Limits to the spatial, energy and momentum resolution of electron energy-loss spectroscopy

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Abstract

We discuss various factors that determine the performance of electron energy-loss spectroscopy (EELS) and energy-filtered (EFTEM) imaging in a transmission electron microscope. Some of these factors are instrumental and have undergone substantial improvement in recent years, including the development of electron monochromators and aberration correctors. Others, such as radiation damage, delocalization of inelastic scattering and beam broadening in the specimen, derive from basic physics and are likely to remain as limitations. To aid the experimentalist, analytical expressions are given for beam broadening, delocalization length, energy broadening due to core-hole and excited-electron lifetimes, and for the momentum resolution in angle-resolved EELS.

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1. Introduction

Many considerations affect the capability of electron energy-loss spectroscopy (EELS), in combination with transmission electron microscopy (TEM), to solve problems in materials or life science. Some of them relate to instrument design, such as the electron-optical design of the spectrometer and microscope column. Others are partly environmental, such as the electrical and mechanical stability. There are also important human considerations, including the knowledge, skill and patience of the researcher. But over the last few decades, the knowledge base and level of instrument performance have improved to the extent that a third kind of factor becomes important: performance limits arising from basic physical principles. This paper reviews all of the relevant factors but gives emphasis to these fundamental limitations. Although the physical principles involved are well established, they are presented here in a form designed to be convenient for the experimentalist.

2. Spatial resolution

In EELS, spatial resolution refers to the smallest diameter (lateral dimension within a thin specimen) from which spatial information can be obtained. In energy-filtered (EFTEM) imaging, the equivalent quantity is the minimum useful pixel size, below which there is no substantial gain in information content.

2.1. Electron-optical considerations

Because spectroscopy and scanning-transmission (STEM) imaging are usually carried out using a tightly focused beam (electron probe), one obvious limit is the smallest beam size that can be produced by a given instrument. In a modern TEM, the minimum probe size is well below 1 nm, thanks to the efficient exploitation of electromagnetic lenses. Use of a Schottky or a cold field-
emission (CFE) electron source helps to ensure that there is sufficient current (e.g. 1 nA) in such a small probe. Correction of the spherical aberration of the probe-forming lens allows a further increase in probe current and can reduce also the full width at half maximum (FWHM) of the probe to below 0.1 nm [1–3]. By removing aberration tails that otherwise contain a substantial proportion of the current, the corrector should provide a "cleaner" current-density profile.

Although the probe size is determined by the electron-source size, lens aberrations and electron diffraction at the condenser aperture, it can in principle be degraded by Coulomb interactions between the electrons within the TEM illumination system. Fortunately, the TEM uses a relatively low beam current, giving conditions that correspond to the "pencil-beam regime" where the statistical Coulomb broadening depends on the third power of the beam current [4]. So for accelerated electrons, the statistical broadening appears to be negligible, even for aberration-corrected lenses forming a high-intensity probe, where the current density can exceed 1 MA/cm².

2.2. Beam broadening within the specimen

Inside the specimen, the electron beam spreads laterally due to electron scattering. Even without scattering, it would broaden by 2πt (of the order of 1 nm for a tightly focused probe and thin specimen) for a probe of convergence semi-angle z focused onto the top surface of a specimen of thickness t. For an amorphous specimen, elastic scattering increases the beam broadening by an amount [5]:

\[
b \approx (625 \text{cm})(Z/E_0)(\rho/A)^{1/2}[t(\text{cm})]^{3/2} \\
\approx (0.47 \text{nm}) (\rho Z)^{1/2}(100 \text{keV}/E_0)[t/50 \text{nm}]^{3/2},
\]

where \( \rho \) is the specimen density in g/cm³, \( E_0 \) the incident-electron energy in keV. For \( E_0 = 100 \text{ keV} \) and \( t = 50 \text{ nm} \), \( b = 1.8 \text{ nm} \) for carbon, \( 2.9 \text{ nm} \) for Al, \( 7.6 \text{ nm} \) for Cu and \( 17 \text{ nm} \) for Au, values that agree rather well with the statistical Coulomb broadening provides a "cleaner" current-density profile. This effect may be added in quadrature to the beam-divergence effect (2πt) in a first approximation.

