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Electron Energy-Loss Spectroscopy

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Electron energy-loss spectroscopy (EELS) involves measuring the energy distribution of electrons that have passed through a thin specimen in a TEM, usually by adding a magnetic spectrometer beneath the viewing chamber (Fig. 1). The spectral energy resolution is largely determined by the energy width of the electron source: 1 – 2 eV for a thermionic source, 0.5 to 0.7 eV for a field-emission gun and 0.1 – 0.2 eV for a FEG followed by a monochromator. Since the electron beam at the specimen can if necessary be focussed into a probe of sub-nm dimensions, this spectral information can be obtained with very good spatial resolution.

If the electron probe is scanned over the specimen and a narrow slit (followed by a single-channel electron detector) used in the spectrum plane, an *energy-filtered* STEM image is obtained. If a parallel recording detector is used to record an entire spectrum at each pixel, a *spectrum-image* of large information content can be recorded for subsequent analysis.

Alternatively, the focusing properties of a magnetic spectrometer can be exploited to form an energy-filtered (EFTEM) image from a stationary and broadly-focused incident beam. The spectrometer (followed by magnifying lenses) may be mounted below the TEM (as in the Gatan GIF system; Fig. 1) or built into the TEM imaging system (as in the LEO omega filter).

Figure 2 shows a simplified energy-loss spectrum. For very thin specimens, the most prominent feature is the zero-loss peak (area I_0, representing purely *elastic* scattering). The plasmon peak, due to *inelastic* scattering by outer-shell (valence) electrons in the specimen, is centered around a plasmon energy E_p, generally in the range 10 - 30 eV. Plural scattering of the transmitted electrons gives rise to additional peaks, at multiples of E_p. Allowing for such multiple scattering, the total inelastic intensity I_p in the low-loss region (up to about 100 eV) is given by: $t = \lambda\, ln[(I_p+I_0)/I_0]$, which enables the specimen thickness t to be measured in terms of a plasmon mean free path λ (typically 100-200 nm for 200kV accelerating voltage). With some computer processing, the low-loss spectrum can yield an absolute value of thickness [1].

At higher energy loss, ionization edges occur due to inelastic excitation of inner-shell (*core*) electrons. They are superimposed on a falling background representing the tail of lower-loss inelastic processes, which usually approximates to a power law: AE^{-r} where A and r are constants within a limited range of energy loss E. The threshold energy of each edge is the binding energy of the corresponding atomic shell and is tabulated for all elements and electron shells (K, L, M, etc.), allowing elements present in the specimen to be identified.

Elemental quantification is achieved by integrating the spectral intensity over an energy range Δ (typically 50 - 100 eV) above the threshold. The pre-edge background is fitted to a power law in order to subtract a background integral and obtain core-loss intensity I_c. The amount of each element (N atoms per unit area) is given by: $I_c = N (I_0+I_p) \sigma_c$, where σ_c is a core-loss cross section obtained by calculation [2,3] or from experiment using a standard specimen [4].

The energy-loss spectrum also contains *fine structure*, in the form of intensity oscillations or local peaks. A peak around 6 eV arises from π-electron excitation in an unsaturated organic compound, and is an indication of double bonding. Fading of this peak can be used as a measure of radiation damage due to bond scission [5].

Energy-loss *near-edge* structure (ELNES), in the form of pronounced peaks just above an ionization-edge threshold, can be related to chemical bonding or electronic band structure (density of states). For example, *white-line* peaks occur at the L_2 and L_3 edges of transition metals and the M_4 and M_5 edges of rare earths, due to the excitation of core electrons to a high density of d- or f- states located just above the Fermi level. The L_3/L_2 or M_5/M_4 intensity ratio has been found to be an indication of the *oxidation state* of the metal [6]. *Extended* energy-loss fine structure (EXELFS), a weaker intensity modulation starting at 50 eV or more from the ionization edge, can be analyzed to give the distance of nearest-neighbor atoms.

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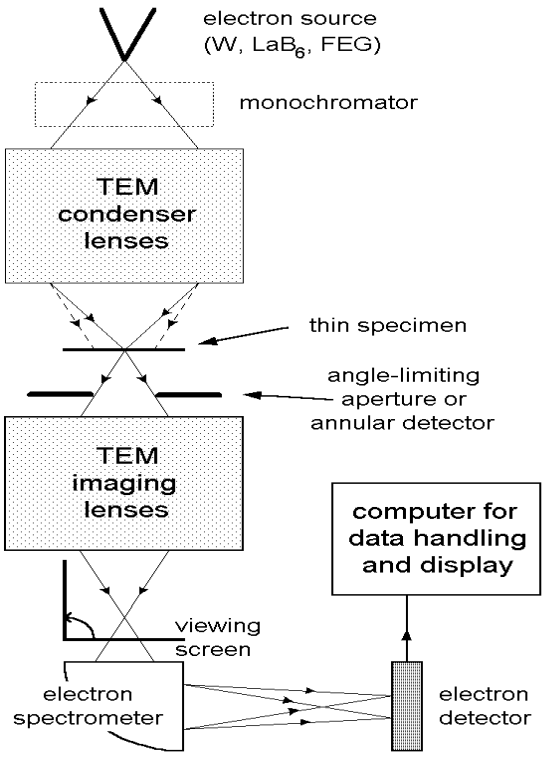

FIG. 1. Schematic of a spectrometer system for recording energy-loss spectra and energy filtered images. Electron paths are arrowed.

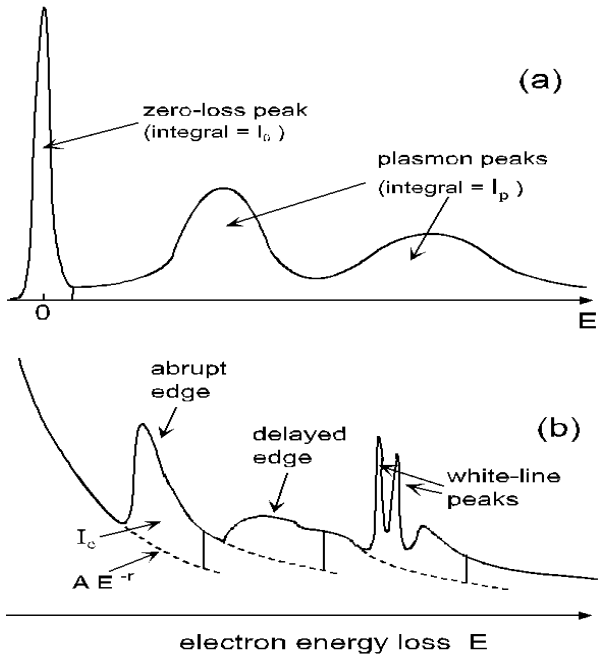

FIG. 2. (a) Low-loss spectrum and (b) the core-loss region (recorded with higher detector sensitivity) showing several basic shapes of ionization edge, each superimposed on a spectral background (dashed curves).

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