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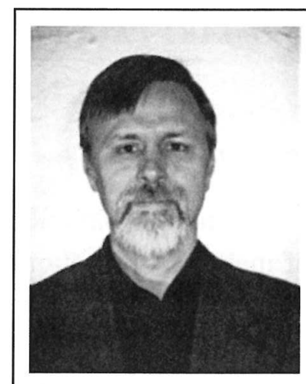
X-RAY MICROANALYSIS AND ELECTRON ENERGY-LOSS SPECTROSCOPY (EELS) IN THE TEM



*János L. Lábár**

Hungarian Academy of Sciences, Research Centre for Natural Sciences, Institute for Technical Physics & Materials Science
P.O. Box 49, HU-1525 Budapest-114, Hungary
** e-mail: labar.janos@ttk.mta.hu*

INTRODUCTION: EXCITATION AND DE-EXCITATION

Here we will discuss special topics from inelastic scattering, the excitation of the inner shells of the atoms and the ensuing de-excitation process. The primary process (excitation) leads to the generation of the electron energy-loss (EELS) signal, while one of the two secondary processes (de-excitation) emits X-rays that we detect with an EDS detector (Fig. 1). Since the energies of the inner shells are quantized, the electronic transitions that involve them act as fingerprints, identifying the atoms. Both EELS and X-ray emission (referred to as EDS after the detection method) are used to determine the atomic composition of the analysed sample. Application of these two methods in the TEM is introduced in the present paper.

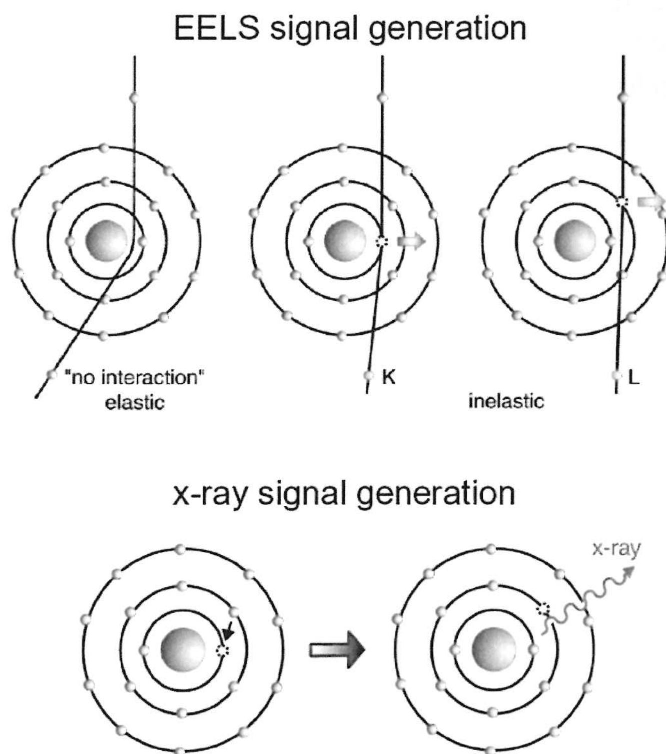


Figure 1. The primary process of excitation of inner shells that leads to the EELS signal, followed by one of the two de-excitation possibilities that produce X-rays.

PRIMARY PROCESS: EXCITATION OF ATOMIC SHELLS, ENERGY-LOSS FOR THE ELECTRONS OF TEM

The EELS hardware

The thin sample in the TEM is illuminated by monochromatic electrons. It is the range of inelastic interactions of the electrons with the sample that produces a spectrum of electrons with different energies. Measuring that electron energy spectrum, actually we obtain an electron energy-loss spectrum (EELS), the loss being measured from the energy of the illuminating electrons. The EELS spectrum is a consolidated history of electron-sample interactions that can be used to decipher the interactions, and hence determine the properties of the sample. The EELS as analytical signal contains both element specific and not element-specific information components.

The EELS spectrum is recorded by a spectrometer, whose principal component is a sector magnet. The principal options for the geometry, applied to record the EELS spectrum are shown in Fig. 2. The focussing effect of the sector magnet is shown in Fig. 3. By proper selection of the geometric parameters of the sector magnet, a double-focussing spectrometer can be constructed, characterized by the same focal lengths at two perpendicular planes. Electrons with different energies are deflected differently in the constant magnetic field of the sector magnet and a spectrum of electron energies can be recorded at the „energy dispersive plane". In practice, the small energy dispersion of the sector magnet is further enhanced by additional multipole lenses and the spectrum is recorded over a line of detectors (diode array), or alternatively on a two-dimensional (2D) set of recording elements, a CCD. In the latter case, integration over pixels, perpendicular to the energy dispersive direction (i.e., pixels corresponding to the same energy-loss) enhances statistics.

Very frequently a combined, spectrometer / energy filter is installed in contrast to a simple spectrometer. Energy filtering is reached by inserting an aperture into the energy dispersive plane and allowing electrons with pre-selected energy to continue their passage. Electrons with all other energies are filtered out by the aperture. Additional lenses in the filter reconstruct the same image or diffraction pattern that was originally present at the viewing screen of the TEM and an energy filtered version of the same image or diffraction pattern is recorded on the CCD. Image and its magnification, or diffraction pattern and its camera length are controlled by selecting the TEM settings. The filtered energy interval is selected by the aperture within the energy filter. Changing between spectrometer mode and energy filter mode not only implies removal or insertion of the energy selecting aperture, but also re-tuning both the pre-magnet and post-magnet lenses within the spectrometer / energy filter.

