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"Structural & Chemical Analysis of Materials by Advanced Transmission Electron Microscopy Technique"

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Please note: These are preliminary notes intended for internal distribution only.

Structural and Chemical Analysis of Materials by Advanced Transmission Electron Microscopy Technique

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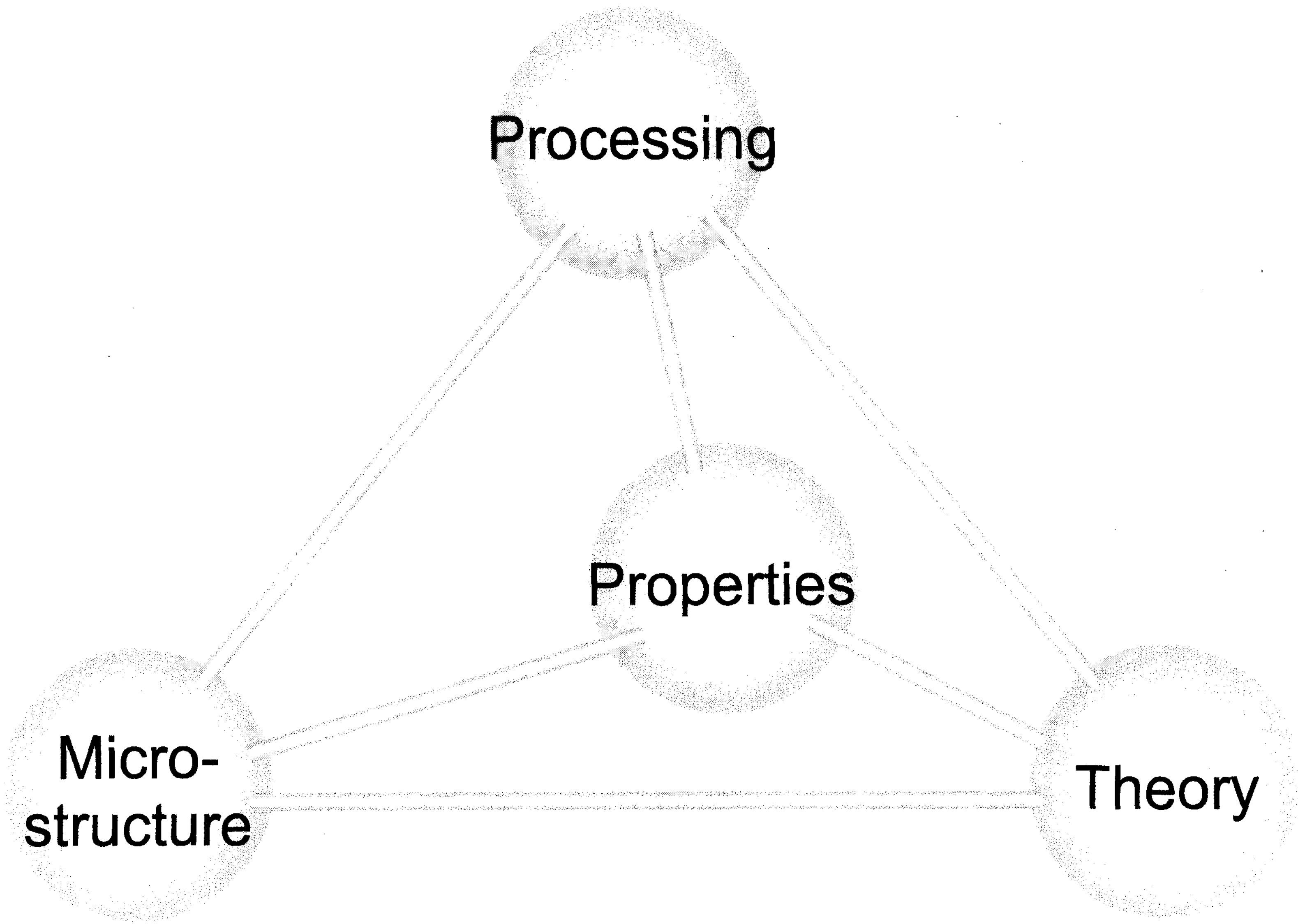
Materials Science



Outline

Introduction: Pathways of microstructural analysis bridging length scales over many dimensions

Transmission Electron Microscopy:
Different Techniques
Advantages and Problems

Case Studies
- Defects in Metals (Cu, NiAl, ...)
- Defects in Ceramics (Al_2O_3, $SrTiO_3$, ...)
- Defect at Metal/Ceramic Composites

Nature of Defects
- O-dimensional: point defects, point defect cluster
- 1-dimensional: dislocation
- 2-dimensional: interfaces
- 3-dimensional: inclusions

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K. van Benthem, S. Krämer, C. Scheu, W. Sigle

Specimen preparation: W. Kurtz, T. Wagner
TEM specimen preparation: U. Salzberger, A. Strecker, M. Sycha

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DFG (German Science Foundation)
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State of Baden-Württemberg
Max Planck Society

Microstructural Parameters

Parameter	Technique
Phases present in materials	X-ray techniques, microprobe
Grain sizes	OM, quantitative analysis
Grain size distribution	SEM
Grain shape	
Misorientation of grains ("special" boundaries)	OIM, SAD (in TEM)
Composition of regions close to the GB	Q-AEM
Atomic structure of specific GBs	Q-HREM
Bonding	ELNES: fingerprints and quantitative analysis

Microscopy of Materials:

Many lenght scales!

Optical Microscopy

Conventional Optical Microscopy
Laser-Scanning Microscopy
Near Field Optical Microscopy
Video Microscopy

Electron Microscopy

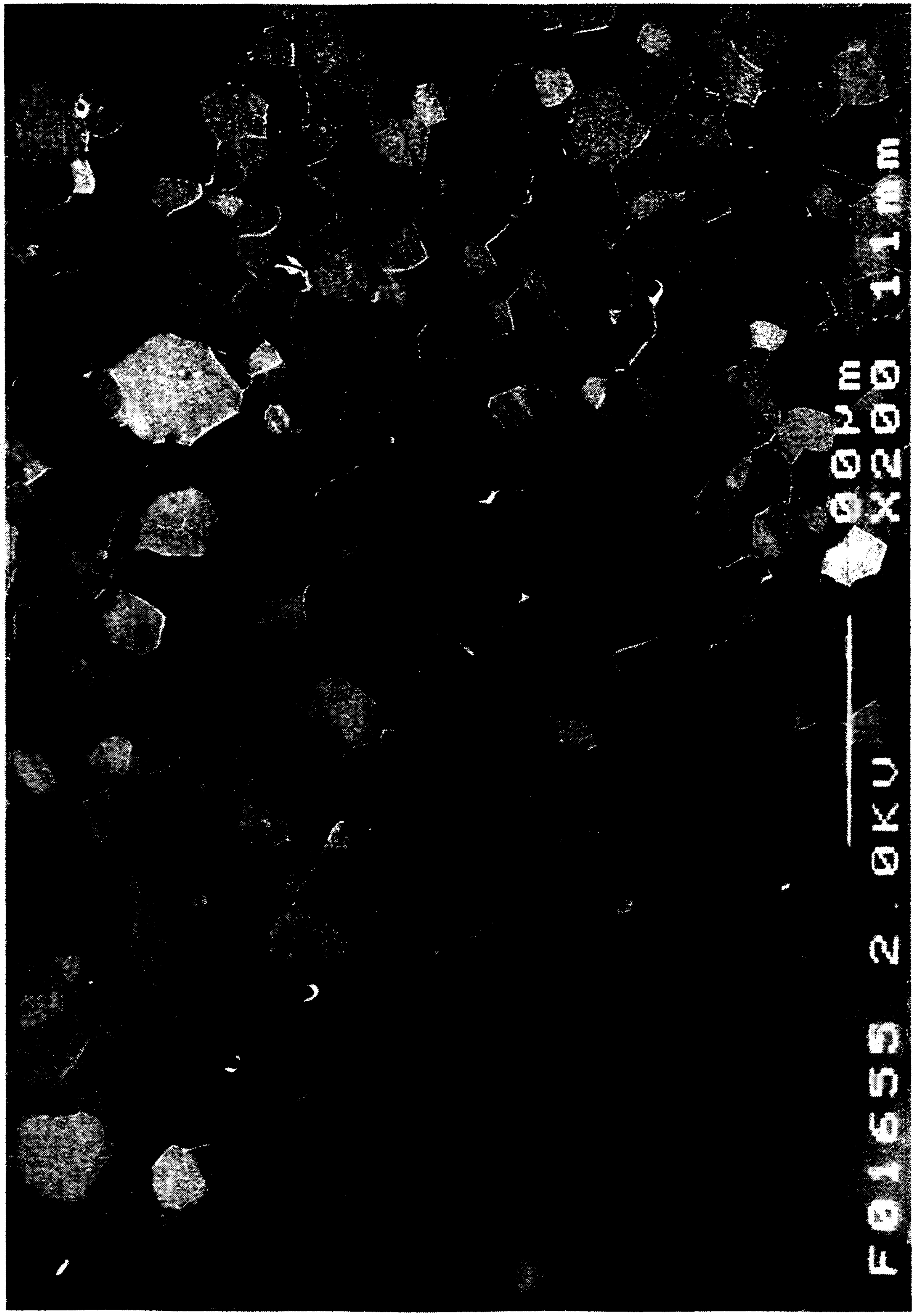
Scanning Electron Microscopy
- Imaging
- Chemical Analysis

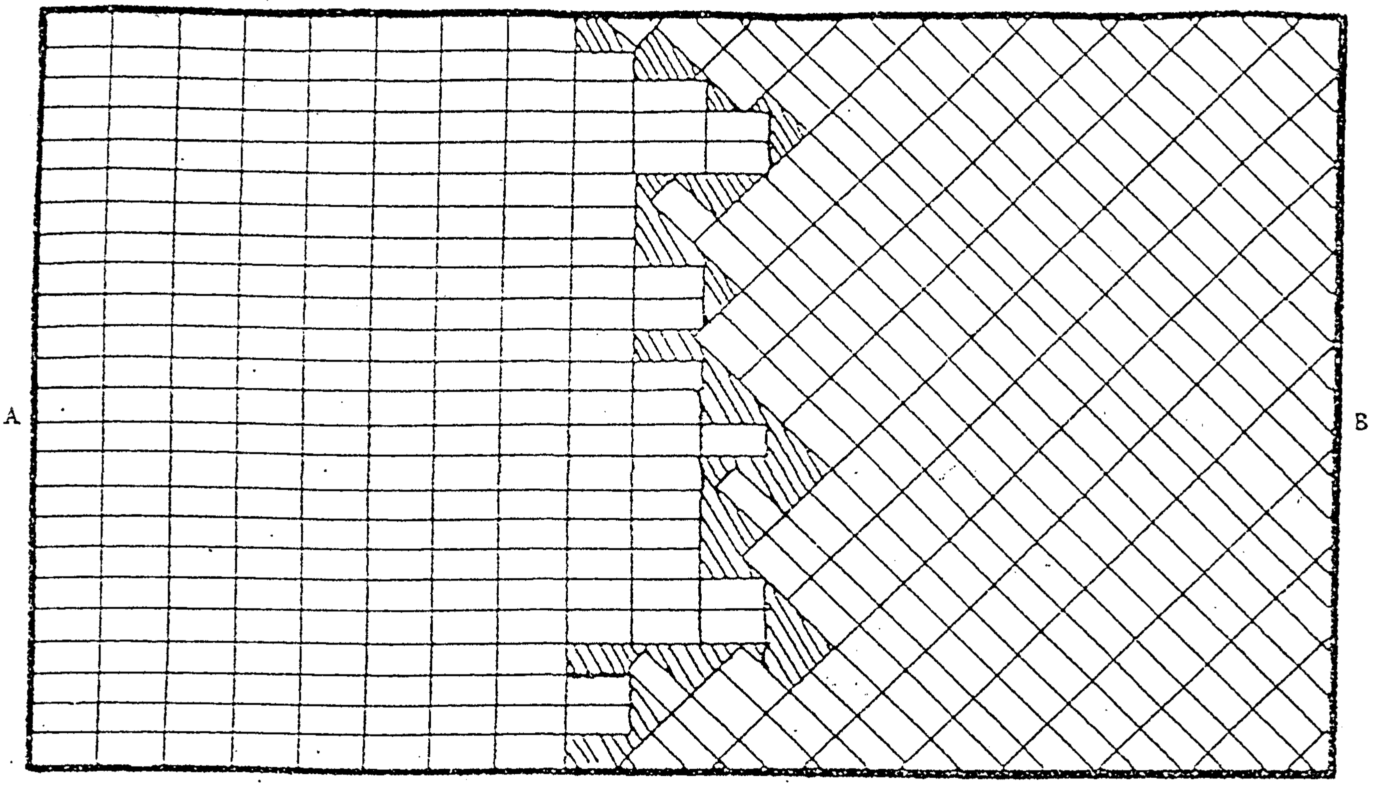
Transmission Electron Microscopy

Diffraction Studies
Diffraction Contrast
Atomic-Resolution Microscopy
Analytical Studies
- Energy Dispersive Studies
- Electron Energy Loss Spectroscopy
- Electron Loss Near Edge Structure

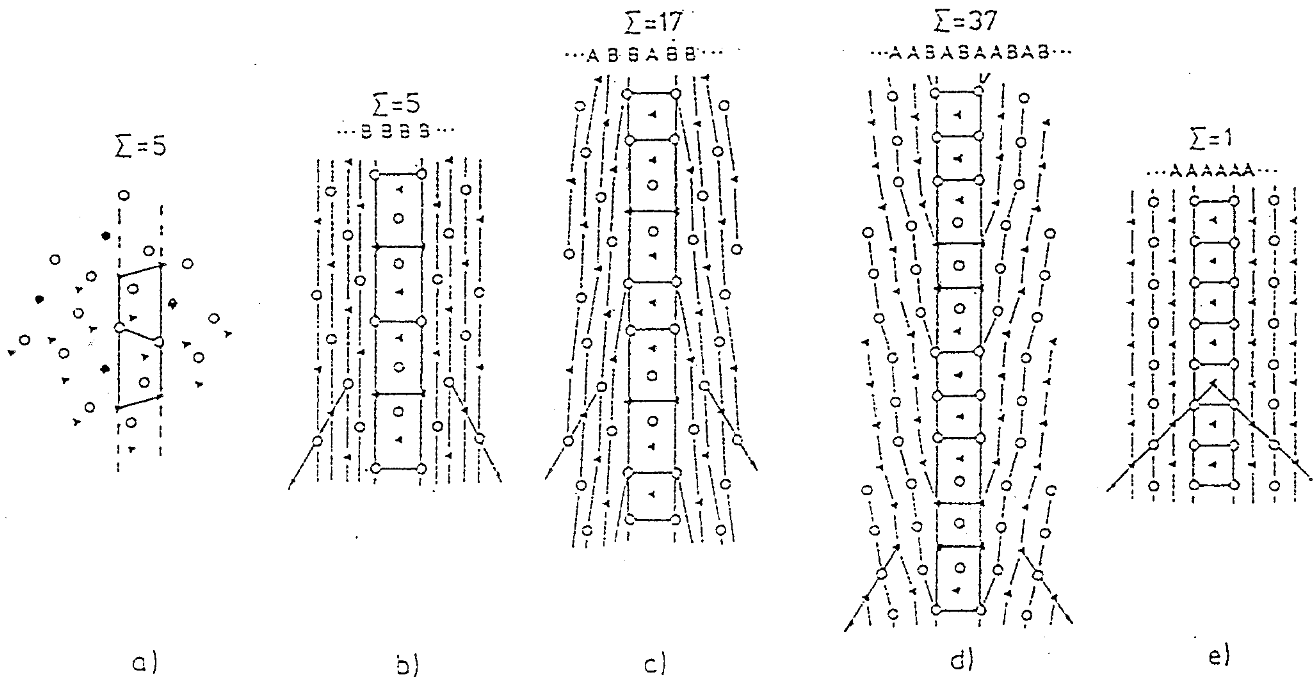
Atom Probe Field-Ion Microscopy

Probe Techniques:
- Scanning Tunneling Microscopy (STM)
  - Scanning Tunneling Spectroscopy
- Atomic Force Microscopy (AFM)

