X-Ray diffraction on a μm size self-assembled nanoparticle supercrystal

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Fundamental research on magnetic nanostructures is an important part of today's scientific effort in information technology [1]. In particular, self-assembled structures of magnetic nanoparticles are candidates for a new generation of improved magnetic storage media [2]. The understanding and control of the structure in 2D and 3D self-assembled particles is of great interest for application, as it allows low-cost mass production of very small structures. The purpose of this study was to use a completely new approach: Performing a diffraction experiment on a 3D μm size self-assembled nanoparticle supercrystal with a micro focused x-ray beam. Thus it was possible to measure the nanoparticle superstructure peaks without powder average and without background from disordered regions, as was the case in previous experiments [3, 4]. The investigated samples consist of cubic iron oxide nanoparticles with an edge length of 10.9 nm and a narrow size distribution [5]. These 3D ordered arrangements of nanoparticles are called mesocrystals, in analogy to crystals formed by atoms. The performed experiment is not only interesting from a scientific point of view, but enters a new level of crystallography. The nanoparticles as new building blocks and the diminutiveness of the mesocrystal with a height of 215 nm and a diameter of 4.5μm makes this experiment an exciting challenge.

A diffraction study under small angles was performed at P08 in order to determine the structure of a single highly ordered mesocrystal (Fig. 1). A special setup was built to fix the single mesocrystals on the sample holder and goniometers were used to adjust the position with the (00l) direction of the mesocrystal lattice parallel to the axis of the phi circle (vertical to the beam), in order to rotate around the z-axis to reach different directions in the plane while keeping the l-component fixed. The detector position was fixed at 77 cm distance from the sample and the energy at 12.4 keV to have sufficient q-range to reach as many reflections as possible at a time, to avoid beam damage to the sample and to have a optimized wavelength for the Roper Scientific detector. To be able to investigate crystals of μm size some requirements are absolutely mandatory: the x-rays have to be focused down to the size of the crystal to achieve high photon flux densities (in our case: 5μm vertically and 10μm horizontally), the beam has to stable within a fraction of the sample diameter, the background has to be virtually zero and the motor resolution has to be significantly better than the sample size and the width of the Bragg reflections. These absolutely necessary conditions make this experiment extremely challenging. For instance, the xyz-position has to be realigned for each crystal orientation to bring the mesocrystal into the beam center as the sphere of confusion of the six-circle was in the order of the beam size. For a measurement with lower focusing (see results of report [6]) more background from other regions around the sample and low intense peaks are visible. So we decided to use a more focused beam.

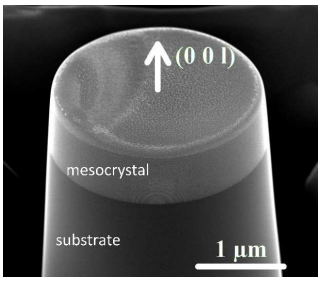
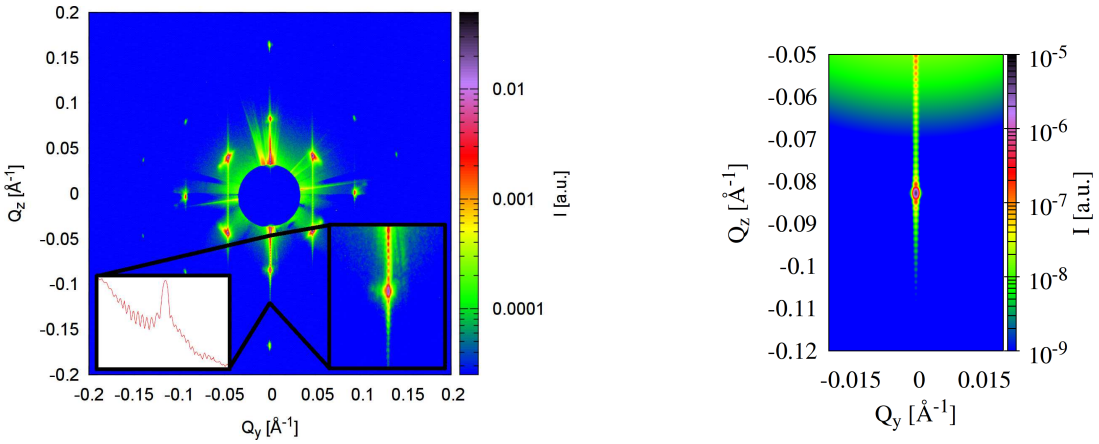


Figure 1: SEM picture of a single mesocrystal

Different scattering planes were reached, optimized in the position and measured by rocking the crystal in both ω and φ. In detail, images were exposed while continuously moving φ for 5 omega positions ("cmesh"). One background cmesh for each image was measured for 60 seconds. These measurements were repeated a number of times in dependence of the expected scattering intensity from the investigated plane. Such a measurement was done for every reached plane. Reflections for



(a) Measurement of the (h0l) plane.

(b) Simulation

Figure 2: Measurement of the (h0l) plane of a single mesocrystal with cubic particles. The zoom shows a nice Laue-Oscillation, which could be well reproduced by a simulation.

four of the reciprocal space planes (h0l, hhl, h2hl, hmhl) for the mesocrystal with cubic building blocks have been measured. The (h0l) plane as an example is shown in Fig. 2(a). Repetitions of selected planes have been verified, proving a fourfold rotation axis parallel to c. The peaks are consistent with the expected I4/mmm space group derived from an ensemble of crystals [3, 4]. The mesocrystal shows a single crystalline structure, in contrast to the mesocrystal out of spherical particles, which was measured in the previous experiment, featuring a twined structure [6]. The width of the peaks depend on the size of long range ordered domains within the crystal. The height of the mesocrystal measured by SEM correspond to the width in the Q_z direction of the peak. The peak tails in Q_z direction show Laue-oscillations, which indicate a high degree of order within sample, a flat surface and a relatively small height. The simulations in Fig.2(b) for a perfectly ordered cubic system fits the observation nicely. The Laue-Oscillations introduced by the mesocrystal shape are in good agreement. Variation of the particle size, as well as the measurement procedure are not considered, which is the reason for the intensity differences of the peaks and background. A preliminary integrated Intensity analysis shows that a new cubic form factor is necessary to accurately describe the data.
This challenging experiment proved the feasibility of the investigations on single, small mesocrystals of nanoparticles to open a new field for further investigations of the mesocrystal structure. The analysis of the intensities and the rocking curves is still in progress.

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