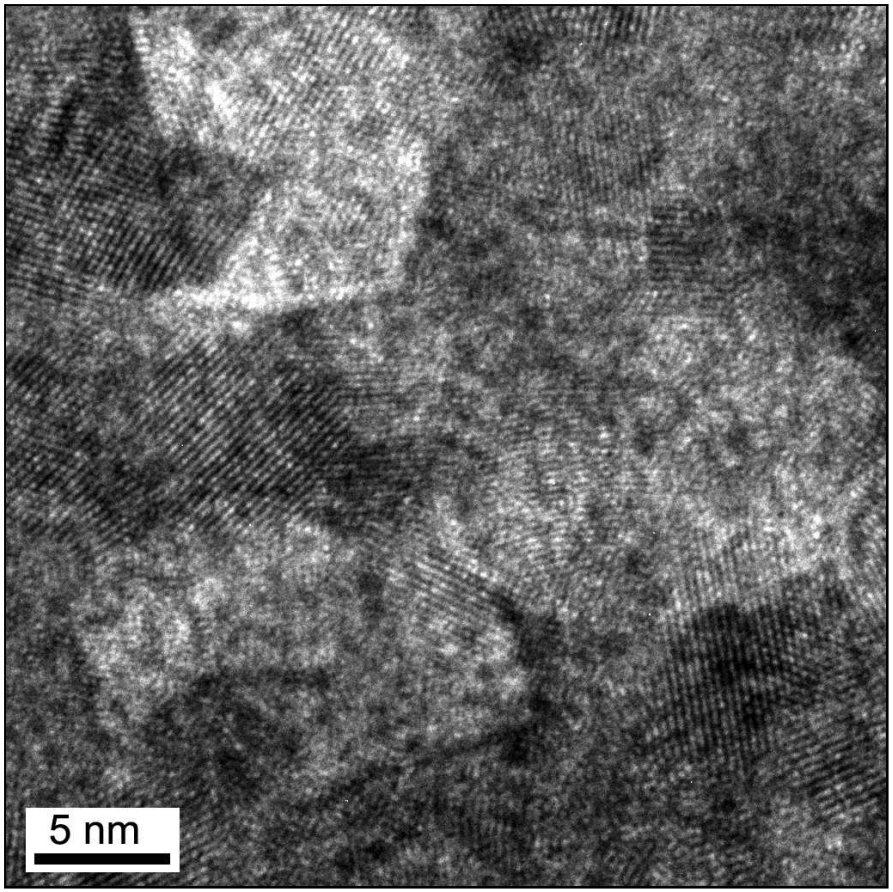
SAND2008-3583P

A brief introduction to TEM



Chad Parish
Luke Brewer

Materials Science and Engineering

Sandia National Laboratories

National Nuclear Security Administration

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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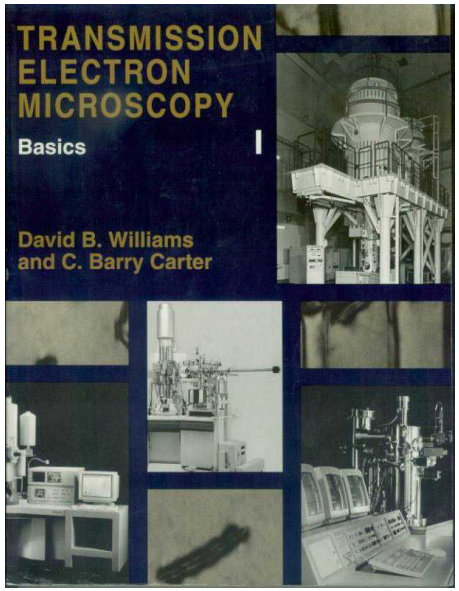
For more information

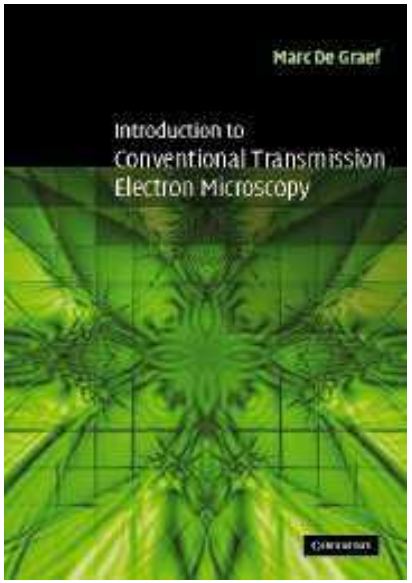
TEM has been around since the 1940s – there's plenty to read if you want more information

Most recent choices:

Williams & Carter, 1996:
Best general introduction
Diffraction, imaging, chemical microanalysis



De Graef, 2003:
Mathematical and computational
Imaging and diffraction



Classic references:

Williams, Introduction to Analytical Electron Microscopy, 1984; Goldstein et al., Principles of Analytical Electron Microscopy, 1986: both cover chemical microanalysis. Somewhat out of date, but still valuable.

Hirsch et al., Electron Microscopy of Thin Crystals, 1965: Theory of imaging from the people who invented it.

Journals to watch:

Microscopy and Microanalysis, Ultramicroscopy, Journal of Microscopy, Journal of Electron Microscopy, Journal of Applied Physics, Applied Physics Letters, and others

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Why do TEM?

- **Ability to directly visualize the structures of materials down to the atomic scale**
- **Ability to measure crystallographic parameters down to nanometer scales**
- **Sensitivity to crystallographic defects**
  - **Dislocations (original use of TEM in materials science)**
  - **Grain boundaries/phase boundaries**
  - **Twins**
- **Measure and Map elemental composition down to atomic scales**
  - **EDS**
  - **EELS**
- ***Ability to combine all of these measurements…***
  - *In one instrument!*
  - *On one sample!*
  - *In one area!*

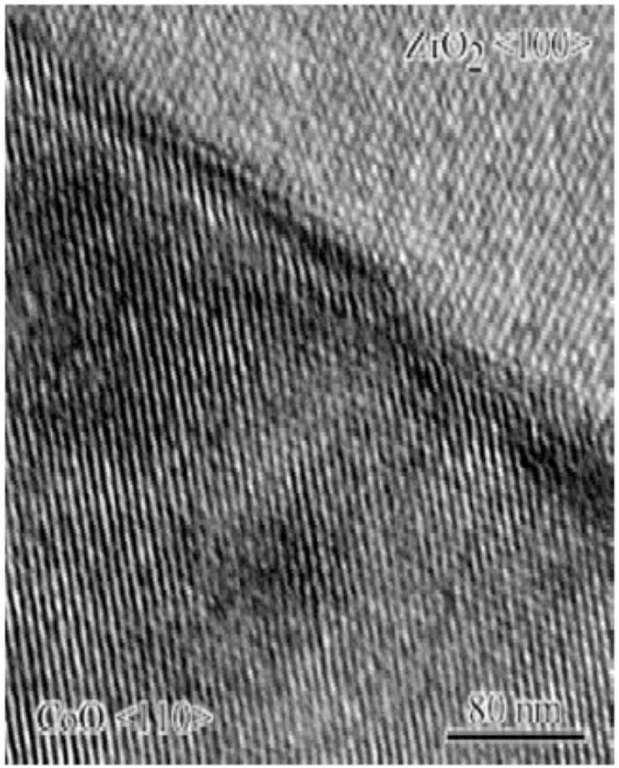

FIG. 4. HREM lattice image of CoO/ZrO_2 showing atomic-level abruptness between phases without the presence of a tertiary phase.

J. Mater. Res., Vol. 17, No. 4, Apr 2002

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Why shouldn't we do TEM?

- Can a suitable sample be found?
  - Difficulty in sample preparation—need thin (<200 nm) samples
  - Stable
  - Representative
- Could we get the information by an easier/faster means?
  - Powder XRD or EBSD
  - X-ray fluorescence or microprobe
  - AFM or SEM
- Will there be difficulty in interpretation of the results?
  - *TEM is a 2D projection of a 3D reality!*
  - Data (images, spectra) can be susceptible to artifacts
- Cost?
  - TEM cannot be done in ½ hr
  - TEMs are expensive instruments ($750K--$4M)

What is a TEM?

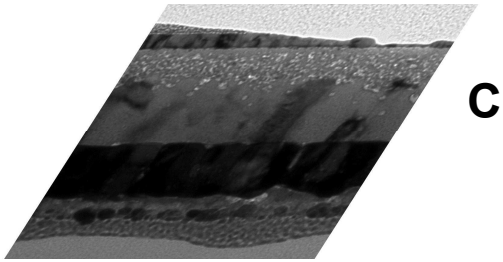
Conceptually:

Illumination stage: Produces a bright electron beam

Electron beam

Thin sample (<200 nm)

Projector stage: Sends electron beam to the detectors



Detectors: CCD camera, fluorescent screen, etc.

Practically:

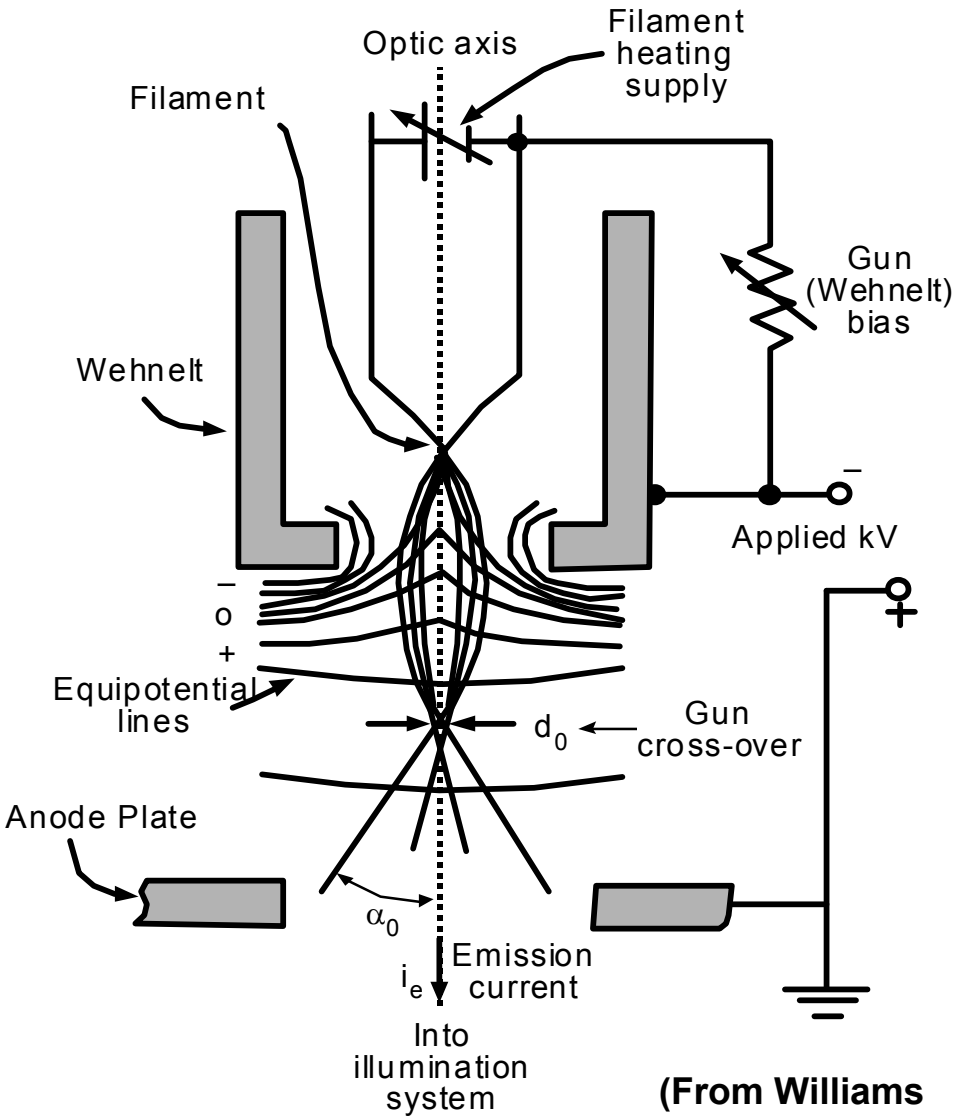
First thing: we need high-energy electrons

There are several types of electron guns

Example: termionic electron source

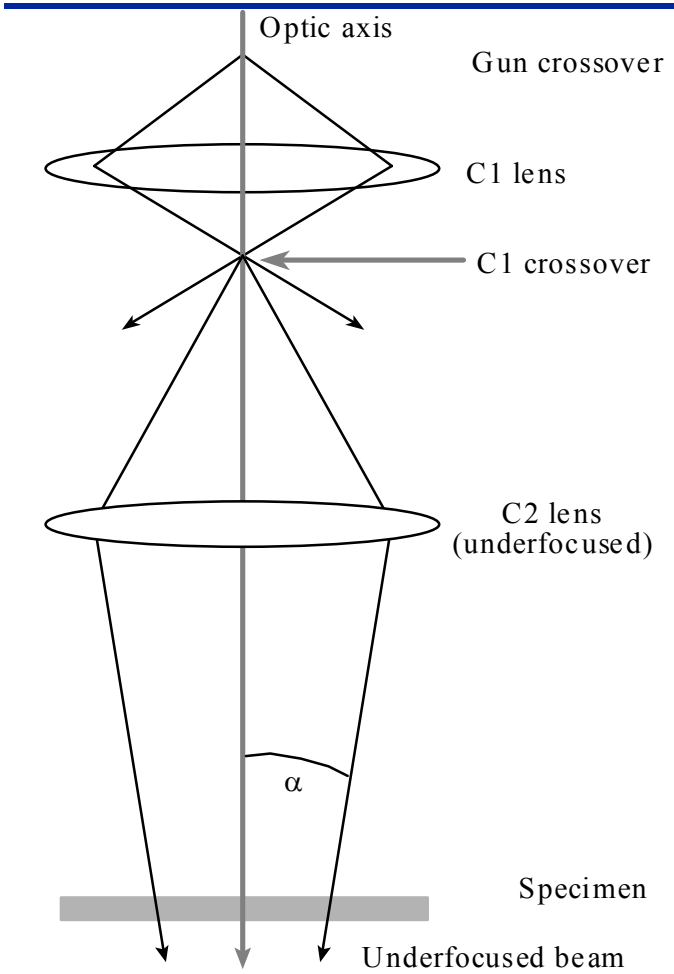
A filament (W or LaB_6) is heated white-hot, which allows electrons to escape →similar to a lightbulb

