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by

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Note: The principal investigator during most of the period covered by this grant was
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I. Introduction

Over the four year period covered by this grant, we have carried out extensive research involving polarized atoms and nuclei. Using laser optical pumping, high polarizations can be produced in alkali-metal vapors. From this starting point, angular momentum can be transferred to other atoms and nuclei through several different types of spin-exchange collisions. This powerful technique enables us to study a wide variety of spin interactions and spin related phenomena. Among the systems we work with are polarized noble gases, which display extremely long spin-relaxation times that vary from several minutes to many weeks.

The use of optical pumping and spin exchange has grown enormously over the past four years. Examples outside of our laboratory include investigations of ^3He in the magnetic resonance laboratory of Texas Instruments,¹ investigations of local Lorentz invariance and possible non-linearity of quantum mechanics by Tim Chupp's group at Harvard,^{2,3} and the enhancement of NMR signals for studies of surfaces and solids by Alex Pines' group at Berkeley.⁴ Spin-exchange with optically pumped alkali-metal vapors has also been important for the production of polarized nuclear targets. Members of our own group have been involved in experiments at the Los Alamos Meson Physics Facility (LAMPF) to produce polarized muonic helium.⁵ Examples outside our lab include work with deuterium at Argonne National Laboratory,⁶ work with ^3He in pion scattering at TRIUMF,⁷ and work with ^3He in electron scattering at the MIT Bates Linear Accelerator.⁸

In addition to the examples given above, all of which build upon, either directly or indirectly, work begun in our laboratory, there are many broader connections between our work and technologies which are of interest to the Air Force. For example, the atomic clocks used on the GPS satellite system operate with optically pumped Rb absorption cells, very similar to cells being investigated in our laboratory. Also, the extremely long spin relaxation times exhibited by noble gas nuclei make them potentially valuable for the construction of atomic gyroscopes and magnetometers. Finally, virtually all of our experiments are strongly influenced by spin interactions that occur between polarized atoms and the surfaces of the containers in which the gases are confined. These surface interactions result in both frequency shifts as well as spin relaxation, phenomena that we are actively engaged in researching. Our findings will have potential impact for work with time standards, both of the sort used in the GPS system as well as devices such as hydrogen masers. Thus, while our research tends to focus on fundamental issues, the number of applications of our work in other areas of physics is enormous, and the potential for future applications of a more practical nature is quite intriguing.

Over the course of the four years covered by AFOSR grant # 88-0165 we have produced 19 publications. In order to convey most naturally the development of our interests, we will discuss the research contained in these publications according to several loosely defined areas, including spin exchange, spin interactions at surfaces, spin interactions in solids, and relaxation due to magnetic field inhomogeneities. For brevity, we have also grouped together (some rather diverse) activities that involve collaboration with researchers supported by sources outside of this grant. In each area discussed, we list, within the the text, the publications to come out of the work. These publications are *lettered* to more easily facilitate referring to them. *Numbered* references are still used for additional

citations as needed.

II. Spin exchange: Polarization transfer and frequency shifts

- A• S. G. Redsun, R. J. Knize, G. D. Cates and W. Happer, *Production of Highly Spin-polarized Atomic Hydrogen and Deuterium by Spin-exchange Optical Pumping*, Phys. Rev. A **42**, 1293 (1990).
- B• S. R. Schaefer, G. D. Cates, Ting-Ray Chien, D. Gonatas, T. G. Walker and W. Happer, *Frequency Shifts of the Magnetic-resonance Spectrum of Mixtures of Nuclear Spin-polarized Noble Gases and Vapors of Spin-polarized Alkali-metal Atoms*, Phys. Rev. A **39**, 5613 (1989).
- C• S. R. Schaefer, G. D. Cates and W. Happer, *Determination of Spin-Exchange Parameters between Optically Pumped Rubidium and ^{83}Kr* , Phys. Rev. A **41**, 6063 (1990).
- D• G.D. Cates, R.J. Fitzgerald, A.S. Barton, P. Bogorad, M. Gatzke, N.R. Newbury, and B. Saam, *Rb- ^{129}Xe spin exchange rates due to binary and three body collisions at high Xe pressures*, Phys. Rev. A **45**, 4631 (1992).
- E• T. G. Walker, *Estimates of Spin-Exchange Parameters for Alkali-Metal Noble-Gas Pairs*, Phys. Rev. A **40** 4959 (1989).
- F• K. D. Bonin, T. G. Walker and W. Happer, *Relaxation of Gaseous Spin-Polarized ^3He Targets Due to Ionizing Radiation*, Phys. Rev. A **37**, 3270-3282 (1988).

There are actually two types of spin-exchange interactions that we study. In one type, two paramagnetic atoms collide, such as hydrogen and rubidium, and spin exchange occurs between the two valence electrons associated with each of the atoms. The cross section for this process is extremely high, and we exploited it in an experiment by Redsun *et al.* (listed above as publication A) in which we polarized both hydrogen and deuterium.

The other variety of spin exchange occurs between the valence electron of an alkali-metal atom and the nucleus of a rare gas atom. While this is a much weaker process than than Rb-H spin exchange, it provides a powerful method for producing polarized nuclei. Another important manifestation of the spin-exchange interaction between alkali-metal atoms and noble gas nuclei is the appearance of frequency shifts of the magnetic resonance spectra of both the electron paramagnetic resonance (EPR) lines of the alkali-metal atoms, and the nuclear magnetic resonance (NMR) lines of the noble gas nuclei. These frequency shifts occur whenever there is a mixture of spin-polarized alkali-metal atoms and noble-gas atoms. The spin-polarized nuclei of noble-gas atoms will cause a shift in the electron paramagnetic resonance (EPR) frequency of the alkali-metal atoms, and similarly the spin-polarized valence electrons of alkali atoms will cause a shift of the NMR frequency of noble gases. We have performed the first comprehensive study of these frequency shifts, both theoretically and experimentally, in work conducted by Schaefer *et al.* (pub. B). We have also used the frequency shifts as a new method for characterizing the spin-exchange interactions that occur between Rb and ^{83}Kr (pub. C). An example of such shifts is shown in Fig. 1.

The frequency shifts are due to the Fermi-contact interaction $\alpha\mathbf{K} \cdot \mathbf{S}$. When, for instance, alkali-metal atoms are mixed with a sample of nuclear polarized noble-gas, they

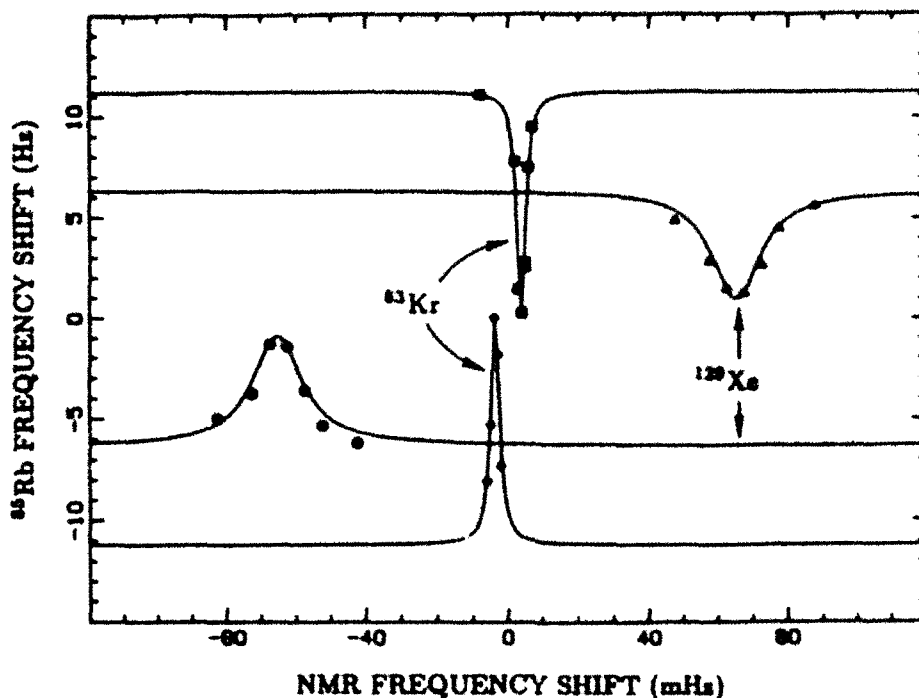


Figure 1. Experimental determination of the NMR frequency shifts of ^{129}Xe and ^{83}Kr due to Rb vapor that is maintained at high polarization by optical pumping with a laser. The lower(upper) two curves are for $\langle S_z \rangle$ and $\langle K_z \rangle$ parallel(antiparallel) to the external magnetic field. Both the ^{129}Xe and the ^{83}Kr were in the same sample cell, thus this measurement yields an accurate measurement of the ratio of κ_0 for the two isotopes. From publication B.

