Hydrogen Atoms in Impurity-Helium Solids

S. I. Kiselev, V. V. Khmelenko, and D. M. Lee

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501

Electron spin resonance (ESR) is employed to study atomic impurities (H and D) stabilized in impurity-helium (Im-He) solids at 1.35–1.5 K. The kinetics of the low temperature tunneling exchange reactions $(D + H_2 \rightarrow H + HD, \ D + HD \rightarrow H + D_2)$ are investigated in Im-He samples containing several different mixtures of hydrogen and deuterium impurities. The ESR line structures help determine the local environment of atoms trapped in Im-He solids. High concentrations of atomic hydrogen stored in Im-He solids may ultimately find applications in energy storage, matrix-isolation spectroscopy, and studies of different quantum statistical effects.

Impurity helium (Im-He) solids are porous gel-like materials created by injecting a mixed beam of helium gas and an impurity gas into superfluid ^{4}He by means of a method first introduced by Gordon *et al.* [1]. Van der Waals forces lead to the formation of thin layers of solid helium around individual impurities or clusters of impurities which are all bound together by van der Waals forces to form a structure with nanoscale pores [2,3]. Matrix isolation of free radical impurities by the surrounding helium in Im-He solids leads to unusually high concentrations of these impurities. This makes systems involving Im-He solids well suited for studying exotic chemical reactions, for applications to energy storage using the isolation of reactive species by inert matrices, and for studying the flow of liquid helium in nanoscale porous materials. Here we report electron spin resonance (ESR) studies of Im-He solids containing atoms and molecules of hydrogen and/or deuterium. We have performed studies of exchange tunneling reactions in which deuterium atoms replace hydrogen atoms bound in H_2 and HD to produce large populations of free hydrogen atoms. The detailed ESR line structures have enabled us to determine that the hydrogen atoms are not perfectly isolated by helium but are found in association with HD or H_2 molecules.

H and D atoms are produced by sending gaseous helium with a small (1%–5%) admixture of impurities (H_2, D_2) through a high frequency discharge into superfluid helium at $T \sim 1.5$ K contained in a small sample beaker. This technique has been described in detail previously [3]. After sample collection was completed, the beaker is lowered into a hole at the top of a TE_{011} microwave resonant cavity. Electron spin resonance signals in a steady magnetic field of 0.3 T modulated at 100 kHz are detected by a 9.1 GHz continuous wave reflection homodyne spectrometer. Using this method we record the derivatives of the ESR absorption peaks. In Fig. 1(a), the main features of the atomic hydrogen and deuterium derivative spectra of a sample prepared from an initial gas mixture in the ratio of H_2:D_2:He = 1:4:100 are shown. We observe the allowed hyperfine transitions of

H and D atoms [4], as well as a small forbidden line of the hydrogen atom which involves a simultaneous spin flip of the electron and proton. Magnetic dipole selection rules for allowed electron spin flip transitions require the microwave field in the cavity H_{rf} to be perpendicular to the applied steady field H. For observation of the forbidden line we need $H_{rf} \parallel H$ [5]. This condition is easily met in our experiment because we operate with macroscopic samples occupying a considerable part of the cavity, including areas with significant components $H_{rf} \parallel H$ (especially at the top and the bottom of the cavity). The intensity (corresponding to the area under the absorption line) of the forbidden line is about 200 times
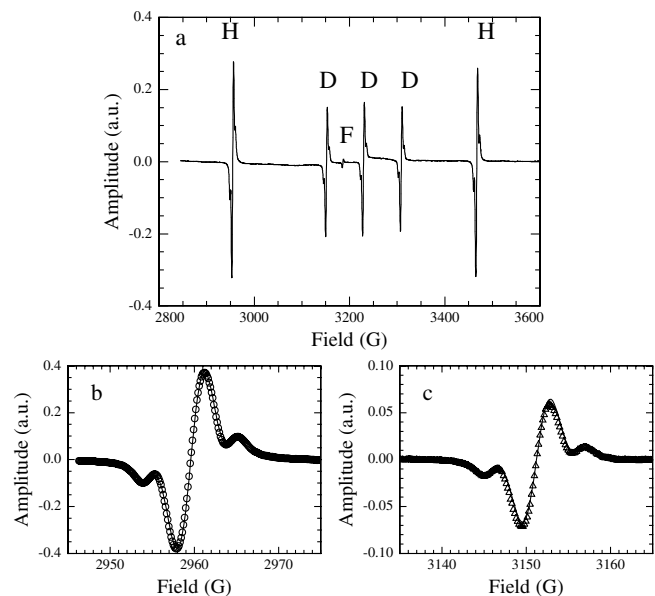

