Véronique Pierron-Bohnes
(IPCMS, Strasbourg)
"Electron holography on Magnetic nanoparticles"

- Magnetic properties of bulk materials
  - Dia-para-ferromagnetism
  - Susceptibility
  - Applications
- Magnetic properties of nano-objects
  - Moments and Curie temperature
  - Energies in competition
  - Applications
- Electron holography
  - Principle
  - Examples

Electron holography

nanometric samples:

Electron holography : sensitive to the phase changes of the electronic wave – resolution: 5 nm

Electron holography—basics and applications
Hannes Lichte and Michael Lehmann
Rep. Prog. Phys. **71** (2008) 016102

Electron Holography for the Study of Magnetic Nanomaterials
John Meurig Thomas, Edward T. Simpson, Takeshi Kasama, and Rafal E. Dunin-Borkowski
Acc. Chem. Res. 41, 665 (2008)

Electrons = particles:

$\vec{F} = -e\vec{E} - e\,\vec{v}\otimes\vec{B}$

$$p = \sqrt{2em_0U_a^*},$$

Relativistic effects:

$$U_a^* := U_a\left(1 + \frac{eU_a}{2m_0c^2}\right)$$

Electrons = wave:

$$\left[\frac{1}{2m_0}\left(-i\hbar\,\nabla + e\vec{A}\right)^2 - eV\right]\psi = E\psi$$

Schrödinger equation

Relativistic effects:

Klein–Gordon equation

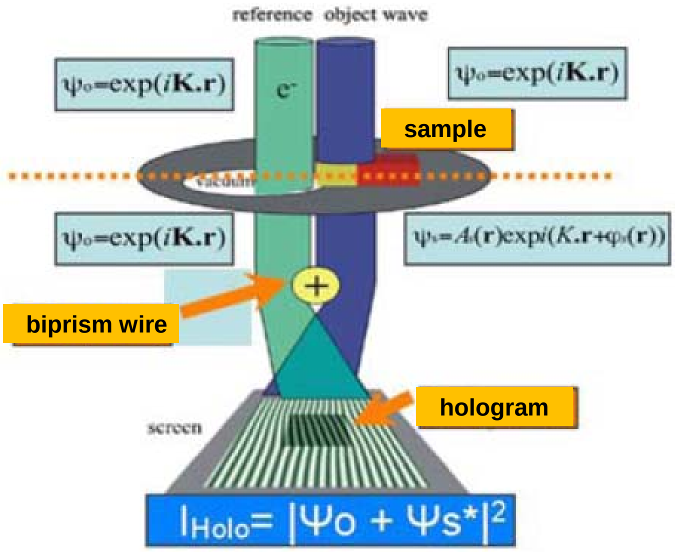
$$\vec{k} = \frac{\sqrt{2em_0(U_a+V)^*}}{\hbar}\vec{e}_p - \frac{e}{\hbar}\vec{A}$$

In vacuum: V=0 and **A**=0
$$\begin{cases} \vec{p} = \hbar\vec{k}_0 \\ k_0 = \dfrac{\sqrt{2em_0U_a^*}}{\hbar} \end{cases}$$

$\Psi(r,t) = a\exp(i(k_0.r - \omega t))$; $E = \hbar\omega$

Electron holography

Possible thanks to field emission guns (spatial and energetic coherence)



Holographie électronique

Hologram writing

Coherent beam

Field emission electron gun

Separated in 2 beams

Sample over half of the beam

Deviation of beams for interference

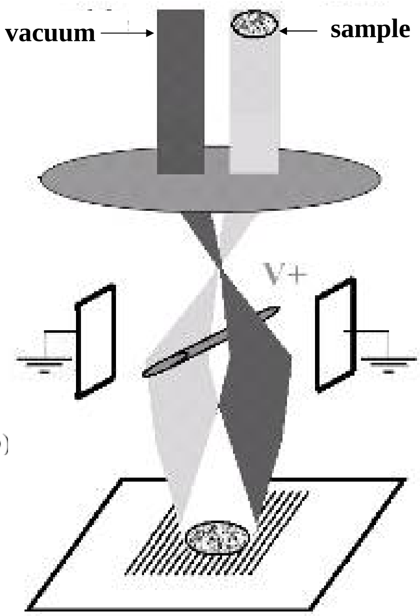
Wire at + potential (biprism)

$$I(\vec{r},t) = (\psi_1 + \psi_2)(\psi_1 + \psi_2)^{cc}$$

$$I(x,y) = I(x) = \underbrace{a_1^2 + a_2^2}_{\text{particle number}} + 2a_1a_2\cos(q_c x + \Delta\varphi)$$

