Entropy-Driven Stabilization of a Novel Configuration for Acceptor-Hydrogen Complexes in GaN

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We present a model for the microscopic structure of Mg-H complexes in GaN, explaining the unusual bond angle observed in recent vibrational spectroscopy studies. The structure is not the lowest-energy configuration at $T = 0$, but it is stabilized at elevated temperatures due to the large entropy associated with a set of low-energy rotational excitations. The rotational excitation spectrum is calculated using a quantum-mechanical model in which the hydrogen atom moves in a weak corrugation potential. Consequences for experiment are discussed.

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It is well known that hydrogen can passivate dopants in semiconductors, resulting in the formation of electrically inactive dopant-hydrogen complexes [1]. This process plays a critical role during the growth of acceptor-doped GaN, where incorporation of H results in complete neutralization of the acceptors. A post-growth anneal is required to remove H from the vicinity of the acceptors, yielding the desired p-type conductivity. A thorough understanding of complex formation and dissociation is deemed essential for optimizing the activation process and enhancing the conductivity. Experimentally, vibrational spectroscopy has proven an excellent tool for monitoring the presence of acceptor-hydrogen complexes [2]. Identification of the complex responsible for a particular line, however, is possible only in conjunction with first-principles theory. For instance, the local vibrational mode (LVM) at 3125 cm^{-1} observed in Mg-doped GaN [3,4] occurs at a much higher frequency than expected for Mg-H bonds. Computations have shown, however, that the hydrogen atom in the Mg-H complex is strongly bonded to a nitrogen neighbor of the Mg atom [see Fig. 1(a)], explaining the high frequency of the observed vibrational mode [5].

Recently, infrared spectroscopy using polarized light produced additional information about the Mg-H complex: Clerjaud *et al.* [4] found that the electric dipole induced by the vibration (which should roughly correspond to the orientation of the N-H bond) formed an angle of 130° with the c axis of the GaN wurtzite crystal. This large deviation from the expected angle of 109° in the $\mathrm{AB}_{\mathrm{N},\perp}$ (antibonding) configuration [see Fig. 1(a)] is very puzzling. Our calculations show that a distorted $\mathrm{AB}_{\mathrm{N},\perp}$ configuration in which the N-H bond forms an angle of 130° with the c axis (as shown in Ref. [4]) is unstable and immediately relaxes back to the regular configuration with $\theta = 109°$. The first goal of this Letter is to propose a new model for the configuration of the Mg-H complex, illustrated in Fig. 1(b): in this structure (which we label $\mathrm{OA}_{\parallel}$), the N-H bond is *not* aligned in the same direction as the Mg-N bond [as in Fig. 1(a)]; rather, the Mg-N bond is oriented (roughly) along [0001], and the interaction between H and the Mg atom changes the angle θ to approximately 130°. Both this angle and the calculated vibrational frequency for this structure (reported below) are in very good agreement with experiment [4]. However, one mystery remains: the calculated total energy of this configuration is *higher* (by 0.19 eV) than the energy of the $\mathrm{AB}_{\mathrm{N},\perp}$ configuration. The magnitude of this energy difference would render experimental observation of $\mathrm{OA}_{\parallel}$ very unlikely.

The second goal of this Letter is to provide an explanation for the stabilization of the 130° configuration. The relative occupation of the two configurations is determined at high temperatures, where the H atom is sufficiently mobile to explore various local minima. The stability of the candidate configurations is thus determined by their *free energy*. It turns out the 130° configuration gives rise to a set of low-energy excitations, which contribute significantly to the *entropy* of the complex. At sufficiently high temperatures the entropy term lowers the free energy of the

