High Field Electron Nuclear Double Resonance and Dynamical Nuclear Polarization

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Overview

- Electron Nuclear Double Resonance
- Pulsed EPR and ENDOR
- K_3NbO_8 with CrO_8^{3-}
- Nitrogen centers in SiC
- DNP via PONSEE
- Nuclear relaxation
- Electrical/optical detection

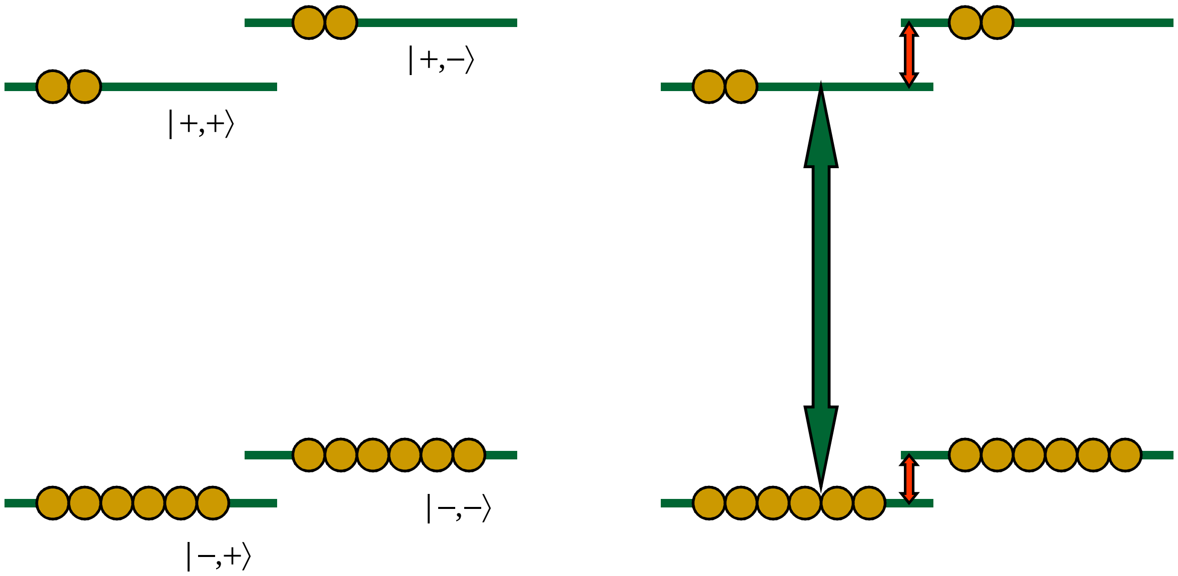
Electron Nuclear Double Resonance (ENDOR)

Combination of Electron Paramagnetic Resonance and Nuclear Magmetic Resonance in which EPR (mwave / mm-wave) transitions and NMR transitions (RF) are excited simultaneously or sequentially.

- NMR transitions are detected by changes in the EPR
- Measure NMR with the sensitivity of EPR
- Measure selectively:
  - Only nuclei coupled to the electron spin via hyperfine interaction are detected
  - Site selection
  - Orientation selection

- Why Terahertz ?
  - NMR state of the art 900 MHz or 21 Tesla, corresponding to an EPR frequency of 0.55 THz

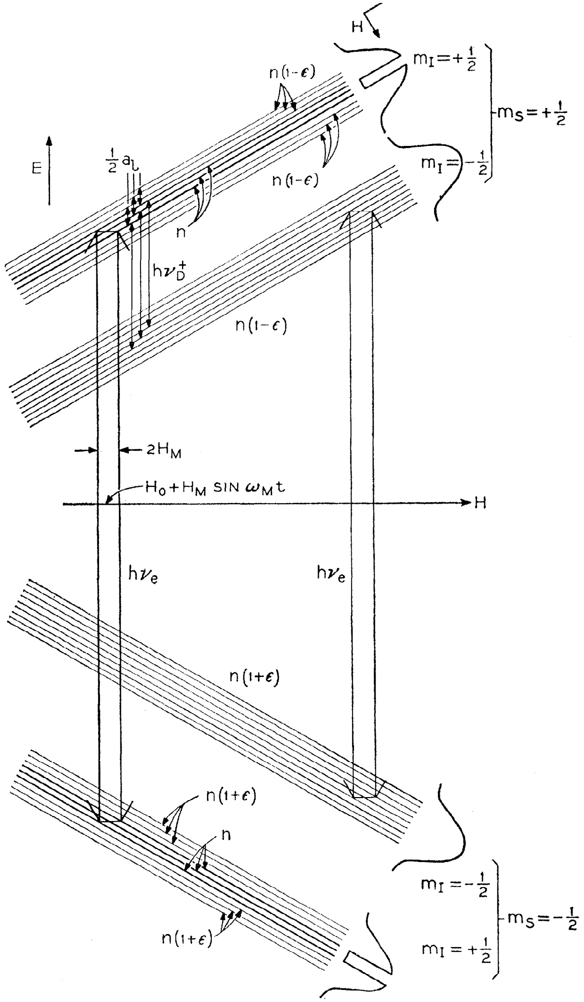
The basic idea of ENDOR

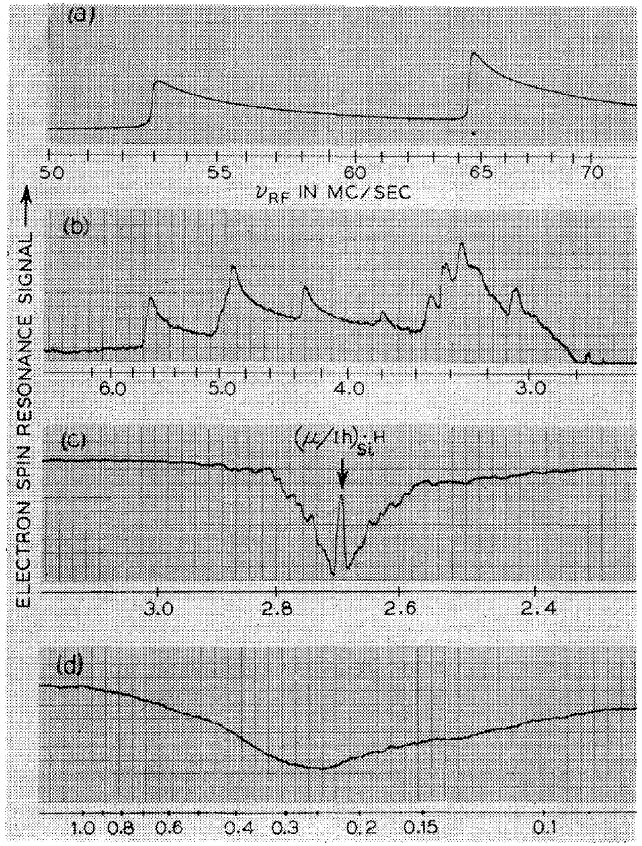


PHYSICAL REVIEW VOLUME 114, NUMBER 5 JUNE 1, 1959

Electron Spin Resonance Experiments on Donors in Silicon. I. Electronic Structure of Donors by the Electron Nuclear Double Resonance Technique

G. FEHER
Bell Telephone Laboratories, Murray Hill, New Jersey

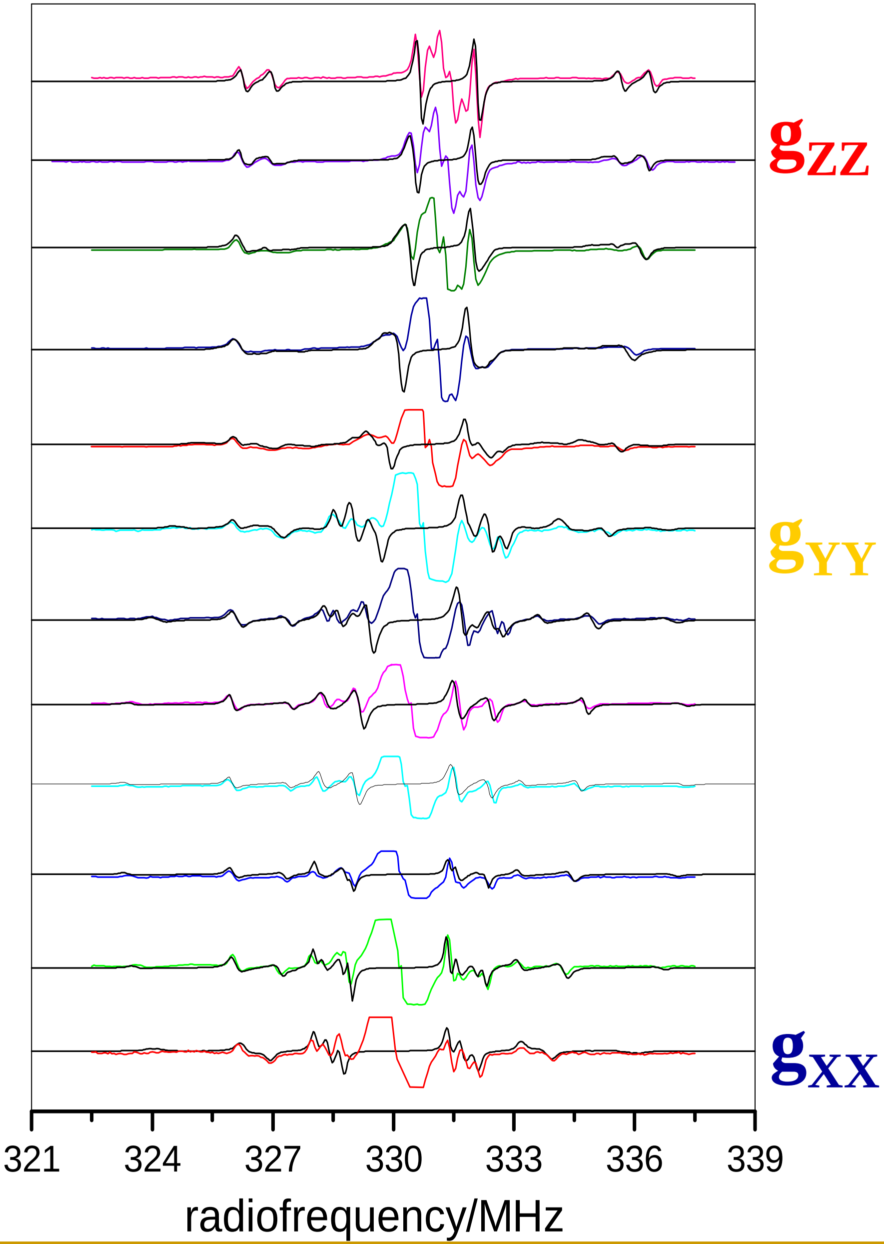




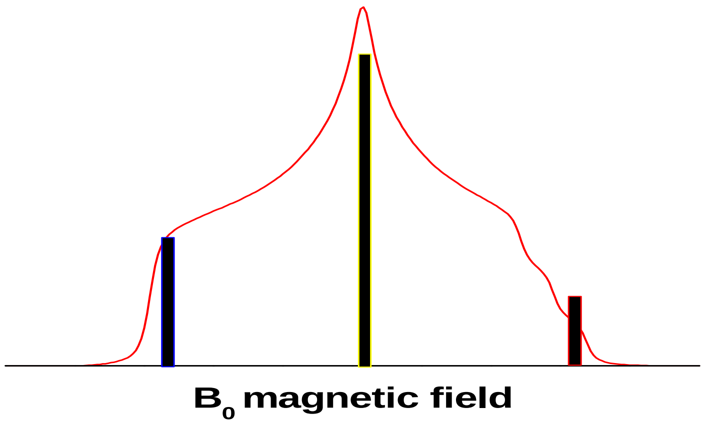
^{31}P

^{29}Si

^{29}Si



ENDOR spectra at 218 GHz and T= 5K along with simulations*.



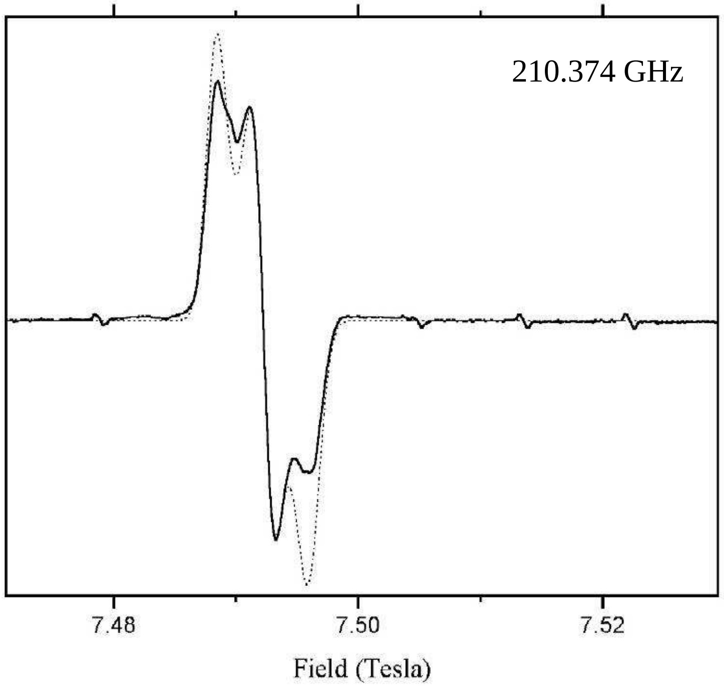
High Field => Orientation selection

"Quasi-crystalline" ENDOR for non-oriented samples

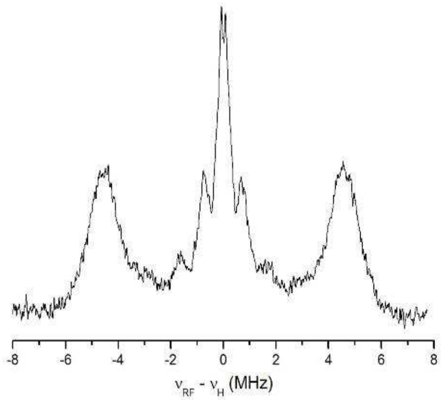
Anna-Lisa Maniero et al. in **Very High Frequency (VHF) ESR/EPR (Biological Magnetic Resonance Vol 22), Springer (2004)**

*Simulated spectra shown in black

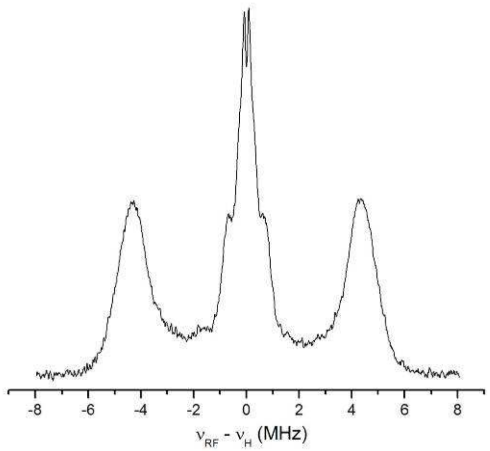
Bacteriochlorophyll *a* radical anion



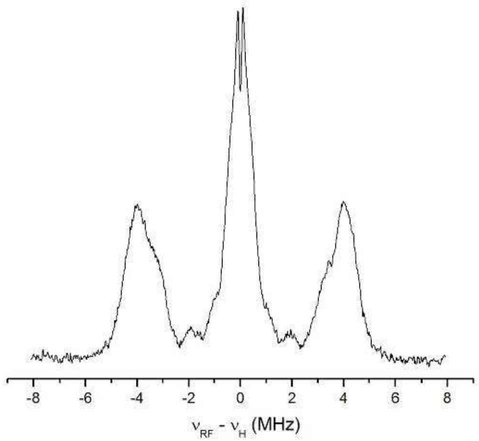
g_x = 2.004265
g_y = 2.003232
g_z = 2.002198



