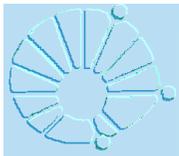


**XXVII OFICINA DE FÍSICA  
RAIOS-X E APLICAÇÕES**

**DIFRAÇÃO DE RAIOS-X : DOS SEUS  
PRIMÓRDIOS ÀS APLICAÇÕES  
RECENTES NO ESTUDO DE MATERIAIS**

*Prof. LISANDRO PAVIE CARDOSO  
LPCM, DFA, IFGW, UNICAMP*



# XXVII OFICINA DE FÍSICA RAIOS-X E APLICAÇÕES

**Introdução histórica** – descoberta dos raios-X

**Cristais** – estruturas, planos atômicos, índices de Miller

**Produção de raios-X**

**Lei de Bragg** e difratometria de policristais

**Método de Rietveld** com aplicações:

Arquitetura (prédios históricos)

Alimentos (polimorfismo, cristalização de gorduras)

**Difração múltipla de raios-X**

Difração Bragg-Superfície (BSD) - híbridas

Aplicação como sonda para:

a piezeletricidade

a transição de fase por temperatura (dilatometria)

impurezas nas redes cristalinas

a implantação de íons



# Introdução histórica

Descoberta dos raios-X (1895)

Wilhelm Conrad Röntgen - raios catódicos  
(<1 ano: 49 livros e 1.000 artigos ) Nobel, 1901

Natureza dos raios-X

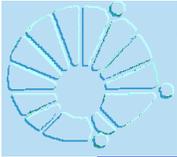
G.G. Stokes → ondas (difração)

W.H. Bragg → corpuscular  
(ionização gases – colisão entre partículas)

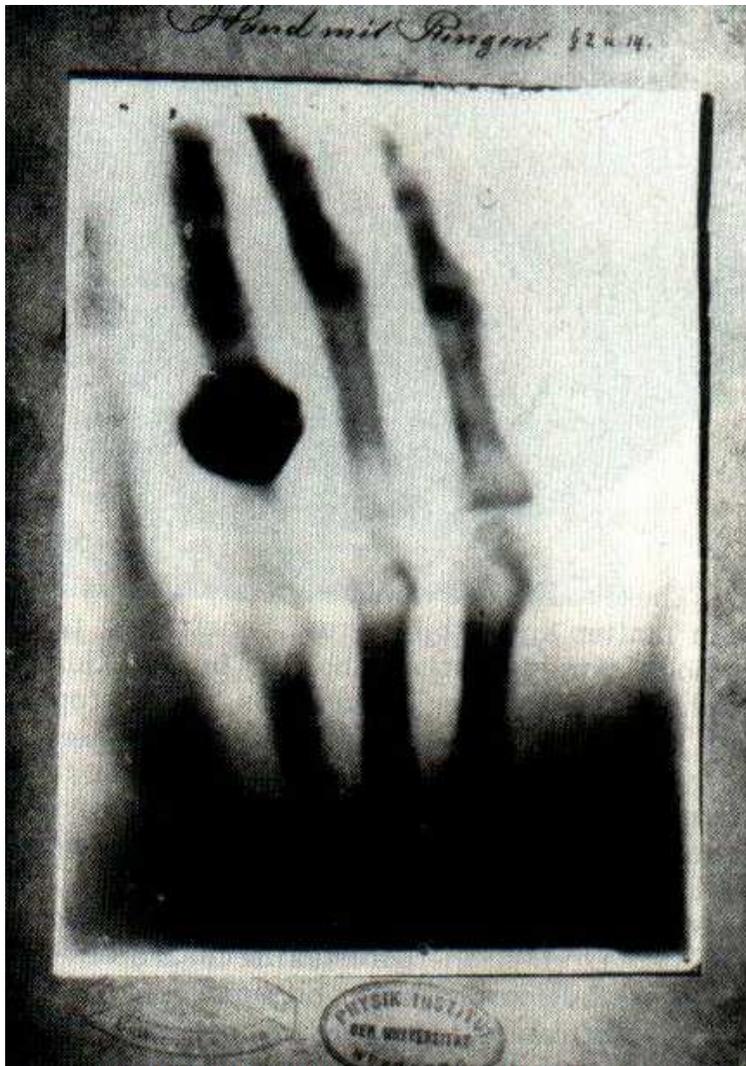
Primeiras experiências científicas

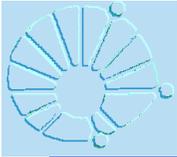
Max von Laue (Nobel, 1914), Walter Friedrich → Estrutura regular dos cristais  
Paul Knipping (Univ. Munique, Alemanha, 1912) natureza ondulatória

W. H. Bragg e W.L. Bragg → Determinação estruturas cristalinas  
(Nobel, 1915) com difração de raios-X



## Radiografia de uma mão e W.C. Röntgen (Nobel, 1901)





## Thomas Edison (4 meses após a descoberta)

**X-Ray-Apparatus**  
of All Kinds,  
For Professionals and Amateurs. ❖❖❖



(1) Ruhmkorff Coils  
(oil immersion type).  
(2) High Frequency Sets  
(for alternating current).  
(3) Modern Holtz Machines  
(4) Crookes Tubes  
a. Regular.  
b. Single focus.  
c. Double focus, with adjustable vacuum.  
(Thomson Universal.)  
(5) Fluoroscopes.  
(6) Fluorescent Screens.  
(7) Calcium Tungstate.

**Complete Outfits  
For X Ray Work**

Our Thomson Universal Double Focus Tube is pronounced by experts the most efficient tube ever made for the production of X Rays.

It is the only tube made that provides for adjustment of vacuum. ❖

Our Ruhmkorff coils of the larger size are of the oil immersion type.  
❖ thus insuring the highest degree of insulation. ❖

Miniature and Decorative Lamps and Electric Signs.  
**EDISON DECORATIVE AND MINIATURE LAMP DEPT.**  
❖ ❖ ❖ HARRISON, N. J. ❖ ❖ ❖

radiograph made with Thomson Universal Tube on 5 inch disk. Exposure 2 minutes.

THE EDISON APPROACH to x rays. This advertisement appeared in *Electrical Engineer* only four months after the announcement of Röntgen's discovery.

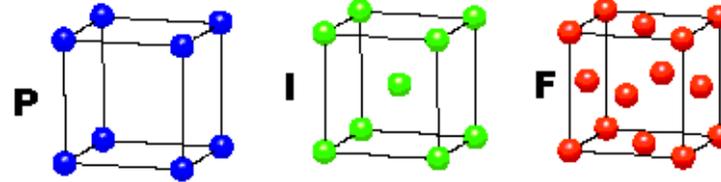


# REDES DE BRAVAIS

As 14 redes  
de Bravais  
distribuídas  
segundo  
os 7  
Sistemas  
Cristalinos

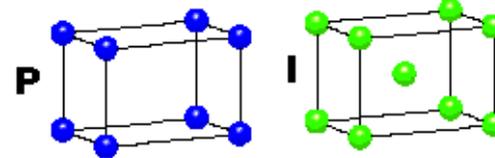
## CUBIC

$$a = b = c$$
$$\alpha = \beta = \gamma = 90^\circ$$



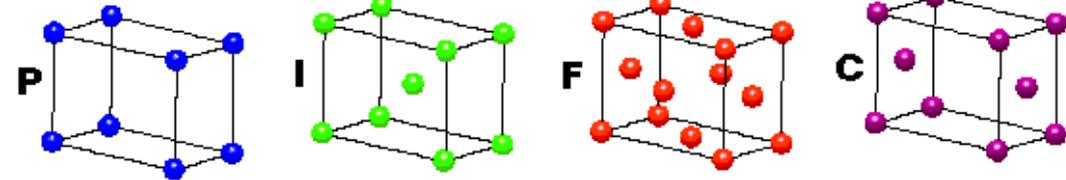
## TETRAGONAL

$$a = b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$



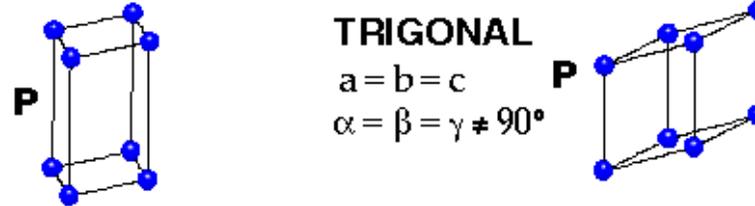
## ORTHORHOMBIC

$$a \neq b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$



## HEXAGONAL

$$a = b \neq c$$
$$\alpha = \beta = 90^\circ$$
$$\gamma = 120^\circ$$

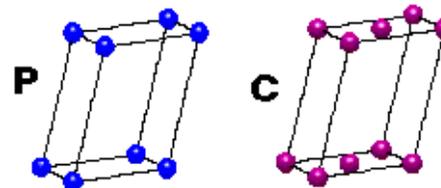


## TRIGONAL

$$a = b = c$$
$$\alpha = \beta = \gamma \neq 90^\circ$$

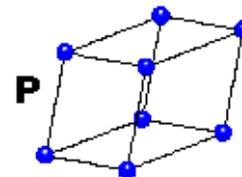
## MONOCLINIC

$$a \neq b \neq c$$
$$\alpha = \gamma = 90^\circ$$
$$\beta \neq 120^\circ$$



## TRICLINIC

$$a \neq b \neq c$$
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



4 Types of Unit Cell

P = Primitive

I = Body-Centred

F = Face-Centred

C = Side-Centred

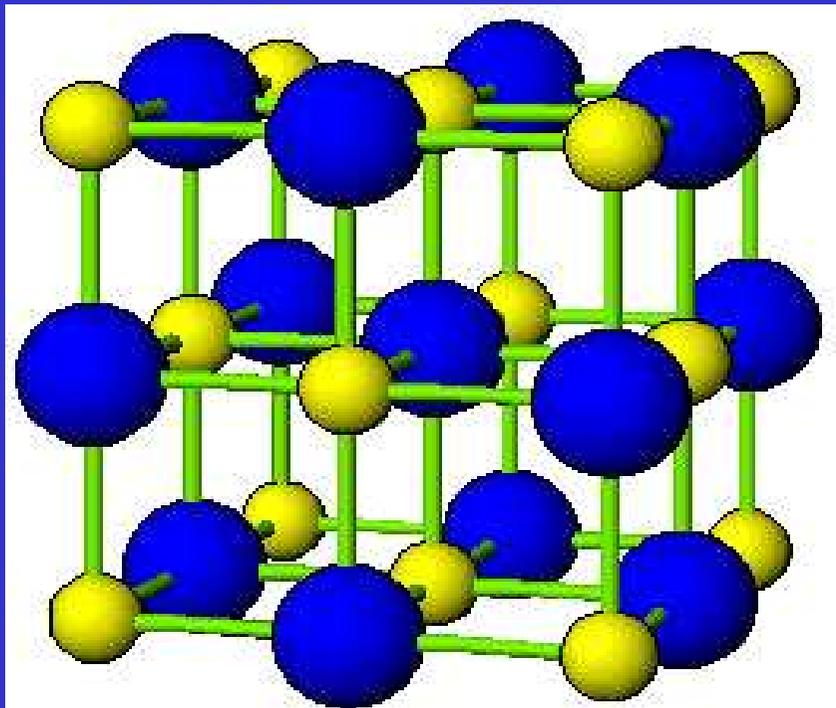
+

7 Crystal Classes

→ 14 Bravais Lattices

# Cristais e suas estruturas

- Cristais são arranjos atômicos ou moleculares cuja estrutura se repete numa forma periódica tridimensional

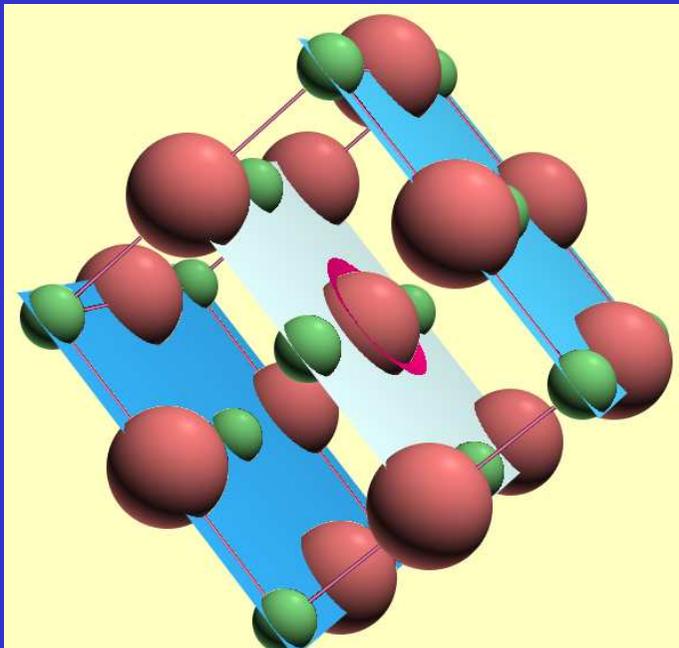


**Célula unitária do NaCl**

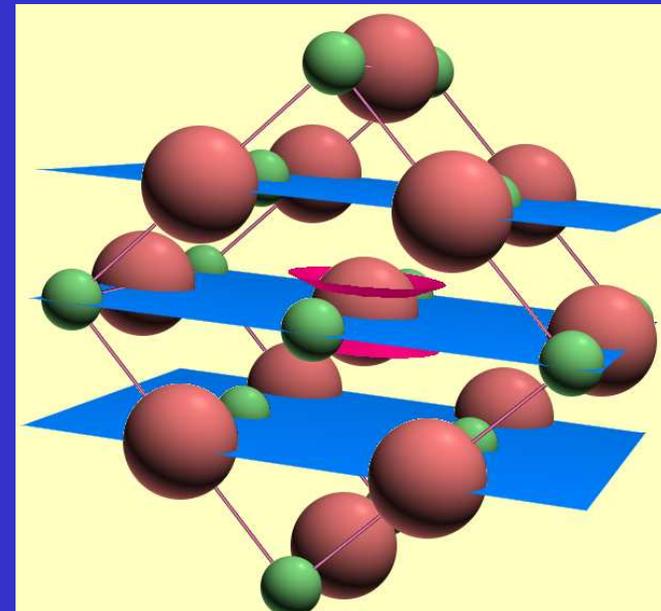
Célula unitária é a menor estrutura que representa um cristal, isto é, um cristal é formado por diversas células unitárias arranjadas tridimensionalmente

# Planos atômicos

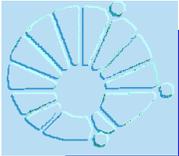
Plano (200) do NaCl



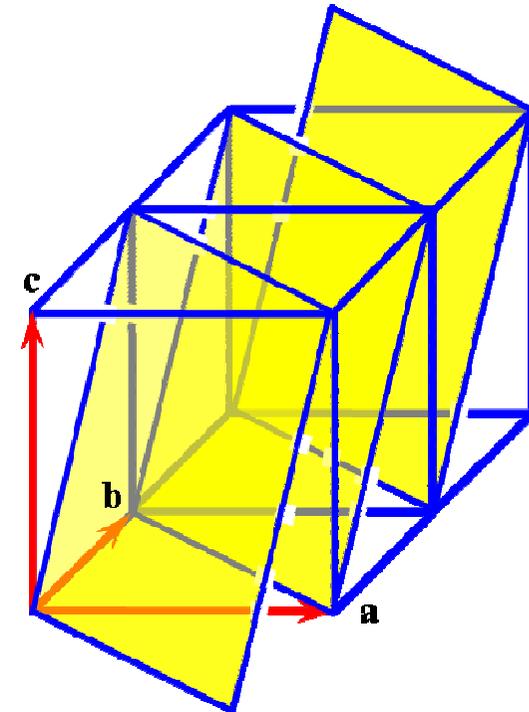
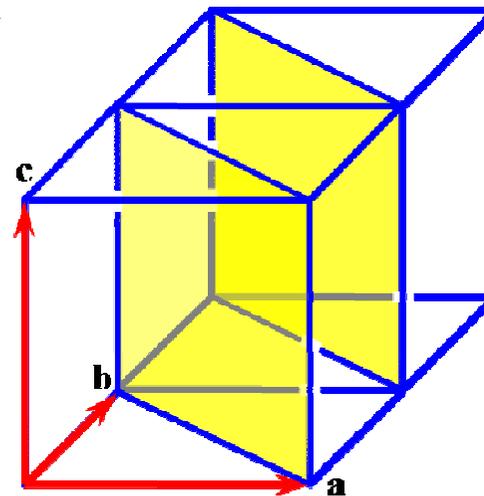
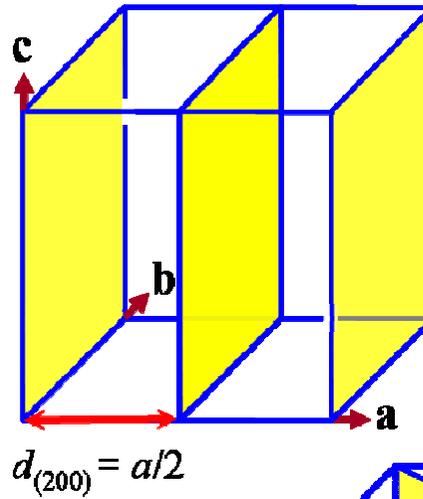
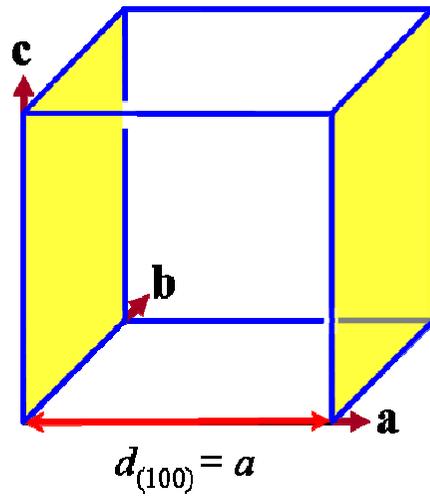
Plano (220) do NaCl



- Os planos atômicos são usados para definir direções e distancias no cristal.
- Planos cristalinos são identificados por Índices de Miller

