Magnetic decoupling of ^{129}Xe nuclear spin relaxation due to wall collisions with RbH and RbD coatings

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Data are presented on the wall-induced nuclear spin-relaxation rate of ^{129}Xe in glass cells in which the interior walls are coated with either rubidium hydride (RbH) or rubidium deuteride (RbD). The relaxation rates have been measured as a function of both magnetic field ($0.08 < B < 1.0$ T) and temperature ($205 < T < 323$ K). Spin relaxation was observed to decrease significantly with increasing magnetic field in both RbH- and RbD-coated cells at all temperatures studied. At temperatures above roughly 250 K, there is strong evidence that relaxation is due to long-range dipolar interactions with paramagnetic sites.

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I. INTRODUCTION

The nuclei of the noble gases ^{3}He and ^{129}Xe can be polarized using spin-exchange optical pumping [1,2], and ^{3}He can also be polarized using metastability exchange optical pumping [3]. Improvements in the understanding of the underlying atomic physics as well as in laser technology have made it possible to polarize large quantities of noble gases for many useful applications, including both polarized nuclear targets [4–7] and magnetic resonance imaging of lungs [8,9]. An issue that is often important for both the production and storage of polarized noble gases is the minimization of spin relaxation at the walls of the container, often glass cells, within which the polarized noble gas is held.

Early in work with spin-polarized noble gases, the suggestion was made that the dominant source of spin relaxation due to wall collisions was interactions with paramagnetic sites (by this we mean something with a magnetic moment of the order of a Bohr magneton) [10]. Several decades later, however, the exact nature of those paramagnetic sites, or even a clear understanding of when paramagnetic sites are the dominant source of relaxation, is still the subject of active research. For example, data were presented on the temperature dependence of the spin relaxation of ^{3}He in borosilicate glass containers and were shown to fit well to a model based on the presence of (paramagnetic) Fe^{3+} ions [11]. Shortly thereafter a different study was published in which spin relaxation in similar glasses was shown to be largely independent of the concentrations of Fe^{3+} ions [12]. The authors of Ref. [12] argued that the relaxation was probably due to paramagnetic dangling bonds on the surface of the container walls, which can have strong effects because of Fermi contact interactions. In both cases, however, it is not entirely clear that relaxation due to something other than paramagnetic sites was completely ruled out. While most workers in the field would probably agree that paramagnetic sites are frequently if not usually the dominant source of wall-induced spin relaxation, it seems clear that a more thorough understanding of these effects is desirable.

There are important examples of wall-induced spin relaxation that are unrelated to paramagnetic sites. Driehuys *et al.* showed that in cells with silane coatings, ^{129}Xe relaxation was due not to paramagnetic sites but rather to dipolar interactions with the protons in the coating [13]. Silane coatings provide an important means for suppressing wall-induced spin relaxation of ^{129}Xe [14]. It has also been shown that ferromagnetic particles within the glass of the container walls, once magnetized by large fields, can cause spin relaxation of polarized ^{3}He [15]. The existence of well-established causes of wall-induced spin relaxation that are unrelated to paramagnetic sites underscores the value of establishing clean experimental signatures that can help distinguish between different mechanisms. The study of the magnetic decoupling of nuclear spin relaxation has played an important role in understanding the underlying physics of spin-exchange optical pumping [16] and was also used in the above-mentioned study of wall relaxation on silane coatings. In the work presented here we show that the magnetic decoupling of the spin relaxation of ^{129}Xe on RbH and RbD coatings provides strong evidence that spin relaxation is probably being caused by long-range dipolar interactions with paramagnetic sites.

We have studied both the magnetic-field dependence and the temperature dependence of wall-induced spin relaxation of ^{129}Xe in sealed glass cells in which the interior walls were coated with either rubidium hydride (RbH) or rubidium deuteride (RbD). Several factors caused us to choose to study RbH and RbD coatings. For example, RbH coatings have been shown to reduce wall-induced spin relaxation of ^{131}Xe [17]. Even though ^{131}Xe has a nuclear spin $I = \frac{3}{2}$ and relaxes, at least in part, through quadrupolar wall interactions [18], the studies described in Ref. [18] provide numerous insights that were useful background for the present work. More recently the nuclei of alkali-metal hydride (and other alkali-metal salt) coatings have been explored as targets for polarization transfer from optically pumped alkali-metal atoms [19]. Finally, and most importantly, we chose RbH and RbD because of a previously reported observation of a reduction in spin relaxation of ^{129}Xe (which has a nuclear spin $I = \frac{1}{2}$) with increasing magnetic field [20]. While the measurements described in Ref. [20] were limited in scope,

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the author speculated, we believe correctly, that he might have been observing a signature of relaxation due to paramagnetic sites. We believed that it would be worthwhile to undertake a careful study of these coatings, and performed measurements of the longitudinal spin relaxation rate $1/T_1$ of polarized ^{129}Xe gas over a broad range of magnetic fields and temperatures. We consistently observed magnetic decoupling in all our RbH and RbD cells for all temperatures studied, and for the reasons presented below, argue that the relaxation, at least at temperatures above roughly 250 K, is due mostly to dipolar interactions with paramagnetic sites.

II. EXPERIMENTAL TECHNIQUE

The measurements of $1/T_1$ for ^{129}Xe for our samples were performed using a custom-built pulse NMR system that included a set of 11 solenoidal probes. Each probe could be tuned and matched at one or two frequencies, could accept a spherical sample cell up to 2.5 cm in diameter, and could connect to a flowing-gas system that provided temperature control from roughly 205 to 323 K. We were able to make measurements at magnetic fields ranging from 0.08 to 1.00 T. The samples of ^{129}Xe were contained in sealed spherical Pyrex cells approximately 2.5 cm in diameter. Each cell contained roughly 7 amagats of xenon, approximately 200 Torrs of N_2, and in all but our control cell, a quantity of either H_2 or D_2. Once sealed, the cells were placed in an oven and allowed to cure at 80 °C for at least two weeks during which RbH or RbD would form on the inner surface of the glass.

