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Morphological and crystallographic orientation of hematite spindles in applied magnetic field†

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1 Supplemental Material

1.1 Halbach magnet setup

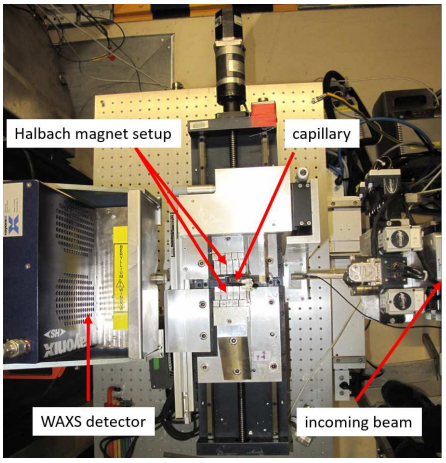

Fig. S 1 Photo of the Halbach magnet setup from SAXS/WAXS experiment.

1.2 SAXS/WAXS Intensity calibration

Data reduction of the WAXS and SAXS measurements were performed by the SAXS program package using the SX parametrization and SPD program from P. Bösecke at ID02 instrument [1]. All corrections were done according to Bösecke *et al.* [2], starting with the dark image subtraction continuing with spatial distortion correction (consisting of the horizontal and vertical displacement of each pixel), division by the flatfield and ending with the normalization to primary beam (measured by a PIN diode atop the beamstop) and conversion to the scattering cross section. The absolute intensity per unit volume is obtained by dividing the scattering intensity I_Ω by sample transmission T and the thickness d:

$$\mathrm{d}\Sigma/\mathrm{d}\Omega = I_\Omega/Td. \tag{1}$$

Correction to the reference material is done by measuring of uncalibrated sample $(\mathrm{d}\Sigma/\mathrm{d}\Omega)^{\mathrm{sample}}$ as well as the reference sample (water in this experiment) with known scattering intensity $(\mathrm{d}\Sigma/\mathrm{d}\Omega)^{\mathrm{ref}}_{\mathrm{cal}}$. The scattering pattern of the reference material is corrected according to the above mentioned procedure. In the last step, the solvent background is subtracted from the sample scattering cross section. Azimuthal average of the data were performed using the SAXSutilities software developed by Michael Sztucki *et al.* [4]. In case of WAXS experiments, 2D data were corrected in the same way as 2D SAXS data except of the background subtraction. Moreover, polarization correction to the 2D WAXS data was applied according to Bösecke [2]. After radial integration, the obtained 1D WAXS data was then corrected for the background by the DataTools program of the SAXSutilities package [4].

1.3 Rietveld refinement

For the Rietveld refinement, we applied a linear combination of the spherical harmonics for the space group no. 167 (space group $R\,\bar{3}\,c$). The integral breadth of the reflection **H** can be described by:

$$\beta_{\mathbf{H}} = \frac{k\lambda}{\cos\theta} \sum_{\mathrm{lmp}} a_{\mathrm{lmp}} y_{\mathrm{lmp}}(\theta_{\mathbf{H}}, \phi_{\mathbf{H}}), \tag{2}$$

where $y_{\mathrm{lmp}}(\theta_{\mathbf{H}}, \phi_{\mathbf{H}})$ are the real spherical harmonics (with the polar angles $\theta_{\mathbf{H}}, \phi_{\mathbf{H}}$), and a_{lmp} are the coefficients[5]. Refinement of the data using spherical harmonics allows us to visualize the average form of the crystallites using GFourier[6,7] as presented in **Fig.** S 2.

