PrF$_3$ Van Vleck paramagnet as a promising material for the nuclear dynamic polarization of $^3$He.

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Abstract. We suggest using insulating Van Vleck paramagnet PrF$_3$ as a solid substrate for the dynamic polarization of $^3$He nuclei at high magnetic fields. The exploring of solid effect for this purpose assumes the knowledge of the optimal conditions for transfer of polarization from the Pr$^{3+}$ electron shell in PrF$_3$ to $^{141}$Pr nuclear spins as well as the existence of effective channel for magnetization transfer from $^{141}$Pr nuclear spins to nuclear spins of liquid $^3$He (so-called magnetic coupling phenomenon). To study solid effect in PrF$_3$ the magnetic field dependencies of the Stark energy levels of $^3$H$_4$ ground state multiple were calculated for high magnetic fields up to 40 T using the set of crystal-field parameters obtained early from magnetization measurements and exchange charges model. Also the results of searching for a direct magnetic coupling between nuclei of the liquid $^3$He and $^{141}$Pr nuclei in the system "PrF$_3$ powder - liquid $^3$He" by pulse NMR method are represented. Also the surface effects in the PrF$_3$ crystal were studied by SQUID and optical microscopy measurements. Other aspects of the nuclear polarization transfer are discussed.

1. Introduction

The obtaining the high-polarized state for liquid (or gaseous) $^3$He nuclear spin system is of interest for fundamental physics as well as for the promising applications of hyperpolarized gaseous $^3$He in medicine and biology [1, 2]. However the methods used now to polarize liquid $^3$He demand very low temperatures about few mK and high-magnetic fields (so-called ”brute-force” method [3, 4]), or possess a rather low productivity (optical pumping method [5]). As an alternative way to get the spin-polarized state of nuclear spins in liquid $^3$He the dynamic nuclear polarization methods [6] can be considered. One of them, the ”solid-effect” method, is based on the transfer of polarization from impurity paramagnetic centers to nuclear spin system. To use insulating Van Vleck paramagnets for dynamic polarization of liquid $^3$He was proposed in Refs. [7, 8]. In this case the Van Vleck ions are at the sites of a regular crystal lattice and act as paramagnetic centers in the transfer of polarization to nuclear spins of Van Vleck ions or diamagnetic atoms. The polarization of nuclei of host Van Vleck ions can be transferred to nuclear spins of liquid $^3$He being in the contact with solid substrate by means of resonant magnetic coupling since the effective gyromagnetic ratio of the nuclei of Van Vleck ions depends on orientation of applied magnetic field and a cross-relaxation might occur in certain orientation. The detailed investigations of magnetic properties of insulating Van Vleck paramagnets thulium ethylsulphate (TmES) [9, 10] and LiTmF$_4$ [10, 11] have eliminated the exceptional importance of
solid state surface quality and the existence of surface paramagnetic centers preventing effective magnetization transfer from Van Vleck ions to liquid $^3$He nuclear spins. In the present work we propose to use insulating Van Vleck paramagnet PrF$_3$ as possible solid substrate to polarize liquid $^3$He.

2. PrF$_3$ electron-nuclear system

As the first step to verify the possibility for dynamic nuclear polarization one should investigate the polarization transfer to the nuclei of the host Van Vleck ions. In a PrF$_3$ single crystal the ground multiplet $^3H_4$ of Pr$^{3+}$ $(4f^2)$ ion is split by electric crystal field into nine singlets, the ground singlet is separated from the first excited level by energy interval $\Delta \sim 65 \text{ cm}^{-1}$ [12]. The nuclear spins $^{141}$Pr are effective coupled to the Pr$^{3+}$ electron shell by a hyperfine interaction. But the static nature of the hyperfine interaction doesn’t allow to transfer a high spin polarization of electron shell to nuclear spins and the electron shell must be put into excited state (or it must be "depolarized"). During relaxation from this excited state the part of the electron polarization will be transferred to the nuclear spin system through a hyperfine interaction.

We have calculated the magnetic field dependence of the Stark levels for the ground multiplet $^3H_4$ of Pr$^{3+}$ ion in external magnetic field up to 40 T. In these calculations the crystal field parameters obtained by us early [13] in the framework of exchange charges model were used. Note that unlike the parameters proposed early this set of the crystal field parameters lead to a rather good agreement of the calculated Stark structure with experimental data [14] for the ground multiplet of Pr$^{3+}$ ion as well as for the excited multiplets [13].

The field dependence of the ground energy level and two nearest excited energy levels of Pr$^{3+}$ ion ground multiplet is shown in Figure 1. Because of a rather big energy distance between ground energy level and these excited levels only far-infrared laser emission [15] must be used to excite the electron shell of Pr$^{3+}$ ion. The application of high magnetic fields is crucial in this case - the variation of magnetic field allows to make the energy distance between the ground level and the excited level equal to some laser output line. The successful observation of high-frequency EPR of Van Vleck ion Tm$^{3+}$ in TmES [16] due to the transitions between non-magnetic ground singlet and the nearest excited states with energy distance $\sim 32 \text{ cm}^{-1}$ should be mentioned here. Also it is believed that ballistic pulses [17] could be used to excite Pr$^{3+}$ electron shell.

