Tech Talk

A brief introduction to energy dispersive spectrum (EDS) and electron energy loss spectrum (EELS)

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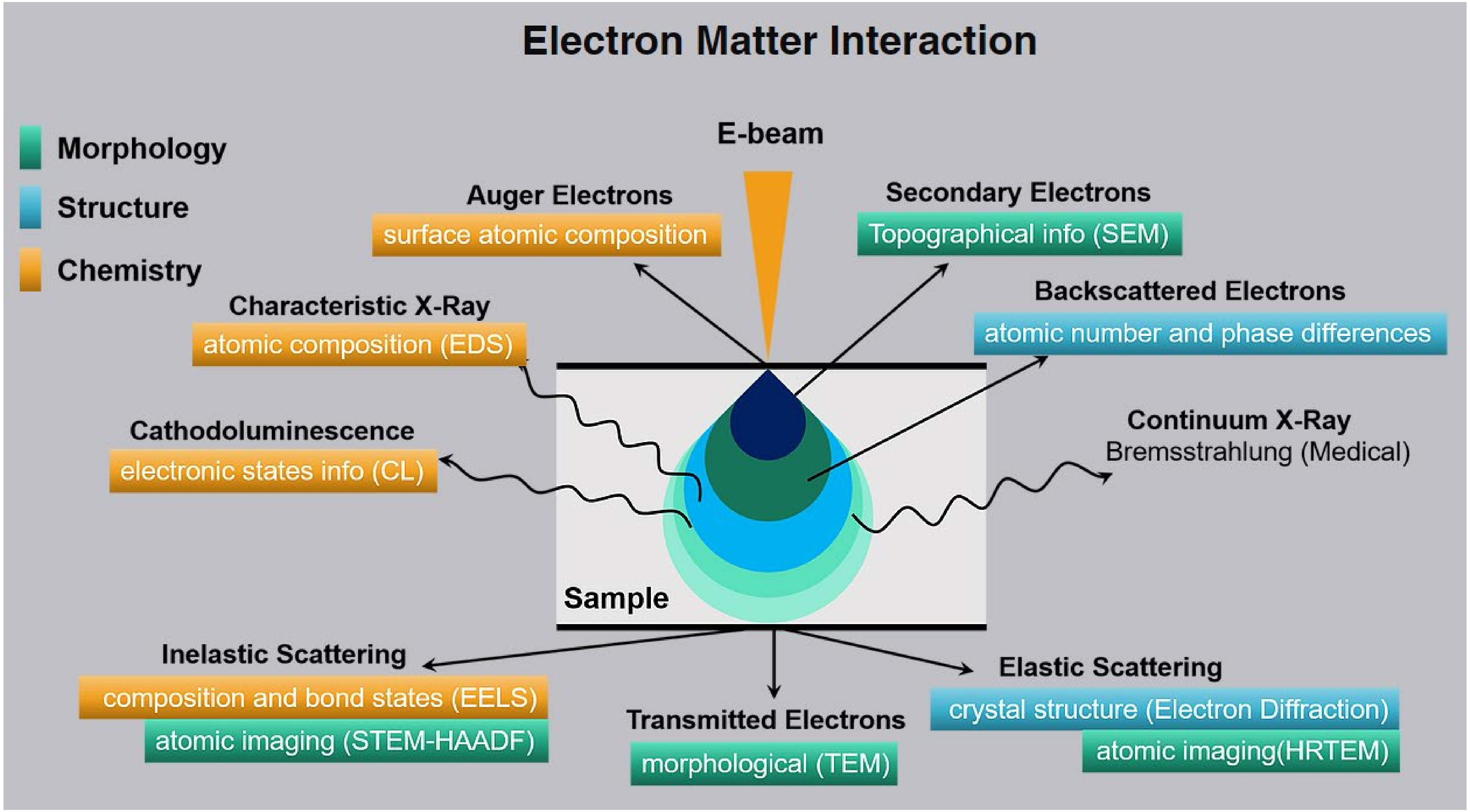
May 20, 2021

Outline

- Principles of EDS and EELS
- Key points/parameters for EDS
- Application of EDS
- Key points/parameters for EELS
- Application of EELS

Quantification methods of EDS and EELS will be covered in future lectures.

Principles of EDS and EELS



Key points/parameters for EDS

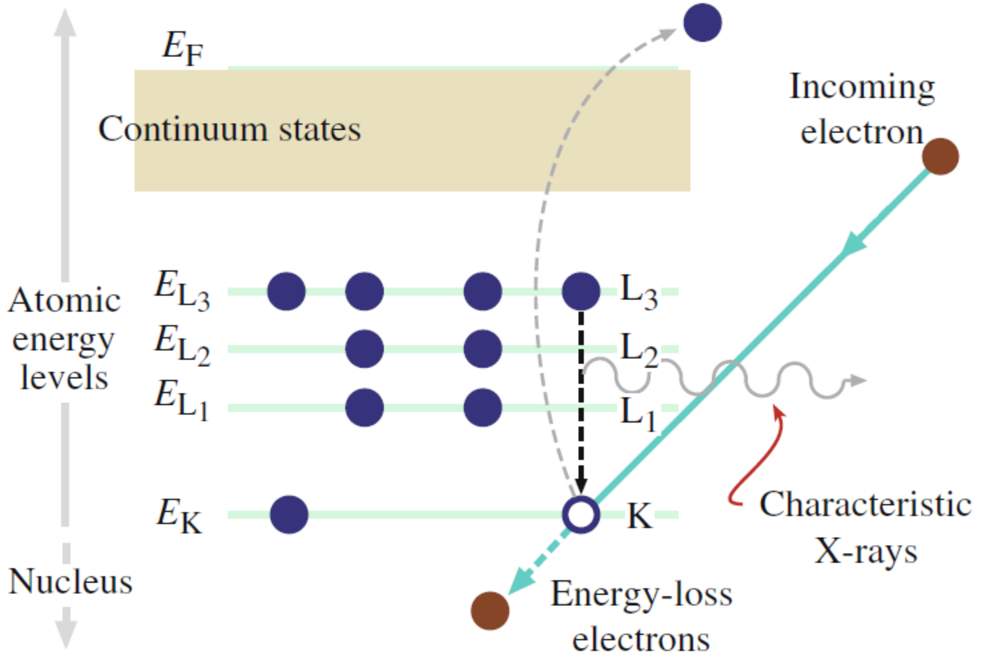
➢ **X-ray emission**

- An ionized atom does not have to lose energy by giving off a characteristic X-ray but can emit an Auger electron instead.
- Fluorescence yield (ω) describes the probability of X-ray versus Auger emission.

$$\omega = \frac{Z^4}{a+Z^4} \text{ (for K shell, } a \sim 10^6\text{)}$$

For C-K edge, $\omega \sim 10^{-3}$;

For Ge-K edge, $\omega \sim 0.5$;



That's why EDS is not the best way to analyze the light elements such as Li, Be and B.

➢ Bremsstrahlung X-rays (braking radiation)

- When electrons interact with the Coulomb field of nucleus, there will be substantial momentum changes and it may emit an X-ray during this process.

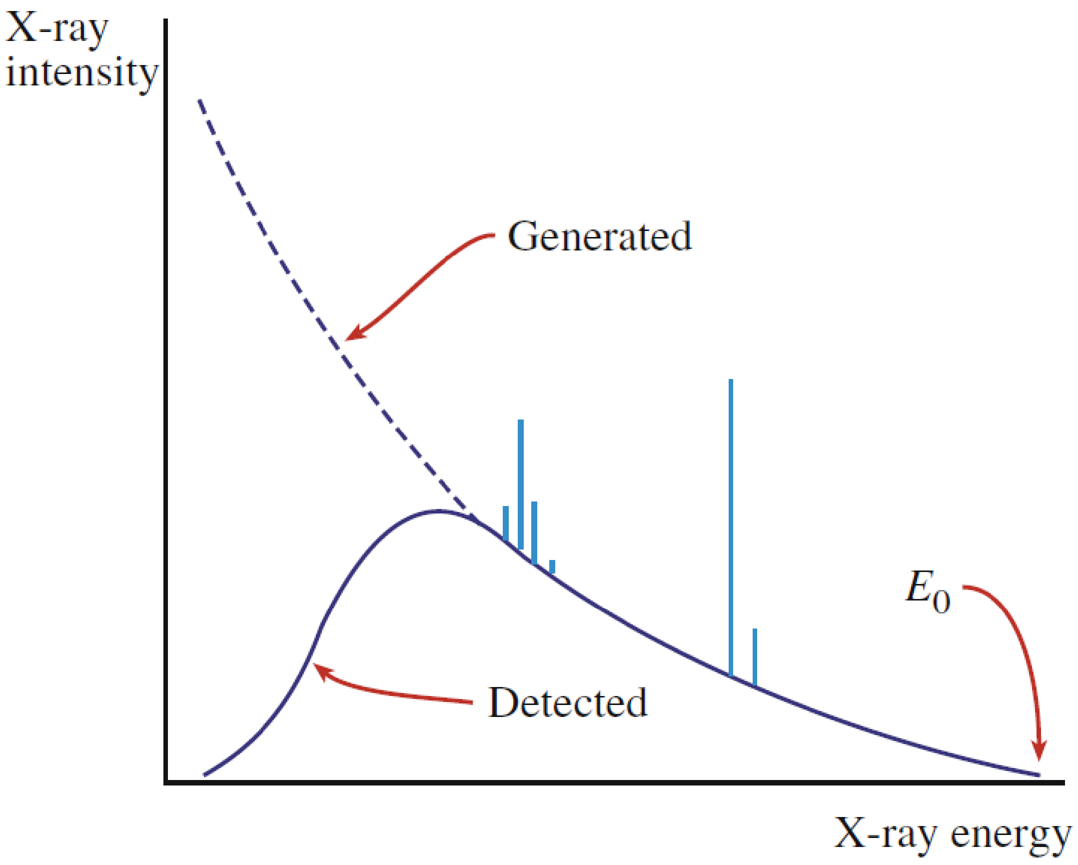
- The approximate expression used is:

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

  N(E): number of bremsstrahlung photons with energy E;

  Z: atomic number; K: Kramers' constant;

  E0: electron energy



Bremsstrahlung X-rays contributes to the continuum background.

