

Materials Analysis with fast ions using the 1.1MV tandem electrostatic Pelletron Particle Accelerator at Union College



Introduction to Ion Beam Analysis

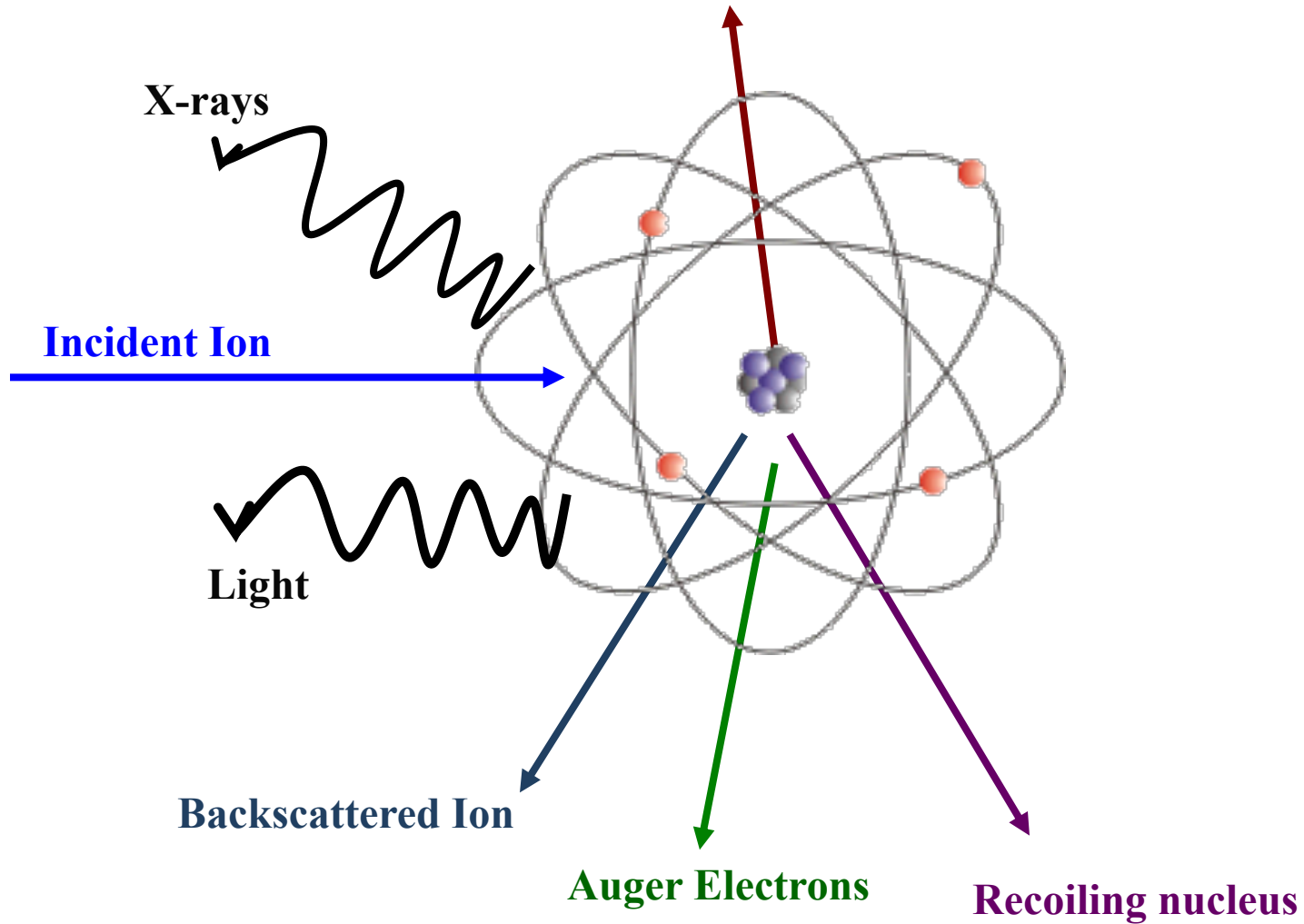
→ Ion –Target Interaction

- Elastic Atomic Collisions
 - Very low energies, typically a few keV
 - Surface composition and structure
 - Ion Scattering spectrometry (ISS)
- Elastic Nuclear Collisions
 - Rutherford Backscattering (*RBS*)
 - Mainly for $Z > Z_{ion}$ (usually He^{++})
 - Elastic Recoil Detection Analysis (*ERDA*)
 - Mainly for $Z < Z_{ion}$ (only H in this case)
- Inelastic Atomic Collisions
 - Ionization of target atoms
 - Characteristic x-ray emission
 - Particle Inducted X-Ray Emission (*PIXE*)
 - Detection of elements with $Z > 6$
- Inelastic Nuclear Collisions
 - Nuclear Reactions can occur
 - Nuclear Reaction Analysis (NRA)
 - Gamma ray production (*PIGE*)

