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S. Sheludiakov , D. M. Lee, V. V. Khmelenko , J. Ahokas , J. Järvinen, and S. Vasiliev



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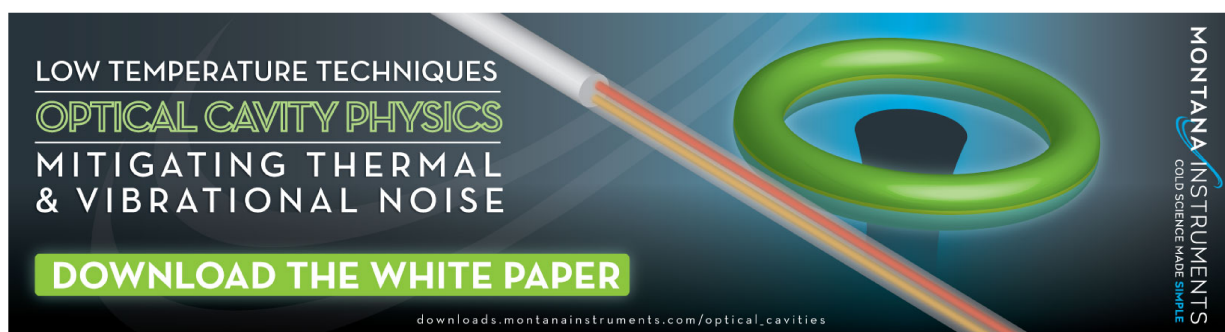
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Studies of nuclear polarization of hydrogen atoms embedded in solid molecular hydrogen and hydrogen deuteride films

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S. Sheludiakov,^{1,a)} D. M. Lee,¹ V. V. Khmelenko,¹ J. Ahokas,² J. Järvinen,² and S. Vasiliev²

AFFILIATIONS

¹Institute for Quantum Science and Engineering, Department of Physics and Astronomy, Texas A&M University, College Station, TX, 77843, USA

²Department of Physics and Astronomy, University of Turku, Turku 20014, Finland

^{a)}E-mail: seshel@physics.tamu.edu

ABSTRACT

We report on an electron-spin resonance study of nuclear polarization of hydrogen atoms embedded in solid H₂ and HD films at temperatures 0.1–1.5 K and in a high magnetic field of 4.6 T. Similar to our previous work [Phys. Rev. Lett. **122**, 225301 (2019)], we observed a build-up of the spontaneously ($p \simeq 0.35$) and highly ($p \simeq 0.75$) nuclear polarized phases of H atoms in the as-deposited H₂ films. However, we did not obtain an enhanced nuclear polarization of H atoms in the regions of their small local concentration. We also failed to observe enhanced nuclear polarization for H atoms in the annealed H₂ films as well as in the as-deposited HD sample. These observations tend to support our previous explanation for the build-up of high nuclear polarization due to the formation of weakly-bound triplet H₂ molecules.

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1. INTRODUCTION

Solid molecular hydrogen along with the helium solids represents a special class of so-called quantum crystals. Similar to the solid helium isotopes where He atoms remain essentially delocalized, light impurities, H atoms, embedded in solid molecular hydrogen below 1 K travel through the matrix by a repetition of the exchange tunneling reaction $H + H_2 \rightarrow H_2 + H$.¹ A number of phenomena related to the exchange interaction or Bose-Einstein condensation (BEC) of H atoms in solid H₂ might be expected at a high enough H atom concentration and low temperatures. The H atom ground state population, in contrast to He, can be probed directly from the measurement of nuclear spin polarization.

A large overpopulation of the ground $|a\rangle$ state for H atoms in a solid H₂ matrix [Fig. 1(a)] was first reported by Ahokas *et al.*² and then observed again in the following studies^{3–5} carried out in two experimental setups located at the University of Turku and Cornell University. Hazzard and Mueller⁶ examined several mechanisms including local Bose-Einstein condensation of H atoms in solid H₂ in order to explain the deviation of nuclear polarization from the Boltzmann distribution. However, neither mechanism was able to provide a full explanation for all the observed phenomena.

