

Nuclear magnetic relaxation of liquid ^3He in the pores of oriented LiTmF_4 powder

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(Submitted 10 November 1989)

Zh. Eksp. Teor. Fiz. **97** 1175–1187 (April 1990)

The relaxation of the longitudinal and transverse nuclear magnetization of liquid ^3He in the pores of magnetically oriented powder of the Van Vleck paramagnetic LiTmF_4 (the particle size ranged from tenths of a micron up to $57\ \mu\text{m}$) at temperatures of $0.075\text{--}1.5\ \text{K}$ was studied by the method of pulsed NMR at frequencies ranging from 4 to 16 MHz. It was found that the diffusion of helium atoms in the strong nonuniform field generated by the magnetized particles of the crystalline powder play an important role in the relaxation of the transverse nuclear magnetization of ^3He . At 1.5 K in a field oriented along the direction of maximum magnetization of the LiTmF_4 powder the nuclear relaxation times T_1 and T_2 of ^3He , measured at the frequency $\nu_{\text{He}} = 8\ \text{MHz}$, are greater than 500 and 0.3 ms, respectively, while in a field oriented along the direction of minimum magnetization of the powder they decrease approximately to 14 and 0.012 ms. The acceleration of the relaxation of ^3He nuclei in the latter case is connected with the participation of the nuclear spins of ^{169}Tm , whose Larmor frequencies are close to ν_{He} , in the process of transfer of the magnetization of helium.

1. INTRODUCTION

The question of the nature of the relationship between the nuclear magnetic moments of liquid ^3He and the dipole magnetic moments in the solid bounding the helium arose more than 20 years ago¹ and has still not been adequately studied. There are very few reliable experimental results illustrating the striking effects of the magnetic coupling between the solid and ^3He . Thus far essentially only one system has been studied — a system with ^{19}F nuclei in finely dispersed ($0.2\ \mu\text{m}$) powder of DLX-6000 polytetrafluoroethylene.^{2–9} Progress in the study of the magnetic coupling of the nuclei of liquid ^3He and nuclei in solids requires, first of all, the accumulation of facts in experiments with different samples of solids. These samples must satisfy three requirements: they must be chemically stable, they must have an extended surface, and they must contain nuclei whose gyromagnetic ratios are as close as possible to the gyromagnetic ratio of ^3He nuclei. In this paper we propose a new type of partner-sample for ^3He , namely, oriented finely dispersed powders of Van Vleck paramagnetics, and we present the results of the first experiments on NMR of liquid ^3He in the pores of such a sample of LiTmF_4 .

2. INFORMATION ABOUT THE CRYSTAL

The LiTmF_4 crystal has the structure of scheelite (CaWO_4). In a crystal electric field with S_4 symmetry the ground state multiplet 3H_6 ($J = 6$) of the Tm^{3+} ion is split into seven singlets and three doublets, and the lowest Stark level is a singlet while the closest excited state lies $32\ \text{cm}^{-1}$ higher (48 K). At liquid-helium temperature the paramagnetic susceptibility of the crystal is independent of the temperature ("Van Vleck susceptibility"), and the maximum values of the components of the susceptibility parallel and perpendicular to the tetragonal axis \mathbf{c} differ by a factor of 39 (Ref. 10):

$$\chi_{\parallel}^0 = 0.010\ \text{cm}^3/\text{mole}, \quad \chi_{\perp}^0 = 0.392\ \text{cm}^3/\text{mole}. \quad (1)$$

At room temperature the anisotropy of the paramagnetic

susceptibility is appreciably smoothed. A calculation using the wave functions from Ref. 11 gives

$$\begin{aligned} \chi_{\parallel}^{300\ \text{K}} &= 0.0158\ \text{cm}^3/\text{mole}, & \chi_{\perp}^{300\ \text{K}} &= 0.0291\ \text{cm}^3/\text{mole}, \\ \chi_{\perp}^{300\ \text{K}} / \chi_{\parallel}^{300\ \text{K}} &= 1.84. \end{aligned} \quad (2)$$

Our measurements using the KLY-1 apparatus (produced in Czechoslovakia) gave for this ratio at room temperature the value 1.91.

Because the electronic $4f$ shell of the Tm^{3+} ion intensifies the external magnetic field the "hyperfine" field at the ^{169}Tm nucleus (the spin $I = 1/2$ and the natural abundance is 100%), like the paramagnetic susceptibility, is strongly anisotropic, so that at low temperatures ($T < 4\ \text{K}$) the NMR of ^{169}Tm is described by the spin Hamiltonian

$$\mathcal{H}_I = -\gamma_{\perp} \hbar (H_x I_x + H_y I_y) - \gamma_{\parallel} \hbar H_z I_z \quad (3)$$

with parameters differing by a factor of 25 (Ref. 10):

$$|\gamma_{\parallel}/2\pi| = 0.965\ \text{kHz/Oe}, \quad |\gamma_{\perp}/2\pi| = 24.11\ \text{kHz/Oe}. \quad (4)$$

The LiTmF_4 crystal is interesting to study in experiments with ^3He because at a certain orientation of this crystal in a magnetic field (the angle ϑ between the \mathbf{c} axis of the crystal and the field \mathbf{H}_0 is equal to 7.4°) the effective gyromagnetic ratio of ^{169}Tm nuclei

$$\gamma(\vartheta) = (\gamma_{\parallel}^2 \cos^2 \vartheta + \gamma_{\perp}^2 \sin^2 \vartheta)^{1/2}$$

is equal to the gyromagnetic ratio of ^3He nuclei ($\gamma = 2\pi \times 3241\ \text{s}^{-1} \times \text{Oe}^{-1}$), as a result of which cross-relaxational coupling of ^{169}Tm and ^3He nuclei is possible through the boundary of the crystal with the liquid helium.¹² The crystal contains, in addition to thulium nuclei, ^{19}F nuclei ($I = 1/2$, $\gamma = 2\pi \times 4007\ \text{s}^{-1} \times \text{Oe}^{-1}$) and ^7Li nuclei ($I = 3/2$, $\gamma = 2\pi \times 1655\ \text{s}^{-1} \times \text{Oe}^{-1}$).

