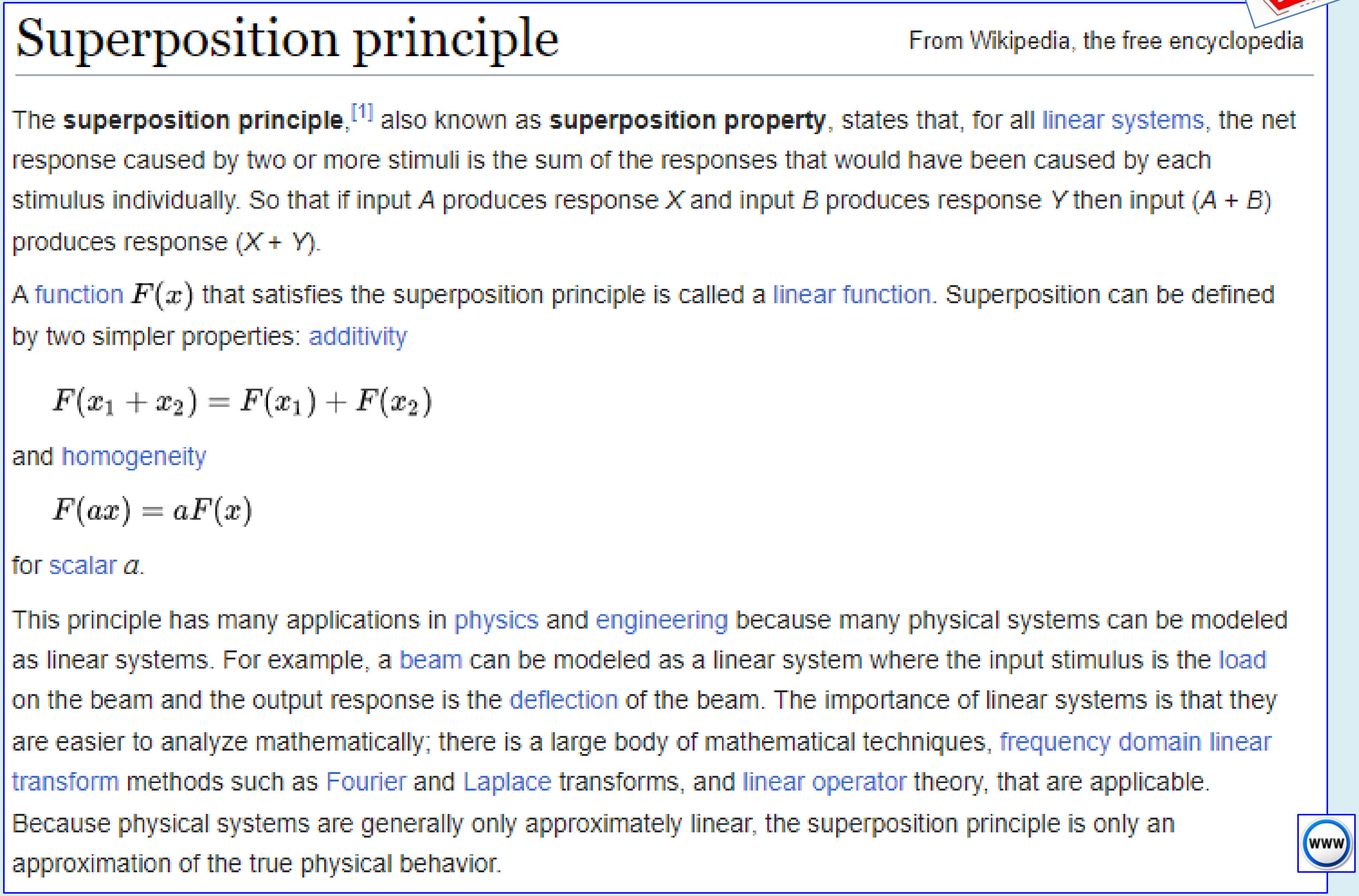
Unidade 5
Difração: Fundamentos

PMT3301
Fundamentos de Cristalografia e Difração
1º semestre de 2023

Introdução

Interferência de Ondas



Superposition principle

From Wikipedia, the free encyclopedia

The **superposition principle**,[1] also known as **superposition property**, states that, for all linear systems, the net response caused by two or more stimuli is the sum of the responses that would have been caused by each stimulus individually. So that if input *A* produces response *X* and input *B* produces response *Y* then input (*A* + *B*) produces response (*X* + *Y*).

A function $F(x)$ that satisfies the superposition principle is called a linear function. Superposition can be defined by two simpler properties: additivity

$$F(x_1 + x_2) = F(x_1) + F(x_2)$$

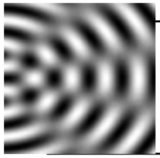
and homogeneity

$$F(ax) = aF(x)$$

for scalar a.

This principle has many applications in physics and engineering because many physical systems can be modeled as linear systems. For example, a beam can be modeled as a linear system where the input stimulus is the load on the beam and the output response is the deflection of the beam. The importance of linear systems is that they are easier to analyze mathematically; there is a large body of mathematical techniques, frequency domain linear transform methods such as Fourier and Laplace transforms, and linear operator theory, that are applicable. Because physical systems are generally only approximately linear, the superposition principle is only an approximation of the true physical behavior.

Fonte: https://en.wikipedia.org/wiki/Superposition_principle

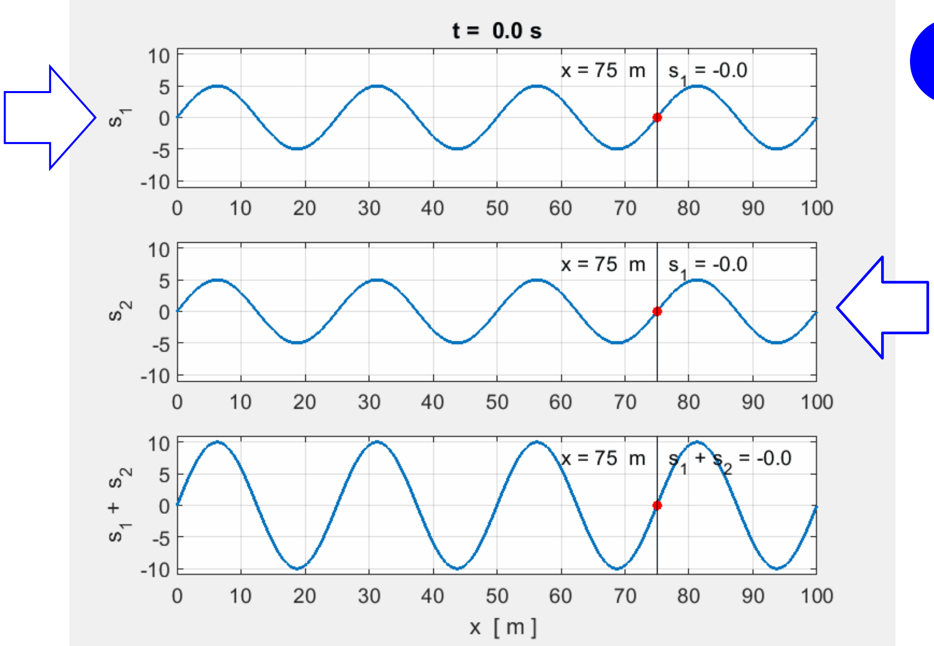


Interferência de Ondas

- O princípio da superposição pode ser usado para descrever o comportamento de ***interferência*** e de ***difração*** de ondas *(tais como as radiações eletromagnéticas → ondas de rádio, luz, raios-X...)*.
- Na visão clássica do universo, as partículas não obedecem ao princípio da superposição, portanto, as partículas não interferem umas nas outras e, portanto, não sofrem difração.
- *...mas nosso universo é muito mais interessante no nível atômico.* Usando os conceitos da mecânica quântica, as ondas têm propriedades semelhantes a partículas e as partículas têm propriedades semelhantes a ondas. Isso é conhecido como Princípio da Dualidade Onda-Partícula.
- *Experimentos mostram que partículas como elétrons podem ser associados um comprimento de onda e podem produzir padrões de difração. E outros experimentos mostram que ondas, como as ondas de luz visível, podem ser associadas a partículas (os fótons...).*

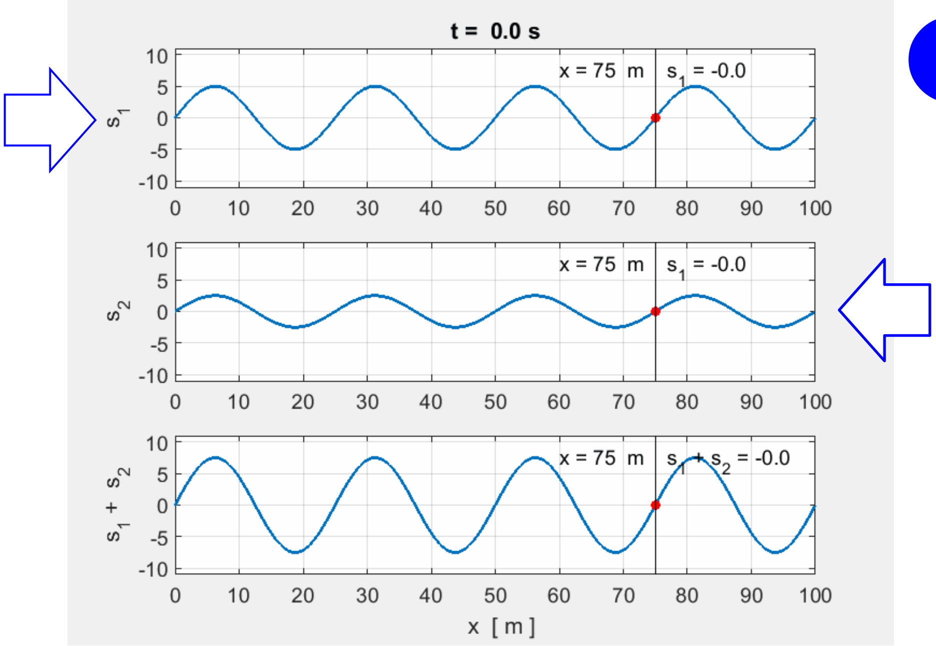
Interferência em ondas na água

①



...quais são as diferenças entre esses exemplos de interferências de ondas?

②



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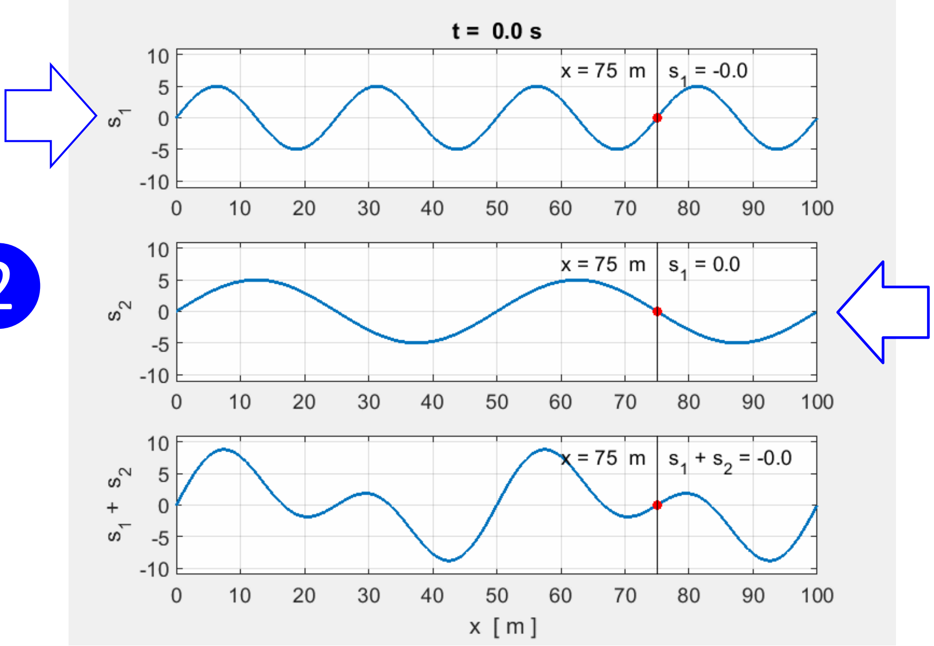

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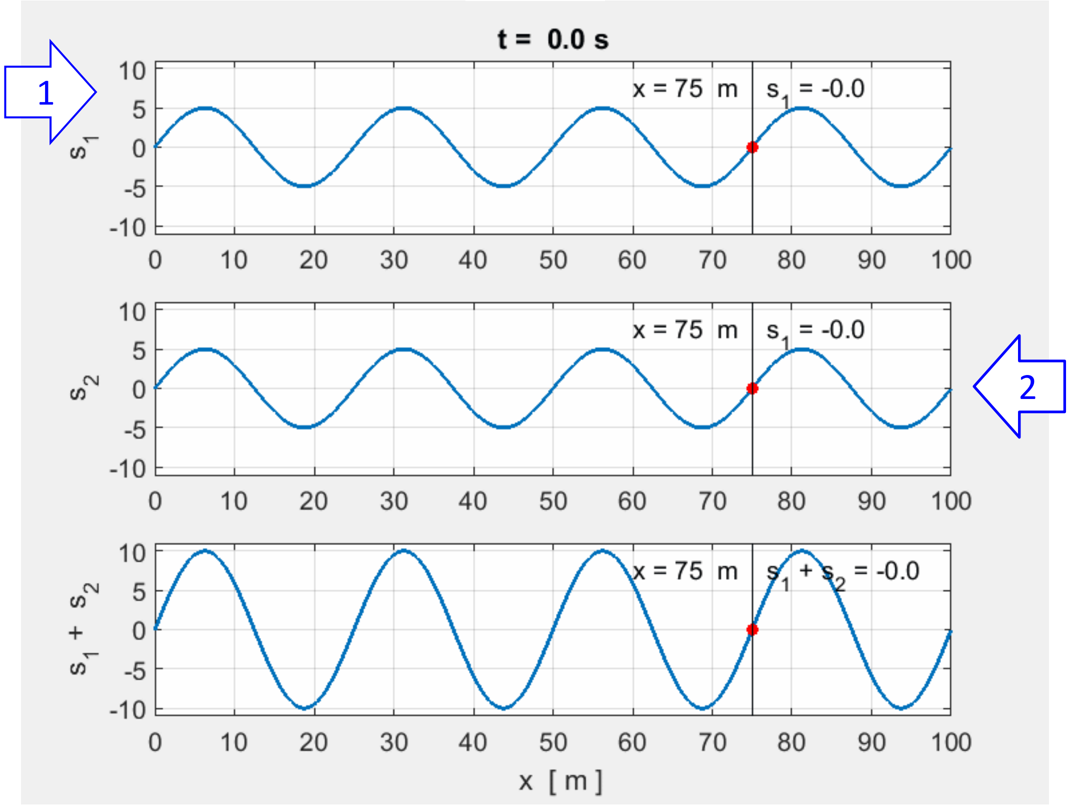


Onda #1 (→)

Amplitude = 5,0 u.a. , λ_1 = 25 m , f_1 = 0,080 Hz , $v_1 = 2{,}0\ m.s^{-1}$

Onda #2 (←)

Amplitude = 5,0 u.a. , λ_2 = 25 m , f_2 = 0,080 Hz , $v_2 = -\ 2{,}0\ m.s^{-1}$

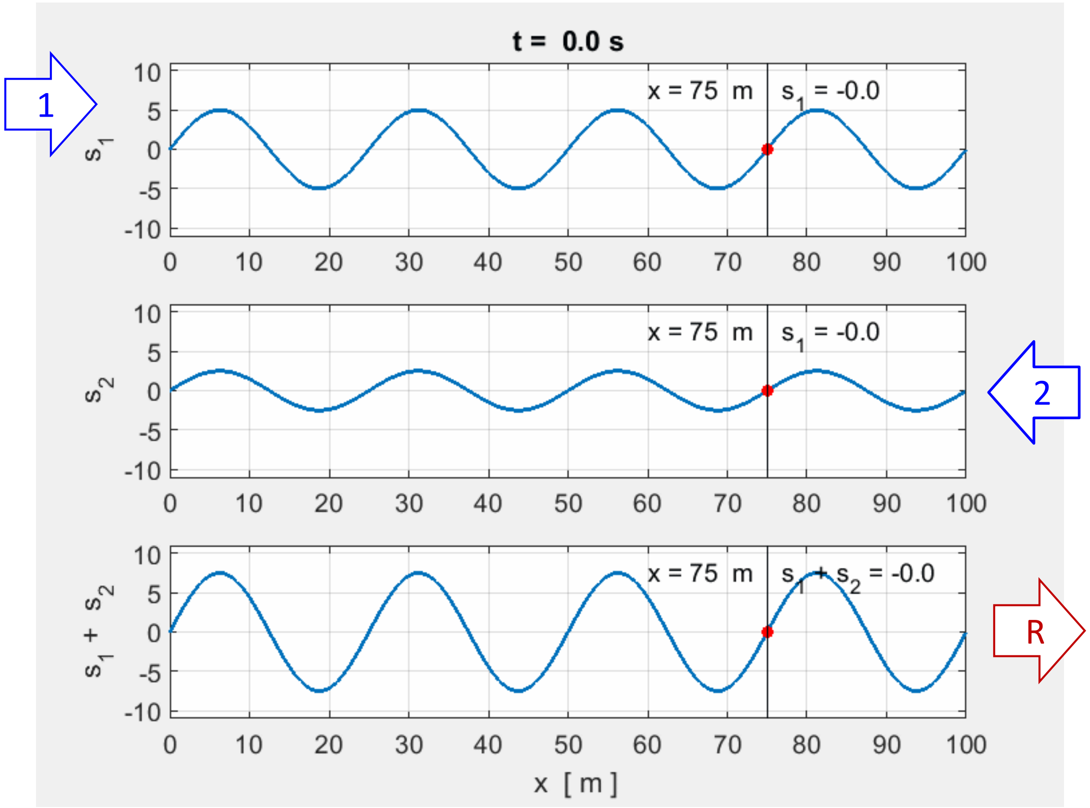
RESULTANTE

Amplitude = 10,0 u.a. , λ_1 = 25 m , f_1 = 0,080 Hz , $v_1 = 0\ m.s^{-1}$

- *A onda resultante é ESTACIONÁRIA !!*
- *Ocorre interferência totalmente destrutiva, e a interferência construtiva é máxima...*

Fonte:www.physics.usyd.edu.au/teach_res/hsp/sp/mod31/m31_superposition_files/image009.gif

②



Onda #1 (→)

Amplitude = 5,0 u.a. , λ_1 = 25 m , f_1 = 0,080 Hz , $v_1 = 2{,}0\ m.s^{-1}$

Onda #2 (←)

Amplitude = 2,5 u.a. , λ_1 = 25 m , f_1 = 0,080 Hz , $v_1 = -\ 2{,}0\ m.s^{-1}$

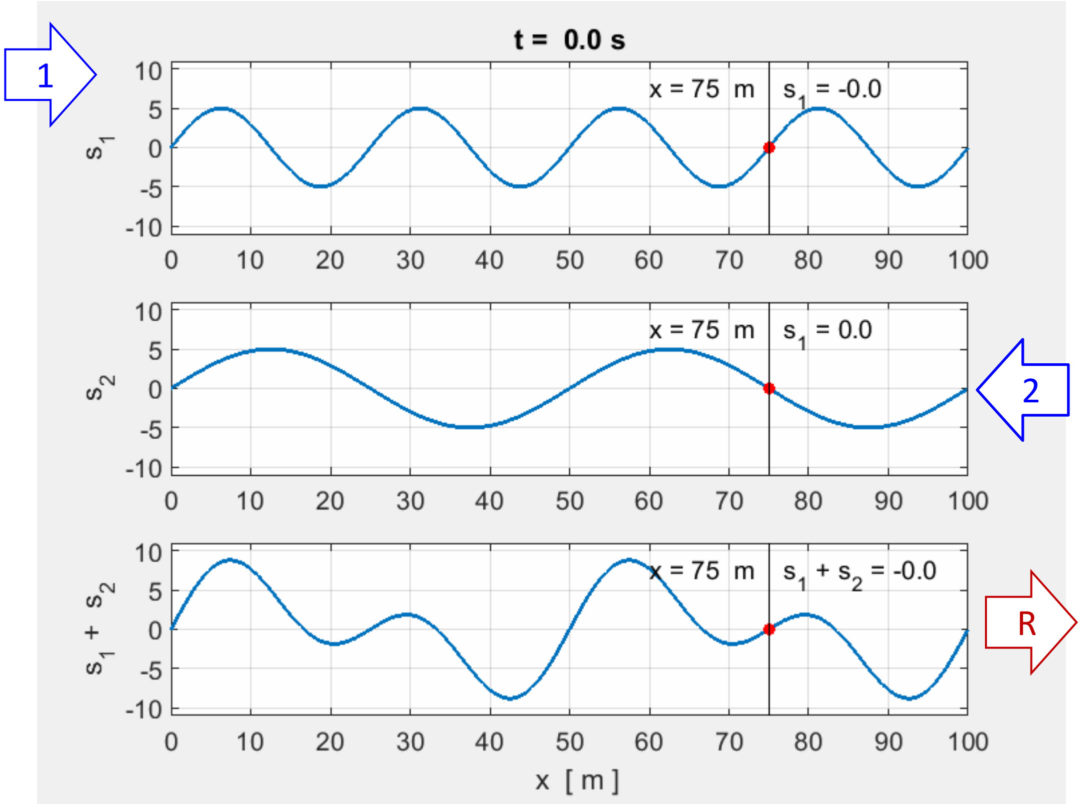
RESULTANTE

Amplitude = 7,5 u.a. , λ_1 = 25 m , f_1 = 0,080 Hz , $v_1 = 2{,}0\ m.s^{-1}$

- *A onda resultante é uma onda SENOIDAL, movendo-se para a direita.*

Fonte:www.physics.usyd.edu.au/teach_res/hsp/sp/mod31/m31_superposition_files/image010.gif

