castaing and Henry in 1962. The drawback to the mirror-prism is the need to split the high-voltage supply and raise the mirror to the same voltage as the gun. So Zeiss now uses a magnetic Ω filter, as does JEOL, currently the only other TEM manufacturer with an in-column filter. The filter is placed in the TEM column between the intermediate and projector lenses and consists of a set of magnetic prisms arranged in an Ω shape which disperses the electrons off axis, as shown in Figure

37.13A but, in the end, brings them back onto the optic axis before entering the final projector lens. Although it is not shown, each of the four prisms is machined with curved faces (like Figure 37.2B) to reduce aberrations. There isn't much to see externally on the TEM except an asymmetry on the side of the (somewhat taller) column, which you can also see if you go back and look at the picture of the Zeiss UHRTEM in Figure 1.9.

The multiple steps necessary for ETEM imaging via an in-column filter are shown in Figure 37.13B. As shown in this figure, we usually project an image into the prism which is focused on a DP in the back-focal plane of the intermediate lens (i.e., image mode in our terminology). Therefore, the entrance aperture to the spectrometer selects an area of the specimen and β is governed by the objective aperture. Electrons following a particular path through the spectrometer (the red ones in Figure 37.13B) 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 CCD. EFTEM has several advantages over conventional TEM images; there's much more about EFTEM in the companion text.

If you change the focus of the projector lens onto the dispersion plane of the filter (where the energy-selecting slit is located in Figure 37.13B) and then remove this slit, you'll see a spectrum on the viewing screen/CCD. The spectrum appears as a line of varying intensity (see Figure 37.14A), which you can imagine as looking down from above on a traditional spectrum display such as Figure 37.1. Since the spectrum is recorded digitally on the CCD, it is simple to select a line through this spectrum and have the computer display a traditional spectrum of counts versus energy loss, as shown in Figure 37.14B.

As with PEELS, you can also change the TEM optics and project a DP into the prism, thus producing an energy-filtered DP on the CCD, as we've already described back in Chapter 20. If you then 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. Such angular (or momentum)-resolved
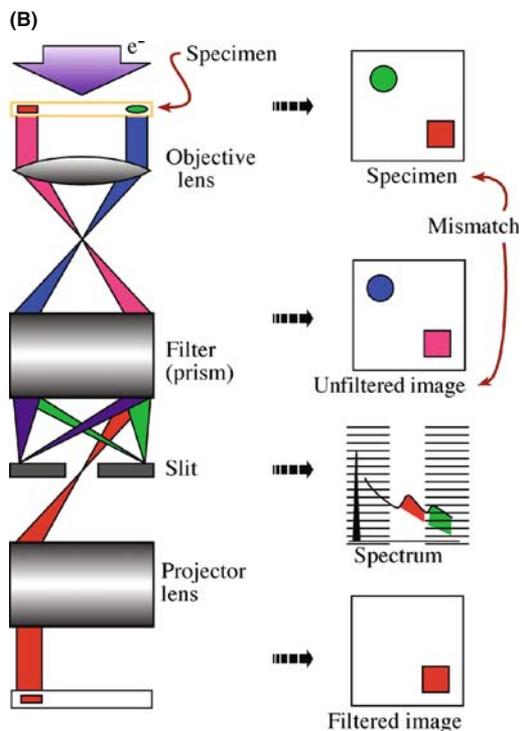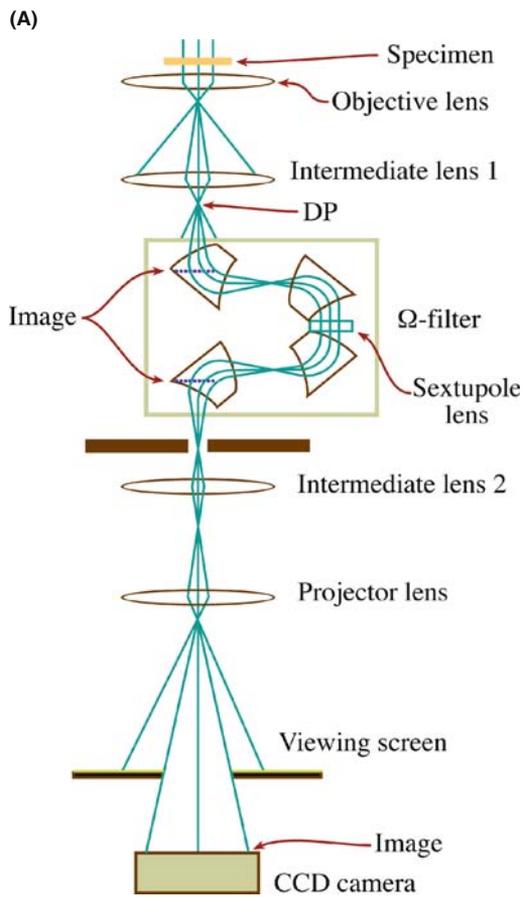
FIGURE 37.13. (A) Schematic diagram of an in-column Ω filter inserted in the imaging lens system of a TEM. (B) Schematic ray diagram of the steps needed to create an EFTEM image.
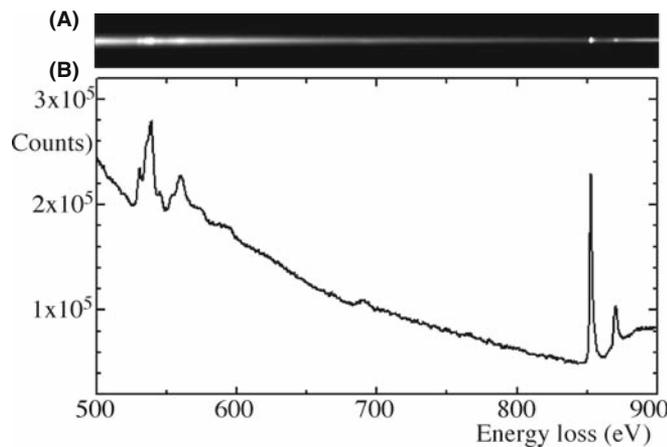