@ g_x



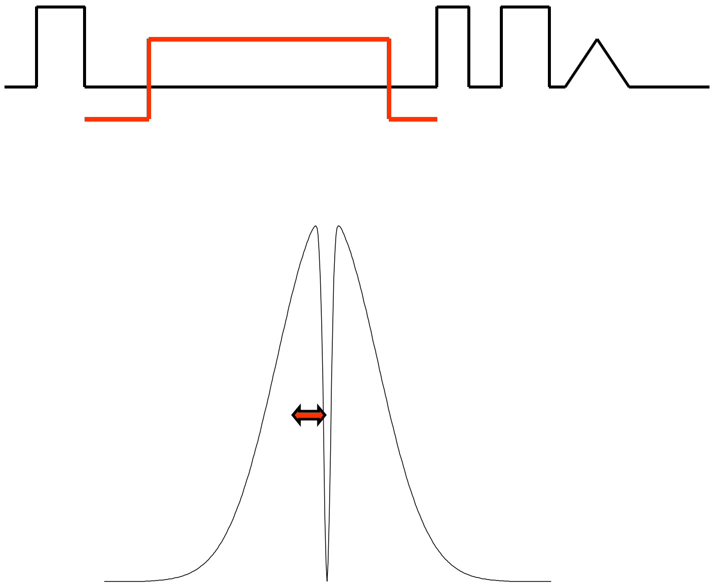
@ g_y



@ g_z

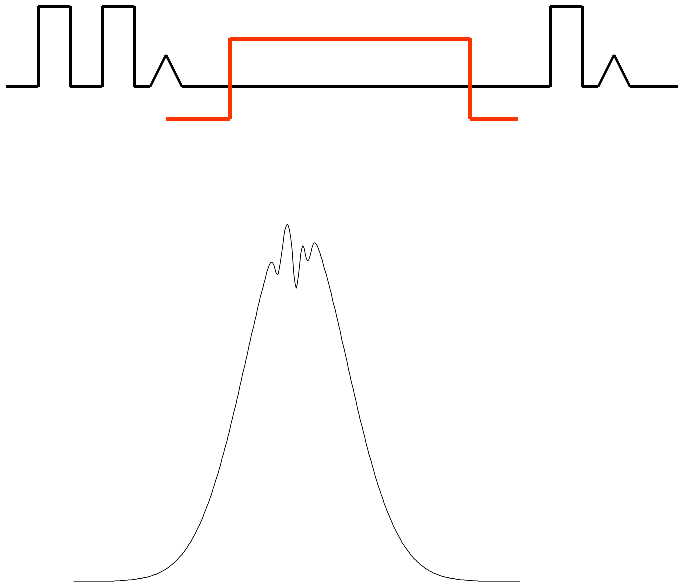
Pulsed ENDOR

- Davies ENDOR



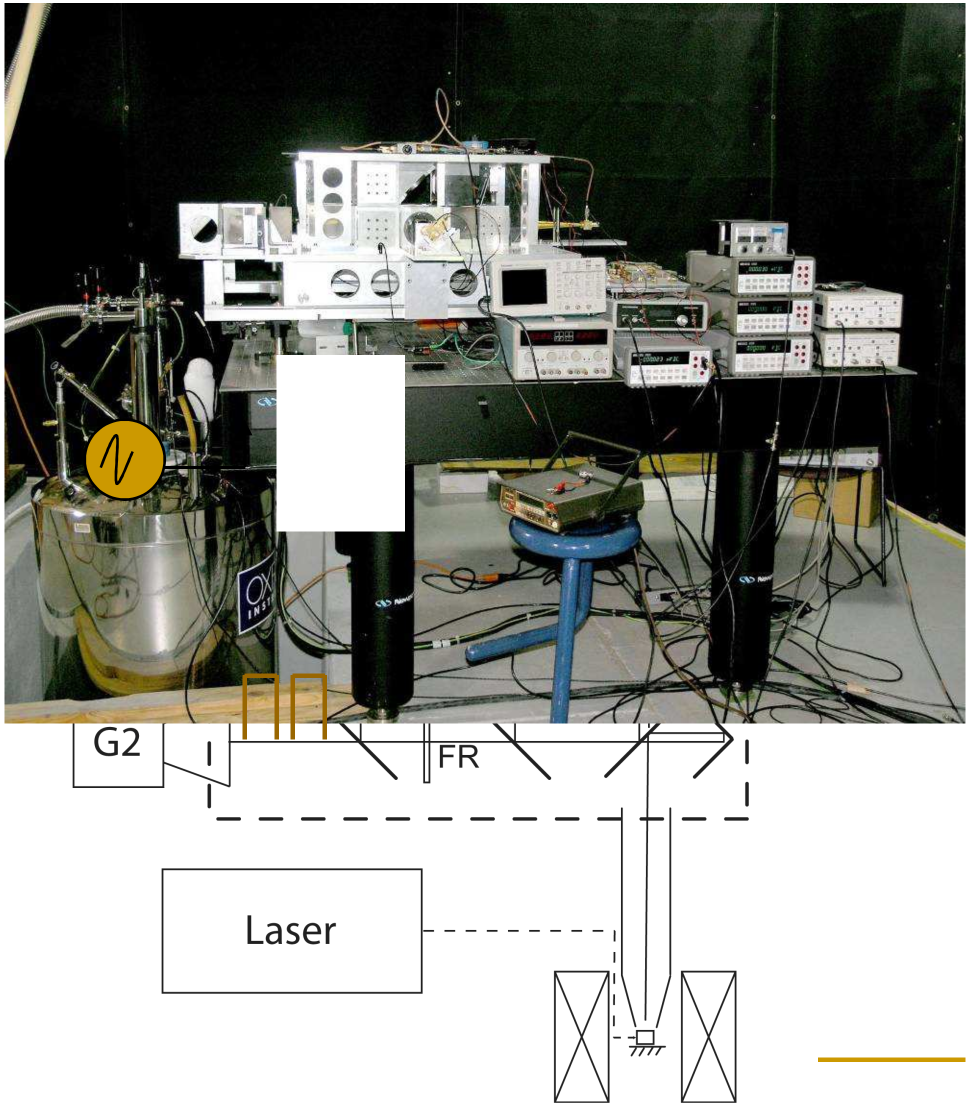
Resonant RF diminishes the population inversion

- Mims ENDOR

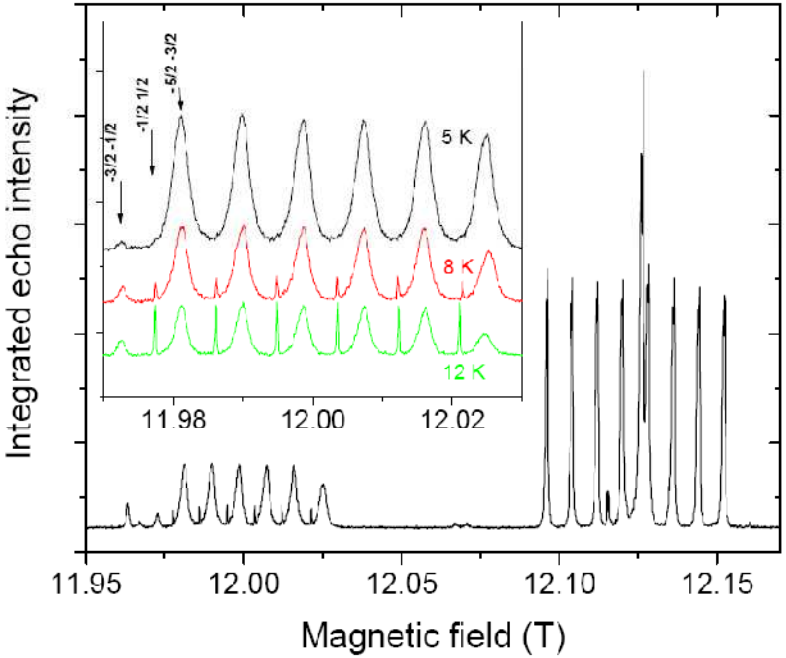


ENDOR destroys coherence between spin populations (and stimulated echo)

Instrumentation



- Home-built
- Quasi-optic
- Multifrequency
  - 120, 240, 336 GHz
- CW EPR/ENDOR
- Pulsed EPR/ENDOR



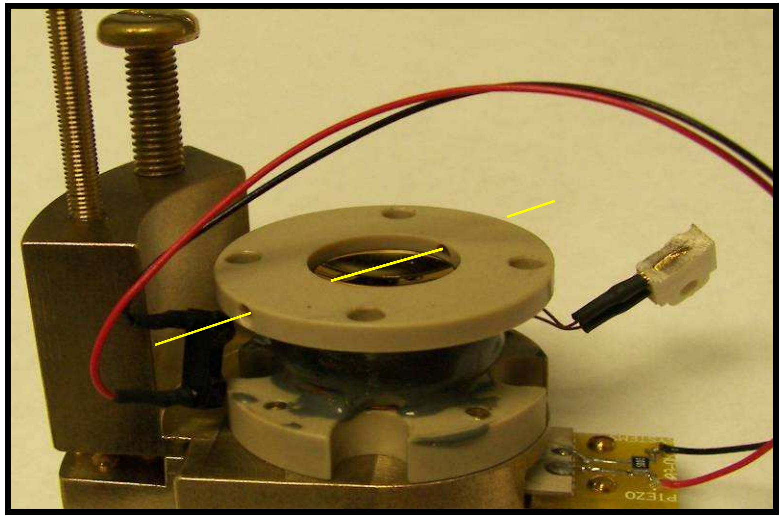
Rev. Sci. Instrum. **79**, 064703 (2008)

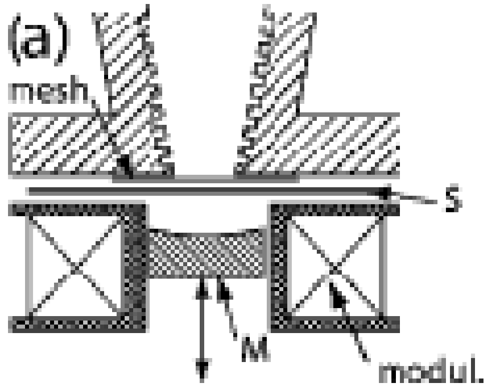
Pulsed ENDOR at 240 GHz

Sample holders:

Fabry Perot Resonator with simple ENDOR coil

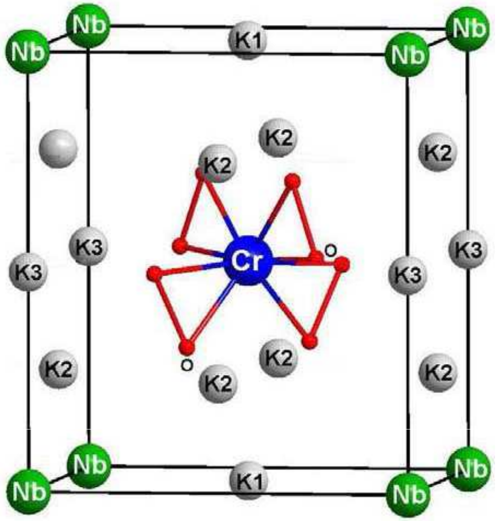
No resonator with helmholtz coil





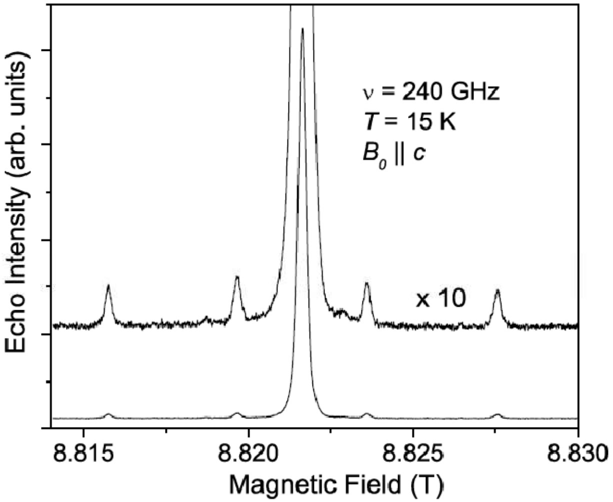
Nellutla et al. **Phys. Rev. B**, **78** (05), 054426 (2008)

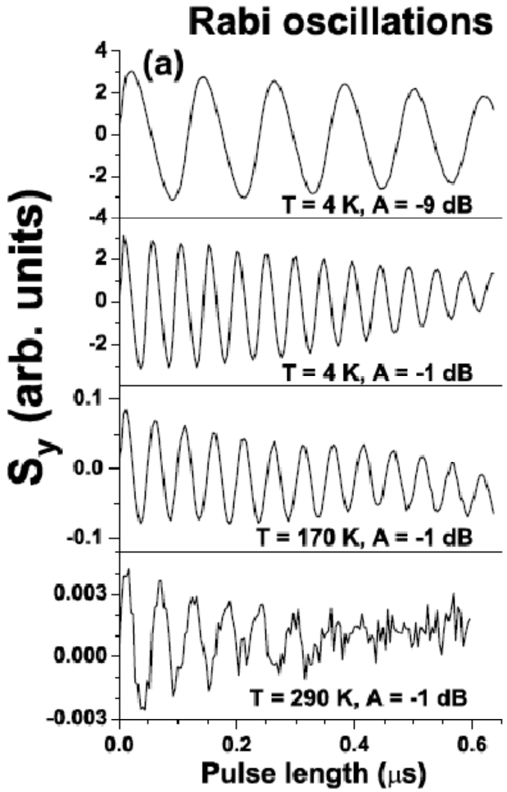
Transition ion system $K_3NbO_8:Cr^{5+}$



Suggested standard for hf-EPR, simple $3d^1$ system.

