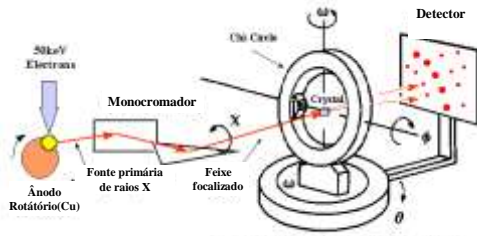


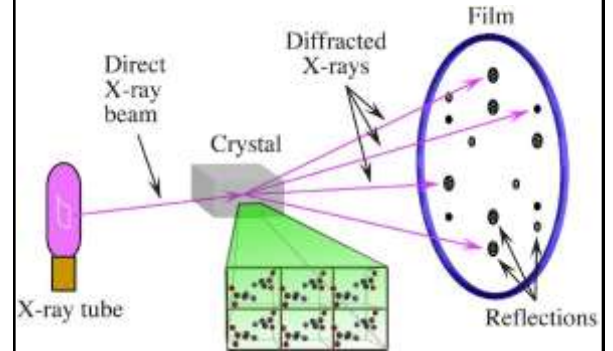
Representação esquemática da fonte de raios X



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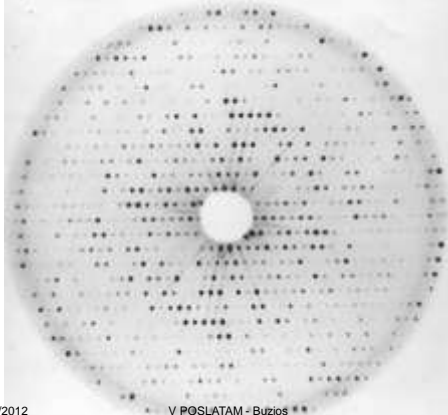
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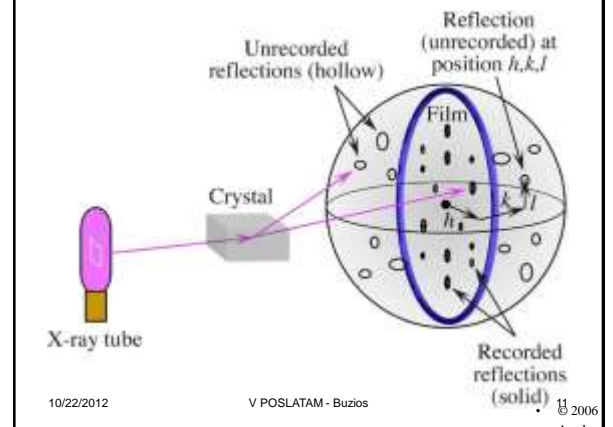
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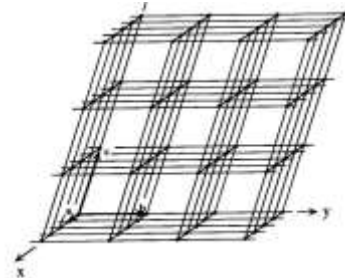
Rede cristalina

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A crystal lattice is a 3-D stack of unit cells

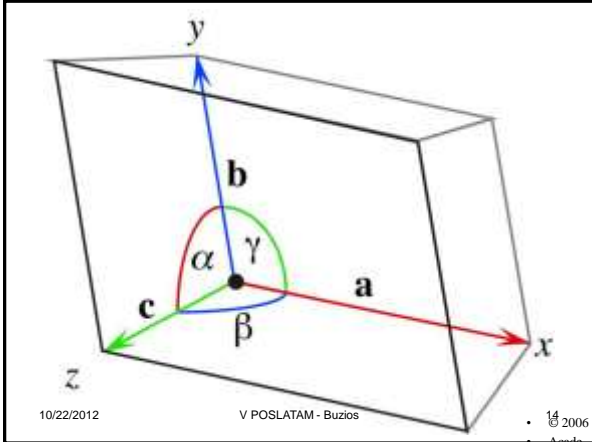


Crystal lattice is an imaginative grid system in three dimensions in which every point (or node) has an environment that is identical to that of any other point or node.

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Miller indices

A Miller index is a series of coprime integers that are inversely proportional to the intercepts of the crystal face or crystallographic planes with the edges of the unit cell.

It describes the orientation of a plane in the 3-D lattice with respect to the axes.

The general form of the Miller index is (h, k, l) where h, k, and l are integers related to the unit cell along the a, b, c crystal axes.

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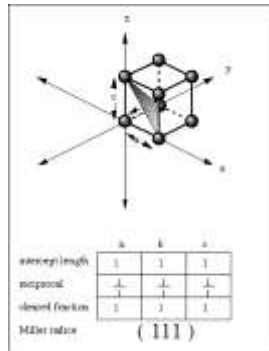
15

Miller Indices

Rules for determining Miller Indices:

1. Determine the intercepts of the face along the crystallographic axes, in terms of unit cell dimensions.
2. Take the reciprocals
3. Clear fractions
4. Reduce to lowest terms

An example of the (111) plane (h=1, k=1, l=1) is shown on the right.



