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Interstitial H_2 in ^{29}Si

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The ortho-para conversion of interstitial H_2 in single-crystalline natural Si (^{nat}Si) and ^{29}Si (enrichment 96.2%) is studied by Raman scattering. The conversion process was found to be practically independent of the isotope composition of Si. The characteristic ortho-to-para conversion time at 77 K was found to be 220 ± 35 and 200 ± 35 h for ^{29}Si and ^{nat}Si, respectively, whereas at room temperature the back conversion occurs with a characteristic time of 8.8 ± 1.5 and 10.5 ± 1.5 h for ^{29}Si and ^{nat}Si, respectively. These values agree very well with the transition rates found in previous IR absorption studies by Peng *et al.* for ^{nat}Si [Phys. Rev. B **80**, 125207 (2009)]. Our findings imply that an interaction of H_2 with the nuclear spin of nearby ^{29}Si has marginal, if any, effects on the ortho-para conversion rate of molecular hydrogen in silicon.

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I. INTRODUCTION

Hydrogen has long been recognized to be an important impurity for modifying the electrical and optical properties of semiconductors [1]. In particular, molecular hydrogen (H_2) was suggested to be present in silicon already in the early 1980s [2,3], but due to its very low infrared and electrical activity it took more than a decade until it was directly observed by Raman scattering and IR absorption [4,5].

Molecular hydrogen in Si occupies a tetrahedral interstitial site and is a nearly free rotator whose center of mass is also in motion [6–12]. H_2 consists of two protons with nuclear spin 1/2. According to the Pauli principle the total wave function of this quantum mechanical system is antisymmetric with respect to permutations of the nuclei. Because of symmetry requirements for the total wave function, for the nuclear spin $I = 1$ (ortho state, o-H_2), only odd values of the rotational quantum number J are allowed, whereas for $I = 0$ (para state, p-H_2), J has to be even [13]. As a result, under "normal" conditions (low-pressure gaseous phase, nonparamagnetic host, no magnetic impurity nearby) the two states do not thermalize and once formed, remain independent. For example, the ortho-para transition rate of an isolated H_2 is 6.2×10^{-14} yr^{-1} [14]. The presence of an external electromagnetic field, however, renders this transition allowed [15] which has been documented in various systems such as solid H_2 [16–20], H_2 adsorbed on surfaces [21–24], H_2 in the liquid and gaseous phase [25], as well as in semiconductor hosts [26–31].

Ortho-para transitions of interstitial H_2 in Si were first observed by Raman scattering and were accounted for by the interaction of the molecule with the nearby ^{29}Si [26,27]. Natural silicon (^{nat}Si) consists of three stable isotopes ^{28}Si, ^{29}Si, and ^{30}Si with abundances of 92.2%, 4.7%, and 3.1%, respectively, of which only ^{29}Si has a nonzero nuclear magnetic moment. The Wigner mechanism [15] of the ortho-para conversion, which takes into account collisions of H_2 with paramagnetic ^{29}Si, was called for to fit the experimental data [26,27]. Since within this approach the conversion rate strongly depends on the collision distance r (as r^{-6} according to Wigner or as r^{-8} according to Ilisca [32]), the ortho-para transition should be a multiexponential process that arises from an interaction of H_2 molecules with ^{29}Si atoms in different neighbor shells. Experimental data presented in Refs. [26,27] seemed to be in line with the proposed model though relatively large error bars did not allow the authors to claim with certainty that the conversion process is indeed multiexponential.

Subsequently, Peng *et al.* employed IR absorption to study the ortho-para conversion of interstitial H_2 in Si [30]. The authors have demonstrated that the ortho-to-para and back conversion can be described by a single exponent whereby the time constants of the process at 77 K and room temperature (RT) were found to be 229 ± 14 and 8.1 ± 0.5 h, respectively. These findings ruled out the interaction with ^{29}Si as the *dominant* mechanism of the ortho-para conversion of interstitial H_2 in natural silicon.

Even though the nuclear magnetic moment of ^{29}Si cannot account for the ortho-para conversion of molecular hydrogen in ^{nat}Si, it would be reasonable to expect that this process will be accelerated in isotopically enriched ^{29}Si. Here, we report

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the results of a Raman scattering study of the ortho-to-para and back conversion of interstitial H_2 in ^{29}Si (enrichment 96.2%). Our findings imply that even in this case the interaction with the magnetic moment of silicon is marginal and does not speed up the ortho-para conversion.

