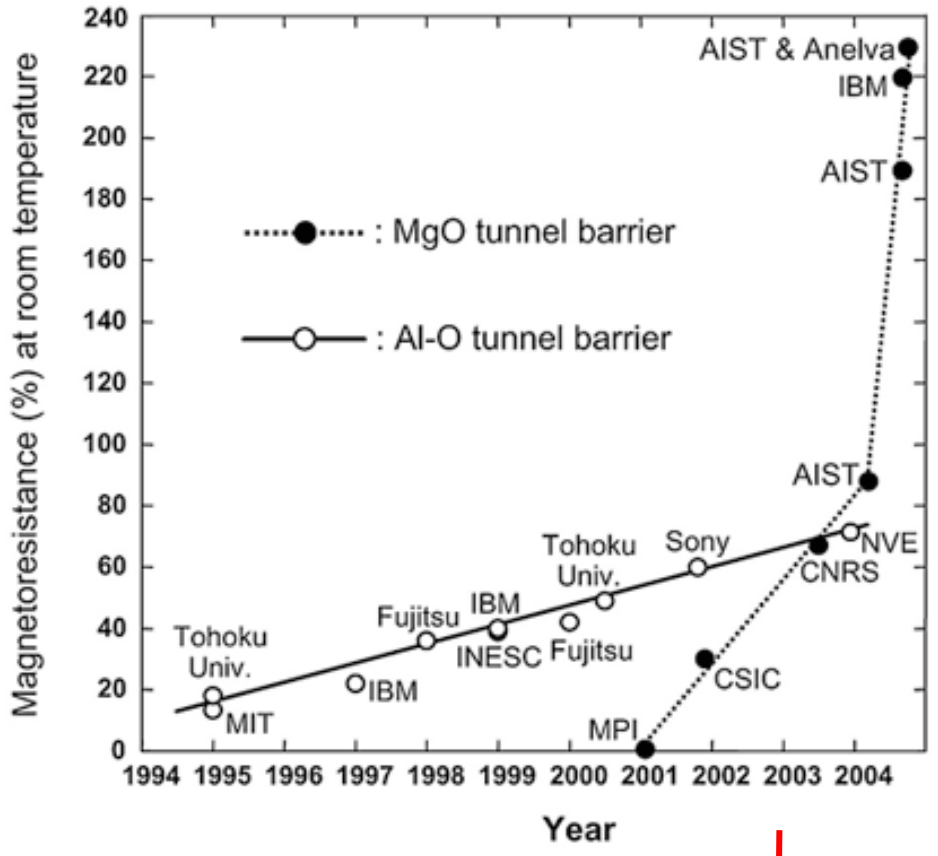
History of improvement in performance of MTJ devices (magnetoresistance ratio)



We need to check the crystallographic structure of our media:

a) on a large scale

b) at different depths

c) in real time

Electron diffraction

Amorphous | **Single crystal**

Increased performance by improving and controlling the crystallographic order at the interfaces

Structural analysis: Electron diffraction

Due to the wave-particle duality, the electron beam may be equally regarded as a succession of electron waves (plane waves) incident normally to the sample. These waves will be scattered by regions of highly localized electron density, i.e. the atoms, acting as point scatters.

The wavelength of the electrons is given by the de Broglie relation :

$\lambda = h / p$ (where p = electron momentum)

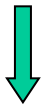
Now , $p = m v = (2 m E)^{1/2}$ with $E = eV$

$$\lambda = \frac{h}{\sqrt{2 m E}}$$ non-relativistic approximation

h Planck constant = 6.6 10^{-34} J s
m electron mass = 9.1 10^{-31} kg
v electron velocity
E electron kinetic energy
e electron charge = 1.6 10^{-19} C

Example:

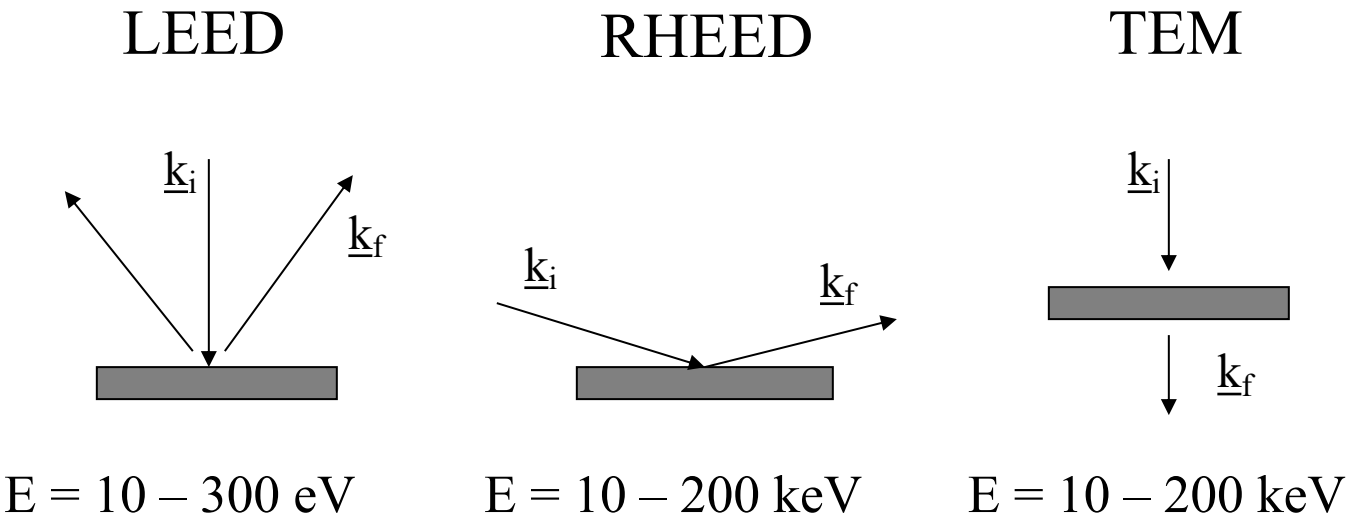
1) Electron energy = 20 eV -> Wavelength = 2.7 Å
2) Electron energy = 200 eV -> Wavelength = 0.87 Å



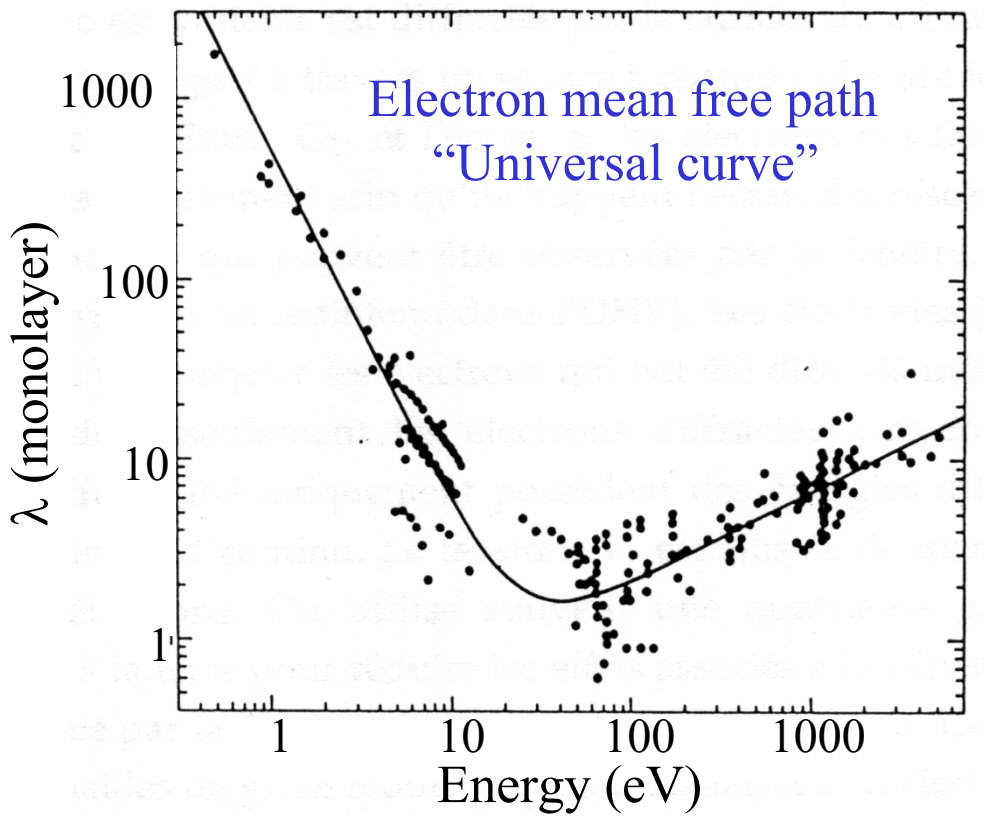
λ comparable to the atomic spacing

Structural analysis: Electron diffraction

LEED: Low Energy Electron Diffraction
RHEED: Reflection High Energy Electron Diffraction
TEM: Transmission Electron Microscopy



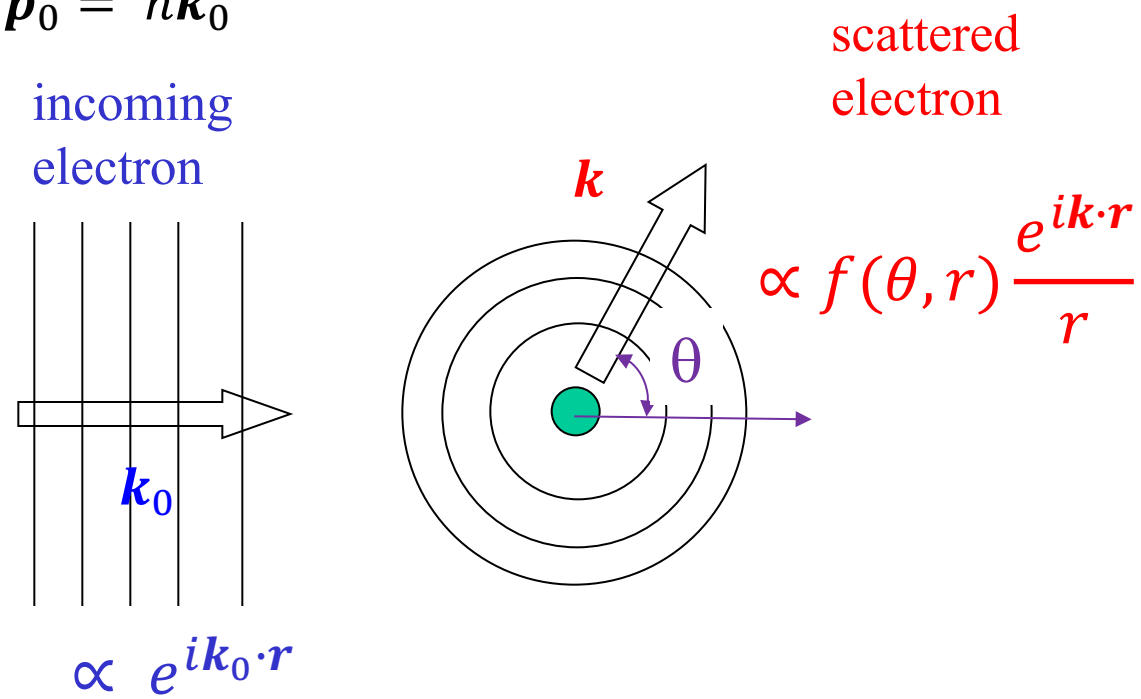
Electron energy and geometry
are chosen considering the electron mean free
path and the spatial resolution



Note: Electron energy = 2 eV → Wavelength = 8.5 Å
The hypothetical "RLEED" would have low resolution

Plane wave scattering (single scatterer)

