Mini-Curso
Fabricação e Caracterização de Nanoestruturas

CBPF - Rio de Janeiro, 20-24 Março, 2006

Unidade 2: Técnicas de Microscopia Eletrônica de Transmissão

Aula 3 – HRTEM – EDS - EELS

Por:

Antônio J. Ramirez
Laboratório Nacional de Luz Síncrotron

2006/3-1

Microscopia Eletrônica de Transmissão Antônio J. Ramirez

Conteúdo

- Introdução
  - Definições
- Ótica Eletrônica
  - Fontes de elétrons
  - Lentes magnéticas
  - Aberrações
- Interação Elétron Matéria
  - Sinais
  - Dano na amostra
- Microscopia Eletrônica de Transmissão (TEM)
  - Configuração do equipamento
  - Microscopia de transmissão por varredura
  - Difração de elétrons
  - Tipos de imagem
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  - Aplicações
  - Preparação de Amostras
  - Microscopia de alta resolução – contraste de fase
- Espectroscopia de Raios –X Dispersiva em Energia (EDS)
- Espectroscopia de Elétrons (EELS)

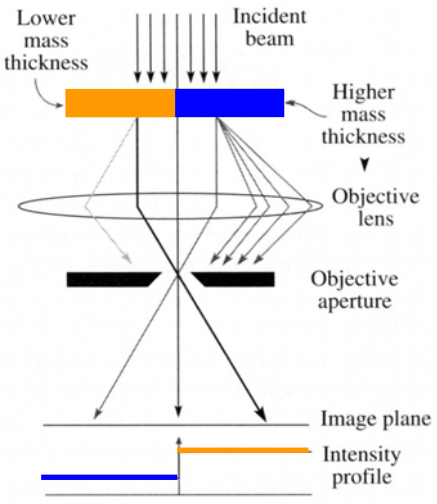
2006/3-2

Contraste

- Contraste de massa – espessura
- Contraste de difração
- Contraste Z (grandes angulos de espalhamento)
- Fase (alta resolução)

2006/3-3

Contraste de Massa - Espessura



Espalhamento Elástico
(Predominantemente Incoerente)

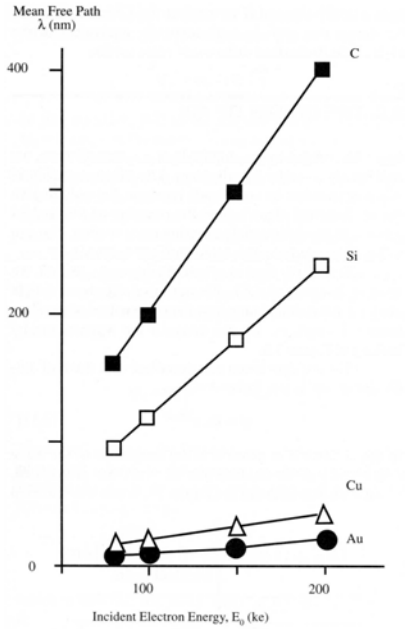
Importante para:

•Amorfos

•Polímeros

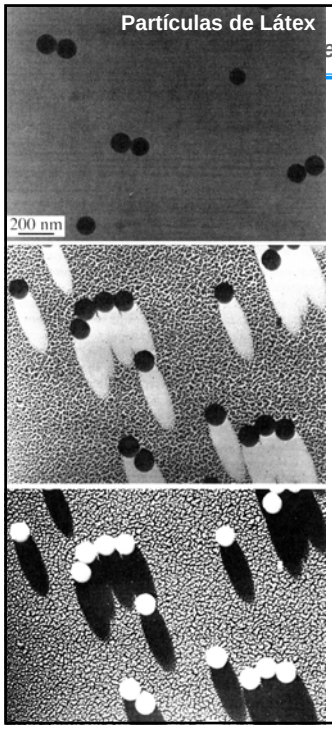
•Amostras Biológicas

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Caminho Livre Médio - TEM

2006/3-9

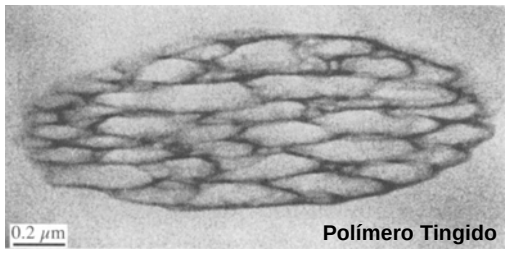


Contraste de Massa – Espessura TEM

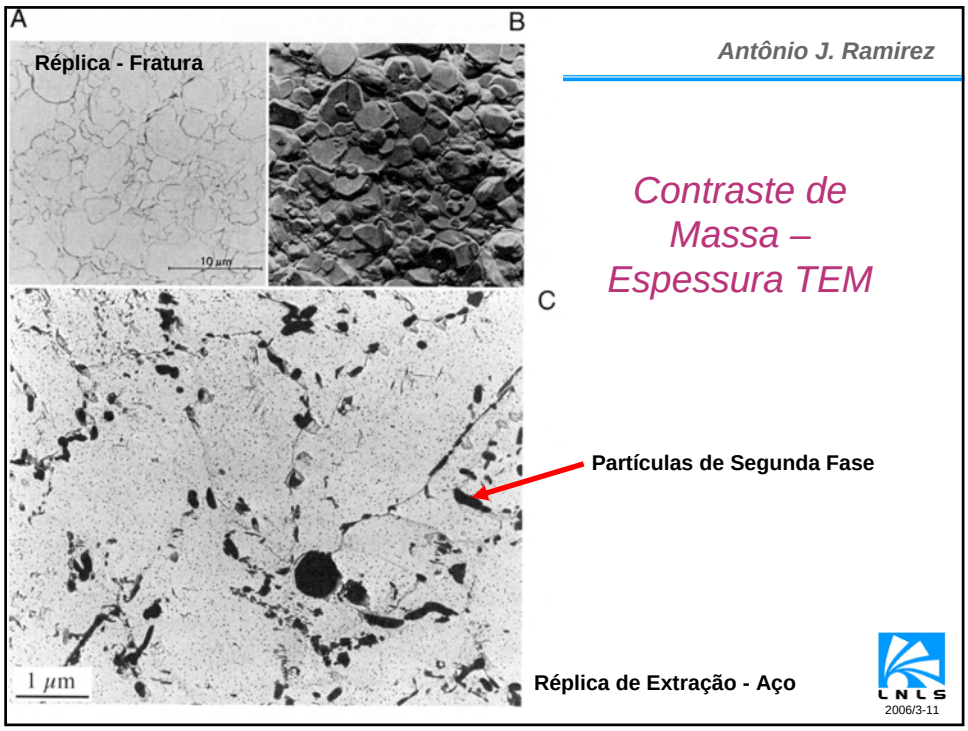
Sombreamento

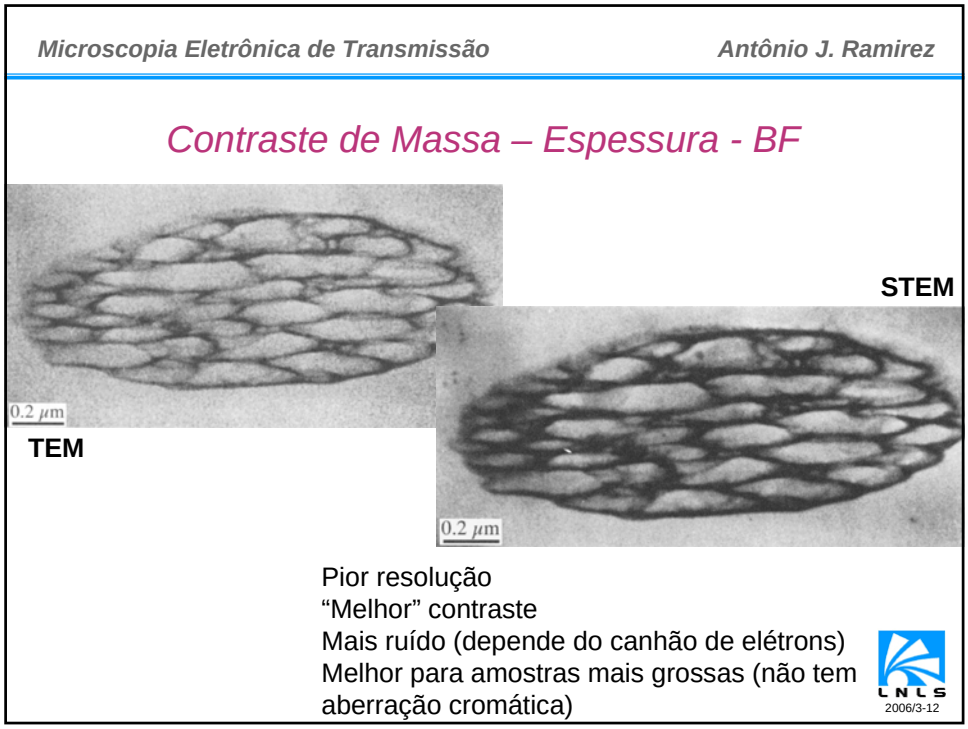
Tingimento

Melhorar:
< abertura
< kV



2006/3-10


A
B
Réplica - Fratura
10 μm
C
1 μm
Antônio J. Ramirez
Contraste de Massa – Espessura TEM
Partículas de Segunda Fase
Réplica de Extração - Aço
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2006/3-11

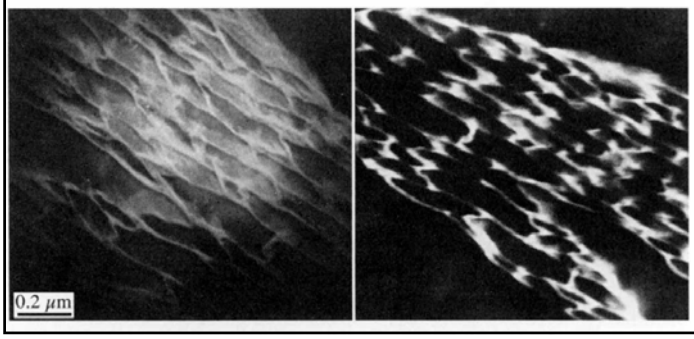

Microscopia Eletrônica de Transmissão
Antônio J. Ramirez
Contraste de Massa – Espessura - BF
STEM
0.2 μm
TEM
0.2 μm
Pior resolução
"Melhor" contraste
Mais ruído (depende do canhão de elétrons)
Melhor para amostras mais grossas (não tem aberração cromática)
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Contraste de Massa – Espessura – DF (ADF)

STEM ADF:

Coleta mais elétrons
< ruido
< resolução

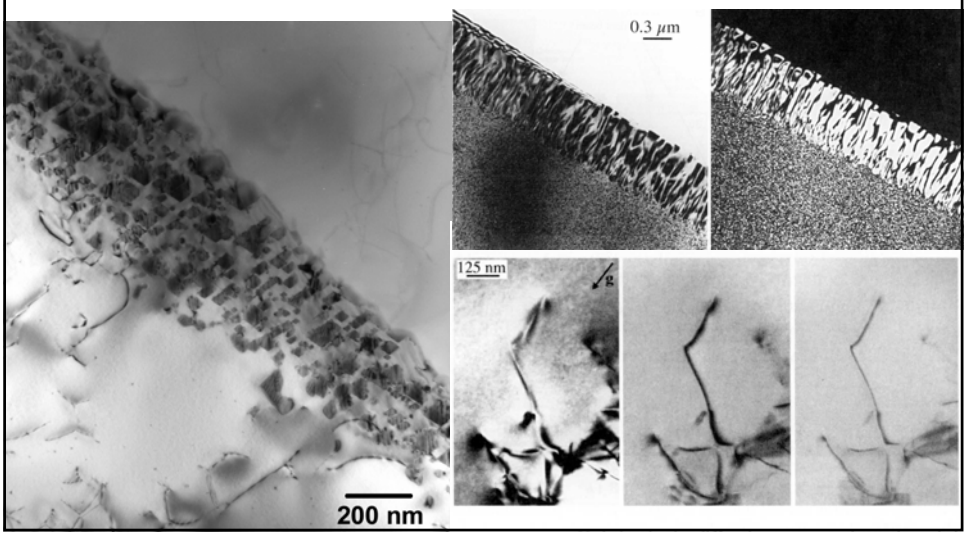
A **TEM** **STEM** B



2006/3-13

Contraste de Difração

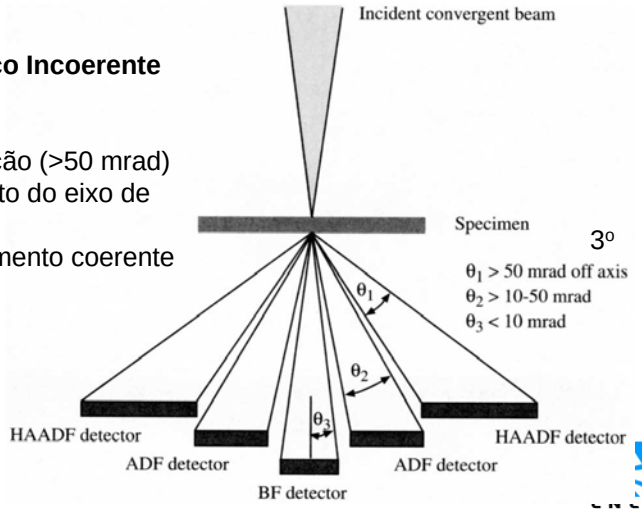
Limitado em STEM



Contraste Z

Espalhamento Elástico Incoerente

>> ângulos
Não contraste de difração (>50 mrad)
Não em two beam (perto do eixo de zona)
Não esfriar (> espalhamento coerente HOLZ)

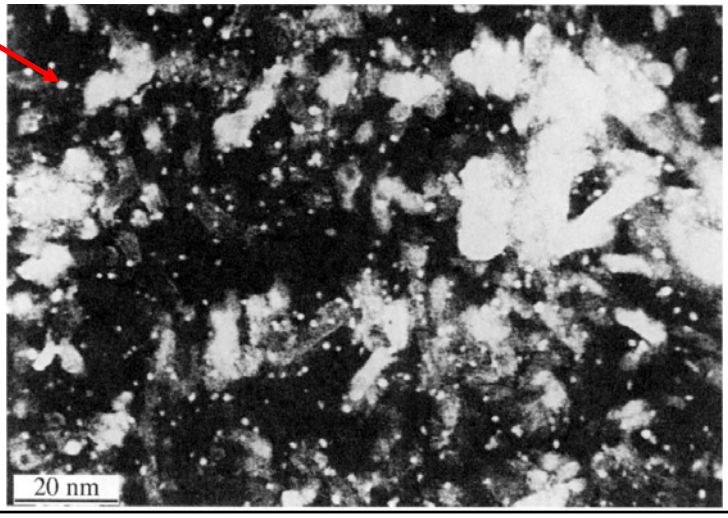


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Contraste Z (low Angle)

