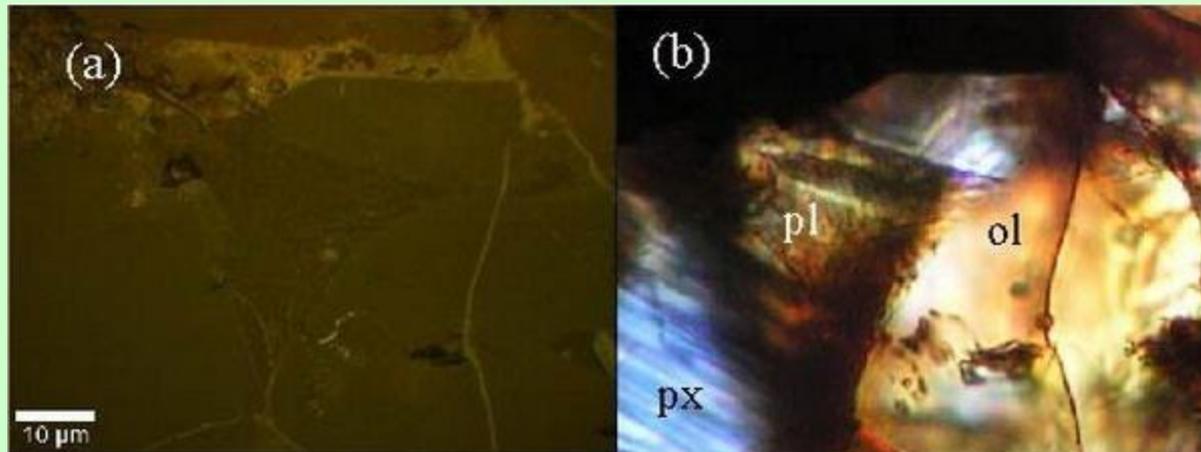


Nano-Microscopy. Lecture 3.

Microanalysis in Electron Microscopy (EDS and WDS)

Pavel Zinin

HIGP, University of Hawaii, Honolulu, USA



Electron Structure of Atoms and Quantum Numbers

Max Planck in 1900 first began to analyze atomic structure in terms of the then-developing *quantum theory* of energy. Plank proposed that an oscillating (ionized) atom could not have any arbitrary energy, but rather only certain selected energy values (quanta) were possible. Plank reasoned that if only certain energy levels were possible, there ought to be a relationship between the energy of an atom undergoing change and both the energy and wavelength of the radiation emitted during the process. He suggested that the wavelength of electromagnetic radiation, λ , its frequency, ν , and its energy, E , are related:

$$E = nh\nu = \frac{nhc}{\lambda}$$

where n is a positive integer, h is Planck's constant (6.626×10^{-34} Joule·sec), and c is the speed of light (3.0×10^8 m/s). In x-ray physics, E is measured in *electron volts*, eV, and is a unit of energy (1.6021×10^{-19} J/eV), such that $E\lambda = hc = 12.397$ (eV·Å).

Bohr's atom model

At the beginning of the 20th century, scientists were perplexed by the failure of classical physics in explaining the characteristics of atomic spectra. Why did hydrogen emit only certain lines in the visible part of the spectrum? Furthermore, why did hydrogen absorb only those wavelengths that it emitted?

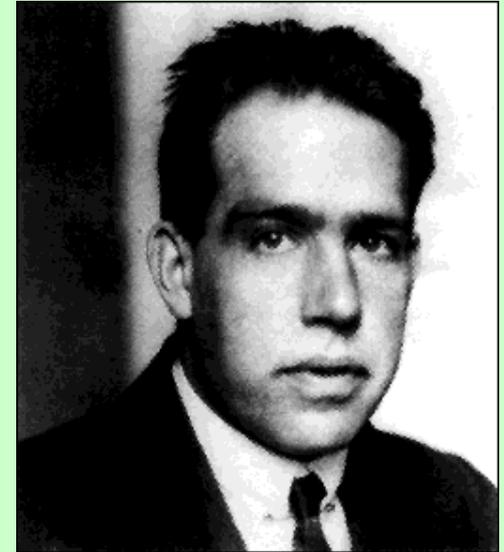


In 1913, the Danish scientist Niels Bohr (1885- 1963) provided an explanation of atomic spectra that included some features contained in the currently accepted theory. Bohr's theory contained a combination of ideas from classical physics, Planck's original quantum theory, Einstein's photon theory of light, and Rutherford's model of the atom. Bohr's model of the hydrogen atom contains some classical features as well as some revolutionary postulates that could not be justified within the framework of classical physics. The Bohr model can be applied quite successfully to such hydrogen-like ions as singly ionized helium and doubly ionized lithium.

Bohr Model

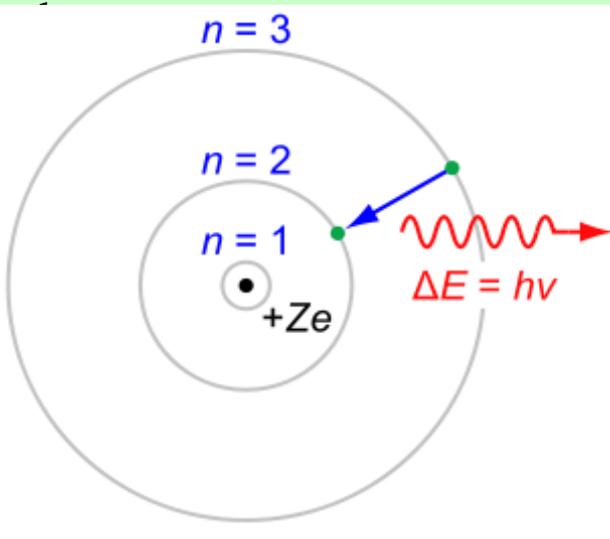
The first application of the quantum theory of atomic structure was made in 1913 by Niels Bohr. Bohr developed a model of the hydrogen atom, which allowed him to explain why the observed frequencies (i.e., wavelengths) of energy emitted obeyed simple relationships. Although it was later shown to be too simplistic, Bohr's model allowed him to calculate the energies of the allowed states for the hydrogen atom.

Introduced by Niels Bohr in 1913, the model's key success lay in explaining the Rydberg formula for the spectral emission lines of atomic



Niels Bohr

Niels Henrik David Bohr
1879-1962



The Rutherford–Bohr model of the hydrogen atom ($Z = 1$) or a hydrogen-like ion ($Z > 1$), where the negatively charged electron confined to an atomic shell encircles a small, positively charged atomic nucleus and where an electron jump between orbits is accompanied by an emitted or absorbed amount of electromagnetic energy (Wikipedia 2009).

Quantum Numbers

1. 1. The electron moves in circular orbits about the nucleus (the planetary model of the atom) under the influence of the Coulomb force of attraction between the electron and the positively charged nucleus.

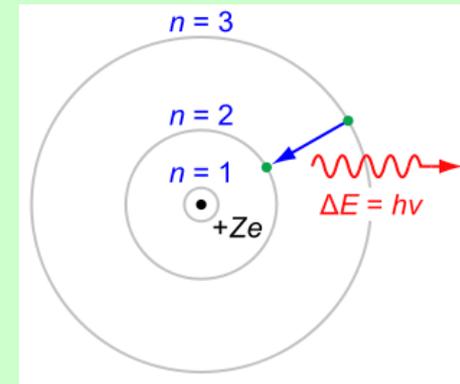
2. The electron can exist only in very specific orbits; hence the states are quantized (Planck's quantum hypothesis). The allowed orbits are those for which the angular momentum of the electron about the nucleus is an integral multiple of $h/2\pi$, where h is Planck's constant. The angular momentum of the electron is mvr , where m is the mass of electron, r is radius of the orbit, V is the linear velocity. Applying the condition that the angular momentum is quantized, we have

$$mVr = nh/2\pi$$

Bohr could determine the energy spacing between levels using rule 3 and come to an exactly correct quantum rule: the angular momentum L is restricted to be an integer multiple of a fixed unit:

$$L = n \frac{h}{2\pi}$$

where $n = 1, 2, 3, \dots$ is called the principal quantum number. The lowest value of n is 1; this gives a smallest possible orbital radius of 0.0529 nm known as the Bohr radius. Once an electron is in this lowest orbit, it can get no closer to the proton.

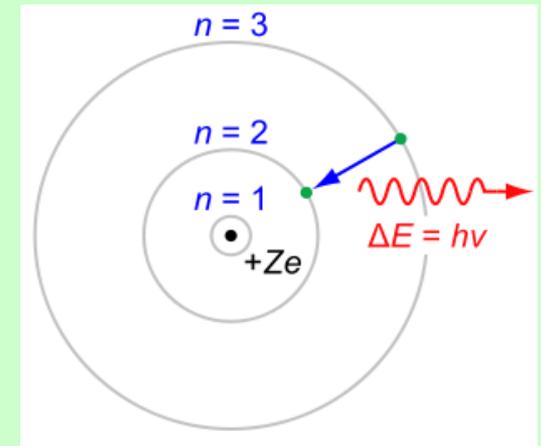


Quantum Numbers

3. The electrons do not continuously lose energy as they travel. They can only gain and lose energy by jumping from one allowed orbit to another, absorbing or emitting electromagnetic radiation with a frequency ν determined by the energy difference of the levels according to the Planck relation

$$\Delta E = E_2 - E_1 = nh$$

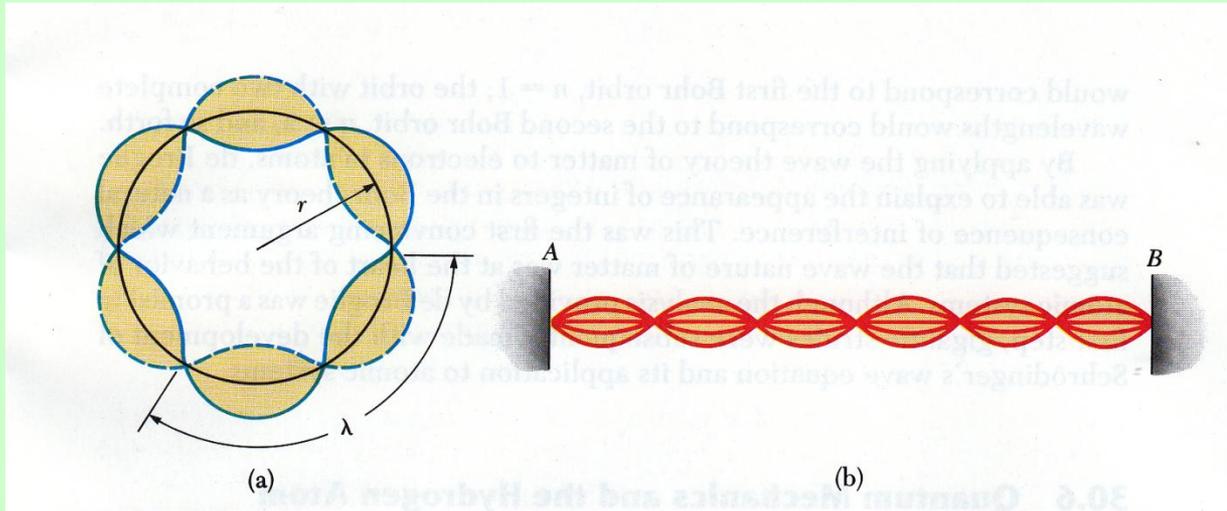
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4. The frequency of the radiation emitted at an orbit of period T is as it would be in classical mechanics; it is the reciprocal of the classical orbit period:

$$\nu = \frac{1}{T}$$

De Broglie Waves and the Hydrogen Atom



(a) Standing wave pattern for an electron wave in a stable orbit of hydrogen. There are three full wavelengths in this orbit.
(b) Standing wave pattern for a vibrating stretched string fixed at its ends. This pattern has three full wavelengths

In general, the condition for a de Broglie standing wave in an electron orbit is that the circumference must contain an integral multiple of electron wavelengths. We can express this condition as