In our recent work,⁷ we reported on the formation of two nuclear polarized phases of H atoms in solid H₂ characterized by different deviations of nuclear polarization, p , from the Boltzmann statistics, where $p = (n_a - n_b)/(n_a + n_b)$ with n_a and n_b being populations of the $|a\rangle$ and $|b\rangle$ energy levels [Fig. 1(a)]. The first phase, the spontaneously nuclear polarized phase (SNPP) with $p \simeq 0.35$ developed spontaneously during the course of sample storage in a high magnetic field at temperatures 0.1–0.8 K. The highly nuclear polarized phase (HNPP) with $p \simeq 0.75$ could be obtained at temperatures 0.1–0.55 K by a consecutive application of dynamic nuclear polarization (DNP) followed by nuclear spin-lattice relaxation. We considered three possible mechanisms for the overpopulation of the H atom ground state: effects related to statistical correlations between H atoms related to BEC, nuclear magnetic ordering, and gradual nuclear spin alignment as a result of the H atom interaction via a $^3\Sigma_u^+$ potential which may lead to the formation of a weakly bound or transient triplet H₂ molecular state.

In the present work, we continued our study of the H atom nuclear-polarized phases in the same experimental condition of $T = 0.1$ –1.5 K and a high magnetic field $B = 4.6$ T. We examined the influence of H₂ film annealing on the H atom nuclear polarization build-up and extended our study further to solid HD films. Similar

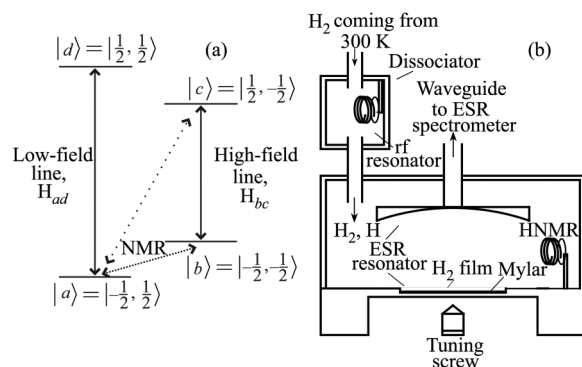


FIG. 1. (a) H atom energy level diagram in high magnetic field. The electron and nuclear spin states are labeled as $|m_s, m_I\rangle$. The allowed ESR transitions are shown by solid arrows. (b) The sample cell schematic.

to the previous work, we were able to obtain both nuclear polarized phases, the SNPP and HNPP, of H atoms in thick as-deposited H_2 films. However, we failed to create a high nuclear-polarization for H atoms in pure HD films and in the regions of solid H_2 with a small, $n < 10^{18} \text{ cm}^{-3}$, local concentration of H atoms as well as for H atoms in annealed H_2 films. We provide possible explanations for these observations.

2. EXPERIMENTAL DETAILS

The experimental apparatus is based on a commercial Oxford 200 dilution refrigerator capable of cooling the sample cell (SC) down to $T \simeq 0.1 \text{ K}$. This setup was also used previously for our experiments at Cornell University.⁵ The SC is located in the center of a 4.6 T superconducting magnet and anchored to the mixing chamber of the dilution unit. The main diagnostic tool in our experiments is a cryogenic 128 GHz heterodyne electron spin resonance (ESR) spectrometer with a sensitivity of $\sim 10^{10}$ spins.⁸ The ESR resonator has an open Fabry-Perot design which also makes it possible to arrange an auxiliary rf resonator (HNMR) tuned to the H_{ab} NMR transition frequency, $f = 910 \text{ MHz}$. The SC design is presented schematically in Fig. 1(b).

The top mirror of the ESR resonator is made of copper and has a semi-spherical shape. The bottom mirror is also made of copper and covered with a $\simeq 20 \mu\text{m}$ thick Mylar foil [Fig. 1(b)]. In this work, we mainly focused on studying thick, 10–200 μm , H_2 and HD films created by solidifying molecular hydrogen isotopes from the liquid phase.⁵ Prior to that, the H_2 or HD gas was condensed into the SC from a room temperature reservoir while the SC temperature was stabilized at 15–20 K. Next, the cell was slowly cooled down to $T \simeq 0.5\text{--}0.7 \text{ K}$ and a small amount, $\sim 1 \mu\text{mole}$, of He gas was condensed into the SC in order to run the rf discharge in helium vapor. The electrons created during the discharge have energies of order 100 eV and are able to dissociate a fraction of H_2 and HD molecules in a rather shallow surface layer $\simeq 100 \text{ nm}$.⁹ The discharge is stopped when the local concentrations of H atoms in solid H_2 (or H atoms in solid HD) level off at the value $\simeq 10^{19} \text{ cm}^{-3}$. After that we proceeded to evacuate the superfluid

helium film from the sample cell for about 1 day. This allowed us to cool the SC to $T \simeq 0.1 \text{ K}$.

