Wall Relaxation of ^{3}He in Spin-Exchange Cells

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The ^{3}He longitudinal spin-relaxation rate T_1^{-1} is crucial for production of highly polarized ^{3}He by spin-exchange optical pumping. We show that T_1^{-1} is increased by a factor of 2–20 solely by exposure of spin-exchange cells to a few-kG magnetic field. The original T_1^{-1} can be restored by degaussing the cell. The effect is attributed to magnetic surface sites and has been observed in both Pyrex and aluminosilicate-glass cells. Our results both advance the understanding of wall relaxation and demonstrate the use of ^{3}He as an extremely sensitive probe of surface magnetism.

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Large nonequilibrium nuclear polarizations can be obtained in certain noble-gas isotopes by spin exchange with an optically pumped and polarized Rb vapor [1]. Polarizations $O(0.1)$ are routinely achieved for liter quantities of ^{3}He and ^{129}Xe at 350–450 K in applied magnetic fields $B_0 = O(10)$ G. These hyperpolarized (HP) gases have been studied and applied in diverse scientific realms [2–4], perhaps most dramatically as the signal source in magnetic resonance imaging (MRI) of the lung air space [5]. Indeed, we are concerned here with HP ^{3}He as prepared for most MRI experiments, where one requires large ($\geq$40 cm^3) valved glass vessels (cells) which can be repeatedly polarized, emptied, and refilled with ^{3}He to pressures approaching 10 atm.

The production and subsequent storage of highly polarized gas depends crucially on the nuclear spin-lattice relaxation rate T_1^{-1}, which shorts out the delivery of angular momentum by Rb-^{3}He spin exchange. Since the characteristic spin-exchange time for Rb-^{3}He is at least several hours [6], a stable T_1 of many tens of hours is required to generate and preserve substantial magnetization. T_1^{-1} is usually dominated by interactions with the cell surface (wall relaxation). Bulk relaxation from ^{3}He-^{3}He collisions [7] also contributes at sufficiently high pressure (greater than several atm). Despite decades of research, relatively little is known about the nature of ^{3}He wall relaxation at most surfaces. This has generally led to irreproducibility in cell fabrication. Several types of glass have been tried with varying degrees of success [8–10], but documented fabrication protocols yielding consistent results are generally lacking, especially for large-volume valved cells.

In this Letter we present evidence that magnetic sites, showing remanence and hysteresis, significantly affect, if not dominate, wall relaxation in spin-exchange cells. We demonstrate that large reversible changes in T_1^{-1}, and hence in the corresponding surface relaxation sites, are induced in such cells solely by exposing them to a large (10 kG) magnetic field and that this effect (termed "T_1 hysteresis") is correlated with the presence of Rb in these cells. The presence of Rb is also strongly correlated with reduced wall relaxation rates (by as much as an order of magnitude) compared to bare-wall glass cells. Our results represent the first explicit evidence of the nature of a surface-relaxation mechanism for ^{3}He in spin-exchange cells. Further study of this mechanism will likely yield vital information for the efficient and reproducible production of highly polarized ^{3}He by spin exchange.

Our valved Pyrex cells have 10 cm of 0.5–1.0 mm i.d. capillary separating the valve (glass stem with O-rings) from the $\approx$50 cm^3 main chamber. Each cell was attached to a glass manifold and baked (except for the valve) under high vacuum (base pressure 2×10^{-8} Torr) for 2–4 days at $\sim$400 °C. Rb metal (100–300 mg; >99.93% pure) was then distilled in prior to flame sealing each cell under vacuum from the manifold. A separate gas-handling system was used to fill and refill the cells with ^{3}He to 8 atm at room temperature [11]. A sidearm protruding from the valve body, normally used for gas filling and dispensing, defines two physical orientations of a cell with respect to an applied magnetic field; these are termed "north" and "south" according to whether the sidearm points to the north or south pole of the magnet.

All relaxation measurements were made at room temperature using 100 kHz NMR detection at $H_0 \approx 30$ G [12]. Very low flip angles were used to generate large-amplitude free induction decays (FIDs) with negligible loss of longitudinal magnetization. The initial height of the FID was recorded as a function of time and fit to an exponential decay to extract T_1^{-1}.

