Dynamic Jahn-Teller effect of the $NV^-$ center in diamond by DFT

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Ground $^3A_2$ and excited $^3E$ states of $NV^-$

- 512-atom cell; negligible cell-cell interactions
- Excited state: 1 electron from $a_1\downarrow$ to an $e\downarrow$ level.
PBE vs. HSE for $\text{NV}^-$

- As the gap opens, majority-spin states shift down relative to the VBM but only slightly; the occupied minority-spin $a_1$ state moves up somewhat, while empty minority-spin $e$ states move up considerably.

Red: majority spin
Blue: minority spin
Fewer bulk bands in the HSE results due to the smaller supercell (i.e., fewer band folding)
E⊗e Jahn-Teller vibronic model for excited $^3E$


- **The electronic part:**

  $H^{el}(Q_x, Q_y) = H^{el}(Q_x = Q_y = 0)\]
  
  $+ \frac{K}{2}(Q_x^2 + Q_y^2)\sigma_z + F(Q_x\sigma_z - Q_y\sigma_x) + G[(Q_x^2 - Q_y^2)\sigma_z + 2Q_xQ_y\sigma_x]$

  where $Q_x$ and $Q_y$ are defined by

  and $K$, $F$, and $G$ are the phenomenological parameters and $\sigma_i$ are the Pauli matrices.

  - no net $x$ comp.
  - a breathing mode
  - no net $y$ comp.
Define polar variables \((\rho, \phi)\) such that \(\rho = \sqrt{Q_x^2 + Q_y^2}\) and \(\phi = \tan^{-1}\left(\frac{Q_y}{Q_x}\right)\); the solutions for \(H^{el}(Q_x, Q_y)\) are \(\epsilon(\rho, \phi) = \frac{1}{2} K \rho^2 \pm \rho \sqrt{F^2 + G^2 \rho^2 + 2FG \rho \cos(3\phi)}\).

- If \(G = 0\), \(\epsilon(\rho, \phi) = \frac{1}{2} K \rho^2 \pm F \rho\).
Solutions of the model

The lower-energy branch would be

\[ \epsilon_{LE}(\rho, \phi) = \frac{1}{2} K \rho^2 - F \rho, \]

which has the shape of a Mexican hat.
The adiabatic potential energy surface (APES)

- Of course, $G \neq 0$, which leads to the APES shown to the right.
- There are 3 local minima as a result of Jahn-Teller distortion.
Three key parameters

- 1\textsuperscript{st}: displacement from the origin to a minimum, $\rho_0 = \frac{F}{(K - 2G)}$
- 2\textsuperscript{nd}: the corresponding energy lowering, $E_{JT} = \frac{F^2}{2(K-2G)} = \frac{F}{2} \rho_0$
- 3\textsuperscript{rd}: energy barriers between local minima, $\delta = 4E_{JT} G/(K + 2G)$

- PBE results: $\rho_0 =$ 0.068 Å, $E_{JT} = 25$ meV, and $\delta = 10$ meV
- HSE+SOC: $E_{JT} = 42$ meV, $\delta = 9$ meV. (Thiering & Gali, 2017)
An example of the $Q_y$ modes

- Red arrows are displacement vectors, which sum to zeros in the x- and z-directions.
- Moving away from the vacancy, displacements decay but do not quickly diminish.
Dynamic Jahn-Teller effect

- From the PBE results for $\rho_0$, $E_{JT}$, and $\delta$, we obtain $F = -0.74$ eV/Å, $G = 1.76$ eV/Å$^2$, and $K = 14.5$ eV/Å$^2$

- Using the $K$, we estimated the energy ($\hbar \omega$) for the local vibrational mode (LVM) to be 71 meV

- For a Mexican hat potential ($G = 0$), the system dynamics involves a radial vibration and a free rotation along the bottom of the trough in the Mexican hat

- However, since $G \neq 0$ and $\hbar \omega \gg \delta$ ($= 10$ meV), the dynamics is better described as a hindered internal rotation, namely, we have a dynamic Jahn-Teller system [Fu, et al., PRL103, 256404 (2009)].
A complete E⊗e vibronic model for $^3E$

$$H^{JT} = H^{el}(Q_x, Q_y) - \frac{\hbar^2}{2M} \left( \frac{\partial^2}{\partial Q_x^2} + \frac{\partial^2}{\partial Q_y^2} \right) = 7.25 \text{ (eV/Å}^2\text{)} (Q_x^2 + Q_y^2)\sigma_z - 0.74 \text{ (eV/Å)} (Q_x\sigma_z - Q_y\sigma_x) + 1.76 \text{ (eV/Å}^2\text{)} [(Q_x^2 - Q_y^2)\sigma_z + 2Q_xQ_y\sigma_x]$$

