Magnetic Sample Environment for in-situ SAXS/WAXS Measurements on Magnetic Nanoparticles with Shape Anisotropy

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Abstract. A vacuum-compatible magnetic sample environment has been developed and installed at the four-crystal monochromator beamline of the Physikalisch-Technische Bundesanstalt (PTB) at the synchrotron radiation facility BESSY II in Berlin, Germany. The design is based on a water-cooled electromagnetic coil setup and is aimed to provide a magnetic flux density of up to 900 mT at the sample position. The magnetic field is applied in order to align or arrange magnetic nanoparticles which can then be measured using small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS). This can be beneficial in the analysis of particles with arbitrary shape. The corresponding scattering patterns are collected as 2D images on vacuum-compatible variants of the PILATUS 1M and PILATUS 100K detectors.

1. Motivation

Magnetic nanoparticles link the important field of nanotechnology with magnetism, which results in many interesting properties and applications. They are used in various technical, environmental, medical applications [1, 2] and fundamental research [3]. Their characteristics depend strongly on the type of material, size and shape of the nanoparticles.

Beside imaging techniques like transmission electron microscopy (TEM), which can only sample a limited amount of particles, also ensemble based methods like small-angle X-ray scattering (SAXS) are well suited to determine the size distribution with good statistics. In a classical SAXS experiment the sample is measured in solution in a diluted form and is contained in a glass capillary. As a result all orientations are present in the sample and averaging leads to a loss of information in the scattering pattern. For nanoparticles with a shape anisotropy (e.g. cubes, rods) this produces ambiguous data models and inaccessible particle dimensions. Applying magnetic fields can solve this problem for magnetic nanoparticles by aligning their easy axis of magnetization and thus pinning their movement in one direction. In addition, field dependent effects can be investigated by changing the field intensity [4] and the formation of arrangements and (super)structures [5, 6] can be induced.

There are two ways to apply a magnetic field, either using permanent magnets [7, 8] or using electromagnets [9, 10], both of which have their own advantages and disadvantages. We chose the latter because it offers more flexibility in magnetic fields (e.g. easy ramping, changing the direction of current and wiring of the coils, or high-frequency fields if coils without a core are used). Soft X-rays require a vacuum, whereas nearly all conventional magnetic sample environments are operated in air at higher photon energies. The few vacuum-compatible versions are complete chamber designs that can reach flux densities of only about 270 mT[11, 12].

In this work, we present the development of a compact, modular, water-cooled, vacuum-compatible magnetic sample environment based on electromagnetic coils that can be used in soft X-ray scattering experiments. This setup can reach flux densities of about 900 mT. The components and control system as well as the magnetic properties are described and the results of the first experiments are given.

2. Experimental Setup

The setup is built for X-ray scattering experiments at the four-crystal monochromator (FCM) bending magnet beamline in the laboratory of PTB [13], the National Metrology Institute of Germany, at the electron storage ring BESSY II and is located inside of the UHV reflectometer [14].

