Transmission Electron Microscopes

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Chapter 1 – The transmission electron microscope

No other scientific instrument can offer such broad range of characterization techniques with such high spatial and analytical resolution, coupled with a completely quantitative understanding of the various techniques. In TEM, your specimen is usually in focus from the top to the bottom surfaces at the same time, independent of its topography, so long as it's electron transparent.

The resolution-limiting factor in light microscope is the wavelength, this doesn't apply to electrons - here other limiting factors play their part, as imperfect lenses. An integral part of any electron microscope plays electron intensity as light intensity. Good to remember is that the unit *V* is used for the accelerating voltage of the microscope, and *eV* refers to the energy of electrons in the microscope. Smaller apertures are the ones that give better depth of focus and depth of field.

Electrons are one type of ionization radiation, i.e. radiation that can remove core electron from their atoms by transferring some of its energy. One of the advantages of using ionizing radiation is that
it produces a wide range of secondary signals from the specimen.
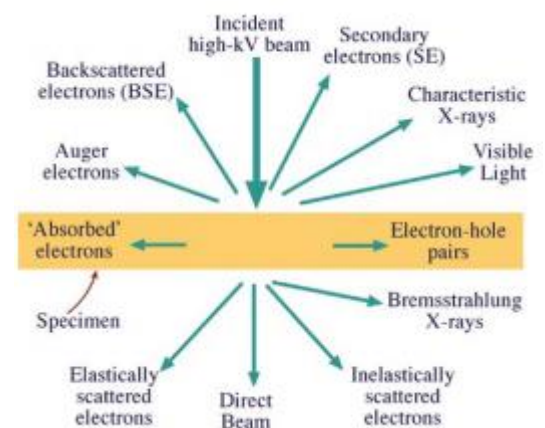
Limitations

With a high-resolution imaging technique you can only look at a small part of your specimen at any one time. The higher the resolution, the worse the sampling abilities. TEM also presents us with 2D images of 3D specimens, and have no depth sensitivity - it's hard to interpret the images. Use a sequence of images taken at different tilts to create a 3D image. Also, ionizing radiation can damage your specimen, particularly polymers. Under about 100 keV, we cannot ignore relativistic effects.

Chapter 2 – Scattering and diffraction

We cannot see anything in electronic microscopes unless the specimen interacts with and scatters the electrons in some way. In the TEM we are usually most interested in electrons that don't deviate far from the incident-electron direction. Other forms of scattering, *BE* (backscattered electrons) and *SE* (secondary electrons ejected from the specimen) are also of interest – but mostly in SEM. However they scatter, the end result is a non-uniform distribution of electrons emerging from the exit surface of the specimen. Scattering can be divided in different ways:

- **Elastic/in-elastic scattering**. This describes scattering that results in no loss of energy or in some measurably loss of energy.
- **Coherent/incoherent** which refers to their wave nature. Elastically electrons are usually coherent and inelastic incoherent. *Coherent* = essentially in phase with another and of a fixed wavelength.

- **Forward/ back scattering**. Refer to the angle of scattering with respect to the incident beam and the specimen that in normal to the beam. *Forward scattered* = scattered through <90˚.

As the specimen gets thicker, fewer electrons are forward scattered and more are backscattered. From bulk, only backscattered incoherent electrons are the remnants from the incident beam. Electrons can be scattered more than once, losing energy on the way.
- *Single scattering* – Approximately all scattering in a TEM if the specimen is very thin.
- *Plural scattering* – electrons scattered more than once.
- *Multiple scattering* – electrons scattered < 20 times. The greater the number of scattering events, the more difficult to interpret the images.
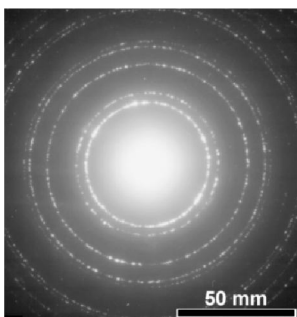
Cross section – determines the chance of a particular electron undergoing any kind of interaction with an atom. Each possible interaction has a different cross section which depends on the energy of the particle. The larger the cross section, the better the chances of scattering. It does not represent a physical area but when divided by the actual area of the atom it represents a probability that a scattering event will occur. Elastic cross sections for transition metals bombarded by 100 keV electrons are ~10^{-22} m^2, and elastic cross sections generally smaller and range from ~10^{-22} m^2 -~10^{-26} m^2.

Mean free path – average distance that the electron travels between scattering events. If we know this, we can decide how thin to make our specimen so plural scattering won't be significant.
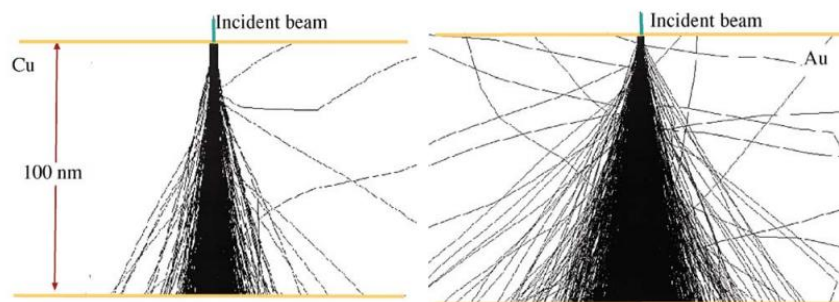
The scattering angle and the amount of BE increases with atomic number. Also, high-density regions scatter more than low-density regions. You can control the cross section through the acceleration voltage (i.e. the electron energy) – higher energy decreases the total cross section, thus higher acceleration gives less scattering.

Diffraction pattern – Forms in some of the TEM detectors as a way of describing the incoming waves as they encounter the crystal structures of the specimen. The pattern forms in the back focal plane of the objective lens in TEM. From these, you can tell a lot about the structures. In a DP, distances on the film correspond to angles of scatter as the specimen. The angular spacing of the features in the diffraction pattern is inversely proportional to the dimensions of the object causing the diffraction.


Crystalline diffraction pattern

A *selected area diffraction* aperture (*SAD*) in the image plane is used to select the diffracted region of the specimen.

Powder diffraction pattern

Chapter 3 – Elastic scattering

The elastically scattered electrons are the major source of contrast in TEM images. Scattering can occur either as a result of electrons interacting with the negatively charged electron cloud (small angular deviation) or by attraction toward the positive nucleus (much larger scattering angles). The intensity of the low-angle scattering is strongly affected by the arrangement of the specimen atoms and is referred to as *diffraction* (here we look at electrons as waves). The atomic number Z of the atom controls the elastic interaction with the nucleus, but the electron-electron scattering is more a function of the incident-beam energy.
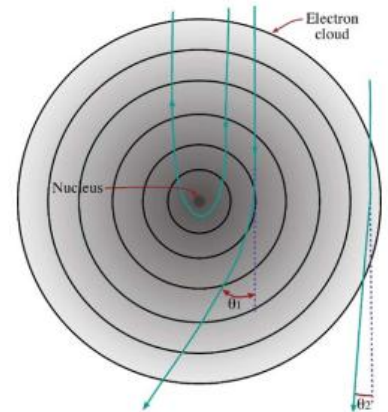
The cross section cannot be calculates exactly as long as we ignore the wave nature of the electron beam. A good approach of waves to cross sections is the concept of the *atomic-scattering* factor $f(\theta)$. It's a measure of the amplitude of an electron wave, and $|f(\theta)|^2$ is proportional to the scattered intensity. The factor depends on the electron wavelength λ, the angle θ (0° for the incident-beam direction) and the atomic number Z. It decreases with increasing θ, decreases with decreasing λ and increases with Z. Both the differential cross section and the scattering factor simply are measures of how the electron-scattering intensity varies with θ.

$f(\theta)$ is for individual atoms scattering electrons, what happens when a lot of electrons are stacked together in a crystal structure? The structure factor $F(f(\theta))$ is a measure of the amplitude scattered by a unit cell of a crystal structure. It's defined as the sum of the $f(\theta)$ terms from all the *i* atoms in the unit cell multiplied with a phase factor. It's influenced by type of atom ($f(\theta)$)m the position of the atom in the cell (*x,y,z*) and the specific atomic planes (*hkl*).

