T E M —

the Transmission Electron Microscopy,

a Powerful Tool for Imaging, Diffraction and Spectroscopy in Materials Science

Lecture -- II

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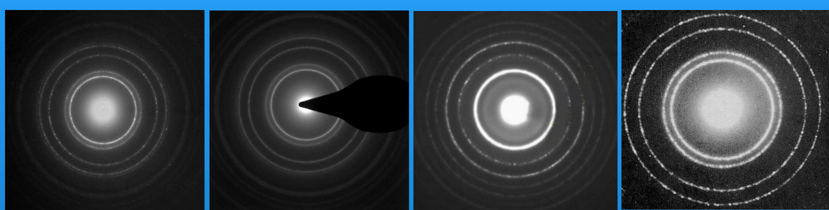
07 - 02 - 2023

(continued – Part 2)

Learn to be an expert to recognize things!

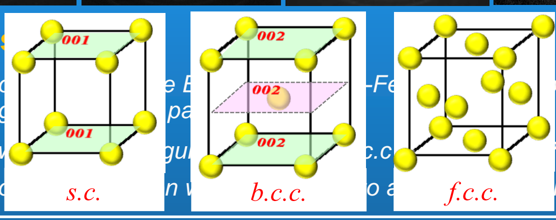
The following four EDPs are taken from Au, Cu, Al and α-Fe polycrystalline respectively. Au ... has b.c.c structure. Their lattice constants are given: a(Au)=0.408nm, a(Cu)=0.361nm, a(Al)=0.405nm, a(α-Fe)=0.286nm.

Questions: Why?



Question

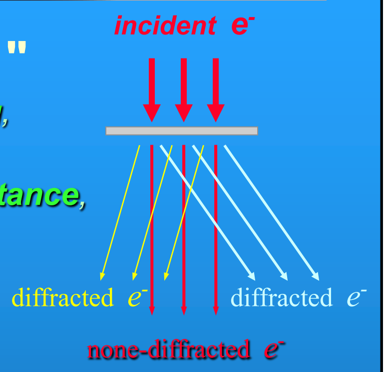
1. Can y... ...e E... ...-Fe ...ly by a quick ... pa...
2. How w... ...gu... ...c.c...
3. What ... ...n w... ...o a... ...n 2 ?



Basic laws for electron diffraction

☞ What is "diffraction" " 衍射 "

Diffraction is, firstly, a ***scattering****, which follows certain* ***rules****, and features a basic nature of* ***inheritance****, namely, the* ***genetics*** *!*

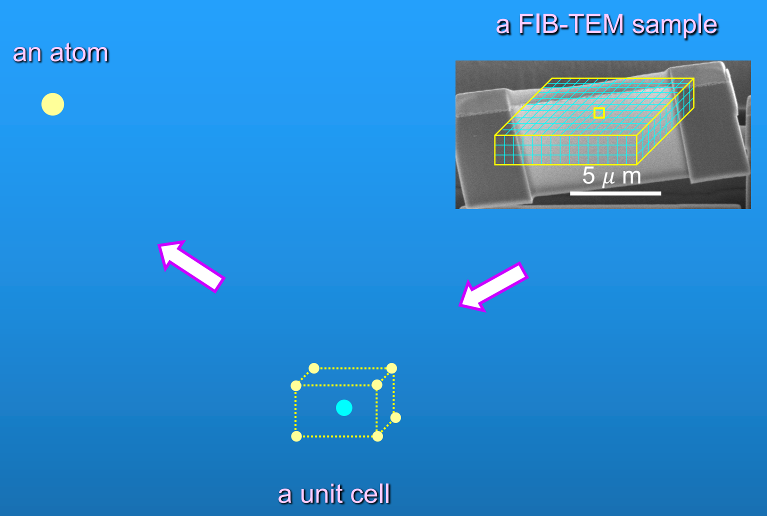


- In what *directions* would electron be diffracted? -- *Geometry analysis*
- How *strong* are the diffracted electron beam along certain directions ? --- *Intensity analysis*

How the direction and the intensity of a diffraction beam inherit the structure information of your specimen ??

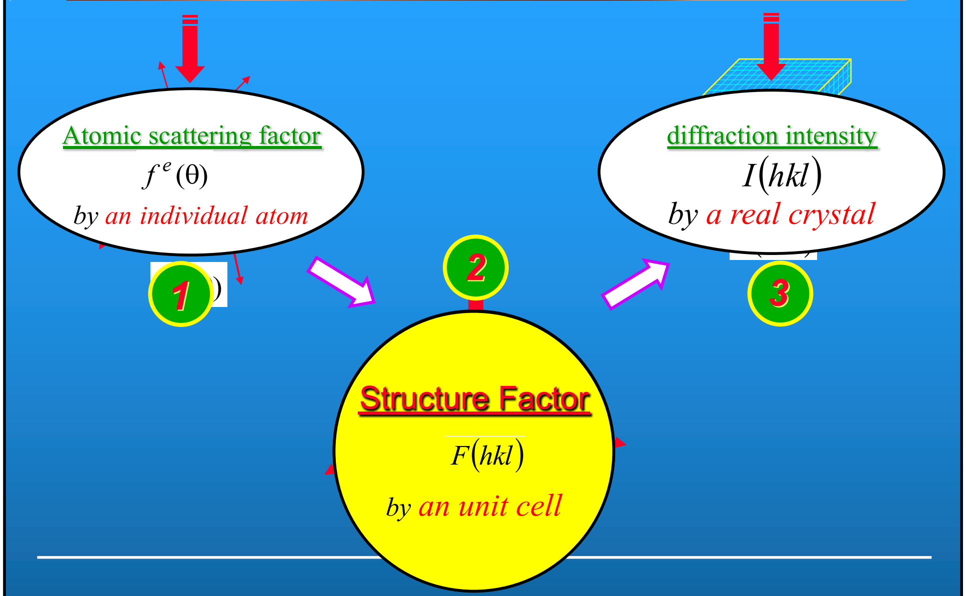
3

Diffraction intensity



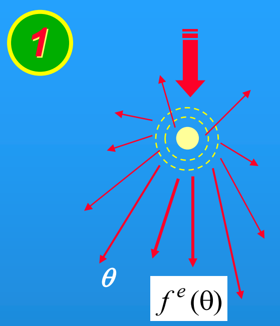
4

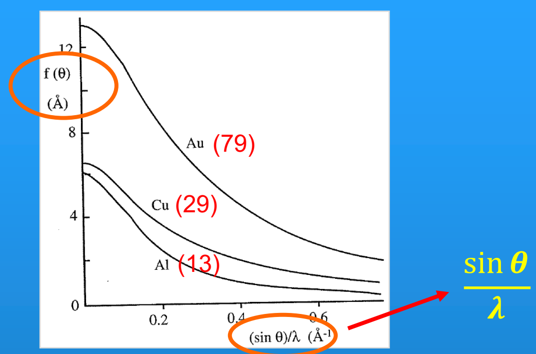
Understanding diffraction intensity



5

The Atomic Scattering Factor $f^e(\theta)$





$f^e(\theta)$ *depends on λ, θ, and Z: it decreases when*

- scattering angle θ *increased;*
- Atomic number *Z is low.*
- wavelength λ *decreases, or high-voltage increased;*

6

The Structure Factor: $F(hkl)$

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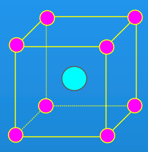
$$F(hkl) = \sum_{j=1}^{N} f_j^e \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]$$



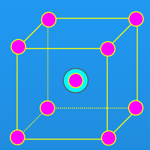
a unit cell

- atom A : f_A^e $(x_1, y_1, z_1) = (0,0,0)$
- atom B : f_B^e $(x_2, y_2, z_2) = (1/2, 1/2, 1/2)$