In our lab we have the ability to do *PIXE*, *PIGE*, *RBS* & *ERDA*

Introduction: Ion –Target Interaction

Nuclear Reactions producing n , γ -rays, ions



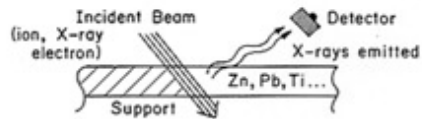
Proton Induced X-ray Emission Spectroscopy

PIXE

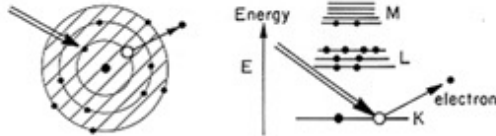
- First observation by Chadwick (the discover of the neutron) (Phil. Mag. 24 (1912) 54)
- X-ray emission induced by charged particles from a radioactive source. We're going to produce protons on our accelerator and shoot them at a target to produce x-rays.
- Moseley in 1913: the energy of the x-rays scales with Z^2
- First application T.B. Johansson et al, Nucl. Instr. Meth. B 84 (1970) 141
- 2022: most widely used technique in materials analysis, atmospheric aerosols, archaeology, paleontology, archaeometry, criminology, biology, geology, environmental sciences.....

PIXE: The Basics

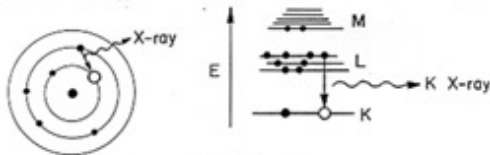
Ion-, Electron- and X-ray-Induced X-ray Analysis



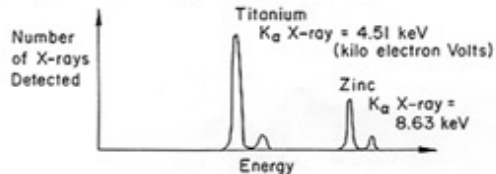
- Incident particle knocks electrons out of the occupied states around the atom leaving empty states (vacancies)



- Electron in occupied state makes transition to unfilled vacancy. X-ray is emitted to conserve energy.



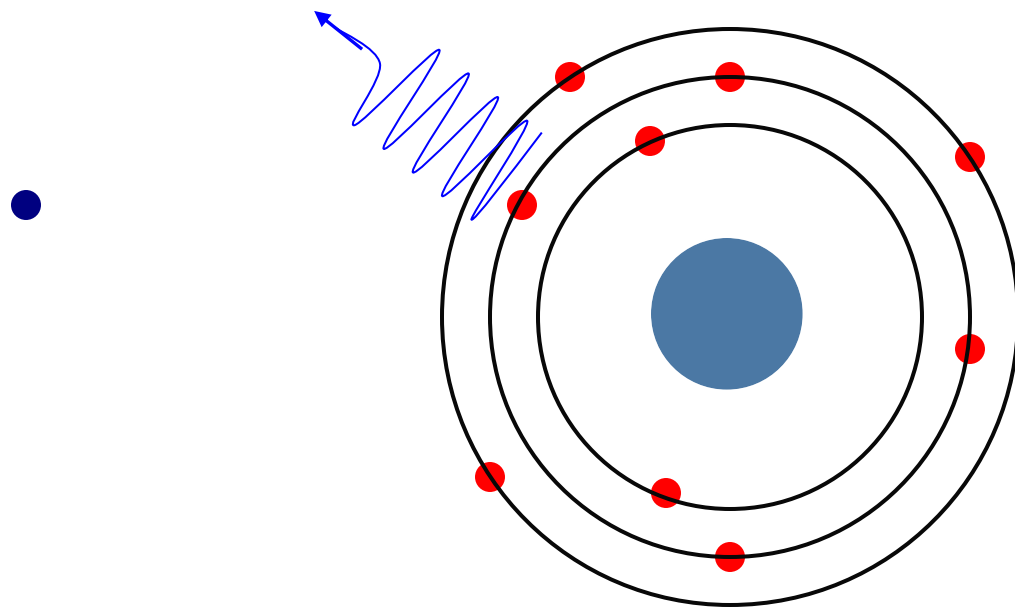
- Energy of the X-ray identifies the atom



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- Incident proton interacts with electrons in the material ejecting electrons.
- This creates a vacancy in a shell that is usually filled with an electron from a higher orbit.
- For the electron to fill this vacancy it needs to lose energy.
- The energy difference is the difference from where the electron is currently to where it wants to go, and this is typically on the order of several keV and higher.
- When the electron transitions an x-ray photon of that energy difference is emitted and the spectrum of all x-ray photons are plotted and identified.