II. EXPERIMENTAL PROCEDURE

Three silicon samples were employed in this study: a natural boron-doped ($p \approx 3\times10^{14}$ cm^{-3}) (100) Czochralski (Cz) Si wafer, phosphorous-doped ($n \approx 2\times10^{15}$ cm^{-3}) ^{28}Si (enrichment 99.995%), and boron-doped ($p \approx 1.5\times10^{16}$ cm^{-3}) ^{29}Si (enrichment 96.2%). They were hydrogenated in a remote dc plasma at 230 °C. The gas pressure during the treatment was held at 1.5 mbar.

In order to study the ortho-to-para conversion rate of interstitial H_2, the samples were stored in the dark at 77 K in liquid nitrogen. For the para-to-ortho back conversion, the samples were kept in the dark at room temperature in air.

Raman measurements were performed in a pseudobackscattering geometry using the frequency-doubled 532-nm line of a Nd:YVO_4 laser for excitation. For this wavelength, the estimated probing depth $(2\alpha)^{-1}$ is about 410 nm [33]. The incident laser beam made an angle of 40° with the sample normal.

The backscattered light was analyzed using a single grating spectrometer and a liquid nitrogen (LN_2) cooled Si CCD detector array. The spectral resolution was 2 cm^{-1}. The measurements were performed with the sample mounted in a cold finger cryostat using liquid helium for cooling. The typical integration time was 90 min.

During the measurements, the temperature in the bulk of the sample (T_b) could be varied by an electrical heater. All measurements were performed at nominally 4.2 K. The actual temperature within the excitation area (T_a) was determined from the Stokes to anti-Stokes ratio of the Γ-phonon line (see Fig. 1). This allowed us to control temperatures down to approximately 60 K, since for lower temperatures the anti-Stokes intensity was too low to be determined with certainty. For temperatures below 60 K, the actual temperature was estimated by extrapolation of the functional dependence of T_a vs T_b.

III. RESULTS AND DISCUSSION

Figure 1 shows Raman scattering spectra taken at cryogenic temperatures for three silicon samples employed in this study. The section around 520 cm^{-1} is normalized at the intensity of the Γ-phonon line, which for ^{29}Si, $^{\text{nat}}$Si, and ^{28}Si has a frequency of 512.4, 520.4, and 521.3 cm^{-1}, respectively. The frequency ratio $512.4/521.3 = 0.983$ coincides with the square root of the mass ratio $\sqrt{28/29}$, which confirms the isotopic composition of the ^{29}Si and ^{28}Si samples. The Γ-phonon frequency of the $^{\text{nat}}$Si sample is close to that of ^{28}Si, thus reflecting the natural abundances of the stable silicon isotopes: ^{28}Si (92.2%), ^{29}Si (4.7%), and ^{30}Si (3.1%). Note that the Γ-phonon frequencies of isotopically enriched ^{29}Si and ^{28}Si (enrichment 99.9%) were recently reported to be 512.55 and 521.3 cm^{-1} [34], which practically coincides with our findings.

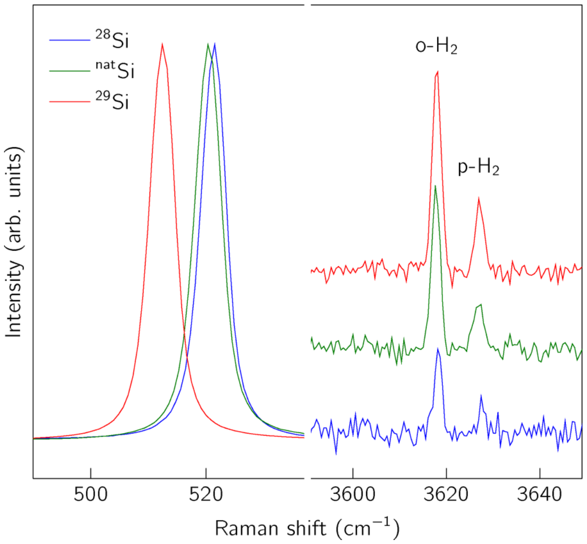

FIG. 1. Raman scattering spectra taken at $T < 60$ K for Si samples employed in this study after exposure to a hydrogen plasma at 230 °C. The section around 520 cm^{-1} is normalized at the intensity of the Γ-phonon line. The spectra of interstitial H_2 are offset vertically for clarity.