experience an effective magnetic field increment

$$\delta B_A = \frac{8\pi}{3} \frac{\mu_K}{K} \kappa_{AX} [X] \langle K \rangle \quad (1)$$

in addition to any externally applied static field. Here $[X]$ is the number density of noble gas atoms and $\langle K \rangle$ is their mean nuclear spin.

The enhancement factor κ_{AX} , originally introduced by Grover⁹ is the factor by which the mean magnetic field exceeds the classical magnetic induction of a polarized sphere. In the high-pressure limit the enhancement factor approaches a pressure independent limit given by

$$\kappa_0 = \int_0^\infty |\Psi(R)|^2 e^{-V(R)/kT} 4\pi R^2 dR \quad (2)$$

where $V(R)$ is the van der Waals potential which describes the force between an alkali-metal atom and a noble-gas atom, and $\Psi(R)$ is the wave function of the alkali-metal atom valence electron at the location of the noble-gas nucleus. At lower pressures, molecular

lifetimes are longer, and the frequency shifts are slightly suppressed. In practice, however, the pressure dependence of the frequency shifts is always small, even for heavy gases like xenon which readily form van der Waals molecules. It is of both theoretical and practical value to determine the parameter κ_0 in systems with which we work quite often. In addition to the work described in the papers listed above, we are continuing to study frequency shifts under funding provided by the successor grant to 88-0165.

Another area in which we worked was the study of spin exchange between Rb and ^{129}Xe at high pressures of Xe (pub. D). In earlier work with Xe the pressures considered were much lower, on the order of a few torr.^{10,11} As work with Xe within our own lab and elsewhere becomes more prevalent, however, there have been numerous reasons to try to work at higher pressures. In this study, we characterized certain relevant parameters, such as the binary spin-exchange cross section, that had not been previously measured.

We mention briefly two additional efforts. The large body of work done in our lab over the last few years put us in a position to make reasonably good theoretical estimates of many of the parameters that characterize spin-exchange in the numerous possible alkali-metal-noble-gas pairs. Such estimates are extremely valuable because they preclude the necessity of performing experiments if one only needs a rough idea of how a particular system would behave. In work that was in part an outgrowth of his thesis, Thad Walker calculated most of the relevant spin-exchange parameters for nearly all of the alkali-metal-noble-gas pairs. This work was performed while Thad worked with our group as a post-doc after receiving his degree. His results are described in publication E. Lastly we mention some calculations performed by Keith Bonin, Thad Walker, and Will Happer, in which they considered spin relaxation of ^3He due to ionizing radiation (pub. F). This work was undertaken in response to repeated inquiries concerning our estimates of the size of the effect. Later in this document we will discuss experimental tests of these calculations.

III. Spin relaxation due to magnetic field inhomogeneities

- G• G. D. Cates, S. R. Schaefer and W. Happer, *Relaxation of Spins Due to Field Inhomogeneities in Gaseous Samples at Low Magnetic Fields and at Low Pressures*, Phys. Rev. A **37**, 2877-2885 (1988).
- H• G. D. Cates, D. J. White, Ting-Ray Chien, S. R. Schaefer and W. Happer, *Spin Relaxation in Gases Due to Inhomogeneous Static and Oscillating Magnetic Fields*, Phys. Rev. A **38** 5092 (1988).
- I• K. C. Hasson, G. D. Cates, K. Lerman, P. Bogorad and W. Happer *Spin Relaxation Due to Magnetic-Field Inhomogeneities: Quartic-Dependence and Diffusion-Constant Measurements*, Phys. Rev. A **41**, 3672 (1990).
- J• S.D. Stoller, W. Happer, and F. J. Dyson, *Transverse spin relaxation in inhomogeneous magnetic fields*, Phys. Rev. A **44**, 7459 (1991).

Because the spin relaxation times of polarized noble gases can be so long, it is often the case that they relax predominantly because of magnetic field inhomogeneities. Prior to our work on this subject, a description of spin relaxation due to magnetic field inhomogeneities was limited to a few special cases. For instance, the longitudinal spin-relaxation rate, $1/T_1$, which describes the relaxation of spins oriented parallel to the magnetic field, was discussed in two early papers by Gamblin and Carver,¹² and also by Schearer and Walters.¹³ These

early papers, however, considered only a high pressure limit where diffusion times are slow compared to the Larmor period. The transverse relaxation rate, $1/T_2$, which describes the relaxation of precessing spins which are oriented transverse to the magnetic field, had been described only approximately.¹⁴

We have developed, in a series of four papers, a comprehensive description of relaxation due to magnetic field inhomogeneities covering a wide variety of conditions. In the first paper, we developed general expressions for both $1/T_1$ and $1/T_2$ that were valid at all pressures. An interesting feature of our findings is that at low pressures, where the atoms are free to diffuse rapidly, a type of motional narrowing occurs. Previous expressions^{12,13} for $1/T_1$ indicated that relaxation is slower at high pressures, and faster at lower pressures. While that is true up to a point, we identified a "relative pressure" below which relaxation decreases. Our expression for the transverse spin relaxation rate $1/T_2$ was, as far as we know, the first rigorous result to appear in the literature. The high pressure limit of our result has a particularly simple form:

$$\frac{1}{T_2} = \frac{8R^4 |\vec{\nabla} \Omega_z|^2}{175D} \quad (3)$$

where D is the diffusion constant of the atoms carrying the spin, R is the radius of the spherical cell containing the sample, and $\Omega_z = 2\pi\gamma B_z$, where γ is the gyromagnetic ratio. This result is extremely useful in experiments that make use of long-lived precessing noble-gas spins, which as discussed above, are becoming increasingly numerous. It is also of central importance to future applications of polarized noble gases in such areas as magnetometry.

Having examined the effects of inhomogeneities in the presence of a static magnetic field, we went on to consider the case of two crossed magnetic fields, one static, and the other oscillating. This configuration is of great importance for magnetic resonance experiments. We developed expressions for what we called $1/T_{r1}$ and $1/T_{r2}$, the longitudinal and transverse spin relaxation rates in the *rotating frame*. We also performed a series of experiments to verify our results. One example of our data is shown in Fig. 2, in which we show the spin-relaxation rate $1/T_{r2}$ as a function of an applied magnetic field gradient. The dotted line represents a best fit assuming a quadratic dependence, which is seen to be fairly reasonable.

As our work progressed we noticed that for $1/T_{r2}$, the second-order perturbation theory on which we had relied to develop theoretical expressions was inadequate to describe our observations. Whereas $1/T_{r2}$ is proportional to the square of the magnetic field gradient for sufficiently small magnetic field inhomogeneities, $1/T_{r2}$ shows some quartic dependence as well as the inhomogeneities get larger. An example of relaxation as a function of applied inhomogeneity in which the quartic dependence is pronounced is shown in Fig. 3. We thus expanded our theory to include fourth order effects, and performed a number of studies to verify our results, measuring several diffusion constants in the process.

