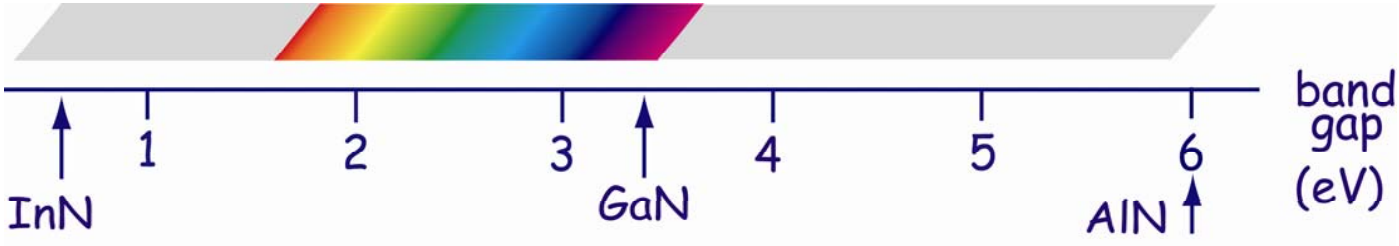
Cation Vacancies in Nitride Semiconductors: A Possibility of Intrinsic Ferromagnetism

In collaboration with Dr. Yoshihiro Gohda (Univ of Tokyo)

GaN, InN & AlN:

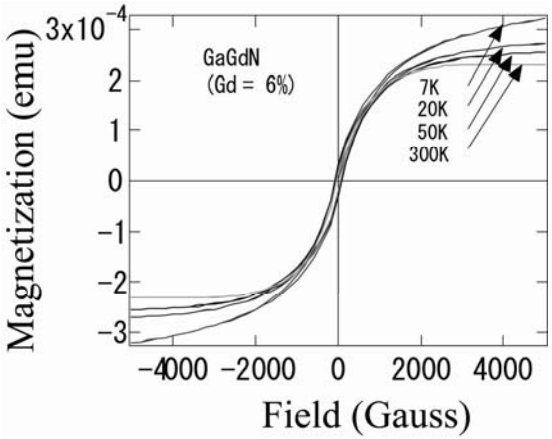
Direct-gap Semiconductors with band gaps,



Environment-friendly semiconductors for optoelectronic devices

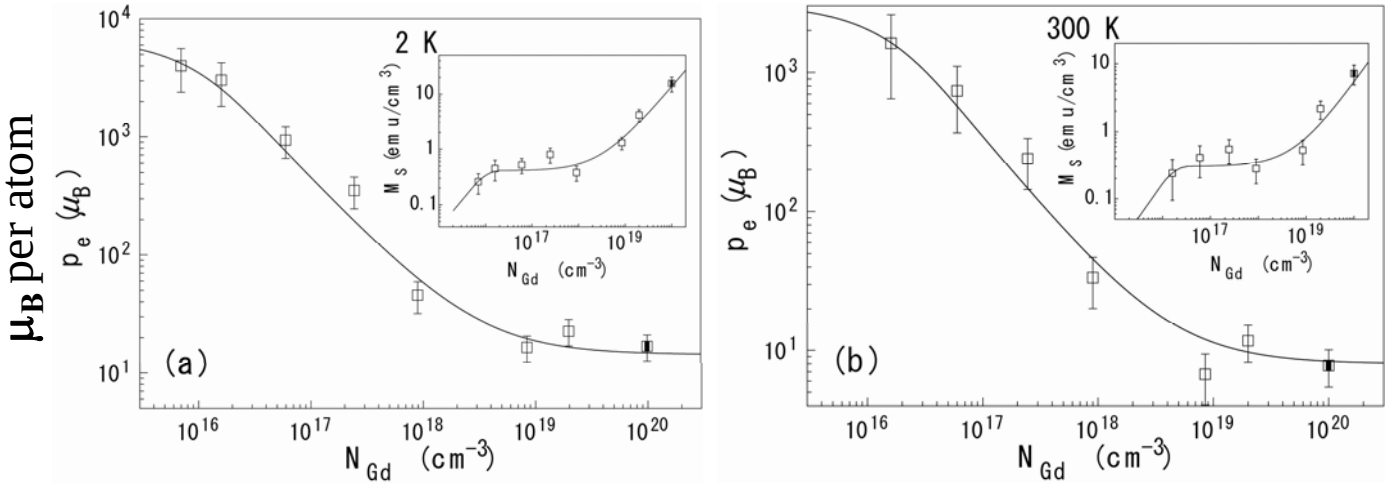
But that's not all ….

Ferromagnetic behavior in GaN doped with magnetic impurity



- Hysteresis has been observed even at Room temperature in Gd-, Cr-, Eu-doped GaN
- Gigantic magnetic moment of 4000 μ_B per Gd atom in epitaxially grown sample, and more in implanted sample (cf. Gd atom 8 μ_B)

Tearguchi et al: SSC (2002), Asahi et al: JPhys C (2004)



Dhar et al: PRL (2005), APL (2006)

Something fascinating but puzzling

⇒ Role of Vacancy?

GGA (+ U) Calculations for Atomic Vacancy in Gd-doped and undoped GaN and other Nitrides

- Consider:
  - Atomic structure, electron states and spin states of mono-, di- and tri-vacancy for various charge states?
  - Interaction among vacancies and Gd atom?

Gd: $(4f)^7(5d)^1(6s)^2$, $8\mu_B$

- Have found:
  - Cation mono-vacancy, di-vacancy and tri-vacancy are spin-polarized.
  - They interact ferromagnetically and thus likely to be responsible for gigantic magnetic moment.