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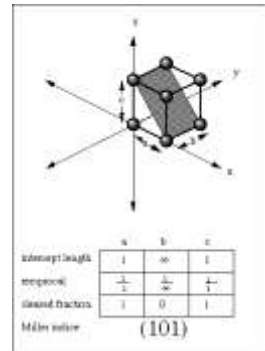
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Another example:

Rules for determining Miller Indices:

1. Determine the intercepts of the face along the crystallographic axes, in terms of unit cell dimensions.
2. Take the reciprocals
3. Clear fractions
4. Reduce to lowest terms



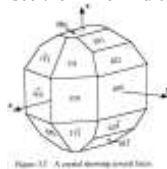
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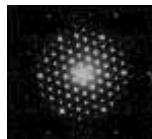
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Where does a protein crystallographer see the Miller indices?

• Common crystal faces are parallel to lattice planes



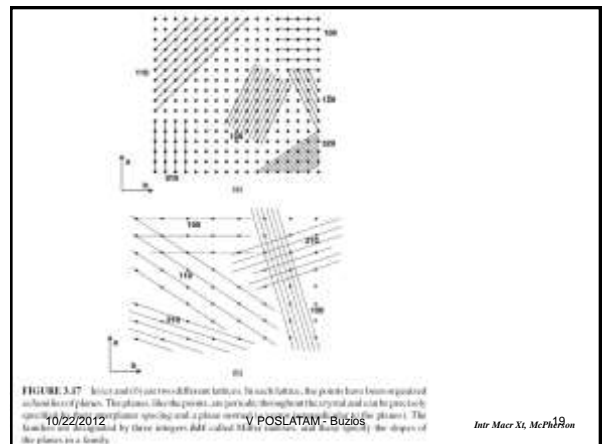
• Each diffraction spot can be regarded as a X-ray beam reflected from a lattice plane, and therefore has a unique Miller index.



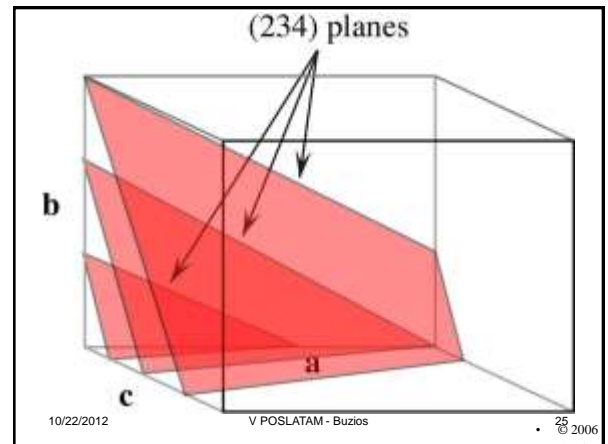
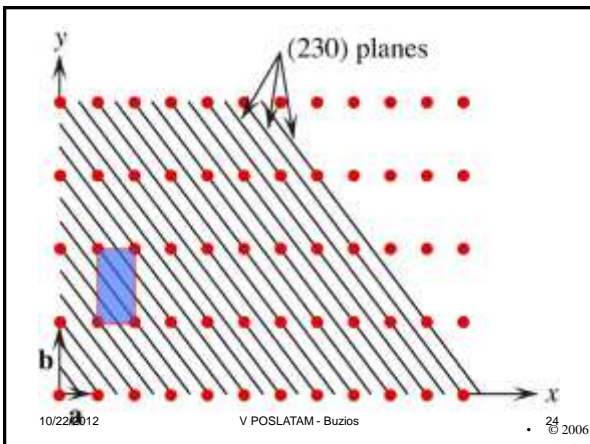
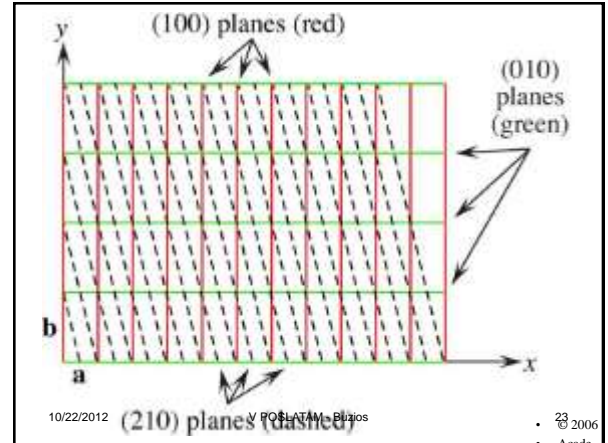
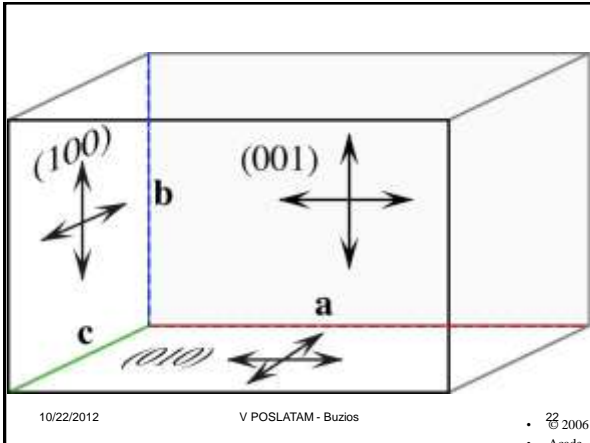
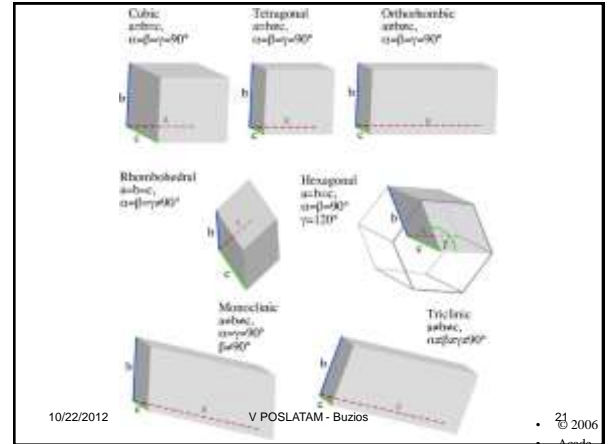
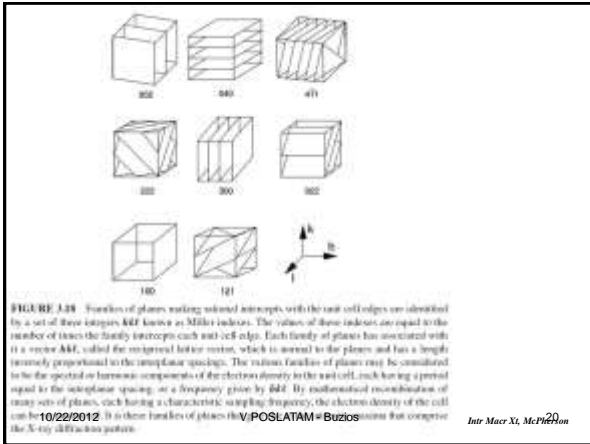
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18