FIGURE 37.14. (A) Spectrum from an Ω filter. The axis of the line is energy loss and the intensity varies along the line. (B) Conventional spectrum of intensity versus energy-loss obtained from (A).

EELS is a whole separate field of study which we'll discuss in Section 40.8.

37.6.B The GIF

The GIF is a Gatan PEELS with an energy-selecting slit after the magnet and a 2D slow-scan CCD detector, rather than a 1D PDA, as the detector. Figure 37.15A shows a schematic diagram of a GIF interfaced to a TEM and Figure 37.15B shows an exploded view of a GIF (which shows the internal parts of the spectrometer shown back in Figure 37.3). Compared to a standard spectrometer, there are many more quadrupoles and sextupoles in the optics of the GIF. The dispersion of the spectrometer onto the slit has to be magnified and the quadrupoles after the slit have two functions. Either we project an image of the spectrum in the plane of the selecting slit onto the CCD or we compensate for the energy dispersion of the magnet and project a magnified image of the specimen onto the CCD. 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. While the spectrometer is double focusing as we saw, the aberration correction is good only for a single plane so astigmatism is introduced and this has to be corrected by a further combination of sextupoles and octupoles. 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 software. One potential operational difficulty is that the magnification of the GIF system is such that the actual TEM screen magnification needs to be rather small in order to observe a filtered image with reasonable magnification. More recent AEMs satisfactorily compensate for this magnification differential, but others do not and
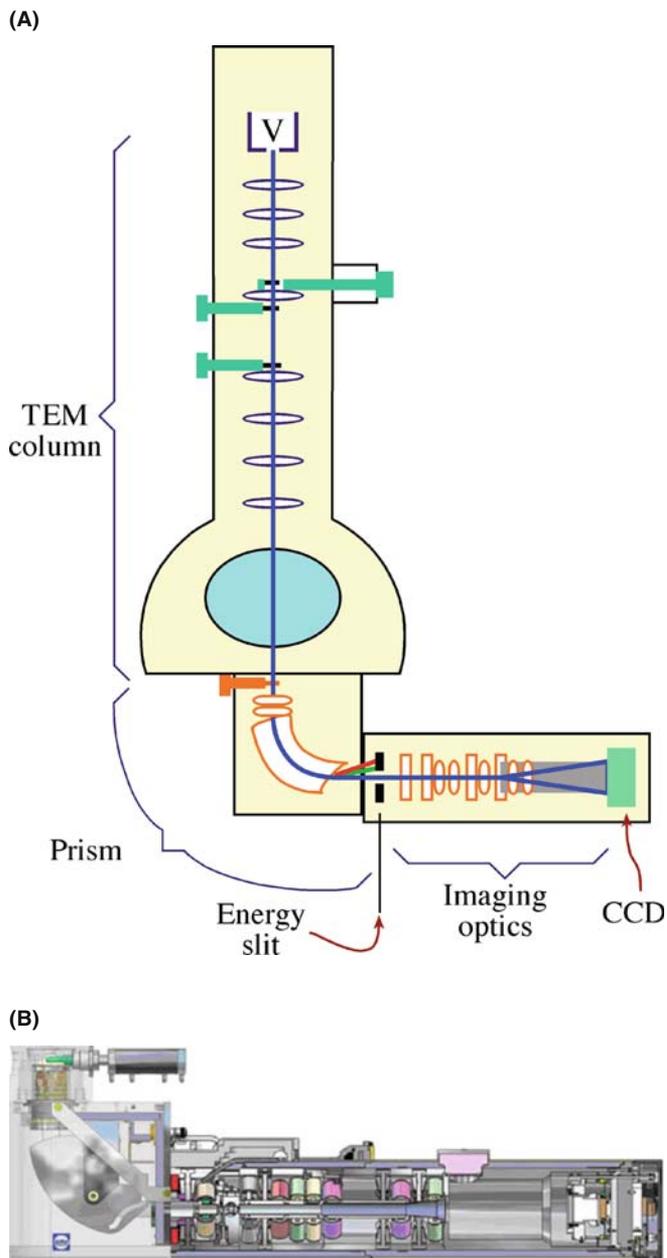
(A)

