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Hydrogen molecules in semiconductors

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Abstract

Molecular hydrogen, the simplest of all molecules, allows a direct insight into the fundamental properties of quantum mechanics. In the case of H_2, the Pauli principle leads to two different species, *para*-H_2 and *ortho*-H_2. A conversion between these species is prohibited. Vibrational mode spectra reflect the fundamental properties and allow an unambiguous identification of the H_2 molecules. Today, we have experimental evidence for the trapping of hydrogen molecules in the semiconductors Si, Ge and GaAs at the interstitial sites, within hydrogen-induced platelets, in voids and at impurities (interstitial oxygen in Si). Interstitial H_2 is a nearly free rotor with a surprisingly simple behavior. We review on interstitial H_2 in semiconductors and report on the unexpected preferential disappearance of the *para*-H_2 or *ortho*-D_2 species. The origin of the detected *ortho–para* conversion will be discussed.

Keywords: Hydrogen molecules; Raman spectroscopy; *Ortho-/para*-hydrogen; LVM

1. Introduction

Hydrogen (H) atoms are the most abundant atomic species in our universe. Experimental studies of the electronic excitations in this atom laid the foundation of quantum mechanics at the beginning of the 20th century. Atomic hydrogen has an electron spin of $S = \frac{1}{2}$ and a nuclear spin of $I_N = \frac{1}{2}$ There are two more isotopes of hydrogen: deuterium (mass 2, $I_N = 1$) and tritium (mass 3, $I_N = \frac{1}{2}$). On earth, isolated hydrogen is not stable and forms molecular hydrogen (H_2), the simplest of all molecules.

In semiconductors, hydrogen is incorporated by many technological processes. The detection of electrical passivation of detrimental defects by atomic hydrogen has initiated strong research activities in the last years. In contrast, molecular hydrogen is electrically passive in the semiconductor lattice and its properties were not in the focus of technology. However, H_2 is a possible source of atomic hydrogen which is activated, e.g., by implantation damage or heat treatments. The understanding of the basic properties of H_2 in semiconductors is a prerequisite to avoid unwanted passivation effects or the creation of hydrogen-induced defect states.

In this review, we summarize the present knowledge on H_2 in semiconductors. In particular, emphasis is given to the fundamental behavior of the *ortho/para* states in the lattice.

2. Free molecular hydrogen

Two hydrogen atoms form the homonuclear molecule H_2. The protons are 0.74 Å apart and the two electrons form a singlet ground state ($^1\Sigma_g^+$). The electron charge density decreases rapidly, making the molecule appear almost spherical rather than dumbbell shaped [1].

Molecular hydrogen exists in two species, due to the requirement on the symmetry of the wave function by Pauli's principle. H_2 is a fermionic system and the total wave function has to be antisymmetric with respect to permutations of the nuclei. This leads to restrictions in the rotational states depending on the arrangement of the nuclear spins. The two H_2-species are labeled *ortho*- and *para*-hydrogen. *Ortho*-H_2 (o-H_2) exhibits a nuclear triplet state $I_{mol} = 1$ and is associated with rotational states with odd spatial symmetry (rotational quantum numbers $J = 1$, 3, 5…). *Para*-H_2 (p-H_2) exhibits a pure nuclear singlet state ($I_{mol} = 0$) and couples only to rotational states ($J = 0$, 2,

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4…) with even spatial symmetry. If hydrogen atoms bind to form H_2 molecules, the concentration ratio of *ortho-/para*-hydrogen is $\frac{3}{1}$, according to the degeneracies of the nuclear spin states.

Deuterium atoms are bosons and the total wave function has to be symmetric. Therefore, the *para*-D_2 state ($I_{\mathrm{mol}} = 1$) couples only to odd rotational states ($J = 1, 3,\ldots$) and the *ortho*-D_2 states ($I_{\mathrm{mol}} = 0,\ 2$) couple to the even rotational states ($J = 0,\ 2,\ldots$). The ratio of degeneracies of *ortho-/para*-D_2 is $\frac{2}{1}$.

In HD molecules, the nuclear spin has no inflections on the rotational states. For all nuclear spin states I_{mol}, one sees the same rotational spectrum [1].