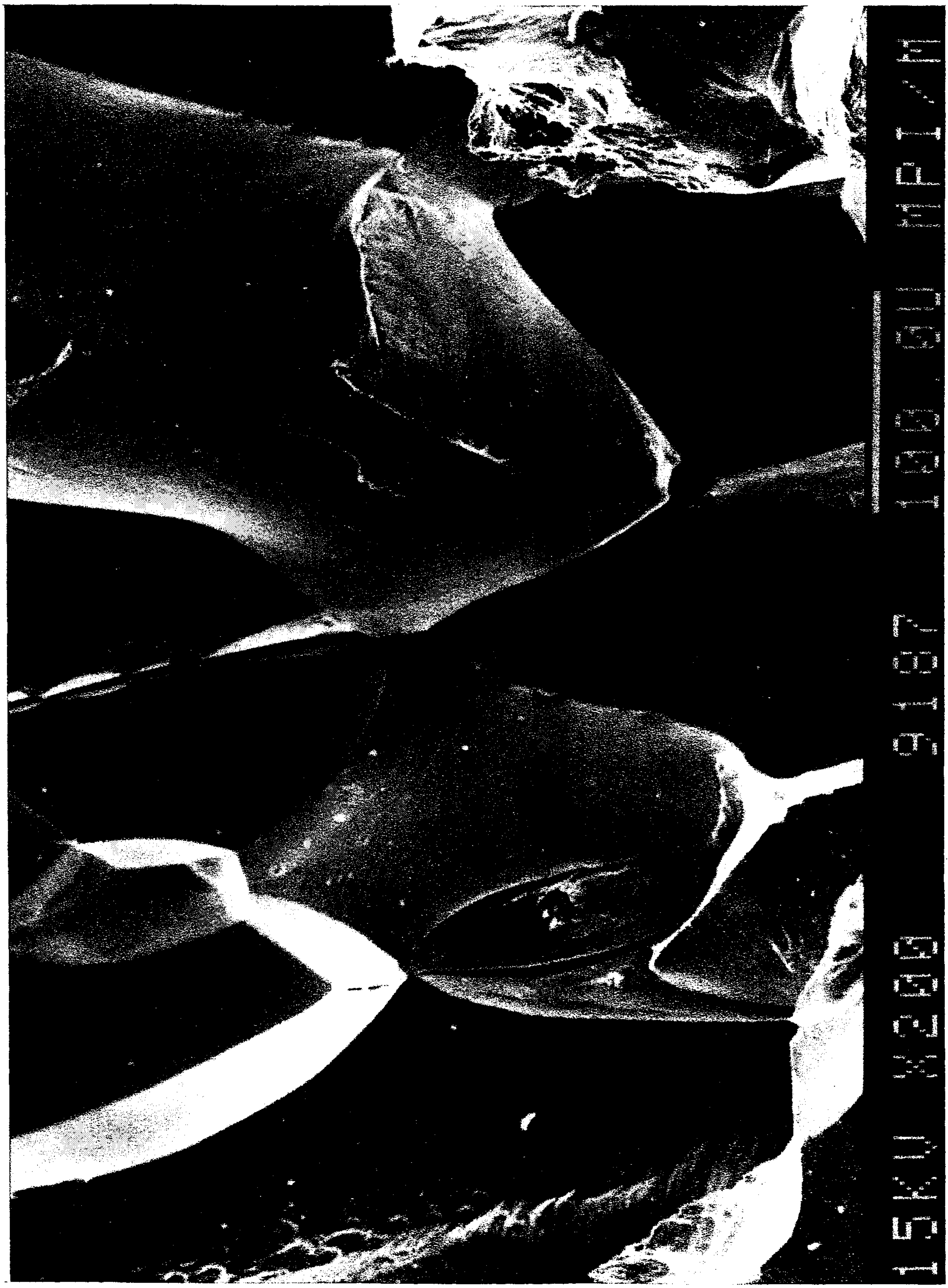

F01655 2.0KV
X200 11mm

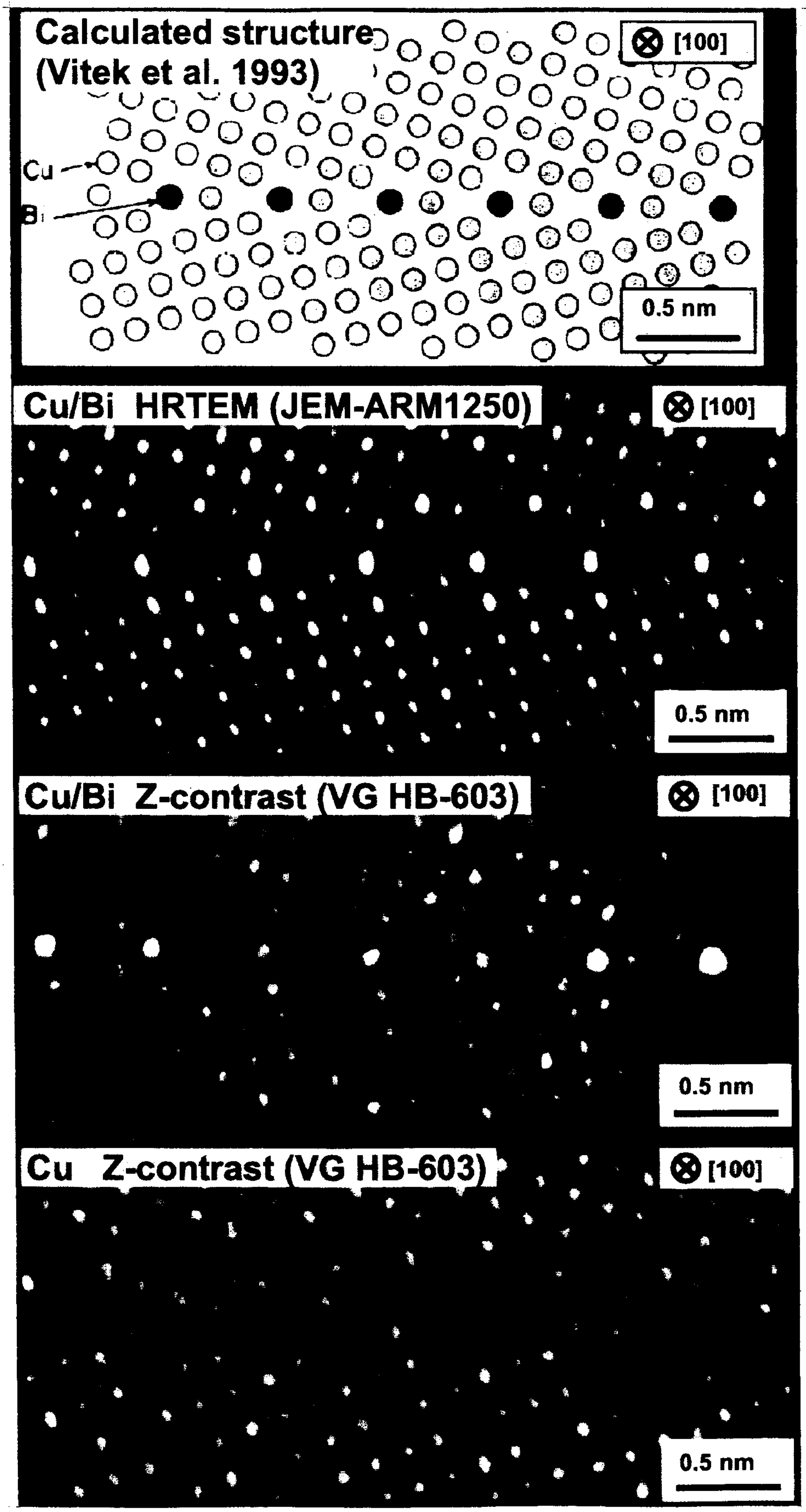


Rosenhain, Ewen 1912

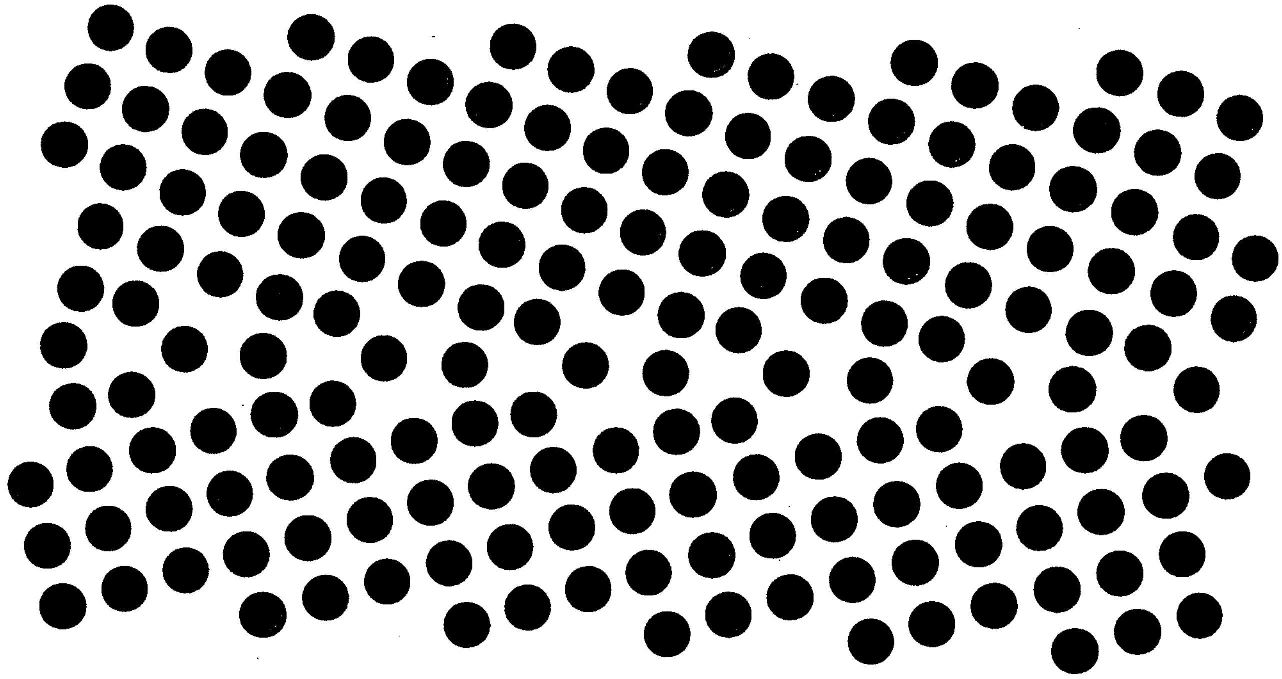


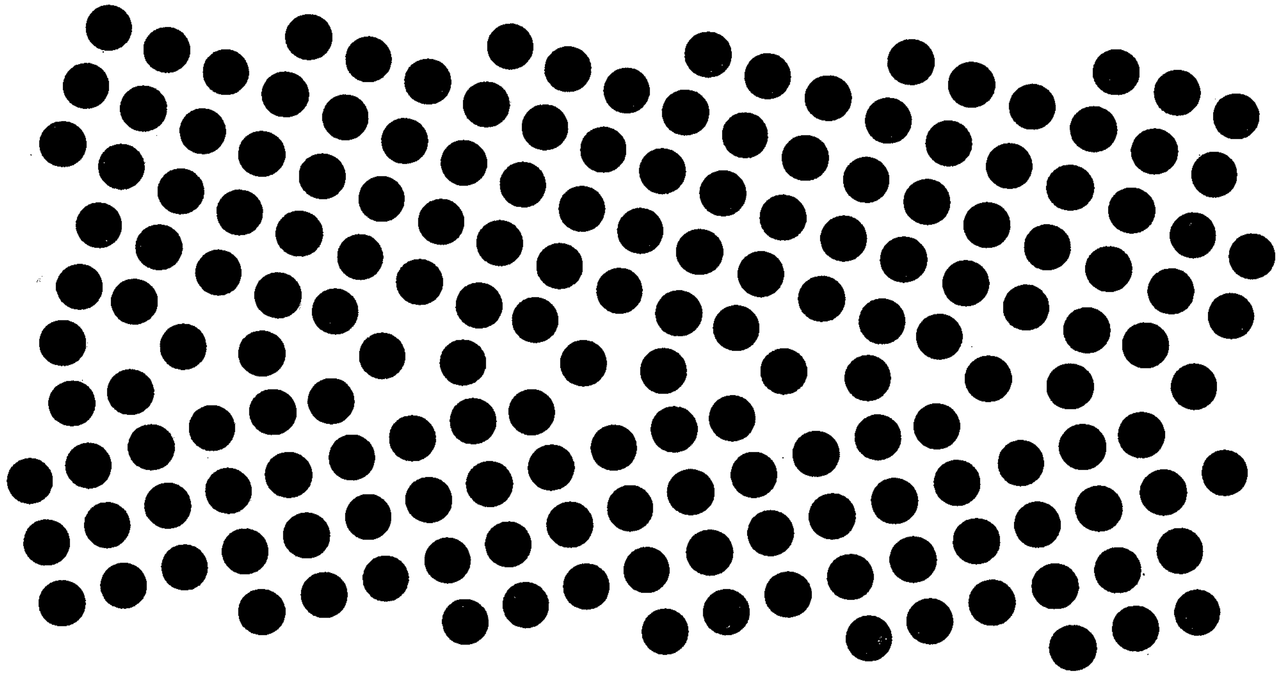
Sutton, Vitek 1983


15KV X200 9187 100.0U MPI/M


Calculated structure
(Vitek et al. 1993)
[100]
Cu
Bi
0.5 nm
Cu/Bi HRTEM (JEM-ARM1250)
[100]
0.5 nm
Cu/Bi Z-contrast (VG HB-603)
[100]
0.5 nm
Cu Z-contrast (VG HB-603)
[100]
0.5 nm

← (c)





Transmission Electron Microscopy

<u>Conventional TEM</u>

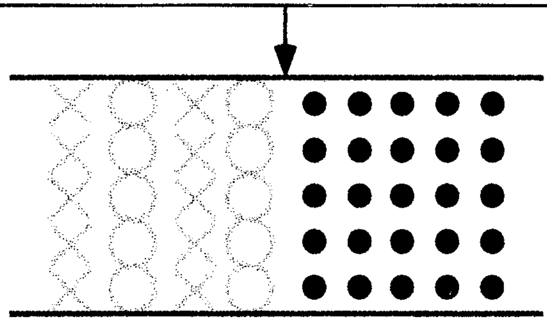
BF/DF/SAD

- Morphology
- Phase Distribution
- Defect Analysis
- *in situ*-Experiments
  - heating
  - cooling
  - deformation

<u>Spectroscopy and CBED</u>

(high spatial resolution)

- EDS
  - compositions
  - gradients
- EELS
  (EXELFS, ELNES)
  - compositions
  - gradients
  - electronic states



Information on chemistry and bonding

<u>Lattice Imaging</u>

HREM

- Structure of materials
  - oxides
  - HT superconductors
- Structure of defects
  - interfaces
  - dislocations

Complicated evaluation:
lens aberration of HREM
scattering within specimen

Experimental studies

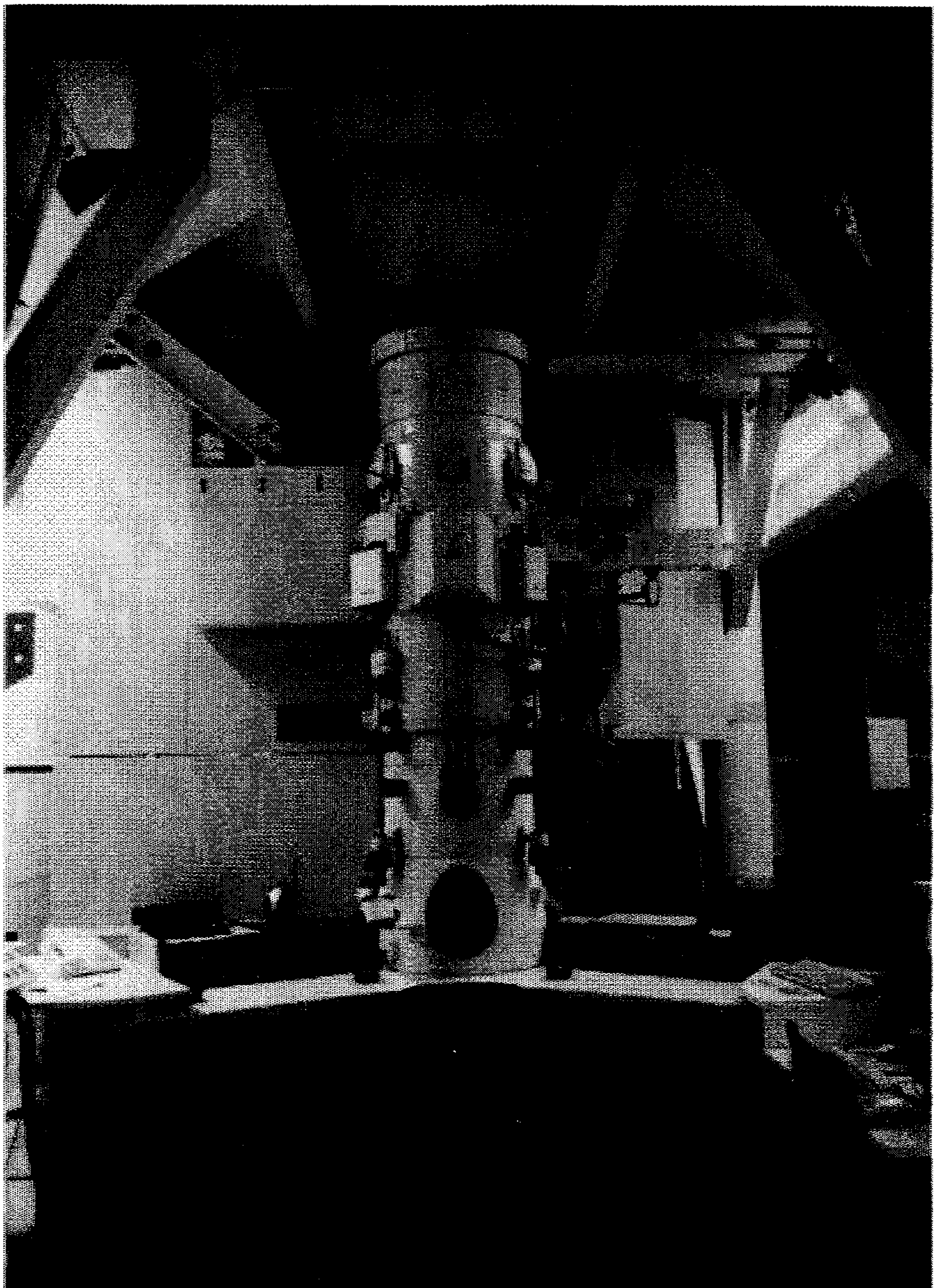
⇔

Image simulations

point-to-point 1.0 Å
information limit 0.8 Å } 1250 kV

STUTTGART "ATOMIC RESOLUTION MICROSCOPE"

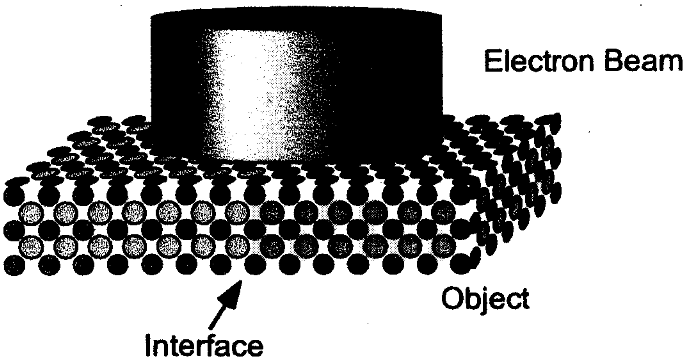
JEM-ARM1250

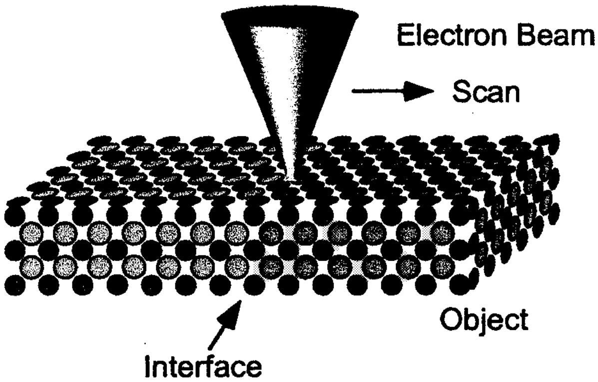


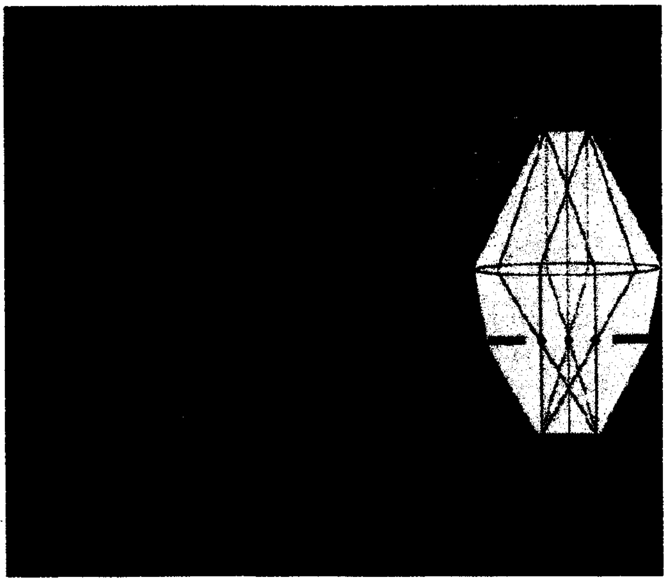
High-Resolution Transmission Electron Microscopy

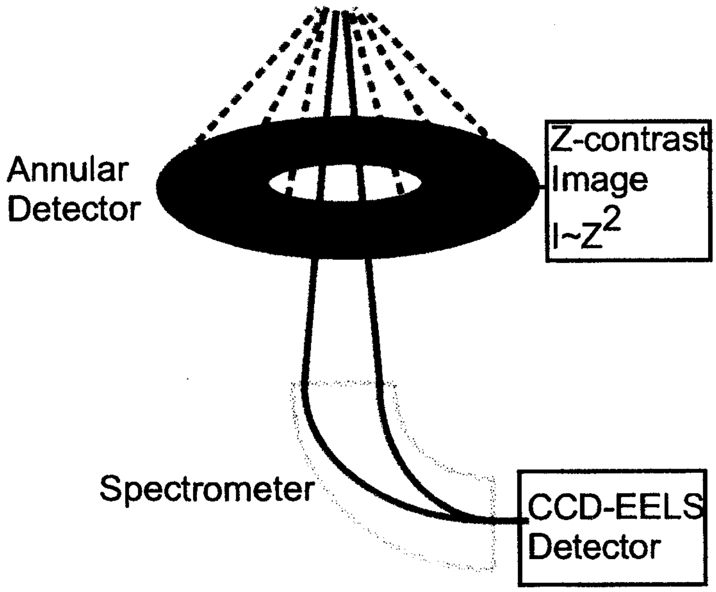
coherent imaging

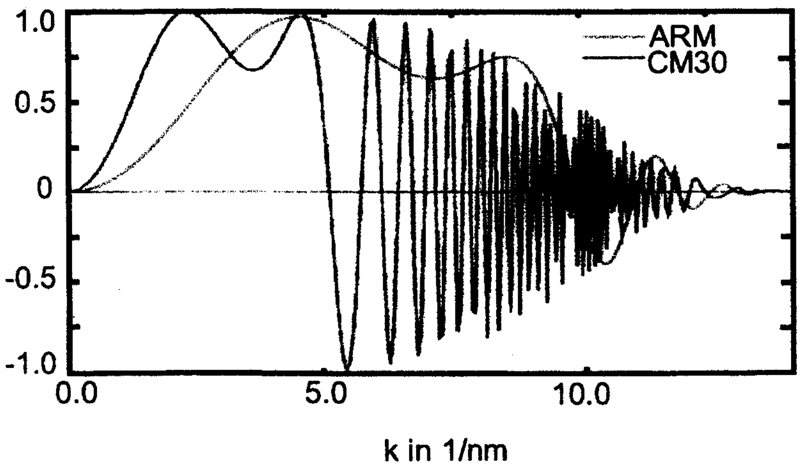
incoherent imaging
(Z-contrast)

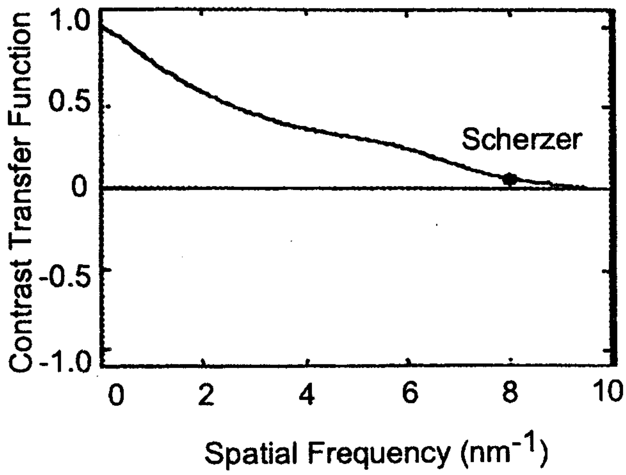




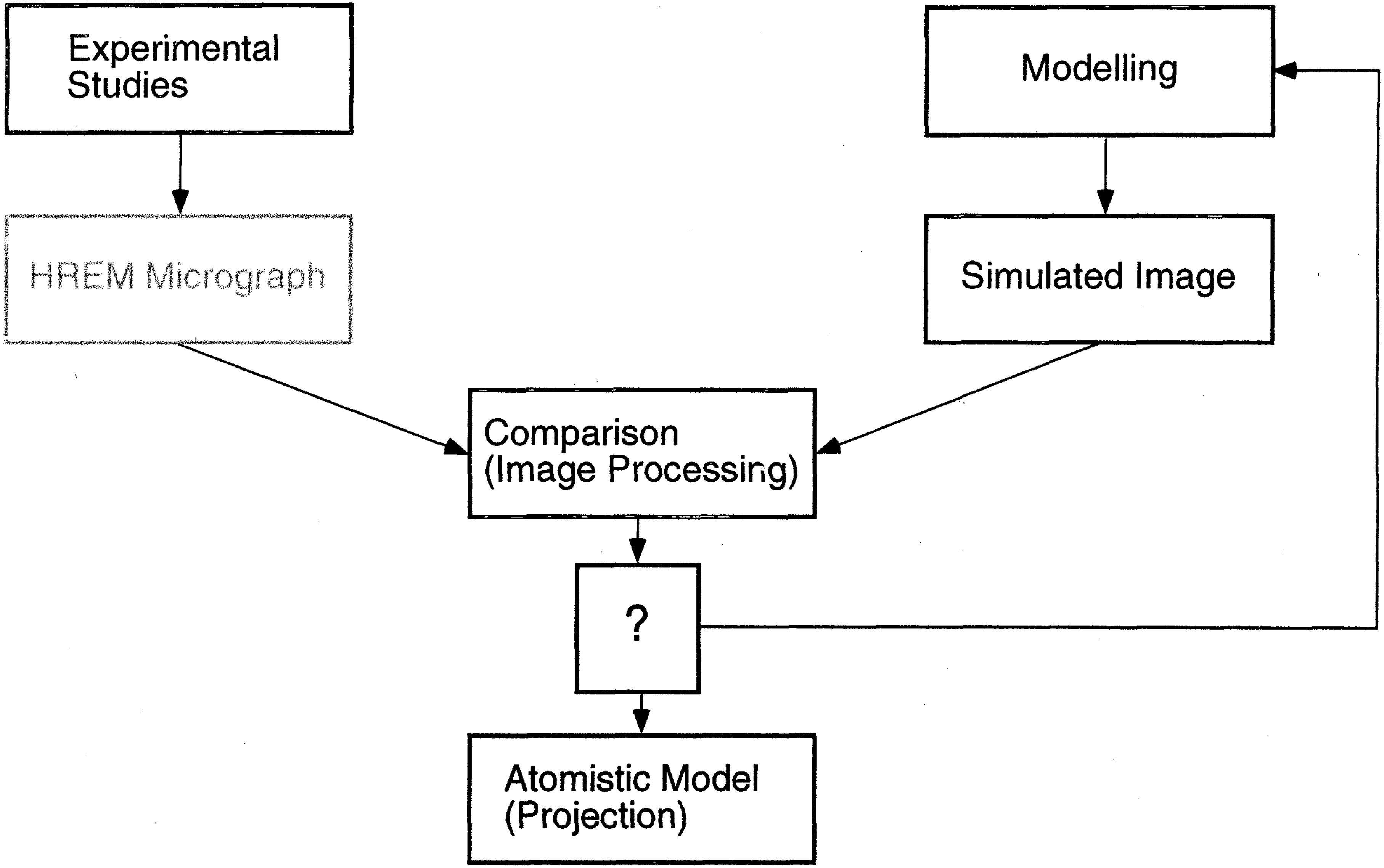




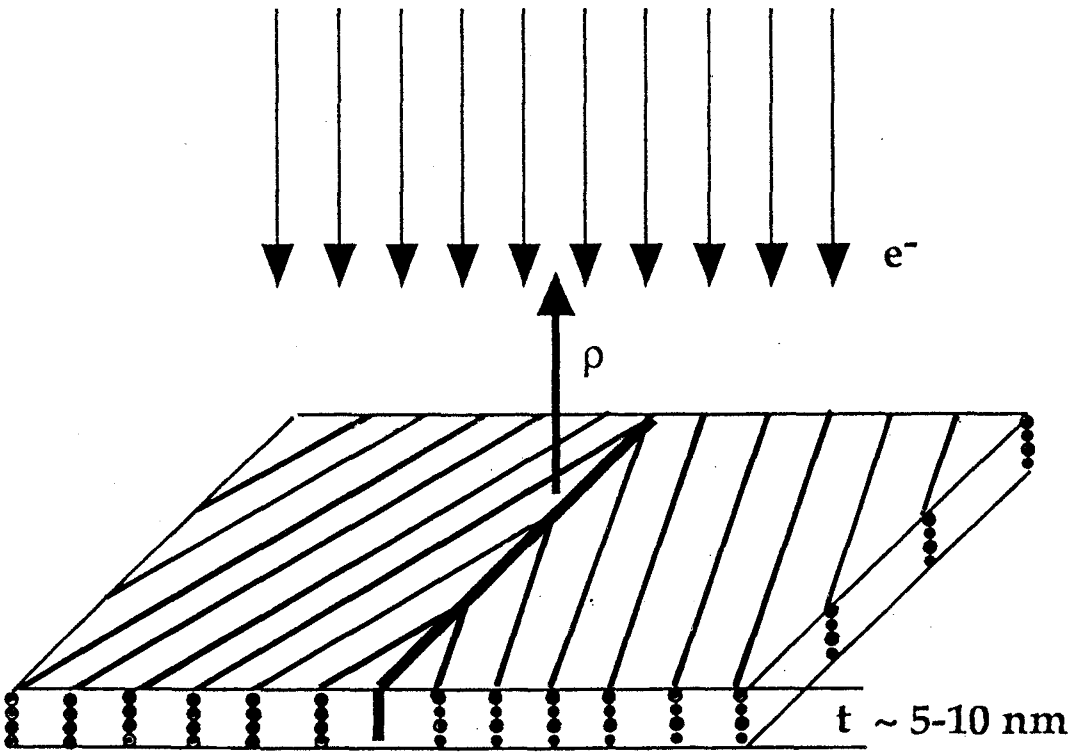




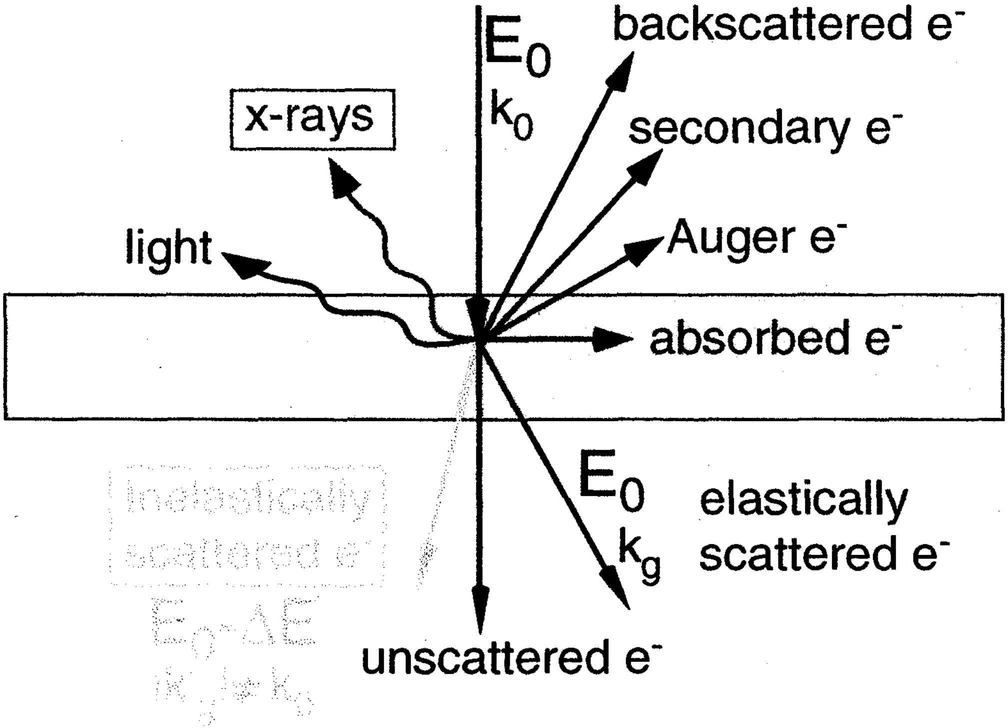
Quantitative High-Resolution Electron Microscopy

