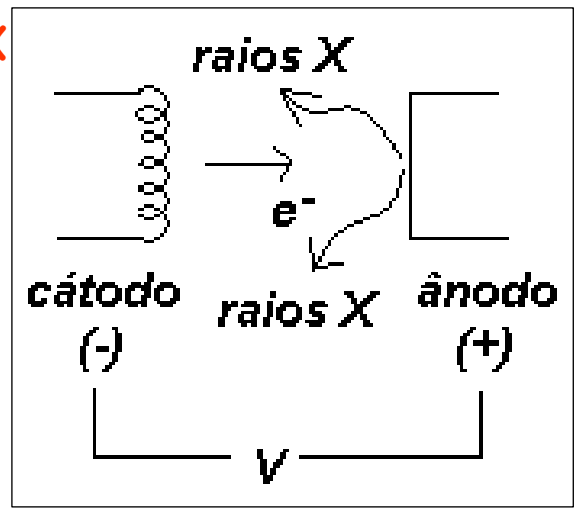
# Difração de raios X aplicada ao estudo de materiais

- **Difração**: Interferência de ondas eletromagnéticas. Interação entre radiação e matéria.
- **Raios X**: Átomos nas estruturas cristalinas estão localizados em planos cujas distâncias são da ordem de grandeza dos comprimentos de onda na faixa dos raios X.
- **Aplicada**: Estudo de monocristais, policristais e materiais amorfos. Técnica de estado sólido capaz de determinar compostos.
- **Materiais**: Não há restrições.

## Propriedades dos raios X

- Descoberto em 1895 por Roentgen.
- Radiação eletromagnética $0,5 < \lambda < 2,5$ Å.
- Produção: $e^-$ decelerado
  espectro contínuo (branca)
  linhas característica (ânodo)



# Técnicas

- <u>Monocristal:</u> método fotográfico de Laue
  difratômetro de duplo cristal
- <u>Policristal:</u> método de pó
  câmara de Debye -Scherrer
  difratômetro
- <u>Amorfos:</u> espalhamento a baixo ângulo e a alto ângulo (EXAFS)
- Detecção: filme, contadores Geiger, multicanal.

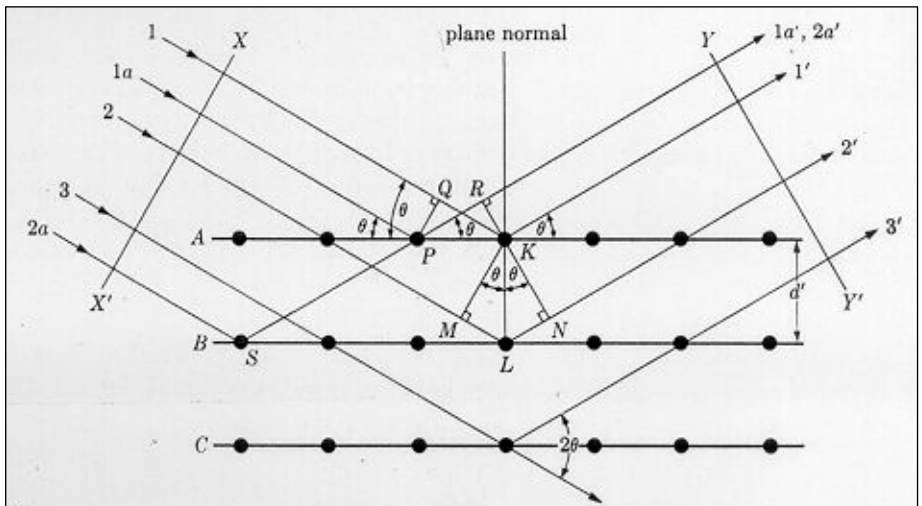



Fig. 3–2 Diffraction of x-rays by a crystal.

B.D. Cullity. "Elements of X-Ray Diffraction", 1956

Diferença de caminho óptico

$2x = ML + LN = 2ML = 2LN$

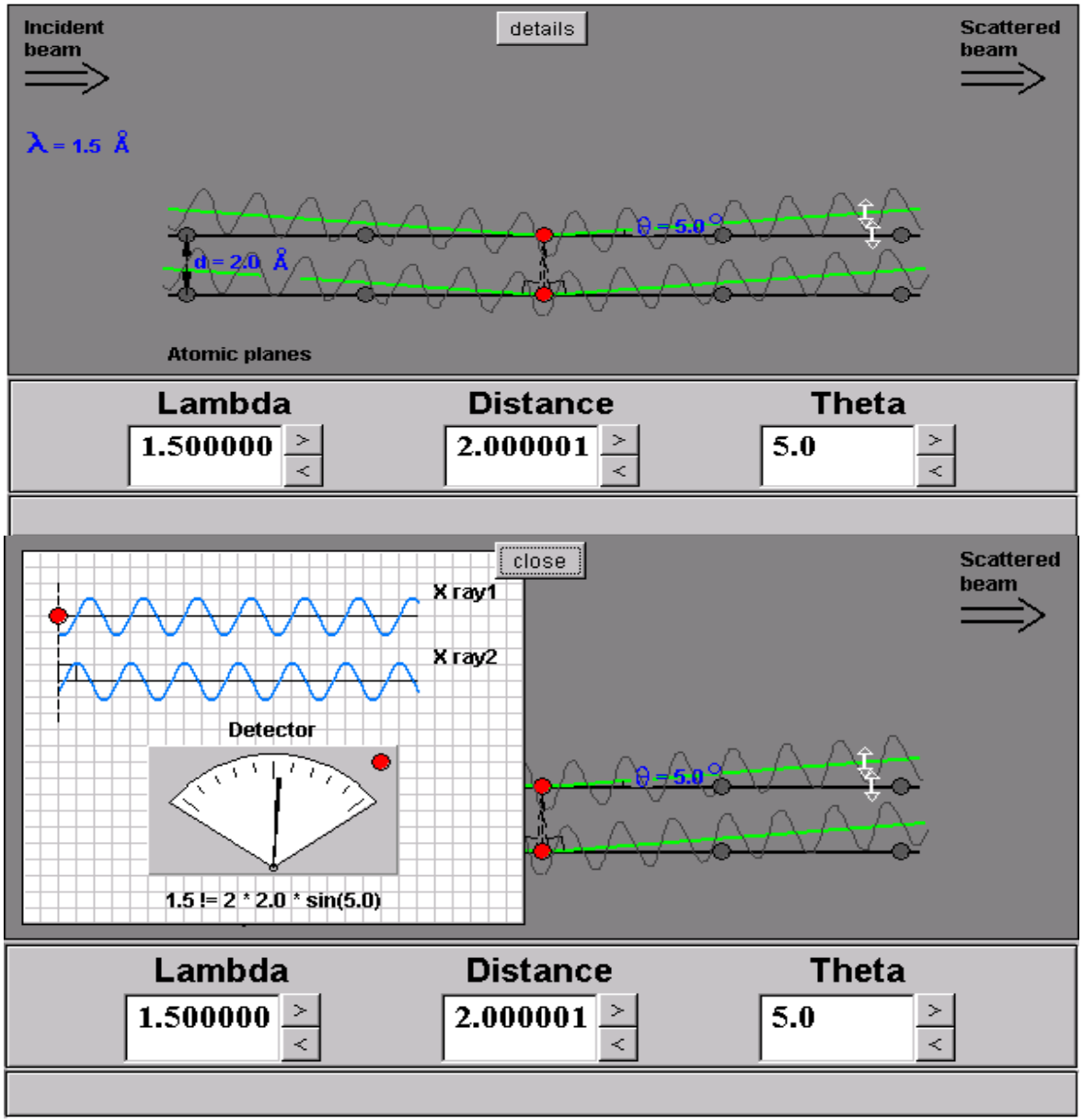
$2x = m\lambda$ (interferência construtiva)