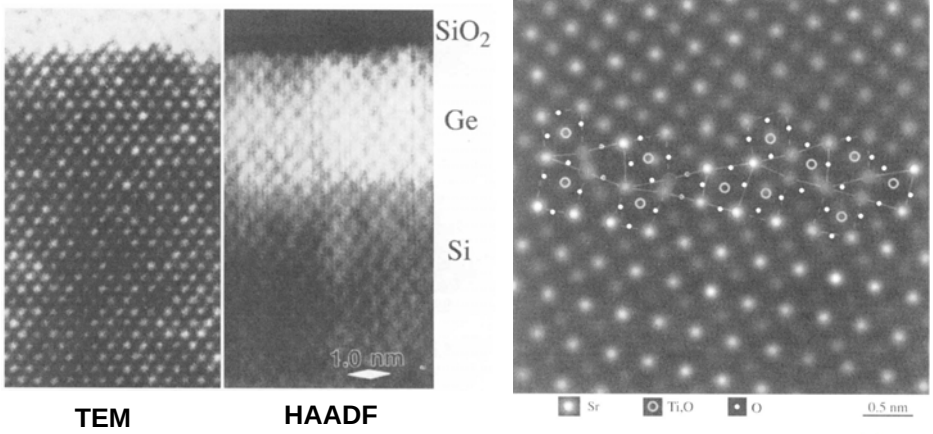
Matriz Al_2O_3

Pt



2006/3-17

Contraste Z (High Angle)



TEM HAADF

$SrTiO_3$

2006/3-18

Contraste de Fase

Diferenças de fase entre os feixes espalhados dentro da amostra

Interferência entre estes feixes (por exemplo 2 feixes)

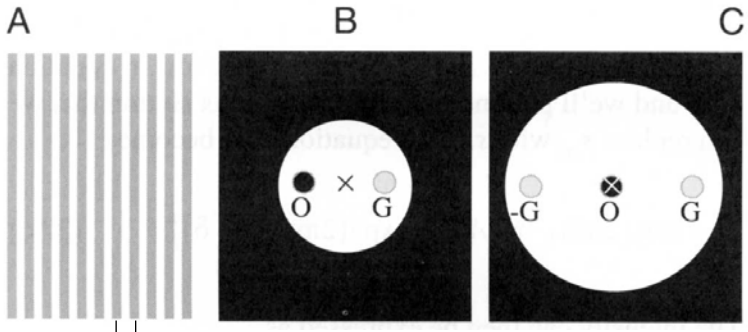
$$\psi = \varphi_0(z) \exp 2\pi i(\mathbf{k}_I \cdot \mathbf{r}) + \varphi_g(z) \exp(2\pi i \mathbf{k}_D \cdot \mathbf{r})$$

$$\mathbf{k}_D = \mathbf{k}_I + \mathbf{g} + \mathbf{s}_g = \mathbf{k}_I + \mathbf{g}'$$

$$I = A^2 + B^2 - 2AB \sin(2\pi \mathbf{g}' x - \pi s t)$$

2006/3-19

Contraste de Fase



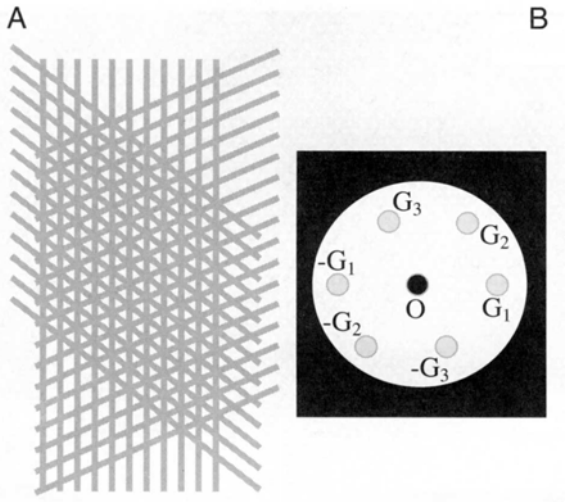
Como um dos faixes é O: $|\Delta g|^{-1} = d$

$|\Delta g|^{-1}$

$$I = A^2 + B^2 - 2AB \sin\left(2\pi \mathbf{g}' x - \pi s t\right)$$

2006/3-20

Contraste de Fase



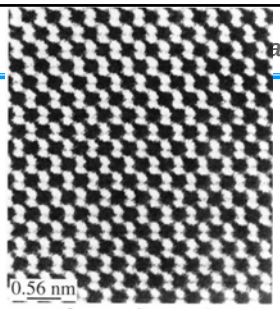
Si

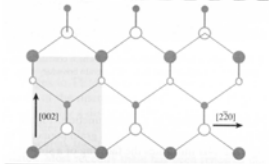
[111]

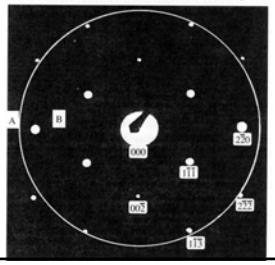
2006/3-21

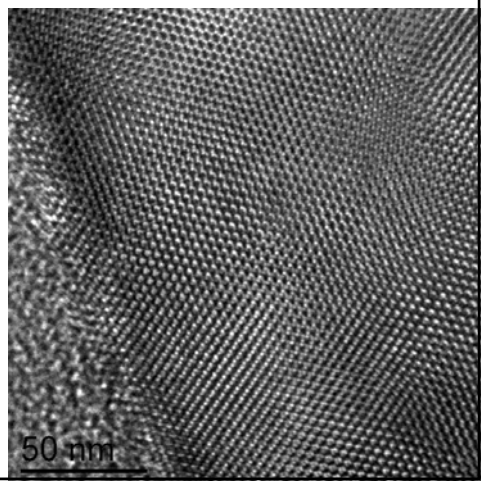
Contraste de Fase - HRTEM

Si Dumbbells









Contraste de Fase - HRTEM

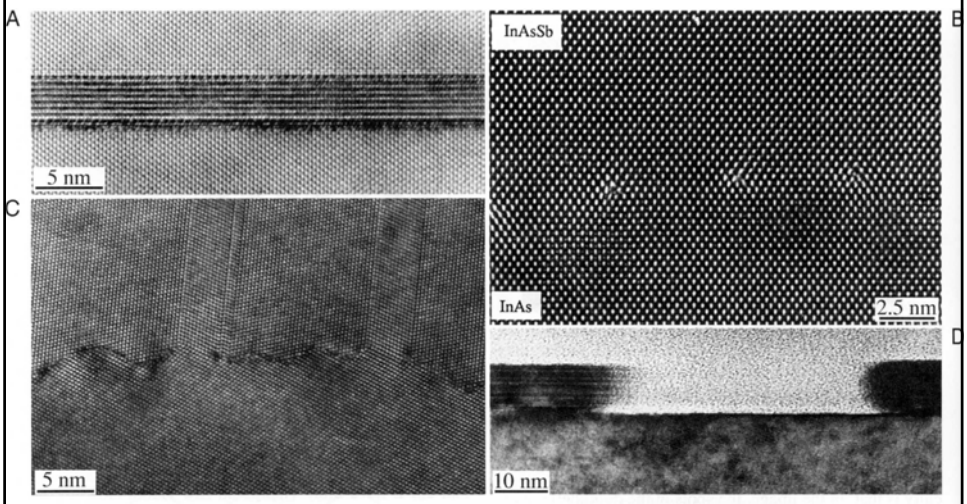
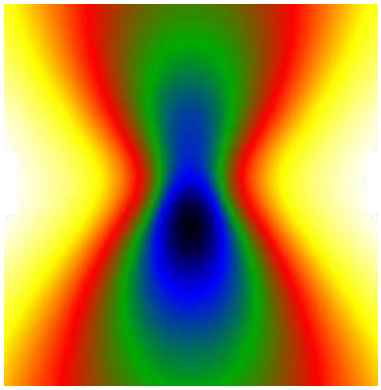


Figure 27.4. Illustrations of lattice images which contain easily interpreted information. (A) The spinel/olivine interface; (B) dislocations at a heterojunction between InAsSb and InAs; (C) a grain boundary in Ge faceting on an atomic scale; (D) a profile view of a faceted surface.

Microscopia Eletrônica de Transmissão Antônio J. Ramirez

Geometric Phase Analysis



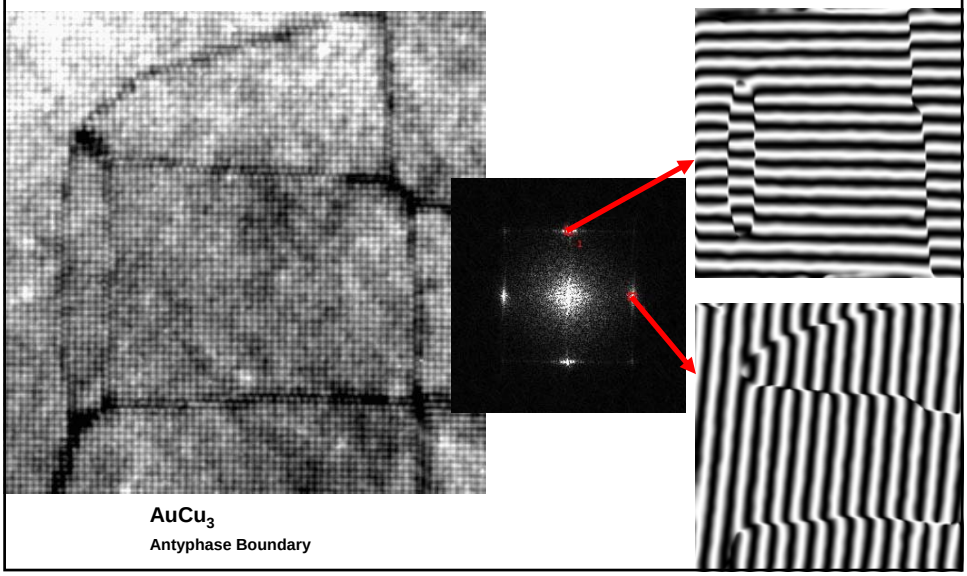


Dislocation Analysis

2006/3-24

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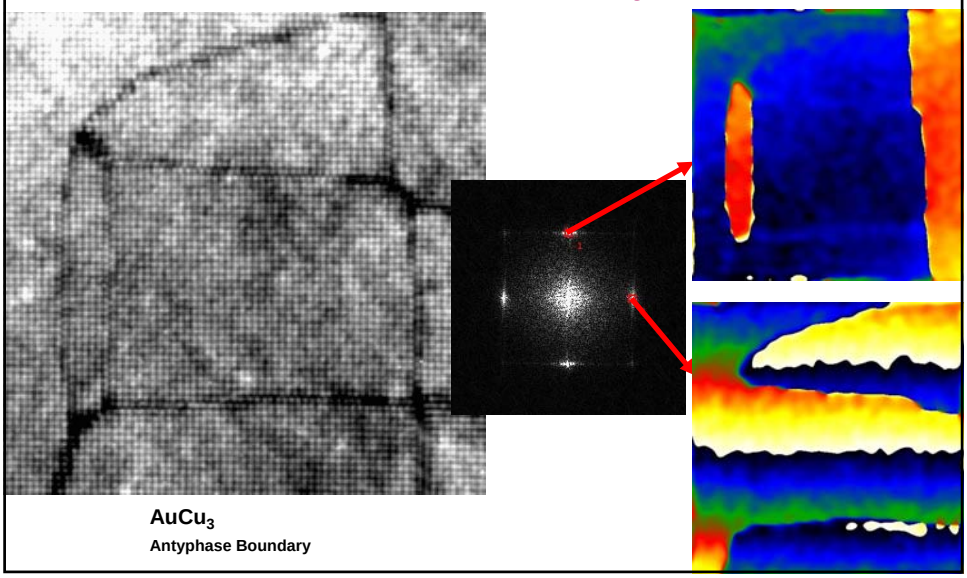
Geometric Phase Analysis



$AuCu_3$

Antyphase Boundary

Geometric Phase Analysis

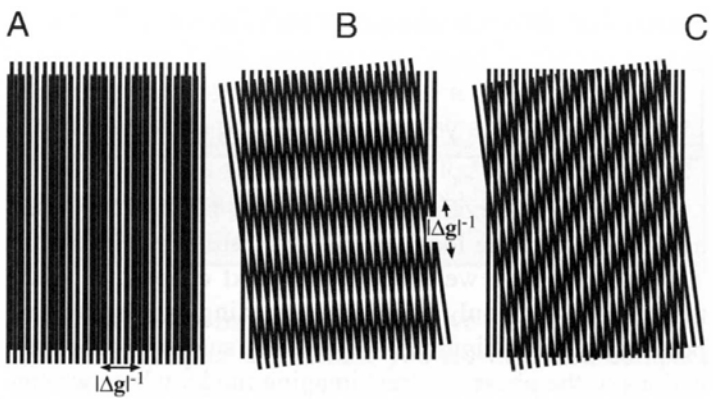


$AuCu_3$

Antyphase Boundary

Microscopia Eletrônica de Transmissão Antônio J. Ramirez

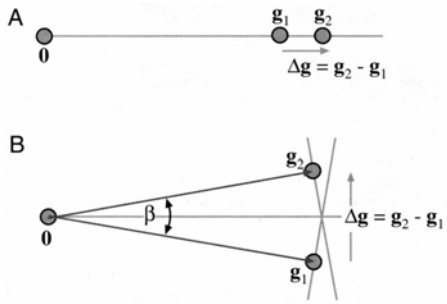
Contraste de Fase – Franjas de Moiré



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Contraste de Fase – Franjas de Moiré