- By diagonalizing $H^{JT}$, we obtain vibronic levels and transition energies:

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Energy (meV)</th>
<th>$\Delta E$ (meV)</th>
<th>Expt. (meV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>36.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_1$</td>
<td>71.7</td>
<td>$E \to A_1$ (3$\Gamma$): 35</td>
<td></td>
</tr>
<tr>
<td>$A_2$</td>
<td>103.8</td>
<td>$E \to A_2$: 67</td>
<td>60</td>
</tr>
<tr>
<td>$E$</td>
<td>114.8</td>
<td>$A_2 \to E$: 11</td>
<td>10</td>
</tr>
</tbody>
</table>

Zero phonon line (ZPL) dephasing rate

- Fu, et al. [PRL103, 256404 (2009)] showed that the dephasing of the ZPL at low temperature ($T$) is dominated by a coupling between the electronic $E$ doublet and $e$ phonons.

- A $T^5$-dependence of the linewidth was explained by a two-phonon Raman process, which results in a dephasing rate:

$$ W = \frac{2\pi}{\hbar} \int_0^{\hbar \omega_D} dE n(n + 1) \rho_{DOS}^2(E) \frac{V^4(E)}{E^2} $$

where $V$ is related to $F$(DFT) by $V(E) = F \sqrt{\hbar^2/2ME}$

- We simplified $W$ to

$$ \frac{8\pi}{\hbar} \left( \frac{\Omega_{cell}}{2\pi^2 \hbar^3 v_{sound}^3} \right)^2 C^4 (k_B T)^5 I_4 \left( \frac{\hbar \omega_D}{k_B T} \right) $$

where $I_4$ is a Debye integral.
Comparison with experiment

- Our approximation for $W$ can cover a wider range of temperatures.
- Agreement with experiment, which were carried out on several different NV centers, is rather good.
Current status of the model


“interestingly, (the measured) $\omega_c$ closely approaches the calculated tunneling splitting (here) of 35 meV, suggesting possible electronic depolarization ...”

<table>
<thead>
<tr>
<th>$\omega_{\text{measured}}$ (cm$^{-1}$)</th>
<th>$\omega_{\text{literature}}$ (cm$^{-1}$)</th>
<th>$\omega_{\text{theory}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>736 ± 18</td>
<td>-</td>
<td>734 (ref. 24)</td>
</tr>
<tr>
<td>1,028 ± 22</td>
<td>1,040 (ref. 36)</td>
<td>1,030 (ref. 24)</td>
</tr>
<tr>
<td>1,166 ± 22</td>
<td>1,130 (ref. 13, 36)</td>
<td>1,182 (ref. 24)</td>
</tr>
<tr>
<td>1,339 ± 31</td>
<td>1,332$^+$ (refs 26, 36)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>or 1344 (refs 13, 36)</td>
<td></td>
</tr>
<tr>
<td>1,525 ± 26</td>
<td>1,510$^+$ (ref. 26)</td>
<td>1,555 (ref. 24)</td>
</tr>
</tbody>
</table>

Issues with $NV^-$ centers in diamond

- Exact positioning is difficult; In addition,
  - near-surface NV suffers from surface-charge fluctuations: blinking due to jumps between $NV^-$ and $NV^0$ / spectral diffusion due to jumps within NV sublevels; and
  - in an ambient condition, water adsorption converts $NV^-$ to $NV^0$
- Low light-collection efficiency due to high refractive index
- Low qubit yield. This is because (a) the N-to-NV conversion efficiency is low, typically a few % and (b) the ZPL of the NV center is relatively weak compared to other photonic transitions.
NV-like center in not h-boron nitride

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Electron counting and the \((V_B - O_N)^0\) center

- To make an \(NV^-\) requires the removal of 4 els with C and the addition of 2 els: one by \(N_C\) and one by the (-) charge. Effectively, the \(NV^-\) center is a 2 e-deficient system.

