

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

S. Sheludiakov, D.M. Lee, and V.V. Khmelenko

*Institute for Quantum Science and Engineering, Department of Physics and Astronomy, Texas A&M University, College Station, TX, 77843, USA*  
E-mail: seshel@physics.tamu.edu

J. Ahokas, J. Järvinen, and S. Vasiliev

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

Received August 23, 2019, published online December 27, 2019

We report on an electron-spin resonance study of nuclear polarization of hydrogen atoms embedded in solid H<sub>2</sub> 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 ( $p \approx 0.35$ ) and highly ( $p \approx 0.75$ ) nuclear polarized phases of H atoms in the as-deposited H<sub>2</sub> 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 H<sub>2</sub> 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 H<sub>2</sub> molecules.

Keywords: hydrogen atoms, solid molecular hydrogen, nuclear polarization.

## 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 H<sub>2</sub> 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 H<sub>2</sub> 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 Mueller [6] examined several mechanisms including local Bose–Einstein condensation of H atoms in solid H<sub>2</sub> in order to explain the deviation of nuclear polariza-

tion 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 H<sub>2</sub> 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  $p \approx 0.35$  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  $p \approx 0.75$  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 H<sub>2</sub> molecular state.

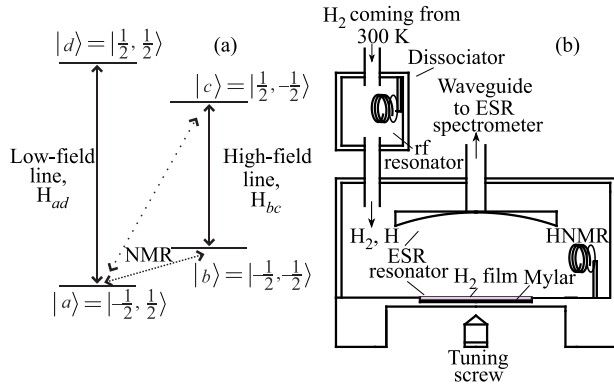


Fig. 1. (a) H atom energy level diagram in high magnetic field. The electron and nuclear spin states are labeled as  $|m_s, m_I\rangle$ . The allowed ESR transitions are shown by solid arrows. (b) The sample cell schematic.

In the present work, we continued our study of the H atom nuclear-polarized phases in the same experimental condition of  $T = 0.1\text{--}1.5$  K and a high magnetic field  $B = 4.6$  T. We examined the influence of  $\text{H}_2$  film annealing on the H atom nuclear polarization build-up and extended our study further to solid HD films. Similar to the previous work, we were able to obtain both nuclear polarized phases, the SNPP and HNPP, of H atoms in thick as-deposited  $\text{H}_2$  films. However, we failed to create a high nuclear-polarization for H atoms in pure HD films and in the regions of solid  $\text{H}_2$  with a small,  $n < 10^{18} \text{ cm}^{-3}$ , local concentration of H atoms as well as for H atoms in annealed  $\text{H}_2$  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  $T \approx 0.1$  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,  $f = 910$  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  $\approx 20$   $\mu\text{m}$  thick Mylar foil (Fig. 1(b)). In this work, we mainly focused on studying thick, 10–200  $\mu\text{m}$ ,  $\text{H}_2$  and HD films created by solidifying molecular hydrogen isotopes from the liquid phase [5]. Prior to that, the  $\text{H}_2$  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  $T \approx 0.5\text{--}0.7$  K and a small amount,  $\sim 1$  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  $\text{H}_2$  and HD molecules in a rather shallow surface layer  $\approx 100$  nm [9]. The discharge is stopped when the local concentrations of H atoms in solid  $\text{H}_2$  (or H atoms in solid HD) level off at the value  $\approx 10^{19} \text{ cm}^{-3}$ . 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  $T \approx 0.1$  K.