LiTmF_4 crystals exhibit giant magnetostriction in a strong field perpendicular to the \mathbf{c} axis.¹³ The magnetostriction effect is observed in experiments on pulsed NMR in the form of high-frequency magnetoacoustic oscillations

("ringing") of the sample after it is irradiated with an rf field in the presence of a constant external field.¹⁴ In pressed powder the ringing effect is suppressed. An attempt to cool liquid ³He by means of adiabatic demagnetization of LiTmF₄ powder immersed in it was unsuccessful;¹⁵ this lack of success could have been due to magnetostrictional heating of the sample.

3. PREPARATION OF THE SAMPLES

In the experiments described below we employed four samples—LiTmF₄ powders consisting of particles of size < 57 μm (I), < 20 μm (II), 2–4 μm (III), and < 1 μm (IV). After pulverization in an agate mortar and sifting through an appropriately sized sieve sample I was poured into a cylindrical mold made of beryllium bronze. The mold was placed in a constant 15 kOe magnetic field and slowly turned in it (at a rate of 2 rpm); as a result of this, the crystallographic *c* axes of separate particles were aligned predominantly along the rotational axis *c'*, i.e., perpendicularly to the magnetic field. The mold was then pressed with the help of a hydraulic press, so that the pressure in the sample reached 200 MPa. Pressing partially reduced the degree of orientation of the powder, but it made it possible to set the orientation. The 6 mm in diameter and 8.5 mm high cylindrical tablet obtained in this manner (the filling factor was equal to 0.72) was placed in a container made of Stycast 1266 epoxy resin. One or two stainless steel capillaries 0.6 mm in diameter, along which the ³He was introduced, were glued into the container. The sample took up the entire interior volume of the container, and the liquid could be contained only in the pores of the powder.

Sample II was prepared by a similar method, except that, in order to make it easier to orient the finely dispersed powder, the mold was filled with ethyl alcohol. Measurements of the susceptibility at room temperature gave the value $\chi_i^{300K}/\chi_i^{300K} = 1.37$; the indices *l* and *t* denote, here and below, the orientation of the magnetic field parallel and transverse to the *c'* axis of the sample.

Sample III was prepared in the same manner as the sample II. The preliminary separation of the fraction with particle sizes ranging from 2 to 4 μm was made based on the rate of settling of the powders suspended in anhydrous ethyl alcohol; the particle sizes were monitored with the help of an optical microscope. As the particle size decreases the binding force between the particles, which sets their mutual orientation, increases. Using this fact, the sample IV, which consisted of submicron-size particles, was prepared without any additional pressing: orientation (in the mixture with alcohol) and subsequent drying of the sample were performed directly in the container, slowly rotating in a magnetic field.

In addition to the four paramagnetic samples, for monitoring purposes we also prepared sample V from LiYF₄ powder (the diamagnetic analog of LiTmF₄) with particle sizes not exceeding 57 μm. In the experiments ³He containing no more than 0.05% ⁴He as an impurity was employed.

4. EXPERIMENTAL APPARATUS AND PROCEDURE

The relaxation times of the ³He and ¹⁶⁹Tm nuclei as well as the shifts and inhomogeneous width of the NMR lines of ³He were measured in this work with the help of a wideband coherent pulsed NMR spectrometer. Because the NMR signals from ³He are weak, which is a result of the strong broad-

ening of the lines owing to the inhomogeneity of the magnetic fields in the pores of the magnetized powder, fast digital storage elements with a novel construction were employed in the experiments. Most of the experiments were performed at 1.5 K: the containers with the samples and rf frame coils, ensuring that the fields *H*₁ and *H*₀ are orthogonal for any orientation of the constant field, were placed directly in liquid ⁴He. Experiments at temperatures below 1.5 K were performed only with sample I; in these experiments the cell with the sample was cooled through a coolant duct consisting of 144 copper lines 0.08 mm in diameter, thermally coupled with the chamber of a ³He/⁴He dilution refrigerator.

In pulsed NMR experiments it is convenient to estimate the inhomogeneous linewidth Δ*ω* based on the width Δ*t* of the spin-echo signal. If the NMR line has a Gaussian shape, then the shape of the echo signal is also Gaussian and

$$\Delta\omega_{1/2} = \frac{2 \ln 2}{\Delta t_{1/2}}; \quad (5)$$

here the index 1/2 denotes the half-width of the corresponding curve at half-maximum. The decay time *T*₂^{*} of the transverse magnetization in a nonuniform field, which time is also measured as the half-width of the echo signal at the 1/*e* level, is related with the quantity Δ*t*_{1/2} by the factor (ln 2)^{-1/2}, while the second moment of the inhomogeneously broadened NMR line is equal to

$$M_2 = \frac{2}{T_2^{*2}} = \frac{2 \ln 2}{\Delta t_{1/2}^2}. \quad (6)$$

In this work the true relaxation time *T*₂ of the transverse magnetization was estimated from the decay of the amplitude of the spin echo *M*(2*τ*) as the interval *τ* between the probing π/2- and π-pulses was increased. In all experiments we were able to fit the decay curve with the expression

$$M(2\tau)/M(0) = \exp[-(2\tau/T_2)^n] \quad (7)$$

with appropriate values of *T*₂ and *n*.