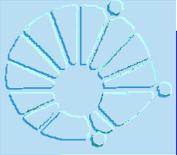


# Índices de Miller

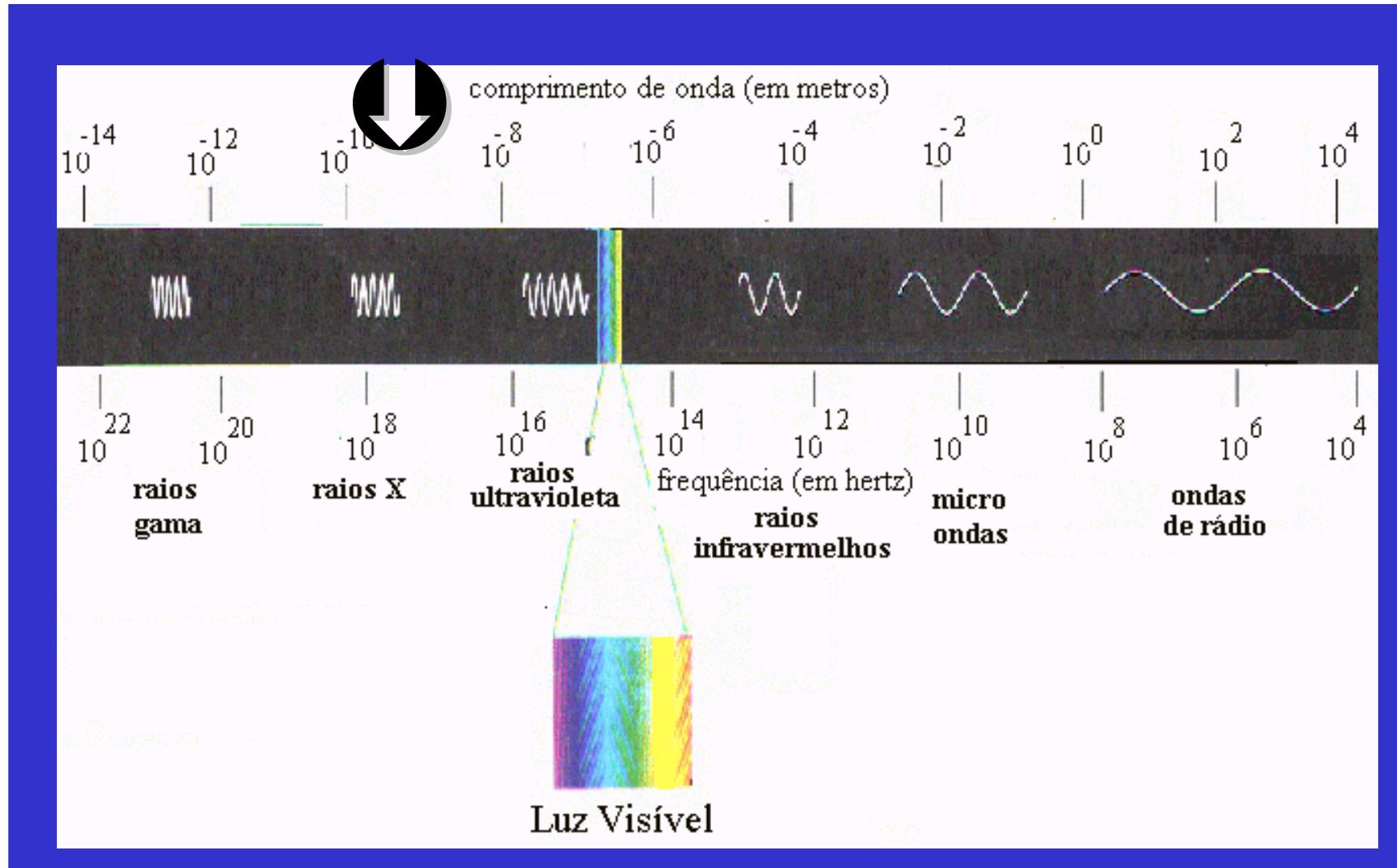


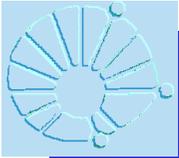
$$\frac{1}{d_{(111)}^2} = \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}$$

$$\frac{1}{d_{(110)}^2} = \frac{1}{a^2} + \frac{1}{b^2}$$



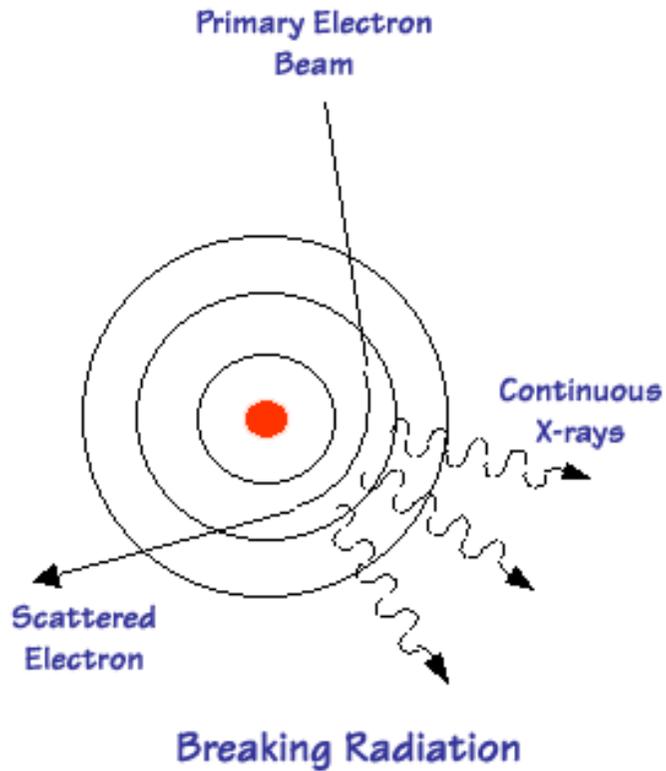
# ESPECTRO ELETROMAGNÉTICO



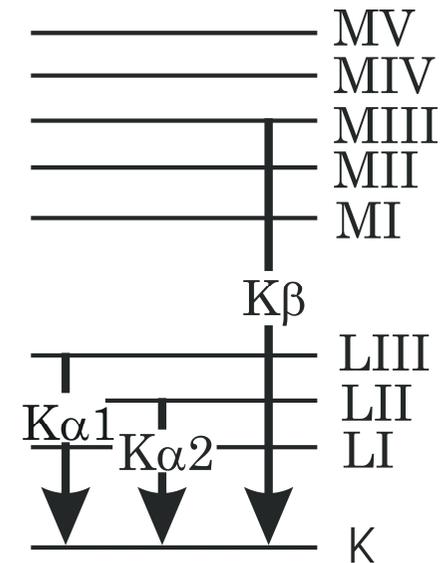
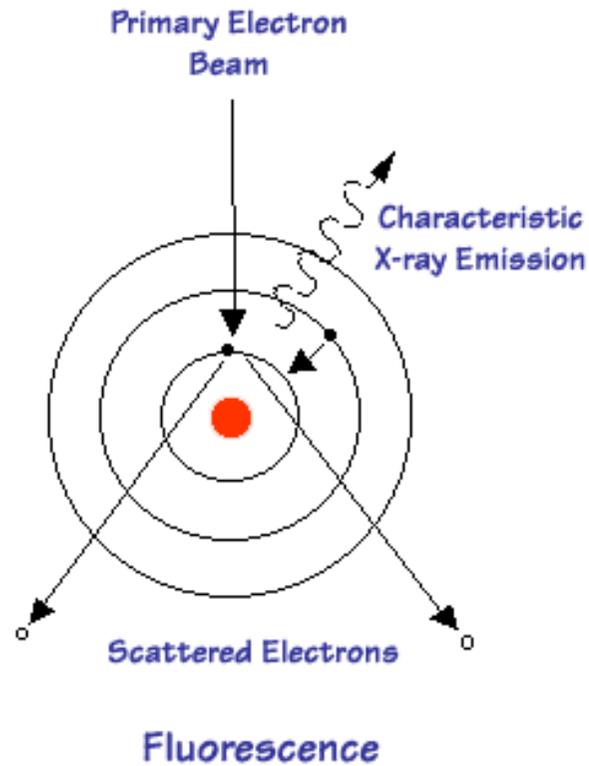


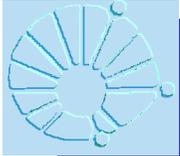
# Ilustração da geração dos dois tipos de espectro de radiação X

## Radiação contínua



## Radiação característica





# Espectro característico de raios-X

Forma-se acima de um determinado

potencial de excitação, característico do metal

do alvo. Exemplos:

Mo (Z=42): 20 kV

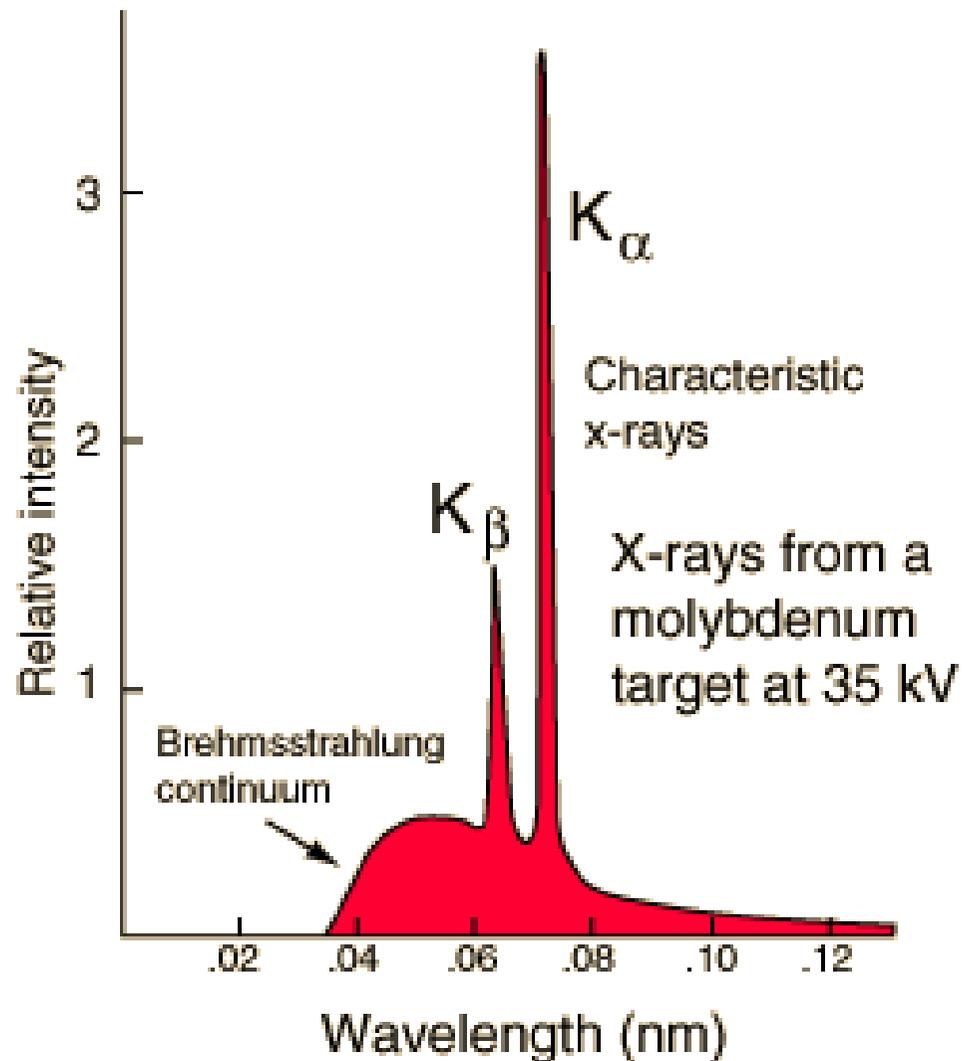
Cu (Z=29): 8,86 kV

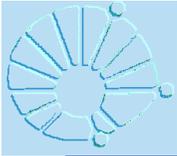
Ni (Z=28): 8,29 kV

Co (Z=27): 7,71 kV

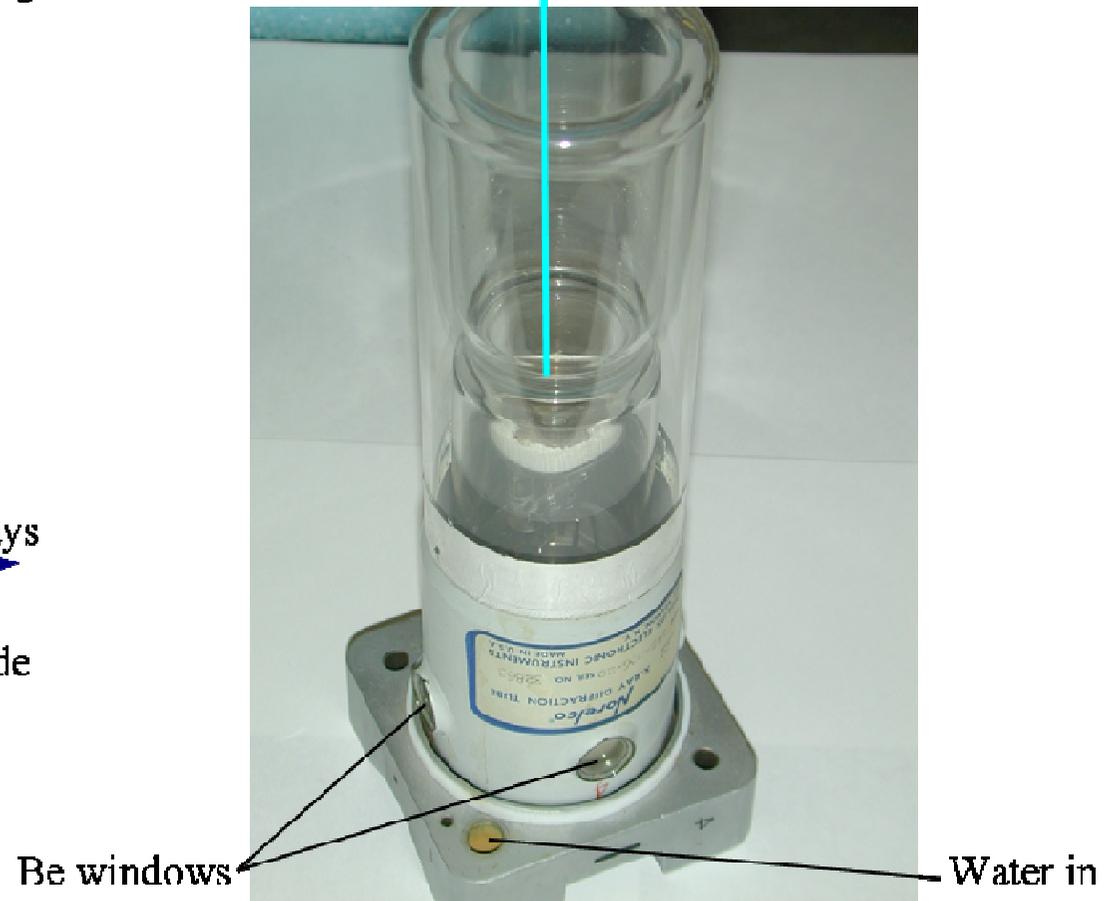
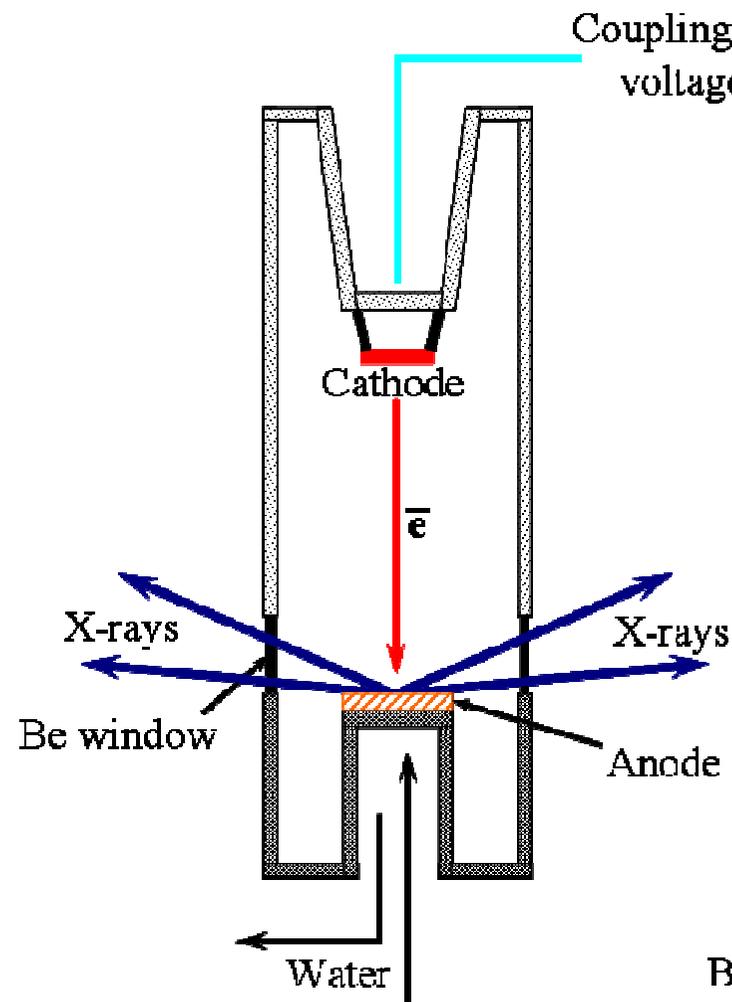
Cr (Z=24): 5,98 kV

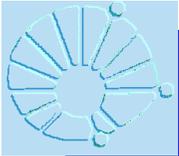
( $Z = \text{número atômico}$ )



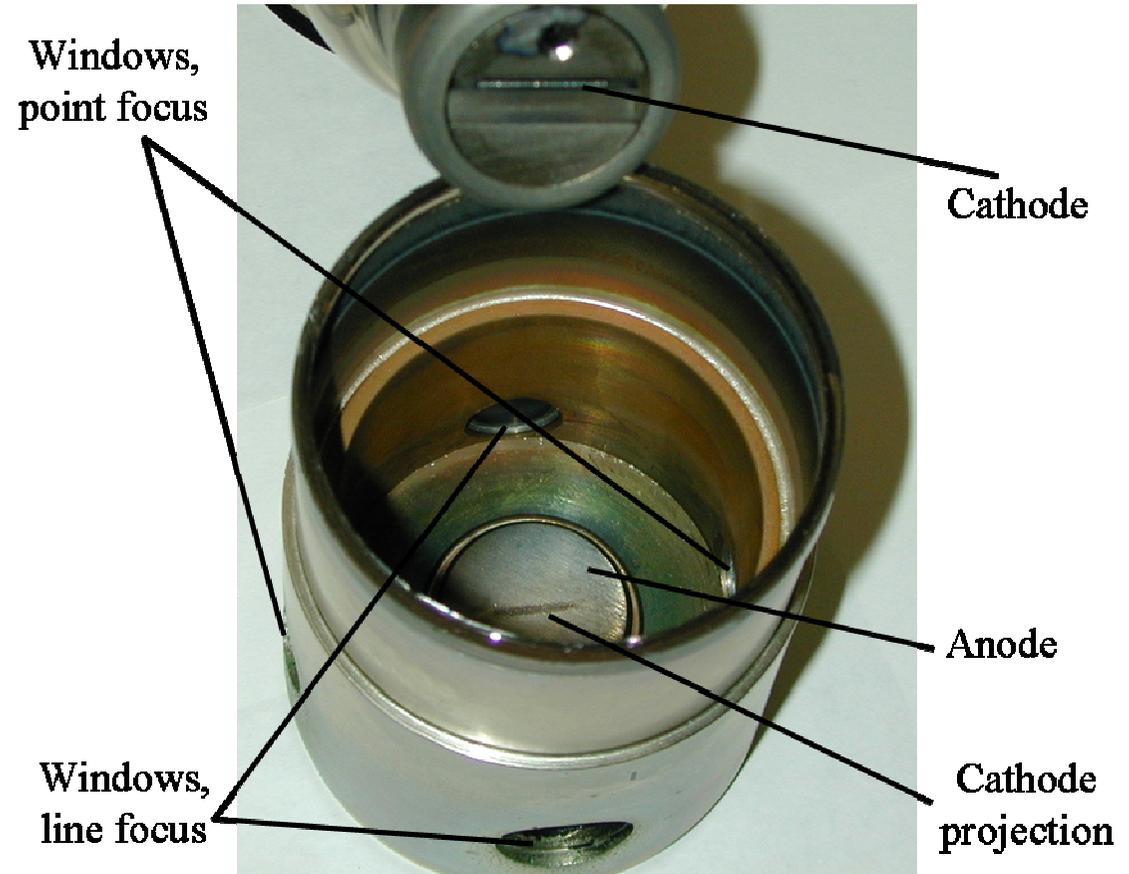
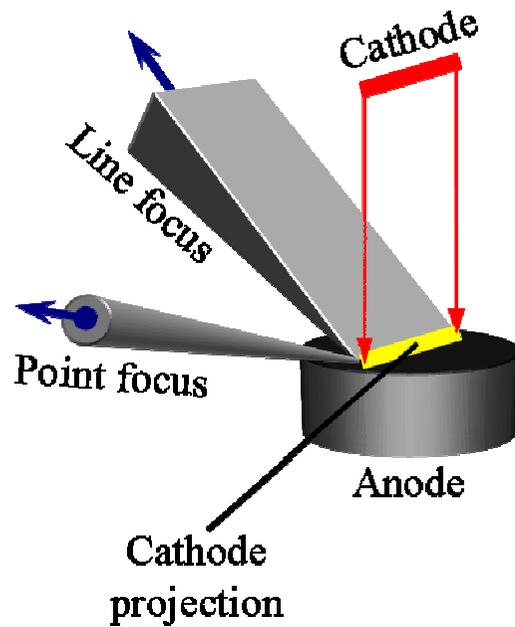


