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ROTATIONAL STATES OF THE HYDROGEN MOLECULE IN THE CRYSTALLINE SILICON MATRIX

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Results of a theoretical study of the atomic and electronic structure of the hydrogen molecule in the crystalline silicon matrix are presented. An analytical expression for the rotational potential energy function of the interstitial hydrogen molecule in the crystal at the tetrahedral position is derived. The rotational terms and the corresponding wavefunctions as well as the ortho-para splitting of the Raman spectral lines are calculated. It is shown that the interstitial hydrogen states with $l < 2$ can be treated within the framework of the free molecule approach; however, a noticeable splitting of the rotational terms with $l \geq 2$ indicates a substantial influence of the semiconductor matrix on the properties of the system.

Keywords: crystalline silicon, interstitial hydrogen, rotational states, ortho-para splitting.

INTRODUCTION

Crystalline silicon plays a vital role in the development and production of semiconductor devices and components. Interstitial hydrogen has a significant influence on the physical and chemical properties of the material [1] which in turn is important for many technological processes. Hydrogen penetrates into the structure of semiconductor devices at almost all stages of their production and fabrication, for example, during annealing, sintering, dry and wet etching, or cleaning by solvent processes. The presence of atomic hydrogen leads to the appearance of shallow and deep donor levels. Some of the hydrogen atoms that penetrated into the semiconductor crystalline structure form molecular hydrogen [2] which has practically no influence on the electrical and optical properties of the crystal, and as a consequence, its detection is quite difficult. However, these *hidden* defects can be reactivated into their atomic form, for example, during heating which leads to changes in the electronic and optical properties of the sample.

The stability of molecular hydrogen in the crystalline silicon was first predicted more than 30 years ago by two independent groups [3, 4]; however, the detection of H_2 in semiconductors had remained for many years a complicated problem, which was finally resolved with the help of Raman spectroscopy [2]. From an analysis of the available results of experimental and theoretical studies of effects caused by H2 presence in semiconductors (see, e.g., [1–17] and references therein) it follows that the hydrogen molecule interacts quite strongly with the silicon matrix which leads to a noticeable increase in the length of the H–H bond and a decrease in the vibrational frequencies. However, along with this, H_2 behaves as a nearly free rotator, i.e., the rotational degrees of freedom are not *frozen* and an interpretation of the existing spectra of the interstitial defect is possible employing the free molecule model. In the equilibrium configuration the H_2 center of mass is found at the tetrahedral position (T site) of the Si crystal lattice, and the molecule is oriented along the [100] or [111] crystallographic direction with a rotational potential barrier on the order of 0.01 eV.

In this work the results of an analysis of the H_2 and D_2 rotational states in the crystalline silicon matrix are presented using a model problem. The structure symmetry and the influence of the rotational potential barrier on the spectra of the interstitial objects are considered. Taking into account significant basic and applied interest to the

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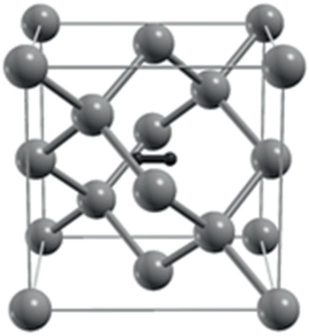

Fig. 1. Supercell consisting of 8 silicon atoms and one hydrogen molecule at the *T* site located exactly at the center of the cube that was used in the calculations.

problem, this work can be regarded as a part of the consecutive detailed study of the effects caused by hydrogen presence in silicon and other semiconductors.

1. COMPUTATIONAL METHOD

The atomic and electronic structure calculations of the H_2–Si system have been performed using the density functional theory with the exchange-correlation functional PW91 [18] in the generalized gradient approximation [19, 20], implemented in the CRYSTAL09 code [21].