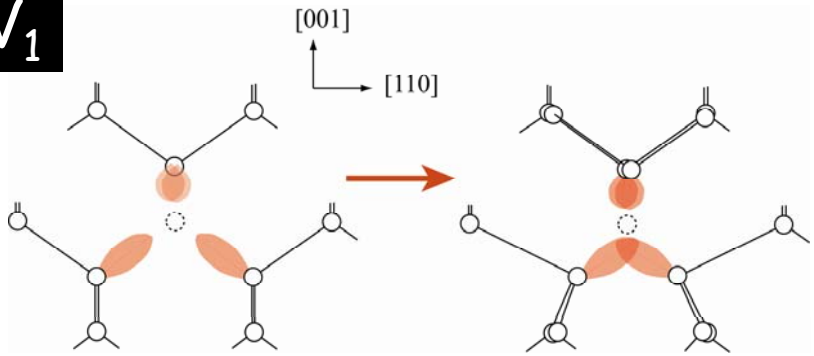
Vc: (degenerate gap state)^3, $3\mu_B$

Some details of GGA (+ U) calculations

- Ga: *(3d)*, *(4s)*, *(4p)*, N: *(2s)*, *(2p)* and Gd: *(5s)*, *(5p)*, *(4f)*, *(5d)*, *(6s)* as valence states
- Core states treated in PAW scheme
- GGA by Perdew, Burke and Ernzerhof
- Hubbard U (6.7 eV) and J (0.7 eV) for 4f states following the work in the past
- Plane-wave basis set with 400 eV cutoff
- Supercell model with 96 – 576 atomic sites

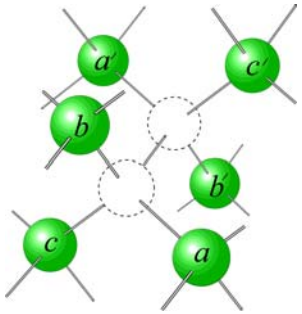
Vacancies in Si

V_1

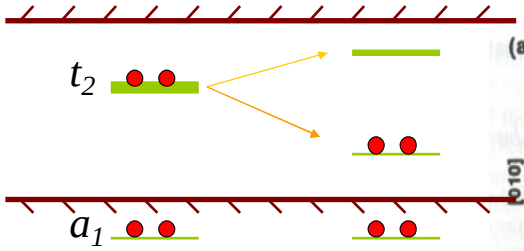


Symmetry-lowering (Jahn-Teller) distortion makes it stable

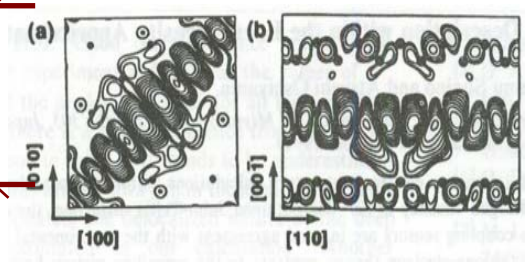
V_2



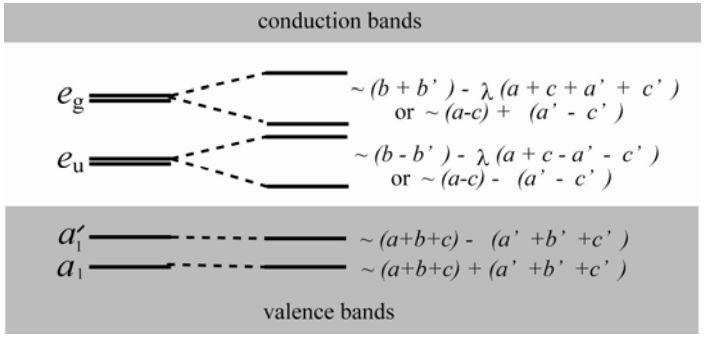
Symmetry-lowering,
pairing or resonant-bond distortion
makes it stable



T_d D_{2d}



actual wavefunction of deep state in V_1



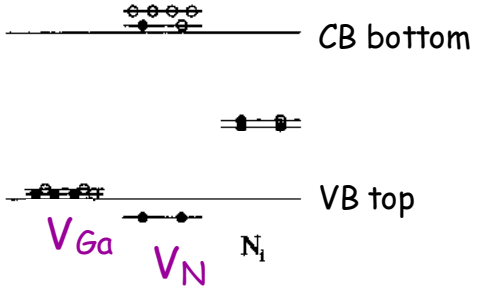
D_{3d} C_i

Quantitative agreement:
Sugino& Oshiyama, PRL (1992);
Saito & Oshiyama, PRL (1994),
Ogut & Chelikowski, PRL (1999)

Rebonding that gains covalent energy, though cost of distortion, is a principal factor

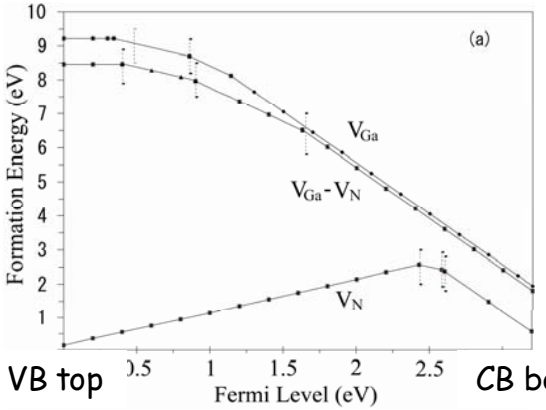
Vacancy in GaN

Defect levels in GaN



Neugebauer & Van de Walle: PRB (1994)

Formation energies



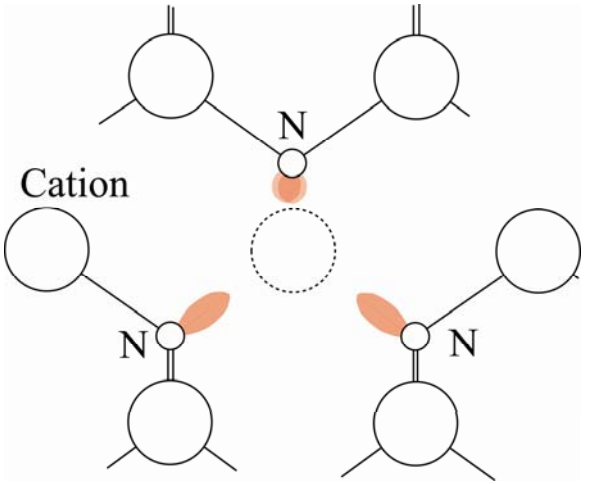
VB top CB bottom

Ganchenkova & Nieminen: PRL (2006)

Limpijumnong & Van de Walle: PRB (2004)

Symmetry keeping breathing relaxation is a principal factor

Nitrogen is too small to rebond!