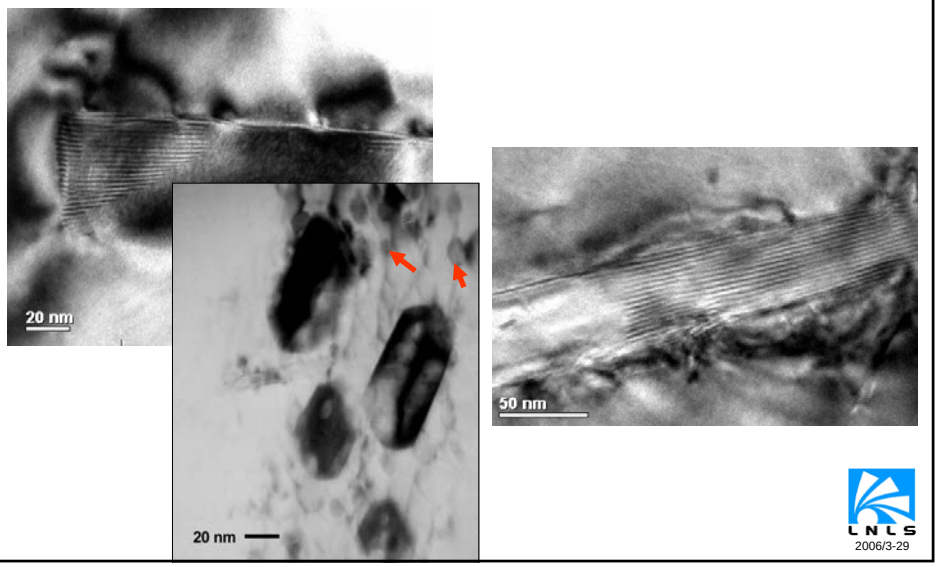
$$d_{tm} = \frac{1}{g_{tm}} = \frac{1}{g_2 - g_1} = \frac{\frac{1}{g_2} \cdot \frac{1}{g_1}}{\frac{1}{g_1} - \frac{1}{g_2}}$$

$$= \frac{d_2 d_1}{d_1 - d_2} = \frac{d_1}{1 - \frac{d_2}{d_1}}$$

$$d_{rm} = \frac{1}{g_{rm}} = \frac{1}{2g \sin \beta/2} = \frac{d}{2\sin \beta/2}$$

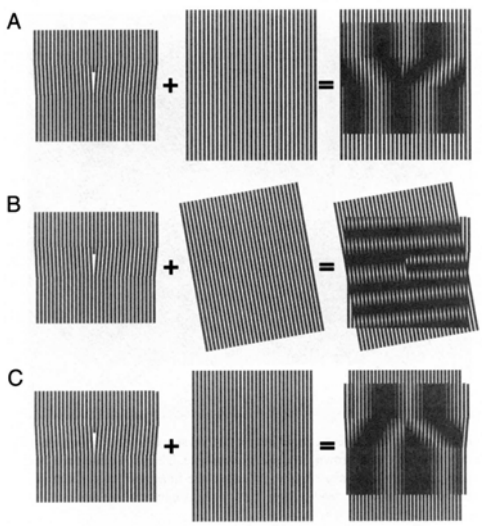
2006/3-28

Contraste de Fase – Franjas de Moiré



2006/3-29

Contraste de Fase – Franjas de Moiré



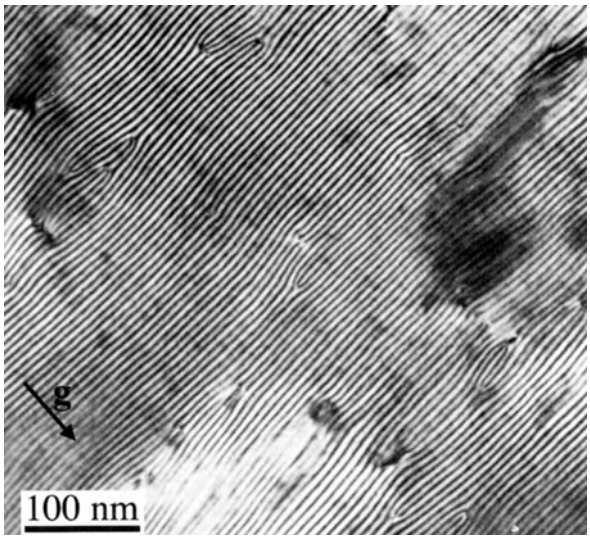
Mesmo espaçamento

Mesmo espaçamento

Diferente espaçamento

2006/3-30

Contraste de Fase – Franjas de Moiré



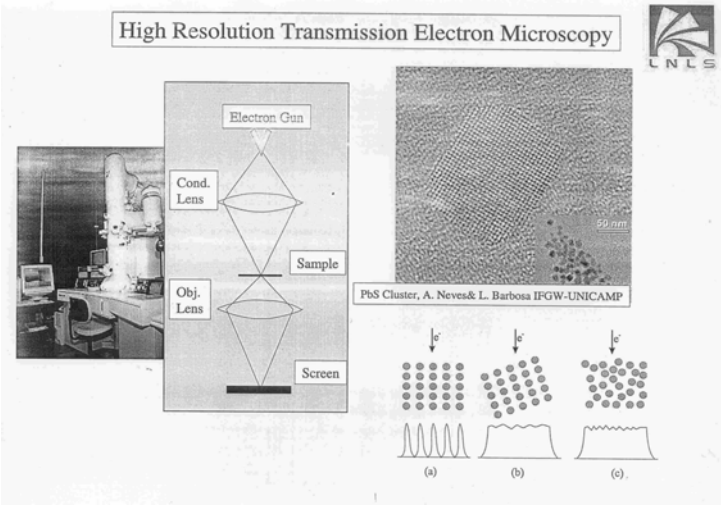
CoCa

Crescido em

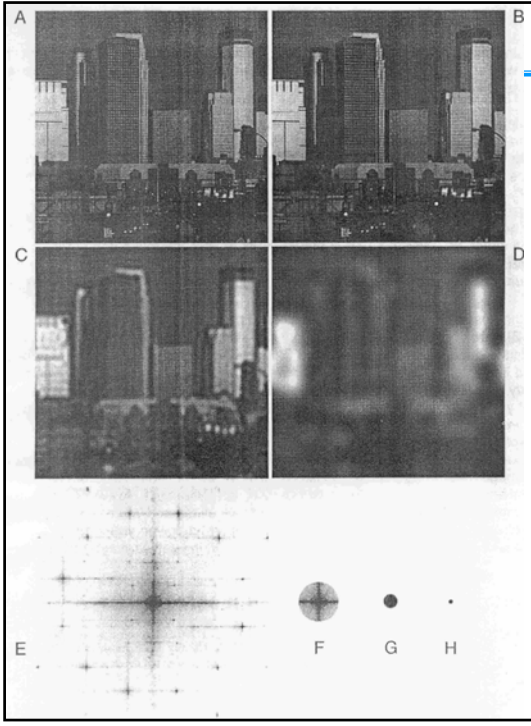
GaAs

2006/3-31

HRTEM



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HRTEM

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Optic System

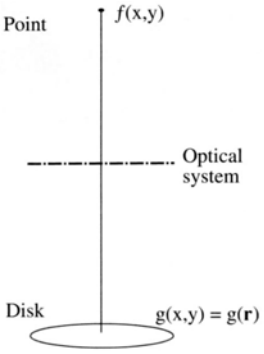
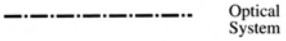
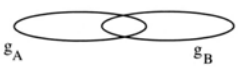


Figure 28.1. An optical system transforms a point in the specimen (described by $f(x,y)$) into a disk in the image described by $g(x,y)$. The intensity in the image at point (x,y) can be described by the function $g(x,y)$ or $g(\mathbf{r})$. It has a unique value for each value of (x,y) so we say that $g(\mathbf{r})$ is a representation of the image.

Optic System







$$g(\mathbf{r}) = \int f(\mathbf{r}')\, h(\mathbf{r}-\mathbf{r}')\, dr'$$

$$= f(\mathbf{r}) \otimes h(\mathbf{r}-\mathbf{r}')$$

h(r) = Describes how the point spreds into a disk (point-spread function)

G(u) = F(u) H(u)

- G(u) = F g(r)
- F(u) = F f(r)
- H(u) = F h(r)

- H(u): Contrast Transfer Fuction

Optic System

$$G(\mathbf{u}) = H(\mathbf{u})\,F(\mathbf{u})$$

The factors contributing to $H(\mathbf{u})$ include:

Apertures	→ The aperture function	$A(\mathbf{u})$
Attenuation of the wave	→ The envelope function	$E(\mathbf{u})$
Aberration of the lens	→ The aberration function	$B(\mathbf{u})$

We write $H(\mathbf{u})$ as the product of these three terms

$$H(\mathbf{u}) = A(\mathbf{u})\,E(\mathbf{u})\,B(\mathbf{u})$$

$$B(\mathbf{u}) = \exp\left(i\chi(\mathbf{u})\right)$$

$$\chi(\mathbf{u}) = \pi\,\Delta f\,\lambda\,u^2 + \frac{1}{2}\pi\,C_s\,\lambda^3\,u^4$$

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Sample

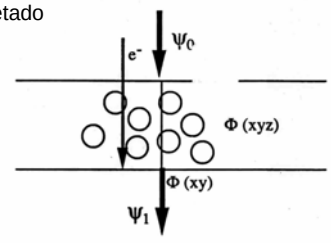
Phase Object Approximation

Scattering angles ≈ 10^{-2} mrad, and thickness ~ 100 Å
very little lateral displacement of the electron beam.

First approximation:
electron beam suffers a phase change that depend only on the potential distribution along a straight path through the sample.

Potencial Projetado

$$\Phi(xy) = \int \Phi(xyz)\,dz$$



Transmission function including phase change and absorption

$$f(xy) = \exp[-i\sigma\,\Phi(xy) - \mu(xy)]$$

$$\psi_1 = \psi_0\,f(xy)$$

Remark: non linear nature of electron scattering

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Weak Phase Object

Weak Phase Object Approximation (WPOA)

$f(xy) = \exp[-i\sigma\Phi(xy)]$ $\qquad \sigma = 2\pi m e \lambda / h^2$

$\cong 1 - i\sigma\Phi(xy)$

Objective Lens Transfer Function

$$T(\mathbf{u}) = A(\mathbf{u})\,E(\mathbf{u})\,2\sin\chi(\mathbf{u})$$

For WPOA, T(u) is called Contrast Transfer Function

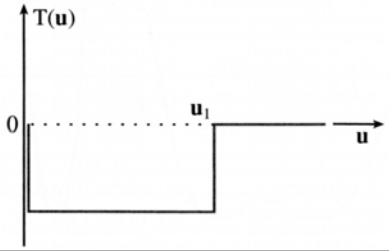
Contrast Transfer Function

$$T(\mathbf{u}) = A(\mathbf{u})\,E(\mathbf{u})\,2\sin\chi(\mathbf{u})$$

- Máximos ($\chi(u) = \pm \pi/2$) e Mínimos ($\chi(u) = \pm \pi$)
- T(u) < 0 (Contraste de fase positivo – âtomos brancos)
- T(u) > 0 (Contraste de fase negativo – âtomos pretos)

Ideal CTF

T(u)=0 em u_1



Contrast Transfer Function

$$\chi = \pi \Delta f \lambda u^2 + \frac{1}{2}\pi C_s \lambda^3 u^4$$

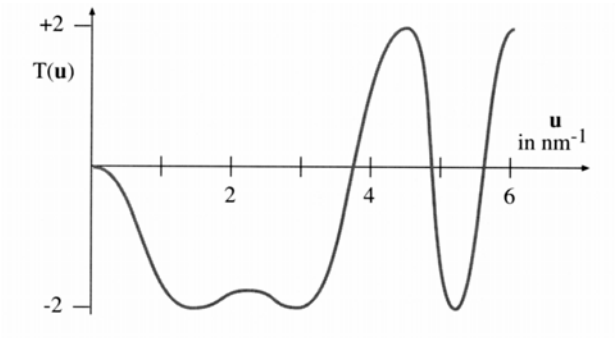
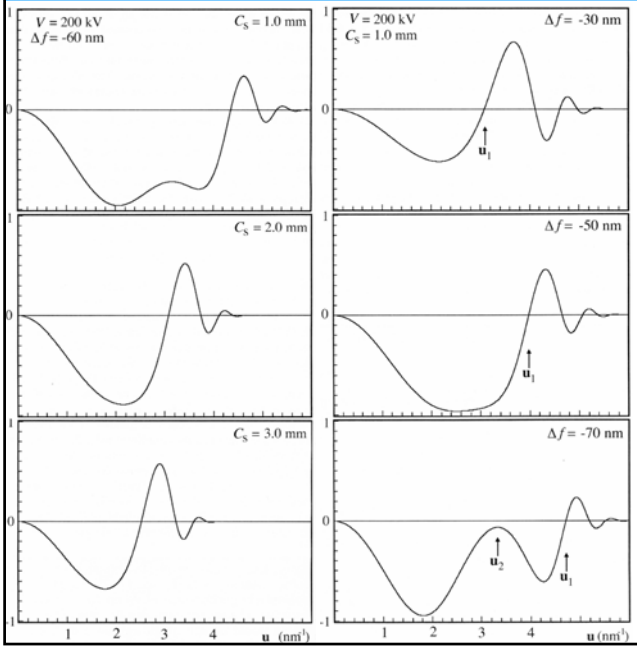


Figure 28.4. A plot of $T(\mathbf{u})$ versus $\mathbf{u}$ (C_s = 1 mm, E_0 = 200 keV, Δf = −58 nm).