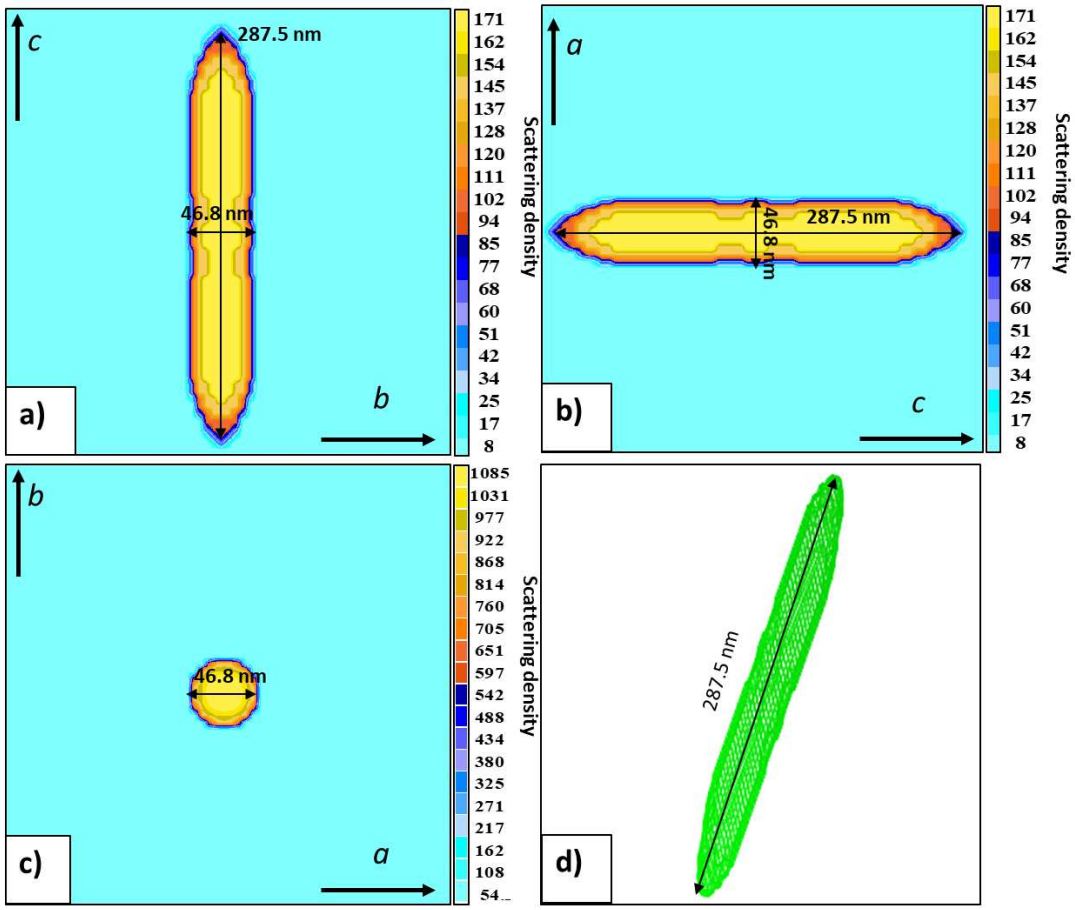

Fig. S 2 a-c) Visualization in 2D and **d)** 3D of the average crystallite shape.

