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The Microscopy Opening Symposium

Wednesday July 4th, 2012

Materials and Analytical Science Centre Building
University of Warwick, CV4 7AL

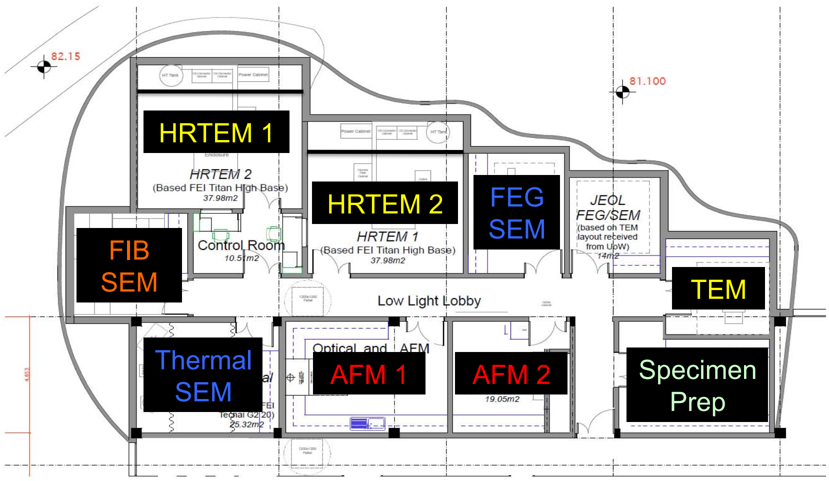
Jeremy Sloan
Richard Beanland
Ana Sanchez
Neil Wilson

gatan

JEOL

Q: So what are we celebrating today ?
A: <u>Not</u> the opening of the MAS building <u>but</u> rather the opening of the new Warwick Microscopy Suite (red box)…and the new microscopes !

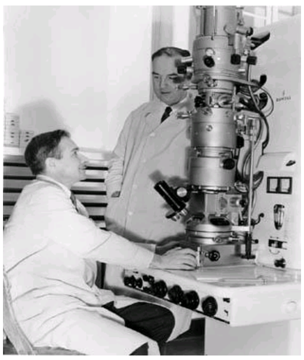
We have a dedicated specimen preparation suite and additional facilities include AFM (several flavours), Environmental FEG-SEM (with EBSD and Cryoprep Stage), Thermal SEM (CL) and conventional TEM with microanalysis



warwick microscopy

Introduction to Transmission Electron Microscopy, High Resolution Imaging and Spectroscopy *Jeremy Sloan*

1931 Ernst Ruska and Max Knoll build the first TEM (1931)



Commercial TEMs (1939+)

ARM200F

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Introduction to Microscopy

11th-13th December 2013 4

Overview

HRTEM: High Resolution Transmission Electron Microscopy

- Overview
- Design of a TEM – comparison with optical microscope
- What's the best electron source ?
- Formation of images and diffraction patterns, defects in materials
- Advanced TEM supports
- Application of HRTEM to the study of nanostructured materials
- Extended resolution – software and hardware C_s correction
- In the next lecture, the **next generation** instrumentation will be discussed…

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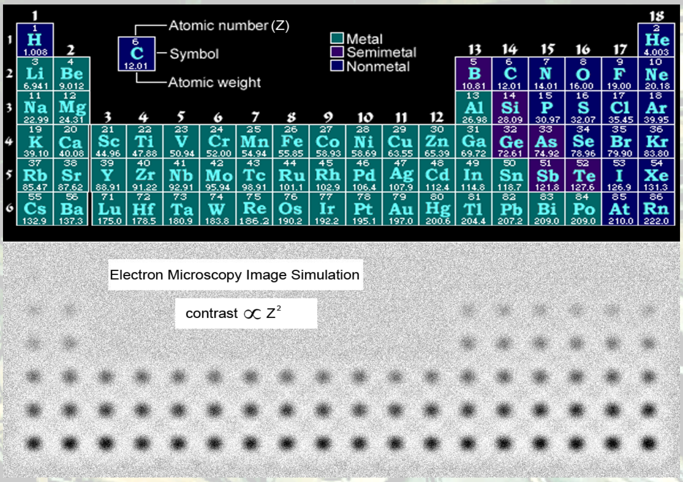
Overview



A 'periodic table' of atom image contrast in a HRTEM (contrast ∝ atomic No.)

What we see in a **Transmission Electron Microscope** is governed by a number of factors:

(I) The **resolving power** of the microscope
(II) The individual **scattering power** of the atoms comprising the specimen
(III) The **number of atoms** in the cross section of the sample (i.e. the specimen thickness)
(IV) The **crystallinity** of the sample.
(V) The **sensitivity** of the sample to the **electron beam**

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So why HRTEM ?

- High Resolution Electron Microscopy can resolve object details smaller than 1 nm (10^{-9} m).
- It can be used to image the interior structure of the specimen (comparing to atomic resolution scanning tunneling microscopy, only at the surface).
- Comparing to atomic resolution provided by X-ray diffraction (average information), HREM can provide information on the local structure.
- Using the related technique of electron diffraction, we can also do crystallography
- Direct imaging of atom arrangements, in particular the structural defects, interface, dislocations.
- Like SEM, HRTEM can be combined with spectroscopic techniques to give more chemical (and other) information about a specimen