Another question that came to interest us is the connection between relaxation due to magnetic field inhomogeneities in the systems we typically study, which are usually gaseous samples with relatively fast diffusion, and systems that are historically more common, such as liquids or very high pressure gases, where diffusion is considerably slower. It had been

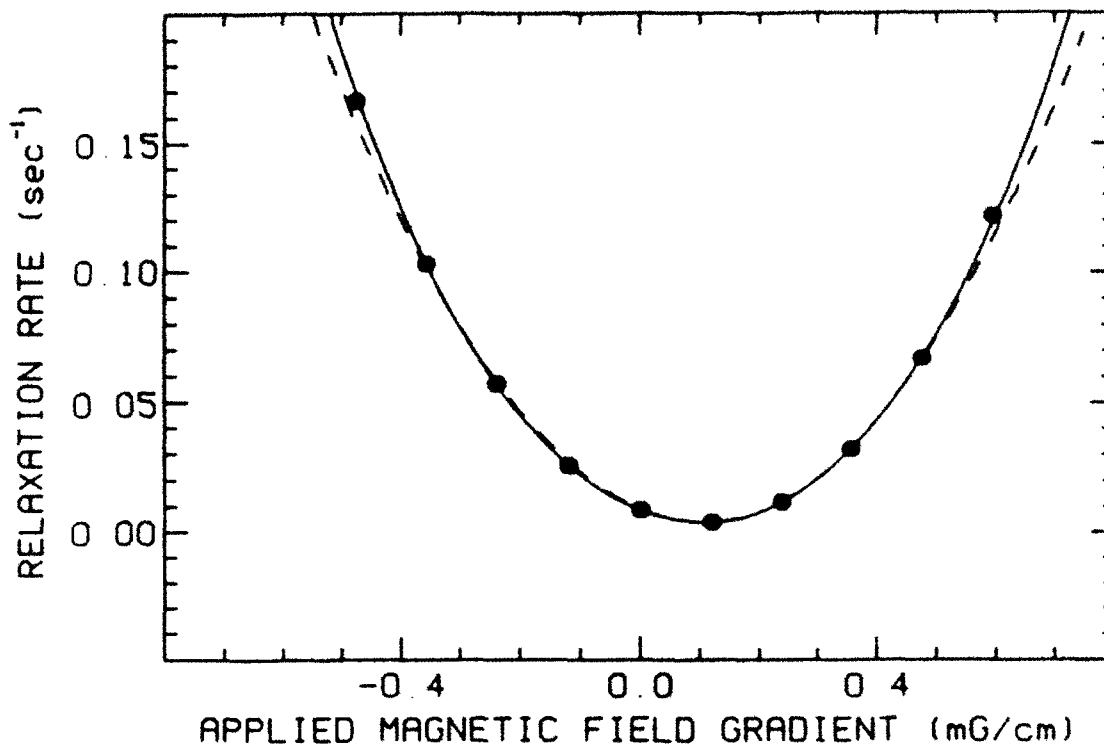


Figure 2. Data showing the spin-relaxation rate $1/T_{r2}$ as a function of an applied magnetic field gradient $\partial B_z/\partial z$. The dotted line shows a best fit to a quadratic dependence. The solid line is a best fit that includes both a quadratic and a quartic dependence. From publication I.

shown by Hahn¹⁵ that the decay of polarization during certain spin echo experiments can be described by the relation

$$\exp \frac{-D|\nabla\Omega_z|^2 t^3}{3}, \quad (4)$$

where D is the diffusion coefficient of the spin-bearing molecules or atoms in the liquid or gas, and Ω_z is the component of the local Larmor frequency along the z axis. On the other hand, we found in our work that the corresponding relaxation was described by the strictly exponential expression

$$\exp \frac{-8|\nabla\Omega_z|^2 R^4 t}{175D}, \quad (5)$$

which is valid for a spherical cell of radius R . These two expressions differ in a profound way; in one case polarization decays exponentially with t^3 , whereas in the other case the exponential decay goes simply like t .

The resolution of this question came about through studying solutions to the deceptively simple *Torrey equation*¹⁶ which has the form:

$$\frac{\partial\psi}{\partial\tau} = \frac{\partial^2}{\partial\zeta^2}\psi + i b\zeta\psi. \quad (6)$$

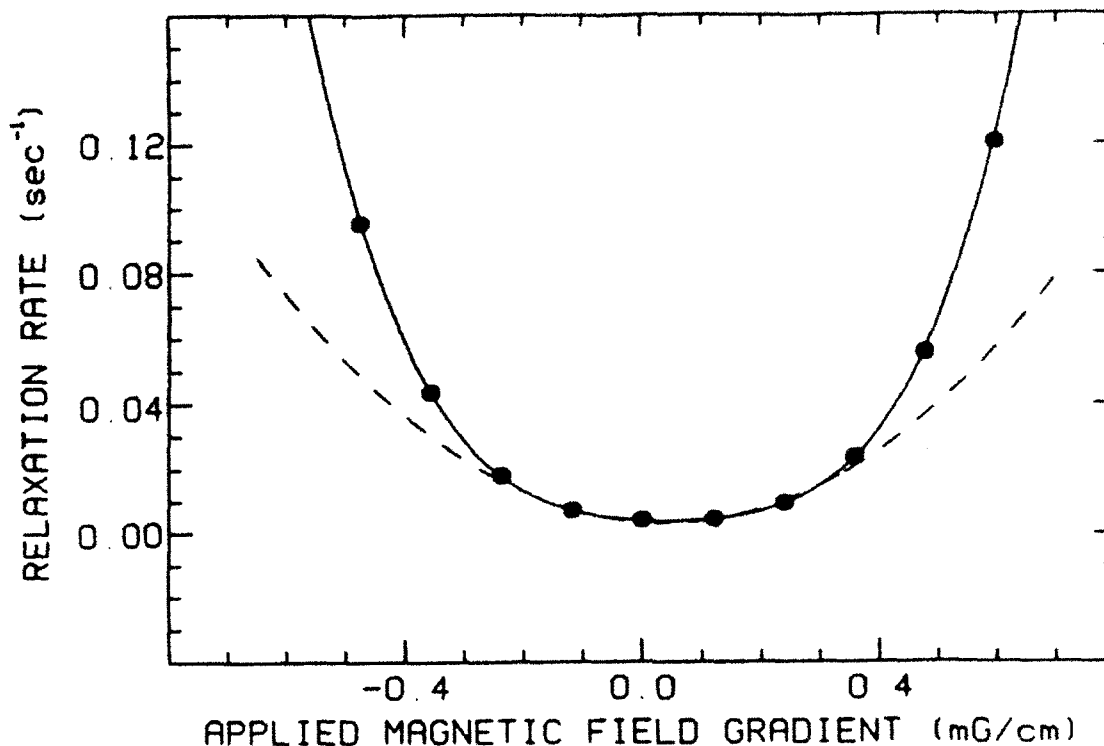


Figure 3. Data showing the spin-relaxation rate $1/T_{r2}$ as a function of an applied magnetic field gradient $\partial B_z/\partial z$. The dotted line shows a best fit to a quadratic dependence. The solid line is a best fit that includes both a quadratic and a quartic dependence. The data shown here clearly require the inclusion of a quartic term for a good fit. From publication I.

where ψ is an appropriately defined transverse polarization, τ and η are dimensionless variables describing time and space, and b is proportional to the magnetic field gradient. The solutions can be expressed in terms of Airy functions. Not only did this work resolve outstanding questions concerning spin relaxation, it was also interesting from a mathematical point of view. The work was carried out as a collaboration between Will Happer, Freeman Dyson, and a Princeton senior named Scott Stoller. Mr. Stoller won a position as an Apker Award finalist for his work.

IV. Spin polarized solid xenon

- K• G. D. Cates, D. R. Benton, M. Gatzke, W. Happer, K. C. Hasson and N. R. Newbury, *Laser Production of Large Nuclear Spin Polarization in Frozen Xenon*, *Phys. Rev. Lett.*, **65**, 2591 (1990).