A special chamber, the H_2 dissociator, was arranged above the sample cell in order to provide a flux of H atoms in the gas phase created by running the rf discharge there. The ESR lines of atomic hydrogen gas were used as a reference for determination of the spectroscopic parameters of H atoms embedded in solid H_2 . The local H atom concentrations were determined based on the concentration-dependent ESR line broadening due to dipolar interaction between the H atom electron spins.⁴

The upper energy levels, $|c\rangle$ and $|d\rangle$, in the high magnetic field of our experiments, $B = 4.6 \text{ T}$, remain unoccupied up to temperatures of $T \simeq 1.5 \text{ K}$. As a result, the H_{ad} and H_{bc} ESR line areas are proportional to the occupations, n_a and n_b , of two lower hyperfine levels, $|a\rangle$ and $|b\rangle$ [Fig. 1(a)]. This provides a simple and reliable method for determination of the nuclear polarization, $p = (n_a - n_b)/(n_a + n_b)$.

3. EXPERIMENTAL RESULTS

In the present work, we provide further insight into the build-up of nuclear polarized phases of H atoms in pure H_2 , the HNPP and SNPP, first observed in our previous study⁷ by examining the effect of sample annealing. In addition, a sample of H atoms in a solid HD film was studied in order to compare the nuclear polarization behavior to that of H atoms in pure H_2 films.

3.1. H_2 samples

We studied four 100 μm H_2 films prepared from the H_2 gas with a normal ortho-para content. The first two samples (Samples 1 and 2) were studied as deposited, whereas the two other samples (Samples 3 and 4) were first annealed at $T = 4\text{--}7 \text{ K}$ for a few hours and then the H atoms were accumulated there by running the rf discharge.

The H atom ESR lines after running the discharge for five days in both as-deposited and annealed samples had a composite shape and contained two components, C1 and C2 [Fig. 2(a)]. We also observed that restarting the SC rf discharge for the as-deposited Sample 2 led to increase of the C1 and C2 components as well as to emergence of an additional narrow, 0.15 G wide, component on both ESR lines of H atoms [C3 in Fig. 2(b)]. The C2 and C3 components correspond to the regions of high and low local H atom concentration regions, respectively. As a result, they appear shifted from each other due to concentration-dependent magnetization.⁴ The C3 component had regular spectroscopic parameters corresponding to trapping of H atoms in the substitutional sites of the H_2 matrix at a very low concentration. All three components observed in this sample had a Lorentzian shape (Figs. 2(a) and 2(b)). The spectroscopic parameters for all three components of the ESR lines of H atoms observed in the as-deposited H_2 Sample 2 are collected in Table I.

The H atom nuclear polarization for the as-deposited Samples 1 and 2, behaved identically to that described in our previous work.⁷ Right after stopping the rf discharge and pumping He film from the sample cell, we stabilized the SC temperature at $T = 0.3 \text{ K}$ in order to monitor the spontaneous build-up of H atom nuclear polarization. The SNPP, $p \simeq 0.37$ [Fig. 3(a)], was built up during sample storage for seven days and after that the HNPP was

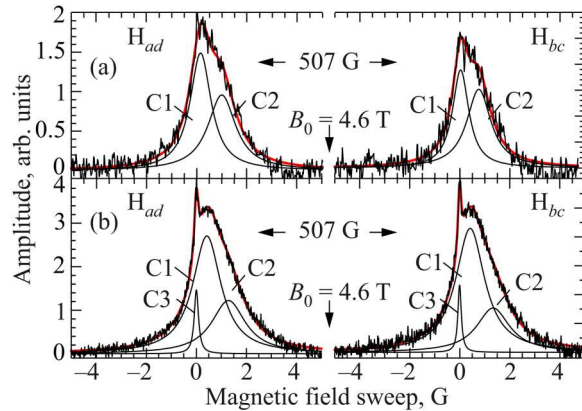


FIG. 2. (a) ESR spectra of H atoms in the as-deposited Sample 2 recorded after first H atom accumulation by running the rf discharge (b) after restarting the discharge in the SC.