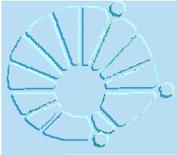
# Tubo de difração de raios-X selado



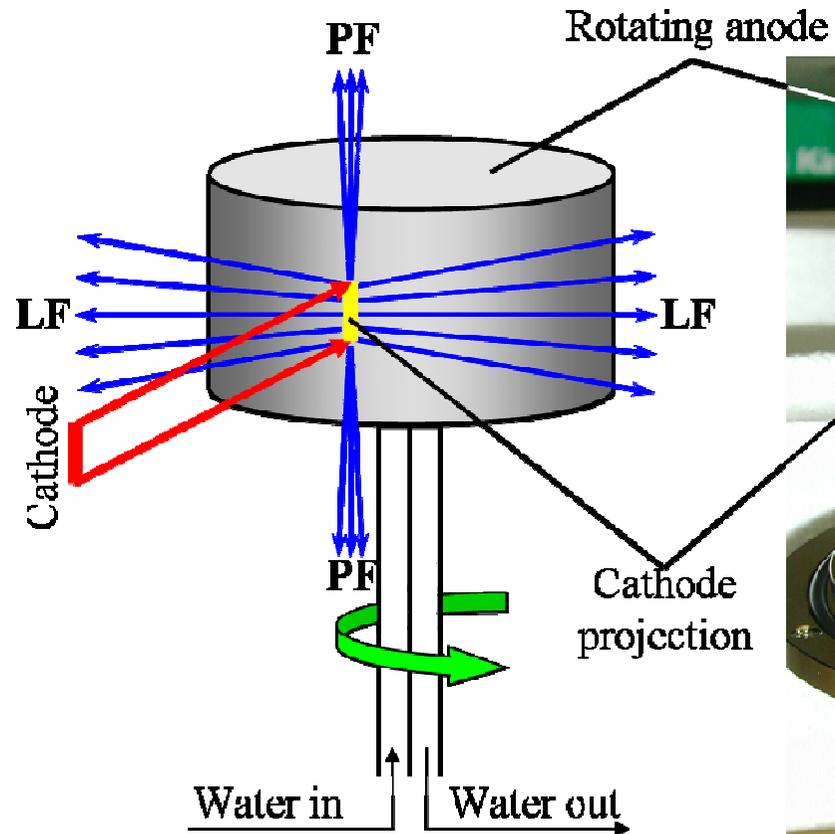


# Geometrias do foco de raios-X no tubo



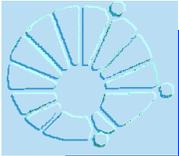


# Gerador de raios-X de Anodo rotatório



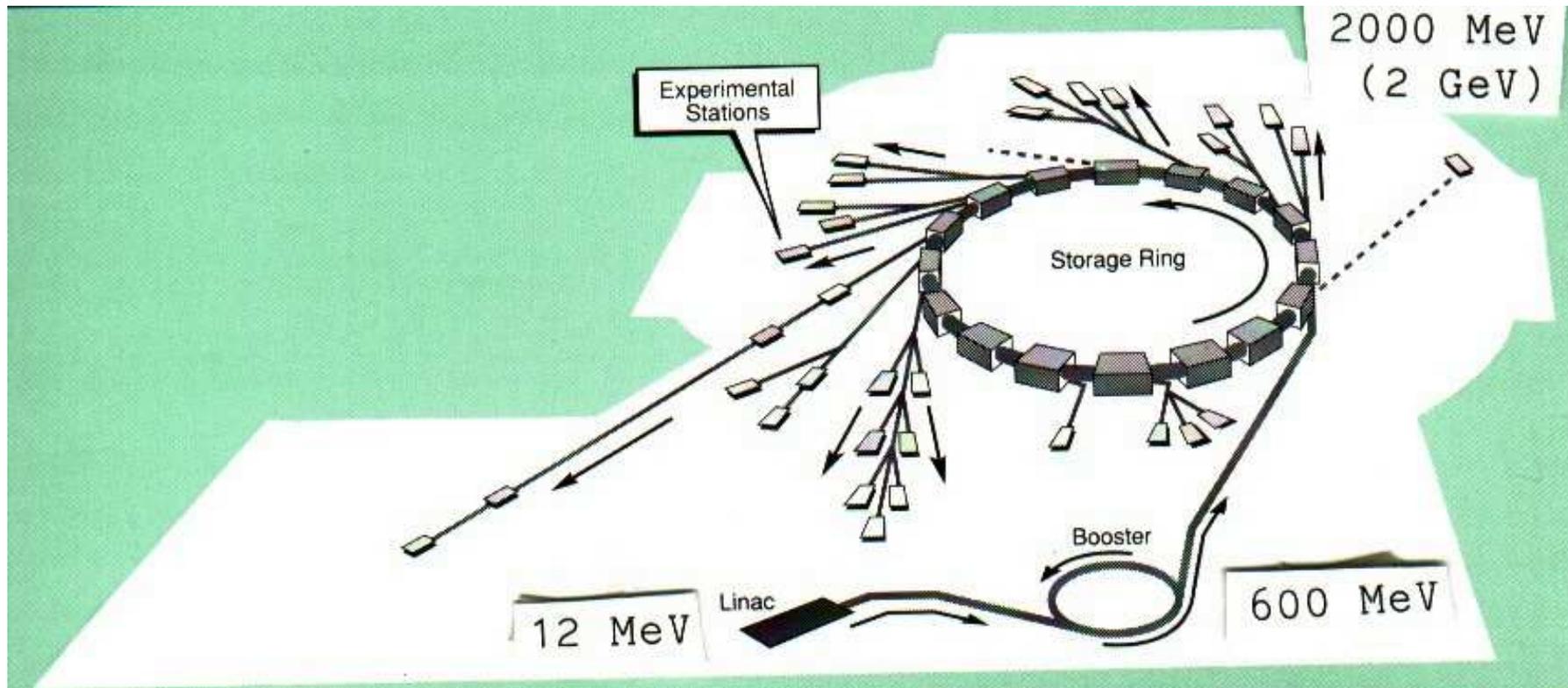
PF – point focus

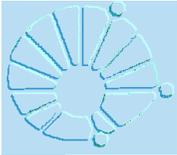
LF – line focus



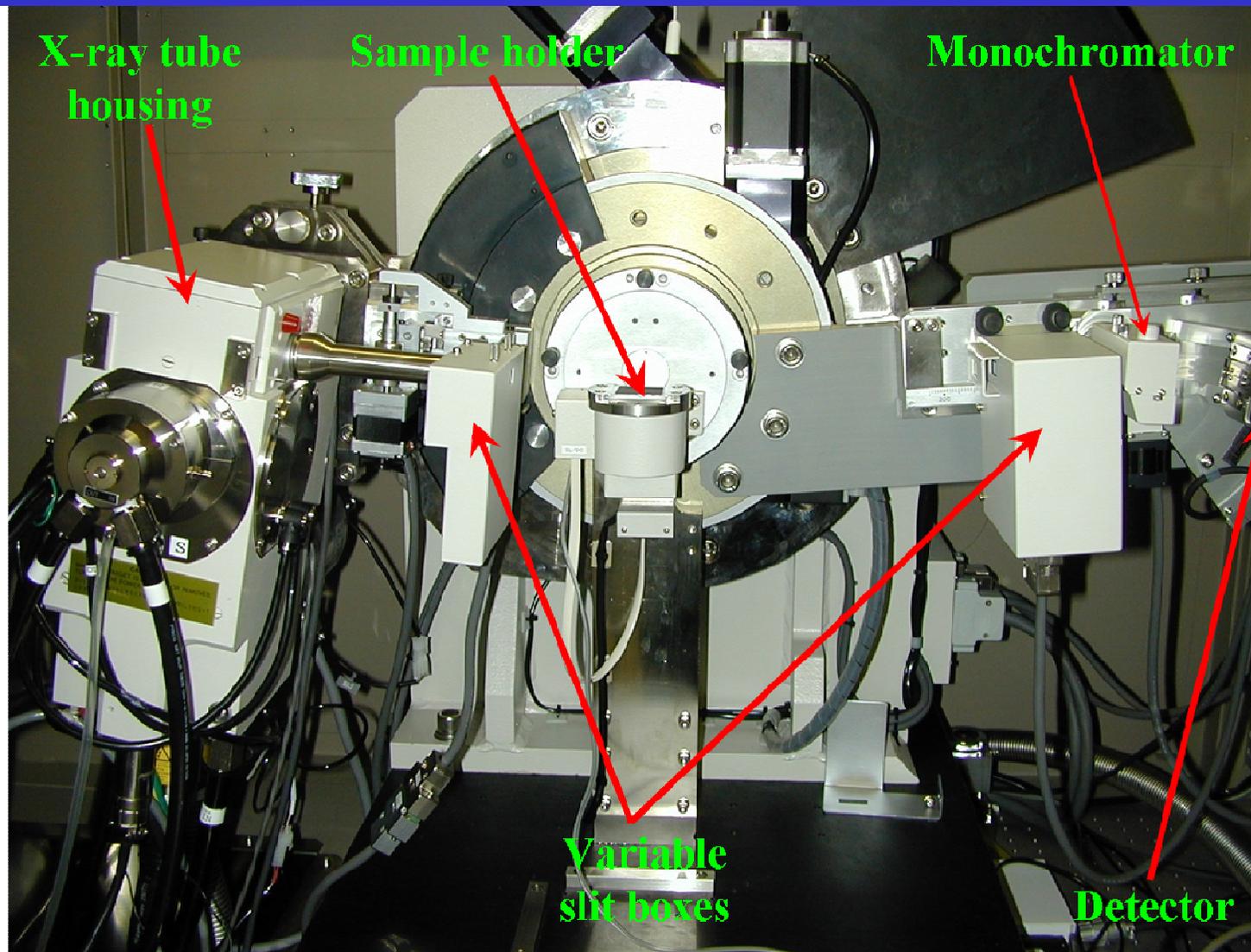
# Radiação síncrotron

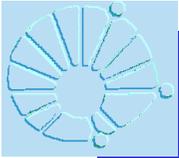
## Laboratório de Daresbury, Warrington, Inglaterra



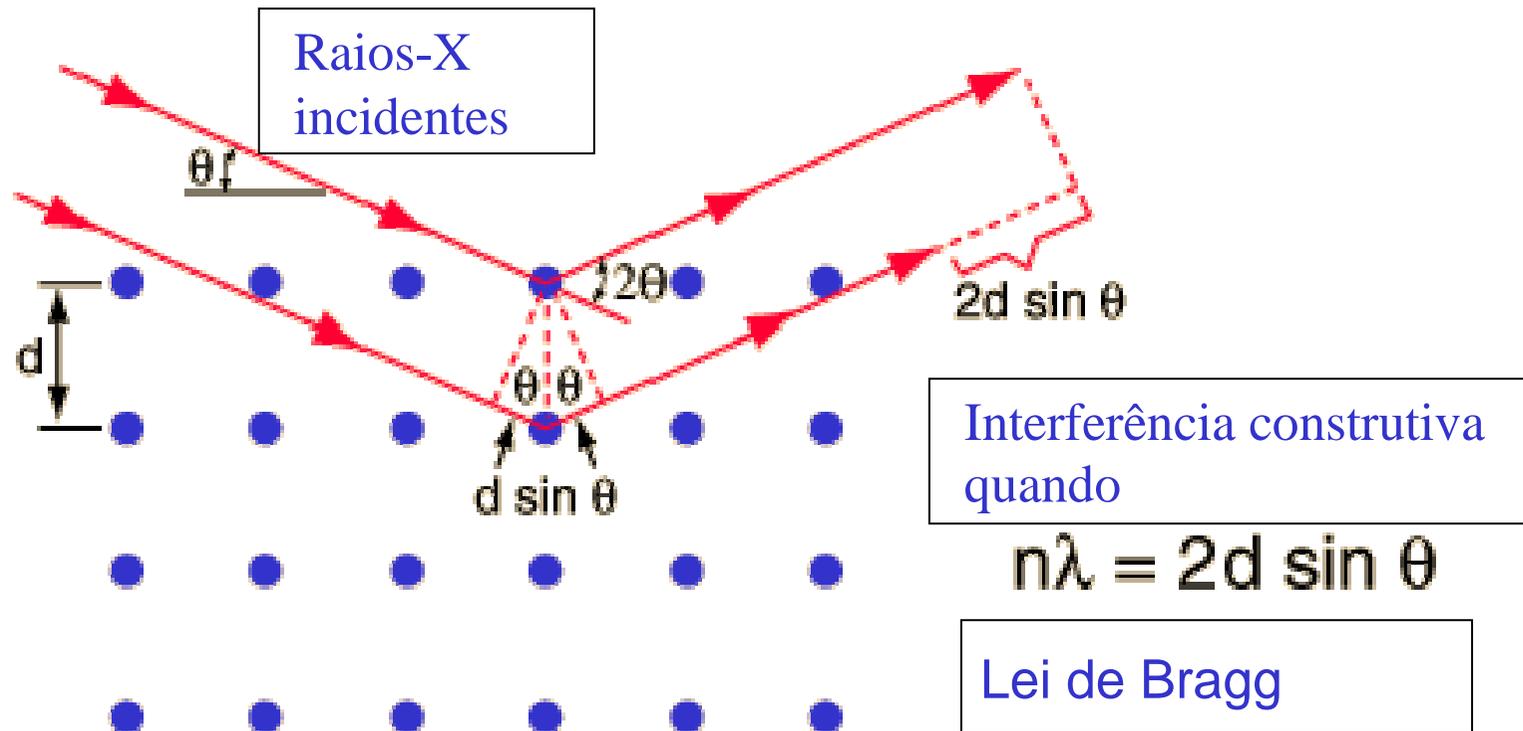


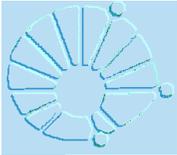
## Difratômetro de raios-X para policristais



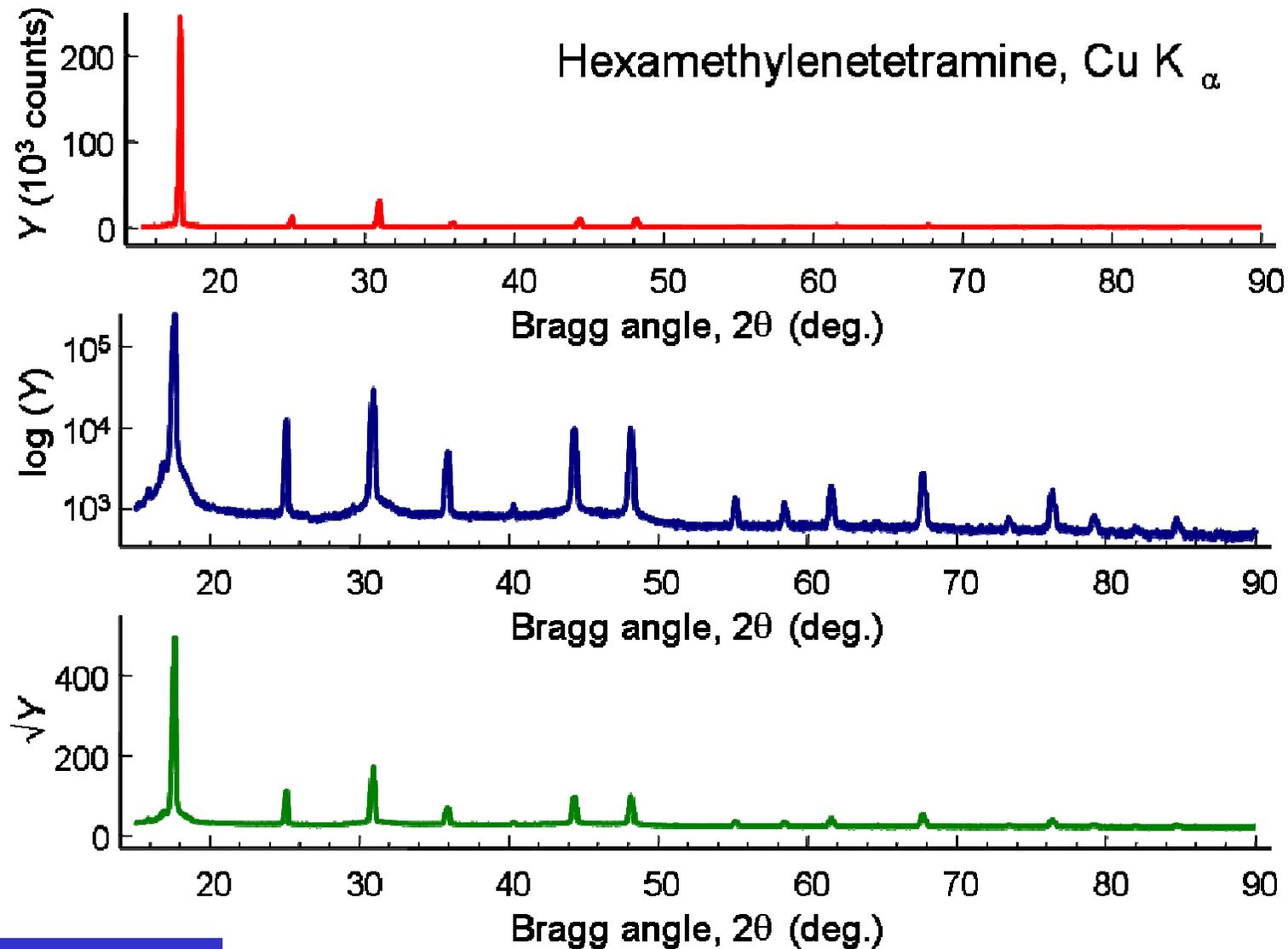


# DIFRAÇÃO DE RAIOS-X – LEI DE BRAGG





# Representação de difratogramas obtidos



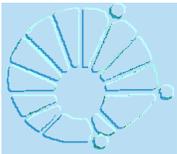


# Padrão para análise de difração de policristais

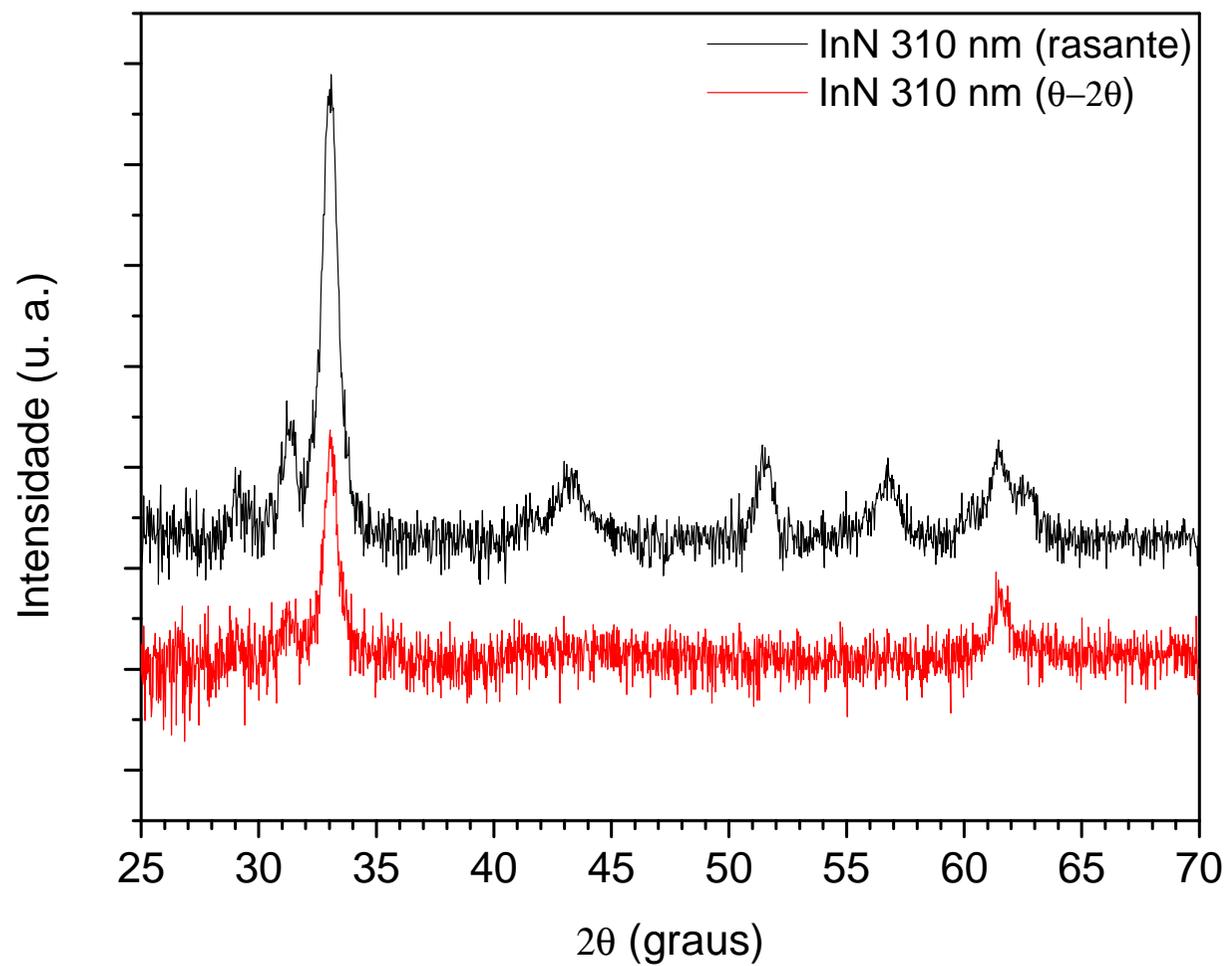
1	48-1152	Quality: Indexed
2	Li <sub>0.6</sub> V <sub>1.67</sub> O <sub>3.67</sub> · H <sub>2</sub> O Lithium Vanadium Oxide Hydrate	
3	Rad:CuKα1    Lambda:1.54056    Filter:    d sp:Diffractionmeter Cutoff:    Int:Diffractionmeter    I/lor:	
	Ref:Whittingham, M., SUNY at Binghamton, MaterialsResearch Center, NY, USA.Chyrayil, T., Zavalij, P., Whittingham, M., (1	
4	Sys:Tetragonal    S.G.:I4/mmm a:3.7047±0.0003    b:    c:15.804±0.002 α:    β:    γ:    Z:2    mp	
	Ref2 Dx:2.53    Dm:2.541    SS/FOM: F30=46.5(0.0161,40)    Volume[CD]:216.91	
5	εα:    ηωβ:    εγ:    Sign:    2V:	
6	Ref3 Color:	
7	Prepared by hydrothermal treatment of tetramethylammonium hydroxide, vanadium pentoxide and \Li O H\ acidified to pH 2-5 for 3 days at 200 C. Pattern taken at 23(1) C.	