An Illustration of the *PIXE* process



L_{α} transition in an atom

The incident proton ejects an electron from the $n = 2$ orbital and creates a vacancy in the $n = 2$ orbital. An electron from the $n = 3$ orbital de-excites to fill the vacancy created in the $n = 2$ orbital and emitting an x-ray in the process that we can detect.

PIXE: The Basics

- For an incident proton energy of 1 – 4 MeV, elements with atomic numbers up to about 50 (Sn) are generally determined through their *K shell* X-rays (typically K_{α} line).
- Heavier elements (greater than $Z = 50$) are measured through their *L shell* X rays because the beam energy is not enough to eject the tightly bound *K shell* electrons.
- The concentration of a particular element is deduced from the intensity of the measured x-ray line together with parameters obtained either theoretically and/or experimentally.

PERIODIC TABLE OF ELEMENTS

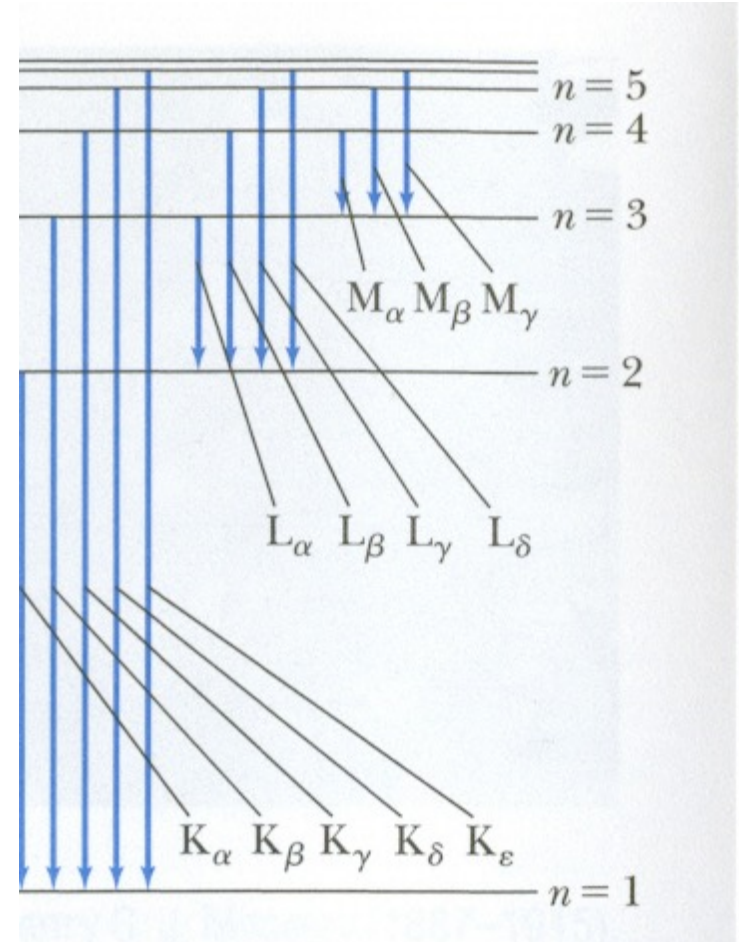
PubChem																							
1 H Hydrogen 1s ¹																	2 He Helium 1s ²						
3 Li Lithium [He] 2s ¹	4 Be Beryllium [He] 2s ²																	5 B Boron [He] 2s ² 2p ¹	6 C Carbon [He] 2s ² 2p ²	7 N Nitrogen [He] 2s ² 2p ³	8 O Oxygen [He] 2s ² 2p ⁴	9 F Fluorine [He] 2s ² 2p ⁵	10 Ne Neon [He] 2s ² 2p ⁶
11 Na Sodium [Ne] 3s ¹	12 Mg Magnesium [Ne] 3s ²																	13 Al Aluminum [Ne] 3s ² 3p ¹	14 Si Silicon [Ne] 3s ² 3p ²	15 P Phosphorus [Ne] 3s ² 3p ³	16 S Sulfur [Ne] 3s ² 3p ⁴	17 Cl Chlorine [Ne] 3s ² 3p ⁵	18 Ar Argon [Ne] 3s ² 3p ⁶
19 K Potassium [Ar] 4s ¹	20 Ca Calcium [Ar] 4s ²	21 Sc Scandium [Ar] 3d ¹ 4s ²	22 Ti Titanium [Ar] 3d ² 4s ²	23 V Vanadium [Ar] 3d ³ 4s ²	24 Cr Chromium [Ar] 3d ⁵ 4s ¹	25 Mn Manganese [Ar] 3d ⁵ 4s ²	26 Fe Iron [Ar] 3d ⁶ 4s ²	27 Co Cobalt [Ar] 3d ⁷ 4s ²	28 Ni Nickel [Ar] 3d ⁸ 4s ²	29 Cu Copper [Ar] 3d ¹⁰ 4s ¹	30 Zn Zinc [Ar] 3d ¹⁰ 4s ²	31 Ga Gallium [Ar] 3d ¹⁰ 4s ² 4p ¹	32 Ge Germanium [Ar] 3d ¹⁰ 4s ² 4p ²	33 As Arsenic [Ar] 3d ¹⁰ 4s ² 4p ³	34 Se Selenium [Ar] 3d ¹⁰ 4s ² 4p ⁴	35 Br Bromine [Ar] 3d ¹⁰ 4s ² 4p ⁵	36 Kr Krypton [Ar] 3d ¹⁰ 4s ² 4p ⁶						