Intr. Macr. XI, McPherson



Onda

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$$f(x) = F \cos 2\pi (kx + a)$$

$$f(x) = F \sin 2\pi (kx + a)$$

In these functions, $F(x)$ specifies the vertical height of the wave at any horizontal position x along the wave. The variable x and the constant a are angles expressed in fractions of the wavelength, that is, $x = \lambda$ implies a position of one full wavelength (2π radians or 360°) from the origin. The constant F specifies the amplitude (the height of the crests and troughs) of the wave. For example, the crests of the wave $f(x) = 3 \cos 2\pi x$ are three times as high and the troughs are three times as deep as those of the wave $f(x) = \cos 2\pi x$ (compare to with in Fig. 2.13).

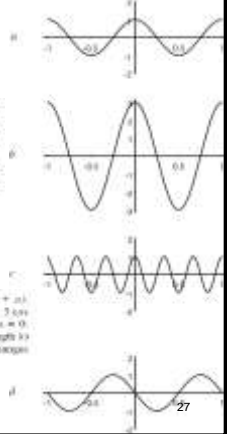
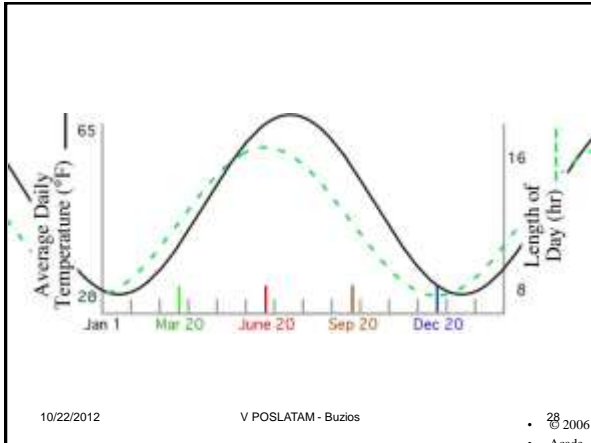


Figure 2.13 Graphs of four simple wave equations $f(x) = F \cos 2\pi(kx + a)$: (a) $F = 3, k = 1, a = \pi/4$; (b) $F = 1, k = 1, a = 0$; (c) $F = 1/2, k = 1, a = 0$; (d) $F = 1, k = 3, a = 0$. Increasing F increases the amplitude of the wave. Increasing k increases the frequency (or decreases the wavelength λ) of the wave. Changing a changes the phase (position) of the wave.

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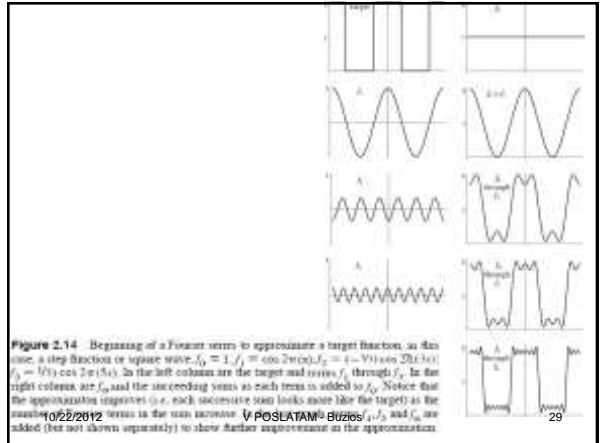


Figure 2.14 Beginning of a Fourier series to approximate a target function as the sum of a step function or square wave. $f_0 = 1, f_1 = \cos 2\pi(x), f_2 = 1/4 \cos 4\pi(x), f_3 = 1/9 \cos 6\pi(x), f_4 = 1/16 \cos 8\pi(x)$. In the left column are the target and series f_0 through f_4 . In the right column are f_0 and the succeeding sums as each term is added to f_0 . Notice that the approximation approaches f_0 as each successive term looks more like the target as the number of terms increases. **V POSLATAM - Buzios** f_0, f_1 and f_2 are added (but not shown separately) to show further improvement as the approximation.

