Raman spectroscopy on surfacted ferrofluids in a magnetic field

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We investigated the effect of an external magnetic field up to 0.25 T on the Raman spectra of surfacted ferrofluids with various magnetic-particle concentrations. With increasing magnetic field the Raman spectra, which display the characteristic broad bands associated with vibrations of surfactant and water molecules, show a pronounced decrease in intensity in the range up to 50 mT. We interpret this behavior as due to an increase of the local particle concentration in the magnetic fluid. At larger fields a magnetic excitation with an intensity growing in proportion to the magnetization of the ferrofluid becomes apparent at around 4400 cm^{-1}. We consider both effects as evidence for the formation of a solid structure by the magnetic nanoparticles in the presence of a magnetic field.

I. INTRODUCTION

Magnetic fluids are complex liquids forming stable colloidal systems, which consist of magnetic nanograins, e.g., iron oxide, dispersed in an organic or inorganic carrier liquid [1]. The particles have typical dimensions between 5 and 20 nm. Because of their small size the most favorable magnetic state of the nanoparticles is of a single domain. Therefore, magnetic fluids display superparamagnetic behavior [2]. Stability of the ferrofluid is attained by balance of counteracting interactions. On one hand, thermal motion and electrostatic or surfactant-mediated repulsion keep the grains apart; on the other hand, van der Waals forces and magnetic dipole interactions lead to particle attraction [3]. To prevent the agglomeration of particles various mechanisms of repulsion are applied. According to the different types of stabilization, magnetic fluids are divided into two groups called ionic (IFF) and surfacted (SFF) ferrofluids [4]. The stabilization of the IFFs is achieved by charging the magnetic particles electrostatically [5], in which case OH^- or H_3O^+ ions are adsorbed at the grains. Steric repulsion in the SFFs is achieved by covering the grains with a protective layer, for example, oleic acid or a tenside [6,7].

Great interest in magnetic fluids resides in their manifold and peculiar physical and chemical properties [8,9]. In recent years, special emphasis has been laid on the investigation of the interactions between magnetic particles in the fluid and particularly the formation of structures, clusters, and other configurations under the influence of a magnetic field [10–13]. A few studies have dealt with the field-induced phase and structural behavior of dipolar colloids. For instance, the theoretical work by Sano and Doi [14] predicts a magnetically induced phase transition from the gaseous to the liquid state, whereas Monte Carlo simulations even yield evidence for the formation of nanoparticle clusters with long-range order with and without magnetic field [15–17]. The generation of structures as a function of magnetic field were explored experimentally by means of transmission spectroscopy [18] and birefringence measurements [19,20]. In the former case, it was found that structure formation occurs in two steps corresponding to the phase transitions from gas to liquid and from liquid to solid. Furthermore, the effects of clustering on water diffusion was investigated by means of nuclear magnetic resonance spectroscopy [21]. Light scattering in general and Raman spectroscopy in particular are a very powerful and sensitive tool to search for particle interactions and structures. First measurements on ferrofluids using transmission Raman spectroscopy were performed to study the effect of the magnetic particles on OH^--related modes in water [22].

The present study focuses on the behavior of surfacted magnetic fluids in a homogeneous magnetic field up to 0.25 T using Raman spectroscopy in backscattering geometry and with particular emphasis on the possible formation of superstructures. For that purpose we systematically varied temperature and magnetic field as well as the particle concentration of the samples. Measurements were performed with parallel and crossed linear polarization of the incident and scattered light in order to assess Raman selection rules. The effects of an external magnetic field on the Raman spectra of surfacted ferrofluids can be summarized as follows: the overall intensity of the Raman-scattered light decreases with increasing field in a similar manner as it does for higher particle concentrations. In addition, at high fields a broad peak appears in the spectra at about 4400 cm^{-1}. Its intensity exhibits as a function of magnetic field the same saturation behavior as the magnetization of the ferrofluid, thus, we attribute this peak to a magnetic excitation. All these effects are no longer observed at low particle concentrations. Our results can be consistently explained if one assumes that in the presence of a field there is a local increase in the concentration of magnetic particles because of the formation of an ordered structure due to an enhanced magnetic-dipole interaction between nanomagnets. Further evidence for the generation of structures in SFFs was obtained from Raman measurements where the samples were first frozen in a magnetic field and then thawed without field.