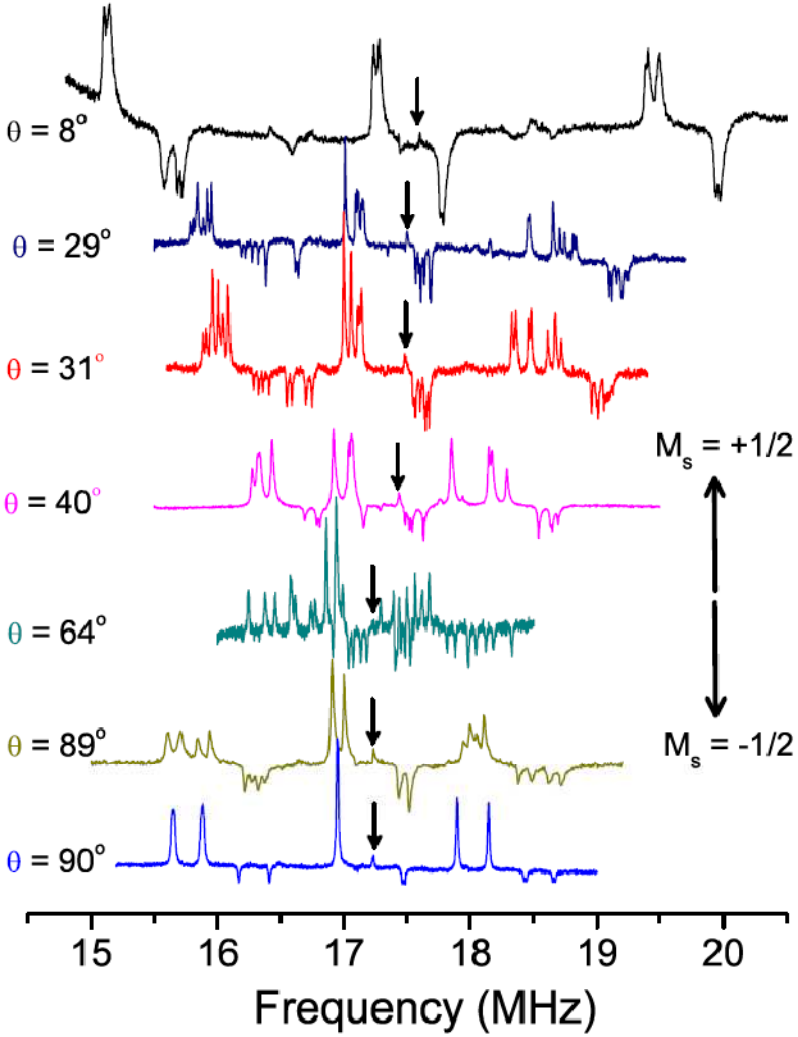
Transition ion "qubit" with S=1/2 and I=0 or I=3/2

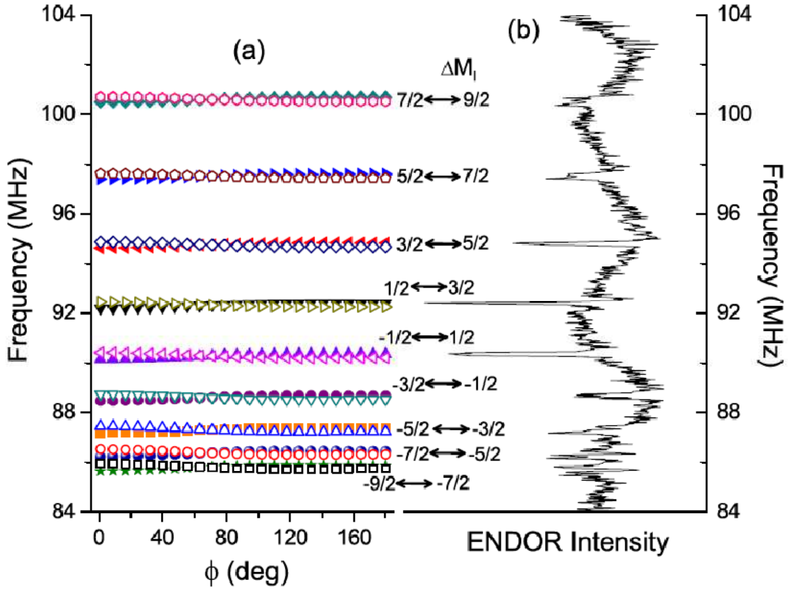




Phys. Rev. Lett. 99, 137601 (2007)

Pulsed ENDOR at 240 GHz





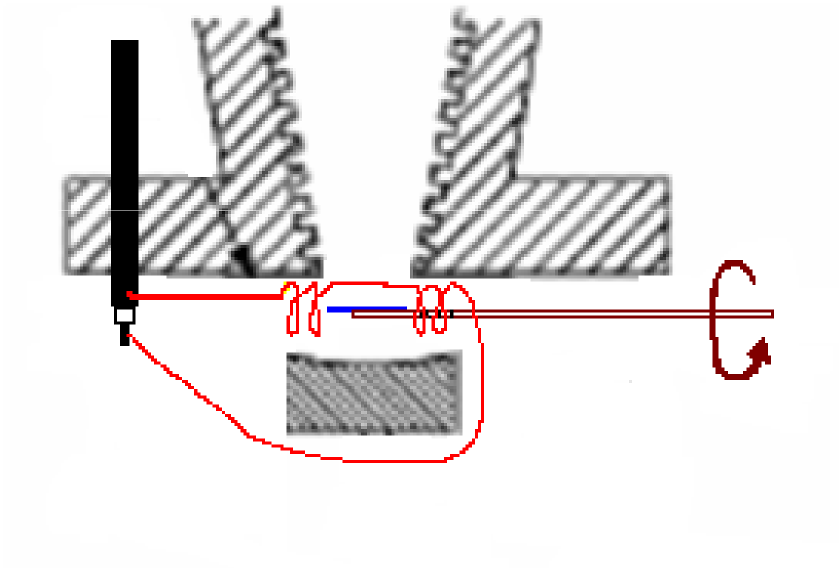
^{39}K, ^{93}Nb ENDOR

→ Hyperfine and quadrupolar couplings
Spin density distributions

Phys. Rev. B, **78** (05), 054426 (2008)

Setup without resonator

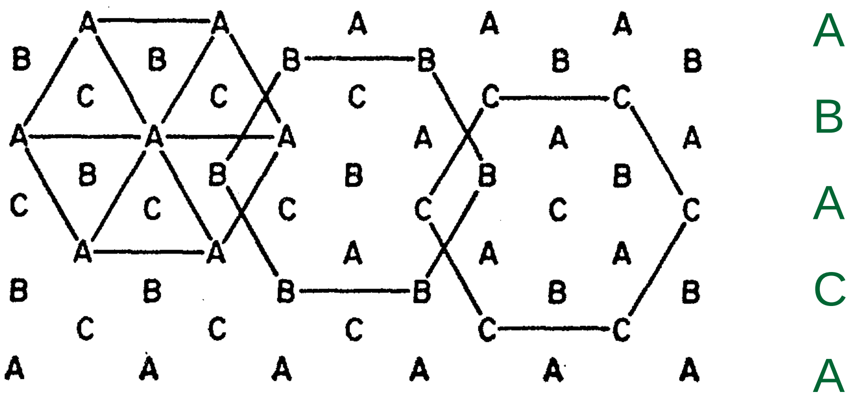
- Sample size (~3x3x1 mm plate)



No resonator

SiC

- High power, high temperature semiconductor
- Drawback: many polytypes (2H, 4H, 6H, …)
- Wavefunction of trapped donor electrons not well known



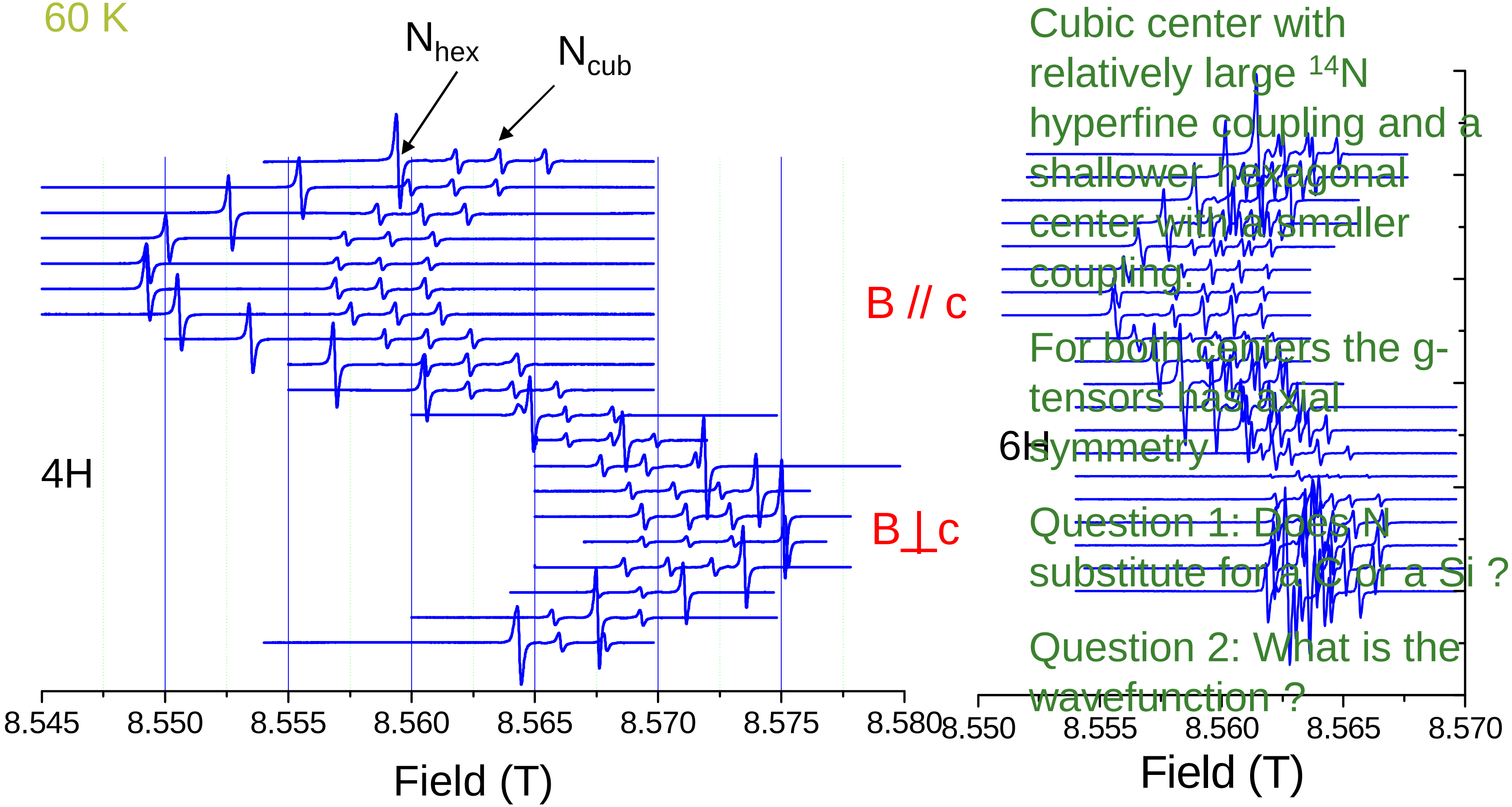
4H-SiC

In 4H-SiC 2 types of substitutions:
Substitution A : cubic site (N_c)
Substitute B/C : hexagonal site (N_h)

Probe the wavefunction of electrons trapped at the donor site by measuring the hyperfine coupling with surrounding ^{13}C, ^{29}Si nuclei.

High-Frequency EPR and ENDOR of N centers in SiC

240 GHz
60 K



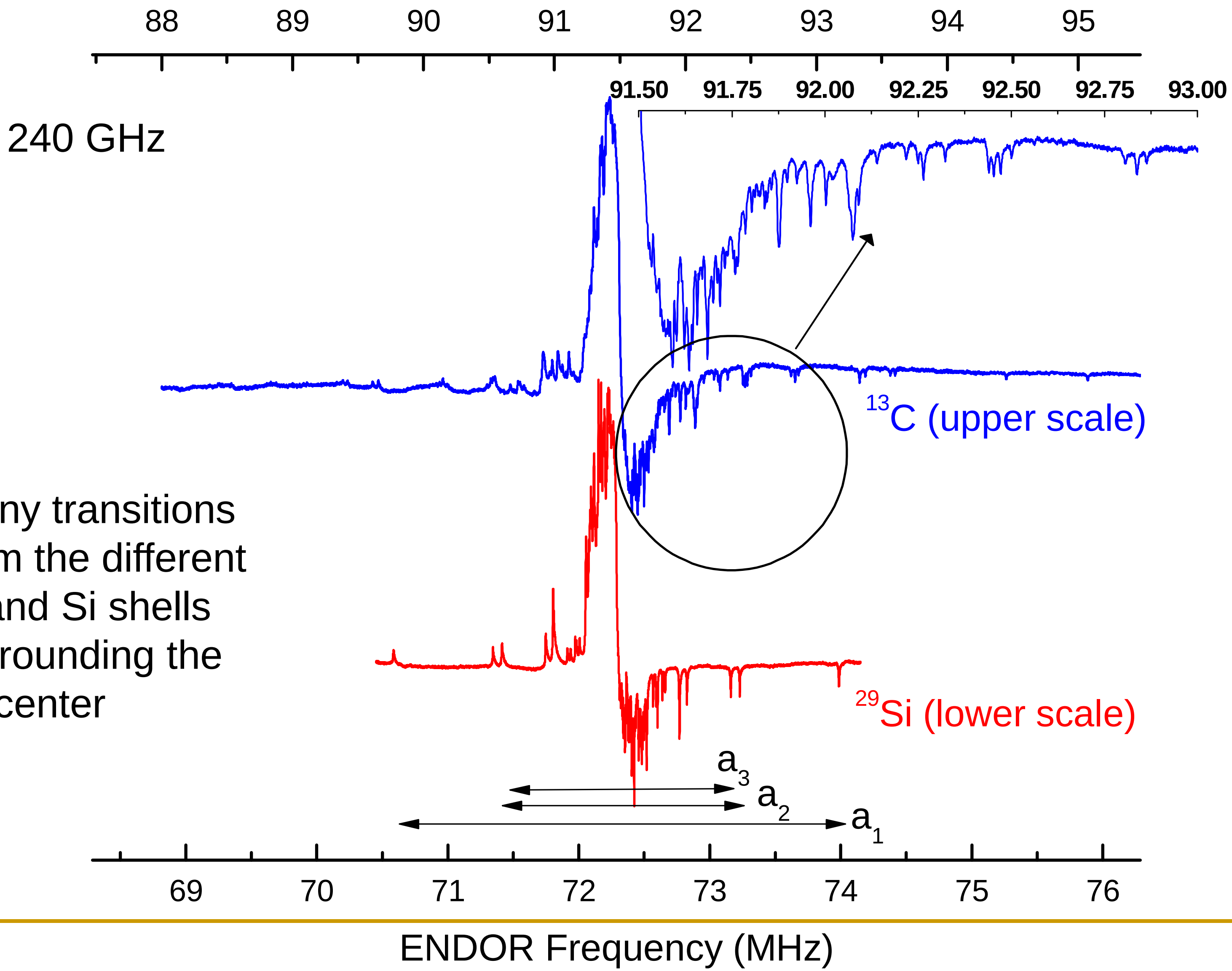
Cubic center with relatively large ^{14}N hyperfine coupling and a shallower hexagonal center with a smaller coupling.

For both centers the g-tensors has axial symmetry

Question 1: Does N substitute for a C or a Si ?