The system was treated within the framework of the cubic supercell model with the periodic boundary conditions. The size of the cell was chosen so as to exclude the interaction of the hydrogen molecule with its images. In these calculations supercells consisting of 4 and 32 primitive cells of crystalline silicon were used, containing 8 and 64 silicon atoms, respectively. Massive calculations were carried out mainly using the small cell; however to check our results and to investigate critical case structures, the calculations for selected atomic configurations were repeated for the large cell.

The small supercell is shown in Fig. 1. In calculations of the H_2–Si potential energy the Si atoms were fixed at their equilibrium positions in the corresponding crystal. The energetics analysis was performed for a large number of possible H_2 configurations inside of the cell. The *ab initio* calculations were carried out using an $8 \times 8 \times 8$ grid of *k*-points for the small cell and a $4 \times 4 \times 4$ grid for the large one. Based on the analysis of the results for the model structure (its reproduction and different properties), the optimized Si basis set from [22] and the DZP basis set for the hydrogen atoms [23] were chosen. Owing to the localized basis functions employed in our calculations, the basis set superposition error (BSSE) correction was always taken into account.

Our calculations show that, as expected, the H_2 center of mass in the equilibrium configuration is always found at the *T* site of the Si crystal lattice. However, the molecule is found to be oriented in the [100] and equivalent crystallographic directions only. In fact, the molecule orientation in the [111] direction at the tetrahedral position corresponds to the energy maximum, although an artificial local minimum for the given direction may arise as a result of an unaccounted BSSE. It should be noted that our value of the silicon lattice parameter ($a = 5.47$ Å) differs from its experimental one ($a = 5.43$ Å) by not more than 0.7%. The calculated H_2 bond length was found to be 0.7487 Å (slightly greater than the experimental value 0.7414 Å [24]) for the free molecule and 0.7810 Å for the hydrogen in the silicon crystal. The latter value was used in the investigation of the rotational states of H_2 in Si.

The *ab initio* energy values of the system corresponding to various hydrogen molecule orientations at the *T* site were then used to construct a symmetrized analytical function of the rotational potential energy $V = V(\theta, \varphi)$, where θ and φ are spherical coordinates. The rectangular coordinate system was chosen such that its axis directions coincided with the computational cell ones. The zero value of θ corresponded to the molecule orientation along the *Oz* axis. The obtained potential function $V(\theta, \varphi)$ was used to calculate the rotational energy states and wavefunctions of the H_2 molecule in the Si crystal by solving the stationary Schrödinger equation using a variational approach.

2. RESULTS AND DISCUSSION

From the geometric analysis of the H_2–Si system it follows that the proper point symmetry group is O_h. This fact significantly reduces the number of configurations of the hydrogen molecule at the interstitial T site needed to reconstruct the potential energy function $V(\theta, \varphi)$. It also imposes corresponding restrictions on the analytical form of this function. The symmetry properties of the system were taken into account while deriving the potential function and for the subsequent classification of the rotational states.

2.1. Rotational Potential Energy

The rotational potential energy function was obtained in the following form:

$$V(\theta,\varphi)=\sum_{l=0}^{6}\sum_{m=-l}^{l} g_{lm} Y_l^m(\theta,\varphi)\,, \tag{1}$$

where $Y_l^m(\theta,\varphi)$ are the spherical harmonics and g_{lm} are the expansion coefficients. The parameters g_{lm} were fitted to the calculated energy values of the system by means of the least squares technique. As a consequence of the symmetry properties of $V(\theta, \varphi)$ and $Y_l^m(\theta,\varphi)$ for $l \le 6$, only three of the coefficients g_{lm} are symmetrically independent, and expression (1) can be rewritten as

$$V(\theta,\varphi)=G_0Y_0^0+G_4(5Y_4^{-4}+\sqrt{70}Y_4^0+5Y_4^4)+G_6(7Y_6^{-4}-\sqrt{14}Y_6^0+7Y_6^4)\,. \tag{2}$$

The fitted expansion coefficients have the following values:

$$G_0=177.763898\ \text{cm}^{-1},\ G_4=-7.6168172\ \text{cm}^{-1},\ G_6=0.761302\ \text{cm}^{-1}. \tag{3}$$

In the fit we used 90 *ab initio* energy values of the system for uniformly spaced coordinates θ and φ. The standard deviation in the potential energy function calculations is 1.026843 cm^{-1}.