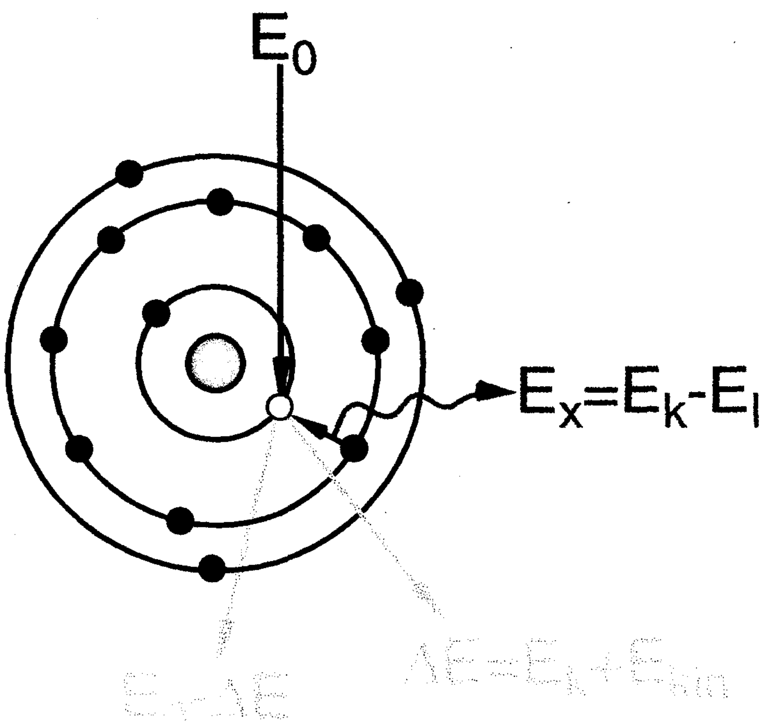


High Resolution Electron Microscopy of Interfaces



Elastic and Inelastic Scattering Process



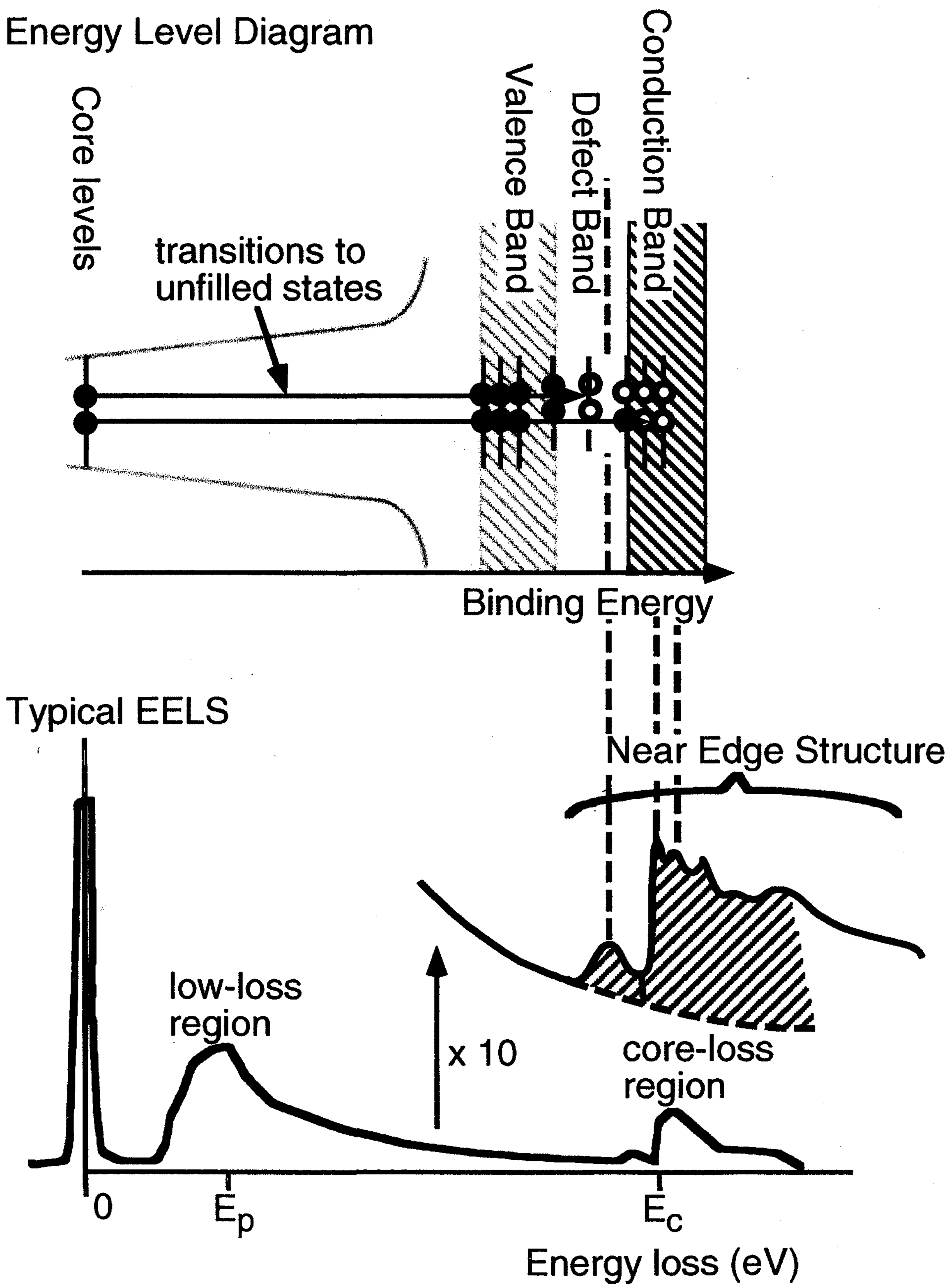


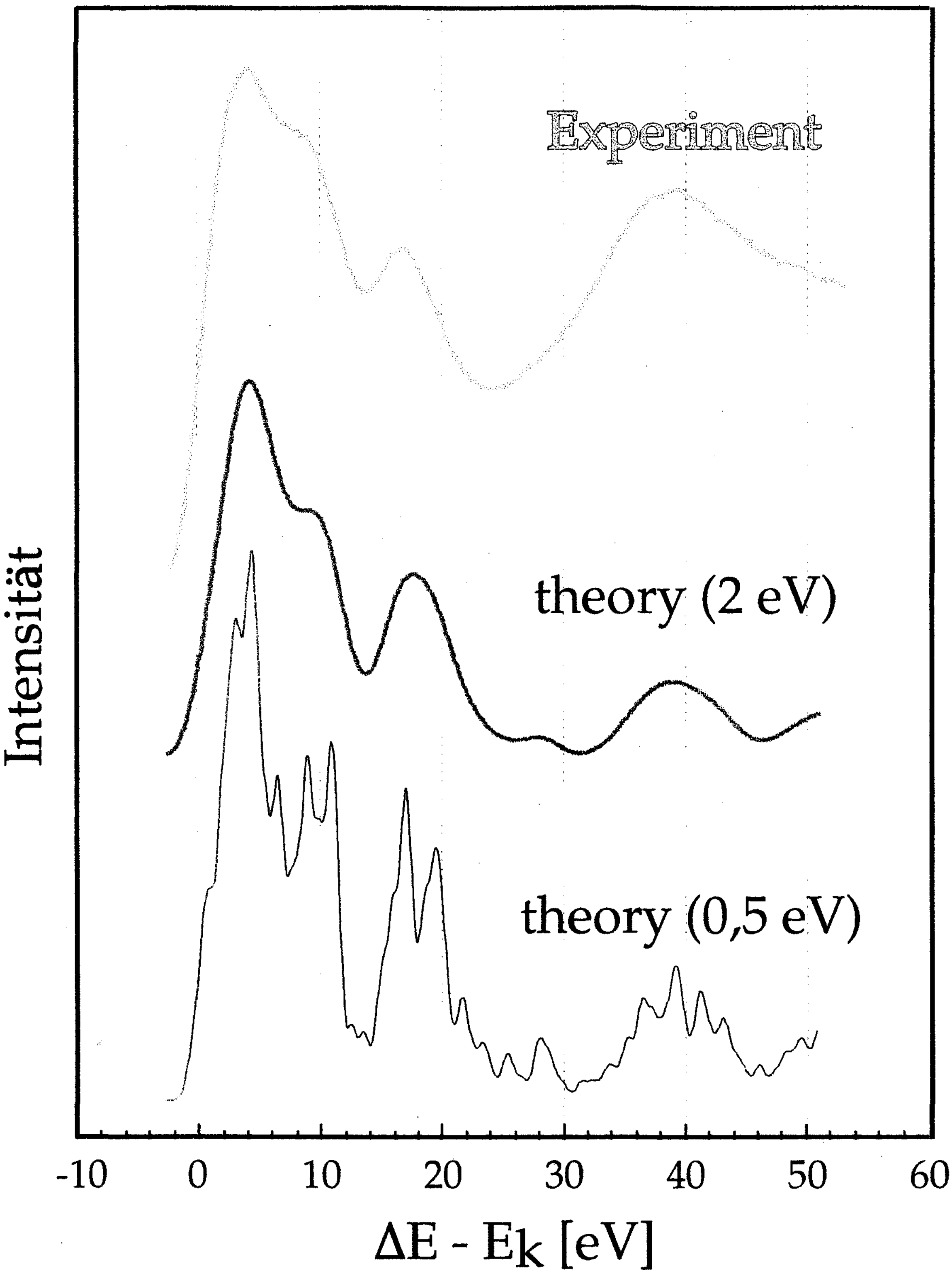
EDS
Energy Dispersive
Spectroscopy

EELS
Electron Energy
Loss Spectroscopy

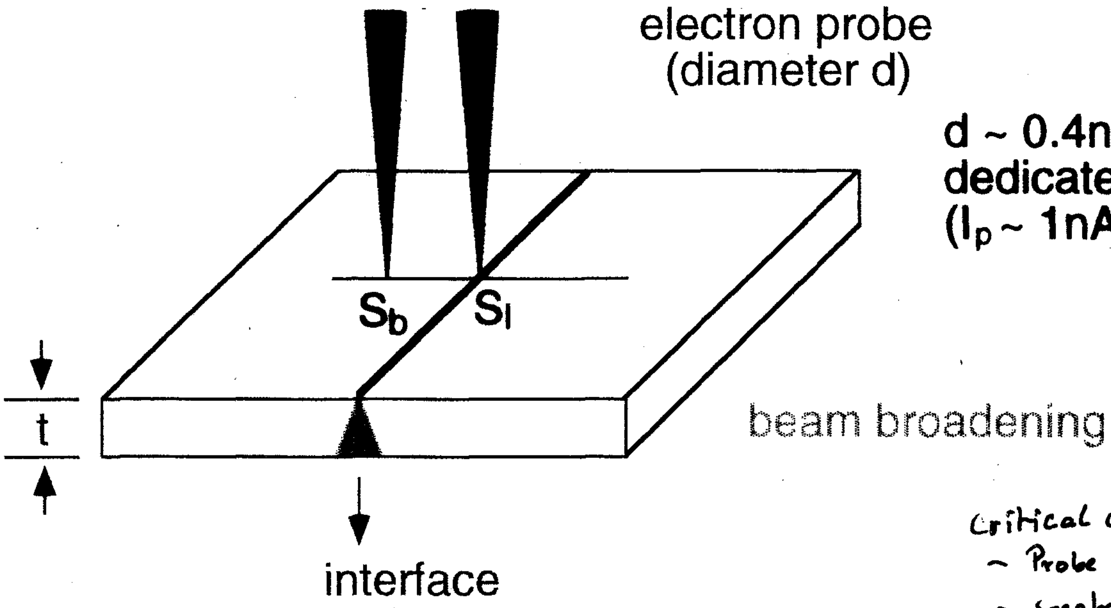
ELNES

(electron energy-loss near edge structure)




Experiment
theory (2 eV)
theory (0,5 eV)
Intensität
-10
0
10
20
30
40
50
60
ΔE - Ek [eV]

Analytical Electron Microscopy with High Spatial Resolution



d ~ 0.4nm (d → 0.1nm)
dedicated STEM
(I_p ~ 1nA)

critical components
- probe
- spectrometer
- detector

Comparision of S_b and S_l : (EDS and EELS)

- Segregation
- ELNES -> information on local bandstructures

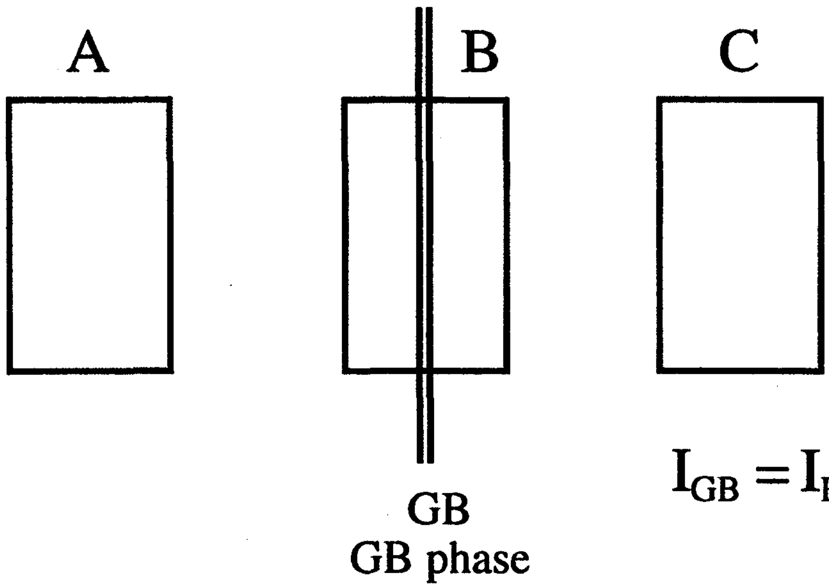
SREELS : Spacially Resolved

Special techniques (with dedicated instruments)

space charges at interfaces

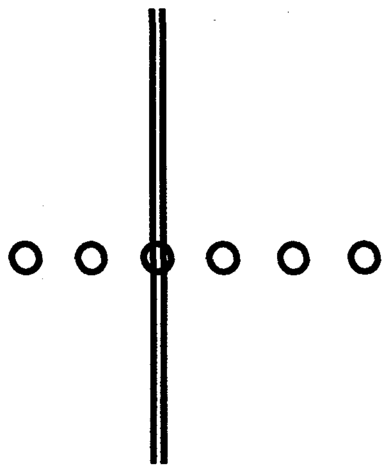
EELS (ELNES) of Grain Boundaries

Spatial difference technique



$$I_{GB} = I_B - \alpha \cdot I_A - \beta \cdot I_C$$

spot mode



spot size
≈ atomic columns!

Spatial difference technique

- information on composition
- information on ELNES at interfaces

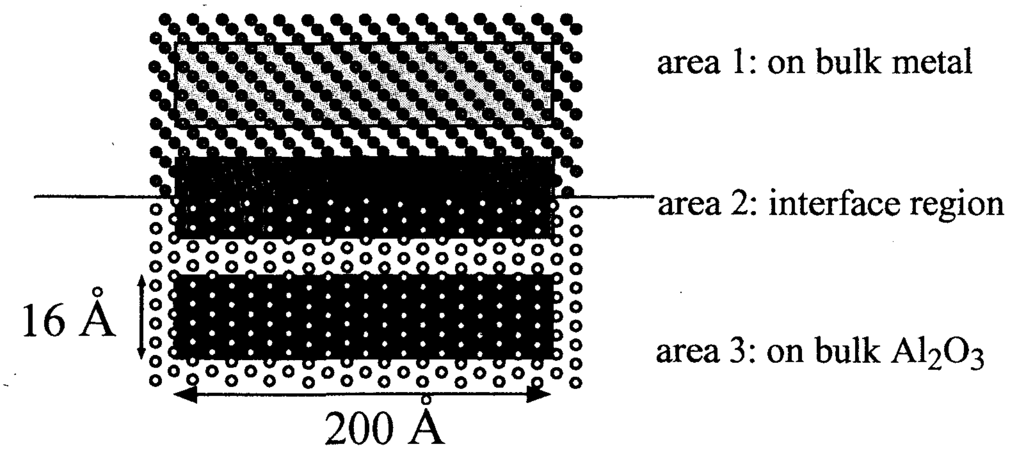
assumption: intensities of incoherent scattered electrons can be added

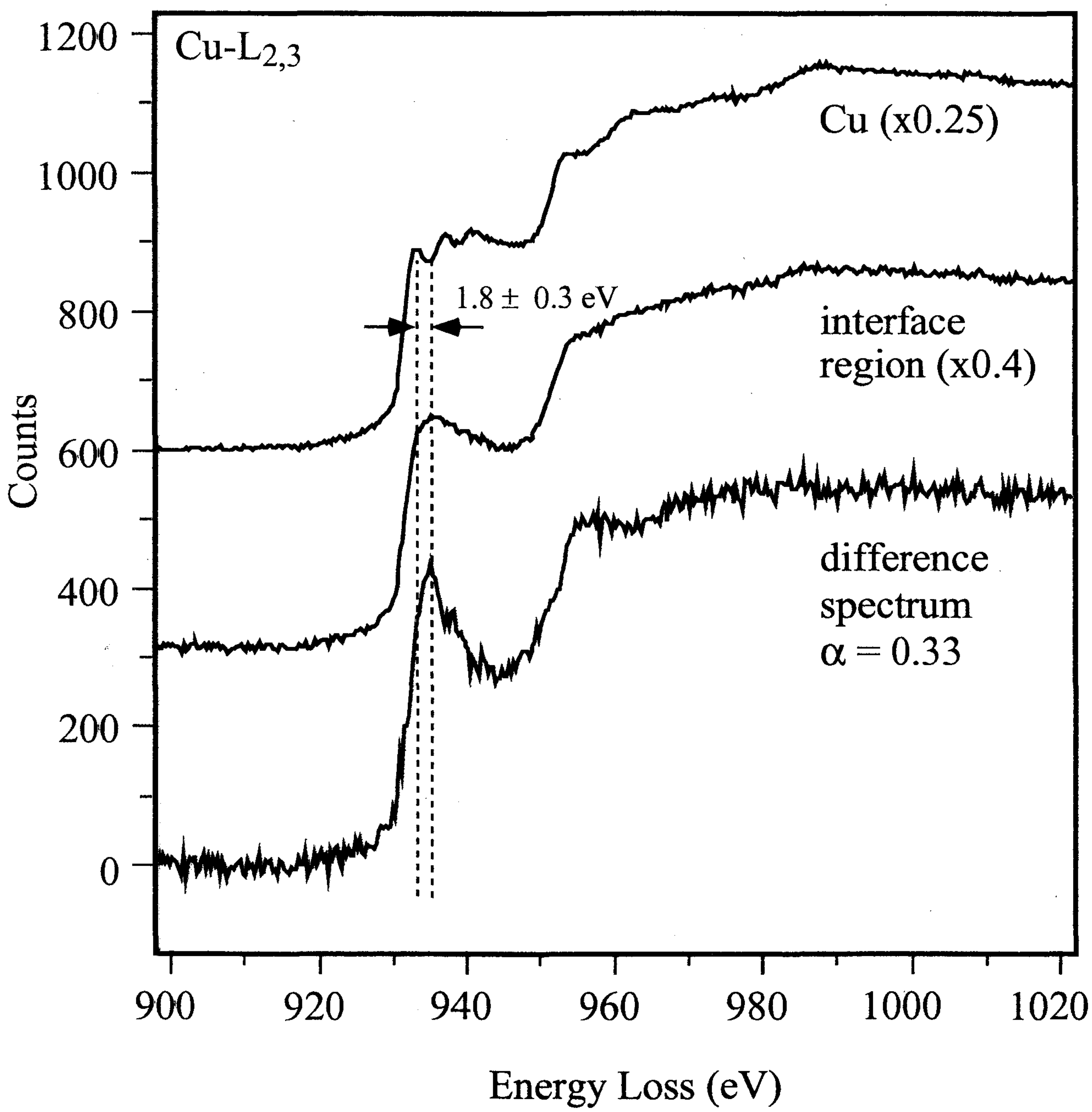
experimental "proof": C. Scheu

theoretical "proof": G. Möbus

Results Cu/(0001)Al_2O_3 (MBE-Stuttgart T=600°C)

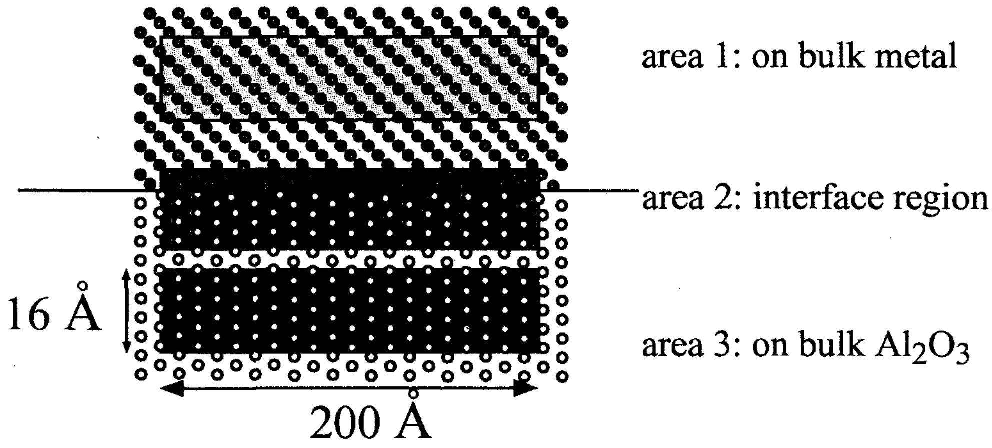
symmetrical case:





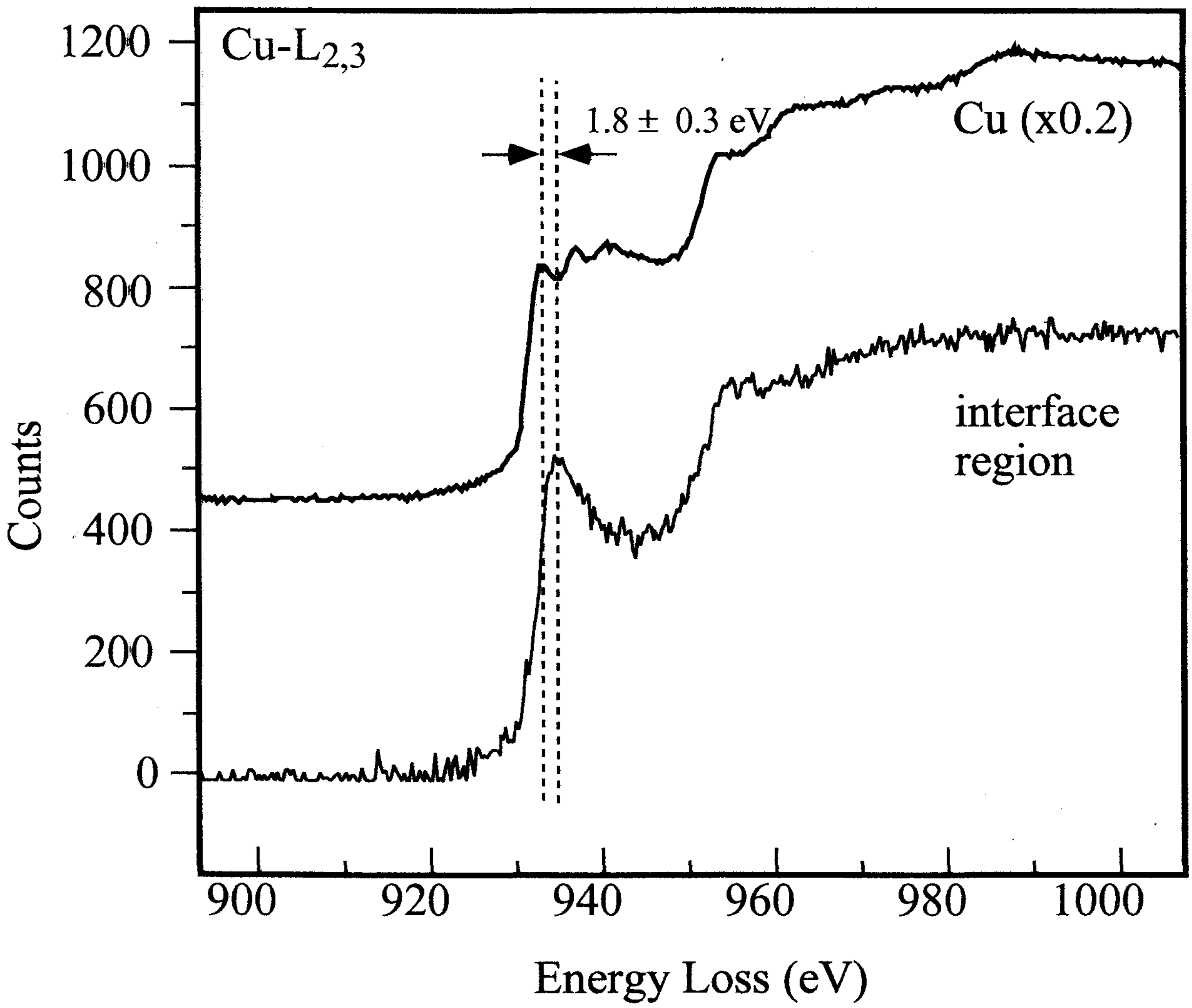
Cu/(0001)Al_2O_3 (T=600°C)

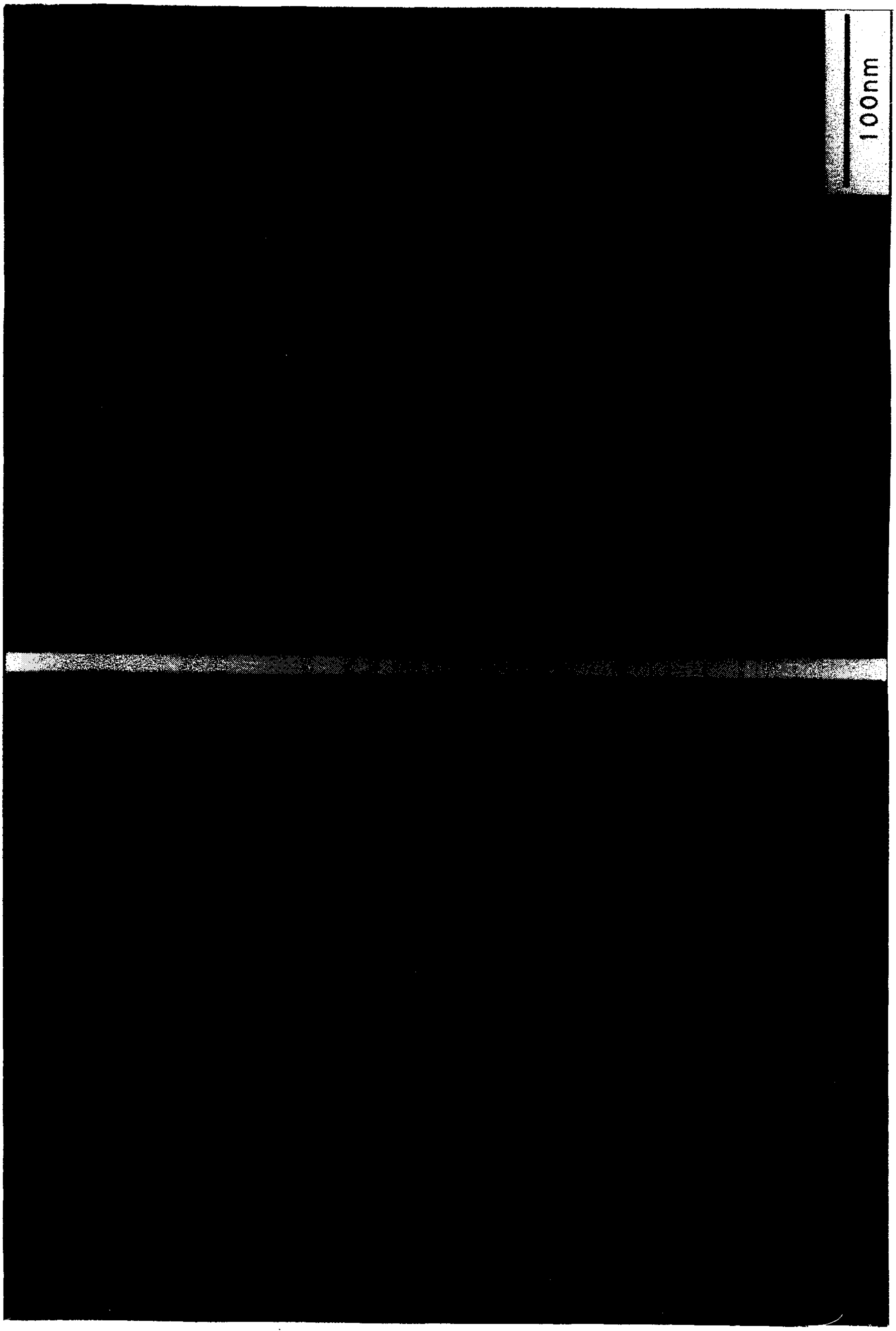
asymmetrical case:



estimation of $\alpha = 0.08$

➡ only 1.28 Å of the scanning area contains bulk Cu atoms!

