Chapter 9

Energy Dispersive X-ray spectrometer:

The Introduction and Application

(Chapter 32, 33)

9.1 X-ray analysis: Why bother?

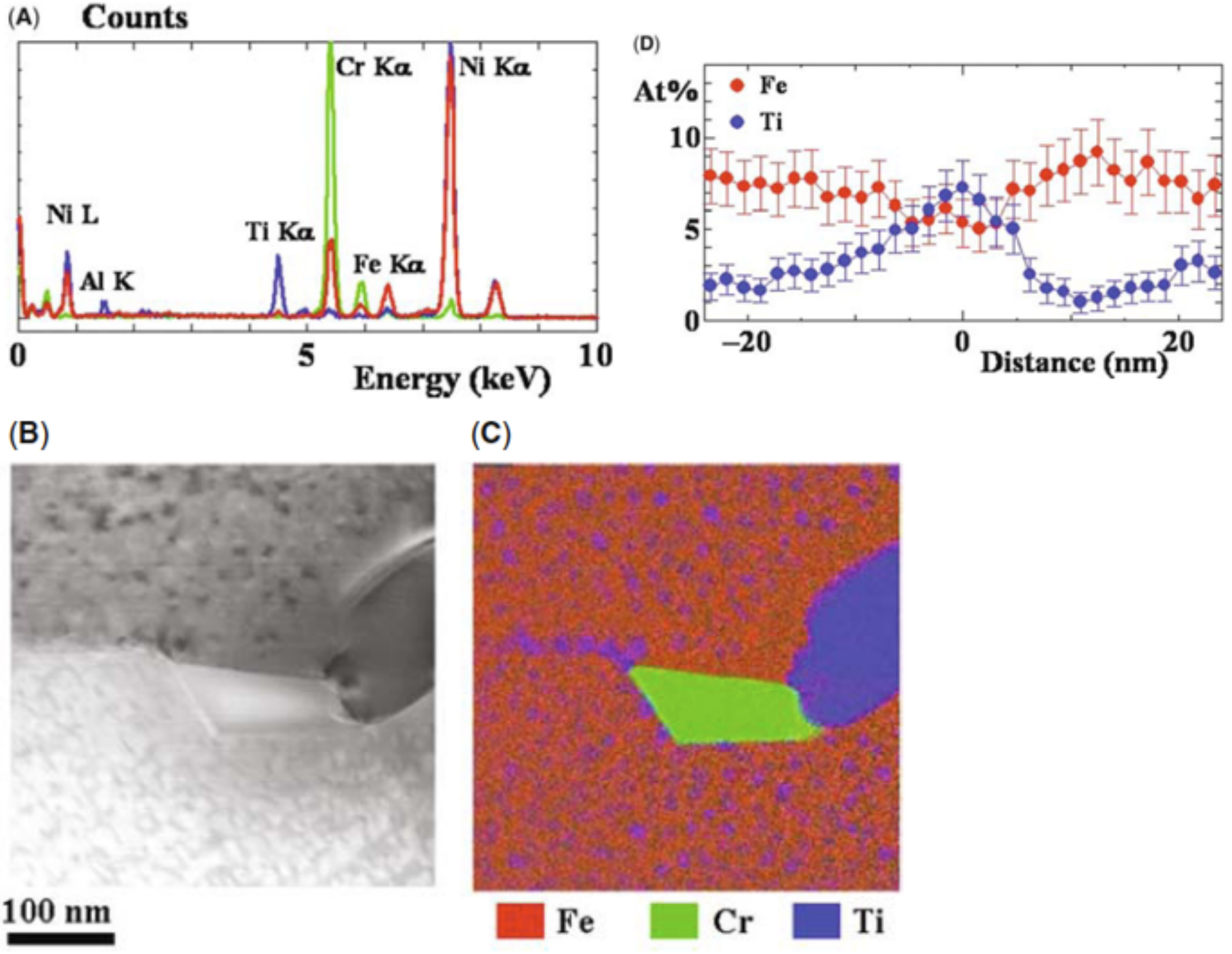
AEM: ***analytical electron microscope***

⇨ EDX: ***X-ray energy-dispersive spectrometer***

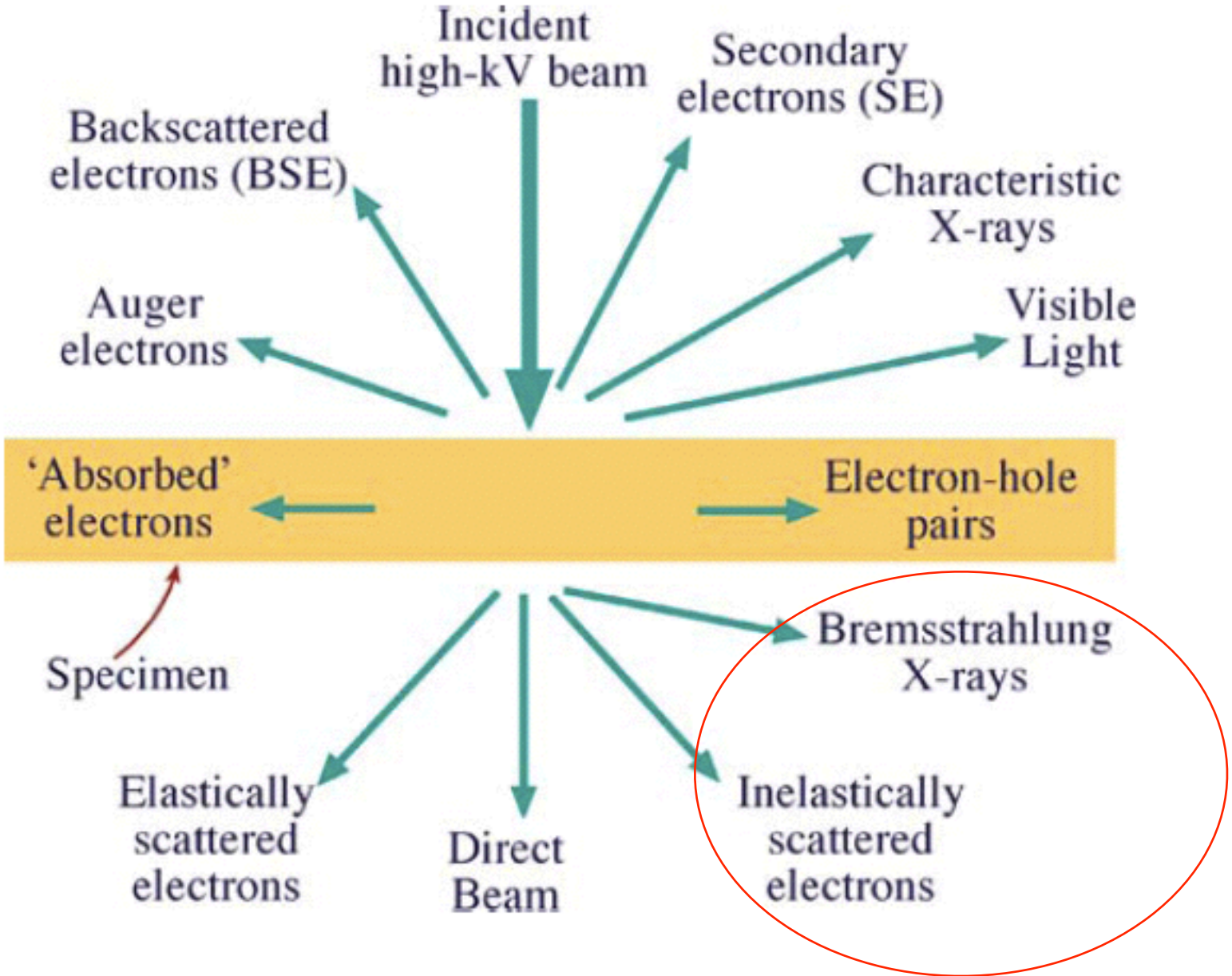
Why bother?

TEM gives us two-dimensional projected images of 3D transparent specimens.

The operator need substantial experience in order to interpret the images correctly.


(A)
Counts
Cr Kα
Ni Kα
Ni L
Ti Kα
Fe Kα
Al K
0
5
10
Energy (keV)
(D)
At%
Fe
Ti
10
5
0
−20
0
20
Distance (nm)
(B)
100 nm
(C)
Fe
Cr
Ti

9.2 TEM beam-specimen interactions and signals



X-RAY EMISSION

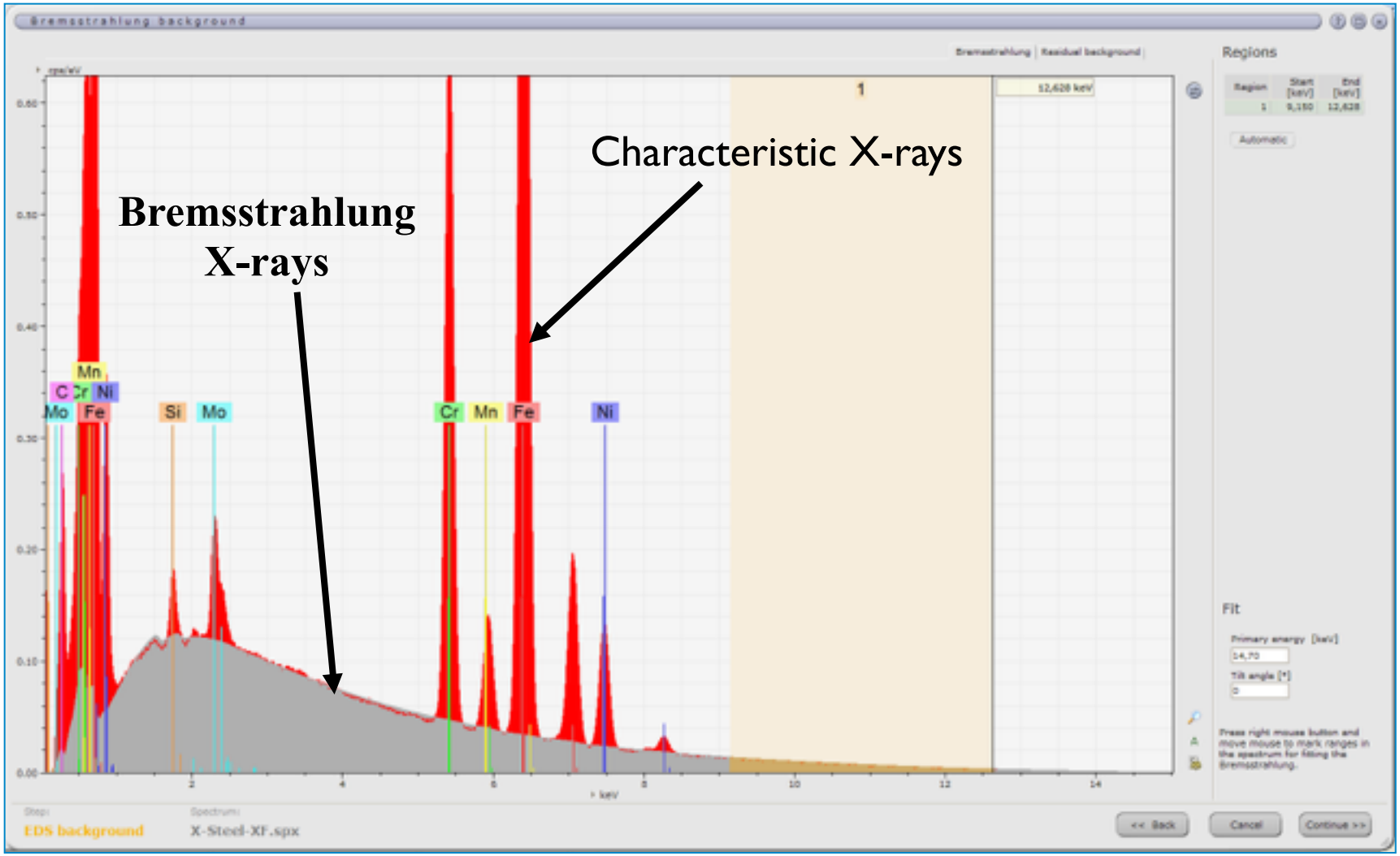
What we get from X-ray?

- Element constitute
- Quantify the amount of element

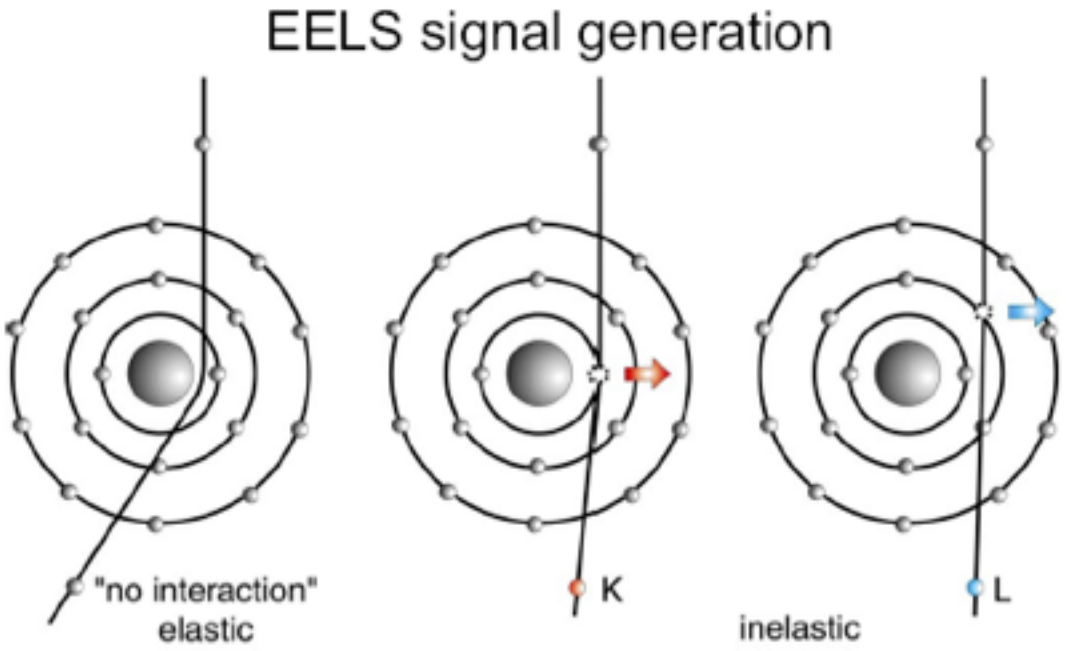
Two kinds of X-rays are produced:

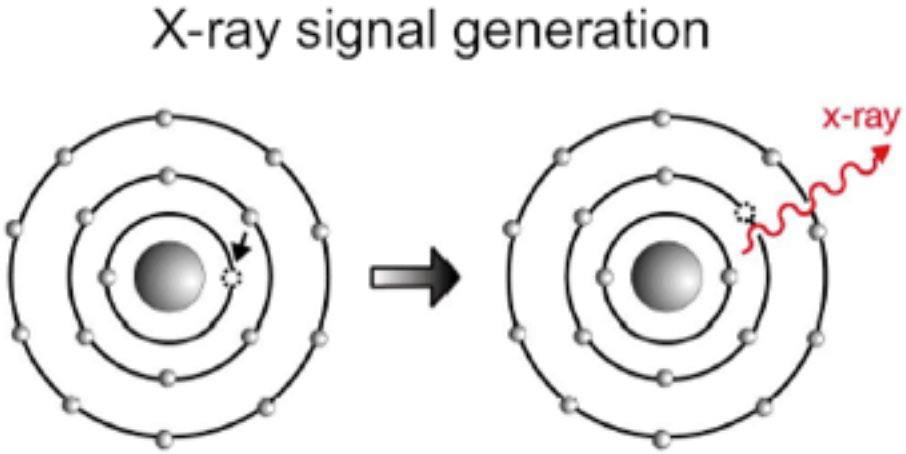
- Characteristic X-rays: useful to the materials scientist
- Bremsstrahlung X-rays: useful to the biologist

→ electron decelerated by the Coulomb field of the nucleus,it emits Bremsstrahlung X-ray.