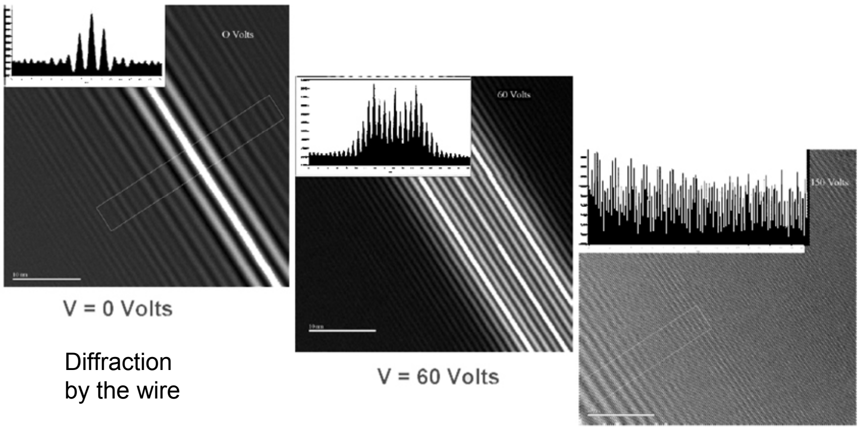
Contrast

$$0 \leqslant C = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} = (2a_1a_2)/(a_1^2 + a_2^2) \leqslant 1$$



Holographie électronique

reference hologram



V = 0 Volts

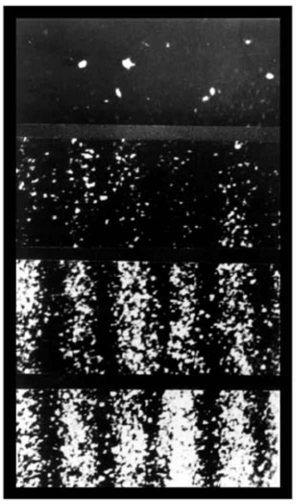
Diffraction
by the wire

V = 60 Volts

V = 150 Volts

Holograms without sample at different biprism polarisations
apparatus response (microscope + biprism + optics after sample).

Electron holography



0.02 s

10 s

60 s

120 s

exposure time

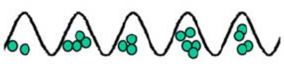


Figure 3. Single electron interference. At very short exposure times, seemingly stochastic impacts of single electrons are found. With increasing exposure time, this shot noise adds up forming a cosinusoidal interference pattern. Since the time of flight of the electrons is five orders of magnitude smaller than the time distance between two impacts, at any one time only a single electron is present in the interferometer.

Möllenstedt G and Düker H 1956 Beobachtungen und Messungen an Biprisma-Interferenzen mit Elektronenwellen *Z. Phys.* 145 377–97

Schmid H 1985 Ein Elektronen-Interferometer mit 300 μm weit getrennten kohärenten Teilbündeln zur Erzeugung hoher Gangunterschiede und Messung der Phasenschiebung durch das magnetische Vektorpotential bei metallisch abgeschirmtem Magnetfluss *Dissertation* University of Tübingen

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$\Psi(r,t) = a \exp(i(k_0.r - \omega t))$; $E = \hbar\omega$

Electron holography

Klein–Gordon equation

$$\vec{k} = \frac{\sqrt{2em_0(U_a+V)^*}}{\hbar}\vec{e}_p - \frac{e}{\hbar}\vec{A}$$

In sample: V ≠ 0 and **A** ≠ 0
$$\begin{cases} p = \hbar k \\ k = k_0\,(1 + V/2U_a) - e/\hbar\ \mathbf{A.e}_p \end{cases}$$

$\Psi(r,t) = a \exp(i(\mathbf{k.r} - \omega t)) = a \exp(i(\mathbf{k}_0\mathbf{.r} + \varphi - \omega t))$

$$\varphi = \frac{e}{\hbar v}\int V\,\mathrm{d}s - \frac{e}{\hbar}\int \vec{A}\,\mathrm{d}\vec{s}$$

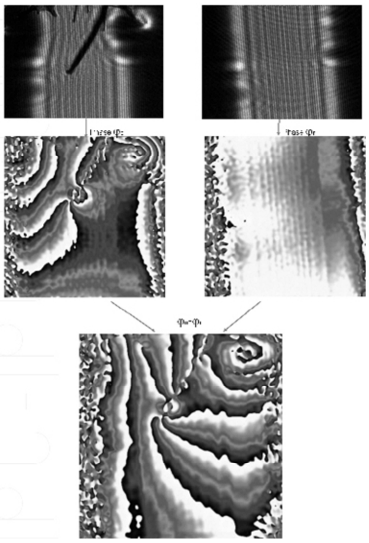
v : the electron velocity

magnetic phase ⟶ magnetisation, stray B field

inner electric field phase ⟶ thickness, electron density, stray E field

Electron holography

Analysis of an electronic hologram:



Sample and reference hologram
of a Ni needle

Calculation of phases

Difference ⇒ phase due to sample

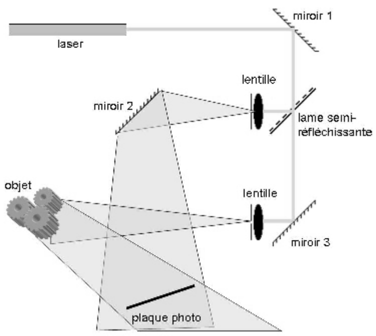
Optical holography

principe de l'holographie optique

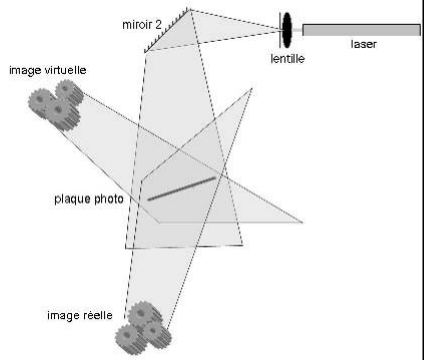
écriture :	lecture :
faisceau très cohérent	faisceau très cohérent
référence / échantillon	hologramme
enregistrement Interférences phase et amplitude onde échantillon	phase et amplitude de l'onde échantillon

Optical holography

Writing



Reading



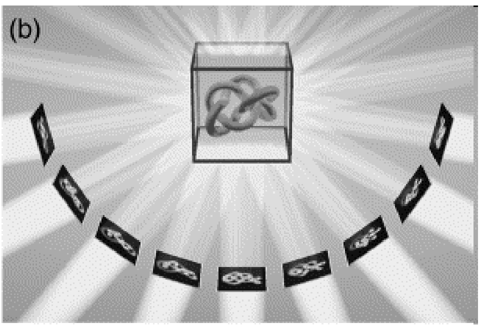
$E = (O + R)(O + R)^*$
$\quad = OO^* + RR^* + OR^* + RO^*$

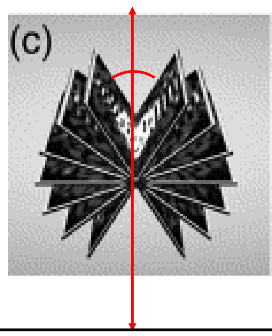
transmittance
$t = 1 - A\,E$

$U = t\,R = A\,[(C+D)R + OD + R^2 O^* O + RO^* R\,]$

Electron Tomography

principle –PhD thesis Iliana Florea or Lucian Roiban (Ovidiu Ersen) IPCMS Strasbourg





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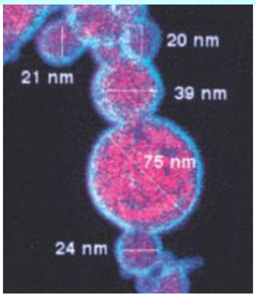
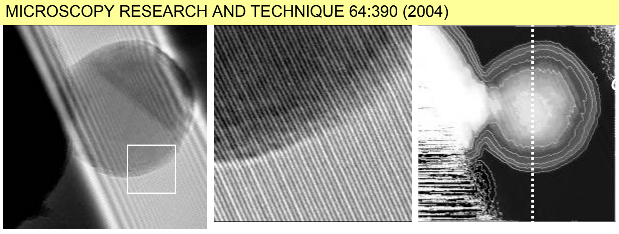
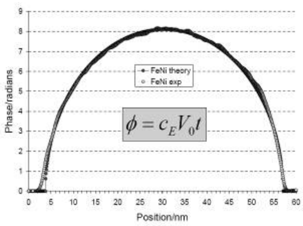
Electron holography



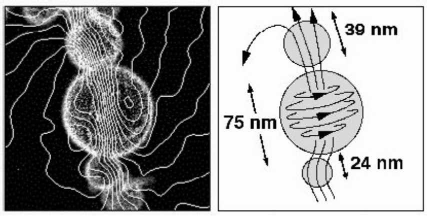
Fe (red), Ni (blue). $Fe_{0.56}Ni_{0.44}$ nanoparticles