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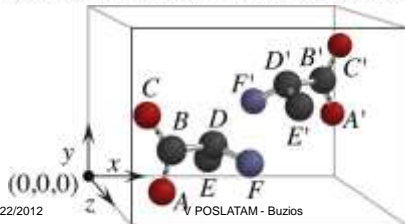
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If diffraction by atom A in Fig. 2.15 is represented by f_A , then one diffracted ray (producing one reflection) from the unit cell of Fig. 2.15 is described by a structure-factor equation of this form:

$$F_{(hkl)} = f_A + f_B + \dots + f_{A'} + f_{B'} + \dots + f_{F'}. \quad (2.3)$$

The structure-factor equation implies, and correctly so, that each reflection on the film is the result of diffractive contributions from all atoms in the unit cell. That is, every atom in the unit cell contributes to every reflection in the diffraction pattern. The structure factor is a wave created by the superposition of many individual waves, each resulting from diffraction by an individual atom.



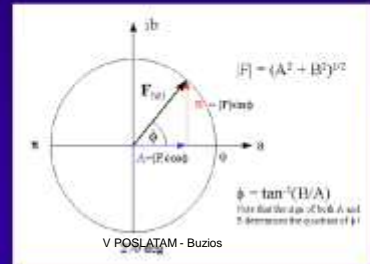
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Calculation of structure factors

$$F_{(hkl)} = \sum_{j=1}^N f_j \exp[2\pi i (hx_{j1} + ky_{j1} + lz_{j1})]$$



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Calculation of Fourier maps

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} \exp[-2\pi i(hx + ky + lz)]$$

Diffraction Experiment

$$I_{hkl} = |F_{hkl}|^2 \cdot LP \cdot A$$



The structure factor and the electron density function are Fourier inverses of one another

$$F_{hkl} = \int_V \rho(x,y,z) \exp[+2\pi i(hx + ky + lz)] dV$$

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} \exp[-2\pi i(hx + ky + lz)]$$

- Note that the electron density is **real** but the structure factor is **complex**.
- The **phase information** must be included in the Fourier synthesis that produces the electron density!
- This has to be recovered, because the **diffraction experiment measures the intensity** of diffraction, which is the square of the structure factor:

Para que a estrutura cristalográfica de um determinado composto (hábil ou anorgânico) possa ser determinada pela técnica de difração de raios-X, é necessário que se estabeleçam relações matemáticas entre o conteúdo da célula e os dados medidos. É possível mostrar que as reflexões de uma estrutura, as grandezas físicas que as expressões recebem o nome de "fator de estrutura" (F_{hkl}). A definição geral para essas grandezas é apresentada na equação 5.3.

$$F_{hkl} = \sum_j f_j(M_j) \exp[2\pi i(hx_j + by_j + cz_j)] = F_{hkl} \exp(i\phi_{hkl}) \quad \text{Eq. 5.3}$$

onde F_{hkl} e ϕ_{hkl} são, respectivamente, de amplitude e fase do fator de estrutura F_{hkl} . Os índices h, k e l que aparecem aqui são os índices de Miller, vistos anteriormente. Os termos $x_j, y_j, z_j = f_j(M_j)$ são as coordenadas atômicas e o fator de espalhamento atômico do j -ésimo átomo (de um total de N átomos) dentro da célula unitária de cristal. O fator de espalhamento atômico $f_j(M_j)$ é uma grandeza que pode ser calculada para cada tipo de átomo, pois é definido por:

$$f_j(M_j) = \int_V \rho_j(x',y',z') \exp[2\pi i(hx' + ky' + lz')] dV' \quad \text{Eq. 5.4}$$

onde $\rho_j(x',y',z')$ é a densidade eletrônica do átomo j e a integral é feita sobre o volume V' do átomo. Assim, se a estrutura cristalográfica de um determinado composto é conhecida a priori, o conteúdo da equação 5.3 permite o cálculo dos valores de F_{hkl} (ou F_{hkl} e ϕ_{hkl}) para cada valor de h, k e l .

uma lista de estruturas quaisquer F_{hkl} para um cristal conhecido nos eixos cartesianos da célula unitária e a representação de F_{hkl} em um plano de Argand.

