Electron Energy Loss spectroscopy in Microchemical analysis

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Introduction

Study of materials has reached advanced levels since a few decades. This has been made plausible due to the rapid advances in the modern technology and its impact on the instrumental developments. On such manifestation is the ability of electron microscope to study ultra structure, identify the phases and simultaneously yield information on its composition. Although electron diffraction and imaging are conventionally employed together in transmission electron microscopy, Analytical Electron Microscope (AEM) enables us in elemental analysis using Energy Dispersive Xray analysis (EDXS) and electron energy loss spectroscopy (EELS). Besides, the ability to form fine electron probe can give crystallographic information through Convergent Electron Beam Diffraction (CBED). As far as, analytical information from sub micron levels is concerned, EDXS and EELS complement each other.

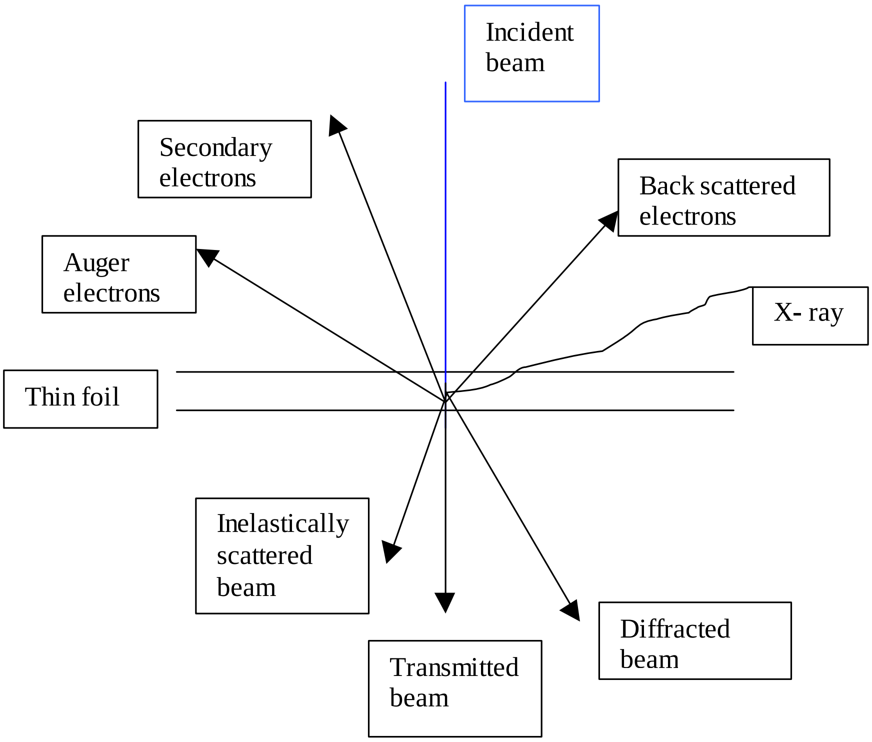


Fig.1 Signals arising from high energy electron interacting with a thin foil

Consider the electron beam interaction with a thin foil. Electron beam interaction may be elastic or inelastic in nature. As a result a number of signals are generated (Fig.1). It is the inelastic scattering that results in energy loss is of importance for EELS. In other words, the primary beam energy loss is being studied. The transmitted beam is directed into a spectrometer which separates the electrons according to their kinetic energy and produces an electron loss spectrum showing the scattered intensity as a function of the decrease in kinetic energy of the fast electron. A typical spectrum is shown in Fig.2.

A typical EELS spectrum will have three regions:

I)Zero loss peak (ZLP);II) Low loss and III) core loss edges

Zero loss peak represents the elastic scattering signal.

Region II – Low loss- specifically representd by Plasmon loss. This arises from outer shell inelastic scattering which may involve many atoms leading to collective effect called **Plasma resonance**. This creates a pseudo particle called Plasmon whose energy is given as e**p** = h*Wp, where Wp is plasmon frequency which is proportional to square root of valence electron density. e**p** for metals is usually 5-30eV.

Core loss edges occur as a result of removal of electrons from the core of the atom resulting in energy losses which would be seen as edges in the spectrum. Since it is characteristic of the atom, these edges are used in elemental analysis. Fig.3 depicts the physics of the energy loss processes. Fig.3 a shows the signal for EELS, Fig.3b the low loss due to plasmon and Fig.3c, the core loss.

