ESRF	**Experiment title:** Development of the Rosensweig instability on the liquid ferrofluid surface: reflectivity study in subcritical magnetic fields.	**Experiment number**: SI-1302
Beamline: **ID10B**	**Date of experiment**: from: 21 Sept. 2005 to: 25 Sept. 2005	**Date of report**: 28 Oct. 2005
Shifts: 15	**Local contact(s)**: O. Konovalov	*Received at ESRF:*

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Report:

The aim of the experiment was observation and analysis of the **field-dependent rearrangement** of the magnetic nanoparticles in the top layer of the ferrofluid (FF). Specifically, we wanted to prove that Rosensweig instability (RI) develops on two substantially different scales – first, on microscopic scale in subcritical fields ($H<H_C$) and then on macroscopic scale at $H=H_C$ (conventional RI). Here H_C is the critical value of the magnetic field determined in the classical Ferrohydrodynamics [1,2]. For this purpose we used specular x-ray reflection and grazing incidence x-ray scattering (GISAXS and GID).

The samples were colloidal suspension of magnetite particles in heavy water. The particles are stabilized with a double layer of surfactant molecules, which makes them hydrophilic and provides stability of the system. The samples with volume concentration of magnetite C=2% and C=7% are called hereafter FF2 and FF7 respectively. The mean size of the particle D_m in FF2 is supposed to be two times smaller than in FF7, where D_m is about 10 nm. Schematic construction of the stabilized particle and electron density values for its components are shown in Fig.1.

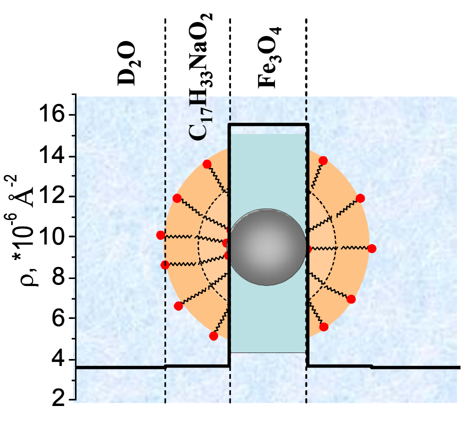

Fig.1. Construction of the magneto-colloidal particle and electron density (ρ) values for the component of the ferrofluid.

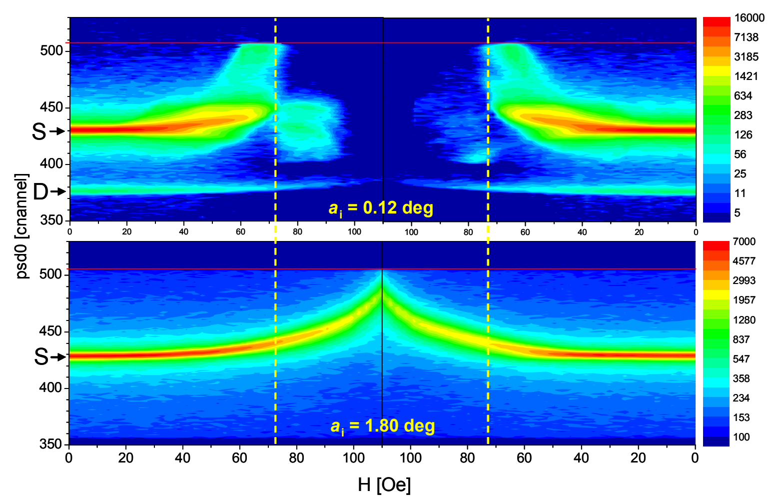

Fig.2. Exit-angle intensity distribution obtained for FF7 during field increasing-decreasing cycle at α_i =0.12° (top) and α_i=1.80° (bottom). Yellow dashed line indicates the value of the critical field according to the conventional theory, red horizontal line – top edge of the PSD. "S" – position of the specular beam at H=0, "D" – a trace of the direct beam at H=0.

Assuming that particle reorganization in the external filed should give rise in drastic change of the surface roughness, we observed, first, an evolution of the reflected beam parameters at fixed angle of incidence α_i during field increasing-decreasing cycles. The result for FF7 is shown in Fig.2 as obtained at α_i=0.12° (top) and α_i=1.80° (bottom). One can see that specular beam not simply changes its intensity but also gets broader, changes its position in space and even splits at higher fields in the case of lower angle of incidence. Different behavior at different α_i is related to the beam footprint (24 and 1.6 mm respectively). The larger footprint the large surface deformations it "feels". This means that from Fig.2 one can estimate a characteristic lateral size of the humps growing on the FF surface at different field values (also at $H<H_C$!). The slope of the humps can be calculated from the specular beam position as compared to the initial values. For example, at H=110 Oe this slope makes an angle 0.12° with the original sample surface plain at H=0.

