Detecting rare earth elements via optically detected magnetic resonance (ODMR) and spin-relaxometry using nitrogen vacancy centers in nanodiamonds

NATIONAL ENERGY TECHNOLOGY LABORATORY

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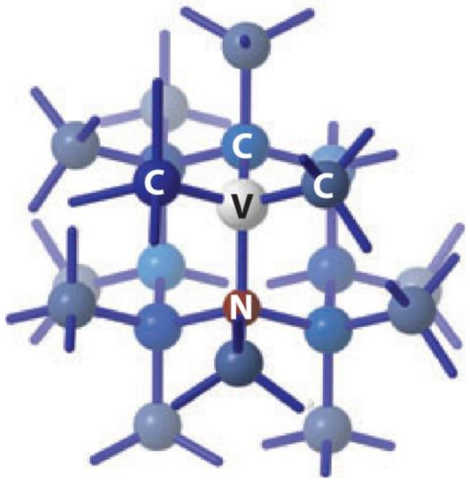
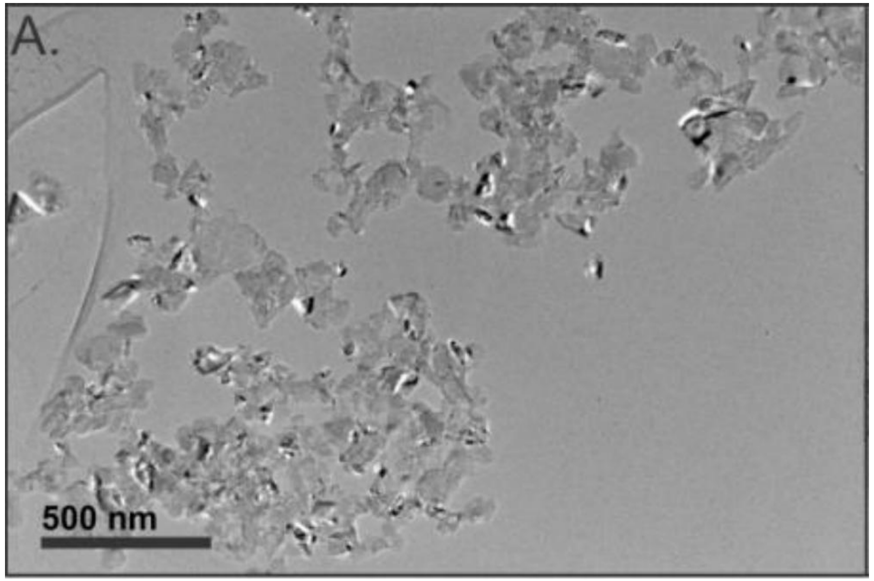
Motivation

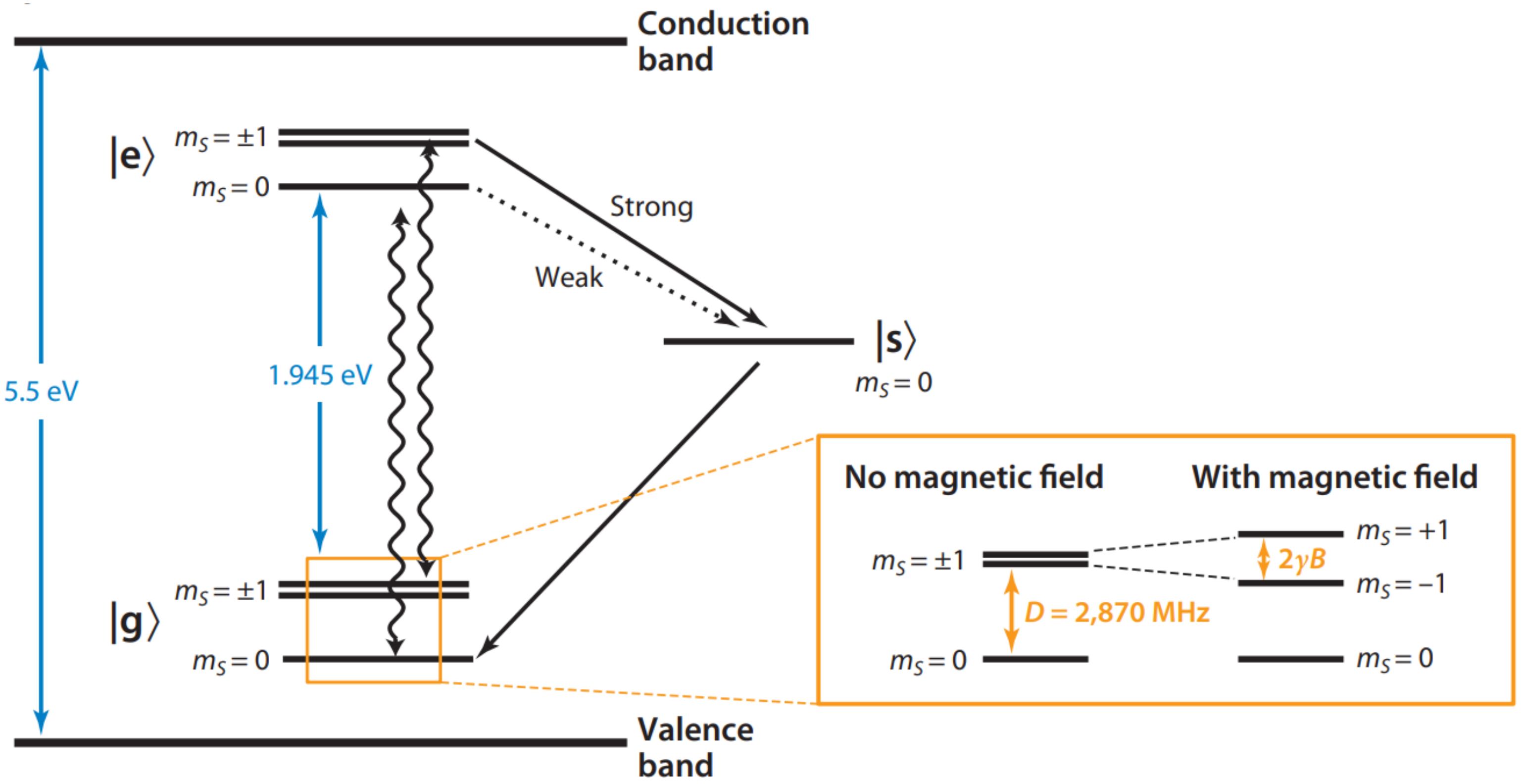
- ODMR can be used as a quantum sensor: nanoscale sensing and more sensitive (nT/ √ Hz).
- Nitrogen vacancy (NV) centers in diamond exhibit a tiny magnet. (works at room temperature and sensitive to local field)
- Physical quantities (e.g., magnetic field, electric field, temperature, and strain) affect crystal lattice, which affect energy levels and spin relaxation time.
- Magnetic field sensing capabilities offer rare earth elements (REE) detection.





