Dipolar and scalar $^3$He-$^{129}$Xe frequency shifts in mm-sized stemless cells

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We describe a $^3$He-$^{129}$Xe comagnetometer operating in stemless anodically bonded cells with a 6 mm$^3$ volume and a $^{129}$Xe spin coherence time of 300 s. We use a $^{87}$Rb pulse-train magnetometer with co-linear pump and probe beams to study the nuclear spin frequency shifts caused by spin polarization of $^3$He. By systematically varying the cell geometry in a batch cell fabrication process we can separately measure the cell shape dependent and independent frequency shifts. We find that a certain aspect ratio of the cylindrical cell can cancel the effects of $^3$He magnetization that limit the stability of vapor-cell comagnetometers. Using this control we also observe for the first time a scalar $^3$He-$^{129}$Xe collisional frequency shift characterized by an enhancement factor $\kappa_{\text{HeXe}} = -0.011 \pm 0.001$.

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Atomic spin comagnetometers [1] are used in a number of precision fundamental physics experiments [2]. Recent efforts on miniaturization of atomic sensors [3, 4] have also led to the development of chip-scale systems for polarization of nuclear spins that have been used to search for new short-range spin-dependent forces [5] as well as for inertial rotation sensing [6–10], for magnetometry [11], and microfluidic NMR detection [12, 13]. These applications use mm-sized vapor cells containing alkali metals and noble gas isotopes with nuclear spins, such as $^{129}$Xe or $^{131}$Xe, which are polarized by optical pumping and spin exchange. The sensitivity in such experiments is determined by the nuclear-spin coherence time, which is often dominated by spin interactions with cell walls and is typically short in small cells that have a large surface-to-volume ratio. Here we demonstrate batch fabrication of stemless anodically bonded cells containing $^3$He and $^{129}$Xe with nuclear-spin coherence times of 4 hours and 300 s, respectively. This is a factor of 10 to 100 improvement in the $^{129}$Xe coherence time compared with prior results and the first detection of $^3$He signals in micro-fabricated cells.

Batch cell fabrication using anodic bonding allows for excellent control of the cell geometry. Typical glass blown or optically contacted cells have a glass stem for cell filling and sealing [8, 14]. Others have made stemless cells by allowing $^3$He to diffuse through quartz walls at a high temperature [15]. The cell shape affects the dipolar magnetic interactions between spin-polarized nuclei [16] that can cause significant frequency shifts in precision measurements using nuclear-spin comagnetometers [17] and are subject of some controversy [18]. Here we form cells using a silicon wafer with an array of 2 mm diameter drilled holes covered on both sides with anodically-bonded alumino-silicate glass plates. By making a slight wedge in the Si wafer we fabricate a number of cylindrical cells in one batch with varying height to diameter aspect ratios.

We systematically study the effects of nuclear-spin dipolar fields in a new regime where atomic diffusion is much faster than other time scales, unlike previous NMR experiments on liquids and gases [19, 20]. We find that for a certain cylindrical cell aspect ratio the average dipolar fields are eliminated, in good agreement with our theoretical analysis. An optimal and well-defined geometry will improve stability of nuclear-spin comagnetometers.

Control of long-range dipolar fields allows us to resolve a small scalar frequency shift between $^3$He and $^{129}$Xe nuclear spins mediated by a second-order electron Fermi-contact interaction. Such through-space $J$-coupling in van der Waals molecules has been theoretically studied in NMR [21, 23] and was first observed experimentally between $^{129}$Xe and $^1$H in a liquid mixture of Xe and pentane [24]. Here we report the first observation of spin-spin $J$-coupling between nuclear spins in the gas phase.

