Nitrogen Vacancy Center in Diamond for Stress and Field Sensing Applications

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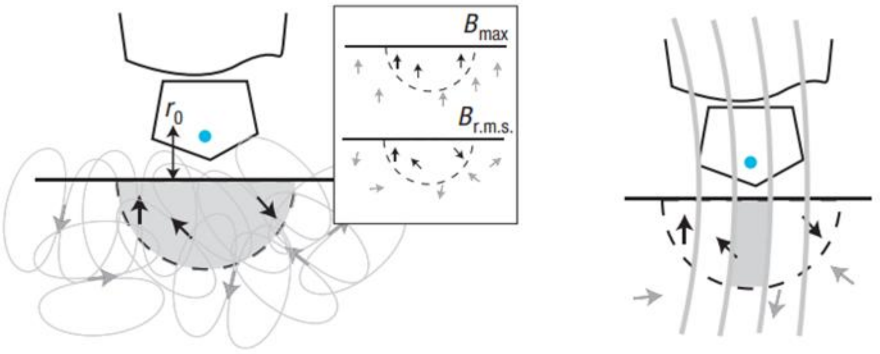
Presentation Outline

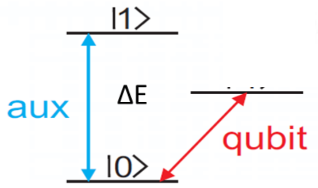
- Quantum materials' electronic and optical features
  - Diamond: A promising candidate material for sensing
  - Experiments: Metal organic framework (MOF) encapsulated nanodiamonds
  - Theoretical modeling: Band structures, density of states, response to strains
  - Theoretical model: Level splitting/shifting under stress
- Technological merits
- Conclusion

Quantum Materials for Sensing

Nitrogen vacancy centers in diamond is a promising quantum sensing material.

- Atomic impurity (N, Si, Sn, etc.) and carbon vacancy in a diamond lattice: spin qubits
  - Optically-Detected Magnetic Resonance (magnetometry, thermometry, electrometry)
  - Spin Relaxometry (field and stress sensing)
  - Zero Phonon Line Emission (thermometry)
  - Room Temperature Operation

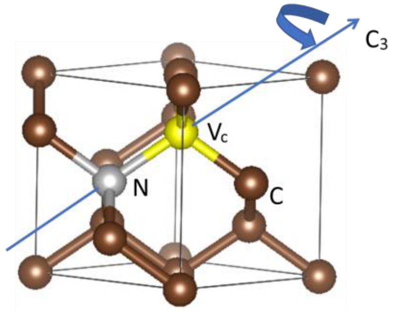




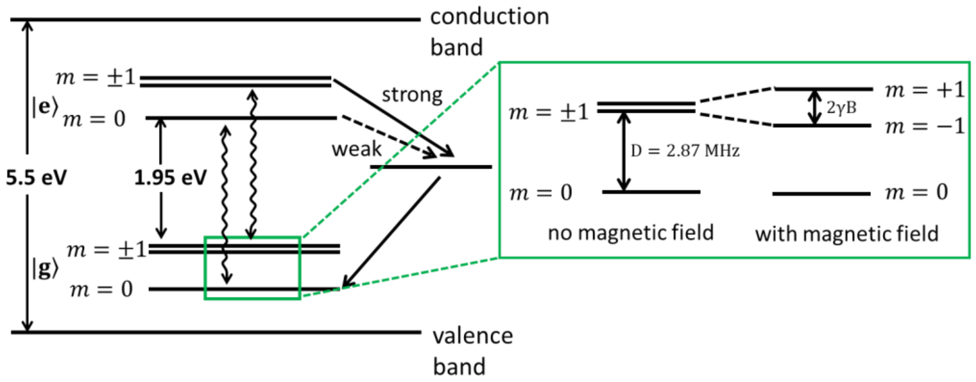
Solid state quantum system

$$\eta_{\mathrm{sp}}^{\mathrm{ensemble}} \approx \frac{\hbar}{\Delta m_s g_e \mu_B} \frac{1}{\sqrt{N\tau}}$$

Field sensitivity 8 nT/sqrt(Hz) @ T = 300 K.



Vacancy in diamond.



Electronic bands of NV center in diamond.

PHYS. REV. APPLIED 17, 044028 (2022)

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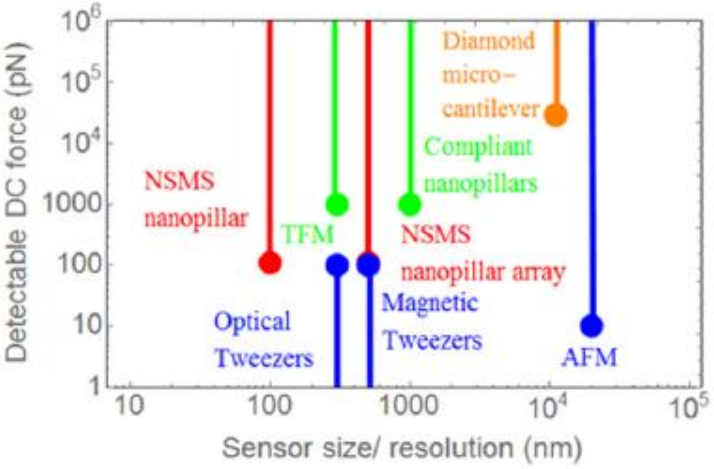
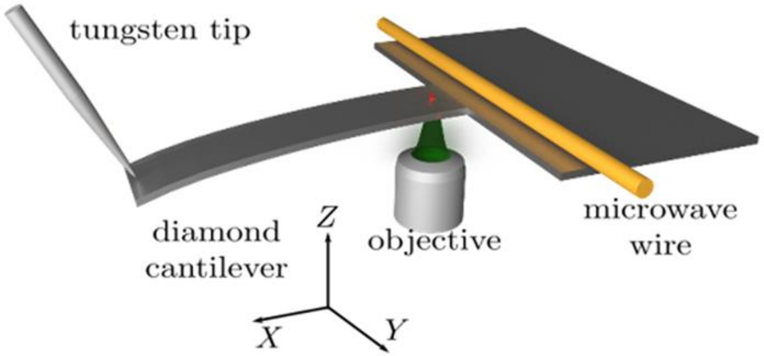
An unprecedented level of field sensitivity could be achieved using NV center in a diamond.

