

## Local Vibrational Modes of Isolated Hydrogen in Germanium

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Two distinct isolated hydrogen defects are observed in crystalline Ge by *in situ* infrared absorption spectroscopy. Implantation of protons into Ge at cryogenic temperatures gives rise to two intense absorption lines at 745 and 1794  $\text{cm}^{-1}$ . The lines originate from distinct defects, each of which contains one H atom located on a  $\langle 111 \rangle$  axis. The 1794- $\text{cm}^{-1}$  line is assigned to bond center H in the positive charge state, whereas the 745- $\text{cm}^{-1}$  line is ascribed to negatively charged H located on a  $\langle 111 \rangle$  axis close to the tetrahedral site.

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Hydrogen is an important impurity in semiconductors because of its ability to react with a wide variety of lattice imperfections like intrinsic point defects, impurities, interfaces, and surfaces. Such reactions may affect the electronic properties of the material by removal of electronic states from the band gap, and H in semiconductors has therefore been studied extensively experimentally and theoretically [1–4]. The natural starting point for investigating the effects of H incorporation is to determine the properties of isolated H atoms interacting with a perfect semiconductor crystal. However, despite the vast amount of work on H in semiconductors, only isolated H in Si has been identified to date.

In this work we present the first experimental observation of isolated H in Ge. *In situ* infrared absorption spectroscopy (IRAS) on Ge implanted with protons at cryogenic temperatures reveals two very intense absorption lines at 745 and 1794  $\text{cm}^{-1}$ , which originate from local vibrational modes (LVMS) of distinct H-related defects containing one H atom. Uniaxial stress measurements show that both defects have trigonal symmetry, which implies that the H atoms are located on a  $\langle 111 \rangle$  axis. The properties of the 1794- $\text{cm}^{-1}$  mode are essentially identical to those of the stretch mode of bond center H in Si, and we therefore assign it to this defect in Ge. On the contrary, the 745- $\text{cm}^{-1}$  line has no Si analog. The experimental results strongly suggest that the 745- $\text{cm}^{-1}$  line originates from an isolated H species, most likely negatively charged H located close to the tetrahedral site. Although predicted by theory more than a decade ago, the present work provides the first direct observation of this isolated H species in a semiconductor.

Most of the knowledge about isolated H in semiconductors comes from studies of Si, and we shall therefore briefly review the properties of isolated H in this material.

According to theory, isolated H in Si can exist in three different charge states:  $\text{H}^{(+)}$ ,  $\text{H}^{(0)}$ , and  $\text{H}^{(-)}$  [4–9]. In the positive and negative charge states, H is predicted to be located at, respectively, the bond-center site (*BC*) and at (or near) the tetrahedral site (*T*), shown in Fig. 1 [4–9]. For the neutral charge state, most theories find that isolated H has energy minima at both sites, with the *BC* site being the global minimum [5,6,8,9]. Theory furthermore predicts that isolated H in Si is a negative-*U* system, i.e., that  $\text{H}^{(0)}$  has higher energy than  $\text{H}^{(+)}$  and/or  $\text{H}^{(-)}$  for all Fermi-level positions [7,9].

Isolated H in Si is problematic to study experimentally because of its high mobility and reactivity, which causes it to react with lattice imperfections below room temperature. One way to circumvent this problem is to incorporate H by ion implantation at cryogenic temperatures and perform the measurements *in situ*, i.e., without heating the sample between implantation and experiment. Using this approach, bond center H ( $\text{H}_{BC}$ ) in Si has been observed with a variety of experimental techniques [10–17].  $\text{H}_{BC}$  was first directly observed by Bech Nielsen with ion channeling [10]. The first definite identification of neutral  $\text{H}_{BC}$  in Si ( $\text{H}_{BC}^{(0)}$ ) was made by Gorelkinskii and Nevinnyi using *in situ* electron paramagnetic resonance (EPR) [11]. The EPR measurements were subsequently reproduced by Bech Nielsen *et al.* [12], who also showed that the EPR signal has the same annealing behavior as the donor level

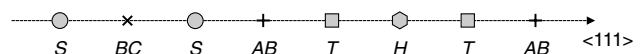


FIG. 1. High-symmetry sites on  $\langle 111 \rangle$  axes in the simple-cubic unit cell of the Ge lattice. The sites are denoted: substitutional (*S*), bond center (*BC*), antibonding (*AB*), tetrahedral (*T*), and hexagonal (*H*).

