Interaction of ^{3}He spins with the spins of protons from water adsorbed on the surface of silica

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We have measured the longitudinal magnetic moment of ^{3}He in the system consisting of liquid helium-3 plus protons from water adsorbed on the surface of porous silica under conditions where the NMR signal from the protons is saturated by an RF field. This quantity is 0.55 ± 0.1 of the equilibrium magnetic moment of ^{3}He when the pores are covered by $\simeq 1$ monolayer of water (physisorbed) at temperatures 0.05 to 0.5 K in magnetic fields of 22 and 44 Oe. We also made measurements on a sample of silica dried in vacuum, on whose surface some chemically bonded water remained.

I. INTRODUCTION

The interaction of the spins of liquid ^{3}He with substrates of various types has been discussed in many papers, among them the recent detailed studies of the liquid helium–Teflon system reported in Refs. 1–5. In these papers it was shown that the magnetizations of the spins of the ^{3}He and ^{19}F nuclei are coupled, and that the magnetization of the helium nuclei decreases when the fluorine is subjected to an RF field. However, the magnitude of this effect reported by various authors has exhibited considerable scatter for Teflons of various types, down to the absence of any coupling whatsoever.[1] Furthermore, the possible influence of electron paramagnetic impurities remains unclear. Gramila *et al.*[6] investigated the ^{3}He–^{19}F system on a substrate made of CaF_2. Gonen *et al.*[7] measured the nuclear spin–lattice relaxation times for various substrate atoms caused by coupling with the spins of liquid ^{3}He. Finally, Egorov *et al.*[8] investigated the coupling between the spins of liquid ^{3}He and ^{169}Tm.

Although the ^{3}He–^{1}H system is probably analogous to the case of helium–fluorine, it is less studied. Ahonen *et al.*[9] observed that the signal from protons in Mylar increased with increasing temperature of the liquid ^{3}He, which indicates a coupling between the spins of ^{3}He and ^{1}H. Engel *et al.*[10] produced a dynamic polarization of ^{3}He nuclei in porous carbon by using hydrogen atoms on the surface. Swanson *et al.*[11] observed that for porous polycarbonate material the interaction of ^{3}He with ^{1}H was $\sim 10^2$ times weaker than that of ^{3}He with ^{19}F. In our paper (Ref. 12) we reported observing a coupling of ^{3}He–^{1}H at the surface of epoxy resin. In this paper we investigate the interaction of liquid ^{3}He spins with the spins of protons from water adsorbed chemically or physically on the surface of porous silica.

2. EXPERIMENTAL PART

In preparing our samples, we used industrial-grade KSKG silica gel. The gel was first washed in concentrated hydrochloric acid to remove impurities from the surface,[13] and then in distilled water. It then was ground up in an agate mortar, after which it was pressed into a cylinder of diameter 4.6 mm and length 10 mm, with an opening along the axis whose diameter was 0.8 mm. The sample was then steam processed for two hours at a temperature of 155 °C, in order to decrease the surface area. Before being placed in an experimental cell, the sample was heated in vacuum at 200 °C for a period of 30 minutes. The area of the sample surface, which was determined from the adsorption isotherms of ^{3}He at a temperature of 2.0 K and N_2 at a temperature of 77 K, was $S = 13$ m^2. The volume of pores, calculated from the weight of the dried sample, was equal to 67% of its volume. The average pore diameter in the sample, which we estimated from the expression $d = 4V/S$ given by Neimark *et al.*,[14] where V is the pore volume, was 350 Å. Using the filling line to the experimental chamber, with diameter 1 mm and length 0.7 m, we were able to pump out the sample and thereby remove physisorbed water. The sample was dried by heating it to a temperature of 40 °C for five to seven days. This process leaves chemisorbed water at the surface of the sample pores.[13] Again using the filling line of the experimental chamber, we were able to pump water vapor into the chamber in amounts corresponding to coverage of the pore surfaces to a thickness of ~ 1 monolayer. In order to prevent migration of water vapor before the cell was cooled, at the beginning of the experiment we pumped the helium-3 to be used in the experiment into the cell at a pressure of 50–100 torr. We also performed a number of experiments using a sample that had not been washed in advance with hydrochloric acid; this sample had a sizable concentration of paramagnetic impurities.