$\boldsymbol{p}_0 = \hbar \boldsymbol{k}_0$

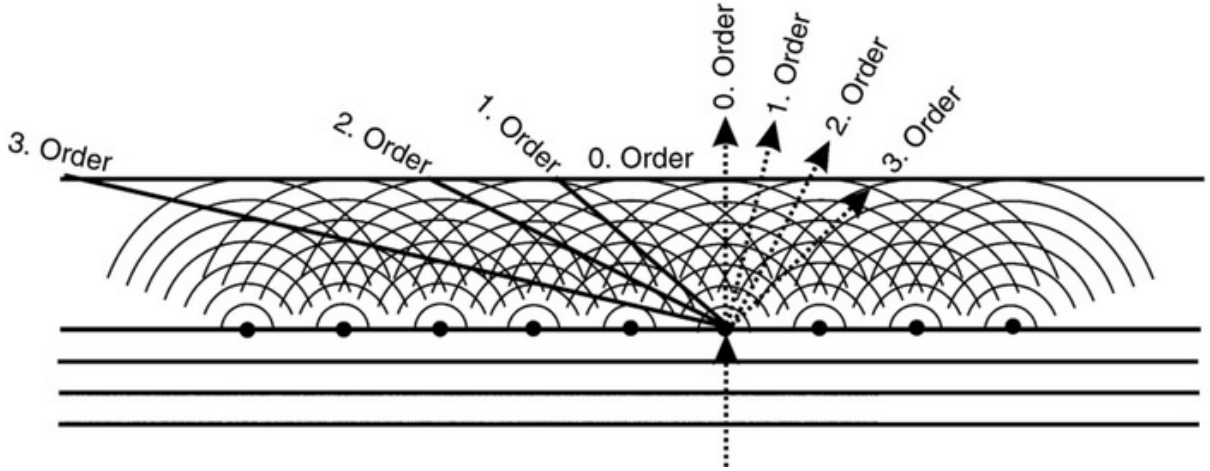


$f(\theta, r)$ is the atomic form factor:
it reflects the atomic electron density

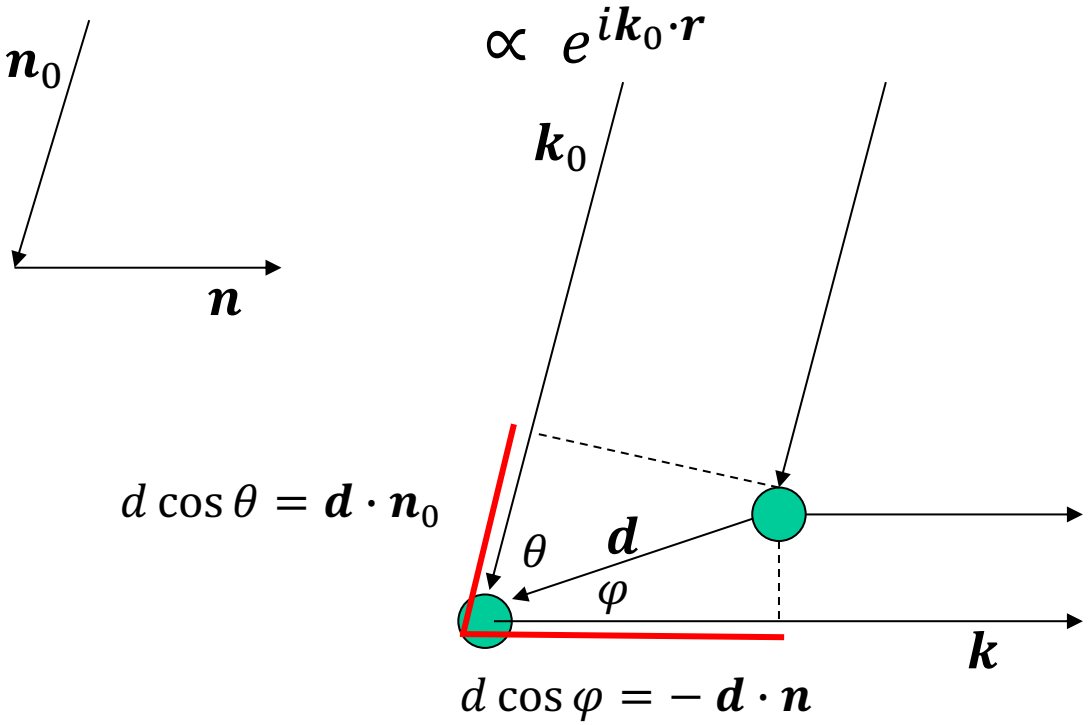
In the case of many scatter points the scattered wave is given by:

$$\propto \sum_j f_j\,(\theta, r_j) e^{i\boldsymbol{k} \cdot \boldsymbol{r}_j}$$

Diffraction spots are the result of the interference pattern generated by the spherical waves scattered by the atoms in the crystal lattice



Two points scattering



$$\boldsymbol{k}_0 = \frac{2\pi}{\lambda}\boldsymbol{n}_0$$

$$\boldsymbol{k} = \frac{2\pi}{\lambda}\boldsymbol{n}$$

1) Elastic scattering:
incident and reflected rays have the same wavelength λ
$|\boldsymbol{k}| = |\boldsymbol{k}_0|$

2) Constructive interference:
difference in path length = multiple of wavelength
$d\cos\theta + d\cos\varphi = \boldsymbol{d}\cdot(\boldsymbol{n} - \boldsymbol{n}_0) = m\lambda$
or
$\boldsymbol{d}\cdot(\boldsymbol{k} - \boldsymbol{k}_0) = 2\pi m \qquad m \in \mathbb{Z}$

3D Bravais lattice

Constructive interference verified by all the lattice points,
$\boldsymbol{R} \cdot (\boldsymbol{k} - \boldsymbol{k}_0) = 2\pi m$ with $\boldsymbol{R}$ Bravais lattice vector, $m \in \mathbb{Z}$

$\boldsymbol{k} - \boldsymbol{k}_0 = \boldsymbol{G}$
$\boldsymbol{G}$ is a reciprocal lattice vector

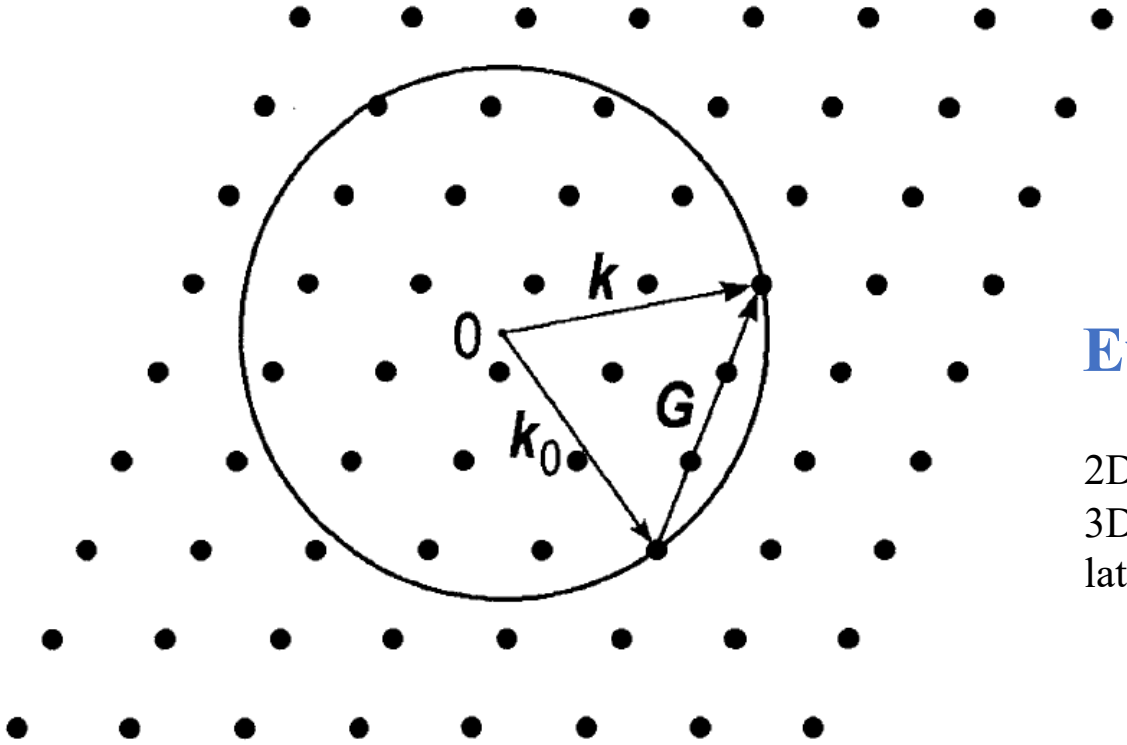
$$\boldsymbol{G} = \sum_i m_i \boldsymbol{a}_i^*, \qquad \boldsymbol{a}_1^* = 2\pi \frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{\boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3}$$

$$\boldsymbol{a}_i \cdot \boldsymbol{a}_j^* = 2\pi\, \delta_{ij}$$

Laue diffraction condition

$$|\boldsymbol{k}| = |\boldsymbol{k}_0|$$

$$\boldsymbol{k} - \boldsymbol{k}_0 = \boldsymbol{G}$$



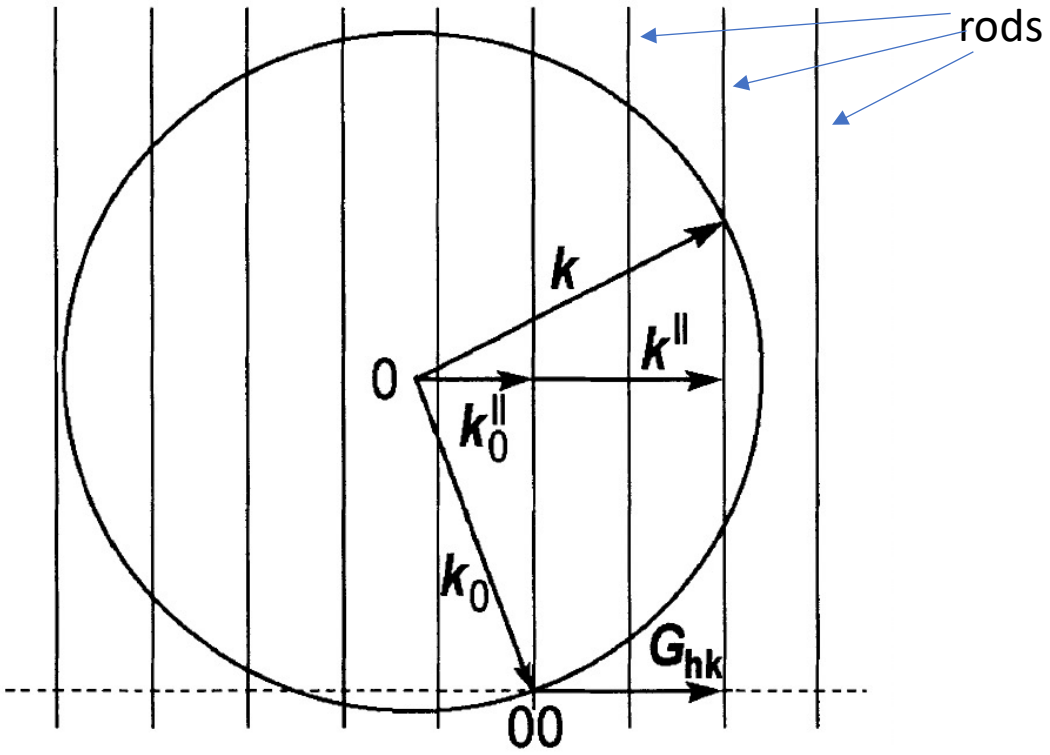
Ewald sphere

2D plane in a 3D reciprocal lattice

2D case: surface scattering

At the surface, the bulk periodicity is truncated and the Laue equation (3 equations) reduces to 2 equations concerning the components of the incident and scattered wave vectors parallel to the surface.

In contrast to the 3D reciprocal lattice points, here reciprocal lattice rods perpendicular to the surface are attributed to every 2D reciprocal lattice point. (An ideal 2D lattice can be conceived as a 3D lattice with infinite periodicity in the normal direction. This will lead to infinitely dense reciprocal lattice points along the normal direction, thus forming rods.)



