

## Electronic Level of Interstitial Hydrogen in GaAs

B. Clerjaud, F. Gendron, and M. Krause<sup>(a)</sup>

*Laboratoire d'Optique de la Matière Condensée, Université Pierre et Marie Curie,  
4 Place Jussieu, F-75252 Paris CEDEX 05, France*

W. Ulrici

*Zentralinstitut für Elektronenphysik der Akademie der Wissenschaften der Deutschen Demokratischen Republik,  
DDR-1086 Berlin, German Democratic Republic*

(Received 22 March 1990)

The carbon-hydrogen complex in GaAs is evidenced by its stretching local mode of vibration. It is shown that even though carbon and hydrogen are present, this complex is not formed in *n*-type material; it only appears in *p*-type material. This is explained by the necessity for hydrogen to be in the positive charge state for the carbon-hydrogen complexes to be formed. The corresponding hydrogen electronic level is shown to be located around 0.5 eV above the top of the valence band.

PACS numbers: 61.70.At, 71.55.Eq, 78.50.Ge

It is now well established that hydrogen can passivate shallow and deep impurities in semiconductors.<sup>1,2</sup> However, a challenging issue is the understanding of the mechanisms of the formation of the hydrogen-impurity complexes and in particular the determination of the charge states of diffusing hydrogen.<sup>3</sup> In silicon experimental and theoretical results<sup>4-11</sup> suggest that diffusing interstitial hydrogen has both a donor and an acceptor level within the band gap. In elementary compound semiconductors, the knowledge about the charge state of diffusing hydrogen is poorer than in silicon; the diffusion characteristics of deuterium in *p*-type GaAs and InP suggest that in these materials, hydrogen diffuses as a positively charged species<sup>12</sup> and very recently the motion of positively charged hydrogen has been evidenced in *p*-type GaAs.<sup>13</sup> The aim of this Letter is to show that in GaAs, hydrogen is positively charged when the Fermi level is lower than 0.5 eV above the top of the valence band.

We have studied a whole GaAs ingot grown by the liquid encapsulation Czochralski (LEC) technique from a quartz crucible in a normal pressure puller; wet boric oxide was used for encapsulation. The ingot was intentionally doped with nickel whose concentration is in the range  $(0.3-1.2) \times 10^{16} \text{ cm}^{-3}$ . This impurity was chosen because it is known to act as a double acceptor;<sup>14-16</sup> because of its segregation it allows one to sweep the Fermi level through the ingot from the nickel double-acceptor level 0.4 eV below the conduction-band minimum at its seed end down to the first acceptor level of nickel 0.2 eV above the top of the valence band<sup>14-16</sup> at the tail end of the ingot. In addition to nickel, the ingot contains the usual residual contaminants of GaAs: silicon coming from the quartz crucible, carbon, sulfur, and iron. Hydrogen is also present, as in all the LEC-grown GaAs ingots,<sup>17,18</sup> the source of contamination being the water present in the encapsulant. The  $\text{Ni}^{2-}$ ,  $\text{Ni}^-$ , and  $\text{Fe}^-$  charge states are monitored by their internal optical ab-

sorptions whereas neutral nickel and iron are monitored by their electron paramagnetic resonance; all the experiments are performed at liquid-helium temperature and allow, by the detection of the different charge states of the impurities, a rough location of the Fermi level in every piece of samples studied. "Isolated" carbon- and hydrogen-related centers are studied by the infrared absorption of their local modes of vibration (LVM).

In the *n*-type (seed end) and semi-insulating parts of the ingot, one observes hydrogen-related LVMs slightly above  $2000 \text{ cm}^{-1}$  as already reported.<sup>17,18</sup> The centers responsible for these LVMs result from the complexing of hydrogen with lattice defects; the main one characterized by a LVM at  $2001 \text{ cm}^{-1}$  has been attributed to a gallium vacancy having one of its dangling bonds saturated by hydrogen.<sup>19</sup> The well-known LVM absorption line at  $582 \text{ cm}^{-1}$  due to isolated carbon is strongly observed in this part of the ingot.