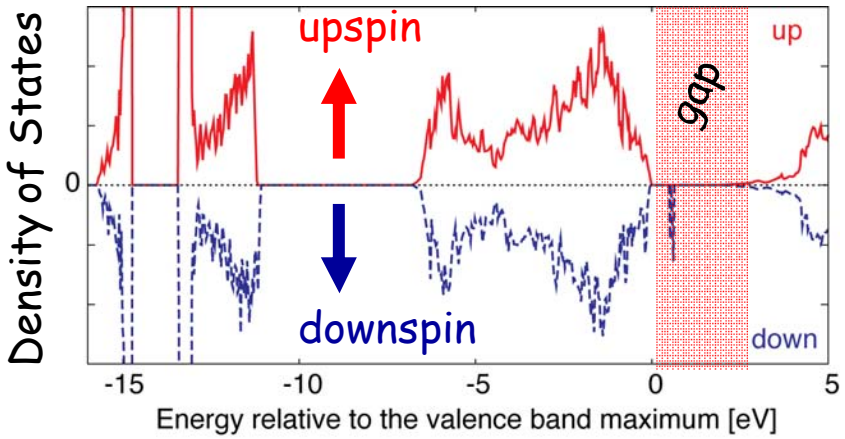


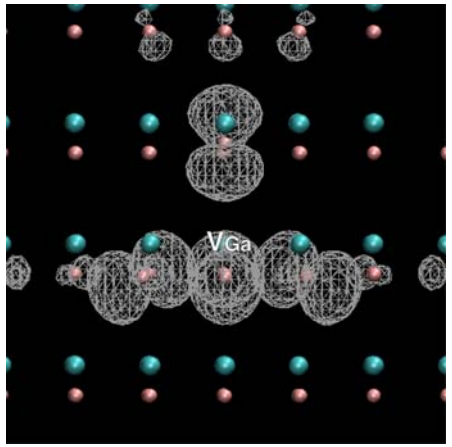
Covalent radii:
0.75 A (N)
1.26 A (Ga)
1.44 A (In)
1.18 A (Al)

Then,
what has been overlooked is:
Exchange interaction among gap states originated from N dangling bonds
⇒
Possibility of spin polarization

Spin-Polarized Cation Vacancy in Nitrides

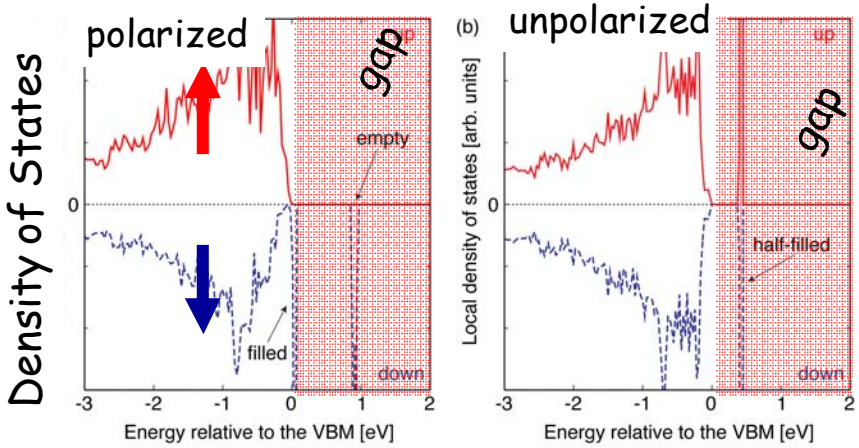
V_{Ga} in GaN





Electron orbitals responsible for spin

V_{Al} in AlN



Nearly degenerate 3-fold defect levels near valence-band top split due to exchange interaction, causing spin polarization with $\mu = 3\mu_B$

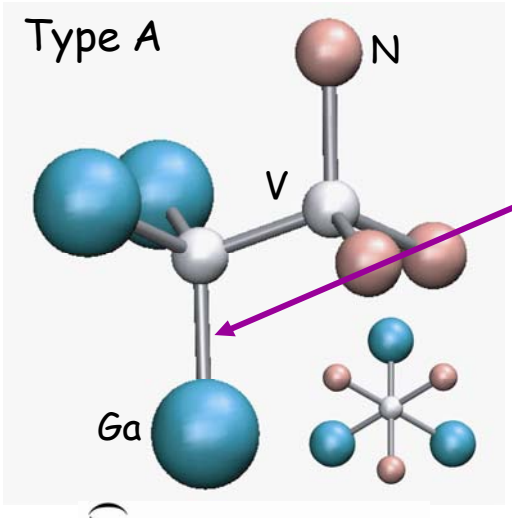
Energy gain due to spin polarization = 0.5 eV ~ 0.9 eV

