GISAXS by long range ordered assemblies of iron oxide nanoparticles

Intensive research has been dedicated to magnetic nanostructures, both because of their possible applications, e. g. in medical imaging, catalysis, information storage, and owing to the interest in fundamental understanding of their magnetic properties. Magnetic nanoparticles, compared to bulk materials, show unique physical properties such as superparamagnetism or enhanced anisotropy constants. Scattering methods are best suited for investigating both intraparticular phenomena, such as the magnetization distribution or the spin structure of individual magnetic nanoparticles, and interparticular interactions of such nanoparticles in higher dimensional nanostructures. However, before addressing the problems of magnetization distributions or magnetic interactions between magnetic nanoparticles, the availability and the precise structural characterization of highly monodisperse nanoparticles and highly ordered nanostructures is required.

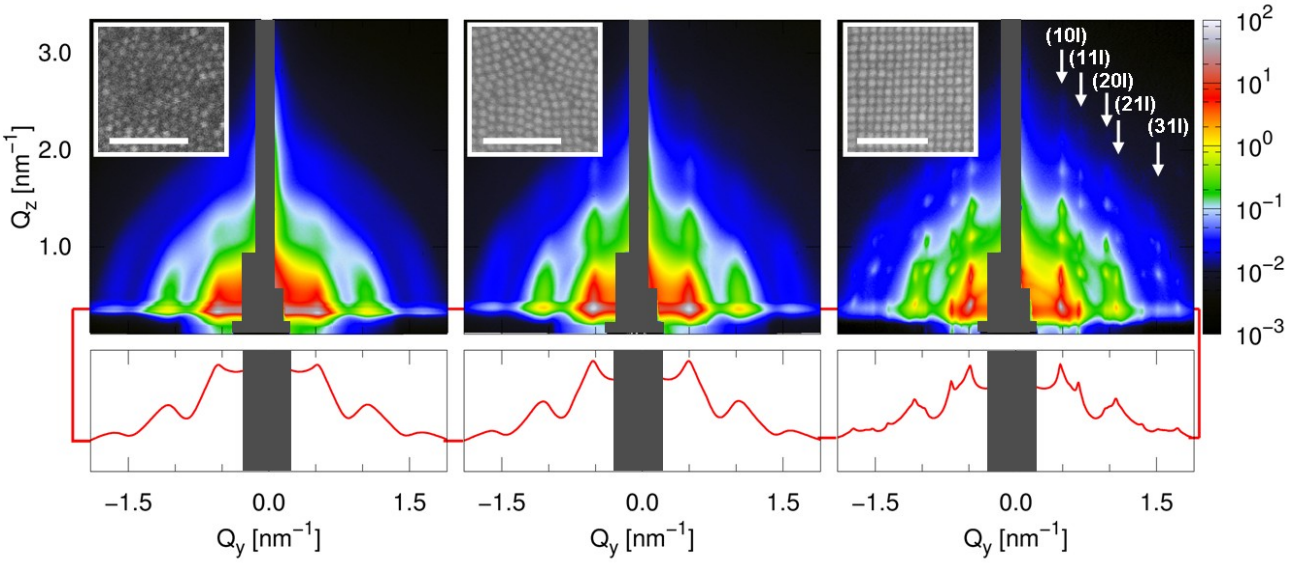

Figure 1: GISAXS patterns of assemblies of iron oxide nanocubes. The nanoparticles were deposited by (a) spin coating, (b) drop casting, and (c) drop casting under a perpendicular magnetic field. The inserts are representative SEM images of the resulting nanoparticle arrays. Scale bars represent 100 nm. The lateral scattering contributions taken at Q_z = 0.34 nm^{-1} in the respective GISAXS patterns are shown on a logarithmic scale at the bottom.