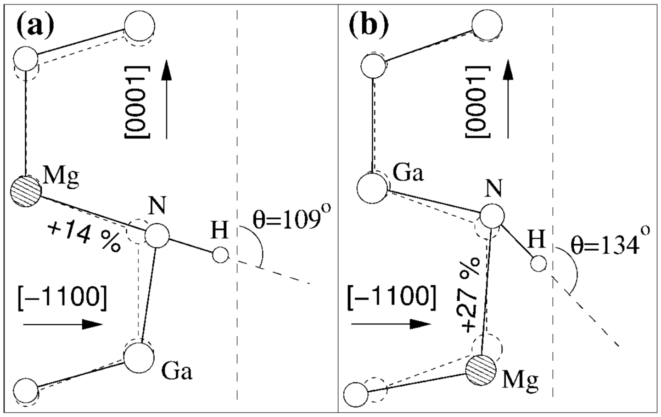

FIG. 1. Schematic representation of atomic positions in the (11-20) plane for a Mg-H complex in wurtzite GaN, with H at the (a) $\mathrm{AB}_{\mathrm{N},\perp}$ site and (b) $\mathrm{OA}_{\parallel}$ site. Large circles represent Ga atoms, medium circles N atoms, shaded circle the Mg atom, and the small circle the H atom. Dashed circles indicate ideal atomic positions, dashed lines bonds in the ideal lattice. Changes in Mg-N bond lengths are given as a percentage of change from the bulk Ga-N bond lengths.

$OA_{\parallel}$ configuration below that of $AB_{N,\perp}$. We will show quantitatively that this entropy-driven mechanism stabilizes the $OA_{\parallel}$ configuration at the temperatures relevant for the GaN:Mg-H system. Other consequences of the presence of low-energy excitations will be discussed.

Our results are based on first principles calculations using density functional theory in the local density approximation [6] and norm-conserving pseudopotentials, with a plane-wave basis set [7]. We have performed calculations both with explicit inclusion of the Ga $3d$ states (requiring a plane-wave cutoff of 60 Ry) and with the "nonlinear core correction" (nlcc) [8] (with a cutoff of 40 Ry); the results are not sensitive to this approximation, and the numbers reported below were obtained with the nlcc. A supercell geometry was employed, with supercells containing 32 or 64 atoms for zinc blende, and 32 or 96 atoms for wurtzite, with at least 24, 36, 24, and 46 atoms, respectively, allowed to relax. The larger supercells yield converged results for all the relevant energy differences, while the smaller cells are adequate for extracting the energy differences needed to calculate vibrational frequencies.

These frequencies are obtained by calculating energies for configurations in which the H is displaced from its equilibrium site, in accordance with a stretching- or bending-mode vibration. Because of the small mass of the H atom, displacements of the host atoms can be neglected; we have shown, by explicit comparison with evaluating the dynamical matrix [9], that this is a very good approximation, provided the reduced mass of the N-H system is used in evaluating the frequencies based on force constants. These constants are obtained from fitting a fourth-order polynomial to the calculated data points; the third- and fourth-order terms allow us to derive anharmonic corrections, which are sizable in the case of a light atom such as H [10]. The numerical error bars associated with this approach are fairly small, but a systematic error results from the fact that our pseudopotential-density-functional calculations overestimate the N-H bond length by 0.6%. We have checked the systematic nature of this deviation in a series of calculations on many different configurations of H in GaN as well as on NH_3 molecules [11]. The deviation results in an underestimation of the vibrational frequencies of stretch modes by 75 cm^{-1}.

The first step in our investigations is to establish all candidate configurations for the Mg-H complex. The AB_N and BC (bond center) configurations have previously been investigated for both the zinc-blende [5] and the wurtzite [12] structures, with the AB_N site showing lower energy. In the wurtzite structure, there are two types of each AB_N and BC: one type has threefold symmetry and is associated with bonds oriented parallel to the c axis; we label these sites $BC_{\parallel}$ and $AB_{N,\parallel}$. The other type is associated with the bonds that are *not* parallel to the c axis; although these are not exactly "perpendicular" to the c axis, we use the notation $BC_{\perp}$ and $AB_{N,\perp}$.

