

Difração de raios X

Lucas Barboza Sarno da Silva

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 - Descoberta
 - Ondas eletromagnéticas
 - Raios X característicos e contínuos

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 - Geometria
 - Tubo de raios X
 - Detetores

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 - Difração e Lei de Bragg
 - Planos de Bragg
 - Exemplos

- **Exemplos de aplicação**
 - Identificação de fases
 - Refinamento da estrutura
 - Cálculo do tamanho de partícula

Raios X



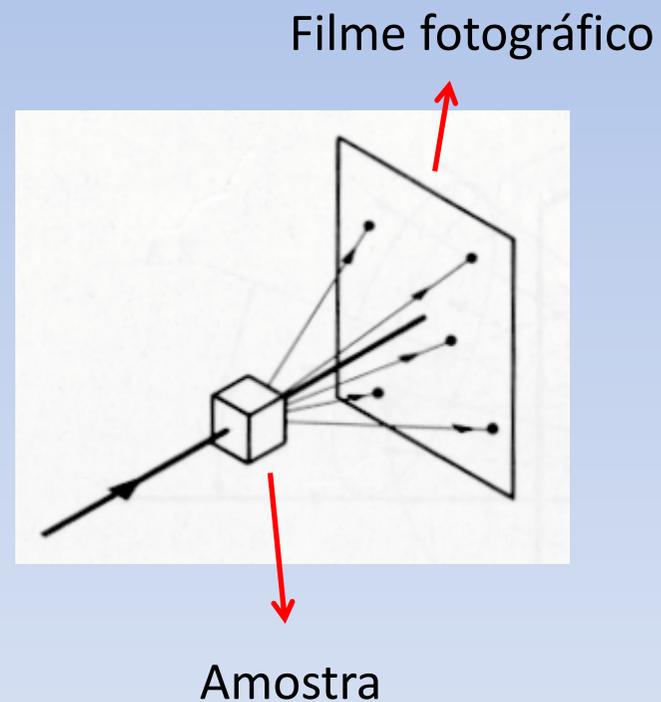
Descoberta dos raios X

1895



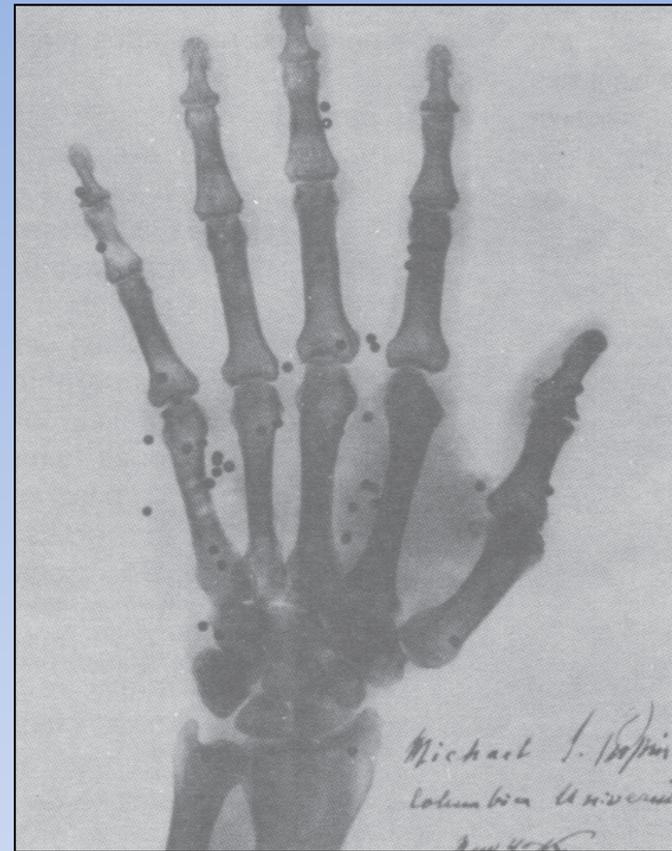
Wilhelm Konrad Röntgen
(1845-1923)

Válvulas
(Tubos de raios
Catódicos)



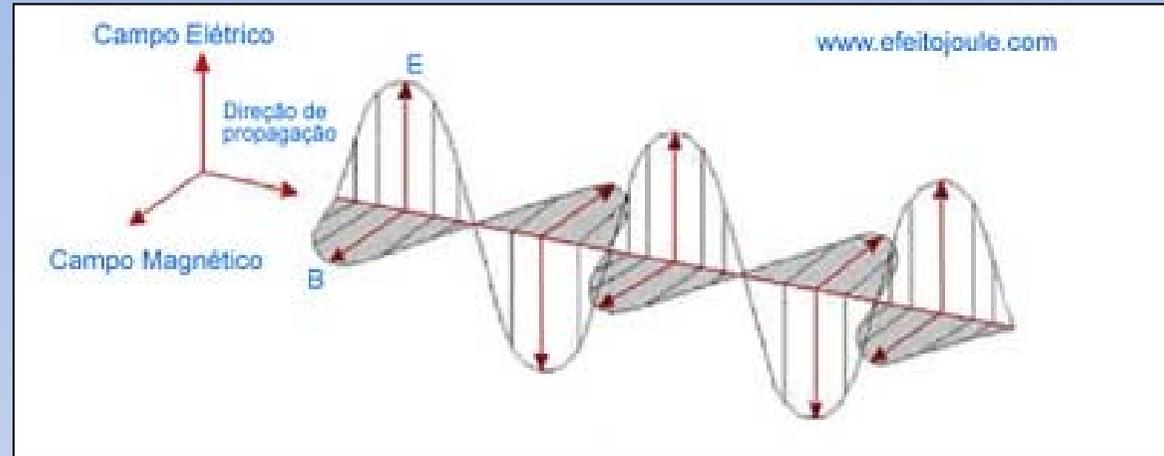


Primeira radiografia realizada no mundo, mostrando a mão da esposa de Röntgen. Note o anel no dedo anular.



Apenas um mês após Roentgen tirar a primeira radiografia, o professor Michael I. Pupin, da Universidade de Columbia, radiografou a mão de um caçador que sofrera um acidente com sua espingarda. As bolinhas negras representam cerca de 40 pedaços de chumbo que estavam ali alojadas.

Ondas eletromagnéticas



Raio-X é radiação eletromagnética com comprimento de onda no intervalo de 10^{-11} a 10^{-8} m (0,1 a 100 Å), resultante da colisão de elétrons produzidos em um catodo aquecido contra elétrons de anodo metálico

$$E = hf$$

$h = 6,625 \times 10^{-34}$ J.s
(constante de Planck)

THE ELECTROMAGNETIC SPECTRUM

Penetrates Earth Atmosphere?



Wavelength (meters)



10^3 10^{-2} 10^{-5} $.5 \times 10^{-6}$ 10^{-8} 10^{-10} 10^{-12}

About the size of...

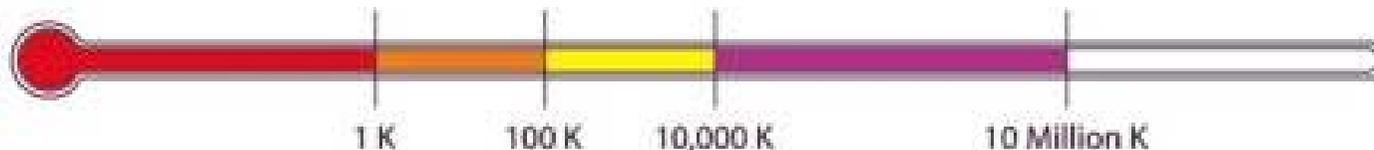


Buildings Humans Honey Bee Pinpoint Protozoans Molecules Atoms Atomic Nuclei

Frequency (Hz)



Temperature of bodies emitting the wavelength (K)



Geração de raios X característicos

$$\Delta E = E_f - E_i$$

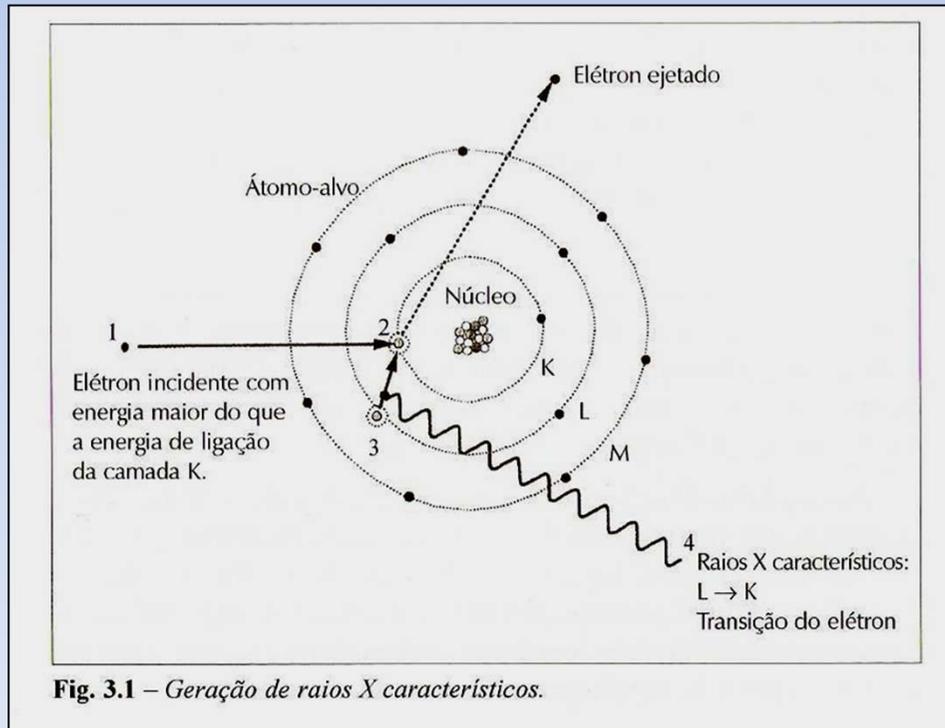
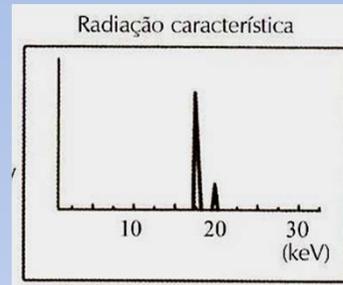
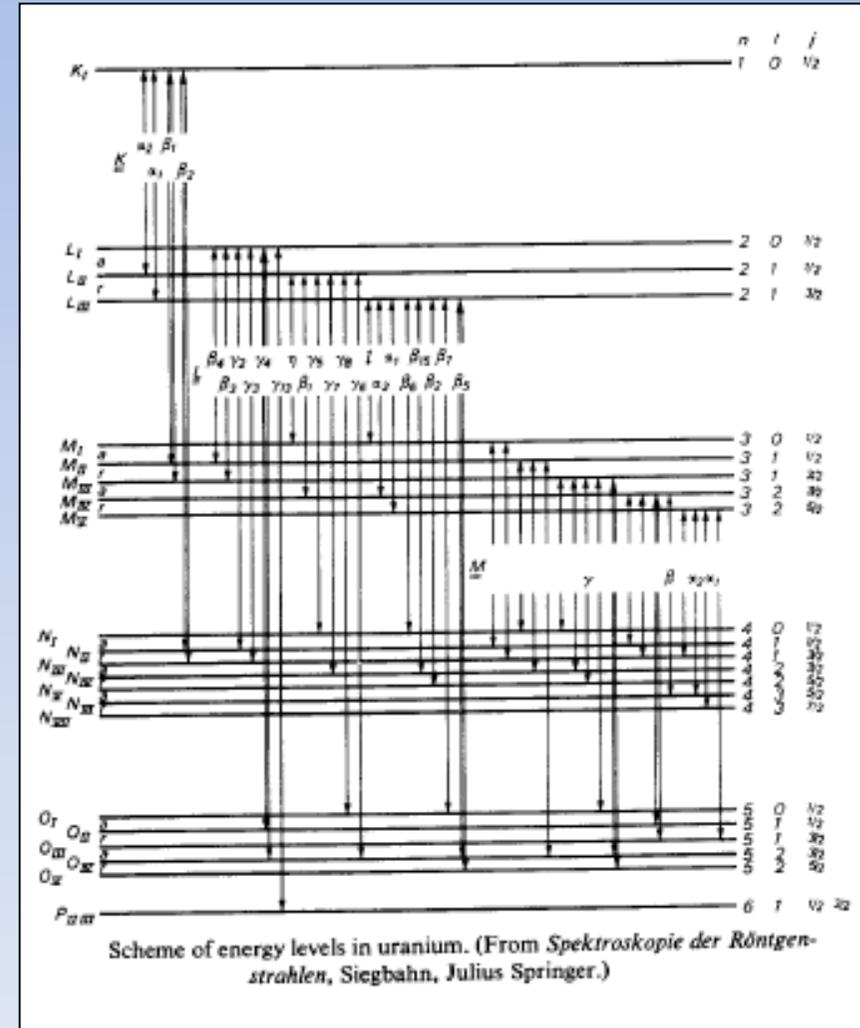
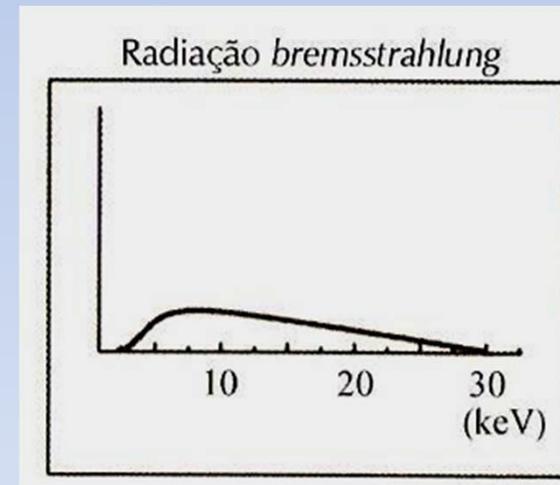
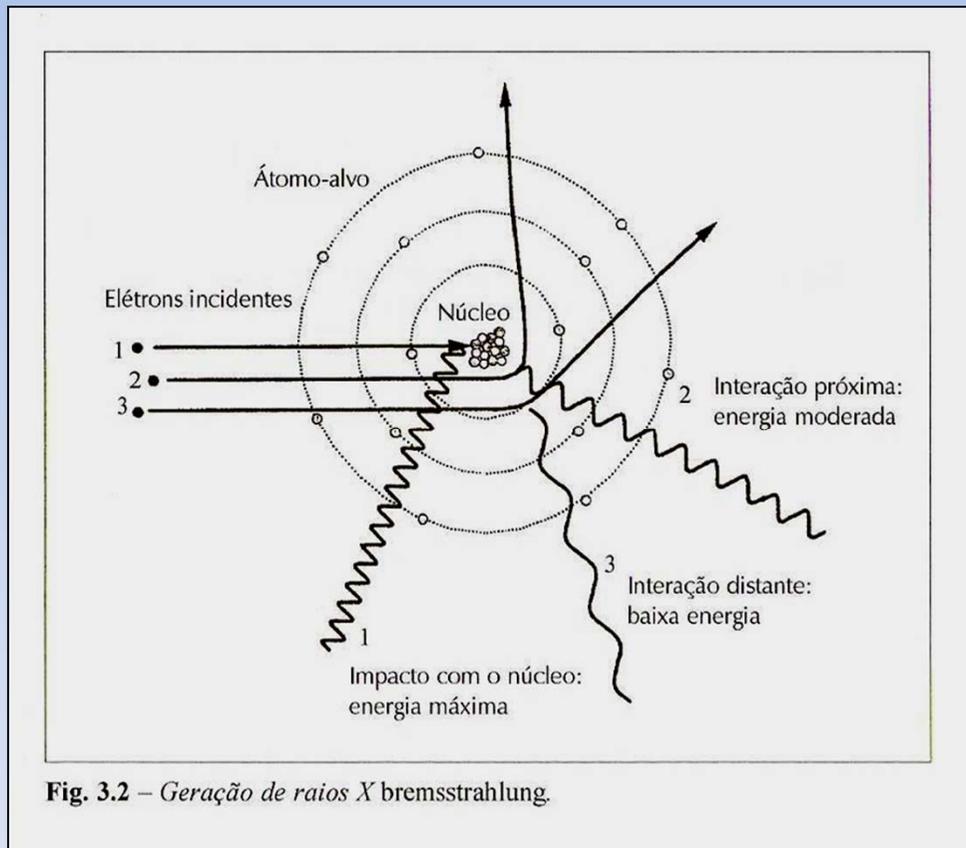