NV Center Nanodiamond as a Pressure Sensor

Nanomechanical Sensing

Nanomechanical microscopy

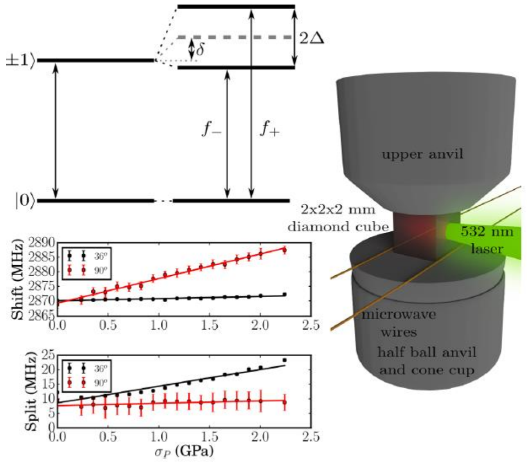




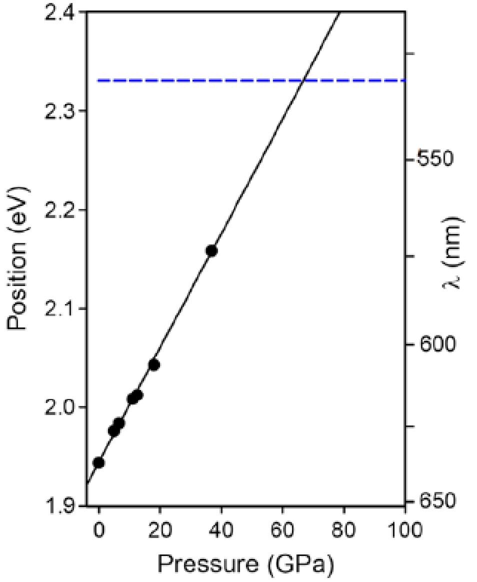
Nano Lett. 2017, 17, 1496–1503.

$$\eta_{gs} = \frac{1}{2\pi \frac{dD(p)}{dp} K \sqrt{T_2^*}}$$

Nano-spin mechanical system (NSMS) sensor high-resolution and low minimum detectable force field.



Shift and split of the spin manifold.

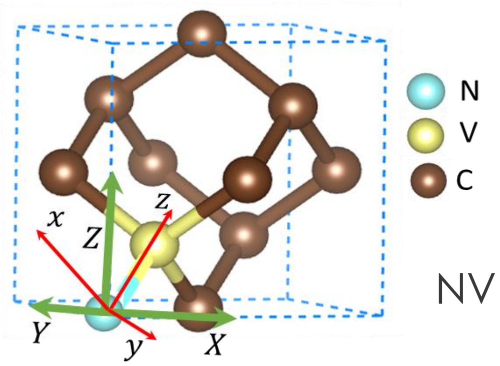


Change in zero phonon line (ZPL)

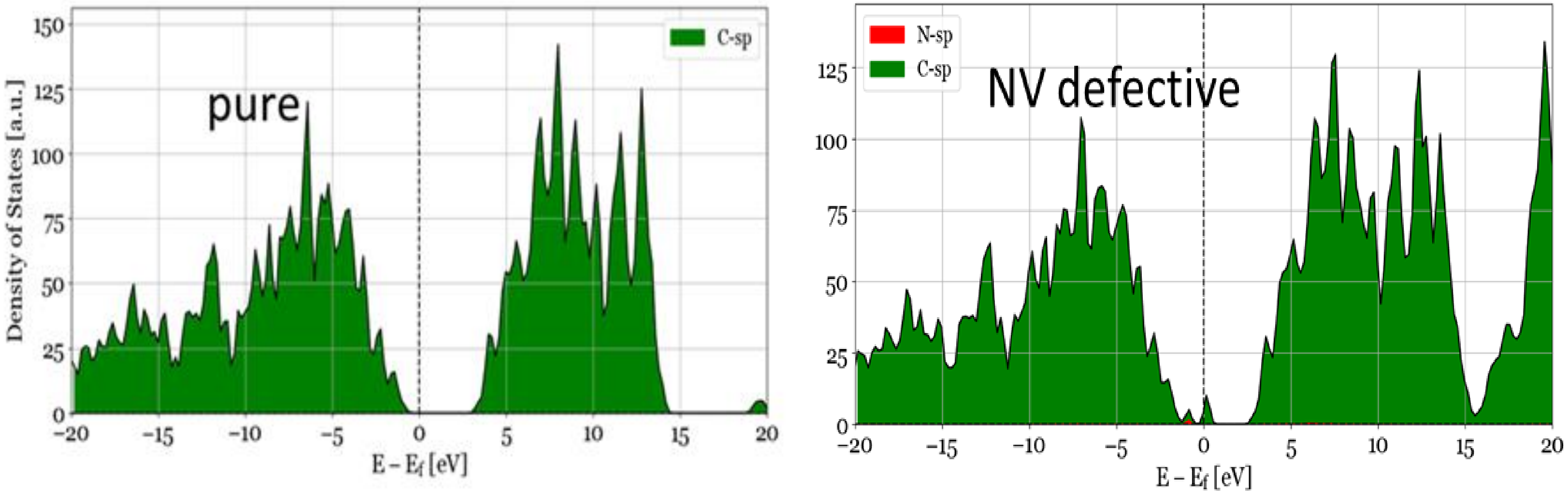
PRL 112, 047601 (2014).

