Calculation of the ortho–para conversion of hydrogen in a \( p \)–type silicon lattice using a dwell time approach

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Abstract. Quantitative spectroscopic studies of hydrogen in a \( p \)–type silicon lattice at room temperature and at reduced temperature have led to rates for the ortho–para conversion process. The characteristic relaxation time at room temperature is about 8 hours. Explanations of this rate on the basis of the interaction between the interstitial H\(_2\) and naturally occurring \( ^{29}\)Si using the Wigner rate expression encounter several difficulties, the principal being that the decay would involve multiexponential decay, in contradiction to observation.

In an earlier work we calculated the rate assuming that the ortho–para conversion was effected during scattering of holes from the hydrogen molecules. The result was smaller than observed by several orders of magnitude. In the present work it is assumed that \( sp_z \) holes diffuse randomly throughout the Si lattice, dwelling on effective areas associated with \( sp_z \) sites. The transition matrix elements are the same as for the scattering mechanism. The resultant characteristic time at room temperature we find to be 1000 hr. Considering the uncertainties in the calculation the discrepancy between our result and observation is not sufficient as to negate our physical picture.

1. Introduction

It is possible to obtain interstitial H\(_2\) in crystalline Si by cooling the silicon from a melt in a hydrogen atmosphere. H\(_2\) has been observed in Si by Raman [1] and by IR spectroscopy [2], the IR spectrum being ascribed to an interaction-induced dipole moment [3]. The ortho and para isomers were identified through Raman spectroscopy by Chen et al. [4]. Quantitative spectroscopic studies of hydrogen in a \( p \)–type silicon lattice at room temperature and at reduced temperature have led to determination of rates for the ortho–para conversion process [6, 7]. The characteristic relaxation time at room temperature is about 8 hours. An attempt to explain this rate on the basis of the interaction between the interstitial H\(_2\) and naturally occurring \( ^{29}\)Si using the Wigner rate expression [7] was given by Hiller et al. [5]. Their explanation was found to be incompatible with experiment by Peng et al. [8], the principal difficulty being that the Wigner mechanism would necessitate a superposition of different decaying exponentials corresponding to the presence of \( ^{29}\)Si in nearest, next nearest, etc. neighbours, leading to a complicated multiexponential decay, as opposed to observation. A second difficulty is discussed below.
It is worth noting that the ortho–para conversion of a given ortho molecule in pure hydrogen has been quantitatively explained as due to the magnetic dipolar fields of neighbouring ortho molecules [9]. At very high densities a different mechanism becomes important, in which the emerging excitations are coupled to the converting molecules via electric quadrupole–quadrupole interactions [10].

All of the mechanisms given here involve the nuclear spins of the hydrogen molecule interacting with other nuclear spins. In this work and its predecessor [11] we will evaluate the effects of holes interacting with the proton spins of the hydrogen. While the holes are typically of very low density, say $10^{15}$ cm$^{-3}$, their magnetic moments are $O(10^4)$ times nuclear spin magnetic moments, and they are highly mobile. This mechanism therefore merits consideration as a serious contender in OP conversion of hydrogen in silicon lattices. In this paper, therefore, the ortho–para conversion is assumed to be due to the unpaired electron spins accompanying holes, interacting with the nuclear spins of the interstitial H$_2$ primarily by the Fermi contact interaction, and the electron density at these spins is enhanced by exchange at the H$_2$ nuclear spins. The exchange interaction is readily included using a technique introduced by Herman[12].

We first consider the geometry of the Si lattice, and then derive the interaction between holes in a silicon lattice, and interstitial H$_2$.

2. H$_2$ tetrahedral Trapping Sites in Crystalline Silicon

Crystalline silicon is known to have the zincblende structure, with Si atoms occupying both the Zn and S sites in the structure. To visualise the situation, consider a face centred cubic structure with corners located on a cubic lattice having side length $a = 5.40$ a.u., with sides oriented parallel to Cartesian axes, $x$, $y$, $z$. It is well known that any atom in the fcc structure could be placed at the origin of coordinates, $(x, y, z) = (0, 0, 0)$ without preference. To obtain the zincblende structure, a similar fcc structure is added, with each atom displaced by $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ from each of the original atoms in the fcc structure, with displacements understood to be in units of $a$. For purposes of discussion we will refer to these as the primary and secondary sublattices. Of course, the secondary sublattice could have been produced with any similar displacement from the primary but once established, the displacements will continue as being similar throughout the entire crystal. So let us discuss the situation as described above.

