Further Study on Trapping Sites of Hydrogen Atoms in Solid Hydrogen at 4.2 K Analyzed by the ESR Linewidths

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(Received March 15, 1993)

Synopsis. The ESR linewidths of H(D) atoms, produced in γ-irradiated solid hydrogen, depend significantly upon the matrices of the hydrogen isotopes. The ESR linewidth has been calculated by considering the dipole interactions of the electron spin magnetic moments of a trapped hydrogen atom with the nuclear magnetic moments of the surrounding hydrogen nuclei in addition to the Fermi interactions. It is concluded from a comparison of the experimental ESR linewidths with the theoretical ones that the H atoms in solid H_2 are trapped at substitutional sites, while the H-(D) atoms in solid HD and D_2 are trapped at interstitial octahedral sites.

Hydrogen atoms in solid hydrogen at 4.2 K show interesting quantum phenomena, such as a tunneling reaction and tunneling diffusion. Miyazaki et al.[1] have studied the tunneling reactions regarding $H_2(D_2$, HD)+H(D) in solid hydrogen at ultralow temperatures. H atoms diffuse through solid H_2 by tunneling below 4.2 K.[2,3] In order to study the quantum phenomena of hydrogen atoms, information concerning the trapping sites of hydrogen atoms in solid hydrogen is fundamentally important.

An analysis of the ESR spin-flip lines of H atoms gave information concerning the trapping sites of H atoms in solid HD[4] and H_2.[5] We recently found that the ESR linewidths of H and D atoms depend significantly upon the matrices of the hydrogen isotopes.[6] The trapping sites of hydrogen atoms have been considered based on an analysis of the ESR linewidths. The linewidth is caused by superhyperfine interactions of a hydrogen atom with surrounding hydrogen molecules. In a previous paper,[6] however, only Fermi interactions between an electron of a trapped hydrogen atom and the nuclei of the surrounding hydrogen were taken into consideration. The dipole interactions of the electron spin magnetic moments of a trapped hydrogen atom with nuclear magnetic moments of the surrounding hydrogen were not previously estimated. Thus, many comments have been given concerning the previous treatment.

In this study the ESR spectra of H atoms in n-H_2 and p-H_2 solids were measured. The values of the dipole interactions were estimated based on the difference in the ESR linewidths of trapped H atoms in the two matrices. The trapping sites of hydrogen atoms in solid hydrogen isotopes were then investigated based on an analysis of the ESR linewidths in terms of the dipole interactions as well as the Fermi interactions.

Experimental

The samples of hydrogen isotopes, such as n-H_2 (75% o-H_2; 25% p-H_2), p-H_2 (>95% p-H_2; <5% o-H_2), HD (98 mol%), D_2 (99.5 mol%), and D_2-H_2 (1 mol%), were solidified at 4.2 K. The sample was irradiated at 4.2 K with γ-rays from a Co-60 source to a total dose of ca. 1 KGy. The trapped hydrogen atoms, produced by the γ-radiolysis of hydrogen, were measured at 4.2 K using a JES-FE2XG ESR spectrometer. The ESR spectra of hydrogen atoms were shown in previous papers.[6,7] The details concerning the experimental procedure were also described in previous papers.[5,7]

Results and Discussion

Experimental ESR Linewidths Figure 1 shows the low-field ESR spectrum of H atoms produced in γ-irradiated n-H_2 and p-H_2 at 4.2 K.[7] The spectrum of H atoms in p-H_2 is much narrower than those in n-H_2. The ESR linewidths (ΔH_{msl}) at the maximum slope is shown in Table 1. The experimental linewidths for H-(D) atoms in HD and D_2 are quoted from Ref. 6, and are also shown in Table 1. The linewidths depend remarkably upon the matrices of the hydrogen isotopes. The linewidths are related to the superhyperfine interactions of a H(D) atom with the surrounding hydrogen

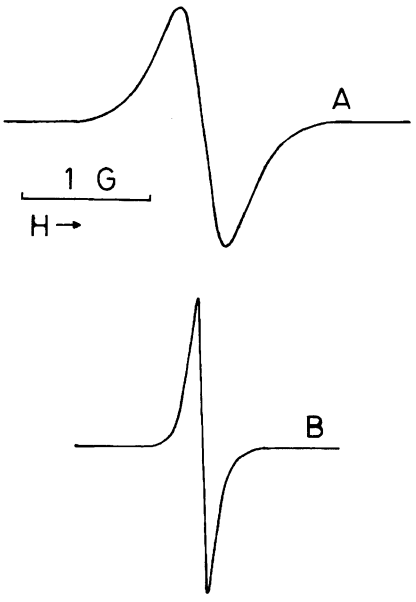

Fig. 1. Low-field ESR spectra of H atoms produced in γ-irradiated hydrogen at 4.2 K.[7] (A) H in n-H_2, (B) H in p-H_2.

Table 1. Comparison of Experimental ESR Linewidths (ΔH_{msl}) of Hydrogen Atoms with Theoretical Ones in Hydrogen Matrices at 4.2 K (all values in G)

Type of sites[a]	Theoretical linewidth[b]			Experimental linewidth	
	Fermi	Dipole	Total	H atoms	D atoms
p-H_2 matrix					
Int. tetra.	9.6	0	9.6		
Int. Octa.	4.2	0	4.2		
Sub.	0.24	0	0.24	0.11	
n-H_2 matrix					
Int. tetra	9.6	0.76	10.4		
Int. octa.	4.2	0.53	4.7		
Sub.	0.24	0.23	0.47	0.34	
HD matrix					
Int. tetra.	6.8	0.81	7.6		
Int. octa.	3.0	0.56	3.6	2.7	2.6
Sub.	0.17	0.25	0.42		
D_2 matrix					
Int. tetra.	2.4	0.16	2.6		
Int. octa.	1.1	0.11	1.2	1.2	1.2
Sub.	0.061	0.047	0.11		

a) Int. tetra., int. octa., and sub. represent an interstitial tetrahedral site, an interstitial octahedral site, and a substitutional site, respectively.
b) Fermi and Dipole represent Fermi interaction and dipole interaction, respectively.

nuclei. The interactions are Fermi and of the dipole type.