Pressure sensitivity ~ 0.6 MPa/sqrt(Hz) at T = 300 K; 68 Pa/sqrt(Hz) @ T < 12 K.

Electronic Structures



NV dipole orientation along [111].

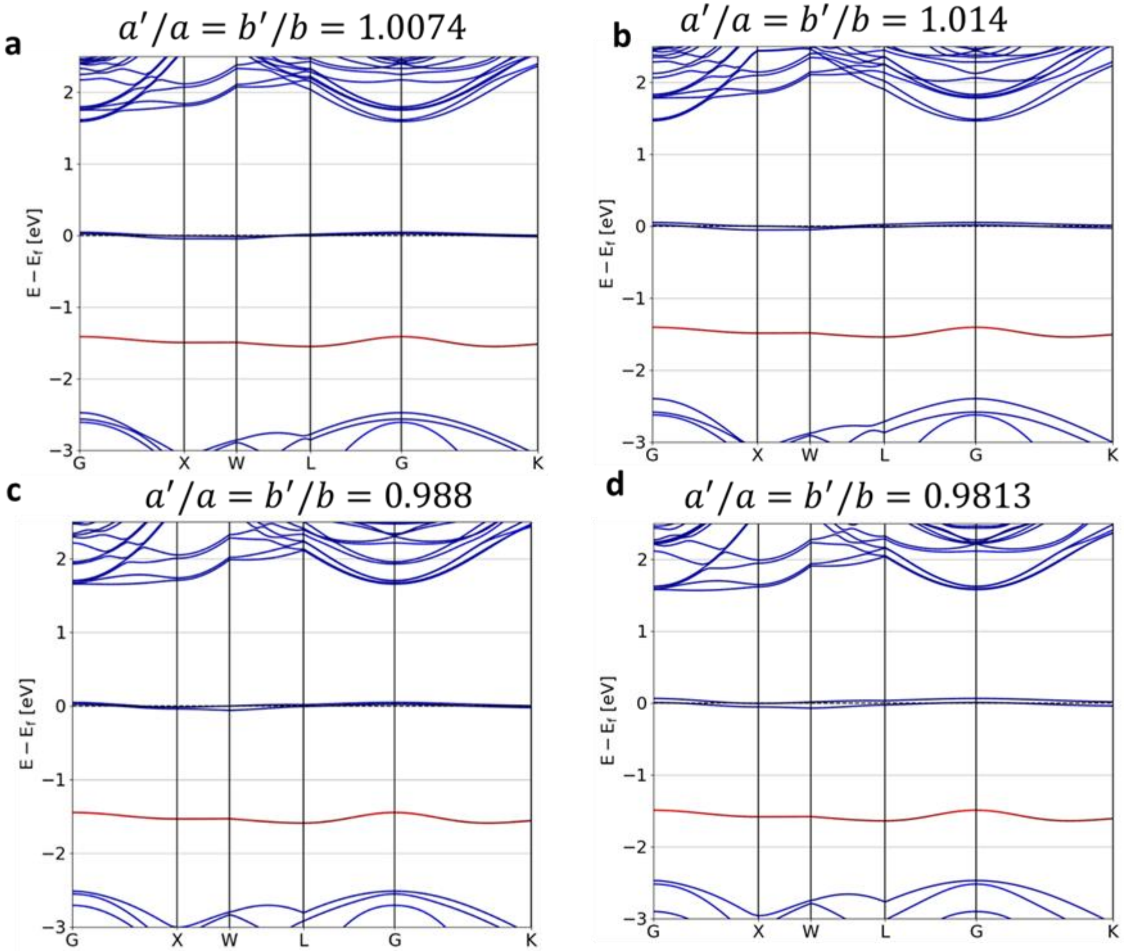


Electronic density of states with negative NV defect.

