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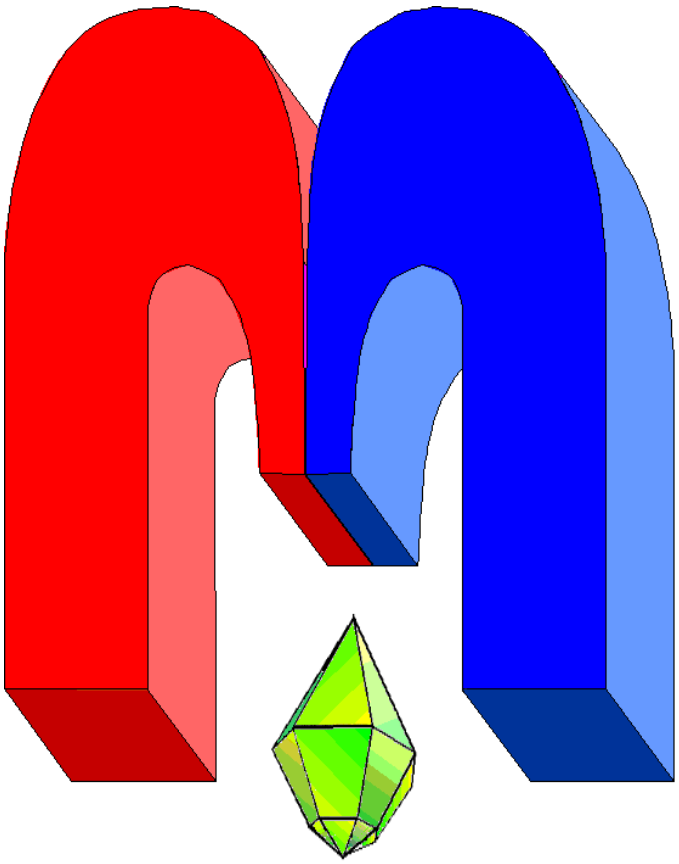

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Anomalous ^{141}Pr nuclear magnetic relaxation in PrF_3 Van Vleck paramagnet†

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The magnetic nuclear spin-lattice relaxation has been studied in PrF_3. It was found that ^{141}Pr spin-lattice relaxation rate is untypically high for the Van Vleck insulator. According to all existing experimental data the only relaxation channel for enhanced nuclear moments at low temperatures is interaction with paramagnetic impurities and typical nuclear relaxation rate in rare earth Van Vleck paramagnets at liquid helium temperatures is 1 s^{-1}. The measured value is 100 s^{-1}. At the assumption that relaxation is caused by the strong 4f-4f cooperative interaction mediated by phonons [1], we measured ^{141}Pr relaxation rates in a number of $Pr_xLa_{1-x}F_3$ samples and found that in diluted samples relaxation slows down to the usual for insulators values.

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1. Introduction

The properties of insulating rare earth Van Vleck paramagnets including spectral and relaxation parameters are most fully described in [2]. Hamiltonian of the rare earth ion with non-zero nuclear spin in crystals includes a number of terms

$$H = H_{\text{cef}} + g_J \beta \mathbf{HJ} + a_J \mathbf{JI} - \gamma_I \hbar \mathbf{HI} + H_Q , \tag{1}$$

where the first term describes the interaction with the crystal electric field, the second is electron Zeeman interaction Hamiltonian, the third corresponds to hyperfine interaction, the fourth is nuclear Zeeman Hamiltonian, the last is nuclear quadrupole interaction term, g_J is Lande factor, β is Bohr magneton, a_J is hyperfine interaction constant, **J** is total electron moment operator, **I** is nuclear spin operator, γ_I is nuclear gyromagnetic ratio, $\hbar$ is Planck constant, **H** is magnetic field. Such an approach sometimes is called single ion model or static model, since no 4f-4f or electron-phonon interaction is taken in account. In case of non-Kramers ions ground state can be a singlet. In this case the system of such ions is called Van Vleck paramagnet. At the temperatures satisfying condition $kT \ll \Delta$, where Δ is the energy of the nearest excited state, temperature independent magnetic (Van Vleck) susceptibility is observed. The nuclear magnetic resonance of Van Vleck ions nuclei is not observed at high temperatures due to the broadening caused by hyperfine interaction. At low temperatures this interaction leads to phenomenon known as enhanced nuclear magnetic resonance. Hyperfine interaction leads to enhancement of nuclear magnetic moments. The effective Hamiltonian, including only nuclear spin operators has the following form

