
CENTRO BRASILEIRO DE PESQUISAS FÍSICAS
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MICROSCOPIA ELETRÔNICA

ANDRÉ LUIZ PINTO

CBPF

Roteiro



- Introdução
- Fundamentos
  - Fontes de elétrons
  - Lentes de elétrons
  - Interação elétron-matéria
- Microscópio Eletrônico de Varredura
- Microscópio Eletrônico de Transmissão
- Aplicações à Nanotecnologia
- Comentários Finais
  - LabNano

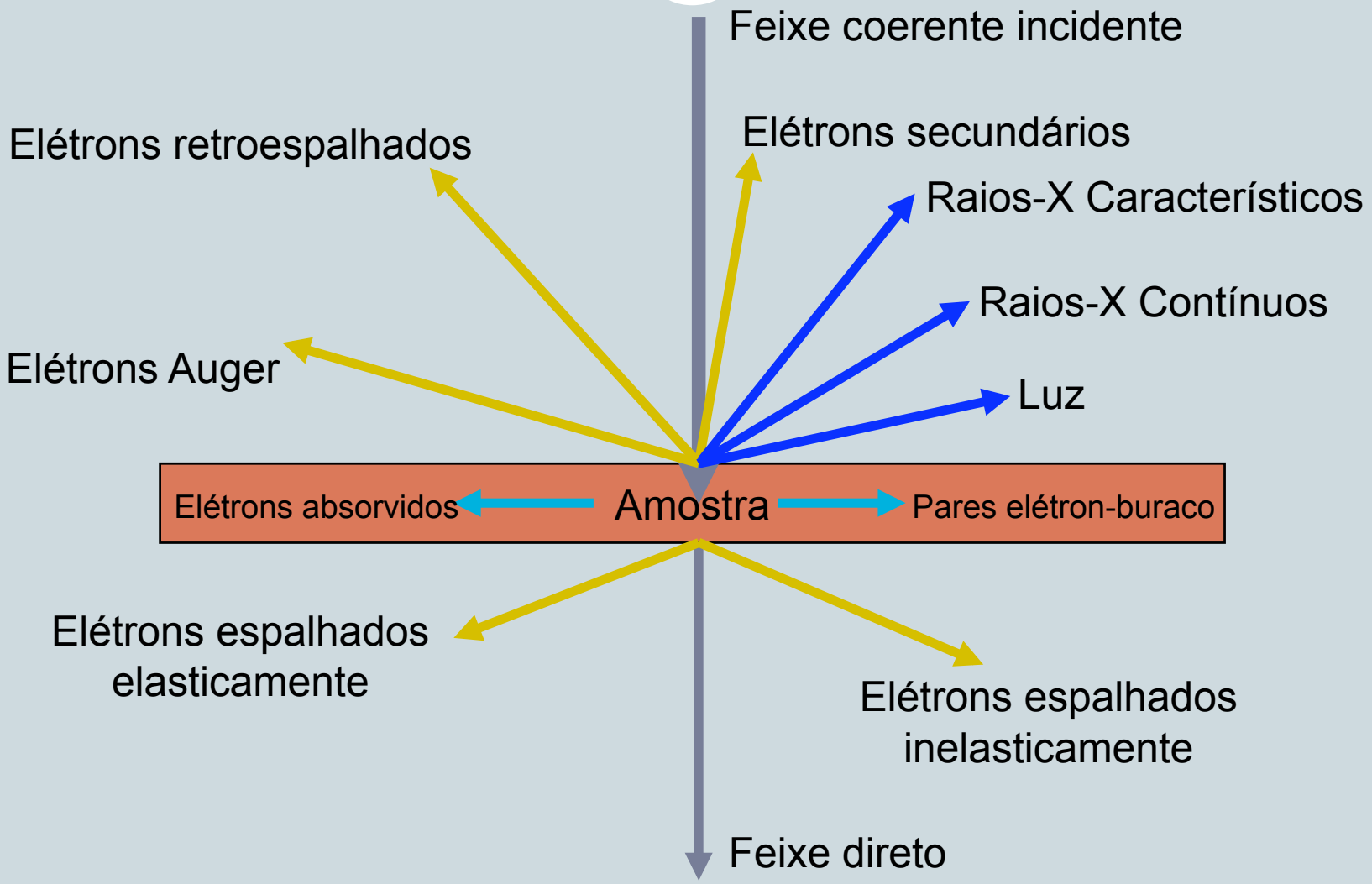
Opções para visualizar a microestrutura

- Aumento x Resolução (lateral)

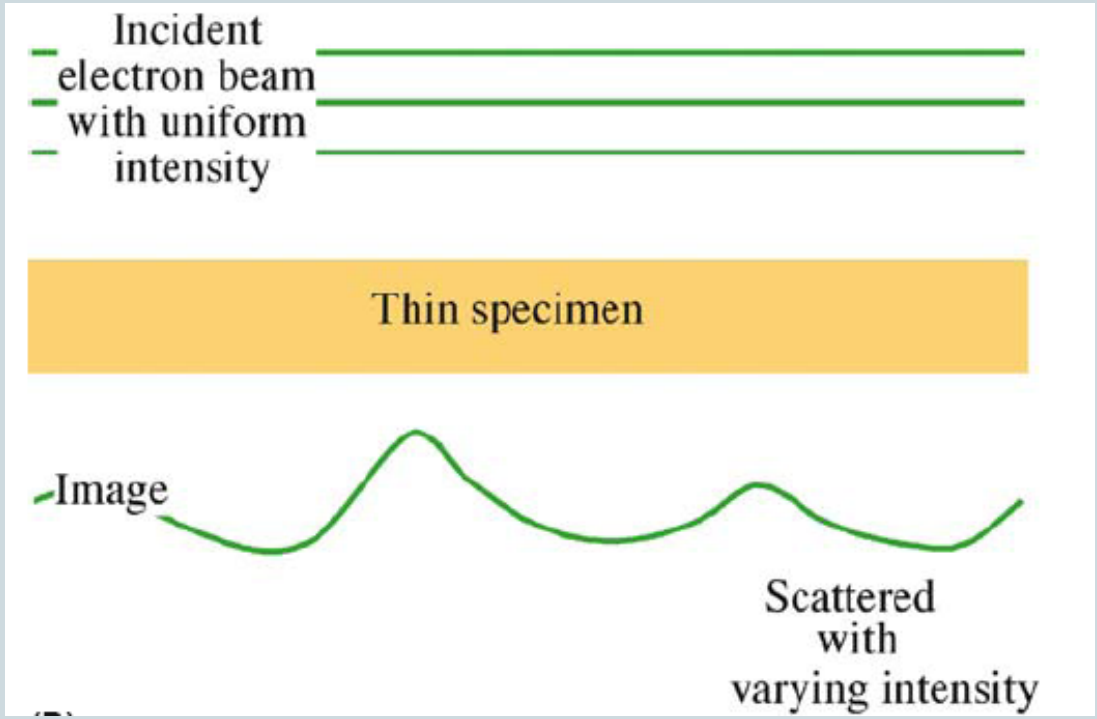


- Olho humano – 0,1 mm
- Microscopia Ótica – 0,5 μm
- Microscópio Eletrônico de Varredura (MEV) – 1 - 4 ηm
- Microscópio Eletrônico de Transmissão (MET) – 0,8 - 1,4 Å
- Microscópio de Ponta de Prova (SPM) – 0,3 Å

Interação Elétron-Amostra

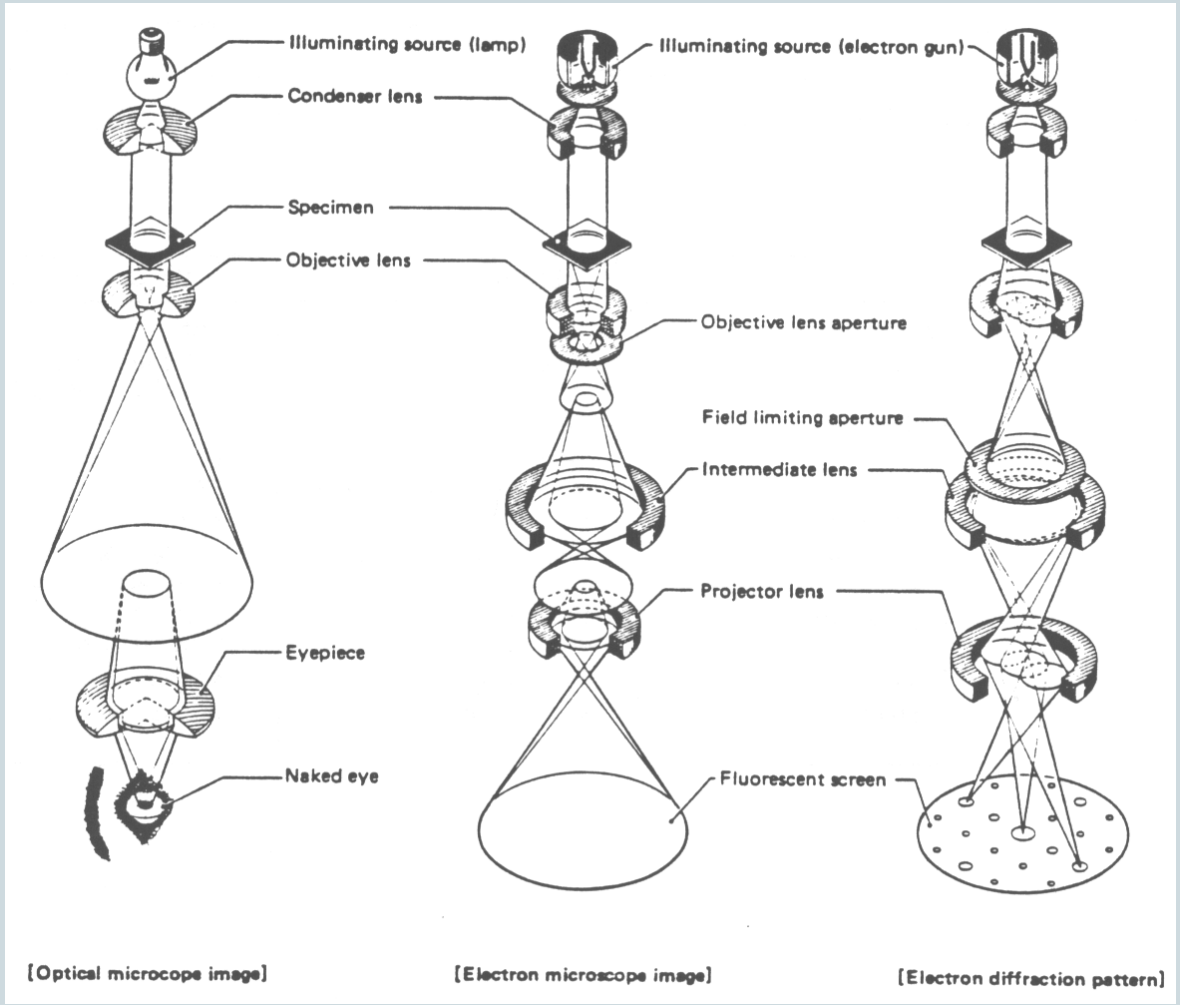


Interação Elétron-Amostra



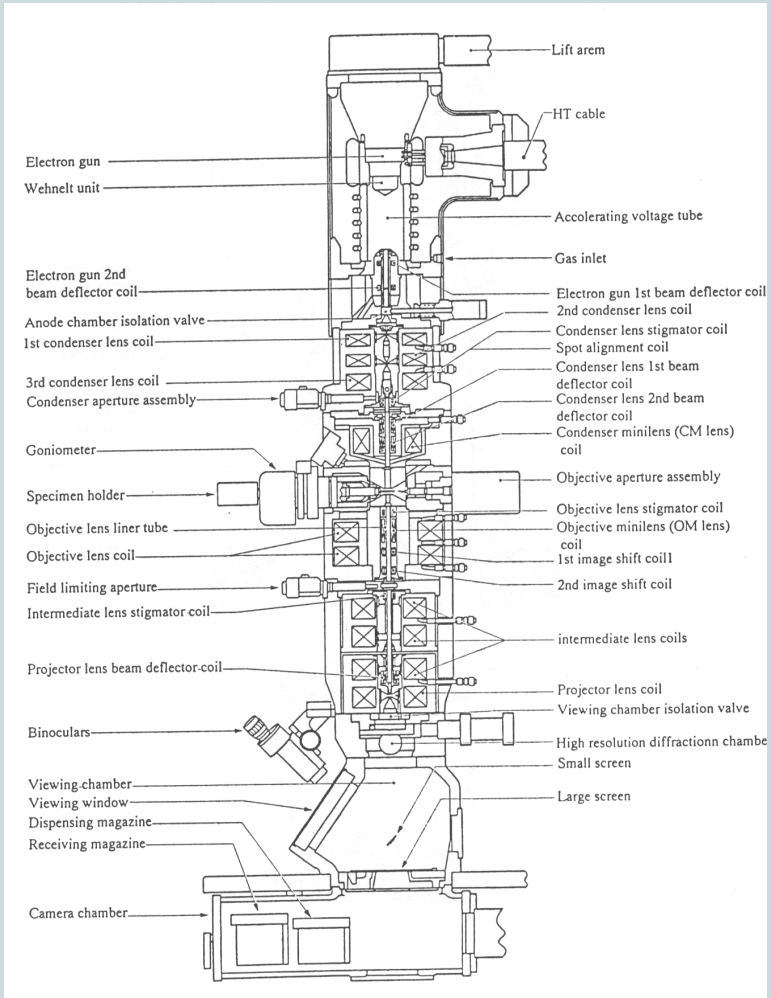
Williams e Carter

Arquitetura



Jeol

Um MET moderno



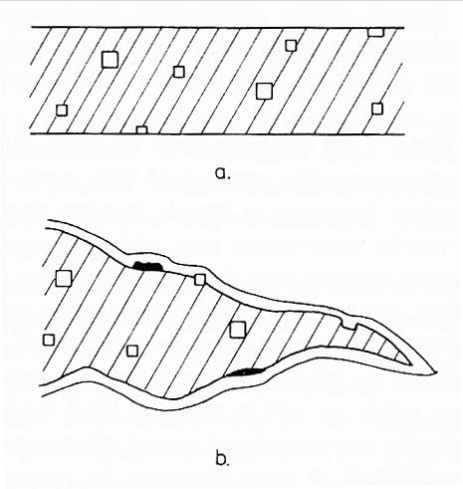


Jeol

Amostras para MET

Suposição de um só evento de choque

Espessura < 100 ηm

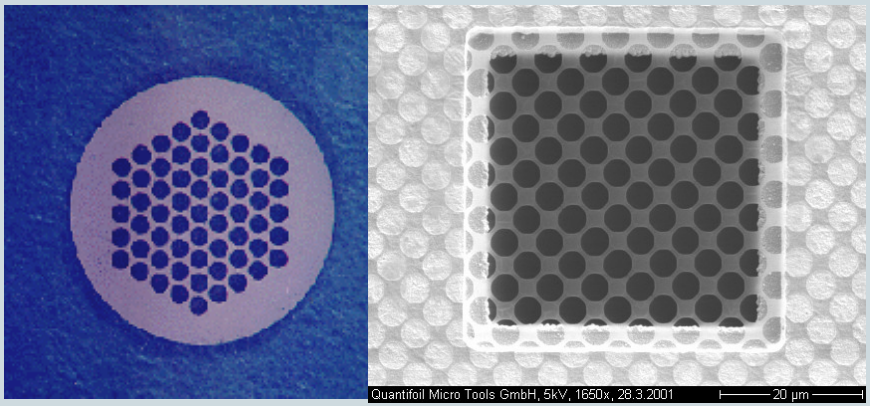


Pergunta básica:

- **Amostra de Folha Fina**

ou

- **Grade**

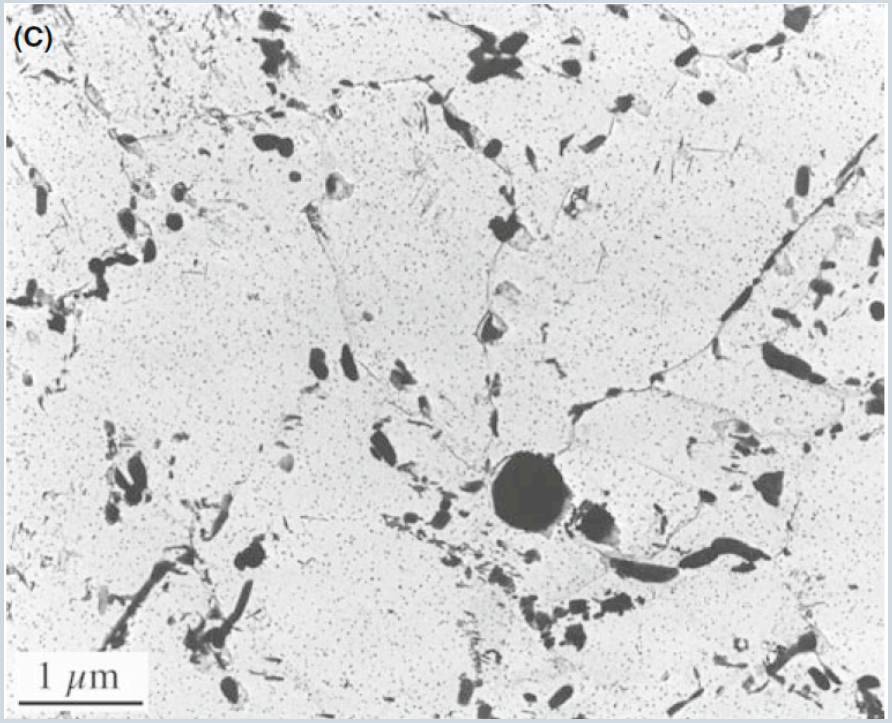


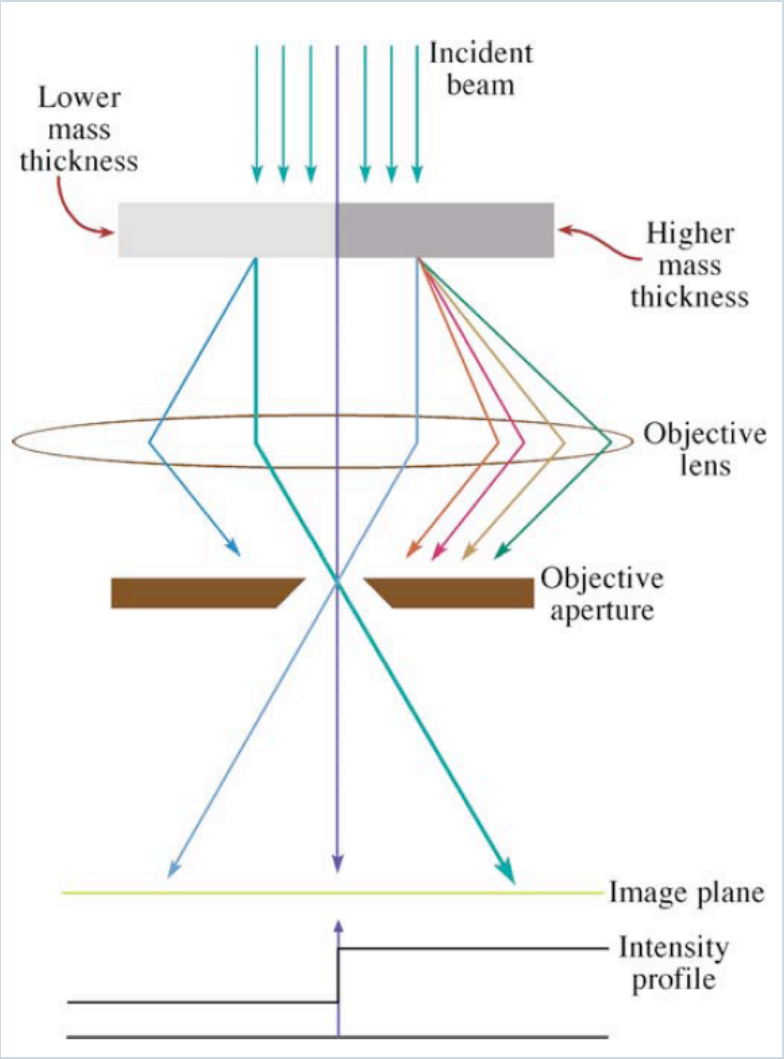
SPI

Contraste de Massa e Espessura

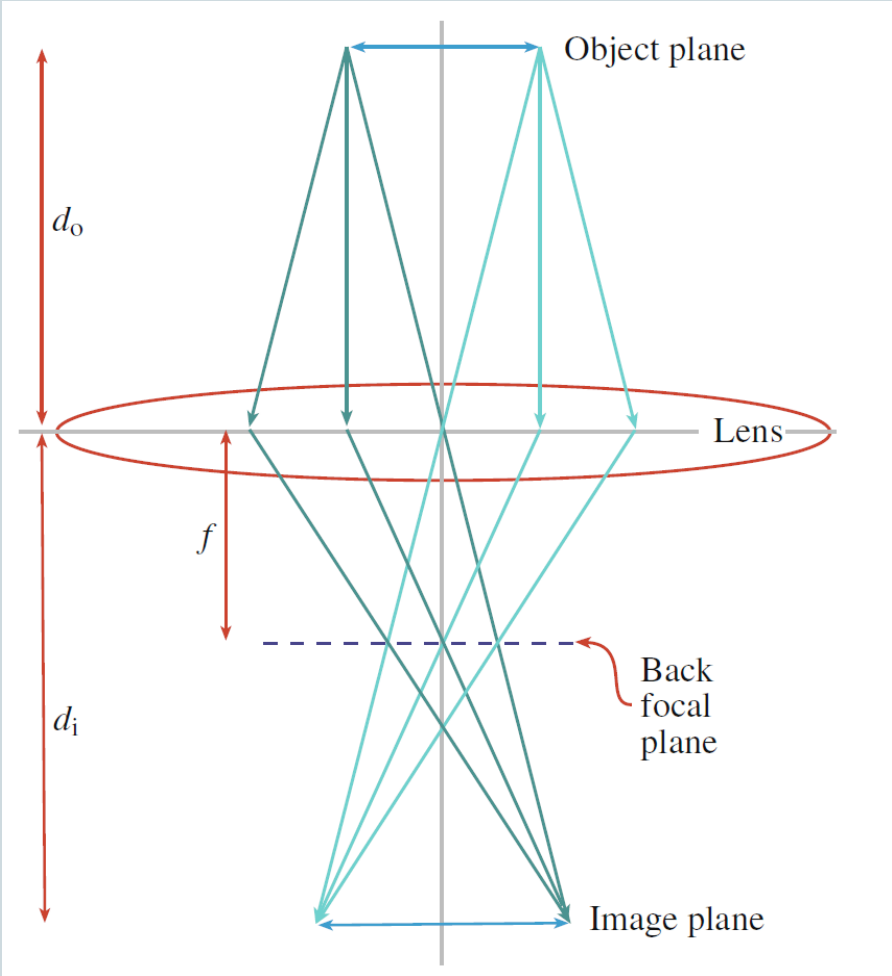
Williams e Carter

Precipitados em aço CrMo





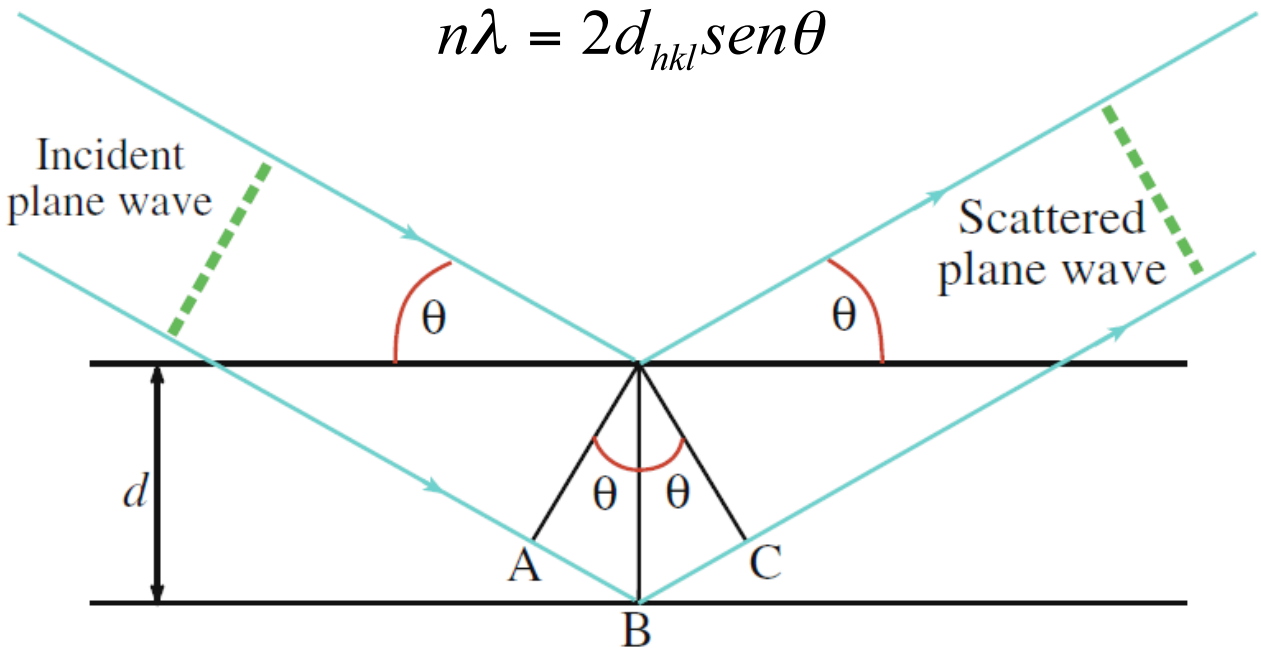
O Plano Focal da Lente Objetiva



Williams e Carter

Condição de Bragg

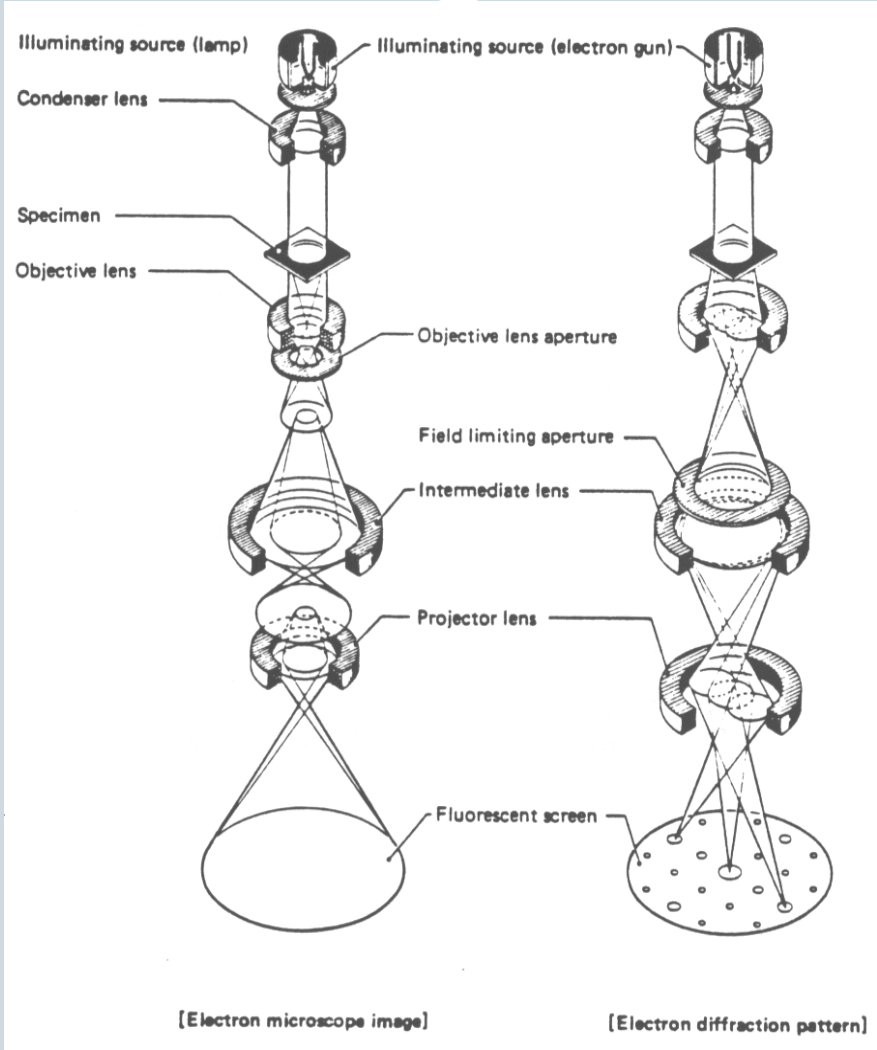
$$n\lambda = 2d_{hkl}sen\theta$$



Williams e Carter

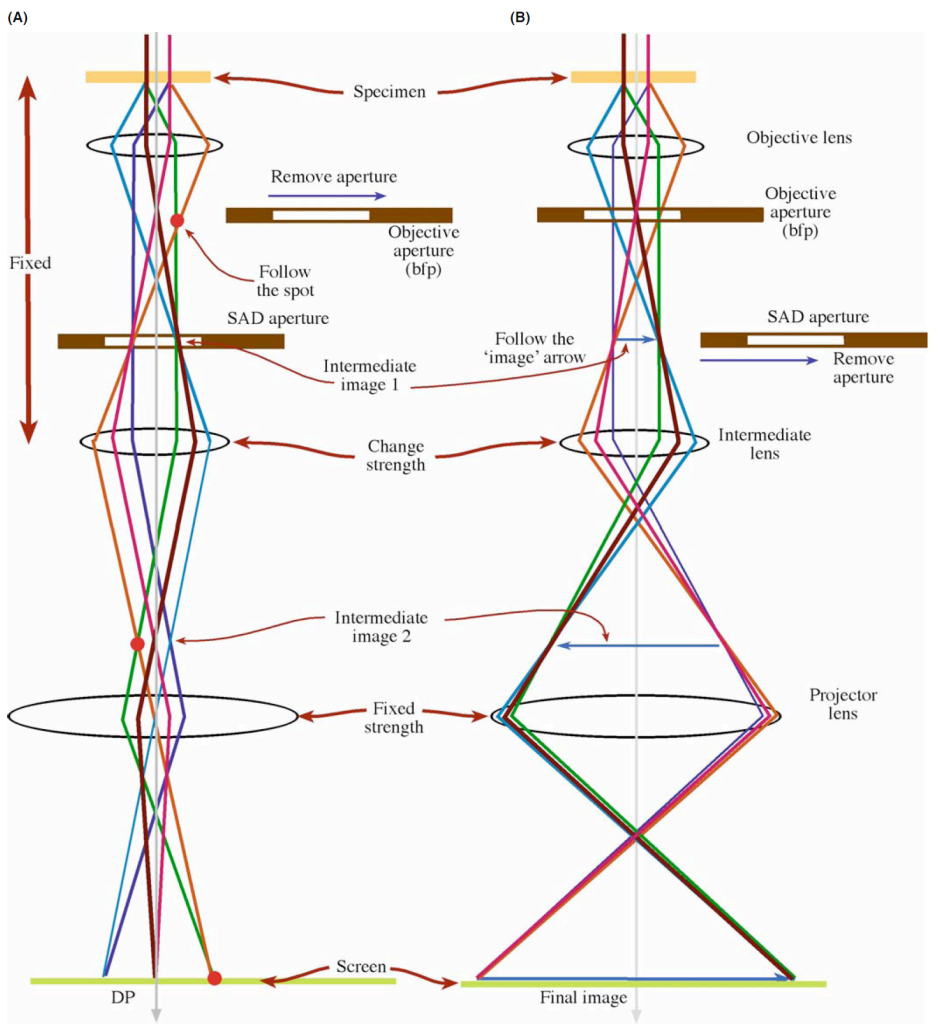
Amostras Cristalinas

A figura de difração e a formação de imagem.