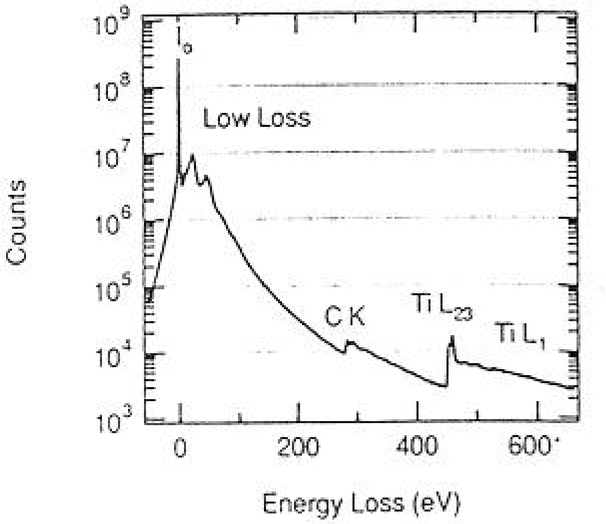


Fig.2 shows the three regions of an electron energy loss spectrum

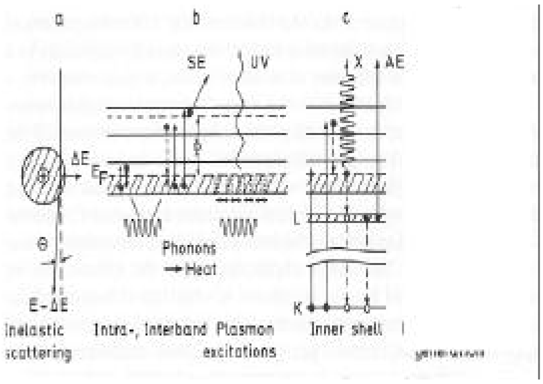


Fig.3 The physics of the different energy loss process

Use of Plasmon loss

1) Thickness (t) of the sample can be measured by relating to mean free path (λ) of the electron in the material as:

$$\boxed{t / \lambda = \ln (I/I_o)}$$

where Io is the intensity of Zero Loss peak (ZLP)

I is the intensity upto selected energy width

2) Application to determine the phase diagram

Alloying additions lead to outer shell electron density changes. Since the plasmon losses are proportional to outer shell electron density, it can be used to determine the phase diagram.

Plasmon losses (e**p)** varies as a function of composition (**Ci)**:

$$\boxed{e_p(c_i) = e_p(o) + C_i \, (d\, e_p / d\, C_i)}$$

where e**p(o)** is the plasmon loss for pure element

A typical example is Al-Mg phase diagram. The Plasmon loss corresponding to pure Al decreases linearly as Mg is added with in single phase. On the other hand, the plasmon loss in a two phase region exhibits two losses –one corresponding to either phase extremes. Thus the study of Plasmon loss helps in determination of Phase boundary.

Core loss region:

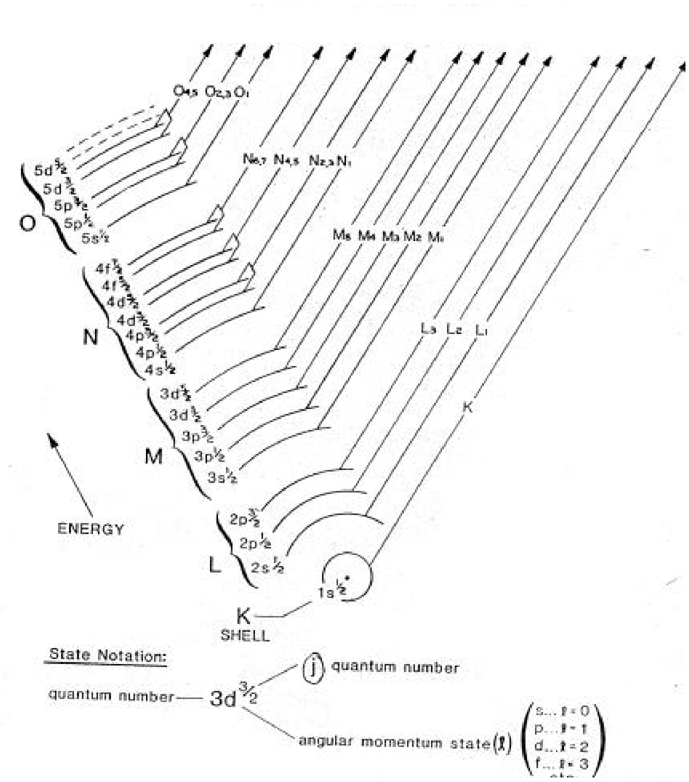


Fig.4

When electron beam interacts with material, Core electrons from sub shells are knocked to continuum. The energy loss associated with such process lead to K, L, M, N edges. These edges have different shapes. The edges can be used in elemental analysis.Fig.4 shows the different edges and their notation. Depending on the J quantum number (J=l+s), the notations are assigned.

Atoms get ionised by electron beam when energy of the electron is greater than the E_k. The intensity of the edges is given by

$$\boxed{I_E = Io.N.\sigma.\eta}$$

Where

I_E represents the intensity of the edge

Io is intensity of ZLP

N no of atoms in irradiated volume

σ.Partial ionisation cross section

η Efficiency factor

Cross section

It represents the probability of an event.

$\boxed{\sigma_{total} = \sigma_{elastic} + \sigma_{ineleastic}}$

The angular dependance of the cross section is given as a differential, $d\sigma/d\Omega$

The cross section is a function of electron beam energy and scattering angle.

Efficiency

1) Collection efficiency depends on the collection angle. The objective aperture determines the collection angle. The high collection angle gives very good intensity while the spatial resolution comes down. In order to improve the spatial resolution, optimum collection angle is chosen.

2) Detection efficiency depends on the detector. Photo Diode arrays (PDA) can read billions of electrons in seconds. Their Detector Quantum Efficiency (DQE) is improved if one operates the microscope with beam in near saturated condition.

Shapes of the edges: The elemental edges in EELS spectra can be either saw tooth like or with a delayed maximum.

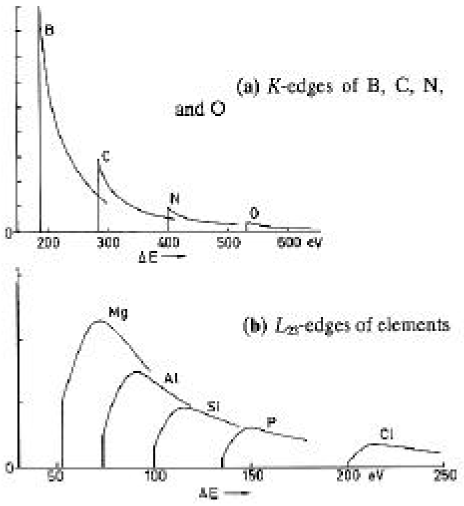


Fig.5 shows examples of spectra.

It can be noted that the edges from K shell are saw-tooth like while those from L, M shell will have a delayed maxima. This can be ascribed to the shape of the shells namely spherical nature of K shells and non-spherical nature of L, M etc. respectively.

For elemental analysis, K edges are used for Li to Si; for Al to Ar $L_{2,3}$ edges are used; for K to Cu white lines can be used and for Cu to Br the L,M edges