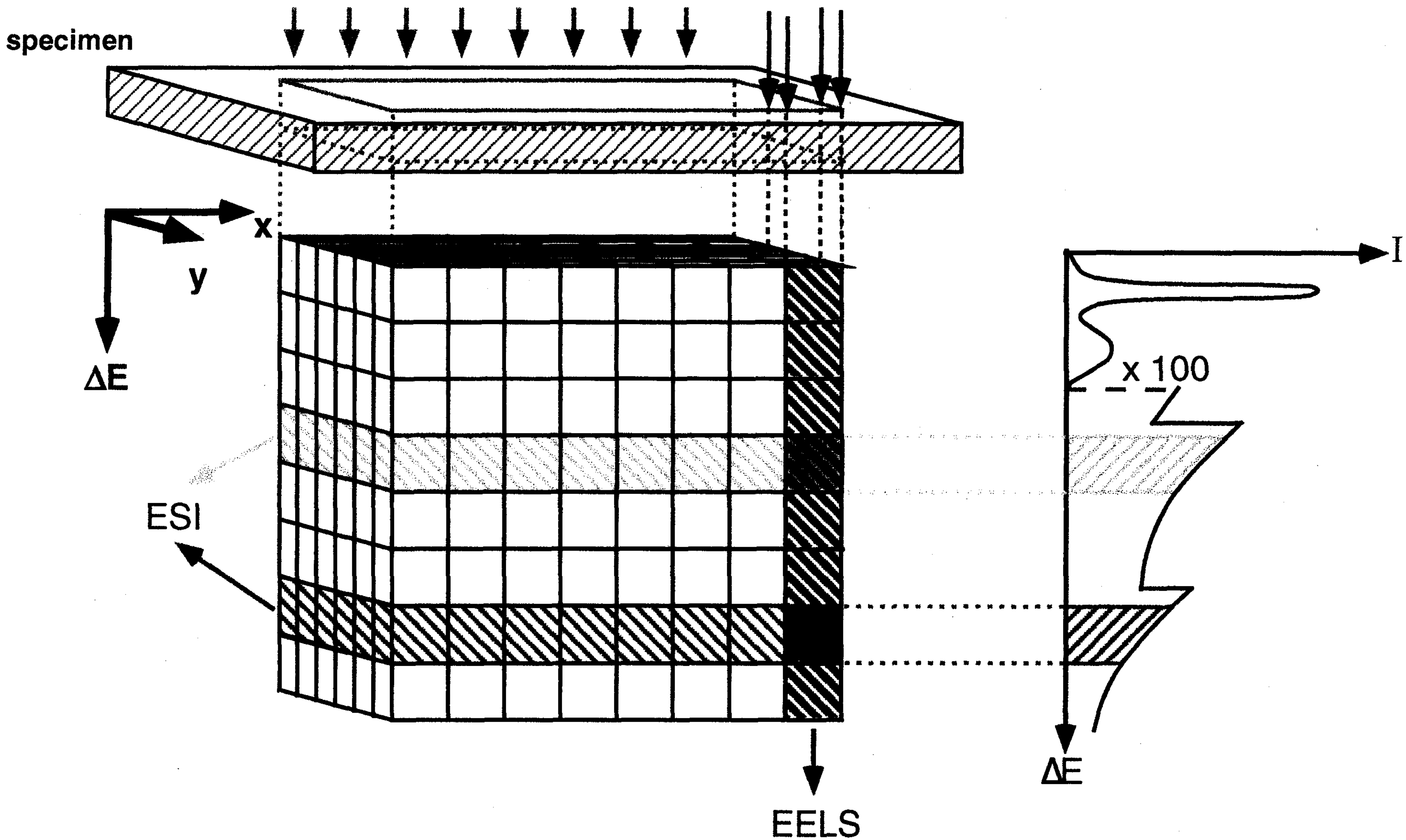



100nm

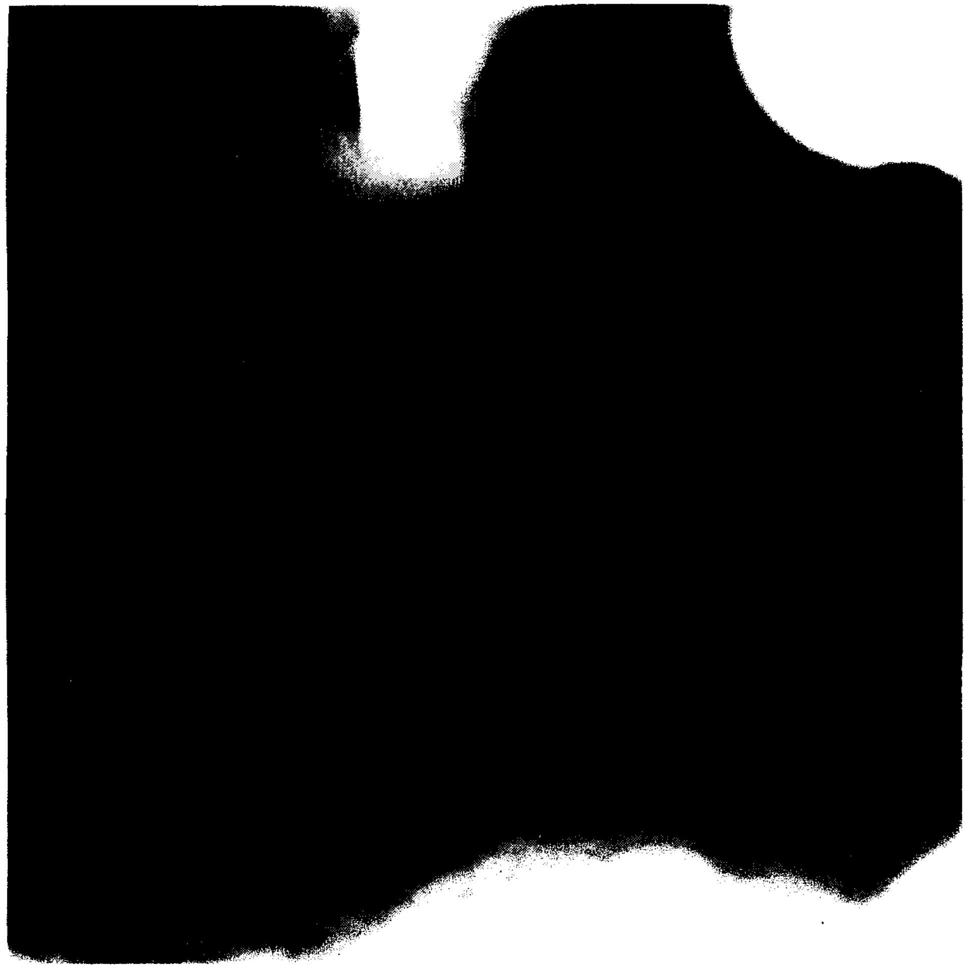
[redacted]

ESI

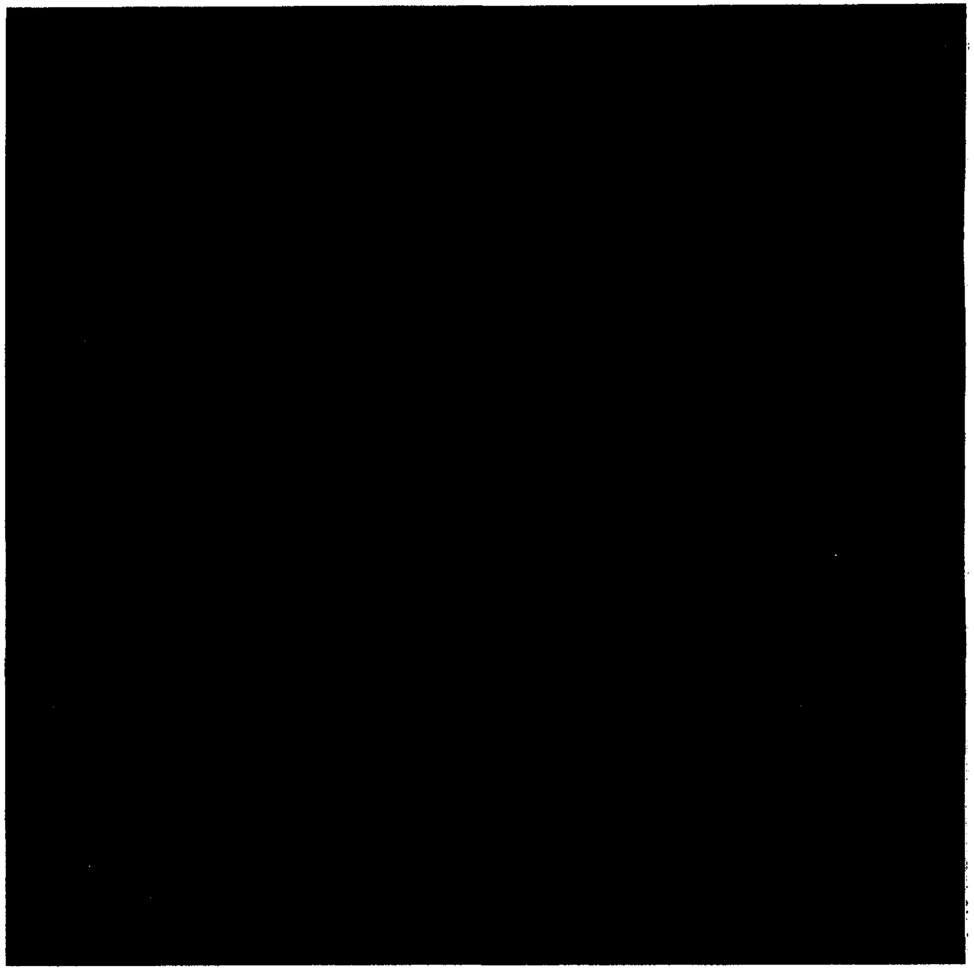
Image mode: $I = I(x, y, \Delta E)$



Sintered polymer derived Si_3N_4/SiC-composite



(bright field image)

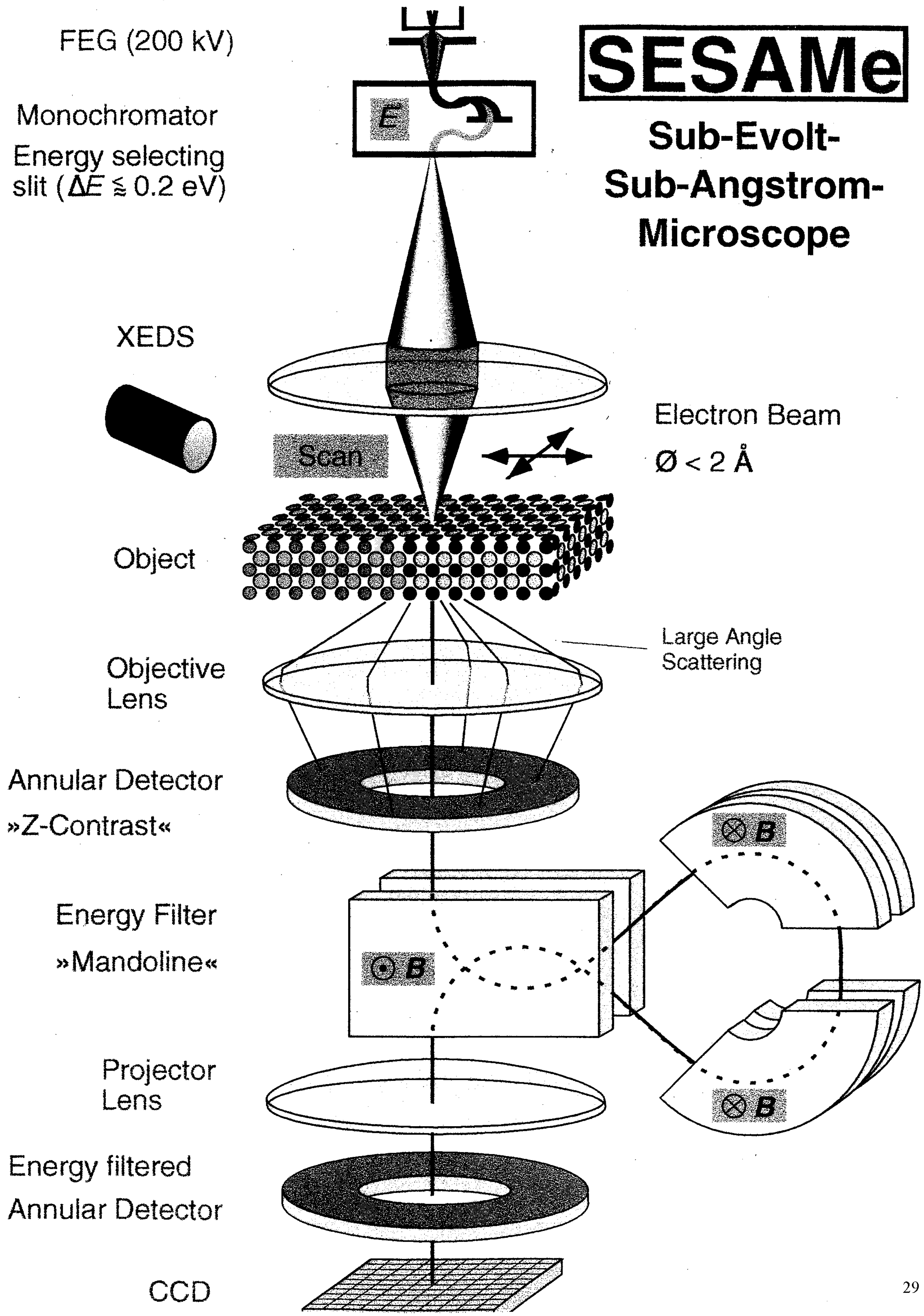


red: C (SiC)
green: N (Si_3N_4)
blue: O (am. oxide)

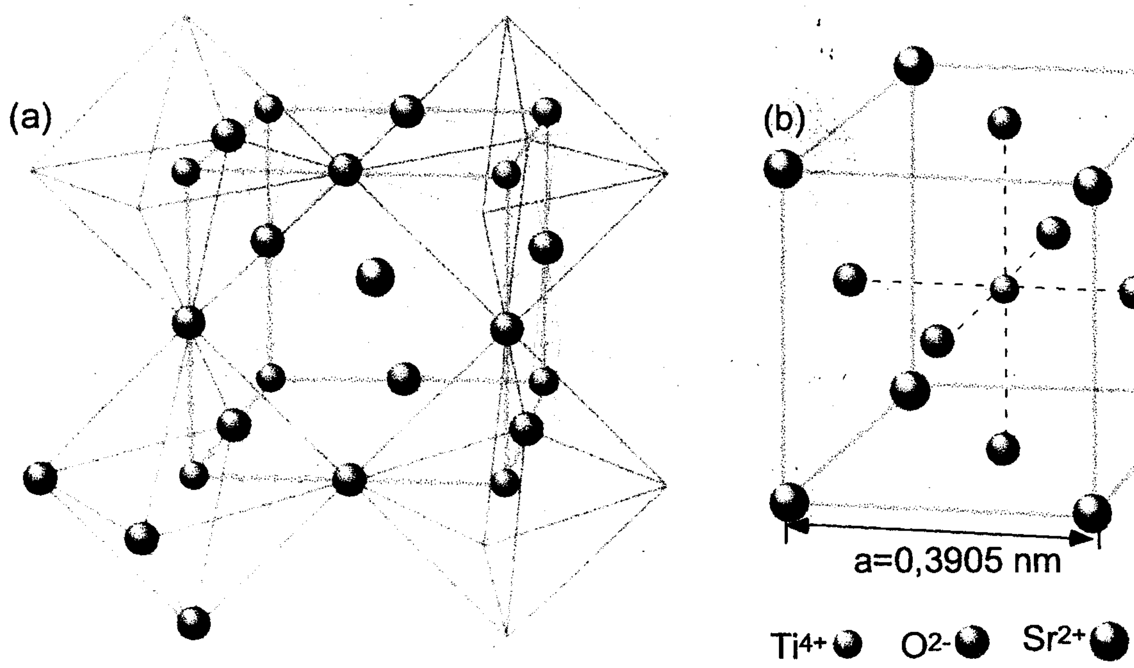
energy resolution
spatial resolution

Revolutionary Developments in Instrumentation of TEM

- Spherical aberration (C_S) of magnetic lenses can be corrected! (Haider, Rose, Urban)
- Monochromators for electron source will soon be available (Rose)
- Energy filter for electrons with high transmittivity are available (Mandoline filter)
- Advanced detection systems allow collection of each electron (low noise CCD cameras)


FEG (200 kV)
Monochromator
Energy selecting slit ($\Delta E \lessapprox 0.2$ eV)
SESAMe
Sub-Evolt-
Sub-Angstrom-
Microscope
E
XEDS
Scan
Electron Beam
Ø < 2 Å
Object
Large Angle Scattering
Objective Lens
Annular Detector
»Z-Contrast«
B
Energy Filter
»Mandoline«
B
Projector Lens
B
Energy filtered Annular Detector
CCD

$SrTiO_3$ - Crystal Properties



Crystal structure of $SrTiO_3$. Titan is in 6-fold coordination by Oxygen.

<u>Selected properties of $SrTiO_3$</u>

Crystal structure : Perowskite
cubic ⟶ highly symmetrical
complex structure

Lattice constant : a = 0.3905 nm

Space group : $Pm\bar{3}m$

Moos hardness : 6...6.5

Single crystal orientation : (001) and (110)

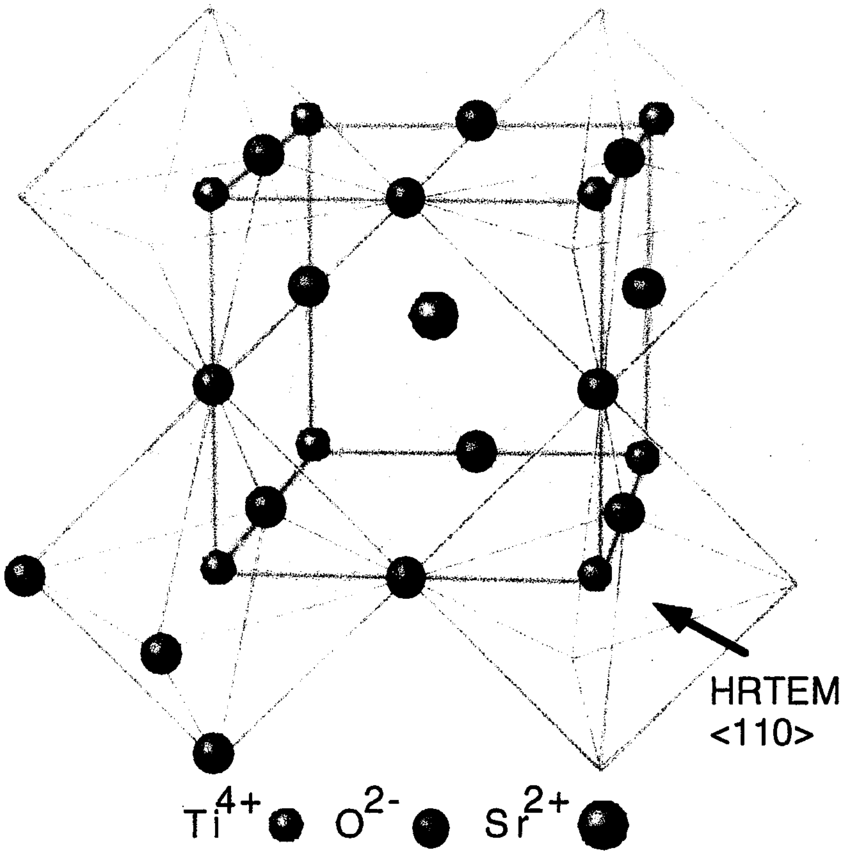
scattering factors?
charge density distribution?