Jeol

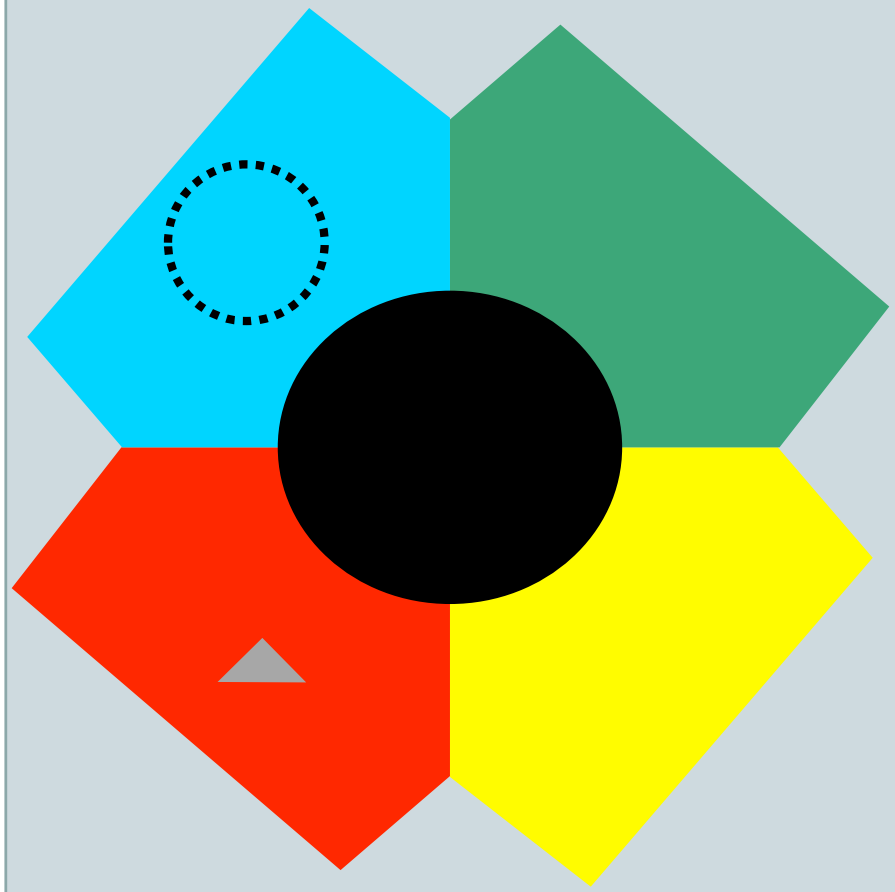
Amostras Cristalinas



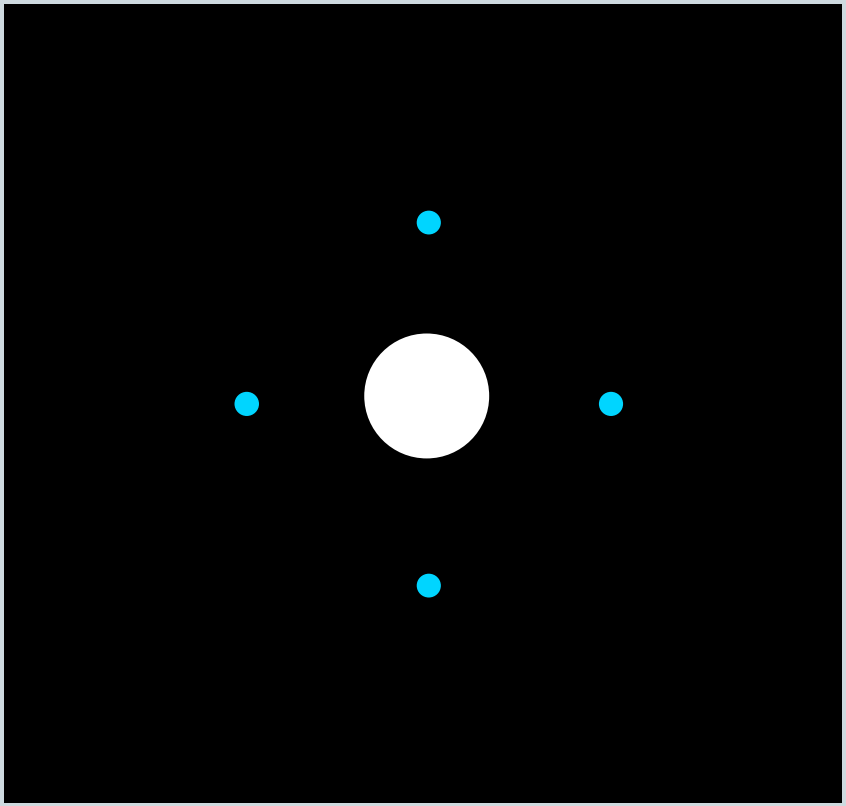
A figura de difração e a formação de imagem.

Williams e Carter

Experimento Mental

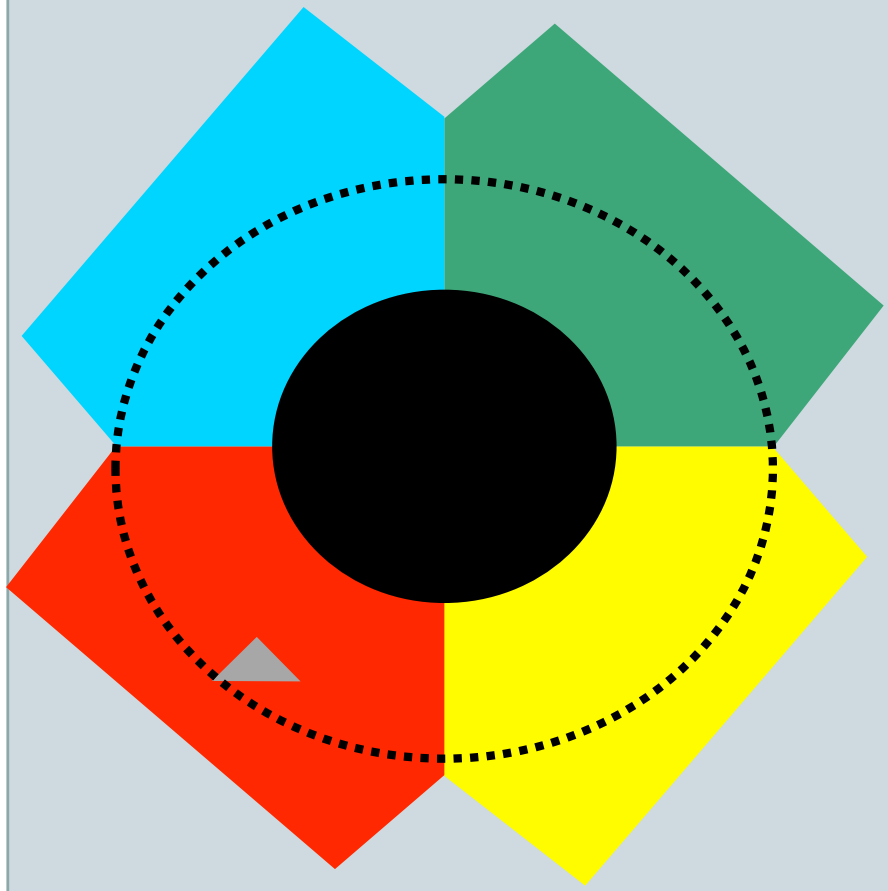


Plano Imagem

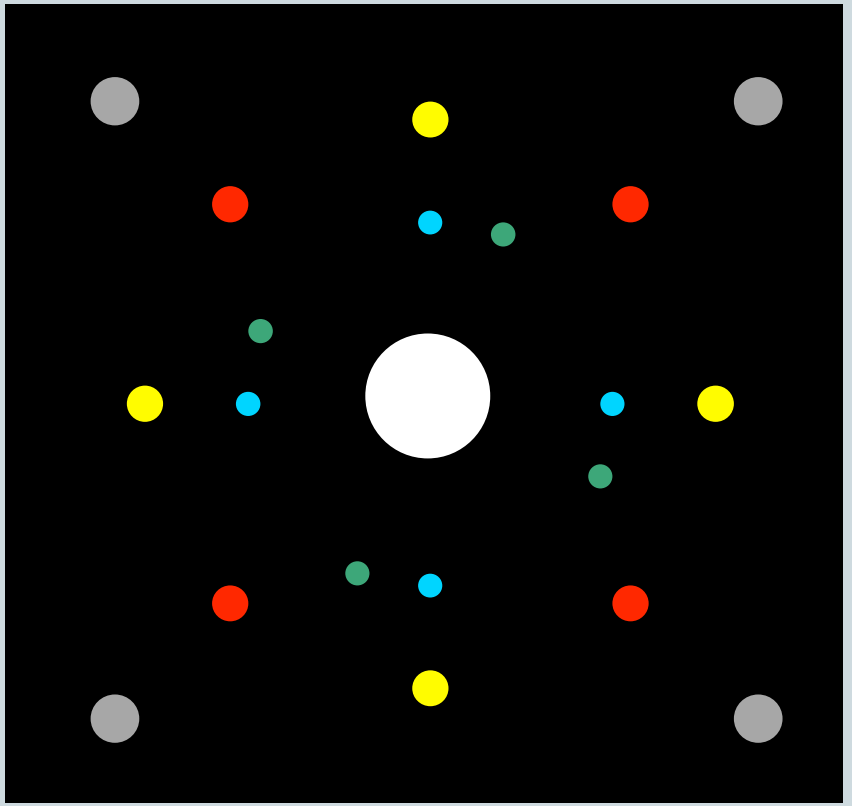


Plano Focal

Experimento Mental

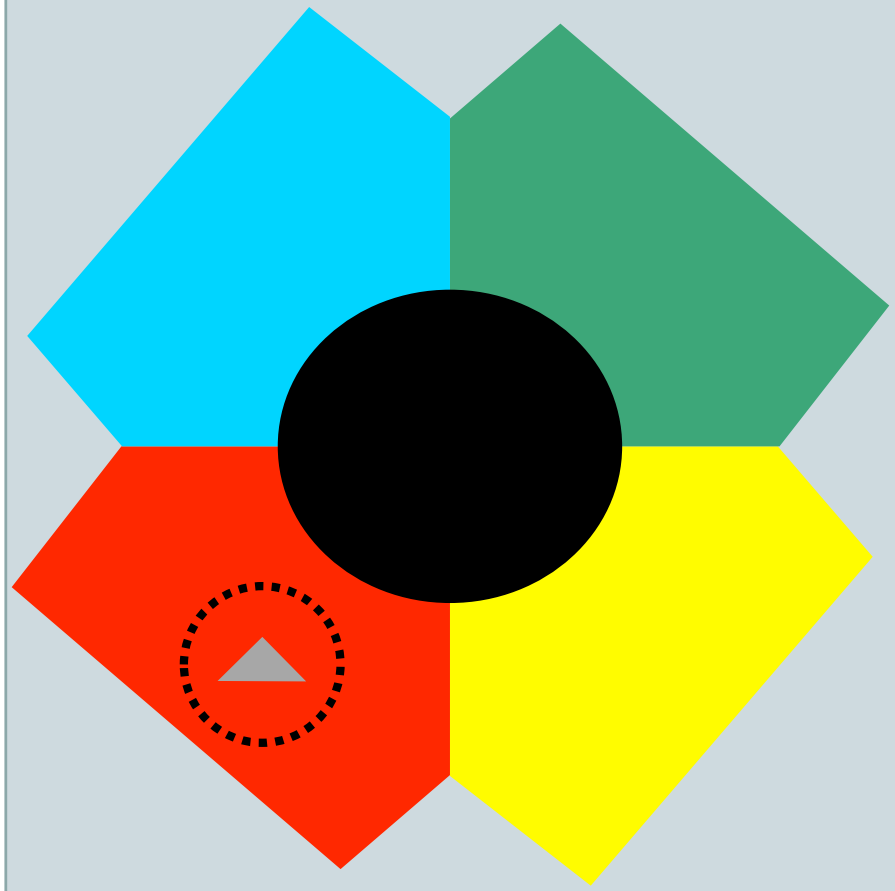


Plano Imagem

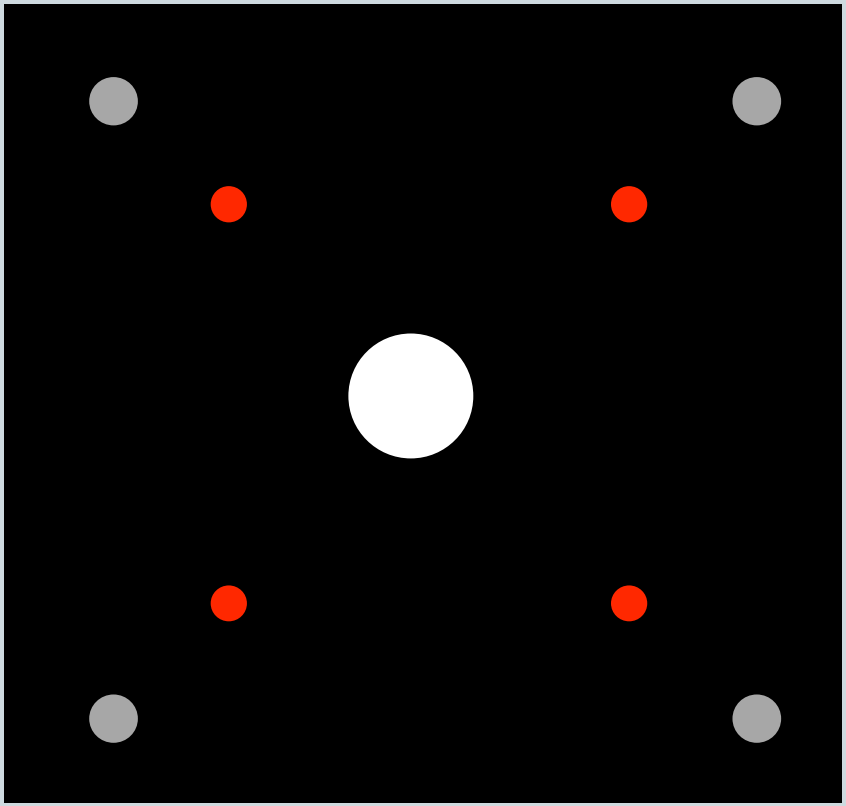


Plano Focal

Experimento Mental

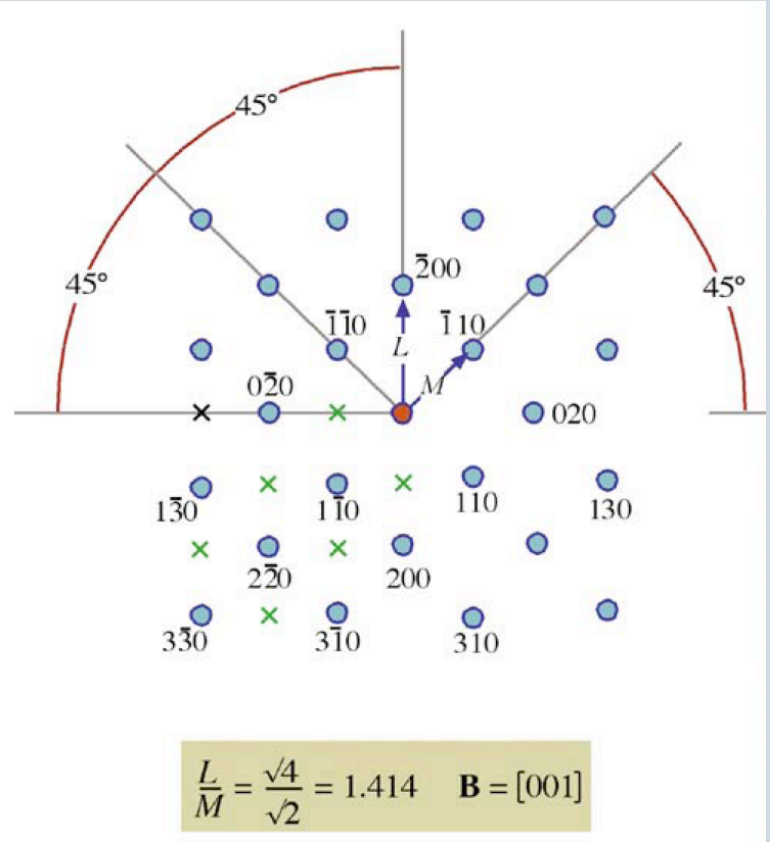


Plano Imagem

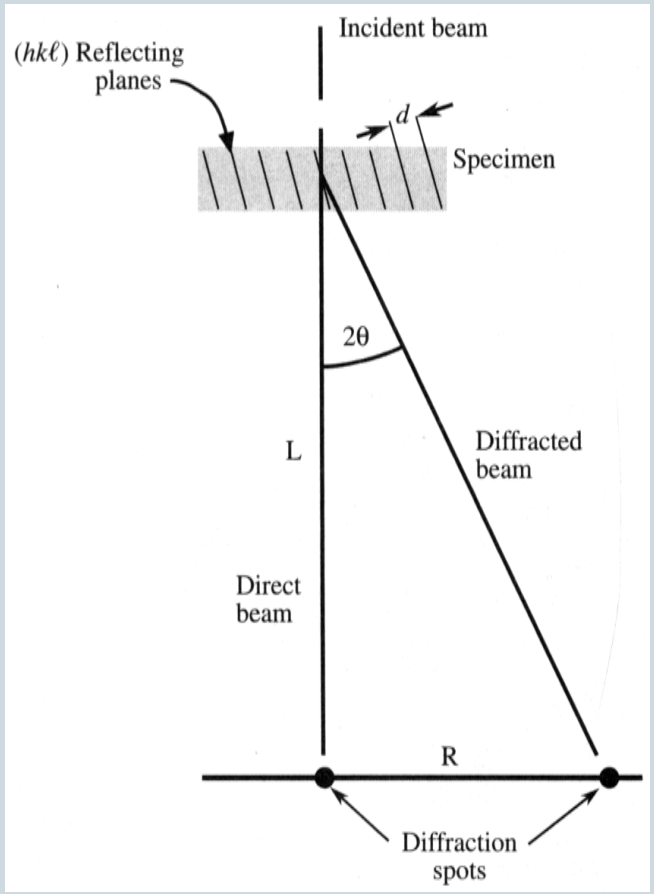


Plano Focal

Identificação da Figura de Difração



$$Rd = L\lambda$$



Williams e Carter

Figura de Difração

Material amorfo

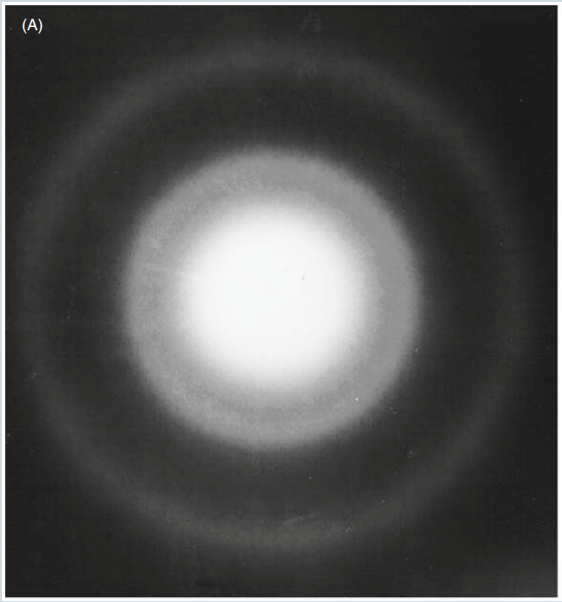


Figura de difração de policristais

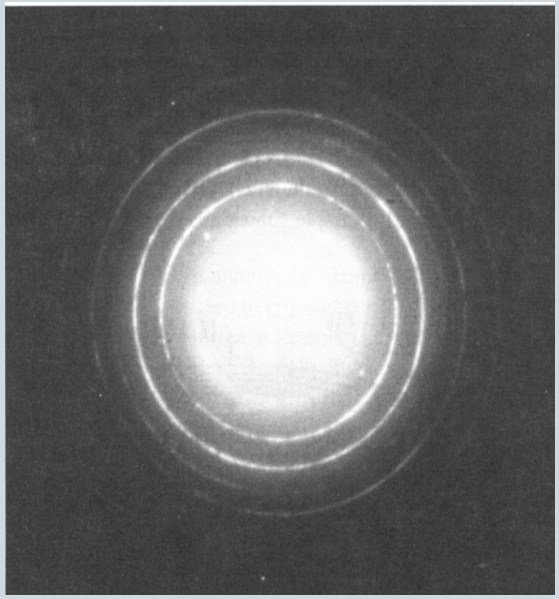
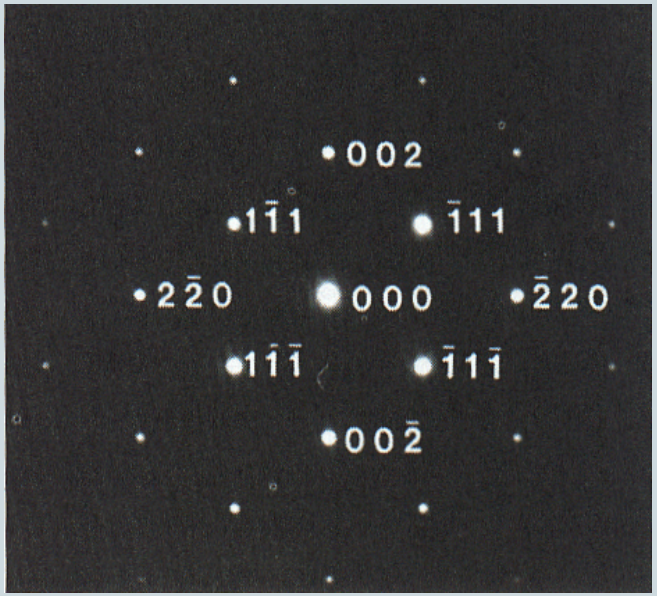