F(hkl) describes contributions from: **atom types, numbers, position.**

Zero Structure Factor -- Forbidden diffraction

Give an example: For iron (Fe), a typical b.c.c. structure



b.c.c Fe

- Fe
- C

b.c.c --> s.c.

$$F(hkl) = \sum_{j=1}^{2} f_{Fe}^e \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right]$$

$$= f_{Fe}^e \exp\left[2\pi i(0+0+0)\right] + f_{Fe}^e \exp\left[2\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{l}{2}\right)\right]$$

$$= f_{Fe}^e + f_{Fe}^e \exp\left[\pi i(h+k+l)\right] \sim (-1)^{h+k+l}$$

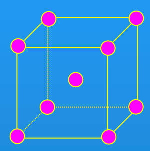
$$h+k+l = \begin{cases} 2n, & F(hkl) = 2f^e \\ 2n+1, & F(hkl) = 0 \end{cases}$$

Zero structure factors

$F(100) \neq 0$	$F(111) \neq 0$	$F(113) \neq 0$
$F(110) = 2f_{Fe}^e$	$F(200) = 2f_{Fe}^e$	$F(112) = 2f_{Fe}^e$

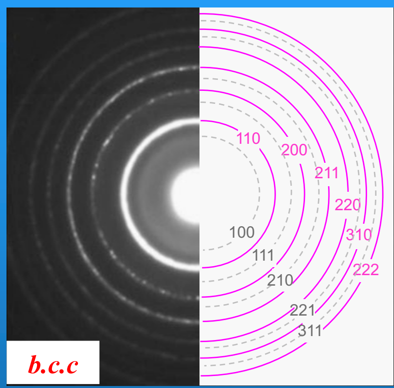
Missing rings in Polycrystalline diffraction

Zero structure factors results in missing rings in Polycrysta…



b.c.c Fe

● Fe

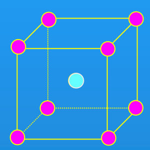


$F(100) = 0$	$F(111) = 0$	$F(113) = 0$
$F(110) = 2f_{\mathrm{Fe}}^{e}$	$F(200) = 2f_{\mathrm{Fe}}^{e}$	$F(112) = 2f_{\mathrm{Fe}}^{e}$

9

Missing rings in Polycrystalline diffraction

What if the centered Fe is substituted by a different atom?
or, the centered atoms are just missing?

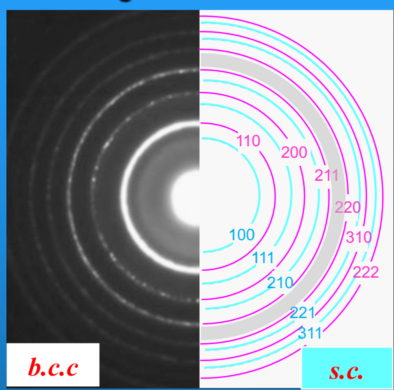


b.c.c. Fe

● Fe

s.c. Fe-C

● C

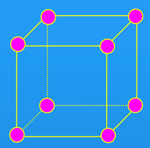


$F(100) \neq 0$	$F(111) \neq 0$	$F(113) \neq 0$
$F(110) = 2f_{\mathrm{Fe}}^{e}$	$F(200) = 2f_{\mathrm{Fe}}^{e}$	$F(112) = 2f_{\mathrm{Fe}}^{e}$

10

Ring patterns of a Simple Cubic (s.c.) structure

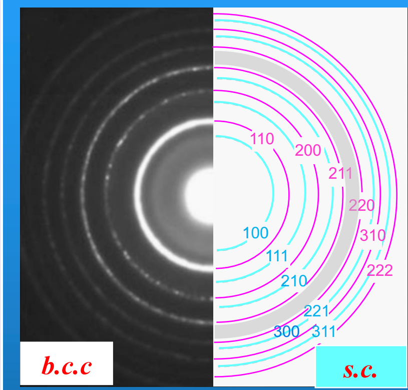
How to recognize a S.C. structure from ring patterns?



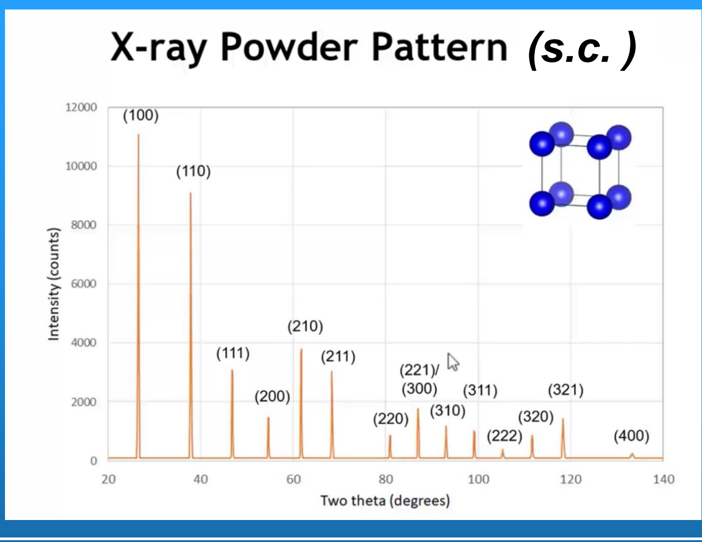
For a S.C. structure, all possible (h,k,l) must be counted:

$$h^2 + k^2 + l^2 = ?$$

(hkl)	$h^2+k^2+l^2$
(100)	1
(110)	2
(111)	3
(200)	4
(210)	5
(211)	6
(220)	8
(221)/(300)	9
(310)	10
(311)	11
(222)	12
(320)	13
(321)	14
(400)	16

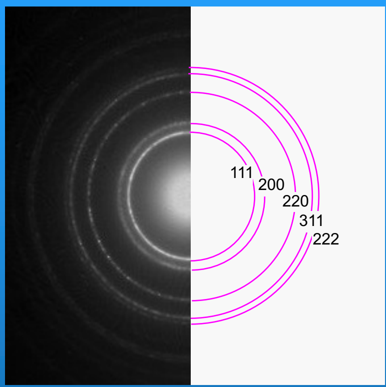


Similar rules applied in X-ray diffraction

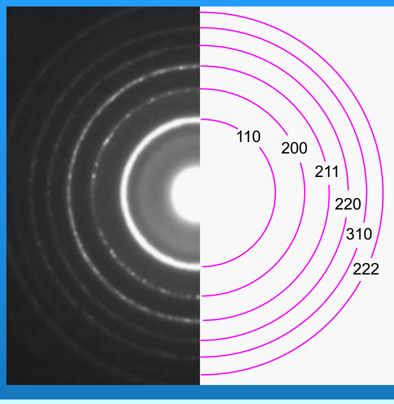


Recognize EDPs from b.c.c or from f.c.c ?

f.c.c. structure



b.c.c. structure



$h^2 + k^2 + l^2 = ?$

$f.c.c$: $3, 4, 8, 11, 12 \ldots$ $b.c.c$: $2, 4, 6, 8, 10, 12 \ldots$

Summary:
(h, k, l) rules for important structures

Simple cubic (s.c.): *all h, k, l* allowed

Body-centered (b.c.c) : $h + k + l = 2n$

face-centered (f.c.c.): h, k, l all odd, *or* all even

Hexagonal close-packed (h.c.p.):

$h + 2k \neq 3n$ (n is an integer)

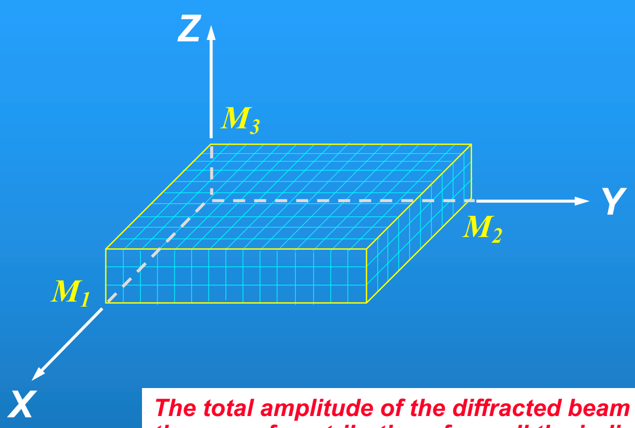
or $h + 2k = 3n$ and l is even;

Note: All possible (h, k, l) combinations:

(1,0,0), (1,1,0), (1,1,1), (2,0,0), (2,1,0), (2,1,1), (2,2,0), (2,2,1), (2,2,2), (3,0,0), (3,1,0), (3,1,1), …

A "real" thin TEM specimen

3



The total amplitude of the diffracted beam takes the sum of contributions from all the individual unit cells in the sample.