The longitudinal relaxation time *T*₁ was estimated from the curve of restoration of the longitudinal magnetization after it was rotated by an rf field into a plane perpendicular to the constant external field. We employed the four-pulse method: π/2-*τ*-π-*t*-π/2-*τ*-π. In most cases the magnetization restoration curve could not be described by a single exponential function,

$$1 - M(t)/M(\infty) = \exp(-t/T_1), \quad (8)$$

and to compare the results of different experiments we took for *T*₁ simply the time of restoration of magnetization up to the level $1 - M(t)/M(\infty) = 1/e$.

5. NMR OF THULIUM

We were able to observe the spin echo of ¹⁶⁹Tm nuclei in all samples with the magnetic field oriented perpendicular to the *c'* axis. At a temperature of 1.5 K the maximum echo signal at 8 MHz was observed in a magnetic field corresponding to an effective gyromagnetic ratio of thulium nuclei |*γ*/2π| = 23.1 kHz/Oe. When the orientation of the magnetic field was changed in the direction toward the *c'* axis no appreciable shifts occur in the NMR line in strong fields, but the signal becomes weaker and is unobservable for angles between the field *H*₀ and *c'* axis less than 45°.

Measurements of the spin-lattice relaxation time *T*₁ of

thulium nuclei in three samples at a temperature of 1.5 K gave the following results: 1.25 s (I), 1.2 s (III), and 36 ms (IV). For comparison we point out that at the same frequency (8 MHz) the times T_1 for thulium in the crystal from which the samples I and II were prepared were equal to 0.65 s in the field $\mathbf{H}_0 \parallel \mathbf{c}$ and 1.0 s in the field $\mathbf{H}_0 \perp \mathbf{c}$. The relaxation times T_1 of ^{169}Tm nuclei at temperatures below 1.5 K were not measured, but the qualitative picture of the spin-lattice relaxation is known from preceding studies:¹⁶ in the presence of accompanying paramagnetic impurities (in thulium fluoride, which was used to synthesize LiTmF_4 , the total content of the rare-earth impurities exceeded 0.01% with respect to Tm^{3+} ions) the nuclear spin-lattice relaxation of ^{169}Tm proceeds with the participation of the dipole-dipole reservoir of impurity centers, and its rate is determined by the expression

$$1/T_1^{\text{Tm}} = B[1 - \text{th}^2(\delta/2kT)], \quad (9)$$

in which δ is the Zeemann splitting of the bottom energy levels of the impurity centers, while the parameter B is of the order of $1\text{--}100 \text{ s}^{-1}$. Measurements of the EPR spectra of rare-earth ions gave the following impurity composition in our samples (as a percentage with respect to Tm ions): I, II—Er (0.017), Tb (0.0005); IV—Nd (0.03), Gd (0.001), Er (0.0005); and, V—Er (0.027). It is obvious that the high content of Nd impurity in sample IV is responsible for the fast spin-lattice relaxation of thulium nuclei at $T = 1.5 \text{ K}$. The spin-spin relaxation time of thulium nuclei (T_2) in our samples is equal to about $4.5 \mu\text{s}$.

6. NMR OF HELIUM-3

1. Shift, inhomogeneous width, and intensity of the NMR line

The nuclear spins of ^3He in the space between the paramagnetic particles of the powder are exposed not only to a constant external field, but also to the fields generated by the particles. This results in screening of the external field: resonance of helium-3 in LiTmF_4 powder is observed at a fixed frequency in an external field stronger than in LiYF_4 powder. Thus in sample I at the frequency $\nu_{\text{He}} = 8 \text{ MHz}$ the shift ΔH was equal to 15 and 45 Oe, respectively, in the orientations $\mathbf{H}_0 \parallel \mathbf{c}'$ and $\mathbf{H}_0 \perp \mathbf{c}'$, while in sample II the corresponding shifts were equal to 15 and 47 Oe, respectively. The shift ΔH increases linearly with the field \mathbf{H}_0 , similarly to the magnetization of LiTmF_4 .

Another consequence of the magnetization of the particles is the extreme nonuniformity of the magnetic fields in

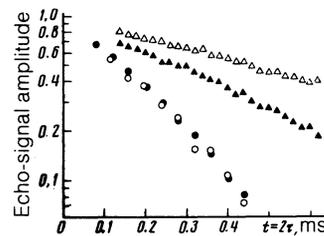


FIG. 1. The decrease of the transverse magnetization of ^3He nuclei in sample I at a temperature of 1.5 K: \blacktriangle — $\mathbf{H}_0 \parallel \mathbf{c}'$, $\nu = 8.0 \text{ MHz}$, $T_2 = 0.45 \pm 0.02 \text{ ms}$, $n = 1.27 \pm 0.05$; \triangle — $\mathbf{H}_0 \perp \mathbf{c}'$, $\nu = 8.0 \text{ MHz}$, $T_2 = 0.66 \pm 0.02 \text{ ms}$, $n = 1.02 \pm 0.05$; \bullet — $\mathbf{H}_0 \parallel \mathbf{c}'$, $\nu = 16.5 \text{ MHz}$, $T_2 = 0.22 \pm 0.01 \text{ ms}$, $n = 1.26 \pm 0.05$; \circ — $\mathbf{H}_0 \perp \mathbf{c}'$, $\nu = 16.5 \text{ MHz}$, $T_2 = 0.24 \pm 0.04 \text{ ms}$, $n = 1.38 \pm 0.23$.

the pores of the LiTmF_4 powder, so that the external field need not be nonuniform in order to observe the spin echo of ^3He nuclei. The nonuniformity of the internal field, just like the magnetization of the sample, increases linearly with the strength of the external field \mathbf{H}_0 , so that as the NMR frequency increases the linewidth also increases. Table I gives an idea of the characteristics of the inhomogeneously broadened NMR line of ^3He in samples I, III, and IV.