NV⁻ diamond as a Sensing Material

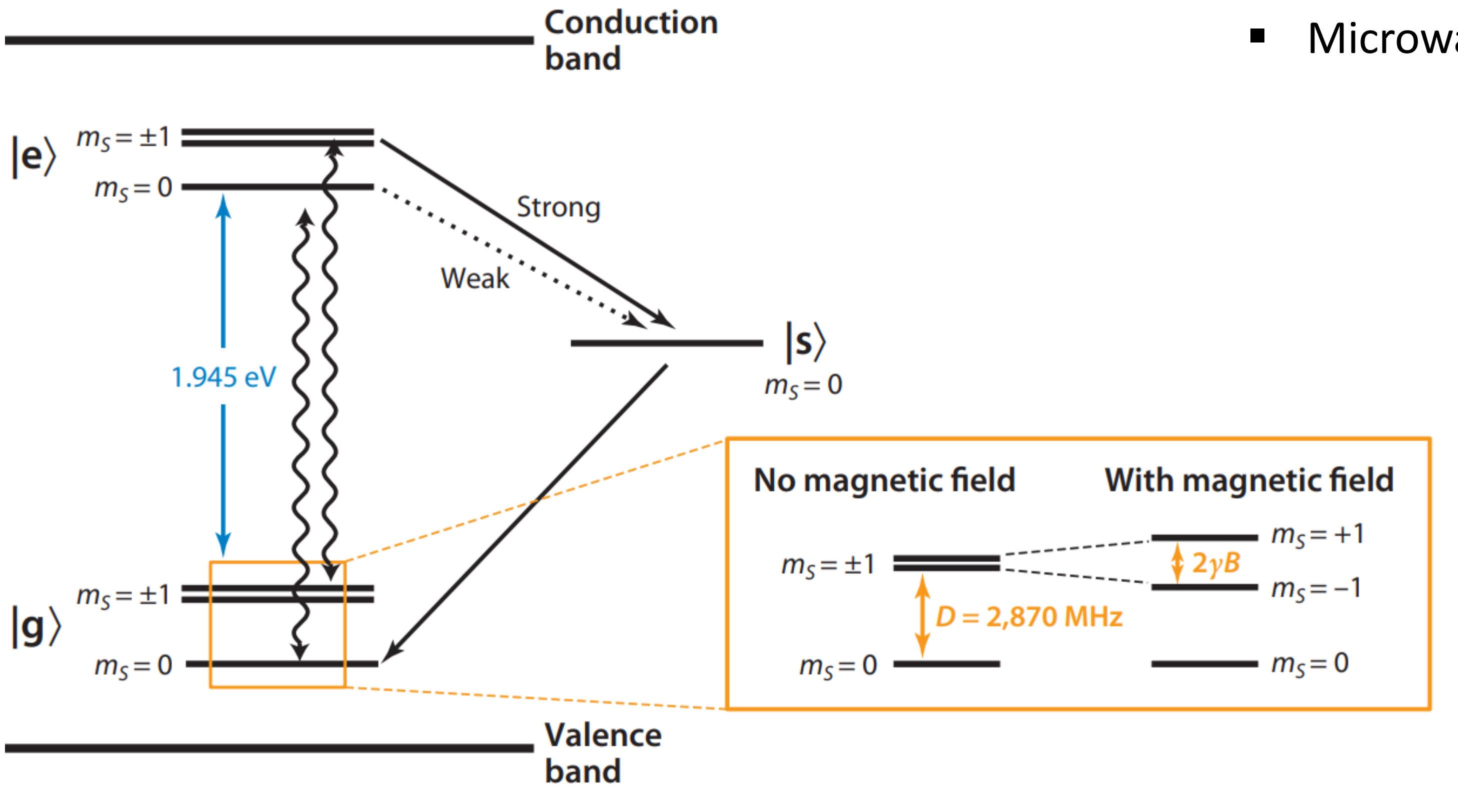
Energy labels of NV⁻ diamond



- NV center provides intra-band states.
- External magnetic field induces Zeeman splitting of $m_s = \pm 1$ states.
- $\Delta f = 2\gamma B = B \times 56\ MHz/mT$; *where, γ is Gyromagnetic ratio.*

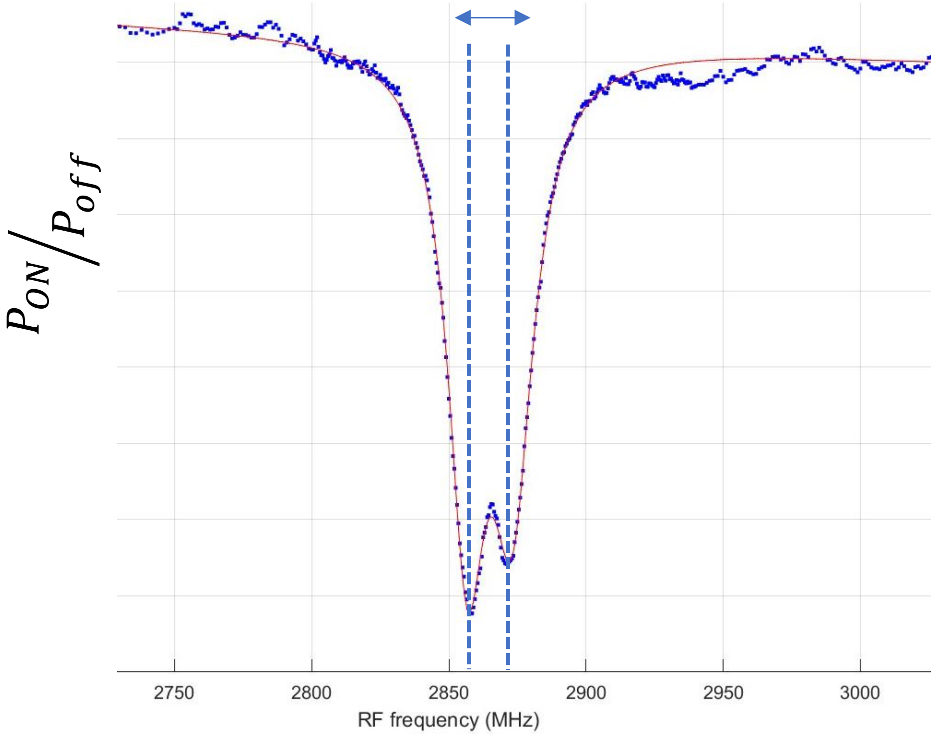
NV^- diamond as a Sensing Material

Energy labels of NV^- diamond



- Zeeman Splitting is measured via photoluminescence
- Microwave radiation populates to $|m_s=\pm1>$ states.

$$\Delta f = 2\gamma B = B \times 56\ MHz/mT$$



Magnetic Characterization Signature

$$U = -\boldsymbol{\mu}.\boldsymbol{B} = m_j g \mu_B B$$

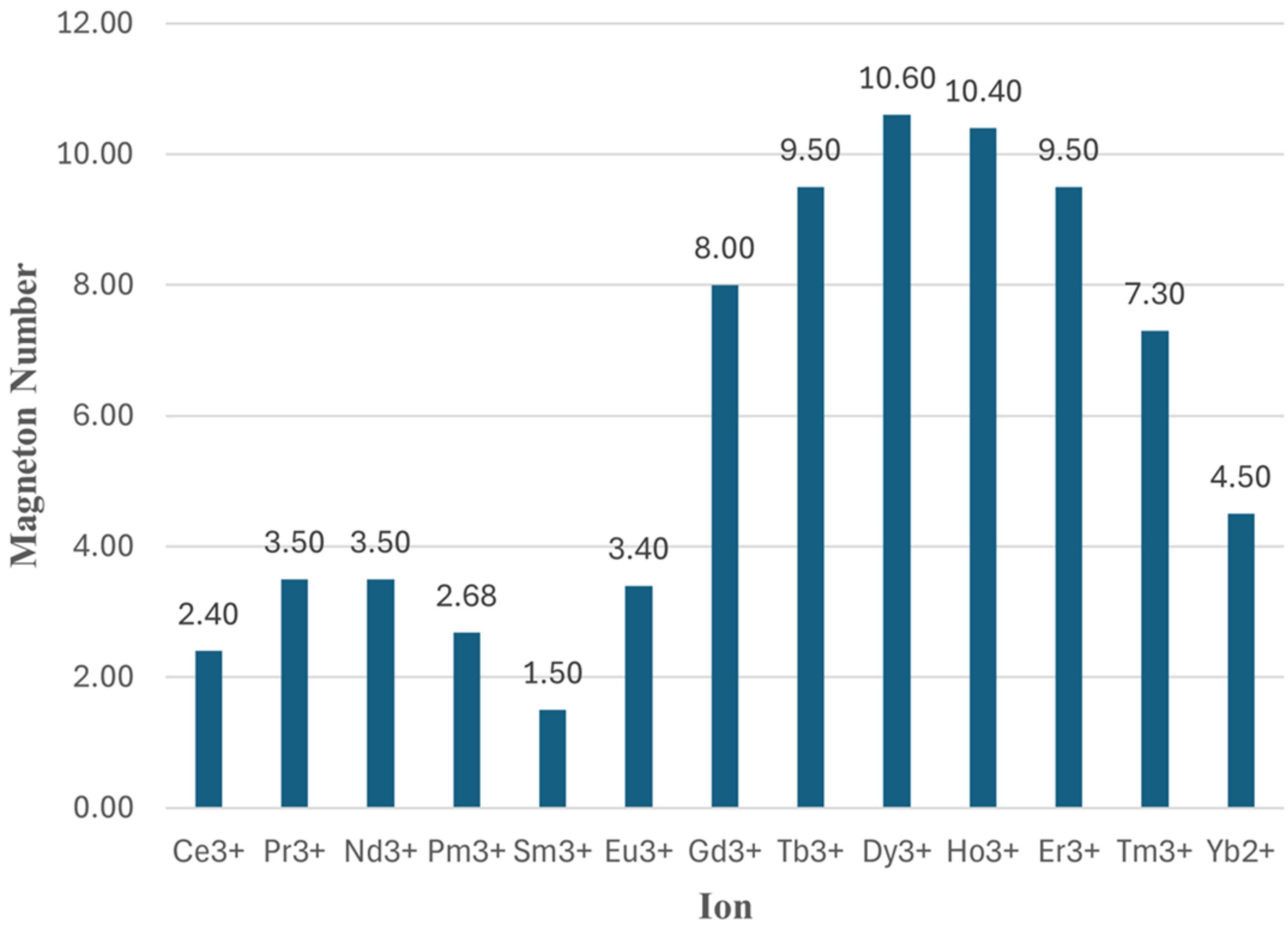
Magnetic Susceptibility of paramagnetic atoms