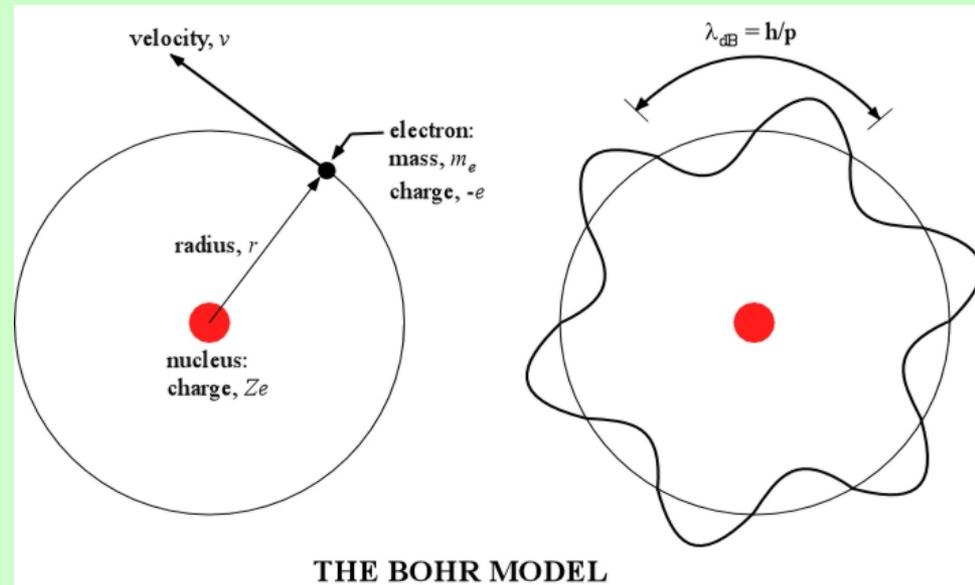
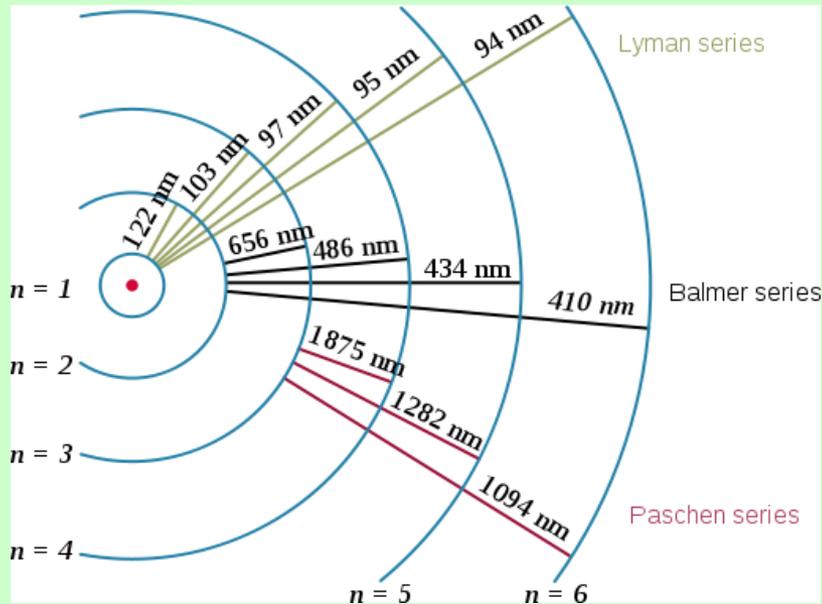
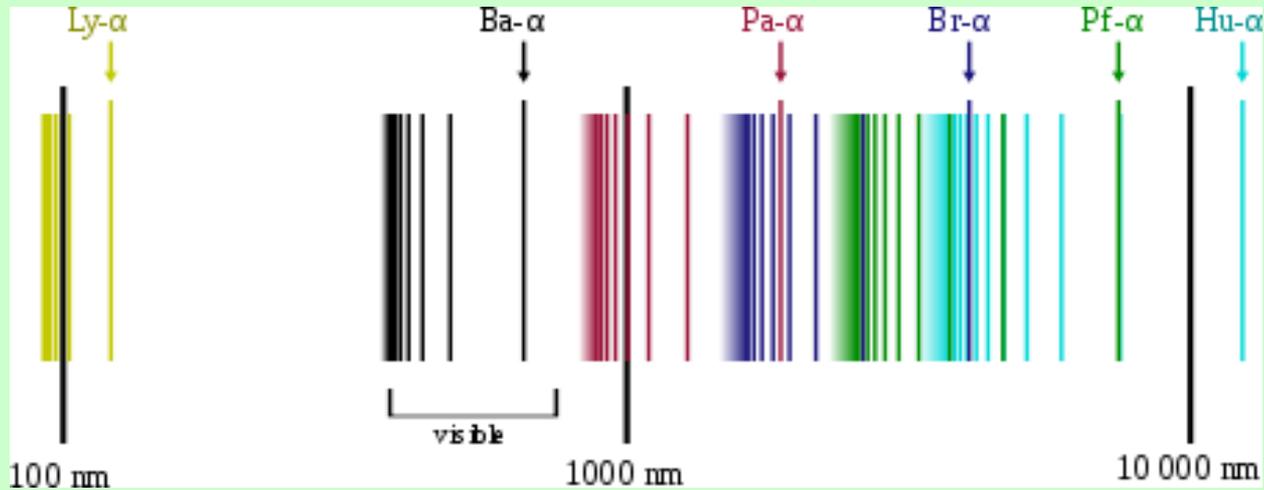
$$2\pi r = n\lambda$$

De Broglie's equation for the wavelength of an electron in terms of its momentum is

$$\lambda = nh/mv \Rightarrow 2\pi r = nh/2\pi$$

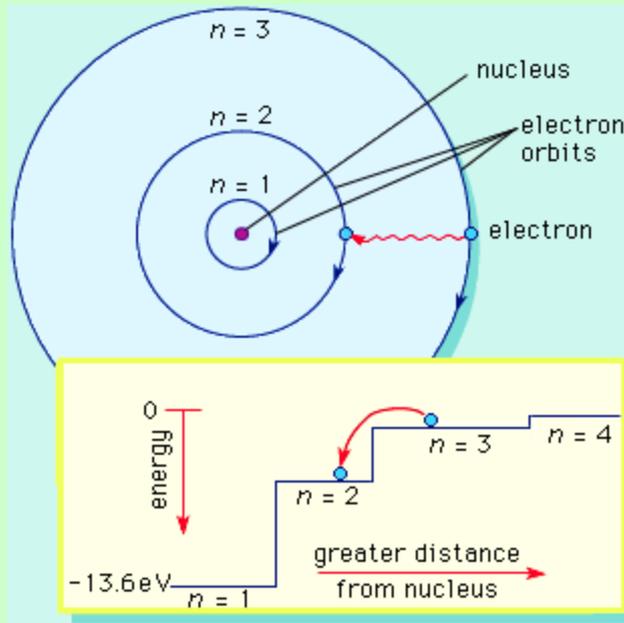
This is precisely the quantization of angular momentum condition imposed by Bohr in his original theory of hydrogen. The electron orbit shown in Figure contains three complete wavelengths and corresponds to the case where the principal quantum number n equals three. The orbit with one complete wavelength in its circumference

Quantum Numbers



Quantum Numbers

There are a set of quantum numbers associated with the energy states of the atom. The four quantum numbers n , l , m , and s specify the complete and unique quantum state of a single electron in an atom called its wavefunction or orbital. No two electrons belonging to the same atom can have the same four quantum numbers which is shown in the Pauli exclusion principle.



$n \equiv$ principal quantum number

The bound state energies of the electron in the hydrogen atom are given by:

$$E_n = \frac{-13.6 \text{ eV}}{n^2}$$

$$n = 1, 2, 3, 4, \dots$$

The principle quantum number (n): The principle quantum number (n) can include any positive integral value. It determines the major energy level of an electron. It is designated **K**, **L** and **M** for $n = 1$, 2 and 3 respectively. The maximum number of electrons allowed is $2n^2$.

Number of Electrons

Maximum number of electrons in any electron shell = $2n^2$

$$n = 1 \quad 2(1)^2 \quad = \quad 2$$

$$n = 2 \quad 2(2)^2 \quad = \quad 8$$

$$n = 3 \quad 2(3)^2 \quad = \quad 18$$

Each principal energy level, which is known as a **shell**, has **one or more subshells**

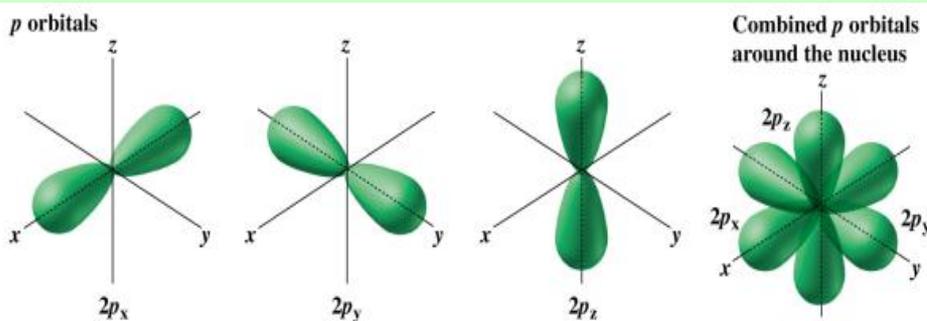
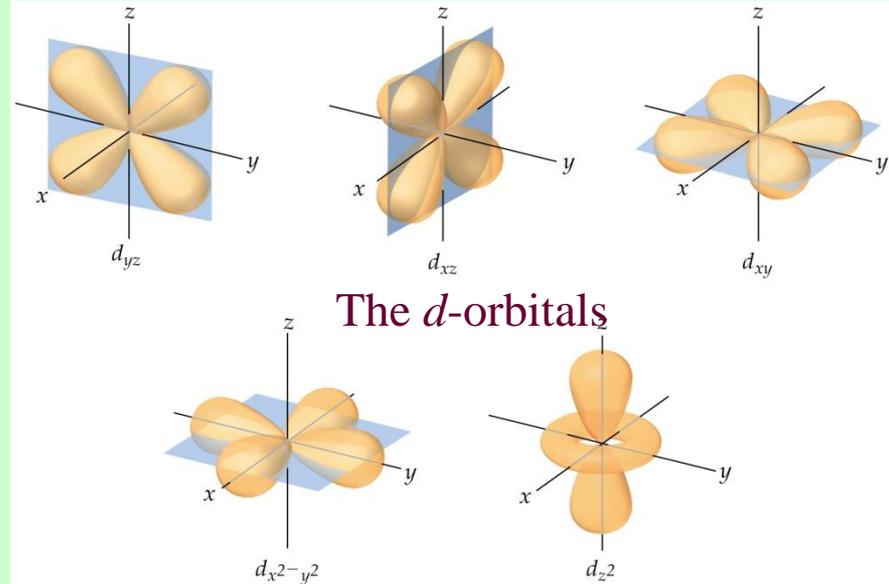
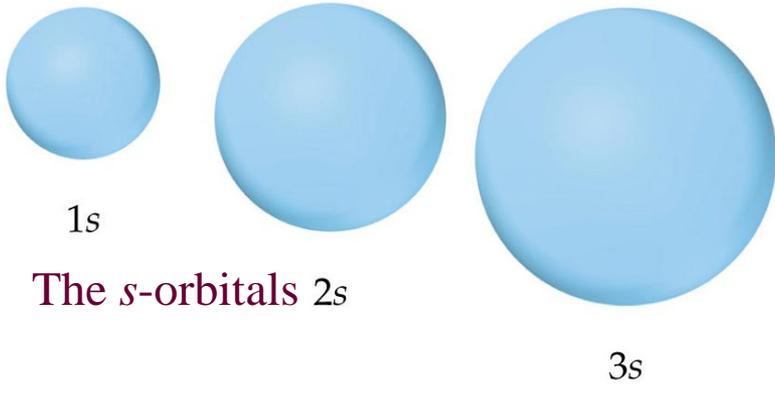
NOTE: Electrons generally fill into shells with smallest n first; however, the filling order gets more complicated after Argon (element 18).

For the first 20 electrons:

<i>Shell</i>	1	2	3	4
	2e	8e	8e	2e

Quantum Numbers

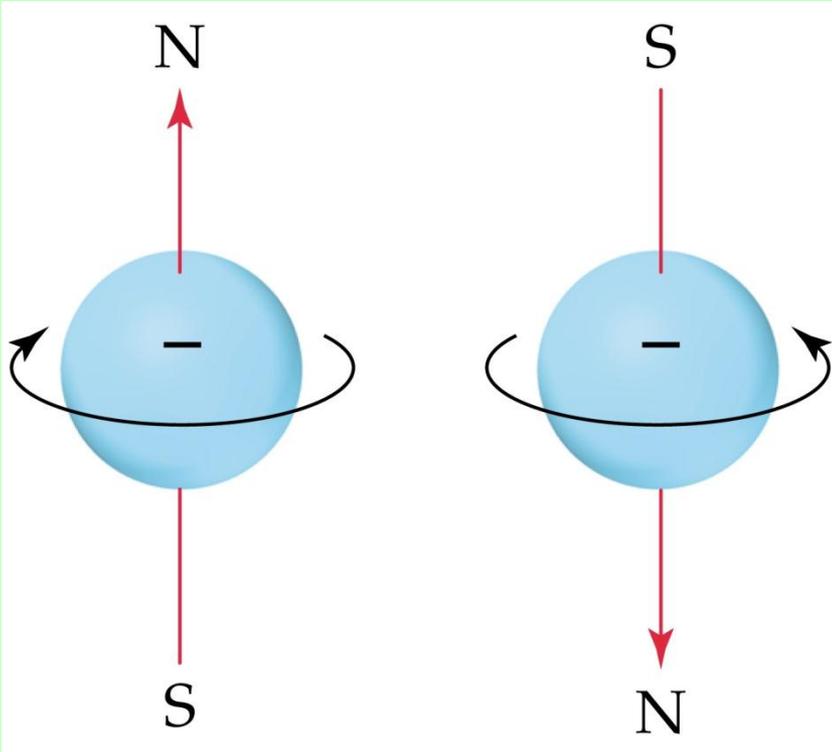
- The azimuthal momentum quantum number (l): The azimuthal or angular momentum number (or orbital angular momentum quantum number, second quantum number) symbolized as l , is a quantum number for an atomic orbital that determines its orbital angular momentum and describes the shape of the orbital. Higher values of l correspond to greater angular momentum. l may assume integer values from 0 to $n-1$. The orbitals are s , p , d and f for $l = 0, 1, 2$ and 3 respectively. The orbitals have distinctive shapes. The maximum number of electrons allowed is: $s = 2$, $p = 6$, $d = 10$ and $f = 14$.



The magnetic quantum number (m): An electron with angular momentum generates a magnetic field. m can assume any integer from $-l$ to $+l$.

Quantum Numbers

- The spin quantum number: A small "particle", like an electron, spinning on its own axis also behaves as a small magnet, hence the electron itself has an intrinsic magnetic property. We say that the electron has a spin and describe it as being either $+1/2$ or $-1/2$.



