Quantitative electron tomography of magnetite nanoparticles embedded in mesoporous silicon

T. Uusimäki[1,2], G. Margaris[3], K. N. Trohidou[3], P. Granitzer[4], K. Rumpf[4], M. P. Morales[5], M. Sezen[1,2,6] and G. Kothleitner[1,2]

1. Institute for Electron Microscopy, Graz University of Technology, Graz, Austria
2. Center for Electron Microscopy, Graz, Austria
3. Institute of Material Science, NCSR "Demokritos", Athens, Greece
4. Institute of Physics, University of Graz, Graz, Austria
5. Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain
6. Currently at Nanotechnology Research and Application Center, Sabancı University, Istanbul, Turkey

toni.uusimaeki@felmi-zfe.at
Keywords: electron tomography, magnetite nanoparticles, mesoporous silicon

Mesoporous silicon infiltrated with Fe_3O_4 nanoparticles comprises a nanocomposite system with interesting magnetic properties spanning a wide range of applications from controlled drug delivery and hyperthermia in the medical field to data storage and optical devices in the material science area [1]. Within this study, a three dimensional characterization was performed using electron tomography with a scanning transmission electron microscope (STEM).

The mesoporous silicon was fabricated by anodization of highly doped n-type silicon wafer in aqueous hydrofluoric acid solution. By adjusting the electrochemical parameters, oriented pores grow along the (100) direction. Samples with a typical average pore diameter of 80 nm and mean pore wall width of 40 nm was used in the frame of this work. The Fe_3O_4 nanoparticles were prepared with high temperature decomposition and were further coated with oleic acid in hexane to prevent oxidation and agglomeration before infiltration to the silicon matrix [2].

For characterization the sample was prepared using focused ion beam (FIB) milling under cryo conditions. A pillar shaped sample was milled to prevent self-shadowing from the sample at high tilt angles and to minimize the missing wedge, which deteriorates the quality of the reconstruction [3]. STEM tilt series from -79° to 78° with 1° tilt increments was acquired on a Tecnai F20 equipped with a Schottky field-emission gun and Fischione high angle annular dark-field (HAADF) detector (model 3000). The tilt series was aligned using a custom made manual alignment program, where the projections of the individual image being aligned, are enhanced in the one-plane 2D reconstruction. With further filtering, it was then possible to identify where the line projections originate and to translate the image accordingly. A three dimensional reconstruction was then calculated using simultaneous iterative reconstruction method (SIRT) with 30 iterations (Fig. 1a). To facilitate the highly important segmentation procedure for correct analysis, a plug-in was written to Digital Micrograph™ to integrate the vast public library of image manipulation tools called Insight Toolkit.

Of further interest was the particles' docking site in the supporting matrix. For this the local curvature was analyzed in terms of shape index, which was extracted in two different ways: By defining rings in the triangulated surface around the particles and taking the mean value of the calculated curvature of these points; a similar approach was reported in [4]. Alternatively, we implemented polynomial regression to fit a surface to an area of points around the particles and taking the curvature value from the centre of the fitted surface (Fig. 1c). The former method yields always a Gaussian distribution centred close to zero (Fig. 1d), while the latter gives two Gaussians centred at -0.5 and 0.5 (Fig. 1e), clearly fitting better to the visual interpretation of the reconstructed data.

Principal component analysis was used to fit an arbitrary ellipsoid to the edge points of the segmented magnetite particles. From the eigenvalues one can estimate the radii of the semi axes, which were further used to calculate the demagnetizing factors for every particle. The eigenvectors also give the directions of these semi axes. The demagnetizing field is minimized along the longest axis of the ellipsoidal particle, hence this direction, if it exists, is assumed to be the easy axis of the particle. Within these restrictions one can then map the distribution of the directions of the easy axes against all principal coordinate axes along with the demagnetizing factors (Fig. 2a).

J.L Dormann [5] stated that interparticle magnetic interactions are characterized by three degrees of disorder: surface topology, volume distribution and the random distribution of the easy axes.

Here we show, that electron tomography can readily solve the first two of these problems and also the third one with some restrictions. The spatial (Fig. 2b, 2d) and volume distribution (Fig. 2c, 2e) of the segmented nanoparticles were used, as an input to Monte Carlo simulations [6] to calculate the hysteresis curves and the zero field cooled / field cooled (ZFC/FC) magnetization curves. To our knowledge, this is the first reported experiment to use real acquired data to simulate magnetic interactions within nanometer scale.