A special chamber, the  $\text{H}_2$  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  $\text{H}_2$ . 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  $|b\rangle$ , in the high magnetic field of our experiments,  $B = 4.6$  T, remain unoccupied up to temperatures of  $T \approx 1.5$  K. As a result, the  $H_{ad}$  and  $H_{ac}$  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  $\text{H}_2$ , the HNPP and SNPP, first observed in our previous study [7] 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  $\text{H}_2$  films.

### 3.1. $\text{H}_2$ samples

We studied four 100  $\mu\text{m}$   $\text{H}_2$  films prepared from the  $\text{H}_2$  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  $T = 4\text{--}7$  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

Table 1. 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<sub>2</sub> 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 <sub>2</sub> | 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)   | –         | –           | –        |

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 H<sub>2</sub> matrix at a very low concentration. All three components observed in this sample had a Lorentzian shape (Figs. 2(a) and (b)). The spectroscopic parameters for all three components of the ESR lines of H atoms observed in the as-deposited H<sub>2</sub> Sample 2 are collected in Table 1.

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  $T = 0.3$  K in order to monitor the spontaneous build-up of H atom nuclear polarization. The SNPP,  $p \approx 0.37$  (Fig. 3(a)), was built up during sample storage for seven days and after that the HNPP was 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<sub>2</sub> and as-deposited HD samples discussed later. The temperature dependence of the inverse  $T_{1N}$  times for the same as-deposited H<sub>2</sub> 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 component corresponds to H atoms trapped in the region of H<sub>2</sub> film with a low concentration, deeper in the H<sub>2</sub> film as compared with those residing closer to the film surface and corresponding to the components C1 and C2.

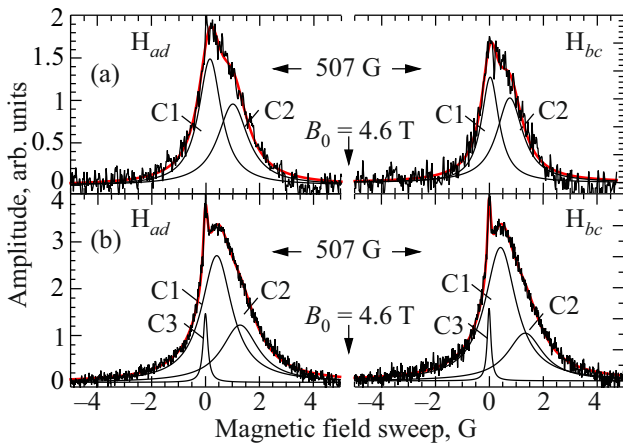


Fig. 2. (a) ESR spectra of H atoms in the as-deposited Sample 2 recorded after first H atom accumulation by running the rf discharge (b) after restarting the discharge in the SC.

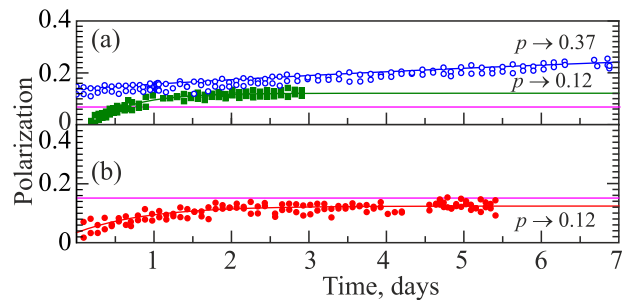


Fig. 3. (a) Spontaneous build-up of nuclear polarization of H atoms in the as-deposited H<sub>2</sub> Sample 1 at  $T = 0.3$  K (open blue circles), in the annealed Sample 3 (filled green squares) at  $T = 0.3$  K and (b) in HD (filled red circles) at  $T = 0.15$  K. The values of Boltzmann nuclear polarization 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  $p(t) = p + a \exp(t/T_{1N})$ .

