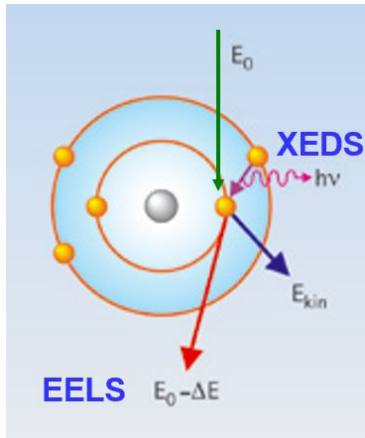# Microanalysis in the Electron Microscope

(XEDS SDD - JEM-ARM200CF; XEDS Si(Li)- JEM-3010, JSM-6320F, S-3000N, EELS - JEM-ARM200CF)

*< Schematic of the electron/specimen interaction*

The interaction of the electron beam with the atoms in the sample can give result in the ionization of the atom (creation of an inner shell vacancy). Energy is transferred from the incident electron beam to an inner shell electron that is ejected from the atom (secondary electron) and the incident electron suffers an energy loss (EELS). The ionized atom can lose energy in a number of ways, one of which is for an outer shell electron to jump into the vacant inner shell, losing the excess energy in the form of a X-ray photon (XEDS) characteristic of the element and the energy difference between original and final shells.

X-Ray Energy Dispersive Spectroscopy (XEDS)

Chemical analysis using X-ray spectrometry has been available in electron beam instruments since the 1950's. The first X-ray detector used in an electron microscope was the wavelength dispersive spectrometer (XWDS). Although this has excellent wavelength resolution, the wavelength ranges for each detecting crystal were restrictive and only one wavelength could be analyzed at a time making it a time consuming process. Originally found only on electron microprobes, where they are still used in conjunction with XEDS, they were also tried on TEMs during the 1960s. However, it was the development of the first energy dispersive spectrometers in the late 1960s which revolutionized microanalysis.

There are two main types of XEDS detector used on electron microscopes. Since the 1970s Lithium Drifted Silicon (Si(Li)) detectors have been used although now largely replaced by Silicon Drift Detectors (SDD) which have a number of advantages including not needing liquid nitrogen to keep the detector cold.
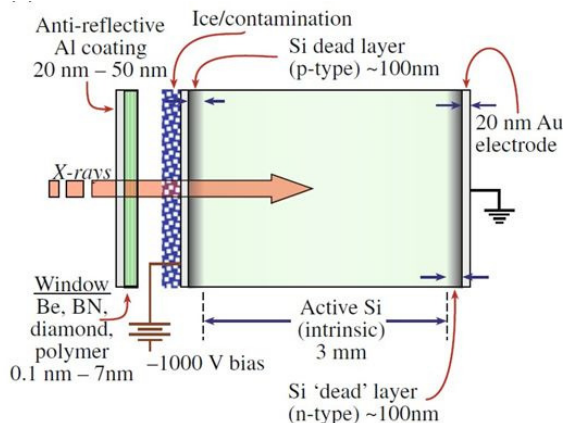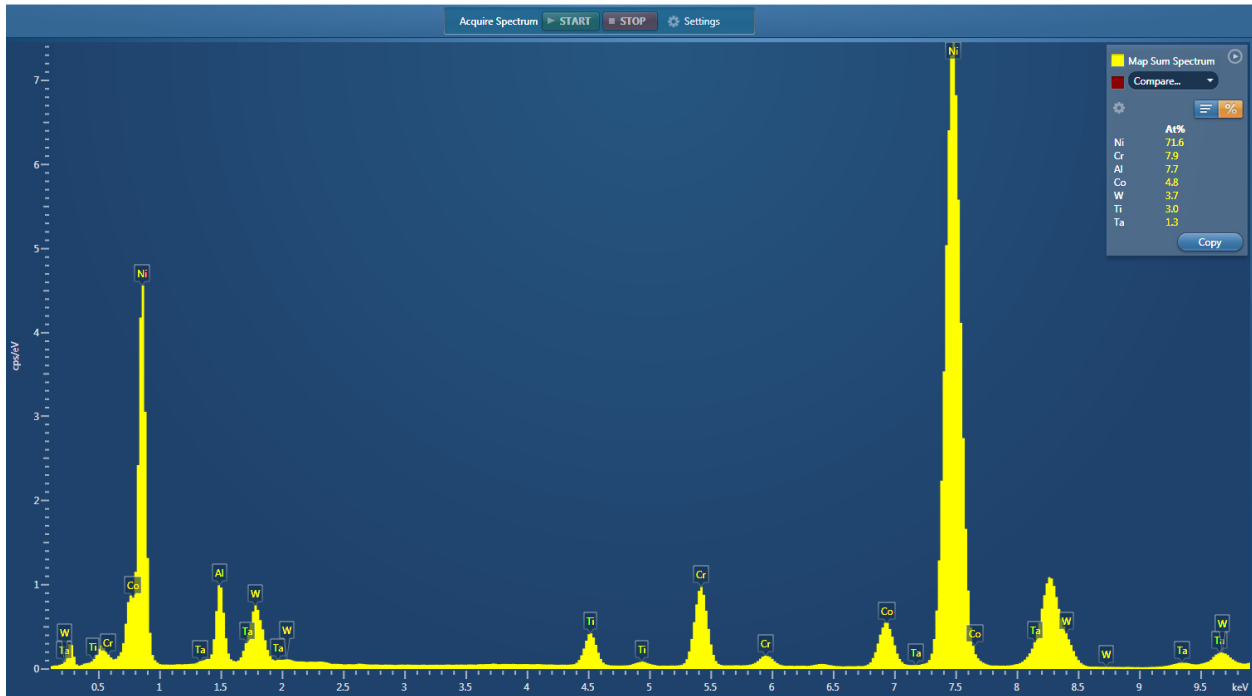