References

[1] M. P. Pileni *et al, Scientific and Clinical Applications of Magnetic Carriers,* Plenum, London 1997
[2] P. Granitzer *et al*, J. Mag. Mag. Mat., **157** (7) K145-K151, (2010)
[3] P.A. Midgley, M. Weyland, Ultramicroscopy **96** 413–431 (2003)
[4] E.P.W. Ward *et a*l, *J. Phys. Chem. C, Vol.* **111***, No. 31, (2007)*
[5] J.L. Dormann *et al,* J. Mag. Mag. Mat 202 251-267, (1999)
[6] K.N. Trohidou *et al*, (2012) Monte Carlo Simulations on the magnetic behaviour of nanoparticle assemblies, in Nanoparticles Featuring Electromagnetic Properties: From Science to Engineering
[7] The author and co-authors gratefully acknowledge funding from the EC FP7 “CopPer”- project (grant number 216474) and from the FWF (project number P 21155). Also the contributions from P. Pölt and M. Weyland are greatly appreciated.

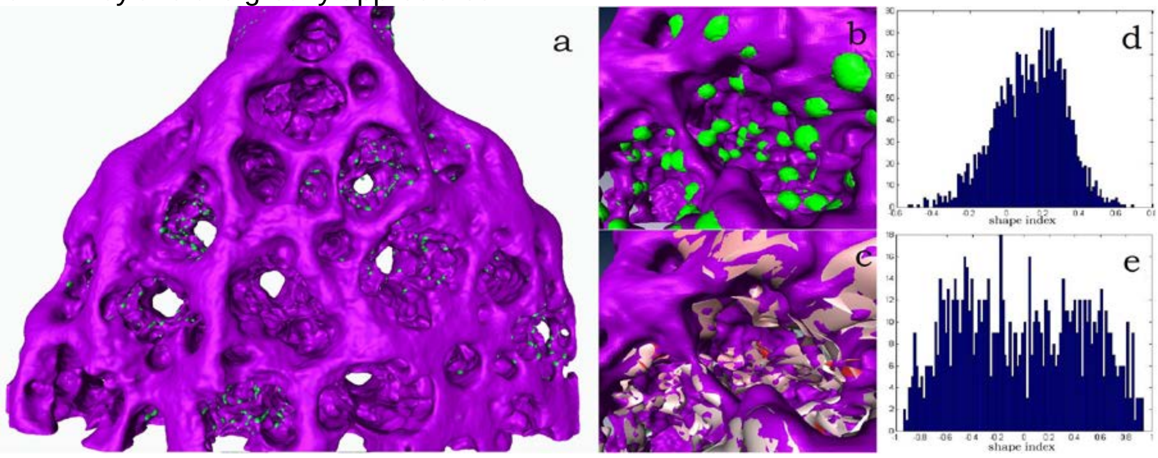

Figure 1. *a) Surface rendered reconstruction. b) Fe_3O_4 particles in a pore. c) polyfitted surface. d) curvature distribution from the average of three rings around the particles. e) curvature distribution from polyfitted data.*

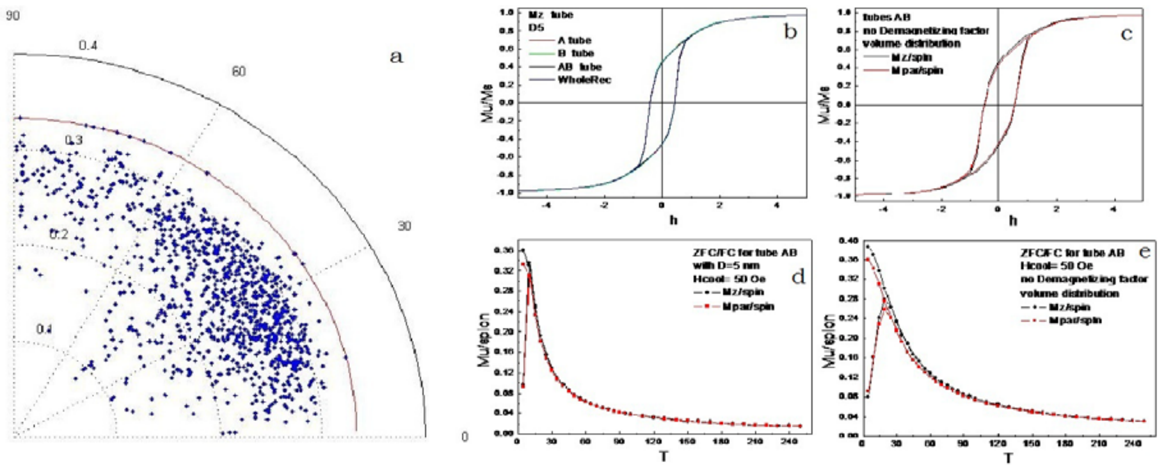

Figure 2. *Demagnetizing factors and the angle of the easy axis of the particles with respect to the coordinate axis, which is parallel to the pores. The red line shows the value of 1/3 for spherical particles. Simulated hysteresis (upper) and ZFC/FC (lower) magnetization curves b) using only the spatial distribution of the reconstructed particles with an assumption of 5 nm diameter spherical particles. c) using also the volume distribution of the reconstructed particles. d) same as in b. e) same as in c.*