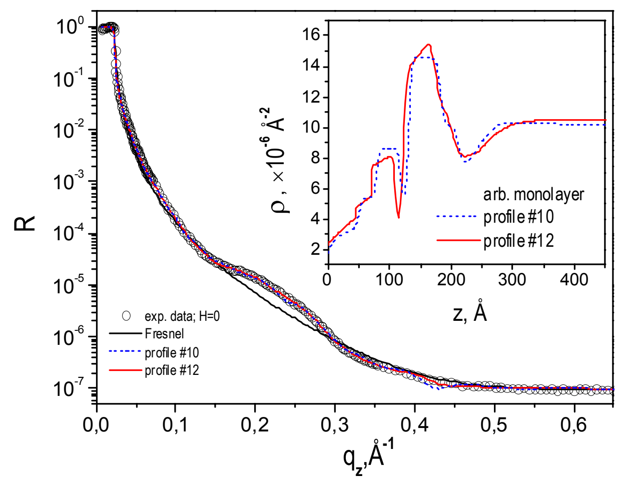

Fig.3. Reflectivity obtained for FF2 at zero field. Circles – experimental data, black line – Fresnel reflectivity, blue and red lines – fit results corresponding to the model profiles shown in the inset.

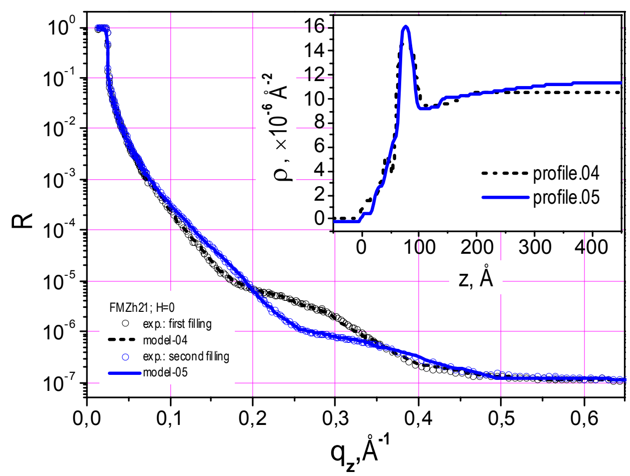

Fig.4. Reflectivities obtained for FF7 at zero field. Black and blue circles – data for the first and second filling respectively, black and blue lines – appropriate fit results according to the model profiles shown in the inset.

Specular reflectivity measurements performed at zero field revealed rather complicated depth profile for both samples as shown in Fig.3 and Fig.4. It was not possible to fit these data with a simple Parrat model consisting on one or two layers on top of the bulk. The main feature of all best fit models is the magnetite enriched layer covered with a layer of lower electron density, which could be water or surfactant molecules (see Fig.1). Electron density in the "bulk" (i.e. at z>200 Å) is about two time higher than the value calculated for the homogeneous sample. The structure remains stable during at least 10 hours as it was proved by the recurrent reflectivity measurements.

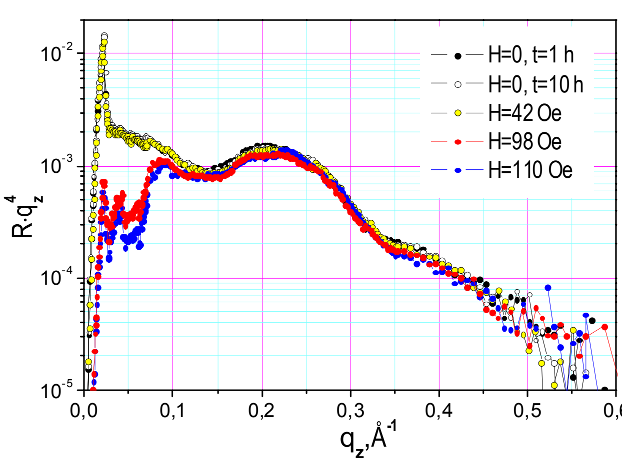

Fig.5. Reflectivity data (Rq_z^4) obtained for FF2 at different value of external field.

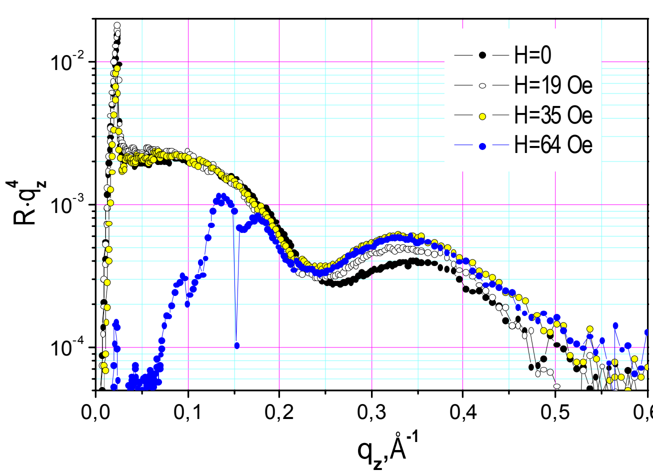

Fig.6. Reflectivity data (Rq_z^4) obtained for FF2 at different value of external field.