obtained by applying a few sequences of dynamic nuclear polarization using the Overhauser effect followed by nuclear-spin relaxation. The Overhauser effect is based on saturation of the allowed H_{bc} ESR transition followed by cross-relaxation through the forbidden H_{ac} transition [Fig. 1(a)]. We call this measurement procedure a saturation-relaxation sequence (SRS). The asymptotic polarization, p , was obtained by extrapolating the polarization relaxation data, $p(t)$, measured for three days with a fitting formula $p(t) = p + a \exp(-t/T_{1N})$ where a is the free fitting parameter and T_{1N} is the H atom nuclear spin-lattice relaxation time [Fig. 4(a)].

After the SNPP in the as-deposited samples had been established, we applied only two SRSs which increased the asymptotic H atom nuclear polarization to $p = 0.53$ in accordance with that described in our previous work.⁷ We present these results in Fig. 5(a) to compare with those obtained for the annealed H_2 and as-deposited HD samples discussed later. The temperature dependence of the inverse T_{1N} times for the same as-deposited H_2 sample is presented in Fig. 5(b).

The nuclear spin-lattice relaxation time, T_{1N} , for C3, $\sim 10^3$ s, was nearly two orders of magnitude shorter than that for the main ESR line which was a sum of C1 and C2 components [Fig. 4(b)]. In contrast to the main ESR line, the C3 component did not exhibit any deviation from the Boltzmann statistics in the temperature range 0.1–1 K within the line fitting accuracy. Unlike C1 and C2, the C3 component was also very stable at high temperatures and did not change after raising the SC temperature from 0.15 to about 1.5 K. These observations led us to the conclusion that the C3

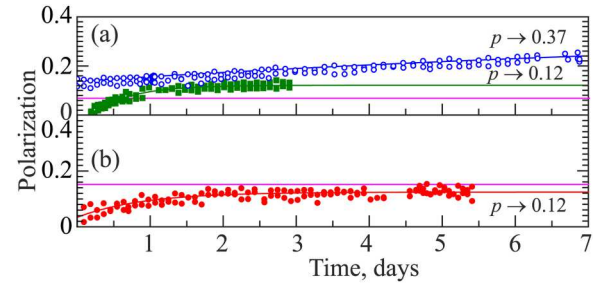


FIG. 3. (a) Spontaneous build-up of nuclear polarization of H atoms in the as-deposited H_2 Sample 1 at $T = 0.3$ K (open blue circles), in the annealed Sample 3 (filled green squares) at $T = 0.3$ K and (b) in HD (filled red circles) at $T = 0.15$ K. The values of Boltzmann nuclear polarization at $T = 0.3$ K ($p = 0.07$) and $T = 0.15$ K ($p = 0.15$) are shown only for comparison by solid magenta lines in (a) and (b), respectively. The solid blue, green, and red lines were obtained by fitting the experimental data by the formula $p(t) = p + a \exp(-t/T_{1N})$.

component corresponds to H atoms trapped in the region of H_2 film with a low concentration, deeper in the H_2 film as compared with those residing closer to the film surface and corresponding to the components C1 and C2.

At the next stage, we studied two samples (Samples 3 and 4) where the H_2 films were annealed prior to accumulating H atoms there. After Sample 3 was annealed at $T = 4$ K for several hours, the SC was cooled down to $T \simeq 0.7$ K and the H atoms in the H_2 film were accumulated to the concentration $7 \cdot 10^{18} \text{ cm}^{-3}$. When the helium film had been evacuated from the SC, we stabilized the SC temperature at $T = 0.3$ K. The spontaneous nuclear polarization build-up during storage of Sample 3 is presented in Fig. 3(a) by green squares. The nuclear polarization leveled off at $p = 0.12$ after about 3 days of storage. Therefore, we were unable to reach the SNPP with $p = 0.37$ in this annealed sample.

For Sample 4, which was annealed at 5–7 K, we did not try to build up spontaneous polarization since we failed to obtain it in Sample 3, but started applying the SRSs in order to reach the highest possible stationary polarization right after stopping the rf discharge and evacuating the helium film from the SC. The H atom concentration in this sample after cooling the sample cell to $T = 0.15$ K was $3 \cdot 10^{18} \text{ cm}^{-3}$. We emphasize that we observed the high nuclear polarization in the as-deposited H_2 samples with such a H atom concentration in our previous work⁷ as well as in the pioneering work² where the H atom ground state overpopulation was reported for the first time.