The basic experimental sequence consisted of three pairs of T_1^{-1} measurements made with the cell oriented north and then south (or vice versa). Each measurement pair was made with no intermediate removal of the cell from the 30 G field, no heating, and no exposure to laser light; the cell was simply rotated 180° about its capillary axis and a new T_1^{-1} measurement was initiated. The first pair was performed after the cell was fabricated and filled for the first time (before any exposure to high field); the second

pair was done after the cell was magnetized north or south, i.e., exposed for ≈30 sec to the 10 kG field of an iron-core electromagnet in the specified orientation (N.B., the word "magnetize" here refers to the cell walls and not to the ^{3}He spins); the third pair was made after the cell was degaussed. A magnetized cell is degaussed by rotating it at ≈1 Hz about the capillary axis in the field of the electromagnet as the field is gradually lowered from 10 kG to the electromagnet's remanent field (≈30 G). The rotation is maintained as the cell is slowly withdrawn from the magnet. The second and third pairs of measurements were repeated after magnetizing the cell in the opposite cell orientation.

We have performed this sequence of measurements on 20 cells. All cells we have examined show significant and consistent increases (factors of 2 to 20) in wall relaxation rate due solely to exposure to the 10 kG field. All cells previously exposed to the 10 kG field show a nearly complete restoration of the original relaxation rate after being degaussed. In addition, all magnetized cells show a consistent dependence of T_1^{-1} on physical orientation (north or south) in the 30 G field; this change is typically 20%, but factors of 2–3 have been observed. Cells that have been magnetized north (south) at 10 kG have a larger T_1^{-1} oriented north (south) with respect to the 30 G measurement field. These results are reproducible over several exposures to the 10 kG field, several degaussing procedures, several refills with ^{3}He, and several repolarizations. Figure 1 is a plot of relaxation rate vs chronological history of magnetic-field exposure for a single representative cell demonstrating all of the described effects. The initial

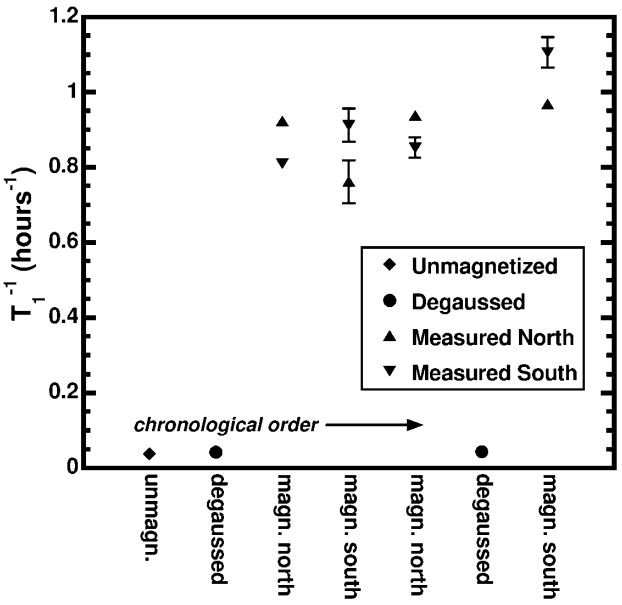

FIG. 1. Relaxation rate at 30 G is plotted vs the chronological history of intervening exposure to a 10 kG field for a single cell. The cell was both magnetized and measured in each of two physical orientations, labeled "north" and "south." Mere exposure to the large field increased the rate by about 20 times. Rates were slightly greater when the magnetizing and measuring fields were in the same direction with respect to the cell's orientation.

lifetimes vary among the cells from tens of minutes to tens of hours, but the qualitative behavior shown in Fig. 1 is the same for all.