$\text{sen}\,\theta = x/d \longrightarrow x = d\,\text{sen}\,\theta$

$$m\,\lambda = 2\,d\,\text{sen}\,\theta$$

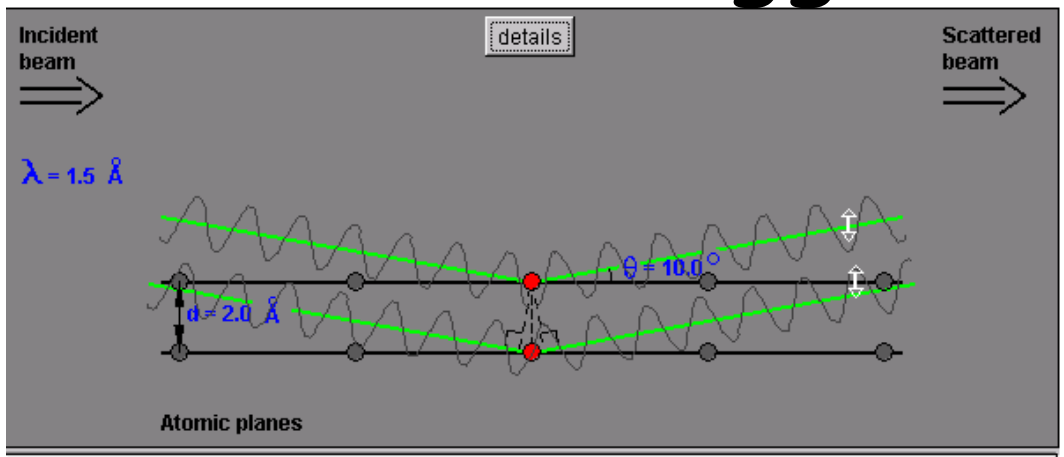
Lei de Bragg

# Lei de Bragg

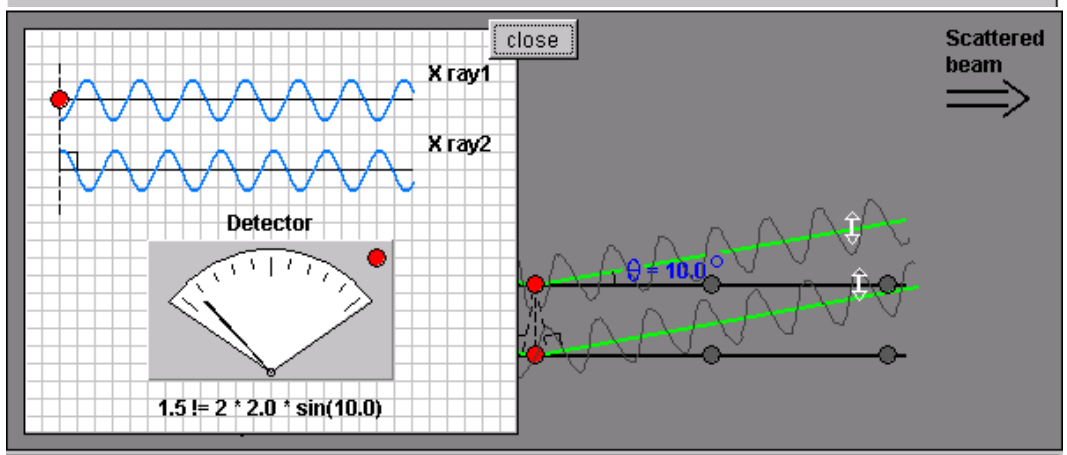



http://www.eserc.stonybrook.edu/ProjectJava/Bragg/index.html

# Lei de Bragg

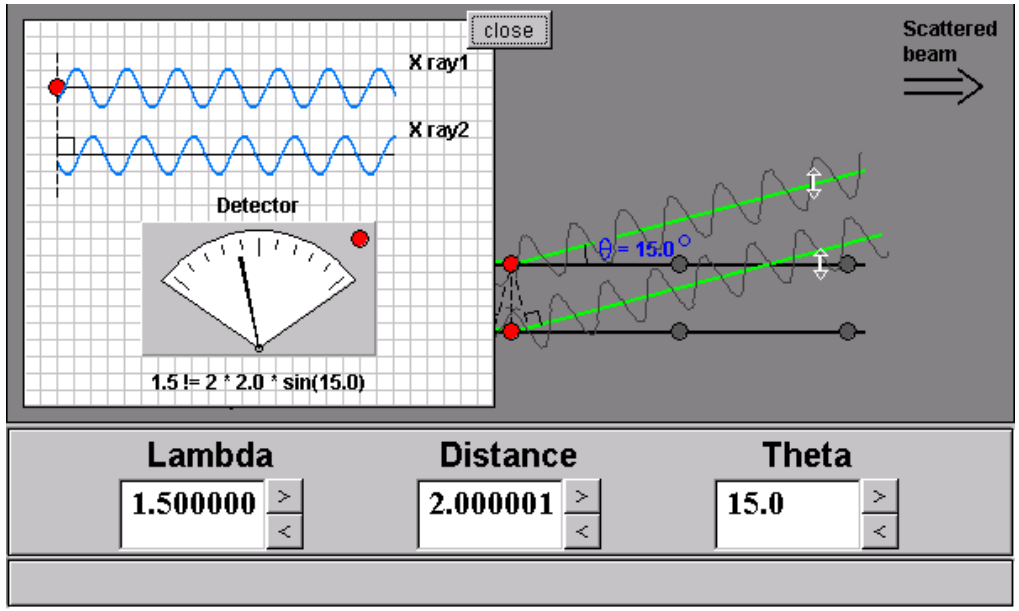


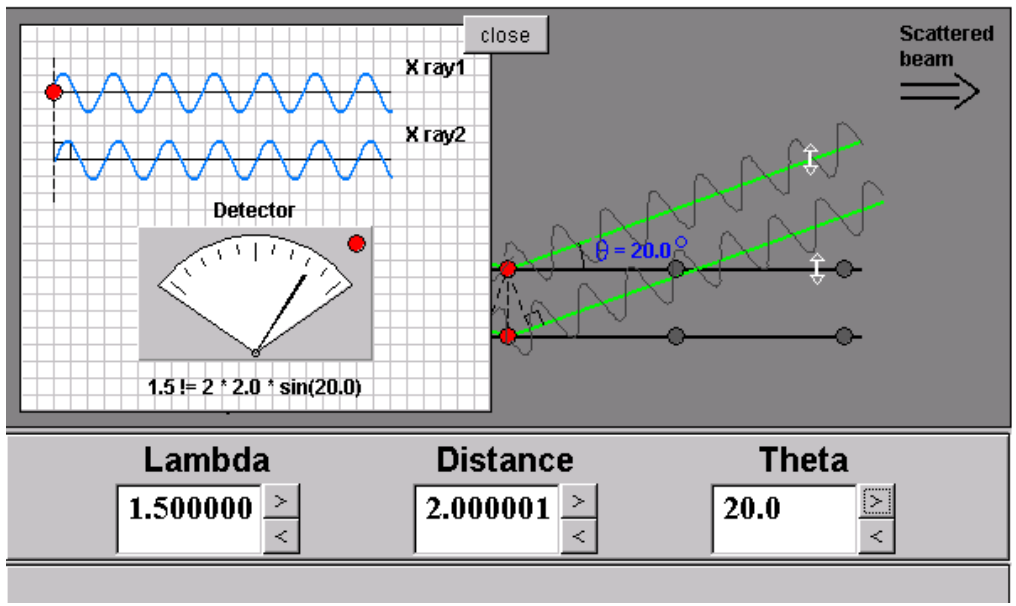

| Lambda | Distance | Theta |
|---|---|---|
| 1.500000 | 2.000001 | 10.0 |

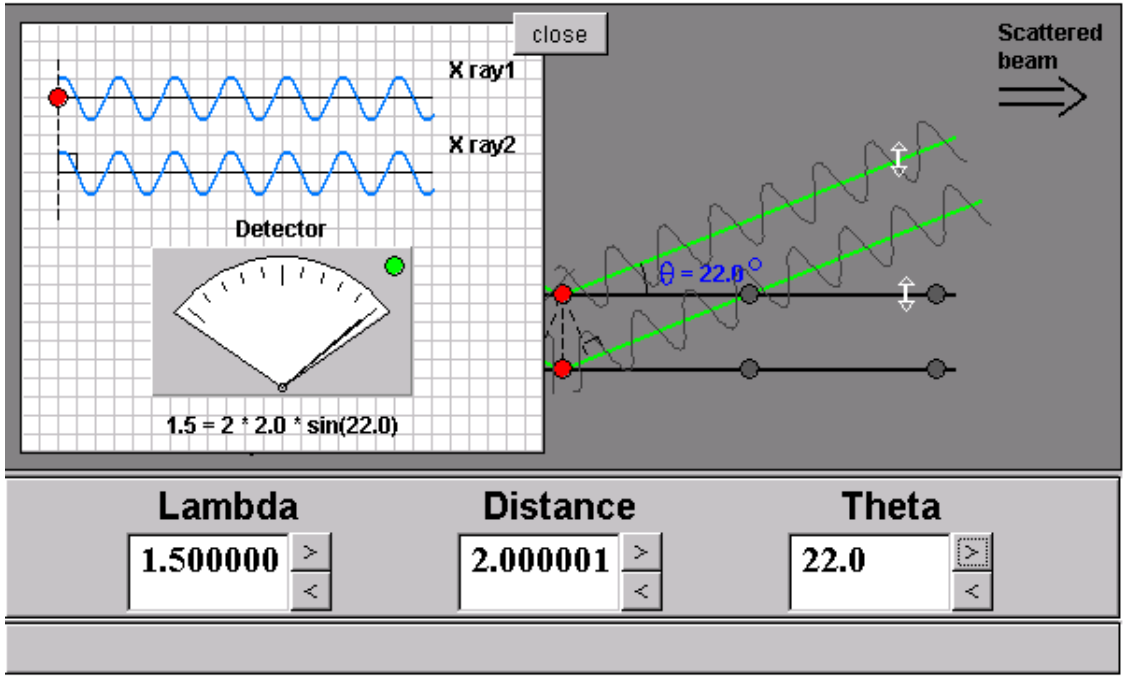



| Lambda | Distance | Theta |
|---|---|---|
| 1.500000 | 2.000001 | 10.0 |

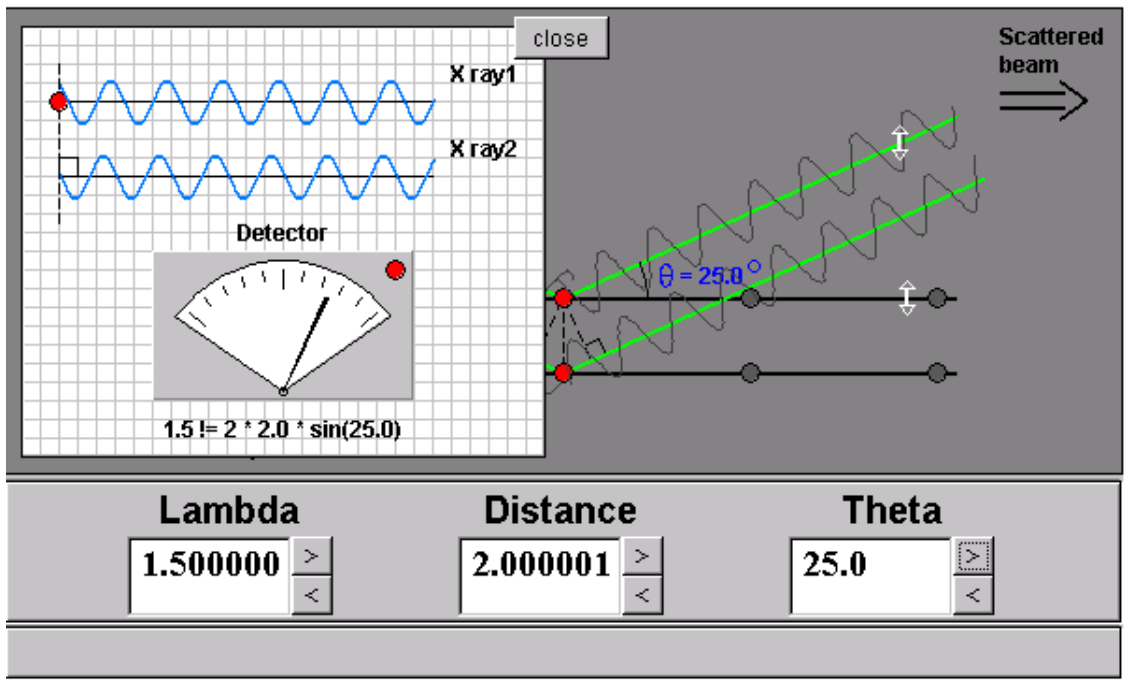
# Lei de Bragg


close
X ray1
X ray2
Detector
1.5 != 2 * 2.0 * sin(15.0)
Scattered beam
θ = 15.0°
Lambda
1.500000
Distance
2.000001
Theta
15.0

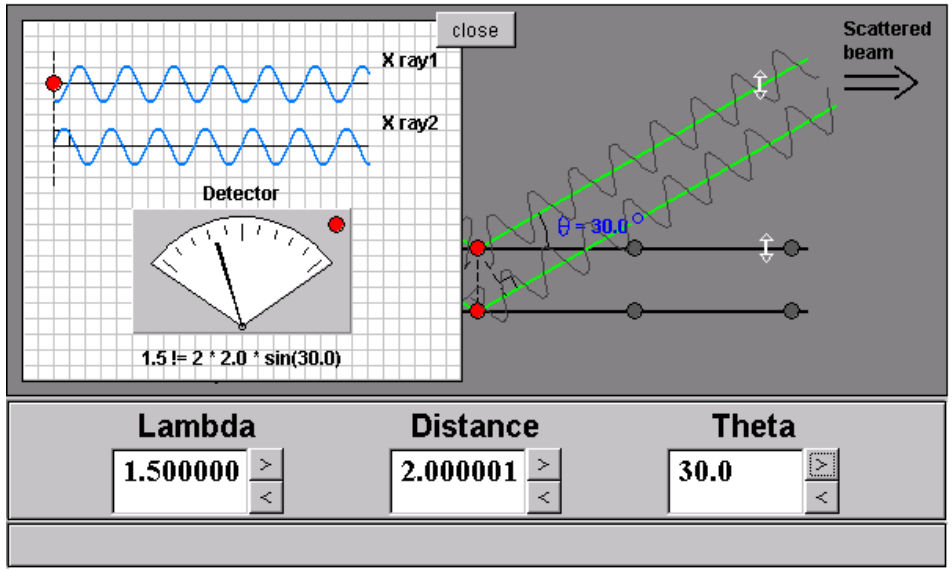

close
X ray1
X ray2
Detector
1.5 != 2 * 2.0 * sin(20.0)
Scattered beam
θ = 20.0°
Lambda
1.500000
Distance
2.000001
Theta
20.0

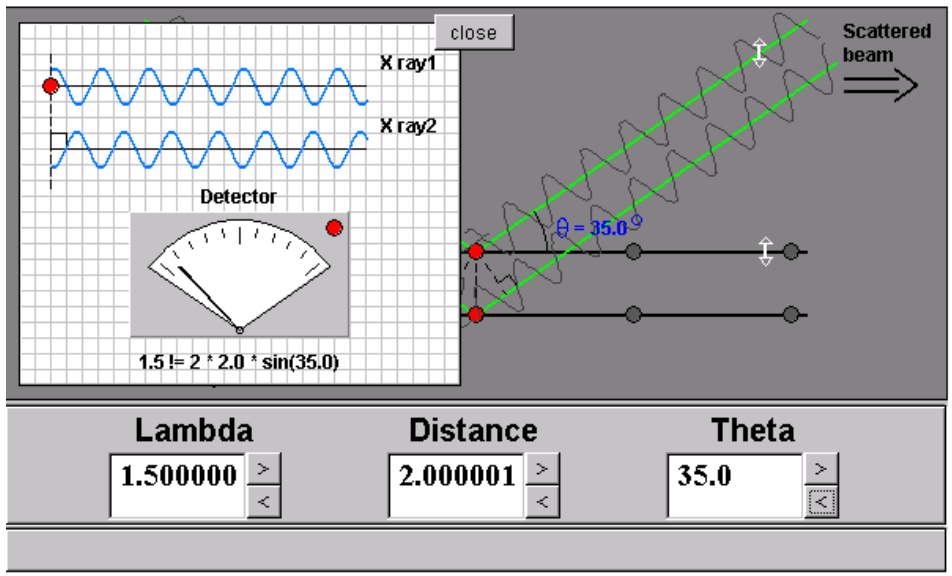

close
X ray1
X ray2
Detector
1.5 = 2 * 2.0 * sin(22.0)
Scattered beam
θ = 22.0°
Lambda
1.500000
Distance
2.000001
Theta
22.0

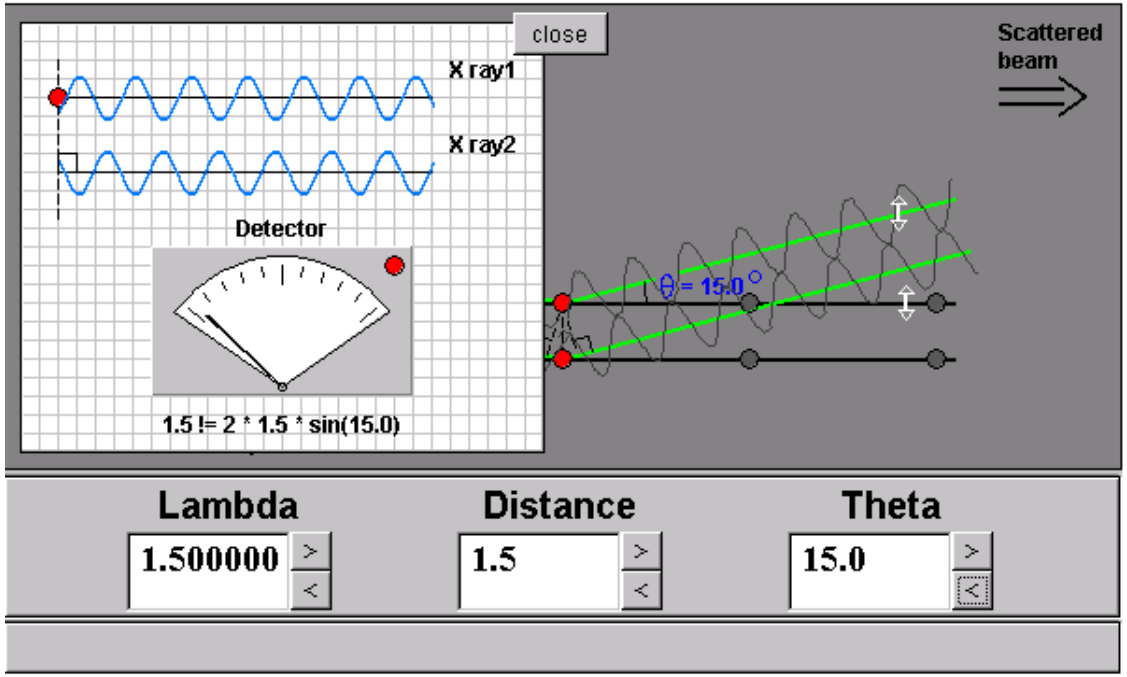
# Lei de Bragg


close
X ray1
X ray2
Detector
1.5 != 2 * 2.0 * sin(25.0)
Scattered beam
θ = 25.0°
Lambda
1.500000
Distance
2.000001
Theta
25.0

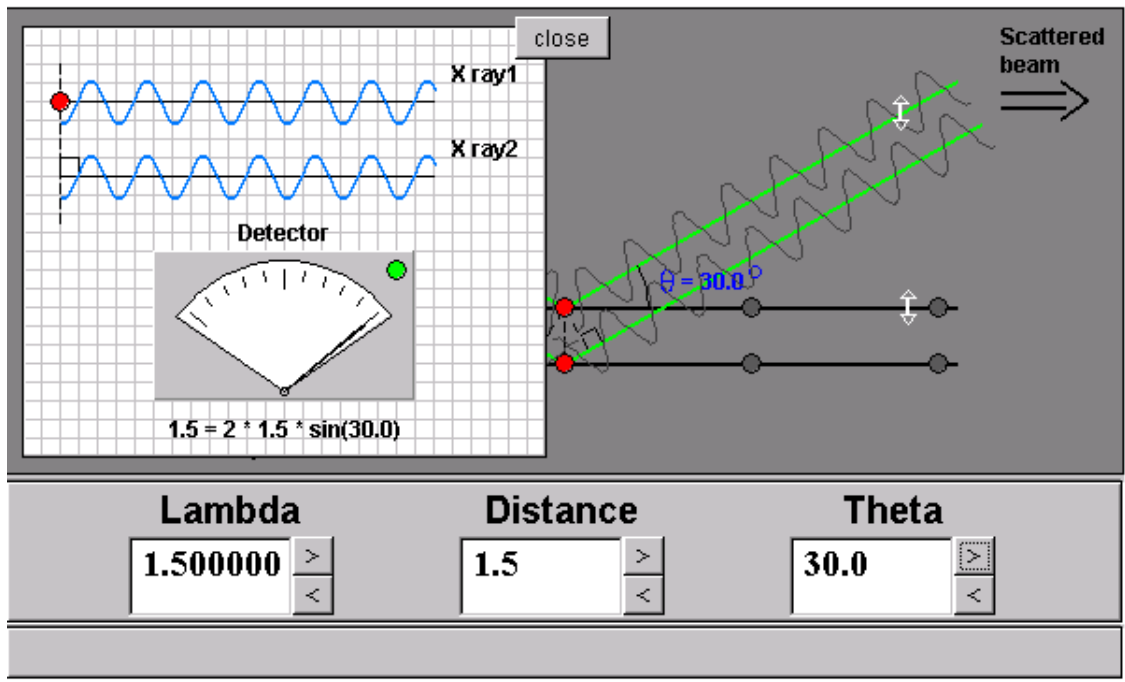
# Lei de Bragg


close
X ray1
X ray2
Detector
1.5 != 2 * 2.0 * sin(30.0)
Scattered beam
θ = 30.0°
Lambda
1.500000
Distance
2.000001
Theta
30.0