II. EXPERIMENTAL SETUP

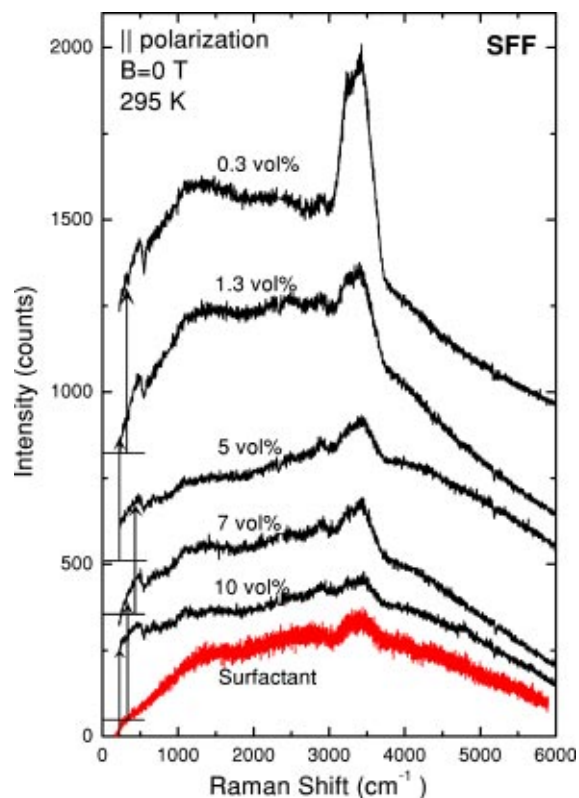The magnetic liquids used in this study are SFF consisting of a colloidal water solution of magnetite (Fe_3O_4) nan-

FIG. 1. Room-temperature Raman spectra for different nanoparticle concentrations of a water-based surfaced ferrofluid (SFF) taken with parallel linear polarization. The spectra were shifted vertically for clarity and the corresponding baselines are indicated. For comparison, the Raman spectrum of an aqueous solution with roughly 10 vol % surfactant is also shown.

ograins with a surfactant bilayer of dodecanoic (laurin) acid and marlipal. The average diameter of the grains is around 10 nm. Starting at 10% by volume, a given ferrofluid was diluted several times so that the concentration ranged between 10 and 0.3 vol %. For the Raman experiments we used a single-grating spectrometer of the LABRAM type equipped with a notchfilter for rejection of the laser light and a microscope for micro-Raman measurements in backscattering. Spectra were excited using the 514.5 nm line of an Ar-ion laser. The samples were loaded into quartz tubes to avoid water evaporation. The tubes were mounted on a brass block that was kept at a constant temperature with a Peltier cooling unit. During the measurements in the frozen state the tubes were placed into a cold-finger cryostat and cooled down to liquid nitrogen temperature. The magnetic field was generated by two permanent supermagnets and applied perpendicular to the direction of the incident laser beam. The strength of the magnetic field was varied by changing the separation between pole pieces.

