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Spin Kinetics of ^{3}He in Contact with Synthesized PrF_3 Nanoparticles

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Abstract Two nanosized PrF_3 samples were synthesized using two different procedures. The X-ray and HRTEM experiments showed high crystallinity of synthesized samples. Comparison of enhanced ^{141}Pr NMR spectra of microsized (45 μm) and nanosized PrF_3 powder is presented. Experimental data on spin kinetics of ^{3}He in contact with PrF_3 nanoparticles at $T = 1.5$ K are reported.

Keywords He-3 · Surface · Surface effect · Cross-relaxation · Magnetic coupling · van Vleck · Helium · 3He · Nanoparticles · NMR · Nuclear magnetic resonance · Low temperature · Magnetic relaxation

1 Introduction

The ^{3}He and its magnetic properties at low temperatures are studied widely since 1970s and a lot of interesting effects was discovered, like superfluidity [1] and spin superfluidity [2]. The properties of ^{3}He in porous media is the matter of interest, for example an aerogel suppress superfluid transition of ^{3}He, because the length scale of an open geometry of aerogel is the same order of magnitude as the superfluid coherence length [3]. A lot of NMR experiments studied magnetic properties of adsorbed

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^{3}He films and surface effects in bulk ^{3}He (see, for example, review sec. [4]). The magnetic properties and spin kinetics of ^{3}He at temperatures above Fermi temperature of liquid ^{3}He are also studied extensively. For instance, the influence of a porous media on NMR characteristics of liquid ^{3}He can be used as a tool for study porous substrates [5]. Another interesting effect was discovered in 1980s, which is a magnetic coupling between liquid ^{3}He and nuclear spin systems of solid state substrates [6–8]. The resonance magnetic coupling between ^{3}He and van Vleck paramagnet TmEs was discovered [9].

The "PrF_3–liquid ^{3}He" system is of interest because of the possibility of using the magnetic coupling between the nuclei of the two spin systems for the dynamic nuclear polarization of liquid ^{3}He [10]. Van Vleck paramagnets are known to have high anisotropy of the effective nuclear magnetogyric ratio [11]. As a result, a direct interaction between magnetic moments of equal magnitude at the liquid ^{3}He–solid state substrate interface becomes possible.

The resonance magnetic coupling between liquid ^{3}He nuclei and the ^{141}Pr nuclei of microsized (45 μm) Van Vleck paramagnet PrF_3 powder has been discovered [12, 13]. Using nanosized PrF_3 powder would create a highly-coupled ^{3}He–^{141}Pr spin system and could show new aspects of effects discovered earlier.

2 The Samples

The nanosized PrF_3 samples were synthesized by using the methods described in [14]. In a typical synthesis, 2.48 g of praseodymium oxide was dissolved in 160 ml of a 10% nitric acid solution to form a transparent solution, then 1.9 g of NaF (F:Pr = 3:1,) was added into the above solution under violent stirring. A light green colloidal precipitate of PrF_3 appeared immediately. The pH of the suspension was adjusted by ammonia to about 4.0–5.0. Deionized water was filled into the suspension to make the volume up to 300 ml. After stirring for about 20 min, the suspension was finally transferred into a 500 ml round flask and placed in a microwave oven (650 W, 2.45 GHz). The suspension was heated by microwave irradiation for 20 min at 70% of the maximum power under refluxing. The resulting product was collected by centrifugation and washed several times using deionized water and ethanol. Thus, two samples were obtained: sample A (without microwave radiation), sample B (with microwave radiation).

The crystal structure of the samples has been characterized by X-ray diffraction (XRD) (Fig. 1). 1-st line—sample A, 2-nd line—sample A (seven weeks aging at STP), 3-d line—sample B. All of the diffraction peaks can be readily indexed from the standard powder diffraction data of the hexagonal phase PrF_3. Figure 1 also confirms the hexagonal phase of the of PrF_3 particles crystal structure. As shown in Fig. 1, the narrow and sharp peaks indicate high crystallinity of the samples.

High-resolution transmission electron microscopy (HRTEM) images were obtained by using JEM—2100 F/SP with resolution—0.14 nm using an accelerating voltage of 200 kV (Fig. 2 and Fig. 3).