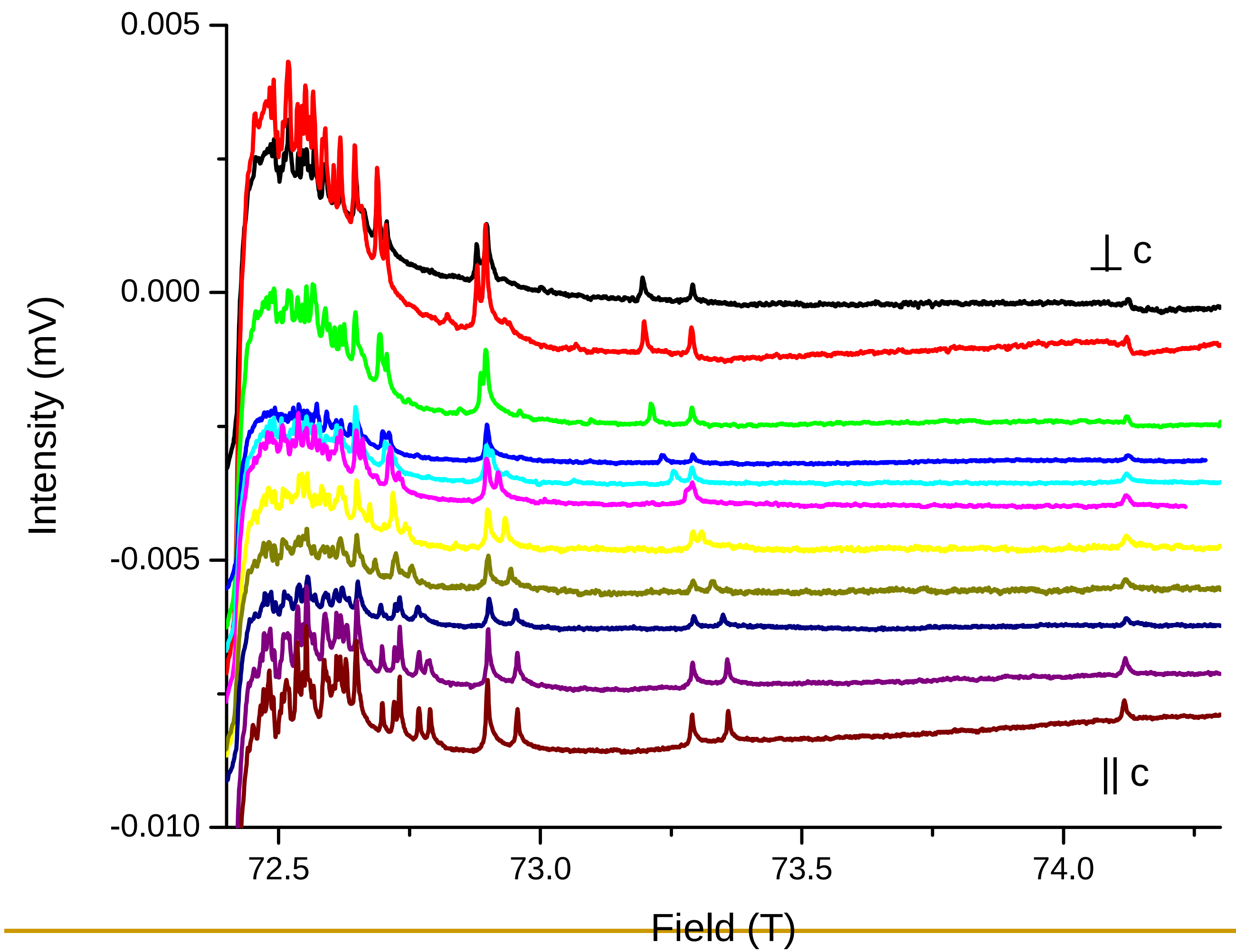
Question 2: What is the wavefunction ?

Pulsed ENDOR on 4H-SiC hexagonal site

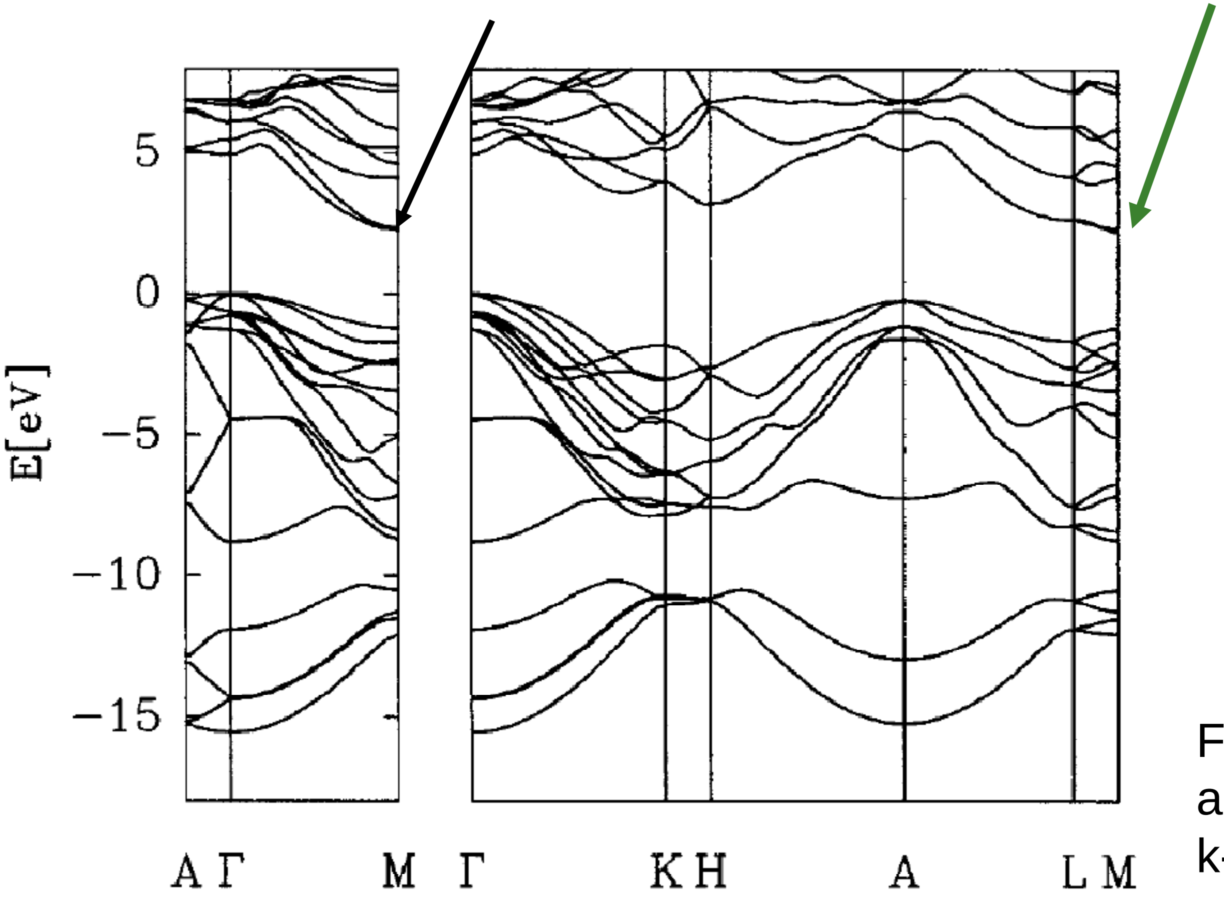


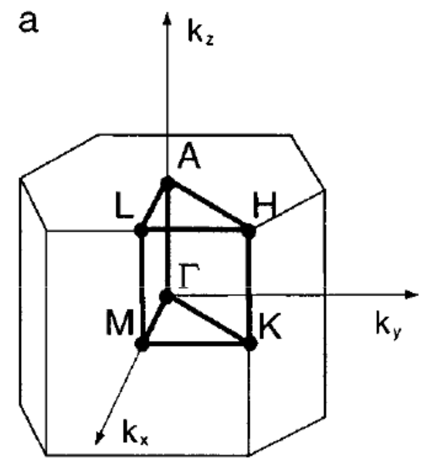
Many transitions from the different C and Si shells surrounding the N_h center

Orientation dependence ^{29}Si



Band structure



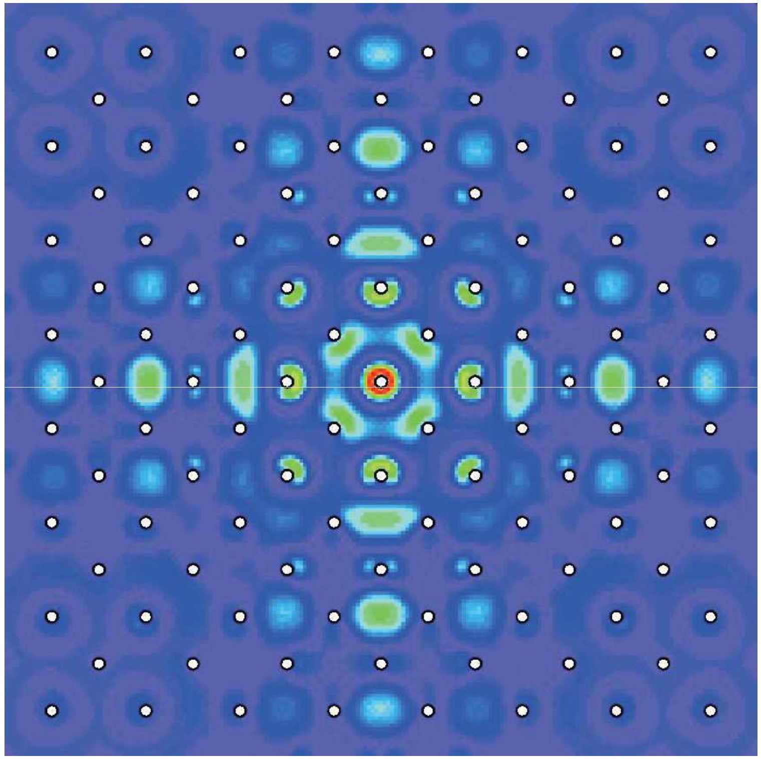


For 4H the minima are along the M-point in k-space

Interference with multivalley conduction band structure (Kohn-Luttinger)

Wellenhofer et al. Phys Stat Sol b, 1997

Strongly modulated spin density



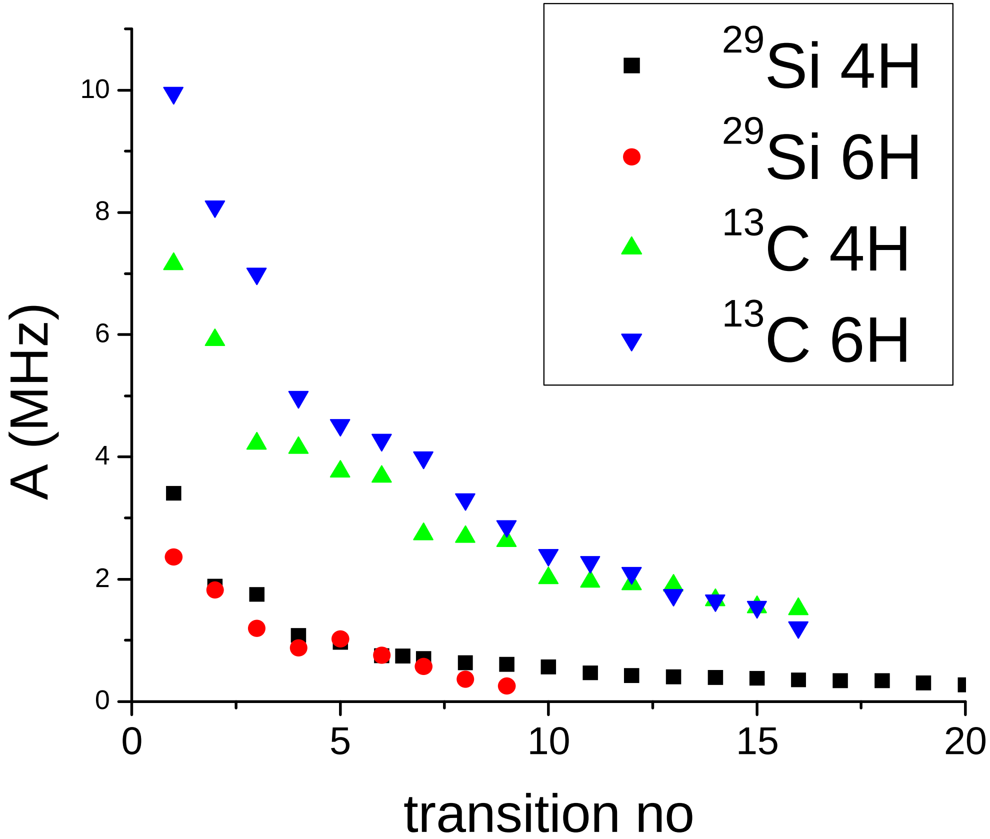
For Si:P in the (100) plane,
Koiller et al. Anais da Academia Brasileira de Ciências (2005) 77(2): 201–222

In Si:P, of the 23 well defined experimental sites (shells), most have now been assigned.

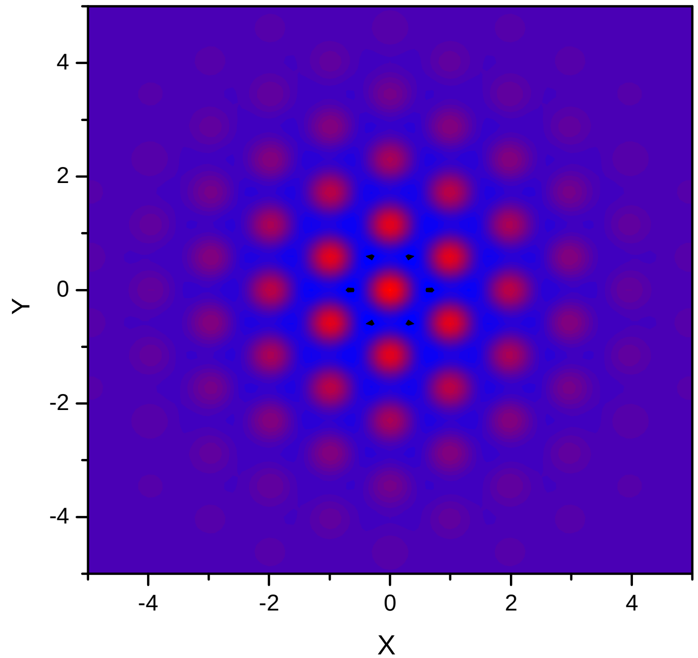
Questions about the calculations and what to include remains (see e.g. Castner PRB 77, 205208 (2008).

The data form a benchmark for the theory.