III. RESULTS AND DISCUSSION

Figure 1 shows polarized Raman spectra for five different concentrations of the SFF dilution series measured without magnetic field. The spectra display a broad but structured background extending over the whole spectral range up to

6000 cm^{-1}, which is attributed to light scattering by the surfactant (marlipal and laurin acid). Surfactant molecules not only cover the nanoparticles but are also present in free form in the liquid. This assumption was verified by measurements of marlipal and laurin acid diluted in an aqueous solution without magnetic particles, which shows a similar Raman spectrum as the ferrofluid. Furthermore, the well-defined peaks at around 430 cm^{-1} and at 3400 cm^{-1} are associated with molecular vibrations of water. The low-energy peak corresponds to rotational vibrations, the so-called librations of the H_2O molecule, whereas the superposition of the main OH-stretching modes of water at 3233 cm^{-1}, 3393 cm^{-1}, and 3511 cm^{-1} give rise to the broad peak centered at 3400 cm^{-1} [22,23]. Obviously, the less the concentration of magnetic particles and thus of surfactant, the stronger are the OH-stretching modes as compared to the background.

An interesting observation concerns the change in overall intensity of the Raman spectra for the dilution series, which in absolute terms decreases with increasing particle concentration (see Fig. 1). Ferrofluids are nontransparent liquids in the visible range owing to the strong dispersion of light by the nanometer-size particles of the colloid. This leads to small effective volumes for Raman scattering. As the distances between the nanograins get larger when the particle concentration decreases, the scattering volume and thus the intensity of the whole Raman spectrum increases. Particularly the intensity of the OH-stretching modes increases noticeably because the ferrofluid was diluted with water. We show below that a somewhat similar behavior of the Raman intensity is observed for a given SFF when a magnetic field is applied.

Figure 2 displays parallel as well as crossed polarized Raman spectra of the ferrofluid with a concentration of 7% by volume for different magnetic fields up to 0.2 T. The OH-stretching modes of water exhibit clear polarization selection rules since they are absent in depolarized spectra [Fig. 2(b)] with exception of the peak at 3511 cm^{-1} which corresponds to a stretching mode [22,23]. The effect of the applied magnetic field on the Raman spectra of the SFF in both polarizations is twofold: with increasing field the background decreases in intensity, whereas a broad peak centered at around 4400 cm^{-1} with full width at half maximum $\sim$3000 cm^{-1} becomes increasingly apparent in the spectra [dashed curve in Fig. 2(b) for crossed polarization]. Both effects of the magnetic field were observed for all samples of the dilution series, but they were much less pronounced at low concentrations.

The integrated intensity of the background and a Gaussian peak at a fixed energy of 4400 cm^{-1} for three concentrations are plotted in Fig. 3 as a function of the applied magnetic field together with the measured magnetization of the SFF [24]. From these data it becomes clear that the decrease of the background intensity goes together with the appearance of the high-energy peak. The intensity of the latter follows the saturation behavior of the magnetization, as the external field increases. As expected for a fluid with superparamagnetic behavior, the saturation field does not depend on concentration. In contrast, the absolute value of the
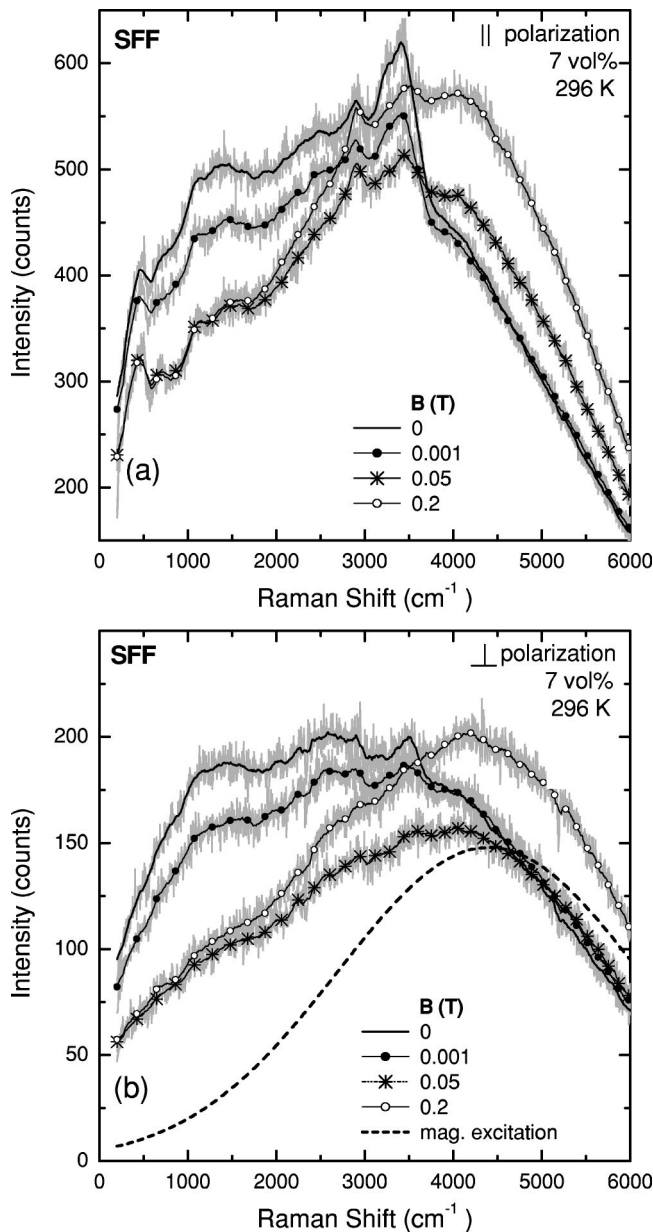
FIG. 2. Raman spectra (unshifted) of the surfacted ferrofluid with a concentration of 7 vol % for different external magnetic fields taken at room temperature with (a) parallel and (b) crossed polarization. The dashed curve represents the Gaussian peak associated with the magnetic excitation used for fitting the 0.2 T spectrum.