32 reflections in pattern.

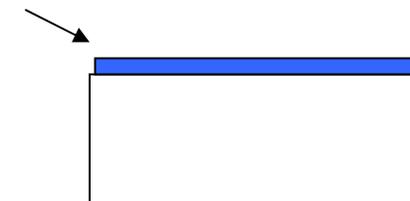
2 θ	Int.	h k l	2 θ	Int.	h k l	2 θ	Int.	h k l	2 θ	Int.	h k l
11.2026	100	0 0 2	50.5721	8	0 2 2	72.0262	4	2 2 0	83.7228	1	0 1 13
22.4967	19	0 0 4	54.6668	3	0 2 4	73.1843	2	2 2 2	84.1343	1	0 3 5
24.6618	9	0 1 1	55.7443	2	1 2 1	76.5173	1	2 2 4			
29.4652	50	0 1 3	58.0669	3	0 1 9	77.4598	1	0 3 1			
33.9955	1	0 0 6	58.3367	13	1 2 3	79.4091	2	1 2 9			
34.2095	14	1 1 0	58.3367	13	0 0 10	79.6864	4	0 3 3			
36.0710	1	1 1 2	58.4543	4	1 1 8	79.6864	4	0 2 10			
37.3772	4	0 1 5	63.3383	3	1 2 5	81.7407	2	1 1 12			
47.1058	19	0 1 7	69.4008	10	1 1 10	82.1813	2	1 3 0			
49.1443	16	0 2 0	70.4377	7	1 2 7	83.3159	1	1 3 2			



## Difração de raios-X ( filme fino) - geometria rasante

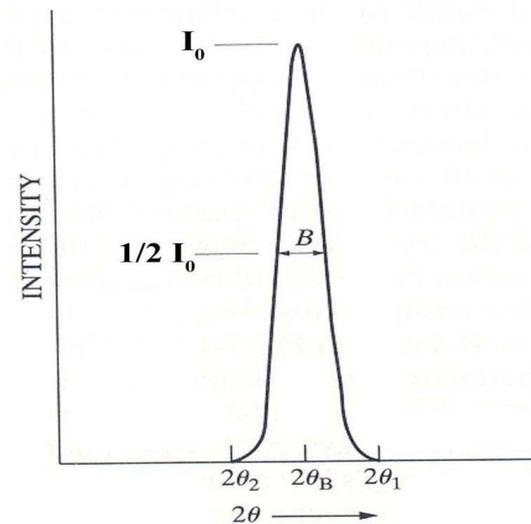
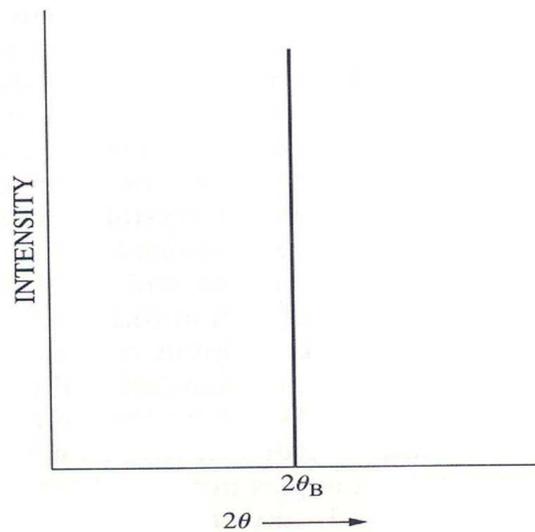
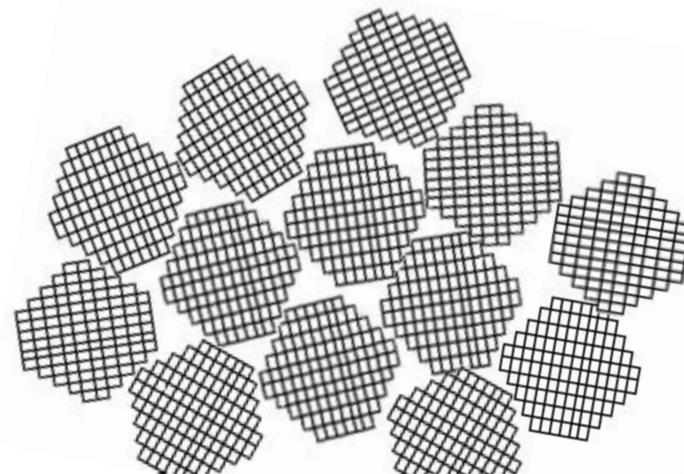
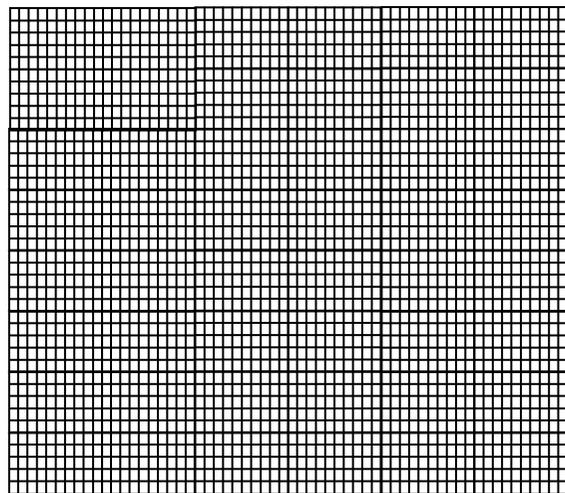


InN filme (310 nm)





# Tamanho de Cristais x alargamento do pico DRX



# Fórmula de Scherrer

$$t = \frac{K * \lambda}{B * \cos \theta_B}$$

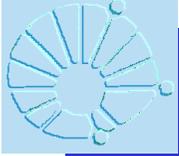
$t$  = tamanho de cristalito

$K$  = constante dependente do formato de cristal (0.89)

$\lambda$  = comprimento de onda dos raios-X

$B$  = FWHM (largura a meia altura do pico)

$\theta_B$  = ângulo de Bragg



# Método Rietveld

Intensidade das reflexões de Bragg:

$$I_k = SM_k L_k |F_k|^2 P_k$$

$S$  = Fator de escala

$M_k$  = Fator de multiplicidade

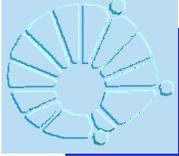
$L_k$  = Fator de polarização de Lorentz

$|F_k|^2$  = Fator de estrutura

$P_k$  = Orientação preferencial\*

---

\* Se não houver orientação preferencial,  $P_k = 1$ .

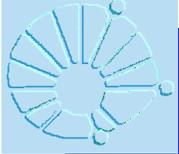


# Método Rietveld

Fator de estrutura:

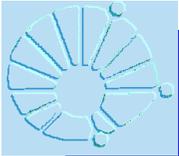
$$F_k = \sum_{j=1}^n f_j \exp[2\pi i(h_r^t r_j - h_k^t B_j)]$$

- $f_j$  = fator de espalhamento atômico (varia com  $\sin\theta/\lambda$ )  
 $h_k$  = matriz que representa os índices de Miller,  
 $r_j$  = coordenadas atômicas  
 $B_j$  = vibração térmica anisotrópica



## Refinamento Rietveld - Parâmetros envolvidos

- ✓ Parâmetros de estrutura cristalina:
  - coordenadas (x, y, z);
  - fator de ocupação;
  - parâmetro de rede (a, b, c)
  - ângulo entre os vetores ( $\alpha$ ,  $\beta$ ,  $\gamma$ );
  
- ✓ Parâmetros de perfil: largura das reflexões, assimetria e forma;
  
- ✓ Parâmetros de intensidade: fator de escala;
  
- ✓ Parâmetros de correção de orientação preferencial.



# Método Rietveld

$R_{wp} = R$  ponderado

$$R_{wp} = \left[ \frac{\sum w_i (y_{io} - y_{ic})^2}{\sum w_i y_{io}^2} \right]^{1/2}$$

Índice a ser analisado para ver se o refinamento está convergindo

$$R_{exp} = \left[ \frac{N - P}{\sum w_i y_{ik}^2} \right] \quad \text{Valor estatisticamente esperado para } R_{wp}$$

$$\frac{\sum w_i (y_{io} - y_{ic})^2}{N - P} - \left[ \frac{R_{wp}}{R_{exp}} \right]^2$$

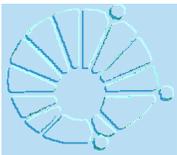
N = número de pontos usados no refinamento  
P = número de parâmetros refinados

## Significado dos fatores R's

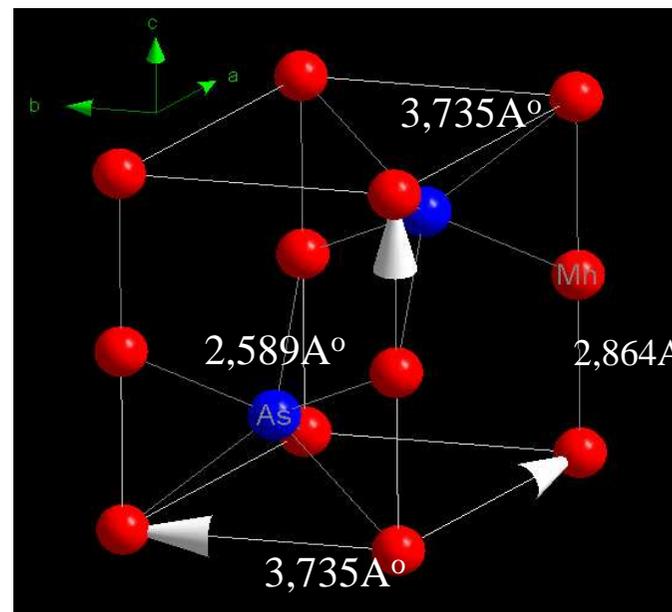
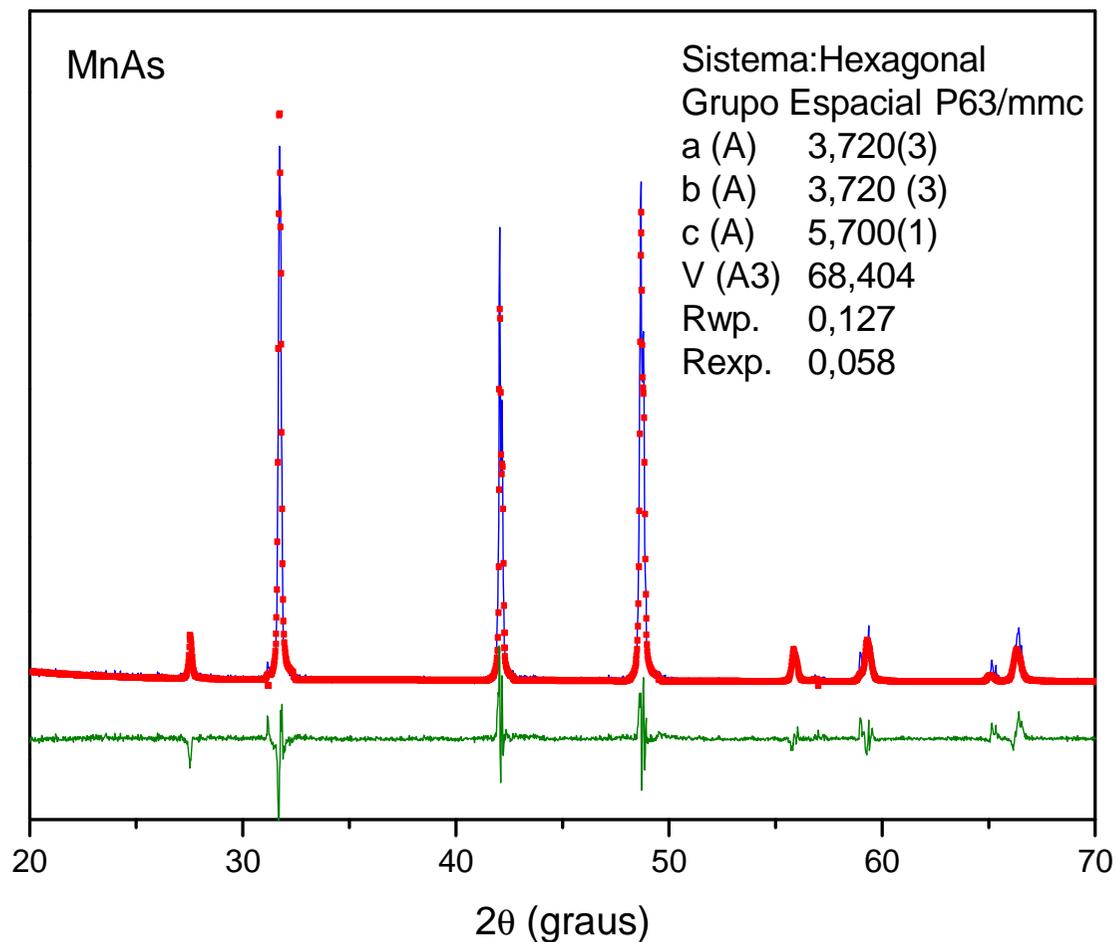
Como a intensidade integrada está relacionada com a estrutura cristalina, o  $R_B$  é o índice a ser considerado para avaliar a qualidade do modelo refinado da estrutura cristalina.

$$R_B = \frac{\sum |I_{kc} - I_{ko}|}{\sum I_{ko}}$$

$$S = \frac{R_{wp}}{R_{exp}} \quad \text{“Goodness of Fit”}$$

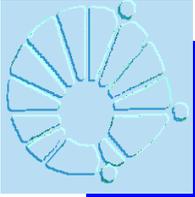


# Refinamento Rietveld - MnAs



## Posições atômicas

Mn (2a)	0	0	0
Mn (2a)	0	0,50	0,50
As (2c)	0,33	0,66	0,25
As (2c)	0,66	0,33	0,75



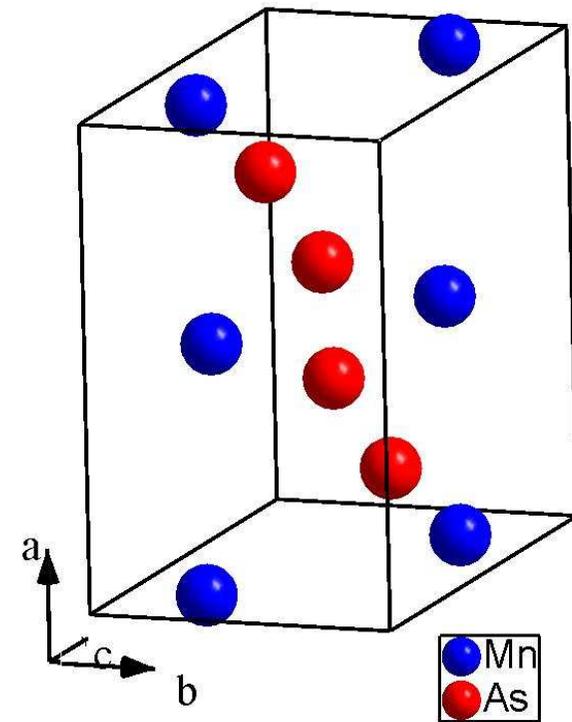
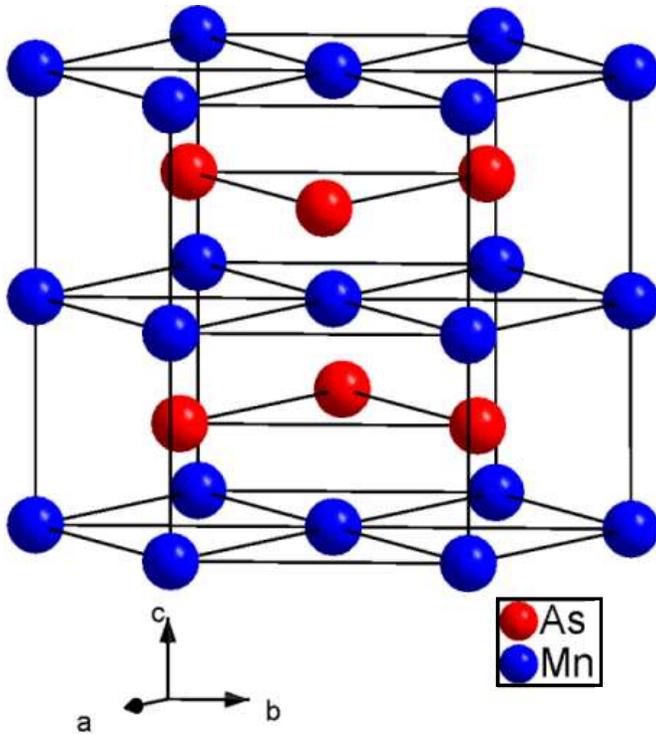
# Estruturas cristalinas - MnAs

