Optically Detected Magnetic Resonance (ODMR) for Characterization of Carbon Nanostructures

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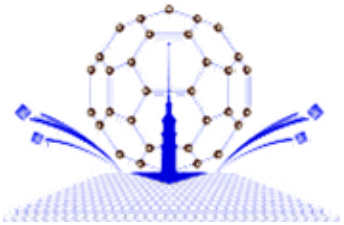
International school for young scientists
"Carbon Nanostructures Diagnostics"



Joint International Conference
Advanced Carbon Nanostructures
ACN'2011

• St Petersburg, Russia • July 4-8, 2011•

Electron Paramagnetic Resonance (EPR) and EPR based methods

- are the most informative tools for detecting defects and excitations in solids
- offer a uniquely sensitive probe of local structural order, chemical identification, charge state, the atomic-scale environment of the defect
- can provide details of electron wave-function density distributions

The microscopic structure of many intrinsic and impurity defects and their clusters in diamonds and other carbon-related materials was studied by EPR. An understanding of the structure and constituents of defects in nanodiamond and other carbon nanostructures is important since their presence can greatly affect the properties of the material

Why Optically Detected Magnetic Resonance – ODMR?

- Direct measurements of EPR in nanostructures are often difficult because of the small total number of spins, therefore ODMR is much better suited for the measurements in such systems.

- In ODMR a microwave-induced repopulation of Zeeman sublevels is detected optically, i.e., there is a giant gain in sensitivity since an energy of optical quntum is by several orders of magnitude higher compared with microwave one, it becomes possible to detect a very small number of spins **down to single spin !**

- ODMR is a “trigger detection” in that the absorption of a resonance microwave photon triggers a change in emission (absorption) of an optical photon due to the selective feeding of the magnetic sublevels. At the root of the selective feeding are spin selection rules for the optical transitions and equally strong selection rules for the radiationless decay.

ODMR studies of nitrogen, nitrogen and oxigen based defects in the ground and excited states in diamond and nanodiamonds will be discussed as an example of the characterization of carbon nanostructures

- ODMR study of NV defects consisting of a nitrogen atom (N) and a vacancy (V) in adjacent lattice sites are of paramount importance.

- NV defect is the only known solid-state system where there exist possibility of detecting and manipulating the spin states of a single localized electron at room temperature.

- Coupling between the NV and N spins in NV –N pair (triplet-doublet interaction) due to a cross-relaxation and coupling between electron NV spin with C-13 nuclear spins give rise to new possibilities for spin manipulation.

- Defects in nanodiamond and possibly carbon clusters in other materials open up an avenue to practical quantum computing, nanoscale imaging magnetometry in the biological and physical sciences.

- Due to ODMR the diamond age of quantum electronics (in general, carbon-related age) could be just around the corner [Scientific American (2007)].

- Nanocarbons in SiC – perspective matter for single defect spectroscopy

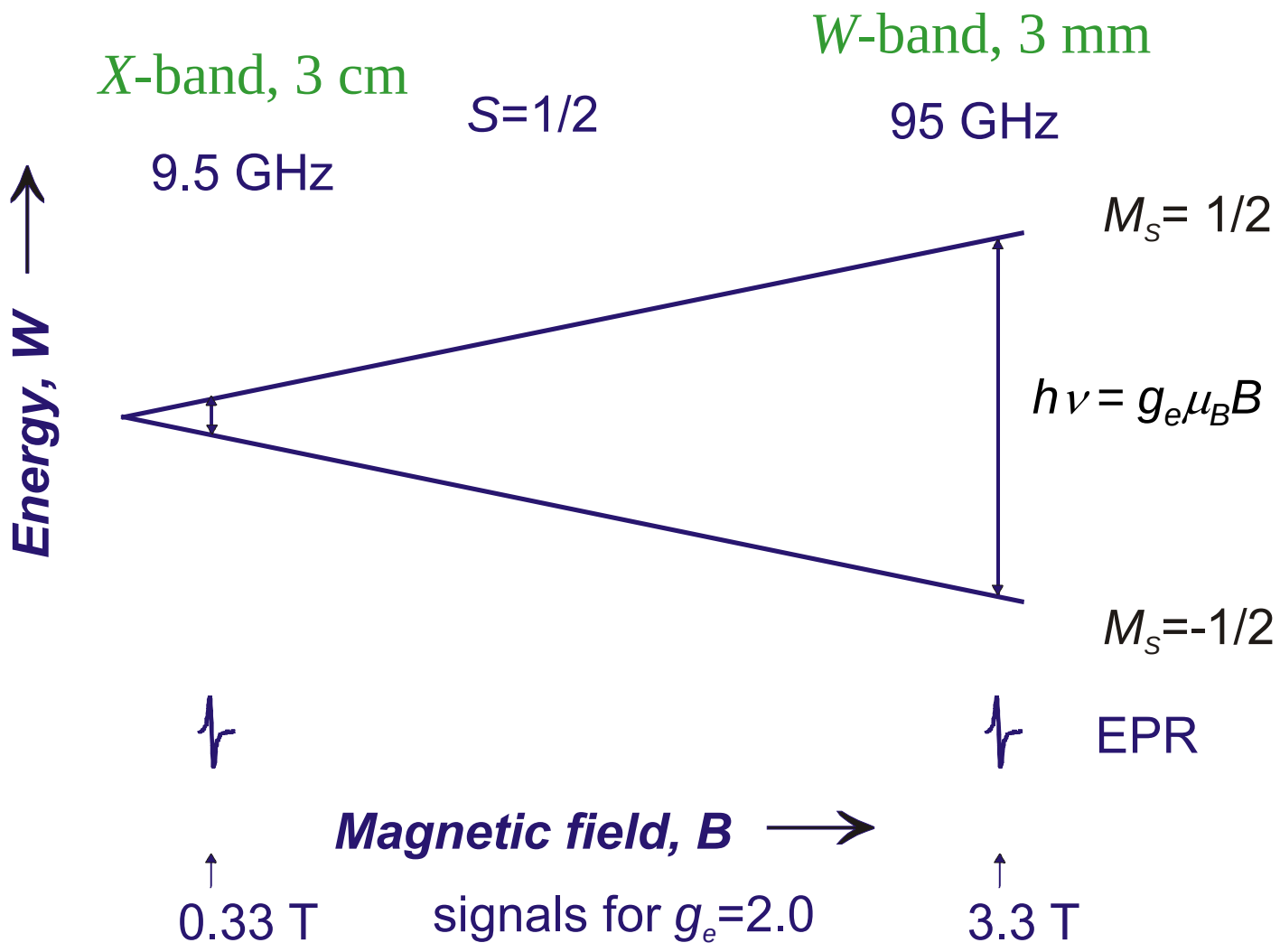
Systems with unpaired electrons:

Transition and rare-earth elements
Donors and acceptors
Radiation defects (radicals, color centers)
Optical excitation (excitons, donor-acceptor pairs),
Products of chemical reactions,
Primary processes in photosynthesis, in photovoltaics,
etc.

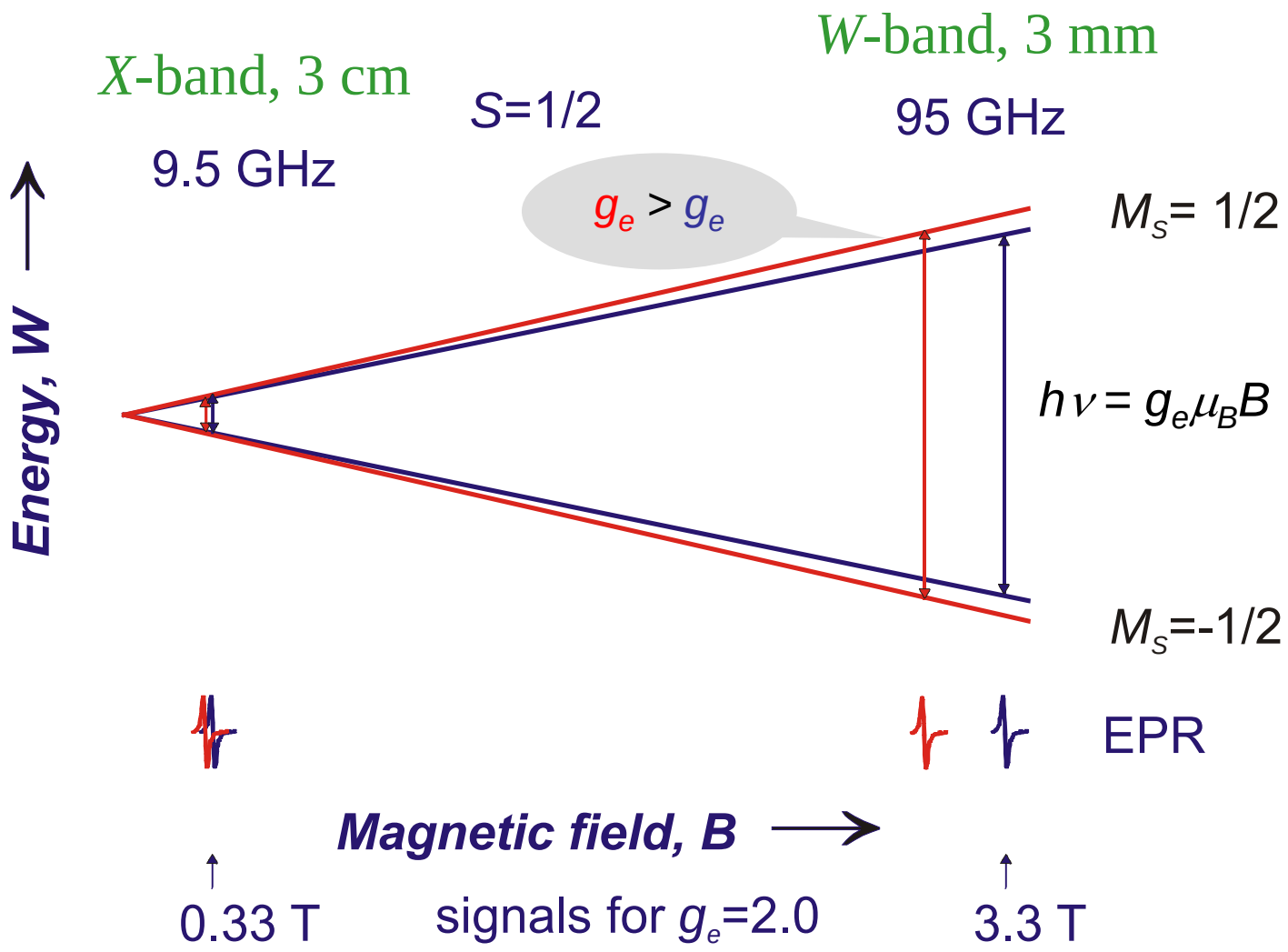
Medium:

Inorganic materials
Organic structures, polymers
Biophysical systems
Nanostructures
Etc.

