Chapter 9

Energy Dispersive X-ray spectrometer:

The Introduction and Application

(Chapter 32, 33)

9.1 X-ray analysis: Why bother?

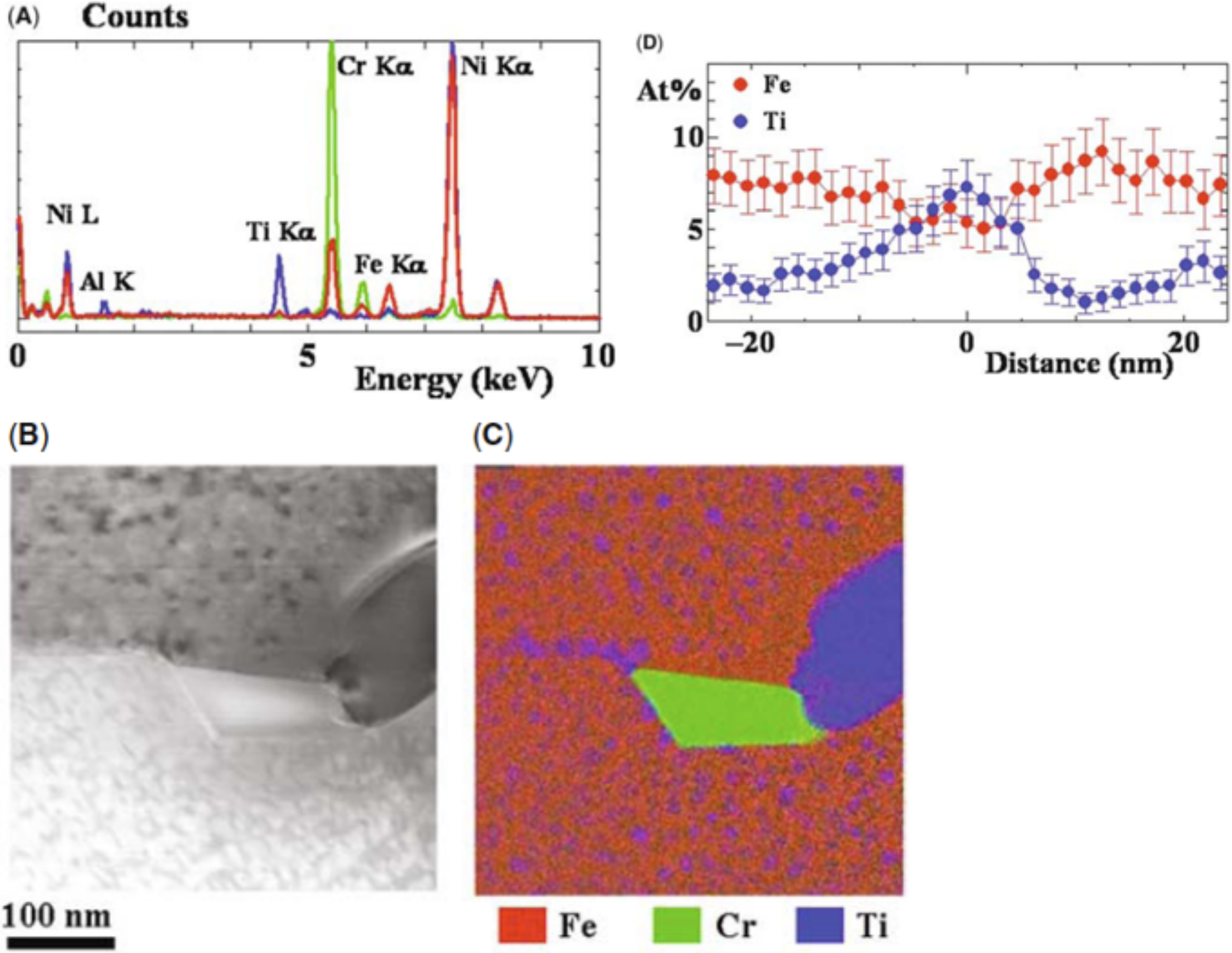
AEM: *analytical electron microscope*

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

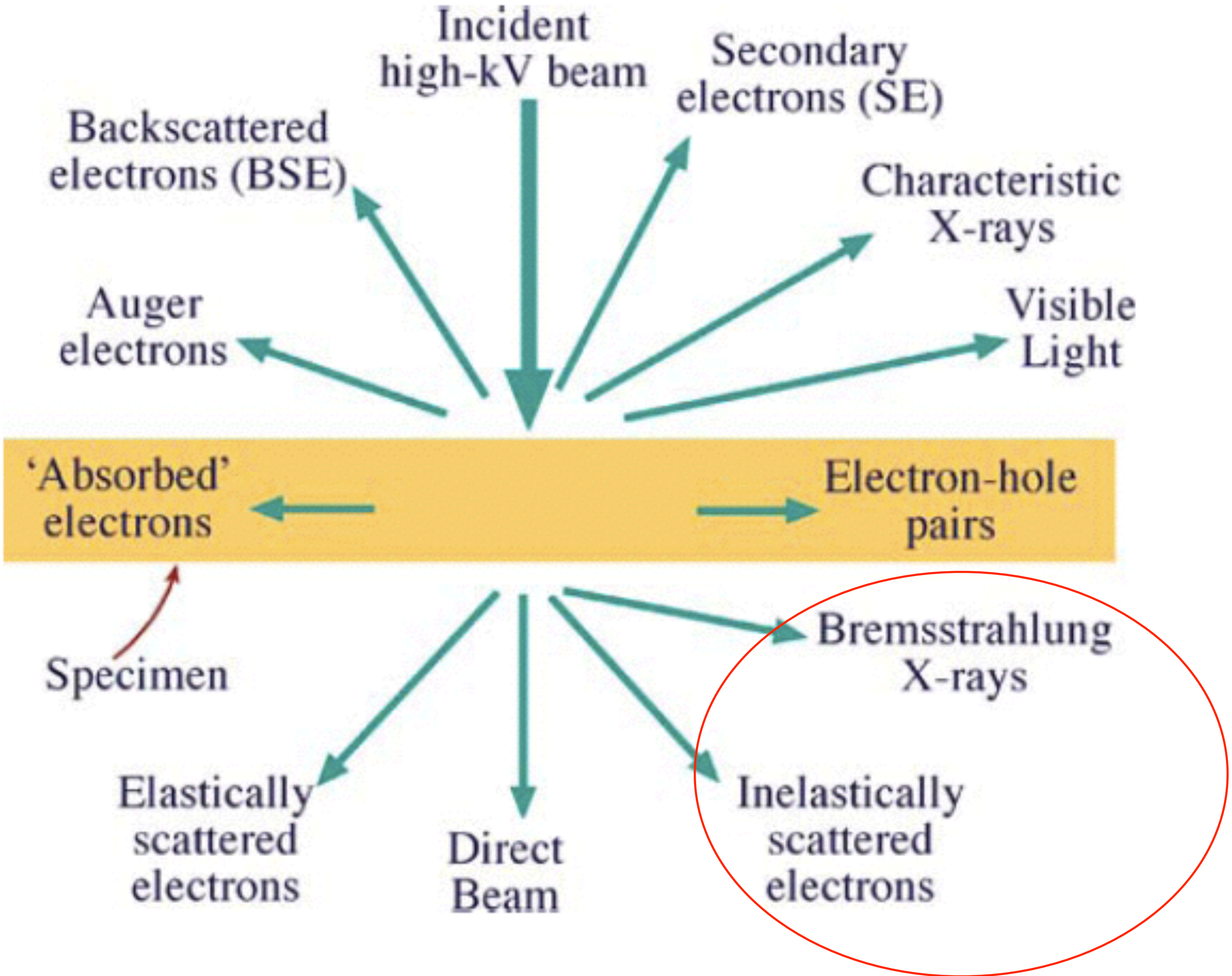
Why bother?

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

9.2 TEM beam-specimen interactions and signals



X-RAY EMISSION

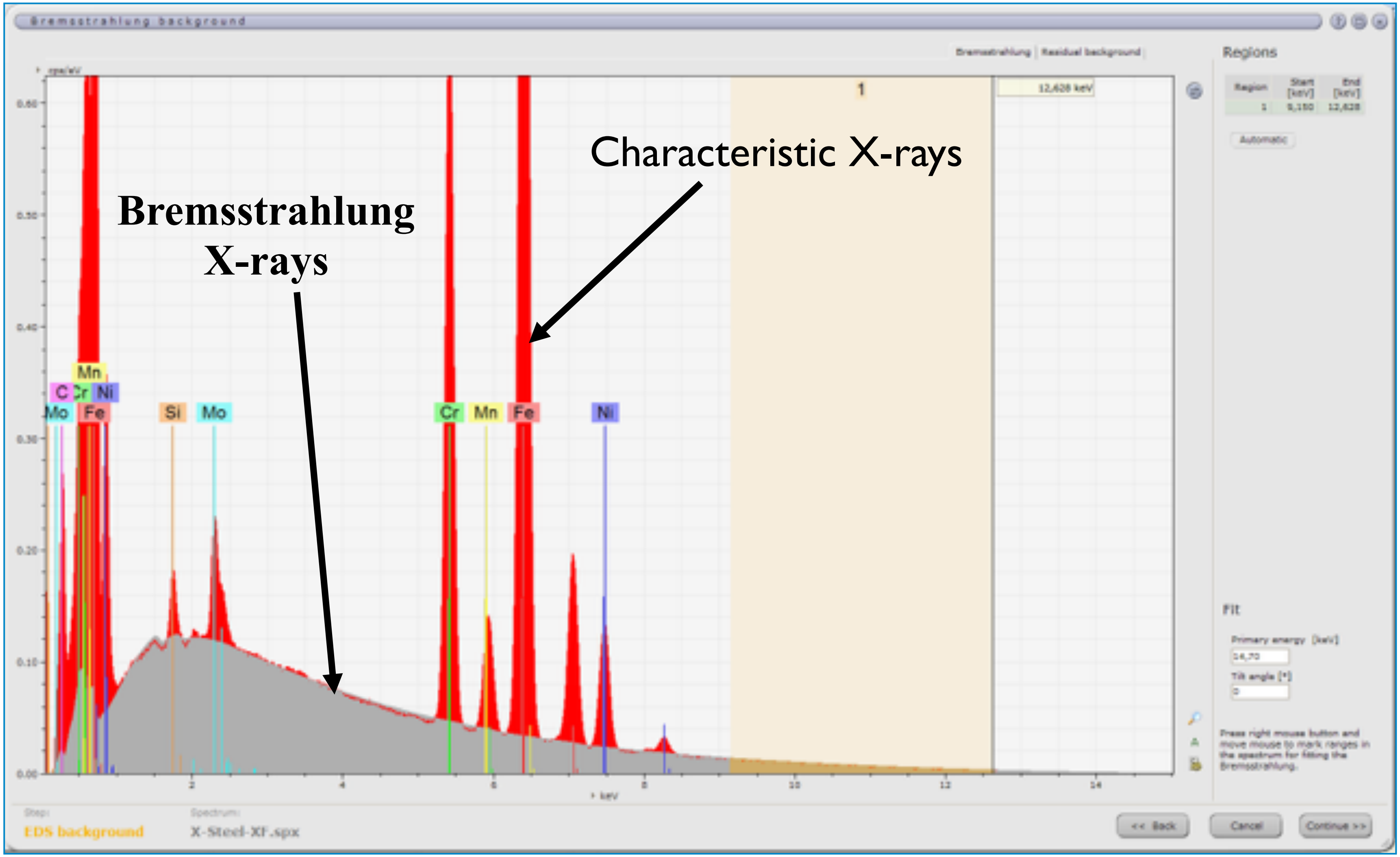
What we get from X-ray?

- 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.