3



Onda #1 (→)

Amplitude = 5,0 u.a. , λ_1 = 25 m , f_1 = 0,080 Hz , v_1 = 2,0 m.s^{-1}

Onda #2 (←)

Amplitude = 2,5 u.a. , λ_1 = 50 m , f_1 = 0,040 Hz , v_1 = - 2,0 m.s^{-1}

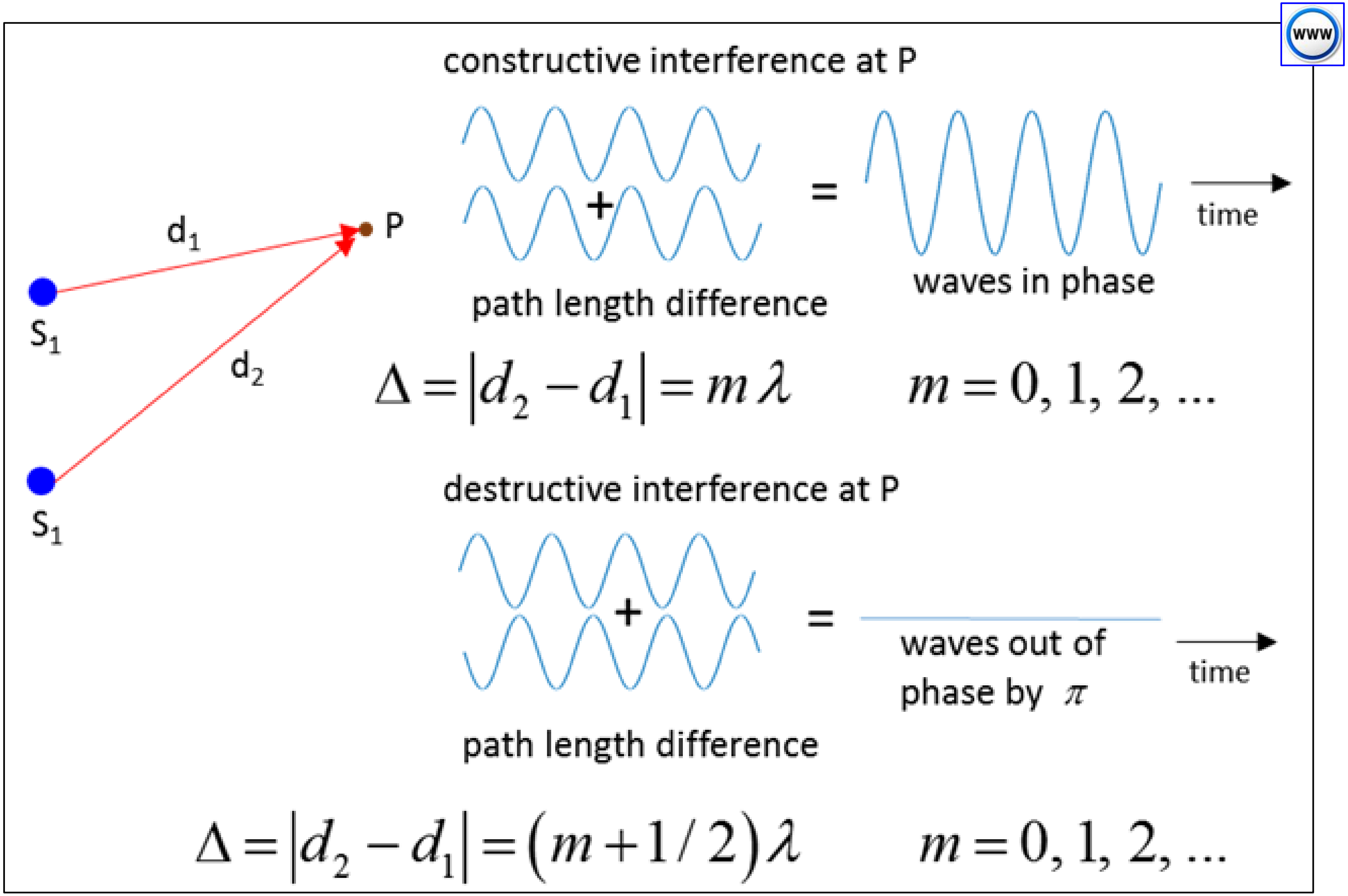
RESULTANTE

Amplitude = 5,0 u.a. , λ_1 = 50 m , f_1 = 0,040 Hz , v_1 = 2,0 m.s^{-1}

- *A onda resultante é uma onda COMPLEXA, movendo-se para a direita.*

Fonte:www.physics.usyd.edu.au/teach_res/hsp/sp/mod31/m31_superposition_files/image011.gif

Interferências: Construtiva e Destrutiva

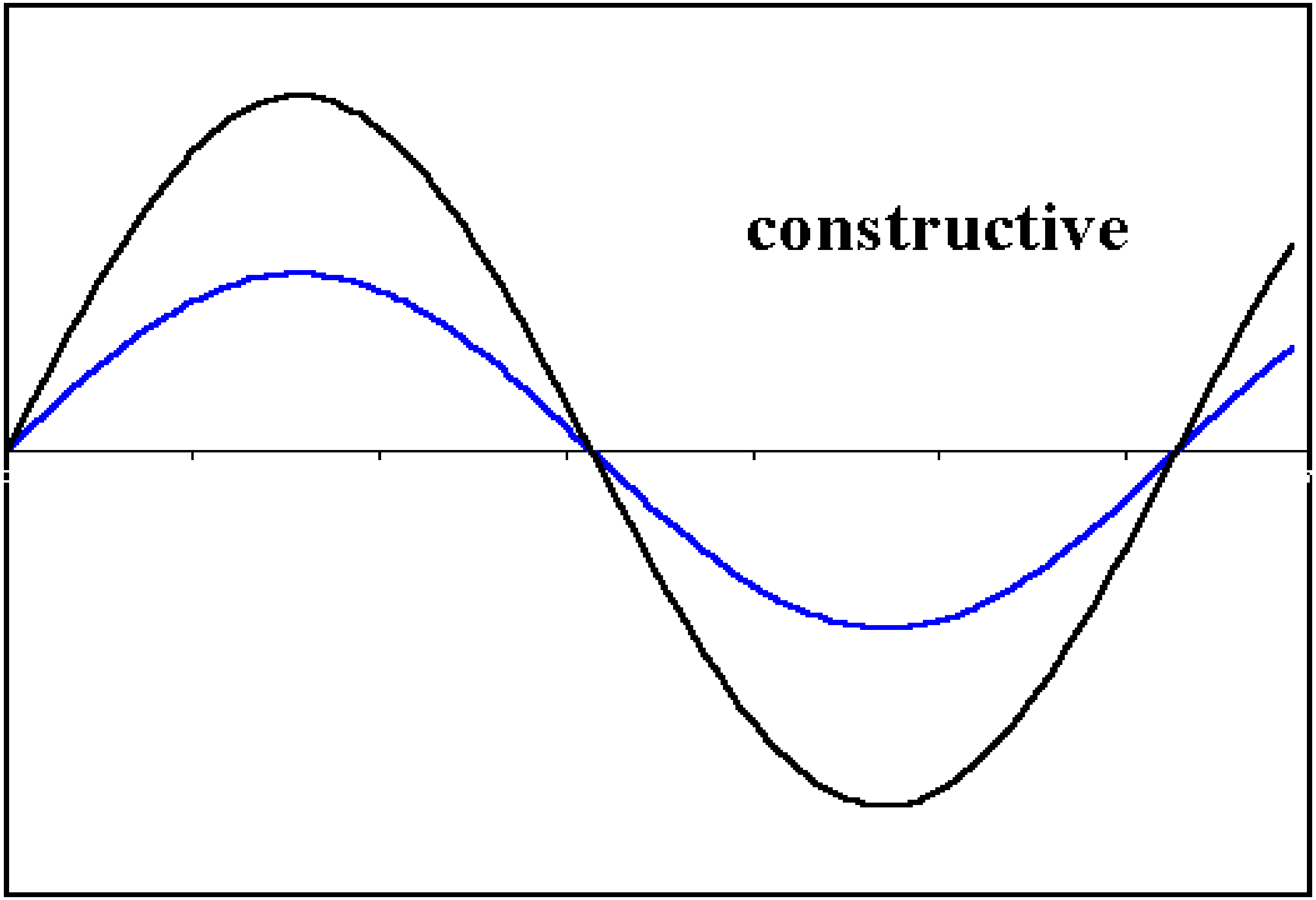


$$\Delta = |d_2 - d_1| = m\lambda \qquad m = 0, 1, 2, \ldots$$

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

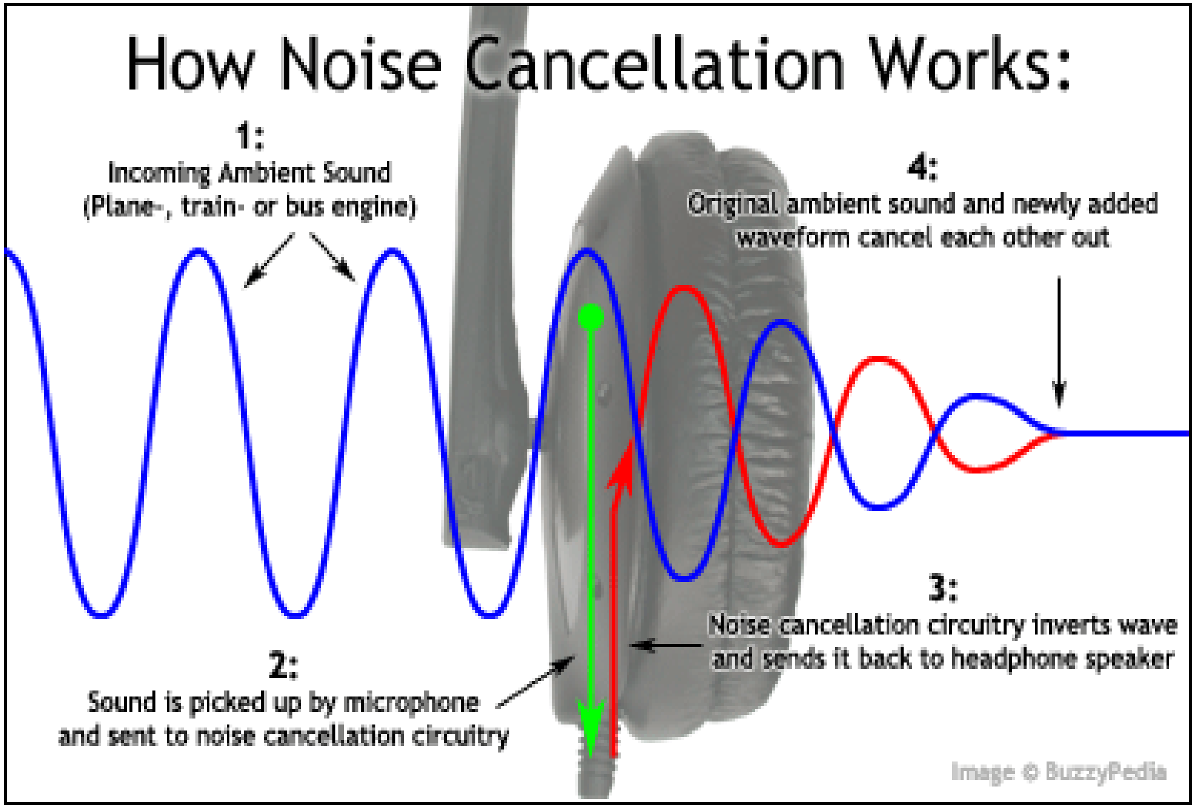
Fonte: www.physics.usyd.edu.au/teach_res/hsp/sp/mod31/m31_superposition_files/image044.png

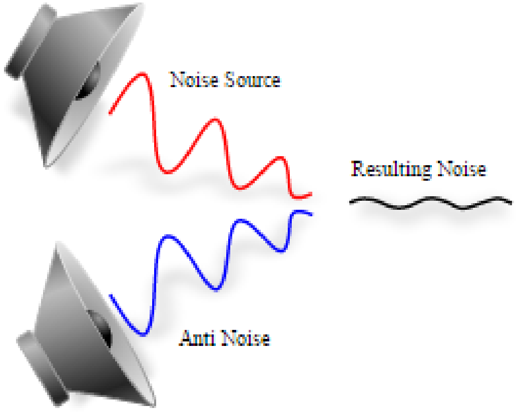
Interferências de Ondas: Construtiva e Destrutiva



Fonte: http://ircamera.as.arizona.edu/NatSci102/NatSci102/lectures/light.htm

... uma aplicação de interferência destrutiva de ondas... sonoras !





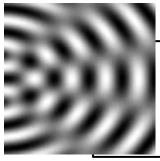
Interferência Destrutiva

...nos sites abaixo, você ***criar*** *ou* ***ouvir*** *interferências de ondas sonoras...*

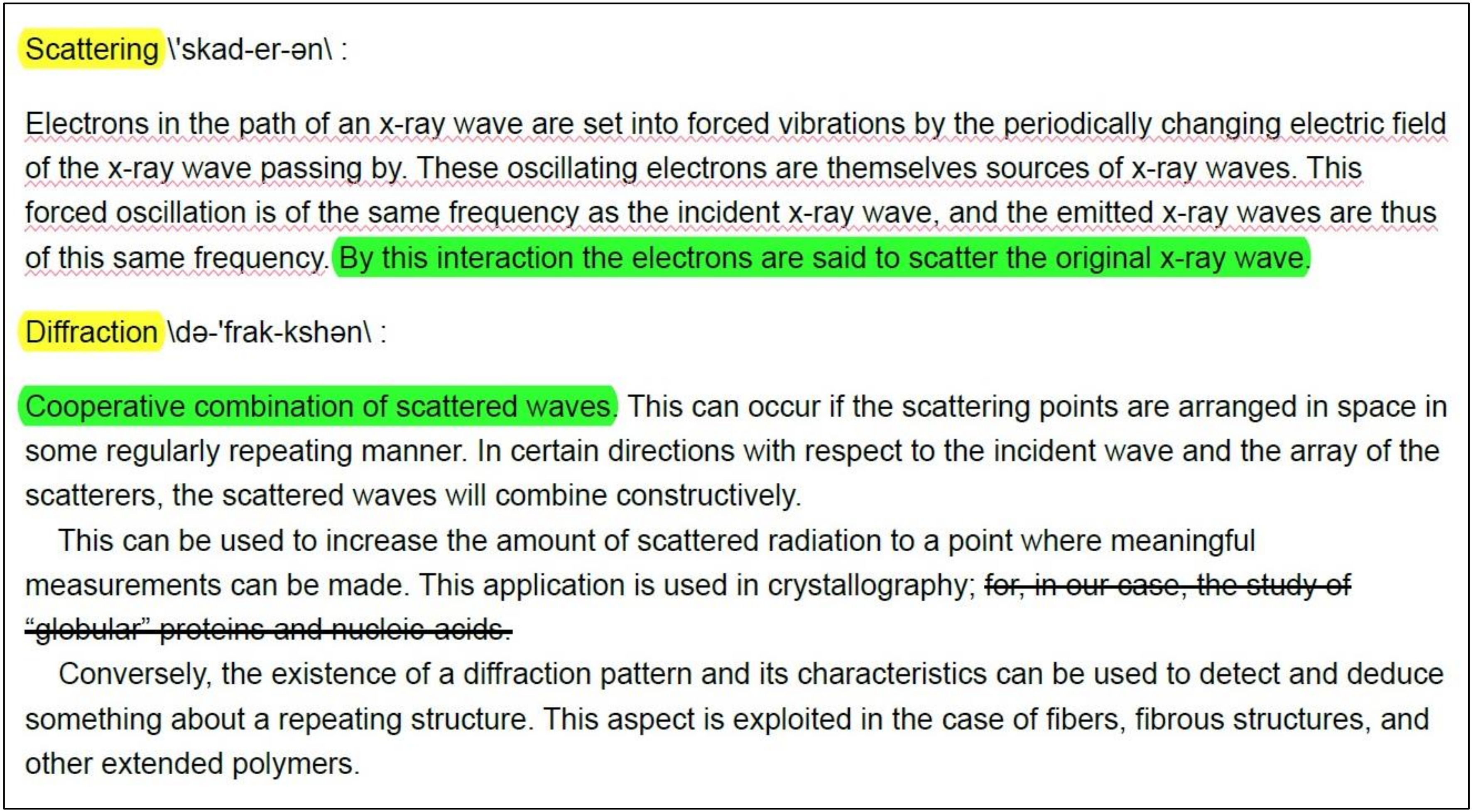
http://www.szynalski.com/tone-generator

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

Espalhamento e Difração



Definições: Espalhamento e Difração



Scattering \'skad-er-ən\ :

Electrons in the path of an x-ray wave are set into forced vibrations by the periodically changing electric field of the x-ray wave passing by. These oscillating electrons are themselves sources of x-ray waves. This forced oscillation is of the same frequency as the incident x-ray wave, and the emitted x-ray waves are thus of this same frequency. By this interaction the electrons are said to scatter the original x-ray wave.

Diffraction \də-'frak-kshən\ :

Cooperative combination of scattered waves. This can occur if the scattering points are arranged in space in some regularly repeating manner. In certain directions with respect to the incident wave and the array of the scatterers, the scattered waves will combine constructively.

This can be used to increase the amount of scattered radiation to a point where meaningful measurements can be made. This application is used in crystallography; ~~for, in our case, the study of “globular” proteins and nucleic acids.~~

Conversely, the existence of a diffraction pattern and its characteristics can be used to detect and deduce something about a repeating structure. This aspect is exploited in the case of fibers, fibrous structures, and other extended polymers.

Fonte: http://kinemage.biochem.duke.edu/teaching/braggEquation

DIFRAÇÃO – *um pouquinho de história...*

O 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.

Fonte:https://en.wikipedia.org/wiki/Francesco_Maria_Grimaldi

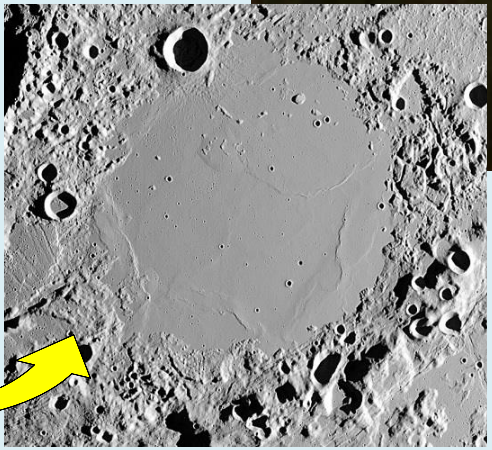
He was the first to make accurate observations on the diffraction of light (although by some accounts Leonardo da Vinci had earlier noted it).

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.

★1618 - †1663

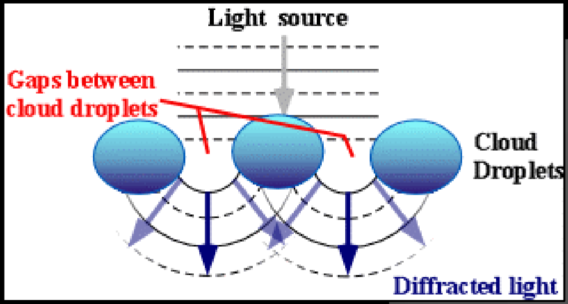


https://finkh.wordpress.com/2019/12/25/riccioli-and-grimaldi-craters/

DIFRAÇÃO

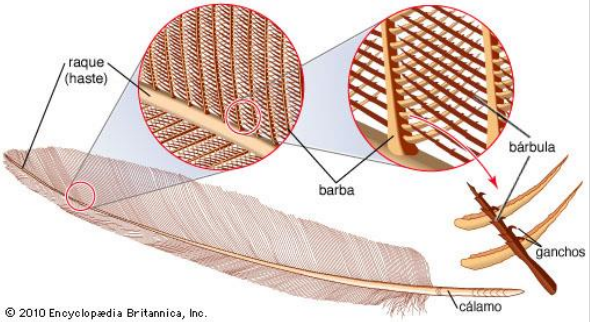
- Em física clássica, o fenômeno da difração é descrito como uma aparente “flexão” de ondas em volta de pequenos obstáculos, ou como o fenômeno de interferência coletiva de muitas ondas espalhadas por “centros de espalhamento” – que podem ser fendas ou átomos (ou qualquer tipo de oscilador...).
- O fenômeno da difração acontece com todos os tipos de ondas, incluindo ondas sonoras, ondas mecânicas na água e ondas eletromagnéticas (como luz visível, raios-X e ondas de rádio) → a comprovação da difração da luz visível e da difração de raios X foi de vital importância para constatar a natureza ondulatória dessas radiações.
- Ainda que a difração ocorra sempre quando ondas em propagação encontram centros de espalhamento *(“scattering centers”: fendas em anteparos opacos à radiação incidente; objetos; partículas; átomos...)*, seus efeitos geralmente são mais marcantes quando o comprimento das ondas é comparável à distância entre os centros de espalhamento.

- A difração é observada recorrentemente nas ondas de rádio - as ondas FM, que tem comprimento de onda da ordem de metros, são muito comumente espalhadas por construções em cidades, sofrendo interferências que diminuem a qualidade do sinal.
- O fenômeno de interferência/difração pode ser facilmente observado também em ondas sonoras, pois são ondas com comprimento de onda da ordem de cm até m. Interações sonoras de ondas com comprimento de onda entre 2 cm a 20 m são facilmente perceptíveis para os seres humanos.
- A difração da luz também é relativamente comum de ser percebida, mesmo tendo em vista o pequeno comprimento de onda da luz visível (400 a 700 nm) → exemplos são os arco-íris, a iridescência em asas de borboletas, em manchas de óleo na superfície da água, em penas de aves quando atravessadas pela luz solar, em padrões claro-escuros observados quando luz atravessa tecidos formados por fios finos em tramas igualmente finas...