Measurements of the temperature dependence of the intensity of the NMR signal from ^3He (proportional to the paramagnetic susceptibility) made it possible for us to determine the magnetic Fermi temperature $T_f^{**} = 0.55 \text{ K}$, which is virtually identical to the value 0.54 K given in Ref. 5.

2. Relaxation of the transverse magnetization

We studied the relaxation of ^3He in sample I in the greatest detail. The basic results of these experiments are as follows.

a) The decay of the transverse magnetization is described by the expression (7), in which the value of the exponent n ranges from 1 to 3, depending on the conditions of the experiment. The typical decay curves are shown in Figs. 1 and 2. The typical values of T_2 lie in the interval from 0.2 to 0.7 ms. We note that such short (for ^3He) times T_2 are usually observed only in systems with very small channels and pores at ultralow temperatures. For example, in ZSM-5 zeolite with channels 5–6 Å in diameter at temperatures below 0.3 K we have $T_2 = 0.6 \text{ ms}$ (Ref. 17), while in Vycor glass with pores 17 Å in diameter $T_2 = 0.65 \text{ ms}$ at $T = 12 \text{ K}$ and $T_2 = 0.43 \text{ ms}$ at $T = 0.5 \text{ mK}$ (Ref. 18).

TABLE I. The half-width of the spin-echo signal ($\Delta t_{1/2}$), the half-width ($\Delta\omega_{1/2}/\gamma$), and the second moment (M_2) of the NMR line of ^3He in samples I, III, and IV at 1.5 K (the echo is a Gaussian).

Sample	ν_{He} , MHz	Orientation of H_0	$\Delta t_{1/2}$, μs	$\Delta\omega_{1/2}/\gamma$, Oe	M_2 , 10^{10} s^{-2}
I	8.0	$l(\mathbf{H}_0 \parallel \mathbf{c}')$	13.5	5.0	0.76
		$t(\mathbf{H}_0 \perp \mathbf{c}')$	6.5	11	3.3
III	8.5	l	7.5	9.1	2.5
		t	3.7	18	10
IV	8.0	l	17.0	4.0	0.48
		t	7.1	9.6	2.8
IV	8.0	l	2.6	26	20
		t	5.1	13	5.3

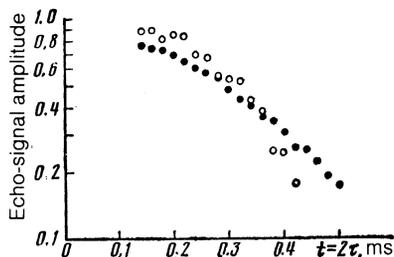


FIG. 2. The decrease of the transverse magnetization of ^3He nuclei in the superfluid solution 25% ^3He + 75% ^4He in the pores of sample I at a temperature of 1.5 K: ● — $\mathbf{H}_0 \parallel \mathbf{c}'$, $\nu = 11.1$ MHz, $T_2 = 0.39 \pm 0.02$ ms, $n = 1.85 \pm 0.09$; ○ — $\mathbf{H}_0 \perp \mathbf{c}'$, $\nu = 11.1$ MHz, $T_2 = 0.36 \pm 0.02$ ms, $n = 3.34 \pm 0.38$.

b) For both orientations of the sample in an external field ($\mathbf{H}_0 \parallel \mathbf{c}'$ and $\mathbf{H}_0 \perp \mathbf{c}'$) the relaxation times T_{2l} and T_{2t} decrease as the field increases (Fig. 2).

c) In a field of 4590 Oe ($\nu_{\text{He}} = 16$ MHz) T_{2l} is approximately equal to T_{2t} , while in a field of 2475 Oe ($\nu_{\text{He}} = 8$ MHz) T_{2l} is appreciably shorter than T_{2t} (Fig. 1).

d) In the superfluid solution 25% ^3He + 75% ^4He the exponent n increases (Fig. 2), and the decay of the transverse magnetization of ^3He in a field $\mathbf{H}_0 \perp \mathbf{c}'$ proceeds more rapidly than in a field $\mathbf{H}_0 \parallel \mathbf{c}'$.

e) Lowering the temperature of ^3He has a different effect on the time T_{2l} measured at frequencies of 8 and 16 MHz: T_{2l} ($\nu_{\text{He}} = 8$ MHz) decreases while T_{2l} (16 MHz) increases (Fig. 3).

The relaxation of the transverse magnetization of ^3He in samples III and IV was studied only at a temperature of 1.5 K. The measurements of T_2 in pure ^3He at $T = 1.5$ K in all three samples are summarized in Table II.

The extremely fast relaxation of ^3He in sample IV, consisting of submicronsize particles, in a magnetic field oriented parallel to the direction of minimum magnetization of the sample is interesting.

