Comments on the cross-relaxation effect between adsorbed 3He and PrF3 nanoparticles

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Comments on the cross-relaxation effect between adsorbed ^{3}He and PrF$_3$ nanoparticles

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The spin kinetics data of ^{3}He 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 ^{3}He and ^{141}Pr nuclei. © 2015 AIP Publishing LLC.
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Introduction

Direct transfer of nuclear magnetization trough the interface between liquid ^{3}He and solid substrate is a fundamental effect discovered in 1980s. First observation of magnetic dipole interaction between the nuclear spins of liquid ^{3}He and ^{19}F nuclei in ^{3}He-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 ^{3}He.[2–6] For an existence of this effect it is necessary to have the Zeeman energy level splitting of ^{3}He to be equal to that of the substrate nuclei.

The possibility of using dielectric Van Vleck paramagnets for dynamic nuclear polarization of ^{3}He via direct magnetic coupling between Van Vleck ion and ^{3}He nuclei was suggested earlier.[7] Later on the cross-relaxation between ^{141}Pr nuclei of PrF$_3$ crystalline powder and liquid ^{3}He 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 transition from micro- to nanometers PrF$_3$ particles sizes significantly increases the surface area, which should increase efficiency of the magnetic coupling between ^{3}He nuclei and the solid state substrate nuclei.

The main goal of present work is to show the presence of cross-relaxation in the ^{3}He 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 Refs. 9 and 10. To synthesize samples with different particles sizes microwave irradiation of colloidal solution was used.[11]

The set of samples includes nonradiated and 20 min microwave irradiated ones: sample 1—nonradiated PrF3 (average particles size (21 ± 9) nm) sample 2—irradiated PrF$_3$ (average particles size (31 ± 10) nm), sample 3—non-radiated 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 methodics.[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 ^{3}He were investigated.

It was shown earlier[10,12] that relaxation of the longitudinal magnetization of ^{3}He nuclei in contact with PrF$_3$ in external magnetic field occurs through two channels: a high-field relaxation due to the ^{3}He atoms motion in local field inhomogeneities and low-field relaxation via adsorbed layer. The relaxation of ^{3}He 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 ^{3}He 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
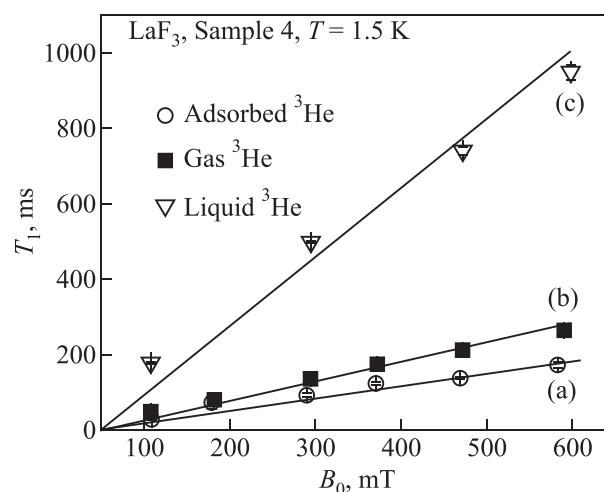

FIG. 1. Magnetic field dependence of the relaxation time of the longitudinal magnetization of the ^{3}He nuclei in the systems LaF$_3$-adsorbed ^{3}He (a), LaF$_3$–gas phase ^{3}He (b) and LaF$_3$–liquid ^{3}He (c) at a temperature of 1.5 K. Solid lines are eye-guide of the experimental data.
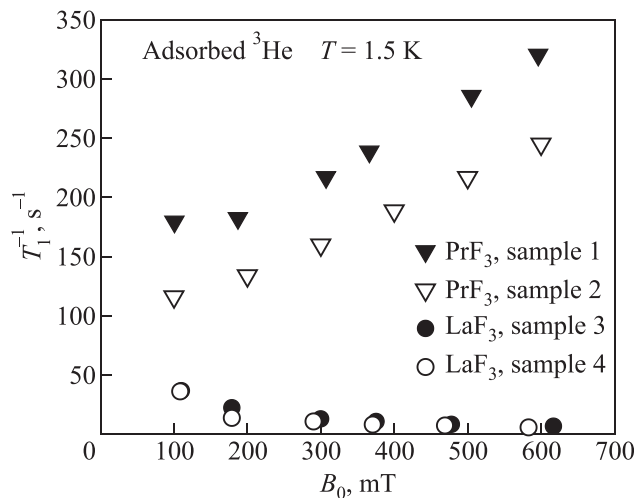
FIG. 2. Magnetic field dependence of the longitudinal magnetization relaxation rate of the adsorbed layer ^{3}He nuclei in contact with LaF$_3$ (circles) and PrF$_3$ (triangles) at the temperature of 1.5 K.