Fig. 3.1 – Geração de raios X característicos.



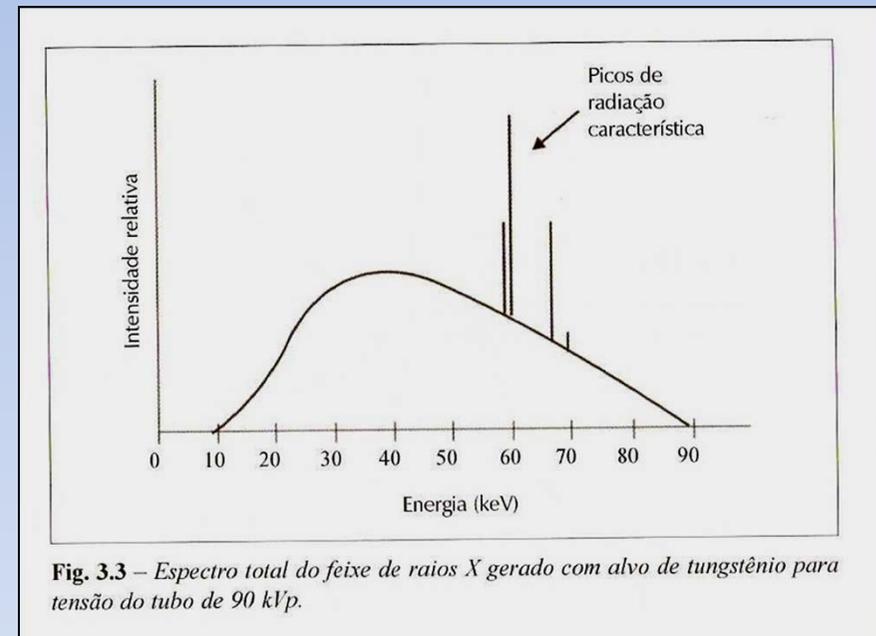
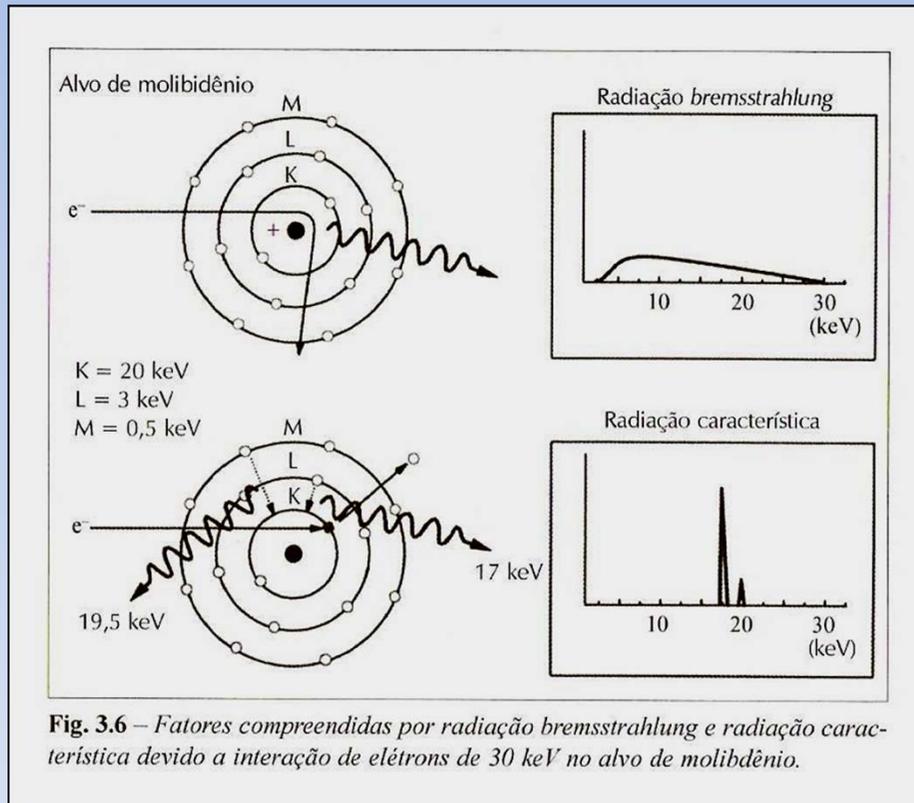
Produção de raios X por bremsstrahlung

Perda de energia por frenamento



Espectro contínuo

Convolução entre os espectros de raios X



Propriedades dos raios X

- Raio invisível
- Propaga-se em linha reta
- Propaga-se com a velocidade da luz ($v = c = 3 \cdot 10^8$ m/s)
- Difração, refração e polarização
- Capacidade de escurecer chapas fotográficas
- Capacidade de produzir fluorescência e fosforescência em algumas substâncias
- Capacidade de liberar fotoelétrons
- Capacidade de danificar e matar células vivas e produzir mutações genéticas

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Figuras características

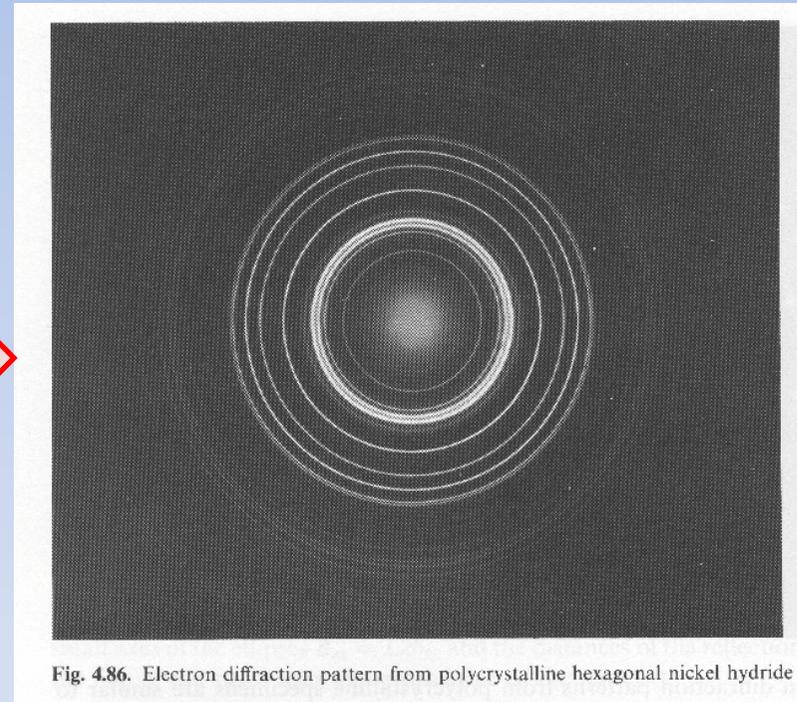
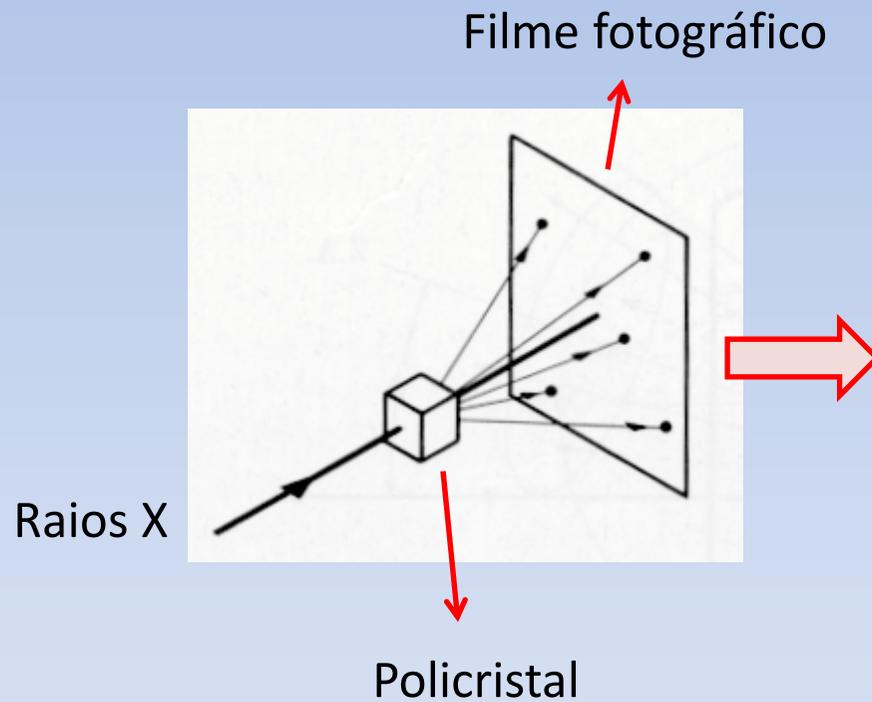