We measured asymptotic nuclear polarization for Sample 4 by applying the SRSs at several temperatures starting from $T = 0.15$ K

TABLE I. The spectroscopic parameters (A , g_e) and full widths at half maximum for the C1, C2, and C3 components of ESR lines of H atoms in pure H_2 Sample 2 and the HD film studied in this work.

	C1			C2			C3		
	A, MHz	g_e	Width, G	A, MHz	g_e	Width, G	A, MHz	g_e	Width, G
H_2	1417.3(1)	2.002284(5)	1.4(2)	1417.3(1)	2.002264(7)	1.5(2)	1417.3(1)	2.002284(5)	0.15(5)
HD	1417.3(1)	2.002284(5)	3.4(3)	1417.2(2)	2.002214(7)	4.3(4)	—	—	—

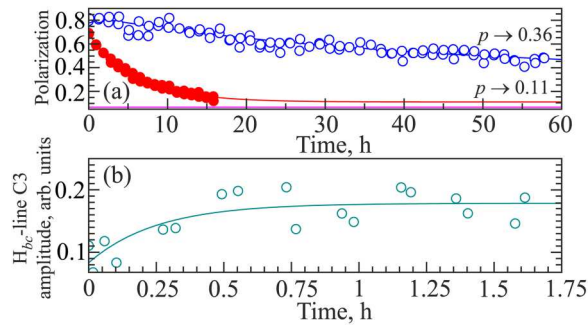


FIG. 4. (a) Relaxation of H atom nuclear polarization after applying the Overhauser effect DNP in as-deposited H_2 Sample 1 (open blue circles) and HD sample (red circles) measured at $T=0.8$ K. H atom nuclear polarization at $T=0.8$ K according to Boltzmann statistics is shown by a solid magenta line. Note the large difference in the T_{1N} times for H_2 and HD samples. The solid blue and red lines were obtained by fitting the experimental data by the formula $p(t) = p + a \exp(-t/T_{1N})$. (b) Amplitude of the H_{bc} -line C3 component after applying the Overhauser effect DNP measured in as-deposited H_2 Sample 2 at $T=0.9$ K. The dark cyan line was obtained by fitting the experimental data by the formula $A(t) = A + a \exp(-t/T_{1N})$ where A is the H_{bc} ESR line amplitude.

and then gradually ascending to $T=0.8$ K as presented in Fig. 5(a) (by green squares). The asymptotic nuclear polarization reached $p=0.35(7)$ at $T=0.3$ K after application of ten SRSs during ten days. We thus failed to reach the HNPP in this sample even after multiple SRSs as presented in Fig. 5(a).

3.2. H atoms in solid HD matrix

In our previous study,⁷ we suggested that the mobility of H atoms in the solid H_2 matrix may have a drastic effect on the H

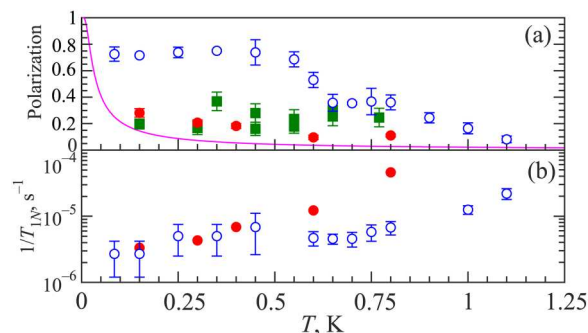


FIG. 5. (a) Asymptotic nuclear polarization of H atoms obtained by SRSs presented as a function of temperature in the annealed H_2 Sample 4 (green squares) and as-deposited HD film (filled red circles) both studied in this work. Nuclear polarization in the as-deposited H_2 film measured by applying the SRSs measured in our previous work⁷ is shown by open blue circles for the sake of comparison. Boltzmann polarization is shown by a solid magenta line. (b) Dependence of the inverse T_{1N} time of H atoms on temperature for the as-deposited H_2 sample measured in previous work (open blue circles) and H atoms in the HD film (filled red circles).