Off-Axis Electron Holography of Magnetic Nanowires and Chains, Rings, and Planar Arrays of Magnetic Nanoparticles
R.E. Dunin-Borkowski, T. Kasama, A. Wei, S. L. Tripp, M. J. Hytch, E. Snoeck, R. J. Harrison, A. Putnis
MICROSCOPY RESEARCH AND TECHNIQUE 64:390 (2004)



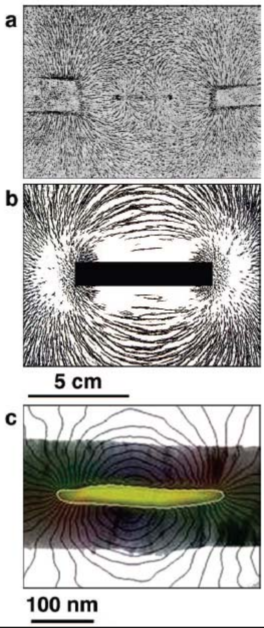


Profile of electric potential phase



magnetic phase image of FeNi particles and scheme of corresponding magnetic configuration deduced from comparison with simulations

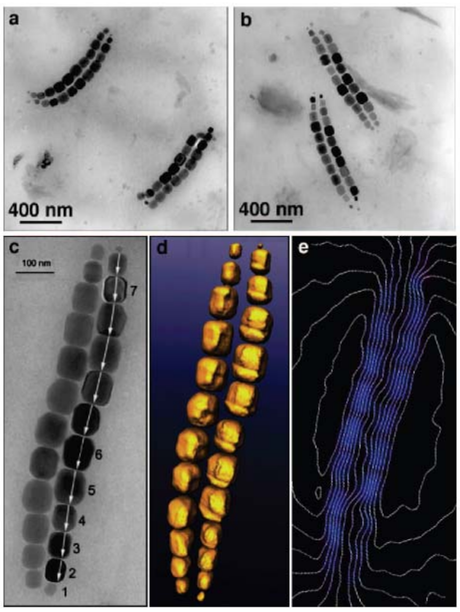
Electron holography



(a) Michael Faraday's image of "magnetic lines of force", formed using magnets and iron filings (this image is shown in Figure 24 on p 47 of ref 1), (b) a contemporary image similar to that shown in panel a formed using a single bar magnet and iron filings, and (c) magnetic phase contours recorded using off-axis electron holography from a multiwalled carbon nanotube, approximately 180 nm in diameter, containing a 36-nm-diameter encapsulated iron crystal (in yellow). The contours, which were generated from the phase image, were overlaid onto a bright-field TEM image of the crystal.[4]

Electron Holography for the Study of Magnetic Nanomaterials
John Meurig Thomas, Edward T. Simpson, Takeshi Kasama, and Rafal E. Dunin-Borkowski
Acc. Chem. Res. 41, 665 (2008)

Electron holography



magnetotactic bacteria

Low-magnification bright-field images

Bright-field TEM image

dark-field tomographic reconstruction

Magnetic induction map

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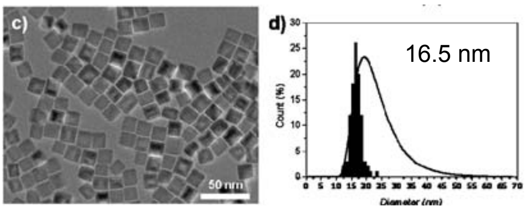
Ferrite nanocubes

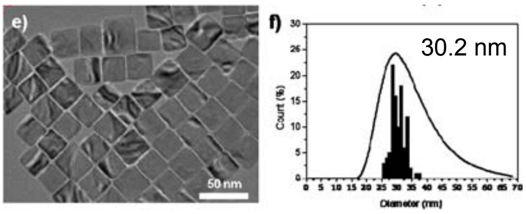
Preparation

Fe(oleate)$_3$ complex
in octadecene
(boiling point: 318°C)
in the presence of oleic acid (OA)+Na^+
molar ratio
R= OA / Fe(stearate)$_2$ = 2
heating rate to 1°C min^{-1}



*a) TEM micrograph and b) size distribution (histogram) and dynamic light scattering (DLS) measurements (line) of iron oxide nanoparticles **NC16** with cubic-shaped morphology.*

Fe(oleate)$_3$ complex
in eicosene
(boiling point: 350°C)
in the presence of oleic acid (OA)+Na^+
molar ratio
R= OA / Fe(stearate)$_2$ = 2
heating rate to 1°C min^{-1}