< Schematic of a Si(Li) X-ray detector

The Si(Li) XEDS detector was developed in the late 1960s. The typical detector consists of a single crystal of silicon up to 40mm^2 in size and 3mm thick and is doped with lithium. When X-rays deposit energy in a semiconductor electrons are transferred from the valence band to conduction band leading to the formation of electron-hole pairs. Each electron hole pair takes ~3.8eV of energy to form so a typical X-ray will generate several hundreds to thousands. These are swept away by the applied bias (on gold contact layers either side of the detector) to form a charge pulse. This pulse is converted to a voltage pulse by a preamplifier and this signal is further amplified and shaped by a pulse processor before being displayed on a histogram of intensity against energy. The detector and preamplifier are held at liquid nitrogen temperatures and have to be isolated from the microscope vacuum, to prevent icing. Originally a thin beryllium window was used which significantly absorbed all X-rays below about 1KeV but modern

detectors have an atmospheric thin window (ATW) made from a number of materials which allows X-rays down to boron to be detected. In STEM mode XEDS maps and linescans can be acquired.

The XEDS spectrum obtained consists of a number of discrete peaks, characteristic of specific energy transitions in elements. These are superimposed on a continuous background caused by the incident electrons being elastically scattered by the nuclei in the specimen and emitting electromagnetic radiation - this is known as *Bremsstrahlung* radiation (German for braking radiation). The background is more noticeable in the SEM where all electrons are stopped in the specimen.

XEDS spectrum from a Ni based superalloy showing the characteristic peaks of the elements in the specimen (ARM200CF 200keV)
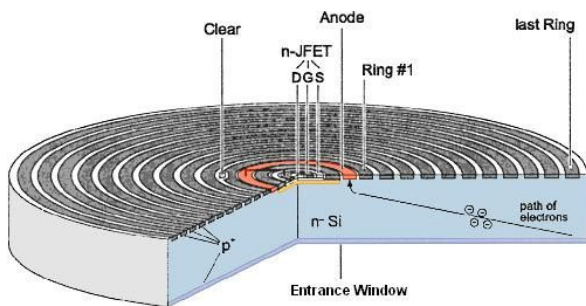