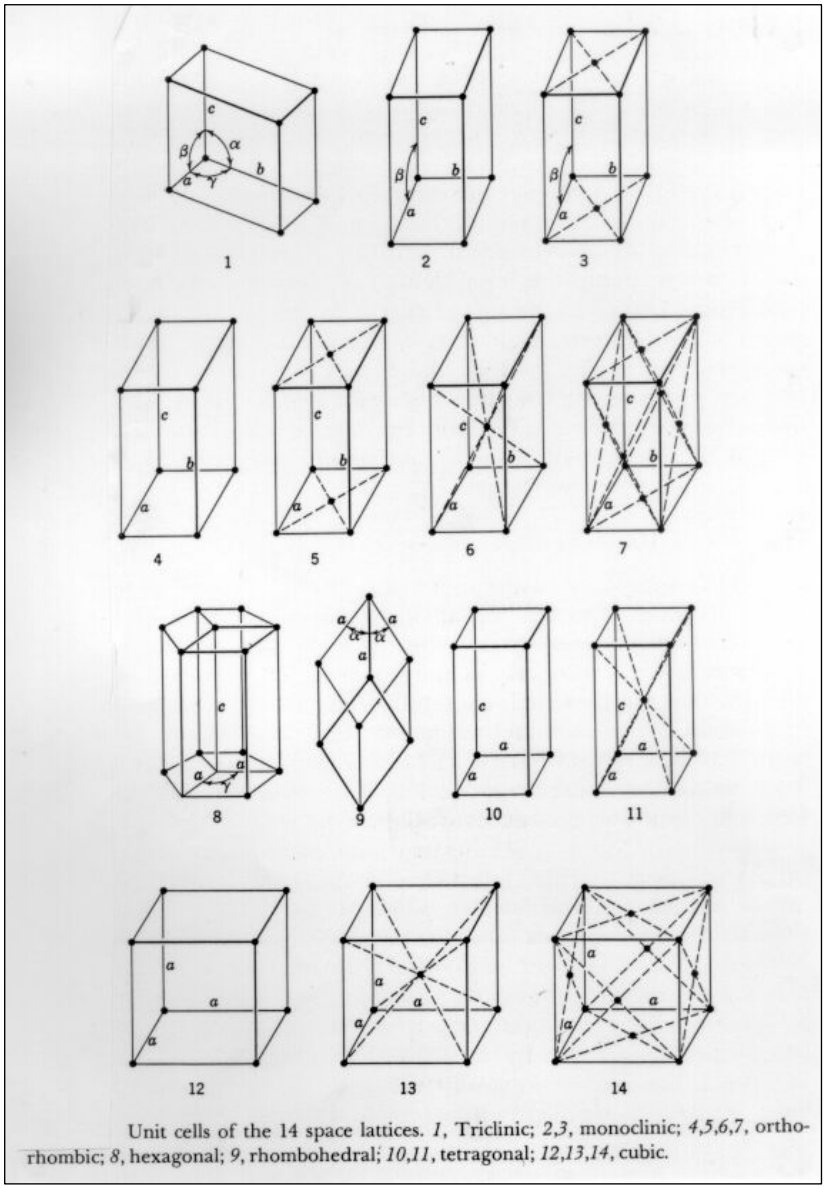

close
X ray1
X ray2
Detector
1.5 != 2 * 2.0 * sin(35.0)
Scattered beam
θ = 35.0°
Lambda
1.500000
Distance
2.000001
Theta
35.0


close
X ray1
X ray2
Detector
1.5 != 2 * 1.5 * sin(15.0)
Scattered beam
θ = 15.0°
Lambda
1.500000
Distance
1.5
Theta
15.0

# Lei de Bragg


close
X ray1
X ray2
Detector
1.5 = 2 * 1.5 * sin(30.0)
Scattered beam
θ = 30.0°
Lambda
1.500000
Distance
1.5
Theta
30.0

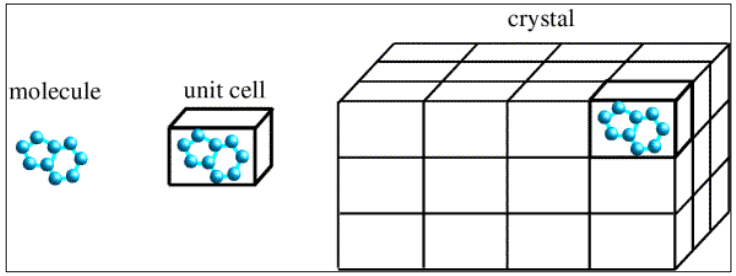
# 14 redes de Bravais

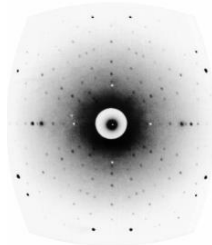



Unit cells of the 14 space lattices. *1*, Triclinic; *2,3*, monoclinic; *4,5,6,7*, orthorhombic; *8*, hexagonal; *9*, rhombohedral; *10,11*, tetragonal; *12,13,14*, cubic.

B.D. Cullity. "Elements of X-Ray Diffraction", 1956.

- **Monocristal**: arranjo periódico de longo alcance de celas unitárias perfeitamente empilhadas.



- **Policristal**: arranjo periódico de celas unitárias de tamanho finito orientadas ao acaso.

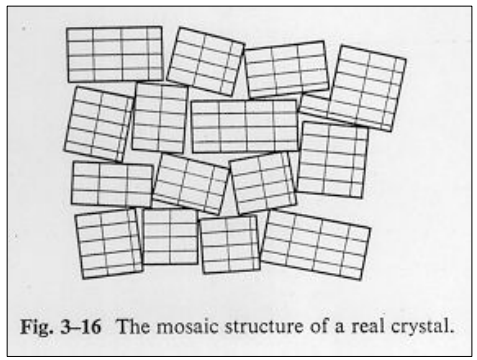
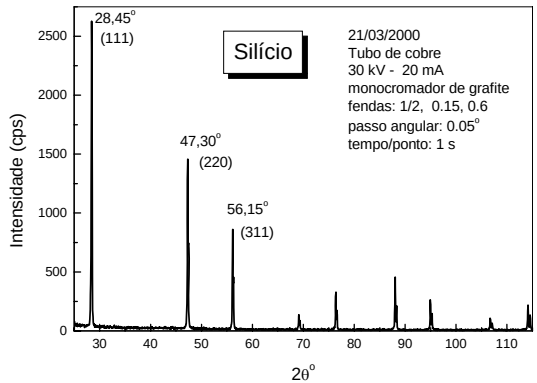
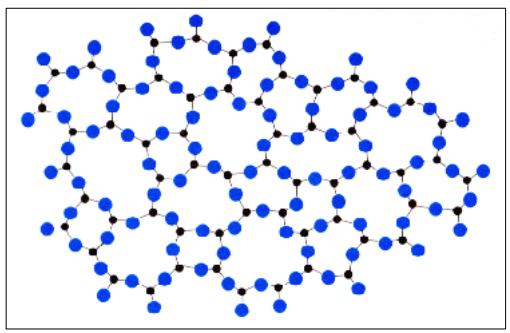


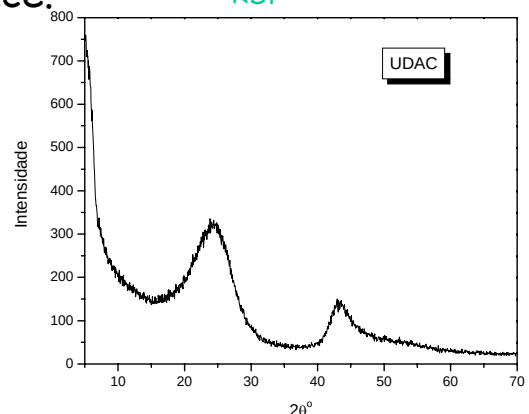
Fig. 3–16 The mosaic structure of a real crystal.




- **Amorfo**: arranjo não periódico de longo alcance. Correlação a curto alcance.



RDF



# Grau de cristalinidade

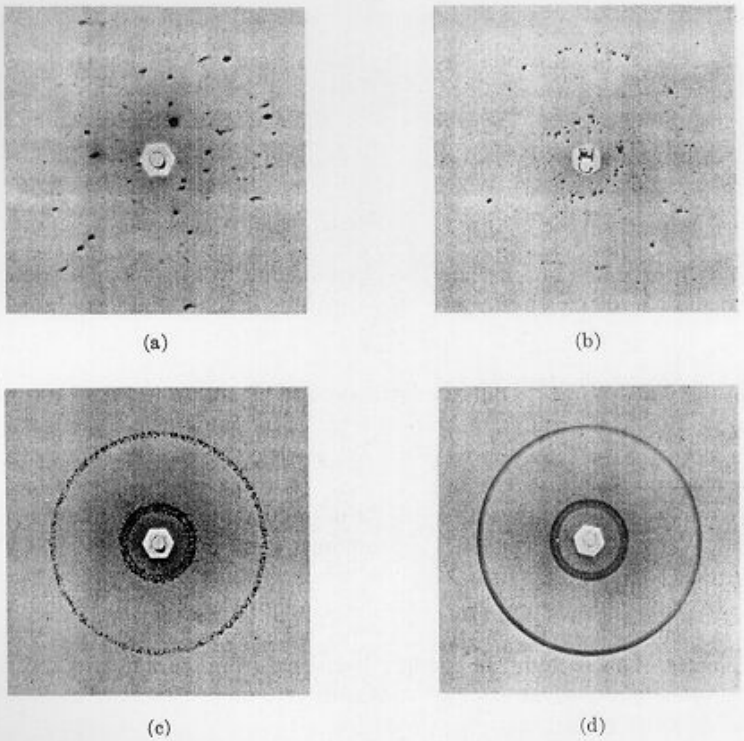



**Fig. 9–1** Back-reflection pinhole patterns of recrystallized aluminum specimens; grain size decreases in the order (a), (b), (c), (d). Filtered copper radiation.

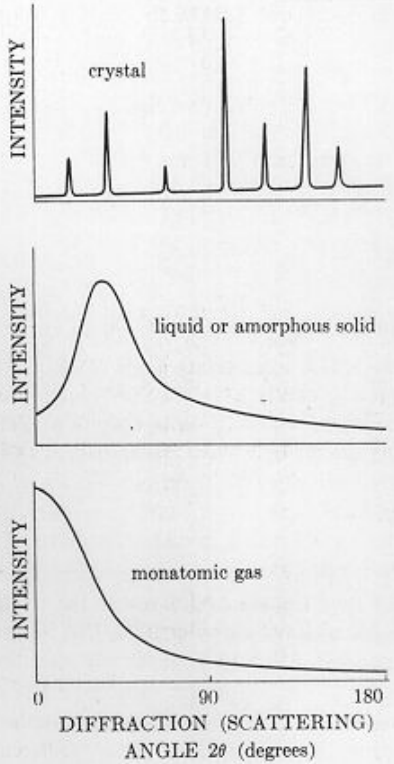



**Fig. 3–18** Comparative x-ray scattering by crystalline solids, amorphous solids, liquids, and monatomic gases (schematic). The three vertical scales are not equal.

B.D. Cullity. "Elements of X-Ray Diffraction", 1956.

# Produção de raios X

## Tubos

- Convencional

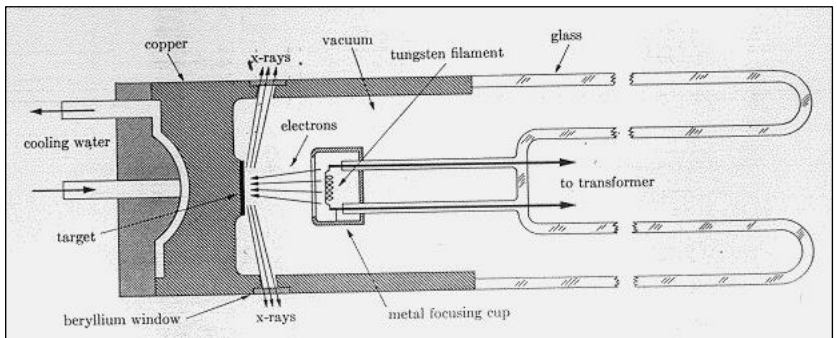



Fig. 1–15 Cross section of sealed-off filament x-ray tube (schematic).

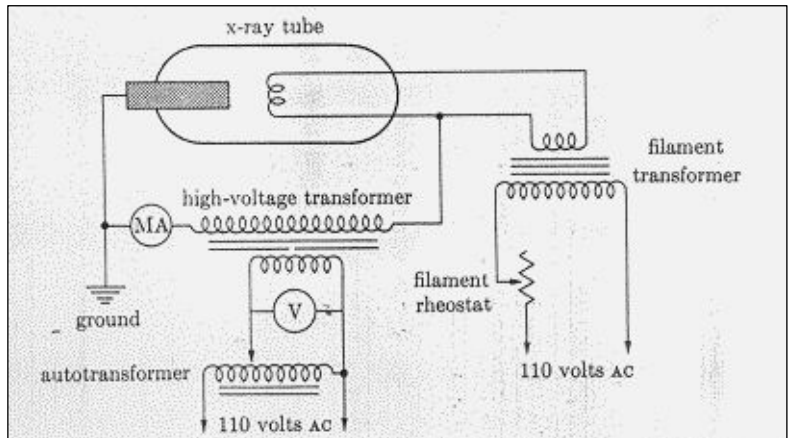



Fig. 1–16 Wiring diagram for self-rectifying filament tube.

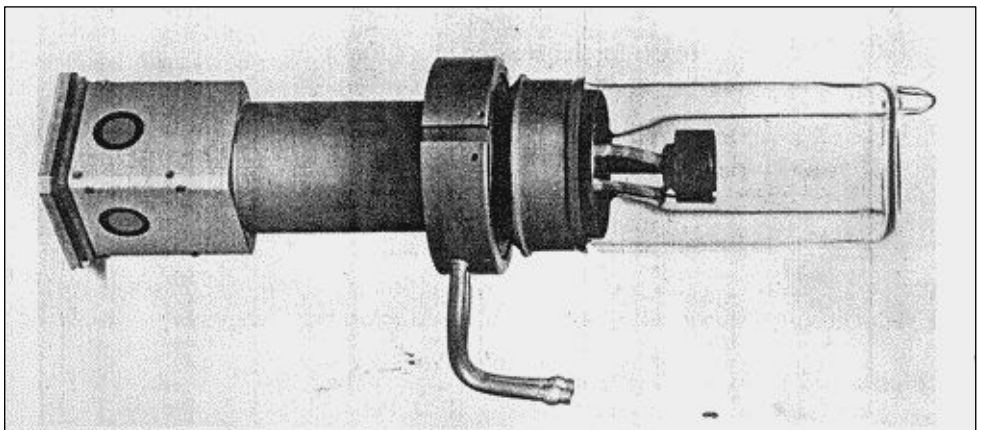


Fig. 1–14 Sealed-off filament x-ray tube. Cooling-water tubes at center connect with internal ducts leading to anode at left end. Three windows: two for projecting square focal spots and one for projecting a line focal spot. Focal spots of three sizes are available with this tube (Type A-5): 1.2 × 12.5 mm, 0.75 × 12.5 mm, and 0.45 × 12.5 mm. (Courtesy of Machlett Laboratories, Inc.)