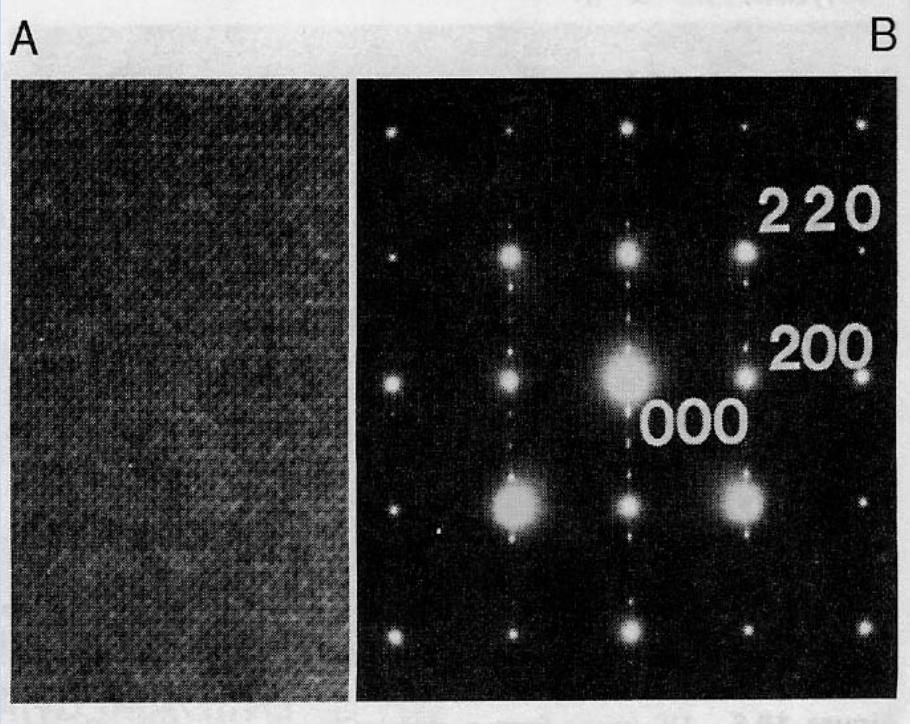
Figura de difração de um monocristal



Williams e Carter

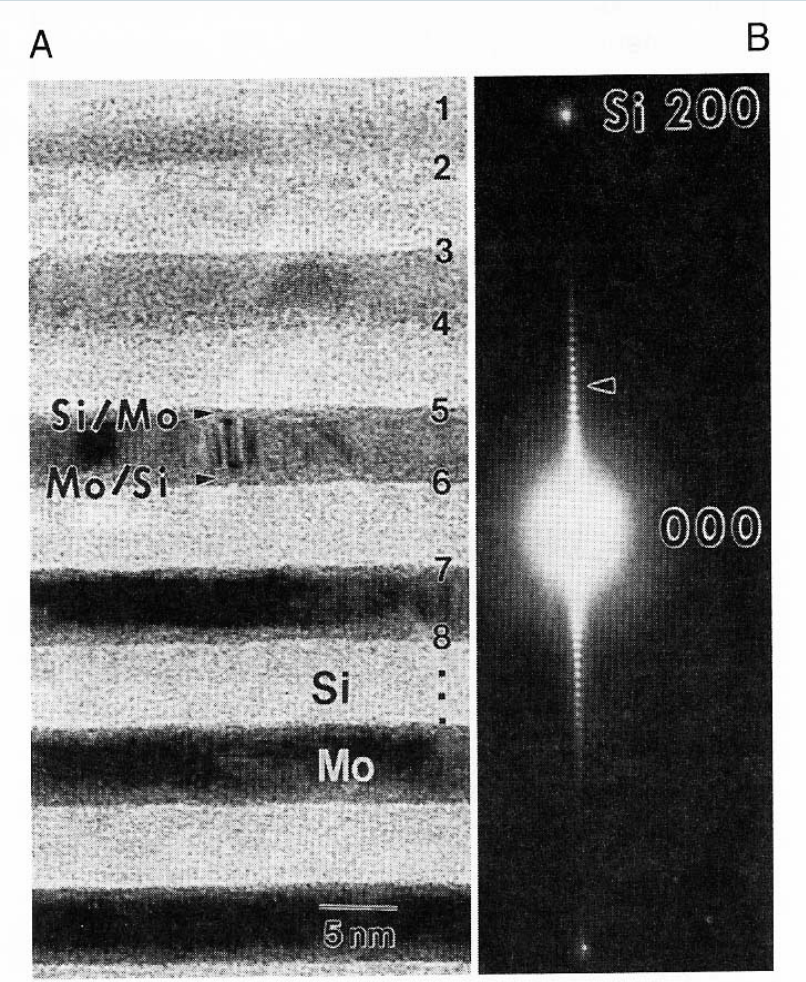
Difração de Superredes

Estrutura artificial $GaAs/Al_xGa_{1-x}$



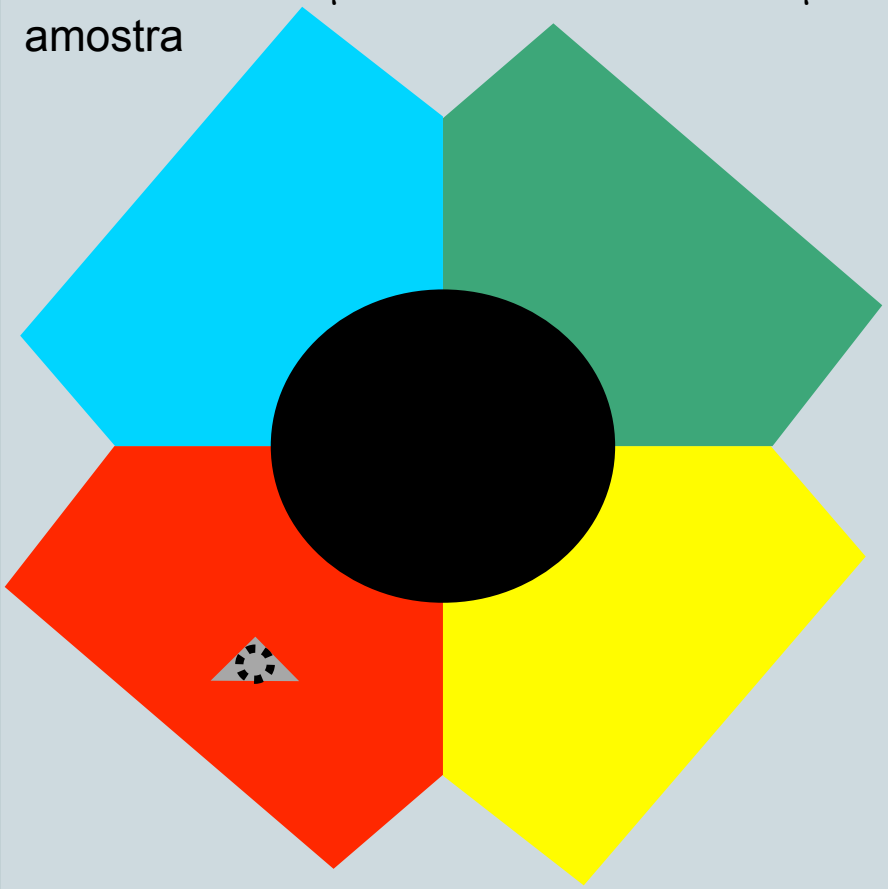
Williams e Carter

Superrede artificial de Si e Mo



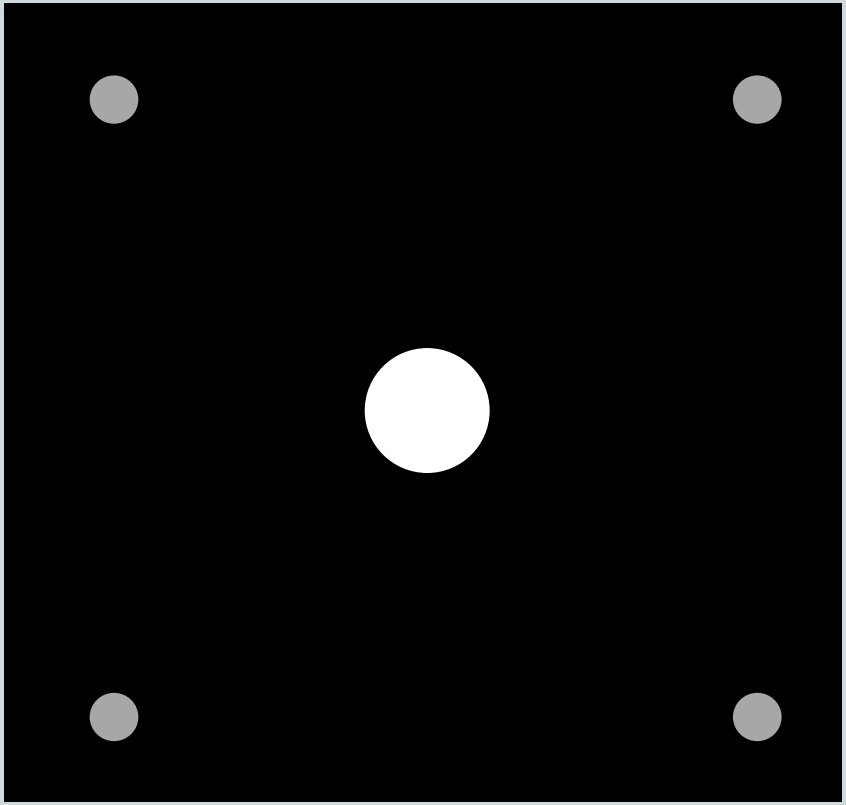
Resolução Espacial

Abertura SAD no plano Imagem
Aumento de aprox. 25x (M)
Abertura de 50 μm seleciona área de 2 μm na amostra



Plano da Amostra

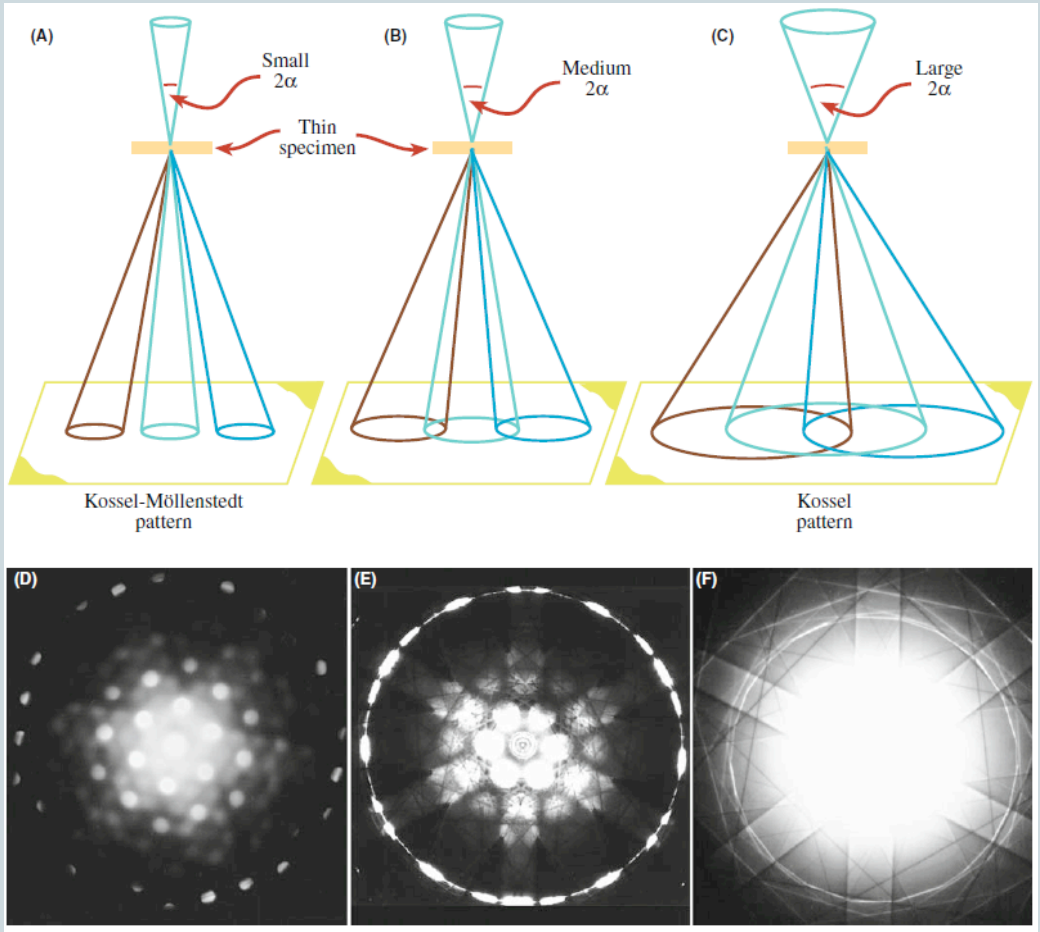
Menor abertura ~ 10 μm
Resolução ~0,5 μm



Plano Focal

Feixe Convergente

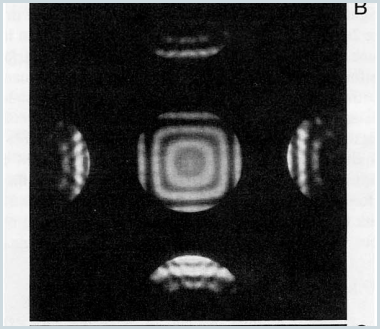
Variação do ângulo de convergência

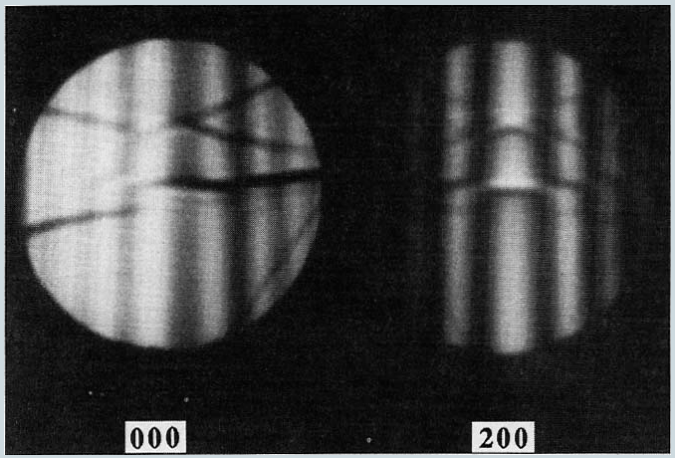


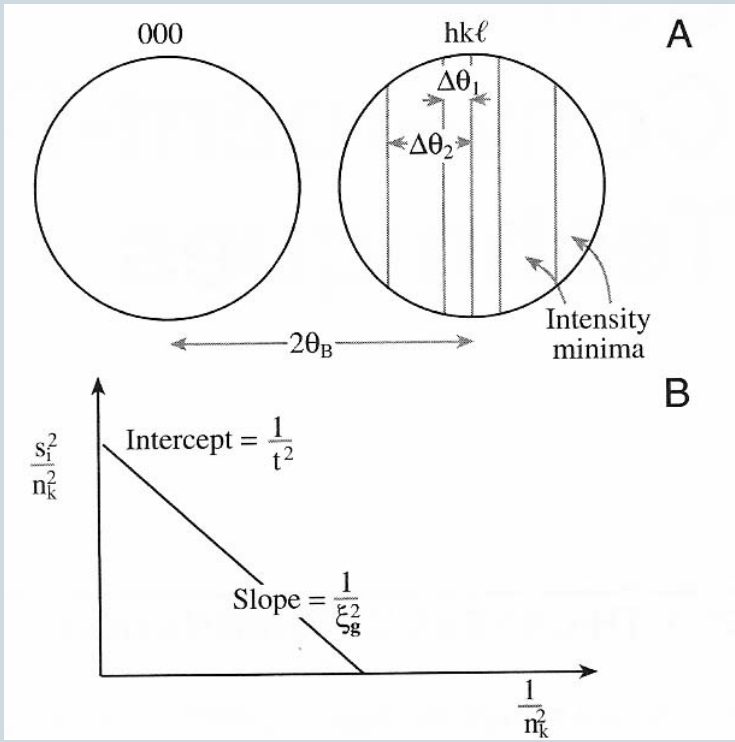
Williams e Carter

Feixe Convergente

- Franjas de Kossel-Möllenstedt (K-M) permitem a determinação da espessura

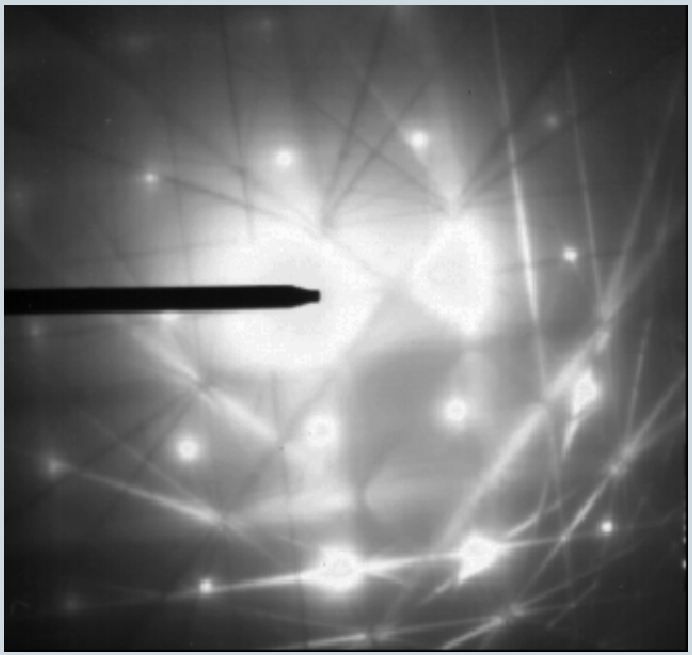


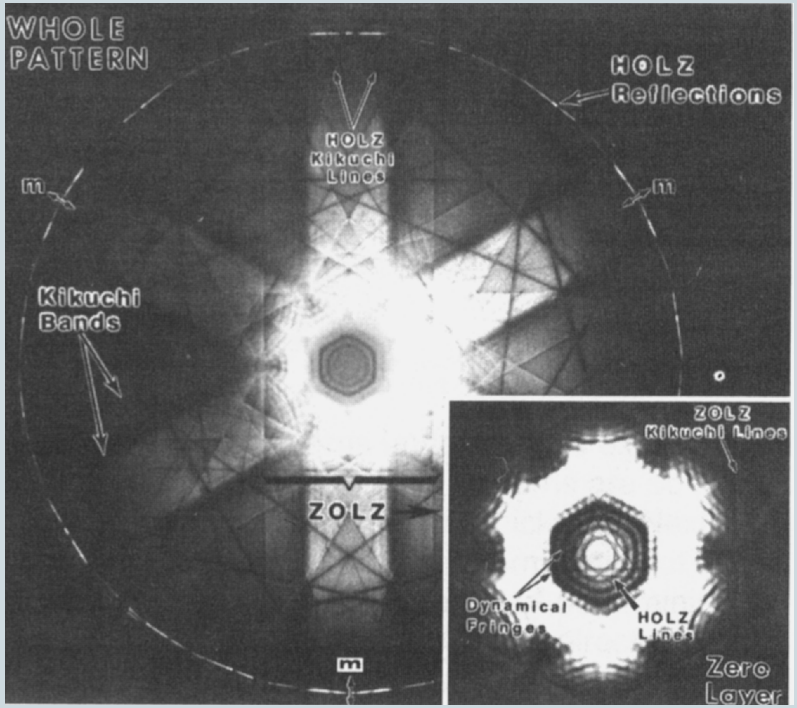




Feixe Convergente

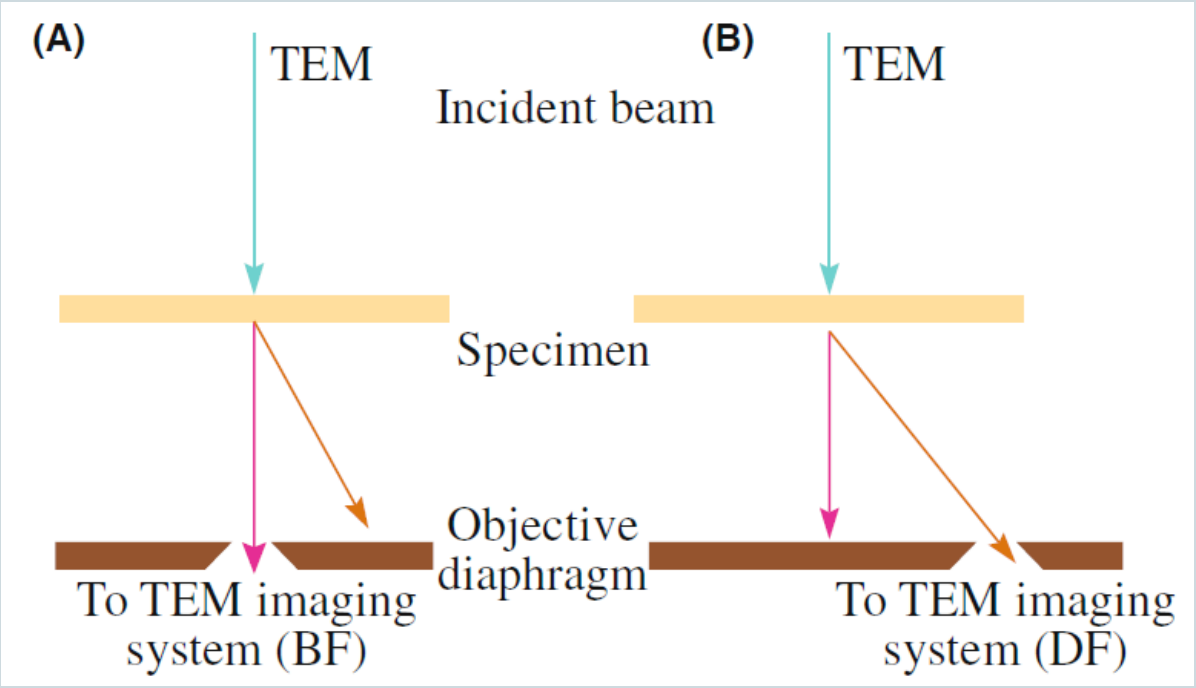
Precisão angular ~0,1º





Williams e Carter

Campo Claro e Campo Escuro

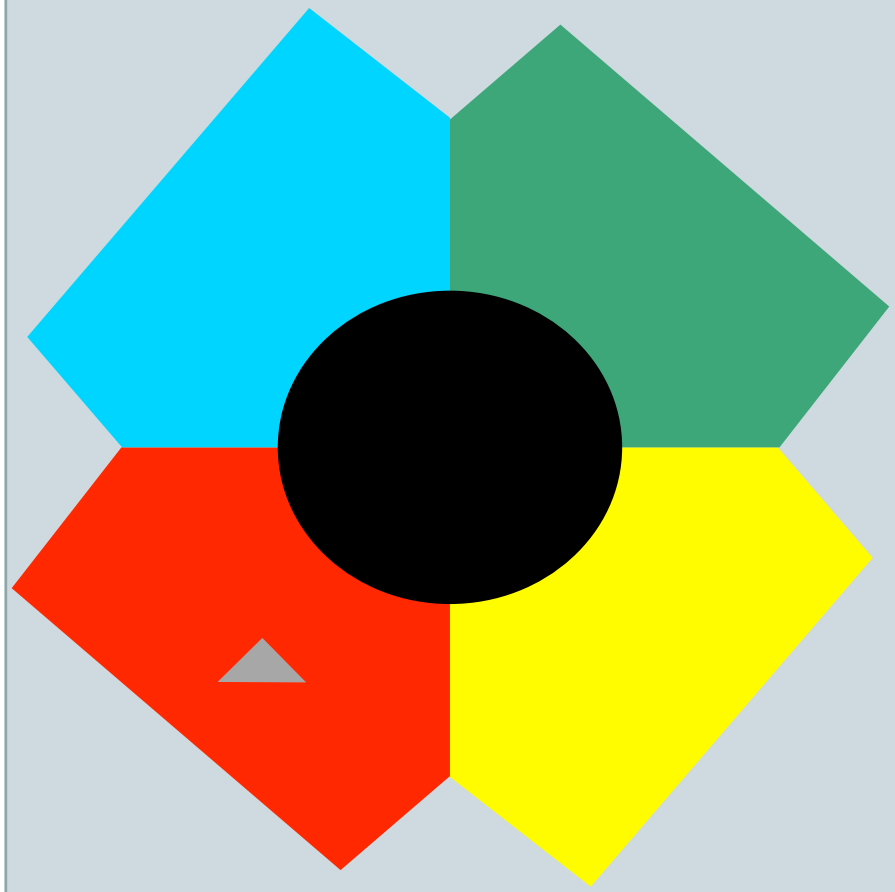




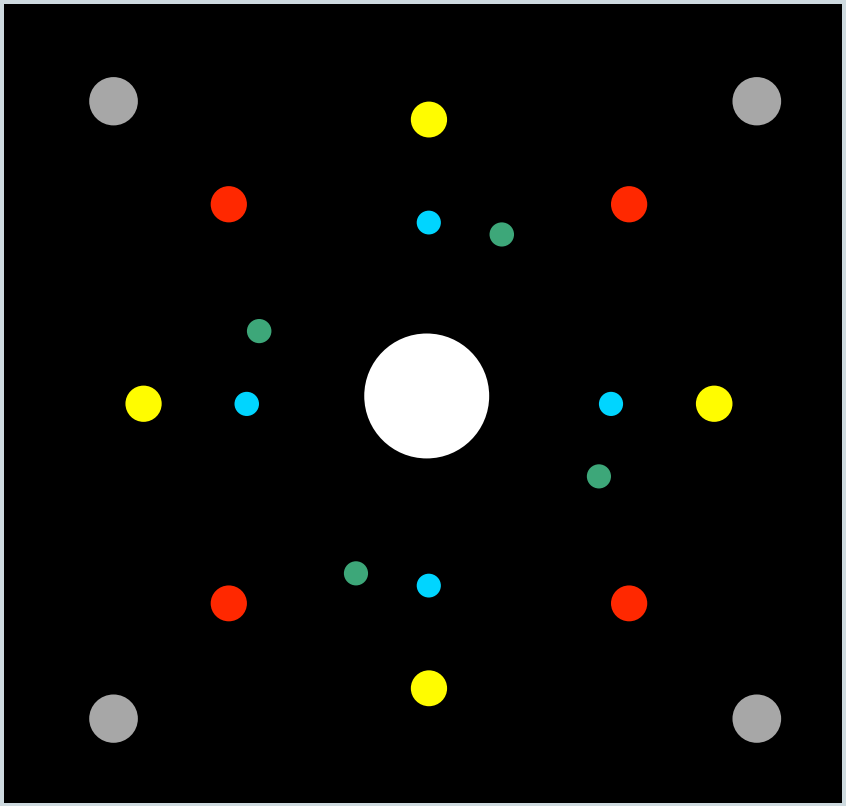
Williams e Carter

Campo Claro: Toda imagem que inclui o feixe direto
Campo Escuro: Toda imagem que deixa de incluir o feixe direto

