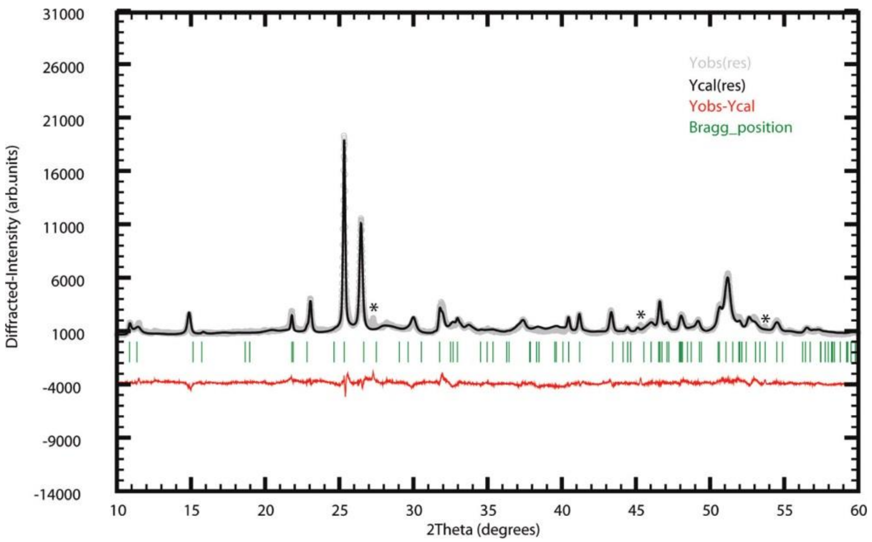
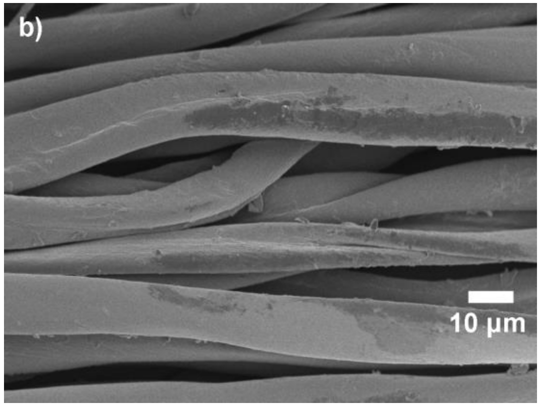
# Lecture 7:
# X-Ray techniques and microscopies

- Miller indices
- Overview of diffraction techniques
- Powder X-Ray Diffraction (XRD)
  - Powder pattern databases
  - Phase idenfication with powder XRD
- Microscopic methods
  - Scanning Electron Microscopy (SEM)
  - Transmission Electron Microscopy (TEM)




Figures: AJK

# Structure of crystalline solids

## 1. Local structure / Defects

Spectroscopy
- IR, Raman
- NMR, ESR
- X-Ray spectroscopies
- Electron spectroscopies

## 2. Unit cell (average crystal structure)

Diffraction techniques
- X-Ray diffraction (XRD)
- Neutron diffraction
- Electron diffraction

## 3. Nanostructure

Microscopy and diffraction
- Transmission electron microscopy
- Scanning electron microscopy
- X-Ray diffraction (particle size)
- Pair distribution function analysis

## 4. Microstructure (grains, grain boundaries, surfaces)

- Scanning electron microscopy
- X-Ray diffraction (particle size)
- X-Ray tomography
- Elemental analysis

Ref: West p. 230

# Miller indices

# Miller indices (1)

See also [Solid State Chemistry Wiki]

- A very fundamental concept in XRD is the ***lattice plane***.
  - Introduced with Bragg's law of diffraction
- Lattice planes are labelled by assigning three numbers known as ***Miller indices***
- In the figure, the origin of the unit cell is at point 0
- The figure shows two planes which are parallel and pass through the unit cell
- A third plane in this set passes through the origin
- Each of these planes continues out to the surface of the crystal and cuts through many more unit cells
- There are many more planes parallel to the two shown, but they do not pass through this particular unit cell

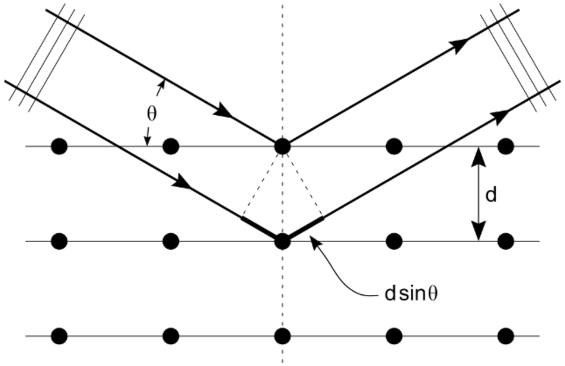
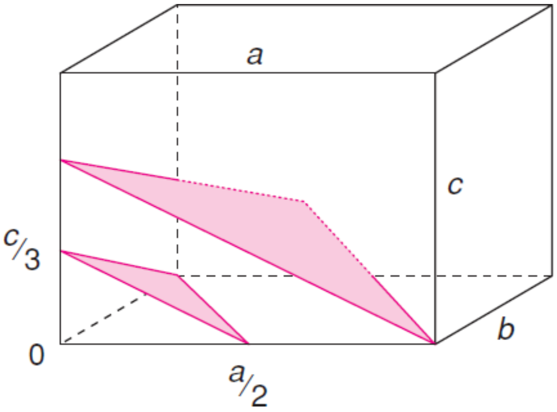



Figure: Wikipedia



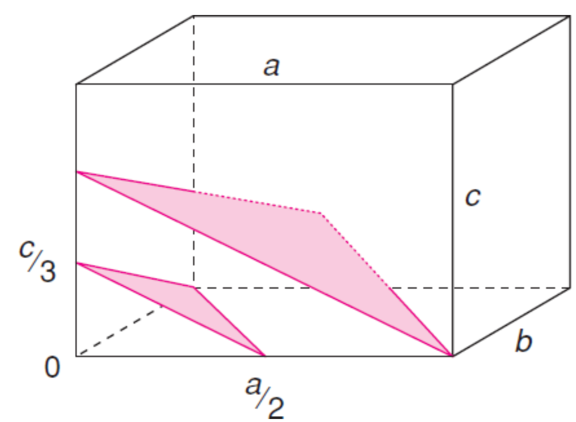

**VESTA has excellent tools for the visualization of lattice planes!**
**See MyCourses -> Software -> VESTA documentation -> Advanced**

Ref: West p. 16

# Miller indices (2)

In order to assign Miller indices to a set of planes, there are four stages:

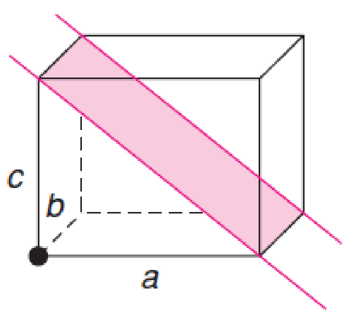
1. Identify the unit cell, choose the origin and label the axes *a*, *b*, *c* and angles *α* (between *b* and *c*), *β* (between *a* and *c*) and *γ* (between *a* and *b*).
2. For a particular set of lattice planes, identify the plane which is adjacent to the one that passes through the origin.
3. Find the intersection of this plane on the three axes of the cell and write these intersections as fractions of the cell edges.
   - The plane in the figure cuts *x*-axis at *a*/2, *y*-axis at *b* and *z*-axis at *c*/3 -> the fractional intersections are 1/2, 1, 1/3.
4. Take reciprocals of these fractions and write the three numbers in parentheses; this gives (213). These three integers, (213), are the Miller indices of the plane and all other planes parallel to it (separated by the same *d*-spacing).