Each measurement of $1/T_1$ began by polarizing the xenon using spin-exchange optical pumping. The cells were heated in an oven while in a holding field of roughly 1 mT, at approximately 95 °C while being irradiated with ∼40 W of light from two fiber-coupled high-power diode-laser arrays. The wavelength of the diode lasers was centered at 795 nm, and the linewidth of the lasers was roughly 2 nm. After 10–20 min the cells were removed from the oven and placed into one of the NMR probes which was fixed between the pole faces of an iron-core magnet. A measurement of $1/T_1$ consisted of five successive measurements of the relative polarization of the cell, each of which involved the application of an rf pulse, the observation of a free-induction decay (FID), and fitting the FID using a fast Fourier transform. At the beginning of a measurement of $1/T_1$, a series of quick pulses were applied to determine the "tip angle," and hence polarization loss, resulting from each rf pulse. The entire process, which we refer to as a "spin-down," was automated to ensure good reproducibility. An example of a spin-down is illustrated in Fig. 1.

Data were collected from each of five cells. Two of them, designated X12 and X16, were initially filled with 20 and 100 Torr of H_2 respectively, and thus had RbH coatings. Two more cells, designated D1 and D3, were initially filled with 80 and 20 Torr of D_2 respectively, and thus had RbD coatings. One cell, into which no hydrogen was introduced, was used as a control and is designated as cell X9. Data were typically collected during two types of studies. In a "magnetic-decoupling" study, in which the temperature was held fixed, $1/T_1$ was measured as a function of magnetic field. In a "temperature-dependence" study, in which the field was held fixed at 0.0824 T (corresponding to a resonance frequency

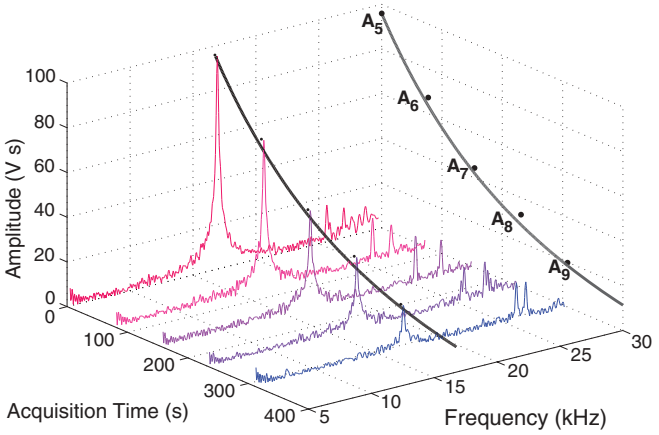

FIG. 1. (Color online) Data from a spin-down in which the longitudinal spin-relaxation rate $1/T_1$ of ^{129}Xe is measured by studying the fast Fourier transforms of five sequential free-induction decays. Also shown is a fit to the data.

for ^{129}Xe of 970 kHz), $1/T_1$ was studied as a function of temperature. Due to the many different values of temperature and magnetic field studied, and due to the fact that we typically repeated measurements for each set of conditions three or more times, the results presented here represent roughly 1000 spin-downs in all.

One of our concerns when beginning our studies was that the conditions in a particular cell would evolve with time, thus making it difficult to obtain reproducible data. When Wu *et al.* studied RbH surfaces in the work described in Ref. [18], they found that they could change their results by redistributing the rubidium in their cells through heating with a hand torch. Their measurements involved observations of Rabi precession in samples of ^{131}Xe that had been polarized using spin-exchange optical pumping. Their signal, which was proportional to the longitudinal polarization of the sample, would slowly oscillate and decay with time. The oscillations showed beats, however, that provided a measure of quadrupole interactions between the nuclei and the cell walls. After redistributing the rubidium, Wu *et al.* found that the beat frequencies could change by as much as a factor of 2. In contrast, however, they found that the relaxation rate would change by only around 25%.

Given that we were interested only in ^{129}Xe, which has no quadrupole interactions, and that the thermal cycling of our cells was going to be much less severe than would occur with a hand torch, we were hopeful that our samples would display reasonably stable behavior. This indeed turned out to be the case. For the plots shown in this paper, measurements of $1/T_1$ (for particular values of temperature and magnetic field) were typically repeated three or more times, and were generally separated in time as either the magnetic field or temperature was cycled through values of interest. The errors we assigned accounted for both the noise inherent in the spin-down itself as well as the scatter between repeated measurements, and were almost always under 5%. In Fig. 2 we show four magnetic decoupling curves for the cell X12, each of which was taken at the indicated fixed temperature. The smoothness of the field dependence makes it clear that the reproducibility was more than good enough to study the effects in which we were interested. We note, however, that the χ^2 for these fits