Experimento Mental

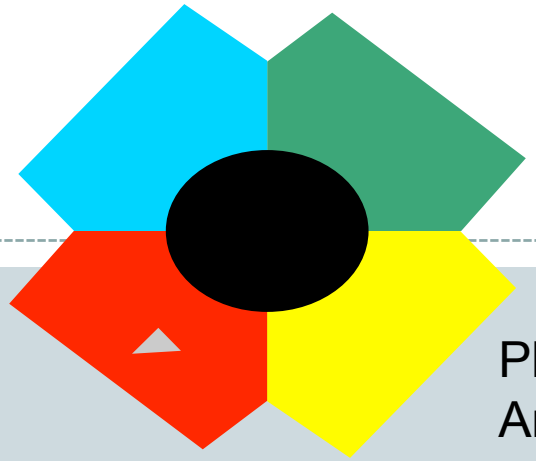


Plano da Amostra

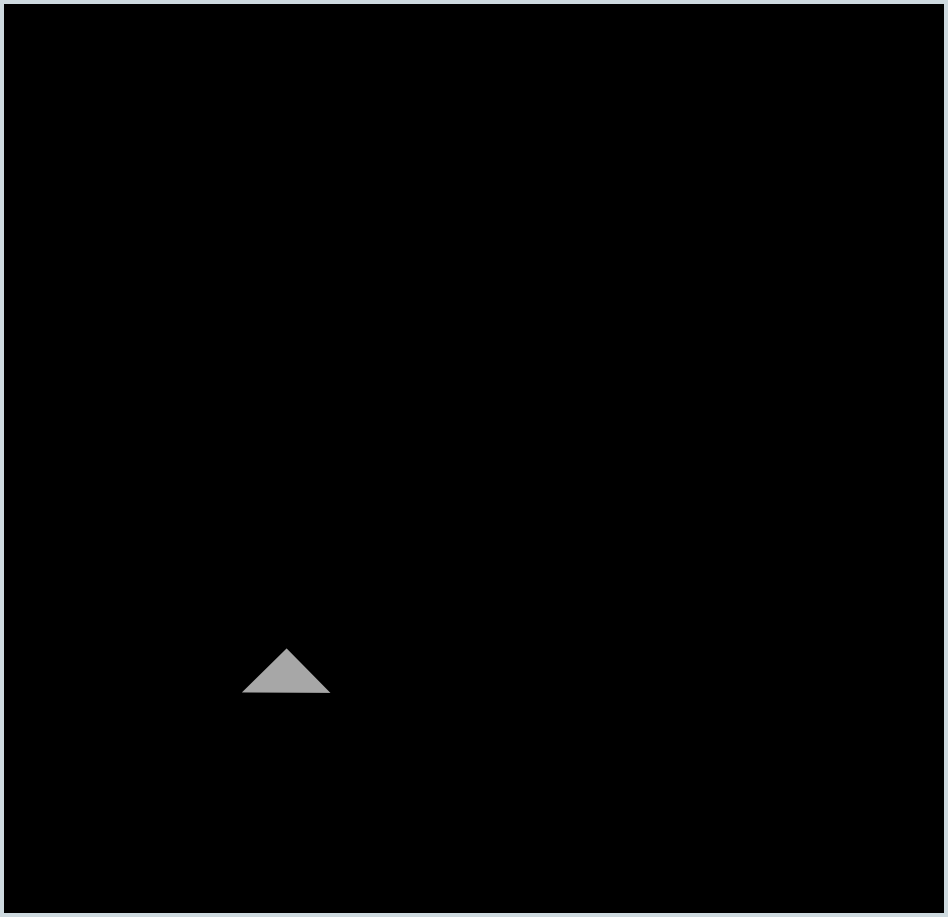


Plano Focal

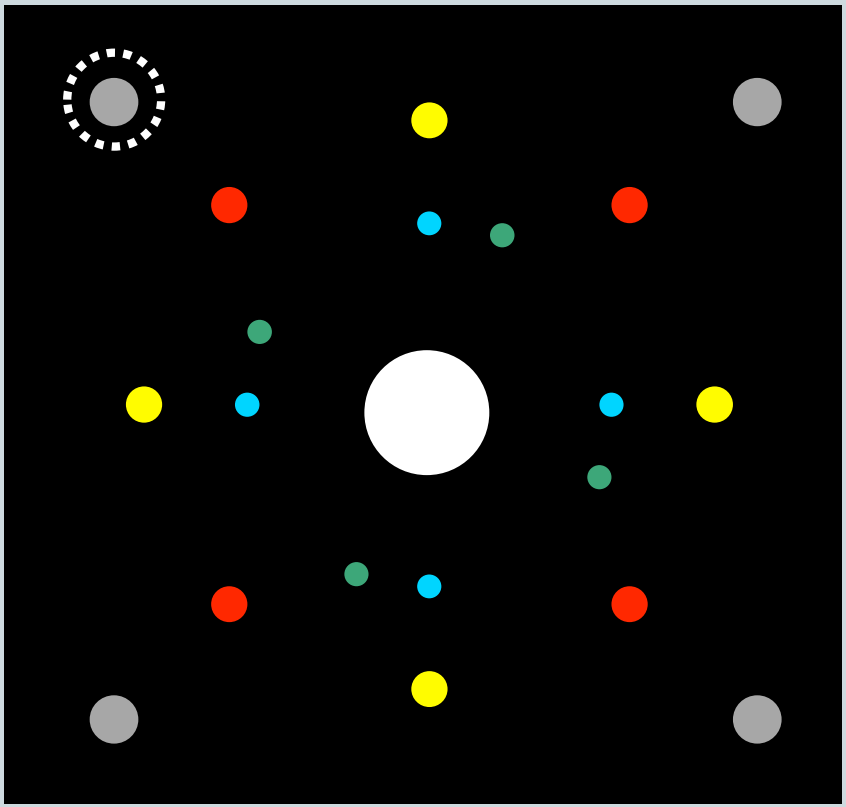
Experimento Mental



Plano da Amostra

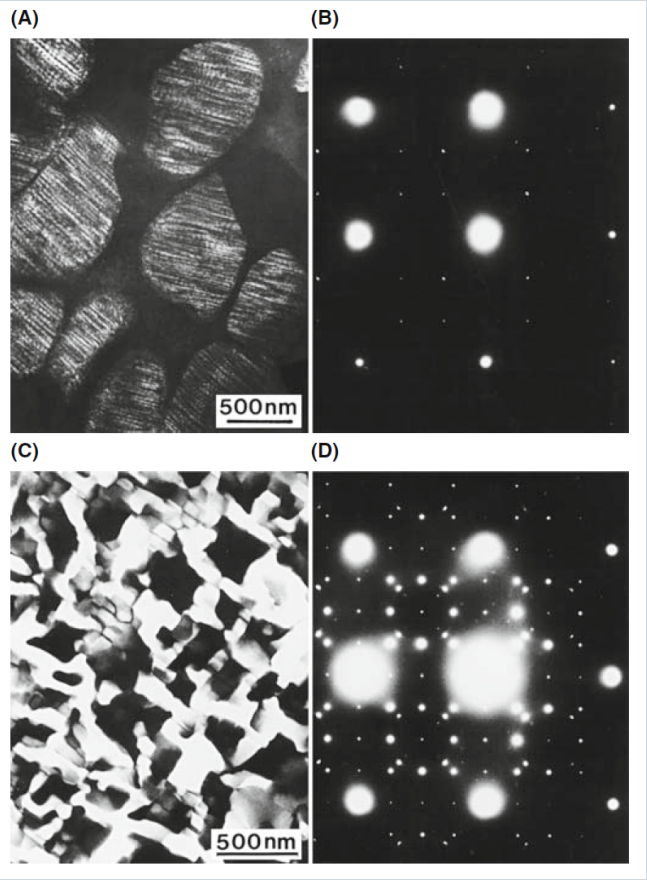


Plano Imagem

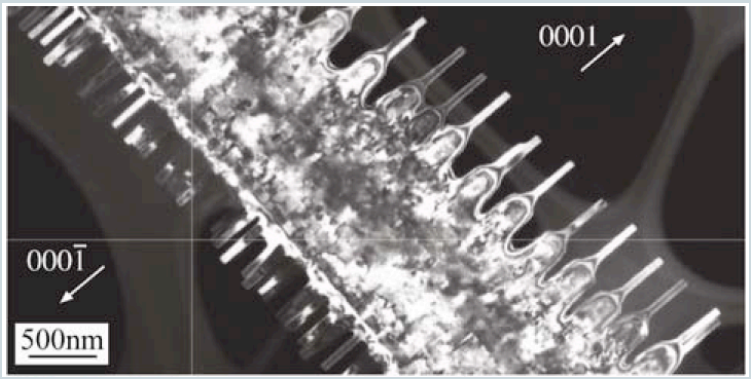


Plano Focal

Campo Escuro



Precipitado V_6C_5 e seu padrão de difração.

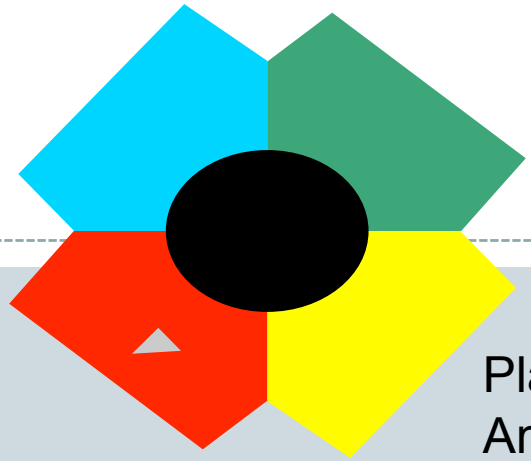


Nanoestrutura de ZnO

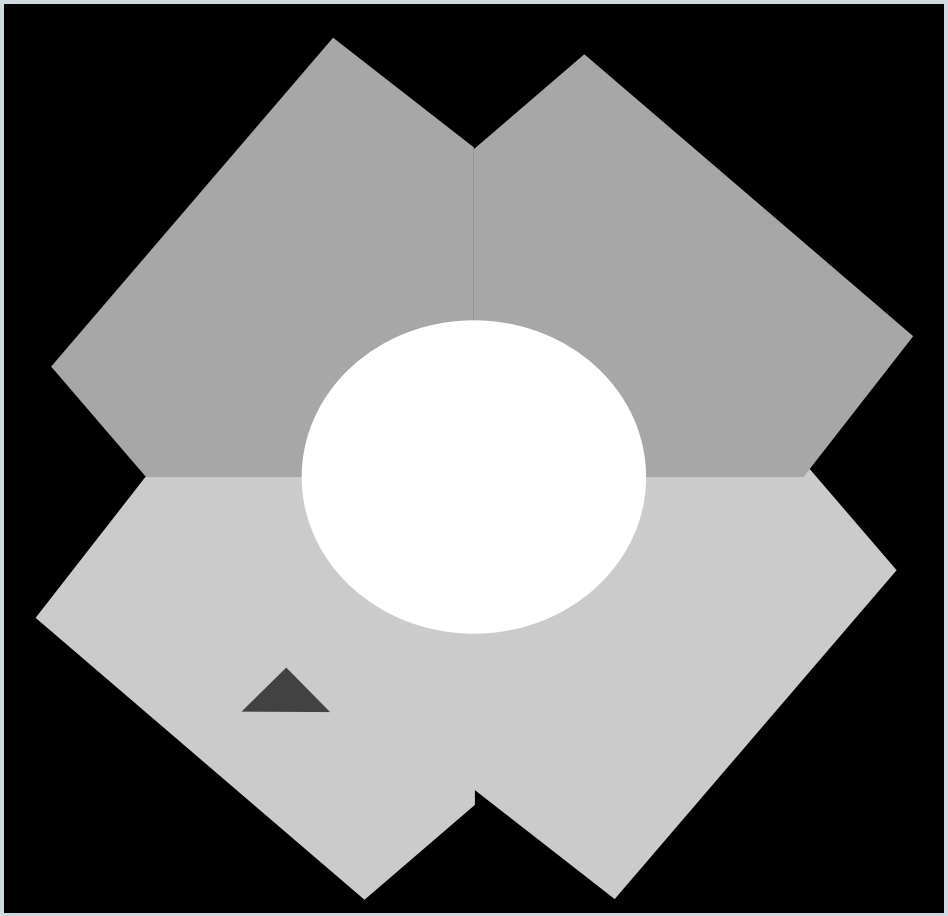
Precipitado V_8C_7 e seu padrão de difração.

Williams e Carter

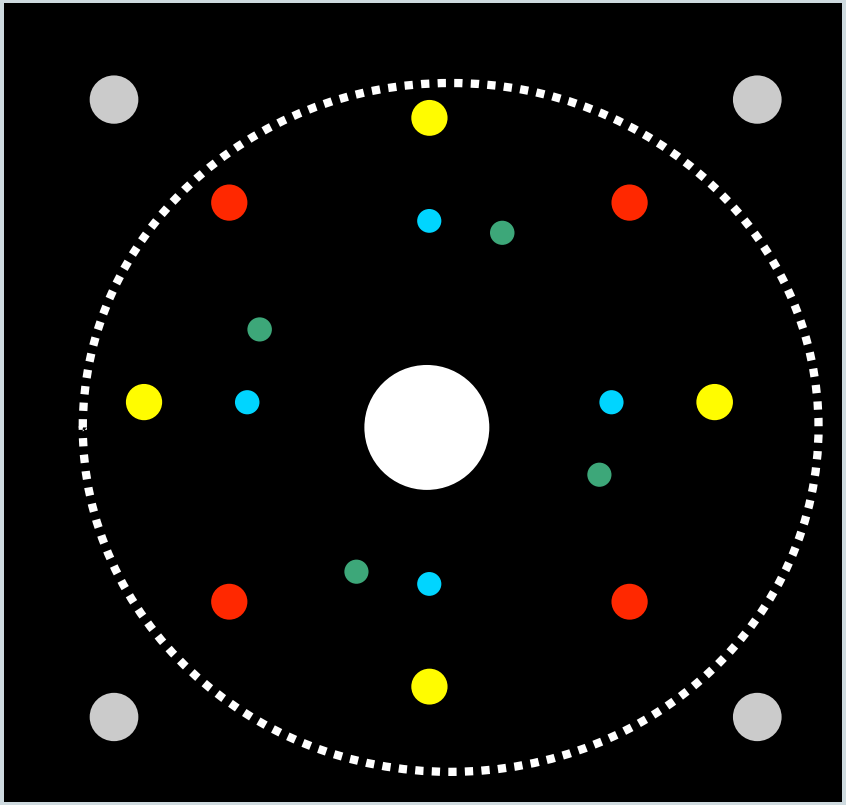
Experimento Mental



Plano da Amostra

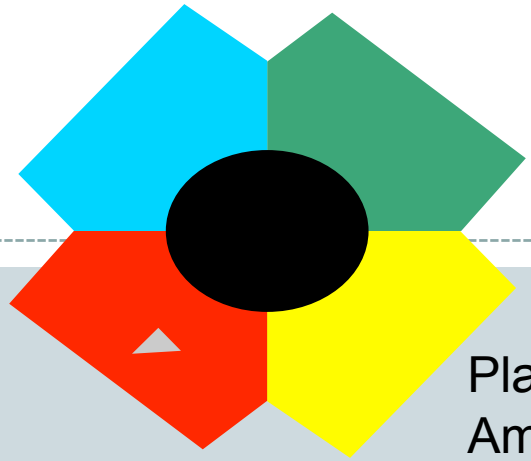


Plano Imagem

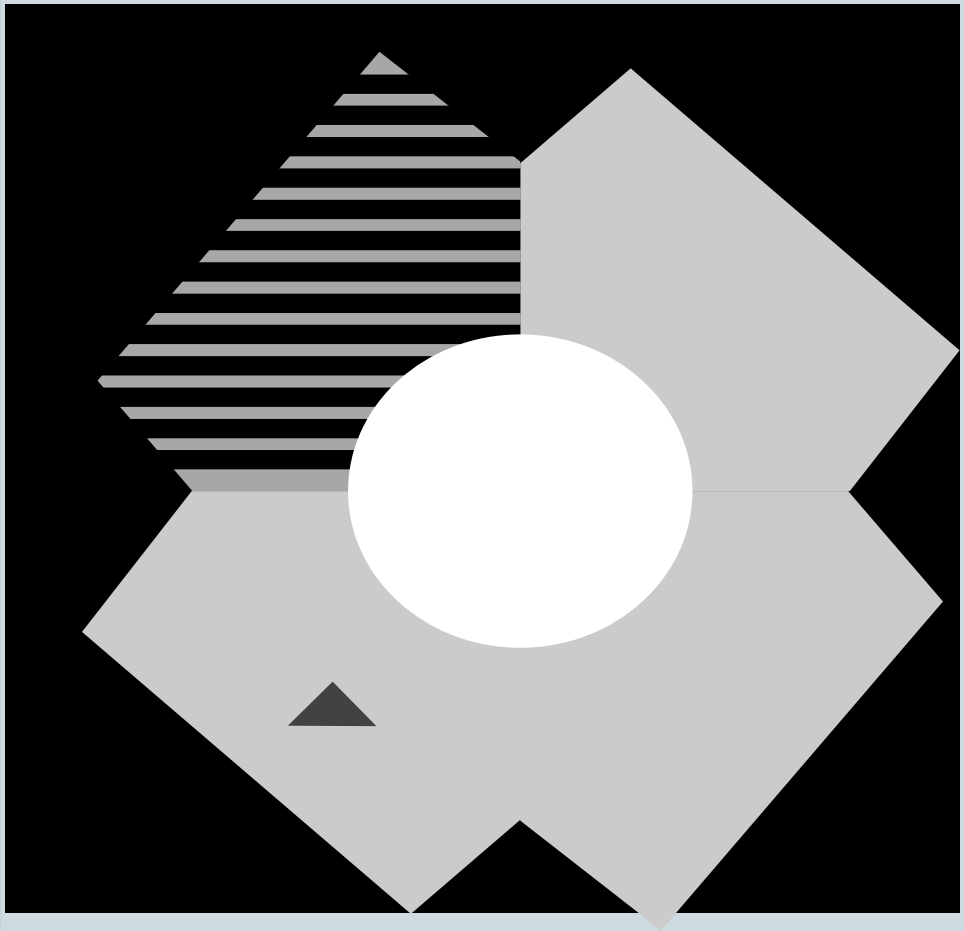


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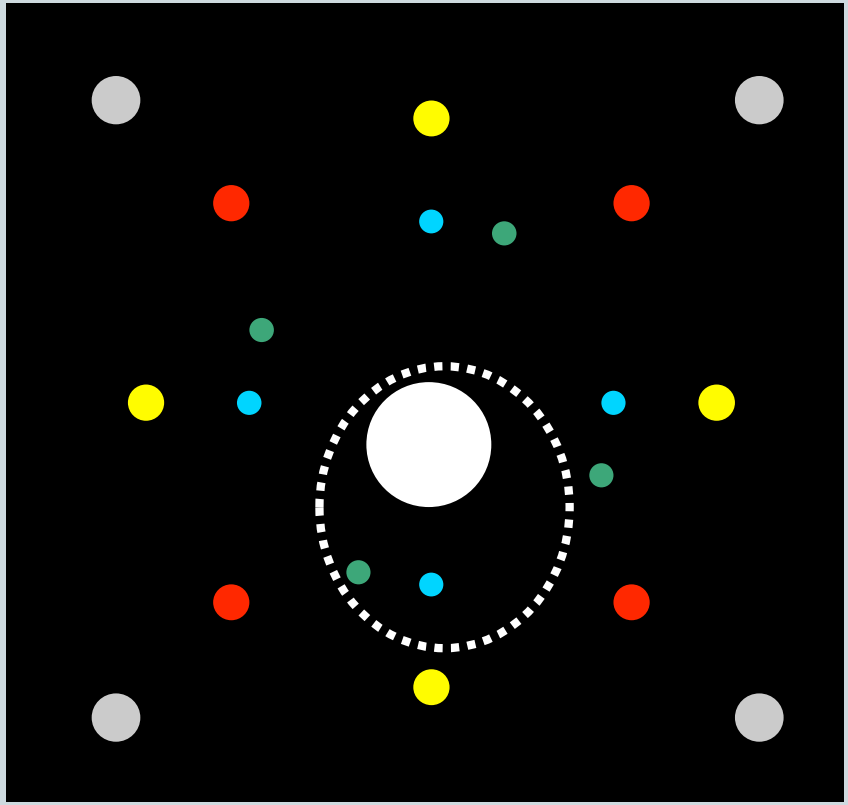
Experimento Mental



Plano da Amostra

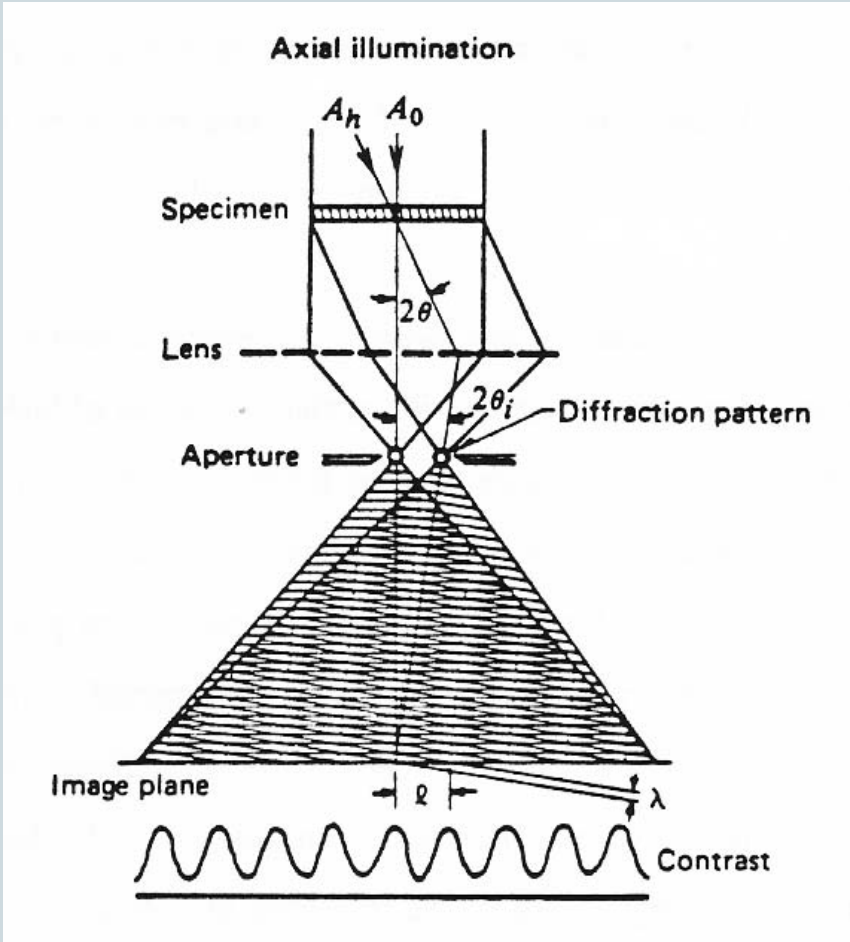


Plano Imagem



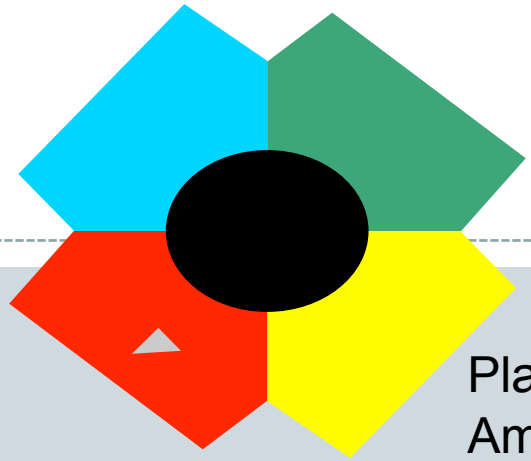
Plano Focal

Contraste de Fase

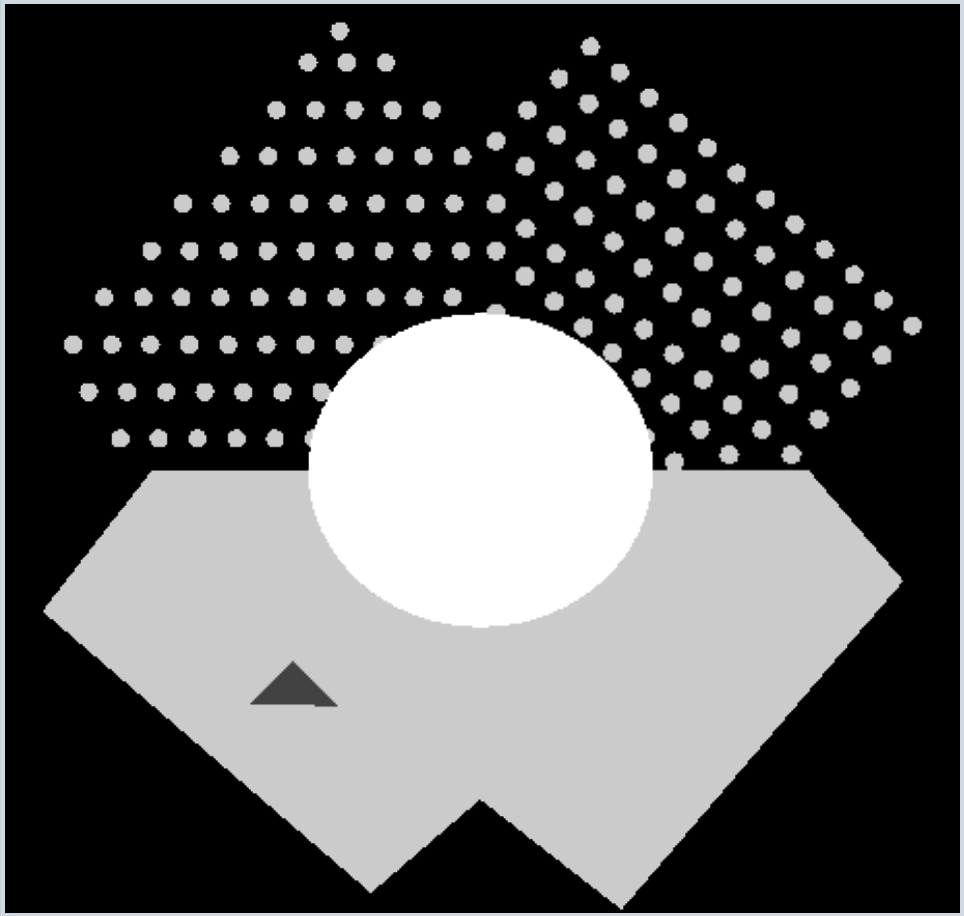


Jeol

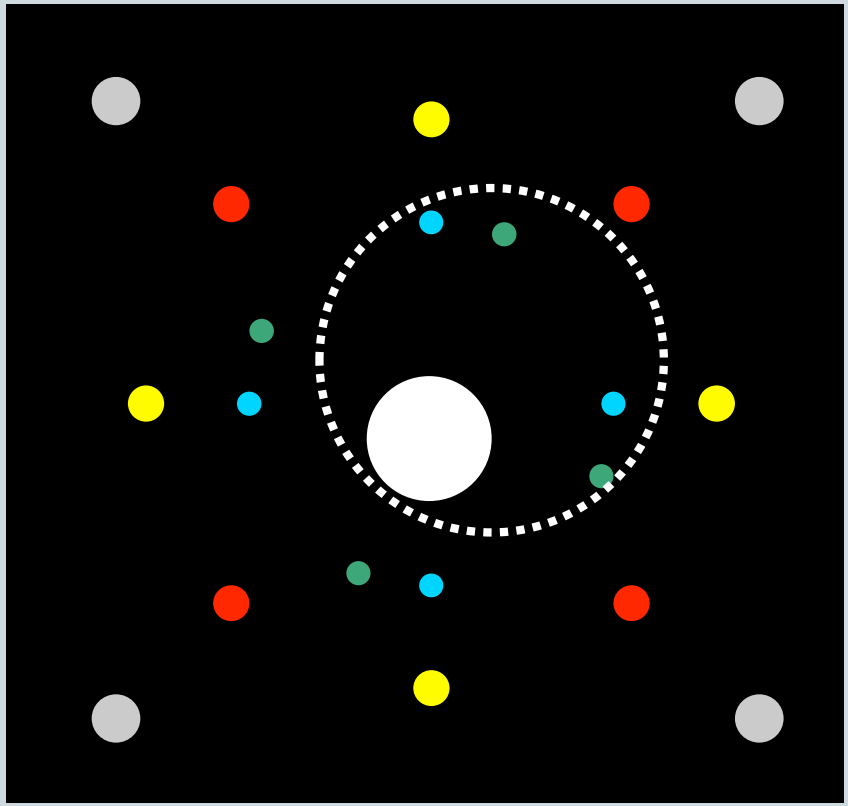
Experimento Mental



Plano da Amostra

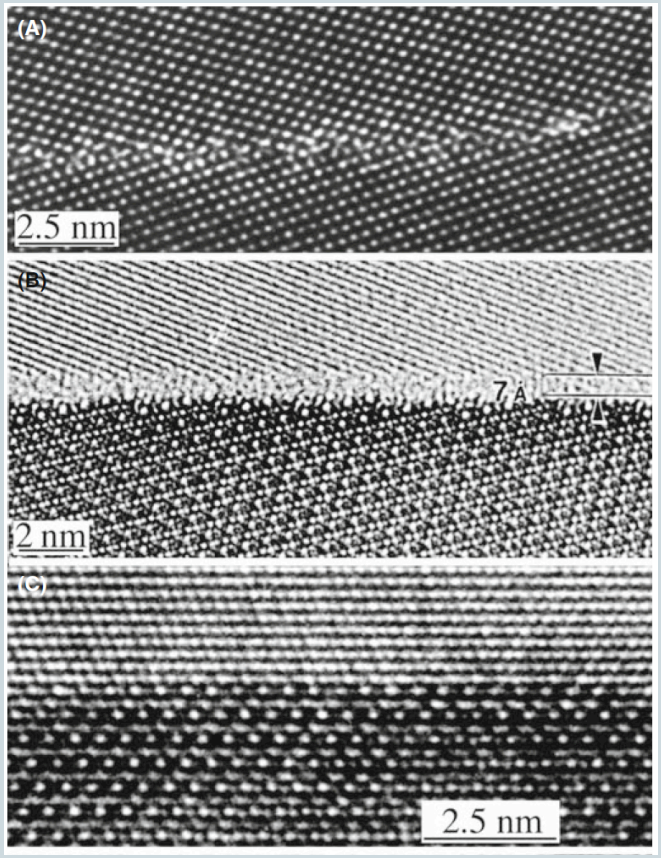


Plano Imagem



Plano Focal

HRTEM



CG em Ge

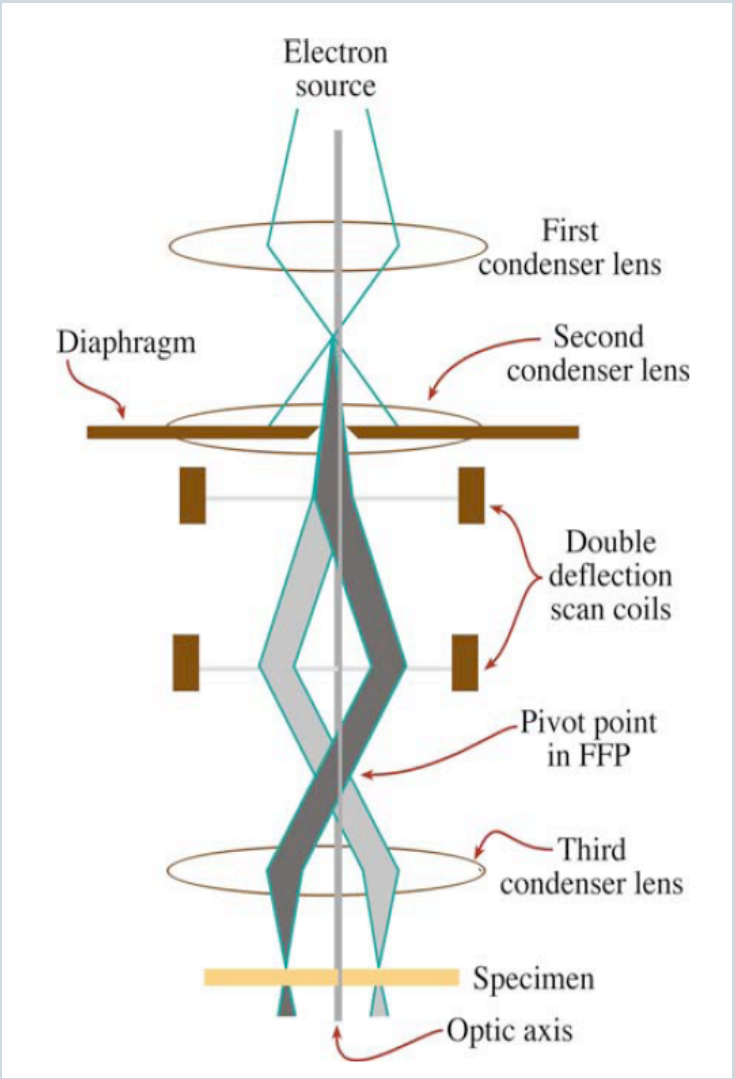
CG em Si_3N_4 com camada amorfa

Interface entre NiO e $NiAl_2O_4$

Williams e Carter

STEM

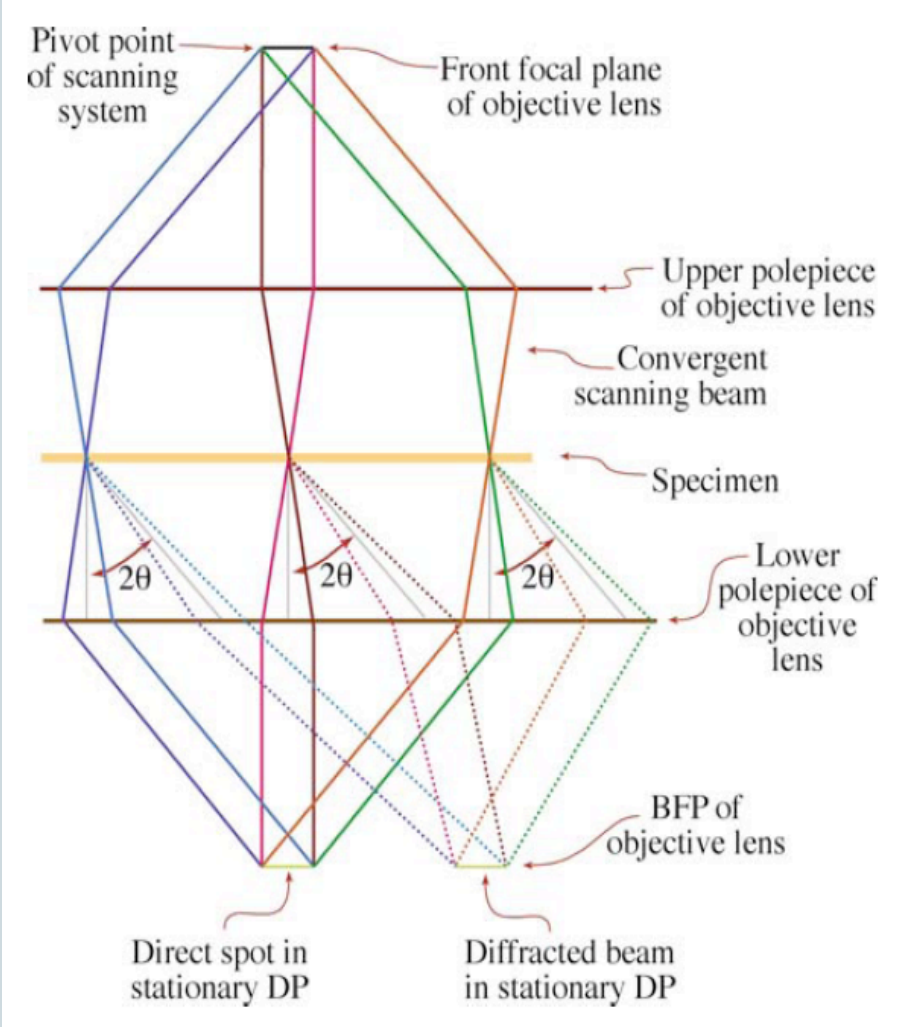
No STEM, um feixe convergente tão pequeno quanto possível varre a amostra sem variação de inclinação simulando a incidência paralela de um TEM.