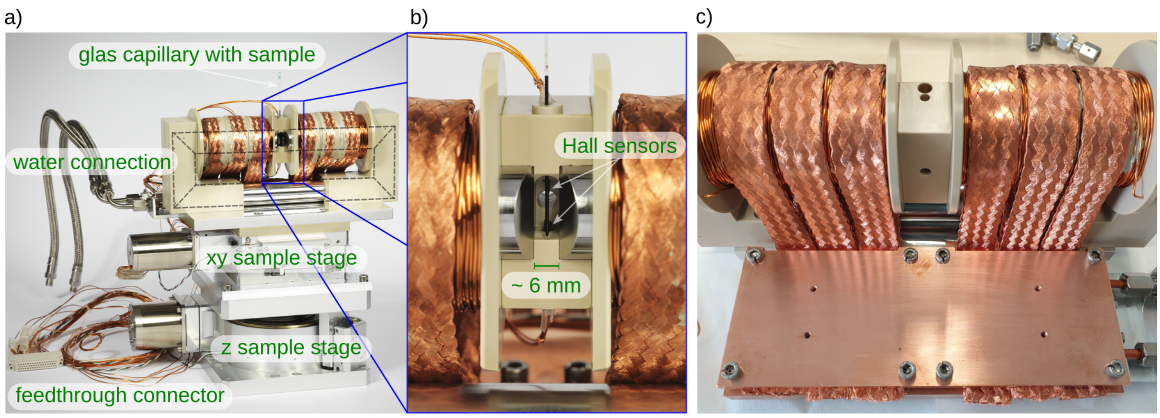

Figure 1. a) Vacuum part of the magnetic sample environment. The gray dashed lines depict the path of the segmented iron core behind the peek mounting. b) Zoom of the sample area between the iron yoke. The hole in the back is the entrance point of the X-ray beam. c) Backside of the sample environment during the building process. Visible is the clamping of the copper stranded wire to the water-cooled copper block.

The design is based on a set of coils, formed by a copper wire with a diameter of 1 mm and a length of $l \approx 130$ m) wrapped around a soft magnetic iron core (ASTM A848 Type 1 - Vim Var Core Iron, Nicofe Materials Ltd.). This iron core is formed by five rod shaped segments, each with a diameter of 25.0 mm (Fig. 2a inlay), which are held together by peek blocks (Fig. 1a). The dimensions of the iron yoke are 85 mm × 255 mm (height × width). The sample is positioned between a gap with a width of 6 mm at which the iron rods have a cut-off to access higher scattering angles, which are needed for the wide-angle scattering detector [15]. Next to the sample above and below the X-ray beam are GaAs Hall-sensors (CYSJ902, ChenYang Technologies) to measure the magnetic field during the experiment. To remove the thermal load, three copper stranded wires per coil are directly glued on to the coil wires with silver adhesive and clamped to an actively water-cooled copper block (Fig. 1c). The cooling water is supplied by a thermostat (Huber Minichiller 280). In addition, each coil is equipped with a Pt100 resistance temperature sensor that monitors the temperature on the outside of the coil. The setup is mounted on top of a xy and z sample stage (HUBER) for positioning relative to the X-ray beam, which is parallel to the x axis in Fig. 2. They are chosen so that they can bear the weight of the electromagnet of approx. 2.5 kg (iron poles + copper coil). A 50 pin Sub-D feedthrough

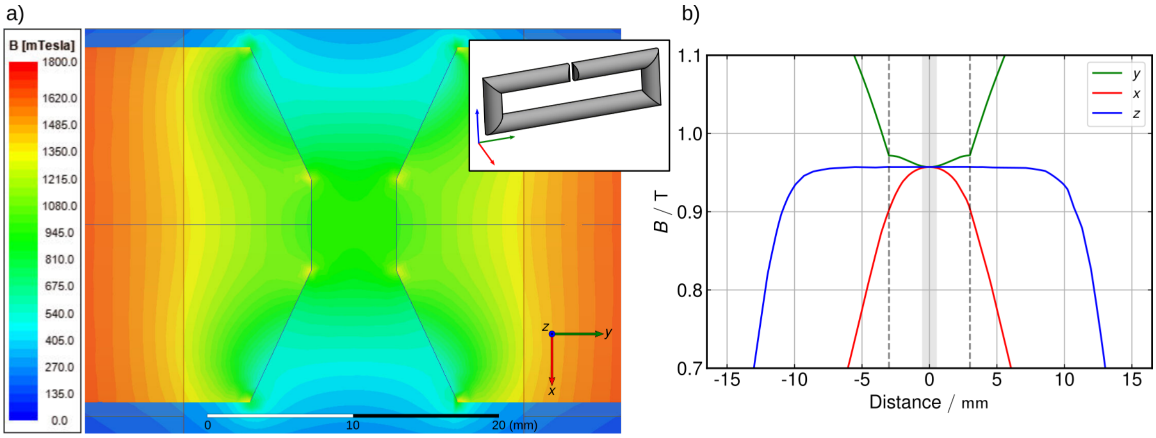

Figure 2. a) Simulated field in the xy-plane of the sample region at the gap for a coil current of 3 A. The inlay shows a 3d model of the yoke. b) Simulated field along the unit directions centered inside the gap. The dashed lines depict the size of the gap and the shaded area is the sample region covered by a standard 1 mm SAXS capillary.