37 Rb Rubidium [Kr] 5s ¹	38 Sr Strontium [Kr] 5s ²	39 Y Yttrium [Kr] 4d ¹ 5s ²	40 Zr Zirconium [Kr] 4d ² 5s ²	41 Nb Niobium [Kr] 4d ⁴ 5s ¹	42 Mo Molybdenum [Kr] 4d ⁵ 5s ¹	43 Tc Technetium [Kr] 4d ⁵ 5s ²	44 Ru Ruthenium [Kr] 4d ⁷ 5s ¹	45 Rh Rhodium [Kr] 4d ⁸ 5s ¹	46 Pd Palladium [Kr] 4d ¹⁰	47 Ag Silver [Kr] 4d ¹⁰ 5s ¹	48 Cd Cadmium [Kr] 4d ¹⁰ 5s ²	49 In Indium [Kr] 4d ¹⁰ 5s ² 5p ¹	50 Sn Tin [Kr] 4d ¹⁰ 5s ² 5p ²	51 Sb Antimony [Kr] 4d ¹⁰ 5s ² 5p ³	52 Te Tellurium [Kr] 4d ¹⁰ 5s ² 5p ⁴	53 I Iodine [Kr] 4d ¹⁰ 5s ² 5p ⁵	54 Xe Xenon [Kr] 4d ¹⁰ 5s ² 5p ⁶						
55 Cs Cesium [Xe] 6s ¹	56 Ba Barium [Xe] 6s ²	57 La Lanthanum [Xe] 5d ¹ 6s ²	58 Ce Cerium [Xe] 4f ¹ 5d ¹ 6s ²	59 Pr Praseodymium [Xe] 4f ³ 6s ²	60 Nd Neodymium [Xe] 4f ⁴ 6s ²	61 Pm Promethium [Xe] 4f ⁵ 6s ²	62 Sm Samarium [Xe] 4f ⁶ 6s ²	63 Eu Europium [Xe] 4f ⁷ 6s ²	64 Gd Gadolinium [Xe] 4f ⁷ 5d ¹ 6s ²	65 Tb Terbium [Xe] 4f ⁹ 6s ²	66 Dy Dysprosium [Xe] 4f ¹⁰ 6s ²	67 Ho Holmium [Xe] 4f ¹¹ 6s ²	68 Er Erbium [Xe] 4f ¹² 6s ²	69 Tm Thulium [Xe] 4f ¹³ 6s ²	70 Yb Ytterbium [Xe] 4f ¹⁴ 6s ²	71 Lu Lutetium [Xe] 4f ¹⁴ 5d ¹ 6s ²							
87 Fr Francium [Rn] 7s ¹	88 Ra Radium [Rn] 7s ²	89 Ac Actinium [Rn] 6d ¹ 7s ²	90 Th Thorium [Rn] 6d ² 7s ²	91 Pa Protactinium [Rn] 5f ² 6d ¹ 7s ²	92 U Uranium [Rn] 5f ³ 6d ¹ 7s ²	93 Np Neptunium [Rn] 5f ⁴ 6d ¹ 7s ²	94 Pu Plutonium [Rn] 5f ⁶ 7s ²	95 Am Americium [Rn] 5f ⁷ 7s ²	96 Cm Curium [Rn] 5f ⁷ 6d ¹ 7s ²	97 Bk Berkelium [Rn] 5f ⁹ 7s ²	98 Cf Californium [Rn] 5f ¹⁰ 7s ²	99 Es Einsteinium [Rn] 5f ¹¹ 7s ²	100 Fm Fermium [Rn] 5f ¹² 7s ²	101 Md Mendelevium [Rn] 5f ¹³ 7s ²	102 No Nobelium [Rn] 5f ¹⁴ 7s ²	103 Lr Lawrencium [Rn] 5f ¹⁴ 6d ¹ 7s ²							