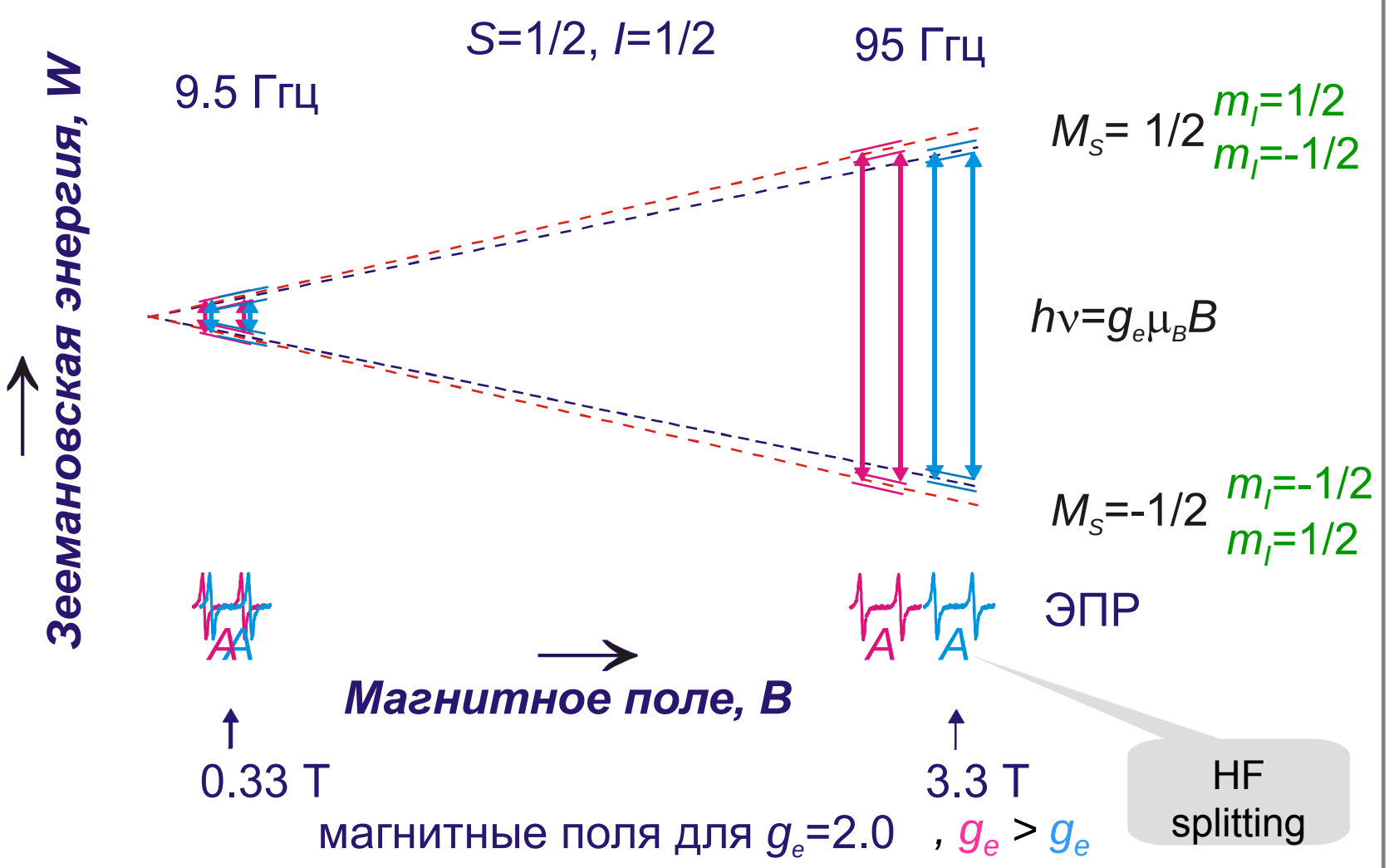
Energy levels in magnetic field for S=1/2



Energy levels in magnetic field for S=1/2



Energy levels in magnetic field for S=1/2, I=1/2



Hyperfine (HF) Interaction Constant (isotropic) $A \sim |\Psi(0)|^2$

Spin Hamiltonian

The *spin Hamiltonian* contains the operators of the electronic spins *S*, of the nuclear spins *I* and the components of the magnetic field *B* which interact and contribute to the energy levels

$$\mathcal{H} = \mathcal{H}_{EZ} + \mathcal{H}_{FS} + \mathcal{H}_{HF}$$

$\mathcal{H}_{EZ} = \mu_B \boldsymbol{S}\cdot\boldsymbol{g}\cdot\boldsymbol{B}$ - electron *Zeeman* interaction

$\mathcal{H}_{FS} = \boldsymbol{S}\cdot\boldsymbol{D}\cdot\boldsymbol{S}$ - fine-structure interaction (S>1/2)

$\mathcal{H}_{HF} = \boldsymbol{I}\cdot\boldsymbol{A}\cdot\boldsymbol{S}$ - hyperfine-structure interaction

where ***g, D, A*** are symmetrical tensors

EPR sensitivity

Constant filling factor
(V_{sample} /V_{cavity} = const)

$N_{min} \sim 1/(\omega^{3/2})$

9.5 GHz (3 cm, *X*-band) $N_{min} \sim 10^{11}$ spins/G
95 GHz (3 mm, *W*-band) $N_{min} \sim 3 \times 10^{9}$ spins/G

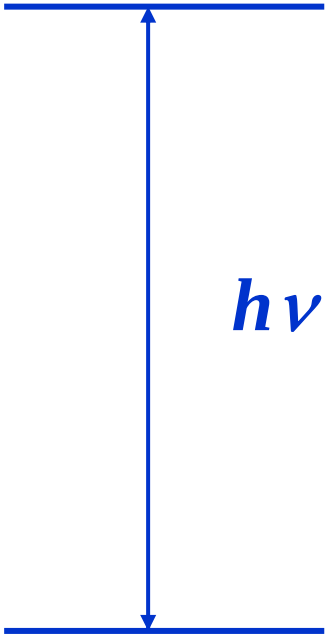
For small sample

$N_{min} \sim 1/(\omega^{9/2})$!

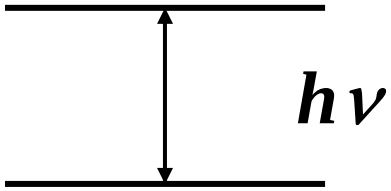
ODMR sensitivity - *down to 1 spin*!