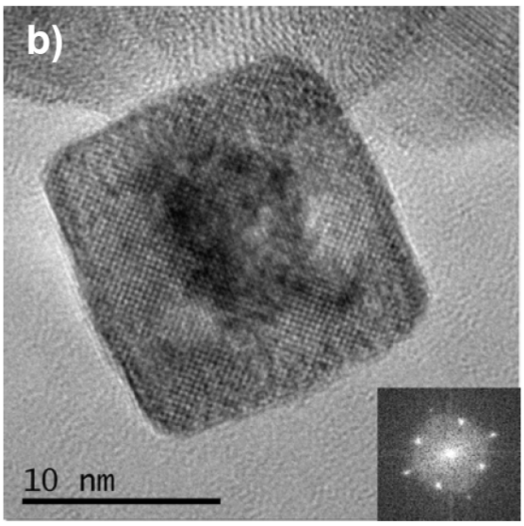


*a) TEM micrograph and b) size distribution (histogram) and dynamic light scattering (DLS) measurements (line) of iron oxide nanoparticles **NC30** with cubic-shaped morphology.*

choice of size
narrow distribution
cubic shape in projection

Benoit P. Pichon, Olivier Gerber, Christophe Lefevre, Ileana Florea, Solenne Fleutot, Walid Baaziz, Matthias Pauly, Maxime Ohlmann, Corinne Ulhaq, Ovidiu Ersen, Véronique Pierron-Bohnes, Pierre Panissod, Marc Drillon, Sylvie Begin-Colin
Microstructural and Magnetic Investigations of Wüstite-Spinel Core-Shell Cubic-Shaped Nanoparticles
Chem.Mater. 23 (2011) 2886

High Resolution Transmission Electron Microscopy

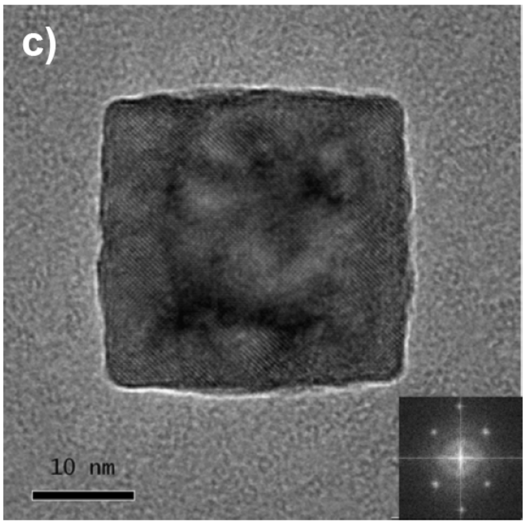


High resolution TEM micrographs of cubic-shaped **NC16** nanoparticles and fast Fourier transform related to the observed isolated nanoparticles.

High Resolution Transmission Electron Microscopy (2)

High resolution TEM micrographs of cubic-shaped **NC30** nanoparticles and fast Fourier transform related to the observed isolated nanoparticles.