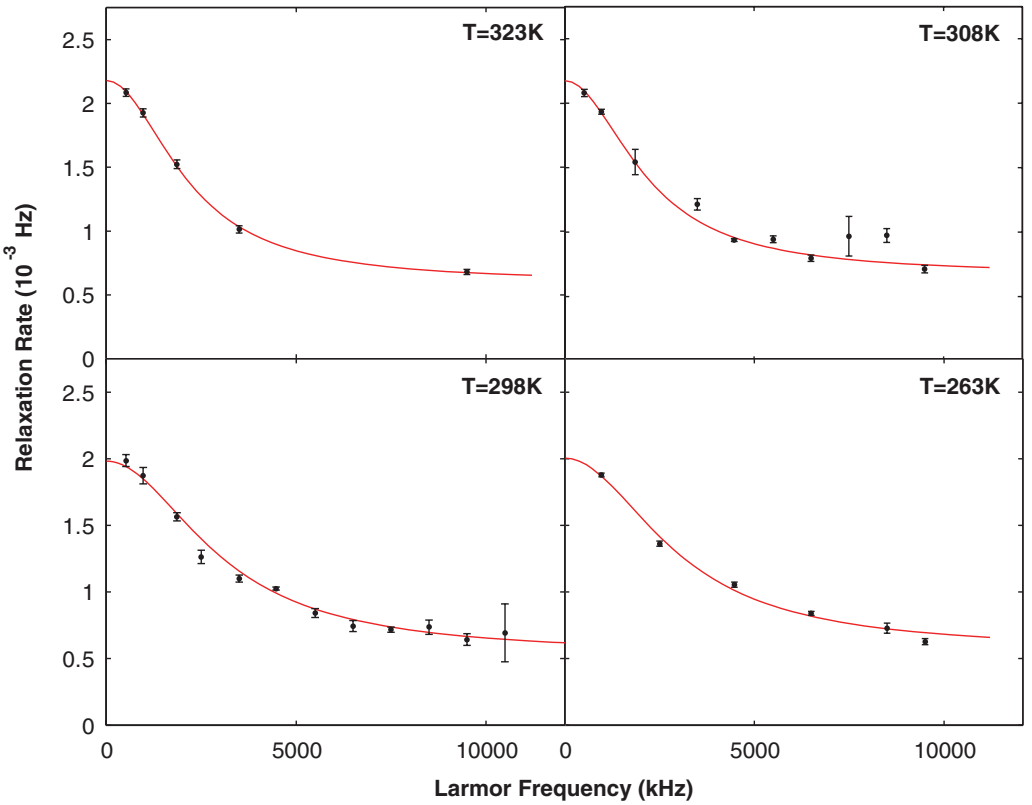

FIG. 2. (Color online) $1/T_1$ as a function of magnetic field and for cell X12, which has a RbH coating, for the four highest temperatures studied. Also shown are fits, discussed more in the text, to a single Lorentzian with a constant background.

suggests that the scatter of our measurements due to lack of reproducibility was perhaps slightly larger than indicated by our assigned errors. This is taken into account in the errors we quote for our fit parameters. It is clear that the reproducibility of our measurements was significantly better than was observed by Wu *et al*., but this is not surprising since our temperature cycling was far less drastic than would occur when redistributing the Rb using a hand torch.

III. OVERVIEW OF TRENDS IN THE DATA

There are two striking trends that appeared in all of our RbH and RbD cells. First and foremost, at every temperature studied, the spin-relaxation rate was observed to decrease with increasing magnetic field. As will be discussed more below, the details of this "magnetic decoupling" provide valuable insight into the microscopic relaxation mechanisms. Second, the spin relaxation showed very little temperature dependence above roughly 250 K, something we found quite surprising. Both of these trends are readily apparent in Figs. 3 and 4 in which all of our measurements from cells X12 (RbH) and D3 (RbD) are shown. We note that we use 250 K somewhat arbitrarily as a boundary separating different types of behavior mostly because it is a round number that falls between two of the temperatures at which we studied magnetic decoupling. Each figure shows the spin-relaxation rate $1/T_1$ as a function of both magnetic field and temperature. We have presented the data in these two figures in a manner that is intended to accentuate the different types of studies that were performed. For example, in Fig. 3, it can be seen that magnetic-decoupling studies were performed at each of seven fixed temperatures. At each temperature the data were fitted to a simple Lorentzian with a constant background (discussed more below). The results of each fit are shown with two-dimensional surfaces while the data themselves are shown with either solid circles or solid squares. For clarity, between adjacent temperatures, we alternate between circles and squares. As is readily apparent, strong magnetic decoupling was observed at all temperatures. In Fig. 3, where the overall spin relaxation was relatively slow

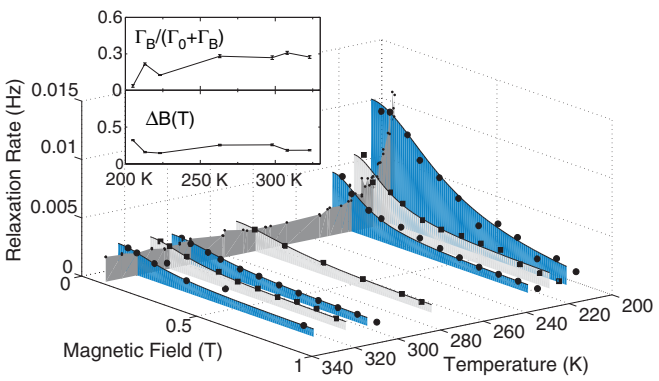

FIG. 3. (Color online) $1/T_1$ as a function of magnetic field and temperature for cell X12 which has a RbH coating. The fits to each magnetic-decoupling study are shown as two-dimensional surfaces. The inset shows the ratio of fit parameters $\Gamma_B/(\Gamma_0+\Gamma_B)$ (see the text) and the decoupling width ΔB as a function of temperature.

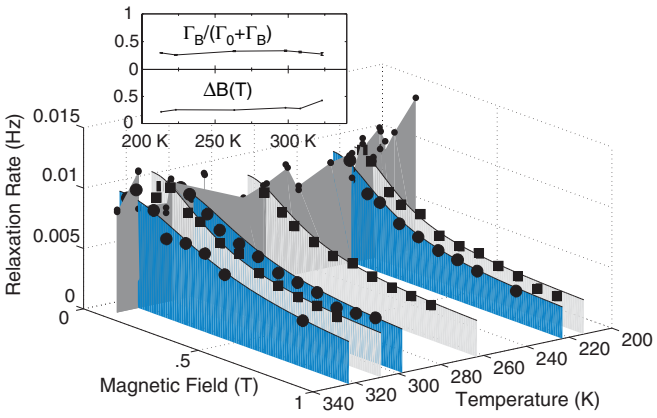

FIG. 4. (Color online) $1/T_1$ as a function of magnetic field and temperature for cell D3 which has a RbD coating.

for the four highest temperatures, it is difficult to clearly see the decoupling. In relative terms, however, the decoupling was just as pronounced, as can be seen by referring back to Fig. 2 where the four highest-temperature decoupling studies from cell X12 are each plotted separately.