2006/3-42



Contrast Transfer Function

Sen χ

2006/3-43

Scherzer Defocus

$$\Delta f_{\mathrm{Sch}} = -\,1.2\,(C_s\lambda)^{\frac{1}{2}}$$

$$u_{\mathrm{Sch}} = 1.51 C_s^{-\frac{1}{4}}\,\lambda^{-\frac{3}{4}}$$

$$r_{\mathrm{Sch}} = \frac{1}{1.51}\,C_s^{\frac{1}{4}}\,\lambda^{\frac{3}{4}} = 0.66 C_s^{\frac{1}{4}}\,\lambda^{\frac{3}{4}}$$

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Evelope Function - Information Limit

$$T_{\mathrm{eff}}(\mathbf{u}) = T(\mathbf{u})\,E_c\,E_a$$

Ec: Chromatic Aberration Envelope

Ea: Source Spatial Coherence Envelope

Virtual Aperture

Minimum contrast

$$\sin\chi(\mathbf{u}) \simeq 0.3$$

$$\Delta f_{\mathrm{MC}} = -\,0.44\,(C_s\lambda)^{\frac{1}{2}}$$

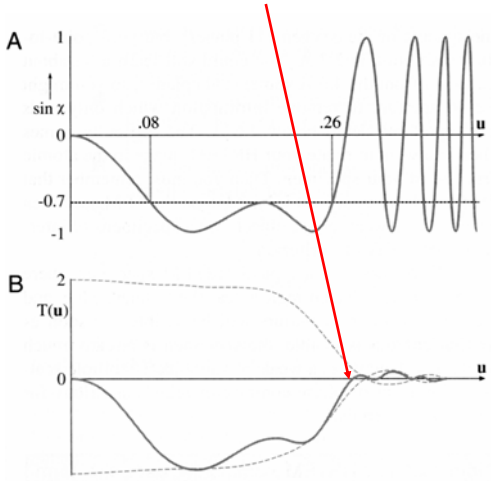
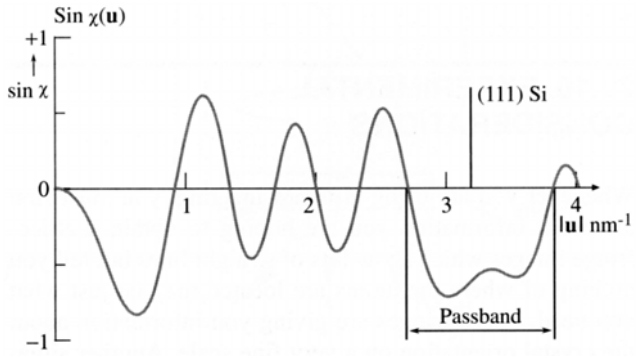


Figure 28.7. (A) $\sin\chi(\mathbf{u})$ versus $\mathbf{u}$ without damping of the higher spatial frequencies. (B) $T(\mathbf{u})$ versus $\mathbf{u}$ modified by the damping envelope (dashed line); $\Delta f = -100$ nm, $C_s = 2.2$ mm.

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Passbands



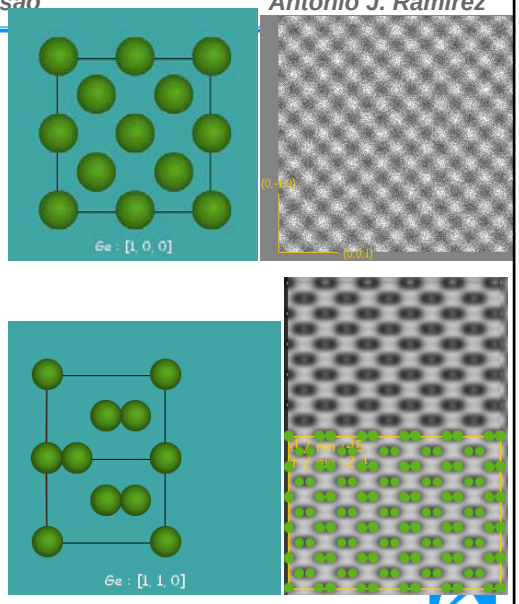
$$\Delta f_p^n = \left\{ \left(\frac{8n+3}{2} \right) (C_s \lambda) \right\}^{\frac{1}{2}}$$

n=0 Scherzer

2006/3-46

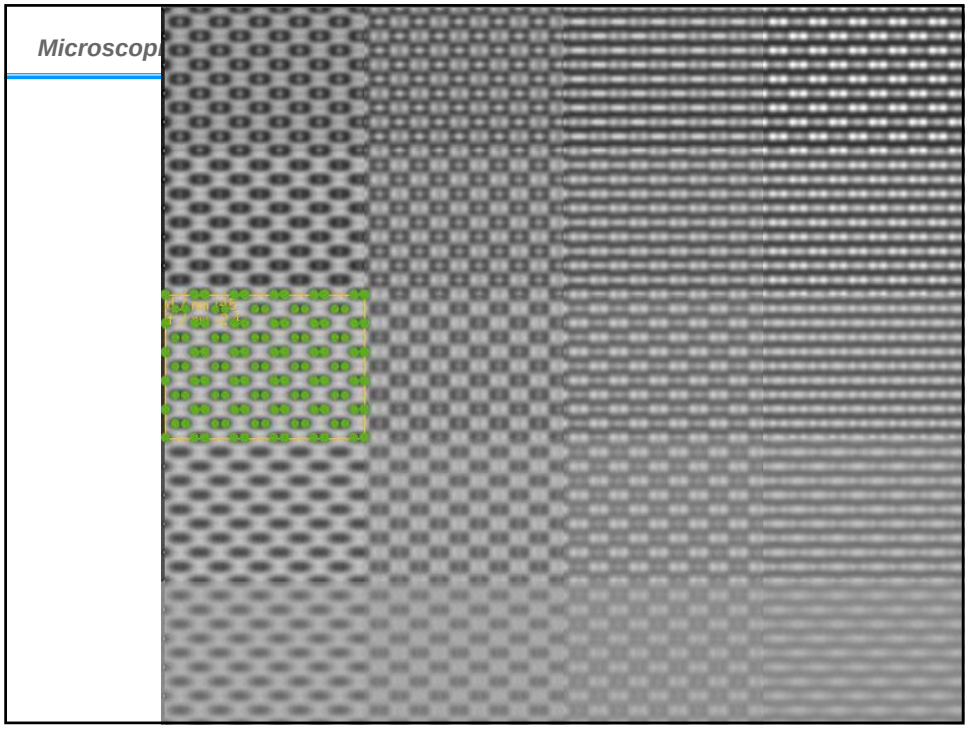
Ge

Ge

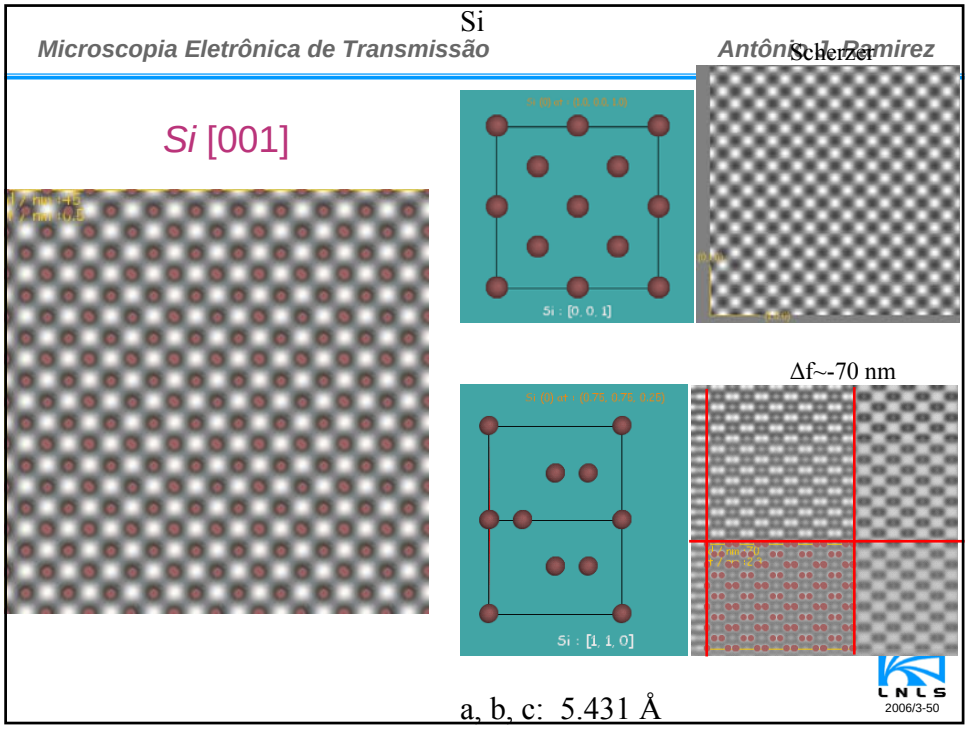


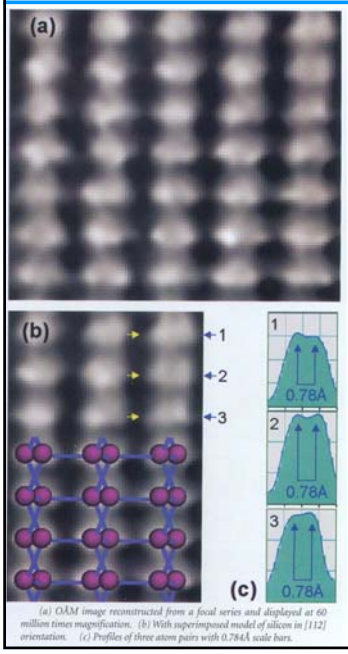
a, b, c: 5.689 Å

2006/3-48


Microscopi

Si


Microscopia Eletrônica de Transmissão
Antônio J. Ramirez
Scherzer
Si [001]
Si : [0, 0, 1]
Δf~-70 nm
Si : [1, 1, 0]
a, b, c: 5.431 Å
LNLS
2006/3-50

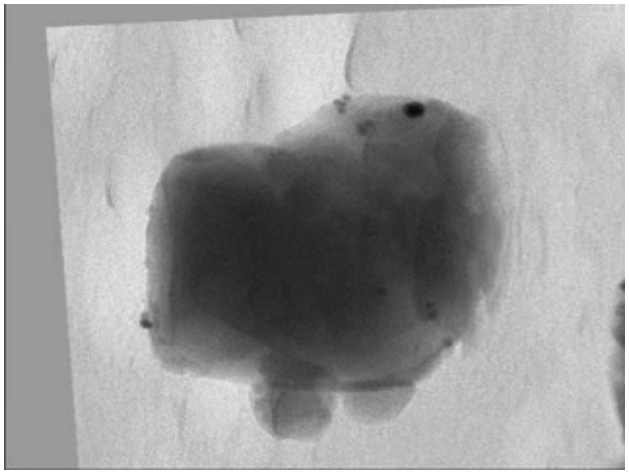


Alta Resolução



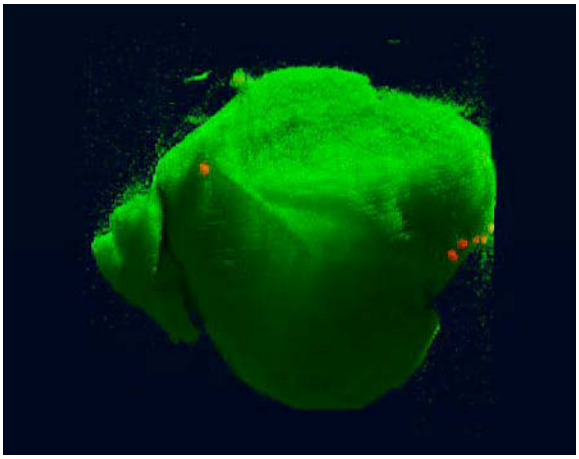
2006/3-54

Tomografia



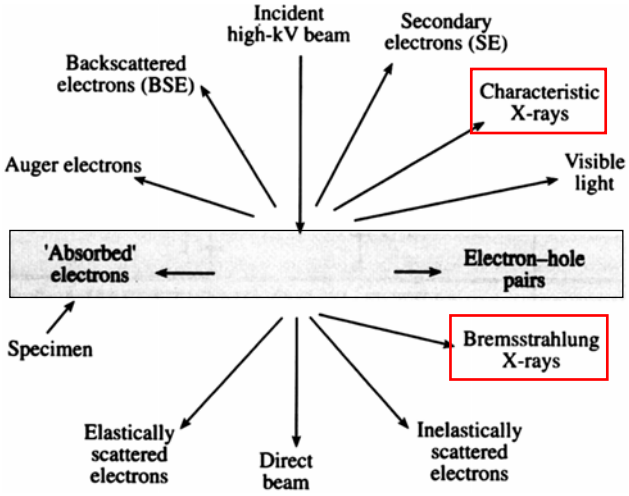
2006/3-55

Tomografia



EDS

Feixe de Elétrons



LNLS
2006/3-64

EDS

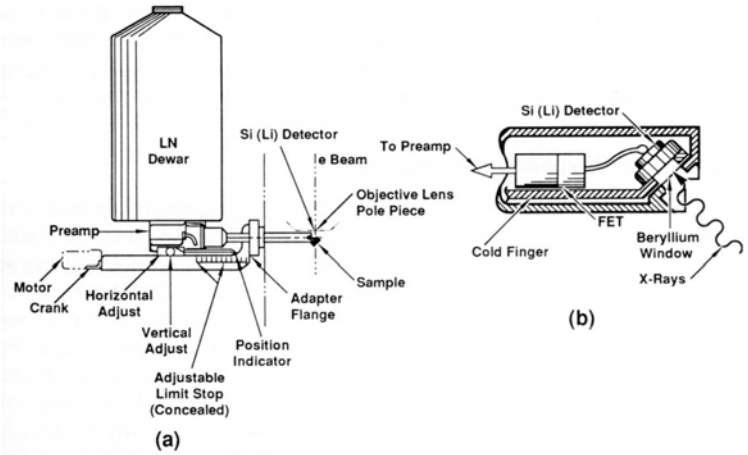
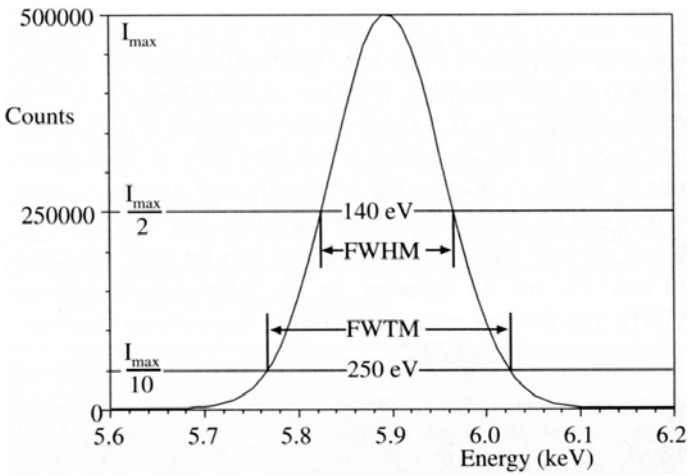


Figure 5.21. (a) Physical appearance of a retractable detector and associated preamplifier electronics. (b) Detail of Si(Li) mounting assembly.