crystallography

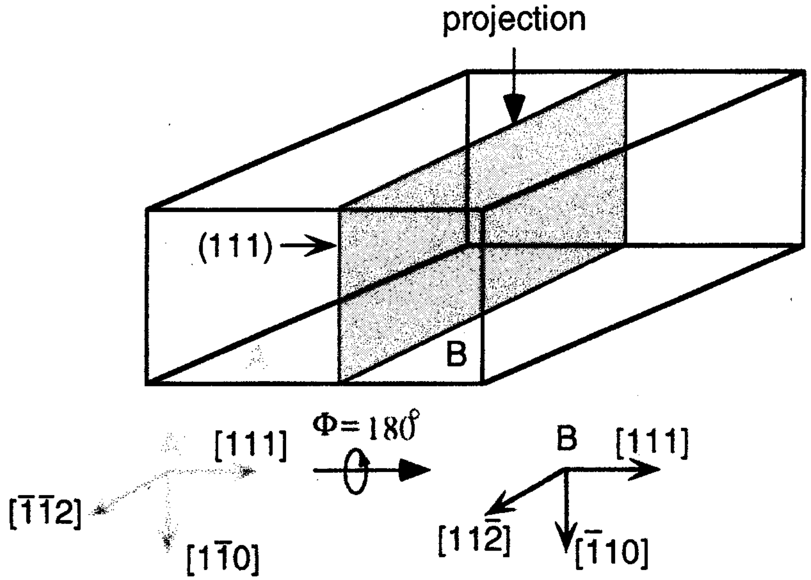
crystal structure of $SrTiO_3$

Perovskite

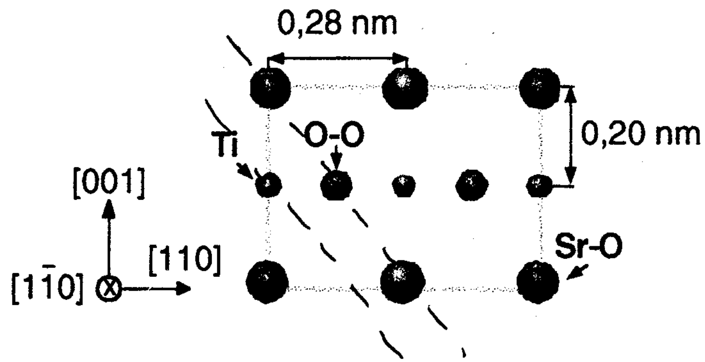
$Pm\bar{3}m$; a = 0,3905 nm



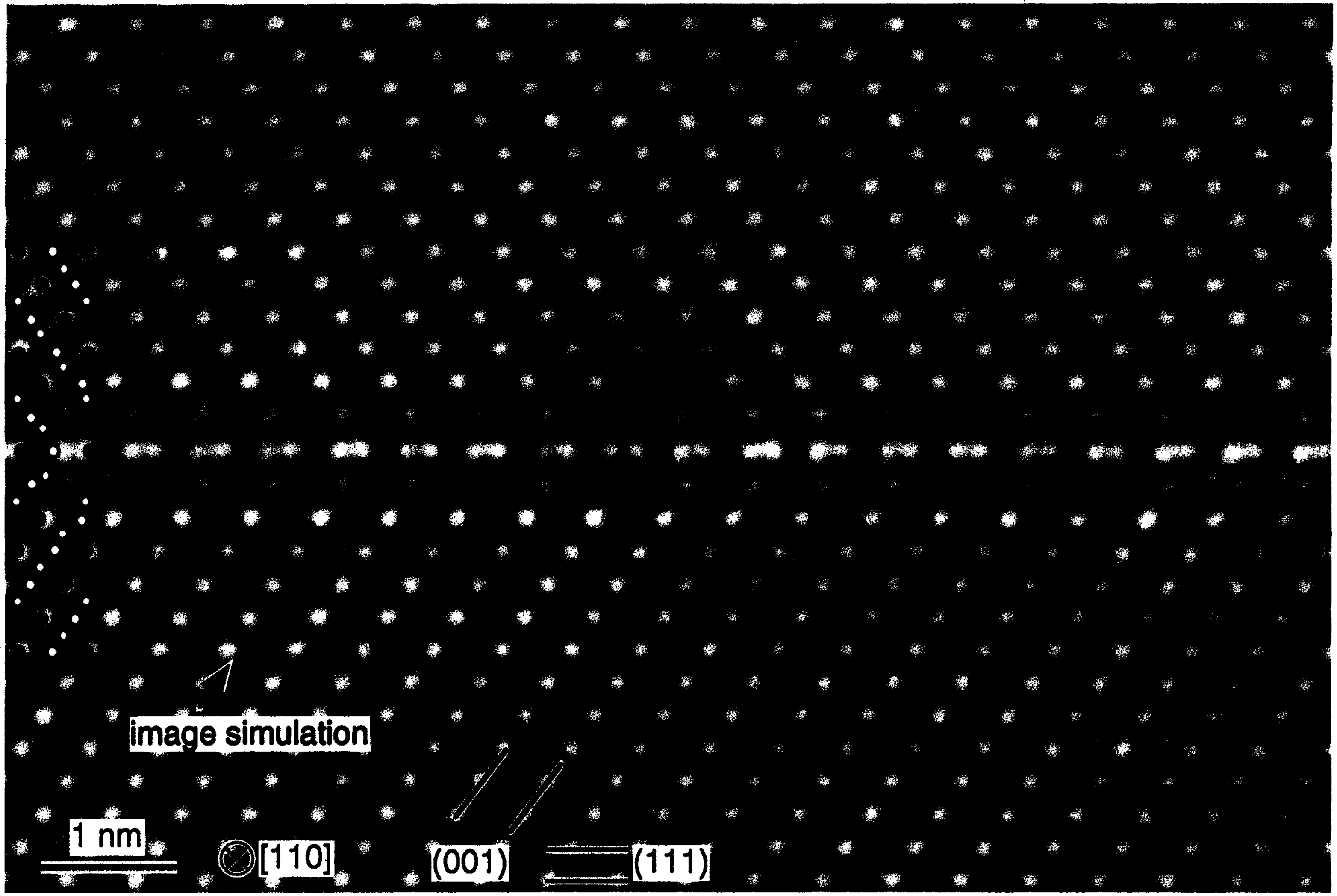
grain boundary crystallography



unit cell in <110> projection



Σ=3, (111) grain boundary in <110> projection

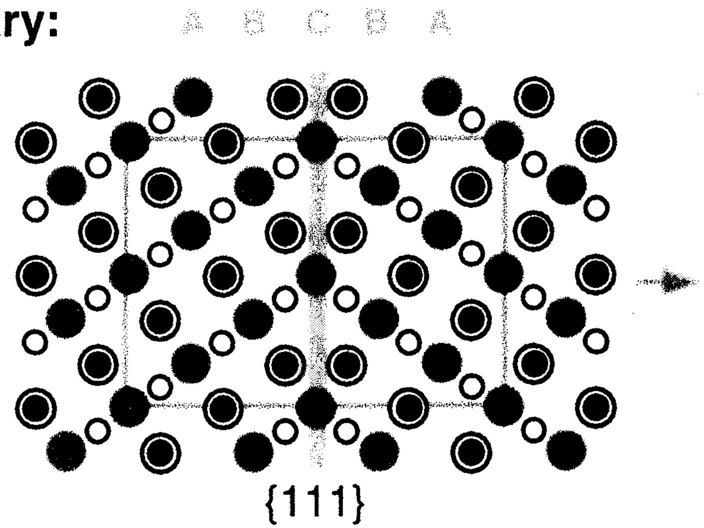


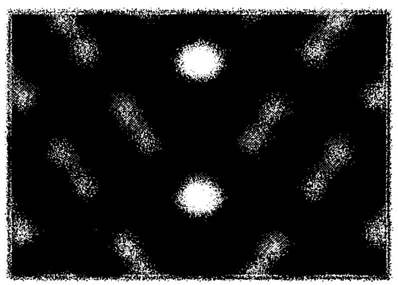
Kienzle

$SrTiO_3$ $\Sigma3$ (111) preliminary models

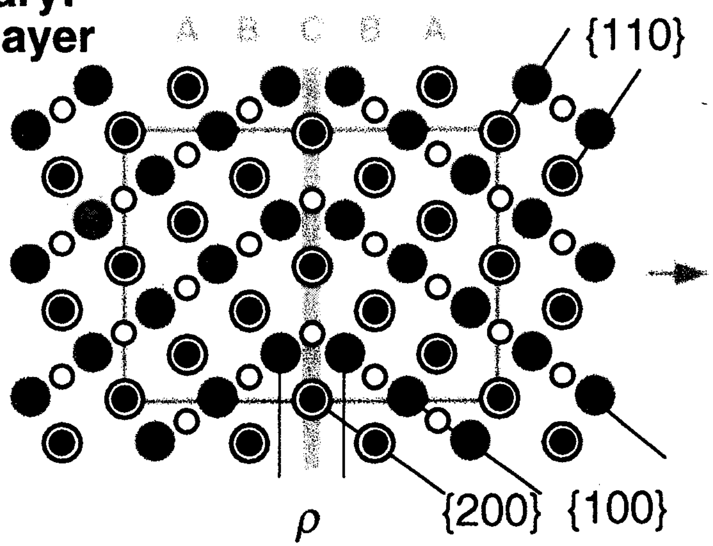
structure models | **image simulations** t = 6 nm, f = 46 nm | **experimental image** t = 6 nm, f = 46 nm