FIG. 3. Magnetic-field dependence of the integrated intensity of the background (full symbols) and the Gaussian peak at 4400 cm^{-1} (open symbols) from polarized spectra measured at room temperature for three different particle concentrations. Dashed curves represent the magnetization data (right axis).

magnetization in saturation decreases proportionally to the density of magnetic moments, i.e., nanograins. In full accordance, the magnetic-field induced changes in the Raman spectra are the same but weaker as the particle concentration is reduced. In fact, for the most diluted fluid (0.3 vol %) the background decreases very little in intensity and the high-energy excitation is barely observable.

By comparing the effect of magnetic field on the background with the changes in the Raman intensity as a function of concentration we are led to the conclusion that the field, while it magnetizes the ferrofluid, gives rise to an increase in the local density of fer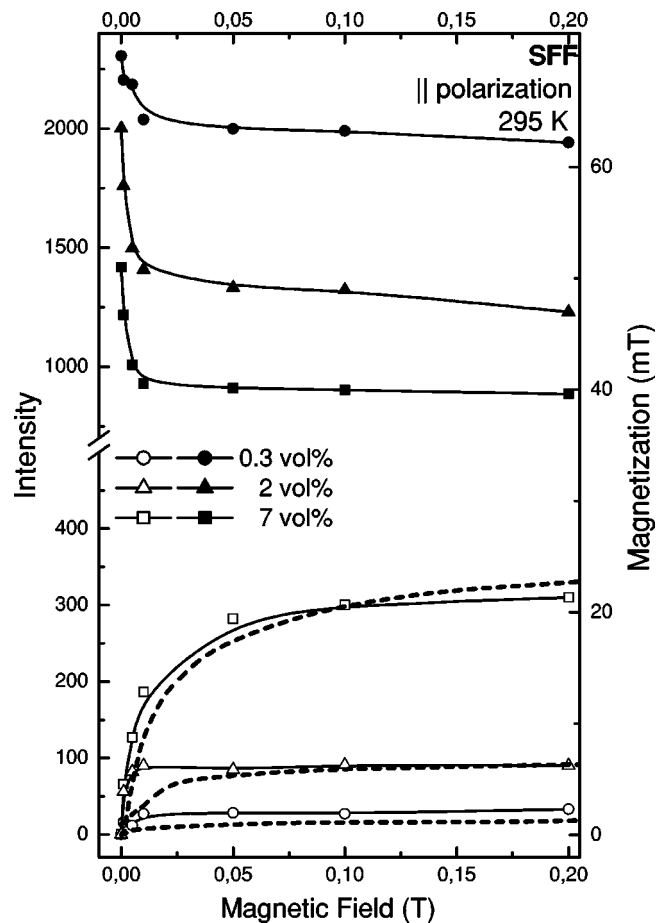romagnetic particles. This results in a decrease in the effective scattering volume and consequently in the intensity of the Raman spectra. Such a change in the local concentration of magnetic particles can be explained only by assuming that the nanograins attract each other due to dipole-dipole interactions when the magnetic moments orient themselves in the external field. In this case, it is likely that nanoparticles form needle-shaped structures and clusters, as predicted by Monte Carlo simulations [15,16] and observed in optical microscopy [18]. Due to the local nature of the changes in particle density, significant concentration gradients are expected to occur depending on the local strength of the magnetic field. As a matter of fact, the ferrofluids exhibit pronounced magnetostriction effects. In principle, the detection of those gradients is possible using our microscope setup. Such experiments are under consideration and will be published elsewhere.

