Investigating the influence of nuclear fluctuations on magnetic quantum tunneling

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TECHNION
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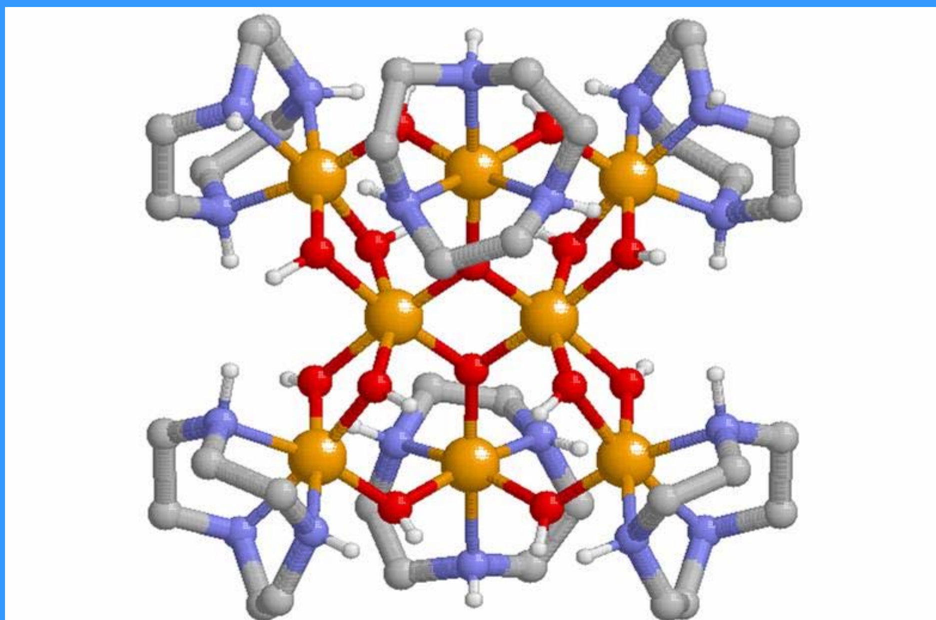
Fe8 Molecule – Single Molecule Magnet

$[Fe_8O_2(OH)_{12}(C_6H_{15}N_3)_6]^{8+}$



- Iron
- Oxygen
- Nitrogen
- Carbon
- Hydrogen

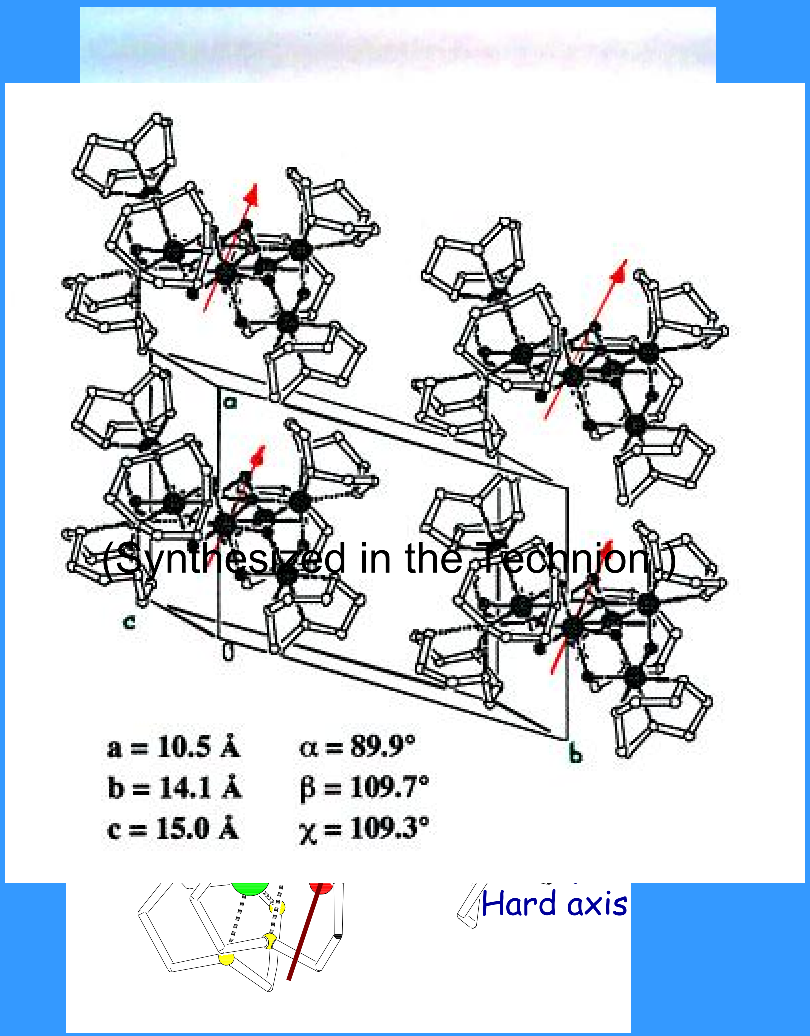
K. Wieghardt, K. Pohl, I. Jibril and G. Huttner, Angew. Chem. Int. Ed. Engl. 23 (1984), 77.

• The magnitude of magnetic interactions between the spins of the ions is between 20 to 170K.

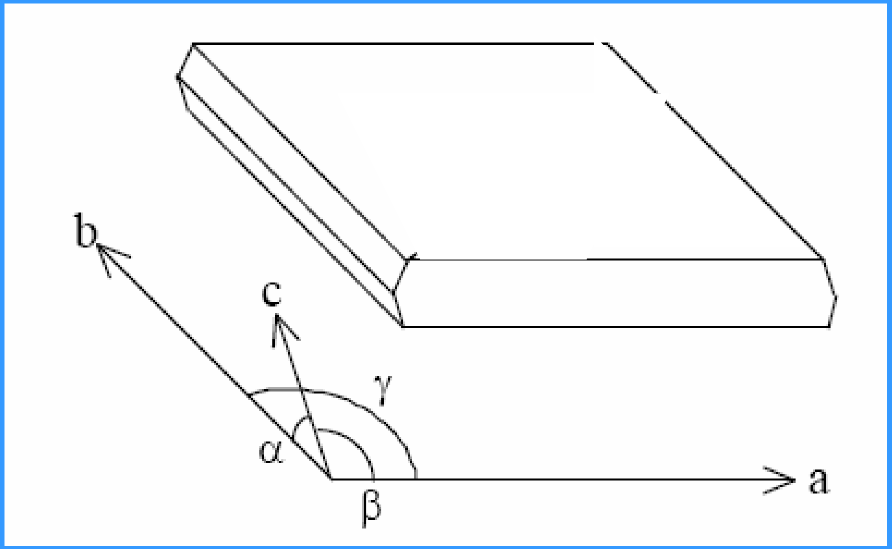
• The magnetic interactions between the molecules are negligibly small (~0.05K).

Single crystal of Fe8

- Single crystal of Fe8 (array of nanomagnets)

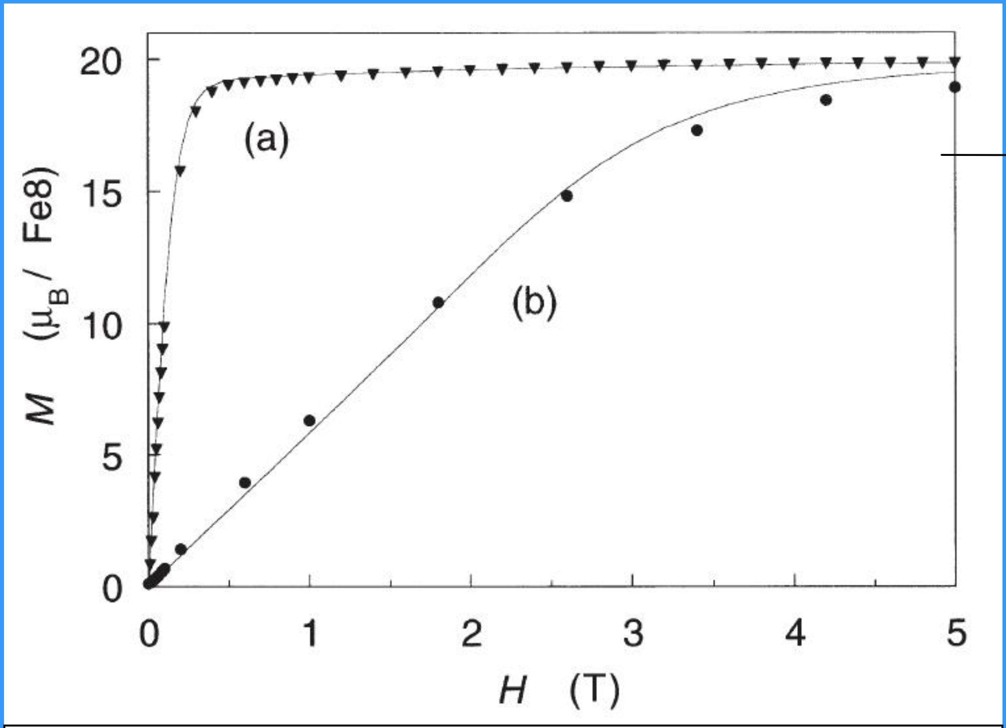


The magnetization is preferentially oriented parallel to an axis called the "easy axis“.



a = 10.5 Å	α = 89.9°
b = 14.1 Å	β = 109.7°
c = 15.0 Å	χ = 109.3°

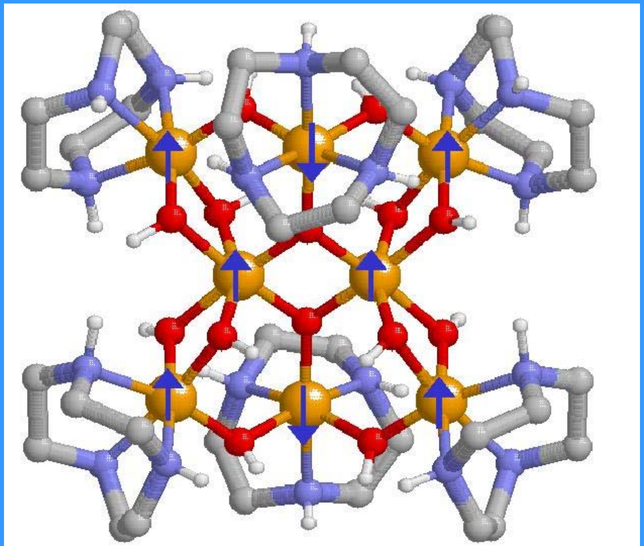
The molecular spin in low temperatures



M. Ueda & S. Maegawa, J. Phys. Soc. Jpn. 70 (2001)

***S*=10**

$$S_{Fe^{3+}} = 5/2$$



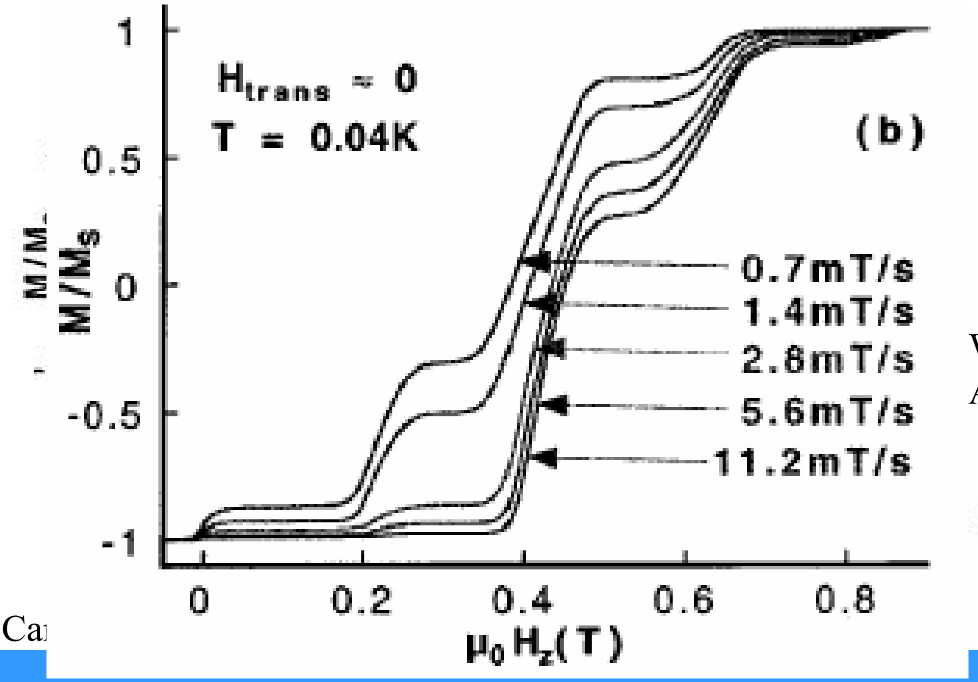
(a) is parallel to the easy axis.

