

Comments on the cross-relaxation effect between adsorbed ^3He and PrF_3 nanoparticles

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The spin kinetics data of ^3He in contact with PrF_3 and LaF_3 nanosized powders are reported. All experiments have been carried out by pulse NMR methods at temperature 1.5 K. The analysis of obtained data testifies in favor of cross-relaxation presence in the nuclear spin–lattice relaxation data, which takes place between ^3He and ^{141}Pr nuclei.

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Introduction

Direct transfer of nuclear magnetization through the interface between liquid ^3He and solid substrate is a fundamental effect discovered in 1980s. First observation of magnetic dipole interaction between the nuclear spins of liquid ^3He and ^{19}F nuclei in ^3He -polytetrafluoroethylene (DLX-6000) system has been reported by Richardson *et al.* [1]. Further investigations revealed such coupling between several substrates and in different spin-systems in contact with ^3He [2–6]. For an existence of this effect it is necessary to have the Zeeman energy level splitting of ^3He to be equal to that of the substrate nuclei.

The possibility of using dielectric Van Vleck paramagnets for dynamic nuclear polarization of ^3He via direct magnetic coupling between Van Vleck ion and ^3He nuclei was suggested earlier [7]. Later on the cross-relaxation between ^{141}Pr nuclei of PrF_3 crystalline powder and liquid ^3He was observed by authors [8]. Typical dimensions of sample powder particles were tens of micrometers in reported experiments.

Decreasing of particles sizes to the order of nanometers shortens the nuclear spin diffusion times over the crystal lattice. Shorter spin diffusion times should provide faster spin-temperature equilibrium achievement over whole spin system during the time of the experiment. Also, the transi-

tion from micro- to nanometers PrF_3 particles sizes significantly increases the surface area, which should increase efficiency of the magnetic coupling between ^3He nuclei and the solid state substrate nuclei.

The main goal of present work is to show the presence of cross-relaxation in the ^3He spin kinetics data in contact with PrF_3 nanosized powders.

Results and discussion

Crystalline nanodimensional powders of Van Vleck paramagnet PrF_3 and its diamagnetic analogue LaF_3 were used as samples. They were synthesized by a method well-described in [9,10]. To synthesize samples with different particles sizes microwave irradiation of colloidal solution was used [11].

The set of samples includes nonradiated and 20 minutes microwave irradiated ones: sample 1 — nonradiated PrF_3 (average particles size (21 ± 9) nm), sample 2 — irradiated PrF_3 (average particles size (31 ± 10) nm), sample 3 — nonradiated LaF_3 (average particles size (21 ± 7) nm) and sample 4 — irradiated LaF_3 (average particles size (31 ± 7) nm).

These samples were investigated by x-ray analysis, high-resolution transmission electronics microscopy, nuclear magnetic and nuclear pseudoquadrupole resonance methods [12–14]. The following results were achieved:

the crystal structure changing by microwave irradiation has been observed; water clusters have been discovered in the internal cavities of the nanoparticles; the parameters of the nuclear spin Hamiltonian have been determined; relaxation times of ^{19}F , ^{141}Pr and ^3He were investigated.

It was shown earlier [10,12] that relaxation of the longitudinal magnetization of ^3He nuclei in contact with PrF_3 in external magnetic field occurs through two channels: a high-field relaxation due to the ^3He atoms motion in local field inhomogeneities and low-field relaxation via adsorbed layer. The relaxation of ^3He nuclei in contact with LaF_3 samples is supposed to avoid the effect of local magnetic field inhomogeneities and absence of high-field relaxation mechanism.

The experiments on ^3He relaxation times were carried out by a home-build pulse nuclear magnetic resonance spectrometer [15]. The spin–lattice relaxation times were measured by the “saturation–recovery” technique and measurement of the amplitude of the free induction decay signal after 90° rf pulse. The temperature of 1.5 K in the experimental cell was reached by pumping of liquid helium vapors from the cryostat. The magnetic field dependence of the ^3He spin–lattice relaxation times in contact with LaF_3 nanoparticles for various ^3He aggregate states has been obtained and is shown in Fig. 1.