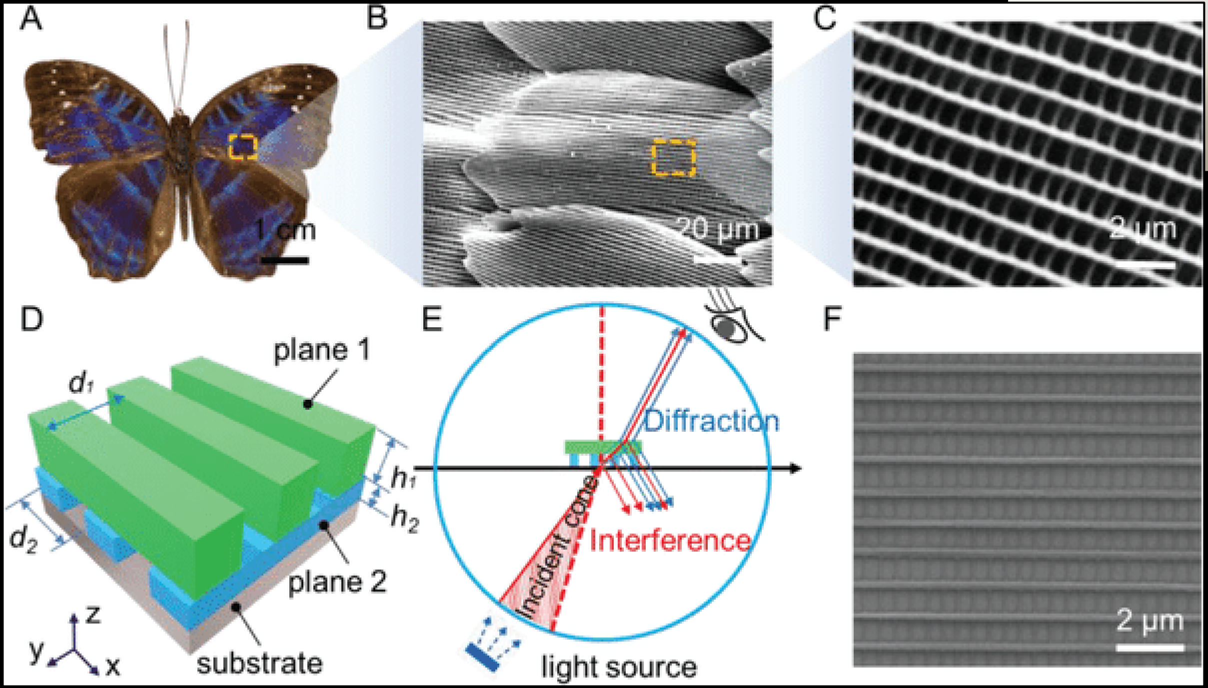
Arco-Íris

Fonte: https://optography.org/diffraction/



Penas de Aves

Fonte: https://www.nhm.ac.uk/wpy/gallery/2016-rainbow-wings



Asa de Borboleta

Fonte: Adv. Mater. 2022, 34, 2109161.
DOI: 10.1002/adma.202109161

"No one has ever been able to define the difference between interference and diffraction satisfactorily. It is just a question of usage, and there is no specific, important physical difference between them. The best we can do, roughly speaking, is to say that when there are only a few sources, say two, interfering, then the result is usually called interference, but if there is a large number of them, it seems that the word diffraction is more often used."

Richard Feynman, The Feynman Lectures on Physics, 30 .
(https://www.feynmanlectures.caltech.edu/I_30.html)

Interferências de Ondas

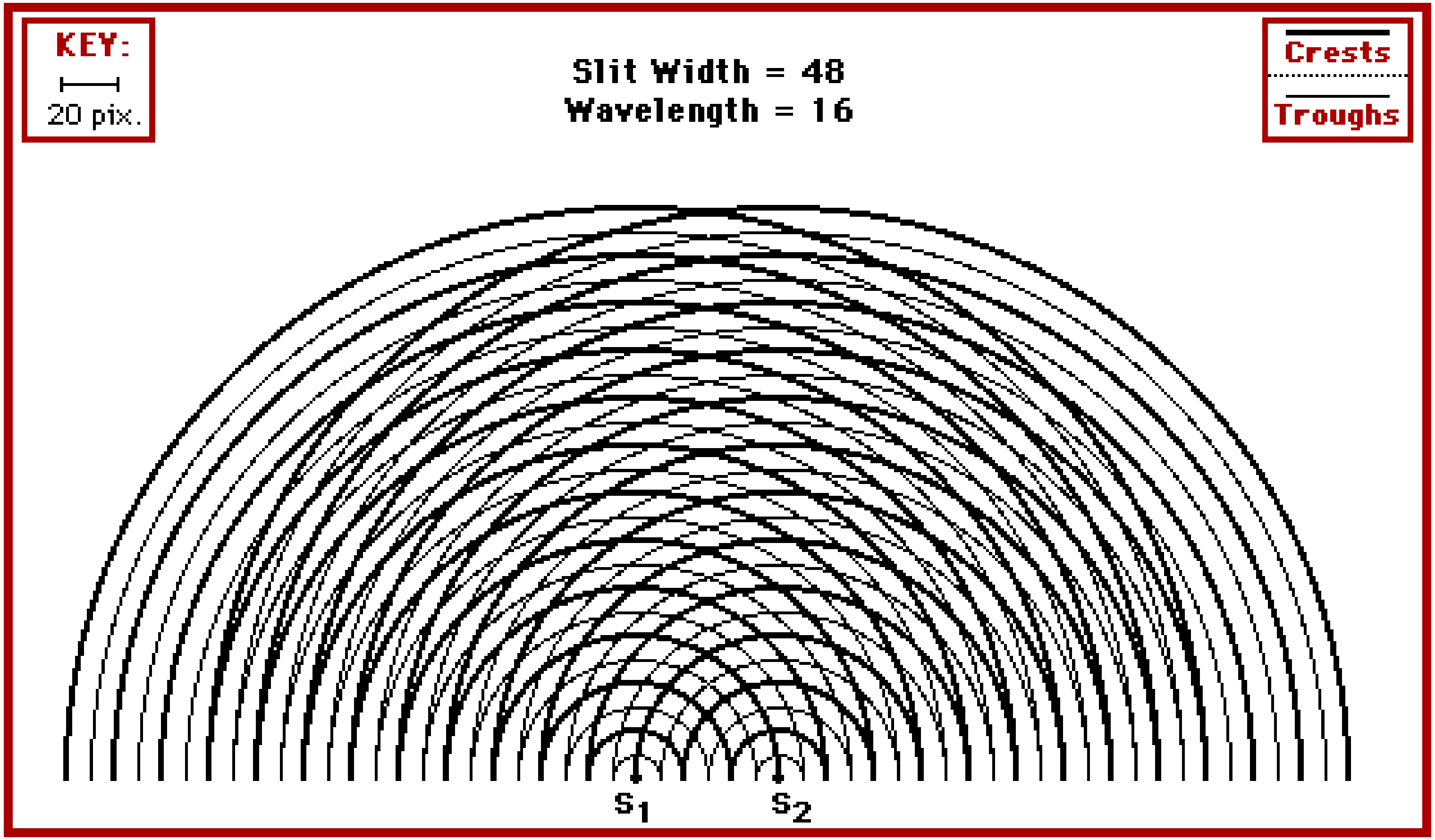
- *Wave interference* is a phenomenon which occurs when two waves meet while traveling along the same medium.
- Wave interference can be *constructive* or *destructive*.
- *Constructive interference* occurs wherever a crest of one wave meets a crest of a second wave (or when a trough of two waves meet). When a crest meets a crest, the resultant displacement of the medium at that location is larger than the displacement of either of the two individual wave crests. A new and larger wave is constructed.
- *Destructive interference* occurs wherever a crest of one wave meets a trough of a second wave. When a crest meets a trough, the two individual waves combine to produce a new wave which has a resultant displacement which is smaller than the displacement of the larger wave. That is, the two waves combine to either partially or completely destroy each other.
- The interference of two sets of circular waves with the same frequency and the same amplitude results in a *standing wave pattern*.

Fonte: http://phys.bspu.by/static/infoteka/mmedia/waves/ipd.html

- These standing wave patterns are known as *two-point source interference pa*tterns since they result from the interference of circular waves from two sources.
- A standing wave pattern is a wave pattern in which there are points along the medium which appear to be standing still. These points are called *nodes* - points of no displacement.
- ***Nodes** are produced when **destructive interference** always occurs at the same location*; a crest and a trough with the same magnitude of displacement interfere to provide complete destructive interference and no resulting displacement of the medium.
- In a standing wave pattern, the nodes are separated by *anti-nodes*. Anti-nodes are points along the medium which oscillate between a large negative displacement and a large positive displacement. ***Anti-nodes** result from the **constructive** interference of two waves*. A crest meets a crest to produce a large positive displacement; and moments later, a trough meets a trough to produce a large negative displacement.

Fonte: http://phys.bspu.by/static/infoteka/mmedia/waves/ipd.html

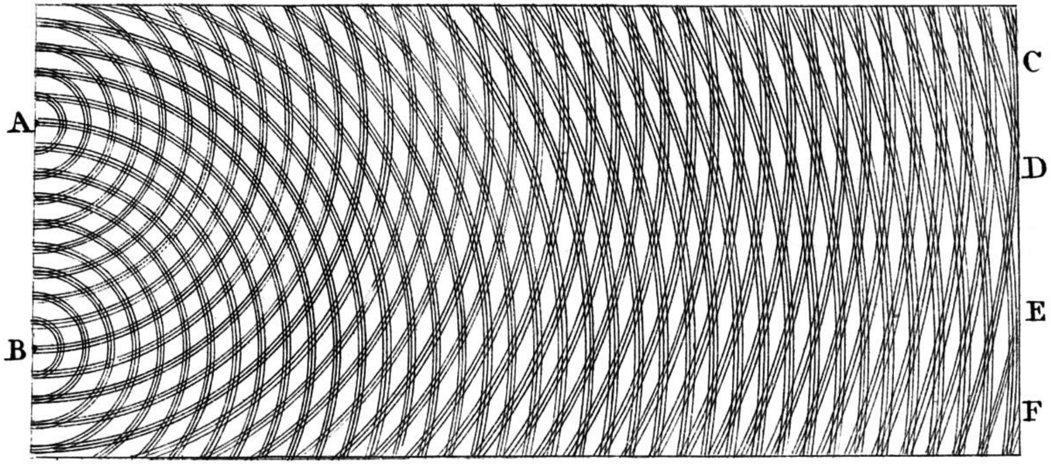
- The diagram below shows several two-point source interference patterns. The crests of each wave is denoted by a thick line while the troughs are denoted by a thin line. Subsequently, the anti-nodes are the points where either the thick lines are meeting or the thin lines are meeting. The nodes are the points where a thick line meets a thin line.



Fonte: http://phys.bspu.by/static/infoteka/mmedia/waves/ipd.html

- Observe that the nodes of the pattern are oriented along lines - known as *nodal lines*. Similarly, the anti-nodes in the pattern are also oriented along lines - known as *anti-nodal lines*.
- *The spacing between these lines is related to the distance between the sources*. The two sources are represented by S_1 and S_2 in the diagram. As the sources move closer together, the spacing between the nodal lines and the anti-nodal lines increases. That is, the nodal and anti-nodal lines spread farther apart as the sources come closer together.

- *In 1801, Thomas Young used a two-point source interference pattern to measure the wavelength of light. Young passed monochromatic light through two slits (acting as the sources) and upon a screen some distance away. The projection of the nodal and anti-nodal lines on the screen produced an alternating pattern of dark and bright lines.*
- *Young used wave principles to establish that the wavelength of light could be mathematically related to the separation distance, the distance to the screen, and the distance between anti-nodal lines (bright spots). Young made accurate measurements and determined the wavelength of light.*



Fonte: https://commons.wikimedia.org/wiki/File:Young_Diffraction.png

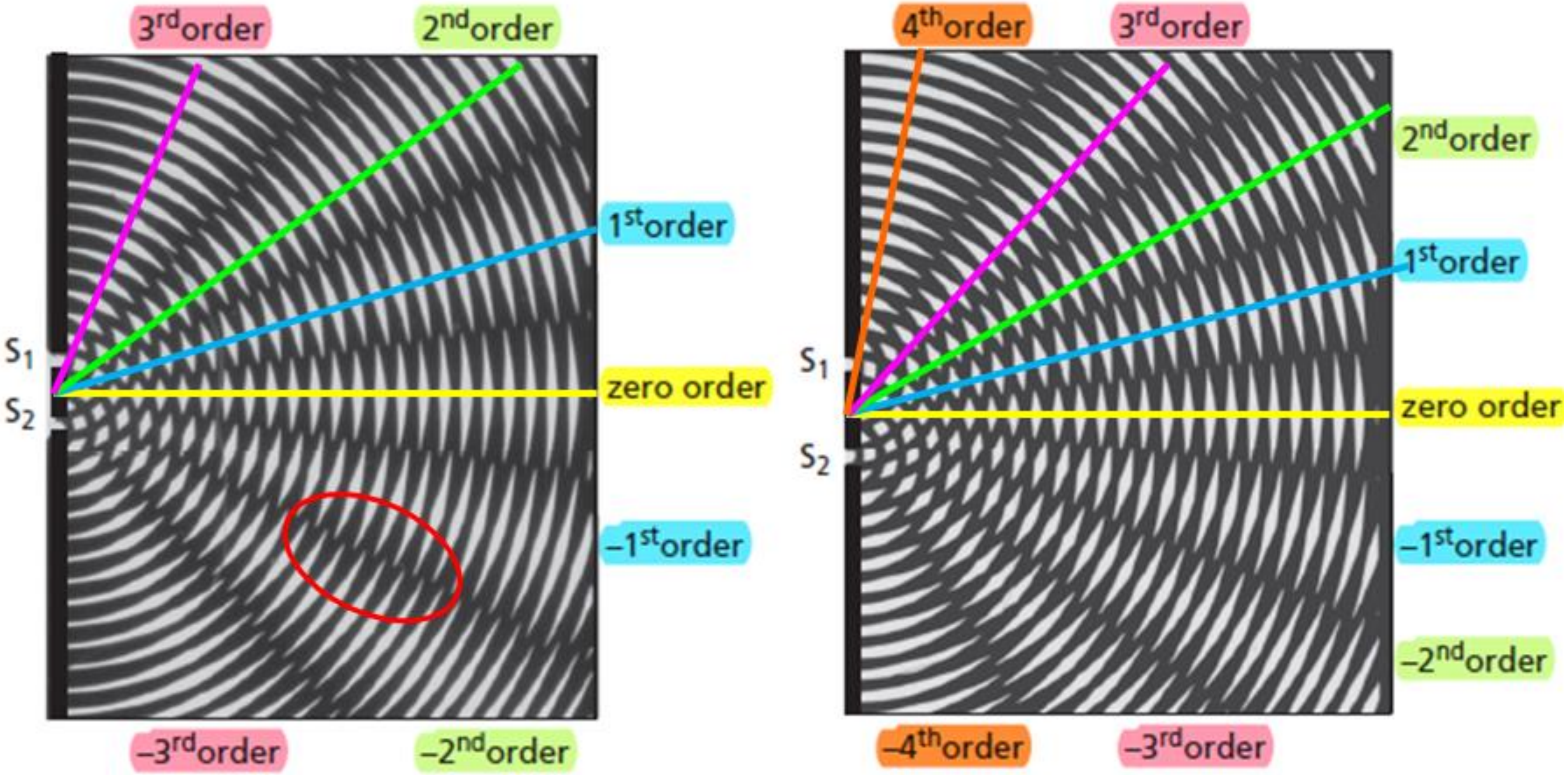
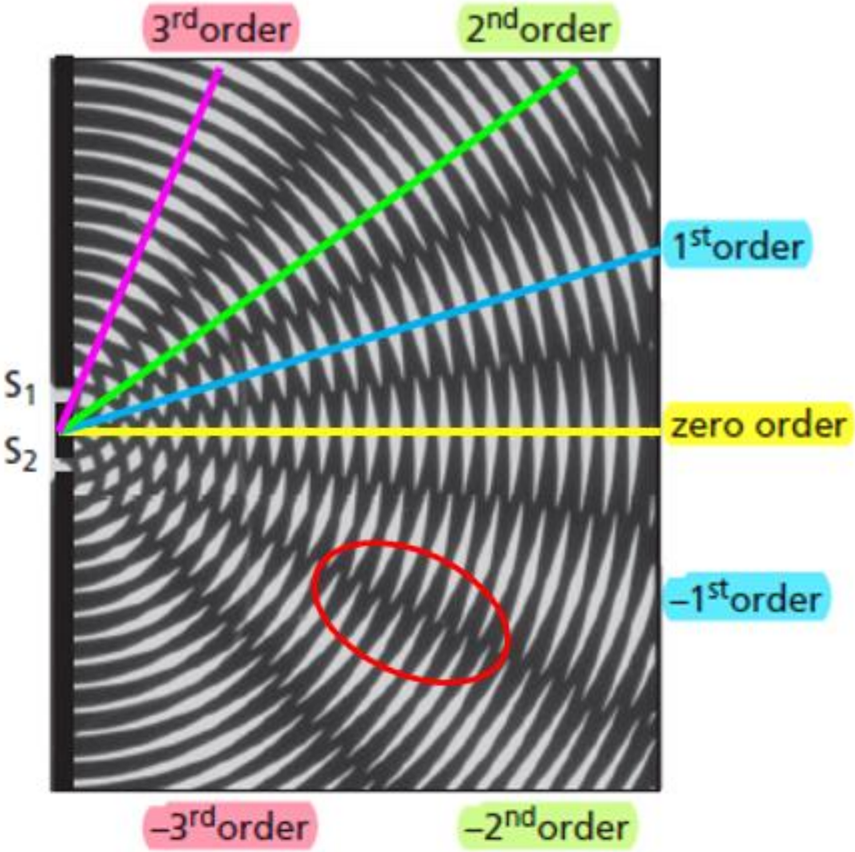


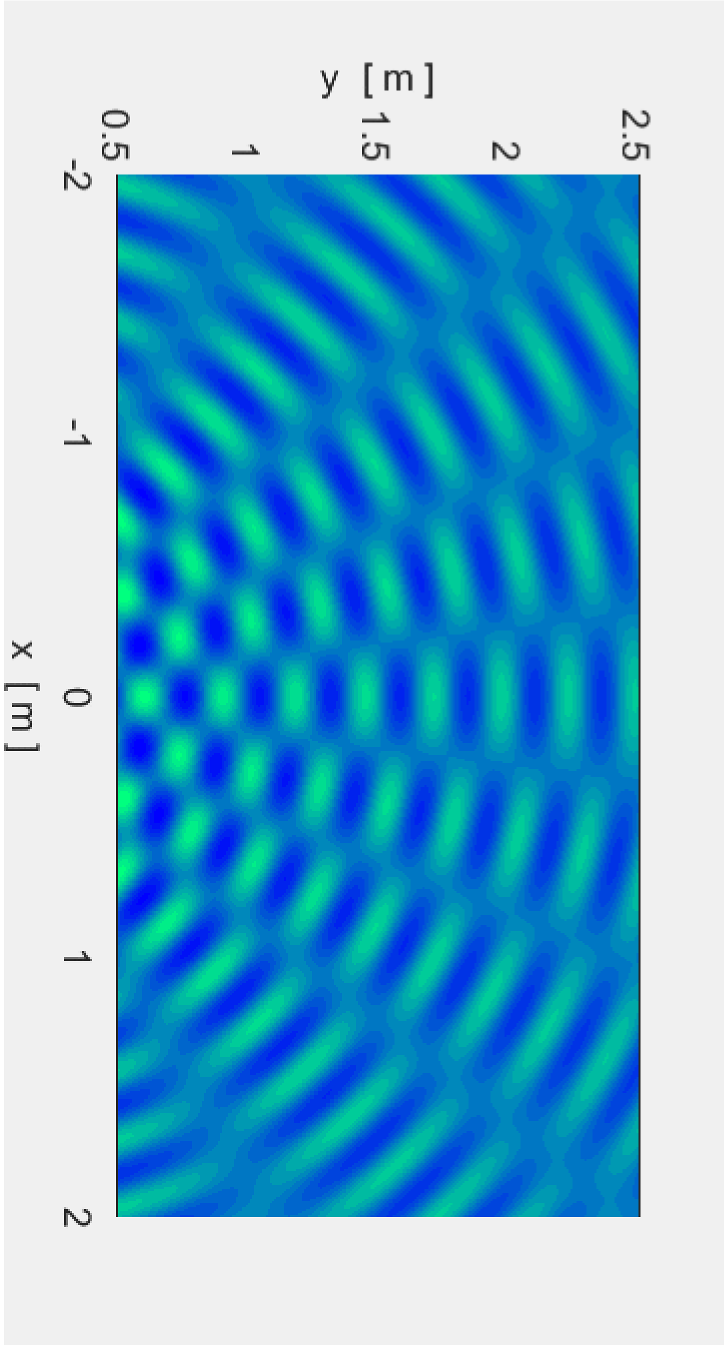
Fig. 7.4. A diagram **(a)** of a distant point source emitting coherent wavetrains and a single slit S in a screen which is the source of secondary waves (Huygens' construction). In **(b)** and **(c)** the wavetrains fall on two slits S_1 and S_2, the waves from each of which interfere to form the diffraction pattern. Note the phase shift of π between alternate diffracted beams and the **smaller** the separation of the slits (Fig. 7.4(b)) the **larger** are the angles of the diffracted beams.

...guardem essa informação...

Fonte: Hammond, C. The Basics of Crystallography and diffraction. 2015. Caps. 7.



Fonte: Hammond, C. The Basics of Crystallography and diffraction. 2015. Caps. 7.