Figura de interferências característica

Geometria Bragg-Bretano

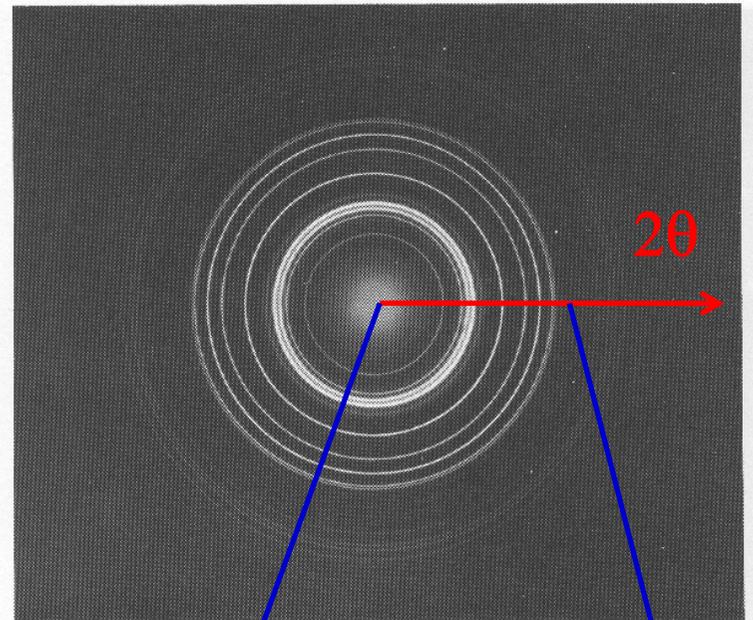
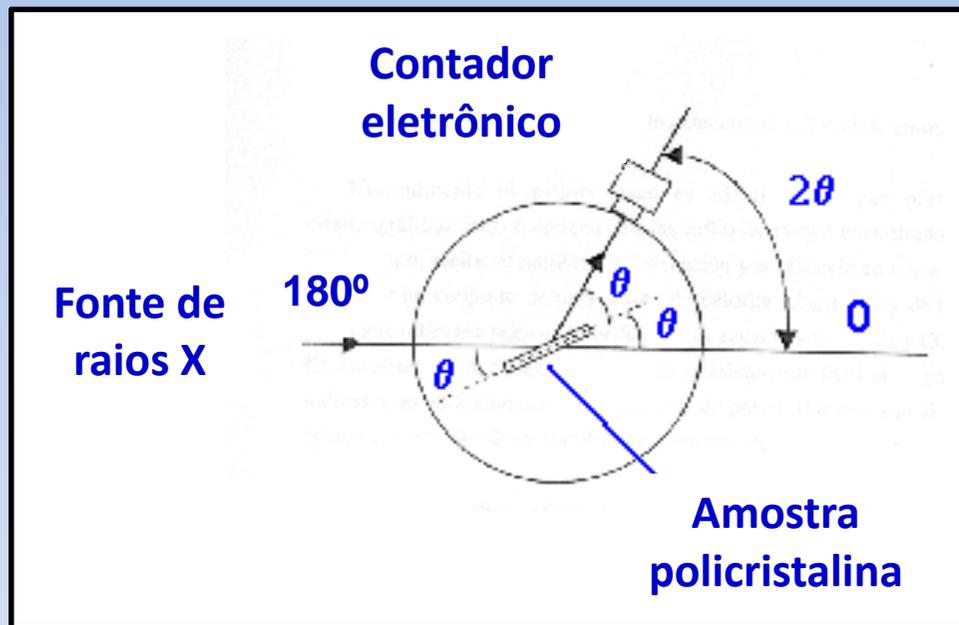
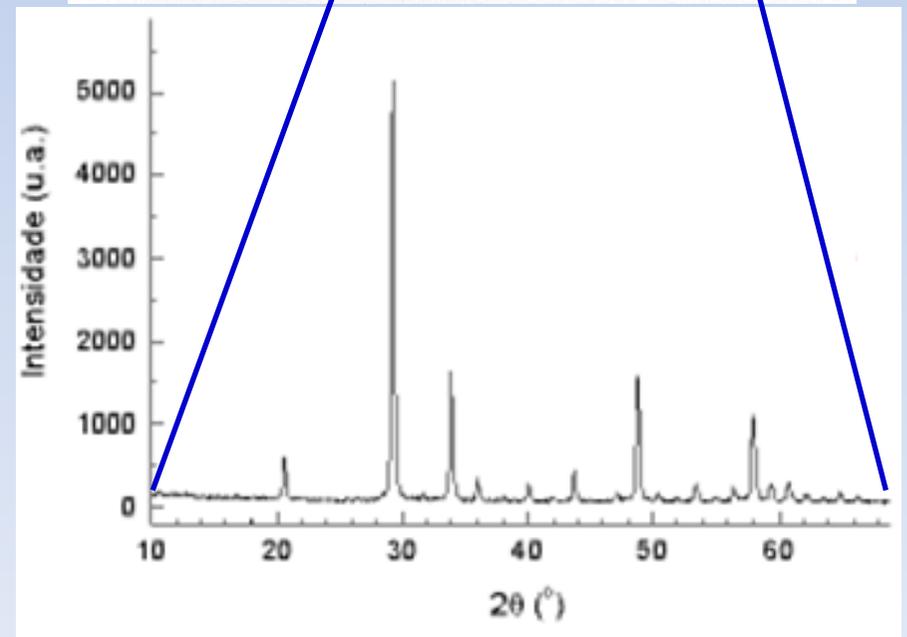
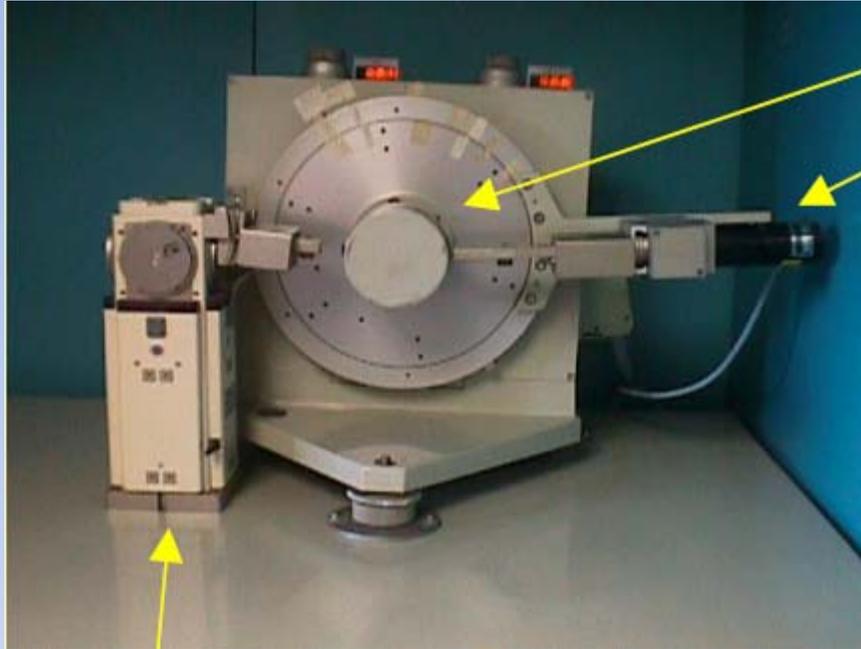


Fig. 4.86. Electron diffraction pattern from polycrystalline hexagonal nickel hydride



Difratômetro de raios X



Tubo de raios X

Suporte de amostra

Detector de raios X

Geometria Bragg-Bretano

Contador

Condições de medida:

- amostra na forma de pó
- 40 kV x 30 mA
- intervalo angular: $10^\circ \leq 2\theta \leq 90^\circ$
- passo angular: $0,05^\circ$
- tempo de contagem: 3 s

poli cristalina

Tubo de raios X

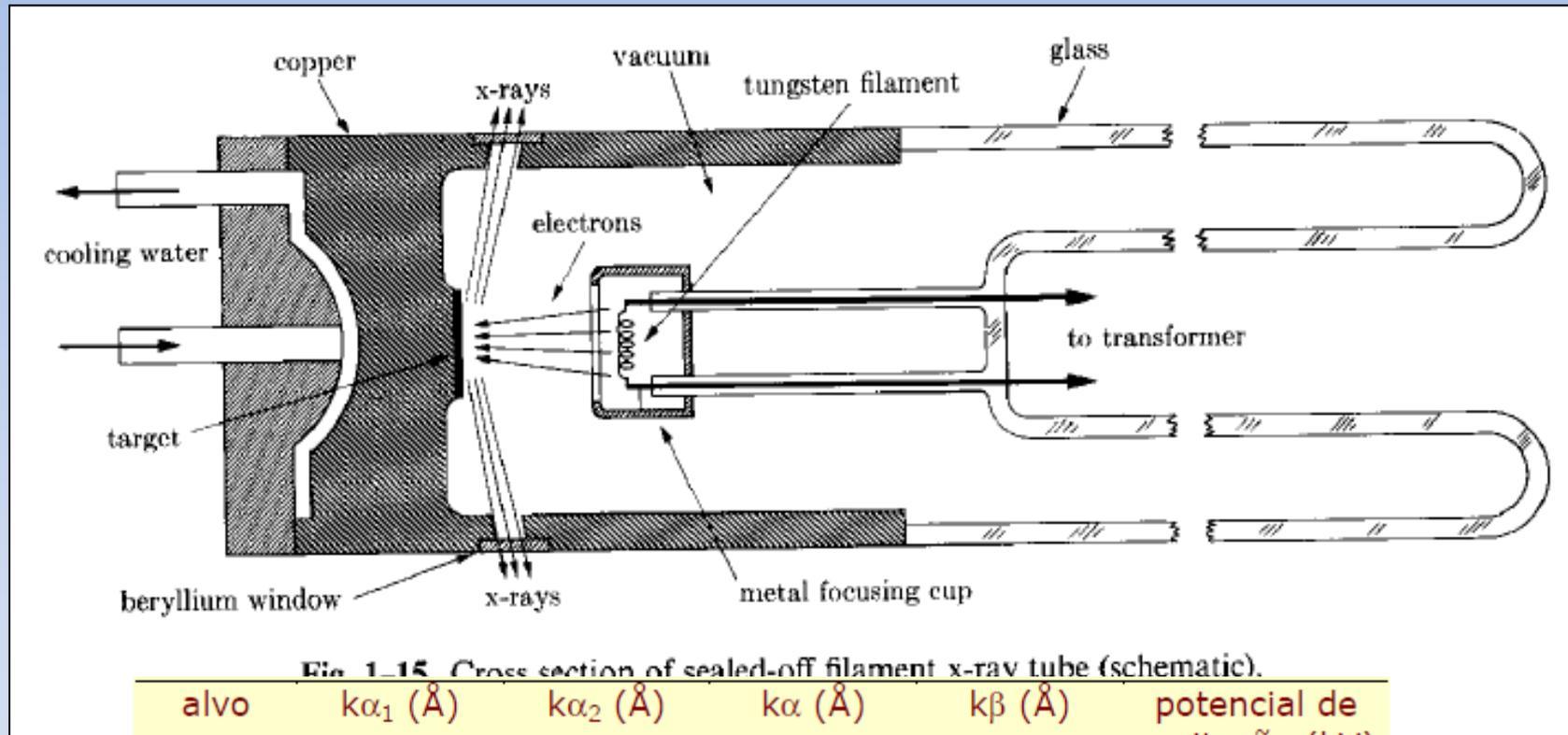
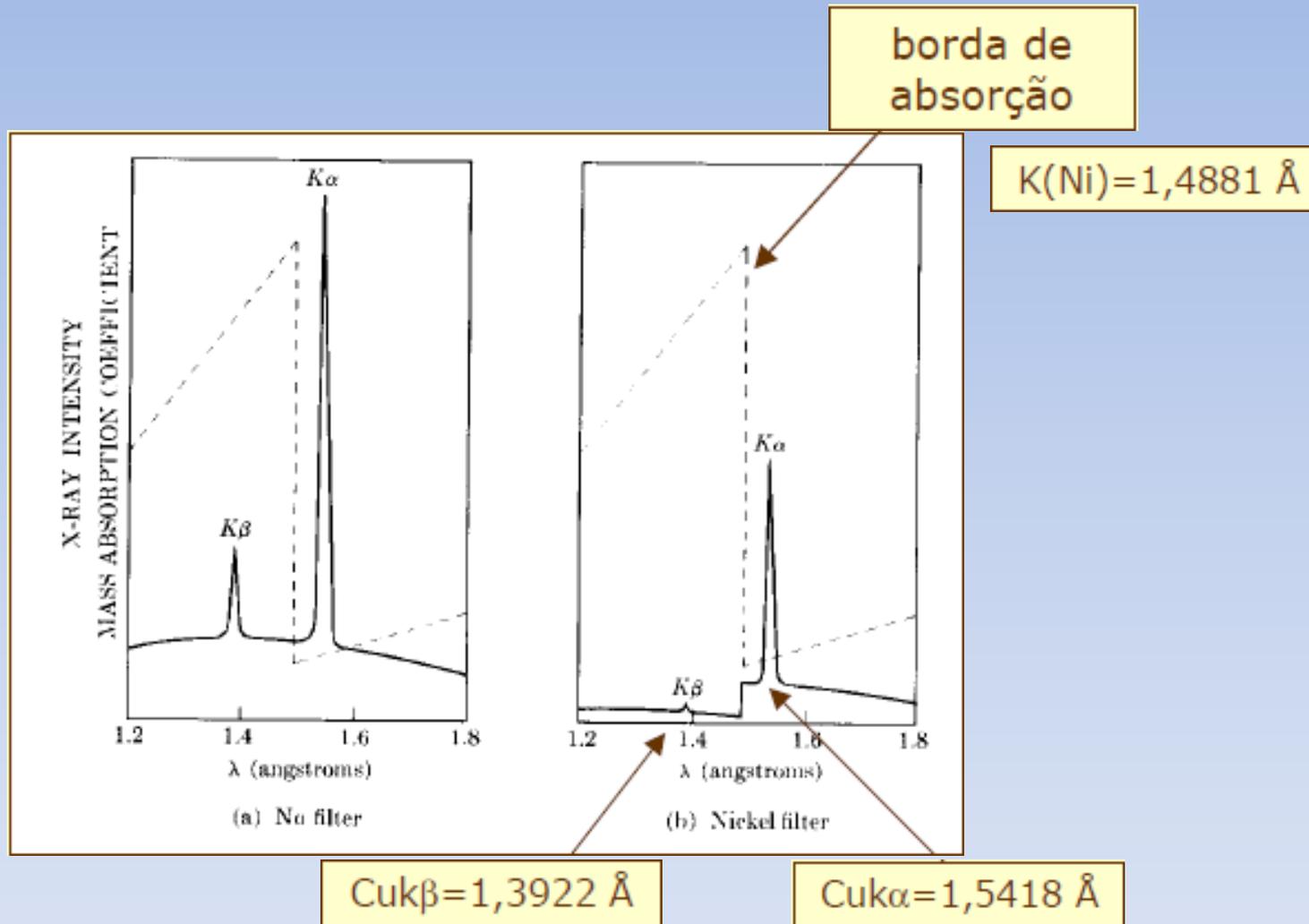


Fig. 1-15. Cross section of sealed-off filament x-ray tube (schematic).

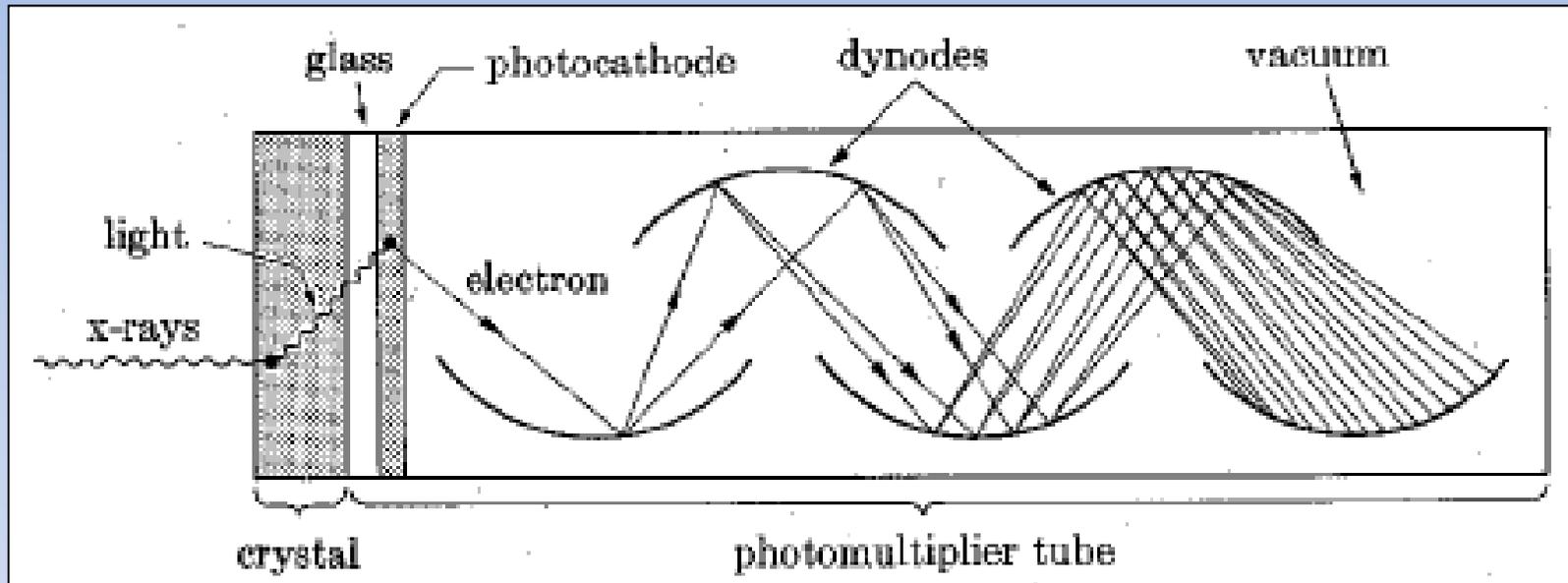
alvo	$k\alpha_1$ (Å)	$k\alpha_2$ (Å)	$k\alpha$ (Å)	$k\beta$ (Å)	potencial de excitação (kV)
Ag	0,55941	0,56380	0,56084	0,49707	25,52
Mo	0,70930	0,71359	0,71073	0,63229	20,00
Cu	1,54056	1,54439	1,54184	1,39222	8,98
Co	1,78897	1,79285	1,79026	1,62079	7,71
Fe	1,93604	1,93998	1,93735	1,75661	7,11