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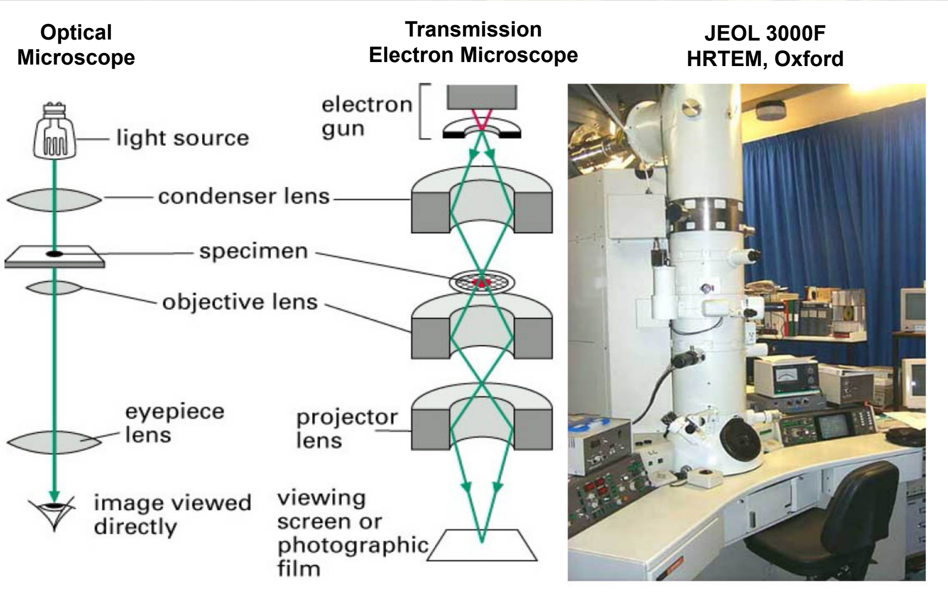
TEM- comparison with optical microscope



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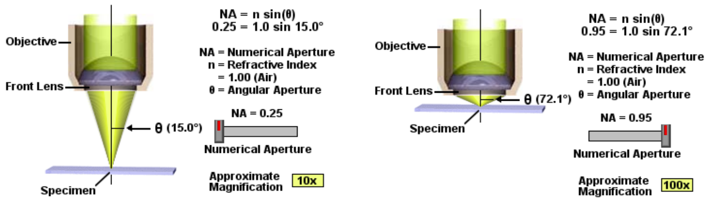
Numerical aperture & Rayleigh Criterion for optical miroscope resolving power

The light-gathering ability of a microscope objective is quantitatively expressed in terms of the **numerical aperture**, which is a measure of the number of highly diffracted image-forming light rays captured by the objective. Higher values of numerical aperture allow increasingly oblique rays to enter the objective front lens, producing a more highly resolved image.



Resolution: smallest distance between two points on a specimen that can still be distinguished as two separate entities.

$R = 0.61\lambda/NA$ (1)
$R = 1.22\,\lambda/(NA(obj) + NA(cond))$ (2)

Raleigh criteria expressed for a **single lens (1)** and an optical microscope with **two lenses (2)**

Note resolving power $\propto \lambda$ $\therefore$ for a light microscope, (shortest wavelength = violet (380 nm) resolution is limited to ~<u>200nm (0.2 μm)</u>

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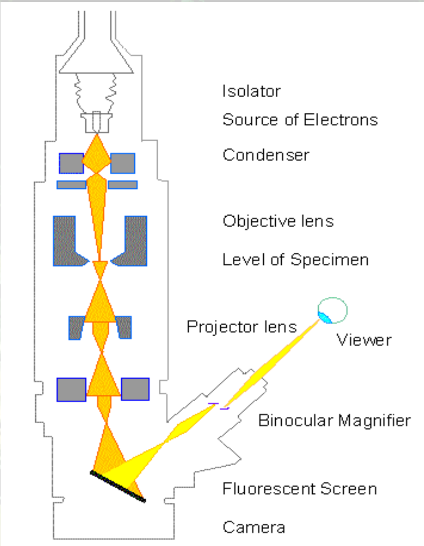
9

TEM – electron wavelength



Ultimate resolution ~ <u>0.5(?)</u>-0.2 nm

- We know that electrons are small particles with wave-like characteristics, i.e.
  $\lambda = h/p$

  (h = Planck's constant; p = momentum (=mv); λ = electron wavelength)

  $\therefore$ $E = 1/2\, m_0 v^2$ or

  $\therefore$ $\lambda = h/(2m_0 eV)^{0.5}$

  taking into account <u>relativistic effects</u>

  $\lambda = h/[2m_0 eV(1+eV/(2m_0c^2))]^{0.5}$

  - c = speed of light; e and m_0 are the charge and rest mass of the electon respectively

10

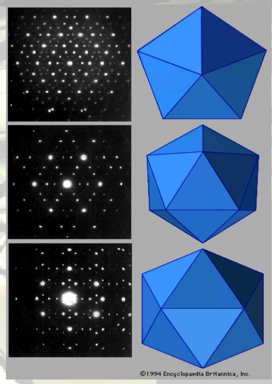
Electron wavelengths

Equation for the electron wavelength (λ)

$$\lambda = h/[2m_0eV(1+eV/(2m_0c^2))]^{0.5}$$

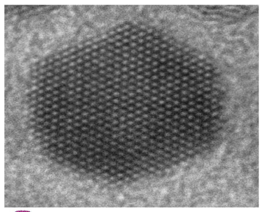
m_0 = electron rest mass
V = voltage
e = electron charge
c = speed of light, h= Planck's constant
…apart from V, all are constants on RHS

Electron diffraction



- V: accelerating voltage, non-relativistic
  - 100kV→ 0.0038nm,
  - 200kV→ 0.0035nm
  - 400kV→ 0.0023nm
- But electrons have speeds close to speed of light
- Relativistic wavelength
  - 200kV→ 0.0033nm, $2*10^8$m/s
  - 400kV→ 0.0016, $2.5*10^8$m/s
  - Increase in mass m/m_0= 1.78