Chapter 4 – Inelastic scattering and beam damage

Unlike elastic scattering, in inelastic scattering the electrons loose energy. This generates a whole range of signals that gives information about the specimen, and in addition of the electrons themselves are the characteristic X-rays, secondary electrons (*SE*) and sometimes visible light. One downside with inelastic scattering is that it deposits energy in the specimen which can be damaged if it's beam sensitive.

Because some of the incident-beam electrons lose energy, these signals are related to the general topic of electron energy-loss spectrometry (*EELS*). These signals in company with the x-ray signals constitute analytical electron microscopy (*AEM*).

When a high-energy electron encounters an atom it penetrates the outer more loosely bound electron cloud and then passes the more tightly bound core shell electrons and finally may encounter the nucleus. The deeper the electron penetrated into the atom, the greater the energy that may be lost. It's very rare that the electron loses all its energy in a single nuclear interaction. We can separate the inelastic processes into three components:

1. Those that generate X-rays
2. Those that generate secondary electrons
3. Those that result from collective interactions with many atoms or electrons

X-rays

From X-rays we can quickly find out what elements that constitutes the interacting part of the specimen. We can also quantify the amount of each element.

1. *Characteristic X-rays* – useful for local elemental analysis of nano-structured materials and crystal defects –XEDS (see chapter 32).
2. *Bremsstrahlung X-rays* – useful to the biologist, but generally regarded as a nuisance by most materials scientists.

Characteristic X-rays

If more than a critical amount of energy is transferred by the initial beam to an inner-shell electron, it ejects and leaves a hole in the inner shell. The ionized atom can return to its lower energy state but filling that hole with an electron from an outer shell, accompanied by emission of an X-ray or an Auger electron (the energy of the emission is characteristic for the energy difference between the shells – unique to the atom). *XEDS* is the analysis of these generated when beam it's the specimen, and provides elemental information (chapter 32).

These shells start with the lowest energy shell K, the next innermost is the L-shell and so on. All the shells except the K-shell have subshells. We only consider bigger significant energy jumps, i.e. those to K-, L- and M-shells. A family is a group of X-ray lines and each member of the family has a different relative intensity. The differences in energy increase with increasing Z.

An ionized atom does not have to lose energy by giving off a characteristic X-ray, it can emit an Auger electron instead. The probability of X-ray versus Auger emission is described by the *fluorescence yield*. The best way to analyze light elements is EELS (se later chapter) because we can always detect the energy-loss electron whether or not it has generated an X-ray (making it better than XEDS).

Bremsstrahlung X-rays

Electrons penetrating all the way to the atom nucleus can interact with the charge field, suffering a change in momentum. During this, it may emit an X-ray called *bremsstrahlung* which energy can differ all the way up to the beam energy though it's usually quite small. It is also highly anisotropic, showing strong forwards scattering which increases as the beam energy increases. The intensity depends on the average Z and is therefore of interest to biologists. The bremsstrahlung has a continuous energy spectrum as the background in XEDS on which the characteristic X-rays are superimposed, have a narrow energy range and appear as sharp peaks.
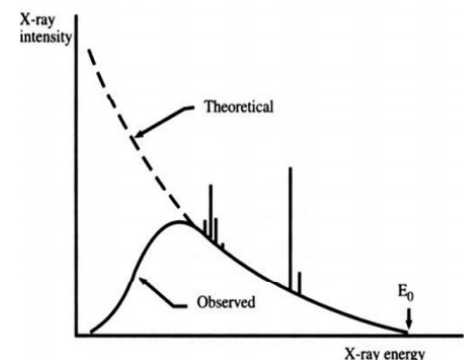

Secondary electrons

Electrons within the specimen that are ejected by the beam electrons. If the electrons are in the valence/conduction band it doesn't take a lot of energy, at most around 50 eV. If they are ejected from an inner shell by the energy released when an ionized atom returns to the ground state, then they are called *Auger electrons*. SE emission is a far less likely process than all the other inelastic processes, but is still useful in the TEM. Because they are weak, they can only escape the specimen if they are close to the surface. While SEs are standard signal in SEM, they can also be used in STEM (where they have better resolution than in SEM). The number of SEs rises to a maximum around 50 eV, and their angular distribution is not important as the detector gathers them with a magnetic field – only the number is important. Tilting the sample gives more SE, and also edges (edge contrast!)

Auger: "A form of SE". An alternative to X-ray emission as an ionized atom returns to its ground state. They have a characteristic energy dependent on the electronic structure of the ionized atom, but so low energies that the ones that do escape come from very close to the surface, containing

chemical information. They are in the energy range of a few hundred eV up to a few keV and strongly absorbed within the specimen.

Backscattered electrons

Not the same as SE, but still used in the same way as SE in SEM, only they travel farther into the specimen and up again and gives more depth of field. Their energy range is typically almost all the way up to the acc. Voltage. The amount of BSE increases with Z. A change of acc. voltage changes especially the depth of travelling, and you get about the same single but better resolution with less BSE. The BSE detector is sensible to composition, surface geometry and angle to detector.
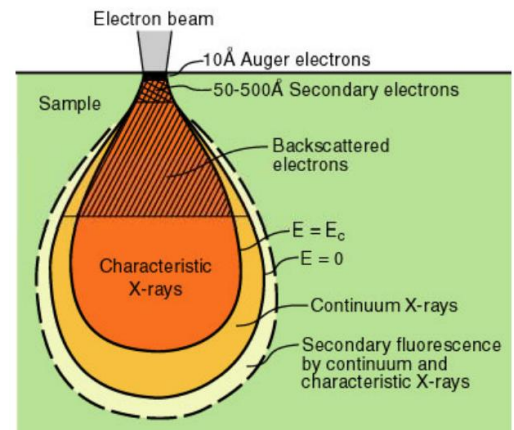
The striped part will make it up to the surface again. SE gives resolution at 1-5 nm, BSE at 100 nm depending on ACC voltage and Z.

Plasmons and phonons

Plasmons – collective longitudinal oscillations of free electrons that occur when a beam electron interacts with the free electron cloud. Energy 15-25 eV forward scattering.

Plasmons are "analogous to sound waves". They create regions of varying electron density. The plasmon process has the largest cross section, making it the by far most common inelastic interaction in materials. Plasmon peaks are also strong features in EEL spectra (see chapter 38). They occur predominantly in metals, especially those with a high free-electron density like aluminum.

Phonons – collective oscillations of atoms in a solid that arise when the atomic lattice is struck by a beam electron. Result in specimen heating, energy loss <0.1 eV but high scattering angle. Phonons can be generated by, except for direct beam on lattice, processes within the atom; the energy of Auger or x-ray emission. They don't carry useful chemical or contrast information about the specimen. Phonon scattering increases with Z and with the temperature. You can reduce the number of phonons by cooling your specimen.

Beam damage

Heating by phonons is worst for thermal conductivity materials.
Radiolysis is the most important damage in light elements, and is the breaking of chemical bonds. Atoms are knocked out of place which increases with beam energy, and sputtering at a bit less energies that displaces atoms.

Chapter 5 – Electron sources

A reliable source of electrons to illuminate the specimen is a very important part of the TEM. Therefore the requirements are many, and we use two different types of source producing the beam:

- *Thermionic* sources is still used in a majority of TEMs
- *Field-emission* sources is best performing

Schottky sources combine the two with both heat and field-emissions.

Thermionic emission

Heat can give the electrons sufficient energy to overcome the natural barrier that prevents them from leaking out form the surface. The only viable thermionic sources are either materials with a high melting point or those with a very low work function ϕ. Before that W filaments were used. Higher heat gives higher current density, but too high temperature shortens the source life through evaporation and/or oxidation -> compromise.
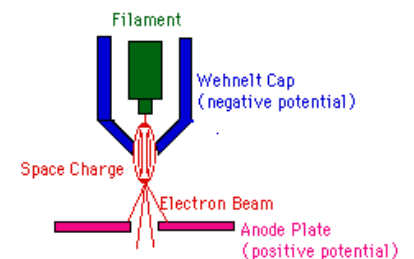
Field emission

Usually called *FEGs* (field-emission guns) and the principle is that the strength of an electric field is considerably increased at sharp points (small areas). A potential at the W needle tip lowers the work-function barrier for electrons to tunnel out of it. Applying high field imposes a severe stress on the tip, it must be mechanically strong to remain intact.