In the *p*-type part of the ingot (tail end), none of the "usual" hydrogen-related LVM lines around  $2000 \text{ cm}^{-1}$  are observed. However, a rather strong absorption line is observed at  $2635.13 \text{ cm}^{-1}$ . To our knowledge, this absorption which is shown in Fig. 1 has not been published up to now.<sup>20</sup> When the temperature is raised up to more than 100 K, this transition stays quite sharp which means that it has a vibrational nature. As the energy of this LVM is very high, a very light impurity must be involved and, in fact, hydrogen is the most likely candidate. The energy of this LVM is too high for hydrogen to be bonded to an arsenic atom (as is the case for the LVMs around  $2000 \text{ cm}^{-1}$ ) or to a gallium atom. This means that hydrogen must be bonded to an impurity atom. If one looks carefully at Fig. 1, one notices that a smaller line is present at  $2628.39 \text{ cm}^{-1}$ . The ratio of the intensities of the two lines is sample independent and slightly above 1%. This means that both lines are related: They correspond to the LVMs of two defects having the same microscopic structure but with two different

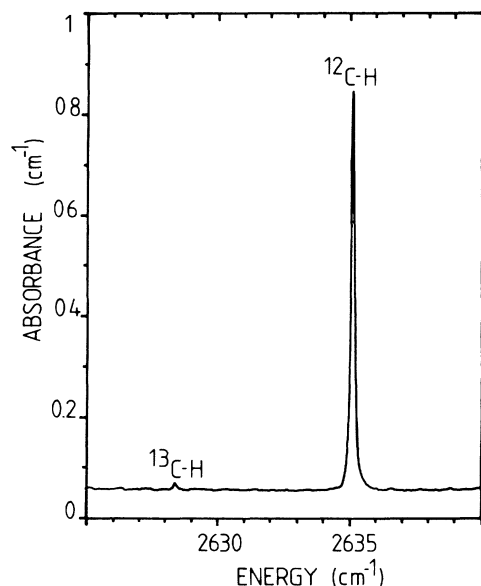


FIG. 1. Absorption of the C-H local modes of vibrations. Both  $^{12}\text{C}$ - and  $^{13}\text{C}$ -related modes can be observed.

isotopes of the impurity. This allows one to determine the impurity to which hydrogen is bonded as we know that the ratio of the natural abundance of the heavy isotope to the light isotope is slightly above 1%. A check of an isotope table indicates that the best candidate is carbon as  $[^{13}\text{C}]/[^{12}\text{C}] = 1.12\%$ . The observed isotopic shift confirms this assignment: The isotopic shift expected for an imaginary C-H molecule having an energy of vibration of  $2635\text{ cm}^{-1}$  (for  $^{12}\text{C}$ ) is  $-7.81\text{ cm}^{-1}$  whereas the observed one is  $-6.75\text{ cm}^{-1}$ . The fact that the observed value is below the calculated one is due to the extra bonding of the carbon atom to three gallium atoms. In order to support this assignment, we have looked at intentionally carbon-doped GaAs LEC-grown samples: In such samples these LVMs are also observed. We are therefore confident that this new LVM at  $2635.13\text{ cm}^{-1}$  and its associated isotopic one are due to the vibrations of C-H bonds. Additionally, we have performed experiments under uniaxial stress. It is out of the scope of the present Letter to detail their results; they show that the  $2635.13\text{-cm}^{-1}$  LVM corresponds to the stretching mode of vibration of bonds aligned along trigonal axes of the sample. It is to be noted that we could not detect any wagging mode of vibration related with the same center. This means that the hydrogen atom is located in a bond-centered position rather than in an antibonding one. We are therefore able to specify the microscopic nature of the carbon-hydrogen complexes. This structure, which is schematized in Fig. 2, is analogous to the one proposed for  $\text{Si}_{\text{As}}\text{-H}$  complexes in GaAs;<sup>21</sup> it is reminiscent of that of the B-H complex in Si.<sup>22</sup> It is to be noted that the hydrogen passivation of carbon acceptors has been evidenced by transport and luminescence measurements,<sup>23,24</sup> but the direct evidence of the resulting com-