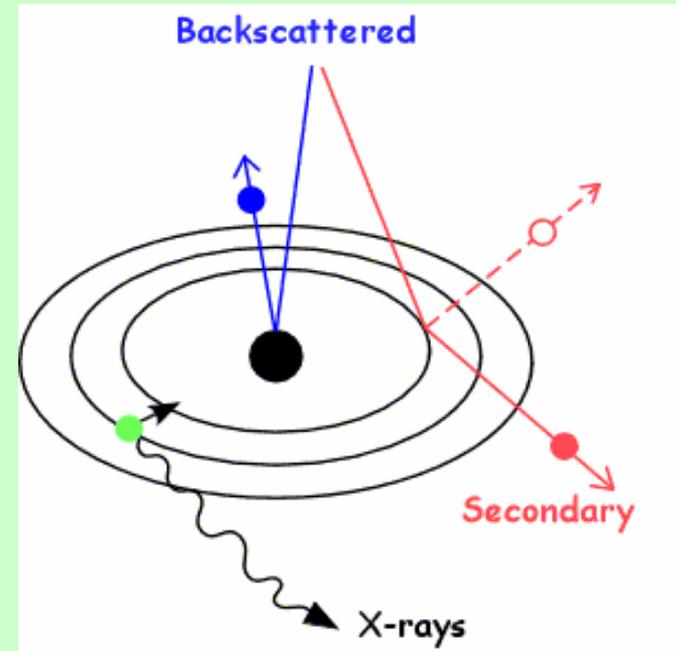
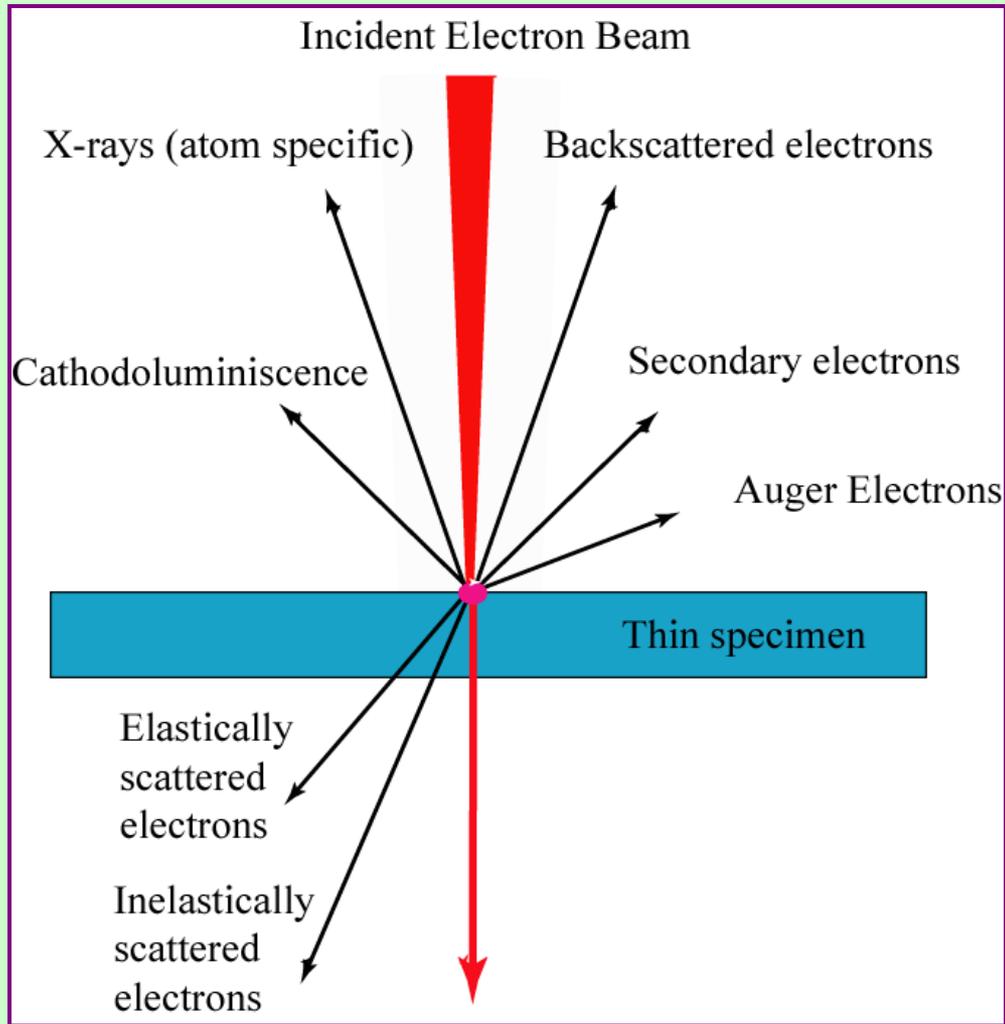
Electron Spin and the Pauli Exclusion Principle

Since electron spin is quantized, we define $m_s = \text{spin quantum number} = \pm 1/2$.

Pauli's Exclusions Principle: no two electrons can have the same set of 4 quantum numbers. Therefore, two electrons in the same orbital must have opposite spins.

The specific quantum numbers assigned to the electrons are determined by thermodynamic considerations that require the occupation of states having the lowest energies first, and the Pauli Exclusion Principle.

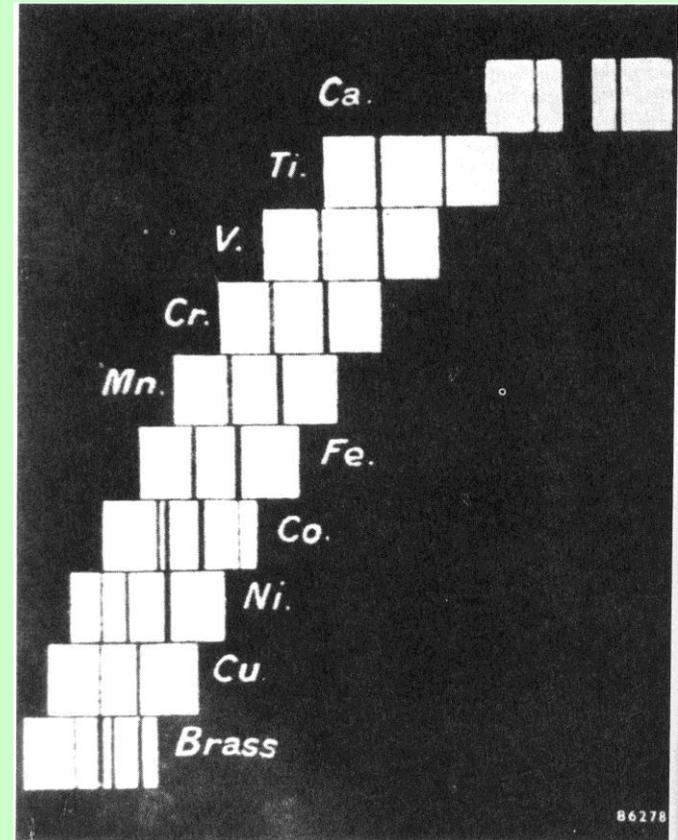
Interaction of electrons with matter in an electron microscope



- Back scatter electrons – compositional
- Secondary electrons – topography
- X-rays – chemistry

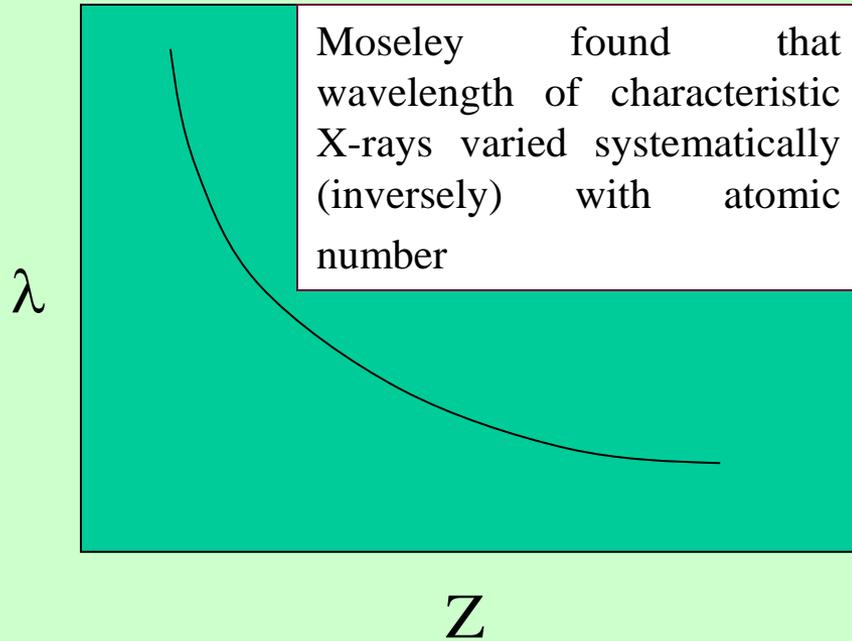
History of X-rays and EDS

- 1912, von Laue, Friedrich and Knipping observe X-ray diffraction. Laue demonstrated with the dispersion of x-rays that their wavelength must be on the order of atomic dimensions. Subsequently, the wavelengths of characteristic x-ray radiation were measured to be in the range of 10^{-8} to 10^{-11} meters, and the dimensional unit angstrom ($\text{\AA}=10^{-10}\text{m}$) was introduced.
- The theory of diffraction of x-rays, originally proposed by Laue, was conclusively demonstrated by W.H. Bragg and W.L. Bragg in 1913 by obtaining the first x-ray diffraction pattern a sodium chloride crystal.
- 1913, Henry G.J. Moseley was researching the characteristics of x-ray emission from different target materials. He noticed a systematic progression of x-ray wavelengths with increasing atomic number of the material generating the radiation. Based on this regularity, the previously unknown elements hafnium and rhodium were discovered with x-ray spectral analysis.



Photographic recording of $K\alpha$ and $K\beta$ x-ray emission lines for a range of elements

History of X-rays



$$\sqrt{f} = k_1(Z - k_2)$$



Henry G. J. Moseley
(1887-1915)

where: f is the frequency of the main or K x-ray emission line k_1 and k_2 are constants that depend on the type of line. For example, the values for k_1 and k_2 are the same for all K lines, so the formula can be rewritten thus:

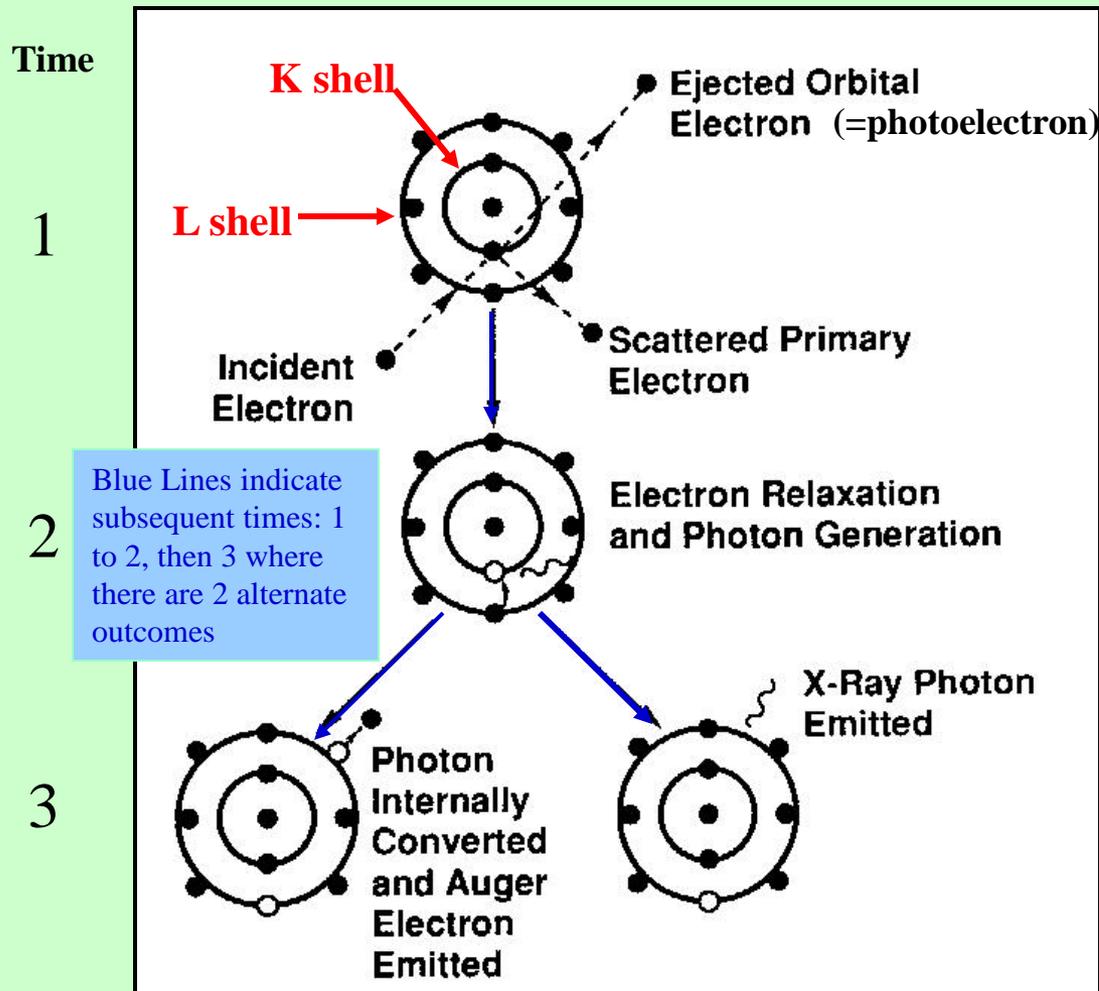
$$f = (2.47 \times 10^{15} \cdot (Z - 1)^2 \text{ Hz})$$

The next year, he was killed in Turkey in WWI. “In view of what he might still have accomplished (he was only 27 when he died), his death might well have been the most costly single death of the war to mankind generally,” says Isaac Asimov (Biographical Encyclopedia of Science & Technology).