The body of the experimental chamber (Fig. 1) was made of Dacron film glued together with Staycast-1266 epoxy resin. By using a current transformer coupled to an RF SQUID, whose detector coil was glued to the body of the cell and had 21 turns, we were able to measure the longitudinal magnetic moment of the sample. In order to shunt pickup from the RF field, we connected a resistance of $3 \cdot 10^{-4}$ Ω into the line between the detector and signal coils, which were surrounded by a shield made of bronze foil tinned with superconducting solder. The output of the SQUID was recorded by a computer.

After the experimental gas was condensed, the sample was soaked with liquid helium, which was drawn up along a fiberglass braid whose lower end was in contact with the helium. This procedure ensured that the sample pores were

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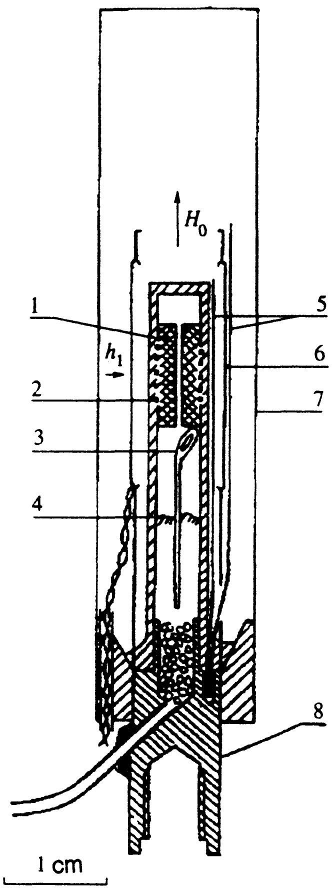

FIG. 1. Experimental chamber: *1*—sample, *2*—detector SQUID coil, *3*—fiberglass braid, *4*—level of liquid helium in the cell, *5*—copper cooling wires, *6*—RF field coil, *7*—screen made of niobium, copper, and Dacron foil, *8*—copper cold finger.

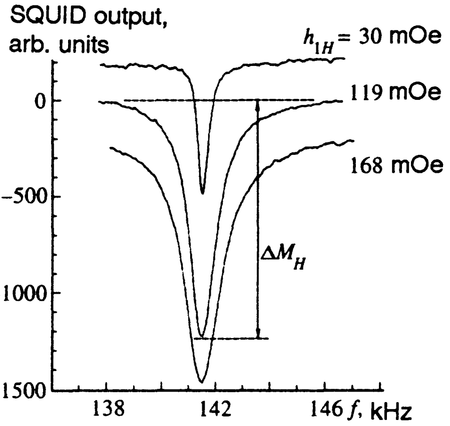

FIG. 2. Trace of the ^{3}He NMR line for various values of the RF field h_{1H}, $H_0=43.8$ Oe, $T=0.10$ K; the frequency sweep rate $df/dt=6.3\cdot 10^3$ Hz/s, and the sample is dried.

filled while leaving the channel in the center of the sample and the portions of the experimental chamber near the sample free of liquid. We determined that all the sample pores were filled based on the NMR signal from a control experiment in which the entire cell was filled with liquid helium.

A DC magnetic field H_0 was created by a superconducting solenoid; upon cooling, this field was trapped by the niobium tube of the cell shield. Using two crossed coils made of superconducting wire, we created rotating RF fields h_1, both at the spin resonance frequency of ^{3}He (h_{1H}) and at the proton resonance frequency (h_{1P}); these fields rotated in opposite directions. The value of h_1 was calibrated based on the shift in resonance frequency in the presence of a strong RF field. The body of the cell and the RF coils were cooled with 18 copper wires with diameters 0.2 mm, tinned with an indium-tin alloy and glued to it with epoxy resin. The copper cold finger of the cell was tightly screwed into the mixing chamber of a ^{3}He–^{4}He refrigerator. The temperature of the cell was monitored and regulated using two resistance thermometers in contact with the cold finger. The ^{4}He abundance in the experimental helium did not exceed 0.02%.