We use $^{87}$Rb to polarize the nuclear spins by spin-exchange and detect their spin precession with an in-situ $^{87}$Rb magnetometer [25, 26]. Rb experiences enhanced magnetic fields from nuclear spins due to spin-exchange collisions [27, 29], which gives a high signal-to-noise ratio in the comagnetometer. The pulse-train magnetometer described in [26] is adapted here for use with anodically-bonded cells having only a single optical axis by using counter-propagating pump and probe (Fig. 1a). After an initial pump time of 30-50 sec to polarize nuclear spins along the bias magnetic field $\hat{z}$, the polarization of the on-resonant 795 nm pump laser is switched between $\sigma^+$ and $\sigma^-$ light with an electro-optic modulator (EOM) at 13 kHz. Simultaneously 3 $\mu$s long magnetic field $\pi$ pulses are applied along $\hat{y}$ to flip the $^{87}$Rb polarization back and forth along $\hat{z}$. The high $\pi$ pulse repetition rate allows for spin-exchange relaxation suppression in the bias field $B_0 \approx 5$ mG [26]. The $^{87}$Rb polarization projection on $\hat{z}$ is detected with paramagnetic Faraday rotation of an off-resonant probe beam passing through the cell.
to a balanced polarimeter. An acousto-optic modulator turns on the probe laser only during the π pulses to avoid unnecessary probe broadening during pumping intervals. A constant $B_y$ field causes an advancement or retardation of the $^{87}$Rb polarization phase during the π pulse flip (Fig. 1b). The balanced polarimeter signal is sent to a lock-in amplifier referenced to half the EOM frequency giving a lock-in output proportional to $B_y$. We obtain a sensitivity of 300 fT/√Hz in our miniature cells, and are able to operate this scheme with $B_0$ parallel or perpendicular to the cell’s optical axis.

We make miniature vapor cells using an anodically bonded glass-Si-glass construction in a custom-built system able to fabricate cells containing isotopically enriched alkali metals and noble gases. The Si wafer is 2 mm nominal thickness with a 7 × 7 array of machined holes with a diameter $d = 2.005 ± 0.005$ mm. We polished one side of some wafers at a small angle to obtain a cell height variations of 1.666 mm to 1.988 mm. The wafer is baked under high vacuum inside the fabrication system to remove contaminants. We close the cells with 0.2 mm thick aluminosilicate glass SD-2 that has low $^3$He permeability. After anodically bonding glass on one side of the wafer, we distill 99.9% isotopically pure $^{87}$Rb metal and bond the second glass in an atmosphere of 80 torr N$_2$, 6.5 torr $^{129}$Xe, and 1400 torr of $^3$He. Heating during anodic bonding can cause buffer gas pressure loss in cells of up to 30%. A cryogenic storage system recovers the remnant buffer gas mixture for future use.

The dominant sources of $^{129}$Xe spin relaxation are collisions with cell walls and Rb-Xe collisions. Collisional Xe-Xe and magnetic field gradient relaxations are negligible. $^{129}$Xe is first polarized along a $B_0$ parallel to the optical axis by continuously pumping $^{87}$Rb. We can also polarize $^{129}$Xe with $B_0$ perpendicular to the optical axis by applying fast π pulses with $\sigma_+/\sigma_-$ pumping that give a time-averaged Rb polarization along $B_0$. A tipping pulse places the $^{129}$Xe spins perpendicular to $B_0$ and $^{129}$Xe precession and decay is detected with the pulse-train $^{87}$Rb magnetometer. A representative signal is shown in Fig. 2a. We fit the data to the function $A \exp(-t/T_2) \sin(\omega_{\text{Xe}} t)$. We measure the $^{129}$Xe $1/T_2$ as a function of cell temperature and Rb density as shown in Fig. 2b and extract a $^{129}$Xe wall relaxation time $T_w = 305 ± 5$ s. We check the $^3$He and $^{87}$Rb densities by measuring the Rb absorption spectrum of the probe laser. In this cell we find the Rb absorption FWHM of 23.4 ± 1 GHz corresponding to 1000 torr $^3$He. From the slope in Fig. 2b we find a Rb-Xe spin-exchange rate of $(7.8 ± 0.7) \times 10^{-16}$ cm$^3$/s in agreement with a calculation of the spin-exchange rate $7.2 \times 10^{-16}$ cm$^3$/s based on previously measured cross-sections. This indicates $T_w$ does not change significantly across our temperature range. The inset of Fig. 2 shows the Rb magnetometer can shorten $^{129}$Xe $T_2$ by causing a Rb polarization