$$\chi = \frac{NJ(J+1)g^2\mu_B^2}{3\kappa_B T}$$

$$\chi = \frac{N\mathcal{P}^2\mu_B^2}{3\kappa_B T}$$

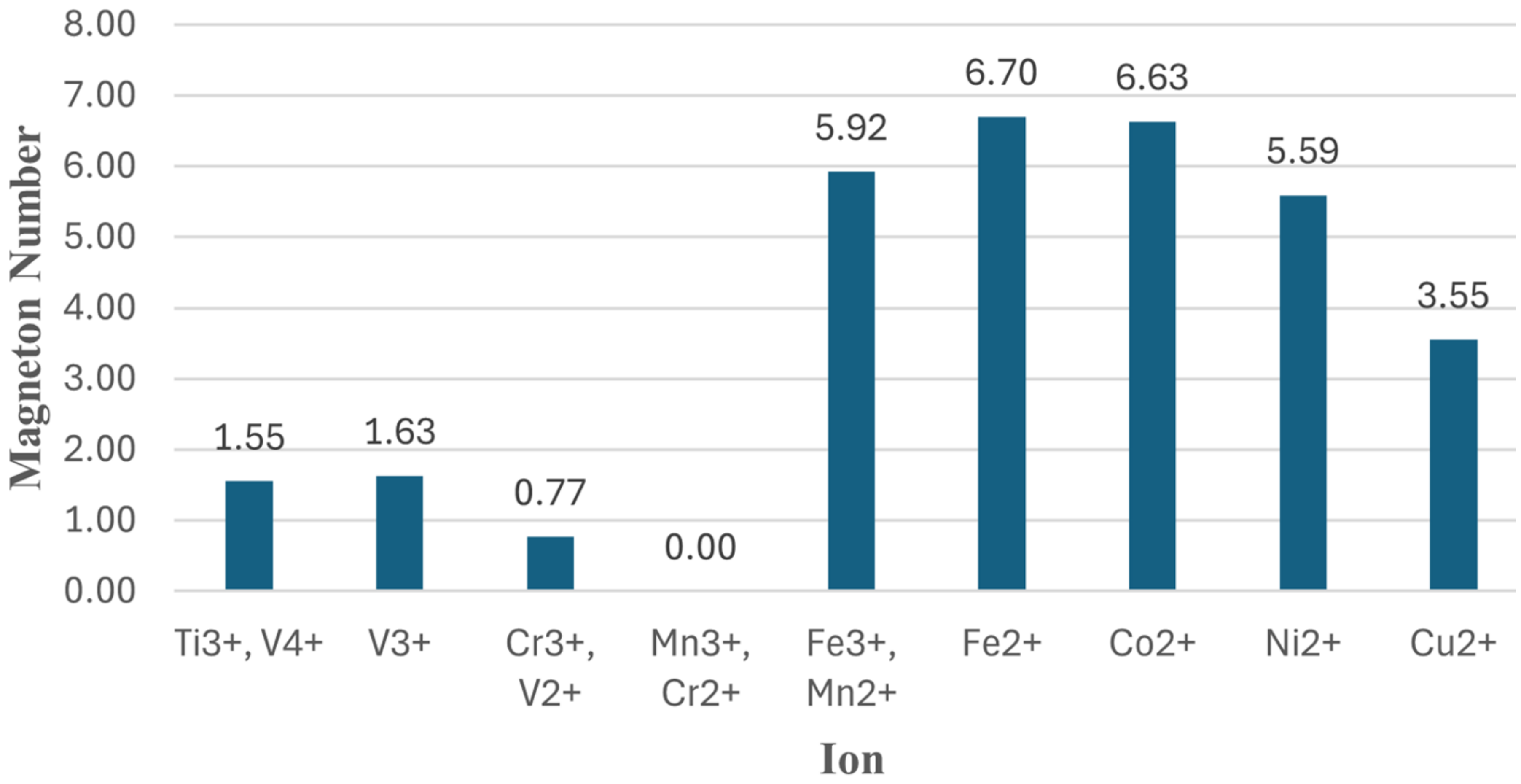
$$\mathcal{P} = g\sqrt{J(J+1)}$$

Magneton Number for Rare Earth Elements



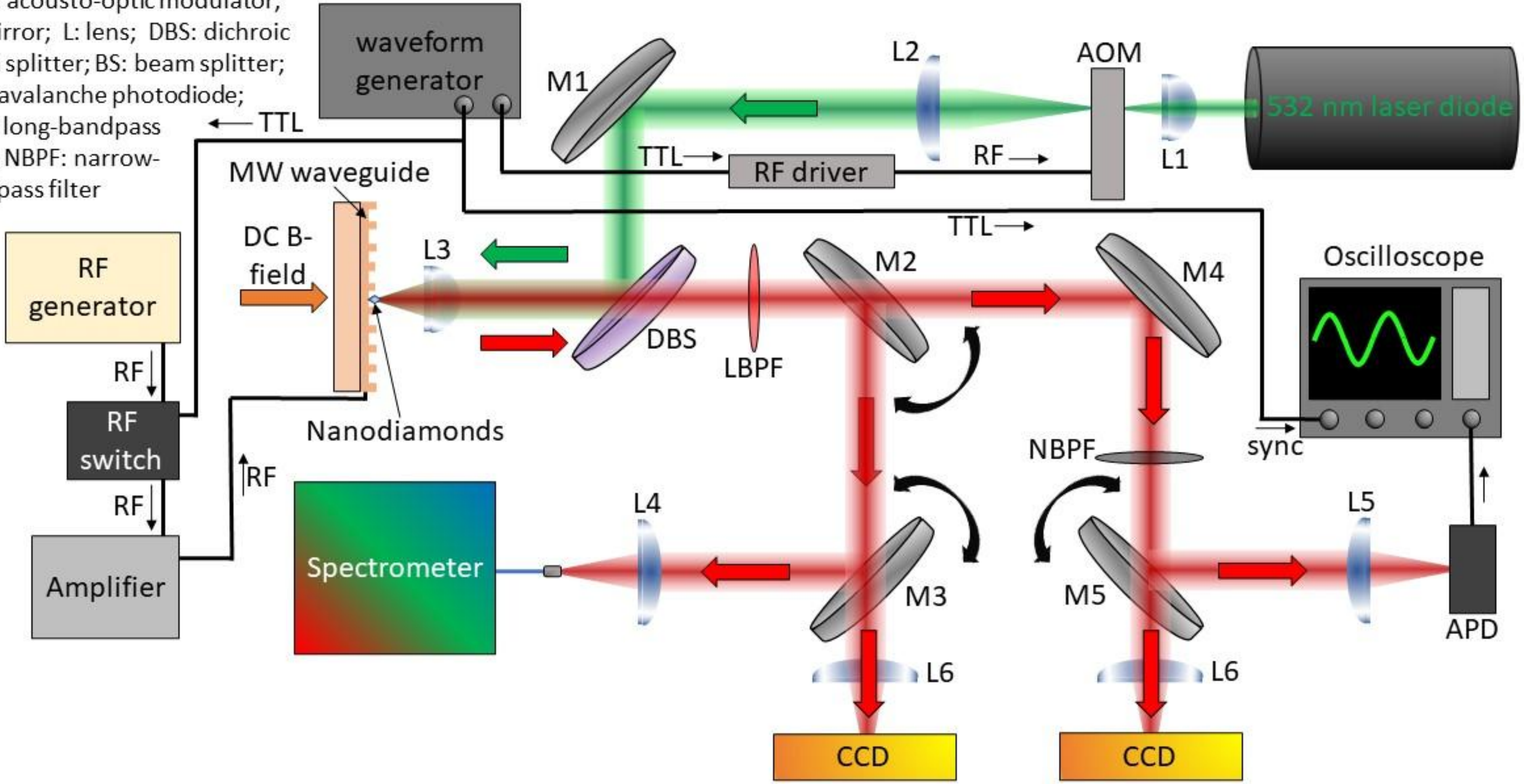
Magnetic Characterization Signature

Magneton Number for Critical Transition Metals



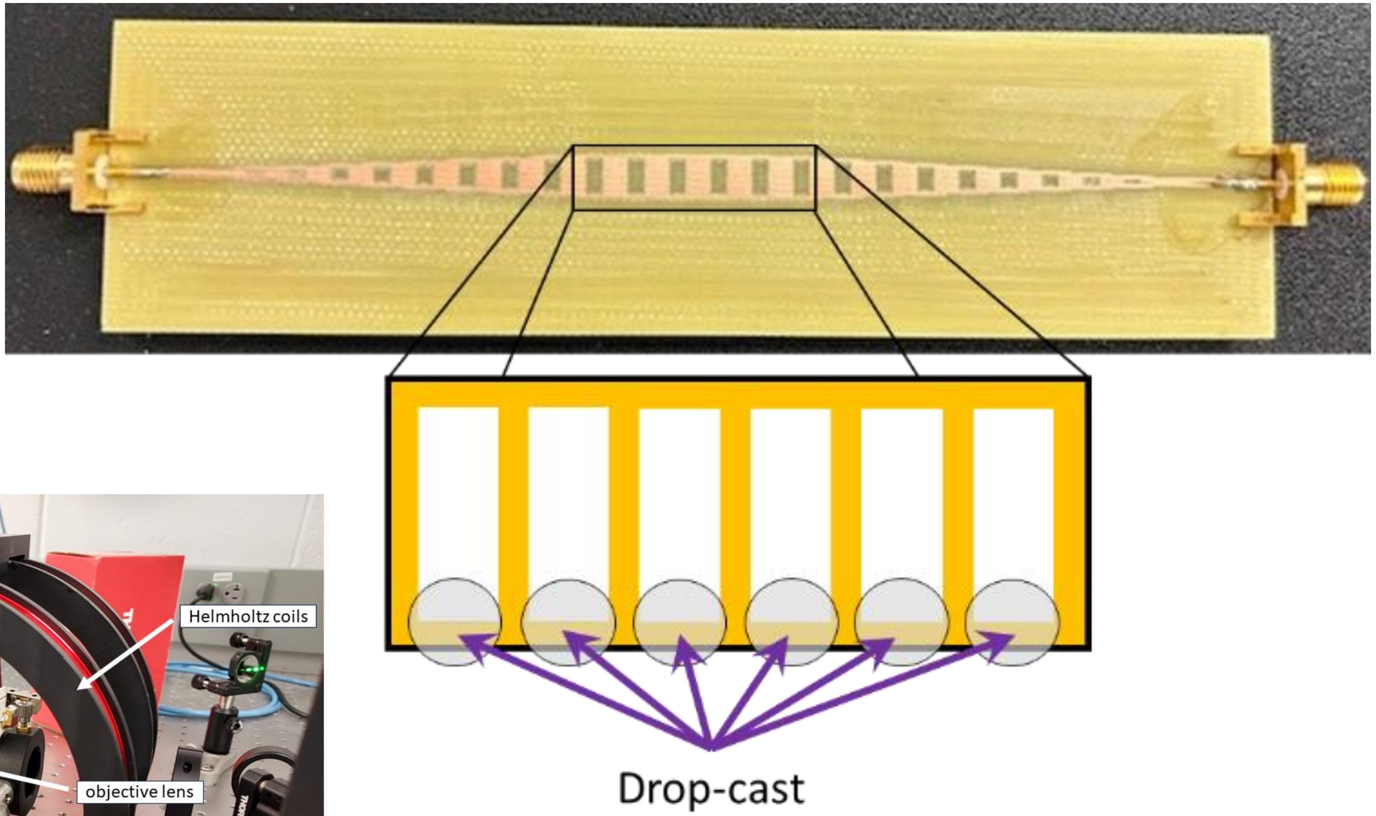
Experimental Set-Up for ODMR and Spin Relaxometry

