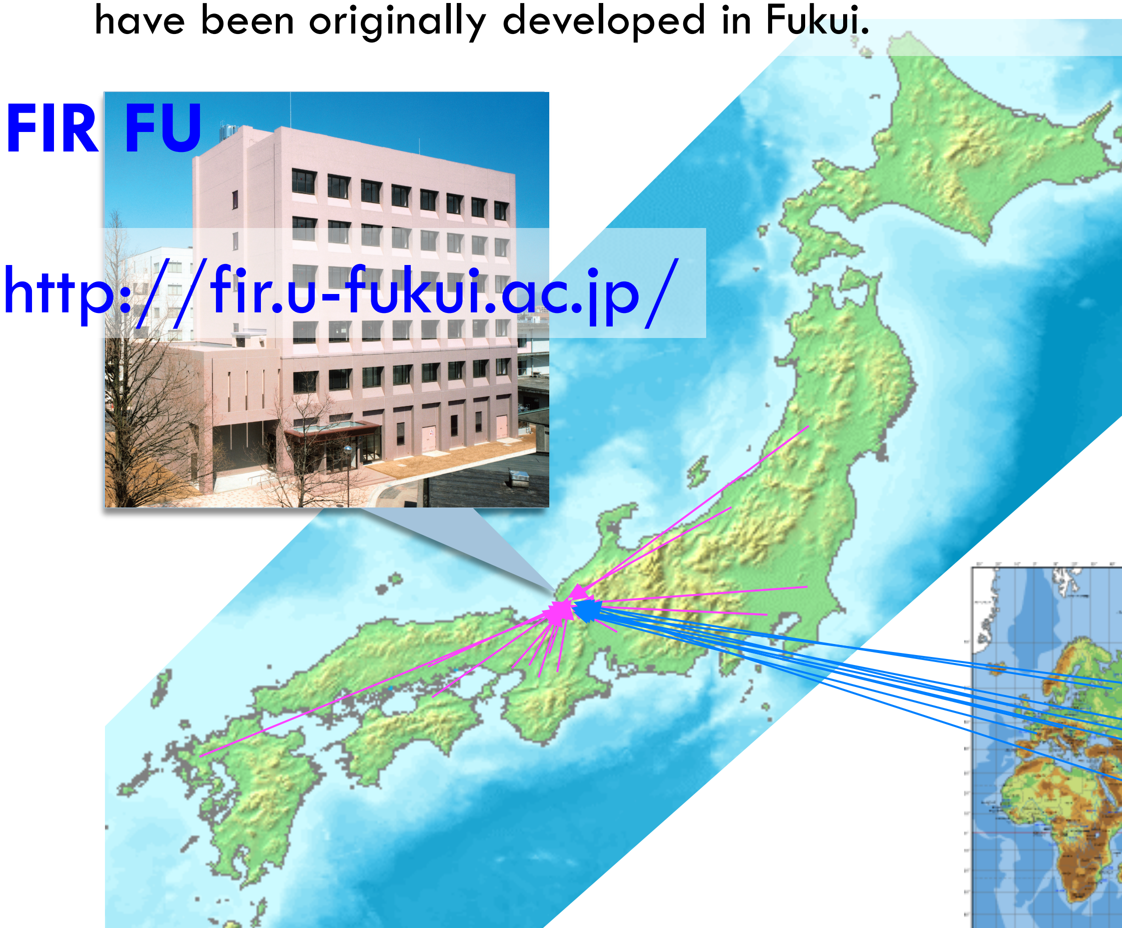
ESR studies of low P-doped Si: T_1 measurement at high fields and DNP at low temperatures

Yutaka Fujii

Research Center for Development of Far-Infrared Region, University of Fukui

NPCQS2012 @Okinawa, 9.40-10:20, Wednesday, April 25, 2012

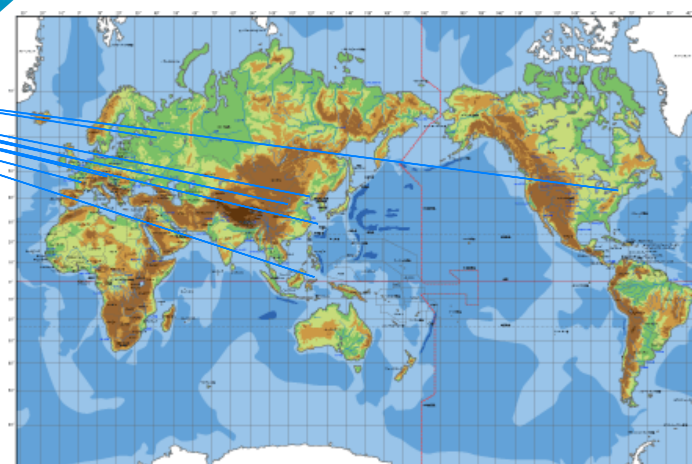
FIR FU is carrying out R&D of the far-infrared region with world class "Gyrotrons" which have been originally developed in Fukui.



World wide collaborations

- Univ. Warwick (UK) (DNP-NMR)
- ESRF (France) (XDMR)
- Princeton Univ. (USA) (Plasma)

etc…



Gyrotron development at Fukui (FIR FU)

Radiation sources of SMMW

- Backward Wave Oscillator
- Molecular Laser
- Free Electron Laser
- ***GYROTRON***

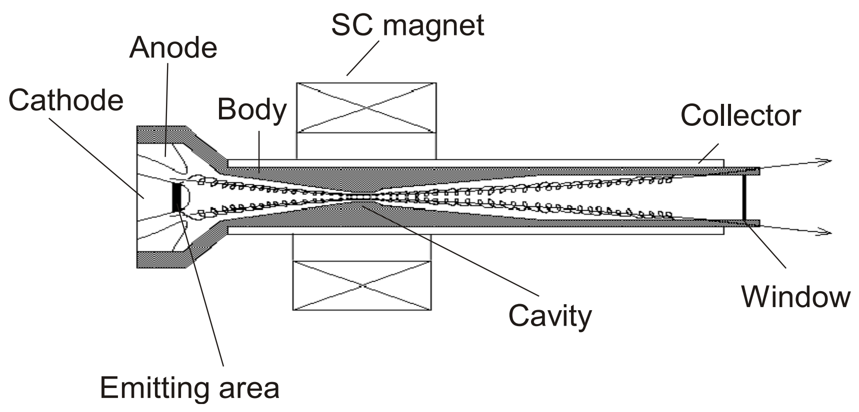
in FIR FU

•High frequency up to 1 THz

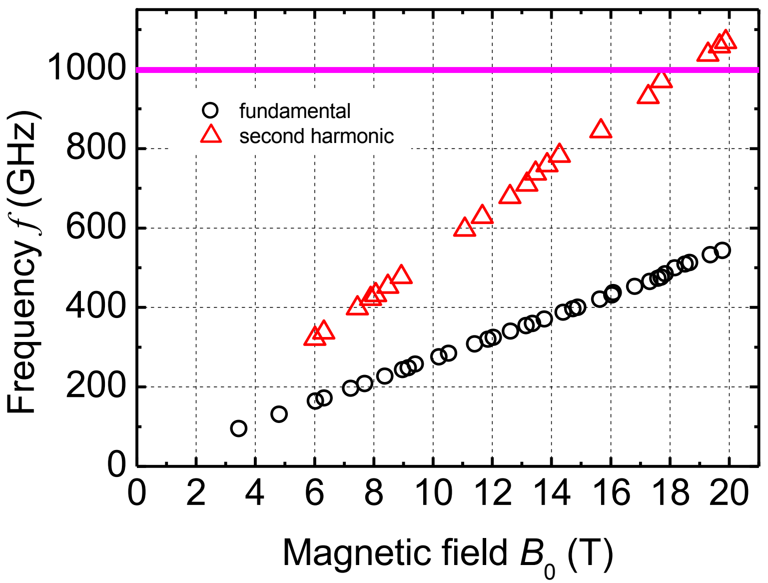
•Tunable frequency (38~889GHz)

•High power radiation with kW class

(World first ESR measurement by using a gyrotron as radiation source)



Vacuum tube of a gyrotron



Outline

1. Introduction:
   - P-doped Si (Si:P)
   - Kane's model of quantum computer
2. cw-ESR set-up and experimental results
3. Numerical solution of Bloch equations under inhomogeneously-broaden line
4. Discussion of field dependence of electron $T_1(T, H)$
5. Dynamic polarization of ^{31}P nuclear spins
6. ESR/NMR double resonance experiment
7. Summary

Refer to M. Song *et al.*, J. Phys.: Condens. Matter **22** (2010) 206001

Co-workers

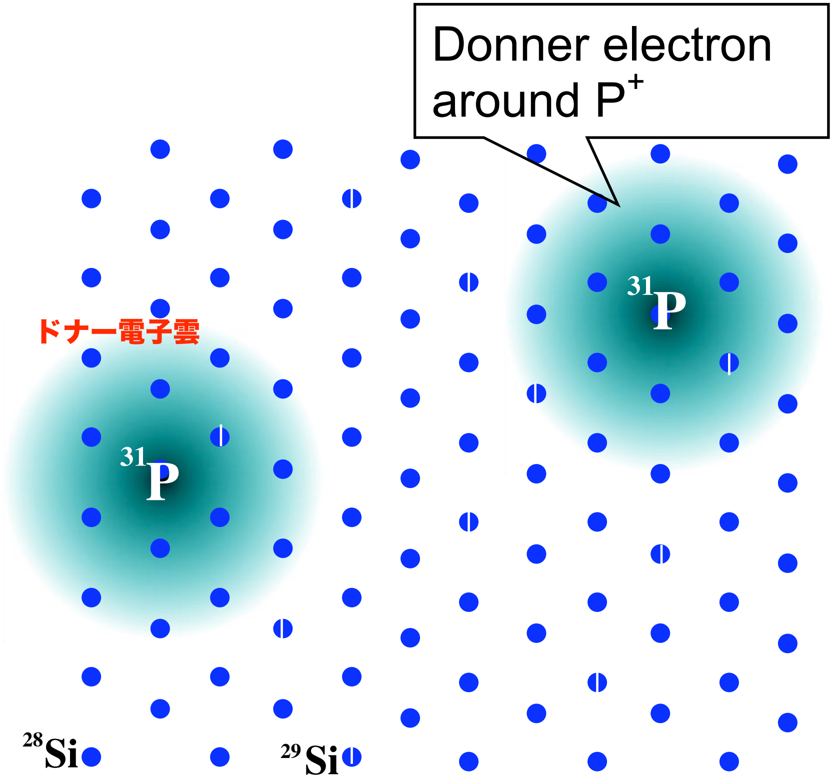
Seitaro Mitsudo[1], Takao Mizusaki[1,5], Hiroshi Aoyama[2], Hikomitsu Kikuchi[2], Meiro Chiba[3],
Tomohiro Ueno[4], Akira Matsubara[5], Akira Fukuda[6],
Myeonghun Song[7], Minki Jeong[7], Byeongki Kang[7], Soonchil Lee[7], Minchan Gwak[8], SangGap Lee[9],
Sergey Vasiliev[10]