(B)

FIGURE 37.15. (A) Schematic diagram of how a post-column imaging filter is attached to the TEM column below the viewing chamber in the same position as a PEELS. (B) Cross section showing the complex inner workings of the Gatan (Tridiem) imaging filter (GIF).

then you have to move between TEM and GIF images and it is not so easy to operate in filtered mode all the time, which would be preferred.

37.7 MONOCHROMATORS

Energy resolution is obviously a key factor in EELS, much more so in fact than in XEDS where we still live with the miserable resolution of the solid-state detector. Resolution of a few eV is more than sufficient for

ionization-loss spectrometry, but as we use EELS more to study such aspects as vibrational modes of atoms, inter/intra band excitations, fine structure, and electronic effects, sub-eV resolution is increasingly of interest. For example, Batson at IBM has pioneered high-resolution (HREELS) in a decades-long research project probing ever deeper into the electronic structure of Si and the Si/SiO$_2$ interface and other materials essential for modern electronics.

If your spectrometer is not a limiting factor, then the gun dictates the ultimate energy resolution. Thermionic sources with ∼3 eV (W) and 1.5 eV (LaB$_6$) resolution, respectively, might be tolerable for ionization-loss spectrometry and basic low-energy plasmon studies. However, EELS really requires that you have a FEG. Either a cold FEG or a Schottky will give you sub-eV resolution, but this is still not sufficient in some cases. So commercial monochromators have become available which offer resolutions ∼100 meV although at very low energy losses (<50 eV) it is even possible to get resolutions of ∼25 meV. Basically, a monochromator is an EELS system fitted on the FEG source and the selecting slit refines the already narrow energy spread still further giving remarkably fine detail in the spectra. The monochromator is usually a Wien filter which has perpendicular electrostatic and magnetic fields which permit the chosen electrons to travel in a straight line down the TEM column. (Again, if you want to learn more, go back to Metherell's early review which has it all.) Figure 37.16A shows the ZLP at 200 keV obtained with and without a monochromator showing the reduction in FWHM. From Figure 37.16A, you can see that the FWHM of a commercial monochromated ZLP is much better than the 600 meV you can get with a Schottky gun and a little better than the ∼ 300 meV delivered by a good cold FEG. The intensity of the beam tail is relatively low in comparison with that of a standard cold FEG. This low-intensity tail results in real improvements for low-loss spectrometry, as we'll see in the next chapter.

Figure 37.16B compares the quality of different spectra of the Co L$_{2,3}$ edges obtained on a variety of instruments and calculated (see Chapter 40 and the companion text for more details on the calculation). Clearly the degree of fine detail in the spectra improves as the energy range of the electron sources gets smaller. The monochromated FEG is similar in quality to the spectrum from the synchrotron source, if a little noisier. The degree of agreement between these latter two spectra and the calculated spectrum is encouraging.

