Difração de Raios X *(XRD)*

Uma Introdução

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Escola Politécnica da USP – 2019

DIFRAÇÃO

- **Difração** é um fenômeno que acontece quando uma onda encontra um obstáculo.
- Em física clássica, o fenômeno da difração é descrito como uma aparente “flexão” das ondas em volta de pequenos obstáculos e também como o espalhamento das ondas após atravessar orifícios ou fendas.
- O fenômeno da difração acontece com todos os tipos de ondas, incluindo ondas sonoras, ondas na água e ondas eletromagnéticas (como luz visível, raios-X e ondas de rádio). Assim, a comprovação da difração da luz foi de vital importância para constatar sua natureza ondulatória.

DIFRAÇÃO

- Ainda que a difração ocorra sempre quando ondas em propagação encontram “obstáculos” (objetos, partículas, fendas...), seus efeitos geralmente são mais marcantes quando o comprimento das ondas é comparável às dimensões do “obstáculo”.
- A difração é observada recorrentemente nas ondas sonoras, pois são ondas com comprimento grande. Interações sonoras com dimensões entre 2 cm a 20 m são facilmente perceptíveis para os seres humanos.
- A difração da luz é mais difícil de acontecer ou de ser percebida, tendo em vista o pequeno comprimento de onda da luz visível (400 a 700 nm).

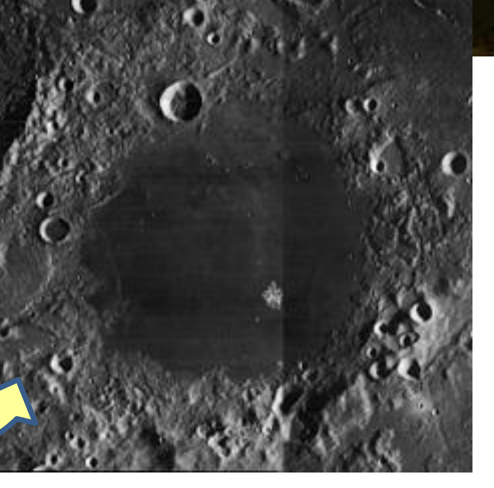
DIFRAÇÃO

- Se o objeto obstrutor apresentar múltiplas fendas, poderá resultar em um padrão complexo de intensidade variável. Isso se deve ao fenômeno de interferência de ondas.
- Richard Feynman escreveu: *“Ninguém nunca foi capaz de definir a diferença entre interferência e difração satisfatoriamente. É somente uma questão de linguagem, e não há diferenças físicas específicas ou importantes entre elas. Tem-se, entretanto, que difração é o fenômeno devido a um obstáculo, já interferência refere-se mais a uma interação entre dois ou mais fenômenos ondulatórios."*

DIFRAÇÃO – *um pouquinho de história...*

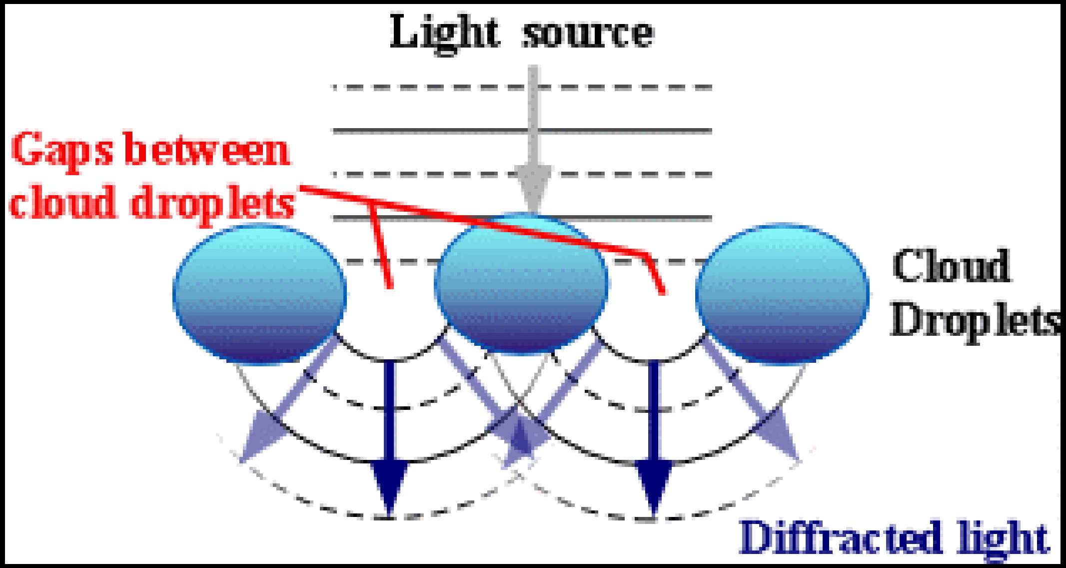
- O cientista italiano Francesco Maria Grimaldi foi o primeiro a empregar o termo "difração" (do latim diffingere, "quebrar em pedaços") e o foi o primeiro a realizar observações detalhadas do fenômeno em 1660.

- He was the first to make accurate observations on the diffraction of light (although by some accounts Leonardo da Vinci had earlier noted it).
- Through experimentation he was able to demonstrate that the observed passage of light could not be reconciled with the idea that it moved in a rectilinear path. Rather, the light that passed through the hole took on the shape of a cone.
- Later physicists used his work as evidence that light was a wave, and Isaac Newton used it to arrive at his more comprehensive theory of light. He also discovered what are known as diffraction bands.
- The crater Grimaldi on the Moon is named after him.



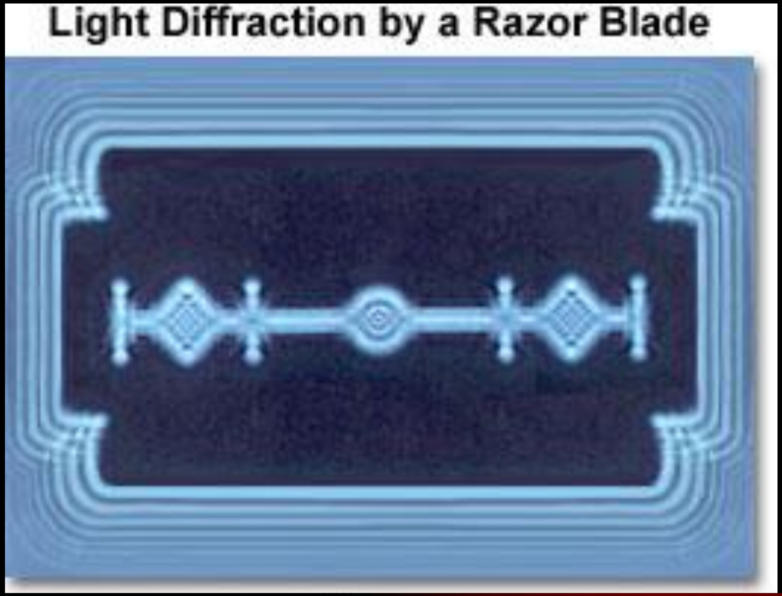
Interferência em ondas na água

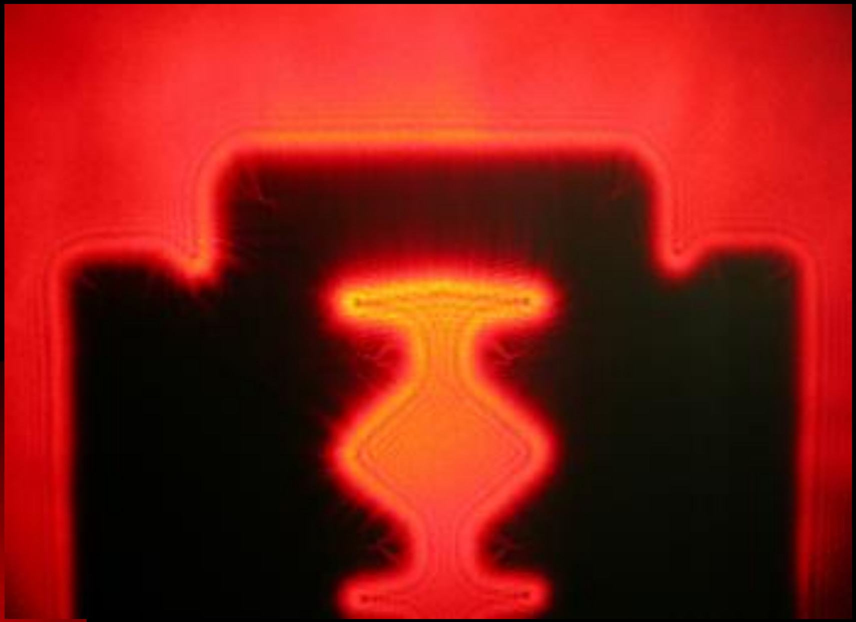
Interferência em ondas na água

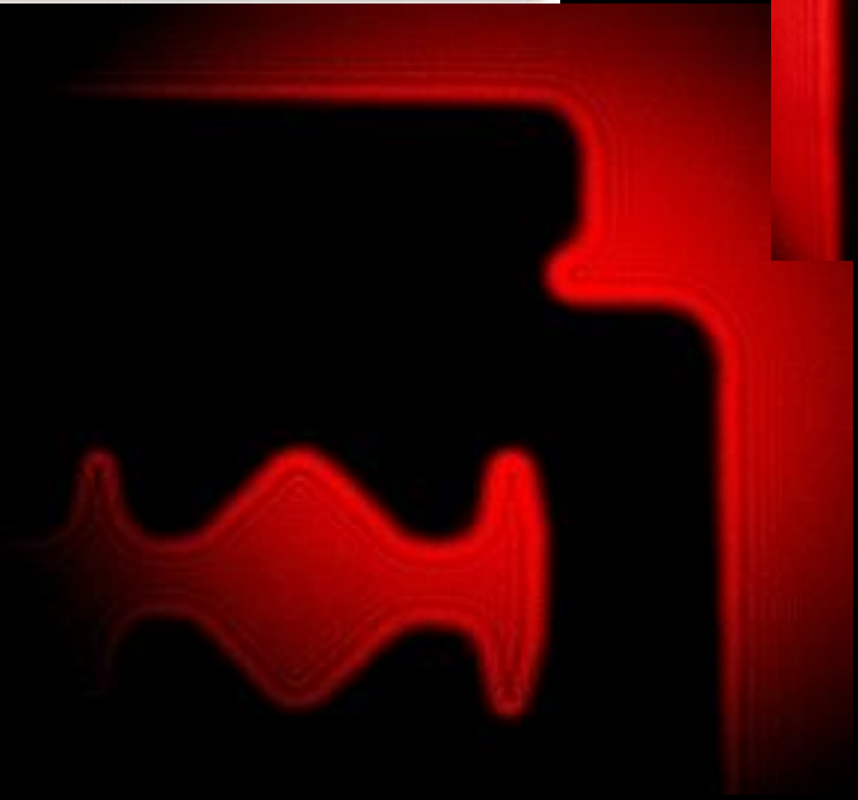

Light source
Gaps between
cloud droplets
Cloud
Droplets
Diffracted light

Arco-Íris

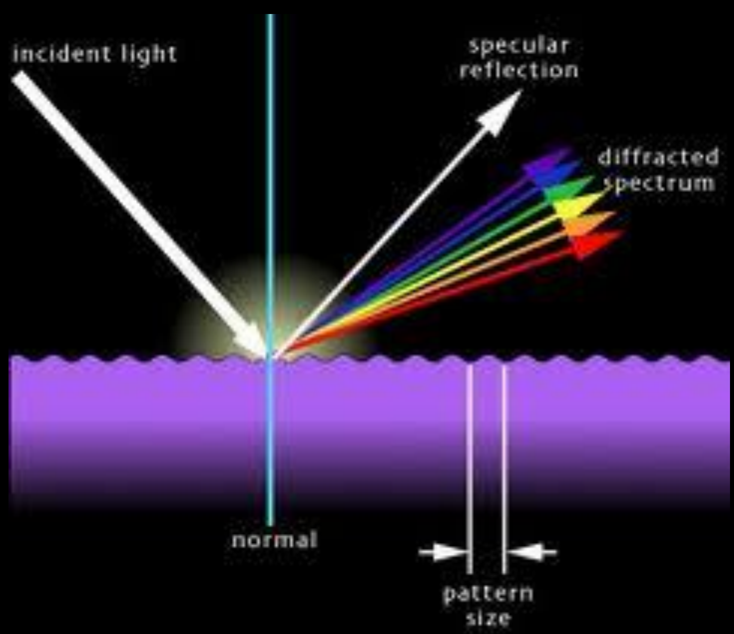
Difração em objetos macroscópicos



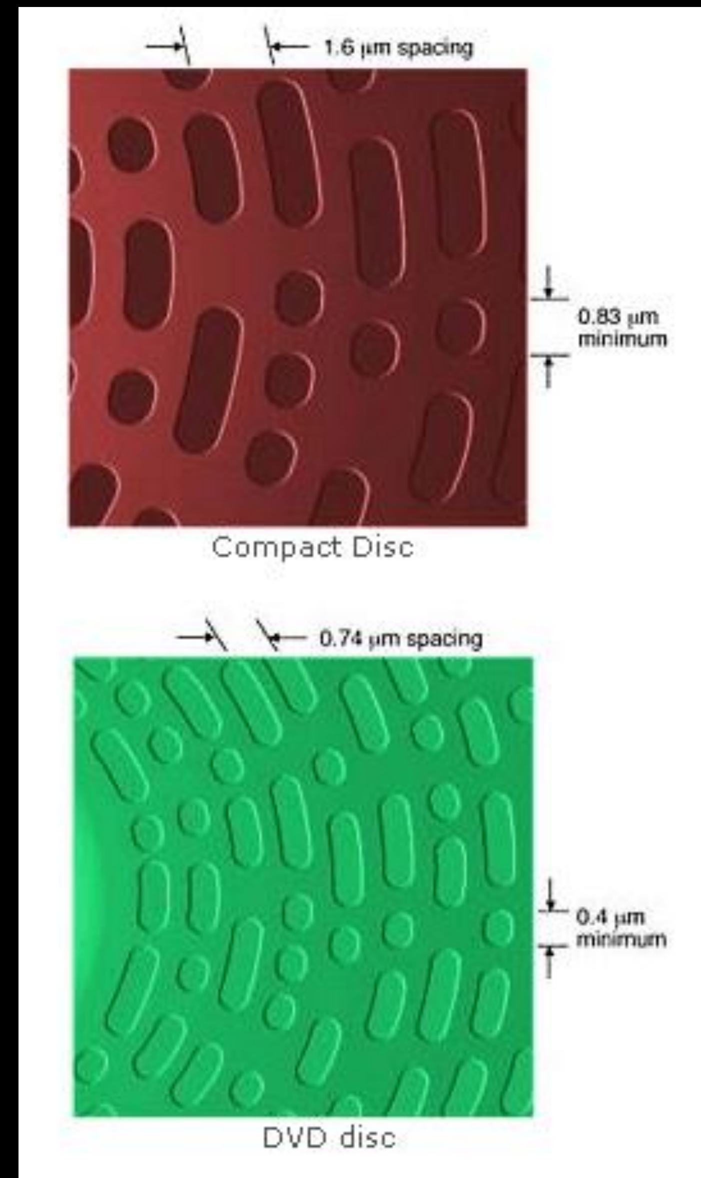




CD - DVD



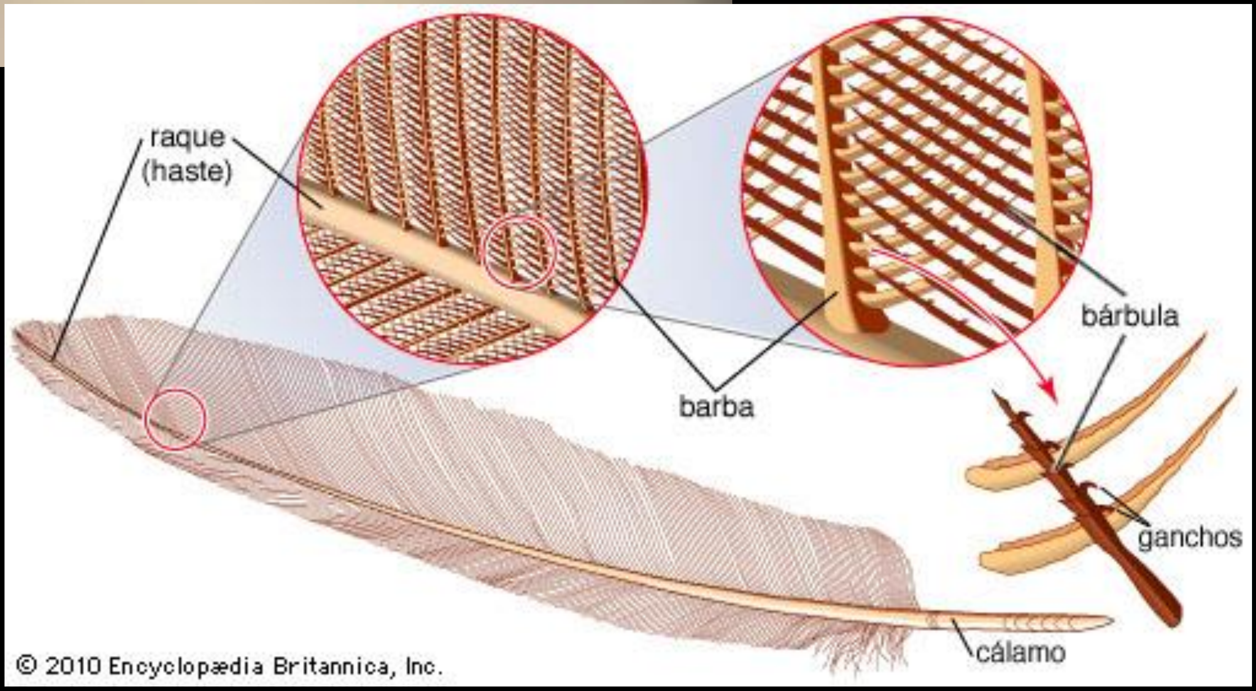
incident light
specular reflection
diffracted spectrum
normal
pattern size



1.6 µm spacing
0.83 µm minimum
Compact Disc
0.74 µm spacing
0.4 µm minimum
DVD disc


© Victor Tyakht

Penas


raque
(haste)
barba
bárbula
ganchos
cálamo
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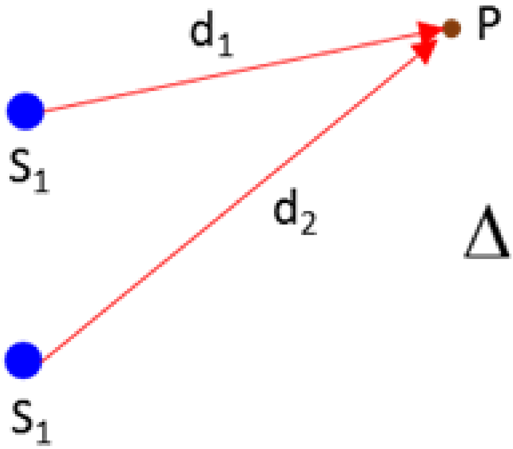
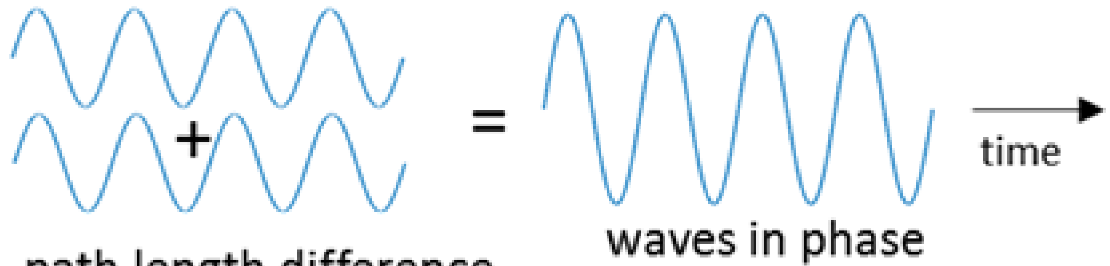
Interferências: Construtiva e Destrutiva