EPR related double resonances: ODMR and ENDOR

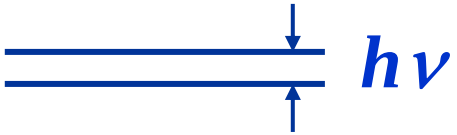
Optical spectroscopy (ODMR) ~ eV



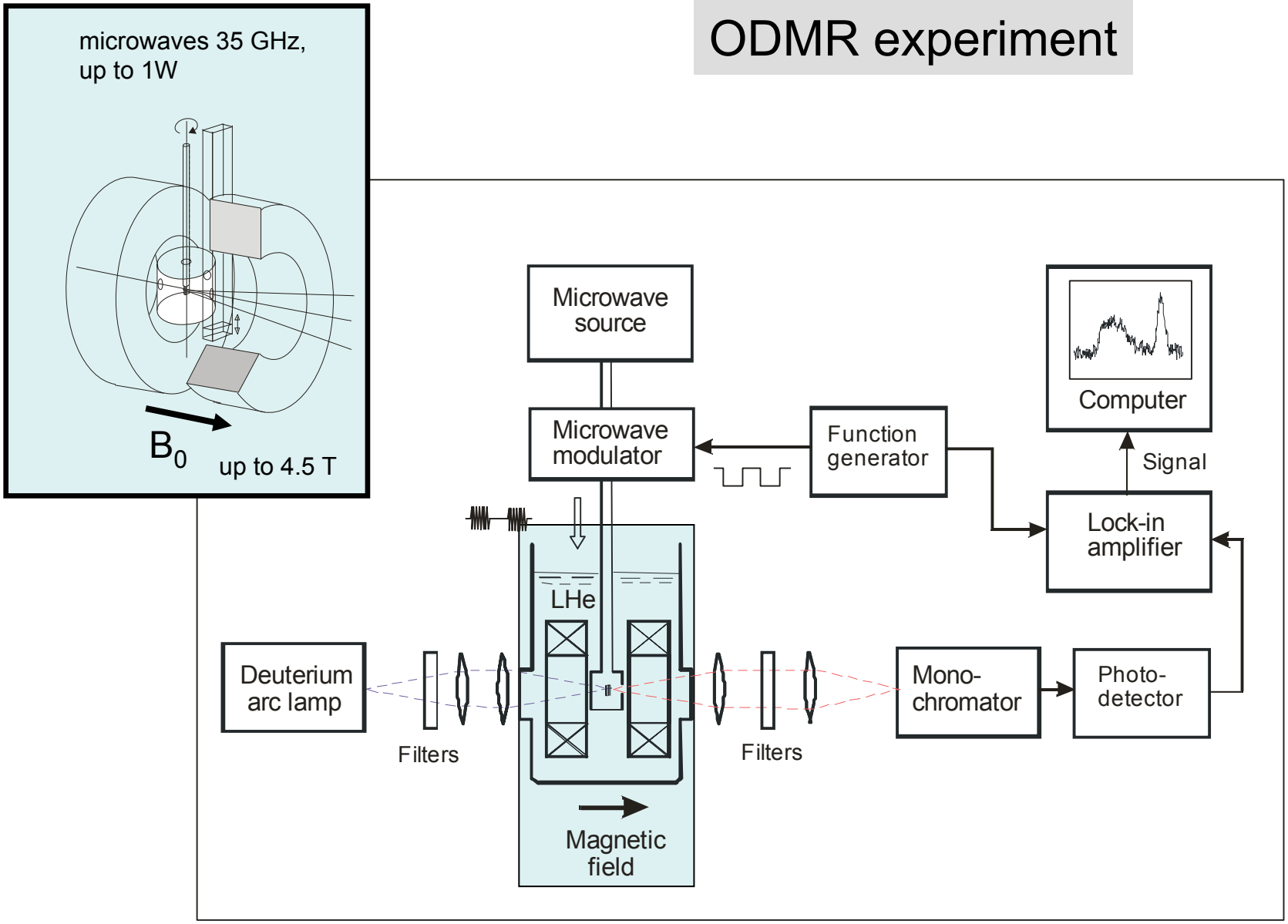
EPR ~ micro eV



NMR (ENDOR) ~ nano eV



ODMR experiment



Example of energy levels in magnetic field for exchange coupled e-h pairs

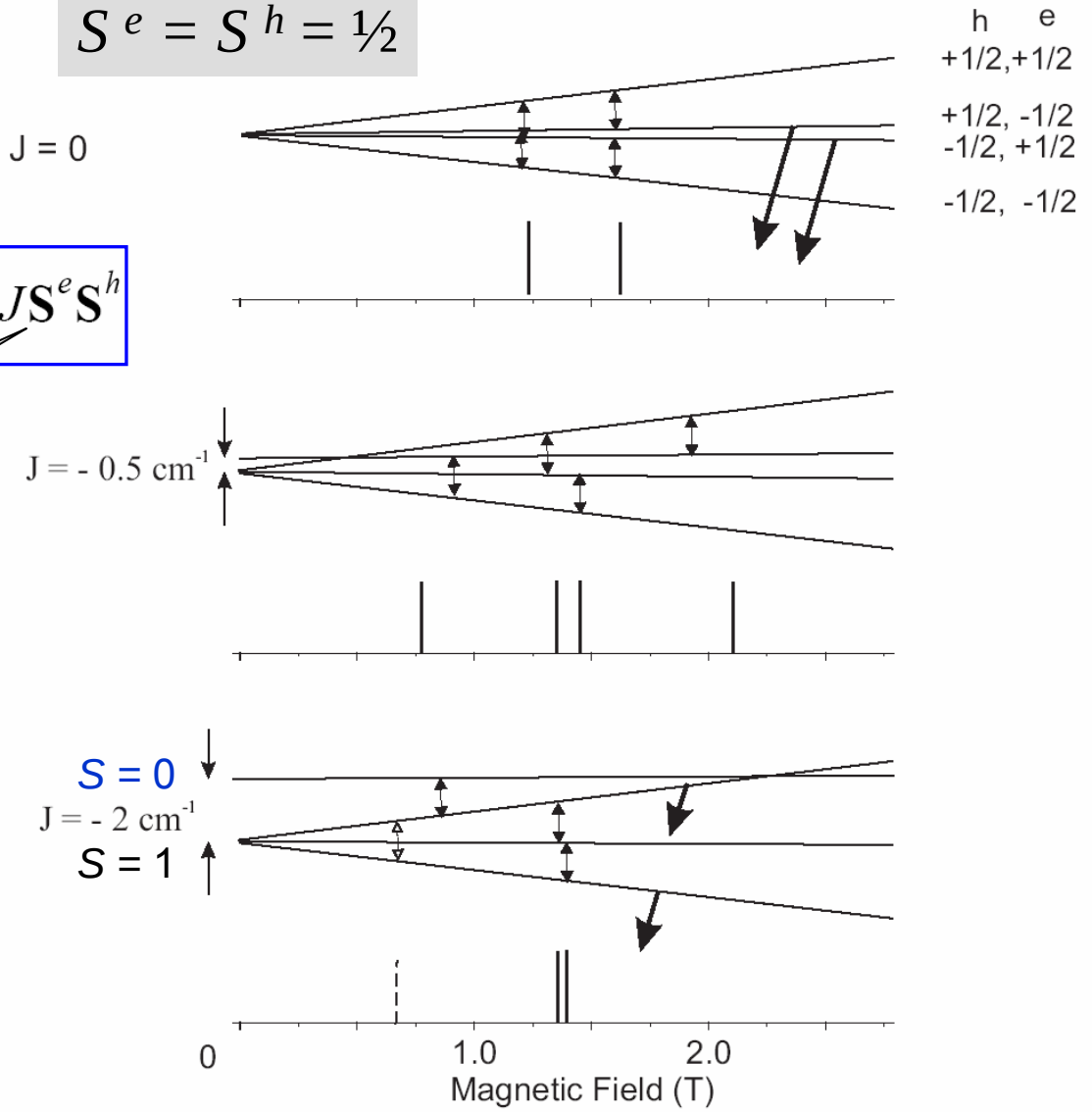
hole *Zeeman* interaction

electron *Zeeman* interaction

$$H = g^e \mu_B \mathbf{S}^e \mathbf{B} + g^h \mu_B \mathbf{S}^h \mathbf{B} + J \mathbf{S}^e \mathbf{S}^h$$

exchange interaction

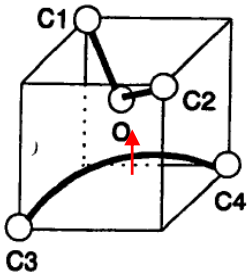
$$S^e = S^h = ½$$



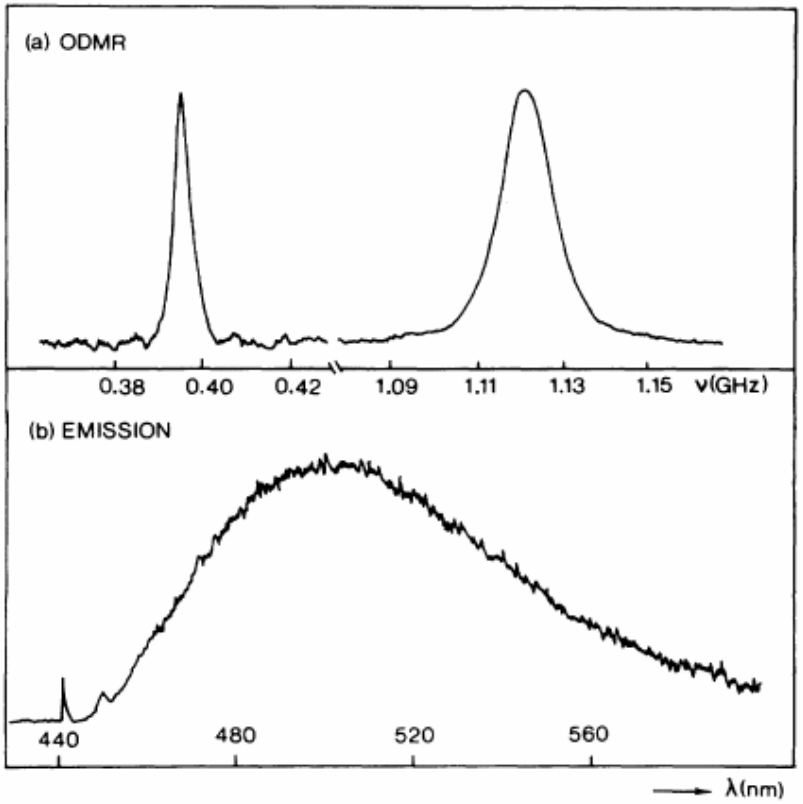
Spin-dependent

electron (e) – hole (h) optical recombination, 35 GHz (Q) band

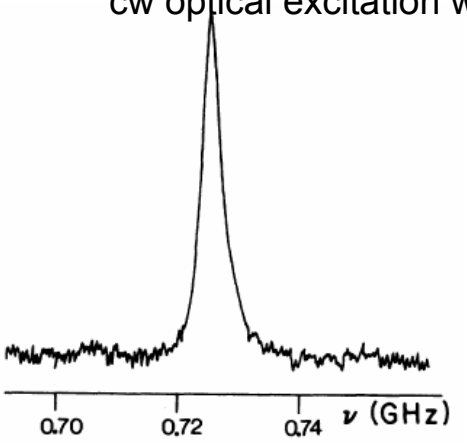
2.818-eV center (V-O) in diamond – ODMR in excited triplet state



S=1



(a) Zero-field ODMR spectrum as observed for the photoexcited triplet state of the 2.818-eV center in brown diamond at 1.4 K.
(b) ODMR intensity as a function of the detection wavelength obtained by phase-sensitive detection of the microwave-induced emission changes of the 1122-MHz transition.
cw optical excitation was at 364 nm.