The Crystal Shape Factor $|G(s_1, s_2, s_3)|^2$

- Kinematic diffraction intensities from actual crystal:

The total scattering amplitude from an actual crystal is the sum of amplitudes from all the unite cells in the specimen :

$$A(hkl) = F(hkl)\sum_{u=0}^{M_1-1}\sum_{v=0}^{M_2-1}\sum_{w=0}^{M_3-1}\exp[2\pi i(\mathbf{g}_{hkl}+\mathbf{s})\cdot(u\mathbf{a}+v\mathbf{b}+w\mathbf{c})]$$

$$= F(hkl)\sum_{u=0}^{M_1-1}\sum_{v=0}^{M_2-1}\sum_{w=0}^{M_3-1}\exp[2\pi i(\mathbf{s}_1 u+\mathbf{s}_2 v+\mathbf{s}_3 w)]$$

---- hence the diffraction intensity for (hkl):

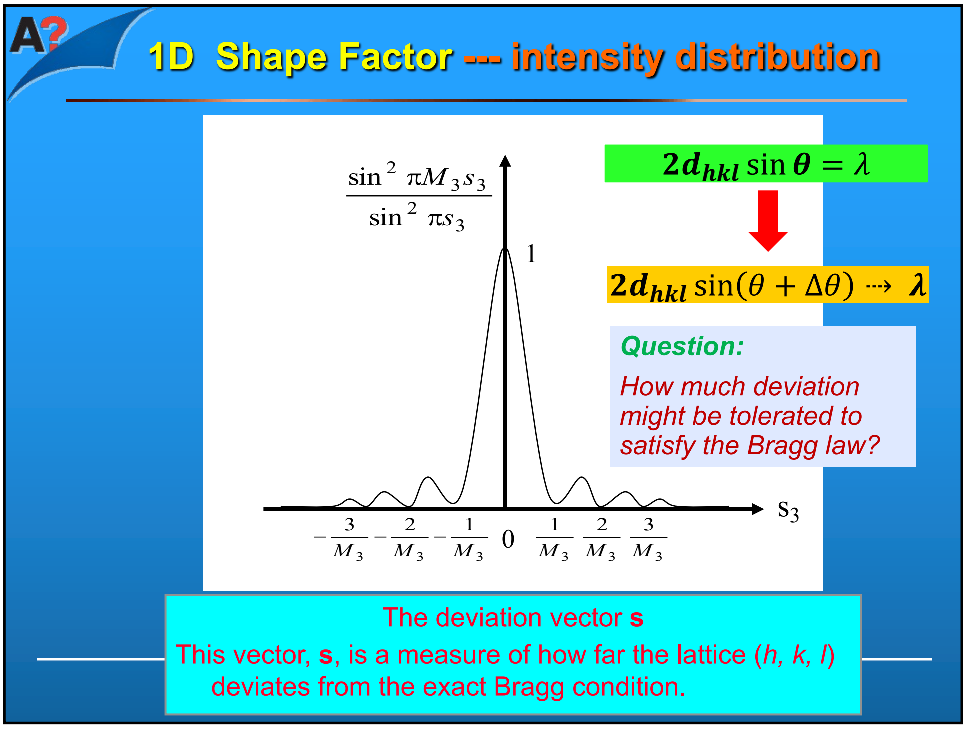
$$I(hkl) = A(hkl)\cdot A^*(hkl) = |A(hkl)|^2$$

$$= |F(hkl)|^2 \times \frac{\sin^2 \pi M_1 s_1}{\sin^2 \pi s_1} \times \frac{\sin^2 \pi M_2 s_2}{\sin^2 \pi s_2} \times \frac{\sin^2 \pi M_3 s_3}{\sin^2 \pi s_3}$$

$$= |F(hkl)|^2 \times |G(s_1, s_2, s_3)|^2$$

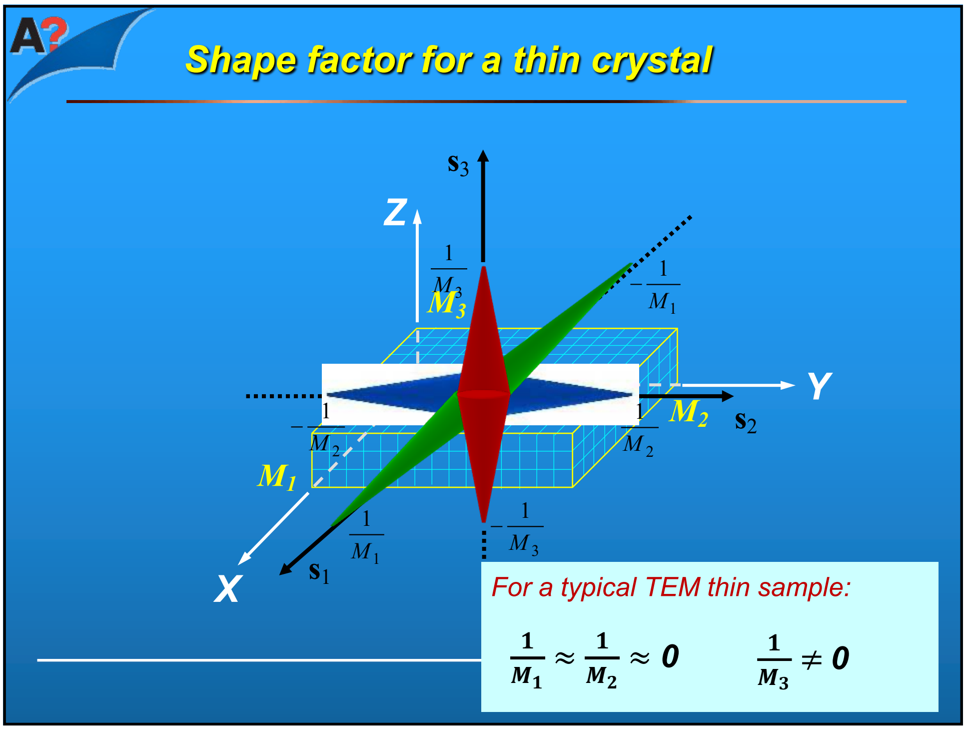
Structure factor

Shape factor for a crystal



1D Shape Factor --- intensity distribution
$\frac{\sin^2 \pi M_3 s_3}{\sin^2 \pi s_3}$
1
0
s_3
$-\frac{3}{M_3}$ $-\frac{2}{M_3}$ $-\frac{1}{M_3}$ $\frac{1}{M_3}$ $\frac{2}{M_3}$ $\frac{3}{M_3}$
$2d_{hkl}\sin\theta = \lambda$
$2d_{hkl}\sin(\theta + \Delta\theta) \dashrightarrow \lambda$
Question:
How much deviation might be tolerated to satisfy the Bragg law?
The deviation vector s
This vector, s, is a measure of how far the lattice (h, k, l) deviates from the exact Bragg condition.