FIG. 1. (a) ESR signal from Im-He sample prepared from gaseous mixture H_2:D_2:He = 1:4:100. "H" marks allowed ESR transitions between hyperfine levels of atomic H; "D" indicates the hyperfine transitions in atomic D, and "F" indicates the forbidden ESR transition of H atoms. At the bottom are shown typical derivative signals for low field hyperfine lines of (b) hydrogen and (c) deuterium atoms showing both the allowed and the accompanying satellite lines.

smaller than the allowed hydrogen line, roughly in accord with theory [5].

Both the deuterium and the hydrogen ESR lines are accompanied by two satellite lines, one on either side of the main line [Figs. 1(b) and 1(c)]. Satellite lines have been previously observed for H and D atoms contained in solid hydrogen by Miyazaki *et al.* [6]. The atoms were produced in very low concentrations by γ irradiation of solid H_2, solid HD, and solid D_2. The satellites are associated with forbidden ESR transitions involving an electron spin flip of a hydrogen or deuterium atom and simultaneous spin flip of protons on neighboring HD or ortho-hydrogen molecules [6], simply as a result of dipolar coupling.

Each of the ESR signals was fitted with a sum of three Gaussians (allowed line plus two satellites). From these fits, shown in Figs. 1(b) and 1(c) by solid lines, the ratio of the intensities of the satellite and main lines is found to be 0.12 ± 0.02. Even if the intensities of these lines change with time, the ratios remain constant. The separations between the main and the satellite lines have also been obtained from the fits. These splittings (4.5 ± 0.1 G) are consistent with proton spin flips in a 3 kG field. Analogous splitting for electron spin-deuteron spin interactions is only 0.7 G, unobservable in our experiments because the ESR linewidths are about 2 G.

The measured ratio of intensities has been compared to the expression obtained by Trammell *et al.* [7],

$$I_{\text{satellite}}/I_{\text{main}} = 3/20(g_e \beta_e/H)^2 \langle r_n \rangle^{-6} n, \qquad (1)$$

to find the trapping sites of atomic species in molecular matrices. In the above equation g_e is the electron g factor, β_e is the Bohr magneton, H is the applied steady field, $\langle r_n \rangle$ is the average distance from an atom to a proton belonging to a neighboring molecule, and n is the number of these protons. This analysis assumes that almost all of the hydrogen atoms or deuterium atoms are close to neighboring molecules. The ratio would be considerably smaller if substantial numbers of totally isolated atoms were present, an entirely conceivable situation for Im-He solids. If we make the reasonable assumption that each atom interacts with one or two protons (from neighboring H_2 or HD), then using Eq. (1) we find that the average distance between the atom and the neighboring proton is 1.9–2.2 Å, which is comparable to the distance between the interstitial sites and the lattice sites in the hcp structure of solid HD or solid H_2, whose lattice constants are 3.6 and 3.8 Å. In the work of Miyazaki *et al.* [6], the H atoms in H_2 matrices were separated from H_2 molecules by 3.6–4.0 Å, whereas for the case of H atoms in HD matrices this distance was 2.5–2.6 Å. The discrepancy between these results and our own may be attributable to the difference in sample composition and sample preparation. Our results provide strong evidence that a large fraction of the hydrogen and deuterium atoms are found in clusters of molecular isotopes of hydrogen.

Estimates of the concentrations of atoms were done by comparing the intensity of the hydrogen and deuterium atomic signals (obtained by double integration of the raw data) with intensity of signals from a small ruby crystal with a known number of atoms. The latter was placed at the bottom of the cavity. The ruby was calibrated prior to the experimental run against a standard organic compound α, α'-diphenyl-β-picrylhydrazyl (DPPH) with a known number of spins.

