Transmission Electron Microscopy (TEM) at UoA

A new Research Journey begins……

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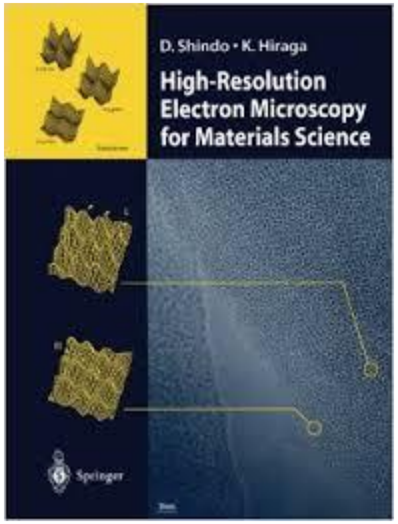
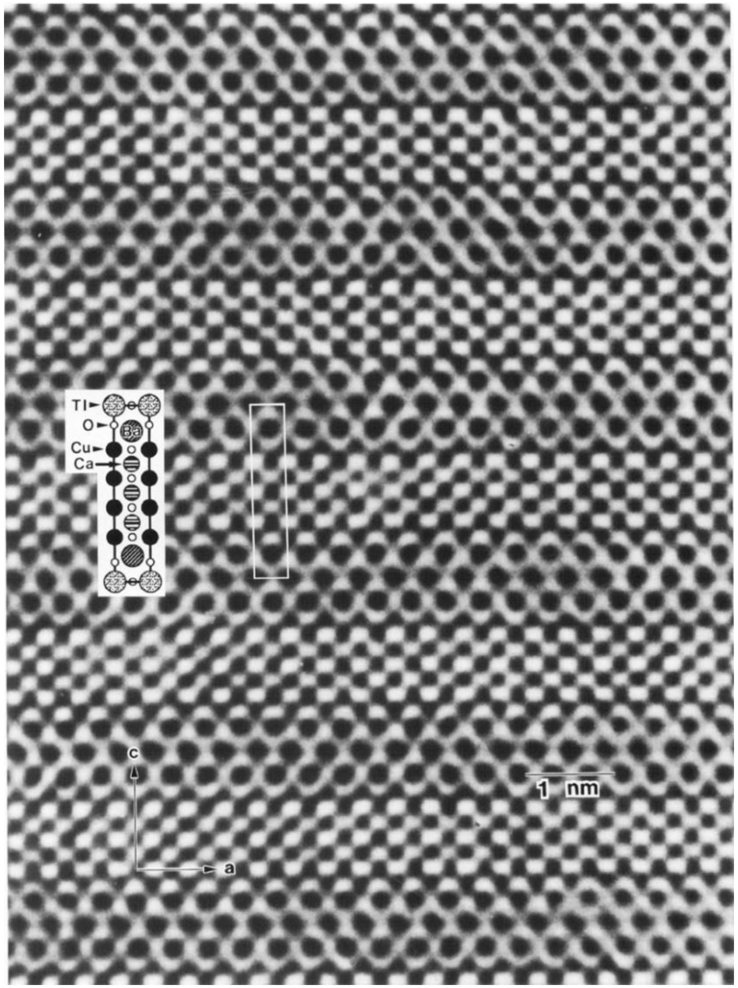
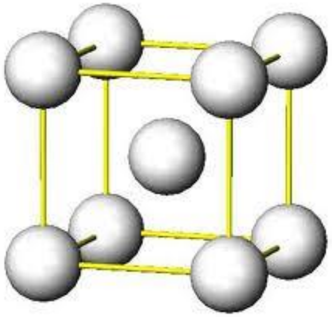
An Unexpected Journey



Copying a few chapters for a Professor



- Large dark spots --- heavy atomic columns such as TI and Ba
- Bright spots --- vacant oxygen



Lattice image (viewed along [010]) + Modeling.

High resolution image of a superconducting oxide $TIBa_2Ca_3Cu_4O_{11}$

My Journey...

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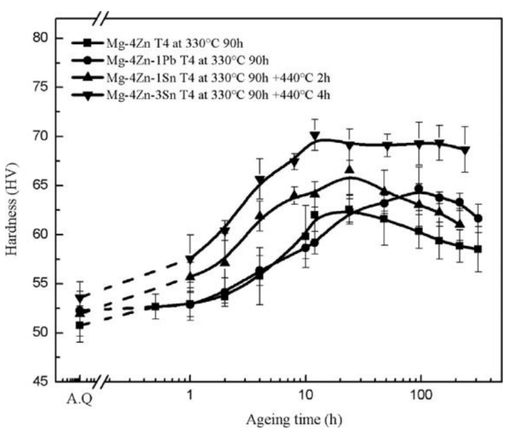
Develop new Mg alloys with high strength and ductility

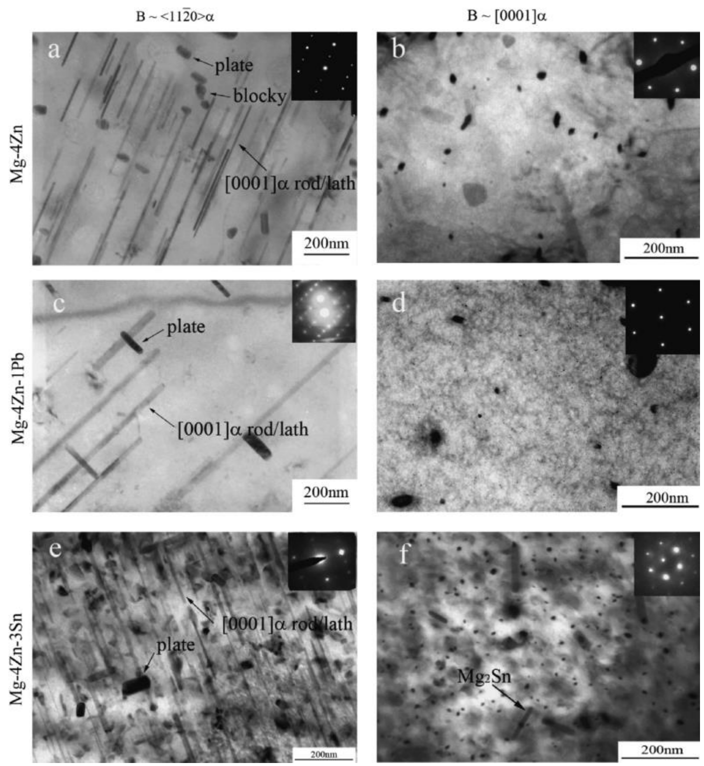
1) Characterisation of the morphology, orientation, and composition of precipitates using BF, SAD, EDS techniques

Magnesium

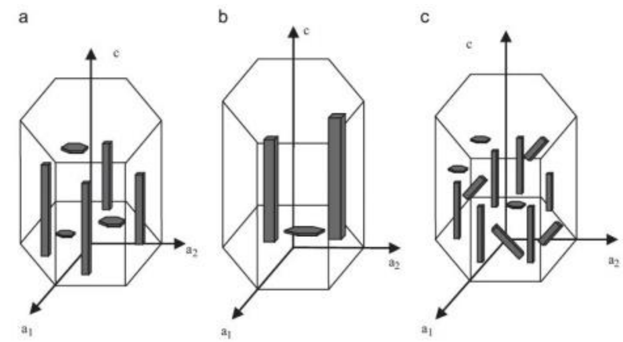
- The lightest structural metal ($\rho_{Mg} < 2/3\rho_{Al}$)



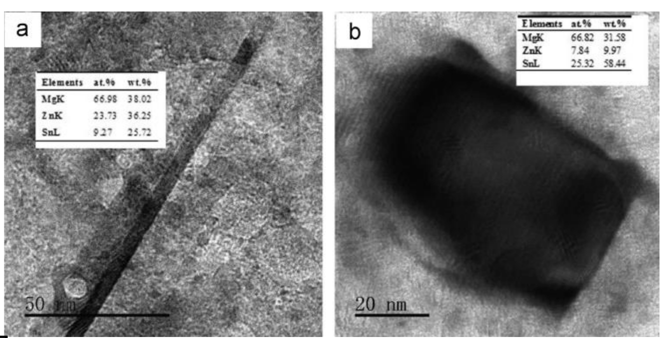
Age-hardening curve of Mg alloys



BF images, viewed along <11-20> and [0001]



Precipitates morphology and habit with respect to matrix



Elements	at.%	wt.%
MgK	66.98	38.02
ZnK	23.73	36.25
SnL	9.27	25.72

Elements	at.%	wt.%
MgK	66.82	31.58
ZnK	7.84	9.97
SnL	25.32	58.44

EDS results of precipitates

My Journey...