The guns

We need to be able to control the electron beam and direct it, by incorporating the source into a gun acting as a lens.

Thermionic guns - The LaB_6 crystals is used as the cathode, in addition to this is a grid called a *Wehnelt cylinder* (works as an electrostatic lens, focus the beam a bit) and an anode at earth potential with a hole in its center. The crystal is bonded to a metal wire which is resistively heated to cause thermionic emission. When electrons leave the cathode they have a negative potential of the acceleration voltage. The grid is applied with a small bias, as the emission current increases, so do the bias. Work the gun just below the saturation condition (when you can't increase the current any more), otherwise you shortens the source life but too low reduces the intensity too much.

Field emission guns – Much simpler in many ways, here we have a cathode and two anodes. The first is positively charged with respect to the tip which produces the extraction voltage to enable electrons to tunnel out of the tip. The second anode accelerates the electrons. The combined fields act as a refined electrostatic lens to produce a crossover but is not very flexible -> incorporating a magnetic lens gives more control and a larger angle. After a while the tip will have contaminations even in UHV conditions, this can be fixed by *flashing* it, i.e. reversing the potential and blowing off atoms and/or heating it up quickly.

Comparison

Source	Thermionic gun	Field-emission gun
Produces electrons...	...when heated	… when a large electric potential is applied between it and an anode.
Made of	LaB_6 crystals (high melting point, low ϕ). Though susceptible to thermal shock, be careful when heating.	fine W needles (mechanically strong, shaped in very thin needles)
Electron energy	Less monochromatic (gives whiter electrons)	More monochromatic electrons. You don't always need that.
Requirements		Needle surface free from contaminants and oxides -> UHV.
Methods		W at ambient temperatures is called a *cold FE*. At poorer vacuum we need to heat the tip.

You can see in the table beneath that cold FEG has a lot of advantages over Schottky, but is need a very high UHV system to work and actually Schottky are the more popular FEG used. LaB_6 is more useful than W because it has a lower ϕ for which the effect on the current density is dominant. It can also be produces with a very fine tip (smaller cross over size -> much higher current densities and 10 times greater brightness). Still, thermionic guns do not even begin to reach the FEG in many aspects. If you require bright, coherent surface use the FEG.

Cold FEG

+ Extremely small source size of a cold FEG → highly spatially coherent →resulting energy spread smallest available without monochromation.
+ UHV gives a gives cleaner specimen stage and prolongs the life time.
- UHV is expensive and complicated.

Use this if you require high brightness and small probe size.

Schottky FEG

+ Provides greater stability of beam current and lower noise.
+ Heating a tip as in Schottky is better than flashing as it lowers the stress and ensures a longer life.
- Larger source size and larger energy spread .

Use this for routine FEG work as the gun is better, more reliable and easier to operate.

	W	LaB_6	Schottky FEG	Cold FEG
Work function ϕ (eV)	4.5	2.4	3.0	4.5
Operating temp (K)	2700	1700	1700	300
Current density	5	10^2	10^5	10^6
Brightness (100 kV)	10^{10}	$5x10^{11}$	$5x10_{11}$	10^{13}
Emission stability (%7hr)	<1	<1	<1	5
Vacuum (Pa)	10^{-2}	10^{-4}	10^{-6}	10^{-9}
Lifetime (hr)	100	100	>5000	>5000

We don't always want the smallest beam – it loses brightness which is hard at lower magnifications as it loses electrons. In scanning we want it small for high resolution.

Chapter 6 – Lenses, apertures and resolution

The lens is basically used to:
- Take all the rays emanating from a point in an object and recreate a point in an image
- Focus parallel rays to a point in the focal plane of the lens

Often we deliberately limit the collection angle with an aperture. The major limit of lenses is that we cannot make them perfect, they suffer from aberrations. In TEMs, the positions of the lenses are fixed but we can change the strength of the lens at will. An aperture is used to select different electron beams to form different images, thus manipulating the image contrast (to control the divergence or convergence of electron paths through the lenses). Under conditions normally found in the TEM strong lenses magnify less and demagnify more.

The objective lens – the most important lens in a TEM, sitting beneath the sample. It forms the images and DPs that are magnified by the other lenses. It is also most difficult to construct since the specimen must be located close to the plane of this lens. Its size controls the collection angle → it determines the effect of the aberrations →it directly influences the resolution.

A magnetic electron lens is made of two components; a polepiece (magnetic cylinder) which most lenses have two of, the other one is a coil of copper wire which surrounds each polepiece. With a current through the coil, a magnetic field is created in the hole of the polepiece. It is the strength of the field in a magnetic lens that controls the electron trajectories or ray paths. With split polepieces you can make them behave differently from each other, making it possible to produce both the

broad beam for TEM and the fine beam for AEM/STEM. For high resolution, we want to keep the focal length of the objective lens short→needs a very strong lens.

The electron spirals through the lens field: a helical trajectory. For electrons with higher keV, we must use stronger lenses to get similar ray paths. You'll notice it because the image or DP rotates on the display screen as you try and focus/change magnification. When we change the TEM acceleration voltage, we change the lenses in the microscope. Resolution in a real EM is limited by imperfections in the lenses, NOT by electron wavelength.

# Chapter 9 – The instrument

The illumination system

Takes the electrons from the gun and transfers them to the specimen giving either a broad beam or a focused beam. You can use this system in two ways: formation of a parallel electrons beam (almost never truly parallel) or a convergent beam (may be divergent).

Parallel beam – two condenser lenses are adjusted to illuminate the specimen with a parallel beam of electrons. The first one, C1, forms an image of the gun crossover. The original thermionic source cross over may be several micrometers away (and demagnified by an order of magnitude or more). The easiest way to create parallel rays is to weaken the second lens C2 so it becomes under focused and at last about parallel. That or use the upper objective lens to focus the cross over very far away. Here there is usually no need to change C1. A small aperture reduces the electron current reaching your specimen, but also you change decrease the angle of beam convergence, making the beam more parallel.

Convergent beam – if you want to minimize the area of the specimen illuminated you need only to change the C2 lens so it is focused rather than defocused and you form an image of the C1 crossover at the specimen. The intensity will be at its greatest and your contrast will be reduced. Ideally, your specimen should be thin enough that you never have to operate with C2 focused, but sometimes we need to scan the specimen. This is standard for STEM and AEM. The convergent beam is a probe, and we use it also to localize the signals coming from the specimen, as HAADF, XEDS and EELS. With a thermionic gun it's not possible to produce the probe using the C1 and C2 lens. We need to introduce a C3 lens – if the objective lens is split into two polepieces we can make the upper polepiece C1 much stronger and maybe even turn C2 off. It still controls the convergence angle of the beam on the specimen.