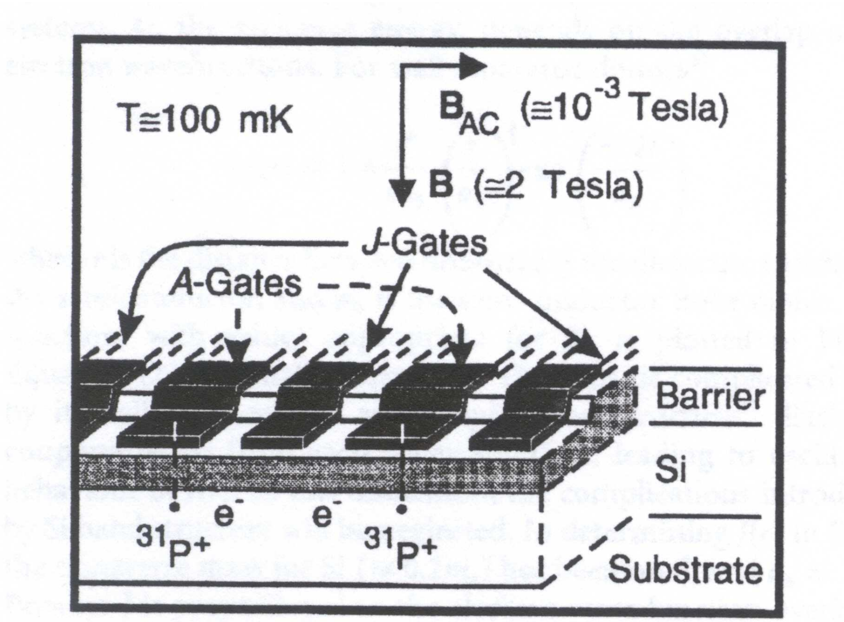
Comparison hexagonal sites in 4H and 6H SiC



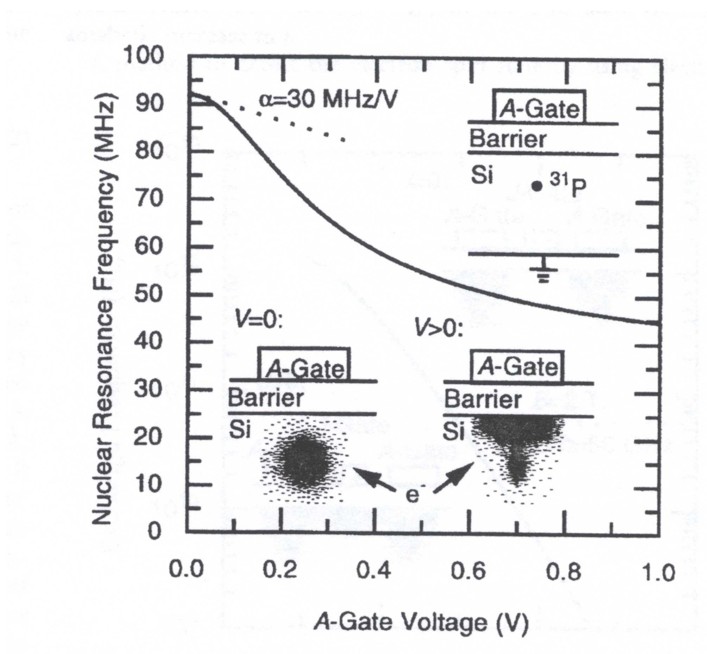
- In 4H slightly smaller carbon spin densities, slightly higher silicon spin densities.

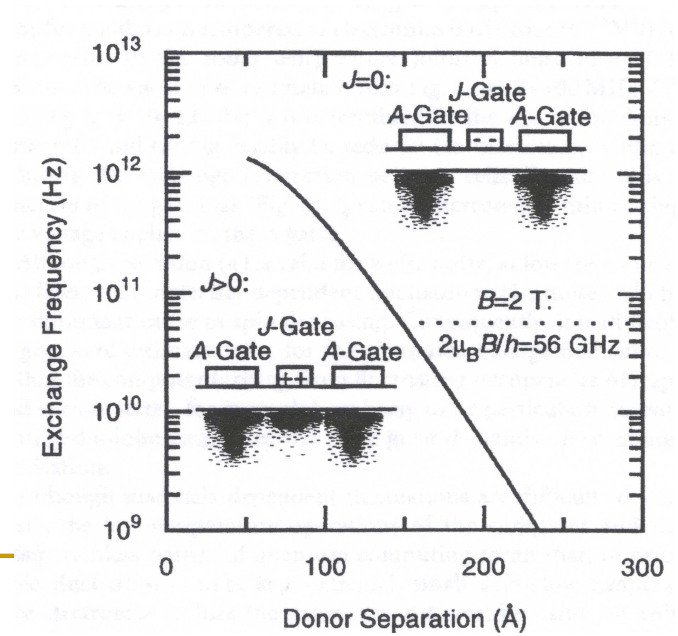


Kane’s model



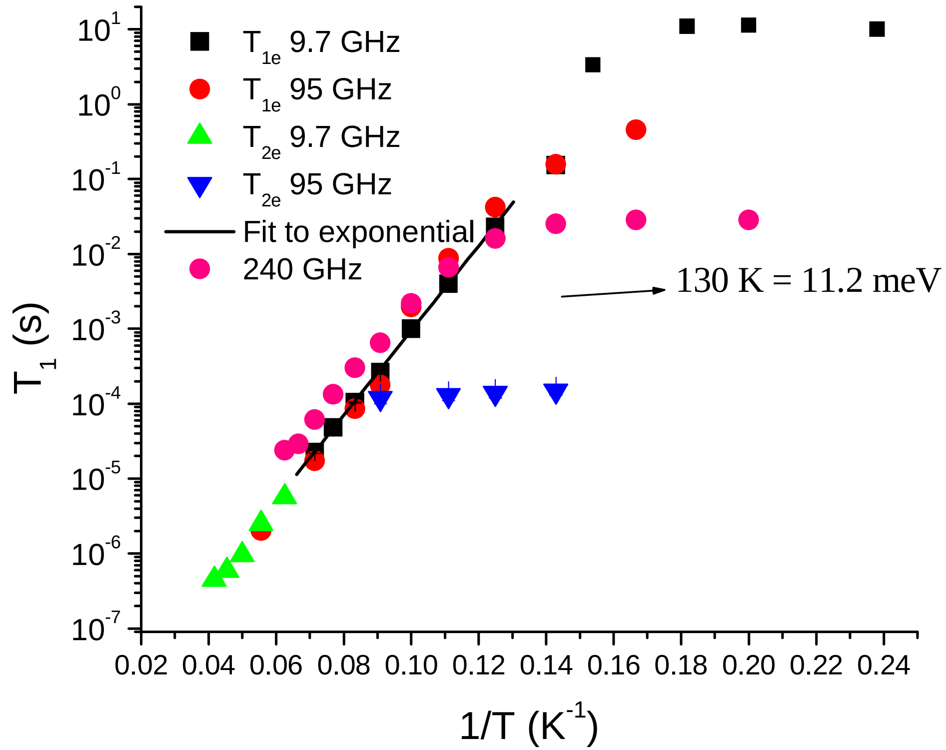
Nature, **393,** 133 (1998).





Si:P ([P] ~10^{15}-10^{16}) Below 20 K no conduction electrons: Nicely isolated from surroundings
Long relaxation times

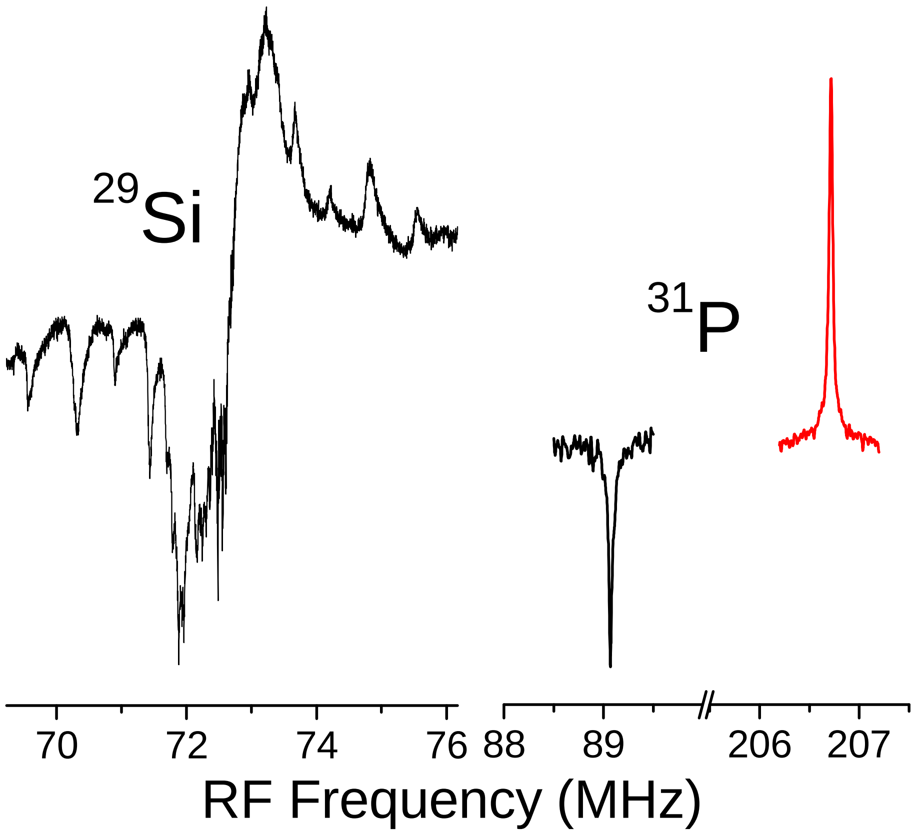
- T_{2e} is constant ~ 200-300 ms due to ^{29}Si
- T_{1e} exponential temp. dependence: shallow donor excited state
- T_{1e} gets significantly shorter at high fields
  - ➢Easier measurements
  - ➢Faster system reset
  - ➢Quantum computing can be faster



240 GHz ENDOR in Si:P

^{29}Si ENDOR from different shells. Strongly coupled Si relax much slower than the weakly coupled Si.

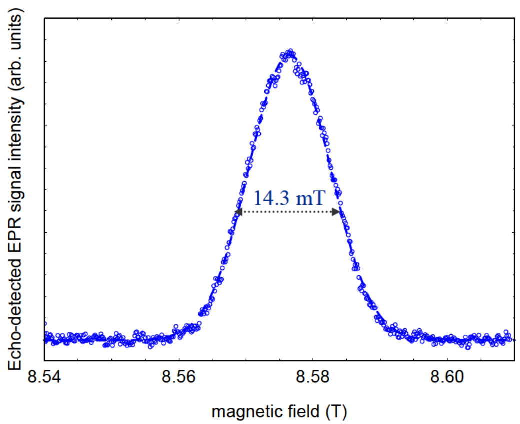
In principle they could add another qubit to the system.

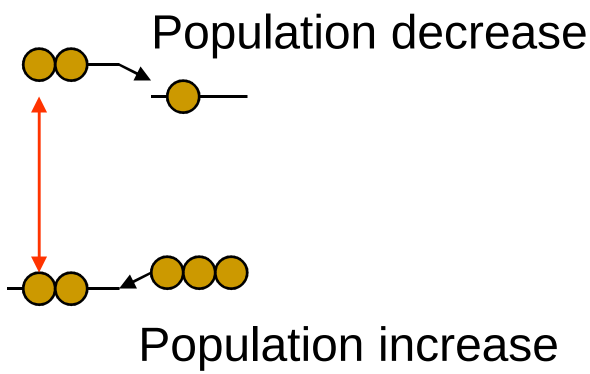


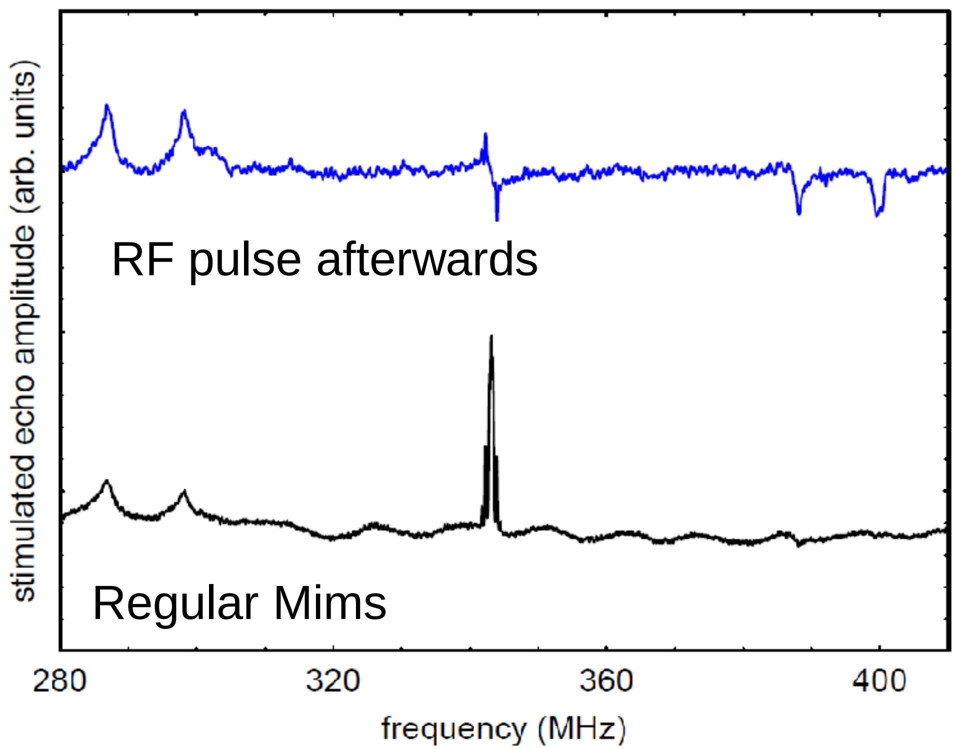
Note the sign change: Due to nuclear polarization induced by the pulse sequence

