Nitrogen-Dihydrogen Complex in GaP

B. Clerjaud, D. Côte, W.-S. Hahn,* and A. Lebkiri
LOS, Université Pierre et Marie Curie, case 80, 4 place Jussieu, F-75252 Paris cedex 05, France

W. Ulrici
Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, D-10117 Berlin, Germany

D. Wasik
Institute of Experimental Physics, Warsaw University, Hoza 69, 00-681 Warsaw, Poland

(Received 5 August 1996)

Detailed infrared studies performed on GaP samples weakly doped with nitrogen and hydrogen have been performed. A trigonal defect involving nitrogen and a pair of nonequivalent hydrogen has been identified, with local vibrational modes at 2885.5, 2054.1, and 1049.8 cm^{-1} for the ^{14}N related complex. ^{14}N-^{15}N isotopic shifts have been observed for the two high wave number modes. All of these modes are attributed to a defect with one hydrogen in bond centered and the other one in antibonding positions around nitrogen. The two hydrogen atoms are bonded mainly to the same nitrogen atom. [S0031-9007(96)01841-8]

PACS numbers: 63.20.Pw, 78.30.Fs

Hydrogen in semiconductors has been a very active subject of investigation during the past years. It is presently known to form complexes with impurities [1]. Most of these defects are trigonal defects which involve only one hydrogen atom [1]. However, it has been reported [2–6] that transition metal impurities can form complexes which involve two hydrogen atoms; this is the case for copper in germanium [2,3] and for platinum in silicon [4–6].

Nitrogen belongs to the column *V* of the periodic table and is an isoelectronic impurity substituting phosphorus in GaP. Nitrogen doping of GaP is used for the production of light emitting devices. Singh and Weber [7,8] reported a reduction of the nitrogen excitonic luminescence after plasma hydrogenation of the samples; this result indicates that hydrogen and nitrogen interact in GaP.

We have performed a spectroscopic investigation of GaP samples containing nitrogen and hydrogen; in this Letter, we report on several local vibrational modes due to the nitrogen-hydrogen complex. Their analysis shows that the complex involves two hydrogen atoms.

The investigated samples are bulk GaP samples grown by the liquid encapsulation Czochralski (LEC) technique. They contain small concentrations of hydrogen ($\leq 10^{16}$ cm^{-3}) and nitrogen ($\leq 10^{17}$ cm^{-3}). Hydrogen is unintentionally present, as is usually the case for LEC grown samples [9–11]. It has been shown [11] that at least part of the contamination comes from the water contained in the wet boric oxide encapsulant. At such low nitrogen concentrations, practically no nitrogen pairs are formed, and only the excitonic luminescence of "isolated" nitrogen is observed. Some of the samples were doped with transition metal impurities which allows one to obtain high resistivity material with various Fermi level locations. The optical absorption experiments have been performed at 5 K using Bomem DA3+ and DA8 Fourier transform interferometers equipped with calcium fluoride or potassium bromide beam splitters and cooled indium antimonide or silicon bolometer detectors. Experiments under uniaxial stress at 5 K have also been performed.

In all the samples investigated in which the Fermi level lies between about 0.5 eV above the top of the valence band and 0.5 eV below the conduction band minimum, three "intense" local vibrational modes (LVMs) are observed at 2885.5, 2054.1, and 1049.8 cm^{-1}. They are displayed in Fig. 1. The highest wave number mode had already been reported and interpreted as being due to a nitrogen-hydrogen complex. It has been used as a probe for locating the donor level of diffusing hydrogen within the GaP energy gap [12]. The ratios of the integrated

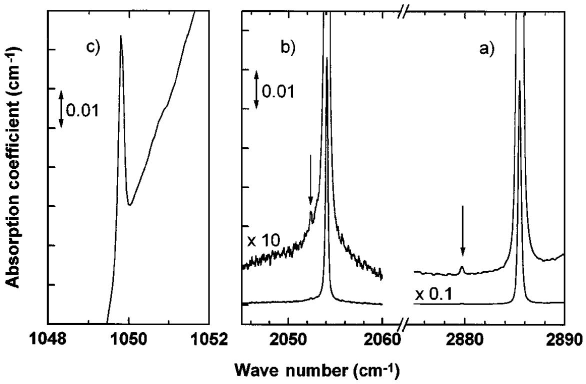

FIG. 1. The three local vibrational modes of the nitrogen-dihydrogen complex in GaP measured at 5 K. The two lines marked by an arrow involve ^{15}N isotope in natural abundance. (a), (b) The two stretching modes; (c) the transverse mode. The linewidths at half maximum are 0.3 cm^{-1} for the 2885.5 cm^{-1} mode, 0.25 cm^{-1} for the 2054.1 cm^{-1} mode, and 0.15 cm^{-1} for the 1049.8 cm^{-1} mode.