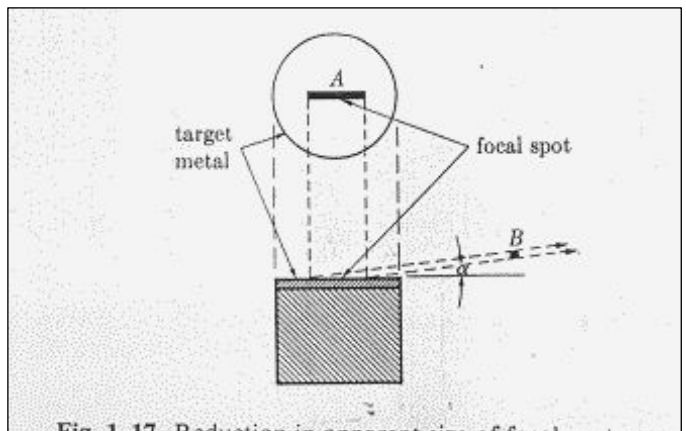
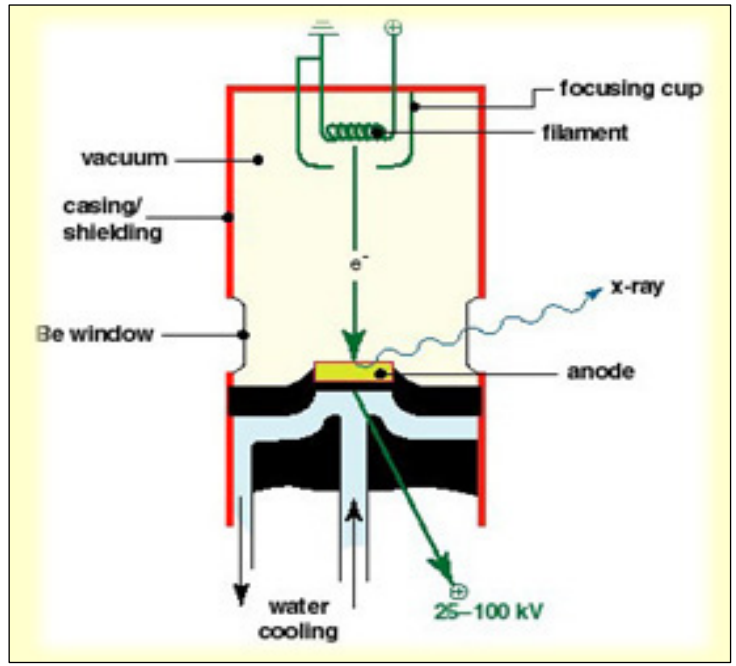



Fig. 1–17 Reduction in apparent size of focal spot.

B.D. Cullity. "Elements of X-Ray Diffraction", 1956.

# Ânodo rotatório



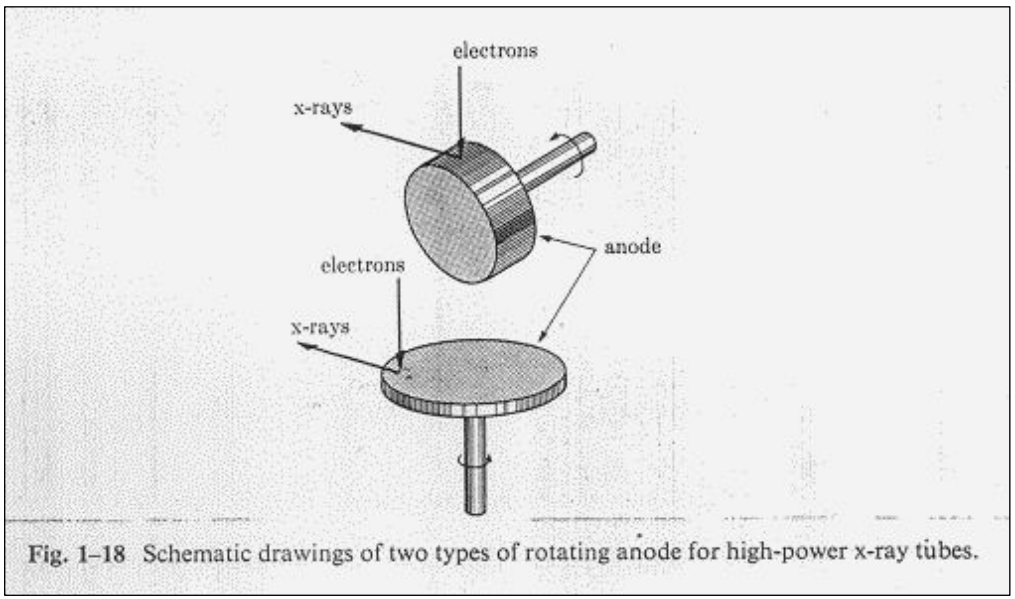
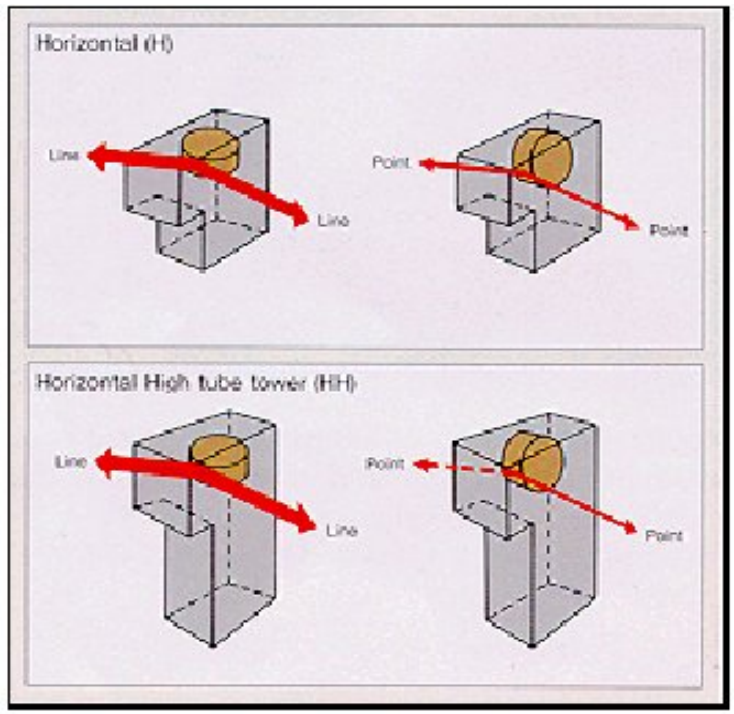
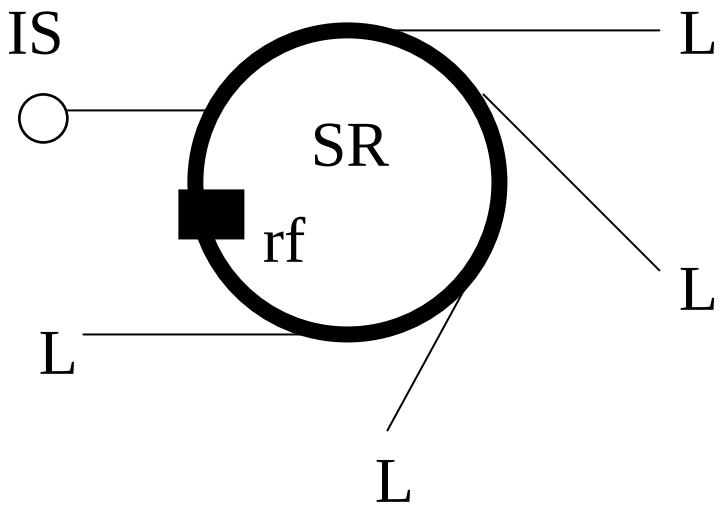




Fig. 1–18 Schematic drawings of two types of rotating anode for high-power x-ray tubes.




B.D. Cullity. "Elements of X-Ray Diffraction", 1956.

# Como gerar radiação síncrotron?

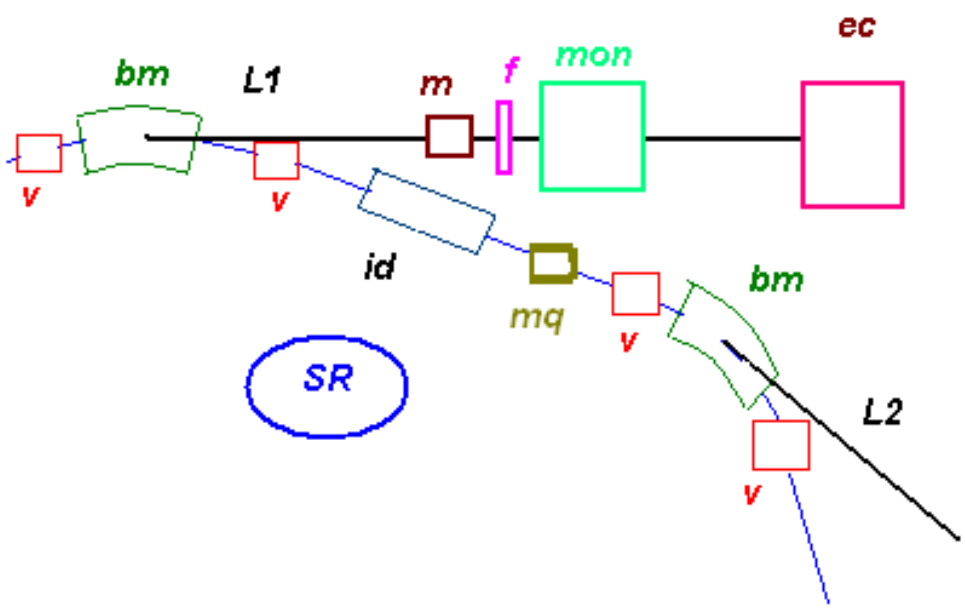



L (beam line) = line

IS = injection system (linac + booster)

SR = storage ring

rf = radio frequency




L1, L2 = line

mq = magnetic quadrupole

bm = bending magnet

id = insertion device

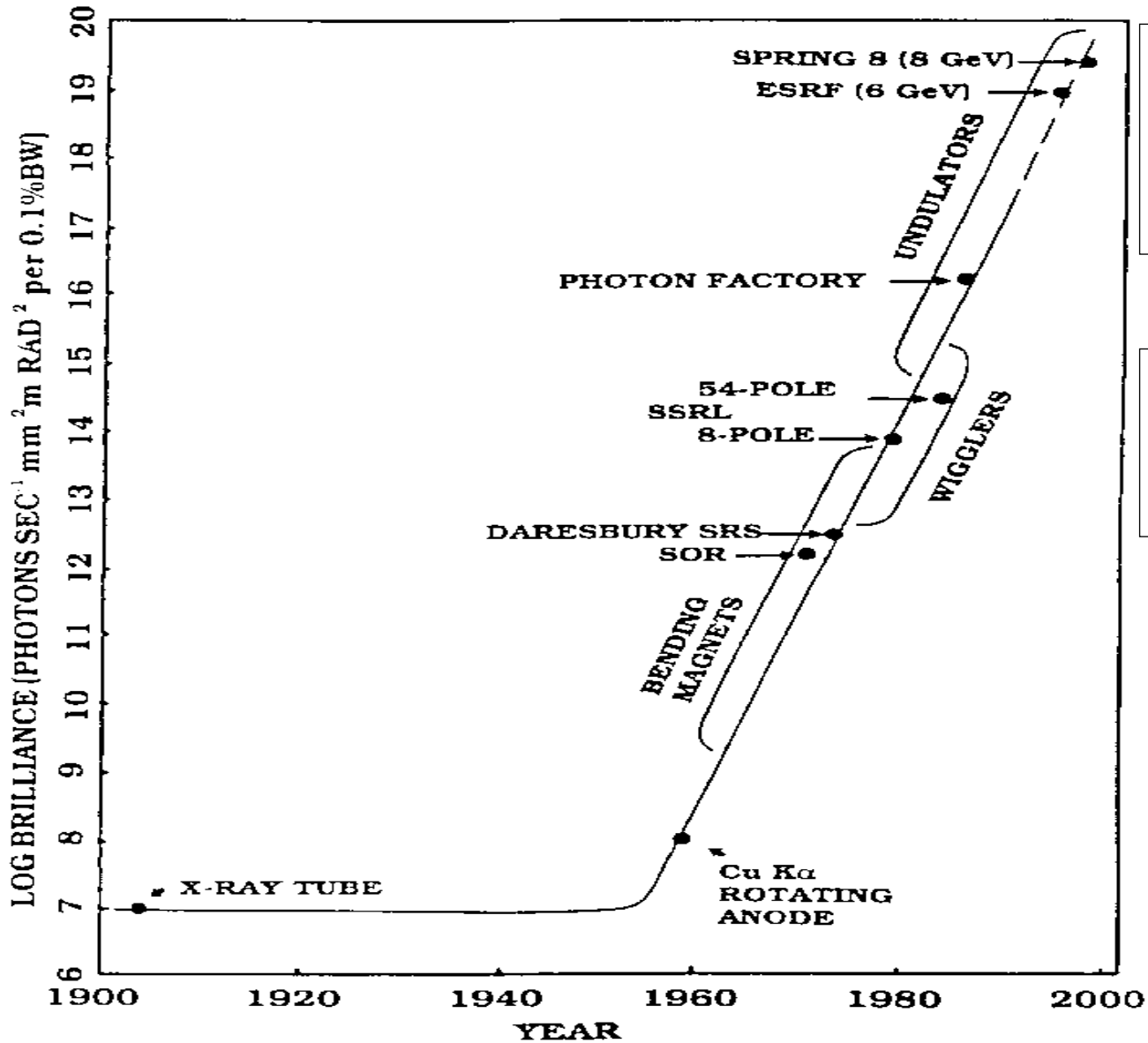
v = valve

m= mirror

f = filter

mon = monochromator

ec = experimental chamber




*The historical development of available X-ray flux*

Daresbury-Inglaterra

Photon Factory & Spring 8 - Japão

SSRL-Stanford Synchrotron Radiation Lab.