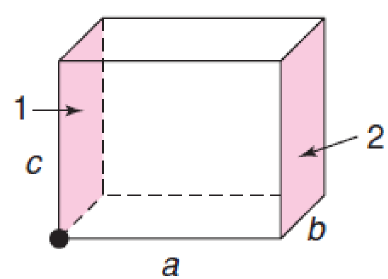

Ref: West p. 16

# Miller indices (3)

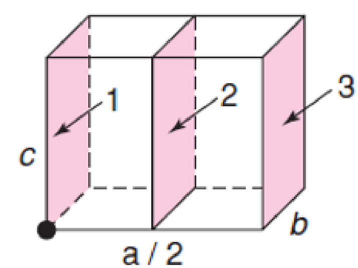
- In (a), the shaded plane cuts *x*, *y* and *z* at 1*a*, ∞*b* and 1*c*, that is, the plane is parallel to *b*. Taking reciprocals of 1, ∞, and 1 gives (101) for the Miller indices
  - Miller index of 0 means that the plane is parallel to that axis
- In (b), the planes of interest comprise opposite faces of the unit cell. We cannot determine directly the indices of plane 1 as it passes through the origin. Plane 2 has intercepts of 1*a*, ∞*b* and ∞*c* and Miller indices of (100)
- (c) has twice as many planes as in (b). To find the Miller indices, consider plane 2, which is the one that is closest to the origin but without passing through it.
  - Intercepts are 1/2, ∞ and ∞ -> the Miller indices are (200).
  - Miller index of 2 -> The plane cuts the relevant axis at half the cell edge.




(a) (101)




(b) (100)




(c) (200)

Ref: West p. 16

# Miller indices and directions

- The general symbol for Miller indices is (*hkl*).
- **Brackets** {} are used to indicate sets of planes that are equivalent
  - Planes (100), (010), and (001) are equivalent in cubic crystals → {100}.
- **Square brackets** [] are used to denote **direction** [*hkl*]
  - For cubic systems, perpendicular to the (*hkl*) plane of the same indices
  - This is only sometimes true in non-cubic systems
- **Angle brackets** <> are used to indicate sets of directions which are equivalent
  - [100], [010], and [001] are equivalent in cubic crystals → <100>.
- Interactive VESTA models of the planes below available in MyCourses -> Materials -> Data files for lectures -> Lecture 07

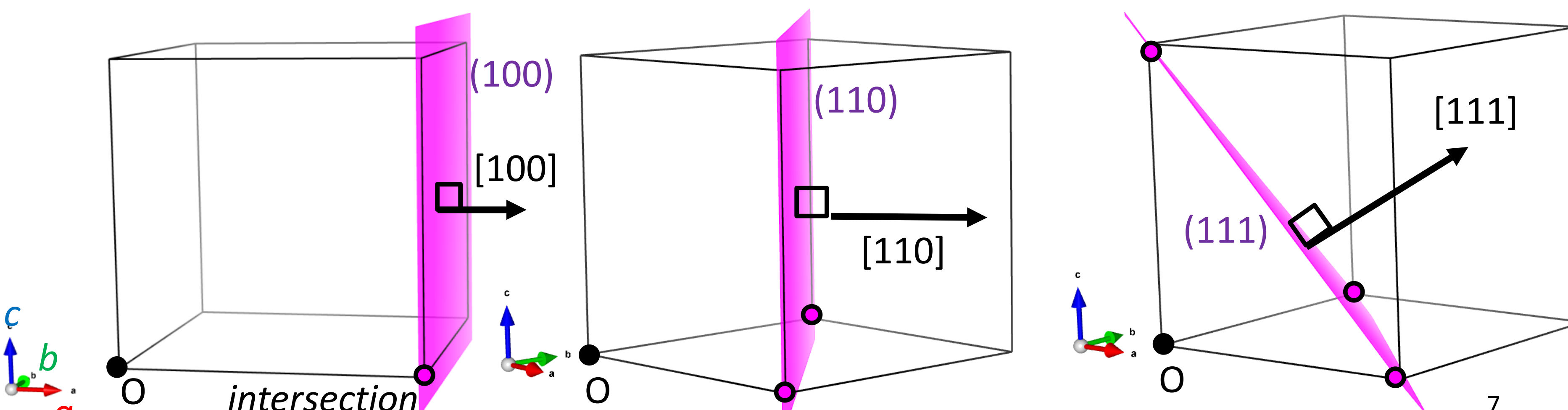
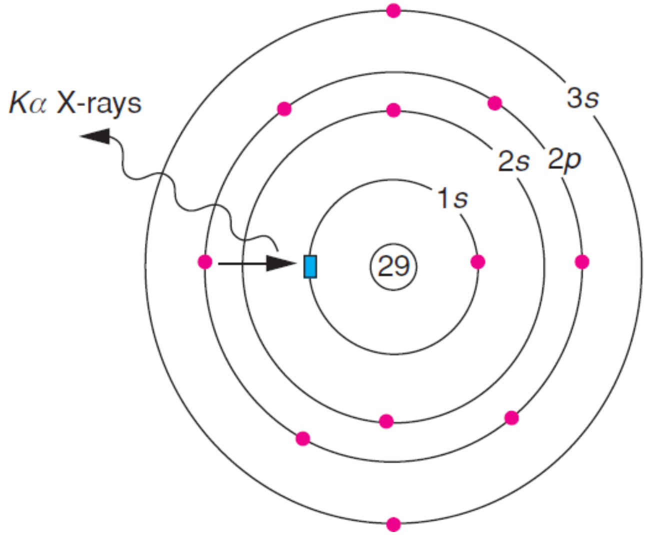


Figure: AJK

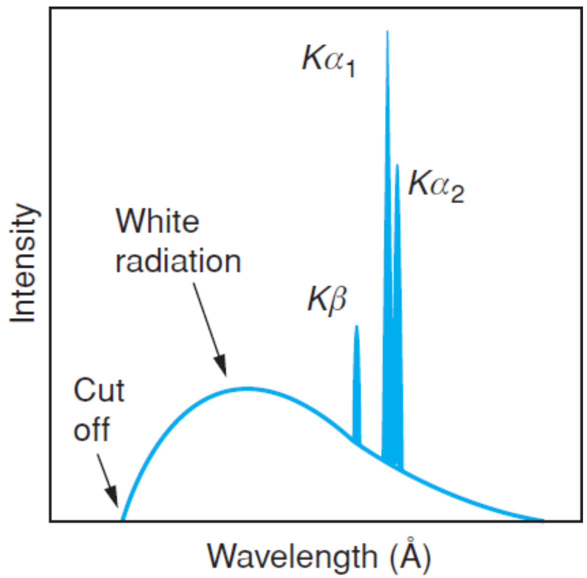
# Diffraction techniques

# Generation of X-rays

- X-rays are produced with X-ray tubes (vacuum tubes converting electricity into X-rays).
- In an X-ray tube, high-energy charged particles, such as electrons accelerated through a voltages of 60 keV, collide with matter.
- For X-ray diffraction experiments monochromatic X-rays are typically used.




Generation of **Cu Kα X-rays**. A 1s electron is ionised, a 2p electron falls into the empty 1s level (blue) and the excess energy is released as X-rays.




Full X-ray emission spectrum of Cu. Particular wavelength, for example **Cu Kα** can be isolated with a monochromator and then used for X-ray diffraction.



Ref: West p. 233

# Bragg's law

- Consider crystals as built up from planes acting as semi-transparent mirrors
- ***Bragg's law***: $2d \sin \theta = n\lambda$, where $n$ = positive integer and $\lambda$ = wavelength
- When **BL** is satisfied, the reflected beams are in-phase and ***interfere constructively***, giving rise to a ***diffraction pattern***, that can be used to solve the crystal structure
- For some simple crystal structures, the planes also correspond to layers of atoms, but this is not generally the case (they are a concept, not physical reality)!

