

## Hyperpolarization of $^{133}\text{Cs}$ nuclei enhanced by ion movement in a cesium salt

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Hyperpolarization of  $^{133}\text{Cs}$  nuclei in CsCl salt is achieved through spin transfer from an optically pumped Cs vapor, with maximum polarizations of 0.1% demonstrated. Motional narrowing of the enhanced NMR line indicates that ion movement facilitates this process by transporting spin-polarized ions from the interface into the salt. The resulting NMR enhancement allows measurement of the polarization and its dynamics in real time. Based upon the NMR frequency and the longitudinal spin relaxation time, we find no evidence that the salt is contaminated by Cs metal or paramagnetic impurities. The Cs nuclear polarization reported here could be improved several orders of magnitude by intense laser heating of the entire sample.

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Recent attempts to polarize nuclei in alkali-metal salts have yielded many discoveries, culminating in the demonstration that a dilute atomic vapor can transfer a considerable amount of its spin polarization to a dense solid [1–4]. Optically polarized alkali-metal atoms transport the angular momentum of their electrons and nuclei to the solid surface, giving some of it to the salt nuclei and enhancing its nuclear magnetic resonance (NMR) signal [1]. Based upon experimental and theoretical studies of this enhancement over a wide range of magnetic fields, the nuclear spin of the vapor was found to be the dominant contribution to nuclear polarization of the salt [2]. In order to determine the mechanism of spin transfer (e.g., the dipolar interaction or atom exchange), a low static magnetic field was preferable for these experiments. To overcome the resulting small signal, fine glass fibers were coated with the salt to provide a large surface area for efficient contact with the polarized atomic vapor [3]. Despite extensive scattering by the glass wool, the randomly polarized and randomly propagating laser light was able to optically pump the vapor, because the magnetic field was still large enough to separate the optical transitions. In addition to the dissociative compound CsH, the stable salt CsCl was also used to obtain a  $^{133}\text{Cs}$  spin polarization of 0.001%, ten times larger than at thermal equilibrium. The transfer rate was shown to be independent of energy for atom exchange; hence, the nuclear dipole interaction is responsible for spin transfer between adsorbed atoms and salt ions [4]. In this paper, we report hyperpolarization of Cs nuclei to a mean polarization of 0.1% by optical pumping and heating. Since the ion mobility is increased at high temperature, the nuclear polarization at the surface is rapidly delivered into the salt, polarizing the bulk and not just the surface. The resulting NMR enhancement enables real-time measurements of spin evolution with and without the laser beam.

CsCl salt was contained in a borosilicate glass cell along with Cs metal, quartz-glass wool, and  $\text{N}_2$  gas [2,3]. The gas pressure was optimized at 2 kPa for optical pumping. In manufacturing the salt cells, coarse grains of CsCl were ground to fine powder, added to the cell along with glass wool, and baked at  $350^\circ\text{C}$  for a few days. In addition to the powder which settled on glass fibers, a chloride film also formed on the fibers by sublimation. This provided a large surface area of salt to be exposed to the polarized Cs vapor. Because

the Cs metal was put into the cell at room temperature, the metal was not mixed with the salt prior to the optical pumping experiment. The optical-pumping NMR experiment has been described in detail [3,4]. Briefly, it consisted of a cylindrical 0.56 T permanent magnet. A solenoid NMR coil transverse to the magnet axis surrounded the cell, which was placed in a heated copper tube within the magnet and illuminated by a laser propagating along the coil axis. The laser light was randomly scattered by glass wool regardless of the original direction of linear polarization and propagation.

Each free-induction decay followed excitation by a single radiofrequency (rf) pulse. The integral of its Fourier transform (here referred to as the NMR area) is proportional to the spin polarization and the number of nuclei in the detection region. We could selectively detect the  $^{133}\text{Cs}$  NMR signal of the salt (molar ratio of cesium,  $m = 0.5$ ) and metal ( $m = 1$ ) because of the Knight shift (1.45%) [5,6]. The resonance frequency of a homogeneous mixture with  $0.5 < m < 1$  is between these frequencies [7]. The Cs vapor density depended on the temperature of glass stem and the optimum signal was observed at  $100^\circ\text{C}$ . Since the electron Zeeman splitting is on the order of the hyperfine splitting of ground-state, the absorption lines overlap across 60 GHz for the  $D_2$  line. Optical pumping produced a positive nuclear polarization both in the vapor and in the salt at a laser frequency  $\nu_P = 351\,718.0$  GHz and negative polarization at  $\nu_N = 351\,731.5$  GHz [2].