1.4 SAXS in applied magnetic field parallel to the incoming beam

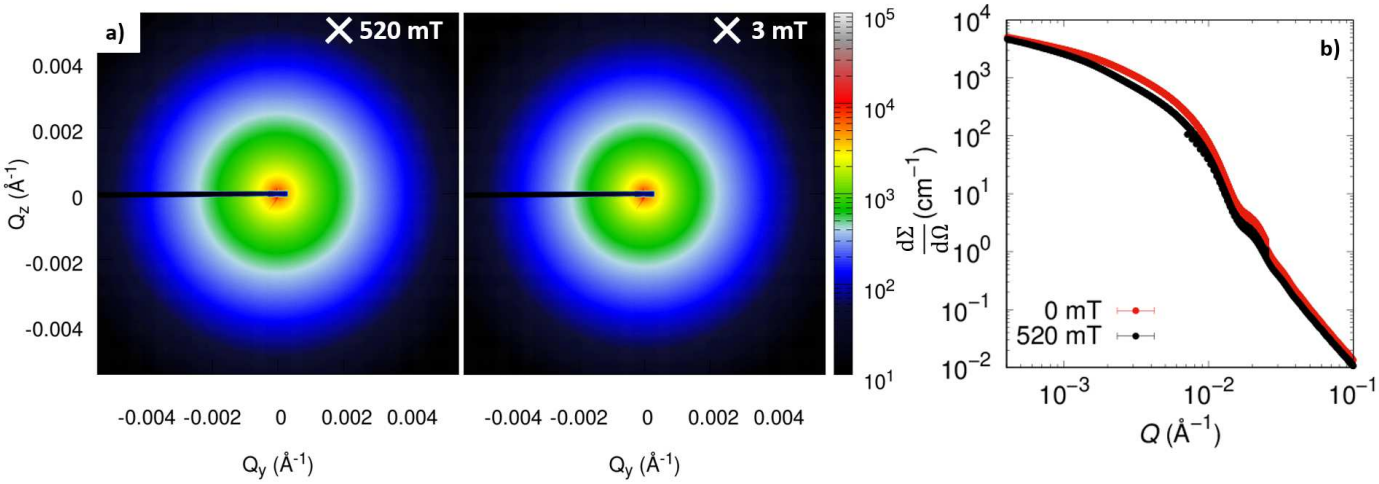

Fig. S 3 a) 2D SAXS and **b)** 1D data of hematite spindles in applied magnetic field of 520 and 3 mT (magnetic field parallel to the beam direction pointing perpendicular to the detector plane, indicated by white cross).

1.5 Field dependence of SAXS sectors integration

In order to visualize the agreement of data and simulation along the horizontal ($\kappa = 0°$) and vertical ($\kappa = 90°$) directions data were scaled as presented in **Fig.** S 4.

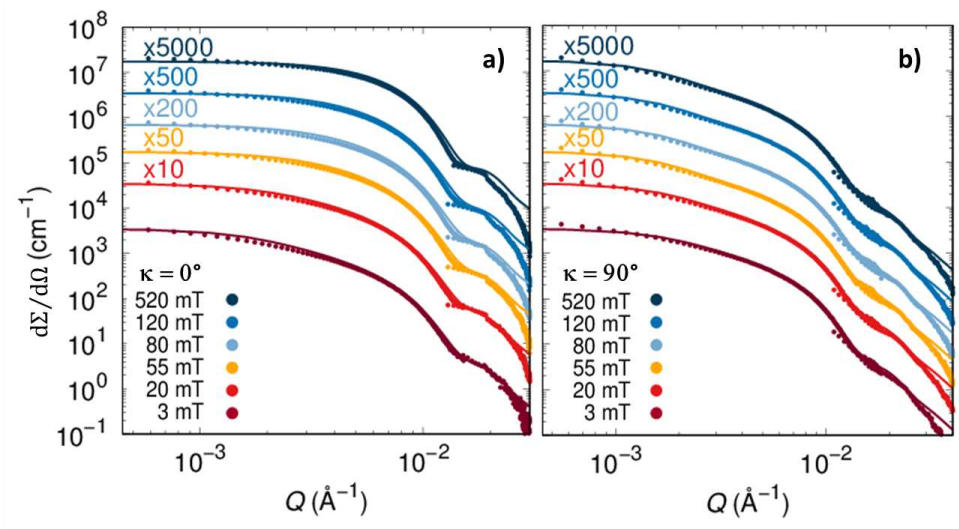

Fig. S 4 Comparison of scaled 1D data (points) with simulation (full lines) of 10° wide sectors around **a)** $\kappa = 0°$ **b)** $\kappa = 90°$. Scaling factor is indicated by numbers.

1.6 Field-dependence of WAXS Reflections

Obtained results from Le Bail fits of the intensity for various WAXS reflections as function of the applied magnetic field are presented in **Fig.** S 5 and summarized in **Table** S 1.

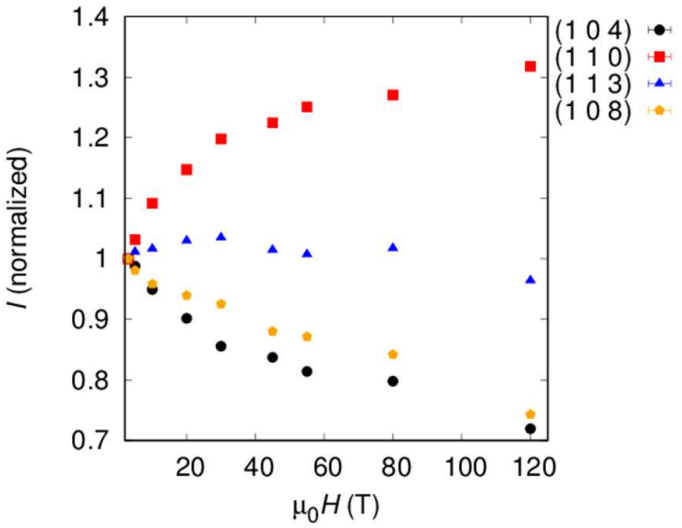

Fig. S 5 Integrated intensities of the WAXS reflections. The data for each reflection are normalized to the intensity measured at 3 mT.

