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Phys. Rev. A **83**, 061401 — Published 16 June 2011

DOI: [10.1103/PhysRevA.83.061401](https://doi.org/10.1103/PhysRevA.83.061401)

Pressure Dependence of Wall Relaxation in Polarized ^3He Gaseous Cells

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We have observed a linear pressure dependence of longitudinal relaxation time (T_1) at 4.2 K and 295 K in gaseous ^3He cells made of either bare pyrex glass or Cs/Rb-coated pyrex due to paramagnetic sites in the cell wall. The paramagnetic wall relaxation is previously thought to be independent of ^3He pressure. We develop a model to interpret the observed wall relaxation by taking into account the diffusion process, and our model gives a good description of the data.

PACS numbers: 33.25.+k, 51.20.+d, 75.70.Rf, 82.65.+r

Spin polarized ^3He gas has been widely used in polarized nuclear targets for lepton scattering experiments [1] and as a signal source in Magnetic Resonance Imaging (MRI) of lung air space [2]. Recently, it has also been used in searches of exotic spin-dependent interactions [3]. These experiments take advantage of large nonequilibrium polarizations of ^3He obtained through spin-exchange with optically polarized Rb or Rb/K vapor mixture. The production and storage of polarized ^3He gas crucially depend upon longitudinal relaxation times (T_1). Among many factors contributing to the T_1 relaxation, the most important ones are the ^3He dipole-dipole interaction [4], magnetic field gradient induced relaxation [5] and wall relaxation. The least understood and hardest to control among these three effects is the relaxation due to the wall.

Although a thorough understanding of the nature of the wall relaxation is lacking, it is widely believed that relaxation rates due to paramagnetic sites in the wall do not depend upon the density of the gas. This is understood in the following way: the wall collision rate per unit area is known as $n\bar{v}/4$, where n is the number density of the gas and \bar{v} is the mean velocity; assuming α is the depolarization probability per collision due to paramagnetic impurities, the relaxation rate $1/T_1$ can be expressed as [6]

$$\frac{1}{T_1} = \frac{\frac{1}{4} \int \alpha n \bar{v} dS}{\int n dV} = \frac{\alpha \bar{v} S}{4V}, \quad (1)$$

where S is the total surface area of the cell, V is the volume of the cell, and n is uniform across the cell. As long as α has no dependence on the gas density or pressure, T_1 is also independent of gas pressure.

In this paper, we present our recent T_1 measurements on polarized ^3He cells which show a linear pressure dependence of T_1 , different from what has been discussed above. In our experiment, the measured T_1 is significantly reduced from tens of hours to tens of minutes by just decreasing the pressure of ^3He gas one hundred times. After excluding dipole-dipole and gradient induced T_1 relaxation, the observed pressure dependence can only be explained by the wall relaxation, which is, however, completely opposite to the pressure dependence observed in the ferromagnetic wall relaxation under the weak collision limit [7]. As the cells tested have never

been exposed to high fields, ferromagnetic relaxation cannot be the dominant relaxation mechanism, and paramagnetic relaxation is the last candidate to account for the observed T_1 relaxation. These T_1 measurements have been carried out on cells with surfaces of Cs/Rb-coated pyrex and bare pyrex, and at temperatures 4.2 K and 295K, suggesting that the observed linear pressure dependence is likely a general property of the paramagnetic wall relaxation regardless of the surface and temperature. We also present a model to explain the observed linear pressure dependence by taking into account the diffusion of the spins. This new model also resolves the discrepancies between theories and experiments found in [8, 9] and explains a recent finding that polarization and T_1 are enhanced by adding ^4He into the cell [10].

The T_1 measurements at 295 K and 4.2 K were carried out using the Free Induction Decay (FID) technique. ^3He was filled and refilled in 48 mm OD spherical detachable cells to 1 or 2 atm, using a $^3\text{He}/\text{N}_2$ gas handling system. The detachable cell was made of Rb-coated pyrex and had an O-ring valve connected to it through a capillary pyrex tubing with an i.d. of 1.5 mm and a length of 18 cm to restrict gas exchange between the valve and the cell, so that the depolarization from the valve was minimized. The detachable cells were always polarized at either 1 or 2 atm, and then diluted to different pressures (0.025 to 0.43 atm) using different dilution volumes. The pressure in the detachable cell was monitored by a pressure gauge connected between the volume and the cell.