- In \(V_B - O_N\), 3 els are removed with B, 1 el is added by \(O_N\). This amounts to a 2-el removal. Hence, the center should be \((V_B - O_N)^0\).

- In contrast in \(C_B - V_N\), 5 els are removed with N, 1 el is added by \(C_B\). One needs 2 additional els to maintain 2e-deficiency \([C_B - V_N]^{2^-}\).
Level shifts relative to $NV^-$ center

- In both cases, the Fermi level is between the minority-spin $e$ and $a_1$ states, so the electron counting model really works.
- Good similarity but in cBN all defect levels move down considerably.
- If we have $CV_N$, instead, these levels would move up considerably.
Optical transitions within Franck-Condon

- Good optical similarities between NV in diamond and OV$_B$ in cBN
- ZPL of 1.60 eV for $(V_B - O_N)^0$ matches the experimental GC-2 center (1.61 eV) in cBN.

HSE calculations for NV and OV$_B$:

<table>
<thead>
<tr>
<th>Defect</th>
<th>$A \rightarrow B$ (eV)</th>
<th>$C \rightarrow D$ (eV)</th>
<th>ZPL (eV)</th>
<th>$\Delta S$ (meV)</th>
<th>$\Delta AS$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NV^-$</td>
<td>2.21</td>
<td>1.74</td>
<td>1.96</td>
<td>258</td>
<td>217</td>
</tr>
<tr>
<td>$(OV_B)^0$</td>
<td>1.75</td>
<td>1.47</td>
<td>1.60</td>
<td>150</td>
<td>130</td>
</tr>
</tbody>
</table>

Dynamic Jahn-Teller Effect
Origin of the optical similarities

- Nearly identical “atomic”-like states between NV and OV$_B$
- Small differences: (a) the OV$_B$ states are more p-like and (b) BN has less donor contribution to the $a_1$ state than diamond does.

- OV$_B$ offers a small variation to NV → good for studying NV physics.
Anything else that supports the GC-2 assignment?

- Define $\Delta R_i = R_i(Q_e) - R_i(Q_g)$ the displacement vector, $p_{\alpha i}$ the polarization vector of the $\alpha$th phonon mode on the $i$th atom, and

$$\eta_\alpha = \sum_i \frac{1}{\sqrt{m_i}} p_{\alpha i} \cdot \Delta R_i$$

the projection of the displacement vector.

Calculated local vibration modes (LVM) and projections:

<table>
<thead>
<tr>
<th>$a_1$ modes</th>
<th>$e$ modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (meV)</td>
<td>$</td>
</tr>
<tr>
<td>51.6</td>
<td>1.5</td>
</tr>
<tr>
<td>53.4</td>
<td>1.0</td>
</tr>
<tr>
<td>57.2</td>
<td>2.1</td>
</tr>
<tr>
<td>64.6</td>
<td>0.5</td>
</tr>
<tr>
<td>67.3</td>
<td>1.0</td>
</tr>
<tr>
<td>81.7</td>
<td>0.4</td>
</tr>
<tr>
<td>89.2</td>
<td>0.0</td>
</tr>
<tr>
<td>$a_2$ mode</td>
<td></td>
</tr>
</tbody>
</table>

- The first three LVMs, weighted by $|\eta|^2$, is 55 meV, which is in good agreement with the experimental result of 56 meV for GC-2.
Electron counting: While one can ignore the bonding along $z$, it takes away 0 and 2 electrons for B and N, respectively. As such, B and N become “equivalent” in the 2D counting.

Primary point defects to consider: $V_B(-3), V_N(-3), O_N(+1), C_B(+1)$, as well as $N_B(0)$ and $B_N(0)$, where electron deficiency (excess) from perfect crystal is indicated. Note that, due to symmetry difference, the 2-electron-deficiency rule for diamond and cBN needs not apply here.

This yields possible 1$^{\text{st}}$ nn pairs: $OV_B(-2), CV_N(-2), B_NV_B(-3)$, and $N_BV_N(-3)$ and 2$^{\text{nd}}$ nn pairs: $CV_B(-2), OV_N(-2), N_BV_B(-3)$, and $B_NV_N(-3)$. 

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Summary

- Reviewed our earlier dynamic Jahn-Teller calculation
- Proposed $OV^0_B$ in cBN for its great similarity to $NV^-$ and suggested it as the experimental GC-2 center.

Thank You for Attention!