We find that the BC sites are not stable or even metastable sites for H. For instance, starting from $BC_{\parallel}$ and moving H slightly off the c axis causes this configuration to relax to the $OA_{\parallel}$ (off-axis) configuration illustrated in Fig. 1(b). This relaxation is caused by the large size of the Mg atom (covalent radius 1.36 Å) which squeezes the H out of the $BC_{\parallel}$ position to the $OA_{\parallel}$ position, where H is displaced by 0.79 Å from the ideal c-oriented Mg-N bond direction. The calculated angle between the N-H bond and the c axis is $\theta = 134°$. The size of the cation as the main driving force for the off-axis configuration is confirmed by comparison with other H-related centers in GaN: The small size of Be (covalent radius 0.90 Å) allows $BC_{\parallel}$ to remain most stable [9], while in pure GaN (Ga covalent radius 1.26 Å), only a very slight displacement (<0.15 Å) off the c axis occurs.

Results for energy differences and lattice relaxations for all relevant structures are listed in Table I. The $AB_{N,\perp}$ configuration [illustrated in Figs. 1(a) and 2(a)] has the lowest energy (which we set to zero in Table I). Next higher in energy is the $OA_{\parallel}$ configuration [illustrated in Figs. 1(b) and 2(b)]. The $OA_{\perp}$ configuration, which is the off-axis version of $BC_{\perp}$, has the highest energy. Within the accuracy of the calculations, $AB_{N,\perp}$ and $OA_{\parallel}$ have essentially the same N-H bond length and very similar vibrational frequencies for the stretch mode (3017 and 3034 cm^{-1}). As mentioned above, the calculated vibrational frequencies underestimate the real value by about 75 cm^{-1}; adding this correction brings the value for $OA_{\parallel}$ up to 3109 cm^{-1}, in very good agreement with the experimental value of 3125 cm^{-1}. While the vibrational frequency itself does not allow us to distinguish between $AB_{N,\perp}$ and $OA_{\parallel}$, the geometry of $OA_{\parallel}$, with the angle θ equal to 134°, is in excellent agreement with the polarized-light results of Clerjaud *et al.* [4], who derived $\theta = 130 \pm 5°$.

$OA_{\parallel}$ thus provides the best match to experiment; however, this configuration is *not* the lowest-energy structure, $AB_{N,\perp}$ being lower in energy by 0.19 eV. While this may seem like a small number, equilibrium occupation of the configurations at the temperatures of interest would result in the lower-energy configuration being overwhelmingly favored. We also expect sufficient accuracy (error bar smaller than ±0.1 eV) in our first-principles determination of this energy difference, because the relevant configurations differ only in the particular arrangement of the atomic

TABLE I. Calculated energy differences ΔE and lattice relaxations for Mg-H complexes in wurtzite GaN, for various lattice locations. The results were obtained from 96-atom supercell calculations. The global minimum ($AB_{N,\perp}$) is chosen as the zero of energy. Δd_{Mg} denotes the displacement of the Mg atom from its nominal lattice site, and Δd_N denotes the displacement of the N atom to which H is bonded, expressed as a percentage of the bond length. $d_{N\text{-}H}$ denotes the N-H distance in Å.

Configuration	ΔE (eV)	Δd_{Mg}	Δd_N	$d_{N\text{-}H}$ (Å)
$AB_{N,\perp}$	0.00	1.7%	14.6%	1.031
$OA_{\parallel}$	0.19	18.0%	10.6%	1.030
$AB_{N,\parallel}$	0.28	1.9%	12.2%	1.031
$OA_{\perp}$	0.31	10.9%	10.4%	1.038