Electronic Bandstructures of NV Center Diamond

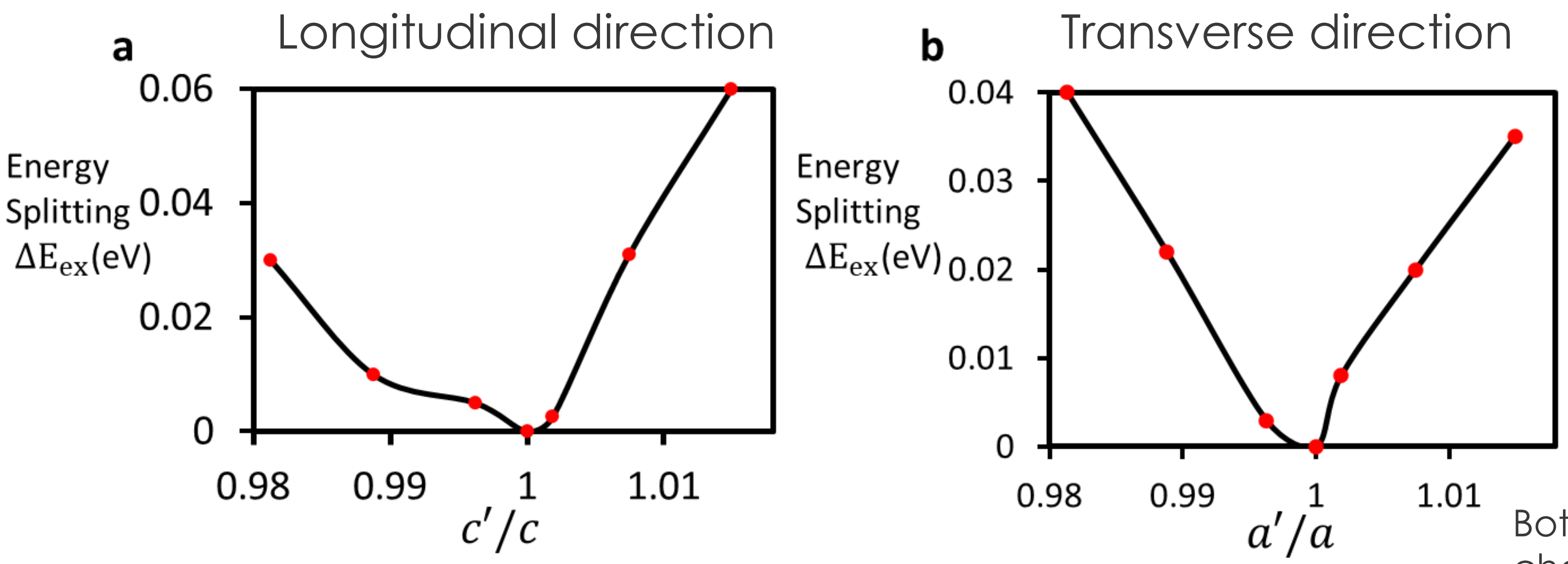
- Shifting of band gap and splitting of band edge under (up to ±2%) changes in the lattice parameters.
- Conduction band edge split by up to 60 milli electron volt (meV) due to compressive strain under up to 2% changes in the transverse lattice parameters (a, b).
- The split is nearly 40 meV due to tensile strain under up to 2% changes in the longitudinal lattice parameters (c).

a, b lattice parameter changes



Band Edge and Band Gap Shift

Band Edge Shift



Both a and b were changed simultaneously.

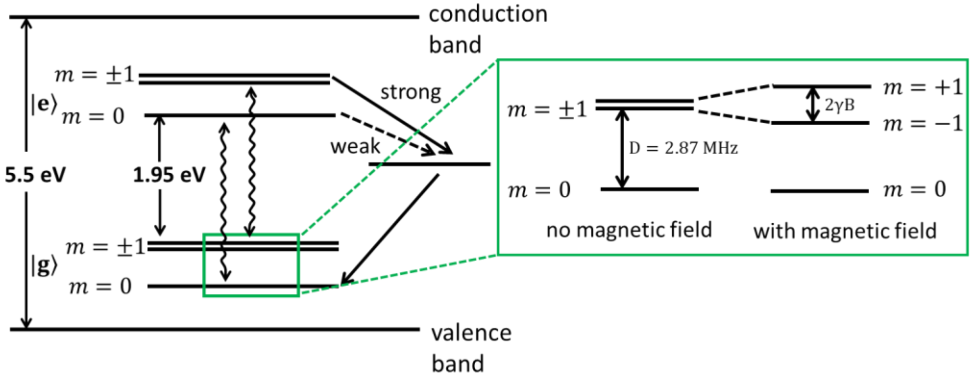
Optical sensor based on the band gap or band edge shift: Wavelength shift per unit stress on the photoluminescence (PL) peak.

For $\sigma_{xx} = \sigma_{yy} \sim 25$ GPa, the conduction band edge shift, $\Delta E_{ex} \sim$ 60 meV.

Band shift per unit GPa, $\frac{\Delta E_{ex}}{\mathrm{DP}} \sim$ 2.4 meV
Wavelength shift per unit GPa, $\Delta\lambda \sim$ 2 nm

Model for Low Energy Hamiltonian

The ground state of negative NV center in a nanodiamond is described by the Hamiltonian:



$H_o = D_0 S_z^2 + \gamma_e \boldsymbol{B} \cdot \boldsymbol{S}$ $D_0 = 2.87$ GHz

For $(0,0,B_z)$= 10 mT, the Zeeman splitting $(\gamma_e B_z)$ ~140 MHz

The transverse components of the field weakly couple to $\boldsymbol{S} = (S_x,\ S_y,\ S_z)$

Under the applied stress:

$$H = D_0 S_z^2 + M_z S_z^2 + N_x\{S_x, S_z\} + N_y\{S_y, S_z\} + M_x\left(S_y^2 - S_x^2\right) + M_y\{S_x, S_y\} + \gamma_e \boldsymbol{B} \cdot \boldsymbol{S}$$