Vc is a magnetic "imperfection" with the configuration of (the gap state)³

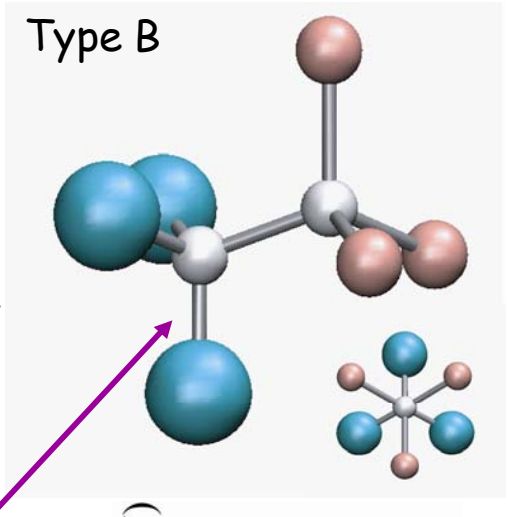
Same was found in $In_{0.5}Ga_{0.5}N$

Structural Bistability in Divacancy: Exchange Splitting vs Electron Transfer through Breathing Relaxation

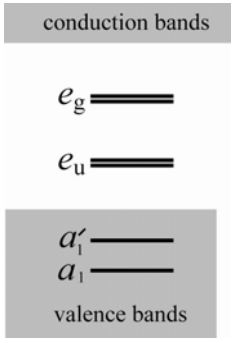
Neutral State

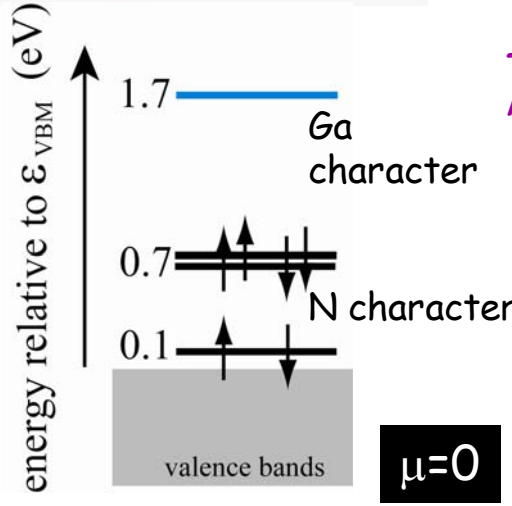


Outward breathing relaxation: +0.37 A
Ga levels shift upward, and then electron transfer

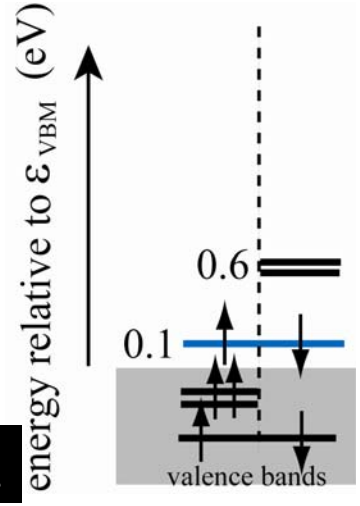


Inward breathing relaxation: -0.11 A
Ga levels shift downward and occupied, and then exchange energy gain at N dangling bonds