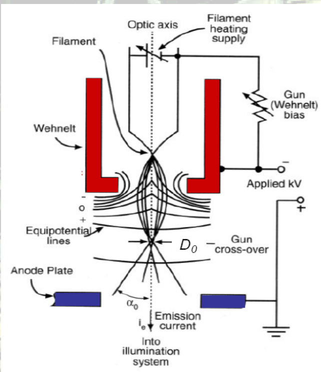
HRTEM



The Rosenthal Group at Vanderbilt
Phase contrast TEM image of a CdSe nanocrystal

Electron sources –Thermionic Emitters

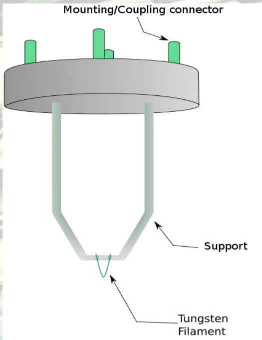
Thermionic emission is the heat-induced flow of charge carriers from a surface or over a potential-energy barrier

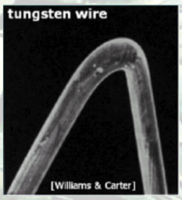


$$J = A_G T^2 e^{\frac{-W}{kT}}$$

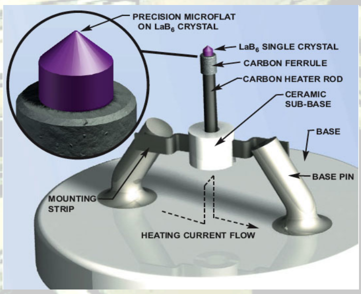
J = emission current density
A_G= 'Richardson's constant'
W = work function

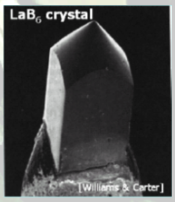
W hairpin





LaB_6 single crystal





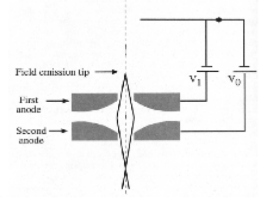
12

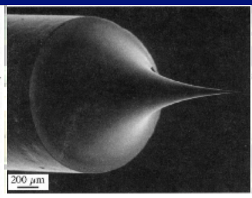
Electron Sources II - Field Emitters

Field emission (FE) is emission of electrons induced by an electrostatic field. Two kinds are common in electron microscopy (i) **Schottky Emission** and (ii) **Cold Field Emission (CFE)**

(i) **Schottky Emission** most electrons escape over the top of a field-reduced barrier, from states well above the Fermi level (**energy spread >0.7 eV**)

(ii) **CFE** most emitted electrons escape by **Fowler-Nordheim tunneling** from electron states close to the emitter Fermi level (**energy spread <0.3 eV**).

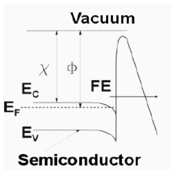


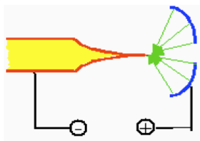


In general, FEG electron sources have much higher coherence and improved electron densities wrt to thermionic emitters

Emission

- Field emission

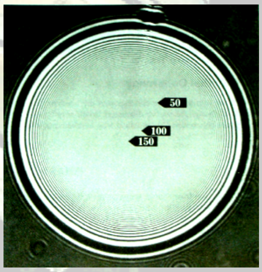




Field emission starts for E > 10^7 V/cm
High current density: $J(E) = A \cdot E^2\ \varphi\ \exp(-B\ \varphi^{1.5}/E)$

Strong nonlinear current-voltage characteristic
Very short switching time (t <ns)

Small spot size due to field enhancement at the tip apex



Fresnel Pattern produced with a W FEG source

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…but can field emission be improved ?

Characteristics of the various emitters

TABLE 5.1. Characteristics of the Three Principal Sources Operating at 100 kV

	Units	Tungsten	LaB_6	Field Emission
Work function, Φ	eV	4.5	2.4	4.5
Richardson's constant	A/m^2K^2	6×10^5	4×10^5	
Operating temperature	K	2700	1700	300
Current density	A/m^2	5×10^4	10^6	10^{10}
Crossover size	µm	50	10	<0.01
Brightness	A/m^2sr	10^9	5×10^{10}	10^{13}
Energy spread	eV	3	1.5	$\boxed{0.3}$
Emission current stability	%/hr	<1	<1	5
Vacuum	Pa	10^{-2}	10^{-4}	10^{-8}
Lifetime	hr	100	500	>1000

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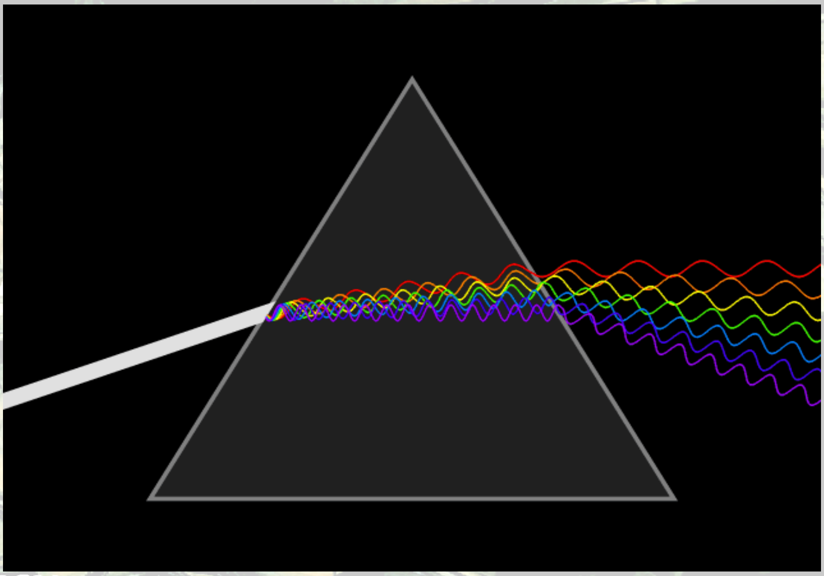
But even field emitted electrons are **not** monochromatic !