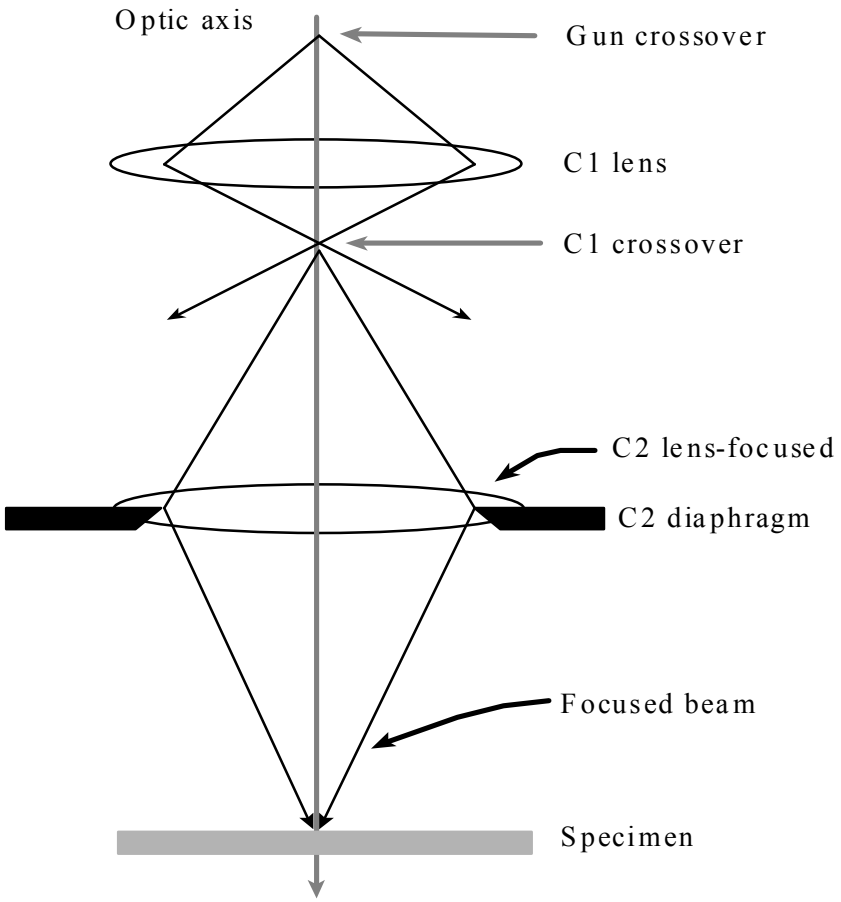
The filament assembly is floated at high voltage (80-300 kV) to accelerate the electrons



(From Williams and Carter)

Next: we must illuminate the sample



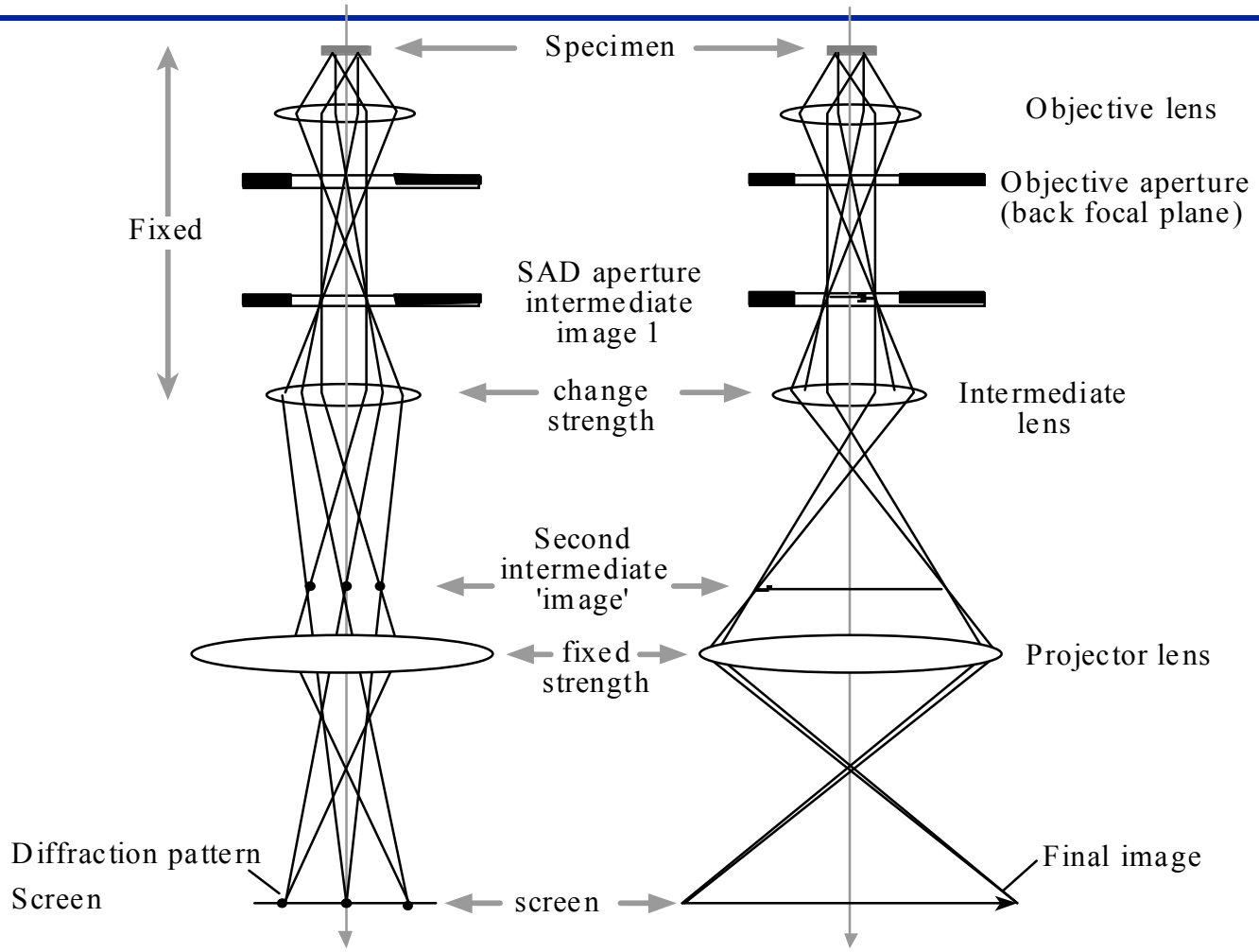


Imaging: nearly-parallel beam

Chemical microanalysis: focused beam

(From Williams and Carter)

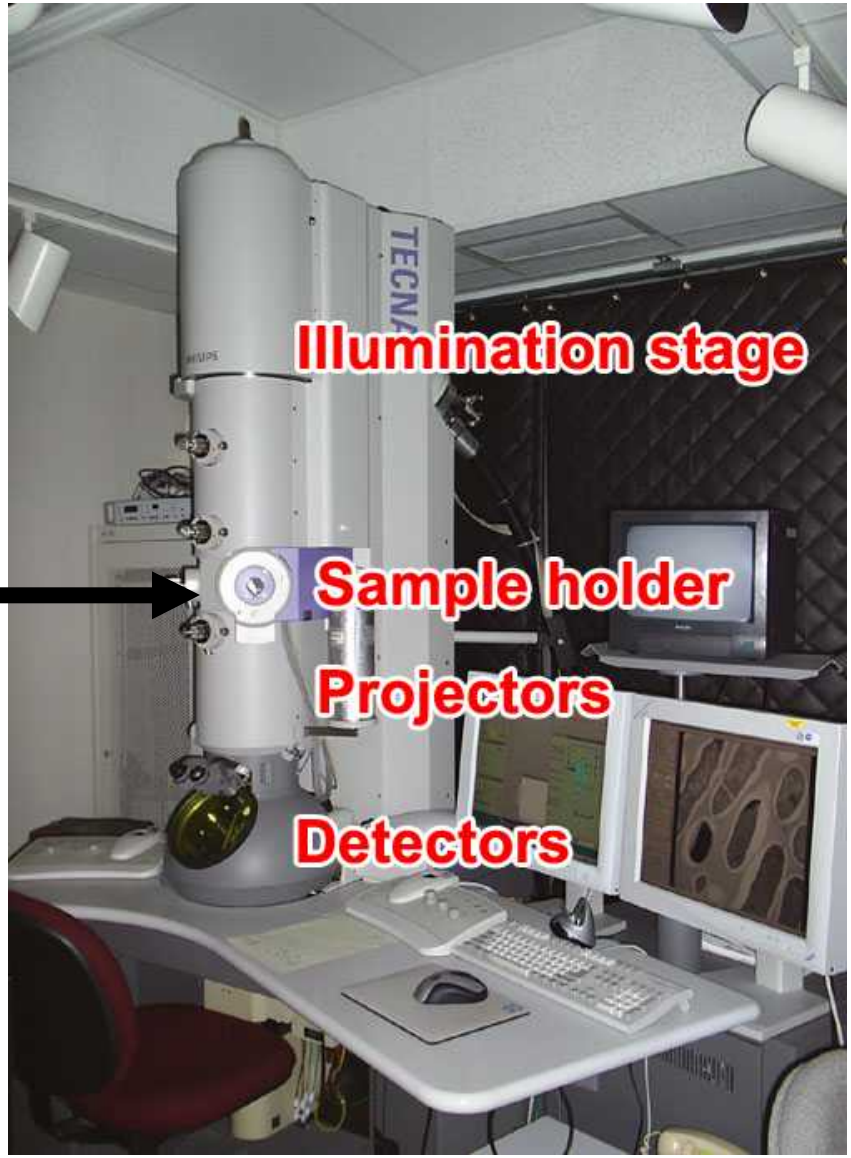
We then project the image onto the detector



(From Williams and Carter)

Limiting factor: the objective lens

Sample + holder enters from the side



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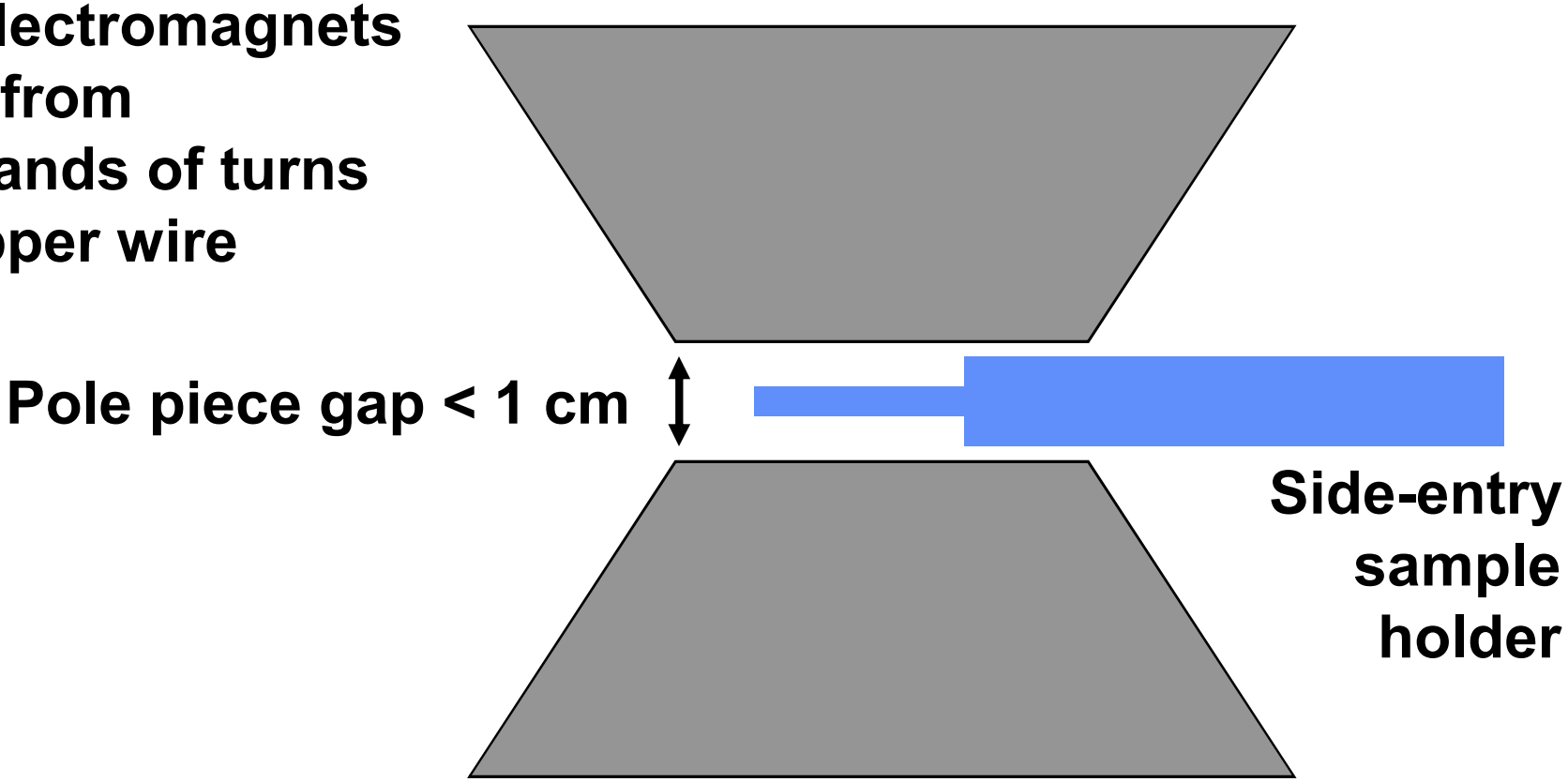
Limiting factor: the objective lens

Objective lens:
Two electromagnets made from thousands of turns of copper wire



Smaller gap → better lensing → image smaller features
2-3 cm (1960s) → 3-4 mm (today)

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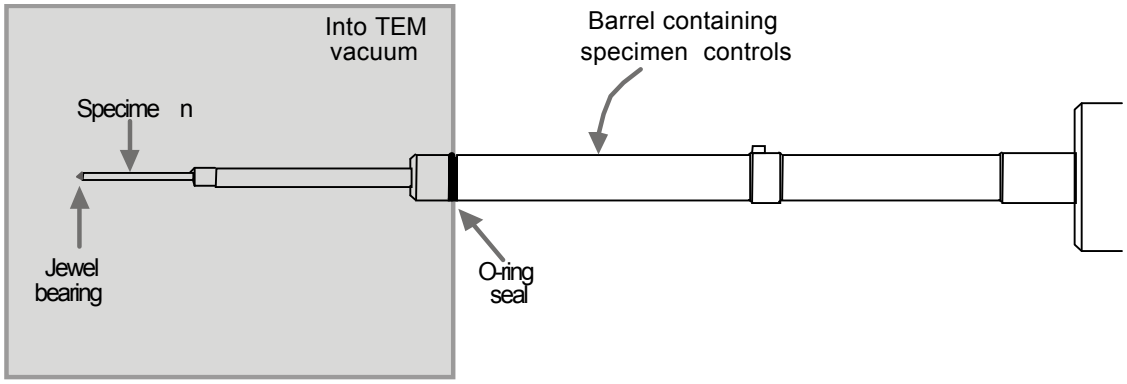
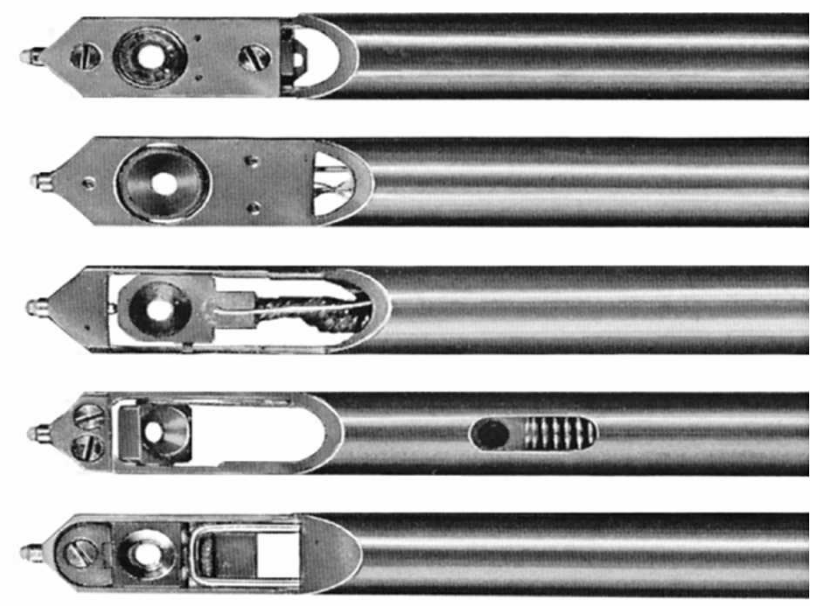
Limiting factor: the objective lens





≈ 1 cm

(From Williams and Carter)

Sample preparation

The small amount of space inside the objective lens limits our sample preparation

Standard sample size for all TEMs: 3mm diameter

How can we make 3mm samples of our materials?