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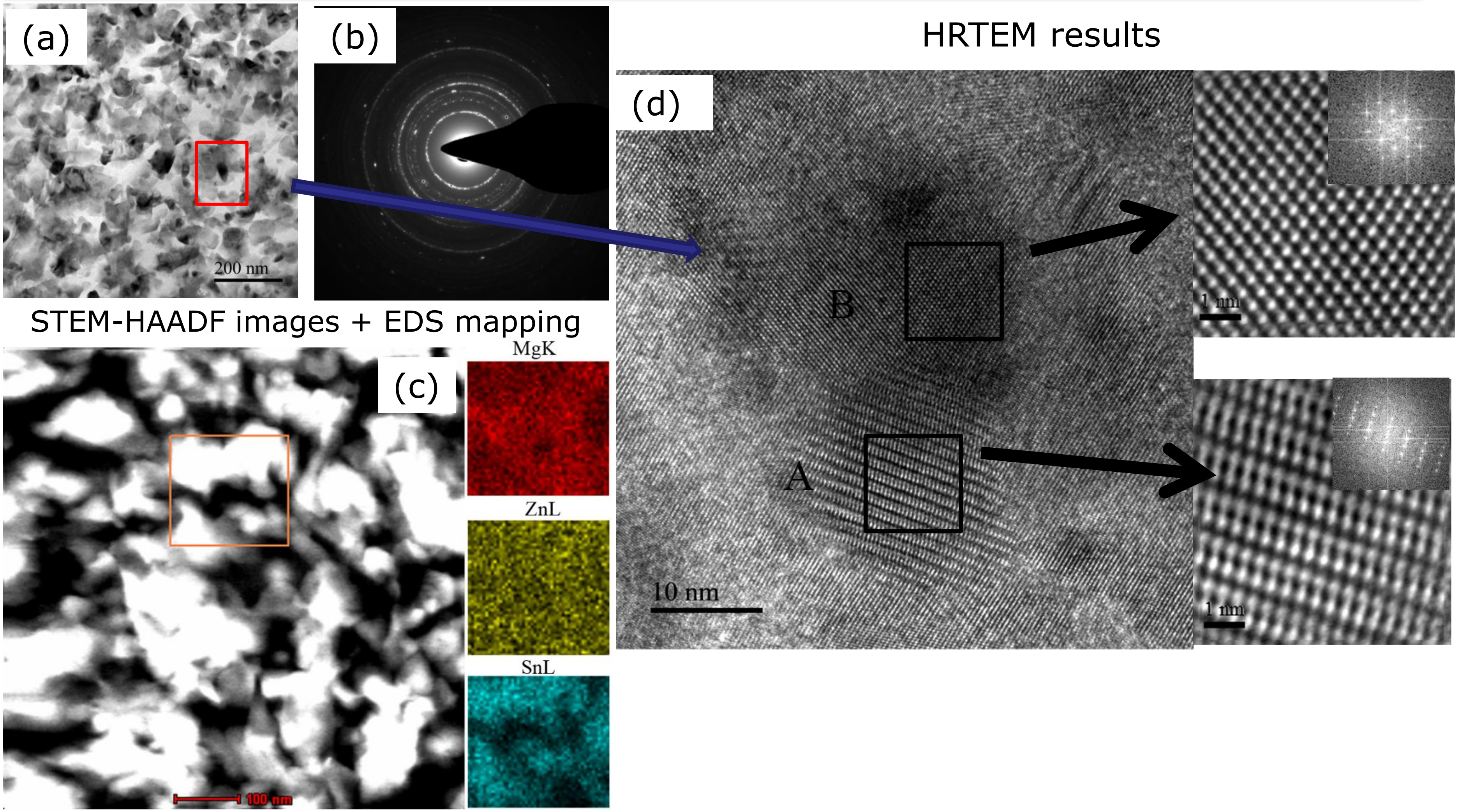
2) Characterisation of nanostructured precipitates using BF, SAD, HRTEM, STEM & EDS



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What is TEM?

- ***TEM is a technique for characterizing materials down to atomic limits.***
  - *Significant impact on fields such as: materials science, biological science, medical science, geology, environmental science, among others.*
  - *Can be used for investigating the morphology and structure in physical and biological science.*
  - *Also enables the investigation of crystal structures, orientations and chemical compositions of phases and nano-structured materials*
- ***A TEM can appear in several different forms, such as HRTEM, STEM, and EFTEM.***

Transmission electron microscope is an extremely expensive piece of equipment!

What is TEM?

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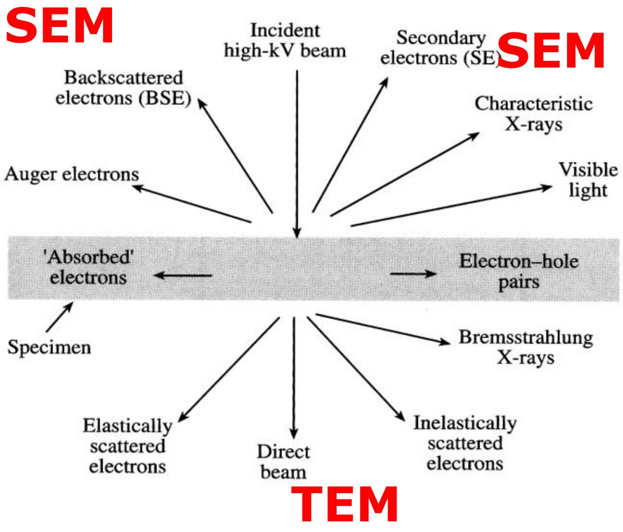
Comparison between SEM and TEM

- **SEM: Invented in 1942. electrons are scanned over the surface of the sample.**
- **TEM: Knoll & Ruska in 1931. electrons are transmitted through the sample.**



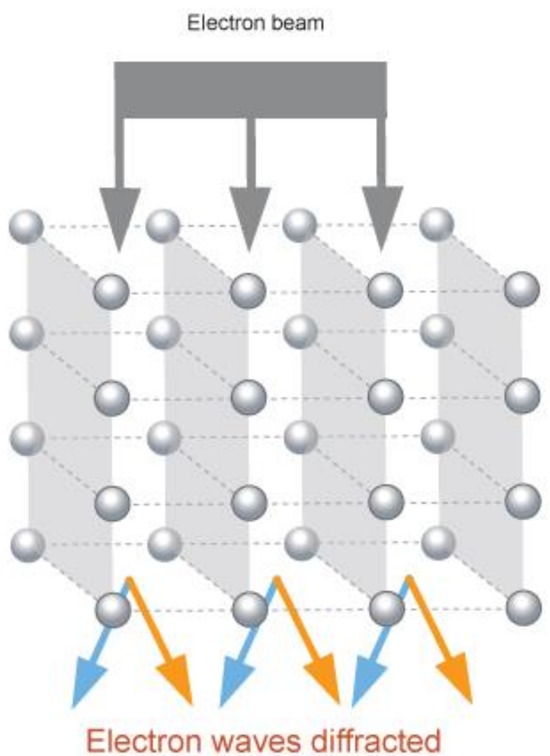
	SEM	TEM
Resolution	Low	High
Sample preparation	Easy	Complex
Results	3D image, representation	2D image, require interpretation
Application	Surface characterization	Structure and crystallographic defects down to nanoscale

TEM Techniques

- Diffraction
  - Selected-area diffraction (SAD)
  - Convergent beam electron diffraction (CBED)
- Imaging
  - Bright/Dark field image
  - High-resolution TEM (HRTEM)
  - Scanning TEM (STEM)
- Spectroscopy
  - Energy-dispersive X-ray (EDX) spectroscopy
  - Electron Energy-loss Spectroscopy (EELS)
- Other techniques
  - 3D Tomography
  - Cryo-TEM

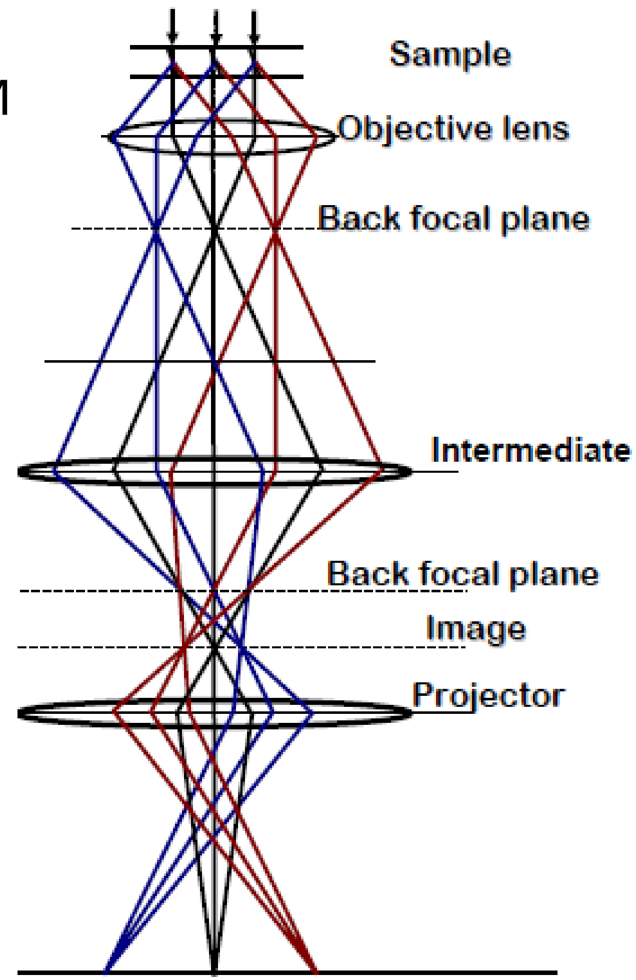
Diffraction

- Imaging of tiny structures in a thin specimen and the diffraction pattern of the same structures --- one of the main advantage of TEM
- The basis of all image formation in the TEM



Diffraction pattern formation

- DP formed in back focal plane of objective lens.
  ---Location of back focal plane determined by strength of objective lens.
- Intermediate lens must focus at this point



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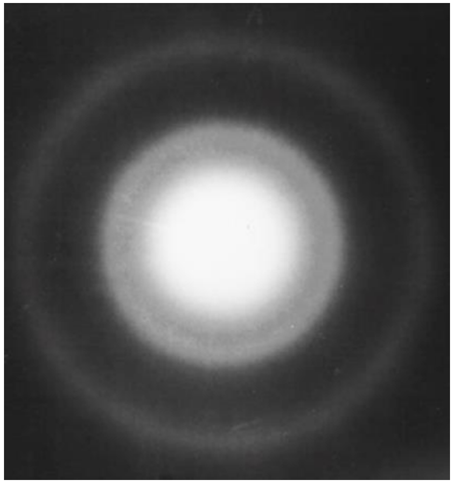
DP Types and Uses