Characteristic X-rays

Bremsstrahlung X-rays

Region	Start [keV]	End [keV]
1	9,150	12,628

Fit

Primary energy [keV] 14,70

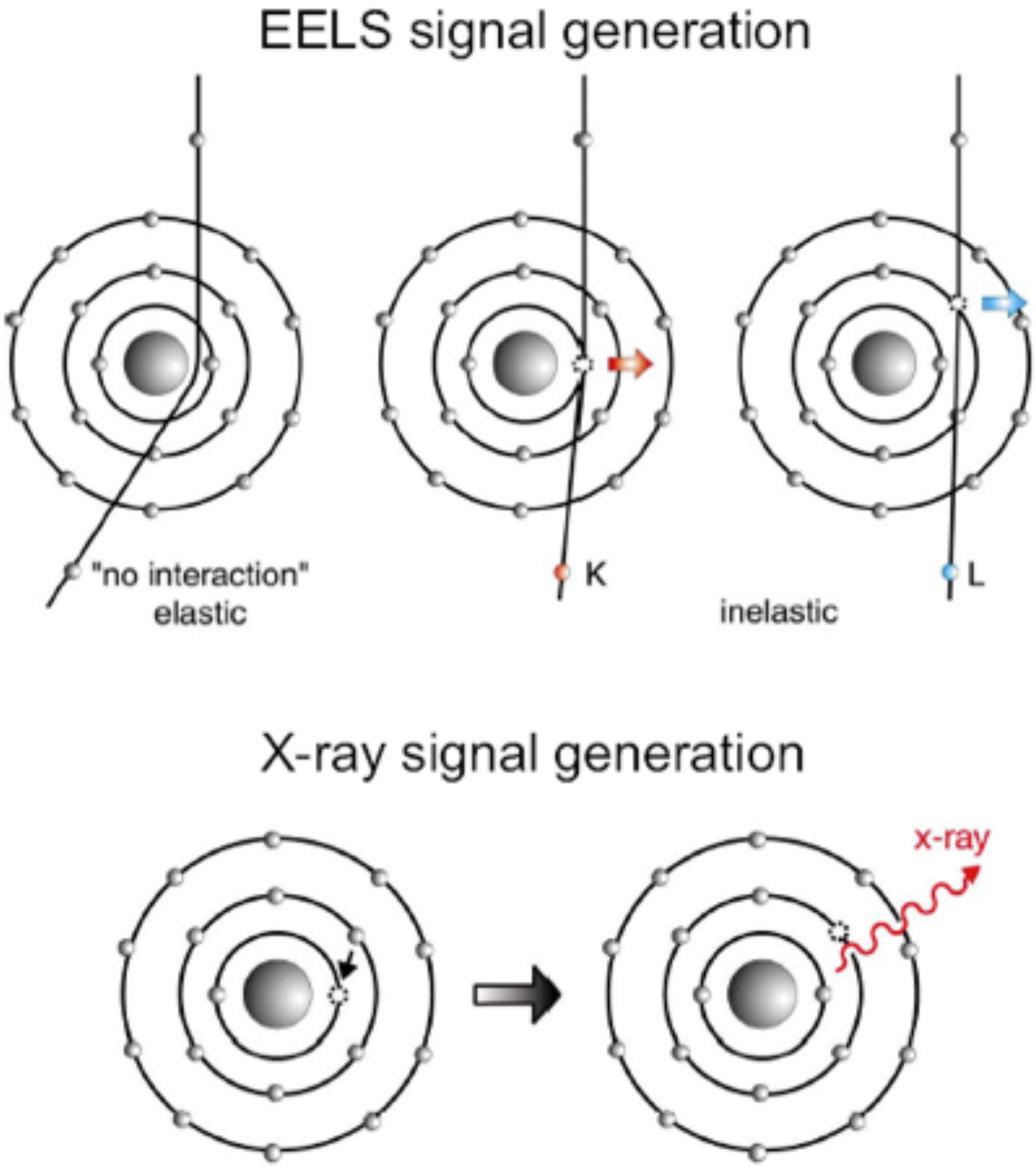
Tilt angle [°] 0

Press right mouse button and move mouse to mark ranges in the spectrum for fitting the Bremsstrahlung.

Step: EDS background

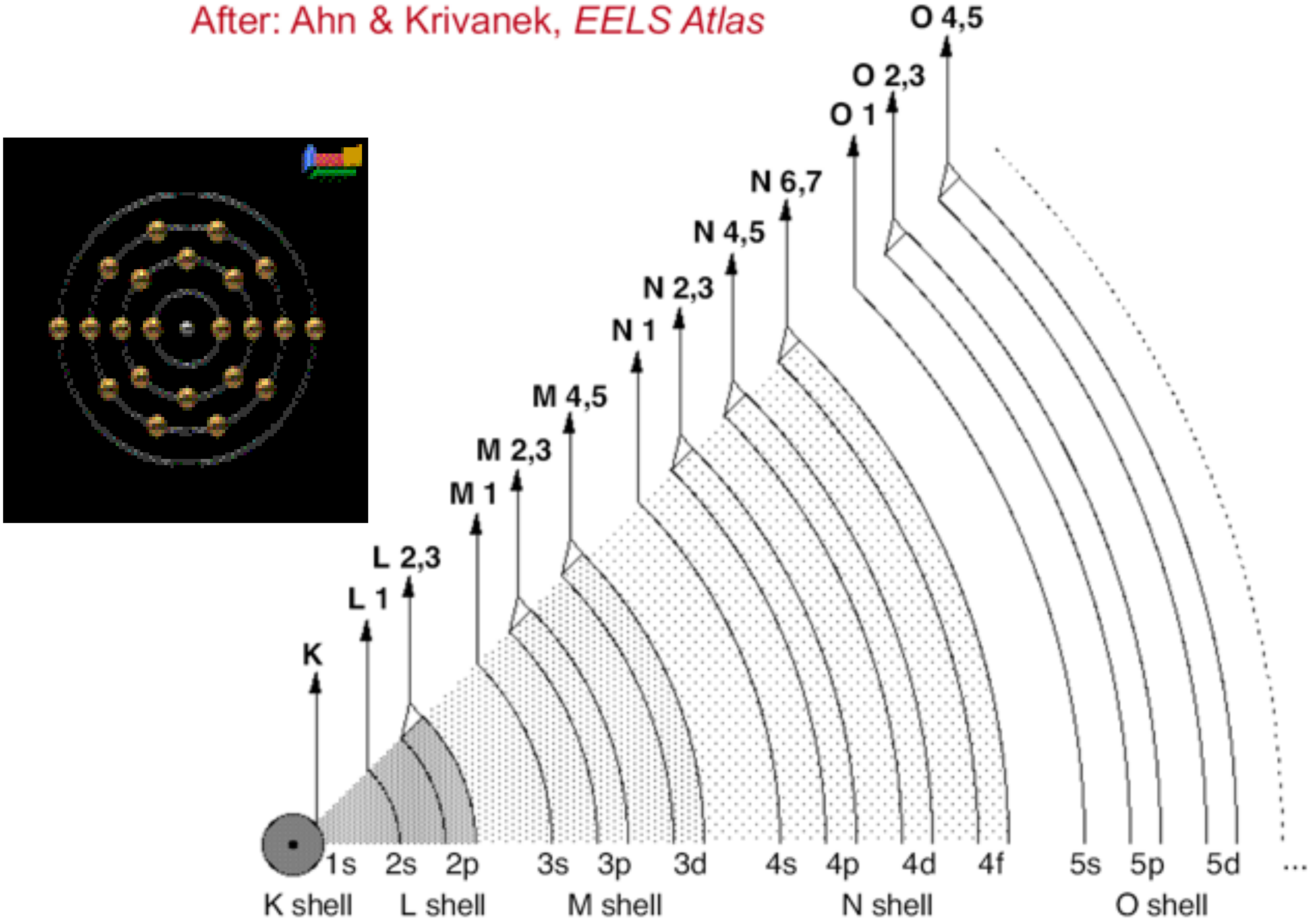
Spectrum: X-Steel-XF.spx

EELS and x-Ray Signal Generation



Nomenclature of EELS ionization edges

After: Ahn & Krivanek, *EELS Atlas*

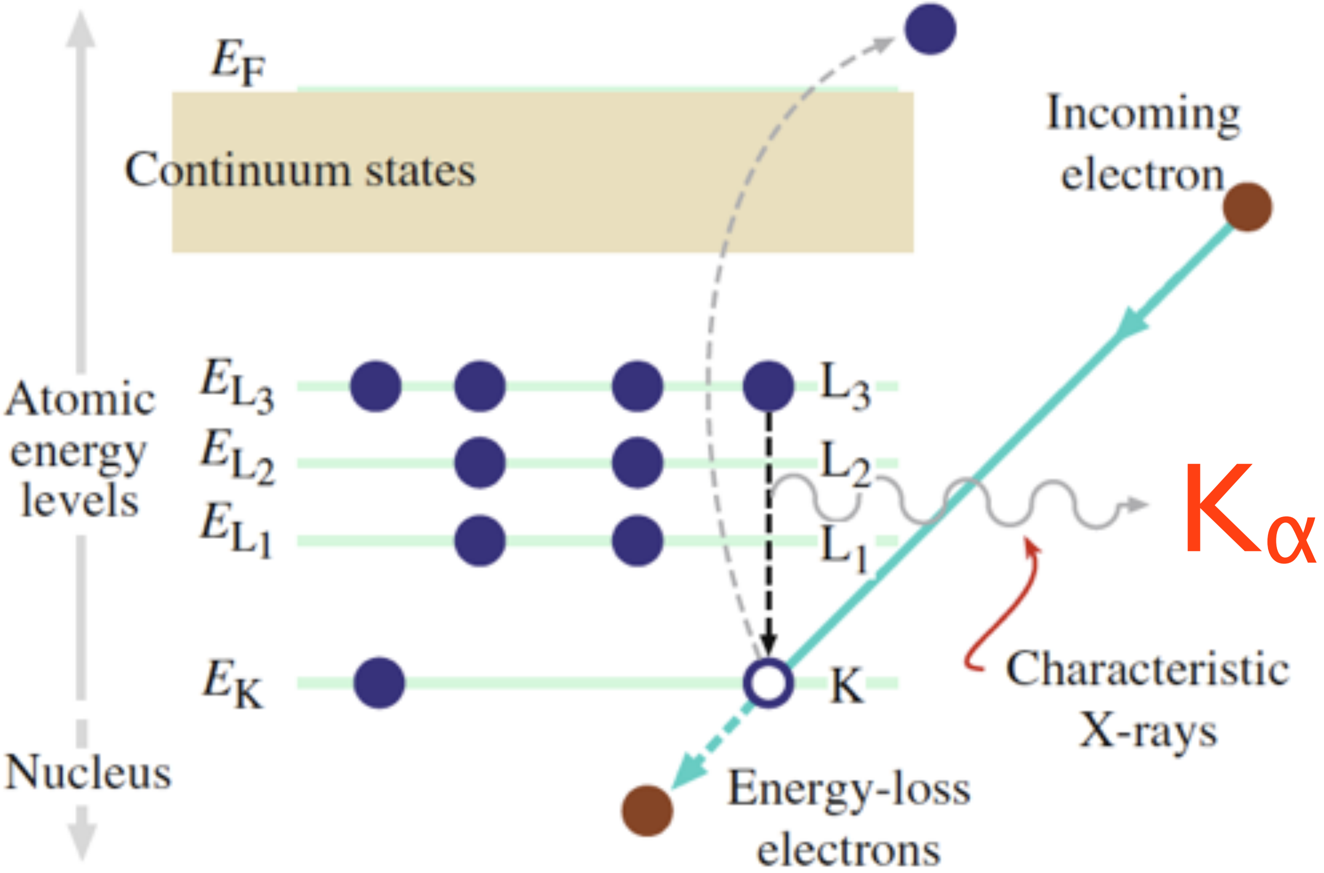


CHARACTERISTIC X-RAYS

How to produce characteristic X-rays?

n=2 l=1
l=0

n=1 l=0



What are they "characteristic"?

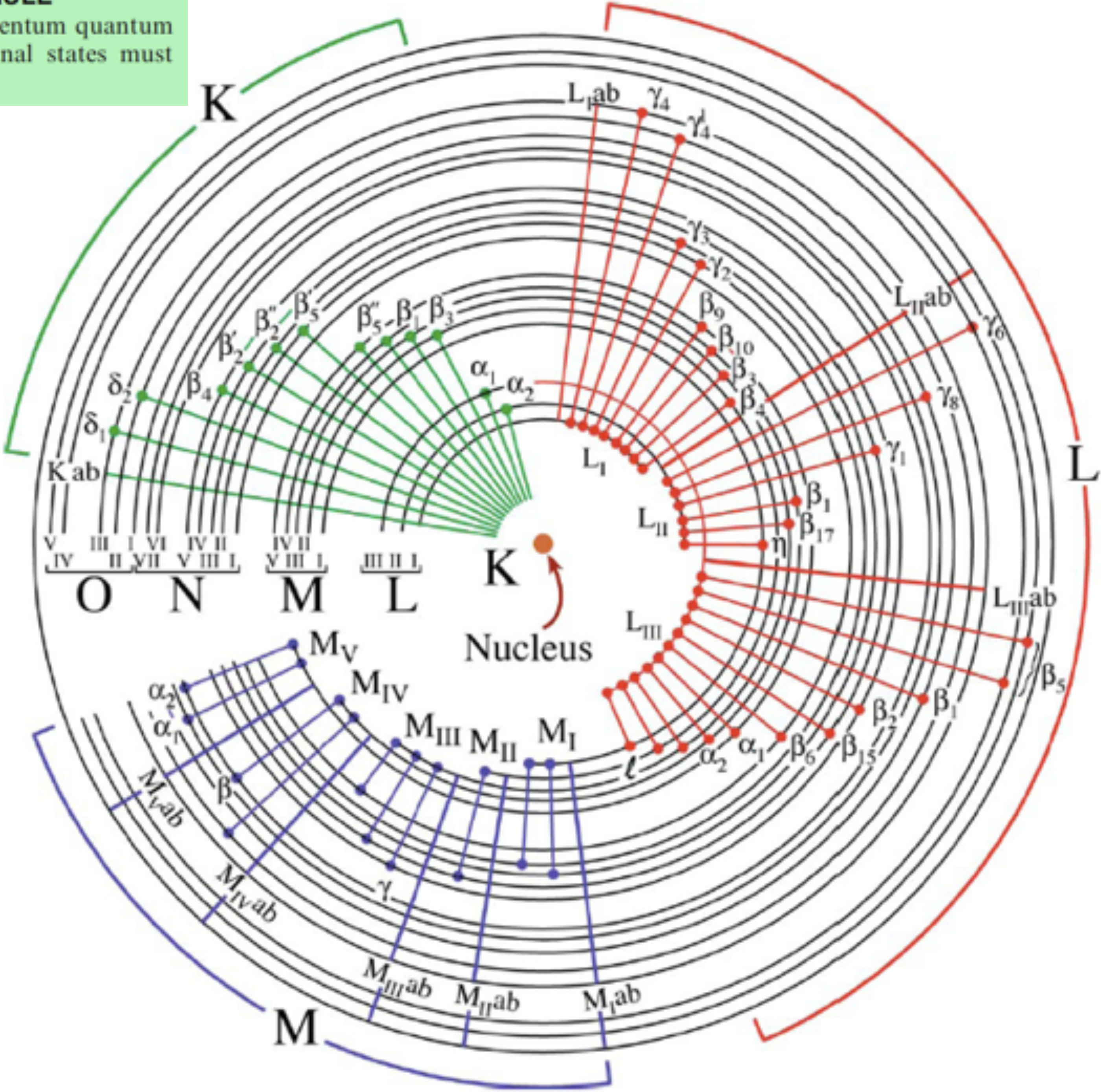
The energy of the emission is characteristic of the difference in energy of the two shells involved and is unique to the atom.