magnetic field (mT)	**(1 0 4)**	**(1 1 0)**	**(1 1 3)**	**(1 0 8)**
3	3.37(1)	1.93(1)	0.97(1)	0.58(1)
5	3.33(1)	1.99(1)	0.98(1)	0.56(1)
10	3.20(1)	2.11(1)	0.99(1)	0.55(1)
20	3.04(1)	2.21(1)	1.00(1)	0.54(1)
30	2.89(1)	2.31(1)	1.01(1)	0.53(1)
45	2.82(1)	2.36(1)	0.99(1)	0.51(1)
55	2.75(1)	2.41(1)	0.98(1)	0.50(1)
80	2.69(1)	2.45(1)	0.99(1)	0.49(1)
120	2.43(1)	2.54(1)	0.94(1)	0.42(1)

Table S 1 Magnetic field dependence of the intensities for the indicated reflections.

1.7 WAXS texture of (1 0 4) reflection

Figure S 6 shows that the texture observed at large applied field of the (1 0 4) reflection. The angle between the c direction (0 0 1) and the (1 0 4) reflection is approximately 38.5° resulting in an angle between the basal plane and the (104) lattice plane of 51.5 and 128.5°, at which a texture of the (1 0 4) reflection should be observed. (This is indicated by the dashed lines in Fig. S 6). The azimuthal scattering intensities around $\kappa = 90°$ are affected by a shadow of the sample capillary during normalization and therefore are not quantitative. However, the general tendency of increased intensity in the direction perpendicular to the applied field confirms orientation of the nanospindles with their polar axis perpendicular to the applied field.

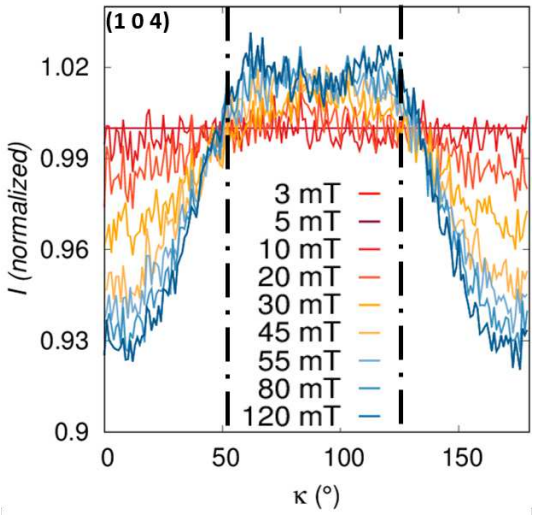

Fig. S 6 Azimuthal angle dependence of the intensity of (1 0 4) reflection measured at various applied magnetic fields. Dashed line represents maxima of reflection angles at 51 and 128°.

Notes and references

1 P. Bösecke, *SAXS program package*, 2013, http://www.esrf.eu/home/UsersAndScience/Experiments/CBS/ID02/available_software/saxs-program-package.html.

2 P. Bösecke and O. Diat, *Journal of Applied Crystallography*, 1997, **30**, 867–871.

3 W. H. De Jeu, *Basic X-ray Scattering Applied to Soft Matter*, Oxford University Press, 2016, p. 160.

4 M. Sztucki and T. Narayanan, *Journal of Applied Crystallography*, 2007, **40**, s459–s462.

5 M. Järvinen, *Journal of Applied Crystallography*, 1993, **26**, 525–531.

6 J. Rodríguez-Carvajal, *Physica B*, 1993, **192**, 55.

7 J. González-Platas and J. Rodríguez-Carvajal, *GFourier: a Windows/Linux program to calculate and display Fourier maps. Program available within the FullProf Suite*, https://www.ill.eu/sites/fullprof/php/programse811.html?pagina=Fourier.