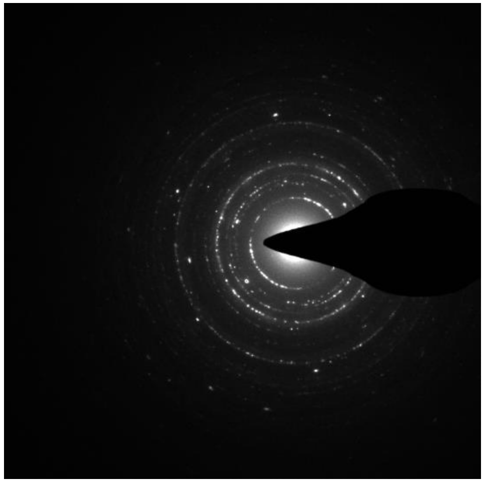
Diffraction patterns can be used:

- ❖ Crystallographic analysis
- ❖ Determine the orientation of crystals or phases
- ❖ Analysis of interfaces, twinning and certain crystalline defects

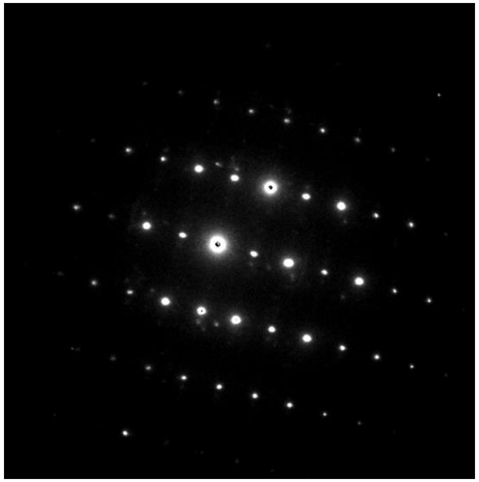
There are several kinds of DP:



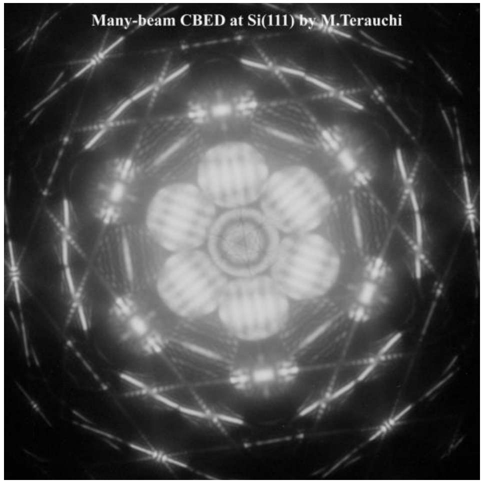
Amorphous carbon



Polycrystalline of Mg alloy



Mg single crystal



CBED pattern for Si [111]

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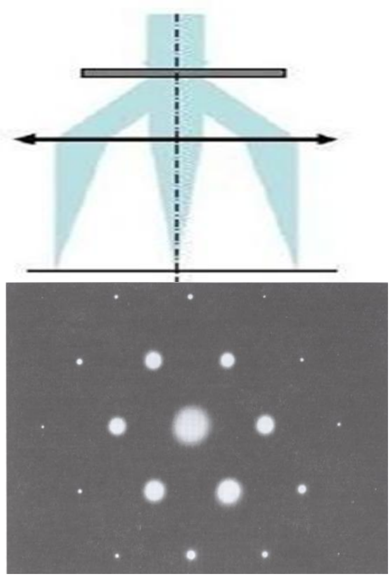
Convergent Beam Electron Diffraction (CBED)

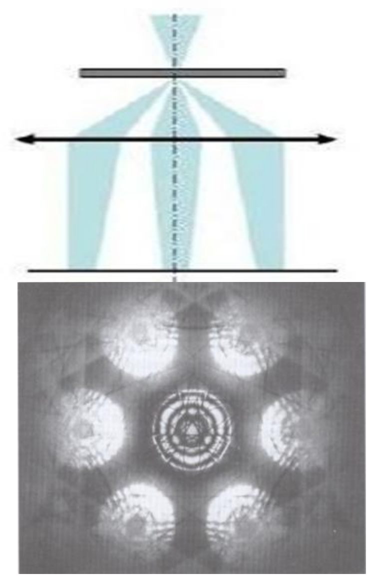
- Very useful for nanocrystalline materials

	SAD	CBED
Incident beam	Parallel	convergent
Selected area	1~10μm in diameter	1~100nm in diameter

Diffraction spots and no visible Kikuchi lines



SAD from [111] Si

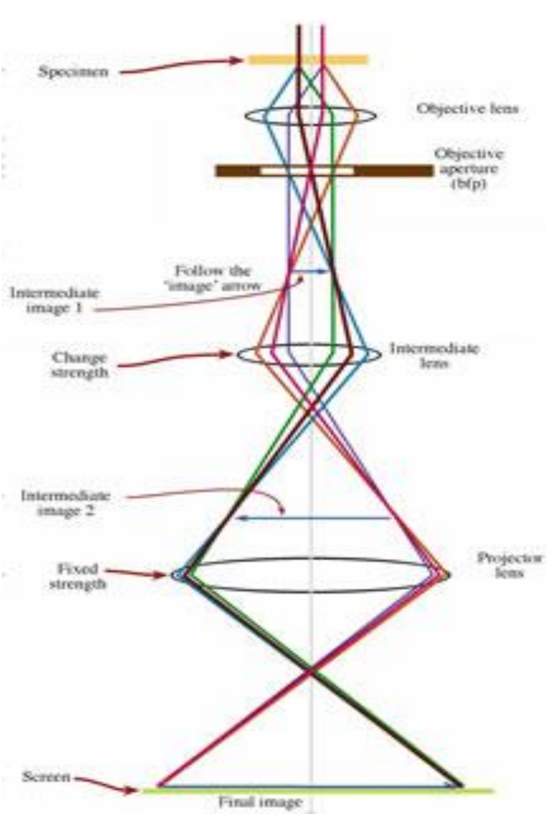


CBED pattern from [111] Si

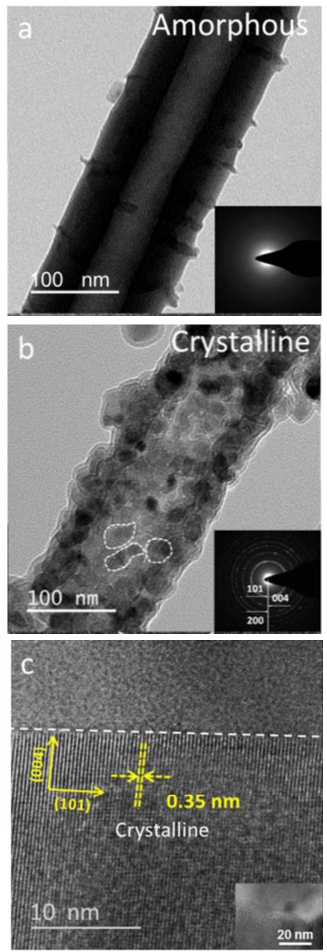
Dynamical contrast within the disks as well as diffuse kikuchi bands and sharp HOLZ lines

Imaging

Formation of TEM image



adapted from Williams & Carter, 2nd ed. (Fig 9.12b)



Contrast of TEM image

Amplitude contrast

- **Mass-thickness contrast**
  - incoherent scattering from the sample
  - Z-contrast imaging
- **Diffraction contrast**
  - Either the direct beam or one of the diffracted beams is selected to form the image

Phase contrast

- Direct and diffracted beams undergo phase shifts in the material

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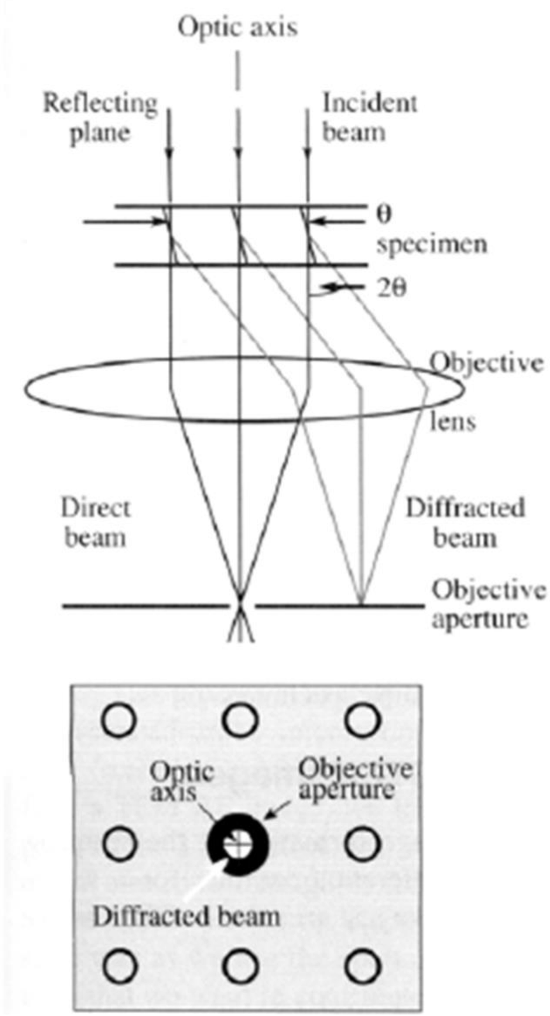
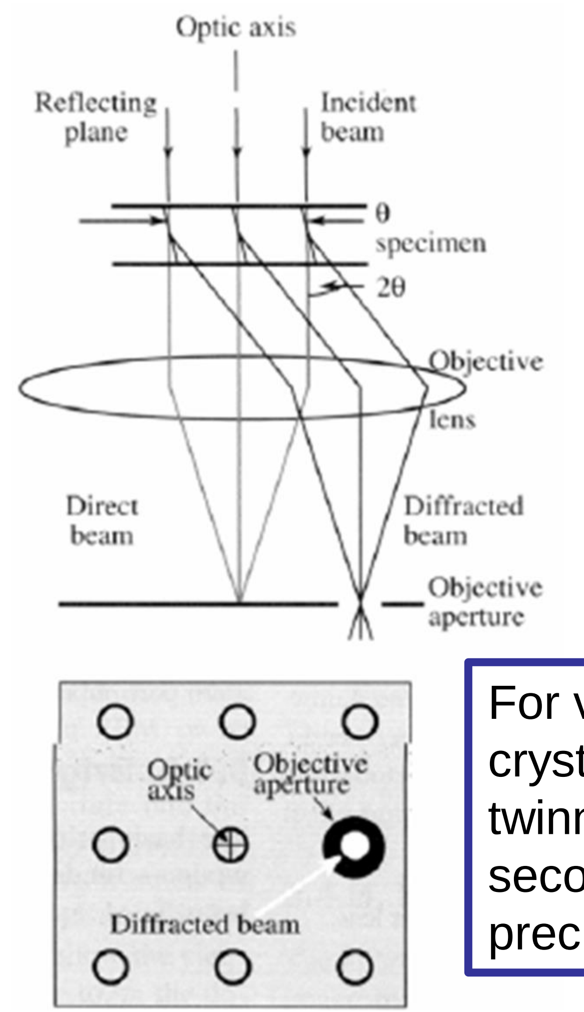
Bright Field / Dark Field Imaging