➢ Energy resolution (～110—140 eV)

Very low and major limitation

$R = (P^2 + I^2 + X^2)^{1/2}$

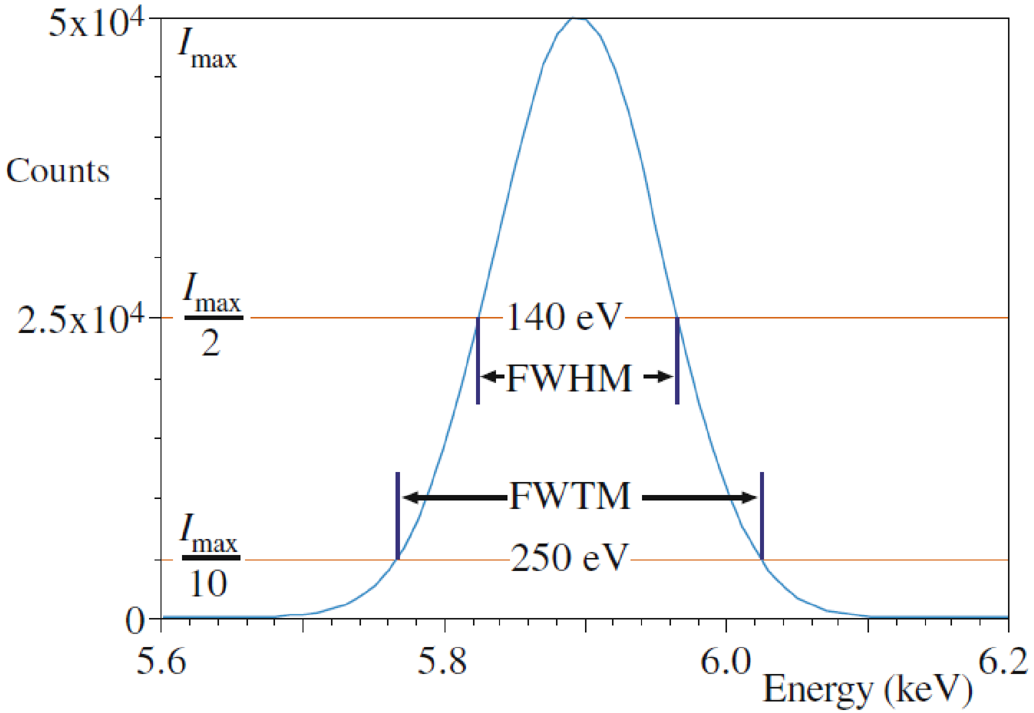
P: Full width at half maximum (FWHM) of a randomized electronic-pulse generator;

X: FWHM-equivalent attributable to detector leakage current and incomplete charge collection;

I: Intrinsic line width of the detector

$I = 2.35*(F*\varepsilon*E)^{1/2}$

(F: Fano factor of the distribution of X-ray counts from Poisson statistics; ε: the energy to create an electron-hole pair in detector; E: the energy of the X-ray line.)

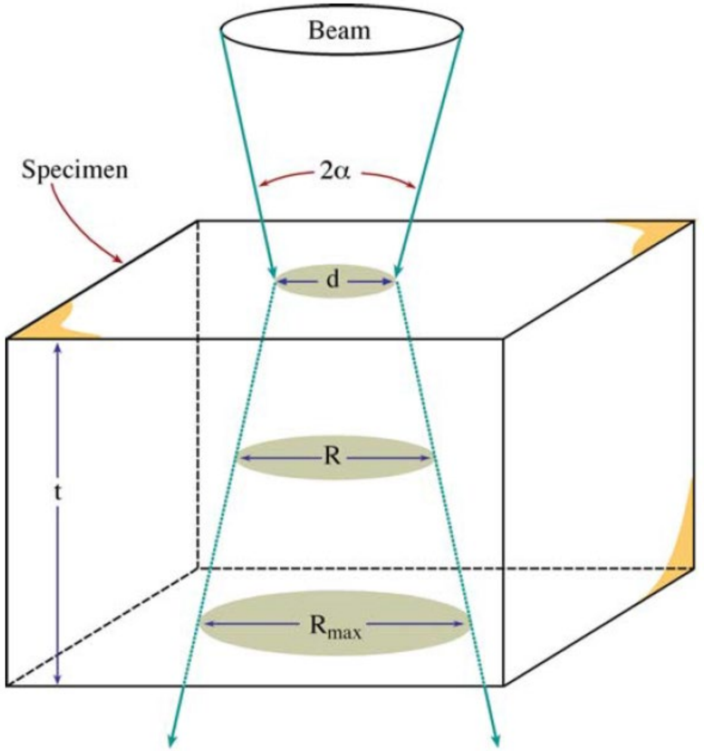


Estimate the energy resolution of Si detector:

- Assume there is no leakage, and the electronics produce no noise (P=X=0)
- F = 0.1; ε = 3.8 eV; for Mn Kα line, E = 5.9 keV
- R = I = 111 eV

➢ **Spatial resolution**

The spatial resolution (R) of EDS is governed by the beam-specimen interaction volume, which is a function of the incident-beam diameter (d_t) and the beam spreading (b).



$$R = \frac{d + R_{max}}{2} \; ; \; R_{max} = (b^2 + d_t^2)^{1/2}; \; b = 8 \times 10^{-12} \frac{Z}{E_0} * N_v^{1/2} * t^{3/2}$$

Z: atomic number;

E_0: incident electron energy in keV

N^v: number of atom/m^3

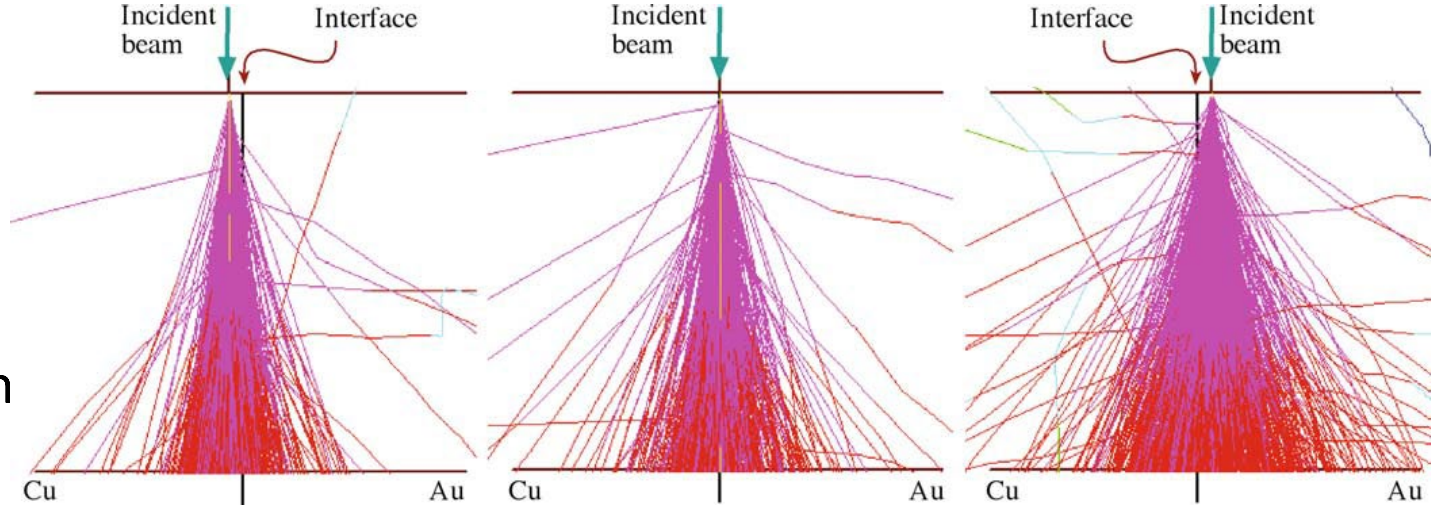
t: foil thickness

$$d_t = (d_g^2 + d_s^2 + d_d^2)^2$$

d_g: beam spread due to gun

d_s: beam spread due to spherical aberration

d_d: beam spread due to diffraction limitation



- **Time constant (τ)** Usually using a shortest τ to maximize the count rate
- τ (～5-100 μs) is the time allowed for the analog processor to evaluate the magnitude of the charge pulse.
- Shorter τ will give a larger counting rate but will give a greater error in assignment of a specific energy to the pulse (poorer resolution).

- **Dead time**
- Dead time is when the detector is not counting X-rays but processing the previous photon.

Dead time in % = $\left(1-\frac{output\ count\ rate\ (Rout)}{input\ count\ rate\ (Rin)}\right)*100\% = \left(\frac{clock\ time - live\ time}{clock\ time}\right)*100\%$

Live time is when the detector is ready to detect an X-ray and not processing any signal;

- Excess of 50-60% indicating the detector is saturated with X-rays and collection becomes increase inefficient. You should find thinner area and reduce the beam current.
- Less than 3% indicating the X-ray signal is not enough. This is the normal case for TEM sample.

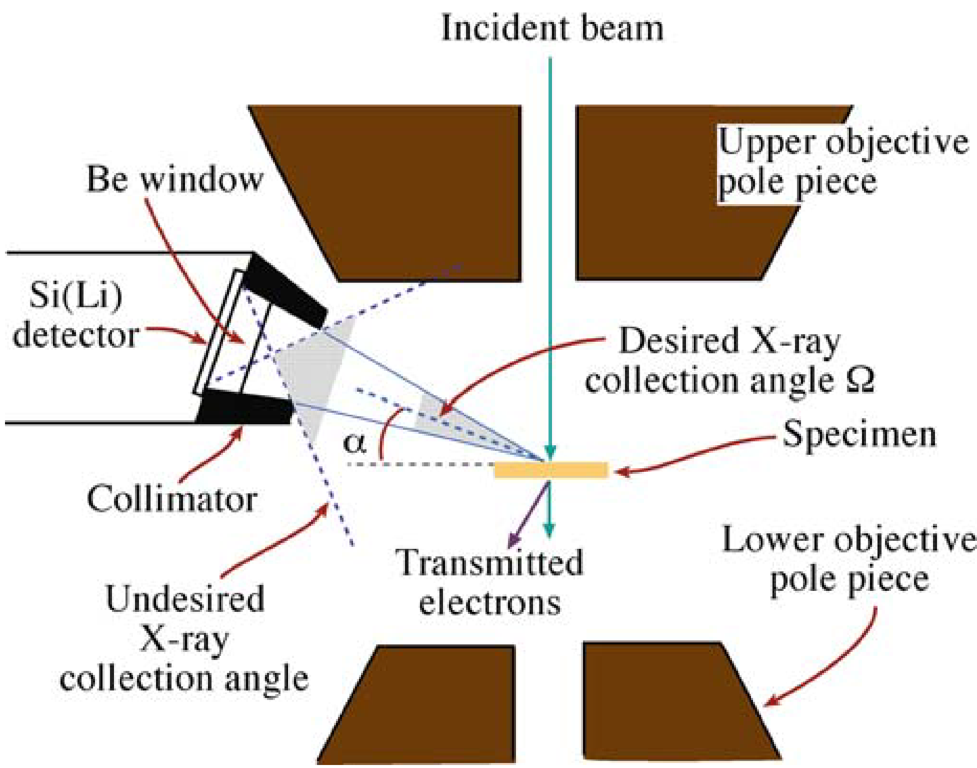
- **Collection angle (Ω)** **The larger the better.**