Sample preparation

- ***Thin***
  - Less than 200 nm preferable, less than 50 nm for good HREM/EELS
  - Good news—nano particles are inherently thin
- High energy electron beam can cause
  - Damage (radiolysis, knock-on)
  - Crystallization
  - Evaporation
- Clean
  - Free of hydrocarbons on surface
  - Oxidation of surface on some metals can be problematic
- ***Representative of the bulk*** (A key question for any microscopy technique)
  - Not so much of a problem for nano particles
  - Very important for dislocation studies in metals—did we relax the material?
  - You don't want the "one representative area"!

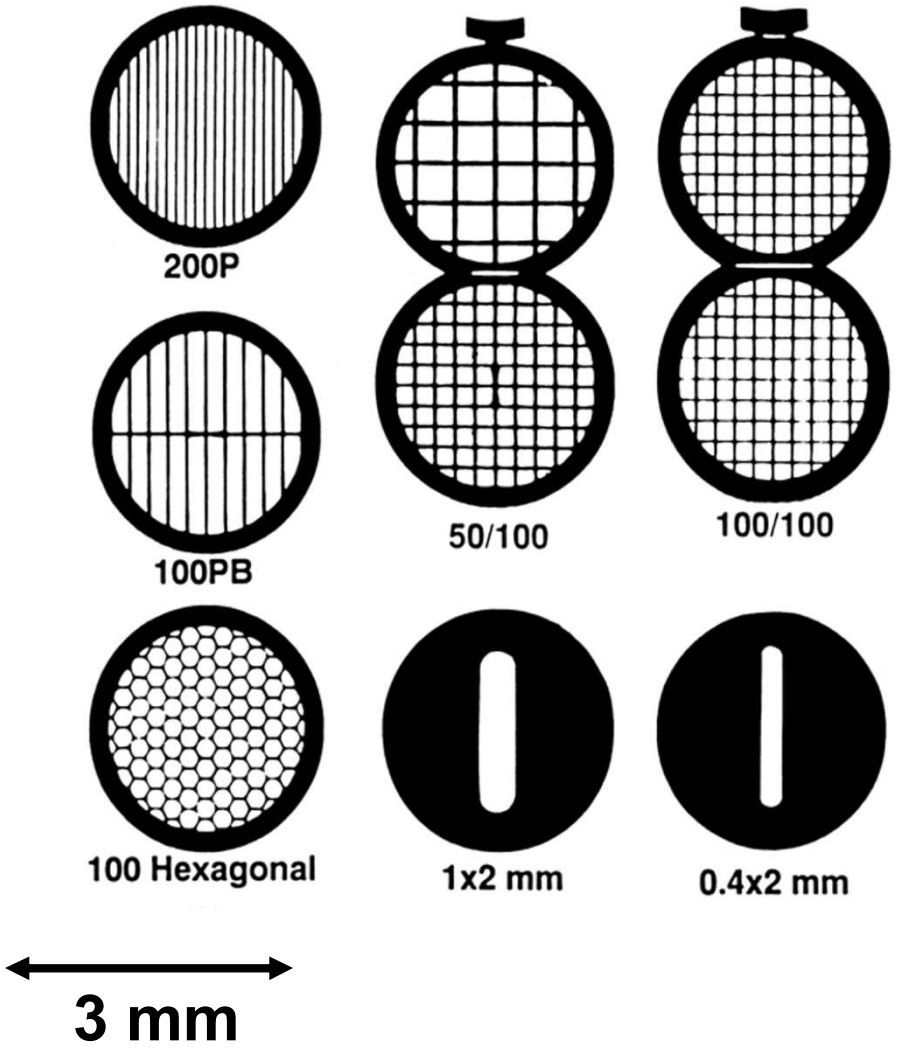
How to hold your sample (particularly nanoparticles)

Common Grid Materials:
Cu Ni Pt Be C Au

Most has a very thin layer of amorphous carbon over a metal mesh

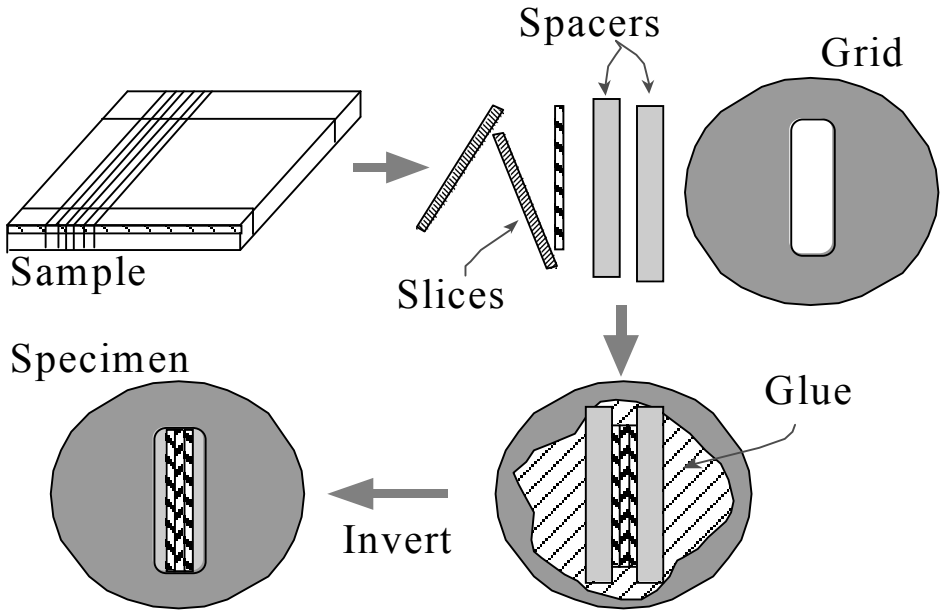
Can have either a continuous film or “holey” carbon

Samples can be prepared by suspending sample in volatile solvent (isopropanol, methanol, etc.) and depositing a *small* amount on the grid



(From Williams and Carter)

Thinning a bulk sample: cutting and mounting



This process used to be the primary means of preparing thin film TEM samples

A grid is used to provide mechanical stability

Quality of glue joints is particularly key

This process takes a lot of practice—dreaded by grad students everywhere!

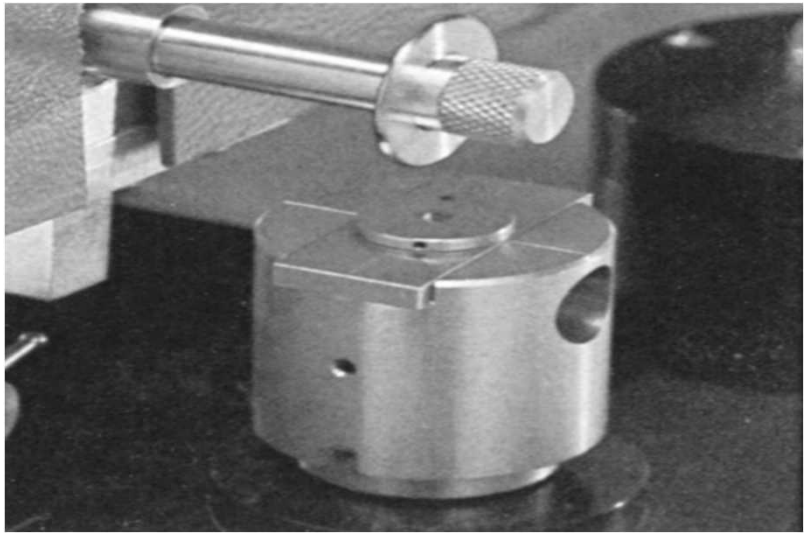
(From Williams and Carter)

Thinning a bulk sample: dimpling

Small wheel rotates on top of solid, polished specimen using abrasive (Si_3N_4 or diamond) slurry

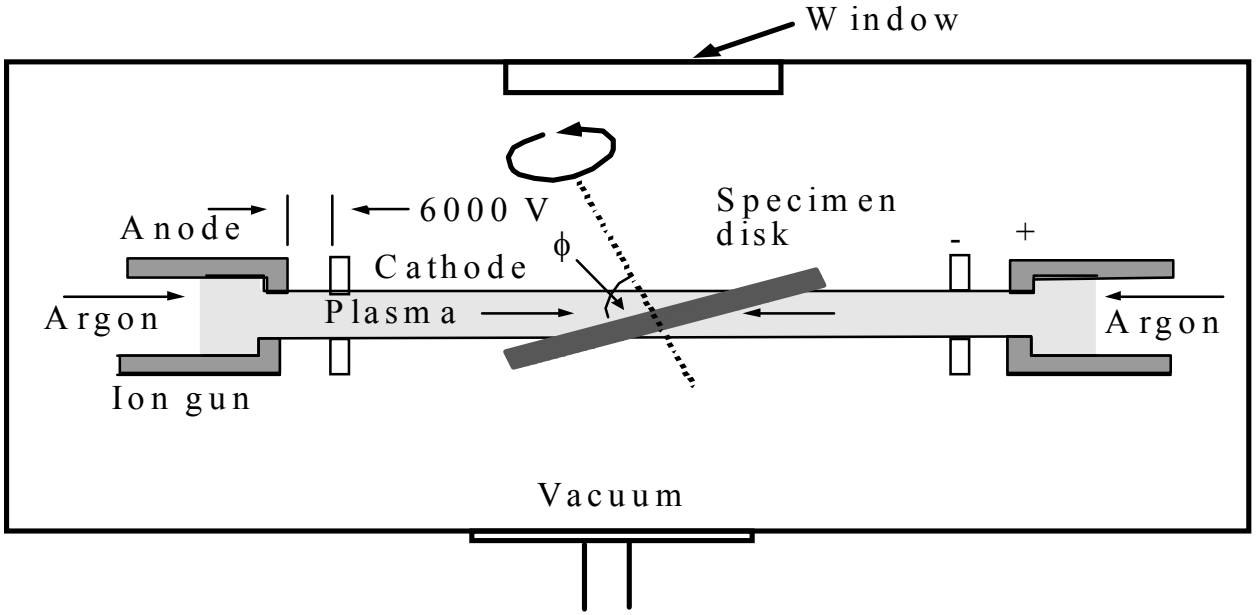
Creates a dimple in the surface of the sample

The result is a sample which is 100μm thick at the edges and <10μm thick at the center



(From Williams and Carter)

Thinning a bulk sample: ion milling



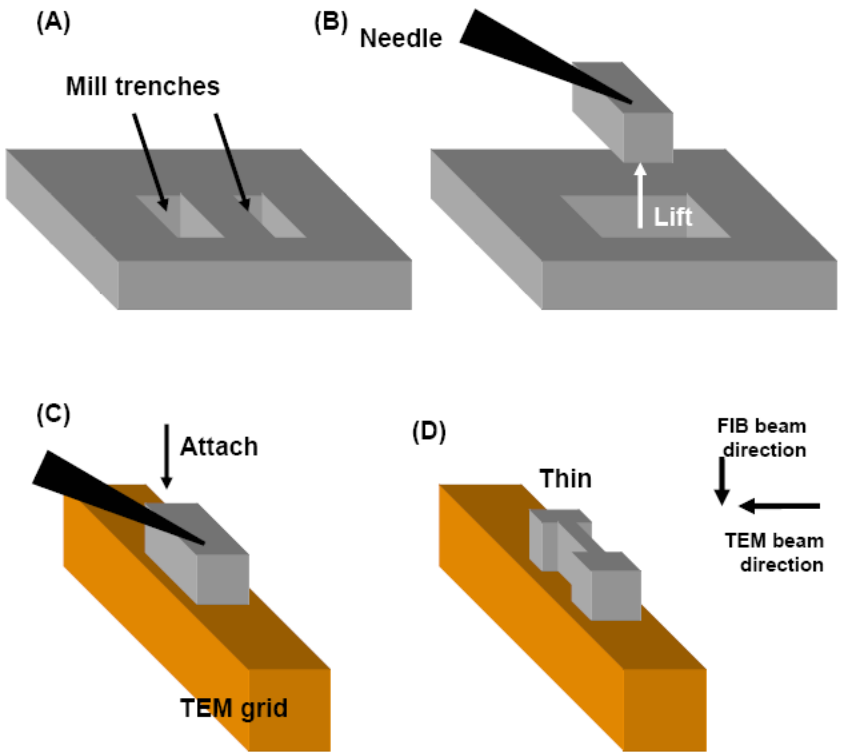
(From Williams and Carter)

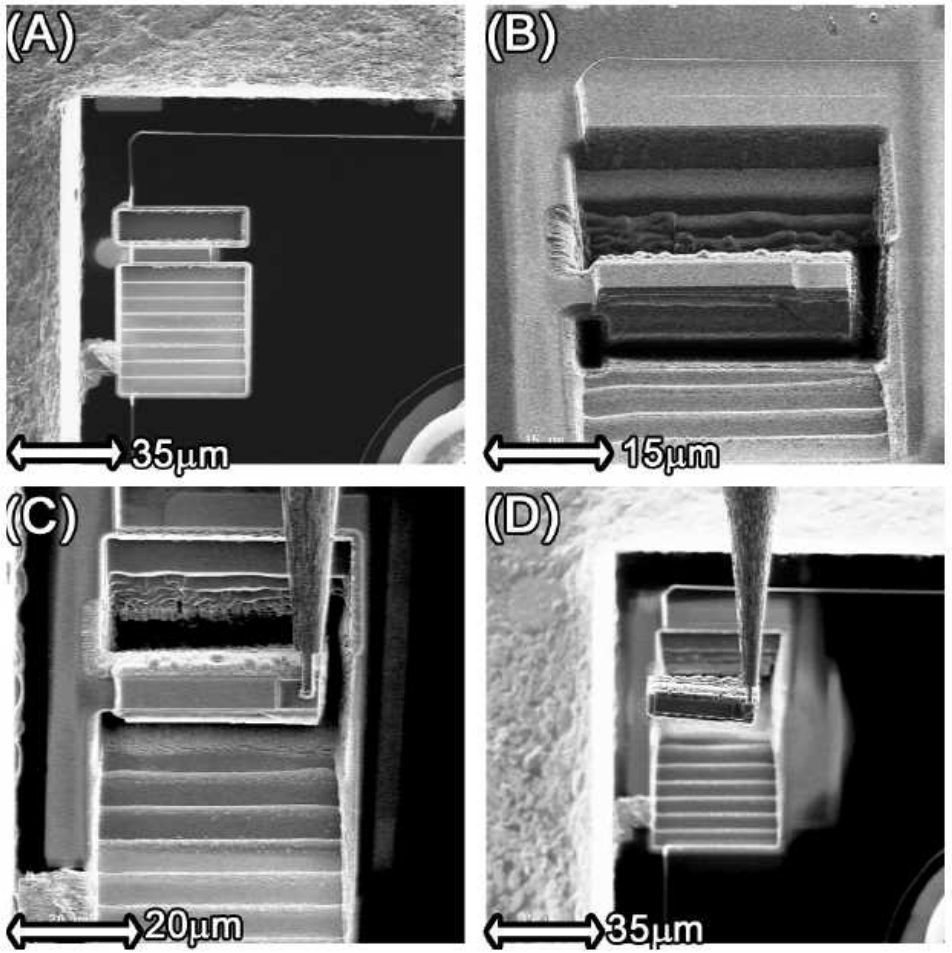
Most samples not electron transparent after dimpling

Ion milling takes sample from thin (~10 μm) down to electron transparent (<200 nm)

Need to be careful about not damaging the sample (Ar implantation, specimen heating, etc.)