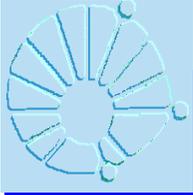
Hexagonal – P63/mmc



~318K

Ortorrômbica - Pnma

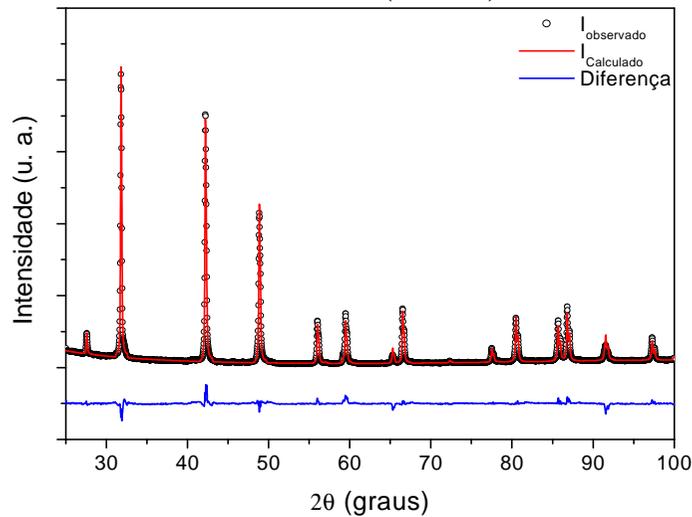




# Resultados

## MnAs- Hexagonal – P63/mmc

T=24°C (298K)



$$R_p = 6,2\%$$

$$R_{wp} = 8,6\%$$

$$a = 3,723(1) \text{ \AA}$$

$$c = 5,708(3) \text{ \AA}$$

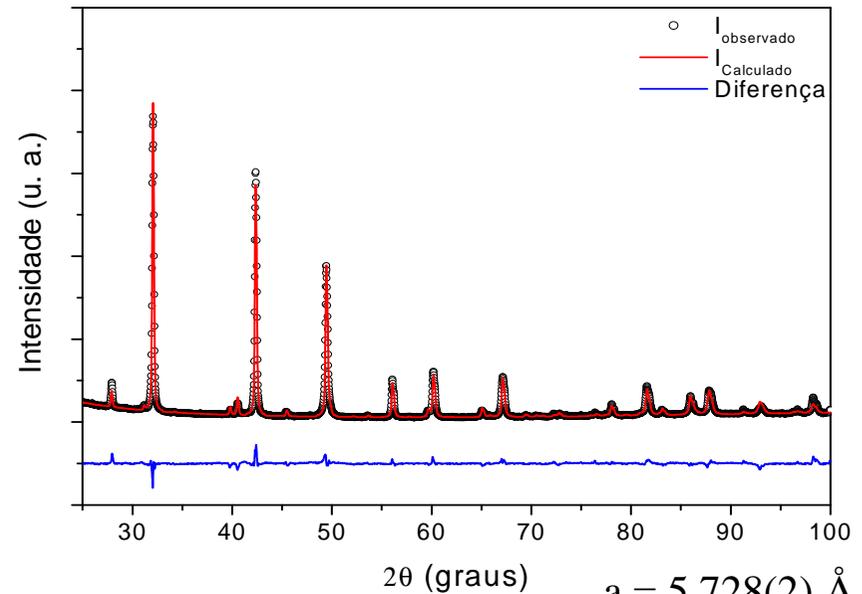
$$V = 68,51 \text{ \AA}^3$$

### Posições atômicas

Mn (2a) 0 0 0

As (2c) 1/3 2/3 1/4

## MnAs - Ortorrômbica - Pnma



$$R_p = 6\%$$

$$R_{wp} = 8,4\%$$

$$a = 5,728(2) \text{ \AA}$$

$$b = 3,678(3)$$

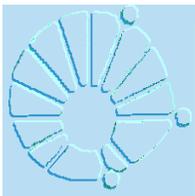
$$c = 6,382(3) \text{ \AA}$$

$$V = 134,41 \text{ \AA}^3$$

### Posições atômicas

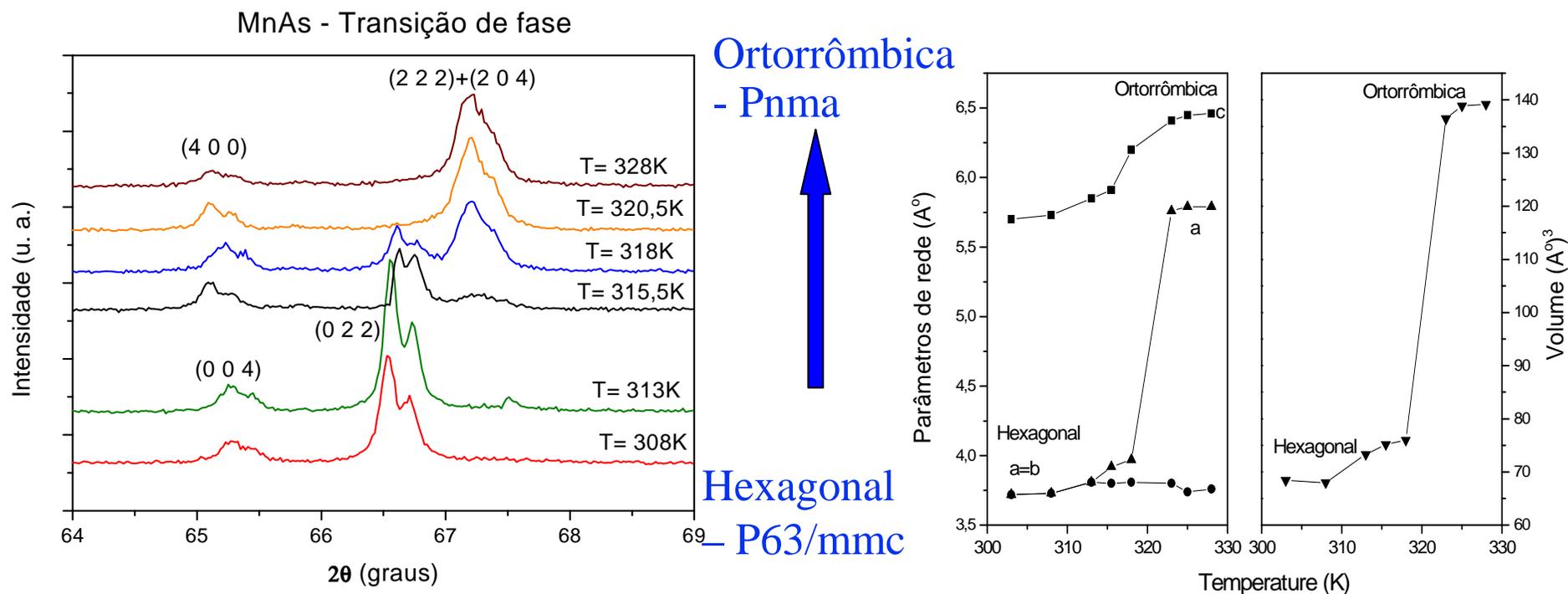
Mn (4c) 0,4952(6) 1/4 0,2771(5)

As (4c) 0,7745(4) 1/4 0,5816(5)

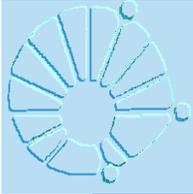


# Resultados

## MnAs - Transição de Fase



“Structural and magnetic study of the MnAs magnetocaloric compound”, Nascimento, dos Santos, de Campos, Gama & Cardoso, Materials Research (2006) 9(1),111-114



# PRÉDIO DA ESTAÇÃO GUANABARA

## Campinas, São Paulo



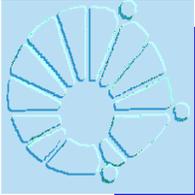
**1938**



**2006**

**Centro Cultural de Inclusão  
e Integração Social  
(CIS-GUANABARA)  
da UNICAMP**

Traços típicos encontrados em edifícios históricos:  
1:1 e 1:2 (cal:areia) e 1:1:2 e 1:3:6 (cimento:cal:areia)



# ANÁLISE DE ARGAMASSA EM PRÉDIOS HISTÓRICOS

## REFINAMENTO RIETVELD – REVELANDO A PRESENÇA DE PORTLANDITA

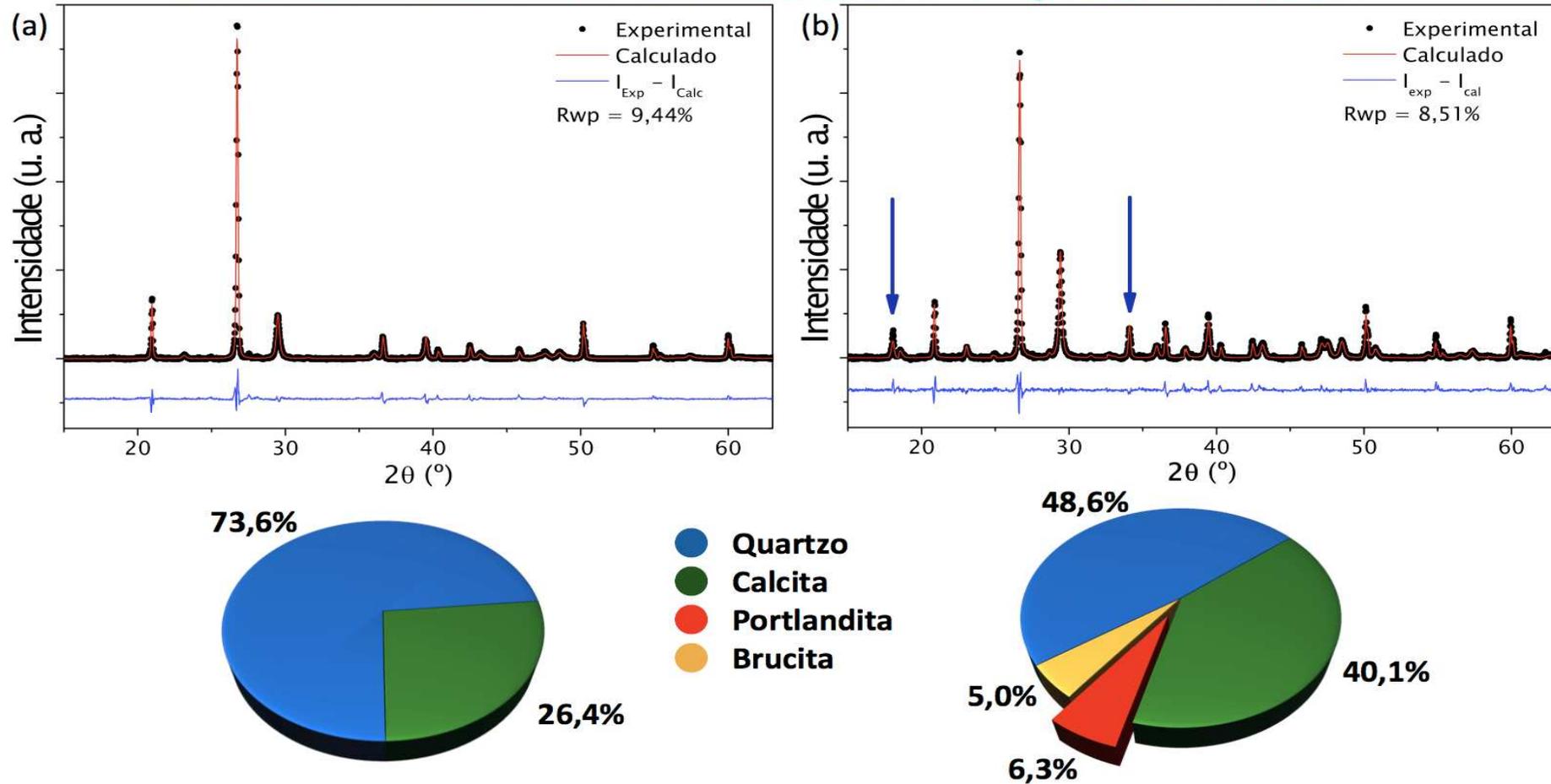
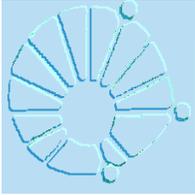


Fig. 1 - Refinamento Rietveld para amostras argamassa. (a) Amostra típica de ambientes de 1893 a 1915 (somente quartzo e calcita); (b) Amostra típica de 1960 (presença de quartzo, calcita, brucita e portlandita - **setas**); As respectivas composições relativas seguem logo abaixo.



# Formação de Cristais

## Solução

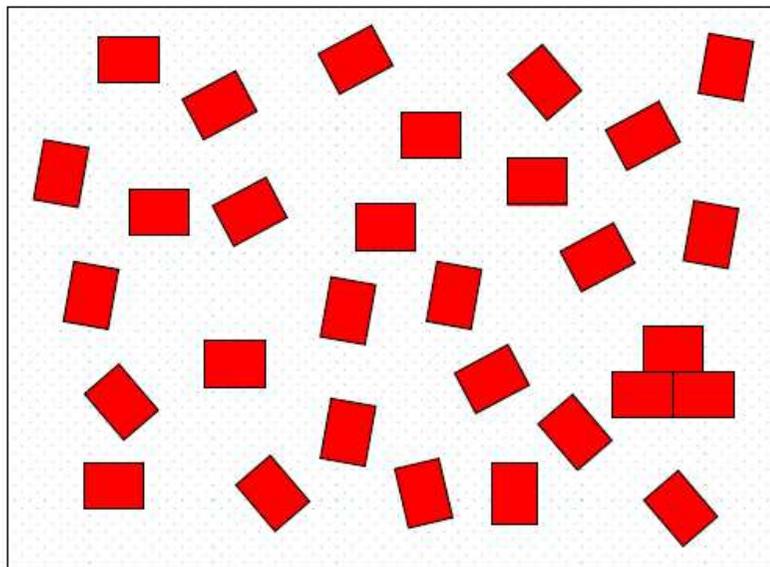
- açúcares – Sais – amido
- Lipídios em solvente orgânico

## Fusão

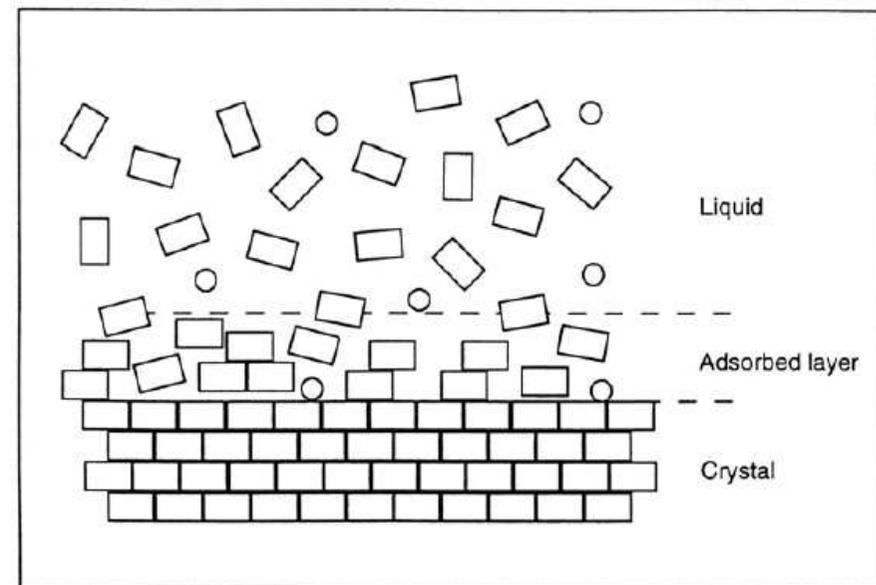
- Lipídios –água –amido

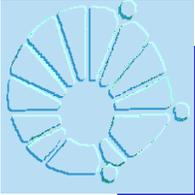
## Exemplo: cristalização da sacarose

### Nucleação



### Formação de cristais

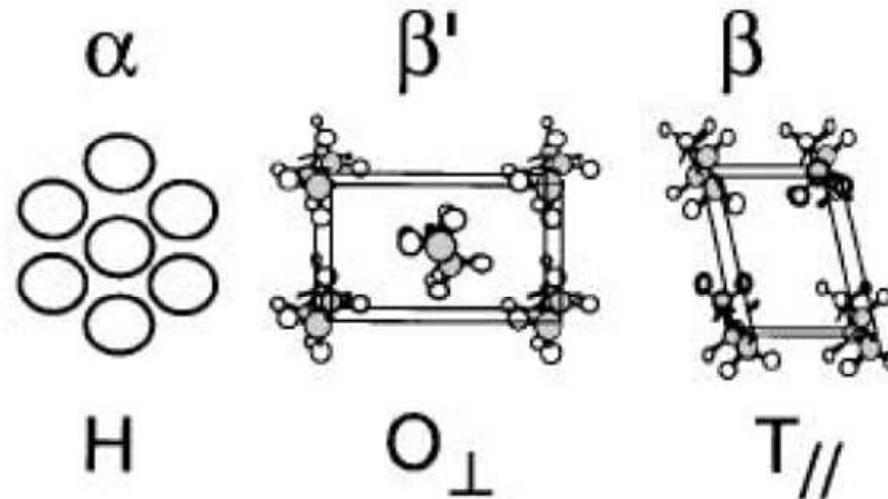




# ESTUDO DE GORDURAS TRANS

Os triacilgliceróis cristalizam-se nas formas polimórficas  $\alpha$ ,  $\beta'$  ou  $\beta$ , embora a forma  $\beta$  seja a mais estável.

A forma  $\beta'$  é o polimorfo de maior interesse para produção de alimentos ricos em gordura (margarinas, produtos de confeitaria e panificação).

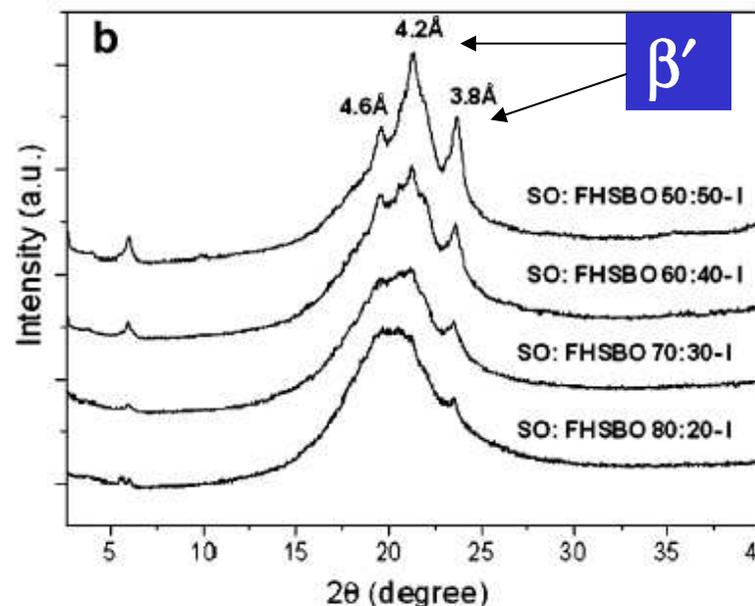
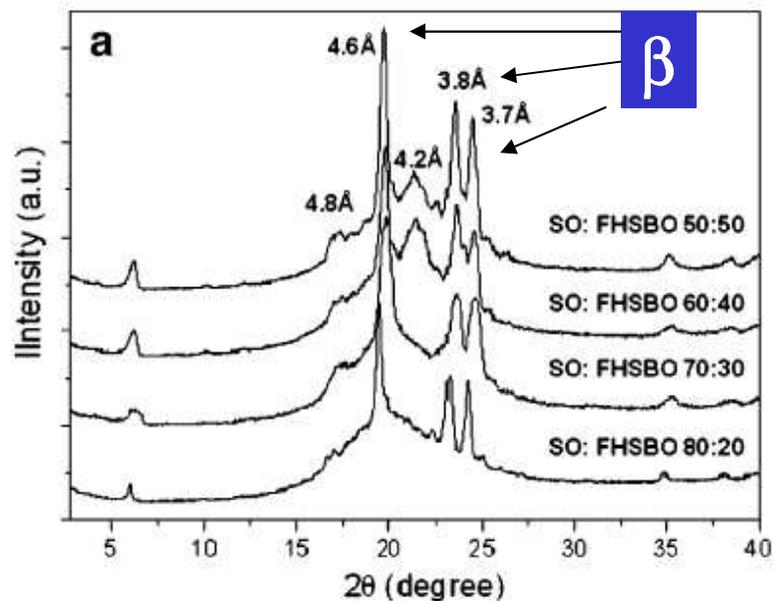


A identificação das formas polimórficas foi realizada a partir das distâncias interplanares.

$$d = \lambda / (2 \text{ sen } \theta)$$



# Microestrutura, Polimorfismo e propriedades de cristalização de gorduras Zero trans de óleo de soja puro (SO) e totalmente hidrogenado (FHSBO)



a) antes

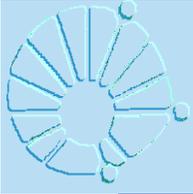
b) após  
interesterificação

Reconfiguração dos três ácidos graxos nos triglicerídeos, que são ligados a uma molécula de glicerol (glicerina). A gordura interesterificada tem qualidades diferentes de fusão (derretimento) e de cozimento.

