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Hyperpolarized cesium ions doped in a glass material

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A R T I C L E I N F O

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Hyperpolarized (HP) ^{133}Cs nuclear magnetic resonance signals were measured from borosilicate glass cell walls during optical pumping of cesium vapor at high magnetic field (9.4 T). Significant signal enhancements were observed when additional heating of the cell wall was provided by intense but non-resonant laser irradiation, with integrated HP ^{133}Cs NMR signals and line widths varying as a function of heating laser power (and hence glass temperature). Given that virtually no Cs ions would originally be present in the glass, absorbed HP Cs atoms rarely met thermally-polarized Cs ions already at the surface; thus, spin-exchange via nuclear dipole interaction cannot be the primary mechanism for injecting spin polarization into the glass. Instead, it is concluded that the absorption and transport of HP atoms into the glass material itself is the dominant mechanism of nuclear spin injection at high temperatures—the first reported experimental demonstration of such a mechanism.

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1. Introduction

Spin polarization of optically-pumped atoms can be transferred to nuclei in a solid [1]. The dilute vapor significantly polarizes the dense nuclear system of the solid. In the sense that spin polarization transfer is caused by spin interaction when the polarized atoms come close to unpolarized nuclei at the surface, it is considered to be similar to spin-exchange optical pumping, where optically polarized atoms exchange spin angular momentum during atomic collisions with unpolarized atoms [2–5]. However, there are still many unknowns on the physics of spin polarization. In the past few years, optically-polarized cesium (Cs) atoms have greatly enhanced nuclear magnetic resonance (NMR) signal of Cs ions in the hydrides, CsH and CsD, and the halides, CsCl and CsI [6,7]. The polarized atoms release valence electrons close to the salt surface, resulting in spin polarized ions. The electronic process is so quick that the atoms never degrade nor enhance their own and salt's nuclear polarization. Since nuclear–nuclear dipole interaction is always on resonance between the ions of the same nuclear species [8], nuclear polarization is efficiently transferred at any magnitude of applied magnetic field [9]. At the temperature of 100 °C, nuclear polarization has been transported in the bulk salt by spin diffusion via dipolar interaction [10]. Despite the difference in each combination of nuclear and electron spins, the above-described spin transfer and transport are induced by the spin interaction, hence the name spin-exchange optical pumping.

In the salt at high temperature, ion migration is important for ionic and electrical conductivity [11,12] and the same holds true for spin transport. Owing to diffusion migration of spin-polarized ions, nuclear spin polarization is transported from the surface to the bulk salt faster than the spin diffusion via dipolar interaction. Therefore, ^{133}Cs NMR signal has been several orders of magnitude enhanced in the polarized salts [7,13]. In the same way as ion migration in the bulk, atom-exchange are also possible at the surface, that is, the polarized atoms can substitute for the surface ions. The mechanism has not been studied previously.

Here, we classify potential mechanisms for spin polarization injection into the salt, as schematically shown in Fig. 1(a) and (b). Although the atom-exchange rate should be significantly different between the hydride that decomposes approximately at 200 °C [14] and the halides that are stable beyond the melting point, similar signal enhancement was observed in both ionic solids [10]. Therefore, nuclear dipolar spin-exchange plays an important role in spin injection into the salts at 100 °C. On the other hand, atom-exchange is expected to dominate at the higher temperature. The large signal of the bulk salt hides the physics about adsorbed ions at the surface [15,16] even by measurements in a wide temperature range. As is the case in spin-exchange via resonant dipolar interaction, atom-exchange is expected to be nearly independent of magnetic field. As the result, separate measurements of the mechanisms have not been successful, and the salt is not the best material for study of atom-exchange at the surface. The studies on the other materials such as solid xenon [17–19] and optical pumping of atoms in solid helium [20] also provide little information on the surface. Alkali-metal atoms and ions at the

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surface of glass and other substrates has been studied by X-ray induced photo-electron spectroscopy [21,22], light induced atom desorption [23,24], and sublevel spectroscopy by evanescent wave [25], posing the challenge for investigation of spin dynamics at the surface. The spin relaxation is accelerated by electric and magnetic fields and their gradient at the surface. Therefore, the spin injection mechanism faster than the relaxation is needed to hyperpolarize the bulk.

This paper presents an NMR study of hyperpolarized (HP) Cs ions in sodium borosilicate glass. We will demonstrate that spin-exchange mechanism shown in Fig. 1(c) is intrinsically inhibited in the Cs-free glass. Instead, the polarized ion injection shown in Fig. 1(d) is measured with no background from the bulk. The measurements can be understood by taking into account doping (absorption) of HP ions and migration (diffusion) in the glass as well as the motional narrowing of NMR signal at high temperature. It means that hyperpolarization survives the entire process of ionization, penetration into the glass, and diffusion into the bulk. The two of them, ionization and diffusion, have been tested by using the salts [6,7,9,10,13]. Therefore, the present work provides the first evidence for polarized ion injection to hot softened materials.

Experimental background is described briefly. Polarized atomic beam is a good probe to detect the surface state which the reflected atoms carry information on [27,28]. It might be capable of doping the atoms into a glass substrate and we could independently control experimental parameters such as atom flux density, injection velocity, and substrate temperature, in return for complicated setup. Instead, we adopt a simple way that Cs atoms diffusing in a buffer gas are optically pumped in a sealed glass cell. On contact with the glass walls, the polarized atoms are doped as polarized ions into the glass. The amount of doped ions is increased when the glass is heated up to the softening temperature. Localized laser heating enables the experiment in a wide range of temperatures in a standard NMR coil, as described below.

