

## Novel configuration of Mg-H complexes in GaN

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### ABSTRACT

We describe a novel configuration of the Mg-H complex in GaN, which is not the lowest-energy configuration at  $T=0$  but is stabilized at elevated temperatures by the large entropy associated with a set of low-energy rotational excitations. We focus on a comparison with two types of experimental results: (1) vibrational spectroscopy using polarized light [B. Clerjaud *et al.*, Phys. Rev. B **61**, 8328 (2000)]; and (2) ion-channeling [W. Wampler *et al.*, J. Appl. Phys. **90**, 108 (2001)]. New results on the predicted quantum-mechanical delocalization of the hydrogen atom and on the effect of replacing hydrogen with deuterium are reported.

### INTRODUCTION

Continued progress in nitride-based devices has been hampered by the limited carrier concentrations in *p*-type material. While various alternative dopants (such as Be) [1, 2, 3] are being explored, most efforts are still focused on improving the doping efficiency with Mg, the most widely used acceptor. Hydrogen is known to play an important role in *p*-type doping, and is abundantly present in the growth environment of many growth techniques used for GaN. Hydrogen passivates the acceptors during growth, rendering the as-grown material highly resistive. A post-growth anneal dissociates the Mg-H complexes, and removes the hydrogen from the vicinity of the acceptors, resulting in *p*-type conductivity. This process can be experimentally investigated by monitoring the local vibrational modes associated with the Mg-H complex. The stretching mode of this complex occurs at  $3125\text{ cm}^{-1}$ , and disappears during the activation process [4].

Despite the established role of hydrogen in the doping process, the details of the microscopic configuration of the Mg-H complex have proved elusive. A frequency of  $3125\text{ cm}^{-1}$  is too high to be associated with a Mg-H bond. Previous computational studies [5, 6] showed that H prefers to bond with a neighboring N atom rather than with the Mg acceptor itself. The vibrational frequencies were calculated for various configurations, and it was found that hydrogen in an antibonding position ( $AB_N$ ) provided the best agreement with the experimental frequency, whereas the bond-center (BC) configuration (H inserted in the bond between Mg and N) is energetically less favorable and yields a much higher vibrational frequency (by several  $100\text{ cm}^{-1}$ ). Since then, discussions of experimental results on Mg-H complexes [7, 8] have focused on the  $AB_N$  configuration. While those experiments have helped to rule out the BC configuration, they did not confirm the  $AB_N$  configuration, and in fact raised some questions about that assignment.

Clerjaud *et al.* [7] performed multitransmission infrared spectroscopy with polarized light. They found that the N-H bond is *not* aligned along the *c*-axis. In fact, they found that the N-H bond (or, at least the electric dipole induced by the mode) forms an angle of  $130\pm 5^\circ$  with the *c*-axis. This value is distinctly different from the  $109^\circ$  angle in the  $AB_N$  configuration.

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Wampler *et al.* [8] performed ion channeling, using an incident analysis beam of 850 keV  $^3\text{He}^+$  ions. Nuclear reaction analysis was used to detect the position of deuterium, using the  $^2\text{H}(^3\text{He},^1\text{H})^4\text{He}$  reaction, and the proton yield was measured as a function of (small) angles between the analysis beam and  $c$ -axis. Wampler *et al.* performed simulations of the yield results for various possible lattice locations of the hydrogen, including  $\text{AB}_{\text{N},\perp}$ ,  $\text{BC}_{\parallel}$ , and C (at the center of the hexagonal channel). Note that the notation “ $\parallel$ ” is used to indicate an orientation of the N-H bond parallel to the  $c$  axis, while  $\perp$  indicates the other orientations (at  $\sim 109^\circ$  with the  $c$  axis). None of the simulated channeling yield curves in Ref. [8] matches the measured one. Wampler *et al.* concluded that the measured yield reflects a mixture of at least two different configurations.