17



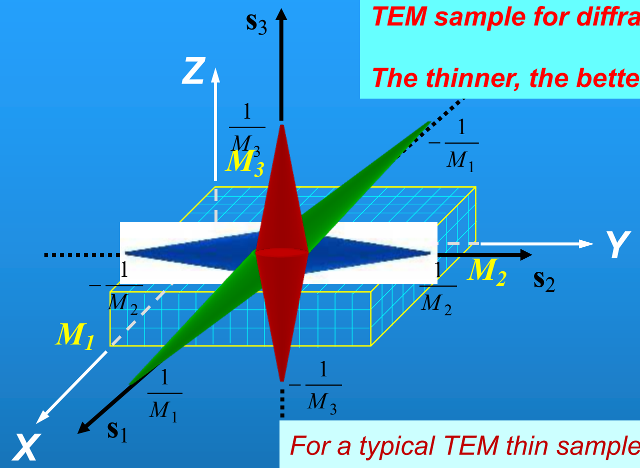
Shape factor for a thin crystal
s_3
Z
$\frac{1}{M_3}$
M_3
$-\frac{1}{M_1}$
Y
M_2
s_2
$-\frac{1}{M_2}$
$\frac{1}{M_2}$
M_1
$\frac{1}{M_1}$
$-\frac{1}{M_3}$
X
s_1
For a typical TEM thin sample:
$\frac{1}{M_1} \approx \frac{1}{M_2} \approx 0$ $\frac{1}{M_3} \neq 0$

18

Shape factor for a thin crystal

TEM sample for diffraction:

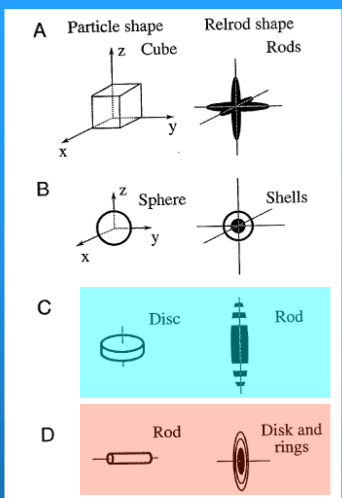
The thinner, the better!



For a typical TEM thin sample:

$$\frac{1}{M_1} \approx \frac{1}{M_2} \approx 0 \qquad \frac{1}{M_3} \neq 0$$

Shapes: Reciprocal Space *vs* Real Space



General rules

"small becomes large"

and

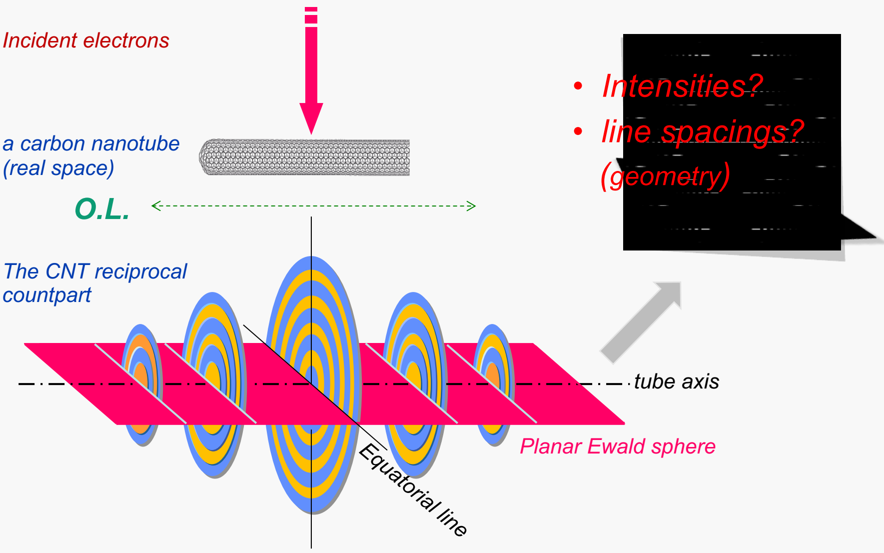
"large becomes small"

Reciprocal principle

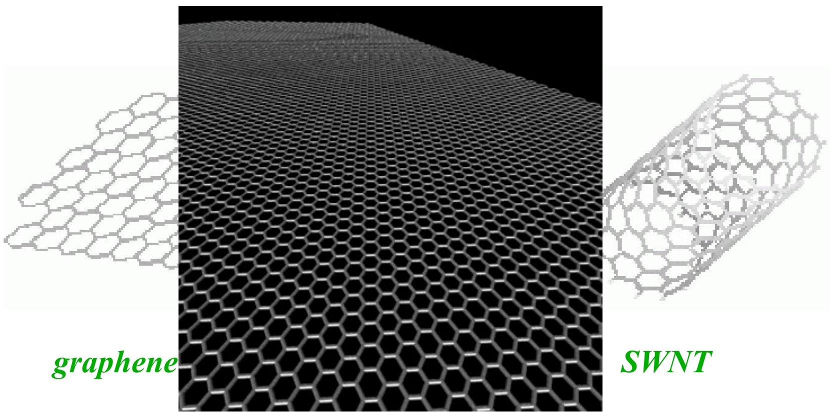
Forming an EDP of a SWCNT in TEM

Normal incidence

--- H Jiang et al, PRB 74 (2006), 035427

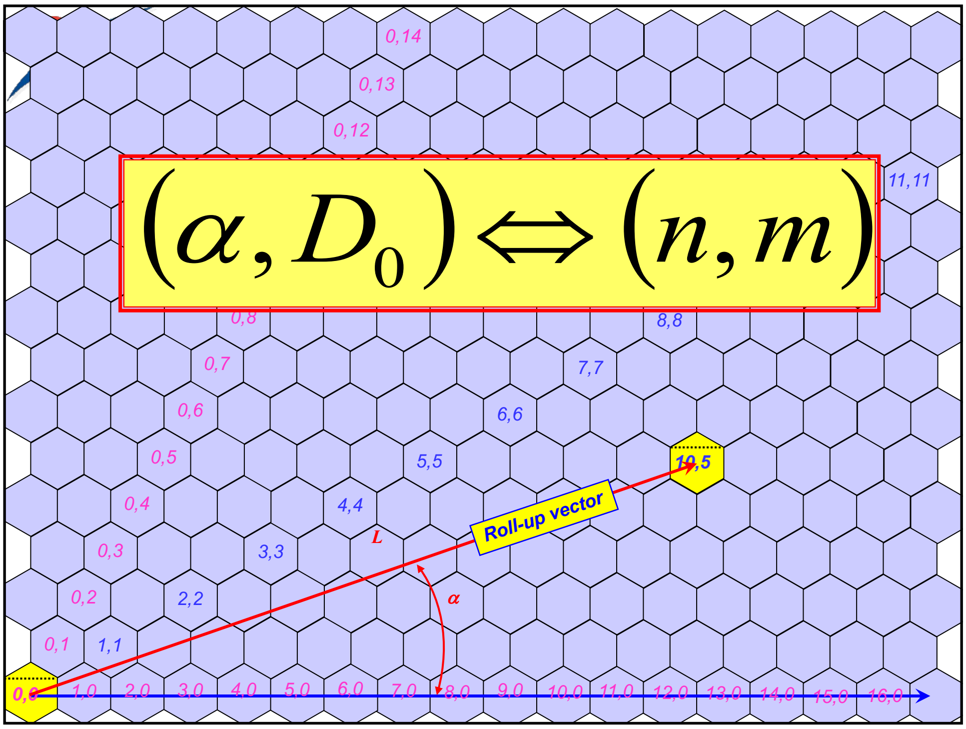


Chirality: Description of CNT structure

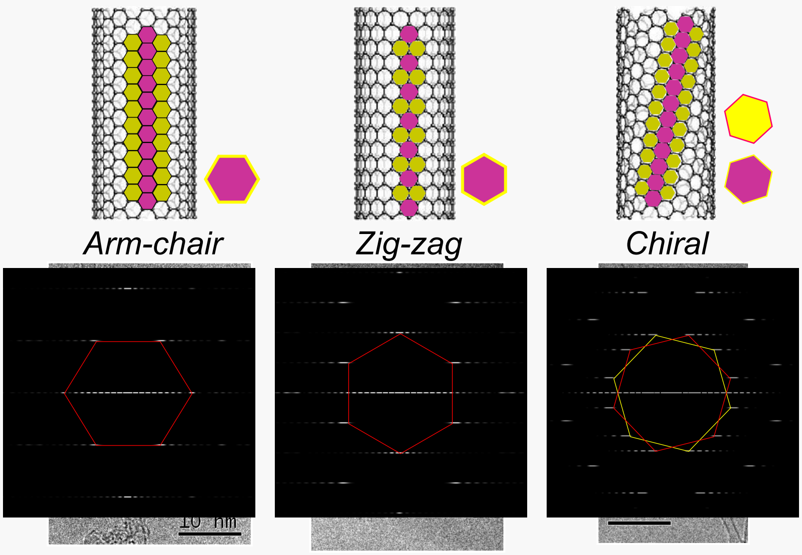


The best way to visualize the property of helicity is to imagine rolling up a piece of graphene sheet into a tube.