Anomalous ENDOR intensities at high fields

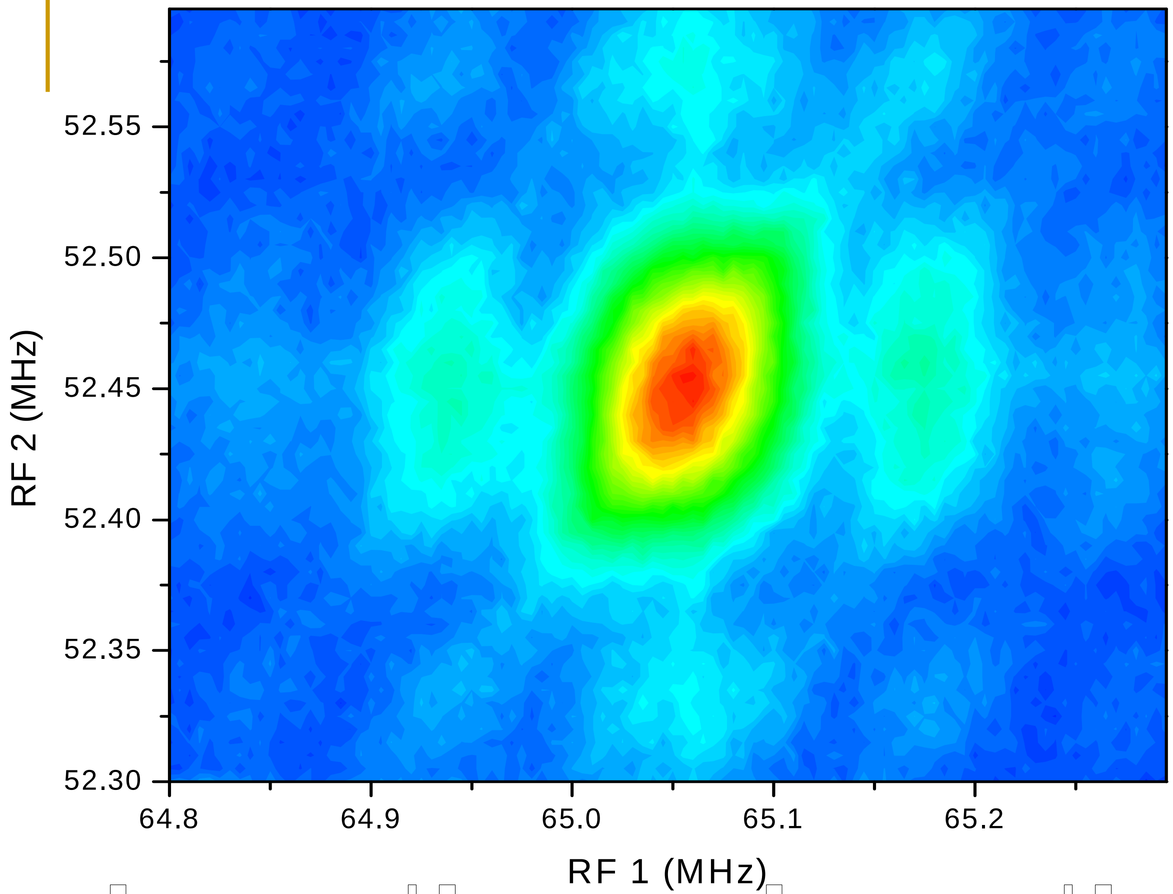
F-center in LiF

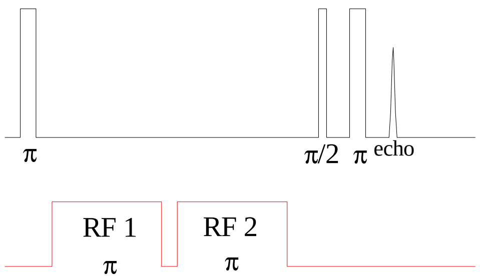




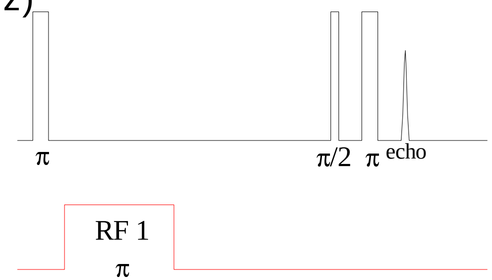


Strong TRIPLE enhancement



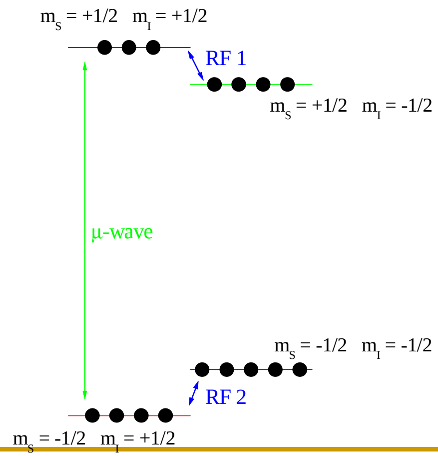


"Davies TRIPLE"



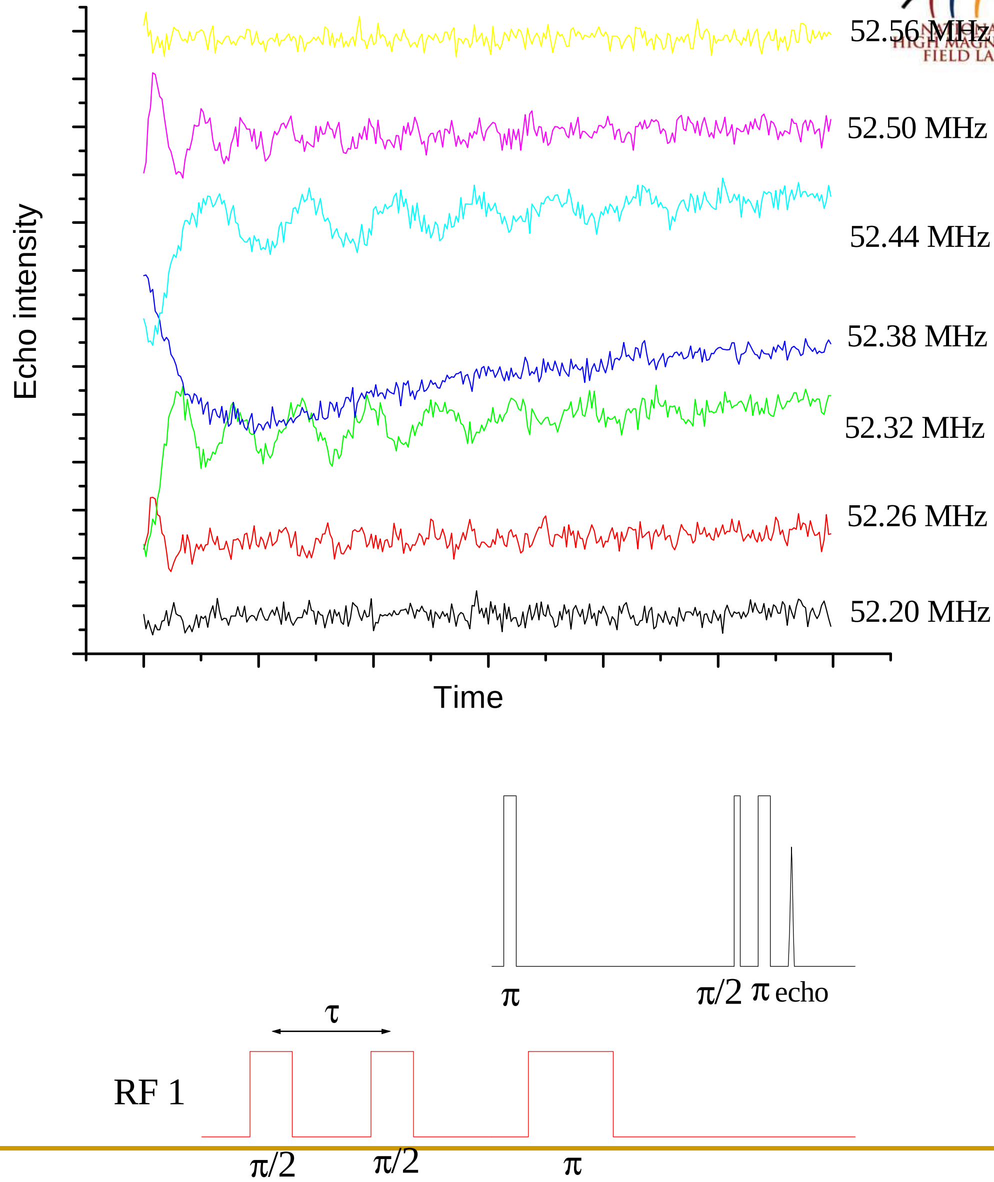
"Davies-ENDOR"

The pulsed ^{31}P TRIPLE spectrum in both Davies and Mims ENDOR is much stronger than the pulsed ENDOR itself, due to the slow relaxation of the nuclear spins. After a typical Davies-ENDOR sequence, followed by electron-spin T_1 decay, the populations of the levels end up as shown below – after the electron spin inversion pulse, the RF pulse has no effect.



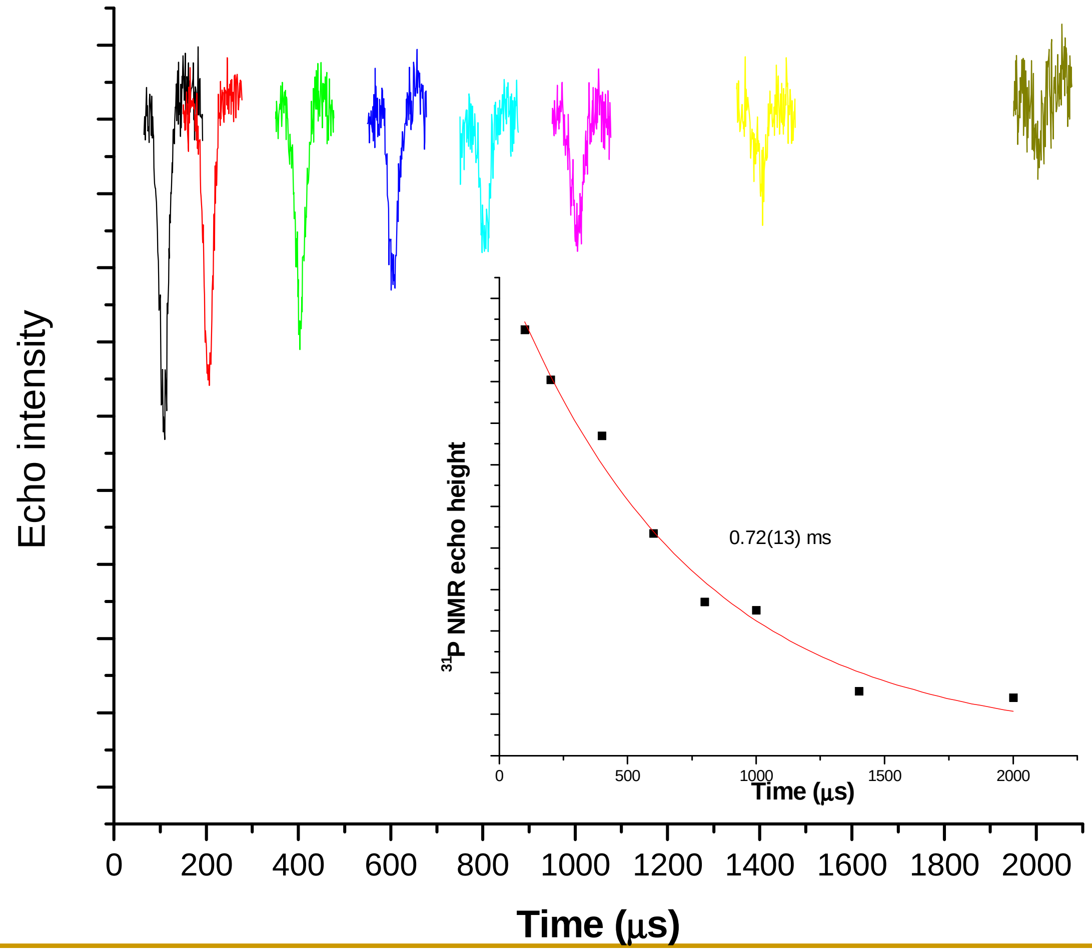
^{31}P free induction decay, measured by "ENDOR"

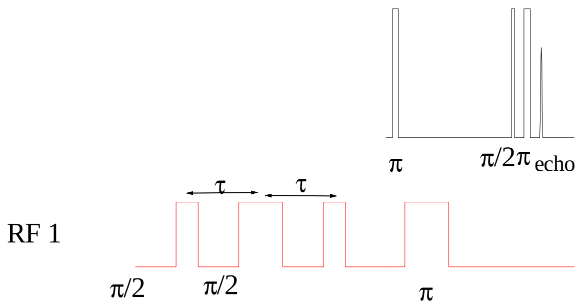
The pulsed-ENDOR sequence can be used to both induce the nuclear polarization and to detect the NMR signal of the ^{31}P nuclei. The repetition rate is slow with respect to the electron spin T_1, but fast with respect to the nuclear T_1. The first RF pulse induces the free-induction decay, the second translates the nuclear coherence to a population difference, and is detected with the pulsed ENDOR sequence



"NMR" echo, detected on EPR/ENDOR signal (10 K)

→ Nuclear coherence time T_{2N} seems to be close to T_{1e}





QC Initialization

High-field dynamic nuclear polarization at $h\nu \gg kT$

→ Creation of close to 100% polarized initial state

Not only Electron Spin Polarization
Aim for High Nuclear Spin Polarization

Dynamic Nuclear Polarization

- Overhauser effect:

  Saturate an allowed transition, and the coupling of the electron and nuclear spins lead to a non-equilibrium nuclear polarization.
- Solid effect.

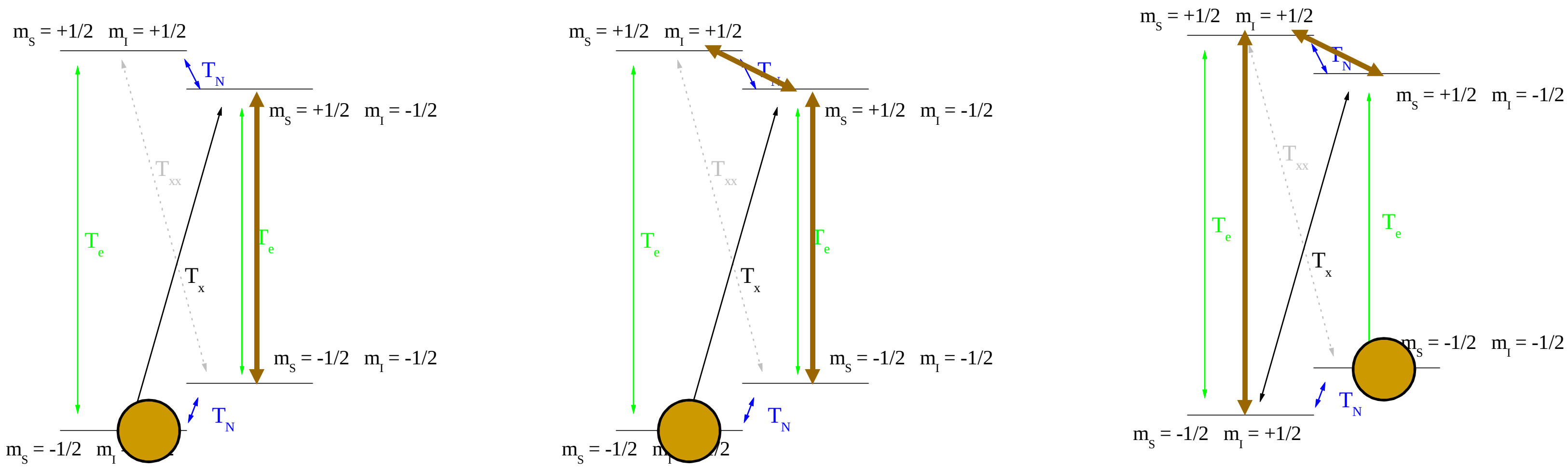
  Excitation of forbidden transitions than involve both an electron and a nuclear spin flip. (of type $S^+I^{+,}$ S^+I^-, etc). Can work in both directions.
- The Cross-effect and thermal mixing, which typically require 2 electron spins and 1 nuclear spin to interact. ($S^+S^-I^+$)
  - The forbidden transitions are less allowed at higher fields, and the solid effect, cross effect and thermal mixing are thought to be less efficient at higher field.