A strong C1 lens results in greater demagnification, giving a smaller beam at the surface. A weaker lens gives a broader probe. This also changes the number of electrons that hit the C2 diaphragm and therefore do not contribute to the current hitting the specimen.
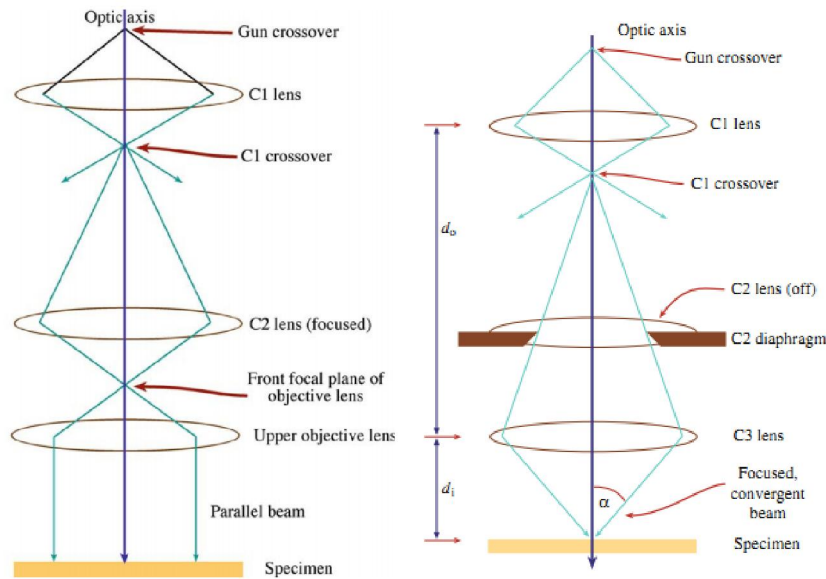
Forming images and DPs

The objective lens takes the electrons emerging from the exit surface of the specimen, disperses them to create a DP in the back focal plane and recombines them to form an image in the image plan. A basic TEM operation is to select a specific area to study to contribute to the DP and reduce the intensity of the direct beam in the DP on the screen. We can reduce the illuminated area in two ways:

- **Make the beam smaller.** Uses C2 and/or C3 to converge the beam at the specimen. The spots in the pattern are not sharply defined but spread into disks.
- Insert an **aperture above the specimen that filters** specific electrons. If you want to use a parallel beam instead. Put the aperture in one of the image planes of the objective lens - *selected-area diffraction*. When the DP is projected onto the CCD, we can use the pattern to perform the two most basic imaging operations in the TEM: bright-field and dark-field.. The pattern will contain a bright central sport that contains the direct-beam electrons – the distribution of which will depend on the nature of your specimen.

For *bright field imaging* select the direct beam, for *dark-field* only electrons that are not in the direct beam. The more off-axis the electrons are, the greater the aberrations and astigmatism they suffer which means that the image will move on the screen as you adjust the objective-lens strength

STEM

It's harder to focus a small probe in STEM than in TEM. The scanning beam must not change direction as the beam is scanned, then the electron scattering incident direction varies and the image contrast would be impossible to interpret. To achieve the parallel scan we use two pairs of scan coils to pivot the beam about the front focal plane of the upper objective polepiece. This lens then ensures them to be parallel to the optic axis. The DP should be formed in the back focal plane.

The STEM image quality depends on the probe which means on a lens. Defects in the *imaging lenses* do not affect the resolution though; the limitation is the beam dimensions. Great advantage is working with a thick sample! The electron detector acts as the interface between the electrons coming from the specimen and the image viewed on the display screen.

BF STEM images – We use an electron detector in the same way as we use an aperture in TEM mode: we only allow electrons that we want to contribute to the image to hit the detector. The beam will vary in intensity depending on the specific point on the specimen illuminated by the probe at a time. When forming a STEM image in a TEM, you operate the TEM in diffraction mode (otherwise in the way for the objective aperture).

DF- STEM images – Works in the same way as for BF, only we filter out other electrons. If we want a specific beam to fall on the BF detector, we can shift the stationary DP so that the scattered beam is on the optic axis and hits the detector. Otherwise, we can use an annular detector which surrounds the BF detector. This is called *ADF imaging*. This image will be complementary to the BF. We can use another annular detector that picks up the electrons scattered out in even higher angles forming *HAADF* images (high-angle ADF) in which Rutherford-scattering effects (Z) are maximized and diffraction-contrast effects (variations in intensity of diffraction) are smoothed out.
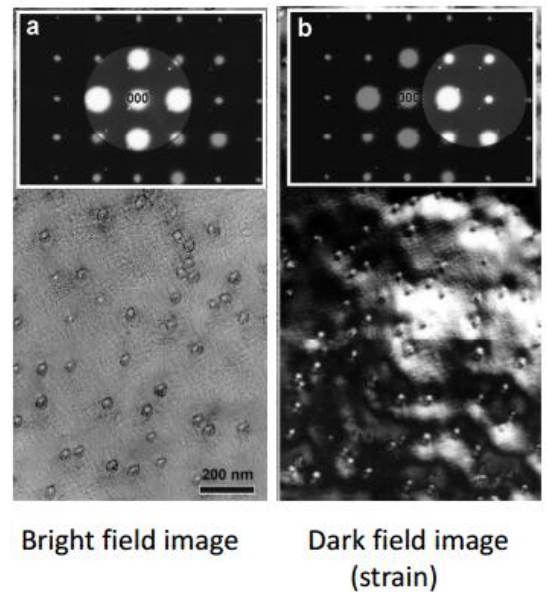
Bright field image   Dark field image (strain)

STEM vs. Conventional TEM

In general		
+ high resolution, see inside structures		
- lack of depth information		
	CTEM	**SEM**
	+ faster than STEM, usually better resolution	+ higher signal/noise, less damage, can be done in SEM
BF	+ atomic structure (phase contrast) - no depth information, confusing contrast for crystalline material	- lower resolution +/- less contribution from diffraction; less confusing but less information
DF	+ more contrast in low-mass materials, distribution of structures easily visible, mapping of strain - slower, less intensity, can be hard to interpret	+ more intensity, HAADF (no diffraction contrast and high Z contrast, more clear thickness information)

Chapter 11 - Diffraction in TEM

Diffraction contrasts arises because the intensity of the diffracted beam is different in different regions of the specimen (because of changing conditions or thickness). These patterns are called diffraction patterns (DP) and give direct crystallographic information about small areas of the specimen. If we see spots, at least the specimen is partly crystalline.

At the Bragg angle the electron waves coming into the specimen interfere constructively. Bragg's law:

$$n\lambda = 2d\, sin\theta_B$$

This gives us a physical picture of the diffraction process because the diffracting planes appear to behave as mirrors for the incident electron beam. It does not matter hos the atoms are distributed on two parallel planes; the scattering from any two points will produce the same path difference $2d\, sin\theta_B$.

Chapter 16 – Diffraction from crystals

How does the crystal symmetry affect the diffraction pattern we expect to see?
The *atomic scattering factor* (*f*) varies with scattering angle, but in this chapter we assume a fix value of *f*. The structure of the crystal imposes certain selection rules which determine which beams are allowed. The *structure factor* (*F*) is the unit cell equivalents of the atomic scattering amplitude, and can be thought of as unit-cell scattering amplitudes.

$$F = f(1 + e^{\uparrow}(\pi i(h + k + l)))$$

F= 2*f* if the sum *h+k+l* is even
F= 0 if the sum *h+k+l* is 0dd

For structures as fcc and bcc for example, a corresponding reciprocal lattice can be described, in which certain reflections are forbidden. It's often not possible to know the structure just by looking at the pattern. Know that with same symmetry, still there's differences: atomic density fcc>bcc>sc → spot density sc>bcc>fcc.

(100)   (110)   (111)
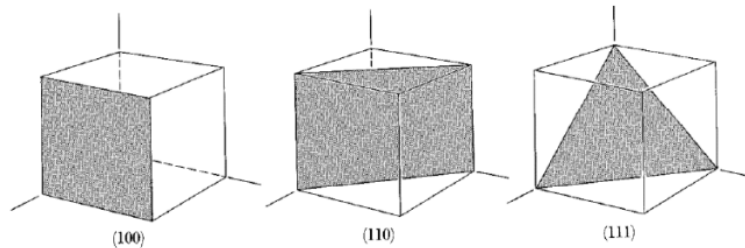
Zone axis – the direction in which the beam passes through the sample. [100] shows as a square, [110] as a rectangle and [111] as a hexagon.

Weiss zone law - reciprocal lattice points visible only if:

$$hU + kV + lW = 0 \qquad r \propto \sqrt{h^2 + k^2 + l^2}$$

If we know the crystal structure we can apply the selection rules: **Example SC [001]**
U=0, *K*=0, *W*=0, which mean *l*=0 too. Only lattice points that fulfill this is in the reciprocal lattice:
For example are those with index $\sqrt{1}$ = 110, 010, ~~001~~ …
This means everyone with something other than *l*=0 is excluded to an empty space in the lattice. Start looking at the smallest frequencies; they should be the ones with largest distance in the reciprocal lattice.