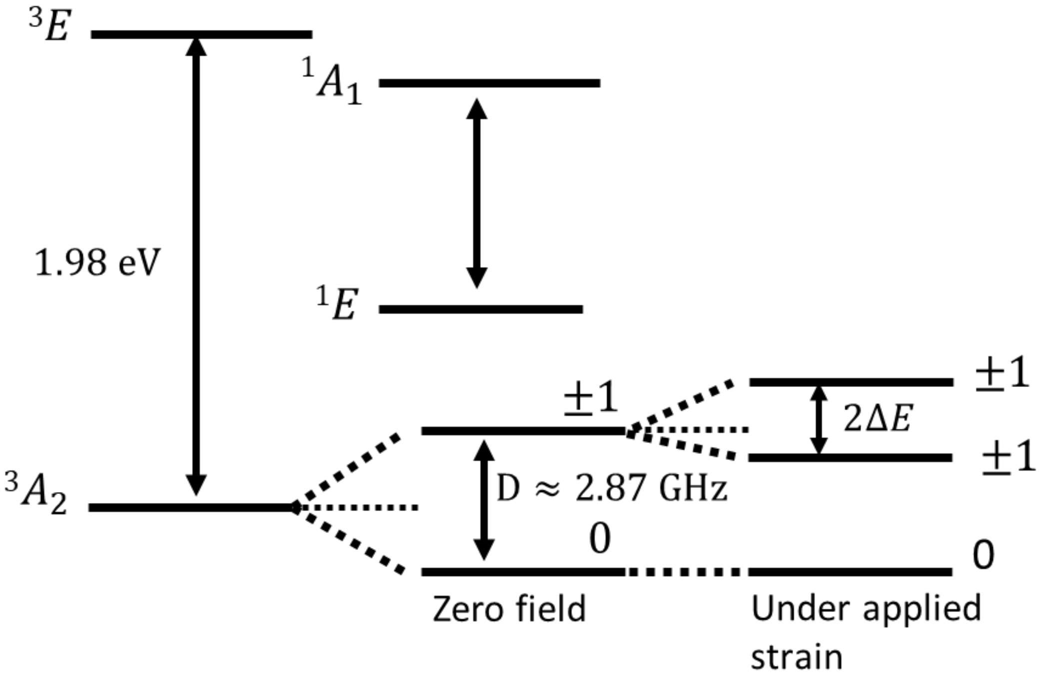
The first two eigenvalues of H (in per GPa)

$$\boxed{\omega_{|\pm 1\rangle} = D_o + M_z \pm \sqrt{(\gamma_e B)^2 + {M_x}^2 + {M_y}^2}}$$

Model for Low Energy Hamiltonian

Energy Splitting for Four Different NV Center Orientations

Applied stress direction	NV sub-ensemble direction	Shift/Splitting per unit pressure
$\boldsymbol{p} \parallel [\mathbf{100}]$	$\boldsymbol{e}_z \in \{111, \bar{1}\bar{1}1, \bar{1}1\bar{1}, 1\bar{1}\bar{1}\}$	$\mathrm{a}_1 \pm 2\mathrm{b}$
$\boldsymbol{p} \parallel [\mathbf{110}]$	$\boldsymbol{e}_z \in \{111, \bar{1}\bar{1}1\}$	$\mathrm{a}_1 + \mathrm{a}_2 \pm (\mathrm{b} - \mathrm{c})$
	$\boldsymbol{e}_z \in \{\bar{1}1\bar{1}, 1\bar{1}\bar{1}\}$	$\mathrm{a}_1 - \mathrm{a}_2 \pm (\mathrm{b} - \mathrm{c})$
$\boldsymbol{p} \parallel [\mathbf{111}]$	$\boldsymbol{e}_z \in \{111, \bar{1}\bar{1}1\}$	$\mathrm{a}_1 + 2\mathrm{a}_2$
	$\boldsymbol{e}_z \in \{\bar{1}1\bar{1}, 1\bar{1}\bar{1}\}$	$\mathrm{a}_1 - 2\mathrm{a}_2/3 \pm 4c/3$



Dependence of splitting/shifting on the direction of stress, and orientation of dipoles.

For $p \parallel [111]$, there is no splitting of the energy level for $e_z \in \{111, \bar{1}\bar{1}1\}$ NV orientations.

Spin Manifold Split and Shift

$(0,0,B_z)$= 10 mT, the Zeeman splitting ($\gamma_e B_z$) ~140 MHz from the center energy line

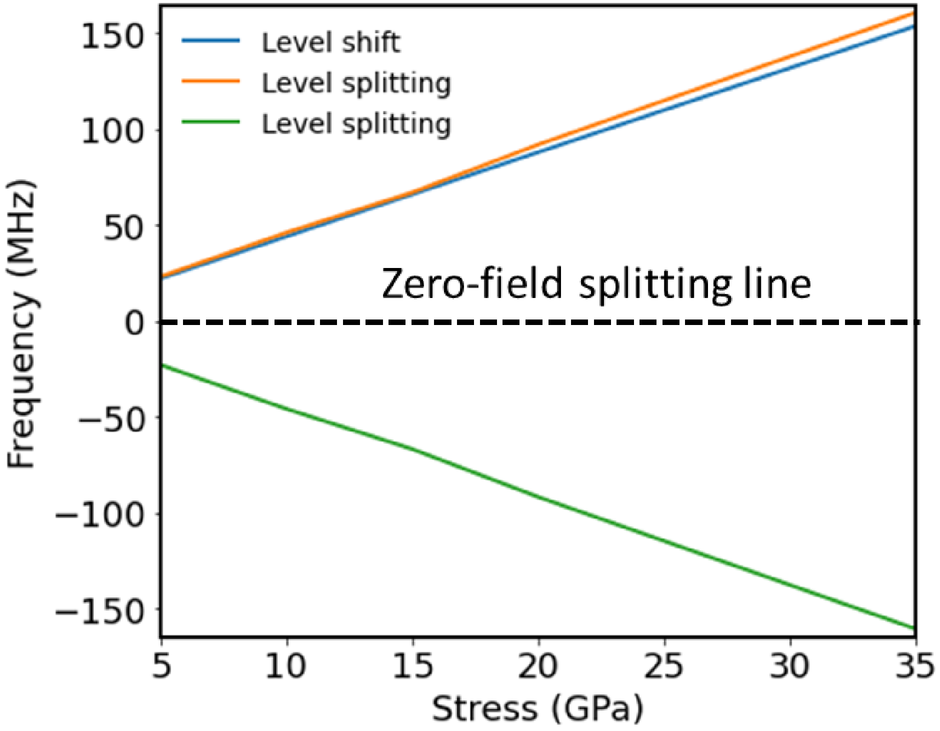
This is equivalent to applying more than 30 GPa pressure!

