

# Dynamic Nuclear Polarization of High-Density Atomic Hydrogen in Solid Mixtures of Molecular Hydrogen Isotopes

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We report on magnetic resonance studies of high-density atomic hydrogen and deuterium in solid hydrogen matrices at temperatures below 1 K. Average concentrations of H atoms  $\approx 3 \times 10^{19} \text{ cm}^{-3}$  are obtained in chemical tunneling reactions of isotope exchange with D atoms. The products of these reactions are closely located pairs of H atoms near  $\text{D}_2$  molecules with strong exchange interactions. We discovered a dynamic nuclear polarization effect on H atoms created by pumping the center of the H electron spin resonance spectrum, similar to the Overhauser effect in metals. Our results indicate that H atoms may be arranged inside molecular matrices at separations equivalent to local concentrations of  $2.6 \times 10^{21} \text{ cm}^{-3}$ . This opens up a way to build a metallic state of atomic hydrogen at zero pressure.

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Among the most spectacular manifestations of quantum behavior in condensed matter physics are the phenomena of Bose-Einstein condensation (BEC) and superfluidity, which occur in systems of neutral atoms at high densities and low temperatures. The possibility of observing quantum phenomena in solids is characterized by a de Boer parameter [1], which is proportional to the strength of the zero-point energy relative to the interaction energy. Helium and hydrogen isotopes are the best candidates for a manifestation of quantum phenomena, because they have small masses and weak interactions. Solid molecular hydrogen containing high densities of atomic hydrogen is thus a very promising system to investigate. The diffusion of H atoms in the  $\text{H}_2$  crystals proceeds via quantum tunneling exchange reactions with neighboring molecules [2,3]. One might expect that BEC and superfluidity could occur at small enough separations between atoms. Collective quantum phenomena of electrons of the atoms are also expected at high enough densities, eventually leading to an insulator to metal transition. In a system of phosphorus donors in silicon crystals, this occurs at a P density of  $\sim 3 \times 10^{18} \text{ cm}^{-3}$  [4]. The onset of the transition to the metallic state is accompanied by dramatic changes of the ESR spectrum. The two hyperfine lines of P atoms, usually separated by 42 G, merge into a single peak at the center of the ESR spectrum. For hydrogen atoms, having a substantially smaller size, this effect would occur at higher densities. This may occur for some groups of atoms or clusters where the local density is larger than average. Studies of exchange tunneling reactions between atoms and molecules of hydrogen isotopes [5,6] and dynamic nuclear polarization of stabilized atoms and HD molecules [7,8] at

low temperatures in a high magnetic field are also worthy of investigation.

In this work, we discovered a method for creating high-density samples of atomic hydrogen in solid matrices. Record-high average H densities of  $3 \times 10^{19} \text{ cm}^{-3}$  were obtained in  $\text{H}_2$  and  $\text{D}_2$  solid mixtures via exchange tunneling reactions between atoms and molecules of hydrogen isotopes. Unlike in other known methods of sample preparation, the relatively small energies released in these reactions do not thermally activate diffusion of the atoms at the preparation stage. As a result, H atoms are generated in pairs adjacent to neighboring  $\text{D}_2$  molecules where the interatomic distance may be substantially shorter than the average. We studied dynamic nuclear polarization (DNP) of H and D atoms by using the Overhauser effect (OE) [9] and the solid effect (SE) [10,11]. Magnetic resonance studies revealed unusual behavior of the DNP of H atoms when the microwave pumping was performed exactly in the center of the H and D ESR spectrum. This may be caused by strong quantum mechanical exchange effects between pairs of H atoms stabilized near  $\text{D}_2$  molecules. We found that these strongly interacting pairs are very stable and do not recombine back to molecules during several days of observation.

