Cation Vacancies in Nitride Semiconductors: A Possibility of Intrinsic Ferromagnetism

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 $\mu_B$ per Gd atom in epitaxially grown sample, and more in implanted sample (cf. Gd atom 8 $\mu_B$)


Something fascinating but puzzling

$\Rightarrow$ Role of Vacancy?
**GGAs ( + 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?

- **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.

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

\[ Vc: (\text{degenerate gap state})^3, 3\mu_B \]
Some details of \textit{GGA ( + U )} calculations

- \textit{Ga: (3d), (4s), (4p), N: (2s), (2p)} and \textit{Gd: (5s), (5p), (4f), (5d), (6s)} as valence states
- Core states treated in PAW scheme
- \textit{GGA} by Perdew, Burke and Ernzerhof
- Hubbard \textit{U (6.7 eV)} and \textit{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

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

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

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

\[ V_{Ga} \quad V_N \quad V_{Ni} \]

Neugebauer & Van de Walle: PRB (1994)

Formation energies

\[ \text{Covalent radii:} \]
\[ 0.75 \text{ Å (N)} \]
\[ 1.26 \text{ Å (Ga)} \]
\[ 1.44 \text{ Å (In)} \]
\[ 1.18 \text{ Å (Al)} \]

Then, what has been overlooked is:
Exchange interaction among gap states originated from N dangling bonds

\[ \Rightarrow \]
Possibility of spin polarization
Spin-Polarized Cation Vacancy in Nitrides

**$V_{Ga}$ in GaN**

- 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 $\approx 0.5$ eV $\sim 0.9$ eV
- $V_c$ is a magnetic "imperfection" with the configuration of (the gap state)$^3$

**$V_{Al}$ in AlN**

- Electron orbitals responsible for spin
- Electron
- Orbitals
- Responsible
- For spin

**In$_{0.5}$Ga$_{0.5}$N**

- Same was found in In$_{0.5}$Ga$_{0.5}$N
Structural Bistability in Divacancy: Exchange Splitting vs Electron Transfer through Breathing Relaxation

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

Inward breathing relaxation: -0.11 Å Ga levels shift downward and occupied, and then exchange energy gain at N dangling bonds
Which Structure? How much is the Spin?

Type A

Type B

Neutral: $E_A < E_B$ by 0.2 eV

Neutral & Positive: Type A

Negative: Type B

Conversion from Type A to Type B makes $\varepsilon(0/-2)$ much lower than 1.7 eV, constituting negative U system
Trivacancy: Charge-state dependent spin center

Neutral $V_{Ga-N-Ga}$ 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: \( \mu = 7.0 \mu_B \)

- Gd 5d electrons contribute to chemical bonding with N
  - Electronic structure remains semiconducting
- Gd 4f 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 $V_{Ga}$

- Linear increase in $\mu$ 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: $\Delta E_{\text{AFM-FM}}=1.12$ eV

⇒ Indicative of intrinsic ferromagnetism due to Ga vacancies
**Ferromagnetic vs Antiferromagnetic:**

\[ \Delta E = E_{AFM} - E_{FM} \]

<table>
<thead>
<tr>
<th>Spin Configuration</th>
<th>( E ) (meV)</th>
<th>( \mu ) (( \mu_B ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd( \uparrow )Gd( \uparrow )V(<em>{Ga})( \uparrow )V(</em>{Ga})( \uparrow )</td>
<td>0</td>
<td>10.00</td>
</tr>
<tr>
<td>Gd( \uparrow )Gd( \uparrow )V(<em>{Ga})( \uparrow )V(</em>{Ga})( \downarrow )</td>
<td>272</td>
<td>7.00</td>
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<tr>
<td>Gd( \uparrow )Gd( \downarrow )V(<em>{Ga})( \uparrow )V(</em>{Ga})( \uparrow )</td>
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<td>3.00</td>
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<tr>
<td>Gd( \uparrow )Gd( \downarrow )V(<em>{Ga})( \uparrow )V(</em>{Ga})( \downarrow )</td>
<td>233</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Site arrangement**

<table>
<thead>
<tr>
<th>Site arrangement</th>
<th>( d ) [A]</th>
<th>( \Delta E ) [meV]</th>
<th>( \mu_{FM} ) [( \mu_B )]</th>
<th>( \mu_{AFM} ) [( \mu_B )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(<em>{Ga})A( \rightarrow )V(</em>{Ga})B</td>
<td>8.30</td>
<td>9</td>
<td>6.0</td>
<td>0.0</td>
</tr>
<tr>
<td>V(<em>{Ga})A( \rightarrow )V(</em>{Ga})C</td>
<td>6.43</td>
<td>-18</td>
<td>6.0</td>
<td>0.0</td>
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<tr>
<td>V(<em>{Ga})A( \rightarrow )V(</em>{Ga})D</td>
<td>4.53</td>
<td>19</td>
<td>6.0</td>
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<tr>
<td>V(<em>{Ga})A( \rightarrow )V(</em>{Ga})( \rightarrow )A(_{perp})</td>
<td>10.48</td>
<td>2</td>
<td>6.0</td>
<td>0.0</td>
</tr>
<tr>
<td>V(<em>{Ga})A( \rightarrow )V(</em>{Ga})( \rightarrow )A(_{palla})</td>
<td>11.14</td>
<td>1</td>
<td>6.0</td>
<td>0.0</td>
</tr>
<tr>
<td>V(<em>{Ga})( \rightarrow )V(</em>{Ga}) (ZincBlende)</td>
<td>9.09</td>
<td>-33</td>
<td>6.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Gd(<em>{A})( \rightarrow )Gd(</em>{B})</td>
<td>8.30</td>
<td>0.0</td>
<td>14.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Gd(<em>{A})( \rightarrow )V(</em>{Ga})( \rightarrow )B</td>
<td>8.30</td>
<td>1</td>
<td>10.0</td>
<td>4.0</td>
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<tr>
<td>Gd(<em>{A})( \rightarrow )V(</em>{Ga})( \rightarrow )C</td>
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<td>38</td>
<td>10.0</td>
<td>4.0</td>
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<tr>
<td>Gd(<em>{A})( \rightarrow )V(</em>{Ga})( \rightarrow )D</td>
<td>4.53</td>
<td>1</td>
<td>10.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**Generally, ferromagnetic favored!**

2 Gd + 2V\(_{Ga}\) with the distances of 6.43 A and 8.30 A

2 Spins at various sites at the distance \( d \)

Cation sites depicted above
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 wurtzite 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 ferromagnetism in GaN, and thus likely to be responsible for gigantic magnetic moment observed.

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