ESRF	**Experiment title:** Nanosized structure and magnetic field induced formation of chains in ferrofluids	**Experiment number**: SC 936
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Report:

Ferrofluids (denoted as FF) are stable magnetic colloids in which nanosized magnetic particles are stabilized against coagulation by coating with organic chain molecules acting as surfactants [1]. They show liquid behaviour combined with superparamagnetic properties. Renewed interest of these materials is motivated by potential biomedical applications [2] based on the superparamagnetic behaviour of nanosized particles which disappears when aggregation would takes place as a consequence of inefficient screening. The fluid properties, viscosity and viscoelasticity, are strongly influenced by the magnetic behaviour. Theoretical explanations of these macroscopic dynamic properties by the microscopic structure predict the aggregation of nano-particles in chains when an external magnetic field is applied [2].

The aim of our proposed experiment was the investigation of field-induced ordering processes (chain-formation) in ferrofluids of different concentration.

Ferrofluid samples based on three different magnetic nanosized core materials Co, Fe_3O_4 or Bariumhexaferrite using different organic shell materials were prepared. This core-shell composite particles are dispersed in different carrier liquids (in case of Co – toluene, Fe_3O_4 – water, Bariumhexaferrite - dodecane). The particle concentrations vary between about 1 vol% up to 6 vol%. All different ferrofluids and some reference samples were filled into small cylindrical quartz glass tubes with diameters between 0.7 mm – 1.2 mm and wall thicknesses of 10 μm. The 3 – 4 cm long tubes were sealed immediately after filling using a hydrogen flame. The samples were measured by SANS before this SAXS experiment took place.

A number of samples were glued together on a sample holder with the glass tube axis oriented by an angle of 45° to the horizontal direction. The sample holder was specially designed (Fig. 1) for this experiment. It was mounted on the ID01 diffractometer head between the pole shoes of an electromagnet. The diffractometer allowed a holder rotation around the vertical axis and a vertical shift of about 4.2 cm to change the samples. The electromagnet yielded homogeneous horizontal magnetic fields up to 0.57 T at the sample position applied perpendicular to the transmitting X-ray beam. The SAXS experiments were performed using a fixed X-ray energy of 7 keV to be well below the K-edges of Fe and Co and make sure to avoid parasitic fluorescence. The scattering curves were detected with a 2-dimensional gasfilled detector. Two sample detector distances of 4.5 m and 1 m were chosen such that a momentum transfer range of $0.05nm^{-1} < Q < 4.5nm^{-1}$ with $Q = 4\pi\sin(\Theta/2)/\lambda$ was covered. Consequently, the scattering curves contain the structure information in a size range of 1.4 nm to 125 nm. The 2-dimensional scattering pictures were corrected for background scattering and detector efficiencies and -distortions and normalised to absolute electron scattering units by comparing the scattering intensity of the samples with that of a calibrated glassy carbon standard sample.

Figure 1: The sample holder and the adapter mountable to the diffractometer tip in the center of Fig. 2 is shown. Filled sample tubes are glued on a frame in the upper part of the holder.

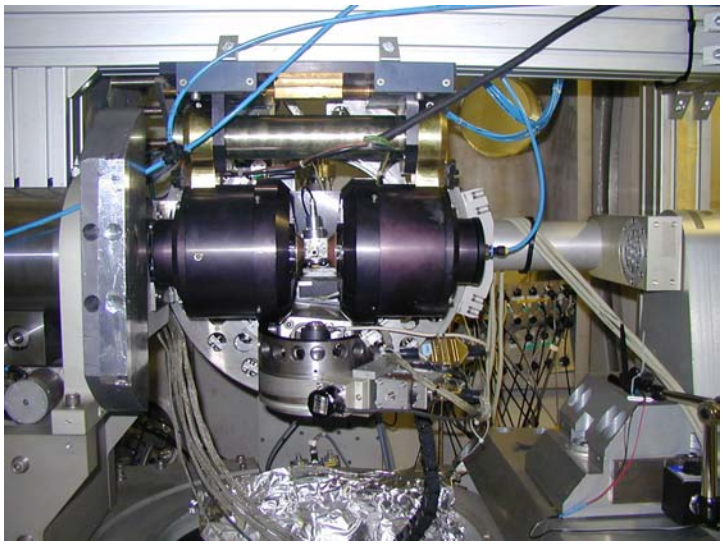

Figure 2: The picture gives a view of the sample holder position. The monochromatic X-ray beam comes from the back and penetrates through the pole shoes in direction perpendicular to the paper. The electromagnet is horizontaly mounted on the diffractometer using a frame.