The measured EELS spectrum; edge types; types of inelastic scattering

The EELS spectrum is collected in a multichannel analyzer. Each channel corresponds to a pre-selected energy interval, typically 0.1 - 0.5 eV/channel. With a typical 2,000 channel,

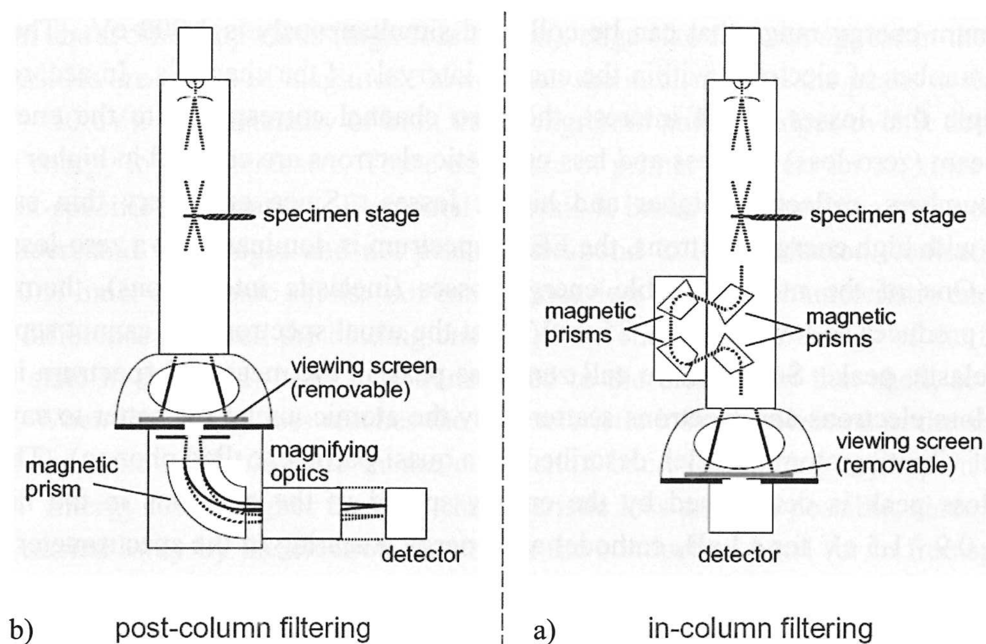


Figure 2. The two existing configurations of EELS in the TEM. The EELS spectrometer / energy filter is always situated below the sample. a) In column filter; the EELS spectrometer / energy filter is manufactured simultaneously together with the TEM. b) Post column filter; the EELS spectrometer / energy filter manufactured separately from the TEM and can be retrofitted later to any existing TEM.

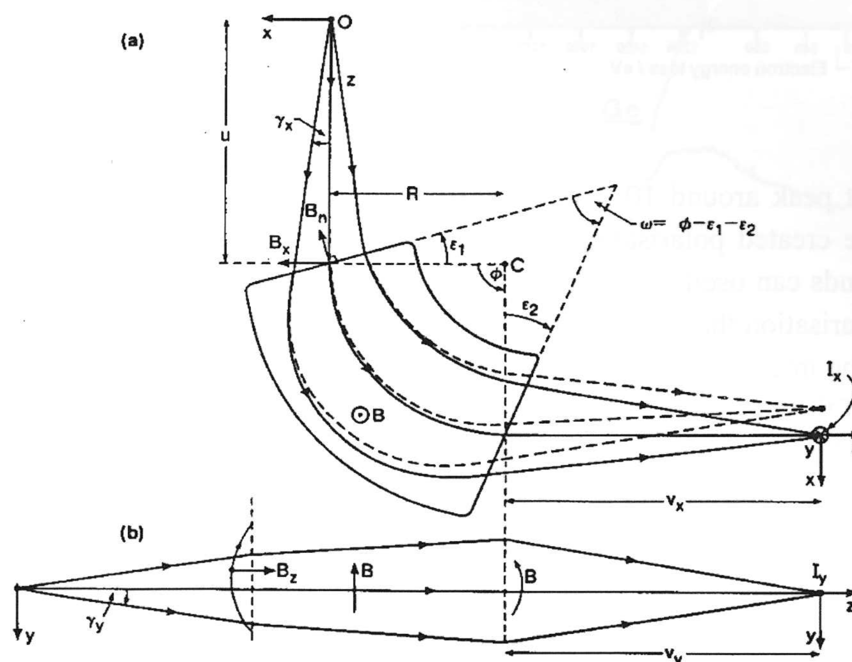


Figure 3. The sector magnet: the basic element of EELS hardware. Two perpendicular planes are shown.

the maximum energy range that can be collected simultaneously is 1,000 eV. The spectrum gives the number of electrons within the energy intervals of the channels. In accordance with the principle that losses are of interest, the zero channel corresponds to the energy of the primary beam (zero-loss) and less and less energetic electrons are counted in higher and higher channel numbers, reflecting higher and higher losses. Since only very thin samples are examined with high energy electrons, the EELS spectrum is dominated by a zero-loss peak (see Fig. 4). One of the most probable energy losses (inelastic interactions), thermal diffuse scattering produces so low losses (~ 25 meV) that the usual spectrometer cannot separate them from the elastic peak. So, what we call zero-loss peak in the measured spectrum is a sum of true zero-loss electrons and electrons scattered by the atomic nuclei (or better to say a weakly joint set of vibrating atomic nuclei, described by a quasi-particle, called phonon). The width of the zero-loss peak is determined by the energy spread of the electrons in the illumination system (~ 0.9 - 1.5 eV for a LaB_6 cathode) and energy smearing of the spectrometer, including both lens properties and stability issues.

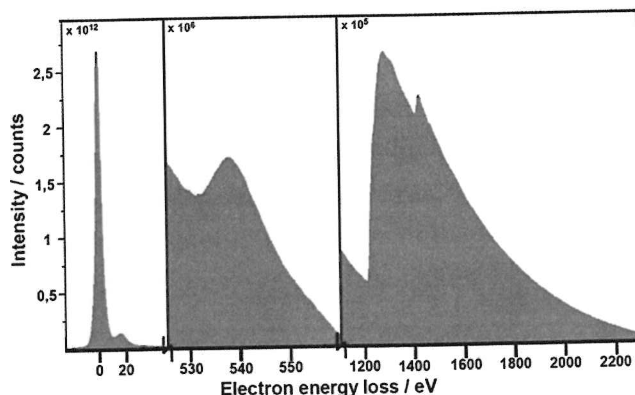


Figure 4. Example of measured EELS spectrum. Partially oxidized germanium. The intensity changes by 7 orders of magnitude over the 2,200 eV energy interval. Left side: zero-loss peak and the Plasmon peak. Central part: oxygen K-edge. Right side: germanium L-edge.