Although beam broadening in the specimen largely determines the spatial resolution of X-ray energy-dispersive spectroscopy (XEDS), its effect on transmission EELS can be considerably less, provided the spectrum is recorded through an angle-limiting aperture that removes electrons that deviate from the optic axis by more than its semiangle \( \beta \). Considering scattering at a distance \( z \) above the bottom surface of the specimen, electrons entering the spectrometer travel through a cone of radius \( \beta z \) and volume \( (\pi/3)\beta^2 z^3 \). Averaging over the specimen thickness \( t \), the diameter containing n% of the detected electrons is:

\[
d_n \approx F_n \beta t,
\]

where \( F_n \approx 0.4 \) for \( n = 50 \) and \( F_n \approx 1.0 \) for \( n = 90 \) [6]. Taking \( t = 50 \text{ nm} \) and \( \beta = 10 \text{ mrad} \) gives \( d_50 \approx 0.2 \text{ nm} \) and \( d_{90} \approx 0.5 \text{ nm} \), values considerably less than the total broadening given by Eq. (1). These estimates may actually be pessimistic since they assume that the scattering (per unit solid angle) is constant up to the angle \( \beta \). If no angle-limiting aperture is used, the beam width in EELS should be given in Eq. (1), at least for an amorphous specimen.

For crystalline specimens, a more correct treatment of beam broadening includes the fact that elastic scattering (except in ultra-thin specimens) is dynamical: for depths in excess of \( \xi_0/2 \), where \( \xi_0 \) is the extinction distance (in the range 25–100 nm for 100 keV electrons), many electrons are scattered back towards the optic axis. As a result, the electron beam spreads less than in an amorphous material (at least for scattering through less than a typical Bragg angle), which benefits XEDS analysis in addition to EELS [7,8]. In addition, the electron density within the beam becomes distributed non-uniformly: at depths exceeding about 5 nm, electrons are channelled preferentially along the columns of atoms, especially for a crystal oriented with a low-index zone axis parallel to the incident beam [9].

2.3. Chromatic aberration

If the electrons transmitted through a specimen are subsequently focused to form an energy-filtered (EFTEM) image, the image resolution is subject to degradation by lens aberrations. Usually chromatic aberration is the most important factor, particularly for core-loss images where the energy and angular widths of the focused electrons can be considerable. Assuming the energy-filtered image is correctly focused for electrons that pass though the center of the energy-selecting slit, the diameter containing 50% of the electrons is increased by an amount \( Fd_c \), where \( d_c = C_c \beta (\Delta/E_0) \), \( C_c \) is the chromatic aberration coefficient of the objective lens and \( \Delta \) is the energy width of the energy-selecting slit. The factor \( F \) depends on the angular width of the inelastic scattering: \( F \approx 0.1 \) for an energy loss \( E = 100 \text{ eV} \) and \( E_0 = 100 \text{ keV} \), increasing to 0.3 for large \( E \) or a thick specimen [10]. The diameter \( Fd_c \) is typically around 0.2 nm for \( \beta = 10 \text{ mrad} \) and \( \Delta = 20 \text{ eV} \). Note that this 50% broadening is substantially less (by factor \( F \)) than the total chromatic width \( d_c \), which is often taken as an estimate of the chromatic effect.

In principle, the EFTEM resolution also depends on the spatial resolution of the electron detector (usually a scintillator/CCD arrangement). However, this factor can be made unimportant by choosing a sufficiently high image magnification.

None of the above factors are fundamental, in the sense that they depend on the design of the microscope and
The concept of delocalization can be introduced in terms of the simple experiment performed in 1974 by Isaacson et al. [11], who scanned a 43 keV CFE probe across the edge of a thin carbon film and recorded line profiles from an annular detector (designed to collect high-angle elastic scattering) and from an energy-loss spectrometer (set to detect the total-inelastic component of the lower-angle inelastic scattering). The inelastic signal changed more gradually than the elastic one, showing inelastic scattering to be more delocalized than high-angle elastic scattering.

This basic experiment has been repeated in greater detail (measuring the inelastic signal as a function of energy loss) by Muller and Silcox [12]. In addition, the spatial distribution of inelastic scattering has been discussed in terms of electron-scattering theory in several important publications [12–22] and reviews [6,23]. Here our aim is to provide an approximate value of the localization distance and its dependence on experimental variables, as well as some insight into the cause of delocalization. We therefore adopt a single-scattering model, assuming that the sample is thin enough to make plural inelastic scattering unimportant and that the effect of elastic scattering can be dealt with separately as beam broadening (as just discussed). In the case of crystalline specimens and core-loss spectroscopy, these assumptions become questionable and a proper treatment requires a simultaneous treatment of elastic and inelastic scattering, using (for example) a combination of multislice and single-inelastic scattering theory [21,22,24] or Bloch-wave methods [18–20].