One of our most important new discoveries during the four years covered by 88-0165 was that polarized gaseous xenon could be frozen with little or no loss of polarization. This discovery is illustrated in Fig. 4, showing NMR signals from a sample of ^{129}Xe , both before and after the sample was frozen. This simple observation opened the door to

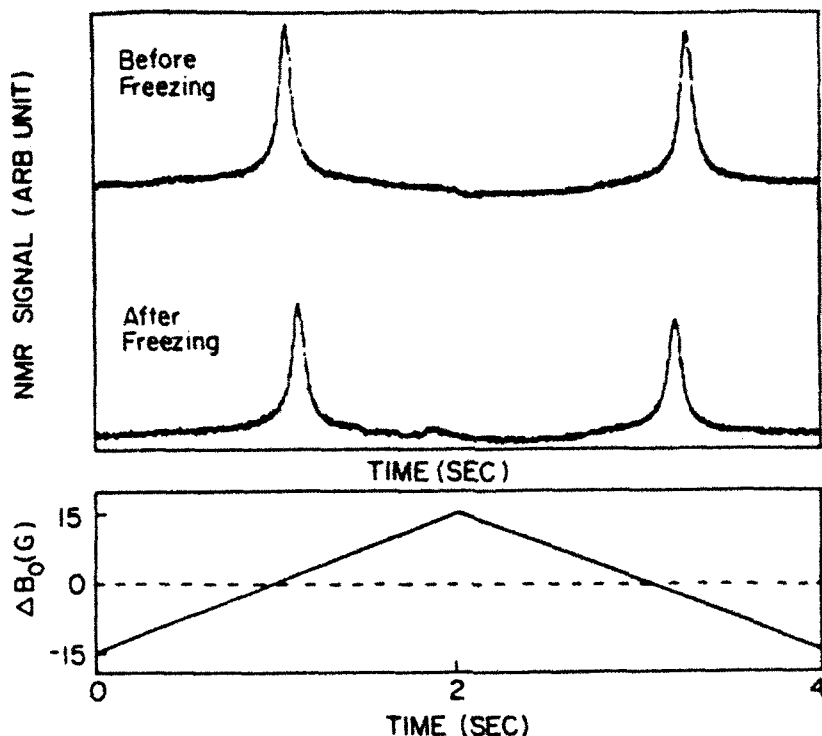


Figure 4. Show is an NMR signal from a sample of ^{129}Xe both before and after the sample was frozen. From publication K.

using spin-exchange optical pumping as a means for producing a highly polarized solid. Perhaps the greatest indication of the importance of this work is the degree to which the techniques we invented are being adopted elsewhere. Our techniques concerning laser polarized solid xenon are now being used by two groups outside of Princeton, Alex Pines' group at Berkeley, and Kurt Zilm's group at Yale. In our own work, we have focused on understanding the sources of spin-lattice relaxation, a subject about which relatively little was known for both solid ^{129}Xe , as well as other members of a wide class of diamagnetic insulators with a nuclear spin of $1/2$. Our early results, summarized in the Physical Review Letter (pub. K) cited above, provide many important new insights. We have reproduced this letter as an appendix to this report.

Our early work established two important facts concerning laser polarized frozen xenon. First, it is possible to produce relatively large samples with very high polarization. With relatively little effort, we produced samples of about 15 milligrams with polarizations of about 25%. In principle, it ought to be possible to produce nearly 1 gram of nearly 100% polarized xenon using a commercially available laser. The second fact is that the samples we produced were experiencing spin relaxation due to some *intrinsic* spin-relaxation mechanism. It had long been believed that spin relaxation in diamagnetic insulating crystals with a nuclear spin of $1/2$ was dominated by the presence of paramagnetic impurities. The spin-relaxation times we observed, however, about 3 hours at 77 K, were clearly due to something other than paramagnetic impurities. We argued that a

reasonable explanation for the relaxation involved the Raman scattering of phonons by a spin-rotation interaction

$$V_{sr} = \gamma_I \mathbf{I} \cdot \mathbf{N}. \quad (7)$$

Here V_{sr} is between the nuclear spin \mathbf{I} of a ^{129}Xe atom and its rotational angular momentum \mathbf{N} with respect to a nearest-neighbor atom in the crystal. Our conclusions were based on a comparison of the estimated size of the interaction with the observed relaxation rate, and the fact the the observed relaxation was insensitive to both magnetic field and isotopic composition as long as measurements were made above approximately 500 G.

Since that time we have accumulated considerable evidence, both theoretical and experimental, that the interaction (7) is in fact the mechanism causing relaxation. Much of the theoretical work was carried out by David Fox, a Princeton Senior, who, like Scott Stoller before him, won a place as a finalist in the Apker Award competition for his work. Mr. Fox found that for a wide range of temperature and magnetic field, $1/T_1$ is well described by the relation:

$$\frac{1}{T_1} \simeq 8.20 \times 10^4 \left(\frac{\gamma_I}{h} \right)^2 \left(\frac{h}{kT_D} \right) f(T^*) \left(1 + \frac{2}{3}\epsilon + 0.122\epsilon^2 \right) \quad (8)$$

Here h is Planck's constant, k is Boltzman's constant, $T_D = 55$ K is the Debye temperature of solid Xe 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 $\epsilon = (\tau_0/\gamma_I)(d\gamma_I/dr)$ 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 $r_0 \simeq 4.4\text{\AA}$.

Only two free parameters appear in (8), γ_I and ϵ . Fortunately, using some of the recent work on laser polarized xenon ice to come out of Pines' group at Berkeley, we can estimate these quantities.

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.²⁰ 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 (8) can be expressed in terms of the chemical shift,²¹

$$\frac{\gamma_I}{h} = \left(\frac{\mu_I}{I\mu_B} \right) \left(\frac{\hbar}{8\pi M r_0^2} \right) (\sigma_s - \sigma_g), \quad (9)$$

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.^{16,17} 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.⁴ We therefore we estimate

$$\frac{\gamma_I}{h} = -27 \text{ Hz}. \quad (10)$$

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 $\epsilon/r_0 = -2.506\text{\AA}^{-1}$,

which has been confirmed by temperature dependence measurements of the chemical shift in solid ^{129}Xe .¹⁹

The preceding estimates for γ_I and ϵ can be used with (8) to predict that $T_1 = 8300$ s at 77 K. In work that has been concluded during the current research period under the successor grant to 88-0165, Mike Gatzke has found that $T_1 = 8500 \pm 800$ s (for fields in excess of 1 kG), in excellent agreement with our expectations. The predictions of (8) and measurements of $1/T_1$ for $B \geq 1$ kG at other temperatures are also in good agreement. We have concluded 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, (as discussed in pub. K) while below about 20 K the large disagreement of the measurements with the predictions of (8) indicates the dominance of yet another mechanism for ^{129}Xe spin relaxation.

Further investigations of xenon ice are continuing during our current research period. A second Physical review letter, based on the thesis work of Mike Gatzke, will appear soon. Also, Brian Saam, a Ph.D. candidate in our group, is doing his thesis on related work.

V. Spin Interactions at surfaces

- L• Z. Wu, S. Schaefer, G. D. Cates and W. Happer, *Coherent interactions of the polarized nuclear spins of gaseous atoms with the container walls*, Phys. Rev. A **37**, 1161-1175 (1988).
- M• Z. Wu, M. Kitano, J. Daniels and W. Happer, *Experimental Studies of Wall Interactions of Adsorbed Spin-polarized ^{131}Xe Nuclei*, Phys. Rev. A **42**, 2774 (1990).

The interaction of polarized atoms with surfaces is important for a variety of reasons. In all of our research involving sealed glass cells, the polarized atoms are constantly undergoing collisions with the cell's interior walls. These collisions cause both spin relaxation, and in some cases, pronounced shifts of magnetic resonance frequencies. While it is important to understand wall collisions, both for fundamental research and for other applications, the study of spin interactions at surfaces is difficult. It is hard to prepare well understood surfaces, and it is also difficult to develop effective surface probes. Over the four years covered by 88-0165 we have had a number of marked successes in this area, as well as preparing the groundwork for future work.