The newest technique: focused ion beam milling





Parish, PhD Dissertation, NC State Univ., 2006

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Sample thinness: main historical problem

Until about 1970, few samples could be made <200 nm thick

The trend was toward higher-energy microscopes (1-3 MeV beam energy) to penetrate thick samples

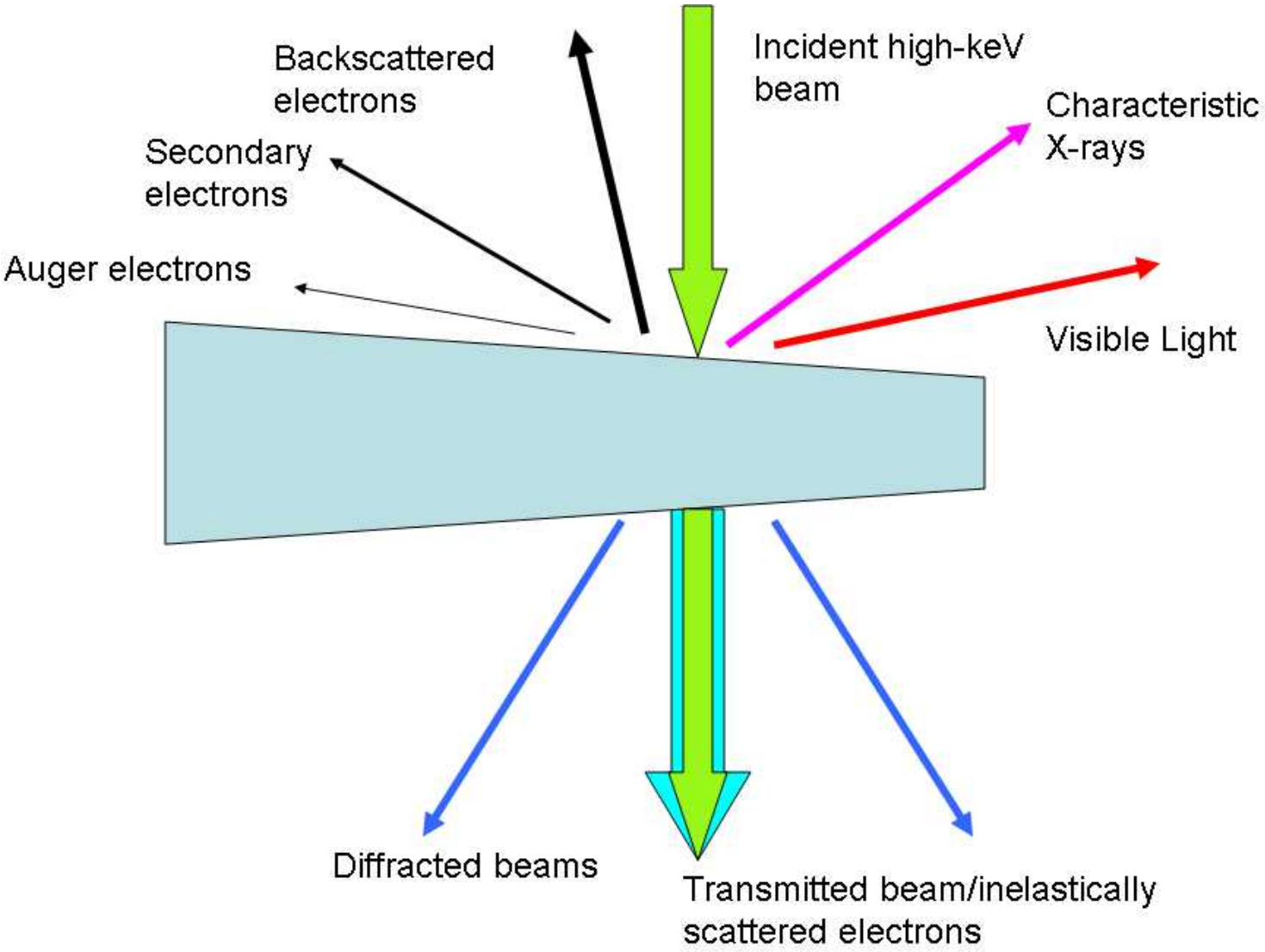
- **Example: US Steel's million volt microscope (1960s)**

With the invention of the ion mill & other tools, TEM voltages dropped to the 80-300 keV seen today

Recap: what we've said so far

1. Electron gun + high voltage generate an electron beam
2. The illumination stage transfers this beam onto the sample
3. The sample is held in a side-entry holder
   - Sample must be thin
   - Sample + holder must fit into a small gap
4. Projector lenses take the transmitted electrons and send them to the detector

What signals do we have to work with?



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Electron diffraction in TEM

$$\lambda = \frac{2d}{n}\sin(\theta)$$

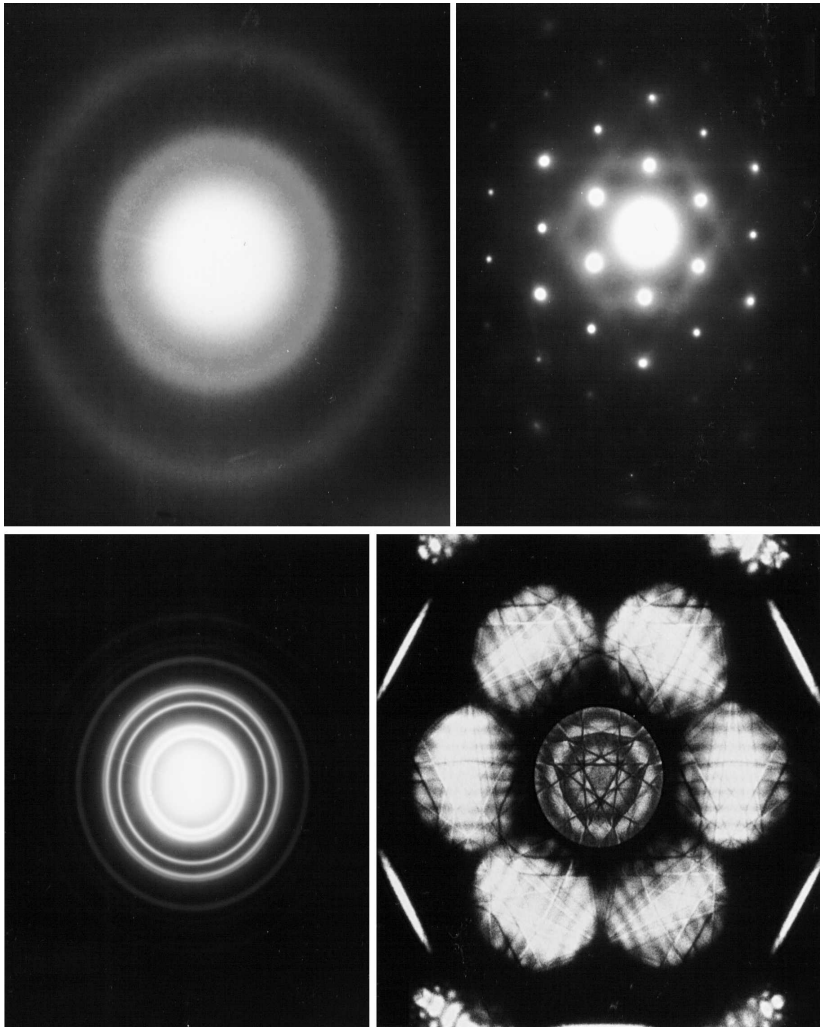
Electrons, just like x-rays and neutrons, are readily diffracted

Kinematic theory (Bragg's law) predicts peak positions

Intensities require dynamical theory → terrifying mathematics

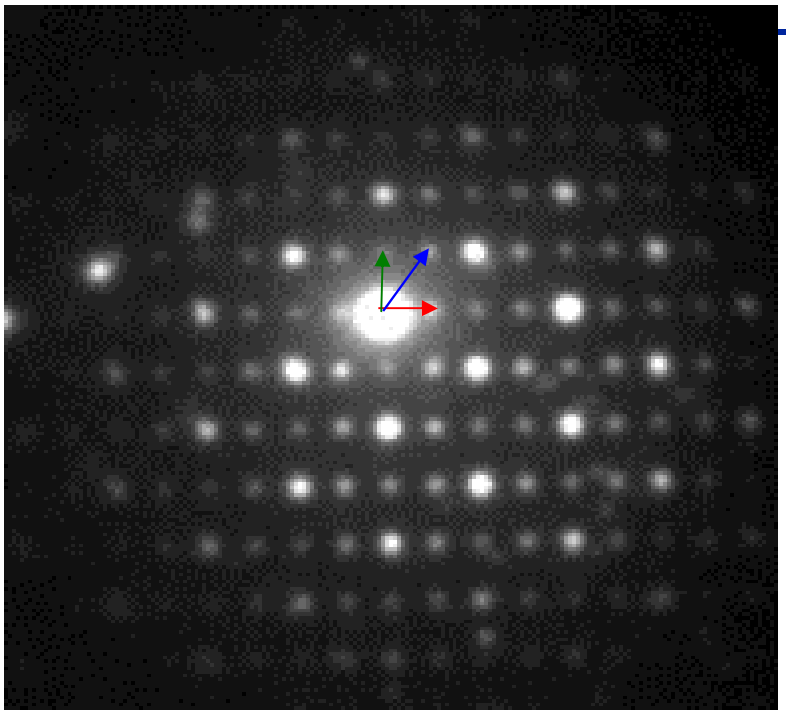
A great deal of information is available with more advanced electron diffraction (CBED, etc.)

- **Space-group analysis**
- **Superlattice ordering**
- **Elastic strain measurement**

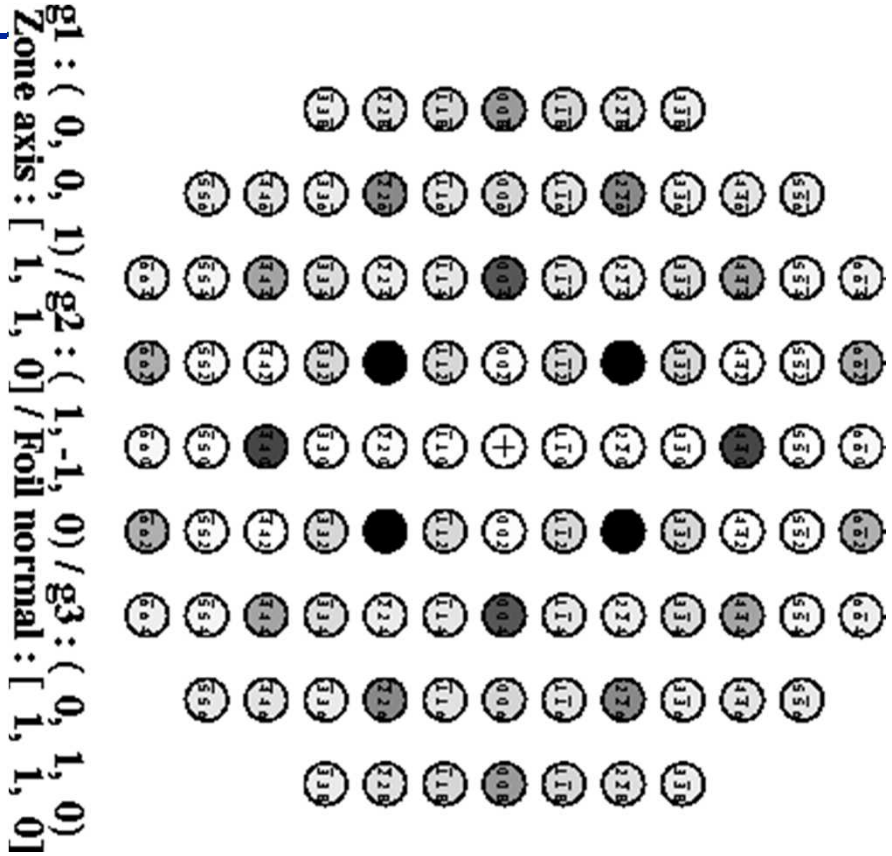


(From Williams and Carter)