Williams e Carter

STEM

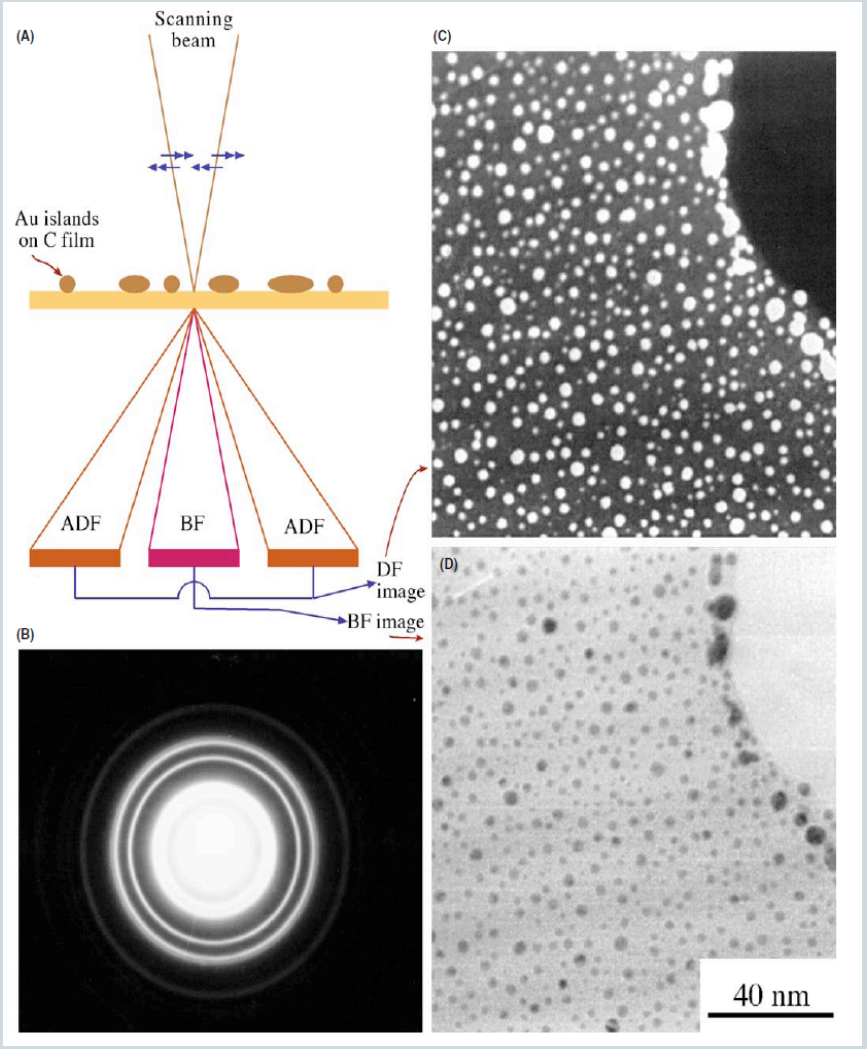
Um detector de elétrons pode ser colocado no plano focal posterior ou em algum de seus planos conjugados se o equipamento for operar como um TEM/STEM.



Williams e Carter

STEM

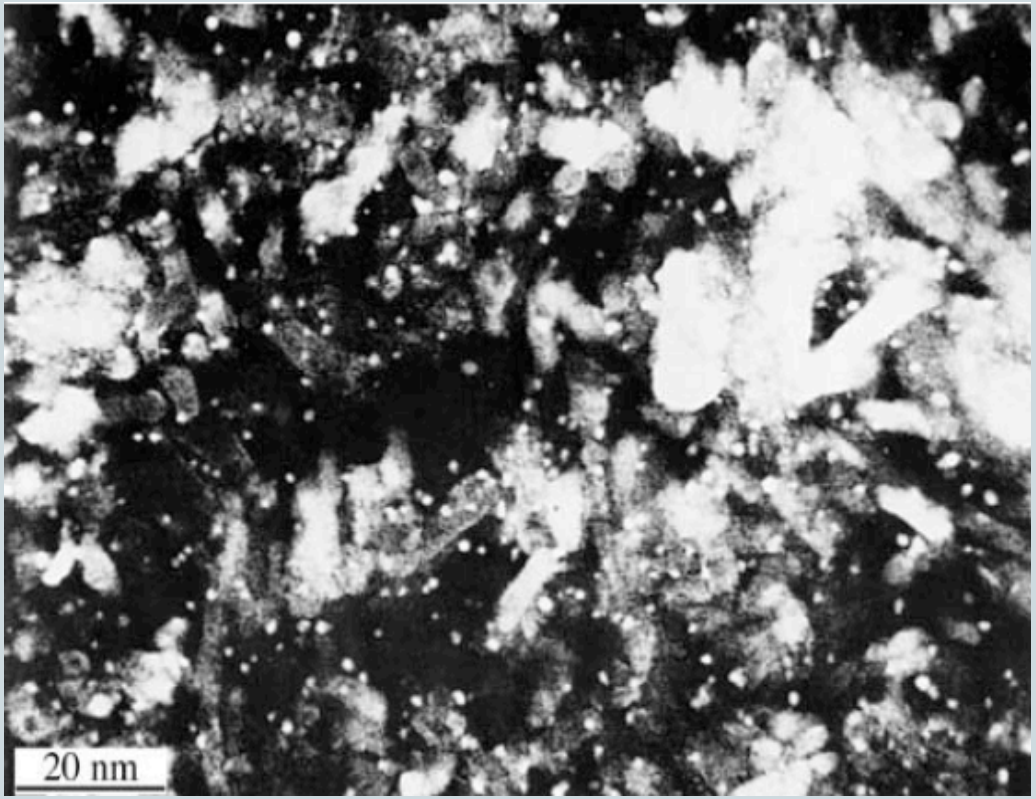
A realização de figura de campo claro ou escuro depende apenas da seleção do sinal de interesse.

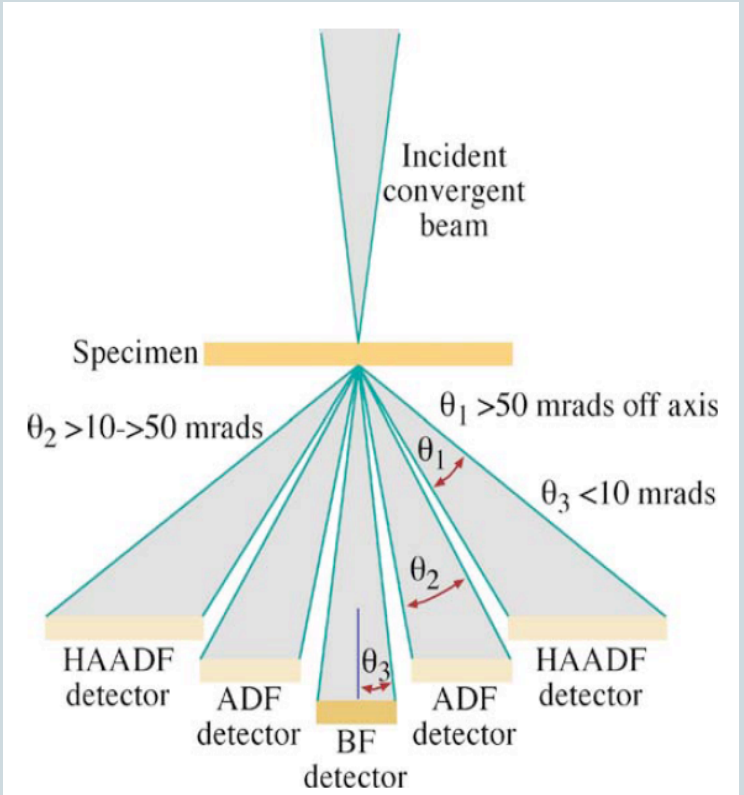


Williams e Carter

STEM

Platina em filme cristalino de Al_2O_3



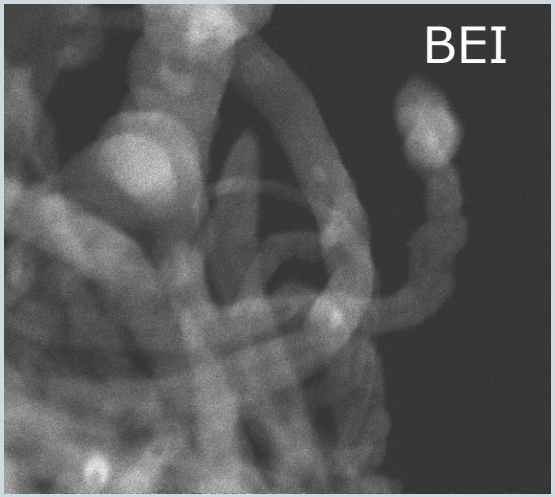


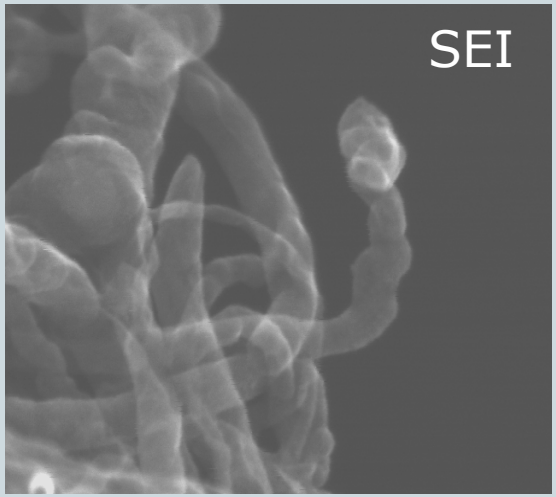
Williams e Carter

STEM

Specimen: Catalyst in the carbon nanotube

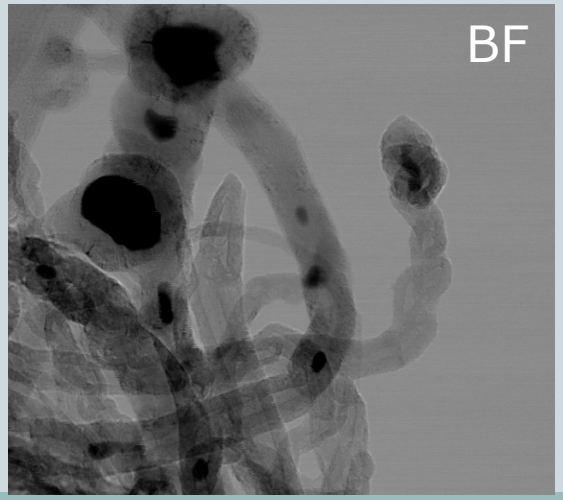
Surface morphology with composition signal

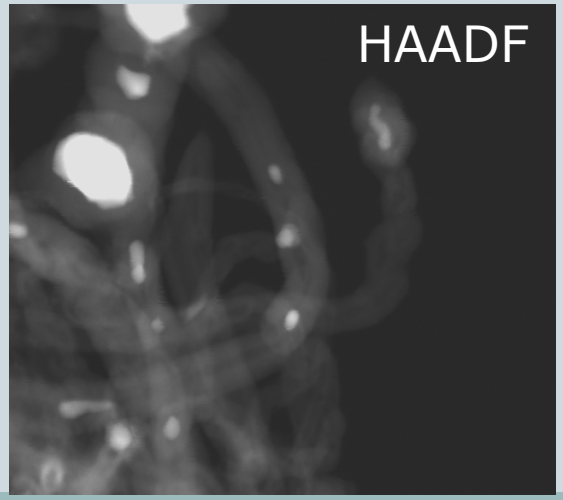




Surface morphology

Transmission





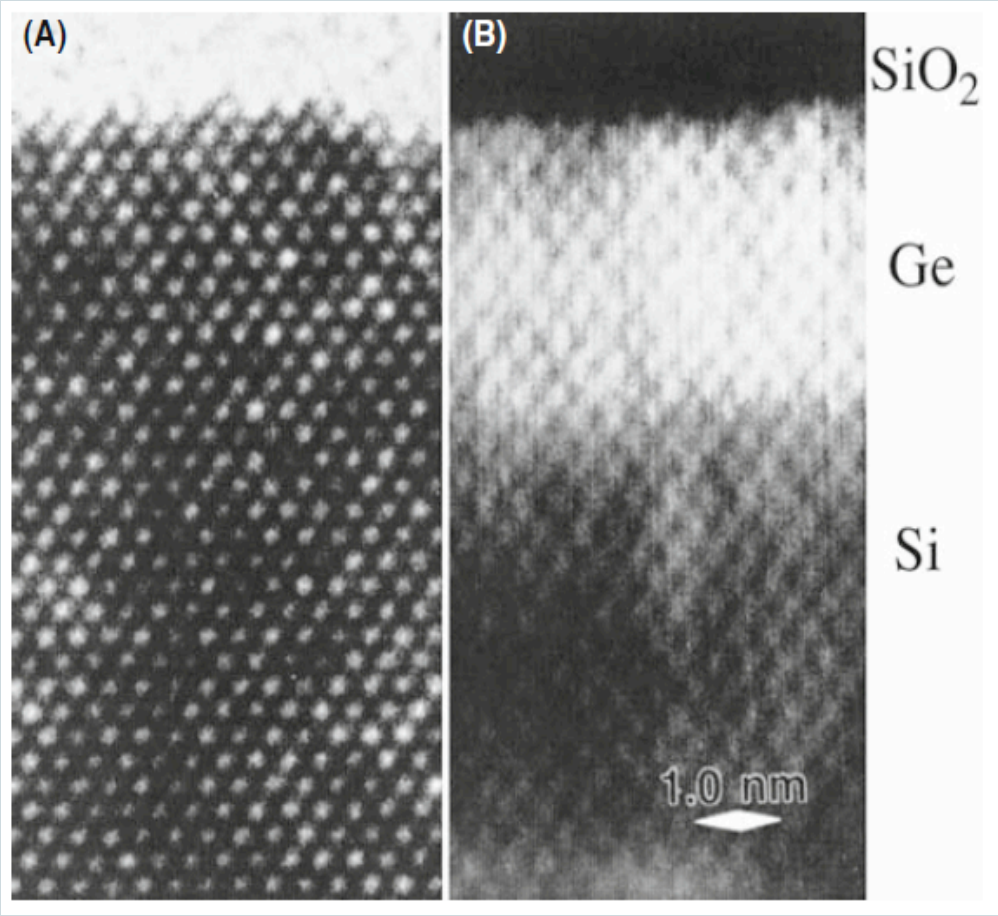
Z-contrast

Jeol

50 nm

STEM

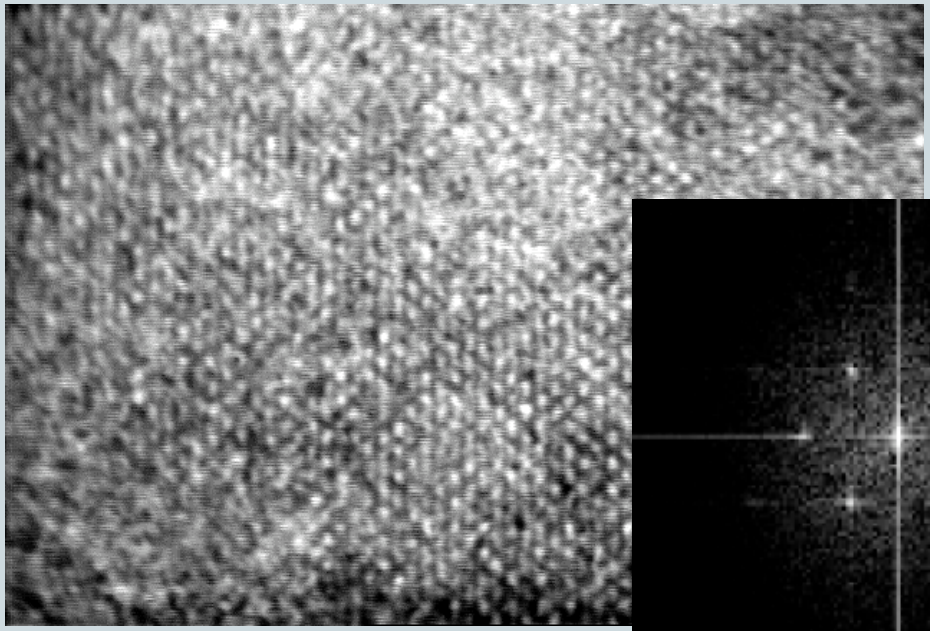
TEM
Contraste de fase



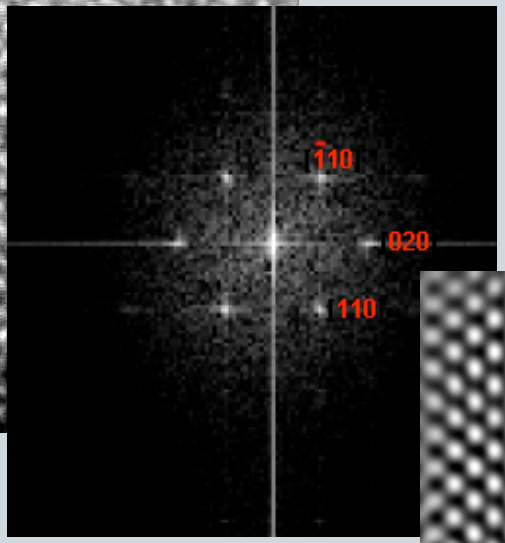
STEM
Contraste de Z

Williams e Carter

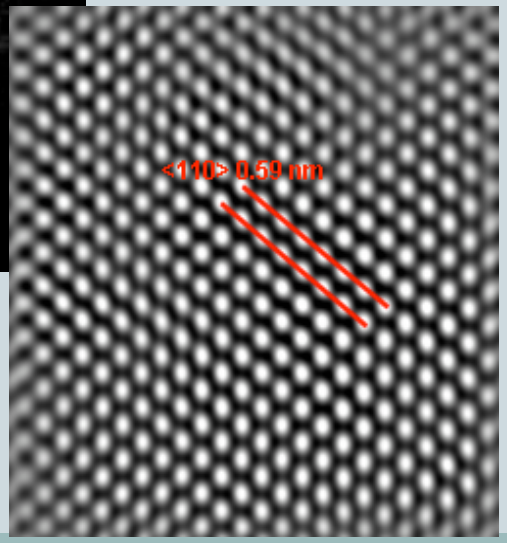
Refinamento por Transformada de Fourier



Micrografia de alta resolução de NbPo-VPO.



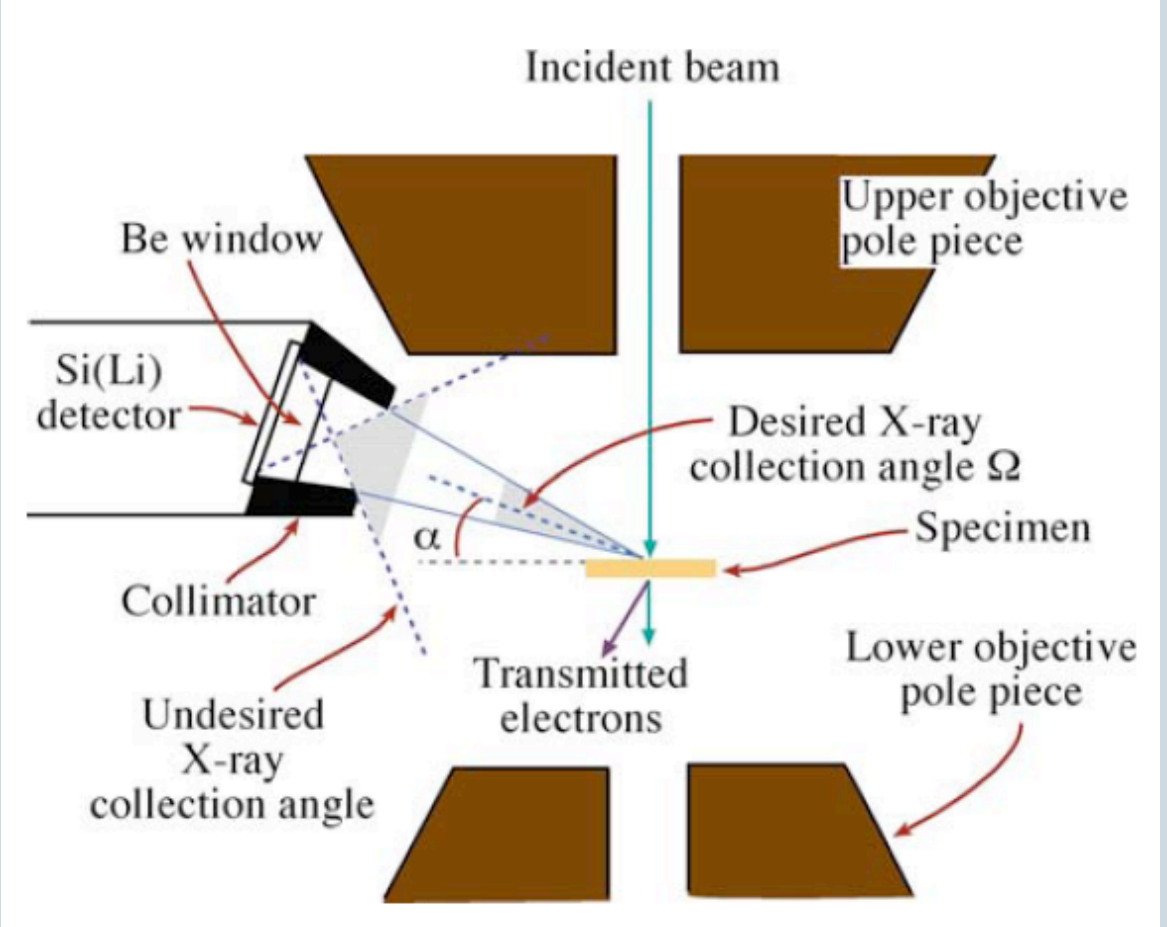
Transformada de Fourier (FFT).



Transformada de Fourier inversa filtrada.