Iron oxide nanocubes of ~ 8.5 nm edge length and nanospheres of 9 nm in diameter – with a narrow size distribution of ~ 6% for each sample - were assembled on germanium substrates, and the obtained assemblies were investigated by GISAXS. GISAXS patterns of the nanocubes assembled by three different deposition techniques are presented in Figure 1. While spin coating was applied in order to prepare a disordered reference sample, some small domains of square order appear in the SEM of the sample prepared by drop casting. Long range order of the nanocubes was achieved by application of a magnetic field perpendicular to the substrate during deposition. The GISAXS patterns of the samples deposited without magnetic field show the typical features of thin films of disordered nanoparticles. The lateral scattering contributions detected in the sample horizon at Q_z = 0.34 nm^{-1} reveal liquid like nearest neighbor correlations with a slightly higher correlation length for the drop casted sample (18 nm as opposed to 16f nm for the spin coated sample). Diffuse streaks of the correlation peaks in the out of plane direction point to the presence of thin (mono- or bi-)layers.

For the magnetically ordered sample different features are observed. The lateral scattering contribution exhibits distinct reflections with correlation lengths beyond the resolution limit

of 65 nm. Also in direction of Qz, sharp reflections are observed rather than diffuse streaks, suggesting the presence of long range ordered nanoparticle mesocrystals instead of disordered thin films. Indeed, the lateral scattering contribution can be indexed according to the square plane group *p4mm*, in agreement with the SEM results. Taking into account the refractive contributions for scattering perpendicular to the substrate, all the appearing reflections were indexed to a tetragonal space group, revealing a tetragonally body centered packing of the oriented iron oxide nanocubes.

Similar to the nanocubes, long range ordered, three dimensional assemblies of iron oxide nanospheres were produced. While SEM images suggest a hexagonal lateral order, the question of the 3D stacking type - either *hcp* or *fcc* – was studied by GISAXS.
Analysis of the lateral and out of plane scattering contributions revealed the hexagonal plane group *p6mm* in agreement with the SEM results, as well as a rhombohedral space group for the entire three dimensional structure. Thus, the stacking preference of these highly monodisperse iron oxide nanospheres has been determined to *fcc* by GISAXS.

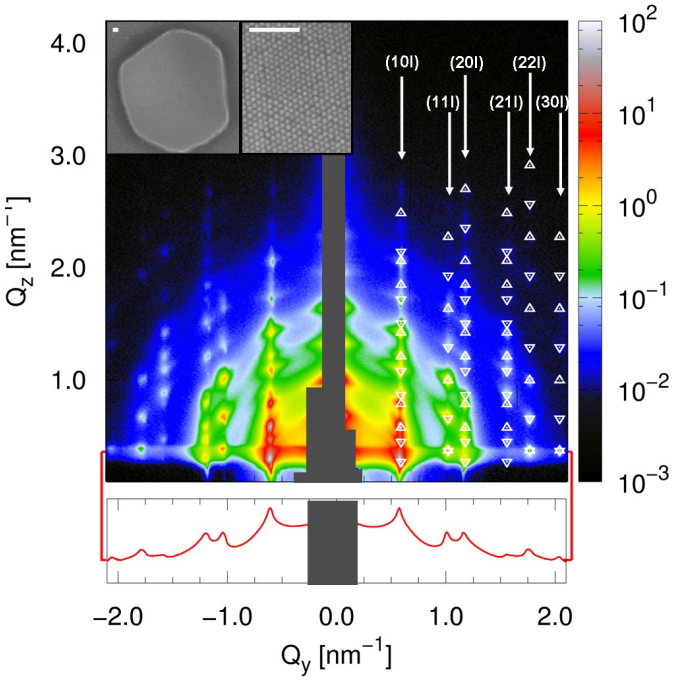

Figure 2: GISAXS by assemblies of iron oxide nanospheres. Rhombohedral reflections with (Δ) and without (∇) reflection of the beam at the substrace are indexed. The insets are representative SEM images of one nanospheres mesocrystal (left) and ordered nanosphered on top of the mesocrystal (right). Scale bars represent 100 nm. The lateral scattering contribution taken at Q_z = 0.34 nm^{-1} is shown on a logarithmic scale at the bottom.