Selected Area Diffraction Patterns -- Er_2O_3 particle



<110> zone axis

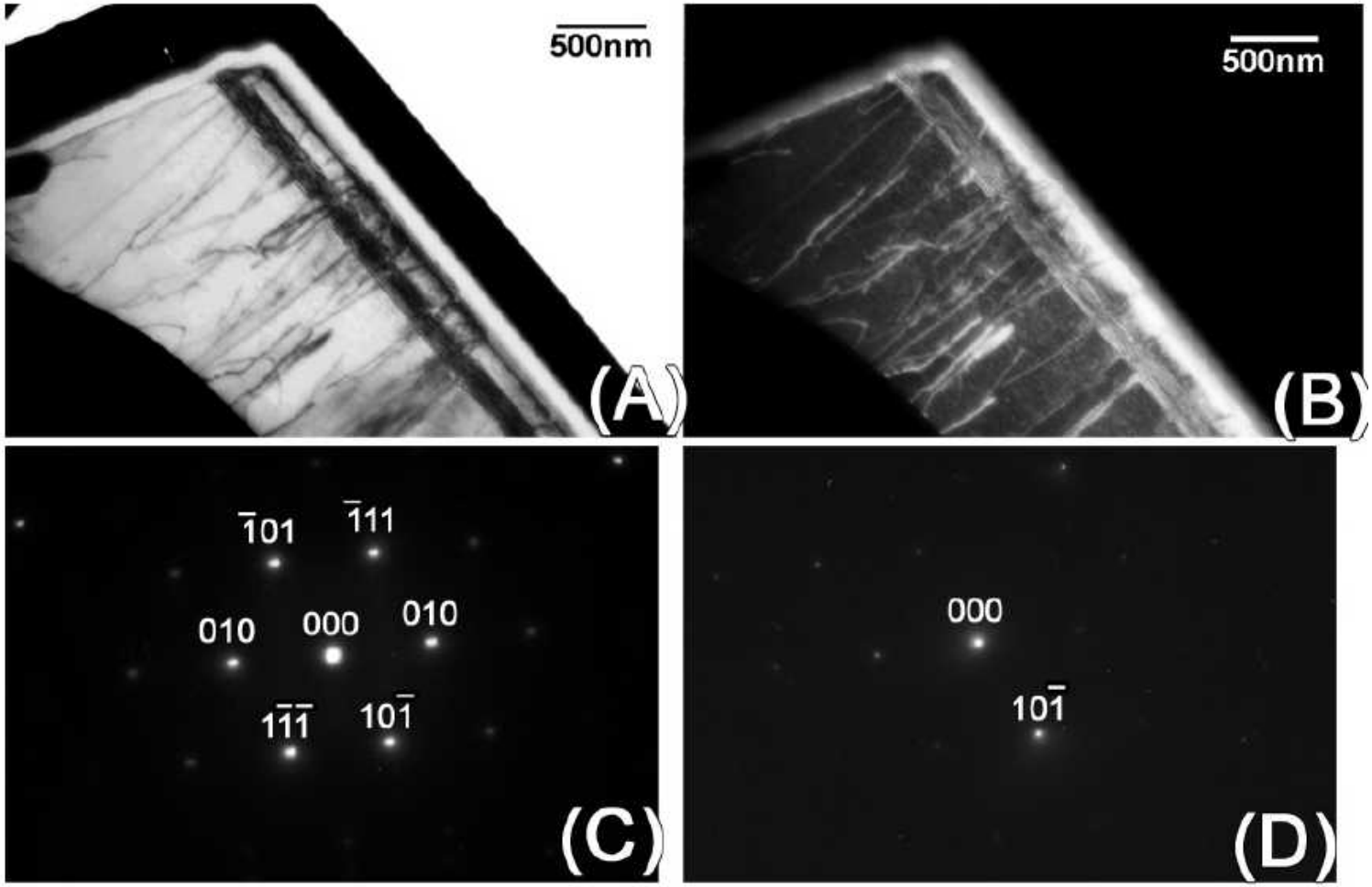


Measured d_{011}=7.2Å (7.45Å)
Measured d_{200}=5.19Å (5.27Å)
Measured d_{211}=4.14Å (4.30Å)

Measured Ratio R_{200}/R_{011}=1.39(1.41)
Measured Ratio R_{211}/R_{011}=1.74(1.73)

All values in parentheses represent calculated values.

Conventional TEM imaging – ideal for crystallographic defects



Parish, PhD Dissertation, NC State Univ., 2006

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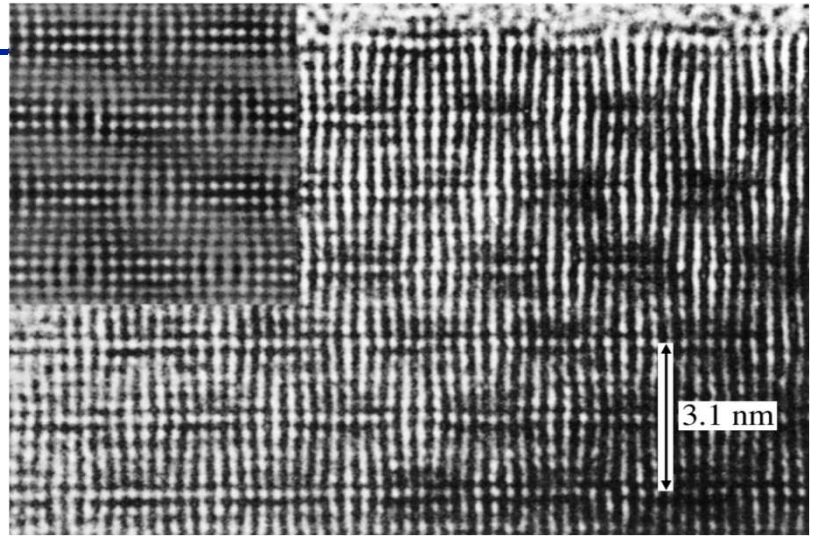
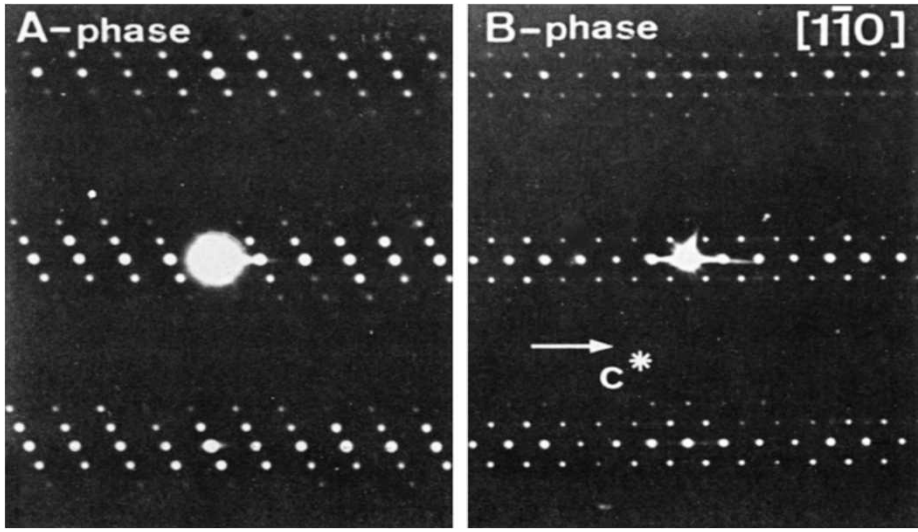
High Resolution Electron Microscopy (lattice imaging)

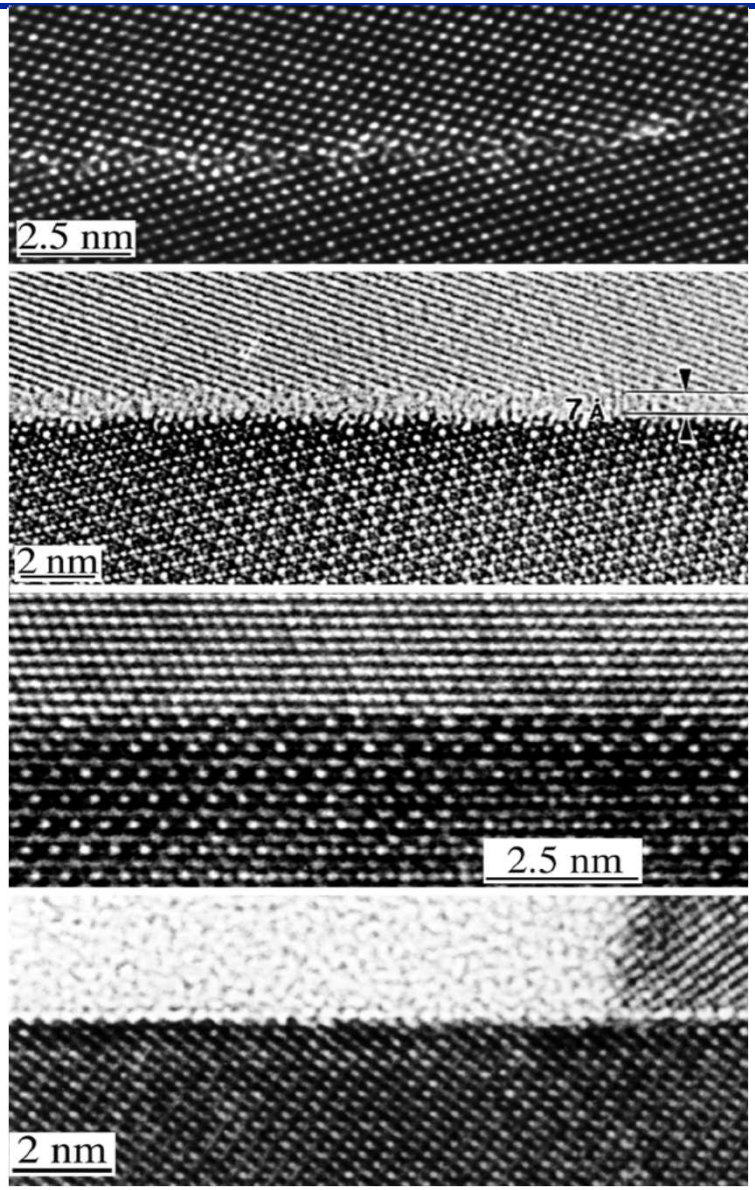
- If we form an image using multiple diffraction spots, we get a very useful interference pattern—an HREM lattice image
- Lattice images can be used to confirm crystallinity of an area
- With careful calibration, can be used to measure d-spacings and look for defects (e.g. misfit dislocations)
- Quantitative structural determination from HREM images requires detailed modeling





(From Williams and Carter)

Examples of HREM images



Ge

Si_3N_4

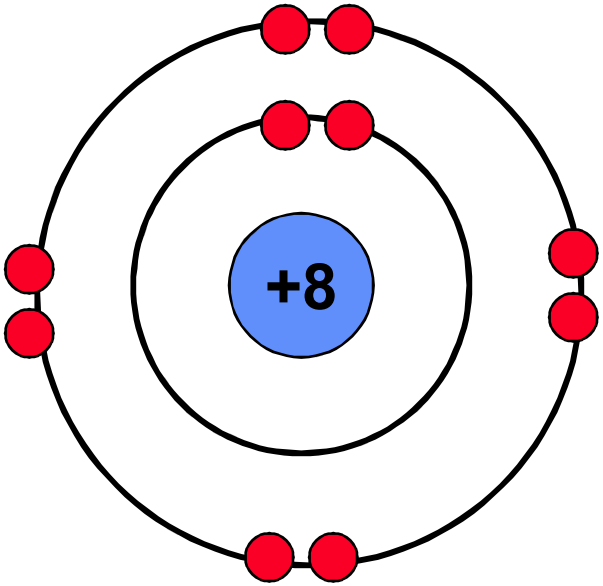
NiO/spinel

Fe_2O_3

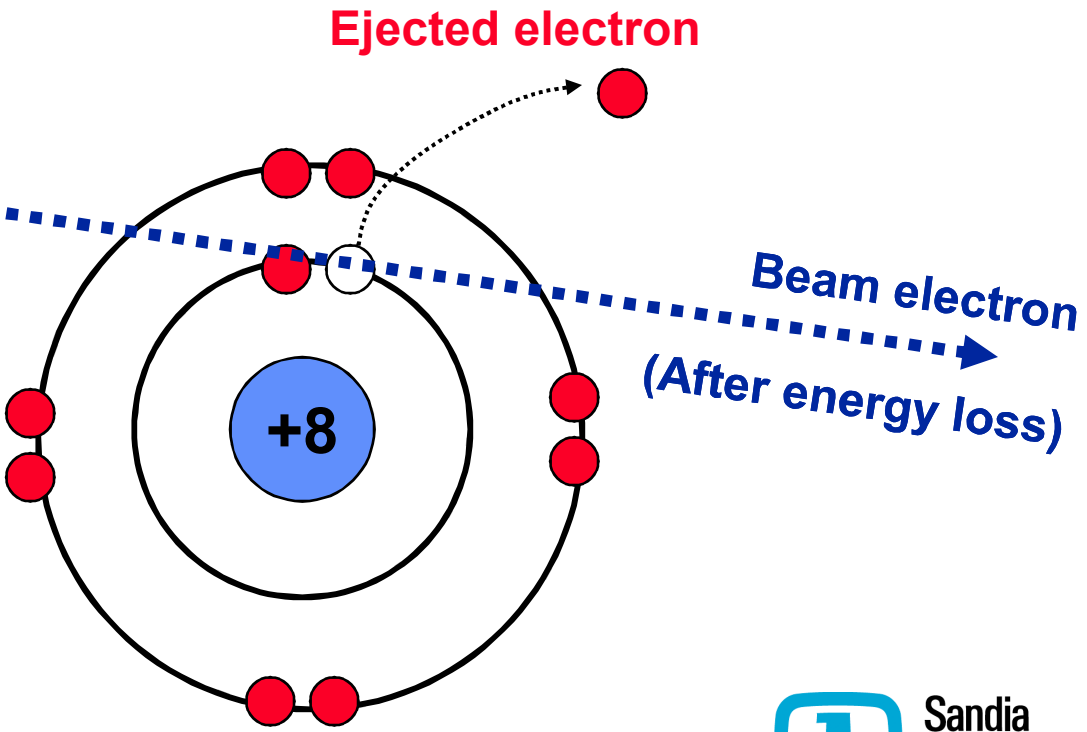
(From Williams and Carter)

Chemical analysis also possible

An atom in the solid…



…can have an inner-shell electron ejected by a beam electron



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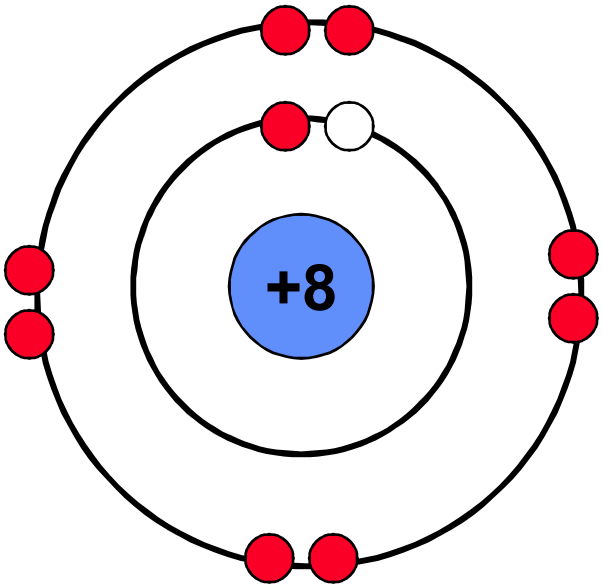
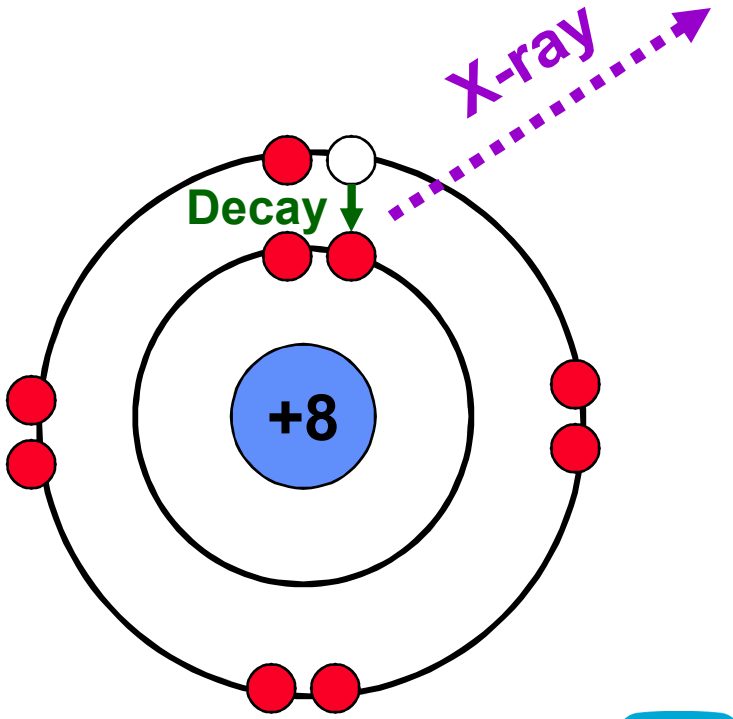
Chemical analysis also possible