We performed a number of checks to confirm that high-field exposure is the sole and direct cause of the change in T_1^{-1} observed before and after magnetizing or degaussing a cell. For most cells, several measurements are possible without need of repolarizing the gas. In many cases, all that transpires between radically different T_1^{-1} measurements at 30 G is that a cell is transported in a portable solenoid back and forth from the 30 G Helmholtz coils to the electromagnet in order to be exposed to the 10 kG field. We have verified that a partial or sloppy degaussing procedure (e.g., slowly removing the rotating cell from the magnet without turning down the field) only partially restores the original T_1^{-1}. One of us (J. C. L.) has observed T_1 hysteresis in two valved Pyrex cells fabricated and filled using a different glass blower, vacuum system, and filling system. The effect has also been observed unambiguously in two aluminosilicate-glass cells, one of GE-180 (General Electric) and one of 1720 (Corning). The 1720 cell is a sealed 8 cm^3 spherical cell containing 3.5 atm ^{3}He (at 295 K) and has no valves or capillaries; it was prepared at NIST (courtesy of T. R. Gentile and G. L. Jones).

Our results point to the existence of magnetic sites at or near the glass surface of our spin-exchange cells. These sites are a major source of wall relaxation for cells exposed to fields greater than several hundred Gauss. This conclusion is supported by the data in Fig. 1, which shows that wall-relaxation rates T_1^{-1} in our cells have all of the basic characteristics of magnetic hysteresis, including remanence, orientation dependence, and the ability to be degaussed.

Previously, wall relaxation has almost always been ascribed to isolated paramagnetic impurities at or near the surface [8,13], but such a mechanism has never been explicitly experimentally demonstrated. Surface paramagnetism may well dominate relaxation in bare-wall cells, but it would not show the hysteresis, reversibility upon degaussing, and orientation dependence of T_1^{-1} that we observe in our Rb-coated cells. The large fractional change in T_1^{-1} for cells with a broad range of initial lifetimes (tens of minutes to tens of hours) suggests that the size and/or concentration of magnetic sites may be responsible for the wide variation in relaxation rates that is often observed with spin-exchange cells. Indeed, the data in Fig. 1 actually understate the effect of T_1 hysteresis on many of the cells with longer initial lifetimes, since these also have a significant bulk contribution to the wall rate (about 0.01 h^{-1} at 8 atm [7]), regardless of whether the cell is magnetized.

When a cell is first fabricated and Rb distilled in, the domains in each magnetic site are randomly oriented, or perhaps slightly aligned. Exposure to the 10 kG field aligns the domains and produces a large enhancement of the magnetic moment of each site. A remanent magnetization exists in the cell after it has been removed to 30 G, where an increased T_1^{-1} is then measured. When the domains are

randomized by degaussing, the magnetic moment of each site is reduced, and T_1^{-1} returns to its original value. We propose that the ^{3}He spins relax by interacting with these sites while diffusing near the cell surface. We assume N sites having magnetic moment μ and radius R. In the weak-collision limit [14], where the interaction time τ is much shorter than the ^{3}He Larmor period at 30 G, the longitudinal relaxation rate for one site is $M_2\tau$, where the second moment $M_2 \approx (\gamma\mu)^2/R^6$. Using $\tau = R^2/6D$, where D is the diffusion coefficient, we obtain for the whole cell

$$\frac{1}{T_1} = \frac{N\pi\gamma^2\mu^2}{9RDV}, \qquad (1)$$

where γ is the ^{3}He gyromagnetic ratio, V is the cell volume, and we have factored in the fraction of spins interacting with sites ($\approx 2\pi R^3 N/3V$). This analysis assumes that the mean free path λ for ^{3}He atoms is much smaller than R ($\lambda \approx 24$ nm at 8 atm [15]).

Equation (1) suggests a linear pressure dependence of T_1^{-1} through $1/D$. We have investigated this dependence by measuring T_1 after each of several releases of a known quantity of polarized gas from the cell. Prior to each measurement, the capillary entrance to the cell was blocked by maneuvering a small bead of Rb metal over the opening. Our results from one cell supporting the weak-collision theory are shown in Fig. 2. By contrast, the limit $\tau \gg (\gamma B_0)^{-1}$ would produce an inverse linear dependence on pressure [16]. An upper limit on R can thus be calculated from $R^2 = 6D/\gamma B_0$ and yields $R = 15$ μm for ^{3}He at 8 atm and 30 G, where we have used $D = 0.23$ cm^2/s [17]. Since R must be at least several times λ (or else there is no pressure dependence whatsoever), we place a lower limit on R of ≈ 0.1 μm.