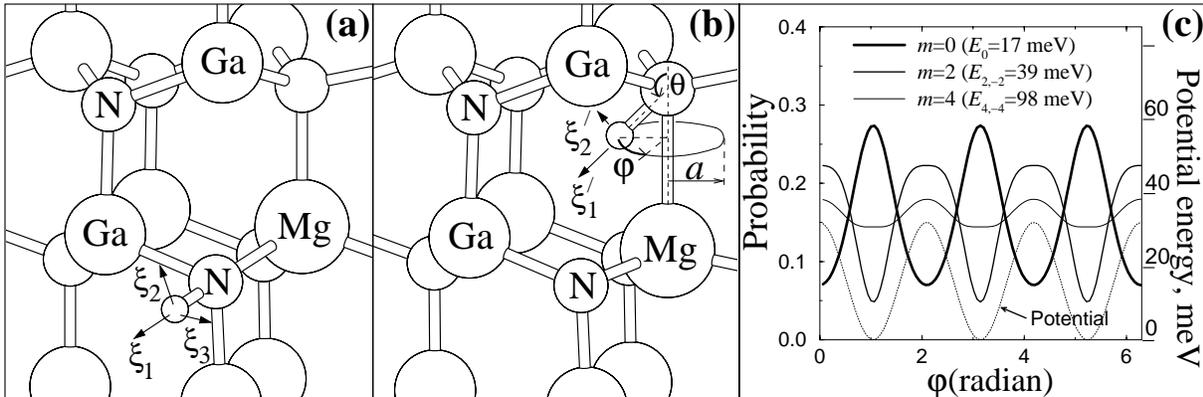


Figure 1: Perspective view of Mg-H complexes in (a) the  $\text{AB}_{\text{N},\perp}$  and (b) the  $\text{OA}_{\parallel}$  configurations. The path of H rotating around the bond axis is also shown in (b). (c) Quantum-mechanical probabilities to find H at an angle  $\varphi$  in the  $\text{OA}_{\parallel}$  configuration, for a few selected states (solid lines). The ground state (with energy 17 meV) is shown as a thick line, the 3rd excited state as a medium line (39 meV) and the 8th excited state as a thin line (98 meV). The potential used in the calculation is shown as a thin dashed line.

We have recently proposed a novel configuration of the Mg-H complex which is microscopically distinct from the  $\text{AB}_{\text{N}}$  and  $\text{BC}$  configurations. The N-H bond in this configuration, which we call  $\text{OA}_{\parallel}$  (for “off-axis”), forms an angle of  $134^\circ$  with  $c$ -axis, in very good agreement with the value  $130 \pm 5^\circ$  measured by Clerjaud *et al.* [7]. The  $\text{AB}_{\text{N}}$  and  $\text{OA}_{\parallel}$  configurations are illustrated in Fig. 1. The  $\text{OA}_{\parallel}$  configuration can be thought of as originating from a  $\text{BC}_{\parallel}$  configuration, but due to the large size of the Mg atom the hydrogen is pushed away from the bond axis. We find, indeed, that the  $\text{BC}$  configurations ( $\text{BC}_{\parallel}$  and  $\text{BC}_{\perp}$ ) are not stable, and that a small distortion leads to a relaxation towards the  $\text{OA}_{\parallel}$  configuration.

The  $\text{OA}_{\parallel}$  configuration is not the lowest-energy configuration at  $T=0$ , but is stabilized at high temperature due to a large entropy contribution. This contribution arises from low-energy rotational excitations: in the  $\text{OA}_{\parallel}$  configuration, the H is not locked into a single position, but can rotate almost freely around the Mg-N bond axis. The free-energy calculations have been described elsewhere [9] and will not be repeated here. In this paper we focus on interpretations of experimental results in light of the novel  $\text{OA}_{\parallel}$  configuration. In particular:

(i) It is unclear whether at the low temperature (5 K) used in the vibrational spectroscopy experiments [7] the hydrogen atom is quantum-mechanically delocalized or not. We will show, however, that even if the hydrogen is delocalized the procedure used in Ref. [7] to derive the angle with the  $c$  axis remains valid. This will involve a generalization of Eq. (1) of Ref. [7].

(ii) The projection of the hydrogen position on the [0001] plane for the  $OA_{\parallel}$  configuration is different from any of the positions used in the channeling-yield simulations of Wampler *et al.* [8]. We will argue that the  $OA_{\parallel}$  configuration may provide a suitable match to their experimental results.

(iii) Isotopic substitution is frequently employed in experimental studies of hydrogen in semiconductors. In fact, deuterium was used in the ion-channeling studies of Ref. [8]. We will investigate the effect of isotopic substitution on the free energy of the  $OA_{\parallel}$  configuration, in order to address whether the stabilization of  $OA_{\parallel}$  also holds in the case of deuterium.