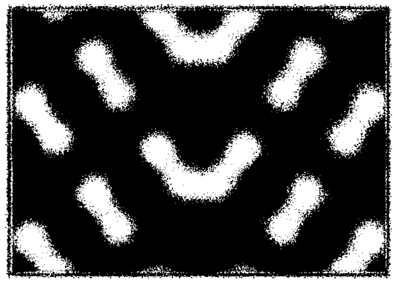
boundary: Ti layer

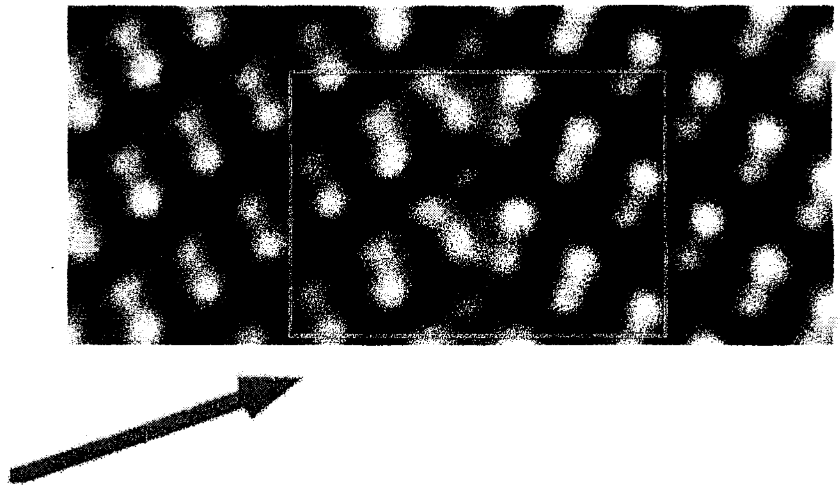




boundary: Sr-O_3 layer





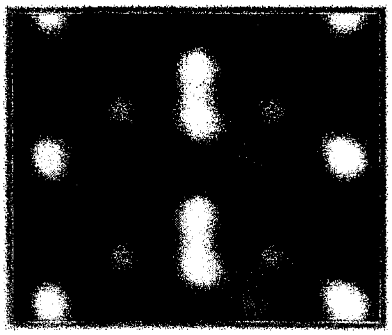


● Ti^{4+} ○ 2 O^{2-} ◉ Sr^{2+} + O^{2-}

Kienzle, Ernst

QHRTEM structure retrieval

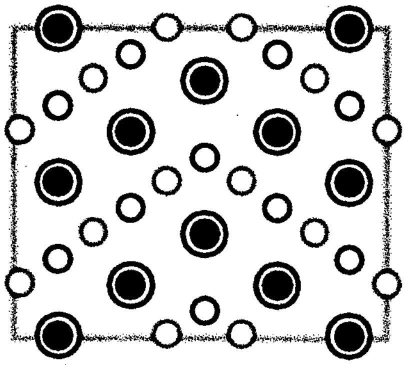
HRTEM image



? →

← image simulation

structure model



Structure retrieval

Determine imaging conditions

sample thickness t, defocus f
sample tilt, beam tilt

↓

Construct

preliminary structure model

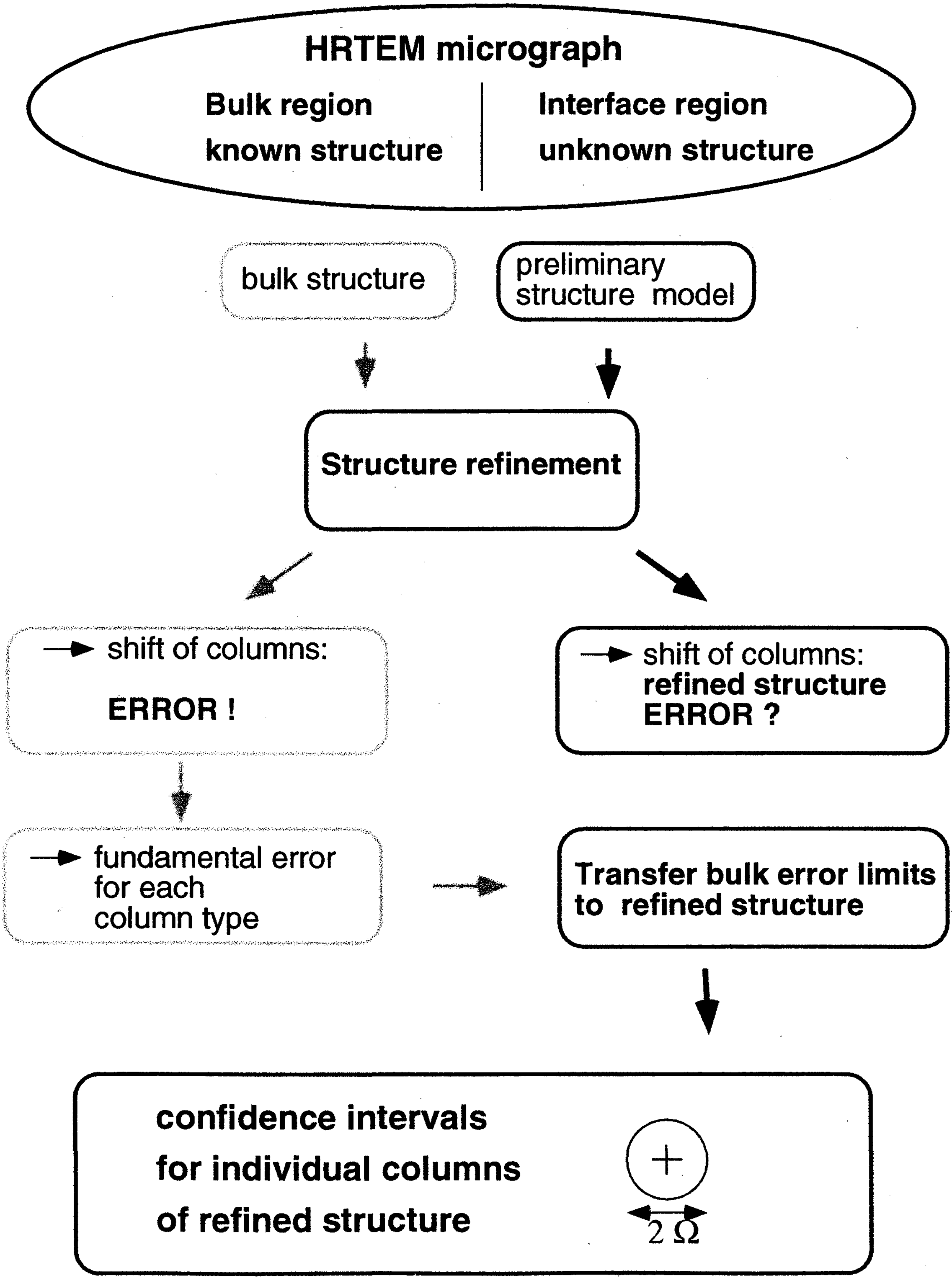
↓

Structure refinement

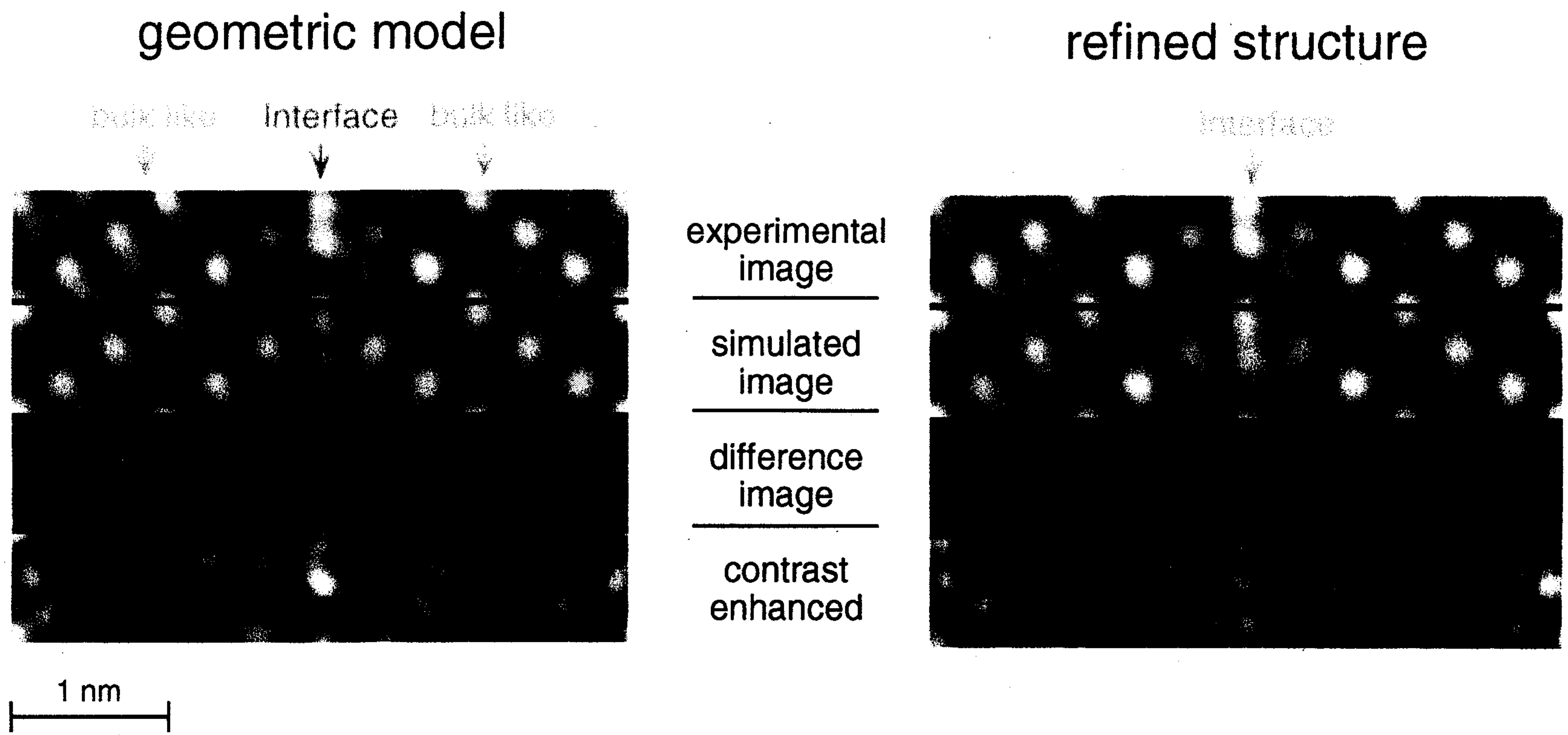
Iterative Digital image matching

D(Sim,Exp) = min

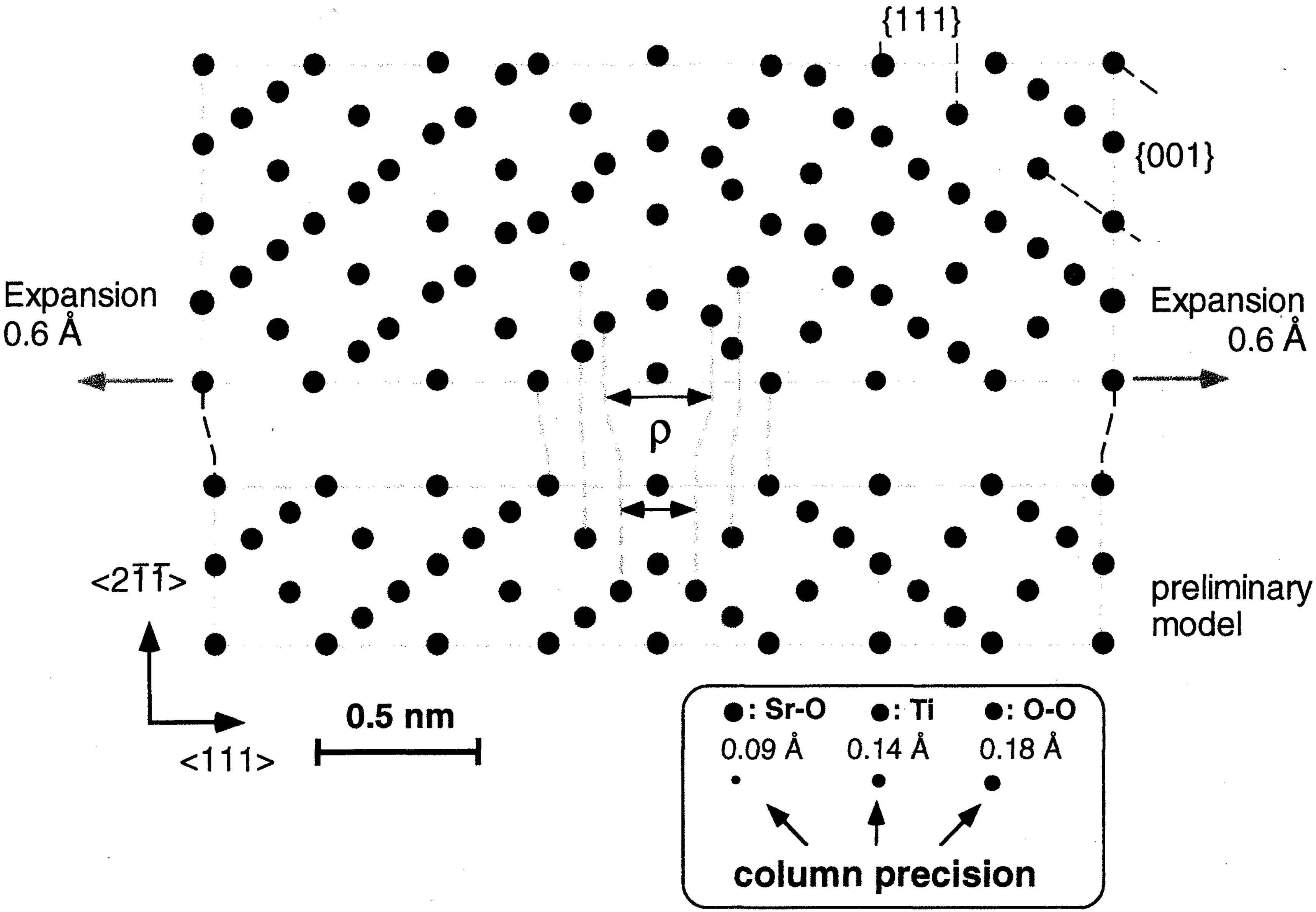
Quantification of error limits



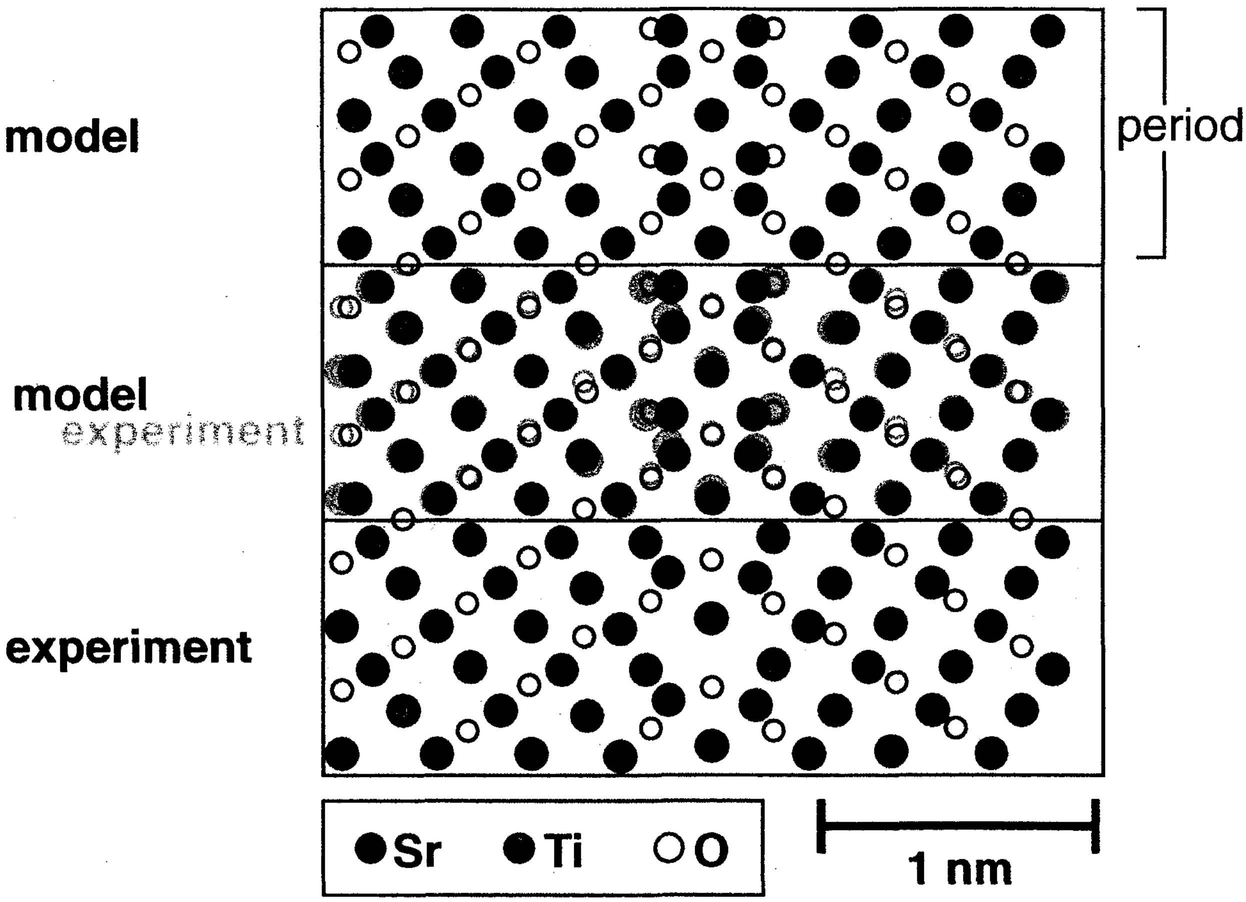
Iterative Digital Image Matching



Refined structure model



computer modelling versus experiment

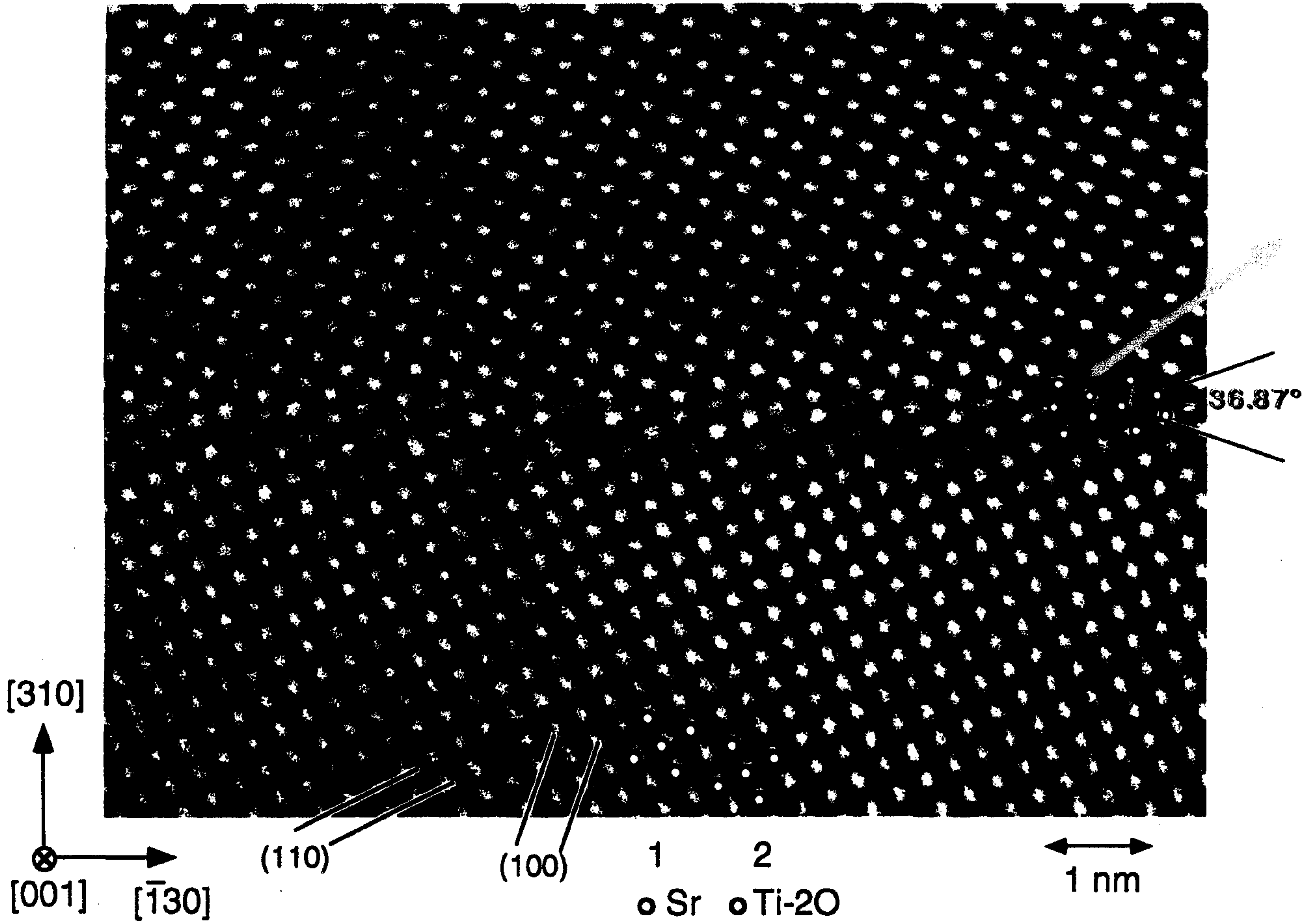


comparision	experiment	modelling	
termination	Sr-O	Sr-O	
coordination	Ti-O octahedra	Ti-O octahedra	
excess volume:	expansion: + 0.6 Å	expansion + 0.3 Å	?
relaxation at gb	Sr-O inward vs Ti low	Sr-O inward vs Ti large	?

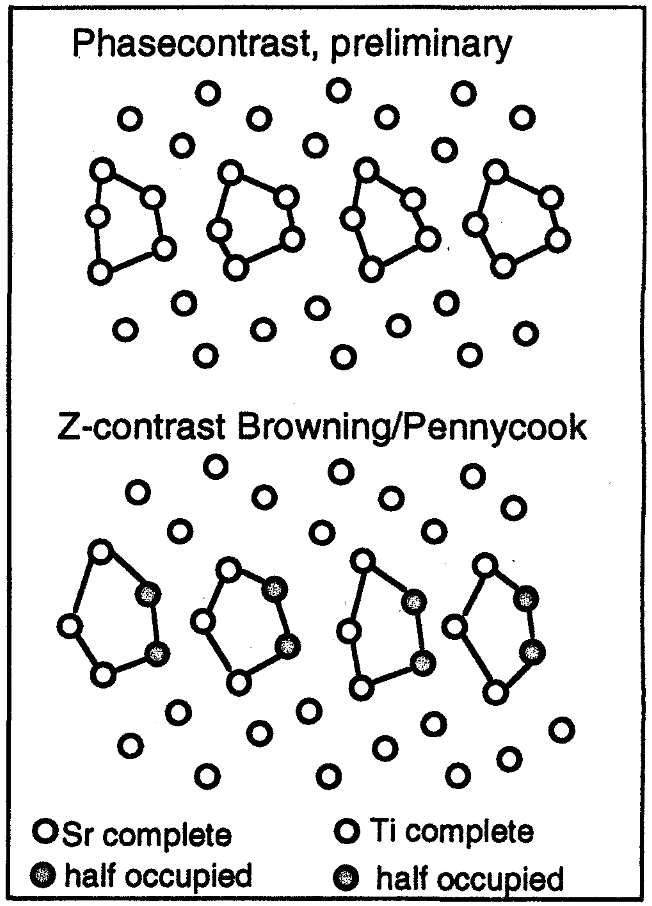
Near ∑5 (310) grain boundary / structure

Doping level: Fe/Ti = 0.01 at.%

HRTEM JEM 4000EX

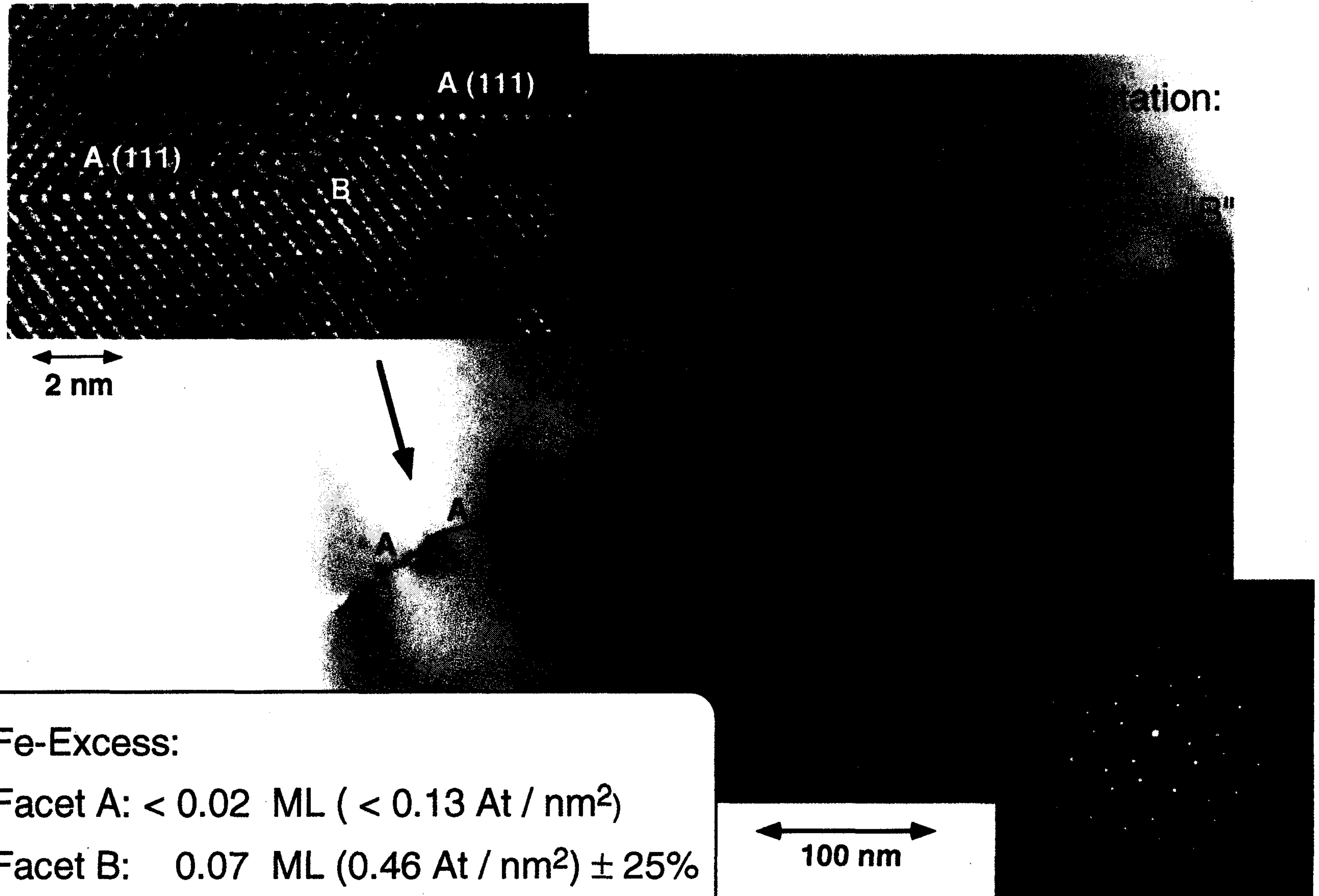


Structure models



Near $\Sigma 3$ (111) grain boundary in polycrystalline $SrTiO_3$

Doping level: Fe / Ti = 0.4 at.%



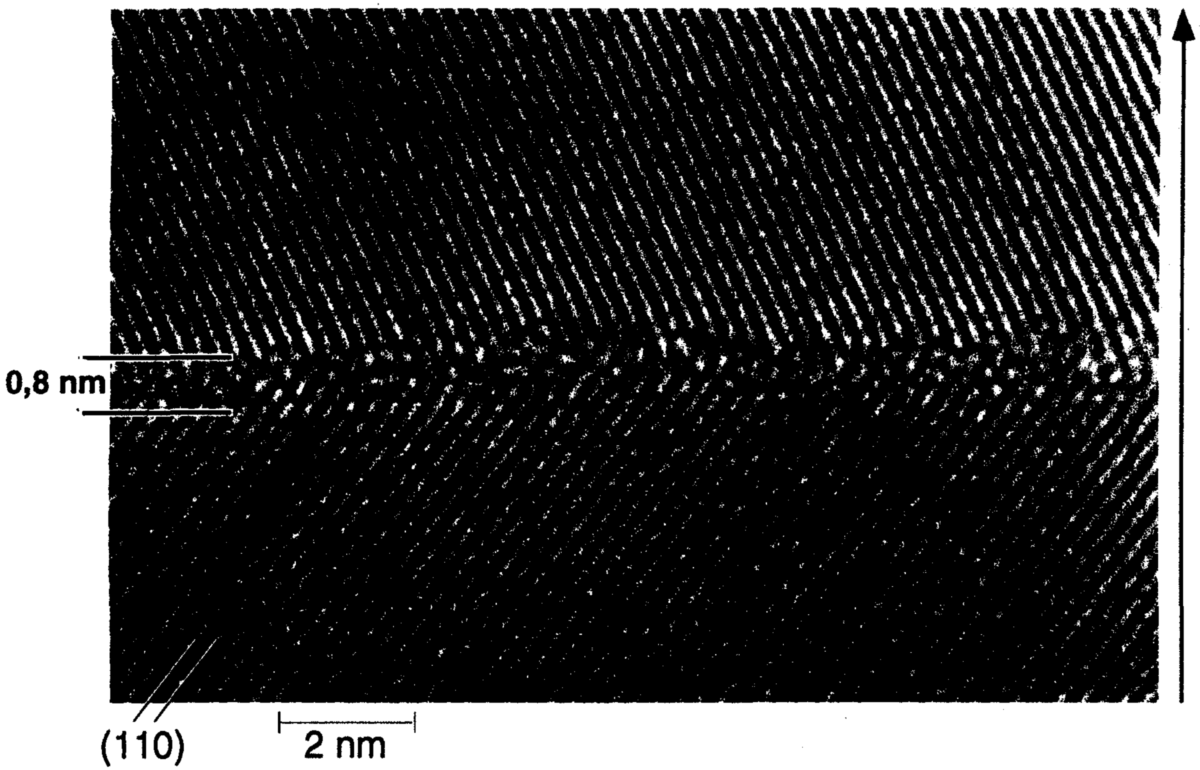
Fe-Excess:

Facet A: < 0.02 ML (< 0.13 At / nm^2)

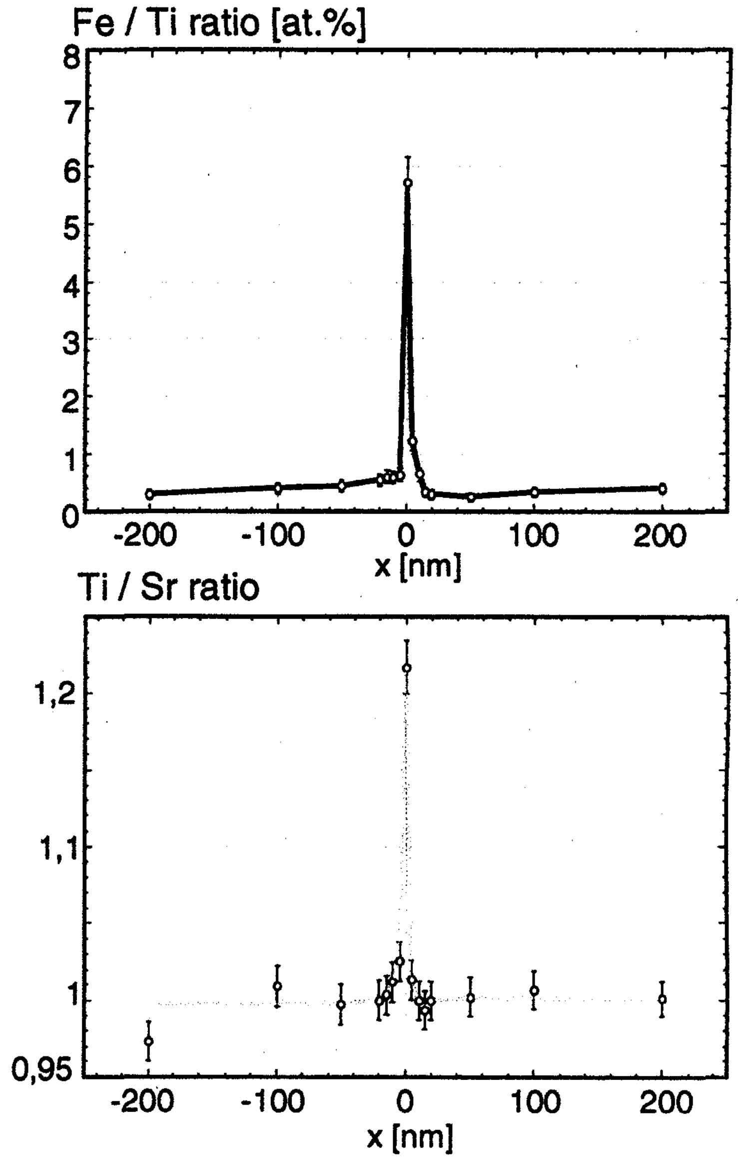
Facet B: 0.07 ML (0.46 At / nm^2) ± 25%

"general" grain boundaries in polycrystalline $SrTiO_3$

Doping level: Fe / Ti = 0.4 at.%



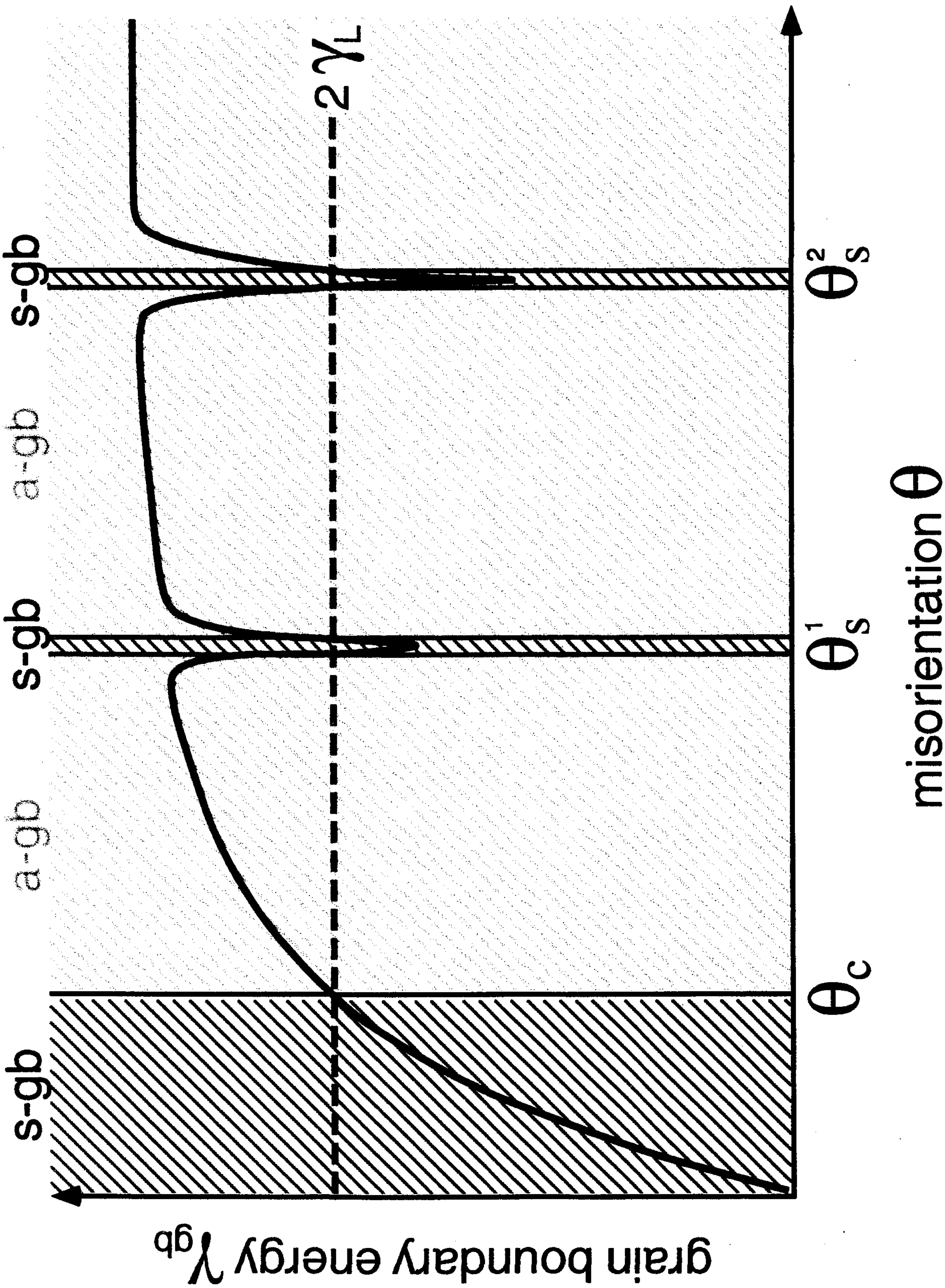
Profiles



EDS

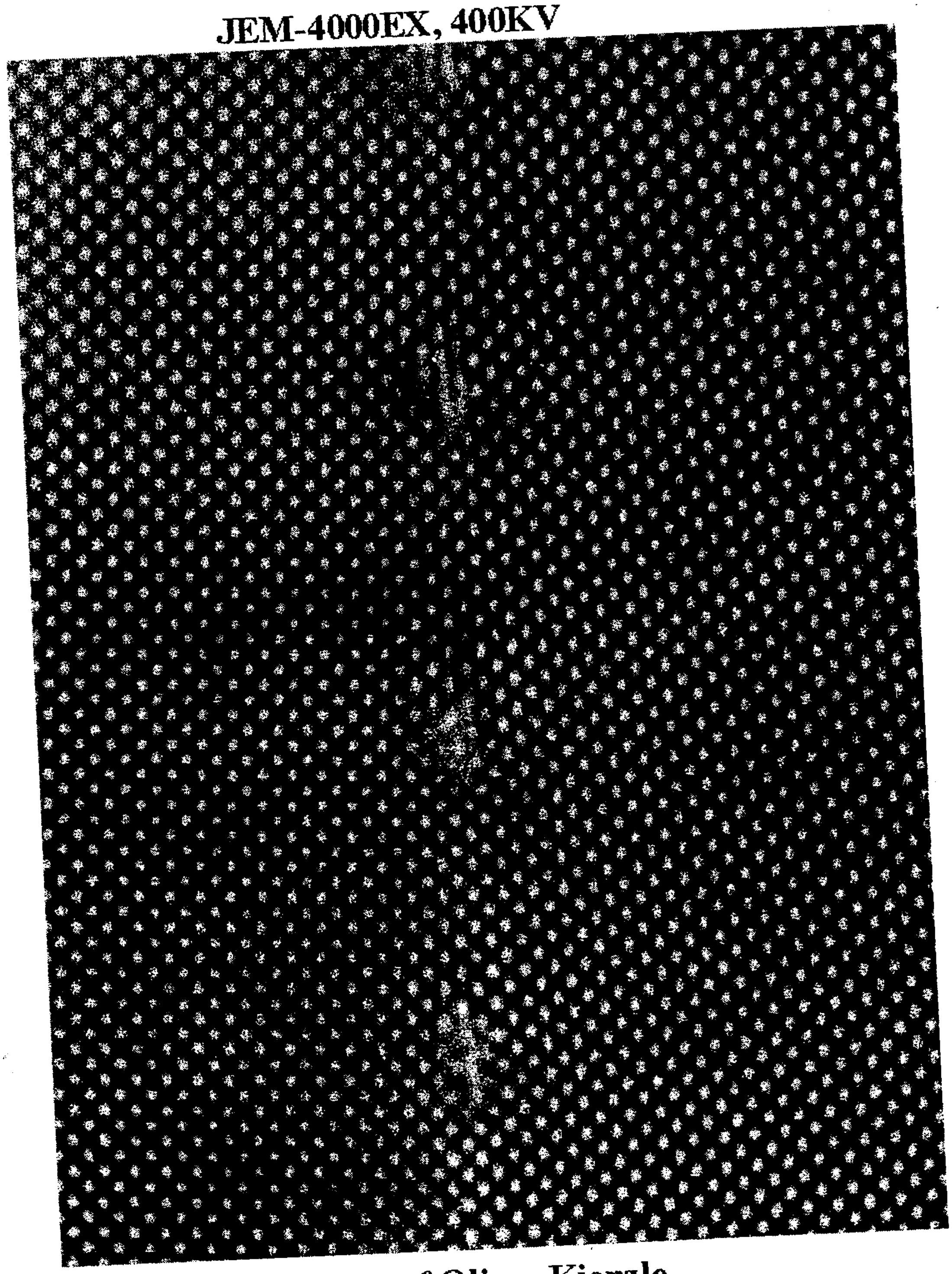
Fe-Excess: (0.61 ± 0.04) ML (4.0 At / nm^2)

Ti-Excess: (1.3 ± 0.14) ML (10.5 At / nm^2)