Selection rules

	Simple cubic	BCC	FCC
In general	F=f for all h,k,l	*F= 2f* if *h+k+l*=even *F =0* if *h+k+l*=odd	*Fcc F=4f* if *(h,k,l)* all odd/even F=0 if mixed.
For [001]		We exclude those with sum 0.	

Chapter 32 – X-ray spectrometry

With X-ray spectrometry, we can detect the X-rays emitted from the specimen and identify from which element they originated. This transforms the TEM into an AEM that can be said to be the combination of imaging and spectroscopy. The spectrometer used is called an X-ray *energy-dispersive spectrometer* (*XEDS*) and is important in both TEM and SEM. The detector generated voltage pulses proportional to the X-ray energy, processing them and translates it into a signal. The counts in the energy channels are then displayed as a spectrum. It is sensitive enough to detect all the elements above Li.

In a XEDS, we would ideally only process one incoming X-ray at one time, and it is therefore switched off between two detected X-rays. The computer tells you the processing conditions, the peak identity, the number of X-rays in a specific channel etc. The three components of an XEDS are the detector, the processing electronics and the computer.

- X-ray detected by semiconductor detector
- Detector generates a charge pulse proportional to the X-ray energy.
- Pulse converted to voltage.
- Signal amplified, isolated and identified.
- Digitized signal is stored in the channel assigned to that energy in the computer display.

Semiconductor detectors

The by far most common detector is the Si detector, and it's a reverse-biased p-i-n diode doped with Li to compensate impurity doping.
When X-rays deposit energy into a semiconductor, electrons are exited and create electron-hole pairs. Thousands of pairs can be generated by a single X-ray; the number is directly proportional to the x-ray photon energy. These still constitute a very small charge pulse so a bias is applied to separate most of the charge. Electrons/holes are separated in a p-i-n diode by a reverse bias and the resulting electron pulse measured.

The detectors have to be cooled not to activate electron-hole pairs that will give a noise level disrupting the signals. It can also affect the intrinsic nature of the detector negatively. They are therefore cooled with liquid N_2, which is an impractical process with some drawbacks. The cooled detectors are usually isolated from the AEM stage with a sealed window to prevent ice buildup. There are three different types of detectors, those with a Be window, those with an ultra-thin window and those without a protective window.

Beryllium-window detectors – use a thin Be sheet which is transparent to most x-rays. Be is expensive, rare and slightly porous which makes a bit thicker sheets more common. It absorbs X-rays

with energies under 1 keV – we cannot distinguish elements below about Na and EELS is often preferable.

Ultra-thin window detectors – use thin polymer films, diamond, boron nitride or silicon nitride which can withstand atmospheric pressure while transmitting 192 eV X-rays. Different window materials absorb light-element X-rays differently. Less X-ray absorption.

Windowless detectors – only appropriate in UHV, but give the best signal.

SDD (Si drift detectors) –Much higher count rates, minimal cooling, less contamination and higher collection angle. Better signal in SEM, but better counts in TEM.

Sometimes Si detectors aren't very good, X-rays with energy over 20 keV can pass through the detector without creating electron-hole pairs which limits the use of the most common detector. One possible solution is to use an intrinsic Ge detector (*IG*). It is more robust and can be warmed up repeatedly. As it only takes 2.9 eV to create a pair in Ge (comparing with 3.8 for Si) a given X-ray produces more pairs in Ge – giving a better energy resolution. Some drawbacks are that the peak intensities are small, and that they are harder to manufacture. Another technique is *WDS* (wavelength dispersive spectroscopy) that have a much better resolution but is very slow.

Chapter 33 – X-ray spectra and images

The spectrum consists of element-specific characteristic peaks with well-defined energies superimposed. The unavoidable presence of scattered electrons and X-rays within the AEM conspire to degrade the quality of the generated spectrum and increase the number of false peaks in the displayed spectrum.

In a characteristic peak, a cascade of electron transitions occurs with each transition filling the hole with an electron from a more weakly bound shell (leaving a shell and so on). Each transition results in either a characteristic X-ray or an Auger electron depending on the fluorescence yield. Lower-energy X-ray peaks are more intense than higher-energy ones and the heavier the element, the more complex the spectrum. The background in the spectrum is the bremsstrahlung radiation and has zero energy at the beam energy and rises as the energy lowers.

Artifacts common to Si XEDS systems

- The detector
- The specimen outside the region of interest
- Elsewhere in the system

Escape peak – The detector do not detect all the X-ray energy, and a small fraction of the energy may be lost, see the picture. Si escape peaks appear in the spectrum 1.74 keV below the characteristic peak position.

Internal fluorescence peak – A characteristic peak from Si or Ge in the detector dead layer (p- or n area). Photons can fluoresce atoms in the dead layer, and the resulting X-rays cannot be identified by the detector and registered as a small peak in the spectrum.

Sum peak – Two photons enter the detector at the same time and are not separated. Will give twice the energy of
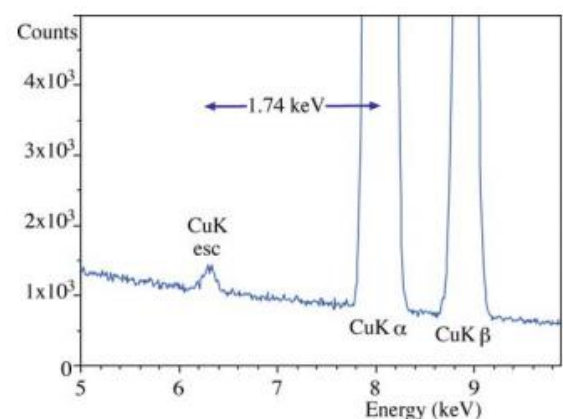
The escape peak in a spectrum from pure Cu, 1.74 keV below the Cu K_α peak. The intense K_α peak is truncated in the display because it is 50–100× more intense than the escape peak.

a major peak. It is likely to occur when the input rate is high, the dead times are > 60% or if there are major characteristic peaks in the spectrum.

The real spectrum

In a perfect AEM, all spectra would be characteristic only of the chosen analysis region. Two factors combine to introduce false information in the real AEM which we call system and spurious X-rays. These factors are:

- The high-voltage electrons which generate intense doses of stray X-rays and scattered electrons in the illumination system.
- The thin specimen which scatters high-energy electrons and X-rays around the limited confines of the AEM stage.

The errors these create in the spectra are not major distortions, but are good to know about. We cannot reduce spurious sources to zero so a spectrum is invariably obtained in all AEMs if you count for long enough (called *hole count*).

Spurious X-rays – Those that come from the specimen but are not generated by the electron probe in the chosen analysis region.

System X-rays – Those that come from parts of the AEM other than the specimen.

Most of the beam electrons scatter in the region of interest, but some are scattered through high enough angles that they strike other parts of your specimen, the support grid, the holder or the objective lens polepiece or other material in the AEM stage. This can often lead to a characteristic Cu peak from the holder in the spectrum and is counted as an artifact in the spectrum. Can reduce this by surrounding the specimen with low-Z material like Be and keep the tilt as low as possible.

Chapter 34 – Qualitative X-ray analysis and imaging

Qualitative analysis requires that every peak in the spectrum be identified with statistical certainty. The best conditions for qualitative analyses require a large probe, a reasonably large area and a large aperture to give the most current – but then you compromise particularly high spatial resolution. The only big requirement for good qualitative analyses is counts! For reasonable qualitative analysis you'll have to accumulate your spectrum for a longer time with a FEG compared to a thermionic source as the FEG gives much less total current. Normally we select a single position in our sample and take a spectrum of counts versus energy. It's also possible to take a single energy and plot counts versus position (spectra corresponding to specific element). Often we select the strongest peak energy, select an area and scan over it. Two methods: dwell time/pixel with collecting counts for a single energy at each pixel and repeat, or scan entire region fast and repeat until satisfied amount of counts.