Bremsstrahlung background
Bremsstrahlung | Residual background
Regions
Region
Start [keV]
End [keV]
1
9,150
12,628
Automatic
12,628 keV
1
Characteristic X-rays
Bremsstrahlung X-rays
Mn
C
Cr
Ni
Mo
Fe
Si
Mo
Cr
Mn
Fe
Ni
cps/eV
keV
Fit
Primary energy [keV]
14,70
Tilt angle [°]
0
Press right mouse button and move mouse to mark ranges in the spectrum for fitting the Bremsstrahlung.
Step:
EDS background
Spectrum:
X-Steel-XF.spx
<< Back
Cancel
Continue >>

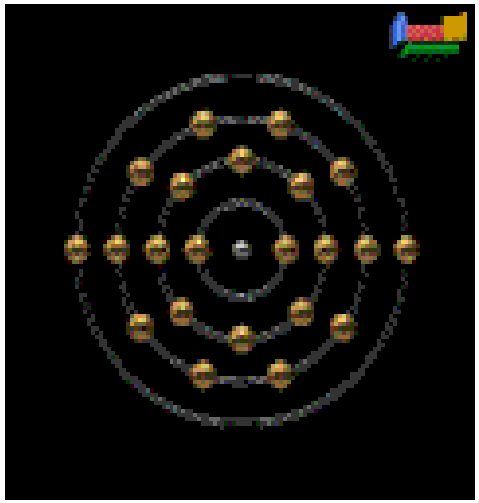
EELS and x-Ray Signal Generation

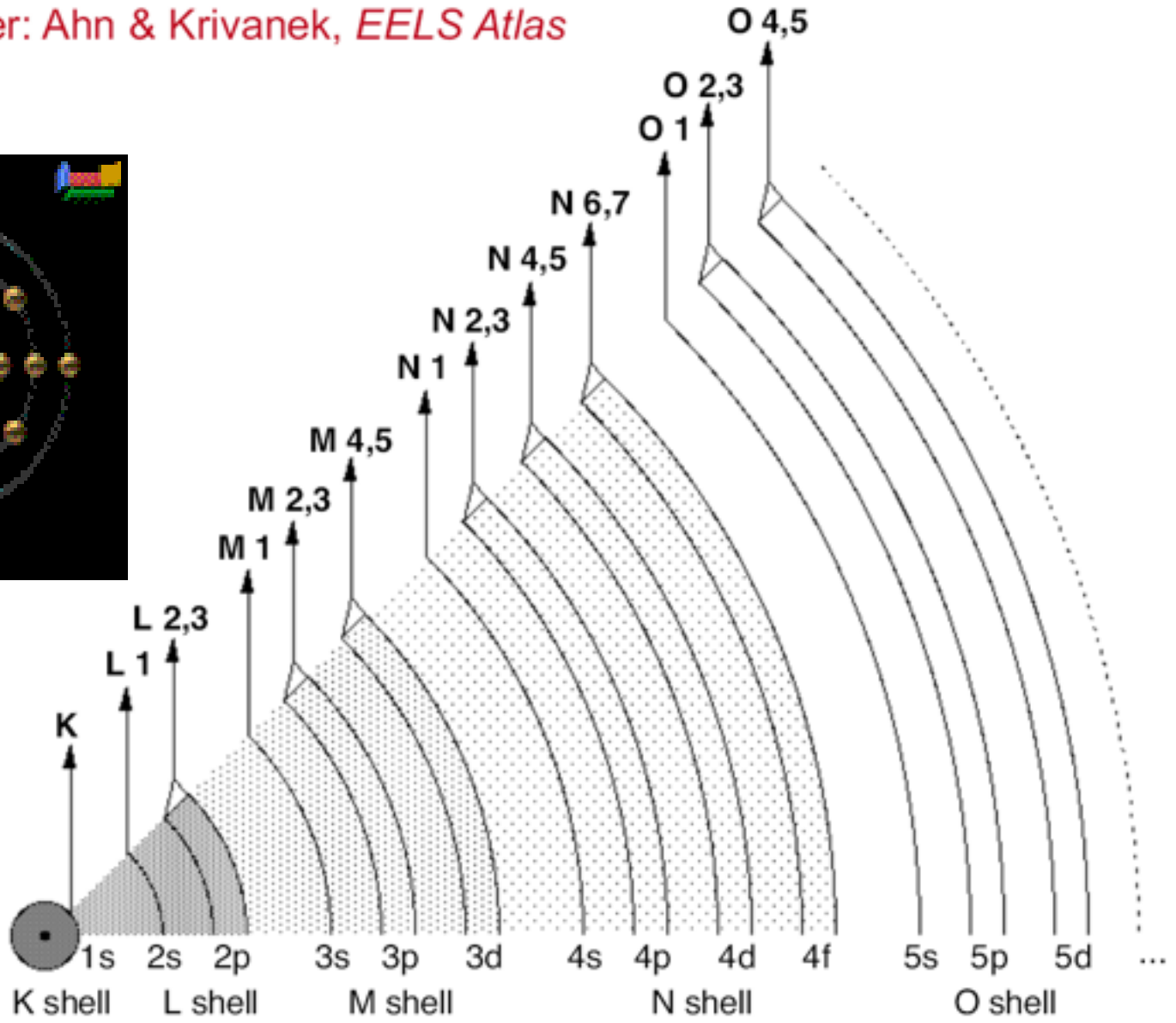




Nomenclature of EELS ionization edges

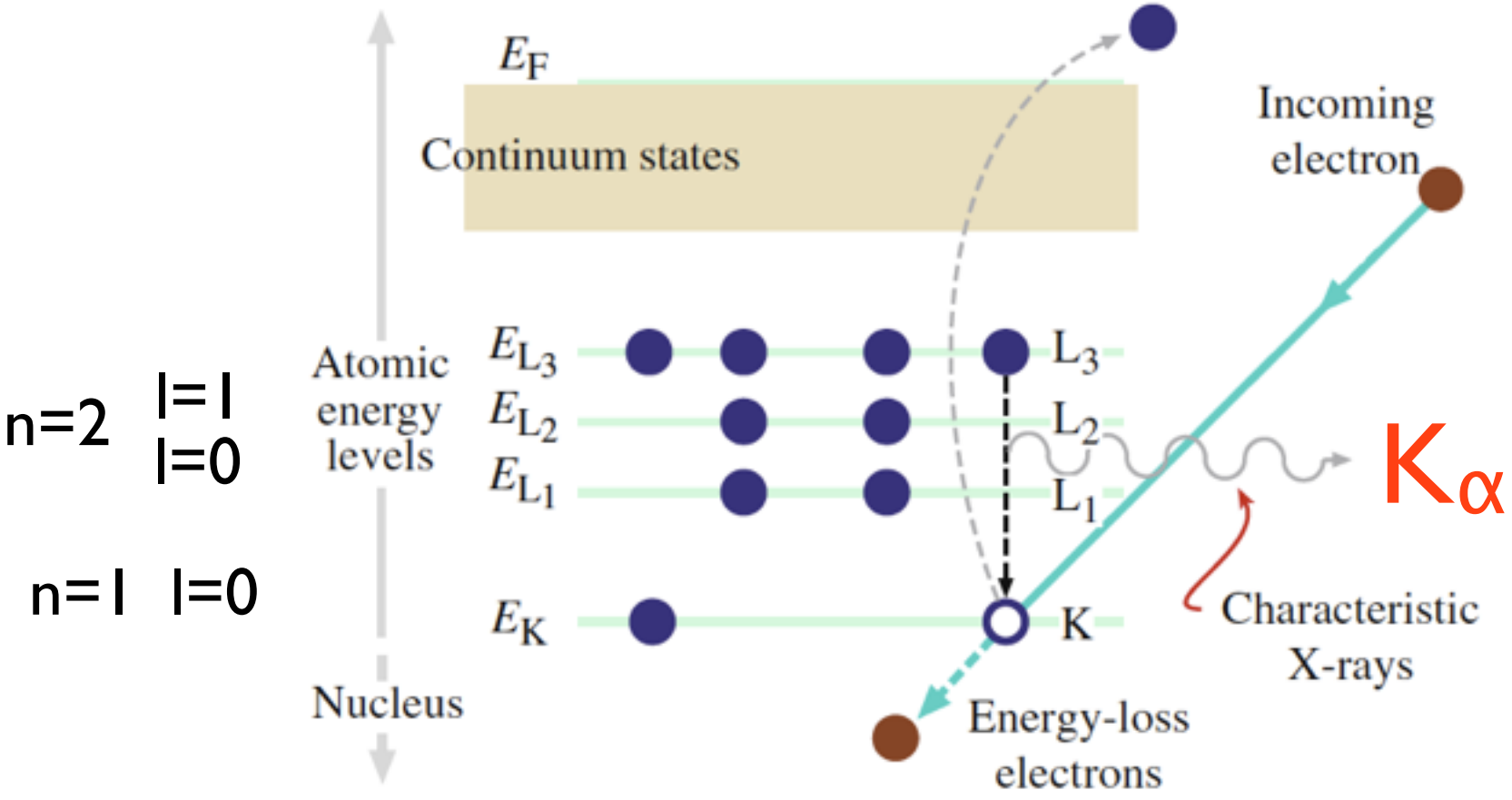
After: Ahn & Krivanek, *EELS Atlas*





CHARACTERISTIC X-RAYS

How to produce characteristic X-rays?



What are they "characteristic"?

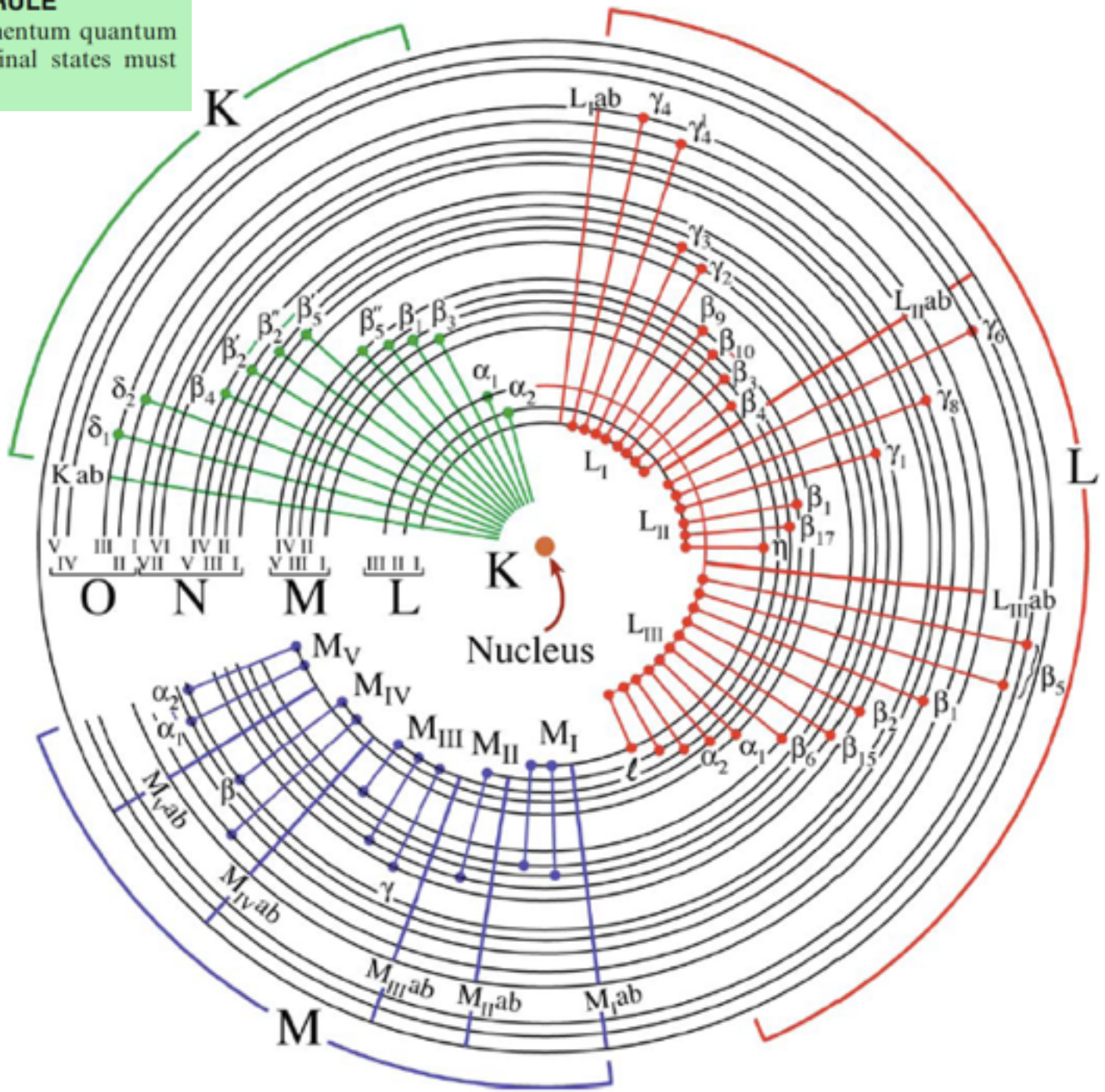
The energy of the emission is characteristic of the difference in energy of the two shells involved and is unique to the atom.

DIPOLE-SELECTION RULE

The change Δl in the angular momentum quantum number between the initial and final states must equal ± 1.