single crystal
or
coherent core-shell

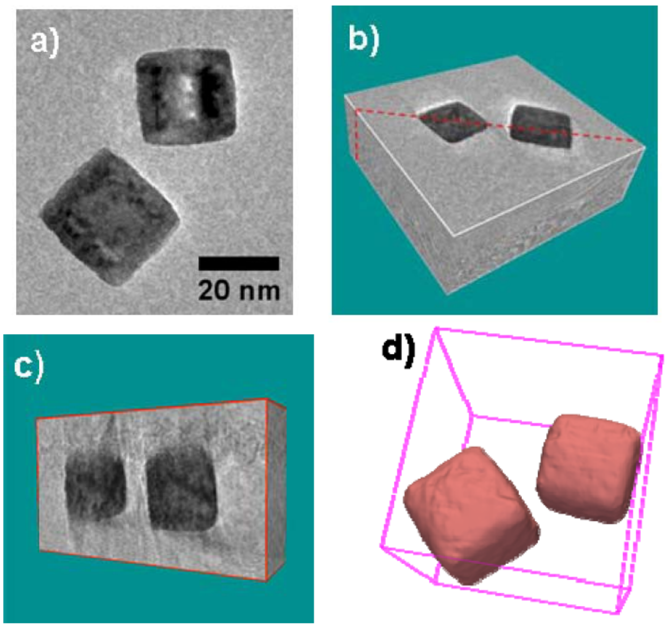


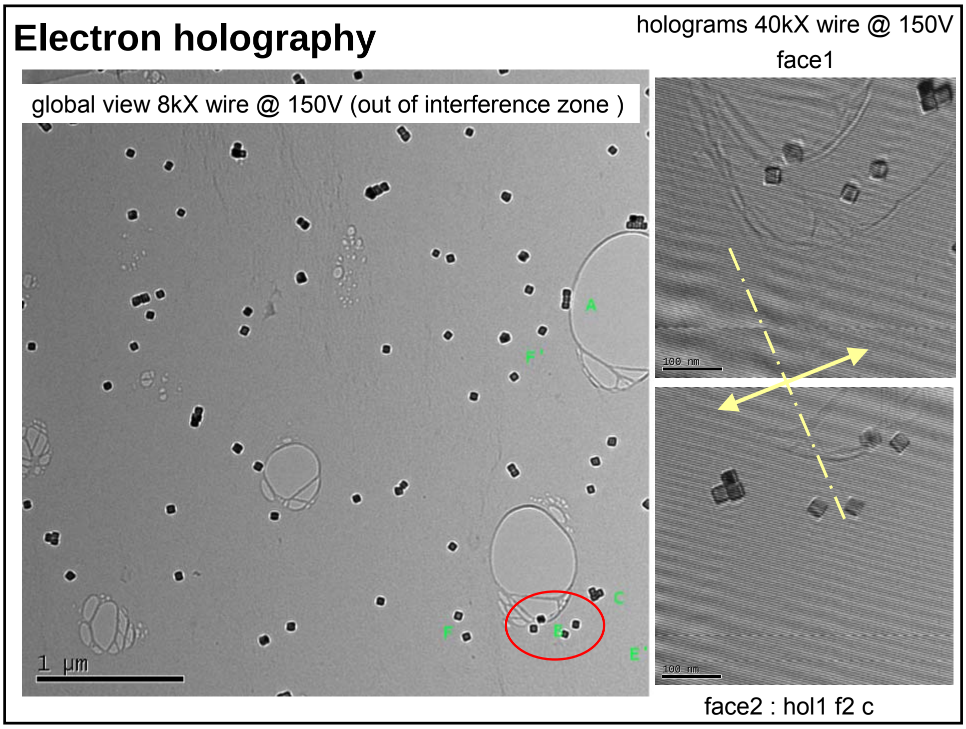
Electron Tomography in classical TEM

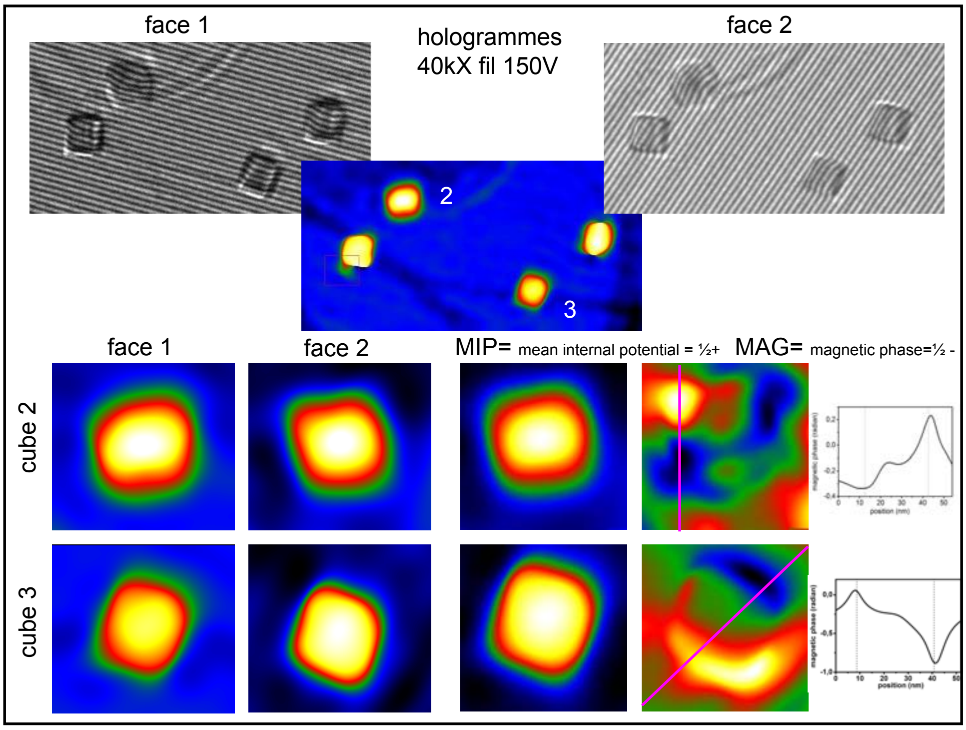
a) Example of 2D-TEM image extracted from the projection tilt series used to reconstruct the 3D structure of the objects **NC30**. b) Typical longitudinal slice through the reconstructed volume perpendicular to the electron beam axis.