The next peak around 10 - 30 eV losses is the so called Plasmon peak. It shows the strength of the created polarisation waves. The loosely bound electrons in the valence and conduction bands can oscillate collectively around the quasi-stationer set of nuclei, producing oscillating polarisation that can be described by a quasi-particle, called Plasmon. For the usual thin samples the intensity of the Plasmon peak is about 1 - 2 order(s) of magnitude lower than the intensity of the zero-loss peak. For very thin samples, only one Plasmon peak is seen. As the sample thickness increases, the probability of creating more than one Plasmon by the same electron is increases and smaller peaks appear at multiples of the Plasmon energy.

Occasionally, a tiny peak can also be observed between the zero-loss peak and the Plasmon peak. It originates from exciting a single electron of the valence band into the next empty state of the conduction band. The energy loss caused by such an interband transition is a few eV.

From about 50 eV upwards (high-loss region), edge-like features appear in the spectrum. Their intensities are orders of magnitude lower than the intensities of the peaks in the low-loss region (< ~ 50 eV). The intensity of both the background and the edges over it decrease very fast as the energy loss is increased. These edges are of primary interest for us, since they carry the element-specific information. Elemental analysis is based on measuring these edges. It is easy to understand why edges and not peaks correspond to the excitation (ionisation) of the tightly-bound inner electronic shells. An energy loss, less than the characteristic energy of the edge (the difference between the binding energy of the shell and the energy of the first empty electronic state in the solid) cannot be transmitted to the electron in that shell, so no loss is observed. When the energy loss reaches the characteristic loss, the electron in the shell can be excited to the next available state in the conduction band (producing a jump in the EELS spectrum). Energy losses higher than the characteristic loss are also possible, since the excess energy is carried away by the electron moving in the conduction band (or in free space if the atom is ionized). Consequently, the increased intensity in the loss spectrum continues up to all possible energy losses (in principle up to the primary beam energy minus the characteristic loss). The result is a saw-tooth-like edge in the EELS spectrum.

Three basic types of edge shapes are known. Saw-tooth-shape for the K-edges of the lightest elements, rounded edges for the L-edge of the medium atomic number elements and edges with „white lines" for the L-edges of transition elements and the M-edges of the lanthanides (see Fig. 5.)

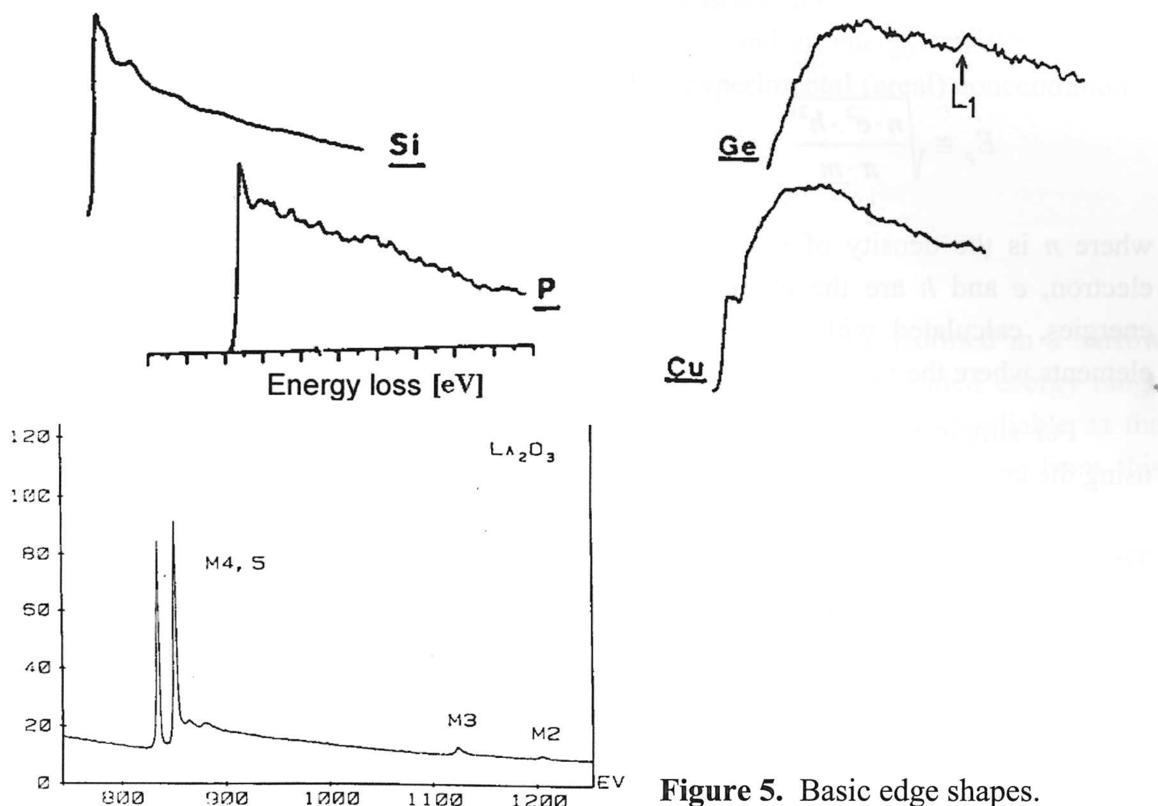


Figure 5. Basic edge shapes.

The low-loss region: sample thickness and the density of „quasi-free" electrons

The value of sample thickness is needed for quantitative EDS analysis (see below), if the X-ray absorption is significant in the examined thin film. One method to determine local sample thickness is provided by EELS. It is based on Beer's law, stating that the intensity of a radiation passing through a sample of thickness ***t*** is varying as an exponential function of the sample thickness. The total number of electrons is given by I, the integral of the EELS spectrum (summing electrons without loss and all energies of losses). The ratio of the elastic peak (I_0) to the total spectrum integral carries the information about thickness.

$$I_0 = I \cdot \exp\left(\frac{-t}{\lambda}\right)$$

where λ is the inelastic mean free path. The sample thickness is given from here by

$$t = \lambda \cdot \ln\left(\frac{I}{I_0}\right)$$

The inelastic mean free path can be calculated as a function of electron energy and sample atomic number.

The local density of the electrons in the valence/conduction band(s) can be determined from the measured energy of the Plasmon peak. A simple theory of a set of quasi-free oscillators predicts that the energy of the Plasmon is proportional to the square root of the electron density:

$$E_p \cong \sqrt{\frac{n \cdot e^2 \cdot h^2}{\pi \cdot m}}$$

where n is the density of the electrons in the valence/conduction band, m is the mass of electron, e and h are the charge of electron and Plank's constant, respectively. Plasmon energies, calculated with the rest mass of electrons agree well with measured values for elements where the valence/conduction band contains electrons with s or p character only.