We now turn to the discussion of the origin of the magnetic field induced peak at 4400 cm^{-1}, whose intensity increases in proportion to the magnetization. This behavior is better appreciated in the spectra of Fig. 2(b) for crossed polarization. On the assumption that the distances between the particles are reduced in a magnetic field, we attribute this peak to a magnetic excitation caused by fluctuations in the

magnetization of the ferrofluid. Within linear-response theory the relation between the electric field of the light **E** and the induced polarization **P** of a magnetic material with magnetization **M** is given by [25]

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E} + i \varepsilon_0 G \mathbf{M} \times \mathbf{E}, \tag{1}$$

where ε_0 is the vacuum permittivity, $\chi(\mathbf{M})$ is the electric susceptibility which, in turn, is a function of **M** and $iG = \partial \chi_{ij}/\partial M_k$ (for ijk any cyclic permutation of xyz) is the susceptibility derivative. The components of the magnetization have thermal fluctuations whose power spectra determine the frequency distribution of the scattered light. The second term of Eq. (1) represents the Faraday-rotation mechanism for light scattering due to the contributions of the average value $\langle M_z \rangle$, where z is taken as the direction of the applied field. In solids, the contribution of the magnetization to the first term in Eq. (1) gives rise to negligible coupling to the light. However, it turns out that this term leads to strong scattering for liquids due to fluctuations of the refractive index. The magnetization power spectrum required for the inelastic light scattering cross section can be determined by the fluctuation-dissipation theorem from the transverse part of the response function due to Faraday rotation. The result for the cross section reads [25]

$$\frac{d^2\sigma}{d\Omega d\omega_S} \propto \omega_I \omega_S^3 V G^2 \hbar \omega \gamma \langle M_z \rangle |(\varepsilon_S \varepsilon_I)_+|^2$$

$$\times [n(\omega)+1] \frac{\Gamma/\omega_0}{(\omega_0 - \omega)^2 + \Gamma^2}, \tag{2}$$

with ω_I, ε_I, and ω_S, ε_S the frequency and polarization vector of the incident and scattered photon, respectively, V the scattering volume, $\hbar\omega$ the Raman shift, $\gamma = g\mu_B/\hbar$ the gyromagnetic ratio of the nanograins in Bohr magneton units, and $n(\omega)$ the thermal occupation number of the magnetic excitation. The transverse cross section (2), which corresponds to scattering with x,z or y,z crossed polarization, has a Lorentzian lineshape centered on the frequency ω_0 and with a width Γ.

