Nitrogen Vacancy Centers in Diamond for Stress Sensing Applications: Theory and Experiments

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American Physical Society, March Meeting 2024

Mar. 6, 2024

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NATIONAL ENERGY TECHNOLOGY LABORATORY

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Presentation Outline

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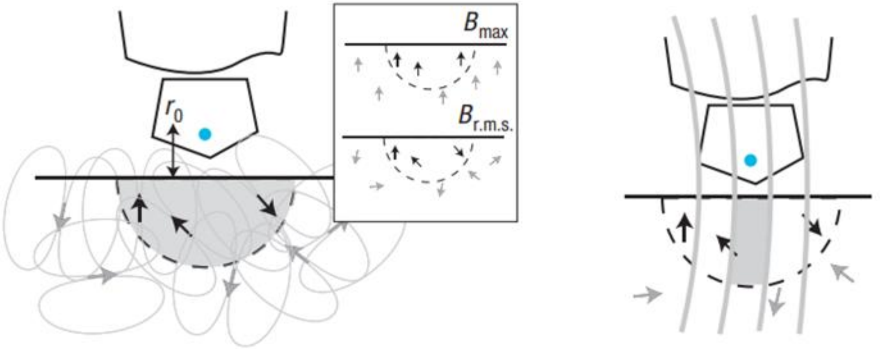
- Quantum materials' electronic and optical features
  - Diamond: A promising candidate material for sensing
  - Experiments: Metal organic framework (MOF) encapsulated nanodiamonds
  - Theoretical modeling: Band structures, density of states, response to strains
  - Theoretical model: Level splitting/shifting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

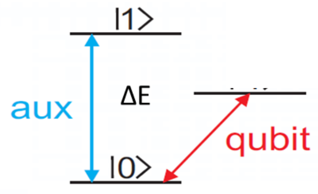
Quantum Materials for Sensing

Nitrogen Vacancy Centers in Diamond

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 Lime Emission (thermometry)
  - Room Temperature Operation

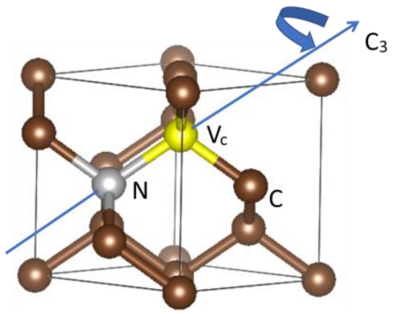




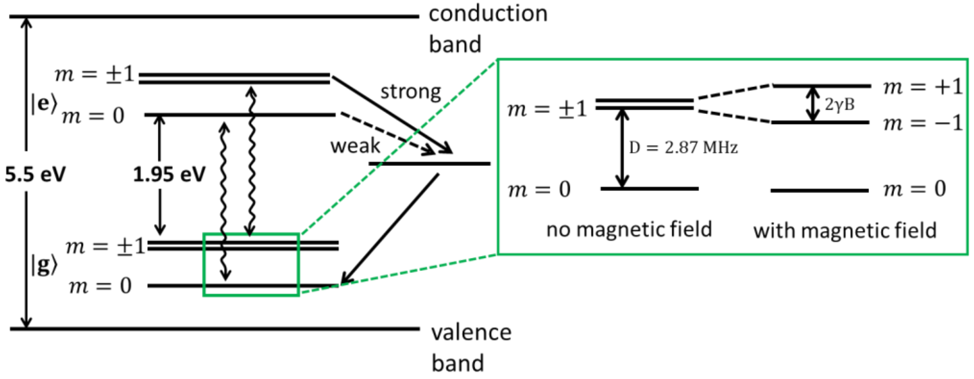
Solid state quantum system

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

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



Vacancy in diamond



Electronic bands of NV center in diamond

PHYS. REV. APPLIED 17, 044028 (2022)

