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The pressure effect on the recombination and relaxation of hydrogen atoms in solid hydrogen

Valeri Shevtsov^{a,b}, Takayuki Kumada^{a,*}, Yasuyuki Aratono^a, Tetsuo Miyazaki^{a,c}

^a Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan
 ^b Russia Research Center "Kurchatov Institute", Moscow 123182, Russian Federation
 ^c Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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Abstract

We have studied experimentally for the first time the properties of hydrogen atoms in solid hydrogen under pressure. The recombination rate constant has activation-type temperature dependence in the pressure range from 0 to 22 MPa. The activation energy increases linearly with external pressure $E_a = (2.4 P + 106 \text{ K})$, as should be expected in the case of a tunneling vacancy mechanism in atom diffusion. Strong pressure effects on the linewidth of the ESR signal and on the spin–lattice relaxation time T_1 were explained by the competition between the local *ortho-para* conversion process around the H atom and the pressure-dependent diffusion. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The hydrogen atom in solid molecular hydrogen is an example of a quantum impurity in a quantum crystal. Since the H atom and H_2 molecule are the lightest stable species in the universe with relatively weak interaction between them, the amplitudes of zero-point motion of both atoms and molecules are comparable with the lattice period of the crystal. This causes a substantial contribution of the quantum effects to both static and dynamic properties of this system. The most interesting manifestations of these effects are the finite mobility at very low temperatures due to the quantum tunneling diffusion of both atoms [1,2] and molecules [3,4] and the tunneling chemical reactions with H and D atoms participating [5,6]. Charged impurities in *para*-hydrogen-like electron bubbles [7] and H_2^- anions [8] also reveal essentially quantum properties.

The quantum diffusion of H atoms in solid H_2 results in the recombination reaction $H + H \rightarrow H_2$. This is a second-order process in the atomic concentration *C*:

$$dC/dt = -2K(T)C^2, \qquad (1)$$

where K(T) is the temperature-dependent recombination rate constant. If the diffusion is homogeneous then the relation between K and the diffusion coefficient D of H atoms is given by $K = 4\pi aD$, where a is the intermolecular distance in solid hydrogen taken as the effective reaction radius [9].

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^{*} Corresponding author. Fax: +81-29-282-5927; e-mail: kumada@popsvr.tokai.jaeri.go.jp

Previously [1], the recombination of H in solid H_2 was studied at zero pressure in the temperature range from 1.35 to 5.9 K. Two distinct types of H atom diffusion were found. At T < 4 K the diffusion proceeds, most probably, via successive repetition of the tunneling exchange reactions $H + H_2 \rightarrow H_2 + H$. The rate was shown to be determined by one-phonon interactions with lattice vibrations, resulting in linear dependence on temperature. At T > 4.5 K the activation-type diffusion prevails, which, however, is assumed to be controlled by the *tunneling vacancy* mechanism [10]. According to this mechanism the diffusion of H atom occurs by tunneling to the nearby vacant position in the lattice. Although the tunneling itself should not depend on temperature. the diffusion coefficient reveals an activation temperature dependence since it is proportional to the relative concentration of vacancies, which is equal to

$$c_v = \exp\left(-\frac{E_0 + Pv}{T}\right),\tag{2}$$

where E_0 is the energy required to remove the hydrogen molecule from the H_2 crystal, P is the external pressure and v is the vacancy volume [11]. The main argument for the tunneling vacancy mechanism was the coincidence of the low-temperature activation energies obtained for the diffusion of various species in solid hydrogen: 103 ± 5 K for H atoms [1], 91 ± 8 K for HD molecules [12], and 96 ± 8 K for o-H₂ molecules [13]. Single activation energy despite different masses and, consequently, different zero-point energies of these particles, can be easily explained by the tunneling vacancy model as the vacancy formation energy $E_0 \approx 100$ K, which is independent of the type of the tunneling particle. Besides, this value is rather close to the value $E_0 =$ 112 K calculated by Ebner and Sung [10].

The experiments to be presented here add pressure as another coordinate to the studies of H atoms in solid H_2 . Thus, according to Eq. (2) the linear pressure dependence of the activation energy of the recombination rate constant, K(T, P) would be direct evidence for the vacancies involved in the diffusion process. That was the primary aim of this study. Also the pressure effect on the relaxation characteristics of H atoms was studied. Although the mechanisms which determine the spin-lattice relaxation

and the ESR line width are quite different, they were shown to depend on diffusion and, consequently, on pressure.