[1]FIR FU, [2]Univ. Fukui, [3]Kinki Univ.,
[4,5]Kyoto Univ., [6]Hyogo Col. Med.,
[7]KAIST, [8]Seoul National Univ., [9]KBSI,
[10]Univ. Turku (Finland)

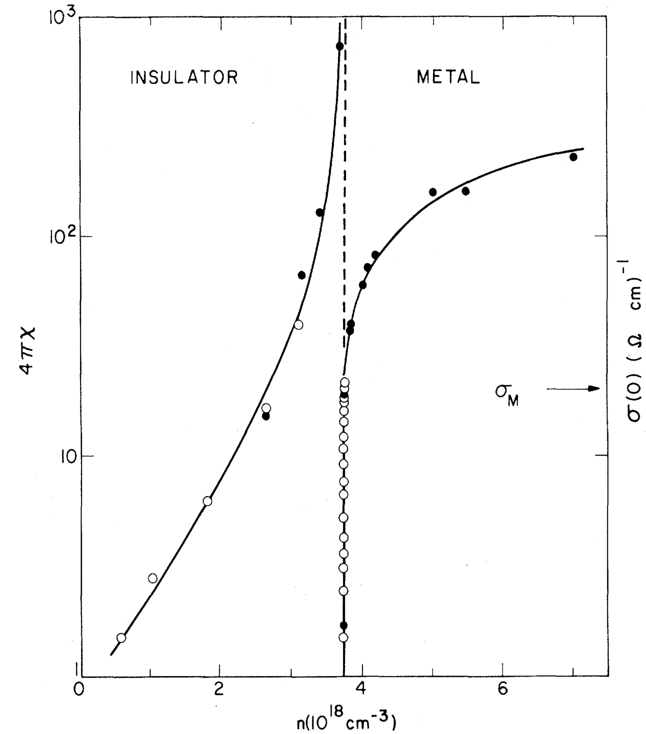
P-doped Si (Si:P) : typical n-type semiconductor

Critical concentration $n_c = 3.7 \times 10^{18}\ \mathrm{cm}^{-3}$
$\rightarrow n_c^{-1/3} \sim 60$ Å

$n > n_c$: metallic
$n < n_c$: insulator



A schematic draw of phosphorus (P) doped silicon (Si)



Metal-insulator transition in a doped semiconductor
T. F. Rosenbaum *et al.*: PRB **27** (1983) 7509

4-levels scheme in Si:P (isolated donor)

Two spin system coupled via hyperfine interaction A (S=1/2, I=1/2)

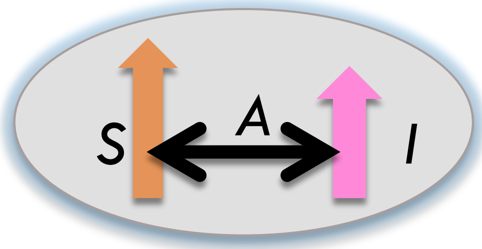
$$\mathcal{H} = -\gamma_S \hbar S^z H_0 + \boldsymbol{S} \cdot \tilde{A} \cdot \boldsymbol{I} - \gamma_I \hbar I^z H_0$$

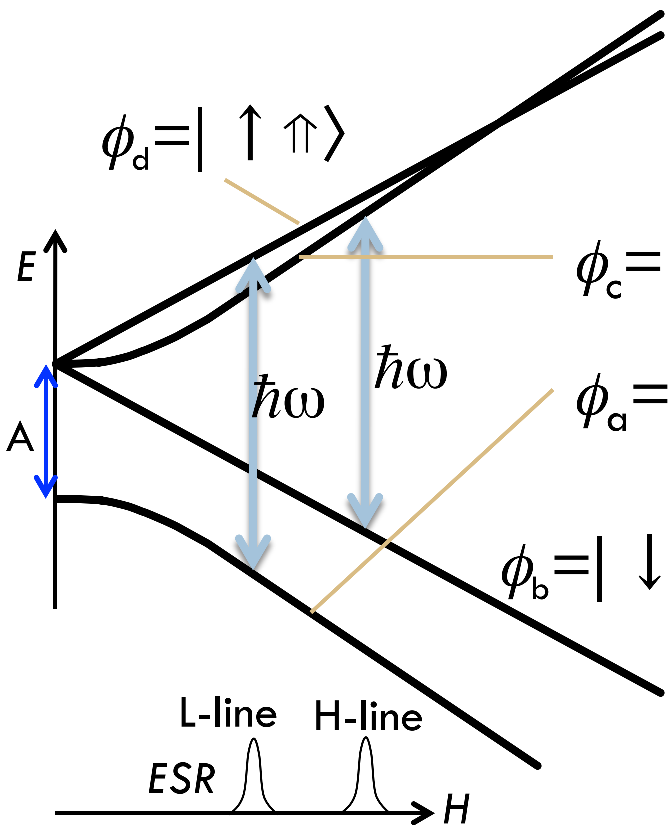
$(H_0 \,//\, z,\ \gamma_S > 0,\ \gamma_I > 0)$

A = Hyperfine coupling energy
(A/h=117.5 MHz for P in Si:P)

$\gamma_I/2\pi$=17.2 MHz/T for ^{31}P

Wavefunction $|m_S, m_I\rangle$ $\quad$ ($m_S, m_I = \pm 1/2$)





$\phi_c = \cos\theta |\uparrow \Downarrow\rangle + \sin\theta |\downarrow \Uparrow\rangle \approx |\uparrow \Downarrow\rangle$

$\phi_a = \cos\theta |\downarrow \Uparrow\rangle + \sin\theta |\uparrow \Downarrow\rangle \approx |\downarrow \Uparrow\rangle$

$$\tan\theta = A/2g\mu_B H$$

4-levels scheme in Si:P and Overhauser effect

Two spin system coupled via hyperfine interaction A (S=1/2, I=1/2)

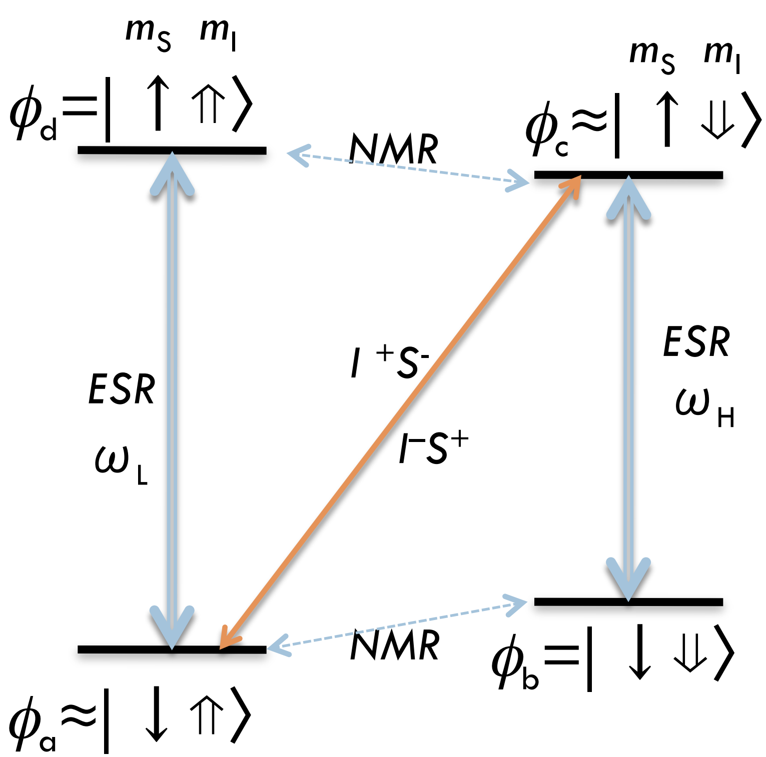
$$\mathcal{H} = -\gamma_S \hbar S^z H_0 + \boldsymbol{S} \cdot \tilde{A} \cdot \boldsymbol{I} - \gamma_I \hbar I^z H_0$$

$$(H_0 \,//\, z,\ \gamma_S > 0,\ \gamma_I > 0)$$

A = Hyperfine coupling energy
(A/h=117.5 MHz for P in Si:P)

$\gamma_I/2\pi$=17.2 MHz/T for ^{31}P

Wavefunction $\left| m_S, m_I \right\rangle$ ($m_S, m_I = \pm 1/2$)



For ^{31}P in Si:P, hyperfine coupling constant A is a scalar so that

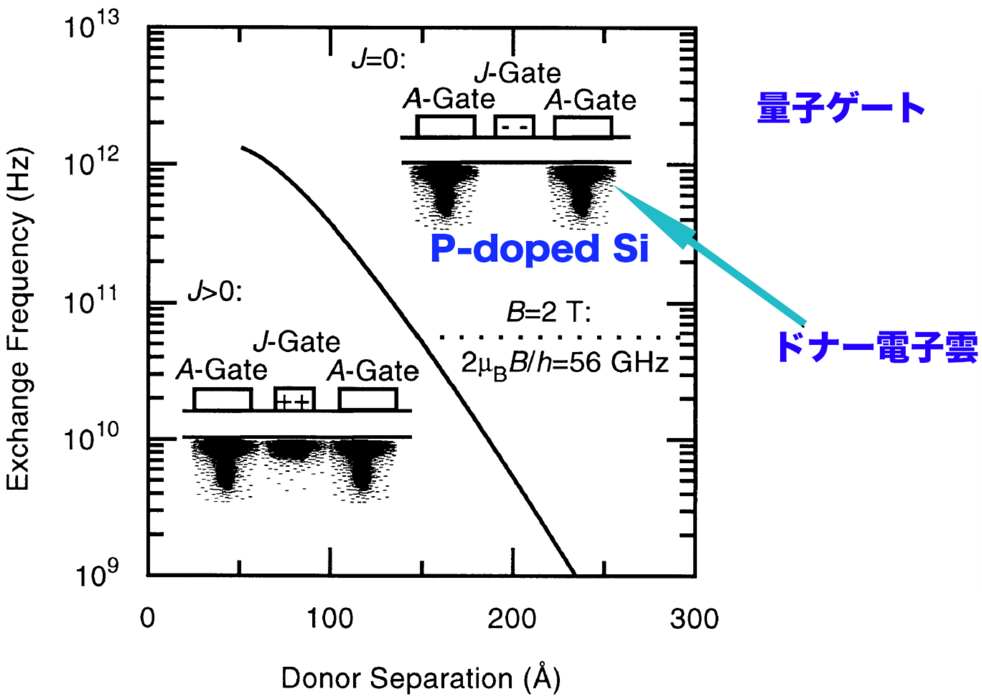
$$\boldsymbol{S} \cdot \tilde{A} \cdot \boldsymbol{I} = A\boldsymbol{S} \cdot \boldsymbol{I} = AS^z I^z + \tfrac{1}{2}\left(S^+ I^- + S^- I^+\right)$$

Thus, S^+I^+ and S^-I^- terms remain strictly forbidden.