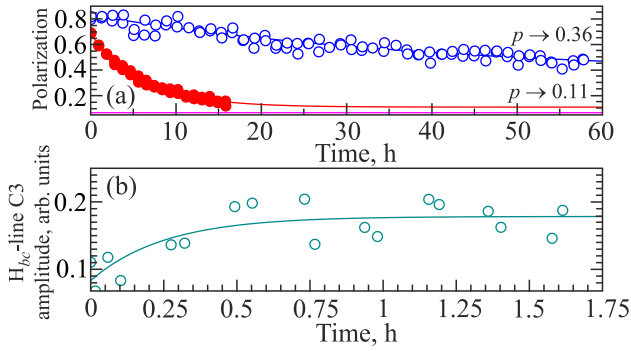


Fig. 4. (a) Relaxation of H atom nuclear polarization after applying the Overhauser effect DNP in as-deposited H<sub>2</sub> Sample 1 (open blue circles) and HD sample (red circles) measured at  $T = 0.8$  K. H atom nuclear polarization at  $T = 0.8$  K according to Boltzmann statistics is shown by a solid magenta line. Note the large difference in the  $T_{1N}$  times for H<sub>2</sub> 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<sub>bc</sub>-line C3 component after applying the Overhauser effect DNP measured in as-deposited H<sub>2</sub> 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<sub>bc</sub> ESR line amplitude.

At the next stage, we studied two samples (Samples 3 and 4) where the H<sub>2</sub> 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  $T \approx 0.7$  K and the H atoms in the H<sub>2</sub> film were accumulat-

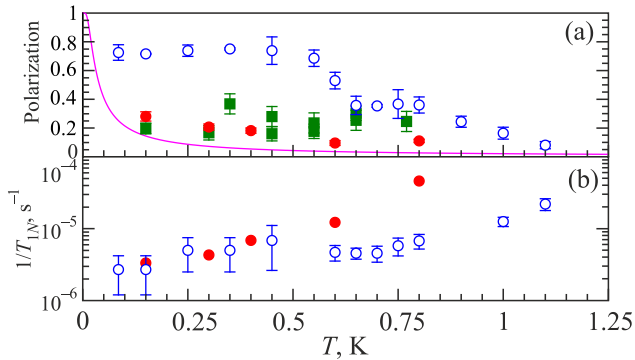


Fig. 5. (a) Asymptotic nuclear polarization of H atoms obtained by SRSs presented as a function of temperature in the annealed H<sub>2</sub> Sample 4 (green squares) and as-deposited HD film (filled red circles) both studied in this work. Nuclear polarization in the as-deposited H<sub>2</sub> film measured by applying the SRSs measured in our previous work [7] 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<sub>2</sub> sample measured in previous work (open blue circles) and H atoms in the HD film (filled red circles).

ed 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<sub>2</sub> samples with such a H atom concentration in our previous work [7] as well as in the pioneering work [2] 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 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<sub>2</sub> matrix may have a drastic effect on the H 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  $\text{H} + \text{HD} \rightarrow \text{HD} + \text{H}$  is two orders of magnitude slower as compared with that in solid H<sub>2</sub> [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<sub>2</sub> matrix. The HD film was 200  $\mu\text{m}$  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  $\text{D} + \text{HD} \rightarrow \text{D}_2 + \text{H}$  [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<sub>2</sub> 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.



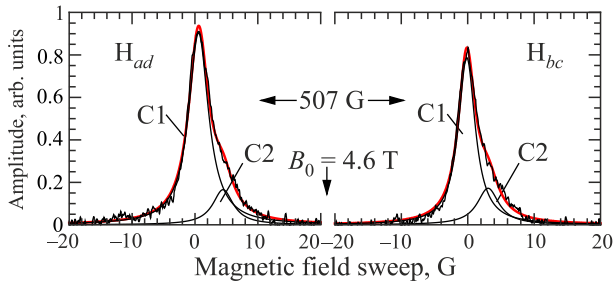


Fig. 6. The ESR spectra of H atoms in HD film.

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 1.

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.