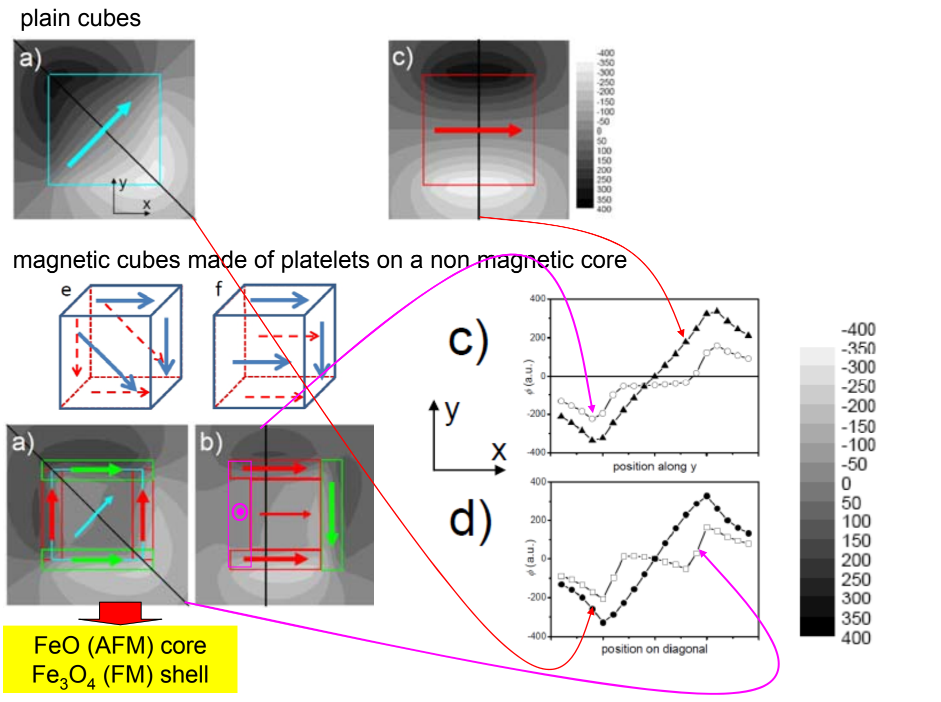
c) Transversal slice, orthogonal to the longitudinal one, taken along the plane marked in red in b). d) 3D representation of the external shapes of the two analysed cubic-shaped nanoparticles.

3D cubic shape




Electron holography
holograms 40kX wire @ 150V
face1
global view 8kX wire @ 150V (out of interference zone)
1 µm
100 nm
100 nm
face2 : hol1 f2 c


face 1
hologrammes
40kX fil 150V
face 2
2
3
face 1
face 2
MIP= mean internal potential = ½+
MAG= magnetic phase=½ -
cube 2
cube 3



Electron Tomography in STEM-HAADF

Scanning Transmission Electron Microscopy In High Angle Annular Dark Field (bright = large $\bar{Z}$)

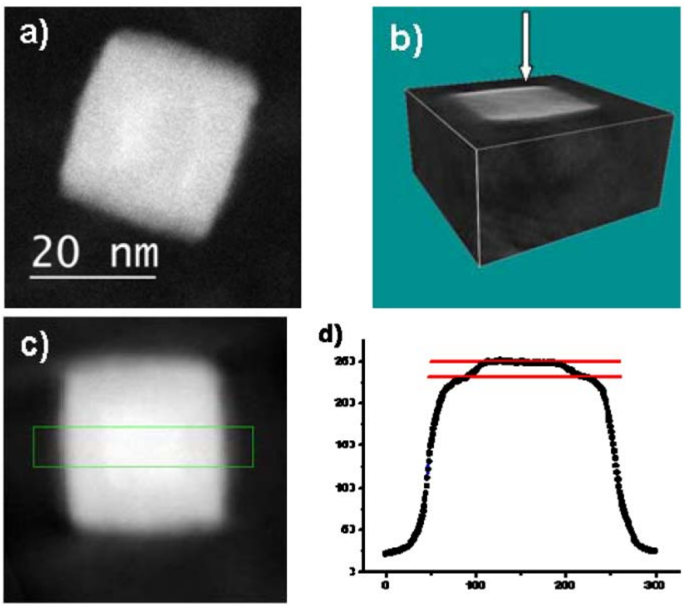
a) 2D STEM-HAADF image at 0° tilt, extracted from the tilt series used to reconstruct the volume of a core-shell **NC30c** (64 days) NP.

b) Slice of the reconstructed volume.

c) Projection computed from the reconstruction in the direction indicated by the white arrow in b).

d) Mean profile obtained by averaging the line profiles contained in the green area drawn on the computed projection of c).

