ESRF	**Experiment title:** Magnetic field-induced assembly of magnetite nanoparticle dispersions	**Experiment number**: SC 3265
Beamline: ID02	**Date of experiment**: from: 16/11/2011 to: 18/11/2012	**Date of report**: 29/02/2012
Shifts: 6	**Local contact(s)**: P. Bösecke	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
S. Taheri*, S. Rosenfeldt*, S. Höhn*, M. Dulle*, S. Förster, University of Bayreuth, Germany

Report:

Magnetic nanoparticles exhibit a rich self-assembly behavior. Understanding the formation of superstructures consisting of magnetic nanoparticles is the key to designed applications in the areas of magnetic drug targeting and magnetic storage devices. Ferromagnetic nanoparticles are regarded as magnetic monodomains. External magnetic fields orient 1D structures according to the easy axis of magnetization. The assembly structure of magnetic iron oxide nanoparticles results from a complex interplay of attractive interaction due to a anisotropic shape (spheres, cubes), magnetic coupling, local gradients (concentration, temperature) and anisotropic local enviroment (influence of stabilizing layer).

During the experiment Sc 3265 we investigated the magnetic field induced self-assembly of superparamagnetic nanoparticle dispersions (spheres and cubes in toluene) by SAXS. Only in case of the nanocubes we find 3D self-assembly (concentrations >10 wt%). This is a strong indication that cubes aggregate mainly due to geometrical reason. Fig. 1 shows a typical series for a nanocube dispersion and the corresponding simulations.Without external magnetic field we observe a set of Debye-Scherrer rings, whose positions can be indexed on a primitive cubic lattice of nanocrystals with space group Pm3m. Application of an external magnetic field leads to orientation of the mesocrystals in the magnetic field. With increasing

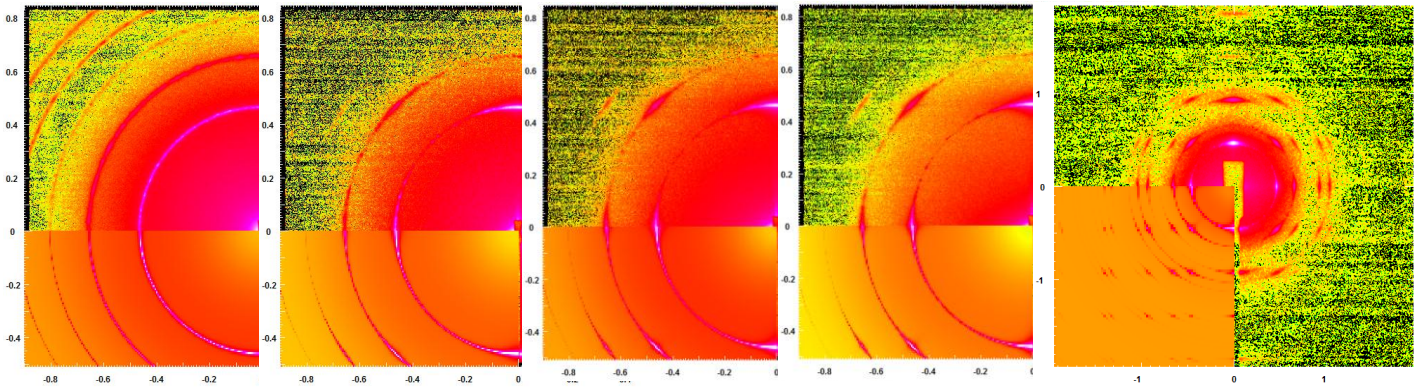

Fig. 1: *Scattering patterns of a magnetite nanocube dispersion (18 wt%) before and after applying an external magnetic field perpendicular to the beam. Left to right: 0.0001 T- 0.0577 T – 0.3828 T- 0.9788 T (last two). The bottom part of the figure on the right depicts the calculated scattering intensity. The detector distance was set to 0.874 m or 5.000 m.*