$E_3'$  observed by deep level transient spectroscopy [13–15]. Finally, the stretch mode of  $H_{BC}^{(+)}$  was recently identified by *in situ* IRAS experiments [16]. Implantation of protons into Si at cryogenic temperature gave rise to an intense absorption line at  $1998\text{ cm}^{-1}$  with the same annealing behavior as the EPR signal, one of the  $BC$  components observed by channeling, and the  $E_3'$  level, which identified the line as the fundamental excitation of the stretch mode of  $H_{BC}$ . In contrast to the EPR signal, which was observed only during illumination with band-gap light, the  $1998\text{-cm}^{-1}$  line was observed without illumination and decreased in intensity when band-gap light was applied. It was therefore ascribed to the positive charge state  $H_{BC}^{(+)}$ . The  $1998\text{-cm}^{-1}$  line was originally observed by Stein, who assigned it to a vacancy-hydrogen complex [17].

Isolated H in Ge has received much less attention than in Si. No experimental studies have been reported, and theoretical studies are much less complete. Theoretical studies were first reported by Khoo and Ong [18]. However, since the calculations were based on the heavily approximated CNDO (complete neglect of the differential overlap) method and did not include lattice relaxations, we shall not address them further here. *Ab initio* density-functional calculations were reported by Denteneer *et al.* [19]. The calculations predicted H to have very similar properties in Ge and Si: In *p*-type material  $H_{BC}^{(+)}$  was found to have lowest energy, whereas  $H_T^{(-)}$  was energetically favored in intrinsic and *n*-type Ge. More recently, Estreicher *et al.* reported a comparative study of the properties of H in diamond, Si, Ge, and  $\alpha$ -Sn using the *ab initio* Hartree-Fock method [20]. In contrast to Si, it was found that  $H_T^{(0)}$  in Ge has slightly lower energy than  $H_{BC}^{(0)}$ , and from this the authors concluded that  $H_{BC}^{(+)}$  changes from being very abundant in Si to being almost nonexistent in Ge. It should be noted, however, that Estreicher *et al.* considered only neutral charge states. Consequently, the calculations may not provide the full picture.

The experiments reported in this Letter were performed using samples cut from high-resistivity, ultrapure Ge single crystals, as described in detail elsewhere [21]. The samples were implanted with protons and/or deuterons at multiple energies yielding a uniform H concentration profile. The widths of the H profiles ranged from 20 to  $250\text{ }\mu\text{m}$ . The samples were mounted in a cryostat attached to the accelerator beam line, and cooled to either  $\sim 20$  or  $\sim 80\text{ K}$  during implantation. After implantation, the cryostat was moved to the infrared spectrometer, while keeping the sample within  $10\text{ K}$  of the implantation temperature. The IRAS measurements were performed at  $\sim 10\text{ K}$  with a spectral resolution better than  $0.8\text{ cm}^{-1}$  using commercial Fourier transform infrared spectrometers. Some of the experiments involved measuring the infrared absorption with uniaxial stresses applied along high-symmetry crystal axes. This was accomplished using specially cut samples and a home-built stress apparatus as described in Ref. [21].

Figure 2(a) shows the infrared absorbance spectrum of Ge implanted with protons at  $\sim 20\text{ K}$ . Implantation of protons gives rise to two intense absorption lines at  $745$  and  $1794\text{ cm}^{-1}$  together with two weak lines at  $1480$  and  $1488\text{ cm}^{-1}$ . This is in marked contrast to the Si case, where one strong line at  $1998\text{ cm}^{-1}$  is observed under similar sample preparation conditions. When deuterons are implanted instead of protons, the two intense lines shift down in frequency by a factor  $\sim \sqrt{2}$  to  $535$  and  $1293\text{ cm}^{-1}$ , which shows that they originate from H-related LVMs. The  $745\text{-}$  and  $1794\text{-cm}^{-1}$  lines are much more intense than other H-related lines observed in proton-implanted Ge at higher temperatures. For instance, the intensities (integrated absorbance) of the two lines shown in Fig. 2(a) are  $I_{745} = 0.65$  and  $I_{1794} = 2.9\text{ cm}^{-1}$ , whereas the sum of the intensities of all the absorption lines observed in the Ge-H stretch region  $1750\text{--}2100\text{ cm}^{-1}$  in the same sample after annealing at  $230\text{ K}$  is only  $0.19\text{ cm}^{-1}$ .