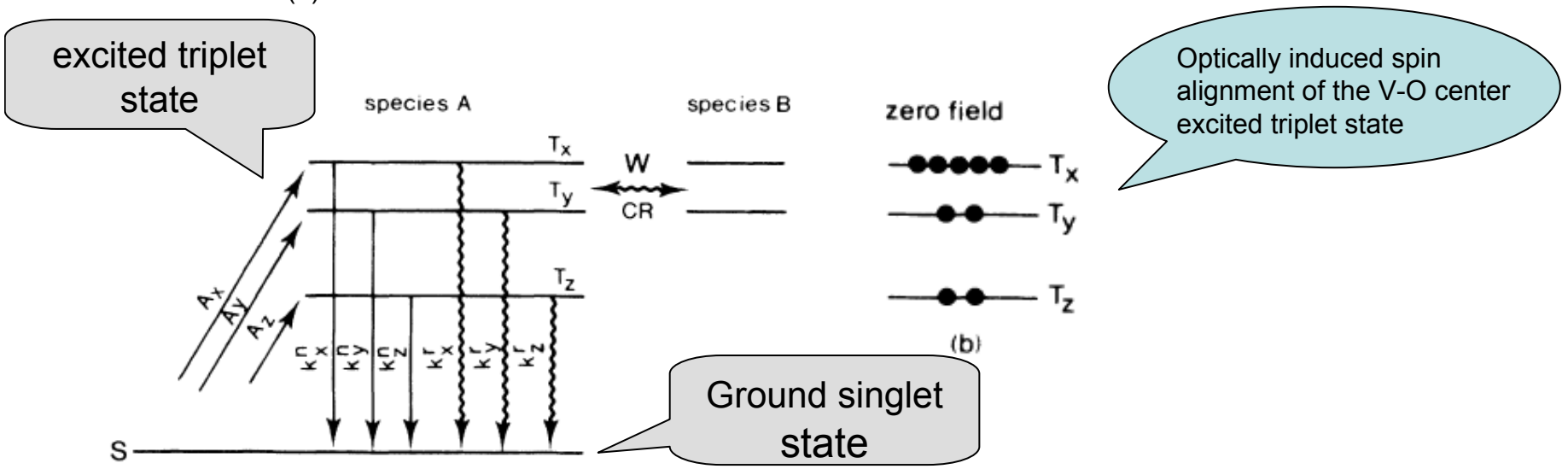


Gated ODMR spectrum showing the /D/—/E/ zero-field transition at 726 MHz of the 2.818-eV defect in the triplet state. Microwave pulses (of 2-ms duration) were applied with a fixed delay time of 6 ms after each optical pulse.

Westra, Sitters, Glasbeek, PRB, 1992

2.818-eV center (V-O) in diamond

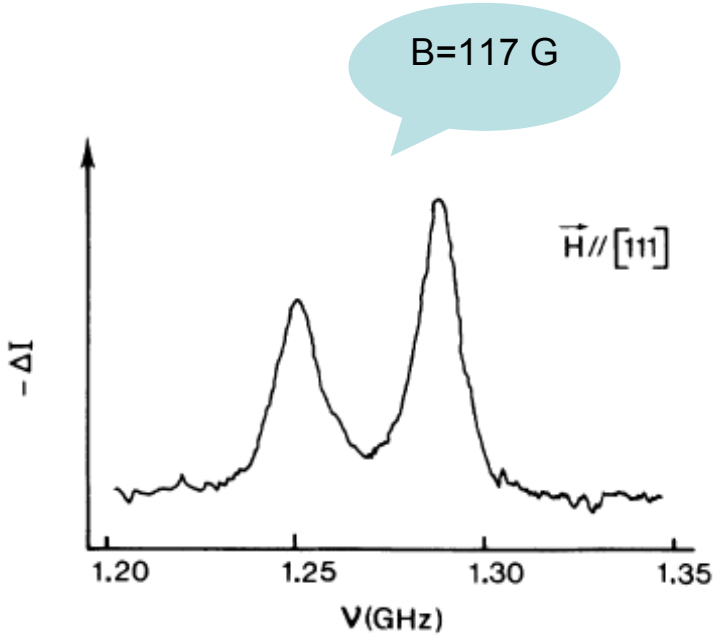
Photoexcitation of a brown diamond sample at 364 nm gives rise to a long-lived luminescence with a zero phonon line peaking at 441 nm (2.818 eV). By means of optically detected magnetic resonance (ODMR) spectroscopy, it was shown that the emission originates from an excited triplet state characterized by g =2.00, /D/ =924(2) MHz, and /E/ =198(2) MHz.



A schematic representation of the energy levels of two species A and B which are resonant and show CR. The four energy levels of species A correspond to the singlet ground state (S) and the excited triplet state (T_X,T_Y, T_Z,). A_i, k_i^r, and k_i^n (i =x,y, z) represent feeding rate, radiative decay rate, and nonradiative decay rate, respectively, of the triplet sublevel T_i.
Species B is resonant to the TX to TY sublevel transition. W represents the cross-relaxation (CR) rate.

Hiromitsu, Westra, Glasbeek, PRB, 1992

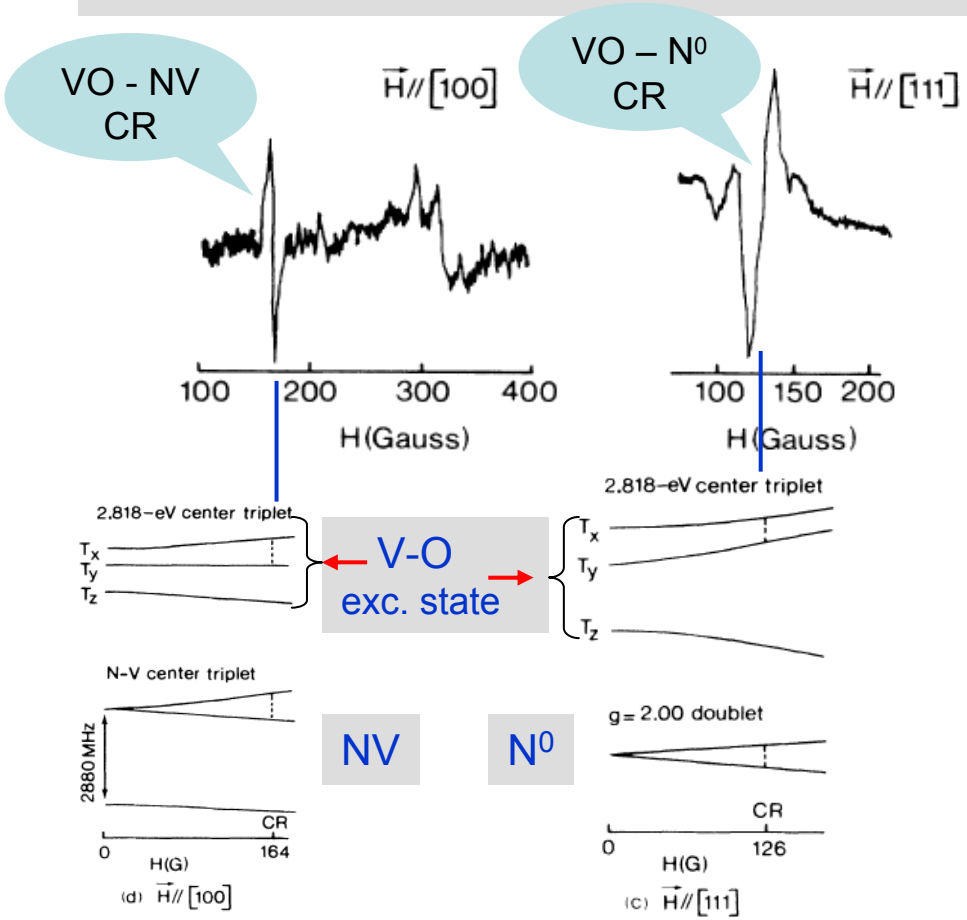
2.818-eV center (V-O) in diamond, ODMR signal



/D/+ /E/ ODMR signals of the 2.818-eV center photoexcited triplet state with the external magnetic field of 117 G applied along the [111] crystal axis. T=1.4 K. The 1.25-GHz and 1.29 GHz signals are due to the different sites of oxygen related centers

Hiromitsu, Westra, Glasbeek, PRB, 1992

2.818-eV center (V-O) in diamond ODMR: LAC and CR



Level anticrossing (LAC) and cross-relaxation (CR) with N^0 and NV ODMR effects

Derivative of the phosphorescence intensity changes of the 2.818-eV center as induced by a magnetic field.
The orientation of the magnetic field relative to the crystal axes is (a) H//[100], (b) H//[111].
Detection wavelength: 490 nm; T =1.4 K.