The time dependence of the concentrations of D atoms in D-D_2-He samples (produced from a D_2:He = 1:20 mixture) and of H atoms in a H-H_2-Ne-He sample (obtained from a H_2:Ne:He = 1:4:100 mixture) is displayed in Fig. 2. The addition of neon was required in the latter sample because, unlike D_2-He samples, the H_2-He solid does not sink to the bottom of the cell, due to its small density. The slow decay of D atoms (with characteristic time $\tau_D = 2500 \pm 500$ min) is attributed to the very slow migration of deuterium atoms through molecular deuterium in the clusters ($D + D_2 \rightarrow D_2 + D$) until recombination with another D atom occurs ($D + D \rightarrow D_2$). The migration of isolated atoms driven by zero point motion may also play a role although we have no evidence of the presence of atoms with only helium neighbors as yet. Much faster migration ($H + H_2 \rightarrow H_2 + H$) can explain the much more rapid decay of the number of hydrogen atoms. The decay time of H atoms shown in Fig. 2 is 150 ± 20 min, an order of magnitude faster than for the deuterium atoms. Kagan *et al.* [8] have investigated theoretically the difference in decay rates for hydrogen and deuterium atoms, respectively, and have found that this difference is not simply a question of mass difference, but rather is determined by differences in phonon processes for the hydrogen and deuterium atom impurities.

The simultaneous presence of deuterium and hydrogen molecules in the makeup gas allows us to form impurity-helium solids containing hydrogen atoms and deuterium atoms as well as hydrogen and deuterium molecules. In Figs. 3(a)–3(c) we show the results of our experiments,
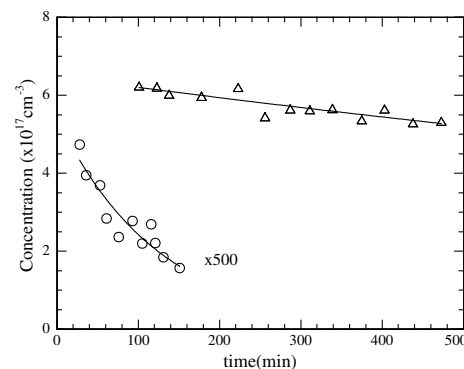

FIG. 2.   Time dependence of concentrations of atomic deuterium [prepared from a D_2:He = 1:20 mixture (open triangles)] and atomic hydrogen [prepared from H_2:Ne:He = 1:4:100 (open circles)] in Im-He solids stored at $T = 1.35$ K.

which dramatically illustrate the time dependence of the hydrogen and deuterium atom concentrations for different initial makeup gas mixtures [9]. In spite of the higher concentration of D_2 compared with that of H_2 in the sample produced from the initial gaseous mixture $H_2:D_2:He = 1:2:60$, the concentration of deuterium atoms is about 2 orders of magnitude smaller than the hydrogen atom concentration and decays more rapidly [Fig. 3(a)]. These results are in sharp contrast to our studies of H_2-Ne-He impurity solids, with no deuterium present, in which the decay of hydrogen atoms due to recombination was much more rapid. The explanation is that when deuterium atoms are present, the supply of hydrogen atoms is replenished via chemical reactions $D + H_2 \rightarrow HD + H$ and $D + HD \rightarrow D_2 + H$. Furthermore, these reactions also explain the faster decrease of the deuterium atom concentration as compared to that in our D-D_2-He sample (Fig. 2). In Fig. 3(b) the population of hydrogen atoms remains almost constant, meaning that the production is almost in balance with recombinational decay in the sample produced from a $H_2:D_2:He = 1:4:100$ mixture. In Fig. 3(c) the population of hydrogen atoms actually shows an increase which is driven by the chemical reactions as time evolves. The large initial supply of deuterium molecules in the gas mixture $H_2:D_2:He = 1:8:180$ means that a copious supply of deuterium atoms is available in the sample, leading to a higher production of hydrogen atoms.

The chemical reactions discussed above were hypothesized by Gordon et al. [10] for impurity-helium solids to explain the unexpectedly high initial populations of hydrogen atoms when impurity-helium solids containing hydrogen and deuterium atoms were formed in their experiments. They were not able to determine the time evolution of the concentrations of the two species in their experiments, however. Later these chemical reactions were employed to study chemical reactions in solid hydrogen matrices by Ivliev et al. [11] via deposition of the products of H_2 and D_2 passing through a radio frequency discharge and Miyazaki et al. [12–16] in experiments on γ-irradiated samples of solid mixtures of H_2 and D_2. Both of these groups monitored the populations of atomic hydrogen and deuterium as a function of time following the deposition or irradiation. Although the concentrations of hydrogen and deuterium atoms were very dilute in their work, time evolutions were found to be similar to the results of our experiments.

