Extraordinarily Slow Nuclear Spin Relaxation in Frozen Laser-Polarized ^{129}Xe

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(Received 16 July 1992)

We studied the very slow nuclear spin-lattice relaxation of solid ^{129}Xe as a function of temperature and magnetic field using laser-polarized nuclei. Relaxation times in excess of 500 h were measured. We present evidence for a new relaxation mechanism which results from a Raman spin-phonon scattering process involving the spin-rotation interaction. We also establish the existence of cross relaxation between ^{129}Xe and the other magnetic isotope ^{131}Xe and demonstrate that laser-polarized ^{129}Xe can be used to cross polarize other nuclei that are present in the lattice.

PACS numbers: 76.60.Es, 29.25.Pj, 32.80.Bx

Recently, Cates *et al.* demonstrated the production of large nuclear spin polarization in frozen ^{129}Xe using polarized laser light [1]. We have since studied the exceptionally slow spin-lattice relaxation of the (spin-1/2) ^{129}Xe nuclei in the polarized solid, and we have found evidence of a spin-rotation interaction as the mechanism for the relaxation. The mechanisms for relaxation of nuclei with spin >1/2 are well understood in most diamagnetic insulators [2]. In many such solids (e.g., rare-gas or ionic solids), to our knowledge no intrinsic interaction of a spin-1/2 nucleus has ever been identified as the source of relaxation at low temperatures, where self-diffusion is negligible [3] (excluding the exotic case of solid ^{3}He [4]). One mechanism for relaxation suggested by Cates *et al.* is a Raman spin-phonon scattering process which results from a nuclear spin-rotation interaction

$$\mathcal{H}_{\rm sr} = \gamma_I \mathbf{I}\cdot\mathbf{N}, \tag{1}$$

where $\mathbf{I}$ is the spin of a ^{129}Xe nucleus, $\mathbf{N}$ is the relative angular momentum of a pair of neighboring atoms, and γ_I characterizes the strength of the interaction. We discuss the relaxation expected from this process and estimate the rate using a recent measurement of the chemical shift by Raftery *et al.* who also utilized laser-polarized ^{129}Xe [5]. Our measurements confirm that this process dominates ^{129}Xe relaxation at many of the temperatures and magnetic fields studied. In addition, at temperatures below 20 K, we suggest that cross relaxation with ^{131}Xe limits the ^{129}Xe spin polarization lifetime T_1 to hundreds of hours at 1 kG. Cross relaxation at low fields has been confirmed by observing the large ^{131}Xe polarization which is created.

Laser-polarized ^{129}Xe is already used in several research programs including our work on spin relaxation, NMR studies of surfaces and solids at Berkeley [5], and matrix isolation NMR at Yale [6]. As suggested by Raftery *et al.*, and demonstrated in this work for the case of ^{131}Xe, laser-polarized ^{129}Xe can be used to cross polarize other nuclei. In addition, polarized ^{129}Xe can be produced at a rate of about 1 g/h using existing lasers [1]; with $T_1 \approx 500$ h, the accumulation of >100 g samples is possible. Potential applications include polarized targets for neutron scattering [7], studies of macroscopic spin-dependent forces [8], and even the enhancement (because of high polarization) of NMR sensitivity [9] for magnetic resonance imaging in biological systems—Xe is known to bind to various proteins.

Our studies were conducted on samples of Xe gas at pressures near an atmosphere contained in sealed cylindrical glass cells along with several milligrams of Rb metal. Some cells also contain other gases, such as He, N_2, or Kr. The ^{129}Xe nuclei of gaseous atoms were polarized by spin exchange with Rb vapor which was optically pumped with a Ti:sapphire laser [10]. The sample cells were then moved to a separate apparatus where the polarized ^{129}Xe gas was frozen into the constricted *pull-off* of the cell by immersing it in liquid N_2. The pull-off was then inserted into a small tuned coil which was part of a balanced Anderson *LR* bridge circuit [11], and the cell and coil assembly were installed into a cryostat to control the sample temperature. The nuclear polarization was measured by detecting the NMR signal which results from a *fast passage* sweep of the magnetic field through the resonance condition [12]. Detection losses were less than 1%. The relaxation was observed by monitoring the polarization over a period of time, which in some cases was more than a week.