In the experiments, the RF fields were switched on for a period of 6 seconds. In order to determine the magnetic moment of the liquid ^{3}He, the frequency of the RF field h_{1H} was swept through the resonance frequency. The curves obtained (Fig. 2) were approximated by a Lorentzian with height ΔM_H. For large values of h_{1H}, the peak height ΔM_H did not depend on the value of h_{1H} (i.e., the resonance was saturated). When an RF field was applied at the proton NMR frequency, the value of ΔM_H decreased. The function $\Delta M_H(h_{1P})$ shown in Fig. 3 is well approximated by the function

$$\Delta M_H(h_{1P})=\Delta M_H(0)(1+aR_H h_{1P}^2)/(1+ah_{1P}^2). \qquad (1)$$

The quadratic dependence on h_{1P} reflects the power adsorbed by the proton system from the RF field. The quantity

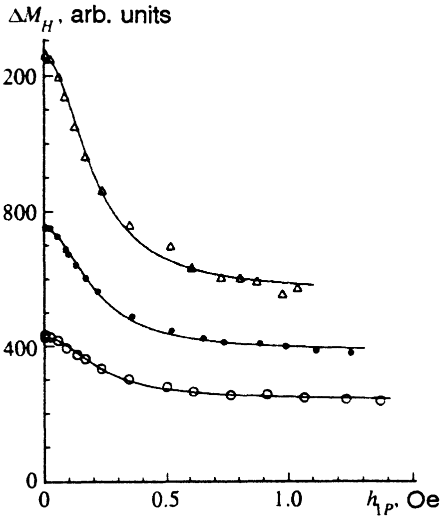

FIG. 3. Dependence of the peak height at the NMR frequency of ^{3}He on the value of the RF field applied at the NMR frequency of the protons; the curves show the approximation by Eq. (1). The sample had added water, $H_0=21.8$ Oe. ○—$T=294$ mK, $h_{1H}=122$ mOe; ●—$T=105$ mK, $h_{1H}=124$ mOe; △—$T=47$ mK, $h_{1H}=155$ mOe.

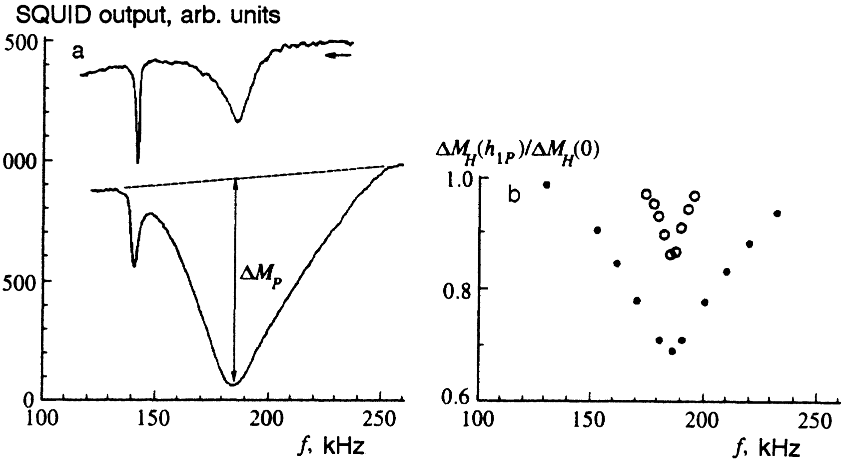

FIG. 4. (a) SQUID output when the RF field is frequency-swept through the NMR proton frequency. $T=0.10$ K, $H_0=43.8$ Oe, $h_{1P}=0.30$ Oe; the direction of rotation of the RF field corresponded to proton NMR, $df/dt=6.3\cdot 10^4$ Hz/s. The upper curve was obtained for a dried sample (the arrows show the direction of scanning of the field), the lower for a sample with added water. To the left, the helium NMR line is visible; it appears because of imprecise tuning of the RF field electronics. (b) Relative peak height at the ^{3}He NMR frequency as a function of the frequency of the RF field h_{1P} rotating in the direction corresponding to proton resonance. h_{1H} =119 mOe, $h_{1P}=0.22$ Oe, $H_0=43.8$ Oe. ○—dried sample, $T=0.07$ K; ●—sample with added water, $T=0.10$ K.