EM Spectrum Lines Produced by Electron Shell Ionization

Number	Name	Permitted Values	Defines
n	Principal	(1, 2, 3, ...)	Electron shell (1=K, 2=L, 3=M ...)
l	Azimuthal	0 to $n-1$	Electron cloud shape
m	Magnetic	$-l$ to $+l$	Electron shell orientation in a magnetic field
s	Spin	$\pm\frac{1}{2}$	Electron spin direction
j	Inner precession	$l \pm \frac{1}{2}$ But $j \neq -\frac{1}{2}$	Total angular momentum

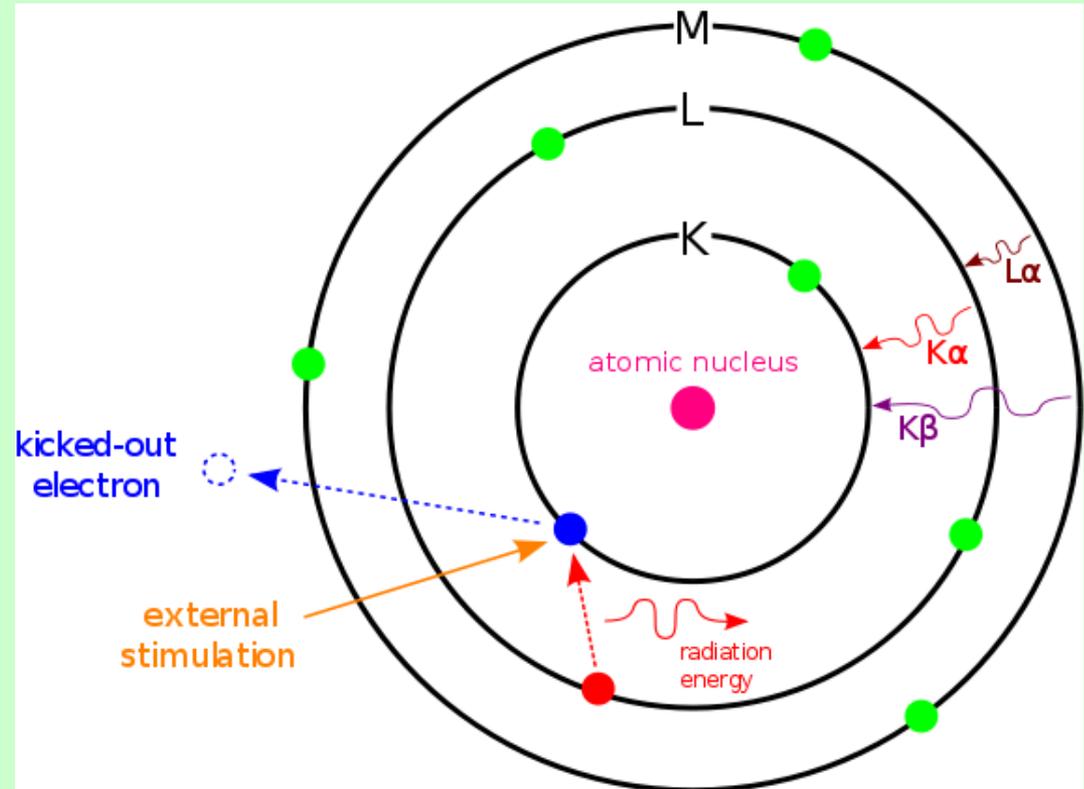
Inner-shell ionization: Production of X-ray



Incident electron knocks inner shell (K here) electron out of its orbit (time=1). This is an unstable configuration, and an electron from a higher energy orbital (L here) 'falls in' to fill the void (time=2). There is an excess of energy present and this is released internally as a photon. The photon has 2 ways to exit the atom (time=3), either by ejecting another outer shell electron as an Auger electron (L here, thus a KLL transition), or as X-ray (KL transition).

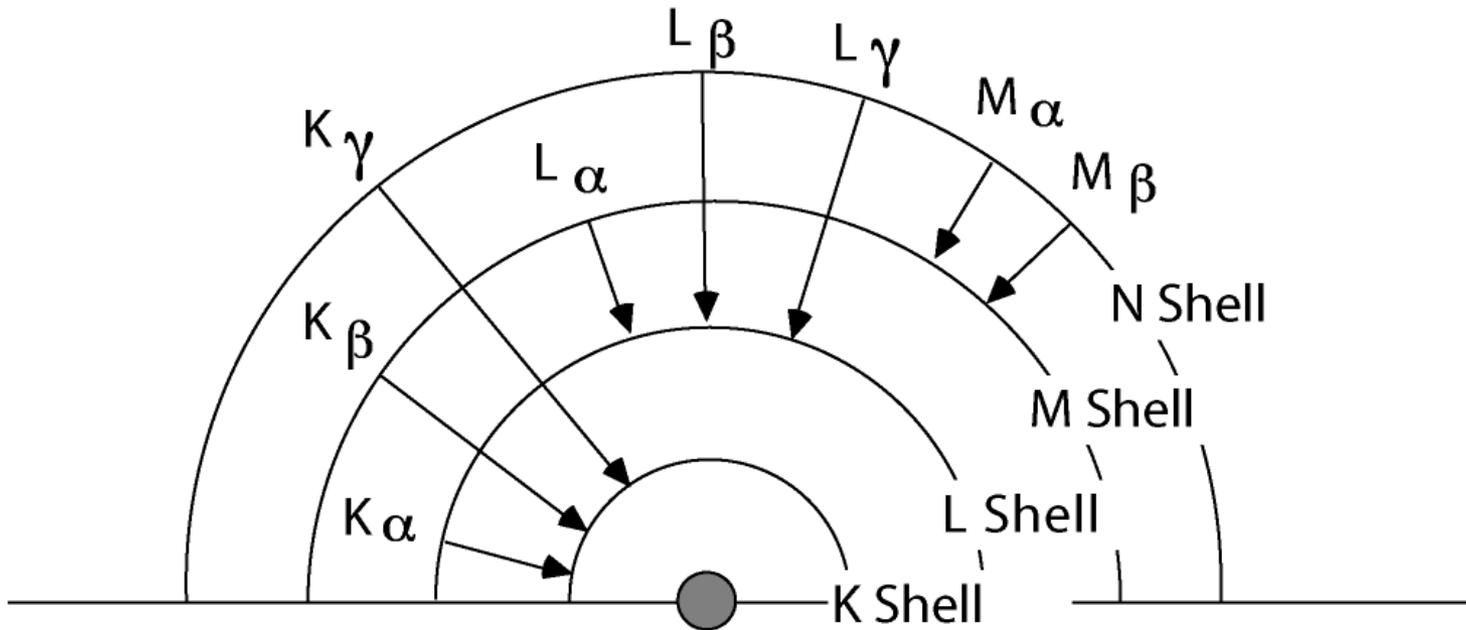
History of the Electron Microprobe Microscopy

In order to return the atom to its normal state, an electron from an outer atomic shell “drops” into the vacancy in the inner shell. This drop results in the loss of a specific amount of energy, namely, the difference in energy between the vacant shell and the shell contributing the electron. This energy is given up in the form of electromagnetic radiation x-rays. Since energy levels in all elements are different, element-specific, or characteristic, x-rays are generated.



EM Spectrum Lines Produced by Electron Shell Ionization

Nomenclature for Principle X-ray Emission Lines



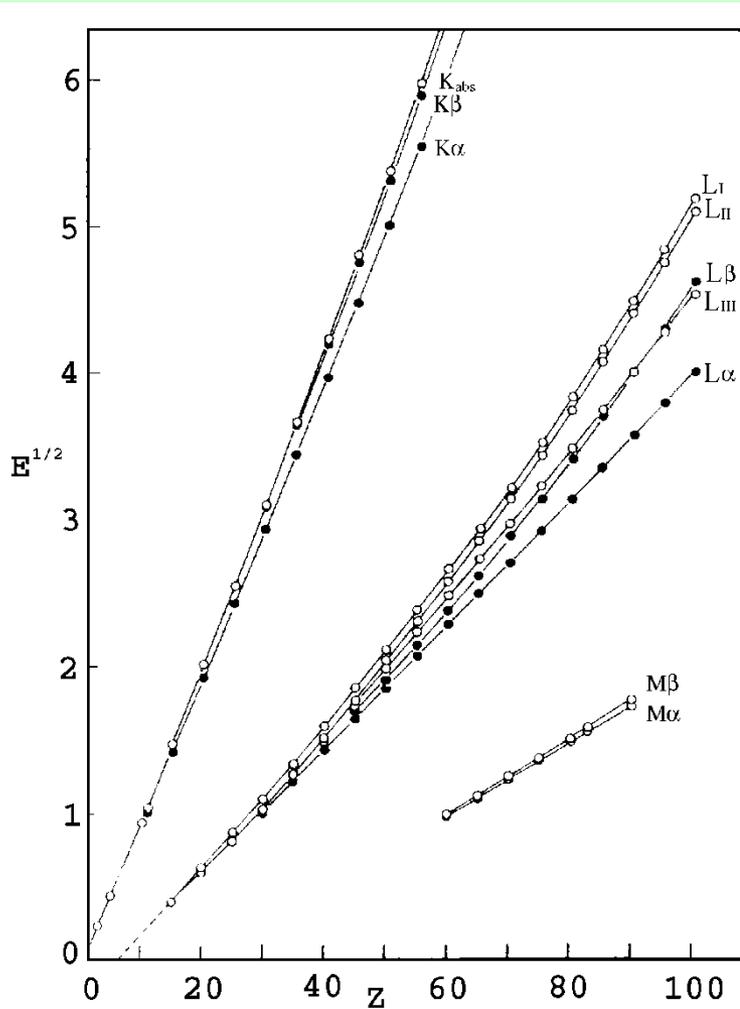
K_{α} X-ray is produced due to removal of K shell electron, with L shell electron taking its place.

K_{β} occurs in the case where K shell electron is replaced by electron from the M shell.

L_{α} X-ray is produced due to removal of L shell electron, replaced by M shell electron.

M_{α} X-ray is produced due to removal of M shell electron, replaced by N shell electron.

Moseley's Law



The amount of energy needed to remove the electron from the inner atomic shell, E_q , which is related to the minimum potential, V_q , required to eject the electron with an electronic charge, e . Moseley's law is a function of atomic number, Z .

$$E_q = eV_q \mu (Zs)^2$$

where the proportionality and the “screening constant”, s , differ depending on which inner shell (K , L , etc.) is ionized

EM Spectrum Lines Produced by Electron Shell Ionization

Energy of characteristic X-rays

$$E(\text{keV}) = K(Z-1)^2$$

where

$K = 1.042 \cdot 10^{-2}$ for the K-shell

$K = 1.494 \cdot 10^{-3}$ for the L-shell

$K = 3.446 \cdot 10^{-4}$ for the M-shell

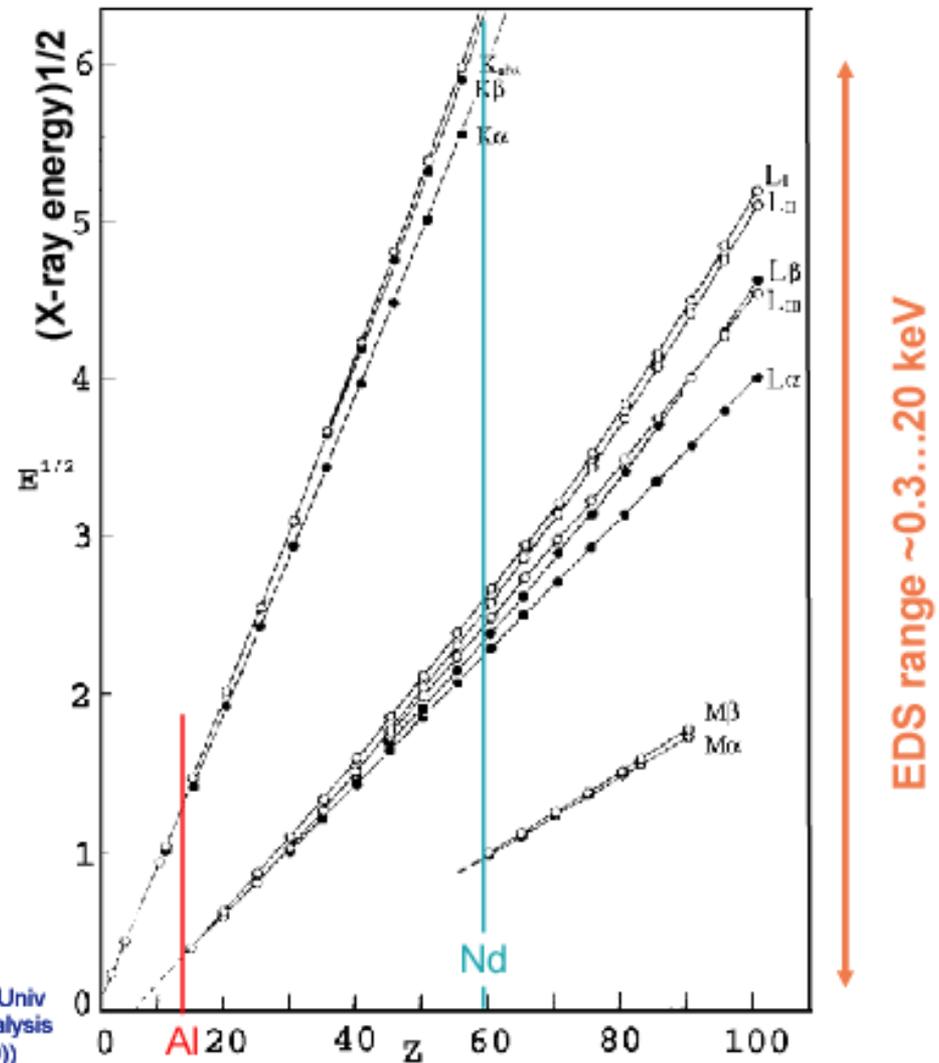
several families K, L, M, N... ($n=1,2,3,4$)

energy within a family increases with Z

$$E_K > E_L > E_M \dots$$

when a level n is excited, all sub-levels $n_i > n$ are also excited and corresponding lines must be observed within the detector capability limit