Energy shift, and the splitting $\{\delta E, \Delta E\}$

$\{3,\ 0\}$ MHz/GPa for $\boldsymbol{p} \parallel [111]$

$\{0.7,\ \pm 5.8\}$ MHz/GPa for $\boldsymbol{p} \parallel [110]$

$\{4.4,\ \pm 4.6\}$ MHz/GPa for $\boldsymbol{p} \parallel [100]$

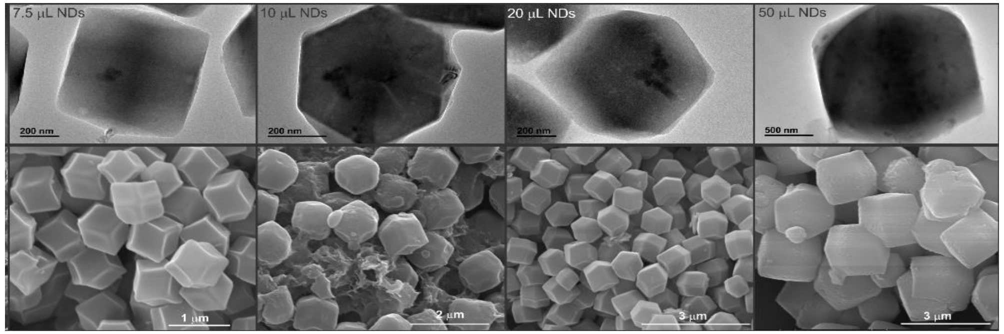


NV center oriented along [111] direction with applied stress along [100].

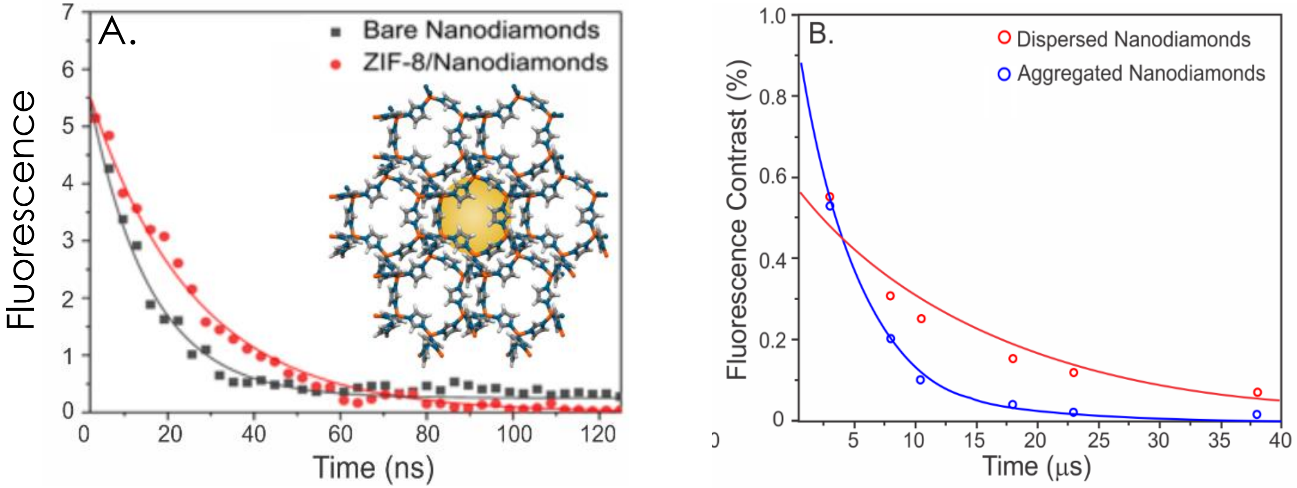
Above pressure limit is equivalent to applying only 1 mT magnetic field!

ODMR for NV Center Diamond

- **Developing functional, tunable materials for target analytes.**
- **The addition of a MOF shell around nanodiamonds for sensitive sensors development:**
  - Simple reaction process to grow ZIF-8 MOFs on nanodiamonds.
  - Optically detected magnetic resonance (ODMR) with and without MOF encapsulation, confirms potential for quantum sensing applications.