Dynamic nuclear polarization (DNP) occurs when populations of sublevels are changed from thermal equilibrium by ESR transitions.
= Overhauser effect

Kane’s model of quantum computer with P-doped silicon (Si:P)

(B. E. Kane : Nature **393** (1998) 133)

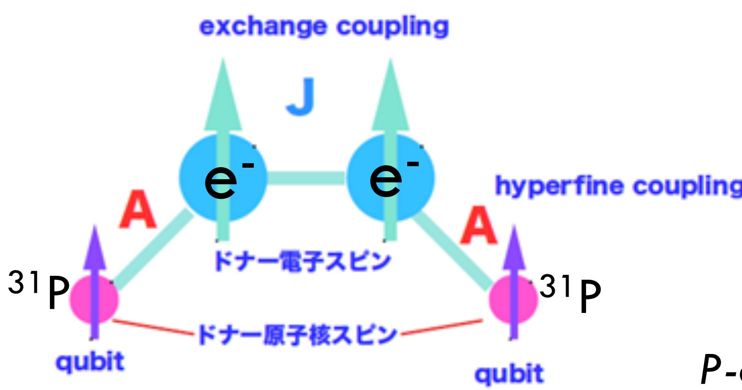


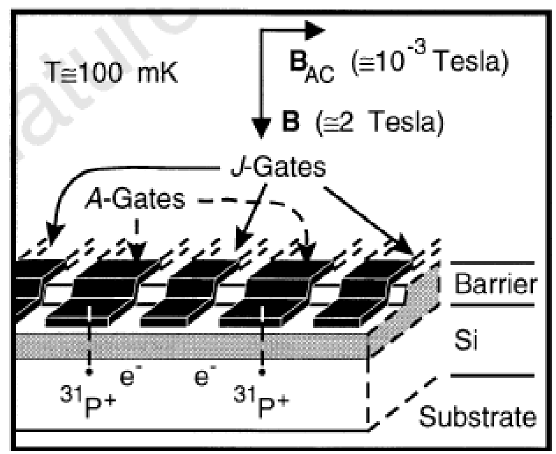
P-doped Si: ^{31}P(I =1/2), Qubit

A-Gate selects a qubit by Stark effect.

J-Gate turns on and off the electron-mediated coupling between nuclear spins.

→ Entanglement can be controlled by J-Gate voltage V_J





P-doped Si is a candidate to realize a quantum computation with ^{31}P nuclear spin.

For realization of Kane's model quantum computer

- Electric field control of hyperfine field
- Spin dynamics at B > 2 T and T ~ 0.1 K (required in order to quench the electron spin freedom)

- Spin dynamics !!
  - DNP can be used to initialize qubits
  - Study in a wide range of B
    - Pulsed ESR studies have been reported at a few values of B.
      →We need more data in a wide range of B.
    - No reports of NMR for insulator Si:P

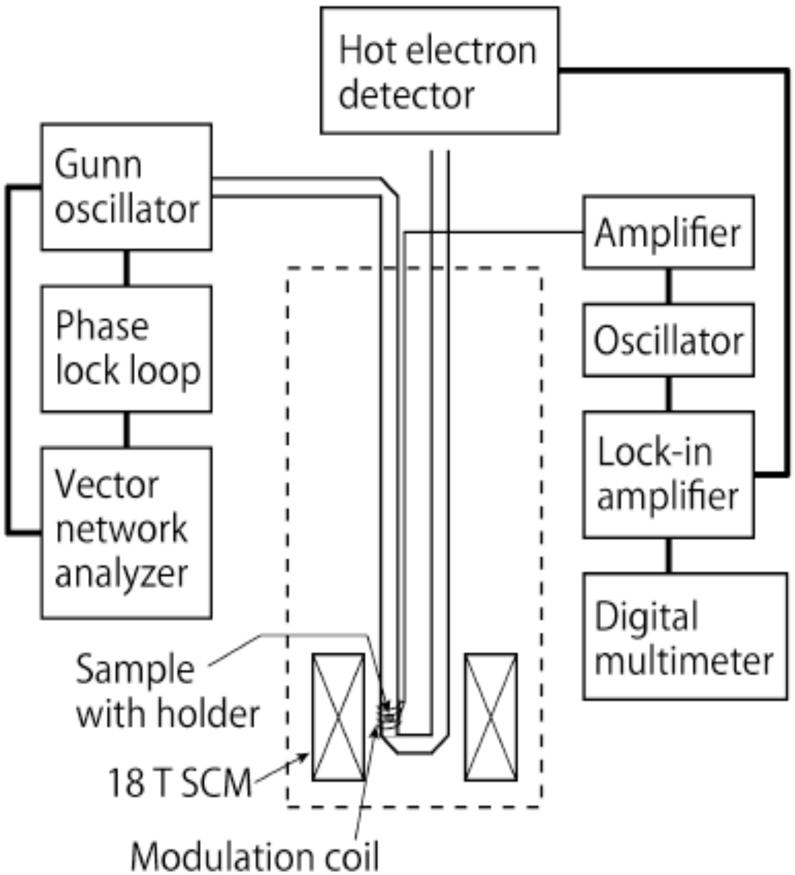
Present work

cw-ESR at high magnetic fields $B \sim 3$ T

- 〈advantage〉 cw-ESR can be performed easily in a wide range of frequency.
- 〈problem〉 Direct measurement of T_1 is difficult.
  - T_{1e} can be measured with a help of numerical calculation
  - Nuclear spin dynamics is also observed via ESR

- Sample: Si:P prepared at KAIST
  - thin film ~ 3 x 3 mm^2
  - P concentration: $n = 6.5 \times 10^{16}$ cm^{-3} << n_c
  - Natural Si (4 % ^{29}Si)

High frequency ESR system with field modulation

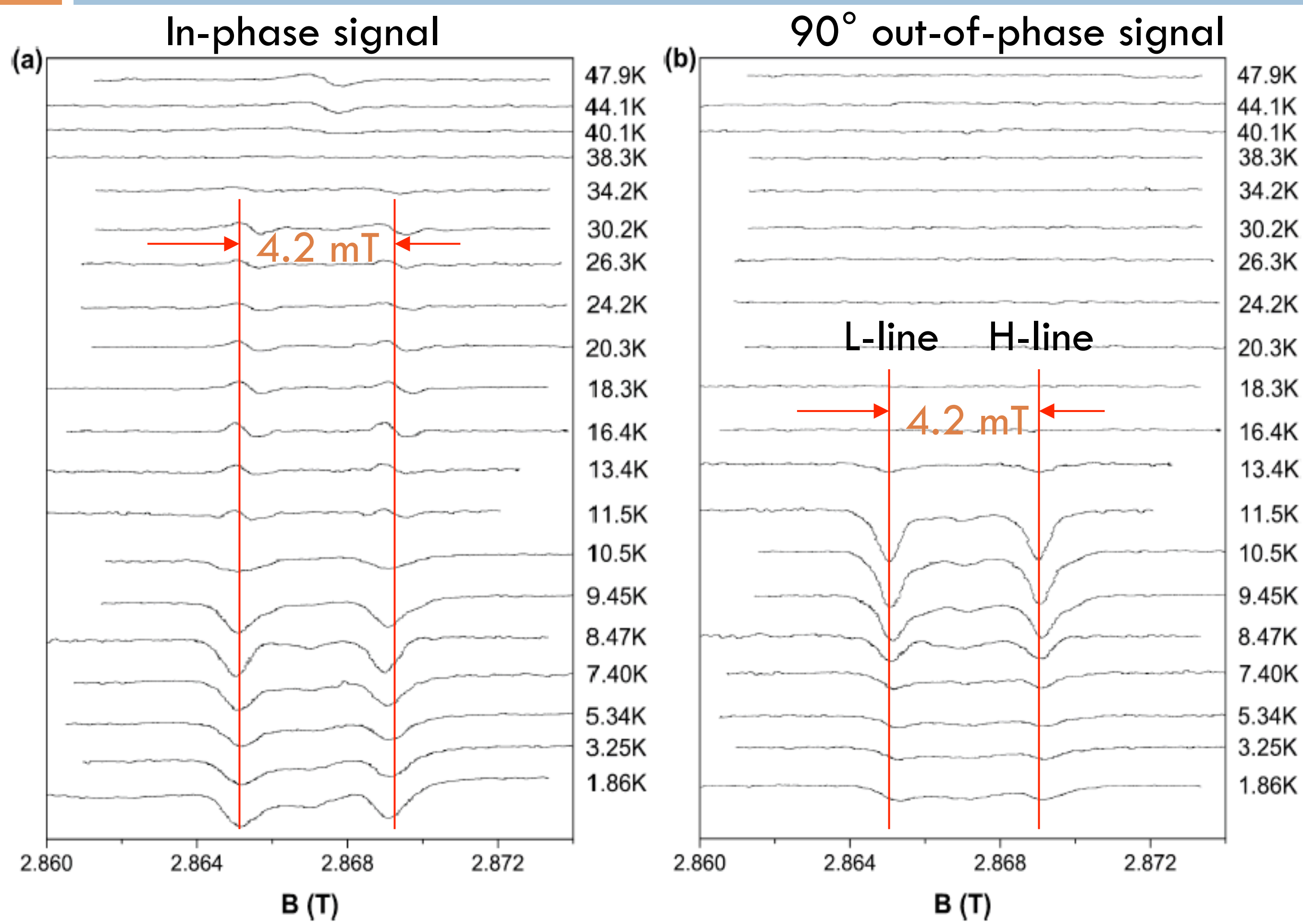


mm-wave cw-ESR of FIR Center, Univ. Fukui

- Gunn oscillator was phase-locked to Millimeter-Wave Vector Network Analyzer. (20 - 600 GHz)
- Hot electron detector (In-Sb) cooled to 4.2 K.
- Field modulation method: In-phase and out-of-phase signals are obtained as the lock-in output with respect to ac-field modulation.
- B = 2.9 T, ω = 80 GHz, ω_m = 330 Hz (590 Hz, 15 kHz)