One of the first attempts to describe the problem mathematically was that of Bohr [25], using entirely classical physics; this work predates Bohr’s quantum model of the atom [26] by 6 months. The incident electron is represented as a particle that interacts via the Coulomb force with a bound atomic electron, represented as a classical oscillator of angular frequency $\omega$; see Fig. 1. Several pages of non-relativistic mechanics lead to an expression for the energy loss $E$ of the incident electron when the latter moves at speed $v$ along an approximately linear path with impact parameter $b$:

$$E(b) = E_R(b \omega/v)^2 [K_0(b \omega/v)^2 + K_1(b \omega/v)^2].$$

Here $E_R = (k_c^2 e^4/E_0)(1/b^2)$ is the Rutherford recoil energy that would be imparted to a stationary and free electron, $k_c = (4\pi \alpha_0)^{-1}$ being the Coulomb constant. For $b \ll v/\omega$, the energy exchange is approximately $E_R$: the atomic electron has insufficient time to move during transit of the incident electron and receives the same momentum as a free electron, according to the impulse approximation. For $b \gg v/\omega$, however, the atomic electron moves in response to the electric field of the incident electron, resulting in very little energy exchange (adiabatic conditions), represented by the rapidly falling modified-Bessel terms in Eq. (3). Therefore the inelastic scattering is often taken to be
confined to impact parameters below \(v/\omega\) and a localization range taken as \(L \approx v/\omega\) according to these classical-physics arguments.

In fact, \(E(b)\) as given by Eq. (3) has a singularity at \(b = 0\) and a long tail extending to moderate values of \(\gamma (bo/v)\), which points to the dangers of representing localization in terms of a single number or at least to the need for careful definition. Considering a circular beam of electrons of diameter greater than \(v/\omega\), \(E(b)\) can be multiplied by \((2\pi b)\) and integrated over \(b\) to evaluate the energy loss for impact parameters up to \(b\). A lower limit of integration \(b_{\text{min}}\) must be introduced [27], corresponding to a maximum scattering angle of \(\pi\) radians or to some smaller value (defined by a spectrometer entrance aperture). Dividing by the total integral (large \(b\)) gives the fraction of energy loss arising from impact parameters less than \(b\), as illustrated in Fig. 1b, which shows that a large part of the energy loss occurs at impact parameters considerably less than \(v/\omega\).

The classical impact parameter \(L = \omega/v\) can be reframed in terms of electron wave properties and made semi-relativistic by using the de Broglie relation \((p = \gamma m_0 v = h/\lambda)\) to replace the fast-electron speed \(v\). Also, \(\omega\) can be taken as the angular frequency of an electron orbiting an atomic nucleus, whose binding energy \(W\) is (according to classical electrodynamics) exactly equal to its kinetic energy and therefore given by \(W = (m/2)(r_n \omega)^2\). For excitation of this electron to a state just above the ionization threshold, the absorbed energy is \(E \approx W = n(\omega/2)(h/2\pi)\) according to Bohr's quantum postulate [26]. Combined with de Broglie's relation, these expressions give:

\[
L = v/w = h(\gamma m_0 \lambda)^{-1}(n h/4\pi E) = n \lambda/(4\pi \theta_E),
\]

where \(\theta_E = E/(\gamma m_0 v^2)\) is the characteristic scattering angle used in EELS theory [6,28]. According to Eq. (4), \(L\) depends on energy loss (through \(\theta_E\)) but also on the quantum number \(n\), and would therefore differ for different edges (K, L, etc.) of similar energy loss. Some experimental data have suggested that this might be true [21].

Alternatively, we can simply write \(E = (h/2\pi)\omega\), implying that the impulse field of the transmitted electron is equivalent to a white-noise spectrum of photons, to which each electron responds appropriately, resulting in:

\[
L = v/w = h(\gamma m_0 \lambda)^{-1}(h/2\pi E) = \lambda/(2\pi \theta_E).
\]

A similar result (without the factor of \(2\pi\)) was deduced by Howie [13], by using the Heisenberg energy-time uncertainty principle. Eq. (5) differs from Eq. (4) by being independent of the quantum number of the excited electron. But in both equations, \(L\) is seen to resemble the Rayleigh expression for the total object-plane diameter (1.22\(\lambda/\alpha\)) of the Airy disk produced when a point object is imaged using a conical beam of waves of wavelength \(\lambda\) and semi-angle \(\alpha\). Here \(\alpha\) is several times \(\theta_E\) but can be assumed to be small so that \(\sin \alpha \approx \alpha\). If we define \(L\) more conveniently as the diameter \(L_{50}\) containing 50% of the inelastically scattered electrons, Eq. (5) becomes

\[
L_{50} \approx (0.52)\lambda/(\theta_E)
\]

in which \(\langle \theta \rangle\) could reasonably be taken as the median angle of inelastic scattering, containing 50% of the scattered intensity. Eq. (6) is consistent with the Heisenberg momentum-position uncertainty principle, since if we take the median transverse momentum to be \(\Delta p = \pm \hbar/(2m_0 \sin (\theta)) \approx (2h/\lambda)(\theta/E)\), the associated uncertainty in position is \(\Delta x \approx \hbar/\Delta p \approx 0.5\lambda/(\theta_E)\).