Electrons must obey when they jumped between shells

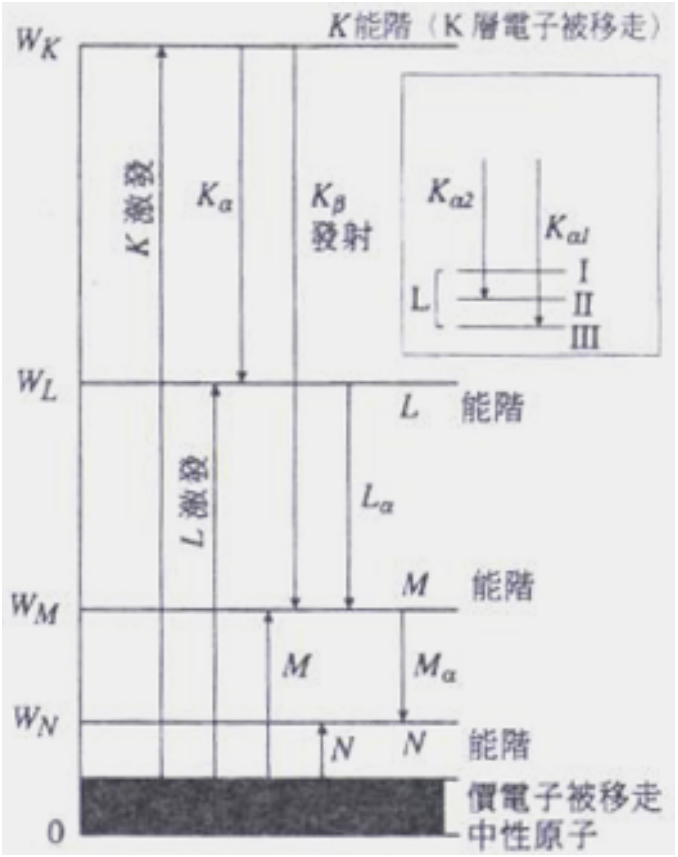
$\Delta l = \pm 1$, $\Delta ml = \pm 1, 0$



Selection rule: ELECTRON SHELLS

Electrons must obey when them jumped between shells ➡ $\Delta l = \pm 1$, $\Delta m_l = \pm 1, 0$

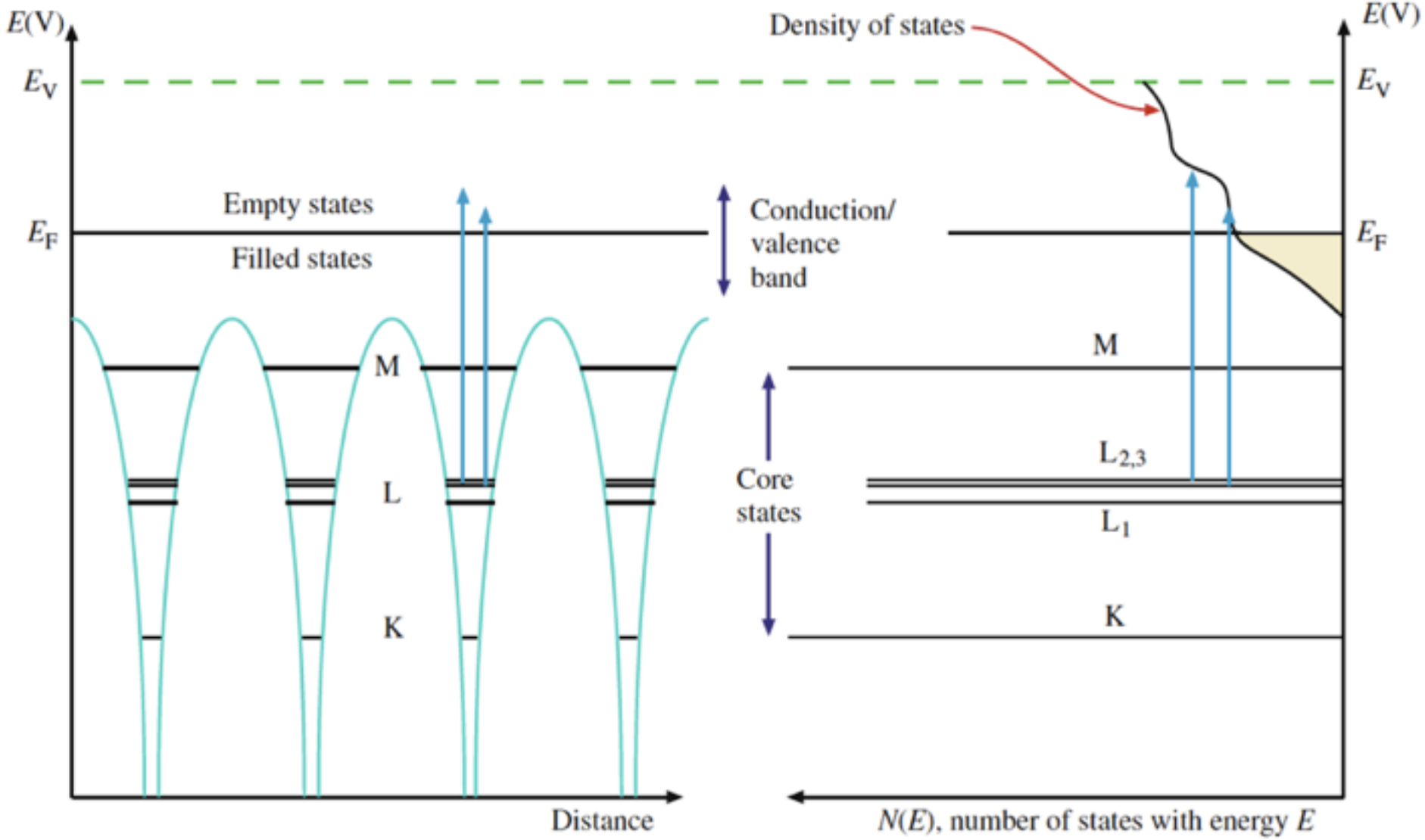
n l ml
1 0 0
2 0 0
3 0 0

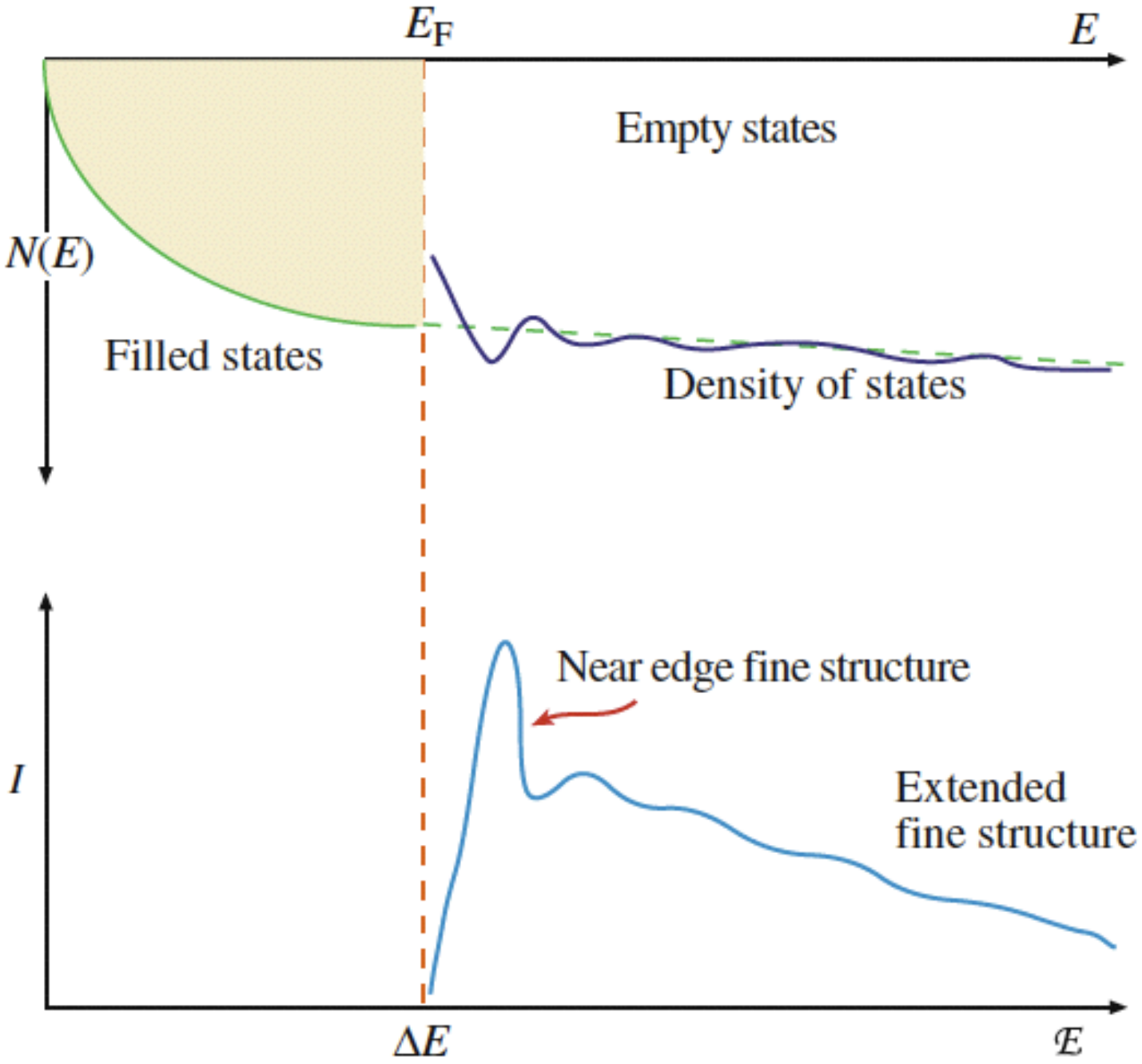


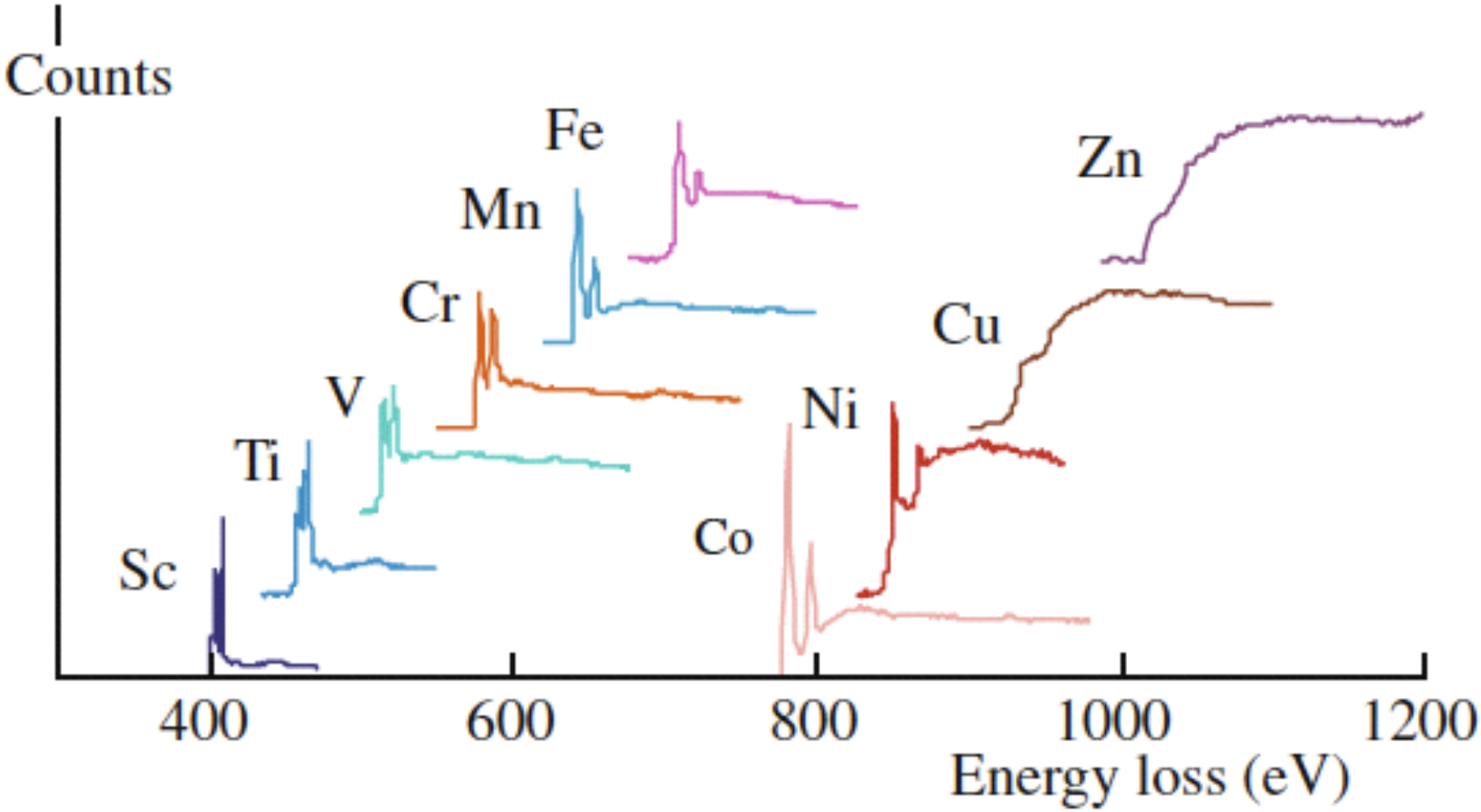
n l ml
2 0 0
2 1 0
2 1 ±1

DIPOLE-SELECTION RULE

The change Δl in the angular momentum quantum number between the initial and final states must equal ± 1.

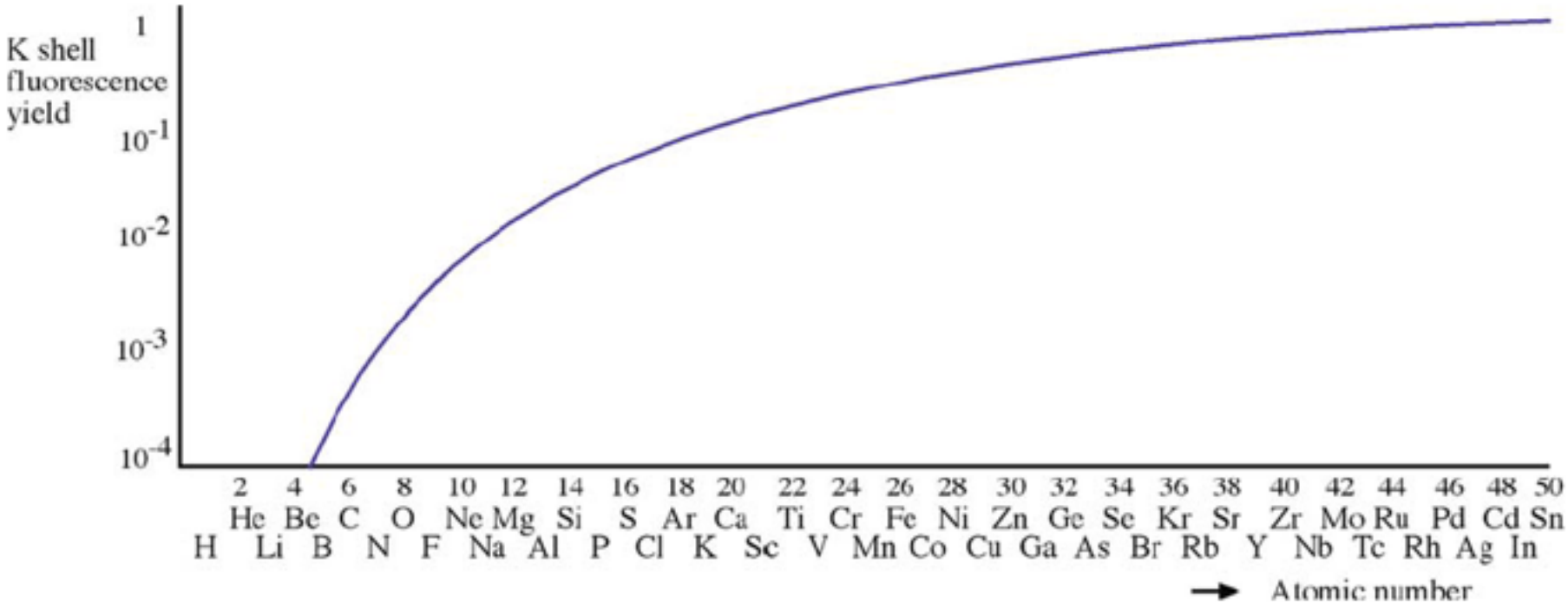

E(V)
E_V
E_F
Empty states
Filled states
M
L
K
Distance
Conduction/
valence
band
Core
states
Density of states
E(V)
E_V
E_F
M
$L_{2,3}$
L_1
K
N(E), number of states with energy E