(b) is perpendicular to the easy axis.

$$S = 6\times\left(5/2\right) + 2\times\left(-5/2\right) = 10$$

(This was confirmed by a polarized neutron-diffraction experiment)

Hysteresis loop of Fe8



A. Ca

W . Wernsdorfer et al. J. Appl. Phys. 87 (2000), 5481

- There is a temperature dependence above 0.4K.
- Equally separated steps can be seen at $H_m \approx n \times 0.22T$.
- The hysteresis shape depends on the field sweeping rate.

Hamiltonian

ZFS

The Hamiltonian of Fe8: S=10

The main part of the spin Hamiltonian:

$$\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z - E \cdot \left(S_x^2 - S_y^2 \right)$$

D – anisotropic constant (~0.27 K)

E – rhombic parameter (~0.046 K)

The energy levels (*E*=0) are:

$$Energy(m) = -Dm^2 - g\mu_B H_z m \longrightarrow H(m) = \frac{D}{g\mu_B} m \approx 0.2m\ [T]$$

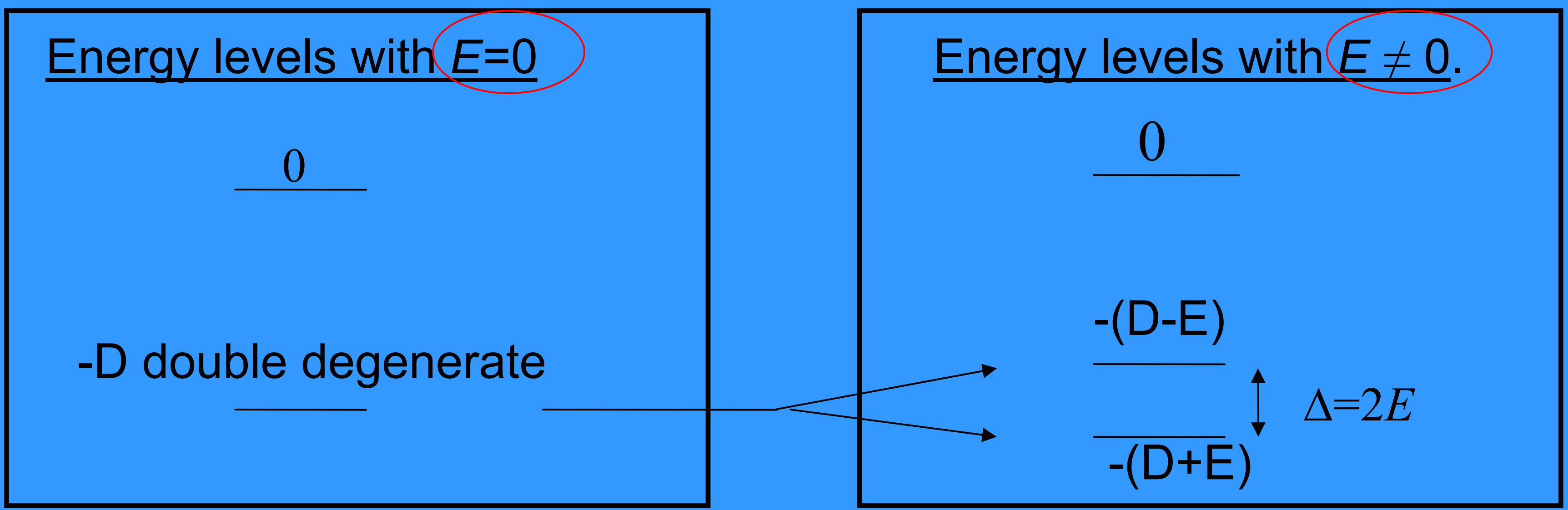
where *m* is the quantum number of the level.

E is responsible for the tunnel splitting.

The concept of tunnel splitting: S = 1

$$\mathcal{H} = -DS_z^2 + E(S_x^2 - S_y^2) = \begin{pmatrix} -D & 0 & -E \\ 0 & 0 & 0 \\ -E & 0 & -D \end{pmatrix}$$

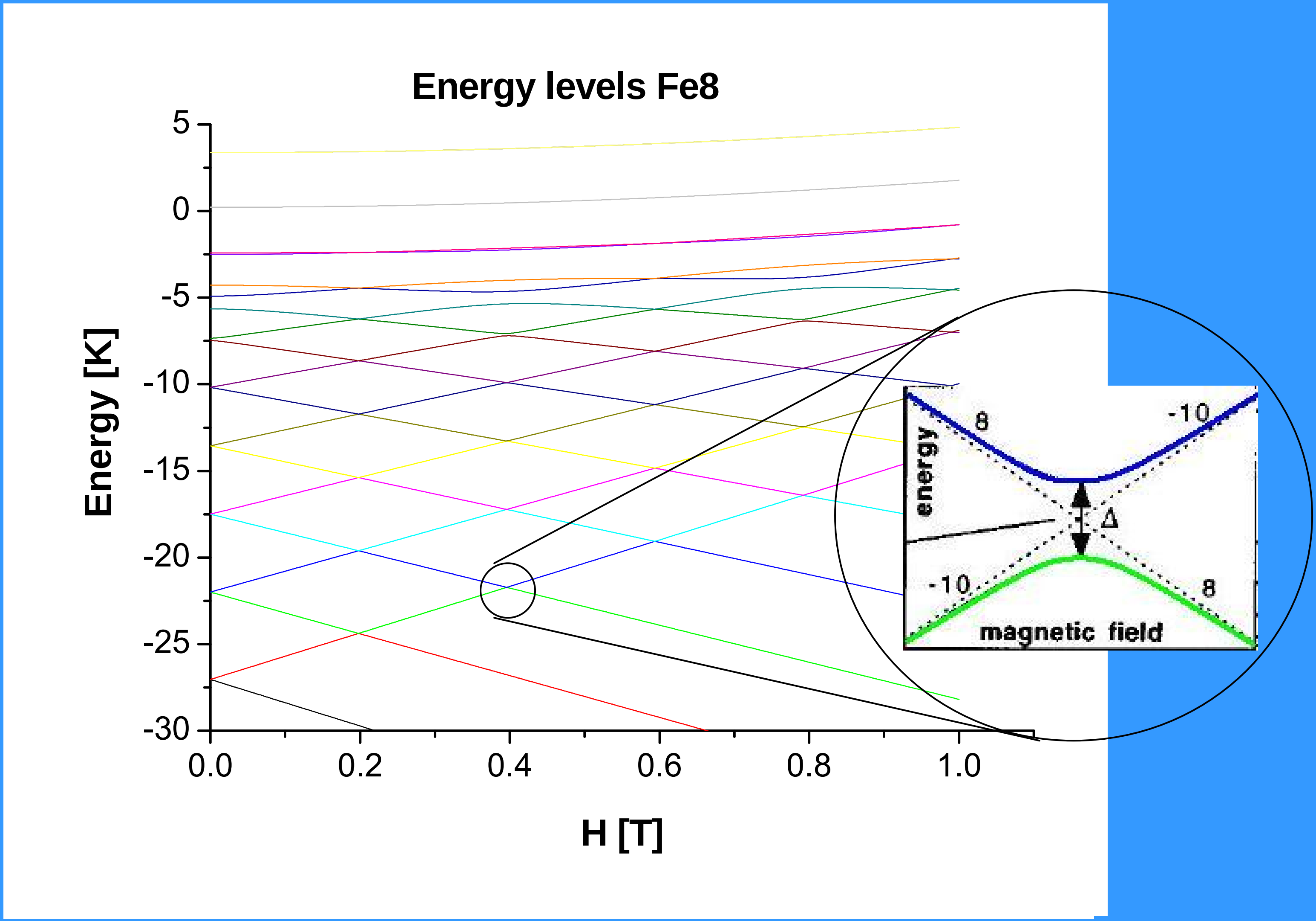
$$|up\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad |middle\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad |down\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$



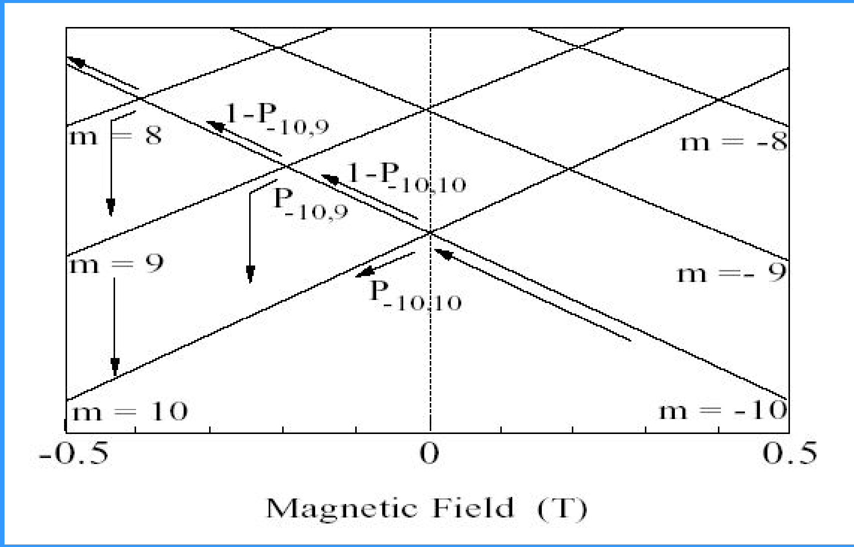
$$\left|\langle down|\exp(-i\mathcal{H}t)|up\rangle\right|^2 = \frac{1-\cos(2Et)}{2} = \frac{1-\cos(\Delta t)}{2}$$

The spin will tunnel at a rate given by Δ from up to down.