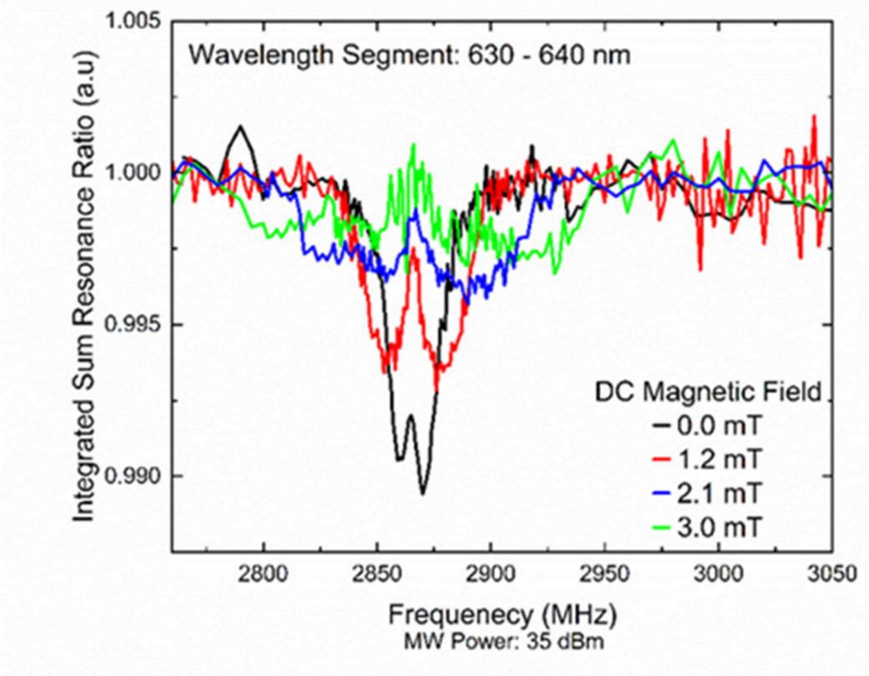


70 *nm* average distribution of nanoparticles.



Shugayev, Crawford, *et al, Chem. Mater.* 2021, **33**, 16, 6365–6373.

ODMR for NV Center Diamond



$$\omega_{|\pm 1\rangle} = D_o + M_z \pm \sqrt{(\gamma_e B)^2 + {M_x}^2 + {M_y}^2}$$

Zero stress limit splitting per unit applied DC field ~16 MHz/mT.

NV Center Stress Sensitivity

Spin relaxation time was recoded up to several microseconds in both encapsulated and bare nanodiamond.

The stress sensitivity: $\eta_{gs} = \left(2\pi C(dD/dP)\sqrt{T_2^*}\right)^{-1}$

ND dipole $\boldsymbol{e}_z \in 111$

Applied stress $\boldsymbol{p} \parallel [111]$,

Level shift $\mathrm{dD/dP} = 3$ MHz/GPa.

Spin dephasing $T_2^* \approx 10\ \mu s$

$$\eta_{gs} \approx 0.32\ \mathrm{MPa}/\sqrt{\mathrm{Hz}}$$

Shugayev, Crawford, *et al*, *Chem. Mater.* 2021, **33**, 16, 6365–6373.

Superiority of NV Center Diamond

Compare resolve frequency per unit pressure with the traditional sensors

Band shift per unit GPa, $\frac{\Delta E}{\mathrm{DP}} \sim 2.4$ meV from the bandstructure calculations

$\approx 3 \times 10^5$ MHz/GPa

Typical spin level shift/split per unit GPa

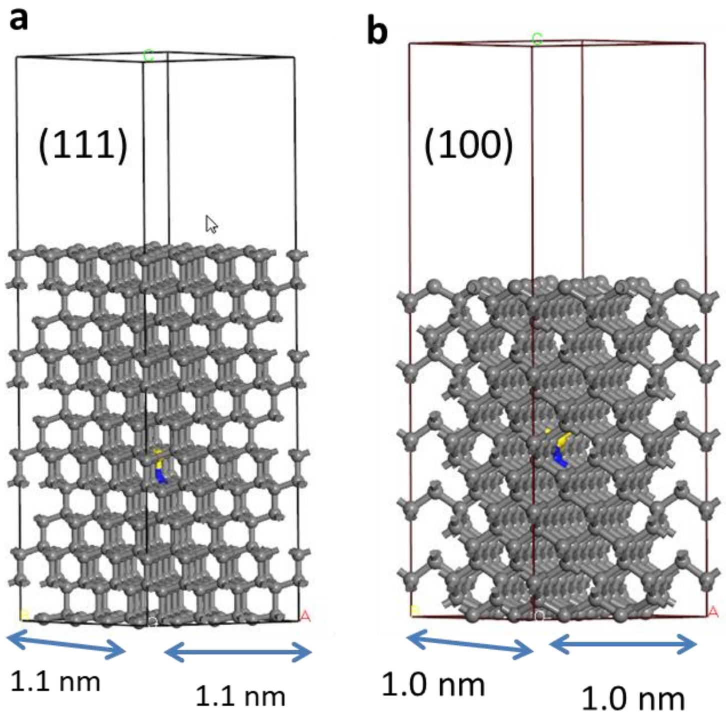
$\approx$ 2-4 MHz/GPa

This is approximately a 4th order of magnitude improvement over traditional optical sensor!

This shows a superiority of stress sensitivity behavior that could be achieved by manipulating the ground state spin levels in NV center nanodiamond over the traditional optical sensor based on the band edge or band gap shifting.