We applied rf pulses to acquire the NMR spectrum both during continuous laser illumination and after turning the laser off. For continuous pumping at an optical power  $P_L = 1.2$  W, the enhanced signal was significantly narrowed, as shown in Fig. 1. The duration of optical pumping was typically 300 s. The amplitude of the narrow NMR spectrum was three orders of magnitude larger than for previously reported signals in CsCl [4]. The residual linewidth was due to the field inhomogeneity of the magnet. Excessive focusing of laser beam caused a decrease of the NMR area since only a portion of salt was illuminated. Therefore, the focus and the position of pump beam were chosen to maximize the NMR area. For continuous pumping at  $P_L = 0.67$  W, we detected a smaller signal with a dipolar-broadened width similar to that of unpolarized CsCl. Although the signal was much larger than at thermal equilibrium, the NMR area of this broad peak was only 20% of that for  $P_L = 1.2$  W. According to the theory of

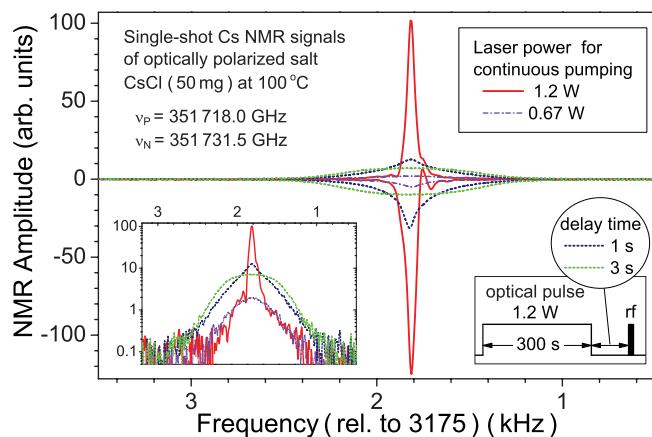


FIG. 1. (Color online) Single-shot  $^{133}\text{Cs}$  NMR signals for CsCl salt. Positive and negative signals were due to optimally focused laser beam at optical frequencies  $\nu_p$  and  $\nu_N$ , respectively. The laser power was varied for continuous pumping as shown in the upper-right inset and the broad components are very similar in both laser powers as shown by the logarithmic plots in the left inset. When the optical pulse was shut off before NMR acquisition, broad but large peaks were observed. The thermal equilibrium signal was smaller than the noise level. The distortions in the wings of the narrow peaks arise from unknown causes.

spin current in atomic vapor, the nuclear polarization of salt should be proportional to  $\sqrt{P_L}$  [1,2]. The large deviation from this prediction suggests additional mechanisms underlying the spin polarization of the narrow signal. We applied an rf pulse within a few seconds of turning off the laser. The NMR signal was large and narrow at the end of optical pulse as in continuous pumping. During the delay time, the enhanced line became successively broader without shifting its center frequency, as shown in Fig. 1. The NMR area of the broad peak was unchanged during this transition.

The crystal structure of CsCl transforms to NaCl type at  $445^\circ\text{C}$  [8]. At this transition, however, the change of static structure such as an internuclear distance is too small to explain the observed narrowing. The observations suggest motional narrowing of enhanced line, according to the fact that the ion mobility increases by several orders of magnitude at high temperature in both the solid and the liquid [9,10]. When cooled down in the dark, the salt presents a broad NMR peak as shown by delayed detection. By weak continuous heating, the ion mobility is insufficient for narrowing. This leads us to propose that the Cs nuclei were highly polarized at the surface by spin transfer from the vapor, and that intense laser heating allows these polarized nuclei to rapidly diffuse into the salt and dramatically enhance the NMR signal.