(Source: Wikipedia)

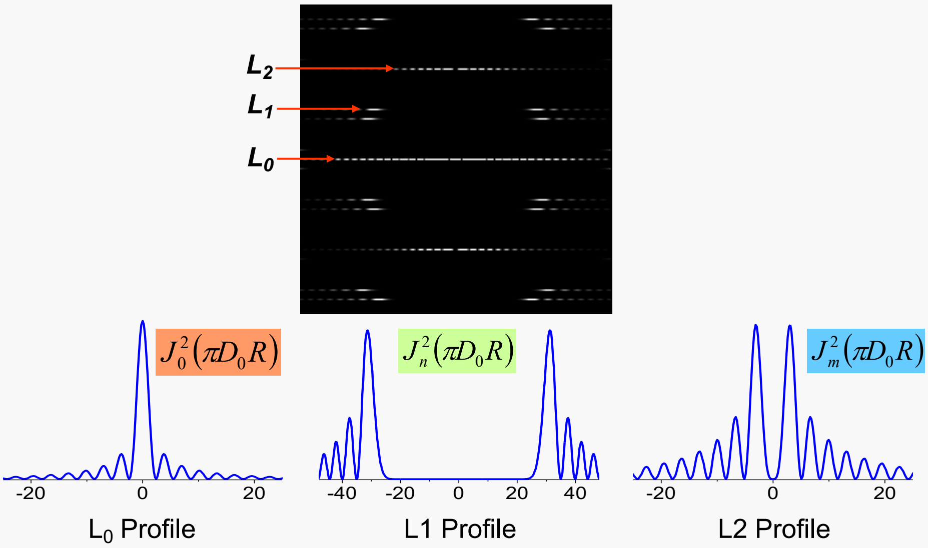


Electron Microscopy for SWCNTs



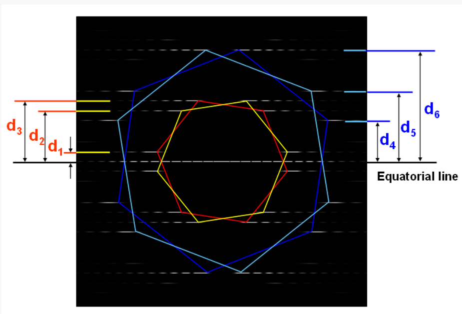
Layer-lines: *by intensity analysis*

--- H Jiang et al, PRB 74 (2006), 035427



Layer-lines: *by geometry analysis*

--- H Jiang et al, Carbon 45 (2007), 662



$$\xi_i = \frac{d_i}{\delta}$$

Layer-line number i	ξ_i^0
1	$\xi_1^0 = \frac{n-m}{\sqrt{3}\pi}$
2	$\xi_2^0 = \frac{n+2m}{\sqrt{3}\pi}$
3	$\xi_3^0 = \frac{2n+m}{\sqrt{3}\pi}$
4	$\xi_4^0 = \frac{\sqrt{3}m}{\pi}$
5	$\xi_5^0 = \frac{\sqrt{3}n}{\pi}$
6	$\xi_6^0 = \frac{\sqrt{3}(n+m)}{\pi}$

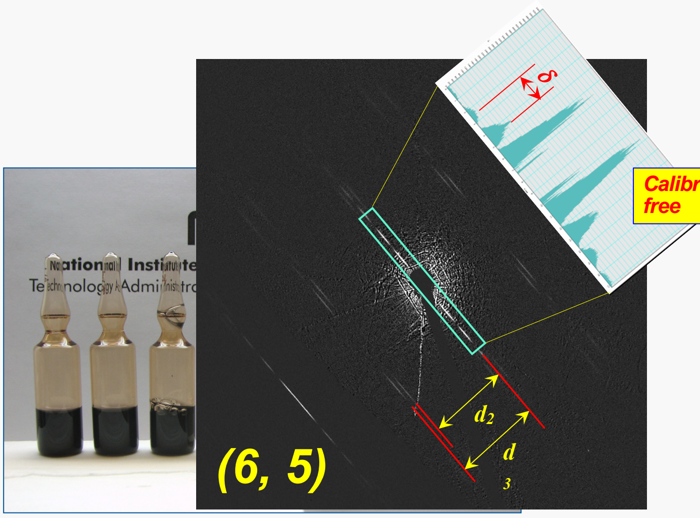
(ξ_2, ξ_3): $n = \frac{\sqrt{3}\pi}{6} \cdot (2\xi_3 - \xi_2)$ $m = \frac{\sqrt{3}\pi}{6} \cdot (2\xi_2 - \xi_3)$

or

(ξ_3, ξ_6): $n = \frac{(3\xi_3 - \xi_6)}{2\sqrt{3}}\pi$ $m = \frac{(2\xi_6 - 3\xi_3)}{2\sqrt{3}}\pi$

Totally calibration-free

Example: *a NIST RM-8281 reference SWCNTs*



$$\xi_i = D_t \cdot d_i = \frac{d_i}{\delta}$$

Calibration free

$$\begin{cases} n = \dfrac{\sqrt{3}\pi}{6} \cdot (2\xi_3 - \xi_2) \\ m = \dfrac{\sqrt{3}\pi}{6} \cdot (2\xi_2 - \xi_3) \end{cases}$$

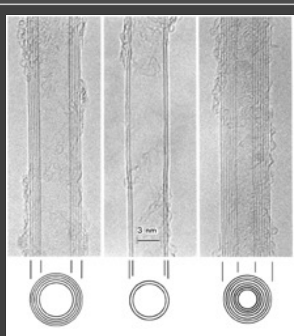
(n, m)	D_t (nm)	α
(6, 5)	0.75	27°

History: *The discovery of CARBON Nanotubes*

Sumio Iijima's web --Nanotubulites --

http://nanocarb.meijo-u.ac.jp/jst/iijima.html

▪THE DISCOVERY of CARBON NANOTUBES



in NEC Co. ＊Sumio Iijima, Nature, 354, 56 (1991).