3. Relaxation of the transverse magnetization

As the experiments showed, the curve of restoration of the longitudinal magnetization in most cases cannot be described by one exponential function (8), so that for quantitative estimates and comparisons we introduce the quantity T'_1 — the time of restoration of magnetization up to the level 0.63 M (∞). The basic results of the observations are as follows.

a) The time T'_1 does not depend on the intensity of the external magnetic field (Fig. 4) and it is much longer in a

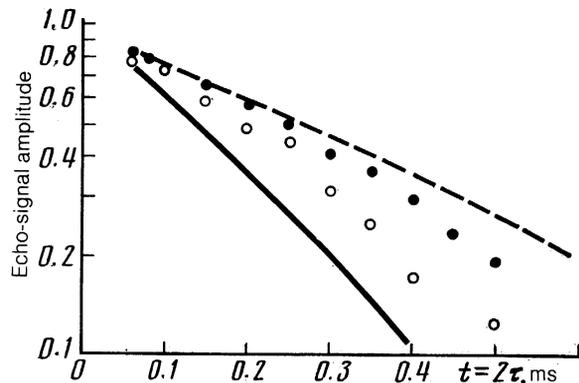


FIG. 3. The decrease of the transverse magnetization of ^3He nuclei in sample I measured at frequencies of 8 and 16 MHz and different temperatures: ● — $\mathbf{H}_0 \parallel \mathbf{c}'$, $\nu = 8.0$ MHz, $T = 0.075$ K; the dashed line is the same at $T = 1.5$ K; ○ — $\mathbf{H}_0 \parallel \mathbf{c}'$, $\nu = 8.0$ MHz, $T = 0.12$ K; the solid line is the same at $T = 1.5$ K.

field $\mathbf{H}_0 \perp \mathbf{c}'$ than in a field $\mathbf{H}_0 \parallel \mathbf{c}'$.

b) As the size of the particles of LiTmF_4 powder decreases the anisotropy of the time T'_1 increases (Fig. 5).

c) The time T'_{1l} in the superfluid solution 25% ^3He + 75% ^4He is shorter than in pure ^3He ; for example, in sample I at $T = 1.5$ K the time $T'_{1l} = 0.11$ s in the solution and 0.13 s in pure ^3He .

d) As the temperature is lowered the time T'_{1l} in pure ^3He decreases. For example, in sample I the time T'_{1l} measured at 16 MHz is equal to 0.17 s at $T = 0.5$ K and 0.05 s at $T = 0.012$ K (Fig. 4).

The measurements of the time T'_1 of pure ^3He in all five samples are summarized in Table III.

7. DISCUSSION

1. Inhomogeneous width of the NMR line

Paramagnetic LiTmF_4 powder containing liquid ^3He in its pores is a very complicated system. The complexity is caused primarily by the magnetization of the particles of the powder and exhibits itself through the extremely strong variation of the internal magnetic field. The intensity of the magnetic field generated by a particle at its surface is equal to $4\pi m/3$, where m is the magnetization of a unit volume of LiTmF_4 , and it can reach 100 Oe in an external field $\mathbf{H}_0 = 2.47$ kOe ($\nu_{\text{He}} = 8$ MHz). This quantity can apparently be employed as an estimate of the inhomogeneous width of the NMR line of ^3He . The observed inhomogeneous width is much smaller (the righthand column in Table I),

TABLE II. The relaxation parameters of the transverse magnetization ^3He nuclei in samples I, III, and IV at $T = 1.5$ K.

Sample	ν_{He} , MHz	$\mathbf{H}_0 \parallel \mathbf{c}'$		$\mathbf{H}_0 \perp \mathbf{c}'$	
		T_{2l} , ms	n	T_{2t} , ms	n
I	16.5	0.22	1.26	0.24	1.38
	8.0	0.45	1.27	0.66	1.02
III	8.5	0.22	1	0.22	1
	4.3	0.32	1	0.46	1
IV	8.0	0.012	1	0.30	1

TABLE III. The relaxation of the longitudinal magnetization of ^3He in LiTmF_4 (I-IV) and LiYF_4 (V) powders at $T = 1.5$ K.

Sample	Particle size, μm	ν_{He} , MHz	T'_{1l} , s	T'_{1t} , s
I	<57	8.0; 16.5	0.16	0.7
II	<20	8.0	0.013	0.5
III	2-4	4.3; 8.5	0.10	0.7
IV	<1	8.0	0.014	1.1
V	<57	8.0	0.35	0.35

and this large difference is, in all probability, caused not so much by the rough character of the estimate as by the averaging of the local fields owing to the diffusion of ^3He atoms. In reality, over the time of observation of the spin echo $2\tau \sim T_2 \approx 0.3$ ms (see Table II) a ^3He atom can diffuse over a distance $l = (D_0 T_2)^{1/2} \approx 1.7 \mu\text{m}$ ($D_0 = 1 \times 10^{-4}$ cm 2 /s is the diffusion coefficient at $T = 1.5$ K). If it is assumed that diffusion occurs in the space between submicron-size particles, then it turns out that over a time ≈ 0.3 ms a ^3He atom not only undergoes repeated collisions with the walls of one pore but it can also diffuse into neighboring pores.