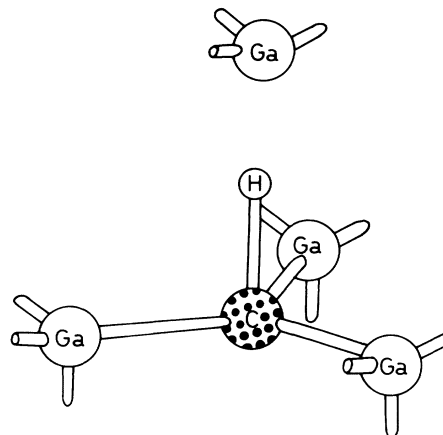


FIG. 2. Schematic representation of the C-H complex.

plexes has not been given up to now. The frequency of the C-H bond in GaAs is about 10% smaller than in molecules, whereas the frequencies of the equivalent Si-H and Ge-H bonds in GaAs<sup>21,25</sup> are about 5% smaller than in molecules; this quantitative difference is probably related with the smaller covalent radius of carbon.

Therefore, it is clear that even though carbon and hydrogen are present in GaAs independently of the Fermi-level location, C-H complexes are formed only in the *p*-type samples. Because of the Fermi-level location, the shallow carbon acceptors are negatively charged in all samples investigated. In order to form C-H pairs, Coulomb interactions require hydrogen to be positively charged. Therefore, we can conclude that "migrating" interstitial hydrogen is in a positive charge state (proton) in strongly *p*-type samples which is not the case in the *n*-type ones.

In order to locate the associated electronic level, we have investigated samples coming from all parts of the ingot. An important result is that there is virtually no part of the ingot where there is a coexistence of the hydrogen-related complexes giving rise to the LVM lines around  $2000\text{ cm}^{-1}$  with the C-H complex; in the few small samples (size  $\sim 1 \times 1 \times 1\text{ mm}^3$ ) where it is possible to observe both types of LVM lines it is quite likely that in fact there is no coexistence at all but juxtaposition of two different zones. The boundary between the two zones corresponds to the crossing between the Fermi level and the hydrogen-related electronic level. Therefore, the determination of the Fermi-level energy ( $E_F$ ) in this part of the ingot would directly give the energy of the electronic level associated with diffusing hydrogen. Fortunately, the study of the unintentional iron impurity allows this determination. Our measurements evidence a correlation between the  $\text{Fe}^-$  absorption and the LVMs around  $2000\text{ cm}^{-1}$ . In the small samples showing both the  $2000\text{-cm}^{-1}$  LVMs and the C-H ones, both  $\text{Fe}^0$  and  $\text{Fe}^-$  charge states are detected. This means that the Fermi level in these samples is close to the iron acceptor

level. This level is well known to be around 0.5 eV above the top of the valence band.<sup>16</sup> Therefore, the electronic level associated with interstitial diffusing hydrogen is located at about 0.5 eV above the top of the valence band ( $E_v$ ).

The above discussion is strictly valid at zero temperature; however, the hydrogen-related complexes are formed during the cooling stage of the process at temperatures of a few hundred degrees centigrade, most probably below 500°C. At 500°C, the carrier concentration below which GaAs becomes intrinsic (Fermi level at midgap) is  $10^{15} \text{ cm}^{-3}$ .<sup>26</sup> In our samples, the total impurity concentration is in the  $10^{16}\text{-cm}^{-3}$  range. This means that in the material we have investigated, up to temperatures around 700°C, the Fermi level is still governed by impurities. Therefore, we believe that our previous conclusions remain true.