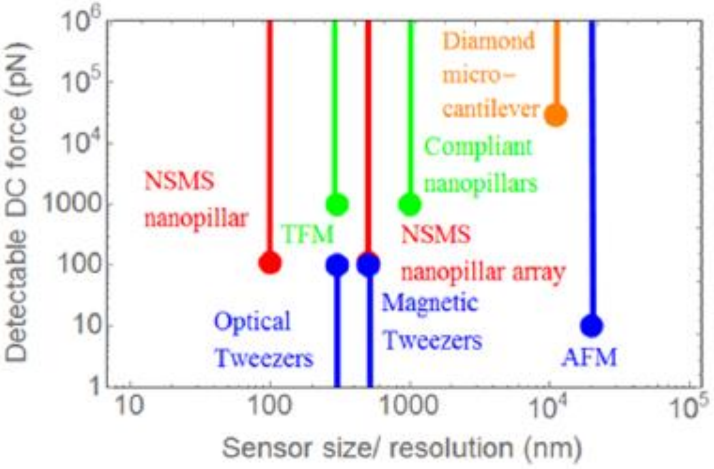
PHYS. REV. APPLIED 17, 044028 (2022)

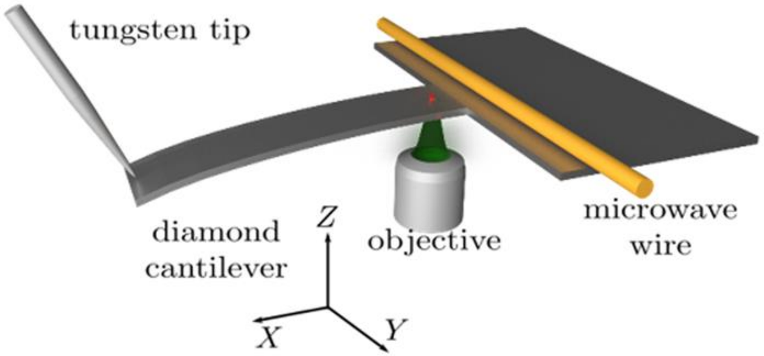
Unprecedented level of field sensitivity could be achieved using NV center in a diamond.

NV Center Nanodiamond as Pressure Sensor

Nanomechanical Sensing

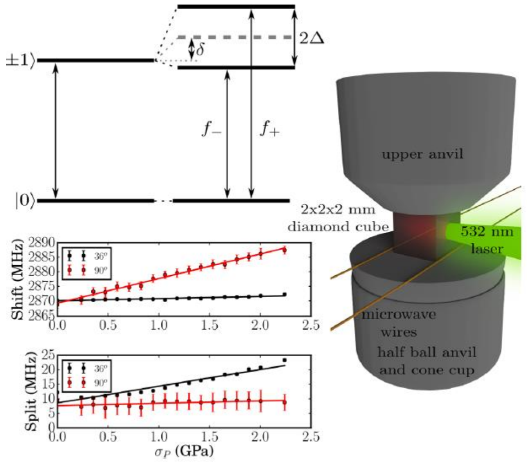
Nanomechanical microscopy



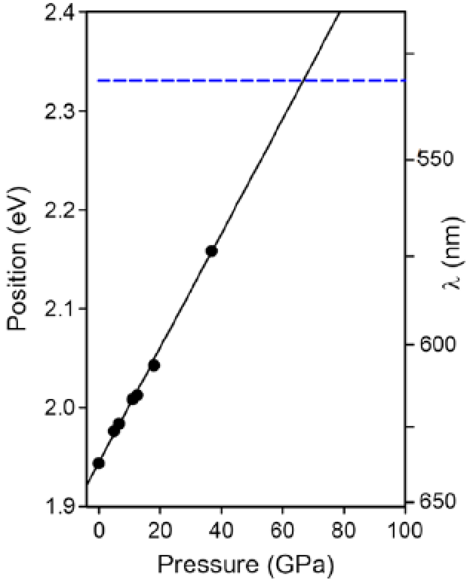


Nano Lett. 2017, 17, 1496−1503

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



Shift and split of the spin manifold



Change ZPL

PRL 112, 047601 (2014)