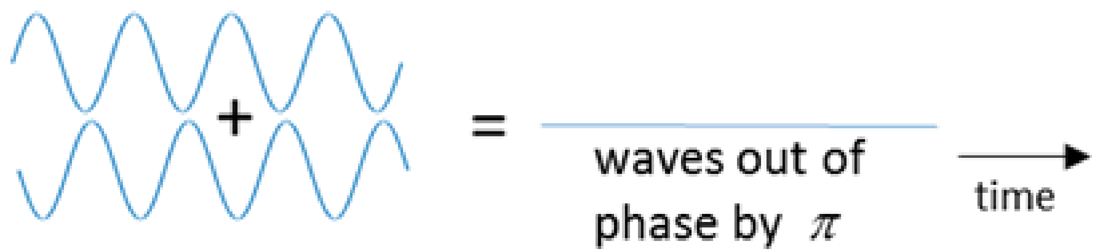
constructive interference at P



path length difference

$$\Delta = \left| d_2 - d_1 \right| = m\,\lambda \qquad m = 0, 1, 2, \ldots$$

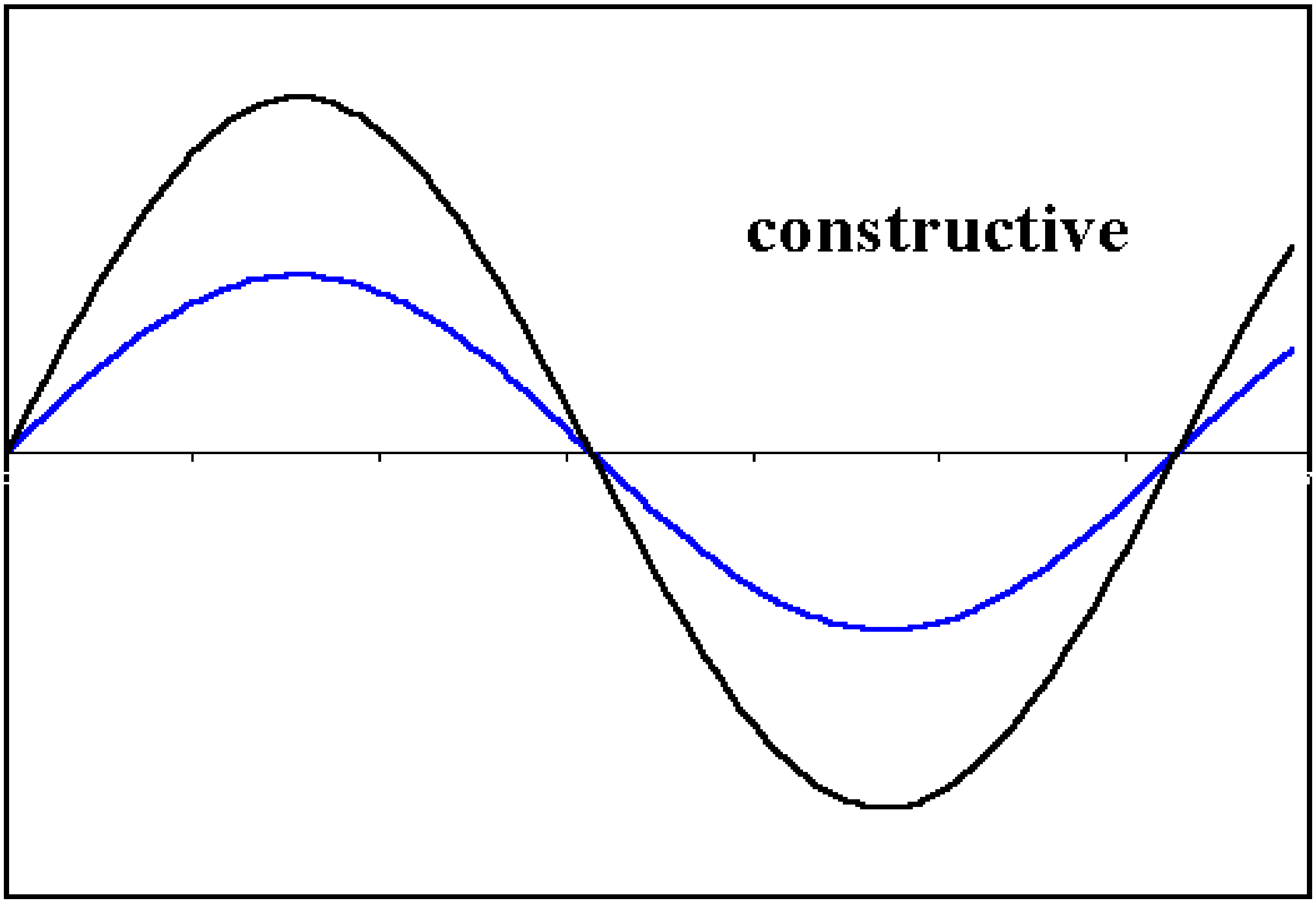
destructive interference at P



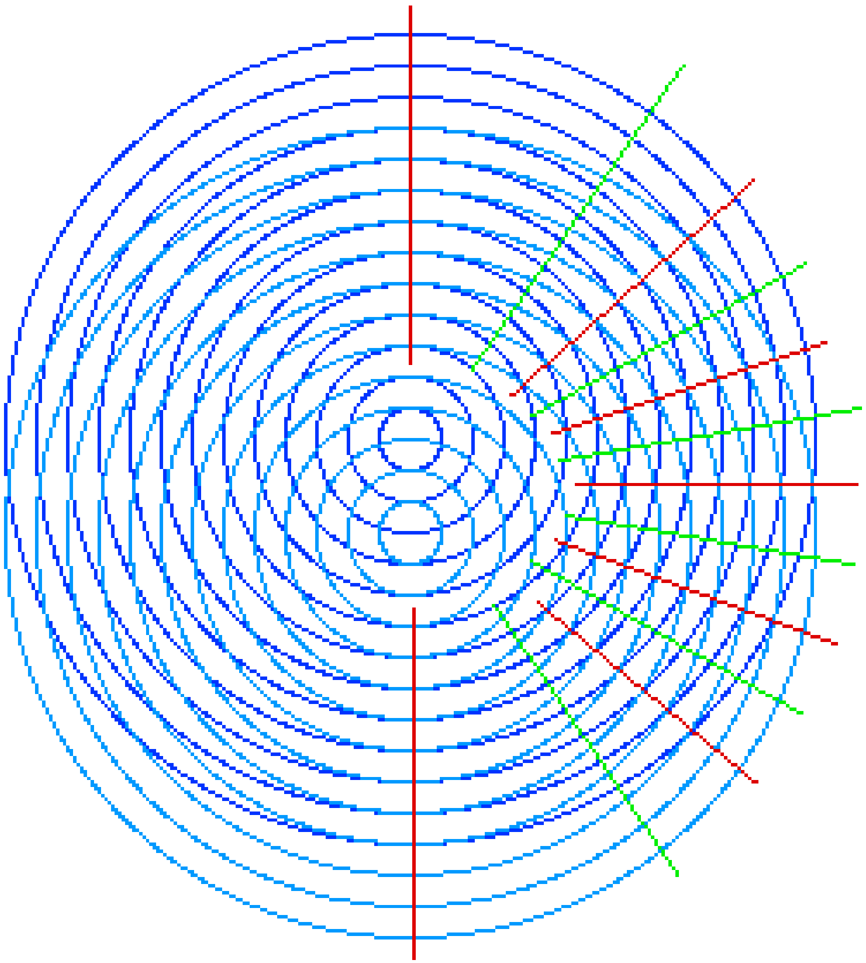
path length difference

$$\Delta = \left| d_2 - d_1 \right| = \left(m + 1/2 \right) \lambda \qquad m = 0, 1, 2, \ldots$$

Interferências de Ondas: Construtiva e Destrutiva



Interferência de duas ondas com a mesma frequência



constructive interference
occurs where the lines, which
represent peaks, cross

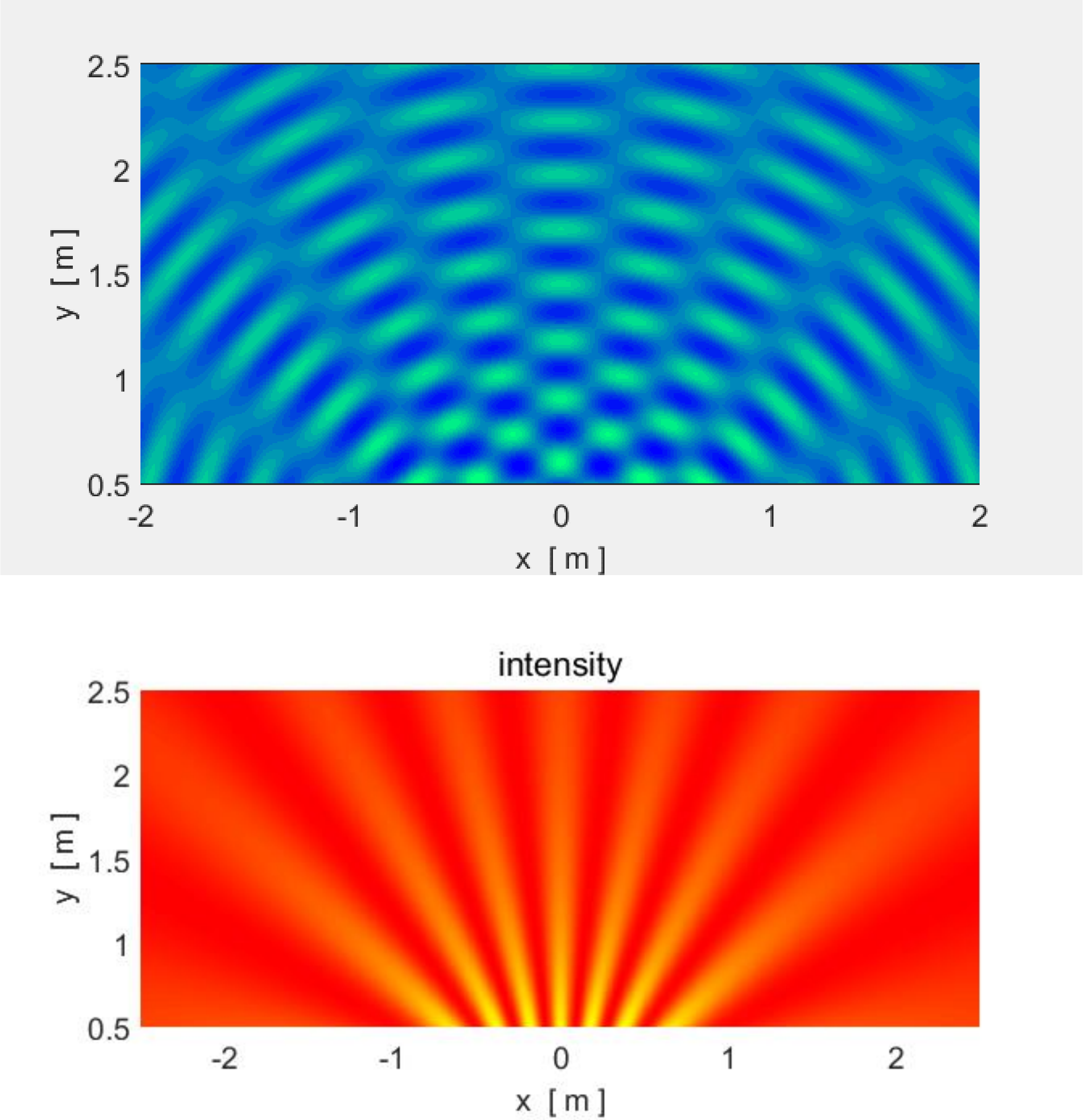
destructive interference
occurs where the two waves are
completely out of phase - a peak
from one lies halfway between
two peaks from the other.

The angles at which constructive and
destructive interference occur
depend on the wavelength and the
separation between the sources.

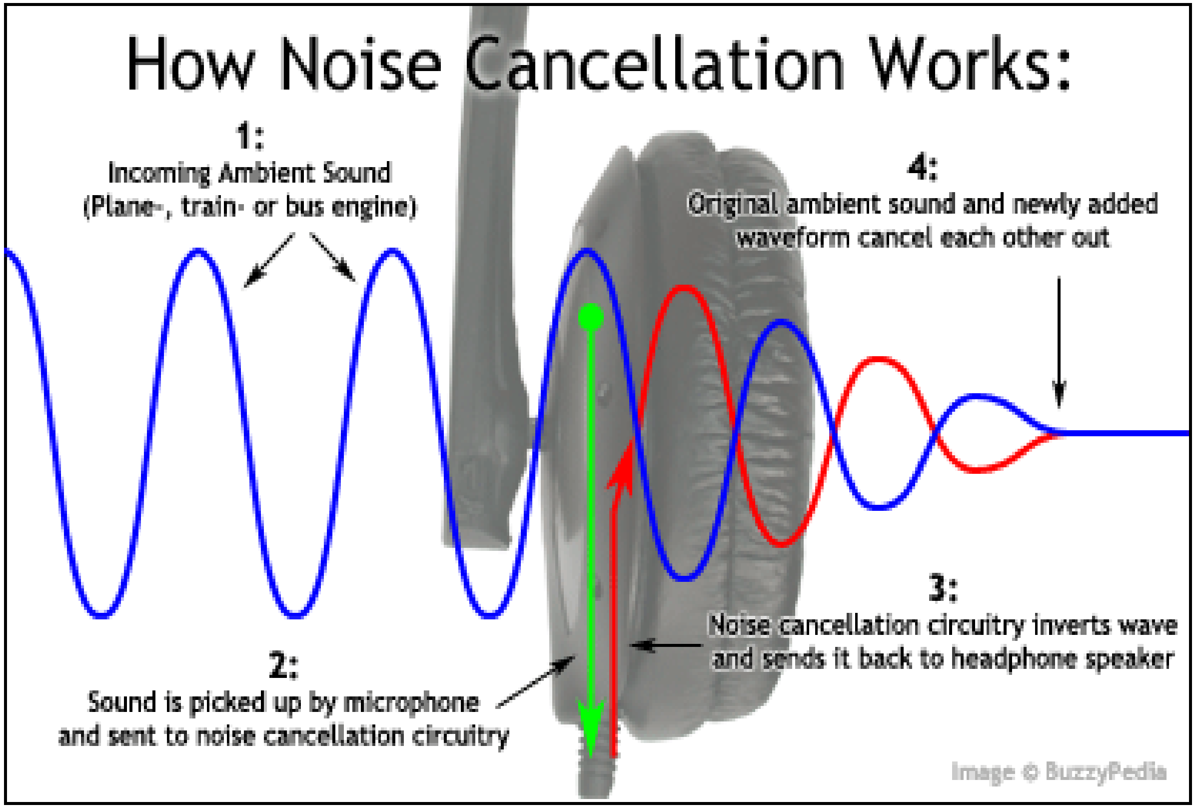
One source is at the center of the light-blue set of circles; the other is
at the center of the dark-blue set.

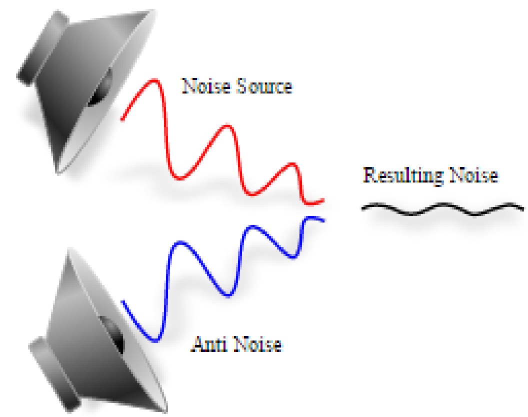
http://physics.bu.edu/~duffy/py105/WaveDiffraction.html

Fonte: http://www.physics.usyd.edu.au/teach_res/hsp/sp/mod31/m31_superposition.htm



Aplicação de Interferências de Ondas: Construtiva e Destrutiva





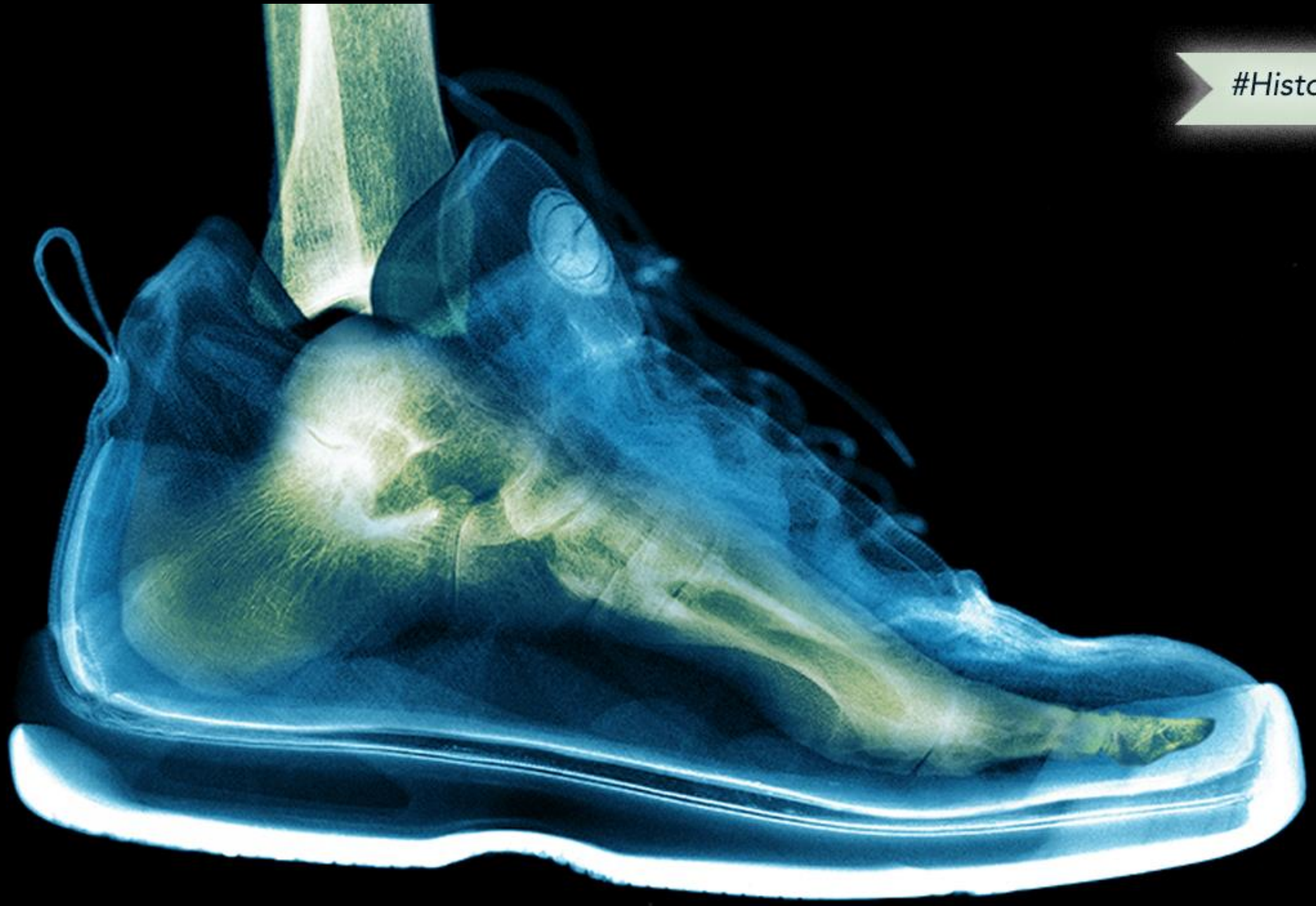
Interferência Destrutiva

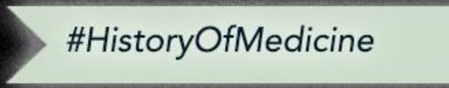
*...nos sites abaixo, você **ouvir** interferências de onda...*

http://www.szynalski.com/tone-generator

https://www.youtube.com/watch?v=V8W4Djz6jnY

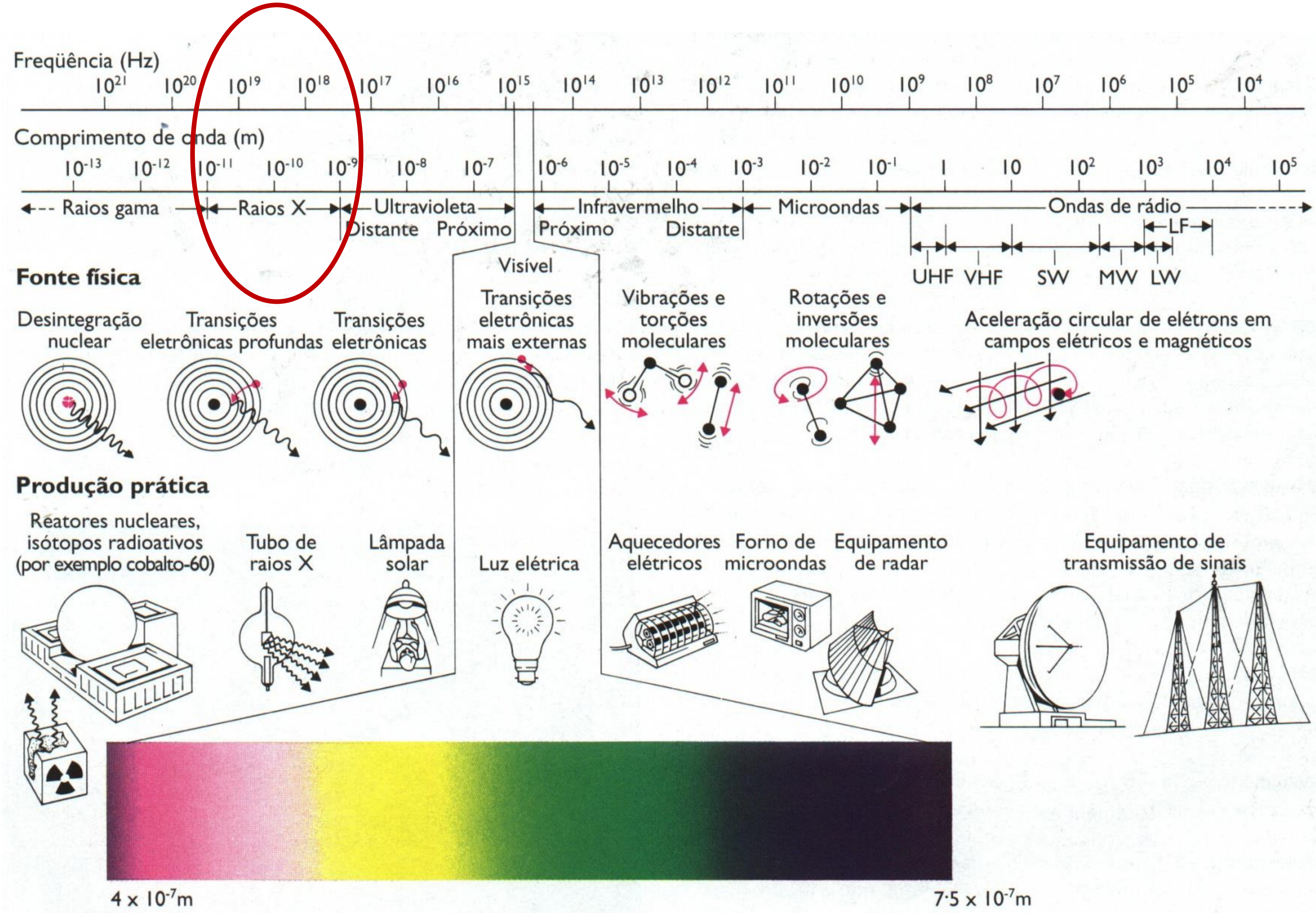
Raios X

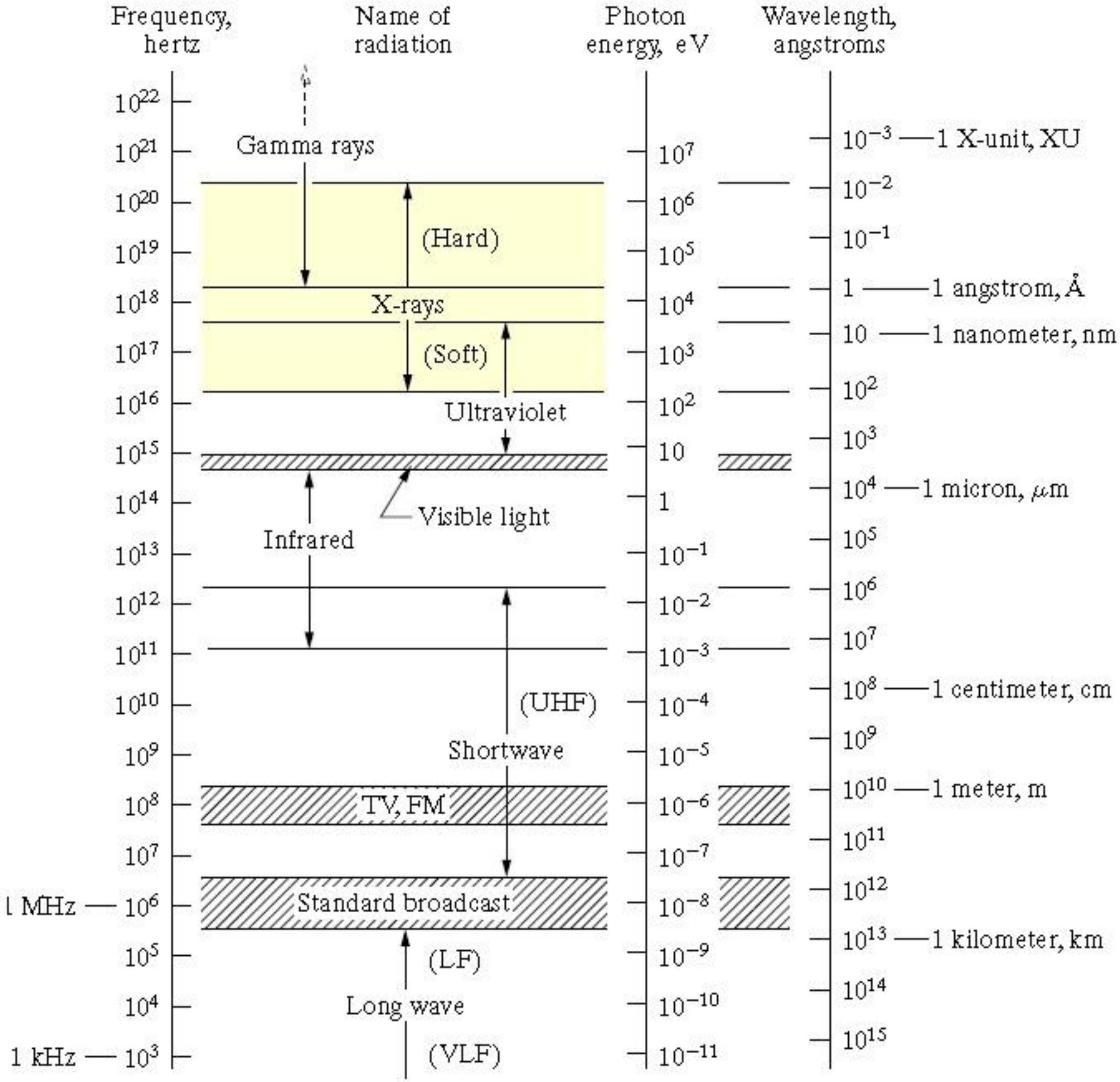




Espectro Eletromagnético

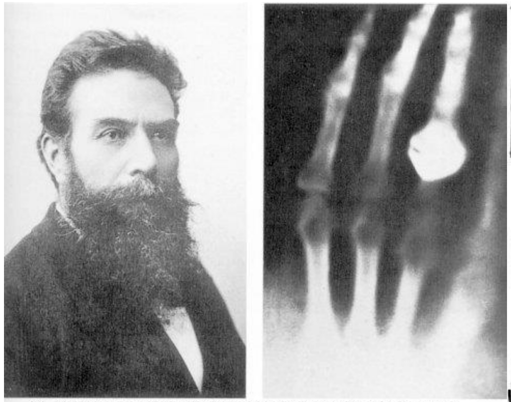
Os raios-X são radiações eletromagnéticas similares à luz, porém com um comprimento de onda muito menor




Frequency, hertz
Name of radiation
Photon energy, eV
Wavelength, angstroms
Gamma rays
(Hard)
X-rays
(Soft)
Ultraviolet
Visible light
Infrared
(UHF)
Shortwave
TV, FM
Standard broadcast
(LF)
Long wave
(VLF)
1 MHz
1 kHz
1 X-unit, XU
1 angstrom, Å
1 nanometer, nm
1 micron, μm
1 centimeter, cm
1 meter, m
1 kilometer, km

Um pouco de História... Os raios-X

- Wilhelm Conrad Röntgen (1845-1923) discovered X-rays on November 8, 1895, at the University of Wurzburg in Germany.
- Röntgen used electrons to bombard inert gas in tubes, and discovered that nearby photographic plates had been exposed by some sort of unknown ("X") radiation.
- He demonstrated that X-rays travel in straight lines and are very penetrative, traversing all materials to varying degrees.
- He received the first Nobel Prize in Physics in 1901 for his discovery, donating the prize money (then about $40,000) to the University of Wurzburg.