FIG. 1. (a) Parallel pump-probe pulsed $^{87}$Rb magnetometer with one optical axis along $\hat{z}$. (b) An EOM square wave alternates $\sigma^+ / \sigma^-$ pump light and $\sigma_{\pm}$ pulses are applied to retain $^{87}$Rb polarization. We shutter the probe laser with an AOM to detect only $^{87}$Rb polarization transitions. Any extra $B_y$ field changes the $^{87}$Rb transition phase and is detected with a lock-in referenced to half the EOM square wave frequency.

FIG. 2. a) Spin precession signal from $^{129}$Xe at 73.3°C with $T_2 = 308$ sec. The inset shows a picture of the cell. b) The dependence of $^{129}$Xe $T_2$ on the Rb number density. The inset shows that at 120°C $^{87}$Rb pump light intensity and deviations of π pulse amplitude from optimal conditions shorten $^{129}$Xe $T_2$ due to Xe diffusion in a $^{87}$Rb polarization gradient.
gradient that $^{129}$Xe diffuses through. The additional relaxation depends on the $^{87}$Rb pump laser power and the accuracy of $^{87}$Rb $\pi$ pulses. We find that increasing the $^{87}$Rb $\pi$ pulse repetition rate reverses the Rb gradient more rapidly and decreases relaxation due to $^{129}$Xe diffusion. For accurate $T_2$ measurements we use proper $\pi$ pulses and low pump power.

We study magnetic dipolar interactions between $^3$He and $^{129}$Xe spins in the regime where atomic diffusion across the cell is much faster than the time scales of dipolar interactions and spin relaxation. Each spin-1/2 species has a uniform nuclear magnetization $\mathbf{M}$ inside the cell, unlike the regime typically studied in NMR [11, 39]. The spin precession frequencies are determined by the volume average magnetic field inside the cell, which can be calculated using the magnetometric demagnetizing factors $\langle H_i \rangle_V = -n_i M_i, (i=x,y,z)$ [39]. An analytical expression for $n_i(\gamma)$ was found for cylinder, where $\gamma = h/d$ is the height over diameter [37, 58]. The demagnetizing factors satisfy $n_x + n_y + n_z = 1$. For a cylinder with $\gamma = 0.9065$, $n_i = 1/3$, the same as for a sphere.

The classical average magnetic field needs to be corrected by separating out the contact term $2\mu_0\delta(t)\mathbf{m}/3$ of the dipolar field for a point dipole $\mathbf{m}$, which can be enhanced or suppressed depending on interactions between atoms that can be parametrized by $\kappa$ [39]. We write

$$\langle B_i^d \rangle_V = \mu_0 \left[M_i - n_i M_i + \frac{2}{3}(\kappa - 1) M_i \right]. \tag{1}$$

Spin precession in the presence of a constant bias field and small nuclear-spin dipolar fields is described by Bloch equations. In our case only $^3$He has a significant magnetization. The dipole field experienced by $^{129}$Xe can be written as $\langle B^d_{Xe} \rangle_V = \mu_0(1/3 - n_z + 2\kappa_{HeXe}/3)M_{He}^d$, where the $z$ axis is defined by the magnetic field direction. The rotating components of the $^3$He magnetization do not have a net effect on $^{129}$Xe precession frequency to first order in $M_{He}^d$. In contrast, the $^3$He precession frequency is affected by the secular co-rotating components of the $^3$He dipolar field but is not affected by the scalar contact interaction. One can write [40, 41]:

$$\frac{\langle B^{He} \rangle_V}{\mu_0} = \left(\frac{n_z}{2} - \frac{1}{6}\right)M_{He}^d + \frac{3}{2} \left(\frac{1}{3} - n_z\right)M_{He}^d \cdot \hat{z}. \tag{2}$$