The conjecture that the narrowing of the inhomogeneously broadened line is caused by diffusion of helium atoms among submicron-size particles is confirmed in Table I. Comparing the values of $\Delta\omega_{1/2}/\gamma$ measured at 8 MHz in a field $\mathbf{H}_0 \perp \mathbf{c}'$ we find that the half-width of the NMR line in the sample III not containing particles with sizes $d < 1 \mu\text{m}$ is much greater than in samples I ($d < 57 \mu\text{m}$) and IV ($d < 1 \mu\text{m}$). Thus the data in Table I cannot give an accurate picture of the inhomogeneity of the internal fields in oriented LiTmF_4 powders: they do not reflect the absolute magnitudes of the inhomogeneity of the fields and the ratios of the components of the paramagnetic susceptibility χ_l and χ_t ; moreover, they can give an incorrect picture of the character of the anisotropy of the susceptibility. Thus one could conclude from the measurements of the width of the spin-echo signal of ^3He in sample IV that the inhomogeneous width of the NMR line and therefore the paramagnetic susceptibility of the sample in a field $\mathbf{H}_0 \parallel \mathbf{c}'$ is not less than but rather two times greater than in the field $\mathbf{H}_0 \perp \mathbf{c}'$. In reality, however, of course, here the ratio $\chi_l < \chi_t$ remains the same as in samples I and III, and the observed inhomogeneous width of the NMR line in a field $\mathbf{H}_0 \parallel \mathbf{c}'$ is apparently greater owing to the very short "lifetime" of the spin of ^3He ($T_2 \approx 12 \mu\text{s}$). During this time interval ^2He atoms can diffuse over a distance not

greater than $0.35 \mu\text{m}$ and they remain within "their own pores" so that averaging of the mean fields in the pores owing to diffusion between the pores does not occur.

2. Relaxation of the transverse magnetization

The problem of the relaxation of the transverse magnetization of nuclei diffusing in a field with a constant gradient G_z in a thin layer of gas (a is the thickness of the layer in the z -direction) was studied theoretically and experimentally in Refs. 19 and 20, where it was shown that the usual form of the decay of the spin echo for NMR experiments in an inhomogeneous field,

$$M(t)/M(0) = \exp(-\gamma^2 G_z^2 D t^3 / 12), \quad (10)$$

changes radically when the diffusion of the atoms is limited by the walls. If the observation time of the spin echo $t = 2\tau$ is short compared with the transit time of an atom from one wall to the other ($t \ll \tau_0 = a^2 / \pi^2 D_0$, where D_0 is the self-diffusion coefficient), then D in Eq. (10) is equal to D_0 and

$$M(t)/M(0) = \exp[-(t/T_2)^3], \quad (11)$$

where

$$1/T_2 = (\gamma^2 G_z^2 D_0 / 12). \quad (12)$$

If, however, $t \gg a^2 / \pi^2 D_0$ holds, then we have

$$D \approx a^4 / 10 D_0 t^2 \quad (13)$$

and the decay is described by a simple exponential function

$$M(t)/M(0) = \exp(-t/T_{2r}), \quad (14)$$

where

$$1/T_{2r} = \gamma^2 G_z^2 a^4 / 120 D_0. \quad (15)$$

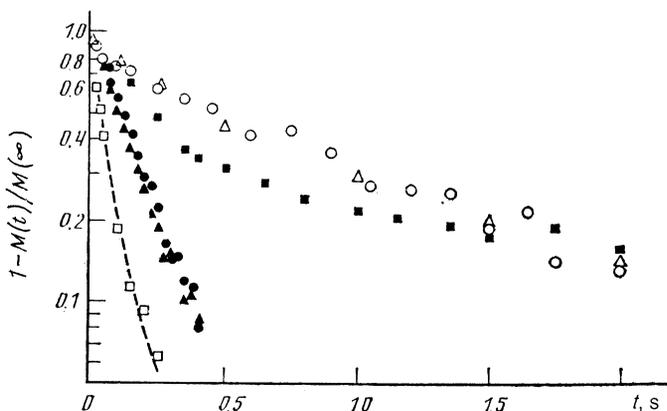


FIG. 4. The restoration of the longitudinal magnetization of ^3He in sample I at $T = 1.5$ K ($\circ, \bullet, \Delta, \blacktriangle, \blacksquare$) and 0.12 K (\square): $\circ - \mathbf{H}_0 \perp \mathbf{c}'$, $\nu = 16.5$ MHz; $\Delta - \mathbf{H}_0 \perp \mathbf{c}'$, $\nu = 8.0$ MHz; $\bullet - \mathbf{H}_0 \parallel \mathbf{c}'$, $\nu = 16.5$ MHz; $\blacktriangle - \mathbf{H}_0 \parallel \mathbf{c}'$, $\nu = 8.0$ MHz; \blacksquare - sample V, $\nu = 8.0$ MHz (for comparison); $\square - \mathbf{H}_0 \parallel \mathbf{c}'$, $\nu = 16.0$ MHz.

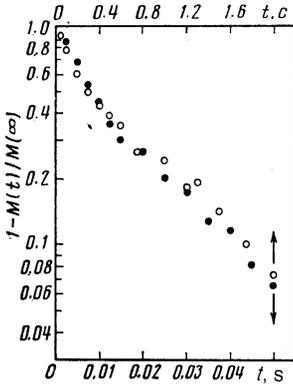


FIG. 5. Restoration of the longitudinal magnetization of ^3He in sample II at 1.5 K; the frequency is equal to 8.0 MHz; $\circ - \mathbf{H}_0 \parallel \mathbf{c}'$, $\bullet - \mathbf{H}_0 \perp \mathbf{c}'$, $T_{1r}/T_{1l} = 40$.