In Fig. 1 we summarize the dependence of the ^{129}Xe spin relaxation rate $1/T_1$ on magnetic field and temperature. The data exhibit little if any dependence on magnetic field and no dependence on the samples' isotopic composition (not shown for clarity) for magnetic fields $H \geq 500$ G and temperatures $T \geq 20$ K. These observations suggest that ^{129}Xe spin relaxation may arise from an inelastic (Raman) spin-phonon scattering process resulting from the interaction in (1) [1]. The rate $1/T_1$ for this process has been computed by Fox and Happer [13] using a simple Debye phonon spectrum in a calculation analogous to van Kranendonk's treatment of quadrupolar nuclear spin relaxation [14]. Their solution is well approximated (to better than 2%) by the expression

$$\frac{1}{T_1} \simeq 8.20\times10^4 \left(\frac{\gamma_I}{h}\right)^2 \left(\frac{h}{kT_D}\right) f(T^*) \left(1+\frac{2}{3}\epsilon+0.122\epsilon^2\right) \tag{2}$$

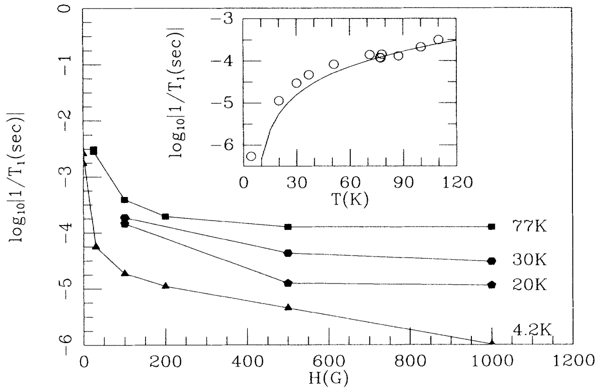

FIG. 1. The magnetic field dependence of T_1 for solid ^{129}Xe. Shown are data at 77 K, 30 K, 20 K, and 4.2 K. The points are connected to guide the eye. The sample cells contain about 600 Torr Xe. In the inset is the temperature dependence of measurements from these and other data taken at a magnetic field $H \geq 1$ kG. The solid line is the prediction of (2) given the estimates of γ_I and ϵ described in the text.

over the temperature range T = 20–120 K. Here h is Planck's constant, k is Boltzmann's constant, $T_D = 55$ K is the Debye temperature of solid Xe [2], and the function $f(T^*) = (T^*)^9 \int_0^{1/T^*} e^x x^8 (e^x - 1)^{-2}\, dx$, where $T^* = T/T_D$. The parameter $\epsilon = (r_0/\gamma_I) d\gamma_I/dr$ accounts for the dependence of the coupling parameter γ_I on the internuclear separation r, with the equilibrium values $\gamma_I \equiv \gamma_I(r_0)$ and $r_0 \simeq 4.4$ Å. We next discuss estimates of γ_I and ϵ with which we can evaluate (2).

The diamagnetic shielding of an isolated atom in an applied magnetic field H is characterized by a shielding parameter σ_g such that the magnetic field experienced by the nucleus is $(1 - \sigma_g)H$. As shown by Ramsey, the shielding parameter for nuclei in solids σ_s is different [15]. Ramsey also pointed out that, as a consequence of Larmor's theorem, the chemical shift $(\sigma_s - \sigma_g)$ is related to the spin-rotation interaction. Using an analysis similar to his, the spin-rotation coupling constant in (1) can be expressed in terms of the chemical shift [13],

$$\frac{\gamma_I}{h} = \left(\frac{\mu_I}{I\mu_B}\right)\left(\frac{\hbar}{8\pi M r_0^2}\right)(\sigma_s - \sigma_g), \tag{3}$$

where $\mu_I = -0.772\mu_N$ is the magnetic moment of ^{129}Xe, μ_B is the Bohr magneton, and M is the average mass of a Xe atom. An analogous relationship was first discussed by Torrey in his explanation of gaseous ^{129}Xe spin relaxation [16]. Comparing the NMR frequencies of laser-polarized ^{129}Xe signals from atoms in both the gas and the solid, the measurements of Raftery *et al.* result in $\sigma_s - \sigma_g = 317 \times 10^{-6}$ at 77 K [5, 17], and therefore we estimate

$$\frac{\gamma_I}{h} = -27\,\text{Hz}. \tag{4}$$

The parameter ϵ has been calculated by Adrian in his treatment of the diatomic contribution to the chemical shift in a dilute ^{129}Xe gas [18]. He found that $\epsilon/r_0 = -2.506$ Å^{-1}, which has been confirmed by temperature dependence measurements of the chemical shift in solid ^{129}Xe [19].