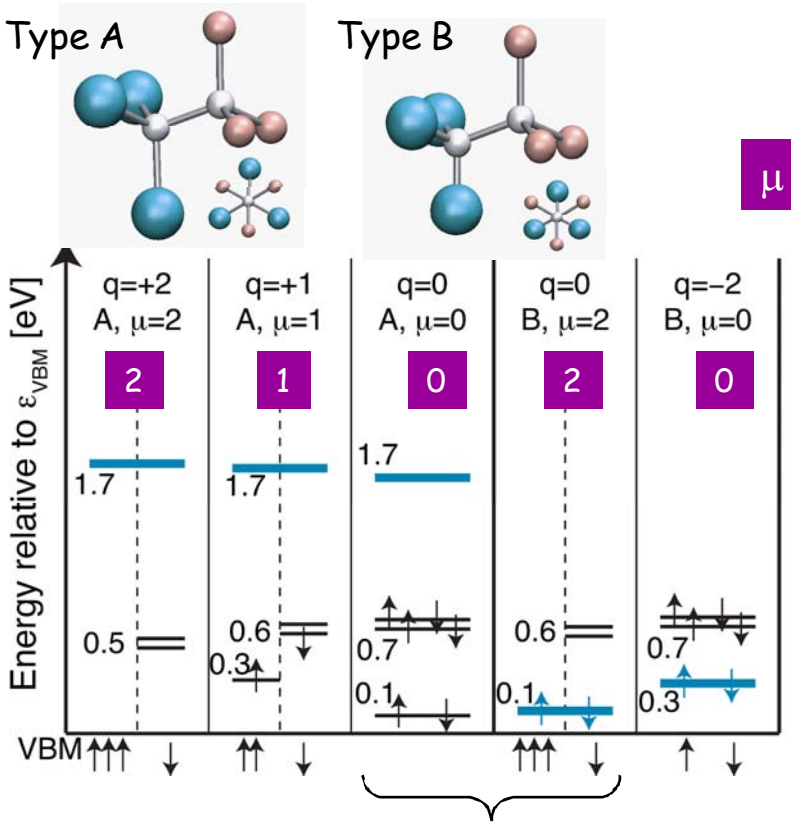


$\mu=0$



$\mu=2\mu_B$

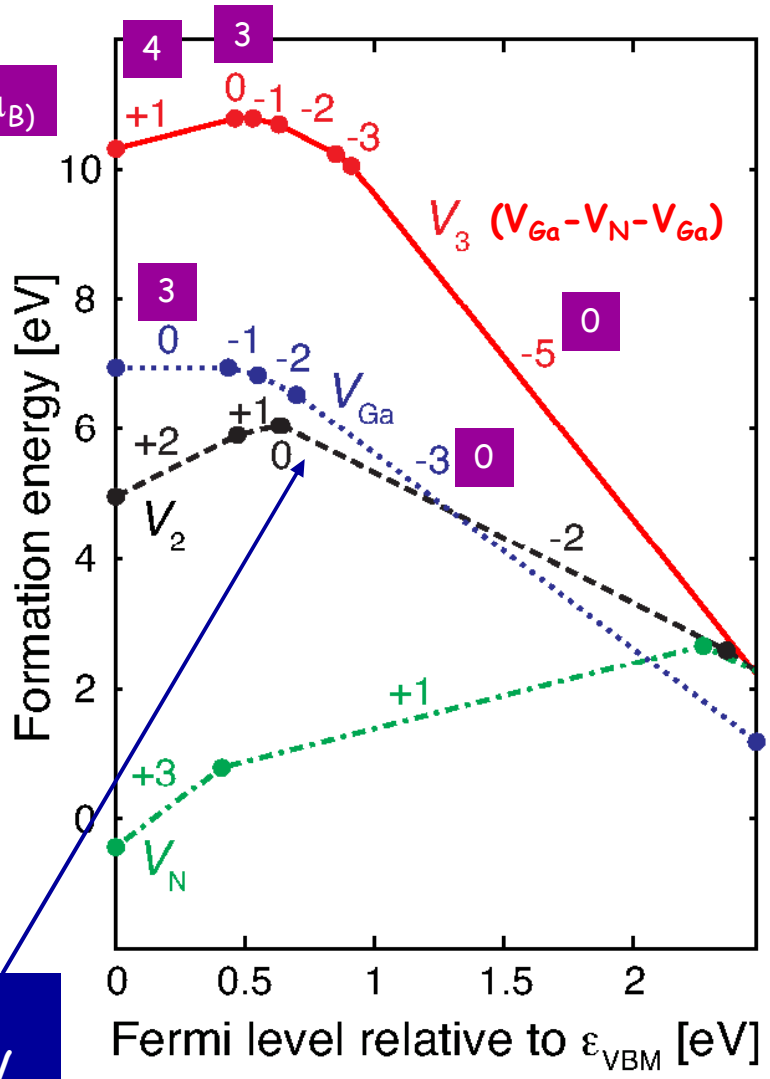
Which Structure? How much is the Spin?



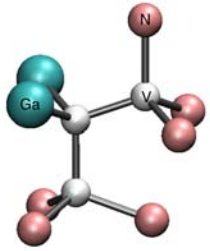
Neutral: $E_A < E_B$ by 0.2 eV

Neutral & Positive: Type A
Negative: Type B

Conversion from Type A to Type B makes ε(0/-2) much lower than 1.7 eV, constituting negative U system

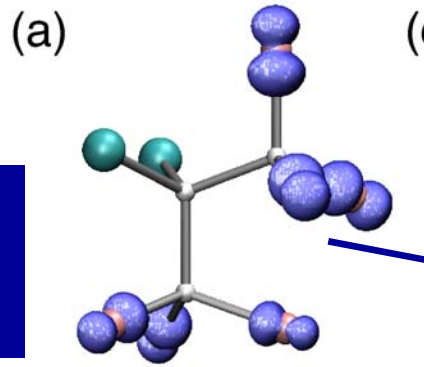


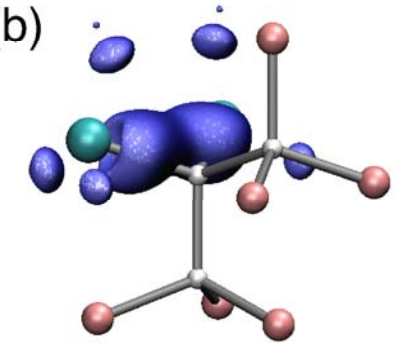
Trivacancy: Charge-state dependent spin center