absorbances of these modes are sample independent and equal to $I_{2885}/I_{2054} = 9.5 \pm 0.5$ and $I_{2885}/I_{1050} = 25 \pm 3$. The accuracy of this last ratio is not excellent because, on the one hand, the intensity of the 1049.8 cm^{-1} line is not very large and, on the other hand, it is superimposed on a three phonon lattice absorption and a 5 cm^{-1} broad oxygen related line, and therefore the "base line" is not very accurately known. Moreover, it is possible to induce a decrease of the absorbances of these three modes by illumination, and, at all stages of the process, these ratios stay constant. This means that the three LVMs are local modes of the same complex.

If one looks carefully at the spectra of samples in which this complex is present in appreciable concentration, one clearly sees two weak LVMs in the low wave number vicinities of the 2885.5 and 2054.1 cm^{-1} lines at 2879.7 and 2052.4 cm^{-1}, respectively. These modes can be seen in Figs. 1(a) and 1(b). The integrated absorbance ratios I_{2880}/I_{2885} and I_{2052}/I_{2054} are both equal to 0.36%. This number corresponds to the natural abundance ratio between the ^{15}N and ^{14}N isotopes. Therefore, it can be concluded that the two modes at 2885.5 and 2054.1 cm^{-1} involve ^{14}N-H bonds. We did not observe any ^{15}N isotopic satellite to the 1049.8 cm^{-1} LVM, but the signal to noise ratio of the 1049.8 cm^{-1} absorption is lower than 1/0.0036 in all of our experiments and therefore too weak for allowing its observation.

In order to determine the symmetry of the complex responsible for these LVMs and the nature of these modes, we have performed absorption experiments under uniaxial stress. There is insufficient space for giving all the details concerning the results of these experiments. All the obtained data show a linear behavior as a function of the applied stress. The two high wave number intense modes at 2885.5 and 2054.1 cm^{-1} are clearly stretching modes of a complex of trigonal symmetry. The piezospectroscopic coefficients [13] describing the behavior of these two modes under uniaxial stress are given in Table I(a).

The 1049.8 cm^{-1} mode splits in two under tetragonal uniaxial stress. The high wave number component is observed only when the electric field vector of the infrared radiation is perpendicular to the stress axis. The low wave number mode is observed with both polarizations with an absorbance ratio I_π/I_σ between the parallel and perpendicular polarizations around 4. Under trigonal stress, this LVM splits into three components, the two high wave number ones being observed only with the polarization perpendicular to the stress axis and the low wave number one with parallel polarization. When the uniaxial stress is applied along a $\langle 110 \rangle$ twofold axis, two components are detected: the low wave number one being polarized parallel to $\langle 110 \rangle$ and the high wave number one parallel to $\langle 1\bar{1}0 \rangle$. The data with stress along fourfold and threefold axes are fully consistent with the behavior of a transverse mode of a complex of trigonal symmetry. However, in such a case, one would expect four components when the stress is applied along a twofold axis. Assuming that the mode is a transverse mode of a trigonal complex, one can extract the four piezo-spectroscopic coefficients [14] from the data obtained with the stress parallel to the fourfold and threefold axes. With this set of coefficients, one can calculate the expected behavior under $\langle 110 \rangle$ applied stress; the observed lines are well predicted and we find that the missing modes, which should be three times weaker than the observed ones, are predicted to be in the high wave number tails of the observed ones. Therefore, even at the highest stress, they could not be resolved. The 1049.8 cm^{-1} mode can be attributed consistently to a transverse mode of a trigonal complex. Its piezospectroscopic coefficients are given in Table I(b).

$\langle 110 \rangle$ stress applied at room temperature does not induce any dichroism at low temperature once the stress is released. This means that the complex does not reorient among its four energetically equivalent configurations at room temperature.