The first term on the right hand side does not generate any frequency shift, since it gives $\langle B^{He} \rangle_V \parallel M_{He}$. The effective dipolar field responsible for a $^3$He frequency shift is given by the second term. It is 3/2 times larger than for $^{129}$Xe and both are proportional to the $M_{He}^d$ projection.

We study dipolar fields in our cells by first polarizing $^3$He for several hours and creating a small $^{129}$Xe polarization. We then apply a tipping pulse calculated to leave a certain percentage of $M_{He}$ along $B_0$ and place $^{129}$Xe magnetization in the transverse plane. Noble-gas precession signals are recorded in a Ramsey-style sequence for about 100 s, with two detection periods separated by a dark period that has a rotating, two-axis decoupling pulse train applied [26]. This decoupling pulse train removes noble-gas frequency shifts due to $^{87}$Rb back-polarization and nulls Bloch-Siegert shifts introduced by the pulse train. Each detection period is fit to two decaying sine waves to extract the phases with which the noble gases enter and leave the dark period. Knowing the number of cycles elapsed during the dark period, we find the in-the-dark free-precession frequencies of the noble gases $\omega_{He}$ and $\omega_{Xe}$. We divide $\omega_{He}$ and $\omega_{Xe}$ by their gyromagnetic ratios $\gamma_{He}, \gamma_{Xe}$ [42] to find the dipolar fields experienced by $^3$He and $^{129}$Xe due to the $\hat{z}$ projection of the $^3$He magnetization $M_{He}^d$. After the Ramsey measurement we place $M_{He}$ along or against $B_0$ by using dumping feedback [13]. We avoid systematic errors from $B_0$ drift and remnant $^{129}$Xe polarization projection onto $B_0$ by using identical tipping pulses while alternating the initial $M_{He}$ projection along $B_0$. $M_{He}$ is found by comparing the amplitude of the fitted $^3$He signal to the $^{87}$Rb magnetome-
ter response from a known magnetic field and dividing by \(2\mu_0\kappa_{RbHe}/3\) to account for Rb–\(^3\)He contact interactions. We neglect a 1% correction from the long-range dipolar effect of \(M_{He}\) on \(^87\)Rb. The Ramsey sequence is repeated for many \(M_{He}\) values and tipping angles to measure the slope \(B^d/\mu_0 M_{He}\).

We plot the effective dipolar field experienced by \(^3\)He and \(^{129}\)Xe due to \(M_{He}^2\) for a cell with \(h = 1.718\) mm, \(d = 2.005\) mm at 120°C in Fig. 3a. We repeat the measurements with \(B_0\) parallel and perpendicular to the optical axis of the cylindrical stemless cell. In Fig. 3b we plot the slope of the dipolar field \(B^d/\mu_0 M_{He}^2\) as a function of the cell aspect ratio \(h/d\) for several cells. Solid lines in Fig. 3 represent first-principles calculations of the dipolar fields using the expression for \(n_i(\gamma)\). The only free parameter is the value \(\kappa_{HeXe} = -0.011 \pm 0.001\), where the error is determined by \(M_{He}^2\) calibration uncertainty. The relative size of the long-range dipolar frequency shifts for the four cases are related to each other by simple ratios shown in Table I, which are applicable for any cell with uniaxial symmetry.