Characteristic X-ray production

- Idea based on the incorrect *Bohr model of the atom*.
- The energy of the photon emitted depends on the energy of the upper state (E_{upper}) and the energy of the lower state (E_{lower}).

$$\Delta E_{photon} = E_{upper} - E_{lower}$$

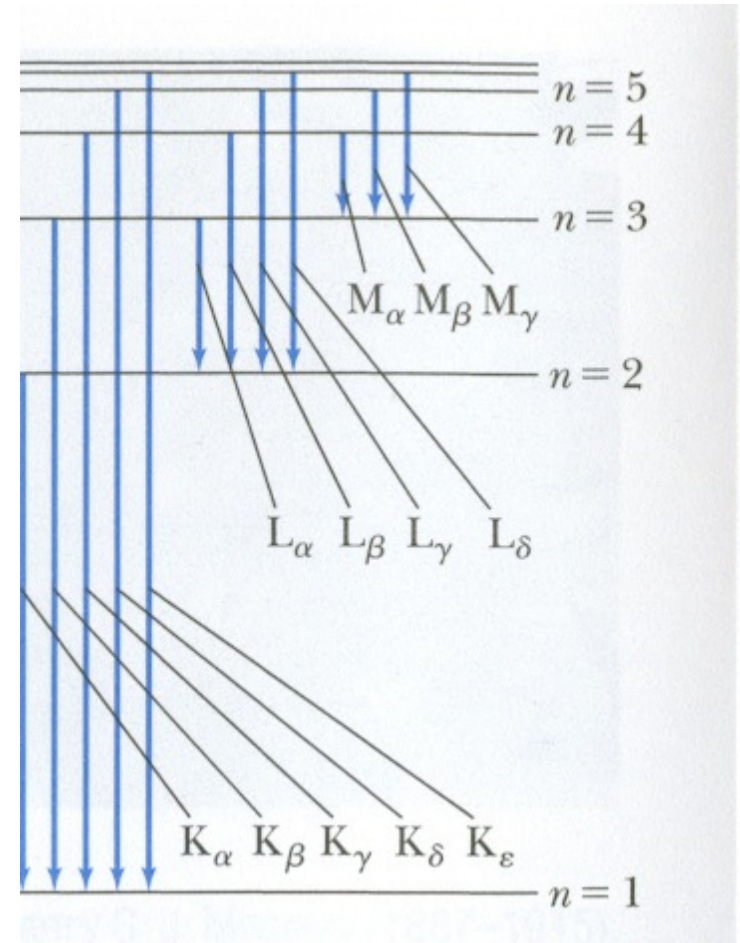
- The n designations correspond to atomic orbitals while the letter designations (K , L , $M...$) correspond to shells in the older spectroscopic notation.
- The actual energies are determined from the Schrodinger equation of quantum mechanics.
- We need to determine a formula for the upper and lower energy states.



Thornton, S., & Rex, A., Modern Physics for Scientists and Engineers, 3rd Ed., Thomas Brooks Cole 151(2006).

Characteristic X-ray production

- Further, the letters are used to designate the shell to which the electron is transitioning.
- The Greek letters are used to designate the higher energy transitions and give the value of Δn .
- For example, the α -transition is a lower energy (higher probability) transition than the β -transition (lower probability), which is in turn lower than the γ -transition.
- The K shell transitions are the highest energy transitions possible.



Thornton, S., & Rex, A., Modern Physics for Scientists and Engineers, 3rd Ed., Thomas Brooks Cole 151(2006).

Characteristic X-ray production

- Moseley in 1913 empirically determined the relationship between the atomic number and the frequency of the x-ray emitted (or the energy of the x-ray emitted as is how we will use it). Plots like those on the right are called Moseley Plots.

- This is the most fundamental idea behind PIXE.