To investigate if the lines are correlated and to determine their thermal stability, an isochronal annealing study was performed. The sample was heated to a series of annealing temperatures  $T_{\text{anneal}}$  for  $15\text{ min}$  in the dark. Between each annealing step, the sample was cooled to  $\sim 10\text{ K}$  and the absorption spectrum was measured. Figure 2(b) shows the normalized intensity of the  $745\text{-}$  and  $1794\text{-cm}^{-1}$  lines as a function of  $T_{\text{anneal}}$ . The intensity of the  $745\text{-cm}^{-1}$  line is constant up to  $100\text{ K}$ , where it starts to decline, reaching

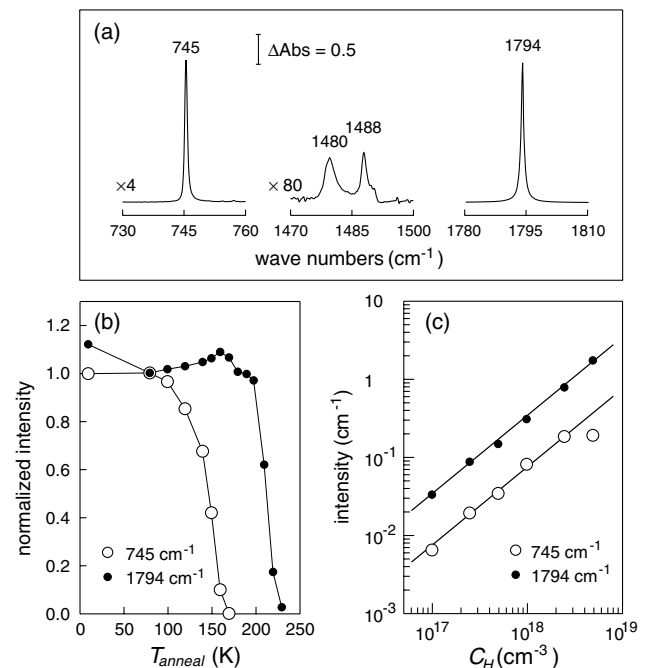


FIG. 2. (a) Absorbance spectrum of Ge implanted with  $2 \times 10^{16}$  protons/ $\text{cm}^2$  at  $\sim 20\text{ K}$ . (b) Normalized intensity of the absorption lines at  $745\text{ cm}^{-1}$  ( $\circ$ ) and  $1794\text{ cm}^{-1}$  ( $\bullet$ ) as a function of annealing temperature. (c) Intensity of the  $745\text{-}$  ( $\circ$ ) and  $1794\text{-cm}^{-1}$  ( $\bullet$ ) lines as a function of H concentration  $C_H$ . The lines shown in the figure correspond to intensities proportional to  $C_H$ .

half its low-temperature value at  $\sim 145$  K. This behavior is clearly different from that of the  $1794\text{-cm}^{-1}$  line, which anneals at  $\sim 210$  K. Consequently, the two lines originate from different defects. In fact, the  $1794\text{-cm}^{-1}$  line increases by about 9% when the  $745\text{-cm}^{-1}$  line disappears, indicative of a conversion to the  $1794\text{-cm}^{-1}$  line. The annealing behaviors of the two weak lines at  $1480$  and  $1488\text{ cm}^{-1}$  are identical to that of the  $745\text{-cm}^{-1}$  line, and since they are very close to  $2 \times 745\text{ cm}^{-1}$  we assign them to overtones of the  $745\text{-cm}^{-1}$  mode.

Figure 2(c) shows the intensities of the two lines as a function of H concentration  $C_H$ . The different  $C_H$ 's were obtained by varying the total implanted dose, while keeping the spatial H profile unchanged. The intensity of the  $1794\text{-cm}^{-1}$  line is proportional to  $C_H$  over the whole range covered. The intensity of the  $745\text{-cm}^{-1}$  line is also proportional to  $C_H$ , but only up to  $2 \times 10^{18}\text{ cm}^{-3}$  at which it saturates. The linear concentration dependencies show that the probability for a H atom to form either a  $745\text{-}$  or  $1794\text{-cm}^{-1}$  defect is independent of the concentration of H and implantation-induced defects. This suggests that the two lines originate from isolated H atoms interacting with a perfect Ge crystal, because the probability of forming complexes involving other H atoms or defects will increase with increasing concentration, and therefore result in a nonlinear  $C_H$  dependence. Involvement of grown-in impurities can be excluded based on the fact that both line intensities are proportional to  $C_H$  up to  $2 \times 10^{18}\text{ cm}^{-3}$ , 2 orders of magnitude above the concentration of impurities in the samples. The conclusion that each defect contains only one H is further supported by H and D coimplantation experiments. Spectra of Ge implanted with overlapping H and D profiles do not reveal any new lines, in addition to the lines observed in samples containing H or D separately.