In the 4.2 K experiment, we measured T_1 of ^3He in cylindrical pyrex cells immersed in liquid ^4He stored in a dewar. The cylindrical cell had an i.d. of 8 mm and a length of 25 mm. The top of the cell was attached to a thin pyrex tube with an i.d. of 3 mm and a length of 68 cm. The other side of the tube was connected to an O-ring valve outside the dewar, where the detachable cell is mounted. A gas flow restriction (0.8 mm i.d. and 3 mm long) was added to the connection point between the tube and the cell to minimize the gas exchange between them. A dilution volume was also connected for diluted T_1 measurements, similar to the 295 K measurement. After dilution, the remaining polarized ^3He gas in the detachable cell was allowed to diffuse into the cylindrical cell. The pressure in the cylindrical cell can be varied from 6.4×10^{-4} atm to 0.19 atm. Four cylindrical

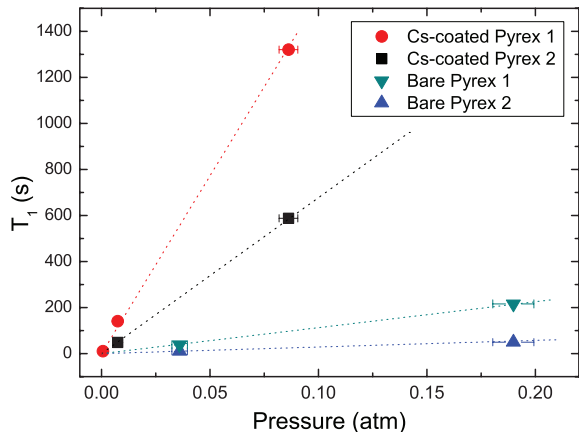


FIG. 1: (Color online) T_1 of ^3He in four cylindrical cells at 4.2 K. Two cells are made of bare pyrex (up-triangle and down-triangle) and the other two are made of Cs-coated pyrex (square and circle).

cells with identical dimensions but different surfaces (two bare pyrex and two Cs-coated pyrex) were used.

The 295 K T_1 measurements were carried out at 39.5 kHz using a homemade FID polarimetry and also at 24 kHz using a commercial polarimetry made by Amersham Health; whereas the 4.2 K measurements were performed at 12 kHz, using Superconducting QUantum Interference Device (SQUID) manufactured by StarCryo. While the 39.5 kHz FID polarimetry has a higher signal-to-noise ratio than the 24 kHz polarimetry, the RF noises from its pre-amplifier are bigger. In all FID measurements, a small tipping angle, resulting in about 1% polarization loss, was applied. This loss was subtracted when extracting T_1 from the data. Two different Helmholtz coil pairs were used and the field gradients were measured to be < 2.3 mG/cm for the 295 K measurement and < 2.2 mG/cm for the 4.2 K measurement. The gradient induced T_1 was more than one thousand hours [5], and was negligible compared to the measured T_1 . The dipole-dipole induced T_1 was calculated [4, 11], and subtracted from the measured T_1 values. Hence, all T_1 s shown below are due to wall relaxation only.

At 4.2 K, when the pressure of the gas is reduced, T_1 decreases proportionally (Fig. 1). From a linear fit of the data (dashed lines), it clearly shows that all the fitted lines pass through the origin, which suggests $T_1 \propto p$. For bare pyrex cells, the minimum T_1 we measured is 10.1 ± 0.3 s at 3.6×10^{-2} atm. If the pressure is further reduced, T_1 becomes so short that a complete T_1 measurement becomes difficult. Cs coating helps increase T_1 by more than two orders of magnitude. This allows the pressure to be further reduced to 6.4×10^{-4} atm. However, even with Cs coating, T_1 at this pressure is only 10.4 ± 0.6 s (the first solid circle in Fig. 1). Therefore, at low pressure, the pressure dependent T_1 relaxation at 4.2 K is the dominant relaxation mechanism.