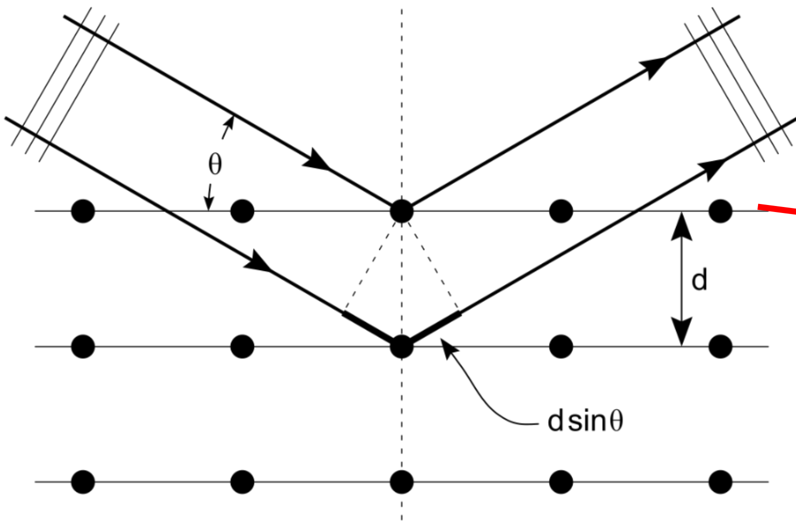



Figure: Wikipedia

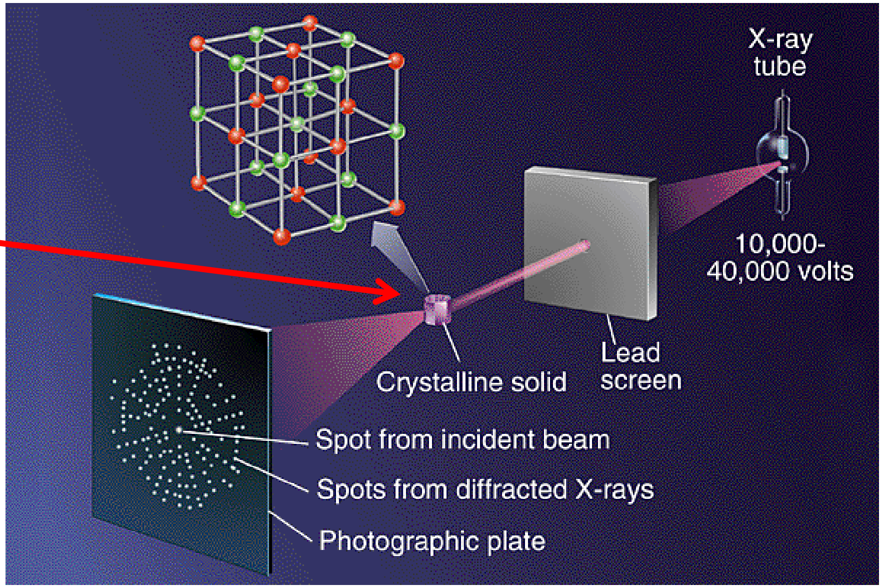
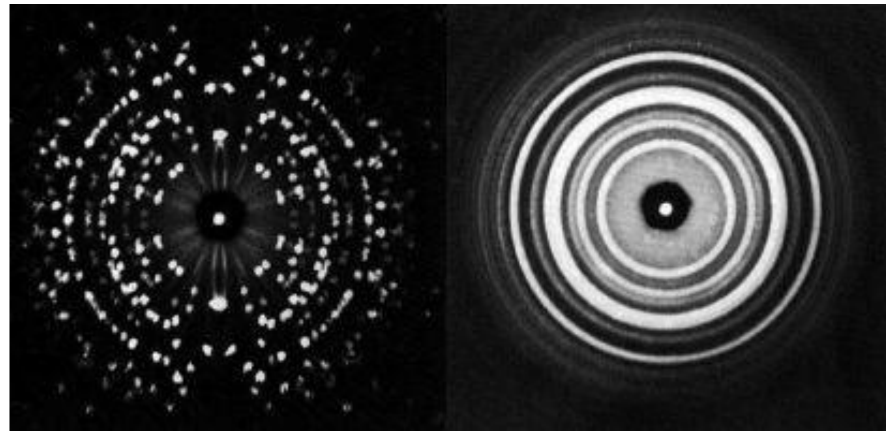


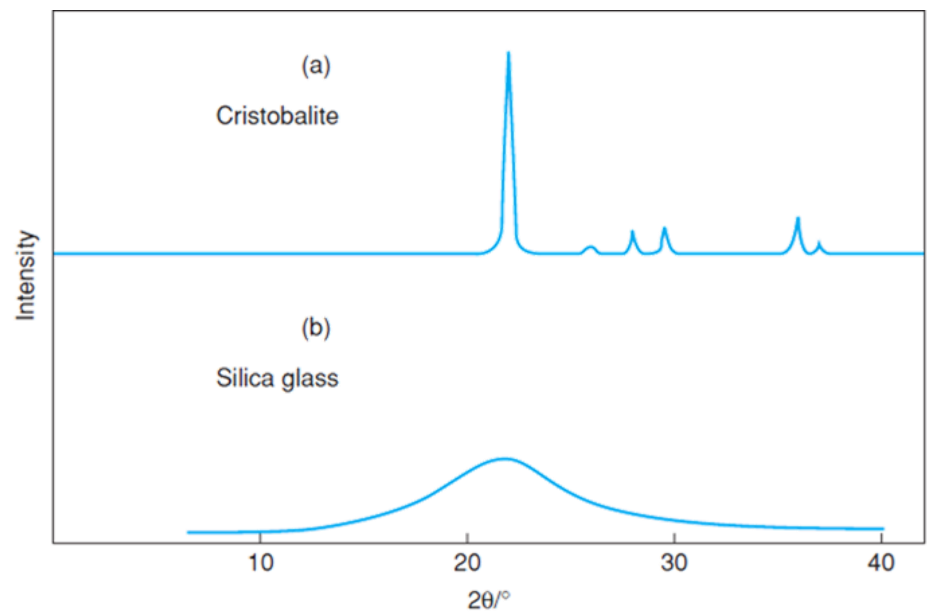

Figure: http://www.scienceiscool.org/solids/intro.html (dead link)

# Single crystal vs. powder X-ray

- The figure shows X-ray diffraction pattern of aluminum single crystal (left) and aluminum powder (right)
- Polycrystalline powder sample has random orientation of crystallites
- 1D summation of 3D diffraction process! [See animation](#).
- The crystal structure might be deduced from a powder pattern with ***Rietveld*** refinement (typically requires a good model structure)
- The figure shows Powder X-ray diffraction pattern of crystalline (top) and amorphous (bottom) $SiO_2$