This is unstable…



…and may result in X-ray generation



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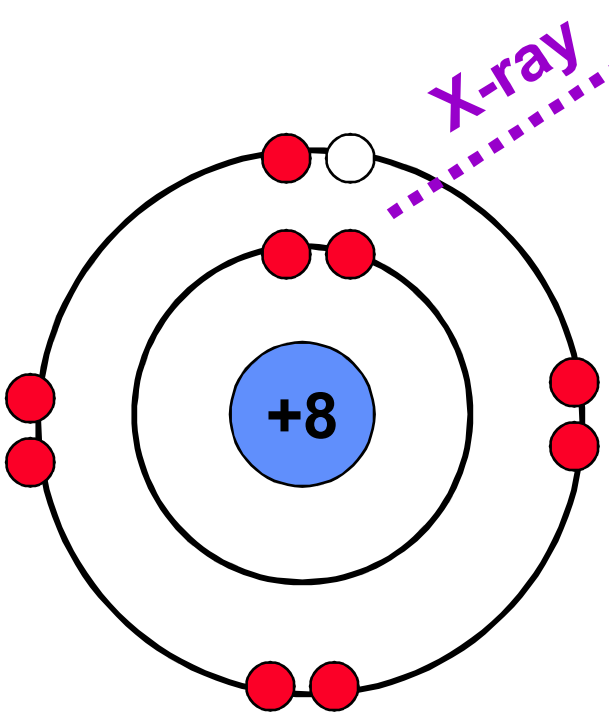
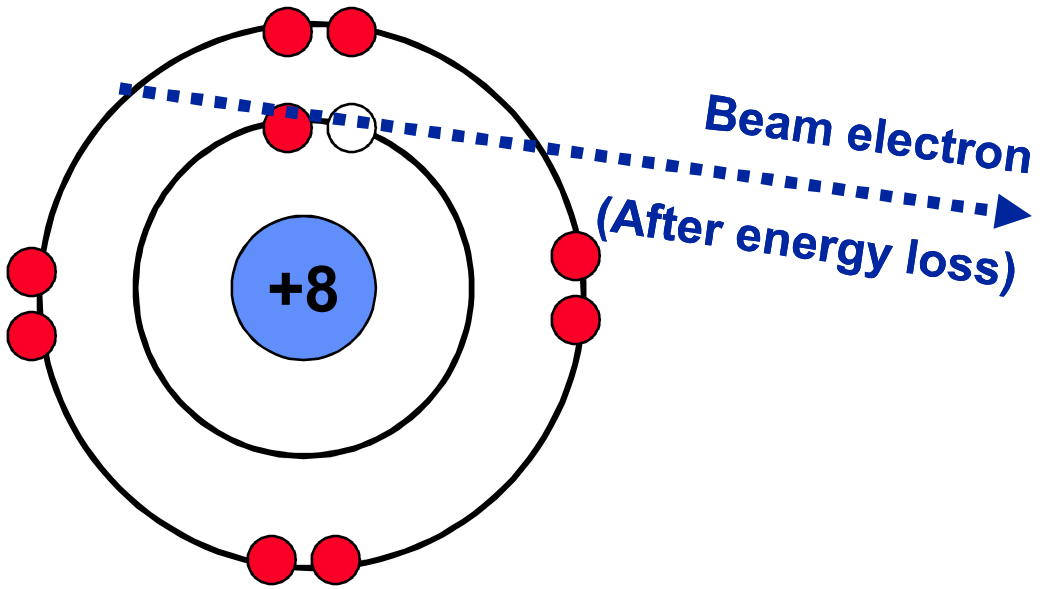
Chemical analysis: two signals to work with





Energy-dispersive X-ray spectroscopy: EDS

Electron energy loss spectroscopy: EELS

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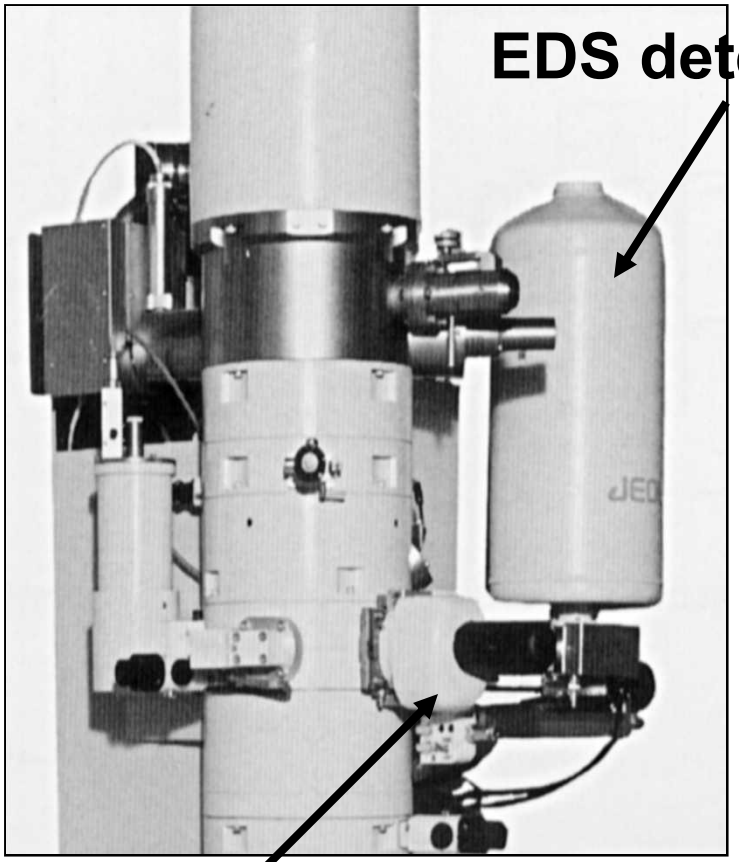
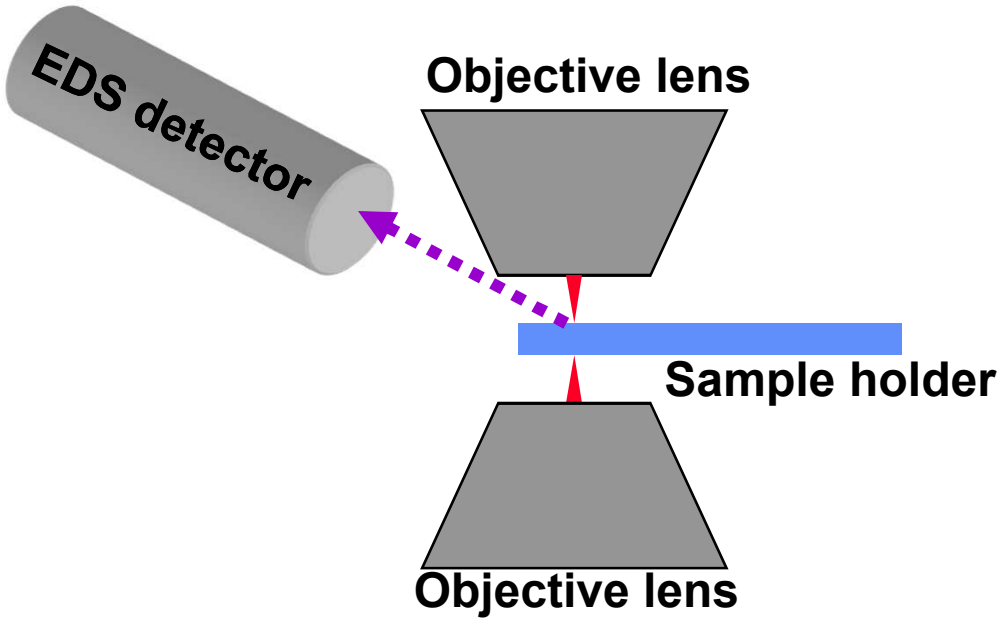
X-ray spectroscopy





The active area of the detector must fit inside the objective lens, along with the sample holder

(From Williams and Carter)

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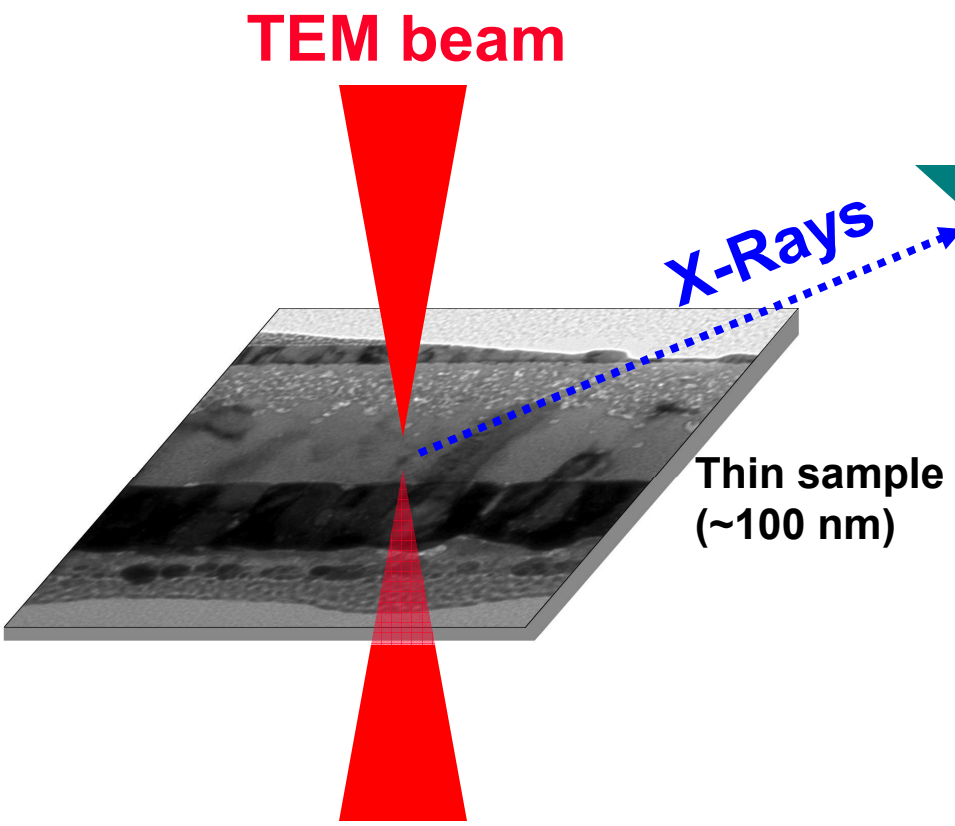
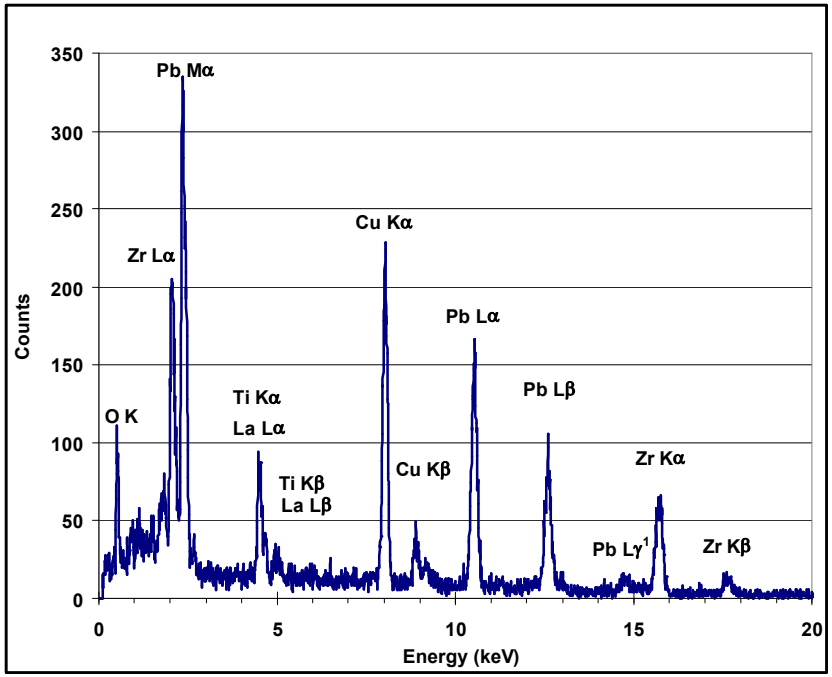
EDS allows us to qualitatively and quantitatively measure chemistry