The right section of the Raman spectra shown in Fig. 1 represents spectroscopic signals of interstitial H_2 formed as a result of hydrogenation. Independent of the isotopic composition of the host lattice, the spectrum consists of two lines due to the vibrational modes of o- and p-H_2 positioned at 3618 and 3627 cm^{-1}, respectively [10,35]. Each species reveals a single line in the Raman spectra since at $T < 60$ K for both o- and p-H_2 only the ground rotational state is populated [36]. The intensity ratio of the two lines 3:1 corresponds to the nuclear spin degeneracy of each species $(2\times1+1):(2\times0+1)$. As can be seen from the figure, the amount of H_2 formed after hydrogenation within the probing depth of a sample depends on the material. Varying parameters of the treatment (temperature and exposure time) did not result in the enhancement of the H_2 signal in ^{28}Si to the level necessary to study the ortho-para conversion. Because of this, in the following discussion we will focus on isotopically enriched ^{29}Si and $^{\text{nat}}$Si taken as a reference.

If a sample is held long enough to establish a thermal equilibrium between o- and p-H_2 the ortho/para ratio $n_o : n_p$ is given by

$$\frac{n_o}{n_p} = 3\frac{\sum_{J=1,3,\ldots}(2J+1)e^{-E_J/kT}}{\sum_{J=0,2,\ldots}(2J+1)e^{-E_J/kT}}, \tag{1}$$

where the factor 3 stands for the degeneracies of the nuclear spin states and the factor $2J+1$ accounts for the degeneracy of the rotational state.

The rotational energy of a diatomic molecule with a rotational quantum number J is given by [13]

$$E_J = \frac{\hbar^2}{2\mu r^2}J(J+1) \equiv BJ(J+1), \tag{2}$$

where μ is the reduced mass and r is the internuclear spacing. The value of $B = 54$ cm^{-1} was determined indirectly by Peng

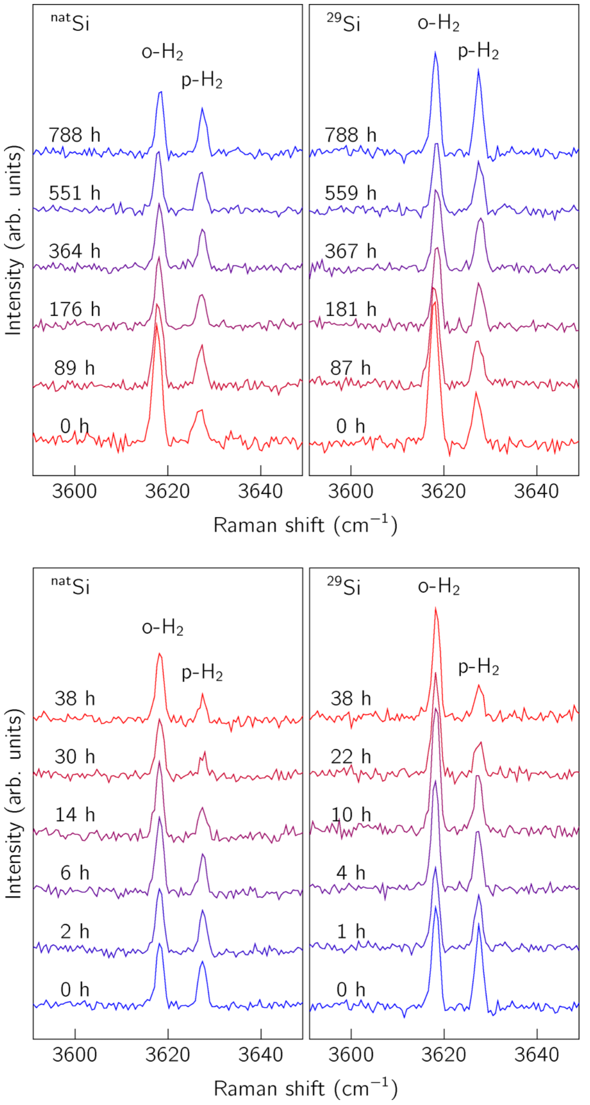

FIG. 2. Raman scattering spectra of interstitial H_2 in ^{nat}Si and ^{29}Si taken at $T < 60$ K. Top: Directly after hydrogenation and after storing the samples at 77 K in liquid N_2. Bottom: After the storage in liquid N_2 for 800 h and subsequent "annealing" at room temperature. The spectra are offset vertically for clarity.

et al. from the rotational levels of HD [30]. It corresponds to the internuclear spacing of 0.788 Å, which agrees with the theoretical calculations [37]. With the known parameter B we obtain that an equilibrium value of $n_o : n_p$ at room temperature and 77 K is 3 and 1.2, respectively.