With the preceding estimates and (2) we compute $T_1 = 8300$ s at 77 K, in good agreement with our average measured value at $H > 1$ kG of $T_1 = 8500 \pm 800$ s [20]. The prediction of (2) and measurements of $1/T_1$ for $H \geq 1$ kG at other temperatures are shown in the inset to Fig. 1; the data follow well the expected temperature dependence. From the compelling agreement of (2) and our measurements, we conclude that the spin-rotation interaction dominates the spin relaxation of ^{129}Xe from about 20–120 K. At higher temperatures dipolar relaxation from diffusing vacancies begins to dominate [1], while below about 20 K the large disagreement of the measurements with the predictions of (2) indicates the dominance of yet another mechanism for ^{129}Xe spin relaxation.

At sufficiently low magnetic field the rate $1/T_1$ depends strongly on magnetic field. At 4.2 K the dependence on field persists up to 1 kG. We find convincing evidence that, in this low temperature regime, ^{129}Xe becomes depolarized by cross relaxation with ^{131}Xe which is also present in the crystal. The isotope ^{131}Xe has spin $I = 3/2$ and therefore a nuclear quadrupole moment which interacts strongly with electric field gradients producing rapid nuclear spin relaxation in accordance with van Kranendonk's theory [14,21]. Thus, ^{129}Xe spin polarization that is transferred to the ^{131}Xe nuclei is quickly lost, making cross relaxation an effective relaxation mechanism for ^{129}Xe. Cross relaxation at low temperatures relies on a degeneracy of the energy levels of the two magnetic species and the presence of dipolar spin-spin interactions which can induce spin exchange transitions between them [22]. This degeneracy is a result of static ^{131}Xe quadrupole interactions with imperfections in the lattice, which previous studies have measured to be equivalent to the ^{131}Xe Zeeman energy at 7 G [23]. Furthermore, our samples are polycrystalline. We expect that ^{131}Xe nuclei near crystal grain boundaries will have very large quadrupole interactions, probably on the order of those experienced in Xe-HCl molecular complexes [24]. Such interactions are large enough to produce cross relaxation even at fields of several kG.

The most dramatic confirmation of cross relaxation as a source of relaxation at low fields is the observation of large ^{131}Xe spin polarization. We performed a series of experiments in which the magnetic field was momentarily lowered to a *mixing* value $H_m \leq 100$ G. As the magnetic field is reduced there are an increasing number of ^{131}Xe nuclei (near defects in the crystal) whose quadrupole interactions are sufficiently large that spin exchange with ^{129}Xe is energetically possible. Just as the ^{129}Xe spin relaxation becomes more pronounced as the field is decreased, the polarization transferred to

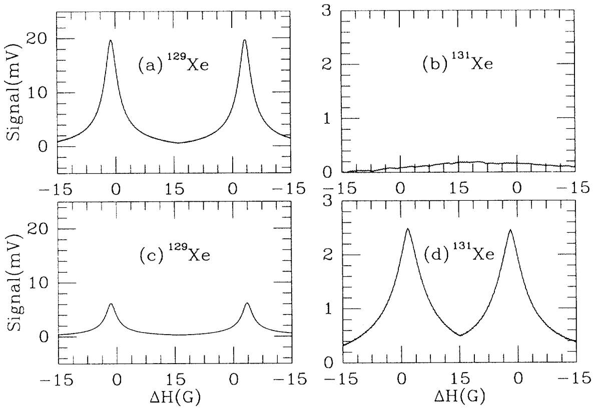

FIG. 2. The cross polarization of ^{131}Xe. Shown are AFP-NMR signals from ^{129}Xe and ^{131}Xe measured before, in (a) and (b), and after, in (c) and (d), briefly lowering the applied field to zero. All signals were acquired at an NMR frequency of 358 kHz with a 40 dB preamplifier. The abscissa shows the *sweep field* ΔH which was added to the applied field H, and swept through the resonance condition twice. The signals in (a), (c), and (d) are from a single run, while (b) is a typical null signal. The ^{131}Xe polarization represented by (d) is about 5%.

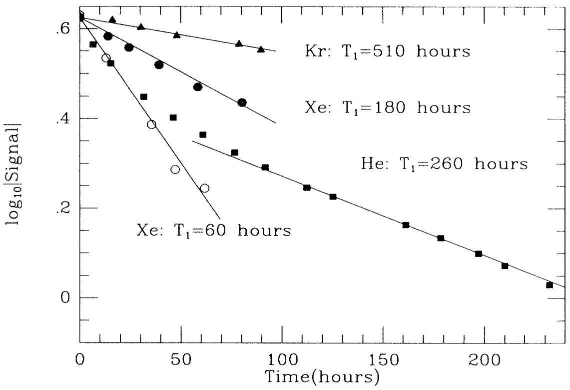

FIG. 3. The decay of polarization for four samples of ^{129}Xe as a function of time. The signals are normalized to be equal at time zero. The solid (open) points are data from isotopically enriched (natural) samples with 80.8% ^{129}Xe and 3.4% ^{131}Xe (26.4% ^{129}Xe and 21.2% ^{131}Xe). The cells labeled Xe contain 600 Torr Xe. The cell labeled Kr contains 300 Torr Xe and 300 Torr Kr, and the cell labeled He contains 600 Torr Xe and 2600 Torr He. Note the pronounced nonexponential decay of the sample containing He. The quoted values of T_1 correspond to the lines shown.