For simple materials, the local sample density can be obtained from electron density, using the known number of electrons per atom in the valence/conduction band.

The core-loss region: elemental analysis

The energy of the edge is characteristic of the element, since it is determined by the quantized energies of atomic electronic shells. So qualitative analysis (i.e., identification of elements) is based on the measurement of the energies of the edges in the spectrum. Quantification (i.e., determination of the quantities of the elements) is based upon the measurement of the integrals of the edges over the background.

The total integral of the EELS spectrum, I, gives the number of electrons that entered the spectrometer (scattered within the acceptance angle of the EELS detector). If the net integral of an edge (of a type atom) could be summed up from the edge energy up to the primary beam energy, I_a, it would give the number of electrons that caused ionisation of the given shell (and scattered into the spectrometer). Their ratio would be the probability of ionisation.

$$\frac{I_a}{I} = n_a \cdot \sigma_a$$

where n is the areal density of atoms [atoms/cm^2] and σ is the ionisation cross-section of the atom in question and the subscript denotes the atom in question. The areal density of a type atom (the concentration of atoms integrated along the beam over the thickness of the sample) is obtained as:

$$n_a = \frac{I_a}{I \cdot \sigma_a}$$

Both I and I_a only contain electrons that were scattered within β, the acceptance angle of the spectrometer. Consequently, the ionisation cross-section is also to be computed for scatterings within the angle β. Furthermore, we are unable to perform integration up to the primary beam energy in practice. Consequently, the „experimental" integral only contains the electrons within the energy interval of the integration window, Δ (as indicated in Fig. 6). As a consequence, the ionisation cross-section is also to be calculated for that energy interval. The ionisation cross-section, calculated for an acceptance angle and an energy window is named partial ionisation cross-section and denoted $\sigma(\beta,\Delta)$. The experimental (areal) concentration of element a is:

$$n_a = \frac{I_a}{I \cdot \sigma_a(\beta, \Delta)}$$

There are three main reasons why the integration can only be performed in a narrow energy window. First, the energy-loss spectrum is only measured in a limited energy range (< 2 keV). Second, extrapolation of the background becomes less and less reliable as the extrapolation distance is increased. Third, overlapping edges would prevent us from this integration anyhow.

Calculation of the partial cross-sections (using the experimentally determined β and the parameter Δ, selected during data reduction) can be based on hydrogen-like atomic electronic functions for K-edges of low atomic number elements and using Hartree-Fock electronic functions for the rest of edges. Calculation of the partial cross-sections comes together with the EELS spectrometer from the manufacturer.

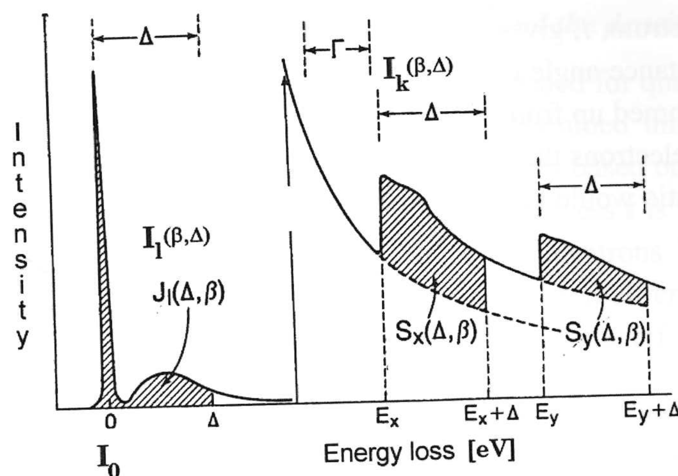


Figure 6. Selection of intervals for both background measurement and post-edge region. Extrapolation from the measured background under the post-edge region is indicated. The post-edge tail of one element serves as background for the overlapping edge of another element. Integration interval for the post-edge region is arbitrarily selected and it is a parameter, needed during the calculation of the partial cross-section, used for quantification.

Practical EELS analysis: TEM coupling; splicing; detected elements and edges; spectral and spatial resolution; detection limit; accuracy

Operation modes of the EELS (spectrometer or energy filter) and operation modes of the TEM (imaging or diffraction) can be controlled separately. In principle, they could be selected independently of each other. However, the coupling between the TEM and the EELS demands interdependent selection of operation modes.

In spectrometer mode of the EELS, the energy dispersive plane of the spectrometer is conjugate to the cross-over of the projector lens. The size (and shape) of the „object" at the projector cross-over is convoluted with the energy spectrum, so it is one factor that determines spectral resolution. The other factor, determining spectral resolution is the energy spread of the beam. If the TEM is in imaging mode, a diffraction pattern is present at the projector cross-over, and the size of the pattern in the projector cross-over is determined by the objective aperture, so its correlation with the area of analysis is not well defined. That is the reason why the TEM must always be in diffraction mode for EELS analysis (spectrometer mode of the EELS). In the TEM diffraction mode, the projector cross-over (SO in Fig. 7) contains a small image of the analysed area. Its size is determined by the size of the analysed area, controlled by the selected area aperture (SAD in the figure). For the analysis of a medium energy edge, the integration window is about 50 eV and the spectral resolution is not a limiting factor even if it is a few eVs, due to a larger area selected for analysis (spectral resolution is a limiting factor only if the optical properties of the sample are being determined from the low-loss region of the EELS spectrum; however, this topic is beyond the scope of the present basic introduction). Spatial resolution is determined by the selected area aperture in that mode. If the analysis is to be restricted to smaller volumes, the illumination is to be restricted by forming a small convergent probe, similarly to what is done in EDS analysis. Best spatial resolution is limited by the probe size if the thinnest samples are used. For TEMs with a field emission gun (FEG),

probe sizes close to the size of atomic columns facilitate separate analysis of individual atomic columns. Z-contrast imaging of FEG-STEMs is especially useful to select the atomic columns for EELS analysis in such cases.