W. Rontgen and his first X-ray photograph of a human shows the hand of his wife with the ring she was wearing.

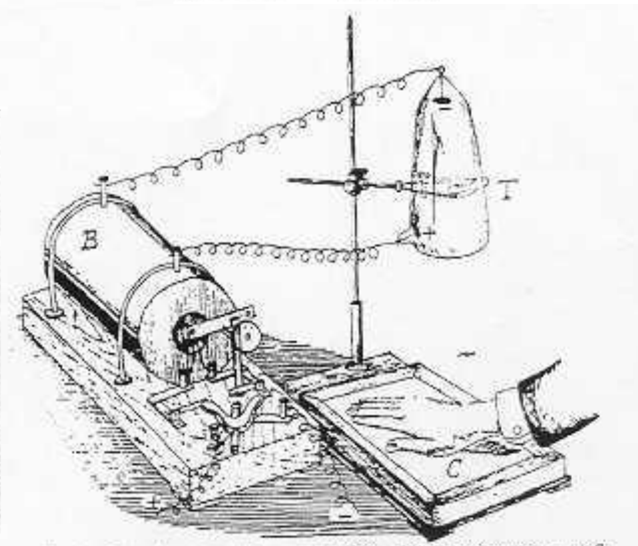


Fig. 1.1. Röntgen's experimental apparatus in 1895. B, Ruhmkorff induction coil; C, photographic plate; T, Hittorf-Crookes evacuated tube.

Um pouco de História... Os raios-X

Uma das primeiras radiografias publicadas

Antiga máquina de radiografia

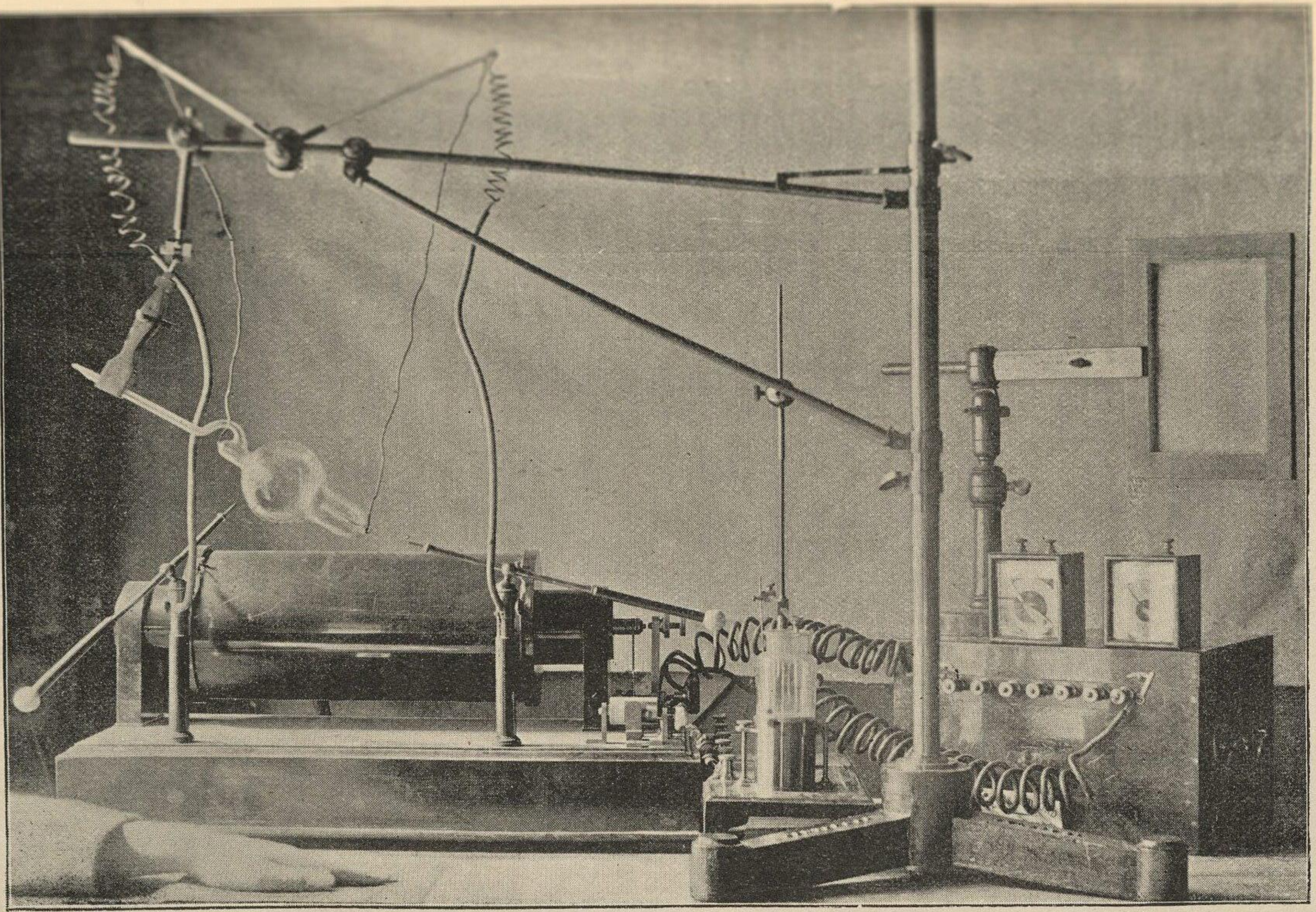


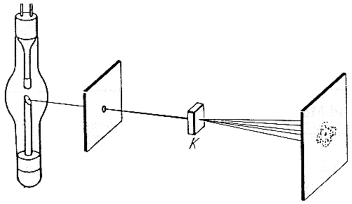
Fig. 17.—Complete Apparatus for Röntgen-Ray Work, consisting of Secondary Battery, Voltmeter, Ammeter, Apps' Induction Coil with Ordinary and Mercurial Break, Rowland's Stand, Focus Tube, Fluorescent Screen on Stand, and Hand in Position upon Photographic Plate.

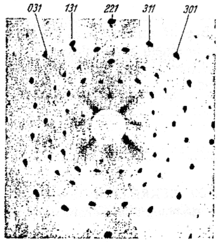
Um pouco de História... DRX (XRD)

- German physicist Max von Laue (1879 – 1960) won the Nobel Prize in 1914, for his work measuring the wavelength of x-rays by their diffraction through the atoms of a crystal.

- This discovery originated when he was discussing problems related to the passage of waves of light through a periodic, crystalline arrangement of particles. The idea then came to him that the much shorter electromagnetic rays, which X-rays were supposed to be, would cause in such a medium some kind of diffraction or interference phenomena and that a crystal would provide such a medium.

- Although his colleagues Sommerfeld, W. Wien and others raised objections to the idea, W. Friedrich, one of Sommerfeld's assistants and P. Knipping tested it out experimentally and, after some failures, succeeded in proving it to be correct.

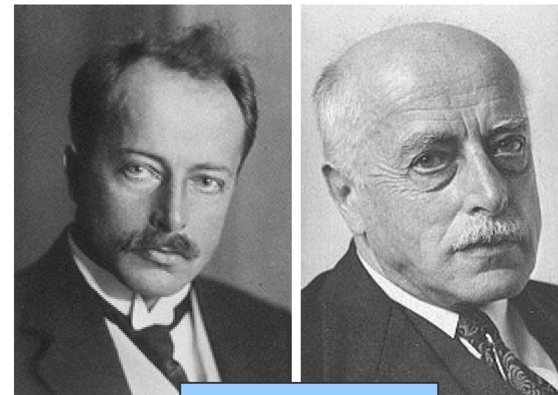




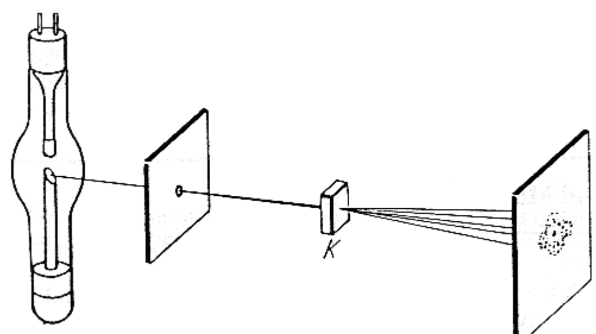
Um pouco de História... DRX (XRD)

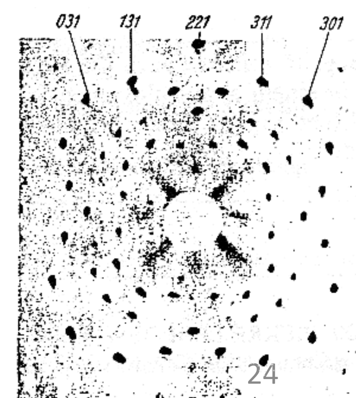
- Von Laue worked out the mathematical formulation of it and the discovery was published in 1912. It established the fact that X-rays are electromagnetic in nature and it opened the way to the later work of Sir William and Sir Lawrence Bragg. Subsequently von Laue made other contributions to this subject .

- As the Nazis came to power in Germany, von Laue openly criticized the governmental stance against "Jewish physics" (i.e., Einstein), and remained in contact with otherwise-isolated Jewish colleagues. During World War II he refused to work on the Nazi program to develop nuclear weapons, and instead wrote a respected book on the history of physics.



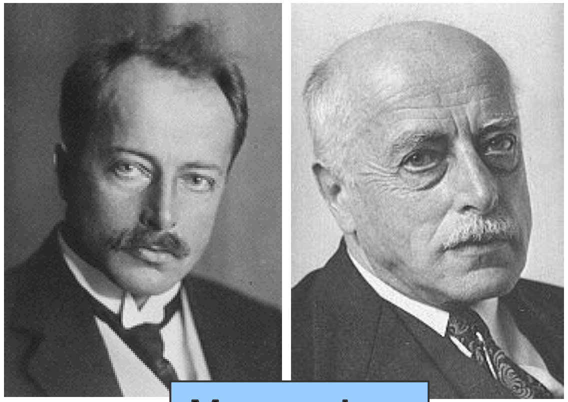
Max von Laue

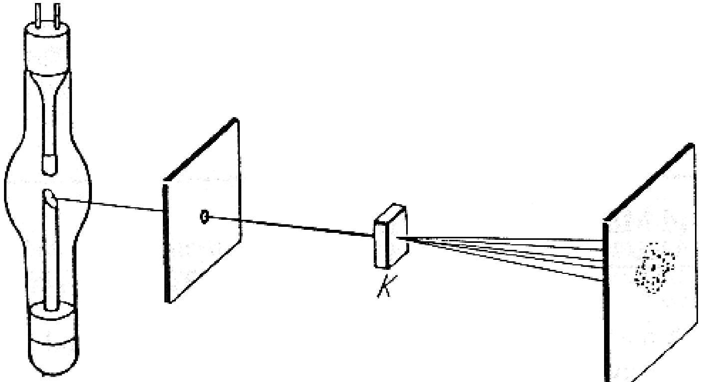




Um pouco de História... DRX (XRD)

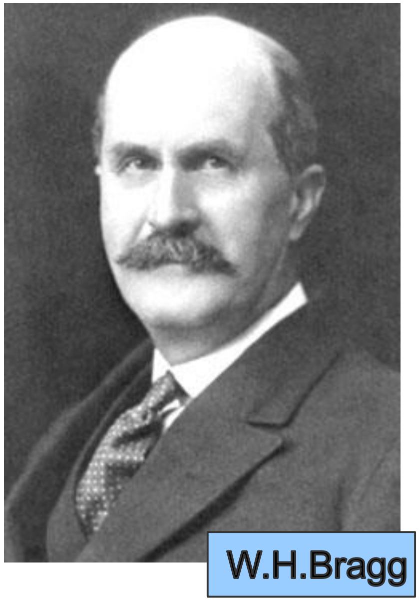
- Still, as one of the leading physicists in Germany, he was among the scientists taken into custody after the war, and was imprisoned for almost a year at Farm Hill in England. During his incarceration he wrote a paper on the absorption of X-rays.
- He was an early and enthusiastic adapter of the automobile, and had a reputation for driving at fast speeds. He was seriously injured in a collision with a motorcycle in Berlin on 7 April 1960 in which the cyclist was killed, and von Laue died of his injuries about two weeks later.

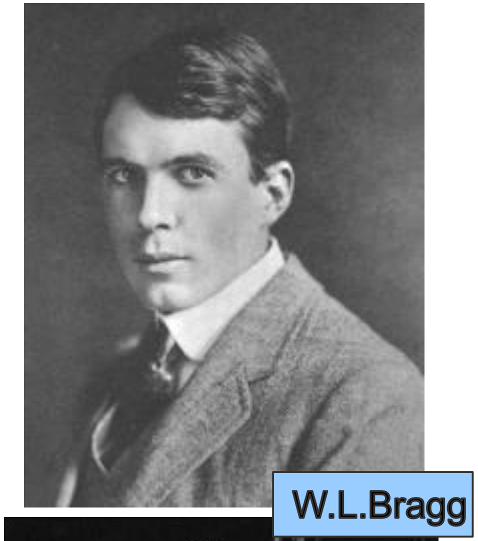

Max von Laue

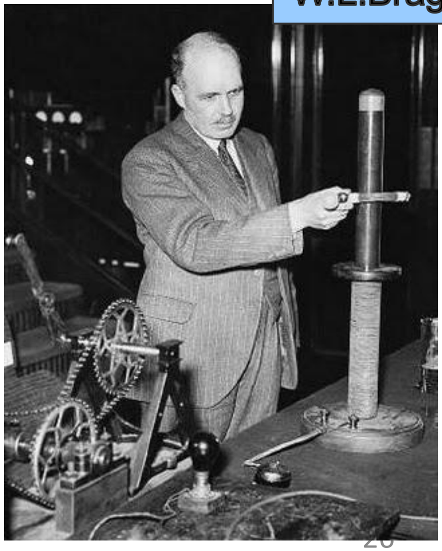


Um pouco de História... DRX

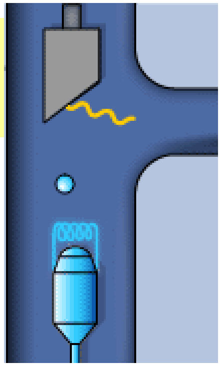
- In 1913, William Lawrence Bragg (1890-1971) observed the first X-ray spectrum, examining the L lines produced from platinum using an NaCl crystal.
- W.L. Bragg confirmed that X-rays produced ionization and also could be diffracted by a regular crystal: the wave-particle duality.
- The older Bragg – William Henry Bragg (1862-1942) – developed developed an X-ray detector that when coupled with the younger Bragg's diffracting crystal is the basis of all X-ray spectrometry.
- The Braggs received the Nobel Prize in 1915 for their work.



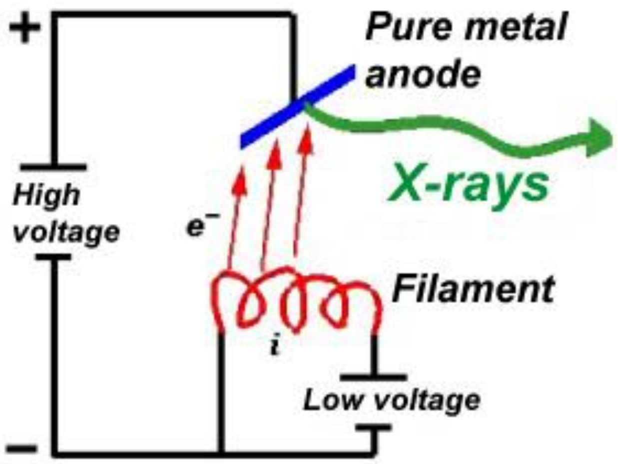


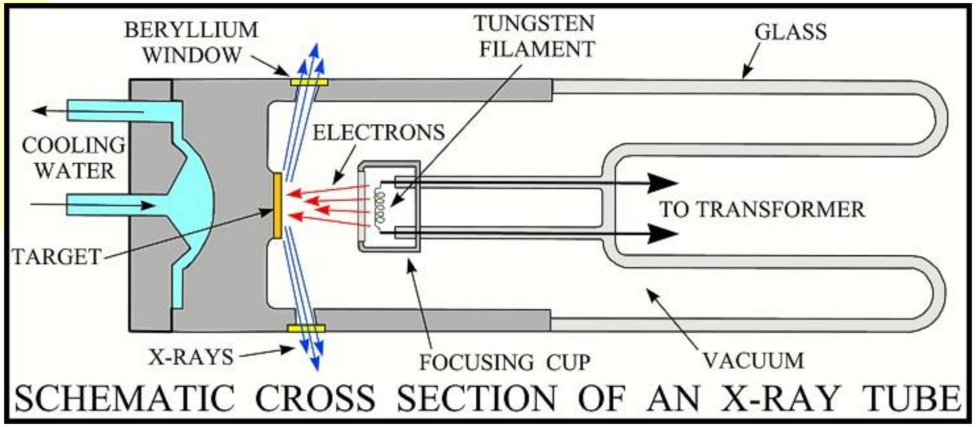


A Fonte de Raios X

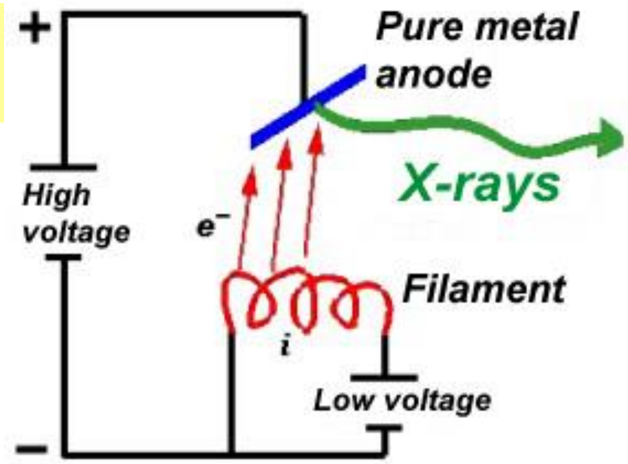


- Elétrons são emitidos no cátodo e acelerados em direção ao ânodo.
- Ao serem bruscamente desacelerados, transferem energia aos átomos do ânodo:
  - parte dessa energia é empregada para ejetar ou excitar elétrons do material do ânodo (fundamento da emissão de raios-X).
  - parte da energia é dissipada em forma de energia térmica (que aquece o ânodo).