At 295 K, the Rb-coated detachable cells have T_1 on

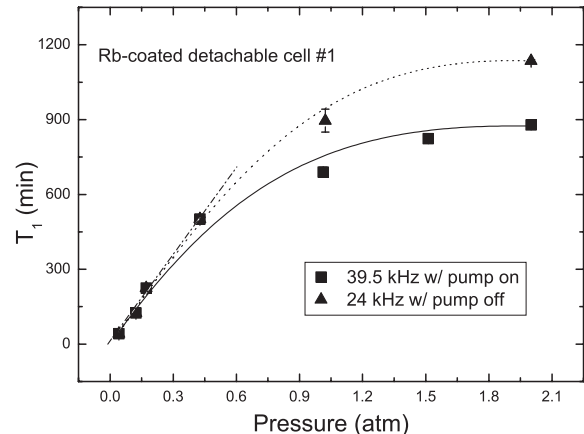


FIG. 2: T_1 of ^3He in the Rb-coated detachable cell at 295 K. The dashed line is the linear fit to the first four data points below 0.43 atm. The dotted line is the fit using Eq. (2) to the four square points below 0.43 atm and the two triangles points. The solid line is the fit using Eq. (2) to all the squares.

the order of tens of hours. This makes the low pressure T_1 measurement easier and also enables us to access the T_1 -pressure relationship for a different surface and temperature in addition to the 4.2 K data. The detachable cells have never been exposed to fields higher than 30 G. Measurements of T_1 have been done to cells before and after degaussing using a commercial demagnetizer, and no changes have been seen within experimental uncertainties. The first detachable cell has $T_1 = 690 \pm 21$ min at 1 atm using the 39.5 kHz polarimetry. When the ^3He pressure is reduced to below 0.43 atm, the measured T_1 exhibits a linear pressure dependence (Fig. 2). By fitting the first four points linearly (dashed line), ranging from 0.042 to 0.43 atm, it yields $T_1 = 1188 \times p$ min. This linear dependence does not hold when the pressure is above 0.43 atm, and T_1 at 2 atm does not change too much from T_1 at 1 atm. This clearly indicates that some other relaxation mechanisms, which are negligible at low pressure, become important at high pressure since the paramagnetic relaxation becomes less pronounced with increasing pressures. In a different experiment, we observed that the continuous RF noise broadcasted by the RF amplifier rendered polarization loss during the T_1 measurement [12]. In this experiment, a mechanical pump and a turbo pump were used to maintain the vacuum of the dilution volume throughout the experiment. We indeed observed that the background noise level in the pickup coil increased with the pumps running. Therefore, we repeated the non-diluted 1 atm and 2 atm T_1 measurements with all pumps off. The less noisy 24 kHz polarimetry was used in these measurements. The repeated measurements showed an increase of T_1 by roughly 200 min and 300 min at 1 atm and 2 atm, respectively. However, in the repeated measurements, T_1 still flattens out at 2 atm. As shown in [13], all their non-magnetized/demagnetized Rb-coated cells exhibit weak ferromagnetic relaxation be-

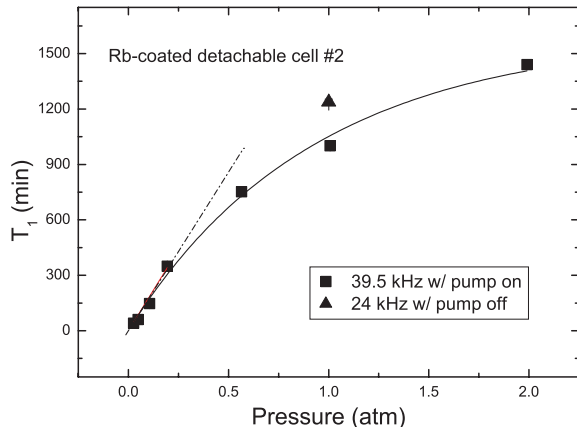


FIG. 3: T_1 of ^3He in the second detachable cell which has longer T_1 at 1 atm. The dashed line is the linear fit to the four data points with pressure below 0.25 atm. The solid line is a fit using Eq. (2) to all 39.5 kHz data labeled as squares.

havior. This leads us to believe that our cells are also subject to ferromagnetic relaxation to some extent. As ferromagnetic relaxation has an inverse pressure dependence $T_1 \propto 1/p$ [7], it is negligible at low pressures; whereas, at high pressures, it becomes more prominent and therefore comparable to the paramagnetic relaxation. This could explain the flattening behavior of T_1 . Hence, the measured T_1 relaxation can be attributed to three mechanisms, expressed as

$$\frac{1}{T_1} = \frac{1}{c_1 p} + \frac{1}{c_2} + \frac{p}{c_3}. \quad (2)$$

The first term is the paramagnetic wall relaxation, which depends on pressure linearly ($T_1 = c_1 p$); the second term is RF noise-induced relaxation, which has no pressure dependence ($T_1 = c_2$); the last term is the ferromagnetic relaxation, which inversely depends on pressure ($T_1 = c_3/p$) [7, 14]. Using Eq. (2) to fit the 39.5 kHz data in Fig. 2 (solid line), one obtains $c_1 = 1288 \pm 110$ min/atm, $c_2 = 2754 \pm 251$ min and $c_3 = 5082 \pm 1641$ min·atm. If the two repeated measurements together with the four data points below 0.43 atm were used for the fit (dotted line), c_2 changes to $c_2 \geq 10086$ min, indicating $1/c_2$ is zero within fitting errors. This suggests that the RF noise in the repeated measurements is negligible.