Figure: Susan Lehman / physics.wooster.edu

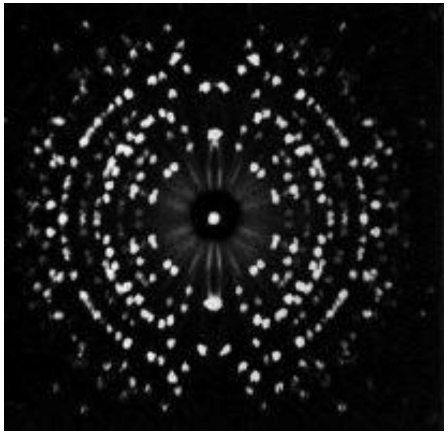




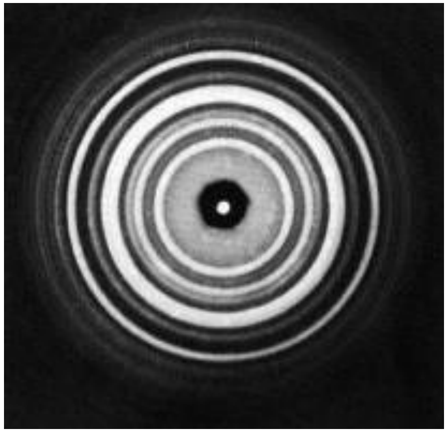

Ref: West p. 245

# Structure determination from single-crystal and powder XRD

- X-ray diffraction has been used for over a century in two main areas
  - **Structure determination** of crystalline materials (single crystal and powder XRD)
  - **Fingerprint identification** of crystalline materials (powder XRD)
- Here the focus is on the fingerprint identification of materials with the help of powder XRD
  - Structure determination is discussed in more detail on the course **Crystallography Basics and Structural Characterization** (CHEM-E4205)
- For thin films, two specialized X-Ray techniques are used for structure determination (links lead to SSC Wiki)
  - Grazing incidence X-Ray diffraction
  - X-Ray Reflection (scattering, not diffraction)



X-ray diffraction pattern of aluminum single crystal



X-ray diffraction pattern of aluminum powder

Figures: Susan Lehman / physics.wooster.edu

# Diffractometers

- First diffractometer was built by Max von Laue in 1912
- Nowadays, numerous different types of diffractometers used for various applications
- Table-top XRD
  - Powder XRD phase identification (very useful in e.g. process control)
  - Small-molecule single-crystal XRD
- Laboratory XRD (single-crystal / powder / thin film)
  - Structures of single-crystals are rather routinely solved
  - Structures of polycrystalline powders can be solved with **Rietveld refinement**
- Sometimes **synchrotron radiation** is required to obtain good enough powder data



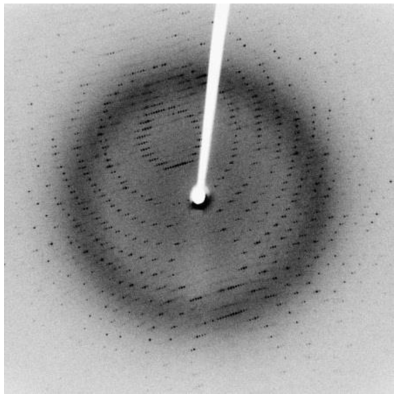
# Synchrotron radiation

- Synchrotrons are particle accelerators that generate very bright X-ray beams
  - High intensity photon beam allows rapid experiments or the use of weakly scattering crystals (https://en.wikipedia.org/wiki/Synchrotron_radiation)
  - High brilliance from highly collimated photon beam
- Large international facilities. For example, ESRF annual figures: budget ~100 M€, ~8000 visitors and ~2000 experiments. Particularly important for biomolecules.

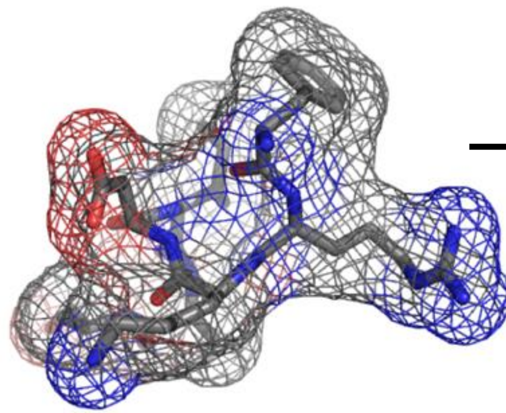
European Synchrotron Radiation Facility (ESRF) in Grenoble

Figure: Wikipedia

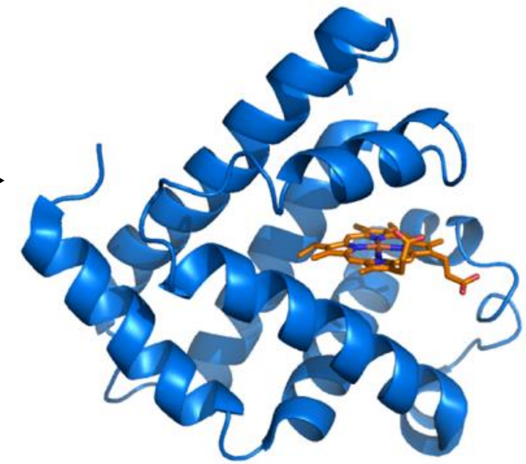
# Structure solution from XRD



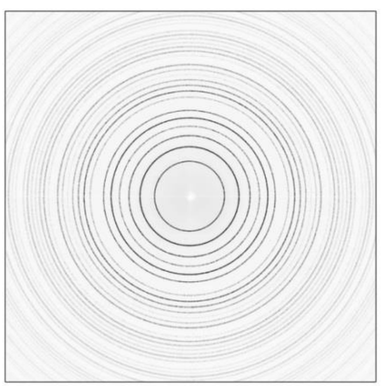
Single crystal diffraction pattern



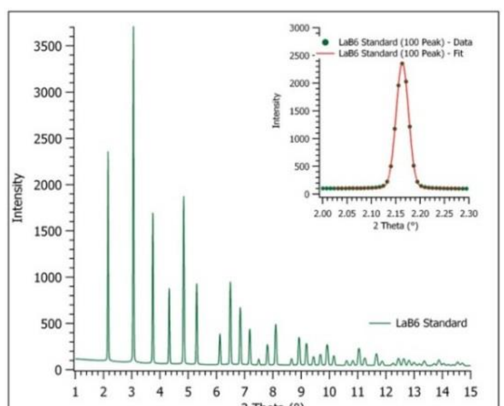
Electron density map



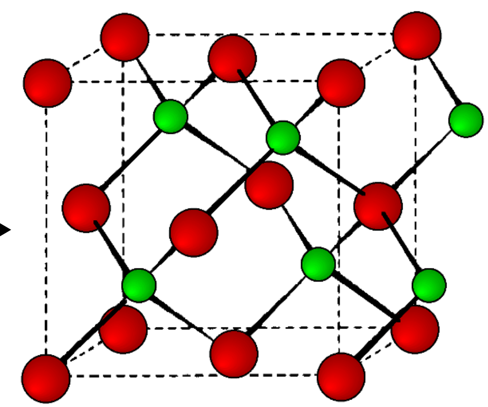
Structural model



Powder diffraction pattern




Rietveld refinement



Structural model

# Neutron Diffraction

- The sample is bombarded with neutrons instead of X-Rays
- Similar to synchrotron XRD, the facilities are very expensive and international collaboration is required
- Neutron beams are usually of low intensity, so large sample sizes are required (at least 1 $mm^3$)
- Typically polycrystalline samples
- Useful for locating light atoms, especially **hydrogens** (not normally possible in XRD)
- Very important application: magnetic structure of materials

Figure: John Loveday

ISIS neutron (and muon) source in Oxford, UK

Ref: West p. 266

# Magnetic structure analysis

- Neutrons possess a magnetic dipole moment and interact with unpaired electrons
- Figure shows neutron diffraction investigation of antiferromagnetic MnO below and above the magnetic ordering temperature (**116 K**)