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 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 study 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  $p \approx 0.35$  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 ( $\epsilon \approx 13$  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<sub>2</sub> 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<sub>2</sub> 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<sub>ab</sub> 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<sub>2</sub> 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<sub>2</sub> films as well as for components 1 and 3 of the as-deposited Sample 2 created from normal H<sub>2</sub> 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 phases of H atoms in the HD sample. The H atom diffusion in solid HD takes place through the exchange tunneling reaction  $H+HD \rightarrow HD+H$  [1] in analogy to the H atom diffusion in solid H<sub>2</sub>. 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,  $p \approx 0.3$ , was much lower than that observed for the HNPP in the pure as-deposited H films,  $p \approx 0.75$ , 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> films at temperatures below 1 K and comparable to those,  $\approx 0.1$  G, observed at  $T \geq 1.3$  K by Kumada *et al.* [19] and Iskovskikh *et al.* [20] for H atoms in solid H<sub>2</sub> and Dmitriev [21] for D atoms in solid D<sub>2</sub>. 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  $10^{18} \text{ cm}^{-3}$ . In contrast to C1, the C3 component followed the Boltzmann statistics for the temperature range studied in this work ( $T = 0.1\text{--}1$  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 atom. 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 H<sub>2</sub> 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 H<sub>2</sub> as well as as-deposited HD matrices. We did not observe enhanced spontaneous nuclear polarization of H atoms in solid HD and annealed H<sub>2</sub> 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 H<sub>2</sub> film. This may also lead to a large mean free path for H atoms in solid H<sub>2</sub> 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 H<sub>2</sub> [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 H<sub>2</sub> 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.

1. T. Kumada, *Phys. Rev. B* **68**, 052301 (2003).
2. J. Ahokas, J. Järvinen, V.V. Khmelenko, D.M. Lee, and S. Vasiliev, *Phys. Rev. Lett.* **97**, 095301 (2006).
3. J. Ahokas, O. Vainio, J. Järvinen, V.V. Khmelenko, D. M. Lee, and S. Vasiliev, *Phys. Rev. B* **79**, 220505(R) (2009).
4. J. Ahokas, O. Vainio, S. Novotny, J. Järvinen, V.V. Khmelenko, D.M. Lee, and S. Vasiliev, *Phys. Rev. B* **81**, 104516 (2010).
5. J. Järvinen, V.V. Khmelenko, D.M. Lee, J. Ahokas, and S. Vasiliev, *J. Low Temp. Phys.* **162**, 96 (2011).
6. K.R.A. Hazzard and E.J. Mueller, *Phys. Rev. B* **82**, 014303 (2010).
7. S. Sheludiakov, P.T. McColgan, D.M. Lee, V.V. Khmelenko, J. Järvinen, J. Ahokas, and S. Vasiliev, *Phys. Rev. Lett.* **122**, 225301 (2019).
8. S. Vasilyev, J. Järvinen, E. Tjukanoff, A. Kharitonov, and S. Jaakkola, *Rev. Sci. Instrum.* **75**, 94 (2004).
9. S. Sheludiakov, J. Ahokas, O. Vainio, J. Järvinen, D. Zvezdov, S. Vasiliev, V.V. Khmelenko, S. Mao, and D.M. Lee, *Rev. Sci. Instrum.* **85**, 5 (2014).
10. T. Takayanagi and S. Sato, *J. Chem. Phys.* **92**, 2862 (1990).
11. S. Sheludiakov, J. Ahokas, J. Järvinen, D. Zvezdov, L. Lehtonen, O. Vainio, S. Vasiliev, D.M. Lee, and V.V. Khmelenko, *Phys. Chem. Chem. Phys.* **18**, 29600 (2016).
12. S. Sheludiakov, J. Ahokas, J. Järvinen, O. Vainio, L. Lehtonen, S. Vasiliev, D.M. Lee, and V.V. Khmelenko, *J. Low Temp. Phys.* **187**, 43 (2017).
13. I.F. Silvera and J.T.M. Walraven, in *Progress Low Temperature Physics*, Vol. 10, D.F. Brewer (ed.), Elsevier (1986), p. 139.
14. T.J. Greytak and D. Kleppner, in *New Trends Atomic Physics. Les Houches Sessions*, Vol. 2, G. Grynberg and R. Stora (eds.), North-Holland, Amsterdam (1982), p. 1125.
15. M.J. Jamieson, A. Dalgarno, B. Zygelman, P.S. Krstić, and D.R. Schulz, *Phys. Rev. A* **61**, 014701 (1999).