atom nuclear polarization build-up. In the present work, we studied H atoms inside a HD matrix where the H atom diffusion due to the tunneling reaction $H + HD \rightarrow HD + H$ is two orders of magnitude slower as compared with that in solid H_2 .¹⁰ The nuclear magnetic moments of HD molecules stimulate nuclear spin relaxation of H atoms which takes place faster than in a pure para- H_2 matrix. The HD film was 200 μm thick and the H atoms were accumulated there to a concentration of $\approx 1.5 \cdot 10^{19} \text{ cm}^{-3}$ by running the rf discharge for seven days. The D atom concentration was an order of magnitude smaller and their ESR lines disappeared due to the exchange reaction $D + HD \rightarrow D_2 + H$ ¹¹ in 2–3 hours after stopping the rf discharge. The ESR lines of H atoms in the HD film consisted of two components, C1 and C2 with the widths of 3.4(3) and 4.3(4) G, respectively, which are much broader than those in the H_2 matrix (1.4 and 1.5 G, respectively) due to the dipolar interaction with the magnetic moments of host HD molecules [Figs. 6 and 2(b)]. The C2 component had a somewhat smaller electronic g-factor as compared with that of C1. The hyperfine constants of both components matched within the estimated error defined by the uncertainty in their relative positions. The spectroscopic parameters and widths for the C1 and C2 components of the ESR lines of H atoms in the HD sample are presented in Table I.

After stopping the discharge in the SC, we proceeded to evacuate the helium film from the sample cell which took about 1 day. The sample cell temperature during this period of time was stabilized at $T=0.5$ K. After that, we stabilized the SC temperature at 0.15 K in order to monitor evolution of the H atom nuclear polarization. The H atom recombination in the solid HD film in the course of pumping He was rather slow. Only 10% of H atoms in solid HD recombined as compared with 20–25% of H atoms recombining in the pure as-deposited H_2 film being stored at the same temperature and having the same initial concentrations.⁷ The ESR lines of H atoms in solid HD had a composite shape which did not change during sample storage. In contrast to the pure as-deposited H_2 Samples 1 and 2 discussed earlier, we did not observe the SNPP formation over the time period of seven days at $T=0.15$ K. The H atom nuclear polarization leveled off at $p=0.12$, close to the Boltzmann value at this temperature, $p=0.15$ [Fig. 3(b)]. At the next stage, we used the SRSs in order to obtain the highest possible stationary polarization in this sample in the temperature range 0.15–0.8 K. The asymptotic nuclear polarization reached $p=0.28(5)$ after the first SRS and did not involve further even after application of four SRSs.

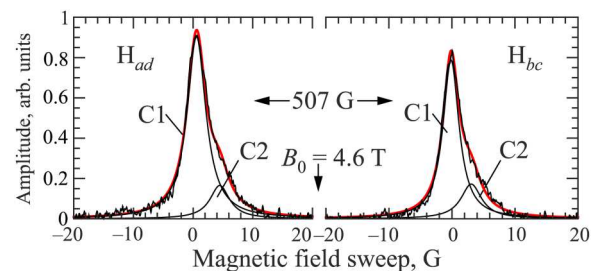


FIG. 6. The ESR spectra of H atoms in HD film.

Finally, we studied the asymptotic nuclear polarization of H atoms in the HD films as a function of temperature. The asymptotic nuclear polarization for each temperature point was acquired using the SRSs with the nuclear polarization relaxation measured for three days at $T = 0.15, 0.3, 0.4$ and 0.6 K, and two days at $T = 0.8$ K. The asymptotic nuclear polarization of H atoms in the HD matrix as a function of temperature is presented in Fig. 5(a) by red circles. The experimental points did not form a plateau similar to those measured in the as-deposited solid H_2 film reported in our previous work.⁷ The T_{1N} times depended exponentially on temperature [Fig. 5(b)] unlike those for H atoms in solid H_2 films where the T_{1N} times were nearly independent of temperature at $T < 1$ K.^{7,12}

4. DISCUSSION AND CONCLUSIONS

In this work, we performed experimental studies of the nuclear spin polarization of H atoms stabilized in solid H_2 and HD matrices. We did not observe any spontaneous H atom nuclear polarization build-up in the annealed H_2 samples, while only a modest deviation from the Boltzmann statistics ($p = 0.3$ instead of 0.15) was observed even after applying a series of SRSs. This drastically differs from the as-deposited H_2 films where the values of $p \simeq 0.35$ and 0.75 for the SNPP and HNPP, respectively, were observed.⁷

The H atom nuclear polarization obtained in the HD sample after the use of SRSs did not form a plateau but had a clear temperature dependence. This can be attributed to a strong dependence of the T_{1N} times of H atoms in solid HD on temperature. This supports our conclusion that the H atom nuclear polarization measured in the experiments is determined by the competition of two factors: the polarization build-up mechanism and nuclear spin-lattice relaxation which tends to restore the Boltzmann occupation of energy levels [Fig. 1(a)] and suppress the gradual nuclear polarization build-up.