For example, if the sites were metallic iron (see below), and we use $V = 50$ cm^3, $R = 0.25$ μm, and a magnetized T_1 of 5 h, we obtain $N = 4 \times 10^4$ sites. Here, we have used the density of iron to obtain an estimate of 5.6×10^9 atoms per site and have assumed that each atom contributes one Bohr magneton at full magnetization. This number of atoms is reasonable for producing the multidomain structure necessary to generate T_1 hysteresis.

Our hypothesis for the cause of the orientation dependence is that the 30 G measurement field causes a slight deviation from the zero-field remanent magnetization of the cell, thus slightly increasing or decreasing the magnetic moments (and hence relaxivity) of the sites. The orientation dependence of T_1^{-1} we observe at 30 G is consistent with this picture in all cells we have tested.

We have also investigated the dependence of wall relaxation and T_1 hysteresis on the presence of Rb in the cell. Two additional cells, otherwise identical to the others, were prepared using the same protocol except that Rb distillation was omitted. HP ^{3}He was transferred to these bare-wall cells from another room-temperature spin-exchange cell, and the measurement sequence described above was perfomed. The bare cells exhibited no T_1 hysteresis. We then remounted the cells to the high vacuum system and distilled in the usual amount of Rb so as to visibly coat most of the cell surface. Again, HP ^{3}He was transferred from another spin-exchange cell, and the standard measurement sequence was performed. Not only did T_1^{-1} decrease significantly after the introduction of Rb, but T_1 hysteresis was also observed; see Fig. 3.

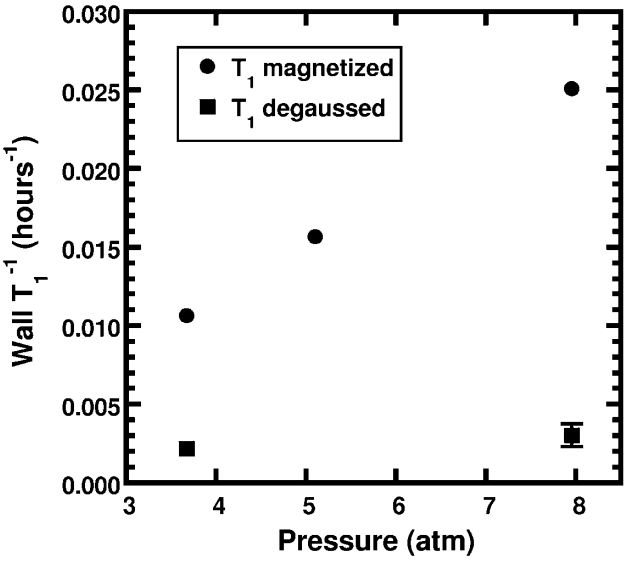

FIG. 2. The appropriate He-He relaxation rate has been subtracted from all data shown to yield the wall-relaxation rate as a function of pressure. The wall rate increases linearly with pressure when the cell is magnetized (supporting the weak-collision theory), but there is no pressure dependence after the cell has been degaussed.