- PONSEE Polarization of nuclear spins enhanced by ENDOR
  - Only allowed transitions are involved.

QC Initialization

High-field dynamic nuclear polarization at $h\nu >> kT$

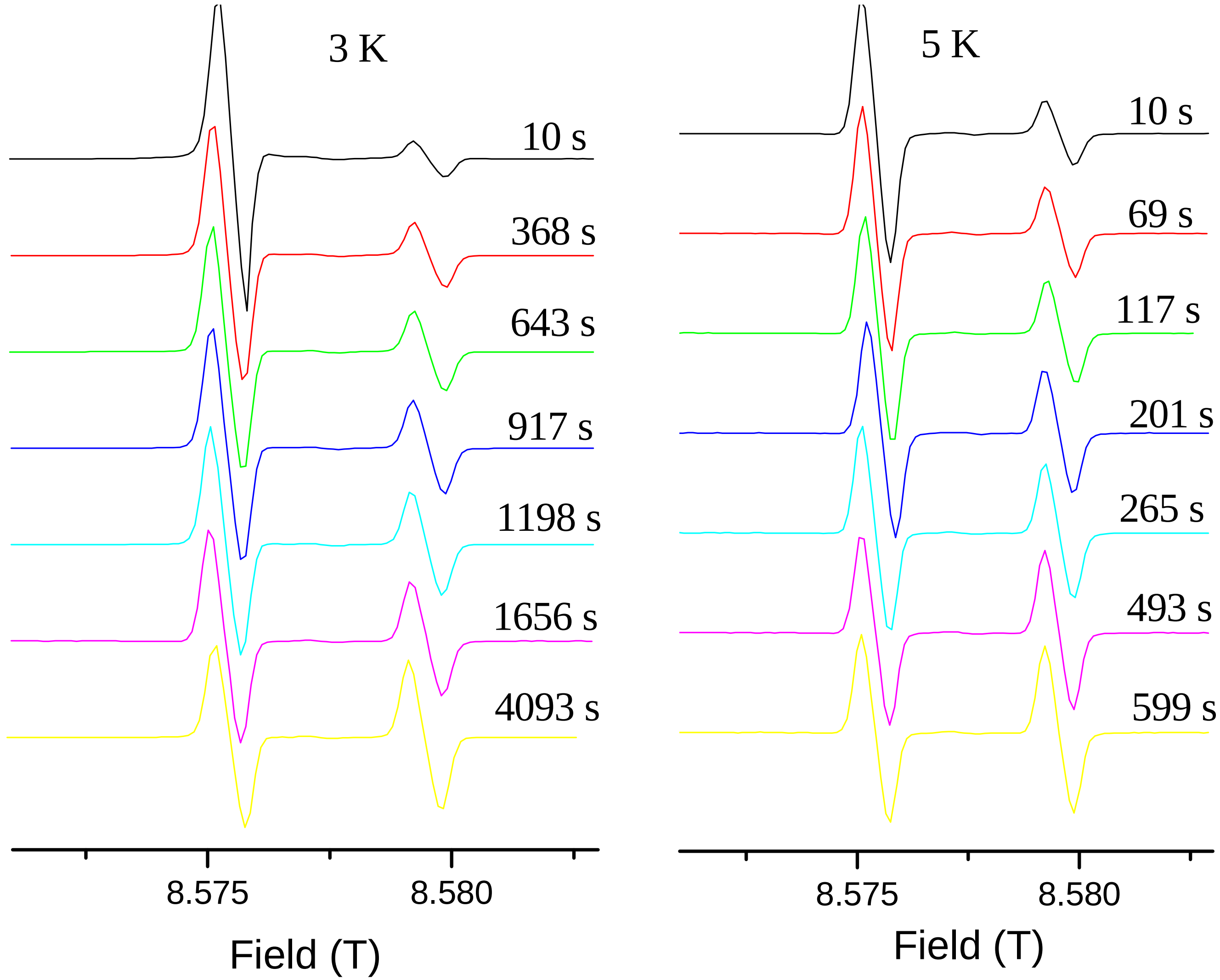
→ Creation of close to 100% polarized initial state



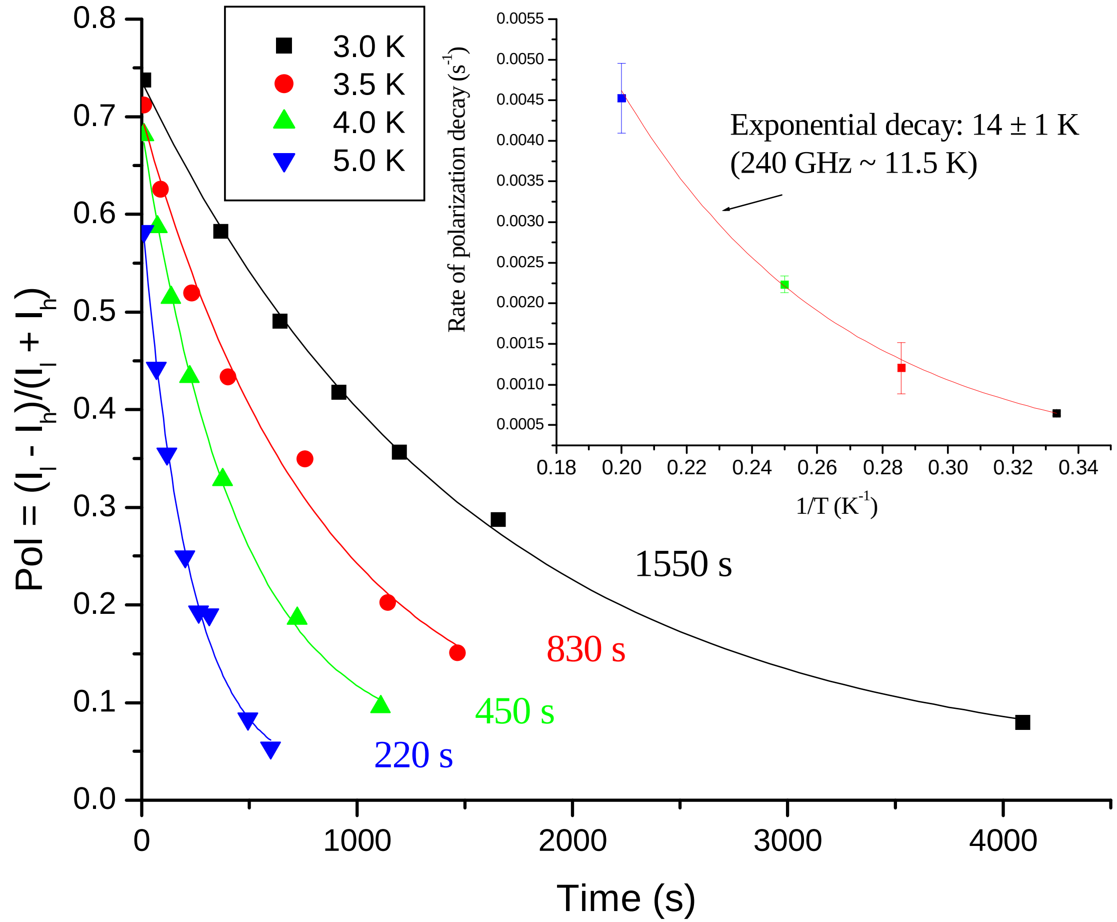
Overhauser

PONSEE

Note that "T_1^{up}" = $e^{h\nu/kT}$ "T_1^{down}"

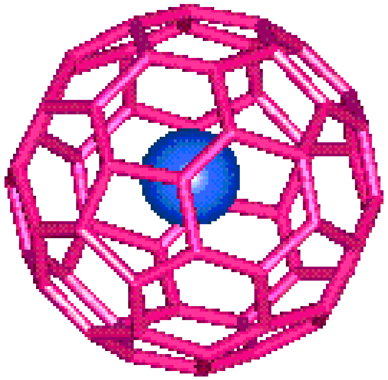

3 K
10 s
368 s
643 s
917 s
1198 s
1656 s
4093 s
8.575
8.580
Field (T)
5 K
10 s
69 s
117 s
201 s
265 s
493 s
599 s
8.575
8.580
Field (T)

Temperature dependence of T_{1n} at 8.6 T



The relaxation to equilibrium spin polarization is well described with a single exponential. The temperature dependence indicates a thermally excited process with an energy close to the electron spin Zeeman splitting at these fields.

N@C_{60}



"Atomic" N is located at high symmetry point in C_{60} cage:

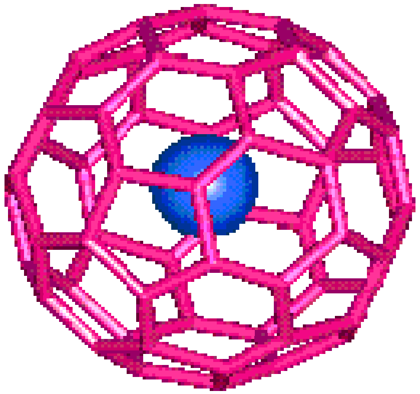
- N retains its S=3/2 spin,
- there is very little interaction between N and cage,
- N@C_{60} is almost indistinguishable chemically from C_{60}.

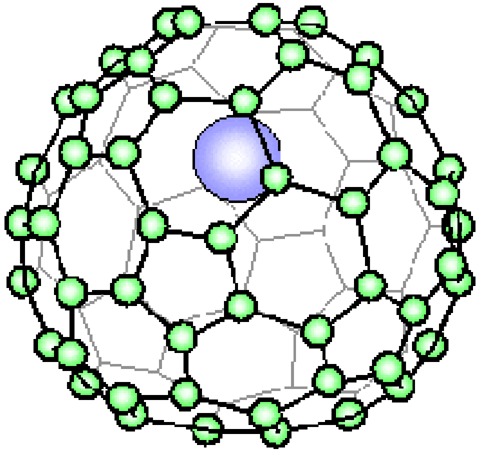
Synthesis by ion implantation or plasma discharge yields ~ 1 N@C_{60} molecule per 10^5 C_{60} molecules:

- purification is a challenge!

Endohedral fullerenes

The fullerene cage can encapsulate other species:





$N@C_{60}$ or $P@C_{60}$:

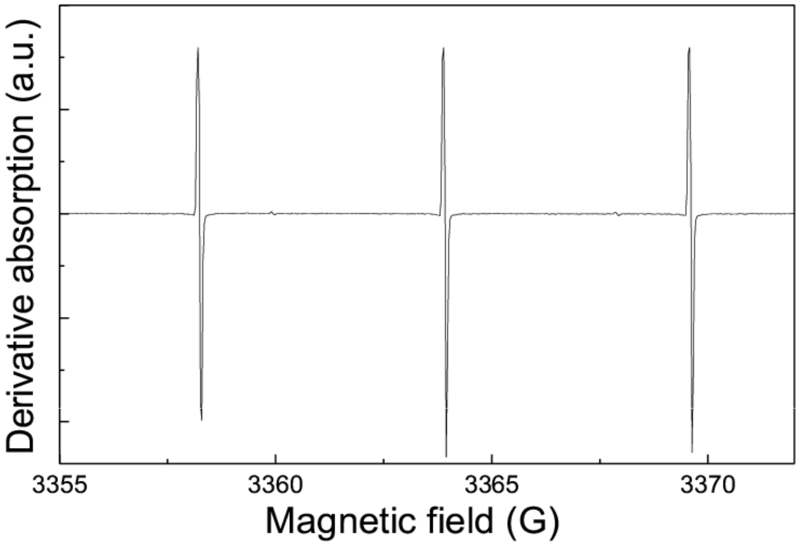
- N and P retain their atomic character

$M@C_{82}$ with
M= Sc, La, Ce, ... :

- M reacts with the cage

Electron spin resonance of N@C_{60}

X-band
(9.5 Ghz)



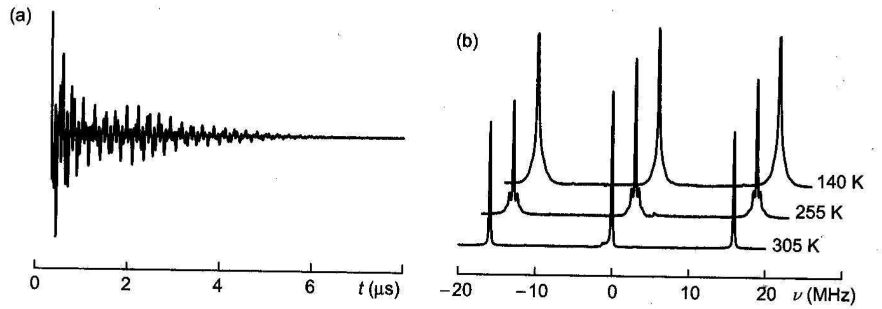


Figure 1.3.1 One-dimensional FT EPR experiments on N@C_{60} in polycrystalline C_{60} above and below the phase transition temperature of 260 K: (a) FID recorded at 255 K (From data provided by K.-P. Dinse); and (b) FT EPR spectra recorded at 305 K, 255 K, and 140 K. (Adapted from Ref. [105].)

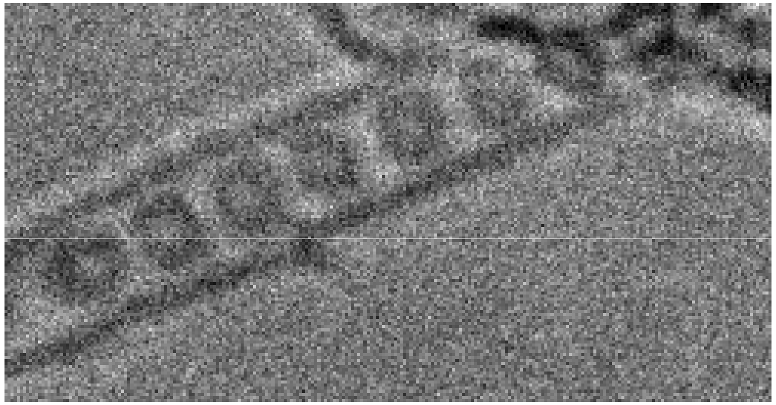
M. Austwick and G. Morley (Oxford)

Three main lines: hyperfine interaction with I=1 ^{14}N nucleus.

Two small lines: hyperfine interaction with I=1/2 ^{15}N nucleus (natural abundance of ~ 0.4%).