R_H is the relative peak height at the NMR frequency of ^{3}He when the proton resonance is saturated by the strong RF field h_{1P}.

3. CONTRIBUTION OF THE PROTON SYSTEM TO THE PEAK HEIGHT AT THE RESONANCE FREQUENCY OF HELIUM

As we pass through the helium resonance line, a change in the longitudinal magnetic moment takes place, associated not only with the helium but also with the proton system. The peak height ΔM_H at the helium resonance frequency equals the difference between the longitudinal moment of the sample when the RF field frequency is detuned far from resonance and the moment at exact resonance. Far from the helium resonance frequency, the magnetic moments of the helium and proton systems have values M_H^0 and M_P^0 that are equilibrium values at the given temperature. At exact resonance, in a sufficiently strong RF field h_{1H}, the longitudinal magnetic moment of the helium vanishes; in this case, because of the interaction of the ^{3}He and ^{1}H spins, the magnetic moment of the proton system changes and becomes equal to $R_P^0 M_P^0$. The quantity R_P^0 denotes the relative magnetic moment of the proton system when a strong RF field h_{1H} is applied at the resonance frequency of the helium. Therefore, the peak height at the helium resonance frequency for a strong RF field h_{1H} (when there is no RF field at the proton resonance frequency) is

$$M_H=M_H^0+(1-R_P^0)M_P^0. \tag{2}$$

In this expression, the quantity $(1-R_P^0)M_P^0$ expresses the contribution of the proton system to the peak height at the helium resonance frequency for large values of h_{1H}. When a strong RF field h_{1P} is applied at the proton resonance frequency, the longitudinal magnetic moment of the proton system vanishes and makes no contribution to the peak height at the helium resonance frequency. For an RF field h_{1H} that saturates the helium resonance, this equals:

$$R_H M_H=R_H^0 M_H^0. \tag{3}$$

The quantity R_H^0 is the relative magnetic moment of the helium when a strong RF field h_{1P} is applied. From (2) and (3) we obtain

$$R_H^0=R_H/(1-(M_P^0-R_P^0 M_P^0)/M_H). \tag{4}$$

The denominator in this expression gives the correction when the quantity R_H is renormalized to R_H^0. The quantities M_P^0 and $R_P^0 M_P^0$ can be determined by measuring the peak height when the frequency of the RF field h_{1P} is swept through the resonance frequency of the protons.

We made these measurements at one sample temperature (0.10 K) with $H_0=44$ Oe. Figure 4 shows the SQUID output as the frequency of the RF field was swept through the proton resonance frequency; the direction of rotation of the RF field h_{1P} corresponded to proton resonance. In order to eliminate the signal from ^{1}H nuclei located on the walls of the experimental chamber, in these measurements we also applied an oscillating RF field at the proton resonance frequency with an amplitude of ≈ 6 mOe. This field was weak, and did not affect the signal from the sample protons; however, it led to complete saturation of the resonance from ^{1}H nuclei on the walls of the chamber.[12] The narrow ^{3}He line, which can be seen on the left-hand portion of Fig. 4a, appears because of imprecise tuning of the electronics; it does not affect the peak height at the proton resonance frequency ΔM_P, which is taken to be the distance from the peak to the straight line passing through the "wing" of the curve in Fig. 4a. It is noteworthy that the ±60 kHz range of swept frequencies around the resonance frequency was sufficiently wide to record the curve for a sample with added water; the half-width of the resonance line determined based on the value of the signal at the NMR frequency of ^{3}He (Fig. 4b) was in the range 22–25 kHz.