Energy levels and tunnel splitting in Fe8

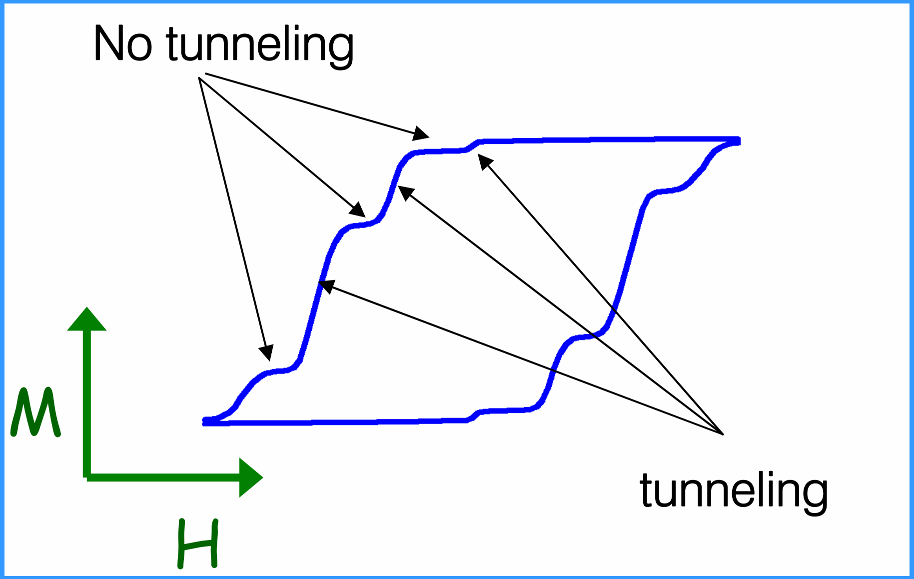


The model and the hysteresis loop

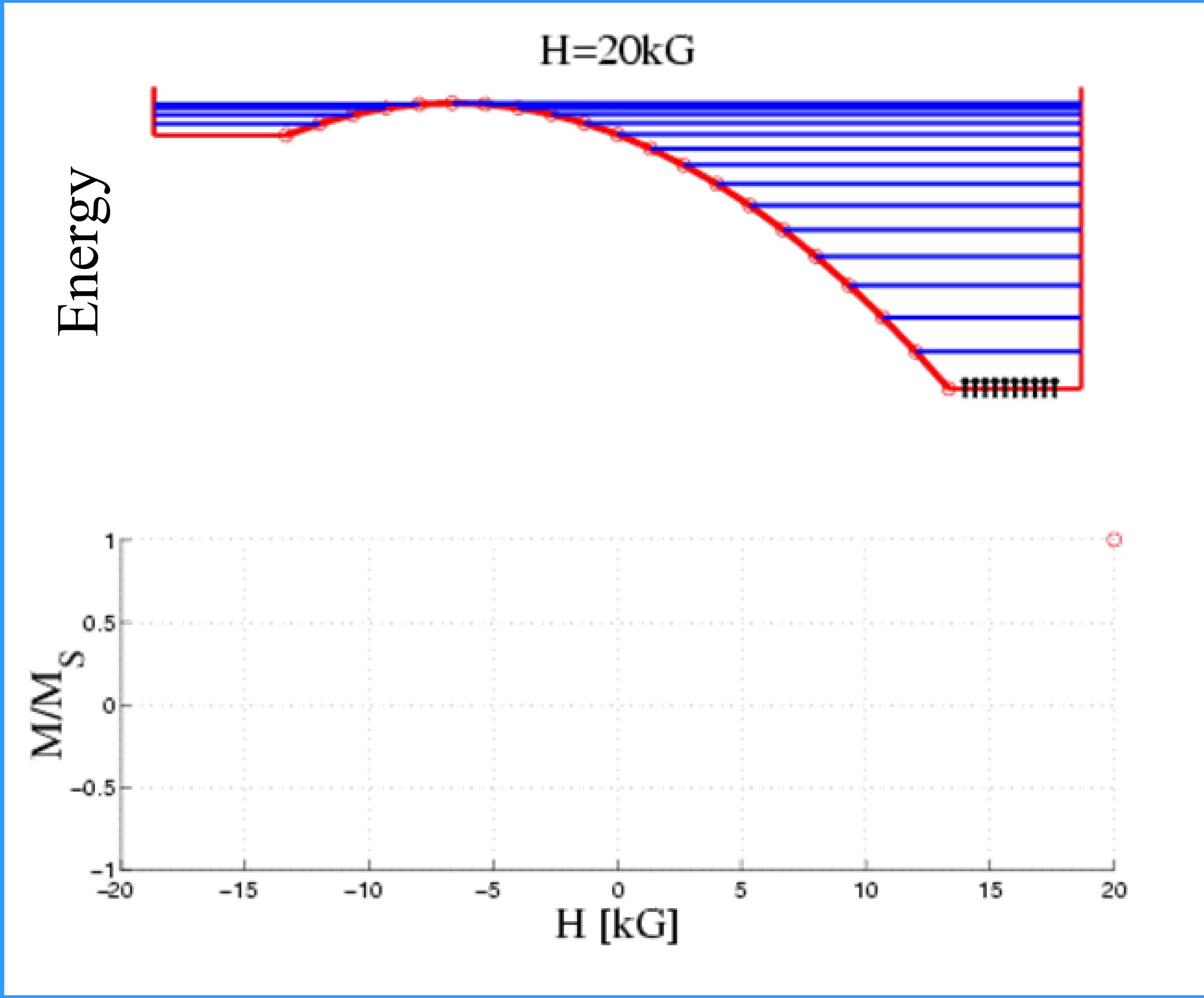


Landau Zener model

$$P_{m,m'} = 1 - \exp\left[-\frac{\pi \Delta^2_{m,m'}}{2\hbar g \mu_B |m - m'| dH/dt} \right]$$



The model and the hysteresis loop



Δ – theory and experiment

Chudnovsky and Garanin: (PRB 87 187203 (2001))

$$\Delta_{-S,S} = \frac{8D}{[(S-1)!]^2}(2S)!\left(\frac{E}{8D}\right)^S \longrightarrow \Delta_{-10,10} \approx 7\cdot 10^{-10}K$$

theory

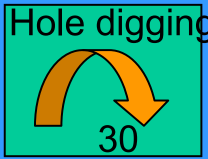
?

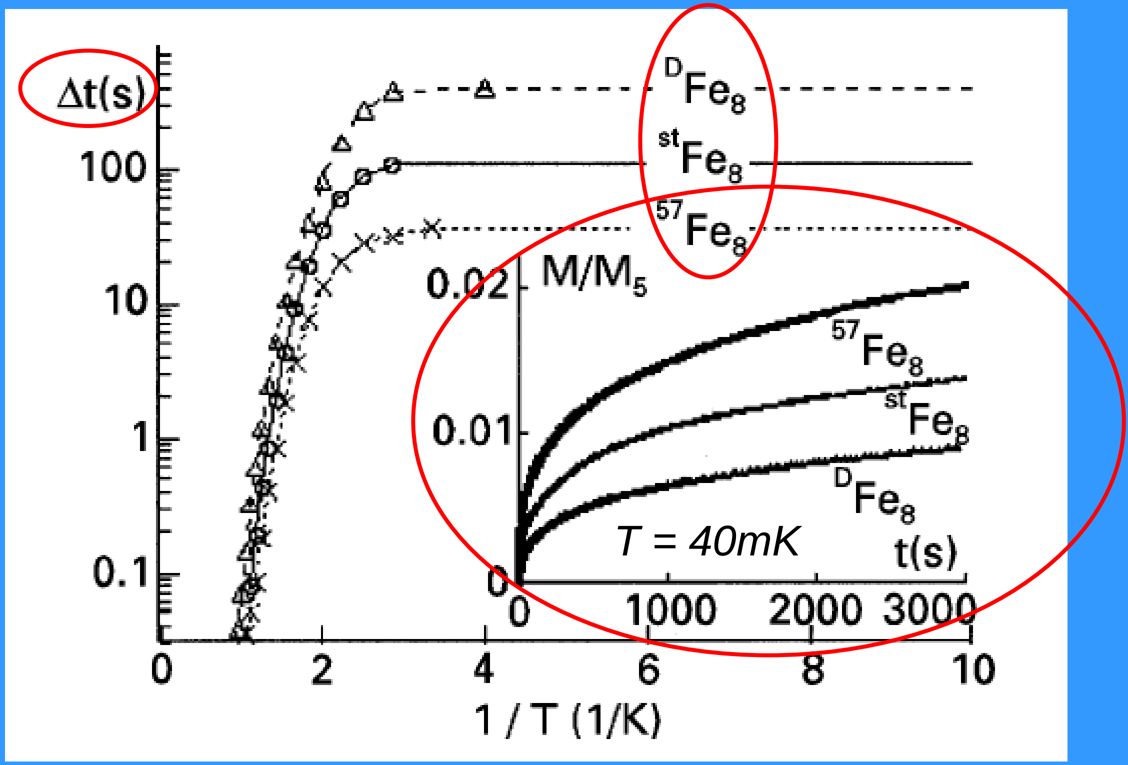
This is only an approximate solution, because even very small higher-order transverse couplings can make an important contribution to Δ_k .

Wernsdorfer et al (J. Appl. Phys. 87 (2000), 5481) have measured Δ_{10} for many different sweeping rates using the Landau-Zener model. Their experiment showed that Δ_{10}~10^{-7}K.

exp

Evidence for the Role of Nuclei in QTM



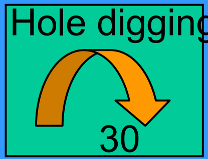


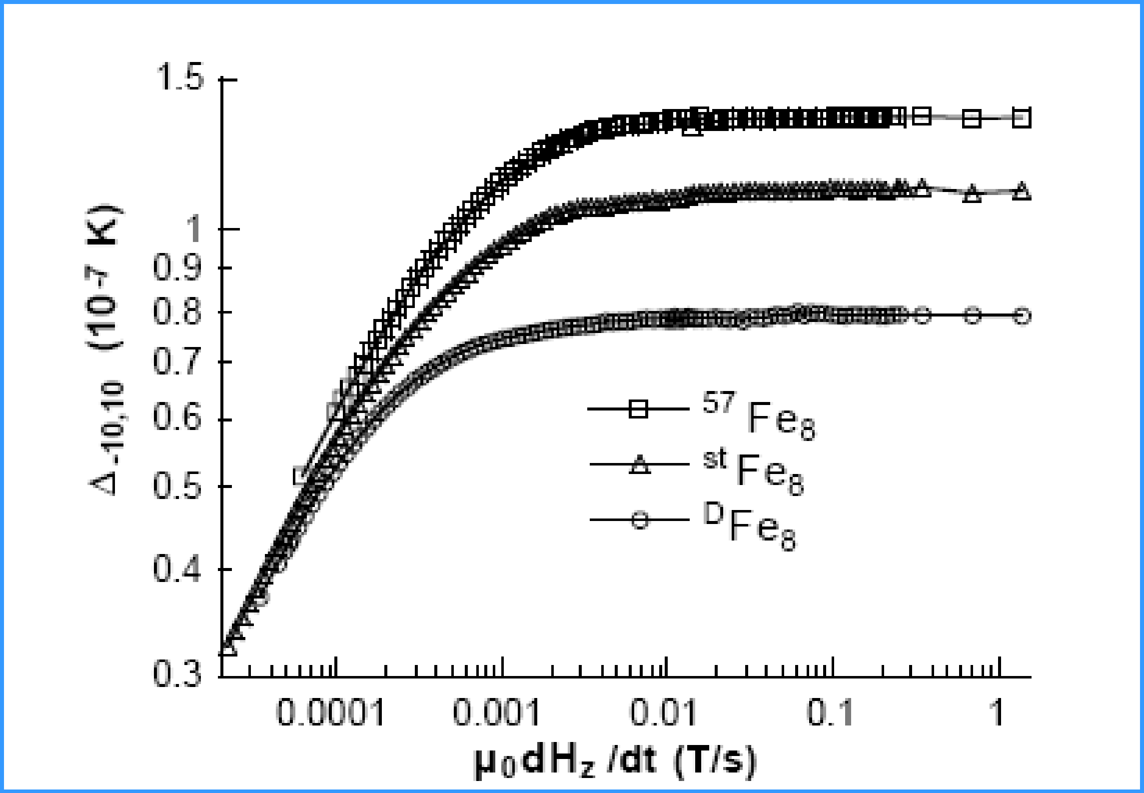
ΔT - The time needed to relax 0.5% of the saturation magnetization