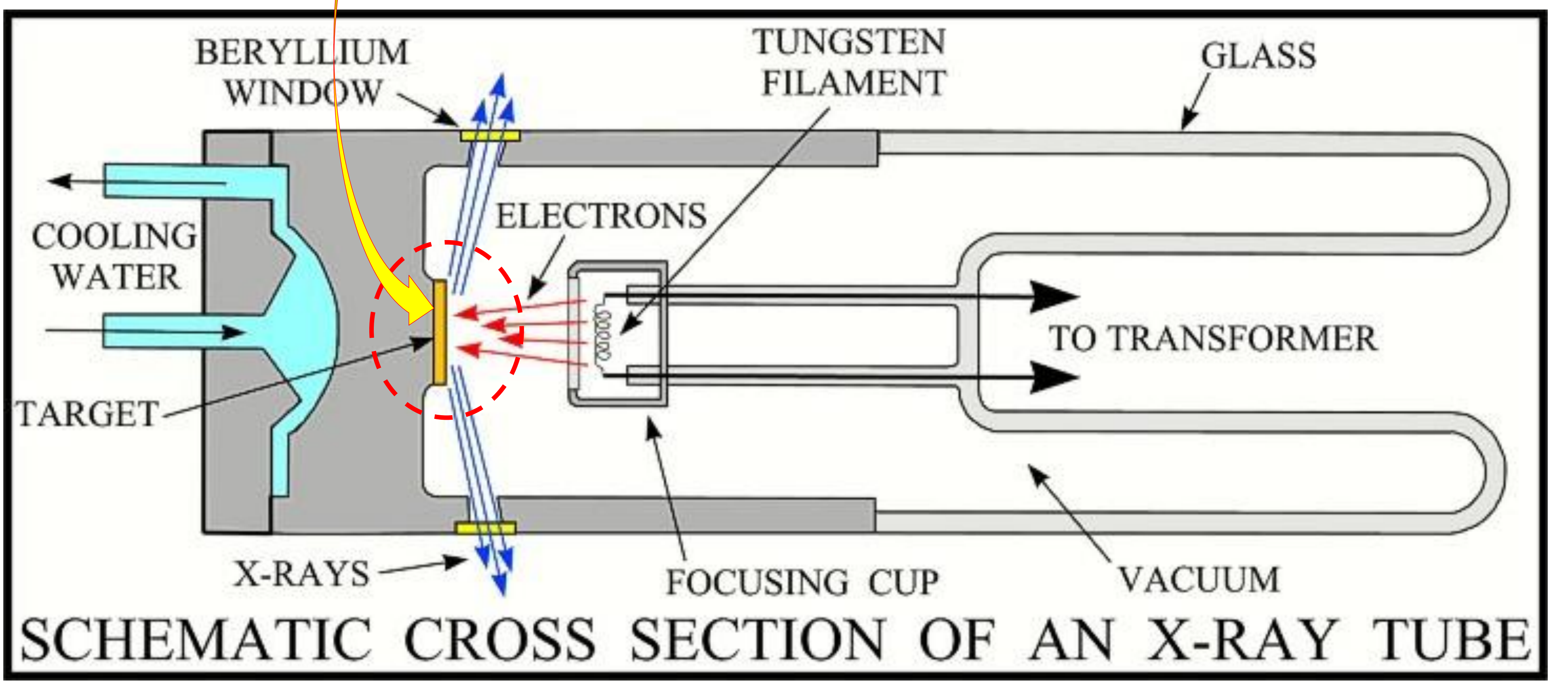




A Fonte de Raios X

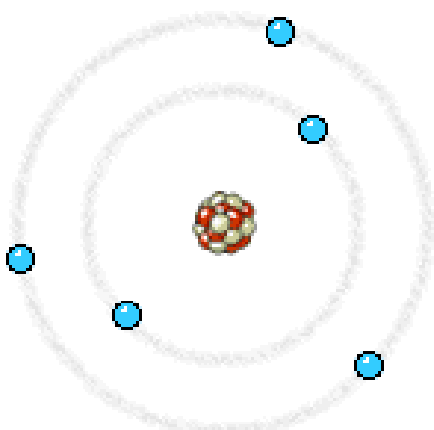


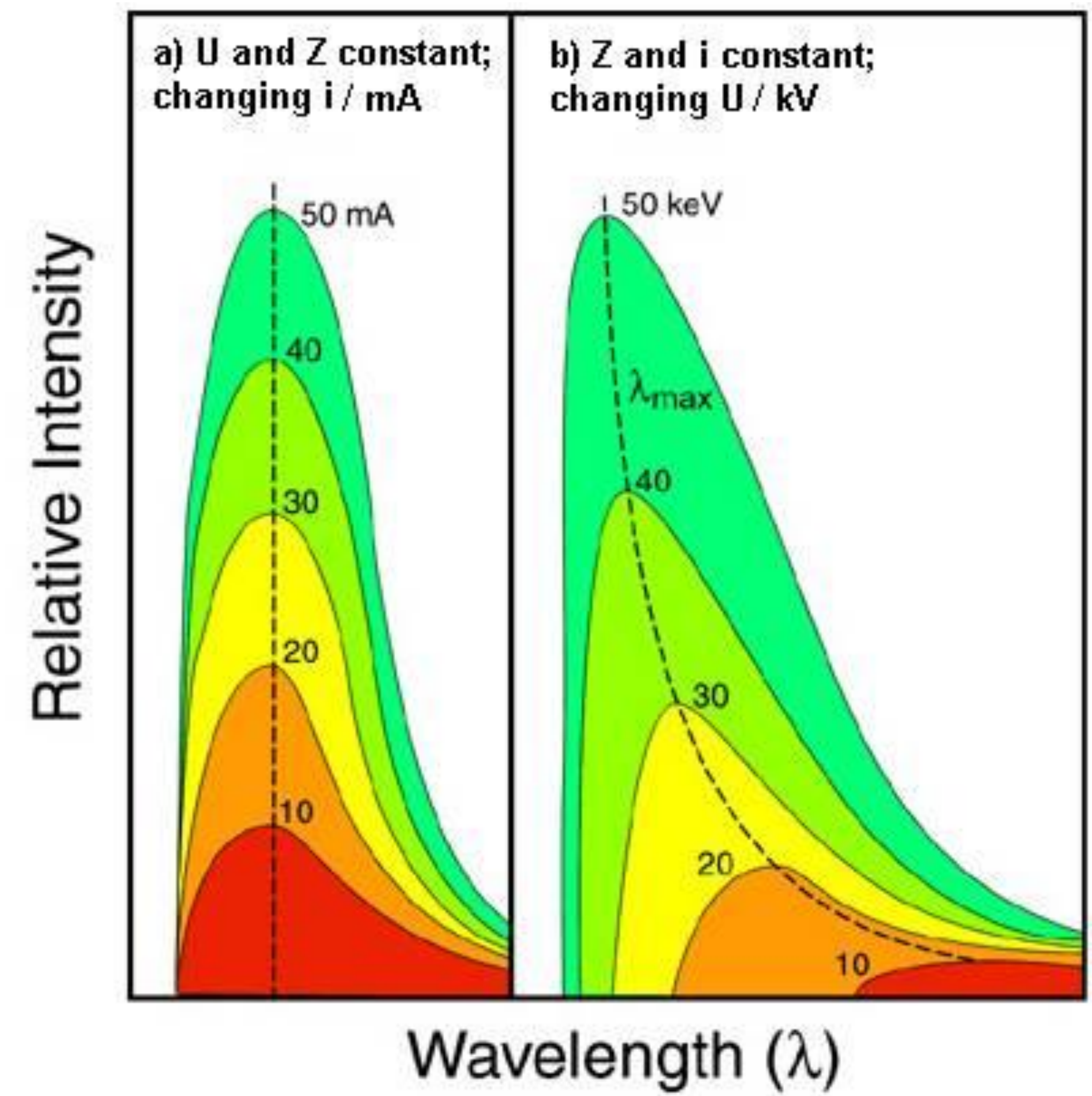
É o material do anodo que define o comprimento de onda



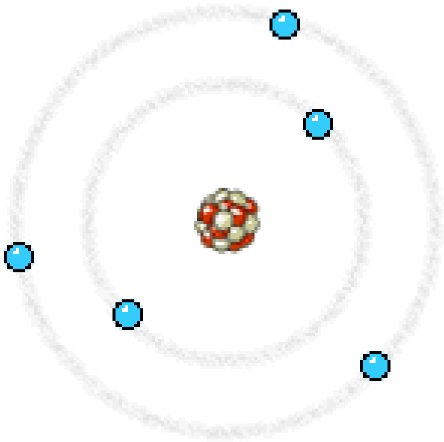
A Fonte de Raios X

- ***Radiação Branca*** - uma forma de radiação que se espalha num espectro contínuo → não é base para obtenção de informações úteis para a difratometria de raios X.



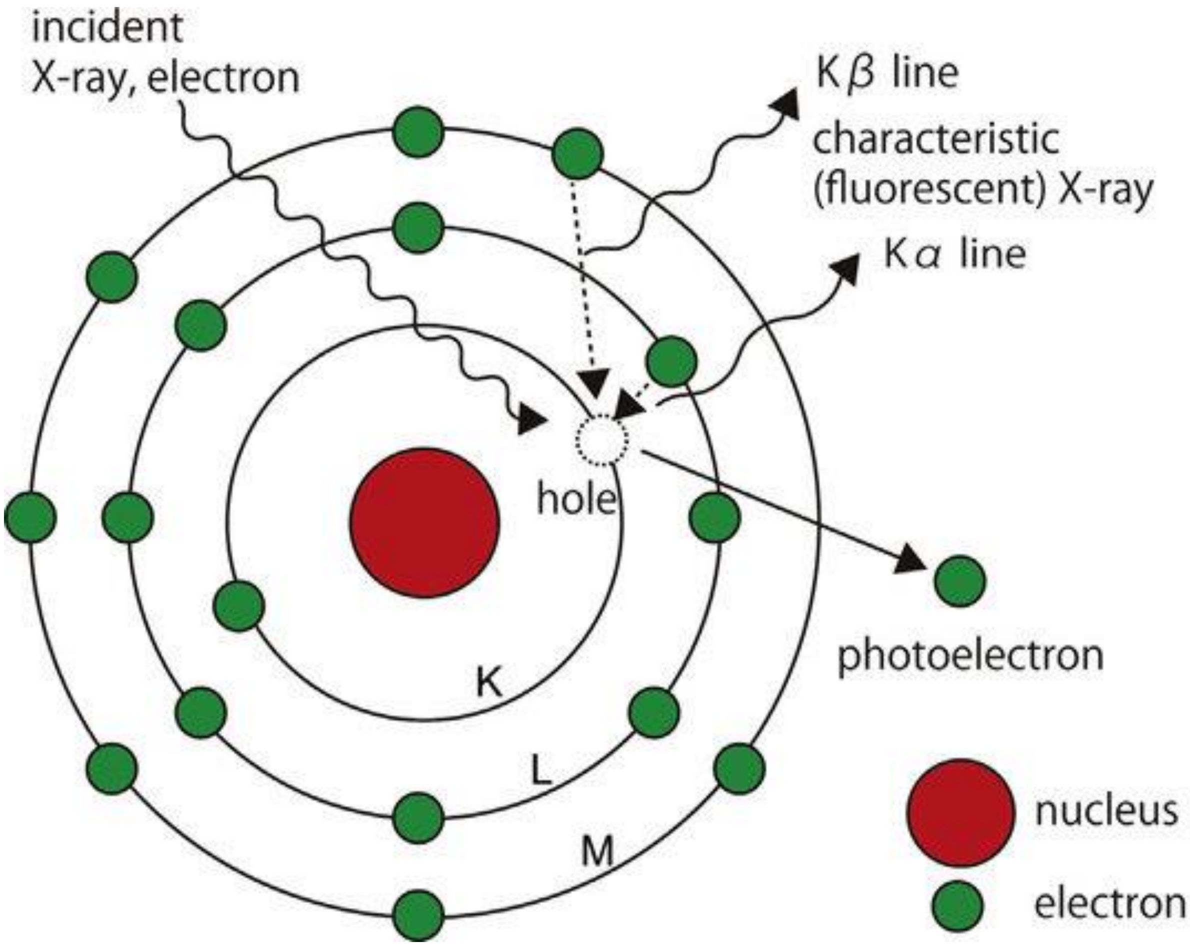


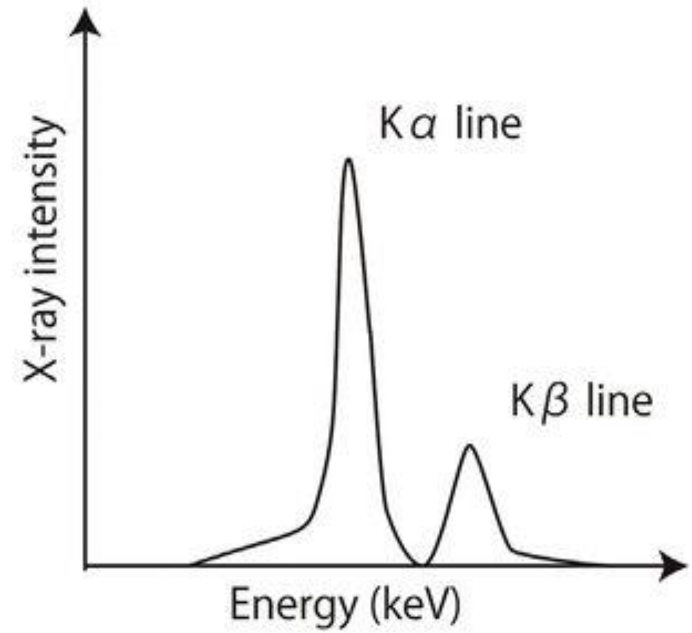
A Fonte de Raios X



- ***Radiação Característica*** → radiação com comprimento de onda (λ) característico do material do anodo.
  - ***e⁻*** incidentes atingem ***e⁻*** das camadas mais internas dos átomos do ânodo.
  - A energia é suficiente para ejetar esses ***e⁻.***
  - As "lacunas" são preenchidas com a passagem de ***e⁻*** das camadas mais externas.
  - A passagem é acompanhada pela emissão de uma radiação X de λ específico.

A Fonte de Raios X





$$E = h\nu = \frac{hc}{\lambda}$$

A Fonte de Raios X

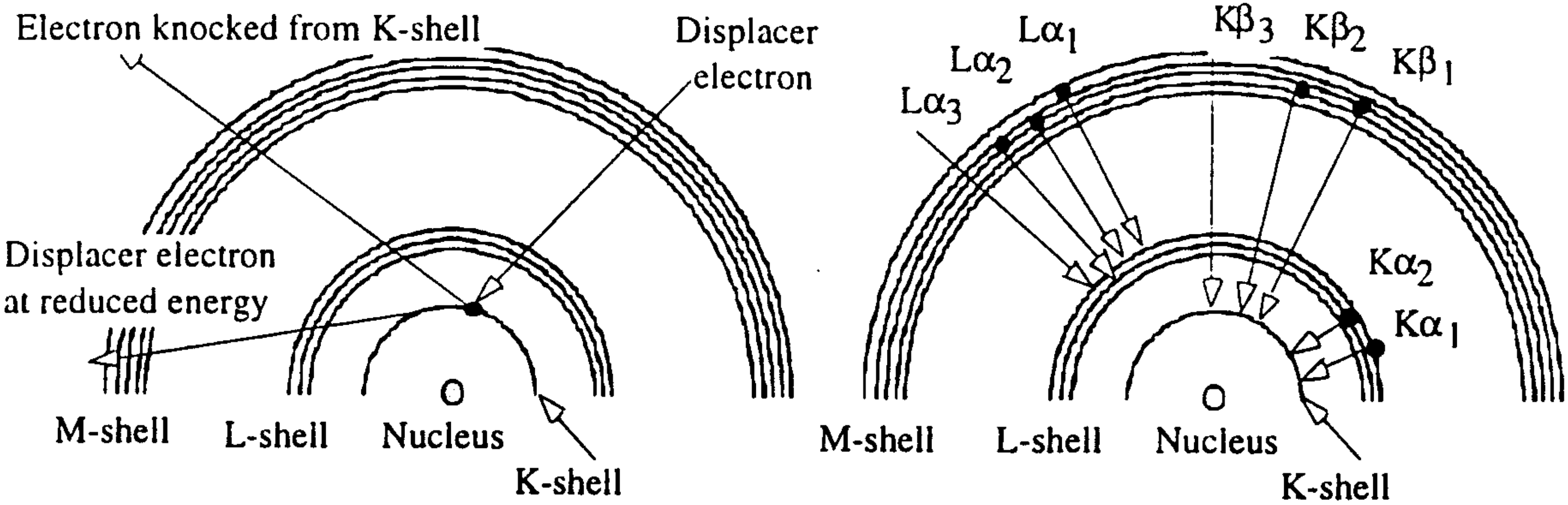
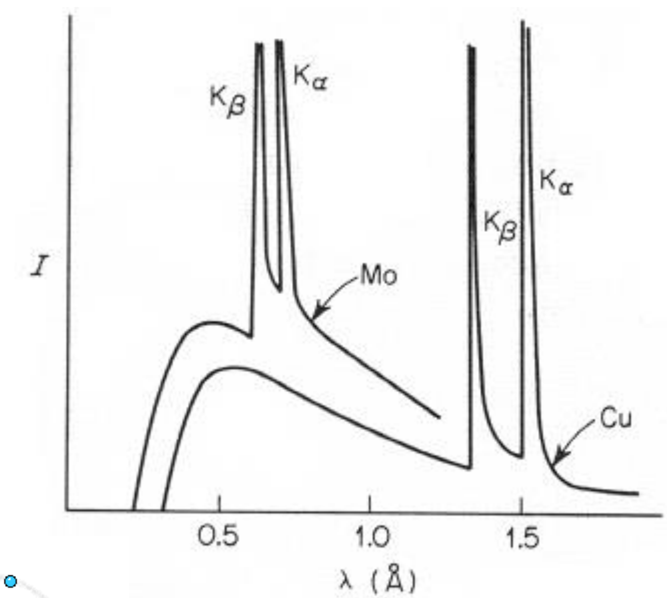


Fig. 2.3. Step 1 shows an electron being knocked from the K shell. The incident electron after impact and the displaced electron, sometimes called a photoelectron, both leave the atom at a wavelength greater than that of the displacer electron as it came into the atom. Step 2 shows many of the possibilities for replacing displaced electrons, only one of which can happen to replace the displaced electron. An X-ray photon is emitted when an electron "drops" from a higher level to refill a shell.

A Fonte de Raios X

- Os **comprimentos de onda λ** nos quais se dá a emissão dessa radiação são característicos do material do ânodo.



$$E = h\nu = \frac{hc}{\lambda}$$

- ***Radiação Característica*** – **série K**
  - série de radiações características dos e^- que decaem da camada L para a camada K
  - constituída por duas raias $\mathbf{K\alpha_1}$ e $\mathbf{K\alpha_2}$ → utilizadas nos aparelhos de difração comerciais.
  - Relação de intensidade entre $\mathbf{K\alpha_1}$ e $\mathbf{K\alpha_2}$ é de aproximadamente 2:1.
  - Além das radiações da série K, outras são geradas, como por exemplo a $\mathbf{K_\beta}$ - produzida pelo decaimento dos e^- da camada M para a camada K.

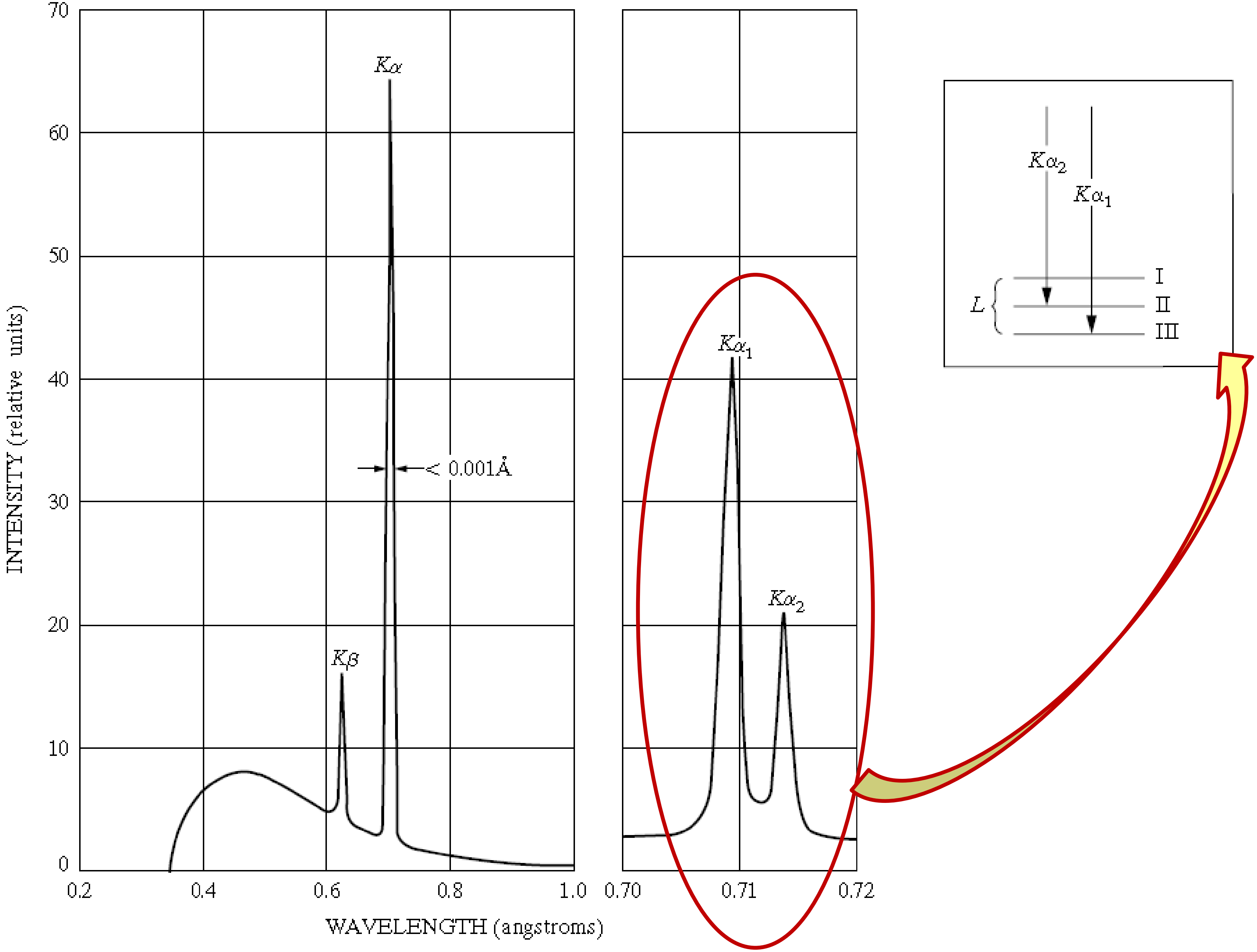
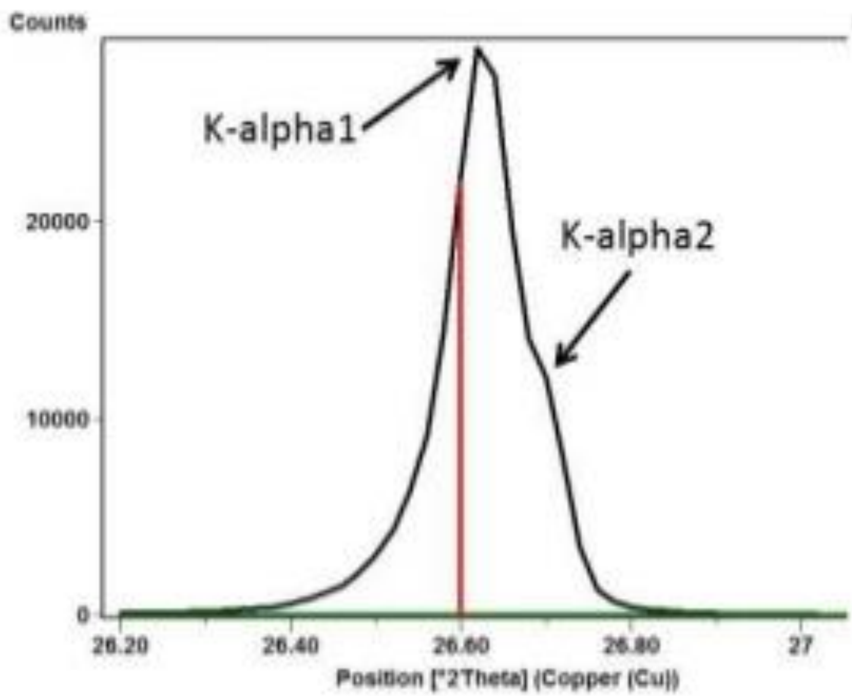
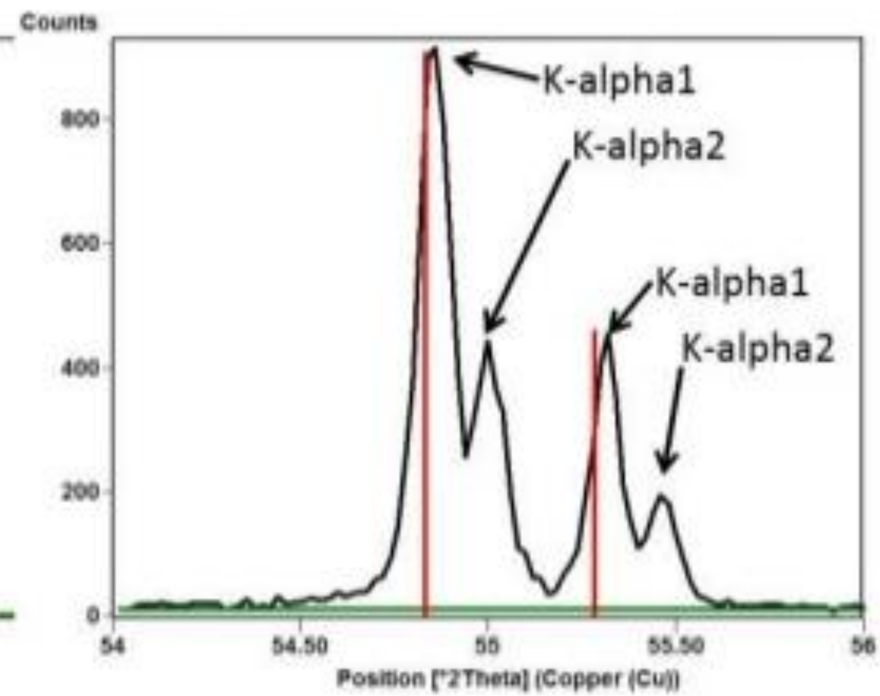


Figure 5 Spectrum of Mo at 35 kV (schematic). Line widths not to scale. Resolved $K\alpha$ doublet is shown on an expanded wavelength scale at right.