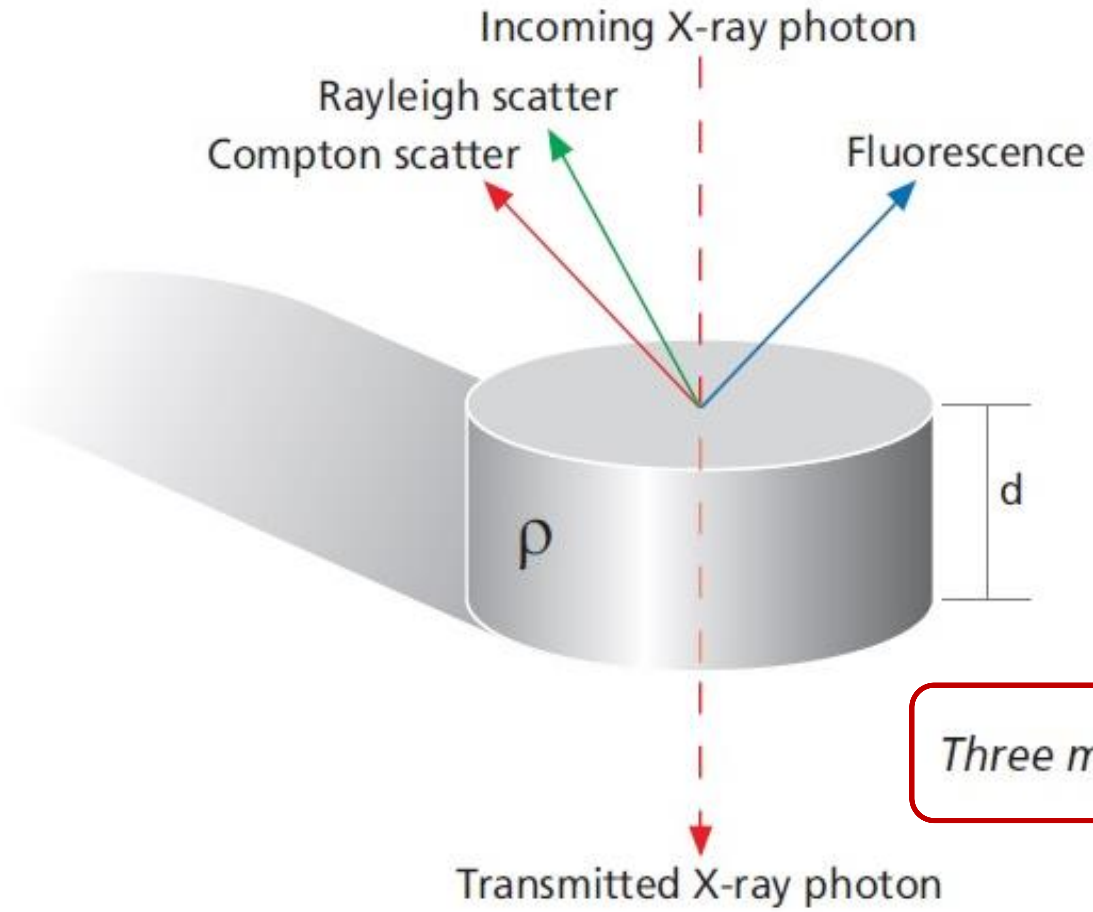


Fonte:http://www.physics.usyd.edu.au/teach_res/hsp/sp/mod31/m31_superposition_files/image045.gif

Difração de Raios X e a Lei de Bragg

Interações dos RX com a matéria - Espalhamento

- Se um feixe de raios X interage com um material, uma fração dos raios é transmitida, uma fração é absorvida (produzindo radiação *fluorescente*) e uma fração é espalhada de volta.
- Dois são os tipos principais de espalhamento → COMPTON e RAYLEIGH / THONSOM



*Espalhamento **COM** perda de energia*
↓
COMPTON

*Espalhamento **sem** perda de energia*
↓
RAYLEIGH / THONSOM

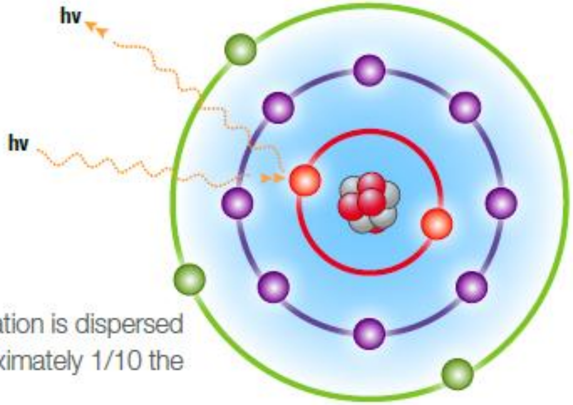
Three main interactions of X-rays with matter

PANanalytical XRF theory.pdf, obtido em:
< http://www.panalytical.com/Xray-fluorescence.htm >

Rayleigh/Compton scatter peaks

Overview

Scattering occurs when incoming X-rays do not produce fluorescence, but rather "collide" with the atoms of the sample which results in a change in the direction of motion of a particle.



Rayleigh scattering

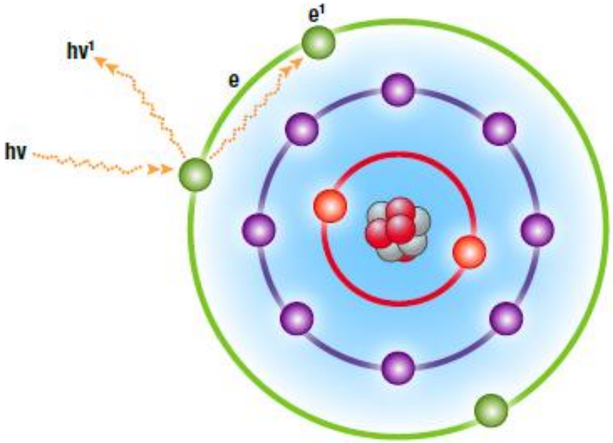
In Rayleigh scattering, electromagnetic radiation is dispersed by particles having a radius less than approximately 1/10 the wavelength of the radiation.

During the Rayleigh scattering process, photons are scattered by tightly bound electrons in which the atom is neither ionized nor excited. The incident photons are scattered with (essentially) an unchanged energy. Rayleigh scattering occurs mostly at low energies and for high atomic weight.

Rayleigh scattering can be compared to a cue ball (the incoming X-ray) bouncing off the side of the table without loss of energy.

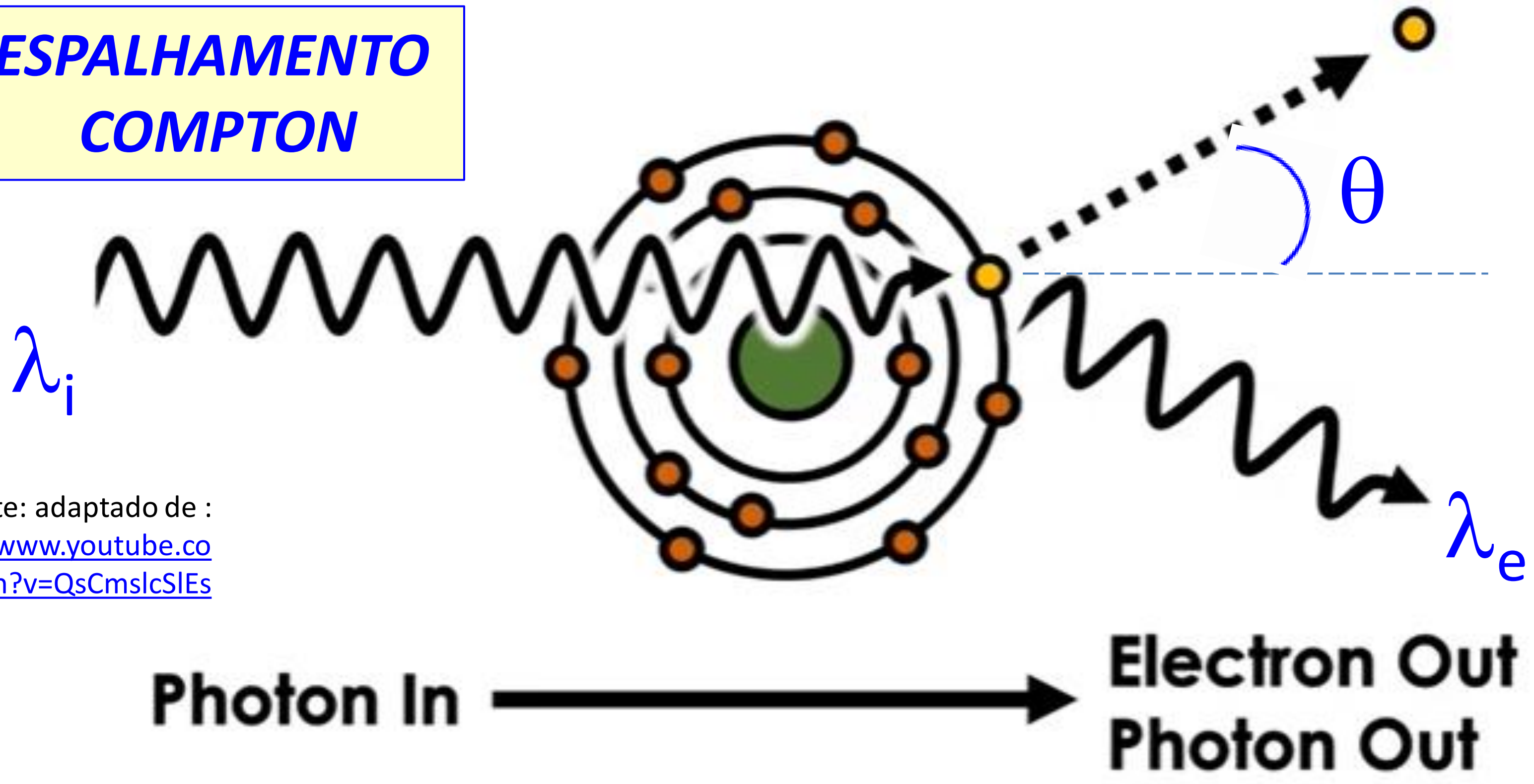
Compton scattering

In Compton scattering, the X-ray strikes an electron of the sample. Since some energy is transferred to the electron in the collision, the X-ray leaves the collision with less energy. That's why we see the Compton peak at an energy lower than the source excitation energy.



Fonte: xrf-technology-lab-eBook-non-scientist-2019.pdf

ESPALHAMENTO COMPTON



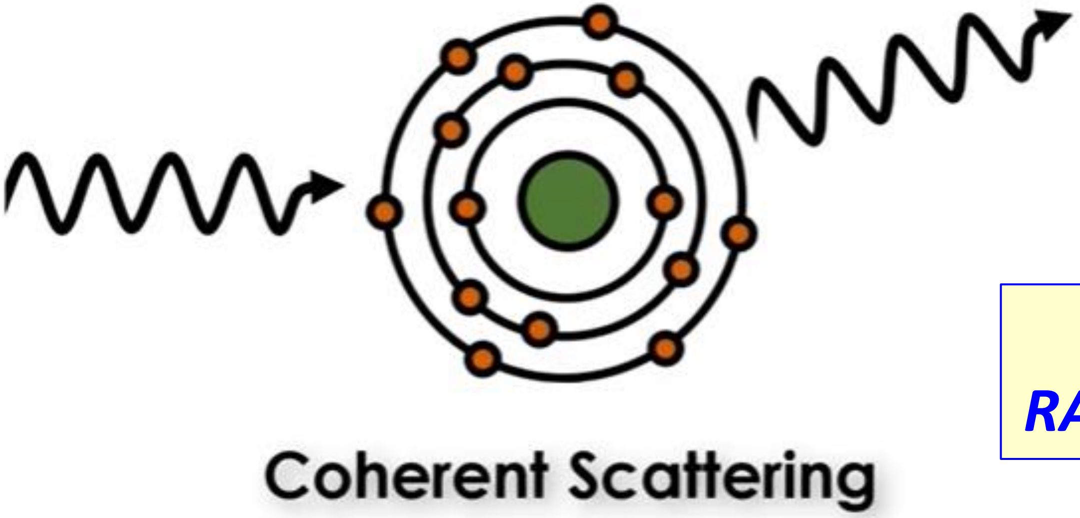
Fonte: adaptado de : https://www.youtube.com/watch?v=QsCmslcSlEs

- *A interação do fóton se dá com um elétron da última camada, que é ejetado.*
- *A diferença de energia entre a energia do elétron ejetado e do fóton incidente (de comprimento de onda λ_i) é liberada por meio de um fóton, de menor energia (comprimento de onda λ_e) do que a do fóton incidente.*

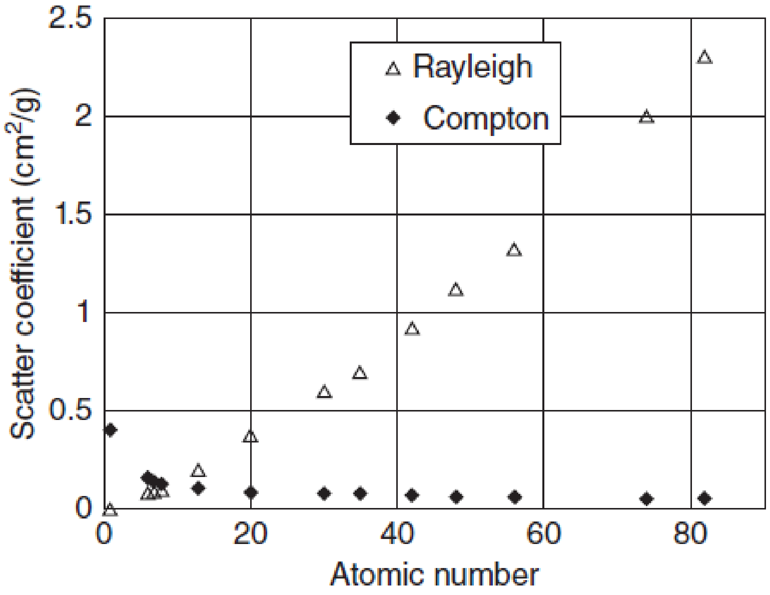
$$\lambda_i - \lambda_e = \frac{h}{mc}(1 - \cos\theta)$$

- *A energia do fóton espalhado não é característica* de nenhuma transição eletrônica do átomo → *não é útil para a análise de DRX*.

ESPALHAMENTO RAYLEIGH / THOMSON



- *O fenômeno de espalhamento Rayleigh / Thomson também pode ser chamado de espalhamento coerente ou espalhamento elástico, e ocorre não somente na interação de fótons de raios X com a matéria, mas também na interação da matéria com fótons de menor energia (luz visível, por exemplo).*
- *A energia do fóton incidente é temporariamente absorvida e o átomo inteiro vibra. O átomo excitado libera essa energia na forma de um novo fóton, que é emitido em uma direção diferente da incidente, e com a mesma energia → não há ionização do átomo, nem perda de energia.*
- *Quando o fóton incidente é de raios X de baixa energia, o espalhamento pode se considerado como sendo o limite de baixa energia do espalhamento Compton, e é chamado de espalhamento Thomson.*
- *São esses raios X que irão sofrer difração.*



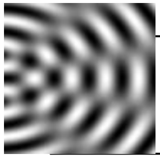
... para uma energia de excitação fixa → ESPALHAMENTO VARIA com NÚMERO ATÔMICO → espalhamento ELÁSTICO (Rayleigh/Thomson) VARIA MAIS do que espalhamento inelástico (Compton)

Figure 2.6 Elastic and inelastic scattering coefficients for selected elements at 20 keV.

X-ray Fluorescence Spectroscopy for Laboratory Applications
Michael Haschke Jörg Flock Michael Haller

2.2.4.2 Scattering

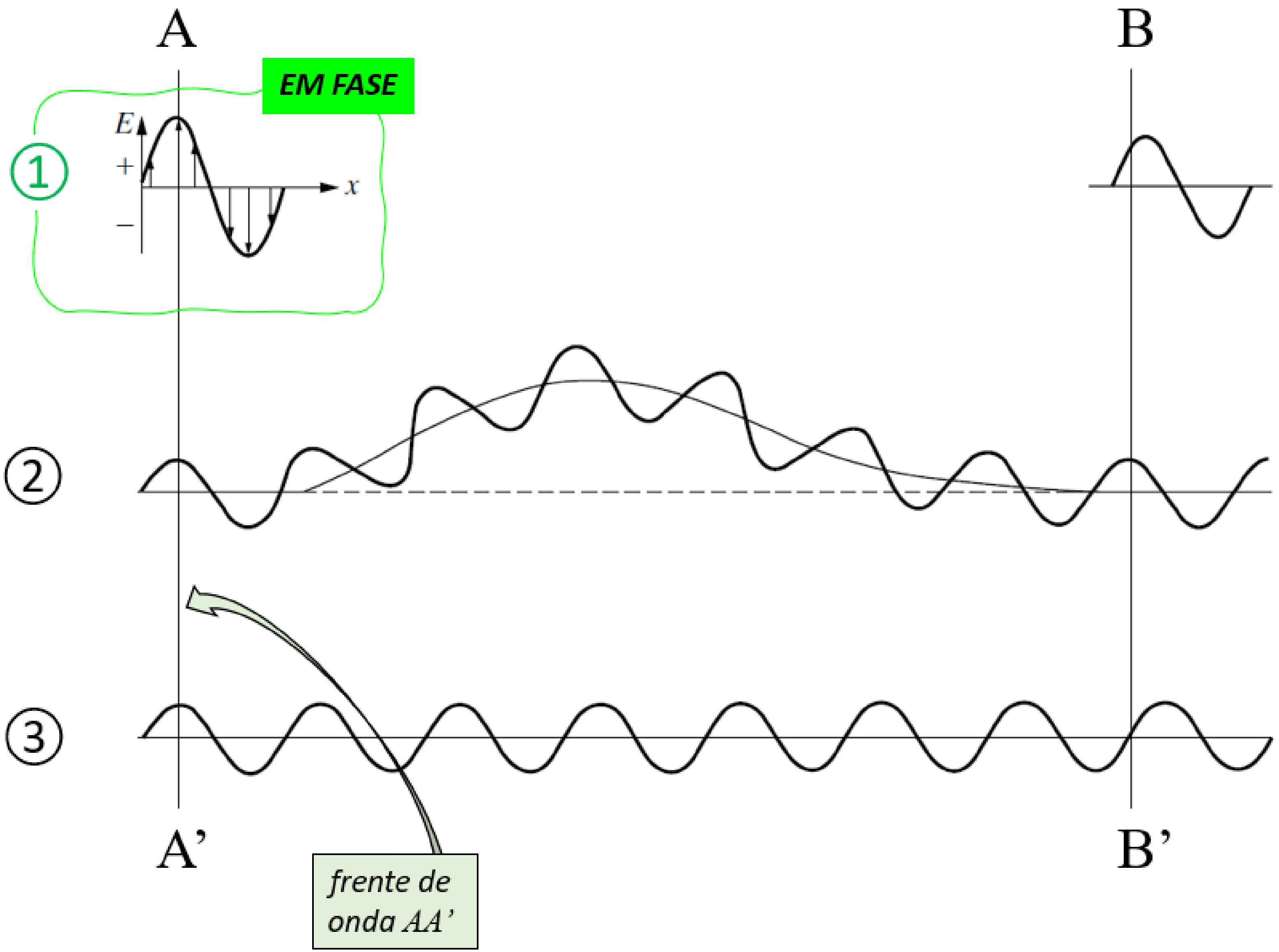
Scattering is the most important origin of the spectral background in X-ray spectrometry. The incident radiation is scattered at the electrons of the atoms of the sample. The scattering can be both elastic (Rayleigh or coherent scattering) and inelastic (Compton or incoherent scattering). All electrons of an atom contribute to the elastic scattering, i.e. the scattering intensity is proportional to the number of electrons or to the atomic number. Inelastic scattering can occur only at weakly bonded, i.e. outer electrons. Therefore, its intensity is mostly independent of the atomic number. This is demonstrated in Figure 2.6 showing the scatter coefficients for a few elements for an energy of 20 keV, which is close to Rh-Kα-radiation, the most often used target material for spectroscopic X-ray tubes (Section 5.3.2.1). The coefficients for the Rayleigh (elastic) scattering increase approximately proportionally with the atomic number whereas the coefficients for the Compton (inelastic) scattering show only a small dependence on atomic number; only for the lightest elements they are slightly larger than for most other elements.