- Solid angle $\Omega = \frac{A * \cos\delta}{S^2}$ (usually <0.5 sr)

  A: the active area of the detector (30-100 mm^2);

  δ: angle between the normal to detector face and a line from detector to specimen; (normally, δ=0)

  S: distance from the analysis point to detector face;

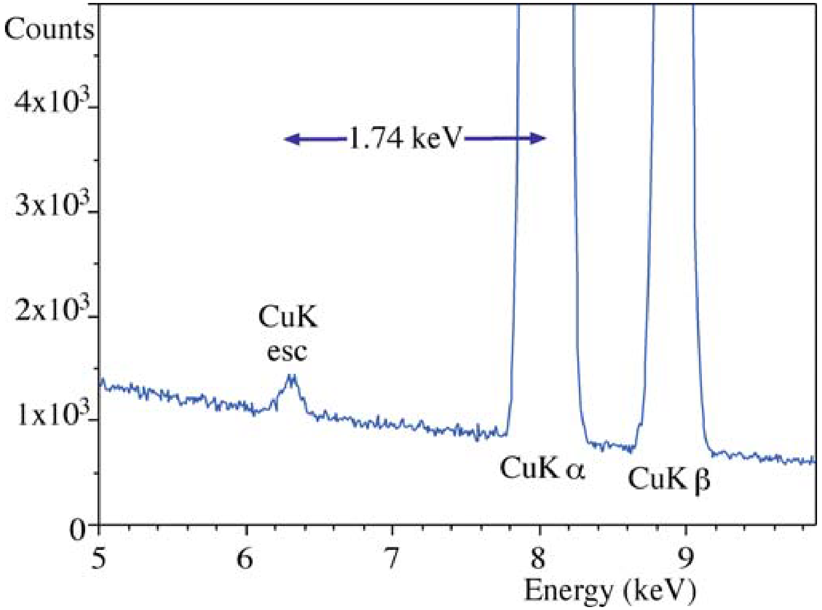


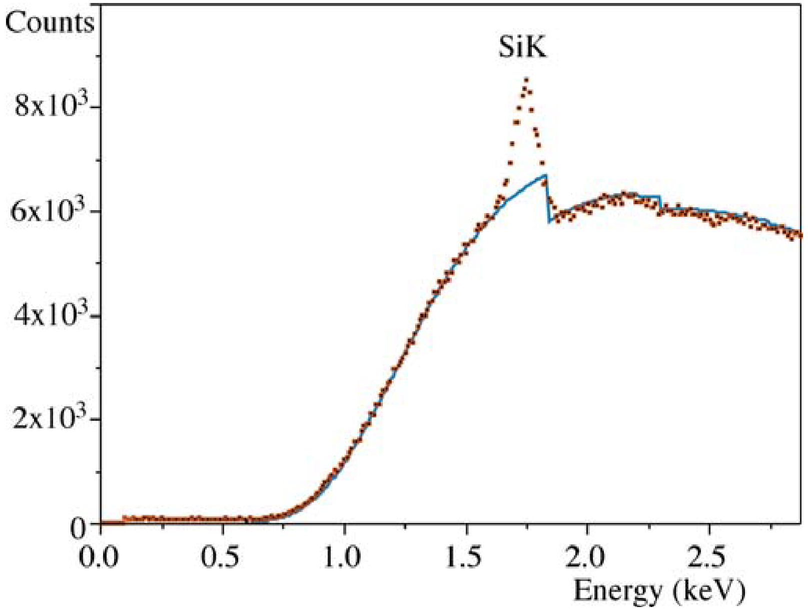
- **Take-off angle (α usually 15°)**

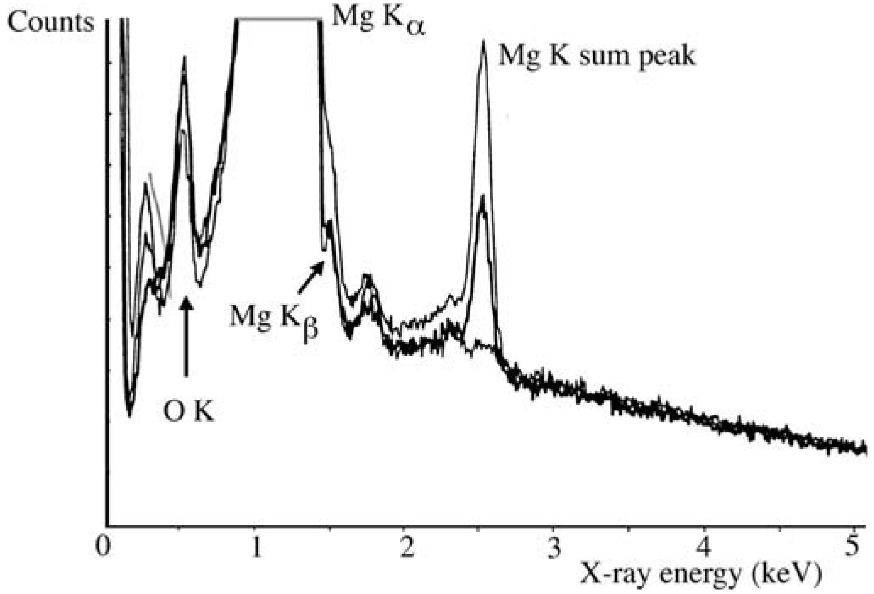
- Detector position was fixed. You can only change this slightly by tilting your sample
- Sample tilt can reduce P/B (peak/background) ratio and increase spurious effects

➢ **Common artifacts from EDS detector**

- Si escape peak (signal detection artifact)
  Detector is not a perfect sink. Incoming photon with energy E is not transformed into electron-hole pairs but fluoresces a Si Kα X-ray with a 1.74k eV energy.
- Internal fluorescence peak (signal detection artifact)
  Incoming photons fluoresce atoms in the dead layer of the detector and result in Si Kα peak
- Sum peak (signal processing artifact)
  Sum peak occurs when the count rate exceeds the electronics' ability to discriminate all the individual pulses and so-called 'pulse pile-up'. Reduce the dead time!!