E_F
E
Empty states
$N(E)$
Filled states
Density of states
I
Near edge fine structure
Extended
fine structure
ΔE
$\mathcal{E}$


Counts
Fe
Mn
Cr
V
Ti
Sc
Co
Ni
Cu
Zn
400
600
800
1000
1200
Energy loss (eV)

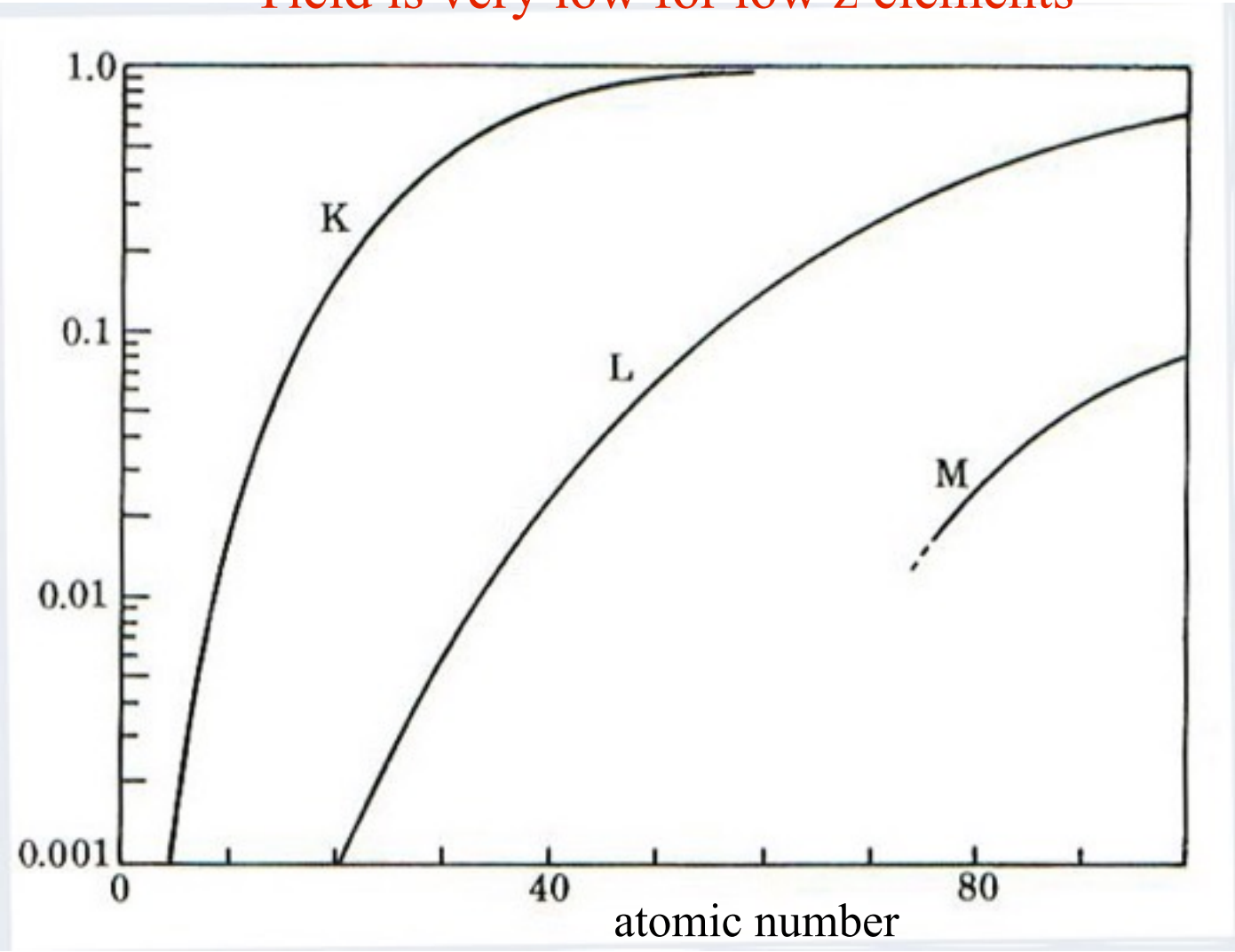
X-ray fluorescence yield

$$\omega = \frac{Z^4}{a + Z^4}$$



X-ray fluorescence yield (log scale) as a function of atomic number

Yield is very low for low z elements



9.3 EDX vs EELS

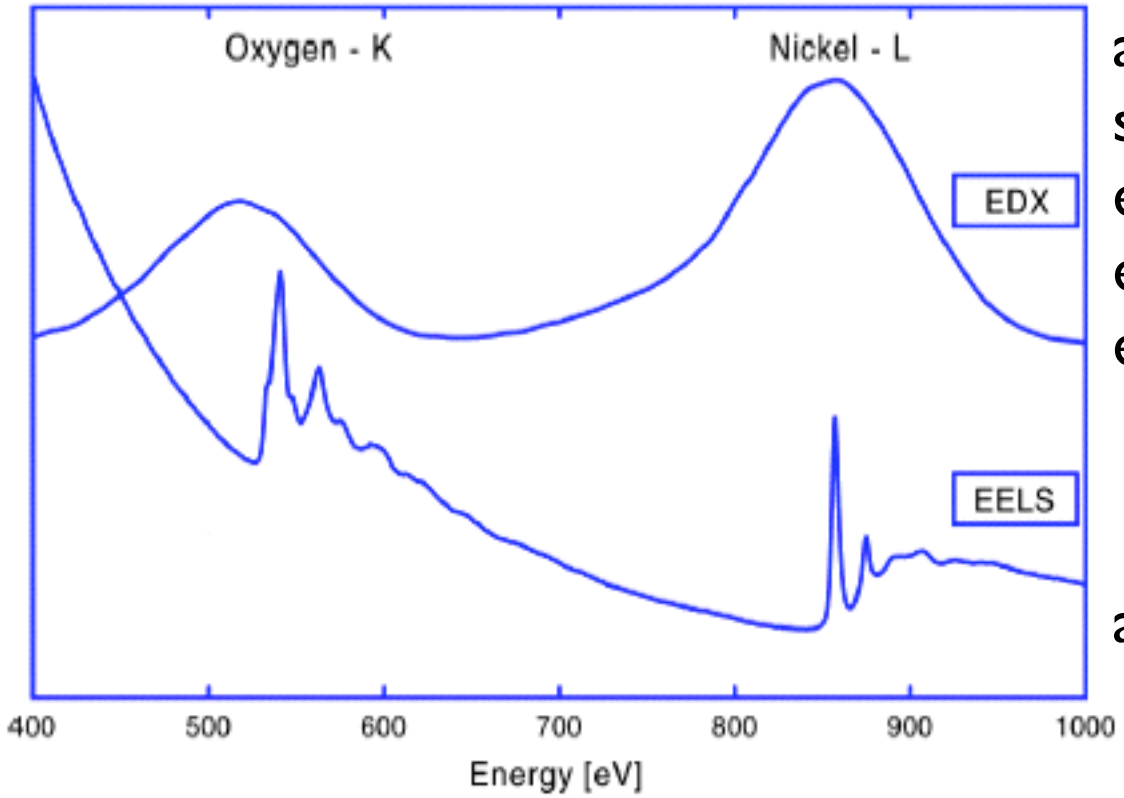
- The ***EELS*** is one step signal, while ***EDX*** is a two step signal (low x-ray fluorescence yield for low Z). In general, the yield rate of the EELS is higher than EDX.

- the signal of EELS concentrates in a small angle range of the transmitted beam, but the EDX signal spans around larger angle range.

(a) These two cause EELS has higher core loss signal
(higher Signal to noise ratio, EELS has less recording time)

X-ray and EELS spectra

(b) EDX has better Signal/ background ratio

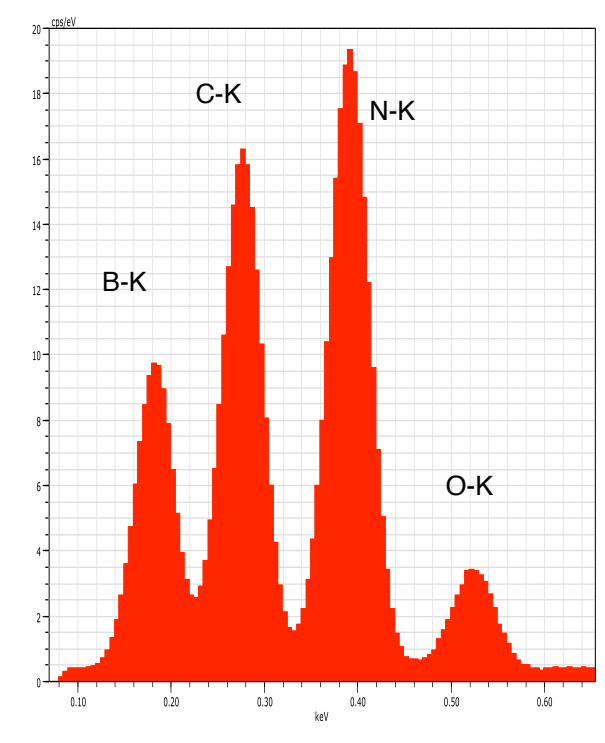


Background of EELS:
arises from the inelastic scattering from the atomic electron whose binding energy less than the edge energy

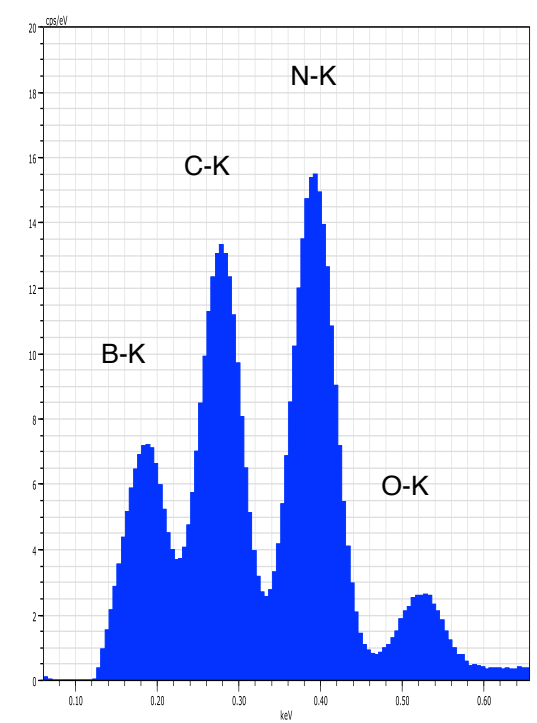
Background of EDX:
arises from bremsstrahlung