cw-ESR study on P-doped Si

Song et al.: J. Phys.: Cond. Matter **22**.(2010) 206001



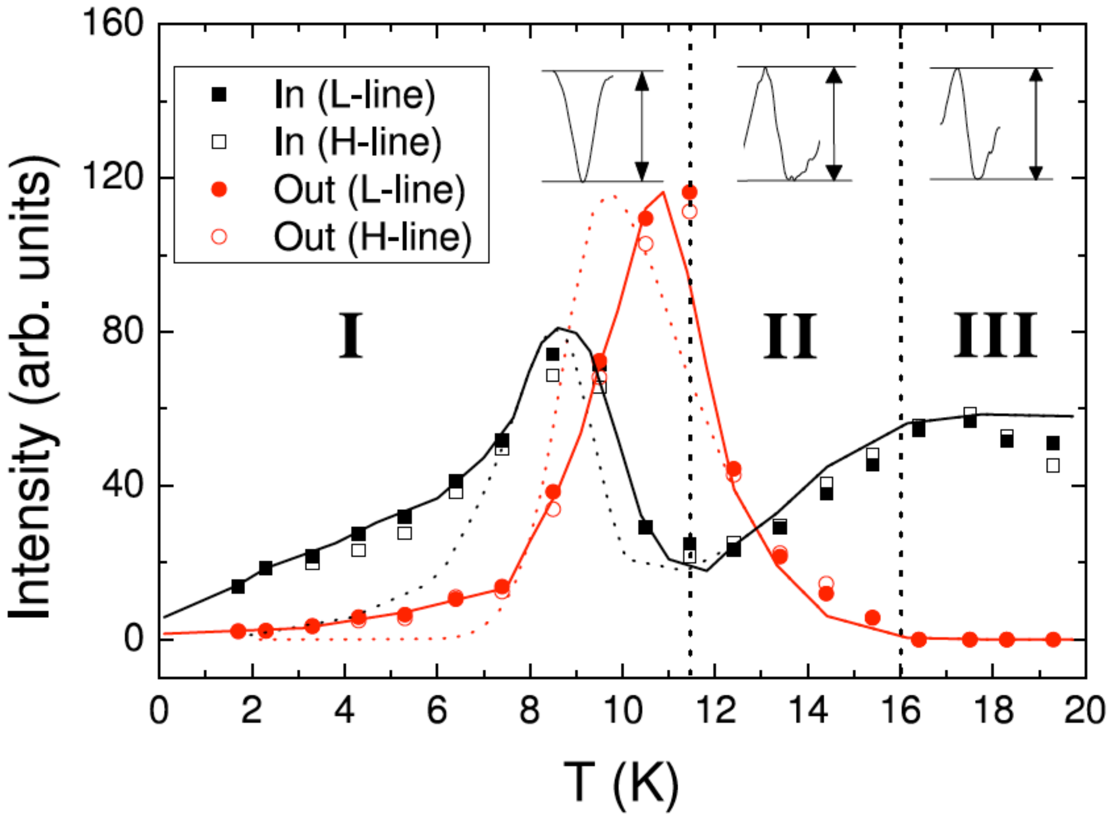
ω = 80 GHz,
ω_m = 330 Hz

Two ESR lines split by hyperfine coupling
L-line (lower field)
H-line (higher field)

$$\mathcal{H} = g\mu_B B S_z + A I \cdot S - \gamma_N \hbar B I_z \;\rightarrow\; \omega_{res} = \frac{g\mu_B}{\hbar}\left(B \pm \frac{1}{2}\frac{A}{g\mu_B}\right), \text{ where } \frac{A}{g\mu_B} = 4.2\text{ mT}$$

T-dependence of normalized ESR signal intensity

Song et al.: J. Phys.: Cond. Matter **22**.(2010) 206001



- Intensity is measured according to the change of the line shape
- Out-of-phase signal appears! Maximum ~12 K
- In-phase signal showed complicated dependence on T: Maxima ~8 K, ~17 K
- Decreasing intensity below 8 K with decreasing temperature.

B_m~0.1 mT
ω_m ~ 2x10^3 rad/s

B_1 *unknown*

Normalized Intensity = I (obs) / $B_S(g\mu_B SH/k_B T)$,

where M_0 ~ $B_S(g\mu_B SH/k_B T)$ is the Brillouin function.

Bloch Equations in a rotating frame with ω'

Bloch eqs.

$$\begin{cases} \dfrac{dM_x}{dt} = -\gamma b_z M_y - \dfrac{M_x}{T_2} \\ \dfrac{dM_y}{dt} = \gamma b_z M_x - \gamma B_1 M_z - \dfrac{M_y}{T_2} \\ \dfrac{dM_z}{dt} = \gamma B_1 M_y - \dfrac{M_z - M_0}{T_1} \end{cases}$$

$$b_z = \frac{(\omega - \omega')}{\gamma} + B_m \cos \omega_m t$$

$$(\delta\omega = \omega - \omega')$$

- M_0 : equilibrium amplitude of $\boldsymbol{M}$
- T_1, T_2 : relaxation constants ➔ T_1 : not known (parameter)

  T_2 : known at low field

  $T_2 = T_1$ for $T_1 < 10^{-4}$ s, $T_2 = 1\text{x}10^{-4}$ s for $T_1 > 10^{-4}$ s

- Solve ➔ time evolution of $\boldsymbol{M}$ (initial condition $\boldsymbol{M} = (0,0,1)$)

  by GNU Scientific Library (GSL) on UNIX

  Embedded Runge-Kutta-Fehlberg method

Passage conditions

ε_A>> 1 : Adiabatic passage $\quad \varepsilon_A = \dfrac{\gamma B_1^2}{B_m \omega_m}$

ε_A=4.7 : (quasi-)adiabatic passage even at the resonance point

ε_R>> 1 : Rapid passage $\quad \varepsilon_R = \dfrac{B_m}{B_1} \omega_m T_1$

ε_F>> 1 : Fast passage $\quad \varepsilon_F = \omega_m T_1 \; < \varepsilon_R$

ε_F= 1

ε_R= 1

Region I
ε_R, ε_F >> 1
rapid and fast

Region II
ε_R>> 1 & ε_F << 1
rapid and non-fast

Region III
ε_R, ε_F << 1
slow (non-rapid) and non-fast

low T
long T_1

high T
short T_1

Numerical solutions of Bloch eqs & lock-in detected ESR signals

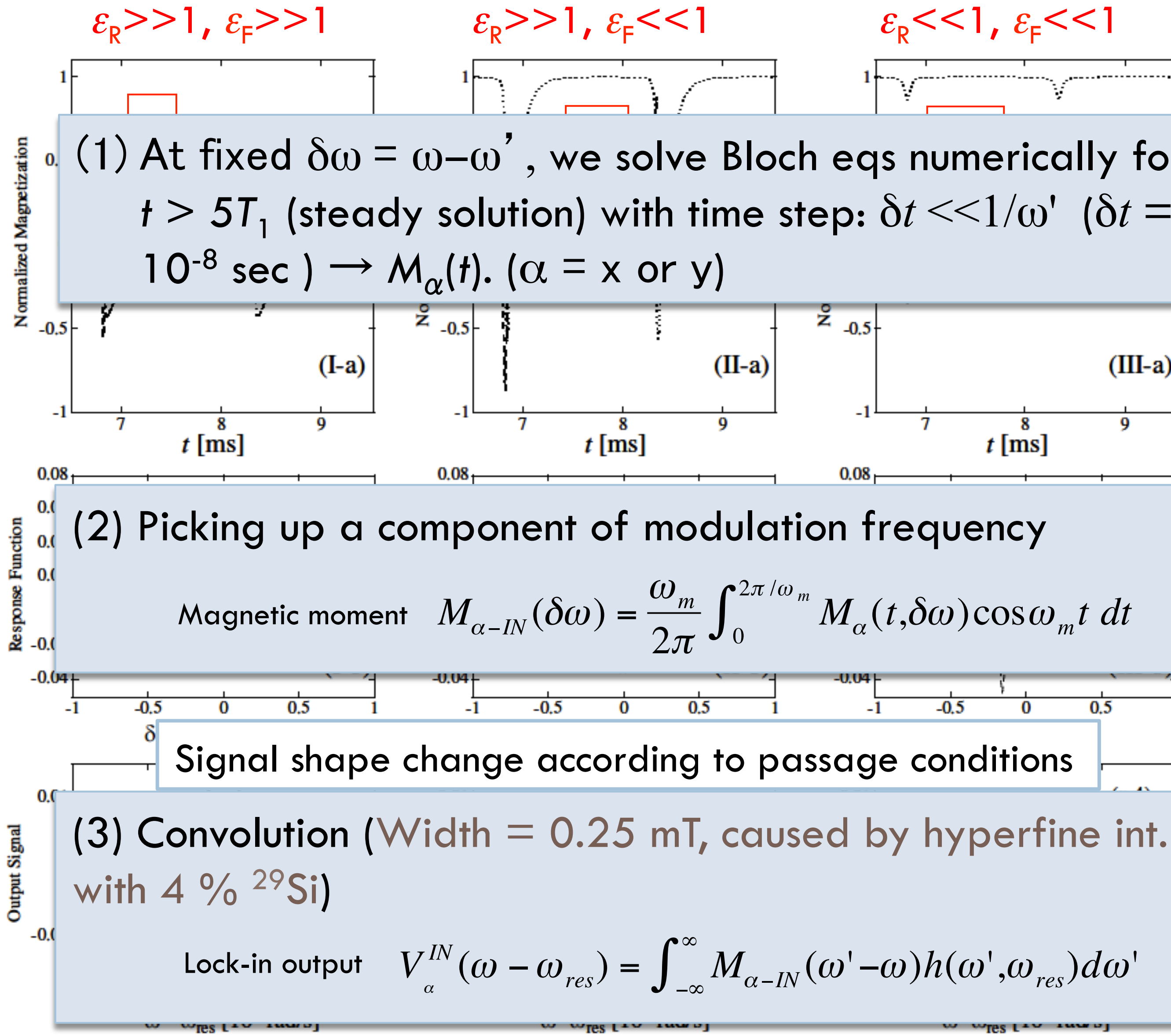
$M_x(t)$, $M_y(t)$

$M_{\alpha\text{-IN}}(\delta\omega)$,

$M_{\alpha\text{-OUT}}(\delta\omega)$

$V_{\alpha\text{-IN}}(\omega-\omega_r)$,

$V_{\alpha\text{-OUT}}(\omega-\omega_r)$



(1) At fixed $\delta\omega = \omega-\omega'$, we solve Bloch eqs numerically for $t > 5T_1$ (steady solution) with time step: $\delta t << 1/\omega'$ ($\delta t = 10^{-8}$ sec) → $M_\alpha(t)$. (α = x or y)