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

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

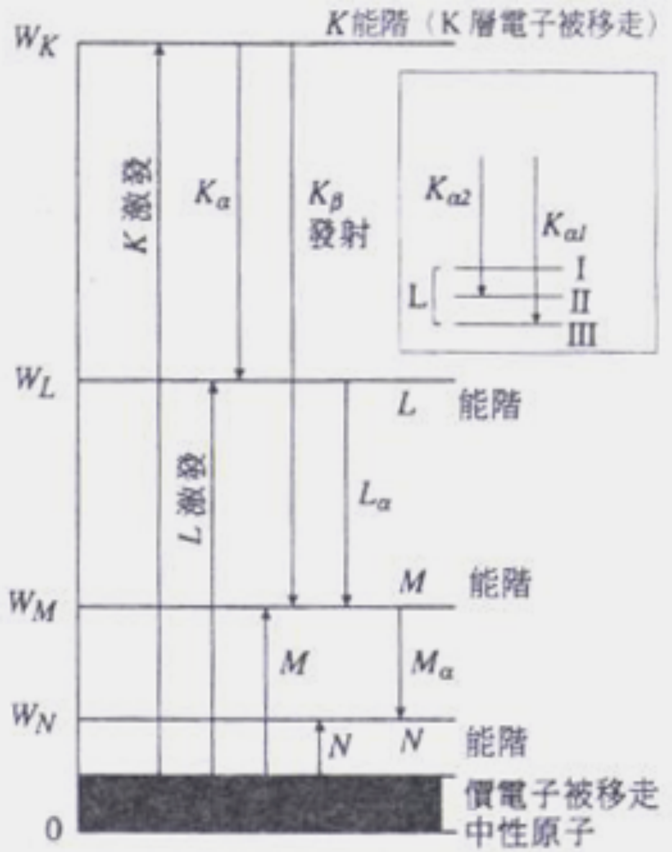


Selection rule:

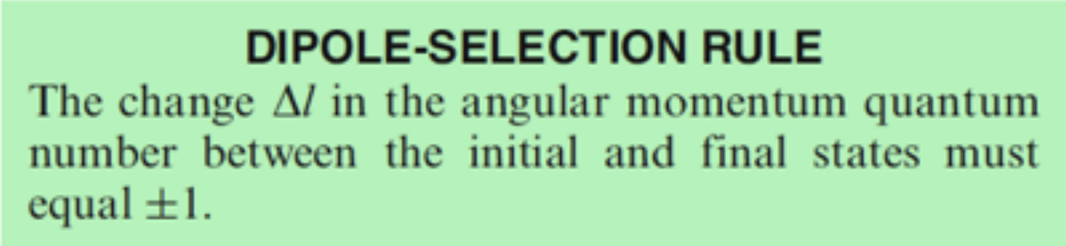
ELECTRON SHELLS

Electrons must obey when they jumped between shells → $\Delta l = \pm 1$, $\Delta ml = \pm 1,0$