One major accomplishment involves both experimental and theoretical studies of quadrupole interactions of polarized nuclear spins with the walls of the glass cells in which they are contained.²²⁻²⁴ The interactions are coherent in nature, and cause shifts of the magnetic resonance frequencies of nuclei such as ^{131}Xe and ^{21}Ne , both of which have a nuclear spin of $3/2$. In the absence of quadrupole shifts, the three m_I transitions, $\frac{3}{2} \leftrightarrow \frac{1}{2}$, $\frac{1}{2} \leftrightarrow -\frac{1}{2}$, and $\frac{1}{2} \leftrightarrow -\frac{3}{2}$, are degenerate. In the presence of quadrupole shifts, however, slight differences in these frequencies appear, and a beating phenomena is observed in NMR precession transients, an example of which is shown in Fig. 5.

The frequency of the beats turns out to be a powerful new probe of electric field gradients at the inner surfaces of the cell. Furthermore, this beating is of critical importance in other fundamental experiments (such as those described in Refs. 2 and 3) in which precessing nuclei are observed.

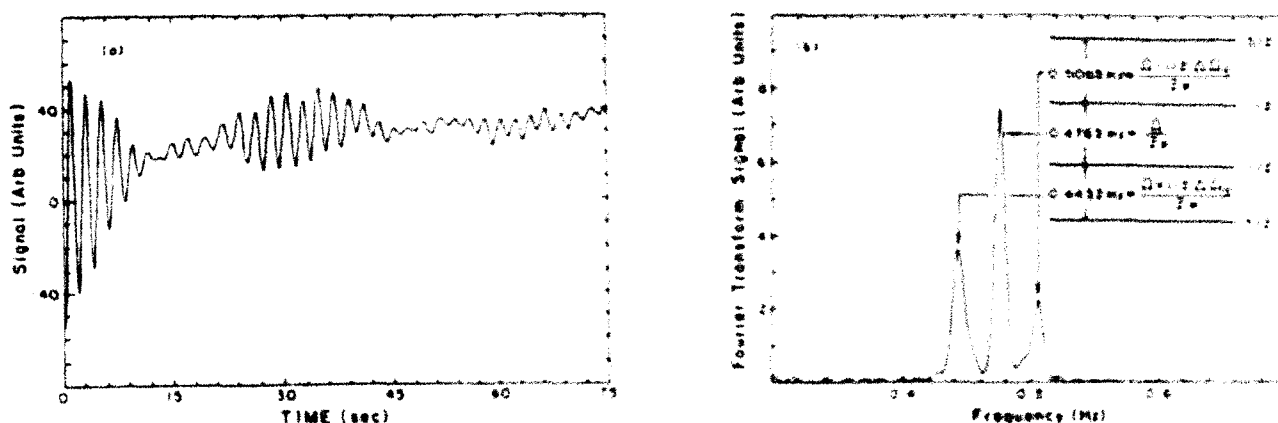


Figure 5. Shown is an NMR transient from ^{131}Xe spins that are undergoing Rabi precession. The “beating” is due to side-bands around the central precession frequency due to coherent quadrupolar interactions with the cell walls. From publications L and M.

More recently, we have succeeded in achieving a goal of long standing interest: the observation of the temperature and magnetic field dependence of wall induced relaxation of polarized noble gases, more specifically of ^{129}Xe . This work was begun as the senior thesis of Jordan Katine, who received his Princeton B.A. in June of 1991, and the senior thesis of Hideo Mabuchi, who received his Princeton B.A. in June of 1992. The results were so encouraging that the research has now become the subject of the Ph.D. thesis of Bastian Driehuys, who has been working with our group since the Fall of 1990.

The origin and significance of temperature and magnetic field dependence in wall induced relaxation can be fairly easily understood. Upon striking the wall of a container, an atom does not necessarily rebound, but may stick to the wall for a certain time.^{25,26} While the atom is on the wall it will vibrate about a site of equilibrium, it may hop from site to site as a result of thermal agitation, and eventually, the atom will acquire enough thermal energy to shake loose from the wall. If an atom binds to every adsorption site on the wall with the same adsorption energy E_a , the average dwell time τ_a of the atom on the wall would be

$$\tau_a = \tau_0 e^{E_a/kT} \quad (11)$$

where E_a is the adsorption energy, T is the absolute temperature, and the coefficient τ_0 depends weakly on temperature and can often be considered a constant. Theoretically,

τ_0 is a measure of the entropy difference between atoms in the adsorbed and gaseous state. Since the travel time between collisions with the walls is long compared to the dwell time on the wall, the wall induced relaxation rate can be expected to be proportional to τ_s . Studies of temperature dependence yield measurements of the adsorption energy E_a . The reason that magnetic field studies are relevant is somewhat more subtle. The magnetic perturbations causing the spin relaxation are basically random, but they are associated with the movement of the atom on the surface, and hence can be characterized by correlation times. For instance, if the motion causing the relaxation is hopping from site to site on the surface, we would expect a correlation time on the order of about a microsecond. On the other hand, if the source of the relaxation is vibrations of the adsorbed atom, we would expect a correlation time of about a nanosecond. The Fourier transform of the perturbation will have a finite bandwidth related to the perturbation. Thus, if a sufficiently large magnetic field is applied to the sample, we expect relaxation to be suppressed, because the Larmor resonance frequency will lie outside the bandwidth of the perturbation. By mapping out the magnetic field dependence of the spin relaxation, we gain information on the correlation times of the responsible mechanisms.

The actual mechanism causing the relaxation must ultimately be a time varying magnetic field. There are several possibilities. One is the magnetic dipole interaction with the magnetic fields generated by nearby nuclei. The field is most effective when the atom hops from adsorption site to adsorption site, since then the fields are strongly time dependent. This hopping will cause the spins to experience a fluctuating field with a magnitude on the order of a few Gauss and with a characteristic frequency on the order of the inverse of the hopping time τ_s of (11). Another possibility is a spin-rotation interaction of the form shown in (7), where in this case N is the rotational angular momentum of the adsorbed atom about the nearest-neighbor atom. This interaction might be expected to be much larger than the fluctuating part of the magnetic field from the nuclei in the wall, but since it depends on the relative motion of the adsorbed atom and the atoms of the wall, it always has a very short correlation time, on the order of a vibrational period. Quite a bit of physics is implicit in the coupling constant γ_I , which involves the second order effects of spin-orbit interactions, Coriolis interactions, hyperfine interactions, etc., and which depend very strongly on the distance R between the adsorbed atom and its nearest neighbor²⁷.

VI. Collaborations with outside groups

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- P• K.P. Coulter, A.B. McDonald, G.D. Cates, W. Happer, and T.E. Chupp, *Measurement of ^3He depolarization rates during bombardment with a ^4He beam*, Nucl. Inst. and Meth. in Phys. Res. **A276**, 29 (1989).
- Q• K.P. Coulter, T.E. Chupp, A.B. McDonald, C.D. Bowman, J.D. Bowman, J.J. Szymanski, V. Yuan, G.D. Cates, D.R. Benton, and E.D. Earle, *Neutron Polarization*

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- S• N.R. Newbury, A.S. Barton, P. Bogorad, G.D. Cates, M. Gatzke, B. Saam, L. Han, R. Holmes, P.A. Souder, J. Xu, and D. Benton, *Laser Polarized Muonic Helium*, Phys. Rev. Lett. **67**, 3219 (1991).

There has been a long and productive tradition of collaboration between those working on the AFOSR program and researchers supported by other sources of funding. We discuss those efforts here, along with the resulting publications. These activities have been of tremendous value, both directly and indirectly, to our central research goals. In addition to providing new information on spin interactions of atoms and nuclei, our collaborations have often sharpened our perception concerning the most relevant directions for our future work. In deed, several of the experiments being completed in the current grant period were inspired by some of the collaborations described here.