Additional reflections from **magnetic** superstructure

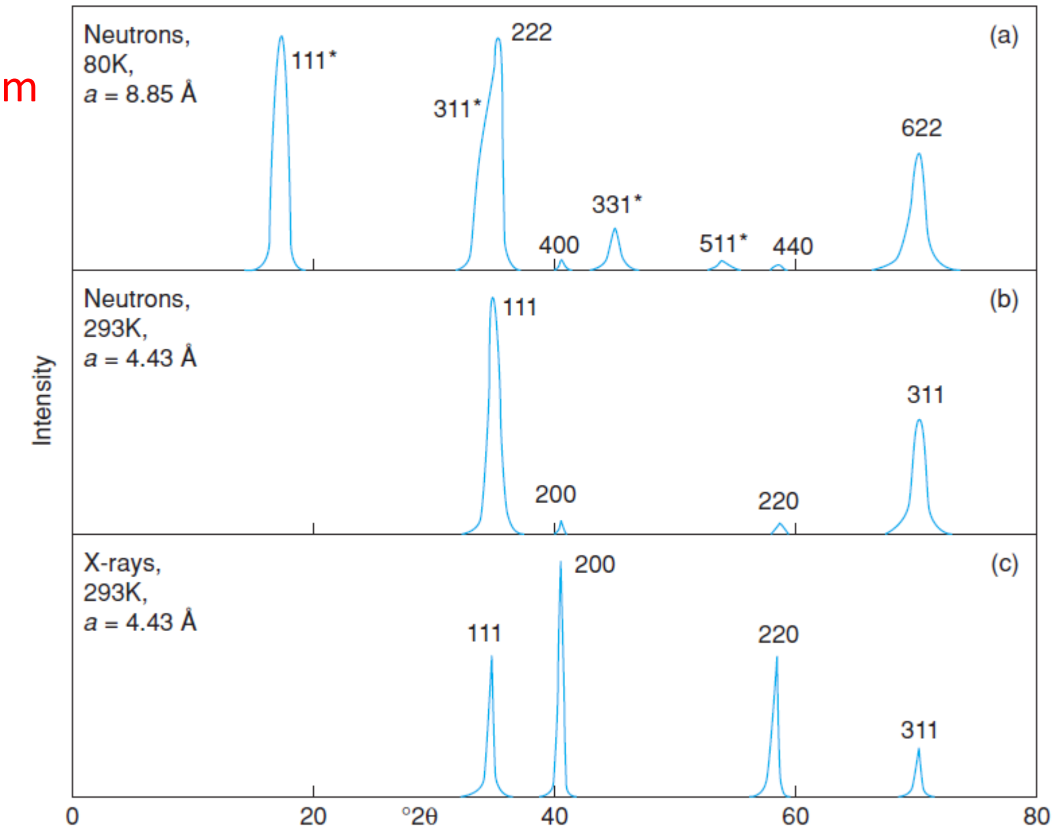


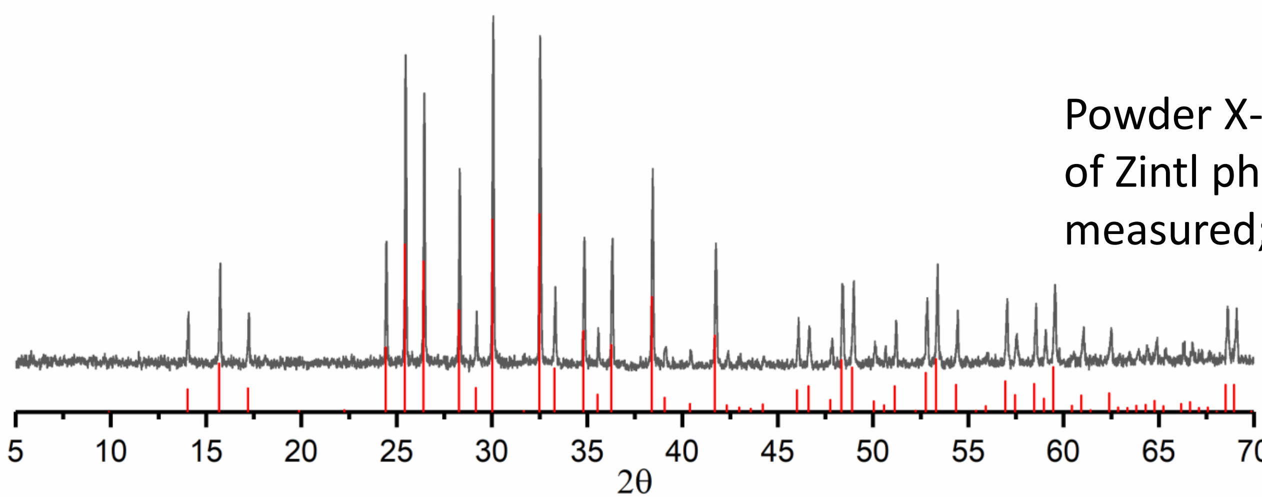

*Figure 5.26* **Schematic neutron and powder XRD patterns for MnO for λ = 1.542 Å. Peaks are assigned Miller indices for the cubic unit cells given. Neutron data adapted from Shull, Strauser and Wollan, Phys. Rev., 83, 333, © 1951 American Physical Society.**

Ref: West p. 269

# Phase identification with XRD

# Phase identification with XRD

- Powder XRD is a very powerful technique for the identification of solid phases
- Each crystalline phase has a characteristic powder XRD pattern which can be used as a fingerprint for identification purposes
  - Powder XRD patterns can be simulated if the crystal structure is known
- The two variables in a powder pattern are
  - **Peak position**, i.e. *d*-spacing, which can be measured very accurately
  - **Intensity**, which can be measured either qualitatively or quantitatively
- The normal practice in using XRD patterns for identification purposes is to pay **most attention to the *d*-spacings** and check that the intensities are roughly correct
- See [animations at DoITPoMS](animations at DoITPoMS).




Powder X-ray diffractogram of Zintl phase $K_4Si_4$ (gray: measured; red: simulated).

Figure: Lorenz Schiegerl / TUM

# Powder pattern matching

See [Solid State Chemistry Wiki]
for further databases

- Powder Diffraction File (PDF)
  – 350 000+ powder patterns
  – Expensive licences, normally fixed to to a single computer
  – Pattern matching software bundled with diffractometers
- Powder pattern matching is also possible with Crystallography Open Database
  – See MyCourses -> Databases -> Full Profile Search Match (Powder COD)
- VESTA can simulate XRD powder patterns
  – See MyCourses -> Software -> VESTA documentation