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

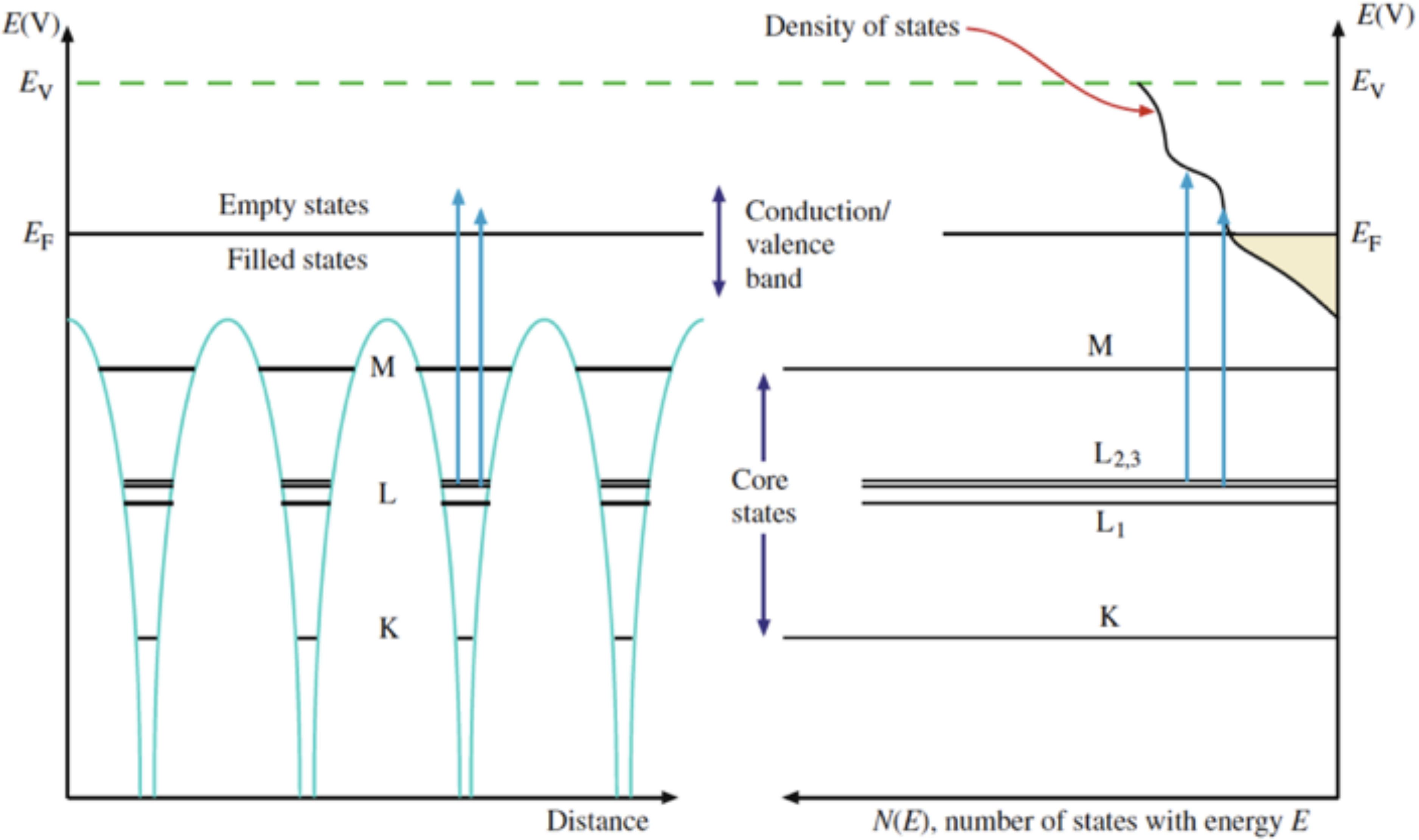


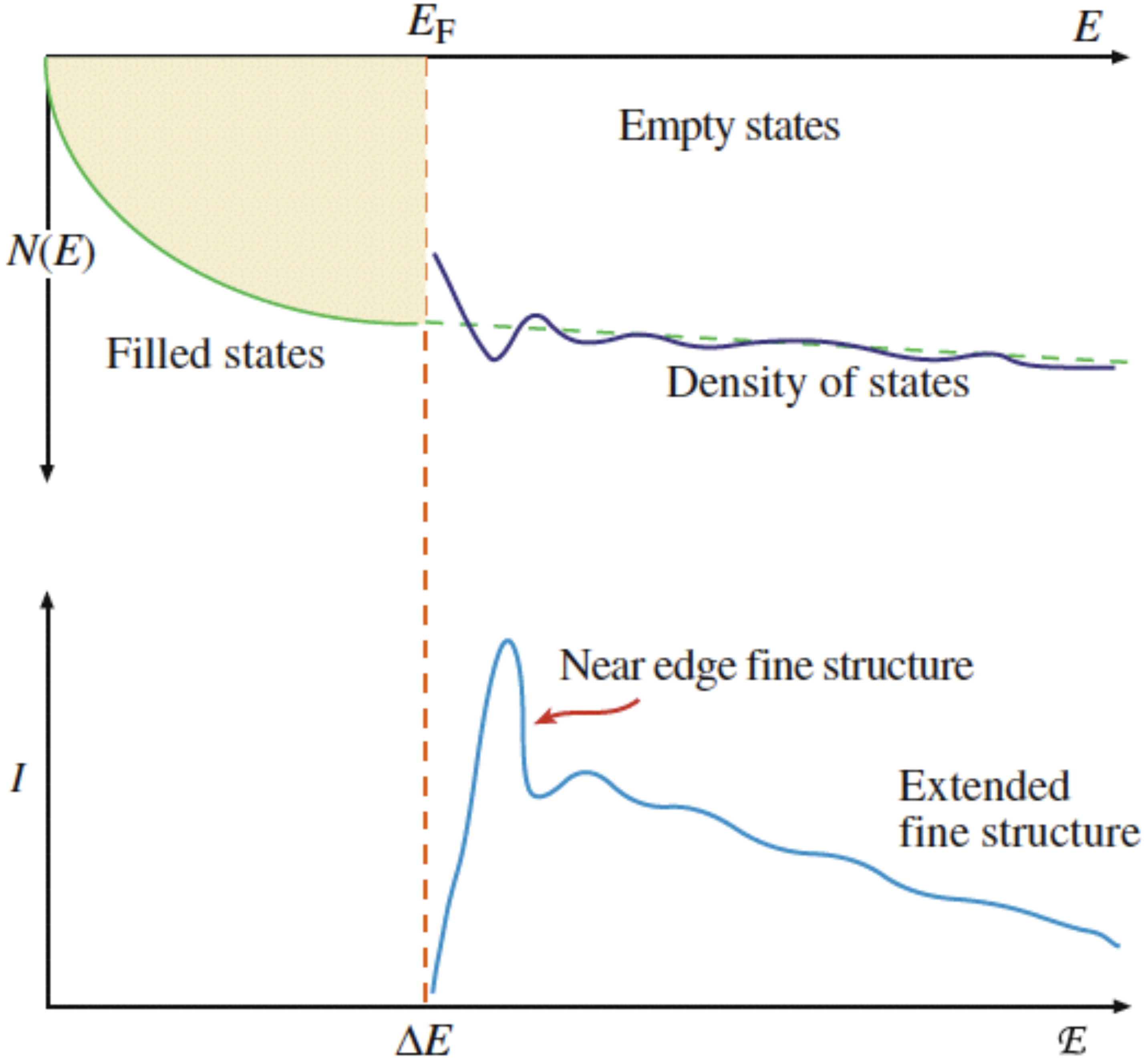
n	l	ml
2	0	0
2	1	0
2	1	±1

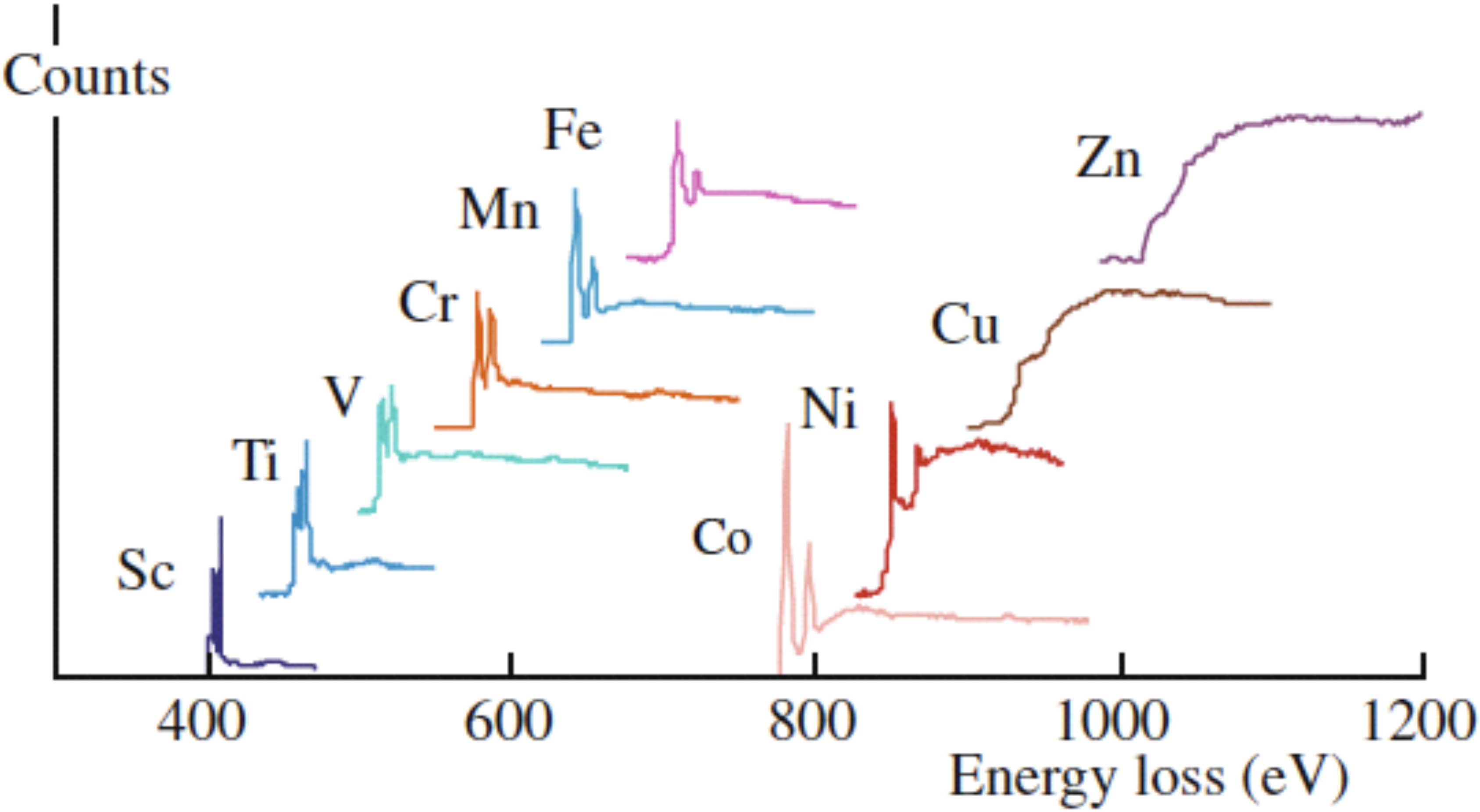


DIPOLE-SELECTION RULE

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

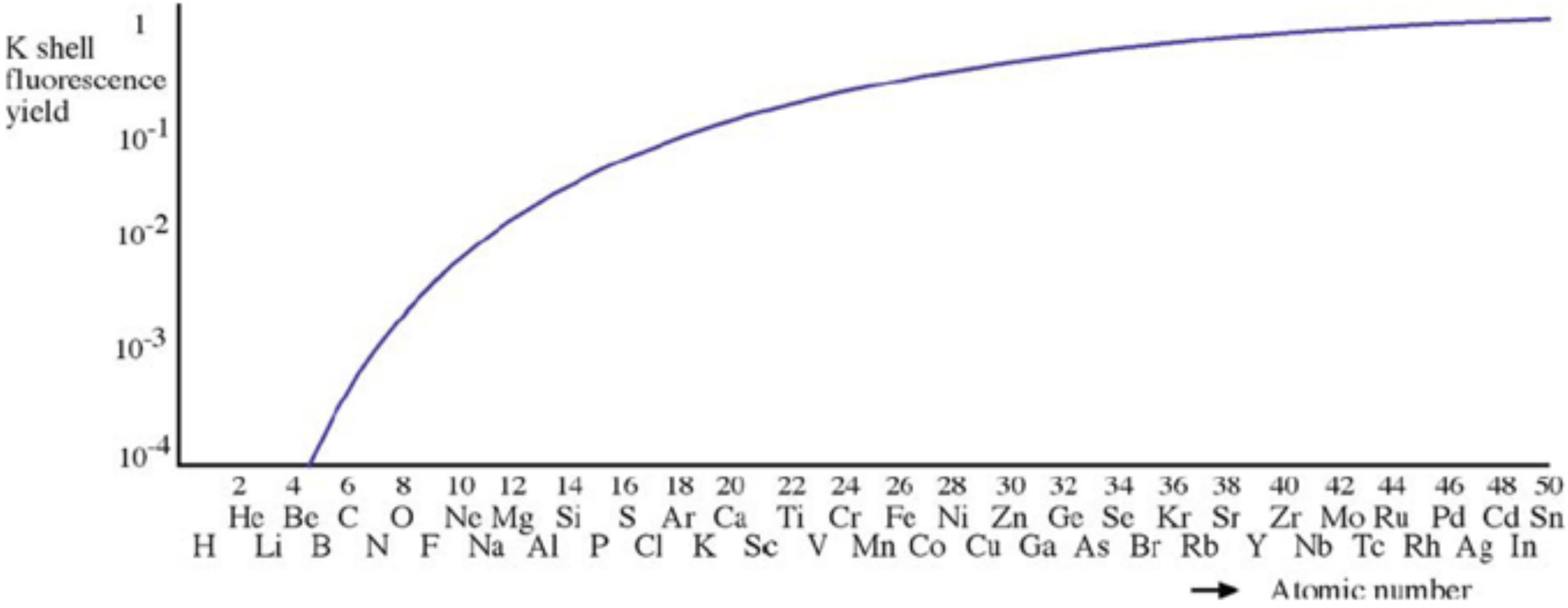

E(V)
E_V
E_F
Empty states
Filled states
M
L
K
Distance
Conduction/ valence band
Core states
Density of states
E(V)
E_V
E_F
M
L_{2,3}
L_1
K
N(E), number of states with energy E


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


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

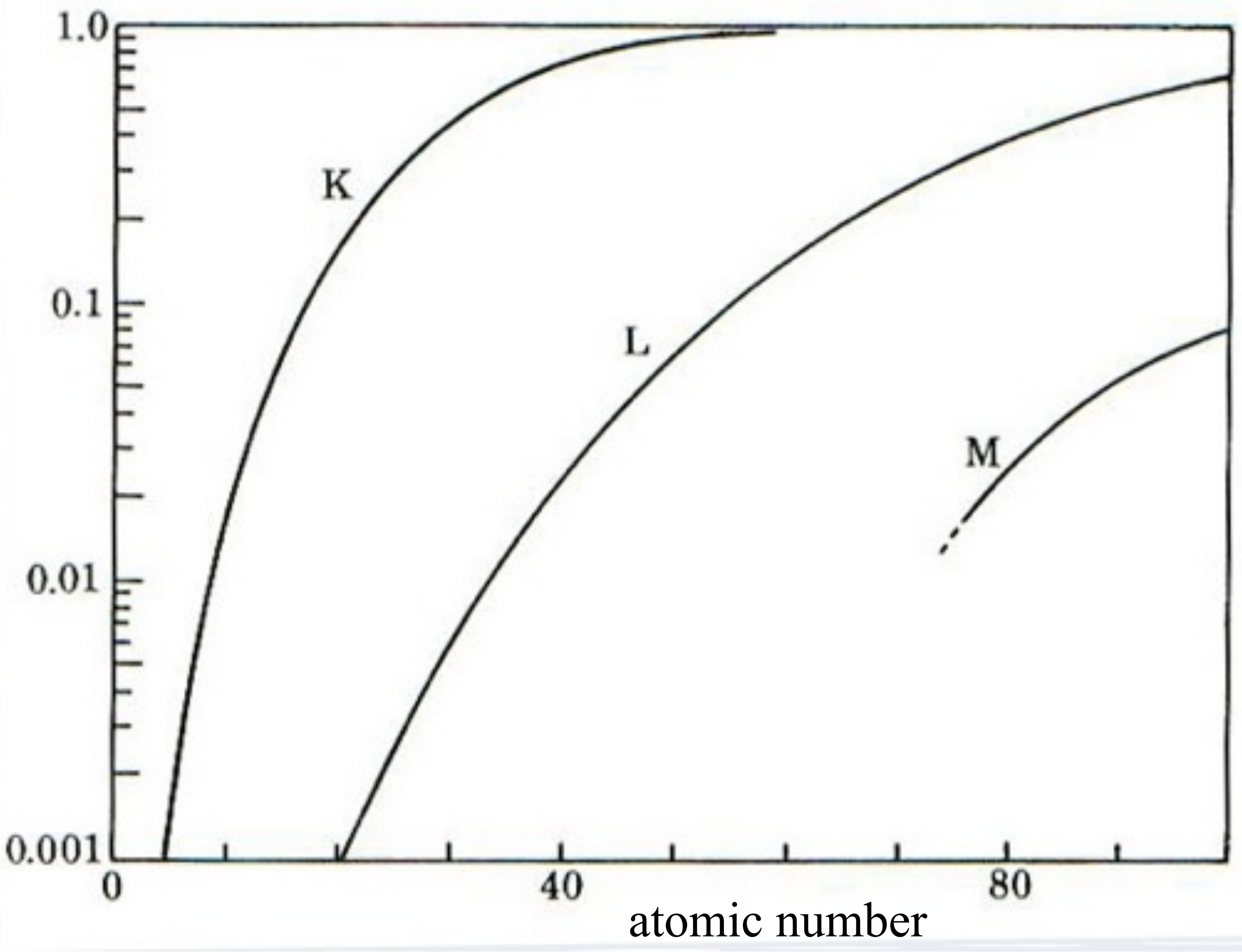
X-ray fluorescence yield

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



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

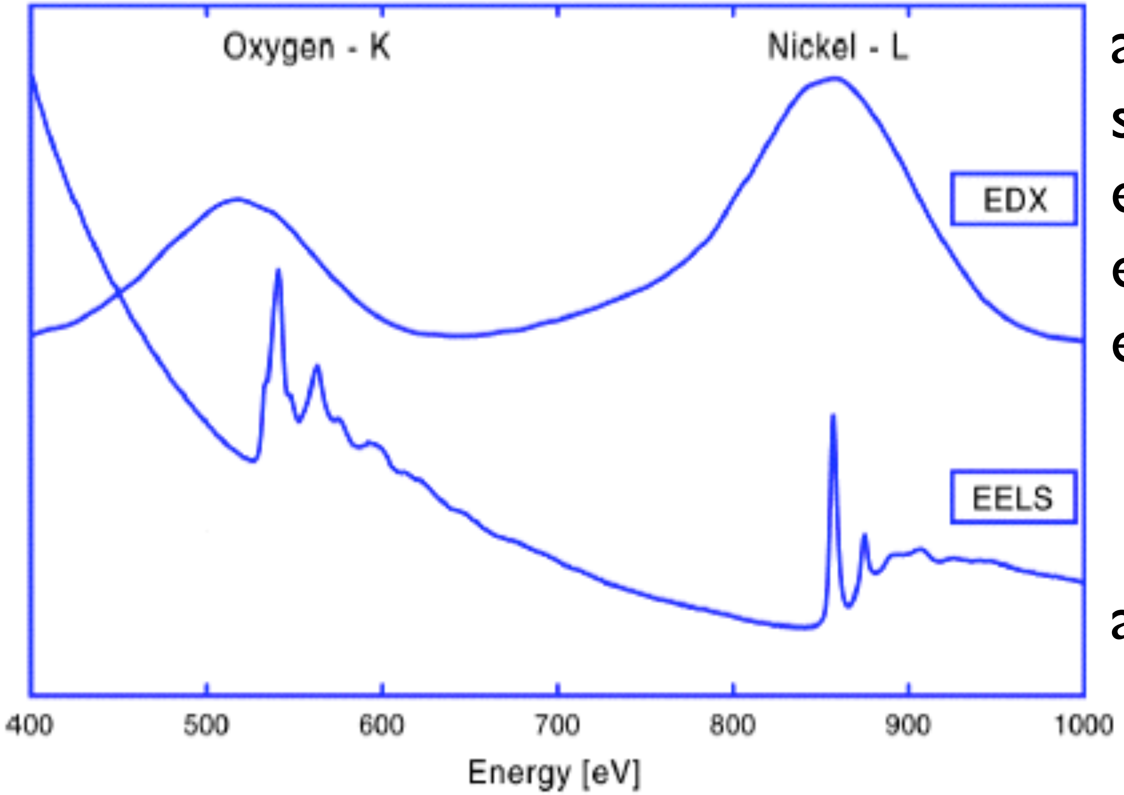
- The ***EELS*** is one step signal, while ***EDX*** is a two step signal (low x-ray fluorescence yield for low Z). In general, the yield rate of the EELS is higher than EDX.