BF image formed from the direct beam



DF image formed from the diffracted beam

For visualising crystalline defects, twinning, and second phase precipitates

BF & DF Imaging…

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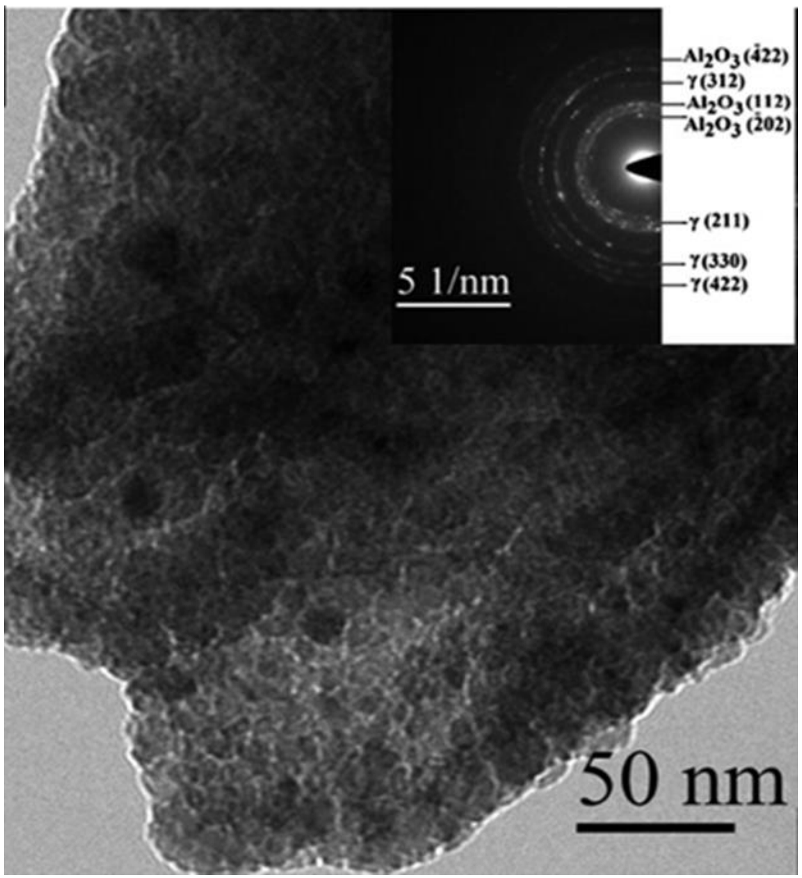
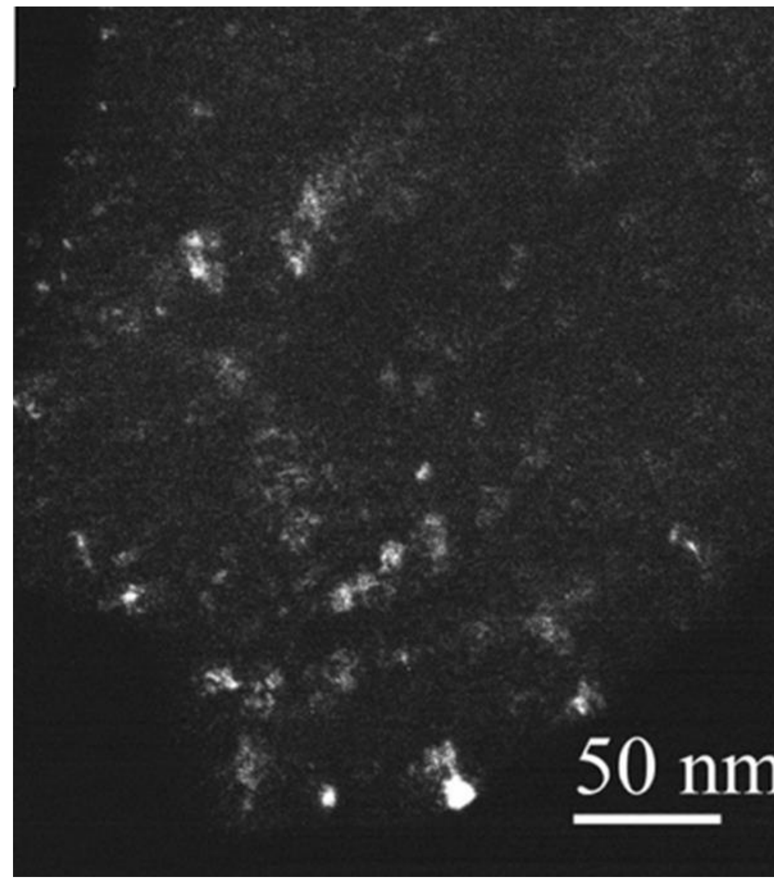
Example



BF image and SAD of Zn-Ni-Al2O3 composite coating



DF image of the same area

TEM Techniques...

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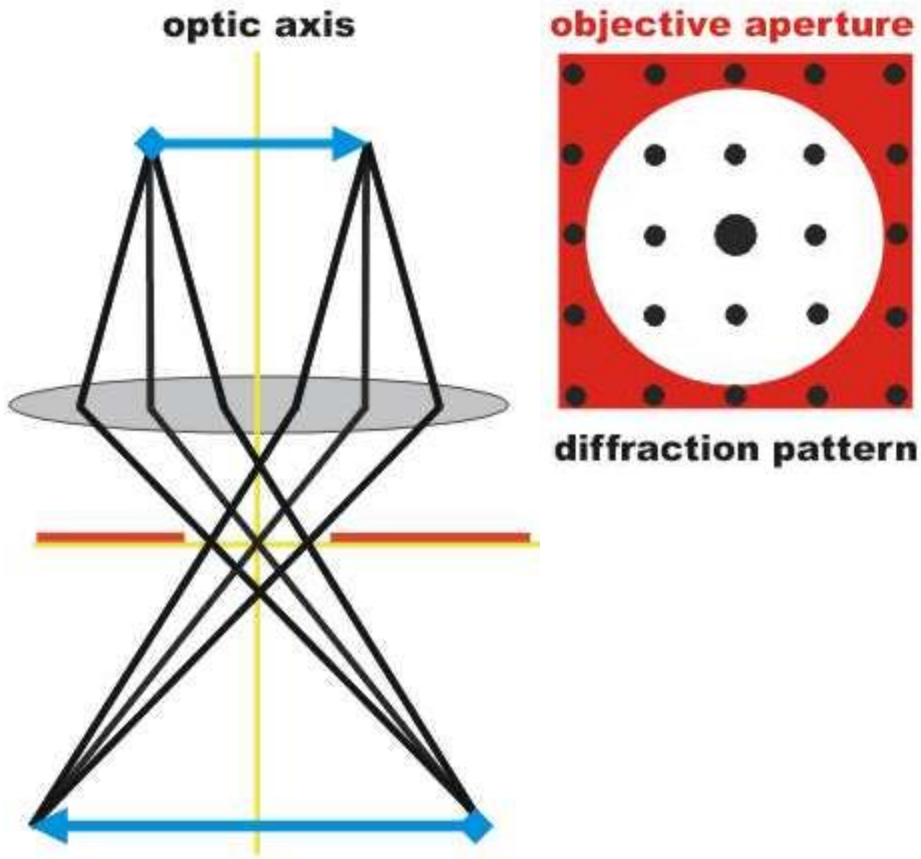
High-resolution TEM (HRTEM)

- The image is formed by the interference of the diffracted beam with the direct beam (phase contrast image)
- The interpretation of HRTEM images has to be confirmed by image simulation, like JEMS
- Typically requires very **thin TEM specimens** free of preparation artefacts.