The suppression of a high nuclear polarization of H atoms in the annealed H_2 samples requires further understanding. In our previous work, we suggested that the gradual nuclear polarization build-up might possibly be related to the mutual interaction of H atoms via the $^3\Sigma_u^+$ potential in the condition of high magnetic field and low temperatures when the H atom electron spins are completely polarized. This potential has a very shallow minimum ($\epsilon = 6.46$ K) with no bound state for free H atoms in the gas phase.¹³ The minimum of the potential becomes deeper in a magnetic field ($\epsilon = 13$ K for $B = 4.6$ T)^{13,14} and it might be suggested that a bound triplet H_2 molecular state exists in the solid H_2 matrix. The symmetry of molecular wavefunction for the ground rotational state of such triplet H_2 molecules requires both electron and nuclear spin to be aligned.¹⁵ Formation of the H_a-H_a pairs (H_a is an atom in the $|a\rangle$ state), in this case, is energetically more favorable and the nuclear spins of H_b atoms (H_b is an atom in the $|b\rangle$ state) can be preferentially flipped when the H_a and H_b atoms approach each other and the weakly bound $^3\Sigma_u^+$ molecule is formed. The nuclear spin can be reversed even without forming a bound molecular state if the H-H atom interaction via the $^3\Sigma_u^+$ potential is strong enough to trigger the nuclear spin flip. After formation of this weakly bound triplet molecule, it can be dissociated back into two H atoms by the zero-point fluctuations or phonons. Atoms after dissociation of triplet molecules should be in the $|a\rangle$ state because they can still possess their nuclear spin alignment due

to very long T_{1N} times, thus contributing to the nuclear polarization build-up observed experimentally.

One of the possibilities would be that the interaction via the triplet potential is most efficient in the presence of lattice defects. The H atom diffusion towards the H_2 lattice imperfections such as vacancies or dislocations is less favorable due to the tunneling energy level mismatch they impose.^{16,17} The H atoms should, therefore, preferentially diffuse within the regions where the H_2 lattice is regular.¹⁸ The lattice imperfections decrease the effective volume available to the H atoms and increase the probability for them to interact via the $^3\Sigma_u^+$ potential. The scarcity of lattice defects in the annealed samples may lead to the less efficient polarization build-up which can be compensated by nuclear spin-lattice relaxation.

One of the intriguing property of the as-deposited samples is the memory effect observed in our previous study.⁷ The memory effect implies a recovery of the H atom nuclear polarization after saturating the H_{ab} NMR transition and equalizing the $|a\rangle$ and $|b\rangle$ level populations once either the HNPP or SNPP was formed. The characteristic time T_{1N} for such a polarization recovery was shorter than the one required to initially build either nuclear polarized phase. This difference in the characteristic times may indicate that the hydrogen atoms migrate and aggregate into specific spatial relative positions, for example, close to the H_2 film surface. The exact nature of such a re-arrangement is not yet known and requires further investigation for which better spatial resolution is required.

The different behavior of H atom nuclear polarization in the as-deposited and annealed H_2 films as well as for components 1 and 3 of the as-deposited Sample 2 created from normal H_2 supports our conclusion that ortho-para conversion is unlikely to influence the H atom nuclear polarization in our samples.