We observed the enhanced narrow peak at temperatures as low as  $40^\circ\text{C}$ , where the saturated vapor density is too low to induce sufficient spin current by optical pumping. It is possible that the metal left on the surface was ablated by the pump laser, thus generating sufficient vapor density, and that the metal coexisted with the salt. The effects of salt-metal mixing on the polarization process are unclear, but seem likely to be small for the following reasons: The phase diagram of the CsCl-Cs mixture shows no monotectic composition—when the ratio of cesium  $m$  increases along the liquidus curve,

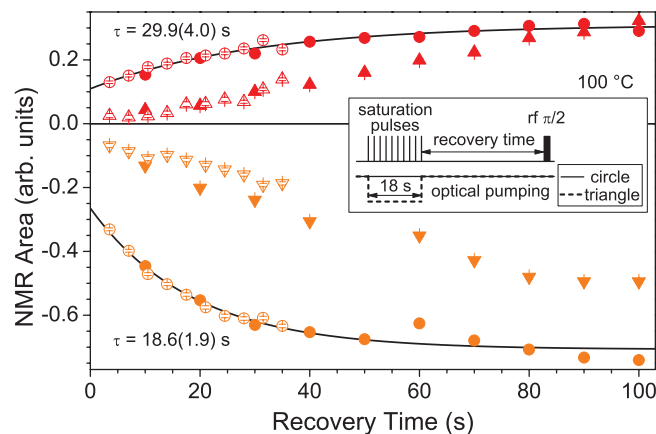


FIG. 2. (Color online) Recovery of NMR signal with a weakly focused pump beam tuned to  $\nu_p$  (positive enhancement) and  $\nu_N$  (negative). Saturation rf pulses were applied with the pumping light on (circles) and off (triangles) as shown in the inset. Different series of measurements are distinguished by the open and the closed symbols. The time constants of the fitting curves,  $A - Be^{-t/\tau}$ , are shown for continuous pumping.

the temperature for the solidification of salt monotonically descends from the melting point of pure salt at  $646^\circ\text{C}$  to the eutectic point very near the melting point of pure metal at  $28.5^\circ\text{C}$  [11]. The electrons released by a trace metal would form localized paramagnetic states in the resulting salt [12]. The magnetic field of these sites is too large for nearby nuclei to contribute to the bulk NMR signal [13]. The mean frequency of the remaining Cs nuclei is shifted by the mean field [14]. The frequency of the narrow line was almost indistinguishable from that of the broad peak, and there were no enhanced signals near the pure metal signal or between these frequencies. Therefore, we estimate the metal impurity to be less than 0.1% in the salt [7]. Because this trace contamination would lead to a very small change in the melting point of the salt, it must have been intensely heated by the laser.

Because no significant narrowing was observed for the unpolarized crystal at  $130^\circ\text{C}$  and because the peak was sufficiently narrowed by pumping at  $40^\circ\text{C}$ , the local elevation of temperature must have been more than  $100^\circ\text{C}$  by laser heating. As shown in Fig. 1, the negative peak was a little acute for  $P_L = 0.67$  W. According to the NMR study of vacancy diffusion in bulk crystals such as Xe [15], LiH [16], LiF [17], and NaCl [18], the linewidth begins to decrease when the jump frequency of  $\text{Cs}^+$  ( $\nu_{\text{Cs}}$ ) and  $\text{Cl}^-$  ( $\nu_{\text{Cl}}$ ) becomes comparable to the width of broad peak ( $\delta\omega$ ). From a rough estimation using the diffusion coefficient,  $\nu_{\text{Cs}}$  and  $\nu_{\text{Cl}}$  are equal to  $\delta\omega$  at  $290^\circ\text{C}$  and  $260^\circ\text{C}$ , respectively [9,17]. Therefore, we expect the temperature of about  $400^\circ\text{C}$  for  $P_L = 1.2$  W. By optical pumping, a bright visible spot could be seen in the glass cell. Based on black-body radiation, the salt and the quartz-glass wool were intensely heated by the focused light. It might be possible that the observed narrow line originated from liquid salt which was relatively uncontaminated by Cs metal.