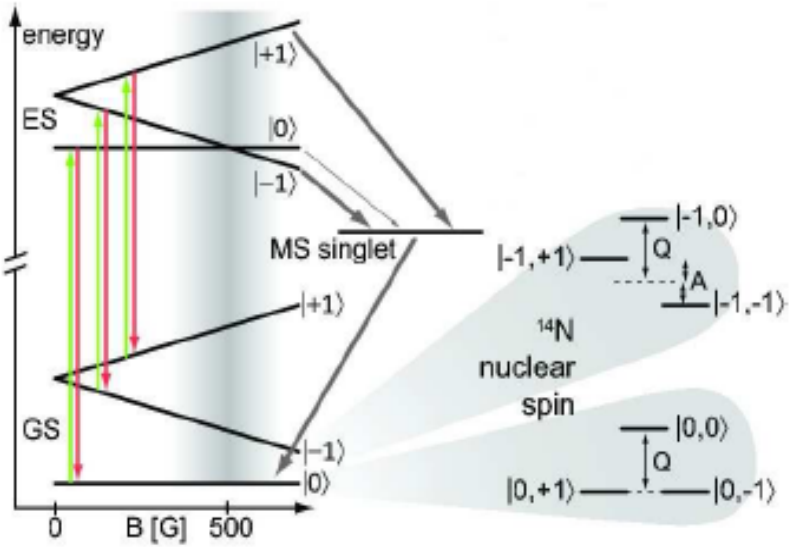
Hiromitsu, Westra, Glasbeek, PRB, 1992

NV centers in diamond

The NV-center levels scheme for triplet ground state (GS) and triplet excited state (ES) with its possible microwave transitions and GS hyperfine structure with ^{14}N nuclear spin

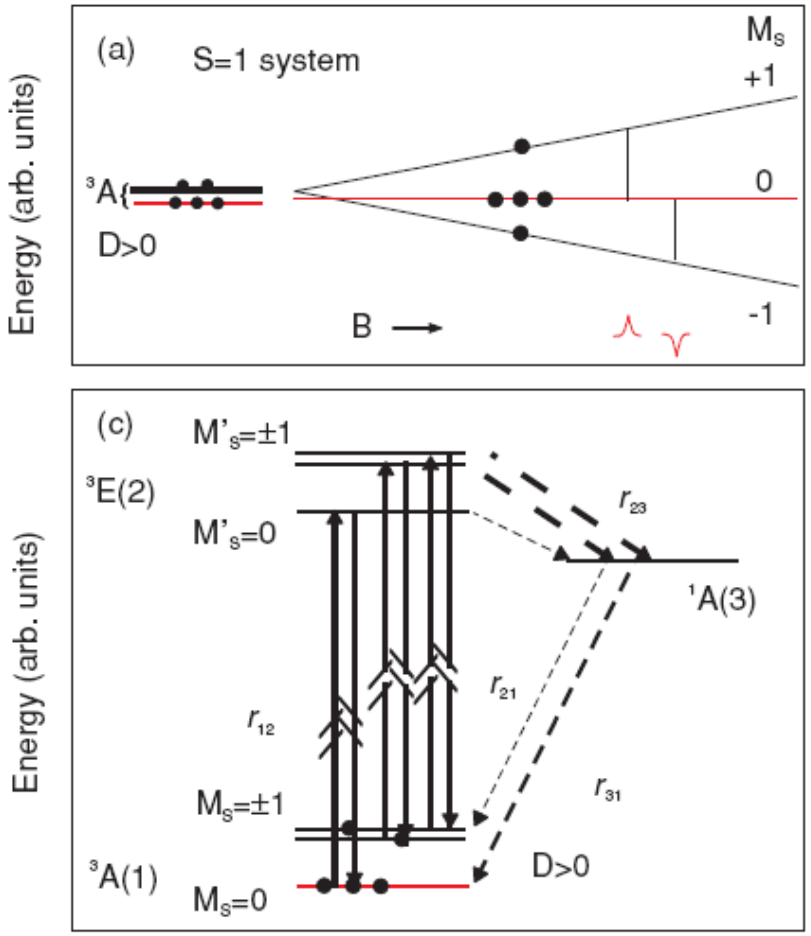
D=1.42 GHz

D=2.87 GHz



J. Wrachtrup, Quantum Memories
A Review based on the European Integrated Project “Qubit Applications (QAP)”, 2010

Energy-levels schemes for optical alignment of the spin sublevels for NV-defect triplet ground state

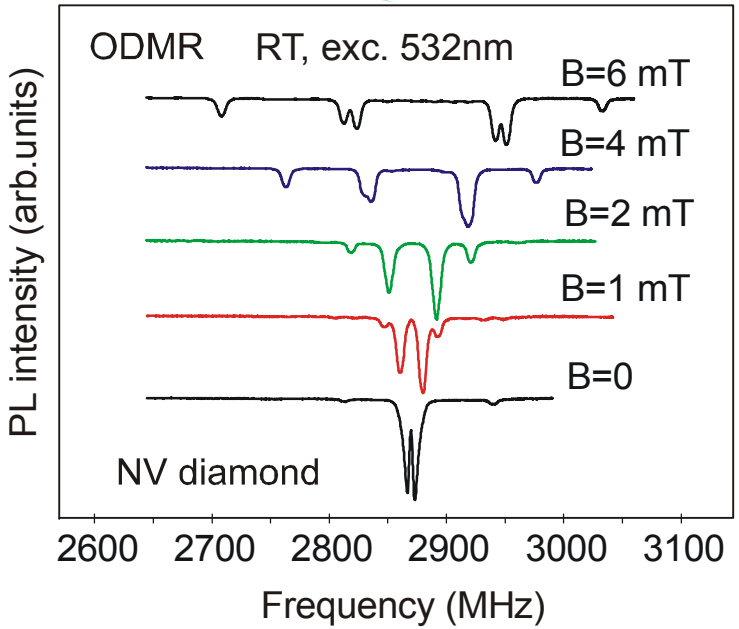


Energy-levels schemes for optical alignment of the spin sublevels for the NV-defect triplet ground state. M_S = 0 level is predominantly populated upon optical pumping, thus the high magnetic-field transition is emissive.
The populations of the ground-state energy levels under optical pumping are indicated by different numbers of filled circles.

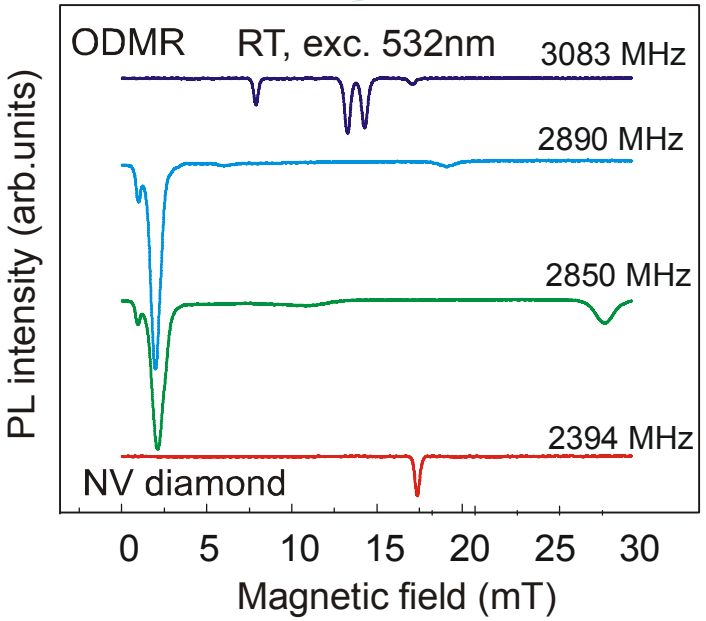
Seven-level models interpreting the optical alignment of the ground-state sublevels in zero magnetic field.
Solid and dashed lines indicate the radiative and nonradiative transitions, respectively. The oblique dashed thick arrow indicates the most probable ISC transition, double line of the upper sublevels for the 3A and 3E states indicates that these levels are doubly degenerate. For the 3E state only the lower three levels are indicated.

Low-frequency ODMR of NV− centers measured in single diamond crystal at room temperature, magnetic field *B* is parallel to <111>

Frequency sweep, *B* is settled

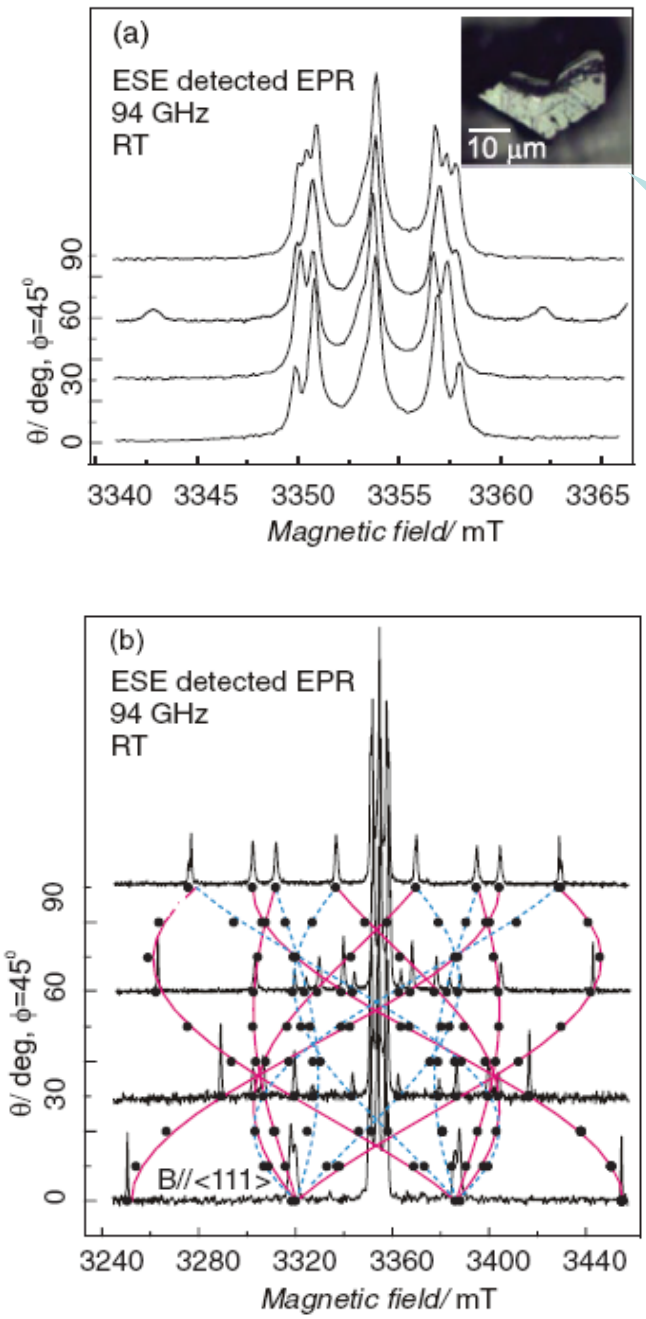


B sweep, frequency is settled



R.A. Babunts, A.A. Soltamova , P.G. Baranov

Enormously High Concentrations of Nitrogen-Vacancy Centers Fabricated by Sintering of Detonation Nanodiamonds (DNDs)