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

0.6 Mpa/sqrt(Hz) at T = 300 K; 68 Pa/ sqrt(Hz) @ T < 12 K

Electronic Bandstructures of NV Center Diamond

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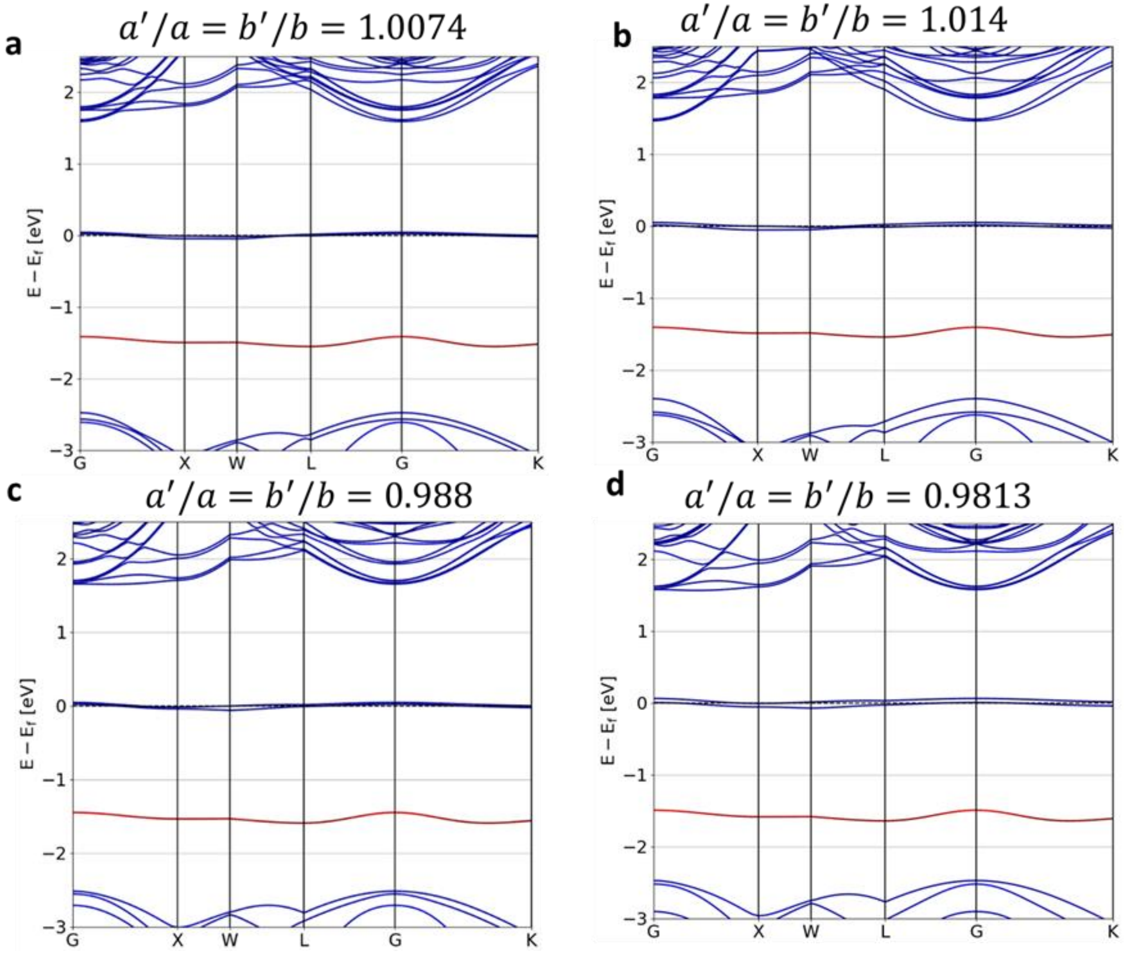
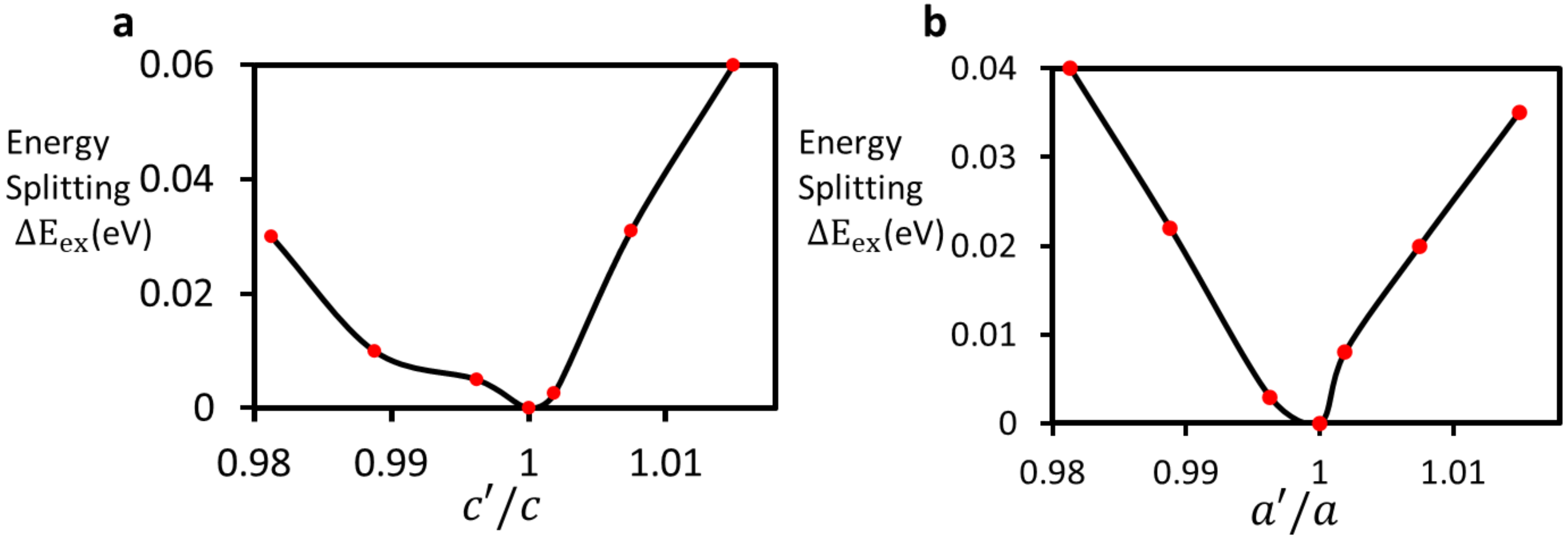
- Shifting of band gap and splitting of band edge under (up to $\pm$2%) changes in the lattice parameters.
- Conduction band edge split by up to 60 milli electron volt (meV) due to compressive strain under up to 2% changes in the transverse lattice parameters (a, b).
- The split is nearly 40 meV due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