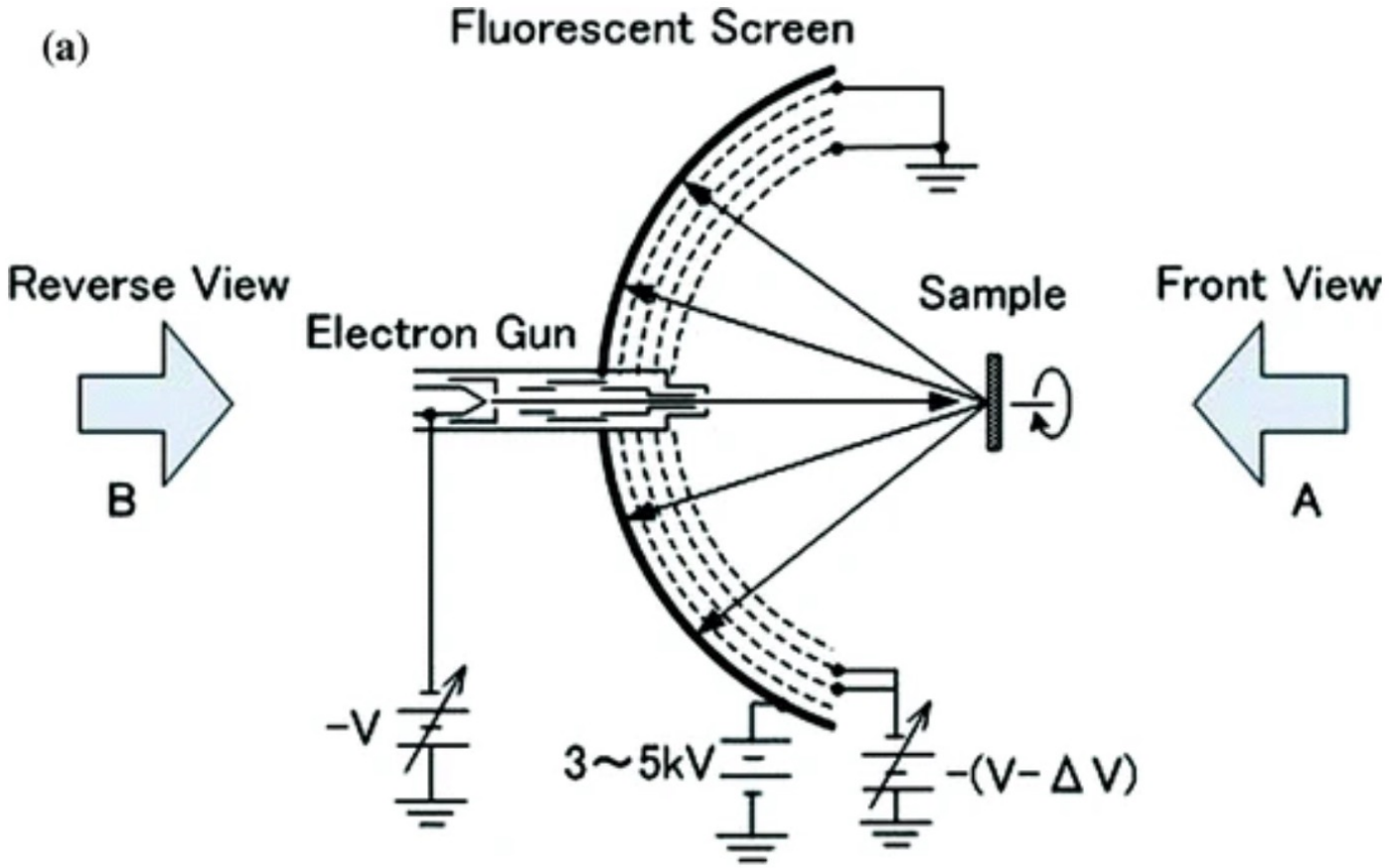
- Scattering from a surface lattice leads to diffracted beams for all incident wave vectors
- Intensity will be higher in correspondence of the points of the bulk reciprocal lattice (limited mean free path for electrons)

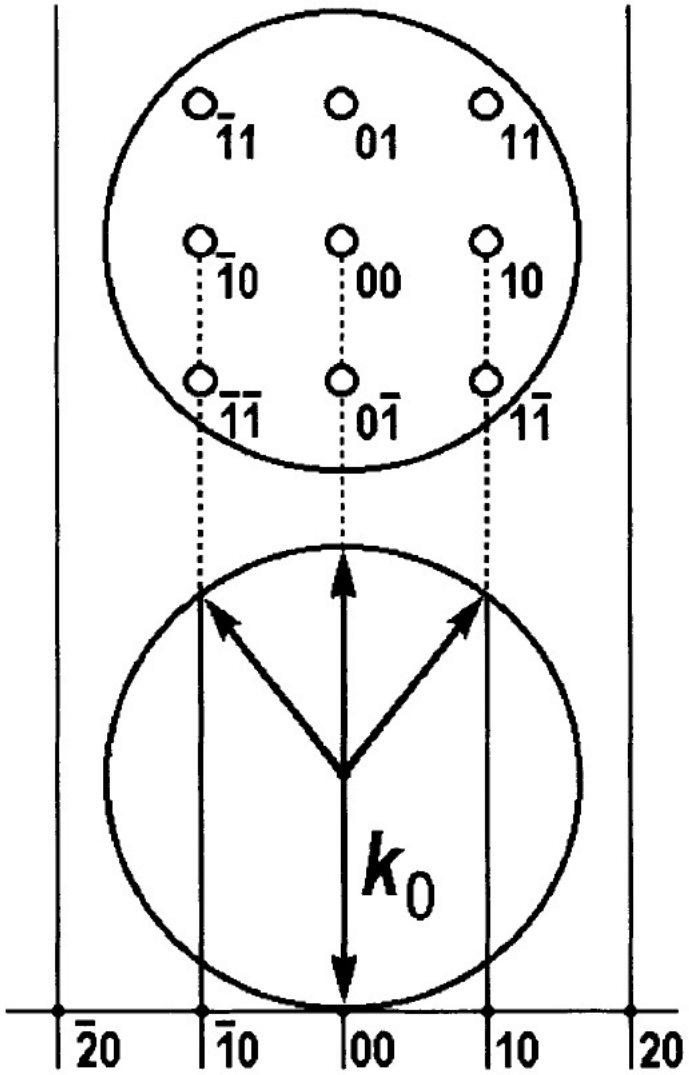
$$\boldsymbol{k}_{\parallel} - \boldsymbol{k}_{0\parallel} = \boldsymbol{G}_{\mathrm{hk}}$$

with $\boldsymbol{G}_{\mathrm{hk}}$ a vector of the 2D reciprocal lattice

The diffraction pattern is a map of the 2D reciprocal lattice

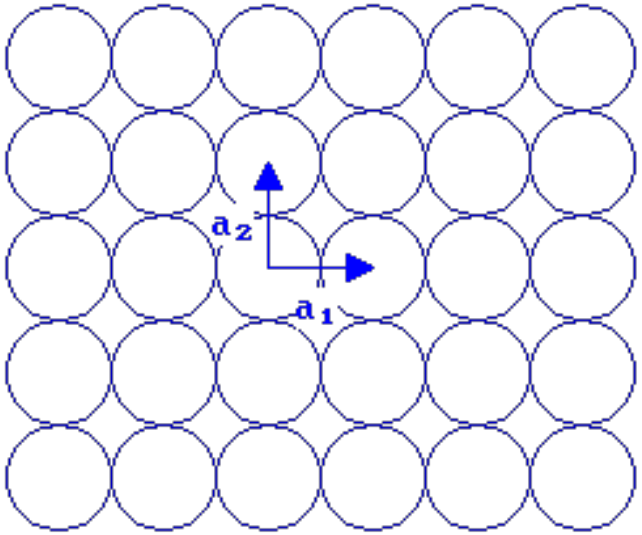
LEED setup

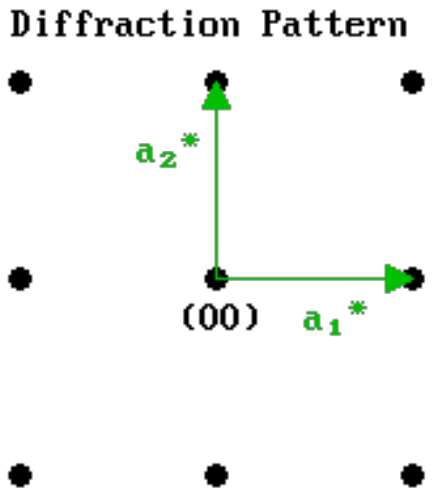




spot labeling →
hk index as for reciprocal lattice vectors

fcc(100)





$\boldsymbol{a}_1^*$ and $\boldsymbol{a}_2^*$ are the primitive vectors in the reciprocal space

$$\boldsymbol{a}_i \cdot \boldsymbol{a}_j^* = 2\pi\,\delta_{ij}$$

$$\boldsymbol{a}_1^* = \frac{2\pi}{a_1}\frac{\boldsymbol{a}_1}{a_1}$$

$$\boldsymbol{a}_2^* = \frac{2\pi}{a_2}\frac{\boldsymbol{a}_2}{a_2}$$

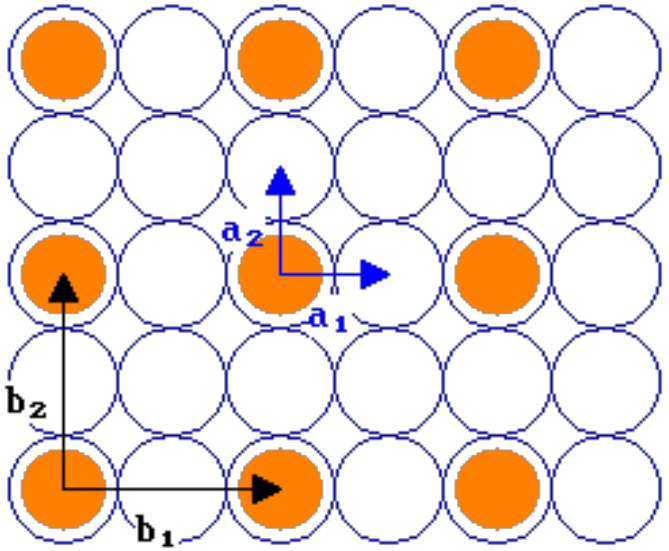
(0,0) corresponds the reflected beam along the surface normal

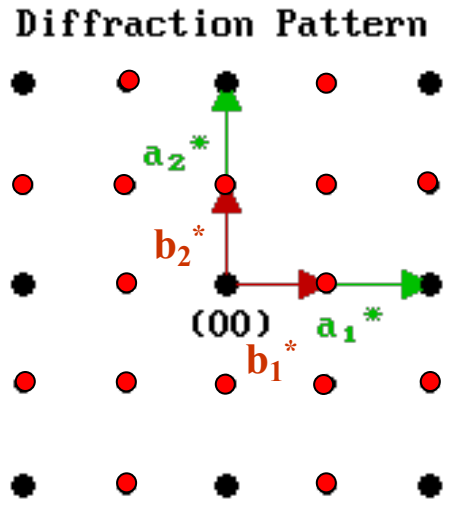
$\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are the primitive vectors in the real space

fcc(100) (2x2)

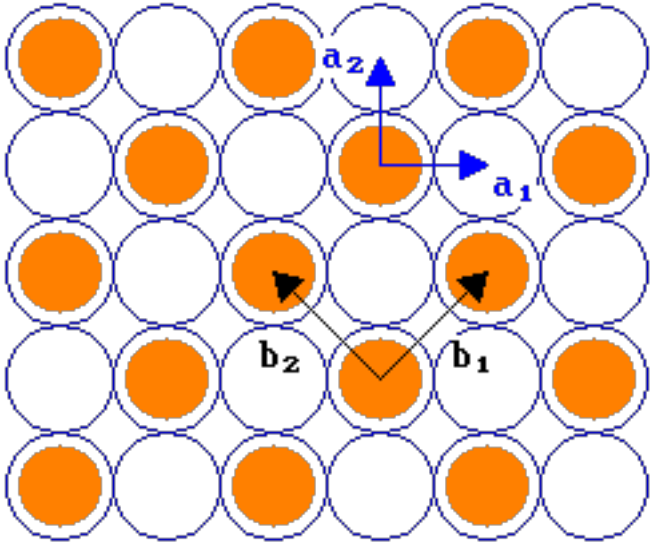
Orange disks represents adsorbate atoms: their periodicity is responsible of the red spots in the diffraction pattern

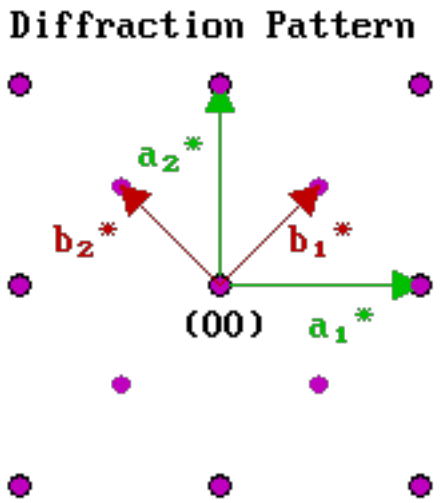
2x2 means that the adsorbates have a double periodicity in both directions with respect to the substrate





fcc(100) c(2x2)