Figure 5 shows the dependence of the quantities ΔM_H and ΔM_P on the values h_{1H} and h_{1P} of the RF fields applied at the helium and proton resonance frequencies. In measuring ΔM_H, the frequency of the RF field h_{1H} was swept through the helium resonance frequency, while the frequency of the RF field h_{1P} was held steady at the proton resonance frequency. Conversely, in measuring ΔM_P, the frequency of the RF field h_{1H} was fixed (at the NMR frequency of ^{3}He), while the frequency of the RF field h_{1P} was swept through the proton resonance frequency. We also measured the peak height at the proton resonance frequency for a sample that was not filled with experimental helium (Fig. 5d). In this case, the sample with added water was cooled to the tem-

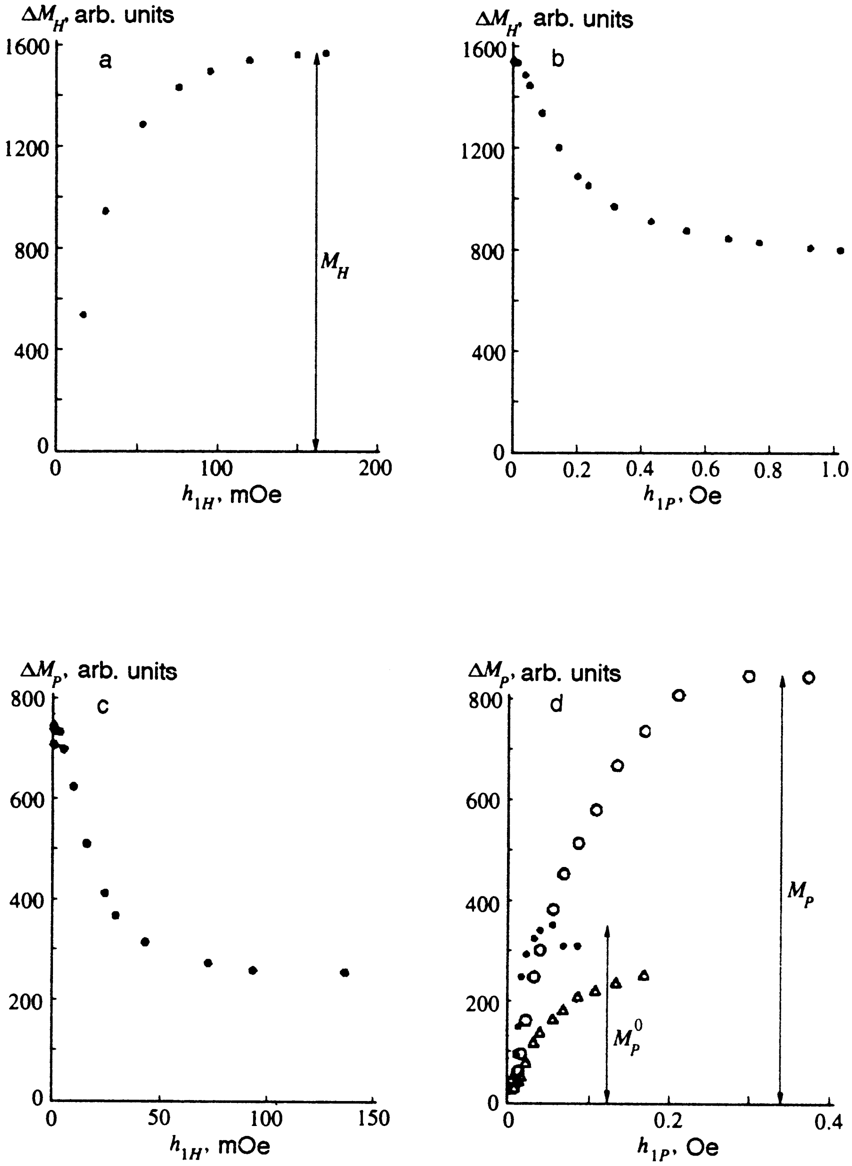

FIG. 5. Dependence of the signals at the ^{3}He and ^{1}H NMR frequencies on the value of the applied RF fields, for a sample with added water: $T=0.10$ K, $H_0=43.8$ Oe. (a) $h_{1P}=0$, (b) $h_{1H}=119$ mOe, (c) $h_{1P}=0.17$ Oe, (d) ○—$h_{1H}=0$; along this curve we show the quantity M_P: △—$h_{1H}=136$ mOe; ●—a sample without ^{3}He, based on the function $\Delta M_p(h_{1P})$, which in this case is determined by the value of M_P^0.

perature of liquid nitrogen in the presence of the experimental helium, which was pumped down at this temperature.