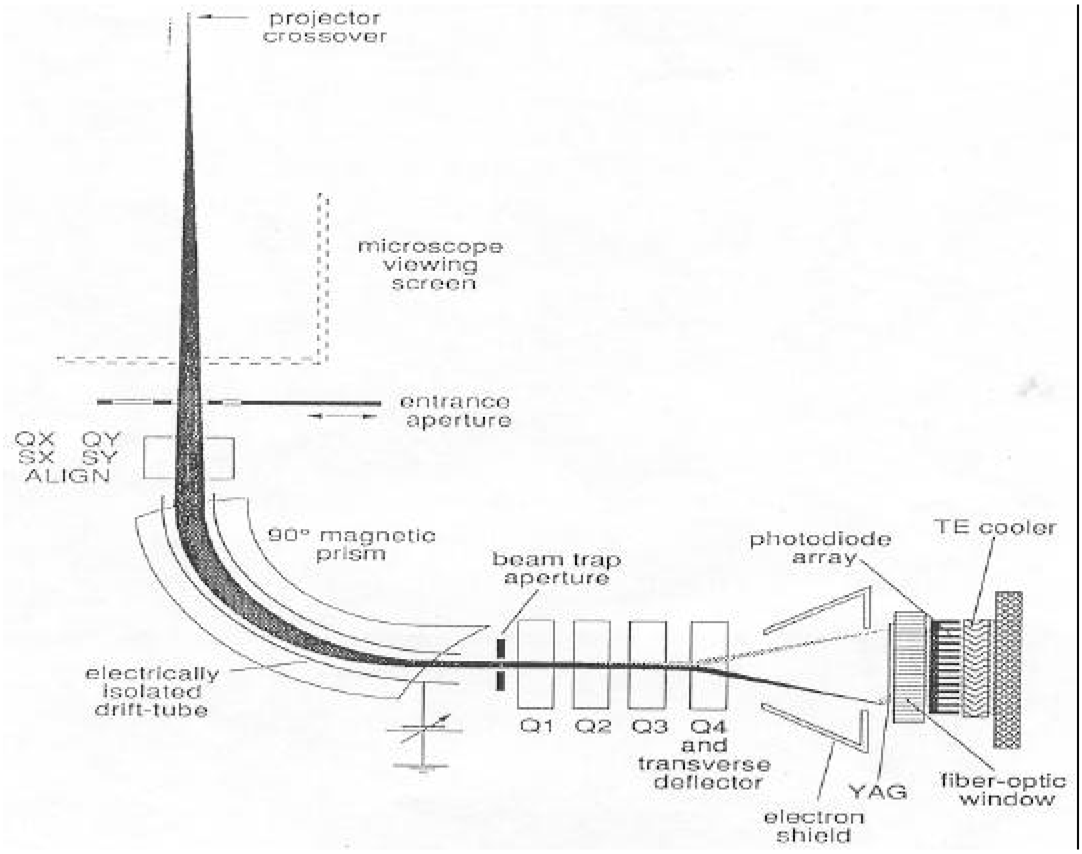


Fig.6. The various components of the PEELS spectrometer

The spectrometer is attached below the microscope column. The main component of the spectrometer is the magnetic prism which collects the electron beam which is composed of electrons that have experienced different energy losses, and bends and disperses them onto the detector. The electron beam first falls on to the scintillator which is basically YAG crystal. The photons generated in the crystal will be directed by fiber optical coupling to photodiode arrays (1024 arrays). The spectrum is read out as pulses and the height of the pulse represent the electron intensity. The signal is fed to multichannel analyser.

Calibration and conditioning of the spectrometer

Dark current calibration

With no beam on the detector, a signal has to be recorded. This signal arises from charge leakage and statistical noise. The dark current recorded will have to be subtracted from the spectrum. Cooling the detector reduces the dark current.

Spectrometer spectrum

With no specimen in the beam, the spectrometer spectrum can be recorded. This arises out of the electron backscattering occurring from the aperture in front of the detector. This also can be subtracted from the spectrum of our interest.

Channel to channel variation

Each of the 1024 diodes will respond differently due to elemental size, quality of optical coupling. This leads to channel to channel variation in gain. This can be observed by spreading the zero loss peak over the complete array. This is called flat fielding and it will give a useful measure of channel to channel variation.

Energy calibration

This can be carried out using a standard namely NiO. A spectrum may be acquired and the energy corresponding to Ni L_3 should be 855eV with respect to zero loss peak. The O k edge can be checked to confirm the calibration.

Spectrum collection

This can be done in two modes of TEM operation. One is image mode and other one is diffraction mode. In the image mode, the object for the spectrometer is the diffraction pattern and hence it is said that spectrometer is diffraction-coupled. In diffraction mode, it is the other way and spectrometer is called image-coupled.