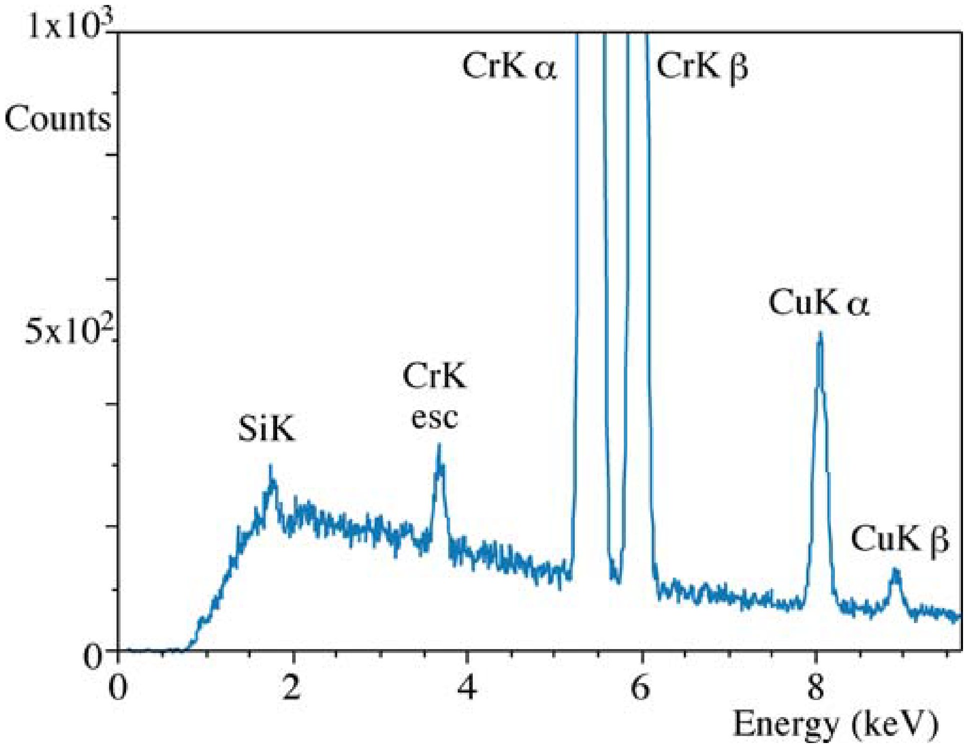


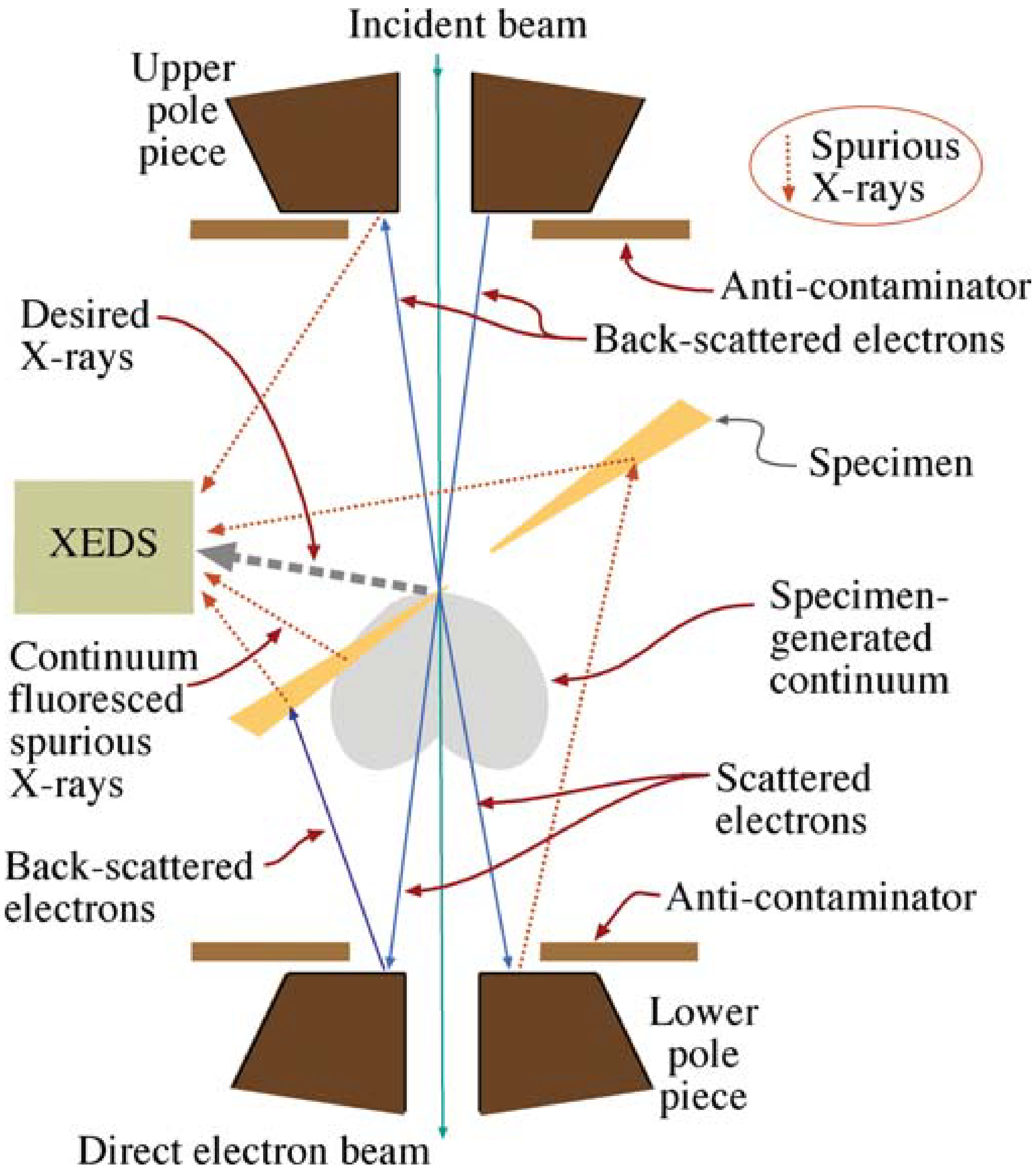




➢ System X-rays

- Cu is everywhere
- Remember to remove the objective aperture before taking EDS signal
- Operate as close to zero tilt as possible





➢ Coherent Bremsstrahlung (CB)

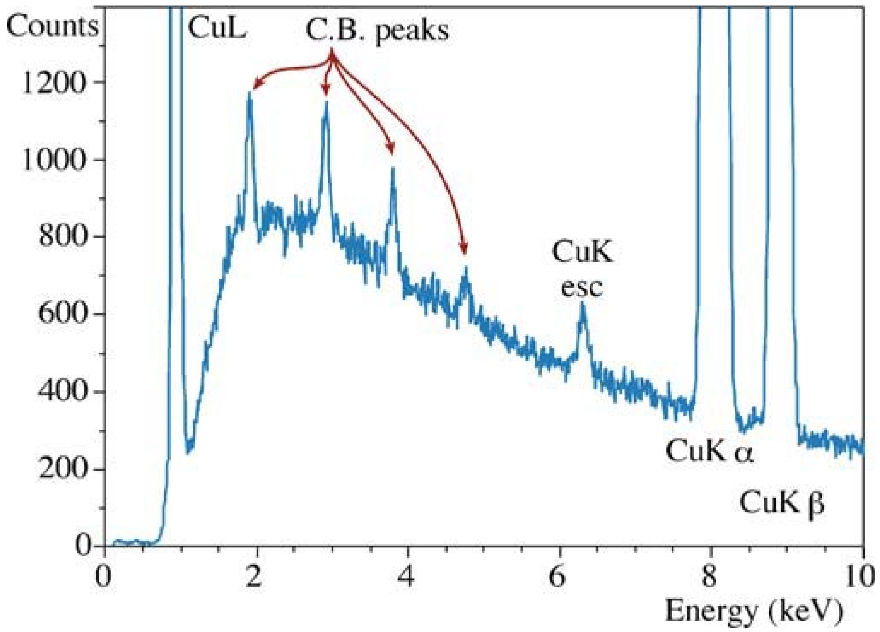
- Continuous bremsstrahlung spectrum usually happens bulk polycrystalline materials by electrons with lower energy (< 30 ekV)
- Within TEM, for single crystalline specimens, CB likely will occur.

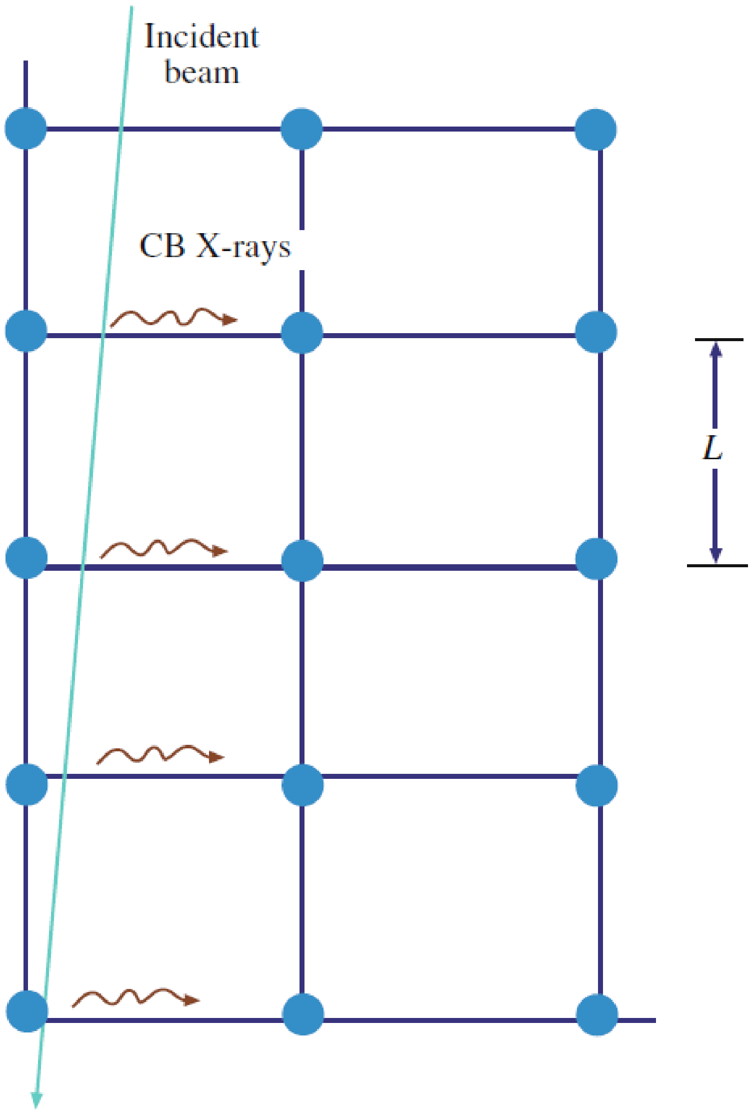
$$E_{CB} = \frac{12.4\beta}{L(1-\beta\cos(90+\alpha)}$$