In the work by Kitano *et al.* (pub. N), spin-exchange optical pumping was used to polarize several radioactive isotopes of radon. This work built on earlier collaborative work polarizing radioactive isotopes of xenon.^{28,29} The magnetic moments of the relevant isotopes were determined quite precisely, and the work has potential value for future studies of T-violating effects. This work also represents the only study of spin exchange in the radon system. We note that M. Kitano was supported jointly by the Air Force and the cyclotron group.

In the work by Coulter *et al.* (pub. P), we were measuring depolarization rates of ^3He due to bombardment with ionizing radiation, more specifically, a beam of ^4He nuclei. We were testing the theoretical predictions described in publication F by Bonin, Walker, and Happer that is mentioned in section II.

In the second paper by Coulter *et al.* (pub. Q), we were participating in an experiment to use polarized ^3He as a spin filter to polarize neutrons. These early efforts were the beginning of what has become a growing new technique. Programs to polarize neutrons using ^3He are now being developed at research reactors at both Grenoble and NIST.

In the work described in the papers by Holmes *et al.* (pub. R) and Newbury *et al.* (pub. S), nuclear polarized ^3He was being used at LAMPF to produce polarized muonic helium. While this work is supported by a separate grant from the DOE, several students supported by the Air Force, most notably Mike Gatzke and Brian Saam, participated in the runs at Los Alamos. In addition to what we learned about spin interactions in muonic atoms, the LAMPF work brought several interesting pieces of physics to our attention. In particular, it was during these efforts that we realized that it was possible to construct ^3He cells in which spin relaxation is dominated by dipole-dipole interactions that occur during ^3He - ^3He collisions. Also, the work with muonic helium inspired some of our recent work with frequency shifts.

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VIII. Personnel

The people listed below received full or partial support from the grant during some portion of the period covered by this report.

Faculty

Dr. William Happer, Professor of Physics
Dr. Gordon Cates, Assistant Professor of Physics
Dr. Keith Bonin, Assistant Professor of Physics

Post Doctoral Research Associates

Dr. Donald Benton (now Univ. of Penn.)
Dr. Thad Walker (now at Univ of Wisconsin)

Graduate students

Note, those whose names are marked with a * received a Ph.D. from work supported by this grant.

- * Dr. Thad Walker (received Ph.D. in Jan. '88, worked with our group as a post-doc (see above), went to JILA, and then to Univ. of Wisconsin.
- * Dr. Steven Schaefer (received Ph.D. in Sept. '88, now at TACAN in Carlsbad, CA)
- * Dr. Sven Redsun (received Ph.D. in December 1989, now at Lawrence Livermore Laboratories)
- * Dr. Michael Gatzke (received Ph.D. in August 1992, now at the University of Virginia)
- Dr. Nathan Newbury (received Ph.D. in August 1992, now at JILA)
- Mr. Paul Bogorad
- Mr. Brian Saam
- Mr. Bastian Driehuys
- Ms. Amy Barton

Undergraduates working on Princeton senior theses

Mr. David Fox, (now at Harvard, Apker Award Finalist)
Mr. Scott Stoller (now at Cornell, Apker Award Finalist)
Mr. Jordan Katine (now at Harvard)
Mr. Richard Fitzgerald (now at Harvard)
Mr. Kenton C. Hasson (now at Harvard)
Mr. David Lopez (now in industry)
Mr. Hideo Mabuchi (now at Cal Tech)

Laser Production of Large Nuclear-Spin Polarization in Frozen Xenon

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The nuclei of gaseous ^{129}Xe atoms are polarized by spin exchange with optically pumped Rb vapor. The Xe gas is subsequently frozen. The nuclear polarizations of up to 25% are largely unaffected by freezing. The spin-lattice relaxation time T_1 was measured as a function of temperature, magnetic field, and isotopic composition. At 77 K and 1800 G, T_1 is limited to about 3 h by a new relaxation mechanism. The potential for accumulating large samples with even higher polarizations makes laser-polarized Xe ice promising for a wide variety of new experiments.

PACS numbers: 76.60.Es, 29.25.Kf, 32.30.Dx, 32.80.Bx

We describe a simple way to produce Xe crystals with high nuclear-spin polarization. We polarize gaseous ^{129}Xe , which has nuclear spin $\frac{1}{2}$, by spin exchange¹ with optically pumped Rb and subsequently freeze the gas in liquid N_2 at 77 K. We have produced 14-mg samples of Xe ice with nuclear polarizations up to about 35%, and spin-lattice relaxation times T_1 of 2–3 h. The gas approaches its equilibrium polarization exponentially with a time constant of about 10 min, much shorter than T_1 in the ice at 77 K. In the gaseous phase, Xe atoms absorb angular momentum at a rate $\frac{1}{2}\eta P/h\nu$, where $\eta \approx 10\%$ is the fraction of Rb angular momentum that is transferred to Xe nuclei,² P is the absorbed laser power, and $h\nu$ is the energy per photon. For 5 W of absorbed laser power, this amounts to about 0.8 g/h. If T_1 is as long as many days at 4 K, as our experiments suggest, one could imagine a flowing gas system that would produce nearly 20 g per day. The equilibrium polarization of the gaseous ^{129}Xe is given by $P_{\text{Xe}} = P_{\text{Rb}}/(1 + T_{\text{ex}}/T_w)$, where P_{Xe} (P_{Rb}) is the average Xe (Rb) polarization ($P \leq 1$), and $1/T_{\text{ex}}$ and $1/T_w$ are the relaxation rates of Xe atoms due to the Rb, and the cell walls.^{1,2} In order to have large quantities of spins in our cells, we chose to operate at pressures of 1–5 atm. At lower Xe pressures, where both P_{Rb} and $1/T_{\text{ex}}$ can be larger, one can achieve polarizations approaching 100%.

Rare-gas solids have long attracted considerable attention. Norberg and co-workers have done extensive NMR studies of both Xe and other noble-gas solids,³ including measurements of spin-spin relaxation times T_2 of ^{129}Xe , and measurements of spin-lattice relaxation effects in systems with nuclear spins $> \frac{1}{2}$ where quadrupole effects cause rapid relaxation. Pipkin and co-workers investigated the possibility of polarizing the nuclei of frozen noble gases by optically pumping trapped alkali-metal atoms, and transferring the electron spin to the surrounding noble-gas nuclei by spin exchange.⁴ Unfortunately, difficulties associated with the effect of the trapping sites on the alkali optical spectra and with short electron spin-lattice relaxation times made the technique impractical. We avoid these problems by polarizing the nuclei in a gas before condensing the gas to a solid.

Tastevin *et al.*⁵ have used a similar technique to liquify optically polarized ^3He . In their work, however, a relaxation time of a few minutes was observed, which is comparable to the expected intrinsic relaxation time (due to dipole-dipole interactions) of weakly polarized bulk liquid ^3He . As will be discussed later, Xe also relaxes quickly due to the same dipole-dipole interaction at temperatures near its melting point of 161 K. Longer relaxation times are required for the accumulation of large quantities of polarized material, which are potentially useful for polarized nuclear targets⁶ and for other interesting experimental possibilities. For example, the ice could be useful in searches for parity- and time-reversal-nonconserving forces of the sort that would arise from various exotic light pseudoscalar particles such as axions.⁷

The gaseous samples consist of $\approx 6.5 \times 10^{19}$ atoms of Xe contained in two types of sealed Pyrex cells: spherical *high-pressure* cells, 0.52-cm³ volume, containing 5 atm of Xe; and cylindrical *low-pressure* cells, 3.1-cm³ volume, containing 1 atm of Xe. Both types of cells also contained about 50 Torr of N_2 to quench the fluorescence of laser-excited Rb atoms, and a few milligrams of Rb metal. All partial pressures quoted above are for 25°C. Samples of both natural isotopic composition and enriched ^{129}Xe concentration (72.9% ^{129}Xe , 5.3% ^{131}Xe) were used. The cells were heated in an oven to temperatures between 80 and 120°C and the Rb atoms were optically pumped with 0.5–5.0 W of circularly polarized 795-nm laser light in a magnetic field of about 30 G. The ^{129}Xe nuclei were polarized by spin-exchange collisions with the Rb atoms.¹ After about $\frac{1}{2}$ h, the ^{129}Xe polarization was typically $\geq 90\%$ of its equilibrium value. The cells were then removed from the oven, carried to a separate apparatus that was equipped to perform NMR measurements, and submerged into a Dewar of liquid N_2 , located at the center of Helmholtz coils, where Xe gas condensed into crystals. Separate experiments showed that polarization losses during transit were typically less than (1–2)%. A magnetic field of ≈ 1800 G was applied during freezing. As indicated by the NMR traces shown in Fig. 1, no significant loss of polar-