DIFRAÇÃO

- A ***difração*** é um fenômeno devido essencialmente à existência de *relações de fase entre duas ou mais ondas* – necessário definir claramente o que se entende por *relações de fase* .
- A discussão será feita a partir da imagem apresentada um pouco mais adiante.
- Vamos considerar um feixe de ondas eletromagnéticas ① se propagando da esquerda para a direita, e por conveniência, consideramos que esse feixe é tal que o vetor do campo elétrico $\mathbf{E}$ está no plano da imagem.
- Imagine que esse feixe ① é composto de duas ondas, ② e ③, ambas com a metade da amplitude de ①, e que essas duas ondas, na *frente de onda* $\mathrm{AA'}$, estão completamente *em fase*.
- *DEFINIÇÃO: frente de onda → superfície perpendicular à direção de propagação do feixe / das ondas.*
- *DEFINIÇÃO: ondas em fase → duas ou mais ondas estão com seus vetores campo elétrico $\mathbf{E}$ com a mesma magnitude e direção no mesmo momento e no mesmo ponto x medido na direção de propagação das ondas.*
- Consideremos o experimento imaginário seguinte:

...continua

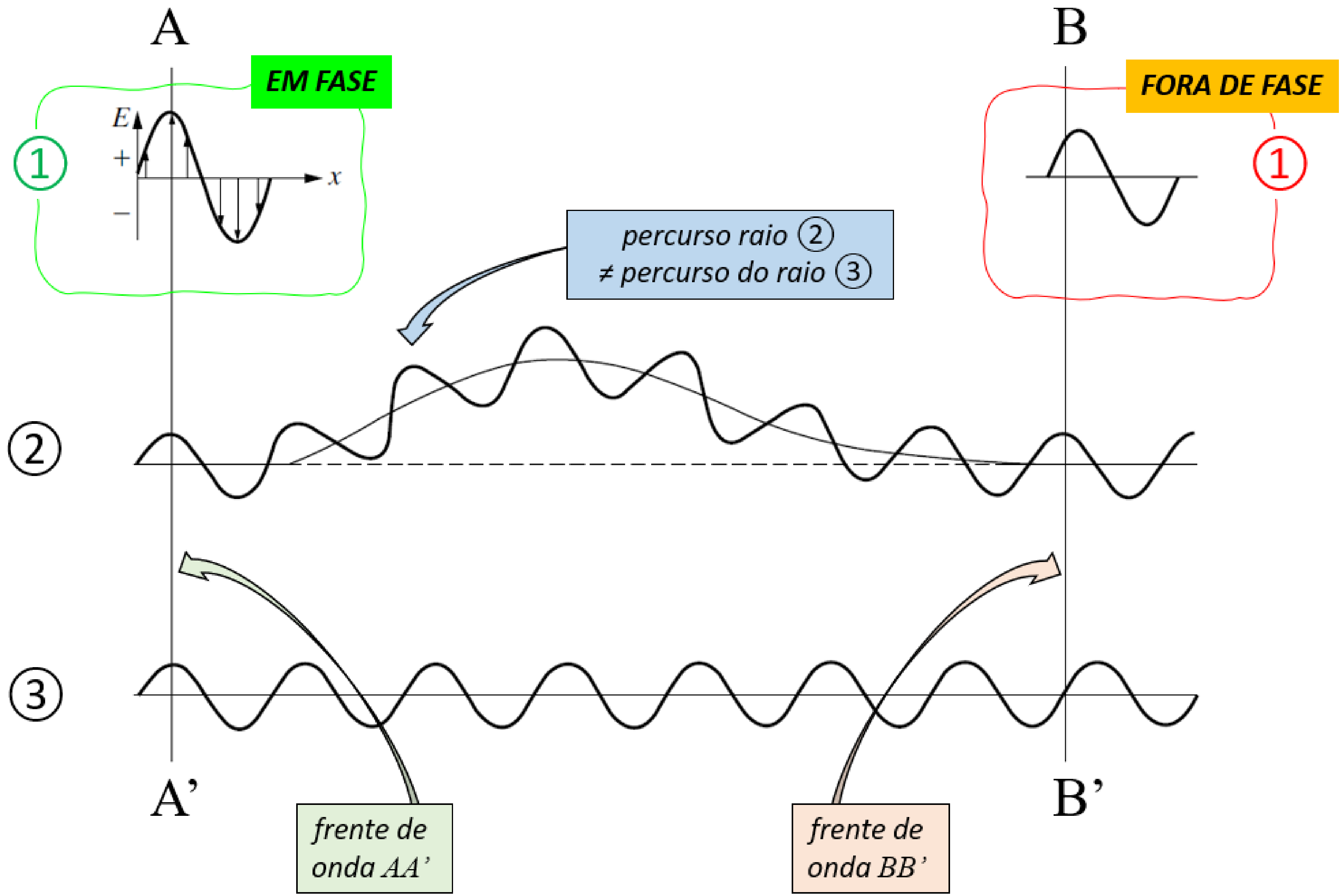


EM FASE

frente de onda AA'

Fonte: adaptado de Cullity, B.D.; Stock, S.R. Elements of X-Ray Diffraction. 3ª Ed. 2014. Cap. 3.

- Consideremos o experimento imaginário seguinte :
  - O raio ③, a partir da frente de onda AA’, continua seu movimento em linha reta até encontrar o raio ② na frente de onda BB’...
  - O raio ②, ao contrário, de alguma forma (não interessa como para os fins da presente discussão), não segue o mesmo percurso, e volta a encontrar o raio ③ na frente de onda BB’ do feixe.
  - Nesse instante, na frente de onda BB’, o raio ② está no máximo de sua amplitude, enquanto a amplitude do raio ③ nesse instante é zero → os dois raios estão *fora de fase*.
  - Para obter a intensidade do feixe 1, somamos os dois raios na frente de onda BB’ → essa intensidade, indicada na figura, mostra claramente que os dois raios estão *fora de fase*.



EM FASE

FORA DE FASE

percurso raio ②
≠ percurso do raio ③

frente de onda AA'

frente de onda BB'

Fonte: adaptado de Cullity, B.D.; Stock, S.R. Elements of X-Ray Diffraction. 3ª Ed. 2014. Cap. 3.

DUAS CONCLUSÕES

1. *Diferenças no comprimento dos percursos das ondas levam a diferenças de fase.*

2. *A introdução de diferenças de fase leva a diferenças na amplitude da onda resultante.*

...as questões centrais desta aula...

- As ***questões centrais*** desta aula :

1. *um feixe de raios X incidindo em um cristal será difratado pelo cristal ?*
2. *caso a difração ocorra, quais são as condições para isso?*

- **DEFINIÇÃO** *: **um feixe de raios X difratado** pode ser definido como sendo um feixe composto por um grande número de raios espalhados que se reforçam mutuamente (...ou seja, que estão **em fase**...).*

- Assim sendo, a *difração de raios X* é essencialmente um fenômeno que envolve *espalhamento* dos raios pelas estruturas cristalinas e *interferência* entre os raios espalhados → não envolve "novas" formas de interação entre os raios X e a matéria *(por exemplo, ionização de átomos, emissão de raios X com λ diferente dos RX incidentes, ...)*.

- **As espécies químicas presentes nos cristais espalham os raios X que incidem sobre eles em todas as direções** → *as figuras que serão apresentadas ao longo da aula mostrarão apenas os feixes nos quais os raios espalhados interferem em fase e, portanto, reforçam uns aos outros formando feixes difratados*.

DRX : A análise de Laue

8.2 Laue's analysis of X-ray diffraction: the three Laue equations

Consider a simple crystal in which the motif is one atom and the atoms are simply to be regarded as scattering centres situated at lattice points.

The crystal may be considered to be built up of rows of atoms in three dimensions: rows of atoms of spacing a along the x-axis, of spacing b along the y-axis and of spacing c along the z-axis. Consider first of all the condition for constructive interference for the waves scattered from the row of atoms along the x-axis—which may simply be reduced to a consideration of the path differences between waves scattered from adjacent atoms in the row (Fig. 8.1(a)).

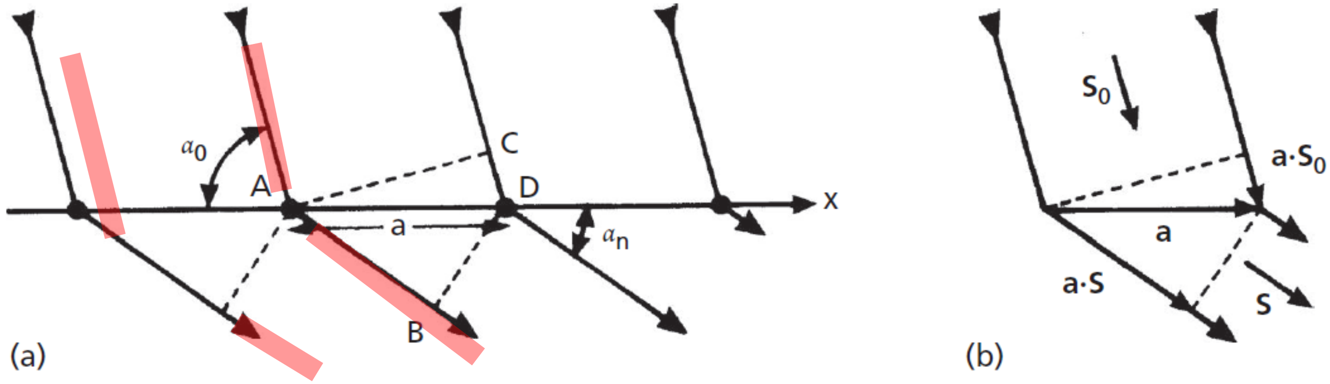
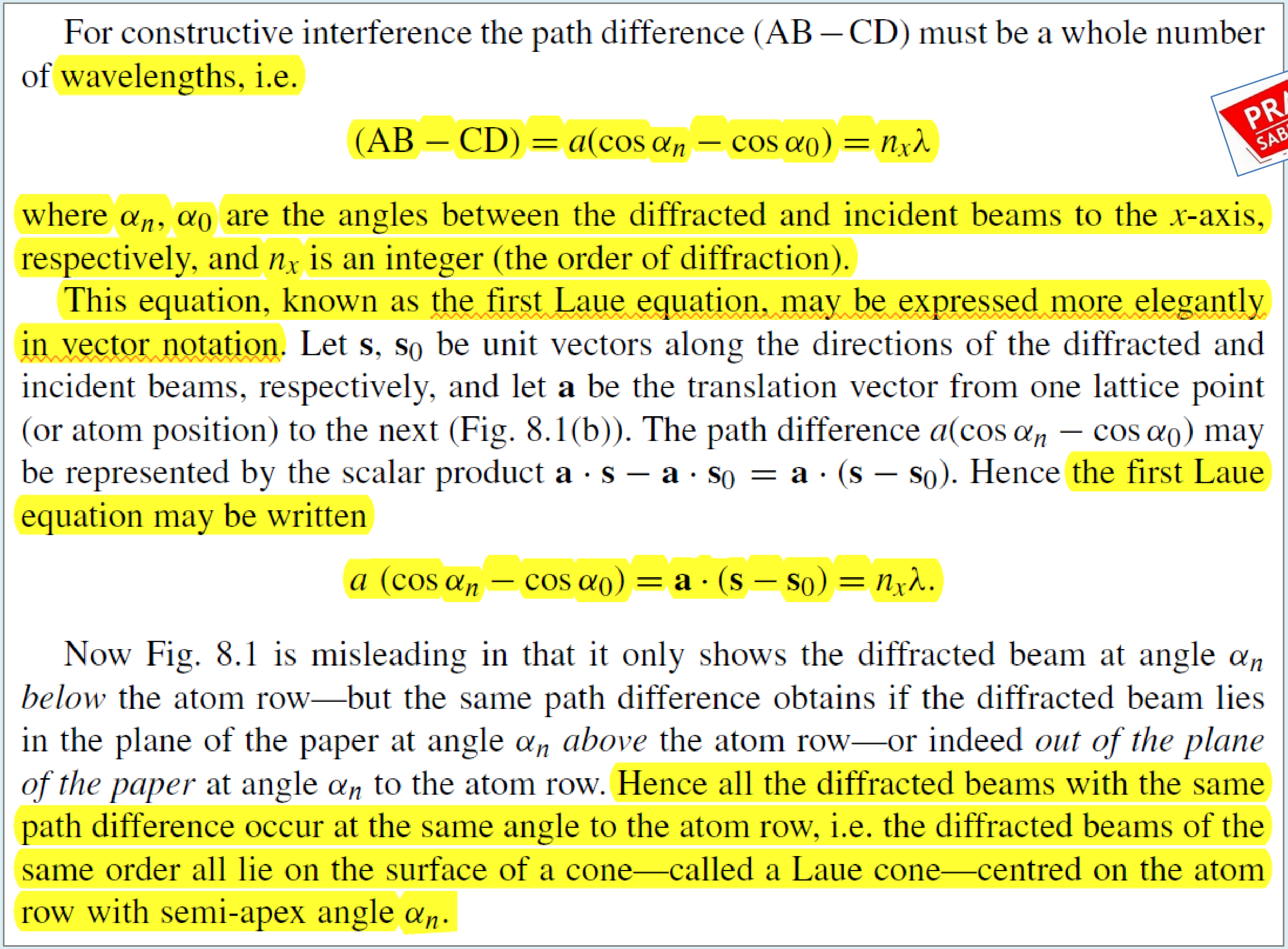


Fig. 8.1. (a) Diffraction from a lattice row along the x-axis. The incident and diffracted beams are at angles α_0 and α_n to the row respectively. The path difference between the diffracted beams = (AB - CD). (b) The incident and diffracted beam directions and the path difference between the diffracted beams as expressed in vector notation.

For constructive interference the path difference (AB – CD) must be a whole number of wavelengths, i.e.

$$(AB - CD) = a(\cos\alpha_n - \cos\alpha_0) = n_x\lambda$$

Fonte: Hammond, C. The Basics of Crystallography and Diffraction. 2015. Caps. 8.



For constructive interference the path difference (AB − CD) must be a whole number of wavelengths, i.e.

$$(\mathrm{AB} - \mathrm{CD}) = a(\cos\alpha_n - \cos\alpha_0) = n_x\lambda$$

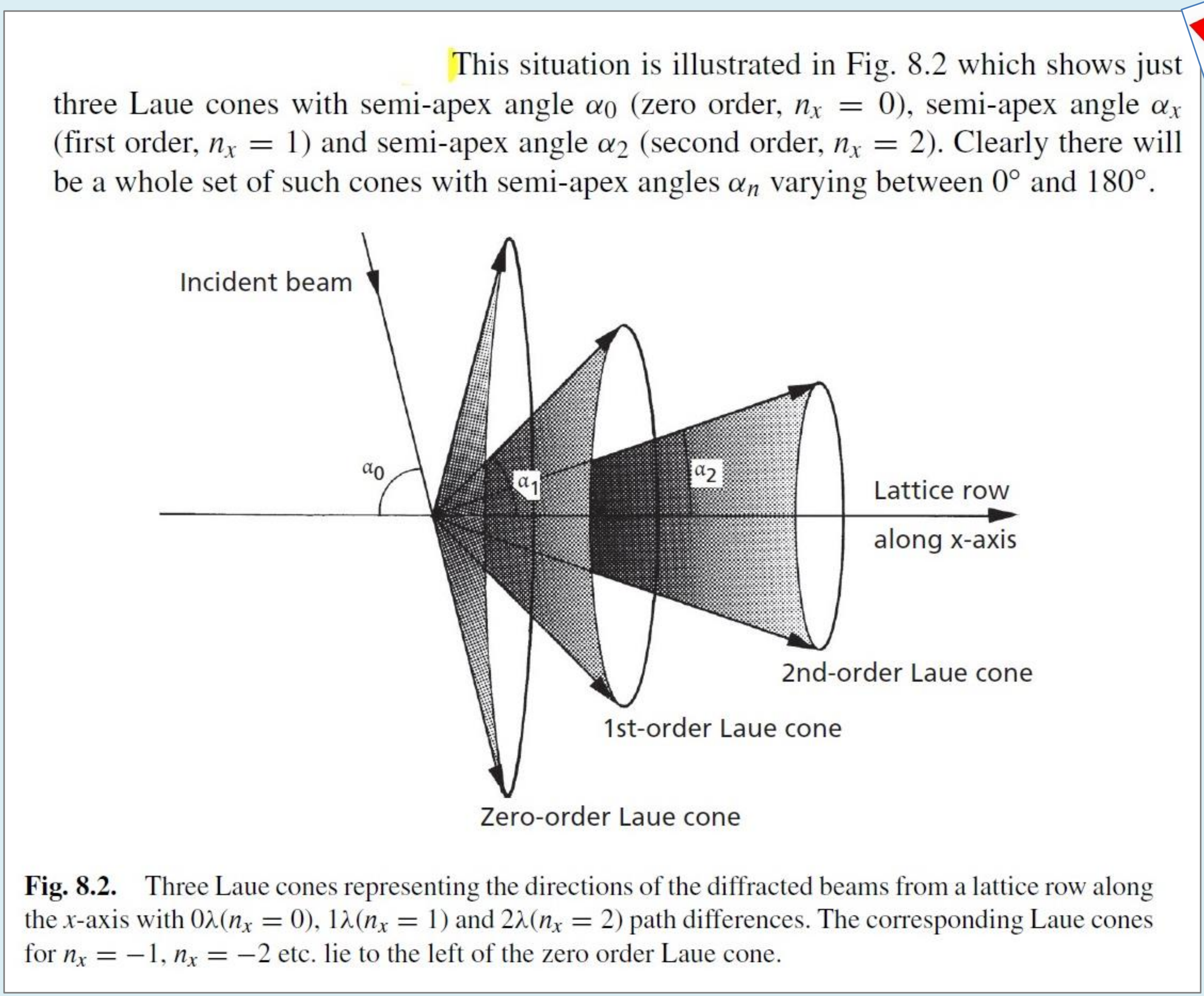
where α_n, α_0 are the angles between the diffracted and incident beams to the x-axis, respectively, and n_x is an integer (the order of diffraction).

This equation, known as the first Laue equation, may be expressed more elegantly in vector notation. Let $\mathbf{s}$, $\mathbf{s}_0$ be unit vectors along the directions of the diffracted and incident beams, respectively, and let $\mathbf{a}$ be the translation vector from one lattice point (or atom position) to the next (Fig. 8.1(b)). The path difference $a(\cos\alpha_n - \cos\alpha_0)$ may be represented by the scalar product $\mathbf{a}\cdot\mathbf{s} - \mathbf{a}\cdot\mathbf{s}_0 = \mathbf{a}\cdot(\mathbf{s} - \mathbf{s}_0)$. Hence the first Laue equation may be written

$$a\,(\cos\alpha_n - \cos\alpha_0) = \mathbf{a}\cdot(\mathbf{s} - \mathbf{s}_0) = n_x\lambda.$$

Now Fig. 8.1 is misleading in that it only shows the diffracted beam at angle α_n *below* the atom row—but the same path difference obtains if the diffracted beam lies in the plane of the paper at angle α_n *above* the atom row—or indeed *out of the plane of the paper* at angle α_n to the atom row. Hence all the diffracted beams with the same path difference occur at the same angle to the atom row, i.e. the diffracted beams of the same order all lie on the surface of a cone—called a Laue cone—centred on the atom row with semi-apex angle α_n.

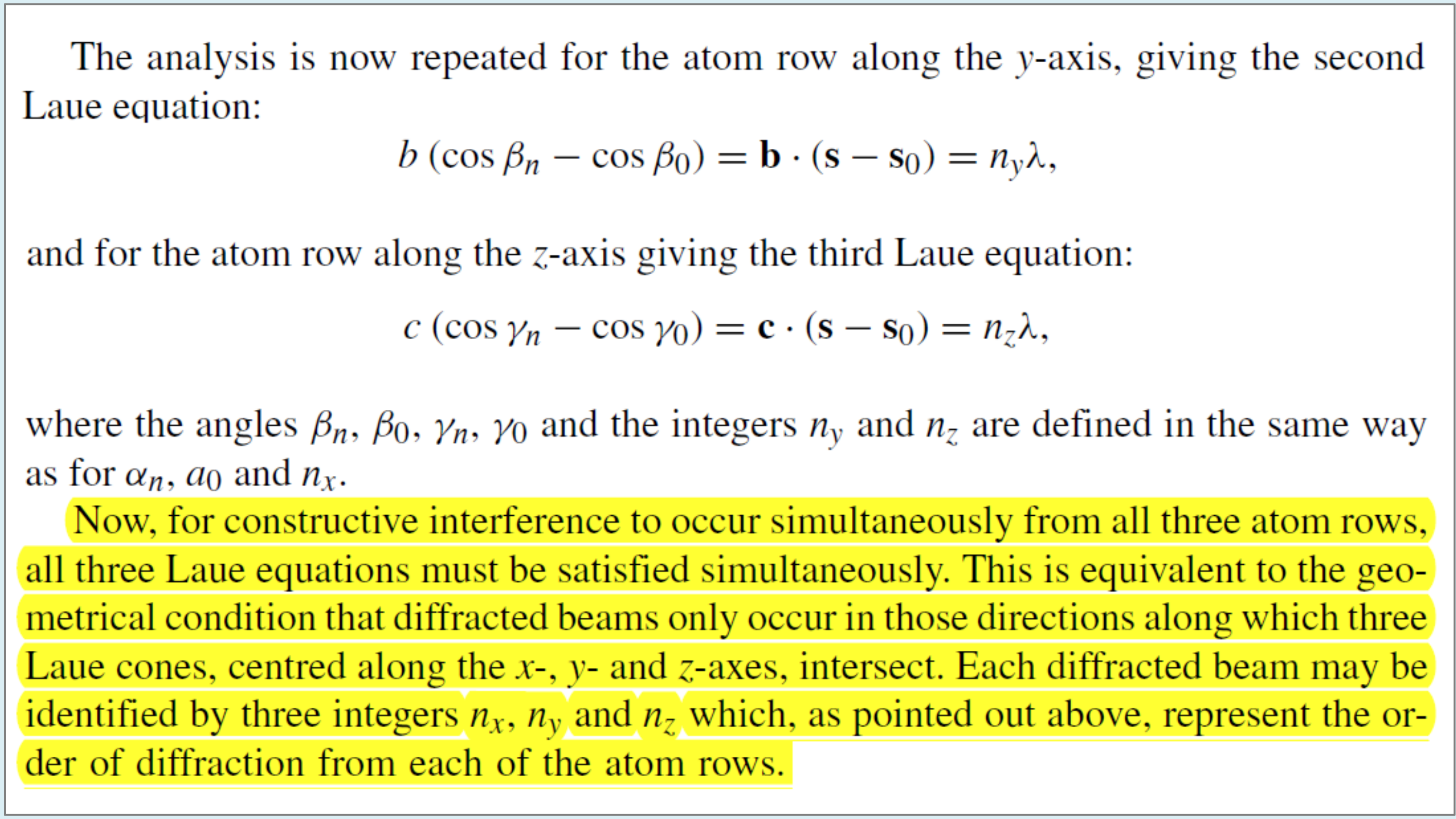
Fonte: Hammond, C. The Basics of Crystallography and Diffraction. 2015. Caps. 8.



This situation is illustrated in Fig. 8.2 which shows just three Laue cones with semi-apex angle α_0 (zero order, $n_x = 0$), semi-apex angle α_x (first order, $n_x = 1$) and semi-apex angle α_2 (second order, $n_x = 2$). Clearly there will be a whole set of such cones with semi-apex angles α_n varying between 0° and 180°.