We also tested another Rb-coated detachable cell, which has a longer T_1 at 1 atm ($T_1 = 1001 \pm 11$ min), measured by the 39.5 kHz polarimetry. This cell also shows the linear pressure dependence with pressure below 0.25 atm (Fig. 3); and beyond this pressure, T_1 starts to flatten out as well. Fitting the data to Eq. (2) yields $c_1 = 1757 \pm 71$ min/atm, $c_2 = 2959 \pm 362$ min and $c_3 \geq 10113$ min·atm. c_2 of this cell is comparable to c_2 of the first one as expected, since the RF noise-induced T_1 should be independent of which cell is used. Both c_1 and c_3 are larger than those of the first cell, which suggests that both paramagnetic and ferromagnetic wall relaxations of the second cell are weaker than those of the

first one. The 1 atm T_1 was also measured using 24 kHz polarimetry with all pumps off. T_1 in this case increases by roughly 236 min.

Once ferromagnetic wall relaxation and RF noise-induced relaxation are excluded, the T_1 relaxation measurements at both 295 K and 4.2 K clearly show the linear pressure dependence, which is contradictory to Eq. (1). The derivation of Eq. (1) implicitly assumes ballistic collisions between spins and the wall, which is only true when spins are in the vicinity of the wall. When far away from it, spins move in a diffusive manner. Hence, the effective speed, at which it moves to the wall, is much slower than its thermal velocity. As majority of the spins are not close to the wall, a more appropriate model to describe the wall relaxation should take into account the diffusion process. In [15], Chupp *et al.* used the diffusion equation to calculate the spatial distribution of ^3He polarization inside a high pressure double cell system. We will also use the diffusion equation, together with depolarizing boundaries, to describe the surface relaxation of ^3He . It should be noted that ferromagnetic relaxation does not fit into this surface relaxation model because it happens not only on the surface but also in the vicinity of the surface. Since ferromagnetic impurities produce much stronger dipole field than paramagnetic impurities, spin can be depolarized even it does not have a contact with the surface. In other words, ferromagnetic relaxation actually occurs in a region adjacent to the surface impurities. In the strong collision limit of the ferromagnetic relaxation, the dipole field is so strong that the adjacent relaxation region extends to the entire cell. In this case, the relaxation rate converges to the gradient-induced relaxation [7, 14].

Let $\rho(r, t)$ represent the polarization of ^3He gas inside a spherical cell as a function of position r measured from the center of the cell and time t . The diffusion equation of the polarization ρ is written as

$$D\nabla^2 \rho = \frac{\partial \rho}{\partial t}, \quad (3)$$

where D is the diffusion constant of ^3He gas. Since spins lose their polarization only at the surface with probability α , the boundary condition is written as

$$\left. \frac{\partial \rho(r, t)}{\partial r} \right|_{r=0} \neq \infty \quad (4)$$

$$\left. \frac{\partial \rho(r, t)}{\partial r} \right|_{r=R} = -\alpha \rho(R, t), \quad (5)$$

where R is the radius of the cell. The solution is

$$\rho(r, t) = \sum_{k=1}^{\infty} A_k j_0\left(\frac{x_k r}{R}\right) \exp\left(\frac{-x_k^2 D t}{R^2}\right), \quad (6)$$

where j_0 is the zeroth order spherical Bessel function, x_k is the k^{th} root of Eq. (5), which can be re-written as

$$x_k j_0'(x_k) + \alpha R j_0(x_k) = 0, \quad (7)$$

and A_k is determined by

$$A_k = \frac{\int_0^R \rho(r, 0) j_0\left(\frac{x_k r}{R}\right) r^2 dr}{\int_0^R j_0^2\left(\frac{x_k r}{R}\right) r^2 dr}. \quad (8)$$