ESRF-European Synchrotron Radiation Facility

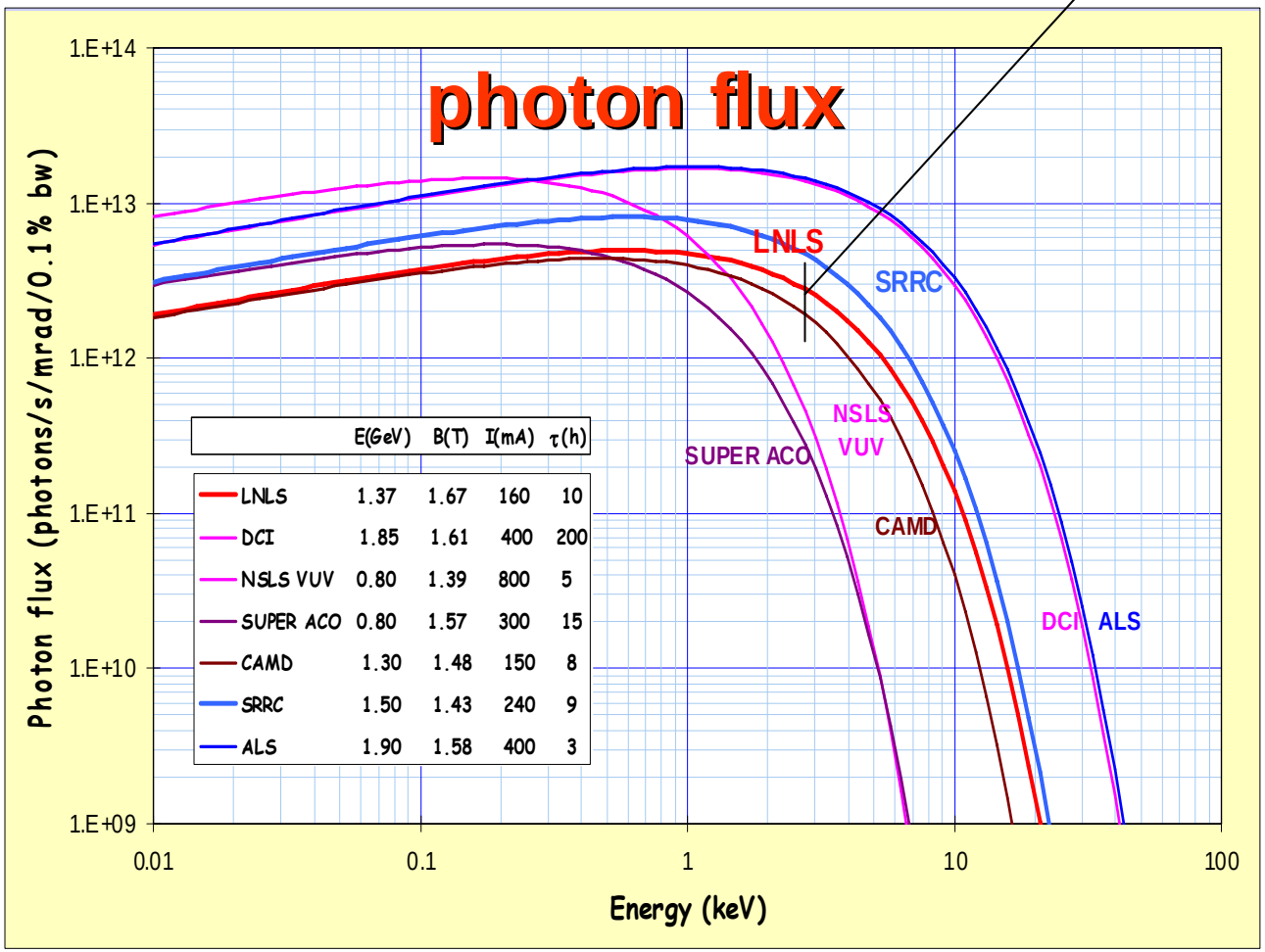
Primeiros experimentos: 1940

Primeira fonte dedicada à luz síncrotron: 1970

Síncrotrons no mundo: mais de 50

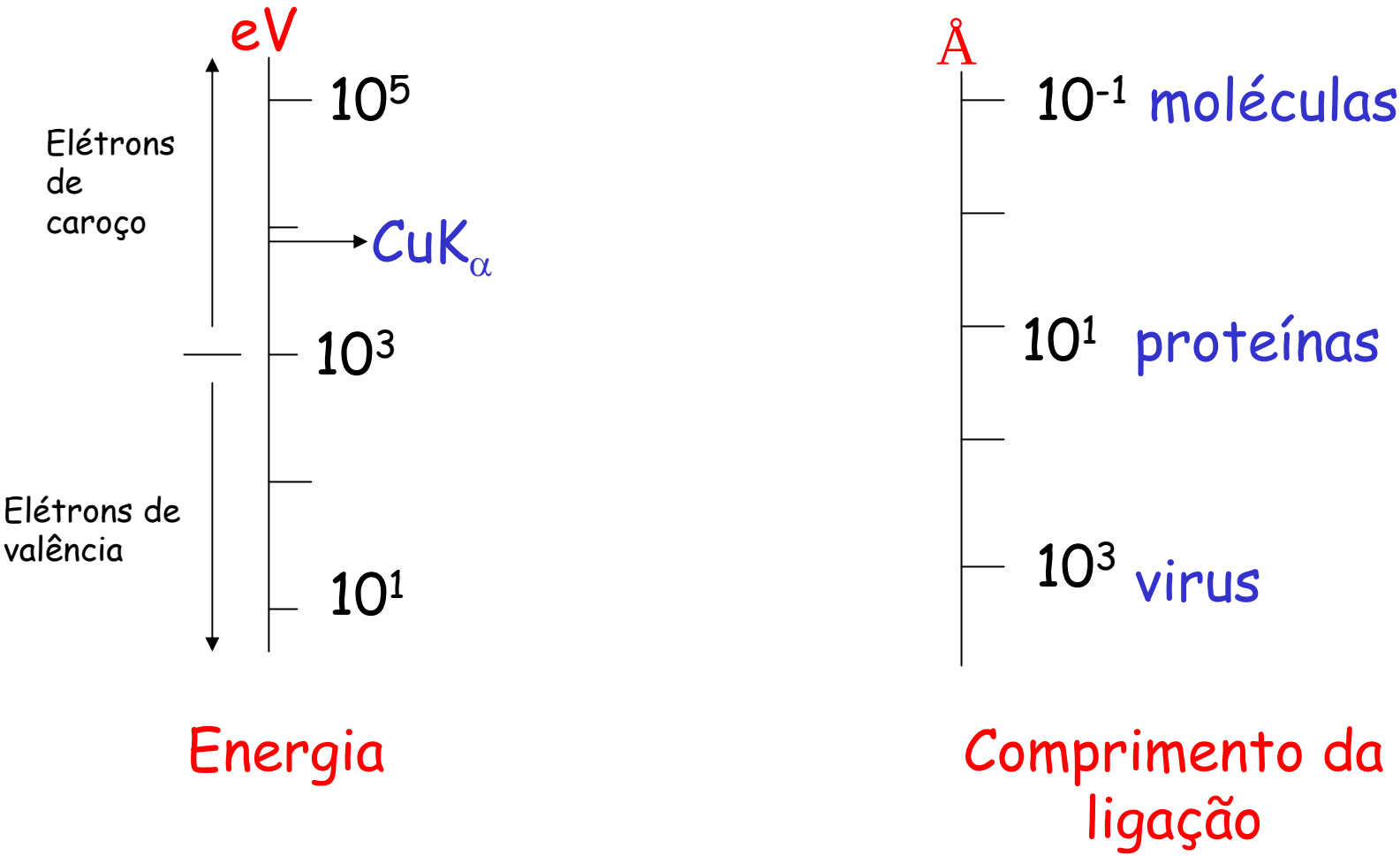
# Características espectrais da fonte de luz

$$\lambda_c = \frac{4\pi m c^2 \rho}{3E_{ac}^{\ 3}}$$




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

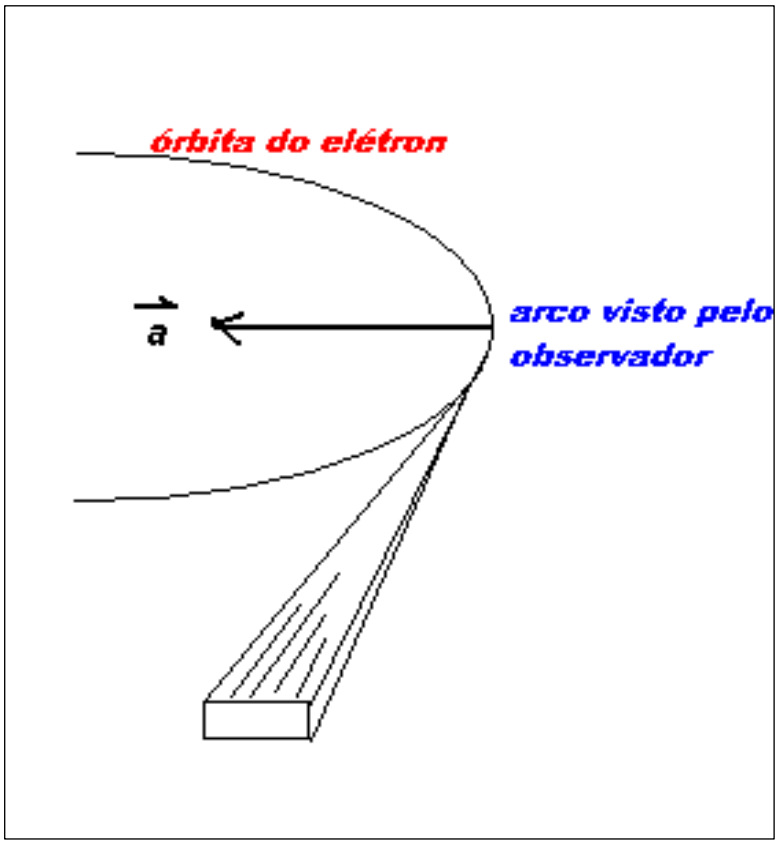
$$E(keV) = \frac{12.4}{\lambda(\text{Å})}$$




# Escolha da energia

# Órbita do elétron

Potência irradiada por uma partícula relativística de massa ***m***, carga ***e***, em movimento circular (raio = $\rho$) e energia $E_{ac}$.

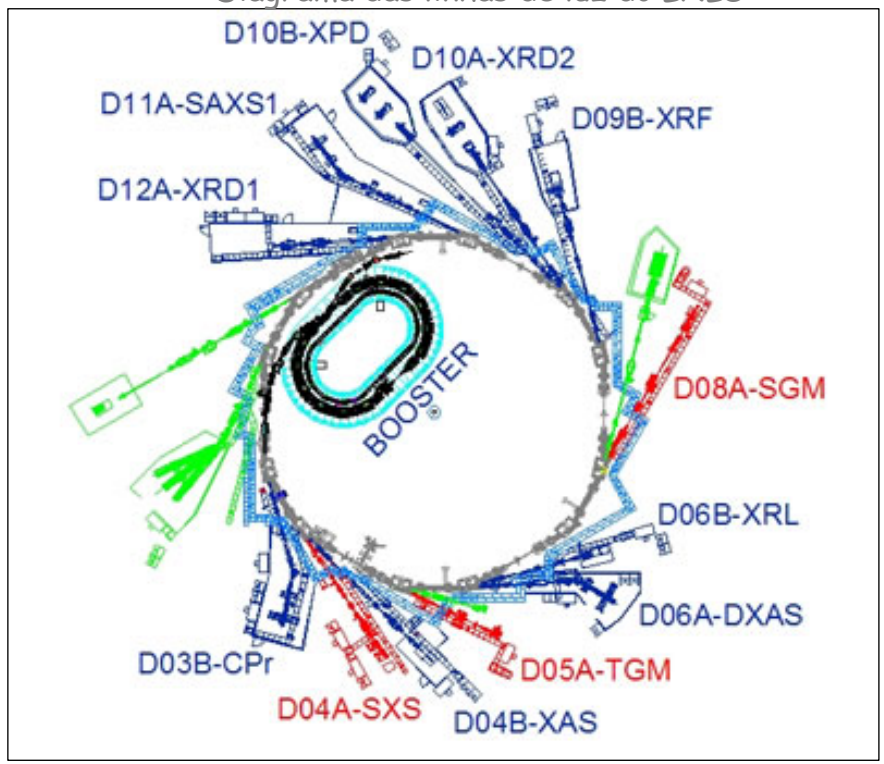



$$P = \frac{2e^2 c\beta^4}{3\rho^2}\left(\frac{E_{ac}}{mc^2}\right)^4$$

$$\beta = \frac{v}{c} \approx 1$$

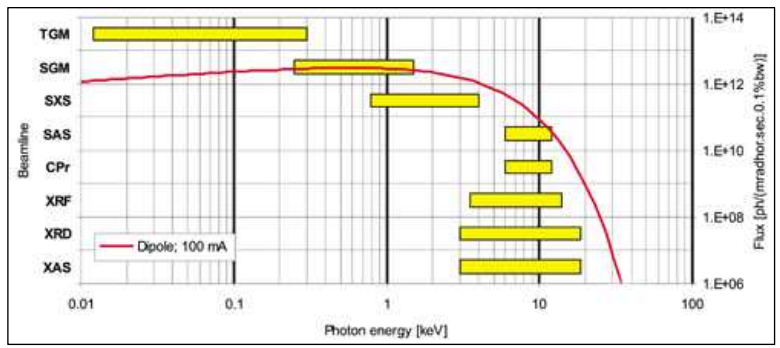
# Fonte BR de radiação síncrotron

Diagrama das linhas de luz do LNLS

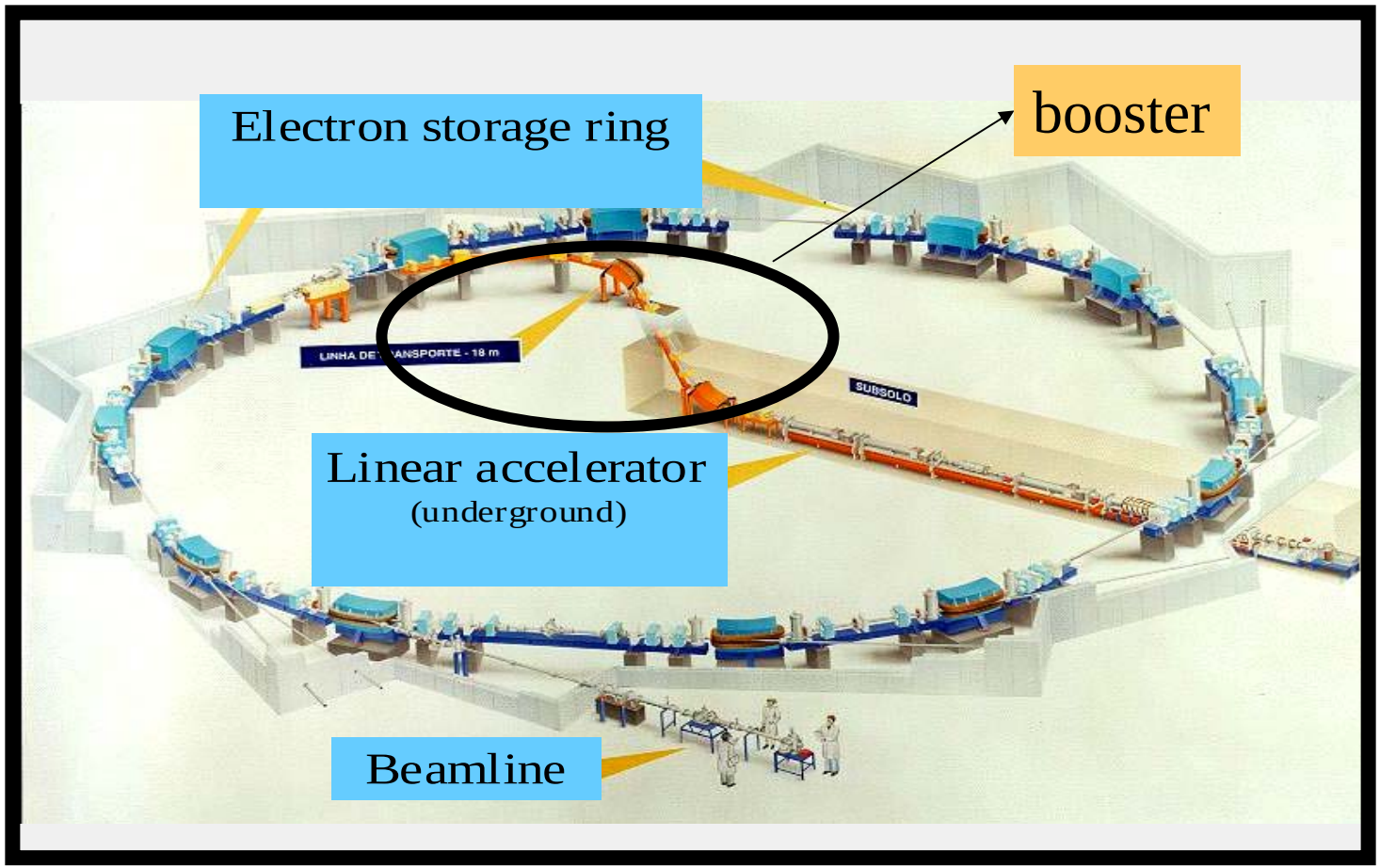



CNPEM

- operacionais em raios-X
- operacionais em ultravioleta e raios-X moles
- novas linhas previstas