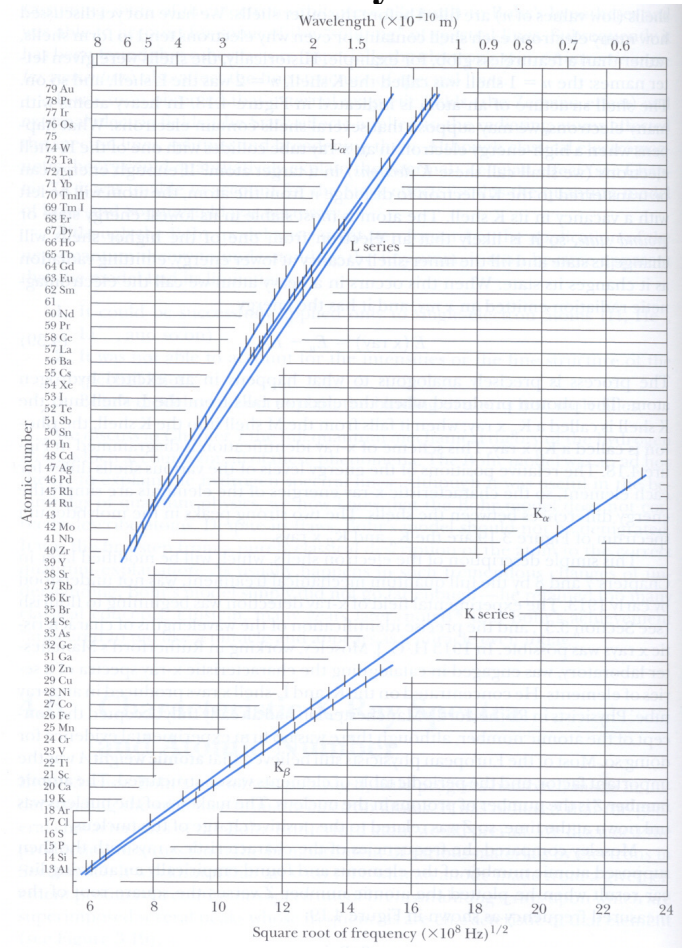
- It shows that for each atomic number (element) there are a characteristic set of x-ray wavelengths and energies emitted.

- Moseley found the relationship to be of the form:

$$Z = a\sqrt{f} + b$$

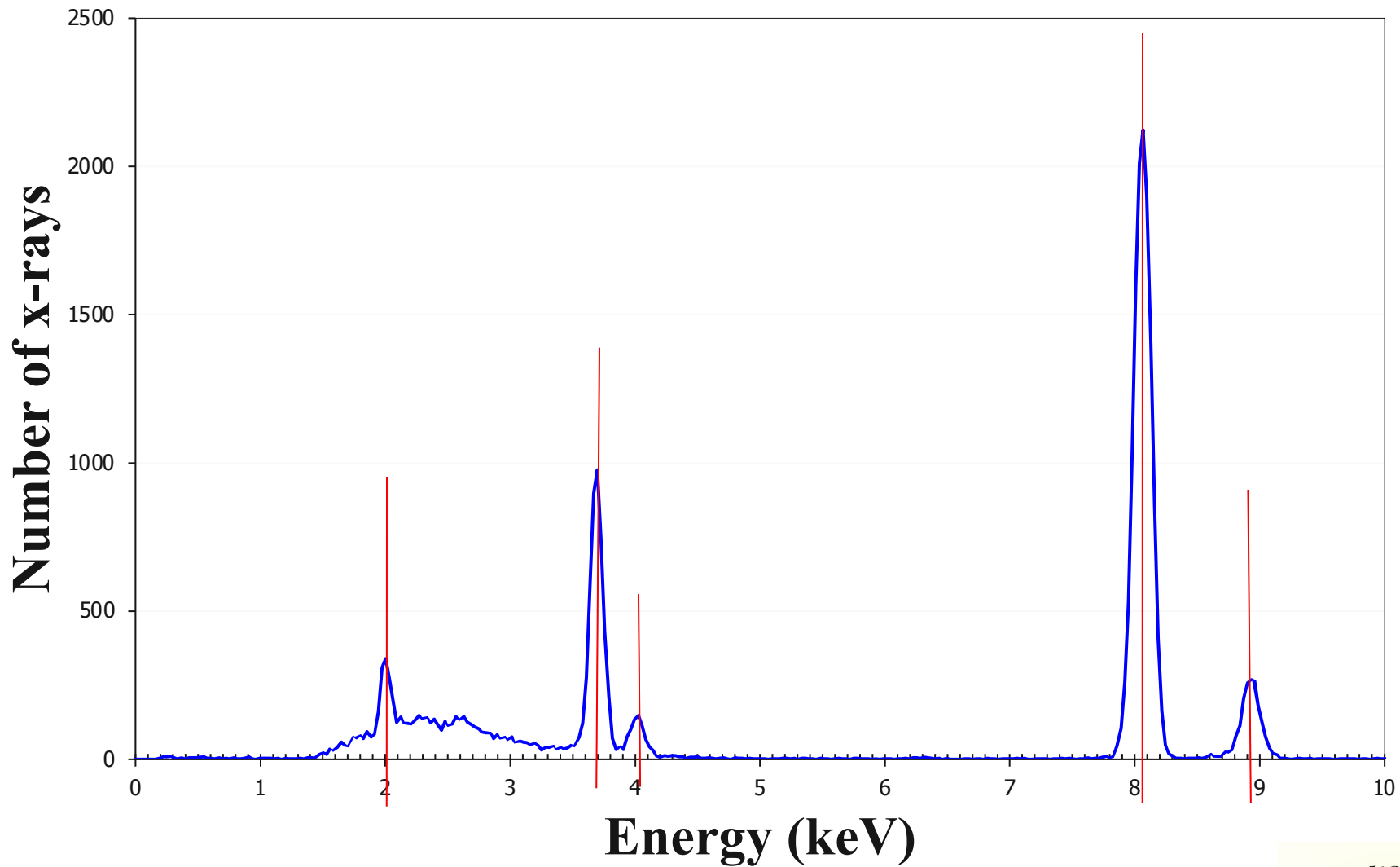
where a and b are constants from the fitting of a line to the data.