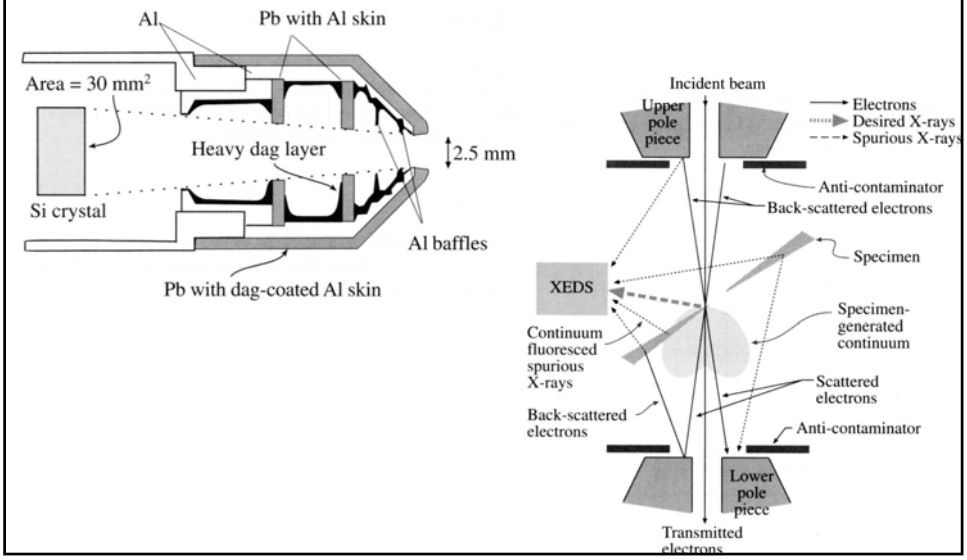
LNLS
2006/3-65

Resolução do Detector



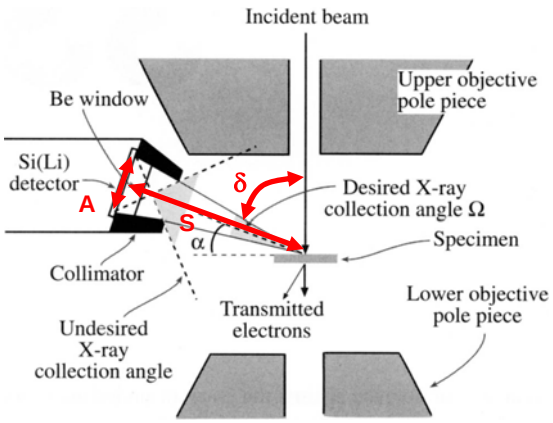
LNLS
2006/3-67

EDS Detector - TEM



LNLS

EDS Detector – Ângulo Sólido

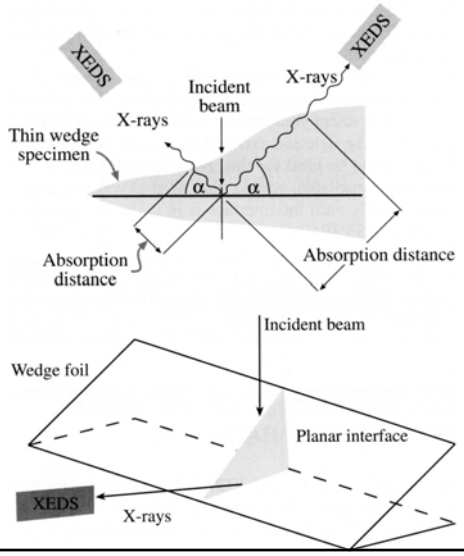


$$\Omega = \frac{A \cos\delta}{S^2}$$

As close as possible

2006/3-70

Ângulo de Escape e Absorção



2006/3-71

EDS Detector

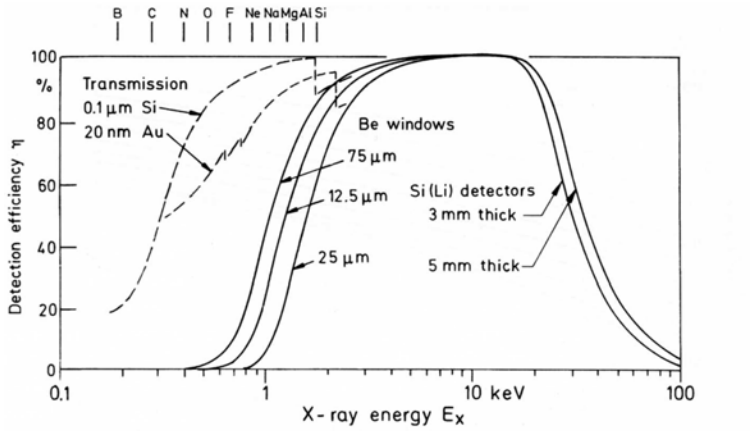


Fig. 10.18. Dependence of the detection efficiency $\eta(E_x)$ of a Si (Li) x-ray detector on quantum energy E_x and on the thicknesses of the Be window and the detector crystal. The transmission through a 20 nm Au film and a 0.1 μm dead-layer in Si decreases the efficiency of a windowless detectors. Energies of the K lines of low Z elements are drawn at the top of the figure

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2006/3-72

EDS Spectral Distribution

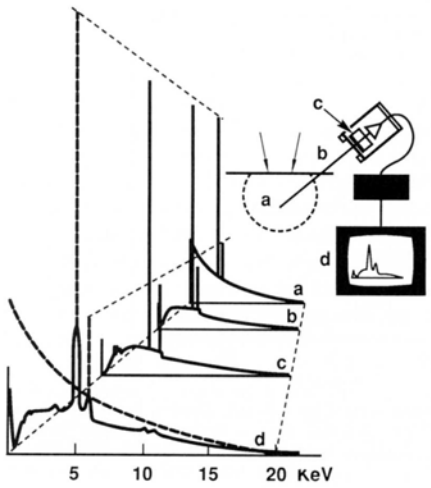
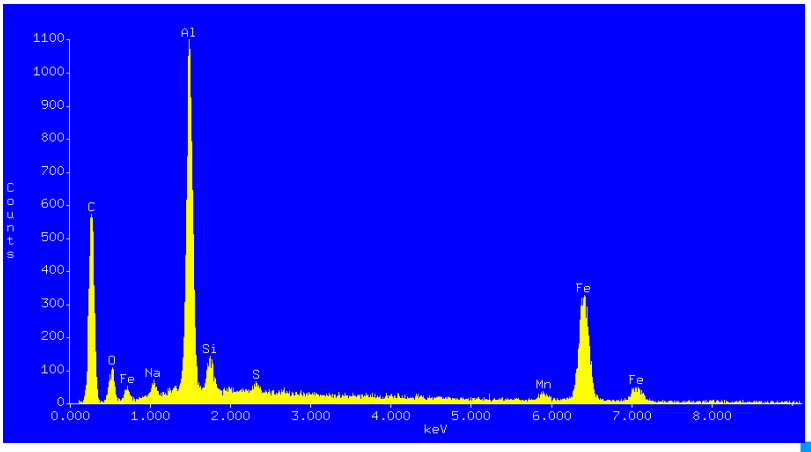


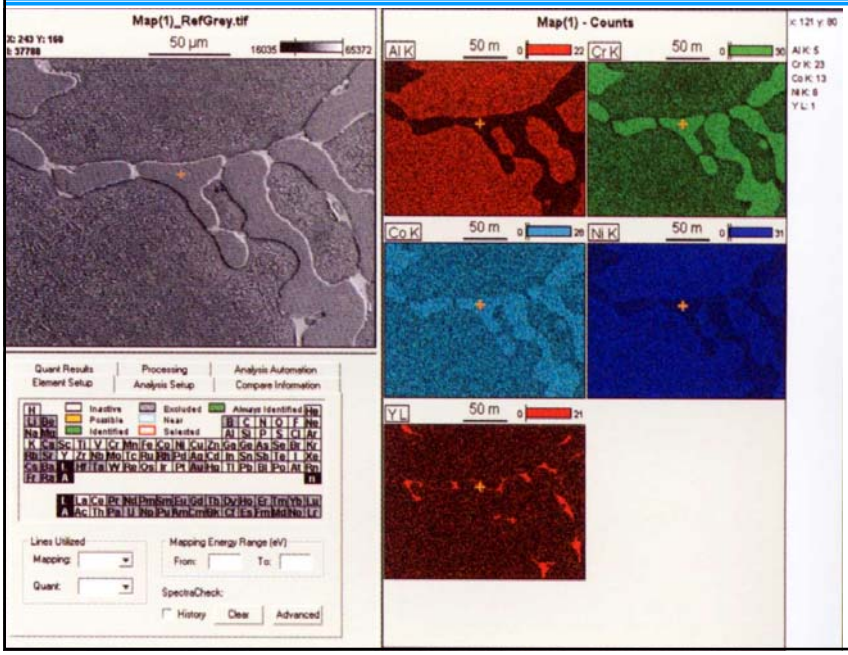
Figure 5.53. Schematic drawing of the relationship between the measured and generated spectral distributions of manganese. (Courtesy of R. Bolon.)

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2006/3-84

EDS Spectrum



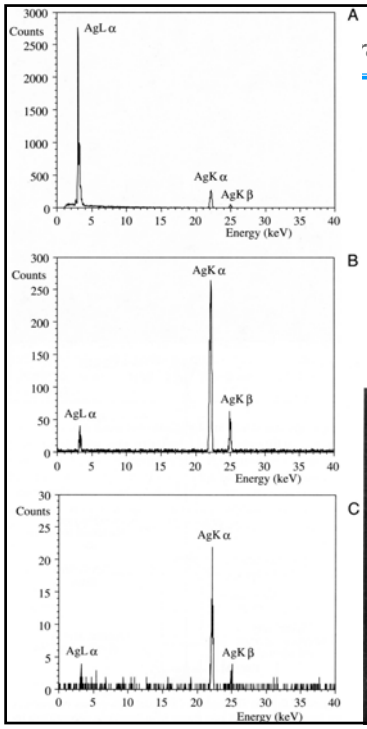
LNLS
2006/3-85



LNLS
2006/3-89

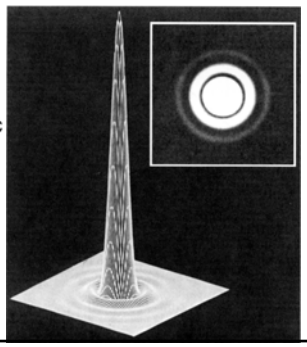
Análise do Espectro

- Efeitos antes da amostra
- Efeitos na amostra e após a amostra
- Efeitos no detector
- Relação peak/background



Efeitos do Feixe

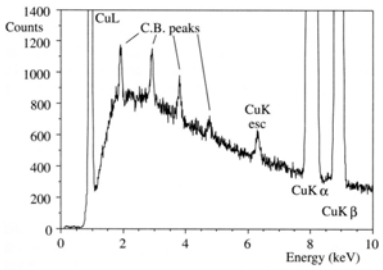
X-ray from C2 aperture and spurious electrons



Solution is a thick and heavy C_2 aperture and a well designed ilumination system

Thin specimen

Epalhamento na Amostra

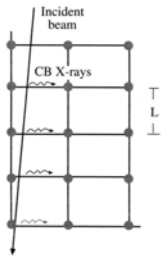


Coherent Bemsstrahlung

$$E_{CB} = \frac{12.4\,\beta}{L(1-\beta\cos(90+\alpha))}$$

$$\beta = \frac{v}{c}$$ Electron velocity

Detector take-off angle



Solution:
Far from low-index zone axis
Tilt de sample or change voltage and verify changes in intensity

2006/3-92

Epalhamento após a Amostra

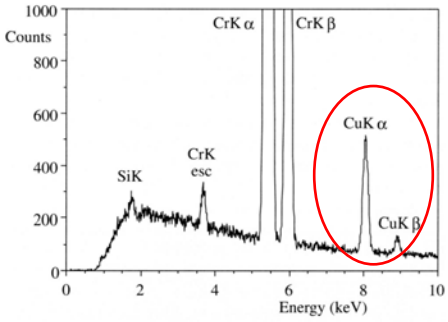
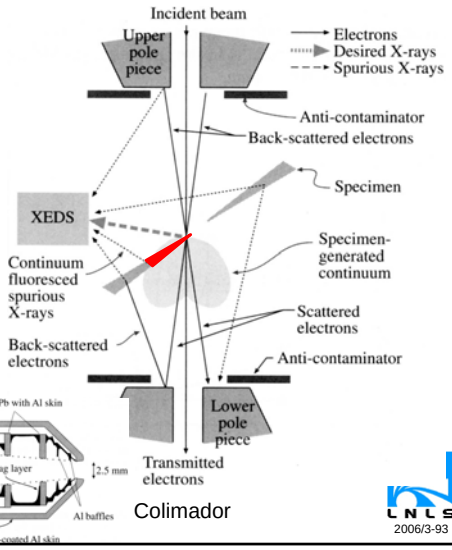
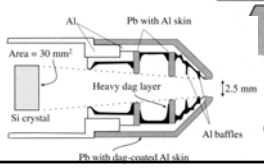


Figure 33.7. Cu peaks in a spectrum from a thin Cr film on a Cu grid. Although the beam is many micrometers from the grid, Cu X-rays are excited by electron scatter and bremsstrahlung from within the specimen and their intensity generally increases with tilt. The Cr escape peak and the Si internal fluorescence peak are also visible.



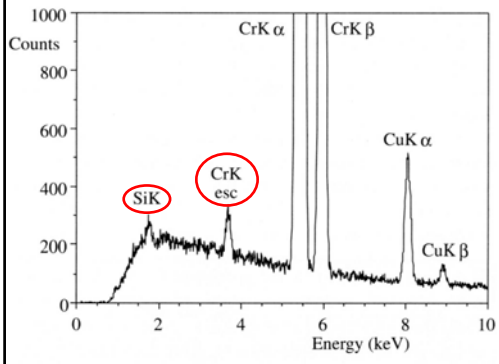


Colimador

Solution:
Baixo tilt <10º
Thin Sample
Adequate Sample Holder

2006/3-93

Epalhamento no Detector



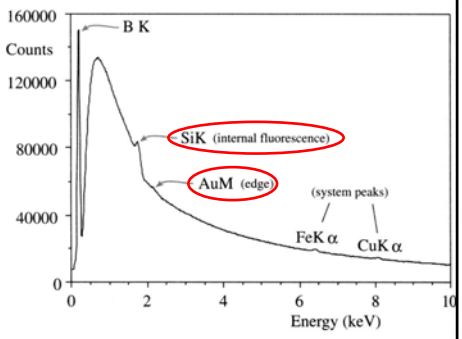


Figure 33.7. Cu peaks in a spectrum from a thin Cr film on a Cu grid. Although the beam is many micrometers from the grid, Cu X-rays are excited by electron scatter and bremsstrahlung from within the specimen and their intensity generally increases with tilt. The Cr escape peak and the Si internal fluorescence peak are also visible.