Estimation of Fermi Interactions The ESR linewidth of trapped hydrogen atoms in solid hydrogen caused by a Fermi interactions can be calculated using the formula[6,8,9]

$$(\Delta H(\text{Fermi})_{msl}/2)^2 = (64/27)\pi^2\mu_N^2[(I_N+1)/I_N]\cdot n|\Psi(N)|^4\cdot 34.13, \quad (1)$$

where μ_N is the magnetic moment of the nearest nucleus (N) of neighboring hydrogen molecules (in units of the nuclear magneton), I_N the spin of the nucleus (N), n the number of nearest nuclei, and $|\Psi(N)|^2$ the unpaired electron density at the nucleus (N).

The crystalline structure of solid hydrogen is a hexagonal-close-packed (hcp) structure.[10] If it is assumed that hydrogen atoms are trapped in the crystal, three kinds of trapping sites can be considered from the structure: an interstitial tetrahedral site, an interstitial octahedral site, and a substitutional site. The ESR linewidths for the three different trapping sites in the crystal were calculated by Eq. 1;[6] the values given shown in Table 1.

Estimation of Dipole Interactions The dipole interactions of the electron spin magnetic moments of a trapped hydrogen atom with nuclear magnetic moments of the surrounding hydrogen nuclei depend upon the orientation of the dipole moments. Since solid hydrogen at 4.2 K is in the hcp orientationally disordered phase,[10] it is difficult to theoretically determine the orientation of the dipole moments.

Figure 1 shows that the linewidth of H atoms in n-H_2, which contains 75% o-H_2, is much broader than that in p-H_2. Since p-H_2 is in a rotational quantum state of zero ($J=0$) at 4.2 K, the orientation of the p-H_2 molecules near to a trapped H atom is isotropic due to the uncertainty principle. The anisotropic dipole interactions are therefore cancelled out in the p-H_2 solid, and only Fermi interactions play a role in the ESR linewidth. n-H_2 contains 75% o-H_2, whose rotational quantum number(J) is 1 at 4.2 K. The o-H_2 molecules near to a trapped H atom in the n-H_2 solid rotate while in various orientations. The dipole interactions in addition to the Fermi interactions should thus be considered to be in the n-H_2 solid. Therefore, the difference in the ESR linewidths between trapped H atoms in the n-H_2 solid and those in the p-H_2 solid correspond to the dipole interactions.

The linewidths of H atoms in p-H_2 can be calculated based on a theoretical model of the Fermi interactions. The experimental linewidth (0.11 G) is much smaller than the values for both interstitial tetrahedral and interstitial octahedral sites, but is approximately similar to the value (0.24 G) for the substitutional sites. Thus, H atoms in the p-H_2 crystal are trapped at substitutional sites. It is reasonable to assume that H atoms in the n-H_2 crystal are also trapped at substitutional sites. The ESR linewidth caused by the dipole interactions is represented by

$$\Delta H(\text{dipole})_{msl} = k\cdot\mu_N\cdot r^{-3}\cdot\sqrt{n}, \quad (2)$$

where k is a constant related to the orientation of the dipoles; r is the distance between a trapped hydrogen

atom and the nearest nuclei (N) of neighboring hydrogen molecules. The nearest-neighbor distances for an interstitial tetrahedral site, an interstitial octahedral site, and a substitutional site are estimated based on the crystalline structure of solid hydrogen as 0.19, 0.23, and 0.34 nm, respectively.

The difference (0.23=0.34−0.11) in the experimental linewidths between trapped H atoms in n-H_2 and those in p-H_2 is considered to be the value ($\Delta H(\text{dipole})_{\text{msl}}$) attributed to the dipole interactions in the n-H_2 solid. When H atoms in the n-H_2 solid are trapped at substitutional sites, r, n (the number of the nearest o-H_2 molecules)[11] and μ_N are known. The constant (k) can thus be obtained from Eq. 2.

The linewidths for the dipole interactions were calculated by using Eq. 2 and are shown in Table 1. In the case of solid n-D_2 comprising 33.33% p-D_2 ($J=1$) and 66.7% o-D_2 ($J=0$), the dipole interactions are caused only by p-D_2 molecules. Table 1 shows that the Fermi interactions are significant in interstitial tetrahedral and octahedral sites, while dipole interactions play a role in substitutional sites, except for p-H_2. The experimental linewidths of the H and D atoms in HD and D_2 matrices are approximately similar to the theoretical linewidths for interstitial octahedral sites. The hydrogen atoms in HD and D_2 matrices are trapped at the interstitial octahedral sites. This conclusion is consistent with the results obtained based on an analysis of the ESR spin-flip lines of H atoms in solid H_2[5] and H atoms in solid HD.[4] The difference in the trapping sites of H(D) atoms may be related to a migration of the hydrogen atoms in solid hydrogen. H(D) atoms, produced in HD and D_2, are initially trapped at the interstitial sites, and do not migrate throughout the solid. On the contrary, even if H atoms in H_2 are initially trapped at interstitial sites, they react quickly with H_2 and migrate throughout the solid by repetition of the tunneling reaction $H_2+H \rightarrow H+H_2$. The H atoms may be finally trapped at substitutional sites during the migration.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

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