Nanodiamond Surface for Functionalization

Surface Models



12 bilayers

10 bilayers

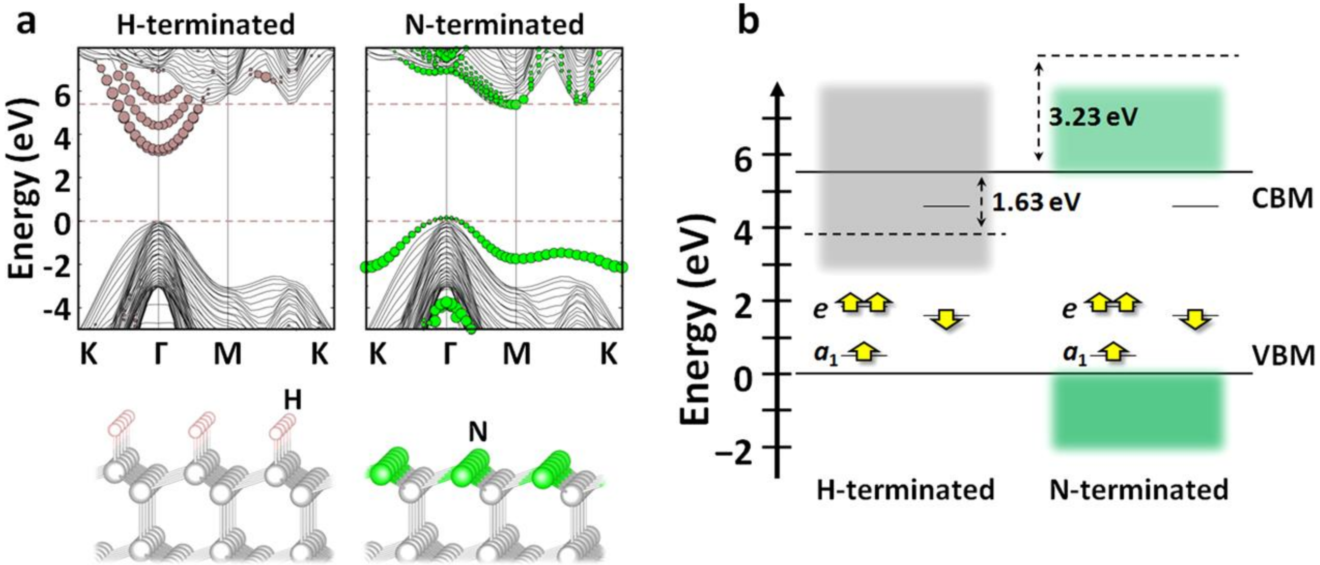
E_{surf} = 0.35 eV/A^2

E_{surf} = 0.96 eV/A^2

- Optimization of nanodiamond surfaces (111) and (100) with 10 and 12 bilayers. NV center (blue and yellow) was introduced after the surface optimization.
- In the experiment, (100) and (111) can be realized but the stability of charges in NV^- is largely determined by type of surface doping.

Diamond Surface Termination

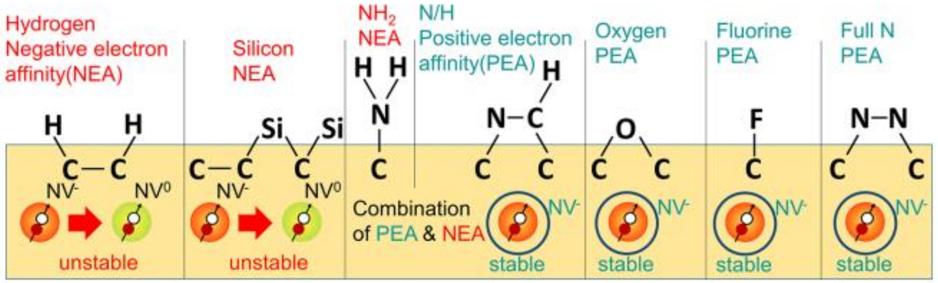
- The metal-organic chemical vapor deposition (MPCVD) growth of diamond results in hydrogen terminated at the surface.
- Has a high electric dipole moment, attracts polar molecule like water leading to the creation of a hole accumulation layer at the surface.
- Results in a negative electron affinity (releases energy when electron is gained), converting NV^- to NV0.
- Results in a blinking effect, low sensor resolution.



Gali et al., Nano Lett. 2017, 17, 2294−2298.

Stability and Surface Termination

- The ODMR contrast reduces significantly due to strain-induced line broadening, interactions with paramagnetic impurities, nontrivial charge dynamics, and inefficient pi-pulse for different NV orientations.
  - For example, the DC magnetic field sensitivity achieved is ~20 pT/√Hz for NV centers in the bulk compared to ~1 μT/√Hz for near-surface NV centers.
  - Positive electron affinity makes NV^- more stable.



Termination	H	Si	NH_2	N/H	O	F	Full N
Electron affinity [eV]	-1.0	-0.86	NEA	0.32	1.7	2.56	3.46
Shallow NV^-	Unstable	Unstable	Stable		Stable	Stable	Stable

Kawai et al, *J. Phys. Chem. C 2019, 123, 3594−36.*

Conclusions

- Discussed the electronic and optical features for NV center nanodiamond using first principles density functional theory approach.
- The band edge splitting/band gap shifting under strain due to changes in the lattice parameters in diamond shows ~2 meV/GPa.
- The low energy Hamiltonian could be used to predict the splitting of energy levels in $\pm$ spin manifold under the applied stress.
- In this experiment, ODMR and spin relaxometry were implemented to quantify the of NV center nanodiamond base devices.
- The quantum sensor is superior in sensitivity over classical sensing.

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