AOM: acousto-optic modulator; M: mirror; L: lens; DBS: dichroic beam splitter; BS: beam splitter; APD: avalanche photodiode; LBPF: long-bandpass filter; NBPF: narrow-bandpass filter

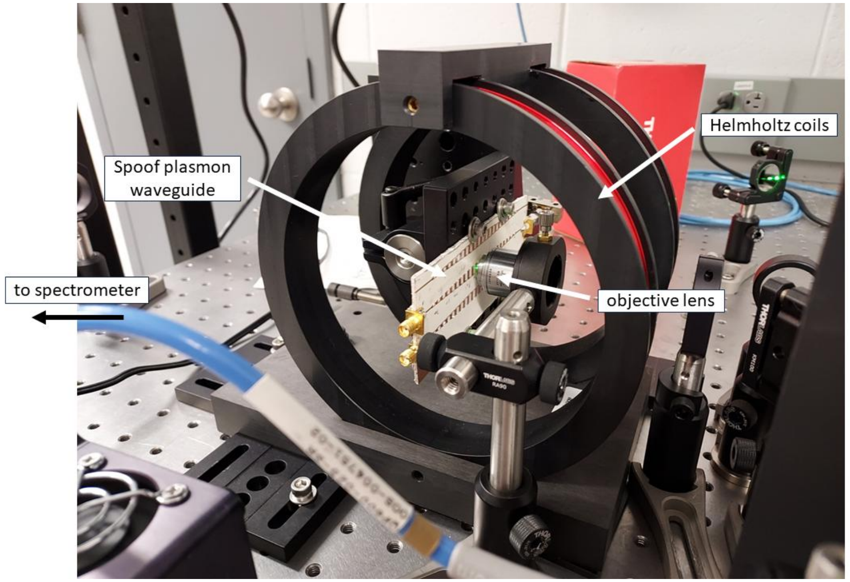


Sample Preparation

- RF voltage applied to spoof plasmon waveguide enhances AC B-field and spin-flip transition.
- Drop-casted nanodiamonds (NDs) and Gd.
- Pure NDs on one side, increasing Gd concentration toward other side.

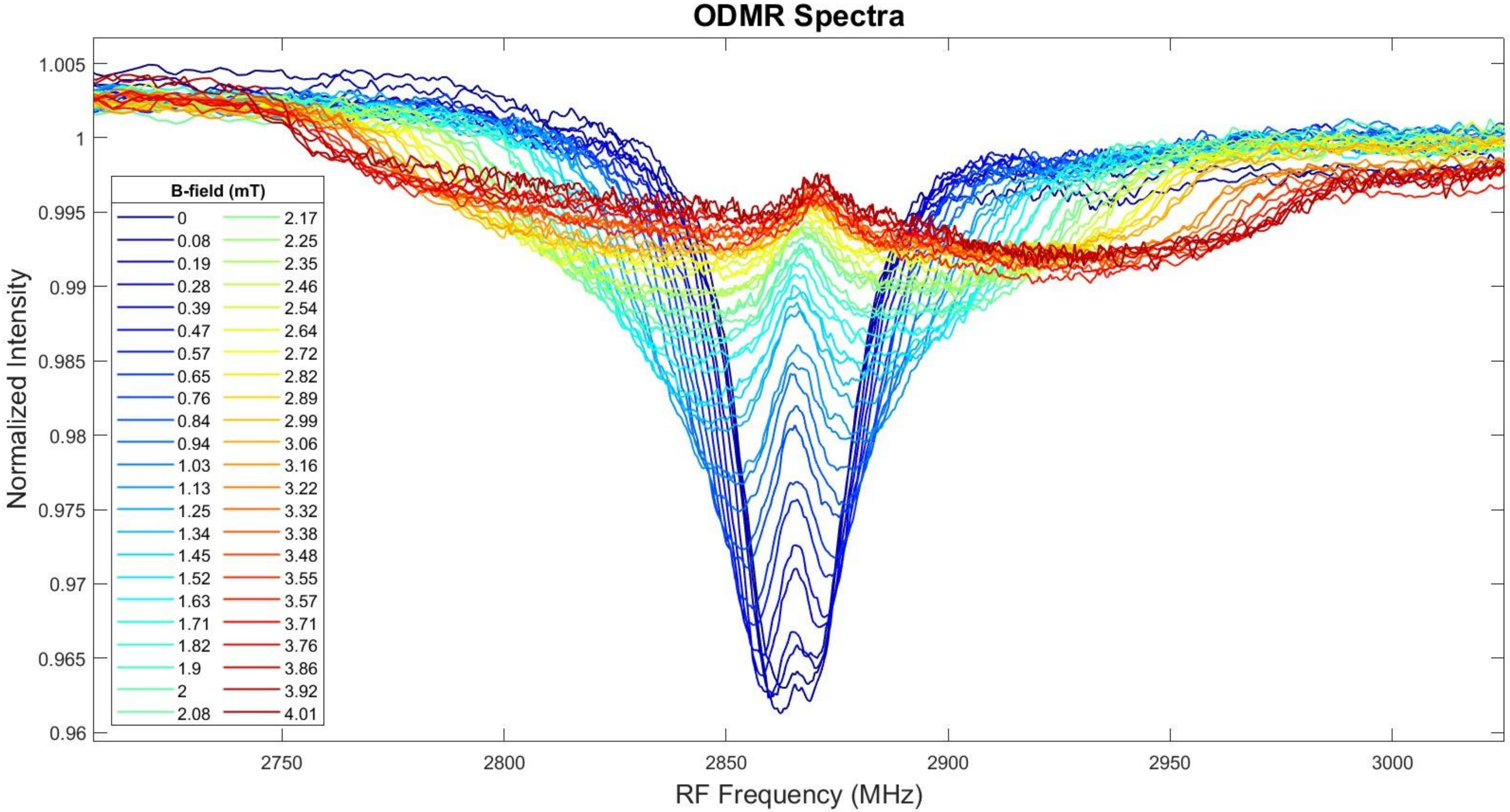


- Sample mounted on XYZ translation stage to move field of view.
- Helmholtz coils supply DC B-field.