As shown in Fig. 2, nanoparticles of sample B are larger than those of sample A and have more regular spherical shape. Figure 3 shows that transition from sample A

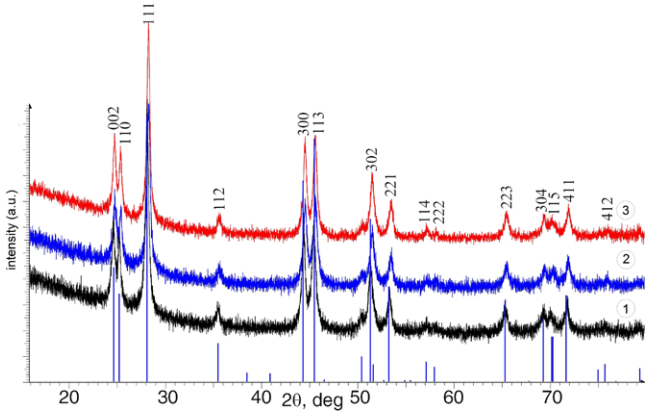
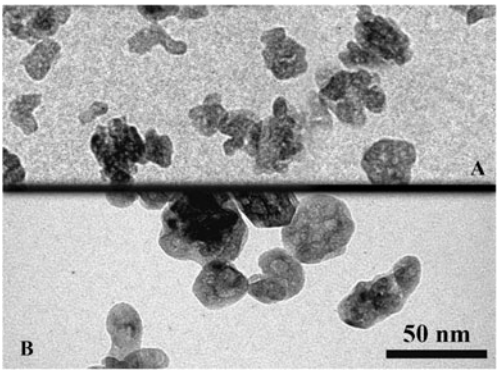


Fig. 1 (Color online) XRD of PrF_3 samples. 1-st line—sample A, 2-nd line—sample A seven weeks old (checking for aging), 3-d line—sample B

Fig. 2 HRTEM image of PrF_3 nanoparticles



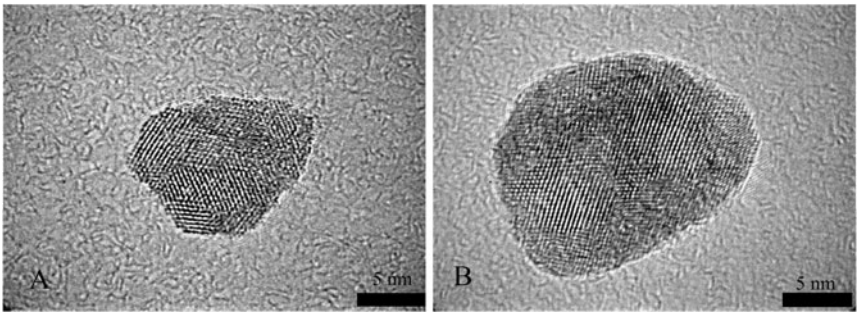


Fig. 3 HRTEM image of an individual PrF_3 nanoparticle

to sample B leads to transition from polycrystalline to single crystal structure. From HRTEM images we can obtain a size distribution of PrF_3 nanoparticles for samples A and B (Fig. 4). Particle sizes are: 20 ± 15 nm sample A, 32 ± 10 nm sample B.

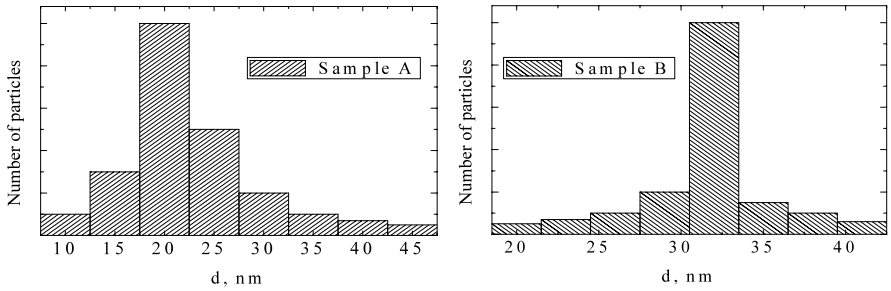


Fig. 4 Distribution of PrF_3 nanoparticles size for samples A and B

3 Experiment and Results

In all presented experiments the synthesized PrF_3 sample B was used, because it has more uniform particles and narrow size distribution. The sample ($m = 345$ mg) was placed in a glass tube which was sealed leak tight to the ^{3}He gas handling system. On the outer surface of the glass tube an NMR coil was mounted. A homebuilt pulse NMR spectrometer (frequency range of 3–50 MHz) was used. The pulse NMR spectrometer is equipped with a resistive electrical magnet that has a magnetic field strength up to 1 T. All experiments were done at the temperature $T = 1.5$ K, which was achieved by helium bath pumping. The longitudinal magnetization relaxation time T_1 of ^{3}He was measured by the saturation recovery method using a spin-echo signal.