The value of the equilibrium magnetic moment of the proton system M_P^0 was defined as the maximum of the function $\Delta M_P(h_{1P})$ for a sample without ^{3}He, Fig. 5d (a certain decrease in the value of ΔM_P in a strong RF field h_{1P} is probably due to heating of the proton system at RF field frequencies that differ from the resonance frequency). By analogy with (3), the longitudinal magnetic moment of the proton system in the presence of a strong RF field h_{1H} is

$$R_P^0 M_P^0 = R_P M_P. \tag{5}$$

Here M_P is the peak height at the proton resonance frequency in a strong RF field h_{1P} (Fig. 5d); R_P equals the relative peak height at the proton resonance frequency when a strong RF field h_{1H} is applied. Our determination of R_P is based on the function $\Delta M_P(h_{1H})$ (Fig. 5c), which we approximate by an expression analogous to (1). From Eqs. (4) and (5) we obtain

$$R_H^0 = R_H/(1-(1-R_P M_P/M_P^0)(M_P^0/M_H)). \tag{6}$$

Equation (6) allows us to calculate the relative magnitude of the longitudinal magnetic moment of helium in a strong RF field h_{1P} based on the relative peak height at the helium resonance frequency. The difference between the quantities R_H^0 and R_H, which is associated with the contribution of the proton system to the peak height at the helium resonance frequency, was about 7% for a sample with added water and 0.5% for a dried sample in a field $H_0=44$ Oe at a temperature 0.10 K.

4. DISCUSSION

The functions $R_H(T)$ that we found are shown in Fig. 6. For a sample with added water, R_H decreases slowly with decreasing temperature. The correction involved in renormalizing the quantity R_H to R_H^0, which was defined by Eq. (6), probably has a temperature dependence governed by the ratio M_P^0/M_H, if we assume that the quantity

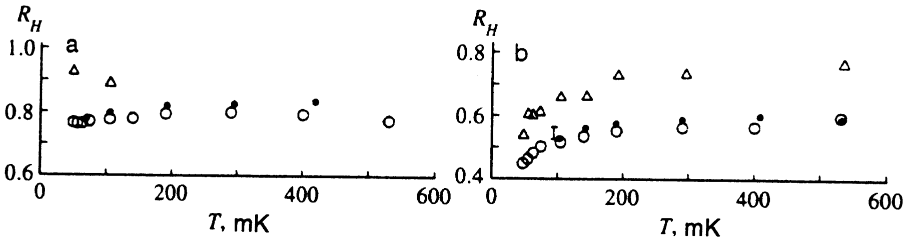

FIG. 6. Relative peak height at the ^{3}He NMR frequency under conditions of complete saturation of the resonance due to ^{1}H nuclei. (a) Dried samples, (b)—samples with added water. ○—H_0=21.8 Oe, ●—H_0=43.8 Oe. The sample was prepared from silica gel washed with acid; the length of the vertical segment shows the correction involved in renormalizing the quantity R_H to R_H^0. △—H_0=21.8 Oe, for a sample with a high concentration of impurities.

$R_P M_P / M_P^0 = R_P^0$ depends weakly on temperature. This correction most likely will increase with decreasing temperature, because M_H increases with decreasing temperature more slowly than $1/T$. The dependence of R_H^0 on temperature thus can be weaker than that of R_H for a sample to which water has been added.