Although partly conjecture, Eq. (6) provides a reasonable approximation to most experimental measurements [12,29–32] and calculations [12,15,21] of the localization distance over a wide range of energy loss, as illustrated in Fig. 2. Exact agreement would hardly be expected: some of the data relate to valence-electron excitation at a planar interface while others represent excitation of core electrons from a single atom. Not all data use the 50% definition of localization width and the measurements involve appreciable experimental error. But in view of the striking correlation with Eq. (6) over a 1000:1 range of energy loss, it appears worthwhile to explore the consequences of this relation, treating it as a useful approximation rather than an exact formula.

For single-electron transitions, Bethe theory predicts a Lorentzian \((\theta^2 + \theta_0^2)^{-1}\) angular distribution of inelastic scattering, but with a more rapid falloff at \(\theta_0 \approx (E/E_0)^{1/2} \approx (2\theta_E)^{1/2}\) due to decrease of the oscillator strength [6,33]. Approximating this decrease as an abrupt termination of the Lorentzian at \(\theta = \theta_c\), the median scattering angle is given [6] by: \(\langle \theta \rangle = \theta_0(1 - 1/2) \approx (\theta_0 \theta_0)^{1/2} \approx 2^{1/4} \theta_0^{1/4}\), leading to:

\[
L_{50} \approx (0.44)\lambda/(\theta_0^{3/4})
\]

Fig. 2. Measurements and calculations of the localization distance for inelastic scattering, plotted as a function of energy loss. Where necessary, the data has been adjusted to 100 keV incident energy. The dashed curve represents Eq. (7) combined with Eq. (9), taking \(\beta = 10\) mrad; the solid line (for \(E < 30\) eV) represents Eq. (10).
Taking $\theta_E = E/(\gamma m_0 v^2)$ in Eq. (7), with $\gamma = (1 - v^2/c^2)$, $L_{50}$ should depend on the incident-electron speed $v$ as follows:

$$
L_{50} \propto \lambda/(\theta_E)^{3/4} \propto \gamma^{-1} v^{-1}/(\gamma^{-3/4} v^{-3/2}) = v^{1/2}(1 - v^2/c^2)^{1/8}.
$$

(8)

For $E_0 > 100$ keV, the right-hand side of Eq. (8) varies only weakly with the kinetic energy $E_0$ of the incident electron; $L_{50}$ is predicted to increase by only about 10% from 100 to 300 keV, as shown in Fig. 3. In terms of Eq. (6), the decrease in electron wavelength almost cancels the fall in median scattering angle above 100 keV. This limited $E_0$-dependence appears compatible with the results of hydrogenic calculations of the root-mean-square impact parameter for $K$-shell ionization [34].

At higher energy loss, the median scattering angle can become comparable to the collection semi-angle used in EFTEM imaging or the probe semi-angle used in STEM, so that the angular distribution of scattering is partly determined by this aperture. One advantage of using the 50% criterion is that it allows optical blurrings to be combined with reasonable accuracy by power-law addition [35]. Accordingly, with nearly parallel illumination and a spectrometer collection angle $\beta$ (the EFTEM case), the localization distance at higher $E$ should be given approximately by

$$
(d_{50})^2 \approx (L_{50})^2 + (0.52\lambda/\beta)^2
$$

(9)

in which the last term represents the diffractive effect (Airy-disk diameter) of an on-axis aperture. The dashed curve in Fig. 2 represents Eq. (9) with $\beta = 10$ mrad, which is applicable to most of the data presented. In the case of STEM or small-probe spectroscopy, the reciprocity principle can be applied to electron intensities [23], in which case $\beta$ in Eq. (9) is the incident-probe semi-angle, assuming a small-angle axial detector.

For energy losses below 30 eV, it may be more appropriate to consider a plasmon model for the inelastic scattering. The angular distribution is again Lorentzian but its cutoff occurs when the magnitude of the plasmon phase velocity ($\omega/q$) approaches the speed $v_F$ of electrons at the Fermi surface and the cutoff angle is:

$$
\theta_c \approx \omega/(k_0 v_F) = 2\pi E/\hbar k_0 v_F).
$$

(10)

This approximation is shown as the solid line in Fig. 2, based on values of $E_p$ and $v_F$ for the elements K, Li, Be, Al and Si [6], and perhaps gives better agreement with the experimental data [12,32].