To understand the tetrahedral trapping sites, let us note that on the principal diagonal in the $(1, 1, 1)$ direction there are atoms located at $(0, 0, 0)$ and $(1, 1, 1)$ (primary lattice sites) and at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (secondary site within the original cubic volume described above). There are no atoms located at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ nor at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and these can be regarded as typical locations for tetrahedral vacancies into which H$_2$ molecules can become trapped. In practice, H$_2$ is diffused into Si at high temperatures, then upon cooling the H$_2$ remain trapped. The site given by $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is surrounded by four Si atoms at equivalent distances, belonging to the secondary lattice, located at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$, $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$. All Si tetrahedral atoms lie a distance 2.34 a.u. from the trapping site. The three latter sites mentioned, which can be viewed as a basal plane in the present coordinate system, lie further from the origin than the originally cited apex atom at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The H$_2$ trapping site located at $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ is similarly surrounded by Si atoms at the primary lattice locations $(1, 1, 1)$, $(1, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 1, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 1)$ with all tetrahedral sites again residing a distance 2.34 a.u. from the tetrahedral vacancy. In this case, the basal plane is located nearer to the origin than the (primary) apex $(1, 1, 1)$. Of course, the Si atom located at $(0, 0, 0)$ would belong to a similar tetrahedron, with the other (basal plane) atoms at $(0, -\frac{1}{2}, -\frac{1}{2})$, $(-\frac{1}{2}, 0, -\frac{1}{2})$ and $(-\frac{1}{2}, -\frac{1}{2}, 0)$. Each Si atom is surrounded by four nearest-neighbours for which bonds can be supported. They also lie at a distance $\sqrt{3}a/4 = 2.34$ a.u. Therefore, it appears to be the case that for every Si–Si bond, there will exist two tetrahedral vacancies lying on the bond axis, to either side of the bond. Since all Si atoms in the primary lattice have identical surroundings it follows that there are as many tetrahedral vacancies as
there are Si atoms themselves. Of course the other apex atoms forming the tetrahedral sites will be similarly bonded to partner Si atoms in directions leading away from the tetrahedral centres. These directions could have served as the directions along which tetrahedral centres could have been described. Because there are four of these special directions within the silicon crystal, and because there are four apex atoms per tetrahedral site, we conclude that all of the sites have become locatable through the analysis above (with the (1, 1, 1) direction being specially labelled), and that the sites so located are properly shared by all of the atoms in the sample.

It should be noted that the tetrahedral atoms surrounding the H₂ molecule do not bond to one another. The distances separating these atoms are given by \( a/\sqrt{2} = 3.82 \) a.u. The Si–Si bonds, other than the ones already noted as lying on the far side of the apex atoms will be occupying tetrahedral directions more of less forming an “umbrella” structure cradling the H₂ molecules. It is these four sets of three bonds each that physically constrain the H₂ to translational states centred about the tetrahedral symmetry points. It is these bonds that effect the H₂ trapping.

Now reassign the former (1, 1, 1) direction as a new \( z \)-direction. Without loss of generality the rates of transition between the \((J, M) = (0, 0)\) and \((J, M) = (1, 0)\) states of H₂ can be analysed relative to these coordinates. Relaxation rates between the other \((J, M)\) and \((0, 0)\) states will be identical. In this way of looking at the situation, each primary lattice Si atom will be bonded to a partner Si atom located in the \( z \)-direction, spaced by a distance \( \sqrt{3}a/4 = 2.34 \) a.u., as well as three other Si partners located in the three other tetrahedral directions (as yet unspecified, though once chosen, to be the same for each of the primary Si lattice atoms, etc. for the secondary lattice). The conduction bands of Si are prolate ellipsoidal in nature with minimum energy being associated with relatively large \( k \)-values, with directions parallel or antiparallel to the tetrahedral bonds present in the crystal. For now, consider the band centered about the large \( k \)-values \( \pm \hat{e}_3 k_0 \). The corresponding hole states will be of \( sp_2 \) type.

### 3. Hole – H₂ interaction

Ortho–para conversion occurs between molecular states such as \( |JMm_{s_A}m_{s_B}\rangle = |10 - \frac{1}{2} - \frac{1}{2}\rangle \), and \( |JM'm_{s_A}'m_{s_B}'\rangle = |00 \frac{1}{2} - \frac{1}{2}\rangle \). \( A \) and \( B \) referring to the two H₂ nuclei, together with \( |00 - \frac{1}{2} \frac{1}{2}\rangle \). The \( |\frac{1}{2} - \frac{1}{2} \rangle \) spin state is a triplet state accompanying a \( J = 1 \) rotational state, while the singlet state is \( (1/\sqrt{2}) (|\frac{1}{2} - \frac{1}{2}\rangle - |\frac{1}{2} - \frac{1}{2}\rangle) \), accompanying (mostly) the \( J = 0 \) rotational state. Any interaction that could cause a transition would have to satisfy three conditions:

- it must be a magnetic interaction with the proton spins in H₂;
- it must have a spatial dependence that can couple to the orientational angles of H₂; and
- there must be a thermal bath capable of absorbing the energy released (or supplying the energy needed in a reverse process) to make the transition \( E_{J=1} \rightarrow E_{J=0} \).