magnetic field strength the rings develop into arcs and finally well-defined Bragg reflections. The Bragg-peaks can be indexed assuming the mesocrystals to be aligned with their [001] direction parallel to the magnetic field (z-direction). The beam passes in perpendicular direction to the magnetic field such that it probes a superposition of random orientations (fibre pattern) including the [100] and [110] directions. After switching off the field, the orientation relaxes slowly due to a huge anisotropy energy. The assembled structures have large dimensions (microns range). When the beam passes parallel to the direction of the magnetic field, Debye-Scherrer rings are observed with and without field, in agreement with the disappearance of the reflection arount 0.8 nm^{-1} (cf. Fig. 2 right). The unit cell size of 13.2 nm agrees very well with the nanocube-nanocube distance observed with cryo-TEM in the one- and two-dimensional assemblies (Fig. 2). It is remarkable that the crystalline order of the nanocubes is translated into the 3D mesocubes bridging 3-4 orders of magnitude in length scale.

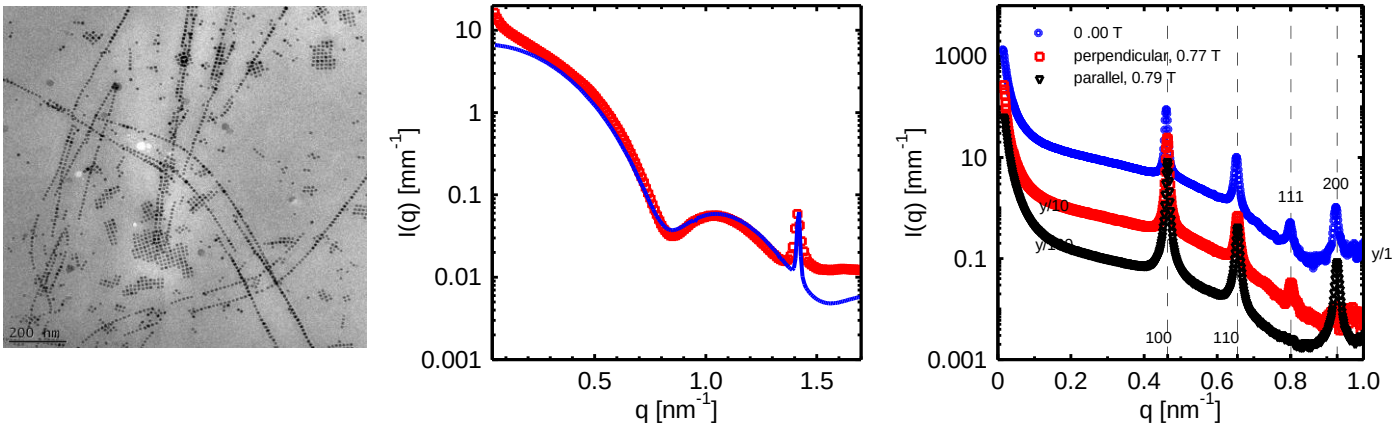

Fig. 2: *Left: Cryo-TEM micrograph on a 1 wt% nanocube dispersion (magnetic earth field). Middle: 1D-scattering intensity of a 2 wt% nanocube dispersion (no additional magnetic field) and corresponding formfactor fit. The Bragg-peak corresponds to the cystallized oleic acid surface layer. Right: Scattering intensities of a 18 wt% dispersions with and without applying an external magnetic field.*

The self-assembly process from nanocubes to mesocubes is very complicated. A closer inspections of the diluted samples by electron microscopy studies revealed the presence of 1D chains/2D bands and small clusters of 2D sheets. The patches and chain structures are never attached, meaning that their dipolar interactions are repulsive (Fig. 2 left). In case of the nanocube disperions the oleic acid layer crystallize around thermal energy leading to a stabilization of the sheet conformations and making the self-assembly pathway even more complicated (Fig. 2 middle).
Based on our results we propose the following self-assembly pathway: (1) At the beginning ferromagnetic linear chains and antiferromagnetic sheets grow. (2) In a secondary growth regime chain/chain and sheet/sheet attachments occur. (3) Field-induced growth leads to the formation of the mesocubes due to sheet/sheet attachments and chain/sheet attachments.

An article on the magnetic self-assembly of iron oxide nanocubes is in preparation.