2. Experimental

The general scheme of the experimental setup is shown in Fig. 1. Solid hydrogen was prepared by slow crystallization from the liquid phase in a quartz sample cell with i.d. 3 mm, which was cooled by a commercial continuous flow cryostat.

The high-pressure system includes hydrogen and helium high-pressure cylinders, a pressure meter and a simple cryogenic 'pressure multiplier'. The latter enables to double the pressure supplied by the highpressure cylinder by changing the temperature of the 'multiplier' cylinder between 77 and 370 K. Pressures lower than 14 MPa were stabilized by an



Fig. 1. The experimental setup.

ordinary pressure reducing valve with accuracy better than $\pm 1\%$. Pressures in the range from 14 to 30 MPa were stabilized by regulation of the temperature in the 'pressure multiplier' system using a computer-controlled heater.

Usually the solid hydrogen sample is pressurized by helium gas and annealed at the temperature close to the melting point at a given pressure in order to assure the uniform pressure distribution along the sample. Special test experiments were made with high pressure achieved using hydrogen gas at P = 13MPa and they give the same results as those using helium as pressure transmitting medium. Thus, despite the finite solubility of helium in *liquid* hydrogen at high pressures, we believe that neither helium atoms dissolve in the solid hydrogen nor, at least, they penetrate into the atomic region on the time scale of the experiment.

The JEOL TE-200 X-band ESR spectrometer was used to detect and investigate H atoms in solid H₂. Hydrogen atoms were produced in situ by white X-ray (50 keV in maximum) irradiation through the window in the microwave cavity of the ESR spectrometer. The height of the irradiated region was determined to be 8.5 mm, resulting in a sample volume of 0.06 cm³. Irradiation time was ~ 5 h at $T \approx 4.8$ K. The maximum atomic concentration obtained is of the order of 0.1 ppm. Certain difficulties in ESR measurements appeared due to strong spurious ESR signals from irradiated quartz parts of the cryostat. Fortunately, they were relatively stable during the measurements and could be obtained by subsequent subtraction after the H atoms in the sample have totally recombined at the temperatures close to the melting point at a given pressure. The absolute amounts of H atoms were measured by comparison with a secondary reference sample of Mn^{2+} in MgO, which was pre-calibrated using the reference sample made of TEMPO solution in benzol having the same size and positioned in the same place as the hydrogen sample.

Unfortunately, the temperature of the sample in the present setup cannot be monitored directly during the ESR measurement, because the introduction of any thermometer with attached conducting wires into the sample region results in deterioration of the Q-value of the ESR cavity. The nearest thermometer is ~ 2.5 cm lower than the sample region. On the

other hand, an unavoidable feature of the continuous flow cryostat used at T > 4.2 K is the temperature gradient along the flow direction, which depends on several factors, the flow rate F being the most important of them. Thus we carried out separate calibration measurements of the sample temperature using a Ge resistance thermometer immersed into the solid hydrogen just in the sample region. Its temperature was measured as a function of the temperature of the other two thermometers and the flow rate of the cold He gas through the cryostat, $T_s =$ $f(T_1, T_2, F)$. If the presence of the calibrating Ge resistor does not change substantially the temperature distribution in the cryostat one may use the obtained calibration to determine the sample temperature in the real experiment. The comparison of our measurements of the temperature dependence of the ESR line width of H atoms at P = 0 (see Fig. 4) with previous studies [14] enabled us to introduce a small correction term to the calibration obtained. making the temperature measurements more accurate.

All the experimental parameters (temperatures, pressure, flow rate) were monitored by a personal computer using self-made software. Besides, the computer controlled the digital temperature stabilizer (Scientific Instrument DTC 9650) and kept the pressure constant if the 'pressure multiplier' was used.

The typical experimental procedure was as follows. Every sample was studied at a fixed pressure, since any pressure change requires a long relaxation time to provide uniform pressure distribution along the sample. (Note, that annealing at high temperatures is impossible after irradiation, since it inevitably results in complete recombination of H atoms.) After the irradiation was finished the temperature of the sample was cycled in a stepwise mode between 4.4 K and the 'measurement' temperatures $T_{\rm m}$ as shown in Fig. 2b. The recombination of H atoms can be observed from the evolution of the intensities of the ESR spectra which are obtained at $T = T_{\rm m}$. However, at high $T_{\rm m}$ it was practically impossible to acquire the ESR signal of H atoms, since the its amplitude decreases with increasing temperature not only because the magnetization is proportional to $1/T_{\rm m}$ but also due to strong temperature-induced line broadening as shown in Fig. 4. In that case the recombination rate was estimated from



Fig. 2. The typical evolution of pressure and temperature during the recombination measurements: (a) external pressure; and (b) sample temperature (solid line), and the concentration of H atoms (closed circles).

the ESR spectra measured at T = 4.4 K before and after the temperature step $T = T_{\rm m}$ and from the duration of the step.