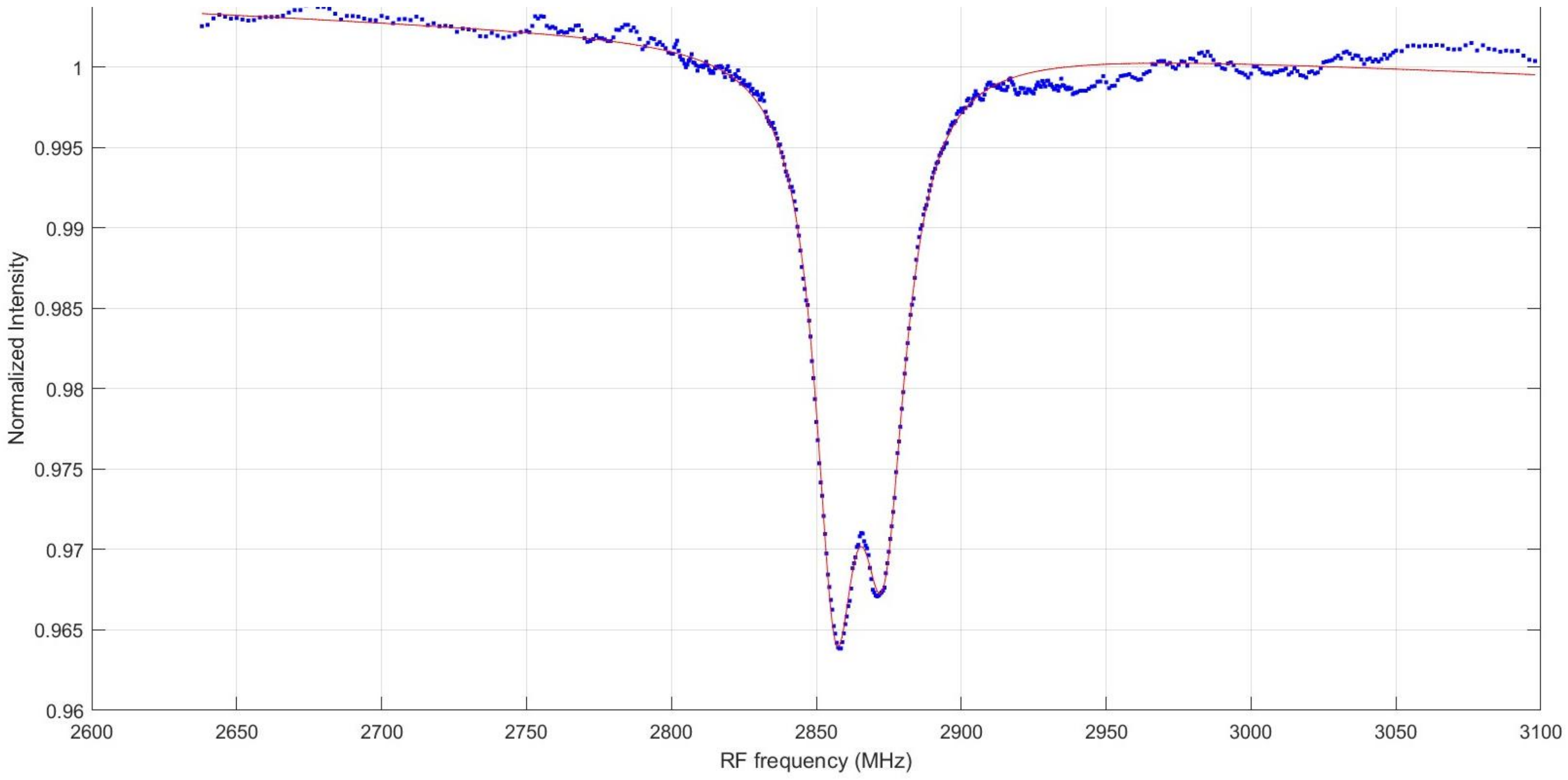
Magnetic Field Dependent ODMR Spectra

- Application of external DC B-field induces Zeeman splitting, two resonances emerge.
- Resonance and splitting can be used to measure local B-field.



ODMR Fits

FWHM and center of resonance is measured from fitting



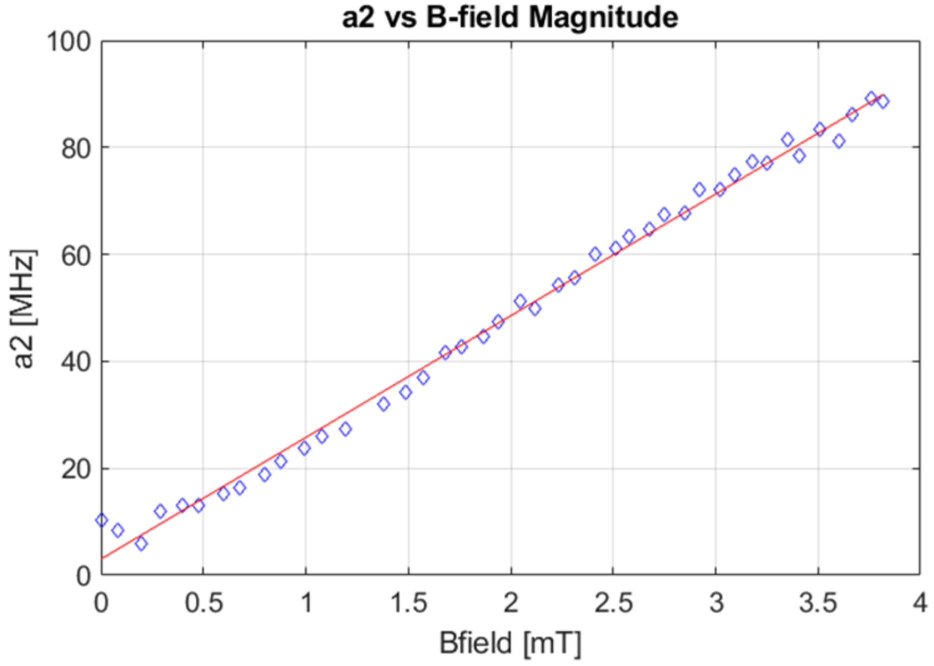
Double Lorentzian with Linear Offset

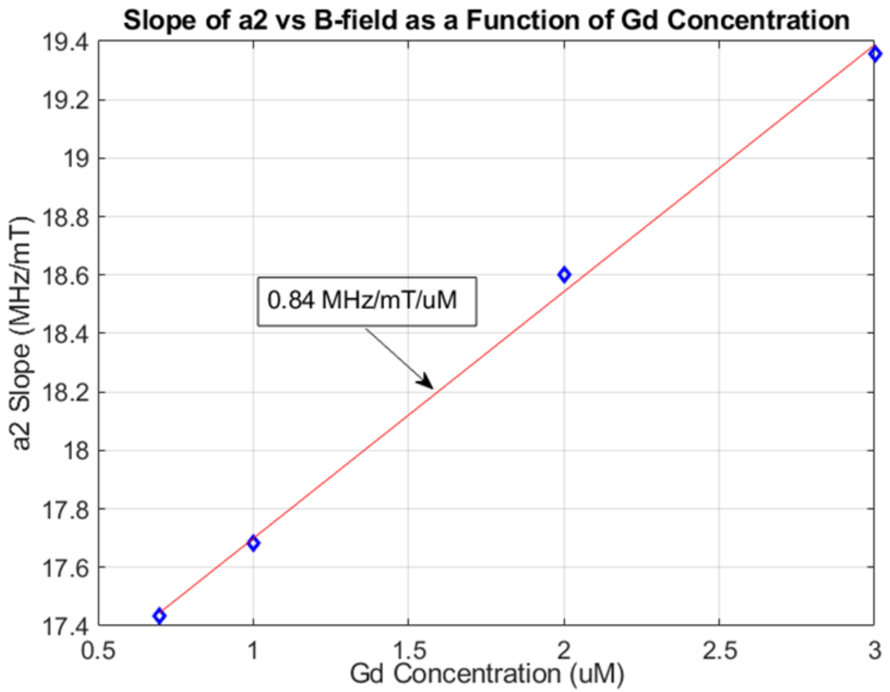
$$ODMR = Ax + B - C\frac{\gamma_1}{\left((x-a_1)^2+\gamma_1^2\right)} - D\frac{\gamma_2}{\left((x-a_2)^2+\gamma_2^2\right)}$$

Result: ODMR Fit Parameters

- Fit center resonance, a_2, as function of DC B-field with linear equation (left).
- Extracted slope of line for each Gd concentration (right).
- Shows detectable magnetic field from presence of Gd.

Linear Fit of Resonance Center





$$ODMR = Ax + B - C\frac{\gamma_1}{\left((x - a_1)^2 + \gamma_1^2\right)} - D\frac{\gamma_2}{\left((x - a_2)^2 + \gamma_2^2\right)}$$

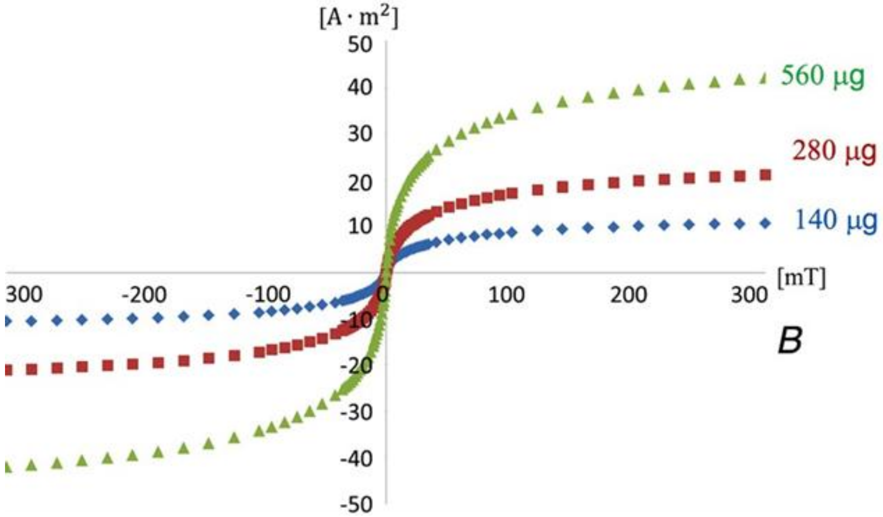
Lander, G. et al. Proc. of SPIE Vol. 13392, 2025