Since all of the experiments involving these chemical reactions are performed at liquid helium temperatures, thermally activated processes can be effectively ruled out. When a deuterium atom is adjacent to a molecule of hydrogen, an intermediate state involving the metastable compound molecule HDH is formed. Then a hydrogen atom is emitted, leaving behind a stable HD molecule. The potential barrier for the formation of the compound molecule is typically of order 4000 K [17] which is far greater than liquid helium temperatures (1–4 K), justifying our statement that the reactions are not thermally activated. Therefore the reactions can be driven only by quantum mechanical tunneling and are thus classified as exchange tunneling reactions.

In studying the sample evolution, we must take into account the reaction rates for the two chemical reactions we have discussed. According to the theoretical work of
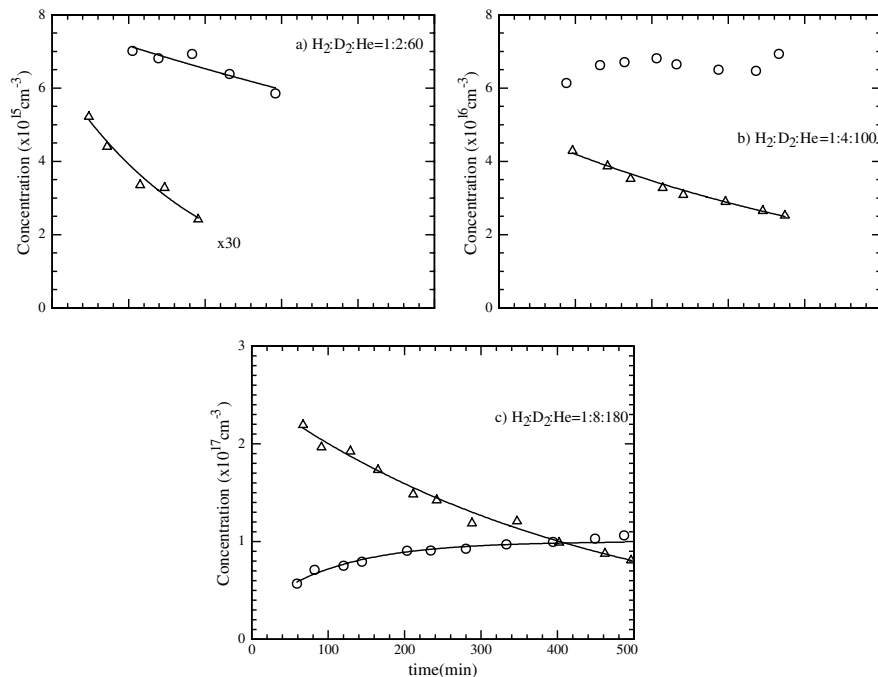

FIG. 3. Time dependence of concentrations of atomic deuterium (open triangles) and atomic hydrogen (open circles) in different Im-He solids stored at $T = 1.35$ K.

Takayanagi *et al.* [18], the rate for the reaction $D + H_2 \rightarrow HD + H$ is 2 orders of magnitude faster than for $D + HD \rightarrow D_2 + H$. The unexpectedly high initial concentrations of hydrogen atoms seen in our work and that of Gordon *et al.* [10] are attributable to the very high rate for the former reaction, where we estimate the time constant to be on the order of 1 min for our samples. The slower decay after sample formation is in large part attributable to the latter reaction. Assuming that the process $D + HD \rightarrow D_2 + H$ is the leading mechanism of depletion of the deuterium atom concentration [D] in the sample prepared from the $H_2:D_2:He = 1:4:100$ mixture, we calculate the rate constant k for this reaction:

$$\frac{d[D]}{dt} = -k[HD][D]. \quad (2)$$

For this sample the measured decay time of [D] is $\tau_D = (\frac{d[D]}{dt}/[D])^{-1} \simeq 550$ min [Fig. 3(b)]. To calculate the concentration of HD molecules [HD] we shall assume complete dissociation of H_2 and D_2 molecules passing through the rf discharge during sample preparation. Recombination reactions will take place in the warm beam as it travels toward the superfluid surface with the resulting formation of H_2, HD, and D_2 molecules, which are in turn incorporated into the impurity-helium solids with the initial molecular ratio $H_2:HD:D_2 = 1:8:16$ [19]. Deuterium atoms react rapidly with the H_2 molecules in the sample, resulting in the formation of additional HD molecules. Therefore after a few minutes the ratio of HD:D_2 will become closer to 9:16. Assuming the cluster density to be close to that of solid deuterium [3], we find an HD concentration of approximately 1.7×10^{22} cm^{-3}. Then $k \simeq 1.1 \times 10^{-3}$ cm^3 mol^{-1} s^{-1}, which is consistent with Miyazaki's value of k for D in a solid HD sample. This agreement provides further evidence that small clusters of impurities are very important in determining the properties of impurity-helium solids.

