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Proton NMR of water colloidal solutions of nanosized crystalline LaF_3 and $\text{LaF}_3:\text{Gd}^{3+}$ particles

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A study of the nuclear magnetic relaxation of water protons in a series of colloidal solutions of nanosized lanthanum trifluoride and lanthanum fluoride particles, doped with gadolinium (0.5%). The proton NMR signal was recorded by a “Proton-20 M (Chromatech)” spectrometer. It is established that the rate of longitudinal relaxation depends on the nanoparticle concentration in the water solution, and on their dimension. It is demonstrated that the proton relaxation rate in the $\text{LaF}_3:\text{Gd}^{3+}$ solution increases with paramagnet concentration in the nanoparticles, and decreases with increasing particle size. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4906340>]

Introduction

Paramagnetic contrast agents are actively used in NMR imaging (MRI), since they can have a pronounced effect on the time T_1 of longitudinal, and time T_2 of transverse, nuclear magnetic relaxation in living tissues. The difference in the relaxation times of neighboring tissues forms the contrast in the MRI images. The contrast agents are divided into two types, as reducing either the transverse or the longitudinal relaxation. The first type is mainly created on the basis of nanoscale iron oxides SPIO (super paramagnetic iron oxide), which have paramagnetic properties, and the second is created based on ions with a large number of unpaired electrons, such as Gd ions, for example. The so-called T_1 -contrast agents have several advantages over T_2 -contrast agents, since as a result of their usage, the contrast and sharpness is higher, and consequently, the imaging quality improves.

Contrast agents are introduced into the organism intravenously or orally, in small concentrations that are safe for the body. In practice, preference is given to nanoscale contrast agents, since they are able to permeate the living tissues more effectively. There are contrast agents that have directional effects, i.e., those that accumulate in a specific tissue or organ. Typically, such agents are based on organic molecules or complexes.^{1–5}

F. Evanics *et al.*⁶ were the first to suggest the use of lanthanum trifluoride doped with Gd^{3+} ions as MRI contrasting agents, during their study of $\text{LaF}_3:\text{Gd}^{3+}$ water colloidal solutions, and their influence on the nuclear magnetic relaxation of protons. In particular, colloidal solutions of gadolinium trifluoride (average size of the nanoparticle being 149.3 nm) and gadolinium-doped lanthanum trifluoride ($\text{LaF}_3:\text{Gd}^{3+}$ (80%), average size of nanoparticle 51.5 nm), were previously studied. In order to increase the stability of the colloidal solution, the nanoparticles were coated with biocompatible passivating shells during synthesis.

We have previously tested the LaF_3 and PrF_3 nanoparticle synthesis technique,^{7,8} and studied the properties of the particles.^{7–13}

The urgent task is to study the influence of the size of the magnetically-diluted $\text{LaF}_3:\text{Gd}^{3+}$ nanoparticles, and the

concentration of the paramagnet in the nanoparticles, on the nuclear magnetic relaxation of water protons in colloidal solutions.

The given investigation is dedicated to the study of the nuclear magnetic relaxation of water protons for a series of colloidal solutions of nanosized lanthanum fluoride, and gadolinium-doped (0.5%) lanthanum fluoride particles (LaF_3 and $\text{LaF}_3:\text{Gd}^{3+}$ (0.5%)), and a comparison of the obtained data with those presented in Ref. 6.

Samples

The stages of the synthesis of nanoscale rare-earth trifluoride samples, are described in detail in Ref. 7, and it was using this method that two of each LaF_3 and $\text{LaF}_3:\text{Gd}^{3+}$ (0.5%) sample was synthesized, with an average particle size of (21 ± 7) and (31 ± 7) nm. Next, the powders were placed in a vial with distilled water, and subjected to sonication at a frequency of 40 kHz in a 120W ultrasonic bath, until the colloidal solution was formed. As a result, we prepared a series of colloidal solutions (Table I).

Experimental Results and Discussion

The obtained colloidal solutions were studied using an NMR-relaxometer, “Proton-20M (Chromatech).” The temperature of the sample during the experiment was 37 °C, and the Larmor frequency was 20 MHz. The “inversion-recovery” sequence was used in order to measure the time of the longitudinal relaxation T_1 .