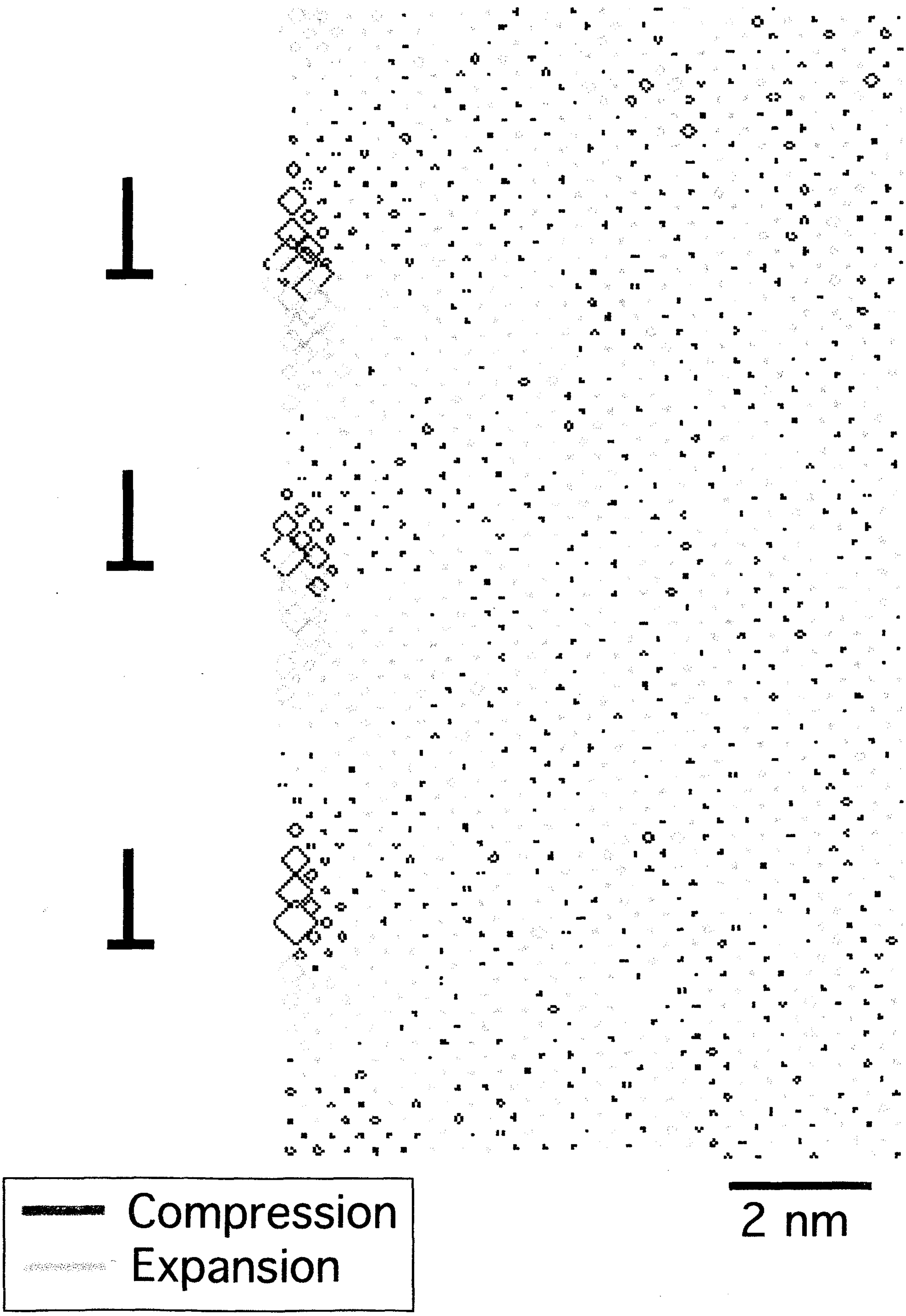
grain boundary energy γ^{gb}
misorientation θ
s-gb
a-gb
s-gb
a-gb
s-gb
$2\gamma_L$
θ_c
θ_s^1
θ_s^2

JEM-4000EX, 400KV



Courtesy of Oliver Kienzle

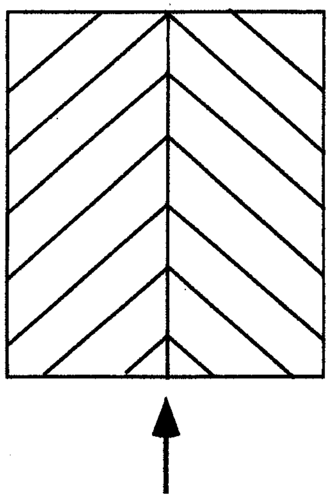
Small-angle grain boundary in $SrTiO_3$



Summary, conclusion and outlook

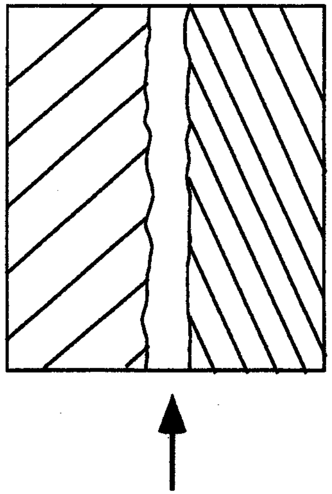
grain boundary structure ⟷ space charge region

a) special boundaries



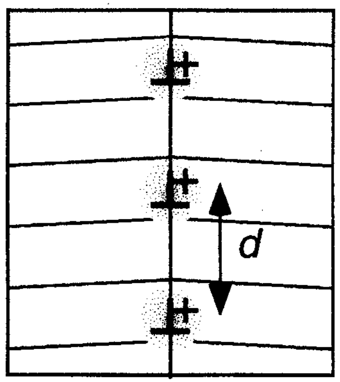
No detectable segregation
$\Sigma=3$, (111) poly / bicrystal
$\Sigma=5$, (310) bicrystal
HRTEM: "perfect structures"

b) amorphous film



Sr-deficient
Ti, Fe segregation
$Ti_{0.75}Fe_{0.25}O_x$
HRTEM, ELNES:
amorphous GB core

c) low angle boundary



outlook

varying *d*
by misorientation
-> diffusion bonding

Correlation to diffusion across GB, electr. properties

S. Hutt(1999)
O. Kienzle
(J. Maier)

Motivation

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Lattice mismatch:

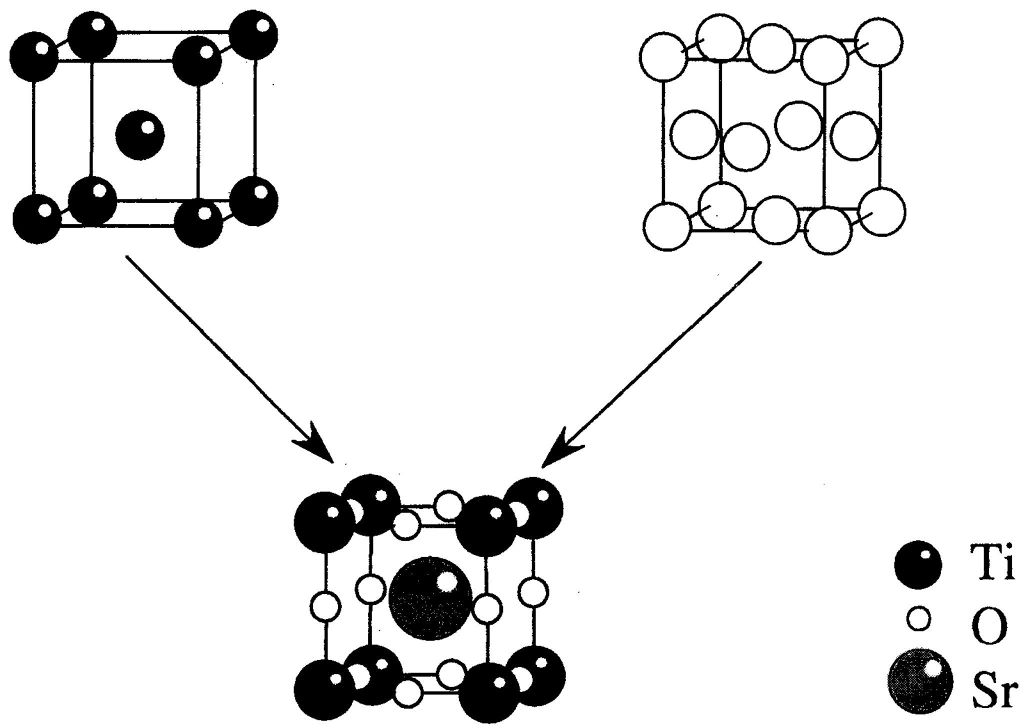
Mo > Ni> Cr > Pd

Reactivity:

Cr > Mo > Ni > Pd

bcc: Cr, Mo

fcc: Ni, Pd



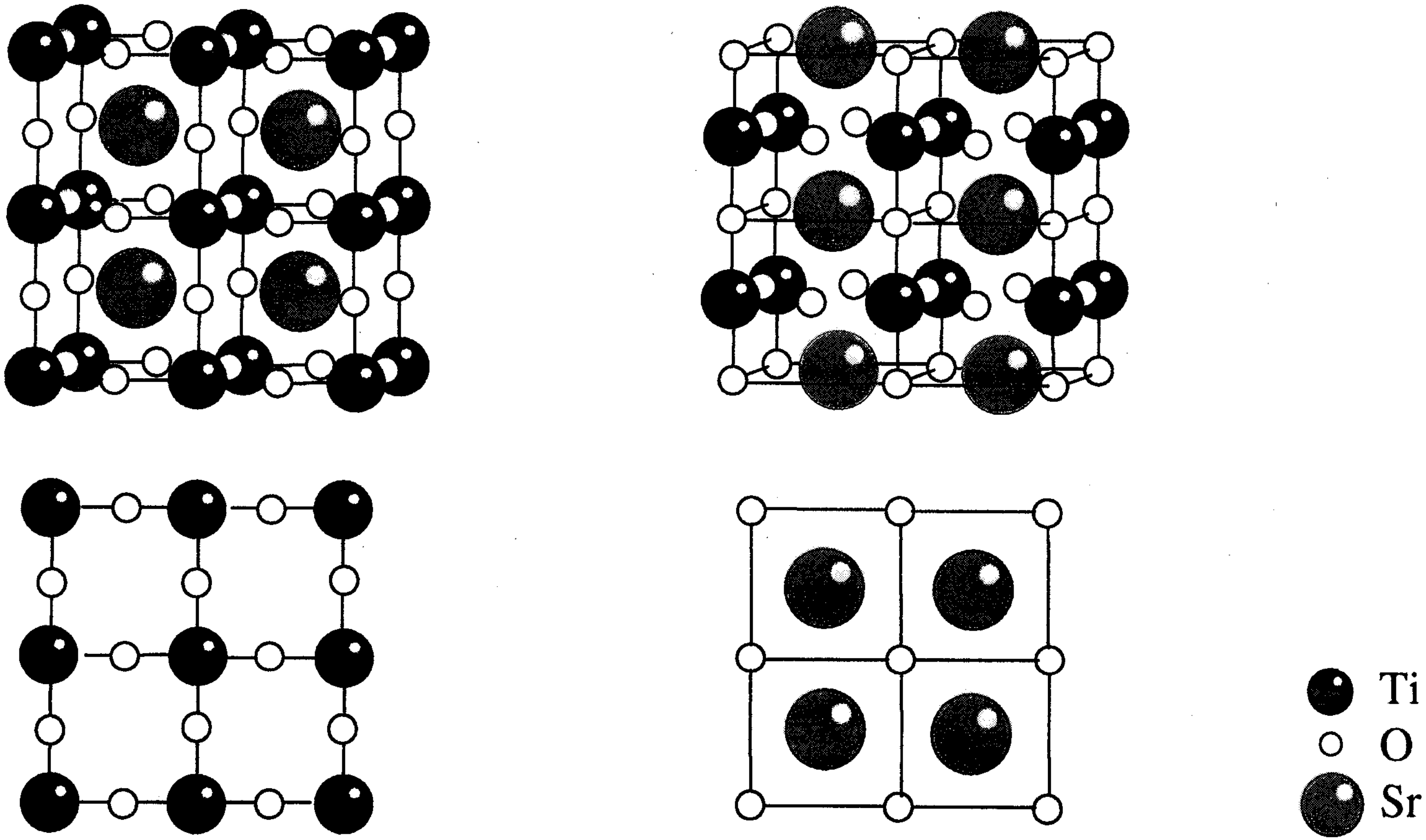
$SrTiO_3$

Surface Termination

TiO$_2$ terminated — SrO terminated

side view

top view



Theory (T. Ochs, T. Classen, C. Elsässer):
metal on top of oxygen is energytically favoured!

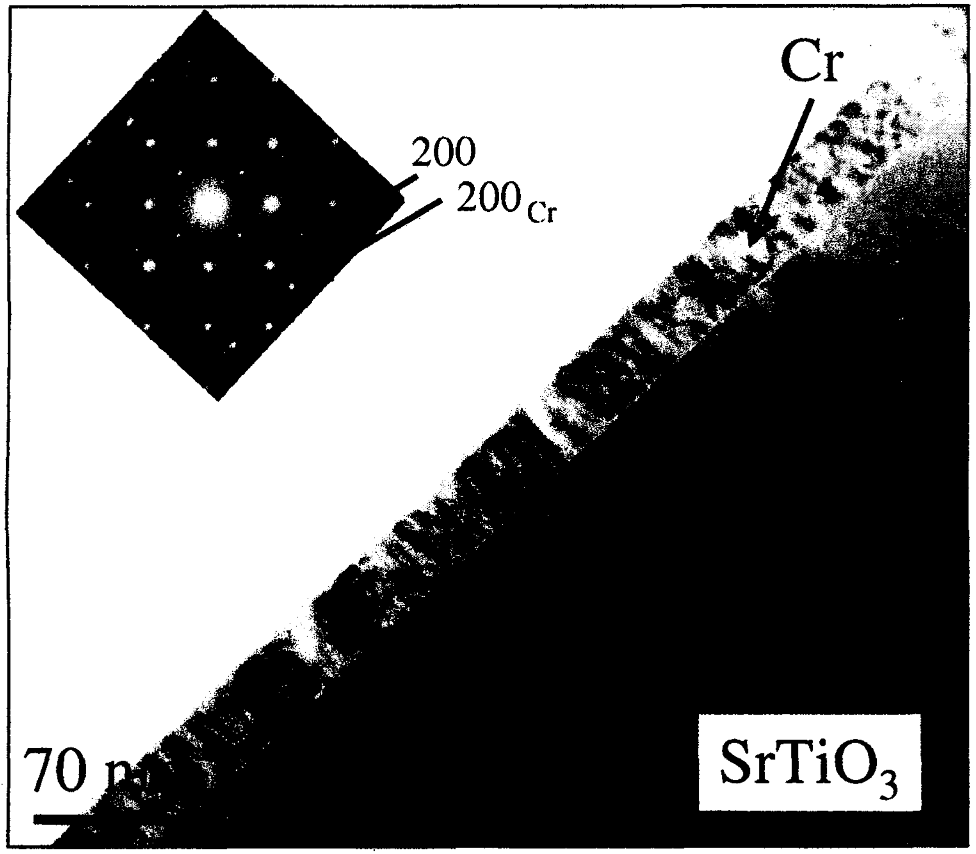
Experimental Details

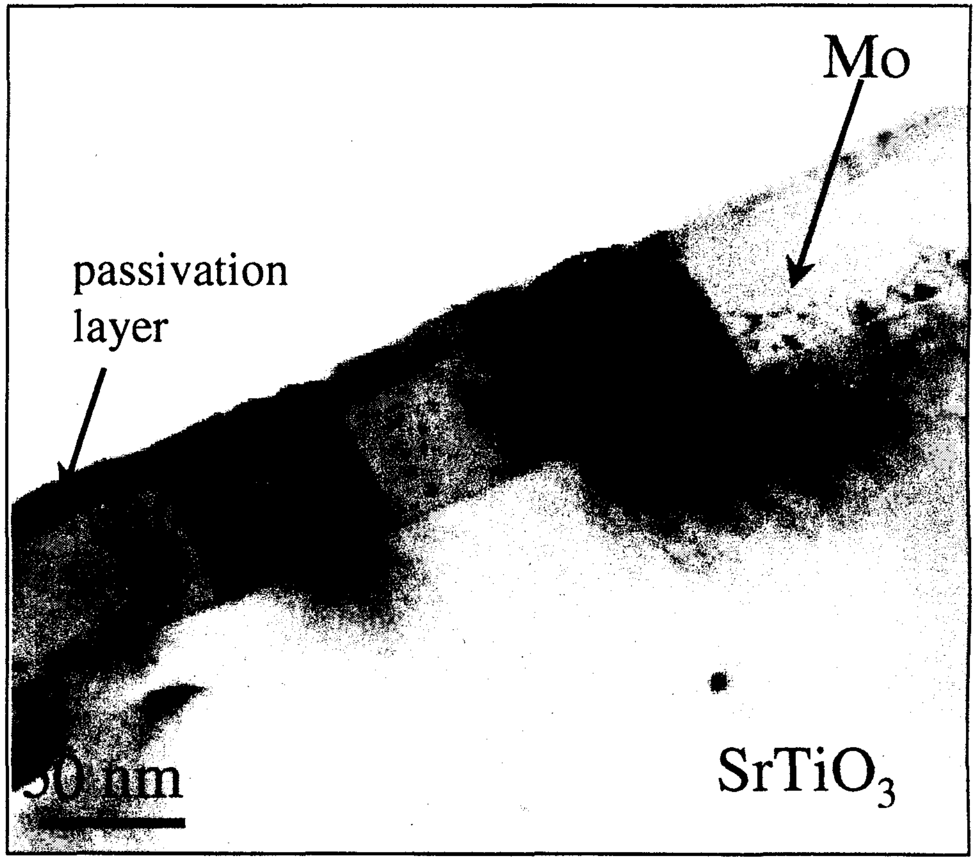
Specimen fabrication

- nominal 35 - 100 nm thick metal films were grown on (001) $SrTiO_3$ by MBE in UHV (10^{-8} Pa)
- substrate temperature was varied between 65°C and 650°C for the various metals to obtain epitaxial films

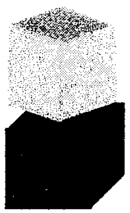
Characterization

- conventional TEM: JEOL 2000FX (200 kV)
- high-resolution TEM: JEOL ARM1250 (1250 kV)
- analytical TEM: VG STEM HB 501 UX (100 kV)





Orientation relationships

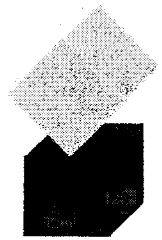


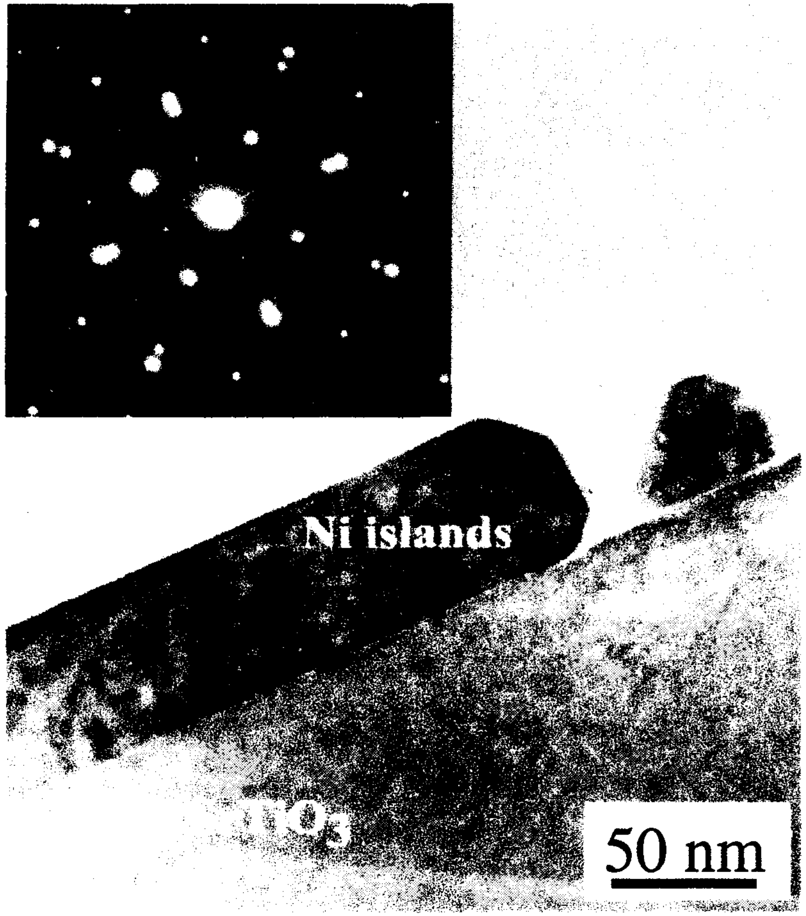
$\{100\}_{Cr} \parallel \{100\}_{SrTiO_3}$