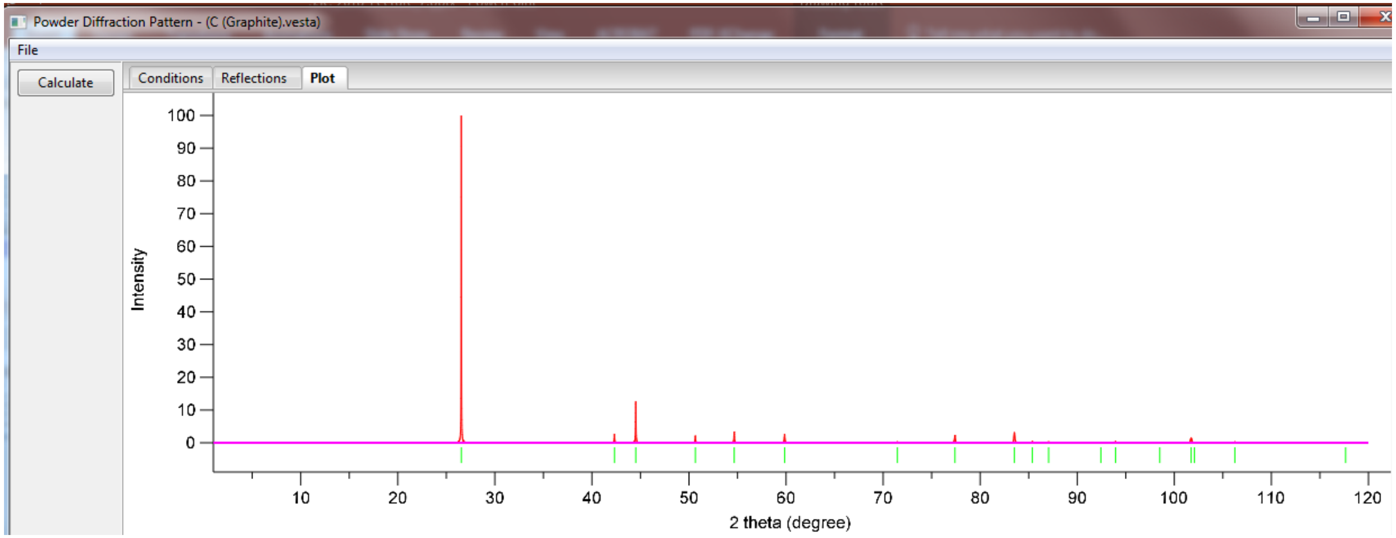
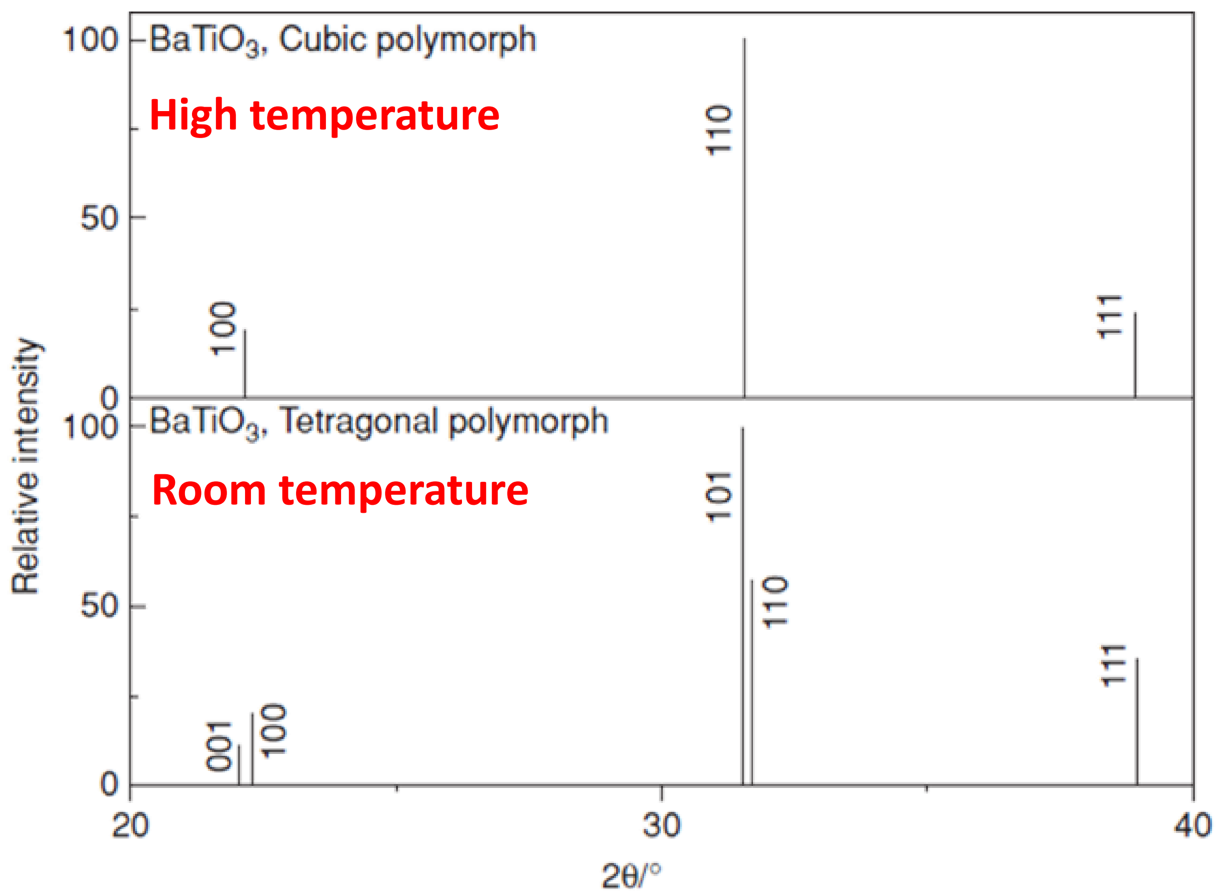
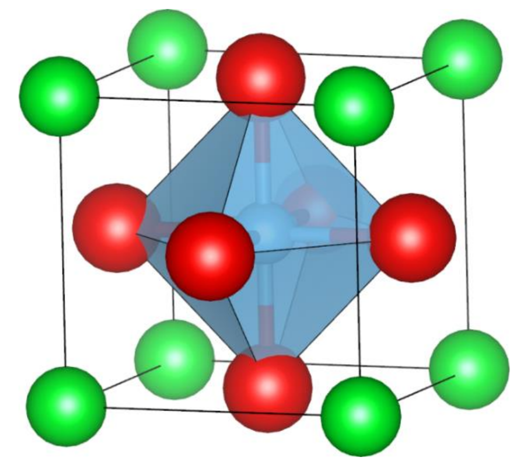



Figure: AJK

# Following phase transitions with powder XRD

$$\text{rhombohedral} \xrightarrow{-110^\circ C} \text{orthorhombic} \xrightarrow{28^\circ C} \text{tetragonal} \xrightarrow{125^\circ C} \text{cubic} \xrightarrow{1470^\circ C} \text{hexagonal}$$



$BaTiO_3$ perovskite

# Microscopic characterization methods

# Microscopic characterization methods

- With optical microscopes, particles down to a few micrometres in diameter may be seen under high magnification
- The lower limit is reached when the particle size approaches the wavelength of visible light, 0.4–0.7 μm
- For submicron-sized particles, it is essential to use **electron microscopy**
  - Features as small as a few Å across can be imaged readily

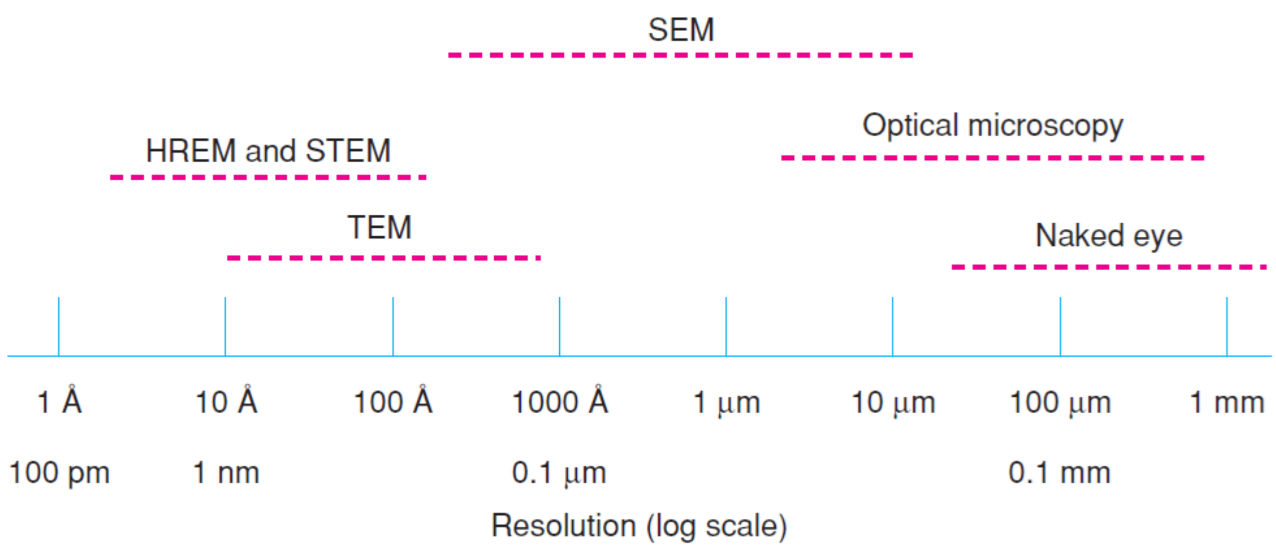



*Figure 6.4 Working ranges of various techniques used for viewing solids. TEM = transmission electron microscopy; HREM = high-resolution electron microscopy; SEM = scanning electron microscopy.*



