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The influence of restricted geometry of diamagnetic nanoporous media on ^3He relaxation

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This is an experimental study of the spin kinetics of ^3He in contact with diamagnetic samples of inverse opals SiO_2 , and LaF_3 nanopowder. It is demonstrated that the nuclear magnetic relaxation of the absorbed ^3He occurs due to the modulation of dipole-dipole interaction by the quantum motion in the two-dimensional film. It is found that the relaxation of liquid ^3He occurs through a spin diffusion to the absorption layer, and that the restricted geometry of diamagnetic nanoporous media has an influence on the ^3He relaxation. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4906335>]

Introduction

Nuclear magnetic relaxation of liquid or gas that is in contact with a solid surface, frequently occurs much faster than relaxation in the bulk. One of the reasons for the acceleration of relaxation when there is surface contact, is a significant change in the motion correlation time, due to changes in the mobility of molecules located at or near a wall. Furthermore, the surface can add additional fluctuating magnetic interactions. The most significant effect on the relaxation comes from paramagnetic ions or other paramagnetic centers, which can be contained at the surface or within the surface proximity, of the solid material.

The exchange between the surface layer and the liquid or gas volume in the pore, creates a finite settlement time for the surface molecules. This rate of exchange largely determines the measurement results. For a liquid located in an isolated pore, in the case of slow exchange, the amplitude of relaxing magnetization will differ according to distances from the pore surface, and the relaxation behavior will be a poly-exponential superposition of the different parts of the pore, depending on its shape.

The simplest situation occurs during a rapid exchange of molecules between the wall layer and pore volume (fast diffusion mode, or slow surface relaxation). The rapid exchange leads to an exponential relaxation of the entire liquid in the pore. This mode is realized if this condition is fulfilled¹

$$T_1 > \frac{r^2}{6D}, \quad (1)$$

where r is the pore radius and D is the diffusion coefficient of the liquid's molecules. In this case, the simplest model that describes the relaxation of the liquid inside the pore, is the two-position model with a rapid exchange,² in which

$$\frac{1}{T_1} = \frac{C_V}{T_{1V}} + \frac{C_S}{T_{1S}}, \quad (2)$$

where C_V and C_S are the proportions of liquid in the bulk and on the surface, respectively, T_{1V} and T_{1S} are corresponding times of T_1 . If we take the volume of the surface layer as being equal to the product of the pore surface S and the thickness of the layer λ , then⁴

$$\frac{1}{T_1} = \left(1 - \frac{\lambda S}{V}\right) \frac{1}{T_{1V}} + \frac{\lambda S}{V} \frac{1}{T_{1S}} \approx \frac{1}{T_{1V}} + \rho \frac{S}{V}, \quad (3)$$

where V is the pore volume and ρ is the coefficient of nuclear spin relaxation at the surface. Very often the first term on the right of expression (3) is small, and can be omitted.

Analogous to times T_1 , the transverse magnetization relaxation times T_2 also decrease for liquids and gases. It is more difficult to interpret the values of T_2 , but porosimetry based on T_2 measurements is applied in practice.³

If the shape of the pores is identical, then the V/S ratio is the measure of pore size. In order to obtain the size of the pore, it is necessary to know the parameter of the surface relaxation, ρ . Calibrations obtained via independent methods of pore size determination are used for these purposes. In the absence of transport between pores, the distribution of relaxation times is responsible for the superposition of individual pore times. If the pores are connected by very narrow channels, the latter can form effective relaxation barriers, leading to pore isolation from the perspective of relaxation measurement.

Ref. 4 shows that an increase in the surface relaxation leads to a decrease in pore connectivity, since faster surface relaxation shortens the distance by which the nuclei can diffuse before relaxation occurs. Therefore, the degree to which the pores are connected depends on the surface geochemistry, the control of which can ease the process of interpreting

NMR data. The authors note that if paramagnetic concentrations are increased (iron ions) at the surface, there is a separation of the distribution into distinct peaks. It is also shown that the pore connectivity affects the relative amplitudes of the fast and slow relaxing signals.