The drawback to monochromation, of course, is that, in filtering out the tails of the Gaussian energy distribution to reduce the FWHM, we reduce the number of electrons significantly. So having spent serious dollars to get the brightest possible electron source for our AEM, we immediately throw away a large amount of it in pursuit of the best energy resolution. This compromise is a real limiting factor and you should rarely contemplate acquiring an AEM with a monochromator.
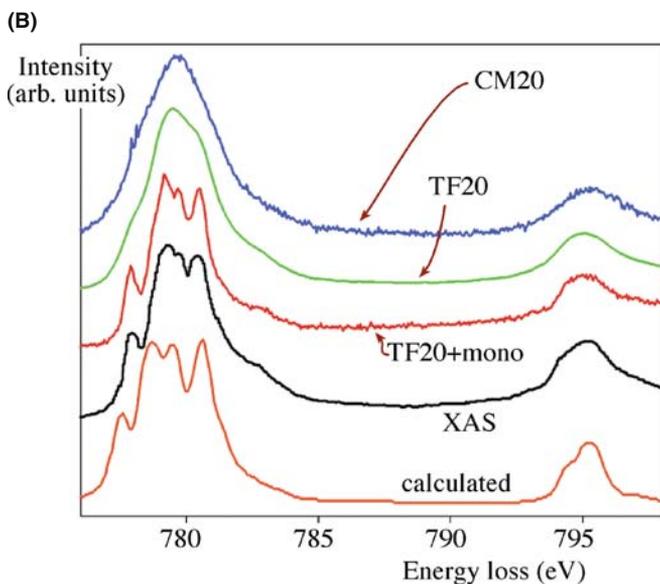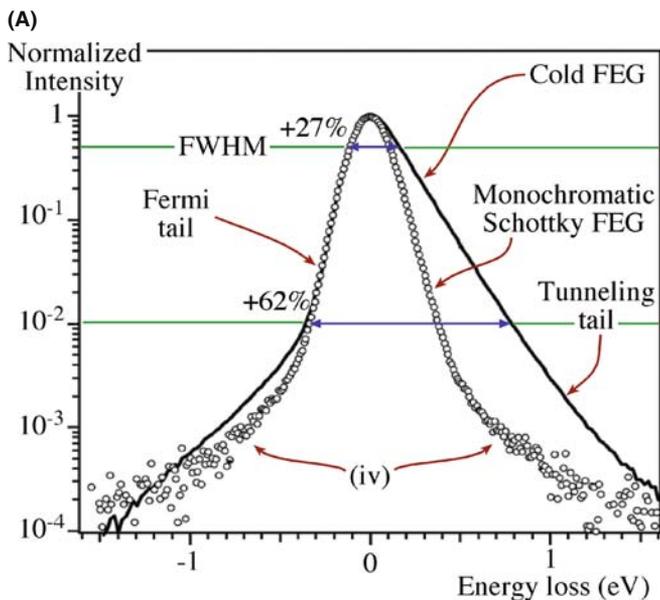
FIGURE 37.16. (A) Typical cold FEG ZLP with and without monochromation. Note that the ordinate is logarithmic so the FWHM is close to the top of the peak. (B) Comparison of Co $L_{2,3}$ spectra from: a Philips CM20 thermionic source, an FEI Tecnai TF20 with a cold FEG, a TF20 with a monochromator, a synchrotron (X-ray absorption spectrum), and a calculated spectrum using crystal-field theory. The improvement in resolution with monochromation is apparent.

> **WAIT BEFORE YOU MONOCHROMATE**
> If HREELS is the *raison d'etre* of the instrument remember that just about all other TEM/AEM operations will be degraded if you switch on the monochromator.

The one thing that you get in EELS is lots of electrons, particularly in the low-loss spectrum. In this case, monochromation is truly an advantage. Of course, it would also help if we could develop even brighter sources than cold FEGs.

There are also software alternatives to physical monochromation of the source and by various deconvolution routines it is possible to obtain spectra with a resolution of about 200 meV (e.g., the papers by Kimoto et al. and Gloter et al.). This approach is a very acceptable alternative to using a monochromator, unless you need the absolute best resolution for exploring the finest details of the electronic structure of nanomaterials (e.g., papers by Kimoto et al. in 2005, and Spence in 2006) when you need to lower both the keV and the beam current to produce sub-100 meV resolution.