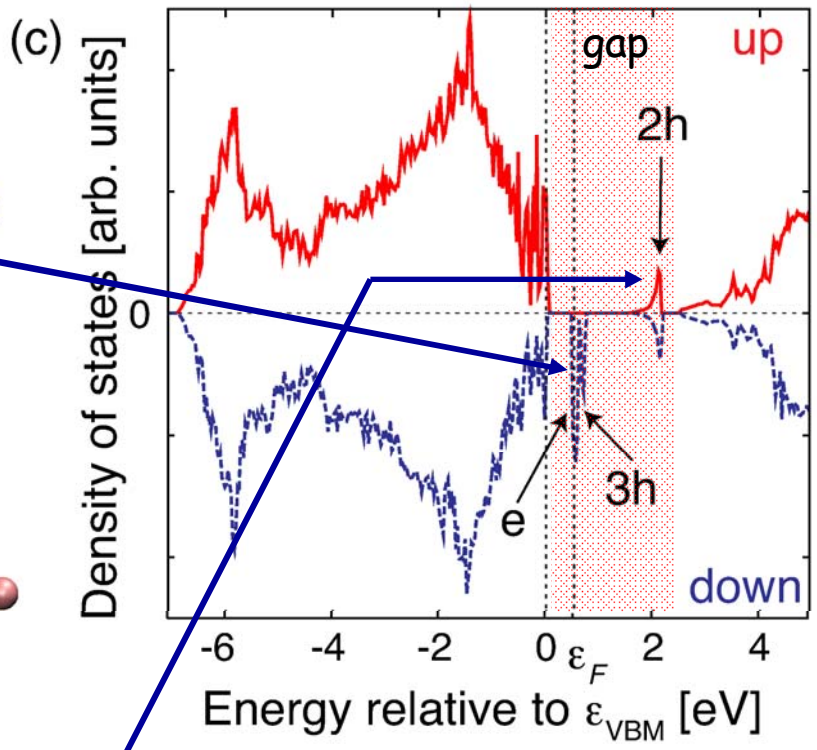


Neutral V_{Ga}-V_N-V_{Ga} Trivacancy $\mu = 3\ \mu_B$

Electron orbital responsible for spin polarization



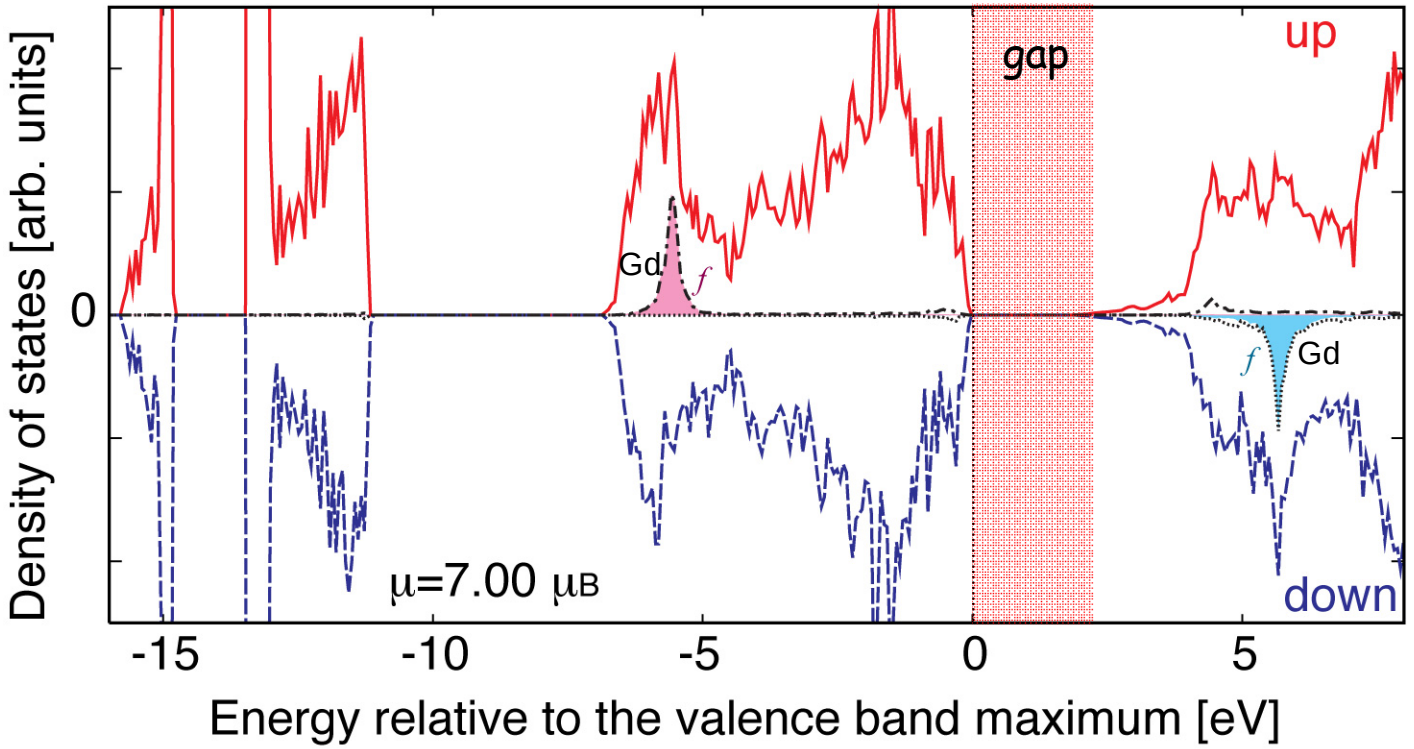




Antiferromagnetic config between the 2 V_{Ga} is less stable than ferromagnetic config by an order of 10 meV, depending on the charge state

Electron orbital with cation character

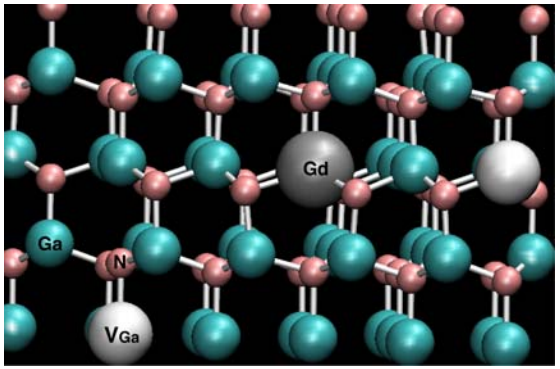
Gd 4f is spin polarized in GaN: μ = 7.0 μ_B



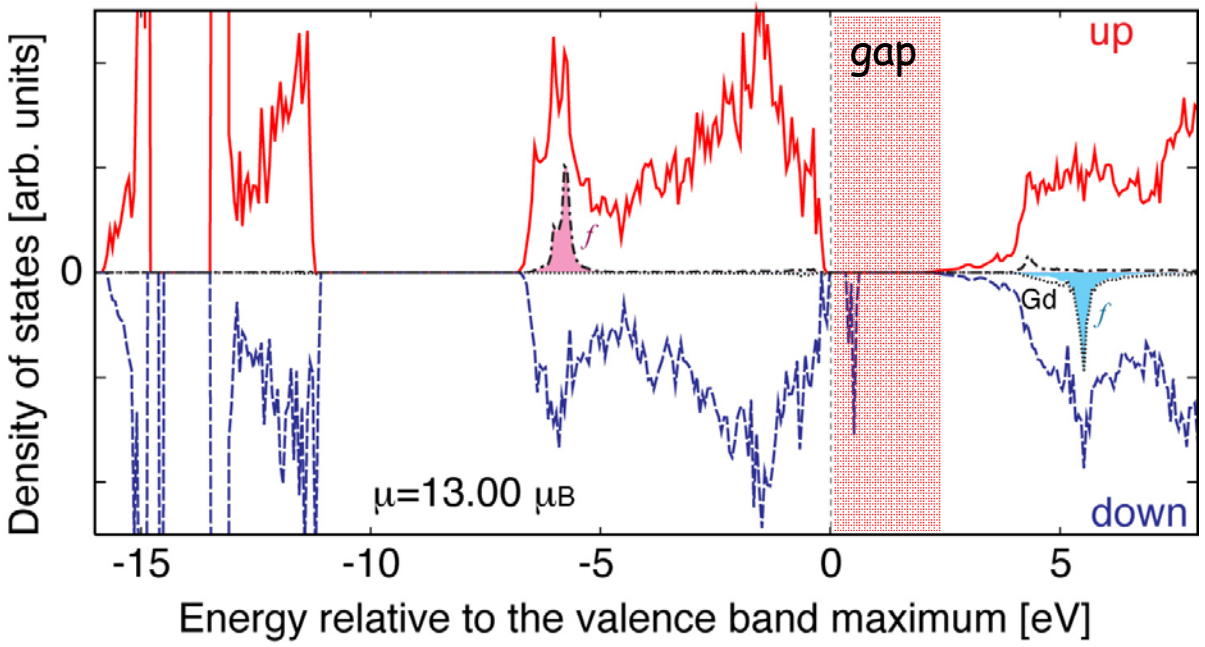
$Gd_{0.02}Ga_{0.98}N$
(96 site cell)