Magnitude of the Conduction Band Edge Shift



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

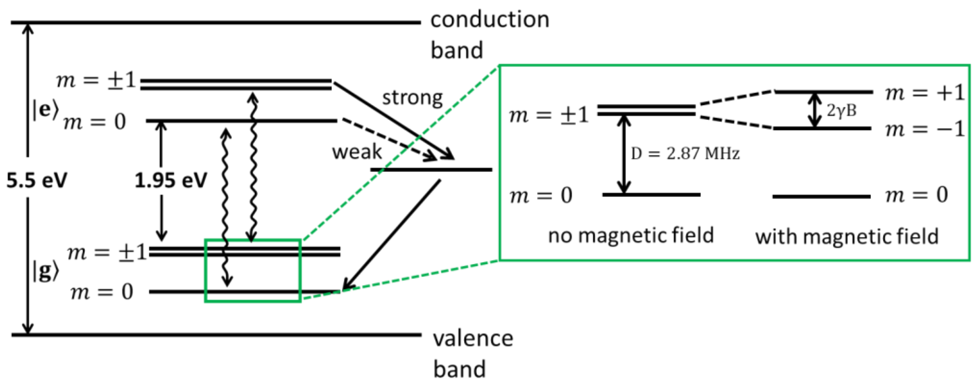
Model for Low Energy Hamiltonian

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

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

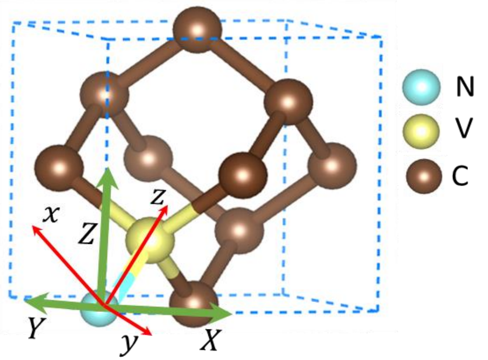
For $(0,0,B_z)$= 10 mT, the Zeeman splitting $(\gamma_e B_z)$ ~140 MHz

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



Under the applied stress

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



NV dipole orientation along [111]