The evolution of interstitial H_2 in ^{nat}Si and ^{29}Si samples kept at 77 K is shown in Fig. 2 (top). After a month of storage the intensity of the p-H_2 signal becomes stronger at the expense of o-H_2 in both ^{nat}Si and ^{29}Si. The process is reversible. After keeping the samples in liquid nitrogen for 800 h the para-to-ortho back conversion takes place if the samples are stored at room temperature. Figure 2 (bottom) shows the evolution the H_2 signals in ^{nat}Si and ^{29}Si at RT. Contrary to 77 K, the back conversion is a much faster process—the equilibrium value is achieved after about 1 day of the room-temperature "annealing." Notably, in both samples the conversion process seems to occur at the same rate.

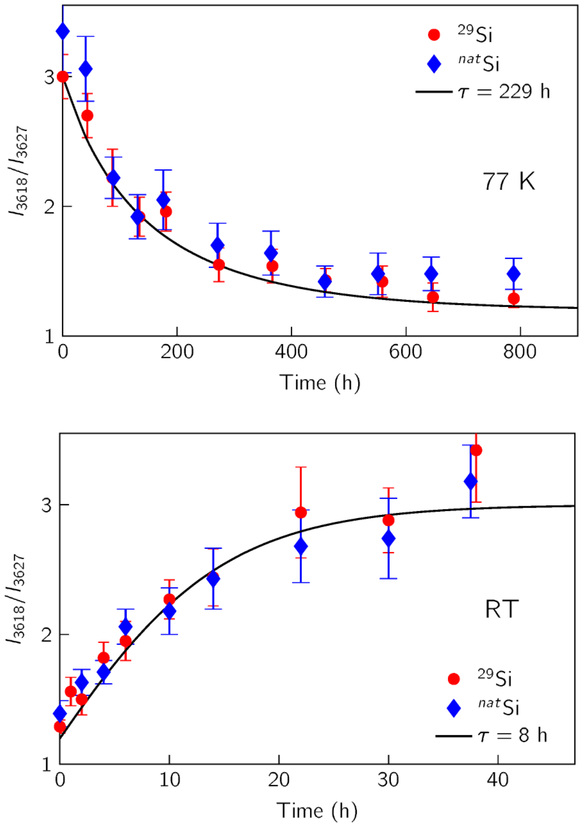

FIG. 3. Development of the intensity ratio of the 3618- and the 3627-cm^{-1} lines of interstitial H_2 vs annealing time at 77 K (top) and room temperature (bottom). Solid lines are time dependences given by Eq. (4a) with the equilibrium values of $n_o : n_p$ obtained from Eq. (1).

The time dependence of the two species population we describe as [26,27,30]

$$\frac{dn_o}{dt} = -\frac{n_o}{\tau_{o\to p}} + \frac{n_p}{\tau_{p\to o}}, \quad \frac{dn_o}{dt} = -\frac{dn_p}{dt}, \tag{3}$$

where $\tau_{o\to p}$ is the time constant for the ortho-to-para conversion, whereas $\tau_{p\to o}$ describes the reverse process. The solution of Eq. (3) is

$$\frac{n_o}{n_p} = \frac{a + b\exp(-t/\tau)}{1 - a - b\exp(-t/\tau)}, \tag{4a}$$

$$a = \frac{\eta_\infty}{1+\eta_\infty}, \quad b = \frac{\eta_0}{1+\eta_0} - \frac{\eta_\infty}{1+\eta_\infty}, \tag{4b}$$

$$\tau = \frac{\tau_{o\to p}}{1+\eta_\infty}, \quad \frac{\tau_{o\to p}}{\tau_{p\to o}} = \eta_\infty, \tag{4c}$$

where η_0 and η_∞ are the equilibrium values of $n_o : n_p$ at $t = 0$ and $t = \infty$, respectively.

Since at cryogenic temperatures only the states with $J = 0$ and $J = 1$ are populated, we assume that $n_o : n_p$ corresponds to the intensity ratio of the 3618- and 3627-cm^{-1} lines. Table I gathers the values of τ, η_0, and η_∞ obtained as a result of the best-fit procedure of experimental data presented in Fig. 3 together with $\tau_{o\to p}$ and $\tau_{p\to o}$ deduced from the best-fit parameters. For the sake of comparison, the values of τ, η_0, η_∞,

TABLE I. Best-fit parameters describing the kinetics of the ortho-para conversion of interstitial H_2 in ^{nat}Si and ^{29}Si at 77 K and RT obtained from Eq. (4).