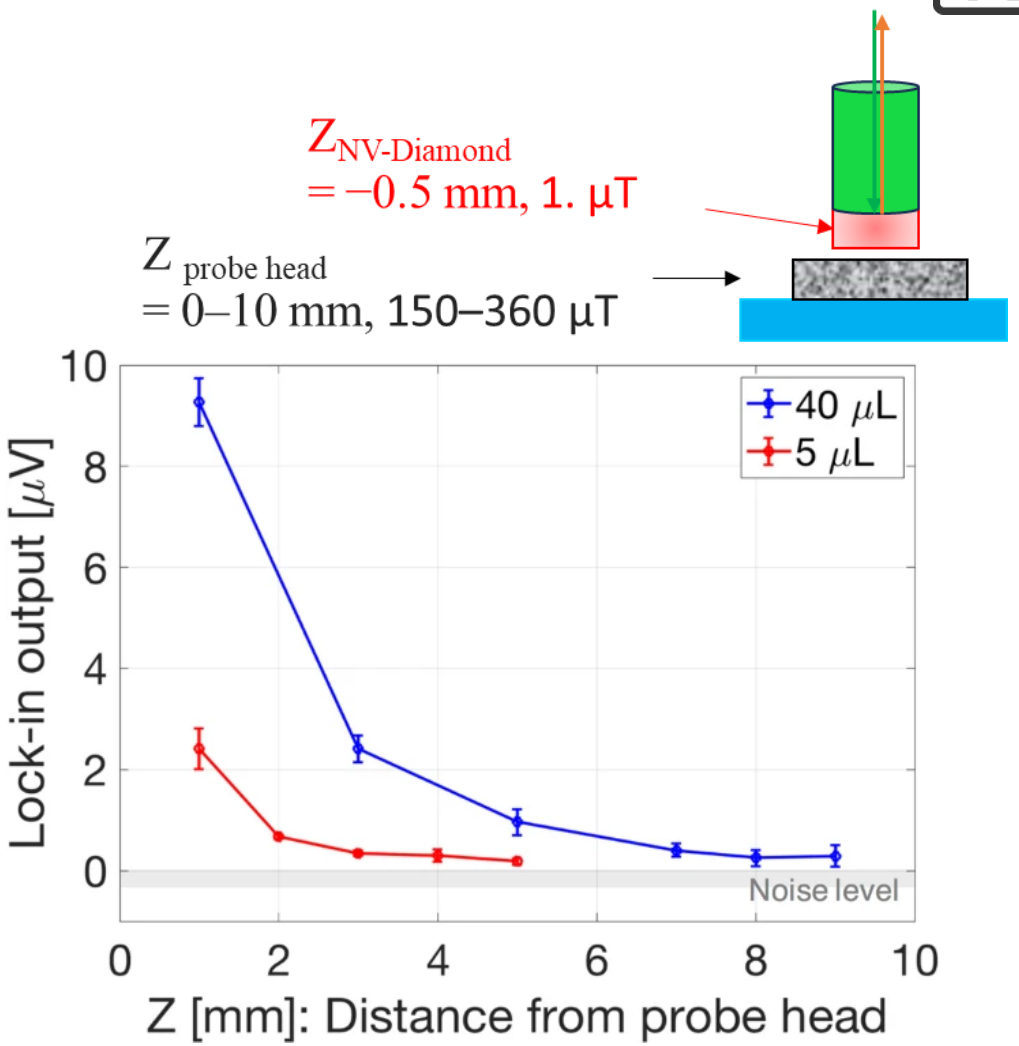
Result from a journal: Magnetic Nanoparticles Detection

$$B_{MNP} = \frac{\mu_0}{4\pi}\left(-\frac{\boldsymbol{m}}{|\boldsymbol{r}|^3} + \frac{3(\boldsymbol{m}\cdot\boldsymbol{r})\boldsymbol{r}}{|\boldsymbol{r}|^5}\right)$$

Superparamagnetic iron oxide nanoparticles (SPIONs), 60 nm, 28 mg/mL

m: magnetic moment





Kuwahata et al., *Sci Rep* **10**, 2483 (2020) https://doi.org/10.1038/s41598-020-59064-6

Bulk Diamond Bulk and Surface for REE sensing

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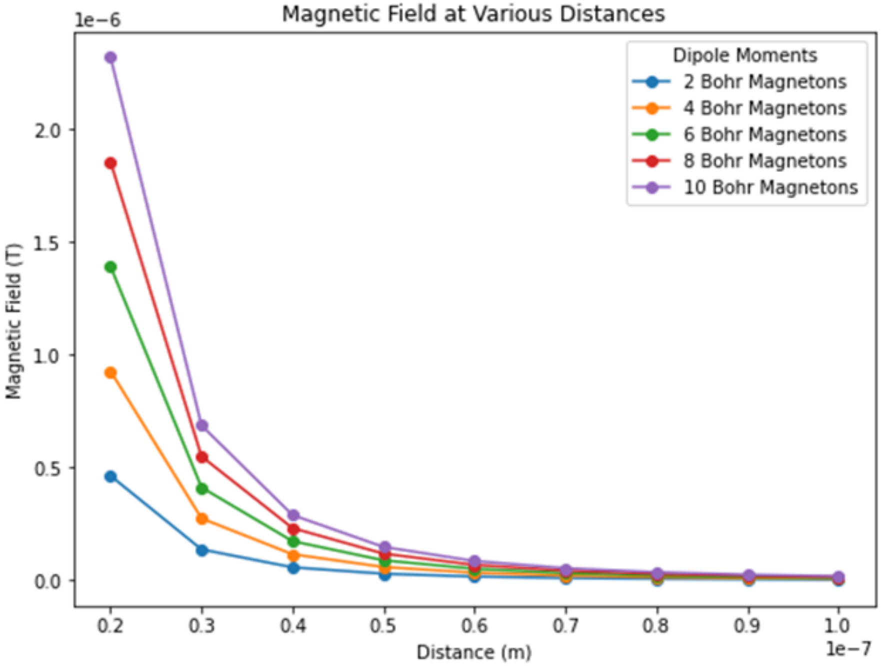
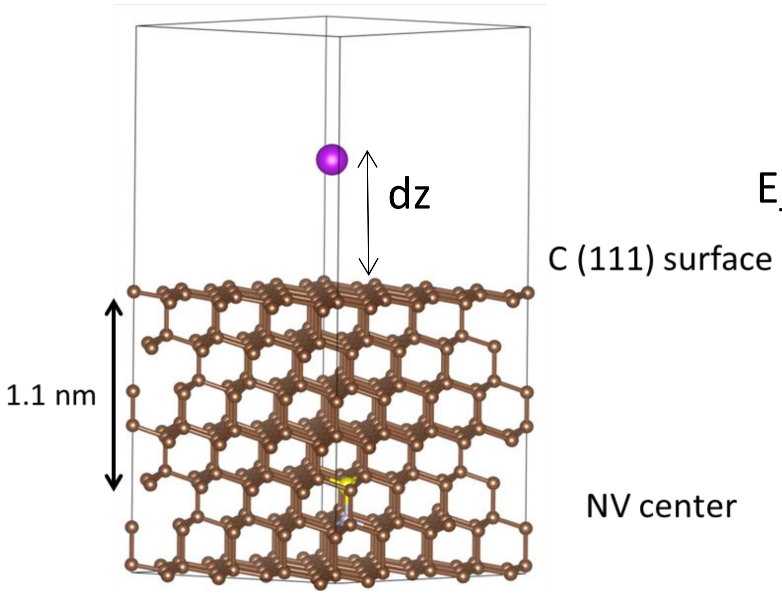
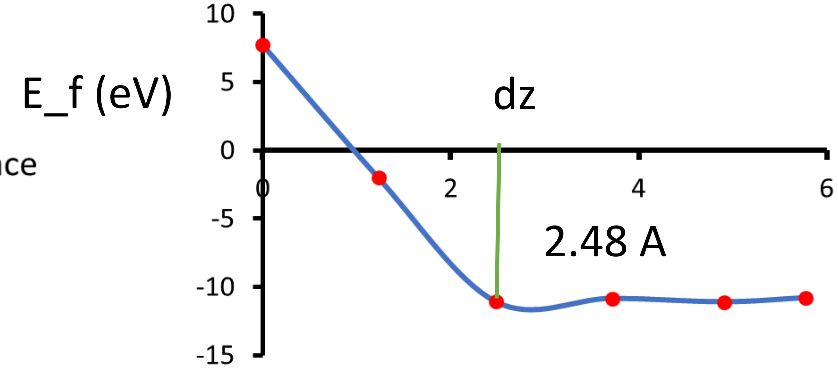
Dipole strength and Formation of Gd





Formation of Gd ion on diamond surface



- Magnetic field variation due to varying point dipoles at perpendicular distance from the source in a nonmagnetic medium
- Formation of Gd ion on the surface of diamond (111) surface at 2.48 A along NV dipole axis.