The reflectivity data obtained for different field values for FF2 and FF7 are presented in Fig.5 and Fig.6 respectively. The experimental reflectivity R was multiplied by q_z^4 and background corrected to give an access to the smallest details. One can see that there is no field-induced *microscopic* change of the depth profile of FF2. (The reflectivity degradation at low q_z is related to the mm-scale deformation of the surface which was explained hereinabove). At the same time FF7 exhibits a slight evolution of the very top layer on the nm level as it is seen from the intensity growth of the interferential maximum at q_z=0.33 Å^{-1}. Interestingly, this evolution stops before the moment when the macroscopic deformation of the surface develops on such level that it destroys completely the specular reflection condition at low angles of incidence (compare yellow and blue points in Fig.6.). Quantitative analysis of such data is accomplished by the absence of the total reflection region on the reflectivity curve which leads to the divergence in the fitting process.

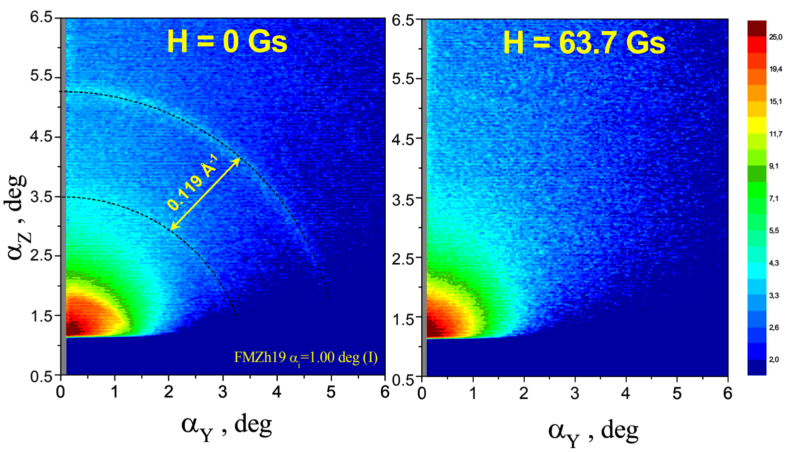

Fig.7. GISAXS intensity distributions obtained for FF2 at zero field (left) and H=63.7 Oe (right) at α_i=1°.

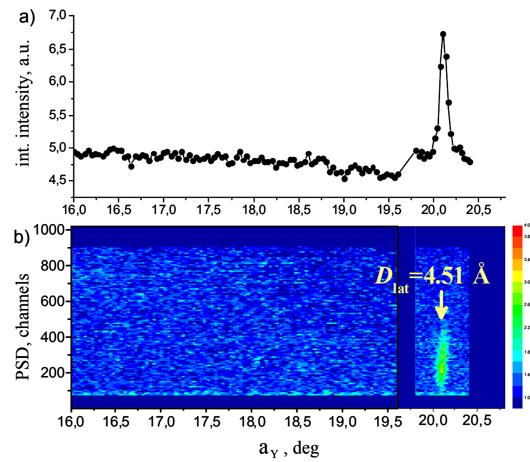

Fig.8. High angular GID peak obtained for FF7 at zero field and α_i=0.11°.

To reveal inplain ordering in the top layer of our samples we performed GISAXS measurements at $\alpha_i<\alpha_C$ and $\alpha_i>\alpha_C$ for different field values. Here α_C=0.155° and α_C=0.160° are the critical angles for FF2 and FF7 respectively. The most interesting result was obtained for FF2 at α_i=1°. It is shown in Fig. 7. At zero field we have found not only scattering from the independent particles (form factor) but also diffraction rings indicating strong correlations in the system. The correlation length calculated from the distance between the rings is found to be 52 Å, which is close to the particle core diameter. When the filed of 63.7 Oe (or higher) was applied the diffraction features of the scattering pattern disappeared, demonstrating dissipation of the ordering. However, after the field was switched off the structure with the same periodicity was recreated.

High angular GID measurement on FF7 at zero field and α_i=0.11° revealed the only diffraction peak at the horizontal angle α_Y=20.1°. This corresponds to the lateral periodicity of 4.51 Å. Most likely, the origin of this peak is hexagonal ordering of the surfactant molecules in a special layer on the top of the whole sample. This means that on the depth profiles shown in the insets of Fig.3 and Fig.4 the very first sublayer is composed of sodium oleate molecules with a long axis oriented perpendicular to the surface.

One can see that surface X-ray scattering experiments performed on ID10b have brought unique information about the structure of the FF layer close to the interface with air. For instance, GISAXS data for the sample FF2 (smaller D_m and low concentration) give a hint that arrangement of the nanoparticles in horizontal plain is strongly influenced by the external magnetic fields H already at $H<H_C$. Surface-in-whole evolution revealed by specular reflection measurements is also very interesting and intriguing. However, complete understanding of the phenomena observed will require more careful data analysis and, definitely, further experiments.

References

1. M. D. Cowley and R. E. Rosensweig, J. Fluid Mech. **30** (1967) 671.
2. Rosensweig R.E. - Ferrohydrodynamics. Cambridge, London, New-York, New Rochelle, Melbourne, Sydney, Cambridge University Press 1985.