## QUANTUM-MECHANICAL DELOCALIZATION

The  $AB_{N,\perp}$  and  $OA_{\parallel}$  configurations are illustrated in Fig. 1. Our calculated N-H bond stretching frequency is  $3092\text{ cm}^{-1}$  for  $AB_{N,\perp}$  and  $3109\text{ cm}^{-1}$  for  $OA_{\parallel}$ . The numbers quoted here include a systematic correction, based on a comparison between calculated and experimental results for  $NH_3$  [9]. Both of these frequencies are very close to the experimental value of  $3125\text{ cm}^{-1}$  [4, 7] and essentially indistinguishable within our calculational accuracy. In order to differentiate between these two configurations, one needs to invoke other experiments that can probe the geometry.

The  $OA_{\parallel}$  configuration has a low energy barrier ( $E_{b\varphi}=32\text{ meV}$ ) for H to orbit around the Mg-N bond [see Fig. 1(b)]. In the case of a free rotor ( $E_{b\varphi}=0$ ), H would exhibit equal probability to occur at any  $\varphi$ , even at  $T=0$ . For the case at hand, the corrugated potential causes an uneven but symmetric (three-fold symmetry imposed by the hexagonal crystal) distribution of the probability  $|\psi_m|^2$  to find H at the azimuthal coordinate  $\varphi$ . For simplicity, we replaced the corrugated potential with an approximation:  $V_{\varphi}(\varphi) = E_{b\varphi}(\cos 3\varphi + 1)/2$ . Since the energy barrier is low, H is delocalized and the probability is non-vanishing at all  $\varphi$ . In Fig. 1(c), the potential is shown with a thin-dashed line and probabilities  $|\psi_m|^2$  for selected states are shown in solid lines.

## DISCUSSION OF INFRARED SPECTROSCOPY RESULTS

Clerjaud *et al.* [7] used polarized infrared light to reveal additional details of the geometry of the Mg-H complex, in particular, the orientation of the electric dipole induced by the bond-stretching mode. They argued that, since hydrogen has the largest amplitude in the stretching-mode vibration, the direction of the dipole is roughly the same as the direction of the N-H bond. They found that the dipole forms an angle  $\theta = 130 \pm 5^\circ$  with the  $c$ -axis. Their conclusion was based on an analysis of the intensities of the lines obtained with different polarizations. In this analysis, it was assumed that the configuration would be static, and that H could occur in any of three equivalent configurations (imposed by the hexagonal symmetry). Here we generalize the analysis of the polarized-light measurements in Ref. [7] to include the delocalization of the hydrogen that occurs in the  $OA_{\parallel}$  configuration.

Clerjaud *et al.* wrote the intensity as a summation over three equivalent configurations:

$$I \propto \sum_{i=1}^3 \cos^2(\mathbf{E}, \mathbf{p}_i) = \sum_{i=1}^3 \left( \frac{\mathbf{E} \cdot \mathbf{p}_i}{E p_i} \right)^2. \quad (1)$$

$\mathbf{E}$  is the electric field of the light, and  $\mathbf{p}_i$  is the electric dipole induced by the vibration of a complex in configuration  $i$ . Applying this analysis to hydrogen in the  $OA_{\parallel}$  configuration, we have to take the delocalization into account. The angle  $\theta$  with the  $c$  axis remains

constant for all hydrogen locations, but hydrogen can occur at a continuum of angles  $\varphi$  [see Fig. 1(c)]. We define  $P(\varphi)$  as the probability that hydrogen appears at an angle  $\varphi$ . Threefold symmetry is maintained, since the probability  $P(\varphi)$  exhibits the symmetry of the crystal [see Fig. 1(c)]. The direction of the dipole is given by the unit vector  $\mathbf{u}(\varphi) = [\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta]$ . We can then write the generalization of Eq. (1) for the intensity of the light absorbed by the  $\text{OA}_{\parallel}$  configuration as:

$$I \propto \int_0^{2\pi} P(\varphi) \left( \frac{\mathbf{E} \cdot \mathbf{p}}{E p_0} \right)^2 d\varphi = \int_0^{2\pi} P(\varphi) \left( \frac{\mathbf{E} \cdot \mathbf{u}(\varphi)}{E} \right)^2 d\varphi \quad (2)$$

We explicitly evaluated Eq. (2) for  $\mathbf{E}_{\text{TE}} = E[1, 0, 0]$  and  $\mathbf{E}_{\text{TM}} = E[0, \sin \alpha, \cos \alpha]$ ,  $\alpha$  defining the angle of the electric field inside the GaN crystal for the TM mode, and taking into account the symmetry of  $P(\varphi)$ . This results in:

$$\frac{I_{\text{TE}}}{I_{\text{TM}}} = \frac{\sin^2 \theta}{(3 \cos^2 \alpha - 1) \cos^2 \theta + \sin^2 \alpha}. \quad (3)$$

This is exactly the same result as reported by Clerjaud *et al.* for the “static” case. Our derivation confirms that the analysis and conclusions of Ref. [7] are equally valid in the case of delocalization of the hydrogen atom, as in the  $\text{OA}_{\parallel}$  configuration.