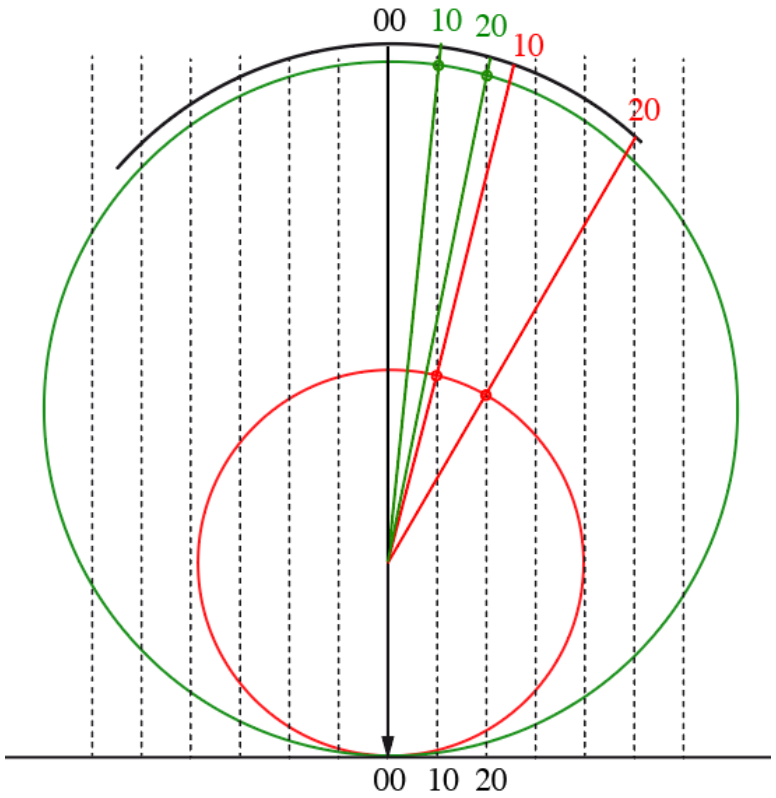
The surface unit cell is rotated by 45° with respect to the substrate one:
$\sqrt{2}$ x$\sqrt{2}$ R45°

However, it is usual to describe this structure as c(2x2), where “c” stays for “centered” to indicate that there is an additional atom in the center of the 2x2 cell. (This kind of nomenclature is used especially for structures with square or rectangular symmetry).

LEED movie

diffraction pattern recorded as a function of the energy of the incident electrons

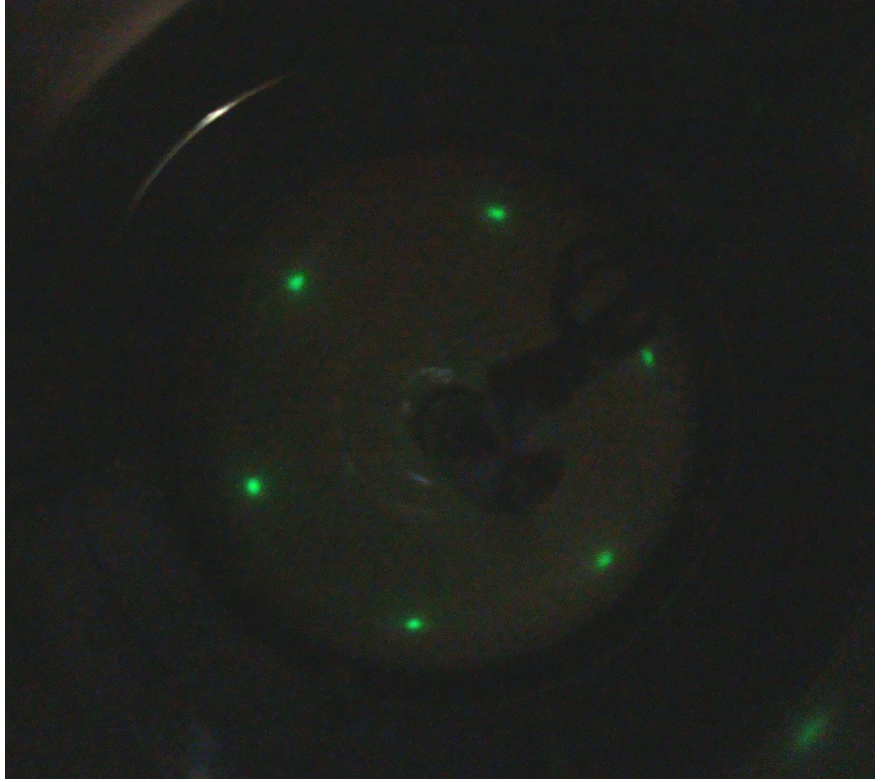
$$E = \frac{\hbar^2 k^2}{2m}$$



https://www.ocivm.com/_low_energy_electron_diffraction.html

Graphene/Ir(111)

Ir(111)

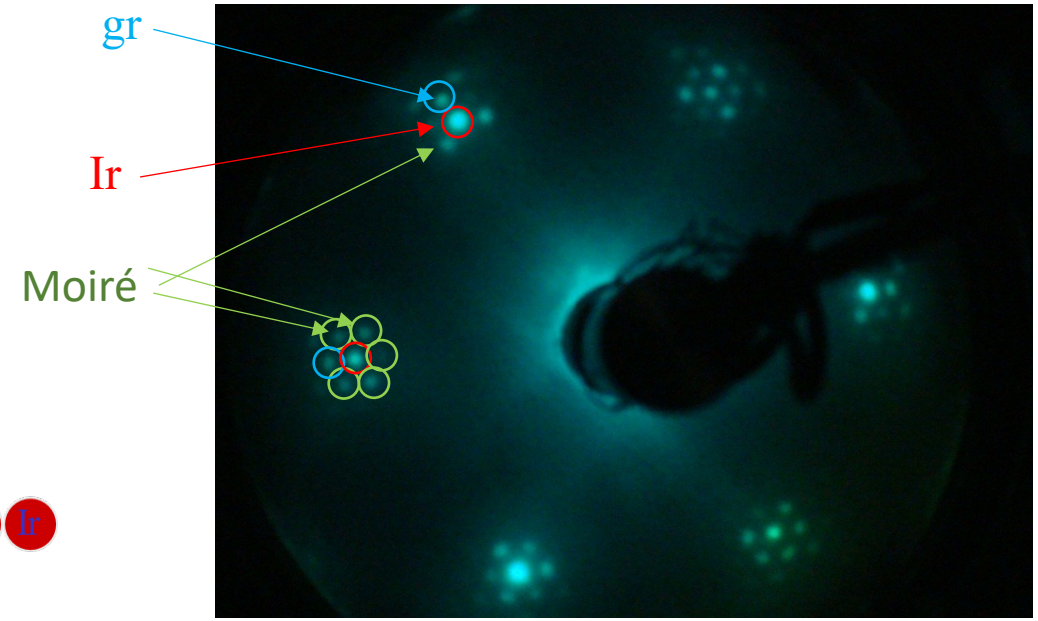


Graphene/Ir(111): modulated surfaces

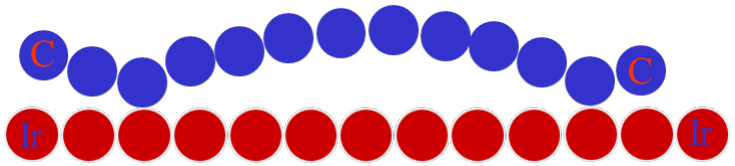
Electrons scattered by
the potential due to :

1) Ir atoms
2) C atoms
3) C-Ir bond formed at sites with minimum C-Ir separation (Moiré periodicity)

satellite reflections
(only the reflections
surrounding the main
reflections are visible)

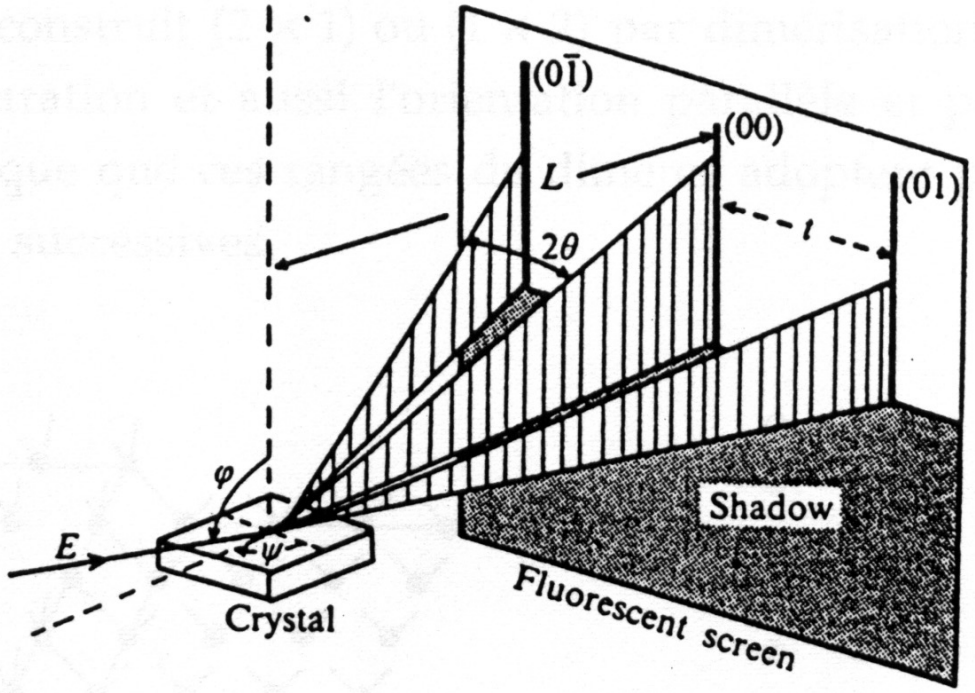


a_{Ir} = 0.27 nm
a_c = 0.245 nm



10 x 10 C atoms over
9 x 9 Ir atoms

RHEED



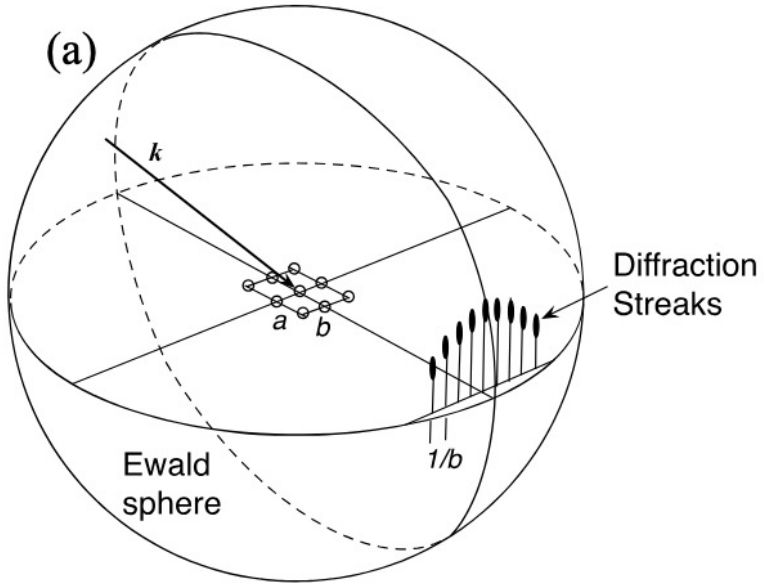
- (0,0) is the specular bar i.e. pure elastic reflection
- Lateral bars are the diffraction ones