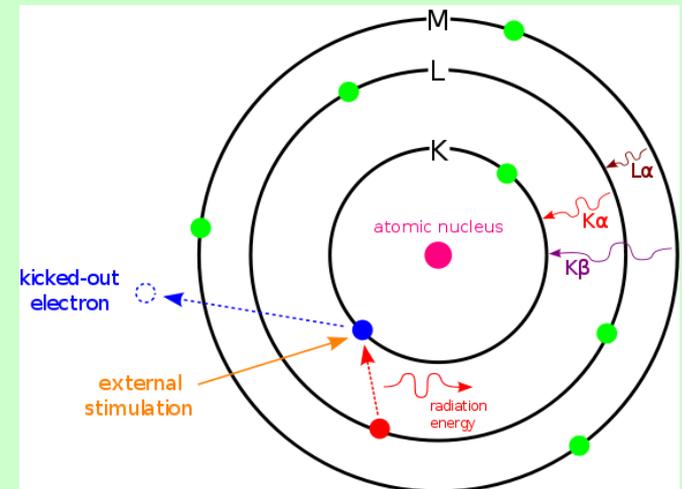
(from CAMCOR Oregon Univ
Electron Beam Micro Analysis
Lecture Notes (Geol 619))



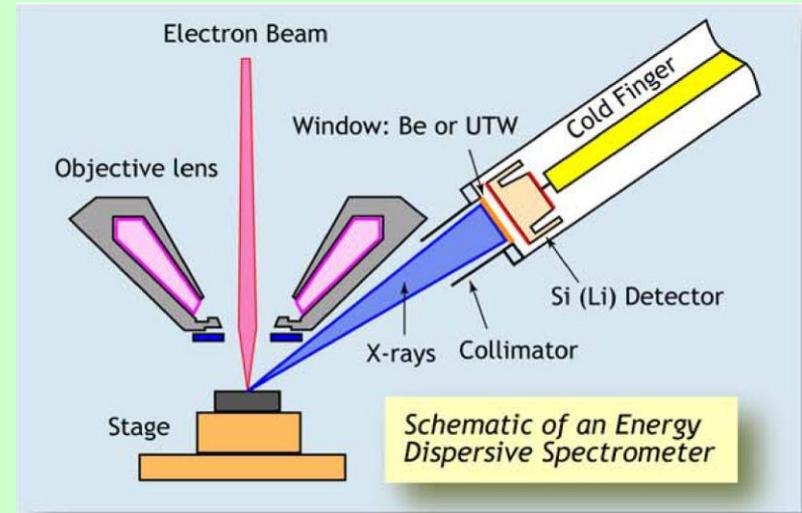
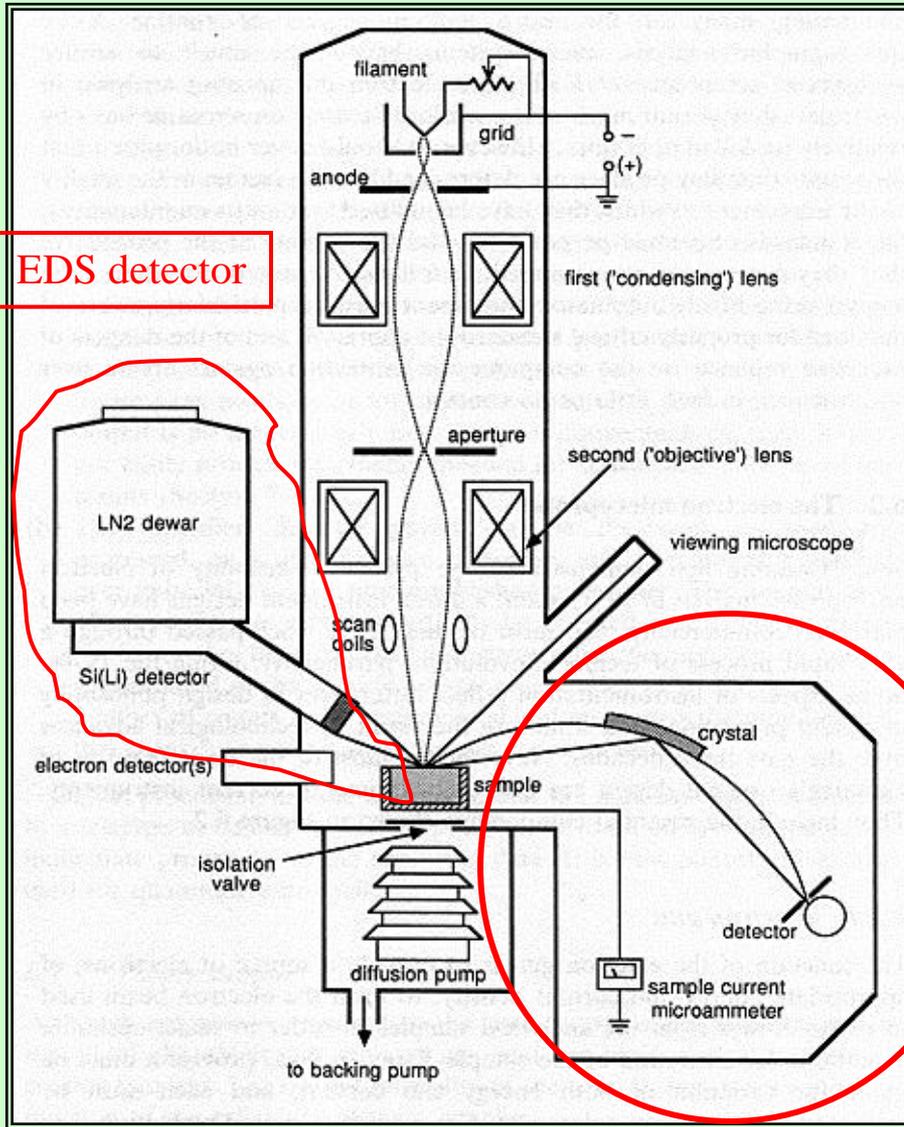
X-ray spectroscopy in SEM

X-ray spectrometers are of two kinds.

- (a) The energy-dispersive (ED) type records X-rays of all energies effectively simultaneously and produces an output in the form of a plot of intensity versus X-ray photon energy. The detector consists of one of several types of device producing output pulses proportional in height to the photon energy.
- (b) The wavelength-dispersive (WD) type makes use of Bragg reflection by a crystal, and operates in 'serial' mode, the spectrometer being 'tuned' to only one wavelength at a time. Several crystals of different interplanar spacings are needed in order to cover the required wavelength range. Spectral resolution is better than for the ED type, but the latter is faster and more convenient to use. X-ray spectrometers attached to SEMs are usually of the ED type, though sometimes a single multi-crystal WD spectrometer is fitted.



SEM with EDS



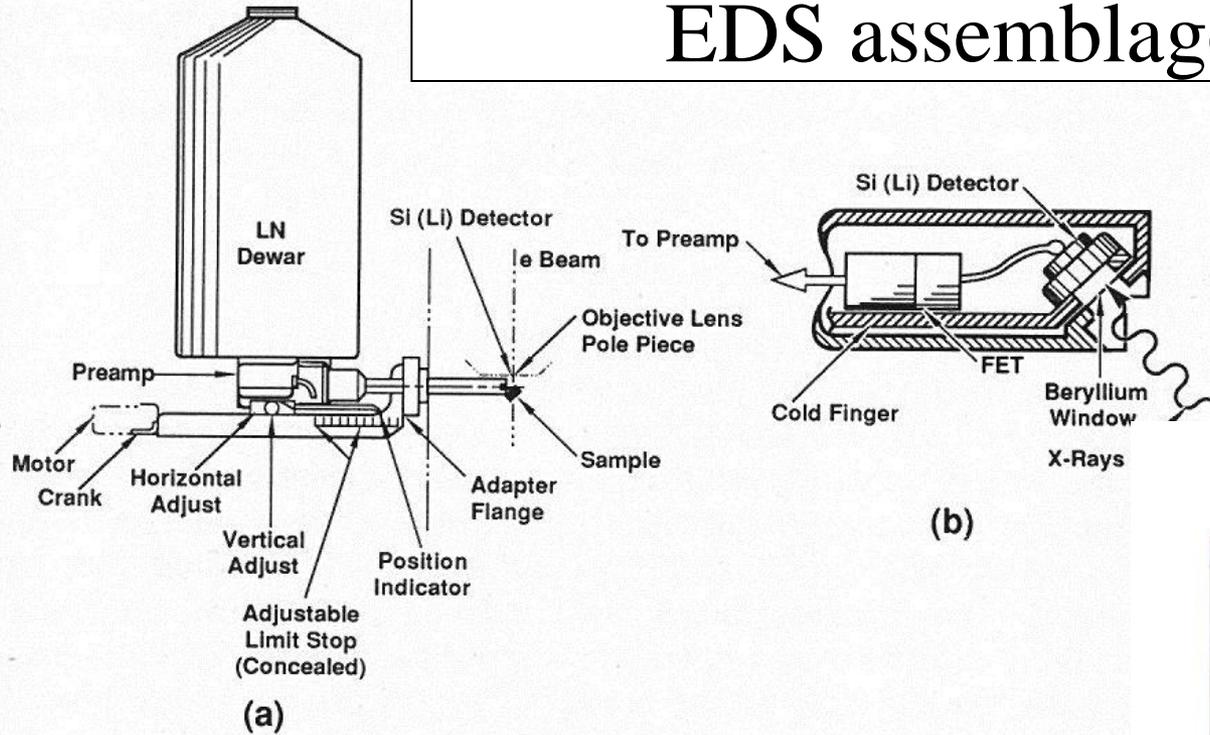
SEM combined with Energy dispersive spectrometer (EDS) and Wavelength Dispersive Spectrometer (WDS).

WDS
spectrometers

How the EDS Detector Works

- The central component of an EDS system is a solid-state detector, consisting of a semiconductor. As each X-ray photon hits the detector, a very small current is produced by knocking out electrons from the semi-conductor.
- How the EDS Detector Works: The EDS detector converts the energy of each individual X-ray into a voltage signal of proportional size. This is achieved through a three stage process. Firstly the X-ray is converted into a charge by the ionization of atoms in the semiconductor crystal. Secondly this charge is converted into the voltage signal by the field effect transistor (FET) preamplifier. Finally the voltage signal is input into the pulse processor for measurement. The output from the preamplifier is a voltage 'ramp' where each X-ray appears as a voltage step on the ramp.
- How the crystal converts X-ray energy into charge: When an incident X-ray strikes the detector crystal its energy is absorbed by a series of ionizations within the semiconductor to create a number of electron-hole pairs. The electrons are raised into the conduction band of the semiconductor and are free to move within the crystal lattice. When an electron is raised into the conduction band it leaves behind a 'hole', which behaves like a free positive charge within the crystal. A high bias voltage, applied between electrical contacts on the front face and back of the crystal, then sweeps the electrons and holes to these opposite electrodes, producing a charge signal, the size of which is directly proportional to the energy of the incident X-ray.
- The charge is converted to a voltage signal by the FET preamplifier.

EDS assemblage



Goldstein et al fig 5.21

There are several types of solid state EDS detectors, the most common (cheapest) being the Si-Li detector. Components: thin window (Be, C, B); SiLi crystal, FET (field effect transistor: initial amp), vacuum, cold finger, preamp, amp and MDA electronics (“multi channel analyzer”).



EM Spectrum Lines Produced by Electron Shell Ionization

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where

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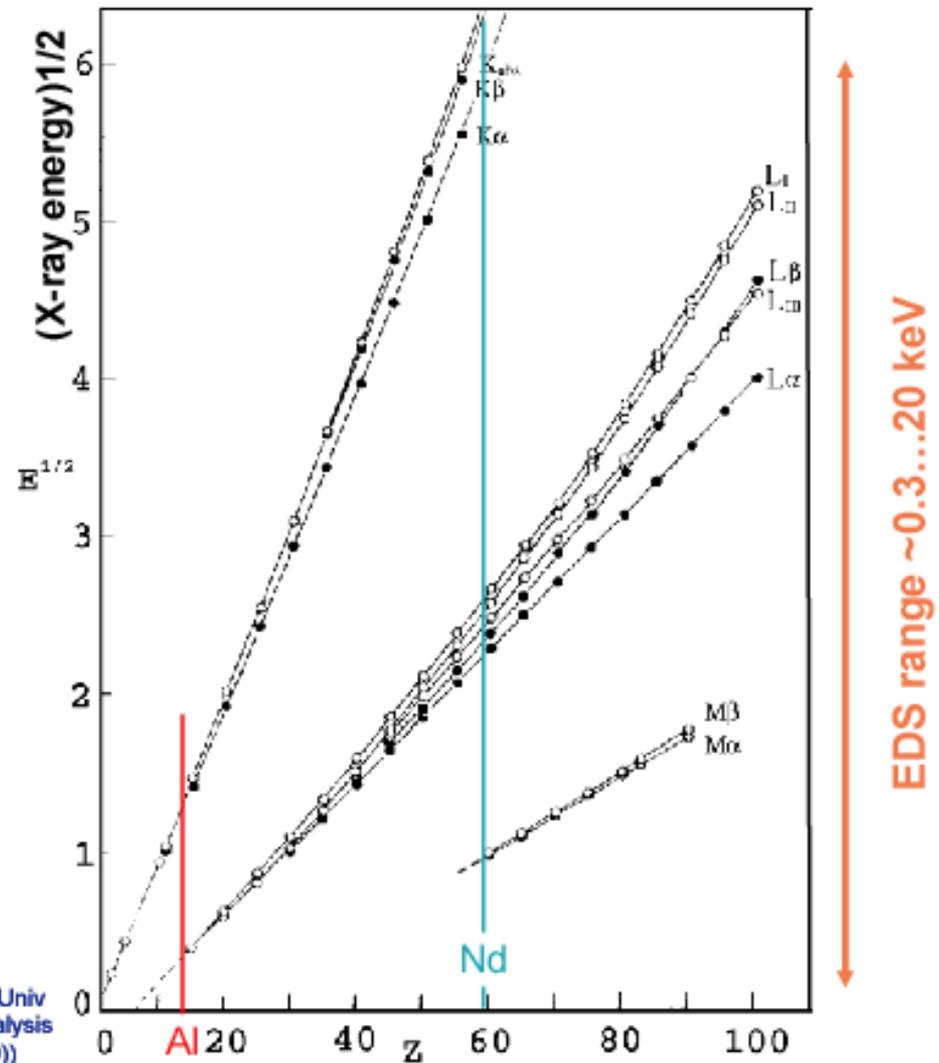
several families K, L, M, N... ($n=1,2,3,4$)