β: electron velocity divided by the velocity of light

L: Lattice spacing in the beam direction

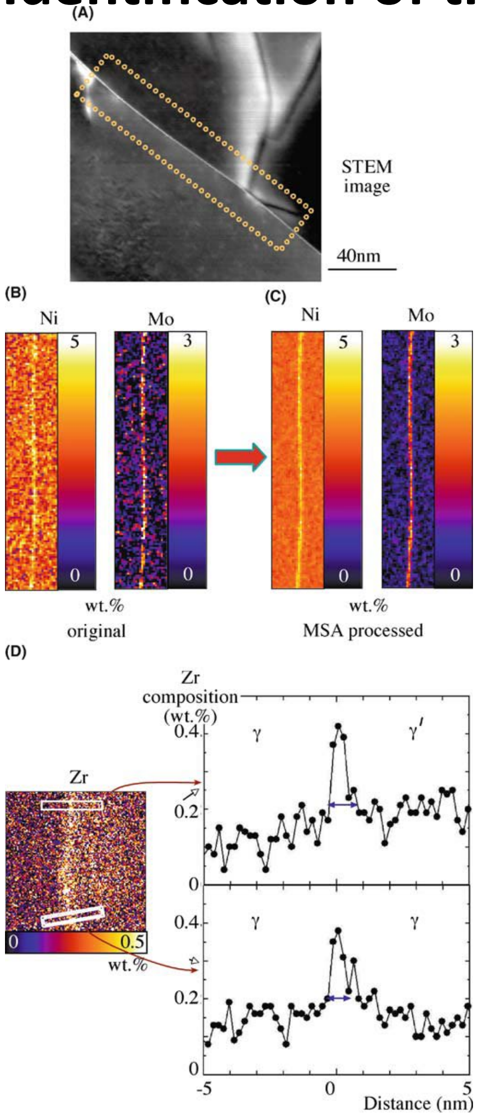
α: take-off angle of the detector



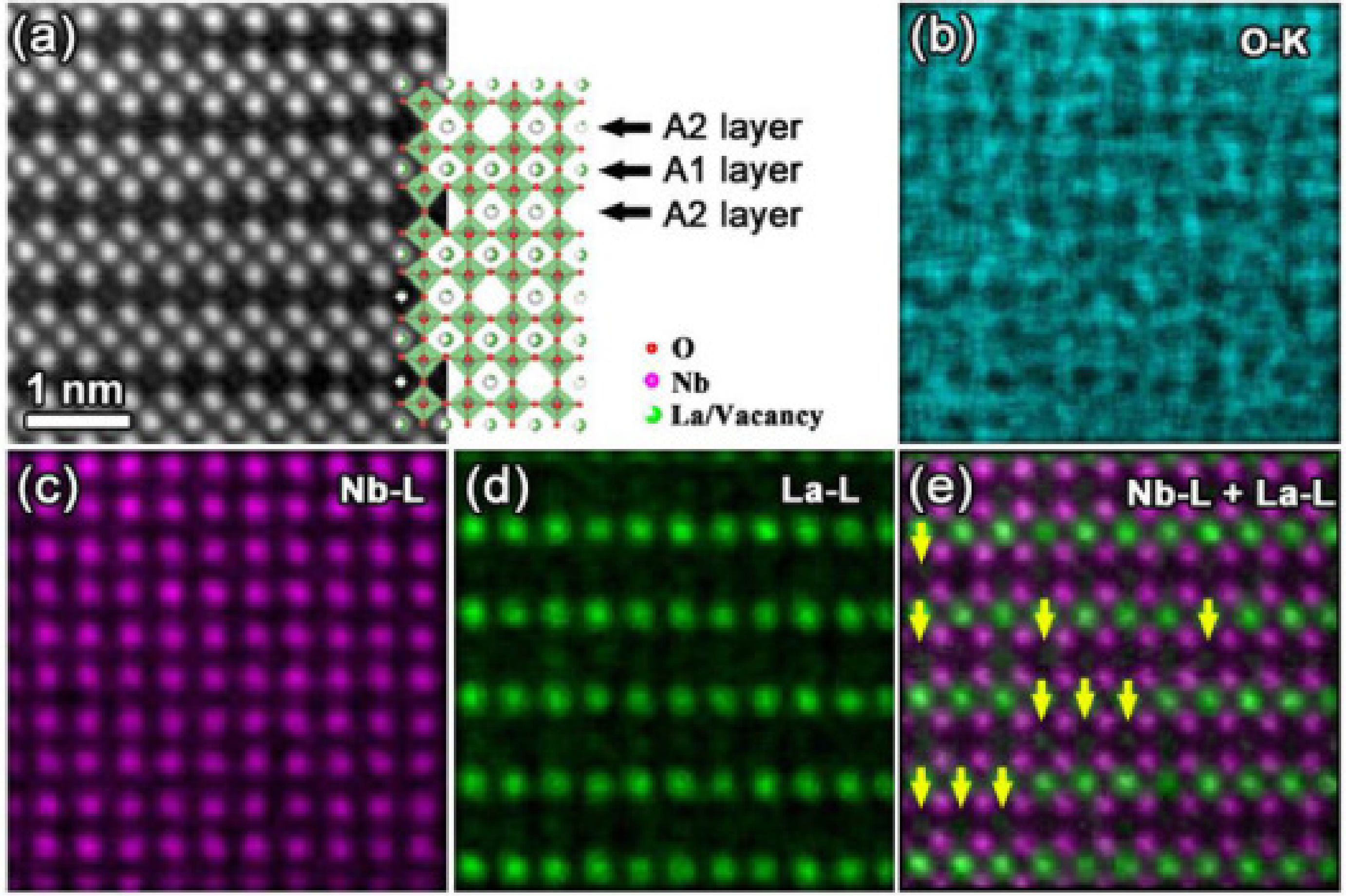


Application of EDS

Identification of the elements and distribution



Elements distribution along grain boundary within a low alloy steel.



Revealing the La-rich and La-deficient within the solid electrolyte directly.

Key points/parameters for EELS

- **Cross-section differential**

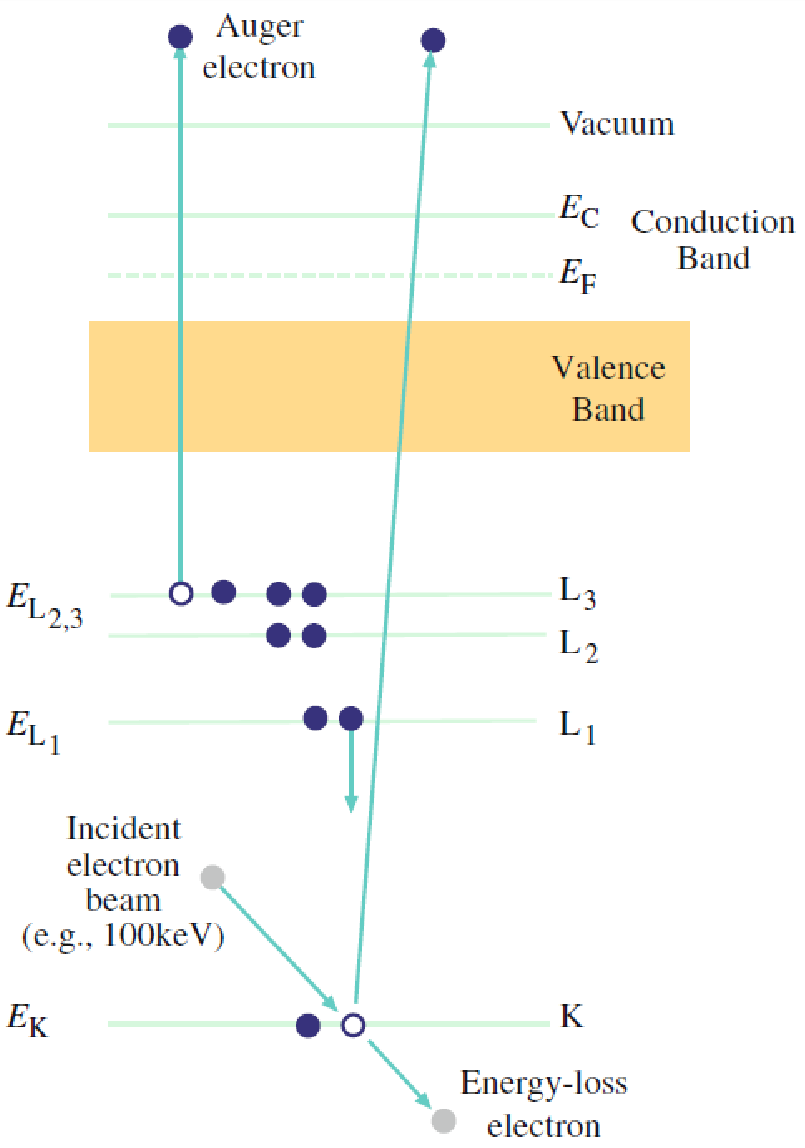
Cross-section differential of the inelastic scattering:

$$\frac{d^2\sigma}{d\Omega dE} \approx \frac{8a_0{}^2R^2}{Em_0v^2} * \left(\frac{1}{\theta^2+\theta_E{}^2}\right) * \frac{df}{dE}$$

1> Higher energy loss has smaller cross-section—Lower signal;

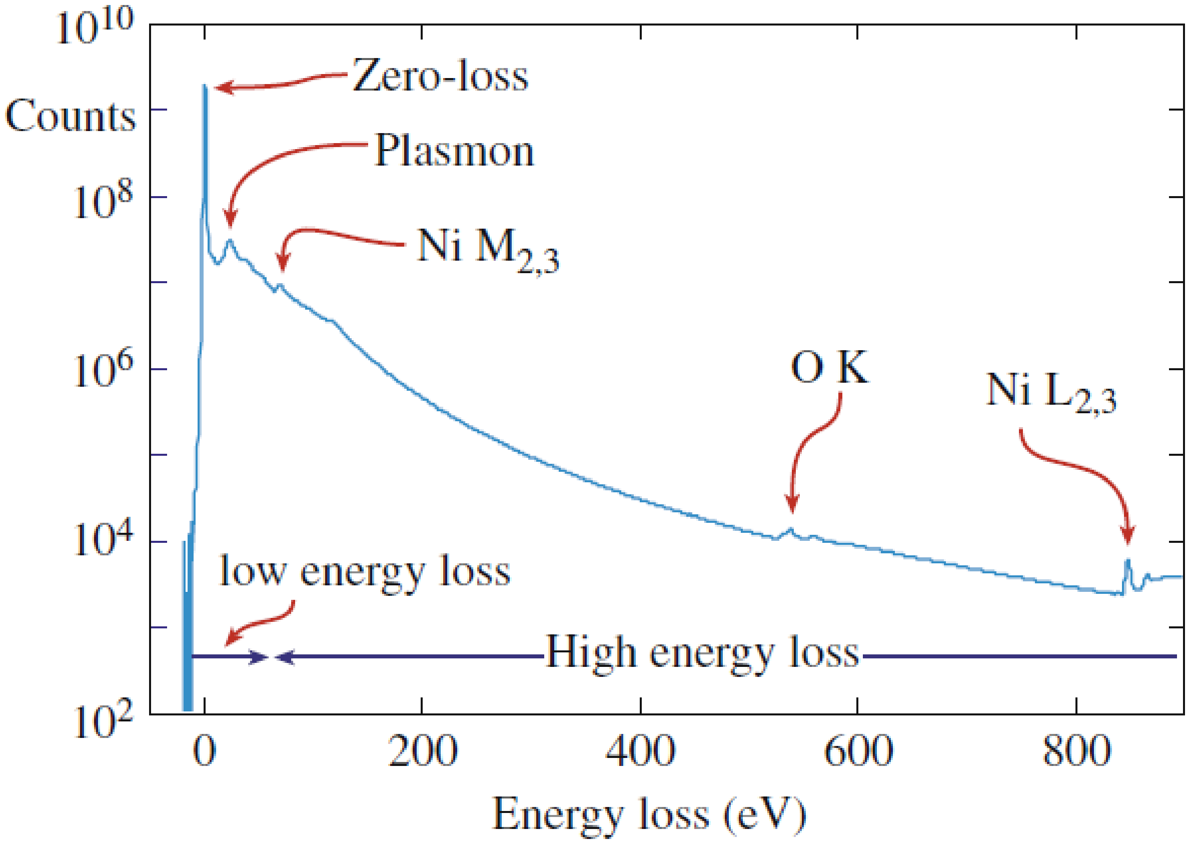
2> Lower incident electron energy has larger cross-section of scattering—Higher signal

σ: Cross-section of the inelastic scattering;
Ω: solid angle;
a_0: Bohr radius, 0.53 Å;
E: Electron loss energy
m_0: rest mass of electron;
R: Rydberg energy, 13.6 eV;
v: velocity of electrons
θ_E: characteristic angle equaling approximately $E/2E_0$;
E_0: Electron energy of the incident electrons
θ: scattering angle;
df/dE: Generalized Oscillator Strength