The data from our temperature studies, for which the magnetic field was fixed at 0.0824 T, are plotted in Figs. 3 and 4 with small black circles. A two-dimensional surface illustrating the temperature studies is also shown, perpendicular to the surfaces representing the magnetic-decoupling studies. The surface illustrating the temperature studies is not a fit; instead the top of the surface corresponds to a line connecting the various measurements at different temperatures. In Fig. 3, for a given value of magnetic field, $1/T_1$ is fairly independent of temperature until T is below something like 250 K. In Fig. 4, the variation of $1/T_1$ with temperature is not very pronounced anywhere.

The behavior for our control cell, X9, was markedly different, as can be seen in Fig. 5. This cell was prepared with no hydrogen or deuterium. Thus, unlike our other cells in which the interior surfaces were presumably largely covered with either RbH or RbD, the interior surface of X9 was presumably covered with several monolayers of Rb [21]. In X9, for $T = 300$ K, no magnetic-field decoupling was

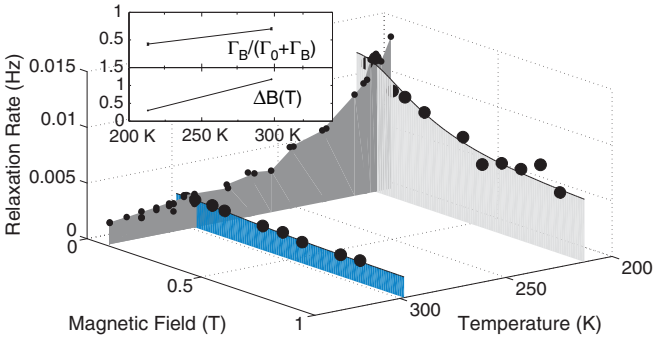

FIG. 5. (Color online) $1/T_1$ as a function of magnetic field and temperature for cell X9 which contained no hydrogen and was our control cell. Magnetic decoupling was clearly evident only at the lowest temperature measured. Also, in contrast to cells containing RbH or RbD, significant temperature dependence of $1/T_1$ was observed over the entire temperature range studied.

observed. Furthermore, in sharp contrast to cells X12, X16, D1, and D3, there was marked temperature dependence that was already quite observable just below room temperature.

IV. MAGNETIC-DECOUPLING STUDIES

To interpret our data quantitatively, we need to consider a specific model for the relaxation mechanism. One possibility is that the ^{129}Xe nucleus experiences a randomly fluctuating magnetic field due to long-range dipolar interactions with various spins that are at or near the surface of the container walls, a mechanism similar to that considered by Bloembergen, Purcell, and Pound within the context of spin relaxation in solids and liquids [22], and considered within the context of the spin relaxation of noble gases by Driehuys *et al.* [13]. Whether those surface spins are paramagnetic sites or nuclear spins, the Hamiltonian for such an interaction would have the form

$$H_{\text{dipole}} = \gamma_I \hbar \mathbf{I} \cdot \left(\frac{\gamma_S \hbar \mathbf{S}}{r^3} - \frac{3\gamma_S \hbar \hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \mathbf{S})}{r^3} \right), \tag{1}$$

where $\mathbf{I}$ and γ_I are the spin and gyromagnetic ratio of the ^{129}Xe nucleus, $\mathbf{S}$ and γ_S are the spin and gyromagnetic ratio of the surface spin, and r is the distance between the two spins. The fields associated with this interaction, summed over all the contributing surface spins, will fluctuate randomly at the location of the ^{129}Xe nucleus as the atom collides with the wall, becomes adsorbed or trapped, and hops from surface site to surface site. The relaxation rate associated with such an interaction as expressed by Driehuys *et al.* is

$$\frac{1}{T_1} = \frac{2}{15} f(T)\, S(S+1) \gamma_I^2 \gamma_S^2 \hbar^2 \tau_c \sum_i r_i^{-6} \left(\frac{1}{1+(\omega_I - \omega_S)^2 \tau_c^2} + \frac{3}{1+\omega_I^2 \tau_c^2} + \frac{6}{1+(\omega_I + \omega_S)^2 \tau_c^2} \right), \tag{2}$$

where $\omega_{I(S)} = \gamma_{I(S)} B$ is the Larmor frequency associated with the spin $I(S)$, B is the applied static magnetic field, and τ_c is the correlation time that characterizes the interaction. The function $f(T)$ is the fraction of ^{129}Xe atoms that are adsorbed onto the cell-wall surface at any one time as a function of the temperature T.

If the Larmor frequency ω_S associated with the surface spins were of the same order as the Larmor frequency ω_I of the ^{129}Xe nuclei, the functional dependence of $1/T_1$ on B would be that of a sum of Lorentzians, tending toward zero for sufficiently large field. This would be the case if the surface spins causing relaxation were nuclear in nature. Under the hypothesis that relaxation is caused by paramagnetic sites, however, $\omega_S \gg \omega_I$ and using Eq. (2) we can write the approximate relation

$$1/T_1 \propto \frac{3}{\left(1+\omega_I^2 \tau_c^2\right)} + \frac{7}{\left(1+\omega_S^2 \tau_c^2\right)}. \tag{3}$$

Furthermore, the large difference in magnitude between ω_S and ω_I guarantees that there will be a large range of magnetic fields over which $\omega_I \tau_c \ll 1$ while $\omega_S \tau_c$ will range from quite small values to values significantly greater than 1. For such magnetic fields, the first term of Eq. (3) will be roughly equal to 3 while the second term of Eq. (3) will be field dependent. It is in this range of magnetic fields that we would expect the

dependence of $1/T_1$ on B to be well approximated by a single Lorentzian and a constant background, the form assumed in the magnetic-decoupling fits shown in Figs. 2–5.