The two-dimensional scattering patterns are taken at zero field followed by measurements at four different fields (0.024T, 0.065T, 0.24T and 0.57T). Finally, measurements at zero fields were done again.
In case of Barium hexaferrite FFs we observed no field depending ordering effect. We assume that this is caused by the very low magnetization of the particles, their known broad size distribution and the existence of aggregates.
In case of the three sorts of magnetite FFs (the sorts differ by their organic shell molecules) we observed a clear field dependent reversible orientation leading to an elliptical shape of the isointensity lines in the center of the 2d-scattering patterns, that means at the lowest Q-values. The long axis of the ellipses was perpendicular to the applied magnetic fields indicating a formation of elongated structures oriented parallel to the field direction. This effect increased with the field and with the concentration of magnetizable cores.
Moreover, in case of Co-FFs the magnetic field induced a queudo-crystalline ordering as revealed by peaks in the right picture of Fig. 3. The field induced order relaxed back to full disorder when the field is switched off, indicating a reversible field induced ordering behaviour. A paper on queudo-crystalline ordering which summarize the results of SANS and SAXS investigations in concentrated Co-FF is already submitted [3].

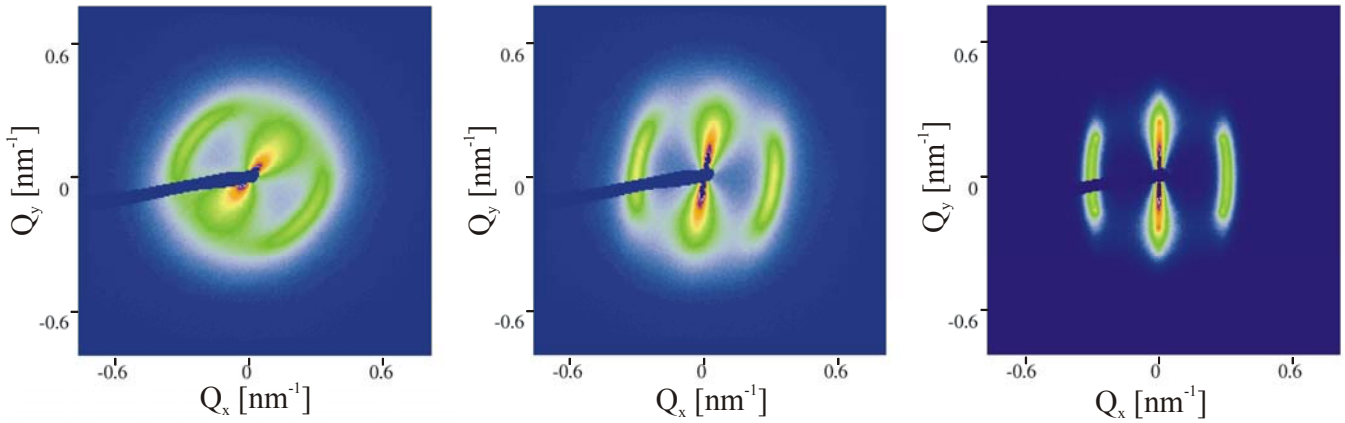

Figure 3: SAXS pattern of Co-3vol % in a horizontal magnetic field of 0.0T (left), 0.065T (centre) and 0.57T (right) applied perpendicular to the photon beam which show the set-up of the pseudo crystalline texture with increasing field. When the field is switched off the texture relaxes back to full disorder. The sample tube axis is mounted to form an angle of about 45° with the horizontal field direction.

An additional interesting effect is observed when the Co-samples are measured in thin tubes at different orientations. Then even in “zero field” the 2d pattern are anisotropic, showing a marked increase of the

intensity perpendicular to the axis of the tube. In the SAXS experiment (Fig. 3) the tube axis was oriented at about 45° to the horizontal direction. When the strength of a magnetic field applied horizontally is increased, the anisotropy moves gradually from the direction perpendicular to the tube axis towards the final direction of 90°, while the "crystalline" peaks are fully established. The anisotropy relaxes back to the original direction when the field is switched off. This anisotropy indicates some spontaneous formation of chain segments aligned along the tube axis. This could result from interactions of particles with the quartz glass container walls.

References:

[1] S. Odenbach, ed., Magnetically Controllable Fluids and their Applications, no. 594 in Lecture Notes in Physics (Springer, 2002).

[2] C. Alexiou and other, JMMM **225** (2001) 187.

[3] A. Wiedenmann, A. Hoell, M. Kammel, P. Boesecke: Field-induced pseudo-crystalline ordering in concentrated ferrofluids, Phys. Rev. E (2003) submitted 12/2002.