NMR investigation of iron-containing magnetically ordered nanomaterial used for preparing of magnetic fluid

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Abstract. The first observation of $^{57}$Fe nuclear magnetic resonance in nanostructured magnetite, used for preparing of magnetic fluid is reported. The radiospectroscopic technique required for the reliable spin echo signal observation is discussed. The data on resonance line associated with physical properties of the material, are presented.

1. Introduction
Magnetic fluids are attractive objects, which have a wide variety of applications in different areas [1]. They are colloids with a solid fraction of magnetically ordered particles, solved in a liquid medium, which possess a number of unconventional physical properties. Now there are many suggestions for their use in photonics [2-5], sensors [6-9], biomedicine [10-13] and other fields. This topic is closely related with the general problem of physics of nanocomposites, containing magnetic phase [14-16].

A question of internal structure of the particles, which determines basic characteristics of such systems, is of a current interest, and a lot of experimental methods were employed to obtain information about it. However, nuclear magnetic resonance (NMR) has never been used, although it is known that it can provide important data, complimentary for such techniques as, for example, magnetometry, neutron scattering and others. This is primarily due to the difficulties of NMR signal registration in very small (nanosized) magnetic objects.

The purpose of this work was to investigate the response of nuclear spin system in nanostructured magnetite, which represents an initial material for the preparing of magnetic fluid, using sensitive radiospectroscopic technique. This approach is a necessary step in the transition to the study of NMR in the solid phase of the colloid.

2. Samples
The samples were prepared by standard procedure as precursors for further fabrication of a magnetic fluid [17]. Initially the synthesis of magnetite colloid was carried out in a solution of FeCl$_3$ and FeSO$_4$ by precipitation with ammonia water. Then the reaction yield, in the form of Fe$_3$O$_4$ nanoparticles, was condensed to the state of a paste. During the synthesis process an admixture of oleic acid was used in order to form a surfactant layer on particle surfaces for preventing their close adhesion. The resulted samples represented paste-like objects, composed of Fe$_3$O$_4$ nanoparticles with the median diameter of
about 10 nm, separated by the layers of an organic substance. Thus, the substance obtained was a true magnetically ordered nanomaterial.

![Figure 1. Schematic depiction of magnetite paste (a) and magnetic fluid, prepared as its 10 % solution (b). Surfactant molecules marked as dashes (a small uncontrollable amount of oleic acid can present in a solvent, for example, kerosene). Normally the particles are consisted of magnetic core and nonmagnetic shell, which outlined in the pictures by different color density. The scale is maintained approximately.](image)

For the comparing with the paste the sample of a bulk Fe₃O₄ (in the form of macrocrystalline powder) was used.

3. Experimental method
The measurements were carried out on Tecmag Redstone radiospectrometer by two-pulse technique of spin echo observation with repetition period of the sequence of 5 ms. The durations of the first and second radio frequency (RF) pulses were 2 μs and 4 μs correspondingly, the delay time t₁₂ between them was 10 μs (for measuring of relaxation time T₂ it was increased by several microseconds). The carrier frequency of RF pulses f was of about 70 MHz, which corresponds to ⁵⁷Fe NMR frequency in most of magnetic iron oxides.

Because ⁵⁷Fe nuclei have very small magnetic moment, natural abundance of ⁵⁷Fe isotope is only of about 2.2 % and, as it is usual for nanostructures, the particles in our paste should have an increased magnetic anisotropy, an expected NMR intensity I in our case had to be extremely low. In order to increase the signal the experiments were carried out at liquid nitrogen temperature (77 K) with the signal accumulation number of 40960.

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4. Results and discussion
⁵⁷Fe NMR spectra for nano- and bulk materials are shown in figure 2. In spite of a small signal-to-noise ratio, spin echo signal in the paste was observable in the range of 68 – 74 MHz (figure 2(a)), demonstrating a general similarity with the same in bulk material (figure 2(b)). According to [18] the resonance lines may be attributed to tetra- (A) and octahedral-like (B) Fe-sites (it should be taken into account that our experiments were carried out lower the Verwey temperature, where the crystalline and magnetic properties of magnetite change). The peculiarities of NMR spectrum in the paste consists in: i) A-peak frequency shifting down (≈ 350 kHz); ii) B-peak frequency shifting up (≈ 800 kHz); iii) considerable increasing of the relative intensity of A-peak; iv) significant broadening of B-peak; v) appearance of a weak signal at lower frequencies (marked by arrow in figure 2(b)).
Note that the resonance line splitting cannot be due to influence of domain walls, because it was observed both in bulk and in nanostructured material, while in the latter case the walls are absent (the particles with diameter of 10 nm should be regarded as single domain). The shift of the peaks preliminary can be explained by the crystal structure distortion, the broadening, most probably, is coming from increased defects amount, typical for nanosized objects and to the increase of the surface contribution in nanocrystalline state. Additional signal at lower frequencies may be ascribed to other magnetic phases.

![Figure 2. $^{57}$Fe NMR spectra. a – NMR spectrum in nanostructural sample; b – NMR spectrum in bulk sample ($T = 77$ K)](image)

It was difficult enough to investigate the relaxation in our paste because of rapid decreasing of the signal amplitude with increased delay time between RF pulses. Nevertheless, with a slight changing of $t_{12}$ it was possible to obtain qualitatively measured dependencies of $I(t_{12})$ and to estimate $T_2$. The spin-spin relaxation time frequency distribution shown in figure 2. As it is seen, $T_2 \approx 2 - 4 \mu$s. It is more than by one order of value lower than in bulk sample. This effect points to a drastic conversion of magnetic processes in nanoparticles and confirms the difference between conventional and nanostructured forms of matter.

![Figure 3. Frequency distribution of relaxation time $T_2$ ($T = 77$ K)](image)
5. Conclusion
The first observation of NMR in nanostructured iron oxide, which is a solid precursor (paste) for the preparing of liquid material (magnetic fluid), presented in this work. It was shown, that using sensitive radiospectroscopic equipment and a large number of accumulations it is possible to observe spin echo signal of iron nuclei and to obtain characteristics of NMR spectrum of this substance. The latter demonstrate a change of magnetite properties when the material prepared in nanostructured form.

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