There is another model for spin relaxation involving paramagnetic sites that is different from that described by Eq. (2). Rather than long-range dipolar interactions, it is possible that paramagnetic sites cause relaxation through scalar contact interactions. Such a possibility was suggested by Schmiedeskamp *et al*. in the context of relaxation of polarized ^{3}He [12], and has also been discussed by Driehuys *et al*. [13]. In the case of Schmiedeskamp *et al*. the authors envisioned the paramagnetic sites to be associated with dangling bonds on the glass surface. As has been discussed by Abragam [23], and has been worked out in some detail by Driehuys in the context of spin relaxation of noble gases [24], a scalar interaction would result in a magnetic-field dependence of the form

$$\frac{1}{T_1} \propto \frac{1}{\left(1+\omega_S^2\tau_c^2\right)}. \tag{4}$$

In contrast to the case of a long-range dipolar interaction, a scalar interaction would result in a field dependence for $1/T_1$ that would be well described by a Lorentzian that tended toward zero with increasing magnetic field, a behavior similar in certain respects to that expected for relaxation due to nuclear surface spins.

To compare our data with Eqs. (2)–(4), we have fitted our data to the functional form

$$\frac{1}{T_1} = \Gamma_B + \frac{\Gamma_0}{1+(B_0/\Delta B)^2}, \tag{5}$$

where Γ_B is a field-independent (background) relaxation rate, Γ_0 is the zero-field limit of a field-dependent term, and ΔB is a decoupling width. For the case of relaxation due to a long-range dipolar interaction with paramagnetic sites as is described by Eq. (3), we would expect the fitted values of the ratio $\Gamma_B/(\Gamma_0+\Gamma_B)$ to be given by 3/10 for the range of B studied. For the case of relaxation due to a scalar interaction with paramagnetic sites as is described by Eq. (4), we would expect the fitted values of the ratio $\Gamma_B/(\Gamma_0+\Gamma_B)$ to be given by 0. For the case of relaxation due to nuclear surface spins, the functional form of $1/T_1$ with B is more complicated, but in general, as long as the coupling is studied over a sufficiently large range of B, we would expect the fitted values of the ratio $\Gamma_B/(\Gamma_0+\Gamma_B)$ to be closer to zero than to 3/10. We note that we also fitted our data to more complicated expressions (and will comment on some of these fits later) but found that Eq. (5) was particularly useful for identifying overall trends and comparing with the expectations associated with different relaxation mechanisms.

We show the fitted values of $\Gamma_B/(\Gamma_0+\Gamma_B)$ for cells X12, D3, and D1 in Table I. We note that we did not perform magnetic-decoupling studies on cell X16. For the four highest temperatures, we find that our data are completely consistent with the expectation $\Gamma_B/(\Gamma_0+\Gamma_B) = 3/10$. In fact, if we treat each measurement as random, we find that the average value of $\Gamma_B/(\Gamma_0+\Gamma_B)$ for the four highest temperatures (more on this choice shortly) is 0.294 ± 0.009. The clustering of our measurements of $\Gamma_B/(\Gamma_0+\Gamma_B)$ around the value of 0.3 is the first of several observations we present that are suggestive of relaxation due to long-range dipolar interactions with paramagnetic sites, at least at the higher temperatures studied.

TABLE I. The fitted values of $\Gamma_B/(\Gamma_0+\Gamma_B)$ [as they appear in Eq. (5)] for cells X12, D3, and D1. n/a indicates not applicable.

T (K)	X12	D3	D1
205	0.035 ± 0.059	n/a	n/a
213	0.217 ± 0.036	0.297 ± 0.022	0.281 ± 0.032
223	0.124 ± 0.007	0.258 ± 0.023	0.299 ± 0.034
263	0.289 ± 0.034	0.324 ± 0.020	n/a
298	0.265 ± 0.025	0.350 ± 0.043	0.319 ± 0.053
308	0.318 ± 0.029	0.307 ± 0.057	n/a
323	0.262 ± 0.018	0.299 ± 0.037	0.348 ± 0.107

For temperatures $T < 250$ K the situation appears to be somewhat more complicated. For cells D1 and D3, each of which has a RbD coating, the ratio $\Gamma_B/(\Gamma_0+\Gamma_B)$ is still consistent with the value 0.3. For cell X12, however, which has a RbH coating, the ratio $\Gamma_B/(\Gamma_0+\Gamma_B)$ is less than 0.3 for the three lowest temperatures studied. In fact, for $T = 205$ K, the fitted value of $\Gamma_B/(\Gamma_0+\Gamma_B)$ for cell X12 is 0.035 ± 0.059, a value that is consistent with zero. The behavior in X12 at $T = 205$ K is thus suggestive of either relaxation due to a scalar interaction with paramagnetic sites, or dipolar interactions with surface nuclei.

Another valuable quantity that comes from fitting our data to Eq. (5) is the "decoupling width" ΔB, which is related to the correlation time τ_c of the interaction by the equation

$$\tau_c = (2\pi\gamma_S\Delta B)^{-1}, \tag{6}$$

where γ_S is the gyromagnetic ratio of the spin causing the relaxation. Using Eq. (6) and an assumed value for γ_S, we can use our decoupling data to calculate a correlation time τ_c. If the resulting value for τ_c is physically reasonable, we have some measure of whether our assumption regarding γ_S was correct. Our measured values for the decoupling widths fell into the range $0.14 < \Delta B < 0.47$ T.