## DISCUSSION OF ION CHANNELING RESULTS

Wampler *et al.* [8] have investigated hydrogen configurations in Mg-doped GaN with ion channeling. They used deuterium instead of hydrogen in order to enable its detection by nuclear reaction analysis (NRA), at room temperature. The angle of the analysis beam (850 keV,  $^3\text{He}^+$  ions) is varied from varied from  $0^\circ$  up to  $2^\circ$  with respect to the  $c$ -axis. For off-axis measurements azimuthal averaging was used. The proton yield was measured as a function of incident beam angle, and simulations of the yield were performed for various configurations of H in the wurtzite lattice. Those configurations are illustrated in Fig. 2.

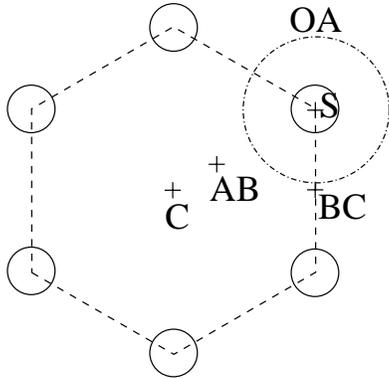


Figure 2: Lattice locations considered for the analysis of ion-channeling measurements by Wampler *et al.* [8]. Projected positions of hydrogen in the  $\text{OA}_{\parallel}$  configuration are shown as the dash-dotted circle.

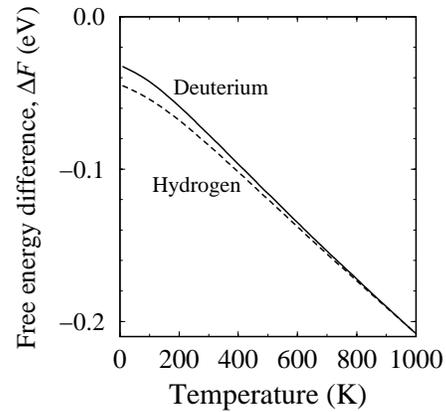


Figure 3: Free energy differences between  $\text{AB}_{\text{N},\perp}$  and  $\text{OA}_{\parallel}$  configurations of Mg-H and Mg-D complexes as a function of temperature.

The simulated yield curves (Fig. 2 of Ref. [8]) have distinctive features that can be understood by inspection of the crystal geometry. Curve C, corresponding to the center of the open channel, exhibits a narrow peak, corresponding to maximum yield when the

analysis beam is parallel to the  $c$ -axis. The C configuration could include isolated interstitial H in the neutral or negative charge states, as well as  $H_2$  molecules. The AB curve is similar to the C curve, although the central peak is lower because H is now closer to the host atoms. This location would be appropriate for the  $AB_{N,\perp}$  configuration of the Mg-H complex (or of isolated H). On the other hand, the S curve, corresponding to a location in-line with the host atoms, exhibits a broad dip, corresponding to minimum yield at  $0^\circ$  because the H atoms are then completely blocked by the host atoms. Once the beam is moved off-axis the H atoms are exposed. We note that the S curve would include  $BC_{\parallel}$  as well as  $AB_{N,\parallel}$  configurations. We found the former to be unstable, while the latter is about 0.3 eV higher in energy than  $AB_{N,\perp}$ . The BC site, finally, which corresponds to  $BC_{N,\perp}$ , also produces a dip, but it is narrower than in the S curve. Again, we found BC sites to be unstable in our calculations.

Experimentally, the clearest results were obtained for “gas charged” samples, which were exposed to deuterium gas at 88 kPa and 700 °C for 4 hours [8]. Other hydrogenation methods (plasma charging or implantation) carry the risk of introducing damage and exhibit a higher degree of hydrogen incorporation in configurations other than Mg-H complexes. The measured yield for the gas-charged sample exhibits a narrow peak at the center (comparable to the AB simulation) plus a broad dip, comparable to the S simulation. In order to fit this yield, Wampler *et al.* had to assume that 20% of the H was in AB sites, 30% in S sites, and 50% was randomly placed. They pointed out that this result seems to conflict with the expectation that most of the hydrogen should be in the lowest-energy configuration, which was thought to be  $AB_{N,\perp}$  for the Mg-H complex. They suggested that hydrogen might be excited into higher energy configurations, possibly due to hot electrons produced by the channeling analysis ion beam.