Moseley Plots



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A typical *PIXE* Spectrum



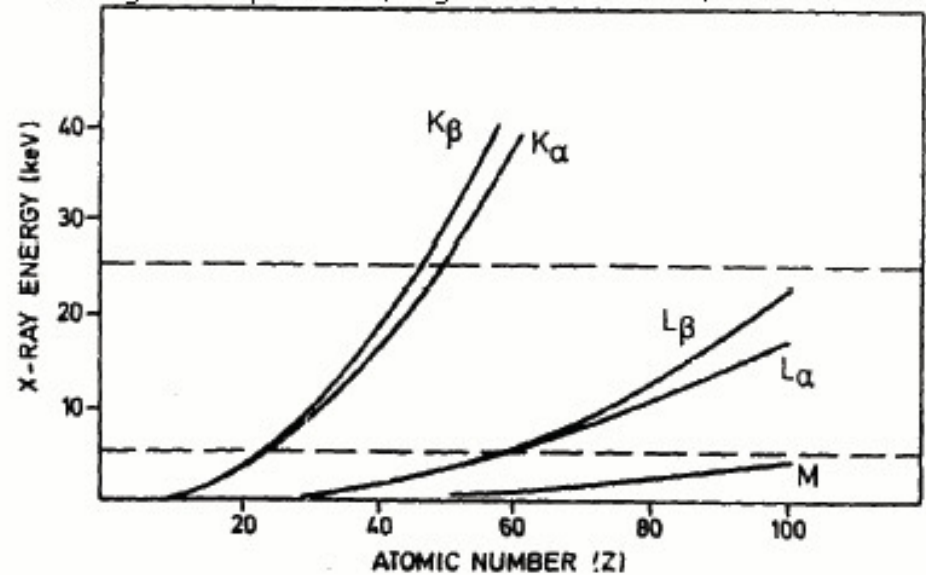
Characteristic X-ray production

- When a vacancy is created in the K shell ($n = 1$ orbital), an electron in the L shell ($n = 2$ orbital) feels an effective charge of $(Z-1)e^-$. This is due to the Ze^- charge of the nucleus and the e^- remaining in the K shell. Thus, the net force on an L shell electron is towards the K shell and a de-excitation occurs.
- The transition energies are given by the Einstein relation

$$\Delta E_{\text{photon}} = E_{x\text{-ray}} = hf \approx -13.57\text{eV} \left(\frac{1}{n_{\text{lower}}^2} - \frac{1}{n_{\text{upper}}^2} \right) Z^2$$

- The x-ray energies go as $(Z - 1)^2$ which produces the parabolic energy curves.
- Notice that if we rearrange the above equation and take a square root, we get the form that Moseley obtained, namely:

$$Z = a\sqrt{f} + b$$



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Comments: Derivation of the Bohr Theory

- Energies and wavelengths are based on the Bohr Theory of the atom for an electron orbiting around a nucleus of charge Ze .

$$F_{\text{centripetal}} = F_{\text{electrostatic}} \rightarrow \frac{m_e v_e^2}{r_e} = \frac{Ze^2}{4\pi\epsilon_0 r_e^2} \rightarrow v_e^2 = \frac{Ze^2}{4\pi\epsilon_0 m_e r_e}$$

- Using the fact that the angular momentum of the electron $L = mv_e r_e$, we can write the above as

$$v_n = \frac{Ze^2}{4\pi\epsilon_0 L}$$

- The angular momentum can also be represented as an integer multiple of Planck's constant, or the angular momentum is quantized.