Principle of monochromation



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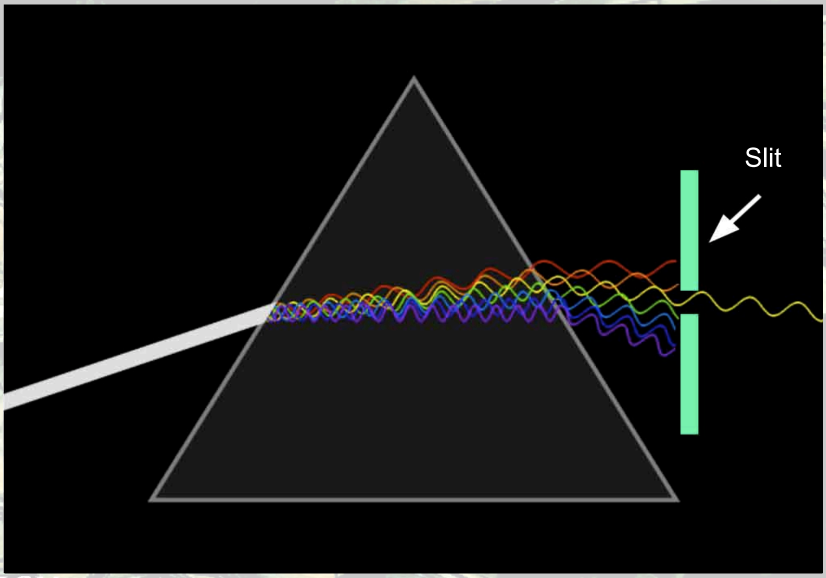
Principle of monochromation



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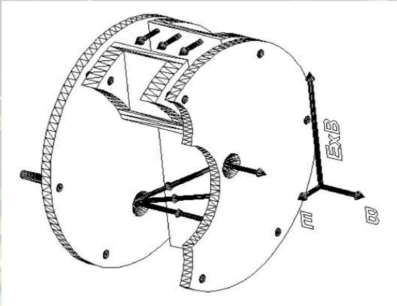
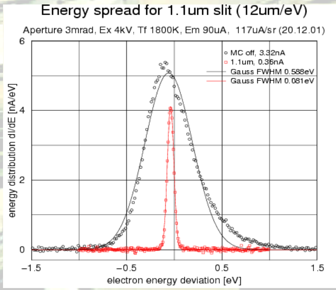
…doing this reduces the beam intensity, however, reducing S/N in spectroscopy

Monochromating the FEG improves the energy and imaging resolution further….



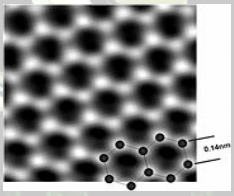
Good for spectroscopy…



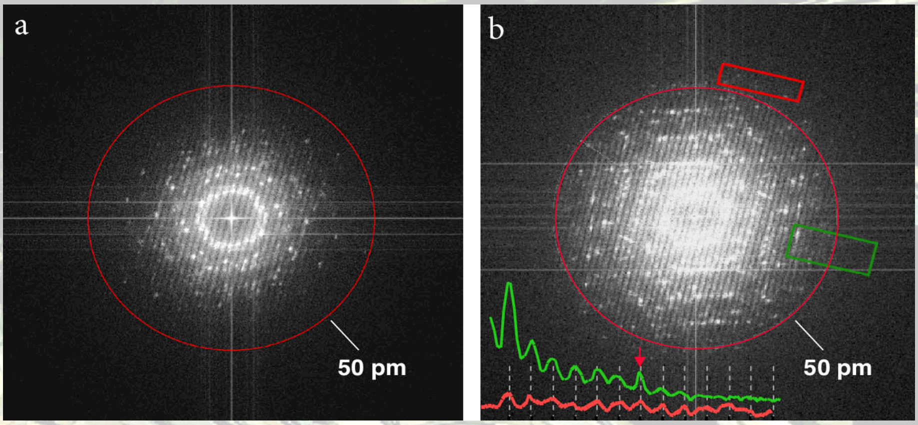
http://www.ceos-gmbh.de/mono.html

Schematic representation of a monochromator
The separation of the electrons occurs in the space with crossed perpendicular homogeneous electrostatic (E) and magnetic (B) fields.

…and for imaging



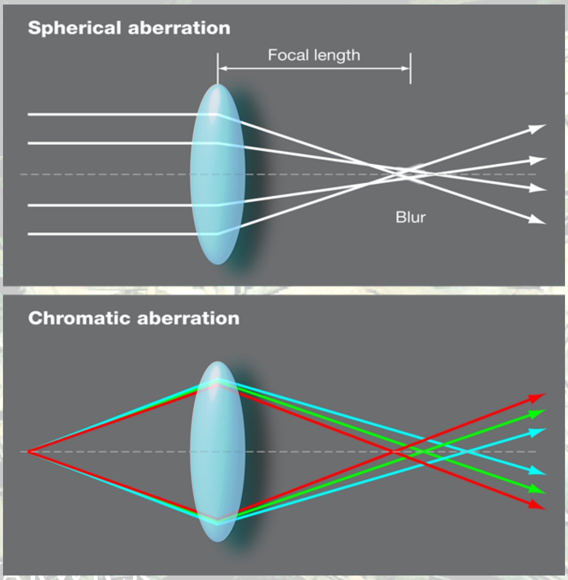
We can even see the effect of monochromation in electron diffraction



Young's fringe experiments with gold nanoparticles suspended on a carbon grid. With the monochromator **switched off**, **(a)**, the fringes extend to about 70 pm. With the monochromator **switched on**, **(b)**, the fringes extent to below 50 pm.

http://ncem.lbl.gov/frames/TEAM0.5.htm

But we still have to worry about those pesky lens aberrations…



These cause problems in **probe formation** – which adversely affects **spatial resolution** in spectroscopy.