The third condition above is stringent. For example, in the proposed spin exchange with \(^{29}\)Si mentioned above this spin exchange would not have been very likely at the outset, simply because the energy exchanged would have to be released into very long wavelength phonons (corresponding to 170 K, compared with the Debye temperature 658K) or would have to be exchanged with translational energies of H₂ constrained to the Si lattice, which are much greater (\( \sim 1070 \) K, by our calculation).

Thus, for this last reason alone, transitions based upon spin exchange with surrounding paramagnetic atoms/nuclei will be considerably suppressed.

The transition matrix elements are the same as for the scattering mechanism [11] with the same exchange enhancement. The contact interaction Hamiltonian responsible for the ortho–
The actual conversion amplitude is
\[ H' = \left( \frac{16\pi}{3} g_n \mu_n \right) \sum_j \sigma_{sz,j} \cdot \left[ \sigma_A \delta (x_j - R_A) + \sigma_B \delta (x_j - R_B) \right] \] (1)

where \( \mu \) and \( \mu_n \) are the Bohr and nuclear magnetons, \( g_n = 5.59 \) is the proton gyromagnetic ratio, and the \( \sigma \) are the Pauli spin matrices. \( R_A \) and \( R_B \) are the positions of the \( A \) and \( B \) protons respectively, while \( x_j \) is the position of the \( j \)th electron. In eq. (1) \( j \) is summed over all Si sites, though only four nearest neighbour sites are important. The \( R^{-b} \) terms from the proton magnetic dipoles make little contribution, principally because they are not exchange-enhanced.

For \( H_2 \), the lowest-lying configuration can be approximated with Heitler–London wave functions, with effective nuclear charge 1.166 as determined by Wang [13]. The small ionic contributions to the \( H_2 \) ground state can be shown to be unimportant, as can more highly excited added configurations. Accordingly, the \( H_2 \) ground state can be represented by
\[ \varphi = \frac{1}{2\sqrt{1 + S_{AB}^2}} \left[ u_A (1) u_B (2) + u_A (2) u_B (1) \right] (\alpha_1 \beta_2 - \beta_1 \alpha_2) \] (2)

where, as above, \( A \) and \( B \) represent the two hydrogen nuclei and 1 and 2 denote the electronic coordinates associated with electrons 1 and 2. \( S_{AB} \) represents the overlap integral \( \langle u_A | u_B \rangle \). The functions \( u_A \) and \( u_B \) are used to represent the modified 1s states centered on the their respective nuclei with \( \alpha \) and \( \beta \) indicating spin up or down states respectively.

Hole wavefunctions were calculated by Density Functional Theory as described previously [11].

After considerable further analysis it is found that the electron spin densities at the two nuclei satisfy the relationship
\[ \text{Spin density at } A - \text{Spin density at } B = -0.0274 \cos \Theta \] (3)

where \( \Theta \) is the \( A \rightarrow B \) displacement vector angle with the \( z \)-axis, for \( H_2 \) above the apex Si atom, with \( A \) being further removed from the Si site than \( B \) for \( \Theta = 0 \). Eq. (3) is not exact; but the next odd term in \( \cos \Theta \) will not connect \( J = 0 \) to \( J = 1 \) rotational states. After integration over electronic coordinates the interaction Hamiltonian yields
\[ V_{fi} = \left( \frac{4\pi g_n \mu_n^2}{3 \times 1836} \right) \times 3.08 \cos \Theta \sigma_{sp_z} (\sigma_A - \sigma_B). \] (4)

4. Hole motility

In the present work it is assumed that \( sp_z \) holes moving with group velocity \( v \) diffuse randomly throughout the Si lattice, dwelling on effective areas associated with \( sp_z \) sites. The dwell time is taken to be the separation between \( sp_z \)- containing planes divided by velocity \( v \).

The dwell time we equate with the planar separation \( d \) divided by velocity. The ortho–para conversion rate will then be
\[ \mathcal{R} = N_{\text{hole}} v A \text{ (conversion amplitude with dwell time } \tau = d/v)^2 \] (5)

with effective area per \( sp_z \) site being \( A = (N_{sp_z} d)^{-1} = 60.2 a_0^2 \), where \( a_0 \) is the Bohr radius. The actual conversion amplitude is \( H_{fi} \tau / i\hbar \).

Overall we have
\[ \mathcal{R} = N_{\text{hole}} N_{sp_z}^{-1} (d/v) \left( \frac{4\pi^2}{3} \right) \left( \frac{g_n}{1836} \right)^2 \left( 0.0137 \right)^2 \left( \frac{4\mu^2}{\hbar a_0^3} \right)^2 \] (6)
The resultant characteristic time at room temperature we find to be about 1000 hr. Considering that the result is the product of several large and small terms each with considerable uncertainty the discrepancy between this and observation is not sufficient as to negate our physical picture.

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