Acontece naturalmente que, em um experimento de difração de raios-X, o resultado medido, ao seja, a intensidade de cada reflexão de difração é um número real combinado como I_{hkl} . Então, como relacionar F_{hkl} com I_{hkl} ? Pode-se mostrar que o quadrado do módulo do fator de estrutura é diretamente proporcional à intensidade da reflexão medida, de forma que

$$I_{hkl} \propto F_{hkl} \cdot F_{hkl}^* = |F_{hkl}|^2 = F_{hkl} F_{hkl}^* \quad \text{Eq. 5.6}$$

(a) Fator de Estrutura

$$F_{hkl} = \sum_j f_j \exp[2\pi i(hx_j + ky_j + lz_j)] = f_1 \exp[2\pi i(hx_1 + ky_1 + lz_1)] + f_2 \exp[2\pi i(hx_2 + ky_2 + lz_2)] + \dots$$

Outra relação importante a ser considerada é a que estabelece o conexão entre o fator de estrutura F_{hkl} e a densidade eletrônica $\rho(x,y,z)$ dentro da célula unitária de um cristal. A partir das equações 5.3 e 5.4, pode-se demonstrar que

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} \exp[-2\pi i(hx + ky + lz)] \quad \text{Eq. 5.7}$$

ou ainda que

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} \exp[i\phi_{hkl}] \exp[-2\pi i(hx + ky + lz)] \quad \text{Eq. 5.8}$$

onde V é o volume da célula unitária e x, y e z são as coordenadas atômicas de um ponto qualquer dentro da célula unitária.

Difração

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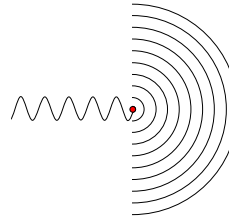
Diffraction: Huygens/Fresnel principle

A small scattering object is a secondary source. The amount of scattering defines the 'scattering cross section'.

Single scatterer:

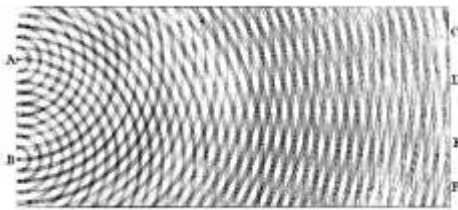
$$F(\mathbf{s}) = \sigma \rho(\mathbf{x}) e^{2\pi i \mathbf{x} \cdot \mathbf{s}}$$

where $F(\mathbf{s})$: intensity scattered in direction ' \mathbf{s} ';
 $\rho(\mathbf{x})$: scattering potential at position ' \mathbf{x} ' (single object: $\mathbf{x}=0$)
 σ : scattering cross section



The emitted radiation is shifted in phase compared to the exciting radiation; the magnitude of the shift ($\pi/2$ to $3\pi/2$) depends on the frequency of the incoming radiation and the resonance frequency of the scattering object.

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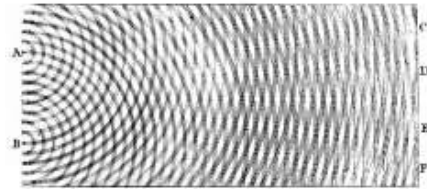
In 1803 **Thomas Young** did his famous experiment observing diffraction from two closely spaced slits.

Explaining his results by interference of the waves emanating from the two different slits, he deduced that light must propagate as waves.

Augustin-Jean Fresnel did more definitive studies and calculations of diffraction, published in 1815 and 1818, and thereby gave great support to the wave theory of light that had been advanced by Christian Huygens and reinvigorated by Young against *Newton's* particle theory.

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Diffraction



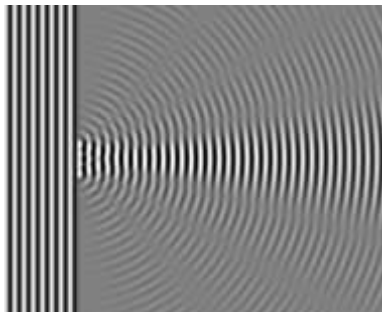
Thomas Young's sketch of two-slit diffraction, which he presented to the Royal Society in 1803

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Diffraction

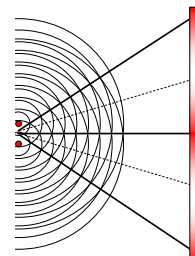


Numerical approximation of diffraction pattern from a slit of width four wavelengths with an incident plane wave. The main central beam, nulls, and phase reversals are apparent

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Diffraction: Young's 'two-slit' interference



Two scattering objects act as coherent secondary sources.

They generate an interference pattern, which at every point is a vector summation of the scattered waves:

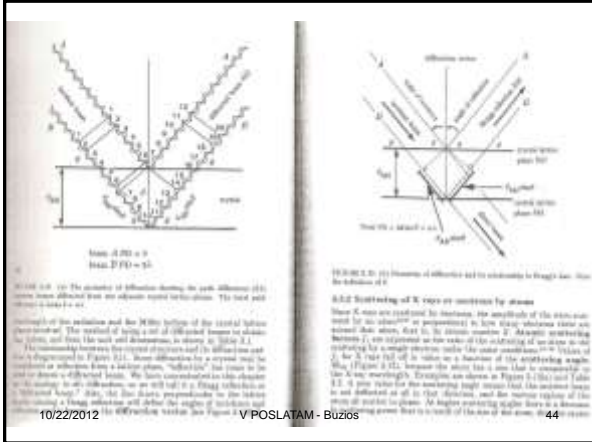
$$F(\mathbf{s}) = \int \rho(\mathbf{x}) e^{2\pi i \mathbf{x} \cdot \mathbf{s}} d\mathbf{x}$$