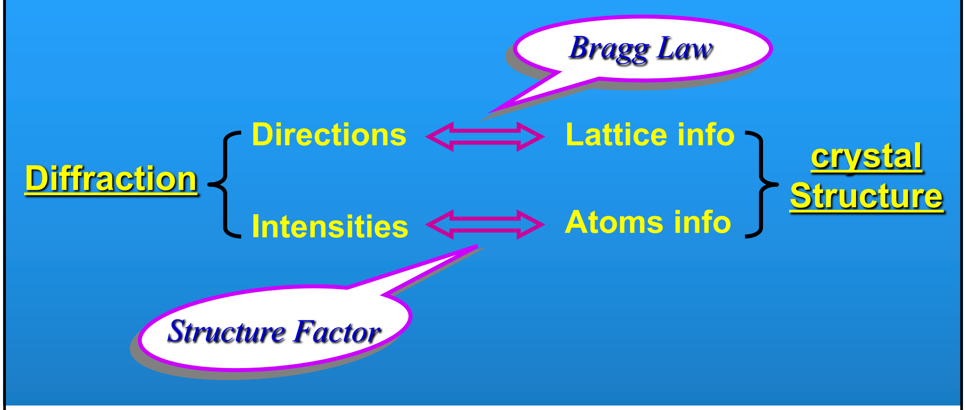
Aalto University Honorary Doctorate, Oct. 10, 2014

Electron diffraction: *things to remember*

1. Electron diffraction takes place in TEM on the focal plane of its objective lens.
2. Diffraction is a reproduction of the sample structure in reciprocal space. Each diffraction spot corresponds to a set of lattice planes (*h*,*k*,*l*) in the crystal.
3. Both the direction and intensity of the diffraction inherit the structure information of your specimen !!

   H O W ?

Electron diffraction: *things to remember*



Purpose of diffraction analysis:

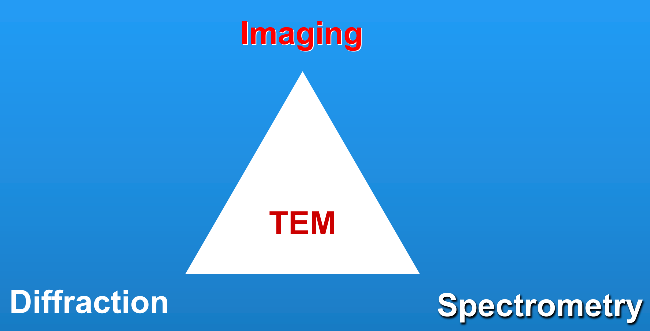
- *From the diffraction direction we get the lattice type information of the structure*
- *By the intensity analysis, we know the atom types, numbers and positions.*

Further thinking about electron diffraction

- Deep learning of Bragg's law for electron diffraction
  - ***Can diffraction always be observed if Bragg's law is satisfied ?***
  - ***If Bragg's law is not (fully) satisfied, can we still observe diffraction ?***

Three angles

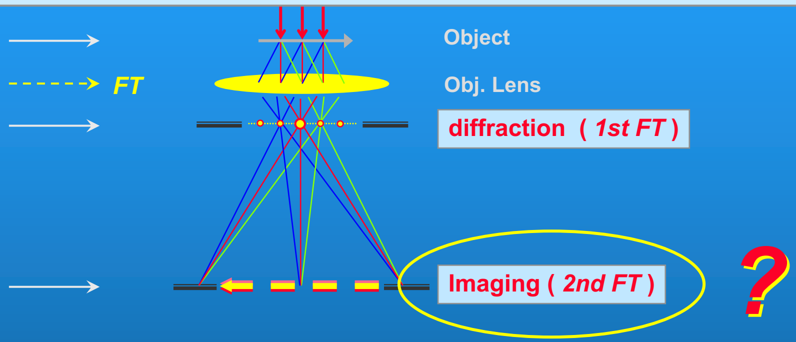
around Electron Microscopy



Overview: Where we are now?

1^{st} FT: *From an object to form a diffraction pattern*

2^{nd} FT: *From the diffraction pattern to form an image*



Questions: *1. What to see from a TEM image?*

2. Can we always trust what we see?

"Imaging" in TEM

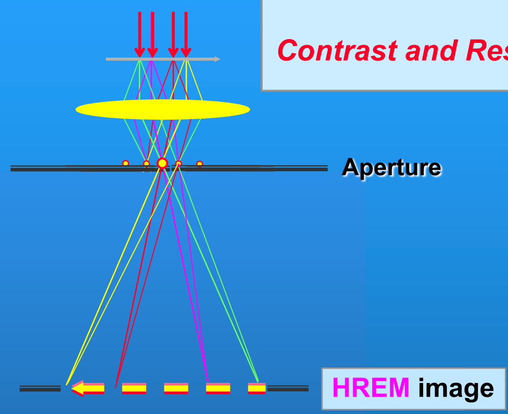
- various imaging modes in TEM
- "contrast"
- "resolution"
- high-resolution TEM imaging

  principle, interpretation, applications

How images form in TEM ?

Two important concepts:

Contrast and Resolution



35

Contrast

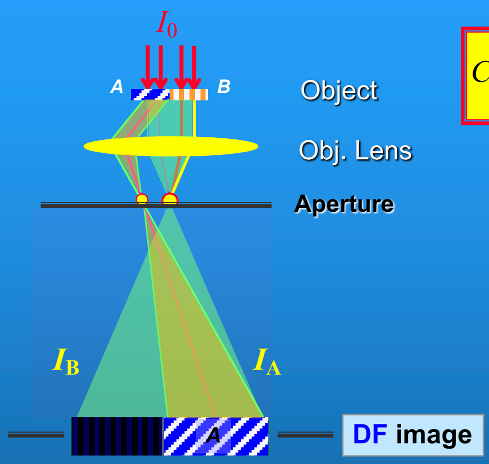
What is contrast ?

*"Contrast" is the appearance of **any difference** in your image.*

What does the difference in the image tell about your sample ?

36

Contrast



$$C = \frac{(I_B - I_A)}{I_B} = \frac{\Delta I}{I_B} > 5-10\%$$

BF mode:

$$I_A = I_0 - I_{scattered}\ , \quad I_B \approx I_0$$

$$C = \frac{I_{scattered}}{I_0}$$

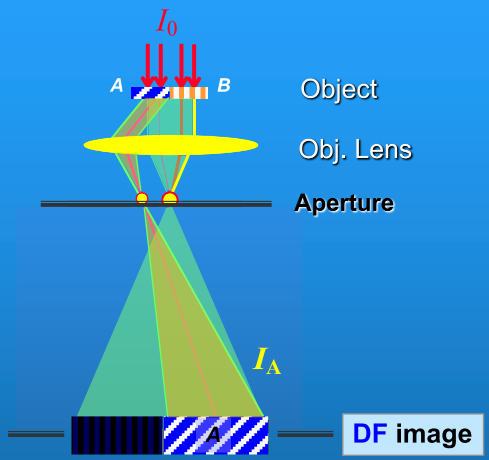
DF mode:

$$I_A = I_{scattered}\ , \quad I_B \approx 0$$

$$C = \frac{I_{scattered}}{I_B} \rightarrow \infty$$

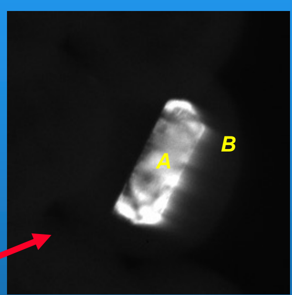
37

Contrast

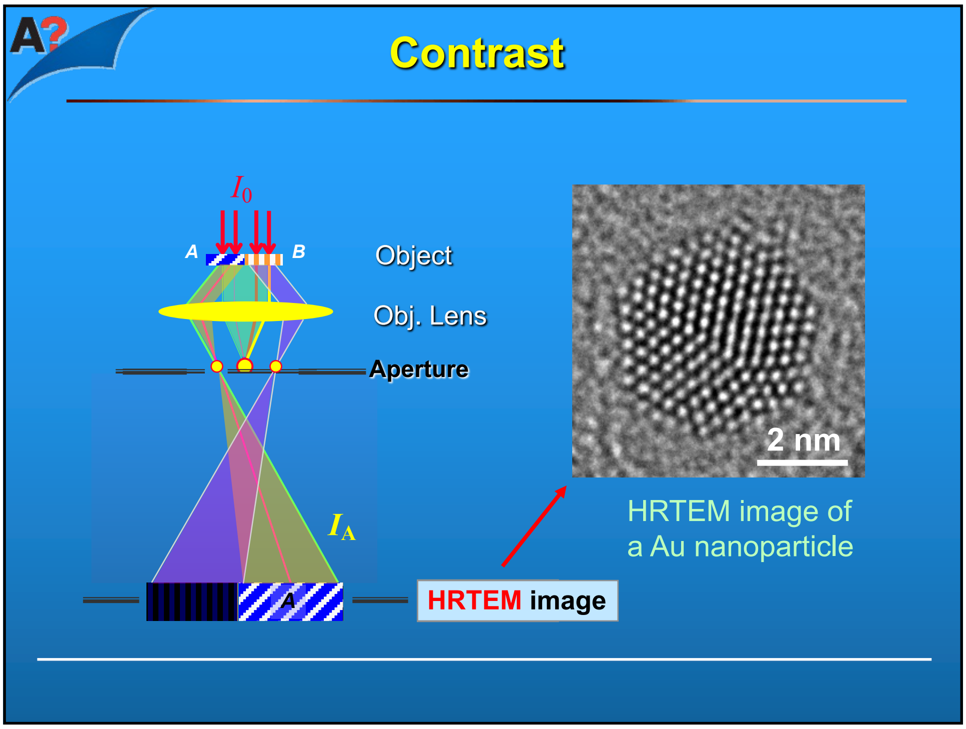


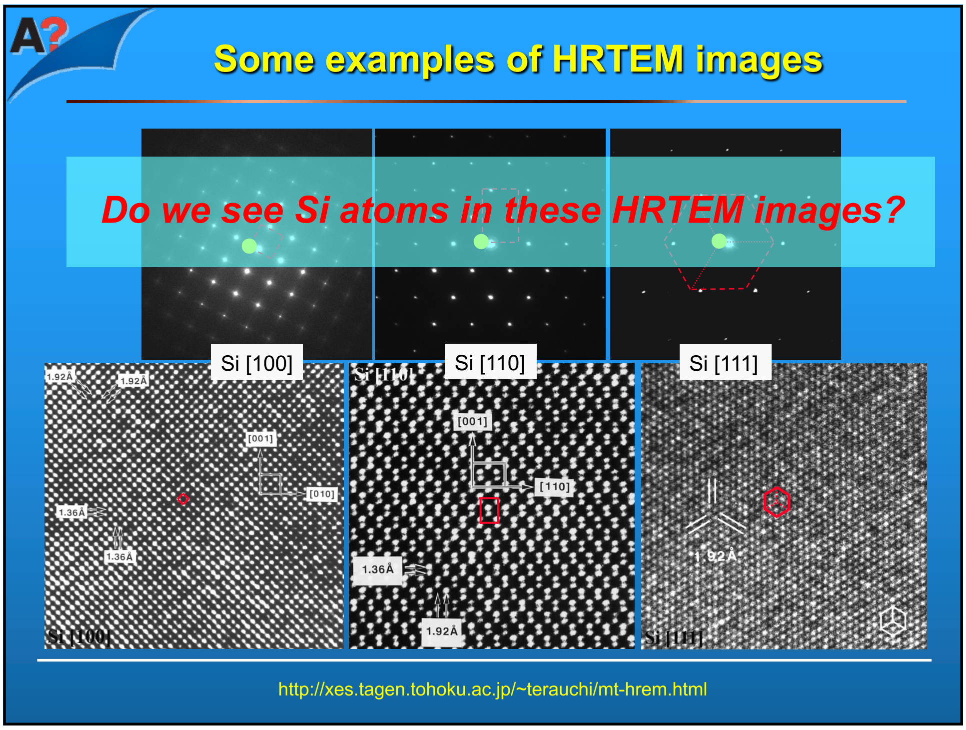
An Example

Feature A: Fe particle
Feature B: SiO_2 coating

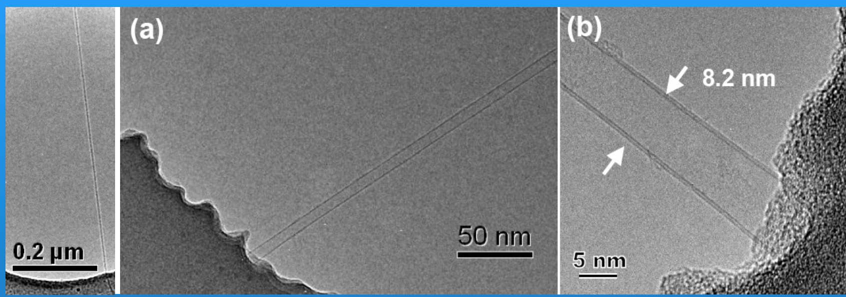


38


Contrast
I0
A
B
Object
Obj. Lens
Aperture
IA
A
HRTEM image
2 nm
HRTEM image of
a Au nanoparticle


Some examples of HRTEM images
Do we see Si atoms in these HRTEM images?
Si [100]
Si [110]
Si [111]
1.92Å
[001]
[010]
1.36Å
[110]
http://xes.tagen.tohoku.ac.jp/~terauchi/mt-hrem.html

An image may mislead us…



We need sufficient resolution to tell us the truth !!!

Resolution

"Resolution" is the smallest feature (distance) in the object that is resoved in your image.

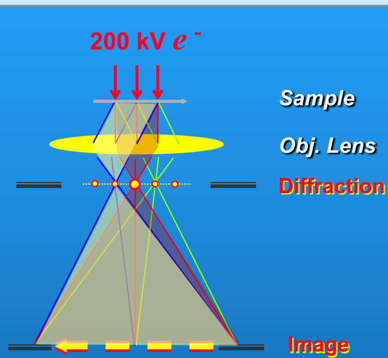
$$2d\sin\theta = n\lambda$$

⇓

$$\theta\uparrow \;\Rightarrow\; d\downarrow$$

⇓

$$resolution\uparrow$$



The resolution of an image depends on how many and what diffraction spots have been allowed for making the image.

Resolutions of typical imaging tools

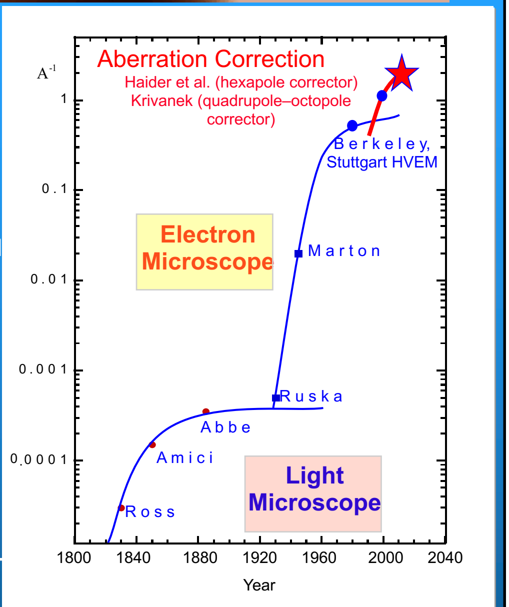
- Resolution of human eyes: ~ 0.1 mm
- Optical microscope: 200 nm
- SEM resolution: ~ 1 nm (optimized)
- TEM resolution: ~ 2 Å (conventional TEM, 200kV)
- HV-TEM: ~ 1 Å (JEOL 1250 kV, Stuttgart 1996)
- Cs-corrected TEM: ~ 1 Å (Philip 200kV, Julich 1997)

1 nm = 10 Å

Where are we NOW?

- Aberration correction removes the barrier that has limited the performance of the electron microscope.
- Successful realization due to advances in computer alignment and electronics.
- Nanoscience and technology needs atomic-level characterization.

Why are we still here?



What limits TEM resolution?

- Limitations of an light microscope ☹

$$d = \frac{0.61\lambda}{n \sin \alpha} \cong \frac{1}{2}\lambda$$

d --- resolution; λ --- light wavelength

Questions:
What limits TEM resolution?