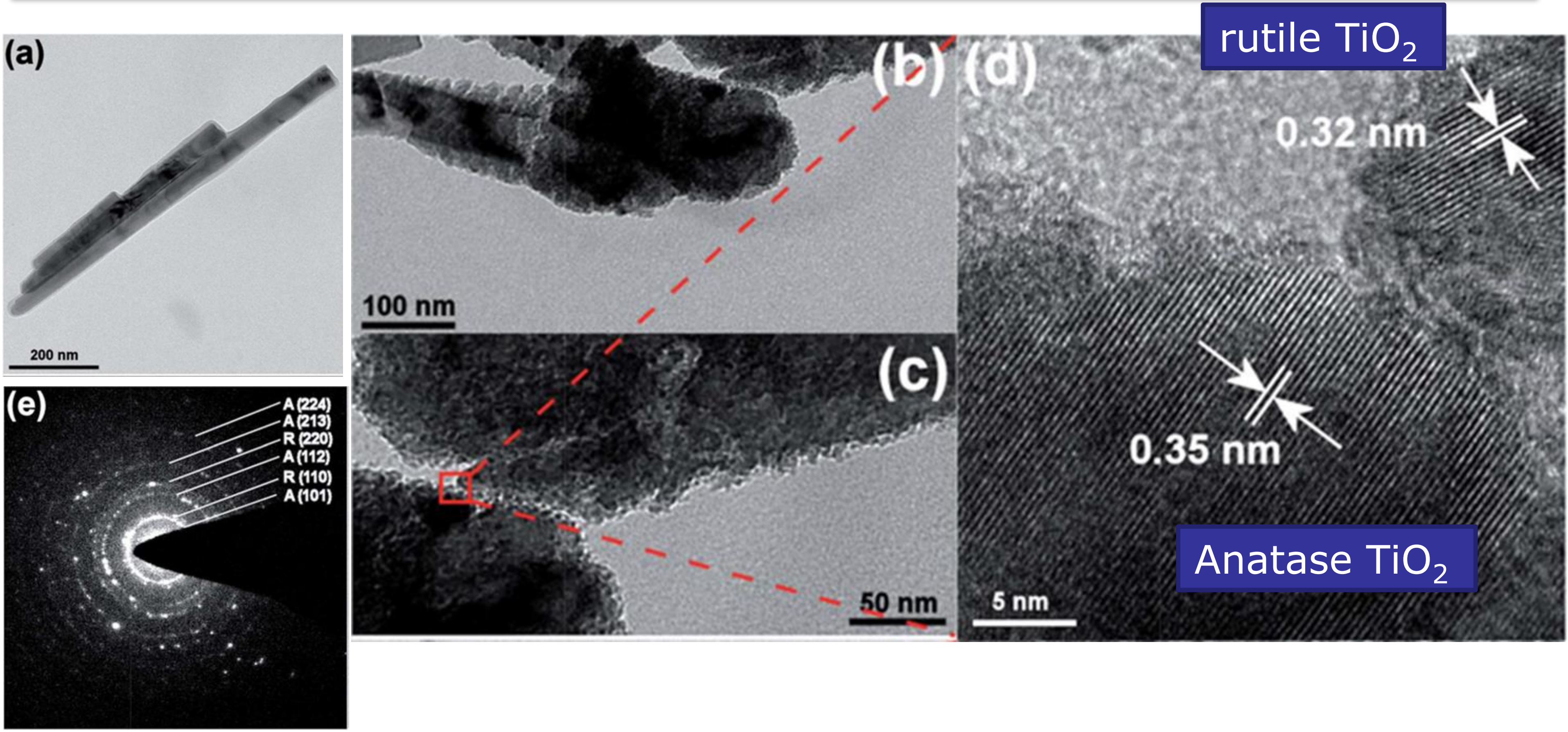
<50nm (the optimum is 5~20nm



HRTEM image

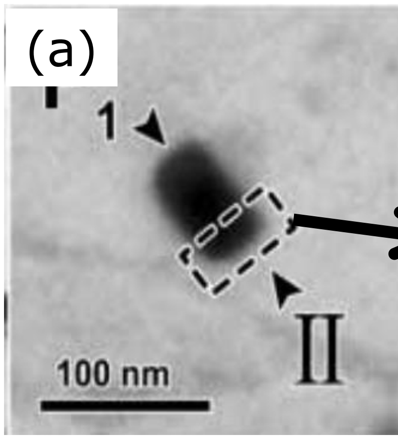
Application & Example

- ***Morphology and crystal structure of nano-structured materials***

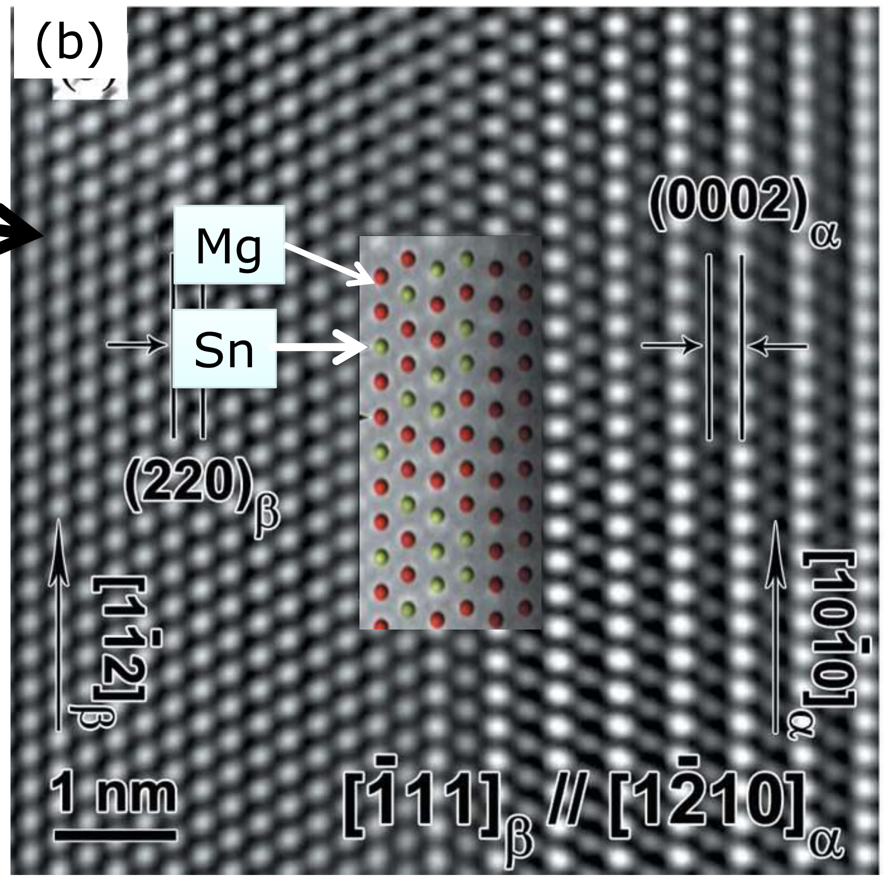


Application & Example

- ***Analysing crystalline defects and interfaces at the atomic scale***



BF image of the heat-treated Mg alloy



The inset shows the proposed atomic structure model of the interface

HRTEM image, along the $[001]_{\beta}//[2\text{-}1\text{-}10]_{\alpha}$ direction

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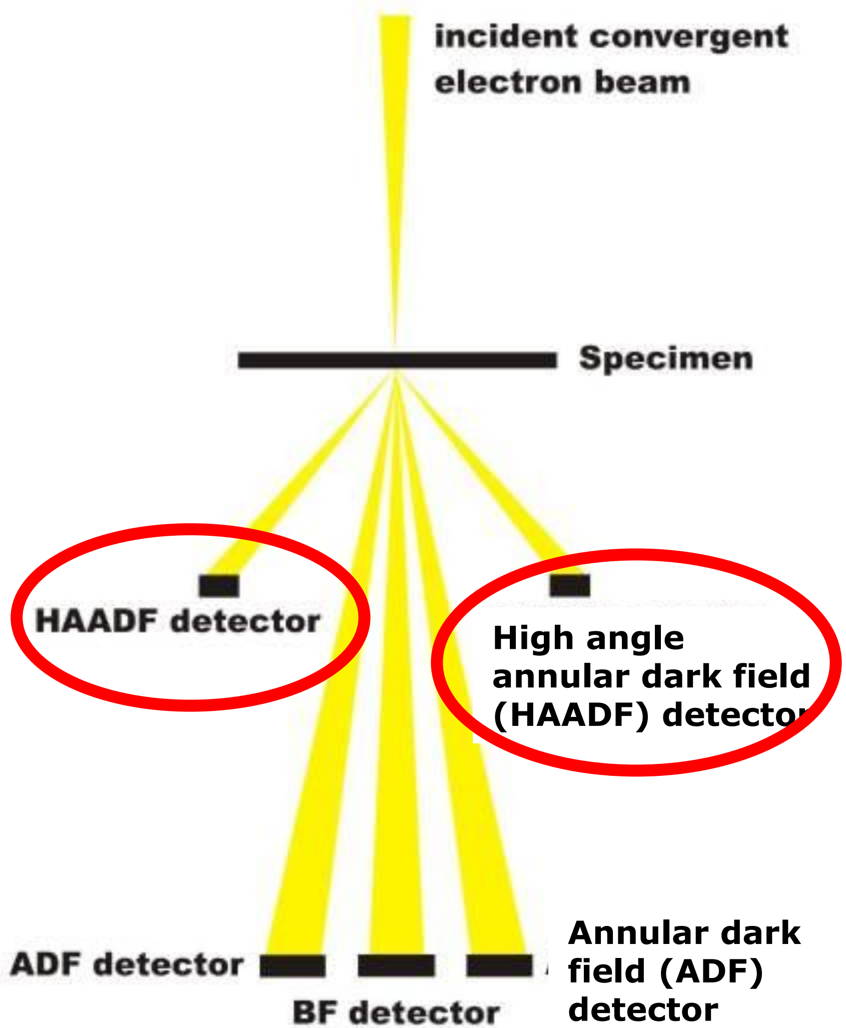
Scanning TEM (STEM)