Williams e Carter

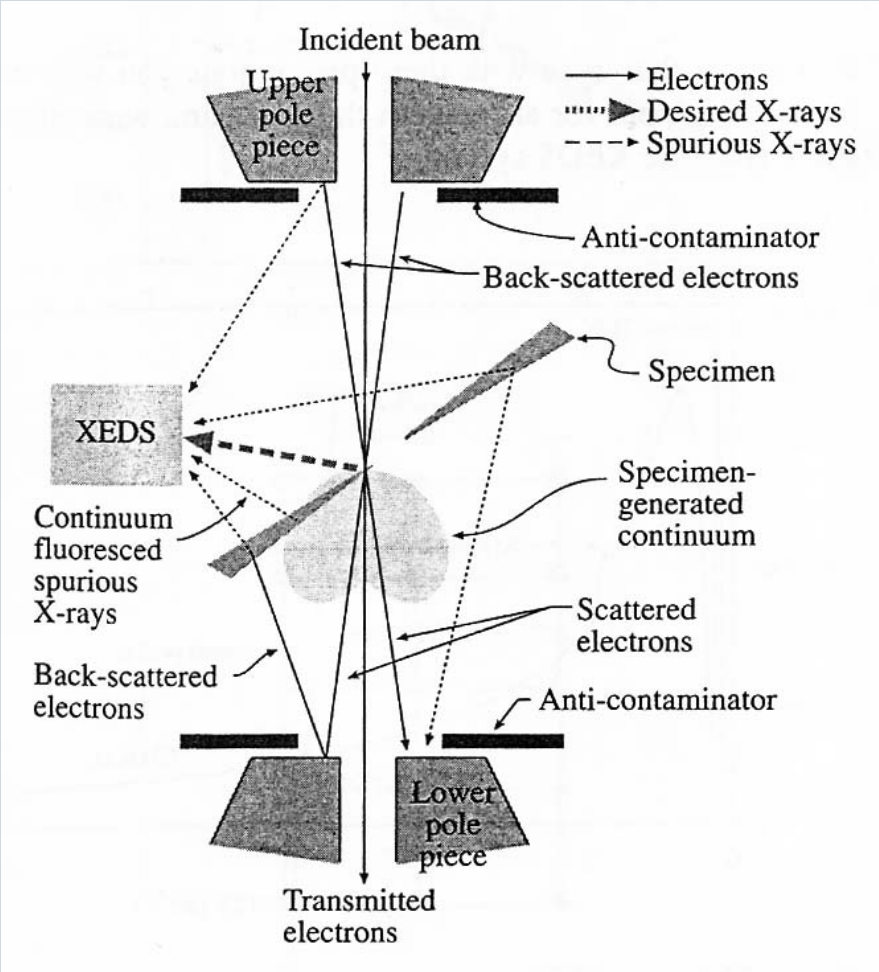
Detector de Raios X (EDS)



Williams e Carter

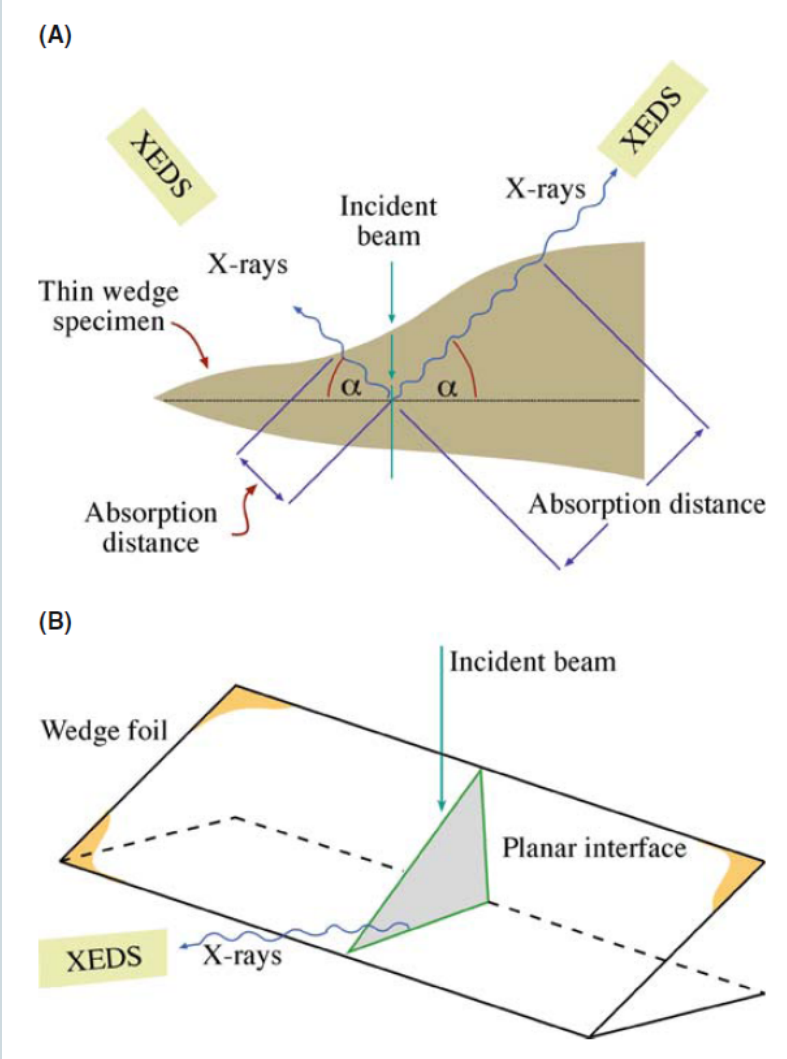
Sinais Espúrios

- Possíveis origens:
  - RX contínuo de alta energia e e^- não colimados podem gerar RX longe do pto de convergência (p/ minimizar: aberturas de Pt espessas e limpas)
  - Espalhamento pela amostra (p/ minimizar: 0º de inclinação, amostra fina e s/ AO)



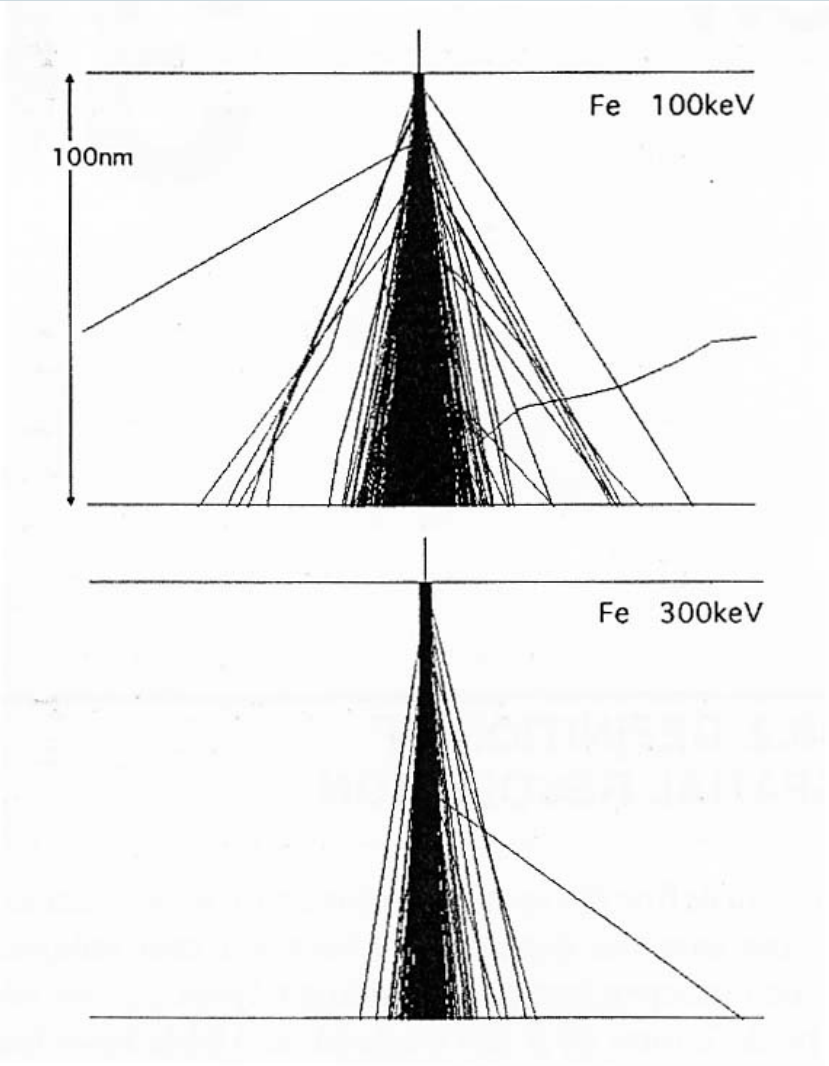
Williams e Carter

Posição Amostra/Detector



Williams e Carter

Resolução Espacial

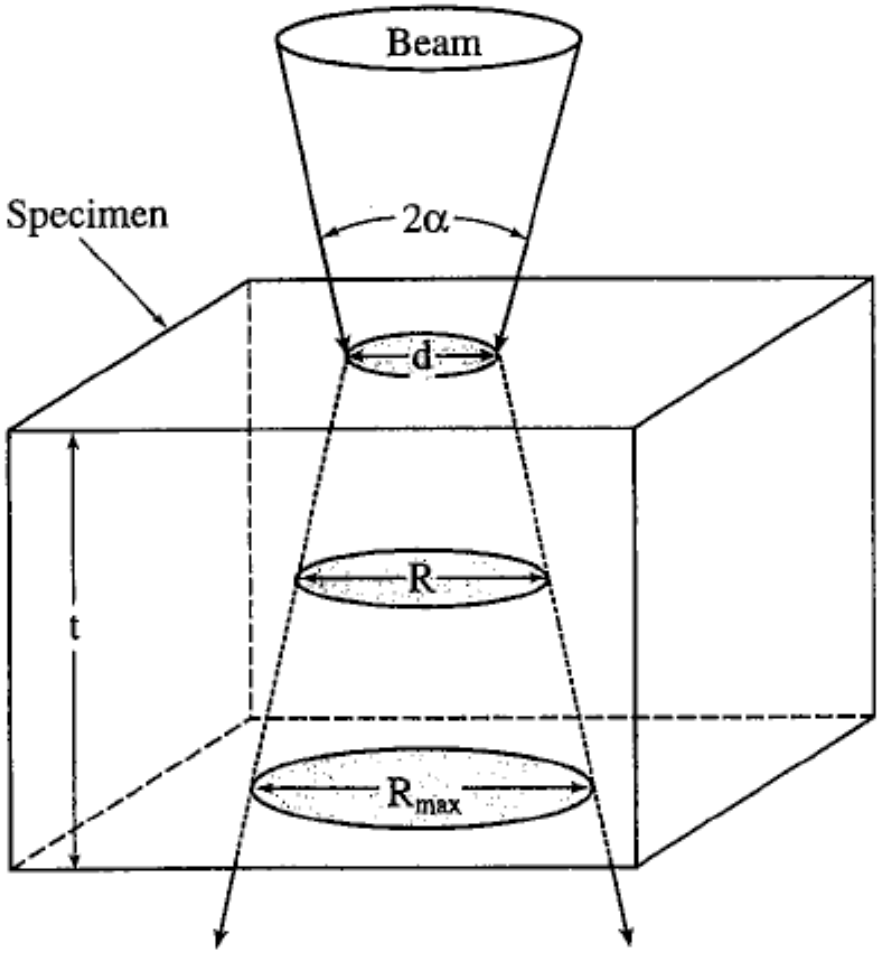


Espalhamento do feixe

$$b = 7{,}21 \times 10^5 \frac{Z}{E_o}\left(\frac{\rho}{A}\right)^{\frac{1}{2}} t^{\frac{3}{2}}$$

Williams e Carter

Resolução Espacial



Resolução

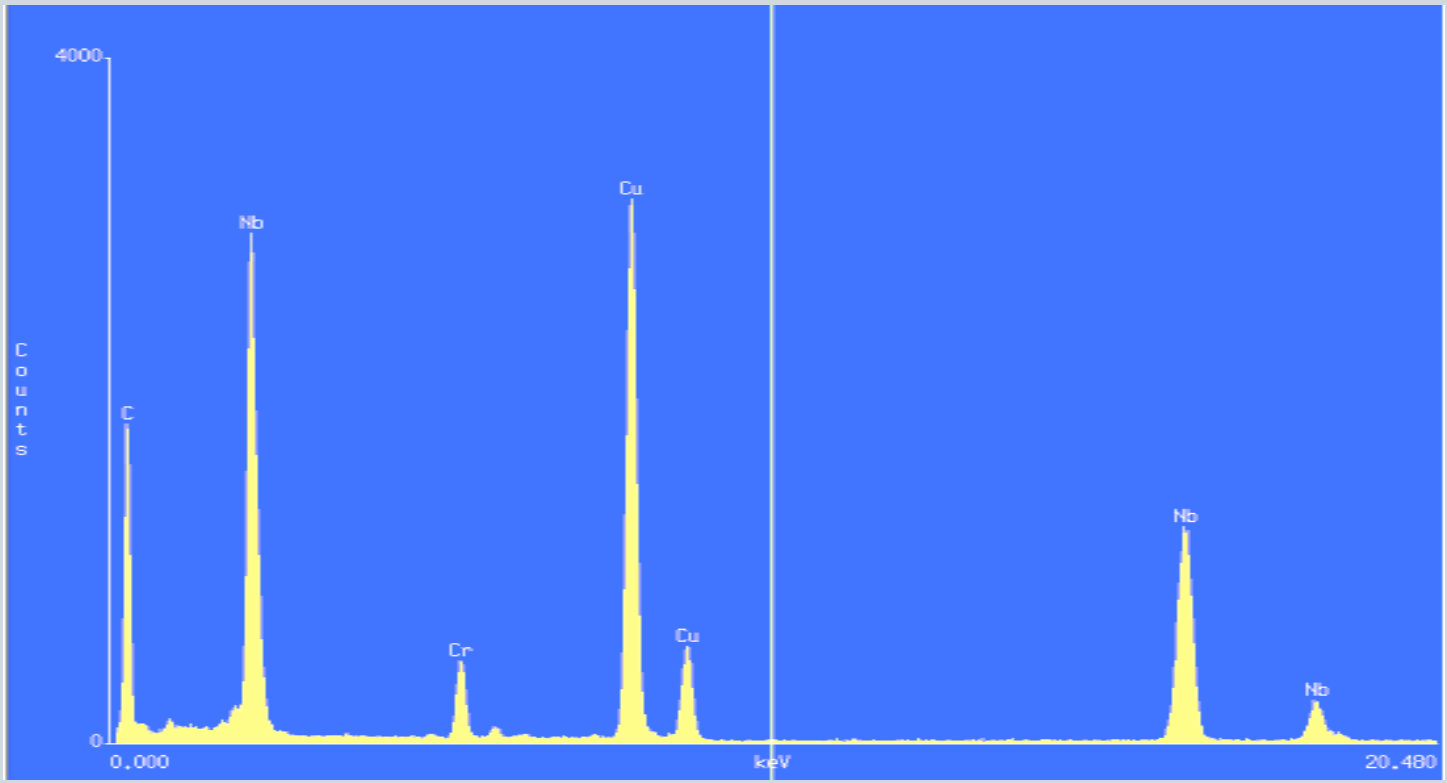
$$R_{Max} = \left(b^2 + d^2\right)^{\frac{1}{2}}$$

$$R = \frac{d + R_{Max}}{2}$$

Williams e Carter

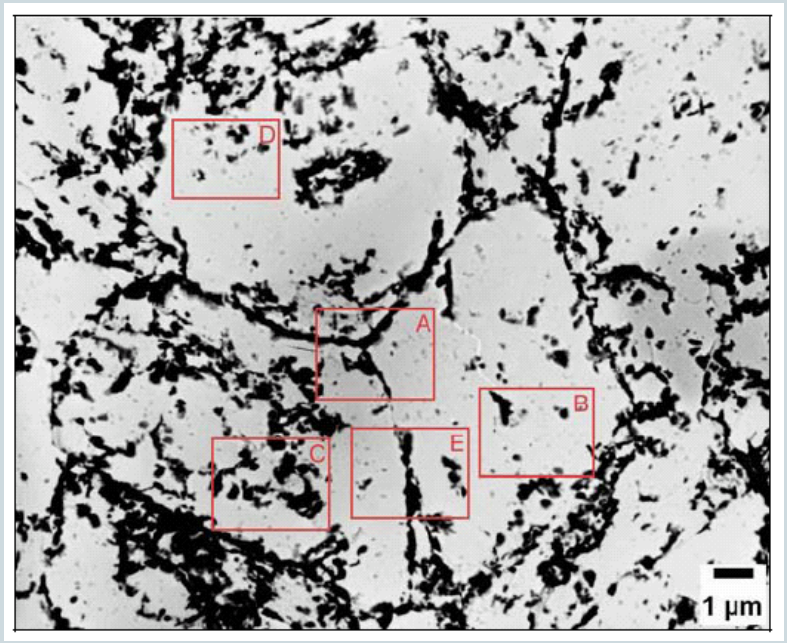
Espectro de EDS

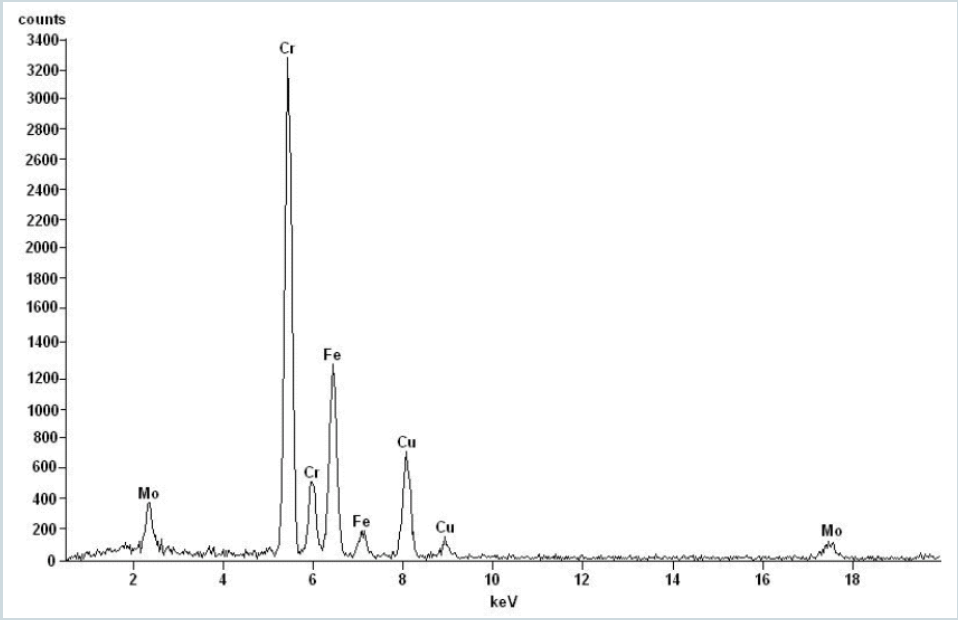
- Permite a análise qualitativa da composição química
- Permite a realização de mapeamentos para localização de elementos químicos
- Permite análises quantitativas



Aplicação de EDS

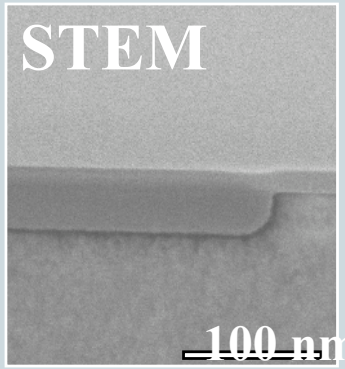
Réplica de uma amostra de aço 2 1/4Cr 1 Mo com precipitados de M_7C_3.

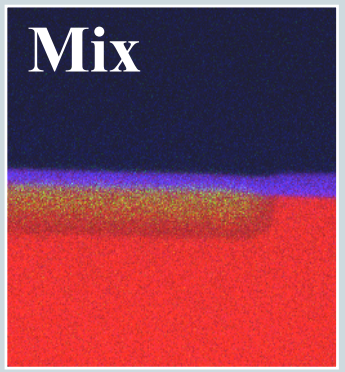




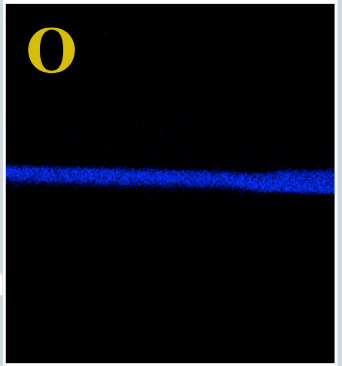
Mapeamento por EDS

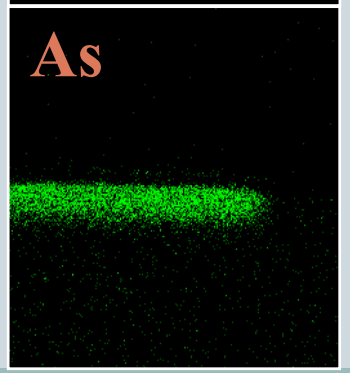
As doping:
25keV, $5e^{15}/cm^2$
No annealing process
256x256, 300,000 x, 60 min







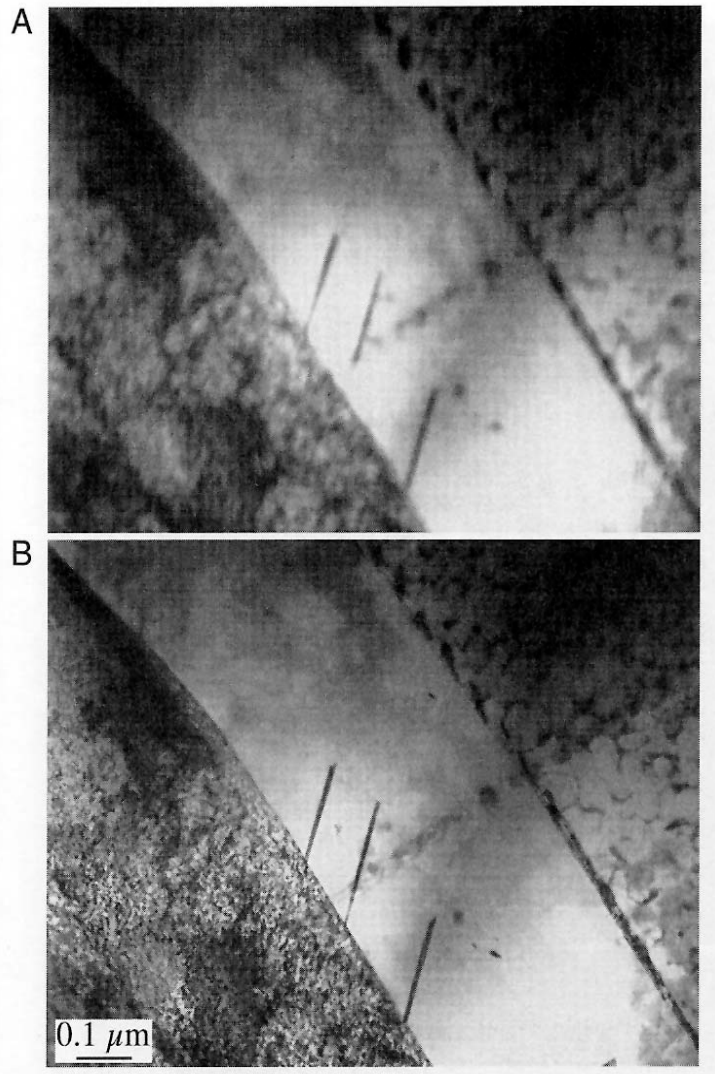




Jeol

Microscopia de Amostras Magnéticas

- Amostras devem estar em redes com grampo
- Objetivas devem ser desligadas durante a inserção
- Se a amostra sumir, desligue o microscópio
- Grande trabalho de alinhamento!!!
- DF centrada requer lentes especiais (Lorentz Microscopy)
- Lorentz Microscopy – lentes objetivas especiais de baixo campo na amostra de modo que os domínios magnéticos da amostra não sejam alterados pela objetiva



Microscopia de Lorentz

É necessário trabalhar com uma lente objetiva que tenha menor campo magnético de modo a não alterar os domínios magnéticos da amostra

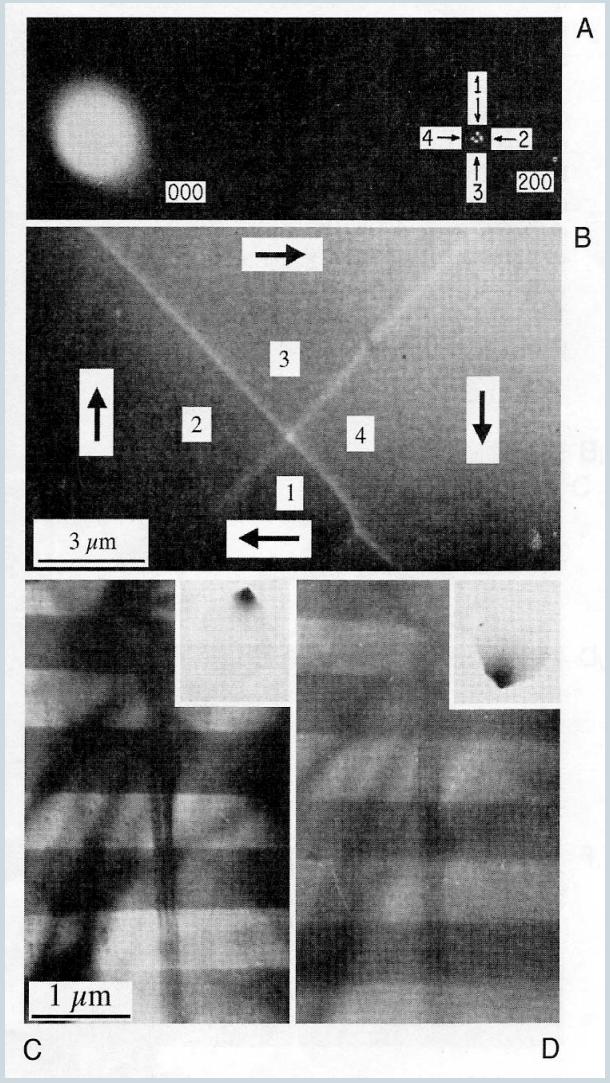
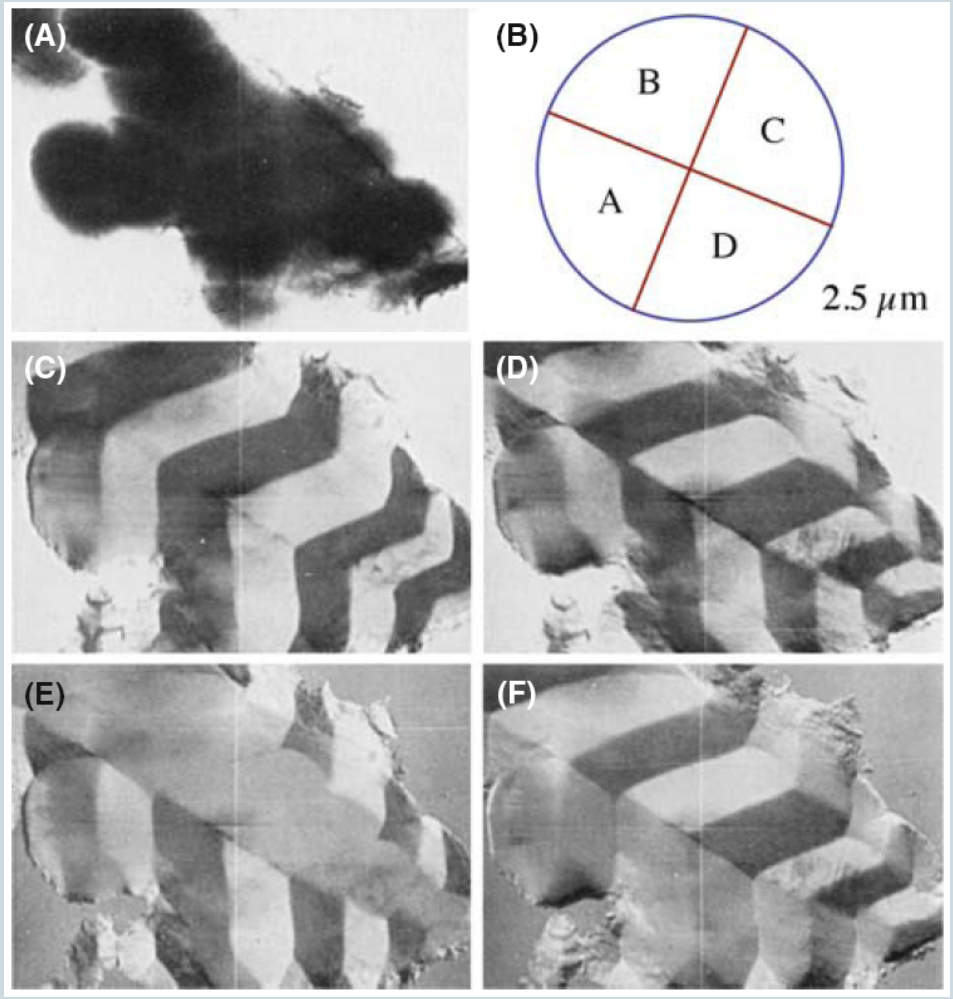