Experiments were performed in the sample cell shown in Fig. 1(a) [12]. It consists of a main sample cell (SC) volume containing a Fabry-Perot resonator (FPR) and two sublimation-type sources for generating beams of  $\text{H}_2$  and  $\text{D}_2$  molecules. The SC is thermally anchored to the mixing chamber of an Oxford 2000 series dilution refrigerator and located at the center of a 4.6 T superconducting magnet. The main diagnostic tools in our experiments are ESR

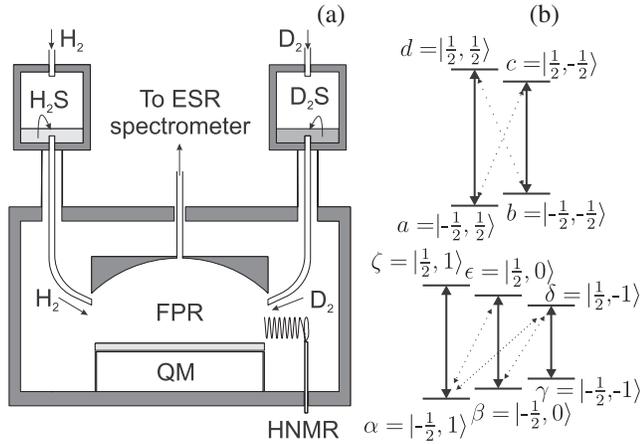


FIG. 1. Schematic drawing of the sample cell. (a)  $\text{H}_2\text{S}$ ,  $\text{D}_2\text{S}$  = molecular hydrogen (deuterium) sublimation sources; FPR = Fabry-Perot resonator; QM = quartz microbalance; HNMR = helical resonator for H- $\text{H}_2$  NMR. (b) Hyperfine-level diagram for hydrogen (upper) and deuterium atoms in a high magnetic field. The numbers in brackets  $|m_s, m_I\rangle$  denote the electron and nuclear spin states. Allowed and forbidden transitions are shown by solid and dashed lines, respectively.

operating at 128 GHz and mass measurement by a quartz crystal microbalance (QM). Molecular hydrogen and deuterium films are deposited onto the QM surface which also works as a flat mirror of the semiconfocal FPR of the ESR spectrometer. The open geometry of the FPR allows installation of a radio frequency (rf) coil for the excitation of NMR transitions for H atoms (HNMR,  $f \approx 910$  MHz) in a 4.6 T field. It can be also used to provide an rf discharge in the cell to produce H and D atoms in molecular films. The deposition of the  $\text{H}_2$  and  $\text{D}_2$  films on the QM surface is accomplished by heating the sublimation chambers to temperatures above 5 and 7 K, respectively. The thickness of the films was determined by the QM. After deposition of the molecular films, the rf discharge is activated in the sample cell in order to produce H and D atoms in the films by electron impact. This method is very efficient for achieving high densities (up to  $2 \times 10^{19}$   $\text{cm}^{-3}$ ) of H atoms in  $\text{H}_2$  films [13].

It is well known that in the solid mixtures of hydrogen isotopes chemical tunneling reactions of isotope exchange  $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ ,  $\text{D} + \text{HD} \rightarrow \text{D}_2 + \text{H}$  proceed with relatively fast rates down to temperatures of  $\sim 1.3$  K [5]. As a result of these reactions, two D atoms associate into a  $\text{D}_2$  molecule, generating two H atoms. This leads to an increase of the H atom concentration and a decrease of the D atom concentration. We found that this process is rather effective at temperatures down to 150 mK and may also be used for production of high concentrations of H atoms utilizing D atoms, generated with the above-mentioned rf discharge.

We studied 100–300 nm films of  $\text{D}_2$  with small HD and  $\text{H}_2$  impurity content ( $\sim 1\%$ ). After deposition of the film

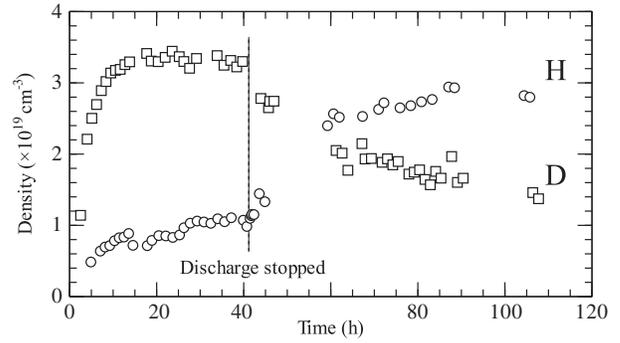


FIG. 2. Evolution of atomic hydrogen and deuterium densities, recorded during the rf dissociation and subsequent tunneling isotope exchange reactions at  $T \approx 300$  mK.