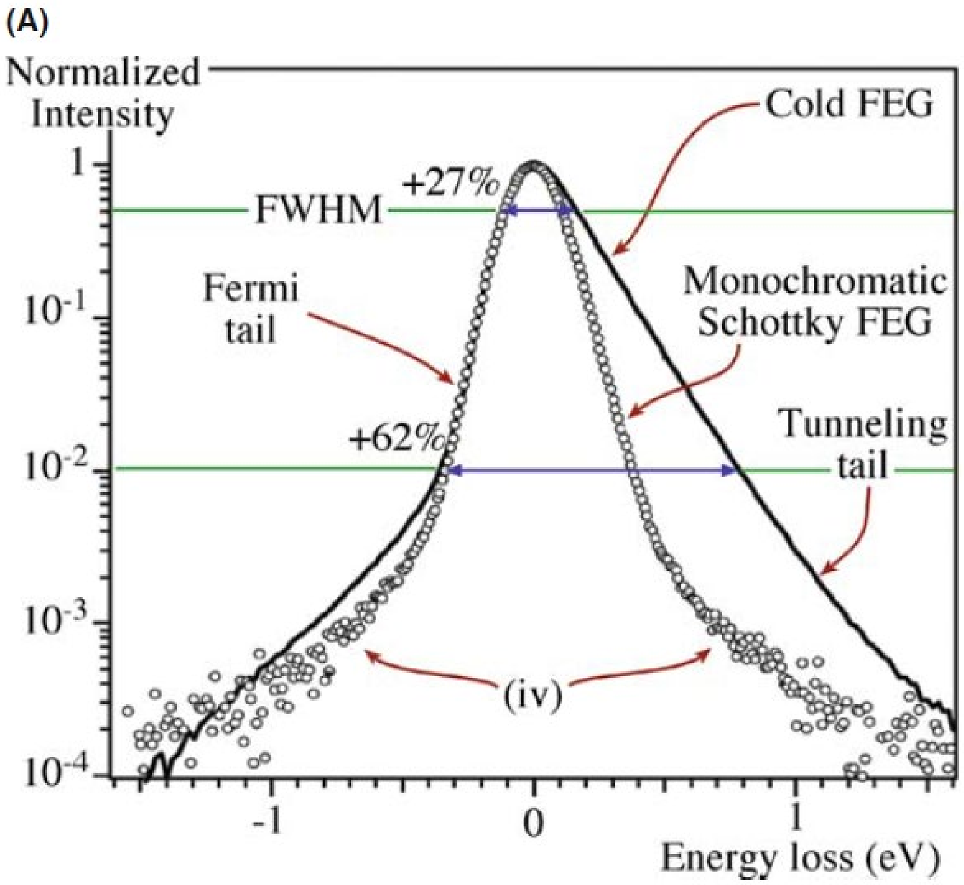
➢ Energy-loss spectrum

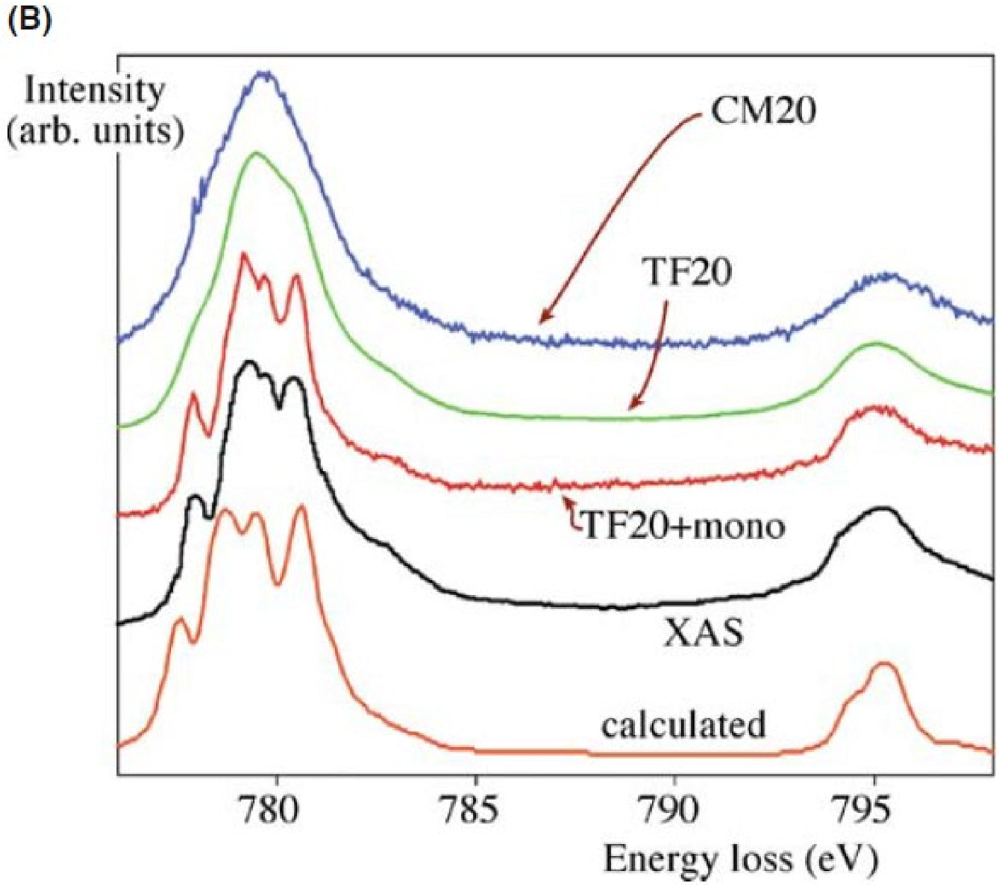
- Zero loss peak (Very intense)
- Low loss regime containing the plasmon peak is relatively intense.
- The ionization edges are relatively low intensity compared to the background.
- Overall intensity drops rapidly with increasing energy loss, reaching negligible levels above ～2keV



➢ Energy resolution

- Higher energy resolution can give you more details.
- The electron gun usually dictates the ultimate energy resolution. (W: 3eV; LaB6: 1.5eV; Cold FEG Gun: 0.35 eV)
- Monochromators can give you very high energy resolution but reduce the signals.



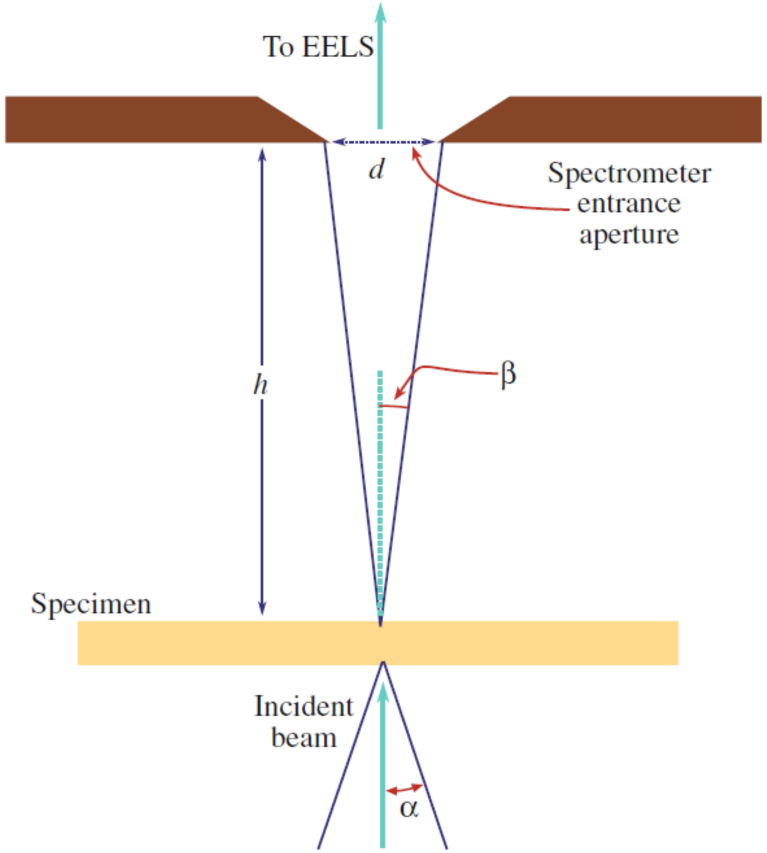


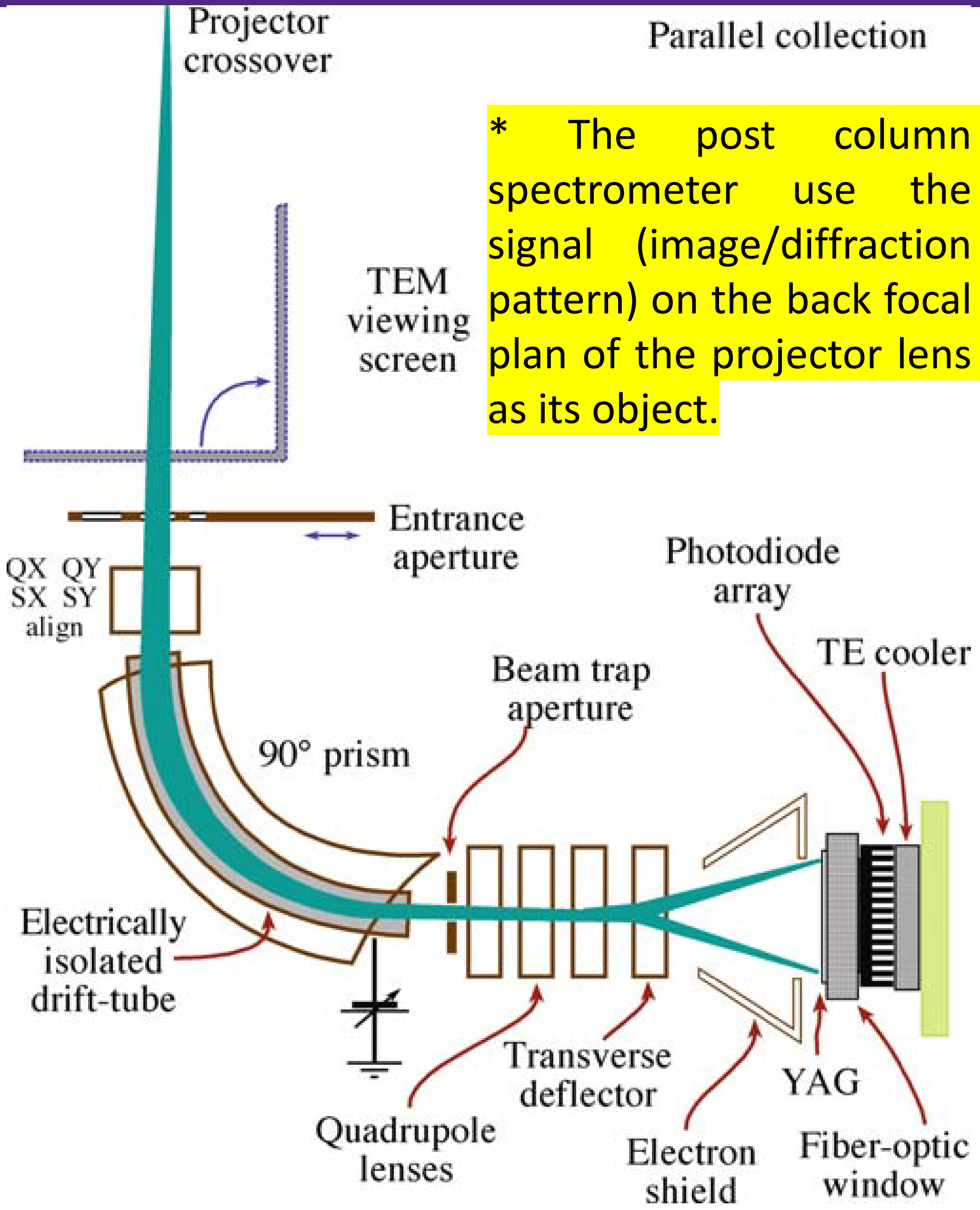
➢ **Collection angle (β)**

- **For dedicated STEM**

Cross-section differential of the inelastic scattering:

$$\beta \approx \frac{d}{2h}$$





* The post column spectrometer use the signal (image/diffraction pattern) on the back focal plan of the projector lens as its object.