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

where γ_α are the components of the effective gyromagnetic ratio. Usually the effective nuclear moments are highly anisotropic. The last terms are similar to the nuclear quadrupole Hamiltonian and

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predict the splitting of the energy levels in the absence of external magnetic field. Actually, they are completely defined by hyperfine interaction and do not depend on nuclear quadrupole moment. Therefore, this special interaction is called pseudoquadrupole. The parameters of the effective nuclear Hamiltonian can be calculated using second order perturbation theory:

$$\gamma_\alpha = \gamma_I + 2g_J\beta\Lambda_\alpha/\hbar, \quad \Lambda_\alpha = a_J\sum_n \frac{\left|\langle g|\mathbf{J}_\alpha|n\rangle\right|^2}{E_n - E_g}, \quad D = a_J\left(\frac{\Lambda_x+\Lambda_y}{2}-\Lambda_z\right), \quad E = a_J\left(\frac{\Lambda_y-\Lambda_x}{2}\right), \quad (3)$$

where E_g is the energy of the ground singlet, $|n\rangle$ are eigen functions of H_{cef} Hamiltonian. The very last analysis of the crystal electric field parameters in PrF_3 was performed for the full $4f^2$ configuration (91 states) [3].

The crystal structure of PrF_3 and isomorphous to it LaF_3, CeF_3 and NdF_3 compounds has a space group D_{3d}^4 ($P\bar{3}c1$) [4, 5]. The rare earth site symmetry is C_2. The ground multiplet $^3H_4$ of the Pr^{3+} non-Kramers ($4f^2$-configuration) in crystal electric field (CEF) of low symmetry splits into 9 singlets. The set of CEF parameters for REF_3 crystals based on comparison with experimental data was proposed in [6]. The ^{141}Pr isotope has 100% natural abundance, spin $I = 5/2$, and gyromagnetic ratio $\gamma_I/2\pi = 12.1$ MHz/T. The ^{141}Pr NMR spectra are well described by Hamiltonian (2) with the following parameters $D/h = 4.31(1)$ MHz, $E/h = 0.30(1)$ MHz, $\gamma_x/2\pi = 33.2(2)$ MHz/T, $\gamma_y/2\pi =$ 32.4(2) MHz/T, $\gamma_z/2\pi = 100.3(2)$ MHz/T [7, 8]. In zero magnetic field nuclear energy levels are split into three doublets. There are two allowed transitions with a frequencies of 9.063(3) MHz and 17.083 MHz [9]. Effective nuclear Hamiltonian parameters for the diluted system Pr:LaF_3 were also obtained using rf-optical double resonance technique $D/h = 4.185(1)$ MHz, $E/h = 0.146(1)$ MHz, $\gamma_x/2\pi = 49.8(4)$ MHz/T, $\gamma_y/2\pi = 25.3(3)$ MHz/T, $\gamma_z/2\pi = 101.6(3)$ MHz/T. The frequencies of the transition are 8.5 MHz and 16.7 MHz [10]. Magnetic relaxation in such multilevel system is not exponential. The solution of kinetic equations for nuclear quadrupole resonance in case of $I = 5/2$ and $\eta \neq 0$ can be used for ^{141}Pr pseudoquadrupole resonance [11]. In this case magnetization recovery function contains two weighted exponents. The weights are different for different transitions and depend on asymmetry parameter. The equivalent asymmetry parameters for the Hamiltonian (2) $\eta = 3E/D$ are 0.21 for PrF_3, and 0.1 for Pr:LaF_3.