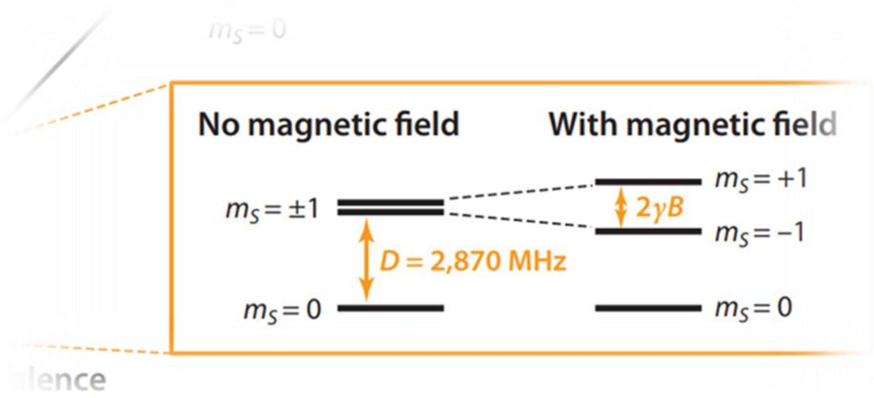
Paudel et al., Nanomaterials **2024**, *14*(8), 675

Bulk Diamond Bulk and Surface

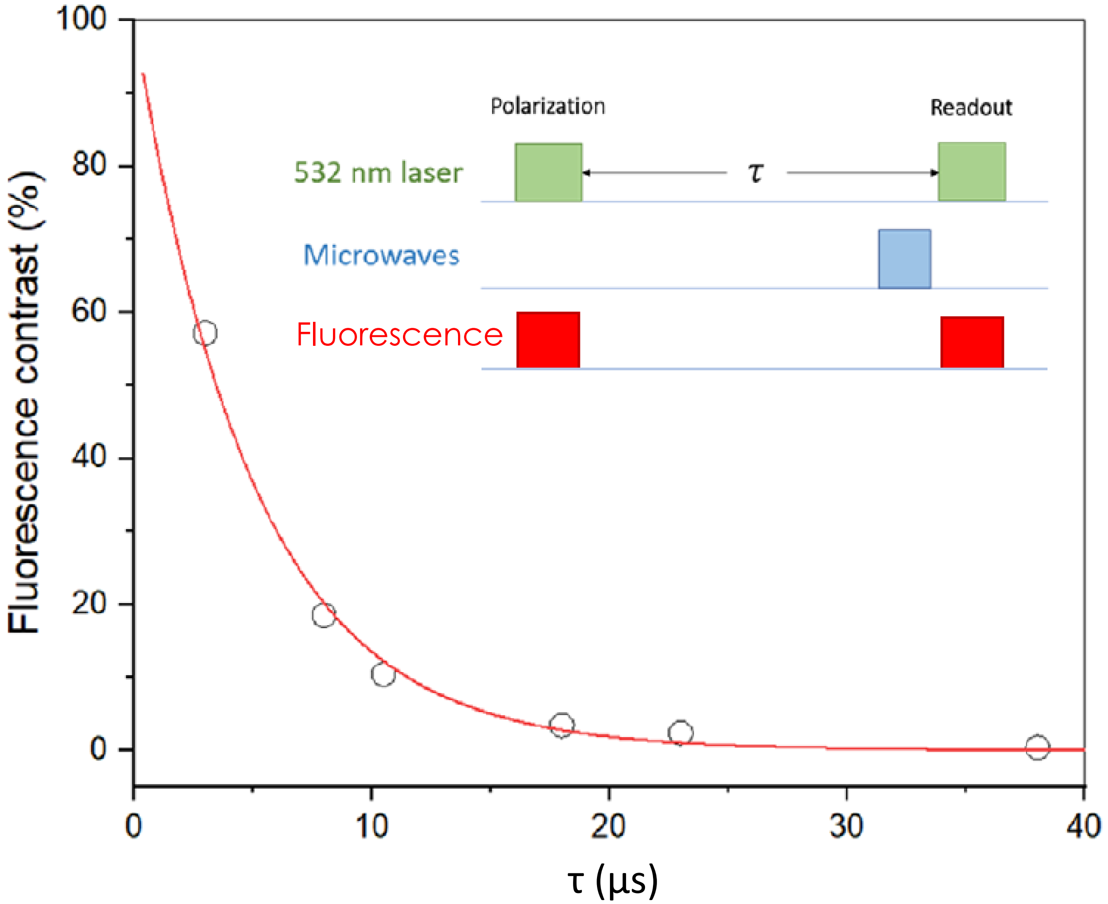
- Computed result shows ~µT range of field due to Gd atom at the NV center embedded in diamond in 10nm depth.

- Magnetic fields sensitivity of ODMR
  $\eta = 2.54\ pT/\sqrt{Hz}$ (Zhang et al. 2023)

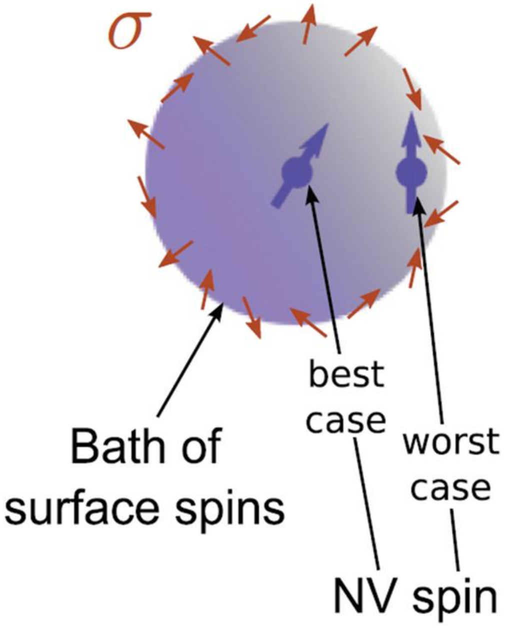
Alternative Method: Spin Relaxometry



- Optical pulse polarizes spin into $|m_s$=0>.
- MW pulse modifies spin state (spin flip), a π-pulse of MW polarizes spin into $|m_s$=±1>.
- We measure contrast between fluorescence pulses (after MW pulse and without MW pulse)
- Vary time between optical pulses, τ.
- Spin relaxation time is measured by fitting contrast vs. τ with exponential function, and it is ~μs order.



Spin casting of Gd^{3+} solution on the NV nanodiamonds



NV nanodiamond size dependent longitudinal relaxation time T1 has been measured

Relaxation rate

$$\frac{1}{T_1} = \frac{1}{T_1^{\mathrm{bulk}}} + 3\gamma_e^2 B_\perp^2 \frac{\tau_c}{1+\omega_0^2\tau_c^2}$$

$$B_\perp^2 = \langle B_x^2 \rangle + \langle B_y^2 \rangle$$

Where, τ_C is correlation time
Ω_0 is electron spin resonance frequency

Estimated sensitivity ≈14 electron spins detected within 10 s

Tetienne et al. Phys. Rev. B **87**, 235436, 2013

Conclusions

- We have successfully detected field due to Gd nano particles using ODMR with NV nanodiamonds.

- The computed field and ODMR's achievable sensitivity are showing their potential for detecting rare-earth elements.

Acknowledgment

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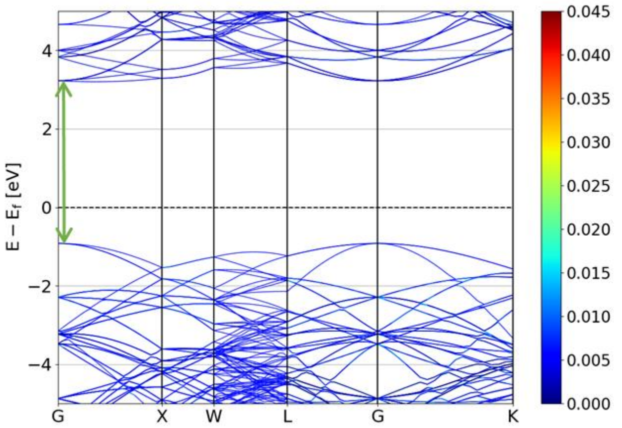
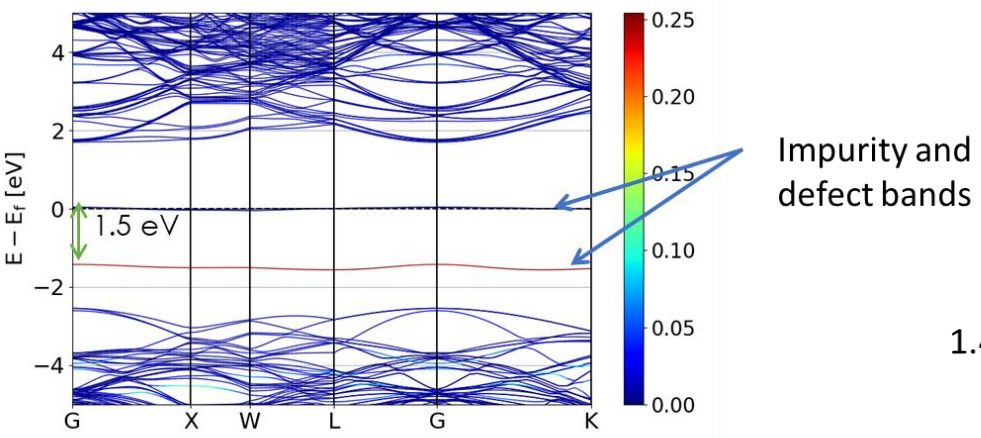
Extra slides

Bulk Diamond with NV center

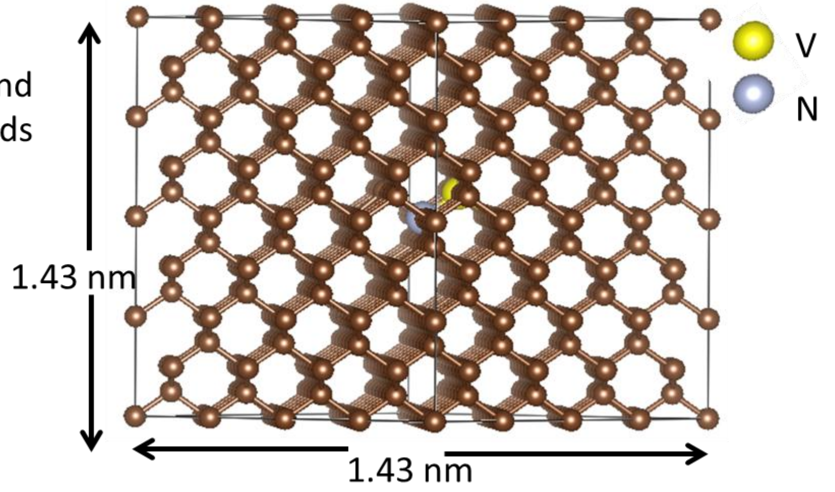
Electronic Properties: Band Structures



Band structures for pure bulk diamond



Band structures for NV$^-$ defective bulk diamond



Diamond 3x3x3 supercell with a NV center

- Impurity and defect energy levels appear with energy gap of 1.5 eV (experiment: 1.95 eV) within diamond bands.
- Regular DFT is unable to reproduce the spin split bands (~2.85 GHz).