- **Gd 5*d* electrons contribute to chemical bonding with N**
  - Electronic structure remains semiconducting
- **Gd 4*f* states are half-filled and spin polarized**
  - $\mu = 7.0\ \mu_B$

Ferromagnetic Coupling between Gd and 2 V_{Ga}

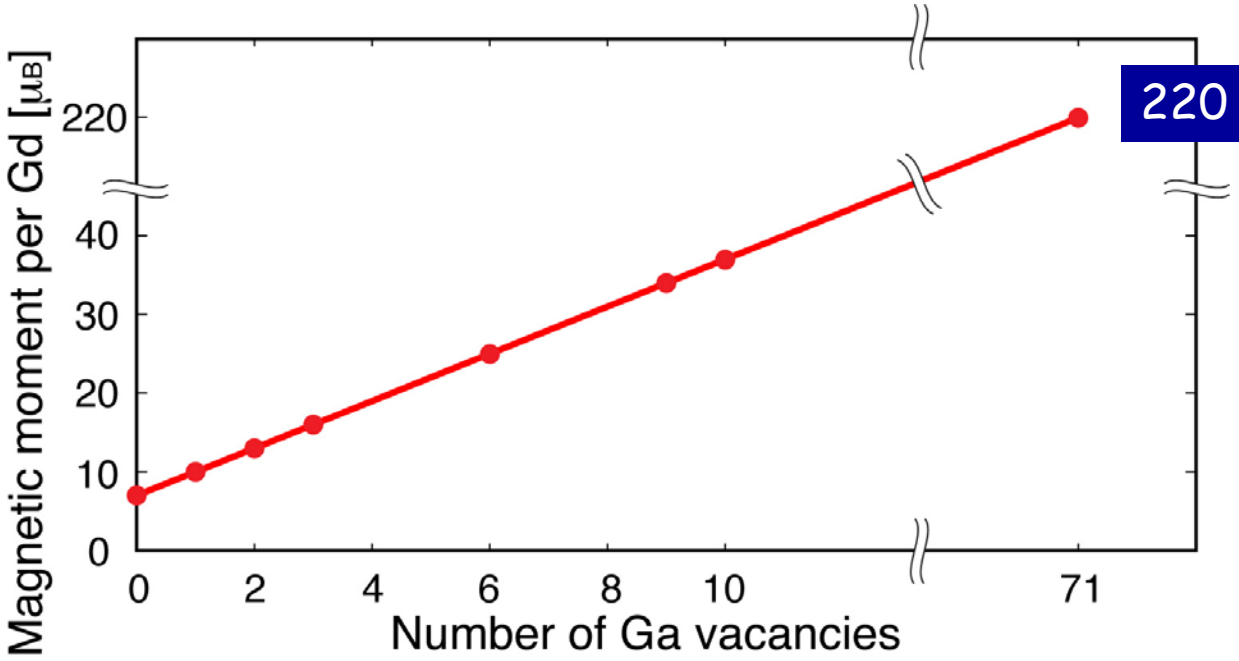


- N-related defect states in the band gap as in V_{Ga}
- Outward breathing relaxation for both V_{Ga} and Gd : No Jahn-Teller Effect



- **Ferromagnetic interaction** among 2 V_{Ga} and Gd, resulting in $\mu = 13.00\ \mu_B$