Therefore it can be concluded from the experiments reported here that the three main LVMs observed belong to the same trigonal defect and that the two longitudinal ones involve N-H bonds. It must be noted that the frequencies of the two stretching modes are relatively low compared with those observed for ammonia molecules (3444 cm^{-1}) or even compared with the N-H complex in ZnSe [15,16] (3193 cm^{-1}). The complex contains only one nitrogen atom since (i) the nitrogen concentration is too small for nitrogen pairs to be formed, and (ii) if these pairs were existing they would interact with hydrogen only in p-type samples in which the Fermi level is lower than 0.3 eV above the valence band maximum [17,18], which is not the case for the samples investigated in this work. The complex must contain two hydrogen atoms to account for two "high" wave number stretching modes; in order to respect the trigonal symmetry, the only way is to have the two N-H bonds located on each side of the nitrogen atom along one of the trigonal axes, i.e., to have one hydrogen in bond center and the second one in antibonding locations

TABLE I. Piezospectroscopic coefficients of the local vibrational modes of the nitrogen-dihydrogen complex in GaP. The coefficients are expressed in units of cm^{-1}/GPa. Compressive stress is taken positive.

(a) Stretching modes of vibration. The definition of the coefficients is given in Ref. [13].

Mode (cm^{-1})	A_1	A_2
2885.5	−2.0	−3.8
2054.1	1.3	−0.1

(b) Transverse mode of vibration. The definition of the coefficients is given in Ref. [14].

Mode (cm^{-1})	A_1	A_2	B	C
1049.8	0.61	0.06	0.57	1.6

around the nitrogen. The complex is schematically shown in Fig. 2. The investigation of samples codoped with hydrogen and deuterium should ultimately confirm that two hydrogen atoms are involved in the complex. Moreover, it would provide information on the interactions between hydrogen and deuterium in the same complex. As a matter of fact, the wetting of the boric oxide encapsulant has been shown to be a suitable technique for doping *III-V* compounds in the bulk with deuterium [11,19]. Unfortunately, we did not succeed in obtaining such samples.

Some facts concerning the stretching modes seem *a priori* surprising: (i) The low wave number mode absorption is about ten times less intense than the high wave number one, and (ii) the ^{14}N-^{15}N isotope shift is much smaller for the low wave number mode than for the high wave number one. These facts can be understood qualitatively on the basis of the proposed model. If one considers a symmetric H-N-H "molecule," it has two stretching modes: a symmetric one and an antisymmetric one at higher energy than the symmetric one. The symmetric mode is infrared inactive, as it does not induce any electric dipole and it does not have any ^{14}N-^{15}N isotope shift as the nitrogen does not move in that mode. If one now considers a nonfully symmetric H-N-H molecule, then the "symmetric" mode will become weakly infrared active and it will show a weak ^{14}N-^{15}N isotope shift as it is observed for the 2054.1 cm^{-1} mode. One can make a rough estimate of the asymmetry of the complex in the frame of a harmonic model of the molecule. The analysis of the wave numbers of the stretching modes of the ^{14}N complex allows the estimation of the spring constants k_1 and k_2 associated with the two N-H bonds: $\frac{1}{2\pi c}\sqrt{\frac{k_i}{m_H}} = 2781$ and 1993 cm^{-1} for $i = 1$ and 2, respectively; m_H is the hydrogen atom mass and c the speed of light in empty space. Using these values, one can calculate the ^{14}N-^{15}N isotope shifts: 7.2 cm^{-1} for the "antisymmetric" mode and 3.4 cm^{-1} for the symmetric one. Both of these values are about 1.5 cm^{-1} higher than the experimentally observed ones. This is not surprising as we used a harmonic model, whereas it is well known [20,21] that anharmonicity plays a crucial role in the determination of these values as well as the coupling of the complex to the lattice [22]; our aim is only to provide a qualitative explanation. With the k_i values given above, each normal stretching mode of vibration of the molecule implies mainly the motion of one of the hydrogen atoms. In fact, the asymmetric environment of the molecule not only affects the spring constants but it also discriminates between the "effective charges" associated with the 2054.1 cm^{-1} and 2885.5 cm^{-1} modes. Therefore the H-N-H model is in qualitative agreement with the observations.