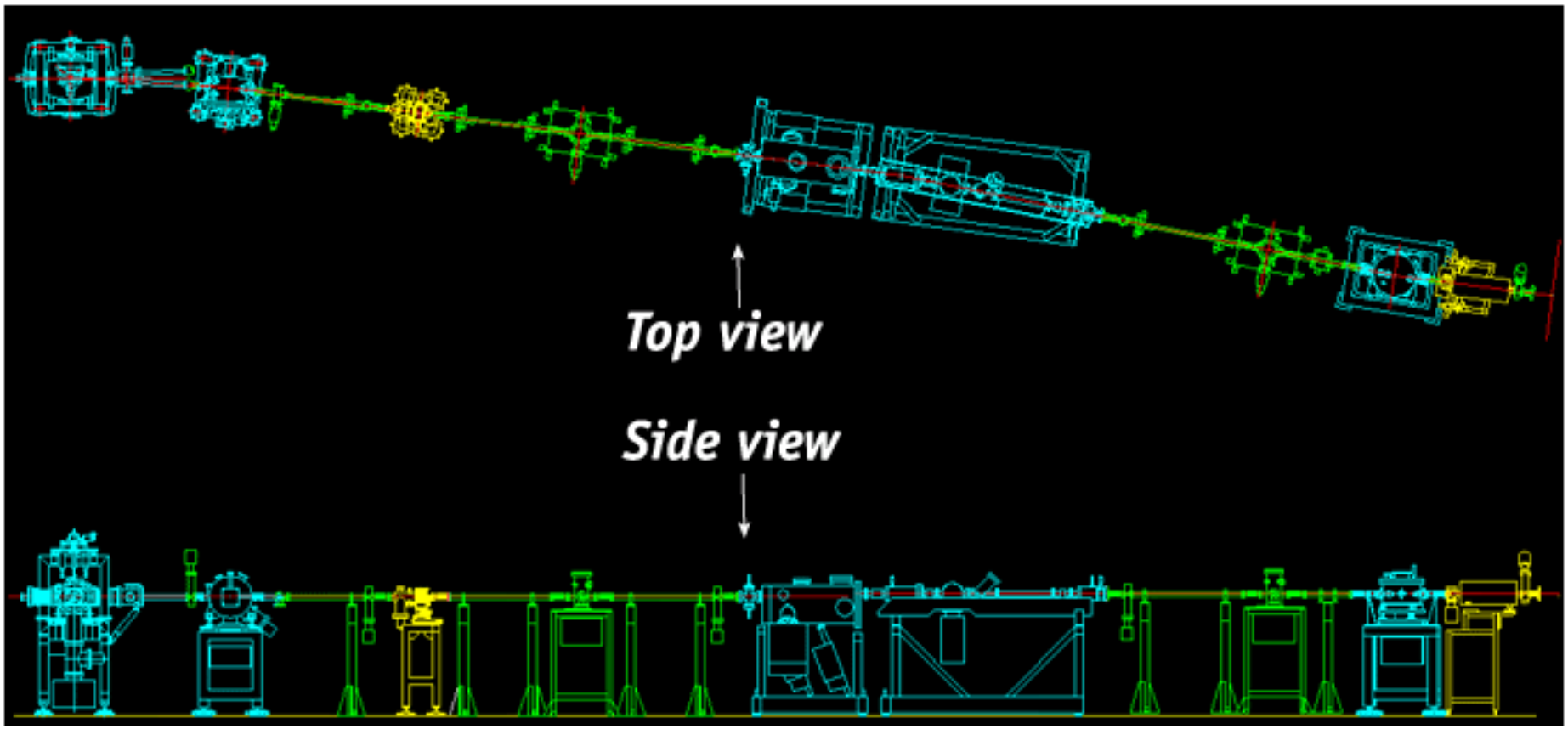
# LNLS (www.lnls.br)




Energia: 1.37 GeV
Corrente: 250 mA
Tempo de vida: 19 hs
Diâmetro : ~ 30m

XAS (3) and SXS (1)
XRD (3) e Cristalografia de proteína (2)
SAXS (2)
Espectroscopia molecular (2)
Fluorescência de raios X (1)

# Linha de luz síncrotron



# Vantagens na utilização da radiação síncrotron

- Produção de radiação X e ultra-violeta pelo menos 5 ordens de magnitude mais intensa que as fontes convencionais.
- Seleção da radiação desejada, através de monocromadores, de um contínuo que vai do infravermelho aos raios X.
- Colimação natural.
- Alta polarização.
- Estrutura pulsada no tempo.
- Ambiente de alto vácuo.
- Fonte de tamanho reduzido.
- Alta estabilidade.

# Áreas de pesquisa beneficiadas

- Física de superfície (EXAFS)
- Química (catálise) (XPS resolvida no tempo)
- Cristalografia de proteínas (dispersão anômala)
- Ciência dos materiais amorfos (XRD, SAXS)
- Análise de traços de elementos (XRF)
- Bioquímica (XRD dependente do tempo)
- Microscopia (~100Å)
- Litografia (circuitos integrados)
- Topografia (defeito em cristais)

- Intensidade $\propto$ I (mA)

  $\propto V^2$ (kV)$^2$

  $\propto Z$

$$Int_{\lambda} = kIZ\left(\frac{\lambda}{\lambda_{\min}} - 1\right)\frac{1}{\lambda^2}$$

$$Int_{\text{integrada}} = 1{,}4 \times 10^{-9}\, IZV^2$$

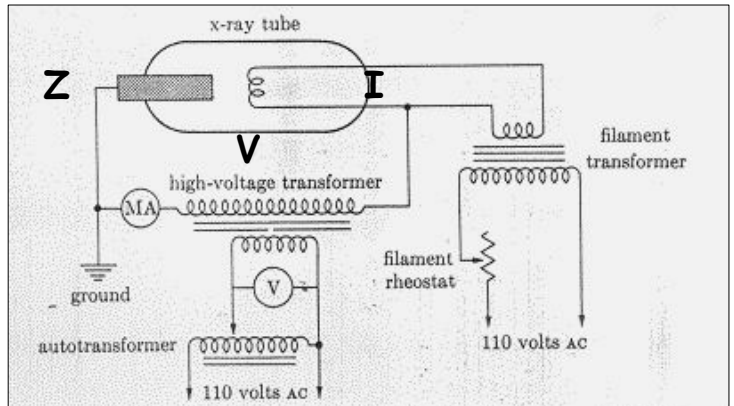



Fig. 1–16 Wiring diagram for self-rectifying filament tube.

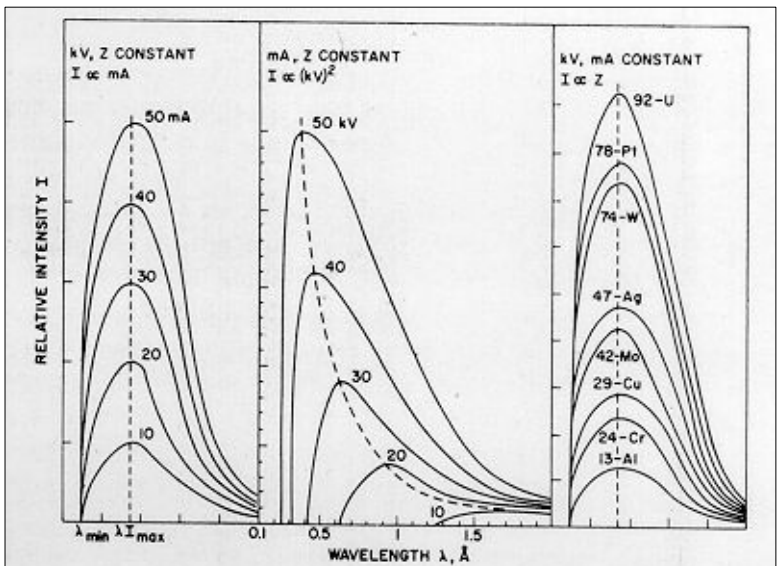



FIG. 1.4. Effect of x-ray tube current, potential, and target atomic number on the continuous spectrum.

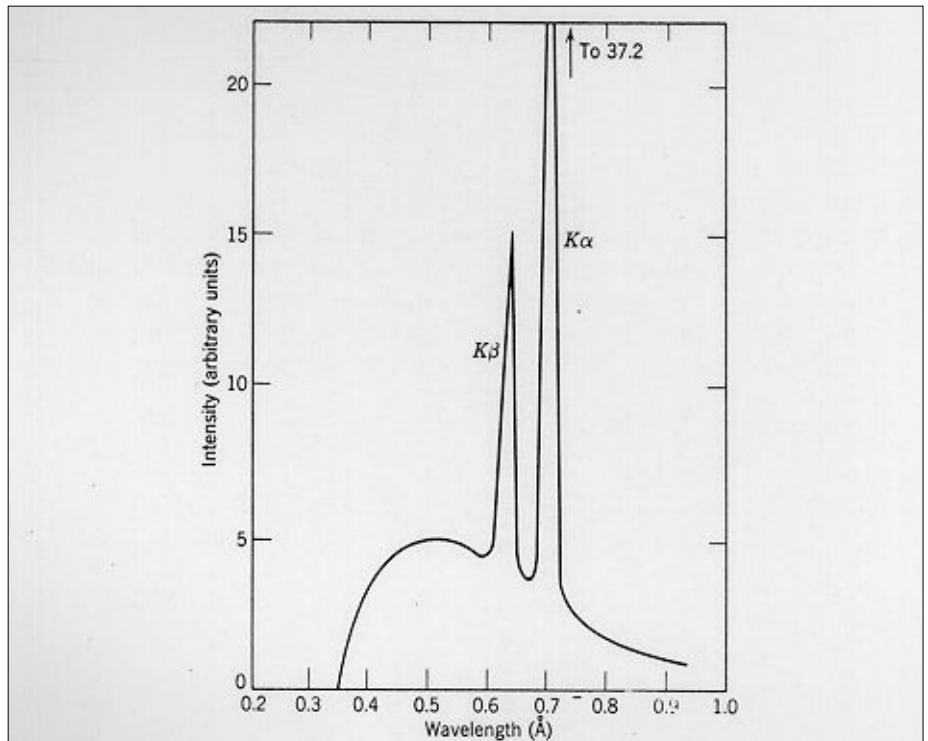



Fig. 2-14. Intensity curve for x-rays from a molybdenum target operated at 35 kV peak. [Courtesy of C. Ulrey, *Phys. Rev.*, **11**, 401 (1918).]

Cullity, 1956 e Bertin, 1975.

# Contínuo

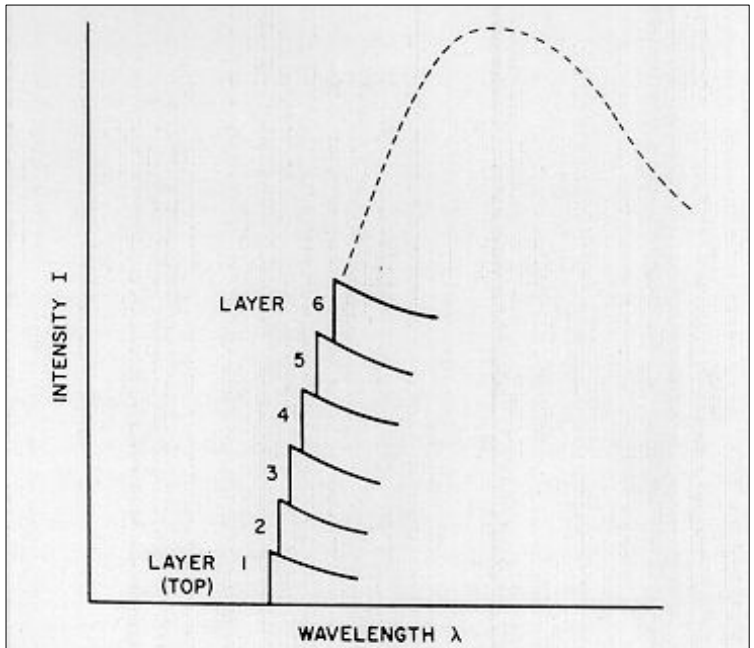



**FIG. 1.3.** Continuous spectrum from an infinitely thick target regarded as the summation of the individual continua from a stack of very thin targets.

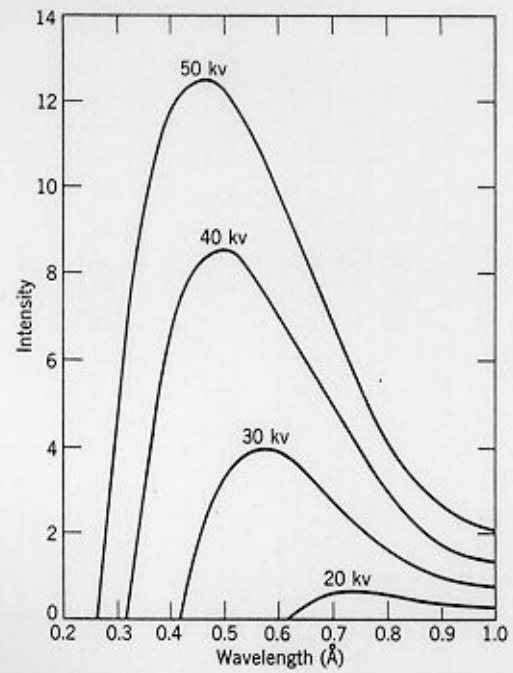



Fig. 2-13. Intensity distribution with wavelength in the continuous x-ray spectrum of tungsten at several voltages. [Courtesy of C. Ulrey, *Phys. Rev.*, **11**, 401 (1918).]