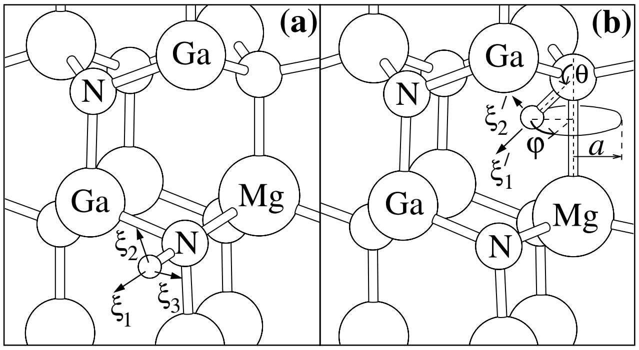

FIG. 2. Perspective view of Mg-H complexes in (a) the $AB_{N,\perp}$ and (b) the $OA_{\parallel}$ configuration. The path of H rotating around the crystal axis is also shown in (b). The directions of vibration for stretching (ξ_1) and bending modes (ξ_2, ξ_3) are indicated by arrows; in (b), ξ_3 is replaced by the azimuthal angle φ describing the rotational motion of H.

constituents. In addition, various checks confirmed the accuracy and reliability, including calculations using explicit inclusion of Ga 3*d* states instead of the nlcc. Interestingly, we obtained the same relative ordering of the energies in the *zinc-blende* structure, indicating that the overall symmetry of the system (hexagonal vs cubic) does not affect this result.

Next we investigated whether extrinsic effects might affect the relative stability of $AB_{N,\perp}$ and $OA_{\parallel}$. The experiments of Ref. [4] were performed on films grown on sapphire, and it is well known that such layers exhibit compressive stress due to the thermal mismatch between GaN and the substrate. We therefore calculated the energy difference between $AB_{N,\perp}$ and $OA_{\parallel}$ configurations when a 1% biaxial compression is applied, accompanied by an expansion of the lattice along the *c* axis. The magnitude of this strain is far larger than the strains typically present in epitaxial layers, which are closer to 0.1%. We found that the presence of this biaxial strain did not affect the energy difference between $AB_{N,\perp}$ and $OA_{\parallel}$.

The $OA_{\parallel}$ configuration actually does exhibit a characteristic that distinguishes it from $AB_{N,\perp}$: a low-energy excitation that qualitatively differs from the stretching and bending modes associated with the N-H bond. Our investigations indicate that it costs very little energy to move H away from the $OA_{\parallel}$ position, maintaining the "polar" angle θ with the *c* axis and changing the azimuthal angle φ [see Fig. 2(b)], effectively rotating the H atom around the *c* axis. If we allow complete relaxation, then for every H position the Mg and N atoms (as well as other host atoms) would assume different positions. The nature of the H motion actually makes it more likely that the surrounding (heavier) atoms will remain fixed, setting up a potential energy surface in which only the much lighter H atom moves. Either way, we find that the barrier for hydrogen rotation is on the order of 0.03 eV.

The presence of such a low-frequency excitation raises the possibility of a large entropy contribution to the free energy; we therefore explicitly calculate the free energy of the system. Since we require only the *difference* between the free energies of two distinct configurations of the Mg-H complex, we focus on those vibrational modes that are expected to be distinctly different in the two configurations, i.e., the modes directly associated with the H atom. For the $AB_{N,\perp}$ configuration, we need to consider one stretching and two bending modes [see Fig. 2(a)]. The calculated frequencies are 3017, 1061, and 1081 cm^{-1}. We express the free energy F in terms of the partition function Z: $F = -kT \ln Z$, with

$$Z = \prod_{i=1}^{3} \sum_{n_i=0}^{\infty} \exp\left(\frac{-E_{n_i}}{kT}\right), \tag{1}$$

where E_{n_i} are the energy eigenvalues for the stretching ($i = 1$) and bending ($i = 2, 3$) mode oscillators. Typically, the harmonic approximation is used, in which $E_{n_i} = \hbar\omega_i(n_i + \frac{1}{2})$ and the sums in Eq. (1) can be evaluated analytically. However, since anharmonic contributions are important (evaluated as described in Ref. [10]), we use the full numerical expression. The three terms in Eq. (1) give rise to free-energy contributions F_1, F_2, and F_3, which are shown in Fig. 3(a). The finite values at $T = 0$ reflect zero-point energies. The decrease in F_i at higher T is due to entropy, which is larger for lower-frequency modes.