3. Results and discussions

We observed several strong pressure effects on the diffusion-related features of the H atoms.

3.1. The pressure effect on the recombination rate

The recombination rate constant strongly decreases with increase of pressure as shown in Fig. 3. For example, at T = 8 K the decrease was about 3 orders of magnitude with pressure increasing from 0 to 22 MPa. The temperature dependence of K(T) becomes stronger at higher pressure, indicating that there also is a pressure-induced increase of the activation energy. Different symbols in Fig. 3 represent the data obtained on eight samples at different external pressures. The solid lines correspond to the fit of the experimental data by the relation

$$K(T, P) = K_0 \exp\left[-\frac{E_0 + Pv}{T}\right]$$
(3)

in accordance with Eq. (2). The parameters obtained are

$$K_0 = (9 \pm 5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1},$$

$$E_0 = 106 \pm 4 \text{ K},$$

$$v = 2.4 \pm 0.1 \text{ K/MPa}.$$
(3a)

The insert in Fig. 3 shows the pressure dependence of the 'individual' activation energies E_a obtained from the fit of the experimental points by the simple Arrhenius expression $K(T) = K_0 \exp(E_a/T)$. The pressure-independent pre-exponent K_0 was chosen here and in Eq. (3), since the 'individual' pre-exponents K_p reveal no specific pressure dependence but show rather large scatter around K_0 because of the relatively narrow temperature interval considered.

Note, that our data at zero pressure are in a good agreement with earlier experiments [1,2] at P = 0, which are represented by the hatched area in the main Fig. 3 and by the open circle in the insert.



Fig. 3. The temperature dependence of the recombination rate constant at various pressures: •, 0 MPa; •, 10.0 MPa; •, 12.0 MPa; •, 13.0 MPa; *, 14.0 MPa; and •, 22.0 MPa. Solid lines represent the results of the fit by Eq. (3) for P = 0, 10, 13 and 22 MPa, respectively. Hatched stripes show the results of previous measurements [1] at P = 0. The insert shows the pressure dependence of the activation energy for the recombination rate constant (closed circles). The open circle represents the result of Ref. [1].

Thus, the obtained dependence K(T, P) indicates that the recombination of H atoms in solid hydrogen at T > 5.5 K and 0 < P < 22 MPa is determined by the diffusion, which includes thermally activated processes. The linear pressure dependence of the activation energy points out that the vacancies are very likely involved in the diffusion of H atoms according to Eq. (2). Finally, the strongest argument in favor of the tunneling vacancy model is the vacancy volume obtained (3a), which is v = 3.4(2) $\times 10^{-23}$ cm³. This value practically coincides with the elementary volume for hcp lattice of H₂ ($n^{-1} =$ 3.8×10^{-23} cm³ at P = 0 and $n^{-1} = 3.5 \times 10^{-23}$ cm³ at P = 26 MPa [15]).

3.2. The pressure effect on the ESR linewidth of H atoms

The ESR linewidth of H atoms in solid H_2 was found [14] to have strong dependence on temperature

at P = 0. Fig. 4 demonstrates that there is substantial dependence of the linewidth on pressure as well. This figure depicts the temperature dependencies of the peak-to-peak width of the first derivative of the low-field hyperfine component of the ESR absorption signals, which were obtained at zero pressure and pressures of ~ 10 and ~ 13 MPa. The crosshairs represent the data of Ref. [14] at P = 0, which are rather close to our data. One can see that the ESR line clearly narrows with increasing pressure at a given temperature. In addition, the temperature, at which the line starts to broaden, becomes higher when pressure increases.