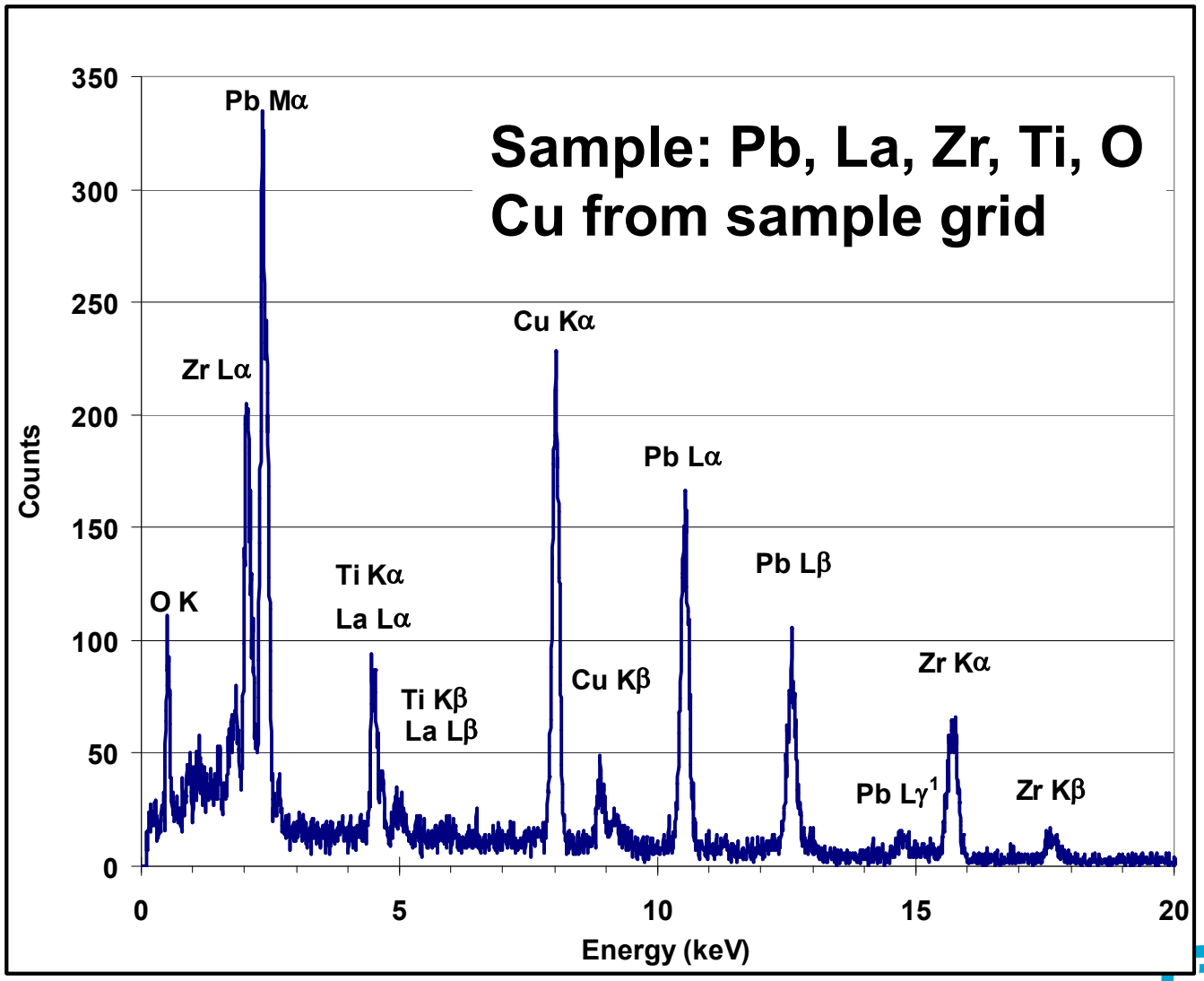


EDS detector

Data



EDS does an excellent job on heavy elements (≥Al in modern instruments)



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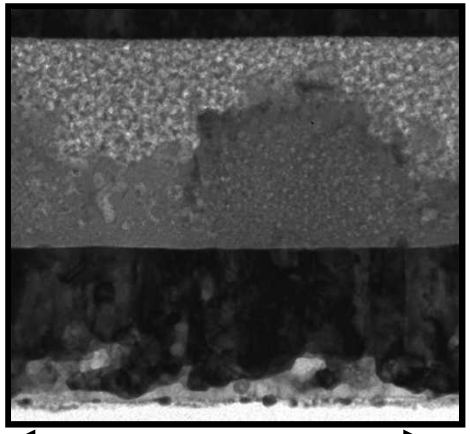
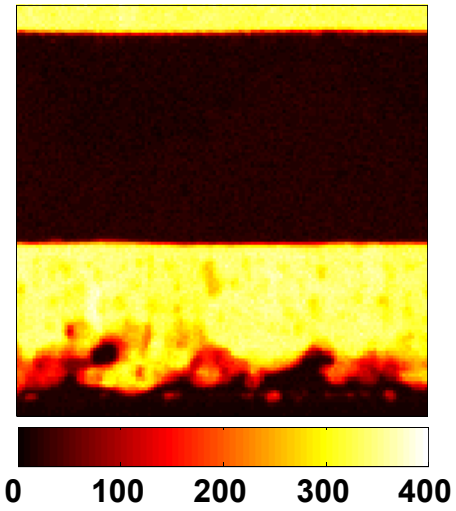
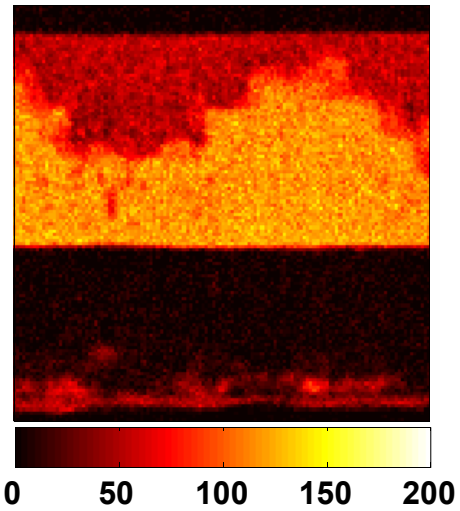
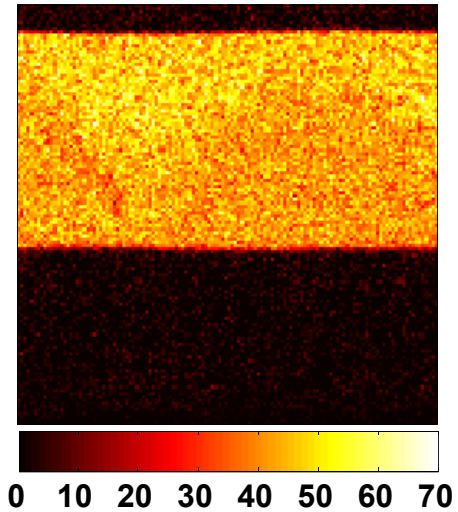
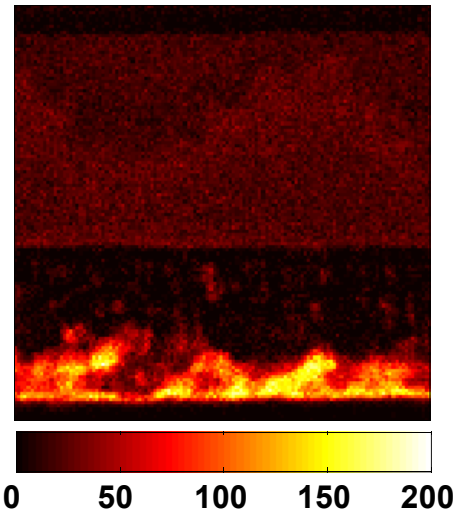
Modern instruments allow mapping of chemistry with ≈few nm resolution

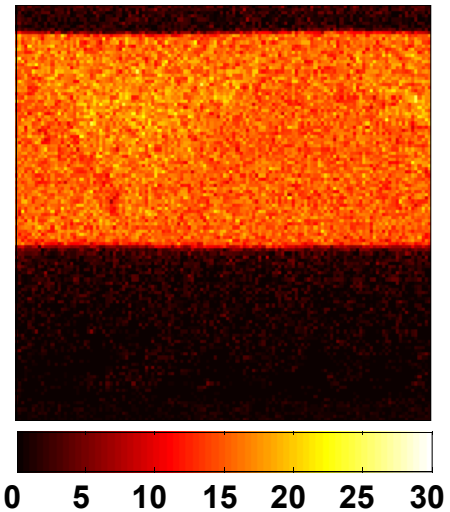




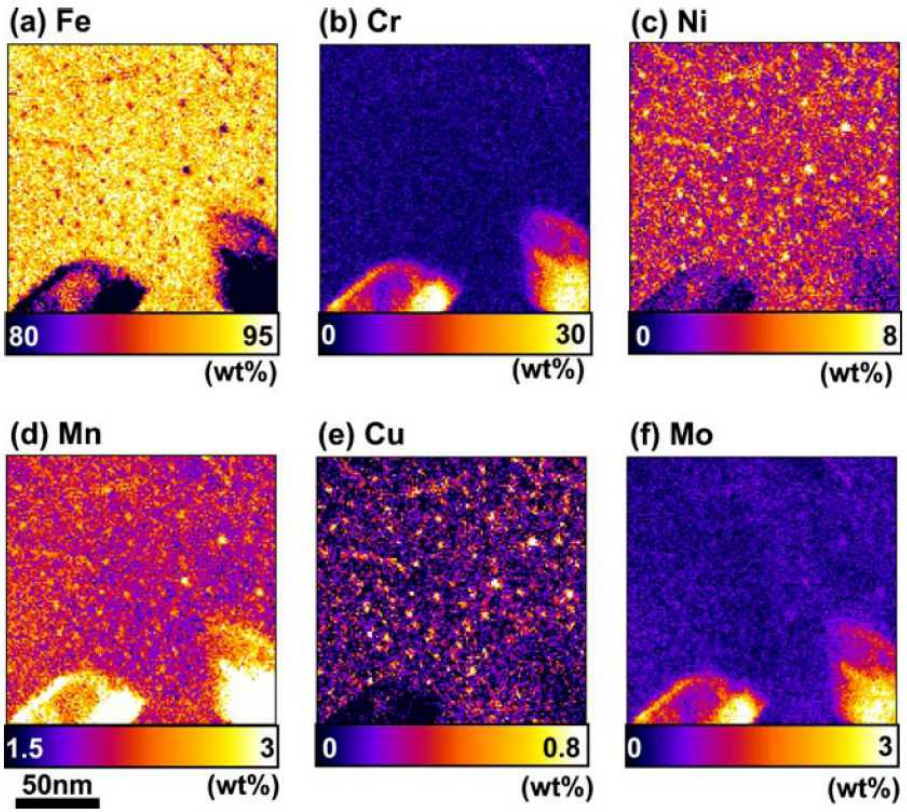




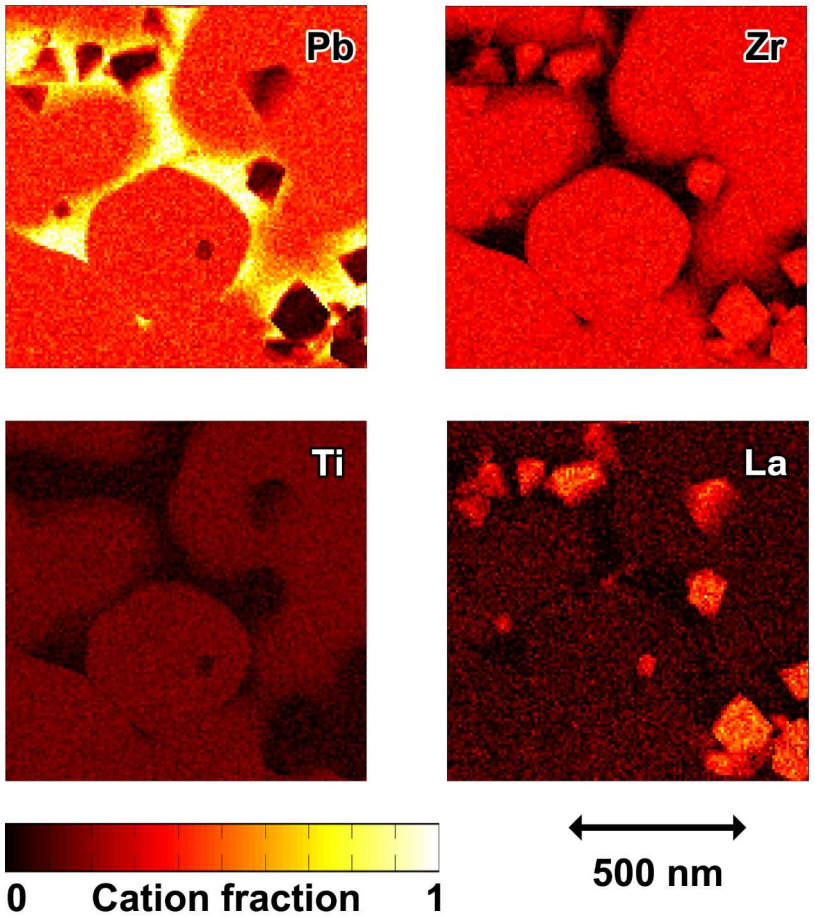




EDS: quantify chemistry at nanometer scale



Burke et al., J Mat. Sci., V41, P.4512 (2006)



Parish et al., to be published

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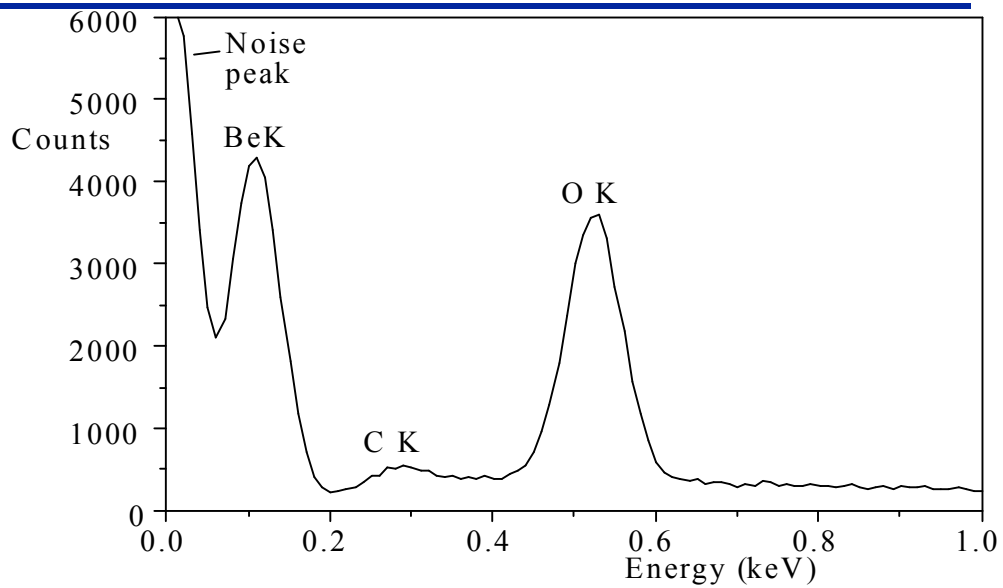
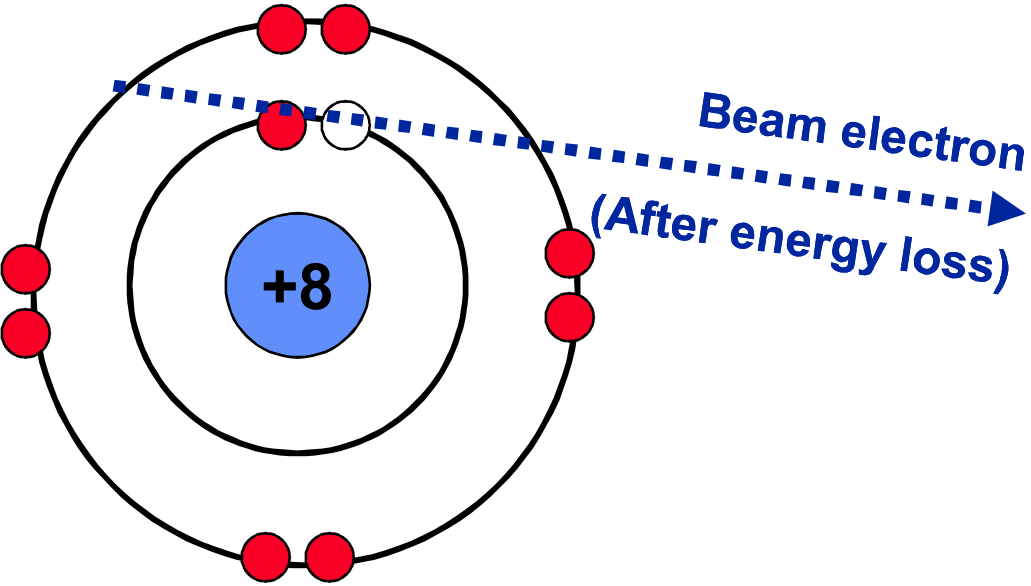
Special Consideration for “Light” Elements