The measurement of the longitudinal magnetization recovery times of the water proton in colloidal solutions LaF_3 (particle dimension 21 nm, sample № 11) and $\text{LaF}_3:\text{Gd}^{3+}$ (0.5%) (particle dimension 21 nm, sample No. 1) have shown (see Fig. 1), that in solutions containing gadolinium, relaxation occurs two orders of magnitude faster (925 ms versus 10 ms). This occurs due to the fact that the Gd^{3+} ion has a huge magnetic moment, and fast electron spin-spin and spin-lattice relaxation time (nanoseconds), whereas pure LaF_3 is a diamagnet.

In order to assess the influence of the $\text{LaF}_3:\text{Gd}^{3+}$ particle dimensions on the longitudinal relaxation, we measured the

TABLE 1. The series of colloidal solutions.

| | Sample | Particle size (nm) | Powder mass (mg) | Water volume (ml) | Gd content in the solution (mg/ml) | Nanoparticle concentration in the solution (mg/ml) |
|----|---|--------------------|------------------|-------------------|------------------------------------|--|
| 1 | LaF ₃ :Gd ³⁺ (0.5%) | 21 | 50 | 0.10 | 2.50 | 500 |
| 2 | LaF ₃ :Gd ³⁺ (0.5%) | 21 | 25 | 0.10 | 1.25 | 250 |
| 3 | LaF ₃ :Gd ³⁺ (0.5%) | 21 | 25 | 0.15 | 0.83 | 167 |
| 4 | LaF ₃ :Gd ³⁺ (0.5%) | 21 | 25 | 0.20 | 0.63 | 125 |
| 5 | LaF ₃ :Gd ³⁺ (0.5%) | 21 | 15 | 0.15 | 0.50 | 100 |
| 6 | LaF ₃ :Gd ³⁺ (0.5%) | 31 | 50 | 0.10 | 2.50 | 500 |
| 7 | LaF ₃ :Gd ³⁺ (0.5%) | 31 | 25 | 0.10 | 1.25 | 250 |
| 8 | LaF ₃ :Gd ³⁺ (0.5%) | 31 | 25 | 0.15 | 0.83 | 167 |
| 9 | LaF ₃ :Gd ³⁺ (0.5%) | 31 | 25 | 0.10 | 0.63 | 125 |
| 10 | LaF ₃ :Gd ³⁺ (0.5%) | 31 | 15 | 0.15 | 0.50 | 100 |
| 11 | LaF ₃ | 21 | 50 | 0.10 | ... | 500 |
| 12 | LaF ₃ | 31 | 50 | 0.10 | ... | 500 |

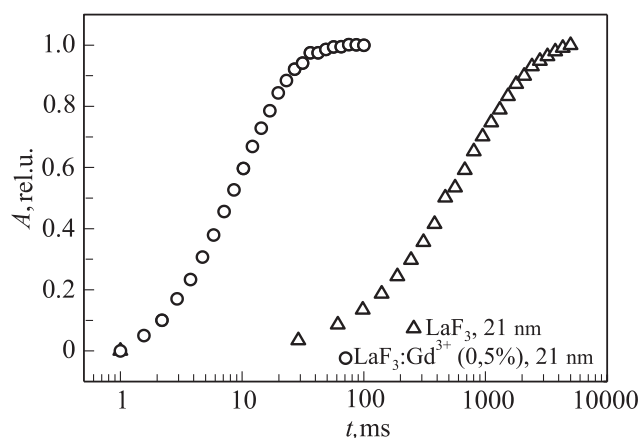


FIG. 1. The effect of gadolinium on the longitudinal magnetization recovery time of ¹H of water for two colloidal solutions: LaF₃, sample No. 11 (Δ); LaF₃:Gd³⁺ (0.5%), sample No. 1 (○).

rate T_1^{-1} of the water proton of the colloidal solutions LaF₃:Gd³⁺, with varying particle sizes and Gd³⁺ mass content in the final solution. The obtained results are presented in Fig. 2. It can be seen that the proton relaxation rate of the LaF₃:Gd³⁺ solution decreases with increasing particle size.