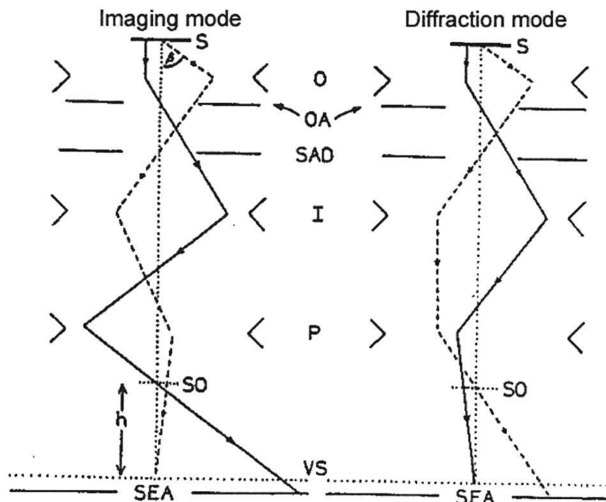


Figure 7. Coupling modes between the TEM and the EELS. In spectrometer mode of the EELS, the energy dispersive plane of the spectrometer is conjugate to the cross-over of the projector lens. The size (and shape) of „object" at the projector cross-over is convoluted with the energy spectrum, so it is one factor that determines spectral resolution. In imaging mode, the projector cross-over contains a small diffraction pattern, so the coupling is through diffraction. In diffraction mode, the projector cross-over contains a small image of the area from where the diffraction comes from, so the coupling is through the image. For EELS analysis the TEM must always be in diffraction mode (so image coupling is to be used).

Since the size of energy interval that can be recorded in a single experiment is restricted by the dynamic range of the spectrum (sections), a complete spectrum over a larger energy interval can only be collected in sections and can be spliced together (by normalising the individual spectra at the overlapping sections).

The energy interval that is recorded in EELS extends to 3 keV (most frequently up to 2 keV), and all elements have at least one characteristic edge in the interval, all elements from Li upward can be detected and analysed in principle. Lack of calculated partial cross-sections for special edges may prevent them from quantification. However, all elements can be analysed by at least one edge.

EELS is not a trace element detection method. Elements present in a concentration of > 1 % are generally detected. Elements with white line can also be detected at lower concentrations, due to the concentration of intensity in a narrow energy interval. Differentiation techniques can further reduce the minimum detection limit.

Precision and accuracy are determined by two main factors. First, small steps on large signal are to be integrated. Uncertainties in the selection of background points and

extrapolation of the background even worsen the situation (undulations due to the presence of extended fine structure of another edge to the left of the measured one makes extrapolation prone to error). Second, uncertainties in the calculated partial cross-section also contribute to the systematic error. Experimental determination of relative values of partial cross-sections is also possible, similarly to the procedure used in EDS. A thin film standard must be measured. From the know ratio of the concentrations of its components and from the measured ratio of the edge integrals, the ratio of partial cross-sections can be determined. Altogether, we can say as a rule of thumb that reliability of EELS analysis is generally not better than 10 % relative for major components.

Fine structure of characteristic edges: ELNES and EXELFS

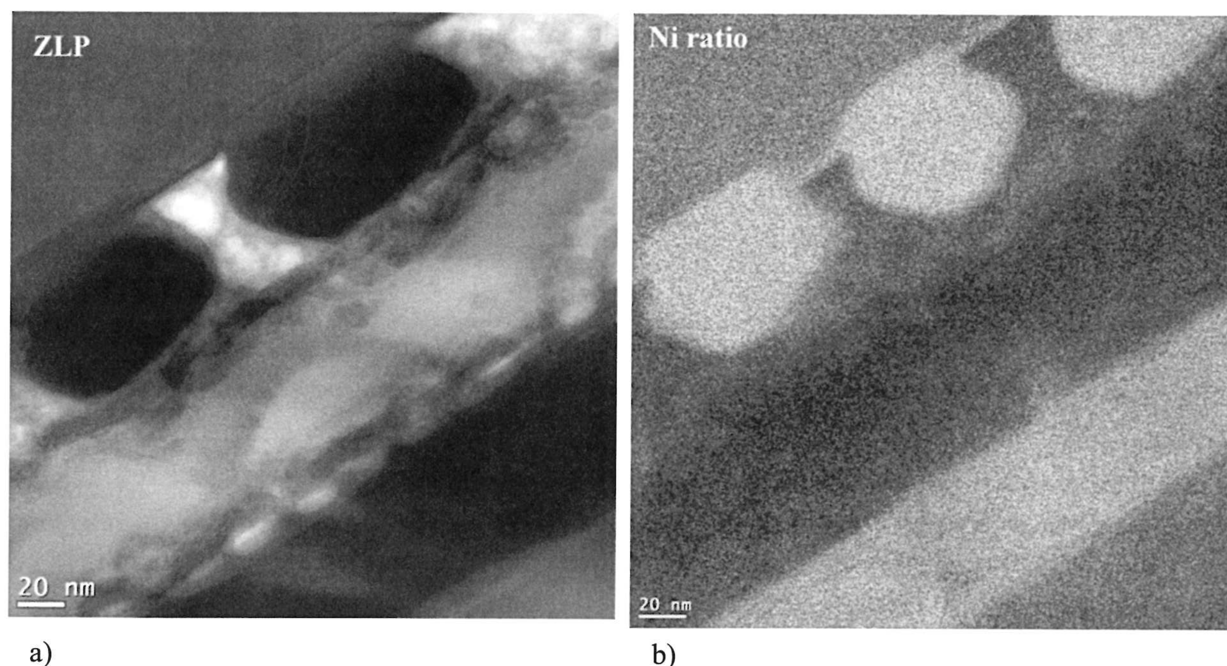
Existence of white lines was one example of the fine structure of an edge. The white lines originate from the presence of unfilled inner shells in the atom. They can serve as final states for electronic transitions, caused by the excitation by the beam electrons. A sharp line is a result of a single final state with quantized energy. It is true in more general that the shape of the edge (close to the onset) is determined by the density of empty states, available as final states for the transition. Consequently, the electron energy-loss near edge fine structure (ELNES) reflects the density of (a subset of) empty states. Since transition selection rules allow only transitions into states with predefined symmetry, it is a symmetry-projected density of states what we see in ELNES.