Escape Peaks, Fluorescence and Absortion



2006/3-94

Peak/Background

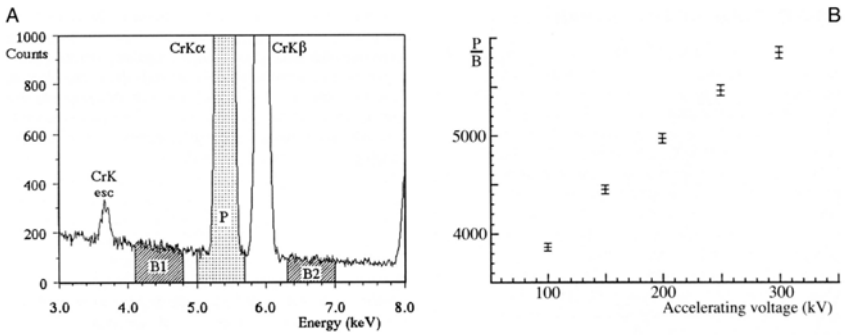


Figure 33.10. (A) The Fiori definition of the peak to background ratio for Cr. The total CrK_α peak intensity *P* is integrated from 5.0 to 5.7 keV. The background windows B1 and B2 are integrated over seventy 10-eV channels from 4.1 to 4.8 keV and from 6.3 to 7.0 keV, respectively. The average of the two windows [(B1 + B2)/2] is B(avg). This B(avg) is divided by 70 to give the background in a single 10-eV channel [B(10 eV)]. The Fiori definition is given by P/B = [P – B(avg)]/[B(10 eV)]. (B) The increase of the Fiori P/B with accelerating voltage in a well-behaved 300-keV IVEM.



2006/3-95



Análise Quantitativa

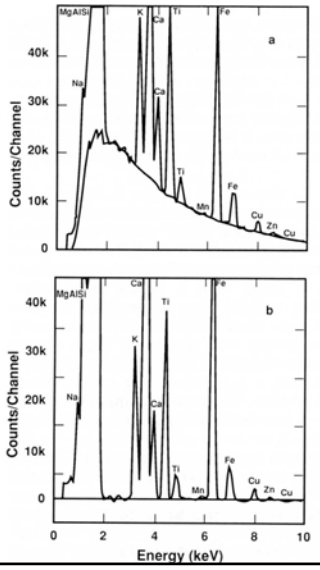
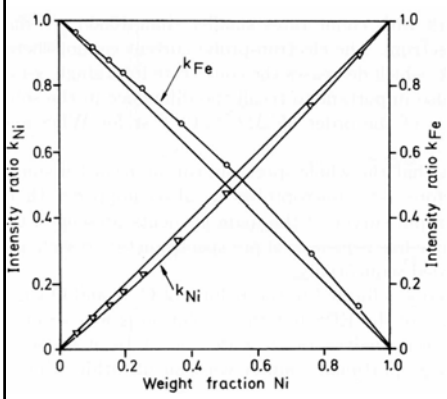
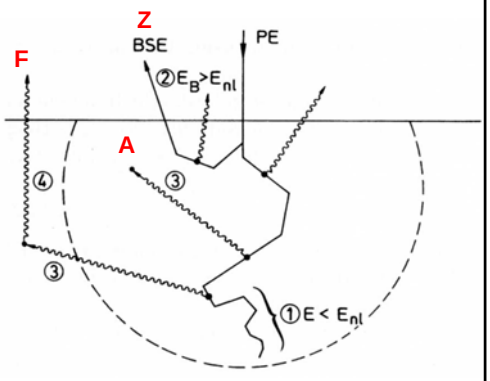


Figure 7.4. Background correction in Kakanui hornblende. (a) Fitted continuum curve calculated by Eq. (7.7); Observed spectrum is superposed. Note the presence of Mn $K\alpha$ peak at 5.9 keV. The concentration of Mn is less than 700 ppm. (b) Background subtracted.

LNLS
2006/3-96

Análise Quantitativa





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2006/3-97

Cliff-Lorimer

$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B}$$

$$C_A + C_B = 100\%$$

$$\frac{C_B}{C_C} = k_{BC}\frac{I_A}{I_C}$$

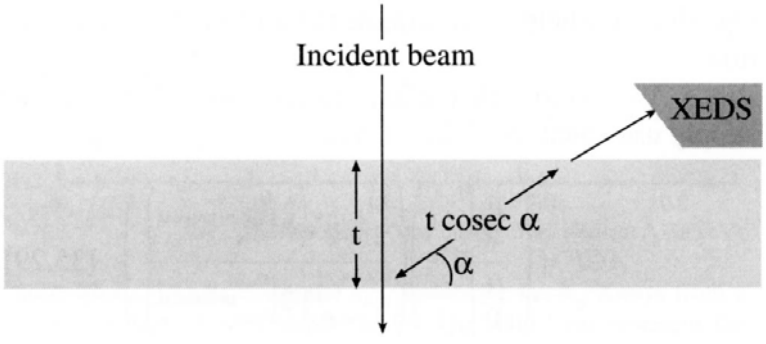
$$C_A + C_B + C_C = 100\%$$

Erro Relativo:

$$\frac{nN^{1/2}}{N}100\%$$

n= 1, 67%
2, 95%
3, 99,7%

Correção por Absorção



Correção por Absorção

$$k_{AB}^* = K_{AB}(ACF)$$

$$ACF = \frac{\int_0^t \left\{ \varphi_B(\rho t)\, e^{-\left(\frac{\mu}{\rho}\right]_{Spec}^{B} \rho t \operatorname{cosec}\alpha} \right\} d(\rho t)}{\int_0^t \left\{ \varphi_A(\rho t)\, e^{-\left(\frac{\mu}{\rho}\right]_{Spec}^{A} \rho t \operatorname{cosec}\alpha} \right\} d(\rho t)}$$

$$ACF = \left(\frac{\left(\frac{\mu}{\rho}\right]_{Spec}^{A}}{\left(\frac{\mu}{\rho}\right]_{Spec}^{B}} \right) \left(\frac{1 - e^{-\left(\frac{\mu}{\rho}\right]_{Spec}^{B} \rho t \operatorname{cosec}\alpha}}{1 - e^{-\left(\frac{\mu}{\rho}\right]_{Spec}^{A} \rho t \operatorname{cosec}\alpha}} \right)$$

$$\left(\frac{\mu}{\rho}\right]_{Spec}^{A} = \sum_i \left(\frac{C_i \mu}{\rho} \right]_i^A$$

$$\sum_i C_i = 1$$

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2006/3-100

Correção por Absorção

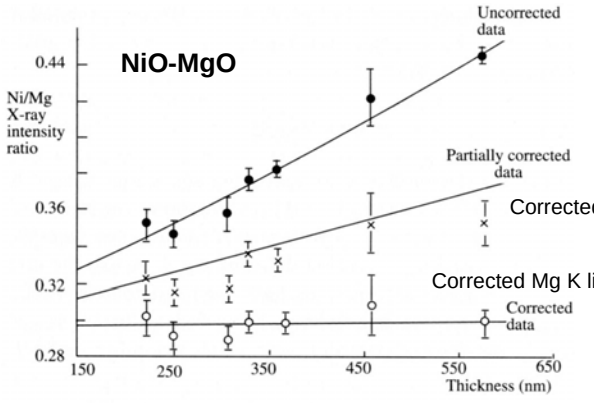


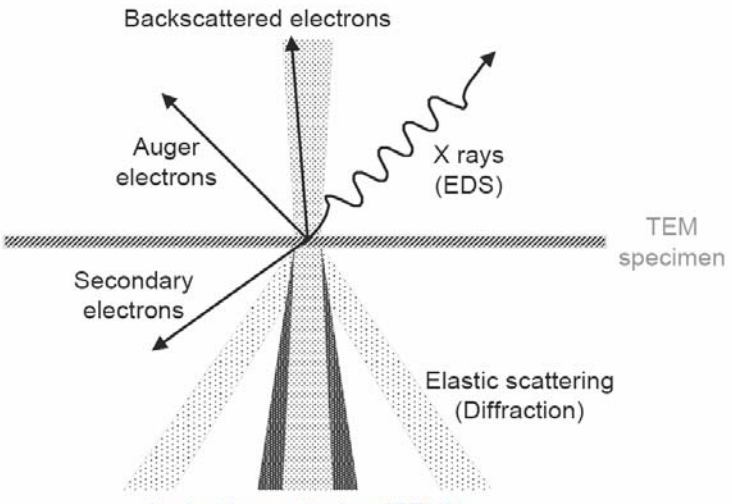
Figure 35.8. The upper curve shows the raw Ni K_α/Mg K_α intensity ratio as a function of thickness in a homogeneous sample of NiO-MgO. The slope indicates strong absorption of Mg K_α X-rays. The middle curve shows the effect of correcting for absorption of the Mg K_α line by Ni and the bottom line shows the effect of a further correction for absorption of the Mg K_α line by O to give the expected horizontal line.

LNLS

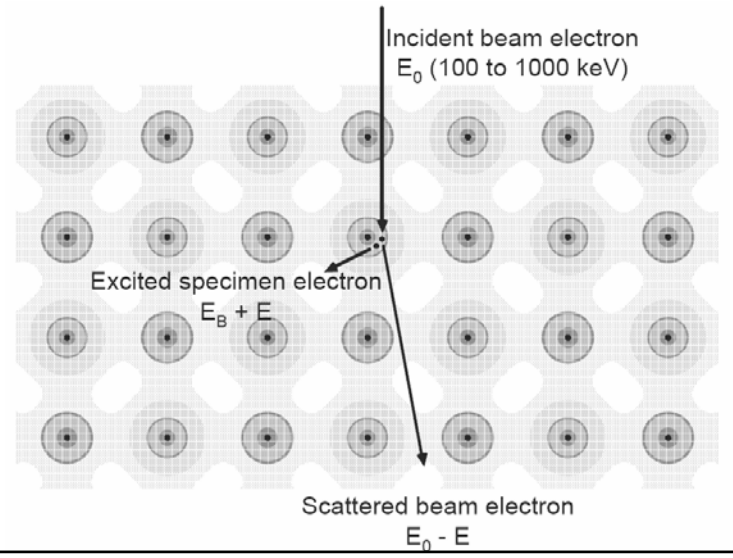
2006/3-101

EELS

Feixe de Elétrons



Perda de Energia



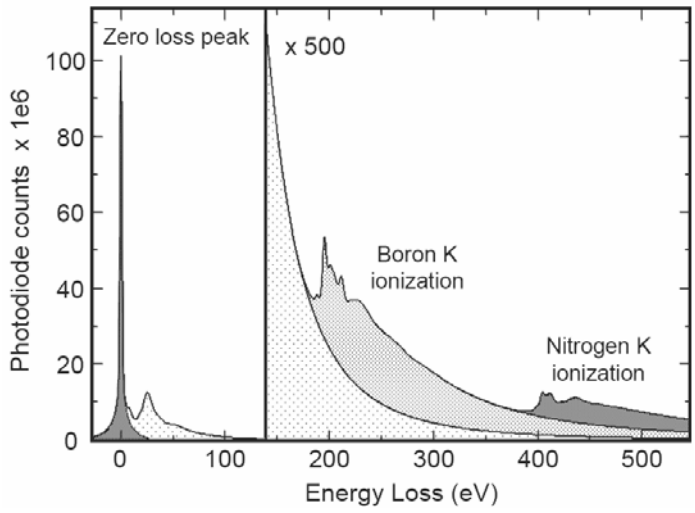
2006/3-104

Difração vs. EELS

- **Difração de Elétrons:**
  - **Distribuição de ângulos de espalhamento**
  - **Identificação de fases e estruturas**
  - **Seleção de ângulo de espalhamento para contraste**
    - **Campo Claro**
    - **Campo Obscuro**
    - **HAADF**
- **EELS**
  - **Distribuição de perdas de energias**
  - **Identificação de fases e composição**
  - **Seleção de perda de energia para contraste**
    - **Elástico (sem cromaticidade)**
    - **Inelástico (composição)**

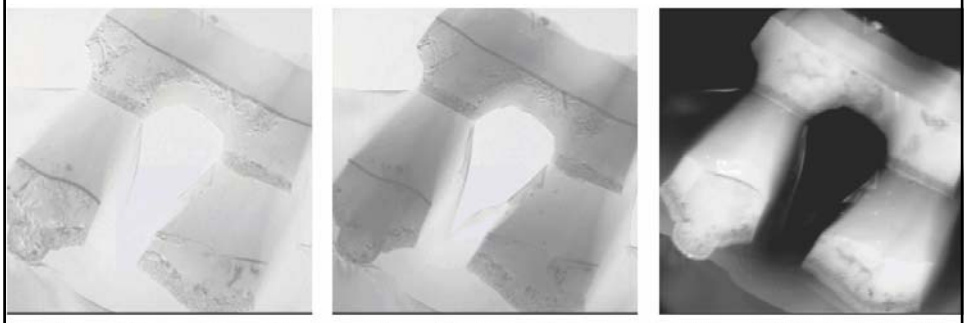
2006/3-105

Espectro EELS



2006/3-106

Imagem Filtrada

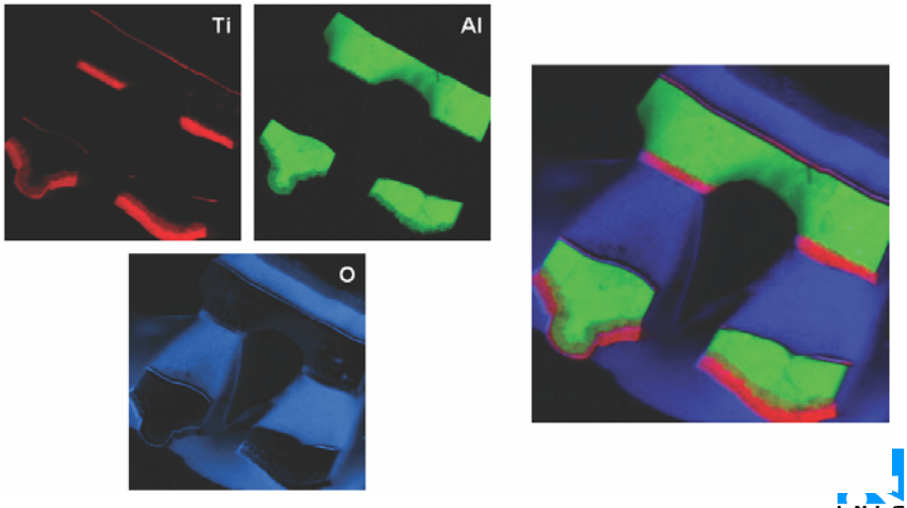


Unfiltered (0 to 1000 eV) Filtered (-10 to 10 eV) Filtered (120 to 140 eV)

