Electronic and vibrational properties of Mg- and O-related complexes in GaN

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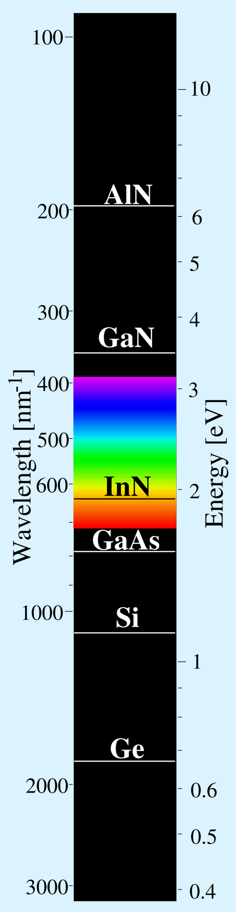
Summary

- Hydrogen plays a crucial role in the passivation of magnesium acceptors in p-type GaN, and a local vibrational mode (LVM) at 3125 cm^{-1} has previously been attributed to a magnesium-hydrogen complex. The angle between the LVM electric dipole and the c-axis has been measured to be 130° degrees, which seems inconsistent with current atomic models. We suggest possible alternatives to current atomic models of this defect by considering complexes of substitutional Mg atoms with intrinsic defects and hydrogen atoms.
- Substitutional oxygen atoms are commonly thought to contribute to the n-type conductivity of as-grown GaN. However, a recent photoluminescence study has linked substitutional oxygen with a 0.88-eV line, suggesting O may be a deep donor. We have also addressed this issue by examining oxygen-related defects possessing deep-donor levels. We find evidence that a deep donor level including substitutional oxygen must result from a complex impurity.

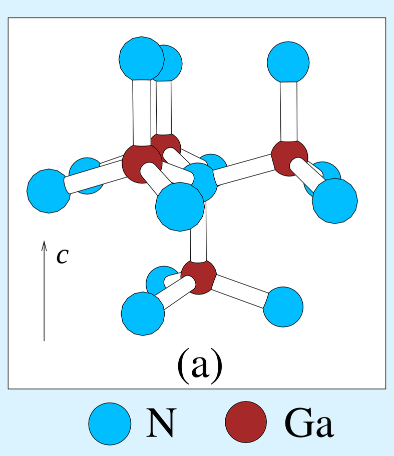
Introduction



- Magnesium is dopant for achieving p-type doping in GaN, but:
  - Compensation by the intrinsic donors V_N^+ and Ga_i^{+++} and by residual O_N^+.
  - Passivation by H in MOCVD-grown samples. H can be removed by a post-growth annealing step in N_2 atmosphere.
- Local vibrational mode at 3125 cm^{-1} is observed in Mg-doped samples before annealing (when sample still insulating / slightly n-type). Annealing at ~600°C activates p-doping and reduces intensity of the 3125 cm^{-1} mode, due to the dissociation of the Mg-H complexes.
- An experimental study of the electric dipole of this LVM [1], obtained by polarised-light absorption, suggests a 130°-angle with the *c*-axis of wurtzite GaN.
- Electron irradiation of undoped GaN with 2.5 MeV electrons produces a 0.88 eV PL line, with a rich phonon sideband that suggests O_N is involved [2].

Methodology

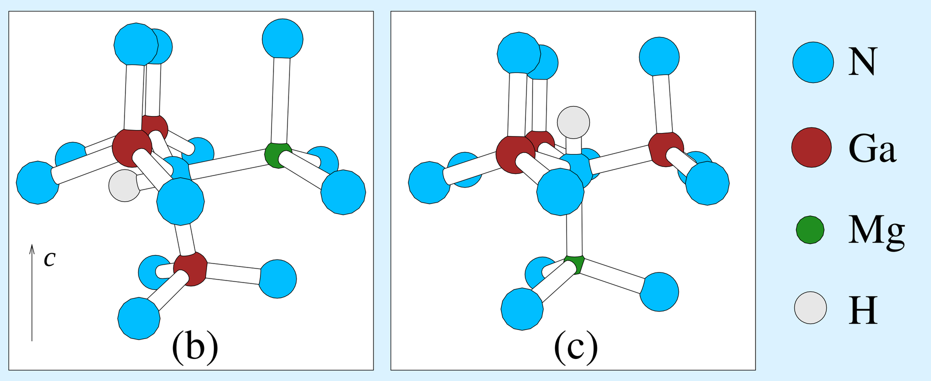
- Self-consistent *ab initio* simulations of wurtzite GaN crystals using AIMPRO, the Ab Initio Modelling PROgramme, within local density functional theory. The wave functions are expanded on a set of *s* and *p* atom- and bond-centred Gaussian orbitals [3].
- Impurities are placed in clusters with 210 atoms, allowing convenient studies of defect levels and charged defects.
- BHS pseudopotentials [4] to describe the valence electrons, thus neglecting the mixing between the Ga 3*d* and N 2*s* electrons.