The same result can be obtained by a different method. An atom carrying nonzero nuclear spin and diffusing in a static inhomogeneous magnetic field in a bounded space is subjected to a fluctuating field $h(t)$. These fluctuations should result, in particular, in relaxation of the transverse nuclear magnetization at the rate²¹

$$1/T_2 = \gamma^2 \langle h_z^2 \rangle \tau_c + \gamma^2 (\langle h_x^2 \rangle + \langle h_y^2 \rangle) \tau_c / [2(1 + \omega_0^2 \tau_c^2)]. \quad (16)$$

It is natural to use here for the correlation time τ_c of the fluctuations the average time interval τ_0 between collisions of an atom with the surface of time magnetized solid body. If the rate of the fluctuations is small compared with the NMR frequency ($\omega_0 \tau_0 \gg 1$), then the first term predominates in the formula (16). In the case when the gradient G_z is constant the average squared z-component of the fluctuating field is equal to²⁰

$$\langle h_z^2 \rangle = G_z^2 a^2 / 12. \quad (17)$$

Substituting this value of $\langle h_z^2 \rangle$ as well as $\tau_0 = a^2 / \pi^2 D_0$, into Eq. (16) and making the assumption that $\omega_0 \tau_0 \gg 1$ we obtain the relaxation rate

$$1/T_{2r} = \gamma^2 G_z^2 a^4 / 12 \pi^2 D_0, \quad (16a)$$

which is the same as Eq. (15).

That the transverse magnetization of ^3He relaxes by the mechanism of bounded diffusion in the inhomogeneous field (BDIF) of the LiTmF_4 powder can be seen in the following facts.

a) The exponent n in the exponential in Eq. (7), describing the experimental decay curves of the transverse magnetization, assumes values from 1 to 3 [see Figs. 1 and 2; compare Eqs. (11) and (14)].

b) The rate of relaxation $1/T_2$ increases as H_0 increases (see Table II), as should happen because $\langle h_z^2 \rangle$ increases.

c) As the temperature is lowered the rate $1/T_2$ decreases (Fig. 3, measurements at 16 MHz), as should happen since the diffusion coefficient increases ($D_0 = 2 \times 10^{-4} \text{ cm}^2/\text{s}$ at $T = 0.12 \text{ K}$) and the correlation time decreases.

Since we have confirmed qualitatively that nuclear relaxation of ^3He occurs by the BDIF mechanism we can make a quantitative estimate of the relaxation time $T_{2r} = 1/\gamma^2 \langle h_z^2 \rangle \tau_0$. For the characteristic width of the gap between the crystallites we take $a_0 = 0.1 \mu\text{m}$, and then the average time between collisions of a ^3He atom and the surface of the crystallites is $\tau_0 = a_0^2 / \pi^2 D_0 = 1 \times 10^{-7} \text{ s}$ at $T = 1.5 \text{ K}$. The quantity $\gamma^2 \langle h_z^2 \rangle$ should be of the order of the second moment of the inhomogeneously broadened NMR line, for example, $M_2 = 2 \times 10^{10} \text{ s}^{-2}$ (see Table I). Then $T_{2r} = 500 \mu\text{s}$, which agrees with the measured values (Table II).

Thus we can see that in our experiments the BDIF mechanism plays an important role in the relaxation of the transverse magnetization of ^3He nuclei. At the same time, this is not the only relaxation mechanism. This is indicated by experimental facts that are not consistent with relaxation by the BDIF mechanism.

d) For magnetic field orientation $\mathbf{H}_0 \perp \mathbf{c}'$ the z-components of the local fields in the pores of the powder are larger than in the case $\mathbf{H}_0 \parallel \mathbf{c}'$, and correspondingly $\langle h_z^2 \rangle$ is maximum for $\mathbf{H}_0 \perp \mathbf{c}'$. As a result of this the time T_{2r} must always be shorter in a field $\mathbf{H}_0 \perp \mathbf{c}'$ than in the field $\mathbf{H}_0 \parallel \mathbf{c}'$. In reality (see Table II), however, in the sample I at $T = 1.5 \text{ K}$ at 16 MHz the time T_{2l} is approximately equal to T_{2r} , while at 8 MHz T_{2l} is even greater than T_{2r} . The same pattern is observed in sample III at 8.5 and 4.3 MHz, and the failure of the BDIF mechanism is especially obvious in the sample IV: $T_{2l}/T_{2r} = 25$ (!).

e) As the temperature decreases the self-diffusion coefficient of ^3He increases, and as a result of this the correlation time τ_0 and the relaxation rate $1/T_{2r}$ should decrease. Experiments with sample I at 8 MHz give the opposite result (Fig. 3).

f) Since it is proportional to the square of the gradient G_r , the relaxation rate $1/T_{2r}$ should vary with the field as H_0^2 . In reality, the dependence of the rate $1/T_2$ on the field is weaker.

g) It is easy to see that for a fixed NMR frequency (and field \mathbf{H}_0) the relaxation rate $1/T_{2r}$ should depend on the sizes of the particles of powder as d^2 and therefore it should decrease from the sample I to the sample IV. The results of measurements of $1/T_2$ (Table II) show the opposite dependence.

The contradictions noted above can be eliminated and

TABLE IV. The relaxation parameters of the transverse magnetization of ^3He in samples I and III at a temperature of 1.5 K.