37.8 USING YOUR SPECTROMETER AND FILTER

So now you've got a thin specimen in your microscope (you'll see later that for most EELS experiments, *very* thin is much better than merely thin) and you want to start acquiring spectra and filtered images. There are several ways to do this and basically they parallel what we've already described for XEDS

1. *Point analyses*: stop the STEM probe from scanning and position it on a selected point in the image over the entrance aperture and record a spectrum (see Figure 37.17A). This was the standard modus operandi for decades, but is (a) biased (because you pick what *you* think ought to be analyzed), (b) statistically poor (only one pixel selected out of a million or so in a typical STEM image), and (c) prone to damaging/contaminating the chosen area of interest by leaving the intense probe on the same point for long periods of time. So don't do point analyses, unless you're just looking quickly around the specimen to see what you can find. If you do, don't necessarily believe that what you find is significant!
2. *Line analyses*: take a series of spectra along a line that traverses some feature of interest (such as a planar interface or defect such as a grain boundary). This process is still biased by your choice of line but at least has the advantage of focusing on something that should provide useful information about the specimen. You can either plot the information from the spectra (e.g., the composition or the dielectric constant or whatever data you extract) or you can display the data as a spectrum-line, as shown in Figure 37.17B which shows changes in chemistry across a nanotube.
3. *TEM filtered images*: using a GIF or Ω filter, gather a filtered image or DP by using the slit to select electrons of a specific energy thus allowing only those electrons to fall on the viewing screen or CCD. If you use this method to filter out all the energy-loss electrons and produce a ZLP image, you can
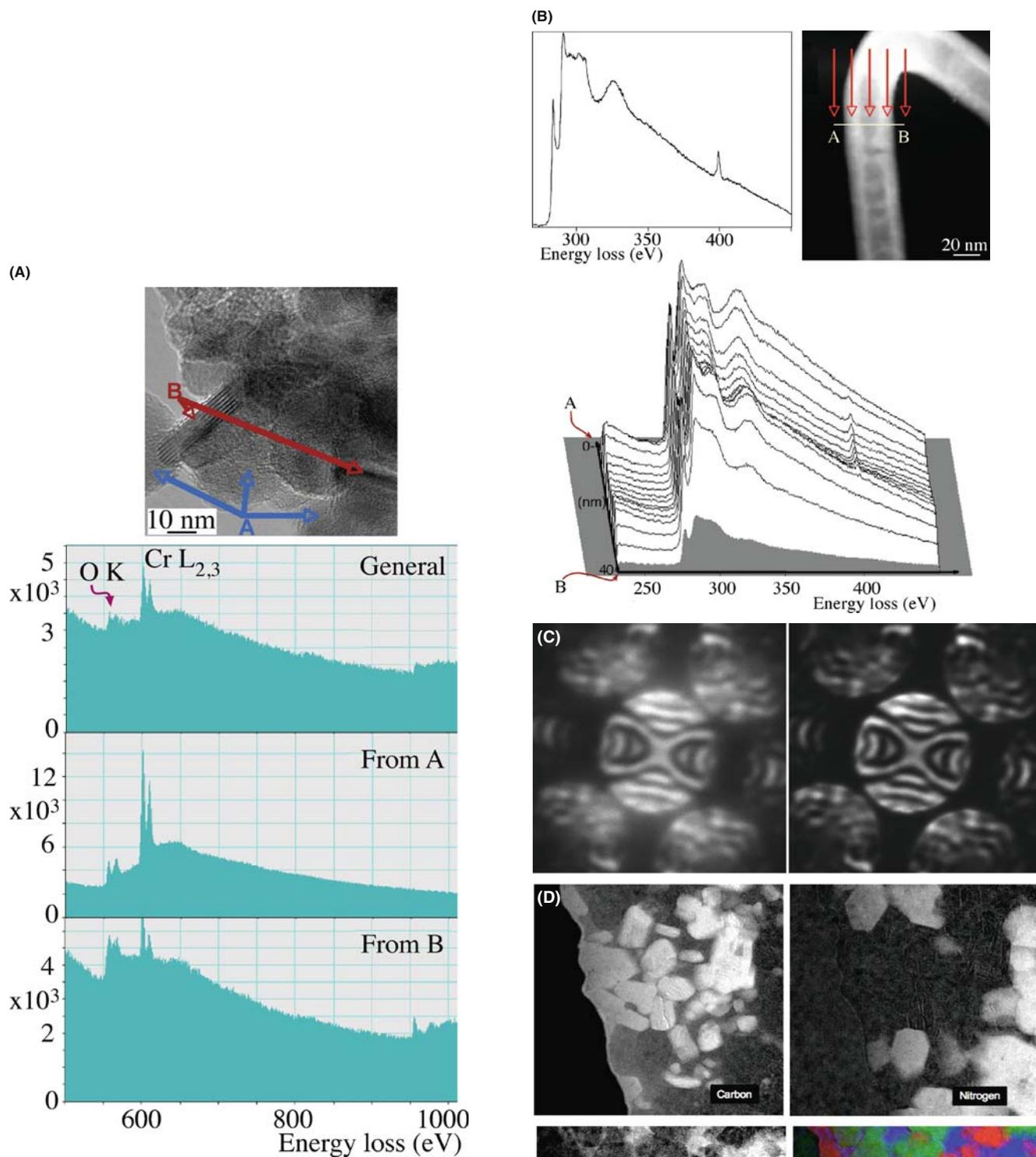
FIGURE 37.17. (A) EELS spectra from individual point analyses from CuCr oxide nanoparticles showing local differences in the three elemental signals. (B) Spectrum-line analysis showing the change in spectral detail along the line A-B across a nitrogen-doped carbon nanotube. The insets show a single spectrum indicating the C-K and N-K edges and a STEM image with arrows indicating from where the spectrum-line profile was taken. (C) Comparison of unfiltered (left) and EFTEM filtered (right) Si [111] CBED pattern. (D) STEM energy-filtered images of a SiC/Si_3N_4 nanocomposite revealing the different elemental distributions and a composite RGB color overlay; carbon (red), nitrogen (green), and oxygen (blue).