The best you could do for gathering more counts is to choose a thicker specimen region, it will degrade the spatial resolution some. A thicker specimen may absorb weak X-rays from light elements that are of interest, but it is possible to proceed with further analyses of smaller samples. The gathering of the counts may take a while and you run the danger of damaging any beam-sensitive specimens.

Basic acquisition requirements:

- Adjust the computer display to the widest possible energy range.
- Collect a spectrum to see the actual energy range over all the detectable characteristic peaks.
- Re-gather if the difference in actual range are present, improving the resolution (<10 ev /channel). Optimize the throughput of counts if possible.

- Next thing is to identify the peaks!

Peak identification

Each X-ray is emitted with very well-defined line energy, but the XEDS system degrades the line to a broad peak.

Basic identification:

1. Look at the most intense peak which should be easiest to identify as a K-, L- or M peak – then work down through the associated family lines. (Use tables for identification).
2. The most intense peak is most likely to have associated artifacts, such as an escape peak (1.74 eV below that peak energy in Si system) and a sum peak (at twice the peak energy).
3. Go to the next most intense peak and repeat etc.
4. Be aware of overlaps, look for spurious-, system- and artifact peaks.

Specific identification:

1. If you find a K_α line, look for the K_β line at 10 % intensity – this must be present but may be overlapped – below 1.74 eV they possibly cannot be resolved.
2. If the two K-lines are fitting, look for the L-lines. Otherwise, look for a L or M line fit for the same energy.
3. If the L_α line fit and are at least Cl, look for accompanying family L-lines (more resolvable at higher energies).
4. The M-lines are usually only visible for elements above La in the periodic table. The pair overlap is difficult to resolve because all the M-lines are < 4keV – if it fits, look for three very small lines.
5. If the M_α line fits, there must be a higher energy L line family and possibly the very high energy K lines.
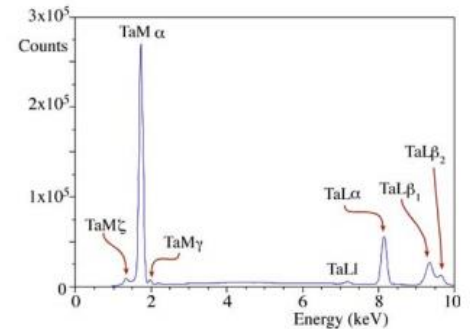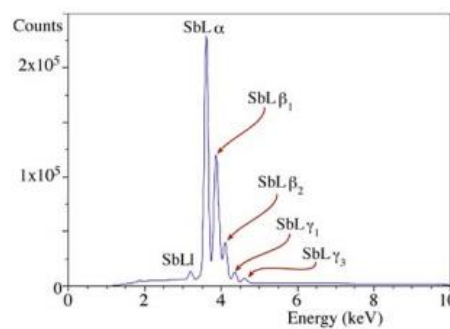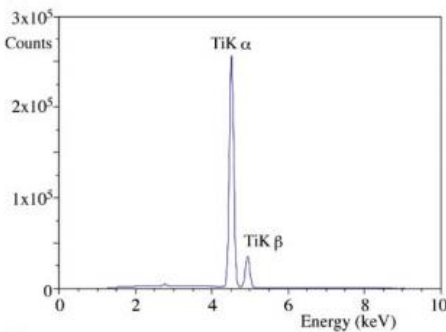
The first picture in the row above shows K-lines in a specimen with Ti, K_β is about 10% of the most intense K_α peak. The next one shows an L family with the familiar assembles of peaks. The $L_{\beta2}$ line is about 50 % of the most intense L_α. The strong M_α line is accompanied with two "shoulders" that sometimes is resolved in the XEDS. Reasons for missing family members:

- Overlapped by another peak. You can try re-gathering the spectrum with longer time constant or use a higher-resolution technique such as EELS.
- The display range may be too small, cutting off the peak.
- The energy of the beam is too low to excite the line (should only be a problem in SEM).

Chapter 35 - Quantitative X-ray analysis

Through the qualitative analysis you can convert it into quantitative data about the distribution of elements in your specimen. We know which elements we have, but how much ad where do we have them?

Cliff-Lorimer ratio technique

We assume that the specimen is thin enough so that we can ignore any absorption or fluorescence. The weight percent of each element C_A and C_B in the specimen can be related to I_A and I_B by:

$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B} \qquad\qquad C_A + C_B = 100\%$$

The term k_{AB} is often termed the Cliff-Lorimer factor and is a sensitivity factor that varies according to the XEDS/TEM and the keV you chooses.

$$k_{AB} = \frac{k_{AC}}{k_{BC}}$$

Practical steps for quantification:
1. Try using K_α lines where possible, use of L and M lines is more difficult because of all the overlapping lines in each family but can be unavoidable.
2. Measure the peak intensities I_A, I_B and so on and then determine the factor k_{AB}. When determining intensities, remove the background counts and integrate the peak counts.

If the peaks lie in the low-energy region where the background is changing rapidly due to absorption, it's not a good technique with subtraction of background radiation. Then you can use a mathematical approach with Kramers' law:

$$N_E = KZ\frac{(E_0 - E)}{E}$$

Z is the average atomic number, E_0 the beam energy in keV and E the X-ray energy in keV. This equation is developed for primarily bulk specimen.

k_{AB} is as said a factor and not a constant, depending on the detector, the microscope and the analysis conditions and your choice of background subtraction. They can therefore only be comparable when obtained under identical conditions. You can determine these experimentally or through a table. Experimentally is can be a problem: there must be possible to make thin specimens, no/minimal X-ray absorption and a stable specimen under beam.

Experimental: Generate a spectrum, obtain the intensity values and calculate in the Cliff-Lorimer equation – if the specimen is thin enough.
Have in mind that you only check a small percentage of the specimen, without knowing it's homogeneity you don't know much about the sample composition. Then you have to take many spectra from different parts – very time-consuming.

Chapter 37 – EELS

EELS – Electron energy-loss spectrometers and filters.
EELS is the analysis of the energy distribution of electrons that have come through the specimen and may have lost no energy or suffered inelastic collisions. These events tell an amount about the chemistry and the electronic structure of the specimen atoms (bonding, dielectrics, density, band gap, thickness...). It is common to form images of the various EELS signals in addition to gathering spectra with an energy filter – the most powerful technique in TEM is the *EFTEM* (energy-filtered TEM).

EELS can, unlike XEDS, detect and quantify all the elements in the periodic table and are especially good for light elements. It has also often a better spatial resolution. It requires very thin specimens and is a bit more challenging as a technique. EELS separates the inelastically scattered electrons into a spectrum. It's these collisions that cause most of the specimen damage.
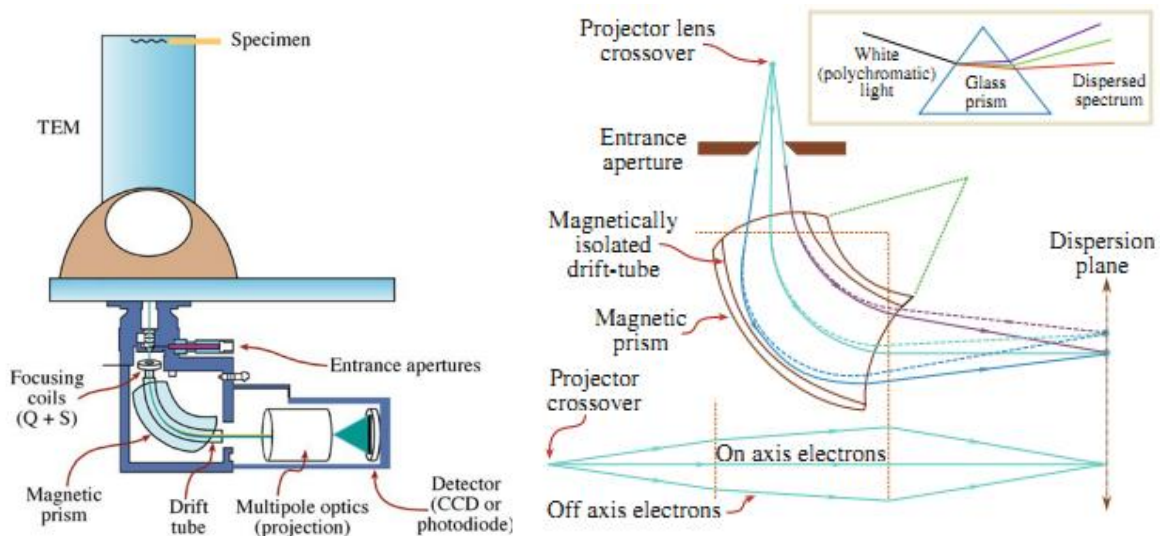
The spectrum