The collection mode affects the intensity and the spatial resolution of the spectrum. If spatial resolution is our concern, it is better to use diffraction mode. But

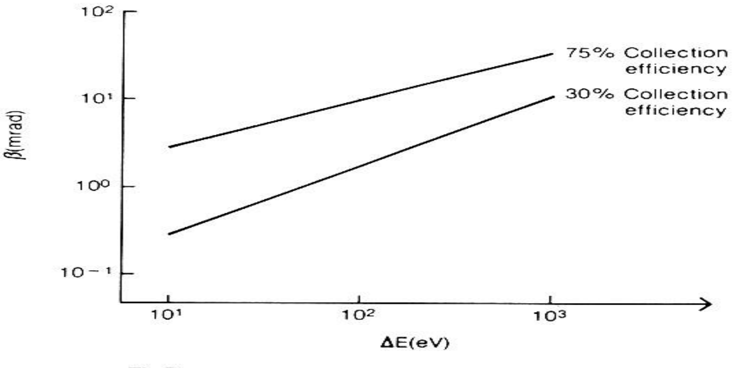


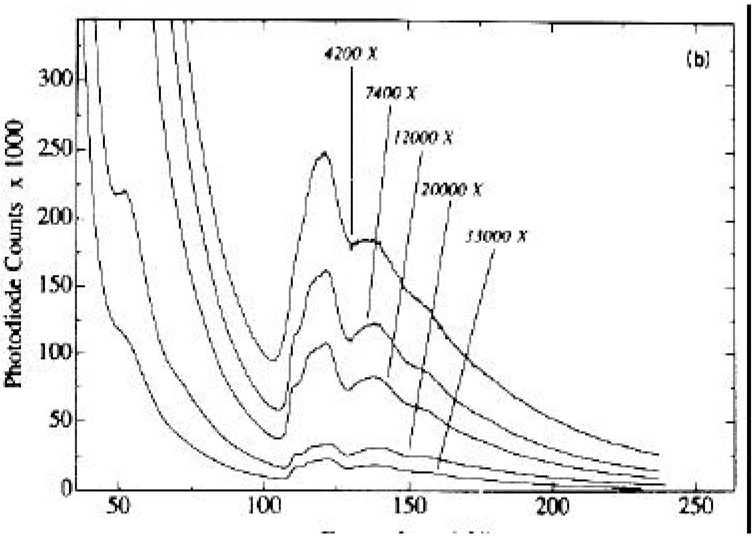
Fig.7 The collection efficiency of the spectrometer as a function of the collection semi angle b and the energy loss of the electron.

NJ).

contamination will be more in this case. Efficiency of collection varies with collection angle (Fig.7). Use of optimum magnification is essential (Fig.8).

Effect of magnification

Increasing magnification will lead to loss of signal intensity and hence optimum magnification is recommended. Fig. 8 shows the variation of signal with magnification.



Energy Loss, eV

Fig.8

It is clear that an optimum magnification is best for good signal to noise ratio. Recording of spectrum can be either serial or parallel since it is faster. Nowadays parallel mode is used.

Storing spectrum

The spectrum can be stored region wise by breaking into two or three ranges and altering the gain of Photo Multiplier Tube.

Processing the spectrum

Background subtraction by suitable models is an essential step. $\boxed{I = AE^{-r}}$

Plural scattering: This is due to thick specimen. It can be identified by checking the intensity of low loss spectrum. If it falls off abruptly, removal by suitable routines is essential.

The microchemical analysis can be done using the equation:

$$\boxed{N_A/N_B = \sigma_B/\sigma_A\,(I_A/I_B)}$$

The partial cross section for each element is to be determined under the same experimental conditions. To do this, we have to use standard elements and acquire spectrum:

As we know N, the No of atoms = thickness *density/mass, We can calculate cross section using the equation: $\boxed{I_A = N_A\,\sigma_A.I_o}$

Theoretical calculation of cross section is possible by computer programs like SIGMAK and SIGMAL. These routines are available nowadays and one can use them to get rapid identification.

Other EELS based techniques for microchemical analysis based structural studies:

1) Energy Loss Near Edge fine Structure (ELNES)- fine peaks around (<50eV) edges

2) Extended Energy loss Fine Structure (EXELFS) – fine peaks around (<200eV) edges

3) Energy Filtered Transmission Electron Microscopy (EFTEM) / Electron Spectroscopic Imaging (ESI) - improving image contrast by filtering inelas.scattered electrons.

Summary

A brief introduction on the physics of the electron energy loss was dealt. The different regions of the spectrum identified and their application discussed. Instrumentation and calibration of the spectrometer for the elemental analysis method were discussed and the required cross section determination briefly reviewed.

References

1) Electron Energy Loss Spectroscopy in Electron Microscope- R.F.Egerton

2) Transmission Electron Energy Loss in Materials Science - C.C.Ahn & B.Fultz.