[Gatan, 2005]

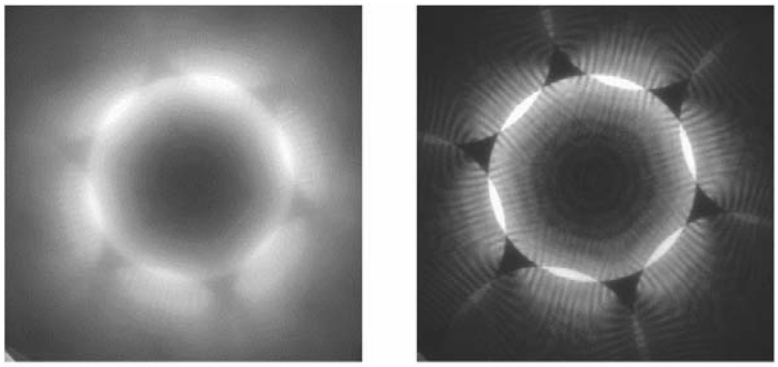
2006/3-107

Imagem Filtrada



[Gatan, 2005]

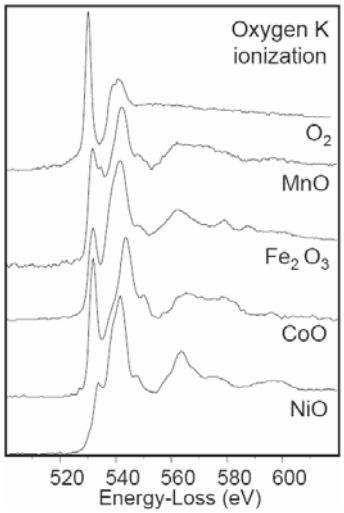
Difração Filtrada



Unfiltered: all E included

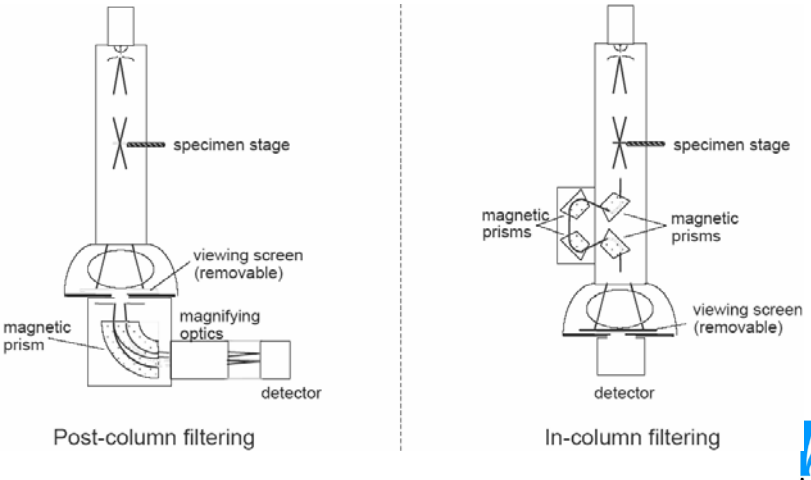
Filtered: E = 0 only

Estrutura Fina



LNLS
2006/3-110

Espectrômetro

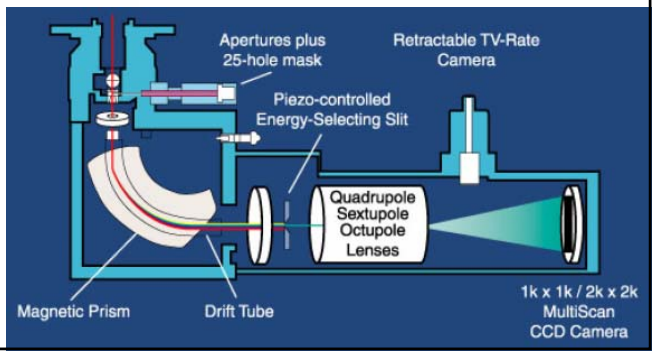


LNLS
2006/3-111

Microscopia Eletrônica de Transmissão Antônio J. Ramirez

EELS

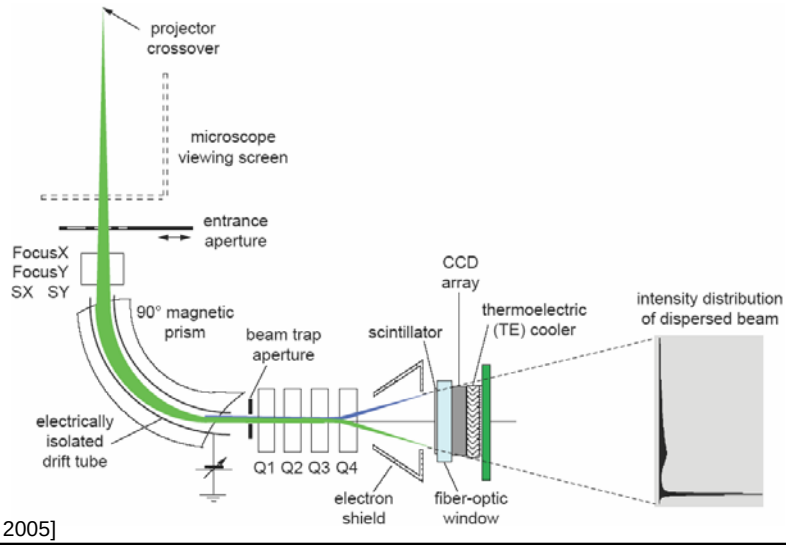




[Gatan, 2005]

Microscopia Eletrônica de Transmissão Antônio J. Ramirez

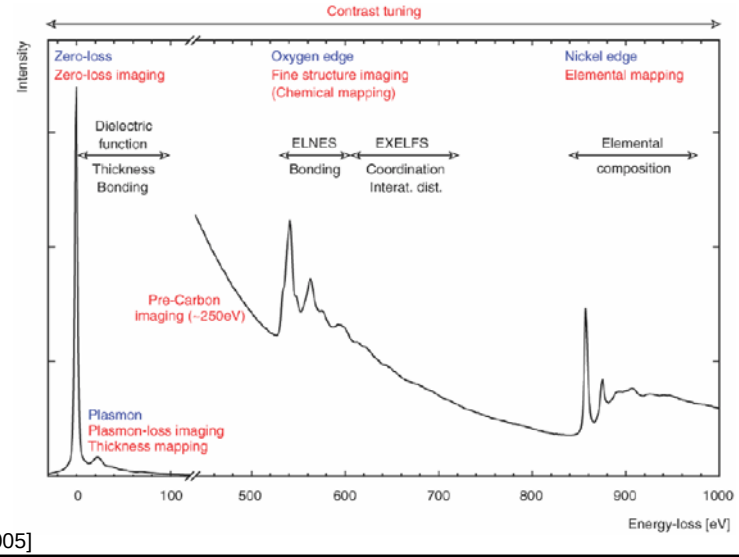
Post-Column



[Gatan, 2005]

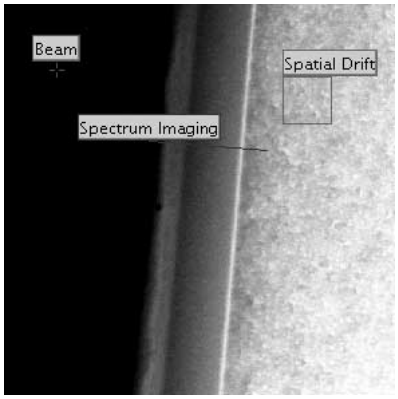
LNLS 2006/3-113

Informações no Espectro



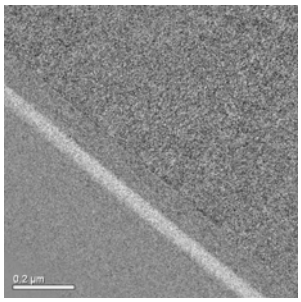
[Gatan, 2005]

2006/3-114

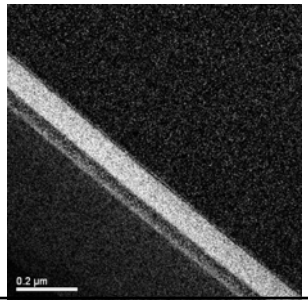


EELS

Ni

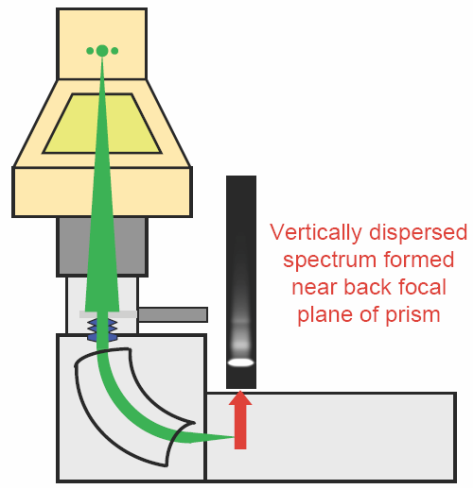


O



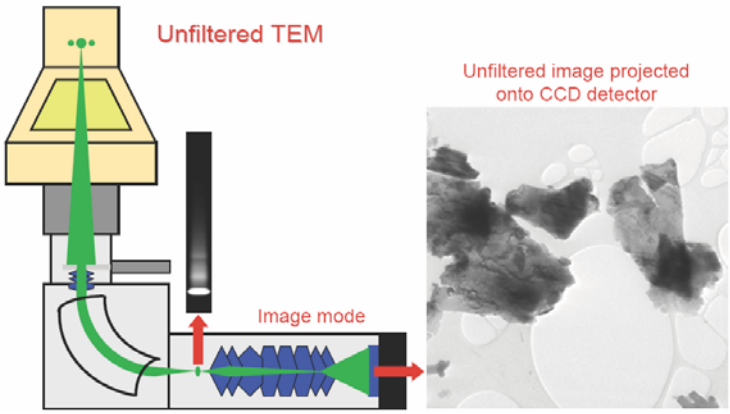
2006/3-115

Espectrômetro



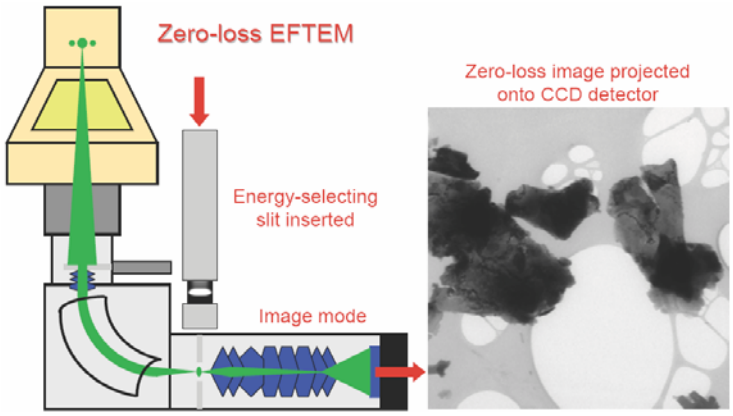
[Gatan, 2005]

Imagem não filtrada



[Gatan, 2005]

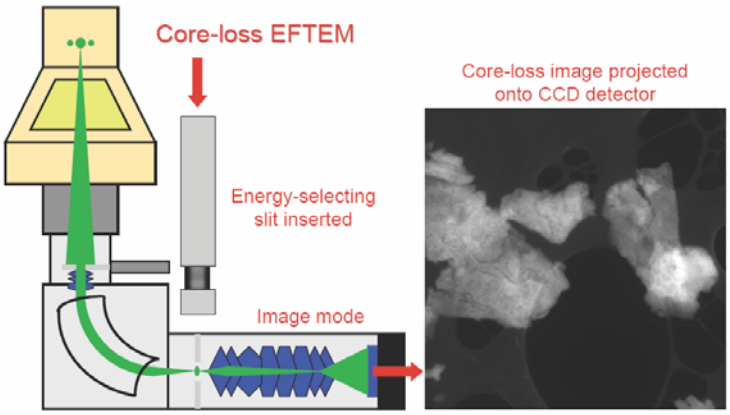
Imagem filtrada



[Gatan, 2005]

2006/3-118

Imagem de Core-loss



[Gatan, 2005]

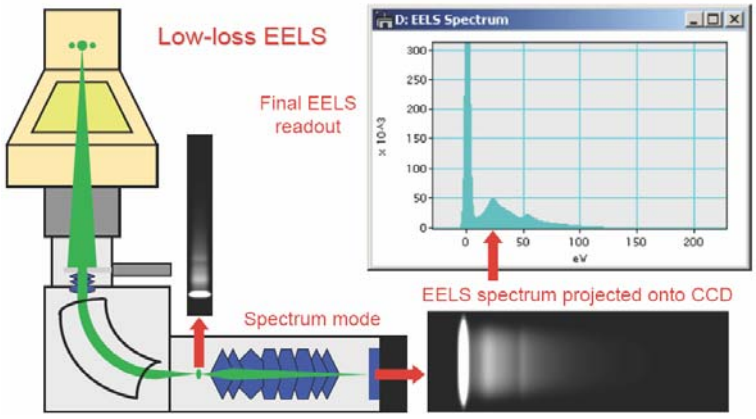
2006/3-119

Imagem Filtrada



2006/3-120

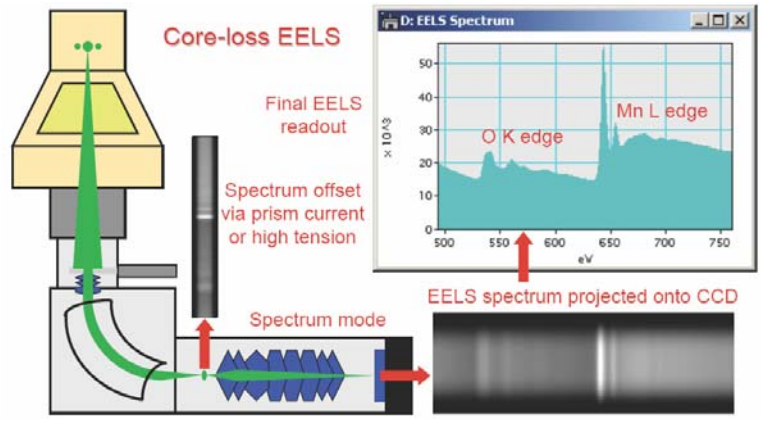
Modo Espectro



[Gatan, 2005]