	77 K					RT				
	η_∞	η_0	$\tau_{o\to p}$ (h)	$\tau_{p\to o}$ (h)	τ (h)	η_∞	η_0	$\tau_{o\to p}$ (h)	$\tau_{p\to o}$ (h)	τ (h)
^{29}Si	1.3 ± 0.1	3.0 ± 0.4	506 ± 44	390 ± 64	220 ± 35	3.1 ± 0.7	1.3 ± 0.2	36 ± 8	12 ± 5	8.8 ± 1.5
^{nat}Si	1.4 ± 0.2	3.3 ± 0.8	480 ± 62	343 ± 87	200 ± 35	3.1 ± 0.6	1.4 ± 0.2	43 ± 8	14 ± 5	10.5 ± 1.5
Ref. [26]	1.5 ± 0.2	3.1 ± 0.4	620 ± 80	419 ± 69	250 ± 35	3.5 ± 0.6	1.5 ± 0.2	32 ± 6	9 ± 3	7.2 ± 1.5
Ref. [30]	1.2	3	504	420	229 ± 14	3	1.2	32.4	10.8	8.1 ± 0.5

$\tau_{o\to p}$, and $\tau_{p\to o}$ obtained earlier from the Raman scattering [26,27] and IR absorption [30] studies of the ortho-para conversion in natural silicon are also shown.

The solid lines in Fig. 3 represent the exponential conversion rate given by Eq. (4a). The equilibrium values of $n_o : n_p$ were obtained from Eq. (1), whereas the conversion time τ was taken from the IR absorption study by Peng *et al.* [30].

It follows from the data gathered in Table I that within the error bars of our current as well as previous Raman scattering and IR absorption studies the ortho-para conversion rate is independent of the isotopic composition of silicon.

After ruling out the interaction of H_2 with the nuclear magnetic moment of nearby ^{29}Si, Peng *et al.* [30] considered alternative models to account for the nuclear spin flip of interstitial H_2. One of them—a “coherent” tunneling motion of H_2 between tetrahedral interstitial sites in Si—was also excluded by Peng *et al.*, since it must be exponentially sensitive to the mass of the molecule which contradicts their experimental finding that the ortho-para conversion rate of D_2 is basically similar to that of H_2.

Another model considered by Peng *et al.* suggests that the dynamical effects of the H_2 rotational, vibrational, and translational motion are responsible for the ortho-para transition [30]. Due to this motion the instantaneous microscopic magnetic fields (generated by electrons in the crystal) acting on the two hydrogen atoms would be different, thereby allowing the mixing of the ortho and para states.

In our recent communications [38] we have suggested that the main mechanism of the ortho-para conversion of the molecular hydrogen in semiconductors is similar to the paramagnetic spin catalysis proposed by Minaev and Ågren [39]. It is realized by the introduction of an unpaired electron which gets activated via an interaction of H_2 with an activator (here, Si crystal). In this case, the electron spin states of the molecule become separated due to the mixing of the ground singlet state $X^1\sum_g^+$, the lowest triplet state $b^3\sum_u^+$, and the crystal states, thus changing the symmetry of the electronic wave function localized in the vicinity of the hydrogen nuclei. This interaction causes a nonzero probability of finding an unpaired electron and one of the protons with identical spatial coordinates. As a result, an effective Fermi contact interaction between the electron and the proton arises which couples the ortho and para states.

The assumption that the driving force of the ortho-para conversion is a mixing of the molecular and crystal orbitals implies that the conversion rate should depend on the distance between the molecule and the Si atoms and hence on the sample temperature. Such a scenario qualitatively agrees with the experimental findings. Indeed, the higher the temperature, the larger the atomic displacements, and thus the closer H_2 approaches the nearby Si atoms. In fact, the idea of spin catalysis is fully consistent with the mechanism proposed by Peng *et al.* [30] and supplements it on the quantum mechanical level.

In summary, the results of our Raman scattering study of the ortho-para conversion of interstitial H_2 in isotopically enriched ^{29}Si lead us to the conclusion that interaction with the nuclear magnetic moment of ^{29}Si has a marginal, if any, effect on the nuclear spin flip of the molecule.

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