< Schematic of a SDD X-ray detector

The Silicon Drift Detector (SDD) detector was developed in the 1990s and consists of high purity Si, in which a transverse electric field is generated by a series of ring electrodes. The detector is thinner than Si(Li) and the size of the anode is small in comparison with the entrance contact. This results in lower capacitance and lower voltage noise, which allows shorter time constants minimizing the effect of leakage current, allowing Peltier cooling to be used instead of liquid nitrogen. The detector has faster readout and can handle higher count rates than Si(Li) detectors. The process of conversion of the X-ray pulse is the same as in a Si(Li) detector. As it no longer requires cryogenic cooling multiple detectors can be mounted on the same chip and larger detector sizes are possible. The JEM-ARM200CF has the prototype $100mm^2$ windowless Oxford X-max100TLE SDD detector. This third generation SDD detector was designed to give the largest possible solid angle in the confined space of the ultra high resolution pole piece on the ARM200CF by optimizing the detector shape. Count rates of 7x those of a standard X-Max80 detector are collected at Ni Kα and 16x at Ni Lα due to the removal of the window.

The main advantage of the XEDS detector is its ability to look at all X-ray energies at once. Its disadvantages are that the energy resolution of the peaks is poor (>100eV) which reduces the peak to background and increases the minimum detectability, and the spectrum can obtain artifacts from the collection process. Si(Li) detectors also cannot handle high count rates without significant pulse pile up, although this is not a problem with SDD detectors.
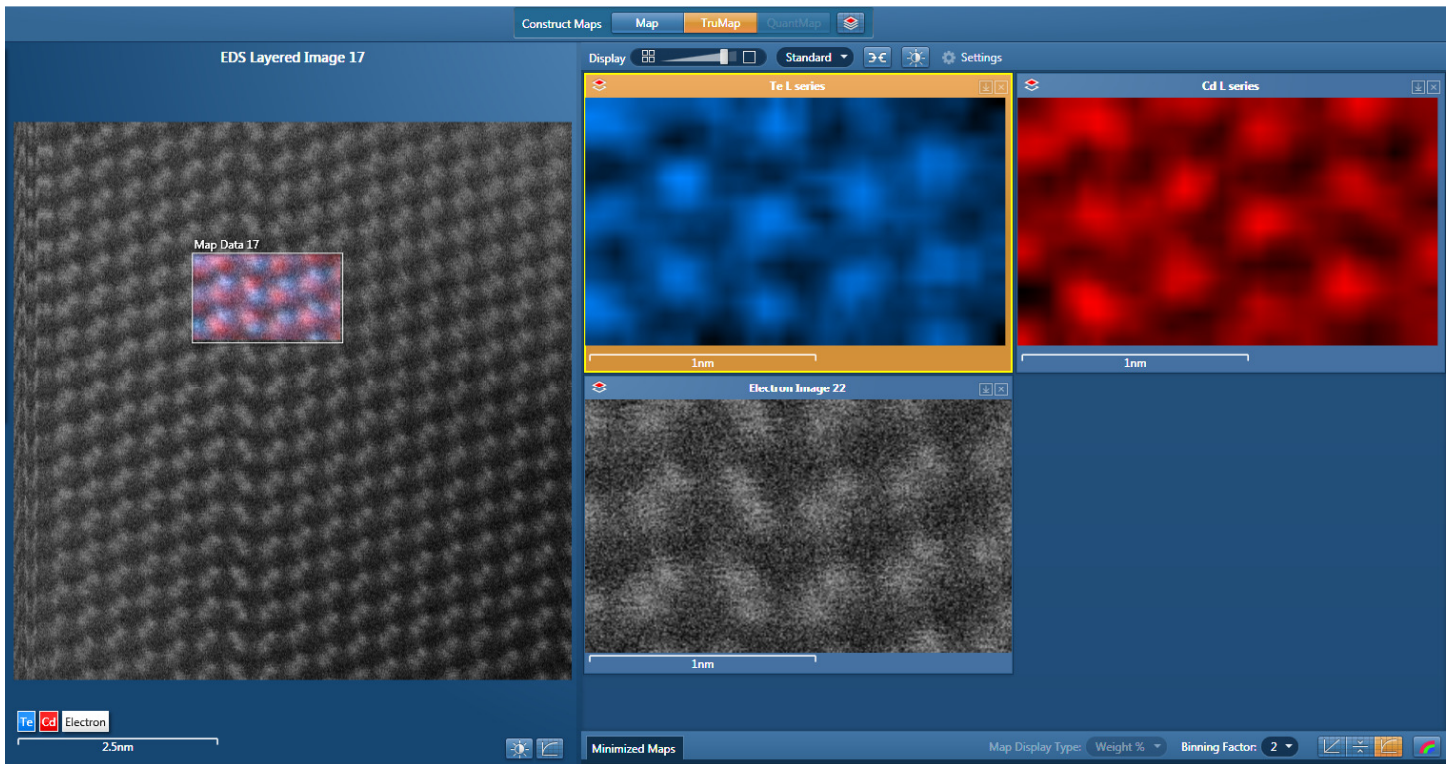
Atomic resolution XEDS map of twins in a CdTe specimen (ARM200CF 200keV STEM 0.1nm probe)