A 3D plot of potential energy function (2) with coefficients (3) is shown in Fig. 2. The magnitude of the radius vector of the point on the surface displayed is equal to $V(\theta, \varphi)$. The minimum value of the rotational barrier is equal to ~60 cm^{-1}, and its maximum value is equal to ~85 cm^{-1}. Note that it does not immediately follow from these results that the hydrogen molecule in the silicon crystal should be an almost free rotator.

2.2. Rotational States

The Hamiltonian of the model system under study has the following form:

$$\hat{H}=\frac{\hat{L}^2}{2\mu R^2}+V(\theta,\varphi)\,, \tag{4}$$

where $\hat{L}$ is the angular momentum operator, R is the hydrogen molecule bond length, and μ is the reduced mass of the molecule. Solutions of the corresponding stationary Schrödinger equation were found in the following form:

$$\psi_n(\theta,\varphi)=\sum_{l,m} a_{lm}^n Y_l^m(\theta,\varphi)\,. \tag{5}$$

TABLE 1. Rotational Terms of H_2 and D_2 Molecules in the Crystalline Silicon, cm^{-1}

n	l	H_2 molecule				D_2 molecule			
		E_n	$E_n - E_0$	$B_0\, l(l+1)$	Exp.	E_n	$E_n - E_0$	$B_0\, l(l+1)$	Exp.
0	0	49.61312	0.00000	0.00000	0.0	49.08332	0.00000	0.00000	0.0
1	1	154.82476	105.21164	105.36676	99	102.08306	52.99974	53.31445	49
2		154.82476	105.21164			102.08306	52.99974		
3		154.82476	105.21164			102.08306	52.99974		
4	2	350.39958	300.78647	316.10027	297	193.82226	144.73894	159.94334	148
5		350.39958	300.78647			193.82226	144.73894		
6		376.26028	326.64716			219.84890	170.76558		
7		376.26028	326.64716			219.84890	170.76558		
8		376.26028	326.64716			219.84890	170.76558		
9	3	673.35244	623.73932	632.20054	–	361.19401	312.11068	319.88668	–
10		673.35244	623.73932			361.19401	312.11068		
11		673.35244	623.73932			361.19401	312.11068		
12		684.24346	634.63034			371.77441	322.69109		
13		684.24346	634.63034			371.77441	322.69109		
14		684.24346	634.63034			371.77441	322.69109		
15		703.48001	653.86690			391.06815	341.98483		
B_0 (crystal)		52.683378				26.657223			
B_0 (molec.)		59.322 [24]				29.901 [24]			

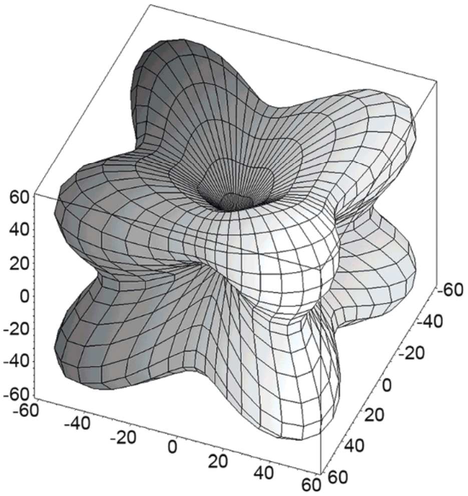

Fig. 2. Rotational potential energy function of the hydrogen molecule in the silicon matrix (cm^{-1}).

The convergence analysis in the calculations of the rotational energies and coefficients a^n_{lm} showed that in order to get accurate values of about 30 lowest lying states, it is sufficient to include terms with $l \le 15$ in expansion (5).