Electron penetration depth λ = 10-30 nm at 40 keV for normal incidence

Surface sensitivity if $\cos \varphi = d/\lambda$ with d = 1- 2 atomic layers

or

φ about 89°

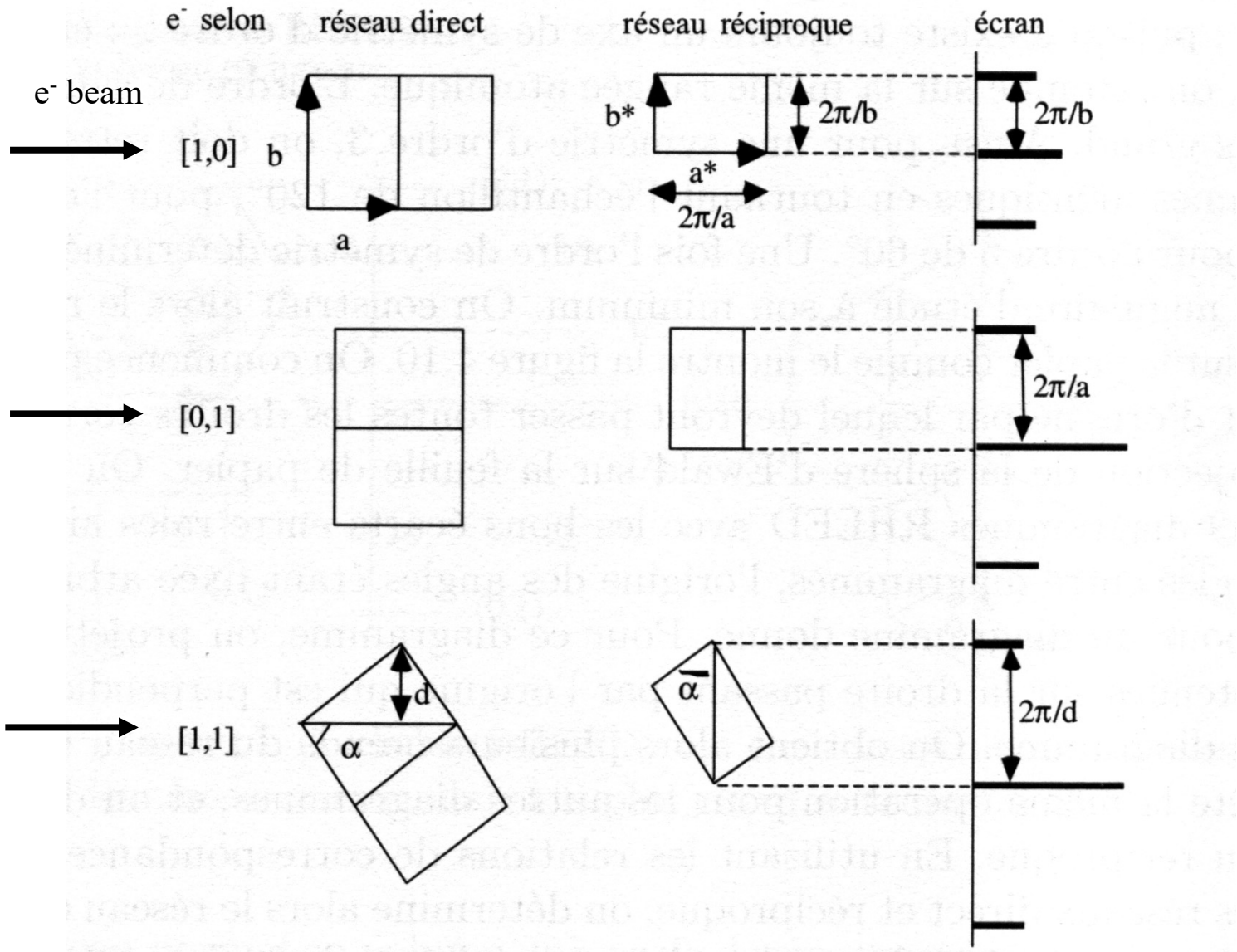


Due to the grazing incidence, the surface is seen as continuous along the incidence direction (no diffraction) and consequently only the periodicity perpendicularly to the incidence direction is detected

Because of the high energy, the intersection of the nearly flat Ewald sphere and rods occurs along their length, resulting in a streaked diffraction pattern

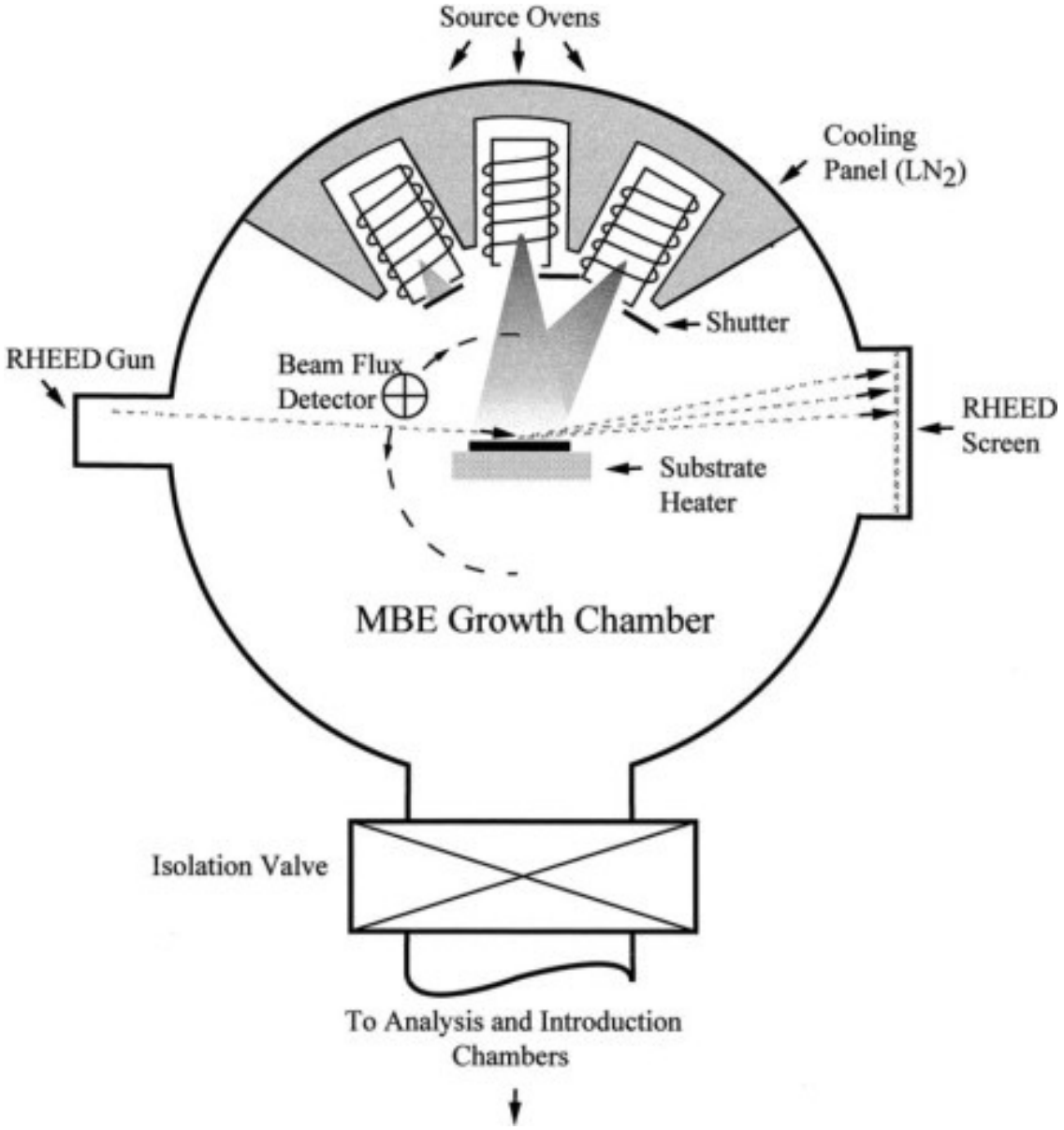
For an overview see also doi.org/10.1533/9780857094957.1.3

RHEED spectrum



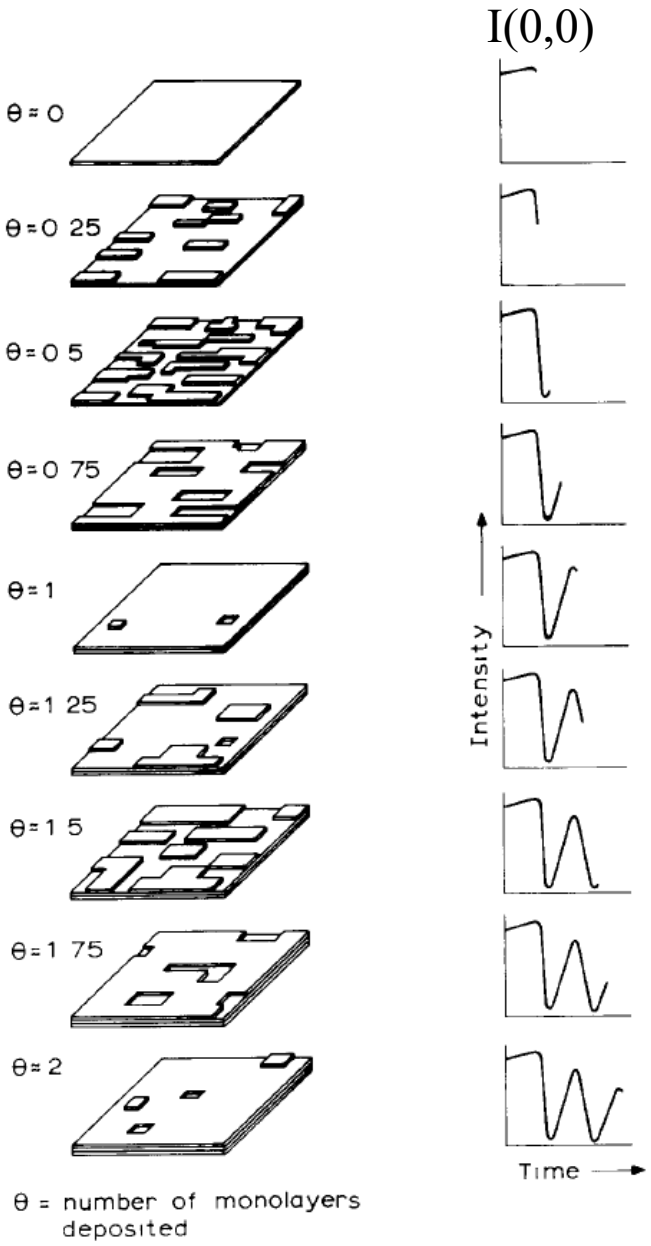
At least measurements at two different angles are needed to get the 2D reciprocal lattice

RHEED for growth control



Evolution of the diffraction spots / strikes intensities are used to check the evolution of the crystal structure

RHEED for growth control



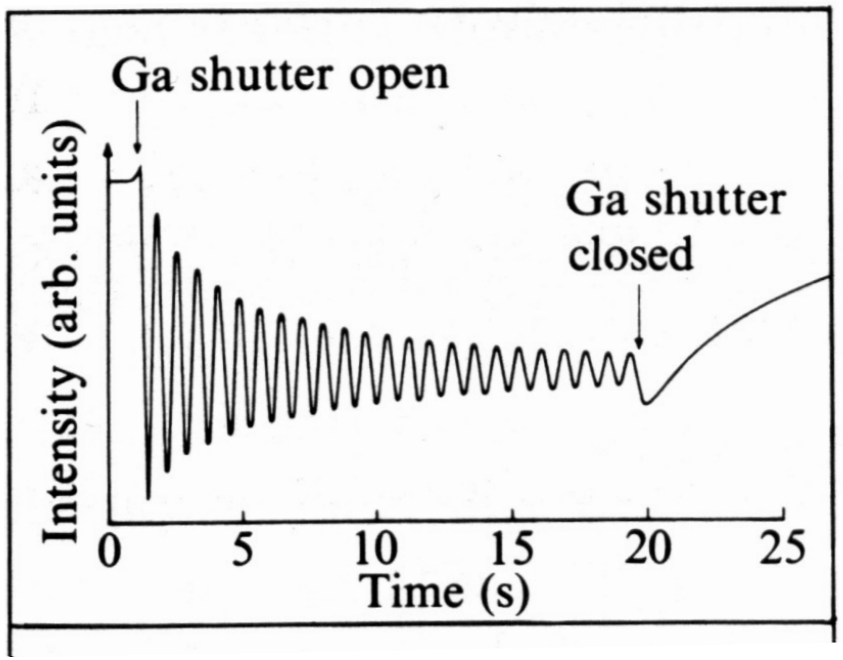
Surface Science **168,** 423-438 (1986)