- 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:

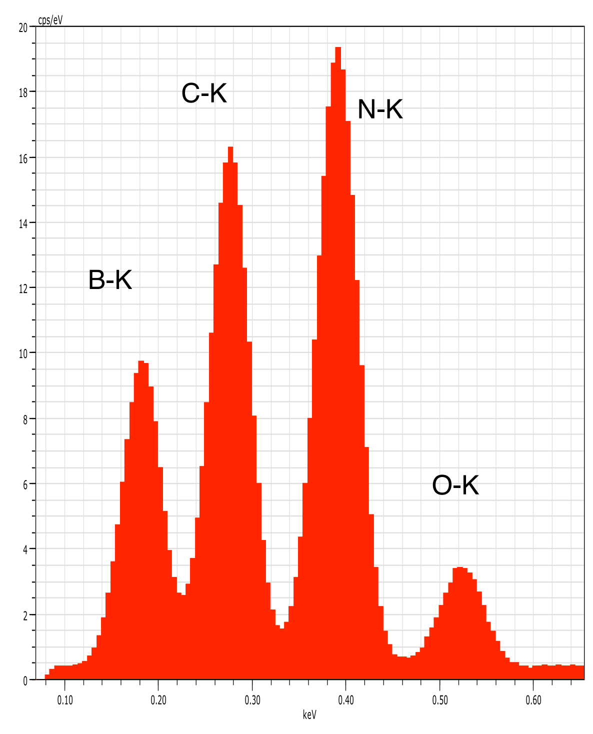
arises from the inelastic scattering from the atomic electron whose binding energy less than the edge energy

Background of EDX:

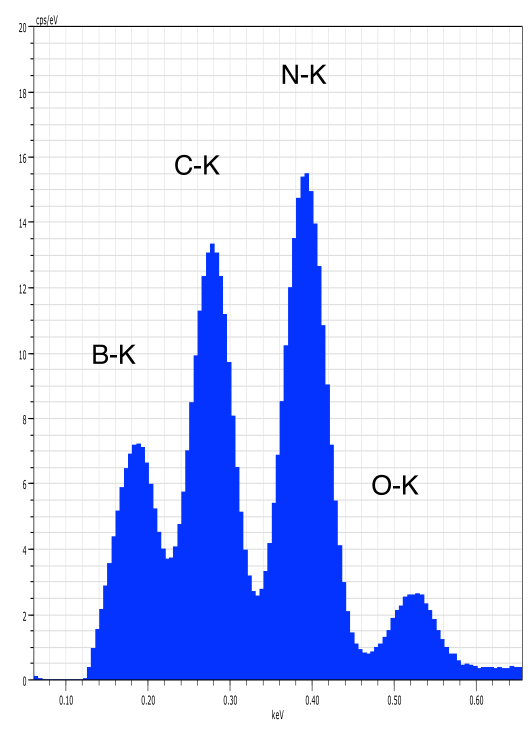
arises from bremsstrahlung

Influence by Resolution changing @ different ICR

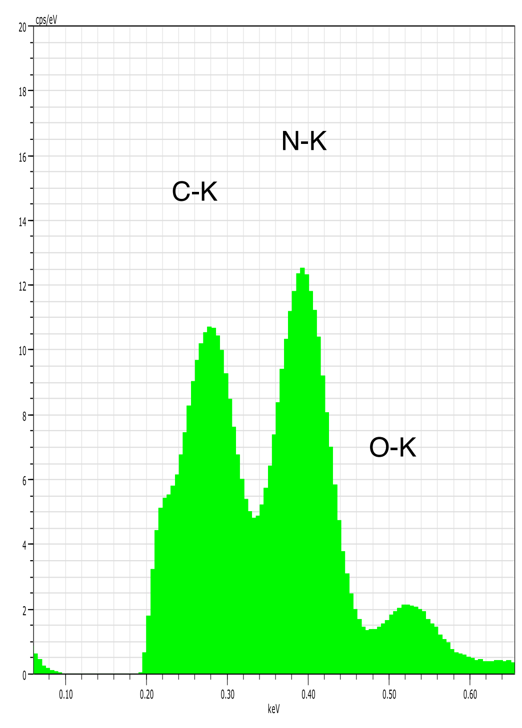
125eV

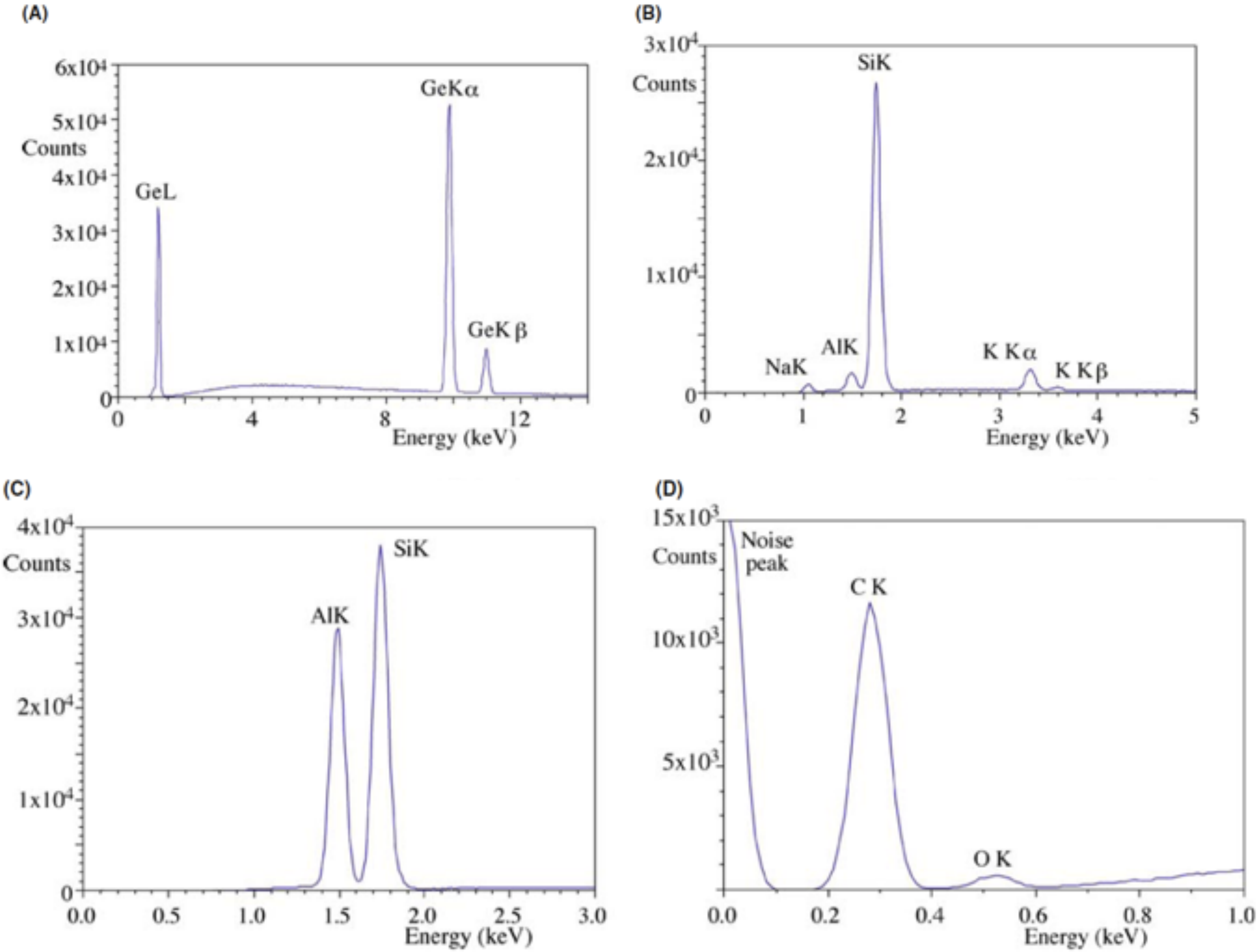


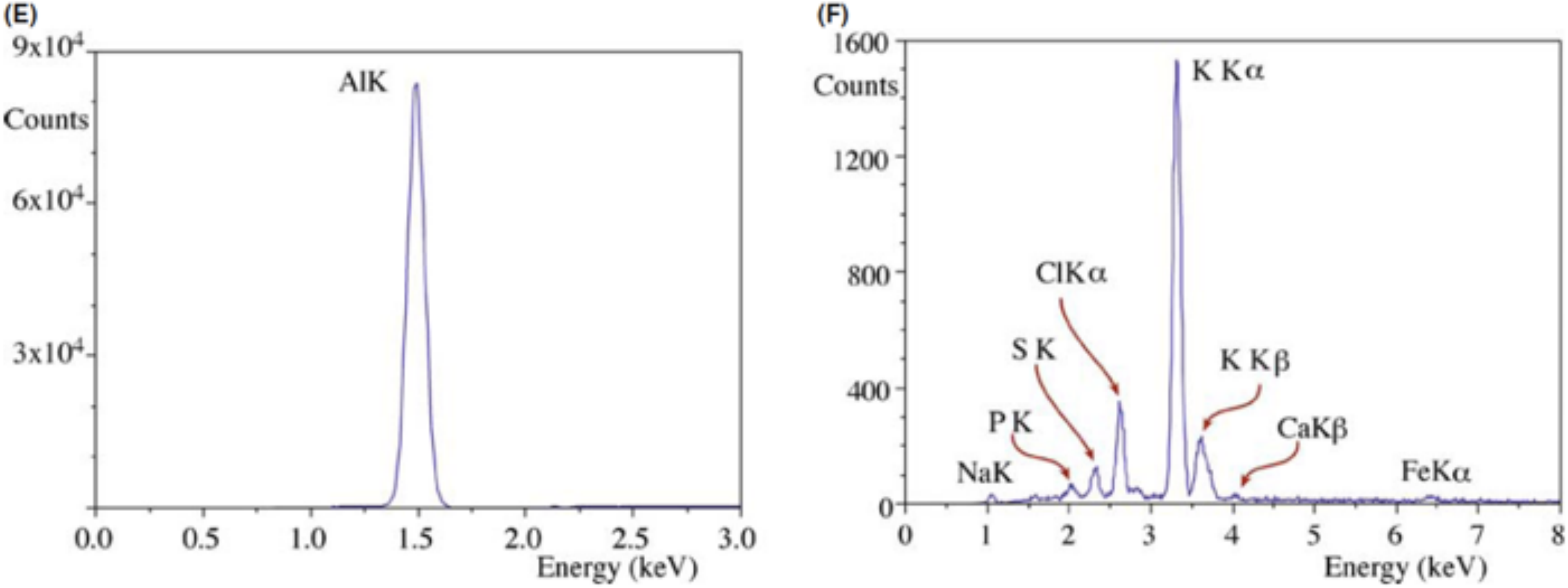
133eV



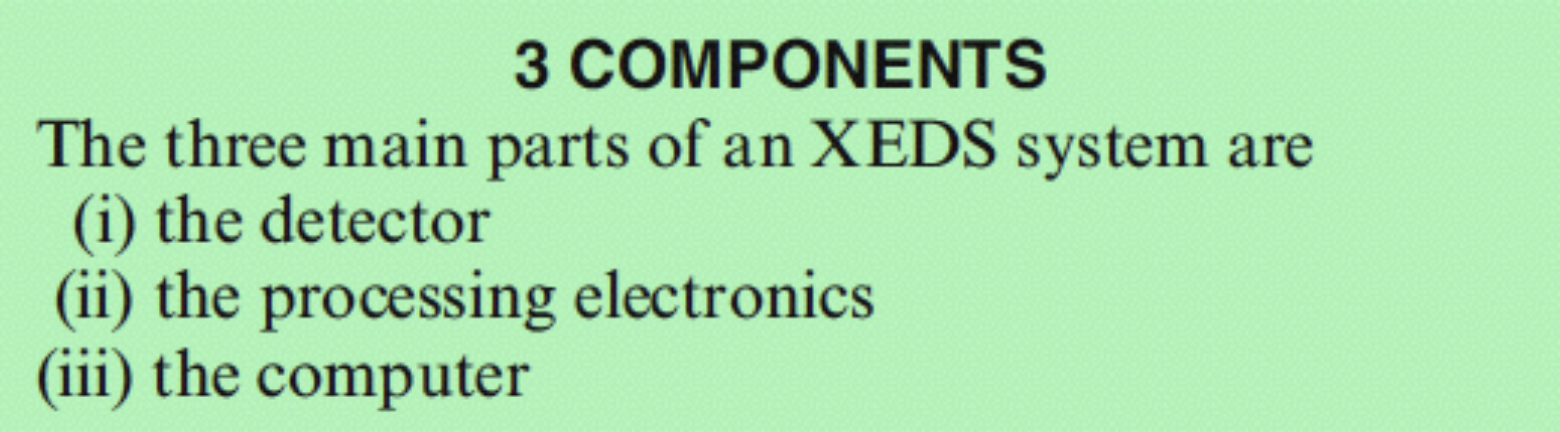
140eV




(A)
6x10^4
5x10^4
Counts
4x10^4
3x10^4
2x10^4
1x10^4
0
GeL
GeKα
GeK β
0
4
8
12
Energy (keV)
(B)
3x10^4
Counts
SiK
2x10^4
1x10^4
0
NaK
AlK
K Kα
K Kβ
0
1
2
3
4
5
Energy (keV)
(C)
4x10^4
Counts
SiK
AlK
3x10^4
2x10^4
1x10^4
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Energy (keV)
(D)
15x10^3
Counts
Noise peak
C K
10x10^3
5x10^3
O K
0.0
0.2
0.4
0.6
0.8
1.0
Energy (keV)


(E)
9x10^4
6x10^4
3x10^4
Counts
AlK
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Energy (keV)
(F)
1600
1200
800
400
0
Counts
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