Influence by Resolution changing @ different ICR

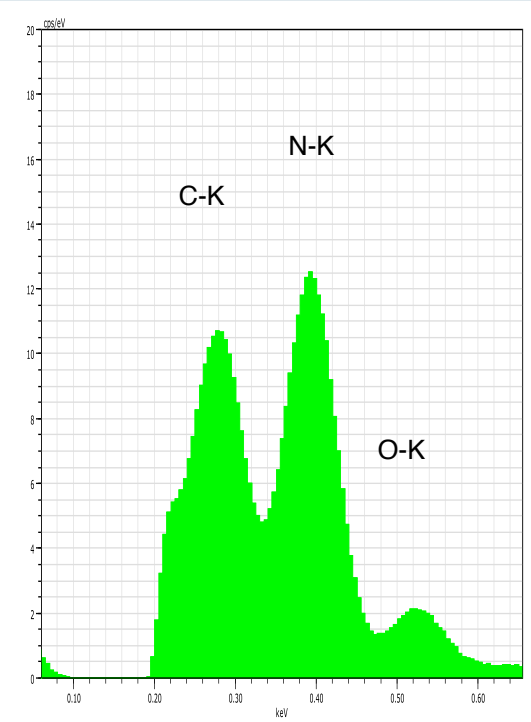
125eV

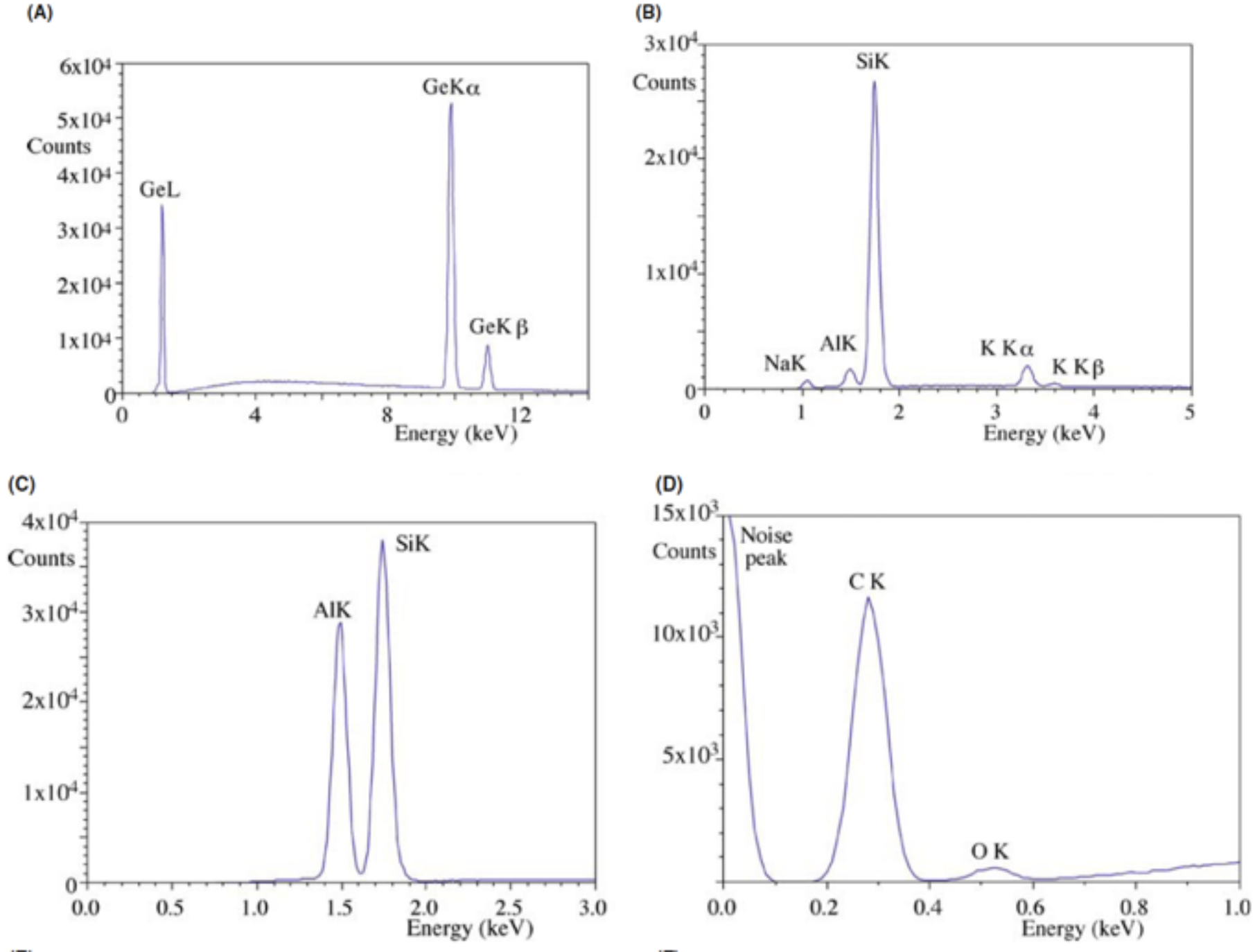


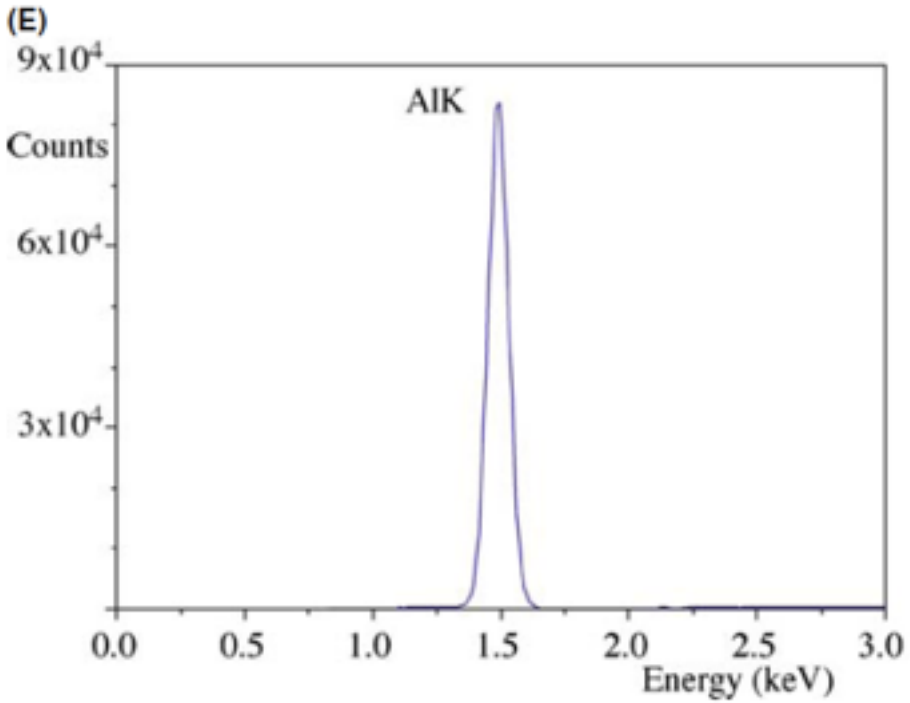
133eV

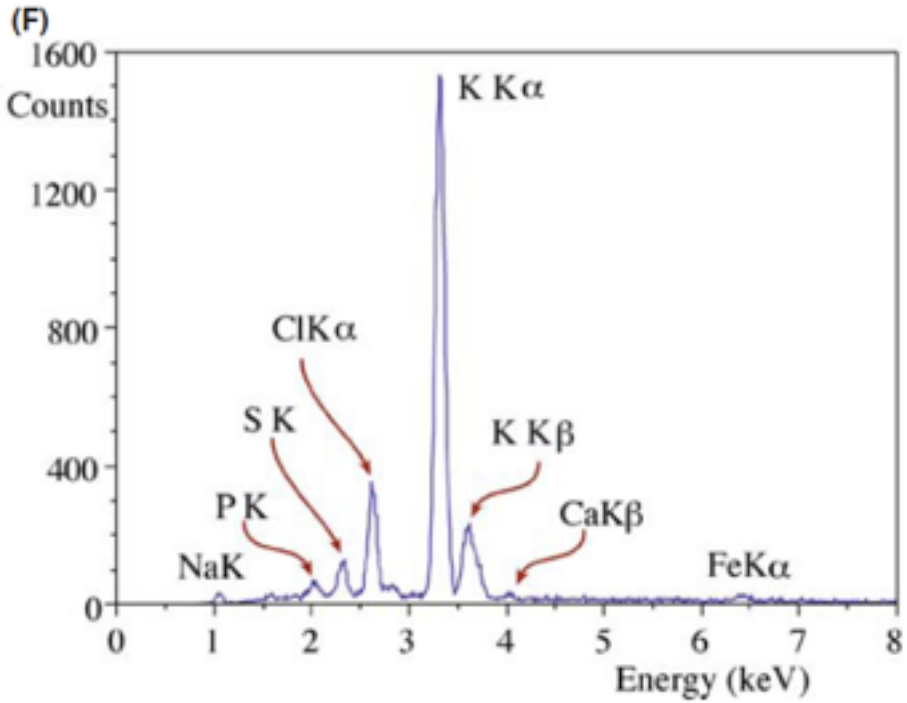


140eV




(A)
6x10⁴
5x10⁴
Counts
4x10⁴
3x10⁴
2x10⁴
1x10⁴
0
GeL
GeKα
GeKβ
0
4
8
12
Energy (keV)
(B)
3x10⁴
Counts
2x10⁴
1x10⁴
0
SiK
NaK
AlK
K Kα
K Kβ
0
1
2
3
4
5
Energy (keV)
(C)
4x10⁴
Counts
3x10⁴
2x10⁴
1x10⁴
0
AlK
SiK
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Energy (keV)
(D)
15x10³
Counts
10x10³
5x10³
Noise peak
C K
O K
0.0
0.2
0.4
0.6
0.8
1.0
Energy (keV)


(E)
9x10^4
Counts
6x10^4
3x10^4
AlK
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Energy (keV)


(F)
1600
Counts
1200
800
400
0
K Kα
ClKα
S K
K Kβ
P K
CaKβ
NaK
FeKα
0
1
2
3
4
5
6
7
8
Energy (keV)

9.4 The Energy-Dispersive Spectrometer

3 COMPONENTS

The three main parts of an XEDS system are

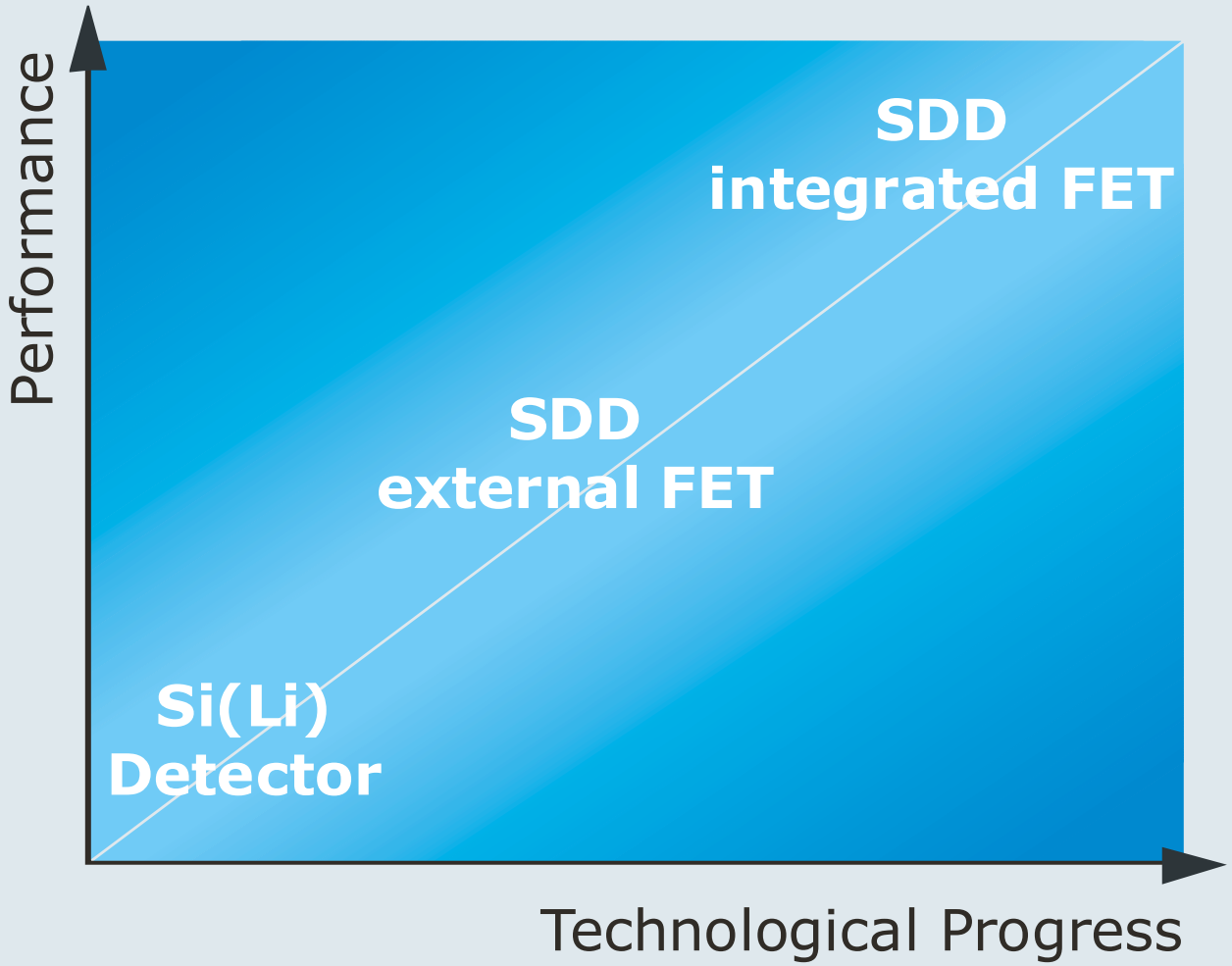
(i) the detector

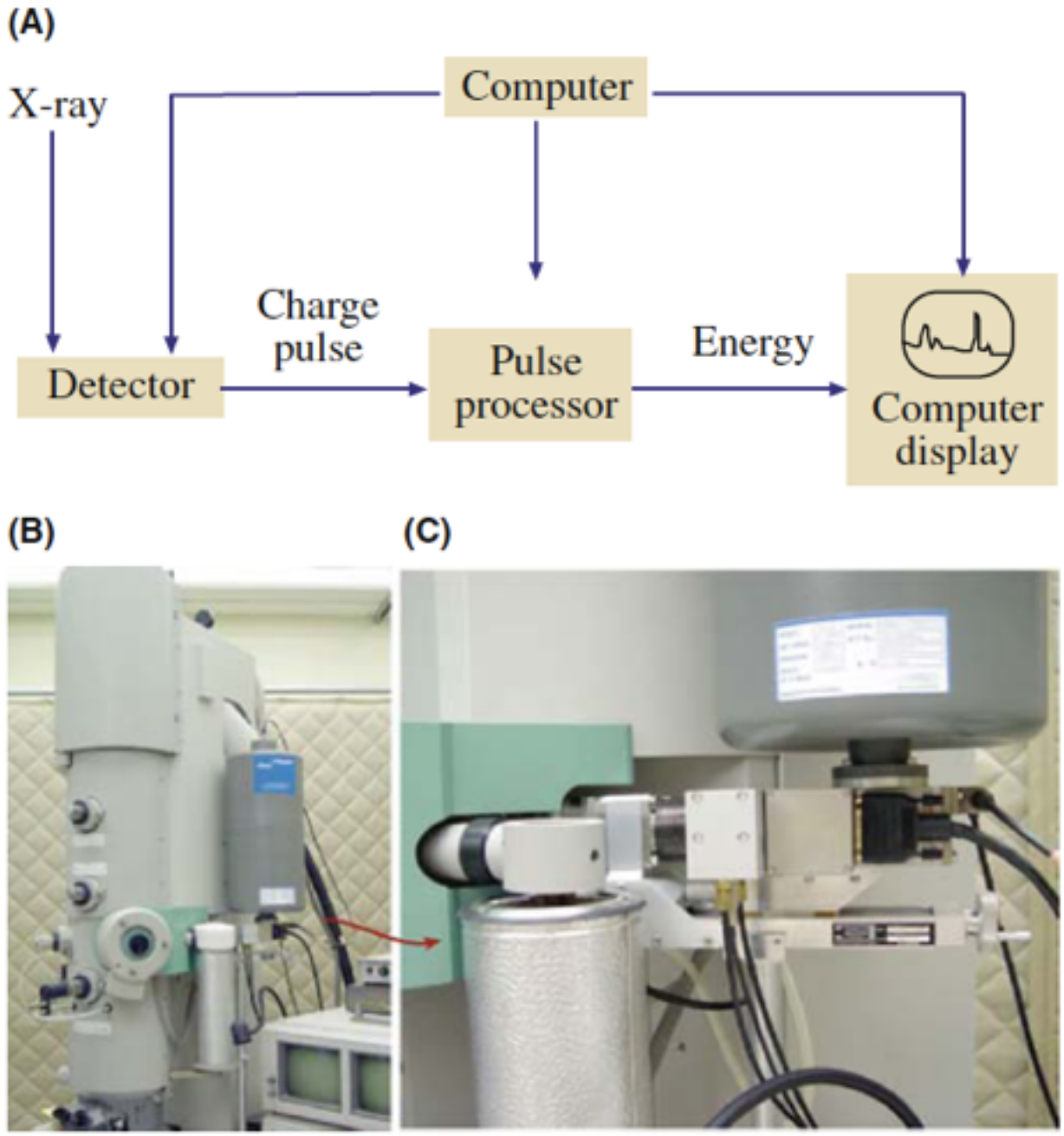
(ii) the processing electronics

(iii) the computer

Si(Li) detector and SDD (Silicon Drift Diode)