onto the surface of the QM, the rf discharge was run for several hours until the concentrations of D atoms reached a maximum value of  $\approx 3 \times 10^{19}$   $\text{cm}^{-3}$ . Evolutions of H and D densities extracted from the ESR data are shown in Fig. 2. The increase of H density and decrease of D density after stopping the discharge clearly demonstrate the above-mentioned isotope exchange reactions. After a period of 120 h, the concentrations of both H and D atoms achieved the stationary levels  $\approx 3 \times 10^{19}$   $\text{cm}^{-3}$  and  $1.4 \times 10^{19}$   $\text{cm}^{-3}$ , respectively. In view of the relatively small initial concentration of  $\text{H}_2$  in the film, the final H atom concentration is spectacularly large. Assuming that the probability of  $\text{H}_2$  and  $\text{D}_2$  dissociation due to the discharge action is the same, we estimate that  $\geq 99\%$  of these atoms are products of the exchange chemical reactions rather than the result of dissociation by electron impact.

After achieving a steady state for the densities of H and D atoms in the sample, we performed a detailed study of the magnetic resonance properties and DNP of the H and D atoms. A schematic of the energy levels and ESR transitions for these atoms is shown in Fig. 1(b). The ESR spectrum consists of two H and three D lines separated by  $\approx 507$  and  $\approx 78$  G, respectively, due to hyperfine interactions. Examples of observed spectra are depicted in Fig. 3. The ESR lines were detected by a heterodyne spectrometer at very low excitation power  $< 1$  nW without field or frequency modulation [14], which provides undistorted absorption and dispersion line shapes free of saturation effects. At the high densities of atoms studied in this work, the ESR lines are mainly broadened homogeneously, due to the electron spin-spin interactions between atoms. A small inhomogeneous broadening is caused by magnetic moments of surrounding ortho- $\text{D}_2$  molecules. The homogeneous broadening is proportional to the atomic density [13]. We used the dependence of the linewidth on density reported in our previous work [13] for determination of the average densities of H and D atoms in our samples. In DNP experiments, we partially saturated ESR transitions by applying a maximum available rf power of  $\sim 0.4$   $\mu\text{W}$  with

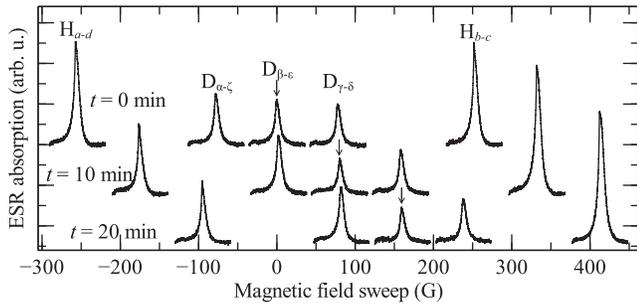


FIG. 3. ESR absorption spectra of H and D atoms and their evolution during pumping at the D atom central line. Upper trace, before pumping; central and lower traces, after 10 and 20 min of pumping, respectively.

a frequency-modulated rf source adjusted to cover the whole or part of the ESR line.