Maximum roughness at 0.5 ML during layer by layer growth

- Oscillation period of I(0,0): 1 atomic layer
- Intensity: decreasing with number of layers

⇩

Imperfect layer-by-layer growth



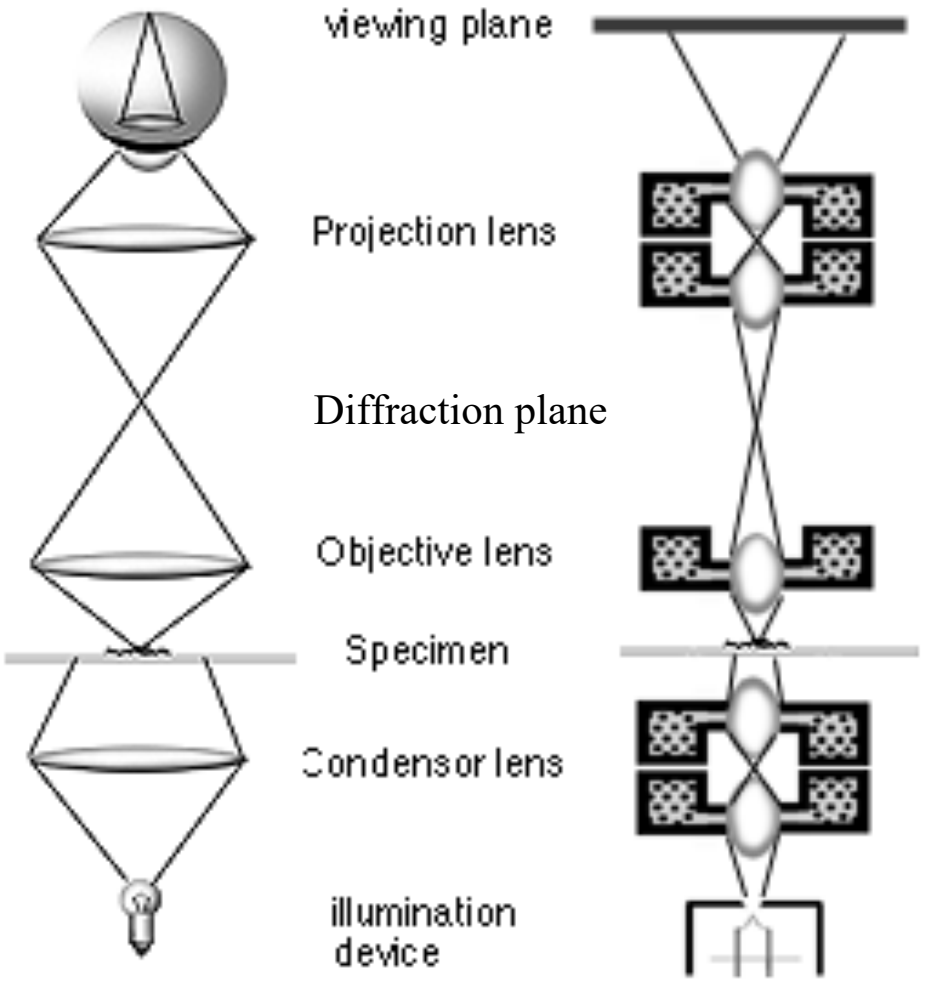
Growth of GaAs(100) by Molecular Beam Epitaxy (MBE)

Neave *et al.* Appl. Phys. **A 31**, 1 (1983)

The intensity oscillations of the specular spot (0,0) can be used to measure the number of deposited layers and surface roughness

Transmission Electron Microscope (TEM)

Conceptually is identical to an optical microscope where electrons are used in place of photons



photons

electrons

$E = 75$ keV -> $\lambda = 0.05$ Å

Theoretical resolution about hundred thousands times better than that of light.

Transmission Electron Microscope (TEM)

Due to the limited penetration depth of electrons in solids, the samples should be very thin: the acceptable thickness is 10-100 nm for conventional microscopes with accelerating voltages of 50-200 keV.

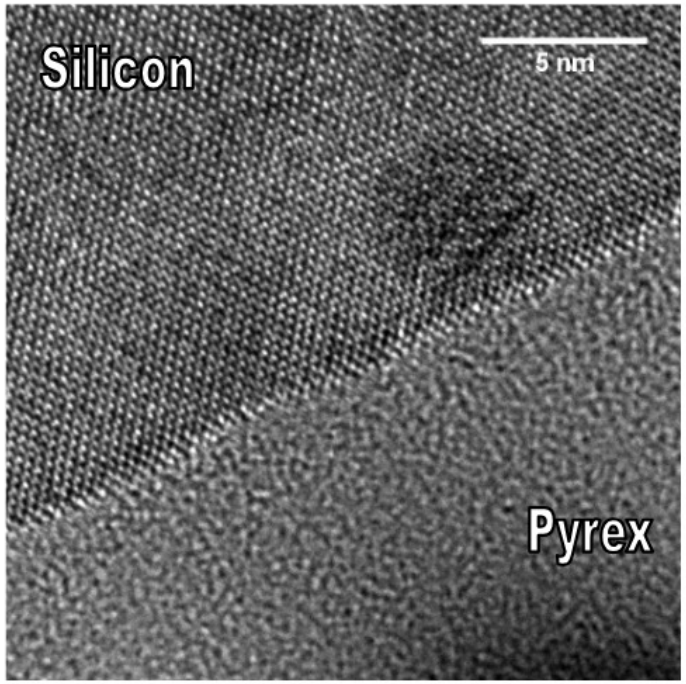
The electron beam loses part of its intensity due to scattering. The loss is greater for thicker regions or regions with species of higher atomic number. The thicker regions and the regions of higher atomic number appear dark.

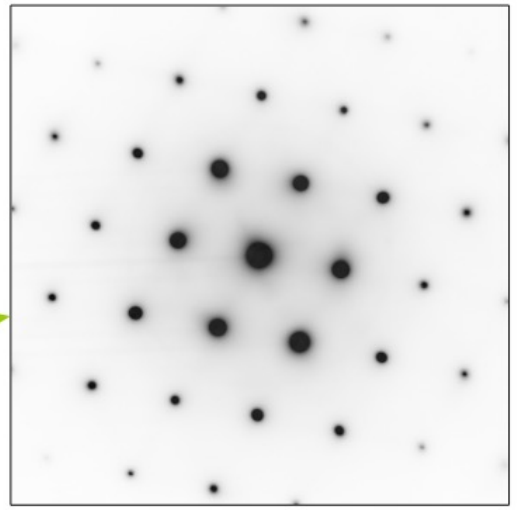
With high-resolution TEM, images showing the atomic structure can be obtained. For complex systems, numerical image simulations are required for the reliable interpretation of the image features in terms of atomic structure.

A diffraction mode is also possible.

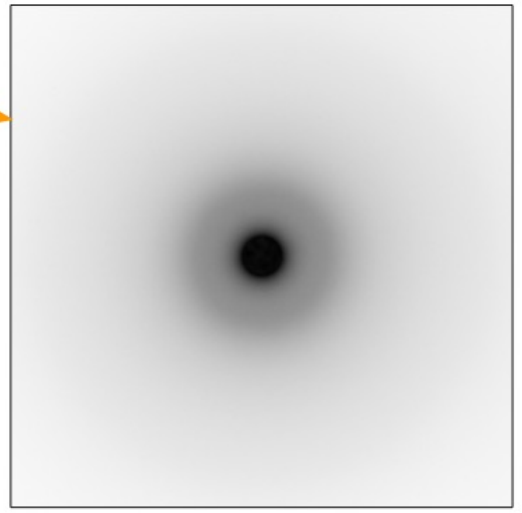
TEM images and diffraction patterns

Silicon – Pyrex® interface





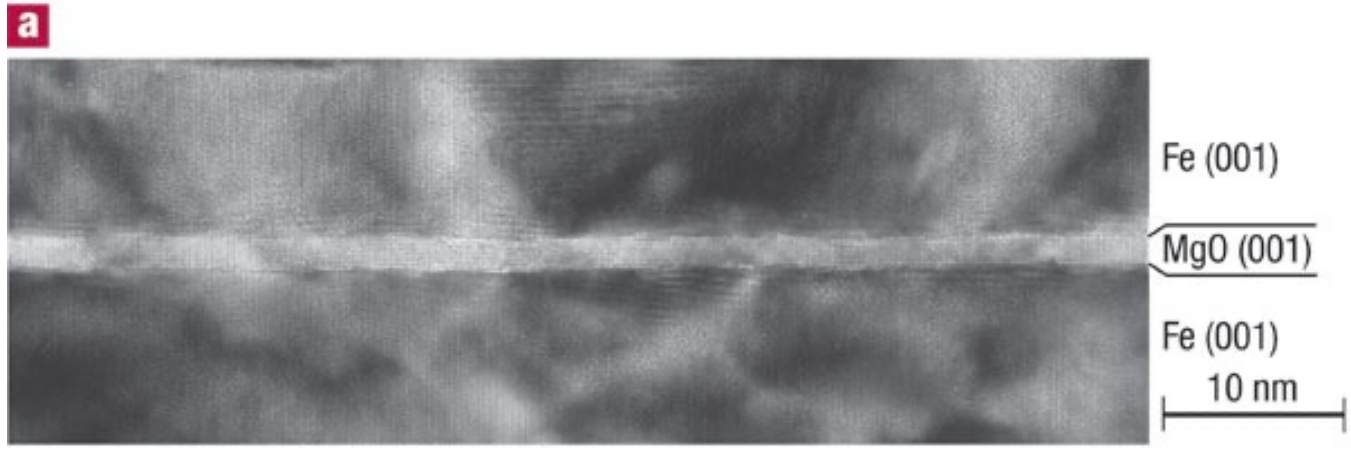
Diffraction pattern of
a crystallized material



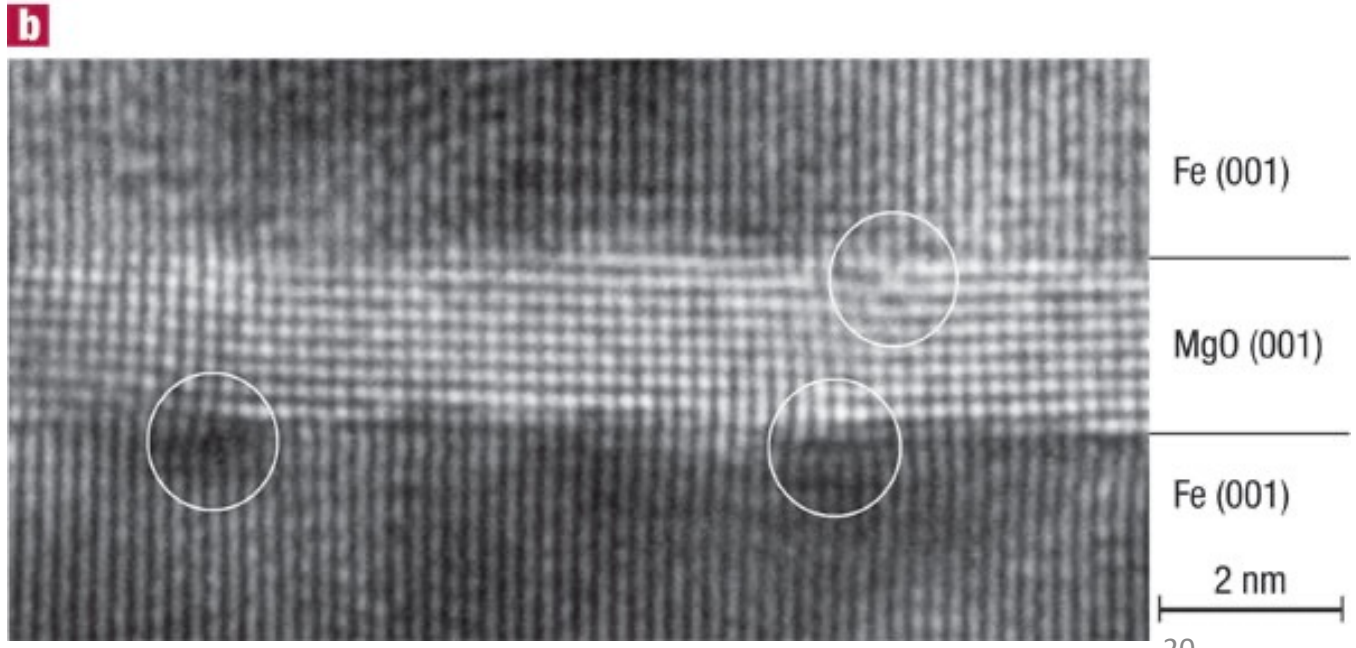
Diffuse rings typical of
amorphous material