(Now $\mathbf{x} \neq 0!$)

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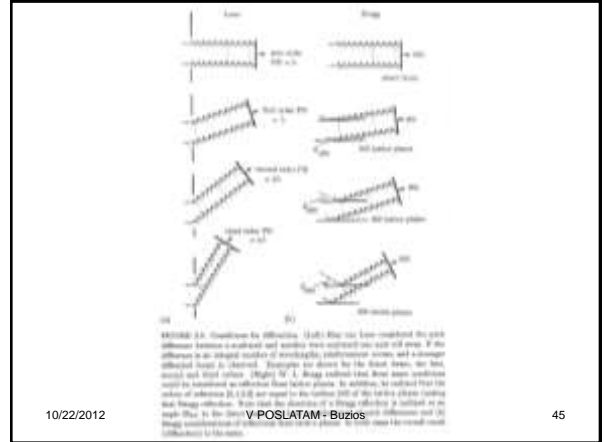
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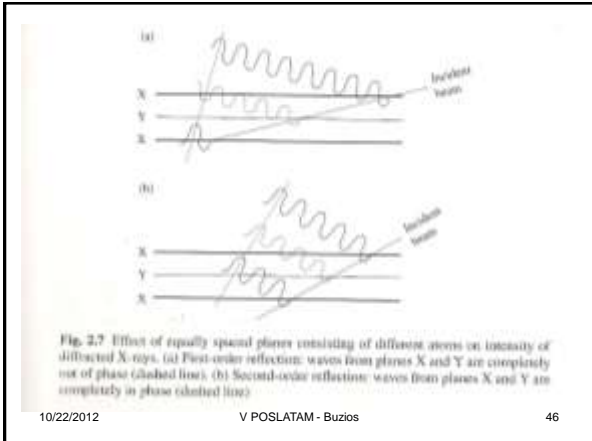
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“I have always felt the association of my name with it [Bragg law] to be an easily earned honour, because it is merely the familiar optical relation giving the colours reflected by thin films, in another guise.”

W. L. Bragg
in *The development of X-ray analysis* (Eds Phillips, D. C., and Lipson, H. F.), p.24. Hafner press (Macmillan), NY, 1975

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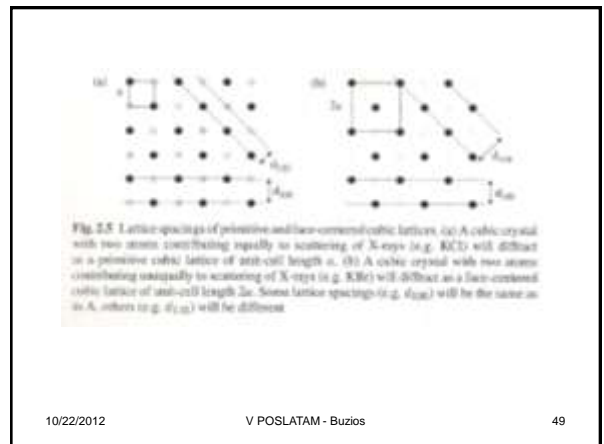
“There was nothing novel about it (the “Bragg equation”). The second (1909) edition of Arthur Schuster’s *An Introduction to the Theory of Optics*, which Bragg had studied as an undergraduate, states that, for a single grating, $2e \sin \theta = n\lambda$, where e is the spacing between the lines. The only reason why Bragg’s name became associated with this relationship was that he showed that it could be applied to diffraction of X-rays by crystals as well as to diffraction of visible light by gratings.”

G. K. Hunyer
in *Light is a messenger*
The life and science of William Lawrence Bragg
p36, Oxford University Press, 2004

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Grade de difração

- Ordem de difração x comprimento de onda

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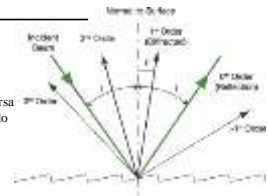
50

Grade de difração

• Grade de difração é um elemento ótico que separa (dispersa) luz policromática em seus elementos constituintes ("cores").

• A luz policromática incidente sobre a grade é dispersa de modo que cada comprimento de onda seja refletido pela grade, emergindo em ângulos ligeiramente diferentes.

• A dispersão provem da divisão da frente de onda e interferência da radiação incidente pela estrutura periódica da grade.



• Grades são compostas de sulcos paralelos, igualmente espaçados, sobre uma superfície reflexiva e depositada sobre um substrato.

• A dispersão e eficiência de uma grade são dependentes da distância entre os sulcos adjacentes e do ângulo dos sulcos.

• Grades geralmente são melhores que prismas, mais eficientes, produzem uma dispersão linear dos comprimentos de onda e não sofrem efeitos de absorção típicos de prismas, o que limita o uso destes.