In Fig. 6 we also show results of measurements performed on a sample prepared from silica gel that was not previously washed in hydrochloric acid. This sample has a large magnetic moment, which was unrelated to the liquid helium or the protons. We observed that the temperature dependence of this magnetic moment followed the Curie law. The value of the impurity-related susceptibility of silica was calculated by comparing with the magnetic moment of liquid ^{3}He. At a temperature of 1 K, this had a value χ (1 K)$=4.7\cdot 10^{-5}$ for an unpurified sample; for a sample prepared from silica gel and purified by washing in acid, χ (1 K)$=1.2\cdot 10^{-5}$ (in cgs units). The concentrations of electronic paramagnetic impurities for these two samples differed by roughly a factor of 4, assuming that the impurities in them are the same. As is clear from Fig. 6b, the value of R_H for these samples changes by only $\approx$30% when water was added. This implies that magnetic impurities remaining after cleaning the surface do not have any significant effect on the value of R_H^0 for a sample with a monolayer of water, which was 0.55 ± 0.1 at temperatures 0.05 to 0.5 K. To measurement accuracy, the values of R_H are the same for $H_0=22$ and 44 Oe.

In our paper (Ref. 12) we measured the relative magnetization of ^{3}He under conditions where the resonance of ^{1}H nuclei on the walls of the experimental chamber, which was made of epoxy resin, was saturated. We observed a strong temperature dependence for this quantity. Since we did not monitor the state of the surface of the epoxy resin in this work, it is possible that adsorbed water was present on it. Our experiments were carried out in the bulk geometry for the liquid helium, which, as we have pointed out in this paper, could have distorted the measurement results for T>0.2 K due to the influence of the intrinsic spin–lattice relaxation of liquid ^{3}He. We measured the dependence of the magnetic moment of ^{3}He on the value of the RF field h_1 applied at the proton resonance frequency at low temperatures because of possible heating. For these measurements, the values of h_1 that we used were probably too low, and extrapolation from them could have led to an overestimate of the measured values at low temperatures. As a whole, the results we obtained, which predict a strong temperature dependence of the quantity R_H^0, are probably not very reliable.

In Refs. 1, 2, and 4, a model was developed for the interaction of liquid helium spins with the spins of the substrate nuclei for the helium–fluorine system in the case where electronic impurities were absent. This model assumed that the interaction was associated with exchange motion of the first surface atoms of a solid layer of helium. From this model, an expression was derived for the relative magnetic moment of ^{3}He under conditions in which the nuclear spins of the substrate are heated by the RF field:

$$R_H^0 = 1 - |\gamma_P / \gamma_H| T_1 / (T_1 + T_C). \qquad (7)$$

In this expression, the time T_1 describes the intrinsic relaxation of ^{3}He associated with modulation of the dipole–dipole interaction by the exchange motion of the ^{3}He; the time T_C corresponds to the interaction of ^{3}He with the spins of the substrate nuclei; and γ_P and γ_H are the gyromagnetic ratios of the ^{1}H and ^{3}He nuclei. This model of the coupling leads us to expect that R_H^0 will be temperature-independent, since the exchange motion is itself independent of temperature. Equation (7) is correct in strong magnetic fields; in weak fields, for which the Larmor frequency is small compared to the atomic exchange frequency, from the relations given by Geng *et al.*[1] we obtain:

$$R_H^0 = 1 - (1/2) |\gamma_P / \gamma_H| T_1 / (T_1 + T_C). \qquad (8)$$

Kondo *et al.*[15] presented an estimate for the minimum exchange frequency: $(J/2\pi) \approx 44$ kHz. In our case, this value is close to the Larmor frequency. The fields 22 and 44 Oe can probably be considered weak. Depending on the ratio T_1/T_C, the quantity R_H^0 given by Eq. (8) can vary from 0.35 to 1.

The time T_C depends on the distance r_{HP} between ^{3}He and ^{1}H nuclei as follows: $1/T_C \propto \langle 1/r_{HP}^6 \rangle$.[4] For dried silica, the value of r_{HP} is found to be larger on the average than for a sample with added water, due to the larger distance between neighboring protons r_{PP}; clearly, this will lead to a larger value of R_H^0 for the dried sample. The average distance between neighboring protons can be estimated based on the width of the resonance line for these nuclei (Fig. 4b):

$$r_{PP} \approx (1.6 - \gamma_P^2 / (2\pi \Delta f))^{1/3},$$

where Δf is the half width at half-height (in Hz). This quantity came to 2.0 Å for a sample with added water, and 3.2 Å for a dried sample.