ELNES extends to ~ 50 eV above the onset of the edge. Fine structure exceeding this energy interval is called extended electron energy fine structure (EXELFS). The undulations in EXELFS are determined by the atomic arrangement close to the ionized atom. Atom specific distribution of nearest neighbours can be determined from EXELFS in principle. However, the measurement is not simple and we cannot find many applications in the literature.

Energy filtered TEM (EFTEM)

When the EELS is switched to energy filter mode of operation, the plane conjugate to the CCD will be the plane of viewing screen of the TEM. While the electrons are travelling from the points of the viewing screen to their conjugate points on the CCD, they pass the energy dispersive plane of the EELS spectrometer, where an energy selecting slit is inserted. Electrons with pre-defined energy are only allowed to follow their path. The rest is filtered out by the aperture.

If the viewing screen contained an image (because the TEM was in imaging mode), an energy filtered image is recorded by the CCD (Fig. 7). If a diffraction pattern was present on the viewing screen (because the TEM was switched to diffraction mode), an energy filtered diffraction appears on the CCD. In either mode, the energy selecting aperture can be set to any preselected value. By selecting the elastic electron, we obtain zero-loss image (or diffraction pattern). If the filter is tuned to characteristic losses, the spatial distribution of the elements can be deduced (these are called elemental maps).



a) b)

Figure 7. Example of energy filtered images from a Ni-InP nanostructure. a) Zero-loss image. b) Elemental map of Ni obtained by the two-window (ratio) technique.

Elemental mapping

To record an elemental map, we need to record three pictures, with three pre-defined energies. Two of them are recorded at two different energies at the pre-edge region. One image is recorded with the energy window containing the highest intensity interval of the post-edge region. The elemental map is obtained by electronic, pixel-by-pixel manipulation of the three images. At each pixel, the background is determined from the first two images and it is extrapolated under the corresponding post-edge pixel in the third image.

Cross-correlation is generally applied between the images to detect drift and to correct for it.

A special trick is also applied to record these images. Since the electromagnetic lenses deflect electrons with different energies differently, we want to ensure that the imaging part of the microscope receive electrons with the same energy all the time, even when we want to record different energy losses. This is done by changing the accelerating voltage of the TEM. E_0 values are tuned in a way that after the different predefined losses, the electrons will always have the same energy. The higher loss we want to observe, the higher E_0 we set.

Zero-loss filtered images and diffraction patterns

For images zero-loss filtering only means that thicker samples can be imaged with the same sharpness, the same resolution.

The most important application of zero-loss filtering is recording diffraction patterns. Many important physical quantities, like the spatial distribution of the chemical bonding electrons can be determined from comparing convergent beam electron diffraction (CBED) patterns with theoretical calculations. Comparison can only be made if the inelastic background is properly removed by zero-loss filtering.

Summary

EELS can detect elements from Li upward if they are present in a concentration > 1 %. The accuracy of the method is around 10 % for major components. Spatial resolution is determined by the selection of the area of analysis. If it is selected by an aperture, the spatial resolution is around 100 nm. If the illumination restricts excitation, the spatial resolution is limited by probe sizes for the thinnest samples and can reach single atomic column resolution for FEG (S)TEMs. Beside elemental composition, a range of other important quantities can also be determined from EELS. They include local sample thickness, the density of electrons in the valence/conduction band, the distances of nearest neighbour atoms and many more. In energy filter mode, elemental maps can be recorded. Zero-loss filtered CBED patterns are used to compare them with calculations.

SECONDARY PROCESS: DE-EXCITATION OF ATOMIC SHELLS

X-ray generation and emission in the TEM; detection; light elements

The high energy electrons cause ionisation in the thin sample similarly as they do in the bulk samples. The ionisation with subsequent X-ray emission (Fig. 8) and X-ray detection is very similar to the situation we learnt for EMPA and EDS of bulk samples in the SEM. However, due to the higher electron energy and due to the presence of a thin sample, there are marked differences from the bulk case. We are discussing these differences here.

Due to the high primary electron energy, the overvoltage for all of the examined ionization edges is high. At that region of overvoltage ($U = E_0/E_c$), the ionisation cross-section (Q) is only slowly varying function of the overvoltage.

Because the sample is thin, the energy loss within the sample (prior to X-ray generation) is small on average. Consequently, the ionisation cross-section can be evaluated at a fix U, and there is no need for integration along a path of slowing down electrons (a situation in contrast to the bulk case).

The thin sample also result is reduced background, as compared to the bulk case (see Fig. 8b). The detector and the detection process is the same as what we learned at a previous talk, so we do not repeat it here.

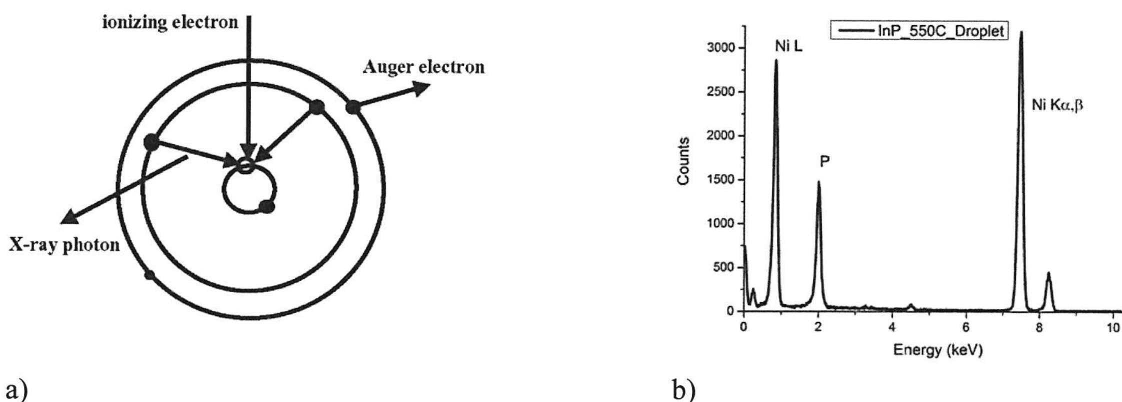


Figure 8. a) Competing processes of de-excitation: emission of an Auger electron versus emission of an X-ray photon. b) A typical EDS spectrum from a Ni-InP nanostructure in a TEM.

The problems of light element detection due to the low fluorescence yield are the same for bulk and thin samples. Light element detection in the TEM is further diminished by the enhanced noise, due to the scattered high energy electrons. As an example, detection of boron is possible in high concentrations only in the TEM, while it is easily detected in the SEM.