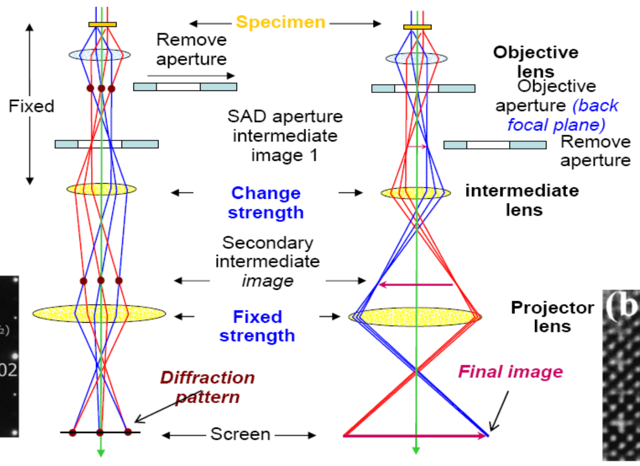
And also **image formation –** these aberrations influence ultimate resolution (more on this later….).

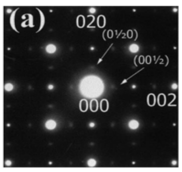
The best electron source is therefore a **high brightness** source that is **monochromated**.

Current state of the art is ~0.08 eV
(still room for improvement !)

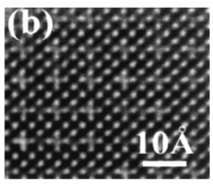
Image and diffraction pattern formation in a HRTEM

Diffraction mode **Image mode**





Electron diffraction pattern

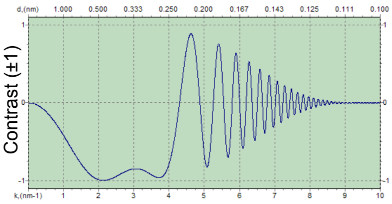


HRTEM Image (white crosses are cation vacancies in $La_xSr_yTiO_3$: an example of defect imaging)

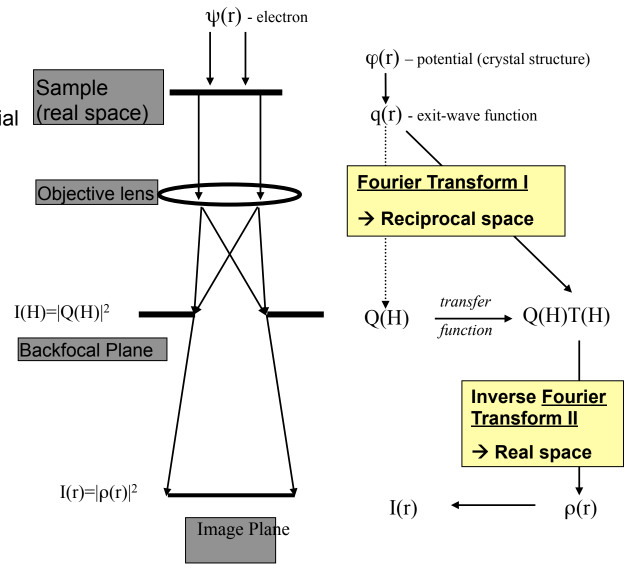
Contrast Transfer Function (T(H))

$T(H)=\sin(\pi C_s \lambda^3 H^4/2+\pi \Delta f \lambda H^2)$.

C_s: Spherical aberration constant; Δf: defocus value; λ = wavelength; H = spatial frequency (~atom periodicity)



Phase contrast transfer function calculated at Δf=-61 nm with Cs=1.0 mm.



Contrast Transfer Function (i.e. CTF or T(H)) & Scherzer defocus (optimum focusing conditions)

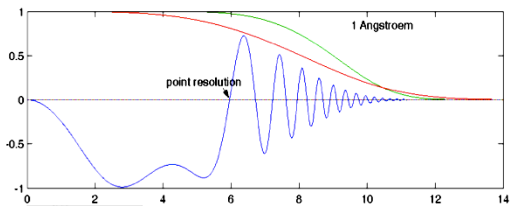
Mathematical Form of the CTF

$$T(H)=\sin\chi=\sin\left(\frac{1}{2}\pi C_s \lambda^3 H^4+\pi \Delta f \lambda H^2\right)$$

C_s: Spherical aberration constant; Δf: defocus value; λ = wavelength; H = spatial frequency (~atom periodicity).

"Sin χ" is the "Contrast"

Graphical Form of the CTF



http://www.maxsidorov.com/ctfexplorer/webhelp/background.htm

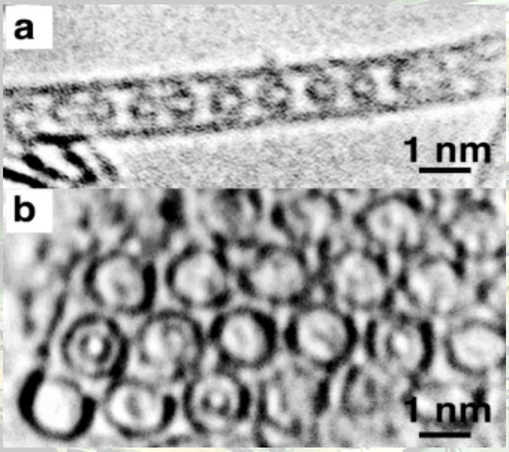
In **Scherzer defocus**, one aims to choose the right defocus value *Δf* whereby low spatial frequencies *u* are transferred into image intensity with a similar phase. In 1949, Scherzer found that the optimum defocus depends on microscope properties like the spherical aberration C_s and the accelerating voltage (through *λ*) in the following way:

$$\Delta f_{Scherzer}=-1.2\sqrt{C_s \lambda}$$

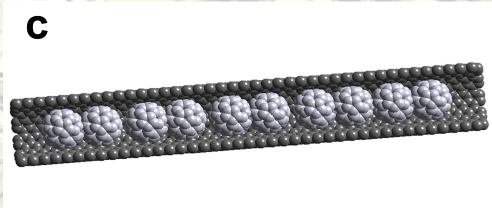
where the factor 1.2 defines the extended Scherzer defocus. For example, when C_s*=0.6* and an accelerating voltage is 300keV result in $\Delta f_{Scherzer}$ *= -41,25 nm*.

In the contrast transfer function (CTF), the **point resolution of a microscope** is defined as the spatial frequency u_{res} where the CTF crosses the X-axis for the first time. At Scherzer defocus this **value is maximized**.

Imaging of molecular structures within SWNTs (C_{60})



SWNT = Single Walled Carbon Nanotube



B.W. Smith, M. Monthioux, and D.E. Luzzi, Nature 396 (1998) p. 323.

A SWNT is one example of an ultrathin specimen support

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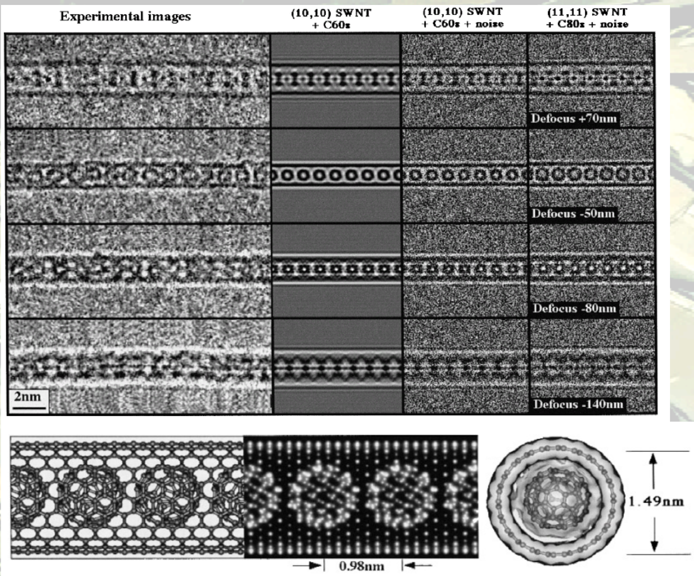
Imaging and simulation of C_{60} and C_{82} within SWNTs

Focal Series



Simulations

Structure model

Projected potential

Chem. Phys. Lett. 316(2000)191–198

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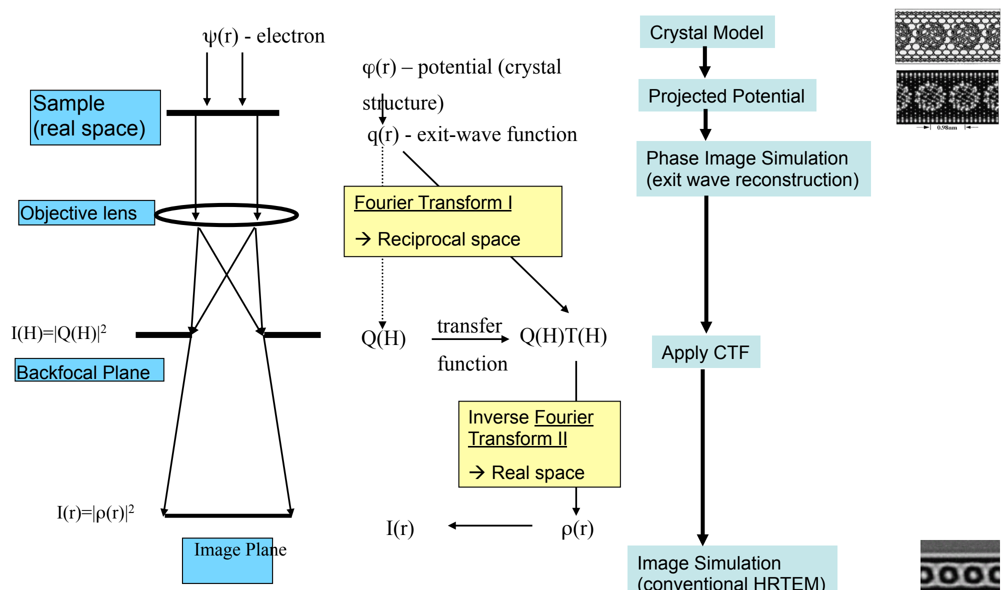
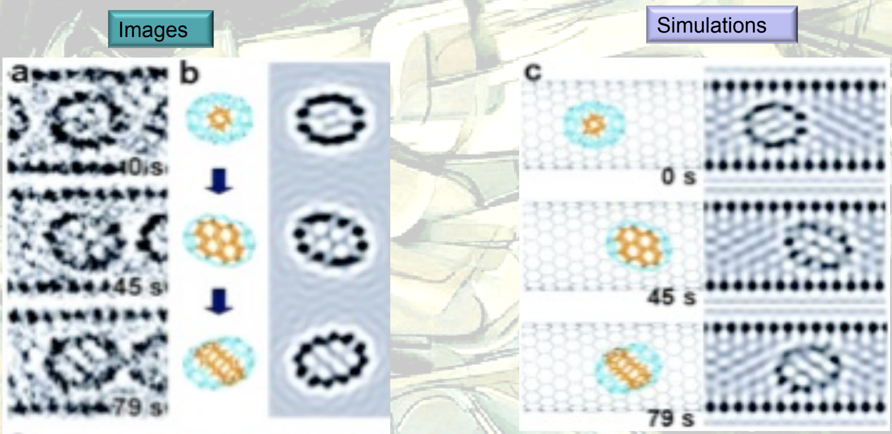
Schematic Procedure for Image Simulation



Cowley, J. M.; Moodie, A. F., Acta Cryst., 1957, 10, 609-619; Goodman, P.; Moodie, A. F. Acta Cryst., 1974, A30, 280290.