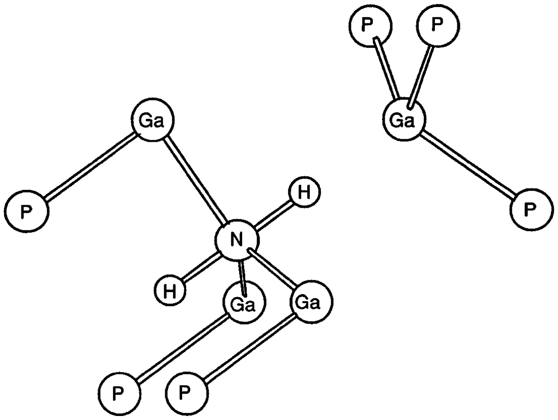

FIG. 2. Schematic representation of the complex.

The experiment does not allow one to state directly which of the N-H bonds has the higher spring constant. Usually, a bond between the same chemical species (for instance, Si-H) has a higher spring constant when it is in a bond centered location than when it is in an antibonding position [1,23,24]. It is also known that, for the Si-H bond in GaAs, the silicon isotope shifts are much smaller than expected from a crude calculation when hydrogen sits in antibonding location [25]. This is also the case in GaAs, where the gallium isotope shift is not observed for Ga-H bonds when hydrogen is in an antibonding site [26–28]. Finally, the effective charges are about three times larger when the moving hydrogen is in a bond centered location than when it is in an antibonding location [29]. This means that the intensity of the mode corresponding to a large motion of the bond centered hydrogen should be 1 order of magnitude larger than for the one involving large movement of hydrogen in an antibonding location. All these arguments lead us to assign the weak bond to hydrogen in the antibonding site and the strong one to bond centered hydrogen. It has to be noted that a harmonic spring calculation including a bonding between the bond centered hydrogen and its gallium nearest neighbor leads to assigning the weakest N-H bond to the bond centered hydrogen [30]. As mentioned earlier, harmonic calculations are not very reliable. Up to now, transverse modes have only been observed when hydrogen is in an antibonding location in semiconductors. Therefore, the 1049.8 cm^{-1} mode is likely due to a transverse motion of the hydrogen in the antibonding location.

In the model represented in Fig. 2, nitrogen looks fivefold coordinated. It has to be noted that, to our knowledge, no molecule with fivefold coordinated nitrogen exists (contrary to phosphorus or arsenic). It is the effect of the crystal which allows nitrogen to be fivefold coordinated in our case. As a matter of fact, in a solid, it should be more appropriate to discuss coordination in terms of electron local density rather than in terms of the number of bonds.

H_2^* defects are trigonal hydrogen related defects which contain two hydrogen atoms located at bond centered and antibonding locations around a host atom. In these centers, which do not involve any extra impurity, the two hydrogen atoms are bonded to first neighbor host atoms. They have been theoretically predicted in diamond [31], silicon [32] and GaAs [33]. To our knowledge, such a defect has only been identified in silicon [34] and germanium [35] up to now. In spite of intensive efforts, we have been unable to observe any evidence of an H_2^* center in GaAs and GaP. In GaP, the partial replacement of phosphorus by nitrogen allows dihydrogenated complexes to be formed. The special nitrogen behavior is very likely related to the large electronegativity of nitrogen and its affinity for hydrogen. In this respect, it would be of interest to investigate experimentally hydrogen in materials such as GaN in order to know whether any H_2^* exists in this material and whether its structure is of the type reported in this Letter.

In this Letter, it has been shown that isolated nitrogen binds two hydrogen atoms, one in a bond centered and one in an antibonding location in GaP, in order to form a new type of trigonal complex. Further theoretical investigations such as those performed in Refs. [31–35] are necessary in order to fully analyze and verify this structure.

We thank C. Naud for the design of our uniaxial stress apparatus.

---

*Present address: Korea Telecom, 17 Seocho-ku Woomyun-dong, Seoul, Korea.

[1] S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer, Berlin, 1992).

[2] J. M. Kahn, L. M. Falicov, and E. E. Haller, Phys. Rev. Lett. **57**, 2077 (1986).

[3] J. M. Kahn, E. E. Haller, and L. M. Falicov, in *Proceedings of the 18th International Conference on Physics of Semiconductors*, edited by O. Engström (World Scientific, Singapore, 1987), p. 1003.

[4] P. M. Williams, G. D. Watkins, S. Uftring, and M. Stavola, Phys. Rev. Lett. **70**, 3816 (1993).

[5] M. Höhne, U. Juda, Yu. V. Martynov, T. Gregorkiewicz, C. A. J. Ammerlaan, and L. S. Vlasenko, Phys. Rev. B **49**, 13 423 (1994).