It's good to theoretically split up the low-loss and high-loss regions in the spectra at about 50 eV. The low-loss region contains electrical information from more weakly bound conduction and valence-band electrons, while the high-loss region contains primarily elemental information from the tightly bound core-shell electrons (and info about bonding and atom distribution). Note that:

- The zero-loss peak is very intense
- The intensity range is enormous
- The low-low regime containing the plasmon peak is relatively intense
- The element-characteristic humps called ionization edges that are relatively low compared to the background
- The overall signal intensity drops rapidly with the increasing energy loss

EELS instrumentation and prism

The magnetic prism spectrometer is the preferred (and when used the EELS is called *PEELS*) because it's compact and easily interfaced to the TEM and it's ideal for analysis through sufficient energy resolution. This spectrometer should be installed beneath the camera system of a TEM, shown in the schematic figure below.

The right picture shows the ray paths through a magnetic prism spectrometer and focusing of the electrons in the image (dispersion) plane of the spectrometer – the spectrum. The spectrometer has to focus the electrons because off-axis electrons experience a different magnetic field to on-axis electrons (and compensate for that).

Dispersion – the distance in the spectrum between electrons differing in energy by *dE*. It's a function of the strength of the magnetic field and of the incident beam.

If your spectrometer is not a limiting factor, then the gun dictates the ultimate energy resolution, and EELS really requires that you have a FEG.

Monochromator – a EELS system fitted on the FEG source and the selecting slit refines the already narrow energy spread, giving very fine detail in the spectra. The drawback is that the filtering of the tails of the Gaussian energy distribution reduces the number of electrons significantly.

EFTEM

Sometimes termed energy-filtered imaging, and to perform this you filter out electrons with a specific energy coming through the spectrometer and forms either an image or a DP. This reduces aberrations and gives a better energy resolution. There are two types of energy filters:

1. *In-column (omega) filters* – placed in the heart of the TEM imaging system, and the recording CCD detector only receives electrons that have come through the filter. Hence, all images/DPs consist of electrons of a specific selected energy.
2. *Post-column (GIF) filters* – placed below the TEM viewing screen just like the magnetic prism spectrometer and therefore you can choose to use it or not.

Omega filter - It consists of a set of magnetic prism arranged in an omega shape which disperses the electrons off axis and in the end brings them back onto the optic axis before entering the final lens.

*GIF filter* - This has an energy-selecting slit after the magnet.
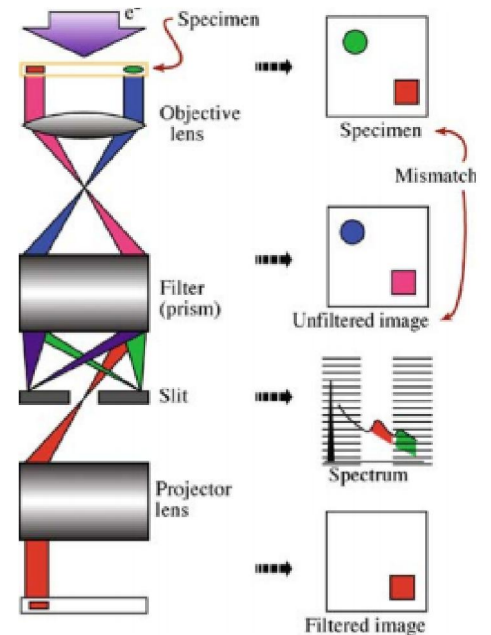
Chapter 38 – Low-loss and no-loss spectra and images

Here we are only interested in inelastic interactions, but we have to consider elastic scattering as well as they are in the spectra too. In the *low-loss region* we have:

- The *zero-loss peak* (*ZLP*) which primarily contains elastic, forward-scattered electrons, but also includes small energy losses. Forming images and DPs with the ZLP electrons has a big advantage over unfiltered images.
- The region up to about 50 eV (called the *plasmon peak*) contains electrons which have interacted with the weakly bound, outer-shell electrons of the atoms and the part reflects the dielectric response of the specimen to high-energy electrons. Images from these reveal information about electronic structure and enhance contrast and resolution in TEM images and DPs. If you instead filter out the ZLP and the high-loss region there is other things to be gained.

The principal inelastic interactions in order of increasing energy are: phonon excitations (0.02 eV – not separable from ZLP), single-electrons scattering (2-20 eV loss in energy), plasmon excitations (5-30 eV) and inner-shell ionizations (50-2000 eV, see chapter 4).

In the picture, apart from the plasmon, the spectrum is relatively featureless but there are still a lot of counts – so extracting data is useful. The other principal features are the ionization edges over 50 eV, that's why this is the limit for the low-loss region. In this region we detect electrons that have interacted with conduction/valence bands that control many electronic properties of the specimen.
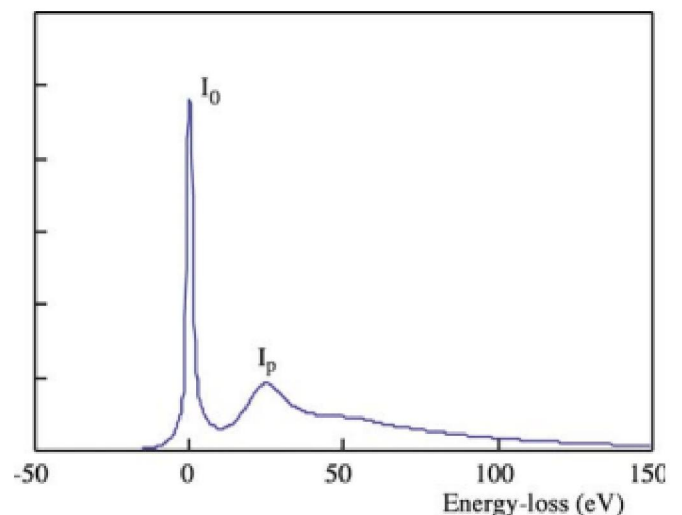
FIGURE 38.1. The low-loss spectrum showing an intense ZLP. The next most intense peak is a plasmon peak and the rest of the spectrum out to the high-loss (> 50 eV) region is relatively low intensity.

We can use the shape of the spectrum to help identify specific phases or features in the TEM image and is used for *fingerprinting* (spectra of known specimens is stored in a library in the computer).

Plasmons

A *plasmon* is a longitudinal wave-like oscillation that occurs when a beam electron interacts with the weakly bound electrons in the conductance/valence band (like the ripples on water when dropping a pebble into it). Unlike in the water the oscillations are rapidly damped. Plasmon losses dominate in materials with free-electrons structures as metals or other materials with loosely bound electrons;, Li, Na, Mg and Al. Plasmon-like peaks occur to a greater or lesser extent in the low-energy spectra from all materials. Plasmon-loss electrons carry contrast information and because they are the most intense energy-loss signal, they are the primary contribution to chromatic aberration in TEM images and it's good to filter them out. We can also use the plasmon-peak intensity to estimate the specimen thickness.

Chapter 39 – High energy-loss spectra and images

The high energy-loss spectrum consists primarily of ionization or core-loss edges on a rapidly decreasing scattering background. From these, elemental data can be extracted, and is good for light element analysis wherein EELS complements XEDS. Both the spatial resolution and minimum detection limits are somewhat better than XEDS. EELS is not affected by the fluorescence-yield limitation that restricts light-element X-ray analysis. This region contains information from the inelastic interactions with the inner core shells, and provides us with direct elemental identification such as bonding and atomic position. We are interested in ionization losses because the process is characteristic of the atom involved, and so the signal is a direct source of chemical information. These signals are called "edges". These have an energy distribution that ideally shows a sharp rise to the critical ionization energy of a specific element and then a slowly decreasing intensity in a more or less triangular shape.