We performed DNP experiments using the OE and SE effects [15]. In the OE DNP, the allowed ESR transitions are saturated. Then subsequent cross relaxation via the so-called forbidden transitions involving simultaneous electron and nuclear spin reversal (flip-flop and flip-flip transitions) leads to enhancement of nuclear polarization. One of the most effective ways of doing OE DNP for hydrogen is to pump the allowed  $b-c$  transition, followed by a  $c-a$  relaxation [see Fig. 1(b)]. This transfers atoms from the  $b$  state to the  $a$  state and creates a nuclear polarization of H atoms  $P = (n_a - n_b / n_a + n_b) \approx 1$ . By pumping an allowed  $a-d$  transition, followed by  $d-b$  relaxation, a negative polarization  $P \approx -1$  is created. In the SE DNP, the forbidden transitions are induced by a resonant rf field. A subsequent relaxation via the allowed transitions leads to DNP. The rate of the OE (or SE) DNP is defined by the relaxation (or rf-induced) transition rates of the forbidden transitions,  $c-a$  and  $a-d$  for H atoms. These transitions become partially allowed because of the anisotropy of the hyperfine interaction, which appears to be rather strong in crystalline solids [15]. Usually, the rate of the flip-flop transition is much faster than that of the flip-flip transition. Thus, we found that for atomic hydrogen  $T_{ca} \approx 65$  s and  $T_{db} \approx 900$  s. Similarly, pumping the central line of D, we create DNP via the faster  $\epsilon \rightarrow \alpha$  relaxation, leading to the enhancement of the low field D atom ESR line (see Fig. 3). In the above-described OE DNP experiments with H atoms, we have not observed any changes of the hyperfine populations of D atoms. In contrast, we noticed that pumping the central line of D also leads to an efficient *negative* polarization of H (seen in the lower traces of Fig. 3), as discussed below.

Next, we studied the efficiency of the hydrogen SE DNP as a function of the magnetic field in the range  $\pm 110$  G around the position of the center of the ESR spectrum. This range includes forbidden transitions for H (dashed traces in Fig. 4). In these measurements, the pumping was performed at various points between the H lines with a

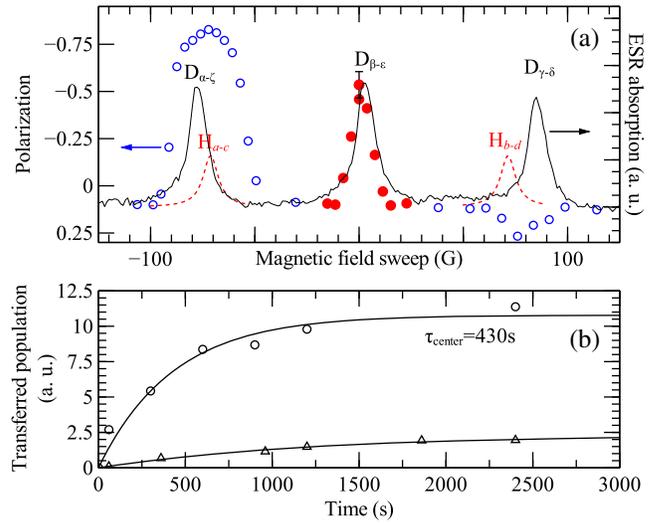


FIG. 4 (color online). (a) DNP of H atoms as a function of the magnetic field (circles), measured at 300 mK. ESR signal of D atoms (thin line) and calculated forbidden transitions of H atoms (dashed lines). Anomalous DNP obtained by pumping in the center of the spectrum is outlined with filled (red) circles. (b) Population transfer for hydrogen (circles) and deuterium (triangles) atoms during pumping of the D atom central line.

$\pm 5$  MHz frequency modulation (FM) of the millimeter-wave source. This allowed an excitation of the atoms in the range of  $\pm 2$  G near the given position. After 1 h of such pumping, the ESR spectra and nuclear polarization of H and D atoms were measured with reduced power ( $P < 1$  nW) and without FM. Then the polarization was restored to a value corresponding to the Boltzmann distribution of the populations for  $T = 300$  mK ( $P = 0.073$ ) using the above-mentioned OE DNP. The process of measurement at the next value of magnetic field was then repeated. The results of these measurements are shown in Fig. 4(a), where the *sign of polarization axis is reversed* and in addition the D atom ESR spectrum is presented. The dependence of the *polarization* value versus the magnetic field has three peaks. The maximum negative polarization ( $P = -0.83$ ) was achieved at the position of the  $a-c$  forbidden transition of H atoms. For the same level of power used for saturation, a maximum positive polarization  $P = 0.25$  was observed at the position of the even more forbidden  $b-d$  transition. These two polarization peaks appear as expected for the resolved solid effect [15].