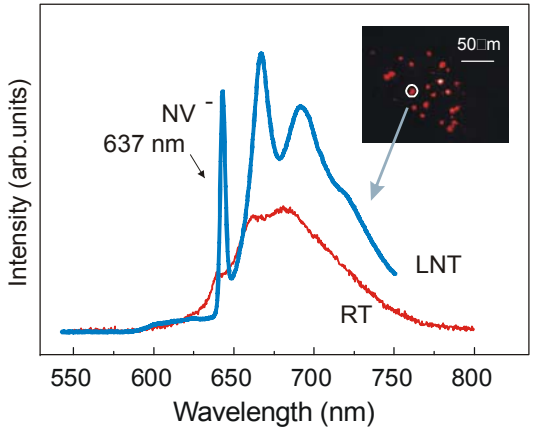
single sintered DND cluster

W-band high-frequency ESE detected EPR in a single sintered DND cluster (see inset)

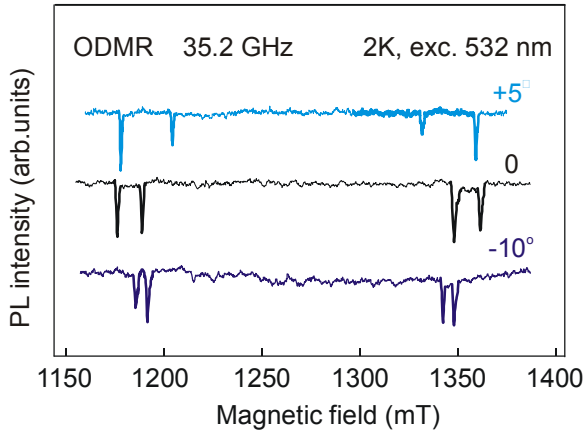
W-band high-frequency ESE-EPR in a single sintered DND cluster.
a) Angular dependence of the central part of the EPR spectra corresponding to isolated nitrogen N donors.
b) Angular dependencies of the whole spectra where dots correspond to experimental data, and solid and dashed lines are simulated angular dependencies for NV defects.

A.A. Soltamova, I.V. Il'in, F.M. Shakhov, S.V. Kidalov, A.Ya. Vul', B.V. Yavkin, G.V. Mamin, S.B. Orlinskii, P.G. Baranov, *JETP Letters, Vol. 92, 102 (2010)*

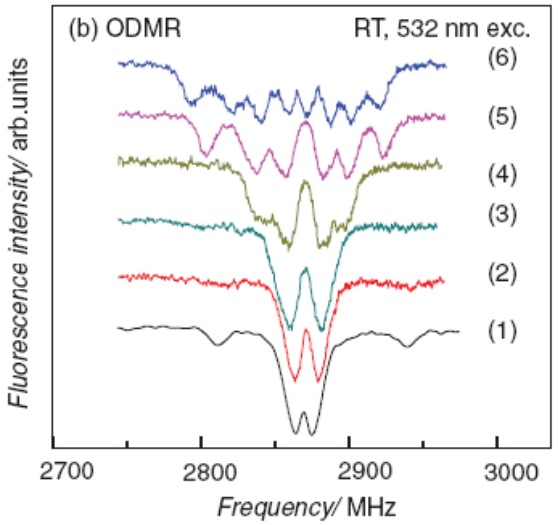
Enormously High Concentrations of Fluorescent Nitrogen-Vacancy Centers Fabricated by Sintering of Detonation Nanodiamonds



Characterization of clusters produced by sintering of the DND powder. Room-temperature and low-temperature fluorescence of a single NV -containing sintered DND cluster. (inset) As-captured image of samples illuminated with the light of solid-state 532-nm laser taken through a standard optical microscope.



ODMR spectra detected in a sintered DND cluster at 35.2 GHz for three different orientations of magnetic field with respect to the NV axis at 2 K.



Low-frequency ODMR of NV− centers registered at room temperature (RT) in increasing magnetic field B = 0 (1), 3 (2), 4 (3), 10 (4), 15 (5), and 20 G (6).

P.G. Baranov ,A.A. Soltamova ,D.O. Tolmachev , N.G. Romanov , R.A. Babunts , F.M. Shakhov , S.V. Kidalov , A.Ya. Vul' , G.V. Mamin , S.B. Orlinskii , N.I. Silkin, SMALL, 2011

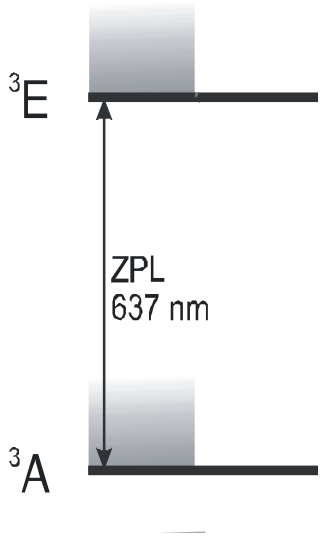
Optically Detected Magnetic Resonance for single NV defect in the triplet ground state in diamond

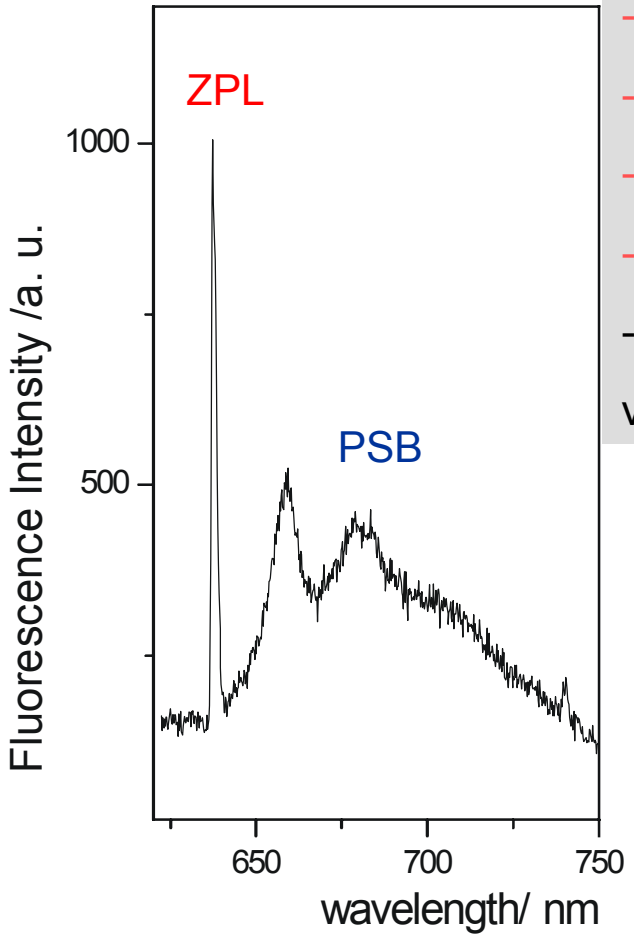
Gruber, Drabenstedt, Tietz, Fleury, Wrachtrup, von Borczyskowski, Science **276**, 2912 (1997);

Kilin, Wrachtrup, Nizovtsev, OSA/ICQI 2001

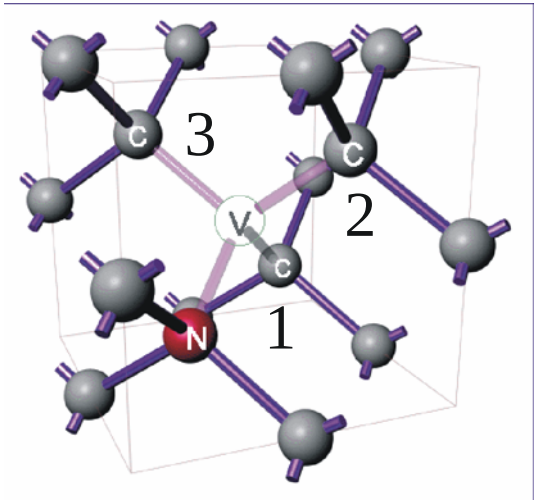
Jelezko, Gaebel, Popa, Gruber, Wrachtrup, *Phys. Rev. Lett*. **92**, 076401 (2004).