In the experiments with ^{3}He three different systems were studied: PrF_3 nanoparticles completely covered by ^{3}He adsorbed layer, PrF_3 sample filled by gas phase ^{3}He and PrF_3 sample filled by liquid ^{3}He. The amount of ^{3}He, necessary for complete coverage of PrF_3 nanoparticles was adjusted as in [15] and was equal to 10 cm^3 STP for our sample. Gaseous ^{3}He was condensed into the sample cell at temperature $T = 1.5$ K in small portions on the order of 0.5 cm^3 STP. After the condensation of each portion, the pressure in the sample cell was checked and, if it turned out to be less than 10^{-2} mbar, the next portion was condensed. The entire sample surface was assumed to be coated by the adsorbed layer of ^{3}He atoms when the equilibrium pressure exceeded 10^{-1} mbar.

The NMR spectra of ^{141}Pr ($I = 5/2$) observed in a PrF_3 single crystal are well described by the nuclear spin Hamiltonian [16]:

$$H = -\hbar \sum_{i=x,y,z} \gamma_i H_i I_i + D\left[I_z^2 - \frac{1}{3} I(I+1)\right] + E(I_x^2 - I_y^2), \tag{1}$$

where $\gamma_x/2\pi = 3.32(2)$ kHz/Oe, $\gamma_y/2\pi = 3.24(2)$ kHz/Oe, $\gamma_z/2\pi = 10.03(5)$ kHz/Oe, $|D/h| = 4.31(1)$ MHz, and $|E/h| = 0.30(1)$ MHz.

The resonance NMR spectra of the powdered PrF_3 sample were measured at frequencies of 6.63 and 19.5 MHz (Fig. 5) by method described in [12] (filled points—PrF_3 nanoparticles, open points—microsized particles [12], the NMR cell was filled by liquid ^{4}He for a good thermal contact with the external helium bath). The simulated NMR spectra of ^{141}Pr for the PrF_3 powders presented in Fig. 6.

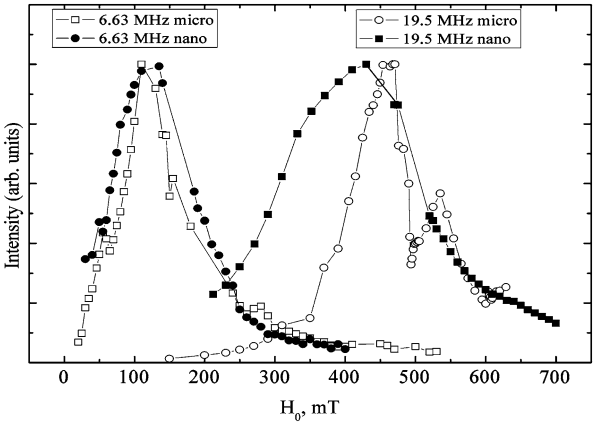


Fig. 5 Enhanced nuclear magnetic resonance (ENMR) spectra of ^{141}Pr in PrF_3 powder obtained at a frequency 6.63 and 19.5 MHz (*filled points*—PrF_3 nanoparticles (sample B), *open points*—microsized particles [12])

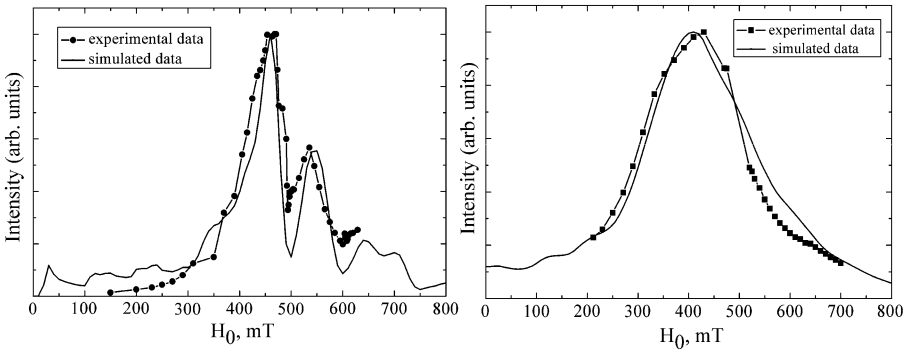


Fig. 6 Simulated nuclear magnetic resonance spectra of ^{141}Pr in PrF_3 powder recorded at the frequency 19.5 MHz. Microsized—*left* fig., nanoparticles—*right* fig.