$M_{ini} = 0$
$H = 0.042$ T

R. Sessoli et. al. JMMM 226 (2001) 1954–1960

Evidence for the Role of Nuclei in QTM



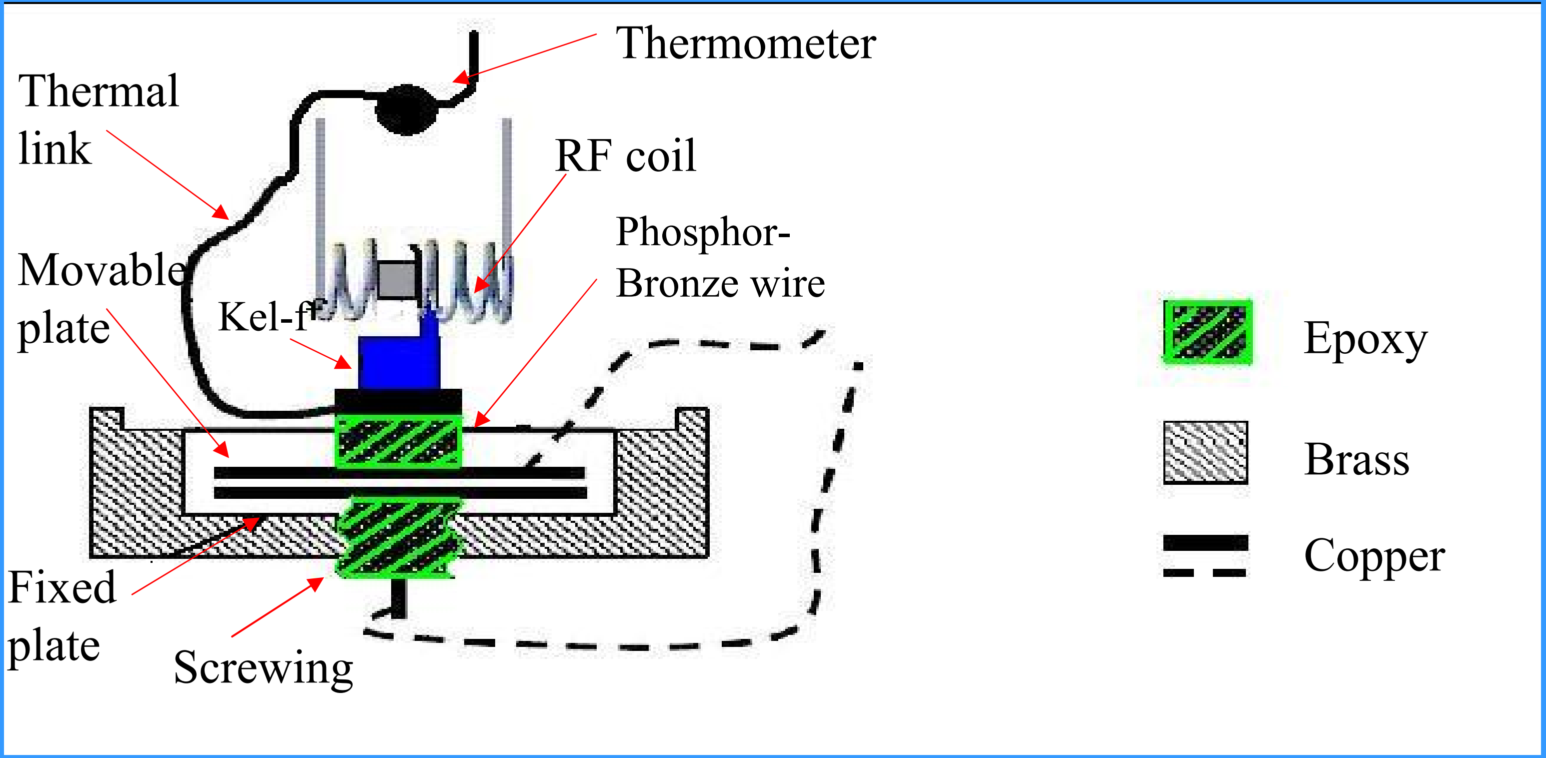


Research Goals

In this research we try to observe the effect of the nuclear spins on the QTM in Fe8 by examining the influence of RF (radio frequency) on its hysteresis loop.

By giving a comb of RF pulses we “warm” the nuclei of the H atoms (more then 100 atoms in every molecule) and look at the effect on the magnetization curve.

Faraday force magnetometer – The load cell



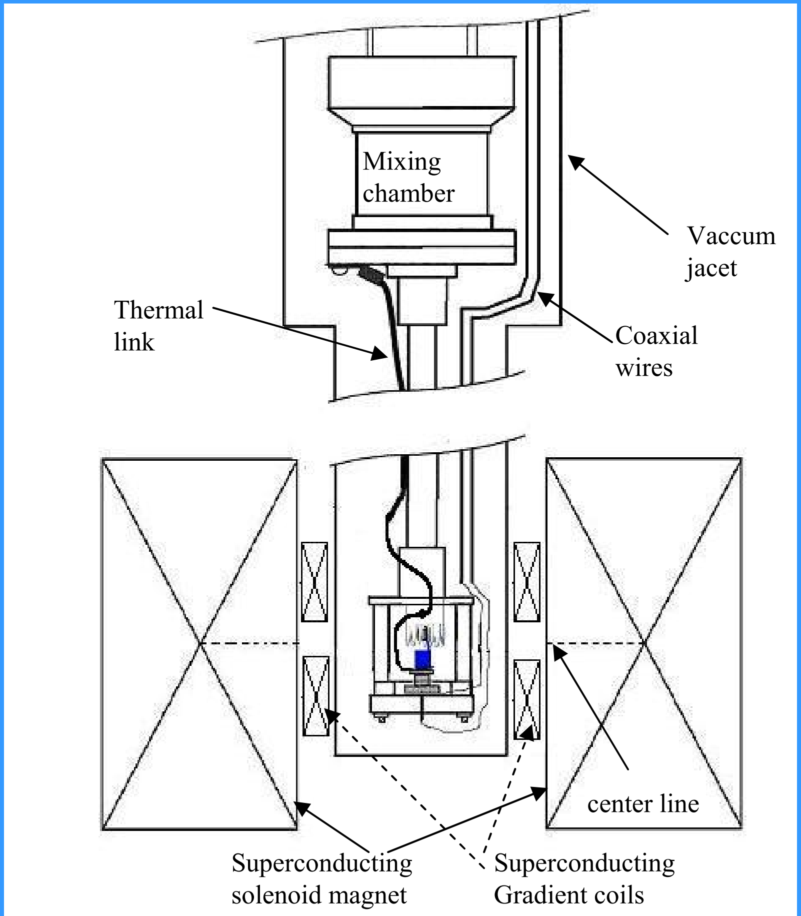
- Measuring the varying capacitance.
- spatially varying magnetic field → magnetic force
- The sample is glued with GE-Varnish to kel-f (without protons) as a thermal link to avoid metallic parts near the coil.

Faraday force magnetometer – inside the DR

DR 48

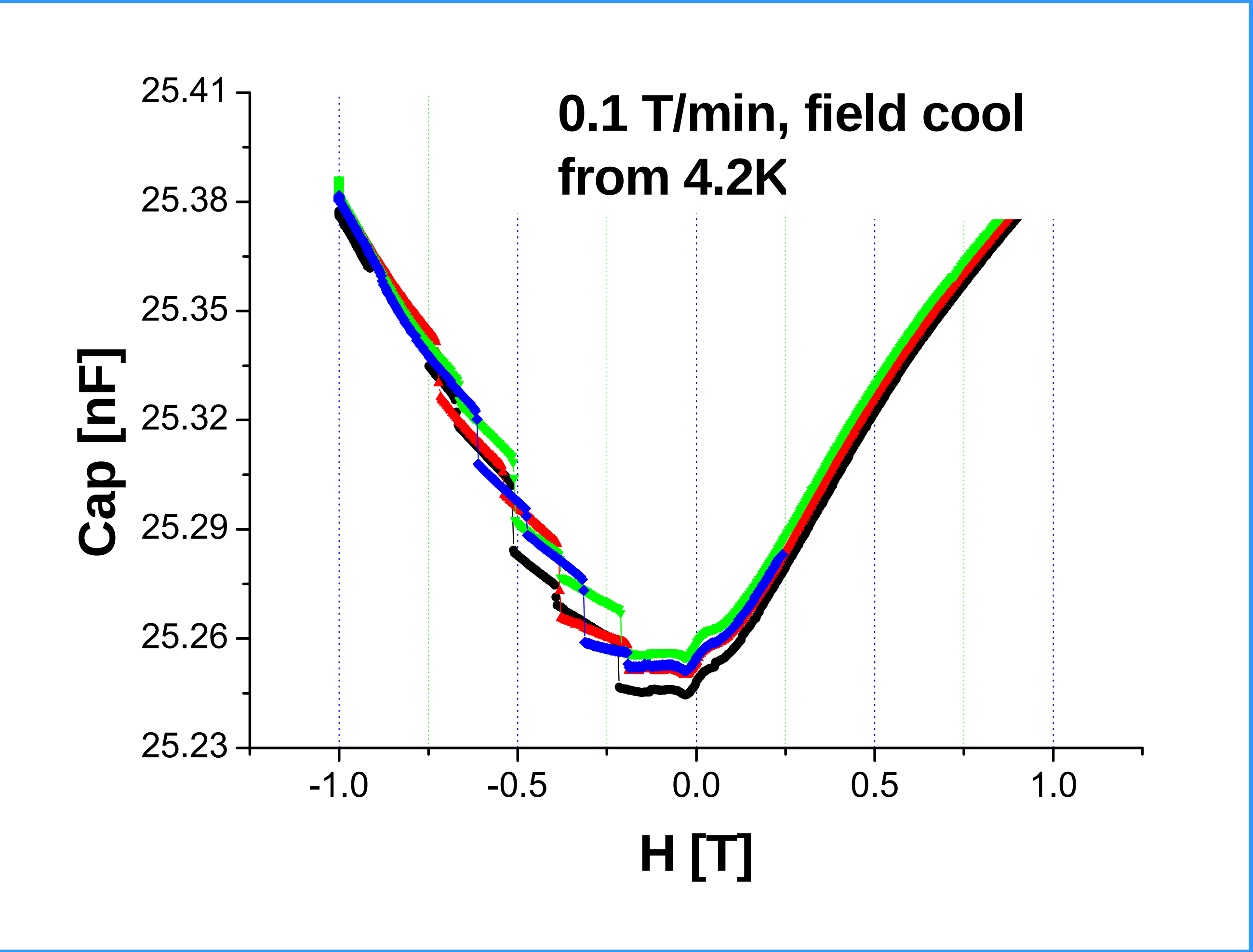
$$C_0^{-1} - C^{-1} = a \cdot M_z \frac{dB_z}{dz}$$

a – Calibration constant



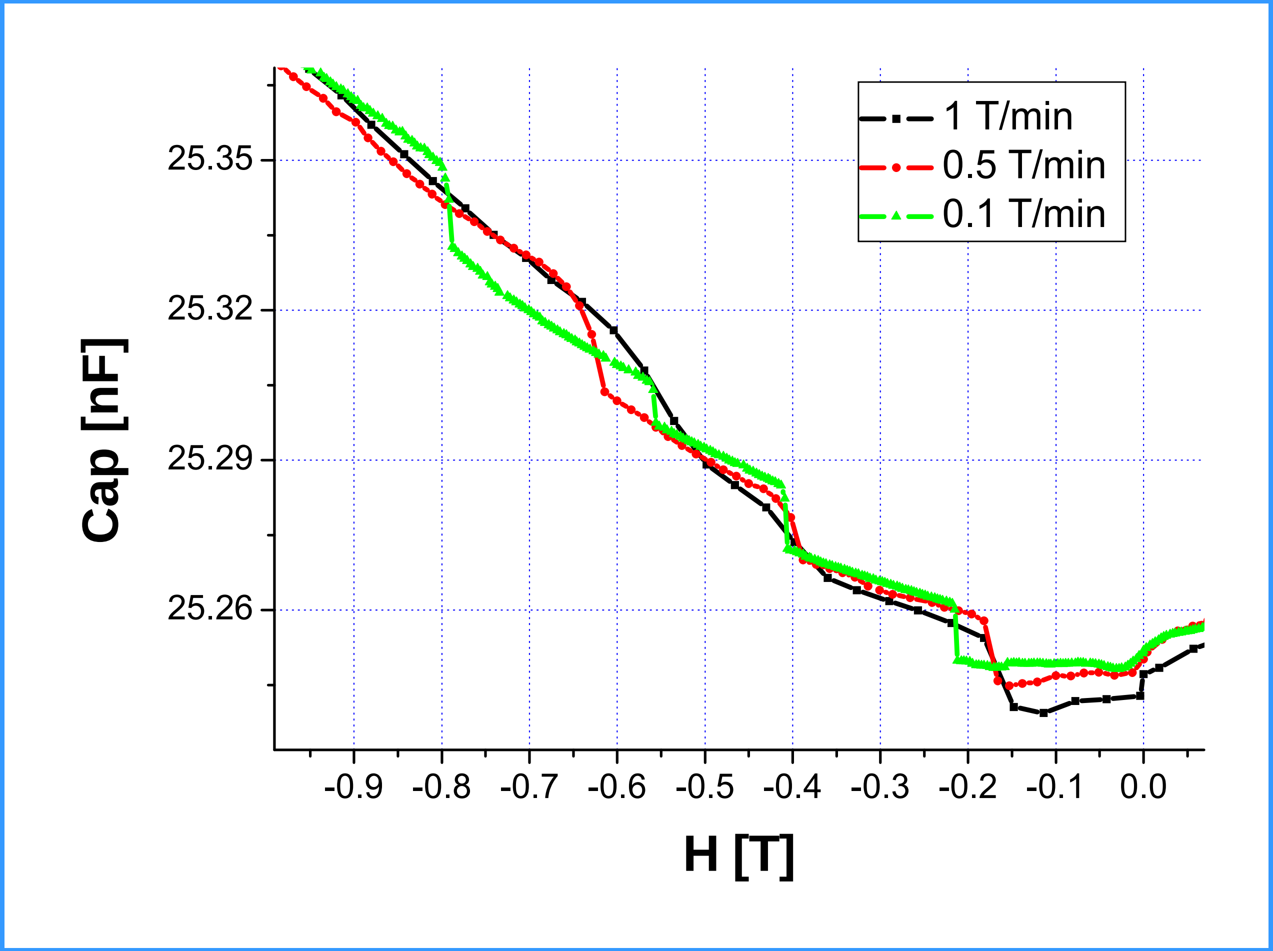
The load cell device, displaced from the center of a solenoid magnet in a dilution refrigerator.