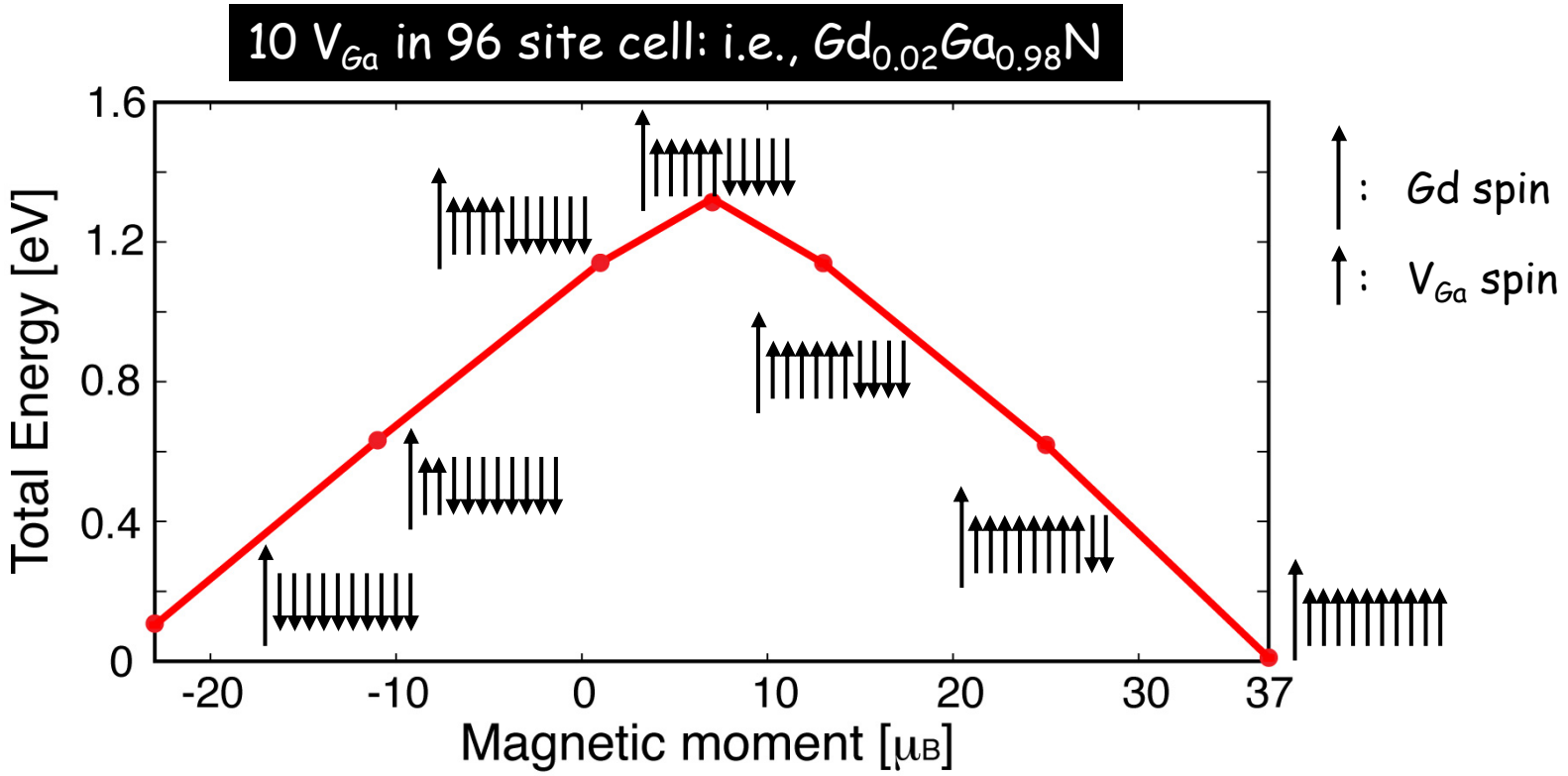
Magnetic Moment Increases with Increasing Number of V_{Ga}



Ferromagnetic Configuration is most stable

- Linear increase in μ with the number of V_{Ga}
  - **Due to 3 holes arising from V_{Ga} with the minority spin**
- Gigantic magnetic moment observed in experiments
  - **Highly attributable to magnetism due to Ga vacancies**

Energetics among Several Spin Configurations



- Ferromagnetic configuration most stable, even for the case without Gd: $\Delta E_{AFM\text{-}FM}$=1.12 eV

  $\Rightarrow$ ***Indicative of intrinsic ferromagnetism due to Ga vacancies***

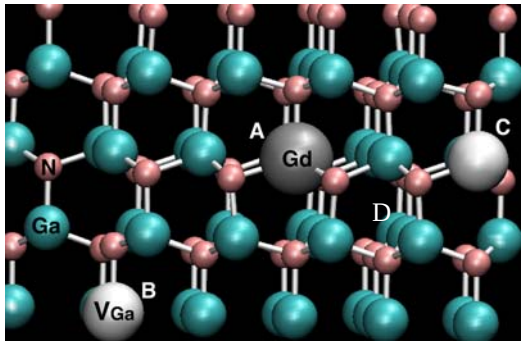
Ferromagnetic vs Antiferromagnetic: $\Delta E = E_{AFM} - E_{FM}$

Spin Configuration	*E* (meV)	μ (μ_B)
Gd↑Gd↑V_{Ga}↑V_{Ga}↑	0	10.00
Gd↑Gd↑V_{Ga}↑V_{Ga}↓	272	7.00
Gd↑Gd↓V_{Ga}↑V_{Ga}↑	41	3.00
Gd↑Gd↓V_{Ga}↑V_{Ga}↓	233	0.00

2 Gd + 2V_{Ga} with the distances of 6.43 A and 8.30 A

Site arrangement	d [A]	ΔE [meV]	μ_{FM} [μ_B]	μ_{AFM} [μ_B]
V_{Ga}@A – V_{Ga}@B	8.30	9	6.0	0.0
V_{Ga}@A – V_{Ga}@C	6.43	- 18	6.0	0.0
V_{Ga}@A – V_{Ga}@D	4.53	19	6.0	0.0
V_{Ga}@A – V_{Ga}@A_{perp}	10.48	2	6.0	0.0
V_{Ga}@A – V_{Ga}@A_{palla}	11.14	1	6.0	0.0
V_{Ga} – V_{Ga} (ZincBlende)	9.09	- 33	6.0	0.0
Gd@A – Gd@B	8.30	0.0	14.0	0.0
Gd@A – V_{Ga} @B	8.30	1	10.0	4.0
Gd@A – V_{Ga} @C	6.43	38	10.0	4.0
Gd@A – V_{Ga} @D	4.53	1	10.0	4.0

2 Spins at various sites at the distance *d*



Cation sites depicted above

Generally, ferromagnetic favored !

Possible Origin of Ferromagnetism

- RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction through carriers, postulated for magnetic semiconductors in the past, are unlikely. No free carriers in the present case
- Coupling of V_{Ga} spin in wultzite network through small covalency is certainly important

???

To Conclude,

- GGA calculations have clarified:
  - Cation mono-vacancy, di-vacancy and tri-vacancy in GaN are spin-polarized, depending on their charge states.
  - Divacancy shows structural bistability caused from exchange splitting and electron transfer accompanied with breathing distortion
  - The vacancy spins interact ferromagnetically, indicating intrinsic ferromagentism in GaN, and thus likely to be responsible for gigantic magnetic moment observed

Gohda & Oshiyama: PRB 78, 161201(R) (2008) & unpublished results