FIGURE 37.17. (Continued).

substantially enhance the quality of CBED patterns, as shown in Figure 37.17C (and also back in Figure 20.10). Also, as we'll see at various times, EFTEM improves mass-thickness contrast, phase contrast, and diffraction contrast. So why wouldn't you use this technique if you have a filter on your AEM?

4. *STEM filtered images*: scan the beam over an area of interest using the slit to select electrons of a specific energy thus allowing only those electrons to fall on the viewing screen or CCD. If you select electrons of a specific energy then you can produce composition maps (Figure 37.17D) similar to many of the XEDS composition maps we have already shown.

5. *Spectrum-images*: store a full spectrum at each pixel (obviously, you need to be operating in STEM to do this). It's much easier to do this in STEM because if you try and do this in TEM mode, you'll have to record hundreds of images at different selected energies and comparing complete images is challenging and time consuming, so not everyone does this; however, this situation is changing. In a similar manner to what we showed you for XEDS, after you've acquired a full spectrum image, you can go into the data cube and select whatever information you want. For example, you can view images at specific energies or spectra from specific points or lines in your specimen, thus removing the bias that affects your choice of spot or line analyses. EELS spectrum imaging was more easily implemented than the XEDS version because of the ease of acquiring large numbers of counts and the broad array of possible images was demonstrated by Hunt and Williams.

We'll use examples of these various methods throughout the next three chapters. Generally speaking, as we've emphasized for X-rays, it makes sense for you to form images of specific features in the spectrum rather than gather spectra from specific points, so that they can at least be compared with your TEM images. Since counts are not a problem in EELS (unlike for XEDS) imaging is relatively straightforward and fast. If you really want to optimize your information then acquire spectrum images.

CHAPTER SUMMARY

We use a magnetic-prism spectrometer for PEELS and a combination of one or more prisms plus imaging lenses for GIF/EFTEM. The prism is a simple device and very sensitive but you have to understand how it functions in combination with different TEM modes, You can operate with your TEM in imaging or diffraction (STEM) mode, or use a DSTEM. You have to know how the software focuses and calibrates the system and how it determines the collection angle, β. Once you can understand this you're in a position to acquire and analyze EEL 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 E and it makes sense, if you can, to view all your images and DPs in filtered mode for reasons we've already mentioned in past chapters and that we'll reiterate in the subsequent chapters. Energy filtering is a rapidly evolving field and systems with reduced aberrations and better energy resolution such as the Mandoline filter on Zeiss's Sub-eV-Sub-Ångstrom Microscope (SESAMe) and Nion's UltraSTEM will offer far more exciting breakthroughs than we can describe here and Egerton gave a brief synopsis of a range of hardware and software advances in 2003.

THE INSTRUMENT

Brydson, R 2001 *Electron Energy-Loss Spectroscopy* 2001 Bios (Royal Microsc. Soc.) Oxford UK. Good introductory text, similar in content and level to much of this chapter and the subsequent ones.

Castaing, R. and Henry, L 1962 *Filtrage Magnétique des Vitesses en Microscopie Electronique* C. R. Acad. Sci. Paris **B255** 76–78. The original design for the mirror prism.