TEM images of a single-crystal MTJ

cross-sectional TEM



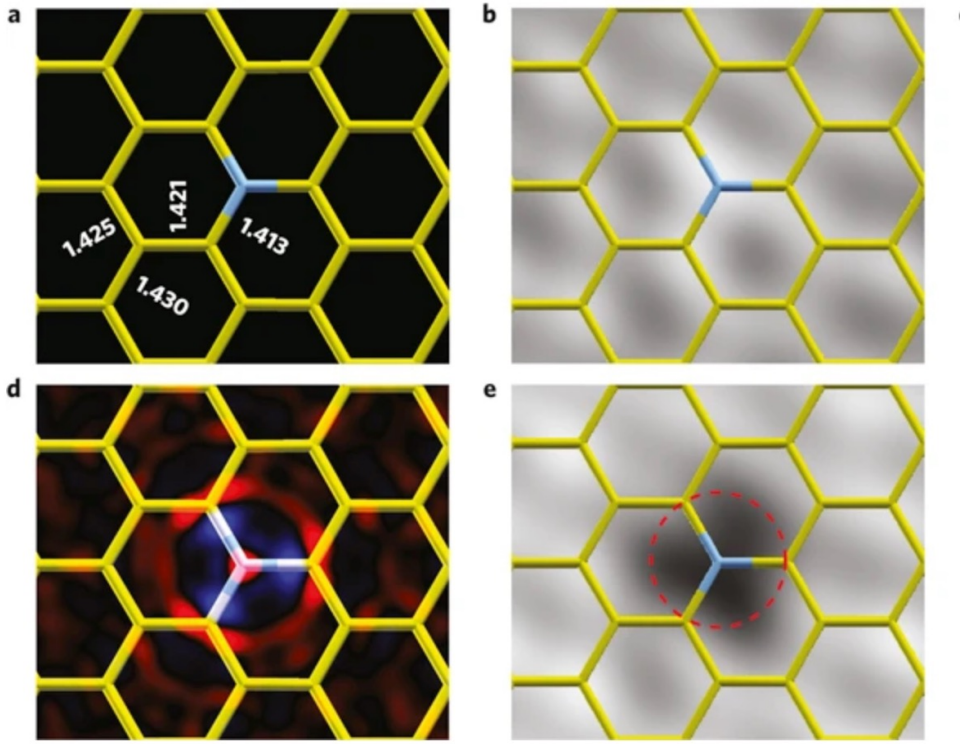
Fe(001)/MgO(001)(1.8 nm)/Fe(001) structure.
b is a magnification of **a**.
Lattice dislocations are encircled.



Nature Materials **3,** 868–871 (2004)

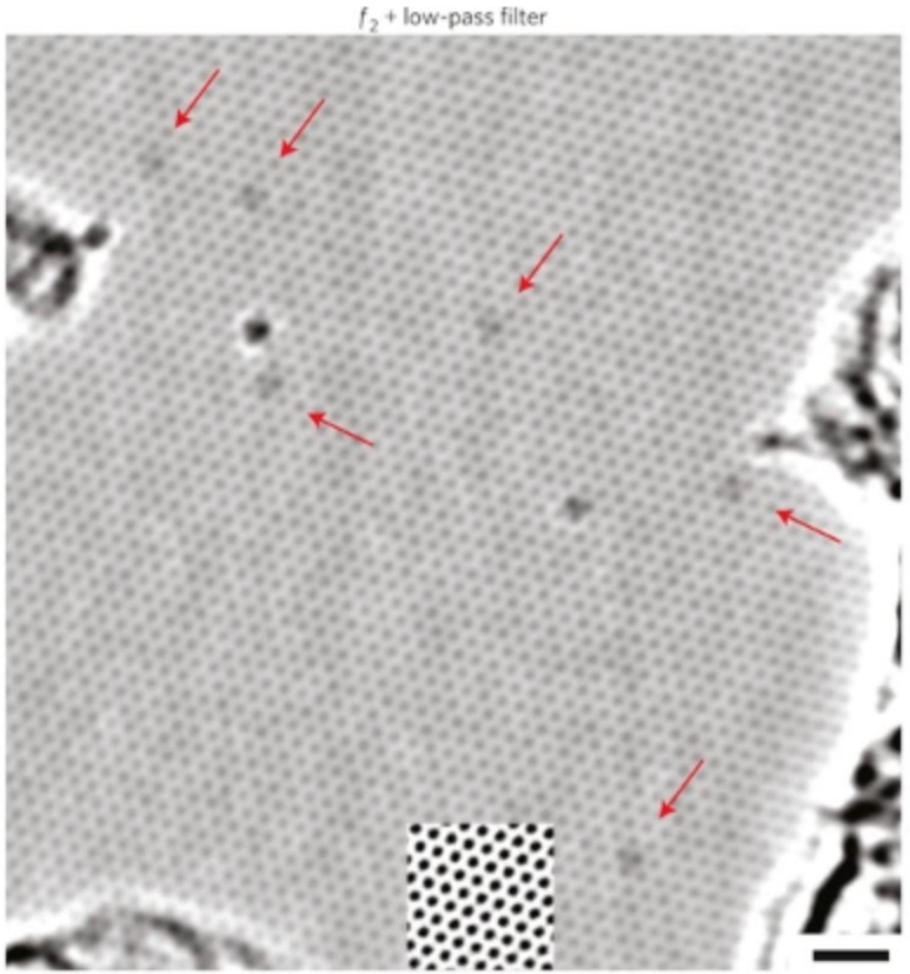
TEM detection of charge redistribution in 2D systems

N-doped graphene



a, Relaxed atomic configuration for a nitrogen substitution in graphene. Bond lengths are given in angstroms. **b**, Projected potential based on the IAM, with the periodic components of the graphene lattice removed, and bandwidth-limited to our experimental resolution (about 1.8 Å). Dark contrast corresponds to higher projected potential values, in accordance with our TEM imaging conditions. **d**, Atomic structure (same bond lengths), with the changes in projected electron density due to bonding shown in colour. Blue corresponds to a lower, red to a higher electron density in the DFT result as compared with the neutral-atom (IAM) case. **e**, Projected potential, filtered as in **b**, based on the all-electron DFT calculation.

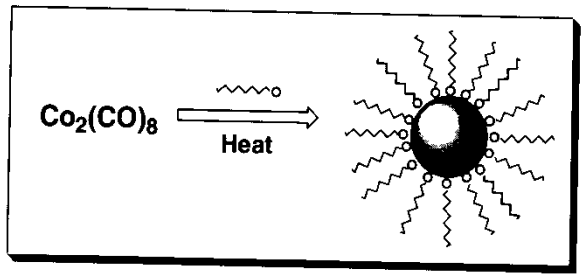
Nature Materials **10**, 209 (2011)



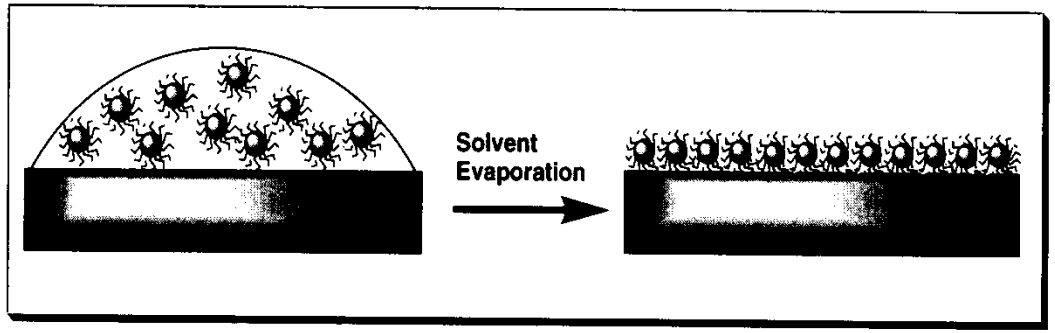
The dopant atom change the local scattering potential. TEM detects the N impurities as darker spots.

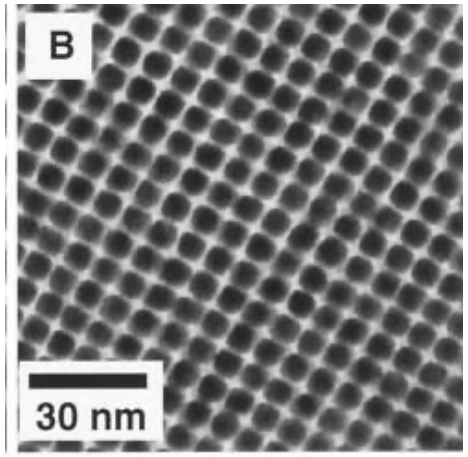
Organo-metallic particles as a magnetic bit

Particles with organic capping



Self-assembly *via* solvent evaporation



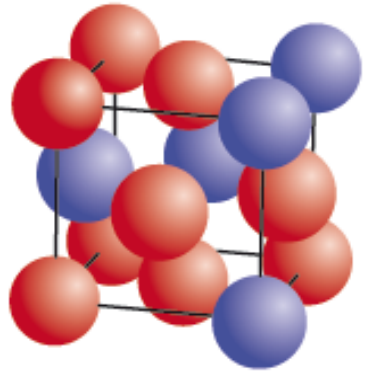


Tunable size in the range 1-10 nm

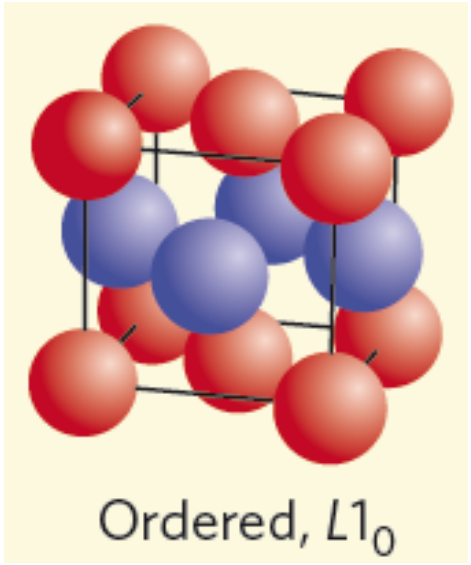
Organic capping used as a spacer to define the array density

FePt alloy as metallic core

Low anisotropy



Annealing to about 600°C



high anisotropy

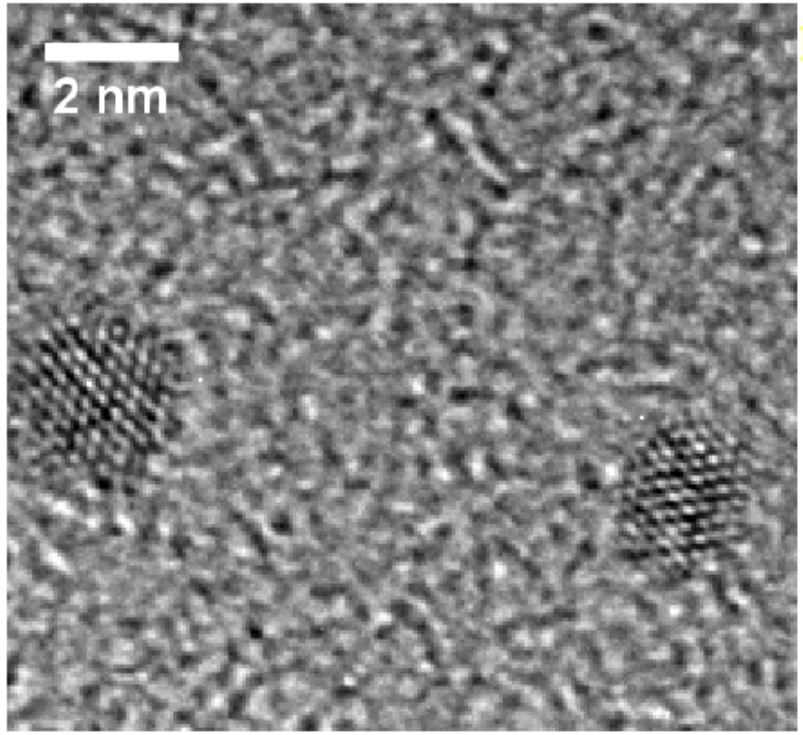
Fe (or Co)