The evolution of the spin polarization during optical pumping is shown in Fig. 2. The nuclei were depolarized with saturation rf pulses either with or without pump light. When the pump light was continuous, the salt remained at

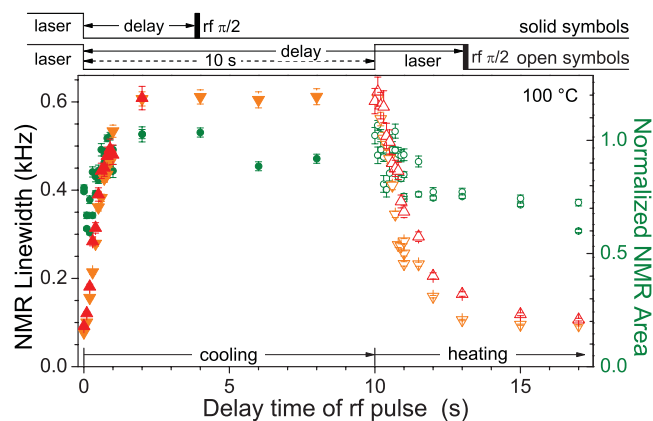


FIG. 3. (Color online) Linewidth (left axis) for positive ( $\blacktriangle$ ,  $\triangle$ ) and negative ( $\blacktriangledown$ ,  $\triangledown$ ) signals was measured with a weakly focused beam. Circles ( $\bullet$ ,  $\circ$ ) show the normalized NMR area scaled by the right axis. The timing chart of optical pumping and rf pulses is shown on the top. The horizontal axis is the delay time of an rf pulse from optical pumping for prepolarization. Fluctuations in the NMR area are due to the varying line shape of the spectrum.

high temperature. In this case the spin polarization built up as  $e^{-t/\tau}$  after an initial rapid polarization period which was less than a second due to unknown causes. This time constant  $\tau$  was smaller than the spin relaxation time previously measured for a CsCl film [4]. When the pump light was interrupted during the rf saturation, the spin polarization rose gradually and the development was not described by a single exponential. Cooling of the salt in the absence of optical pumping delayed the onset of laser heating, reducing the effective spin transfer rate from the polarized vapor.

Following a period of optical pumping, we applied rf pulses to measure the linewidth and the NMR area. The salt temperature changed during the delay of a few seconds. Due to the high polarization established in the salt through spin-transfer optical pumping, the NMR signal was large enough to observe the cooling process, as shown in Fig. 3. The negligible decay of polarization ( $\bullet$ ) rules out additional quadrupole relaxation, implying that the crystal field remained symmetric through this transition. The NMR peak monotonically broadened during the delay time ( $\blacktriangle$ ,  $\blacktriangledown$ ). The cooling was likely fast enough that vacancies were frozen in the crystal. For completely cooled and depolarized salt, the signal remained too small (as shown by triangles in Fig. 2) to observe the heating effects. In order to monitor the heating process, the salt was prepolarized according to the time chart in Fig. 3, allowed to cool without laser illumination for 10 s, and then illuminated again. The signal of this prepolarized salt ( $\circ$ ) was large enough to allow measurement of narrowing ( $\triangle$ ,  $\triangledown$ ) within the subsequent few seconds. Since further motional narrowing would have been hidden by inhomogeneous broadening, we could not observe a stepwise change of linewidth indicating that a phase transition occurred.

Thanks to the signal enhancement it was possible to measure the evolution of the NMR spectrum in real time, as shown in Fig. 4, by NMR detection with small-angle rf pulses. Due to continuous optical pumping and heating, narrow peaks were observed the whole time. When the laser frequency

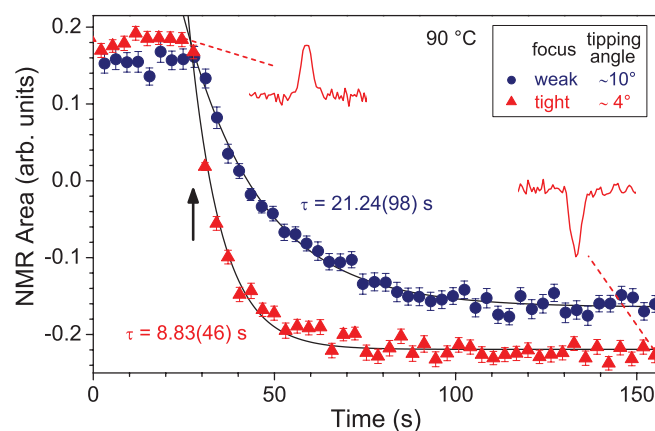


FIG. 4. (Color online) Real time measurement with weak rf excitation of the spin polarization buildup. The laser frequency was changed from  $\nu_P$  to  $\nu_N$  at the time indicated by the arrow. Single exponential curves fit the measurements well. By tightly focusing the laser beam ( $\blacktriangle$ ), the signal inverted more quickly than in the weakly focused case ( $\bullet$ ). The tipping angle was chosen to be different in the two cases to make them exhibit similar NMR amplitudes.