$K_{\alpha 1}$, $K_{\alpha 2}$ e K_{β}

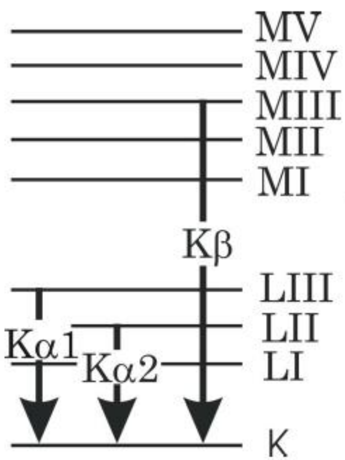
- The $K_{\alpha 1}$ and $K_{\alpha 2}$ components have wavelengths so close together that they are not always resolved as separate lines; if resolved, they are called the K_{α} *doublet* and, if not resolved, simply the K_{α} *line*.
- Similarly, $K_{\beta 1}$ is usually referred to as the K_{β} *line*, with the subscript dropped.
- $K_{\alpha 1}$ is always about twice as strong as $K_{\alpha 2}$, while the intensity ratio of $K_{\alpha 1}$ to $K_{\beta 1}$ depends on atomic number but averages about 5/1.

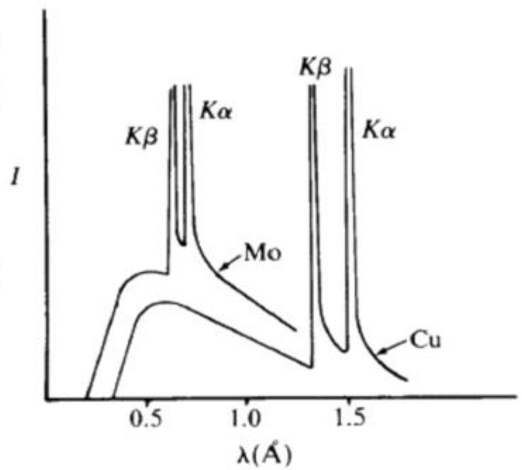


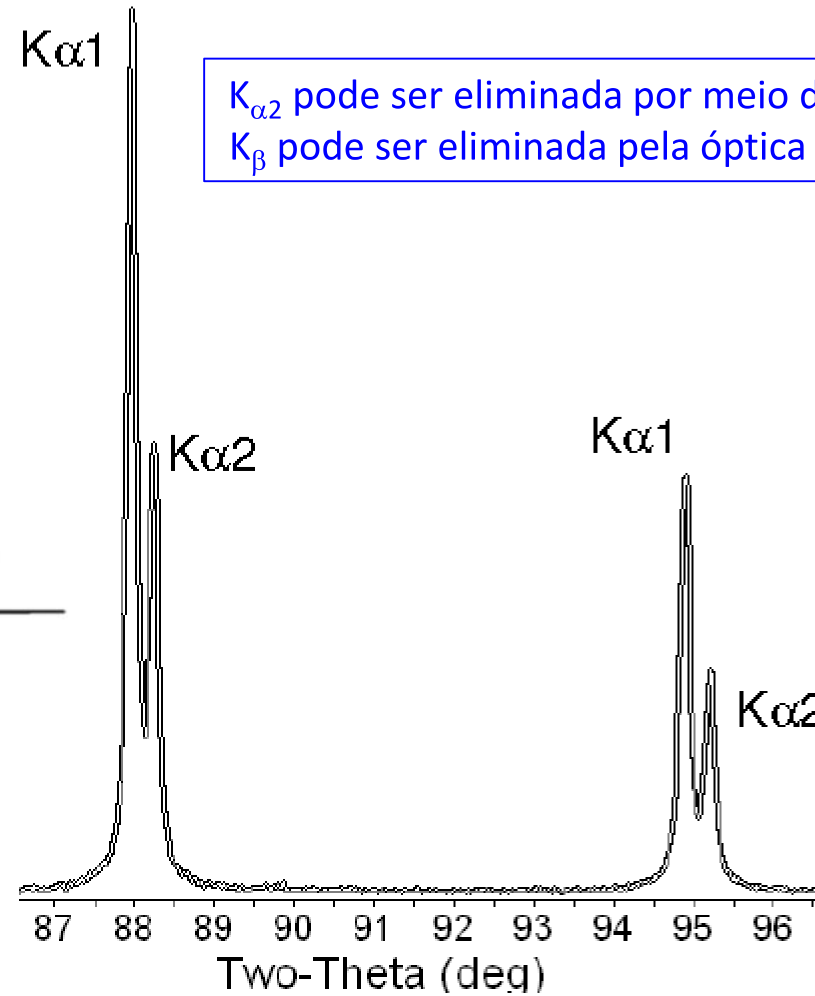


$K_{\alpha 1}$, $K_{\alpha 2}$ e K_{β}

$K_{\alpha 2}$ pode ser eliminada por meio de software
K_{β} pode ser eliminada pela óptica do sistema

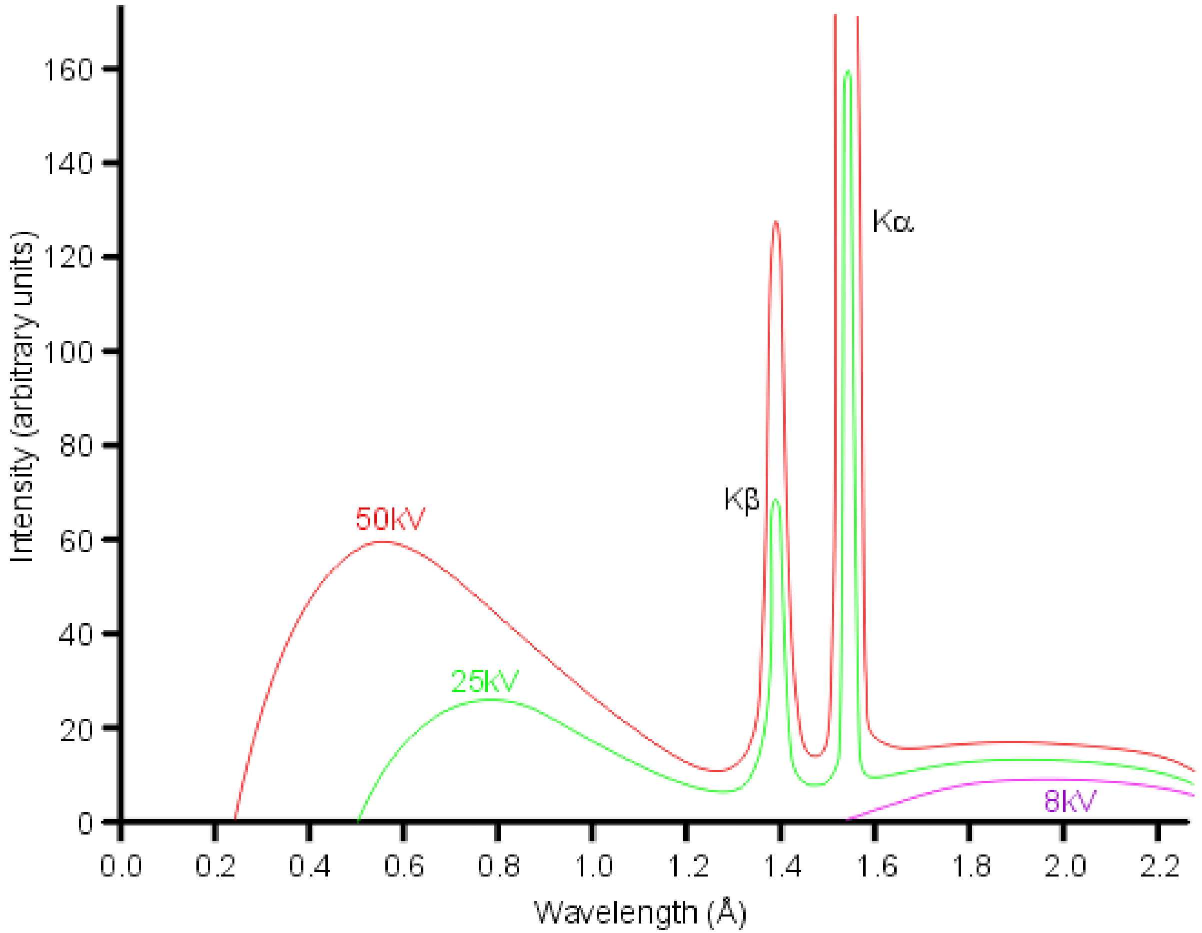


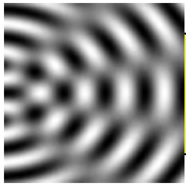




- The Kα1 & Kα2 doublet will almost always be present
  - Very expensive optics can remove the Kα2 line
  - Kα1 & Kα2 overlap heavily at low angles and are more separated at high angles

- X-rays are generated when matter is irradiated by a beam of high-energy charged particles such as electrons.
- In the laboratory, a filament is heated to produce electrons which are then accelerated in vacuum by a high electric field in the range 20-60 kV towards a metal target, which being positive is called the anode.
- The corresponding electric current is in the range 5-100 mA.
- The process is extremely inefficient with most of the energy of the beam being (> 90%) dissipated as heat in the target.
- A typical X-ray spectrum from a copper target is shown on he right → →





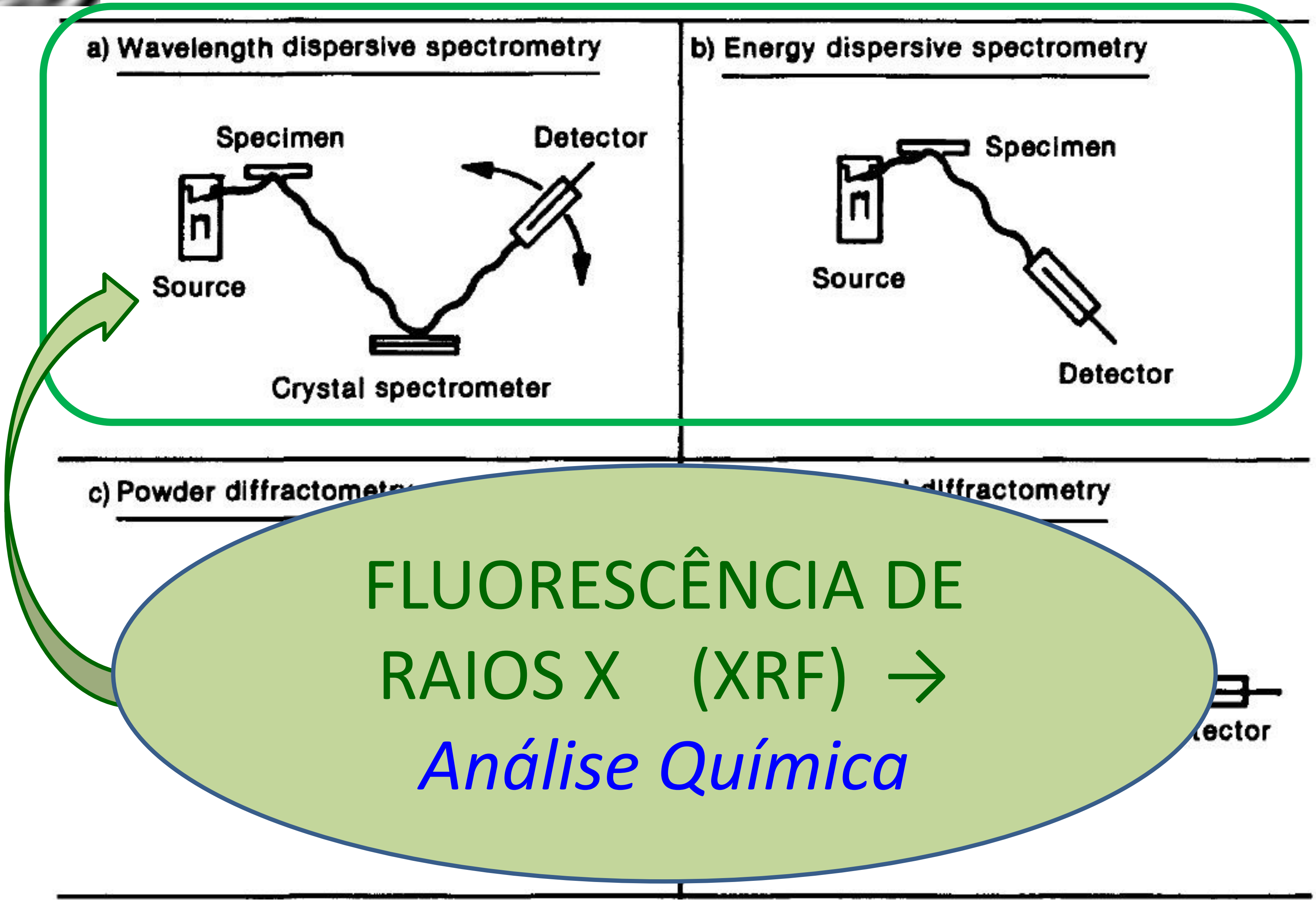
Fontes Comerciais para DRX (XRD)

Wavelengths for X-Radiation are Sometimes Updated

Copper Anodes	Bearden (1967)	Holzer et al. (1997)		Cobalt Anodes	Bearden (1967)	Holzer et al. (1997)
Cu Kα1	1.54056Å	1.540598 Å		Co Kα1	1.788965Å	1.789010 Å
Cu Kα2	1.54439Å	1.544426 Å		Co Kα2	1.792850Å	1.792900 Å
Cu Kβ	1.39220Å	1.392250 Å		Co Kβ	1.62079Å	1.620830 Å
Molybdenum Anodes				Chromium Anodes		
Mo Kα1	0.709300Å	0.709319 Å		Cr Kα1	2.28970Å	2.289760 Å
Mo Kα2	0.713590Å	0.713609 Å		Cr Kα2	2.293606Å	2.293663 Å
Mo Kβ	0.632288Å	0.632305 Å		Cr Kβ	2.08487Å	2.084920 Å

- Often quoted values from Cullity (1956) and Bearden, *Rev. Mod. Phys.* **39** (1967) are incorrect.
  - Values from Bearden (1967) are reprinted in *international Tables for X-Ray Crystallography* and most XRD textbooks.
- Most recent values are from Hölzer et al. *Phys. Rev. A* **56** (1997)
- Has your XRD analysis software been updated?

Aplicações que empregam fontes de raios X

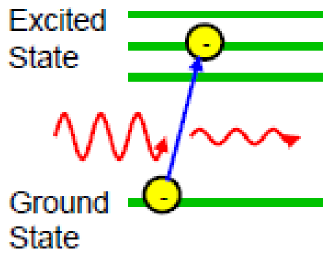


FLUORESCÊNCIA DE RAIOS X (XRF) → *Análise Química*

ATOMIC SPECTROMETRY FUNDAMENTALS

Atomic Absorption

Light of specific wavelength from Hollow Cathode Lamp promotes electron to higher energy level (excitation)

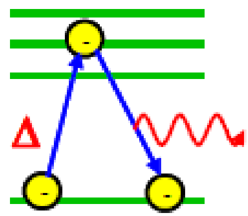


Selectivity based on use of element-specific light source (Hollow Cathode Lamp)

Light absorption is proportional to concentration: **$A = -\log(P/P_0) = \varepsilon bC$**

Atomic Emission

Heat energy from high intensity source (flame or plasma) promotes electron to higher energy level (excitation)

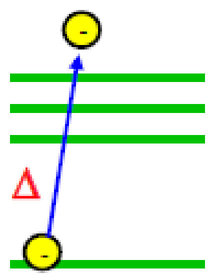


Selectivity based on emission of light at characteristic λ for element

Light emission is proportional to elemental concentration: **$I = kC$**

Mass Spectrometry

Heat energy from high intensity source (plasma) separates electron from atom (ionization)

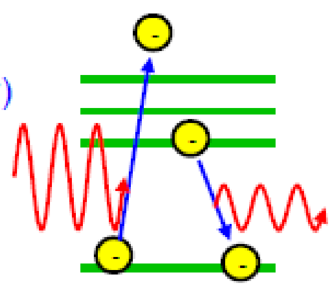


Selectivity based on use of measurement of characteristic mass of elemental ion

Ion intensity is proportional to elemental concentration: **$I = kC$**

X-Ray Fluorescence

Energy from X-Rays (high energy) separates electron from atom (ionization), then inner shell electron fills vacant hole by emitting light



Selectivity based on use of emission of light at characteristic λ for element (X-Ray)

Light intensity is proportional to elemental concentration: **$I = kC$**

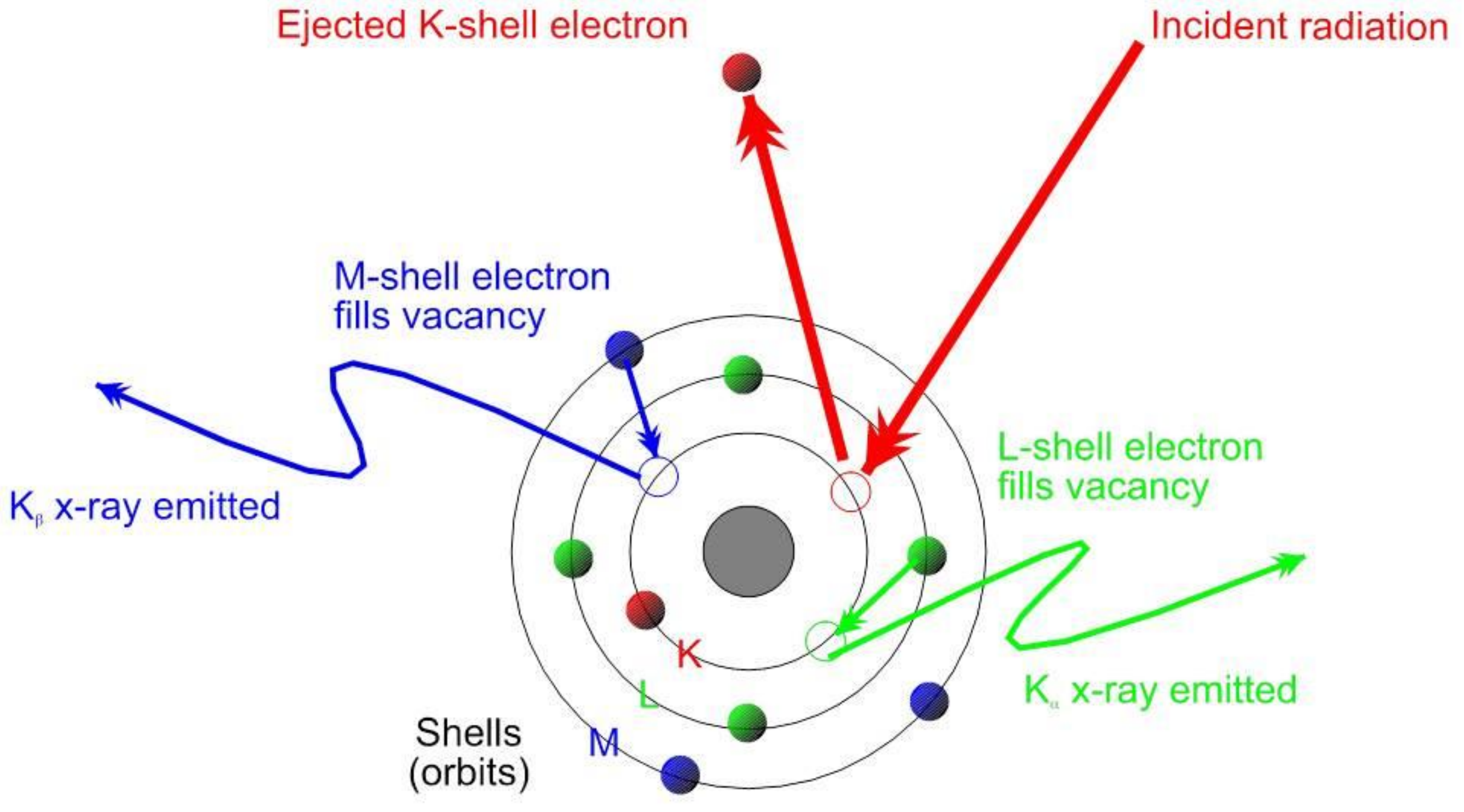
Fonte: Bruker_AXS_Lab_to_Field_Teaching_XRF_Webinar

XRF – Princípio Físico

- Raios X interagindo com um material → podem ser absorvidos ou espalhados.
- Se a energia dos raios X incidentes for suficientemente elevada → durante o processo de absorção, elétrons podem ser ejetados das camadas eletrônicas mais internas dos átomos → *"lacunas eletrônicas" são criadas nas camadas eletrônicas mais internas dos átomos* → átomos "instáveis".
- Para retomar a sua condição de estabilidade → elétrons das camadas eletrônicas mais externas são transferidos para as camadas mais internas.
- Essa passagem de uma camada eletrônica mais externa para um outra mais interna é acompanhada pela emissão de uma ***radiação X*** de comprimento de onda (λ) específico cuja energia é a diferença entre os níveis de energia das camadas envolvidas no processo:
  - a camada mais externa, de onde o elétron se origina,
  - e a camada mais interna, que tem a "lacuna eletrônica" e que receberá o elétron.