Sample	T_{2sl} , ms	$T_{2rl}(8 \text{ MHz})$, ms	T_{2sl} , ms	$T_{2rl}(8 \text{ MHz})$, ms
I	0.66	1.41	1.75	1.06
III	0.38	0.50	0.75	0.30

all observed facts can be explained if it is assumed that aside from the BDIF mechanism there is an additional mechanism of relaxation of the transverse magnetization of ^3He ; the action of this mechanism is all the more noticeable the lower the NMR frequency and the smaller the LiTmF_4 particles from which the magnetically oriented sample is prepared. The rate of this relaxation $1/T_{2s}$ (we call it surface relaxation) can be estimated from the results of experiments with samples I and III at two frequencies, but for this it is necessary to assume that the quantity $1/T_{2s}$ does not depend on the frequency at least in the interval $\nu = 4\text{--}16$ MHz. From two pairs of equations of the type

$$\begin{aligned} 1/T_{2l}(\nu) &= 1/T_{2sl} + 1/T_{2rl}(\nu), \\ 1/T_{2l}(2\nu) &= 1/T_{2sl} + 4/T_{2rl}(\nu), \end{aligned} \quad (18)$$

corresponding to longitudinal (l) and transverse (t) orientations of the field \mathbf{H}_0 , we find four time parameters for each sample. These parameters are summarized in Table IV ($4T_{2r}(2\nu) = T_{2r}(\nu)$). They reveal tendencies that can be described by the inequalities

$$T_{2sl} < T_{2st}, \quad T_{2rl} > T_{2rt}, \quad T_{2sl} < T_{2rl} \quad (19)$$

and formulated in the following generalization. The BDIF mechanism plays an important role in the relaxation of the transverse magnetization of nuclei of liquid ^3He in the pores of magnetically oriented LiTmF_4 powder; it is all the more effective the greater the magnetization of the sample. In addition there exists another mechanism of surface relaxation which plays a dominant role when the field \mathbf{H}_0 is oriented parallel to the direction \mathbf{c}' of minimum magnetization of the sample.

We have a basis for conjecturing that the very short time $T_{2l} = 12 \mu\text{s}$, measured in sample IV at 8 MHz, is completely determined by surface relaxation. Unfortunately repeated experiments with this (unpressed) sample cannot be performed at a different frequency: rotations of the sample in a magnetic field in the course of the measurements still partially reduce the degree of orientation of the powder and change the relaxation parameters (in a repeated experiment the time T_{2l} at 8 MHz increased up to $30 \mu\text{sec}$).

3. Relaxation of the longitudinal magnetization

Analysis of our experimental results (see Table III) permits the following conclusions to be drawn.

a) The relaxation of the longitudinal magnetization of ^3He in a field \mathbf{H}_0 oriented perpendicular to the \mathbf{c}' axis is not related with the Van Vleck magnetization of LiTmF_4 samples (compare T_1 in sample V).

b) This relaxation is also not related with impurity paramagnetic centers. The quantity T'_{1l} in sample IV, containing a large admixture of Nd^{3+} ions, is even longer than the time T'_{1l} in other samples. In addition, T'_{1l} is insensitive to an increase in the degree of polarization of the electron spins $P_0 = \tanh(\delta/2kT)$ as the temperature decreases.

c) The relaxation of the longitudinal magnetization of ^3He in the field \mathbf{H}_0 parallel to the \mathbf{c}' axis likewise is not related either to the Van Vleck magnetization of LiTmF_4 powders (it does not depend on the field \mathbf{H}_0) or to impurity paramagnetic centers.

d) When, the field \mathbf{H}_0 is oriented along the \mathbf{c}' axis a relaxation mechanism of ^3He which is not manifested at all

in a field $\mathbf{H}_0 \perp \mathbf{c}'$ operates. The efficiency of this mechanism increases as the sizes of the LiTmF_4 particles decrease and the surface area of the sample increases.

Since we are talking about the magnetic relaxation of ^3He nuclei and since the only magnetic parameter which we have thus far not discussed is the electron-nuclear magnetization of LiTmF_4 we must look for a relation between the anisotropy of the time T'_1 and the anisotropy of the effective gyromagnetic ratio of ^{169}Tm nuclei.

8. CONCLUSIONS

Generalizing the results of Secs. 7.2 and 7.3 we arrive at the conclusion that the accelerated relaxation of the transverse and longitudinal magnetizations of ^3He nuclei in magnetically oriented LiTmF_4 powder in a field $\mathbf{H}_0 \parallel \mathbf{c}'$ occur for the same reason, related to the presence of a system of "intensified" nuclear moments of ^{169}Tm . An obvious feature of the magnetically oriented LiTmF_4 sample is that for any orientation of the external field the Zeemann splitting of the electron-nuclear energy levels of ^{169}Tm in some particles of powder is identical to the Zeemann splitting of the energy levels of ^3He nuclei, but more of these "resonating" particles correspond to the orientation $\mathbf{H}_0 \parallel \mathbf{c}'$ than to the orientation $\mathbf{H}_0 \perp \mathbf{c}'$. In other words the orientation $\mathbf{H}_0 \parallel \mathbf{c}'$ is distinguished by a large surface area of the particles of powder capable of coming into thermal contact with the nuclear spins of ^3He . We assume that only those ^{169}Tm nuclei that lie on the surface (or close to the surface) of the resonating particles of LiTmF_4 powder participate in the relaxation of ^3He nuclei. They effectively shorten the phase memory time of the nuclear spins of ^3He and also participate in the process of energy transfer from the spin system ^3He into the kinetic-energy reservoir of the helium atoms. If our assumptions are correct, then it will be possible to use finely dispersed oriented powders of dielectric Van Vleck paramagnets to cool ^3He by the method of adiabatic demagnetization.

It is well known that the parameters of the electron-nuclear system of thulium in a TmPO_4 crystal are virtually identical to those in LiTmF_4 . Our experiments on NMR of ^3He in oriented TmPO_4 powder, prepared from particles with sizes $< 57 \mu\text{m}$, gave results which are close to those obtained with sample I.²²

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Translated by M. E. Alferieff