**Table 5** Polymorphic forms and short spacings of the original and interesterified SO:FHSBO blends

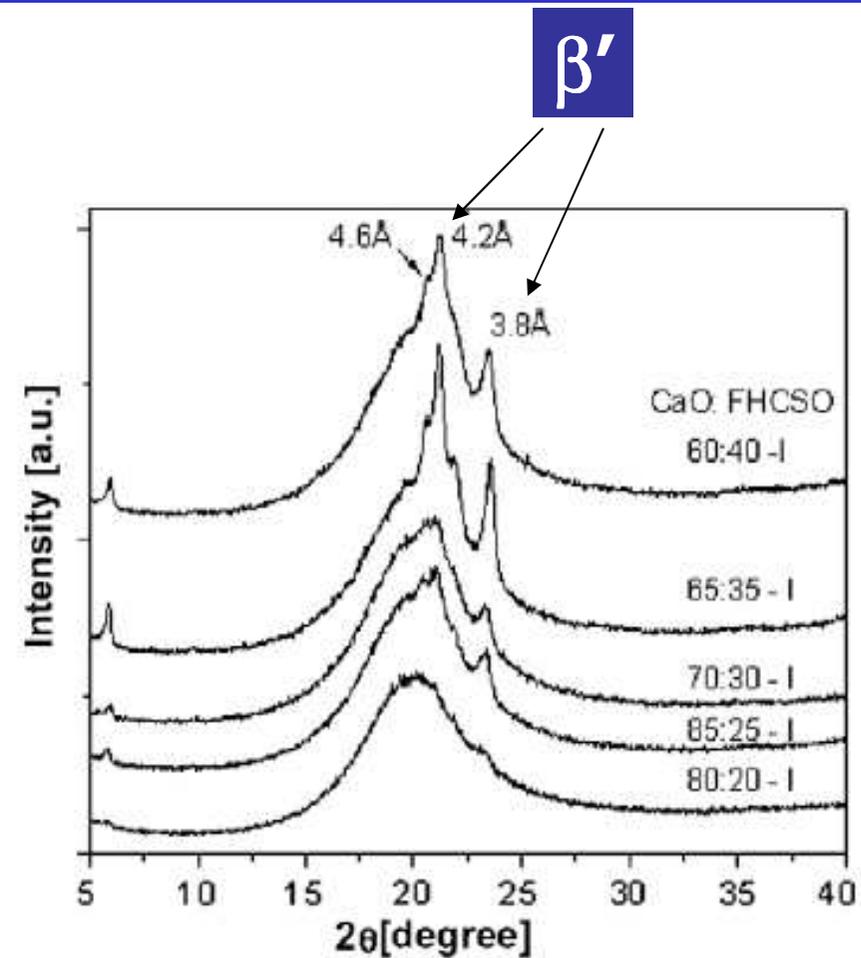
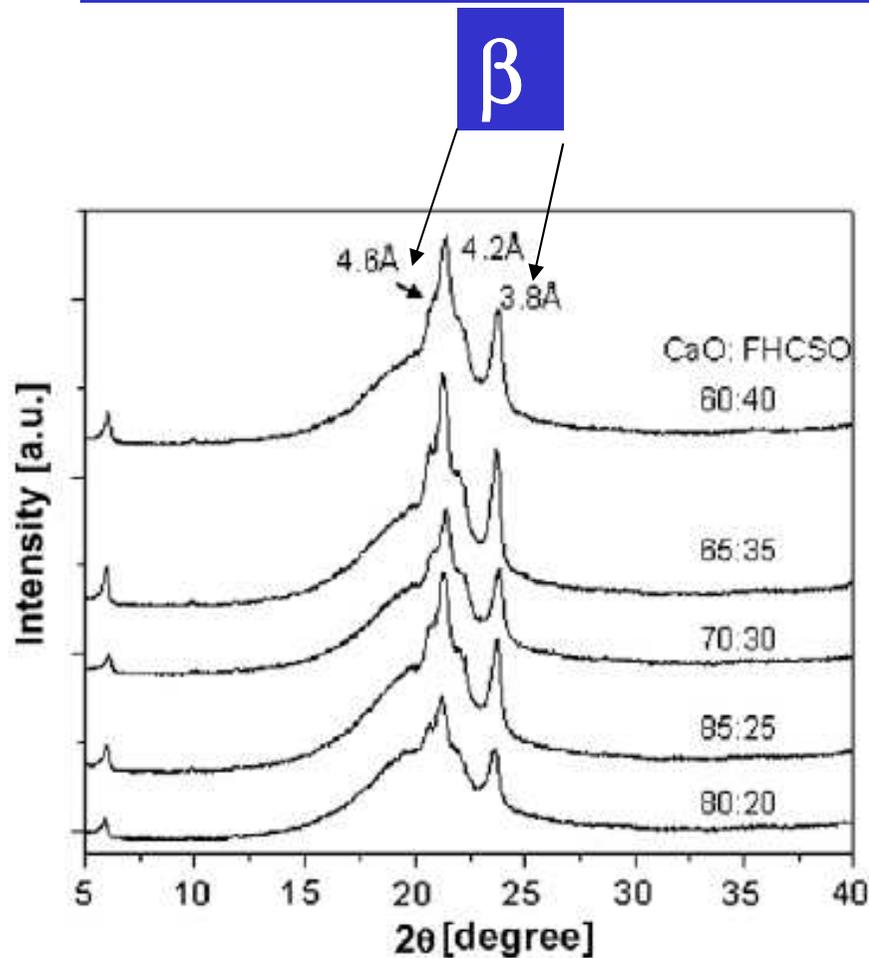
SO:FHSBO	Short spacings (Å)					Polymorphic form
	4.8	4.6	4.2	3.8	3.7	
80:20	4.83 (vw)	4.60 (s)		3.86 (m)	3.70 (m)	β
70:30	4.82 (vw)	4.59 (s)		3.85 (m)	3.69 (m)	β
60:40	4.78 (vw)	4.56 (s)	4.19 (w)	3.77 (m)	3.67 (m)	β > β'
50:50	4.84 (vw)	4.60 (s)	4.22 (w)	3.79 (m)	3.70 (m)	β > β'
80:20-I		4.57 (w)	4.24 (m)	3.84 (m)		β' > β
70:30-I		4.63 (w)	4.23 (m)	3.84 (m)		β' > β
60:40-I		4.58 (w)	4.23 (s)	3.83 (m)		β' > β
50:50-I		4.62 (w)	4.21 (s)	3.80 (m)		β' > β

v very, w weak, m medium, s strong



# ESTUDO DE GORDURAS TRANS

## Óleo de canola + óleo de algodão totalmente hidrogenado

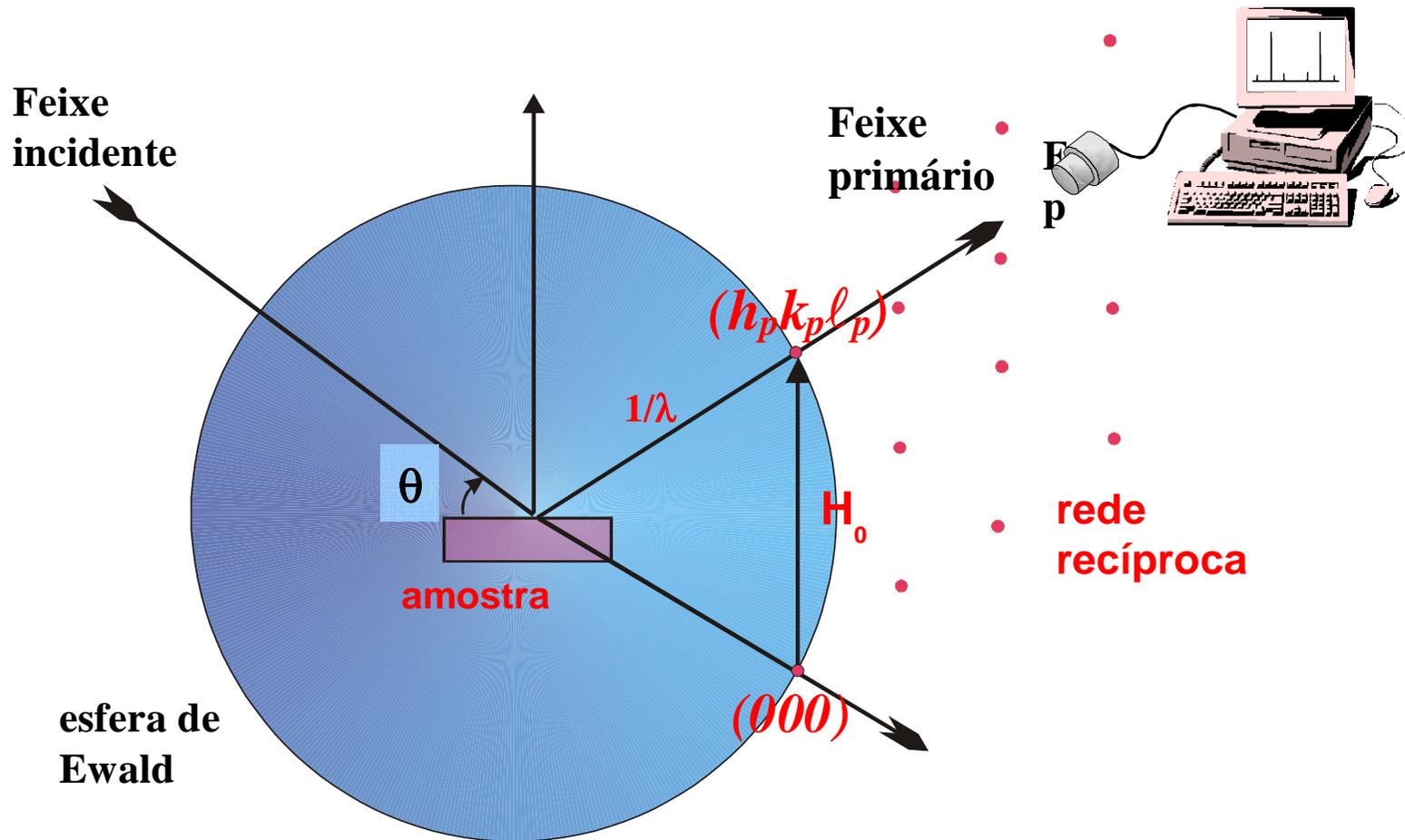


DRX de misturas binárias ANTES

APÓS interesterificação química



# Difração de Raios-X: caso de 2 feixes

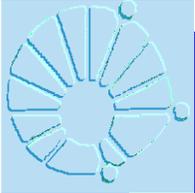


$$|\vec{H}_0| = \frac{1}{d_{hkl}}$$

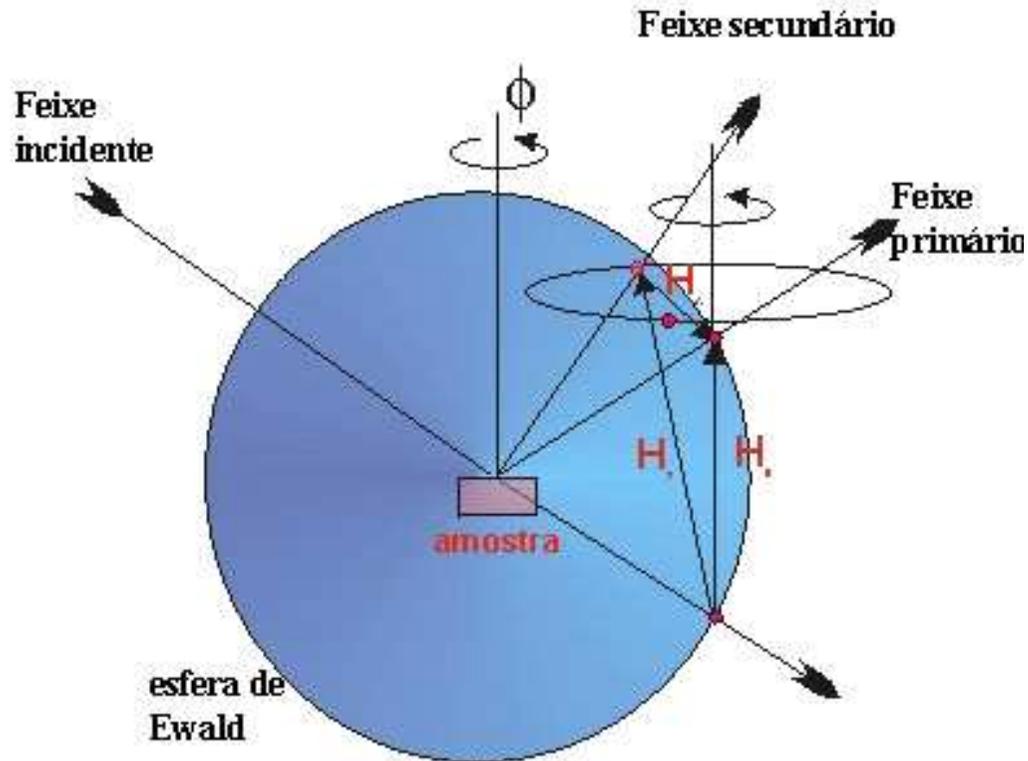
Lei de Bragg

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



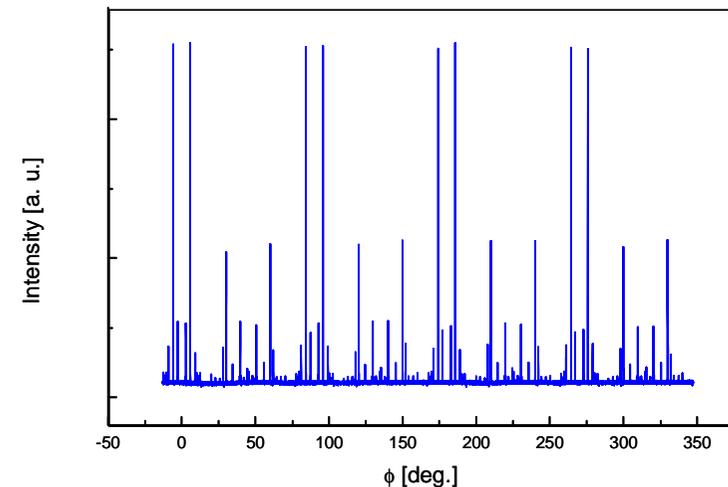


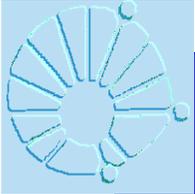
# DIFRAÇÃO MÚLTIPLA DE RAIOS-X (XRMD)



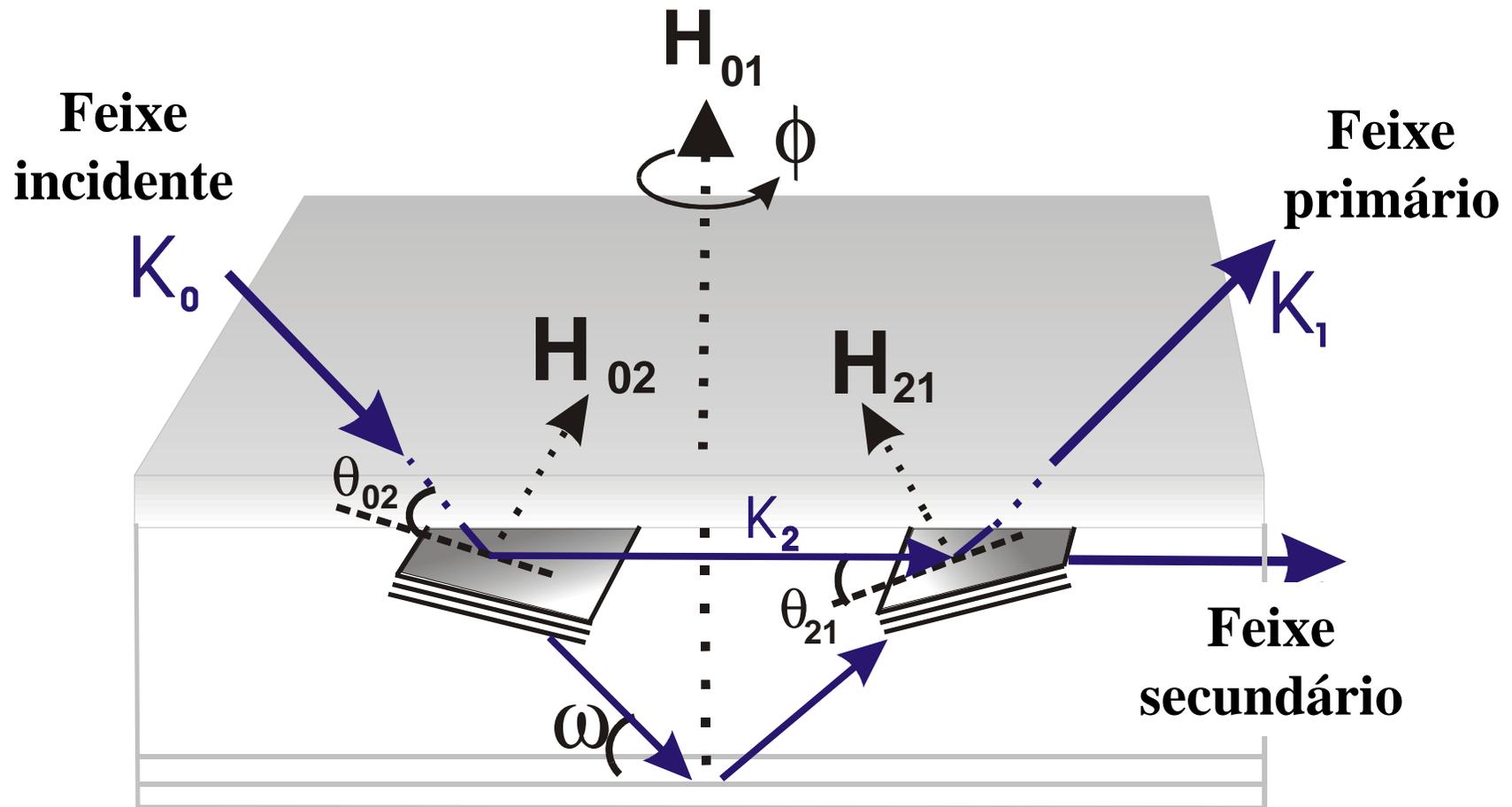
## Vantagens

- Informação 3D simultânea na análise da rede cristalina.
- Alta sensibilidade às pequenas deformações na rede (simetria).
- **Casos Difração Bragg-Superfície** - feixe secundário paralelo à superfície da amostra (interface).



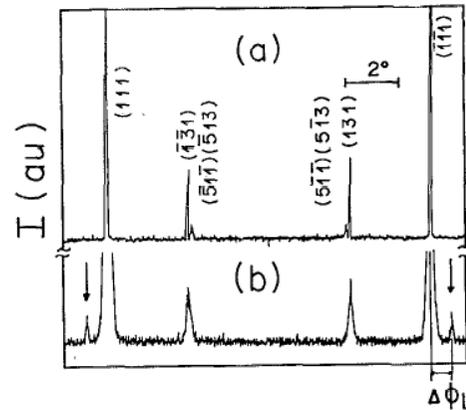


# Representação da Difração Bragg-Superfície (BSD)



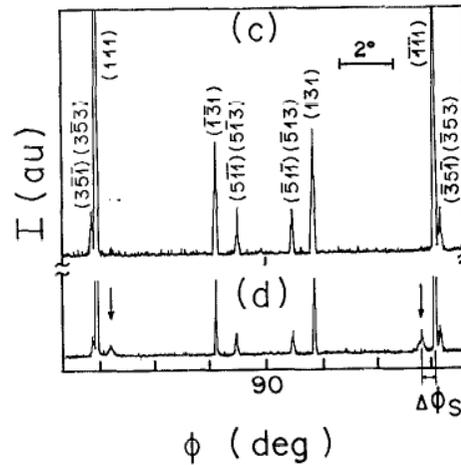


# Reflexões híbridas (SL e LS) em GaAs/Si(002)



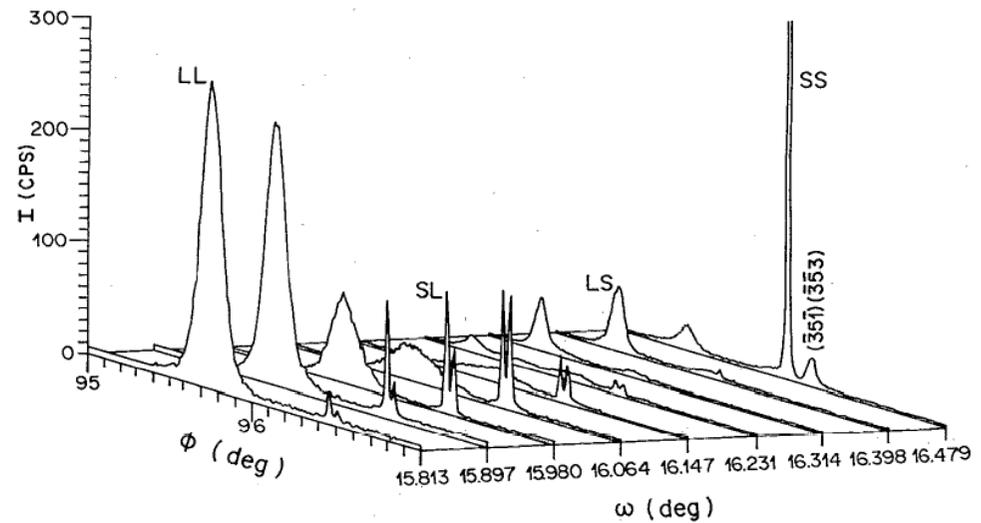
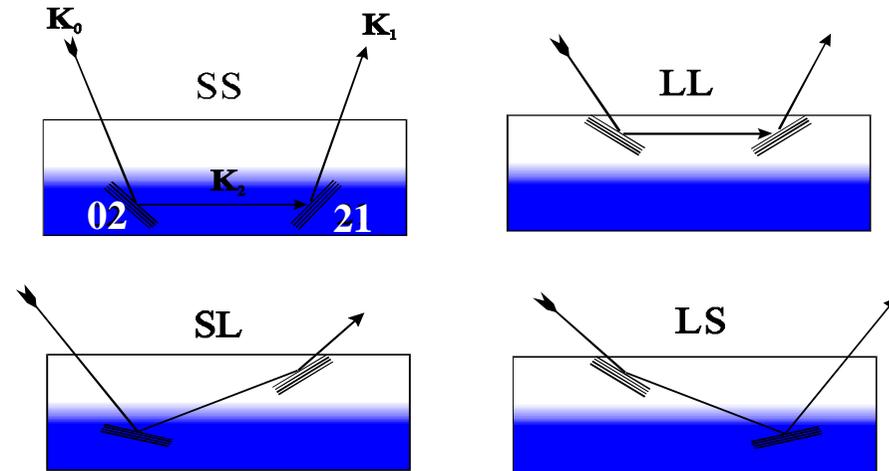
GaAs  
(substrato)