Fig. 8.2. Three Laue cones representing the directions of the diffracted beams from a lattice row along the x-axis with $0\lambda(n_x = 0)$, $1\lambda(n_x = 1)$ and $2\lambda(n_x = 2)$ path differences. The corresponding Laue cones for $n_x = -1$, $n_x = -2$ etc. lie to the left of the zero order Laue cone.

Fonte: Hammond, C. The Basics of Crystallography and Diffraction. 2015. Cap. 8.



The analysis is now repeated for the atom row along the *y*-axis, giving the second Laue equation:

$$b\,(\cos\beta_n - \cos\beta_0) = \mathbf{b}\cdot(\mathbf{s}-\mathbf{s}_0) = n_y\lambda,$$

and for the atom row along the *z*-axis giving the third Laue equation:

$$c\,(\cos\gamma_n - \cos\gamma_0) = \mathbf{c}\cdot(\mathbf{s}-\mathbf{s}_0) = n_z\lambda,$$

where the angles β_n, β_0, γ_n, γ_0 and the integers n_y and n_z are defined in the same way as for α_n, a_0 and n_x.

Now, for constructive interference to occur simultaneously from all three atom rows, all three Laue equations must be satisfied simultaneously. This is equivalent to the geometrical condition that diffracted beams only occur in those directions along which three Laue cones, centred along the *x*-, *y*- and *z*-axes, intersect. Each diffracted beam may be identified by three integers n_x, n_y and n_z which, as pointed out above, represent the order of diffraction from each of the atom rows.

- A análise de Laue é a extensão da ideia da difração em uma dimensão (uma “linha de átomos”) para as três dimensões...

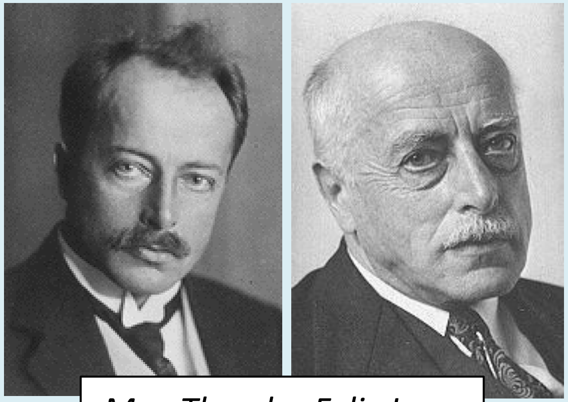
- A análise de Laue tem a desvantagem de ser pouco prática... → necessita calcular 12 parâmetros (seis ângulos: α_0, α_n, β_0, β_n, γ_0, γ_n; três parâmetros de rede: a, b, c; e três integradores: n_x, n_y, n_z), e, por essa razão, teve menos sucesso do que a abordagem de Bragg *(muito mais simples e prática, mesmo não correspondendo exatamente à realidade física do fenômeno...)*.

- Por essa razão, focaremos o curso na análise da difração segundo o modelo de Bragg...

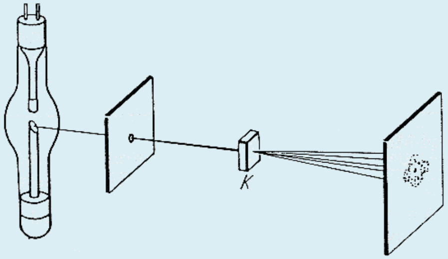
Fonte: Hammond, C. The Basics of Crystallography and Diffraction. 2015. Caps. 8.

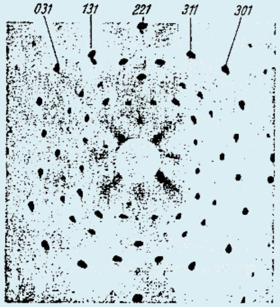
After the preliminary survey of the physics of x-rays and the geometry of crystals, this chapter will fit the two together and discuss the phenomenon of x-ray diffraction, which is an interaction of the two. Historically, this is exactly the way this field of science developed. For many years, mineralogists and crystallographers had accumulated knowledge about crystals, chiefly by measurement of interfacial angles, chemical analysis, and determination of physical properties. There was little knowledge of interior structure, however, although some very shrewd guesses had been made, namely, that crystals were built up by periodic repetition of some unit, probably an atom or molecule, and that these units were situated some 1 or 2 Å apart. On the other hand, there were indications, but only indications, that x-rays might be electromagnetic waves about 1 or 2 Å in wavelength. In addition, the phenomenon of diffraction was well understood, and it was known that diffraction, as of visible light by a ruled grating, occurred whenever wave motion encountered a set of regularly spaced scattering objects, provided that the wavelength of the wave motion was of the same order of magnitude as the repeat distance between the scattering centers.

Fonte: Cullity, B.D.; Stock, S.R. Elements of X-Ray Diffraction. 3ª Ed. 2014. Cap. 3.

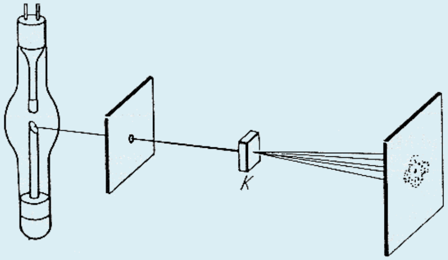


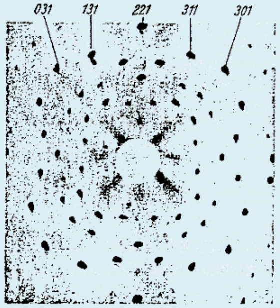
Max Theodor Felix Laue
★1879 - †1960

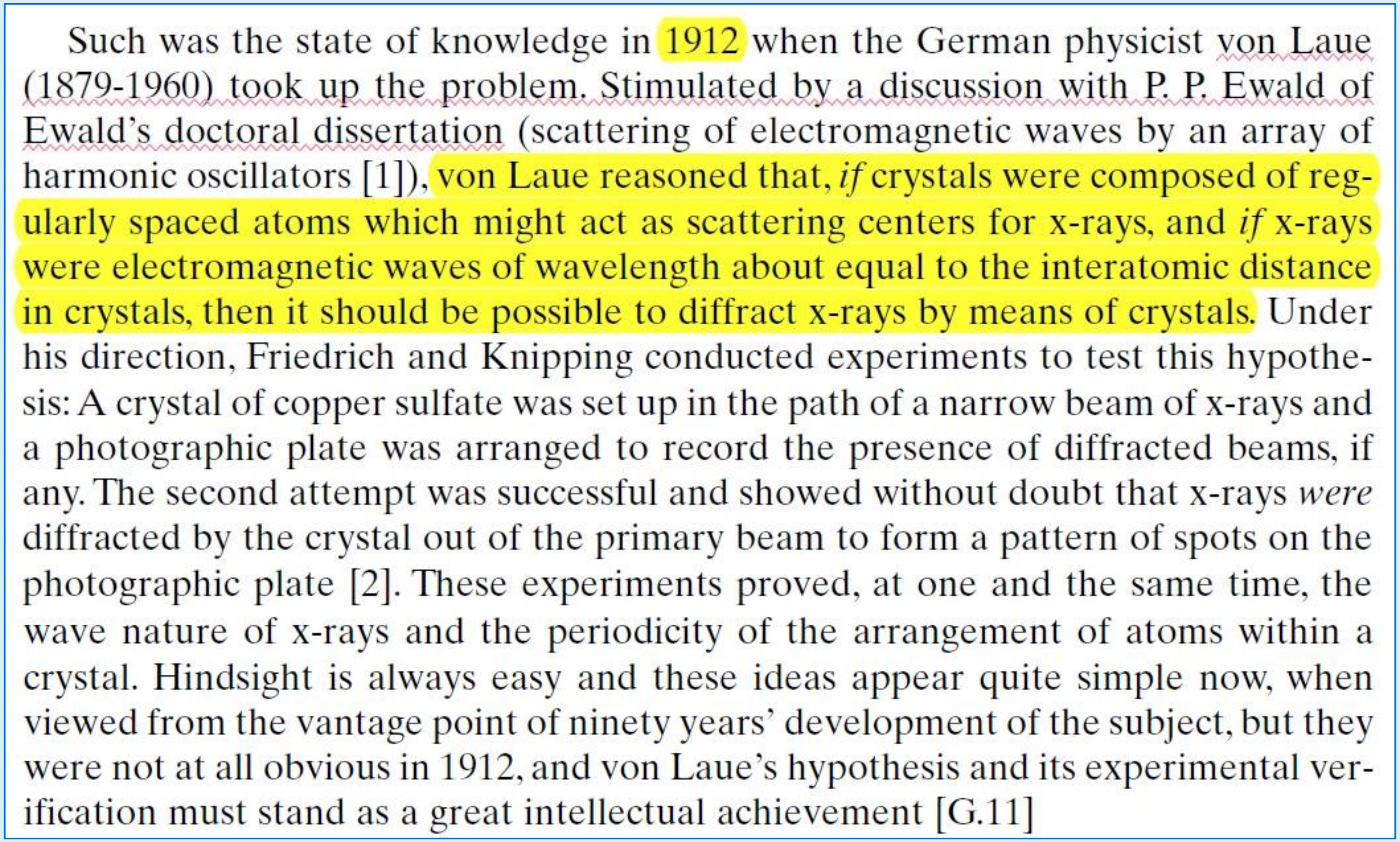




Paul Peter Ewald
★1888 - †1985

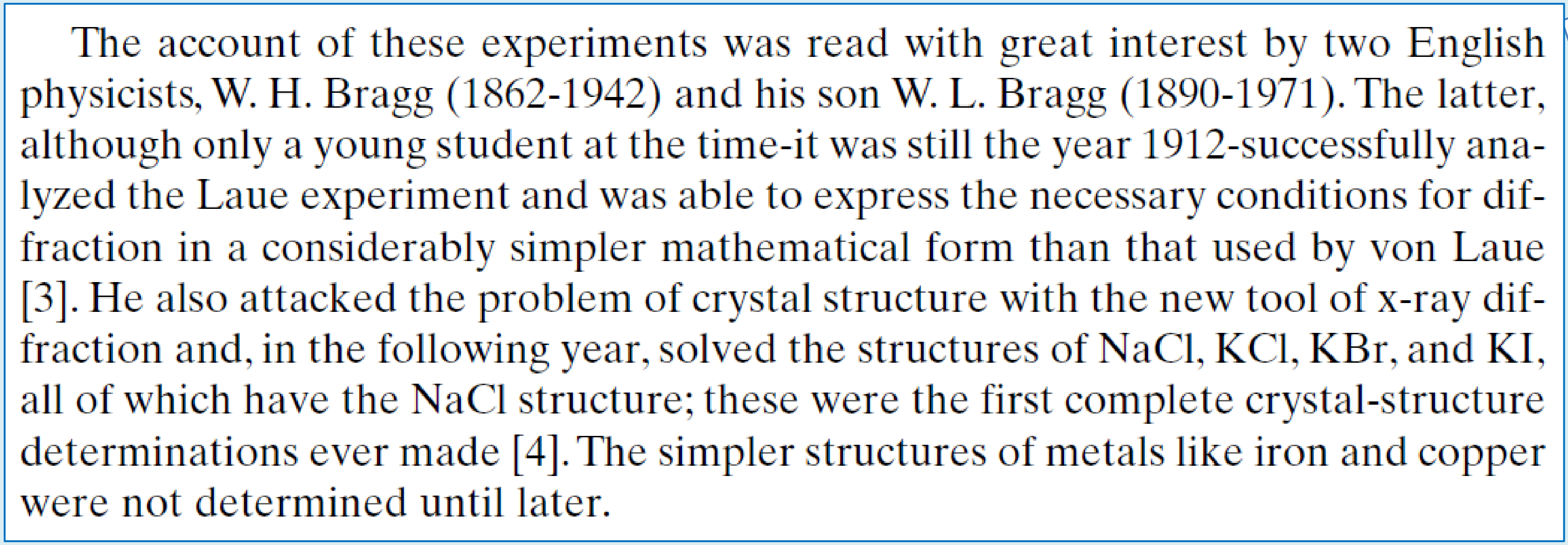






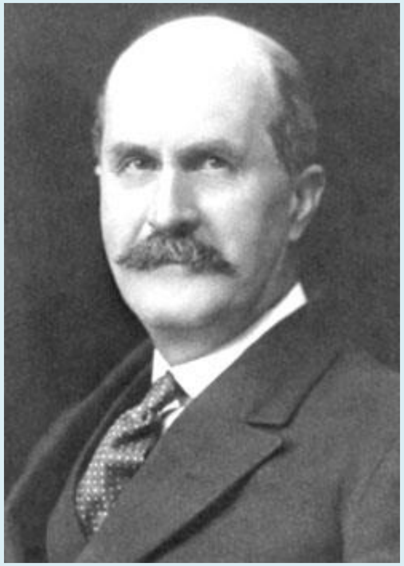
Such was the state of knowledge in 1912 when the German physicist von Laue (1879-1960) took up the problem. Stimulated by a discussion with P. P. Ewald of Ewald's doctoral dissertation (scattering of electromagnetic waves by an array of harmonic oscillators [1]), von Laue reasoned that, *if* crystals were composed of regularly spaced atoms which might act as scattering centers for x-rays, and *if* x-rays were electromagnetic waves of wavelength about equal to the interatomic distance in crystals, then it should be possible to diffract x-rays by means of crystals. Under his direction, Friedrich and Knipping conducted experiments to test this hypothesis: A crystal of copper sulfate was set up in the path of a narrow beam of x-rays and a photographic plate was arranged to record the presence of diffracted beams, if any. The second attempt was successful and showed without doubt that x-rays *were* diffracted by the crystal out of the primary beam to form a pattern of spots on the photographic plate [2]. These experiments proved, at one and the same time, the wave nature of x-rays and the periodicity of the arrangement of atoms within a crystal. Hindsight is always easy and these ideas appear quite simple now, when viewed from the vantage point of ninety years' development of the subject, but they were not at all obvious in 1912, and von Laue's hypothesis and its experimental verification must stand as a great intellectual achievement [G.11]

Fonte: Cullity, B.D.; Stock, S.R. Elements of X-Ray Diffraction. 3^{a} Ed. 2014. Cap. 3.



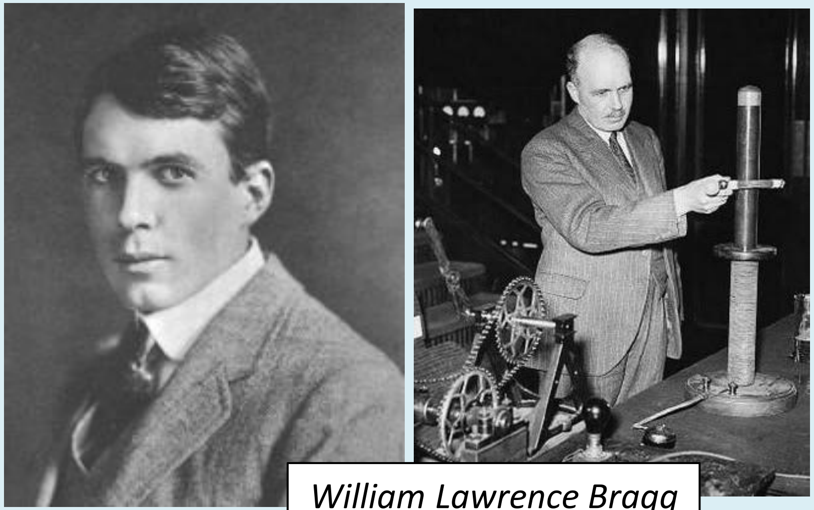
The account of these experiments was read with great interest by two English physicists, W. H. Bragg (1862-1942) and his son W. L. Bragg (1890-1971). The latter, although only a young student at the time-it was still the year 1912-successfully analyzed the Laue experiment and was able to express the necessary conditions for diffraction in a considerably simpler mathematical form than that used by von Laue [3]. He also attacked the problem of crystal structure with the new tool of x-ray diffraction and, in the following year, solved the structures of NaCl, KCl, KBr, and KI, all of which have the NaCl structure; these were the first complete crystal-structure determinations ever made [4]. The simpler structures of metals like iron and copper were not determined until later.

Fonte: Cullity, B.D.; Stock, S.R. Elements of X-Ray Diffraction. 3ª Ed. 2014. Cap. 3.



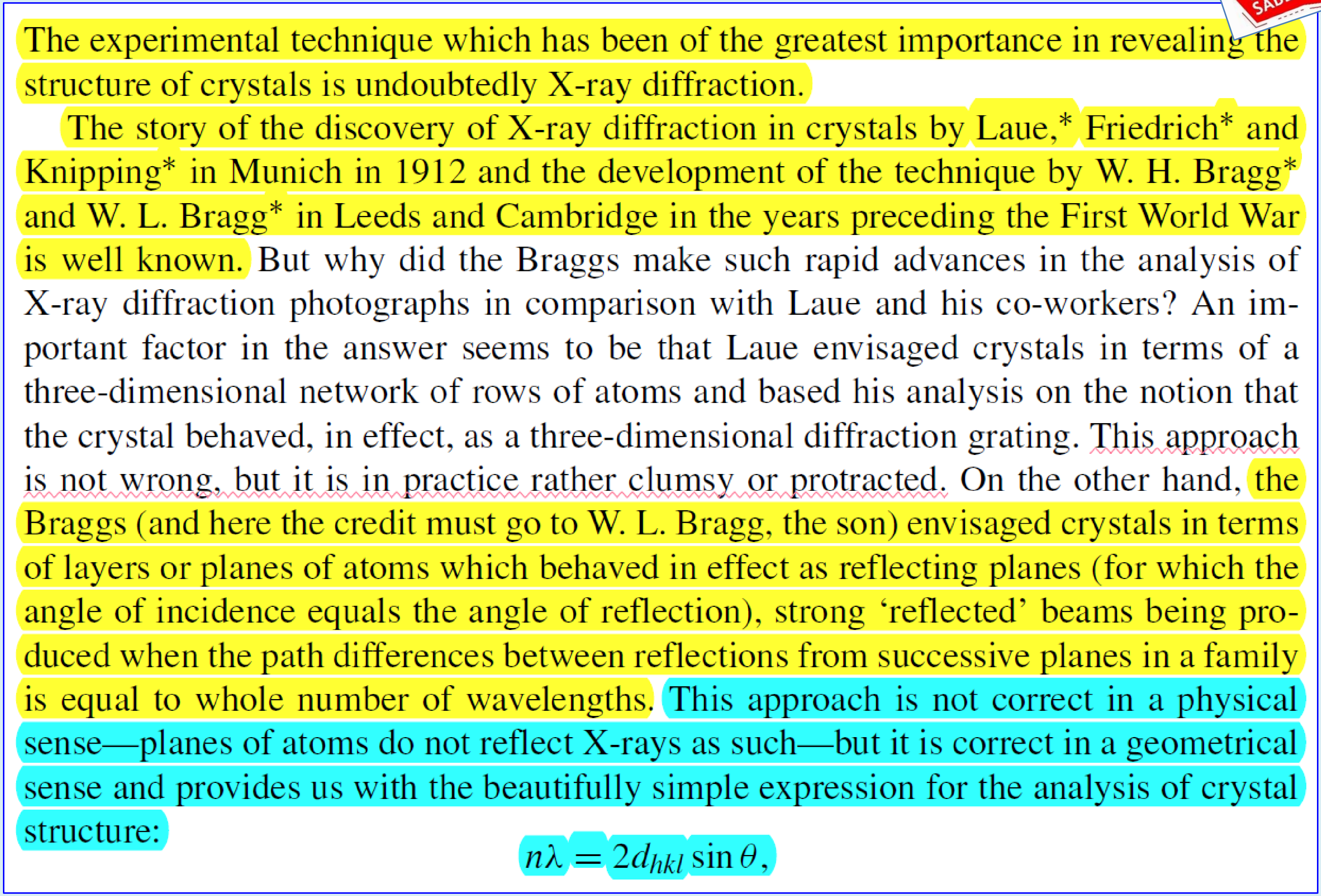
William Henry Bragg
★1862 - †1942

Espectrômetro de RX
de W.H. Bragg



William Lawrence Bragg
★1890 - †1971

Fonte das Fotos: Wikipedia



The experimental technique which has been of the greatest importance in revealing the structure of crystals is undoubtedly X-ray diffraction.

The story of the discovery of X-ray diffraction in crystals by Laue,* Friedrich* and Knipping* in Munich in 1912 and the development of the technique by W. H. Bragg* and W. L. Bragg* in Leeds and Cambridge in the years preceding the First World War is well known. But why did the Braggs make such rapid advances in the analysis of X-ray diffraction photographs in comparison with Laue and his co-workers? An important factor in the answer seems to be that Laue envisaged crystals in terms of a three-dimensional network of rows of atoms and based his analysis on the notion that the crystal behaved, in effect, as a three-dimensional diffraction grating. This approach is not wrong, but it is in practice rather clumsy or protracted. On the other hand, the Braggs (and here the credit must go to W. L. Bragg, the son) envisaged crystals in terms of layers or planes of atoms which behaved in effect as reflecting planes (for which the angle of incidence equals the angle of reflection), strong 'reflected' beams being produced when the path differences between reflections from successive planes in a family is equal to whole number of wavelengths. This approach is not correct in a physical sense—planes of atoms do not reflect X-rays as such—but it is correct in a geometrical sense and provides us with the beautifully simple expression for the analysis of crystal structure:

$$n\lambda = 2d_{hkl}\sin\theta,$$

Fonte: Hammond, C. The Basics of Crystallography and diffraction. 2015. Caps. 8.