Ref: West p. 331

# Scanning Electron Microscopy

See [Solid State Chemistry Wiki]

- In SEM, electrons from the electron gun, accelerated through 5–50 keV, are focused to a small spot, 50–500 Å in diameter, on the sample surface
- Usually, detection of **secondary electrons**
- The main application of SEM is for surveying materials under high magnification and providing information on sizes, shapes and compositions as seen from solid surfaces

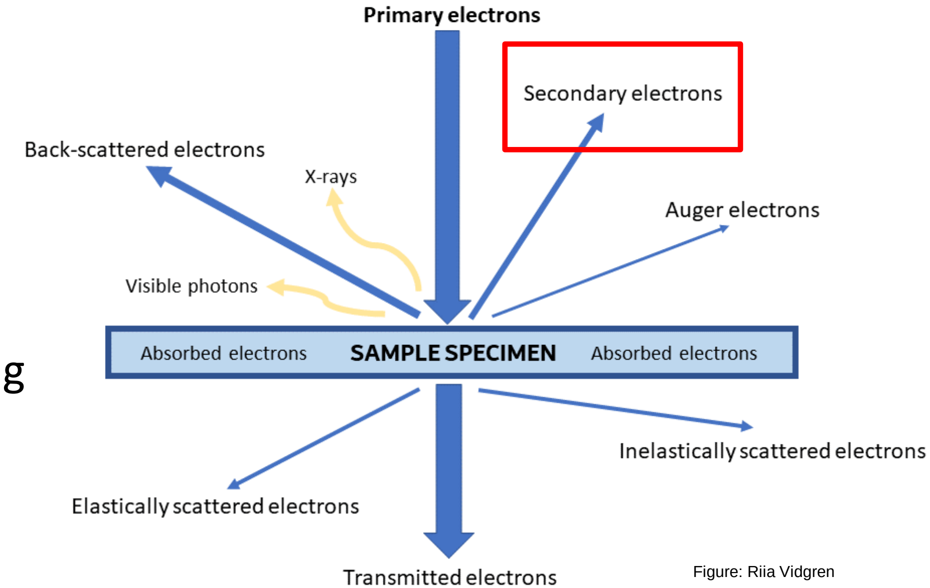



Figure: Riia Vidgren

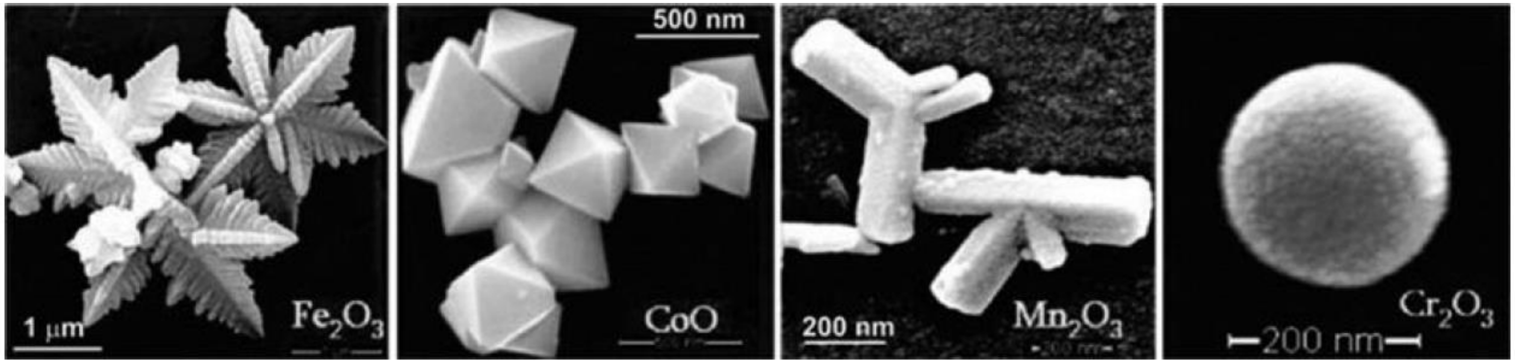



*Figure 4.9 SEM images of various metal oxide nanostructures. Reproduced with permission from I. Bilecka and M. Niederberger, Nanoscale, 2, 1358, © 2010 Royal Society of Chemistry.*

Ref: West p. 204, 281

# Transmission Electron Microscopy

See Solid State Chemistry Wiki

- TEM detects **transmitted** electrons and radiation (SEM is based on **reflection**)
- Nowadays enables even atomic resolution (≤ 1 Å)
- With TEM, both **electron diffraction patterns** and **magnified images** can be obtained from the same sample area
  - Electron diffraction patterns give unit cell and space group information
  - In imaging mode, TEM gives morphological information on the sample
- The first TEM was built by Max Knoll and Ernst Ruska already in 1931 (Nobel 1986)

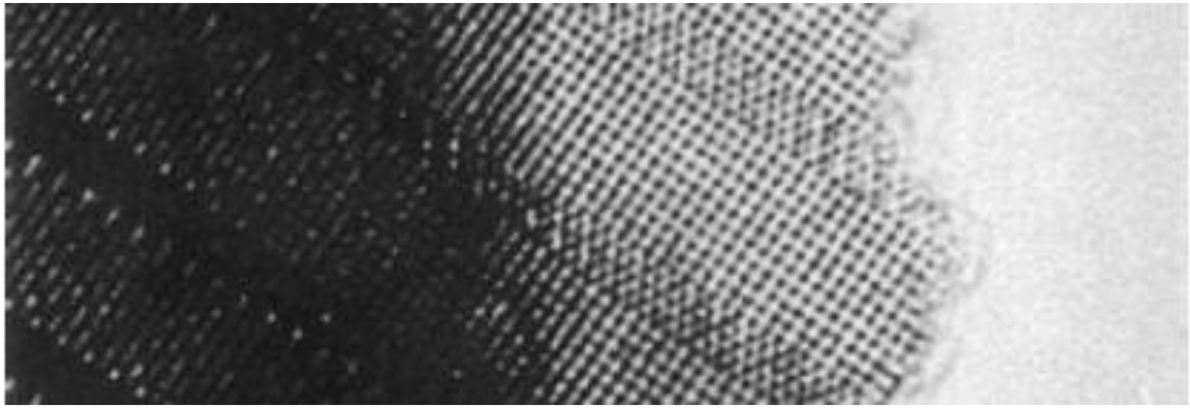


*Figure 6.14 High-resolution electron micrograph of an intergrowth tungsten bronze, $Rb_{0.1}WO_3$. Black dots represent $WO_6$ octahedra. The structure may be regarded as an intergrowth of primitive cubic $WO_3$ (strips of black dots based on a square grid) and hexagonal $WO_3$ containing Rb (narrow strips of black dots on a hexagonal grid). Photograph courtesy of Dr M. Sundberg, University of Stockholm, Department of Chemistry.*