16. Yu. Kagan and L.A. Maksimov, *Sov. Phys. JETP* **57**, 459 (1983).
17. Yu. Kagan, *J. Low Temp. Phys.* **87**, 0022 (1992).
18. S. Sheludiakov, J. Ahokas, J. Järvinen, O. Vainio, L. Lehtonen, D. Zvezdov, V. Khmelenko, D.M. Lee, and S. Vasiliev, *J. Low Temp. Phys.* **183**, 120 (2016).
19. T. Kumada, M. Sakakibara, T. Nagasaka, H. Fukuta, J. Kumagai, and T. Miyazaki, *J. Chem. Phys.* **116**, 1109 (2002).
20. A.S. Iskovskikh, A.Ya. Katunin, I.I. Lukashevich, V.V. Sklyarevskii, and V.A. Shevtsov, *Sov. Phys. JETP Lett.* **42**, 30 (1985).
21. Yu.A. Dmitriev, *J. Low Temp. Phys.* **180**, 284 (2015).
22. V.N. Grigoriev, B.N. Esel'son, V.A. Mikheev, V.A. Slusarev, M.A. Strzhemechny, and Yu.E. Shulman, *J. Low Temp. Phys.* **13**, 65 (1973).

### Дослідження ядерної поляризації атомів водню в твердих плівках молекулярного водню та дейтериду водню

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

Представлено дослідження ядерної поляризації атомів водню в твердих плівках H<sub>2</sub> та HD методом електронного спінового резонансу при температурах 0,1–1,5 К в сильному магнітному полі 4,6 Тл. Як і в попередній роботі [*Phys. Rev. Lett.* **122**, 225 301 (2019)], ми спостерігали утворення фаз спонтанної ( $p = 0,35$ ) та високої ( $p = 0,75$ ) ядерної поляризації атомів Н в осаджених плівках H<sub>2</sub>. Утворення даних фаз не відбувалося в областях з малою концентрацією атомів водню. Ми так само не виявили збільшення ядерної поляризації для атомів Н в відпалених плівках H<sub>2</sub> й свіжоприготовлених зразках HD. Дані спостереження підтверджують наше пояснення збільшення ядерної поляризації атомів Н в процесі утворення слабкоз'язаних триплетних молекул H<sub>2</sub>.

Ключові слова: атоми водню, твердий молекулярний водень, ядерна поляризація.

### Исследования ядерной поляризации атомов водорода в твердых пленках молекулярного водорода и дейтерида водорода

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

Представлено исследование ядерной поляризации атомов водорода в твердых пленках H<sub>2</sub> и HD методом электронного спигового резонанса при температурах 0,1–1,5 К в сильном магнитном поле 4,6 Тл. Как и в предыдущей работе [*Phys. Rev. Lett.* **122**, 225301 (2019)], мы наблюдали образование фаз спонтанной ( $p = 0,35$ ) и высокой ( $p = 0,75$ ) ядерной поляризации атомов Н в осажденных пленках H<sub>2</sub> и свежеприготовленных образцах HD. Мы так же не обнаружили увеличения ядерной поляризации для атомов Н в отпаленных пленках H<sub>2</sub> и свежеприготовленных образцах HD. Данные наблюдения подтверждают наше объяснение увеличения ядерной поляризации атомов Н в процессе образования слабо связанных триплетных молекул H<sub>2</sub>.

ядерной поляризации атомов Н в осажденных пленках Н<sub>2</sub>. Образование данных фаз не происходило в областях с малой концентрацией атомов водорода. Мы так же не обнаружили увеличения ядерной поляризации для атомов Н в отожженных пленках Н<sub>2</sub> и свежеприготовленных образцах HD. Данные наблюдения подтверждают наше объяснение

увеличения ядерной поляризации атомов Н в процессе образования слабосвязанных триплетных молекул Н<sub>2</sub>.

Ключевые слова: атомы водорода, твердый молекулярный водород, ядерная поляризация.