Filtros



elemento	Ag	Mo	Cu	Ni	Co	Fe	Cr
borda de absorção K (Å)	0,4859	0,6198	1,3806	1,4881	1,6082	1,7435	2,0702

Detector de raios X



Cintilação (tubo fotomultiplicador)

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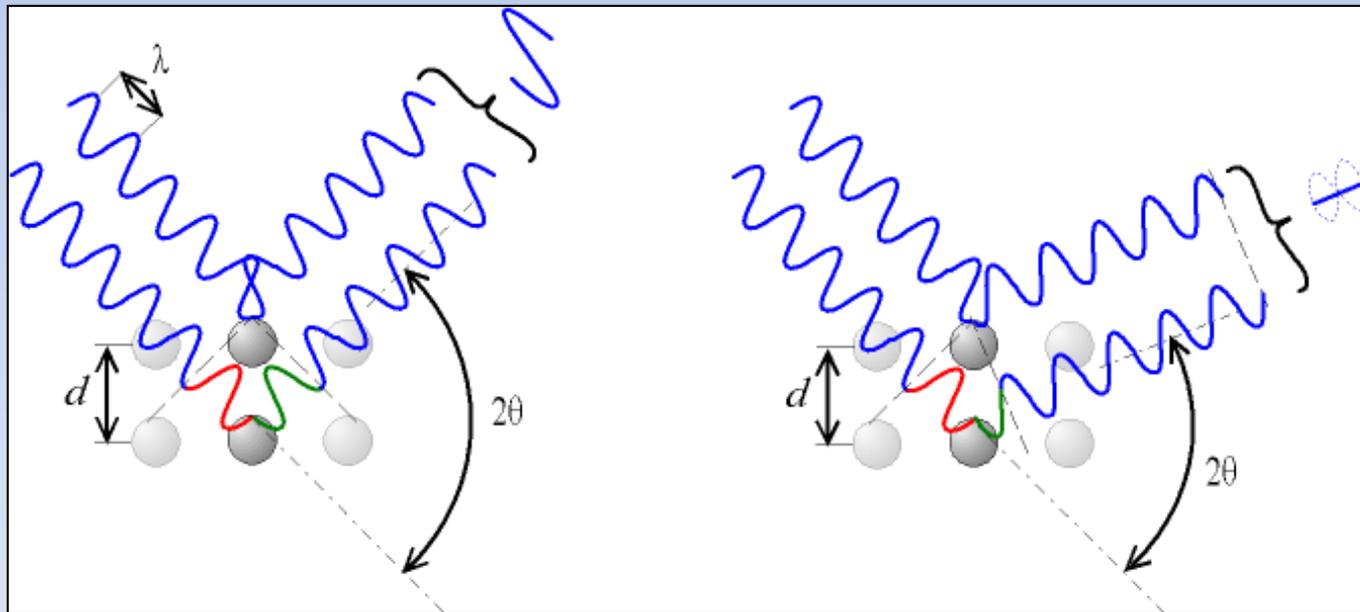
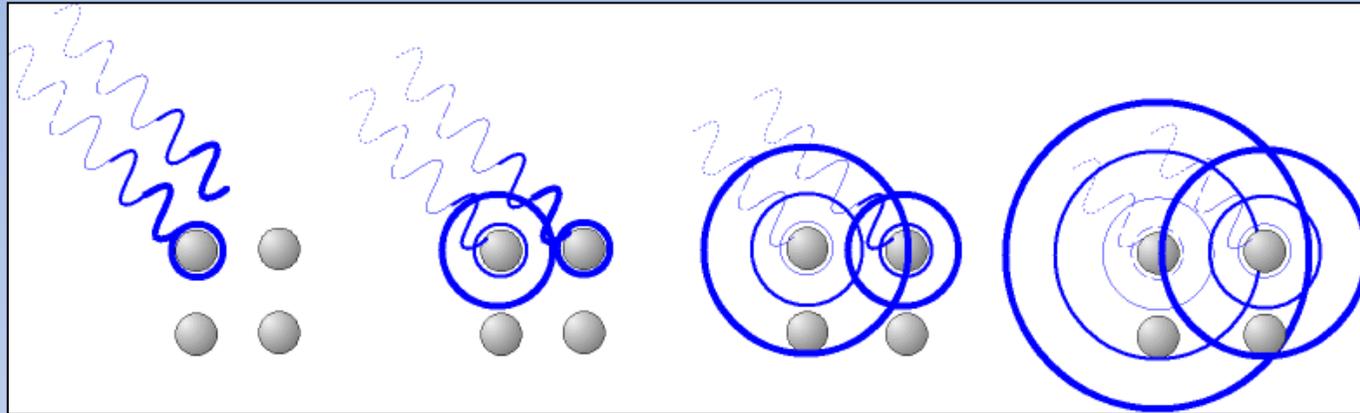
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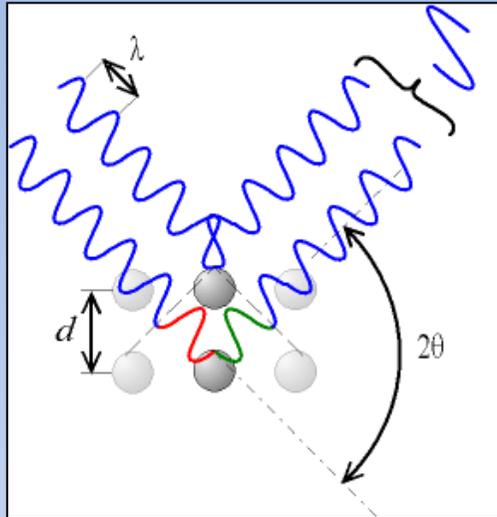
Difração



Interferência
construtiva

Interferência
destrutiva

Lei de Bragg

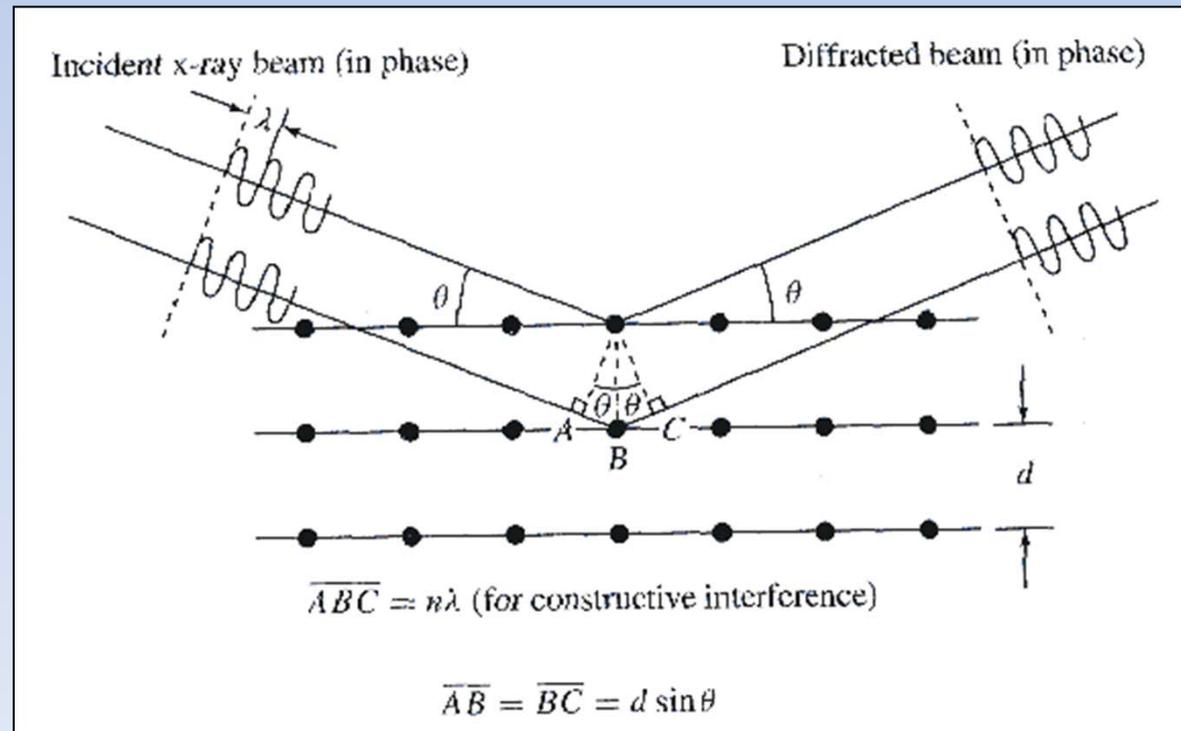


Interferência
construtiva

$$2 d \sin \theta = n \lambda$$

d = distância interplanar

n = ordem da reflexão (número inteiro)



Posição dos picos

Planos de Bragg

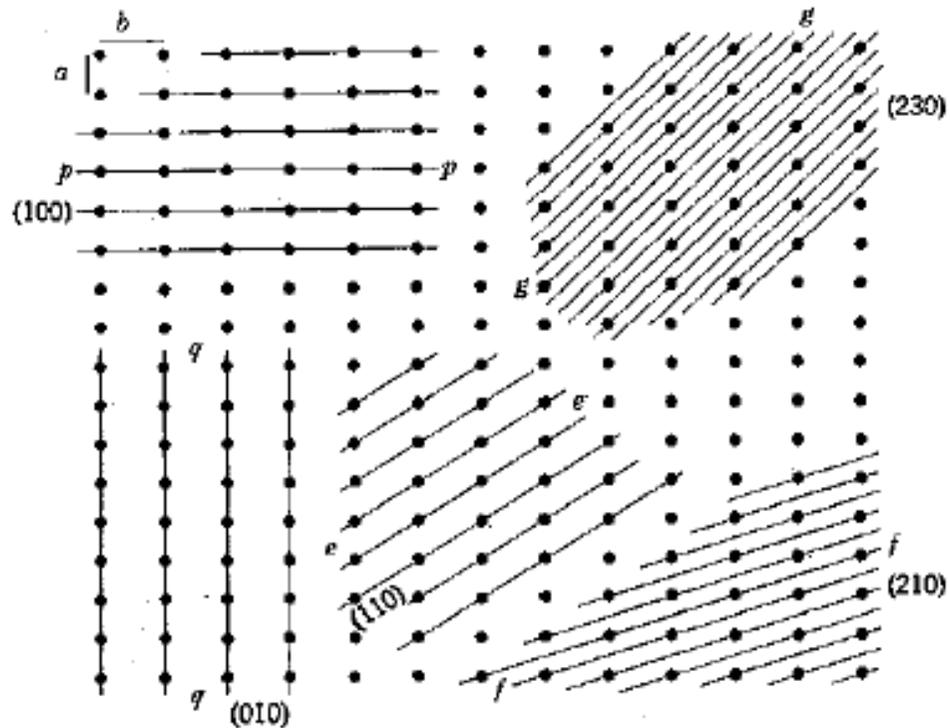


Fig. 1-30. Plane traces on an ab section of an orthorhombic net.

Índices de Miller

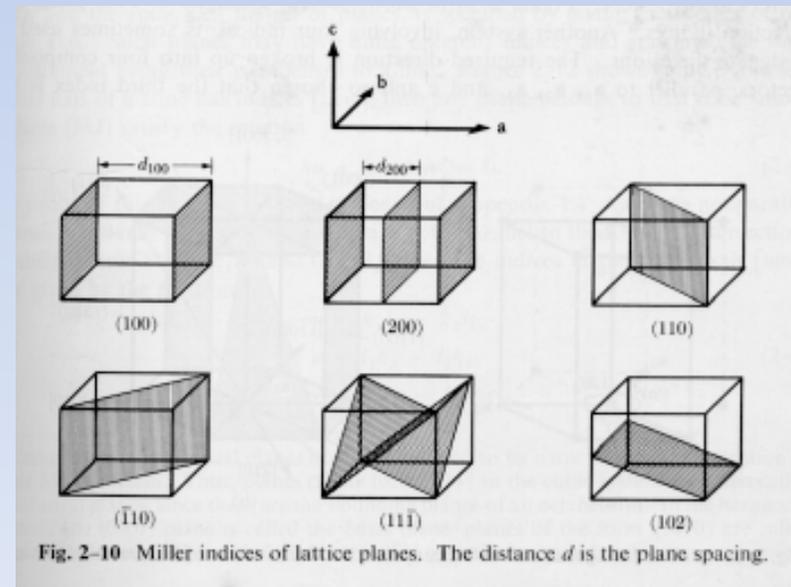
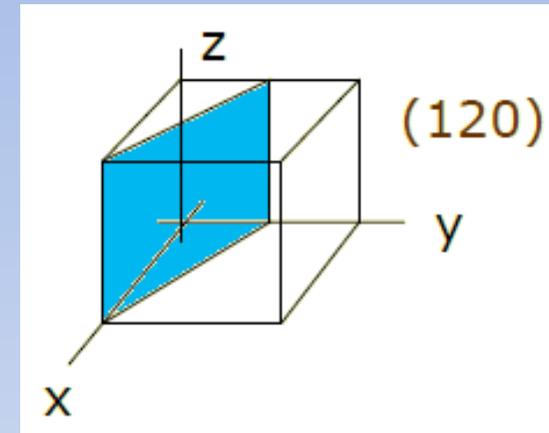
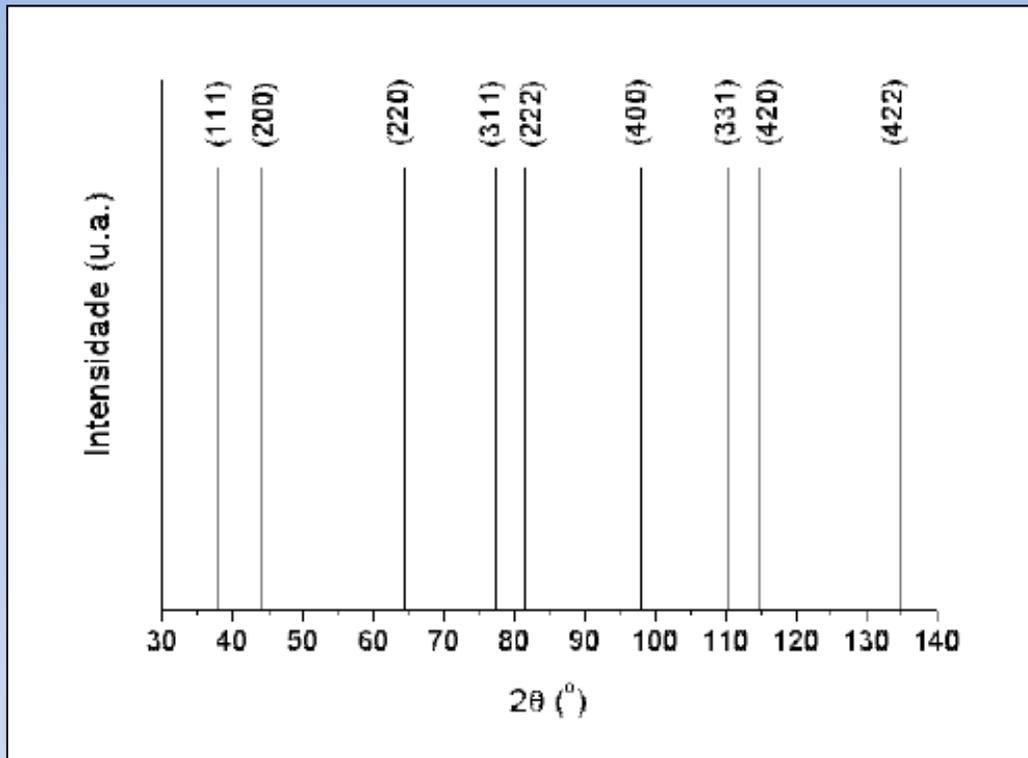