The selection rule for electrical dipole transitions in a rotating diatomic molecule is $\Delta J = \pm 1$. The symmetric stretching vibration of an isolated H_2 molecule in the gas phase does not give rise to an oscillating dipole moment and is therefore infrared inactive [2]. Raman investigations of gaseous H_2, D_2 and HD show ro-vibrational lines [3] corresponding to the Raman selection rules $\Delta v = 0, +1$ and $\Delta J = 0, +2 (v = 0,1,2,\ldots$ denotes the vibrational quantum number) [2]. The existence of *ortho*- and *para*-hydrogen gives proof for a freely rotating H_2 molecule. Extended Raman studies were also performed on liquid and solid hydrogen [4] and on H_2, D_2 and HD molecules trapped in matrices like silica [5], solid Ar, Kr, Xe [6], O_2, or N_2 [7,8].

The conversion between the two H_2 species is not allowed for isolated H_2. However, *ortho–para* conversion is well documented in the solid and liquid phase. Three different mechanisms are discussed for the *ortho–para* conversion. A *paramagnetic* mechanism where the spin flip is caused by the magnetic interaction of hydrogen spins with paramagnetic centers like unpaired electron spins or other magnetic dipoles like nuclear spins. Dipolar magnetic nuclear interactions are usually responsible for very slow conversion rates. The magnetic hyperfine interaction of unpaired electrons leads to faster conversion rates. A *chemical* mechanism uses chemical exchange reactions to produce the spin conversion. The intermediate binding of the molecule to, e.g., transition metals is the preferred conversion mechanisms at surfaces. A *pressure*-dependent mechanism catalyzes the spin conversion by high pressures in solid hydrogen [1].

In 1933, Wigner [9] gave the original explanation on the *ortho–para* conversion based on the paramagnetic mechanism. The non-zero magnetic dipole interaction between the magnetic moment of a catalytic center and the total nuclear spin of H_2 molecules leads to the Wigner rate of spin conversion.

3. Hydrogen in semiconductors

3.1. General properties

In the early 1980's theory predicted that H_2 is compared to isolated H the energetically favorable state in Si [10,11]. Interstitial molecular H_2 was found to be located at a T site.

Another hydrogen dimer (H_2*) was identified in proton implanted Si and Ge [12,13]. This defect is formed by two hydrogen atoms, one sitting close to a bond-centered site (H_{BC}) and the other at an antibonding site (H_{AB}) of two neighboring Si atoms.

Indirect evidence for H_2 molecule formation came from samples treated in hydrogen plasmas. Close to the surface, high amounts of electrically inactive hydrogen atoms were detected. They were attributed to the formation of neutral H_2 molecules [14]. Other indirect evidence for an immobile H_2 species came from annealing studies in hydrogenated n^+p-diodes or p-type Si samples [15,16].

Amorphous Si (a-Si) was the first semiconductor material where H_2 molecules were detected. The existence of H_2 had strong implications on the discussion of the origin of light-induced defects in this material. Hydrogenated a-Si can contain several atomic % of hydrogen. Under these conditions the existence of hydrogen molecules in microbubbles at high pressures (2000 atm) was detected by different techniques. Experimental support came from NMR studies of the proton spin-lattice relaxation in hydrogenated a-Si [17] and thermal calorimetry [18]. Weak infrared absorption was possible through dipole moments induced by collision processes in the H_2 clusters [19]. Isolated molecules were not reported. An *ortho–para* conversion was detected and an ordering of *ortho*-hydrogen occurred at low temperatures [20].

The first direct experimental proof of interstitial H_2 in crystalline semiconductors was found 1996 in GaAs [21] and soon after that in Si by means of FTIR absorption [22,23] and Raman scattering [24]. Today, H_2 is known to exist in Si, Ge and GaAs. Different trapping sites are reported like the interstitial sites, voids and impurities like oxygen in Si.

Theory predicts positive binding energies for H_2 in semiconductors, although the binding energy is smaller than in vacuum. The interaction of H_2 with the host charge density or the size of the surrounding semiconductor cage leads to a reduction of the vibrational frequency and a lowering of the binding energy [25].

3.2. Interstitial H_2 in semiconductors

Low temperature Raman spectra of H, D and HD plasma-treated GaAs samples are shown in Fig. 1. The lines at 3934.1, 2842.6 and 3446.5 cm^{-1} in the samples are identified by the frequency ratios as due to H_2, D_2 and HD stretch modes, respectively [21]. Theory predicted that H_2 is stable at the interstitial tetrahedral (T_{Ga}) site with four Ga neighbors or the T_{As} site close to the four As anions, with a slight energetical preference of the T_{Ga} site [25]. The strong lines seen in Fig. 1 were therefore assigned to different isotopes of hydrogen molecules on the T_{Ga} site in GaAs. The frequencies are lower than the values for free gaseous H_2 and agree with most calculations for the LVM of H_2