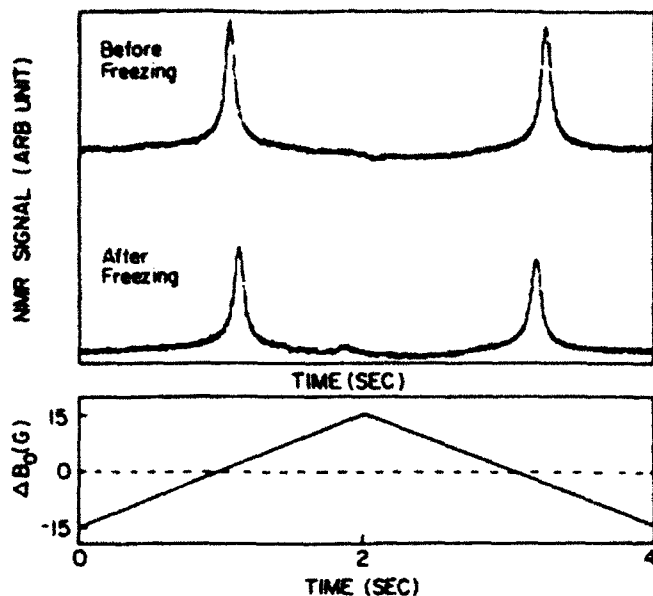


FIG. 1. NMR adiabatic fast passage (AFP) signal of a Xe sample before and after the sample was frozen. As indicated at the bottom, the magnetic field is swept through the resonance condition twice, resulting in two peaks. This facilitates monitoring the losses that occur during an AFP sweep, and also assures that the nuclei are left in the same orientation as before the scan. The height of the signals is proportional to the polarization. Because of the fact that the nuclear spins are spatially distributed differently before and after freezing, the slight difference in peak height is not necessarily an indication of a loss of polarization.

ization occurred as a result of the freezing. During measurements of T_1 , fixed temperatures of 77 or 87 K were maintained in a glass Dewar filled with either liquid N_2 or liquid argon. Temperatures between 100 and 145 K were maintained by flowing cold N_2 gas past the sample and controlling the gas temperature with a heater and a temperature-sensing feedback circuit.

The polarization of the sample was monitored using the NMR technique of adiabatic fast passage (AFP).⁸ An oscillating magnetic field was applied to the sample in a direction orthogonal to the static field. When the static magnetic field was swept through the resonance condition, the ^{129}Xe spins reversed their orientation. As the spins flipped, the precessing magnetization was detected by pickup coils, and produced signals like those of Fig. 1. The static field was ramped through resonance twice. There are two advantages to this: The spins were left in their original orientation, and the relative heights of the two peaks provided a measure of the polarization loss due to the AFP. The amplitudes of the signals were proportional to the polarization of the sample, and were calibrated by comparison with AFP signals from protons-in-water samples. We plotted the natural logarithms of the signal amplitudes (adjusted for AFP losses) as a function of time, and the inverse slopes of the best-fit straight lines to the semilogarithmic plots are

quoted as the longitudinal relaxation time T_1 of the samples. The data must be regarded as somewhat preliminary at present because the semilogarithmic plots were curved slightly upward. Perhaps related to the nonexponential decay is a small but reproducible difference between the relaxation times for our high-pressure and low-pressure cells. For the low-pressure, isotopically enriched cells at 77 K, $T_1 = 7700 \pm 300$ s, while $T_1 = 9800 \pm 600$ s for the high-pressure cells. Both of these effects may be associated with the polycrystalline nature of our samples. More rapid depolarization at grain boundaries could cause spin diffusion from the bulk. We hope to clarify the nature of the slightly nonexponential decay and the dependence on the cell filling pressure with an improved NMR apparatus.

Our initial measurements of T_1 (in the high-pressure cells) yielded 9800 ± 600 and 8500 ± 1000 s for the enriched and natural samples at 77 K and an external magnetic field of 1800 G. It is not clear why these times are not longer. As was first pointed out by Waller,⁹ the most obvious interaction, the magnetic dipole-dipole interaction between neighboring nuclei in the rigid lattice, leads to theoretically predicted relaxation times of months, and is thus irrelevant. This is in contrast to the situation with liquid (or even solid) ^3He where more rapid relative motion of the atoms leads to much shorter relaxation times due to the dipole-dipole interaction. Most often, spin-lattice relaxation of spin- $\frac{1}{2}$ nuclei is attributed to paramagnetic impurities.¹⁰ Let us suppose that paramagnetic impurities were present at a small relative concentration $C = N_S/N_I \ll 1$, where N_S and N_I are the number densities of paramagnetic impurities and ^{129}Xe nuclei. Abragam and Goldman¹¹ derive a resulting contribution to the relaxation rate

$$\frac{1}{T_1} = \frac{8\pi}{5} \frac{S(S+1)}{3} C \left(\frac{\gamma_S}{\gamma_I} \right) \left(\frac{\Delta H_n}{H_0} \right)^2 \frac{\omega_0^2 T_{1e}}{1 + \omega_0^2 T_{1e}^2} \quad (1)$$

where γ_S and γ_I are the electron and ^{129}Xe nuclear gyromagnetic ratios, $\Delta H_n \approx \gamma_I \hbar N_I$ is the nuclear linewidth due to spin-spin interactions in the rigid lattice, T_{1e} is the longitudinal relaxation time of the electronic spin S , and $\omega_0 = \gamma_I H_0 \gg \gamma_I \Delta H_n$ is the Larmor frequency of the ^{129}Xe spins in the external magnetic field H_0 . In the derivation of (1) it is assumed that within a distance $b = (\Delta H_n / \gamma_S \hbar)^{1/3}$ of the paramagnetic center, the ^{129}Xe nuclei have their Larmor frequencies shifted by more than the rigid-lattice linewidth ΔH_n , and are therefore unable to exchange nuclear-spin polarization with other nuclei. All nuclei no closer than b to a paramagnetic impurity maintain spin-exchange equilibrium with each other and are depolarized by the fluctuating dipolar magnetic field of the impurity, which has a correlation time of T_{1e} . The global relaxation rate is just the spatial-average relaxation rate for all nuclei which are no closer than b to the impurity spin.

Equation (1) predicts that $1/T_1 \propto N_I$, and N_I differs

where $\tau_c = \tau_0 e^{E_D/kT}$ is the thermally activated correlation time for vacancy diffusion. The factor f accounts for the isotopic enrichment of the sample; for samples of natural isotopic composition, $f=1$, and for our enriched samples, $f=2.42$. We have plotted (3) in Fig. 3 with a dotted line using Yen and Norberg's measured values of $1/T_2$ and τ_c . Although the order of magnitude of the relaxation predicted by (3) is correct, we obtained a much better fit with $E_D/k=2000$ K, in contrast to Yen and Norberg's measured value of $E_D/k=3727$ K.