## Electron Energy Loss Spectroscopy (EELS)
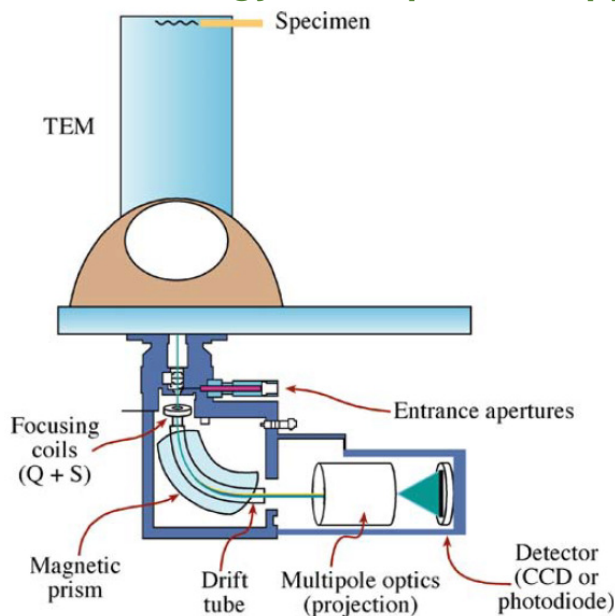
The Gatan EELS detector consists of a magnetic sector. When an electron travels through a uniform magnetic field perpendicular to its travel, its path is constrained by its velocity (energy). Hence electrons of different energies are focused at different positions on a focusing plane. There are a number of different detectors that can be used. In our instrument the electrons are focused onto a CCD array, and this is read out and displayed as a histogram of intensity against energy lost.

< Schematic of major components in an EELS spectrometer

The resolution of the information in the EELS spectrum can be better than 1eV, and depends on electron source type and current. The spectrum can give information about both composition and the electronic state of the atom; however detectability is poor as the edges are superimposed on a rapidly sloping background, and errors in quantification are greater than for X-ray analysis. EELS mapping at atomic resolution is possible in STEM mode.

The full EELS spectrum consists of a number of features:
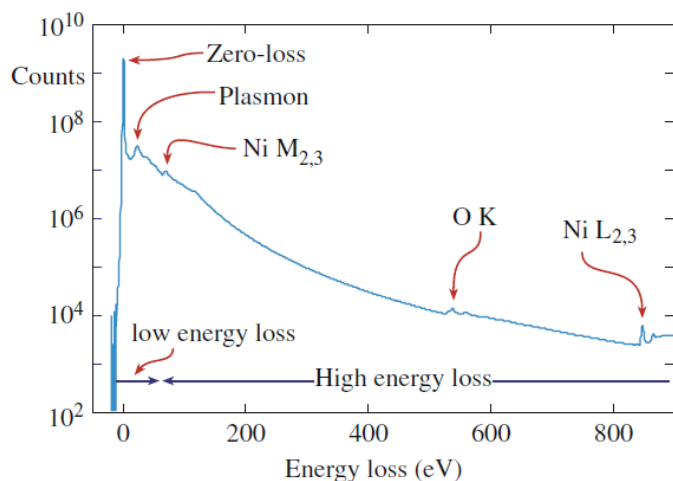
1. A zero-loss peak representing electrons that have not interacted with the specimen or been scattered elastically.
2. One or more peaks below 50eV, which represent inelastic scattering by outer-shell (valence or conduction band) electrons in the specimen. This can take the form of a collective oscillation of many outer shell electrons known as a Plasmon oscillation.
3. A rapidly decaying background, which at any energy, arises from all ionization events (Plasmon and characteristic) occuring before that energy.
4. Inelastic excitation of inner-shell electrons, which gives rise to an abrupt increase in electron intensity (an ionization edge) at an energy loss equal to the inner-shell ionization energy. However, unlike the XEDS case, these are not sharp peaks and the incident electron lose any energy from the ionization energy up to the accelerating energy. Beyond each ionization threshold, the spectral intensity decays more gradually towards the extrapolated pre-edge energy.