We begin by assuming that the spin relaxation is due to paramagnetic sites, and take $\gamma_S = 2.8 \times 10^{10}$ Hz/T. We accordingly find that our measured widths correspond to correlation times in the range of 12–42 ps, and show the individual values in Table II. As will be discussed more in Sec. V, these values are physically reasonable, and are roughly of the order that one would expect for adsorption times. We

TABLE II. The values of τ_c for cells X12, D1, and D3 that result from fitting the data to Eq. (4) and assuming that relaxation is due to spin-1/2 paramagnetic sites.

	τ_c (ps)		
T (K)	X12	D1	D3
205	17.6 ± 2.3	n/a	n/a
213	41.7 ± 10.5	18.1 ± 2.78	26.3 ± 3.97
223	38.7 ± 4.48	22.3 ± 4.48	25.5 ± 1.73
263	22.2 ± 2.61	n/a	22.2 ± 1.53
298	22.0 ± 1.84	15.5 ± 1.73	20.4 ± 1.52
308	30.8 ± 4.38	n/a	17.5 ± 2.10
323	30.6 ± 2.41	12.0 ± 2.66	13.4 ± 1.32

note that unlike the ratio $\Gamma_B/(\Gamma_0+\Gamma_B)$, there is no reason to assume that τ_c should be constant. Adsorption times, for example, should in general be expected to be temperature dependent. More generally, one could also imagine that a correlation time τ_c could be influenced by details that are specific to the cell in question, such as the crystalline structure of the RbH or RbD salt on the cell walls. For instance, a cell with larger crystals might have a different τ_c than a cell with smaller crystals.

An alternative hypothesis is that relaxation is due to interactions with surface nuclei. A rough estimate of the resulting correlation times can be obtained by using Eq. (6) and the gyromagnetic ratio of one of the candidate nuclear surface spins. In fact, we fitted our data using the full form of Eq. (2), and included terms corresponding not just to protons or deuterons, but also to the nuclei of both isotopes of Rb, assuming natural abundance. We assumed one Rb atom for every proton or deuteron. Each fit thus included seven Lorentzian terms. For all temperatures studied, the fitted values of τ_c fell in the range of 10 to 20 ns. Such long correlation times, while certainly not impossible, are difficult to physically motivate, at least at the higher temperatures. As we will discuss later, there may be a suggestion in our data that such long correlation times are not entirely ruled out at the lowest temperatures studied.

To summarize, under the hypothesis that relaxation is caused by long-range dipolar interactions with paramagnetic sites, we expect that each magnetic-decoupling curve will have the form given in Eq. (5), with the ratio $\Gamma_B/(\Gamma_0+\Gamma_B)\approx 3/10$. This is well satisfied by our RbH data for which $T>250$ K, and by all of our RbD data. For the RbH data corresponding to $T<250$ K, however, we find that $\Gamma_B/(\Gamma_0+\Gamma_B)<3/10$, something that would tend to suggest either relaxation due to a scalar contact interaction, or nuclear surface spins. In considering the decoupling widths, we find that the assumption that spin relaxation is due to paramagnetic sites results in correlation times of tens of picoseconds, whereas the assumption that relaxation is due to nuclear surface spins results in correlation times of tens of nanoseconds. Taken together, the magnetic-decoupling data strongly support the hypothesis that spin relaxation is caused by dipolar interactions with paramagnetic sites, at least at the higher temperatures studied. For the lower temperatures some questions remain.

V. TEMPERATURE STUDIES

In addition to performing magnetic-decoupling studies at each of several fixed temperatures, we also performed dedicated studies of the temperature dependence of spin relaxation. These measurements were all performed at a field $B=0.0824$ T, and are shown in Figs. 6 and 7. As we will discuss below, the observed behavior in our RbH and RbD cells does not agree well with some of our naive expectations. Even so, we observed distinctive qualitative behavior that seems to suggest that in addition to the relaxation mechanism that dominates at higher temperatures, we also see evidence for what we will refer to as a low-temperature relaxation mechanism.