3. Cross-relaxation between PrF$_3$ and liquid $^3$He.

For polarization transfer to liquid $^3$He the resonant magnetic coupling between nuclear spins $^3$He ($I = \frac{1}{2}$) and $^{141}$Pr ($I = \frac{5}{2}$) must occur in the system $^3$liquid $^3$He - solid PrF$_3$. The nuclear spin Hamiltonian for $^{141}$Pr in PrF$_3$ reads as follows for moderate magnetic fields[18]:

$$H = -\hbar \sum_{\alpha=x,y,z} \gamma_\alpha H_\alpha I_\alpha + D \left[I_z^2 - \frac{1}{3} I(I + 1)\right] + E(I_x^2 - I_y^2),$$

where $\gamma_x/2\pi = 3.32 \text{ kHz/Oe}$, $\gamma_y/2\pi = 3.24 \text{ kHz/Oe}$, $\gamma_z/2\pi = 10.03 \text{ kHz/Oe}$, $D/\hbar = -4.31 \text{ MHz}$, $E/\hbar = -0.30 \text{ MHz}$. The cross-relaxation between $^{141}$Pr and $^3$He nuclear spins ($\gamma/2\pi = 3.243 \text{ kHz/Oe}$) is possible because of dependence of energy splittings on the magnetic field direction. Such cross-relaxation coupling has been found between $^{169}$Tm and $^3$He nuclear spins in the system "$^3$TmES crystal - liquid $^3$He" [9].

To increase the efficiency of polarization transfer through the boundary "solid substrate - liquid $^3$He" the powders of solids should be used. In Figure 2 two acquired at different excitation conditions pulse NMR spectra for the system "PrF$_3$ powder - liquid $^3$He" are represented. The simulated powder NMR spectrum is also shown. The simulation is integral probability of transitions averaged over all the powder particles. It has been done by use of the method developed in [19] and the Hamiltonian(1).
Figure 1. The field dependence of the ground energy level and two nearest excited energy levels of Pr$^{3+}$ ion ground multiplet in PrF$_3$ single crystal. External magnetic field is applied parallel to c-axis of a crystal.

In the previous investigations of magnetic coupling in the system "LiTmF$_4$ powder - liquid $^3$He" the existence of defect paramagnetic centers on the powder particle surface has been found [20]. These centers located in the nanocracks on powder particle surface create strongly fluctuating magnetic fields which lead to a spread of Larmor frequencies of $^3$He nuclear spins just near particle surface and to a breaking of magnetic coupling. In Ref. [21] the correlation between the appearance of nanocracks on crystal surface and the existence of cleavage plane for the given crystal has been found. It is expected that in PrF$_3$ having the cleavage plane ac the surface mechanical tensions should be resolved by the cleavage along this plane. Consequently the number of defect paramagnetic centers on crystal surface of PrF$_3$ is a rather small. The evidence for that one can get from magnetic susceptibility measurements for the fine-dispersed powders of PrF$_3$ in magnetic field 10 Gauss (see Figure 3). Unlike to LiTmF$_4$ powders [20] the present measurements do not demonstrate an additional paramagnetic contribution to the magnetic susceptibility.

Figure 2. Two pulse NMR spectra acquired at different excitation conditions and the simulated spectrum for the system "PrF$_3$ powder - liquid $^3$He". The particle size of PrF$_3$ powder is less than 1 μm; the temperature, NMR frequency and pulse sequence are also shown.

Figure 3. The temperature dependence of magnetic susceptibility for PrF$_3$ fine-dispersed powders with different average particle size.
4. Conclusion
The insulating Van Vleck paramagnet PrF\(_3\) is believed to be a promising solid substrate for the dynamic nuclear polarization of liquid \(^3\)He. Our preliminary investigations of the nuclear longitudinal spin-lattice relaxation of liquid \(^3\)He being in the contact with the fine-dispersed powder of PrF\(_3\) and with the fine-dispersed powder of its diamagnetic analogue LaF\(_3\) at \(T = 1.5\) K are supported this prediction. In the case of LaF\(_3\) powder the recovering of \(^3\)He longitudinal magnetization is well described by exponential curve \(\exp(-\frac{w_1 t}{T_1})\) with relaxation rate \(w_1 = \frac{1}{T_1} = 12.20(13)\) sec\(^{-1}\) and \(N = 1\) while in the case of PrF\(_3\) the parameters of relaxation were changed to \(w_1 = \frac{1}{T_1} = 14.49(26)\) sec\(^{-1}\) and \(N = 0.75(2)\). The stretched exponent in the last case with \(N < 1\) might be the evidence for some distribution of liquid \(^3\)He longitudinal relaxation rates in the system "liquid \(^3\)He - solid PrF\(_3\)" because of the existence of magnetic coupling between two nuclear systems.

We should underline the importance of high magnetic field usage for the excitation of Pr\(^{3+}\) electron shell. The high magnetic fields also reduce the loss of electron polarization due to the fluctuating magnetic field created by paramagnetic impurities (Er\(^{3+}\), Yb\(^{3+}\), Nd\(^{3+}\) etc.) in trifluorides of rare-earth ions.

One should take into account the existence of the coupled electron-nuclear states of Van Vleck ion in high magnetic fields [8, 22]. Because of very strong mixing of electron and nuclear states it is more correct to consider the polarization of the Van Vleck ions instead of polarization of nuclear spin system.

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