Fig. 2-10 Miller indices of lattice planes. The distance d is the plane spacing.

Exemplo: Prata (Ag)



Radiação de Cu

λ (Cu k_{α}) = 1,54184 Å

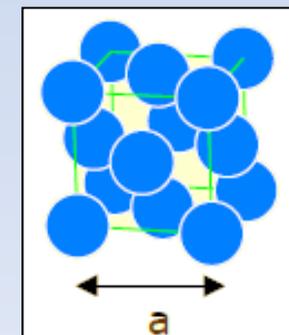
$$\lambda = 2.d.\text{sen}\theta$$

(hkl)	d (Å)	2θ (°)
(111)	2,359	38,11
(200)	2,043	44,30
(220)	1,445	64,44
(311)	1,232	77,39
(222)	1,180	81,53
(400)	1,021	97,88
(331)	0,9374	110,51
(420)	0,9137	114,92
(422)	0,8341	134,87

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Rede: cúbica de face centrada

$$a = 4,0862 \text{ Å}$$

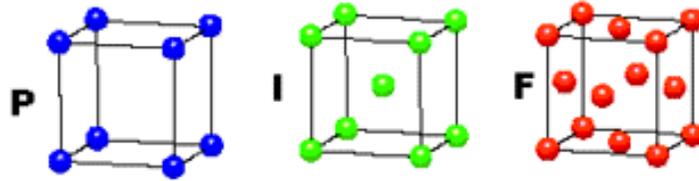


Cálculo de d_{hkl}

CÚBICO

$$a = b = c$$

$$\alpha = \beta = \gamma = 90^\circ$$

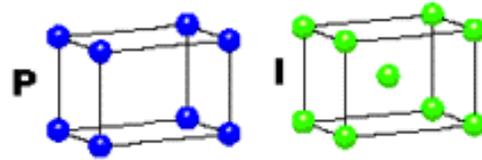


$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

TETRAGONAL

$$a = b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

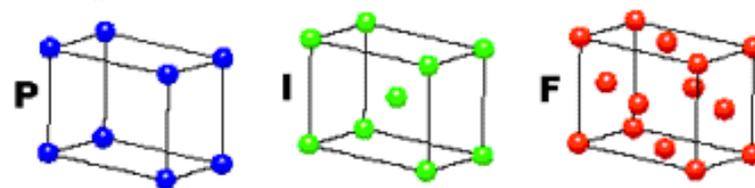


$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

ORTORÓMBICO

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$



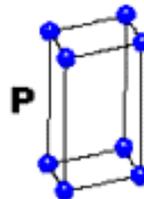
$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

HEXAGONAL

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

$$\gamma = 120^\circ$$



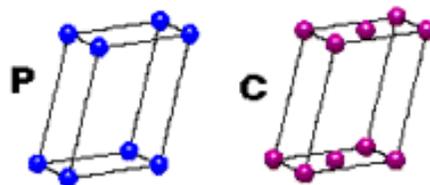
$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

MONOCLÍNICO

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ$$

$$\beta \neq 120^\circ$$

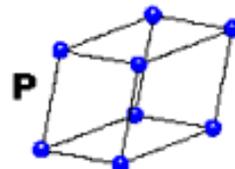


$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2h \cdot l \cos \beta}{a \cdot c} \right)$$

TRICLÍNICO

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



$$\frac{1}{d_{hkl}^2} = \frac{1}{(1 + 2 \cos \alpha \cos \beta \cos \gamma - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma)}$$

$$\times \left\{ \frac{h^2 \sin^2 \alpha}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2 \sin^2 \gamma}{c^2} + \frac{2hk}{ab} (\cos \alpha \cos \beta - \cos \gamma) \right.$$

$$\left. + \frac{2kl}{bc} (\cos \beta \cos \gamma - \cos \alpha) + \frac{2lh}{ac} (\cos \gamma \cos \alpha - \cos \beta) \right\}$$

Intensidade das reflexões:

$$I(hkl) = |F_{hkl}|^2 \cdot p \cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \cdot e^{-2M}$$

(1) (2) (3) (4)

- (1) - Fator de estrutura (depende da célula unitária)
- (2) - Fator de multiplicidade (depende da simetria)
- (3) - Fator de Lorentz-polarização
(depende da geometria do equipamento)
- (4) - Fator de temperatura
(depende da vibração térmica dos átomos)

Difração de raios X

Prof. Paulo A. Suzuki - EEL - USP

policristal

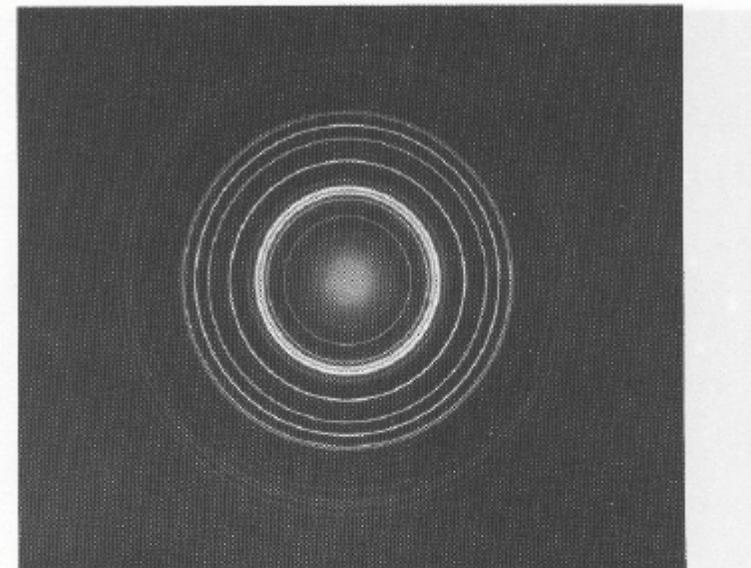
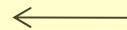
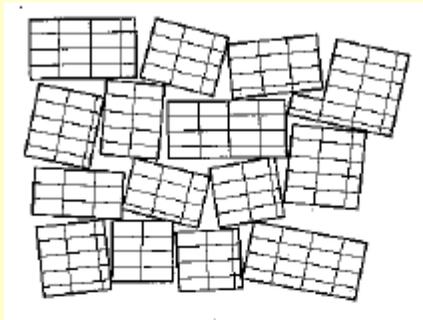


Fig. 4.86. Electron diffraction pattern from polycrystalline hexagonal nickel hydride [4.85]

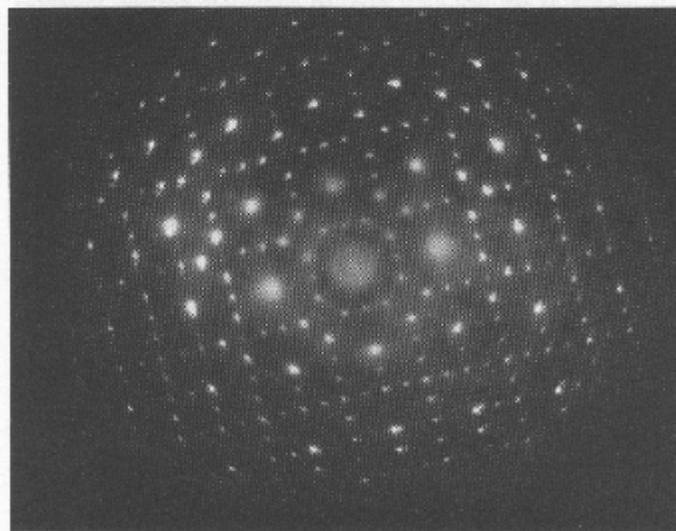
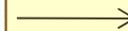
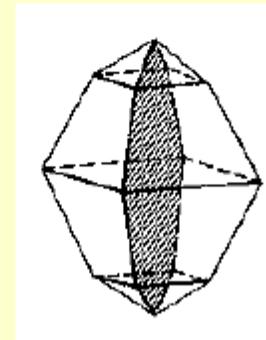


Fig. 4.81. Electron diffraction spot pattern from a mosaic crystal of BaCl₂·H₂O (accelerating voltage 60 kV, L = 700 mm) [4.81]