Nuclear spin-lattice relaxation in insulating Van Vleck compounds at low temperatures has the same nature as in diamagnetic insulators i.e. via paramagnetic centers which are always present in small amount in all rare earth compounds. Van Vleck paramagnets having effective magnetic moments intermediate between nuclear and electronic were used for adiabatic cooling as it was proposed in [12]. Insulators were never used for that purpose since spin-lattice relaxation is very slow. Intermetallic compounds such as $PrCu_6$ were successfully used for that purpose since they have additional Korringa relaxation channel [13]. At higher temperatures the nuclear relaxation is driven by thermally excited states of 4f-ions and the temperature dependence of relaxation rate has a factor $\exp(-\Delta/kT)$. ^{141}Pr spin-lattice relaxation in PrF_3 is anomalously fast at low temperatures. We measured $T_1 = 5$ ms for $\pm 1/2 \leftrightarrow \pm 3/2$ transition in a number of PrF_3 powders at 4.2 K [9], and 7 ms for ^{141}Pr NMR in PrF_3 powder at the frequency of 6.65 MHz at 1.5 K [14].

2. Experimental

A number of single crystals $Pr_xLa_{1-x}F_3$ ($x = 1$, 0.2, 0.1, 0.05, 0.01) were grown using Bridgman-Stockbarger method. ESR measurements have shown that total content of paramagnetic impurities (Er^{3+}, Dy^{3+}, Nd^{3+}, Gd^{3+}) never exceeds 0.01% of the host rare earth ion. We used home-built NMR/NQR pulse spectrometer. All the measurements were provided using nuclear spin-echo technique. The three pulse sequence was used for the measurements of longitudinal nuclear

magnetization recovery: $\pi/2-t-\pi/2-\tau-\pi$. The first saturating pulse is followed by two pulses producing Hahn echo. In case of uniform (single exponent) relaxation of the nuclear magnetization the data should be fitted by the function $S(t)=S(\infty)\left[1-\exp(-t/T_1)\right]$, where $S(\infty)$ is the intensity of unsaturated echo, and T_1 is relaxation time. The energy levels of ^{141}Pr $(I=5/2)$ in all the samples under the study are the three doublets and the recovery curves contain two exponents. Their weights depend on transition: $\pm1/2\leftrightarrow\pm3/2$ or $\pm3/2\leftrightarrow\pm5/2$ and asymmetry of pseudoqudrupole interaction. In order to follow the changes in recovery curves we used the function $S(t)=S(\infty)\left[1-\exp\left(-t/T_1\right)^N\right]$, $N\leq1$. In this case T_1 equals to the time at which magnetization recovers to $S(\infty)(1-e)$ value.

The temperature dependence of ^{141}Pr spin-lattice relaxation in PrF_3 for two pseudoquadrupole frequencies have been measured (Fig. 1). At low temperatures relaxation rate is unusually fast and displays no temperature dependence. At higher temperatures the relaxation is caused by hyperfine field fluctuations caused by thermal excitations of 4f-ion. Therefore experimental data have been fitted by the following function $T_1^{-1}=A+B\exp(-\Delta/kT)$. We obtained $A=220(10)$ s^{-1}, $\Delta=96(3)$ cm^{-1}, and $A=362(16)$ s^{-1}, $\Delta=79(6)$ cm^{-1} at high and low frequencies respectively. The frequencies of the pseudoquadrupole transitions become slightly smaller with the temperature increase. We followed these changes and all the measurements were done at the maximal signal intensity.

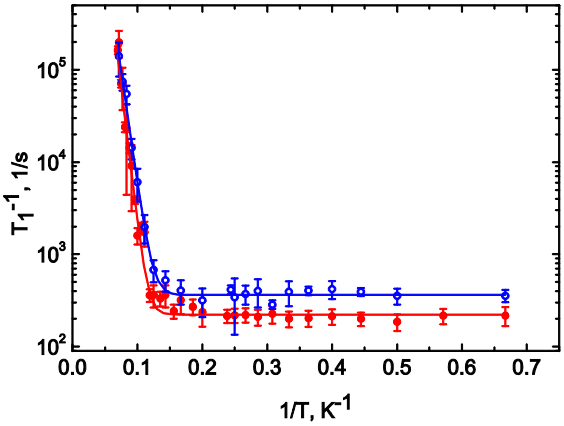

Figure 1. ^{141}Pr nuclei spin-lattice relaxation rate dependence on inverse temperature in PrF_3. Open blue circles correspond to the frequency of 9.06 MHz at 4.2 K, filled red circles present the values obtained at 7.08 MHz, solid lines are fitting curves.