XRF – Princípio Físico

1. **When an X-ray photon of sufficient energy strikes an atom, it dislodges an electron from one of its inner orbitals (recall that X-rays are *ionizing* radiation)**
2. **To regain stability, the atom fills the vacancy with an electron from an outer orbital**
3. **As electron drops to lower energy state, excess energy is released as an X-ray**

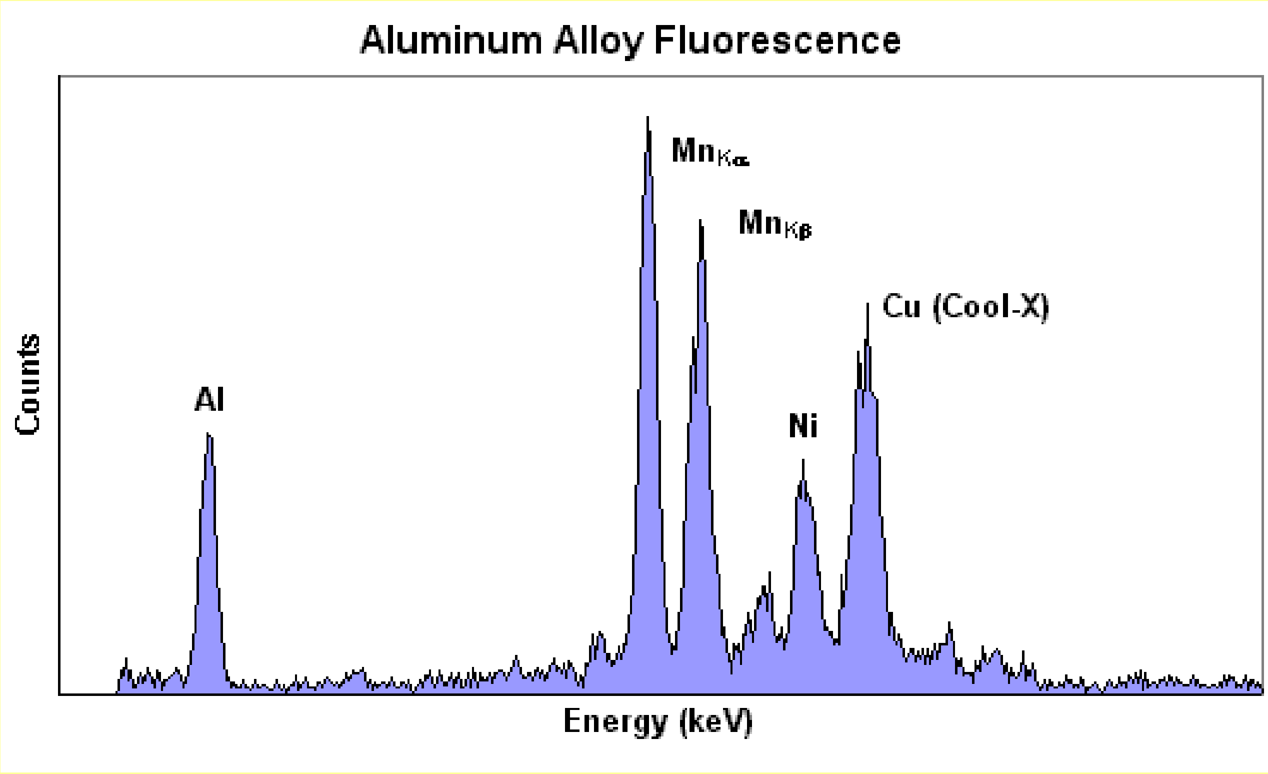


Fonte: Bruker_AXS_Lab_to_Field_Teaching_XRF_Webinar

- Cada elemento tem linhas espectrais características com comprimentos de onda (λ) específicos.

- O espectro gerado consiste das linhas geradas pelos elementos que compõem a amostra.

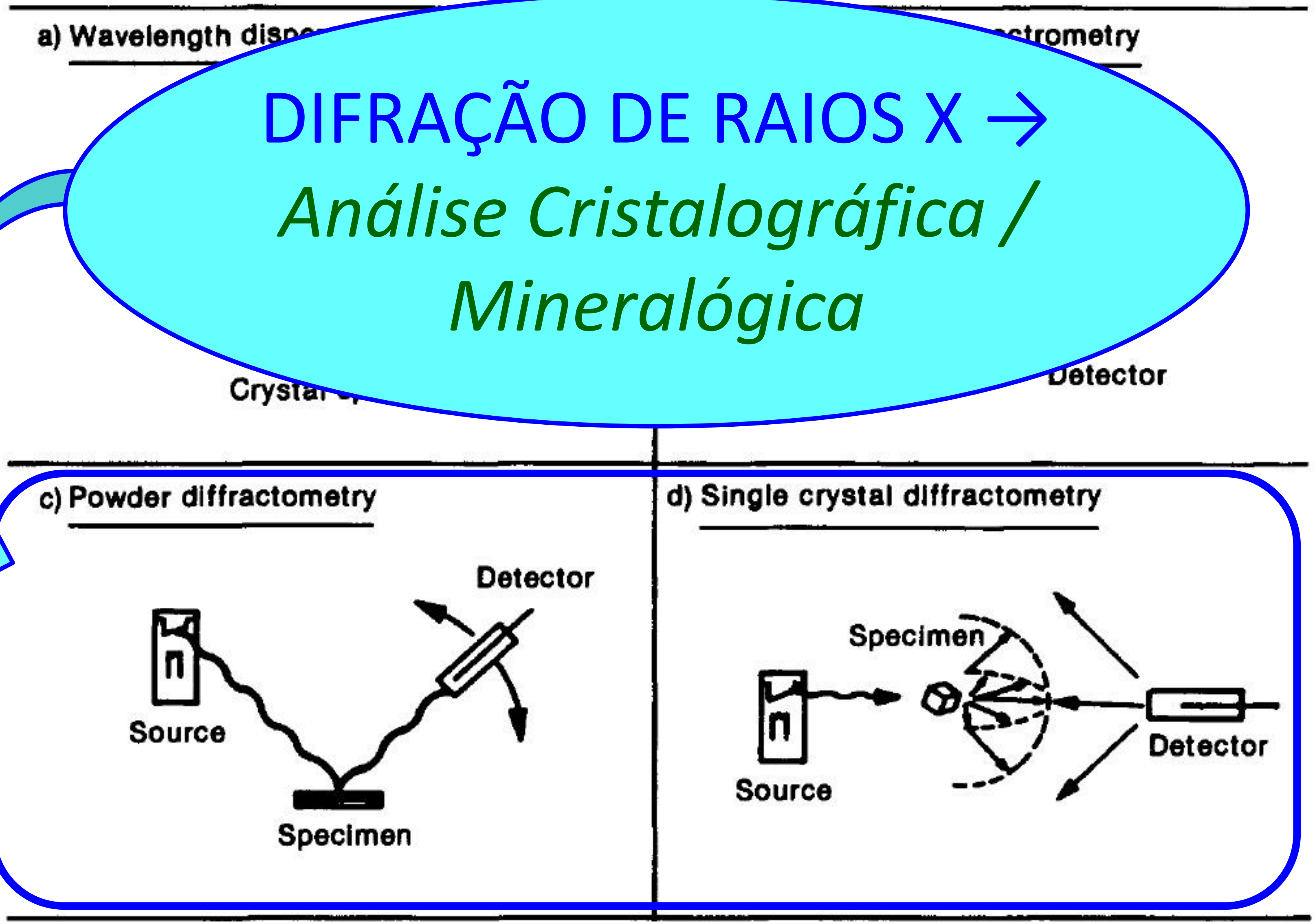
- A análise dos comprimentos de onda dos raios X emitidos permite identificar o(s) elemento(s) presente(s) na amostra → permite identificar a ***composição química*** da amostra.



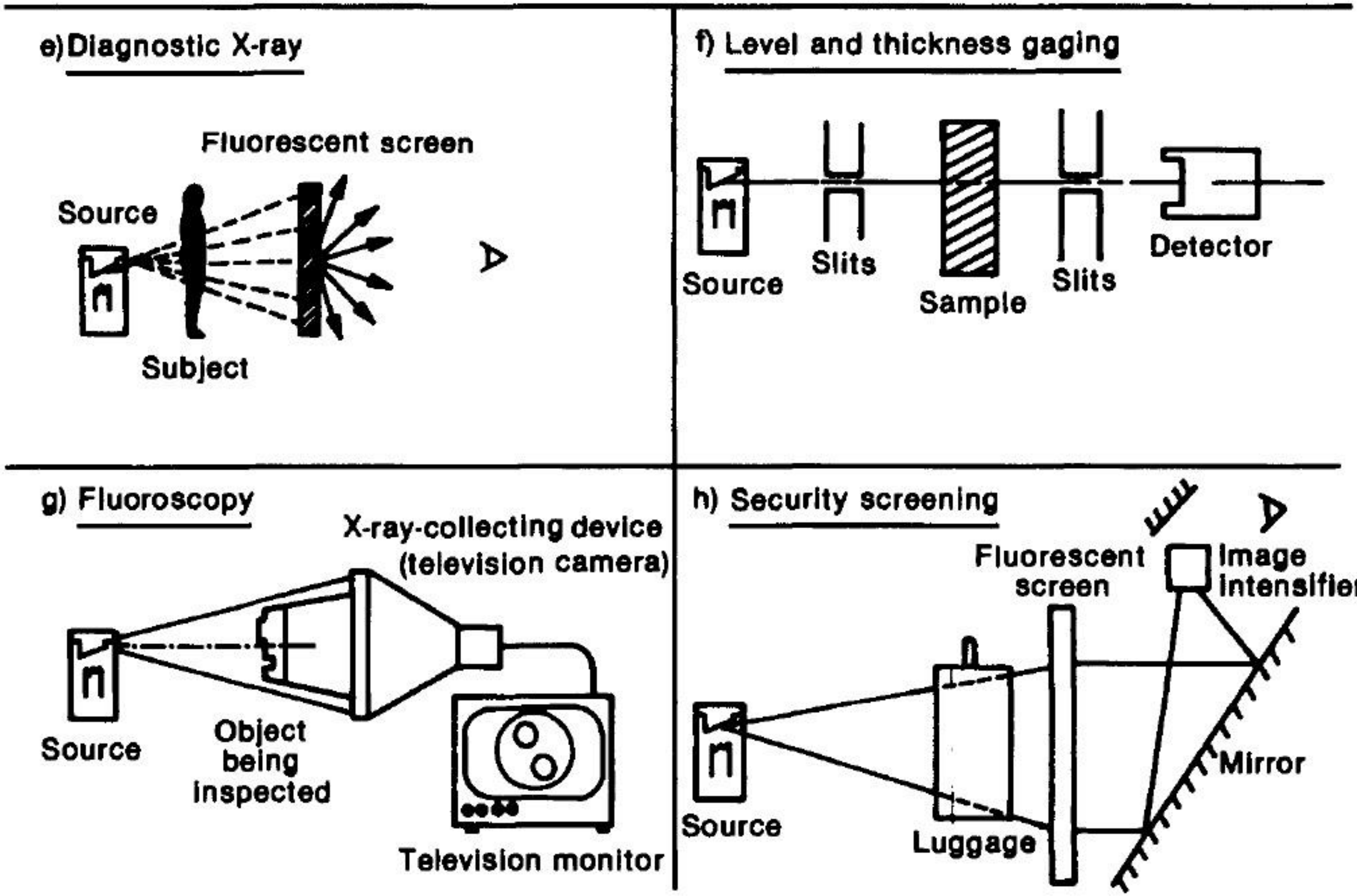
Aplicações que empregam fontes de raios X

DIFRAÇÃO DE RAIOS X →

Análise Cristalográfica / Mineralógica



Aplicações que empregam fontes de raios X



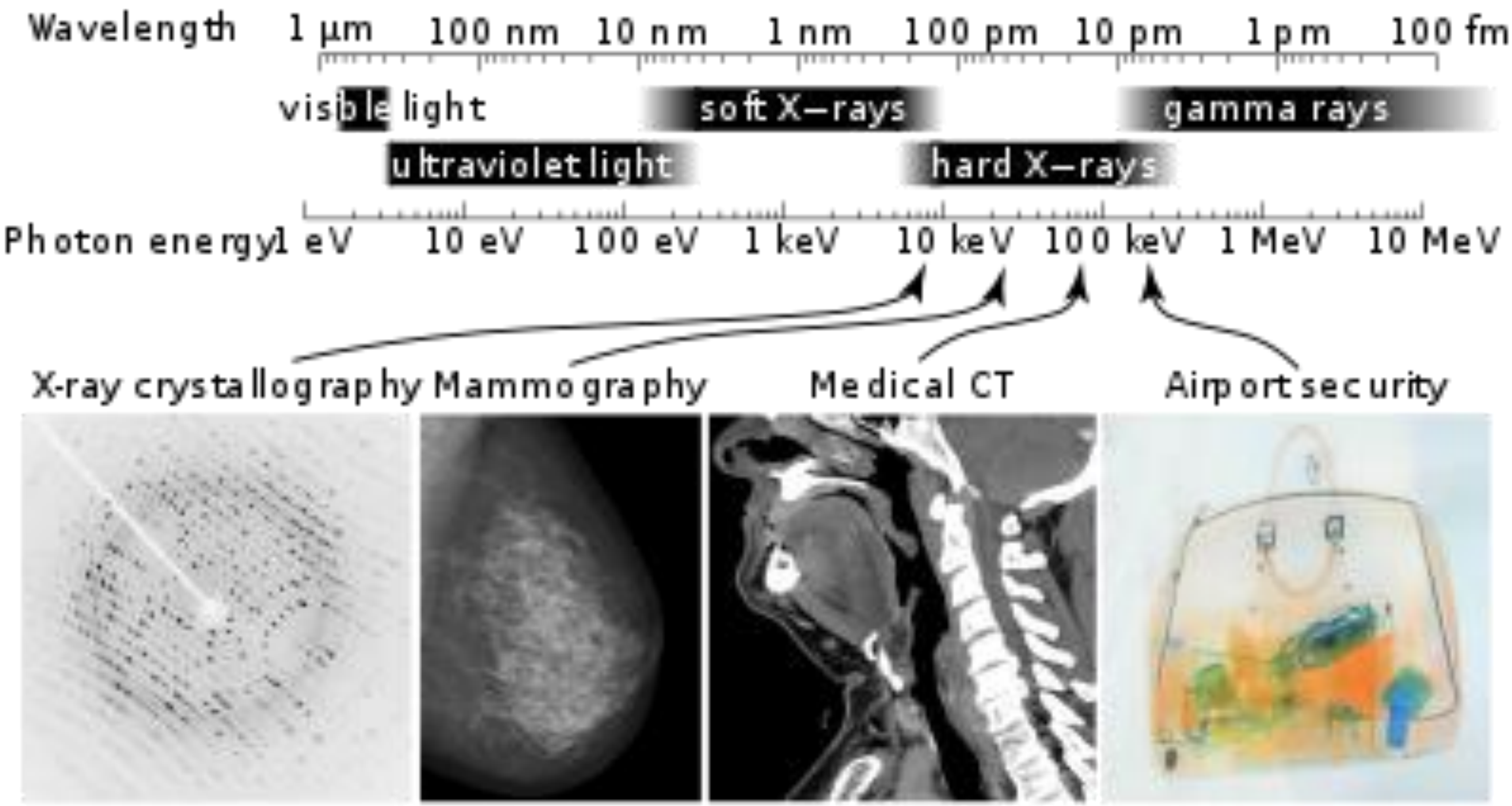
Uses of X-ray methods in industry and research.

Fluoroscopy

Scanners em Aeroportos

- X-rays launched from one side of the machine are picked up by a pair of detectors on the opposite side. As your bag enters through the lead-lined curtains, it crosses the path of these X-rays and absorbs some of the energy they carry. This means that the X-rays that passed through your stuff have less energy than those that sailed straight past.
- When the X-rays hit the first plate-like detector, their energy and position is recorded. They continue towards the second detector, but a filter between the two blocks low-energy X-rays: the second detector collects only high-energy X-rays. By comparing the two detectors' outputs, the machine can construct an image showing not just the position of objects, but also roughly what they're made of and their density.
- Organic materials like paper, food and explosives are orange, while blue or green are used for metals and glass. The denser the material, the darker the colour.

Escalas de Energia



Síncroton

- A synchrotron facility contains a large ring (on the order of hundreds of meters or even kilometers), where electrons move at a very high speed in straight channels that occasionally break to match the curvature of the ring.
- These electrons are made to change direction to go from one channel to another using magnetic fields of high energy.
- It is at this moment, when electrons change their direction, that the electrons emit a very high energy radiation known as ***synchrotron radiation***.
- This radiation is composed of a continuum of wavelengths ranging from ***infrared*** to the so-called ***hard X-rays***.

HOW DOES THE ESRF WORK?

Synchrotron light is produced when high-energy electrons circulating in a storage ring are deflected by magnetic fields. The first synchrotron radiation beam was observed in 1947. Since then, spectacular progress has been made not only in accelerator physics, electronics, and computing, but also in magnet and vacuum technologies. As a result, it is now possible to produce extremely intense X-ray beams for which there is a huge and growing demand.

The linear accelerator (or "linac")

Electrons emitted by an electron gun are packed into "bunches" at the start of the linac and then gradually accelerated using electromagnetic waves until they are travelling very close to the speed of light.

The booster synchrotron

The electrons then enter the booster synchrotron, a ring with a circumference of 300 metres. The electrons travel round this ring several thousand times, gaining a little more energy with every lap. Once they reach their final energy of 6 billion electron-volts, a process which takes barely 50 milliseconds, they are sent into the storage ring.

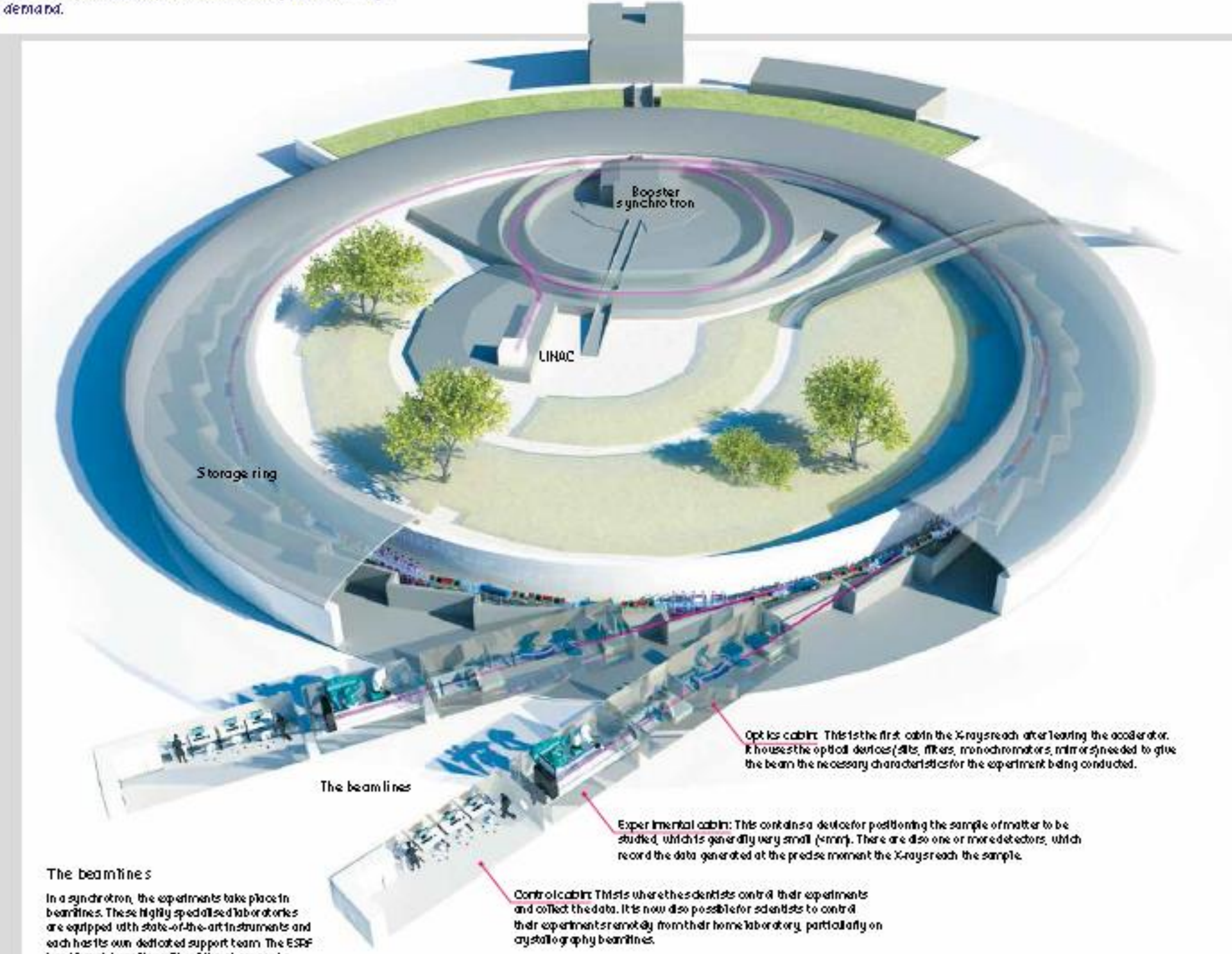
The storage ring

The storage ring has a circumference of 844 metres. The electrons travel for hours around the storage ring at the speed of light inside a tube under ultra-high vacuum conditions (around 10^{-9} mbar). As they travel round, they pass through different types of magnets, such as bending magnets, undulators and focusing magnets. Each time they pass through certain magnets, the electrons lose energy in the form of electromagnetic radiation, known as "synchrotron radiation".

The bending magnets are essential because they force the electrons to change direction. They are also a source of synchrotron light, which is emitted tangentially to the curved path of the electron beam and is directed towards the beamlines.

The undulators are magnetic structures made up of a series of small magnets with alternating polarity. The beams of X-rays they produce are a million times more intense than those generated by the bending magnets and have brightness and coherence properties that are close to lasers.

The focusing magnets, also known as magnetic lenses, are used to focus the electron beam so that the beam is as narrow as possible.



Optics cabin: This is the first cabin the X-rays reach after leaving the accelerator. It houses the optical devices (slits, filters, monochromators, mirrors) needed to give the beam the necessary characteristics for the experiment being conducted.

Experimental cabin: This contains a device for positioning the sample of matter to be studied, which is generally very small (<mm). There are also one or more detectors, which record the data generated at the precise moment the X-rays reach the sample.

Control cabin: This is where the scientists control their experiments and collect the data. It is now also possible for scientists to control their experiments remotely from their home laboratory, particularly on crystallography beamlines.