(2) Picking up a component of modulation frequency

Magnetic moment $$M_{\alpha-IN}(\delta\omega) = \frac{\omega_m}{2\pi}\int_0^{2\pi/\omega_m} M_\alpha(t,\delta\omega)\cos\omega_m t\, dt$$

Signal shape change according to passage conditions

(3) Convolution (Width = 0.25 mT, caused by hyperfine int. with 4 % ^{29}Si)

Lock-in output $$V_\alpha^{IN}(\omega-\omega_{res}) = \int_{-\infty}^{\infty} M_{\alpha-IN}(\omega'-\omega)h(\omega',\omega_{res})d\omega'$$

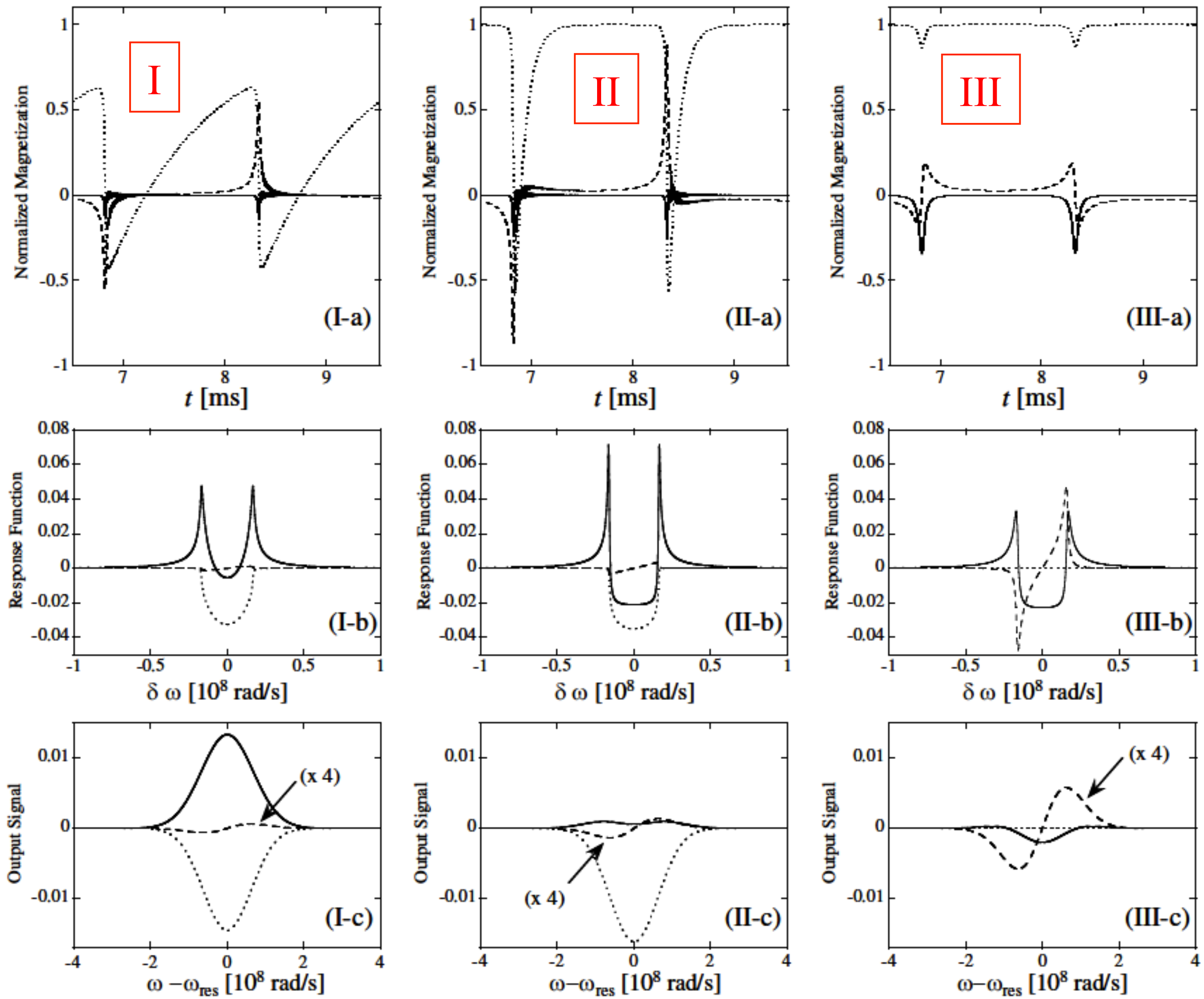
Numerical solutions of Bloch eqs & lock-in detected ESR signals

$\varepsilon_R>>1,\ \varepsilon_F>>1$ | $\varepsilon_R>>1,\ \varepsilon_F<<1$ | $\varepsilon_R<<1,\ \varepsilon_F<<1$

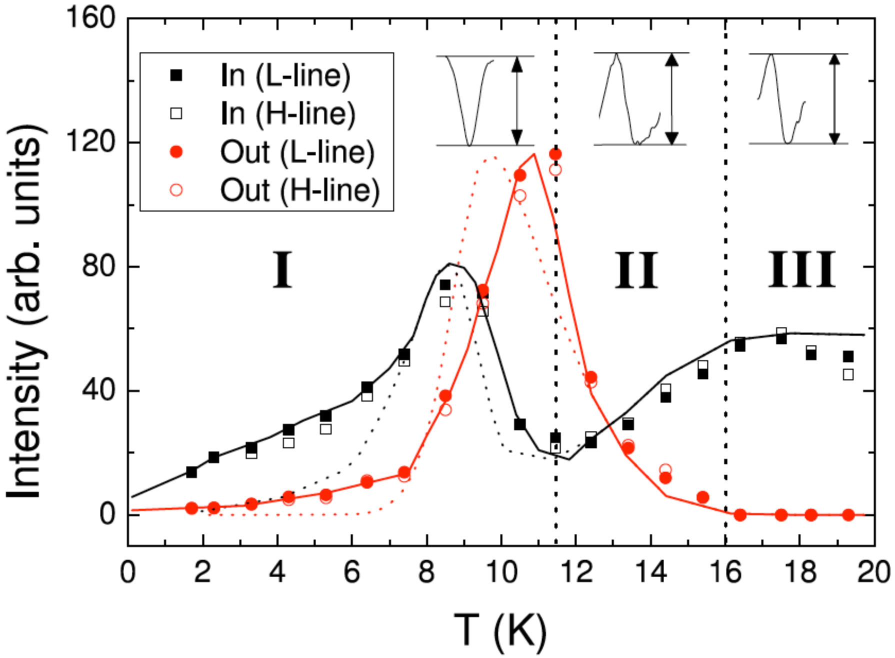
$M_x(t)$, $M_y(t)$

$M_{\alpha\text{-IN}}(\delta\omega)$, $M_{\alpha\text{-OUT}}(\delta\omega)$

$V_{\alpha\text{-IN}}(\omega-\omega_r)$, $V_{\alpha\text{-OUT}}(\omega-\omega_r)$



Normalized ESR signal intensity as a function of T_1 by Bloch eqs.



Solid line: Numerical calculation

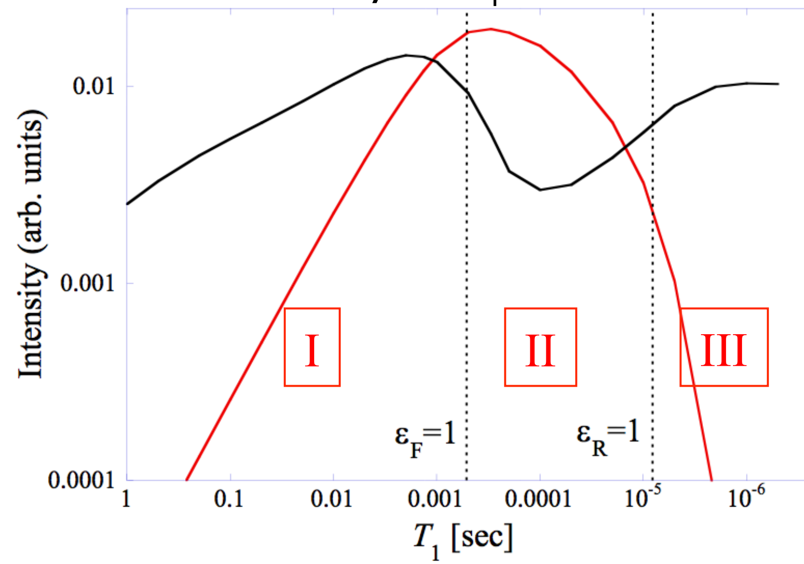
Normalized Intensity = I (obs) / $B_S(g\mu_B SH / k_B T)$

Black: In-phae,

Red: Out-of-phase

$M_y >> M_x$ for $\varepsilon_R >> 1$ and $M_x >> M_y$ for $\varepsilon_R << 1$.