The linewidth of H atoms in solid hydrogen is determined by the magnetic dipole interaction between the electron spin of a H atom and the nuclear spins of neighboring o-H₂ molecules, which increases with the decrease of H–o-H₂ distance. Thus, one might expect the increase of the ESR line to



Fig. 4. The temperature dependence of the peak-to-peak ESR linewidth of hydrogen atoms in solid hydrogen at various external pressures: \bigcirc , P = 0; \Box , P = 10-10.5 MPa; and \diamondsuit , P = 12-14 MPa. Crosshairs represent the results [12] obtained at P = 0. Solid lines are guides for the eye.

broaden with increasing density (pressure). However, the experiment gives just the opposite dependence. The qualitative explanation for this discrepancy is based on the fact that the effective distance $R_{\rm eff}$ between the H atom and $o-H_2$ is substantially larger than the nearest-neighbor distance *a* in solid hydrogen. This can be easily seen from the data presented in Fig. 4. The absolute values of the linewidths are much less than the estimate which can be calculated on the basis of Van Vleck theory of the second moment of dipole interaction [16]. Since the H atom takes the substitutional position in the hcp lattice [17], its linewidth in the case of a normal hydrogen matrix containing 75% of $o-H_2$ should be $\Delta B_{\rm pp} = 254 \ \mu T$.

The abnormally small linewidth was explained [14.18] by the fast *ortho*-to-*para* conversion of the neighboring o-H₂ molecules in the first few coordination spheres of a hydrogen atom, which is catalyzed by its electron magnetic moment. The catalyzed conversion time of atom's nearest neighbors is about 5 orders of magnitude faster than the natural selfconversion process in solid hydrogen and can be roughly estimated as $\tau_{cc} \approx 10$ s [18]. Yet, it strongly increases with distance as $\tau_{cc} \propto R^{12}$. This *local* catalyzed conversion effectively decreases the dipole interaction of the H atom and thus narrows the line. However, the diffusion should obviously increase the local o-H₂ concentration and, therefore, broaden the line. Thus, the linewidth is determined by the competition of two processes: the diffusion of H atoms and the local *ortho-para* conversion around H atoms.

The pressure used in this study practically does not affect the conversion rate [15]. On the other hand, the increase of pressure significantly slows down the diffusion as it was shown above. Hence, the pressure applied should enhance the local *ortho-para* conversion of the neighboring H_2 molecules, and narrow the ESR linewidth.

The line should begin to broaden substantially at temperature T_b when the diffusion jump time becomes smaller than the local conversion time. This qualitatively explains the experimental observation that T_b increases with pressure increase, since the same value of the diffusion rate can be obtained at higher temperatures if the pressure rises.

Thus the pressure effect on the linewidth is in qualitative agreement with the recombination data.

3.3. The pressure effect on the spin-lattice relaxation of H atoms

The longitudinal relaxation of H atoms was studied by pulsed ESR techniques. Special measures were undertaken to remove the contribution from the quartz background signal. The relaxation time T_1 grows from 0.5 to 1.3 s with pressure increasing from 0 to 22 MPa as shown in Fig. 5. The solid line is a linear fit to the data points: $T_1 = 0.5 + 3.4 P$, where T_1 is measured in seconds, and P in MPa.

The spin-lattice relaxation mechanism for H atoms in solid H_2 was proposed in Ref. [19]. It includes two stages, there is: (1) the relaxation of Zeeman energy of the H atom to the quadrupole energy of the o-H₂ system in the solid hydrogen; and (2) relaxation of the energy from the quadrupole system to the lattice vibrations. The last stage is the fastest, since it is determined by strong *electric* quadrupole interaction between o-H₂ molecules. Thus the total relaxation rate is limited by the first stage, which is determined by the *magnetic* dipole interaction between the electron spin of the H atom and the small *rotational* magnetic moment of the o-H₂ molecule.

Therefore, everything that was mentioned in the previous section about the effective dipole interaction between electron and nuclear spin magnetic moments can be applied to understand the pressure effect on the spin–lattice relaxation of H atoms in solid H_2 . The pressure-induced decrease of atom diffusion at an almost constant local conversion rate



Fig. 5. The pressure dependence of the spin-lattice relaxation time of H atoms.

around the H atom causes the increase of the effective $H-o-H_2$ distance, and results in growth of T_1 .

4. Conclusions

The first experiments on H atoms in solid hydrogen, carried out at non-zero pressures, give important results on the pressure effect on the high-temperature diffusion properties of H atoms. The linear pressure dependence of the diffusion activation energy and the obtained effective volume of the vacancy in solid H₂ unambiguously gives an indication on the vacancy mechanism of the diffusion of hydrogen atoms. Practically coincident activation energies for various diffusion species in solid hydrogen infer that the atom-vacancy exchange occurs, most probably, by tunneling. The observed pressure effects on the ESR linewidth and on the spin-lattice relaxation can be explained by the competition between the local ortho-para conversion catalyzed by the H atom and its pressure-dependent diffusion rate.

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