The validity of our conclusion rests on the assumption that there is no reaction that involves the capture of free carriers. For instance, one could imagine a dissociation of the C-H complexes according to the reaction  $\text{C-H} + e \rightarrow \text{C}^- + \text{H}^0$ ,  $\text{H}^0$  being trapped by the lattice defects to form complexes with them. The electron  $e$  should come from an impurity when the Fermi level rises. One could think of an iron effect according to the reaction  $\text{Fe}^- \rightarrow \text{Fe}^0 + e$ ; but in such a case, the observation of hydrogen-lattice defects should be accompanied by the observation of  $\text{Fe}^0$  which is in contradiction with our experimental observations. The same conclusions would be reached when considering the effect of other impurities or defects present in the samples. We are therefore confident of having located an electronic level associated with migrating hydrogen.

It is not clear to us how the hydrogen-related complexes giving rise to the LVM lines around  $2000 \text{ cm}^{-1}$  are formed. Therefore, we cannot specify with certainty what is the charge state of hydrogen when the Fermi level is above  $E_v + 0.5 \text{ eV}$ . Two hypotheses can be done: either hydrogen is neutral or negatively charged. If hydrogen is neutral when  $E_F > E_v + 0.5 \text{ eV}$ , then our results evidence that the deep donor level associated with interstitial hydrogen is at  $E_v + 0.5 \text{ eV}$ . In the second case, if hydrogen is negatively charged when  $E_F > E_v + 0.5 \text{ eV}$ , then hydrogen is a "negative- $U$ " impurity; i.e., its acceptor level is below the donor one. In such a case, the level we have evidenced at  $E_v + 0.5 \text{ eV}$  would be the occupancy level  $E(-, +)$  located midway between the hydrogen donor and acceptor levels. Our results do not allow one to discriminate between these two possibilities.

It is to be noted that in silicon-doped strongly  $n$ -type samples (not issued from the ingot described in this paper), we have simultaneously observed the LMVs around  $2000 \text{ cm}^{-1}$  (already observed in samples when the Fermi level is just above  $E_v + 0.5 \text{ eV}$ ) and the  $\text{Si}_{\text{Ga}}\text{-H}$  one. This could indicate that the same charge state of hydrogen is involved in the formation of the  $2000\text{-cm}^{-1}$  com-

plexes and the  $\text{Si}_{\text{Ga}}\text{-H}$  one. This would mean that there is only one possible hydrogen charge state when  $E_F > E_v + 0.5 \text{ eV}$  and therefore that there is no other hydrogen electronic level in the GaAs band gap. Therefore, our results do not support the suggestion that hydrogen has a donor level in the upper half of the GaAs band gap.<sup>27</sup>

It is of importance to note that the concentration of isolated carbon decreases by a factor of 4 when passing from the zone where the Fermi level is above the hydrogen-related level to the zone where it is below this level. This confirms that carbon is involved in the  $2635\text{-cm}^{-1}$  LVM. We did not observe any LVM in the  $600\text{-cm}^{-1}$  region which could be due to complexed carbon.

In this Letter we have shown that interstitial hydrogen has an electronic level within the GaAs band gap which is very close to the iron acceptor level, i.e., about 0.5 eV above the top of the valence band. It is to be noted that in iron-doped semi-insulating InP, where the Fermi level is pinned by the iron acceptor level, one observes in the same sample the LVMs of defects resulting from the neutralization of zinc acceptors by hydrogen and of hydrogen-lattice defect complexes.<sup>12</sup> One could question whether, also in InP, interstitial hydrogen has an electronic level close to the iron acceptor level, i.e., around 0.8 eV above the top of the valence band.<sup>16</sup>

The Laboratoire d'Optique de la Matière Condensée is a unité associée au Centre National de la Recherche Scientifique. We are very grateful to D. Côte, C. Naud, B. Pajot, and M. Stavola for very helpful discussions.

<sup>(a)</sup>Present address: Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, D-1000 Berlin 45, Germany.

<sup>1</sup>S. J. Pearton, J. W. Corbett, and T. S. Shi, *Appl. Phys. A* **43**, 153 (1987).

<sup>2</sup>J. Chevallier and M. Aucouturier, *Annu. Rev. Mater. Sci.* **18**, 219 (1988).