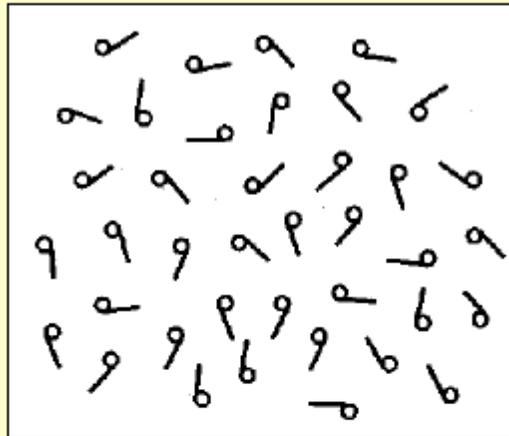
monocrystal



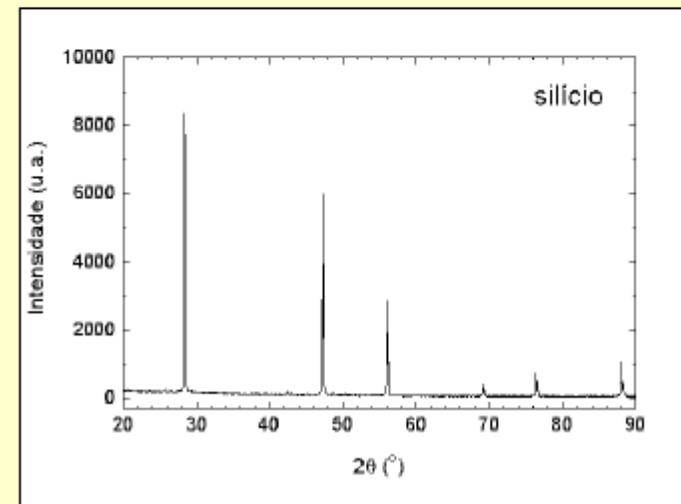
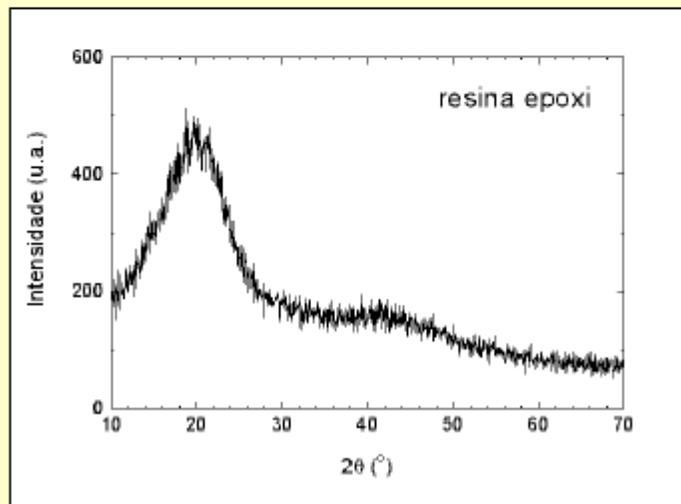
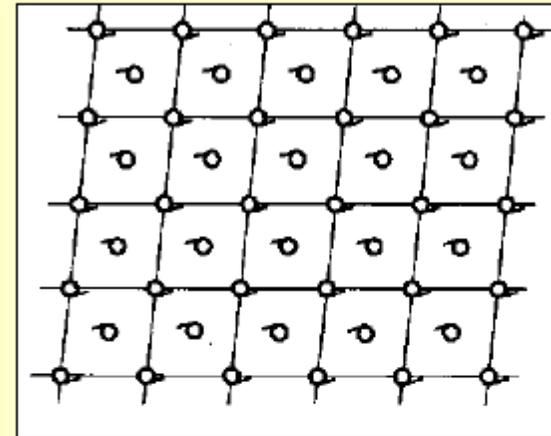
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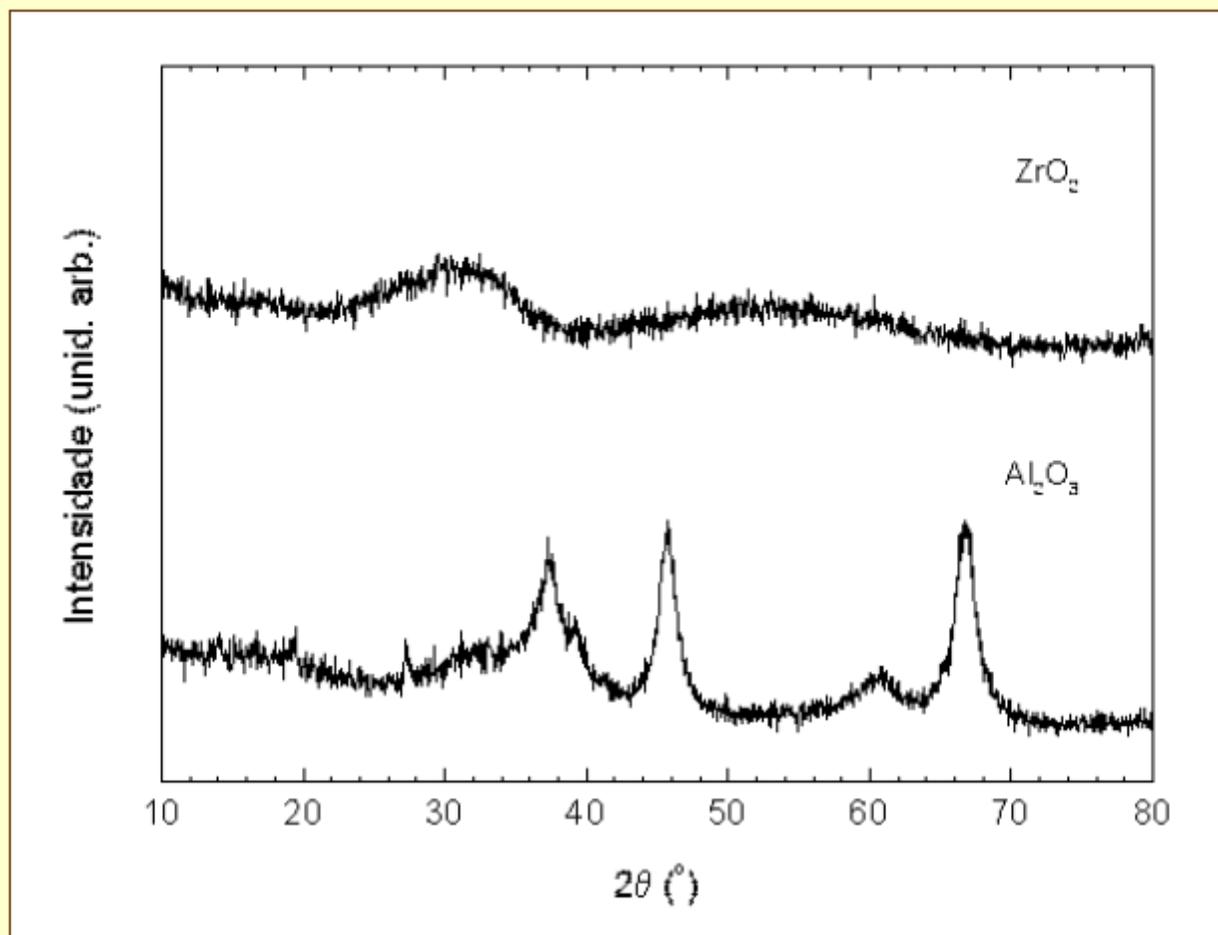
amorfo



cristalino



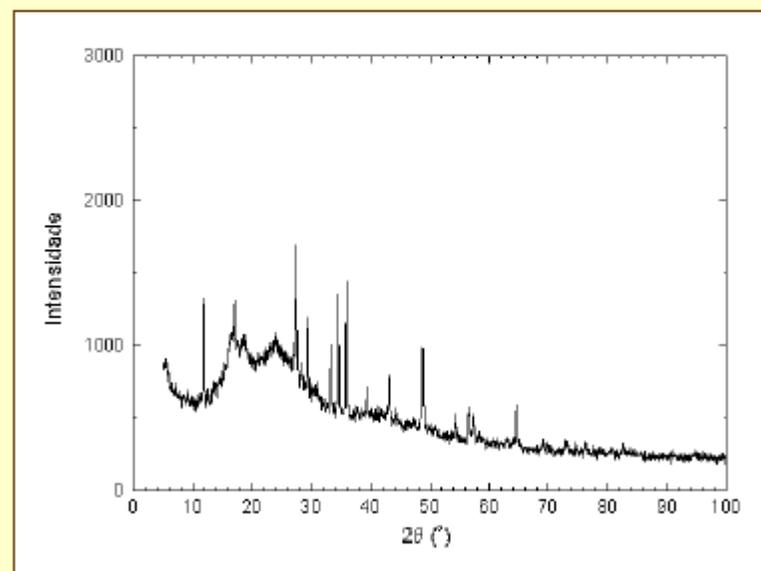
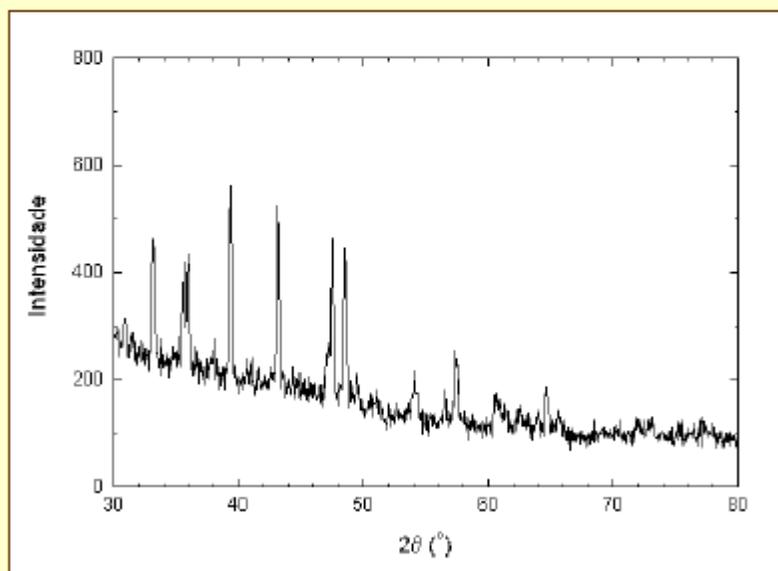
materiais nanocristalinos



polímeros

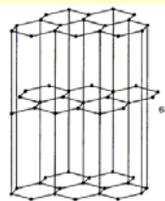
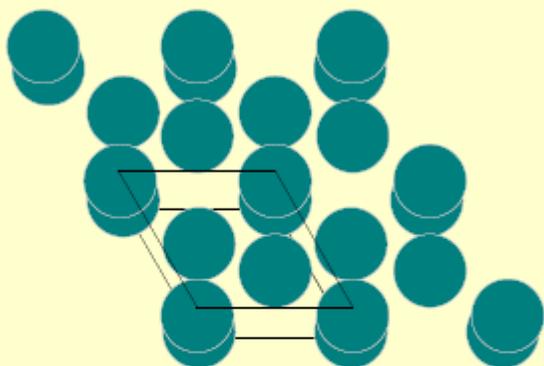
baquelite

PVC

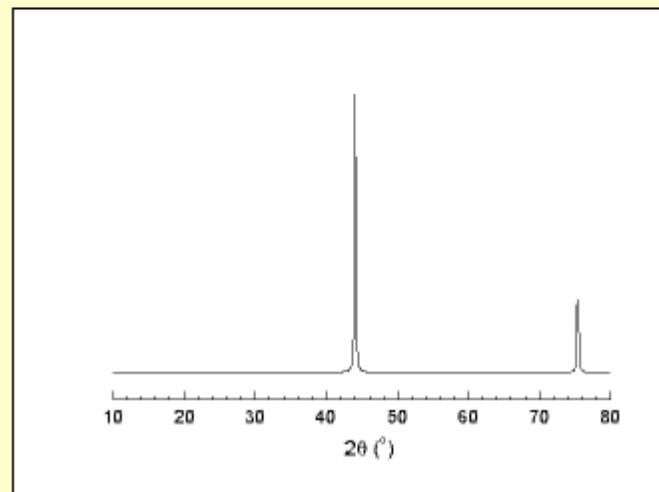
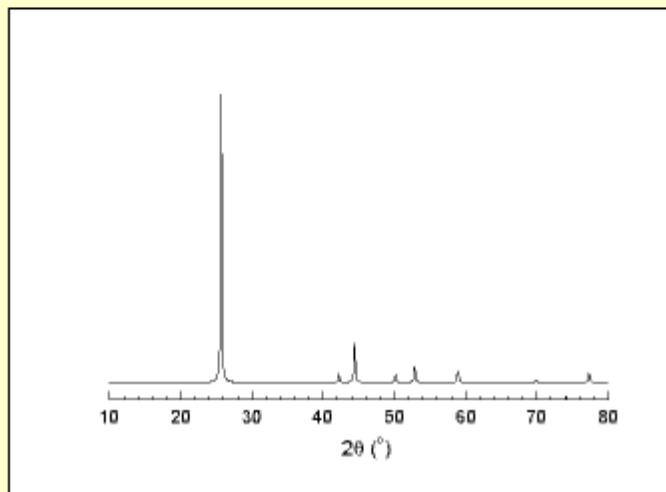
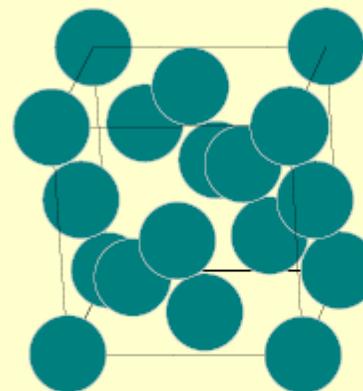


Carbono

grafite

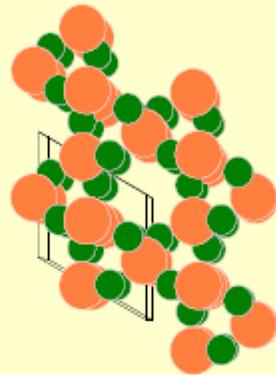


diamante

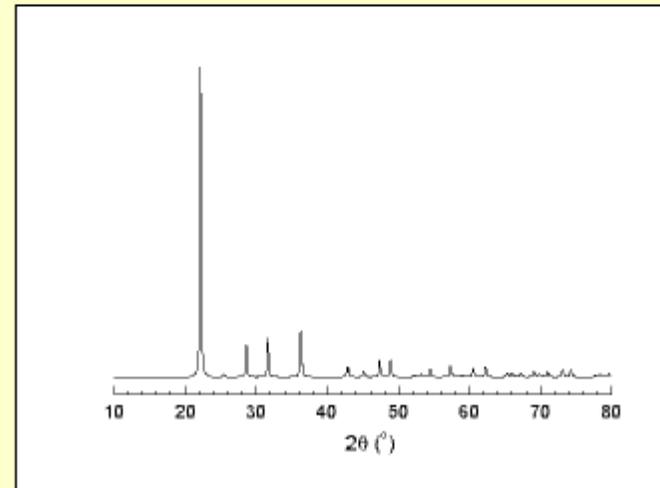
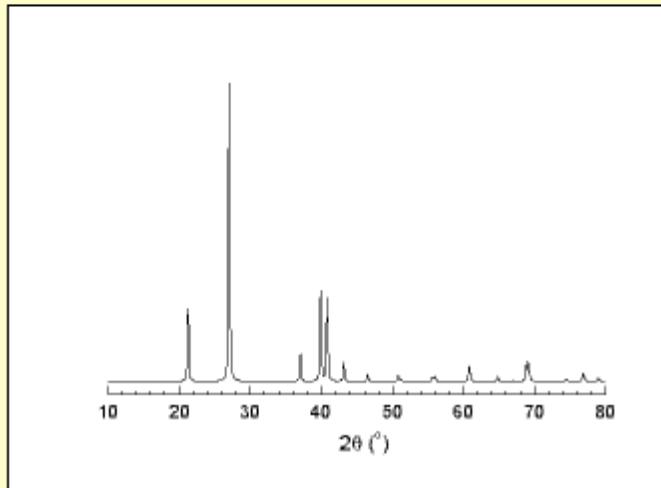
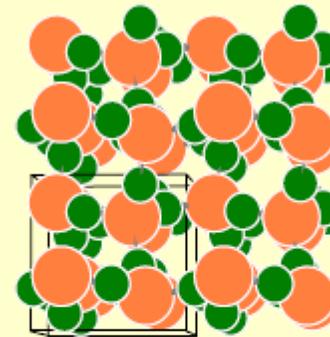




quartzo



cristobalita

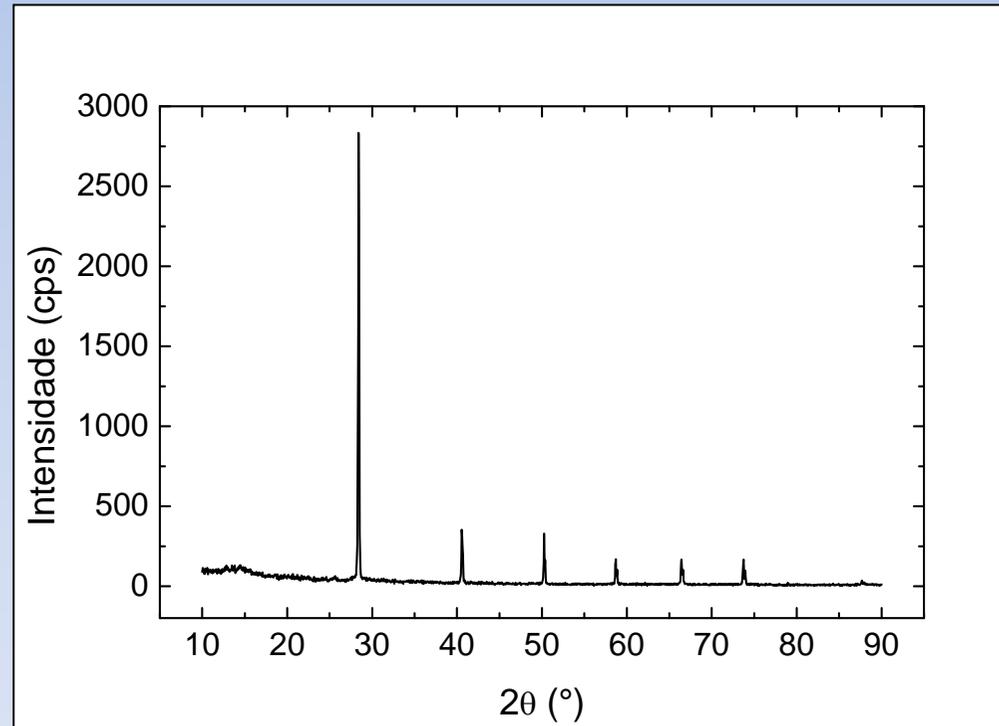


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 - Refinamento da estrutura
 - Cálculo do tamanho de partícula