The obtained rotational term values for H_2 and D_2 molecules in Si are presented in Table 1. One can see that they are in good agreement with the experimental results from [14]. For a comparison, the column labeled as $B_0l(l+1)$ displays the rotational energies of the molecules calculated in the rigid rotor approximation. Theoretical values of the rotational constant B_0 for molecules in the crystal along with experimental values of the same constant for the free molecule are presented in the last row of the table. It can be seen that for $l < 2$, the term values obtained for different models agree within about 0.5 cm^{-1}; at the same time, by virtue of the system symmetry, the rotational states remain

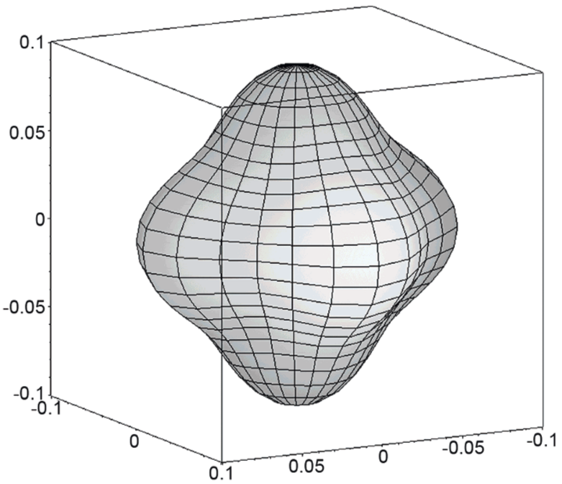

Fig. 3. Rotational probability density function of the ground state of the D_2 molecule in the silicon matrix.

degenerate even in the presence of the potential barrier. The degeneracy is removed only for states with $l \geq 2$. Note that already for the states with $l = 2$, splitting on the order of 26 cm^{-1} is observed indicating a noticeable influence of the rotational barrier on the interstitial defect spectrum.

An analysis of the dependence of the energy spectrum of the system based on Hamiltonian (4) on the magnitude of the rotational potential barrier or, which is equivalent, on its ratio to the average molecule inertia momentum $\min\{V(\theta,\varphi)\}/2\mu R^2$ revealed a weak influence of these quantities on the rotational energy states with $l < 2$. An analogous result was obtained in calculations with an altered symmetry of the system as a consequence of deformation of the crystal. This fact is due to the properties of wavefunctions (5) and correspondingly is a unique characteristic of the system with Hamiltonian (4). Thus, the states with $l < 2$ of the system under study can be described with good accuracy using the free rotor approximation. This fact is confirmed by the experimental results presented in [13–16] according to which the interstitial defects demonstrate rotational properties.

Figure 3 shows a 3D plot of the rotational probability density function for the ground state of the D_2 molecule in the silicon matrix. The shape of the function correlates well with the geometry of the rotational potential energy (see Fig. 2). It is obvious that the maximum probability corresponding to the potential energy minimum grows with an increase of the potential barrier value (or with a decrease in B_0). One can see that the rotational degrees of freedom of the D_2 molecule and consequently also of the H_2 molecule are not frozen. By virtue of the system symmetry and the rotational potential barrier magnitude, the probability density functions for the excited states are *visually similar* to the analogous functions of the free rotator; however, the crystal environment uniquely determines their orientation in space. Here by the *visual similarity* we mean that for fixed n corresponding to the free rotator, coefficients a_{lm}^{n} in expansion (5) make the dominating contribution to the probability density function.