In fact, plasmon excitation provides an alternative way to visualize the delocalization effect, in terms of the variations in potential and charge density induced in the specimen by the transmitted electron. Any charged particle moving through solid matter produces an oscillation in potential (of angular frequency $\omega_p$ and wavelength $2\pi v/\omega_p$) in the wake trailing the particle [36,37]. The wake angle is $\propto (v_F/v) \approx 10$ mrad, so the wavelength measured perpendicular to the particle trajectory is $\approx (2\pi v/\omega_p) \approx 0.5$ nm. The fact that this transverse periodicity is independent of $v$ is consistent with Eq. (8).

Underlying Eqs. (6), (7) and (9) is the wave-optical theory of imaging and Fraunhofer diffraction [38–41]. If the angular dependence of the scattering amplitude $A$ (square root of the intensity $dI/d\Omega$) is used as an aperture function, a point-spread function (PSF) can be calculated:

$$
PSF = FT^2(\Delta) FT^*(\Delta),
$$

(11)

where $FT^2$ denotes a two-dimensional Fourier transform and $*$ represents a complex conjugate.

As an example, Fig. 4 shows the PSF evaluated using a hydrogenic $K$-shell angular distribution for $dI/d\Omega$, together with the fraction of intensity $F(r)$ contained within an object radius $r$. The diameter $L_{50}$ containing 50% of the scattered intensity is about twice the full-width at half maximum of the PSF, indicating that the PSF has an extended tail.

In a Fourier-optics treatment, it is straightforward to include the effect of an angle-limiting aperture or to simulate the effect of an annular detector. In the latter case, the width $L_{50}$ of the PSF falls as the inner diameter of the detector is increased (see Fig. 5), readily explained in terms of the higher spatial frequencies present in the signal. A similar effect is expected on the basis of classical theory but would be interpreted in terms of the reduced impact parameter associated with higher scattering angles [13].

One assumption behind Eqs. (6) and (11) is that the electron waves reaching the detector are incoherent. For coherent radiation, the factor in the Rayleigh formula (for
PSF radius changes from 0.61 to 0.82 if certain assumptions are made [40] or becomes 0.5 or 1.0 under particular conditions [41]. In the case of inelastic (plasmon) scattering of electrons, the degree of coherence of the scattered waves has been measured as 0.3 [42,43], meaning 70% incoherence. Therefore an assumption of incoherence in the scattered waves is unlikely to lead to a large error in the estimate of delocalization.

A related concept is the lateral coherence length associated with inelastic scattering. Holographic measurements suggest that this quantity is also given by Eq. (7) for energy losses in the range 50–400 eV [44]. In a recent theoretical treatment of bulk plasmon losses [45], the coherence length appears closely linked to the angular distribution of plasmon scattering. If so, all information relating to delocalization and lateral coherence is contained within the angular distribution of inelastic scattering.

The beam-broadening effect (discussed earlier) differs from inelastic delocalization in that it increases with specimen thickness. For an amorphous specimen, the two broadening effects could be combined (for example) in quadrature. In a crystalline specimen that is not extremely thin, the elastic and inelastic scattering are more closely coupled and require a more rigorous mathematical treatment [21,22]. Yet even here, there appear to be situations in which the concept of a thickness-independent delocalization distance remains useful: for low-loss spectroscopy or imaging, where the delocalization length is large compared to interatomic distances (the angular width of inelastic scattering is well below the Bragg angle), and at high energy loss where it becomes a fraction of the atomic diameter. This latter case corresponds to the use of a delocalization distance in the analysis of channeling experiments [46–49].

2.5. Radiation damage

Another fundamental limit to spatial resolution is set by radiation damage to the specimen. In order to obtain a statistically meaningful spectrum or image, a large enough number of electrons must be recorded. But as the electron dose $D$ (usually measured in C/cm$^2$) approaches some critical value $D_c$, the specimen undergoes damage and the measurement no longer reflects the original properties of the specimen.

The value of $D_c$ depends on specimen composition, specimen temperature and the incident-electron energy. Organic specimens are the most beam-sensitive and they damage mainly by radiolysis, caused by electronic excitations induced by the inelastic scattering. This damage is manifest as mass loss (specimen thinning or hole formation) and/or structural change, including loss of crystallinity. Radiolysis also occurs in most inorganic compounds but the value of $D_c$ is usually much larger. Metallic and semi-metallic specimens may be immune to radiolysis but are expected to undergo mass loss (for higher incident energies and sufficiently high electron dose) as a result of electron-beam sputtering.
Table 1 shows approximate values of $D_c$ for the three types of specimen. The radiolysis doses are based on experimental data published in several review papers [50–52]. The dose range for hole formation due to sputtering (in a 20 nm specimen) is based on calculations for elements of atomic number below 40, assuming a planar surface potential [53].