- Electron wave is featured by its short electron wavelength ☺

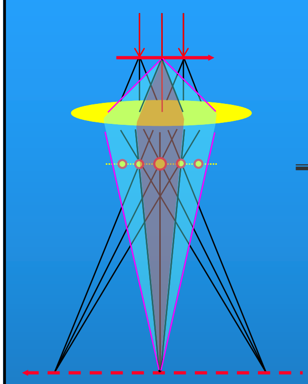
$$\lambda = \frac{12.25}{\sqrt{U(1+0.9788\times10^{-6}U)}} \propto \frac{1}{\sqrt{U}}$$

100 kV: 0.0375 Å
200 kV: 0.0251 Å
300 kV: 0.0197 Å

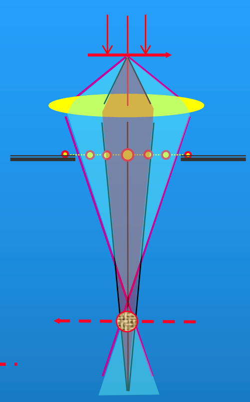
U --- accelerating voltage

45

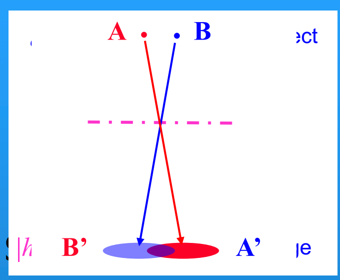
Image formation in TEM
(in real space)



Perfect Lens
(accurate transfer)

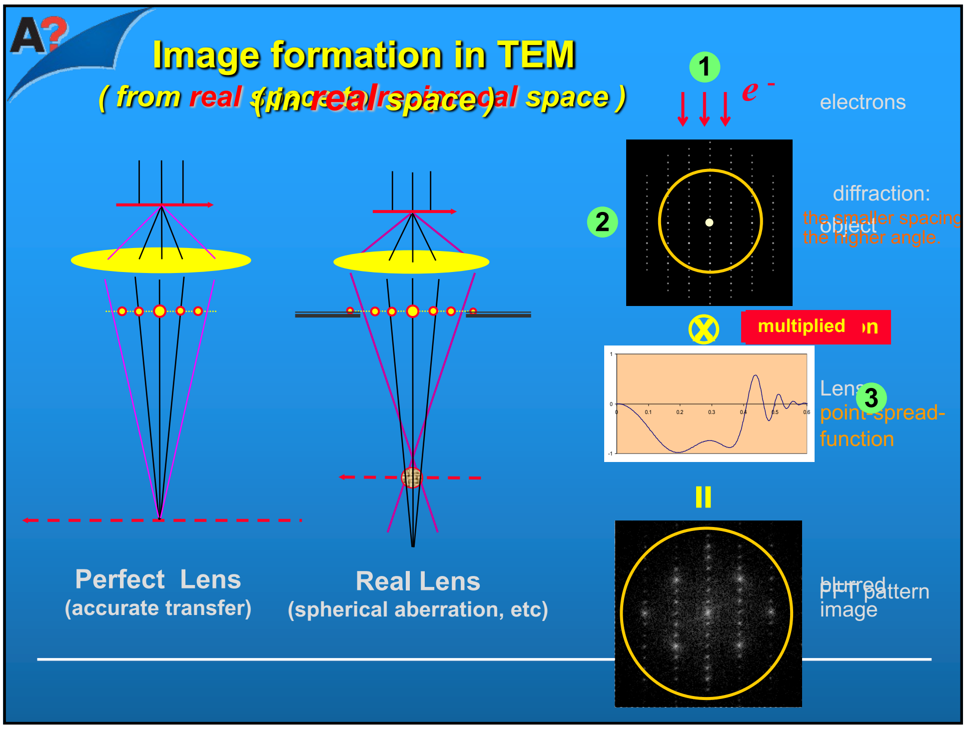


Real Lens
(spherical aberration, etc)



$f\,(x,y)$ specimen function
$\otimes$
$h\,(x,y)$ PSF
=
$g\,(x,y)$ image function

46



1 *Electrons: the messenger*

- **Accelerated elections in vacuum**

$$\text{wavelength}: \quad \lambda = \frac{h}{\sqrt{2meU}} \qquad U: \text{accelerating voltage (200 kV)}$$

Note: 1. non-relativity for simplicity
2. the higher electron energy, the shorter electron wavelength

- **Electrons going through specimen**

$$\lambda' = \frac{h}{\sqrt{2me\left(U + V(x,y,z)\right)}} \qquad V(x,y,z): \text{specimen inner potential}$$

- **Phase shift of electrons carries structural info of the specimen**

$$d\phi \approx \sigma \int V(x,y,z)dz = \sigma V_t(x,y) \qquad V_t(x,y): \text{integrated potential in the z-direction}$$

Note: the phase shift depends ONLY on 2D projection of the object structure;
The electrons carry the structure info after passing the specimen

Note: $\sigma = \pi/\lambda E$ is a small interaction constant.

2 *Object: the specimen function*

- The specimen function is given by

$$f(x,y)=\exp(-id\phi)=\exp[-i\sigma V_t(x,y)]$$

Note: no absorption is considered here for simplicity

Phase-object approximation: a specimen is represented as a **phase object**

- **Weak-phase-object approximation (WPOA) :**

$$f(x,y)=1-i\sigma V_t(x,y) \quad \text{if} \quad V_t(x,y) << 1$$

Thin sample!!!
Specimen potential is WEAK!!

In general, the WPOA only holds for VERY thin specimens.

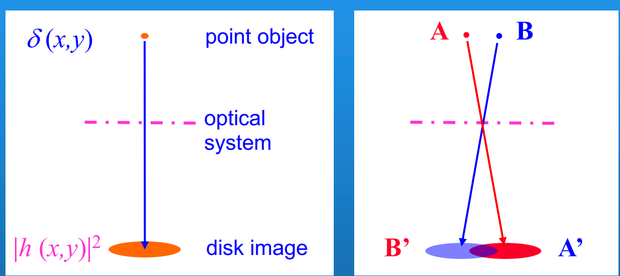
49

3 *Lenses: the point-spread-function (PSF)*

- **Mathematical description of HREM image formation:**

in real space: $g(x,y)=f(x,y)\otimes h(x,y)$

REMEMBER*: an image is not just the structure of your sample but….*



$f(x,y)$	specimen function
$\otimes$	
$h(x,y)$	PSF
$=$	
$g(x,y)$	image function

50

3 Lenses: contrast-transfer-function (CTF)

- Mathematical description of HREM image formation:

in reciprocal space: $G(u,v) = F(u,v) \cdot H(u,v)$

After Fourier transform ($\mathscr{F}$) of the previous equation, a convolution in real space gives multiplication in reciprocal space.

$G\ (u,v)$ gives the Fourier components of an HREM image

$F\ (u,v)$ is the structure factor of the specimen, seen as diffraction

$H\ (u,v)$ is the Fourier transform of PSF, *describing how information (contrast) in reciprocal space is transferred into the image.*

H (u,v) is the Contrast Transfer Function (CTF).

3 The objective lens (III)
the factors contributing to CTF

- CTF is determined by:

$$H(\mathbf{u}) = A(\mathbf{u})E(\mathbf{u})B(\mathbf{u})$$

A (u): the aperture cut-off function, governed by the radius of the aperture
E (u): the envelope function, describing the attenuation of the wave
B (u): the aberration function, coming from the aberration of the lens

B (u) is the only term we are interested in for this moment!!

$$B(\mathbf{u}) = \sin \chi(\mathbf{u})$$
$$\chi(\mathbf{u}) = \pi \Delta f \lambda u^2 + \frac{1}{2}\pi Cs \lambda^3 u^4$$

Δf : the focusing condition;
Cs: the spherical aberration coefficient; a constant for a particular lens.

Δf is the key parameters to TUNE image contrast.

An animation show of CTF