with max. 5 A per pin is used for all conductors including the motor cables. The coils are connected in series and the current for the electromagnet is delivered by a programmable power supply (HMP2020, Rhode & Schwarz). Both the power supply and the motor controller are integrated into the EPICS [16] environment of the laboratory and can be controlled by PTB's own measurement software [17]. Behind the reflectometer a vacuum-compatible area detector (PILATUS 1M, DECTRIS) is located at a variable sample-detector distance of up to 5 m which is part of the SAXS setup [18].

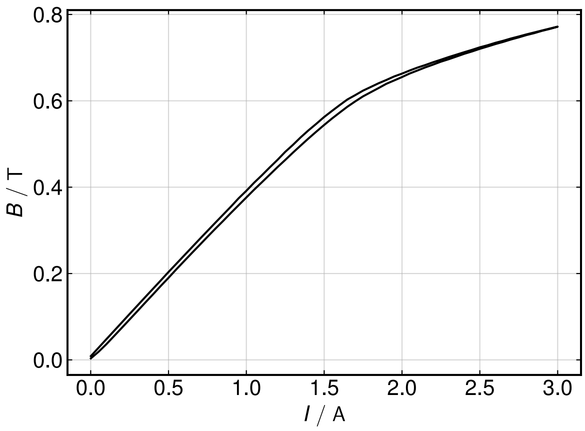

Figure 3. Magnetic flux density measured with a professional teslameter as a function of the coil current for different current ramps. The change of slope in the curve at about 1.5 A is a result of the saturation magnetization of the soft magnetic iron yoke.

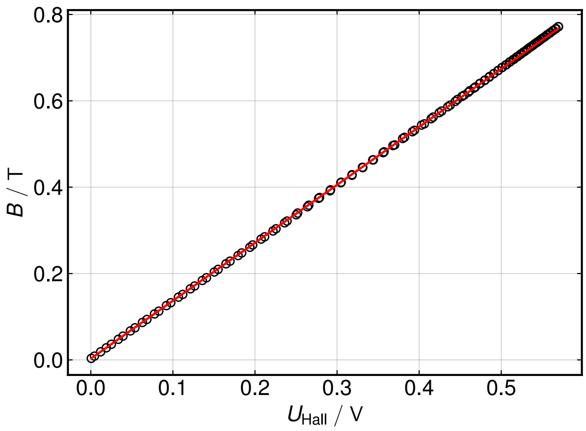

Figure 4. Magnetic flux density measured with a professional teslameter at the sample location vs the hall voltage measured by the Hall sensor ($I_H = 100$ mA).

In Fig. 3 the magnetic flux density at the sample position is measured by a calibrated teslameter (FM302, Projekt Elektronik). Although the core is made from soft magnetic iron, it still shows a hysteresis, which means the field values differ depending on the magnetization

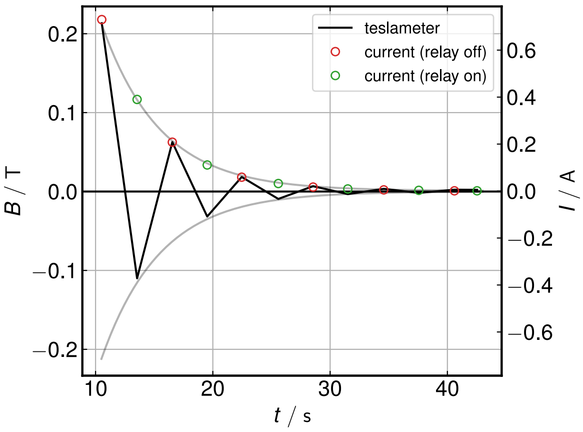

Figure 5. During the demagnetization process, the coil current follows an exponential decay. In combination with a relay that switches the current direction, this results in an oscillating signal that is measured with the professional teslameter at the sample position.