The electron dose $D$ needed for EELS depends greatly on the type of measurement involved. Valence-loss spectroscopy or imaging require relatively low dose, the intensity being relatively high in the low-loss region of the spectrum. Probably the application that demands the least dose is a being relatively high in the low-loss region of the spectrum. Probably the application that demands the least dose is a sputtering (in a 20 nm specimen) is based on calculations for elements of atomic number below 40, assuming a planar surface potential [53].

**Table 1**

<table>
<thead>
<tr>
<th>Damage mechanism</th>
<th>Type of specimen</th>
<th>Damage dose $D_i$ (C/cm$^2$)</th>
<th>Resolution (nm) for</th>
<th>Resolution (nm) for</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td>valence-EELS</td>
<td>350eV-EELS</td>
</tr>
<tr>
<td>Radiolysis</td>
<td>Organic</td>
<td>$10^{-1}–1$</td>
<td>$5 \times 10^{-4}$–0.5</td>
<td>1–300</td>
</tr>
<tr>
<td>Radiolysis</td>
<td>Inorganic</td>
<td>$0.1–10^6$</td>
<td>$&lt;0.05$</td>
<td>0.01–30</td>
</tr>
<tr>
<td>Sputtering</td>
<td>Metallic</td>
<td>2000–40000</td>
<td>$&lt;10^{-6}$</td>
<td>$&lt;0.2$</td>
</tr>
</tbody>
</table>

Ionization damage (radiolysis) should occur largely through the excitation of inner shells, with small cross section but large excitation energy, so that the deposited energy can be larger than for the valence electrons. As a result, the damage should be mainly associated with small impact parameters and in the aloof mode of EELS [54] a highly focused electron beam placed very close to but just outside the specimen should cause less damage than a beam that penetrates the specimen [55]. Unfortunately this argument fails for light elements such as carbon, where the K-shell ionization energy is only a few percent of that of the valence electrons.

**3. Energy resolution**

The energy resolution of an EEL spectrum or energy-filtered image is influenced by several instrumental factors: energy width of the electron source, energy broadening (Boersch effect) arising from electron interaction in the illumination system, electron-optical design of the electron spectrometer, and stability of the high-voltage and spectrometer power supplies. There are also environmental factors: level of AC magnetic fields and mechanical vibrations, although their effects can be minimized by good spectrometer design.

Whereas thermionic (LaB$_6$ and W-filament) sources provide an energy spread in the range 1–2 eV, a Schottky-emission source gives typically 0.7 eV and a cold field-emission (CFEG) source can give 0.5 eV, or even as low as 0.27 eV with fast data recording [56]. The use of a gun monochromator (a spectrometer with a narrow energy-selecting slit) in the illumination system can reduce the energy spread to below 0.2 eV, with some loss of intensity [57,58]. This type of monochromator operates at close to the gun potential and disperses the electrons before they are accelerated, resulting in relatively high dispersion. A disadvantage of the gun monochromator is that its monochromation is relative to the gun potential: any change $\Delta V$ in the high voltage supply results in an equal change ($\Delta V$eV) in kinetic energy of the accelerated electrons.

The highest energy resolutions (in the range 2–100 meV) have been obtained by combining these relative monochromators with relative spectrometer systems; the same high voltage is used to retard the electrons when they are analyzed, so that high-voltage fluctuations are compensated [59–62]. Such an arrangement has the disadvantage of requiring high potential to be applied to the post-specimen portion of the TEM column. However, it would greatly relax the stability needed for the spectrometer and microscope power supplies and might make possible the analysis of vibrational and phonon-mode features (which mostly occur at energy losses below 0.1 eV) combined with the high spatial resolution. The deployment of aberration correctors could make the use of lower acceleration voltages more attractive.
Energy broadening due to electron interaction within the TEM column (e.g. at beam crossovers) appears to be negligible at typical beam currents. The only significant effect may be in the electron gun itself, where the electrons move slowly, which presumably explains why the energy width of an electron source increases with emission current.

As an alternative (or in addition) to the use of a monochromator, the resolution in an energy-loss spectrum can be improved by a useful factor through deconvolution, using either Fourier [6,63,94] or Bayesian techniques [64–66]. In both cases, the maximum resolution enhancement is determined by spectral noise, which (in the absence of instrumental instability) is limited by radiation damage to the specimen. In theory, maximum-entropy deconvolution offers a resolution improvement several times larger than Fourier processing, although it has to be used with care to avoid introducing spectral artifacts [66].