Magnetization measurements



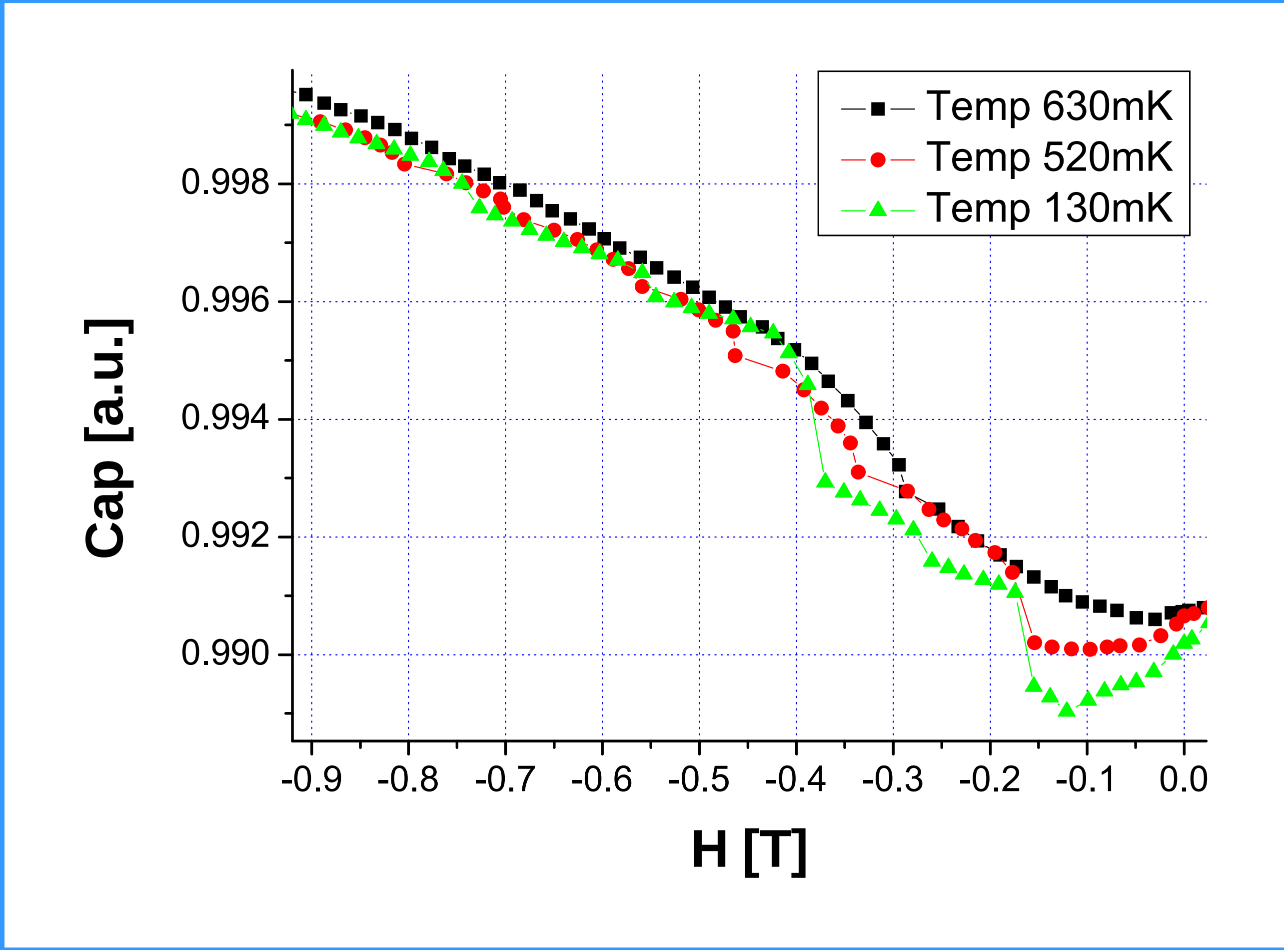
- Because the sample is off-center, the gradient is a function of *H*.

Field sweep rate dependance



- base temperature, 1 [T]/[min]=16.66 [mT]/[sec]

Temperature dependance



- The temperature of the sample is higher then the resistor

(mesearment while cooling, sweep rate 0.5T/min)

NMR Spectrometer

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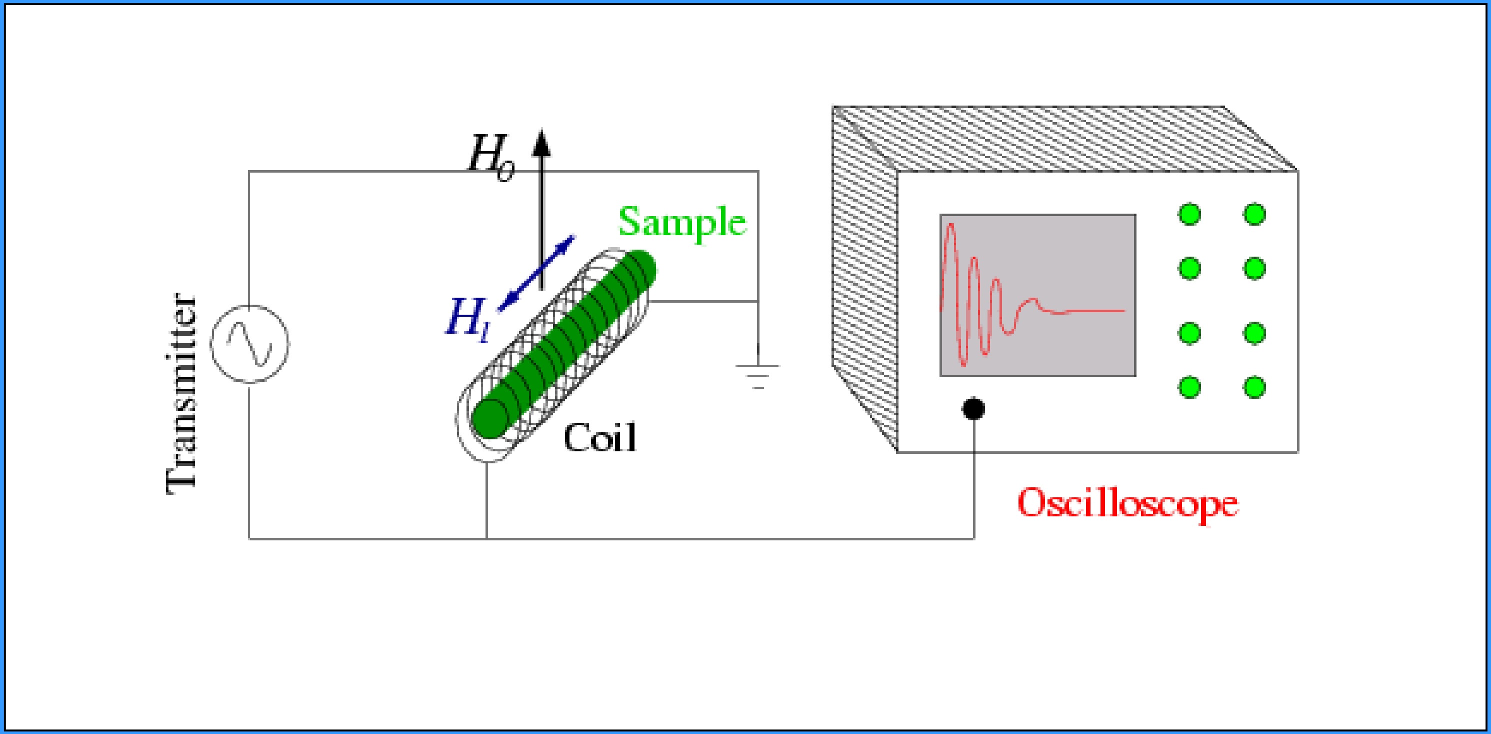
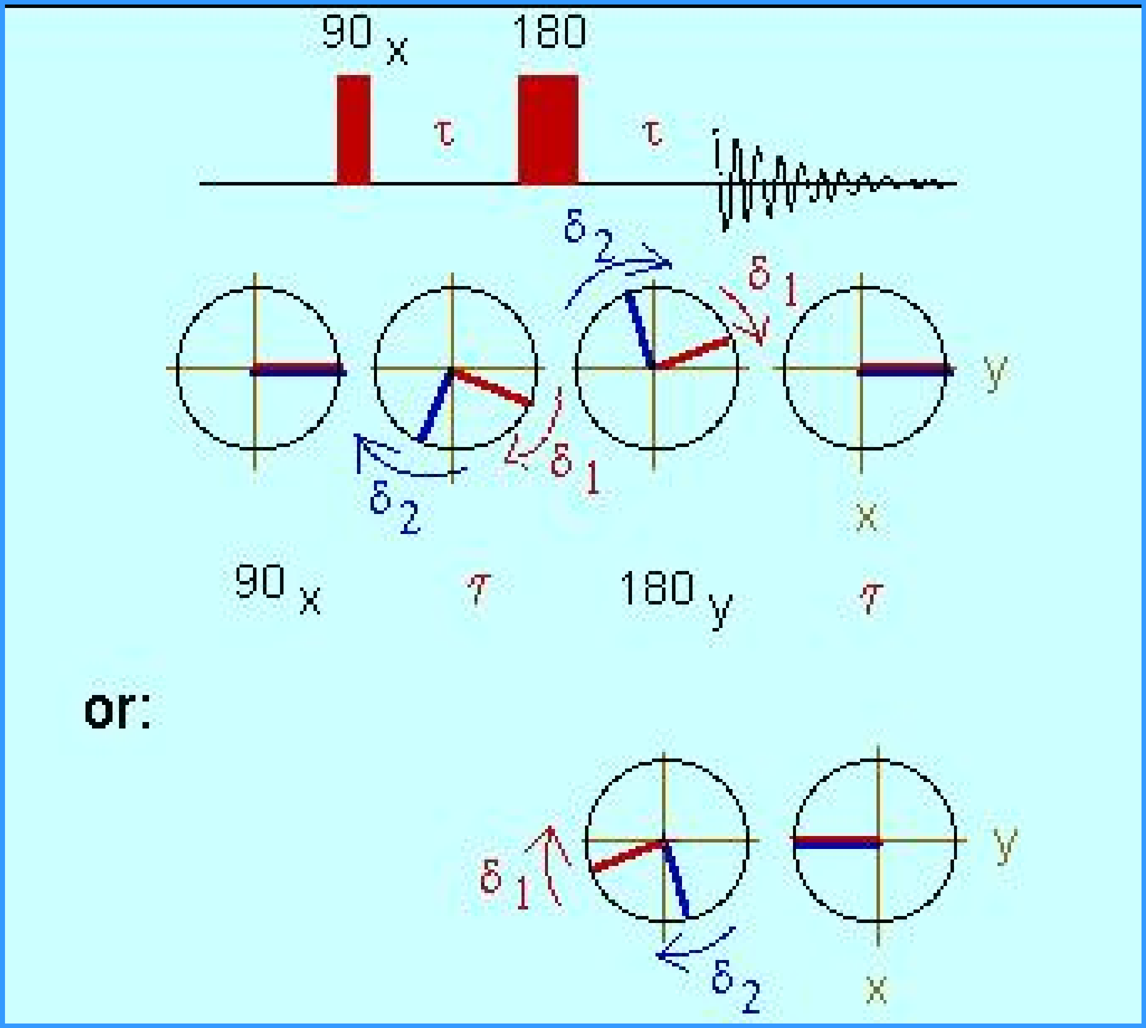
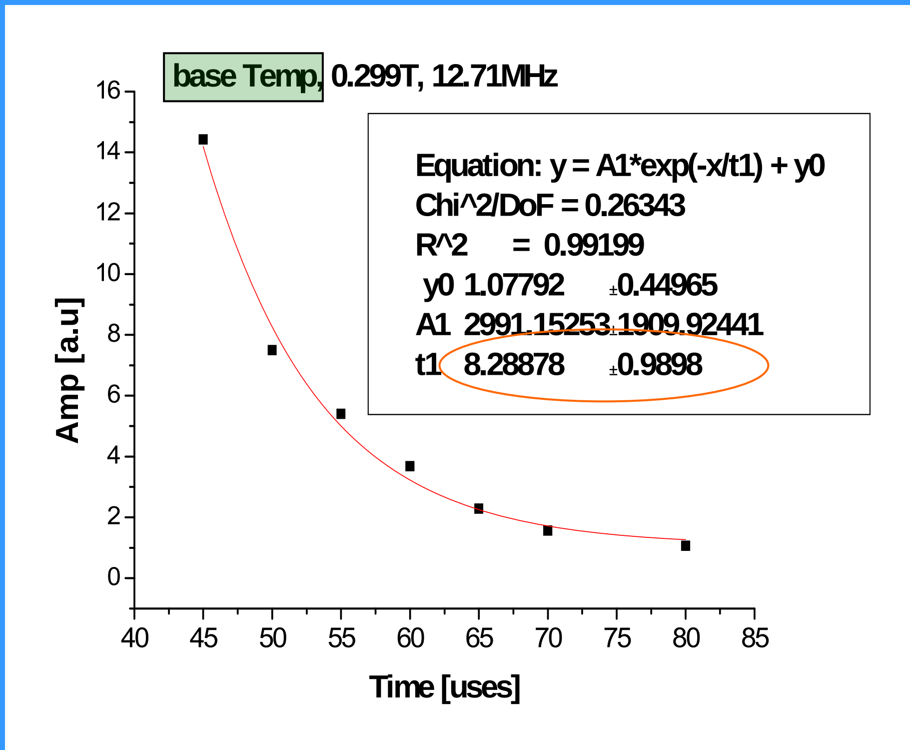