Due to the large dynamic range of the spectrum it is normal to look at a smaller energy range of interest (e.g 480-700eV for the MnO example below).
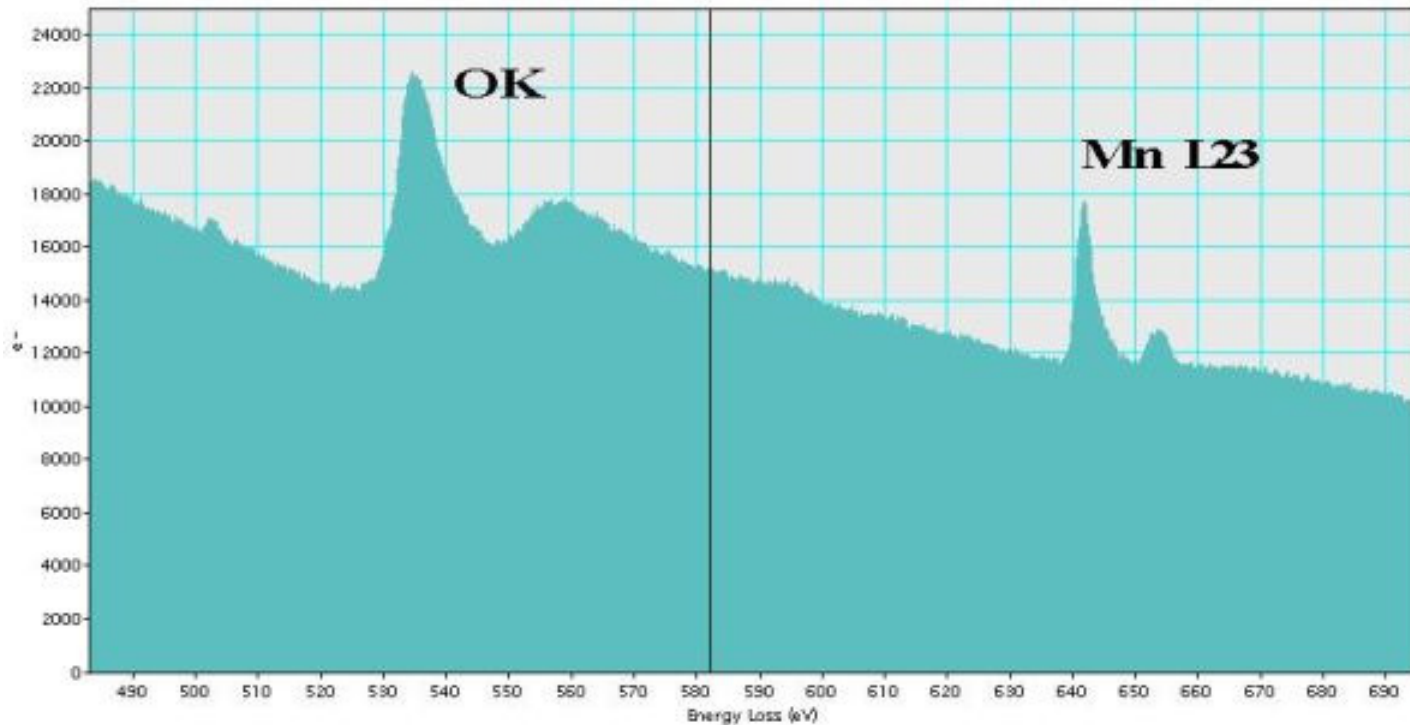
EELS spectrum from manganese oxide showing the edges from O K and Mn L23 superimposed on a sloping background