The beamlines

In a synchrotron, the experiments take place in beamlines. These highly specialised laboratories are equipped with state-of-the-art instruments and each has its own dedicated support team. The ESRF has 43 such beamlines. The different areas of a beamline are described hereafter:

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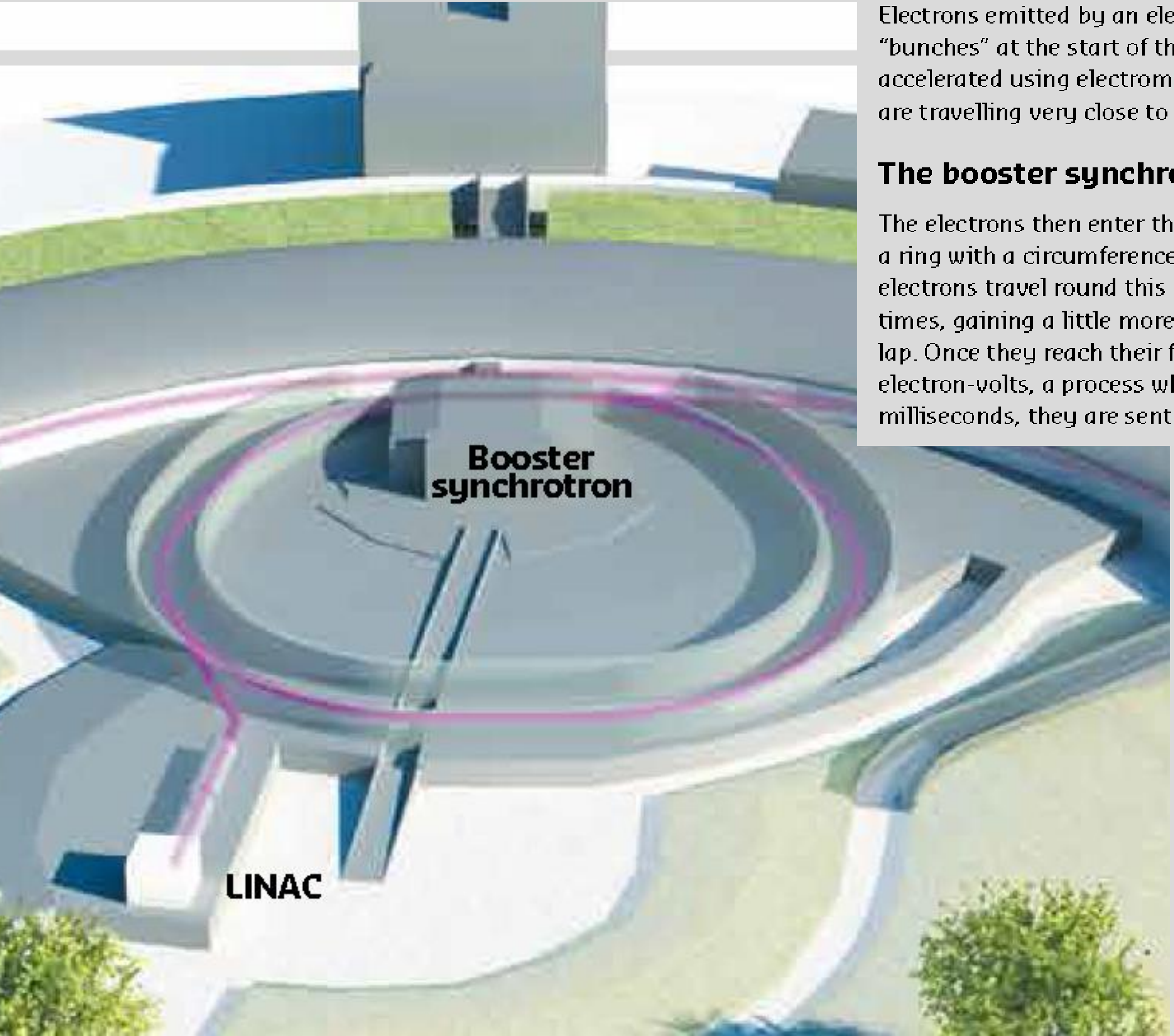

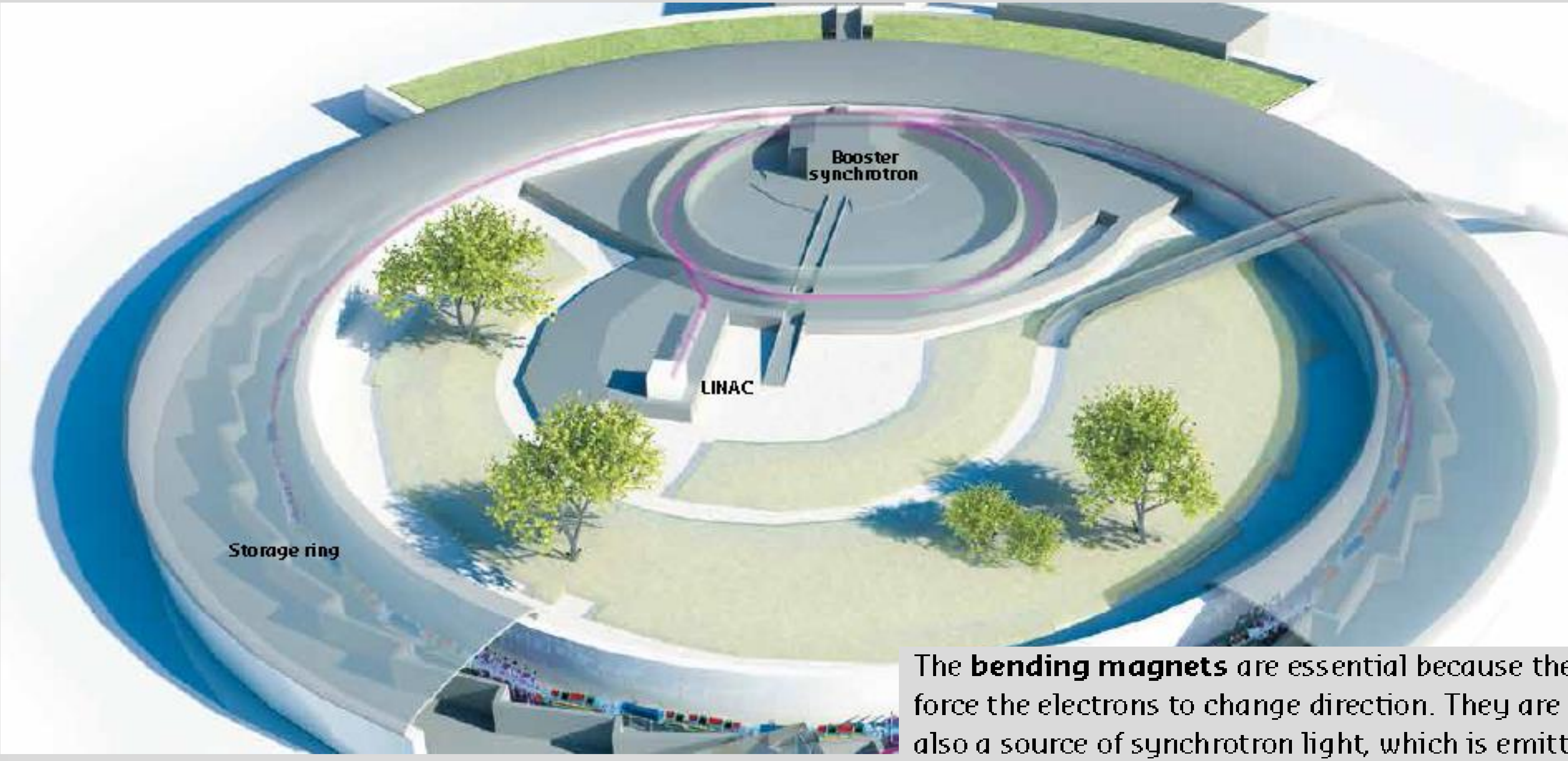

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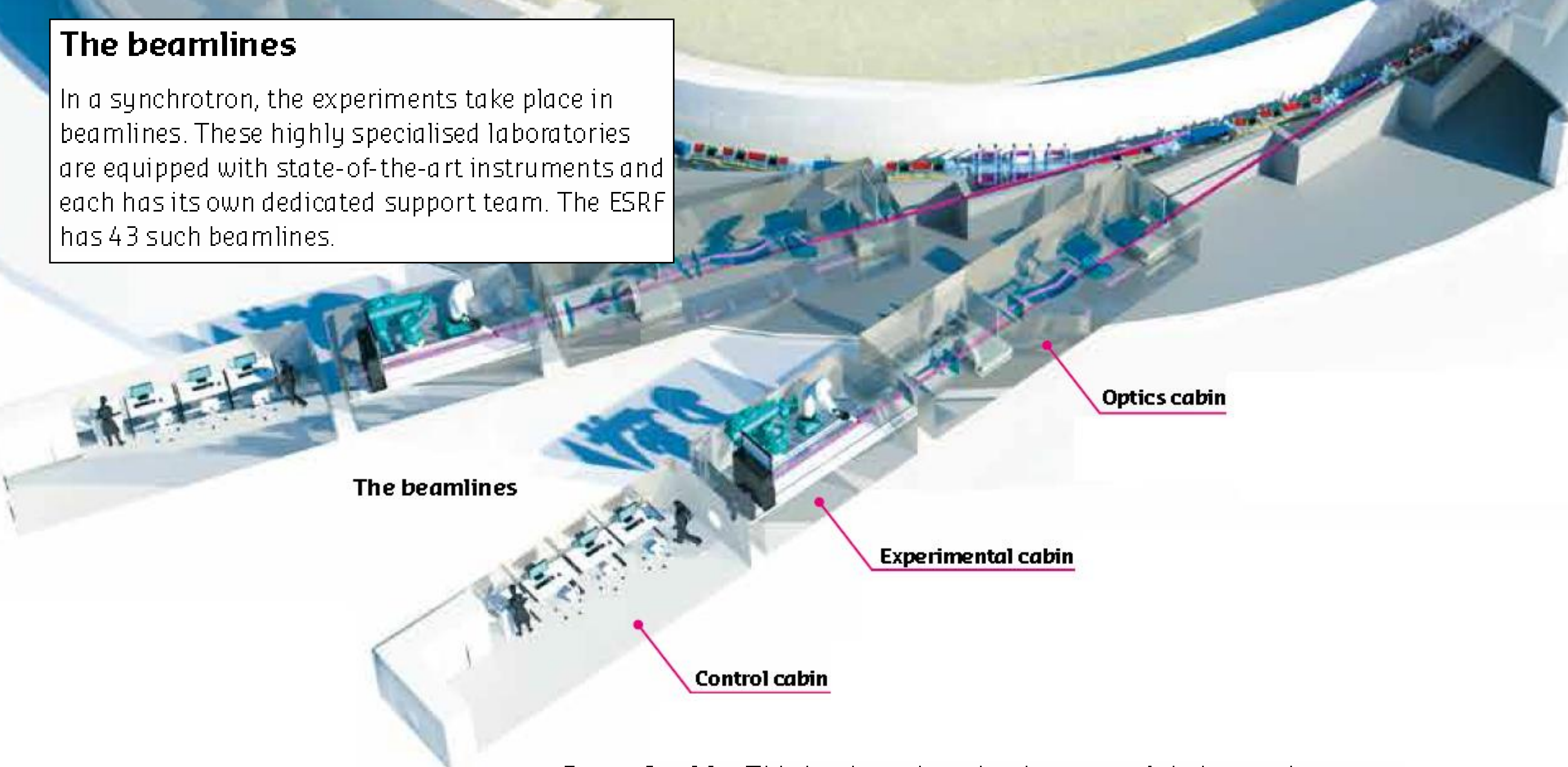

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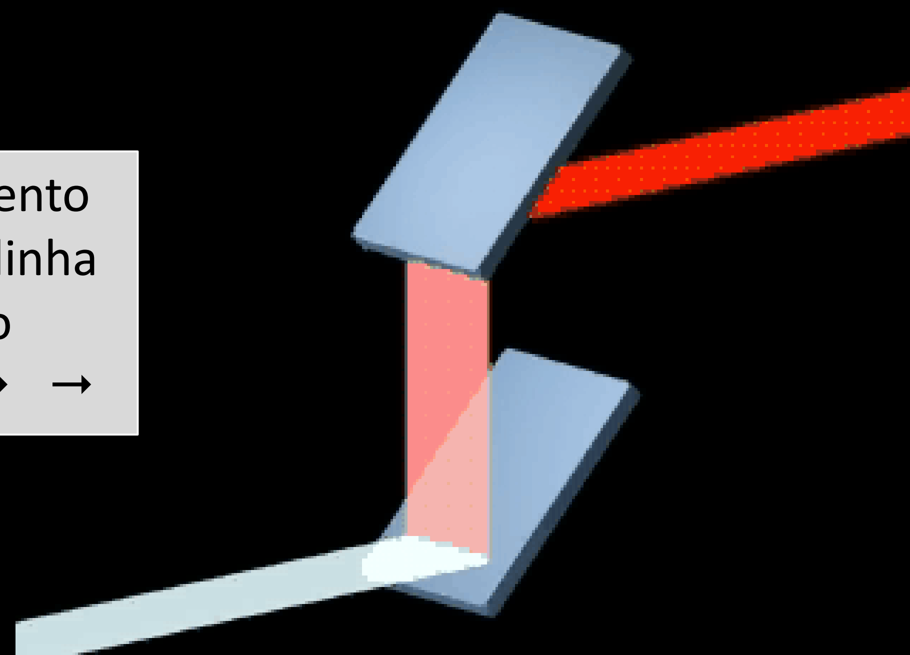
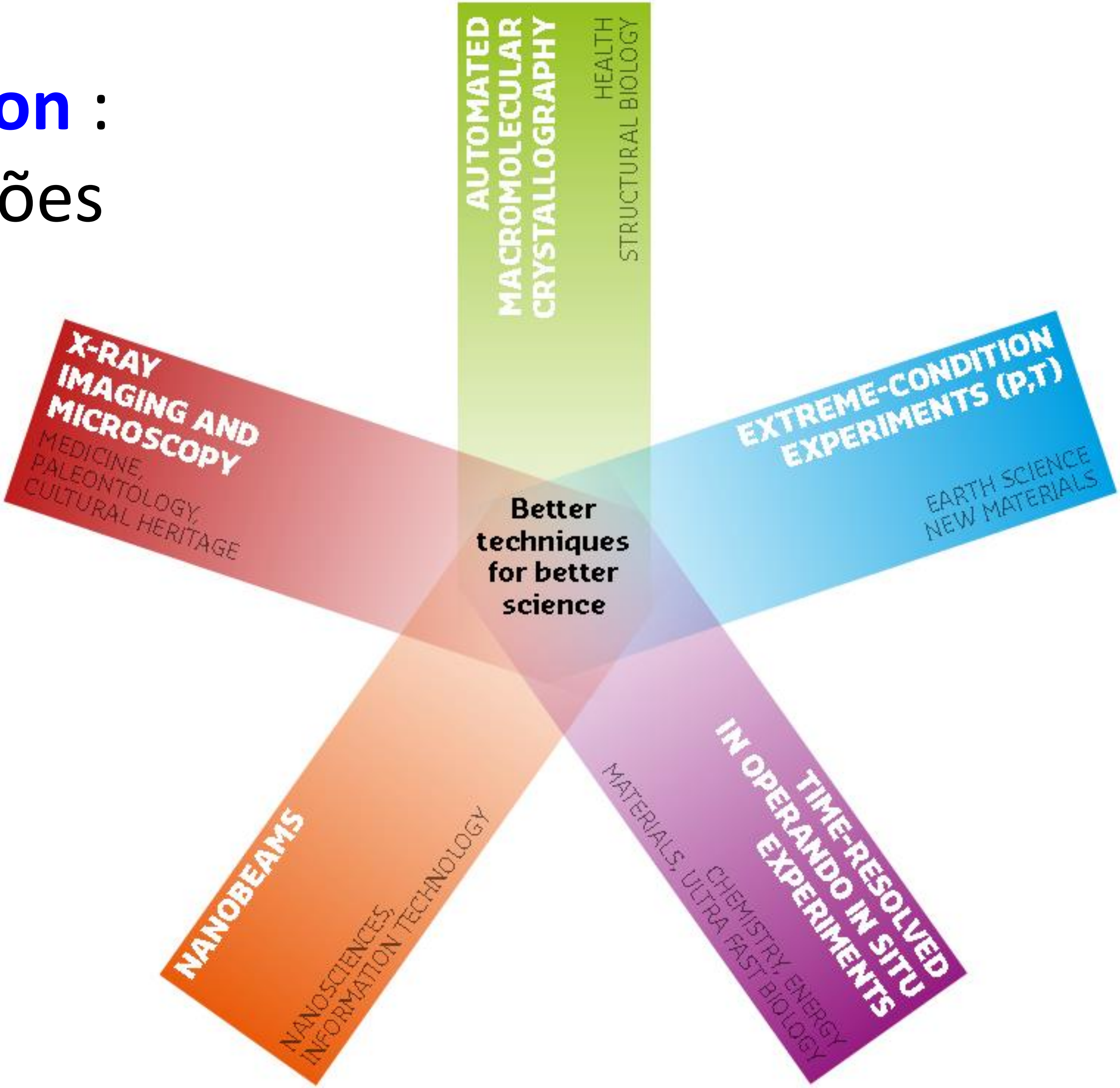
Linhas de Luz

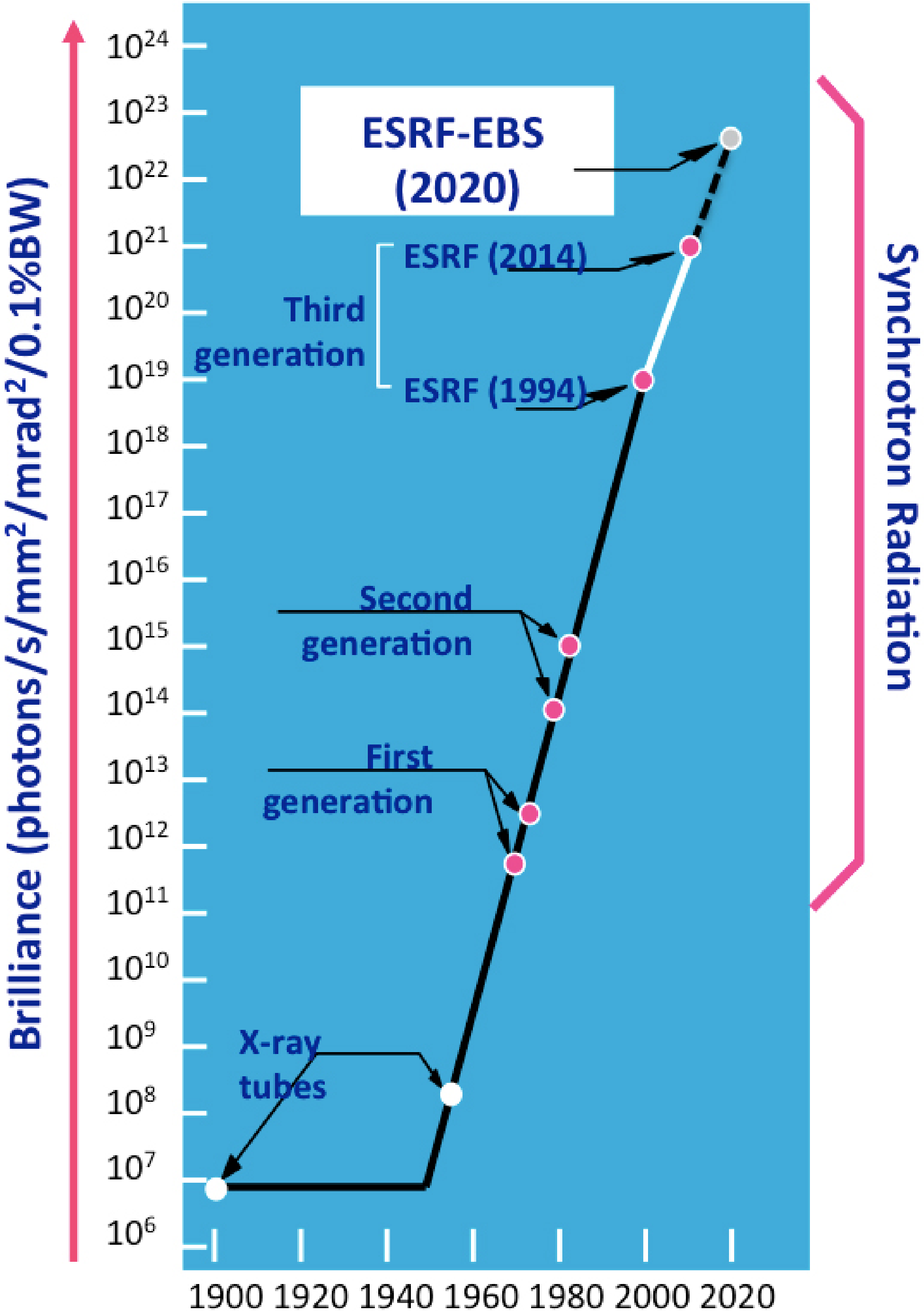
Estações experimentais para onde o feixe de luz síncrotron é conduzido e direcionado até as amostras, de forma a revelar informações sobre o material analisado. As fontes de síncrotron normalmente comportam diversas linhas de luz, e nelas são realizados experimentos usando diferentes técnicas, como espectroscopia do infravermelho ao raio X, espalhamento de raios X, cristalografia, tomografia e outras

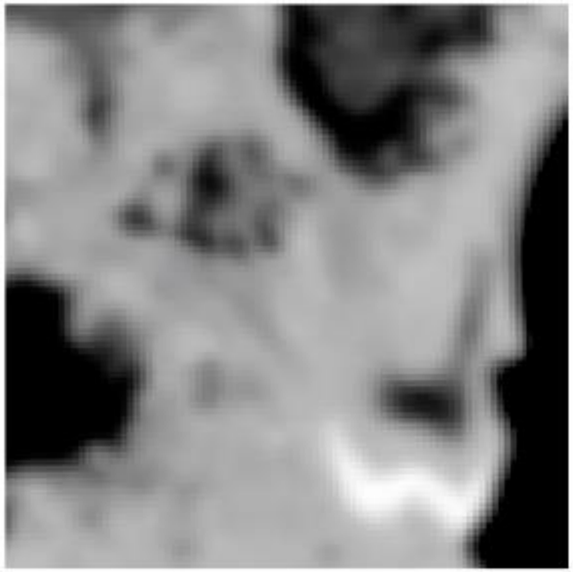
Para selecionar qual o comprimento de onda será utilizado em cada linha de luz, é utilizado um dispositivo chamado *monocromador* → → →



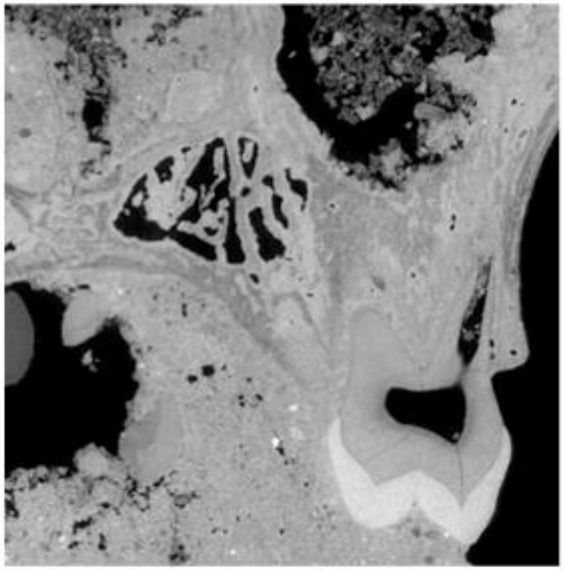
Síncroton : Aplicações





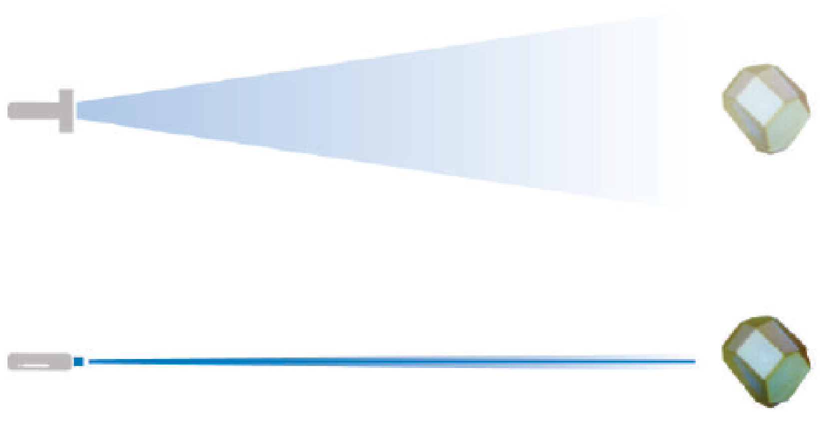


Scan at the hospital



At the ESRF

Brilho e emitância



A emitância de uma fonte de luz sícrotron é o produto do tamanho e da divergência angular do feixe de elétrons. Quanto menor for a emitância, maior é o brilho da fonte

A qualidade de uma fonte de luz é caracterizada pelo seu brilho, que pode ser definido como o número de fótons emitidos pela fonte em uma determinada faixa espectral de energia, por unidade de tempo, por unidade de tamanho e divergência angular da fonte. Quanto maior o brilho, melhor será a qualidade da fonte de luz. O feixe de elétrons de uma fonte de alto brilho emite muitos fótons por segundo em uma faixa estreita de energia, possui dimensões pequenas e é bastante colimado.