- First STEM was built in the 1940s, further development until the 1970s.
- STEM combines the principles of TEM and SEM
- a small electron probe (nanoprobe) scan across the sample (similarly to SEM).
- HAADF detector detects electrons incoherently scattered at high angles --- Z-contrast image

Application:

- *compositional contrast*
- *STEM+EDXS or EELS*
  a powerful technique for analysing compositional variations on nanometric to micrometric scales

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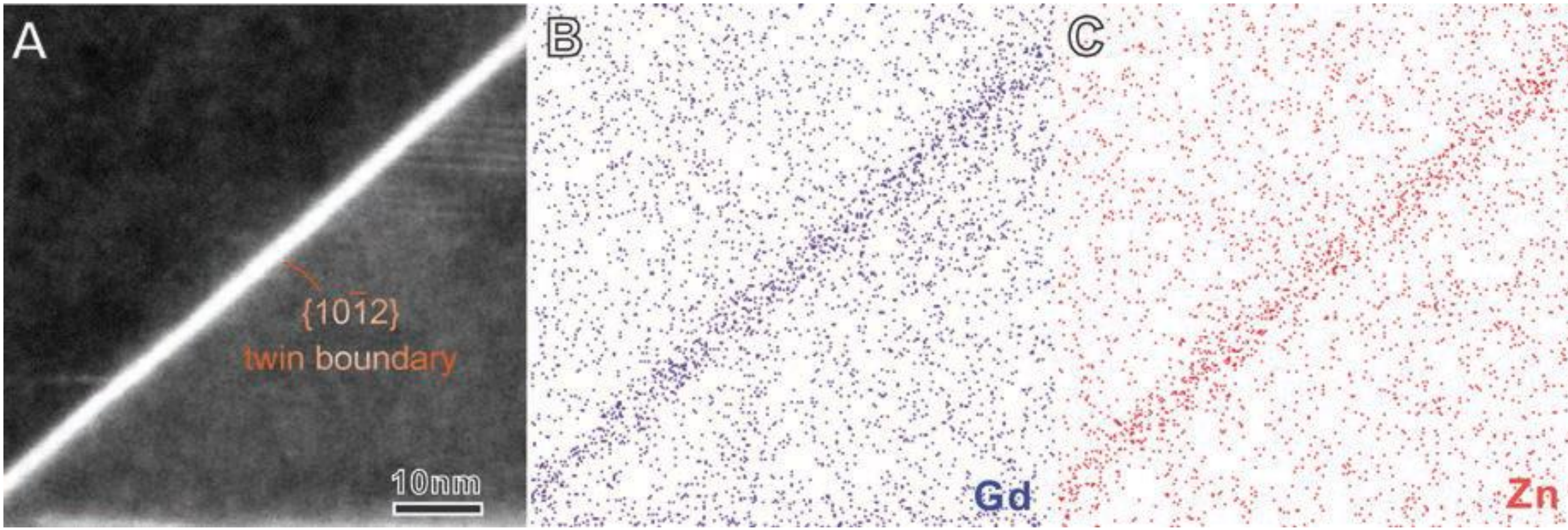
Example

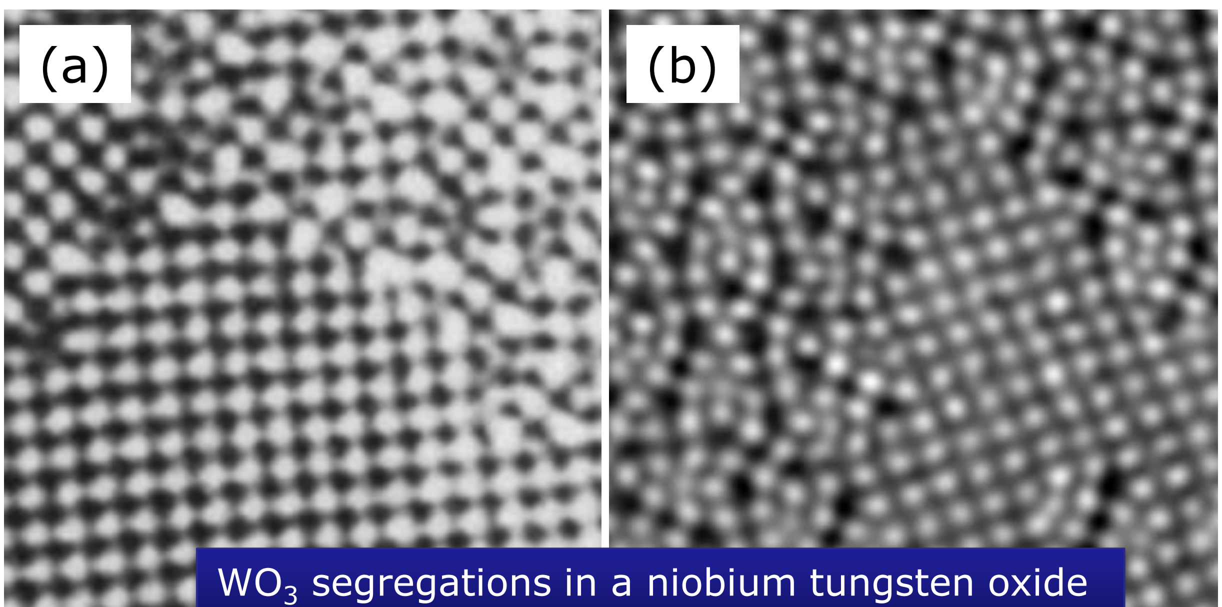


(A) HAADF-STEM image showing a {10-12} twin boundary (TB) in a sample of Mg alloy. (B) and (C) STEM-EDX maps showing the segregation of both Gd and Zn in the TB shown in (A).

HRTEM and HAADF-STEM (Z-contrast)

	HRTEM	HAADF-STEM
Basics	Interference of coherently scattered electron waves	Incoherent scattering
Point resolution	<0.27nm (Our TF20 TEM)	<0.34nm (Our TF20 TEM)
Image interpretation	Confirm with simulations; at Scherzer defocus: atom columns dark	Direct; intensity ~Z^2(Z: atomic number)

HRTEM image dark --- Metal atom columns



WO_3 segregations in a niobium tungsten oxide

HAADF-STEM (Z contrast) image: Bright spots --- metal atoms

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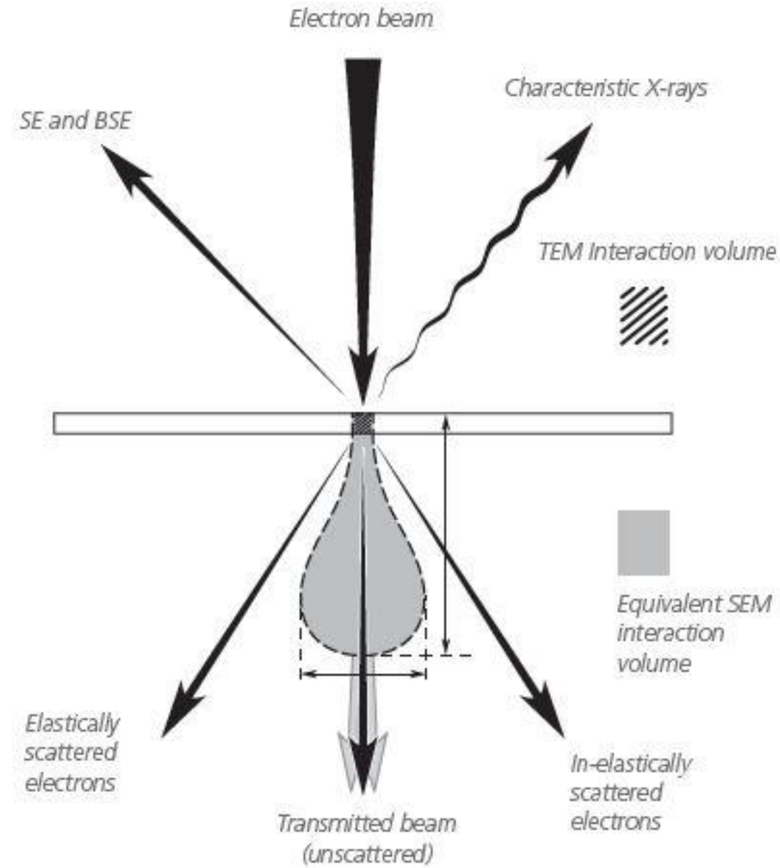
Energy-dispersive X-ray (EDX) spectroscopy

- 1st used on TEMs in the early 1970s
- Chemical composition analysis
- EDS analysis in the TEM can be performed on very small areas due to very small interaction volume.