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 ^{3}He spin–lattice relaxation times in contact with LaF$_3$ nanoparticles for various ^{3}He aggregate states has been obtained and is shown in Fig. 1.

It is clearly seen that the longitudinal relaxation time of ^{3}He nuclei changes linearly with the value of the external magnetic field. And the relaxation rates strongly depend on the amount of ^{3}He 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 ^{3}He nuclei in the gaseous and liquid phases are in a good agreement with the consideration that the magnetic relaxation times are proportional to the He relaxation times in the adsorbed layer and to the ratio of total number of ^{3}He spins to the number in the layer:

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

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

Magnetic field dependence of the ^{3}He 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 ^{3}He relaxation rates in contact with PrF$_3$ between samples 1 and 2 was explained by size effect and described in Ref. 12. Also, a qualitative model of the magnetic relaxation of ^{3}He by two relaxation mechanisms, describing the experimental results has been proposed.

It is well seen from Fig. 2 that ^{3}He 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 ^{3}He atoms motion in local field inhomogeneities, which are almost negligible in case of LaF$_3$ samples.

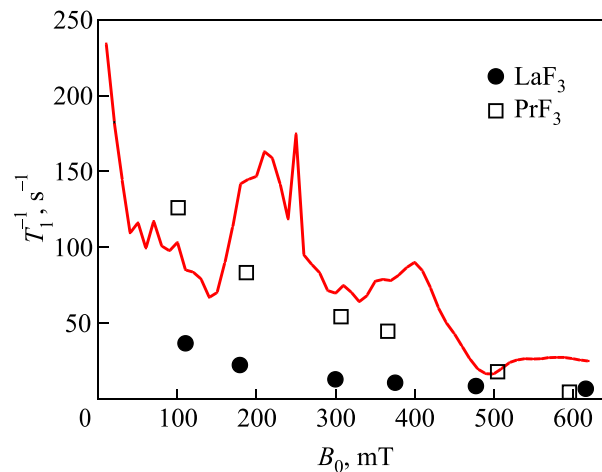Comparison of longitudinal magnetization relaxation rates of the adsorbed layer ^{3}He nuclei in contact with LaF$_3$

FIG. 3. Magnetic field dependence of the longitudinal magnetization relaxation rate of the adsorbed layer ^{3}He 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 ^{3}He nuclei, based on calculated intensity of the NMR signal of ^{141}Pr in the undirected PrF$_3$ powder at the Larmor frequency of He.[8]

and PrF$_3$ without high-field mechanism contribution should provide additional information on the nature of relaxation processes.

Magnetic field dependence of the ^{3}He 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 deducted from experimental data).

Obviously the ^{3}He relaxation rate by Cowan's relaxation mechanism[16,17] in adsorbed layer of He in both cases should have comparable magnitude. Unexpectedly, the longitudinal relaxation of ^{3}He 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 ^{3}He and ^{141}Pr nuclei.

Anisotropy of effective gyromagnetic ratio of ^{141}Pr nuclei (nuclear spin $I = 5/2$) in PrF$_3$, quadrupole and pseudo-quadrupole interactions leads to a fact that similar transition frequencies between ^{141}Pr and ^{3}He 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 ^{3}He (Ref. 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 ^{3}He-PrF$_3$ nanosized crystalline powder system.

Conclusion

The spin kinetics data of ^{3}He 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 ^{3}He and ^{141}Pr nuclei.

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