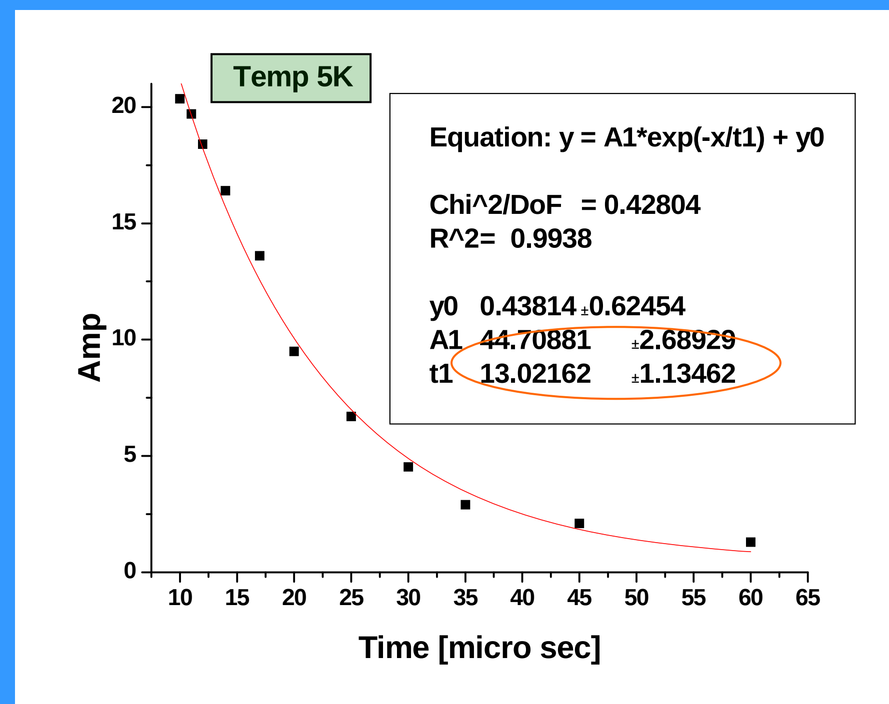
NMR - T_2 measurement



NMR data of Fe8 - T2

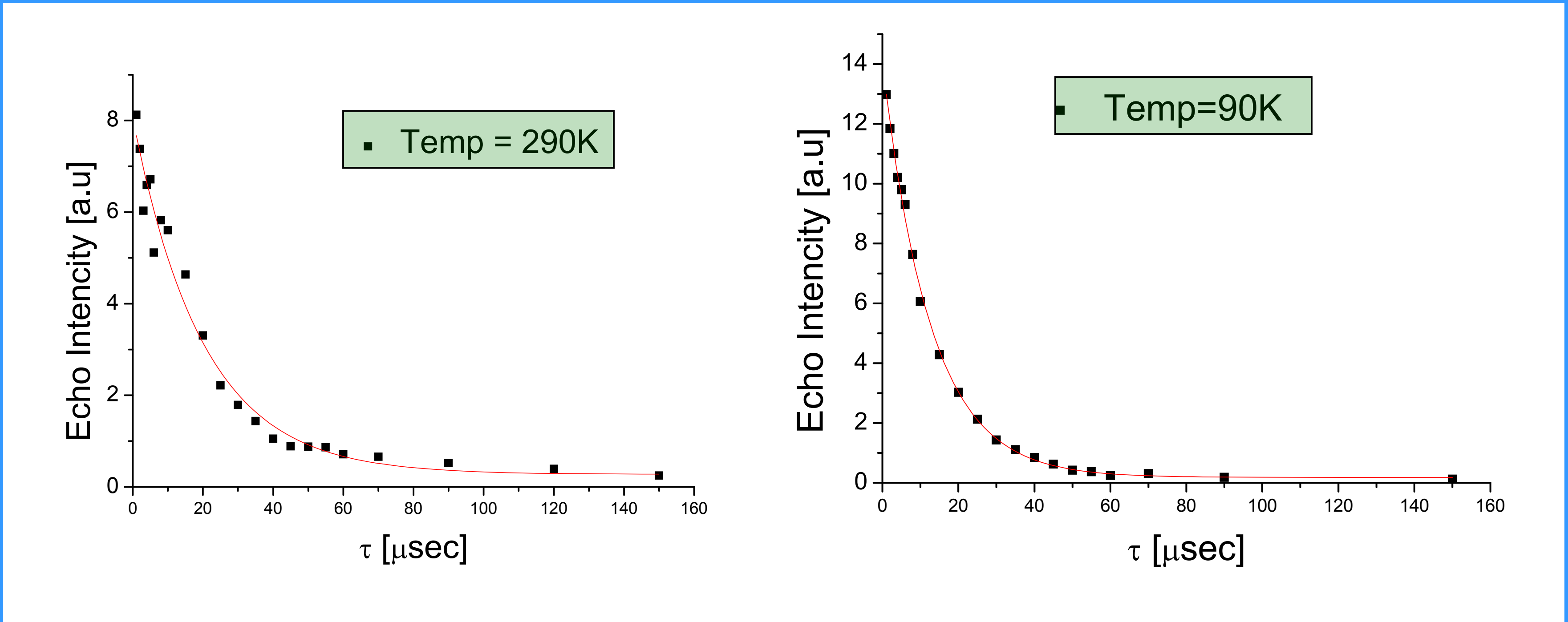
Ueda T2





T_2 NMR – High Temp

pure crystals in NMR system (without G-Varnish)

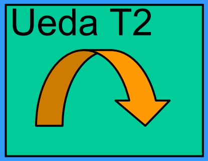


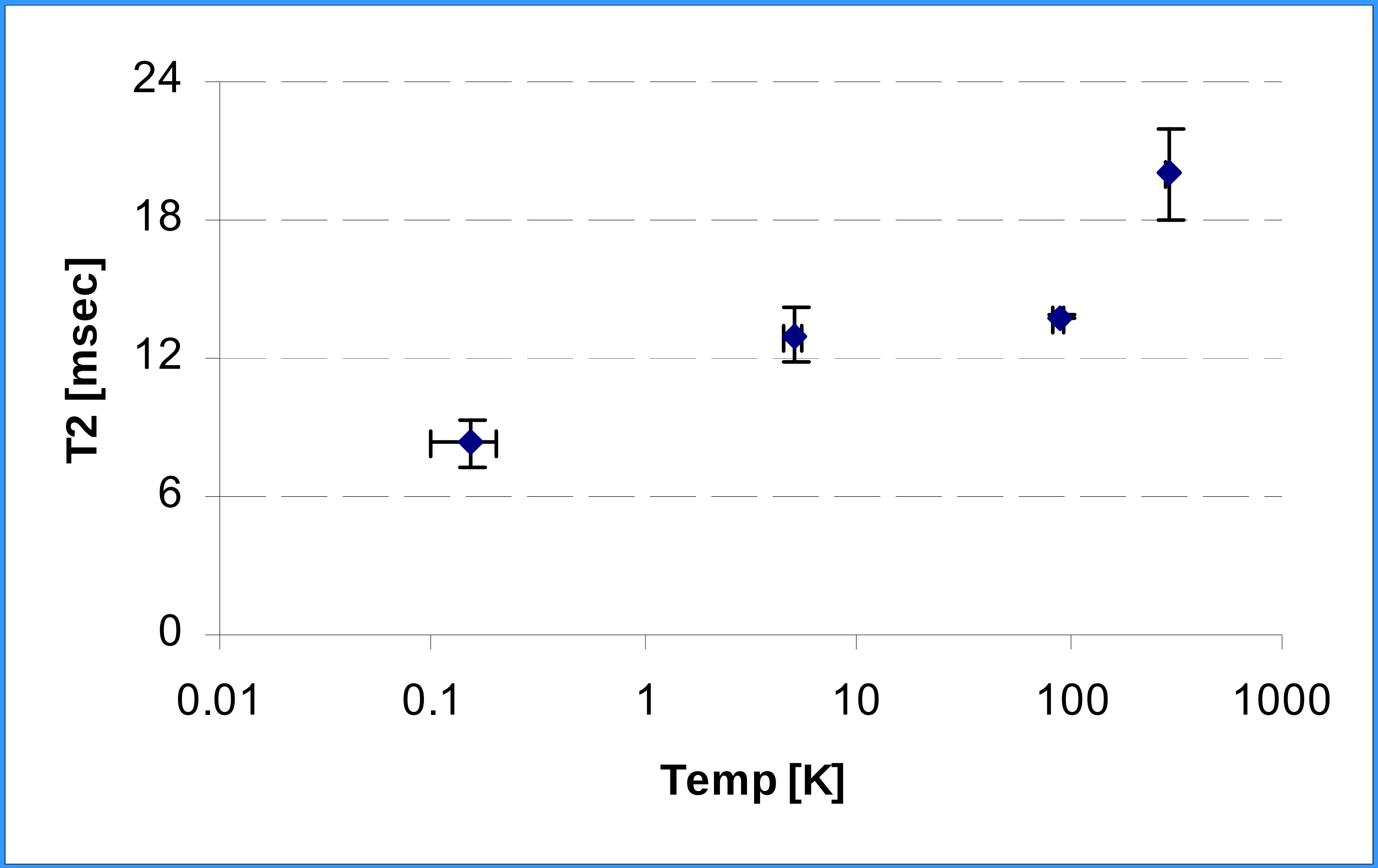
the line is a fit to the function:

$y = A_1 * \exp(-x/T_2) + y_0$

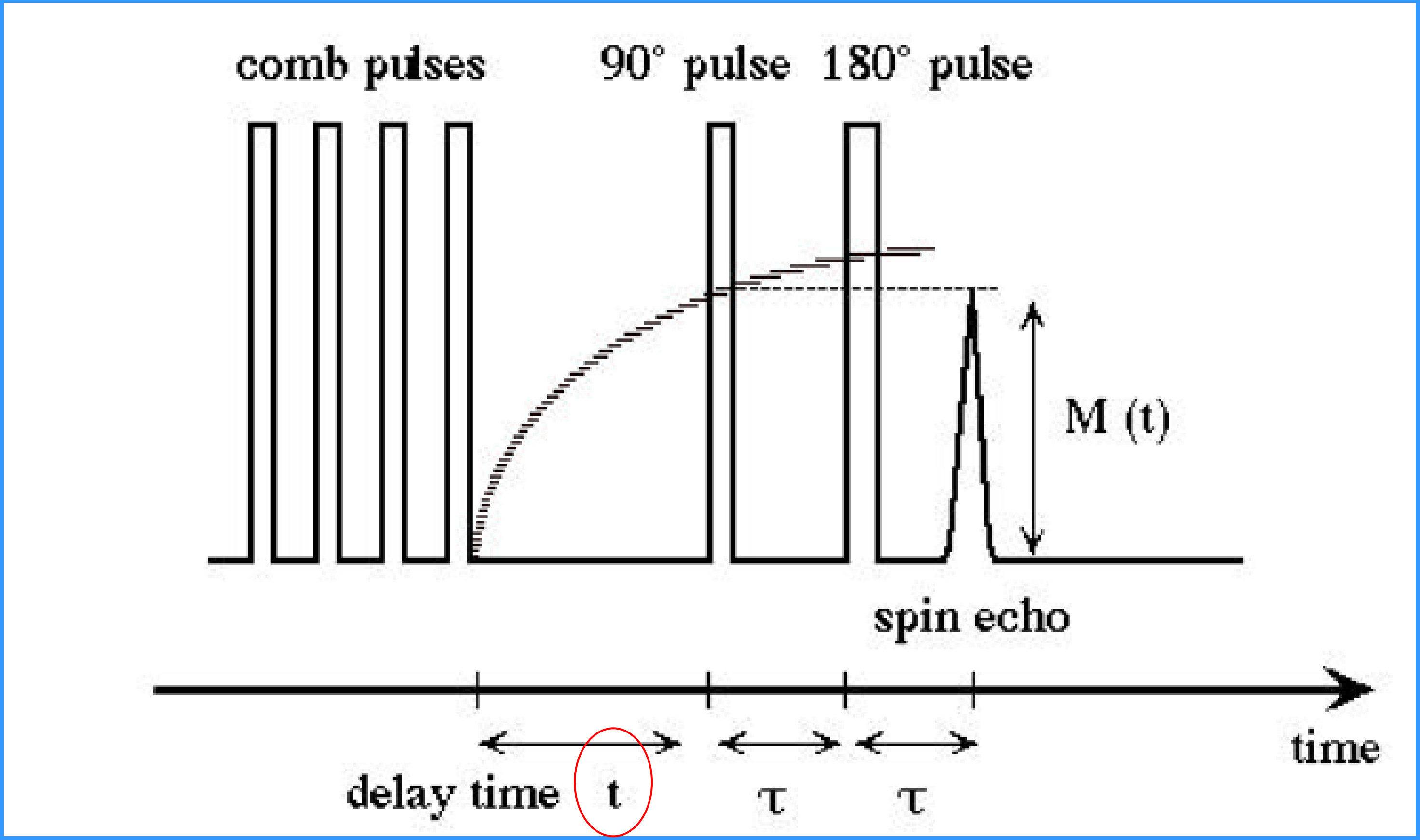
$T_{2\ (290K)} = 20 \pm 2$ [μsec] and $T_{2\ (90K)} = 13.8 \pm 0.13$ [μsec].