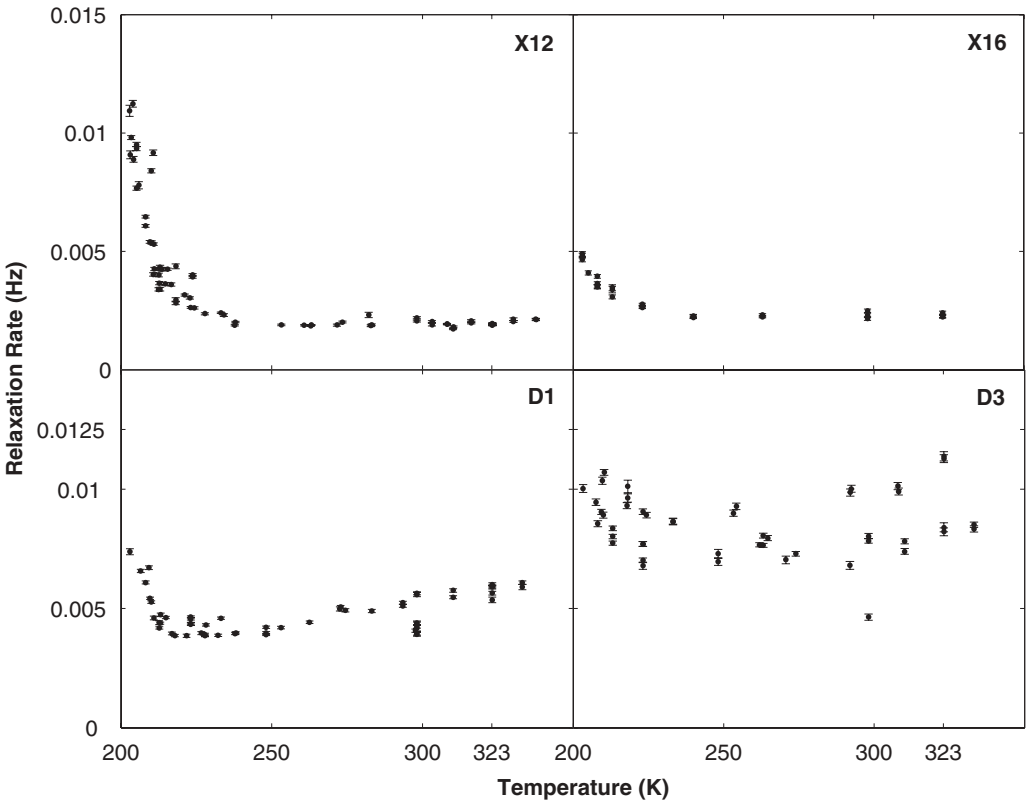

FIG. 6. $1/T_1$ as a function of temperature for cells X12 and X16, whose interior walls are coated with RbH, and cells D1 and D3, whose interior walls are coated with RbD.

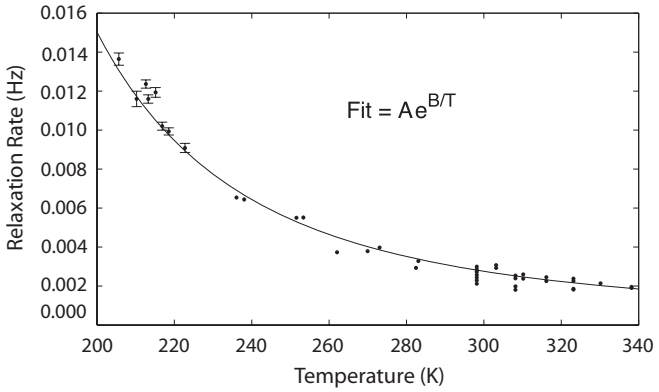

FIG. 7. $1/T_1$ as a function of temperature for cell X9, our control cell that contained no hydrogen. The observed temperature dependence is distinctly different from what was observed in our cells with hydride coatings.

In Fig. 6 we show $1/T_1$ versus temperature for all of our RbH and RbD cells. At higher temperatures, the spin-relaxation rates in the two RbH cells, X12 and X16, are remarkably flat. This is surprising since the dwell time during adsorption on the wall can reasonably be expected to be temperature dependent. For D1, a RbD cell, the spin-relaxation rate at higher temperatures is also only weakly temperature dependent, and even seems to be getting smaller with decreasing temperature, the opposite trend to what we would naively expect. We had a number of problems during our temperature measurements of D3, but apart from the scatter in the data, the behavior is not obviously different from that in D1.

The low-temperature behavior of cell X12 is quite striking. Below roughly 250 K, the spin-relaxation rate can be seen to be sharply rising. While this behavior is most pronounced in cell X12, similar behavior is clearly visible in both X16 and D1. It is very interesting to note that the three magnetic-decoupling curves obtained with X12 for which $\Gamma_B/(\Gamma_0+\Gamma_B) < 3/10$ correspond to precisely this temperature regime. For X12, both the temperature behavior as well as the shape of the decoupling curve seem to suggest that a different spin-relaxation mechanism dominates at low temperatures. Unfortunately, we do not have magnetic-decoupling data for X16. In the case of D1, there are two factors that complicate a direct comparison with X12. First, the overall spin-relaxation rate at higher temperatures was much faster than was the case for X12, which complicates the interpretation. Second, we were not able to obtain a magnetic decoupling curve for D1 at 205 K, the temperature at which, for X12, $\Gamma_B/(\Gamma_0+\Gamma_B) \sim 0$. Even so, we believe the data we have are nonetheless sufficient to suggest that we are probably observing a different relaxation mechanism at low temperatures.

To better understand what we might naively expect to see for temperature dependence, we begin by discussing the behavior of our control cell X9 that has no RbH or RbD coating. There are two factors in Eq. (2) that can be expected to contribute to the temperature dependence of the zero-field limit of $1/T_1$: $f(T)$ and τ_c. The factor $f(T)$, the fraction of atoms that are adsorbed onto sites that cause relaxation at any given time, is estimated in Ref. [13] using the expression

$$f(T) = \frac{N_s V_s}{V} e^{-E_a/k_B T}, \tag{7}$$

where V is the volume of the cell, V_s is the volume associated with an individual adsorption site, N_s is the number of adsorption sites on the cell's interior surface, E_a (a negative quantity) is the adsorption energy, k_B is Boltzmann's constant, and T is temperature. The spin-relaxation rate of X9 as a function of temperature is shown in Fig. 7. These data fit well to a function with the form of Eq. (7), and we find a fitted value for E_a of -0.088 eV, a value that is significantly larger than the value of -0.03 eV reported by Wu *et al.* for bare glass [18].

It is not obvious what to expect for the temperature dependence of τ_c. One possibility, however, is that τ_c is one and the same as the dwell time on the cell wall, τ_d, which can be estimated using Frenkel's law:

$$\tau_d = \tau_0\, e^{-E_a/k_B T}, \tag{8}$$

where $\tau_0 \approx 10^{-12}$ s and the other quantities are defined as in Eq. (7). If this were the case, there would be two factors of $e^{-E_a/k_B T}$ affecting $1/T_1$, and we would expect the zero-field limit of $1/T_1$ to have the form

$$1/T_1 = A e^{-2E_a/k_B T}, \tag{9}$$

where A is a constant. In this case the temperature dependence in Fig. 7 would suggest that $E_a = -0.044$ eV, a value that is much closer to the value of -0.03 eV from Wu *et al.* [18]. If we continue this line of reasoning, the dwell time given by Eq. (8) should be the same as the correlation time obtained from the decoupling width. We consider $T = 213$ K, the only temperature at which we clearly observed magnetic decoupling in X9. Using a range for E_a of -0.03 to -0.044 eV, we find that $1.6 \leqslant \tau_d \leqslant 11$ ps. The decoupling width of X9 at 213 K suggests a correlation time $\tau_c = 23 \pm 7$ ps. Given the approxime nature of Eq. (8) (particularly regarding τ_0), the value of τ_c from the decoupling width may well be consistent with at least the upper range of our estimates for τ_d. While we do not want to suggest that the model presented here, in which $\tau_c \approx \tau_d$, should in any way be considered definitive, it at least appears that we have successfully described the basic trend of the observed temperature dependence.