Klug&Alexander, 1974 e Bertin, 1975

# Característico

## Estrutura atômica

$$\frac{I_{K\alpha 1}}{I_{K\alpha 2}} = \frac{2}{1}$$

$$\lambda_{K\alpha} = \frac{2 \times \lambda_{K\alpha 1} + \lambda_{K\alpha 2}}{3}$$

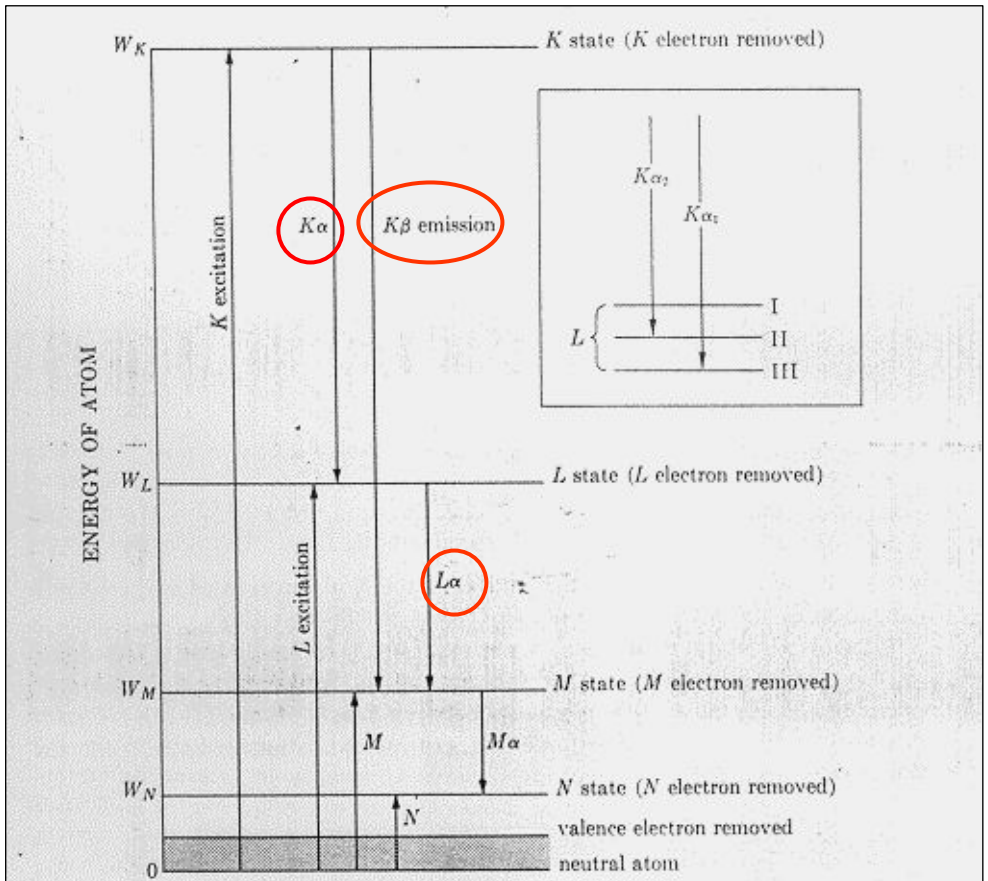



**Fig. 1–11** Atomic energy levels (schematic). Excitation and emission processes indicated by arrows. The insert at top right shows the fine structure of the *L* state. After Barrett [1.7].

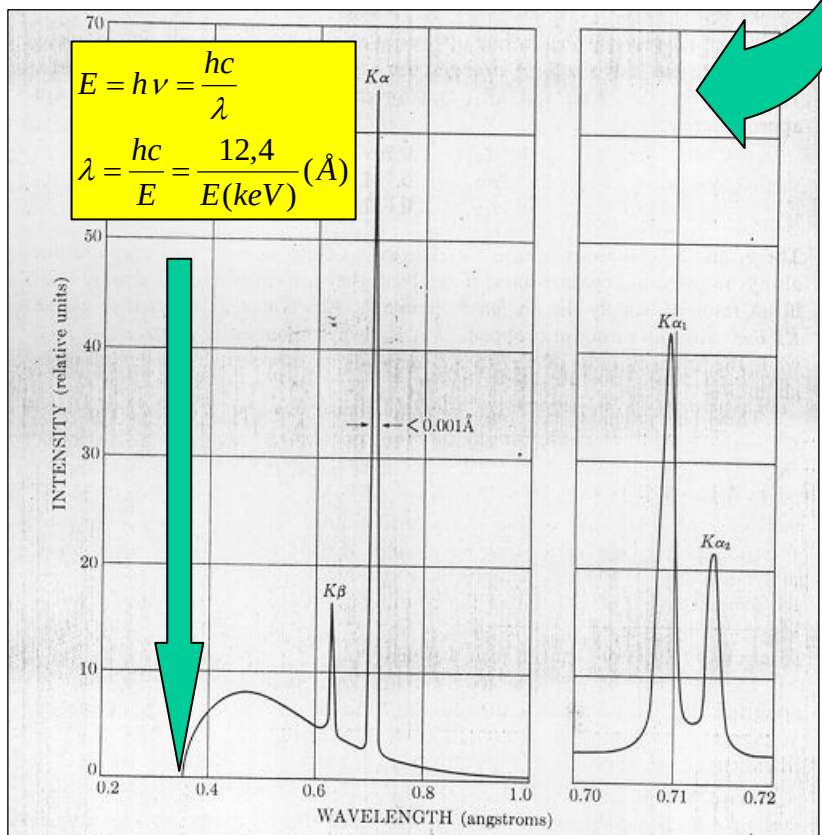



**Fig. 1–5** Spectrum of Mo at 35 kV (schematic). Line widths not to scale. Resolved *Kα* doublet is shown on an expanded wavelength scale at right.

B.D. Cullity. "Elements of X-Ray Diffraction", 1956.

# Escolha da radiação

| Ânodo | $\lambda_{K\alpha}$(Å) | Filtro | $\mu/\rho$ {Metais} |
|---|---|---|---|
| Mo | 0,711 | Zr | todos |
| Cu | 1,542 | Ni | Ni,Cu,Zn |
| Co | 1,790 | Fe | Fe,Co,Ni,Cu,Zn |
| Fe | 1,937 | Mn | Mn,Fe,Co,Ni,Cu,Zn |
| Cr | 2,291 | V | V,Cr,Mn,Fe,Co |

**Metais:** Ti,V,Cr,Mn,Fe,Co,Ni,Cu,Zn.

Sem filtro

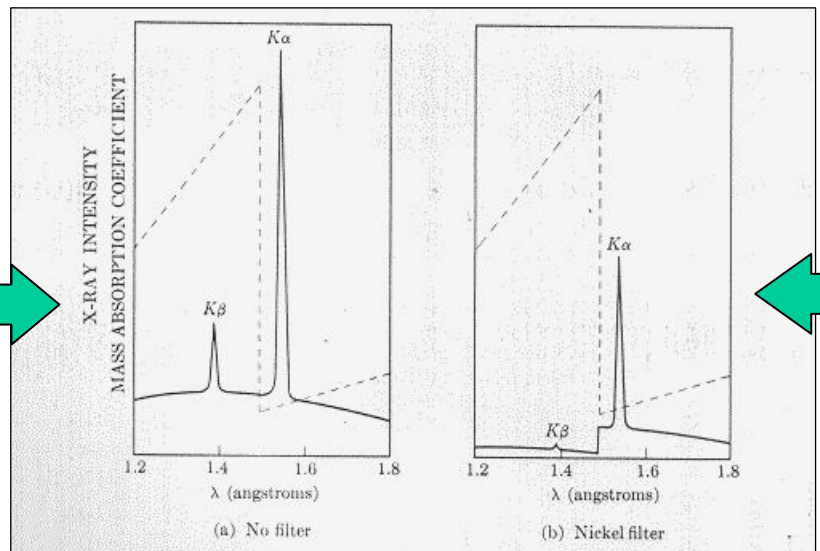



**Fig. 1–13** Comparison of the spectra of copper radiation (a) before and (b) after passage through a nickel filter (schematic). The dashed line is the mass absorption coefficient of nickel.

Com filtro

B.D. Cullity. "Elements of X-Ray Diffraction", 1956.

Radiação: Cu

Filtro: Ni

# Método de Debye-Scherrer

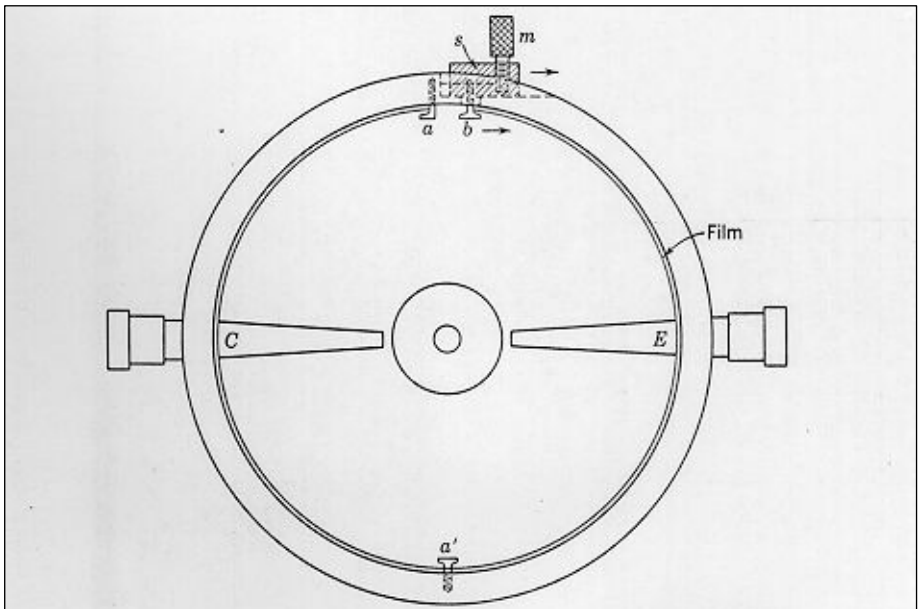



Fig. 4-10. Arrangement involving a movable finger for compressing film against camera wall.

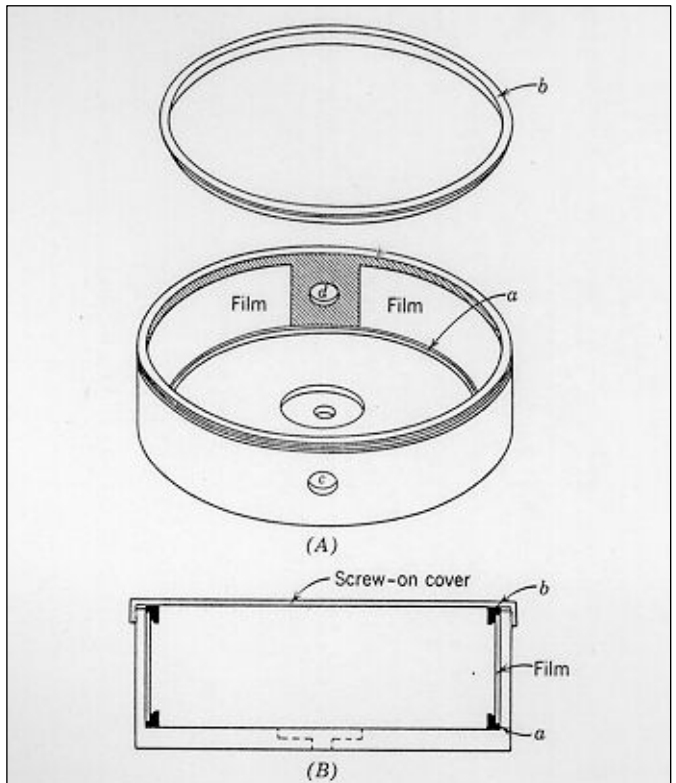
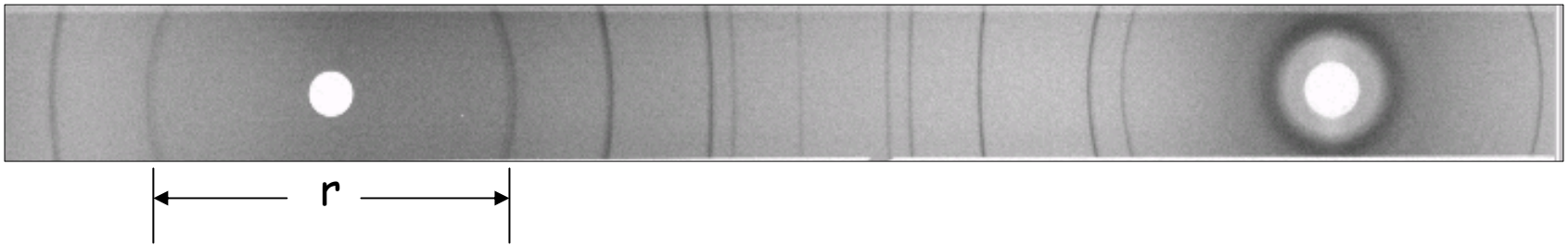



Fig. 4-9. Beveled-ring arrangement for holding film in position.

Klug&Alexander, 1974.

# Método de Debye-Scherrer




$P = 360 \text{ mm} = 2\pi R$

$R = 180/\pi = 57{,}3 \text{ mm}$

$S = R\alpha$ (arco= raio x ângulo)

$P/(S=r) = (2\pi R) / (4\theta R) \longrightarrow$ rad

$360(\text{mm})/r(\text{mm}) = 2\pi/(4\theta^{o} \times \pi/180^{o})$

$r\ (\text{mm}) = 4\theta^{o}$

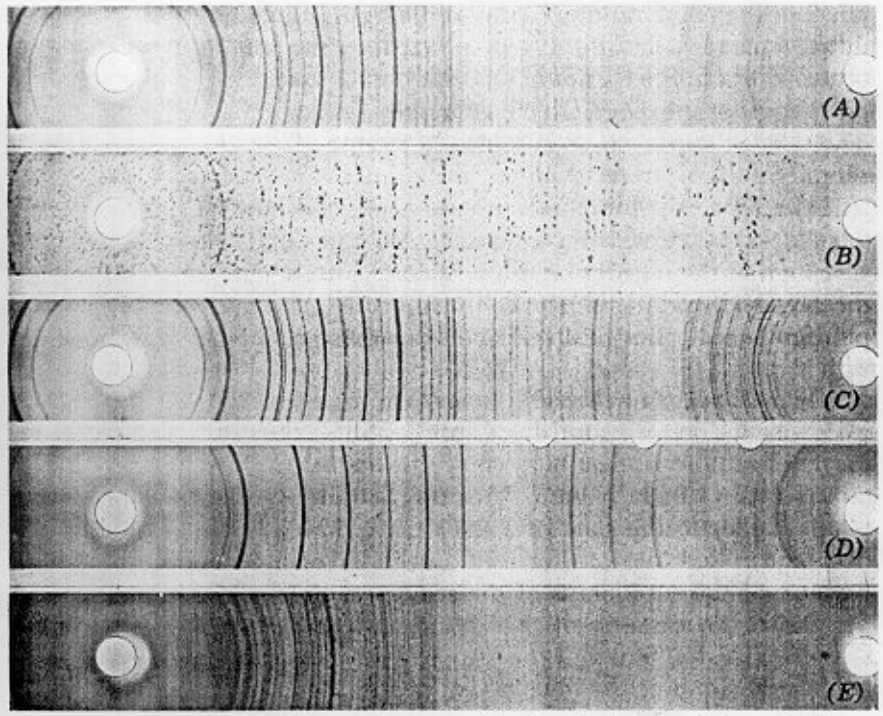



Fig. 4-18. Debye-Scherrer photographs prepared under different conditions. (*A*) Quartz powder, <5 μ, specimen stationary. (*B*) Quartz powder, 15–50 μ, specimen stationary. (*C*) Quartz powder, 15–50 μ, specimen rotating. (*D*) NaCl, <325 mesh, specimen rotating. (*E*) Feldspar, <325 mesh, specimen rotating.

Klug&Alexander, 1974.