Since terms other than $k = 1$ vanish quickly, only $k = 1$ term contribute to the polarization and T_1 is written as

$$1/T_1 = \frac{x_1^2 D}{R^2} \propto \frac{x_1^2}{n R^2} \propto \frac{x_1^2}{p R^2}. \quad (9)$$

The second and third proportionalities use the fact that $D \propto 1/n \propto 1/p$. Therefore, the paramagnetic wall relaxation rate $1/T_1$ does not only depend upon the depolarization probability α (implicitly through x_1) but also on the diffusion constant D . Chen *et al.*[10] found that T_1 of their ^3He cells are increased by filling ^4He into the cell. This can be explained by the decrease of ^3He diffusion constant due to the presence of ^4He in the cell. It should be noted that Eq. (3) can also be used in situations other than pure ^3He gas, for instance ^3He in superfluid ^4He . In this case, D is the diffusion constant of ^3He in superfluid ^4He [16, 17], so Eq. (3) and the following arguments are still valid. Another observation on Eq. (9) is that $1/T_1$ has a quadratic dependence on the surface-to-volume ratio, $1/T_1 \propto 1/R^2 \propto (S/V)^2$ (spherical cell). This quadratic dependence, instead of the linear dependence in Eq. (1), suggests that surface to volume ratio has bigger influence on paramagnetic relaxation T_1 than it is previously believed.

Low pressure cells (a few torr) used in Metastability Exchange Optical Pumping (MEOP) have been reported to have long T_1 from several hours to tens of hours [18–21]. These include both valved cells and permanently sealed cells; and they are usually made of aluminosilicate glass or Cs-coated pyrex with much better glass cleaning process than what we did to our detachable cells. No apparent pressure dependence was observed in the valved MEOP cells, except that, at low enough pressures, the gradient-induced relaxation dominates. This seems to be inconsistent with the pressure dependence we observed. However, these cells usually have hundreds or even thousands of hours of T_1 at 1 atm, considerably longer than our cells (less than 20 hours). Rather than the paramagnetic relaxation, T_1 of those MEOP cells are likely dominated by other relaxation mechanisms, such as the ferromagnetic relaxation and the dipole-dipole relaxation.

T_1 of ferromagnetic wall relaxation has an inverse linear pressure dependence in the weak collision limit, de-

defined as $\omega_0 \tau \ll 1$, where ω_0 is the spin precession frequency and τ is the interaction time of spin with a magnetic site on the surface [7, 14]. In the strong collision limit ($\omega_0 \tau \gg 1$), T_1 becomes linearly dependent on pressure, which in fact can be understood by the gradient-induced relaxation [7]. As the experimental conditions of both 4.2 K and 295 K measurements are clearly not in the strong collision limit which requires large ferromagnetic site on the surface, and our cells have never been exposed to high fields, the observed pressure dependence cannot be explained by the ferromagnetic relaxation in the strong collision limit.

Chapman and Richards [8] also observed the linear pressure dependence of T_1 in ^3He at 4.2 K. They use Eq. (1) to describe their findings and the pressure dependence was ascribed to the pressure dependence of α using a two-phase model with ^3He in the absorbed phase with a shorter T_1 when a complete monolayer was formed on the surface, and ^3He in the bulk phase which has much longer T_1 . However, this two-phase picture cannot explain the pressure dependence seen in the experiment by Lusher *et. al.* [9], in which only a partial monolayer was formed. The binding energies W between ^3He spin and a specific surface determines when a complete monolayer will be formed. For bare pyrex glass, the binding energy is around 100 K [9]. For Cs and Rb-coated cells, the binding energy are 2.3 K and 2.8 K [22, 23], respectively. In our 4.2 K measurement, for sure a complete monolayer of ^3He is formed on the bare pyrex; whereas, in the Cs-coated cell, it is certain that only a partial monolayer is formed. As the pressure dependence is observed in both cases, it further demonstrates that Eq. (1) and the two-phase picture are inadequate to describe the experimental data, and the diffusion process is essential to the wall relaxation.

In summary, we conclude that the linear pressure dependence observed in our T_1 measurements is associated with the paramagnetic wall relaxation. This pressure dependence originates from the diffusion process of ^3He spins and can be well described by the diffusion equation. It also suggests that it is vital to control the paramagnetic wall relaxation when the diffusions are fast.

We thank J. Rishel for making all the cells reported in this work, and Tom Gentile, Jian-guo Liu and Mike Snow for helpful discussions. This work is supported by the U.S. Department of Energy under contract number DE-FG02-03ER41231 and Duke University.

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