Ideal wurtzite GaN

- LVMs estimated by computing 2nd derivatives of total energy with respect to the atomic displacements of defect atoms. For other atoms, 2nd derivatives are estimated from a Musgrave-Pople potential [5].

Structure Mg-N-H

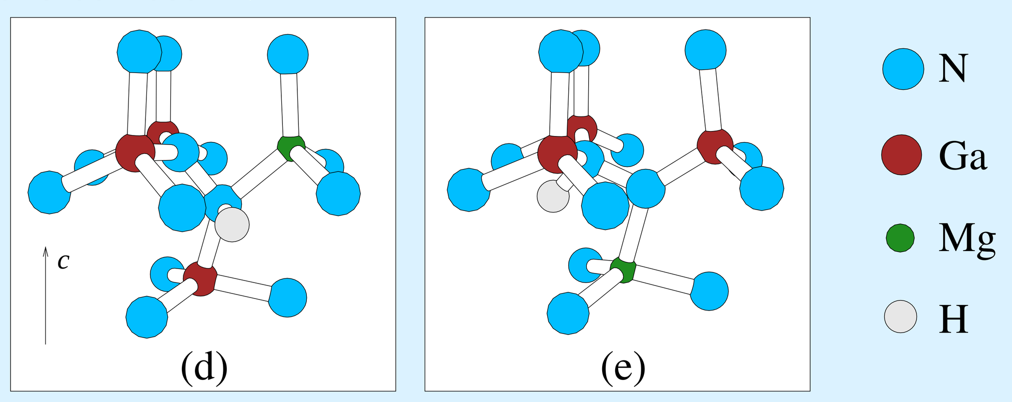


Mg_{Ga}-N-H (C_{1h}) Mg_{Ga}-N-H (C_{3v})

- We explore several possible positions of a single H atom around a Mg_{Ga} substitutional atom, in a wurtzite GaN crystal, shown in (a):
  - Lowest energy structure in the neutral charge state is shown in (b), with H anti-bonded along the Mg-N bond, in a direction off the *c* axis.
  - Structure (b) is 0.2 eV *lower* in energy than with H anti-bonded along the *c*-axis (c).
  - Meta-stable structures with H within the Mg-N bond are 0.3 eV higher in energy.
- High-energy LVMs of structure (b) are estimated to be 3345 cm^{-1} (for H) and 2445 cm^{-1} (for D). These values match the order of magnitude of experimental values at 3125 and 2321 cm^{-1} respectively. Bond-centred-H structures have theoretical LVMs ~4200 cm^{-1} and can thus be rejected as candidates.
- For structure (b), the angle between the N-H bond and the *c*-axis, found to be parallel to the LVM electric dipole, is only 106° in the neutral charge state, significantly lower than the experimental value.

Complexes of Mg, H, and intrinsic defects

- In the search for alternative structures leading to a 130° angle between the *c*-axis and the electric dipole, we consider complexes of Mg, H, and intrinsic defects. Complexes of Mg_{Ga} with V_{Ga}, a second Mg_{Ga}, or a Ga_i atom do *not* support N-H bonds at the correct angle and with the correct LVM.



Two low-energy Mg_{Ga}-N_i-H complexes

- We find that complexes of Mg_{Ga} with N_i support several low energy structures with H. Two such structures are shown in (d) and (e), above. We predict that structure (d) has the lowest energy, and that structure (e) is 0.3 eV higher in energy, in the negative charge state. Both models have high-energy LVMs around 3200 cm^{-1}, and structure (e) has an angle of 137° between the *c*-axis and the N-H bond.

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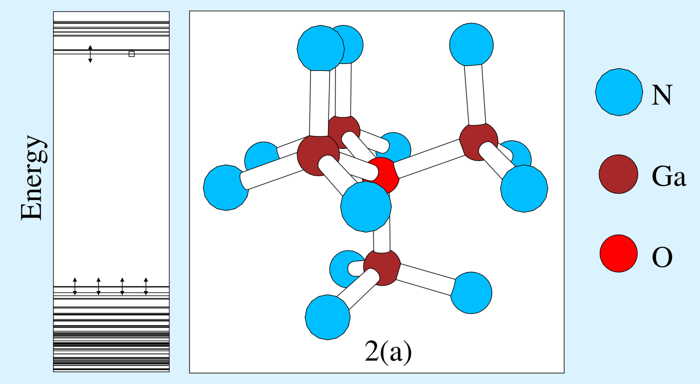
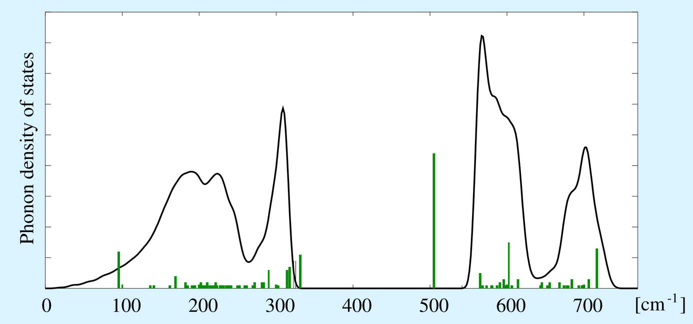
Substitutional Oxygen