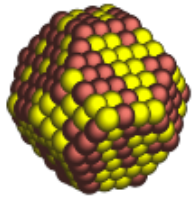
Pt (or Pd)

D. Alloyeau et al., Nat Mater. **8**, 940 (2009); Z.R. Day et al. Nano Lett. **1**, 443 (2001); S. Sun *et al.*, Science **287**, 1989 (2000)

Structural change upon annealing

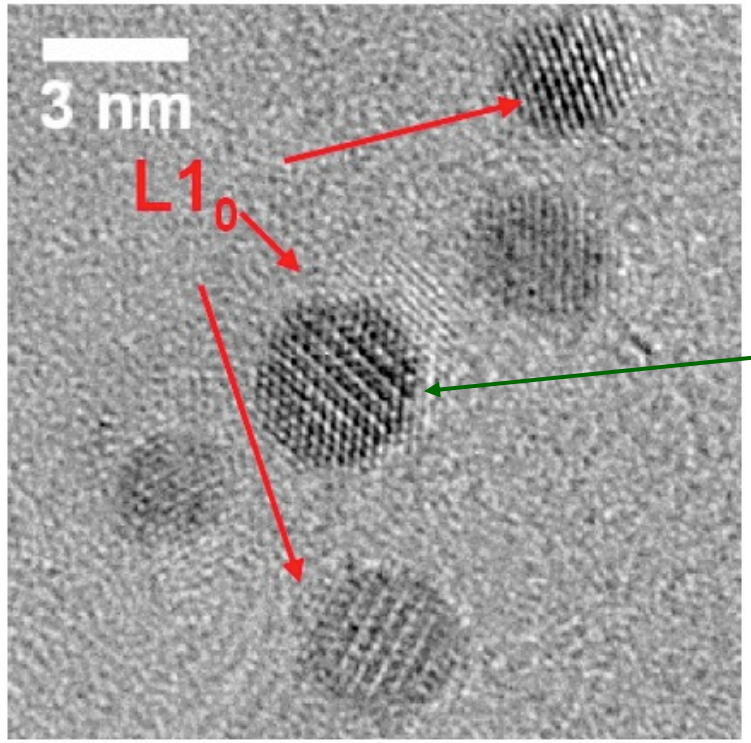
FCC chemically desordered A1 phase

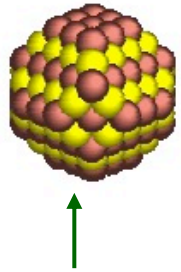




As prepared

Tetragonal chemically ordered $L1_0$ phase





Different contrast for the different atomic planes

N. Blanc, PhD thesis (Lyon Dec. 2009)

Atomic Electron Tomography

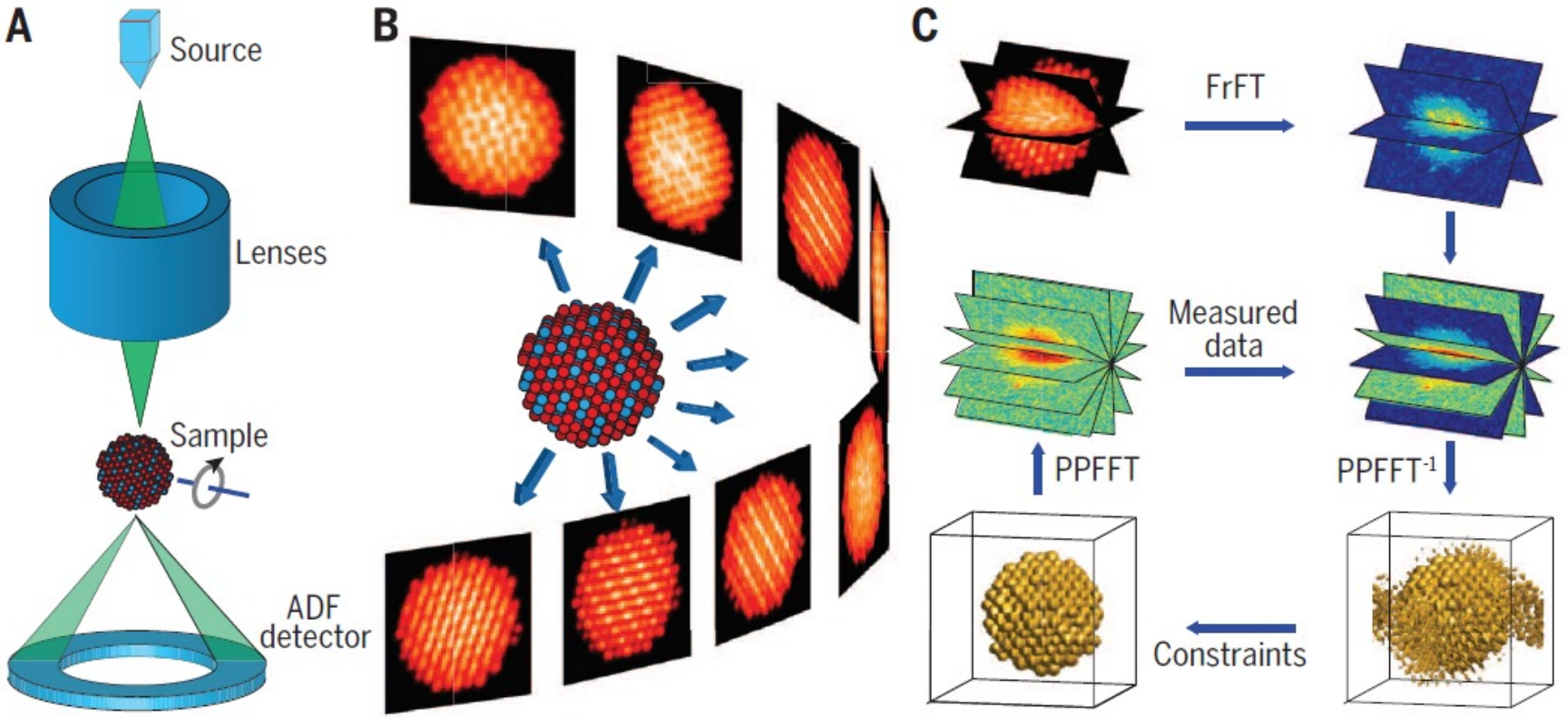


Fig. 1. Schematic layout of AET. (**A**) An electron beam is focused on a small spot and scanned over a sample to form a 2D image. The integrated signal at each scanning position is recorded by an ADF detector. (**B**) By rotating the sample around a tilt axis, a series of 2D images is measured at different tilt angles. (**C**) After preprocessing and alignment, the tilt series is inverted to Fourier slices by the fractional Fourier transform (FrFT). A 3D reconstruction is computed by using a Fourier-based iterative algorithm. From the 3D reconstruction, the coordinates of individual atoms are traced and refined to produce the 3D atomic model of the sample.

10.1126/science.aaf2157

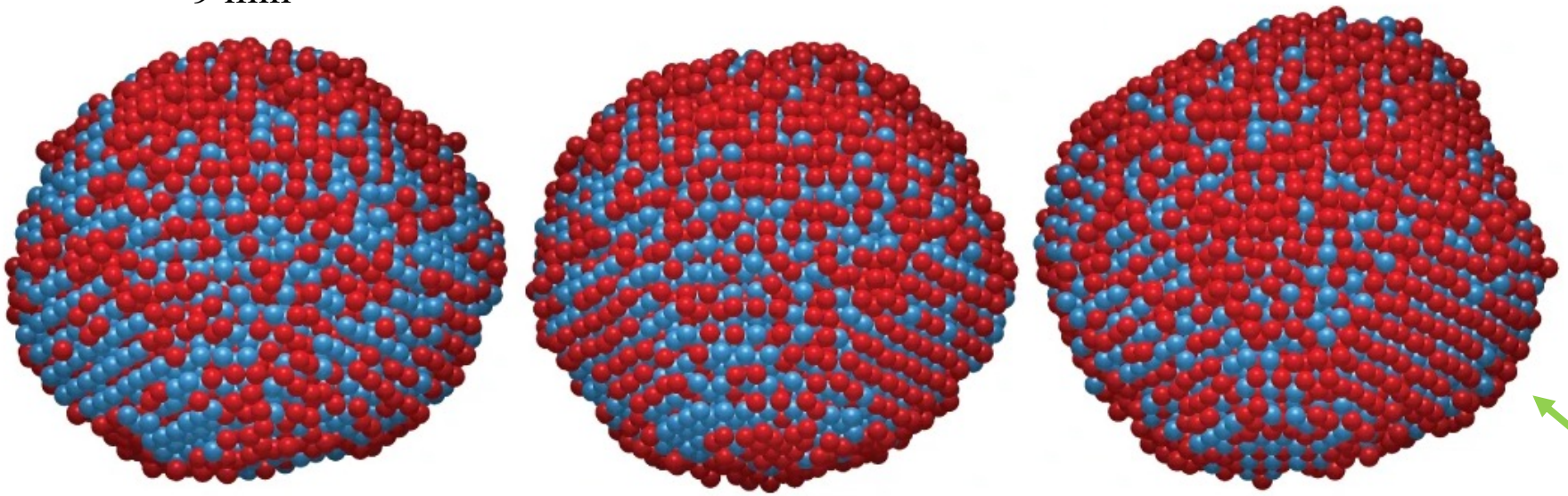
Observing crystal nucleation using atomic electron tomography

Annealing to 520°C

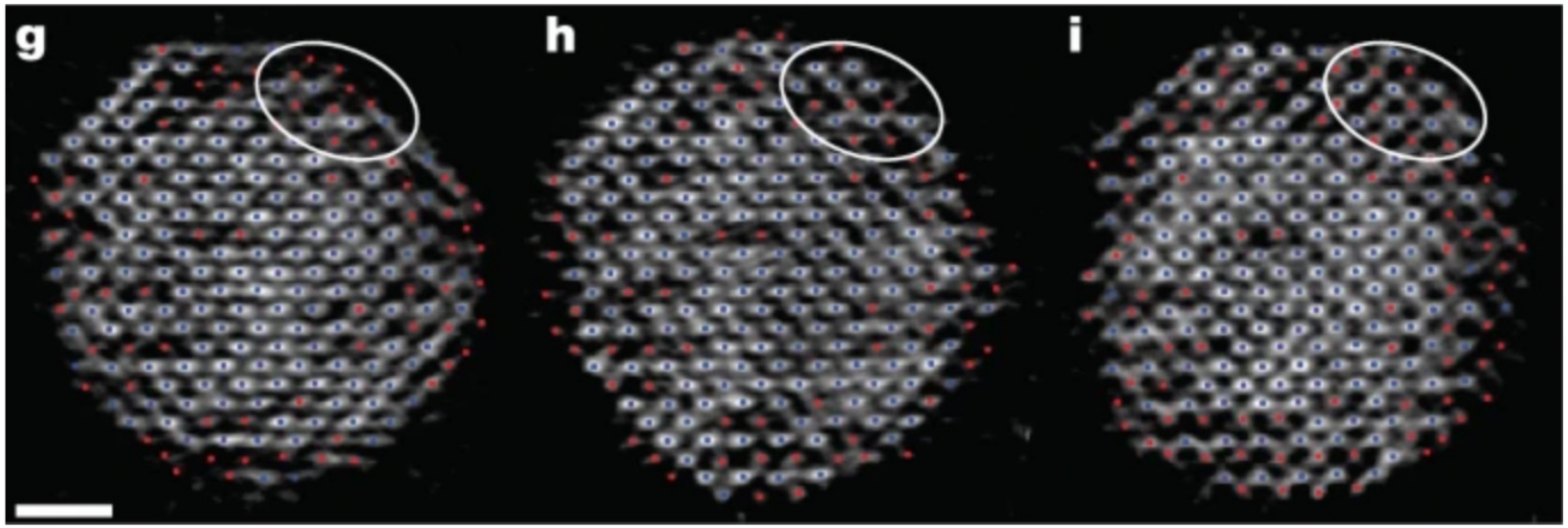
9 min

16 min

26 min



Fe red, Pt blue



$L1_0$ phase
starts to develop

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