A Lei de Bragg

- A análise de Bragg é muito mais simples e prática do que a abordagem de Laue *(que precede este slide, e que não foi discutida na aula presencial...)*.
- A análise de Bragg considera que os cristais são constituídos por planos de átomos.
- A análise de Bragg se aplica independentemente da posição dos átomos nos planos → objetivamente, só a ***distância entre os planos*** precisa ser considerada → as distâncias entre planos cristalográficos são extremamente úteis para o estudo de estruturas cristalinas.
- *A lei de Bragg é completamente representeada em duas dimensões*, como veremos no esquema a seguir → os raios incidentes, os raios "refletidos" (difratados) e a normal aos planos cristalinos estão todos no mesmo plano *(o plano do papel ou da tela...).*

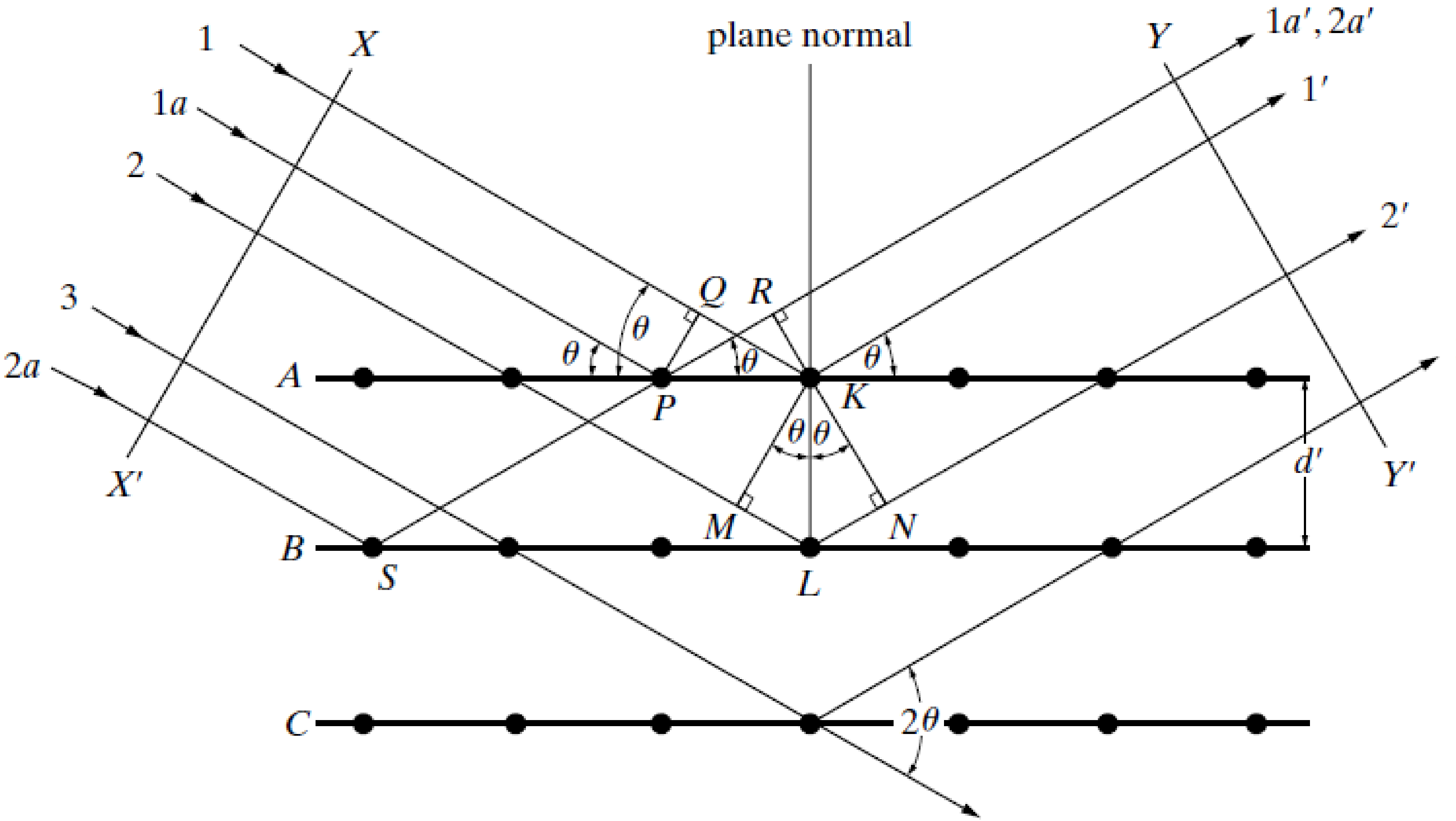
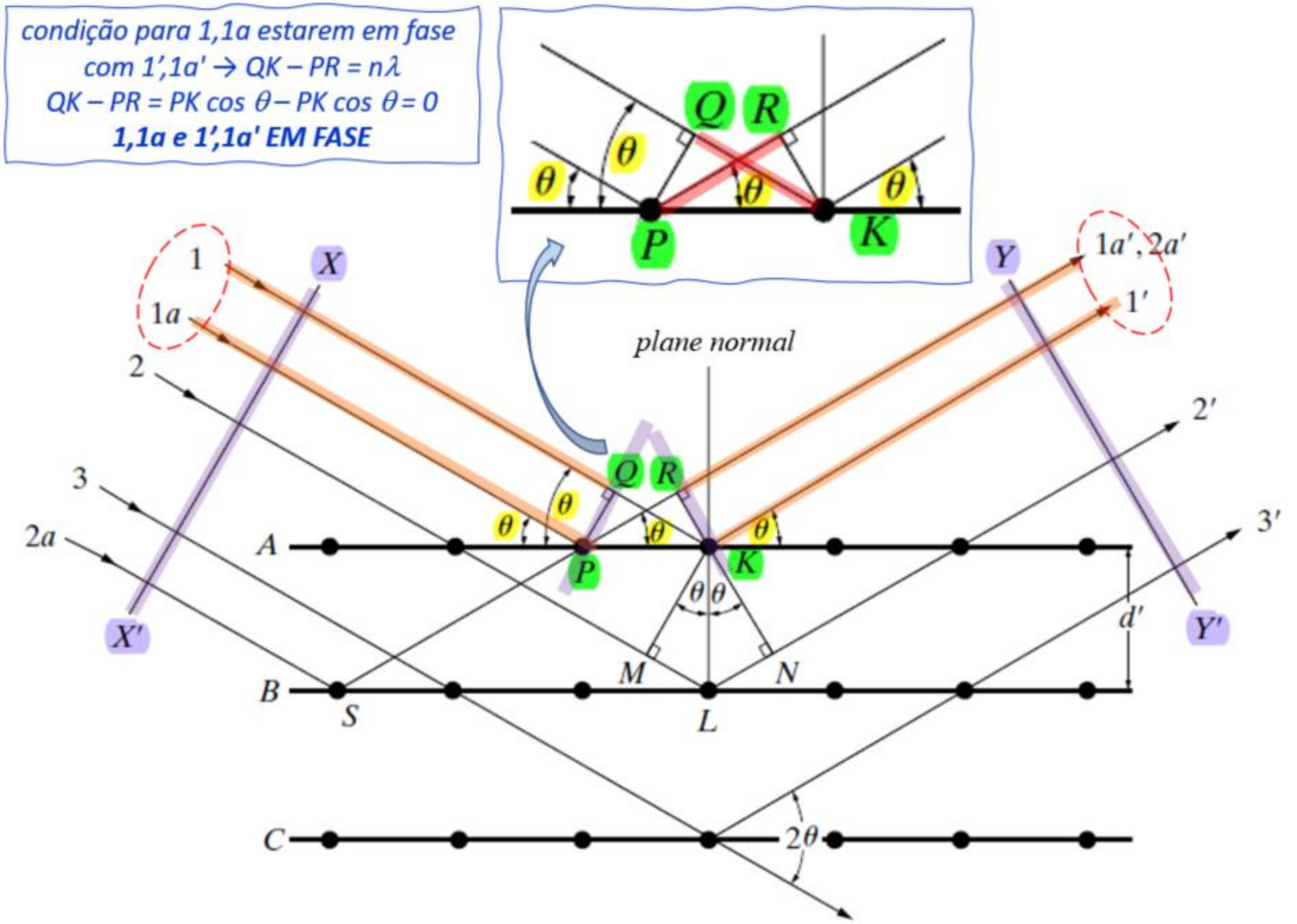


Figure 2 Diffraction of x-rays by a crystal.

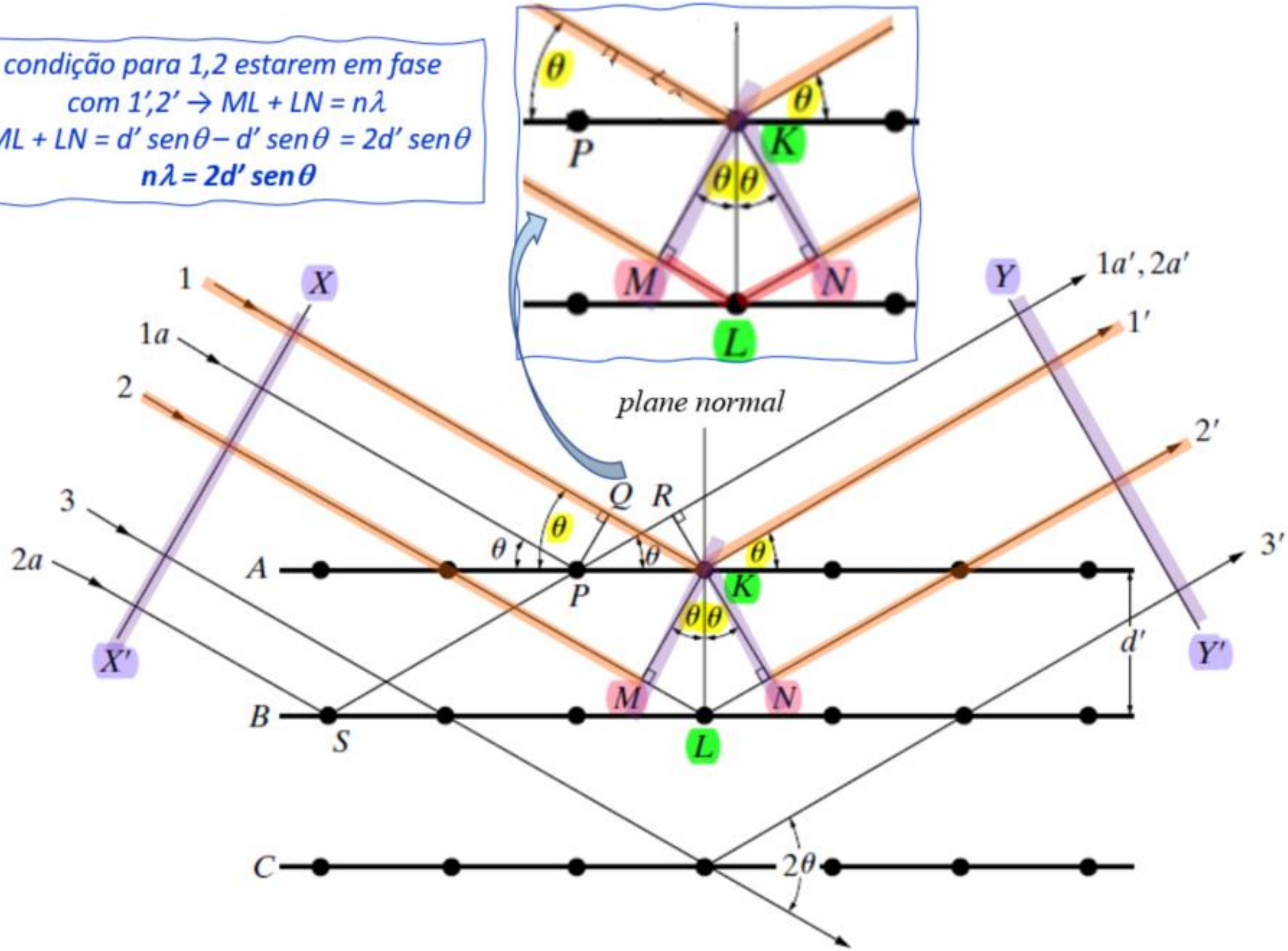
Fonte: Cullity, B.D.; Stock, S.R. Elements of X-Ray Diffraction. 3ª Ed. 2014. Cap. 3.



condição para 1,1a estarem em fase
com 1',1a' → $QK - PR = n\lambda$
$QK - PR = PK\cos\theta - PK\cos\theta = 0$
1,1a e 1',1a' EM FASE

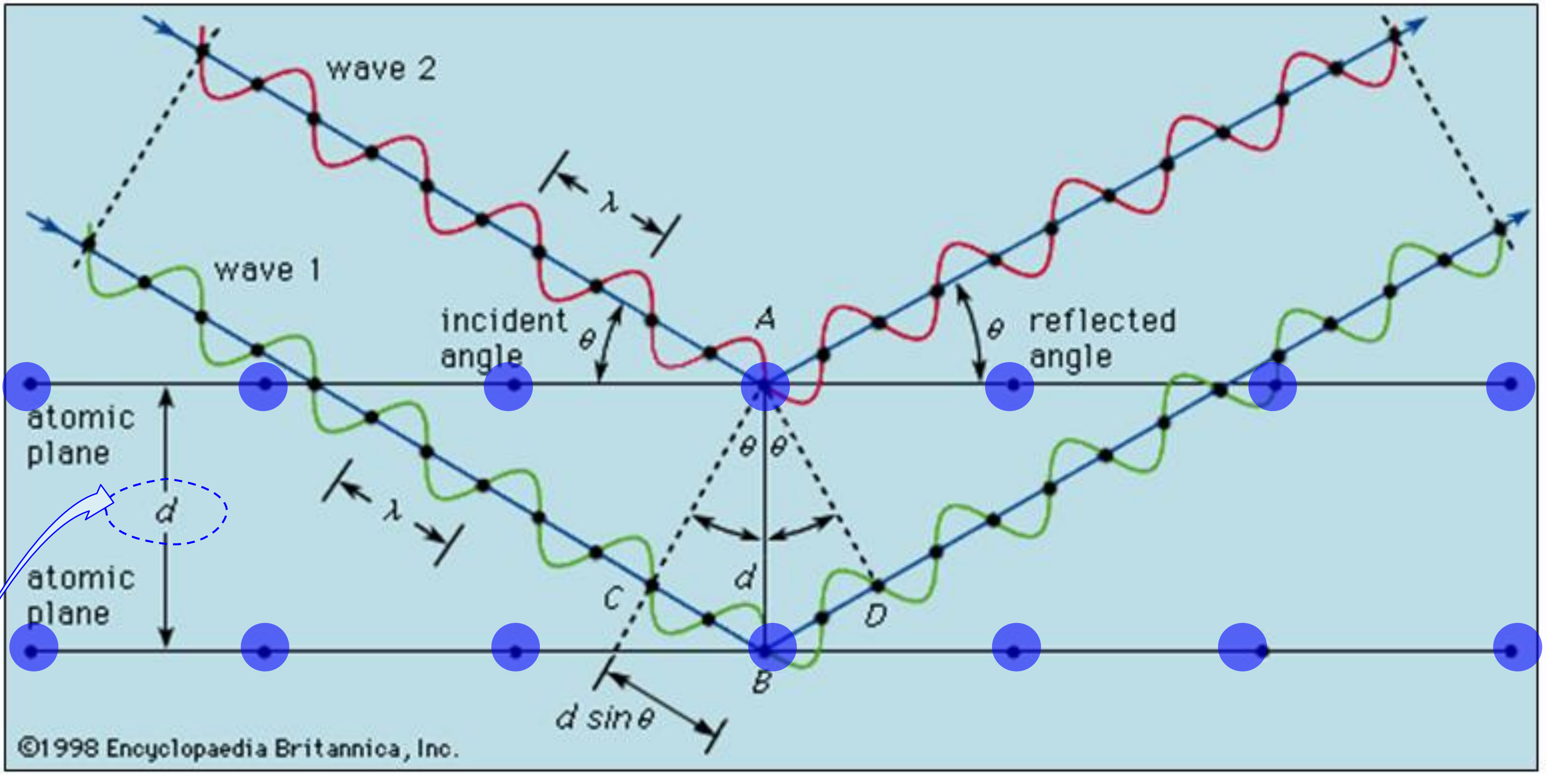
- Todos os raios X espalhados por átomos que estão no primeiro plano atômico (plano A) que tenham direção paralela a 1' estão em fase, interagem de forma construtiva e dão contribuições para o feixe difratado → isso é verdade para todos os planos separadamente.
- No entanto, esse feixe difratado não fornece informação a respeito da estrutura do cristal sobre o qual incidem os raios X → não diz nada a respeito do espaçamento entre os planos cristalinos...

condição para 1,2 estarem em fase
com 1',2' → $ML + LN = n\lambda$
$ML + LN = d' \operatorname{sen}\theta - d' \operatorname{sen}\theta = 2d' \operatorname{sen}\theta$
$n\lambda = 2d' \operatorname{sen}\theta$



- Considerando os raios X espalhados por planos distintos superpostos em um cristal, como por exemplo os planos A e B na figura → o raio 1 é interage com o átomo K situado no plano A, e o raio 2, com o átomo L situado no plano B.
- o percurso 2-2' é maior do que o percurso 1-1' – se a distância (ML+LN) for igual a um número inteiro de comprimentos de onda l, os raios 1' e 2' estarão em fase na frente de onda YY'.
- *Essa relação foi formulada pela primeira vez por W. L. Bragg em 1912.*

Lei de Bragg



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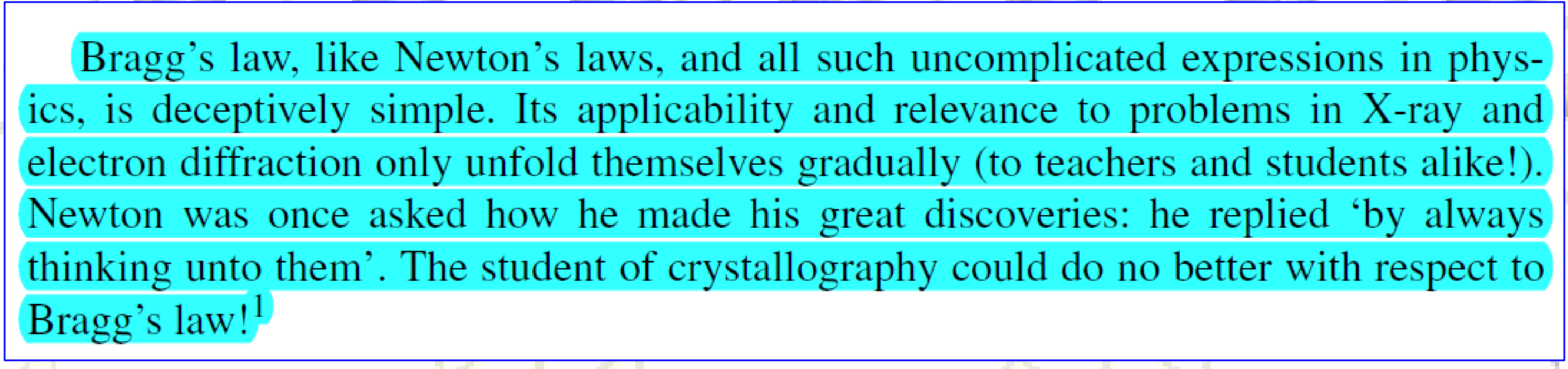
A lei de Bragg fornece informações fundamentais para o estudo das estruturas cristalinas, pois permite a determinação dos espaçamentos entre os planos cristalinos (d) .

BRAGG LAW

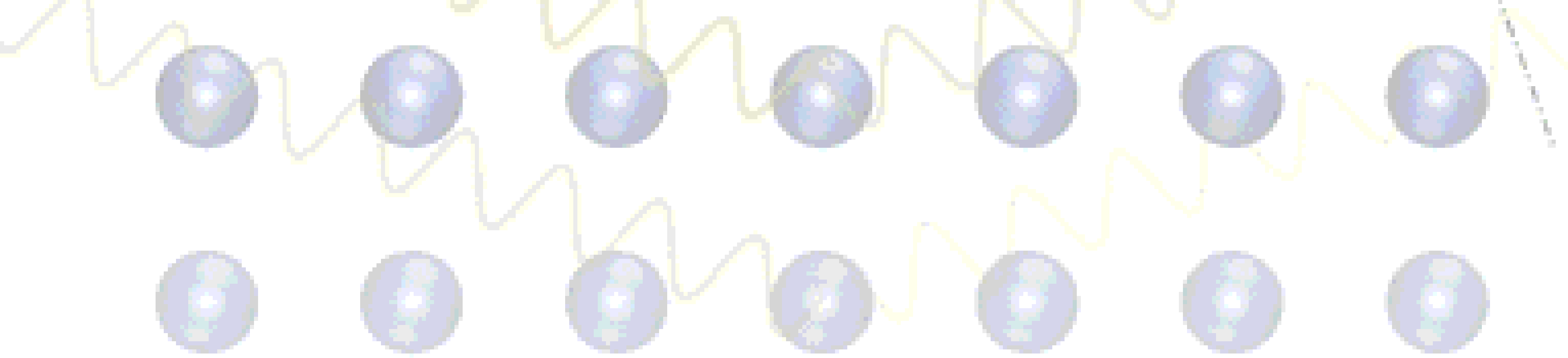
$$2d(\sin\theta) = \lambda_o$$

where:

d = lattice interplanar spacing of the crystal
θ = x-ray incidence angle (Bragg angle)
λ = wavelength of the characteristic x-rays



Bragg’s law, like Newton’s laws, and all such uncomplicated expressions in physics, is deceptively simple. Its applicability and relevance to problems in X-ray and electron diffraction only unfold themselves gradually (to teachers and students alike!). Newton was once asked how he made his great discoveries: he replied ‘by always thinking unto them’. The student of crystallography could do no better with respect to Bragg’s law![1]



Fontes: Hammond, C. The Basics of Crystallography and diffraction. 2015. Caps. 8.
https://www.xtal.iqfr.csic.es/Cristalografia/archivos_05/braggslaw1.gif

Exercício

Mostre que a lei de Bragg vale tanto para um reticulado cristalino ortogonal *(sistemas cúbico, tetragonal, ortorrômbico – representados pela Fig.8.3 (a) abaixo)*, quanto para um reticulado não-ortogonal – como por exemplo o caso mais geral de um reticulado monoclínico representado na Fig 8.3 (b).