Here we propose that the features observed in the measured yield curve can be explained by invoking the  $OA_{\parallel}$  configuration of Mg-H complexes. At room temperature, H in  $OA_{\parallel}$  is orbiting around Mg-N bond (along the  $c$  axis), with almost equal probability of occurring at any azimuthal angle. The projection of the hydrogen path is shown in Fig. 2. The nature of this configuration leads us to expect that the features it would produce in a yield curve would be some combination of the AB, S, and BC curves. We also point out that, in addition to the quantum-mechanical delocalization associated with the angle  $\varphi$ , H at  $OA_{\parallel}$  also exhibits a sizable vibrational amplitude due to a relatively low-frequency bending mode [coordinate  $\xi'_2$  in Fig. 1(b)]. In addition to this classical motion, H may exhibit some quantum-mechanical delocalization in the direction towards the Mg-N bond as well: indeed, while our calculations show  $BC_{\parallel}$  to be unstable, this configuration is only about 0.1 eV higher in energy than  $OA_{\parallel}$ , raising the possibility of tunneling through the bond. All these contributions enhance the “S like” appearance of the yield for  $OA_{\parallel}$ . We also note that the quantum-mechanical delocalization of hydrogen (as opposed to being located at discrete sites) may enhance the appearance of being located in random sites, as was found to be necessary for 50 % of the hydrogen in the simulations of Wampler *et al.* [8]. An explicit simulation of the yield curve for the  $OA_{\parallel}$  configuration would of course provide a firmer confirmation of our proposal.

## DIFFERENCES BETWEEN HYDROGEN AND DEUTERIUM

Deuterium is often used in experimental studies of hydrogen in semiconductors. Using deuterium helps to overcome the sensitivity problems associated with hydrogen in secondary ion mass spectroscopy (SIMS). Vibrational spectroscopy studies often use D to check for isotope shifts, which can help in identification of local vibrational modes. And, as we saw above, the ion channeling studies of Wampler *et al.* [8] were carried out with

deuterium to take advantage of the  ${}^2\text{H}({}^3\text{He}, {}^1\text{H}){}^4\text{He}$  reaction.

The  $\text{OA}_{\parallel}$  configuration of the Mg-H complex is stabilized at elevated temperatures due to the large entropy associated with low-frequency rotational excitations. These excitations are sensitive to the mass of the hydrogen atom. It is therefore important to investigate the differences that occur upon replacing hydrogen with deuterium. We examined the difference in free energies  $\Delta F$  due to vibrational and rotational excitations:  $\Delta F = F' - F$ , where  $F'$  and  $F$  are the free energies of  $\text{OA}_{\parallel}$  and  $\text{AB}_{\text{N},\perp}$  configurations, respectively. The free energies were evaluated following the calculational approach outlined in Ref. [9].

The individual components of the free energy (corresponding to stretching, bending, and rotational excitations) incur sizable changes when we replace H by D. It turns out, however, that those changes largely cancel, producing only a small change in  $\Delta F$ . As can be seen in Fig. 3,  $\Delta F$  for deuterium is very similar to that of hydrogen, particularly in the temperature range of interest for stabilization of the  $\text{OA}_{\parallel}$  configuration. For all the temperatures of interest, the  $\Delta F$  values for H and D differ by less than 0.01 eV. Replacing H with D therefore does not affect our conclusions about the stabilization of the  $\text{OA}_{\parallel}$  configuration at elevated temperatures.

## CONCLUSIONS

We have discussed a novel configuration for the Mg-H complex in GaN ( $\text{OA}_{\parallel}$ ) that is consistent with the recent polarized infrared spectroscopy results of Clerjaud *et al.* [7]. In the  $\text{OA}_{\parallel}$  configuration the N-H bond forms a  $134^\circ$  angle with the  $c$ -axis, in good agreement with the  $130\pm 5^\circ$  measured in Ref. [7]. We have shown that the quantum-mechanical delocalization of the hydrogen does not affect the the analysis leading to the conclusions of Ref. [7]. We also discussed the ion-channeling experiments of Wampler *et al.* [8], pointing out that the  $\text{OA}_{\parallel}$  configuration may provide a better match to the measured yields. Finally, we verified that the entropy-driven mechanisms that stabilize the  $\text{OA}_{\parallel}$  configuration are only very weakly affected by an isotopic substitution (deuterium replacing hydrogen).

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