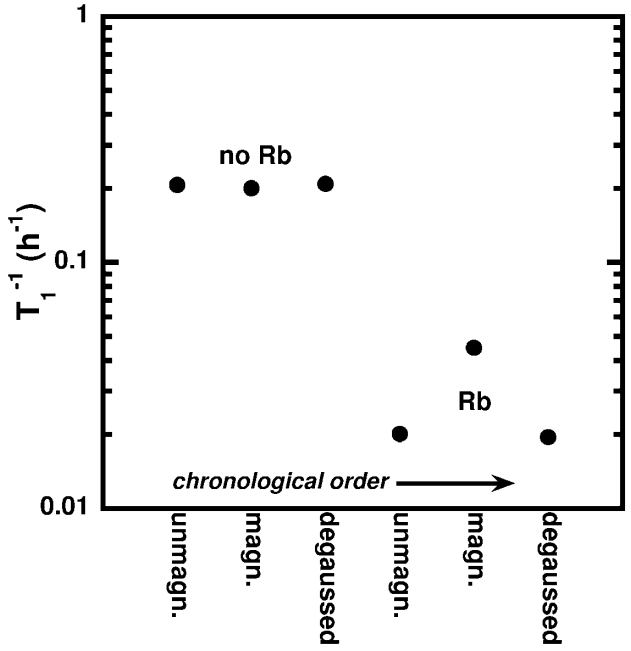

FIG. 3. Relaxation rate is plotted vs the chronological history of preparation of a single cell. This cell was tested before and after introducing Rb metal. For all measurements, hyperpolarized ^{3}He was transferred in from another spin-exchange cell. Rb both greatly reduces the wall relaxation rate and gives rise to T_1 hysteresis.

The data of Fig. 3 suggest that the presence of Rb both inhibits wall relaxation and gives rise to T_1 hysteresis. The former conclusion is in line with earlier work [8,18], and we have confirmed the effect using the same cell, thus reducing uncertainties associated with cell-to-cell variation. We can only speculate at present about how the Rb (itself or in a compound) beneficially affects the cell walls: it may, for example, chemically neutralize paramagnetic sites. It may also act as a physical barrier to surface sites or to helium permeation of the glass. It is further apparent that Rb plays a role in creating magnetic sites, perhaps by acting as a reducing agent on ionic iron impurities in the glass, catalyzing the formation of ferromagnetic iron oxides or metallic iron. Alternatively, the 1 g Rb ampules we use [19] have Fe, Ni, and Co impurities at the $\approx$10 ppm level, although these levels should be reduced by distillation. The characteristic applied field at which cells become magnetized is about 500 G, with saturation occurring at 1–2 kG—reasonable numbers for iron or iron oxide impurities. The bare-wall cells we measured had T_1's between 5 and 12 h, comparable to or longer than T_1's measured for most of the Rb-coated cells when magnetized. It is therefore not likely that the sites are resident initially in the glass and that the Rb is simply removing a more dominant nonhysteretic mechanism. We have initiated studies of Rb-coated Pyrex using ESR, SQUID, and the magneto-optical Kerr effect [20], in order to look for an independent confirmation of magnetic hysteresis as well as to better quantify the size, concentration, and chemical identity of the sites. Results so far are negative. However, we note that ESR and SQUID suffer from decreased filling factor compared with our measurements, which are exquisitely sensitive to the surface alone.

Our understanding of both T_1 hysteresis and the importance of the Rb coating has allowed us to make substantial progress toward reproducible fabrication of Pyrex spin-exchange vessels. Early research suggested that the helium permeability of Pyrex glass leads to large wall-relaxation rates [8]. More recently, Hsu *et al.* [21] showed that long T_1's were possible even for simple Rb-coated Pyrex. Pyrex remains attractive for spin-exchange cells despite its difficulties because it is rugged, inexpensive, ubiquitous, and easy to work compared with most other glasses. Most of our cells have $T_1 > 30$ h when degaussed. Several cells have $T_1 > 60$ h, from which one infers wall-relaxation times $>$150 h using the bulk relaxation rate at 8 atm [7]. Absent exposure to high field, we find these T_1 values to change very little as the cells are repeatedly heated to 160–180 °C, exposed to the 40 W laser, and repeatedly refilled with gas. We routinely produce ^{3}He polarizations $>$40% in these cells; they are robust and well suited to the MRI experiments for which they were designed.

We conclude that ^{3}He T_1 hysteresis is a robust, reproducible, and consistent effect which should be observable to some degree in almost all spin-exchange cells. The effect is observed only in the presence of the Rb needed for optical pumping and may be due to ferromagnetic impurities which are either in the Rb itself or are catalyzed by Rb at the glass surface. Our results suggest an approach to making reproducible spin-exchange cells that greatly narrows the search for effective fabrication techniques to those that are likely to affect the size, concentration, and magnetic moment of the sites responsible for this effect. Our results also demonstrate the first use of hyperpolarized ^{3}He as an extremely sensitive probe of surface magnetism.

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