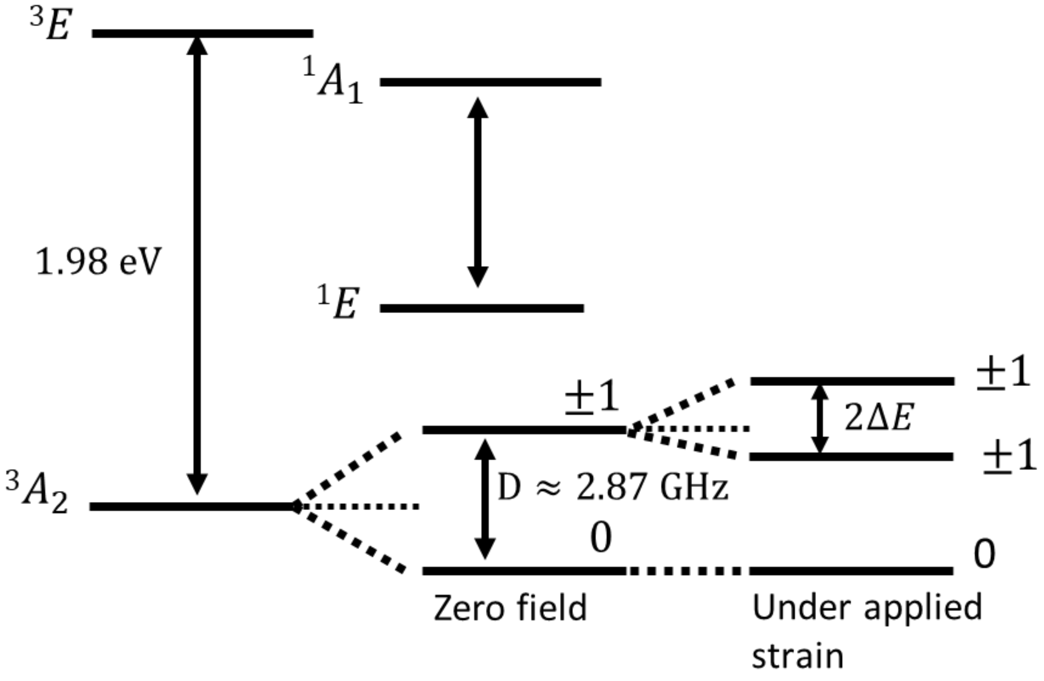
The first two eigenvalues of H (in per GPa)

$$\omega_{|\pm1\rangle} = D_o + M_z \pm \sqrt{(\gamma_e B)^2 + {M_x}^2 + {M_y}^2}$$

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
$\boldsymbol{p} \parallel [\mathbf{100}]$	$\boldsymbol{e}_z \in \{111, \bar{1}\bar{1}1, \bar{1}1\bar{1}, 1\bar{1}\bar{1}\}$	$a_1 \pm 2b$
$\boldsymbol{p} \parallel [\mathbf{110}]$	$\boldsymbol{e}_z \in \{111, \bar{1}\bar{1}1\}$	$a_1 + a_2 \pm (b - c)$
	$\boldsymbol{e}_z \in \{\bar{1}1\bar{1}, 1\bar{1}\bar{1}\}$	$a_1 - a_2 \pm (b - c)$
$\boldsymbol{p} \parallel [\mathbf{111}]$	$\boldsymbol{e}_z \in \{111, \bar{1}\bar{1}1\}$	$a_1 + 2a_2$
	$\boldsymbol{e}_z \in \{\bar{1}1\bar{1}, 1\bar{1}\bar{1}\}$	$a_1 - 2a_2/3 \pm 4c/3$