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

- This is a completely non-classical or quantum mechanical result.

- Therefore, the velocities are quantized, meaning they only have certain allowed values.

$$v_n = \frac{Ze^2}{4\pi\epsilon_0 n\hbar}$$

- Now, returning to angular momentum, we can express the orbital radius in terms of this velocity that we just found.

$$L = n\hbar = mv_n r_n \rightarrow r_n = \frac{n\hbar}{mv_n} = \frac{4\pi\epsilon_0 n^2 \hbar^2}{mZe^2}$$

- The orbital radius is thus also quantized.
- If we have, for example, hydrogen with $Z = 1$, the radius of the 1st orbital, known as the *Bohr radius*, is given as

$$r_1 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

- Substituting the values of the constants gives the value of the Bohr radius

$$r_1 = \frac{4\pi \left(8.85 \times 10^{-12} \frac{C^2}{Nm^2} \right) \left(\frac{6.63 \times 10^{-34} Js}{2\pi} \right)^2}{9.11 \times 10^{-31} kg \times (1.6 \times 10^{-19} C)^2} = 5.31 \times 10^{-11} m$$

- One more thing about orbital radii...

$$r_n = \frac{4\pi\epsilon_0 n^2 \hbar^2}{mZe^2} = n^2 r_1$$

- The radius of the n^{th} orbital can be expressed as an integer multiple of the Bohr radius.
- Now, this is nice and all, but we really want to be able to calculate the energy of individual orbits and then talk about differences in energy levels.
- This will allow us to talk about the x-rays emitted when an electron transitions between an upper orbital and a lower orbital.
- So, how do I calculate the energy of any orbital?
- The energy of an orbit is the sum of the kinetic energy of the electron and a potential energy due to its position with respect to the nucleus.

- The potential energy of a particle of mass m and charge $-e$ a distance r from a heavy nucleus of charge $+Ze$ is given as

$$V_n = -\frac{Ze^2}{4\pi\epsilon_0 r_n}$$

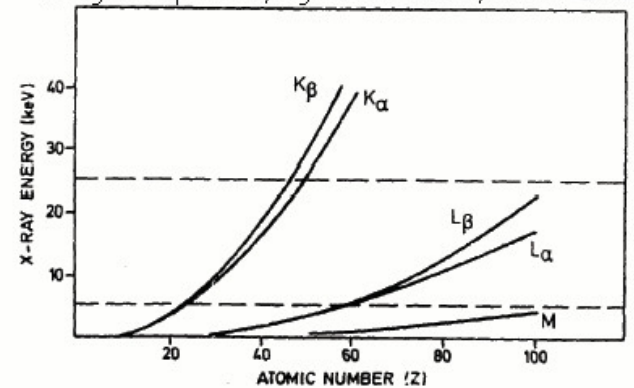
- The energy of the orbit is given as

$$E = \frac{1}{2}mv_n^2 + V_n = \frac{1}{2}m\left(\frac{Ze^2}{4\pi\epsilon_0 n\hbar}\right)^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{4\pi\epsilon_0 n^2 \hbar^2}{mZe^2}$$

- Doing the math... $E_n = -\frac{Z^2 m e^4}{2(4\pi\epsilon_0)^2 n^2 \hbar^2}$

- And here we are, the energy of the n^{th} orbital for a hydrogen-like (1 electron) atom.

- Notice that the energy is proportional to Z^2 and if you plot the energy versus atomic number, you get parabolic energy curves which is what Moseley obtained.



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The X-ray Energies

- The energies of an emitted x-ray are given as the difference between where the electron originates and where the electron is going to

$$\Delta E = E_{upper} - E_{lower}$$

- So, we have:

$$\Delta E = E_{upper} - E_{lower} = -\frac{Z^2 m e^4}{2(4\pi\epsilon_0)^2 n_{upper}^2 \hbar^2} - \left(-\frac{Z^2 m e^4}{2(4\pi\epsilon_0)^2 n_{lower}^2 \hbar^2} \right)$$

$$\Delta E = \frac{Z^2 m e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \left(\frac{1}{n_{lower}^2} - \frac{1}{n_{upper}^2} \right) = hf = \frac{hc}{\lambda}$$

$$\rightarrow \Delta E = -13.6\text{eV} \left(\frac{1}{n_{upper}^2} - \frac{1}{n_{lower}^2} \right) Z^2$$

- Next, we'll examine this formula and see what it tells us.....
- We'll calculate the K_{α} and K_{β} transition energies of a particular element.
- Then we'll discuss how well our results agree with experiments and look at a *PIXE* spectrum for a single element