It should be noted that if surface relaxation dominates, then the rate of change of magnetization at the shortest times is proportional to the ratio of the total surface to the total system volume, regardless of the connectedness of the pore system. Obviously, this exact case is realized with ^3He , due to the extremely long relaxation times in the bulk ^3He . Another feature of ^3He is its very rapid diffusion, which means that it is very rare to have a situation with relaxation barriers, and there is no need to analyze the distribution of relaxation times.

In addition, using ^3He as a probe in porous media is justified by the extremely high sensitivity (NMR signal value) that allows for the direct measurement of the surface relaxation in the adsorbed layer.

^3He in inverse opals SiO_2

We studied two model samples of inverse opals with pore sizes (224 ± 15) nm (sample 1) and (337 ± 5) nm (sample 2). The samples were grown in the Special Design and Technological Bureau “Nauka” KSC SB RAS (Krasnoyarsk). Photos of the test samples, obtained using a transmission electron microscope, are shown in Figs. 1 and 2.

The samples were grown as particles with a large size distribution (from 1 to 10 mm). In order to reduce the spread of particle sizes, they were passed through two sieves with mesh sizes of 800 and 300 μm .

Filling the surface of the inverse opals with ^3He was done using the following technique. Gaseous ^3He condensed in the experimental cell in small portions of about 0.5 cm^3 (under normal conditions). After the condensation of each portion, the pressure inside the cell was controlled. When the equilibrium pressure of $P=10^{-1}$ millibar was exceeded, it was assumed that the entire surface of the test sample was filled with a layer of adsorbed ^3He atoms. Further condensation of ^3He in the cell caused an increase in pressure and the emergence of the gas phase. Upon reaching the saturated vapor pressure of ^3He (66 millibar at 1.5 K) the liquid phase appeared in the cell, and the process of filling it with liquid ^3He was controlled using the

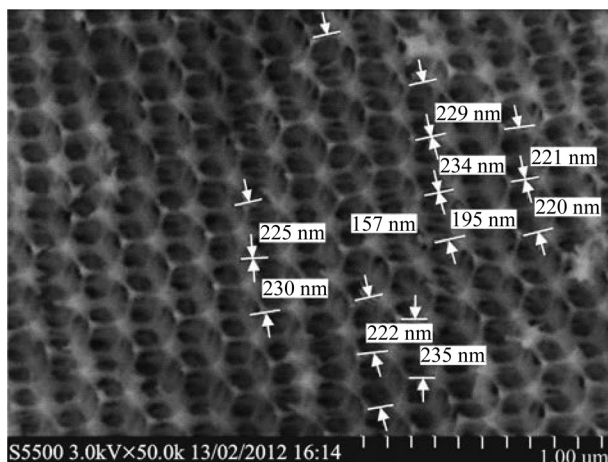


FIG. 1. Inverse opal sample 1, with pore sizes (224 ± 15) nm.

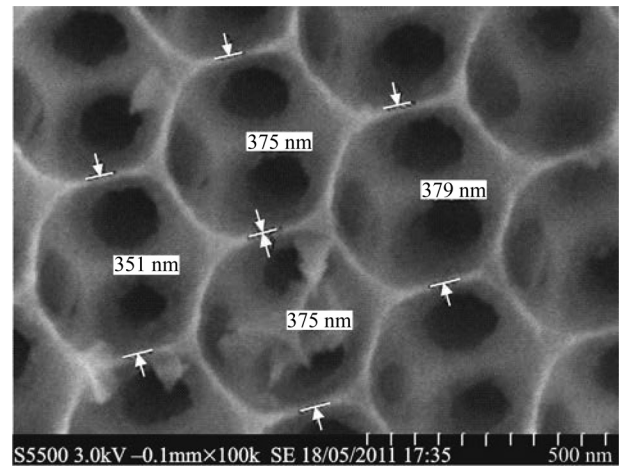


FIG. 2. Inverse opal sample 2, with pore sizes (377 ± 5) nm.

amplitude of the ^3He NMR signal. The adsorption isotherms for both samples are shown in Fig. 3.

In all experiments, there is an observed exponential time dependence of the longitudinal and transverse magnetization decay recovery for the test spin systems: adsorbed ^3He , adsorbed and gaseous ^3He , and adsorbed and liquid ^3He , which is explained by the rapid exchange of ^3He atoms in the system. There was no observable separation between NMR signals from ^3He located between the particles of the inverse opal, and ^3He located in the pores of the sample particles.