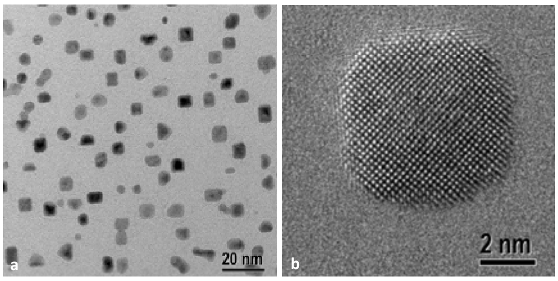
higher density in core
3D cubic shape core



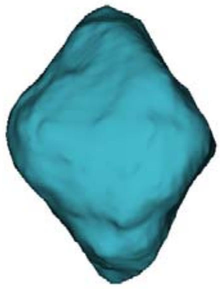
CoPt nanoparticles epitaxied on NaCl transferred on C membrane

Holography ⇒ superparamagnetic

Tomography ⇒ slightly truncated octahedrons



side view



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IPCMS Strasbourg

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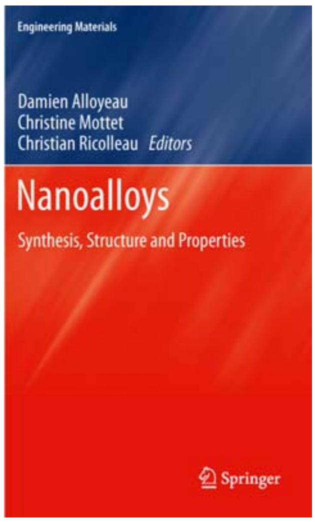
"Electron holography on Magnetic nanoparticles«



- Magnetic properties of nano-objects

  http://www.springer.com/engineering/book/978-1-4471-4013-9

- Electron holography

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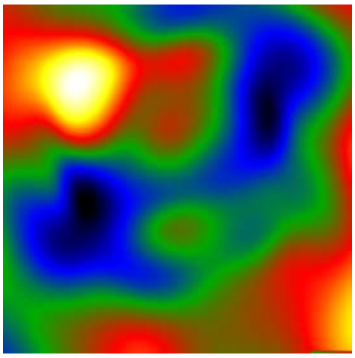
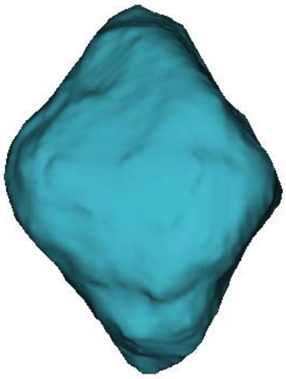
Thank you for attention !





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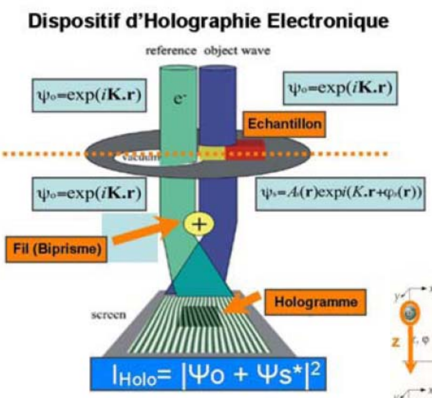
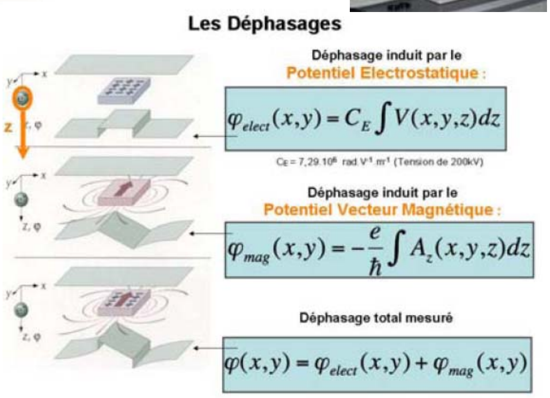
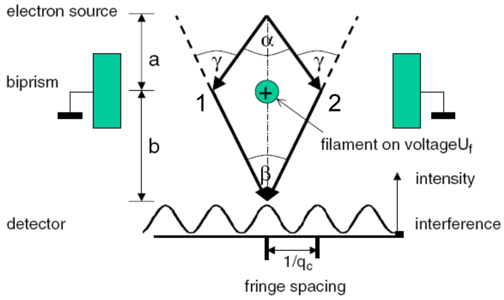




V : scalar
unchanged when sample flipped
A : vector
reversed when sample flipped
→ contribution separation
making 2 measurements

Electron holography



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