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Grade de difração

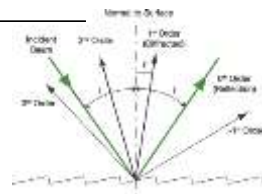
A equação de grade holográfica

• A dispersão por uma grade é governada pela equação de grade, que usualmente é escrita como:

$$n \cdot \lambda = d \cdot (\sin \theta_i + \sin \theta_d)$$

onde: 'n' é a ordem da difração, 'λ' é o comprimento de onda difratado, 'd' é a constante da grade (a distância entre sulcos sucessivos), 'θ_i' é o ângulo de incidência medido a partir da normal, e 'θ_d' é o ângulo de difração medido a partir da normal.

• O diagrama mostra as ordens de difração dos comprimentos de onda. Igualmente para a ordem positiva, a luz pode ser difratada no sentido oposto (i.e. n = -1, -2 etc.). Ordens superiores também podem aparecer, mas com grande decréscimo em intensidade. Usualmente, as primeiras ordens de linhas (n=1 ou n=-1) são as mais intensas.



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Monocromadores: dispersivo vs grade



<http://www.jobinyvon.com/>



www.ssiptics.com/planelazedgratings.html

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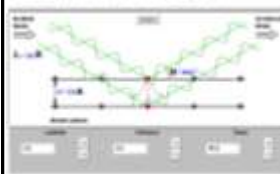
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• Tutorial interativo (Java App) Bragg:

<http://www.bmsc.washington.edu/people/merritt/bc530/bragg/>

The applet was developed by the author as a Java applet for teaching Bragg's law. It is a simple Java applet that can be used to illustrate Bragg's law of diffraction. The applet is written in Java and is available for free. It is a simple Java applet that can be used to illustrate Bragg's law of diffraction.



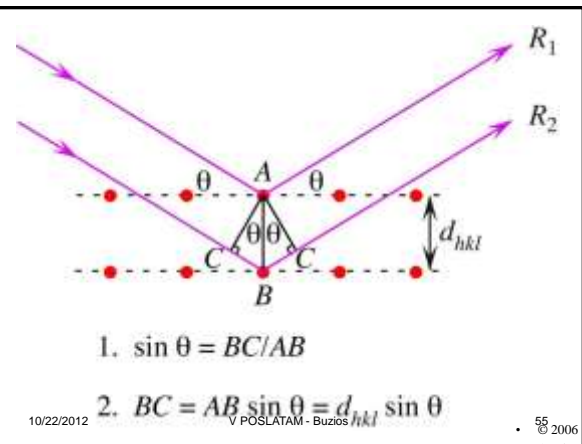
Bragg's Law Applet

Bragg's Law is a simple law that describes the conditions under which the waves in a crystal will be in phase. The law is a simple law that describes the conditions under which the waves in a crystal will be in phase. The law is a simple law that describes the conditions under which the waves in a crystal will be in phase.

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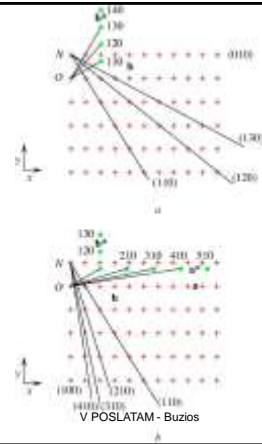
55 © 2006

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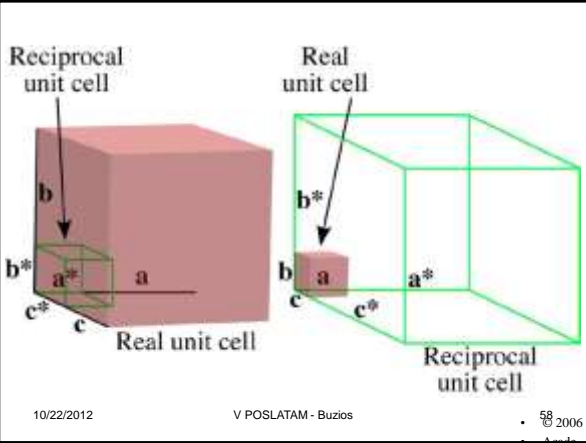
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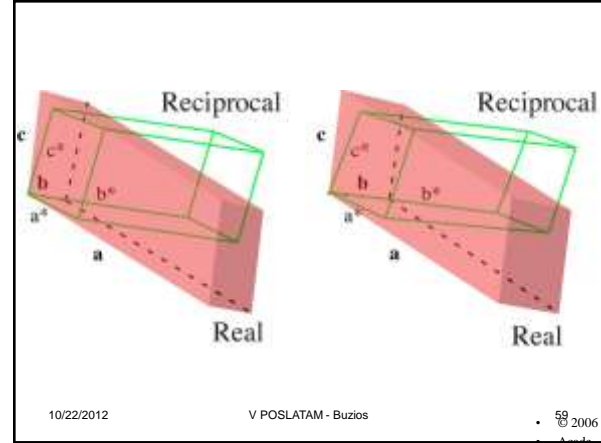
57 2006



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58 2006



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59 2006

Ewald

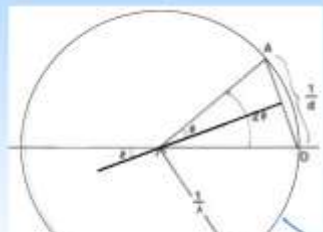
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To relate the planes in the crystal lattice to the points in the diffraction pattern, we make Ewald's construction.