It was discovered that the relaxation time T_1 of the adsorbed ^3He has a linear dependence on the Larmor frequency of the ^3He NMR (Fig. 4), which is the same for both samples, serving as evidence of there being one single mechanism of nuclear magnetic relaxation in the ^3He adsorbed layer.

The longitudinal magnetization recovery curves of liquid ^3He nuclei located in the pores of the inverse opal sample are shown in Fig. 5. It can be seen that the time T_1 for both samples varies by a factor of 2.5, which correlates to the pore size of the samples.

^3He in contact with nanosized LaF_3 particles

Similar to the experiment with inverse opals, the spin kinetics of liquid ^3He are studied in the space between

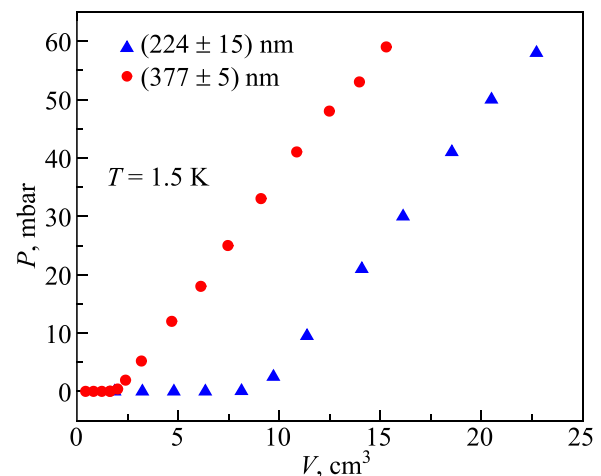


FIG. 3. Absorption isotherms of ^3He on the surface of inverse opal SiO_2 samples, at a temperature of 1.5 K.

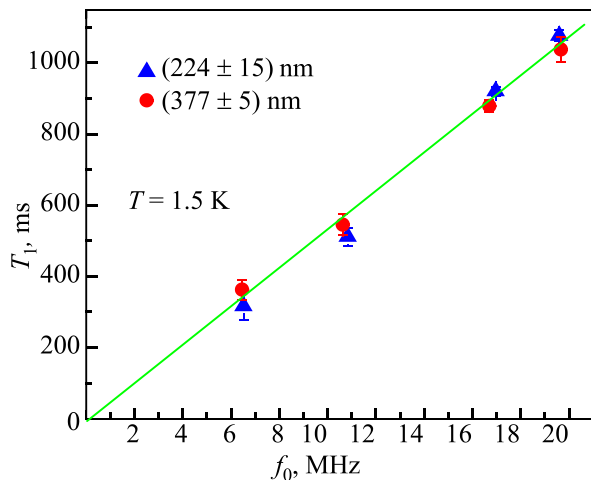


FIG. 4. The frequency dependence of the longitudinal relaxation time T_1 of the absorbed ^3He at the surface of inverse opals.

nanosized LaF_3 particles of different sizes, and at their surface (absorption layer).

Samples 3 and 4 are LaF_3 nanopowders with an average particle size of (21 ± 7) and (31 ± 7) nm, respectively. The stages of synthesis and sample properties are described in detail in Refs. 5–9.

The NMR vial was evenly filled with the nanopowder, and sealed shut. The vial had a hermetically sealed vacuum connection to the ^3He gas control device. Before the NMR process, the samples were pumped out using a cryopump (pressure of about 10^{-3} millibar), in order to rid the sample surface of any absorbed gases. The experimental procedure and setup are described in detail in Ref. 10.

Fig. 6 shows the frequency dependence of the longitudinal relaxation time T_1 of the absorbed ^3He at the LaF_3 surface (samples 3, 4). It is evident that the relaxation time T_1 of the absorbed ^3He , as is the case with the inverse opals described above, has a linear dependence on the ^3He NMR Larmor frequency, and this dependence is the same for both samples. As such, the relaxation mechanism of the absorbed ^3He layer is also carried out through the modulation of the dipole-dipole interaction by the quantum motion in the two-dimensional film.^{11,12}