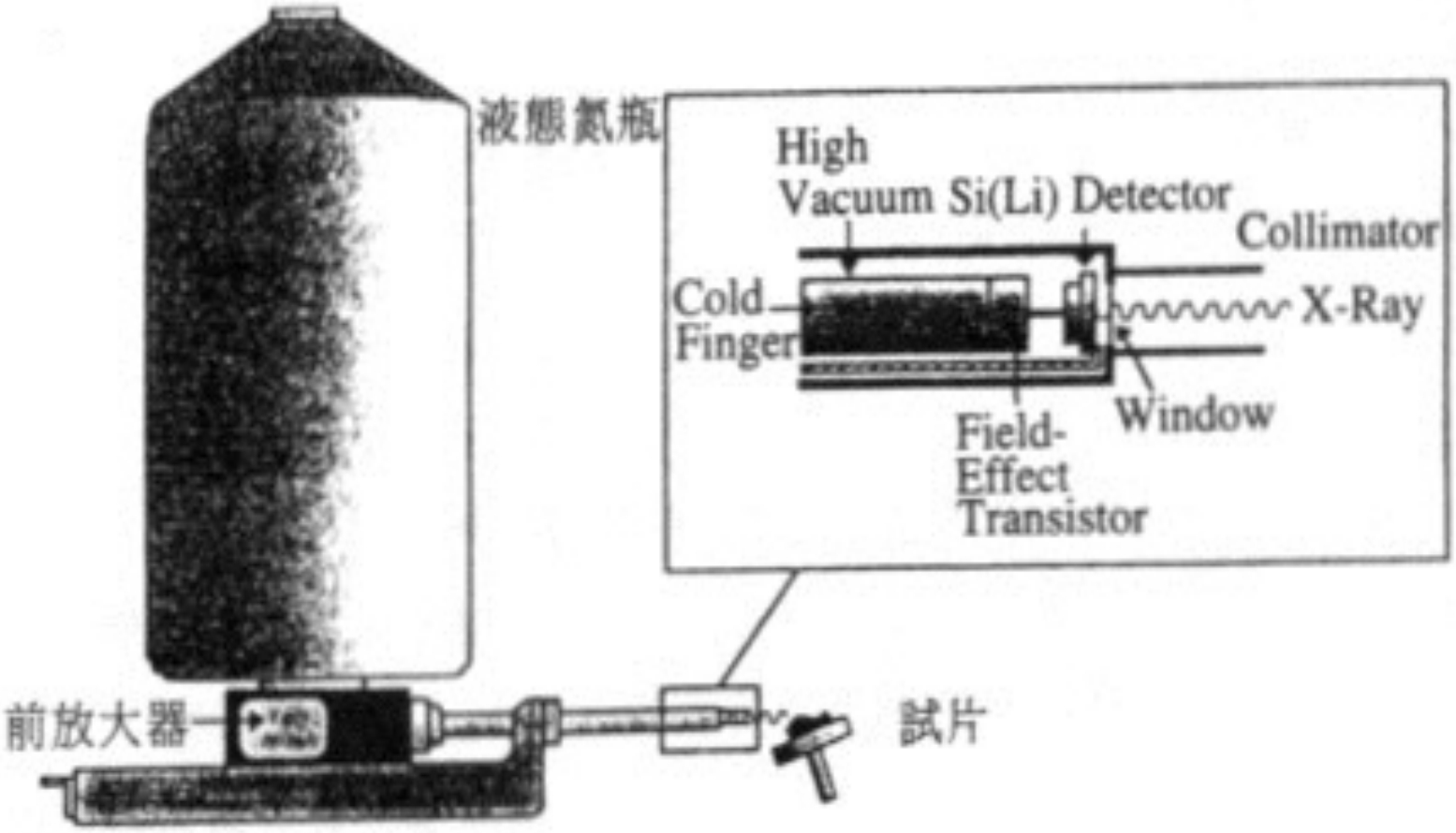
Detector Types

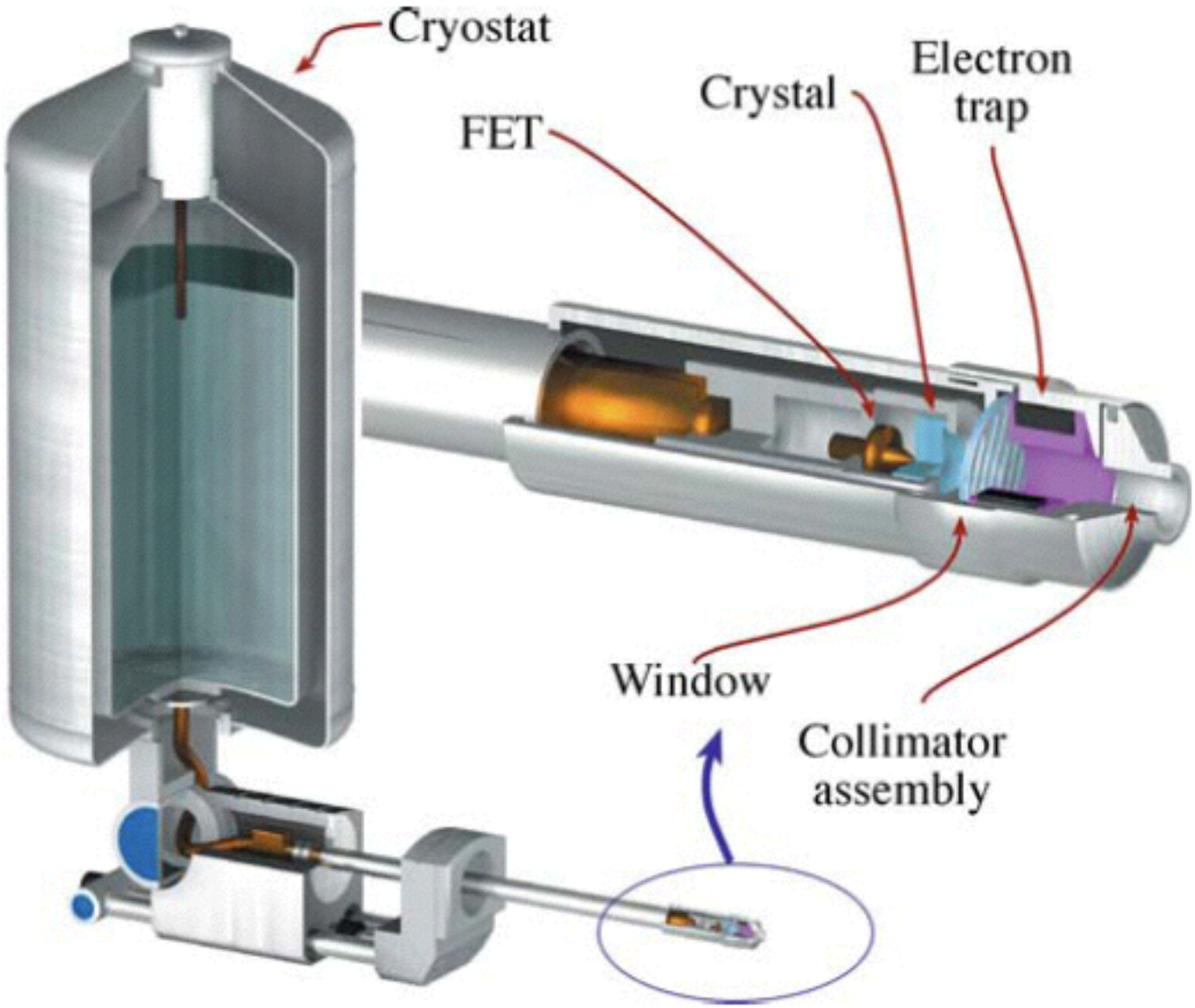


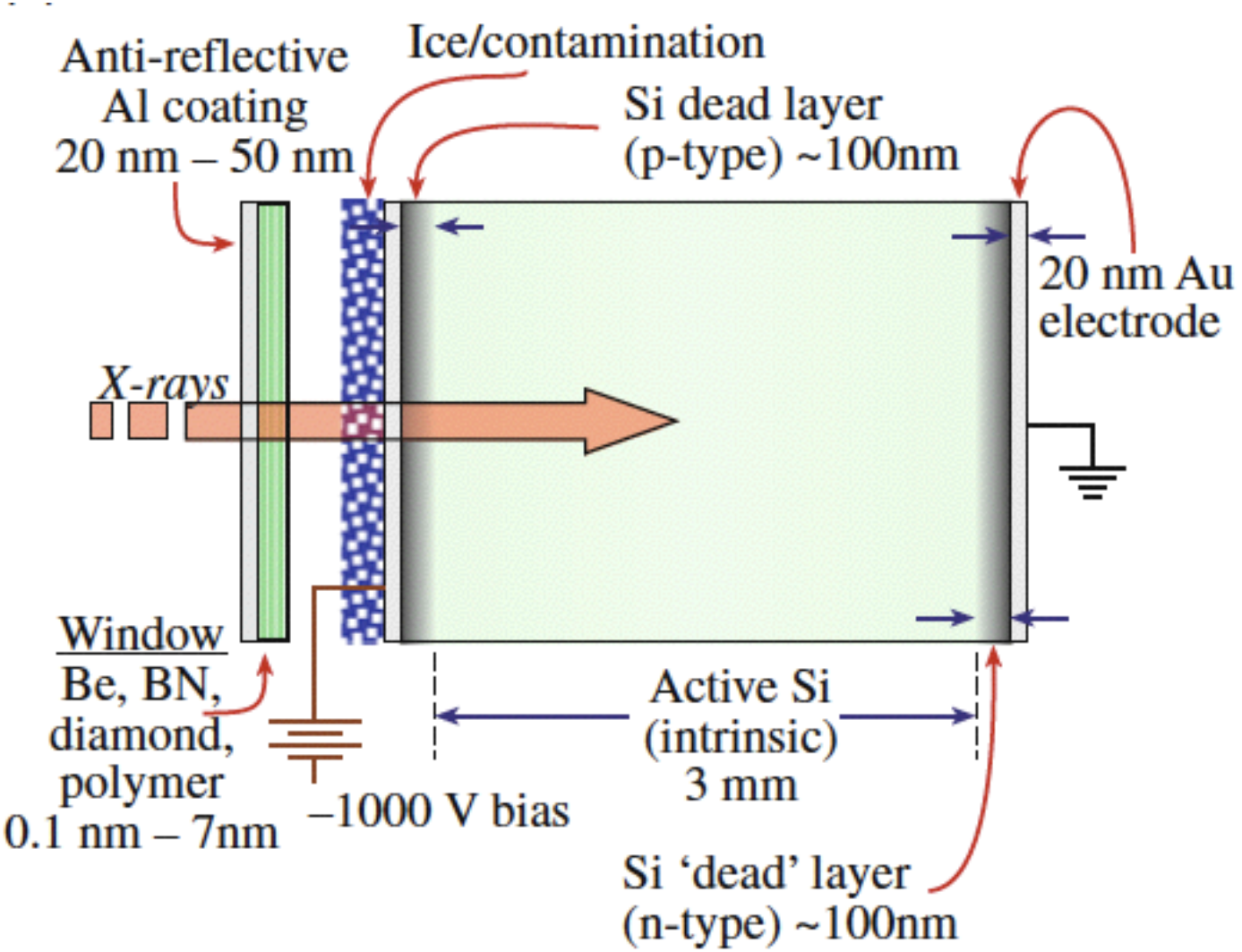

(A)
X-ray
Computer
Charge pulse
Energy
Detector
Pulse processor
Computer display
(B)
(C)

9.4.1 Semiconductor Detector

The XEDS produces spectra which are plots of X-ray counts versus X-ray energy.



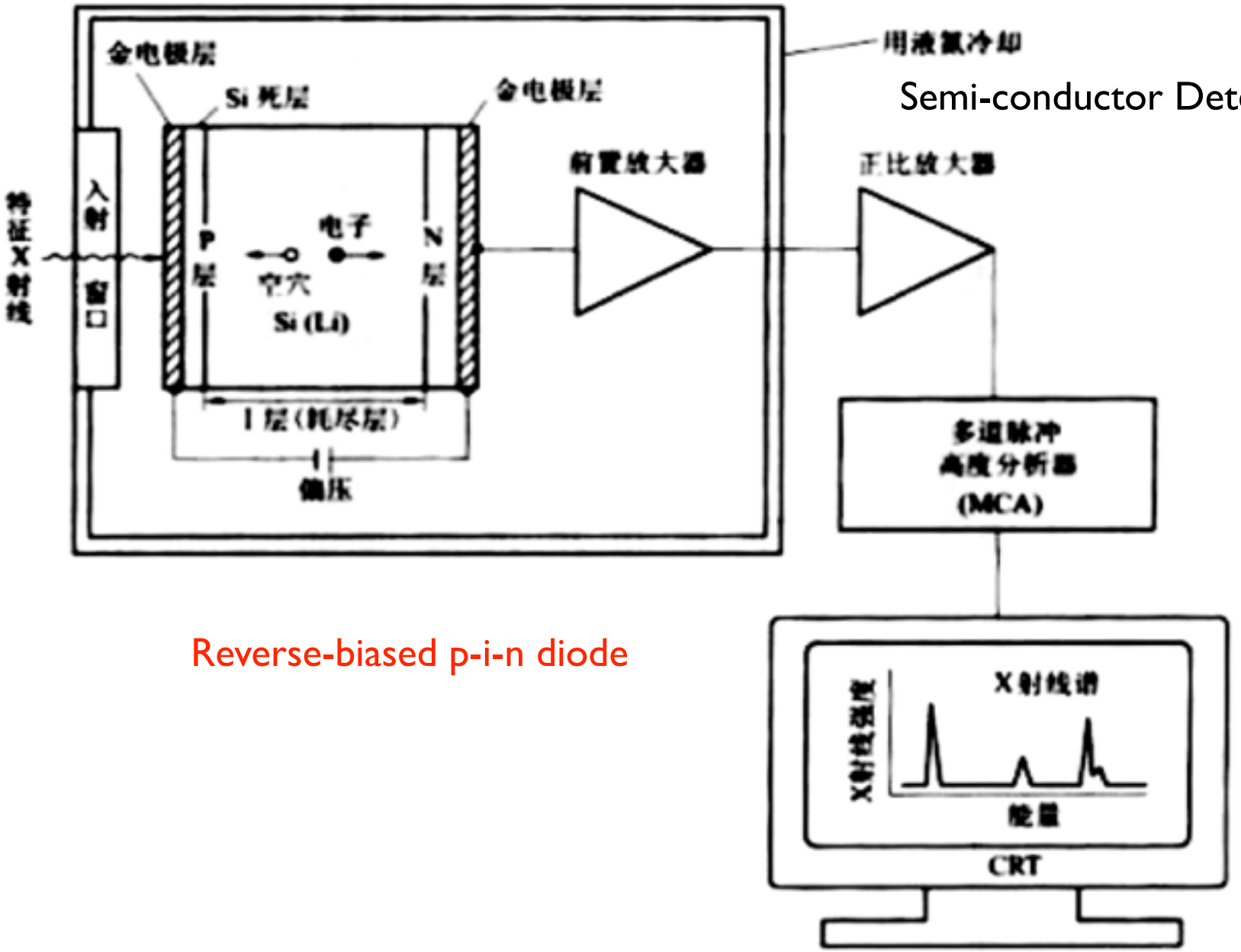

Cryostat
FET
Crystal
Electron trap
Window
Collimator assembly



Usually, Si contains p-type impurity,

We usually compensate with Li to create Intrinsic Si. Si(Li) is operated under LN2 temperature to prevent Li drift

• Si(Li) detector



Semi-conductor Detector Si(Li)

Reverse-biased p-i-n diode

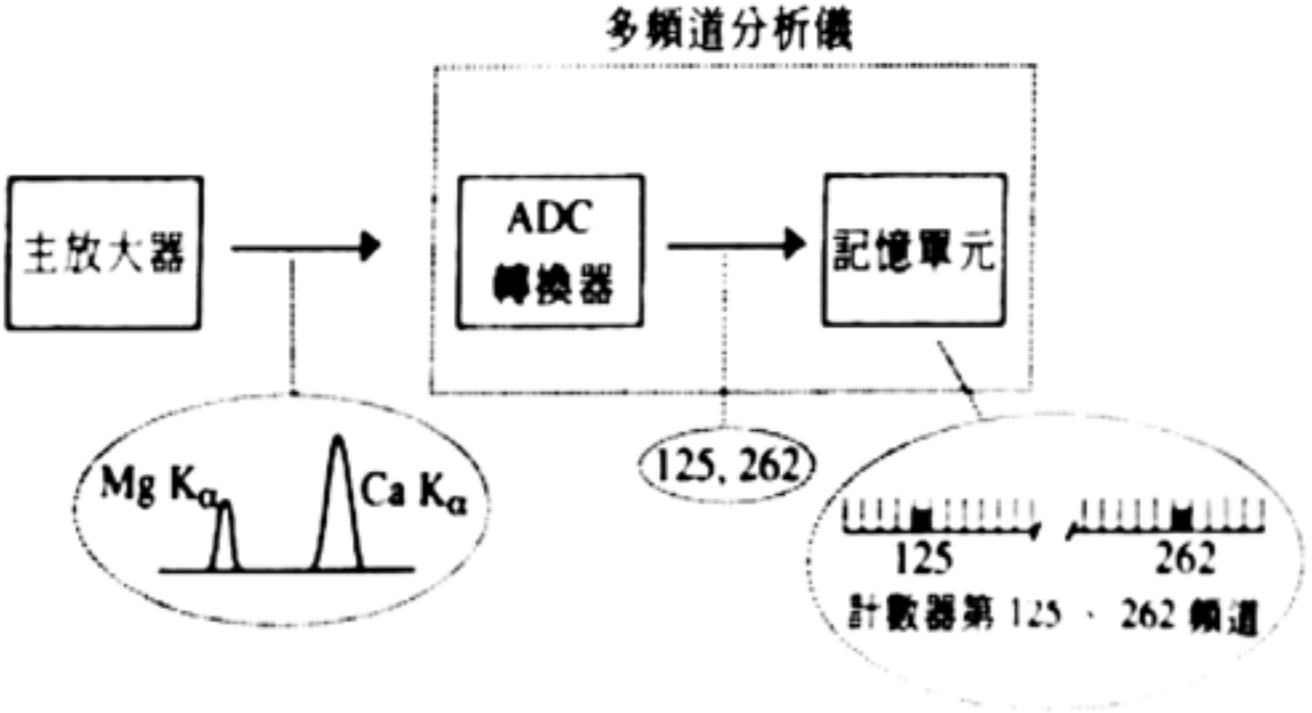
3.8 eV

It takes ~3.8 eV to generate an electron-hole pair in Si, so a Be K_α X-ray will create at most ~29 electron-hole pairs, giving a charge pulse of $\sim 5 \times 10^{-18}$ C!