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

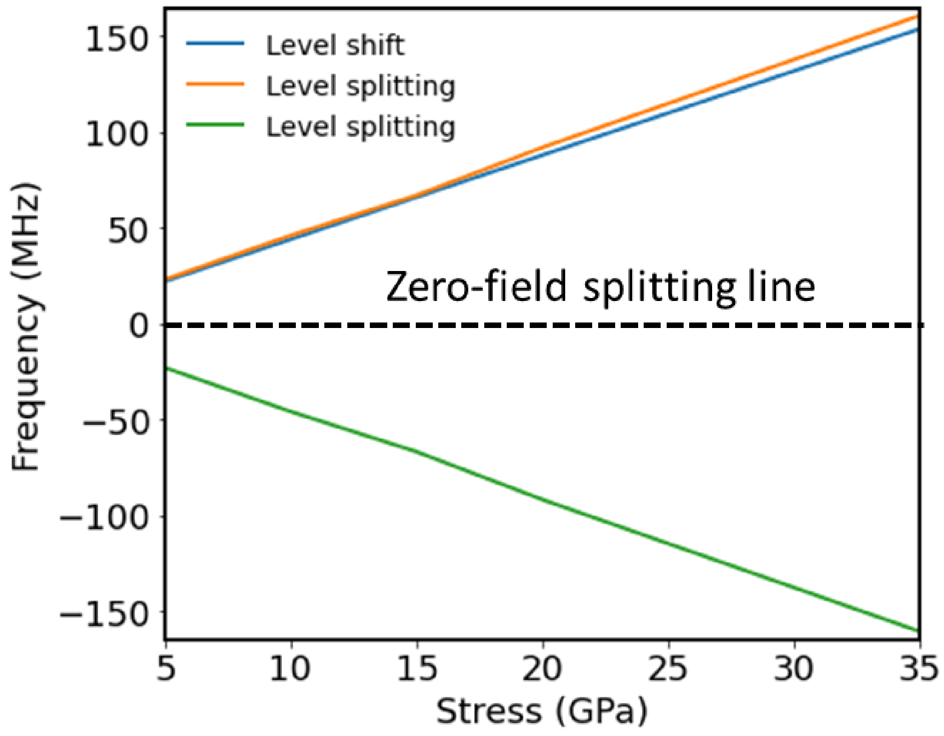
This is equivalent to applying more than 30 GPa pressure!

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 $\boldsymbol{p} \parallel [100]$

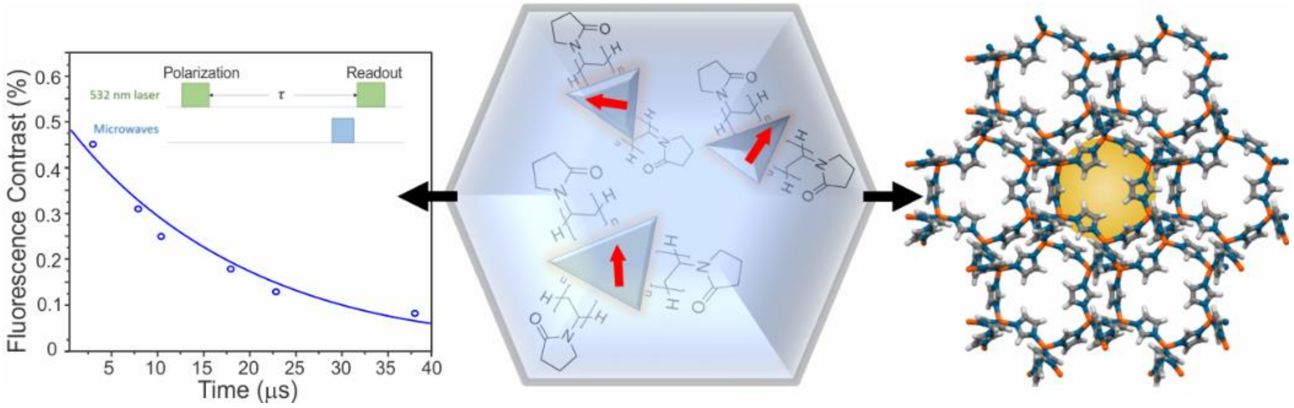


NV center oriented along [111] direction with applied stress along [100]