energy within a family increases with Z

$$E_K > E_L > E_M \dots$$

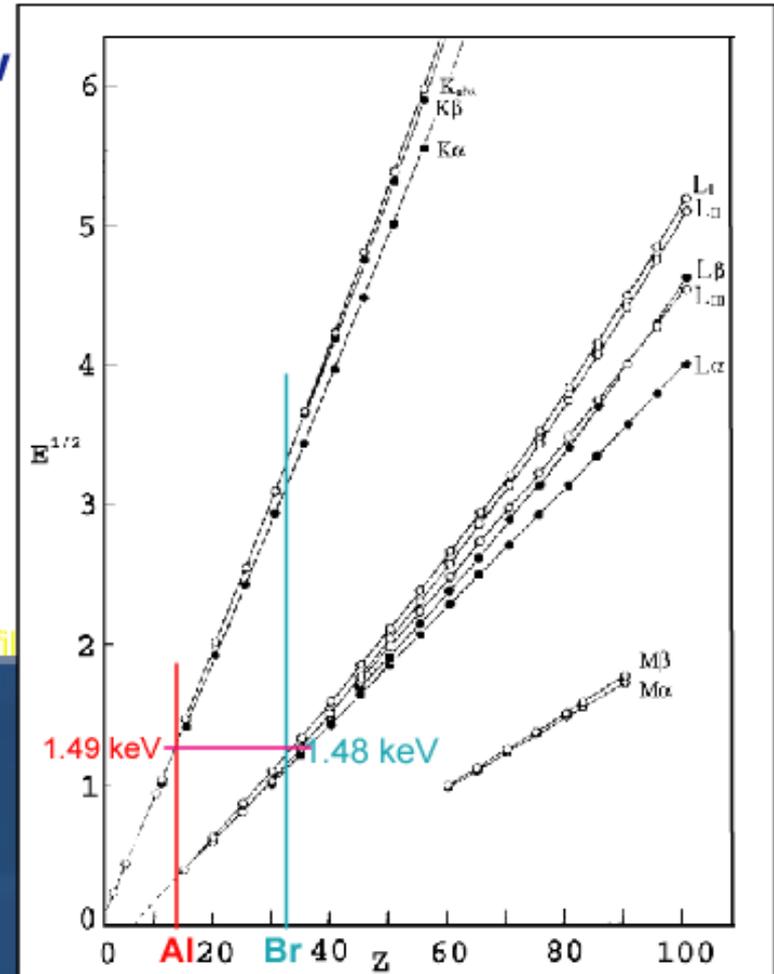
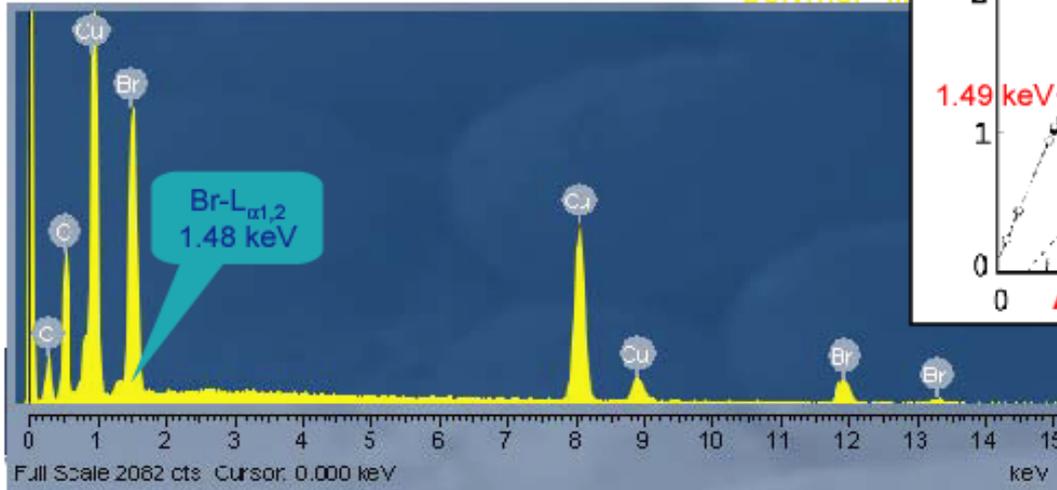
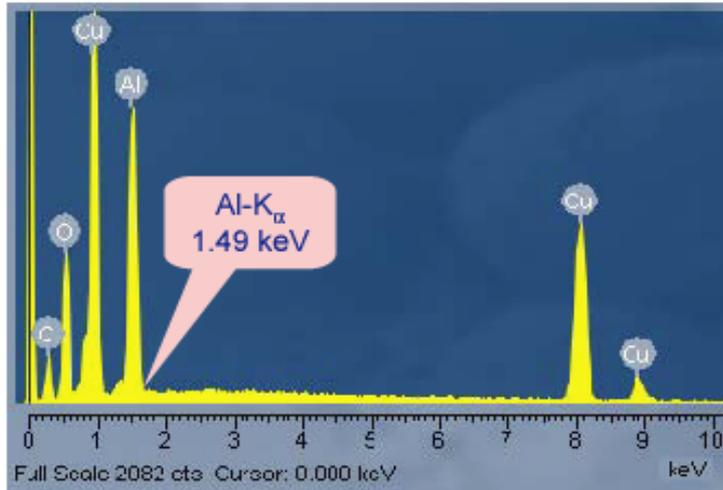
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(from CAMCOR Oregon Univ
Electron Beam Micro Analysis
Lecture Notes (Geol 619))



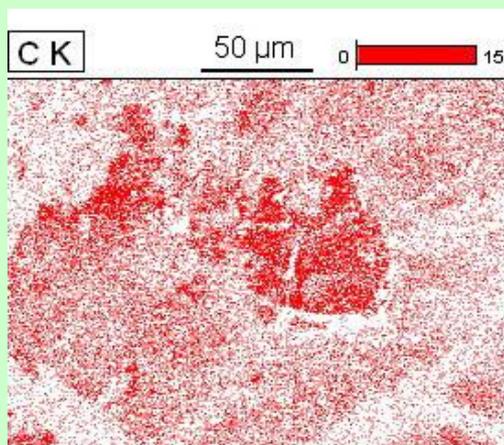
EM Spectrum Lines Produced by Electron Shell Ionization

Characteristic lines: Moseley's Law

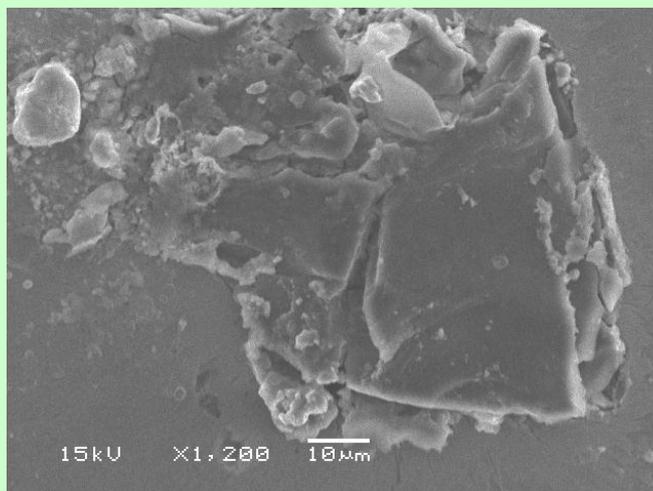


polymer+fil

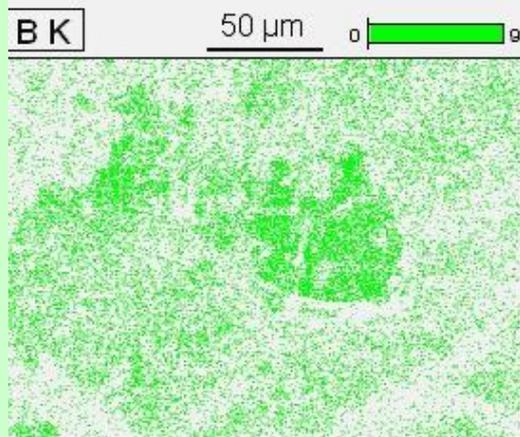
Synthesis of BCx diamonds



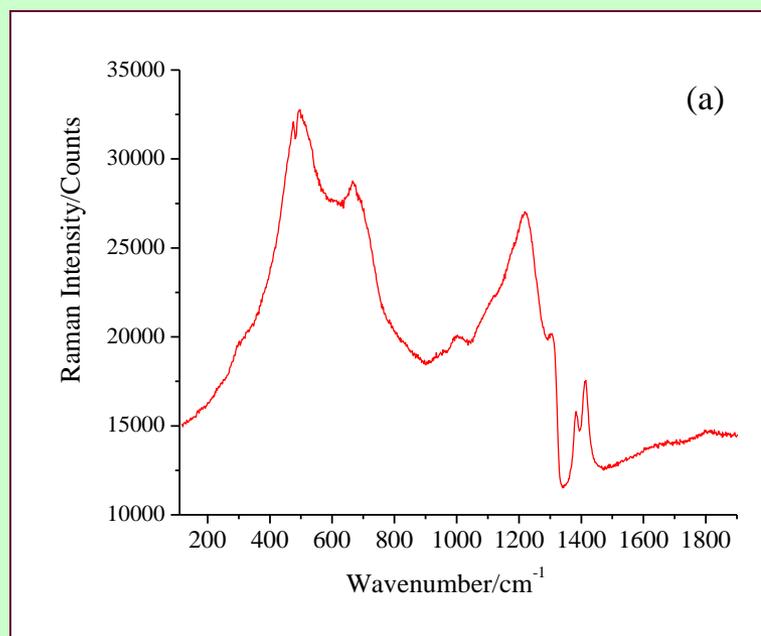
C-K map



SEM image of the post-heated BC3 sample recovered from 50 GPa and 2033 K and with the NaCl layer being removed. Marker is 10 μm.

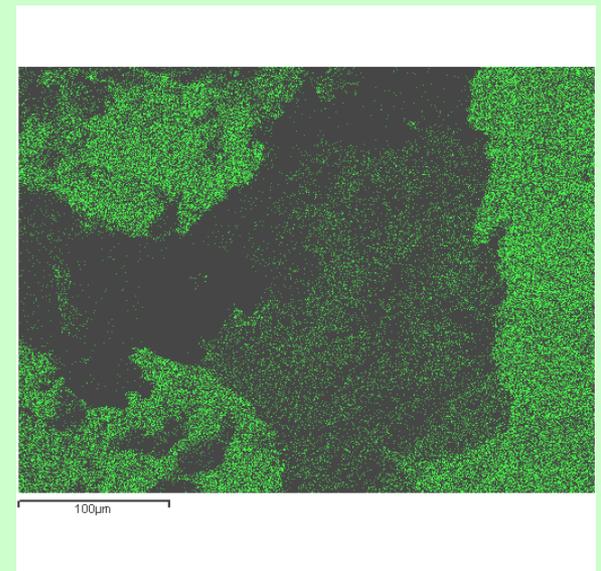
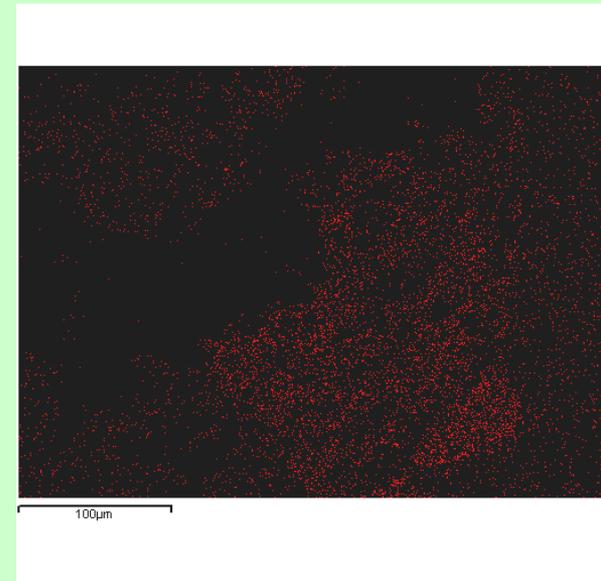
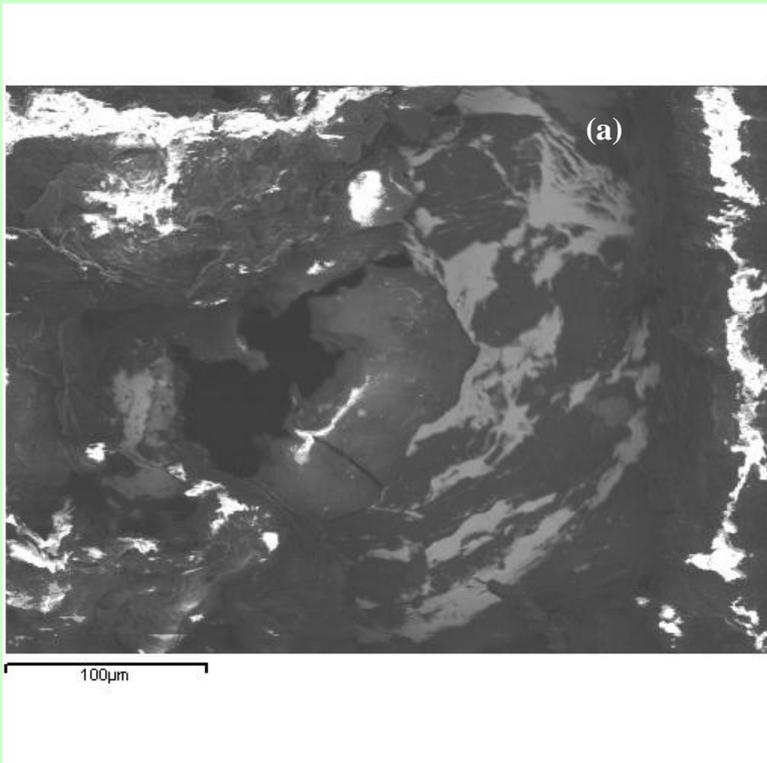