Calculation: intensity vs. T_1

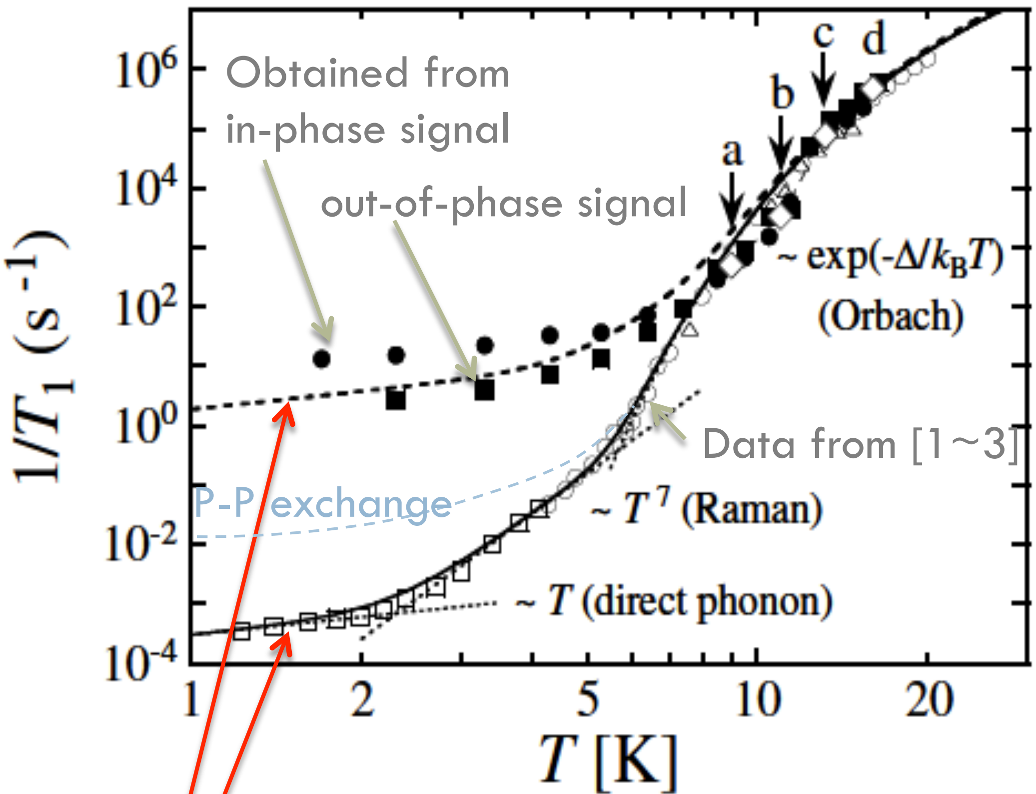


(4) Take peak-peak intensity

Parameter Fitting:

1) B_1 is chosen by fitting $T_1(T)$ at $\varepsilon_R=1$.
2) The mixing ratio between M_y and M_x is chosen by fitting the peak height in $\varepsilon_F<1$ and a constant value in $\varepsilon_R>1$ for the black line :(4 M_y + M_x).

Temperature dependence of $T_1(T)$ at 2.9 T



$$T_1^{-1} = aB^4T + bB^2T^7 + c\exp\left(\Delta/k_BT\right)$$

Solid line: $T_1^{-1}(T)$ for isolated P electrons $n < 10^{16}$ cm^{-3} at $B < 0.3$ T [1~3]

Dashed line: $T_1^{-1}(T)$ for $B = 2.9$ T with the same values of a, b, c and Δ/k_B=122.5 K.

T_{1e} is represented fairly well by 3 relaxation processes which have been discussed at B~0.3 T

T_{1e} process changes at high field for T < 6 K.

- B<0.8 T: P-P exchange for $n > 10^{16}$ cm^{-3} [1]
- B> 1 T: Direct/Raman process overcomes P-P exchange process for $n = 6.5 \times 10^{16}$ cm^{-3}

[1] Feher & Gere: PR **114** (1959) 1245

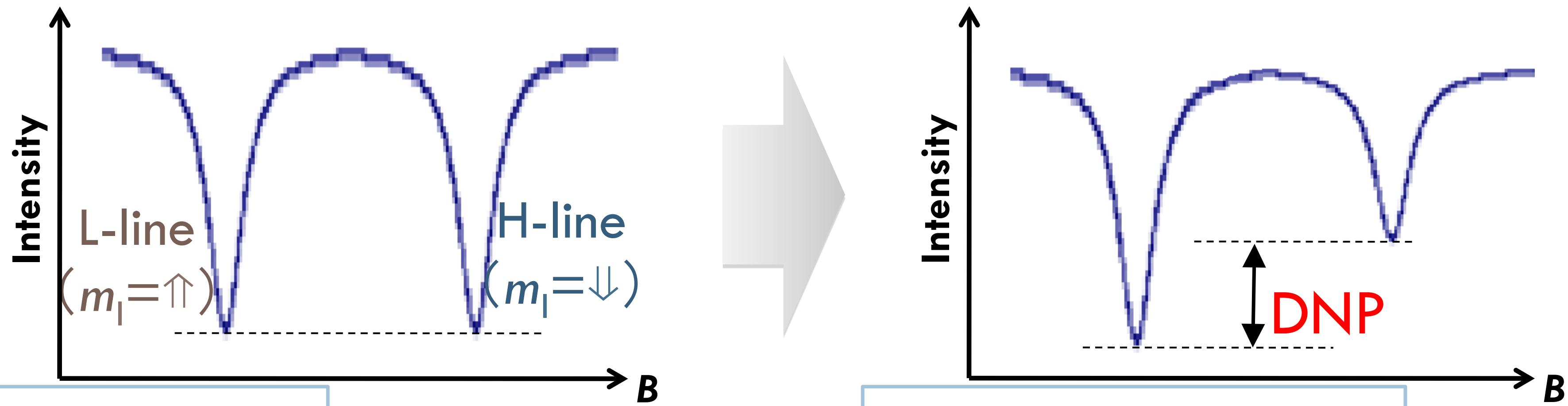
[2] Castner: PR **130** (1963) 58

[3] Tyryshkin *et al.*: PRB **68** (2003) 193207

ESR spectrum of Si:P with DNP

Schematic drawing of field sweep cw-ESR spectrum

☞Each of two lines corresponds a specific direction of nuclear spin.



Thermal equilibrium

After saturating H-line by ESR

<u>Asymmetric spectrum suggests DNP.</u>

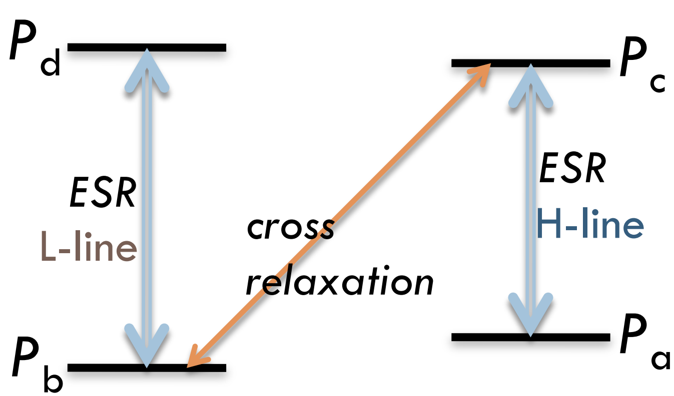
$P_b/P_d=P_a/P_c$

intensity of absorption

$I(\mathrm{L}) \sim P_b - P_d$, $I(\mathrm{H}) \sim P_a - P_c$

$\underline{I(\mathrm{L}) = I(\mathrm{H})}$

P_i : poulations $\Sigma P_i=1$



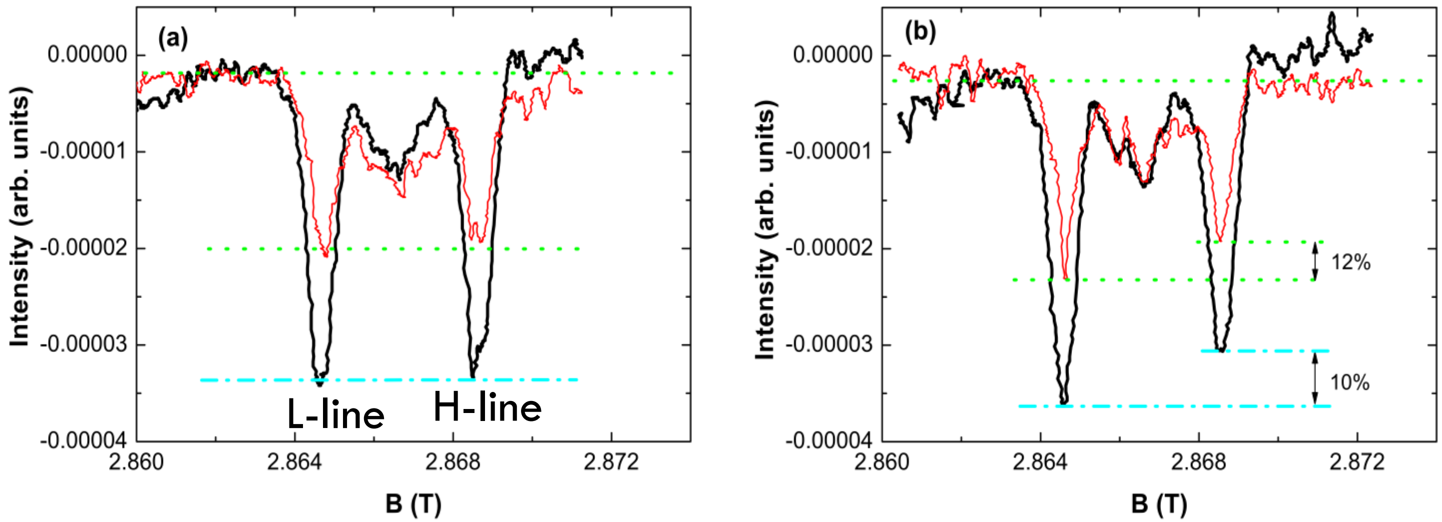
$P_b/P_d >> P_a/P_c$

$P_b >> P_a$

$\underline{I(\mathrm{L}) > I(\mathrm{H})}$

Possibility of dynamic nuclear polarization (DNP) of ^{31}P

Song et al.: J. Phys.: Cond. Matter **22**.(2010) 206001



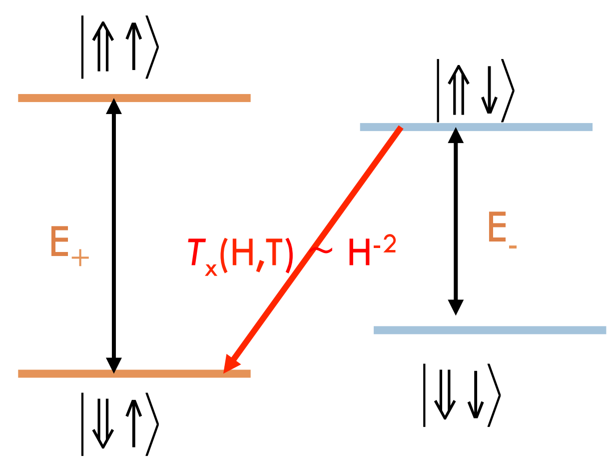
(a) Right after cooling down from 70 K to 6.9 K. (b) After radiation of microwave for 20 minutes at H-line. Black : in-phase signal, red : 90° out-of-phase signal.