The existence of a finite \(\kappa_{HeXe}\) implies that the cell aspect ratio required to cancel the \(^3\)He magnetization effect on the frequency ratio in the comagnetometer is different from the condition \(n_i = 1/3\). Indeed, we find that for our cell with \(h/d = 0.857\), the comagnetometer frequency ratio \(f_r\), is insensitive within errors of \(M_{He}^2\) for \(B_0\) parallel to the cell axis, as shown in the bottom panel of Fig. 3. The temperature dependence of \(\kappa_{HeXe}\), shown in the inset of Fig. 3, is relatively weak. Operation of a \(^3\)He–\(^{129}\)Xe comagnetometer in a well-defined cylindrical cell with this aspect ratio will improve its long-term stability.

The contact spin-spin \(J\) couplings for noble gases have been calculated for \(^{129}\)Xe–\(^{131}\)Xe and for \(^3\)He. For spin couplings in gases and liquids with fast molecular motion it is more convenient to parametrize the interaction in terms of \(\kappa\) [21, 39]:

\[
\kappa = -\frac{3\pi}{\mu_0\gamma_1^2\gamma_2^2 h} \int 4\pi r^2 g(r)J(r)dr
\]

where \(g(r)\) is the radial intermolecular distribution function. For example, for the \(^{129}\)Xe–\(^{131}\)Xe calculation the low gas density limit can be obtained by considering two Xe atoms confined to a spherical cavity of a certain size [44]. It gives \(\kappa_{^{129}\text{Xe–}^{131}\text{Xe}} = -0.27\), which may give observable effects in \(^{129}\)Xe–\(^{131}\)Xe co-magnetometers [1]. The \(^{129}\)Xe–\(^1\)H contact interaction was measured and calculated in [21], \(\kappa_{^{129}\text{Xe–}^1\text{H}} = -0.0014\). The value of \(\kappa\) increases for heavier atomic pairs, as can be expected.

The cells fabricated for this experiment were used to test the comagnetometer and gyroscope performance of the system [20]. In a cell temperature operating at 120°C the Cramér-Rao frequency uncertainty lower bound using the best signal-to-noise ratio measured for \(^3\)He and \(^{129}\)Xe signals was found to be 0.005 deg/\(\sqrt{h}\). We also operated the comagnetometer for an extended period of time to determine its long-term stability. In Fig. 4 we compare the Allan deviation for the Ramsey-style sequence with active Rb depolarization and for continuous measurements with the Rb \(\pi\)-pulse train magnetometer. In both cases the frequency uncertainty is limited by the \(^3\)He frequency error due to low steady-state \(M_{He}\) at a temperature that allows for long \(^{129}\)Xe \(T_2\). Using cells with higher \(^3\)He pressure and the optimum aspect ratio would improve the performance.

In conclusion, we have demonstrated fabrication of miniature anodically bonded vapor cells containing \(^3\)He, \(^{129}\)Xe, \(^{87}\)Rb, and \(N_2\) with very long \(^{129}\)Xe and \(^3\)He coherence times. Precise control over the cell geometry allowed us to make detailed measurements of the long-range nuclear dipolar fields due to \(^3\)He magnetization in the regime of fast atomic diffusion, which are in good agreement with calculations. We observe a small but finite scalar interaction between \(^3\)He and \(^{129}\)Xe. As a result, the optimal cell shape for operation of a comagnetometer is different from a sphere.

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| \(^{129}\)Xe field | \(^{129}\)Xe theory | \(^3\)He field | \(^3\)He theory |
|-------------------|-------------------|----------------|----------------|
| \(B_0\) || 1 | 1 | 1.50 ± 0.02 | 3/2 |
| \(B_0\) ⊥ | -0.44 ± 0.03 | -1/2 | -0.72 ± 0.03 | -3/4 |

TABLE I. Relative size of the slopes \((B^d/\mu_0 M_{He}^2)/(h/d)\) from fits to Fig. 3 scaled to the \(^{129}\)Xe \(B_0\) || case.

FIG. 4. Allan deviation for continuous comagnetometer measurements and Ramsey-style sequence with active Rb depolarization in a batch-fabricated anodically bonded cell at 120°C.

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