For our cells with either RbH or RbD coatings, the temperature dependence of $1/T_1$ is clearly more complicated. The data do not fit well to the form of Eq. (9). Empirically, they appear to have roughly the form

$$1/T_1 = A + Be^{-E/k_B T}, \tag{10}$$

where A and B are constants, and E is an as yet unidentified energy. Fitting to Eq. (10) yields values for E of -0.40, -0.40, and -0.66 eV for cells X12, X16, and D1, respectively, or -0.20, -0.20, and -0.33 eV if, as discussed previously, $\tau_c = \tau_d$. The temperature data from D3 are too noisy to fit. Interestingly, using Eq. (8), an adsorption energy of -0.2 to -0.3 eV would at these temperatures correspond to correlation times of tens of nanoseconds, something that would be consistent with spin relaxation due to surface nuclei. This could be interpreted as evidence favoring surface nuclei over a scalar interaction with paramagnetic sites as the explanation for the sudden rise in spin relaxation at low temperatures,

although more work would be needed to take this hypothesis seriously.

VI. POSSIBLE ISOTOPIC DIFFERENCES

One way to investigate the hypothesis that relaxation is due to nuclear surface spins is to study the differences between RbH and RbD coatings. Protons have a much larger magnetic moment than is the case for deuterons, and according to Eq. (2), this would have several implications. For example, Eq. (2) indicates that spin relaxation should be proportional to $S(S+1)\gamma_S^2$. The relative difference between relaxation due to protons and deuterons, all other factors being equal, should thus be about a factor of 20. The nuclei of the Rb atoms, however, must also be taken into account. Assuming one Rb atom for each proton or deuteron, and assuming Rb with natural isotopic abundance, we would expect relaxation in RbH cells to be about four times faster than in RbD cells.

We first consider possible isotopic differences for $T > 250$ K. We found that the magnitude of the observed spin relaxation was about two to three times *higher* in our RbD cells than was the case in our RbH cells, a trend that is opposite what we would expect from the above argument. This tends to disfavor the hypothesis that the spin relaxation was due to surface nuclei. This conclusion needs to be tempered, however, by the fact that we routinely see large variability in wall-induced relaxation, even when we try to make cells under identical conditions. Still, while it is possible that both D1 and D3 had anomalously high wall-relaxation rates that more than overcame the benefits of replacing protons with deuterons, it seems more likely that we should take the observed behavior of the RbD cells as lending further support to the hypothesis that, at least for $T > 250$ K, spin relaxation is due to paramagnetic sites.

Regarding isotopic differences in decoupling widths, without going into details, we note that the interpretation is complicated by the fact that the nuclear surface spins include not just protons or deuterons, but also the nuclei of the Rb atoms. Furthermore, the observed decoupling widths are a function not just of the gyromagnetic ratios, but also of τ_c, which is quite variable. We comment only that the observed decoupling widths are consistent with any of the hypotheses considered.

Lastly, we comment on what the comparison of RbH and RbD cells tells us about the low-temperature relaxation mechanism. If it were due to nuclear surface spins, we should expect the rise in spin relaxation at low temperatures to be more pronounced in cells X12 and X16 than in D1 and D3. While the increase in relaxation is certainly most pronounced in X12, it is not clear what that means in light of the behavior of X16, in which the increase does not seem particularly large when compared with D1. There are clearly many factors affecting spin relaxation in our cells. If there is an isotopic difference in the low-temperature relaxation mechanism, more work is needed to demonstrate its existence.

VII. DISCUSSION

We have obtained a substantial set of data describing the magnetic-field and temperature dependence of the longitudinal spin-relaxation rate $1/T_1$ of nuclear polarized ^{129}Xe in cells coated with both RbH and RbD surfaces. At all temperatures, strong magnetic decoupling was observed over the range of magnetic field studied. For temperatures above roughly $T = 250$ K, the observed magnetic decoupling supports the hypothesis that spin relaxation is being caused by long-range dipolar interactions with paramagnetic sites. An alternative hypothesis, that relaxation is occurring because of interactions with the spins of surface nuclei, is largely ruled out by two factors: (1) the magnetic decoupling widths are such that the correlation times with the nuclei would need to be tens of nanoseconds, something that is physically unlikely and (2) in contrast with what one would expect if nuclear spins were the source of relaxation, the relaxation was stronger for RbD coatings than it was for RbH coatings. An alternative hypothesis, that relaxation was being caused by a scalar interaction (not a long-range dipole interaction) with paramagnetic sites is not consistent with the observed shapes of the decoupling curves. While one could always postulate a more complex mechanism to explain the data, it seems most likely that relaxation at our four highest temperatures is caused by dipolar interactions with paramagnetic sites.

At the lower end of the temperature range studied, there appears to be evidence that a different relaxation mechanism becomes dominant. It seems most likely that the "low-temperature" mechanism is due to either dipolar interactions with nuclear surface spins or scalar contact interactions with paramagnetic sites. The strong temperature dependence is perhaps providing a hint that the former is more probable, but the isotopic differences between the RbH and RbD coatings do not convincingly support this hypothesis. A better understanding of the low-temperature mechanism will require more work.

Finally, on a more general note, we suggest that this work provides further support for the already well-established utility of magnetic-decoupling studies as a productive avenue for understanding spin-relaxation effects in cells containing polarized noble gases.

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