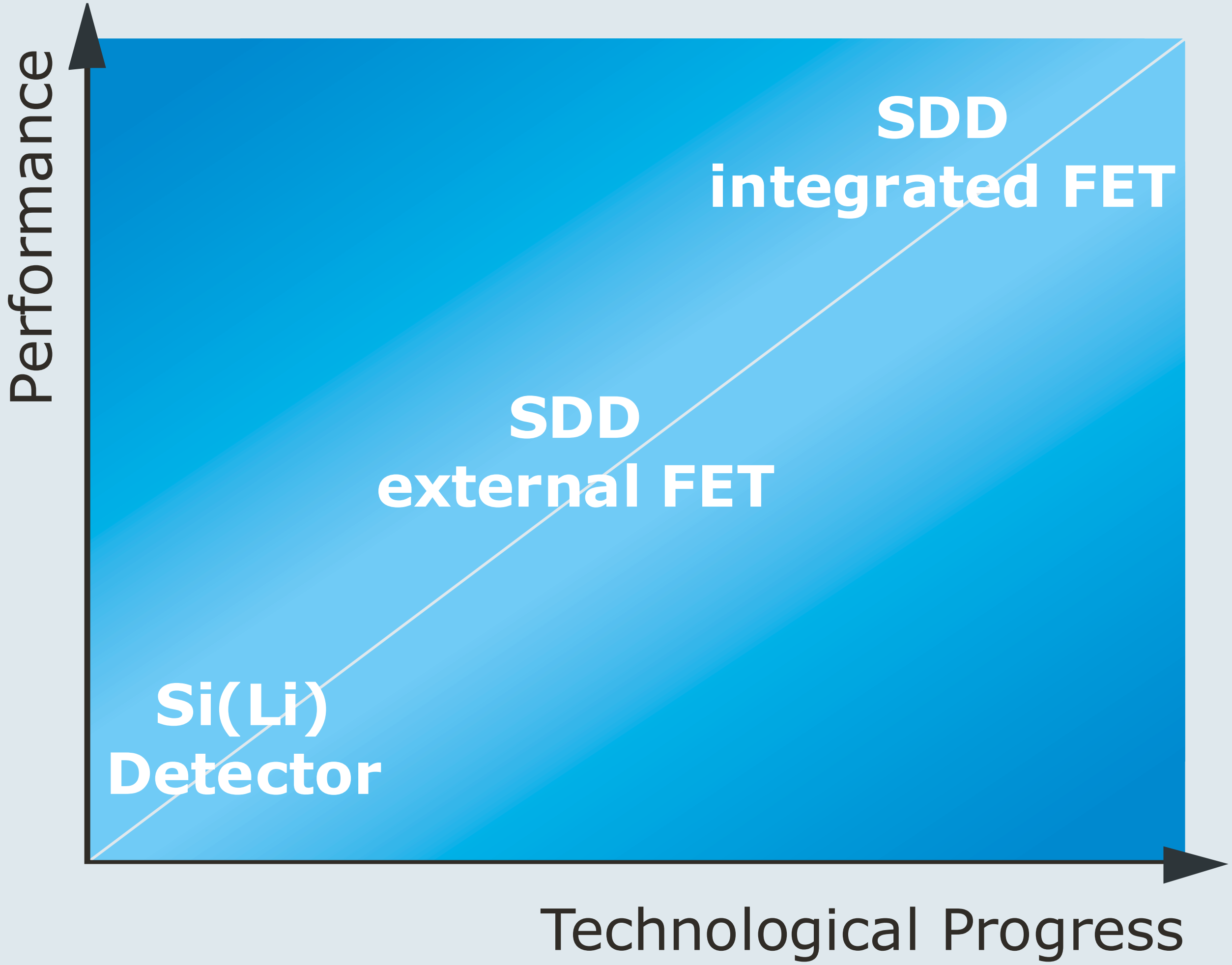
3 COMPONENTS

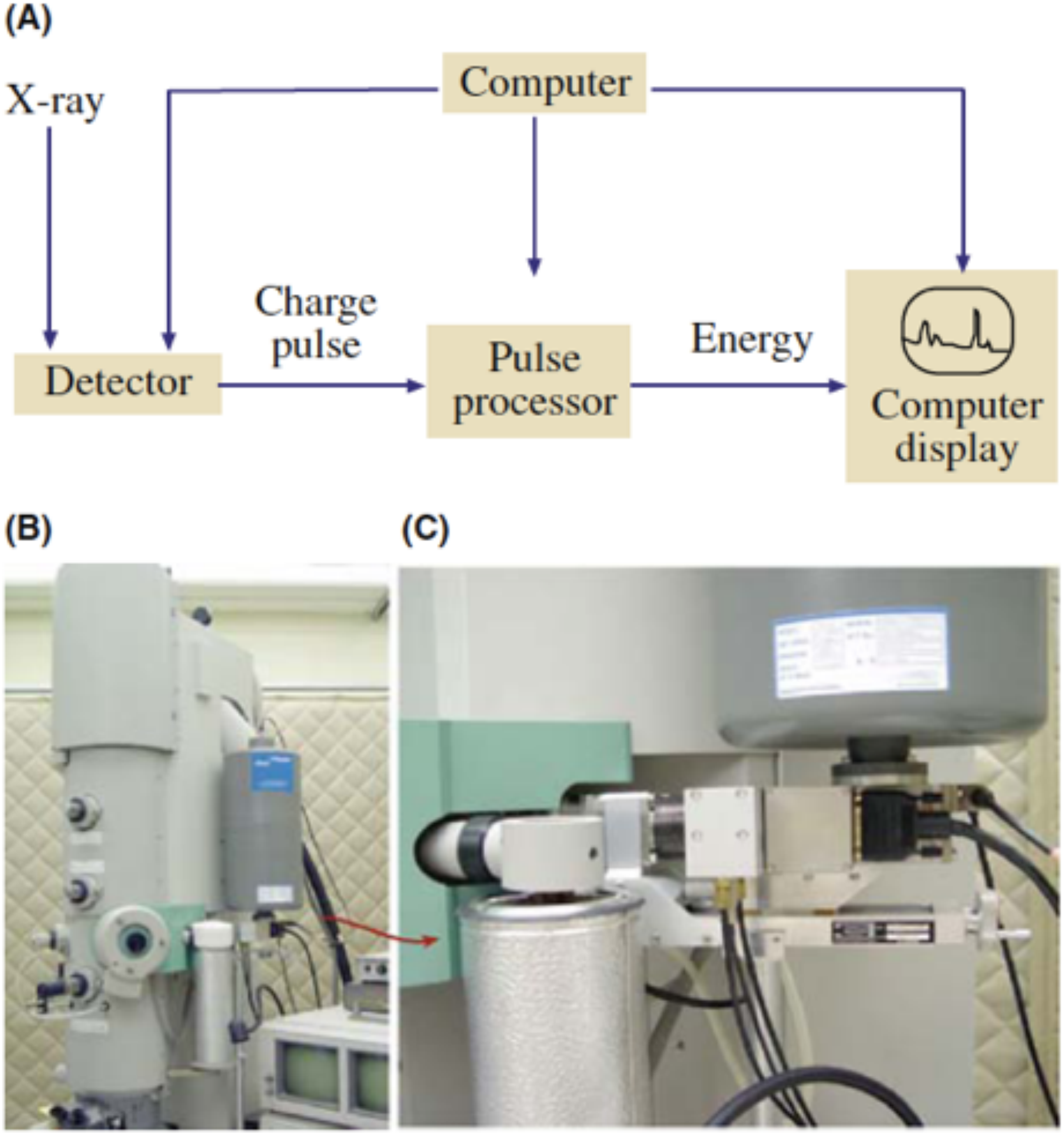
The three main parts of an XEDS system are

(i) the detector
(ii) the processing electronics
(iii) the computer

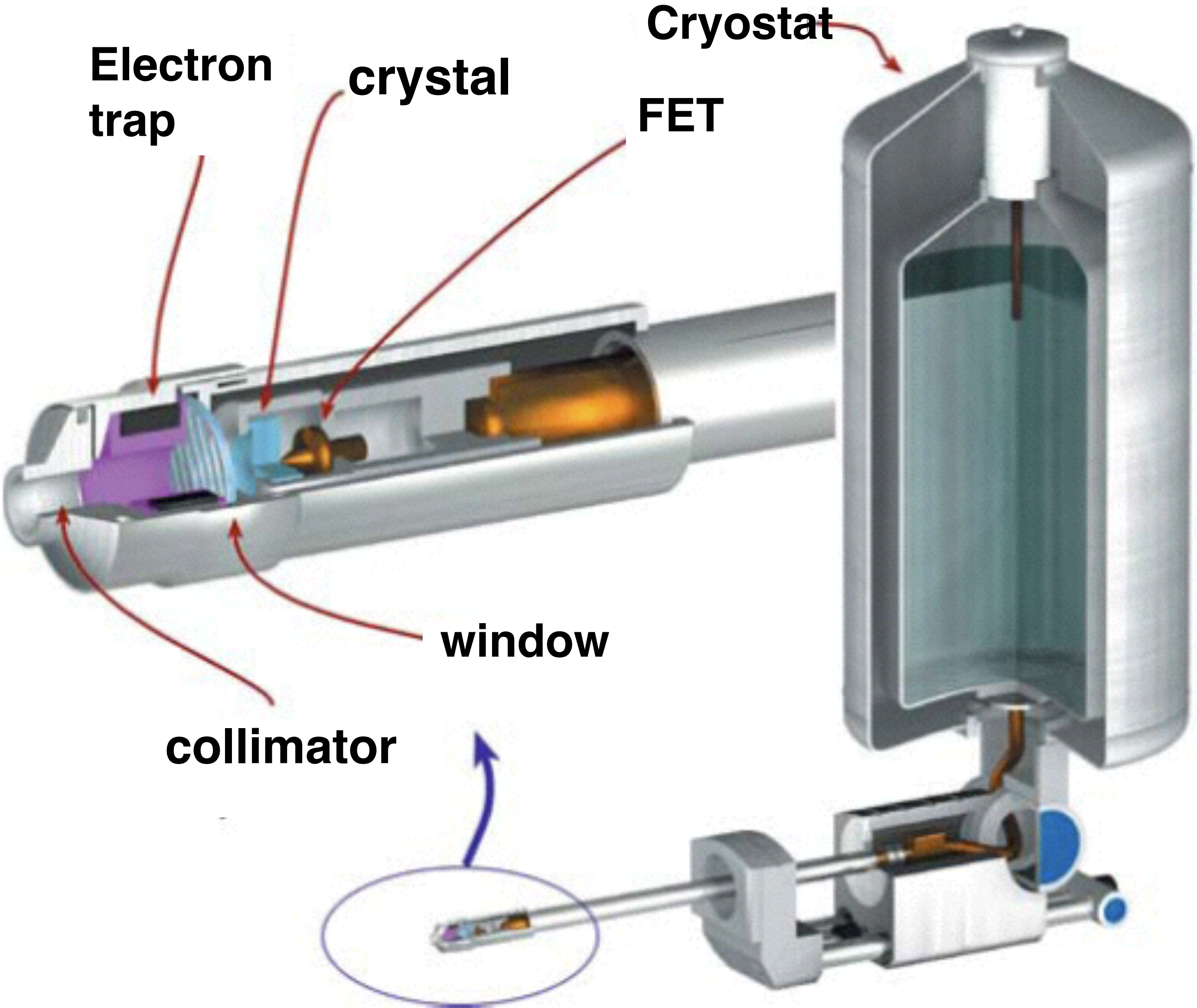
Si(Li) detector and SDD (Silicon Drift Diode)

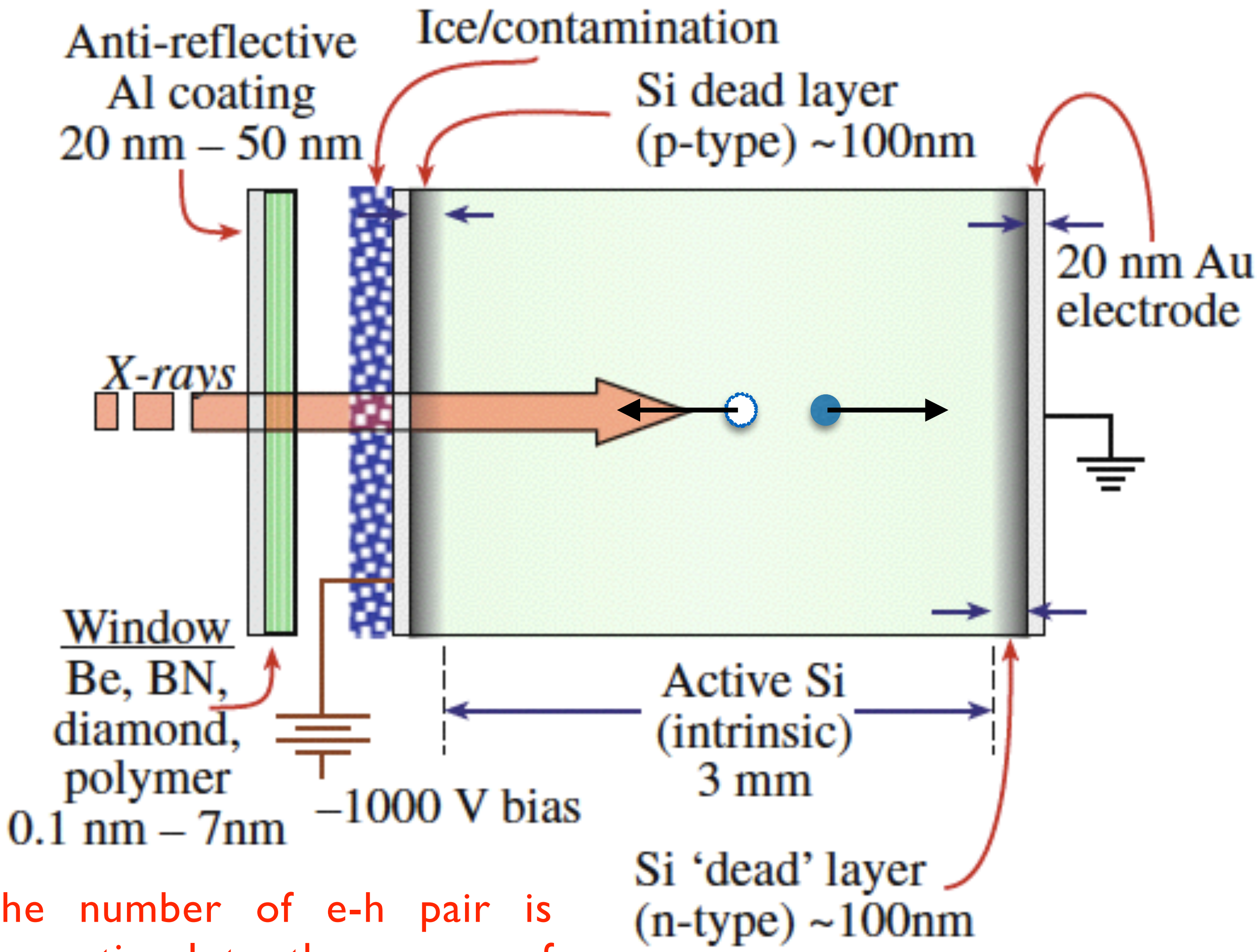
Detector Types




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

9.4.1 Semiconductor Detector





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

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 $\sim 5\times10^{-18}$ C!