Similarly, since the sample is thin and the detector is at reasonable angles above the sample, the absorption path-length (see Fig. 9) is frequently small (no need for the X-ray to get out from deep inside the sample). As a consequence, the absorption is generally not too significant and can be neglected. This is the so-called thin film approximation (its validity is elaborated below). Without significant absorption, secondary fluorescence is also negligible. Altogether, modelling (calculating) X-ray analysis is much simpler in the TEM (thin samples) than in EPMA or SEM/EDS (bulk samples). We shall see below that the ratio of concentrations is proportional to the ratio of measured intensities, where the constants of proportionality are called the Cliff-Lorimer factors. No matrix effects are present in the Cliff-Lorimer factors (Fig. 10). It is hard to imagine a situation simpler than that.

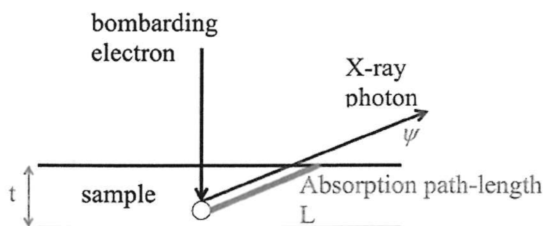


Figure 9. Relation of absorption path length to layer thickness for an ideal geometry of a uniformly thin sample bounded with plan-parallel planes.

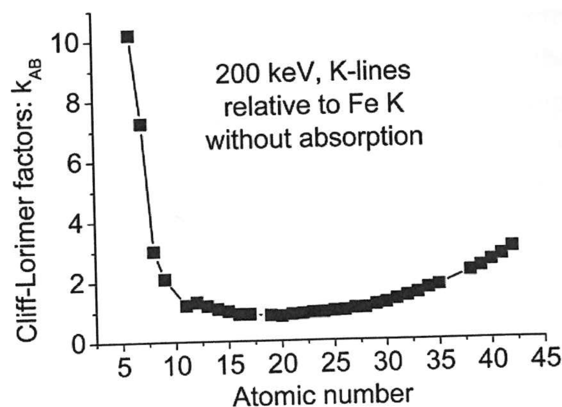


Figure 10. The Cliff-Lorimer factors, related to Fe K-line, for a range of elements.

The detection efficiency in the calculation of the Cliff-Lorimer factors is identical to that learned about EDS in a previous lesson, so it is not repeated here. Thickness and components of the window material determine low energy efficiency, while thickness of the detector determines high energy efficiency.

Protection of the EDS detector

High energy electrons produce a huge amount of electron-hole pairs in the EDS detector. The resulting high current is harmful to the detector, so it must be protected against scattered electrons. Fortunately, backscattering is low probability event in thin samples. Additionally, the magnetic field of the OL deflects many of the scattered electrons from the detector. What must be avoided is a situation when both backscattered electrons and X-rays are produced in large number. This is the case when a thick part of the sample (or sample holder) is hit by the beam. That is why; the EDS is generally withdrawn behind a metal shield, when it is not in use. It is only inserted close to the sample after the thin part for analysis has been selected and the beam is concentrated on the thin part only. Most of the EDS detectors in the TEM give a warning signal and switch off the detector bias when a high current is detected in the EDS, indicating the presence of an unwanted level of ionising radiation. It is generally caused by a careless move of the operator. The detector must only be reinserted after the problem was eliminated.

Quantification; the Cliff-Lorimer factors

The intensity of the ith element of the sample, as detected by a detector extending Ω solid angle is

$$I_i = N \cdot Q_i^*(E_0) \cdot \left\{ N^0 \cdot \rho \cdot t \frac{c_i^w}{A_i} \right\} \cdot \left\{ \int \varphi(\rho z) \cdot \exp(-\chi_i \cdot \rho z) \cdot d(\rho z) \right\} \cdot \omega_i \cdot a_i \cdot \left\{ \frac{\Omega}{4\pi} \varepsilon_i \right\}$$

N is the number of primary electrons. $Q_i^*(E_0)$ is the ionisation cross-section of one atom of type "i", taken at the energy of the primary electrons (E_0). N^0, ρ and t and are Avogadro's number,

the density and thickness of the layer, respectively. The expression in the curly braces is the absorption correction. It is 1, when the thin film approximation holds. The mass fraction, atomic weight, fluorescence yield and weight of line for the ith element is designated by c^{w}_{i}, A_i, ω_i and a_i, respectively, while ε_i is the detection efficiency of the detector for the line of element "i".

Taking the ratio of two such expressions for the ith and j^{th} elements:

$$\frac{I_i}{I_j} = \frac{Q_i^*(E_0)}{Q_j^*(E_0)} \cdot \frac{c_i^w}{c_j^w} \cdot \frac{A_j \cdot \omega_i \cdot a_i}{A_i \cdot \omega_j \cdot a_j} \cdot \frac{\varepsilon_i}{\varepsilon_j} = k_{i,j} \cdot \frac{c_i^w}{c_j^w}$$

In the absence of absorption, the $k_{i,j}$ factors only contain atomic data and detector efficiencies and knowledge of sample thickness is not needed for the evaluation of the concentrations. The $k_{i,j}$ factors only depend on the two elements in question, but are independent of all the other components of the sample. This is the simplest expression one can imagine for converting intensities into concentrations. The $k_{i,j}$ factors are named after the two people, who introduced them. They are the Cliff-Lorimer factors. The ratios of concentrations are converted into true concentration values by a normalising condition: the sum of all concentrations must add up to 100 %. The Cliff-Lorimer factors can be interpreted as relative sensitivity factors for a pair of elements. These sensitivity factors are generally within one order of magnitude if different elemental pairs are compared (see Fig. 10).