C_{60} in single-walled nanotubes

Owing to “graphitic” interlayer interactions, fullerenes save ~0.5 eV each by entering a nanotube of the right diameter:

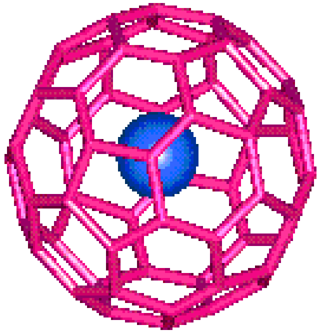


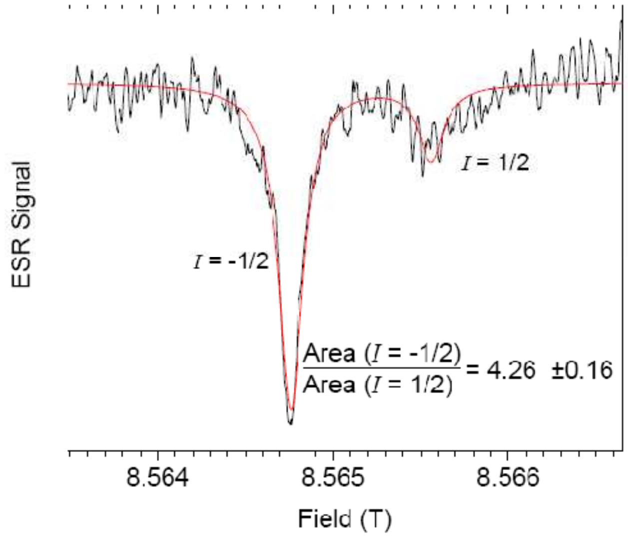
A C60@SWNT “peapod”
A. Khlobystov

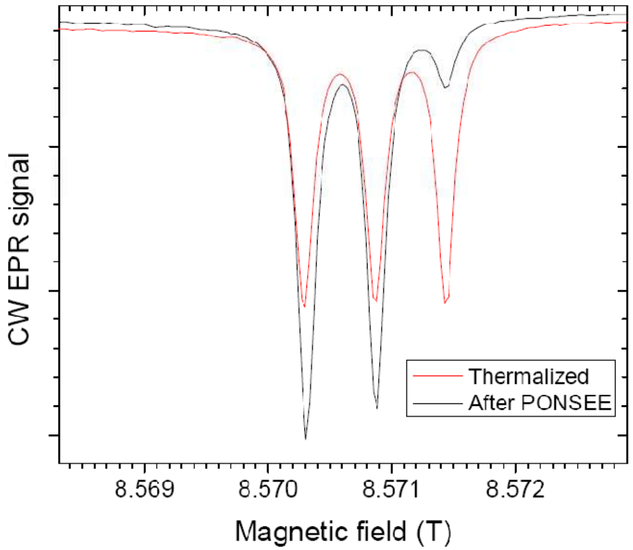
Optimum graphitic layer separation ≈ 0.33 nm,

- defines optimum tube diameter,
- defines fullerene separation inside tube.

N in C_{60}







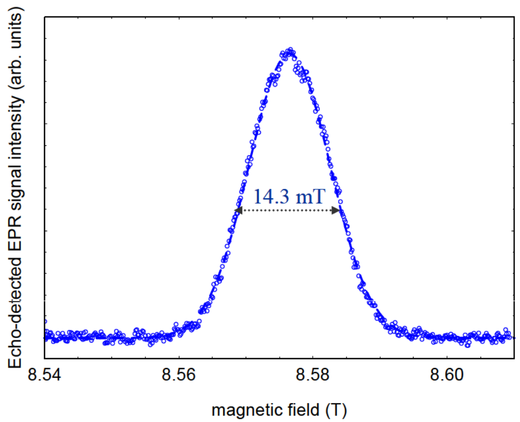
T_{1n} ~ 12 hours at 4.2 K

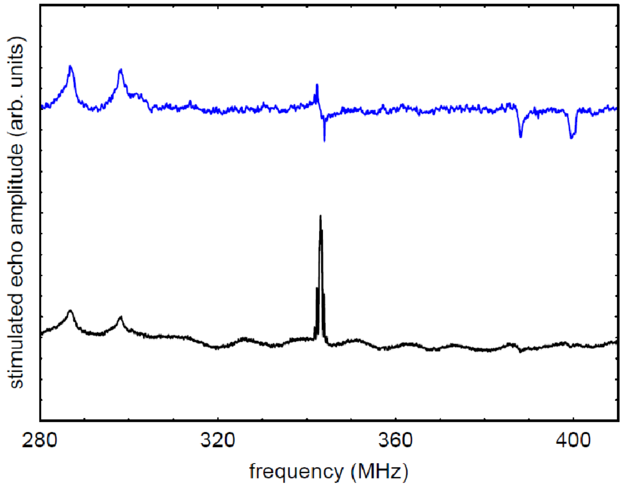
Morley et al. PRL 2007, AMR 2008

Will this work for in general ?

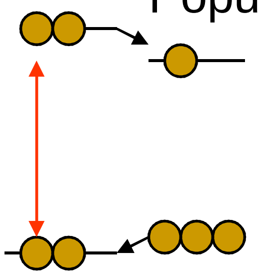
Works for well resolved hyperfine components. What if no resolution in EPR ?

F-center in LiF



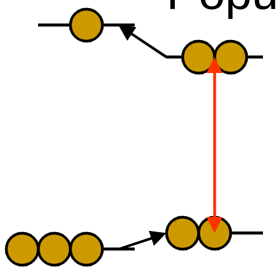


Population decrease



Population increase

Population decrease

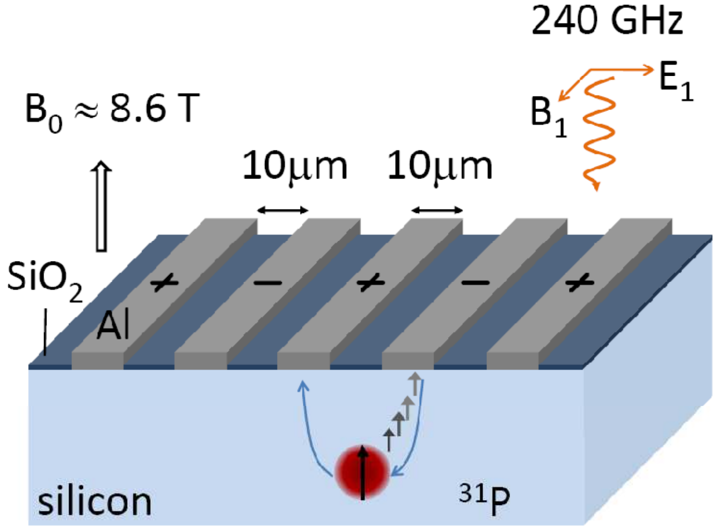


Population increase

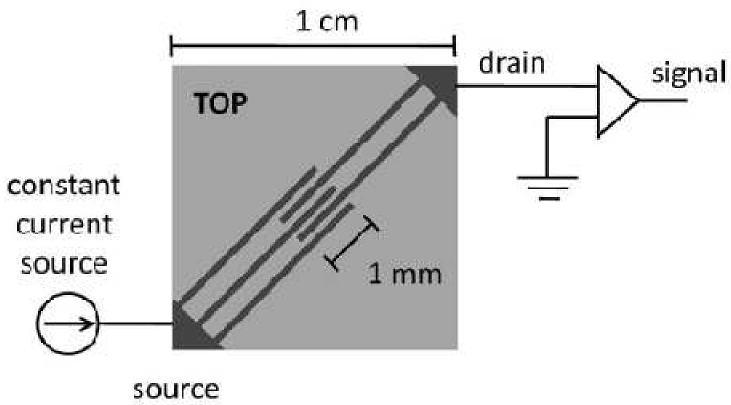
No net effect in center
But net effect on the edges
of the EPR line… To be tested

Electrical detection of Magnetic Resonance (Read out)

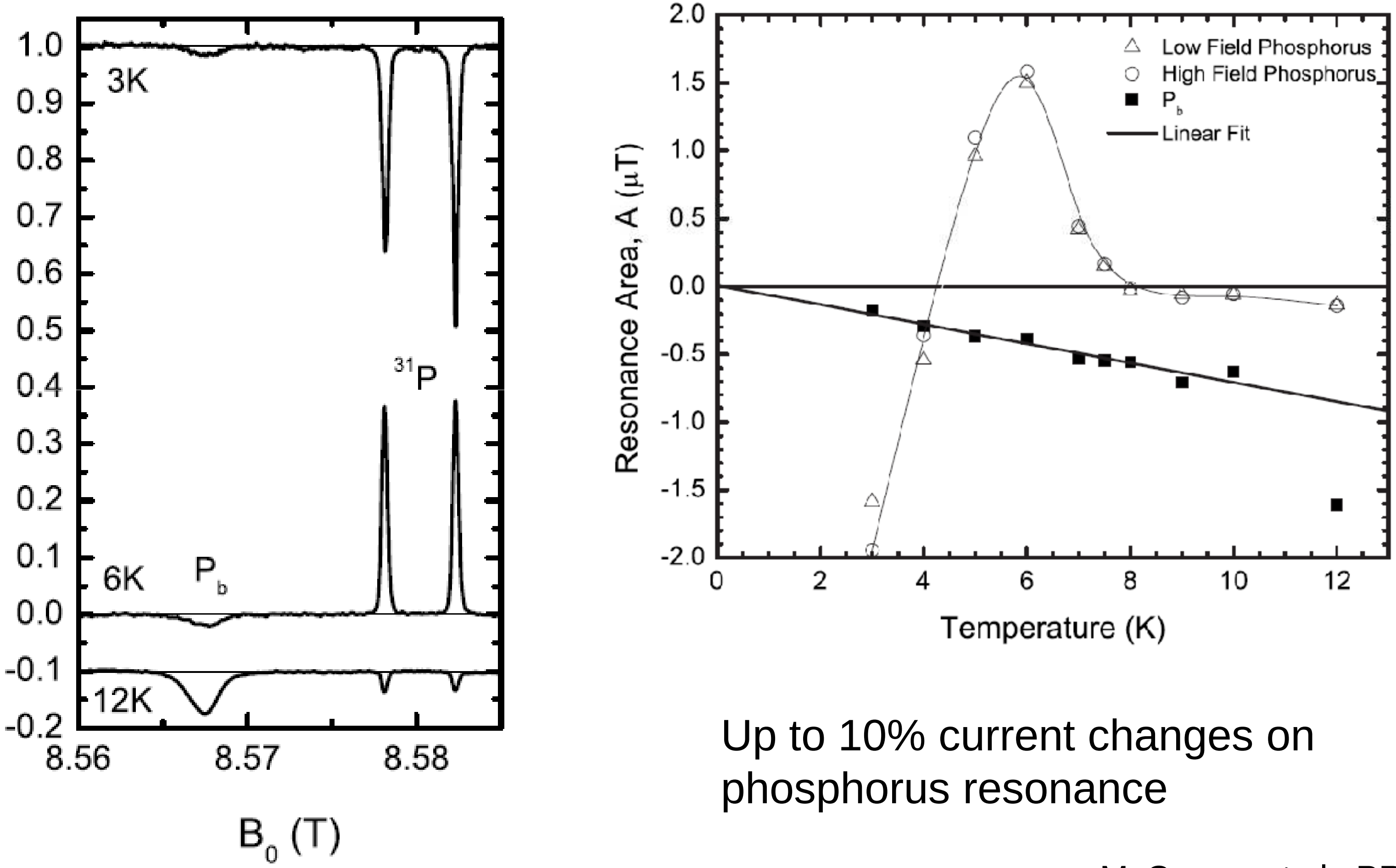
- Electrical detection can be very sensitive
- At low frequencies a P_b (surface) center is involved



  - In order to measure a current we use light excitation to create carriers
    - T_1 is shortened, T_2 more or less unchanged



EDMR spectra

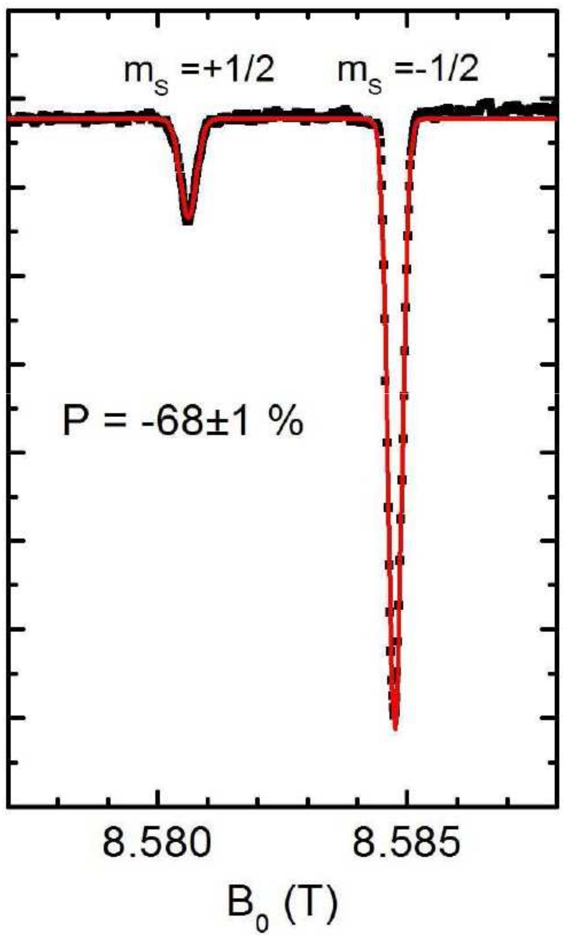


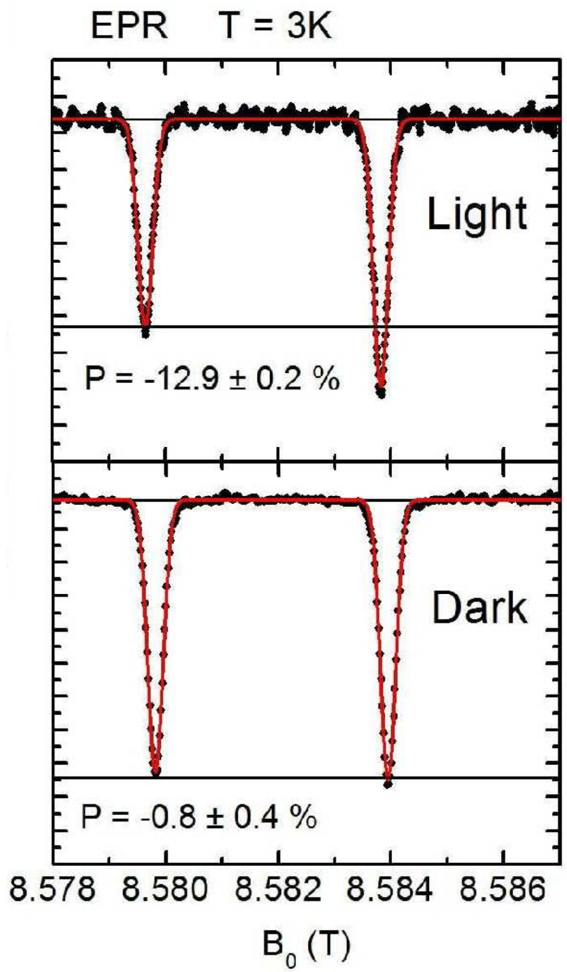
Up to 10% current changes on phosphorus resonance

McCamey et al., PRB 2008

Light Induced Nuclear Polarization

EDMR





Arxiv (McCamey)

Summary

- High-Frequency pulsed ENDOR useful for determining wavefunction of the center
- Direct spin-lattice relaxation significantly faster at high fields => Increase reset speed
- Electron-electron dipolar contribution to spin decoherence can be eliminated at hv>>kT =>increase coherence times
- High nuclear spin polarization can be achieved easily at hν>>kT => initialization in pure (electron nuclear) spin state
- Electrical read-out is efficient at high fields and long coherence can be preserved.

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