In order to clarify the origin of the fast relaxation at low temperature we measured ^{141}Pr spin-lattice relaxation times, as well as spectroscopic characteristics in the set of $Pr_xLa_{1-x}F_3$ single crystals at the temperature of 4.2 K (Table 1). All the measurements were done at the higher frequency ^{141}Pr pseudoquadrupole transition. This frequency systematically changes from 17.08 MHz in PrF_3 to 16.7 MHz in diluted Pr:LaF_3 compound, reflecting the changes in crystal electric field. The line width has the smallest values in the samples with a highest and lowest Pr content, i.e. having the most ordered crystal structure. Spin-spin relaxation time (T_2) increases by a factor of 2, indicating the increasing of the mean distance between the ^{141}Pr nuclei and reduction of this contribution into spin-spin relaxation. The most striking changes occur with a spin-lattice relaxation constant, which value increased by a factor 120 with the x decrease from 1.0 to 0.05. This fact supports the hypothesis that

Table 1. x denotes Pr content in $Pr_xLa_{1-x}F_3$ crystals, ν is the frequency of the pseudoquadrupole resonance transition, $\delta\nu$ is the line width, T_1 is spin-lattice relaxation time, T_2 is spin-spin relaxation time.

x	ν, MHz	$\delta\nu$, MHz	T_1, s	T_2, mks
1.0	17.08(1)	0.134	0.010(1)	10.5(2)
0.2	16.53(2)	0.88	0.21(4)	14.0(6)
0.1	16.50(2)	0.48(4)	0.70(8)	16.3(4)
0.05	16.55(2)	0.28(2)	1.2(2)	18.6(2)
0.01	16.6(1)	0.11(1)	–	–

^{141}Pr spin-lattice relaxation in PrF_3 is driven by some cooperative 4f-4f electron excitations. ^{141}Pr spin-lattice relaxation rate dependence on temperature in $Pr_{0.05}La_{0.95}F_3$ is presented on Fig. 2. The Δ parameter value was estimated to be 55(3) cm^{-1}.

We also studied the form of ^{141}Pr magnetization recovery curves in PrF_3 and $Pr_{0.05}La_{0.95}F_3$ samples at the temperatures of 4.2 K and 7 K. The data is presented at Fig. 3. The stretched exponent $\exp\left[-\left(t/T_1\right)^N\right]$ was used in order to follow the changes of non-exponent relaxation. In case of PrF_3 parameter N does not change within the precision of fitting procedure: $N(7\text{ K}) = 0.34(4)$, and $N(4.2\text{ K}) = 0.39(2)$, approving that the spectral density of magnetic fluctuations is the same for all the nuclei at both temperatures. The most diluted sample under the study $Pr_{0.05}La_{0.95}F_3$ displays at lower temperature smaller N value: $N(7\text{ K}) = 0.78(3)$, and $N(4.2\text{ K}) = 0.59(2)$. This fact indicated that relaxation at lower temperature has a different origin and ^{141}Pr nuclei relax via paramagnetic impurities.

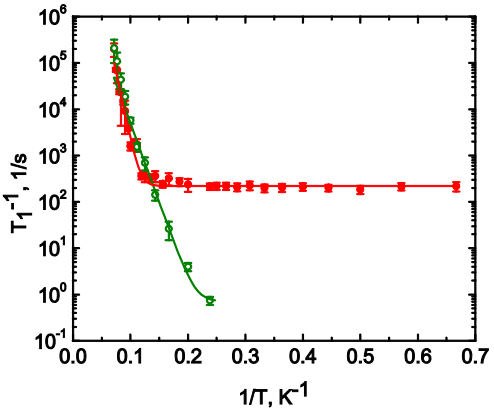

Figure 2. ^{141}Pr nuclei spin-lattice relaxation rate in PrF_3 (filled red circles), and $Pr_{0.05}La_{0.95}F_3$ (open green circles). The solid lines are fitting curves.