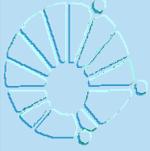
GaAs (0,8µm)  
sobre Si



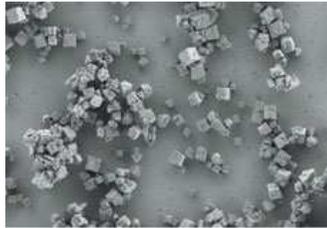
Si  
(substrato)

Si substrato de  
GaAs (0,8µm)





# ENERGIA LIMPA SOB NOSSOS PÉS

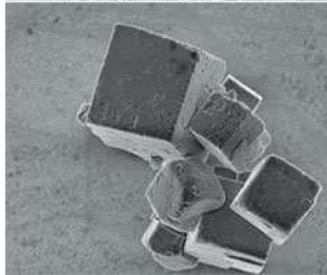


Partículas de cerâmica nanométrica que compõem o material piezoelétrico

POLÍMERO -CERÂMICA (PZT)

PVDF (30-50%PZT – Tf~180oC)

Walter Sakamoto (Unesp-Iha Solteira) e Maria Aparecida Bertochi (Unesp-Araraquara) Fonte: *Pesq. FAPESP (2010) 171, 75*



**Aplicações: pisos piezoelétricos (2008)**

*Casas noturnas (Londres e Roterdã)*

*Estações de metrô em Tóquio*

*Israel –aeroportos e rodovias*

*Estimativa: 20 carros/min – 200 kW/h consumo (casa/mês)*

**Problema: armazenagem (baterias)**

**0,1 kW/ passo (60 kg)**

**NO SAPATO**  
O material poderia ser usado ainda nas solas dos sapatos. A energia seria usada para carregar telefones celulares e tocadores de música de bolso

Fontes: Innowattec, Elson Longo, professor de físico-química da Universidade Estadual Paulista (Unesp), Walter Sakamoto, do Departamento de Física e Química da Faculdade de Engenharia de Ilha Solteira da Unesp



**A**  
A superfície dotada de um material piezoelétrico recebe a pressão dos pés ou dos pneus de veículos

**B**  
Ao ser pressionado, ele libera elétrons, transformando a energia mecânica em elétrica

**C**  
O que é gerado pode ser usado como uma fonte de energia: acender lâmpadas e ligar aparelhos, por exemplo



# DMRX: uma sonda para a piezeletricidade

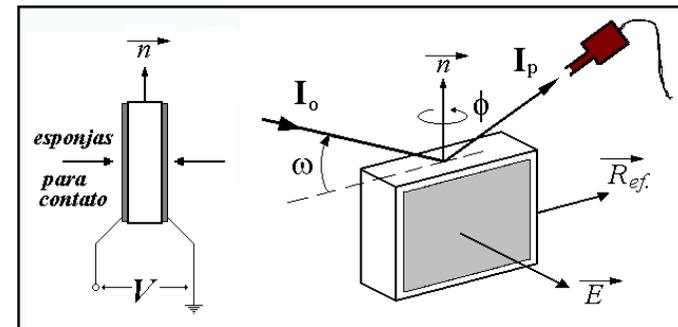
- **Pré-requisito:** Ausência de um centro de simetria
- **Efeito Direto:** Tensão ( $\sigma_{jk}$ )  $\rightarrow$  Polarização  $\rightarrow P_i = d_{ijk} \sigma_{jk}$
- **Efeito Inverso:**

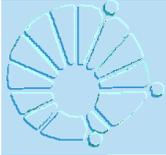
**Campo ( $E_i$ )  $\rightarrow$  Distorção ( $\epsilon_{jk}$ )  $\rightarrow \epsilon_{jk} = d_{ijk} E_i$**

$d_{ijk} \equiv$  **Coeficientes Piezelétricos**

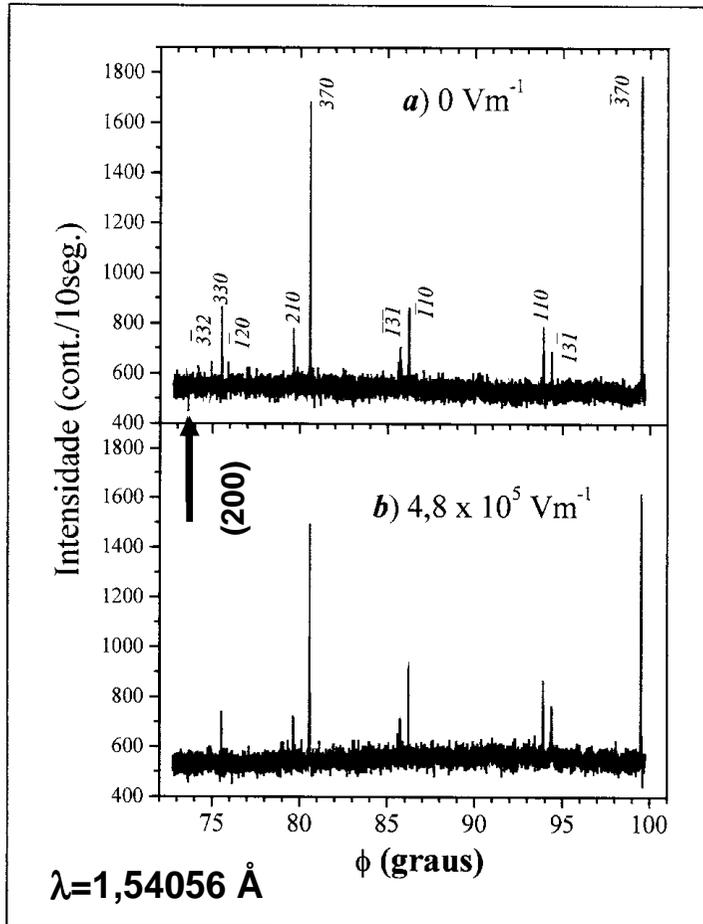
$$\begin{matrix} \vec{E}_x \\ \vec{E}_y \\ \vec{E}_z \end{matrix} \begin{pmatrix} [100] & [010] & [001] & [011] & [101] & [110] \\ 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{pmatrix} \begin{matrix} \text{meta-Nitroanilina (mNA)} \\ \text{ortorrômbico (} mm2 \text{)} \end{matrix}$$

J.F.Nye in: “*Physical properties of crystals*”  
(Clarendon Press, Oxford, 1985).

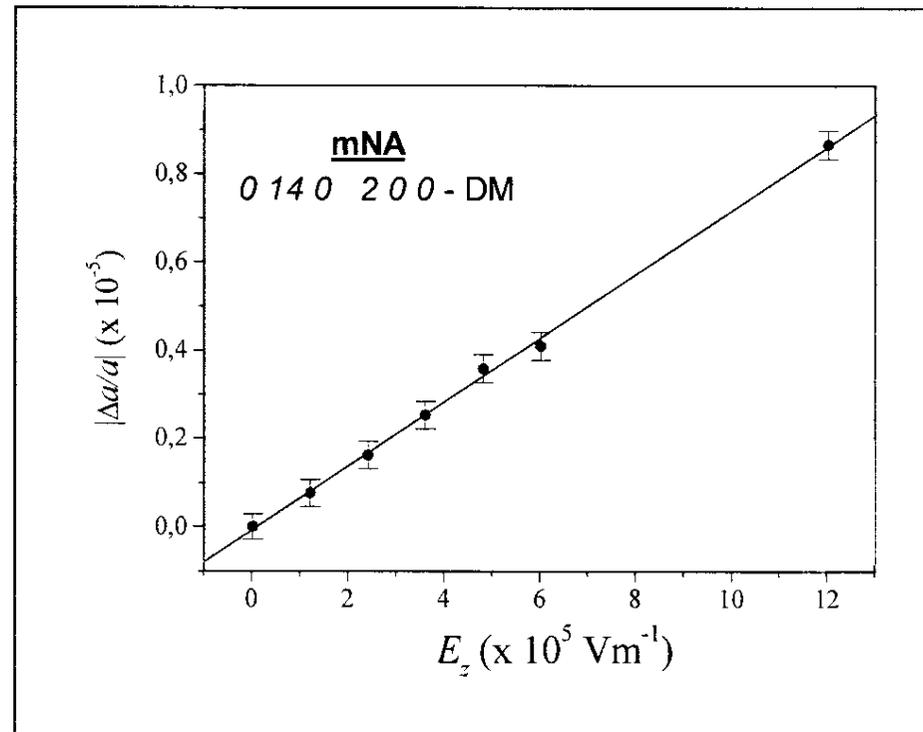




# Coeficiente piezoelétrico $d_{31}$ (mNA)

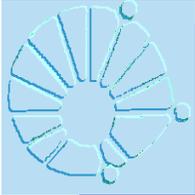


$$\frac{\Delta a}{a} = \operatorname{tg}(\phi^{200} + \phi_o) \Delta(\phi_o^{200} + \phi_o) - \frac{\lambda^2 k_o^2}{4b^2 - \lambda^2 k_o^2} \left( \frac{\Delta b}{b} \right) = \epsilon_{xx} = d_{31} E_z$$



$$|d_{31}| = 7,3(1) \times 10^{-11} \text{ CN}^{-1}$$

Avanci, Cardoso, Girdwood, Pugh, Sherwood & Roberts,  
Phys. Rev. Lett. (1998) **81**(24), 5426



# APLICAÇÕES DO MÉTODO

**mNA (C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>) (ortorrômbico)**  
**(meta-Nitroanilina)**

Phys. Rev. Lett. (1998) **81**(24), 5426

$$\begin{matrix} \vec{E}_x \\ \vec{E}_y \\ \vec{E}_z \end{matrix} \begin{pmatrix} [100] & [010] & [001] & [011] & [101] & [110] \\ 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ 7,3(1) & 16,5(7) & 10,3(8) & 0 & 0 & 0 \end{pmatrix} \times 10^{-11} \text{ NC}^{-1}$$

**MBANP (C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>O<sub>25</sub>) (monoclínico)**  
**[(-)-2-(α-metilbenzilamina)-5-nitropiridina]**

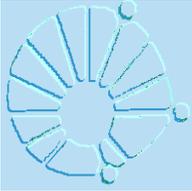
Phys. Rev. B (2000) **61**(10), 6507

$$\begin{matrix} \vec{E}_x \\ \vec{E}_y \\ \vec{E}_z \end{matrix} \begin{pmatrix} [100] & [010] & [001] & [011] & [101] & [110] \\ 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ 0,2(1) & 24,8(3) & 1,3(1) & 0 & 5,9(1) & 0 \\ 0 & 0 & 0 & d_{34} & 0 & d_{36} \end{pmatrix} \times 10^{-11} \text{ NC}^{-1}$$

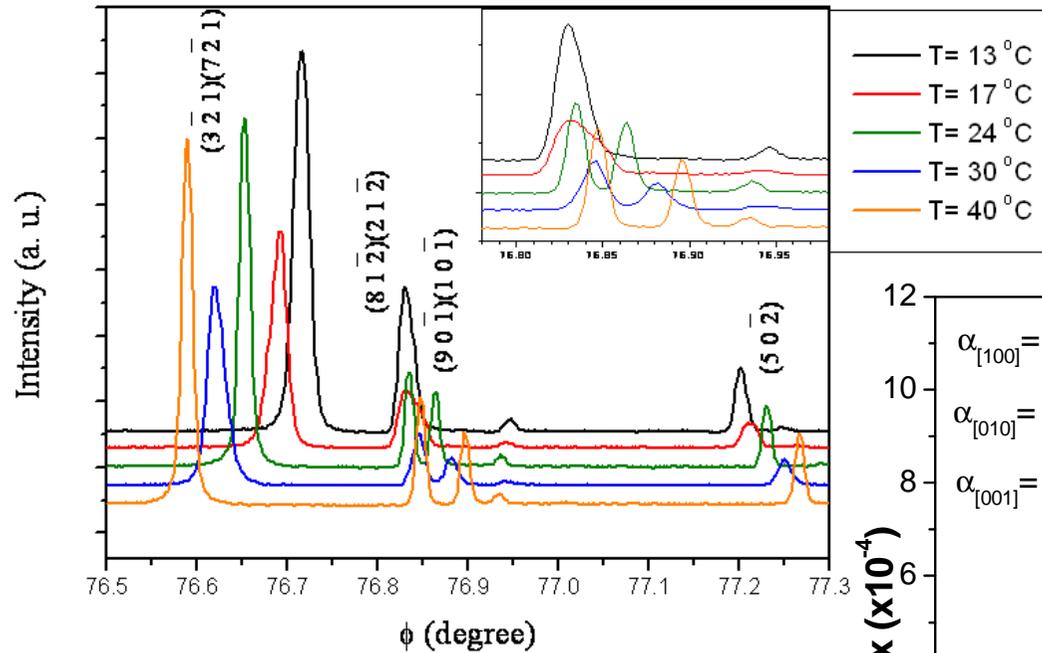
**Sal de Rochelle (monoclínico)**  
**(NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> · 4H<sub>2</sub>O)**

J. Phys: Cond. Matter (2003) **15**(46) 7835

$$\begin{matrix} \vec{E}_x \\ \vec{E}_y \\ \vec{E}_z \end{matrix} \begin{pmatrix} [100] & [010] & [001] & [011] & [101] & [110] \\ 0 & 0 & 0 & 23(3) & 0 & 0.162(6) \\ 70(6) & 220(90) & 210(90) & 0 & 3.7(8) & 0 \\ 0 & 0 & 0 & 78.2(3) & 0 & 1.23(7) \end{pmatrix} \times 10^{-11} \text{ N/C}$$

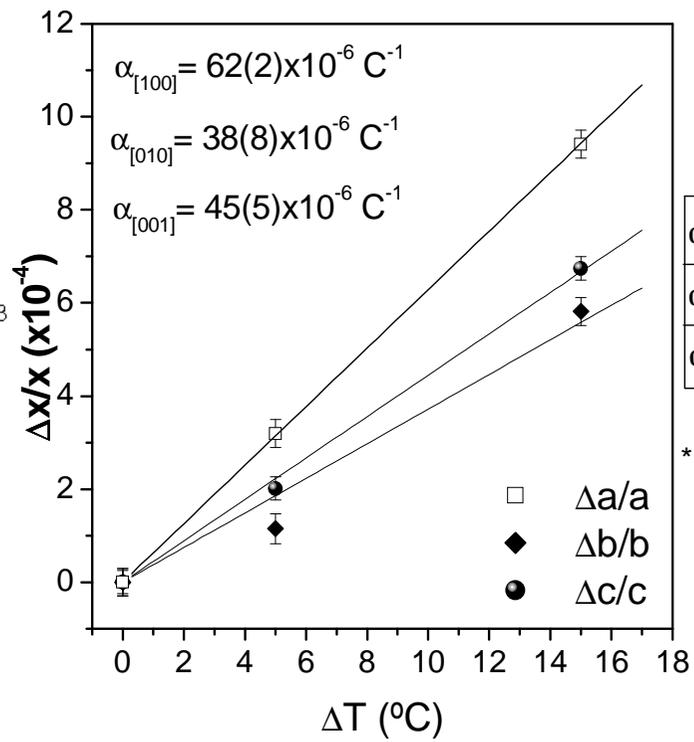


# DMRX: SONDA PARA TRANSIÇÃO DE FASE (TEMPERATURA) E DILATOMETRIA



**Sal de Rochelle**  
**NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> · 4H<sub>2</sub>O**

**Fase monoclinica**  
↓ **T ~ 24°C**  
**Fase ortorrômbica**

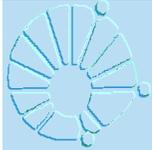


Reference\*

$\alpha_{[100]}$	$(58-62) \times 10^{-6} \text{ C}^{-1}$
$\alpha_{[010]}$	$(42-54) \times 10^{-6} \text{ C}^{-1}$
$\alpha_{[001]}$	$(43-54) \times 10^{-6} \text{ C}^{-1}$

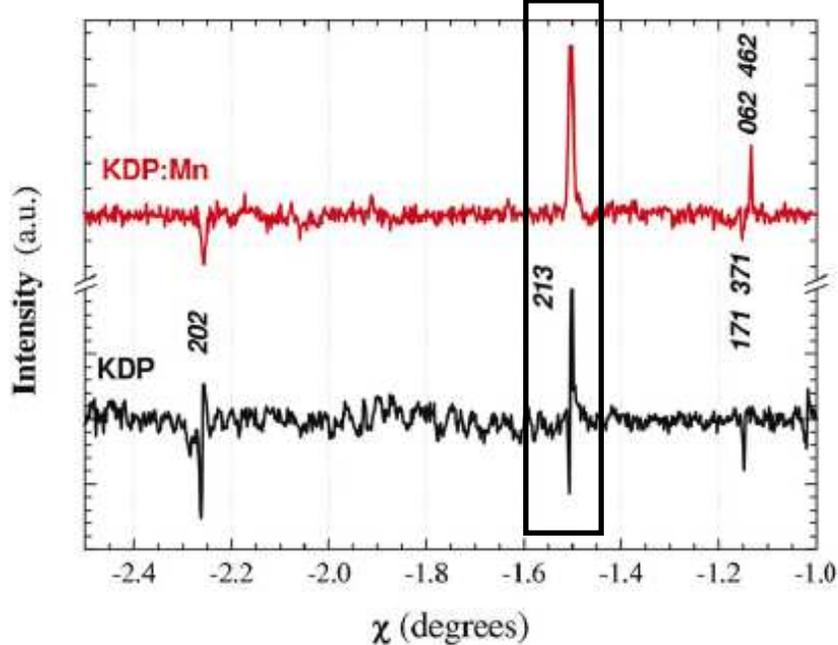
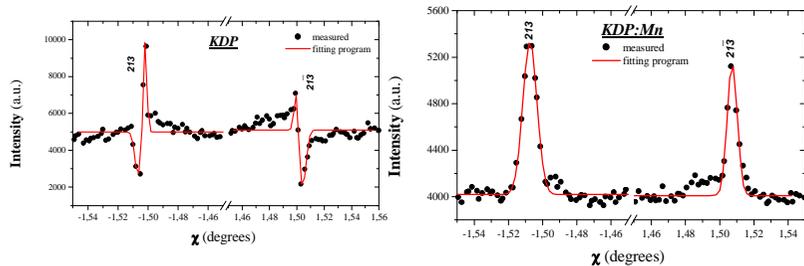
\* W. Bronowska, J. Appl. Cryst. 14, 203 (1981)

**Uma sonda para dilatometria!**



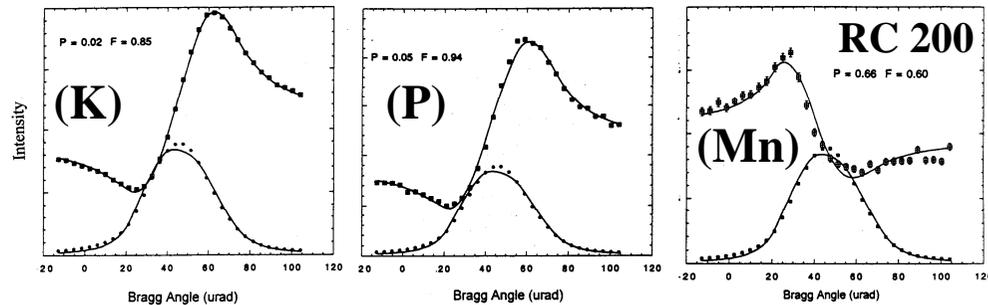
# Modelo de incorporação intersticial em KDP:Mn<sup>3+</sup> (colab. Kevin Roberts, University of Leeds)