Imagem de Foucault
DF centrada

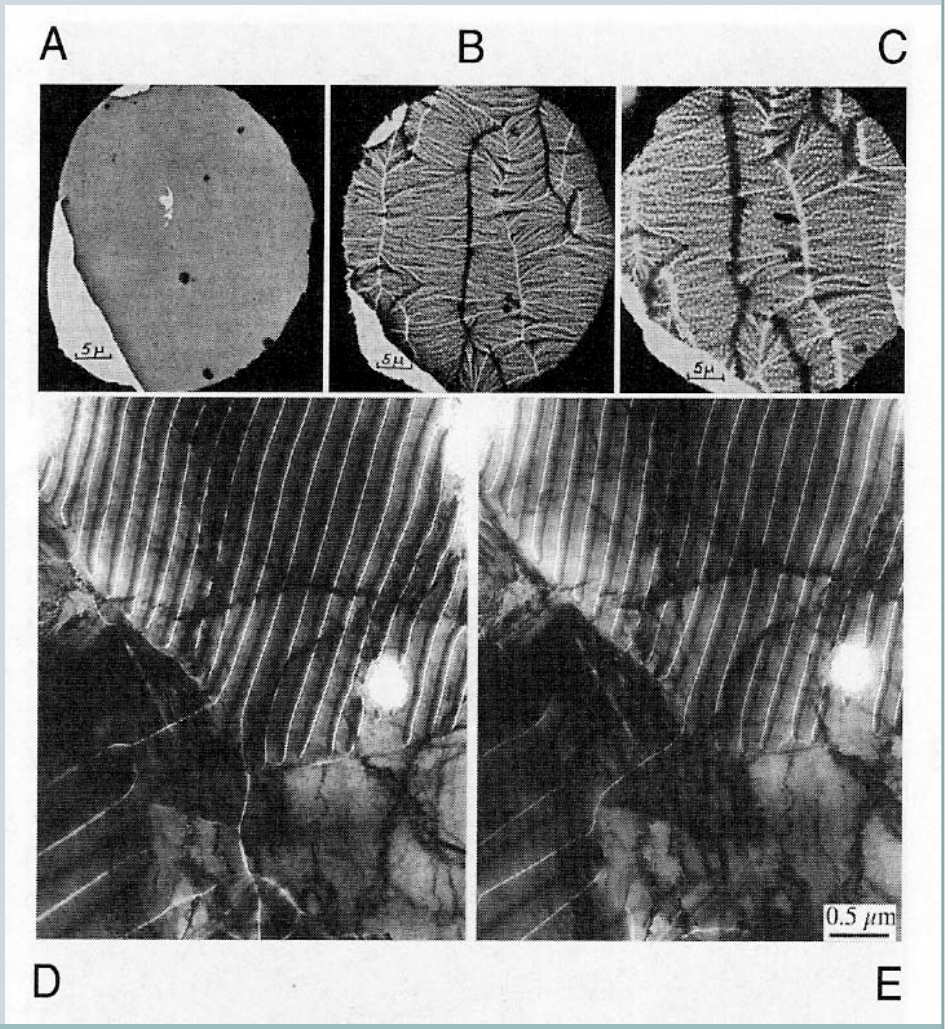
Microscopia de Lorentz



Imagens de Foucault de Fe puro utilizando os diferentes quadrantes de um detector de estado sólido obtidas em um STEM

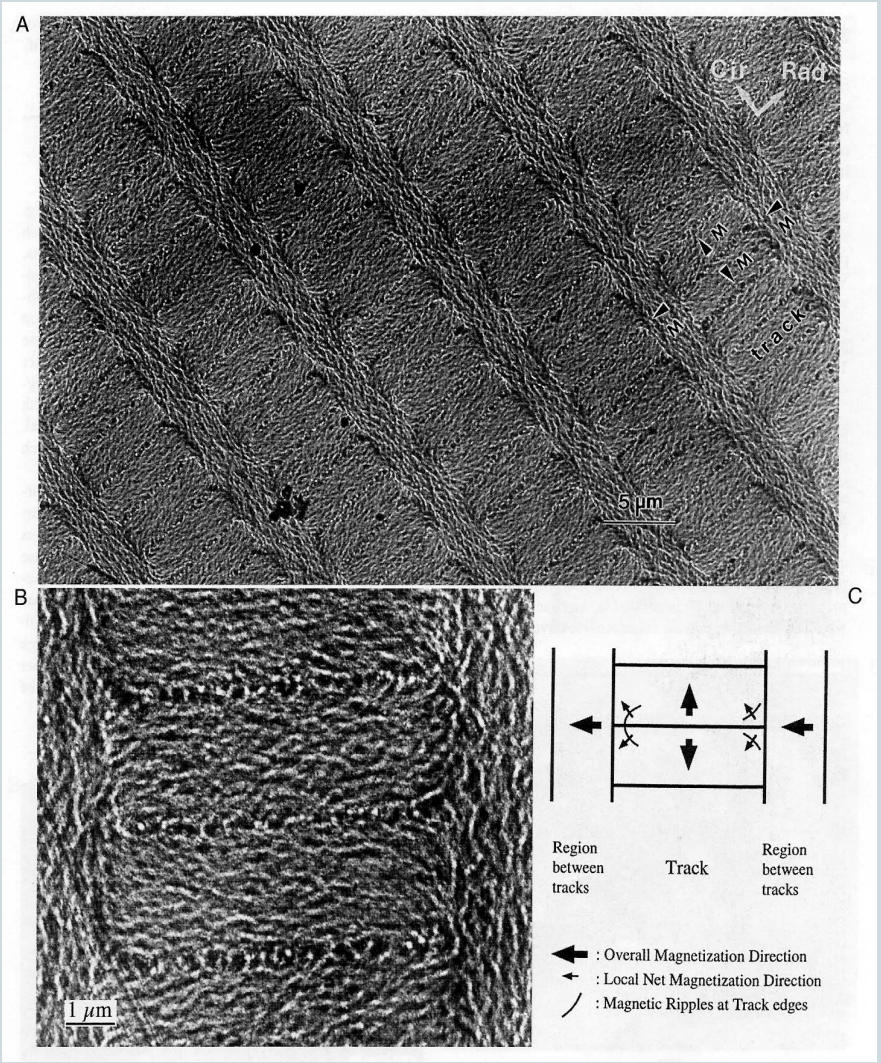
Microscopia de Lorentz

Contraste de Fresnel

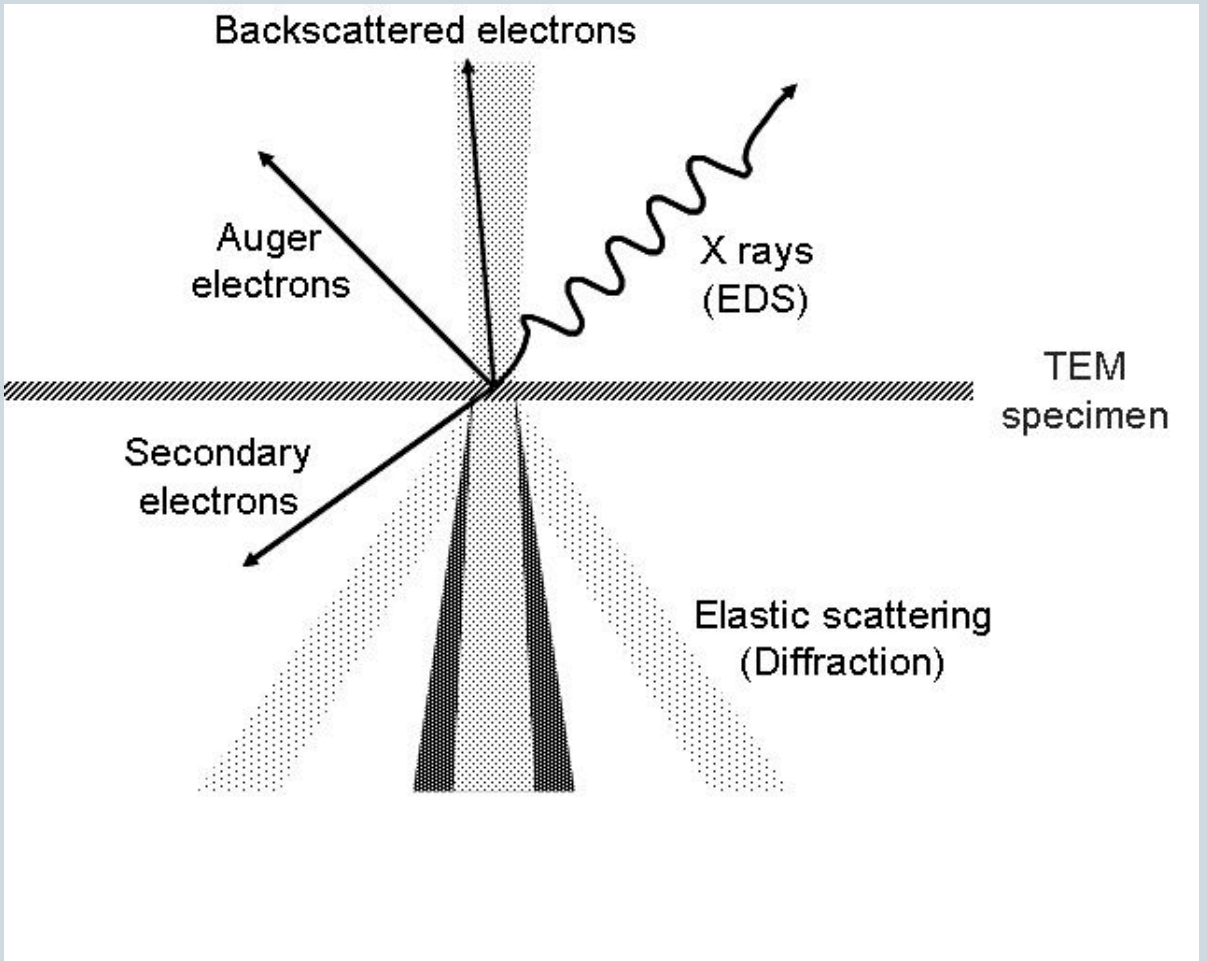


Microscopia de Lorentz

Contraste de Fresnel

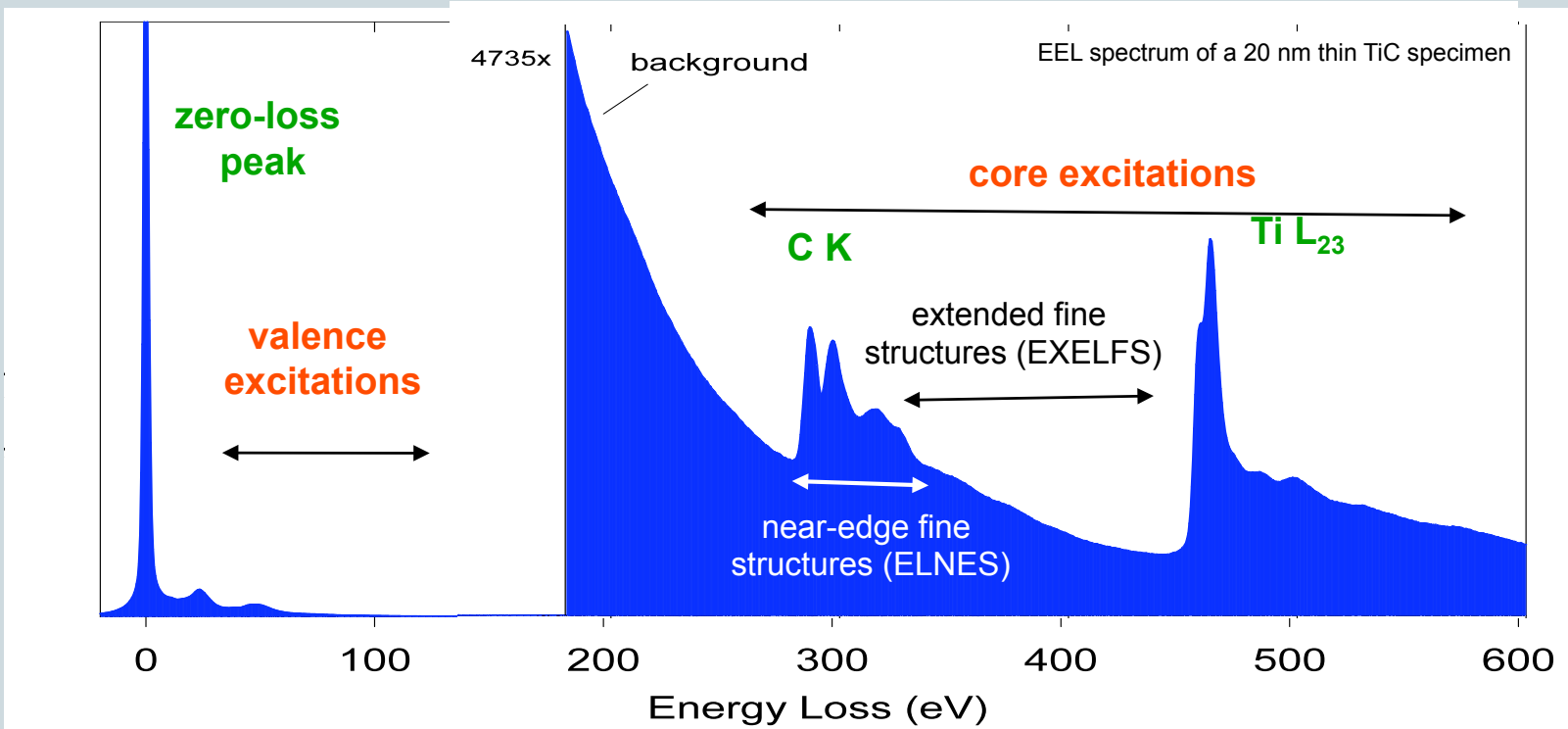


Electron Energy Loss Spectroscopy (EELS)



Inelastic scattering (EELS)

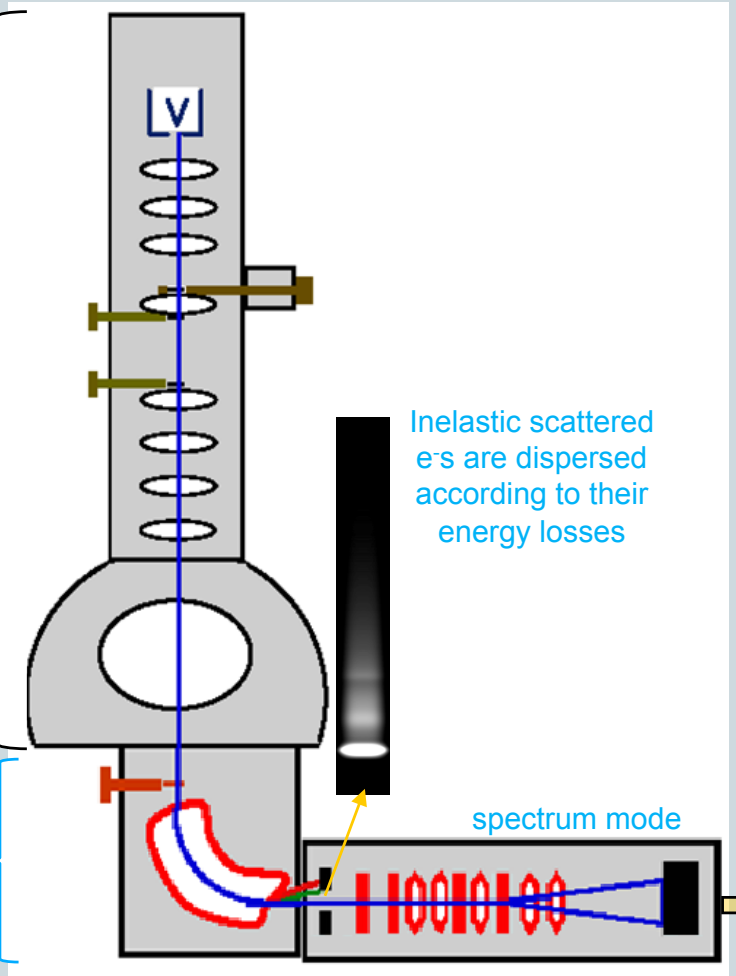
Electron Energy Loss Spectroscopy (EELS)



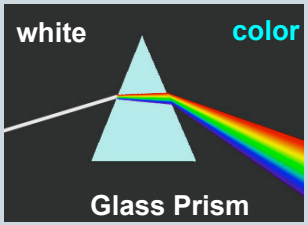
Gatan

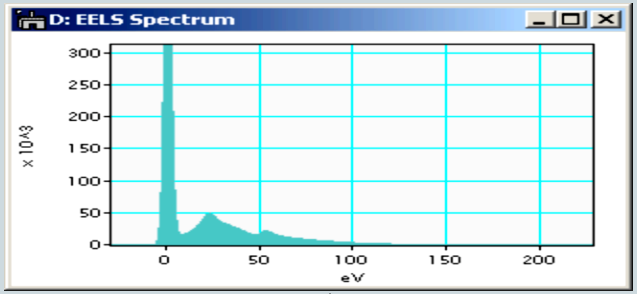
- Zero loss peak / plasmon peak: espessura da amostra
- Valence excitations: densidade eletrônica das bandas de condução/valência, medida de band gap, efeitos de polarização, efeitos dielétricos
- Core excitations: Identificação e quantificação de elementos, investigação do ambiente eletrônico incluindo número de coordenação, estado de valência e tipo de ligação atômica
- Mapeamento elementar

Post-column spectrometer



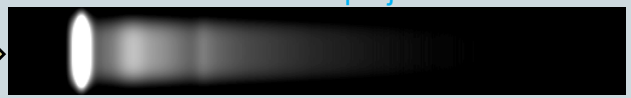
Simply speaking, the major function of an EELS Spectrometer (GIF/PEELS) is dispersing the scattered electrons according to their lost energies into a spectrum.





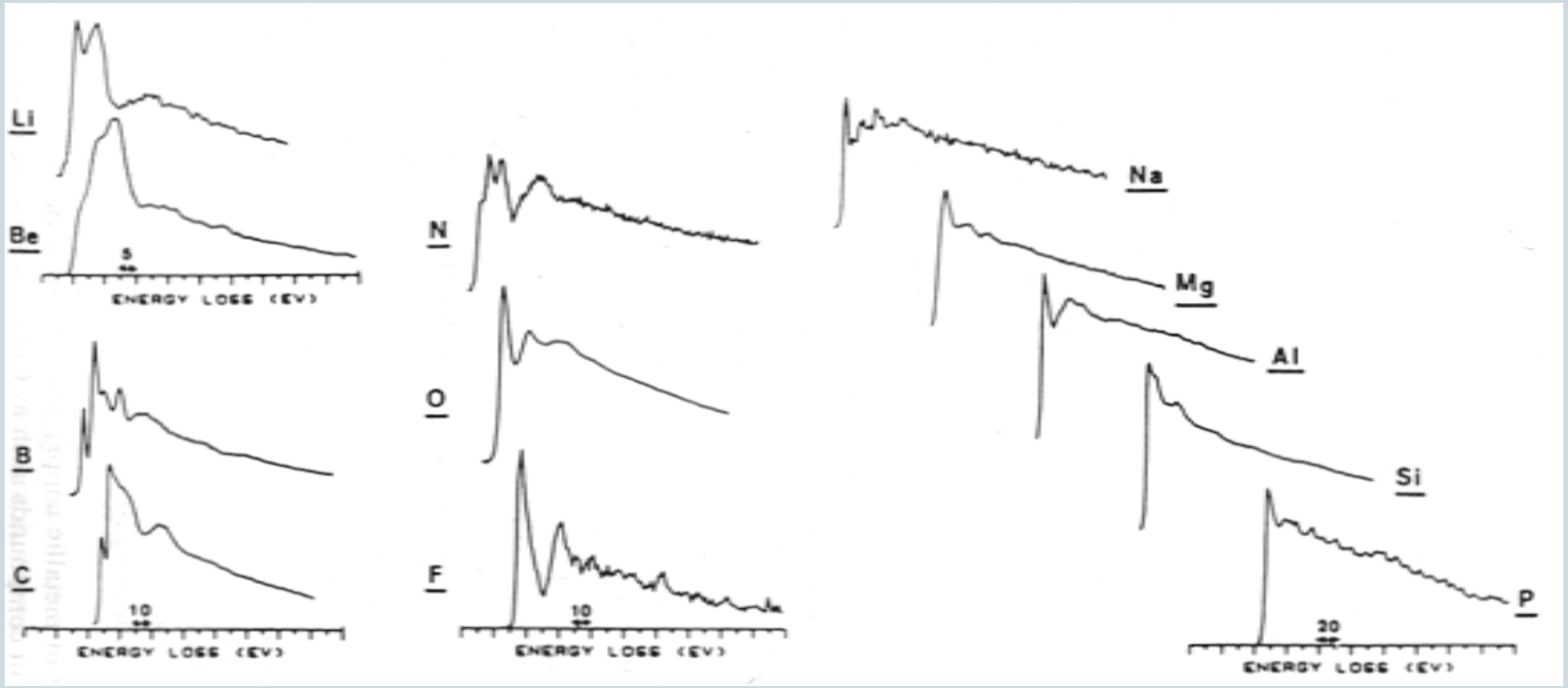
Final EELS readout

EELS spectrum projected onto CCD



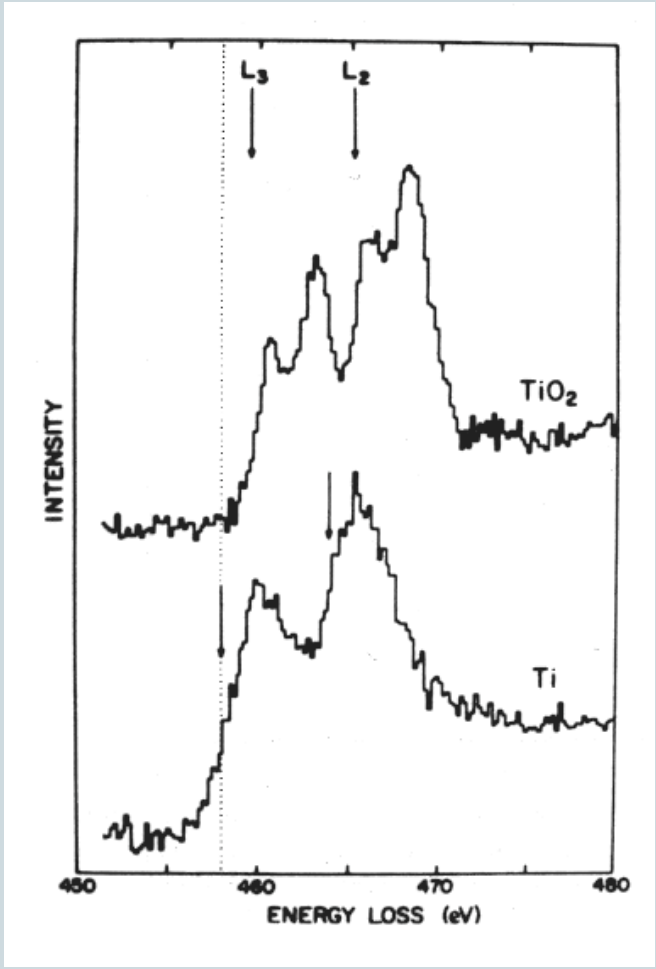
Gatan

Sensibilidade à Composição Química



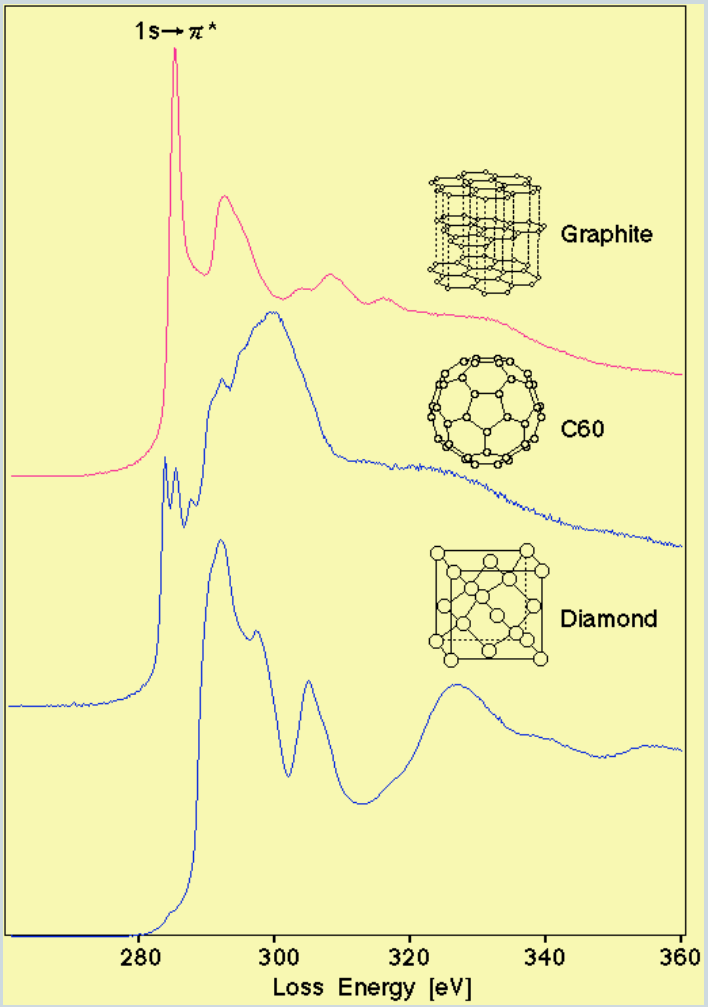
Gatan

Estado de Oxidação



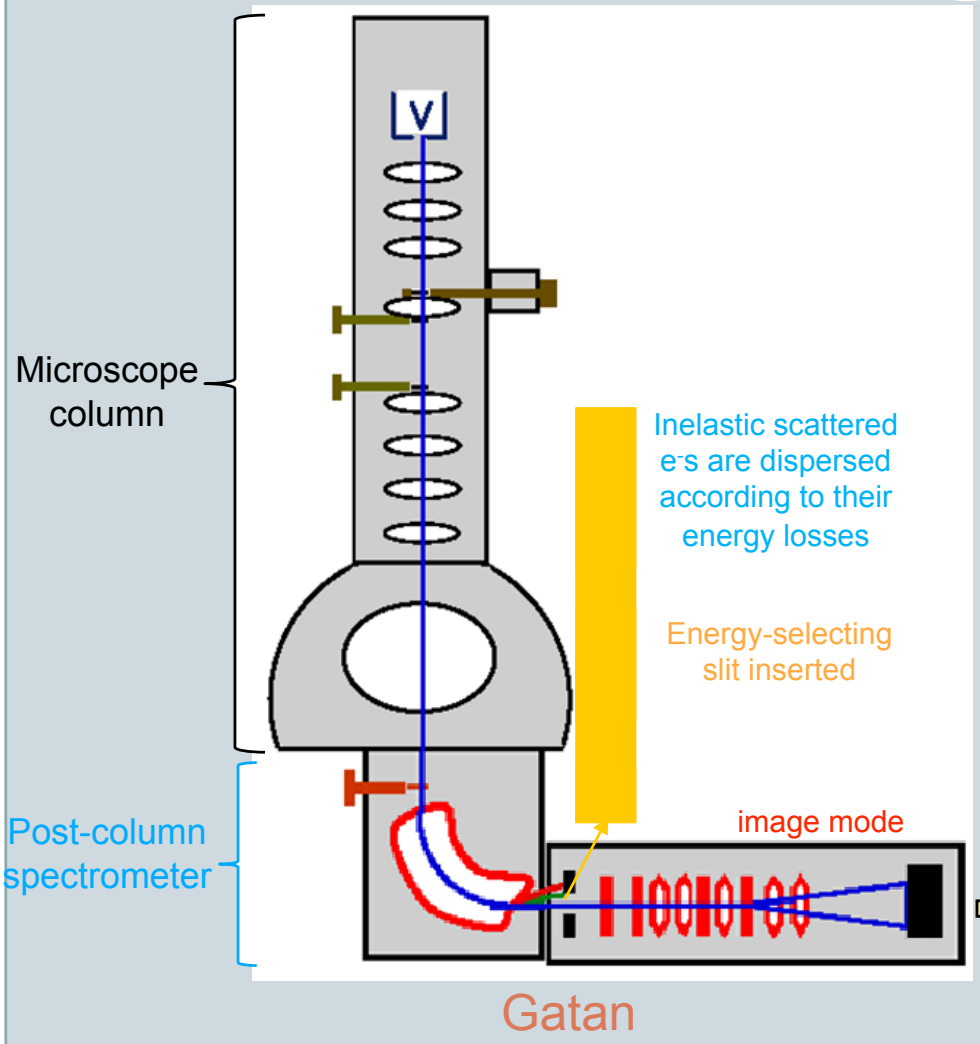
Gatan

Esado de Ligação



Gatan

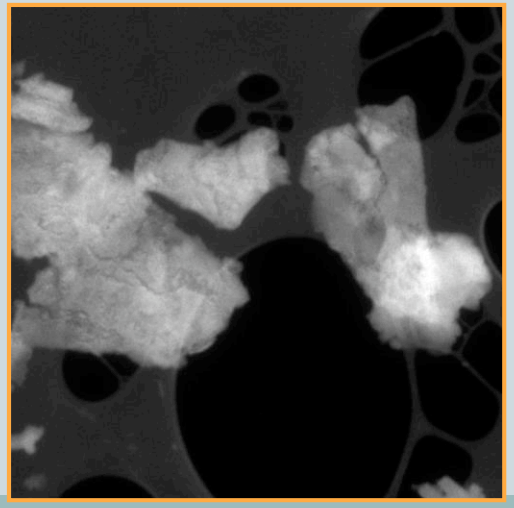
Imageamento por EELS



Energy filtered TEM (EFTEM): select the electrons with certain energy losses for imaging.