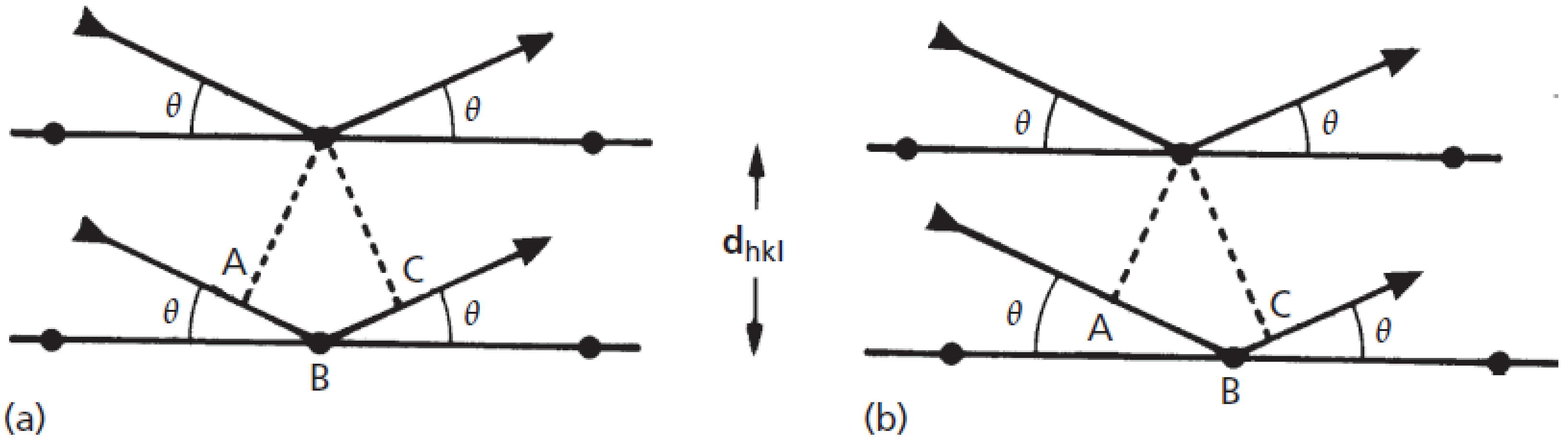


Fig. 8.3. (a) Bragg's law for the case of a rectangular grid, i.e. AB $=$ BC $= d_{hkl} \sin\theta$; the path difference (AB $+$ BC) $= 2d_{hkl} \sin\theta$. (b) Bragg's law for the general case in which AB $\neq$ BC.

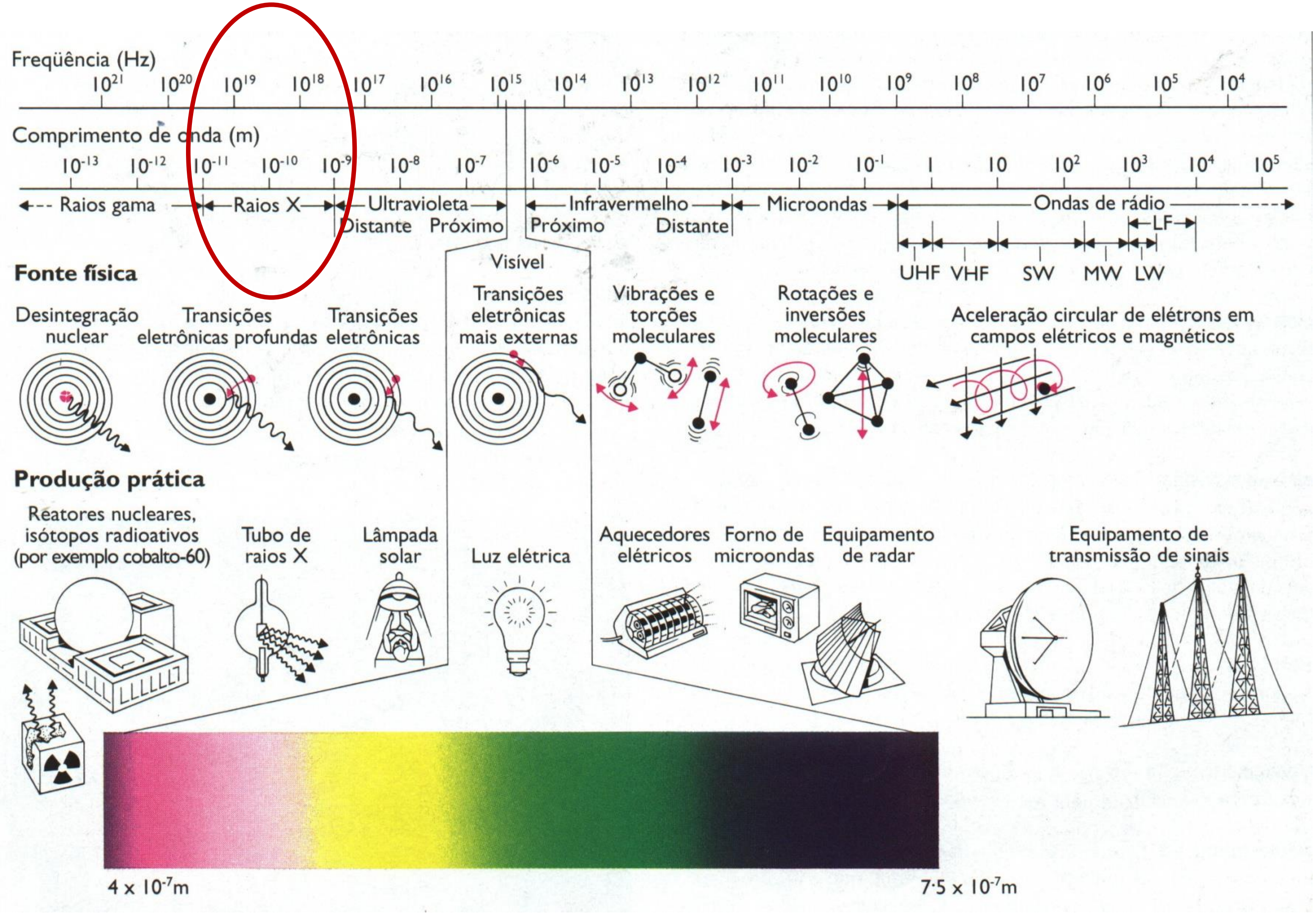
... continue depois de tentar fazer o exercício...

A resolução de todos os exercícios desta unidade se encontra em um arquivo separado na página da disciplina.

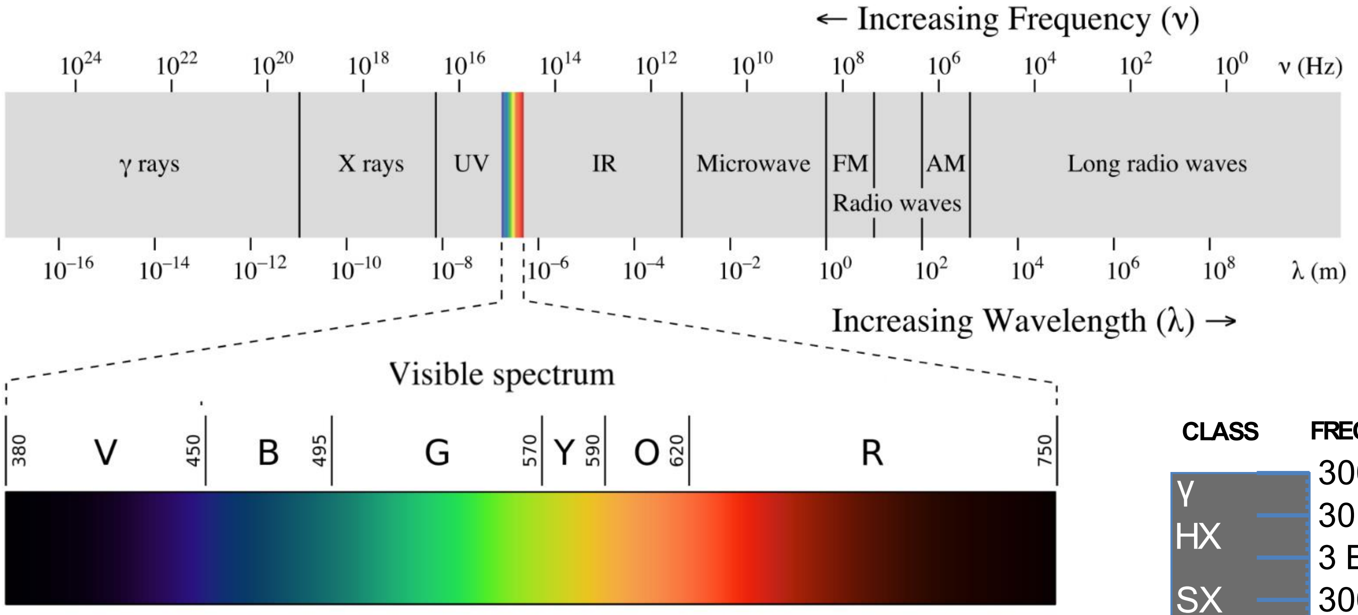
...porque raios X e não luz visível ?

- Ao fenômeno de difração, para ocorrer, necessita: *(i)* de centros de espalhamento de onda *("scattering centers")* que se distribuam no espaço de acordo com um padrão repetitivo; *(ii)* que o comprimento de onda da radiação incidente seja da mesma ordem de grandeza da distância que existe entre os centros de espalhamento.
- Escrevendo a lei de Bragg de uma outra forma: $\frac{n\lambda}{2d} = sen\theta$
- Como $sen\theta \leq 1$, assumindo reflexão de primeira ordem *(n = 1)*, chegamos a $\lambda \leq 2d$.
- Considerando que o espaçamento entre planos em cristais é da ordem de 3 Å ou menos, isso significa que o comprimento de onda da radiação incidente para que seja observada difração em cristais deve ser $\lambda \leq 6$ Å = 0,6 nm → os próximos slides mostram que essa é faixa de comprimento de onda dos raios X...
- Na prática, não somente raios X podem ser utilizados para se obter informações de estruturas cristalinas – elétrons e nêutrons de alta energia *("high energy electrons and neutrons")* também podem ser empregados para essa finalidade.
- A luz visível e a radiação UV tem comprimentos de onda muito grandes → não interagem com os átomos de uma estrutura cristalina provocando difração...

Espectro Eletromagnético



O Espectro Eletromagnético



Legend:
γ = Gamma rays

HX = Hard X-rays
SX = Soft X-Rays

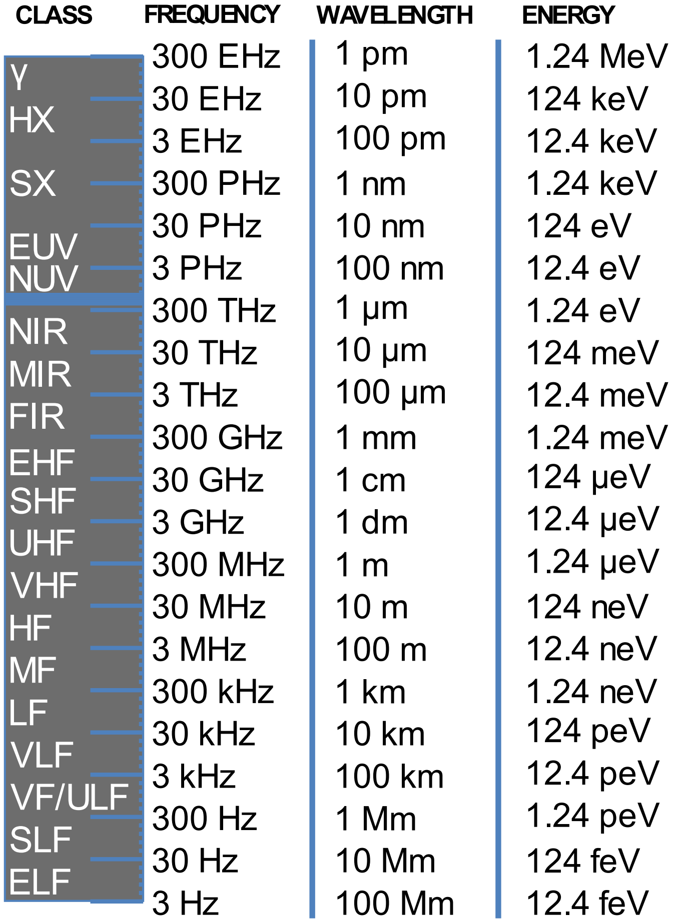
EUV = Extreme-ultraviolet
NUV = Near-ultraviolet

Visible light (colored bands)

NIR = Near-infrared
MIR = Mid-infrared
FIR = Far-infrared

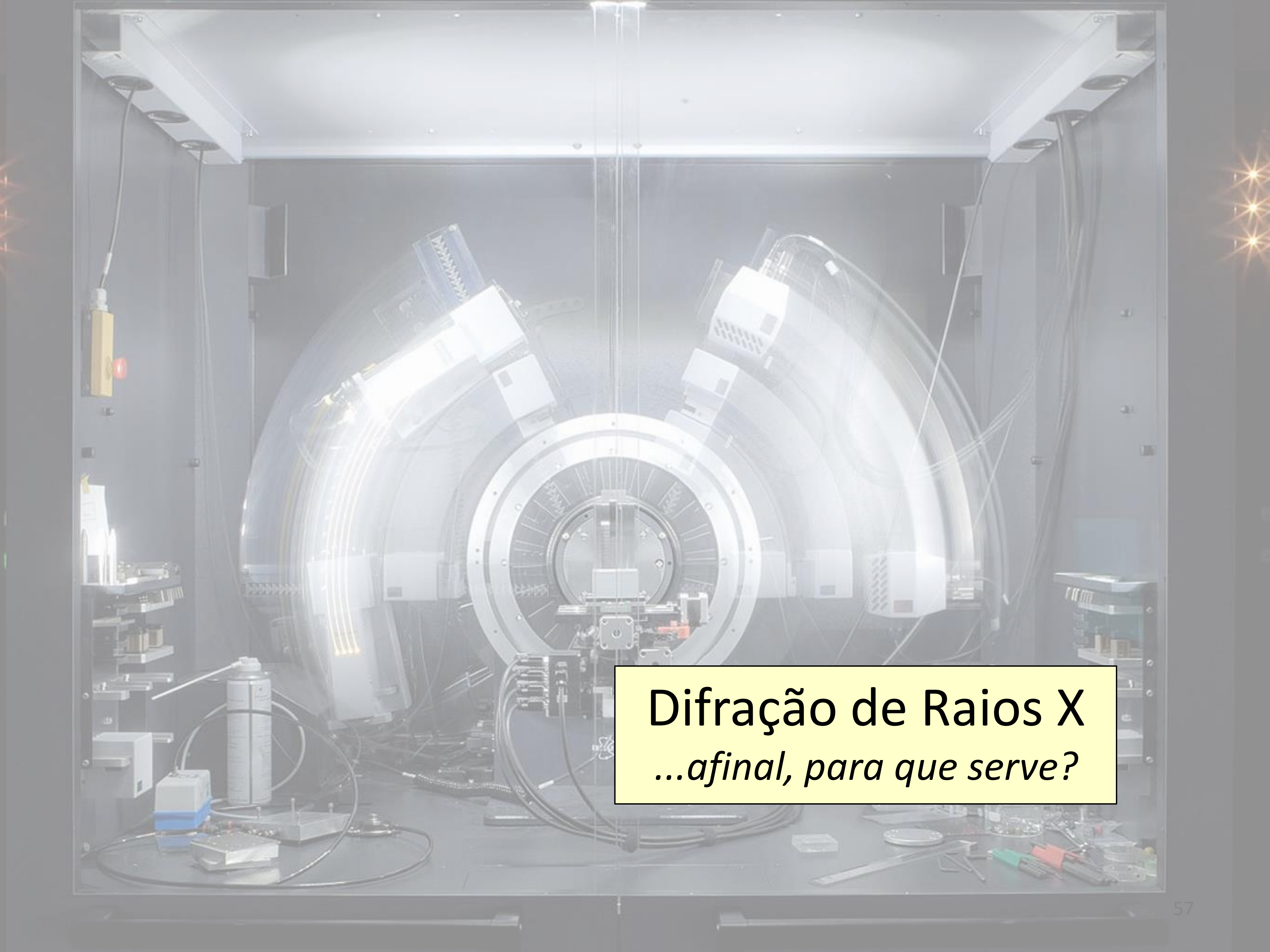
EHF = Extremely high frequency (microwaves)
SHF = Super-high frequency (microwaves)

UHF = Ultrahigh frequency (radio waves)
VHF = Very high frequency (radio)
HF = High frequency (radio)
MF = Medium frequency (radio)
LF = Low frequency (radio)
VLF = Very low frequency (radio)
VF = Voice frequency
ULF = Ultra-low frequency (radio)
SLF = Super-low frequency (radio)
ELF = Extremely low frequency (radio)



CLASS	FREQUENCY	WAVELENGTH	ENERGY
γ	300 EHz	1 pm	1.24 MeV
HX	30 EHz	10 pm	124 keV
	3 EHz	100 pm	12.4 keV
SX	300 PHz	1 nm	1.24 keV
EUV	30 PHz	10 nm	124 eV
NUV	3 PHz	100 nm	12.4 eV
NIR	300 THz	1 μm	1.24 eV
MIR	30 THz	10 μm	124 meV
FIR	3 THz	100 μm	12.4 meV
EHF	300 GHz	1 mm	1.24 meV
SHF	30 GHz	1 cm	124 μeV
UHF	3 GHz	1 dm	12.4 μeV
VHF	300 MHz	1 m	1.24 μeV
HF	30 MHz	10 m	124 neV
MF	3 MHz	100 m	12.4 neV
LF	300 kHz	1 km	1.24 neV
VLF	30 kHz	10 km	124 peV
VF/ULF	3 kHz	100 km	12.4 peV
SLF	300 Hz	1 Mm	1.24 peV
ELF	30 Hz	10 Mm	124 feV
	3 Hz	100 Mm	12.4 feV

Fonte: https://en.wikipedia.org/wiki/Electromagnetic_radiation



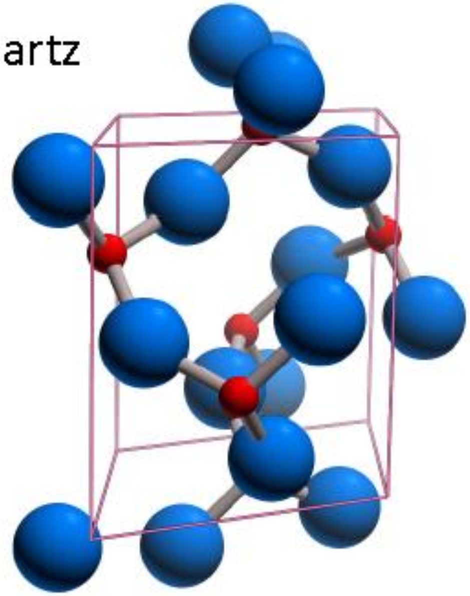
Difração de Raios X

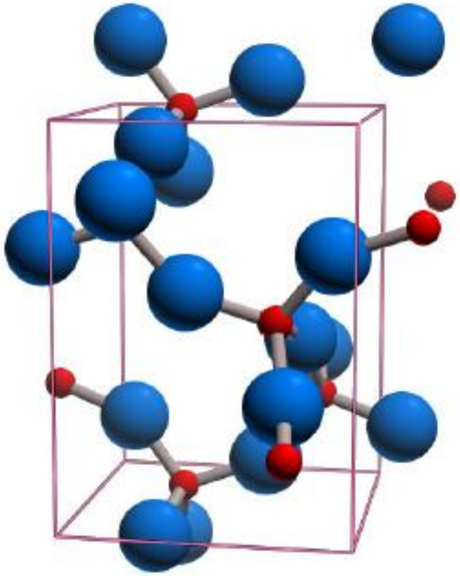
...afinal, para que serve?

A curva de DRX de um material é resultado de sua estrutura cristalina

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

Quartz





Cristobalite

- 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)

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

O que se pode fazer com DRX

- 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
- 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)*

Composição Mineralógica (quantitativa)

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

...finalizando : Difração: Fundamentos

- Ao final do estudo dos conteúdos desta Unidade você deve ser capaz de:
    - descrever qualitativamente os fenômenos de interferência construtiva e destrutiva de ondas;
    - descrever qualitativamente os fenômenos de espalhamento e difração de ondas;
    - deduzir geometricamente a lei de Bragg;
    - construir geometricamente a esfera de Ewald para um dado reticulado recíproco de um cristal, sendo dado o comprimento de onda da radiação que incide sobre esse dado cristal.
    - ter uma noção preliminar de que informações são possíveis de ser obtidas por meio da difração de raios X.

Referências

- **Hammond, C.** The Basics of Crystallography and diffraction. 4th Ed. IUCr / Oxford U. Press. Oxford (UK). 2015. Cap. 8.
- **Cullity, B.D.; Stock, S.R.** Elements of X-Ray Diffraction. 3ª Ed. Pearson. 2014. Cap. 3.
- **CSIC.** Crystallography in a nutshell, 5. Scattering and diffraction *(consultado em fevereiro/2023)* : https://www.xtal.iqfr.csic.es/Cristalografia/index-en.html
- **University of Cambridge.** DoITPoMS - Reciprocal Space *(consultado em fevereiro/2023)*: https://www.doitpoms.ac.uk/tlplib/reciprocal_lattice/index.php ; X-Ray Diffraction Techniques *(consultado em fevereiro/2023)*: https://www.doitpoms.ac.uk/tlplib/xray-diffraction/index.php
- **Speakman, S. A.** Basics of X-Ray Powder Diffraction. *(consultado em fevereiro/2023)* : http://prism.mit.edu/rxay