Fine structure present in an energy-loss spectrum is closely related to the energy dependence of a density of states (DOS) of the material being investigated. For valence-electron losses, this implies a convolution of the conduction- and valence-band DOS, including gap states if the energy resolution is good enough. In the case of an ionization edge, the background-subtracted spectrum reflects the density of unoccupied states above the Fermi level, multiplied by an atomic matrix element (assumed to vary slowly with energy) and convolved with a function that represents the energy width of the core level. The width of this function (essentially the natural linewidth) has been calculated for K and L shells [67] and the results can be parameterized as follows:

\[
\Delta E_K = 0.0216(E)^{0.472} - 0.285, \tag{12}
\]

\[
\Delta E_{L3} = (6.9 \times 10^{-4})E - 0.14 \exp[-(E - 680)/400]^2 - 0.05 \exp[-(E - 30)/90]^2, \tag{13}
\]

\[
\Delta E_{L2} = (7.4 \times 10^{-4})E - 0.16 \exp[-(E - 690)/400]^2 - 0.05 \exp[-(E - 30)/90]^2, \tag{14}
\]

where \( E \) is the appropriate threshold energy in eV. The \( L \)-widths are roughly proportional to threshold energy, the \( L_2 \) width being slightly higher than that of the \( L_3 \) level because Coster-Kronig transitions provide an additional decay channel, decreasing the core-hole lifetime in a solid. However, some data [68–70] differ substantially from the Krause and Oliver values [67], as illustrated in Fig. 6.

This core-level width can be viewed as lifetime broadening of the \textit{initial} state, but there is also \textit{final-state} broadening, representing the fact that the excited electron has a finite lifetime. This electron is subject to the same inelastic scattering processes as a high-energy transmitted electron, so its lifetime \( \tau(e) \) and inelastic mean free path \( \lambda(e) \) (for a given starting energy \( e \)) can be estimated by integrating the low-loss spectrum over all scattering angles and up to an energy loss \( E = e \) [71–75]. This lifetime applies to an energy loss \( e \) above the ionization edge and the corresponding energy broadening \( \Delta E \) can be estimated from the uncertainty principle: \( \Delta E \tau \approx \hbar/(2\pi) \). Recent measurements for aluminum [71,72] are shown in Fig. 7.

Alternatively, the lifetime of the excited electron (energy \( e \) and speed \( v \)) can be taken as \( \tau \approx \lambda/v \), where \( v = (2m_e)^{1/2} \) according to a free-electron approximation, \( m \) being the electron mass, giving:
Fig. 8. Final-state broadening for ionization edges of Al, Ag, Au and Cu, according to Eqs. (15) and (16).

\[ \Delta E \approx \frac{h}{2\pi} / x = h(2\pi \lambda)^{-1}(2e/m)^{1/2}. \]  

(15)

The slow-electron mean free path \( \lambda(x) \) has been measured from photoelectron spectroscopy and the results for several elements have been parameterized (for \( 1 \text{ eV} < \varepsilon < 10^2 \text{ eV} \)) in the form [78]:

\[ \lambda (\text{nm}) = 538 \varepsilon^{-2} + 0.41 a^{3/2} \varepsilon^{1/2}, \]  

(16)

where \( \varepsilon \) is in eV and \( a \) is the atomic diameter (thickness of a monolayer) in nm, given by: \( a^2 = A/(602 \rho) \), where \( A \) is the atomic mass number and \( \rho \) the specific gravity of the specimen (the density in g/cm\(^3\)). The result of applying Eqs. (15) and (16) to aluminum is shown in Fig. (7) and is seen to be in reasonable agreement with the experimental data. For \( \varepsilon > 60 \text{ eV} \), the second term in Eq. (16) is dominant and exactly cancels the \( \varepsilon \)-dependence in Eq. (14), giving:

\[ \Delta E_{\text{max}} \approx (0.93 \text{ eV}) a^{3/2}. \]  

(17)

In other words, the final-state broadening is predicted to reach a limit beyond 60 eV from the edge threshold. Using data from several elements, this limit appears to be between 7 and 9 eV, independent of atomic number; see Fig. 8.

### 4. Momentum resolution

To extract all of the information available from EELS, the spectrum must be recorded as a function of scattering angle \( \theta \), yielding the dependence of the scattering cross section on scattering vector \( q \approx k_0(\theta^2 + \theta_0^2)^{1/2} \) or transferred momentum \( (h/2\pi)q \). This capability has been exploited as a means of exploring the mechanisms of electron scattering in solids [79–88]. In the low-loss region, surface plasmons, bulk plasmons and radiation-loss processes are found to have distinctly different dispersion \( (\omega - q) \) characteristics, so dispersion (or lack of it) can help to identify spectral peaks, even in amorphous materials [89]. The \( q \)-dependence can also be used to investigate the band structure of crystalline materials, especially when combined with measurements made at different sample orientations [86,88]. For this purpose, the \( q \)-resolution should correspond to some small fraction of the Brillouin zone.