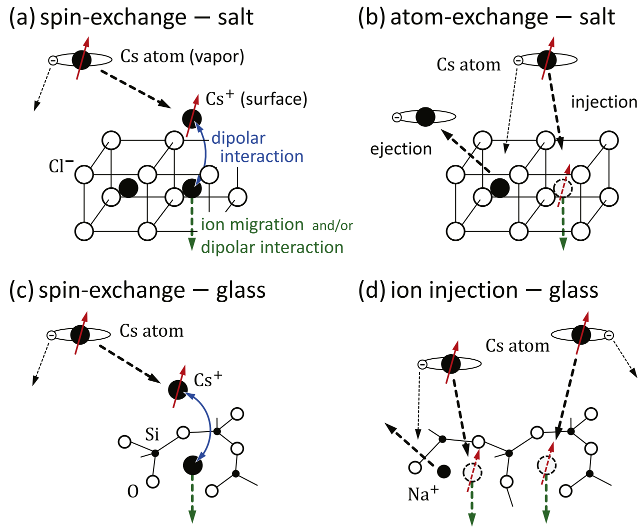

Fig. 1. Schematic diagram of potential mechanisms for spin polarization injection to the salts and the glasses. (a) Spin exchange via resonant nuclear dipolar interaction at the salt surface. Spin polarization is transferred between physisorbed HP ions (formerly vapor atoms) and thermally-polarized ions in the salt when vapor atoms release valence electrons. Since $[\mathrm{Cs}] = [\mathrm{X}]$ in the halide CsX, spin-exchange works effectively. (b) Atom exchange (also called as chemical exchange and cation replacement) at the salt surface. HP ions (formerly vapor atoms) replace the thermal ions or penetrate into vacancy in the salt. (c) Spin exchange via resonant nuclear dipolar interaction between HP ions (formerly vapor atoms) and the thermal ions already at the glass surface. The mechanism is less effective if the thermal ions are dilute at the surface. (d) Ion injection at the glass surface. HP ions (formerly vapor atoms) are injected into the structure of glass. The mechanism that Cs ions replace sodium ions may also be significant because sodium ions are present in sodium borosilicate glass with the proportion of $[\mathrm{Na}] \sim [\mathrm{Si}]/10$ [26]. Electron spin polarization of the atoms contributes little to nuclear polarization in these materials. The released electrons will be trapped in the salt and the glass, emitted as photoelectrons, or reduce end group at the glass surface. Nuclear polarization is transported from the surface into the bulk via dipolar interaction and ion migration, depending on density and mobility of the ions. Because of small electric quadrupole moment, spin polarization of Cs nuclei decays slowly in a local field of cubic symmetry. For example, the decay time is 600 s in CsCl at 100 °C.

2. Experiment

The fabrication details of cylindrical borosilicate glass cells have been described [6]. The glass cell used in this work contains simply Cs metal and N_2 buffer gas, and any Cs compounds have not been intentionally added. Virtually no Cs ions are originally present in the sodium borosilicate glass. Due to magnetic field produced by conduction electrons, the NMR frequency in the Cs metal is higher by the Knight shift of 770 kHz than in the compounds at the applied field of 9.4 T [29,30]. Therefore, no ^{133}Cs NMR signal was observed in a frequency region of interest prior to establishment of optical pumping conditions.

Optical alignment near the NMR coil is shown in Fig. 2. An NMR probe was maintained at 90 °C by an electric heater. In the probe, the glass cell was heated from above by unfocused laser beam at the maximum power of 50 W and at the wavelength of 1060 nm, and also heated from below by focused laser beam of a few watts at 790 nm. Heating from both sides made the Cs metal stay near the bottom. The lasers heated the glass like a torch would. Because the OH-stretch band at 3 μm absorbs the heating lasers at most on the order of 1% [31], impurity bands should have helped the laser heating. We were careful about macroscopic impurities, which would absorb the intense light and make a hole through the glass wall [32]. The heating lasers are far from resonance and unlikely to have a significant impact on atomic transitions. A single-mode laser of 1.2 W for optical pumping was tuned to the D2 line (852 nm) of Cs atoms, linearly polarized, and focused from below. The pumping light heated the glass and also the buffer gas because of quenching of atomic fluorescence. Focusing of the lasers on the metal led to bright spot and sudden increase of vapor density.

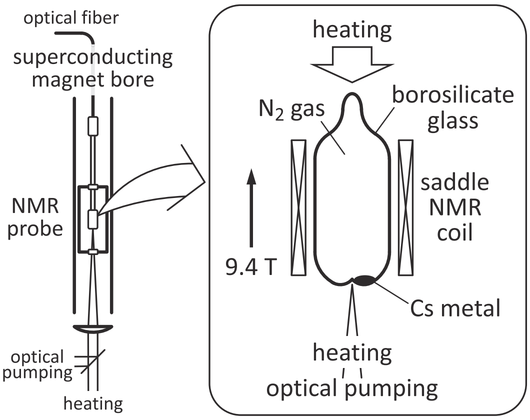

Fig. 2. Optical and NMR setup. A cylindrical glass cell (outer diameter 10 mm) contains Cs metal and N_2 gas at 2 kPa. When the metal stay in the detection region, quality factor of the coil is not so high but sensitive enough for the NMR measurement. Tuning of NMR circuit has been readjusted at each measurement condition. Air temperature in the NMR probe was measured by non-magnetic thermocouple placed about 10 mm from the glass cell, and maintained at 90 °C by an electric heater. The glass walls were hotter than the air due to laser heating. One of heating lasers ($\leqslant$ 50 W, 1060 nm) lighted the glass cell from above introduced with optical fiber. The heating light was scattered by the sealed glass stem and significant part of them warmed the surrounding parts such as the coil, the cell holder, and the inner walls of NMR probe. Another heating laser (a few watts, 790 nm) and optical pumping laser (1.2 W, 852 nm) were focused from below through free space.

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