[6] S. J. Uftring, M. Stavola, P. M. Williams, and G. D. Watkins, Phys. Rev. B **51**, 9612 (1995).

[7] J. Weber and M. Singh, Mater. Res. Soc. Symp. Proc. **104**, 325 (1988).

[8] M. Singh and J. Weber, Appl. Phys. Lett. **54**, 424 (1989).

[9] B. Clerjaud, D. Côte, and C. Naud, Phys. Rev. Lett. **58**, 1755 (1987).

[10] B. Clerjaud, Physica (Amsterdam) **170B**, 383 (1991).

[11] B. Clerjaud, D. Côte, W.-S. Hahn, and W. Ulrici, Appl. Phys. Lett. **58**, 1860 (1991).

[12] B. Clerjaud, D. Côte, W.-S. Hahn, D. Wasik, and W. Ulrici, Appl. Phys. Lett. **60**, 2374 (1992).

[13] A. A. Kaplyanskii, Opt. Spektrosc. **16**, 602 (1964) [**16**, 329 (1964)].

[14] A. E. Hughes and W. A. Runciman, Proc. Phys. Soc. London **90**, 827 (1967).

[15] J. A. Wolk, J. W. Ager III, K. J. Duxstad, E. E. Haller, N. R. Taskar, D. R. Dorman, and D. J. Olego, Appl. Phys. Lett. **63**, 2756 (1993).

[16] A. Kamata, H. Mitsuhashi, and H. Fujita, Appl. Phys. Lett. **63**, 3353 (1993).

[17] B. Clerjaud, D. Côte, and W.-S. Hahn, Mater. Sci. Forum **148-149**, 281 (1994).

[18] M. Mizuta, Y. Mochizuki, N. Takadoh, and K. Asakawa, J. Appl. Phys. **66**, 891 (1989).

[19] F. X. Zach, E. E. Haller, D. Gabbe, G. Iseler, G. G. Bryant, and D. F. Bliss, J. Electron. Mater. **25**, 331 (1996).

[20] R. C. Newman, Semicond. Sci. Technol. **5**, 911 (1990).

[21] R. C. Newman, Physica (Amsterdam) **170B**, 409 (1991).

[22] S. N. Walck and W. B. Fowler, Phys. Rev. B **51**, 13 146 (1995).

[23] J. Chevallier, B. Clerjaud, and B. Pajot, in *Hydrogen in Semiconductors*, edited by J. I. Pankove and N. M. Johnson, Semiconductors and Semimetals (Academic, San Diego, 1991), Vol. 34, p. 447.

[24] M. Stavola, Mater. Sci. Forum **148-149**, 251 (1994).

[25] B. Pajot, R. C. Newman, R. Murray, A. Jalil, J. Chevallier, and R. Azoulay, Phys. Rev. B **37**, 4188 (1988).

[26] R. Rahbi, B. Theys, R. Jones, B. Pajot, S. Öberg, K. Somogyi, M. L. Fille, and J. Chevallier, Solid State Commun. **91**, 187 (1994).

[27] J. Vetterhöffer, J. H. Svensson, J. Weber, A. W. R. Leitch, and J. R. Botha, Phys. Rev. B **50**, 2708 (1994).

[28] J. Vetterhöffer and J. Weber, Phys. Rev. B **53**, 12 835 (1996).

[29] B. Clerjaud and D. Côte, J. Phys. Condens. Matter **4**, 9919 (1992).

[30] W.-S. Hahn, B. Clerjaud, D. Côte, F. Gendron, C. Porte, W. Ulrici, D. Wasik, and W. Wilkening, Mater. Sci. Forum **143-147**, 277 (1994).

[31] P. Briddon, R. Jones, and G. M. S. Lister, J. Phys. C **21**, L1027 (1988).

[32] K. J. Chang and D. J. Chadi, Phys. Rev. B **40**, 11 644 (1989).

[33] L. Pavesi and P. Giannozzi, Phys. Rev. B **46**, 4621 (1992).

[34] J. D. Holbech, B. Bech Nielsen, R. Jones, P. Sitch, and S. Öberg, Phys. Rev. Lett. **71**, 875 (1993).

[35] M. Budde, B. Bech Nielsen, R. Jones, J. Goss, and S. Öberg, Phys. Rev. B **54**, 5485 (1996).