2.3. Ortho-Para Splitting

As shown above, the rotational states of the H_2 and D_2 molecules in the Si crystal with $l < 2$ can be treated in an analogous way to the states of the free molecules. To obtain the potential function $U(R)$ of the H_2 molecule, we calculated the dependence of the potential energy of the system in the equilibrium configuration on the molecule bond length R. If we keep only terms up to the fourth order, this potential function can be written as

TABLE 2. Spectroscopic Parameters and the *Ortho-Para* Splitting Δ_{o-p} for H_2 and D_2 Molecules, cm^{-1}

System	ω_e		$x_e\omega_e$		α_e		Δ_{o-p}	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
H_2	4404.9	4401.2 [24]	116.9	121.3 [24]	2.979	3.062 [24]	5.96	5.9 [13]
H_2–Si	3838.4	4015.0 [13]	175.2	194.0 [13]	4.309	–	8.62	9.0 [13]
D_2	3115.2	3115.5 [24]	59.7	61.8 [24]	1.017	1.079 [24]	2.03	2.1 [13]
D_2–Si	2714.2	–	87.6	–	1.524	–	3.05	3.0 [13]

$$U(R) = \frac{\mu\omega_e^2}{2} R^2 - aR^3 + bR^4 . \tag{6}$$

Employing perturbation theory [25], one can obtain an expression for the rovibrational energy of the molecule with potential (6):

$$E_{v,l} = \hbar\omega_e \left(v + \frac{1}{2} \right) - x_e\hbar\omega_e \left(v + \frac{1}{2} \right)^2 + B_v l(l+1) - D_e l^2 (l+1)^2 , \tag{7}$$

where B_v, α_e, and x_e are the conventional spectroscopic parameters. For potential (6) the parameters α_e and x_e are defined by the following formulas:

$$\alpha_e = \frac{6B_e^2}{\hbar\omega_e} \left(\frac{a\hbar}{\mu\omega_e^2} \sqrt{\frac{2}{\mu B_e}} - 1 \right), \tag{8}$$

$$x_e = \frac{3}{2\hbar\omega_e} \left(\frac{\hbar}{\mu\omega_e} \right)^2 \left(\frac{5a^2}{2\mu\omega_e^2} - b \right). \tag{9}$$

Using Eqs. (7)–(9), it is easy to obtain the magnitude of the *ortho-para* splitting of the Raman transitions $\Delta v = 1$ and $\Delta l = 0$:

$$\Delta_{o-p} = \left(E_{1,0} - E_{0,0} \right) - \left(E_{1,1} - E_{0,1} \right) = 2\alpha_e . \tag{10}$$

From the latter expression it follows that the magnitude of the *ortho-para* splitting is directly related to the anharmonicity of the potential function *U*(*R*) which in turn arises from the interaction of the hydrogen atoms both with each other and with the silicon matrix.

The obtained values of the *ortho-para* splitting Δ_{o-p} and other parameters are listed in Table 2. It can be seen from the table that our calculations are in good agreement with the available experimental data. At the same time, the difference between the theoretical and experimental values of the hydrogen molecule harmonic frequency in the Si crystal is almost 180 cm^{-1}. On the one hand, it properly agrees with the accuracy of the calculations within the framework of density functional theory but, on the other hand, it indicates a stronger dependence of the given parameter on the characteristics of the model system considered. It is quite likely that having obtained a reasonable estimate of the molecule interaction with the matrix, we have underestimated the intramolecular interaction, for instance, owing to the basis set incompleteness.

CONCLUSIONS

In this work we have carried out first principles calculations of the atomic and electronic structure of the hydrogen molecule in crystalline silicon. Within the framework of the proposed model, we have performed an analysis of the energetics of the system and calculated its main characteristics. On the basis of the *ab initio* data obtained we have constructed a symmetrized rotational potential energy function of the H_2 molecule at the T site in crystalline silicon. The minimum value of the rotational potential barrier is found to be approximately 60 cm^{-1}.

We have calculated the rotational energies of H_2 and D_2 molecules. Our analysis of the dependence of the energies of the system on the rotational potential barrier as well as on the symmetry properties shows that the interstitial defects in the states with $l < 2$ can be treated within the framework of the free molecule model. However, the noticeable splitting of the rotational terms for $l \geq 2$ points out the substantial influence of the rotational barrier on the properties of the system.

