Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Structure of hexaferrite-based ferrofluids under applied magnetic field	**Experiment number**: SC-4371
Beamline: ID-02	**Date of experiment**: from: 02.09.16 to: 05.09.16	**Date of report**:
Shifts: 9	**Local contact(s)**: Peter Boesecke	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Ferrofluids (or magnetic fluids) are colloidal suspensions of magnetic nanoparticles in carrier liquids. The majority of presently available ferrofluids are based on the spinel-type ferrites (e.g., magnetite Fe_3O_4, maghemite γ-Fe_2O_3, $CoFe_2O_4$, etc.) in the superparamagnetic state, featuring particles with approximately 10 nm in diameter. Recently in our lab we have developed a method for production of novel type of magnetic colloids based on disc-like hard magnetic hexaferrite ($SrFe_{12}O_{19}$) particles [1, 2].

Since the hexaferrite ($SrFe_{12}O_{19}$) ferrofluids consist of single-domain magnetic particles with large magnetic moment their magnetic interaction should induce formation of spatially ordered structures. One of indirect evidences of such structuring is transition from a diluted "gas" phase to a "condensed liquid" phase in gradient magnetic field. Such spontaneous or field induced particle ordering hasn't been investigated yet.

In our experiment we have used SAXS technique to reveal colloid internal structure in constant and alternating magnetic field. For this purposes we have used specially designed measurement cell with two coils producing nearly uniform magnetic field. Field strength varied from 0 to 500 Oe for static fields. For AC measurements field strength amplitude was 30 Oe at number of frequencies (28,28; 56,56; 112,11; 224,24, 336,36, 400 and 500 Hz). We have performed two types of AC measurements: integral imaging with relatively high acquisition times, corresponding to average state of the particles and time scan, illustrating the process of particles reorganization in the magnetic field.

During the experiment a set of samples containing different types of particles with various concentrations have been analyzed. Best results have been achieved for colloid solution containing aluminum substituted hexaferrite particles. It was presented in two forms: standard "gas" phase colloid and "condensed liquid" phase. "Liquid" phase was also mixed with glycerol for obtaining samples with different viscosity. A colloid solution of non-substituted hexaferrite particles, has also been investigated as a reference sample.

According to the results obtained standard "gas" state colloid has not shown any diffraction reflexes under DC magnetic field, but scattering intensity distribution seriously changed in the applied field. Such behavior corresponds to particles alignment in the applied magnetic field and form-factor intensity redistribution. Measurements in AC field gave qualitatively the same results, those would be used to extract kinetics of colloid particles reorganization.

Condensation process was studied *in-situ* during this experiment. Cuvette with “gas” state colloid was placed in a highly intensive (max. 1500 Oe) gradient magnetic field. Time scan in this case showed appearing of diffraction reflection at the q=0,233 nm^{-1} corresponding to the interparticle distance of ~27 nm. This value seriously exceeds particle width (~5 nm), indicating in-solution magnetic ordering of particles rather than their aggregation. Particles form thread-like columnar structures which are stabilized by the balance of electrostatic repulsion and magnetic attraction.

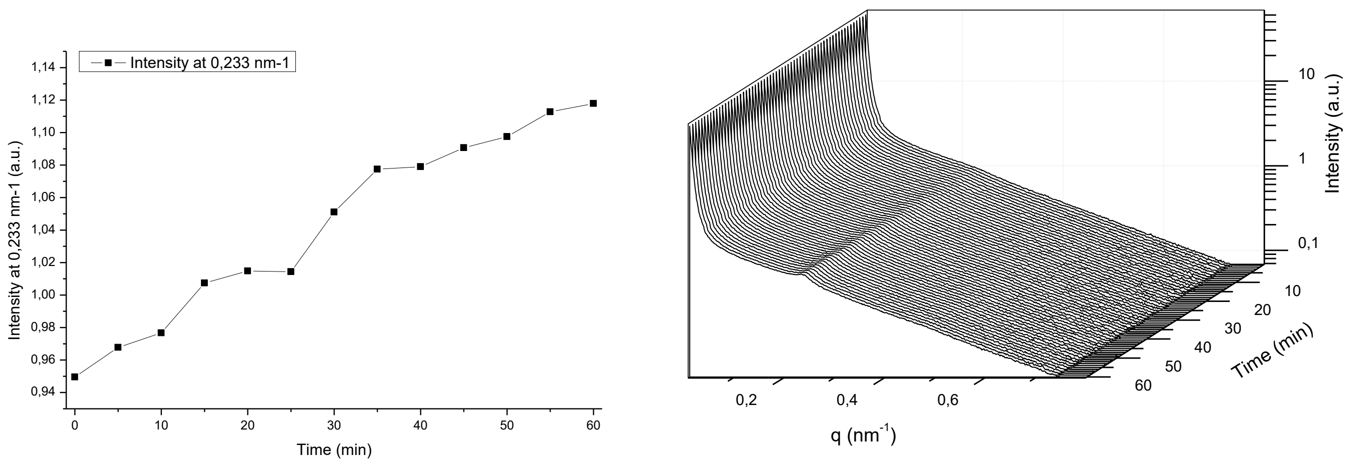

Fig. 1 Time dependence of scattering distribution in the applied field direction and corresponding diffraction peak intensity over scanning time