Figure 6 shows that at a frequency of 19.5 MHz the nanosized sample spectrum is well described by the simulated spectrum with a line width 6 MHz, and microsized—1 MHz. ^{141}Pr energy levels in PrF_3 in the absence of a magnetic field are 9.02 and 17.08 MHz. Figure 7 shows that with the transition from single crystal to the microsized powder, the levels become a zone of a width of 1 MHz, and the transition to nanosized sample widens the zone up to 6 MHz.

The spin kinetics of ^3He in contact with PrF_3 nanoparticles has been studied. Experimental data are presented in Figs. 8 and 9. In all experimental cases (PrF_3 nanoparticles completely covered by ^3He adsorbed layer, PrF_3 sample filled by gas phase ^3He and PrF_3 sample filled by liquid ^3He) only one common ^3He NMR signal was detected. This situation is similar to ^3He NMR in an aerogel samples at low [15, 17] and ultralow temperatures [18] and could be result of fast exchange of ^3He atoms between adsorbed layer and free (gas or liquid) phase.

The magnetic field dependences of the longitudinal magnetization relaxation rate of ^3He nuclei measured by pulse NMR technique in the system PrF_3–^3He are presented in Fig. 8. As can be seen the nuclear magnetic relaxation of ^3He is anom-

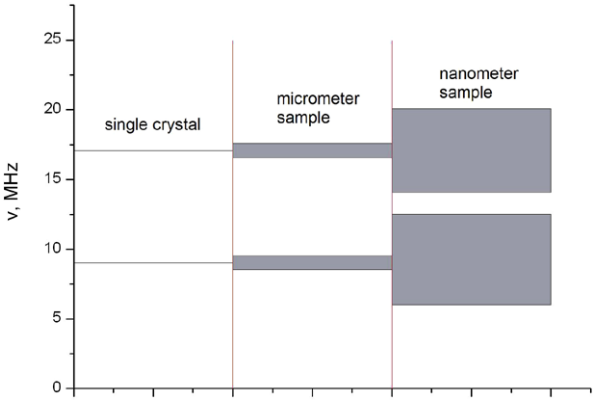


Fig. 7 (Color online) Schematic of ^{141}Pr energy levels in PrF_3 in the absence of applied magnetic field vs. size of sample particles

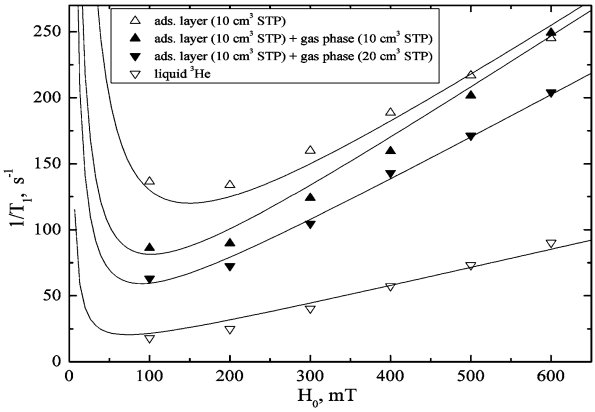


Fig. 8 The magnetic field dependences of the longitudinal magnetization relaxation rate of ^{3}He nuclei in the system PrF_3–^{3}He

alously fast. In normal bulk liquid ^{3}He the longitudinal relaxation time is the order of hundreds of seconds [19].