Calculations of the *ortho-para* splitting and other spectroscopic parameters for the system in states with $l < 2$ have also been performed. The values obtained are in good agreement with the available experimental data.

The numerical calculations were performed on the SKIF-Cyberia supercomputer with the support of the Regional Center for Collective Use of High-Performance Computing Resources of Tomsk State University.

REFERENCES

1. S. J. Pearton, J. W. Corbett, and M. Stavola, Hydrogen in Crystalline Semiconductors, Springer Verlag, Berlin (1992).
2. A. W. R. Leitch, V. Alex, and J. Weber, Phys. Rev. Lett., **81**, 421–424 (1998).
3. A. Mainwood and A. M. Stoneham, Physica, **B116**, 101–105 (1983).
4. J. W. Corbett, S. N. Sahu, T. S. Shi, and L. C. Snyder, Phys. Lett., **A93**, 303–304 (1983).
5. S. K. Estreicher, Mater. Sci. Eng., **R14**, 319–412 (1995).
6. Y. Okamoto, M. Saito, and A. Oshiyama, Phys. Rev., **B56**, No. 16, 10016–10019 (1997).
7. K. G. Nakamura, K. Ishioka, M. Kitajima, *et al.*, Appl. Surf. Sci., **130**, 243–247 (1998).
8. B. Hourahine, R. Jones, S. Oberg, *et al.*, Phys. Rev., **B57**, No. 20, 12666–12669 (1998).
9. C. G. Van de Walle and J. P. Goss, Mater. Sci. Eng., **B58**, Nos. 1–2, 17–23 (1999).
10. Y.-S. Kim, Y.-G. Jin, J.-W. Jeong, and K. J. Chang, Physica, **B273-274**, 231–234 (1999).
11. S. K. Estreicher, J. L. McAfee, P. A. Fedders, *et al.*, Physica, **B308**, 202–205 (2001).
12. W. B. Fowler, P. Walters, and M. Stavola, Phys. Rev., **B66**, No. 7, 075216 (2002).
13. E. V. Lavrov and J. Weber, Phys. Rev. Lett., **89**, 215501 (2002).
14. M. Hiller, E. V. Lavrov, and J. Weber, Phys. Rev., **B74**, 235214 (2006).
15. M. Hiller, E. V. Lavrov, and J. Weber, Phys. Rev. Lett., **98**, 055504 (2007).
16. J. Weber, M. Hiller, and E. V. Lavrov, Physica, **B401-402**, 91–96 (2007).
17. C. Peng, M. Stavola, W. B. Fowler, and M. Lockwood, Phys. Rev., **B80**, 125207 (2009).
18. J. P. Perdew, J. A. Chevary, S. H. Vosko, *et al.*, Phys. Rev., **B48**, 4978–4978 (1993).
19. J. P. Perdew and Y. Wang, Phys. Rev., **B33**, 8800–8808 (1986).
20. J. P. Perdew, Phys. Rev., **B33**, 8822–8824 (1986).
21. R. Dovesi, R. Orlando, B. Civalleri, *et al.*, Z. Kristallogr., **220**, 571 (2005); R. Dovesi, V. R. Saunders, C. Roetti, *et al.*, CRYSTAL09 User's Manual, University of Torino, Torino (2009).
22. F. J. Torres, B. Civalleri, C. Pisani, and P. Ugliengo, J. Phys. Chem., **B110**, 10467–10474 (2006).
23. T. H. Dunning, Jr., J. Chem. Phys., **53**, 2823 (1970).
24. A. P. Babichev, N. A. Babushkina, A. M. Bratkovskii, *et al.*, Handbook of Physical Quantities, I. S. Grigor'ev and E. Z. Meilikhov, eds. [in Russian], Energoatomizdat, Moscow (1991).
25. L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Nonrelativistic Theory), Course of Theoretical Physics, Volume 3, Third Edition, Pergamon Press, Oxford (1977).