Spectroscopy of single NV defect in diamond

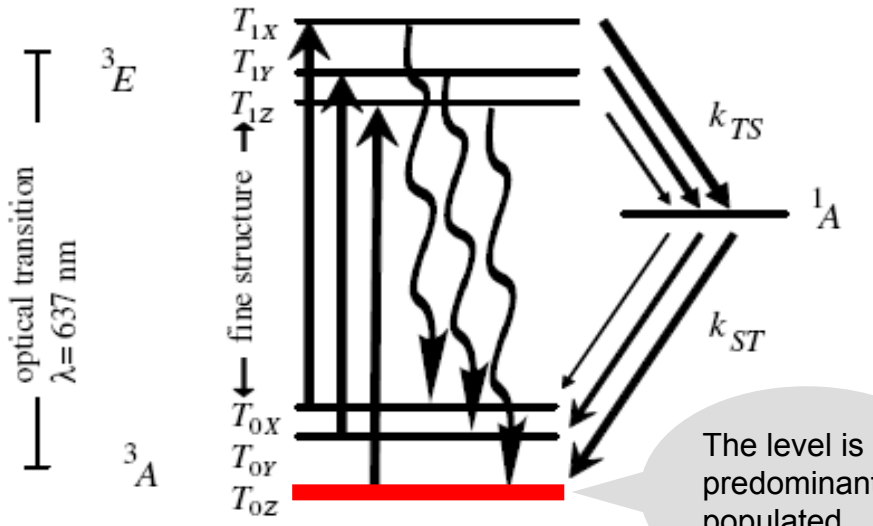




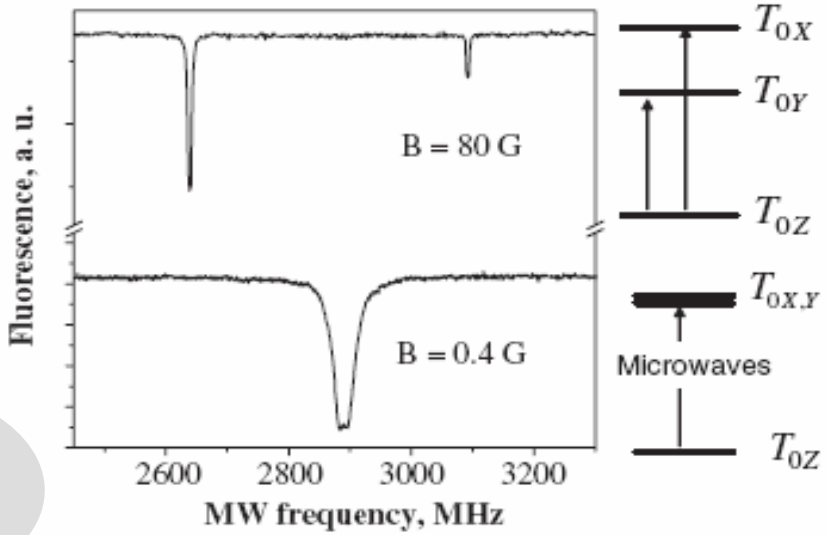
- Ground state: spin triplet ^3A
- Excited state: orbital doublet ^3E
-Zero-Phonon Line (ZPL): 637 nm
- Phonon side band (PSB)
-Line broadening due to strain variation



Single NV defects in diamond



Energy level diagram of a NV centre. Allowed optical transitions between ground (^{3}A) and excited (^{3}E) electronic state sublevels are shown. The strength of the spin-selective intersystem crossing transitions is encoded by the thickness of the arrows.

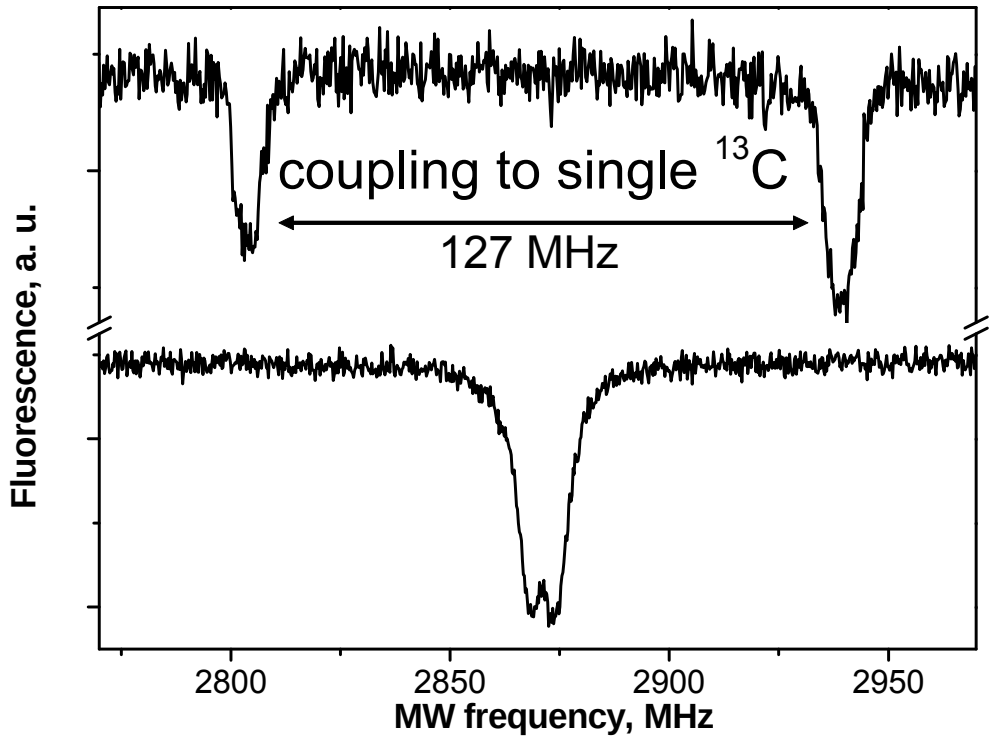


ODMR

Optically detected ESR spectra of single NV defects in zero (lower graph) and weak (upper graph) magnetic fields. Relevant spin transitions are shown on the right side of the graph.

Jelezko, Wrachtrup, J. Phys.: Condens. Matter 16 (2004) R1089–R1104

Single NV defects in diamond



Hyperfine splitting for ^{13}C in the first shell 127 MHz

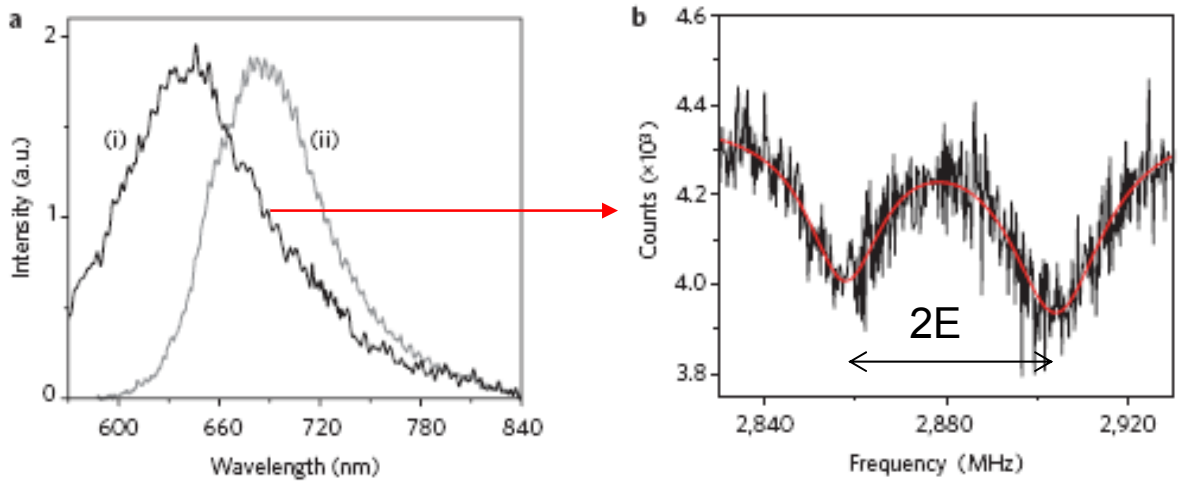
^{13}C spins as qubits:
Kilin, Wrachtrup, Nizovtsev, OSA/ICQI 2001;
Wrachtrup, Opt. Spectr. 91 429 (2001)

Experimental realization using ESR:
Jelezko et al. hys. Rev. Lett. **93**, 130501 (2004)