2006/3-121

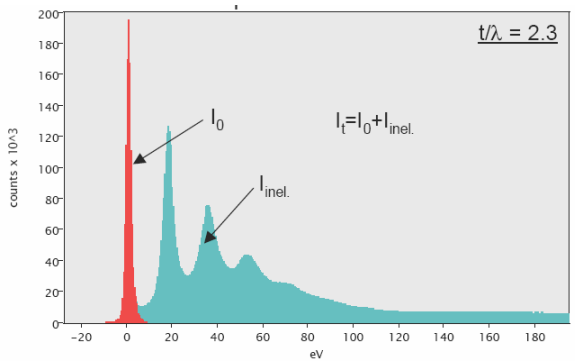
Offset do Espectro



[Gatan, 2005]

2006/3-122

Espessura da Amostra

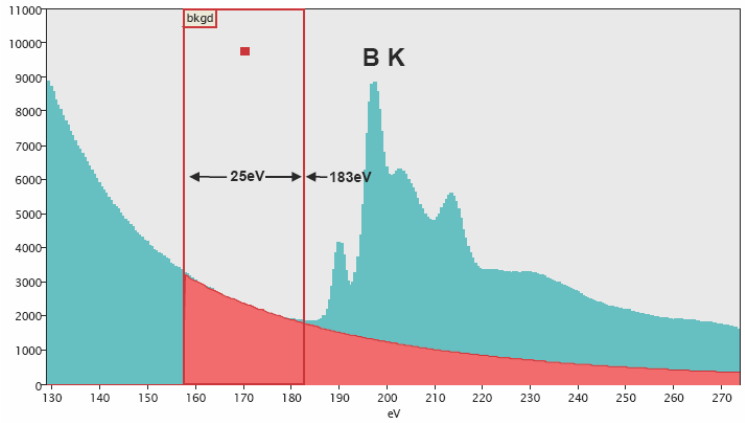


$$t/\lambda = -\ln(I_0/I_t)$$

[Gatan, 2005]

2006/3-123

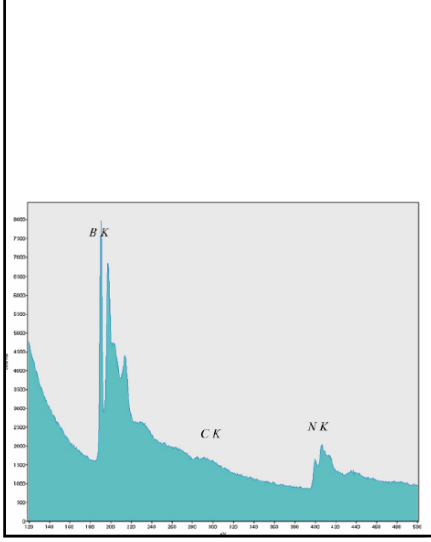
Modelamento do Background

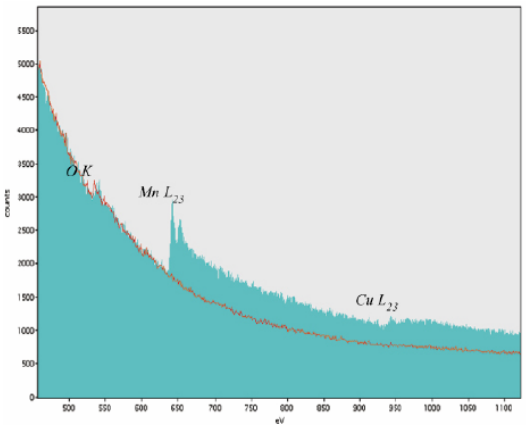


[Gatan, 2005]

LNLS 2006/3-124

EELS

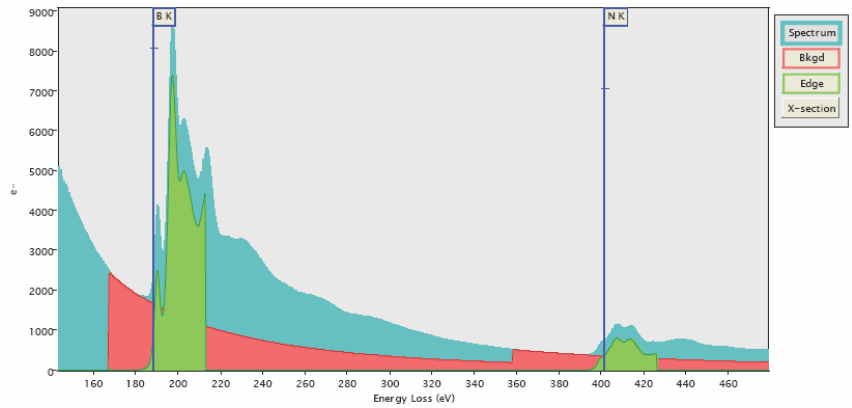




[Gatan, 2005]

LNLS 2006/3-125

Extração do Sinal

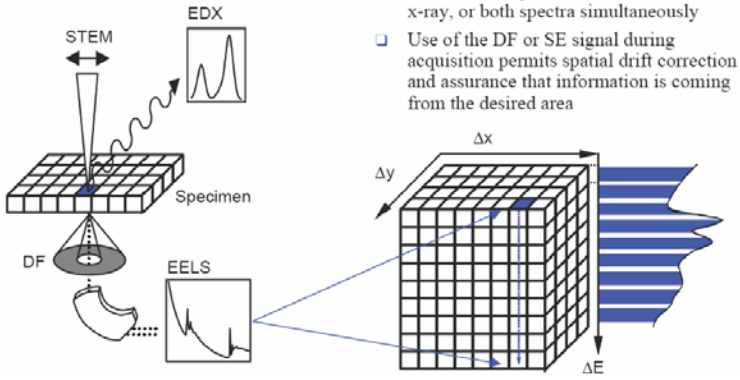


[Gatan, 2005]

2006/3-126

Spectrum Image

- A STEM spectrum image is acquired by stepping a focused electron probe from one pixel to the next
- The spectrum image data cube is filled one spectrum column at a time
- In STEM it is possible to collect EELS, x-ray, or both spectra simultaneously
- Use of the DF or SE signal during acquisition permits spatial drift correction and assurance that information is coming from the desired area

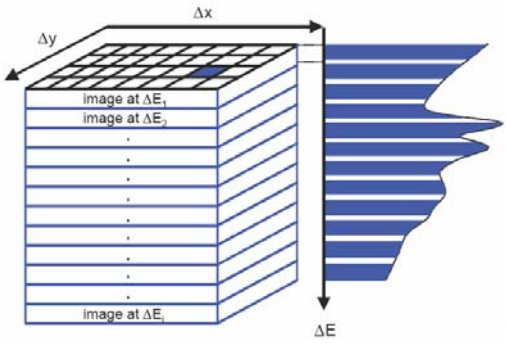


[Gatan, 2005]

2006/3-127

Filtered Image

- An energy-filter (EFTEM) can acquire an image containing a narrow range of energies
- The spectrum image data cube is filled one energy plane at a time
- a.k.a. Imaging spectra mode



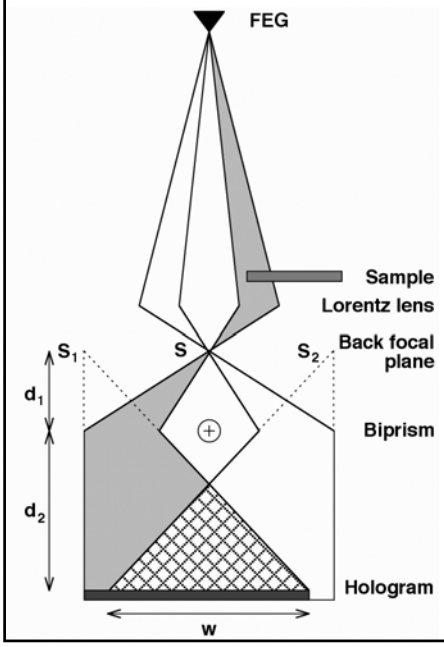
[Gatan, 2005]

LNLS
2006/3-128

Electron Holography

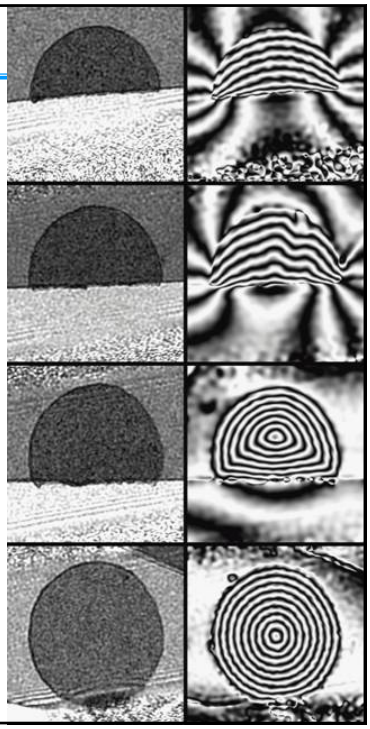
LNLS
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Experimental Setup



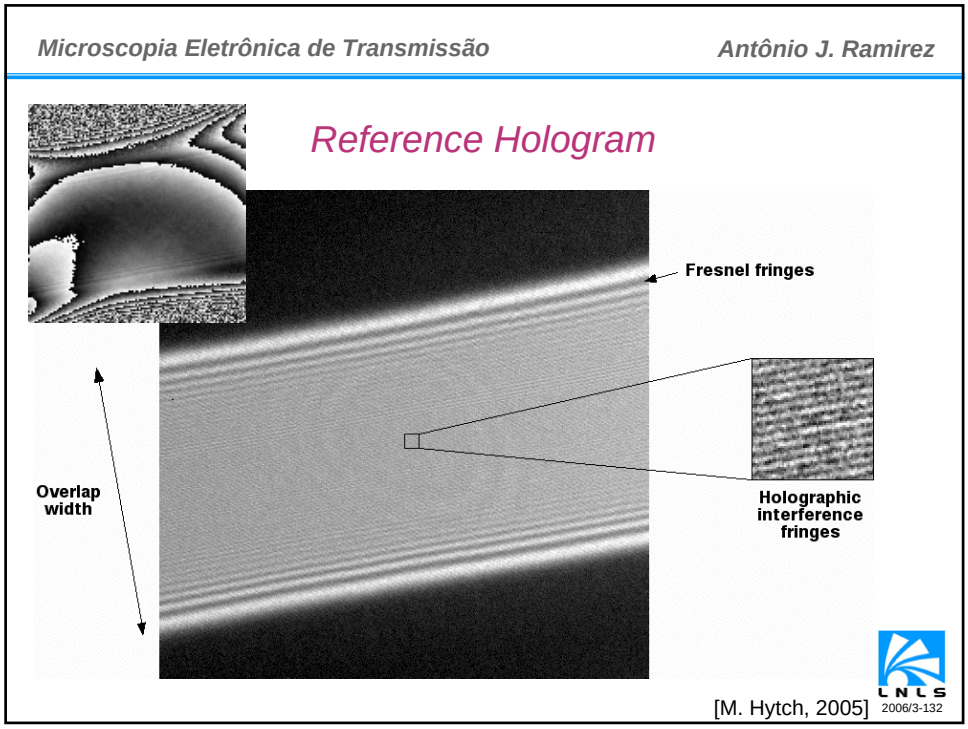
2006/3-130

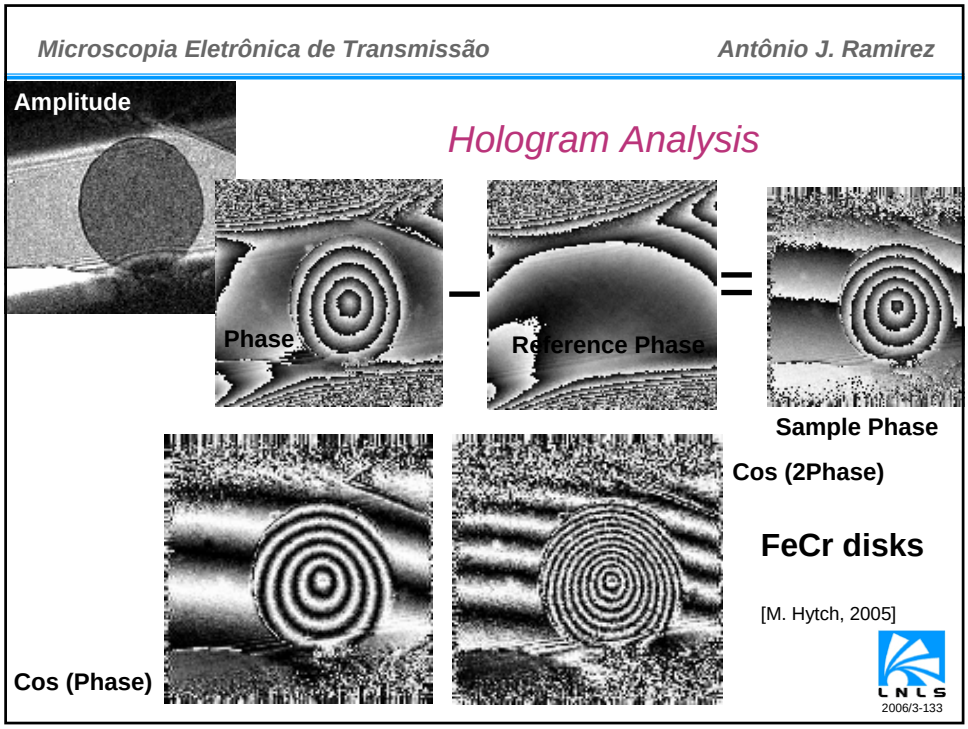
Magnetic Lines of Force



[M. Hytch, 2005]

FeCr Disks


Microscopia Eletrônica de Transmissão
Antônio J. Ramirez
Reference Hologram
Fresnel fringes
Overlap width
Holographic interference fringes
[M. Hytch, 2005]
2006/3-132


Microscopia Eletrônica de Transmissão
Antônio J. Ramirez
Amplitude
Hologram Analysis
Phase
Reference Phase
Sample Phase
Cos (2Phase)
FeCr disks
[M. Hytch, 2005]
Cos (Phase)
2006/3-133