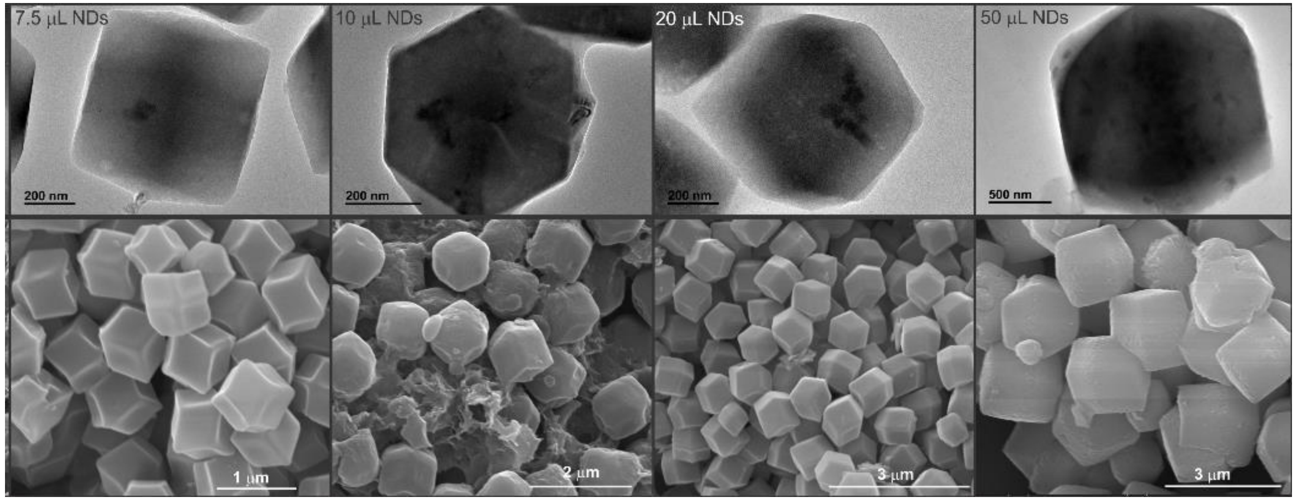
Above pressure limit is equivalent to just applying 1 mT magnetic field!

Nanodiamond Encapsulation

- **Developing functional, tunable materials for target analytes**
- **The addition of a MOF shell around nanodiamonds is a first step for sensitive sensors**
  - Simple reaction process to grow ZIF-8 MOFs on nanodiamonds.
  - Optical properties are unchanged or enhanced following MOF encapsulation, confirming potential for quantum sensing applications.



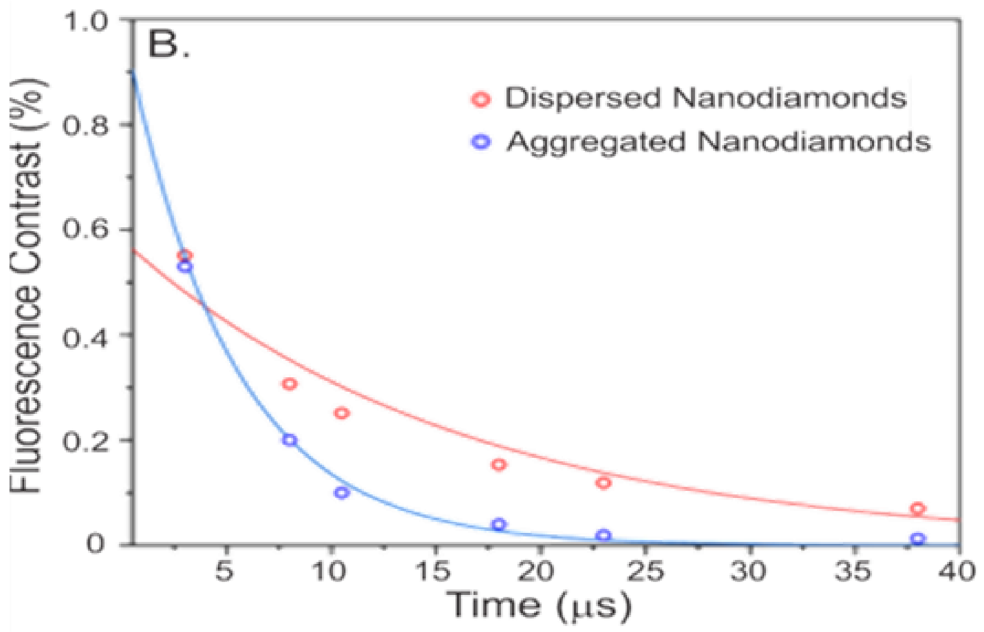
70 *nm* average distribution



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 to the Traditional Sensors Based on the Band Gap or Band Shift.