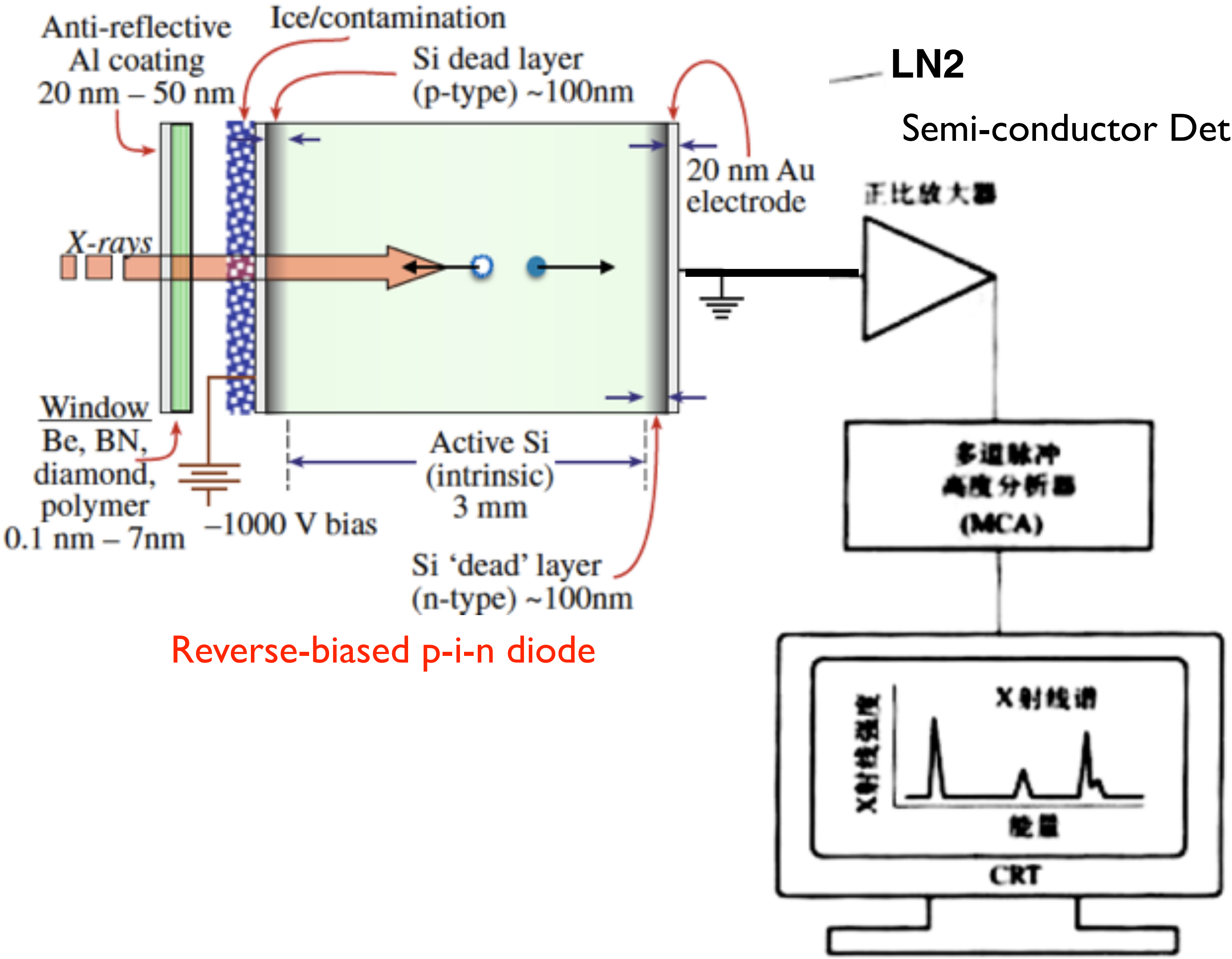
Usually, Si contains p-type impurity,

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

- Si(Li) detector

LN2

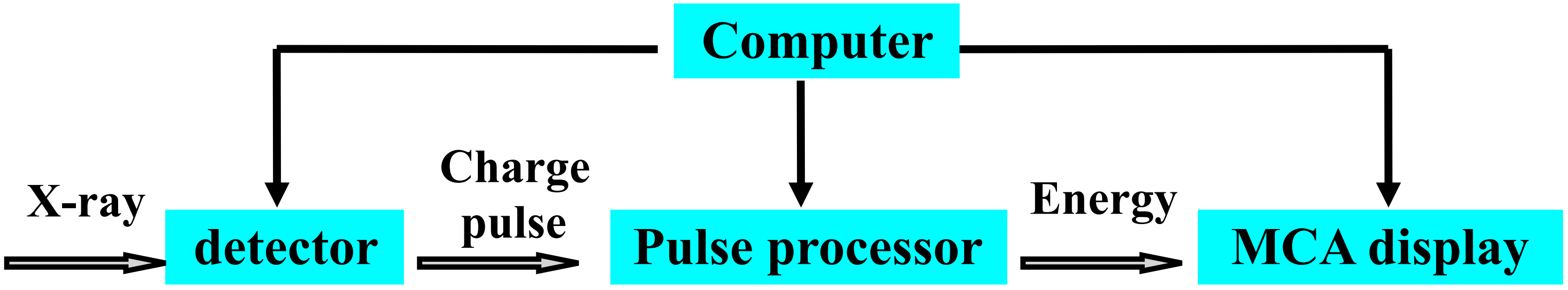
Semi-conductor Detector Si(Li



Reverse-biased p-i-n diode

The three main parts of the XEDS system are …

1. detector 2. Processing electronics 3. MCA display



Computer

X-ray → **detector** → Charge pulse → **Pulse processor** → Energy → **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

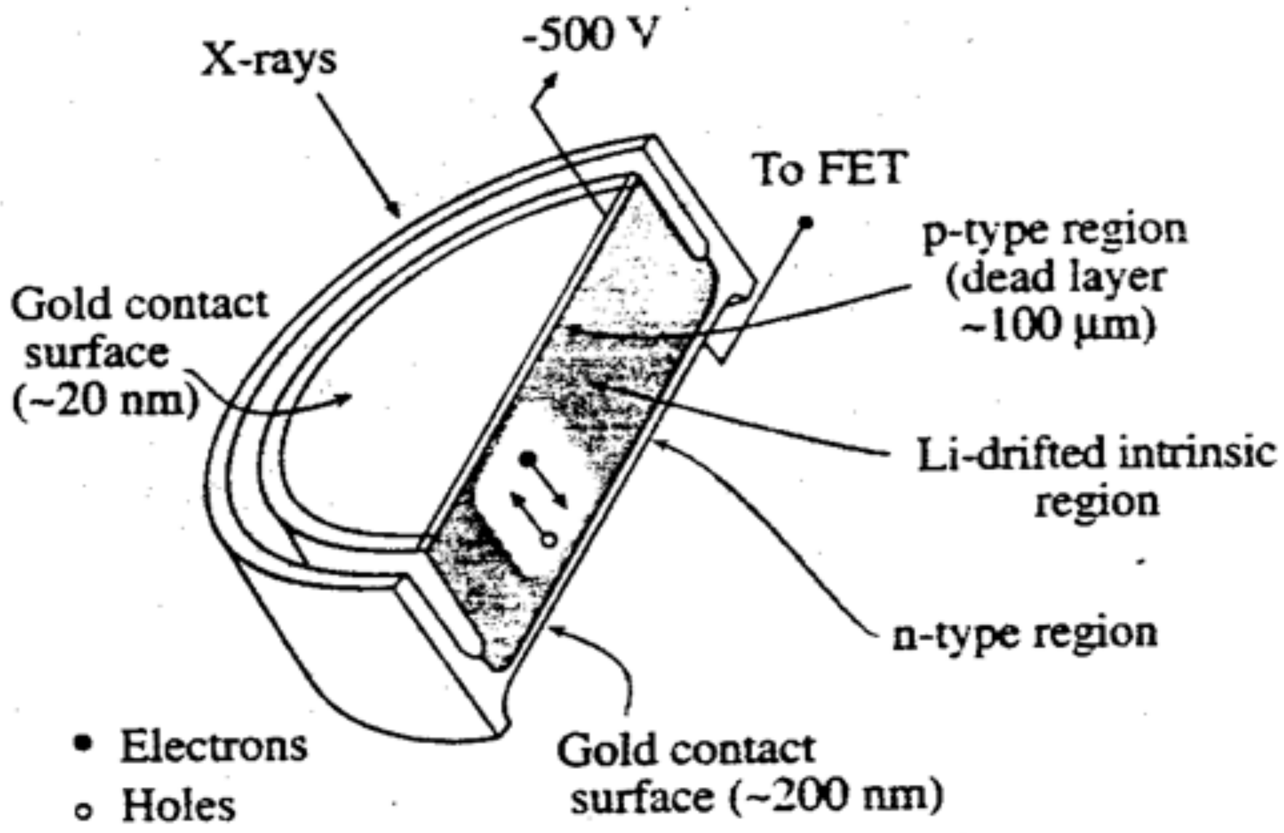


Figure 32.4. Cross section of a Si(Li) detector. The incoming X-rays generate electron–hole pairs in the intrinsic Si which are separated by an applied bias. A positive bias attracts the electrons to the rear ohmic contact after which the signal is amplified by an FET.

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.