Egerton, RF 2003 *New Techniques in Electron Energy-Loss Spectroscopy* Micron **34** 127–139 A concise review of recent advances in instrumentation.

Egerton, RF, Yang, YY and Cheng, SY 1993 *Characterization and Use of the Gatan 666 Parallel-Recording Electron Energy-Loss Spectrometer* Ultramicrosc. **48** 239–250.

Hillier, J. and Baker, RF 1944 *Microanalysis by Means of Electrons* J. Appl. Phys. **15** 663–675. History – it's amazing to read that AEM was essentially all conceived more than 60 years ago.

Metherell, AJF 1971 *Energy Analysing and Energy Selecting Electron Microscopes* Adv. Opt. Elect. Microsc. **4** 263–361 Eds. R Barer and VE Cosslett Academic Press New York. Still the best review of spectrometers.

Uhlemann, S and Rose, H 1996 *Acceptance of Imaging Energy Filters* Ultramicrosc. **63** 161–167.

BACKGROUND DATA

Ahn, CC Ed. 2004 *Transmission Electron Energy Loss Spectrometry in Materials Science* 2nd Ed. Wiley-VCH Weinheim Germany. Updated version of the Disko et al. text (below).

Disko, MM, Ahn, CC and Fultz, B Eds. 1992 *Transmission Electron Energy Loss Spectrometry in Materials Science and the EELS Atlas* TMS Warrendale PA. Multi-author, practical text.

Egerton, RF 1986 *Electron Energy-Loss Spectroscopy in the Electron* Plenum Press New York. The bible of EELS; required reading for all serious spectroscopists.

Egerton, RF 1996 *Electron Energy-Loss Spectroscopy in the Electron Microscope* 2nd Ed. Plenum Press New York. Second edition of the EELS bible.

APPLICATIONS

Batson PE 2004 *Electron Energy Loss Studies of Semiconductors* in *Transmission Electron Energy Loss Spectrometry in Materials Science* 2nd Ed. 353–384 Ed. CC Ahn Wiley-VCH Weinheim Germany.

Gloter, A, Douiri, A, Tencé, M and Colliex, C 2003 *Improving Energy Resolution of EELS Spectra: an Alternative to the Monochromator Solution* Ultramicrosc. **96** 385–400.

Hunt, JA and Williams, DB *Electron Energy-Loss Spectrum Imaging* Ultramicrosc. **38** 47–73.

Kimoto, K, Kothleitner, G, Grogger, W, Masui, Y and Hofer, F 2005 *Advantages of a Monochromator for Bandgap Measurements Using Electron Energy-loss Spectroscopy* Micron **36** 185–189.

Spence, JCH 2006 *Absorption Spectroscopy with Sub-Angstrom Beams: ELS in STEM* Rep. Prog. Phys. **69** 725–758.

THE EELS WORKSHOP REPORTS

The quadrennial EELS workshops (1990, 1994, 1998, 2002, and 2006) pioneered and often organized and edited by Krivanek are a rich source of papers by the leading researchers in the field describing cutting-edge aspects of EELS and related techniques. Often the proceedings are published separately and are divided between methodology/instrumentation and practice. The respective journals (either complete volumes or part thereof) and editors are listed below.

Krivanek, OL Ed. 1991 Microsc. Microanal. Microstruct. **2** (# 2–3).
Krivanek, OL Ed. 1995a Microsc. Microanal. Microstruct. **6** 1.
Krivanek, OL Ed. 1995b Ultramicrosc. **59** (# 1–4).
Krivanek, OL Ed. 1999 Ultramicrosc. **78** (# 1–4).
Krivanek, OL Ed. 1999 Micron **30** (#2) 101.
Krivanek, OL Ed. 2003 Ultramicrosc. **96** (#2–4) 229.
Krivanek, OL Ed. 2003 J. Microsc. **210** 1.
Browning, ND and Midgley, P Eds. 2006 Ultramicrosc. **106** (#11–12).
Mayer, J Ed. 2006 Micron **37** 375.