Compare resolve frequency per unit pressure

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

$\leftrightarrow\ 3 \times 10^5$ MHz/Gpa

Typical spin level shift/split per unit Gpa

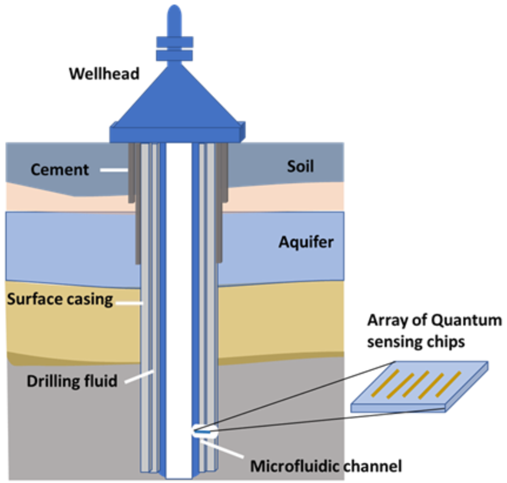
$\approx$2-4 MHz/GPa

Quantitatively this is about 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.

Potential Technological Merits: A "Quantum Manometer"

- Hydraulic fracturing of clay, sand, and rocks requires fluid injection under tens of MPa pressure through high-pressure well bores.
- Monitoring deep geological CO_2 storage and the potential induced seismic vibration triggering earthquakes (stress could reach up to 10-15 MPa).



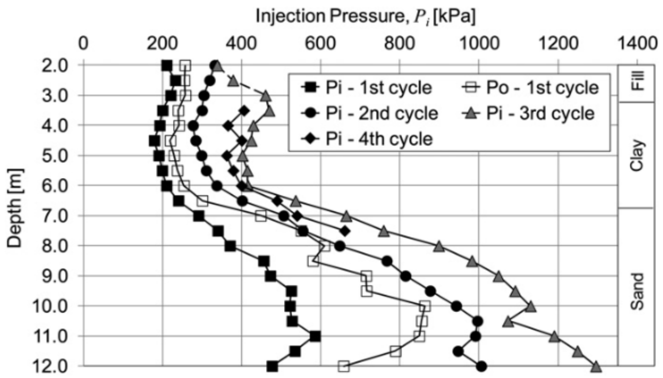
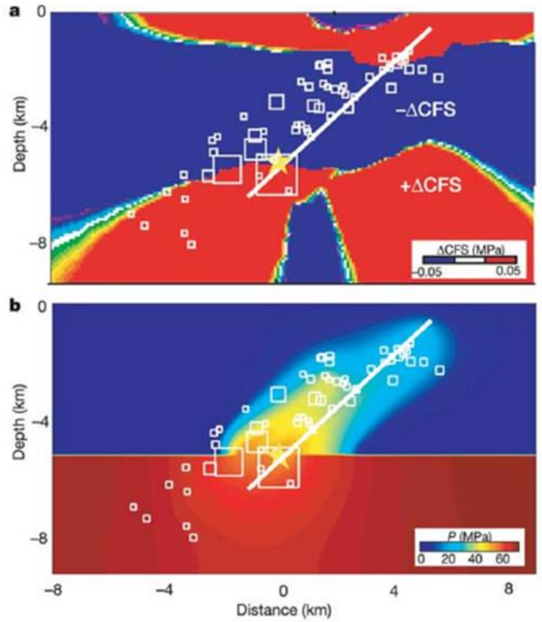


Fig. 9. Average injection pressures at the manometer versus depth for each cycle, and opening pressures at the manometer (open squares) versus depth only for the first cycle

Marchi1; G. Gottardi' 2013, J. Geotech. Geoenviron. Eng



Nature ***2004****, 427 (6976), 724-727*

NV center coated on the fiber could be developed and deployed to monitor the extreme pressure with high accuracy!

Conclusions

- Discussed the electronic and optical features for NV center nanodiamond using first principles density functional theory approach.
- Demonstrated the band edge splitting/band gap shifting strain due to changes in the lattice parameters.
- Implemented the model for low energy Hamiltonian to predict the splitting of energy levels in $\pm$ spin manifold under the applied stress.
- Discussed the experimental approach for the measurement of spin relaxation in in NV center nanodiamond.
- Discussed the superiority of quantum sensing over classical sensing by combining experimental and theoretical results.

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