(a) The energy required for the e-h transfer in Si at LN2 temperature is ~ 3.8eV (this is not the band gap energy, but from statistical)

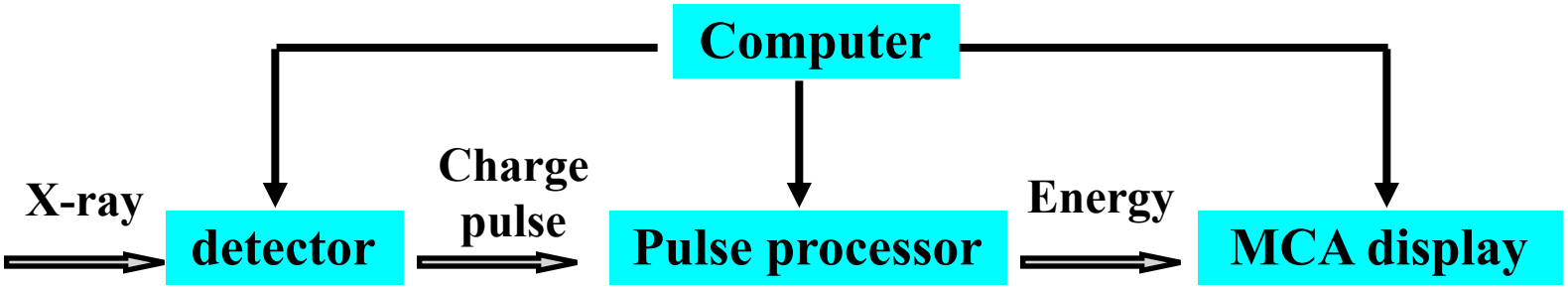
(b) Characteristic X-ray has energy exceeding 1keV that is enough to generate thousands of e-h pairs

(c) The number of e-h pair is proportional to the energy of incoming x-ray



The three main parts of the XEDS system are …

1. detector 2. Processing electronics 3. MCA display



On/ off

(Analyze one x-ray photon at a time)

MCA: ***multi-channel analyzer***

The detector generates a charge pulse proportional to the energy of X-ray

The pulse is first converted to a voltage (detector is off)

The signal is then amplified throught a field effect transistor (FET): detector is off

The EDX detector device

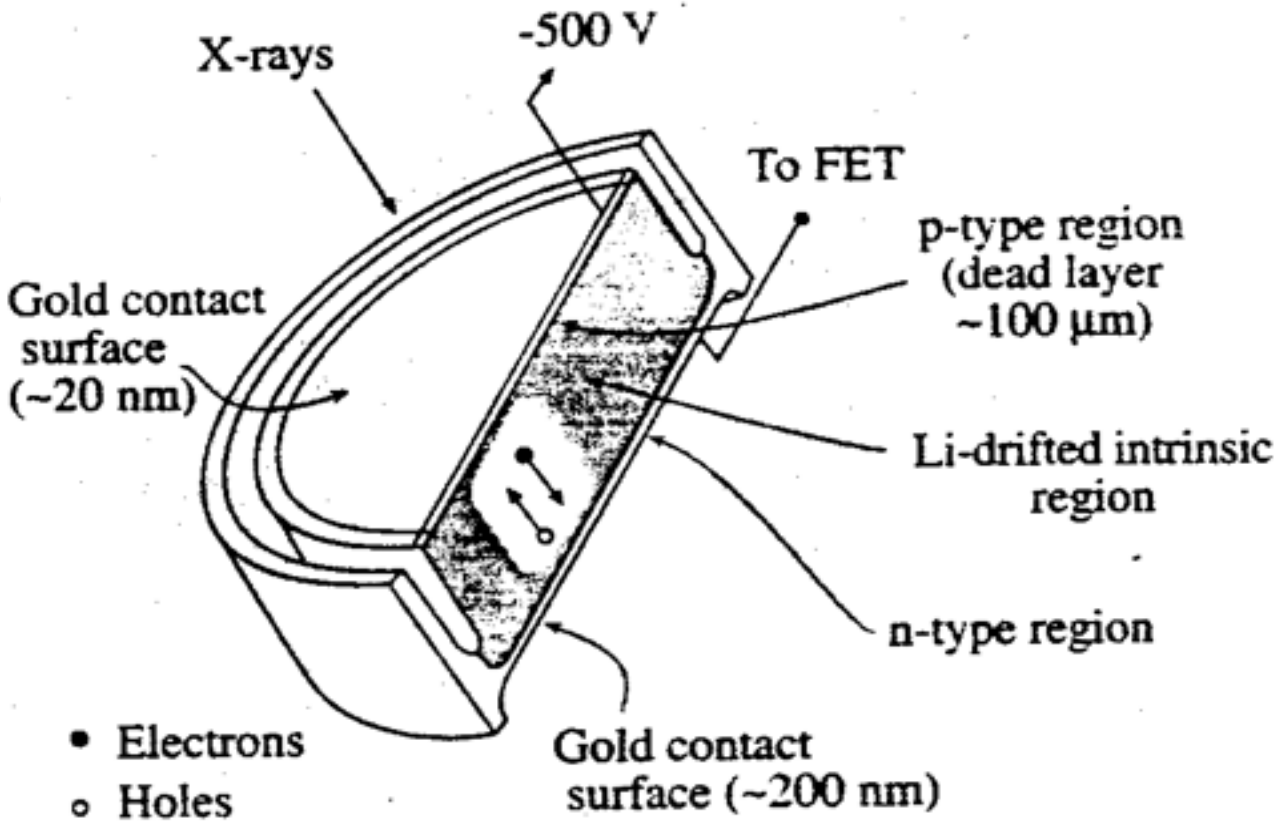
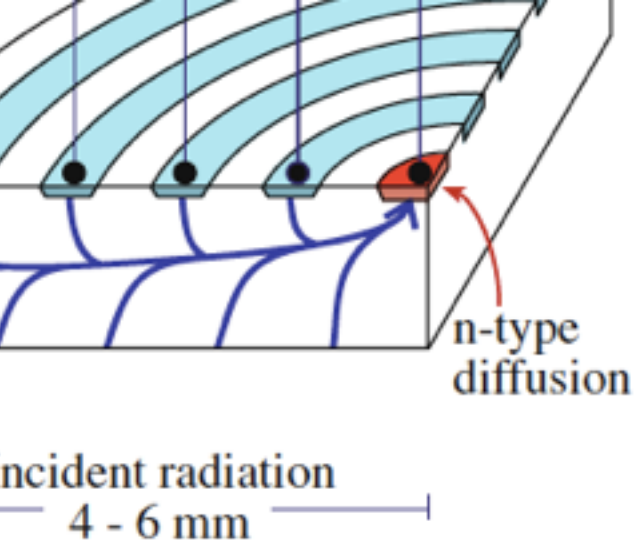
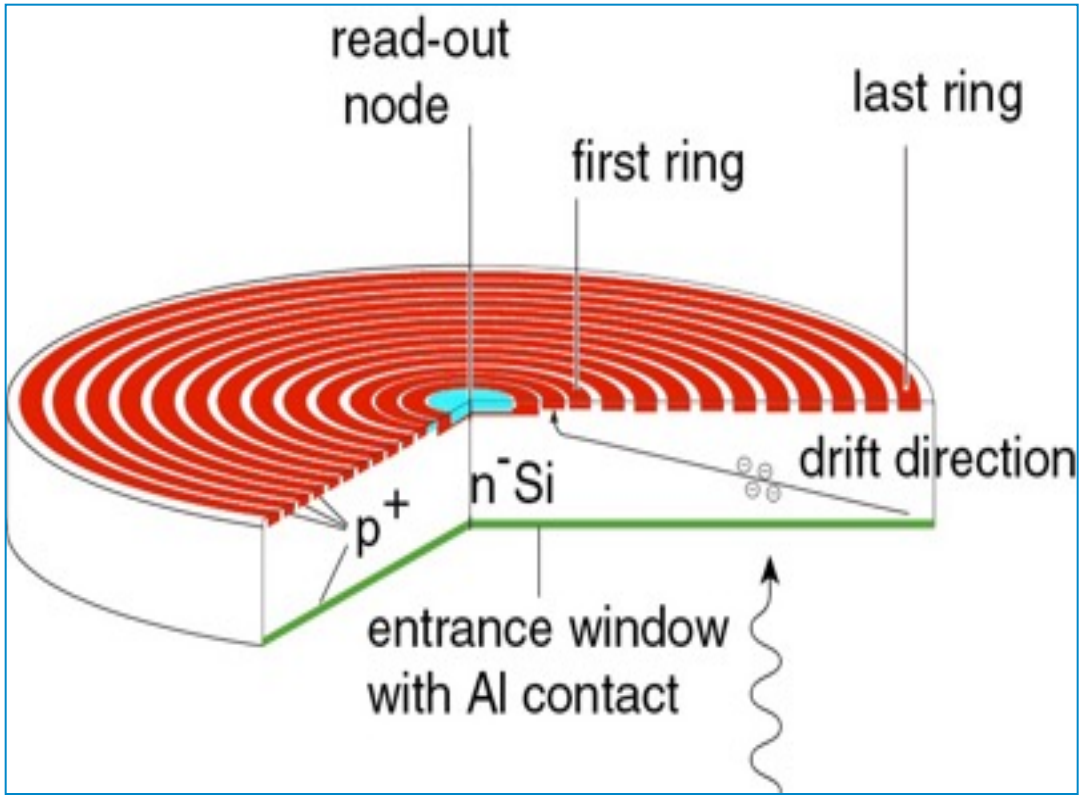


Figure 32.4. Cross section of a Si(Li) detector. The incoming X-rays generate electron–hole pairs in the intrinsic Si which are separated by an applied bias. A positive bias attracts the electrons to the rear ohmic contact after which the signal is amplified by an FET.



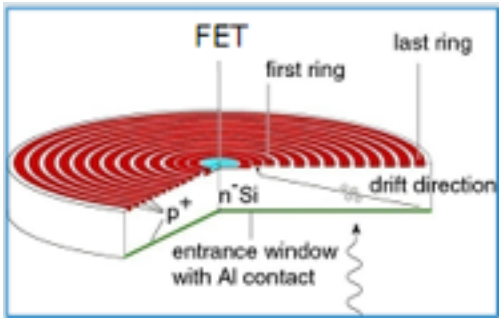
SDD

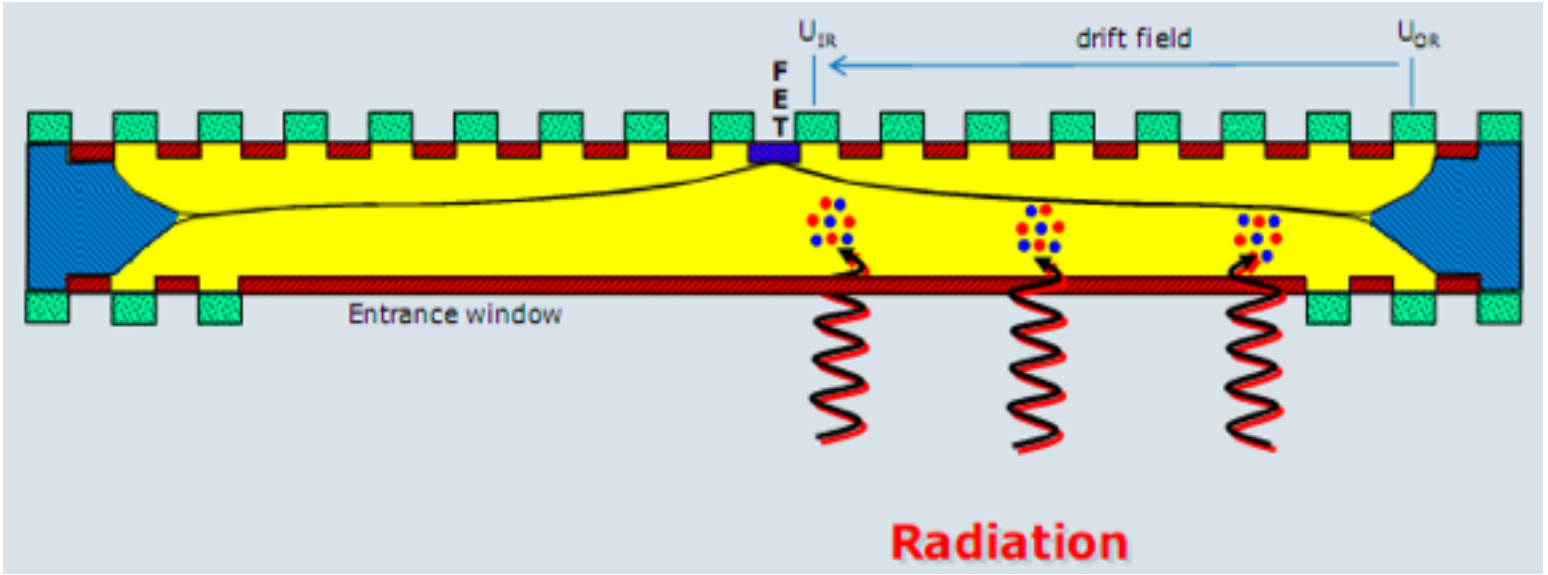
Silicon Drift Diode



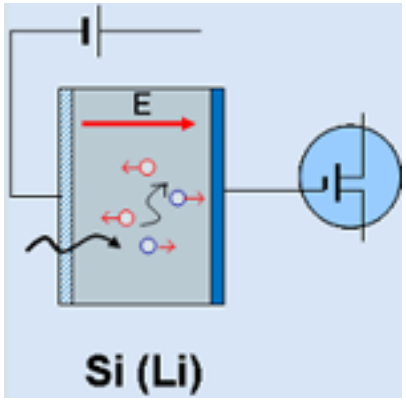
How does the SDD work?