These values of R_H^0 allow us to calculate the ratio of times T_1/T_C. A calculation based on Eq. (8) gives

$T_1/T_C=0.4$ for a dried silica sample; for a sample with a monolayer of water, $T_1/T_C=2.2\pm1$. In Ref. 1, additional information about the quantities T_1 and T_C was obtained by measuring the spin–lattice relaxation time of the fluorine nuclei. Our experiments could be used to provide an estimate of the spin–lattice relaxation time for ^{1}H and ^{3}He nuclei based on the RF field required to saturate the resonances of these nuclei [in terms of the value of "a" from Eq. (1) and Fig. 5a]. At $T=0.05$ K, the half-width of the helium line at half-height for weak RF fields h_{1H} came to roughly 200 Hz, which greatly exceeded the value for $T=0.5$ K (about 60 Hz); this probably is determined by the nonuniformity of the field H_0. An estimate of the relaxation time in this case gives a value of order 10^{-3} seconds. This value agrees with the results obtained by Kondo *et al.*[15] for the relaxation time of liquid ^{3}He in porous glass. We note that for the sample of silica having a large concentration of paramagnetic impurities, the width of the helium line at small RF fields h_{1H} and the value of the inverse spin–lattice relaxation time of helium were found to be only 1.5 times larger (roughly) than for a purified sample.

To sum up, the results of our measurements of the relative magnetic moment of ^{3}He under conditions in which the resonance of the protons of the water adsorbed at the surface of the silica was saturated can be explained by using the model of coupling of the spins of the liquid ^{3}He and the nuclear spins of the substrate proposed in Refs. 1, 2, and 4.

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[1] Q. Geng, M. Olsen, and F. B. Rasmussen, J. Low Temp. Phys. **74**, 369 (1989).

[2] A. Schuhl, F. B. Rasmussen, and M. Chapellier, J. Low Temp. Phys. **57**, 483 (1984).

[3] L. J. Friedman, T. J. Gramila, and R. C. Richardson, J. Low Temp. Phys. **55**, 83 (1984).

[4] A. Schuhl, S. Maegawa, M. W. Meisel, and M. Chapellier, Phys. Rev. B **36**, 6811 (1987).

[5] P. C. Hammel, P. L. Kuhns, O. Gonen, and J. S. Waugh, Phys. Rev. B **34**, 6543 (1986).

[6] T. J. Gramila, F. W. Van Keuls, and R. C. Richardson, Physica B **165–166**, 695 (1990).

[7] O. Gonen, P. L. Kuhns, C. Zuo, and J. S. Waugh, J. Magn. Reson. **81**, 491 (1989).

[8] A. V. Egorov, O. N. Bakharev, A. G. Volodin *et al.*, Zh. Éksp. Teor. Fiz. **97**, 1175 (1990) [Sov. Phys. JETP **70**, 658 (1990)].

[9] A. I. Ahonen, T. Kodama, M. Krusius *et al.*, J. Phys. C **9**, 1665 (1976).

[10] L. W. Engel and K. DeConde, Phys. Rev. B **33**, 2035 (1986).

[11] D. R. Swanson, D. Candela, and D. O. Edwards, J. Low Temp. Phys. **72**, 213 (1988).

[12] I. S. Solodovnikov and N. V. Zavartskii, JETP Lett. **56**, 162 (1992).

[13] R. K. Iler, *Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry,* Wiley, New York (1971), Chs. 5, 6.

[14] I. E. Neimark and R. Yu. Sheinfein, *Silica Gel: Sources, Properties, and Applications* (in Russian), Kiev (1973).

[15] Y. Kondo, T. Mizusaki, A. Hirai *et al.*, J. Low Temp. Phys. **75**, 289 (1989).

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