Beyond the thin film approximation

Depth distribution of ionisations can be regarded constant within a thin film. With this assumption the absorption term for the ith element is

$$f(\chi_i) = \int_0^{\rho t} \exp(-\chi_i \cdot \rho z) \cdot d(\rho z)$$

where

$$\chi_i = \left(\frac{\mu}{\rho}\right)_i \cdot \frac{1}{\sin(\psi)}$$

The definition of the take-of-angle, ψ, is seen in Fig. 9. Now, the mass absorption coefficient for the radiation of element „i" does depend on all the components of the sample. So matrix effects are introduced by the absorption correction, if the thin film approximation does not hold. It is assumed that the sample is of uniform thickness, bounded by plan-parallel boundaries (see Fig. 9). The absorption path length, needed in absorption correction is converted into sample thickness by this assumption about the geometry of both the sample and of the entire measurement arrangement. The necessary sample thickness can be determined by

several alternative methods: form EELS measurement, from the separation of contamination spots and from convergent beam electron diffraction. The first two works for amorphous or polycrystalline samples, while the last one can only be applied to single crystals.

Since the thickness is small, the exponential can be expanded in series. Stopping at the second terms and forming the ratio of such expressions for two elements,

$$\frac{f(\chi_i)}{f(\chi_j)} = \frac{1}{2}\left\{\left(\frac{\mu}{\rho}\right)_i - \left(\frac{\mu}{\rho}\right)_j\right\}\frac{\rho \cdot t}{\sin(\psi)}$$

Depending on the pair of element in question, absorption can also be negligible (i.e., the thin film approximation can hold) even for element of strong absorption, provided the two elements are absorbed similarly. It is obvious that the sample can be "thin film" for EDS and can be "thick" for imaging, or vice versa. Validity of the thin film approximation depends on both members of the pair and not only on any one of them.

Measurement of intensities and standards

Measurement of intensities is done very similarly as in the case of bulk samples. Spectrum processing must remove background and deconvolve peak overlaps. Background is much smaller for thin films.

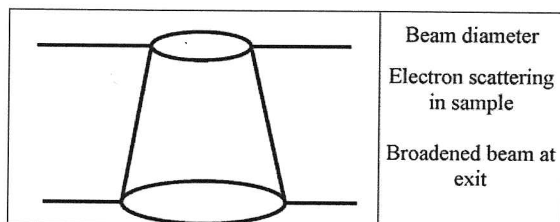
Quantitative analysis requires the knowledge of the Cliff-Lorimer factors. They can be computed or measured from well characterized samples (thin film standards). In the former case we speak of "standardless" analysis. In principle, the calculation is simpler than for bulk samples and standardless approach is applied more frequently than in the case of bulk samples.

Preparation of good thin film standards is more problematic than the preparation of good bulk standards. The main reason is that a very thin film is very easily oxidized or contaminated. However, it is possible to produce such thin film standards and the Cliff-Lorimer factors can also be determined experimentally for a given instrument.

Since absorption is less of a problem in thin films, comparison to pre-measured peak shapes is a working option. The most frequently applied approach is that the filtered EDS spectrum is fitted to pre-measured peak shapes of the elements by least squares. Combining with the Cliff-Lorimer factors, the concentrations are determined.

Detection limits, spatial resolution, Cs-correctors

Spatial resolution in a thin sample is determined by both the probe size and the scattering of electrons within the sample. The latter is a function of both the average atomic number and the thickness of the sample. Broadening within the sample is seen in Fig. 11. It is obvious that the best spatial resolution (approaching the nominal value) can only be reached in very thin samples.



Broadening [nm] due to electron scattering @ 200 keV			
Element / thickness	10 nm	50 nm	100 nm
C	0.08	0.9	2.6
Cu	0.34	3.8	11
Au	0.78	8.6	50

Figure 11. Broadening of the electron beam within the thin film sample.

Two types of detection limits can be defined: the lowest concentration that can be detected as one definition and the lowest number of atoms, as a second definition. Detection of low concentration needs low statistical scatter in the measured signal, i.e., a strong signal. It can be reached if a thicker sample is illuminated over a large area (intense beam). Generally this is not the aim of the EDS measurement in the TEM, since locality is lost under these conditions. The smallest number of atoms can be detected if the smallest volume is excited. Small diameter beam and very thin sample is needed for that detection limit. The experimental conditions are opposite for the two types of detection limits. Detection of low concentration is accompanied by bad spatial resolution, while the lowest number of atoms can only be detected when the best spatial resolution is available. The smallest diameter values can only be achieved when a FEG is available. The key question is how large current can be compressed in the smallest diameter. The smallest diameter is determined by the spherical aberration of the objective lens. Broadening, caused by the spherical aberration is show in Fig. 12.

$$d \approx C_s^{1/4}$$

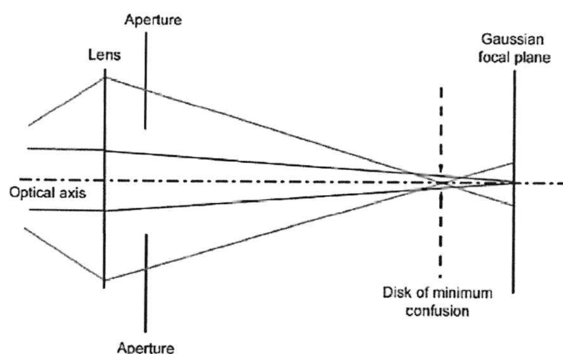


Figure 12. Effect of the spherical aberration on the probe size.

For most of the microscopes used worldwide the value of C_s was determined during manufacturing and cannot be changed later. The newest generation of "C_s-corrected" TEMs and STEMs offers a possibility to vary C_s and improve the spatial resolution that can be obtained in EDS analysis.

Accuracy and precision

Precision is controlled by statistical scatter of the signal (reproducibility). It can be improved by collecting more counts (longer measurement time). This is the value that is calculated by most programmes when the analysis result is presented.

Accuracy is controlled by the presence of systematic errors. The most significant source of systematic errors is the inaccurate knowledge of the Cliff-Lorimer factors. These errors are hard to estimate. Be aware of the fact that the "reliability limits" printed by your programme never contain the contribution from the very important systematic errors. Another source can also be the stray radiation component in the measured EDS spectrum. These artefacts can generally be identified and even eliminated, so they must be less of a problem.

Summary

Elements from boron upward can be detected in thin films by EDS. Quantification is done by applying the Cliff-Lorimer factors. Absorption correction can also be needed for certain samples. The usual accuracy that is reached is about 10 % relative for the main components. The detection limit is about 0.1 wt% for the heavier elements and worse for the light elements. The lowest number of atoms can only be detected by using a FEG and the thinnest possible samples. Detection of a few atoms is achieved in that way.

FURTHER READING

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