Ref: West p. 288

# TEM (2)

- TEM resolution has been pushed to the sub-ångström level with sophisticated ***aberration correction*** techniques
- Important limitation: Extensive sample preparation is required to produce a sample thin enough to be electron transparent
- The structure of the sample may change during the preparation process
- The field of view is relatively small, so the analyzed region may not represent the whole sample.
- The sample may be damaged by the electron beam, particularly in the case of biological materials (lower operation voltage helps)

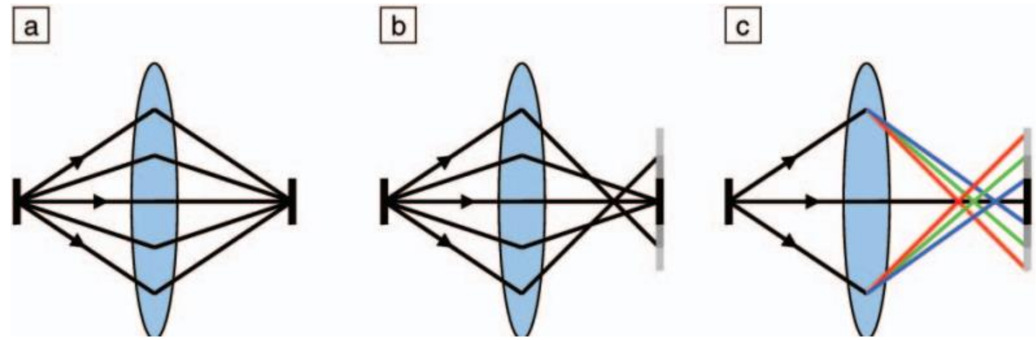
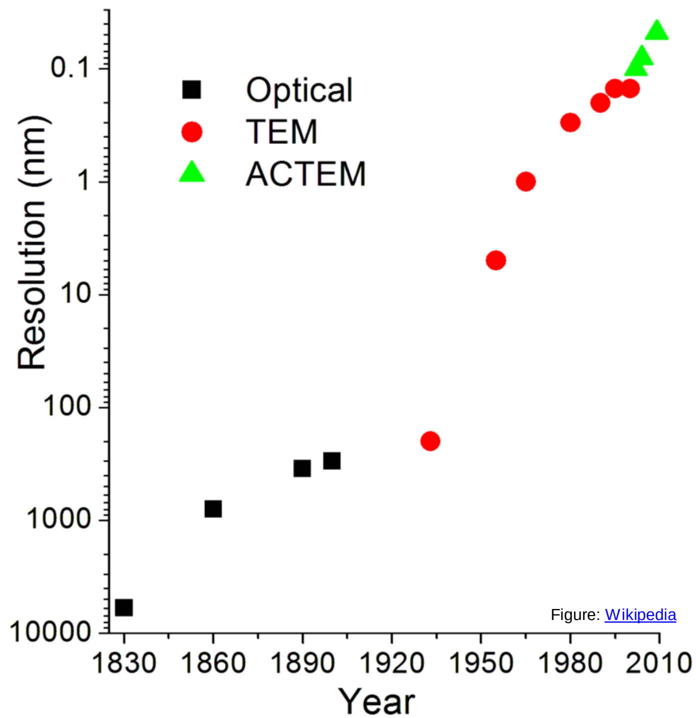


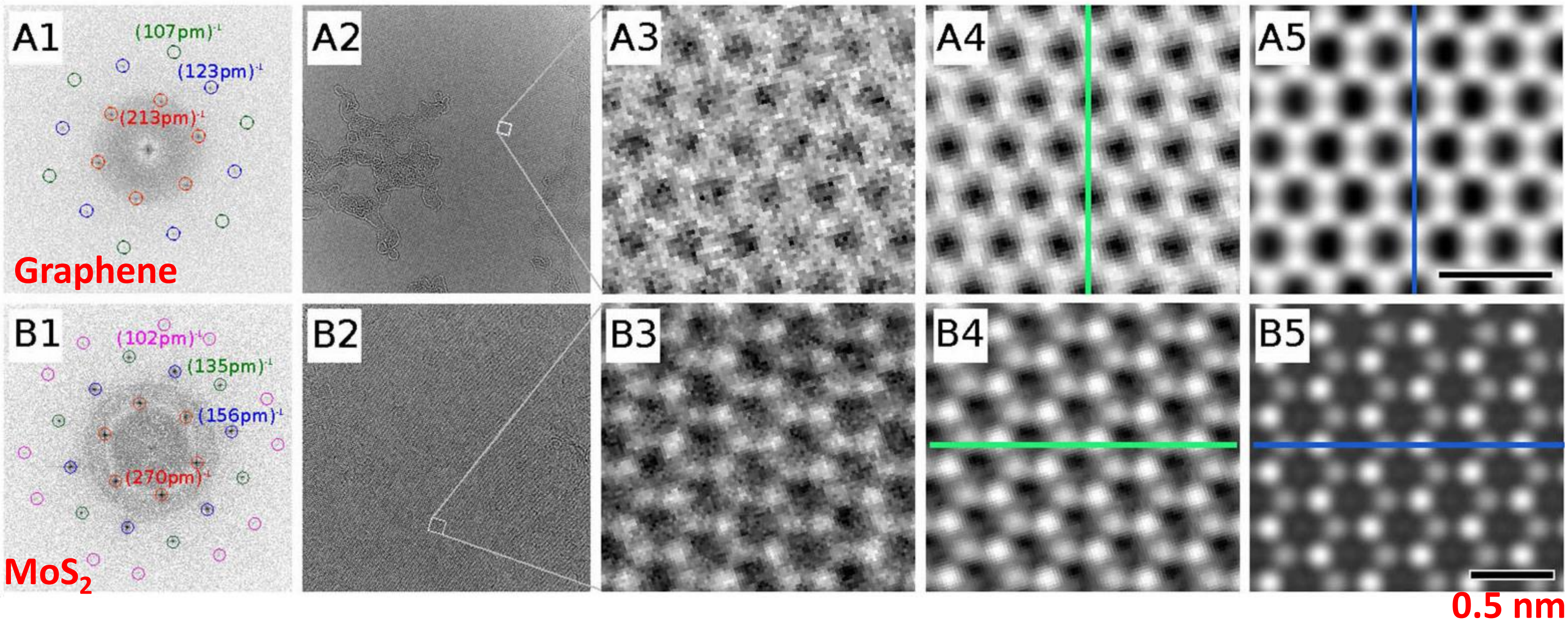

*Figure 2. Illustration of certain lens aberrations. (a) A perfect lens focuses a point source to a single image point. (b) Spherical aberration causes rays at higher angles to be overfocused. (c) Chromatic aberration causes rays at different energies (indicated by color) to be focused differently.* **MRS BULLETIN • VOLUME 31 • JANUARY 2006**

Optical, transmission (TEM) and aberration-corrected electron microscopes (ACTEM)



# Sub-Ångström TEM

Diffractogram | Raw image | Magnified raw image | Averaged image | Simulated image




Experimental and calculated $C_S/C_C$-corrected 30 kV HRTEM images of graphene (A) and $MoS_2$ (B). The diffractograms ($A_1$ and $B_1$) of the experimental raw images of graphene ($A_2$) and $MoS_2$ ($B_2$) in bright-atom contrast (field of view 40 x 40 $nm^2$) indicate the achieved resolution. The magnified raw images ($A_3$ and $B_3$) directly allow for identifying the atomic structure. The averaged experimental images ($A_4$ and $B_4$) show a strong signal-to-noise improvement and are in good agreement with the simulated images ($A_5$ and $B_5$). The scale bars in $A_5$ and $B_5$ correspond to 0.5 nm

http://www.salve-project.de/newspress/SALVE-CC-correction-realized.html