Asymmetric ESR spectrum suggesting DNP effect.

$$\frac{I(\mathrm{L}) - I(\mathrm{H})}{I(\mathrm{L}) + I(\mathrm{H})} = 10\ \% \quad \Rightarrow \quad \frac{\langle I_z \rangle}{\langle I_{\mathrm{equi}} \rangle} = 6 \times 10^2$$

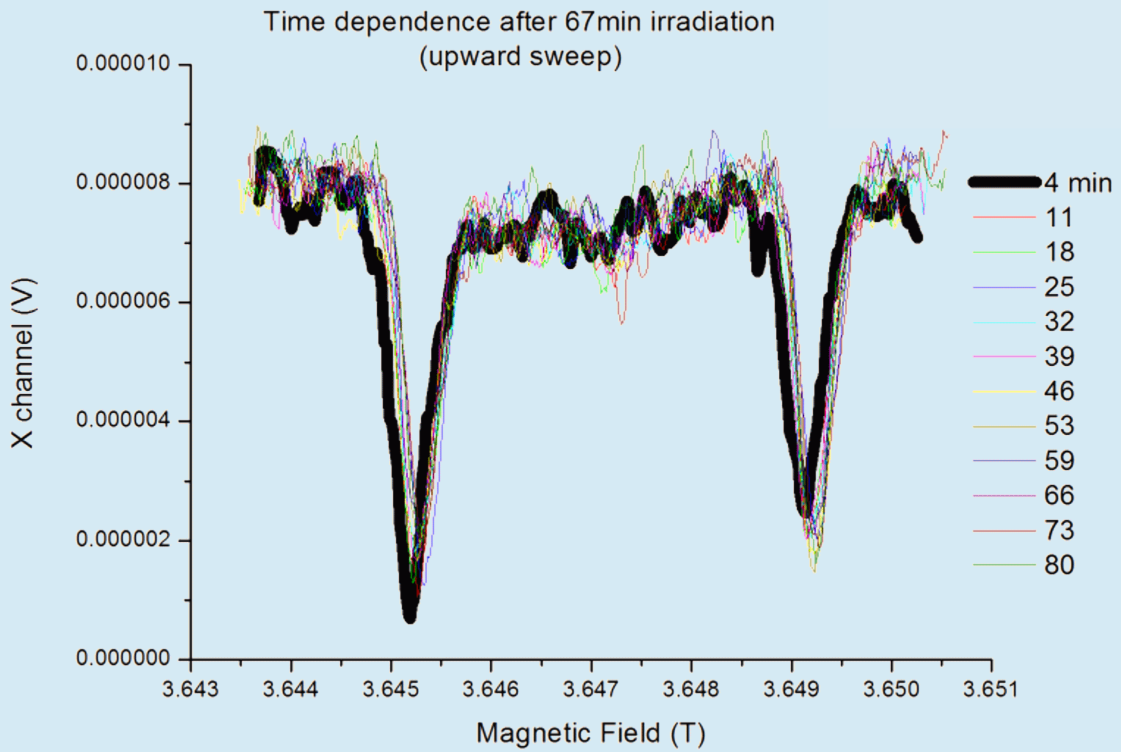
at 6.9 K, 2.9 T

DNP effect



DNP and relaxation to thermal equilibrium

Time evolution of nuclear polarization



in-phase signal

T=1.44 K

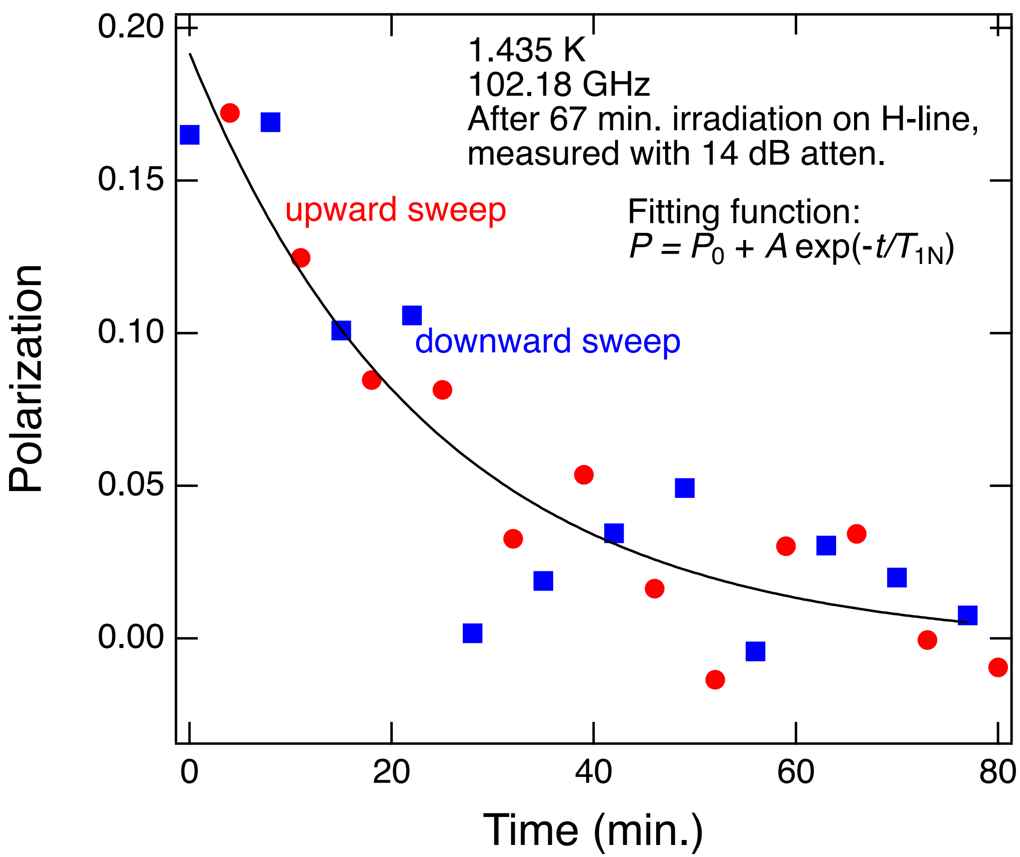
B=3.64 T (102.2 GHz)

Preparation: Irradiation at H-line for 67 min. with full power microwave and field modulation.

Measurement:
Sweep both direction consecutively with attenuated microwave.

Microwave: 102.2 GHz, B_1~2 x 10^{-6} T
Modulation frequency : 541 Hz, Modulation field ~ 0.03 mT

DNP and relaxation to thermal equilibrium (2)



T_{1N} measured by ESR

T_{1N} = 24 ± 7 min.
at T=1.44 K and B=3.65 T

DNP effect

Maximum nuclear spin polarization = 19 %

$$\frac{\langle I_z \rangle}{\langle I_{\mathrm{equi}} \rangle} = 2 \times 10^2$$

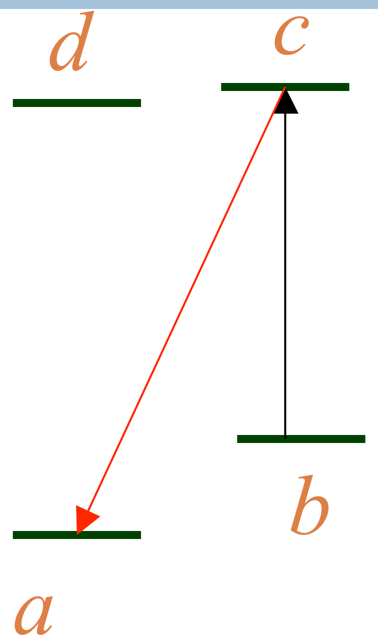
(depends on the sweep direction)

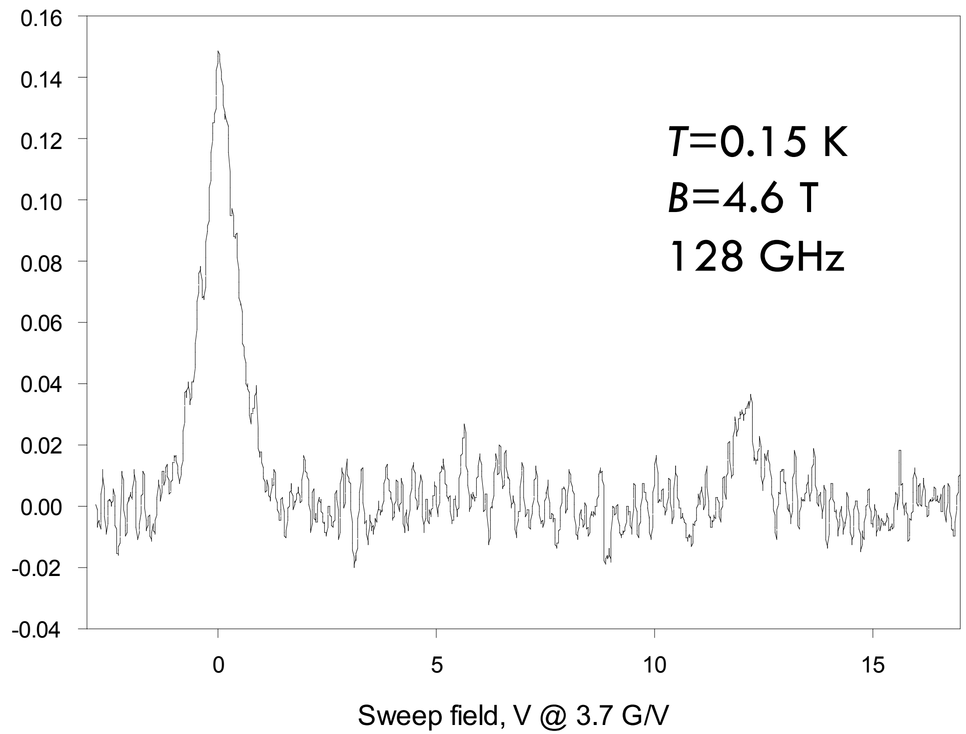
Thermal equilibrium polarization at 1.44 K, 3.65 T
tanh ($g \mu_B H$ / $2kT$) = <u>94 %</u> for electron spin

Imperfect saturation of electron spins?