The edge may also show fine oscillations which are due to bonding effects (*ELNES – energy-loss near-edge structure*). More than 50 eV after the edge, small intensity oscillations may be detectable due to diffraction effects from the atoms surrounding the ionized atom, called *EXELFS* (*extended energy-loss fine structure*). The edge shape generally depends on the electronic structure of the atom.

Compared with plasmon excitation, which requires much less energy, the ionization cross sections are relatively small – as a result the ionization-edge intensity is much smaller than the plasmon peak. The combination of an ionization loss and a plasmon loss is not uncommon, and distorts the spectrum and filtered images. The ionization-loss electrons are very strongly forward-scattered and have an effective collection of information.
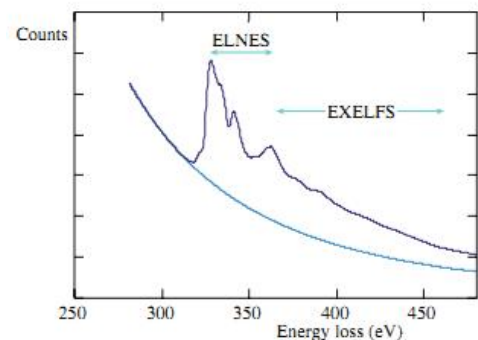
The relative energy levels of the ionized shell (K, L or M) control the position of the ionization edge in the spectrum. There are families of edges, but it is very rare that you would expect to see more than one family of lines from a given element. Edges for Z=19-28 and Z=37-45 are characterized by intense near-edge structure called *white lines*. They appear as lines of varying intensity in the EELS (read more in Chapter 40).

To quantify the spectrum or to form a quantitative image you have to integrate the intensity in the edges by removing the background. Then you have to determine the number of atoms responsible

for the intensity. These are related by a sensitive factor termed the *partial ionization cross section* and work the same way as with the equation in chapter 35. In addition to plural scattering, there can also be single-scattering contributions to the background from the tails of preceding ionization edges. There are two common techniques used to remove the background.

EFTEM

The by far most powerful method of EELS analysis is forming EFTEM images. Either select a given edge from which to form a single image (filters) or gather a spectrum image and select the specific energy later (GIFs).

Qualitative imaging. Using the ionization edge intensities correspond to elemental maps. Do this by subtracting a pre-edge background image from a post-edge image to get a qualitative elemental distribution. It is important that your sample thickness and diffraction conditions remain reasonably constant. If your specimen isn't very thin it's probably not worth bothering with a qualitative approach.

Quantitative imaging. If we at each pixel carry out a background subtraction, edge integration and multiply the resulting intensity by the partial ionization cross section we should get quantitative images of the distribution of specific elements. The most common method is to acquire three images; two from the background preceding the edge, one from under the edge (takes seconds in TEM and maybe even hours in STEM).

Chapter 40 – Fine structure and finer details

From the finer structures in in EELS, we can obtain data on how the ionized atom is bonded, the coordination of that specific atom and its density of states. Now we have the ability to simulate spectra using atomic-structure calculations which helps us to understand the details in the spectra. Both ELNES and EXELFS arise because the ionization process can give more than the critical ionization energy needed. These fine-structure effects can occur in X-ray spectra but the resolution is usually too poor. Some can resolve bonding effects though; *XANES* (X-ray absorption near-edge structure) and *EXAFS* (extended X-ray absorption fine structure).

ELNES – energy-loss near-edge structure

An excited electron from the core shell can reside in any of the unfilled states, but not with equal probability – there are more states within certain energy ranges than in others. This uneven distribution is termed the *density of states* (DOS)*.* Because of the greater probability of electrons filling certain unoccupied states above the Fermi level, the ELNES intensity is greater at the energy losses corresponding to the regions of the DOS that have the greatest density of unfilled states. I.e. ELNES mirrors the unfilled DOS above the Fermi level.

White lines –intense sharp peaks in certain ionization edges that arise because core electrons in certain elements are excited into well-defined empty states rather than into a broad continuum.

ELNES is dependent on details of the local atomic environment (coordination, valence state, type of bonding…) and can give answers about for example where changes in bonding occur over small distances in your specimen. The technique can be used to easily distinguish for example all the new forms of carbon.
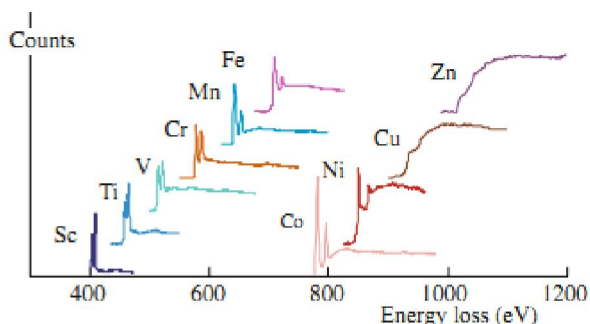
FIGURE 40.4. Spectra from the transition metals show a variation in the L_3 and L_2 white-line intensity ratios reflecting the variation in the number of core L-shell electrons ejected into unfilled d states. Note that Cu and Zn show no white lines because their d shells are full. The L_3 and L_2 white lines in the Fe L edge are the only ones that show the expected $L_3:L_2$ of ~2:1.
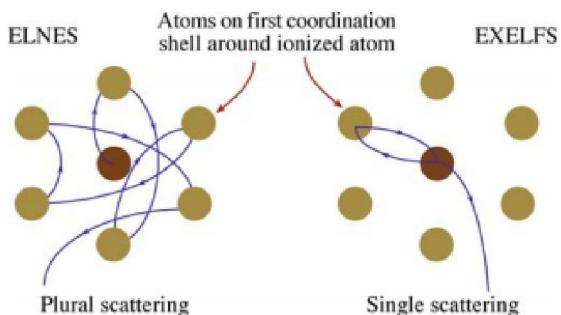
FIGURE 40.1. Schematic diagram showing the source of (A) ELNES and (B) EXELFS. The excess energy retained by the electron escaping above the Fermi level creates a wave radiating from the ionized atom and is scattered by surrounding atoms. The low-energy ELNES arises from plural scatter and is affected by the bonding between the atoms. The higher-energy EXELFS approximates to single scatter and is affected by the local atomic arrangement.

EXELFS – extended energy-loss fine structure

If the ejected electron doesn't fill an empty state but escapes outside the atom, it acts as a free electron. Because its energy is higher than those that gave rise to multiple-scattering ELNES, the diffraction is assumed to be a single-scattering event. We can determine the partial radial distribution function around any specific atom (atomic-structure information).

Difference between EXELFS and *EXAFS* (in synchrotron X-ray spectra) is that the latter results in complete photo absorption of incident X-ray while EXELFS only absorbs a small fraction of the beam electron. Both give structural information from materials with strong, local atomic correlations.

Limitations with EXAFS: Hard access K-edges below 3 keV because it requires thin specimens and low absorption atmosphere. Also gives a relatively low spatial resolution as X-rays cannot easily be focused to a sub-micrometer spot. (EXELFS can obtain atomic/electronic structure with nanometer resolution). EELS is more naturally suited to analysis of low-Z elements than EXAFS because of high vacuum and thin samples.

	ELNES	EXELFS
Arises from	diffraction effects from the atoms surrounding the ionized atom	bonding effects
Electrons	Resides in previously empty state above Fermi level	Escapes outside the atom
Scatters	Multiple scattering (lower energy loss)	Single scattering (higher energy loss)
Data	Bonding	Atomic structure
Occurrence	Around the edge	50 eV post-edge (ELNES can overlap)
Width of "peaks"		20-50 eV wide
Occurrence width		> several hundred eV
Other		High spatial resolution (if thin specimen)