# Método de Laue

- Transmissão

$$tg\,2\theta = \frac{r_L}{D}$$

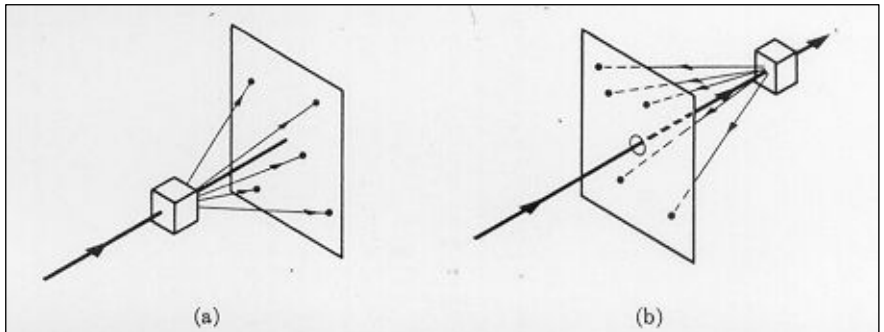



Fig. 3–5 (a) Transmission and (b) back-reflection Laue methods.

Reflexão

$$tg(180^o - 2\theta) = \frac{r_L}{D}$$

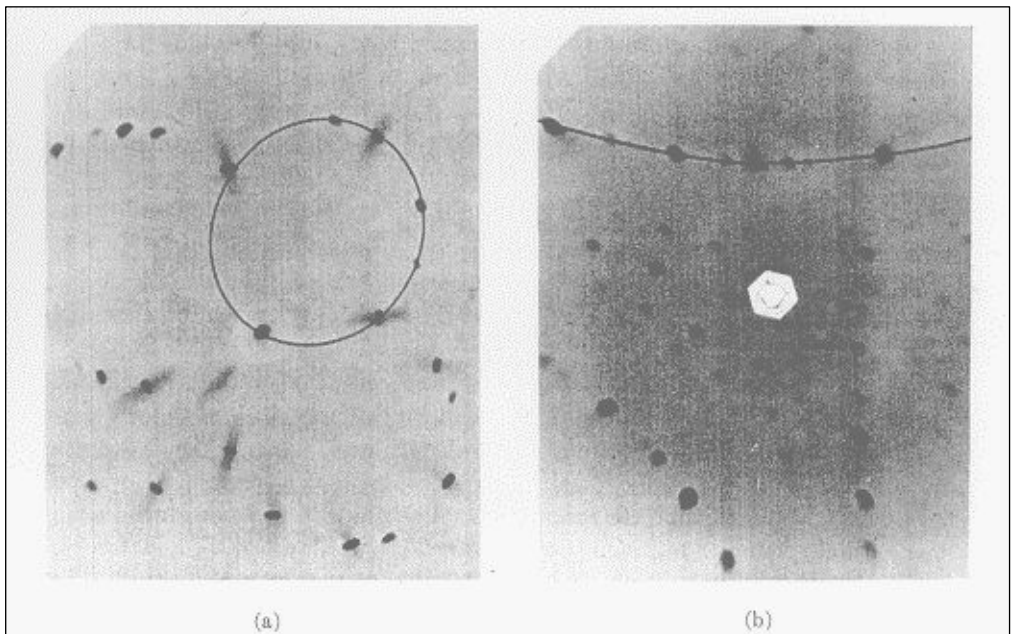
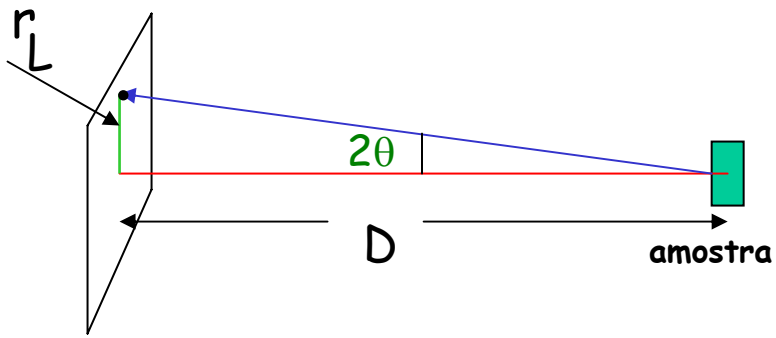
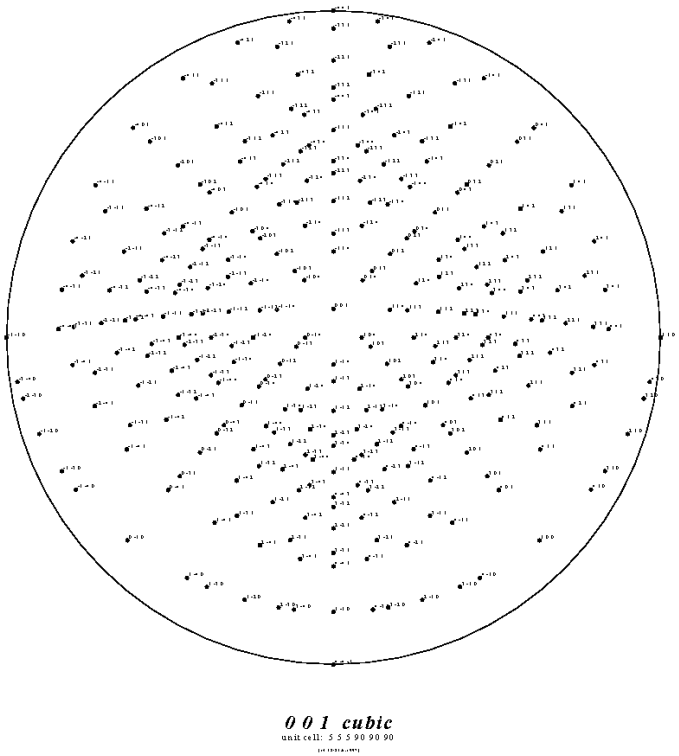



Fig. 3–6 (a) Transmission and (b) back-reflection Laue patterns of an aluminum crystal (cubic). Tungsten radiation, 30 kV, 19 mA.

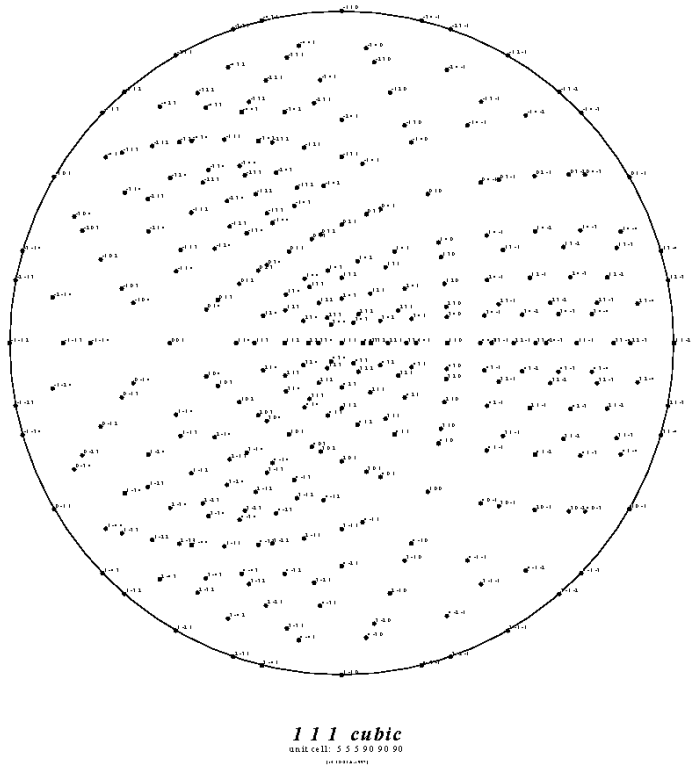



B.D. Cullity. "Elements of X-Ray Diffraction", 1956.

# Método de Laue

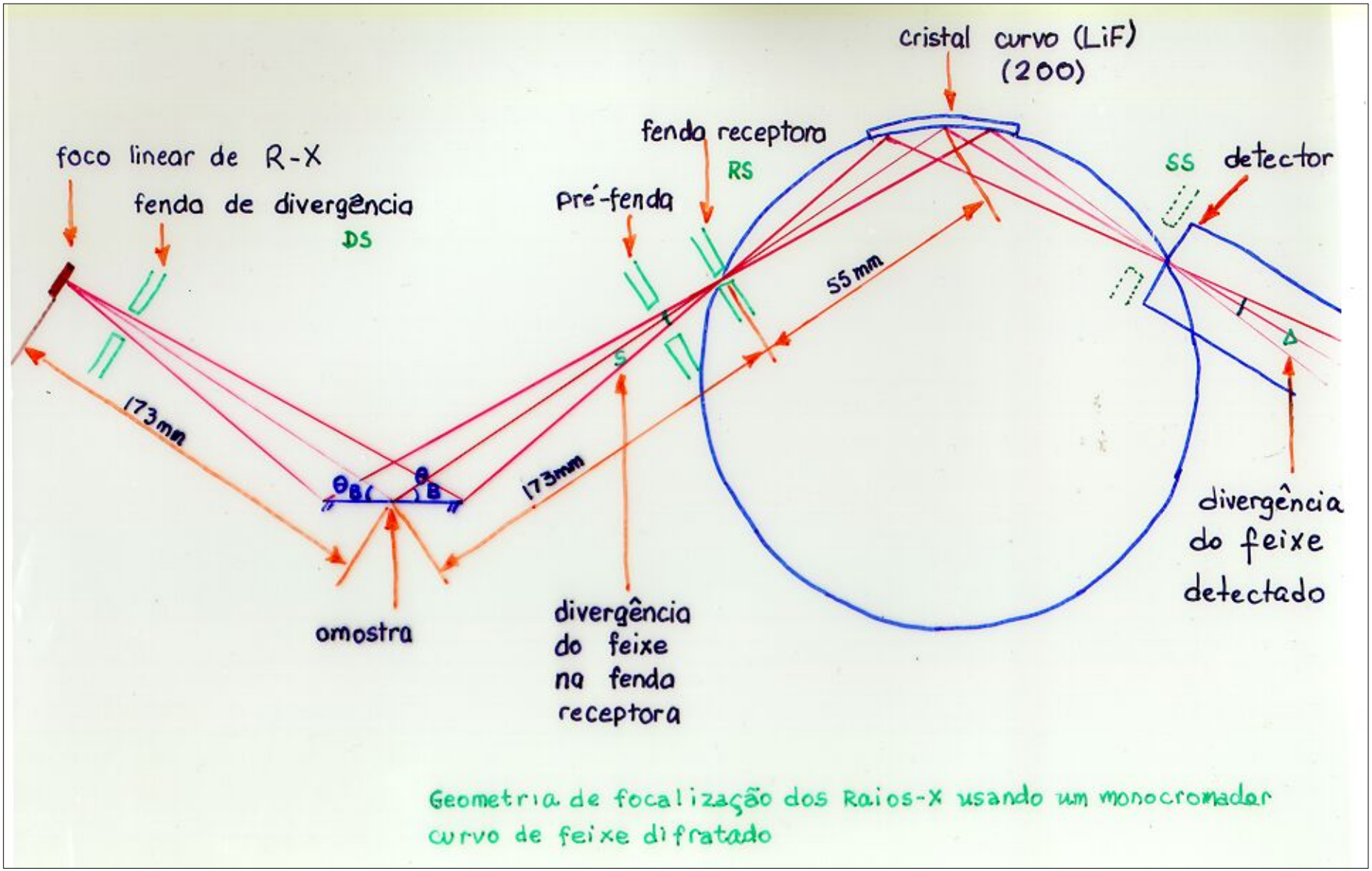



Eixo 4




Eixo 3

# Difratômetro




Geometria de focalização dos Raios-X usando um monocromador curvo de feixe difratado

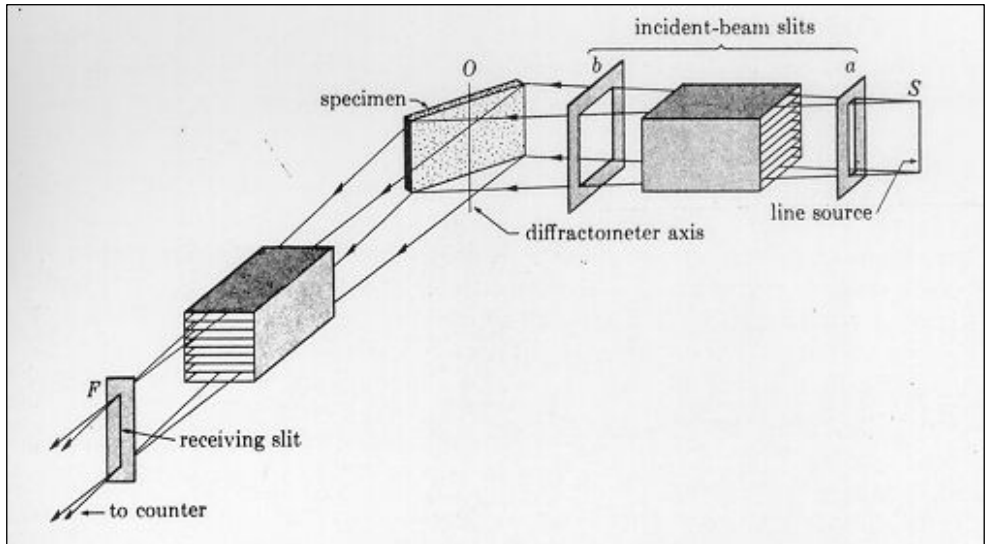



**Fig. 7–8** Arrangement of slits in diffractometer.

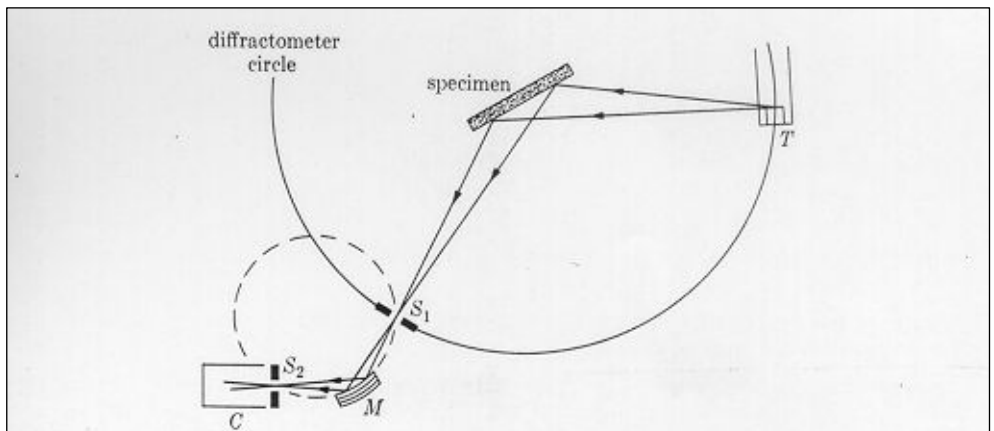



**Fig. 7–28** Diffractometer with monochromating crystal $M$ in diffracted beam. $C$ = counter, $T$ = x-ray tube.



B.D. Cullity. "Elements of X-Ray Diffraction", 1956.