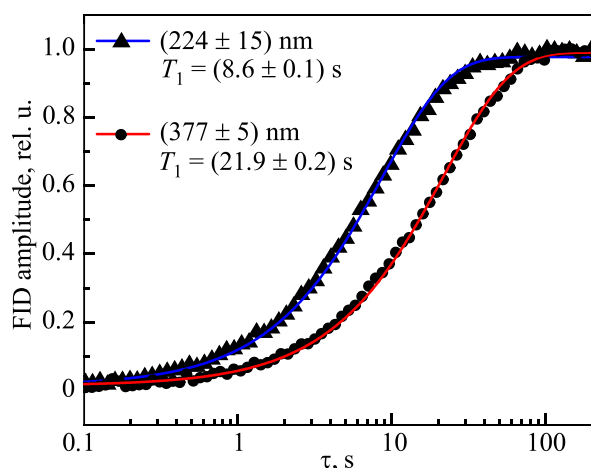


FIG. 5. The longitudinal magnetization recovery curve of liquid ^3He nuclei in the pores of the inverse opal samples.

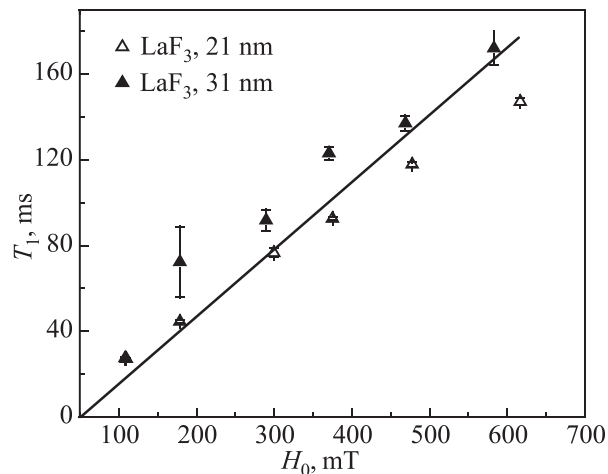


FIG. 6. Frequency dependence of the longitudinal relaxation time T_1 of the absorbed ^3He , at the LaF_3 surface (samples 3 (Δ) and 4 (\blacktriangle)).

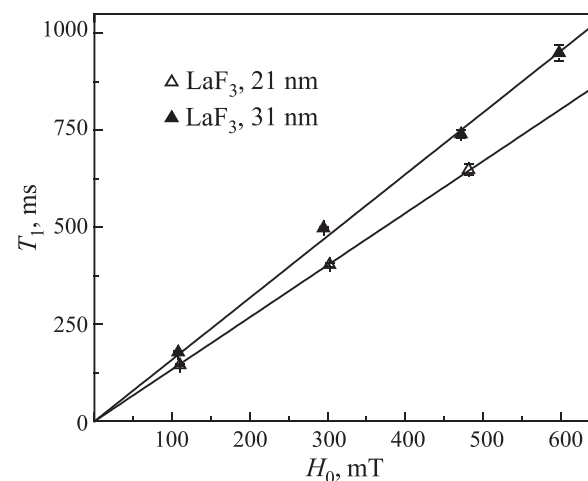


FIG. 7. Frequency dependence of the longitudinal relaxation time T_1 of liquid ^3He at the LaF_3 surface (samples 3 (Δ) and 4 (\blacktriangle)).

Fig. 7 shows the frequency dependence of the longitudinal relaxation time T_1 of liquid ^3He , in contact with LaF_3 (samples 3,4). Time T_1 for the two samples differs by a factor of 1.2, even though according to the average size of the sample particle, the times should vary by a factor of 1.5. Most likely, this discrepancy was caused by non-ideal filling of the NMR vial, and compaction of the sample inside.

Conclusion

Experimental studies of the spin kinetics of ^3He in contact with diamagnetic samples of inverse opals SiO_2 , and LaF_3 nanopowders of varying particle size, are conducted.

It is found that the nuclear magnetic relaxation of the absorbed ^3He for all samples has the same character, and is carried out through the modulation of the dipole-dipole interaction by quantum motion in the two-dimensional film.

It is also found that the nuclear magnetic relaxation of liquid ^3He occurs by way of spin (mass) diffusion from the bulk ^3He toward the absorbed layer.

There is also an observable influence of the restricted geometry of the diamagnetic nanoporous media on the relaxation of ^3He .

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