Nanosized powder has a huge crystal surface which means that relaxation mechanisms due to the adsorbed film [15, 20, 21] should work. Due to the fact that PrF_3 is a van Vleck paramagnet, its particles create a highly inhomogeneous magnetic field between them. Thus, the longitudinal relaxation mechanism of ^{3}He in inhomogeneous field should work [22] and this model assumes the relaxation rate should be proportional to the inhomogeneity of magnetic field between powder particles. According to our measurements of T_2^* versus magnetic field (Fig. 9), the inhomogeneity of magnetic field is proportional to external magnetic field H_0. Taking into account both described mechanisms all experimental data can be fitted by following equation (parameters A and B presented in Table 1):

$$1/T_1 = A/H_0 + BH_0 \tag{2}$$

According to fitting experimental data by (2) and parameters presented in Table 1 the surface mechanism is quite similar to reported earlier (see for instance [15, 17, 21]). Moreover, close look at parameter A and its correlation to the amount

Table 1 Parameters A and B for fitting of experimental data (Fig. 8) by (2)

The system under investigation	parameter A of (2)	parameter B of (2)
PrF_3 nanoparticles completely covered by ^{3}He adsorbed layer (10 cm^3 STP). Equilibrium pressure 0.1 mbar.	8999	0.4
PrF_3 nanoparticles completely covered by ^{3}He adsorbed layer (10 cm^3 STP) + gas phase (10 cm^3 STP). Equilibrium pressure 25 mbar.	4140	0.4
PrF_3 nanoparticles completely covered by ^{3}He adsorbed layer (10 cm^3 STP) + gas phase (20 cm^3 STP). Equilibrium pressure 50 mbar.	2650	0.33
PrF_3 nanoparticles + liquid ^{3}He. Saturation vapor pressure of ^{3}He 75 mbar.	750	0.14

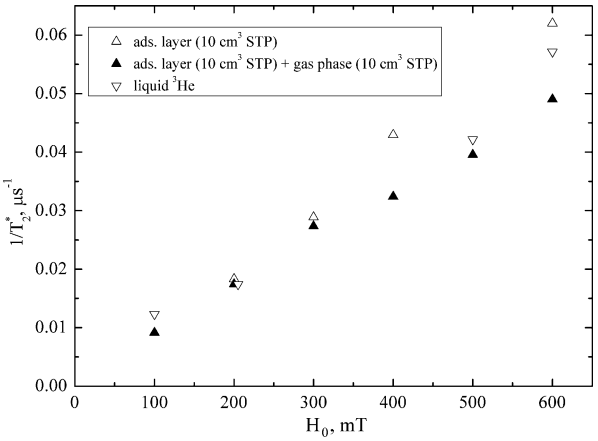


Fig. 9 The dependence of the magnetic field inhomogeneity of the applied external field H_0 between PrF_3 particles, sensed by ^{3}He T_2^* NMR parameter

of gaseous ^{3}He proves the model Hammel-Richardson [15, 23] works perfectly in our case and taking into account that intrinsic relaxation time of bulk liquid ^{3}He is much longer than observed values, the model described analytically [18] also works, in spite of significant difference in temperature. Parameter B in the Table 1 should be proportional to the diffusion rate of ^{3}He, but surprisingly this parameter is the same in the case of complete adsorbed layer of ^{3}He and in the presence of small portion of gaseous (10 cm^3 STP) ^{3}He, which could be also caused by fast exchange between adsorbed layer and gaseous phase.

4 Conclusion

The method of synthesis of nanosized powders of crystalline trifluoride rare earths compounds was tested. As a result, two nanoscopic samples of van Vleck paramagnet PrF_3 with size (20 ± 15) nm and (32 ± 10) nm were synthesized. X-ray analysis established a high crystallinity of the synthesized samples. According to the results of HRTEM, the transition from the first sample to the second sample leads to transition from polycrystalline to single crystal structure.

NMR spectra of ^{141}Pr in the synthesized PrF_3 powders were investigated. The spectrum of nanosized sample is wider than that of microsized PrF_3 sample, investigated earlier [12, 13]. The simulations of ^{141}Pr NMR spectra are in good agreement with experimental data.

Spin kinetics of ^3He in the system "PrF_3–^3He" was investigated. The model of longitudinal magnetization relaxation of ^3He nuclei was proposed. According to this model the longitudinal relaxation of ^3He is carried out both by the ^3He adsorbed film on the surface and due to the modulation of dipole-dipole interaction in strongly inhomogeneous magnetic field, caused by nanosized PrF_3 particles.

At present time according to our experimental data we see no evidence of ^{141}Pr–^3He coupling in our system and it will be the aim of future research.

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