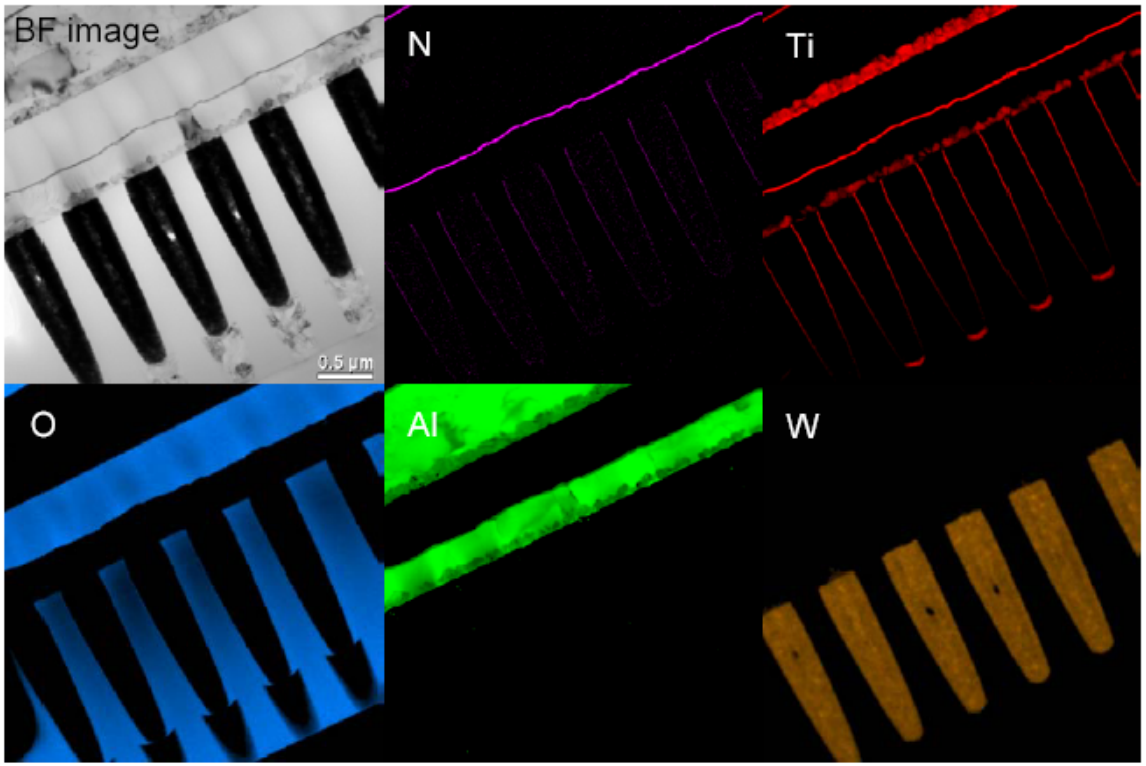
EFTEM has many uses, based on the wealthy information on EELS :

- Contrast enhancement in imaging & diffraction
  - zero-loss filtering; most probable loss imaging; contrast tuning; pre-carbon imaging
- Elemental mapping/Jump ratio imaging
  - 3 window method; 2 window method
- Chemical mapping



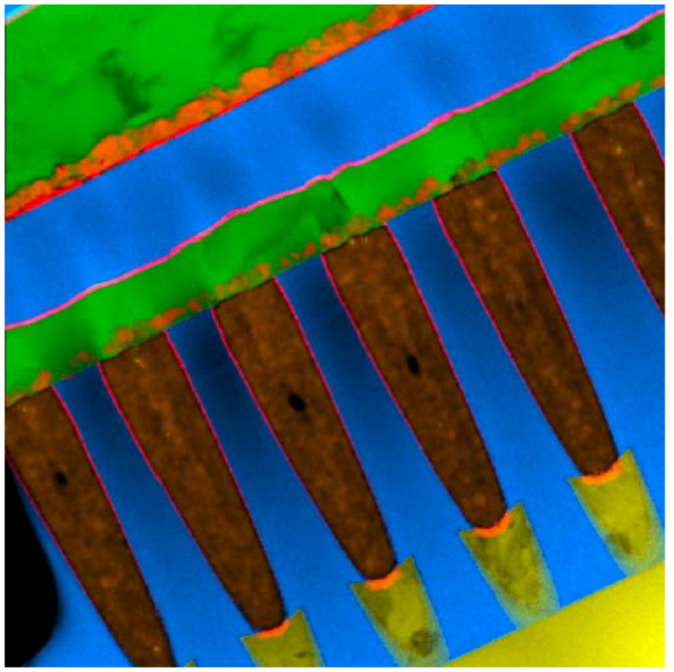
Zero loss filtered image projected onto CCD

EFTEM – Mapeamento e identificação de fases



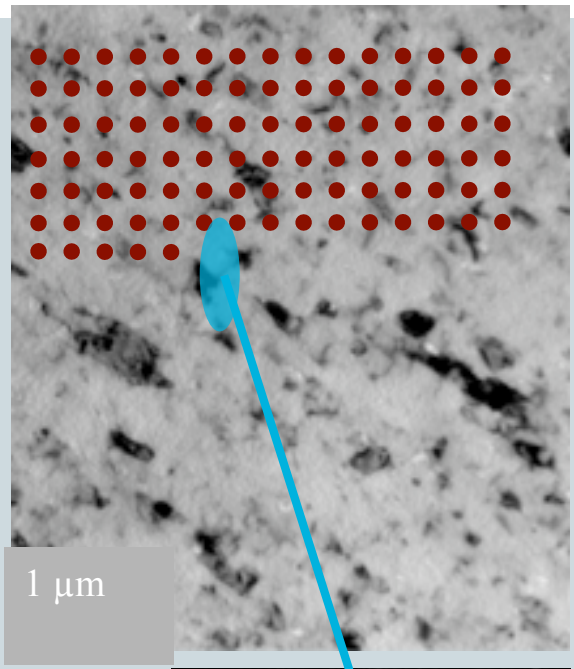
Unfiltered bright-field TEM image of semiconductor device structure and some elemental maps formed from ionization-edge signals of N-K, Ti-L, O-K, Al-K, and W-M.

Gatan

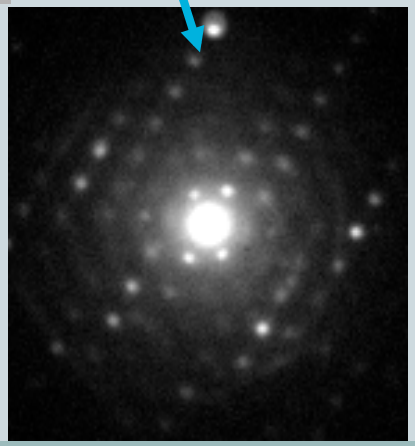


Color composite of the elemental maps displayed on the left, clearly showing the construction of the device.

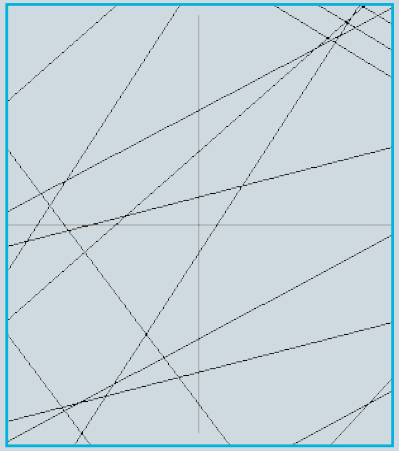
Microscopia de Orientação com Auxílio de Difração com Precessão



Severely deformed 7075 Al. Alloy



Kikuchi pattern

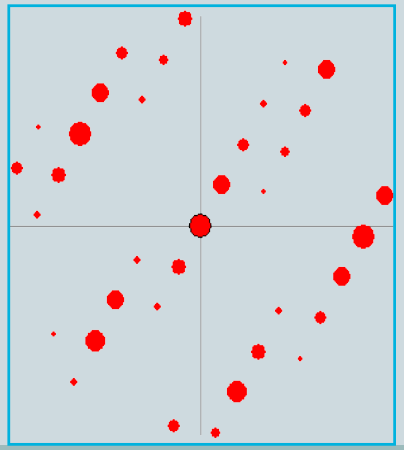


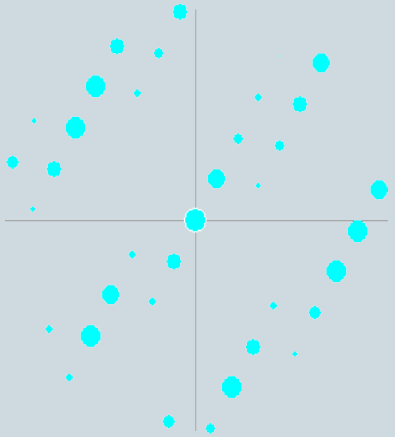
Orientation Ω



Orientation **Ω + Ω'(= Ω +0.1°)**

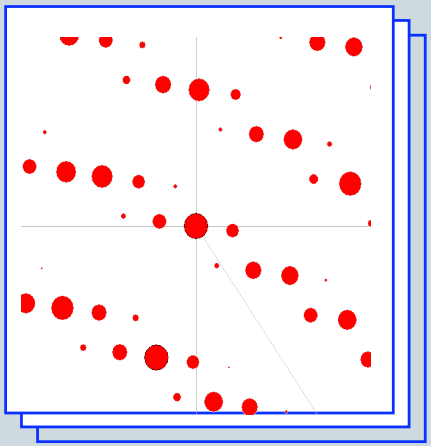
Bragg Spot pattern





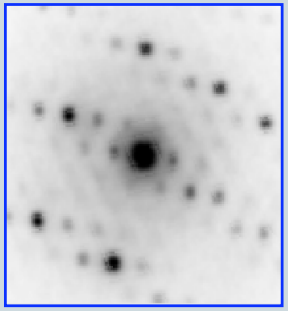
Microscopia de Orientação com Auxílio de Difração com Precessão

Pre-calculated templates

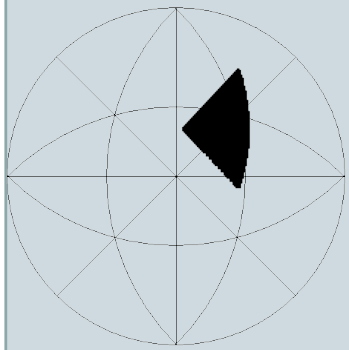


$$Q(i) \sim \sum_{j=1}^{m} P(x_j,y_j)\, T_i(x_j,y_j)$$

Correlation index

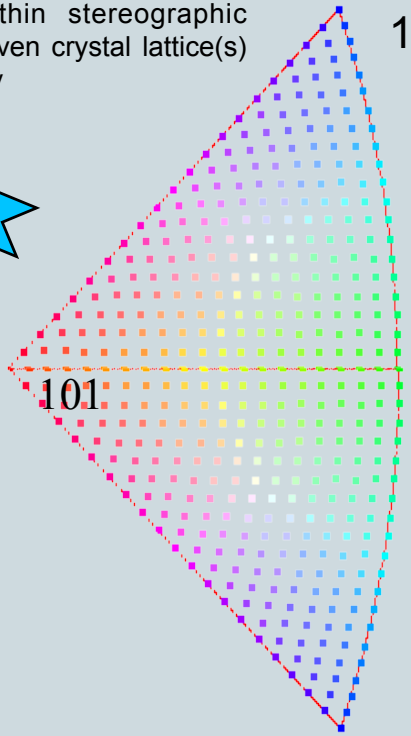


Acquired pattern



Degree of matching between experimental patterns and simulated templates is given by a correlation index ; highest value corresponds to the adequate orientation/phase

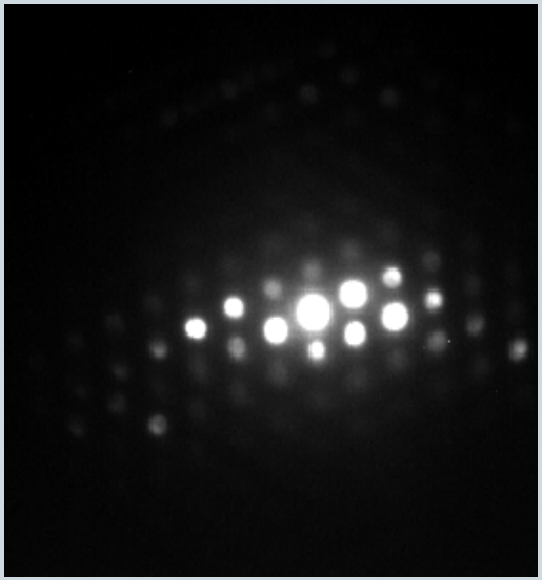
Template generation of all possible simulated orientations (every1°) within stereographic triangle for given crystal lattice(s) and symmetry



Stereographic projection 1-11

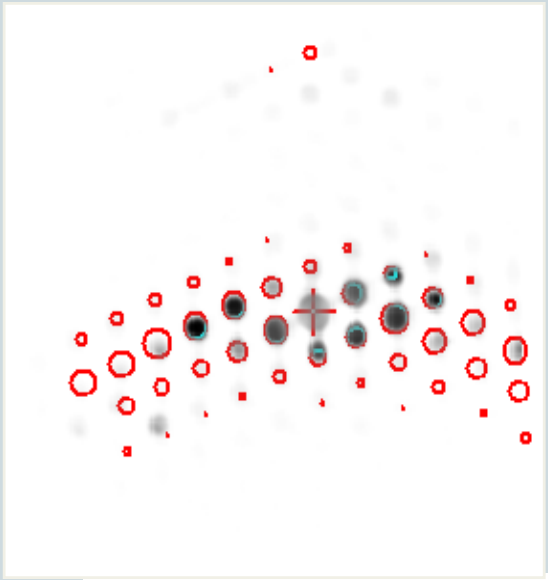
(example ,cubic) ~ **2000 simulated patterns**

Microscopia de Orientação com Auxílio de Difração com Precessão

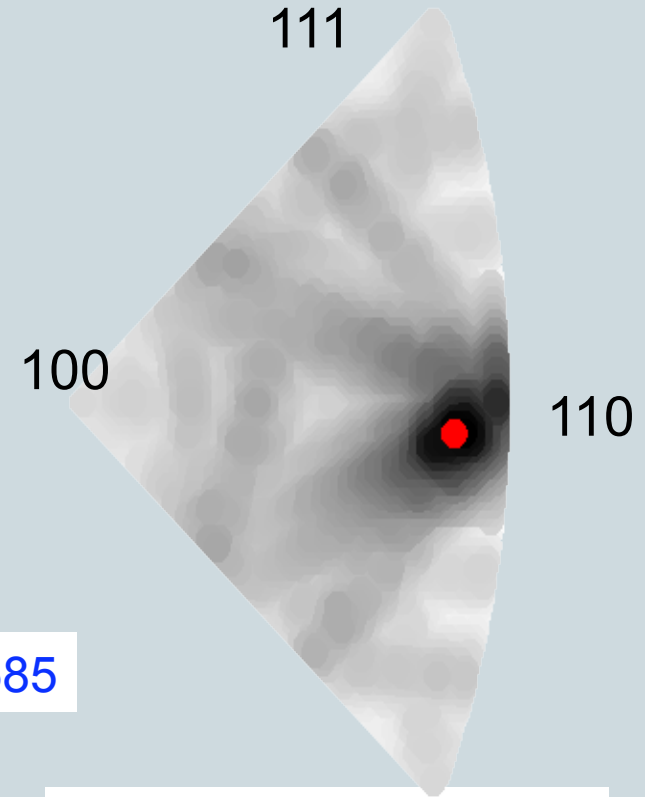


Diffraction pattern

(nanocrystalline cubic copper)



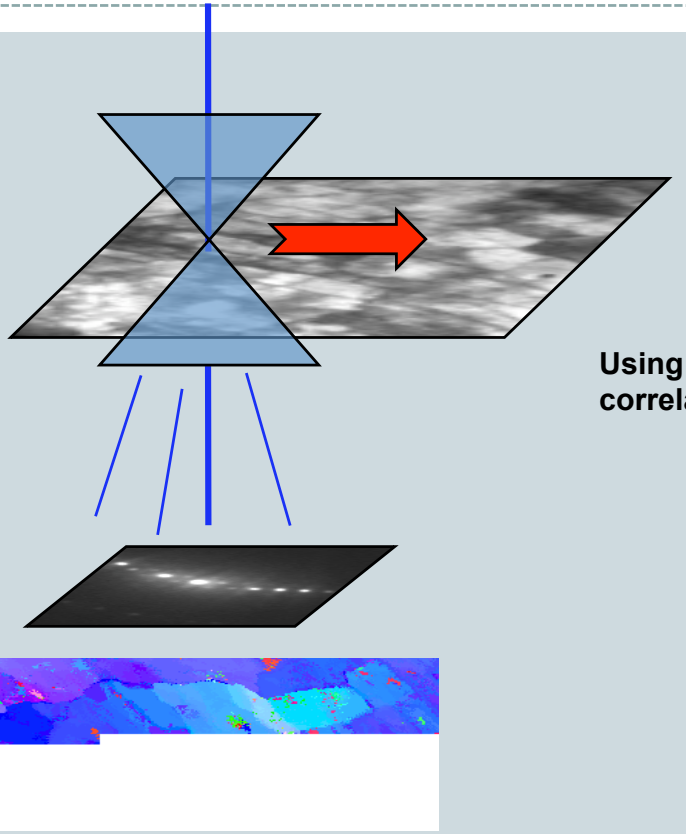
correlation index = 585

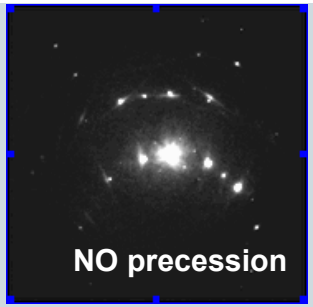


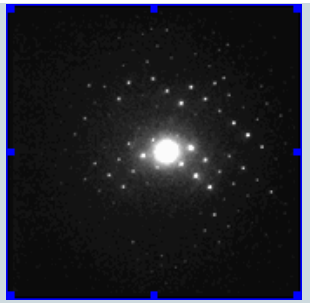
Correlation index map

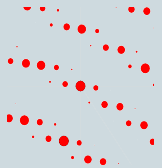
For a given ED pattern, the correlation index map is calculated for all possible template orientations and plotted on a map that represents a portion of the stereographic projection (reduced to a double standard triangle). That resulting map reveals the most probable orientation for every experimental spot ED pattern (in this case ED pattern is found to be close to 110 ZA orientation)

Microscopia de Orientação com Auxílio de Difração com Precessão

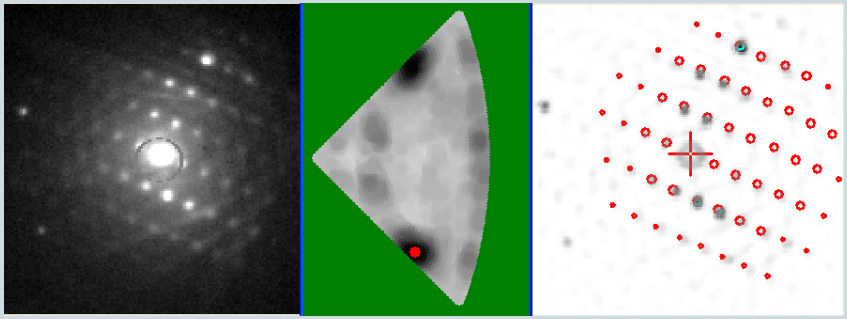




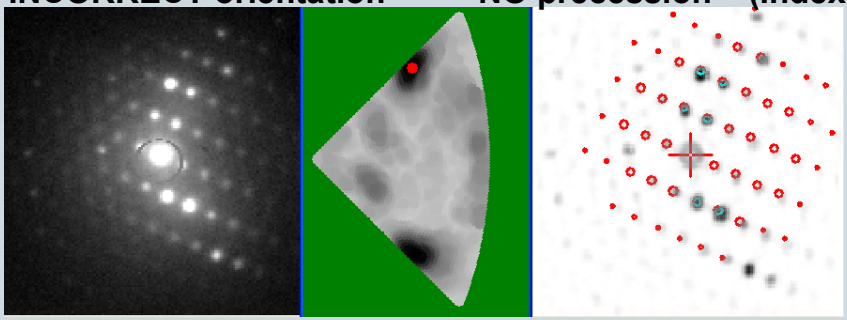




Using precession diffraction the number of ED spots observed increases; correlation index map becomes much more reliable



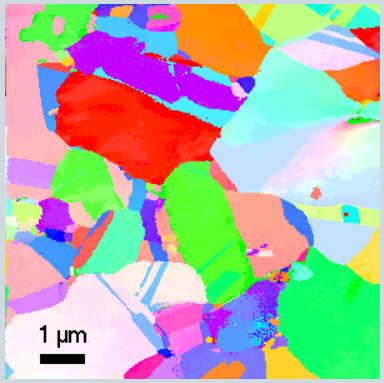
INCORRECT orientation **NO precession (Index 622)**

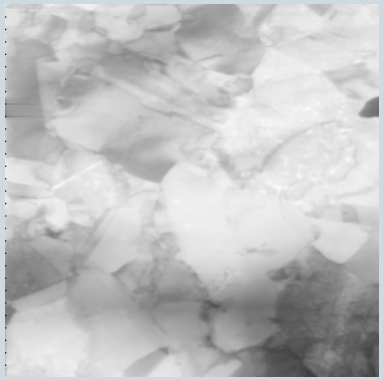


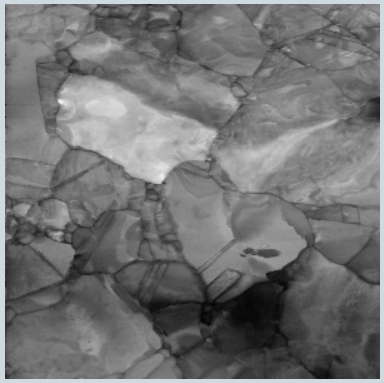
CORRECT orientation **0.5° precession (Index 745)**

In this example (right) a metal particle gives wrong correlation index without precession due to presence of Kikuchi lines; after applying precession (right lower image), index gets correct value as ED quality improves and Kikuchi lines disapear

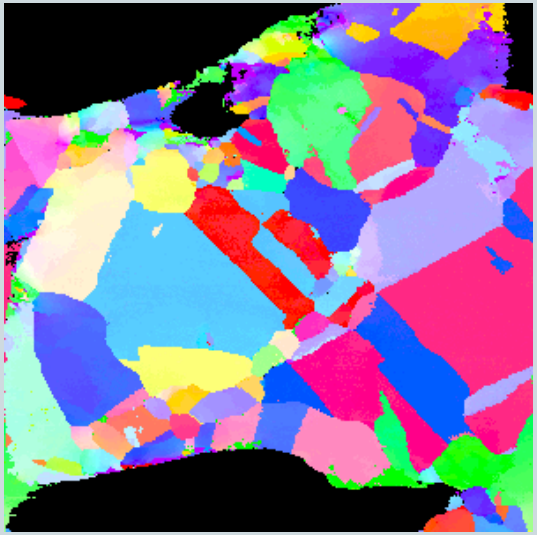
Microscopia de Orientação com Auxílio de Difração com Precessão

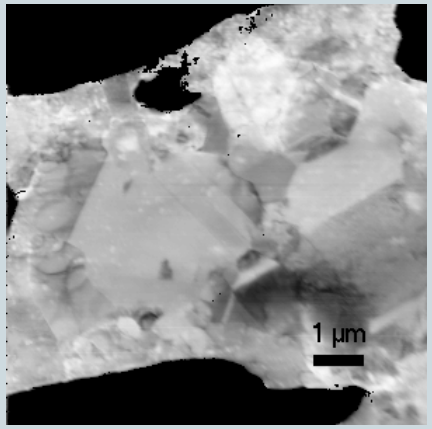


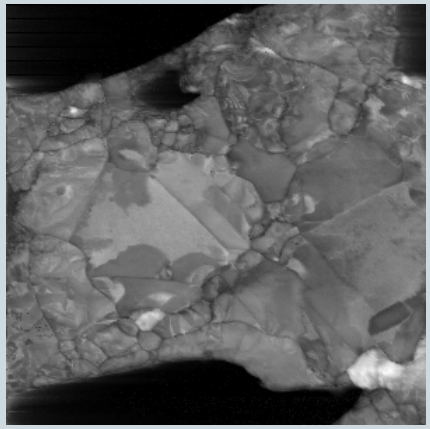


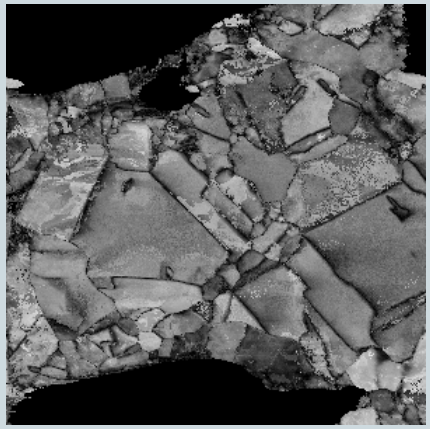












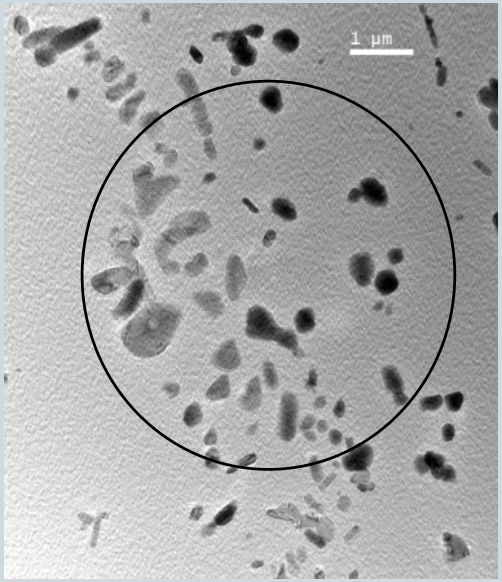
VBF index **reliability**

ASTAR (EBSD -TEM) orientation maps : Nanotwins in Cu CBD mode Jeol 3010 microscope

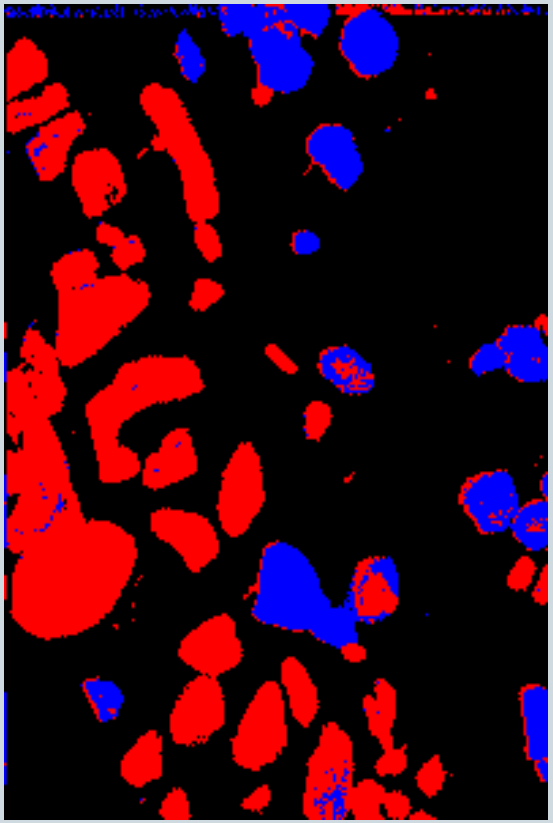
Microscopia de Orientação com Auxílio de Difração com Precessão

Sample : Replica sample extracted from 430 stainless steel contain lot of precipitates NOT possible to distinguish between them from size

$M_{23}C_6$ carbides cubic fcc a = 10.62 A
Cr_2N nitrides hexagonal a = 4.83, c = 4.51 A



TEM



carbides

nitrides

ASTAR crystal phase map, step 22 nm

Referências

- Goldstein, J. I. et alli., “Scanning Electron Microscopy and X-Ray Analysis”, Ed. Plenum, New York, 2003.
- Williams, D. B. e Carter, C. B., “Transmission Electron Microscopy” , Ed. Plenum, New York, 2009.
- Goodhew, P. J. et all, “Electron Microscopy and Analysis”, Ed. Taylor & Francis, London, 2001.

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