In our previous work, we suggested that the H atom mobility is important for the build-up of high nuclear polarization. In the present work, we did not observe the formation of either polarized phase of H atoms in the HD sample. The H atom diffusion in solid HD takes place through the exchange tunneling reaction $H + HD \rightarrow HD + H$ ¹¹ in analogy to the H atom diffusion in solid H_2 . The rate of the former reaction is about two orders of magnitude smaller than that of the $H + H_2$ reaction.¹⁰ The H atom nuclear polarization stimulated by the SRSs in the HD sample, $p \simeq 0.3$, was much lower than that observed for the HNPP in the pure as-deposited H films, $p \simeq 0.75$, studied in this work and reported previously.⁷ It is possible that nuclear spin flips for H atoms in solid HD due to the H-H interaction via the $^3\Sigma_u^+$ potential become much less frequent due to their inferior mobility in the HD matrix as compared with that in the H_2 films. In this case, the rate of such spin flips which may take place after two H atoms approach one another is insufficient to compete with the nuclear spin-lattice relaxation.

Another new observation is the appearance of the narrow C3 component in the ESR spectra of H atoms in the H_2 film. Based on its small linewidth and stability at elevated temperatures, we suggest that the H atoms which correspond to C3 may be trapped deep in the bulk of H_2 film. A similar component with a width of about 0.3 G was reported previously.⁵ The observed linewidth for C3 is smaller than those reported in all previous studies of H atoms in solid H_2 films at temperatures below 1 K and comparable to those, $\simeq 0.1$ G, observed at $T \geq 1.3$ K by Kumada *et al.*¹⁹ and

Iskovskikh *et al.*²⁰ for H atoms in solid H₂ and Dmitriev²¹ for D atoms in solid D₂. The observed T_{1N} time for this component was nearly two orders of magnitude shorter than those of C1 and C2. Based on the C3 width, 0.15 G, we estimate the upper limit for the concentration of H atoms forming it as 10^{18} cm^{-3} . In contrast to C1, the C3 component followed the Boltzmann statistics for the temperature range studied in this work ($T = 0.1\text{--}1 \text{ K}$).

It is possible that the absence of a high nuclear polarization for the narrow C3 component observed in this work may be a result of a too small concentration of H atoms. In this case, the mean free path for the H atoms to approach one another in order to interact via the $^3\Sigma_u^+$ potential and experience the nuclear spin flip is much longer than that for the H atoms in more concentrated regions corresponding to C1. They are far away from each other and their interaction through the triplet molecular potential is negligible. Therefore, the polarization build-up for the C3 component is much less efficient and can be compensated by the process of nuclear spin-lattice relaxation. Based on the unusually small width of C3, we may also suggest that these H atoms are trapped deep in the film where the H₂ lattice is highly regular. In this case, the nuclear polarization build-up might be further suppressed due to the absence of lattice defects similar to that observed in the annealed samples. This may cause the nuclear polarization for the C3 H atoms to obey the Boltzmann statistics.

To summarize, in this work we reported on the results of studying the nuclear polarization of H atoms in solid as-deposited and annealed H₂ as well as as-deposited HD matrices. We did not observe enhanced spontaneous nuclear polarization of H atoms in solid HD and annealed H₂ samples. The absence of nuclear polarization for the narrow C3 component may be a result of a very small concentration of H atoms in some region of the H₂ film. This may also lead to a large mean free path for H atoms in solid H₂ before they encounter another H atom and interact with it via the $^3\Sigma_u^+$ potential leading to a spin reversal. These observations may serve as indirect evidence for the enhanced nuclear polarization build-up process through the interaction of H atoms via the $^3\Sigma_u^+$ potential.

Reminiscences from S. Vasiliev: I've first time got acquainted with Mikhail Strzhemechny in 1985 being a graduate student of Moscow Physical Technical Institute. At that time I was making my MSci diploma at Kurchatov Institute for Atomic Energy in the Laboratory of Gamma-Resonance Spectroscopy headed by Igor Ivanovich Lukashevich (sadly, Igor passed away in 2008). The main subject of our research was quantum diffusion of atomic hydrogen in solid molecular crystals of hydrogen and its isotopes. We were inspired in this work by the results obtained in Kharkov on the quantum diffusion of He in solid H₂.²² Mikhail was the member of the Kharkov team with the major contribution to the theory of this phenomena. We have met several times at Low Temperature and Cryocrystals conferences and discussions with him had a serious impact on our work. In the beginning of 2000s, we renewed studies of H in H₂ crystals in Turku and Cornell University (later moved to Texas A&M University) together with the group of David Lee

and Vladimir Khmelenko, which are actively pursued by both groups at present. We are glad to present in this manuscript new results of our research in this field. Together with my colleagues at Turku and Texas I congratulate Mikhail on his jubilee and wish him further success in research work.

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