We then turn to evaluating the free energy for $OA_{\parallel}$. The stretching mode (ξ_1', at 3034 cm^{-1}) and one of the bending modes (ξ_2', at 1162 cm^{-1}) are very similar to those in $AB_{N,\perp}$ [see Fig. 2(b)]. The third excitation, however, is very different in nature, and corresponds to hydrogen rotating around the *c* axis, described by the azimuthal angle

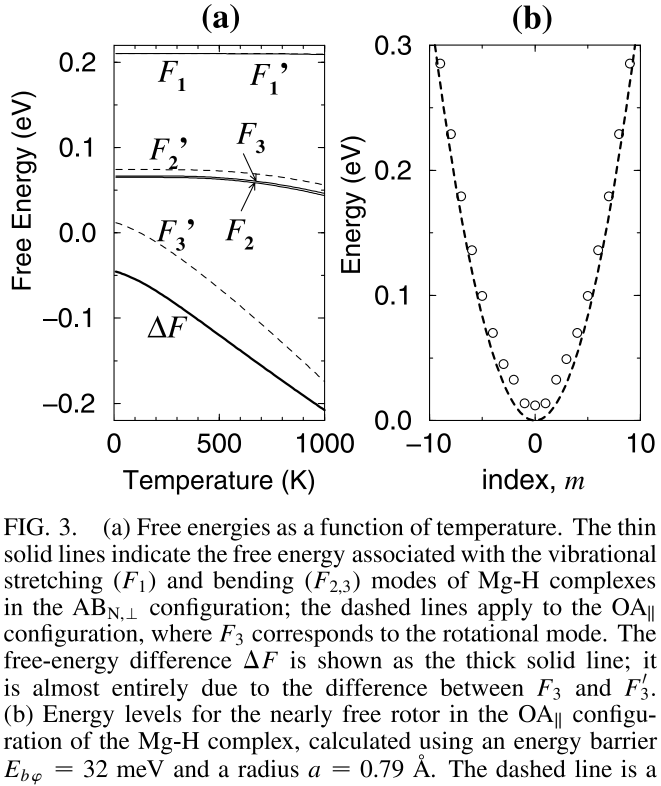

FIG. 3. (a) Free energies as a function of temperature. The thin solid lines indicate the free energy associated with the vibrational stretching (F_1) and bending ($F_{2,3}$) modes of Mg-H complexes in the $AB_{N,\perp}$ configuration; the dashed lines apply to the $OA_{\parallel}$ configuration, where F_3 corresponds to the rotational mode. The free-energy difference ΔF is shown as the thick solid line; it is almost entirely due to the difference between F_3 and F_3'. (b) Energy levels for the nearly free rotor in the $OA_{\parallel}$ configuration of the Mg-H complex, calculated using an energy barrier $E_{b\varphi} = 32$ meV and a radius $a = 0.79$ Å. The dashed line is a perfect parabola, reflecting the solutions for a free rotor.

φ. The potential energy in which the hydrogen moves shows some corrugation. The barrier for hydrogen rotation, when constraining the neighboring Mg and N atoms on the c axis, is calculated by determining the structure of the complex for an intermediate position of the hydrogen (corresponding to $\varphi = 30°$), and then fixing the Mg and host atoms in these positions and evaluating the energy as a function of the hydrogen coordinate. This yields a barrier of 32 meV. This value is not very sensitive to the detailed positions of the Mg and N atoms, which allow us to avoid the issue of coupling between the rotational motion and the other degrees of freedom.