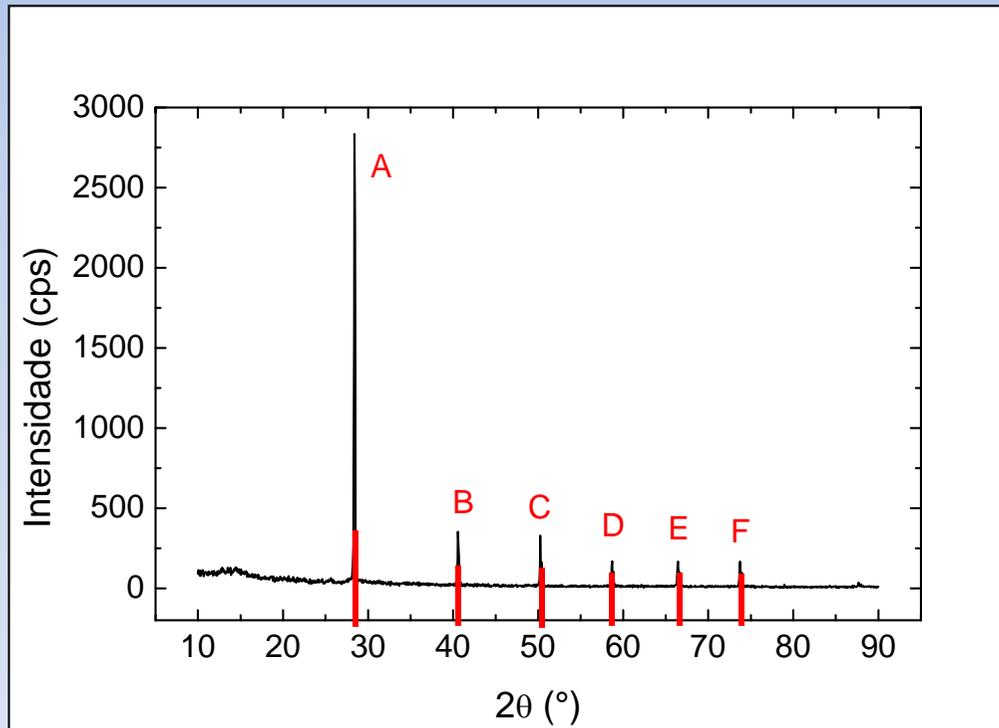
Identificação de fases

Difratograma de raios X



Identificação de fases

Método de Hanawalt



Posição dos picos

<i>Pico</i>	<i>Posição 2θ</i>	<i>Posição θ</i>
<i>A</i>	28,4°	14,2°
<i>B</i>	40,6°	20,3°
<i>C</i>	50,2°	25,1°
<i>D</i>	58,7°	39,3°
<i>E</i>	66,5°	33,3°
<i>F</i>	73,8°	36,9°

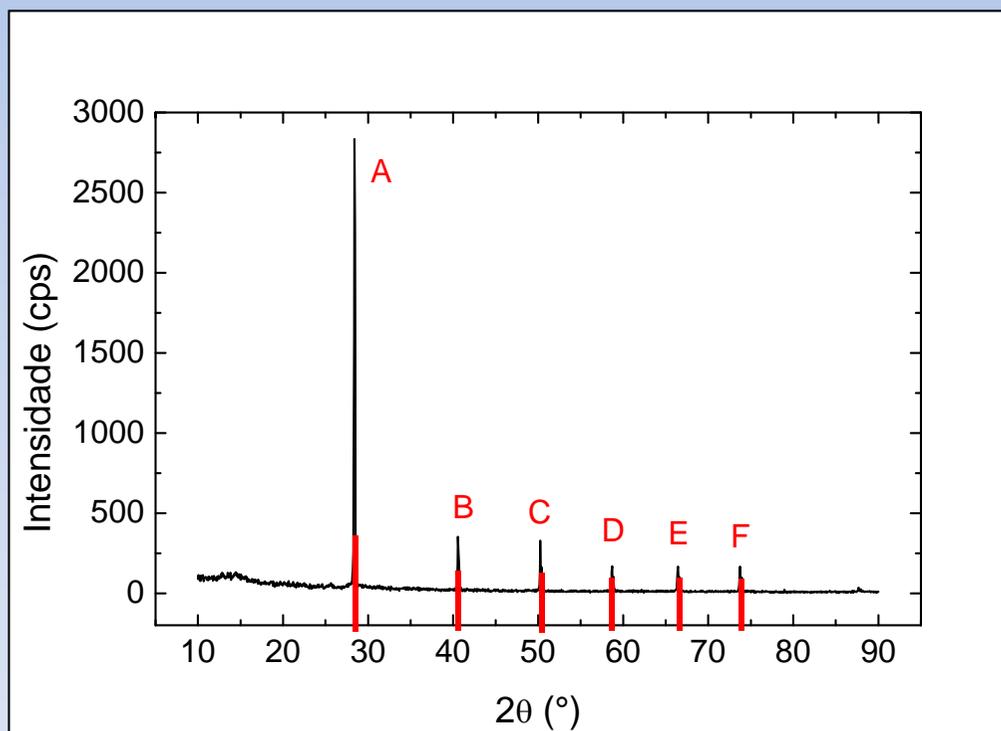
Identificação de fases

Método de Hanawalt

Distância interplanar

$$\lambda = 2.d.\text{sen}\theta$$

$$d = \frac{\lambda}{2.\text{sen}\theta}$$

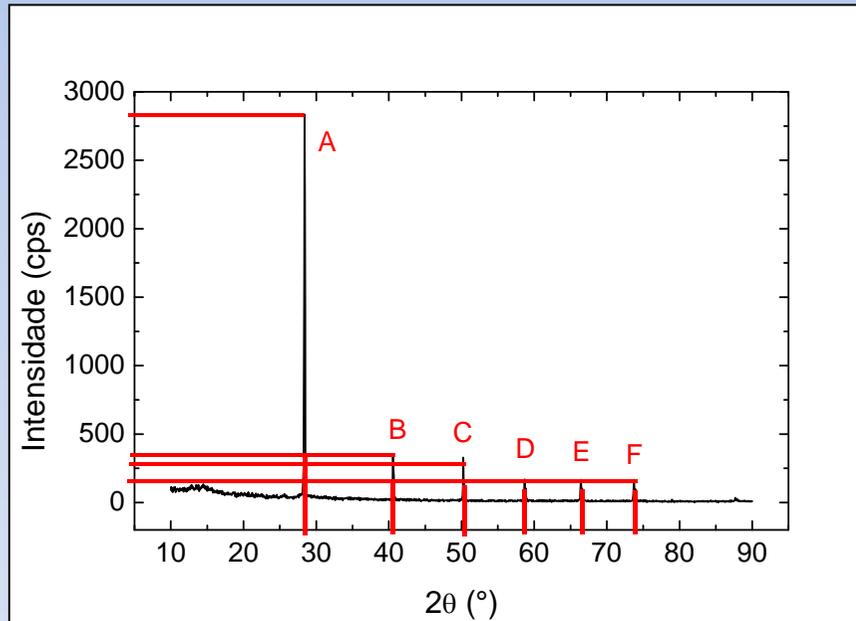


Radiação de Cu
 $\lambda (\text{Cu } k_{\alpha}) = 1,54184 \text{ \AA}$

<i>Pico</i>	<i>2θ</i>	<i>θ</i>	<i>d</i>
<i>A</i>	28,4°	14,2°	3,140 Å
<i>B</i>	40,6°	20,3°	2,220 Å
<i>C</i>	50,2°	25,1°	1,812 Å
<i>D</i>	58,7°	39,3°	1,572 Å
<i>E</i>	66,5°	33,3°	1,406 Å
<i>F</i>	73,8°	36,9°	1,284 Å

Identificação de fases

Método de Hanawalt



Intensidade relativa

Pico A: $I_{100\%} = 2833\text{cps}$

Pico	2θ	θ	d	$I(\text{cps})$	I/I_0
A	$28,4^\circ$	$14,2^\circ$	$3,140 \text{ \AA}$	2833	100%
B	$40,6^\circ$	$20,3^\circ$	$2,220 \text{ \AA}$	351	12,4%
C	$50,2^\circ$	$25,1^\circ$	$1,812 \text{ \AA}$	329	11,6%
D	$58,7^\circ$	$39,3^\circ$	$1,572 \text{ \AA}$	170	6%
E	$66,5^\circ$	$33,3^\circ$	$1,406 \text{ \AA}$	167	5,9%
F	$73,8^\circ$	$36,9^\circ$	$1,284 \text{ \AA}$	166	5,8%

$3,1425_x$ $2,2220_2$ $1,8116_2$ $1,4060_1$ $1,2839_1$ $1,5716_1$

Identificação de fases

Método de Hanawalt

De acordo como o Método de Hanawalt, espera-se que o composto possa ser identificado da seguinte maneira:

3,1425_x 2,2220₂ 1,8116₂ 1,4060₁ 1,2839₁ 1,5716₁

3.11 _x	2.41 ₆	1.62 ₆	1.31 ₂	1.31 ₂	2.11 ₂	1.56 ₁	1.00 ₁	Pyrolusite syn	β -MnO ₂	24- 735
3.13 _x	2.40 ₉	3.47 ₈	2.15 ₈	1.55 ₇	1.83 ₆	6.98 ₅	4.93 ₃	Hollandite	(Ba,K ₂)MnMn ₇ O ₁₆ · ca 2H ₂ O	13- 115
3.10 ₈	2.33 ₈	1.78 _x	4.07 ₆	1.54 ₆	7.00 ₅	2.84 ₄	3.95 ₃	Welinite	Mn ₃ Si _{0.6} W _{0.4} O ₇	20-1389
3.10 ₈	2.33 ₆	1.59 _x	1.94 ₆	4.10 ₆	1.64 ₆	2.48 ₅	1.75 ₄	Behierite syn	TaBO ₄	7- 131
3.13 _x	2.32 ₆	2.00 ₆	1.85 ₆	6.07 ₅	3.71 ₅	1.53 ₅	1.36 ₅	Dussertite	BaFe ₃ (AsO ₄) ₂ (OH) ₅ ·H ₂ O	19- 112
3.12 _x	2.31 ₅	2.12 ₅	4.92 ₄	3.64 ₃	2.61 ₂	1.76 ₂	9.90 ₁	Kawazulite	Bi ₂ Te ₂ Se	29- 248
3.10 _x	2.29 _x	2.11 ₈	1.97 ₈	1.93 ₈	1.64 ₈	1.35 ₈	1.30 ₈	Tetradymite	Bi ₂ Te _{1.65} S _{1.35}	19-1330
3.15 ₈	2.28 ₈	4.55 _x	1.93 ₈	3.34 ₇	2.15 ₆	1.74 ₆	2.07 ₄	Gearksutite	CaAl(F,OH) ₅ ·H ₂ O	5- 283
3.11 _x	2.25 ₇	1.37 ₇	1.42 ₆	2.15 ₆	1.26 ₄	1.88 ₄	1.08 ₇	Antimony syn	Sb	5- 562
3.15 _x	2.22 ₆	1.82 ₂	1.41 ₂	1.28 ₁	1.57 ₁	1.05 ₁	0.84 ₁	Sylvite syn	KCl	4- 587
3.12 _x	2.18 ₇	3.15 _x	2.42 ₆	2.17 ₆	1.56 ₆	1.55 ₆	2.21 ₆	Hollandite, ferrian	BaFeMn ₇ O ₁₆	12- 514
3.11 ₆	2.15 ₆	2.39 _x	1.83 ₄	1.54 ₄	1.42 ₄	6.81 ₃	1.65 ₃	Vernadite	Mn(OH) ₄	15- 604
3.14 ₉	2.14 ₈	2.96 _x	3.08 ₇	1.97 ₇	3.60 ₆	3.47 ₆	2.20 ₅	Jarlite, calcian	Na(Sr,Ca) ₃ Al ₃ F ₁₆	5- 595
3.11 _x	2.13 ₃	2.25 ₂	4.41 ₁	3.66 ₁	1.75 ₁	1.36 ₁	3.36 ₁	Grueningite	Bi ₄ TeS ₃	2- 580
3.09 _x	2.13 ₈	2.25 ₇	1.75 ₆	1.35 ₆	3.63 ₅	1.83 ₅	1.55 ₅	Poubaite	PbBi ₂ (Se,Te) ₄	29- 762

Identificação de fases

Método de Hanawalt

De acordo como o Método de Hanawalt a microficha é a 4-587 para o composto cloreto de potássio.