Another significant part of the experiments was devoted to “condensed” phase colloid itself. Particularly to its structure determination and influence of pH changes as destabilizing factor. According to the acquired data the phase consists of thread-like aggregates described above, resulting in much higher magnetic response but having rheological properties of liquid. SAXS measurements showed presence of these structures without applied magnetic field as circular diffraction reflection due to disorientation of the threads. Magnetic ordering of a condensed phase in DC field leads to appearance of two highly-intensive reflections (spatial ordering of single threads in the liquid), corresponding to interparticle distance in threads.

AC measurements showed that threads are stable and could not be destroyed by high frequency field. Time scan in AC mode indicated periodical orientation-disorientation of the threads with field oscillations.

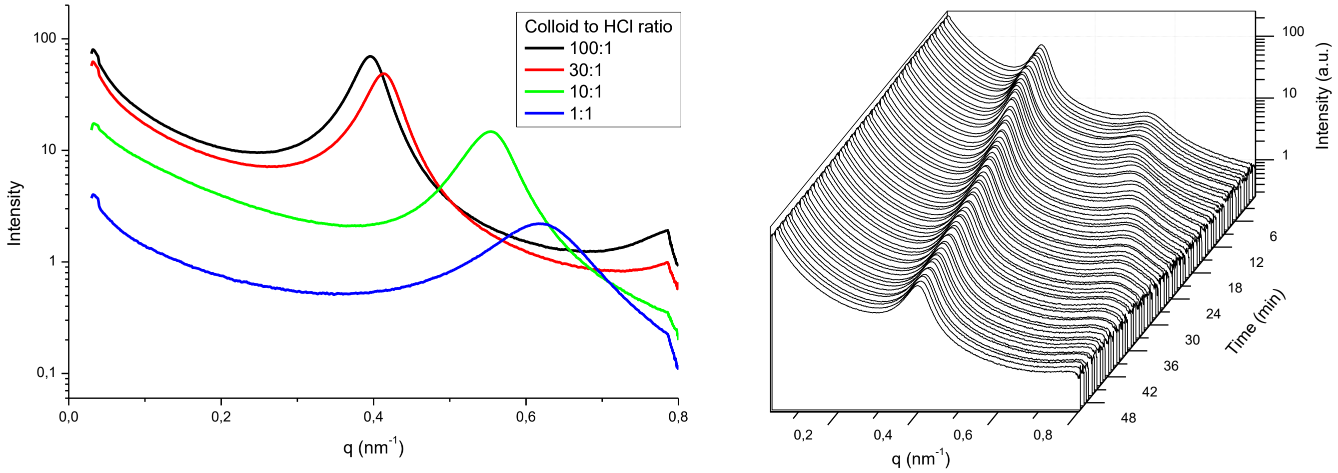

Fig. 2 Influence of pH on “condensed” phase colloid (mixing with 0,6 % HCl (left panel) and acid concentration front movement in time (right panel))

One of the most exciting results obtained was concerned interparticle distance variation with the change of pH value in “condensed” state colloid. In “gas” state colloid such variation of pH value beyond stability region leads to fast particle aggregation and precipitation. In “condensed” state decrease of pH doesn’t destabilize colloid but strongly influences on interparticle distance in threads (Fig. 2). Time scan of concentration front movement (AC field to show only freely rotating non-stuck particles) shows continuous decrease of interparticle distance. Direct mixing with 0,6% HCl also leads to the same results, but much faster. This implies a decisive role of electrostatic repulsion forces on platelets ordering and the interparticle distance. Further theoretical analysis and modelling will allow to give a model description of the observed effects.

[1] Trusov L.A., Vasiliev A.V., et al. Stable colloidal solutions of strontium hexaferrite hard magnetic nanoparticles. Chem. Comm. 2014. V.50. P.14581.
[2] Lukatskaya M.R., Trusov L.A., et al. Controlled way to prepare quasi-1D nanostructures with complex chemical composition in porous anodic alumina. Chem. Comm. 2011. V.47. P.2396.