Relaxed neutral O_N defect. Left panel shows the Kohn-Sham energy levels of structure 2(a) near the gap.

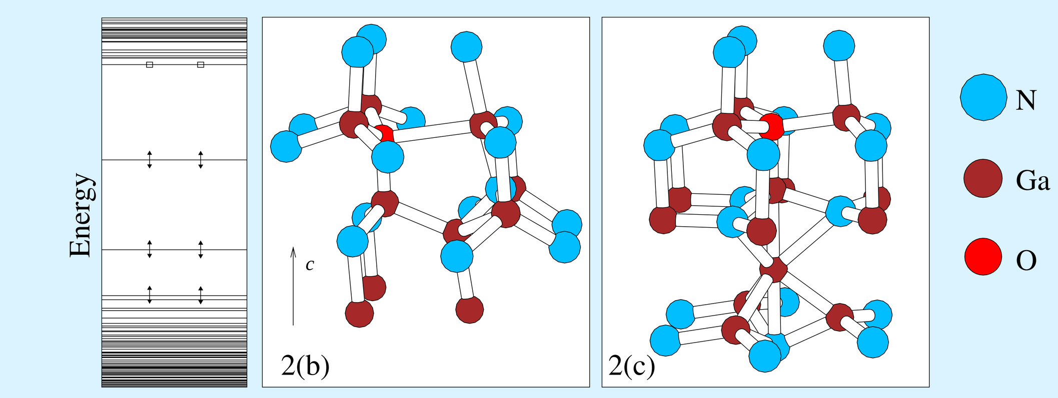
- A single substitutional O_N defect is a shallow donor.
- Local vibrational modes of O_N^+ mix with bulk phonon modes:



Phonon density of states (black) and LMVs near O_N^+ (green). Heights of impulses reflect the localisation of LVMs on O_N and its Ga neighbours.

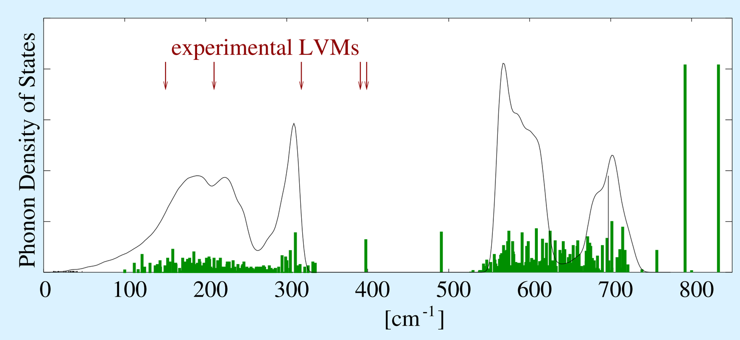
Complexes with O and intrinsic defects

- 2.5-MeV e^- irradiation can produce Ga_i [6]. If they complex with O_N, deep donor levels could be formed.



Two O_N-Ga_i complexes with C_{1h} 2(b) and C_{3v} 2(c) symmetry, neutral charge state. The left panel shows the Kohn-Sham energy levels of structure 2(b) near the gap.

- Although the C_{1h} and C_{3v} structures of a single Ga_i are very close, when paired with O_N, structure 2(b) is lower in energy than 2(c) by 4 eV.
- Several LVMs in GaN phonon gap, qualitatively similar to those seen experimentally by PL [2]:



Phonon density of states (black) and LMVs near O_N-Ga_i of structure 2(b) (green), compared with experimental LVMs (red). Heights of impulses reflect the localisation of the LVMs on O_N.

Conclusions

- For Mg-N-H defects, H in antibonding position
  - lower energy if N-H bond is off the *c*-axis
  - electric dipole of LVM, parallel to N-H bond, at 106° with respect to *c*-axis
- Mg-N_i-H complexes can give rise to a LVM with an angle of ~130° with *c*-axis
- Complexes of O with a Ga interstitial could lead to experimental observations on the 0.88-eV photoluminescence line
- The future:
  - inclusion of full Ga(3*d*)-electrons in the valence band

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