Se compararmos, por exemplo, a emissão de uma lanterna com a de uma ponteira a laser, com a mesma taxa de fótons, vemos que para examinar um objeto ou parte de um objeto pequeno será muito mais eficiente a iluminação a partir da ponteira a laser, cujo brilho é muito maior (ver figura acima).

Um ingrediente-chave para aumentar o brilho de uma fonte de luz síncrotron é, portanto, a emitância do feixe de elétrons, que é a medida do tamanho e da divergência deste feixe. Quanto menor a emitância, maior será o brilho da fonte de luz. A emitância natural de equilíbrio é determinada pelo balanço entre o amortecimento radiativo e a excitação quântica das oscilações das partículas, ambas causadas pela emissão de fótons. A emitância, que é uma constante característica da máquina e depende apenas da configuração da rede magnética do anel de armazenamento, é um dos principais parâmetros de uma fonte de luz síncrotron.

A redução da emitância é uma das formas mais efetivas para aumentar o brilho das fontes de luz, por isso a busca constante por fontes de emitância cada vez menores. Esse é um dos objetivos no projeto e construção de novos síncrotrons. O Sirius está sendo projetado para ter uma das menores emitâncias do mundo atualmente.

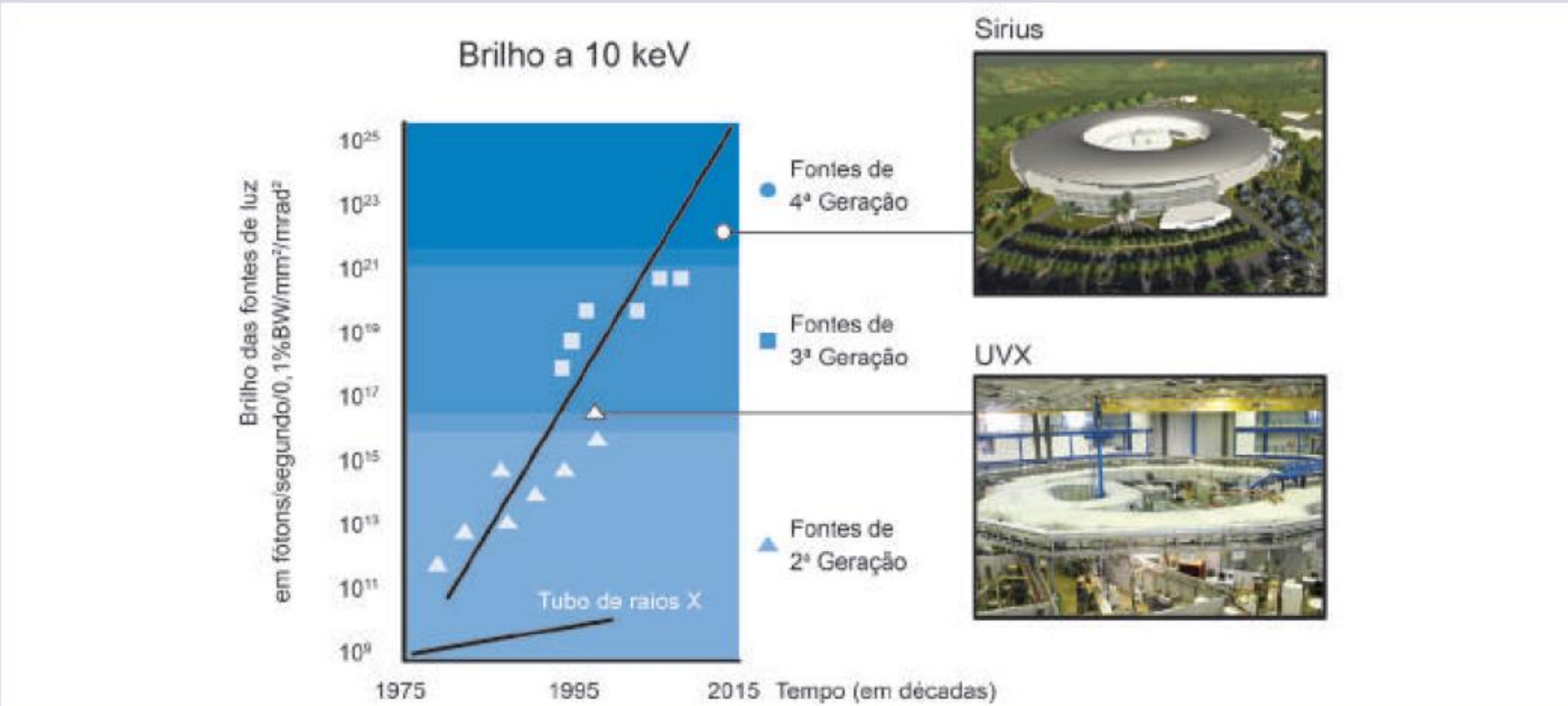
Fonte: http://www.lnls.cnpem.br/wp-content/uploads/2016/08/Livro-do-Projeto-Sirius-2014.pdf

SIRIUS

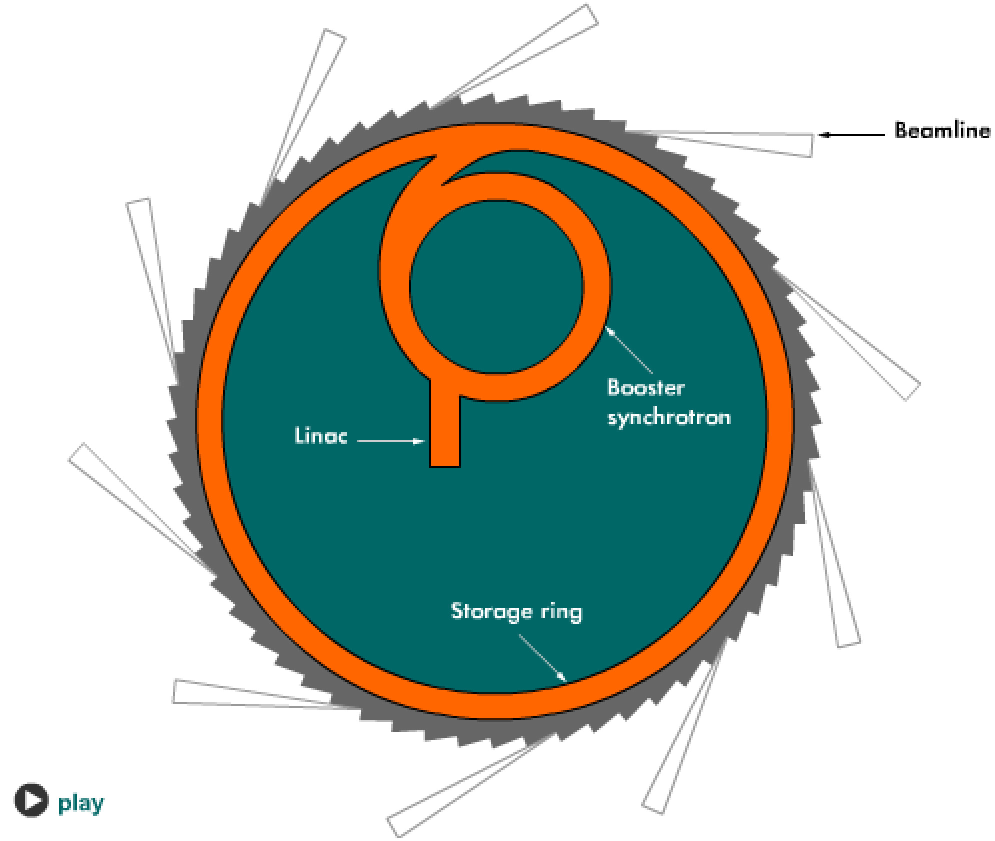
LNLS Laboratório Nacional de Luz Síncrotron

sirius

SIRIUS



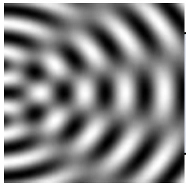
Evolução do brilho das fontes de raios X ao longo da história e comparação entre o brilho do UVX, fonte considerada de 2ª geração, e o do Sirius, que está na fronteira do conhecimento e já é considerado uma fonte de 4ª geração http://www.esrf.eu/about/synchrotron-science/synchrotron-light-animation



Electrons emitted by an electron gun are first accelerated in a linear accelerator (linac) and then transmitted to a circular accelerator (booster synchrotron) where they are accelerated to reach an energy level of 6 billion electron volts (6 GeV).

These high-energy electrons are then injected into a large storage ring where they circulate in a vacuum environment, at a constant energy, for many hours. Each time these electrons pass through an undulator, a device consisting of series of alternating magnets, they emit X-rays, which are directed along beamlines.

Difração de Raios X



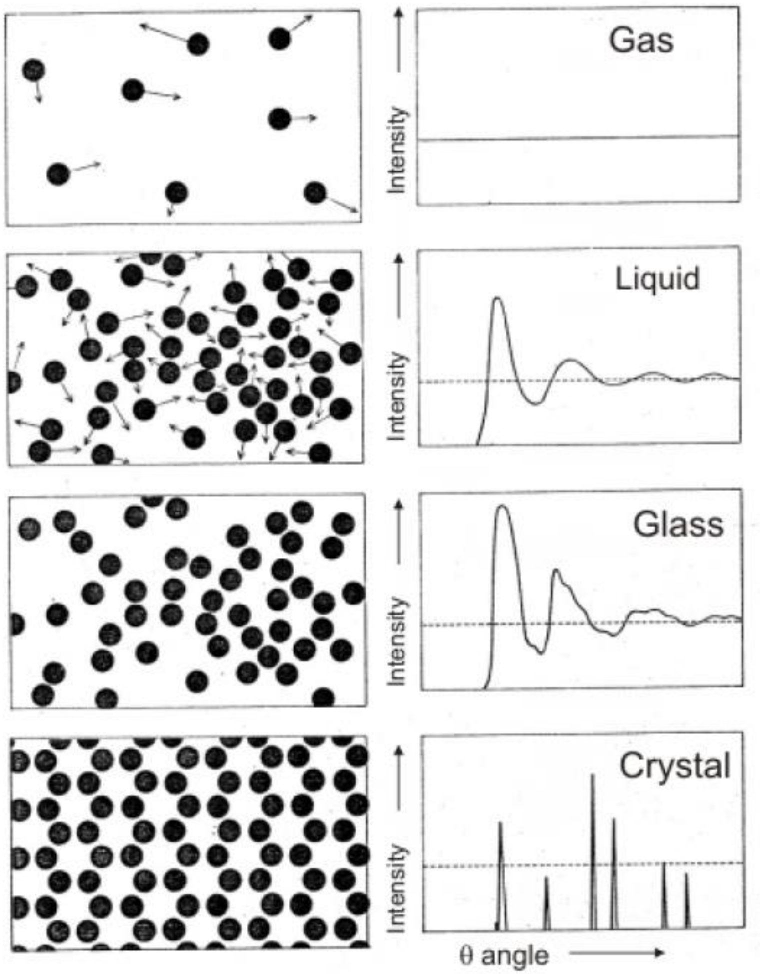
DRX : Cristais !

Diffraction occurs when light is scattered by a periodic array with long-range order, producing constructive interference at specific angles.

- The electrons in an atom coherently scatter light.
  - We can regard each atom as a coherent point scatterer
  - The strength with which an atom scatters light is proportional to the number of electrons around the atom.

- The atoms in a crystal are arranged in a periodic array and thus can diffract light.
- The wavelength of X rays are similar to the distance between atoms.
- **The scattering of X-rays from atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal**

- Amorphous materials like glass do not have a periodic array with long-range order, so they do not produce a diffraction pattern



Scattering diagrams of a monoatomic material in different states.

In the intensity axis we have neglected the background contribution.

The figures mainly represent the effect of the **external interference**, while the **internal interference** (in this case due to a single atom only) is simply reflected by the relative intensity of the maxima.

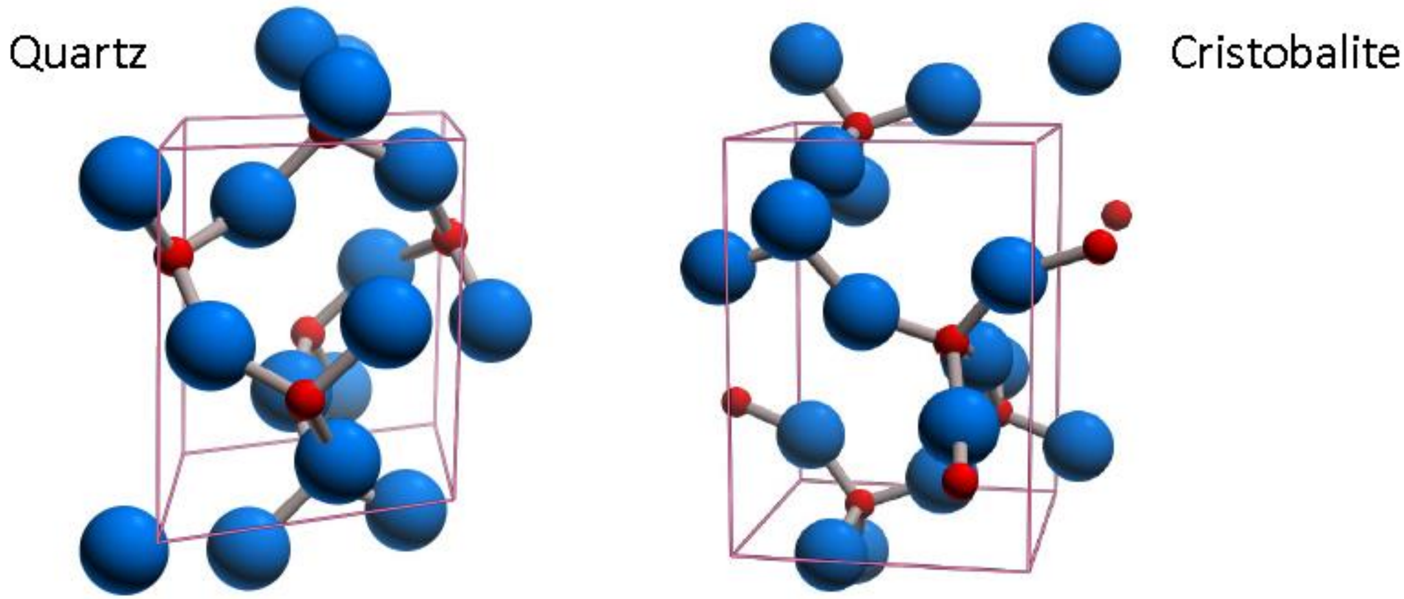
Note how the thermal movement in the liquid softens and reduces the scattering profile, and how the maxima produced by the glass also decrease.

In the crystal, where the phase relations are fixed and repetitive, the scattering profile becomes sharp with well defined peaks, whereas in the other diagrams the peaks are broad and somewhat continuous. In the crystal case the scattering effect is known as **diffraction**.

Note how the scattering phenomenon reflects the **internal order** of the sample -- the positional correlations between atoms.

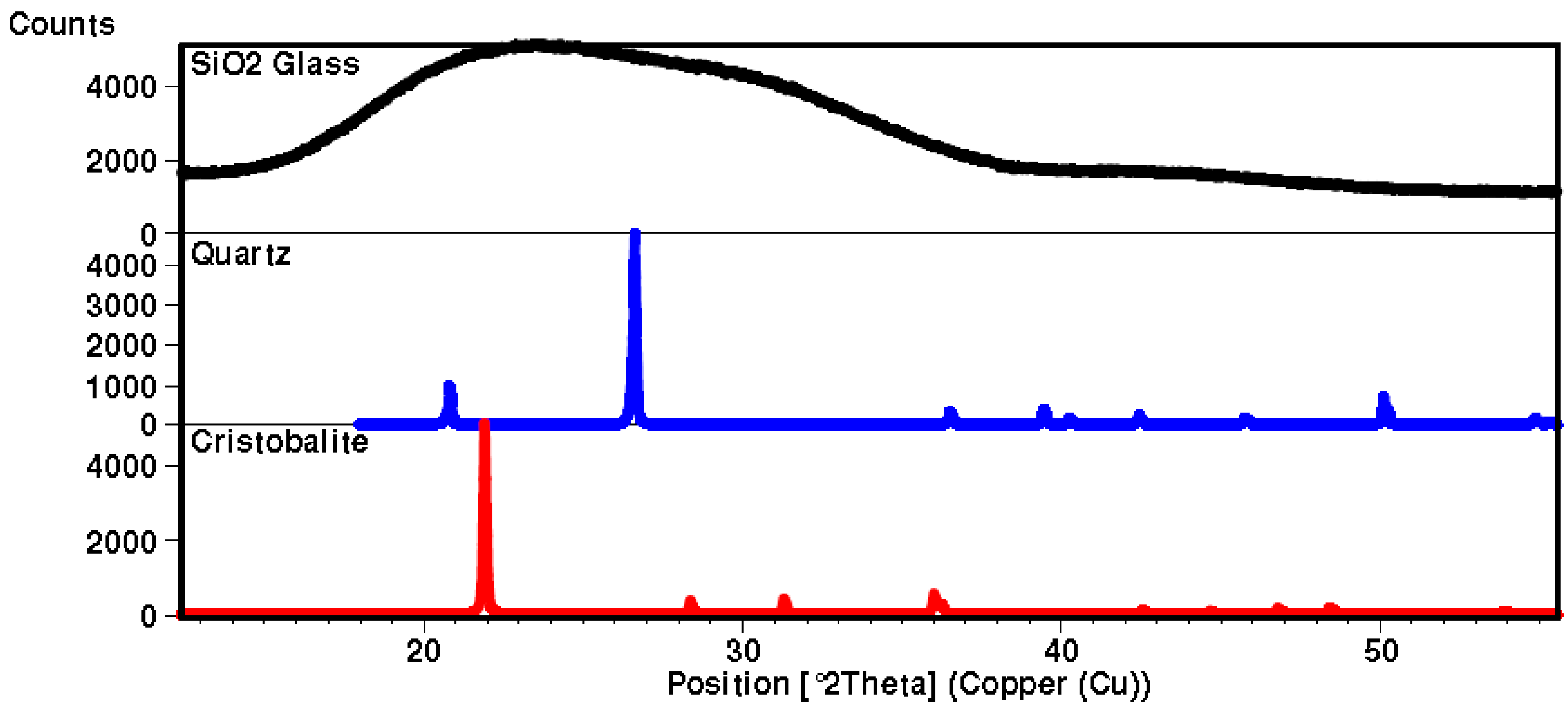
Fonte: http://www.xtal.iqfr.csic.es/Cristalografia/parte_05-en.html

The diffraction pattern is a product of the unique crystal structure of a material



- The crystal structure describes the atomic arrangement of a material.
- When the atoms are arranged differently, a different diffraction pattern is produced (ie quartz vs cristobalite)

The figure below compares the X-ray diffraction patterns from 3 different forms of SiO_2



- These three phases of SiO_2 are chemically identical
- Quartz and cristobalite have two different crystal structures
  - The Si and O atoms are arranged differently, but both have structures with long-range atomic order
  - The difference in their crystal structure is reflected in their different diffraction patterns
- The amorphous glass does not have long-range atomic order and therefore produces only broad scattering peaks

O que se pode fazer com DRX

You can use XRD to determine

- Phase Composition of a Sample
  - Quantitative Phase Analysis: determine the relative amounts of phases in a mixture by referencing the relative peak intensities
- Unit cell lattice parameters and Bravais lattice symmetry
  - Index peak positions
  - Lattice parameters can vary as a function of, and therefore give you information about, alloying, doping, solid solutions, strains, etc.
- Residual Strain (macrostrain)
- Crystal Structure
  - By Rietveld refinement of the entire diffraction pattern **(composição)**
- Epitaxy/Texture/Orientation
- Crystallite Size and Microstrain
  - Indicated by peak broadening
  - Other defects (stacking faults, etc.) can be measured by analysis of peak shapes and peak width
- *We have in-situ capabilities, too (evaluate all properties above as a function of time, temperature, and gas environment)*

Referências

Para as bases da DRX, em livros básicos de Ciência dos Materiais

- Callister, W,D.; Rethwisch, M.S. Materials Scince and Engineering. 8th Ed. Wiley. 2009. Cap.3.
- Shackelford, J. Ciência dos Materiais. 6ª Ed. Pearson/Prentice Hall. 2008. Cap.3.

Livro-texto sobre DRX

- *Cullity, B.D.; Stock, S.R. Elements of X-Ray Diffraction. 3ª Ed. Prentice Hall. New Jersey. USA. 2001.*

Site excelente sobre cristalografia

- http://www.xtal.iqfr.csic.es/Cristalografia/welcome-en.html

Algo mais avançado sobre DRX (com caráter operacional) em sites da web

- Uma apresentação excelente: http://prism.mit.edu/xray/Basics of X-Ray Powder Diffraction.pdf

Site do LNLS – Projeto SIRIUS

- https://www.lnls.cnpem.br/sirius/
- http://www.lnls.cnpem.br/wp-content/uploads/2016/08/Livro-do-Projeto-Sirius-2014.pdf

Site do ESRF – The European Syncroton

- http://www.esrf.eu/home.html
- http://www.esrf.eu/files/live/sites/www/files/Industry/documentation/ESRF-Indus-2018.pdf