URLs

1) http://www.energyloss.com/index.html
2) http://www.gatan.com/ Gatan's web site

SELF-ASSESSMENT QUESTIONS

Q37.1   What's the difference between a GIF and a PEELS system?
Q37.2   Why is it useful for the spectrometer to act as a lens also? Can we achieve the same combination when dispersing visible light?
Q37.3   What is the dispersion plane of the spectrometer and what is a typical value of the dispersion?
Q37.4   How would you measure the energy resolution of the spectrometer?
Q37.5   What's a typical value of the energy resolution and what governs the minimum possible value?
Q37.6   What factors can degrade (i.e., increase the value of) the energy resolution?
Q37.7   Why is the spectrometer collection angle (β) so important?
Q37.8   What controls β in image mode?
Q37.9   What controls β in diffraction mode?
Q37.10 Why might you have to integrate several spectra in your PEELS rather than just acquire a single spectrum?
Q37.11 What controls the spatial resolution in image mode?
Q37.12 What controls the spatial resolution in diffraction mode?
Q37.13 Why is diffraction mode in TEM equivalent to operating a dedicated STEM?
Q37.14 What is the point-spread function and why should you be concerned about it?
Q37.15 How do you correct for this artifact?
Q37.16 Why do you need to calibrate the spectrometer?
Q37.17 How do you calibrate the spectrometer (if the software can't do it for you)?
Q37.18 Why is it necessary to cool the diode array in a PEELS?

Q37.19 What's the difference between a GIF and an Ω filter?

Q37.20 What are the pros and cons of these two types of filter?

Q37.21 Why would you want to form an image from specific electrons in an EELS spectrum rather than just look at the spectrum?

Q37.22 Why is TEM image mode generally a bad choice for gathering spectra?

TEXT-SPECIFIC QUESTIONS

T37.1 Using Figure 37.1 and Figure 32.2A, contrast the principal characteristics of XEDS and EELS spectra, indicating the relevance of your observations to interpreting/quantifying the spectra.

T37.2 Examine Figure 37.2B. Why is the back focal plane of the projector lens used as the object plane of the spectrometer/lens?

T37.3 What is the object of the spectrometer/lens when an image is on the TEM screen?

T37.4 Electrons that have lost energy can be both an advantage and a disadvantage. Explain how such electrons are used to advantage in diffraction and in imaging, and likewise how they can degrade DPs and images (find examples (especially figures where possible) throughout the book to support your arguments).

T37.5 Using Figure 37.9 estimate what fraction of the single channel intensity is lost through the spreading of the point-spread function. What instrument modification might help reduce the point-spread function by keeping the probe more localized?

T37.6 Contrast the specific roles of the objective aperture and the selected area aperture in TEM and EELS.

T37.7 Describe the steps you would take to gather a spectrum with $\beta = 20$ mrad in (a) DSTEM, (b) TEM image mode, or (c) TEM diffraction mode.

T37.8 Can you think of circumstances in which you might get better energy resolution in a non-monochromated spectrum than in a monochromated one?

T37.9 Examine Figure 37.1 and estimate the absolute intensities of the zero-loss peak, the plasmon peak and the Ni L ionization edge above background. What does this tell you about the difficulties that we will encounter with processing EELS spectra? How does the P/B ratio compare with an XEDS spectrum?

T37.10 Although SEELS systems are no longer sold, can you think of an advantage to serial collection over parallel collection?

T37.11 Why is the camera length an important variable if you are operating in diffraction mode (Figure 37.8)? Choose two reasonable values of the camera length and calculate what effect this has on the operation of the spectrometer.

T37.12 Explain under what circumstances the spectrometer entrance aperture, rather than the objective aperture, might control the value of β in TEM mode (Figure 37.7).

T37.13 If the specimen is really thin so that the electrons suffer no significant energy losses while traversing the thin foil, can we totally ignore chromatic-aberration effects?

T37.14 Explain why the specimen you are looking at can affect the spatial resolution of the EELS analysis (in totally different ways to which the specimen controls the spatial resolution for XEDS).

T37.15 If your lab can't afford a monochromator, list all the other ways that you can improve the resolution of your spectra. Give the pros and cons of each method and list them according to their relative costs.

T37.16 What is a typical count rate in an EELS spectrum versus an XEDS spectrum? (If you can't find these data in the book, try a quick experiment on the AEM.)

T37.17 Would you expect a channel-to-channel gain variation in a scintillator-photomultiplier detector on an old SEELS and in a CCD camera in a GIF?

T37.18 How can you minimize the dark current?

T37.19 List the other common artifact in EELS spectra and explain how you would (a) recognize and (b) correct for each one.

T37.20 Why is it not a problem if one of the detectors in the PEELS diode array dies?

T37.21 When might it be better to perform a spectrum–profile analysis rather than an EFTEM analysis?

T37.22 Can you think of any circumstance when point analysis might be better than a line-profile or EFTEM analysis?