was switched from  $\nu_P$  to  $\nu_N$ , the sign of the polarization inverted. The time constant, 21 s, was consistent with that shown in Fig. 2. When the laser beam was more tightly focused, the signal experienced more enhancement and its sign was inverted more rapidly. This can be explained by a spin-transfer rate equation—an increase in spin flux to salt nuclei has compensating benefits for a reduced time constant, with the model that the Cs ion mobility was increased by laser heating, allowing the spin polarization to diffuse more quickly into the salt. The one-dimensional spin diffusion length is  $\sqrt{DT_1}$ , where  $D$  is the diffusion coefficient for the dipole interaction and the motion of Cs ions, and  $T_1$  is the longitudinal spin relaxation time determined by the quadrupole interaction. Because of the different origins for  $D$  and  $T_1$ , it is possible to increase the product  $\sqrt{DT_1}$  and thus the rate of spin transfer by heating of the crystalline salt, whether or not a phase transition occurs. These results suggest that a material of high alkali-ion mobility such as ionic liquid or a superionic conductor could be polarized by optically pumped atoms. Laser heating could also be used for a “ $T_1$ -switch,” which makes it possible to enhance the polarization quickly and store it for later detection. By real-time measurement of the cooled salt, we also observed that  $T_1$  was approximately 350 s in the dark. This slow relaxation gives additional evidence that paramagnetic sites were sparse within the polarized salt. It also implies that the polarization was unaffected by the surface relaxation and the crystallites were larger than the spin diffusion length due to the dipole interaction [4].

Even if the salt is not entirely melted by the optical pumping laser, it is clear that enhanced ion mobility plays a role in the polarization process. This ion mobility is due to vacancy diffusion in the bulk crystal [9], which depends on temperature and is also enhanced by impurities [10]. Since the salt has large surface area in the cells used here, premelting of the pure crystal [19] and surface melting by impurities [20] may also have significant influence on the ion mobility over a wide range of temperatures. In such particles, the spin polarization would be transferred from the vapor to the solid via the liquid

interface. In order to study this possibility, it is useful to control the heating power independently of optical pumping. For this purpose, an additional laser (790 nm, 2.3 W) was used for heating, in combination with the single-mode laser for pumping. Under these circumstances the enhancement became twofold larger than that shown in Fig. 1, corresponding to a nuclear spin polarization of approximately 0.1%. This is a significant result for spin transfer from a polarized vapor to a solid. This figure was calculated based on the enhanced signal from the illuminated portion of the salt and the thermal equilibrium signal in the entire glass cell. Within the focused laser beam, the local nuclear polarization was likely much higher than this mean value. Therefore, illumination of the entire cell with a high-power laser would likely improve the total spin polarization dramatically.

In summary, the  $^{133}\text{Cs}$  NMR signal of CsCl salt was greatly enhanced by optical pumping of a Cs vapor and laser heating of the salt. The salt was deposited on glass fibers and thus had a large surface area in contact with the

polarized vapor. Enhanced ion diffusion within the heated salt allowed the angular momentum to travel into the salt crystals more rapidly than would occur through dipolar spin diffusion, and the nuclear polarization accrued on a time scale of 10 s. The resulting enhancement corresponded to a mean nuclear polarization of 0.1%, thousands of times larger than the thermal equilibrium at this field. The high polarization enabled real-time measurement of the spin development by periodic application of small-tipping-angle rf pulses. Because there was no detectable difference in the NMR frequencies of the narrow and broad lines and because the decay time of the enhanced signal after prepolarization was on the order of  $T_1$  in the bulk solid, the narrow NMR signal likely arose from macroscopic particles with negligible density of paramagnetic sites.

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