According to Eq. (2) we assign the peak at 4400 cm^{-1} to a collective magnetic excitation of the magnetic dipole system in the ferrofluid. The frequency of this excitation, $\omega_0 = \gamma B$, is determined by the strength of the gyromagnetic ratio and the macroscopic magnetic field $\mathbf{B} = \mathbf{B}_0 + \mu_0 \mathbf{M}$, where $\mathbf{B}_0$ is the external field and μ_0 is the vacuum permeability. For single-domain nanoparticles consisting of 10^3–10^4 atoms, as in our case of SFFs of superparamagnetic character [2], it holds that $\gamma \gg 1$ since it is proportional to the number of magnetic atoms in a nanograin. The particle-size distribution is very broad ($\pm 50\%$ of the mean size), which leads to the broad Gaussian peak observed in the Raman spectra at high magnetic fields [dashed curve in Fig. 2(b)]. Furthermore, we notice that Eq. (2) predicts that the scattering intensity of the magnetic excitation should increase linearly with the z component of the magnetization, in agreement with our observations (see Fig. 3). The characteristic frequency ω_0, however, is expected to depend on magnetic
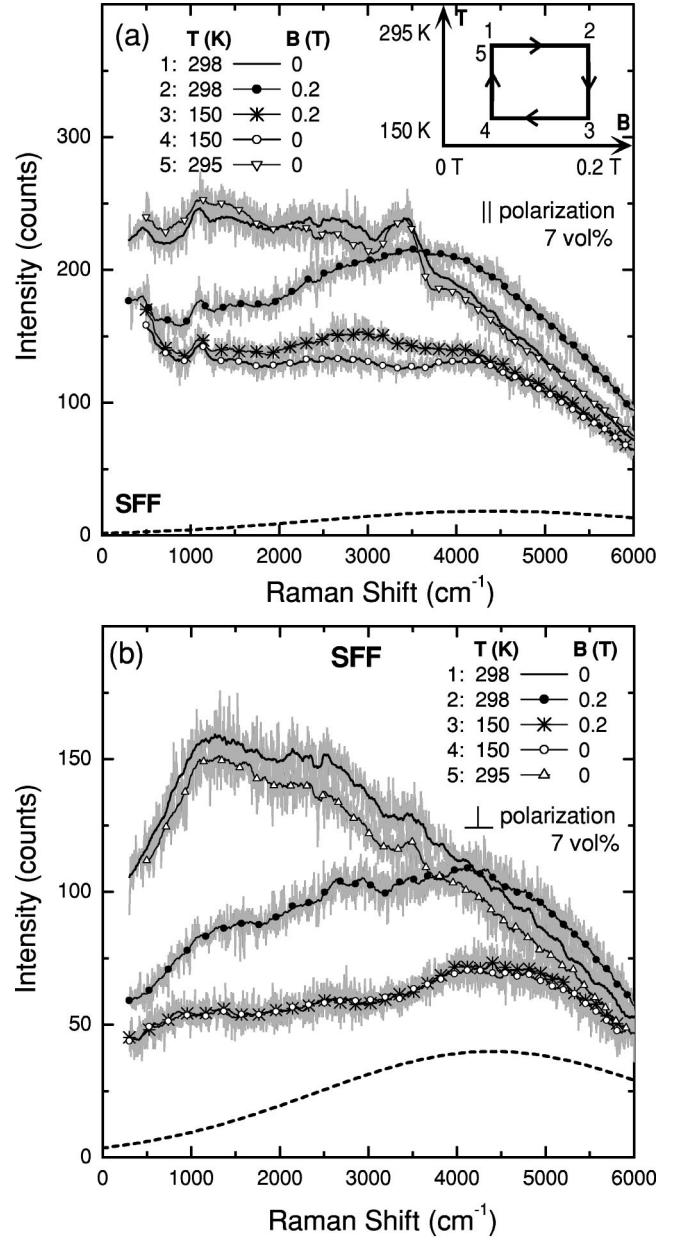