It is clearly seen that the longitudinal relaxation time of ^3He nuclei changes linearly with the value of the external magnetic field. And the relaxation rates strongly depend on the amount of ^3He in the experimental cell. This fact proves that the relaxation occurs through the adsorbed layer [16–18].

Observed values of T_1 relaxation times of ^3He nuclei in the gaseous and liquid phases are in a good agreement with the consideration that the magnetic relaxation times are

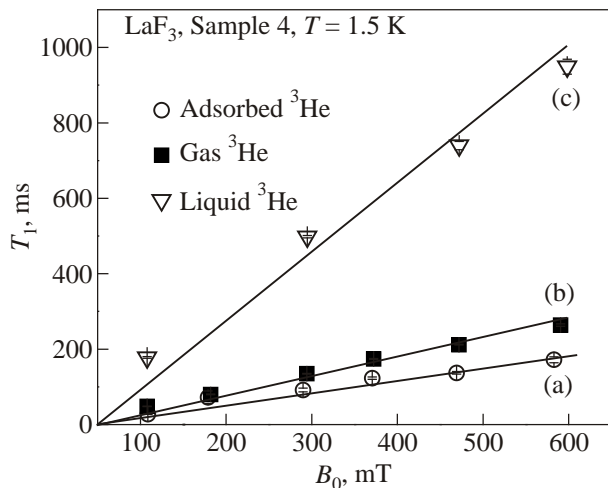


Fig. 1. Magnetic field dependence of the relaxation time of the longitudinal magnetization of the ^3He nuclei in the systems LaF_3 –adsorbed ^3He (a), LaF_3 –gas phase ^3He (b) and LaF_3 –liquid ^3He (c) at a temperature of 1.5 K. Solid lines are eye-guide of the experimental data.

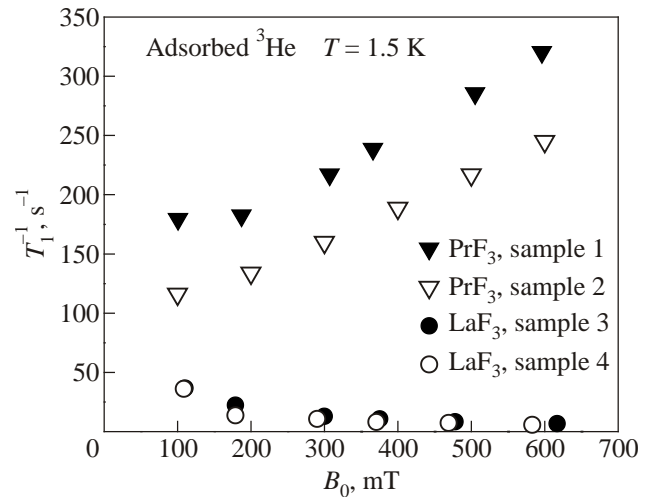


Fig. 2. Magnetic field dependence of the longitudinal magnetization relaxation rate of the adsorbed layer ^3He nuclei in contact with LaF_3 (circles) and PrF_3 (triangles) at the temperature of 1.5 K.

proportional to the ^3He relaxation times in the adsorbed layer and to the ratio of total number of ^3He spins to the number in the layer:

$$T_1 = T_{1S} N_0 / N_S, \quad (1)$$

where T_1 — longitudinal magnetization recovery time, T_{1S} — longitudinal magnetization recovery time for adsorbed layer, N_0 — total number of ^3He spins, N_S — number of ^3He spins in the adsorbed layer.

Magnetic field dependence of the ^3He longitudinal magnetization relaxation rate in the adsorbed layer on the surface of all samples at 1.5 K temperature is shown in Fig. 2.