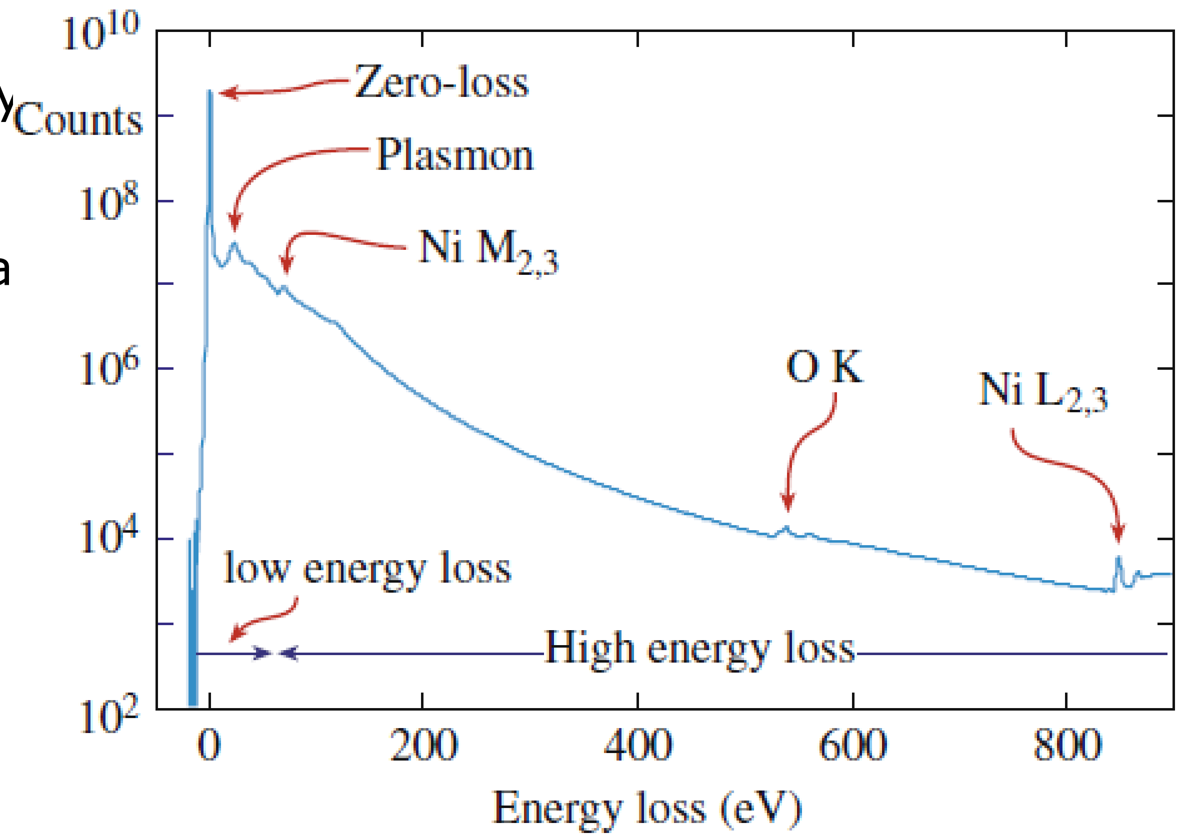


Electron beam/sample interaction

Electron Energy-loss Spectroscopy (EELS)

- Inelastic scattering causes loss of the energy of electrons
- Thin specimen required
- EELS spectrometer has a very high energy resolution
- complementary to X-ray spectroscopy
- can be utilized for qualitative and quantitative element analysis as well
- Can be used in forming energy filtered images

→ EFTEM



Example of EELS spectra

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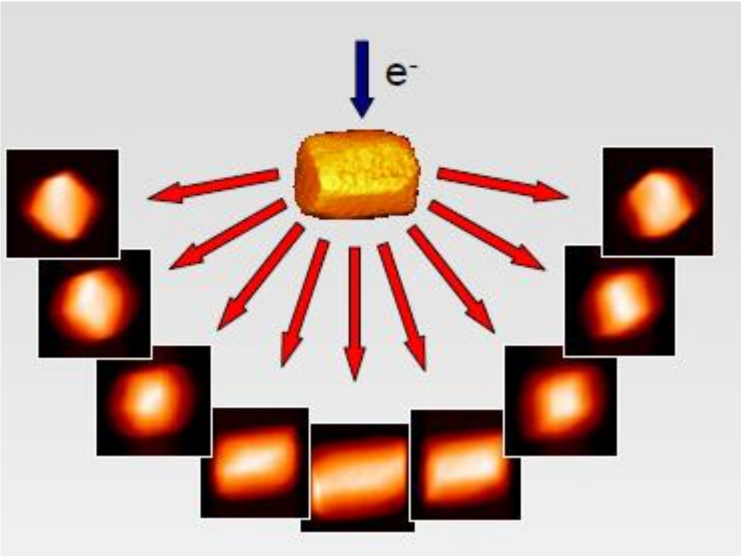
EELS and EDX

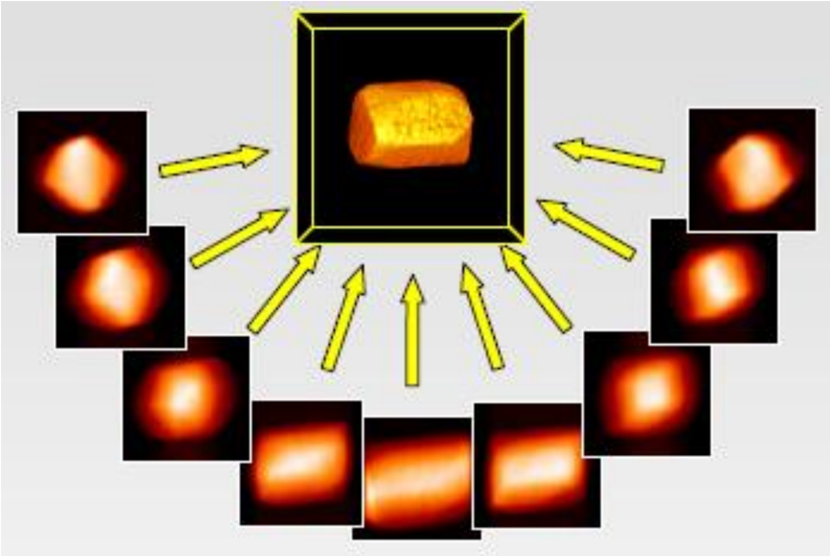
	EELS	EDX
Ease of use	Medium	High
Spatial resolution	Good	Beam broadening
Contamination sensitive	Yes	no
Visibility	Low	High
Peak overlap	No	Can be severe
Qualitative analysis	easy	Easy
Sensitivity light elements	**High**	**Low**
Sensitivity heavy elements	**Low**	**High**
Quantification	Easy	Easy
Accurate quantification	Complicated	Complicated
Energy resolution	High	Low

3D Tomography

- The sample is tilted in the microscope from +70° to −70° with 1 degree increment.
- Powerful computer softwares used to 3D reconstruction, such as Imaris, Amira and AutoQuant.
- Very time consuming process



Acquisition



Reconstruction

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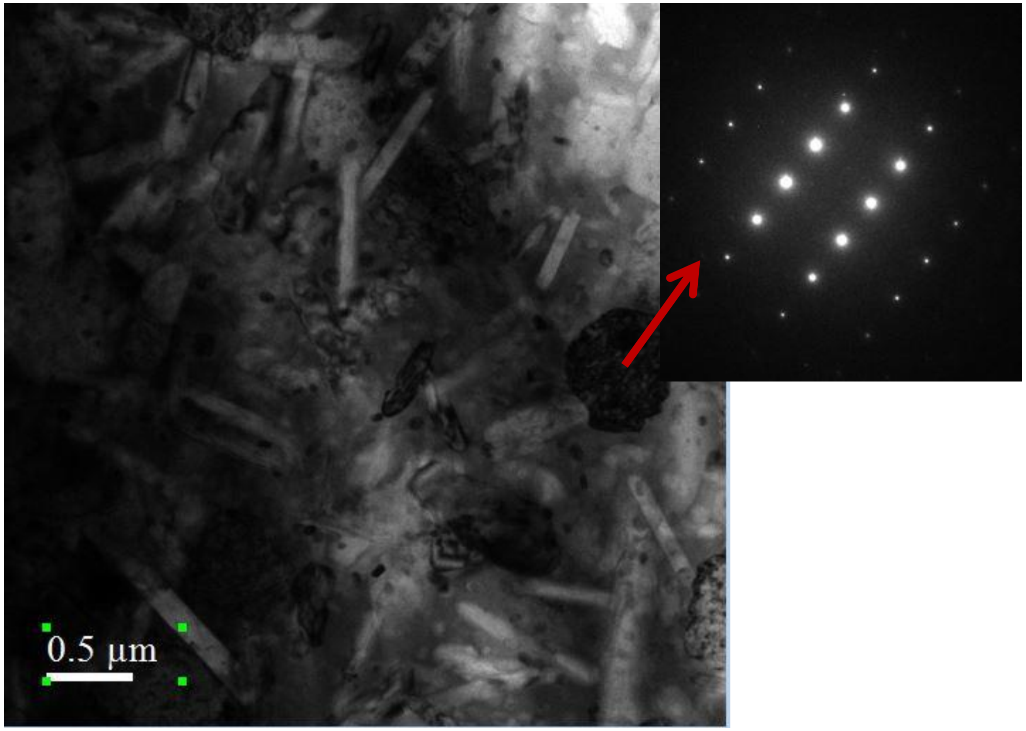
Cryo-TEM for materials science

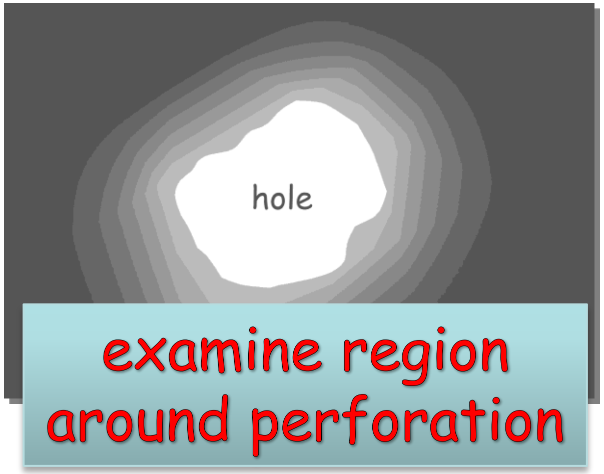
- To minimise the electron beam damage
- Samples are analysed at low temperatures (usually at ~-170ºC cooling by liquid Nitrogen)