ODMR in detonation nanodiamond

Luminescence

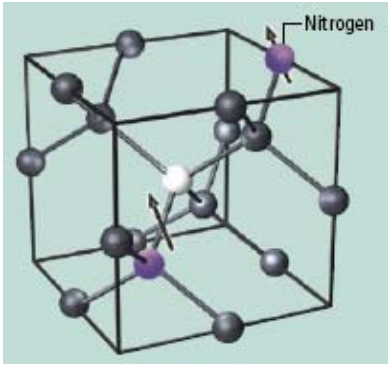
ODMR spectrum

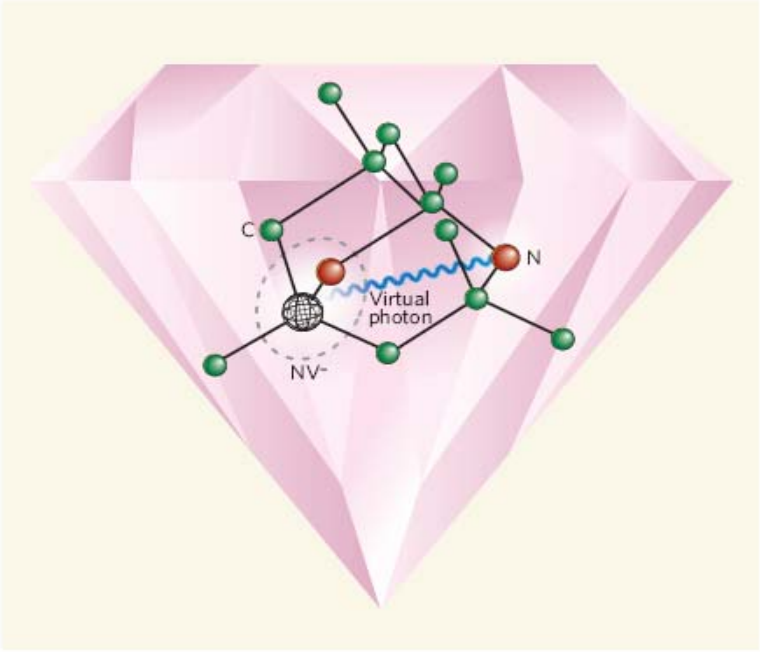


Luminescence and magnetic resonance spectra from detonation nanodiamond. a, Representative NV centre spectra, as acquired in nanodiamonds incorporated in aggregates (i) and in the free-space sample (ii). b, ODMR spectrum associated with the luminescence spectrum (i), showing the two characteristic magnetic resonance dips indicating a strain-induced non-axial splitting of NV spin sublevels in nanodiamonds, which is above 20 MHz!

C. Bradac et al. , NATURE NANOTECHNOLOGY, 2010

Observing coherent coupling between two quantum objects in the solid state has been achieved at room temperature — using nitrogen defects in diamond — opening up an avenue to practical quantum computing. [J.J.L. Morton, nature physics **2**, 365 (2006)]





Pieter Kok and Brendon W. Lovett
NATURE, **444**, 2 (2006)

The N–NV^- system can embody two electron-spin qubits, so these experiments represent a significant steptowards a larger-scale quantum computer based on the NV^- system. The authors suggest that several NV^- centres could be connected through chains of N defects. This interaction allows spin control of the nitrogen defect using optical control of the NV defect, and the combined system **forms a promising two-qubit structure for quantum computing.**

[1] Hanson, R., Mendoza, F. M., Epstein, R. J. & Awschalom, D. D. *Phys. Rev. Lett.* 97, 087601 (2006). [2] **Jelezko, F**., Gaebel, T., Popa, I., Gruber, A. & **Wrachtrup, J**. *Phys. Rev. Lett*. 92, 076401 (2004).

ODMR scanning probe magnetometry with nanoscale resolution

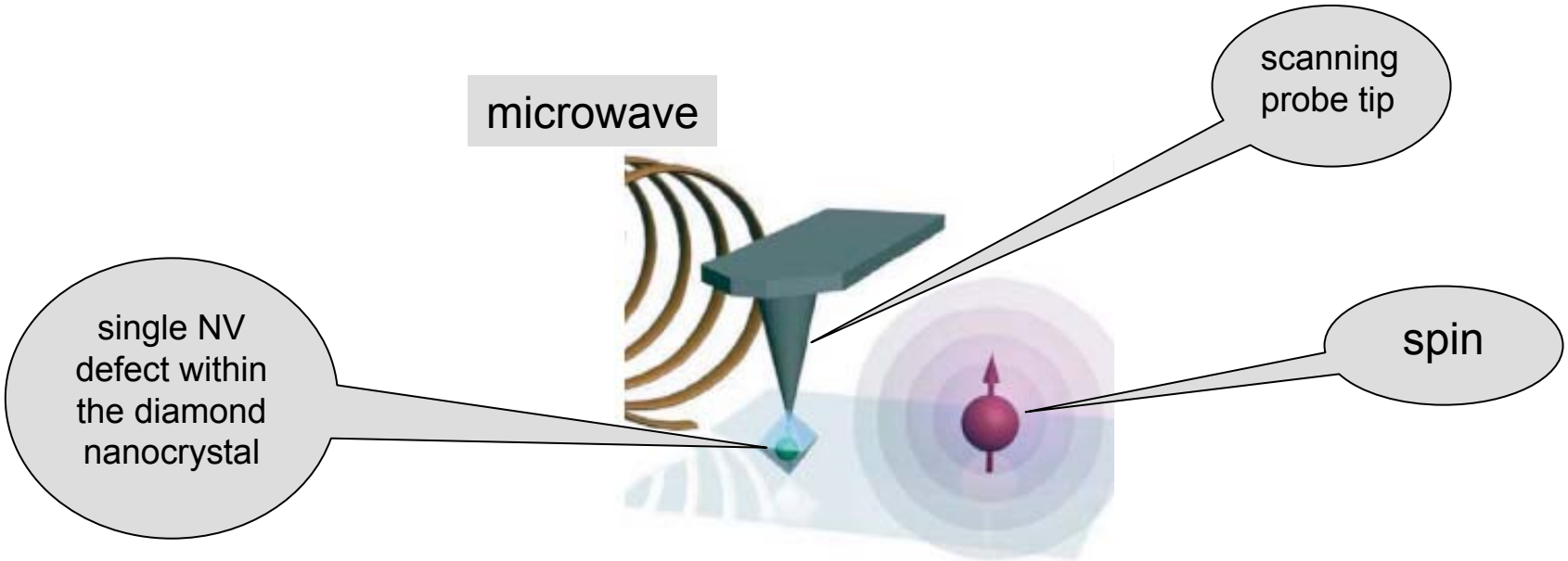


Diagram of the magnetic field imaging experiment
(without optical system)

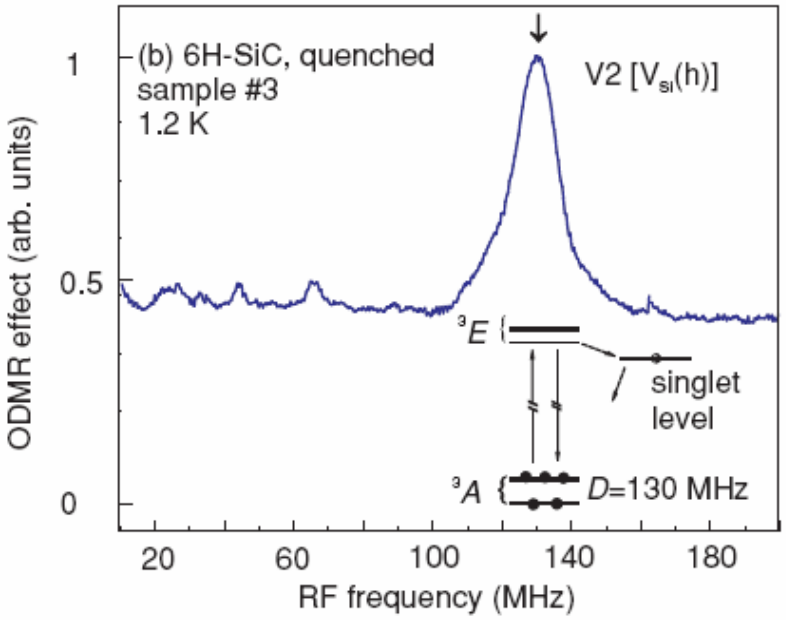
G. Balasubramanian, I.Y. Chan, R. Kolesov, M. Al-Hmoud, J. Tisler, C. Shin, C. Kim, A. Wojcik, P.R. Hemmer, A. Krueger, T. Hanke, A. Leitenstorfer, R. Bratschitsch, F. Jelezko, J. Wrachtrup, Nanoscale imaging magnetometry with diamond spins under ambient conditions, NATURE| Vol 455|2 October 2008

Nanocarbons in SiC – perspective matter for the single defect spectroscopy

Silicon vacancy in SiC as a promising quantum system for single-defect and single-photon spectroscopy

P.G. Baranov, A.P. Bundakova, A.A. Soltamova, S.B. Orlinskii, I.V. Borovykh, R. Zondervan, R. Verberk, J. Schmidt, Phys. Rev. B 83, 125203 (2011); JETP Letters **86**, 202 (2007).

The ODMR spectra for Si vacancy in 6H-SiC obtained with excitation of the *V*2 ZPL with maximum ODMR effect detected at 937 nm



P.G. Baranov, A.P. Bundakova, and A.A. Soltamova, S.B. Orlinskii, I.V. Borovykh, R. Zondervan, R. Verberk, J. Schmidt, PRB 83, 125203 (2011); JETP Letters **86**, 202 (2007)

- A giant change in the luminescence intensity of zero-phonon lines in zero magnetic field (by a factor reaching 2–3) was observed upon absorption of microwave radiation with energy equal to the fine-structure splitting of spin sub-levels of the silicon vacancy ground state in SiC.

- As distinct from the known NV defect in diamond, the silicon vacancy is an intrinsic defect; therefore, a system of a single electron spin localized in an environment free of nuclear spins can be created.

- In this system, the coherence time is extended, and the electron spin can be controlled by low-energy microwave quanta in the range 20–150 MHz, which is two orders of magnitude lower the corresponding energy for the N–V defect in diamond.

"Eventually, other defects in, e.g., SiC, might take over because of easier structuring of host material, defect positioning, or more advanced material science...
...So what will be the future of defect center spintronics? Will spin defects in diamond or, e.g., SiC, be the future quantum hardware? The answer to that question certainly is subject to future investigations."
J.Wrachtrup, Defect center room-temperature quantum processors, PNAS | May 25, 2010 | vol. 107 | no. 21 | 9479–9480

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