A new and surprising effect was the observation of an additional peak of negative polarization of H atoms ( $P = -0.54$ ) when we pumped at the center of the H (and D) ESR spectrum (filled circles in Fig. 4). Since pumping at this position also leads to the D atom polarization via the Overhauser effect, we performed a comparison study of the dynamic polarization of both H and D atoms during such pumping. The time dependencies of the population transferred from the  $H_a$  state to the  $H_b$  state and from the  $D_\beta$  to the  $D_\alpha$  states of deuterium are shown in Fig. 4(b).

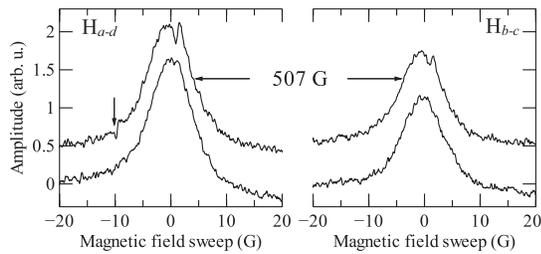


FIG. 5. A demonstration of simultaneously creating holes in the  $a-d$  (left upper trace) and  $b-c$  (right upper trace) lines of atomic hydrogen by pumping the position of the left satellite line of the H atom  $a-d$  line (marked by an arrow) associated with a simultaneous spin flip of an electron on an H atom and a deuteron on a  $D_2$  molecule. Lower traces: ESR lines before pumping.

From these graphs, we can see that the number of polarized H atoms was almost one order of magnitude larger than that for D atoms for the same pumping time.

We tried to make similar DNP experiments with H atoms in films of pure para- $H_2$ , also studied in our previous work [13]. We found that the only possibility for creating DNP was via the Overhauser effect by pumping the  $b-c$  transition. All of our attempts at pumping the  $a-d$  transition, pumping the forbidden transitions (SE effect), and pumping the center of the spectrum were unsuccessful.

One can see that the presence of deuterium dramatically changes the magnetic resonance behavior of atoms in the films. One of the reasons is the presence of large quantities of magnetic dipoles in the lattice; 5/6 of the deuterium molecules in the ground state (ortho- $D_2$ ) possess nuclear spins of 2. Their magnetic moments create anisotropic local fields, which lessen restrictions on forbidden transitions and make DNP substantially more effective.

The presence of molecules with magnetic moments (ortho- $D_2$  or ortho- $H_2$ ) in close proximity to the embedded atoms can be verified by an excitation of the so-called satellite transitions [16] which involve a simultaneous spin flip of the electron of the atom and a nuclear spin of the molecule. The satellite transition corresponding to a  $D_2$  nuclear spin flip located  $\pm 10.3$  G from the ESR lines is too weak to be detected directly. Since the ESR lines have small contributions from inhomogeneous broadening due to the magnetic moments of surrounding molecules, altering  $D_2$  spin states produces a small hole in the ESR line shape. Results of such a measurement are presented in Fig. 5, where we pumped the left satellite of the H  $a-d$  line for 30 min. A clear hole is detected in the adjacent ESR peak. Similar holes were observed when pumping satellites on both sides for all H and D lines. But a new and interesting feature, never observed in previous work, was that pumping the H  $a-d$ -line satellites also leads to the appearance of a hole in the H  $b-c$  line (upper right trace in Fig. 5). No holes were detected in the D lines after such pumping, and pumping D satellites did not create holes in the other H or D lines.

The most intriguing result obtained for the films containing deuterium is the appearance of the nuclear polarization of H atoms after pumping at the center of the ESR spectrum. For an interpretation of this effect, we consider the following mechanisms: (i) polarization transfer from D to H atoms; (ii) strong exchange effects in closely located pairs of atoms. We consider these possibilities in detail below.