In the case of anisotropic materials, measurement of the angular dependence of scattering can provide useful information; a good example is provided by energy-filtered diffraction patterns of graphite, taken above and below the carbon K-edge, which show up the directionality of bonding [90]. To provide a standard “fingerprint”, a collection aperture can be chosen such that the spectrum is independent of orientation, although the “magic angle” (angular range) required is rather small. A recent discovery, following up on earlier work [91], is that the relativistic effects that occur at higher beam energies must be reformulated to correctly account for electron scattering in anisotropic materials [28,92].

It is easy to see that there is a basic-physics limit to the angular or momentum resolution and that this is linked to the spatial resolution of the measurement. High spatial resolution can be achieved by using a focused probe (Fig. 9a) but a fundamental limit to probe size is set by diffraction at the probe-lens aperture and is given by the Rayleigh criterion: \( \Delta x \approx (0.5) \lambda / z \). Increasing the aperture semi-angle \( z \) should improve the resolution, although in most instruments spherical aberration makes things worse for \( z \) greater than about 10 mrad. In an aberration-corrected instrument, \( z \) can increased beyond this value but any appreciable spread in incident-electron direction introduces a spread \( \Delta q = (2\pi / \lambda)(2\Delta z) \) in the scattering vector \( q \). For band-structure studies, \( \Delta q \) needs to be a small fraction of the wavevector \( q_B \) that corresponds to the first Brillouin-zone boundary, equivalent to diffraction (through an angle \( 2\theta_B \)) by atomic planes of spacing \( d_{\text{hkl}} \); see Fig. 9a. Using the Rayleigh criterion and Bragg’s law \( (\lambda = 2d_{\text{hkl}} \theta_B) \), the fractional momentum resolution can be expressed as:

\[ \Delta q / q_B = (2z)/(2\theta_B) = (\lambda / \Delta x)(d_{\text{hkl}} / \Delta x) = d_{\text{hkl}} / \Delta x. \]  

(18)

For 5% momentum resolution, the spatial resolution is therefore limited to \( \Delta x = 20d_{\text{hkl}} \), amounting to 2 nm or more in a typical material. These considerations become limiting when determining the electronic structure of nanowires [89]. Note that Eq. (18), which is equivalent to use of the Heisenberg uncertainty principle \( (\Delta p \Delta x \approx h) \) in the specimen plane, is independent of source brightness and accelerating voltage.

Midgley [93] has described a method for obtaining angular resolution down to a few microradians by...
operating the TEM in image mode. The electron probe is focused at the usual eucentric plane but the specimen is raised by a distance $z$, as in Fig. 9b. Because the probe is out of focus at the specimen, the spatial resolution is no better than $2\alpha z$; see Fig. 9b. From geometry at the eucentric plane, the angular resolution is limited to $\Delta \theta = (2\theta_B) \left[ \Delta x/(2\theta_B) \right] = \Delta x/z = (0.5)\lambda/(\alpha z) = d_{kl}/\theta_B/(\alpha z)$ and the fractional angular or momentum resolution is: $\Delta \theta/2\theta_B = d_{kl}/\Delta x$, in agreement with Eq. (18).

5. Conclusions

The spatial resolution of EELS or energy-filtered imaging depends on the mechanical and electric stability of the instrumentation, and on the design of the electron optics and electron source. But as these aspects are improved, more fundamental limits become significant. Elastic scattering in the specimen causes beam spreading, especially in thicker specimens, degrading the spatial resolution of the inelastic signal. Inelastic scattering itself is somewhat delocalized, especially at lower energy loss. On a classical (particle) picture of scattering, this delocalization reflects the long-range nature of the Coulomb potential. Using a wave-optical description, the degree of delocalization depends on the angular distribution of the electrons reaching the detector. In beam-sensitive specimens, radiation damage imposes a more serious practical limit to resolution, especially at high-energy loss where the scattered signal is weak.

Energy resolution depends on the design and stability of the microscope and spectrometer, the type of electron source and whether a monochromator is used. However, the resolution of core-loss fine structure is considerably affected by the core-level width (initial-state broadening) and scattering of the excited electron (final-state broadening).

To provide additional information about the specimen, the momentum resolution of EELS can be increased, but at the expense of spatial resolution. Again this limit follows from the wavelike nature of the electron, as embodied in the Heisenberg uncertainty relation or the Rayleigh criterion for resolution.

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