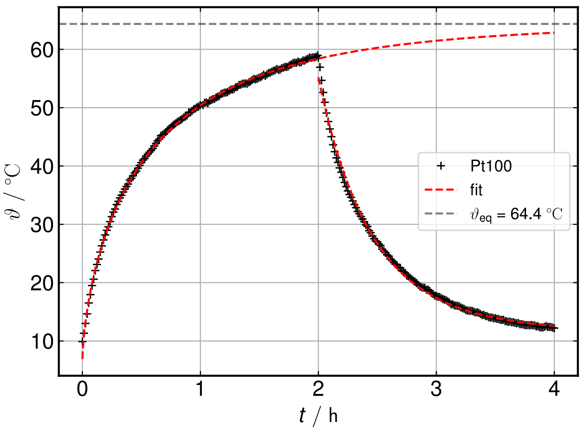

Figure 6. Coil Temperature at a coil current of $I = 3\,\mathrm{A}$. The red dashed line corresponds to a stretched exponential which was fitted to the data to estimate the equilibrium temperature. Thermostat set point is at $\vartheta = 5\,°\mathrm{C}$.

history of the iron core. For this reason, it is also necessary to measure the magnetic field in-situ with Hall sensors. These Hall sensors exhibit a linear behavior and are referenced by the teslameter measurement (Fig. 4). Another side effect of the iron core hysteresis is the remanence. In order to reduce the remaining field at 0 A a demagnetization process is applied after every experiment. This consists of the coil current alternating with decreasing absolute value, which follows an exponential curve (Fig. 5). The alternating behavior is realized by a relay that switches the inputs when a 24 V signal is received. After this step, the remanence is lowered to a constant value of about 2.7 mT. The homogeneity of the magnetic flux density at the sample position is very good with a variation of only $\frac{\Delta B}{B} \approx 0.1\,\%$. In Fig. 6 the coil temperature is shown over a period of 2 h with 3 A coil current and additional 2 h without current. A stretched exponential is fitted to extract the equilibrium temperature of about $\vartheta_{\mathrm{eq}} = 64\,°\mathrm{C}$. Although the current is divided among several pins in the feedthrough and thus a coil current of more than 5 A is possible, it is not recommended to operate the electric coils at more than 3 A for a prolonged period of time in order to avoid overheating the system. Nevertheless, the maximum field strengths achieved at 4 A and 5 A are 855 mT and 920 mT, respectively.

3. Application Example

The magnetic sample environment is used for aligning or arranging magnetic nanoparticles. To test this newly developed system, we have chosen two types of iron oxide nanoparticles (hematite, Fe_2O_3) with different shapes, namely cuboids and spindles.

Fig. 7 display the SAXS images collected at a sample-detector distance of about 5 m with a photon energy of 8 keV. The small images depict the same sample measure by TEM. At a magnetic flux density of $B = 376\,\mathrm{mT}$ both particle systems are aligned with their easy axis of magnetization parallel to the magnetic field. This is clearly visible from the SAXS image. The signal is no longer radially symmetric, as is the case when all directions are present in the sample. From the radial distribution it is already possible to deduce the orientation of particles, which is along the space diagonal for the cuboids and along the short axis of the spindle. The particle is only pinned in one axis, so further rotation about the field axes is still possible and needs to be included in any data model.