- X光打到此元件時，會產生電子雲，
- 在內環與外環加不同的電壓，形成Drift Field，電子雲自然會向中間電極處移動。

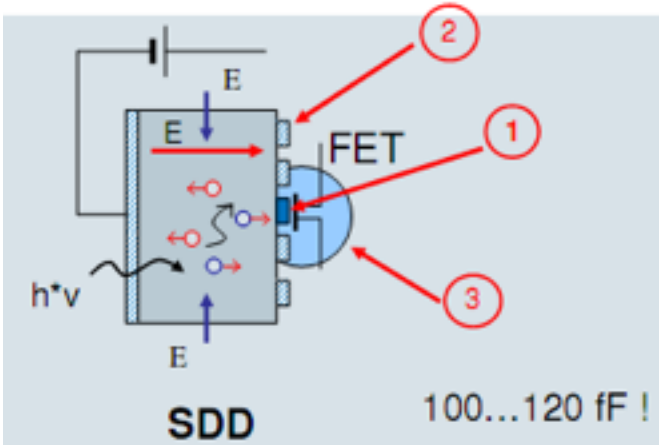




Si- based detector (schematic)



- Si(Li)是由整塊的Silicon去doping Li。當X光打進去時，會產生電子電洞對，電子會向陽極跑去(整個晶體的面都是陽極)，為了要減少雜訊，所以要將電極冷卻到-180度，並且是外接式的FET電晶體



- SDD是個半導體製程的元件，用半導體製程來減少陽極的面積，並且做出了drift ring，這協助電子團移動到設計的陽極處。所以可以用-20度來冷卻，也因此，可以將FET做在同一個半導體元件內。

Windows types:

- **Beryllium (Be) window detector:**

  The thickness of Be is about 7~12μm, it is too thick to detect x-ray. The x-ray energy less than ~1keV are strongly absorbed. Therefore the K_α of Z<11 can't detect.(like B, C, N and O)

- **Ultrathin window(UTW, ATW) detector:**

  The thickness of UTW is usually <100 nm and the composition of polymer, diamond, boron or silicon nitride. The newer UTW like ultrathin diamond or BN or Al/polymer can withstand atmospheric pressure, termed ATWs.

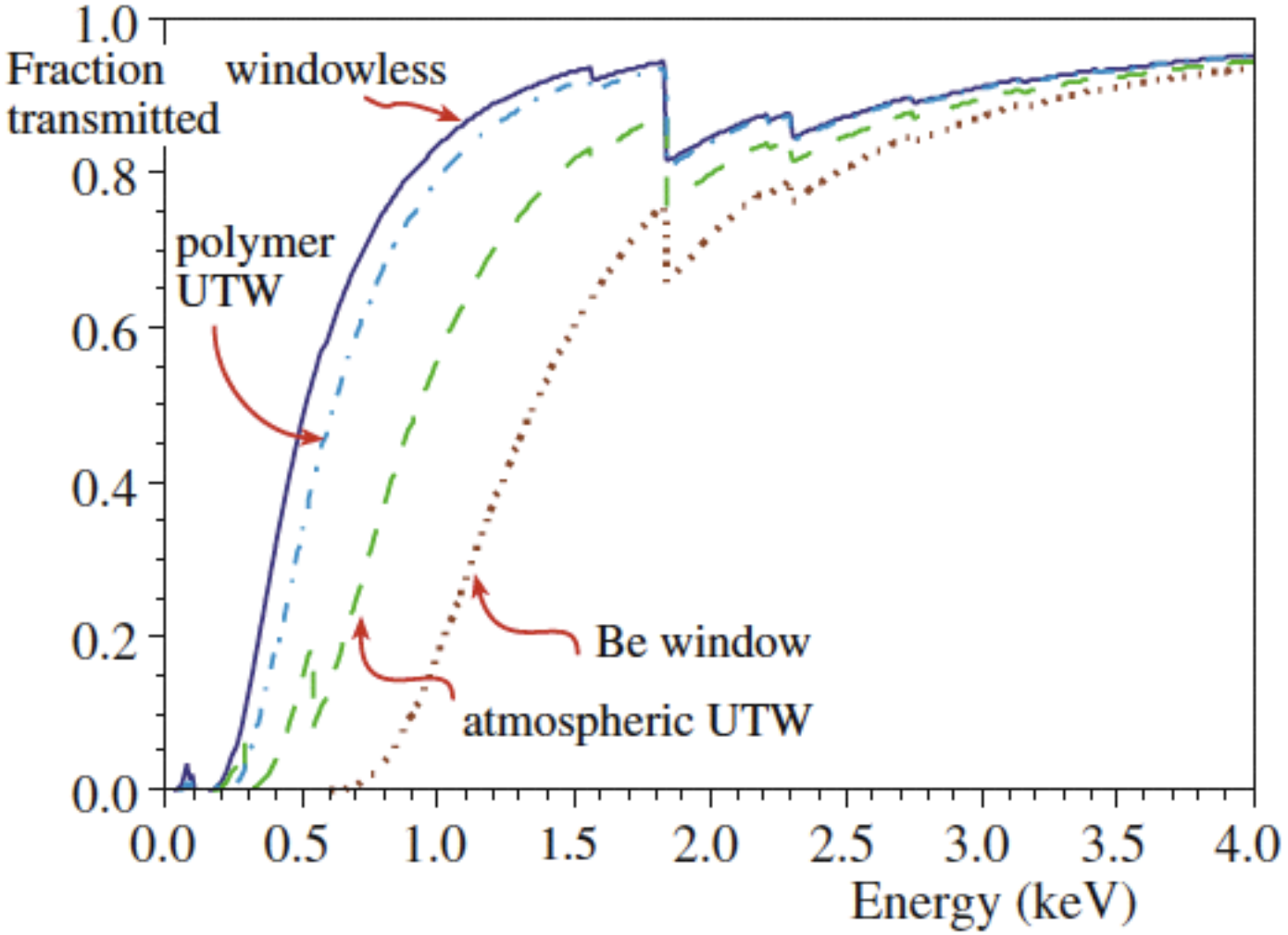
- **Windowless detector:**

  This system require high vacuums, like UHV system(~10^{-8} Pa). The best performance of this system is the detection of Be(110 eV) K_α

Compare the EELS and EDX technique

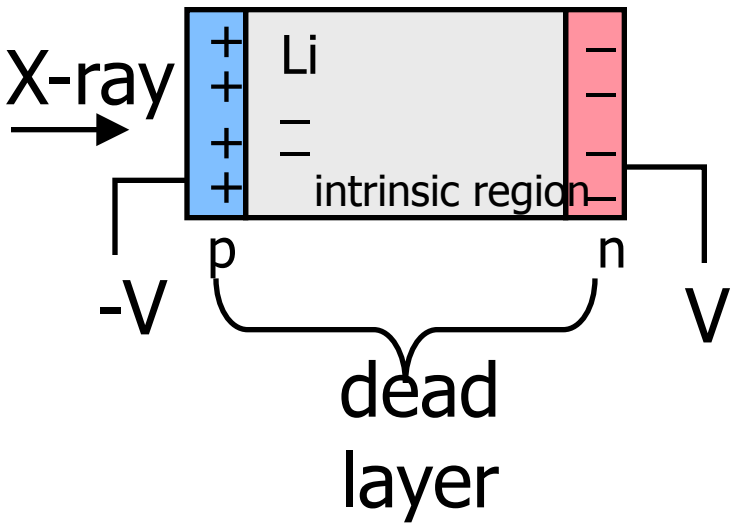
- Prior to the 1980, most EDX detector were protected (from the water vapor and hydrocarbon in the microscope column) by a 10μm thickness beryllium window, which strongly absorbs photons of energy less than 1000eV and percludes analysis of elements of atomic number less than 11.
- With development of ultrathin (UTW) or atmospheric-pressure (ATW), elements down to boron can be routinely detected, making EDX competitive with EELS for microanalysis of light elements in a TEM specimen.

Low energy efficiency calculated for different window types



Dead layer effect:

The p and n regions, at either of the detector, are usually termed "Dead layer"

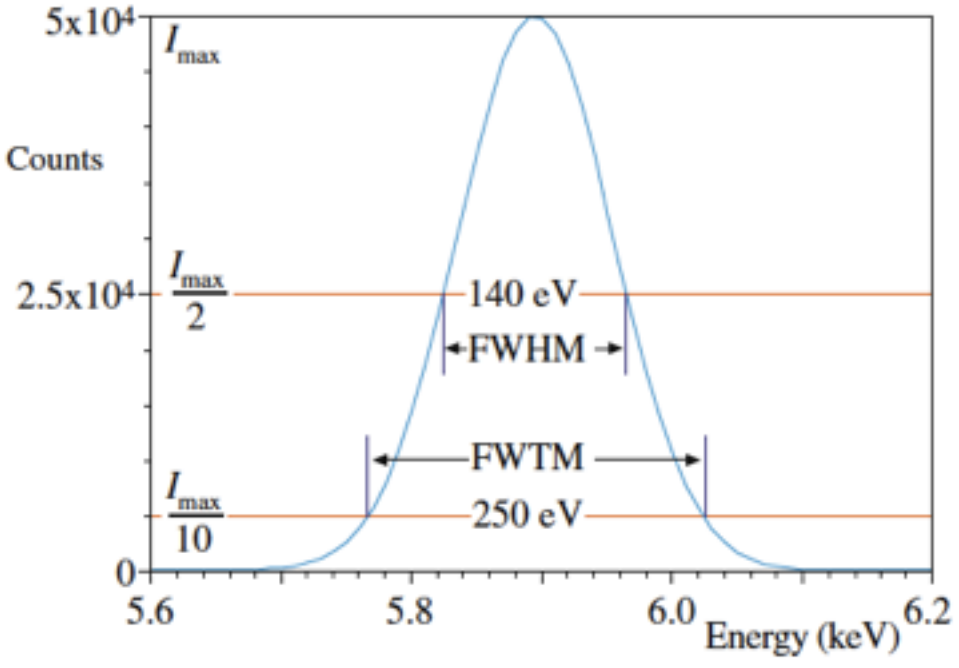


Why use Liquid N_2 cooling ?

1. Thermal energy would active electron-hole pair, **giving a noise level**.
2. The Li atoms will diffuse under applied bias, that will **destroy the intrinsic property**.
3. The noise in FET will **mask the signal** from low-energy X-rays.

- The dead layer effect is more clearly at low-Z element.

Incomplete-charge collection (dead layer effect):



because of the dead layer, the X-ray peak will not be a perfect Gaussian shape. Usually the peak will have a low-energy tail, because some X-ray energy will be deposited in the dead layer and will not create electron-hole pairs in the intrinsic region. You can measure this ICC effect from the ratio of the full width at tenth maximum (FWTM) to the FWHM of the displayed peak,

IDEAL GAUSSIAN

An ideal Gaussian shape gives a ratio FWTM/FWHM of 1.82 (Mn K_α or Ni K_α) but this will be larger for lower-energy X-rays that are more strongly absorbed by the detector.

Intrinsic Germanium Detectors:

The higher purely intrinsic region is easy produced than Si

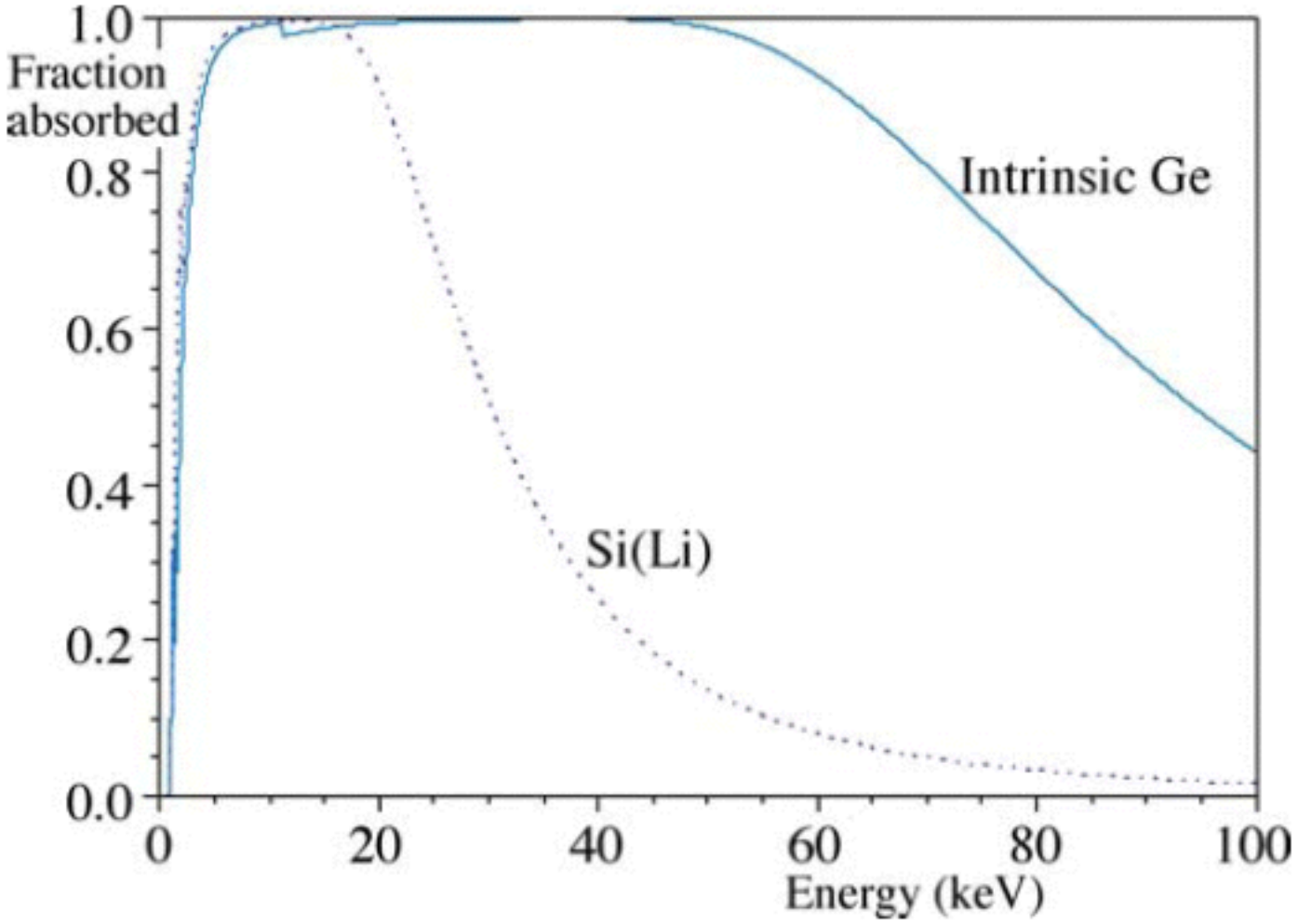
The intrinsic region (IG) is ~5 mm and can 100% efficient detect Pb Kα ~75keV

The energy for e/h pair of IG is about 2.8 eV, smaller than Si(3.8 eV)

PROTECT YOUR DETECTOR

The intense doses of high-energy electrons or X-rays which can easily be generated in an AEM (e.g., when the beam hits a grid bar) can destroy the Li compensation in a Si(Li) detector, but there is no such problem in an IG crystal.

High energy efficiency up to 100 keV X-ray energy caculated for Si(Li) and IG dectoe



- A typical energy range for Si(Li) detector is 20KeV