- # TEM-imaging mode (diffraction coupling)

If there is no objective aperture:

$$\beta \approx \frac{r_0}{L}$$

r_0 : maximum radius of the diffraction pattern in the focal plane of the spectrometer; typically ~ 5 µm

L: camera length;

$$L \approx \frac{D}{M}$$

D: distance from the projector crossover to the recoding plan ~ 0.5 µm

M: magnification of the image in the recording plan

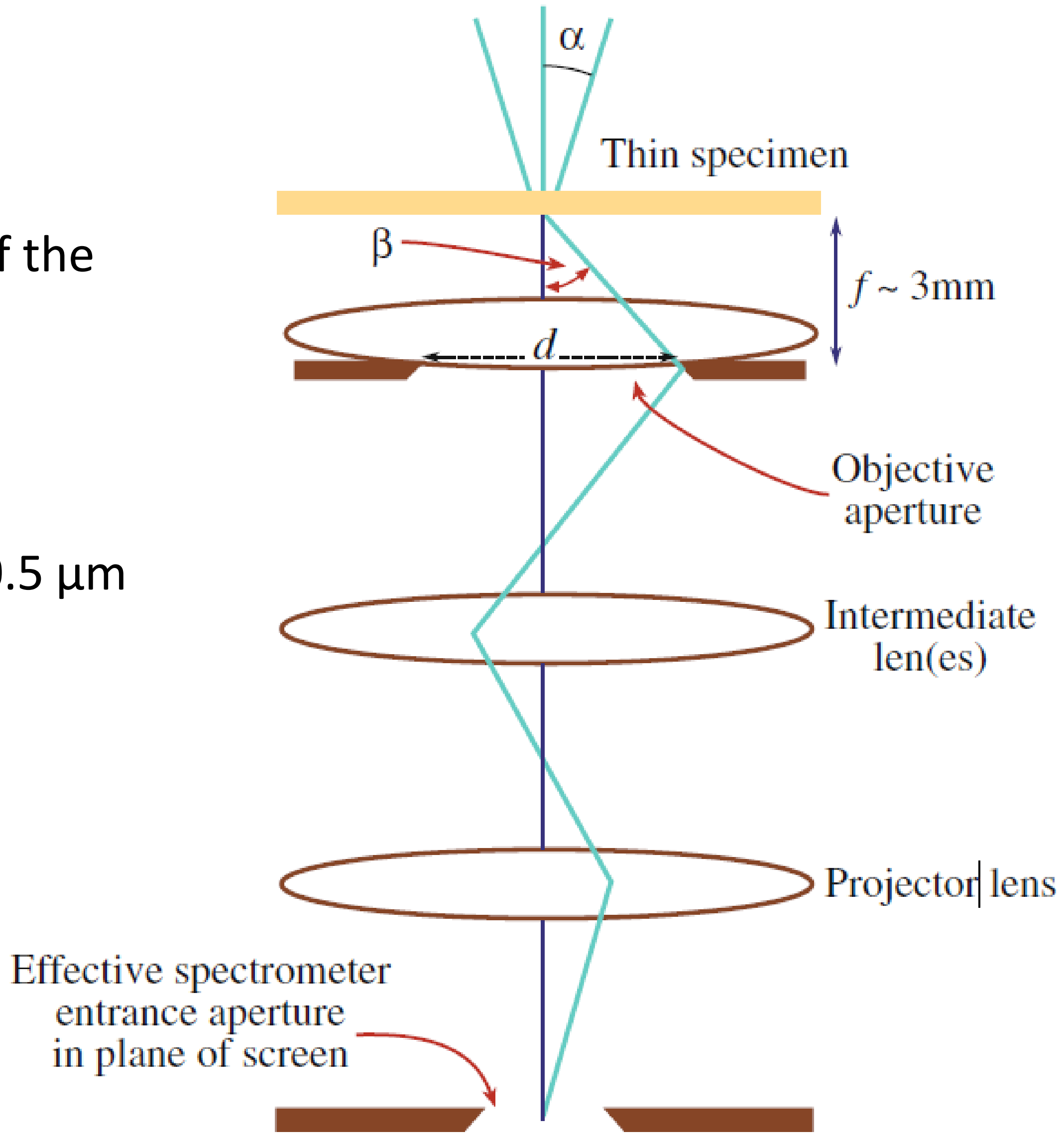
If M=10000, D=0.5 µm, β is around 100mrad.

If there is an objective aperture:

$$\beta \approx \frac{d}{2f}$$ (if d=30 µm, f=3 mm, β is around 5 mrads)

d: diameter of the objective aperture;

f: focal length of the objective lens;



- **TEM/STEM diffraction mode (image coupling)**

Collection angle is mainly limited by the entrance aperture

$$\beta = \frac{d_{eff}}{2} * \frac{2\theta_B}{b} = \frac{D}{D_A} * \frac{d}{L}$$

θ_B: Bragg angle

b: distance between 000 and hkl

d_{eff} : effective aperture diameter

L: camera length on the recording plane

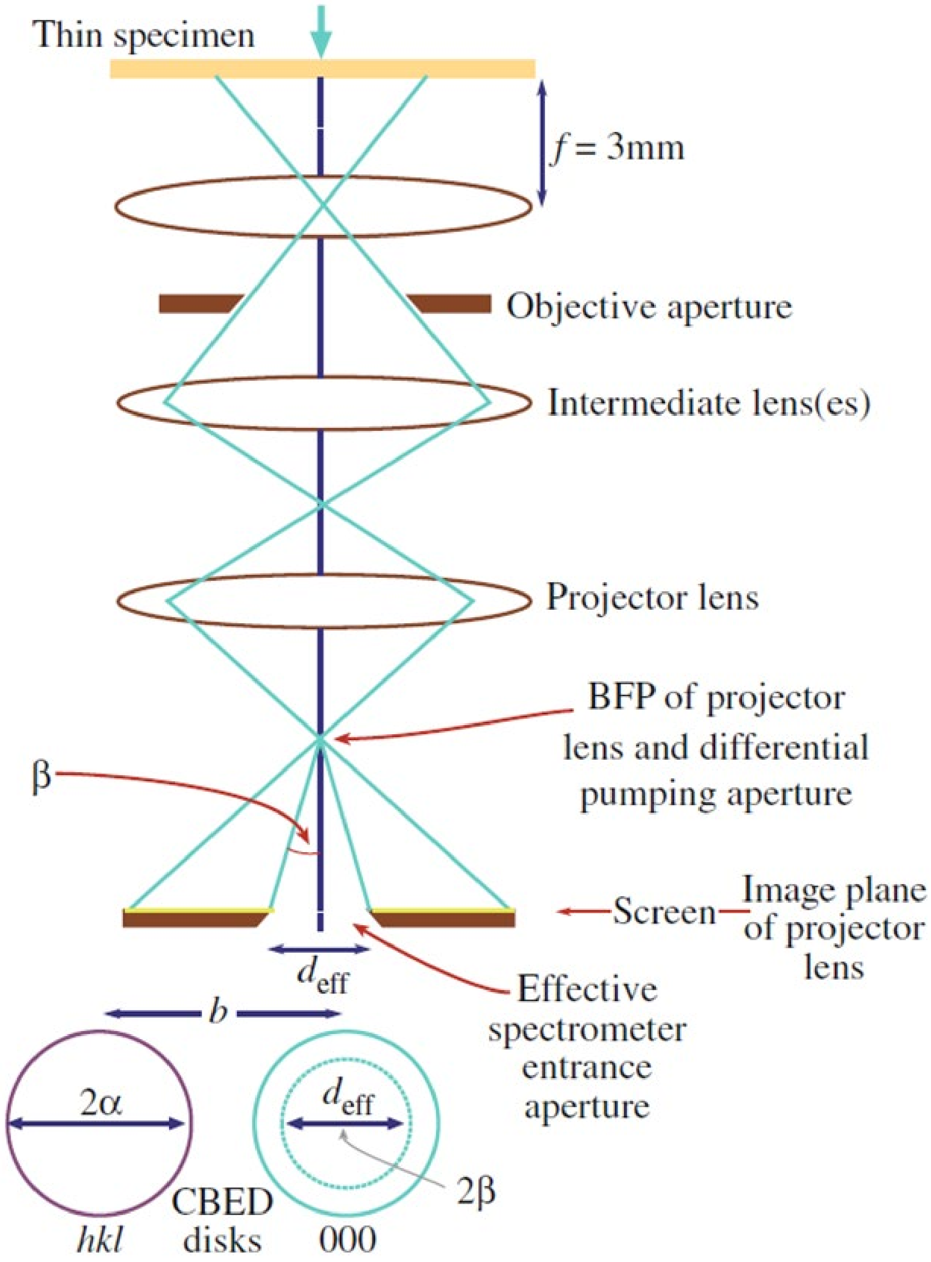
$$d_{eff} = \frac{d * D}{D_A}$$

D: distance from projector crossover to the recording plane (Varies)

D_A : distance between the crossover and entrance aperture (typically 610 mm for Gatan EELS)

For example:

If D=500 mm, L=800mm, GIF aperture 5mm, β is around 5mrads.



➢ Characteristic angle and cut-off angle

- **Characteristic angle**

$\theta_E \approx \frac{E}{2E_0}$ (E: electron energy loss; E_0: incident electron energy)

* The characteristic scattering angles for core-loss electrons range from ～ 0.2 to 10 mrads.