(i) Because of spin-spin interactions, the polarization may be effectively transferred from nuclei of one sort to another. Such transfer effects are well known in the NMR of liquids and solids (see, e.g., [17]). However, the OE after pumping the central line of D leads to a positive polarization of D. After the transfer, H atoms should also gain positive  $P$ , which contradicts our observations. Also, the polarization transfer should work equally well for the transfer of polarization in the reverse direction, from H to D. Such an effect has not been observed at all. Therefore, we think that the polarization transfer may be an unlikely mechanism to explain the negative polarization obtained after pumping the center of the ESR spectrum.

(ii) The second important feature of the samples containing deuterium is the possibility for chemical reactions of isotope exchange  $D + H_2 \rightarrow HD + H$ ,  $D + HD \rightarrow D_2 + H$ . All reverse reactions are endothermic ( $\Delta E \sim 500$  K) and do not proceed at the temperatures of our experiment. This results in the production of a substantial number of stable complexes  $H-D_2-H$ , in which H atoms are separated by only two lattice constants. They cannot move apart from each other because of a lack of mobility of H atoms in  $D_2$  matrices. The strongly interacting H atom pairs would create extra ESR lines at the position in the center of the ESR spectrum. Such central-pair and cluster lines due to the exchange interaction of two, three, or four electrons were observed in silica crystals doped with P atoms at a concentration exceeding  $10^{16}$   $cm^{-3}$  [18,19].

Careful analysis of the ESR spectra of atomic dimers with strong exchange interaction energy  $J$  [20,21] shows that two lines appear at the center of the ESR spectrum, separated by  $A^2/2J$ , with  $A$  being the hyperfine energy. These lines merge into a single peak in the center for very large  $J$ . For the real system of pairs with a random distribution of the interatomic separation, and hence values of  $J$ , this leads to the appearance of a broad peak in the center of ESR spectrum. Saturating this peak with rf power in P-doped silicon leads to a reduction of the ordinary hyperfine ESR lines [20] and may also build nuclear polarization of the atoms of the pair. Then the polarization may propagate through the volume of the crystal due to spin diffusion, which is expected to be very fast at high concentrations of impurity atoms. Thus it is effectively transferred to unpaired atoms in the sample. The sign of the polarization depends on the ratio of the probabilities of the forbidden transitions, which is a complicated function of the anisotropy of the crystal [22]. In the  $H-D_2-H$

complexes, the separation between atoms is the same as it would be in samples having a  $2.6 \times 10^{21} \text{ cm}^{-3}$  concentration of atoms, more than 5 orders magnitude larger than in the example mentioned for P in silicon. It is therefore reasonable to expect that these strongly interacting pairs of H atoms have partially allowed transitions at the center of their spectra. The registration of these transitions is problematical because of their weakness and of the presence of the strong  $D_{\beta-c}$  line at the same position.

Further strong evidence of the presence of large numbers of strongly interacting H pairs is found in the above-described experiment with satellite transitions of the H ESR lines (see Fig. 5). In the case of an unpolarized H sample, we deal with an equal number of  $H_a-H_a$  and  $H_b-H_b$  pairs, twice lower than the number of  $H_a-H_b$  pairs. Flipping the  $D_2$  molecule spin for pairs having  $a$ -state atoms will influence half of the total number of  $b$ -state atoms. Therefore, after pumping the  $a$ - $d$ -line satellite, one would expect the appearance of a hole also in the  $b$ - $c$  line, a factor of  $3/2$  smaller than that in the  $a$ - $d$  line. The relative depths of the holes seen in Fig. 5 qualitatively confirm this prediction.

Our results demonstrate the possibility of the existence of stable pairs of hydrogen atoms with small interatomic separation stabilized near  $D_2$  molecules in solid mixtures of molecular hydrogen isotopes. These atoms experience strong electron exchange effects, leading to effective dynamic nuclear polarization when the center of the H atom ESR spectrum was pumped. Similar behavior is well known for metals where it was originally proposed by Overhauser [9]. Our work suggests that a stable metallic phase of atomic hydrogen can be created inside solid molecular crystals with a large number of embedded H atoms. Recombination of the atoms is suppressed by the  $D_2$  molecules placed between the atoms. Chemical tunneling reactions involving isotope exchange should provide a good opportunity for a practical realization of such systems.

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