Preliminary

Dynamic nuclear polarization after 300 s pumping of *b*-c transition





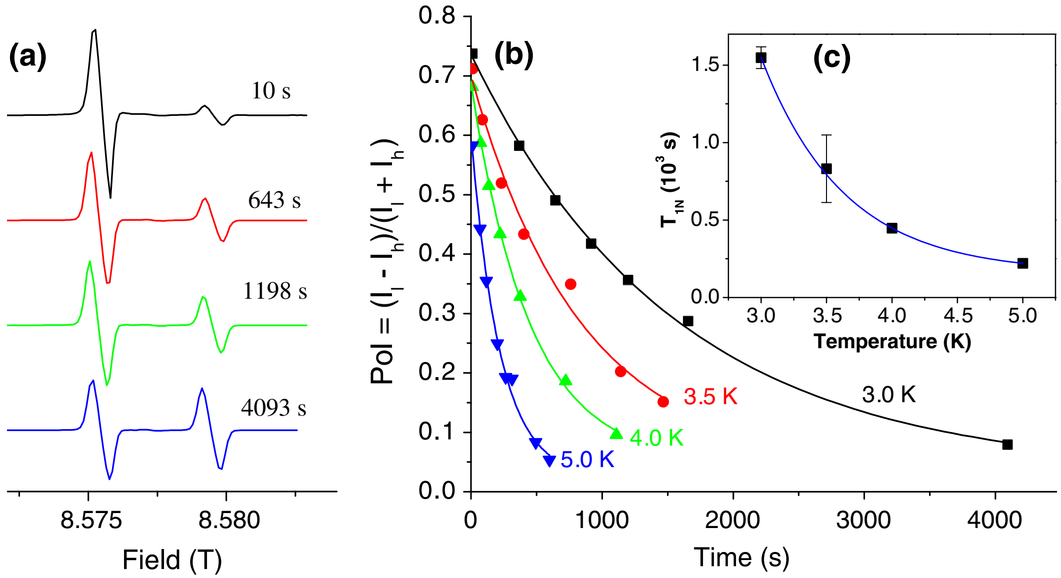
a-c transition probability

$$W_{ac} = \left(\frac{A}{2g\mu_B B}\right)^2 W_{bc} \approx 1.6\cdot 10^{-7} W_{bc}$$

if $T_{1e}=1$ s, then $T_{a\text{-}c\ \mathrm{pumping}} \sim 10^7$ s → much faster in real system

J. van Tol *et al.*: Appli. Magn. Reso. **36** (2009) 259, High-Field Phenomena of Qubits

- Sample: $3x3x1 mm^3$ piece of crystalline silicon from Wacker Siltronic with $[P] = 1x10^{15}$ cm^{-3}
- 240 GHz ESR = 99.99% electron spin polarization is reached at 2.1 K

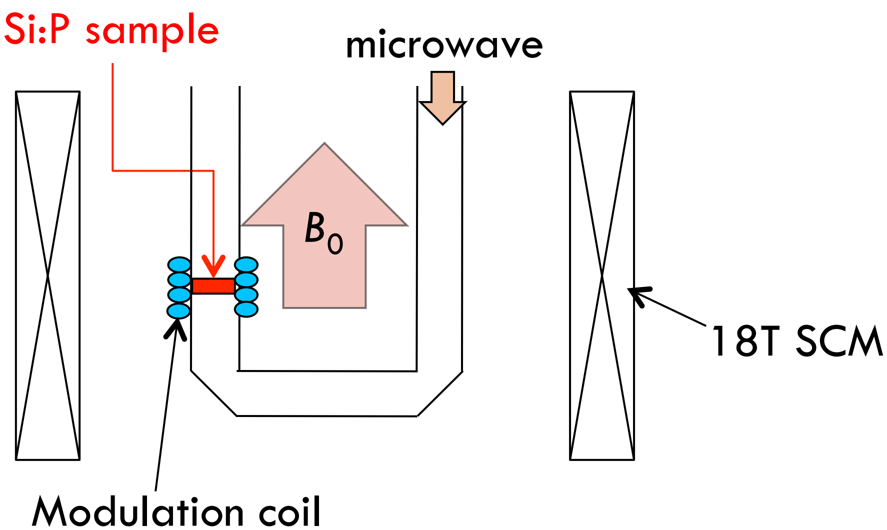


mm-wave source:
Gunn diode, 120GHz 40 mW max., 240 GHz 9 mW max. with doubler

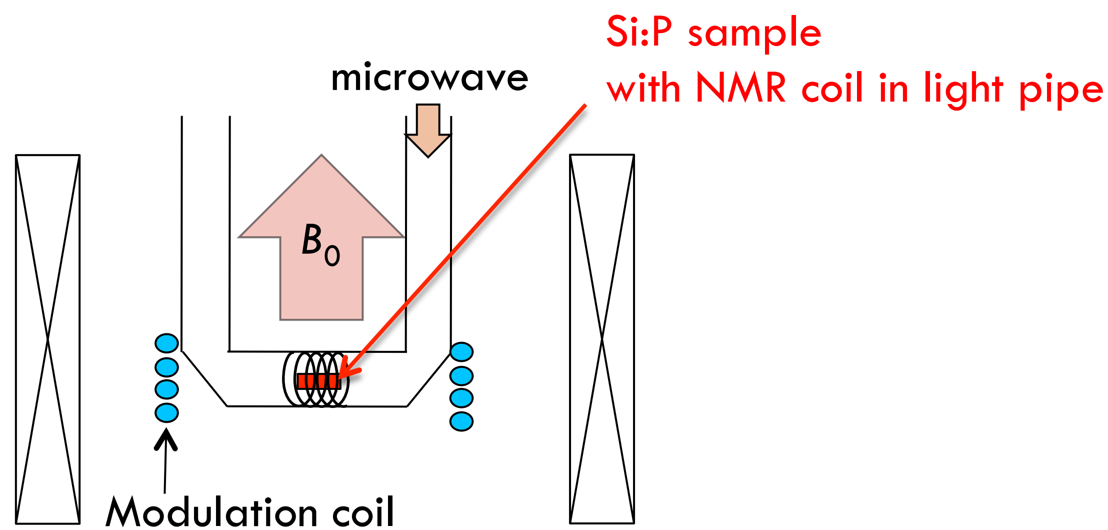
- EPR spectra at 3K measured at very low power after saturating the high-field hyperfine component for 5 min at high power.
- ~75 % polarization below 5 K
- T_{1N} is measured as a decay of polarization. T_{1N} ~3.5 min at 5 K.

Change of sample position for adding NMR coil

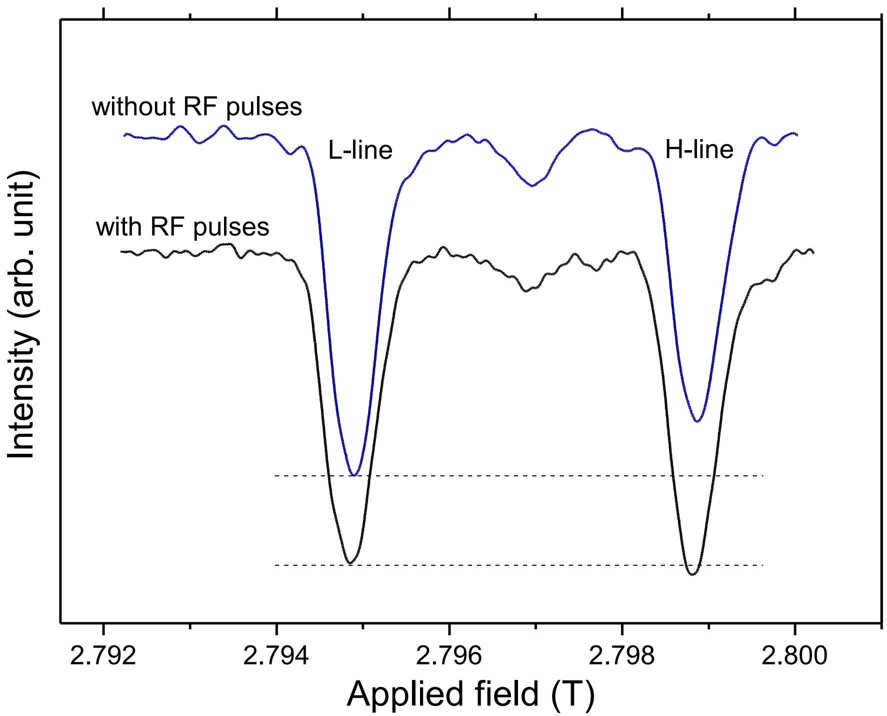
cw-ESR



Double resonance

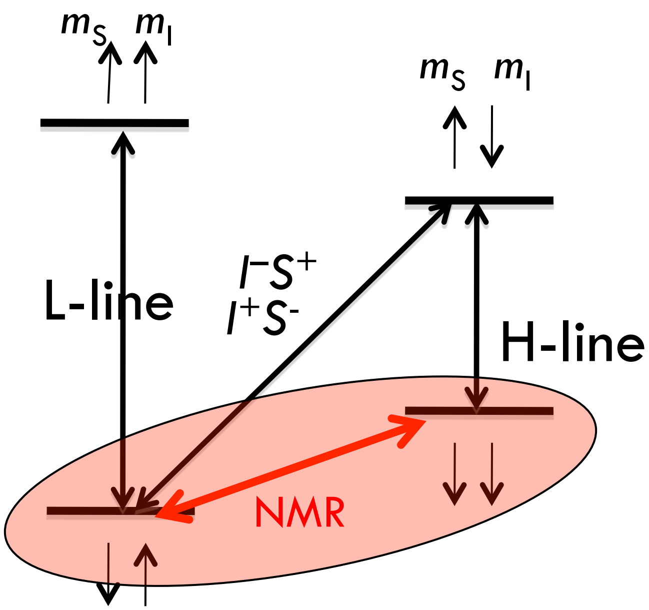


Double resonance experiments



ESR spectra recorded after irradiating H-line for 20 minutes at 1.5 K.

f= 78.45 GHz, f_{RF}= 107.1 MHz



Nuclear spin polarization was changed by applying RF.

Summary

- T_{1e} obtained from cw-ESR spectrum by numerical calculations of time evolution of Bloch equations
  - Shape change according to passage conditions
  - Reasonable T- and B-dependence

$$T_1^{-1} = aB^4T + bB^2T^7 + c\exp\left(\Delta/k_BT\right)$$

- DNP effect found at B=2.9 T and 3.6 T and T<7 K
  - T_{1N} is measured
  - What restrict nuclear polarization?
- ESR/NMR double resonance measurements
  - nuclear spin polarization changed by RF
  - ENDOR

Future plan and prospect

- Future plan
  - Using cavity to increase B_1
  - DNP system with ^{3}He-^{4}He dilution temperature
- ^{31}P-DNP-NMR could be directly observed if nuclear polarization enhances ~10^3
  - $n \sim 10^{19}$ cm^{-3} (metallic) → $n \sim 10^{16}$ cm^{-3} (insulator)

END

Thank you!