Image simulation is an important tool even for the next generation TEMs

Cs –corrected imaging of D_{5d} C_{80} molecular motion in a SWNT



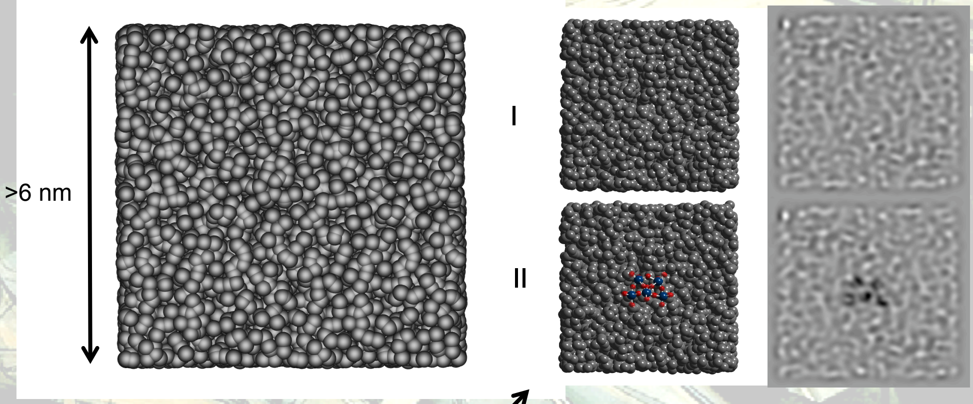
Sato et al Nano Lett., 7 (12), 3704 -3708, 2007

The latest generation HRTEMs can image fullerene-type molecules at atomic resolution at low accelerating voltage

Newly developed specimen supports for TEM

Unfortunately, ordinary carbon supports are rather thick – and amorphous

SIMULATIONS
(two blocks 6 nm thick in the direction of the electron beam)



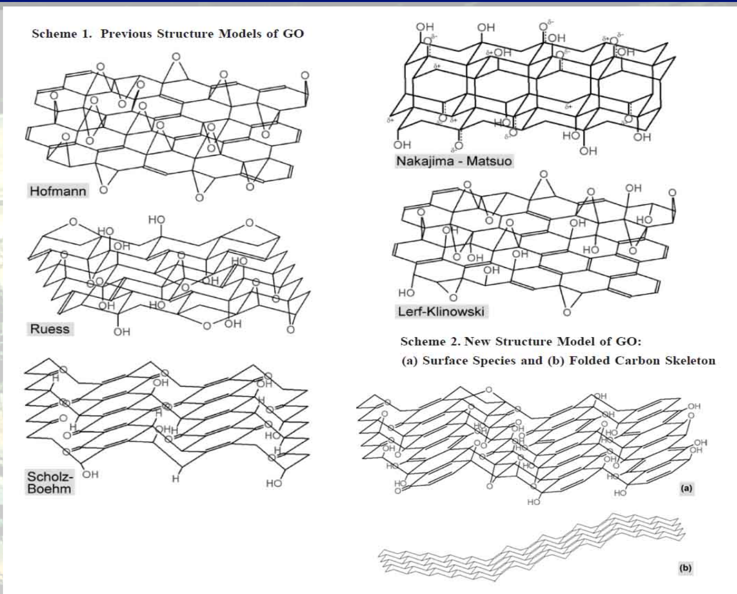
There's a molecule on the surface of this one….

Investigations into new specimen supports for advanced HRTEM imaging

The precise structure of Graphene Oxide (GO) is disputed but nonetheless it is an easier to work with material than graphene.

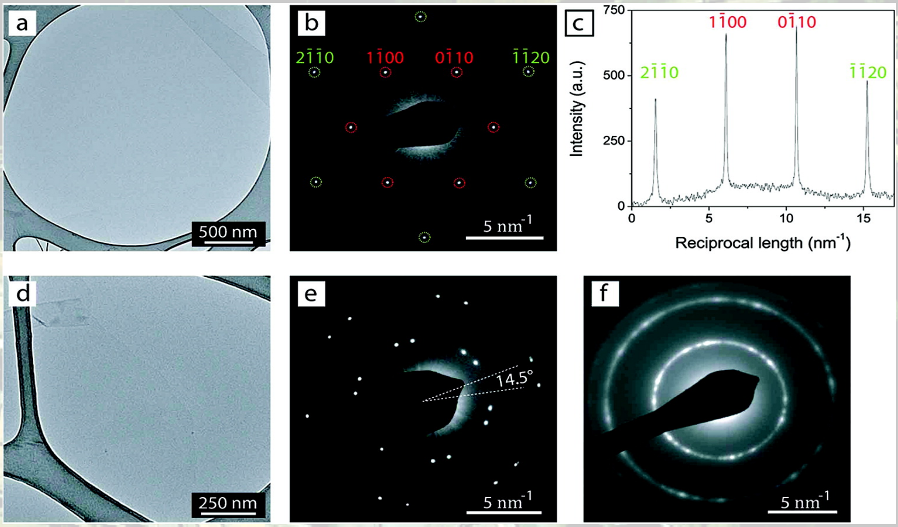
Ideally it is a single layer of partially oxidised graphene with ordered oxidation. In reality, no one seems to really agree on what the actual structure is. Also the oxidation seems to be unevenly distributed over the structure.