FIG. 4. (a) Polarized and (b) depolarized Raman spectra of the surfaced ferrofluid with 7 vol % particle concentration for different temperatures and magnetic fields. The inset illustrates the temperature-field cycle followed in the experiment. Dashed curves represent again the Gaussian peak used for the magnetic excitation to fit the spectra taken at point 3 (see inset).

field. In spite of this, we were able to fit the Raman spectra for different magnetic fields using a constant value of 4400 cm^{-1} for ω_0. This might be an indication that the feature observed at high fields corresponds to an *overdamped* collective excitation of the magnetic moments of the nanograins; a mode which exists in strongly disordered systems [26]. In this case, the light-scattering line shape given by Eq. (2) yields a broad peak centered at the inverse of the relaxation time.

Further insight into the properties of the magnetic excitation and its relation to the build up of structures in the SFF

can be gained from Raman measurements along a temperature-field cycle, as depicted in the inset to Fig. 4. For each point on the cycle denoted by numbers a Raman spectrum of the 7 vol % sample was measured in parallel and crossed polarization, as shown in Figs. 4(a) and (b), respectively. As the magnetic field is raised at room temperature in going from 1 to 2, ordered structures can form in the ferrofluid and the magnetic excitation clearly shows up in the spectra in both polarizations. Then the sample is frozen in a field of 0.2 T, which causes an overall decrease in intensity but the magnetic excitation remains observable mainly in depolarized spectra. This is important for two reasons: First, the observation of the excitation in the frozen state indicates that it is associated with fluctuations in the orientation of the magnetic moments of the nanoparticles but not to the reorientation of the grains themselves, as they were nanomagnets. Second, the weakness of the Raman signal at 4400 cm^{-1} in parallel polarization when the liquid freezes [compare dashed lines in Figs. 4(a) and (b)] is due to the suppression of the mechanism for polarized scattering represented by the first term of Eq. (1), which is only active if magnetization-induced fluctuations of the density and hence of the refractive index are possible. Finally, quenching the field in the frozen state has no influence on the spectra; the magnetic excitation are still observed because the structure formed before cooling remains intact. After raising the temperature to ambient conditions the original spectra are recovered.

Another interesting experiment consists of the reversal of the sequence in the temperature-field cycle. If the ferrofluid is frozen before the magnetic field is applied, the spectra at point 3 differ from that measured otherwise in that the magnetic excitation is absent. This is a clear indication that in order for this excitation to exist, the magnetic moments of the nanoparticles need to interact with each other. This situation is realized when the magnetic particles come closer together undergoing an disorder-order phase transition, hence forming an ordered structure in the presence of a external magnetic field. By applying the field in the frozen state, such phase transformation is inhibited and a magnetic excitation does not appear in the Raman spectra. Further spectroscopical evidence for the nucleation of the ordered phase might be gained from the Rayleigh scattering signal.

IV. CONCLUSIONS

We have investigated the generation of particle structures induced by a magnetic field in surfacted ferrofluids of different concentrations using Raman spectroscopy. Evidence of structure formation and the concomitant reduction of the interparticle distances is obtained from the decrease in intensity of the background in the Raman spectra and the appearance of a magnetic excitation at around 4400 cm^{-1}, as the magnetic field is increased at room temperature. These effects are very weak or absent for low particle concentrations or if the field is applied in the frozen state. Furthermore, we were able to demonstrate that the magnetic excitation has collective character corresponding to an overdamped coherent fluctuation of the orientation of the interacting magnetic dipoles of the nanograins in the structure formed before by the application of an external field. In this way, we provided further insight into the behavior of surfacted ferrofluids in the presence of magnetic fields. Future experiments will aim at revealing the exact mechanism for structure generation as well as their forms, symmetries, and anisotropies.

ACKNOWLEDGMENTS

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