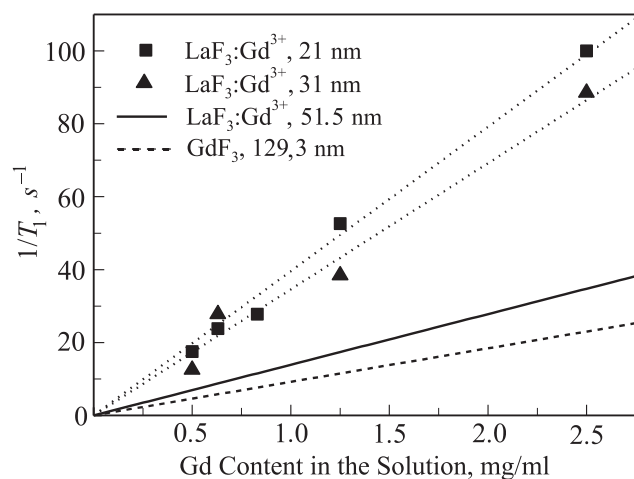


FIG. 2. The rate of longitudinal relaxation NMR ¹H of water of colloidal solutions LaF₃:Gd³⁺, with varying particle size and mass content of Gd³⁺ ions in the final solution. The sample temperature is 37 °C. The results are for samples of LaF₃:Gd³⁺ (average particle size 51.5 nm) and GdF₃ (average particle size 129.2 nm) taken from Ref. 6.

This fact can be related to the significant decrease in the specific surface area of the nanoparticles in the solution, and a decrease in the efficiency of the exchange between water molecules located close to the nanoparticle surface, and the water molecules in outer focal spheres.

For practical applications of the above solutions as contrast agents, the actual concentration of the agent in the solution is of the most importance. This is how, for example, the brightness of the side effect imaging depends on the given concentration. Fig. 3 shows the experimentally-measured dependences of the longitudinal relaxation rate of ¹H of water in colloidal solutions LaF₃:Gd³⁺, on the nanoparticle concentration in the final solution and paramagnet composition, as well as the results of Ref. 6. As can be seen in Fig. 3, the proton relaxation rate of the LaF₃:Gd³⁺ solution increases with paramagnet concentration in the nanoparticles. This type of dependence serves to indicate that the determining factor in the relaxation of water protons in the solution LaF₃:Gd³⁺ is the efficiency of the electron spin-lattice relaxation of the Gd³⁺ ions. This could be confirmed by direct measurements of the electron spin-lattice relaxation time for Gd³⁺ ions using pulsed EPR techniques, in

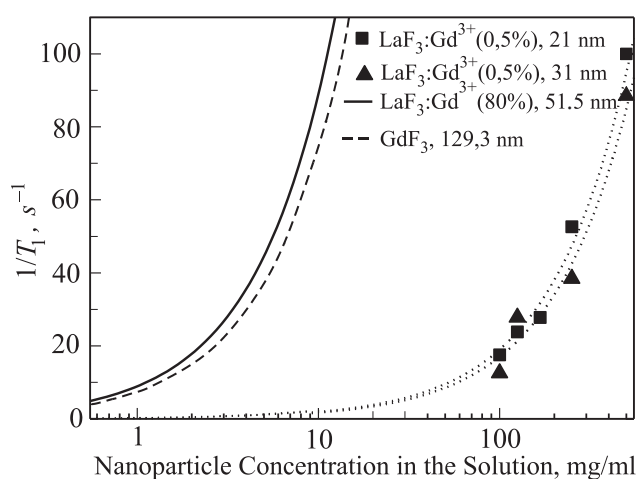


FIG. 3. The dependence of the rate of longitudinal relaxation of ¹H of water of colloidal solutions LaF₃:Gd³⁺, on the concentration of nanoparticles in the final solution and paramagnet content. The temperature is 37 °C. Results for LaF₃:Gd³⁺ samples (80%, average particle size 51.5 nm) and GdF₃ (average particle size 129.3 nm) taken from Ref. 6.

synthesized $\text{LaF}_3:\text{Gd}^{3+}$ nanopowder with varying paramagnet concentrations.

Conclusion

The object of the study is the nuclear magnetic relaxation of water protons in a series of colloidal solutions of magnetically-diluted LaF_3 and $\text{LaF}_3:\text{Gd}^{3+}$ nanoparticles (0.5%). Patterns of experimental dependences of the rate of longitudinal relaxation on the concentration of nanoparticles within the solution, and on their size, are established. It is shown that the rate of proton relaxation in the $\text{LaF}_3:\text{Gd}^{3+}$ solution increases with the paramagnet concentration in the nanoparticles, and decreases with increasing particle size.

It is suggested that the determining factor for the relaxation of water protons in $\text{LaF}_3:\text{Gd}^{3+}$ solution is the efficiency of the electron spin-lattice relaxation of the Gd^{3+} ions, which in this case is the correlation time. In order to confirm this, pulsed EPR measurements of the electron spin-lattice relaxation time for Gd^{3+} ions in synthesized $\text{LaF}_3:\text{Gd}^{3+}$ nanopowder, with varying paramagnet contents, should be carried out.

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