At temperatures below about 120 K, the measured rates are orders of magnitude faster than can be explained by (3), so some other mechanism must dominate the relaxation at the lower temperatures. Brinkmann, Brun, and Staub¹⁵ have already pointed out that the measured spin-relaxation times of ¹²⁹Xe in high-pressure Xe gas are about 1000 times shorter than predicted from the magnetic dipole-dipole interaction. We suggest that at low temperatures, $1/T_1$ is dominated by Raman scattering of phonons by the nuclear spin-rotation interaction

$$V_1 = \gamma_I I \cdot N, \quad (4)$$

which is analogous to the electron spin-rotation interaction.² Here I is the nuclear spin of the ¹²⁹Xe. The coupling coefficient must be of order $\gamma_I \approx nA\gamma_S/E_e$, where n is the effective number of outer-shell electrons that participate in the interaction, $A/h \approx 10^{10}$ Hz is the mean magnitude of the hyperfine interaction between a ¹²⁹Xe nucleus and one of the n electrons, and $E_e \approx 10$ eV is the energy required to excite one of the n electrons. Our data are best fitted by a value of $\gamma_I \approx 35$ Hz. Using the previously measured¹² value of $\gamma_S/h = 1.6$ MHz, our estimate agrees well with our measurement for a value of $n \approx 7$. We note that our measured value of $\gamma_I = 35$ Hz would very nearly account for the results of Brinkmann, Brun, and Staub.

If the rate were proportional to T^2 , as indicated in (2) for temperatures below 120 K, the anticipated longitudinal relaxation time at 4 K would be about 43 days. In fact, if the relaxation is due to phonon scattering, the relaxation time would be even longer than this estimate, since 4 K is well below the 55-K Debye temperature of Xe crystals, and the hot phonons would be frozen out.

To summarize, laser production of large nuclear polarization in frozen Xe is practical, and relatively easy. At 77 K, the relaxation times in the ice are 2-3 h, and ap-

pear to be dominated by a new relaxation mechanism. The long relaxation times make feasible the accumulation of as much as a gram of > 50% polarized material. Indications are that relaxation will become significantly longer at lower temperatures, which would further increase the amount of polarized Xe one could collect. We are undertaking further experiments to better understand spin relaxation in the ice, and we are exploring several other applications including polarized nuclear targets and the study of spin-dependent forces. Laser-polarized Xe ice may be useful for a wide variety of new experiments.

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by a factor of 2.8 for our natural and enriched samples. The fact that we observed T_1 to be nearly independent of N_I is strong evidence that paramagnetic impurities cannot be responsible for the observed relaxation. The magnetic-field dependence of paramagnetic-impurity-induced relaxation requires a knowledge of T_{1c} , about which little is known for alkali-metal atoms in noble-gas matrices. If we assume that Rb atoms are somehow incorporated in our Xe crystals, we can estimate T_{1c} from the well-known¹² spin-rotation interaction $V_S = \gamma_S \mathbf{N} \cdot \mathbf{S}$ between the spin of a Rb atom moving with rotational angular momentum \mathbf{N} about a Xe atom. Raman scattering of phonons by the spin-rotation interaction will cause a relaxation time $T_{1c} \approx 5 \times 10^{-6}$ s which we estimated with a calculation similar to van Kranendonk's¹³ treatment of quadrupolar nuclear relaxation. Thus, if Rb atoms are incorporated into the crystal, (1) implies that the nuclear-spin relaxation rate due to the paramagnetic centers should be proportional to the inverse square of the external magnetic field for fields larger than about 100 G. In Fig. 2, we show the magnetic-field dependence of the relaxation rate at 77 K. The rates are essentially independent of magnetic field and isotopic composition for fields above 500 G in contradiction to the predictions of (1). For fields below 500 G both natural and enriched samples relaxed more rapidly. Even if we assume that our estimate of T_{1c} is wrong and we maximize (1) with respect to T_{1c} , the concentration C needed to cause the observed relaxation at 77 K would be about 1 part in 10^5 , which is much greater than the relative concentration of Rb atoms at room temperature before freezing the Xe. Our Xe crystals should have great chemical purity since the Rb

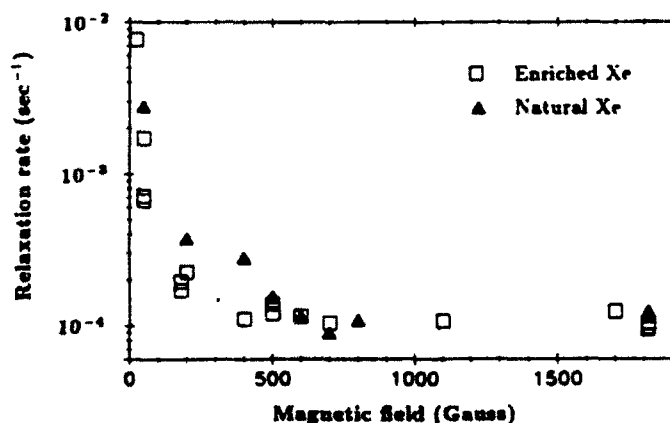


FIG. 2. The spin-lattice relaxation rate $1/T_1$ of ^{129}Xe nuclei as a function of magnetic field for two samples, one containing Xe of natural isotopic composition (26.4% ^{129}Xe and 21.2% ^{131}Xe), and one containing Xe that has been isotopically enriched (72.9% ^{129}Xe and 5.3% ^{131}Xe). We list only the isotopic fractions of Xe isotopes with nonzero nuclear spin. These data were obtained at a temperature of 77 K. Note that above about 500 G, $1/T_1$ is essentially independent of both isotopic composition and magnetic field.

atoms condense almost completely before the temperature drops low enough for the Xe to freeze. The Rb also ensures that the O_2 , another potential paramagnetic contaminant, is absent because of gettering. We therefore conclude that paramagnetic impurities cannot be responsible for the relaxation we observe.

We have systematically measured T_1 as a function of temperature, and the results of these measurements are summarized in Fig. 3. The data are fitted well by the function

$$1/T_1 = aT^2 + be^{-E_D/kT}, \quad (2)$$

where the term in T^2 is to be expected from any relaxation mechanism due to Raman scattering of phonons at temperatures above the 55-K Debye temperature of the Xe ice, and the second term is characteristic of relaxation due to the magnetic dipole-dipole interaction and vacancy diffusion with an activation energy E_D . At the two highest temperatures measured, 135 and 145 K, the measured rates depend noticeably on the isotopic composition, suggesting that a dipole-dipole interaction is contributing significantly to the relaxation. Yen and Norberg showed that the rapid transverse relaxation rate $1/T_2$ of solid ^{129}Xe is well explained by the dipole-dipole interaction, with motional narrowing caused by the diffusion of vacancies taken into account. Using the theory of Kubo and Tomita,¹⁴ we can predict a contribution to T_1 from Yen and Norberg's measured values of T_2 and the correlation time τ_c associated with the diffusion of the vacancies,

$$\frac{1}{T_1} = \frac{4}{3} \frac{f}{(\omega_0 \tau_c)^2} \frac{1}{T_2} \propto \frac{\sigma^2}{\omega_0^2 \tau_c}, \quad (3)$$

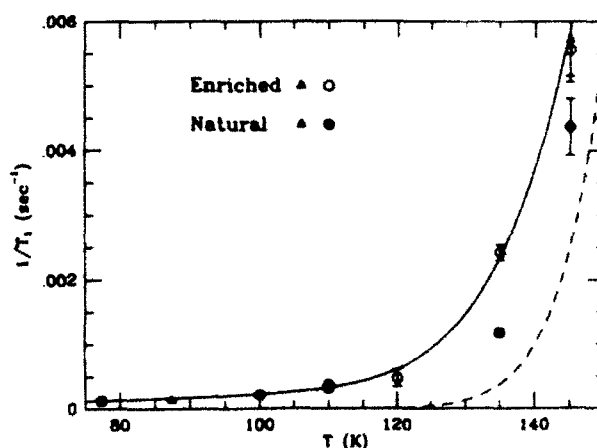


FIG. 3. The spin-lattice relaxation rate $1/T_1$ as a function of temperature. Solid line, a fit by the function given by (2) of the data points corresponding to the low-pressure isotopically enriched samples. Circles (triangles), the low- (high-) pressure cells. Dotted line, relaxation expected from vacancy diffusion given by (3) and the data of Yen and Norberg. Note that at high temperatures the samples with natural isotopic composition have lower relaxation rates.