4 - 5 8 7

d	3.15	2.22	1.82	3.15	KCl	★				
I/I ₁	100	59	23	100	Potassium Chloride (Sylvite)					
Rad. CuK _α λ	1.5405	Filter Ni	Dia.		d Å	I/I ₁	hkl	d Å	I/I ₁	hkl
Cut off		I/I ₁ Diffractometer	I/I _{cor.} = 3.9		3.146	100	200			
Ref. Swanson and Tatge, NBS Circular 539, Vol. 1, 65 (1953)					2.224	59	220			
					1.816	23	222			
					1.573	8	400			
Sys. Cubic		S.G.	Fm3m (225)		1.407	20	420			
a ₀ 6.2931	b ₀	c ₀	A	C	1.284	13	422			
α	β	γ	Z 4	Dx 1.987	1.1126	2	440			
Ref. Ibid.					1.0490	6	600			
					0.9951	2	620			
εα	nωβ 1.490	εγ	Sign		.9486	3	622			
2V	D	mp	Color	Colorless	.9083	1	444			
Ref. Ibid.					.8727	2	640			
					.8410	6	642			
<p>A Mallinckrodt sample; Accompanied by chemical analysis (%): Ba 0.001, insoluble 0.005, Fe 0.003, heavy metals 0.005, neutrality OK, NO₃ 0.003, N 0.001, PO₄ 0.002, Na 0.02, SO₄ 0.005. At 25°C. Merck Index, 8th Ed., p. 853. Halite-galena-periclase group.</p>										

Tipo de rede:

cúbica

Parâmetro de rede:

$$a_0 = 6,2931 \text{ \AA}$$

Grupo espacial:

Fm3m (#225)

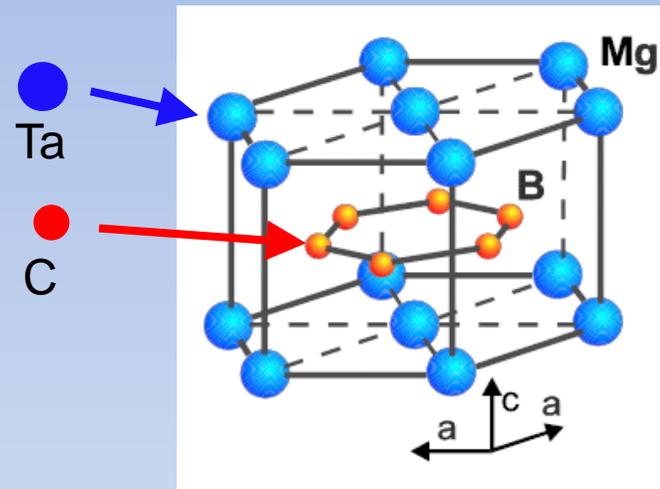
Propriedades supercondutoras do MgB_2

Dopagem:

➤ TaB_2

➤ SiC

Estrutura Cristalina



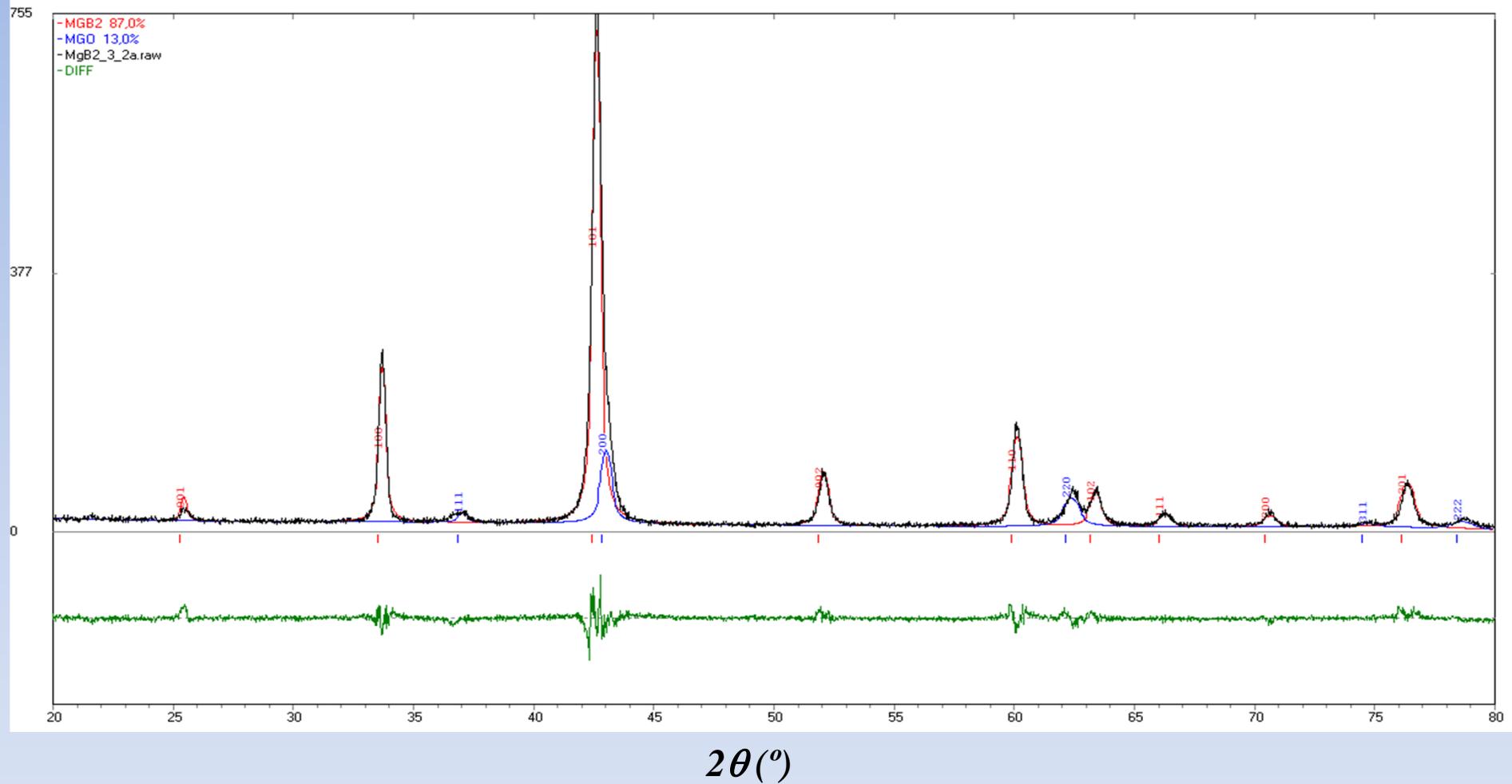
Hexagonal
estrutura do tipo AlB_2

Grupo espacial:
 $P6/mmm$

$$a = 3.084 \text{ \AA}$$

$$c = 3.522 \text{ \AA}$$

Refinamento da estrutura cristalina



- Composição de cada fase
- Parâmetros de rede

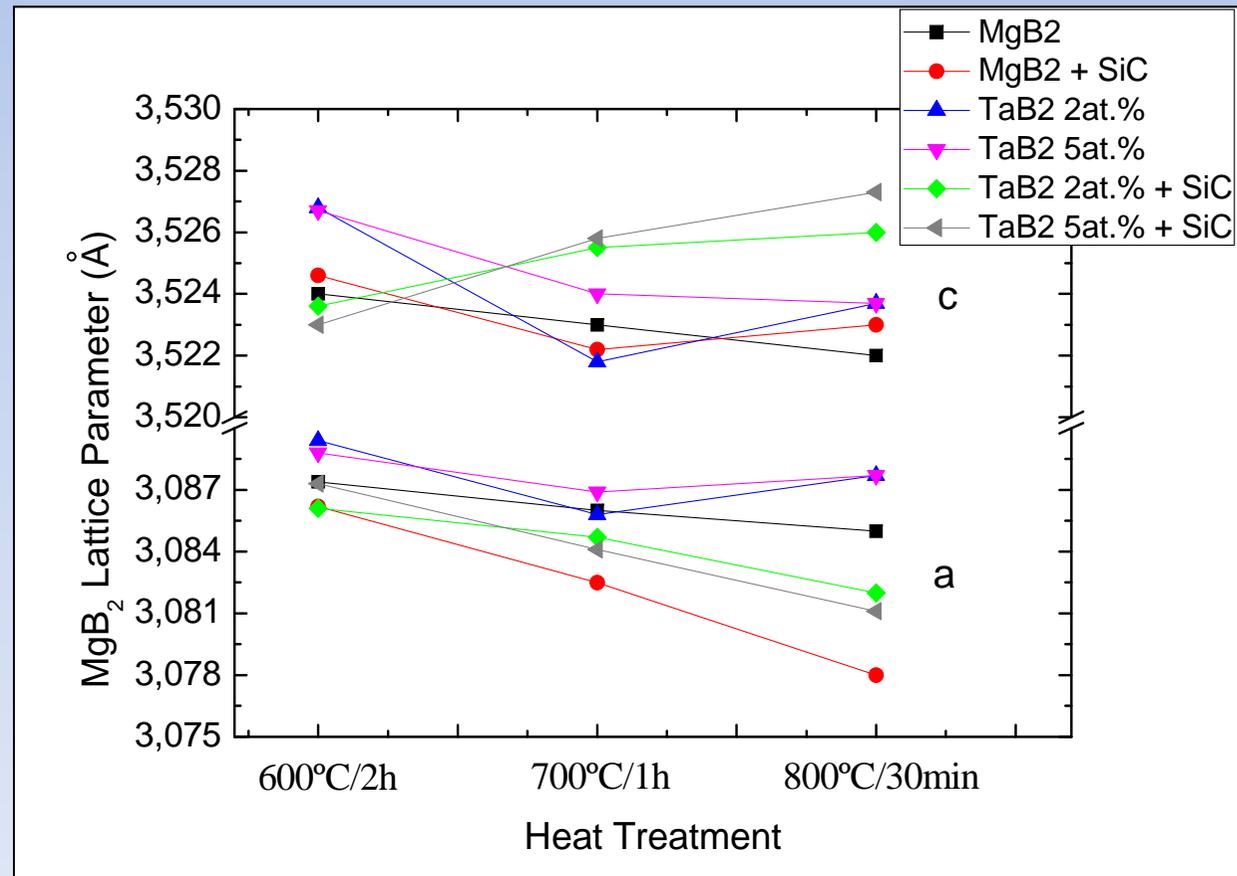
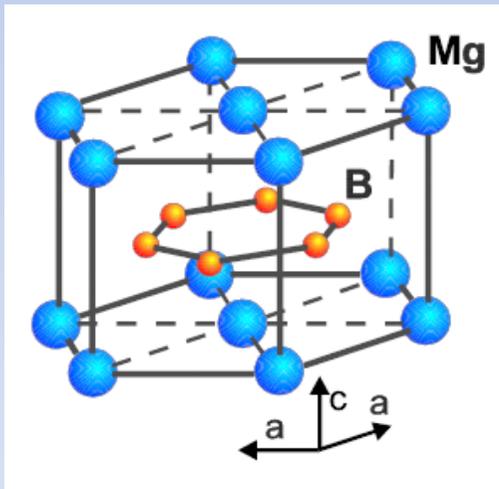
Refinamento da estrutura cristalina

Raio atômico:

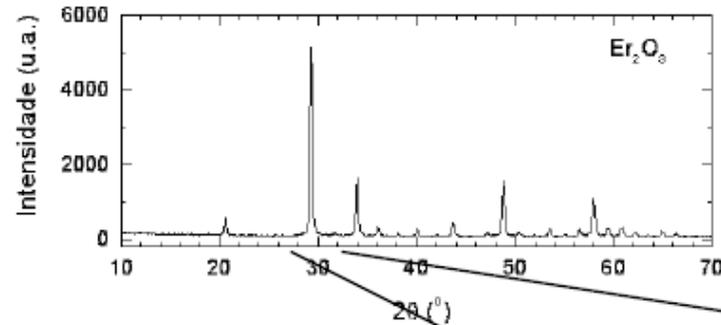

 Mg = 1,72 Å
 Ta = 2,09 Å




 B = 1,17 Å
 C = 0,91 Å



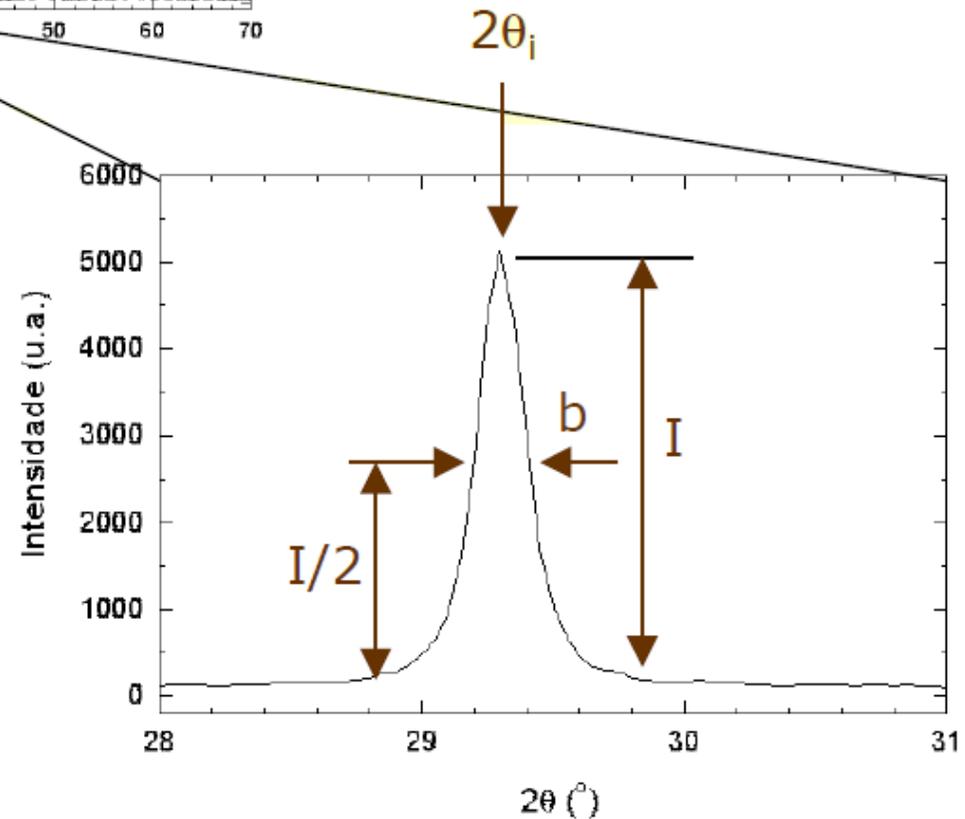
Tamanho de partícula



Largura a meia altura: b_{hkl}

Equação de Scherrer:

$$G_{hkl} = \frac{0,9 \cdot \lambda}{B_{hkl} \cdot \cos \theta}$$

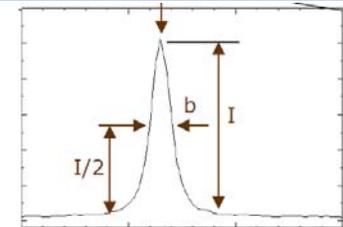


G_{hkl} : tamanho de partícula na direção hkl

Tamanho de partícula

Largura a meia altura: b_{hkl}

G_{hkl} : tamanho de partícula na direção hkl



Equação de Scherrer:

$$G_{hkl} = \frac{0,9 \cdot \lambda}{B_{hkl} \cdot \cos \theta}$$

Fatores a serem considerados:

$$B_{hkl} = b_{hkl} + \beta_{hkl} \quad \beta_{hkl} : \text{Contribuição experimental}$$