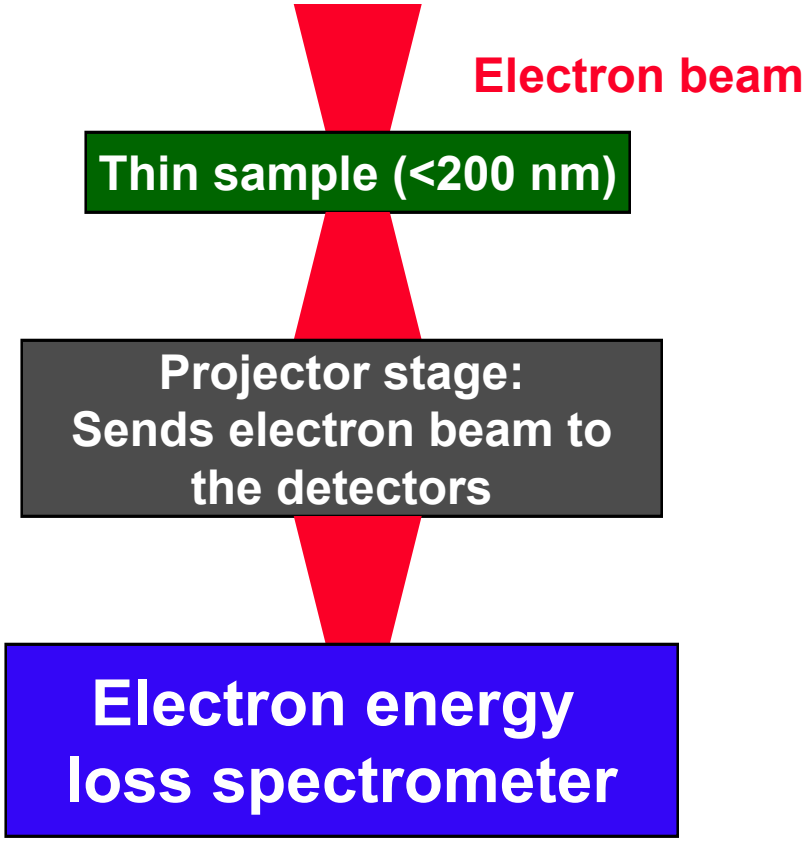


Low Z elements:

- **Don’t produce a lot of X-rays**
- **These X-rays are low in energy and can be <u>readily absorbed</u>**
  - **By the sample—what’s the thickness?**
  - **By the EDX detector window (Be, ultra-thin polymer, windowless**
- **These X-rays are often overlapped with X-rays from higher Z elements (e.g. Cr-L and O-K)**
- **Also, carbon and oxygen tend to be everywhere—did this signal come from your area of interest?**

Electron energy loss spectroscopy





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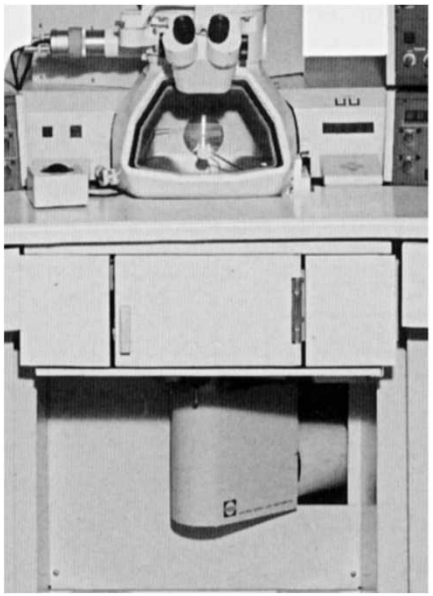
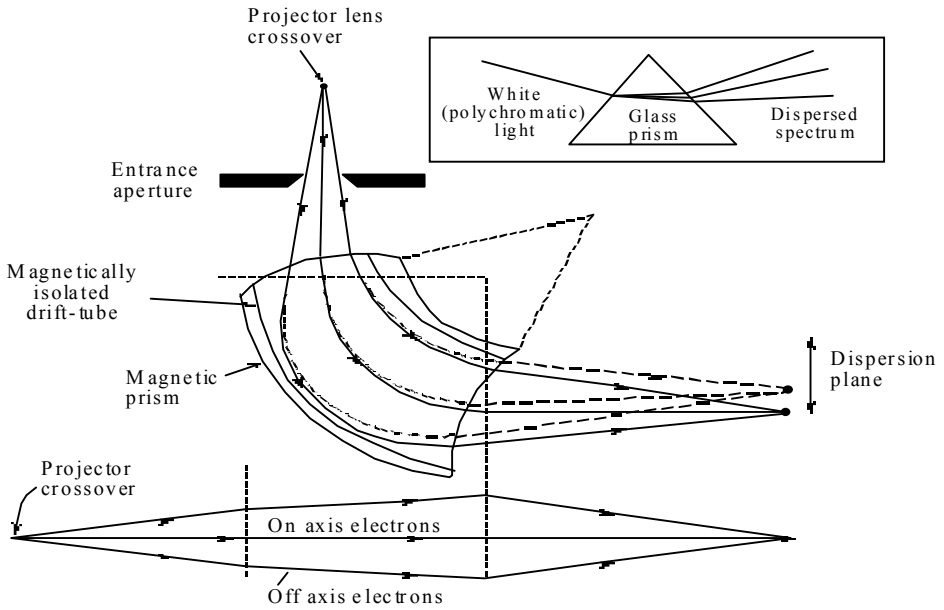
EELS with an Energy Filtered Camera “GIF”





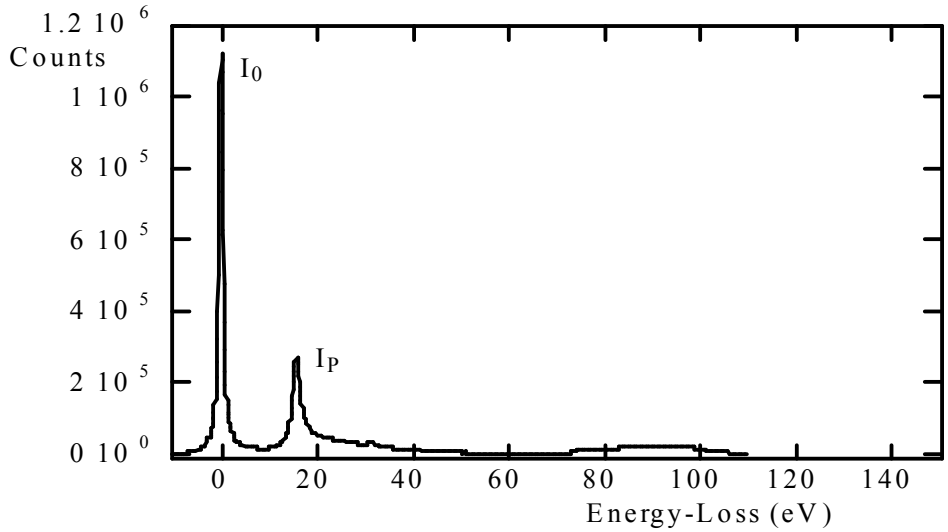
The GIF bolts onto the bottom of the standard TEM column

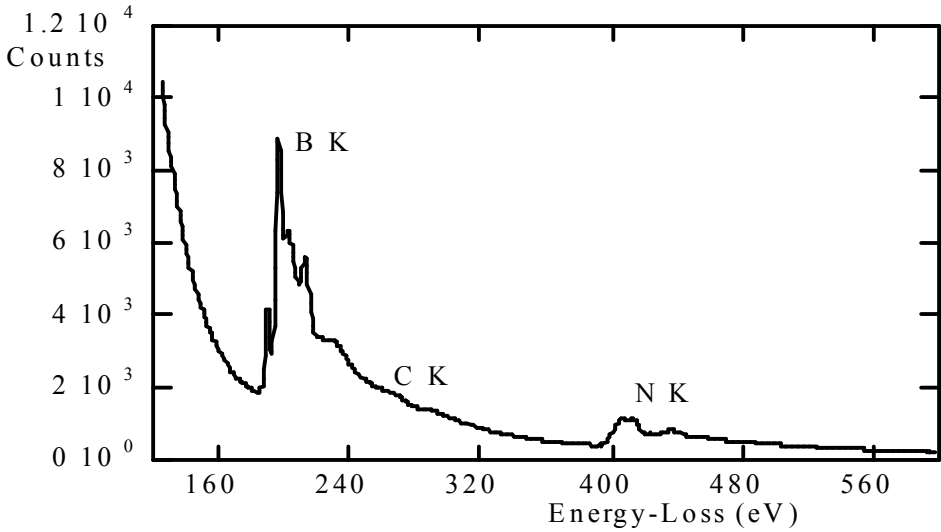
The GIF is a combination of a 90˚ magnetic prism and a set of lenses.

The “white” transmitted electron beam is dispersed onto a CCD camera as a function of energy.

(From Williams and Carter)

Why do EELS?

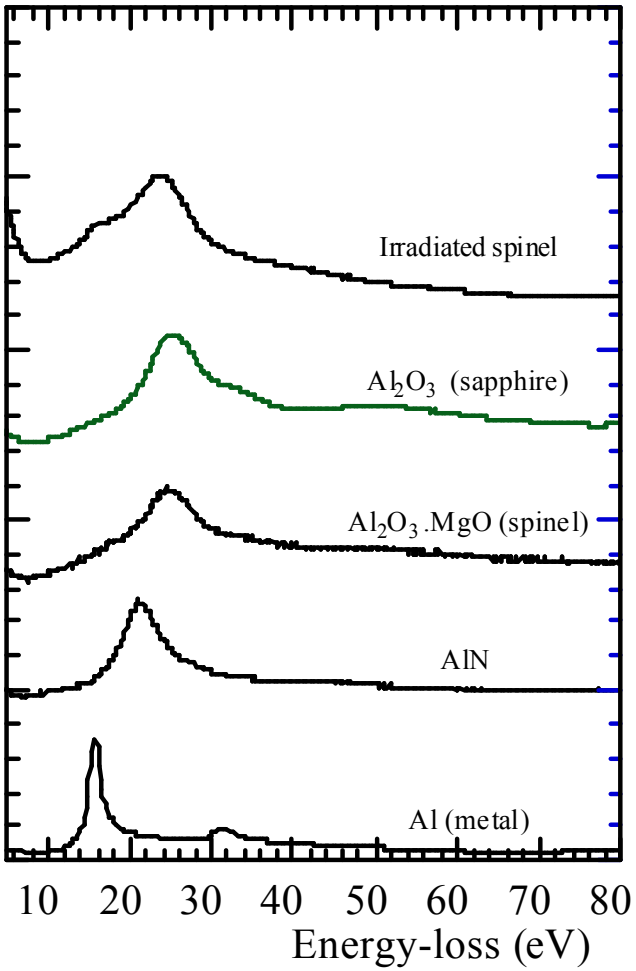


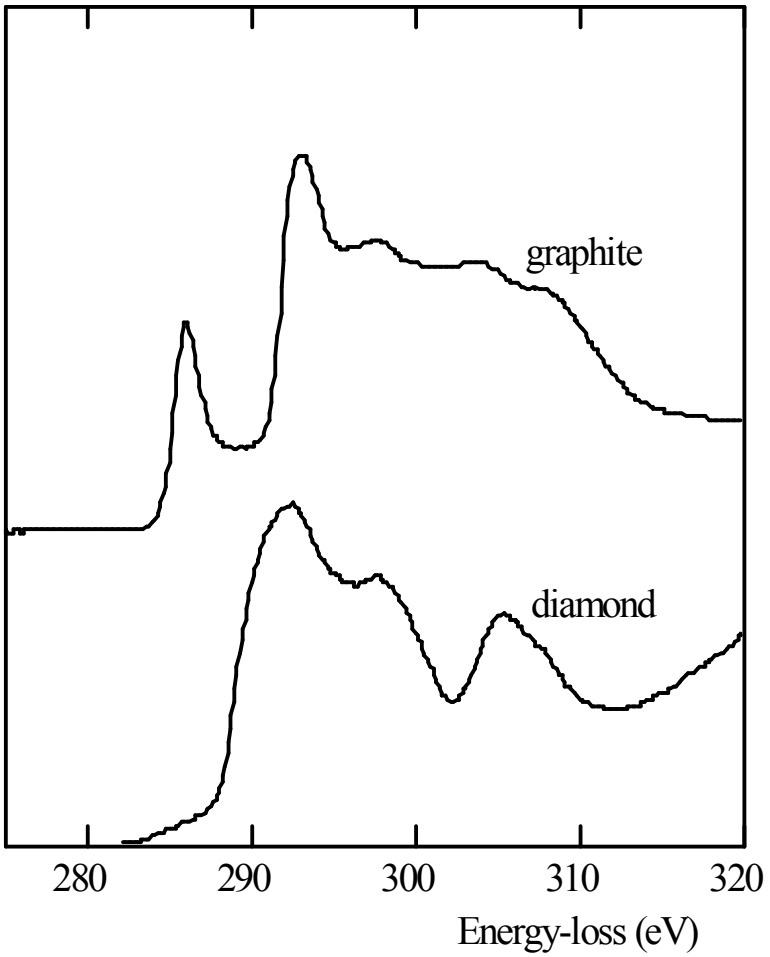


- **Sensitive to light elements**
  - **Light elements don't produce a lot of x-rays**
  - **The problem with low energy x-ray absorption is gone**
  - **Low Z elements produce low loss energy events which are inherently more intense**
- **Can be used for microanalysis**
- **Sensitive to chemical state of materials**
  - **Valence measurement**
  - **Coordination measurement**

(From Williams and Carter)

With EELS, Al is not just "Al"—sensitive to chemical environment





Able to distinguish between graphite and diamond, carbon isn't just carbon

(From Williams and Carter)

Compare: EELS to EDS

	EELS	EDS
Identify light elements	Yes	Sometimes
Identify heavy elements	Sometimes	Yes
Quantify light elements	Yes	With effort
Quantify heavy elements	Not very well	Yes
Valence, bonding, local electronic enviro nment	Yes	No
Mapping	Yes	Yes
Best spatial resolution	≈0.1 nm	≈1-2 nm
Best spectral resolution	≈0.3 eV	≥100 eV
Typical spectral range	0-2 keV	.1-20 keV
Artifacts	Many	Many

Summary: TEM

TEM allows imaging, crystallography, and analysis at the nanometer scale

TEMs cost millions of dollars – use TEM when SEM, XRD, etc., are too coarse to answer your question

Many signals can be measured from the same sample area – synergistic information

Sample preparation is the slowest and most difficult step