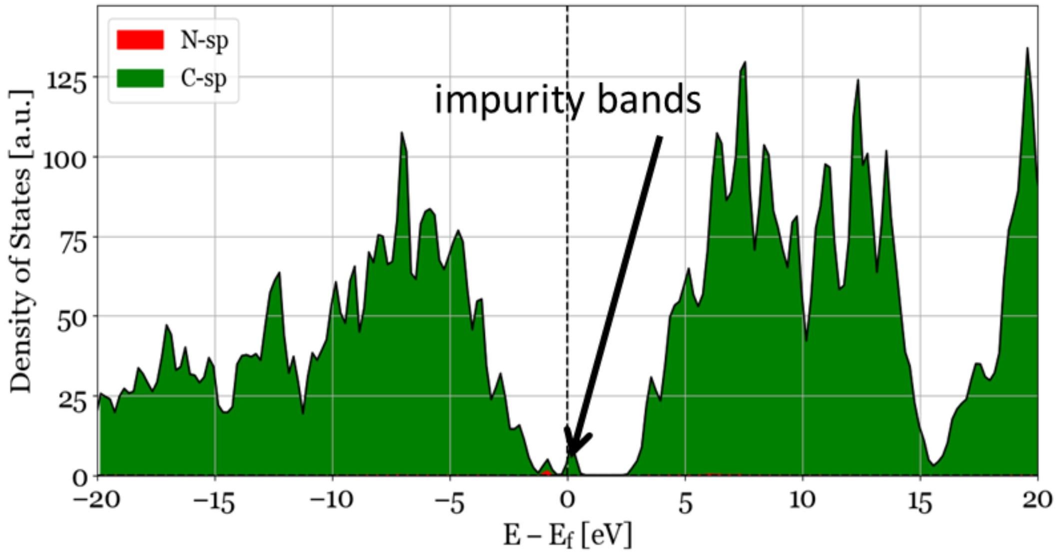
Paudel et al., Nanomaterials **2024**, *14*(8), 675

Bulk Diamond Bulk with NV center

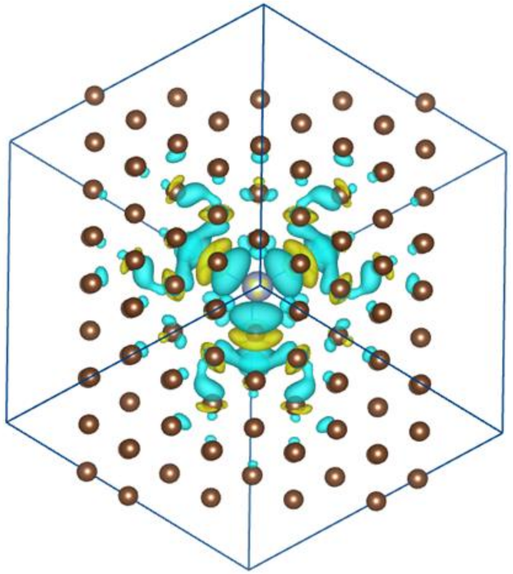
Density of states and charge distribution

- N in NV center neutral gains -0.80 e charges
- N in NV negative gains -0.78 e charges
- N is more positive after putting -1 e
- Band due to N effectively shift towards valence band

NV$^-$ defective bulk diamond



Electronic density of states

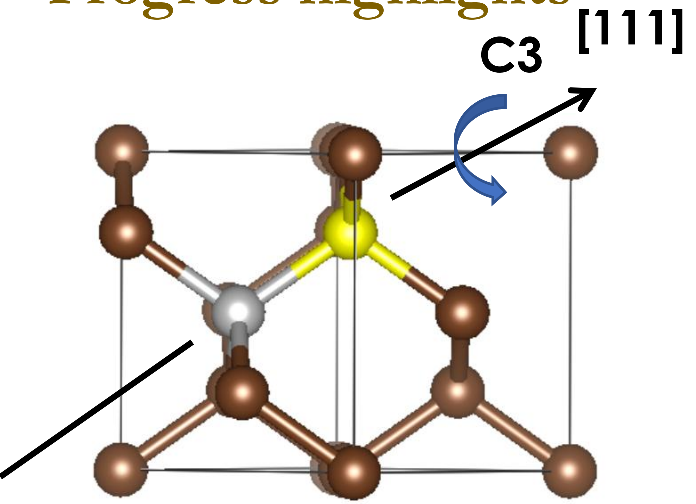


Charge distribution around NV center

Paudel et al., Nanomaterials **2024**, *14*(8), 675

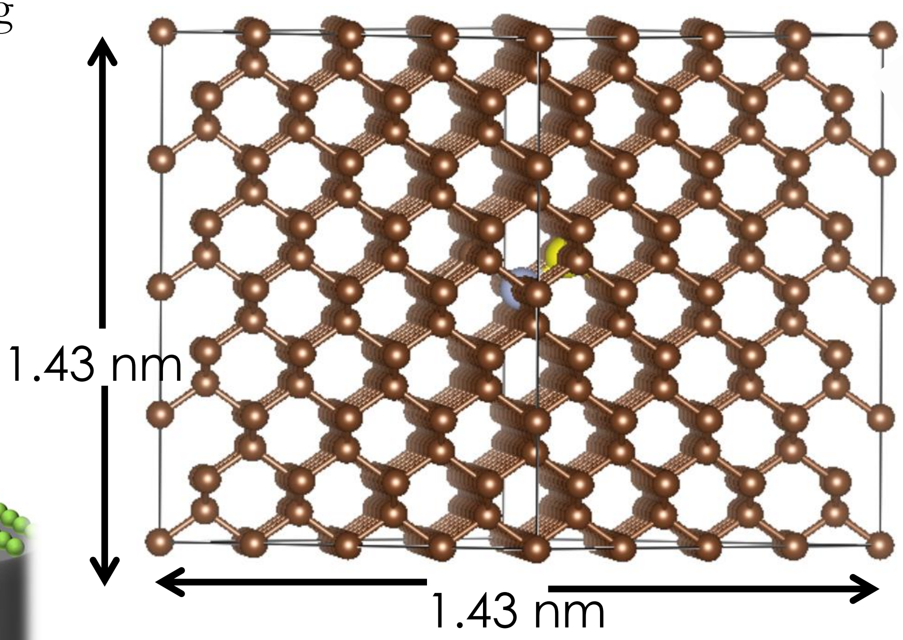
Quantum Sensing for Fossil Energy Applications: Task # 87

Progress highlights



Unit cell of diamond enclosing a NV center

- ❑ Orientation of stable NV center is along [111] direction
- ❑ A C-defect formation is found to be energy = 6.78 eV
- ❑ A 512-atom supercell model is found to be good enough to model a NV center for sensing applications
- ❑ Neutral NV center formation energy = 7.5 eV



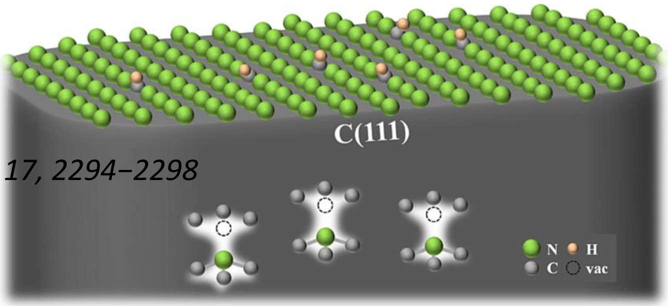
Supercell model (cubic structure) of diamond enclosing a NV center

Number of C atom = 510
Number of N atom = 1
Number of Vacancy = 1

Work under progress

- ❑ NV center electronics structures
- ❑ Surface model for nano-diamond with NV center
- ❑ NV center responses to the external light and magnetic fields

Nano Lett. 2017, 17, 2294−2298



Surface model for nano-diamond with NV center

"A model with dimension 1.43 nm is identified as a good model for calculating NV center properties for sensing applications."