Approximate thickness ca. 0.7 nm



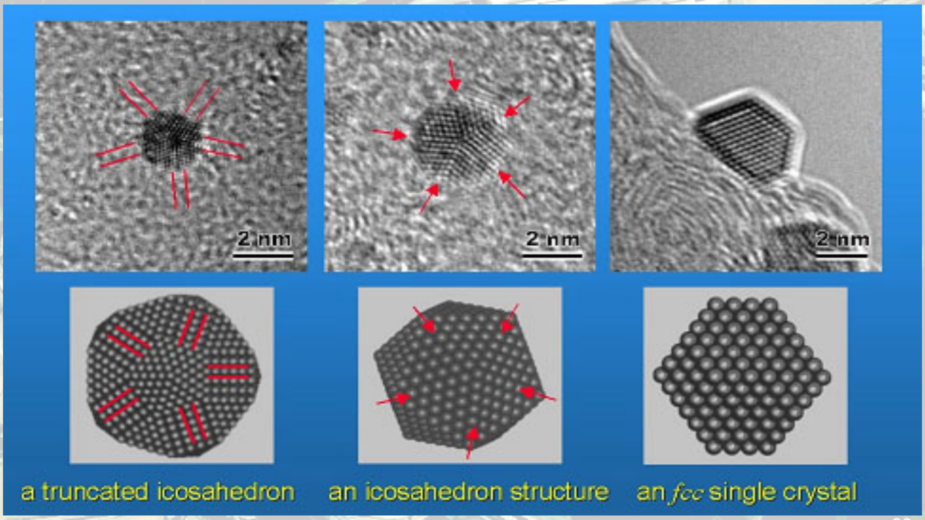
Szabo et al. Chem. Mater., 2006, 18, 2740-2749

Investigations into new specimen supports for advanced HRTEM imaging



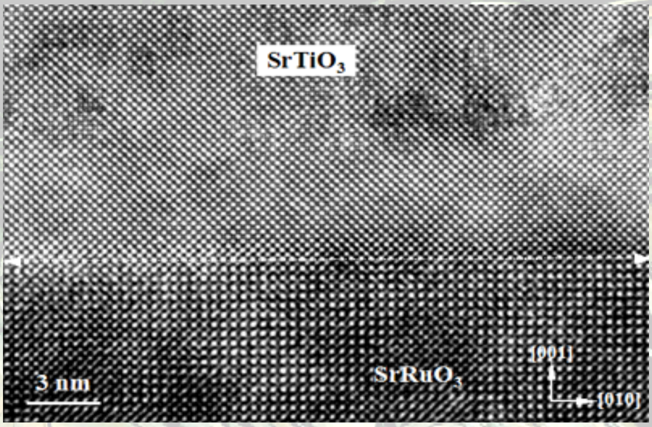
Published in: Neil R. Wilson; Priyanka A. Pandey; Richard Beanland; Robert J. Young; Ian A. Kinloch; Lei Gong; Zheng Liu; Kazu Suenaga; Jonathan P. Rourke; Stephen J. York; Jeremy Sloan; ACS Nano 2009, 3, 2547-2556.
DOI: 10.1021/nn900694t

Applications of HRTEM I: Shape Determination of Au Nanoparticles



30

Applications of HRTEM III: Interfaces



a=0.3905 nm

Misfit=0.64%

a=0.3982 nm

HREM image the coherent $SrTiO_3$/$SrRuO_3$ interface.

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Suggested Reading

'Transmission Electron Microscopy', Volumes 1-4 (or single volume) By David B. Williams and C. Barry Carter, Plenum Press, 1996.

'Electron Microscopy and Analysis' By Peter J. Goodhew, F. J. Humphreys, R. Beanland, Taylor and Francis, 2001.

'Electron Energy Loss Spectroscopy', Rik Brydson, Royal Microscopical Society Handbooks, 2001.

'Electron Energy-Loss Spectroscopy in the Electron Microscope' 2nd Ed. R. F. Egerton, Plenum, 1996.

'Transmission Electron Microscopy; Physics of Image Formation.' L. Reimer and H. Kohl, 5th Ed., Springer, 2008.

+ any recent scientific literature on electron microscopy – the technology is improving all the time !

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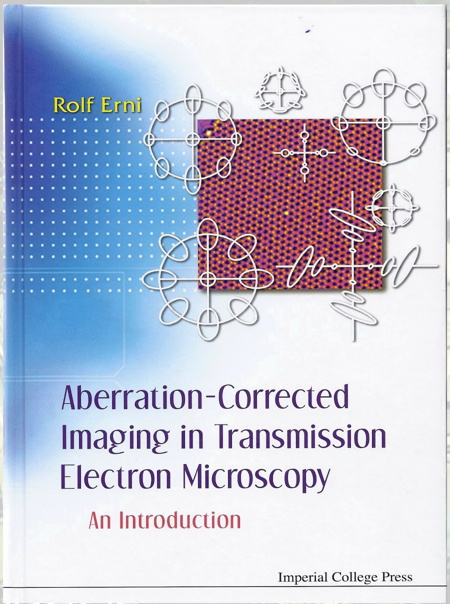
The next generation….



To the list of essential texts for any student of high-end electron microscopy, which will include Williams and Carter, Ray Egerton, any or all of a number of volumes by John Cowley and colleagues, Reimer and Kohl, (insert your favourites here), make a space on your bookshelf for Rolf Erni's "Aberration-Corrected Imaging in Transmission Electron Microscopy – An Introduction"- do it now!

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