<sup>3</sup>N. M. Johnson, in *Proceedings of the Workshop on Hydrogen Effects in InP and Related Compounds*, Lannion, France, 1989 (unpublished).

<sup>4</sup>A. J. Tavendale, D. Alexiev, and A. A. Williams, *Appl. Phys. Lett.* **47**, 316 (1985).

<sup>5</sup>N. M. Johnson, *Appl. Phys. Lett.* **47**, 874 (1985).

<sup>6</sup>M. Capizzi and A. Mittiga, *Appl. Phys. Lett.* **50**, 918 (1987).

<sup>7</sup>S. T. Pantelides, *Appl. Phys. Lett.* **50**, 995 (1987).

<sup>8</sup>T. Zundel, A. Mesli, J. C. Muller, and P. Siffert, *Appl. Phys. A* **48**, 31 (1989).

<sup>9</sup>N. M. Johnson and C. Herring, *Mater. Sci. Forum* **38-41**, 961 (1989).

<sup>10</sup>A. J. Tavendale, S. J. Pearton, and A. A. Williams, *Appl. Phys. Lett.* **56**, 949 (1990).

<sup>11</sup>J. Zhu, N. M. Johnson, and C. Herring, *Phys. Rev. B* **41**, 12534 (1990).

<sup>12</sup>J. Chevallier, B. Clerjaud, and B. Pajot, in "Hydrogen in

Semiconductors," edited by J. I. Pankove and N. M. Johnson, Semiconductors and Semimetals Vol. 34 (Academic, Orlando, to be published).

<sup>13</sup>A. J. Tavendale, S. J. Pearton, A. A. Williams, and D. Alexiev, Appl. Phys. Lett. **56**, 1457 (1990).

<sup>14</sup>B. Clerjaud, J. Phys. C **18**, 3615 (1985).

<sup>15</sup>B. Clerjaud, in *Current Issues in Semiconductor Physics*, edited by A. M. Stoneham (Adam Hilger, Bristol, 1986), p. 117.

<sup>16</sup>B. Clerjaud, in *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology*, edited by M. Schulz (Springer-Verlag, Berlin, 1989), Group III, Vol. 22b.

<sup>17</sup>B. Clerjaud, D. Côte, and C. Naud, Phys. Rev. Lett. **58**, 1775 (1987).

<sup>18</sup>B. Clerjaud, D. Côte, M. Krause, and C. Naud, Mater. Res. Soc. Symp. Proc. **104**, 341 (1988).

<sup>19</sup>B. Clerjaud, M. Krause, C. Porte, and W. Ulrici, in *Proceedings of the Nineteenth International Conference on the Physics of Semiconductors, Warsaw, Poland, 1988*, edited by

W. Zawadski (Polish Academy of Sciences, Warsaw, 1988), p. 1175.

<sup>20</sup>This line is mentioned in D. Côte, thesis, Université Pierre et Marie Curie, 1988 (unpublished).

<sup>21</sup>J. Chevallier, B. Pajot, A. Jalil, R. Mostefaoui, R. Rahbi, and M. C. Boissy, Mater. Res. Soc. Symp. Proc. **104**, 337 (1988).

<sup>22</sup>J. I. Pankove, P. J. Zanzucchi, C. W. Magee, and G. Lukowski, Appl. Phys. Lett. **46**, 421 (1985).

<sup>23</sup>N. Pan, S. S. Bose, M. H. Kim, G. E. Stillman, F. Chambers, G. Devane, C. R. Ito, and M. Feng, Appl. Phys. Lett. **51**, 596 (1987).

<sup>24</sup>I. Szafranek and G. E. Stillman, Mater. Res. Soc. Symp. Proc. (to be published).

<sup>25</sup>R. Rahbi, B. Pajot, J. Chevallier, and M. Gavand (to be published).

<sup>26</sup>S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).

<sup>27</sup>S. J. Pearton, W. C. Dautremont-Smith, J. Lopata, C. W. Tu, and C. R. Abernathy, Phys. Rev. B **36**, 4260 (1987).