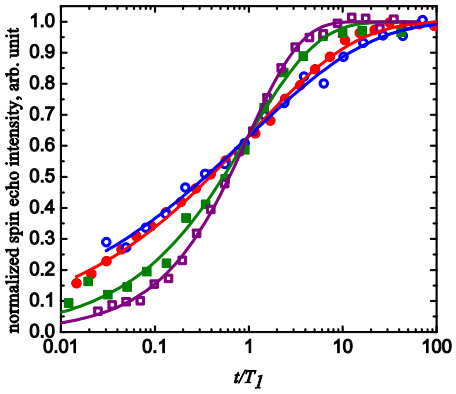

Figure 3. Normalized and scaled over T_1 ^{141}Pr longitudinal magnetization recovery curves. The fitting functions are plotted as solid lines. Filled red circles correspond to PrF_3, $T = 4.2$ K, fitting parameter $N = 0.39(2)$. Open blue circles: PrF_3, $T = 7$ K, $N = 0.34(4)$. Filled green squares: $Pr_{0.05}La_{0.95}F_3$, $T = 4.2$ K, $N = 0.59(5)$. Open purple squares: $Pr_{0.05}La_{0.95}F_3$, $T = 7$ K, $N = 0.78(3)$.

3. Discussion

Our data on ^{141}Pr nuclear spin-lattice relaxation in $Pr_xLa_{1-x}F_3$ single crystals at the temperatures when the population of excited Pr^{3+} singlets becomes substantial obeys the following law $T_1^{-1} = \sum_{i=1}^{8} a_i \exp\left(-\Delta_i / kT\right)$, where Δ_i are the energies of excited levels, the relative values of factors a_i are determined by the wave functions of the electron states [15]. It is hardly possible to determine contribution of each level from the relaxation data. Instead of it, one can fit the data using single exponent process, and the parameter Δ obtained from the fitting procedure should not be smaller than the energy of the lowest excited level. Three closest to the ground Pr^{3+} levels in PrF_3 have the energies of 60, 69, and 134 cm^{-1} [6]. We obtained 96 and 79 cm^{-1} for the high and low frequency ^{141}Pr transitions. The closest to the ground Pr^{3+} levels in Pr:LaF_3 have the energies of 57, 76, and 136 cm^{-1} [16]. The fitting of the data in $Pr_{0.05}La_{0.95}F_3$ sample gave the value of 55(3) cm^{-1}. This facts support the validity of the proposed model of ^{141}Pr relaxation at higher temperatures.

Let us turn to the low temperature region. There is a number of arguments that ^{141}Pr relaxation in Van-Vleck paramagnet PrF_3 cannot be explained by interaction with paramagnetic impurities. a) The relaxation rates are anomalously high. b) These rates are reproduced with high precision for the samples grown using very different starting chemical compounds. We measured the relaxation rate in the sample originally used for acoustic magnetic resonance in 1979 [8] and obtained the same values as for our crystals. c) ^{141}Pr relaxation time in highly diluted Pr:LaF_3 sample at the temperature of 2 K is about 1 s [10] i.e. 200 times longer than our data on PrF_3.

The extensive studies of PrF_3 crystals using Raman and infrared spectroscopy have been provided by M. Dahl et al. and outlined in [1]. Collective magnetic moments and Davydow splitting were observed. The total number of lines in exciton spectrum appeared to be 16 instead of 8. M. Dahl explains it by Davydow splitting. These effects result from Jahn-Teller type coupling of the 4f- and the phonon systems. The identification of the pure phonon and 4f-excitations (excitons) was provided using the studies of a mixed crystals $La_xPr_{1-x}F_3$. The electronic excitations gain intensity in PrF_3 while phonons can be traced from LaF_3 to PrF_3. Our studies show that the ^{141}Pr nuclear relaxation in PrF_3 is driven by the hyperfine field fluctuations caused by 4f-excitations.

The possible explanation of ^{141}Pr nuclear relaxation anomalous temperature dependence possibly can be explained by the narrowing of the lines in exciton spectrum with a temperature decrease, observed by the same authors [1].

4. Conclusion

The analysis of our experimental data supports the idea that ^{141}Pr nuclear magnetic relaxation in insulating Van Vleck paramagnet PrF_3 is governed by a strong phonon mediated 4f-4f excitations.

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