The symmetry of a point defect can be obtained from measurements of the response of its LVMs on uniaxial stress. The top part of Fig. 3 shows the effect of uniaxial stresses parallel to  $[100]$ ,  $[111]$ , and  $[110]$  directions on the  $1794\text{-cm}^{-1}$  line. The line shifts linearly with stress along  $[100]$  but does not split. Stress along  $[111]$  splits the line into two components, only one of which is observed with light polarized perpendicular to the stress direction. This splitting pattern is characteristic for an  $A \rightarrow A$  transition of a defect with trigonal symmetry (see, e.g., Ref. [21] and references therein). The lines in Fig. 3 represent the best fit of the theoretical shifts of such a transition to the data, and are defined by the parameters  $A_1$  and  $A_2$  listed in Table I. The fit is in excellent agreement with the data for all stress directions, thus confirming the assignment of the  $1794\text{-cm}^{-1}$  line to an  $A$  mode of a trigonal defect. The stress pattern of the  $745\text{-cm}^{-1}$  line is shown in the bottom half of Fig. 3 together with the best-fit theoretical shifts for an  $A \rightarrow E$  transition of a trigonal defect [21]. The excellent agreement between the lines and the experimental data for all stress directions shows that the  $745\text{-cm}^{-1}$  line originates from a twofold degenerate mode of a trigonal

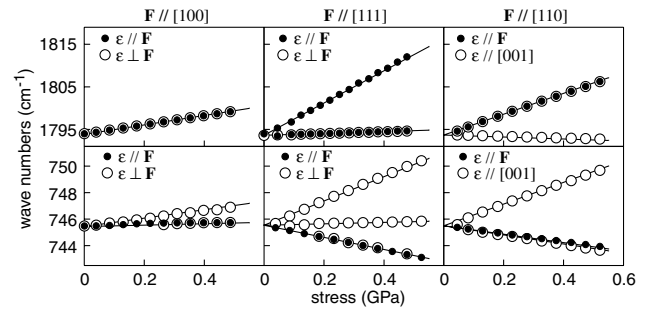


FIG. 3. Frequency shifts induced by uniaxial stresses parallel to  $[100]$ ,  $[111]$ , and  $[110]$  directions. The frequencies indicated by the symbols  $\bullet$  ( $\circ$ ) were obtained with the infrared light polarized parallel (perpendicular) to the stress direction  $F$ . The lines represent the best fit of an  $A \rightarrow A$  (top) and an  $A \rightarrow E$  transition (bottom) of a trigonal center.

defect. Since the  $745\text{-}$  and  $1794\text{-cm}^{-1}$  defects each contain one H atom, the trigonal symmetry implies that the H atoms are located on a  $\langle 111 \rangle$  axis of the Ge lattice. Being an  $A$  mode, the  $1794\text{-cm}^{-1}$  mode corresponds to the vibration of H parallel to this axis, whereas the  $745\text{-cm}^{-1}$  mode corresponds to vibration perpendicular to the  $\langle 111 \rangle$  axis.

The properties of the  $745\text{-}$  and  $1794\text{-cm}^{-1}$  lines are summarized in Table I together with those of the  $1998\text{-cm}^{-1}$  line of  $H_{BC}^{(+)}$  in Si. The lines at  $1794\text{ cm}^{-1}$  in Ge and  $1998\text{ cm}^{-1}$  in Si are very similar. They are observed under the same experimental conditions, are extremely intense, have nearly the same annealing behavior, and are very sensitive to uniaxial stress, as evidenced by the large  $A_1$  and  $A_2$  parameters. Moreover, the ratios  $A_1/A_2$  are equal within experimental error, consistent with the two lines originating from defects with the same bonding configuration. Based on these similarities we assign the  $1794\text{-cm}^{-1}$  line to  $H_{BC}^{(+)}$  in Ge.

TABLE I. Properties of the  $745\text{-}$  and  $1794\text{-cm}^{-1}$  modes in proton-implanted Ge. The properties of the  $1998\text{-cm}^{-1}$  mode of  $H_{BC}^{(+)}$  in Si are shown for comparison.