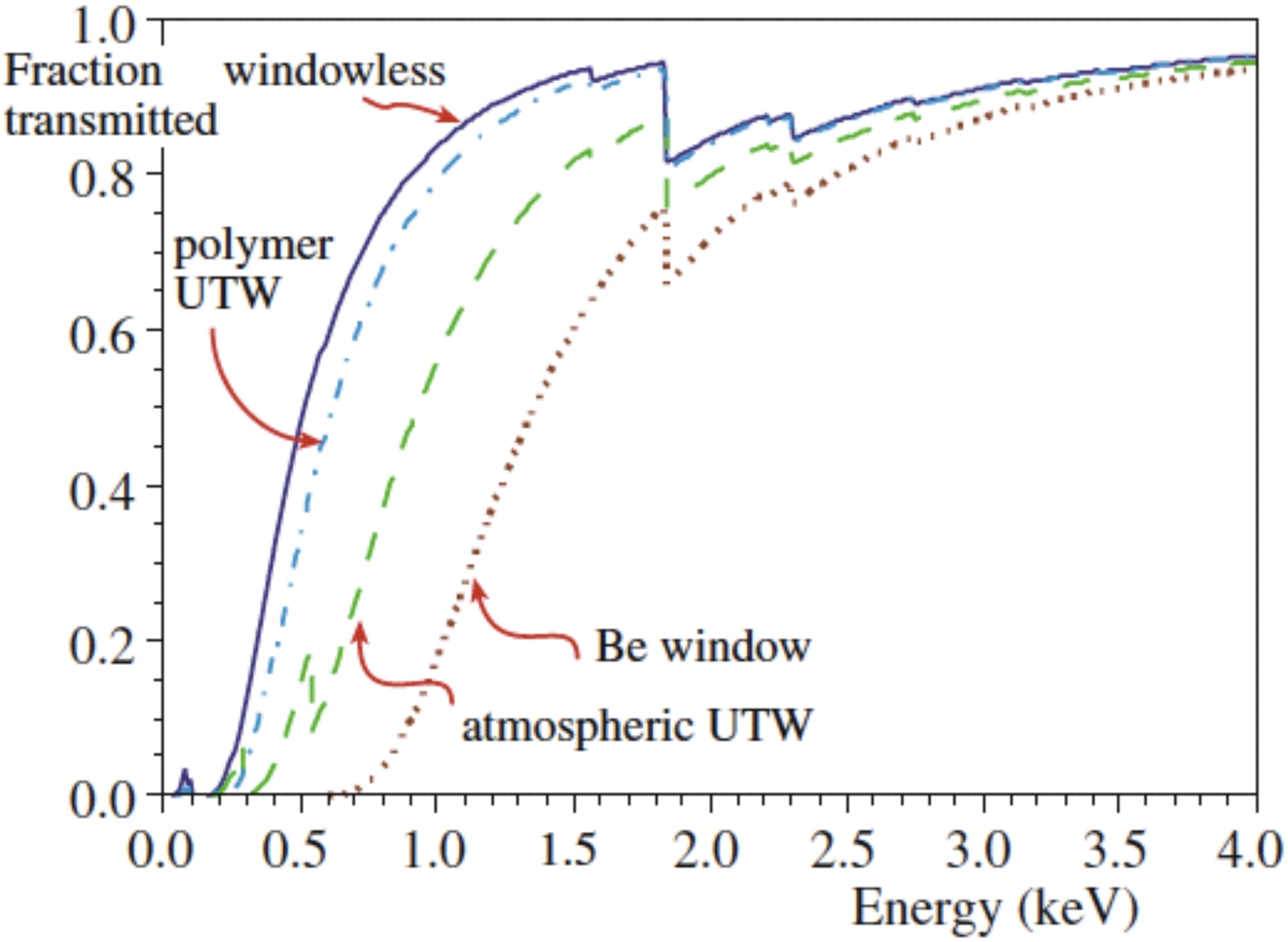
- **Windowless detector:**

  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

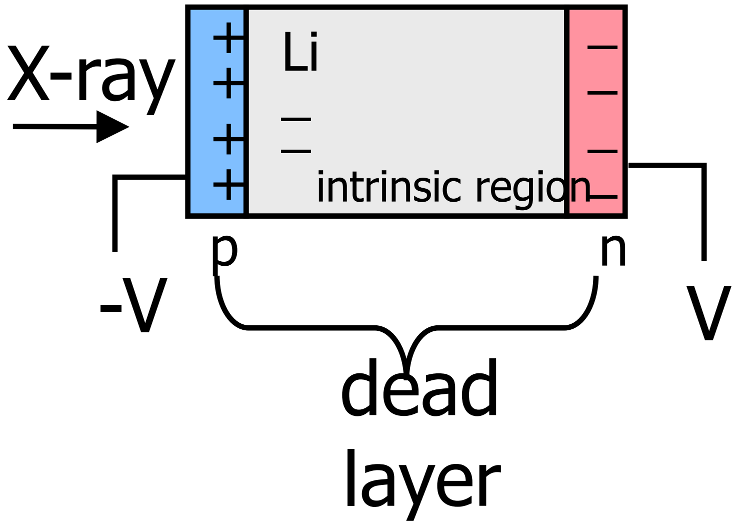
- Prior to the 1980, most EDX detector were protected (from the water vapor and hydrocarbon in the microscope column) by a 10µm thickness beryllium window, which strongly absorbs photons of energy less than 1000eV and percludes analysis of elements of atomic number less than 11.
- With development of 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"

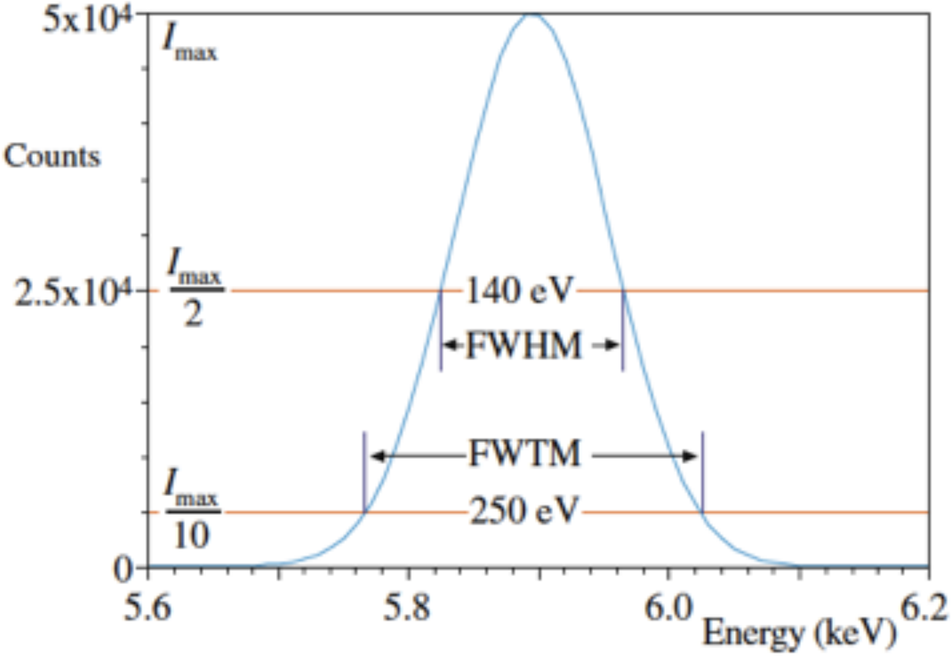


Why use Liquid N_2 cooling ?

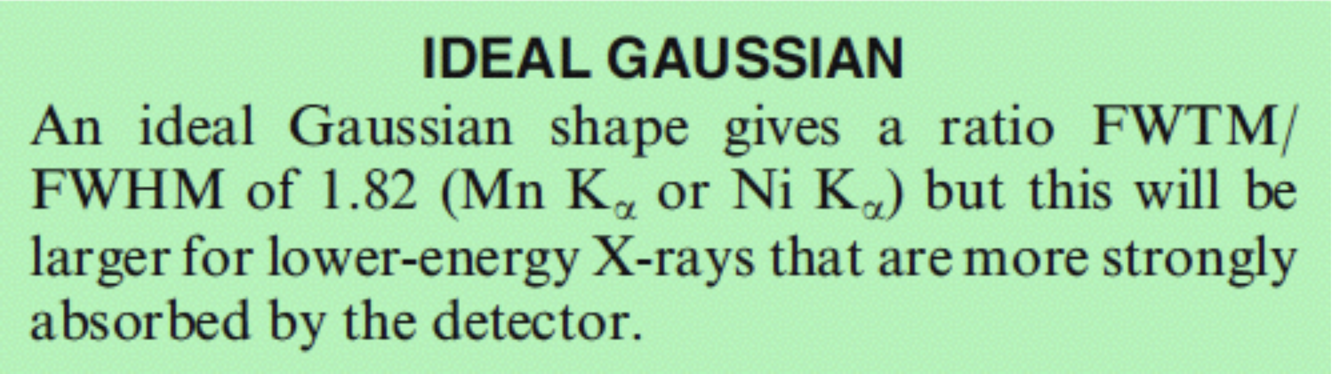
1. Thermal energy would active electron-hole pair, **giving a noise level**.
2. The Li atoms will diffuse under applied bias, that will **destroy the intrinsic property**.
3. The noise in FET will **mask the signal** from low-energy X-rays.

- 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

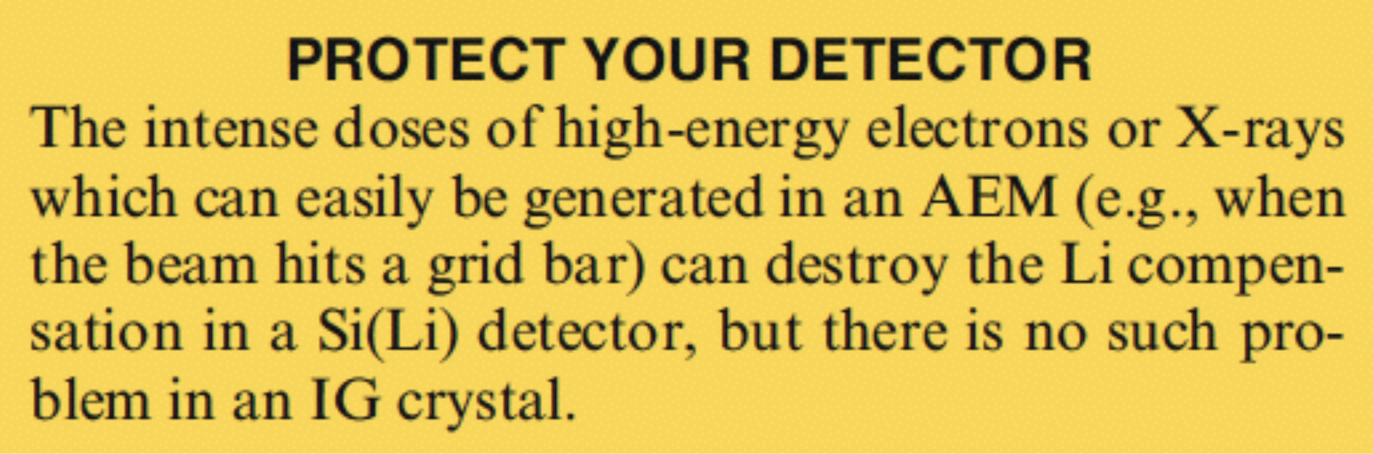
An ideal Gaussian shape gives a ratio FWTM/FWHM of 1.82 (Mn K_α or Ni K_α) but this will be larger for lower-energy X-rays that are more strongly absorbed by the detector.

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 $K\alpha$ ~75keV

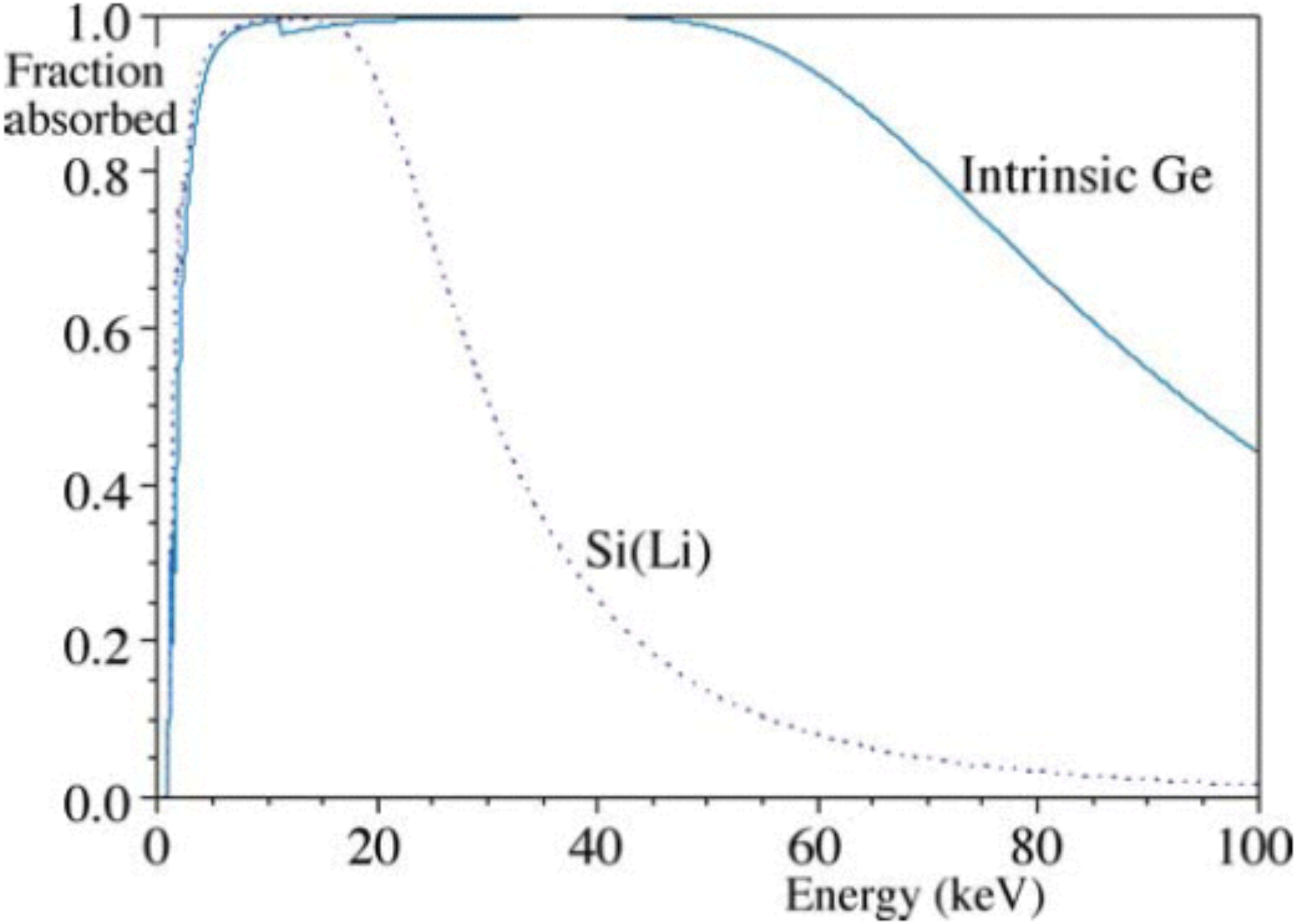
The energy for e/h pair of IG is about 2.8 eV, smaller than Si(3.8 eV)



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