B-K map



Raman spectrum of the BC3 sample after laser heating (50 GPa, 2033 ± 241 K)

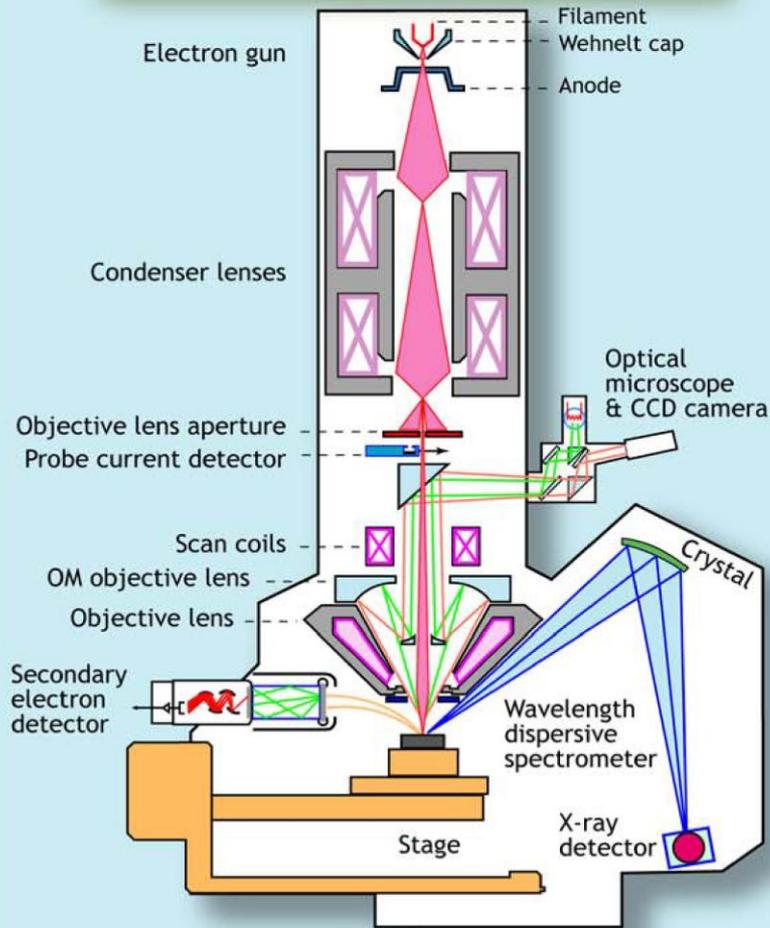
Synthesis of cubic C_3N_4 diamonds



(a) SEM image of the recovered C_3N_4 sample after heating to 2000 K at 33 GPa. Marker is 100 μm . (b) map of the nitrogen distribution; (c) map of the carbon distribution.

Generic EMPA/SEM WDS

Schematic of an Electron Microprobe with a Wavelength Dispersive Spectrometer

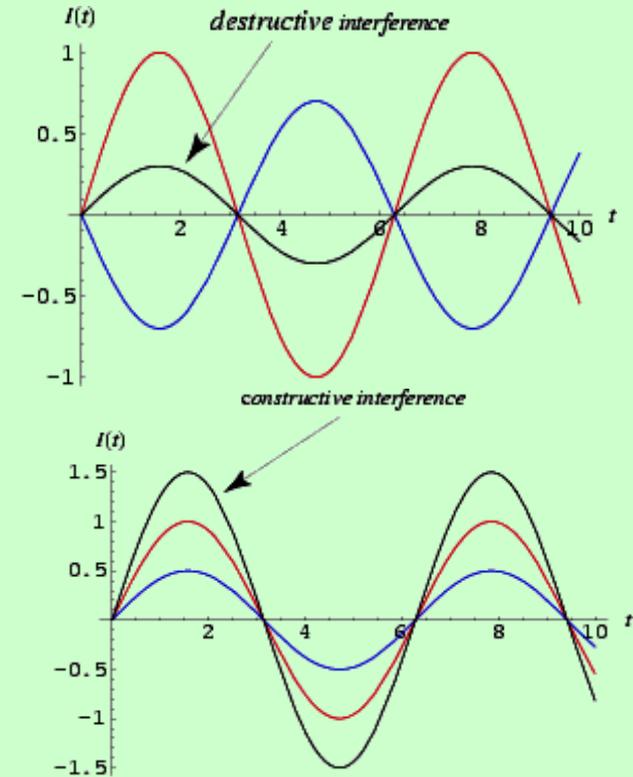
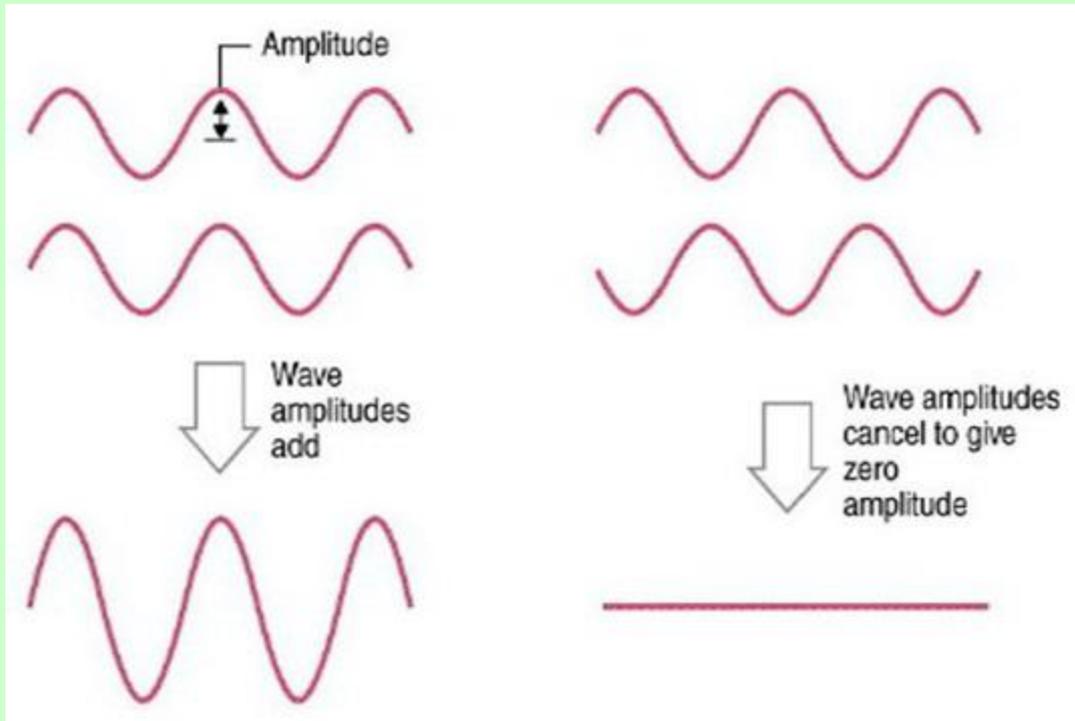


Each element produces a unique set of characteristic X-rays when bombarded with electrons. Each X-ray will have a specific energy and wavelength. Energy dispersive spectrometers (EDS) sort the X-rays based on their energy; while wavelength dispersive spectrometers (WDS) sort the X-rays based on their wavelengths. WDS systems use X-ray diffraction as the means by which they separate X-rays of different wavelengths. The spectrometer consists of an analyzing crystal and a detector. Those X-rays that hit the crystal and diffract will enter the detector. Whether an X-ray photon will diffract depends on its wavelength, the orientation of the crystal, and the crystal's lattice spacing. Only X-rays of a given wavelength will enter the detector at any one time. To measure X-rays of another wave length, the crystal and detector are moved to a new position. Since a specific WDS spectrometer can measure only one X-ray wavelength at a time, it is important that a WDS system has an array of spectrometers in order to work efficiently. Electron micro-probes typically have up to five WDS spectrometers, allowing them to measure five elements simultaneously.

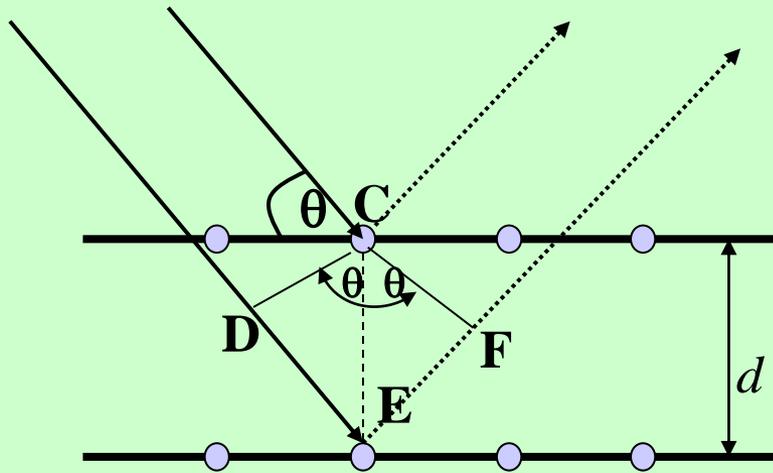
X-ray as a plane wave

The most convenient wave to write down introduce equation describing a plane wave is to use complex exponent $e^{i\alpha}$

$$\exp^{i\alpha} = \cos \alpha + i \sin \alpha : \phi = Ae^{i(kx - \omega t + \phi)} = A \cos(kx - \omega t + \phi) + iA \sin(kx - \omega t + \phi);$$



Deriving Bragg's equation



- The angle of incidence of the x-rays is θ
- The angle at which the x-rays are diffracted is equal to
- the angle of incidence, θ
- The angle of diffraction is the sum of these two angles, 2θ

The two x-ray beams travel at different distances. This difference is related to the distance between parallel planes. We connect the two beams with perpendicular lines (CD and CF) and obtain two equivalent right triangles. $CE = d$ (interplanar distance)

$$\sin \theta = \frac{DE}{d}; d \sin \theta = DE = EF \quad 2d \sin \theta = EF + DE = \text{difference in path length} = \frac{m\pi}{k} = m\lambda$$

Reflection (signal) only occurs when conditions for constructive interference between the beams are met. These conditions are met when the difference in path length equals an integral number of wavelengths, m . The final equation is the BRAGG'S LAW

$$2d \sin \theta = EF + DE = \frac{m\pi}{k} = m\lambda$$

WDS

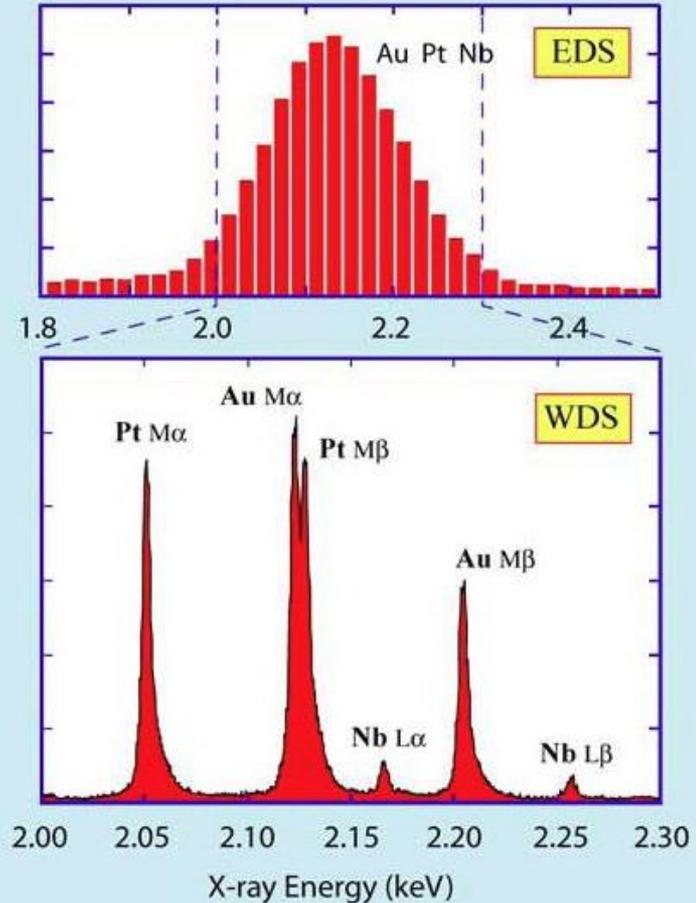
The fact that characteristic x-ray photons are described by either their energy or their wavelength enables us to isolate and count x-rays for a desired element either by discrimination based on energy or by wavelength. This fact produces two principal types of x-ray detection systems:

WDS: wavelength dispersive detection system in which x-rays from different elements are recognized and separated from one another by their wavelength using Bragg diffraction. WDS systems use X-ray diffraction as the means by which they separate X-rays of different wavelengths. The spectrometer consists of an analyzing crystal and a detector. Those X-rays that hit the crystal and diffract will enter the detector. Whether an X-ray photon will diffract depends on its wavelength, the orientation of the crystal, and the crystal's lattice spacing. Only X-rays of a given wavelength will enter the detector at any one time. To measure X-rays of another wavelength, the crystal and detector are moved to a new position. Since a specific WDS spectrometer can measure only one X-ray wavelength at a time, it is important that a WDS system has an array of spectrometers in order to work efficiently. Electron micro-probes typically have up to five WDS spectrometers, allowing them to measure five elements simultaneously. Each spectrometer typically has between two and four analyzing crystals, each with a different lattice spacing, because each type of crystal can diffract only a given range of wavelengths