Crystal structure analysis of glass ceramic lithium disilicate

Limitations

Limitations of TEM

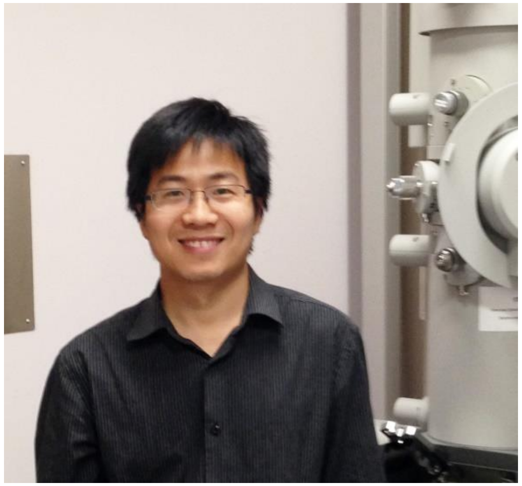


- The field of view is relatively small
- Electron beam damage
- Interpreting TEM images is challenging: an image represents a 2D projection of a 3D specimen
- A major limitation --- thin specimens:
  - The usual sample thickness is ~100-200nm (~10-20nm for HRTEM)
  - The structure of the sample may be changed during the preparation process

Electron Microscope in Image Centre

- Located at the School of Biological Sciences, Thomas building.
- The centre specialises in transmission electron microscopy (including cryo-TEM)

Dr Adrian Turner (Centre Manager)



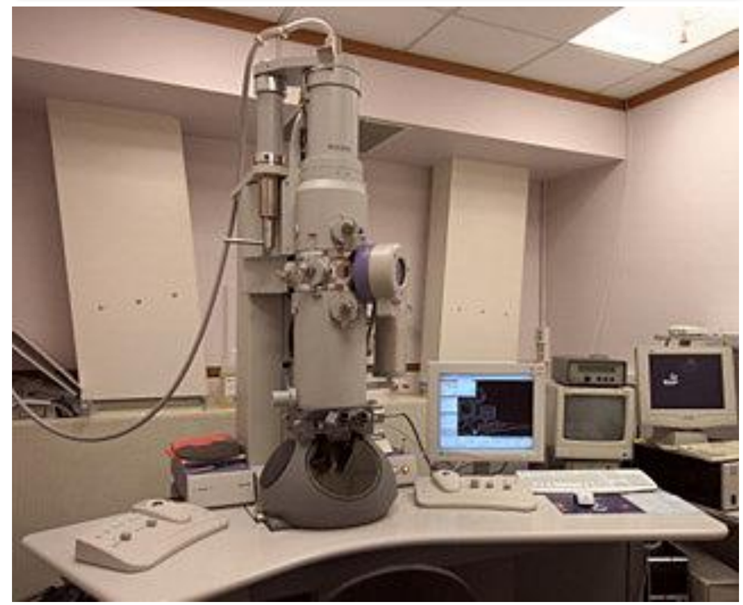
In charge of the materials science and TEM in the Centre

Electron Microscopes in Image Centre

❖ Philips CM12 TEM (CM12)

- ❖ 120 kV
- ❖ single tilt, double tilt, and cryo specimen holders
- ❖ Applications: BF; DF; SAD

❖ FEI Tecnai 12 TEM (T12)



- ❖ 120 kV
- ❖ optimised for Cryo-TEM, with cold stages
- ❖ Single and double tilt
- ❖ Applications: BF, DF, SAD

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Electron Microscope in Image Centre

❖ FEI Tecnai FEG20 TEM (TF20)

- ❖ FEG 200 kV
- ❖ TEM/STEM mode
- ❖ Chemical compositional analysis
  - ❖ Edax EDS.
  - ❖ Gatan energy filter
- ❖ Single, double tilt, tomography and cryo holders.
- ❖ **Techniques:**
  BF; DF; SAD; CBED; HRTEM; STEM; EFTEM, EDS; EELS; 3D tomography…..

- ❖ **TEM resolution:**
  Point: ≤0.270nm
  Line: ≤0.144nm
- ❖ **STEM resolution: ≤0.34nm**

TEM sample

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Inorganic Specimens Preparation

Samples need to be extremely thin (~100nm) so electron beam can penetrate

❖ Powders/particles and soft materials

Powders /particles /friable mass → Add powders to some solvent e.g. ethanol
Powders /particles /friable mass → Crushing with pestle and mortar → Add powders to some solvent e.g. ethanol
Powders /particles /friable mass → Support with Polymerised resin or via freezing
Soft mass → Support with Polymerised resin or via freezing → Ultramicrotomy or Cryo-ultramicrotomy

Add powders to some solvent e.g. ethanol → Mount on grid
Ultramicrotomy or Cryo-ultramicrotomy → Mount on grid

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Specimens Preparation Equipment

Leica EM UC6 Ultramicrotome

- Ultra-thin sectioning of material for TEM (40 and 100 nm).
- Diamond knives and glass knives are used with ultramicrotome

TEM sample

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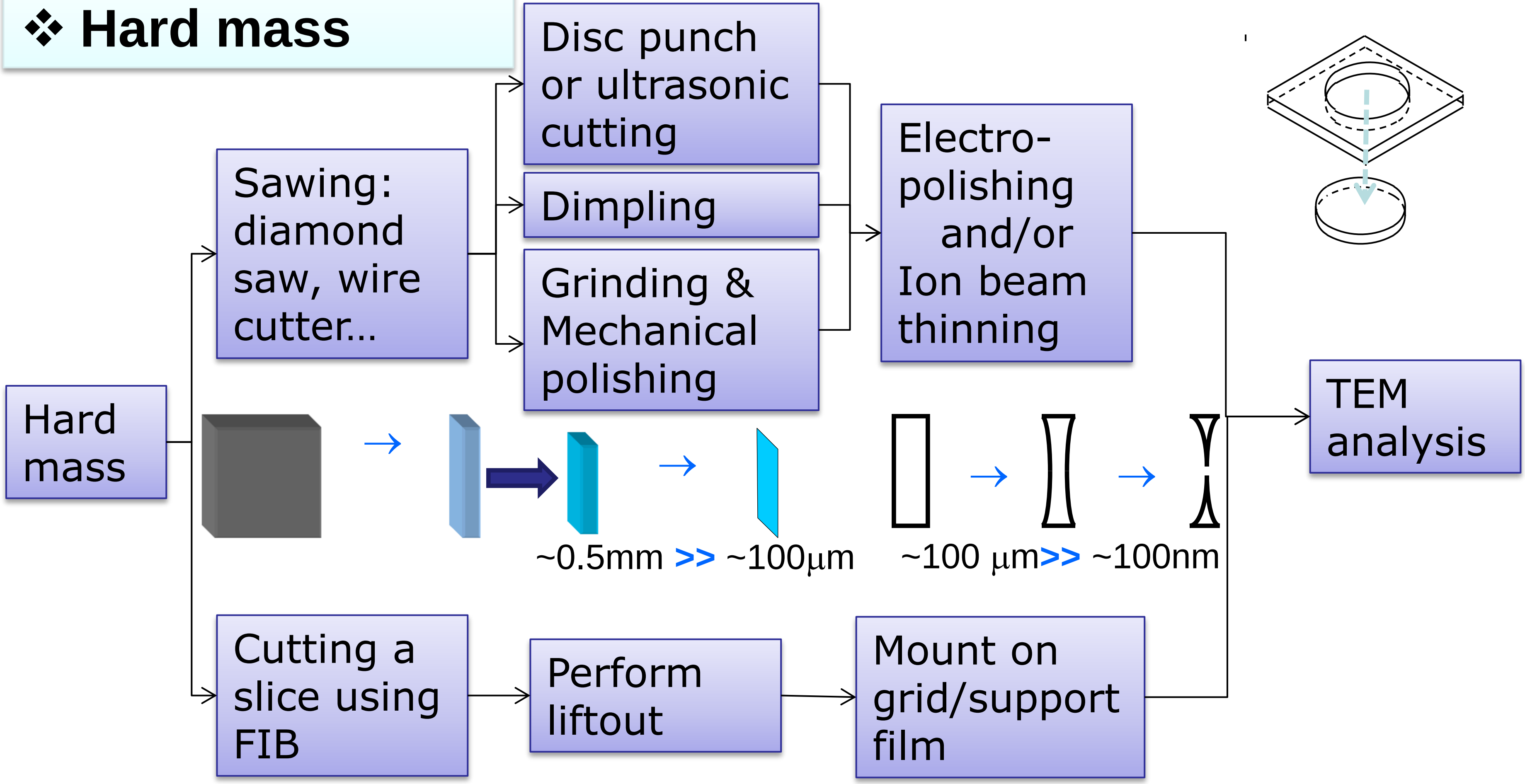
Inorganic Specimens Preparation

- **Hard mass**



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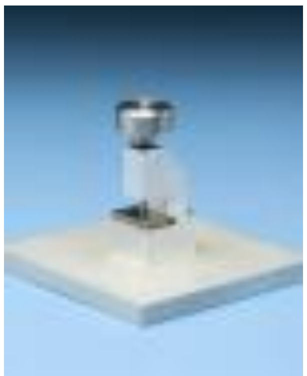
Sample Preparation Equipment

Disc punch



Ultrasonic Cutter

Dimple grinder

Struer Twin-jet electro-polishing system

Fischoine mode 1010 Ion mill

Summary

- TEM is a very versatile analysis technique.
- Many different types of analysis can be performed
- Complimentary information can be obtained from distinct small (nm) regions allowing full nano-scale characterisation.

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Thank you for participating