*Collection angle **β >2-3 θ_E ; A smaller β will cut off intensity in spectrum**

- **Cut-off angle (above which the scattering intensity is zero)**

$$\theta_c = (2 * \theta_E)^{\frac{1}{2}}$$

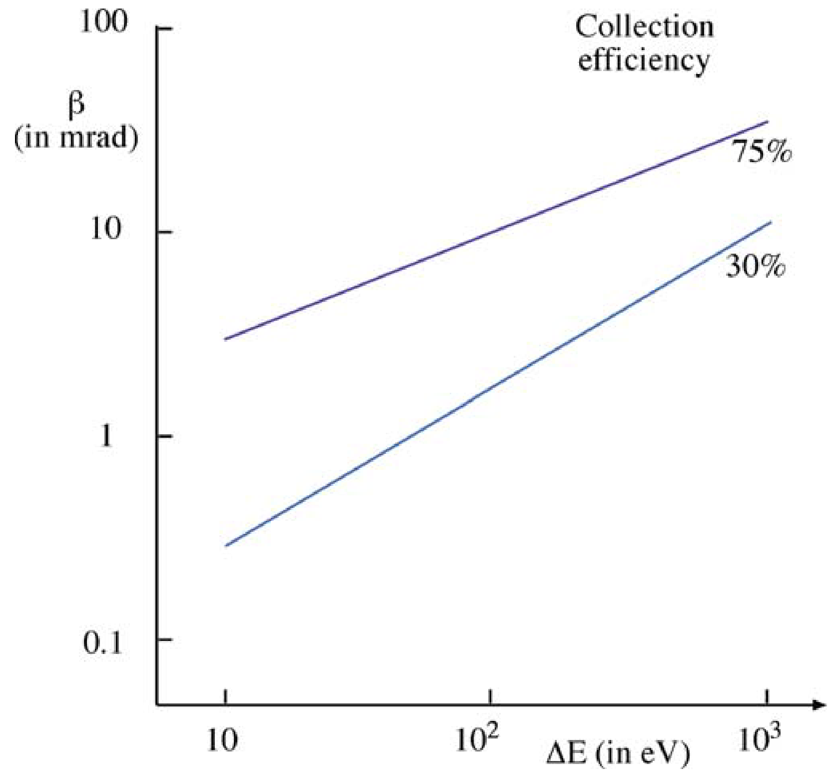
*Be careful to calculate this angle in radians but not in milliradians.

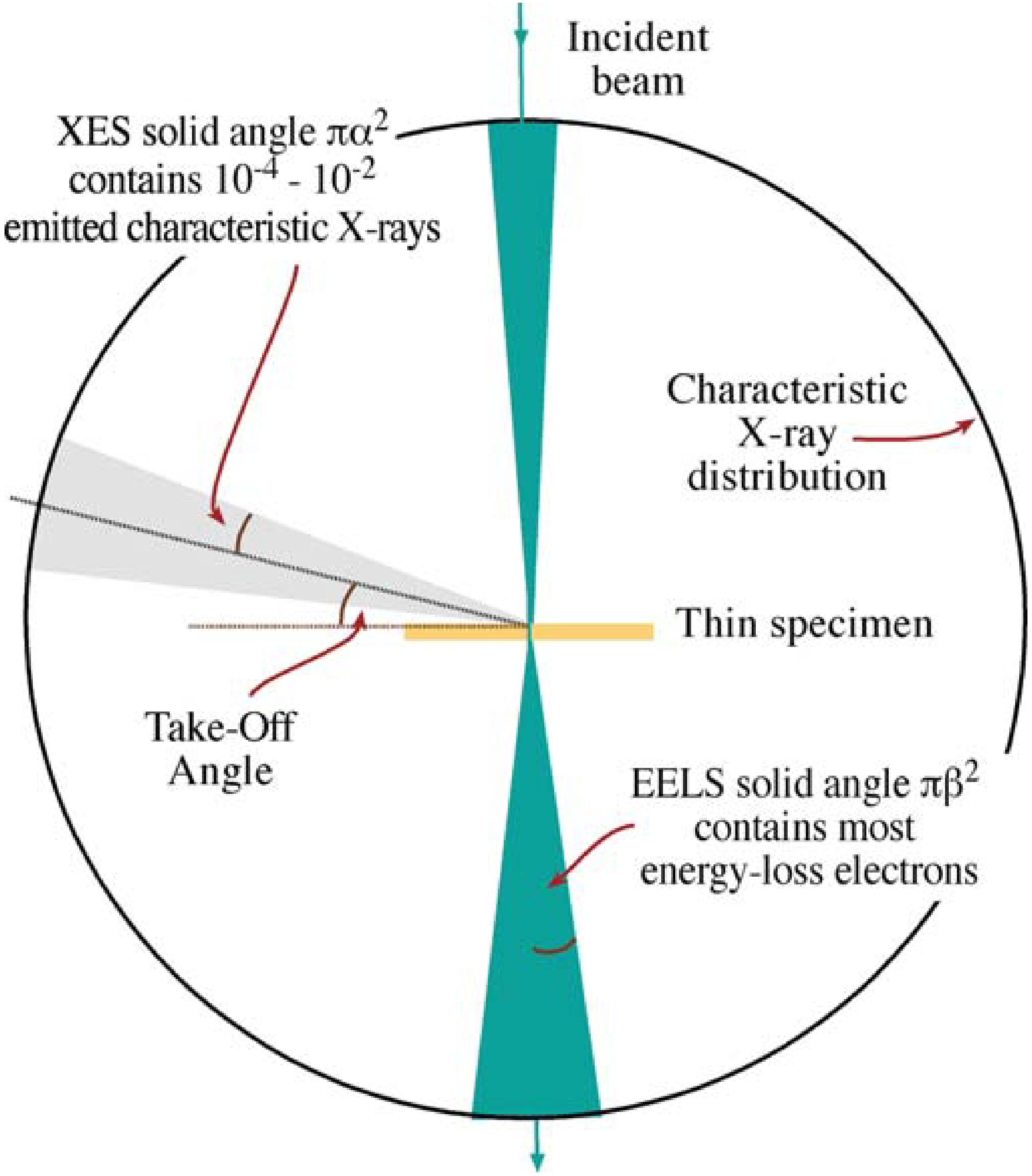
*The characteristic cut-off angles for core-loss electrons range from ～ 25 to 200 mrads;

***Too large β will include many unwanted electrons.**

➢ Detection efficiency

- Ionization-loss electrons are very strongly forward-scattered.
- Detection efficiency of EELS is very high (50-100%)
- Detection efficiency of EDS is usually inefficient.





➢ Spatial resolution

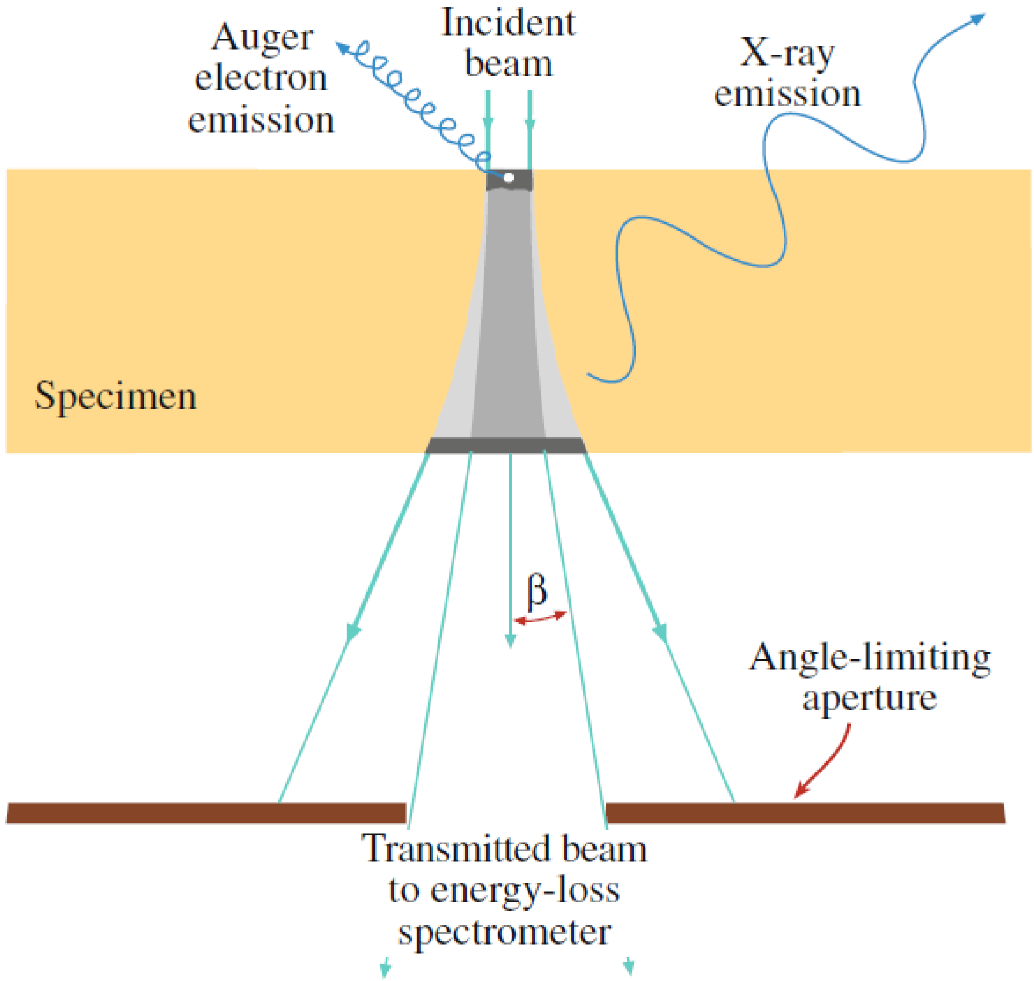
- In STEM/diffraction mode, the resolution is mainly limited by the size of the probe.
- In TEM imaging mode, the selecting aperture (e.g., spectrometer entrance aperture and its effective size at the plane of the specimen) is a limited factor.
- Delocalization **which is the ejection of an inner-shell electron by the passage of a high-energy electron some distance from the atom** is another limiting factor.

Diameter d_{50} contains 50% of the inelastic intensity.

$$d_{50}^2 = \left(\frac{0.5\lambda}{\theta_E^{0.75}}\right)^2 + \left(\frac{0.6\lambda}{\beta}\right)^2$$

For energy loss E= 50 eV, d_{50} is around 1 nm. For E= 300eV, d_{50} is around 0.4 nm.

That is why it is very challengeable for getting the atomic resolution EELS map using light elements (e.g. C and B).



Application of EELS

- **Identification of specific elements and concentration**
- **Identification of valence state of the elements.**
- **Determination of band gap, plasmon and other physics related phenomenon...**
- **…….**

Thank you for your attention!

Q.&A.