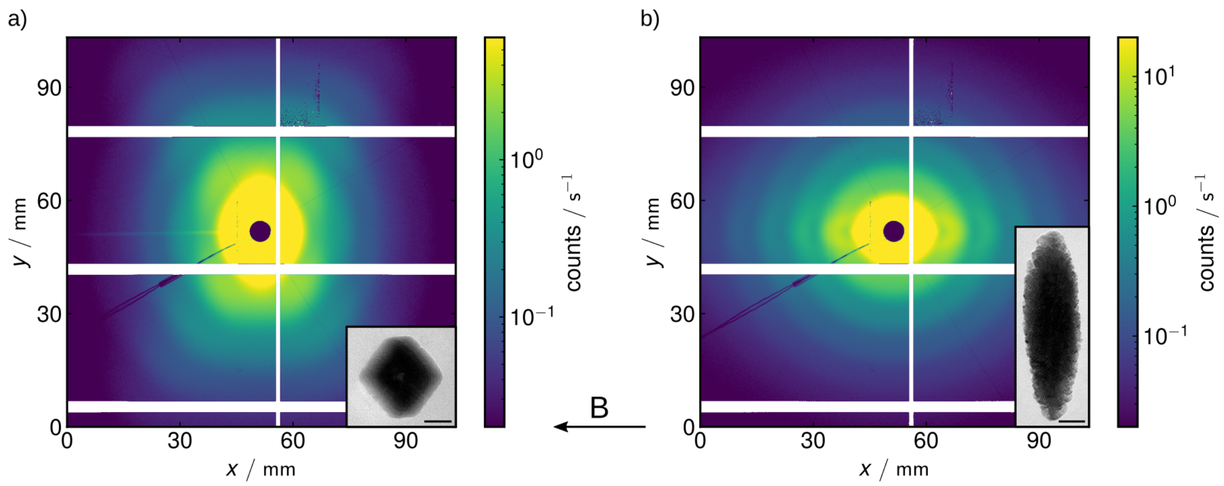

Figure 7. Hematite (Fe_2O_3) nanoparticles with a) cuboid and b) spindle shape. The magnetic flux density of about $B = 376\,\mathrm{mT}$ is parallel to the x axes of the detector image. The scale bar in the TEM images has a length of 25 nm for the cuboid and 50 nm for the spindle.

4. Conclusion and Outlook

In this paper, we have presented the development of a vacuum-compatible sample environment with actively water-cooled electromagnetic coils. The full design is very compact with about $30\,\mathrm{cm} \times 30\,\mathrm{cm} \times 30\,\mathrm{cm}$. The setup is equipped with multiple sensors to measure the magnetic flux density in-situ and to monitor the temperature of the coils. A sample stage can be used to align the sample environment relatively to the X-ray beam. Thanks to the soft magnetic iron core, the sample environment is capable of reaching flux densities as high as 920 mT at coil currents of 5 A. However, to reduce the remanence of the iron core, a demagnetization cycle should be performed between different experiments.

First measurements on magnetic nanoparticles with shape anisotropy show the ability of the setup to align nanoparticles of different shapes. In combination with extensive 2d modeling of form factors, this should provide access to the single particle dimensions. Furthermore, an arrangement of nanoparticles in a magnetic field can lead to superstructures that can provide additional information for the characterization.

Acknowledgments

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References

[1] Lu A-H et. al. 2007 *Angew. Chem. Int. Ed.* **46** 1222-1244
[2] Mohammed L et. al. 2017 *Particuology* **30** 1-14
[3] Afkhami S and Renardy Y 2017 *J. Eng. Math* **107** 231-251
[4] Hinrichs S et. al. 2020 *J. Nanomater.* **10** 2526
[5] Wiedenmann A et. al 2003 *Phys. Rev. E.* **68** 031203
[6] Giersig M and Hilgendorff M 2005 *Eur. J. Inorg. Chem.* **18** 3571-3583
[7] Taheri S M et. al. *PNAS* **112** 14484-14489
[8] Narayanan T et. al. 2001 *Nucl. Instrum. Methods Phys. Res.* A. **467-468** 1005-1009
[9] Bras W et. al. 2014 *IUCrJ* **1** 478-491

[10] Paolasini L et. al. 2007 *J. Synchrotron Rad.* **14** 301-312
[11] Grabis J et. al. 2003 *Rev. Sci. Instrum.* **74** 4048-4051
[12] Lee J-S et. al. 2008 *J. Korean Phys. Soc.* **52** 1814-1817
[13] Krumrey M and Ulm G 2001 *Nucl. Instrum. Methods Phys. Res.* A. **467** 1175-1178
[14] Fuchs D et. al. 1995 *Rev. Sci. Instrum.* **66** 2248-2250
[15] Skroblin D et. al. 2020 *Rev. Sci. Instrum.* **91** 023102
[16] EPICS, `https://epics-controls.org/`
[17] eveCSS, `https://github.com/eveCSS/eveCSS`
[18] Wernecke J et. al. 2014 *J. Synchrotron Radiat.* **21** 529-536