The difference of ^3He relaxation rates in contact with PrF_3 between samples 1 and 2 was explained by size effect and described in [12]. Also, a qualitative model of the magnetic relaxation of ^3He by two relaxation mechanisms, describing the experimental results has been proposed.

It is well seen from Fig. 2 that ^3He spin–lattice relaxation rates are different for various samples. In the case of PrF_3 the rates exceed ones for LaF_3 case by order of magnitude. As was described above, the high-field relaxation mechanism exists due to the ^3He atoms motion in local field inhomogeneities, which are almost negligible in case of LaF_3 samples.

Comparison of longitudinal magnetization relaxation rates of the adsorbed layer ^3He nuclei in contact with LaF_3 and PrF_3 without high-field mechanism contribution should provide additional information on the nature of relaxation processes.

Magnetic field dependence of the ^3He longitudinal magnetization relaxation rate in the adsorbed layer on the surface of samples 1 and 3 at 1.5 K temperature is shown in Fig. 3 (for sample 1 high-field mechanism was deduced from experimental data).

Obviously the ^3He relaxation rate by Cowan’s relaxation mechanism [16,17] in adsorbed layer of ^3He in both

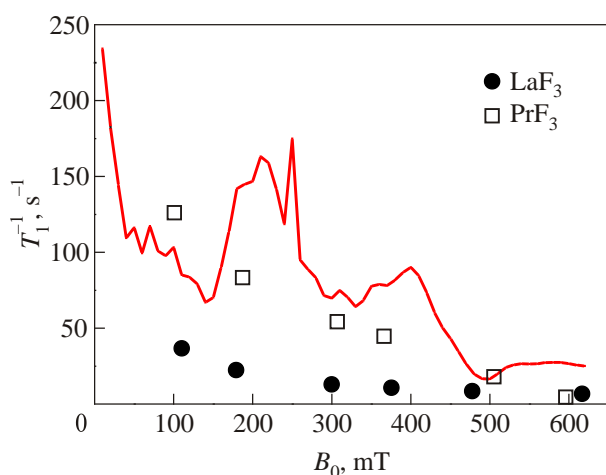


Fig. 3. Magnetic field dependence of the longitudinal magnetization relaxation rate of the adsorbed layer ^3He nuclei in contact with LaF_3 (circles, sample 3) and PrF_3 (squares, sample 1) with the deduction of the relaxation in inhomogeneous magnetic field at the temperature of 1.5 K. The solid line qualitatively displays efficiency of cross-relaxation between ^{141}Pr and ^3He nuclei, based on calculated intensity of the NMR signal of ^{141}Pr in the undirected PrF_3 powder at the Larmor frequency of ^3He [8].

cases should have comparable magnitude. Unexpectedly, the longitudinal relaxation of ^3He is significantly faster in case of PrF_3 . This can be an evidence of the existence of additional mechanism, which can be the cross-relaxation between ^3He and ^{141}Pr nuclei.

Anisotropy of effective gyromagnetic ratio of ^{141}Pr nuclei (nuclear spin $I = 5/2$) in PrF_3 , quadrupole and pseudoquadrupole interactions leads to a fact that similar transition frequencies between ^{141}Pr and ^3He nuclear energy levels can be obtained at certain directions and a certain magnitude of an external magnetic field with respect to the crystallographic axes of the sample particles.

The intensity of the NMR signal of ^{141}Pr in the undirected PrF_3 powder at the Larmor frequency of ^3He [8] is inserted to the plot on Fig. 3. The efficiency of cross-relaxation will be proportional to the intensity of the ^{141}Pr NMR signal. Indeed, there is a slight correlation between cross-relaxation efficiency and experimental data for ^3He - PrF_3 nanosized crystalline powder system.

Conclusion

The spin kinetics data of ^3He in contact with PrF_3 and LaF_3 nanosized powders are reported. The analysis of obtained data testifies in favor of cross-relaxation presence in the nuclear spin-lattice relaxation data, which takes place between ^3He and ^{141}Pr nuclei.

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