## DMRX (Daresbury, UK)

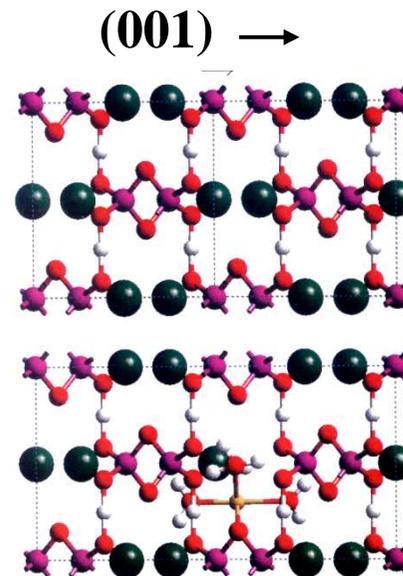


Avanci, Lai, Sasaki, Roberts & Cardoso,  
J. Appl. Cryst. (2003) **36**, 1230

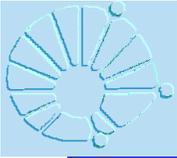
## Standing waves (NSLS, NY, USA)



## EXAFS + modelamento molecular



Lai, Roberts, Bedzyk, Lyman, Cardoso & Sasaki,  
Chemistry of Materials (2005) **17**(16), 4053

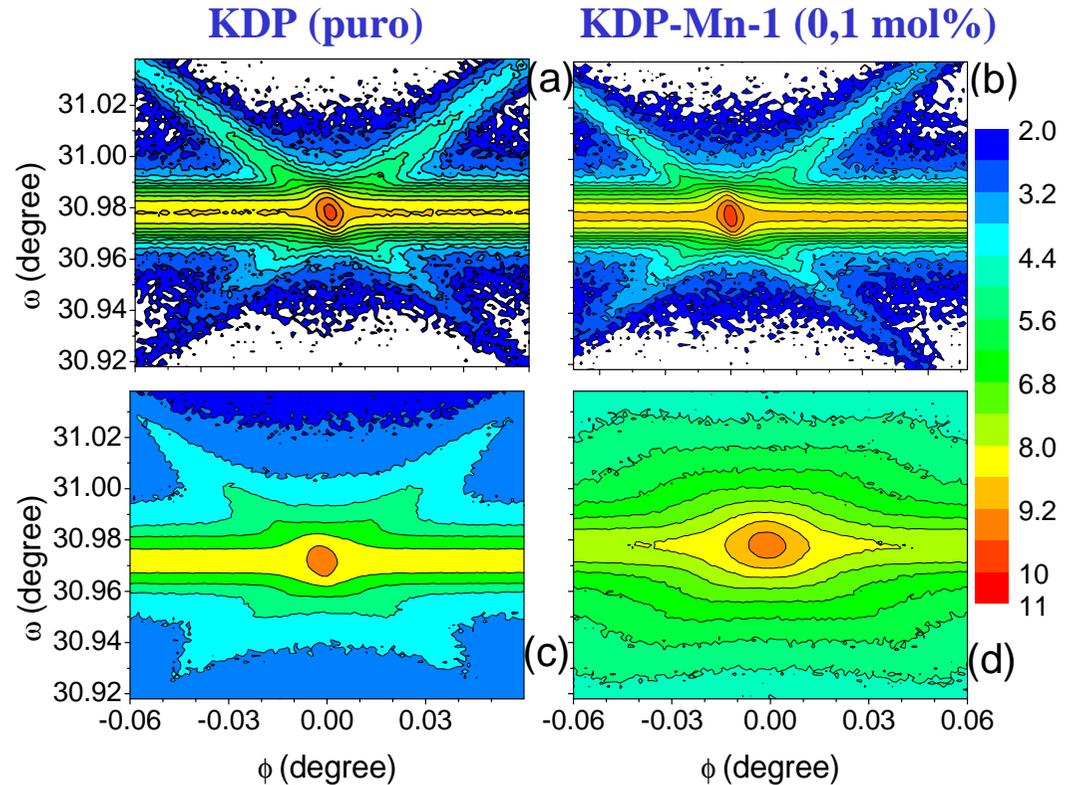
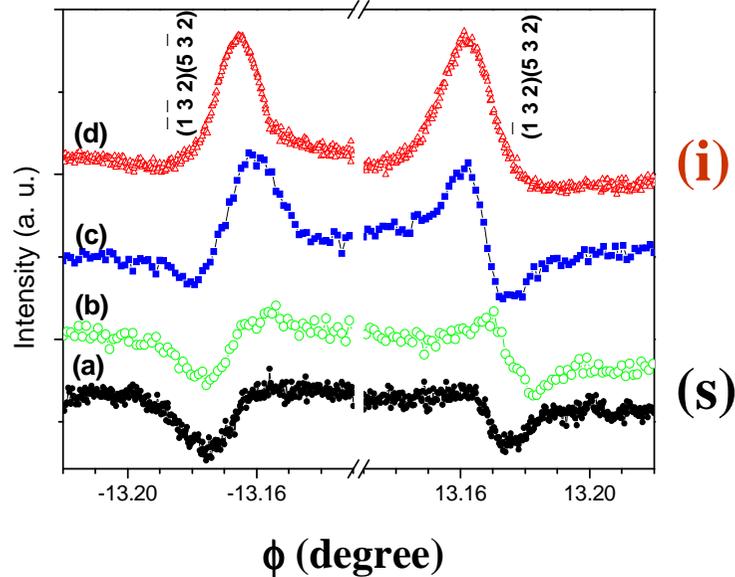


# Evidência experimental da influência da concentração de $Mn^{3+}$ em KDP ( $KH_2PO_4$ )

Colaboração:  
 Prof. Kevin Roberts, Univ. of Leeds  
 Dr. Cláudio Remédios, UFPA

BSD:(000)(400)(220)(2-20)

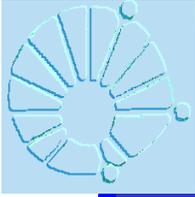
Pico secundário  
 (000)(400)( $\bar{1}32$ )(532)



KDP-Mn-3 (0,3 mol%)

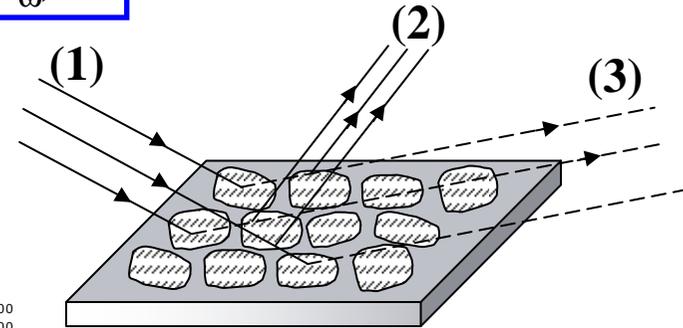
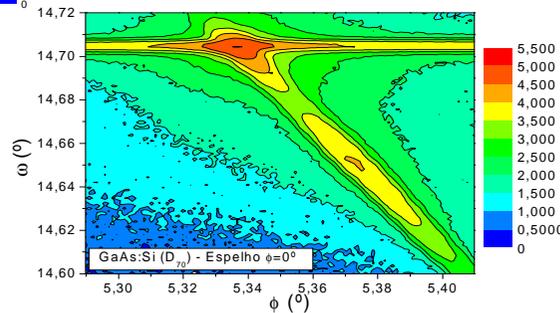
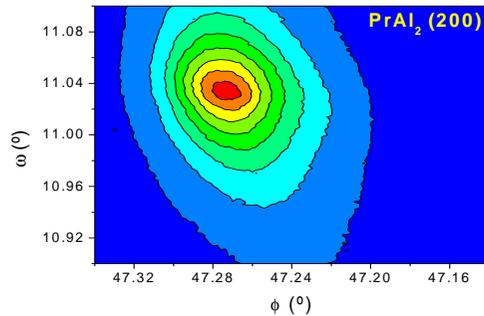
KDP-Mn-9 (0,9 mol%)

Remedios, dos Santos, Lai, Roberts, Moreira, Miranda, de Menezes, Rouxinol & Cardoso, *Crystal Growth & Design* (2010) **10**(3), 1053



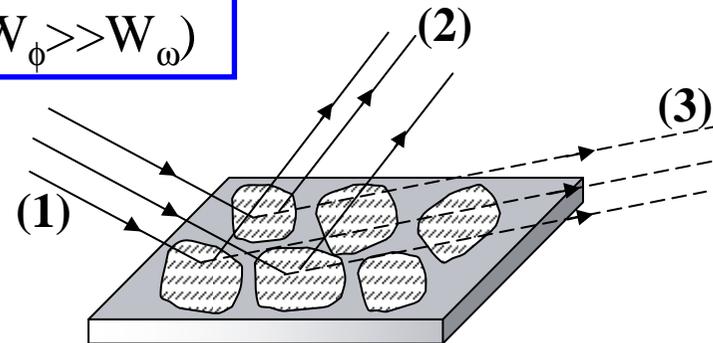
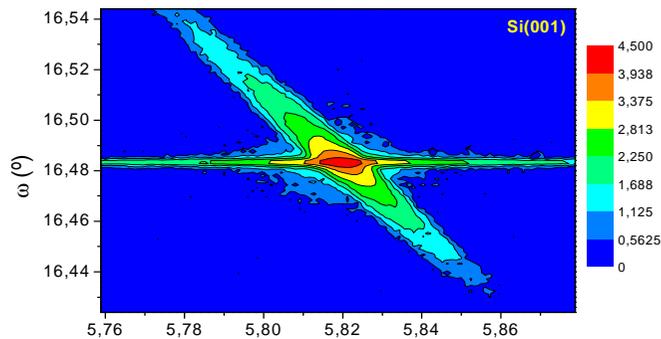
# Mapeamento da reflexão Bragg-Superfície (MBSD)

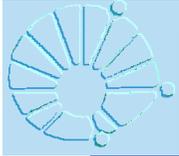
## Cristal mosaico - Teoria cinemática ( $W_\phi \ll W_\omega$ )



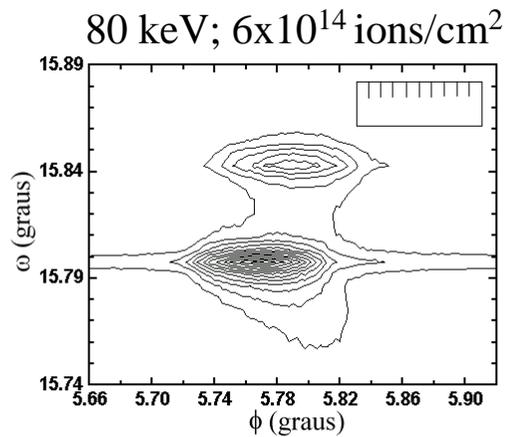
- (1) Feixe Incidente
- (2) Feixe Primário
- (3) Feixe Secundário

## Cristal quase-perfeito - Teoria dinâmica ( $W_\phi \gg W_\omega$ )





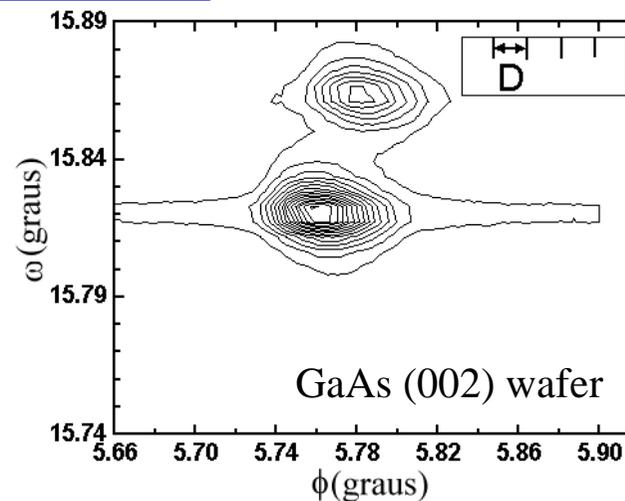
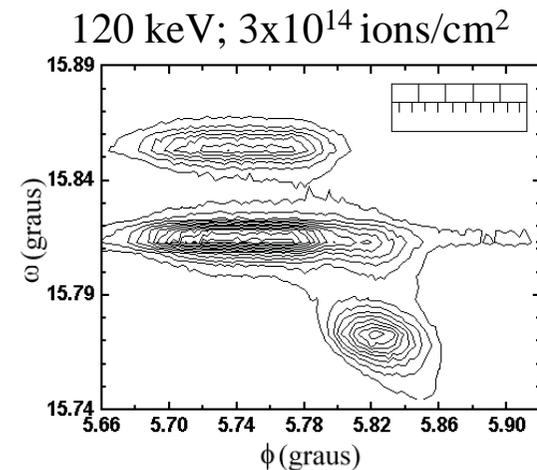
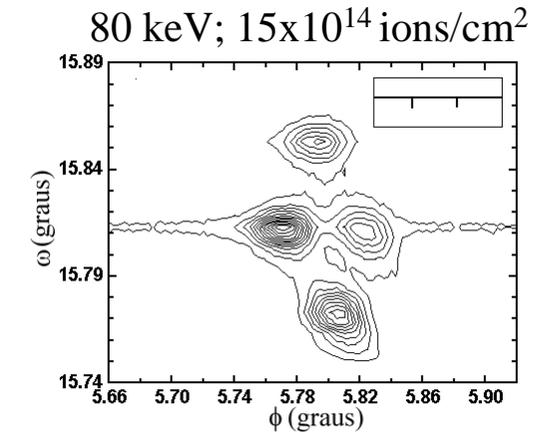
# MBSD: sonda na implantação de íons $\text{Se}^+$ em $\text{GaAs}(002)$ - Reflexão BSD: $(000)(002)(111)$ – LPCM ( $\text{CuK}\alpha_1/\alpha_2$ )



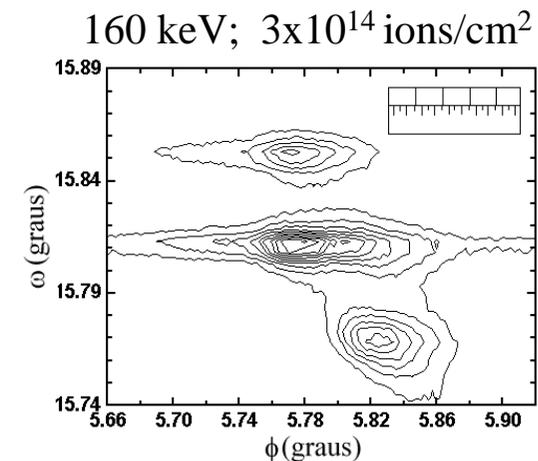
Dose  $\Rightarrow$

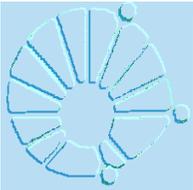
$$D_\phi \propto \left( \frac{1}{W_\phi} \right)$$

Comprimento de coerência  
no plano (implantação)



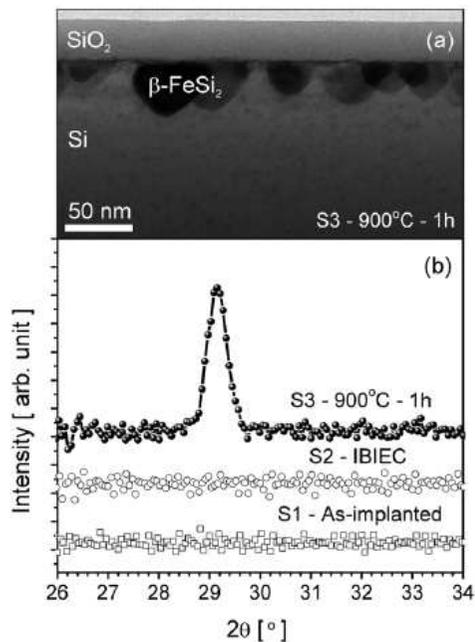
Energia  $\Rightarrow$



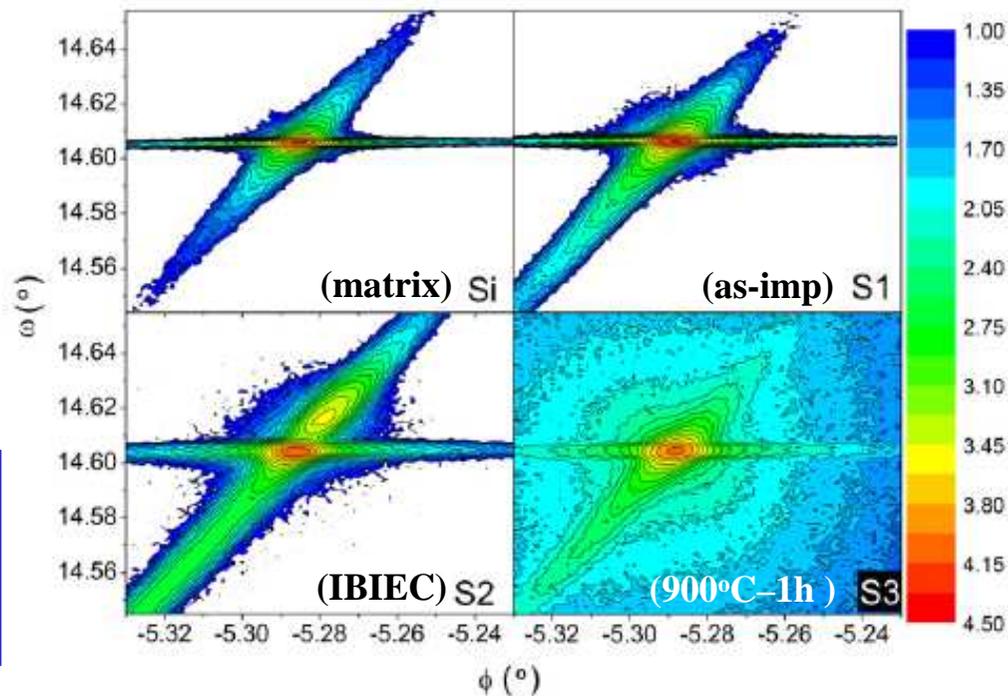
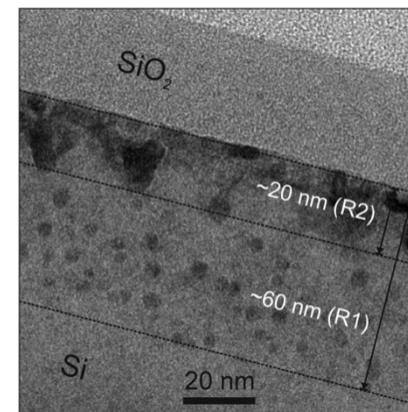
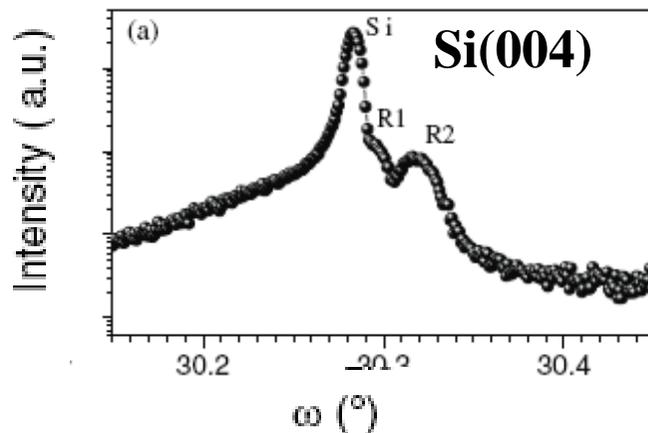


# MBSD: sonda na implantação de íons $\text{Fe}^+$ em $\text{Si}(001)$

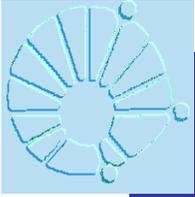
## Reflexão BSD: $(000)(002)(111)$ - LNLS



**(IBIEC - cristalização epitaxial induzida por feixe de íons)**



Colaboração IF, UFRGS (R. Lang e L. Amaral) dos Santos, Lang, de Menezes, Meneses, Amaral, Reboh & Cardoso, J. Phys. D: Appl. Physics. (2009) 42, 195401



**MUITO OBRIGADO  
PELA ATENÇÃO!**

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