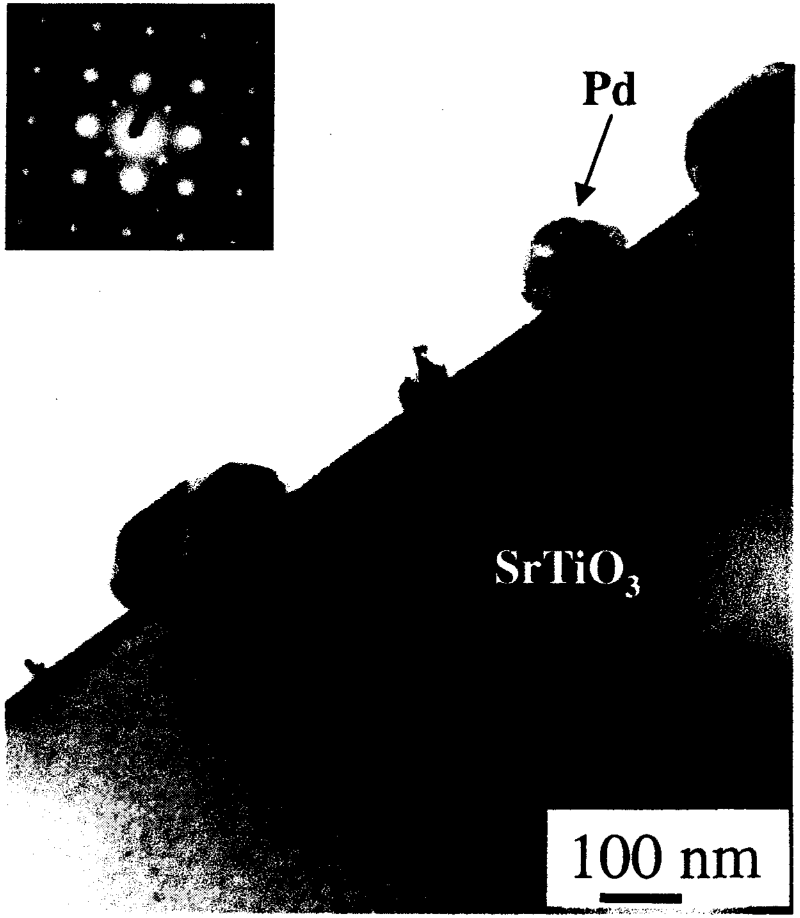
$<110>_{Cr} \parallel <100>_{SrTiO_3}$

$\{110\}_{Mo} \parallel \{100\}_{SrTiO_3}$

$\pm <100>_{Mo} \parallel <100>_{SrTiO_3}$



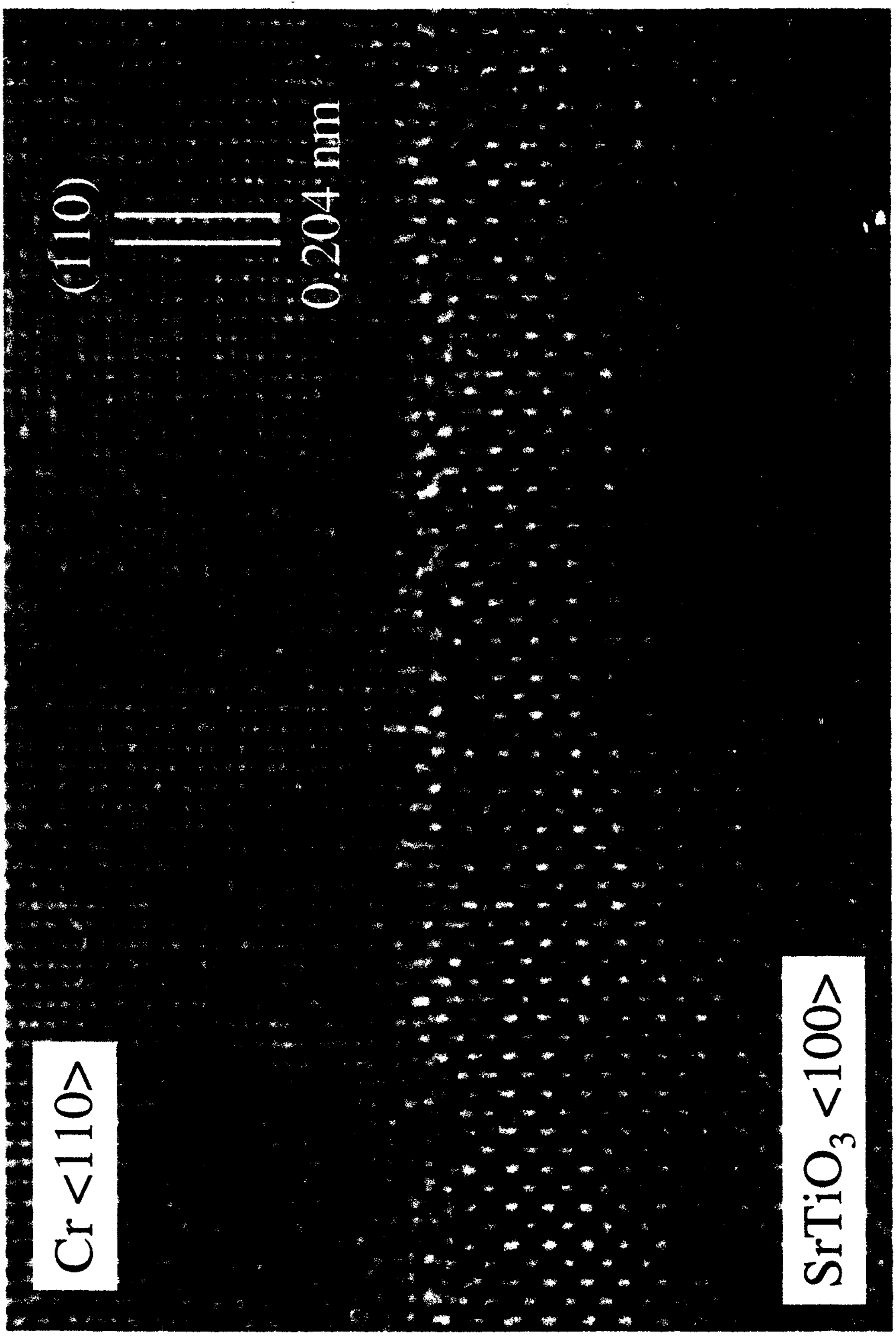




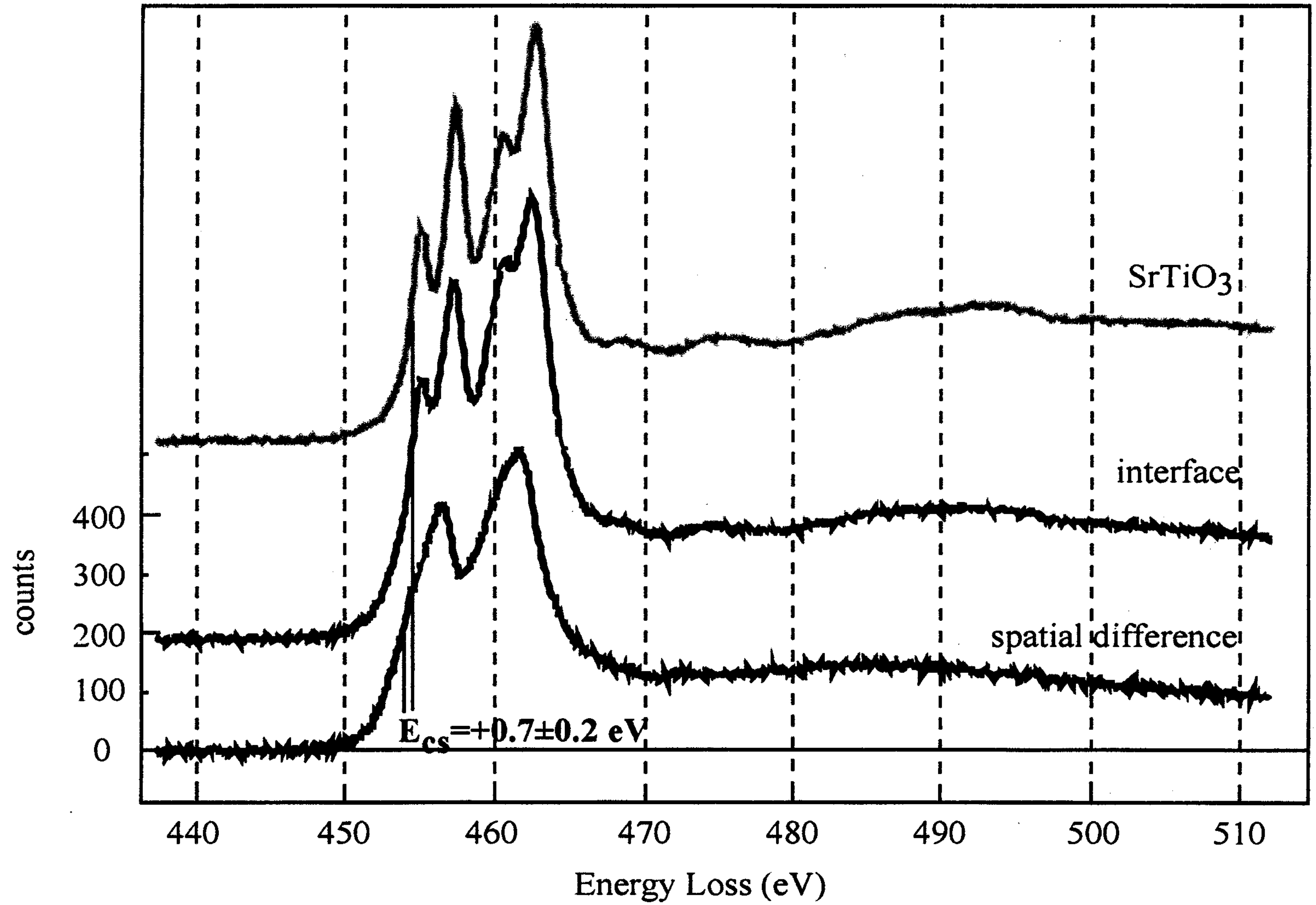
Orientation relationship

$\{100\}_{Metal} \parallel \{100\}_{SrTiO_3}$

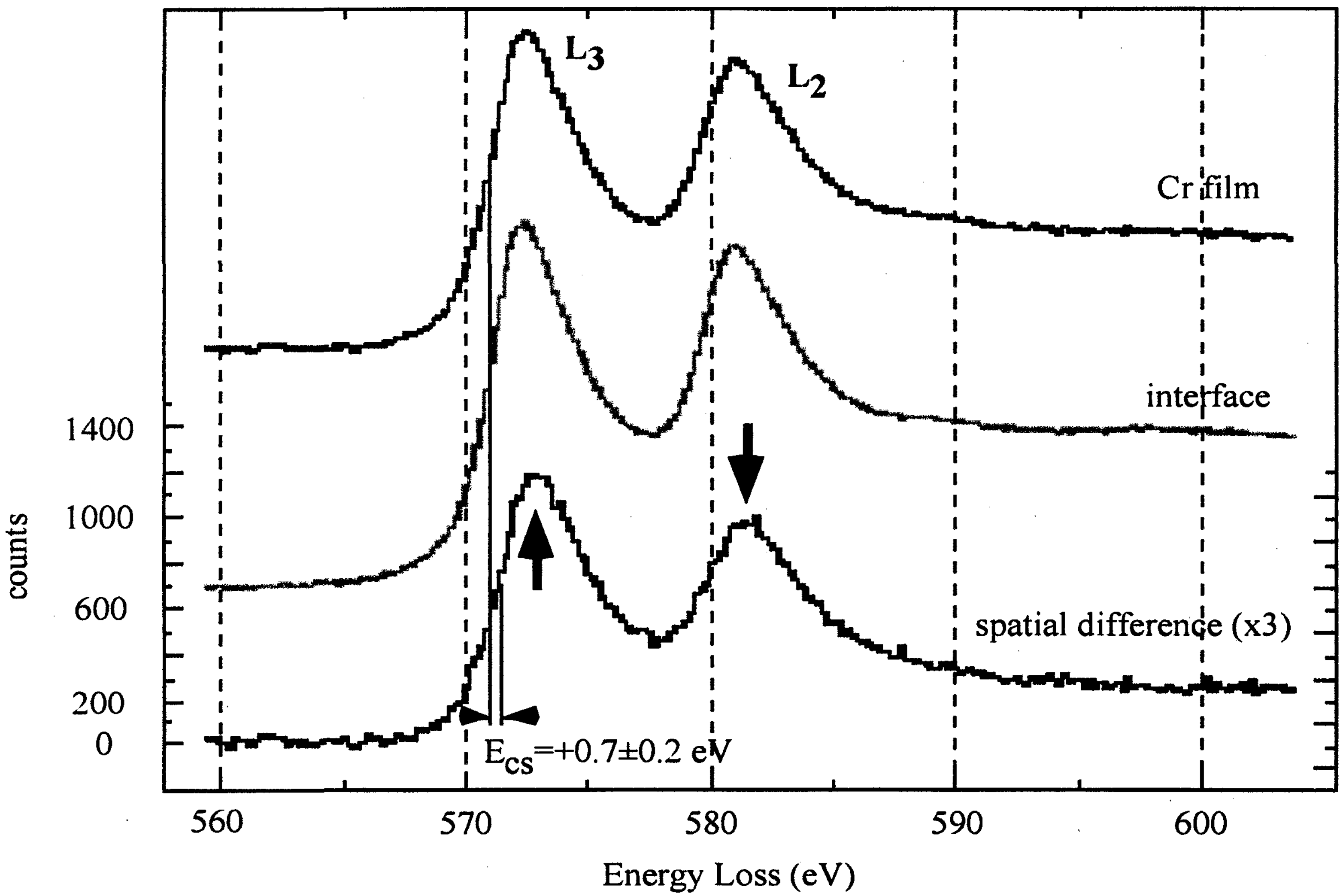
$\langle 100\rangle_{Metal} \parallel \langle 100\rangle_{SrTiO_3}$


(110)
0.204 nm
Cr <110>
$SrTiO_3$ <100>

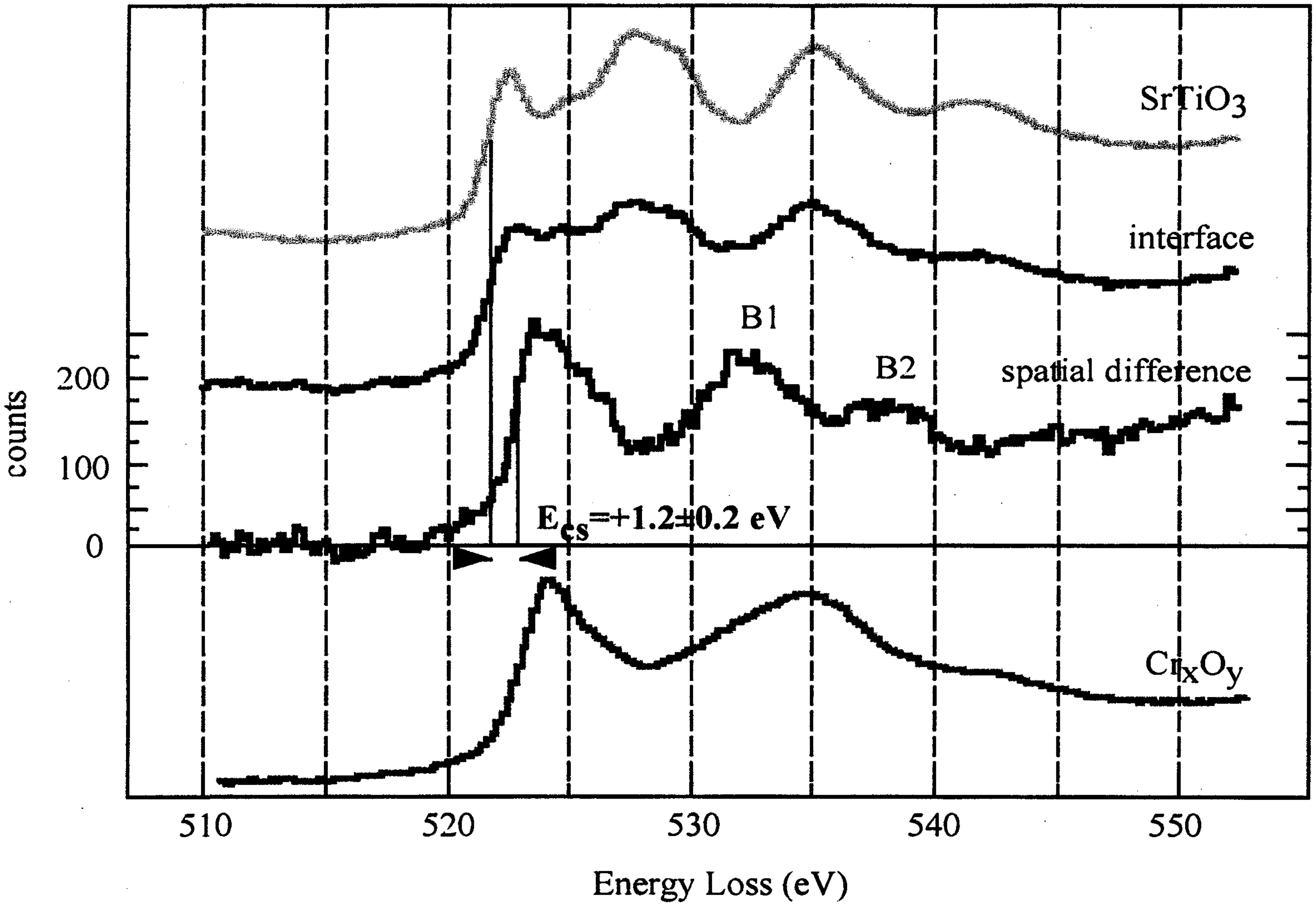
Ti $L_{2,3}$ edge of $Cr/SrTiO_3$



Cr $L_{2,3}$ edge of $Cr/SrTiO_3$



O K edge of $Cr/SrTiO_3$



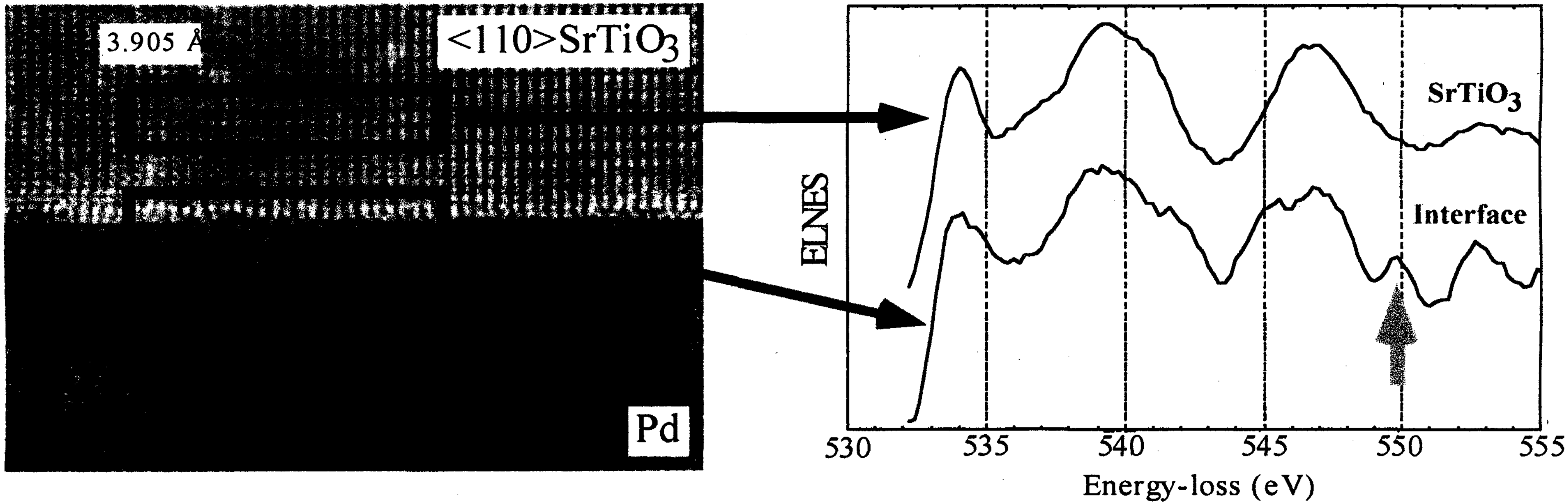
Analysis of the interfacial ELNES of $Cr/SrTiO_3$

- reduction of Ti at the interface
- reduced crystal field splitting
- O 2p - Cr 3d hybridization
- electron transfer from Cr to O

⇒ mixed ionic-covalent bonding between Cr and $SrTiO_3$

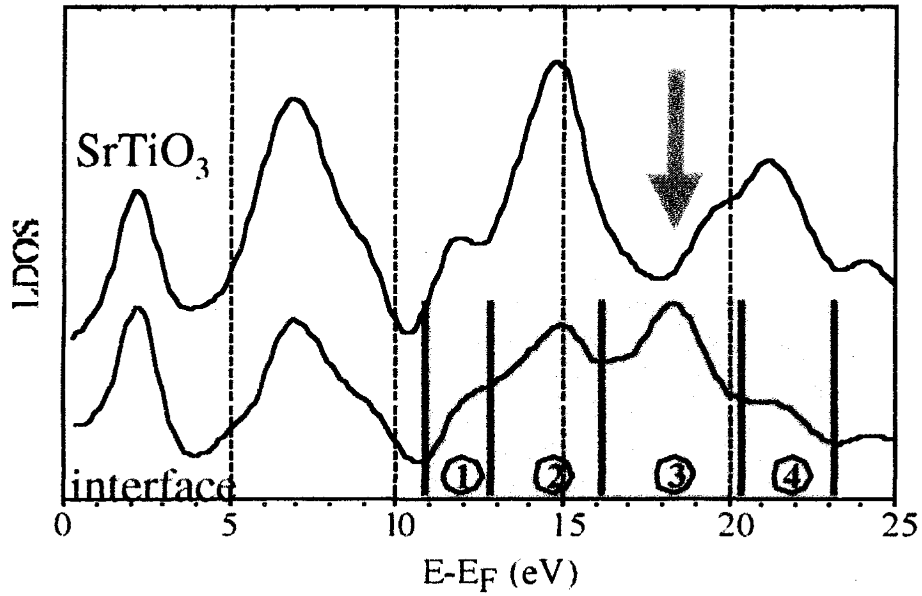
O-K edge of $Pd/SrTiO_3$

Atomistic structure | **Electronic structure**



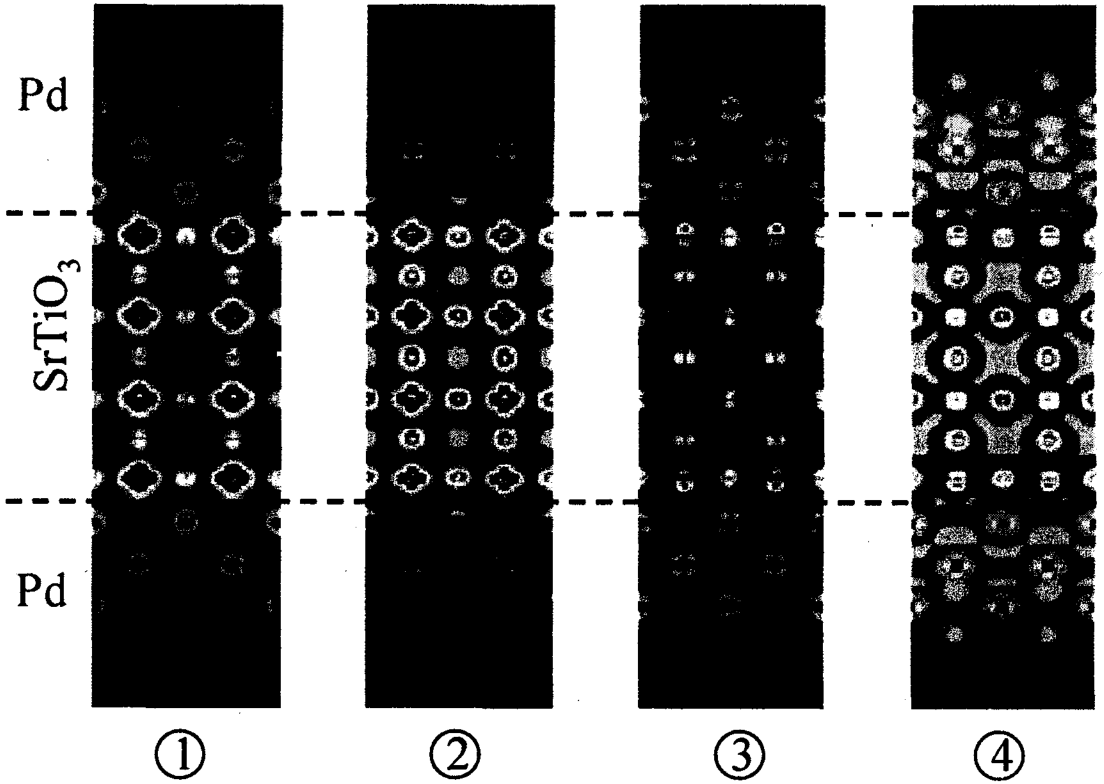
ab-initio calculations of Pd/$SrTiO_3$

Electronic structure



- Oxygen p-PDOS
- additional peak in region 3
- similar line-shapes in comparison to the experimental data

$|\Psi|^2$ distribution maps



- cut through Ti-O plane (i.e. 010,001-plane)
- appearence of interface specific components in region 3

K. van Benthem and C. Elsässer, unpublished

Analysis of the interfacial ELNES of $Pd/SrTiO_3$

- experiment and theory provide the same interfacial ELNES

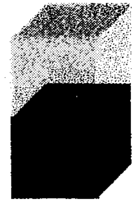
➡

- interaction between Pd and O
- Pd sits above the O of the TiO_2 terminated (001) $SrTiO_3$
- O 2p - Pd 4d hybridization

➡ covalent bonding between Pd and $SrTiO_3$

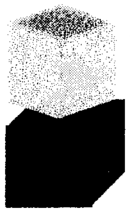
Summary

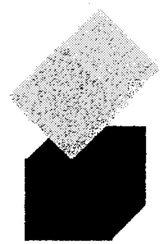
$Pd/SrTiO_3$ and $Ni/SrTiO_3$:



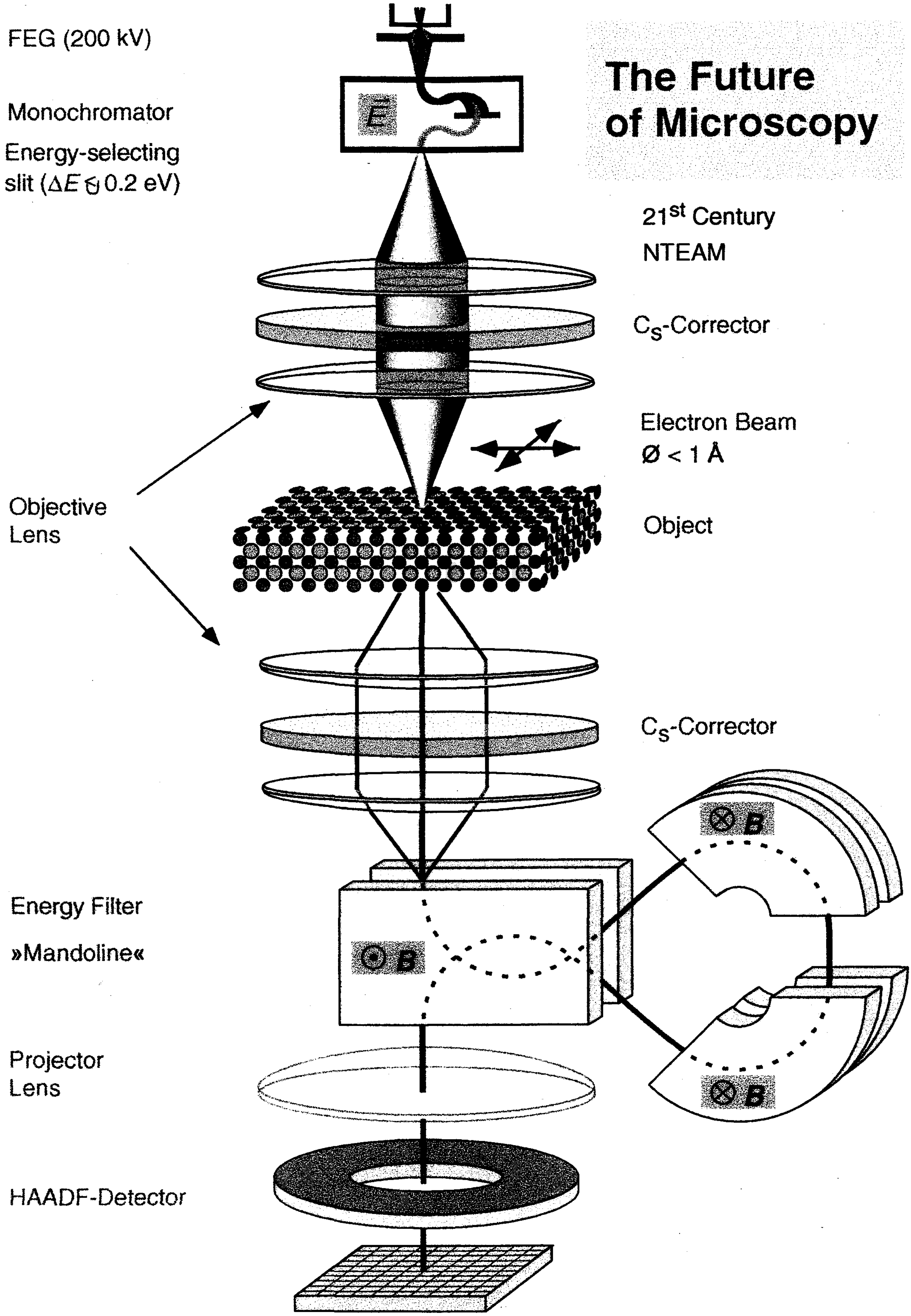
- epitaxial growth with cube-on-cube orientation relationship
- island growth
- the electronic structure of **$Pd/SrTiO_3$** is determined by experiment and theory

$Cr/SrTiO_3$ and $Mo/SrTiO_3$:





- epitaxial growth with cube-on-cube but 45° in-plane rotated for **$Cr/SrTiO_3$** and 45° out-plane rotated for **$Mo/SrTiO_3$**
- continous film layers
- the electronic structure of **$Cr/SrTiO_3$** is determined by experiment


FEG (200 kV)
Monochromator
Energy-selecting
slit (ΔE ≤ 0.2 eV)
E
The Future
of Microscopy
21st Century
NTEAM
CS-Corrector
Electron Beam
Ø < 1 Å
Objective
Lens
Object
CS-Corrector
B
Energy Filter
»Mandoline«
B
B
Projector
Lens
HAADF-Detector