Because the H atom sees a weak corrugation potential associated with the azimuthal angle φ, we can treat it dynamically as a nearly free rotor. The threefold symmetry around the c axis leads to $V_\varphi(\varphi + 120°) = V_\varphi(\varphi)$, allowing us to approximate the potential energy as $V_\varphi(\varphi) = E_{b\varphi}(\cos 3\varphi + 1)/2$, where $E_{b\varphi}$ is the calculated barrier. The φ-dependent part of the Schrödinger equation can be written as

$$HY(\varphi) = \left[-\frac{\hbar^2}{2m_{\mathrm{H}}a^2}\frac{\partial^2}{\partial\varphi^2} + V_\varphi(\varphi)\right]Y(\varphi) = EY(\varphi), \tag{2}$$

where a is the radius of the circular orbit [see Fig. 2(b)]. We have solved this equation using a plane-wave basis set [13]:

$$Y(\varphi) = \sum_{m=-\infty}^{\infty} c_m \frac{\exp(im\varphi)}{\sqrt{2\pi}}. \tag{3}$$

Including 51 plane waves ($m = -25$ to $m = 25$, corresponding to energy levels up to about 1 eV) suffices to converge the partition function. After diagonalizing the Hamiltonian matrix H we obtain the energy levels shown in Fig. 3(b). Note that the eigenvalues are very close to the parabola that would be obtained in the case of a free rotor, where $E_m = (\hbar^2/2m_{\mathrm{H}}a^2)m^2 = (0.0033\ \mathrm{eV})m^2$.

Figure 3(a) shows that the free energy corresponding to the nearly free rotor, F'_3, exhibits a large temperature dependence, reflecting the large entropy associated with this low-energy excitation. Figure 3(a) also shows the free-energy difference $\Delta F = F' - F$ between the $\mathrm{OA}_{\|}$ and the $\mathrm{AB}_{\mathrm{N},\perp}$ configurations; F'_3 obviously makes the largest contribution to ΔF. We see that ΔF equals -0.19 eV (the energy difference between $\mathrm{OA}_{\|}$ and $\mathrm{AB}_{\mathrm{N},\perp}$) at around $T = 900$ K or 627 °C. At higher temperatures, the $\mathrm{OA}_{\|}$ configuration will be stabilized. In the experiments of Ref. [4] the hydrogen was introduced during metal-organic chemical vapor deposition at 1000 °C, a temperature high enough to favor the $\mathrm{OA}_{\|}$ configuration.

An intriguing consequence of our results is that, given the small value of the barrier $E_{b\varphi}$, the hydrogen will tend to be quantum-mechanically delocalized. Indeed, in the limit of a free rotor ($E_{b\varphi} = 0$), hydrogen would exhibit equal probability to occur at any value of the azimuthal coordinate φ even at $T = 0$. Whether or not this delocalization as a function of φ occurs at the low temperatures (5 K) of the experiment in Ref. [4] is a question we feel cannot be answered without a full quantum-mechanical treatment of the hydrogen motion. However, we have checked that the procedure used in Ref. [4] to arrive at the bond angle $\theta = 130°$ is equally valid even if H has equal probability of occurring at any angle φ. The presence of rotational excitations with an energy on the order of a few meV could lead to broadening of the observed vibrational line (1 meV $\approx 8\ \mathrm{cm}^{-1}$). Substantial broadening was indeed observed in the spectra reported in Ref. [4].

In summary, we have presented a model for the structure of the Mg-H complex in GaN that agrees with the unusual bond angle that has been experimentally observed [4]. The structure exhibits a set of low-energy excitations, consisting of a nearly free rotor with a very small barrier for rotation. The entropy associated with this motion plays an essential role in stabilizing the complex. Our work highlights the importance of taking finite-temperature free-energy effects into account when assessing the relative stability of various possible configurations of a defect, impurity, or complex.

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