EDS versus WDS

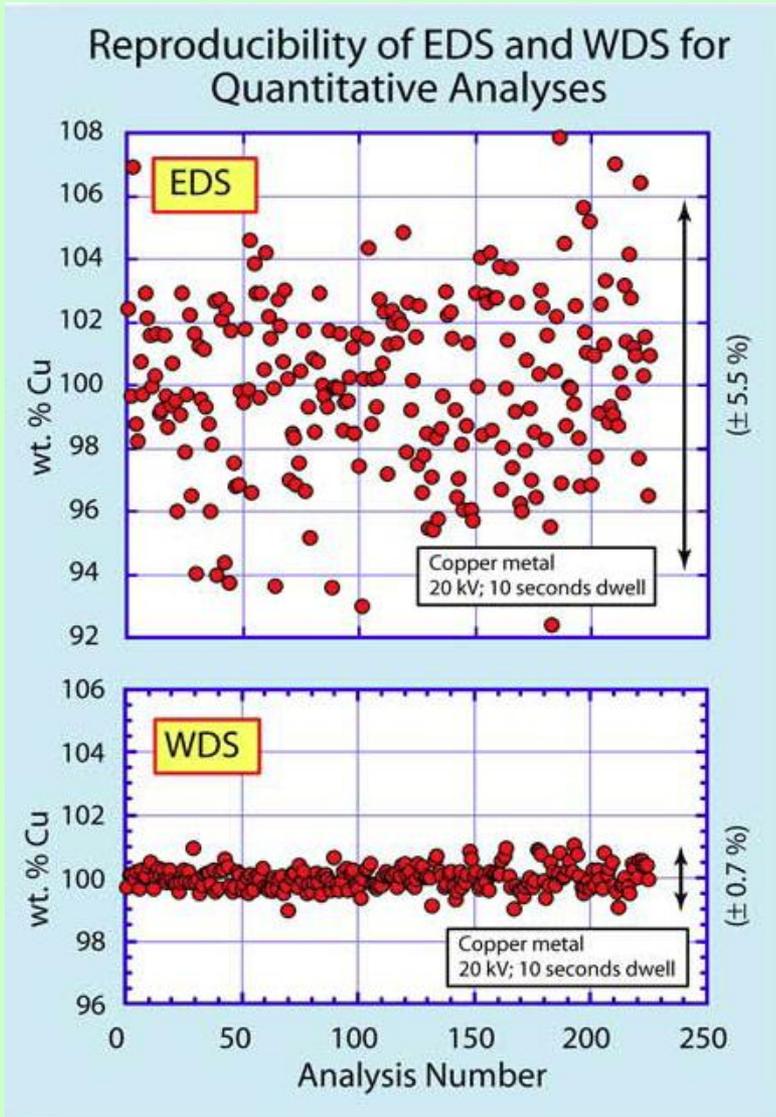
The most significant difference between WDS and EDS systems is their energy resolution. A Mn K α X-ray line on an EDS system will typically be between 135-150 eV wide. On a WDS system, this same X-ray line will only be about 10 eV wide. This means that the amount of overlap between peaks of similar energies is much smaller on the WDS system. To the right is a comparison of spectra collected from a Pt- Au-Nb alloy on a WDS compared to an EDS system. On the WDS system six X-ray lines can be identified, with an overlap occurring only between the Au M α and the Pt M β lines. It would be very straightforward to identify the elements present and to quantify their abundance without resorting to an elaborate deconvolution procedure.

Energy Resolution of EDS vs WDS



On the EDS system, the broad nature of the X-ray lines mask each other and they appear to be a single peak. It would be impossible to reliably deconvolute this peak into the individual X-ray lines.

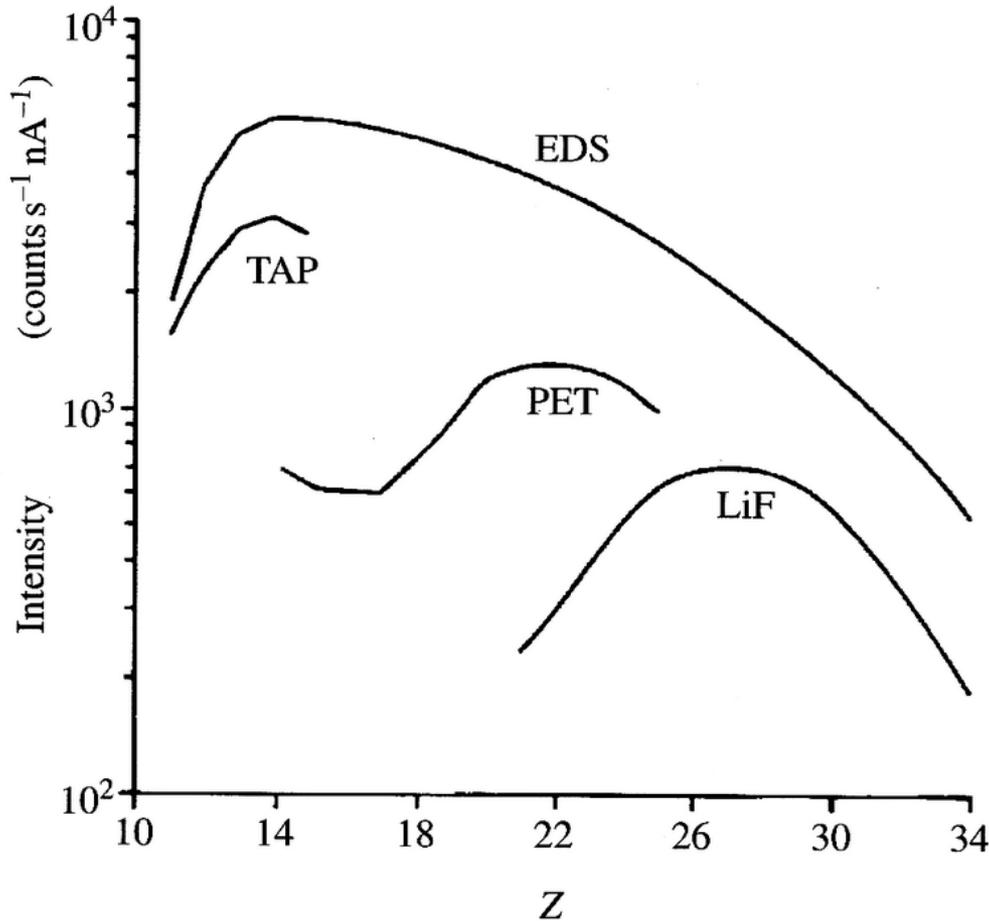
EDS versus WDS



- The second major problem with EDS systems is their low count rates and poor reproducibility. Typically a WDS system will have a count rate about 10x that of an EDS system. There are some EDS systems that can collect at a higher count rate, but they sacrifice even more on the energy resolution — their peaks are even wider.

- To the left is a comparison of the reproducibility of an EDS system and a WDS system. The data were collected simultaneously, so the conditions under which they were collected were identical. The plots show that the EDS data had almost 8x the scatter of the WDS data. For serious quantitative analyses, the EDS data would not be acceptable. The spread on the EDS data could be reduced by counting longer, but that would also improve the WDS data.

EDS versus WDS



- Intensities of K α line for pure elements (Z is atomic number) as recorded by an EDS spectrometer and a WD spectrometer with different crystals (S.J. B. Reed . Electron Microprobe Analysis).

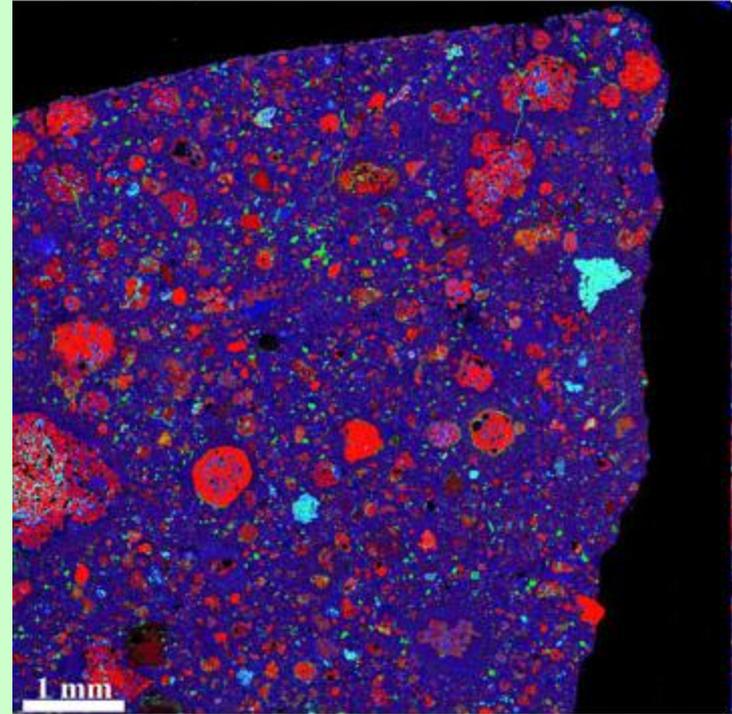
Mapping Elements - WDS

Murchison, CM2 Carbonaceous Chondrite



© Natural History Museum, London.
(Image courtesy of Natural History Museum, London.)

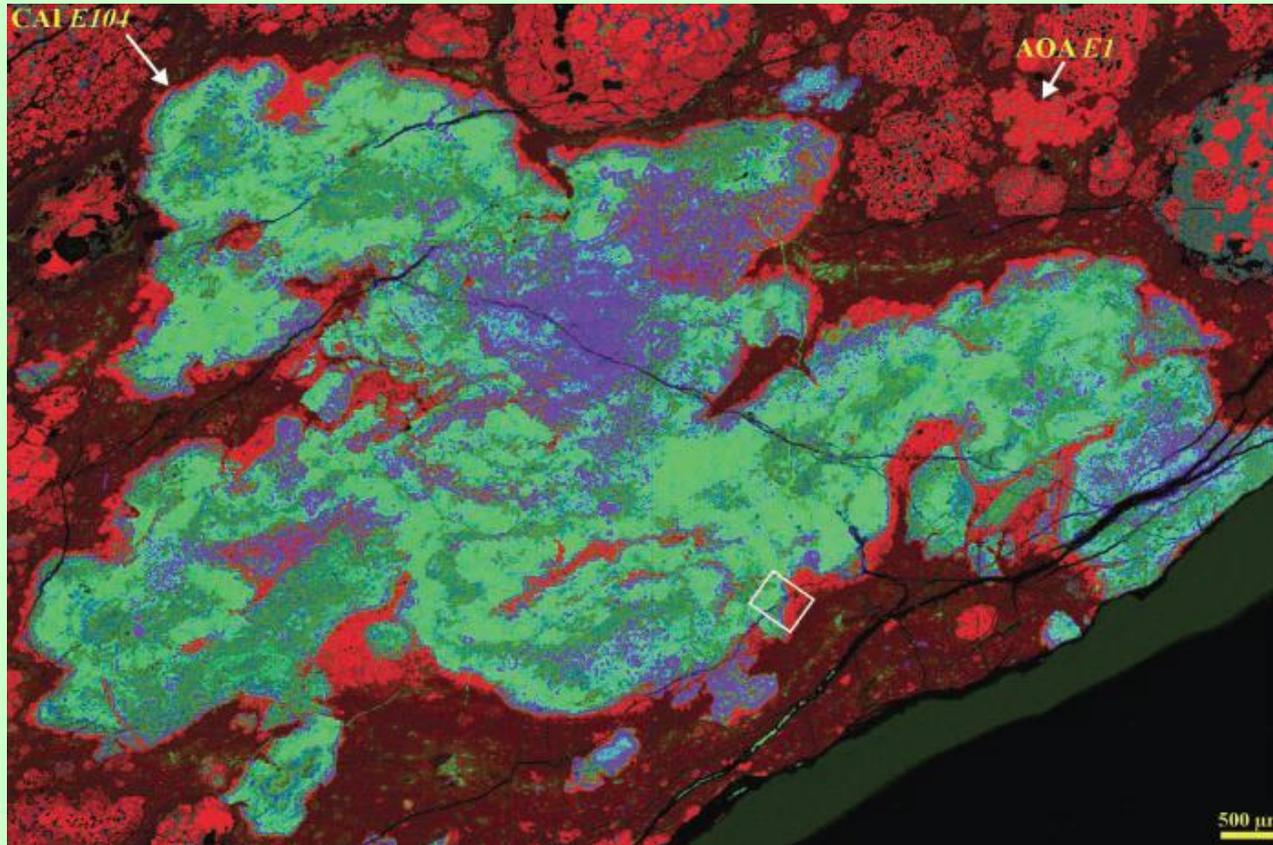
Murchison, CM2 Carbonaceous Chondrite



(Image courtesy of Alexander Krot, University of Hawaii.)

The picture on the [LEFT] shows a large piece of the Murchison meteorite courtesy of the Natural History Museum, London. [RIGHT] This image is known as a 'combined X-ray elemental map.' It was created by combining X-ray intensities due to magnesium (red), calcium (green) and aluminum (blue) from a thin slice of the Murchison meteorite, courtesy of Alexander Krot, a meteorite researcher at the University of Hawai'i. The x-rays were made by bombarding the sample with a beam of electrons in an electron microprobe.

Mapping Elements - WDS



Combined x-ray map composed of Mg K α (red), Ca K α (green), and Al K α (blue) of a polished section of the Efremovka meteorite containing Ca, Al-rich inclusion E104, and amoeboid olivine aggregate E1. The calcium-aluminum-rich inclusion (CAI) consists of spinel (purple), Al-diopside (dark green), anorthite (light blue), and melilite (light green). It is surrounded by a multilayered Wark-Lovering rim and a thick forsterite-rich rim (red). (Krot *et al.*, *Science* **295** 2002).

Home Work

1. Derive Bagg's law (SO).
2. Describe Moseley's law (KK).
3. Describe principles EDS (KK).
4. Describe principles WDS (SO).
5. Provide definition of the atomic numbers (KK).