In conclusion, we point out that matrix isolation of reactive atomic species in impurity-helium solids greatly impedes molecular recombination reactions. The results of our work indicate that the atoms tend to be associated with clusters of other impurity atoms and molecules. They do not appear to simply occur as individual atoms isolated by layers of solid helium. Two pieces of evidence support this conclusion. One of these is that the satellite lines in our ESR spectra indicate that neighboring H_2 and HD molecules are close to the hydrogen and deuterium atoms. The second is that the rate constants seen in the exchange tunneling reactions are consistent with clustering.

The exchange tunneling reactions are capable of producing very high concentrations of hydrogen atoms. The highest concentration achieved, as estimated from the ESR line intensity, was $\sim (7.7 \pm 3.0) \times 10^{17}$ atoms/cm^3. For this concentration the thermal de Broglie wavelength becomes comparable to the mean distance between hydrogen atoms at ~ 10 mK which can possibly be reached by means of a dilution refrigerator, provided that recombinational heat and the heat from ortho-para conversion of hydrogen molecules can be removed efficiently. Quantum overlap phenomena involving quantum statistical effects or magnetic transitions might be observable. The local concentration of hydrogen atoms within a cluster is much larger than the average concentration, so that quantum overlap of the hydrogen atoms may occur at much higher temperatures. If the clusters containing hydrogen atoms are above the percolation threshold, we indulge in the speculation that dramatic transport properties associated with Bose-Einstein condensation (BEC) might be observable. Relevant to this discussion, Toennies and co-workers [20] have recently observed a phenomenon that they have interpreted as superfluidity of H_2 trapped in isolated clusters. Crooker and co-workers [21] performed seminal studies of BEC in a very dilute film of liquid helium trapped in the pores of Vycor glass in the 1980s, anticipating later studies of BEC in the alkali gases and spin polarized hydrogen gas.

Finally, the forbidden line has been observed for the first time in hydrogen atoms trapped in an impurity-helium solid. This sets the stage for possible dynamic nuclear polarization experiments.

[1] E. B. Gordon *et al.*, JETP Lett. **19**, 63 (1974).
[2] E. B. Gordon *et al.*, Chem. Phys. Lett. **155**, 301 (1989).
[3] S. I. Kiselev *et al.*, Phys. Rev. B **65**, 024517 (2002).
[4] N. F. Ramsey, *Molecular Beams* (Clarendon Press, Oxford, 1956).
[5] A. Abragam and M. Goldman, *Nuclear Magnetism: Order and Disorder* (Clarendon Press, Oxford, 1982).
[6] T. Miyazaki *et al.*, J. Phys. Chem. **94**, 1702 (1990).
[7] G. T. Trammell *et al.*, Phys. Rev. **110**, 630 (1958).
[8] Yu. Kagan *et al.*, JETP Lett. **36**, 253 (1982).
[9] S. I. Kiselev *et al.*, J. Low Temp. Phys. **128**, 37 (2002) gives some preliminary results before final calibration.
[10] E. B. Gordon *et al.*, JETP Lett. **37**, 282 (1983).
[11] A. V. Ivliev *et al.*, JETP Lett. **38**, 379 (1983).
[12] H. Tsuruta *et al.*, J. Phys. Chem. **87**, 5422 (1983).
[13] T. Miyazaki *et al.*, J. Phys. Chem. **88**, 4959 (1984).
[14] T. Miyazaki *et al.*, J. Phys. Chem. **93**, 3352 (1989).
[15] T. Kumada *et al.*, Chem. Phys. Lett. **261**, 463 (1996).
[16] T. Kumada *et al.*, J. Chem. Phys. **116**, 1109 (2002).
[17] R. N. Porter and M. Karplus, J. Chem. Phys. **40**, 1105 (1964).
[18] T. Takayanagi *et al.*, J. Chem. Phys. **90**, 1641 (1989).
[19] S. I. Kiselev, Ph.D. thesis, Cornell University, 2002 (unpublished).
[20] J. P. Toennies *et al.*, Phys. Today **54**, No. 2, 31 (2001).
[21] B. C. Crooker *et al.*, Phys. Rev. Lett. **51**, 666 (1983).