the ^{131}Xe increases. At mixing fields near zero, spin exchange is possible with nearly all of the ^{131}Xe nuclei and a common nuclear spin temperature should result [12]. In this case, the fraction m_λ of the initial magnetization expected in a particular isotope ($\lambda = A$ for ^{129}Xe or $\lambda = B$ for ^{131}Xe) after the high field is restored is $m_\lambda = c_\lambda/(c_A + c_B)$, where c_λ represents the nuclear spin heat capacity of that isotope in the crystal [12]. Our measurements of m using adiabatic fast passage (AFP) are in good agreement with this prediction for both ^{129}Xe and ^{131}Xe at $H_m \simeq 1$ G; at lower fields some additional depolarization occurs. We note that the extreme quadrupole broadening of the ^{131}Xe AFP-NMR signals must be accounted for in making these comparisons. In Fig. 2 we illustrate the production of cross polarization in ^{131}Xe near zero mixing field. Shown in the figure are AFP signals for both ^{129}Xe and ^{131}Xe before and after mixing. The large ^{131}Xe polarization that results (about 5%) represents more than 1/3 of the original ^{129}Xe polarization. Not only do these measurements confirm the existence of cross relaxation, they also demonstrate a useful technique for polarizing other nuclei which can be imbedded in the Xe lattice.

Finally, we believe that at 4.2 K cross relaxation dominates the nuclear spin relaxation of ^{129}Xe over the entire range of the magnetic field studied, up to 1 kG. This conclusion is supported by the dependence of the relaxation rate on the fraction of ^{131}Xe. In Fig. 3 we show on a semilogarithmic plot a decay of the nuclear spin polarization with time for four samples at 1 kG and 4.2 K. In the cells containing isotopically enriched ^{129}Xe, only 3.4% of the gas is ^{131}Xe, whereas in the cell containing naturally abundant Xe, 21.2% of the gas is ^{131}Xe. As expected, the cell with natural Xe exhibits faster relaxation. In general, decays at 4.2 K are significantly nonexponential, indicating that the relaxation is partly diffusion limited. This is consistent with the expectation that, at 1 kG, the only sites where quadrupole interactions are likely to be strong enough to produce cross relaxation are localized near the surfaces of crystal grains, and that the transport of spin to these surfaces by spin diffusion is the limiting relaxation mechanism [25]. The slowest decaying diffusion mode associated with a spherical grain of radius R would have a decay rate constant $\Gamma = \pi^2 D/R^2$, where $D \sim 10^{-13}$ cm^2/s is an estimate of the spin-diffusion constant in ^{129}Xe. Consequently, we attempted to vary the relaxation rate by controlling the size of the grains. This was done by introducing buffer gases into our cells. Having observed much slower Xe condensation rates in the cells filled with Kr, compared with cells containing He, we conclude that the Xe frozen in these cells had larger crystal grains. From Fig. 3, the cell containing Kr clearly exhibited much slower relaxation than the cell containing He, as expected. Furthermore, $1/\Gamma = T_1 = 500$ h implies a grain size $2R \sim 30\,\mu$m, which is consistent with previous studies [26]. We note, however, that if relaxation at the grain boundary were truly fast compared to Γ, we would not see the dependence on field that is clearly evident in Fig. 1 at 4.2 K. Future studies are planned at 4.2 K and higher magnetic fields where, according to our cross-relaxation–spin-diffusion model, relaxation should be greatly suppressed.

In conclusion, we have identified two intrinsic nuclear spin-lattice relaxation mechanisms in frozen ^{129}Xe. One results from a nuclear spin-rotation interaction. The other, cross relaxation with ^{131}Xe, suggests a new technique for polarizing other nuclei in the lattice. Together with our original study [1], the dominant nuclear spin relaxation processes for ^{129}Xe have now been determined over the entire solid temperature range above 4.2 K. The extraordinarily long ^{129}Xe spin relaxation times of hundreds of hours, which are the longest ever observed, are likely to be even longer above 1 kG. This ensures that laser-polarized ^{129}Xe can be accumulated and stored over long periods of time, opening many new experimental possibilities.

This work was supported by the U.S. Air Force Office of Scientific Research under Grants No. 88-0165 and No. F49620-92-J-0211.

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