Line	Ge		Si
	$745\text{ cm}^{-1}$	$1794\text{ cm}^{-1}$	$1998\text{ cm}^{-1}$
$\omega_H$ ( $\text{cm}^{-1}$ )	745	1794	1998
$\omega_D$ ( $\text{cm}^{-1}$ )	535	1293	1449
$T_{\text{anneal}}$ (K)	145	210	190
H atoms	1	1	1
Symmetry transition	Trigonal $A \rightarrow E$	Trigonal $A \rightarrow A$	Trigonal $A \rightarrow A$
$A_1$ ( $\text{cm}^{-1}/\text{GPa}$ )	$1.8 \pm 0.3$	$11.1 \pm 0.9$	$9 \pm 1^a$
$A_2$ ( $\text{cm}^{-1}/\text{GPa}$ )	$-0.66 \pm 0.15$	$13.4 \pm 0.4$	$11 \pm 1^a$
$B$ ( $\text{cm}^{-1}/\text{GPa}$ )	$0.53 \pm 0.13$		
$C$ ( $\text{cm}^{-1}/\text{GPa}$ )	$5.16 \pm 0.15$		
Assignment	$H^{(-)}$	$H_{BC}^{(+)}$	$H_{BC}^{(+)}$

<sup>a</sup>M. Budde and B. Bech Nielsen, unpublished.

In contrast, the  $745\text{-cm}^{-1}$  line has no Si counterpart. The experimental data strongly suggest that it originates from isolated H located on a  $\langle 111 \rangle$  axis of the Ge lattice, and that the  $745\text{-cm}^{-1}$  mode corresponds to the vibration of H perpendicular to this axis. The frequency, symmetry, and stress response of the  $745\text{-cm}^{-1}$  mode resemble that of the bend mode of the  $\text{H}_2^*$  defect in Ge at  $765\text{ cm}^{-1}$  [21], which seems to indicate that the  $745\text{-cm}^{-1}$  mode originates from the bend mode of H at the  $AB$  site. However, if this were correct, then an additional absorption line is expected around  $1774\text{ cm}^{-1}$  due to the stretch mode of the Ge- $\text{H}_{AB}$  bond, with the same annealing behavior and similar intensity as the  $745\text{-cm}^{-1}$  line. Despite the very large intensity of the  $745\text{-cm}^{-1}$  line, this stretch mode has not been observed [22]. The observation of a bend mode without an associated stretch mode is highly unusual, and indicates that the H atom involved does not form a typical covalent bond with a Ge atom.

According to theory, the most likely candidates to the line at  $745\text{ cm}^{-1}$  are  $\text{H}_{BC}^{(0)}$ ,  $\text{H}_T^{(0)}$ , and  $\text{H}_T^{(-)}$ . However, none of these defects are consistent with the experimental data.  $\text{H}_{BC}^{(0)}$  has inversion symmetry ( $D_{3d}$  point group) and the overtones of its bending mode are therefore infrared inactive [24], inconsistent with the observation of the overtones at  $1440$  and  $1448\text{ cm}^{-1}$ . This argument also rules out H located at the  $H$  site. H located at the  $T$  site can be excluded because it has cubic ( $T_d$ ) symmetry, in conflict with the uniaxial stress data. In contrast, all the observations are in accordance with the  $745\text{-cm}^{-1}$  line originating from isolated H displaced from the  $T$  site along a  $\langle 111 \rangle$  axis, e.g., towards the  $AB$  site. The large intensity of the  $745\text{-cm}^{-1}$  line furthermore suggests that the defect is in the negative charge state, consistent with the calculations by Denteneer *et al.* [19].

In summary, local vibrational modes of two distinct, isolated H defects have been observed in Ge by low-temperature, *in situ* infrared spectroscopy. The defect giving rise to the  $1794\text{-cm}^{-1}$  mode is identified as  $\text{H}_{BC}^{(+)}$ . The other defect, giving rise to an intense absorption line at  $745\text{ cm}^{-1}$  and two overtones at  $1480$  and  $1488\text{ cm}^{-1}$ , is ascribed to isolated  $\text{H}^{(-)}$  located on a  $\langle 111 \rangle$  axis near the tetrahedral site.

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[2] See *Hydrogen in Semiconductors II: Semiconductors and Semimetals*, edited by N.H. Nickel (Academic Press, New York, 1999), Vol. 61, and references therein.

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