We have that $\sin \theta = (OA/2)/(1/\lambda) = \lambda \times OA/2$, or $\lambda = 2 \sin \theta / OA$. Compare this to Bragg's Law: $\lambda = 2d \sin \theta$. We take $1/OA$ as being equivalent to d . Notice the reflection plane, and that OA is perpendicular to it. The Ewald construction exists in a space with dimensions of reciprocal distance!



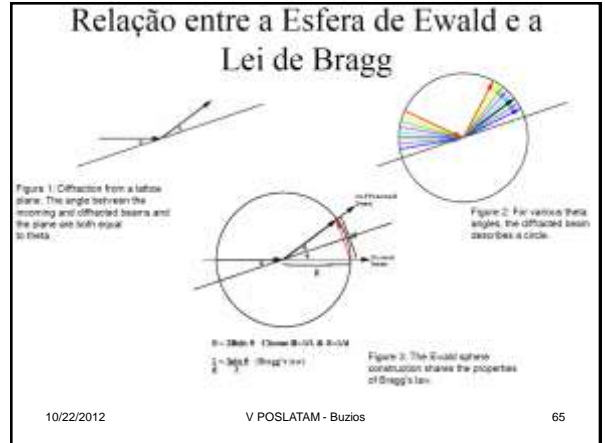
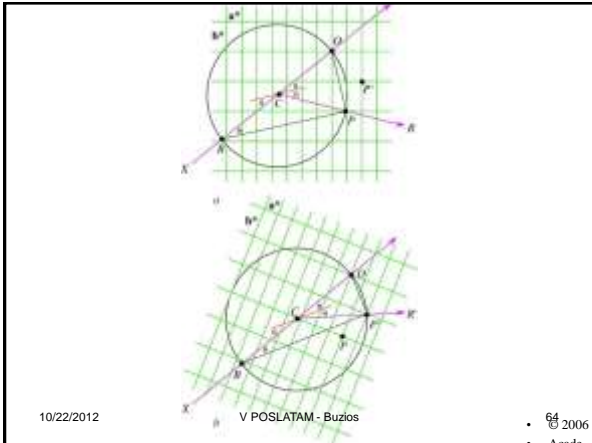
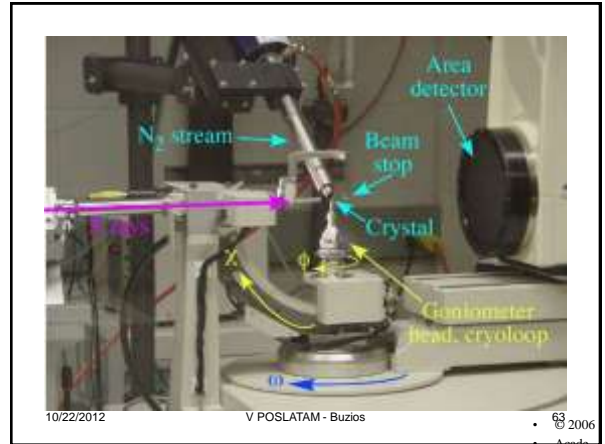
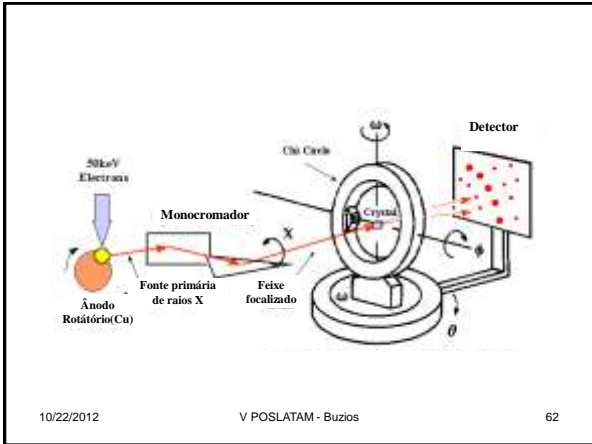
This defines Reciprocal Space! The vector of length $1/d$ is perpendicular to the reflecting plane that lies θ from the "rays."

The Ewald Sphere

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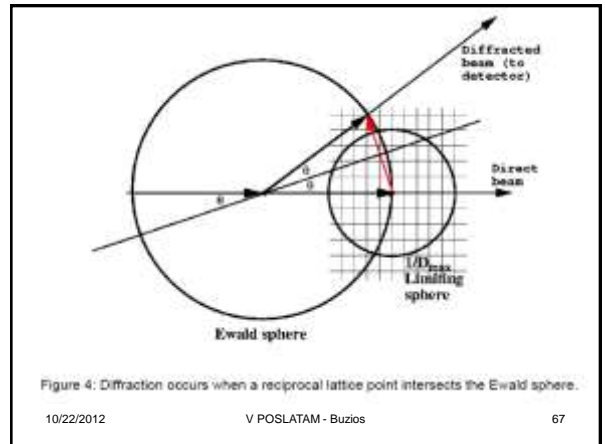


Data collection methods

- Either the crystal has to rotate or the wavelength has to vary.

According to Bragg's law, only these lattice points that intercept with Ewald sphere will give rise to reflections.

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The reciprocal lattice and the geometry of diffraction