T2 - Temperature dependence



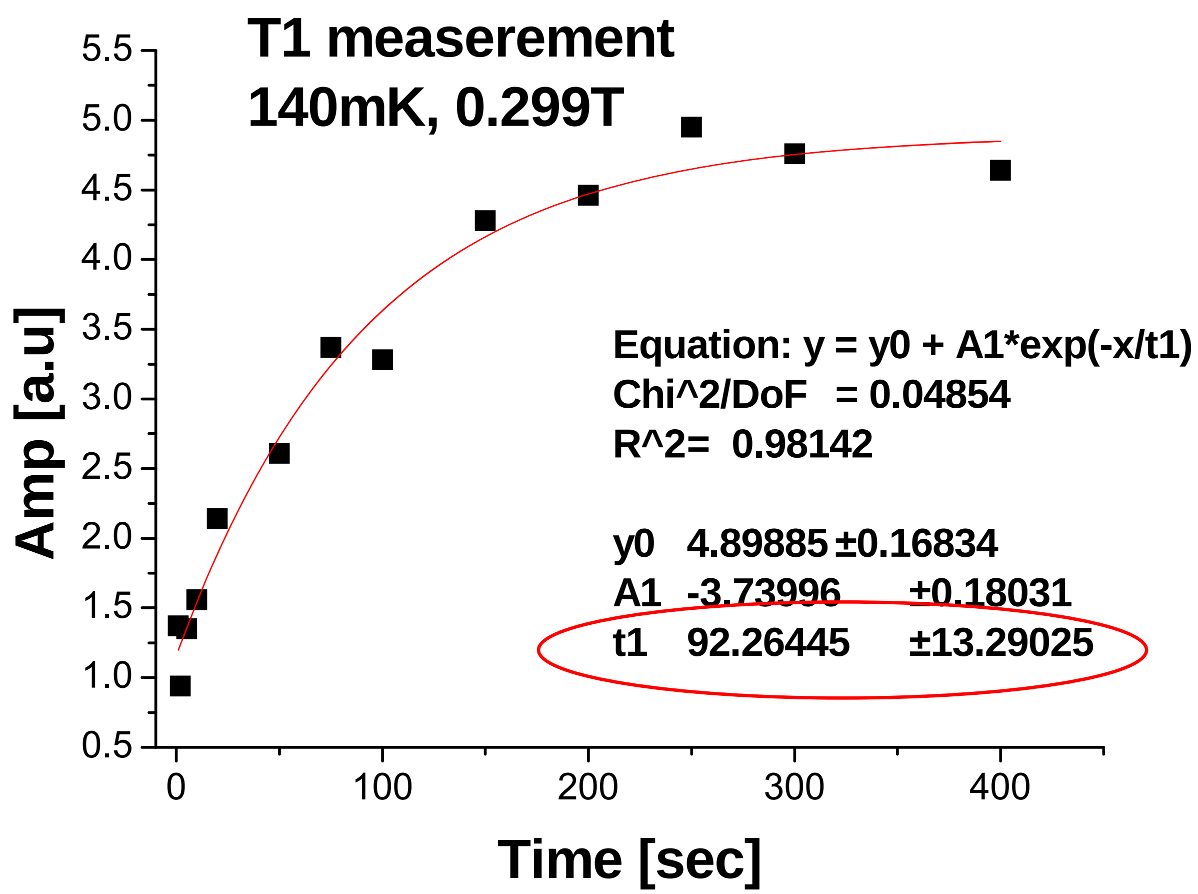


NMR - T_1 measurement



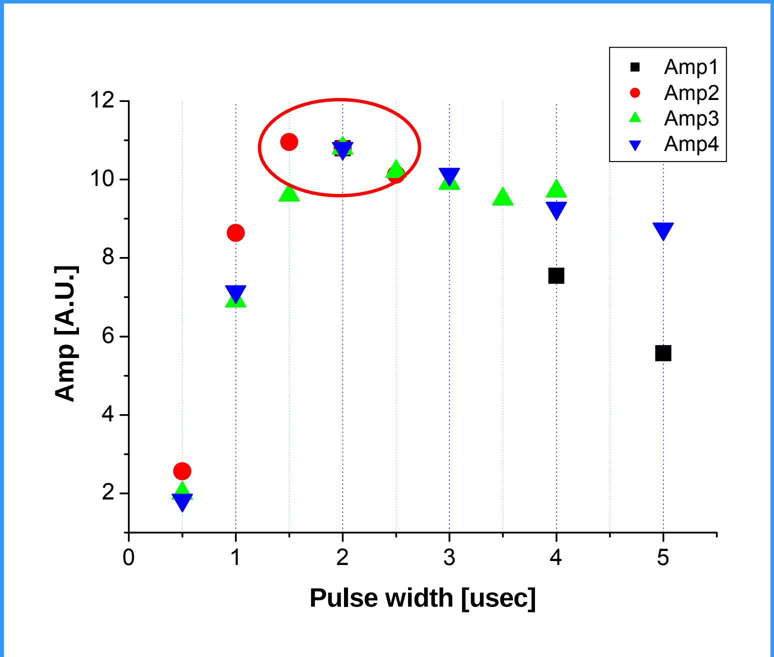
NMR data of Fe8 - T1

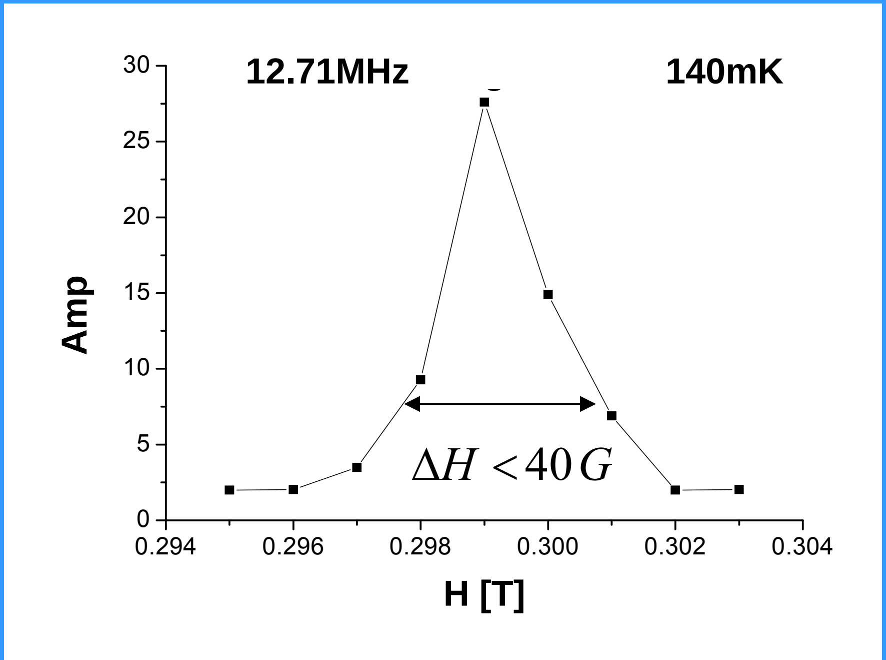
Ueda T2



NMR data of Fe8 - Pulse length

Ueda T2





$$pulse = 2 \pm 0.5\mu \xrightarrow{\omega=\gamma H} H_1 = 120 \pm 30\,G$$

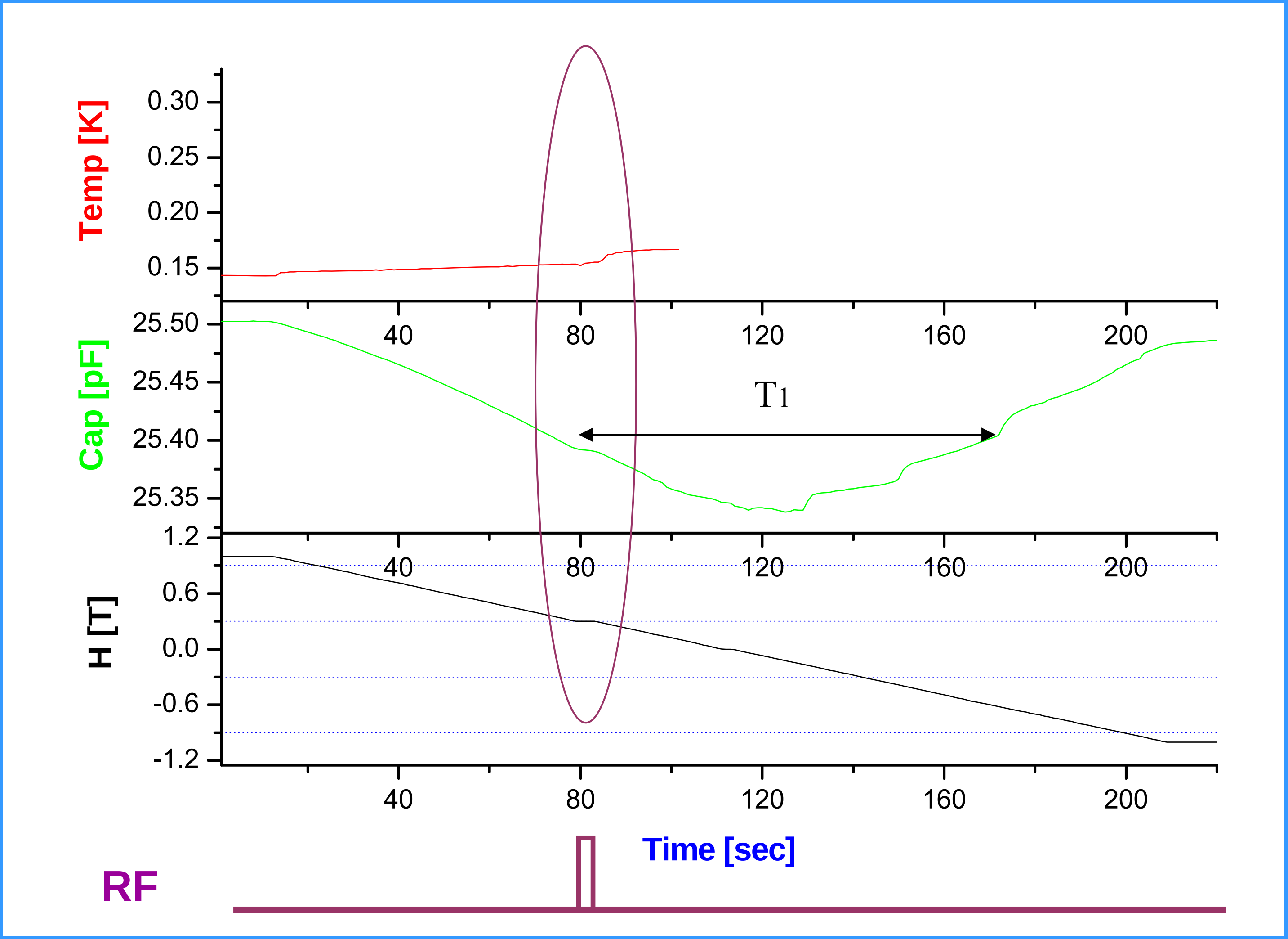
$\Delta H < H_1 \longrightarrow$ The RF excites all the “visible” protons

Measuring with RF

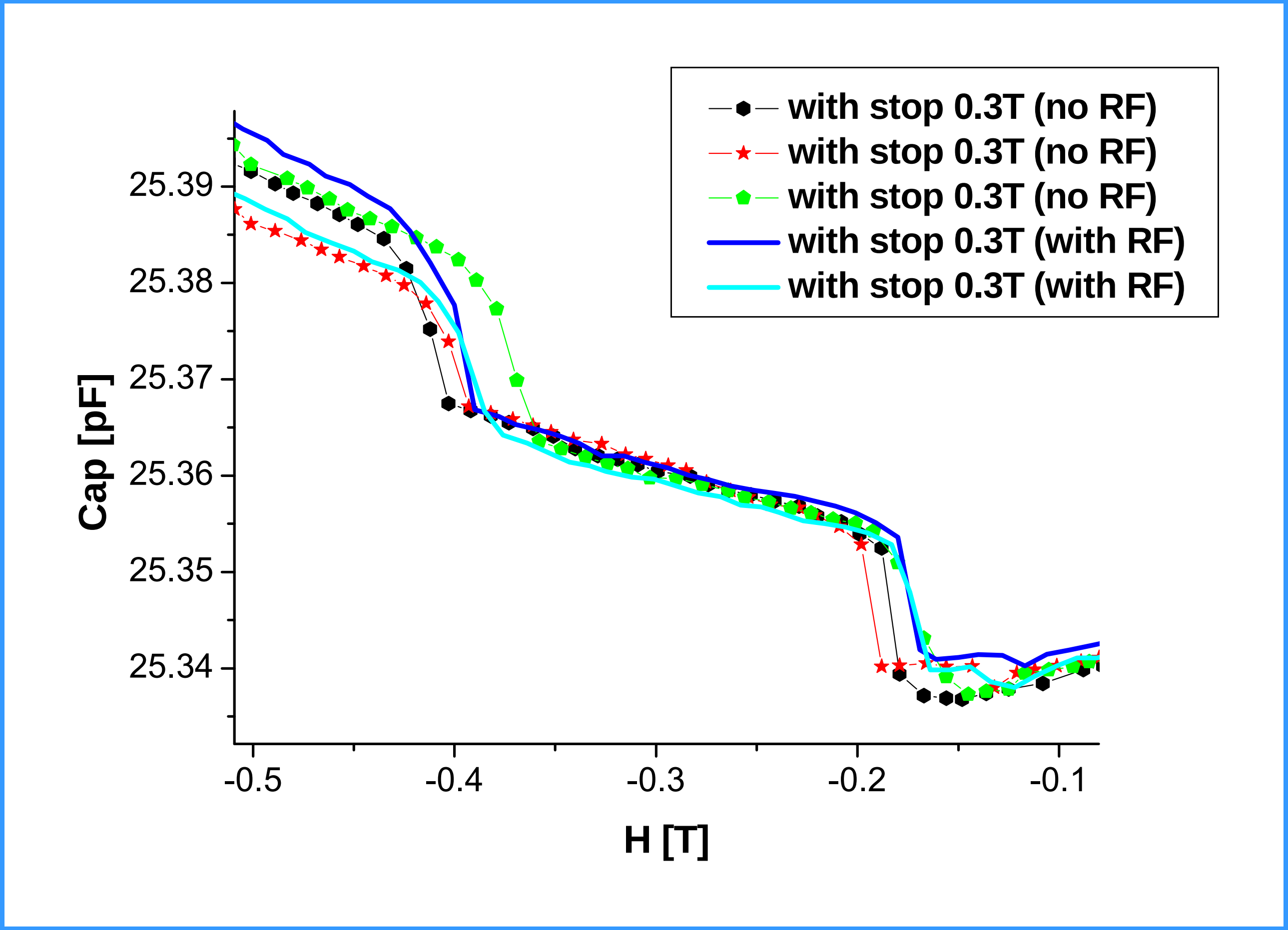
- We saw that we can saturate the nuclei (we give a comb of pulses until the echo is gone).
- For technical reasons we can detect NMR signal only above ~0.3T (12MHz).
- Trying to transmit near or between the jumps cause thermally assisted QTM.
- T1 is in the order of 100 sec.

- Therefore we decided to transmit at 0.3T (when the jumps are expected at negative field) and sweep the field with a rate of 0.5 T/min and see if it is effecting the jumps height.

Measuring with RF



Measuring with RF



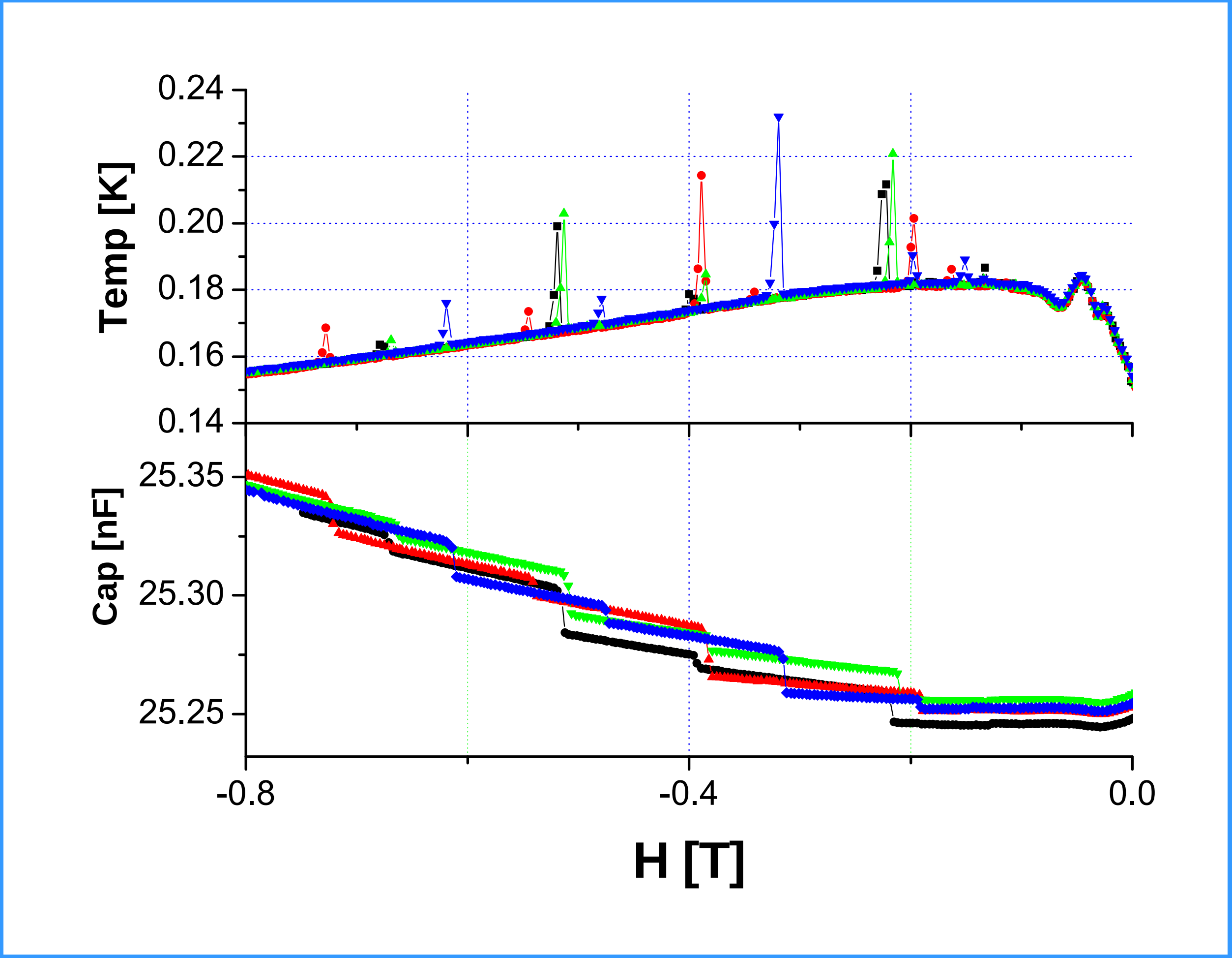
We don't see any effect of the RF radiation.

Conclusions - NMR

- We are convinced that the jumps come from the sample, but we are not sure why they are irreproducible.
- We are confidant at the NMR T_1 and T_2 measurements.
- We don’t see any effect of the RF radiation.

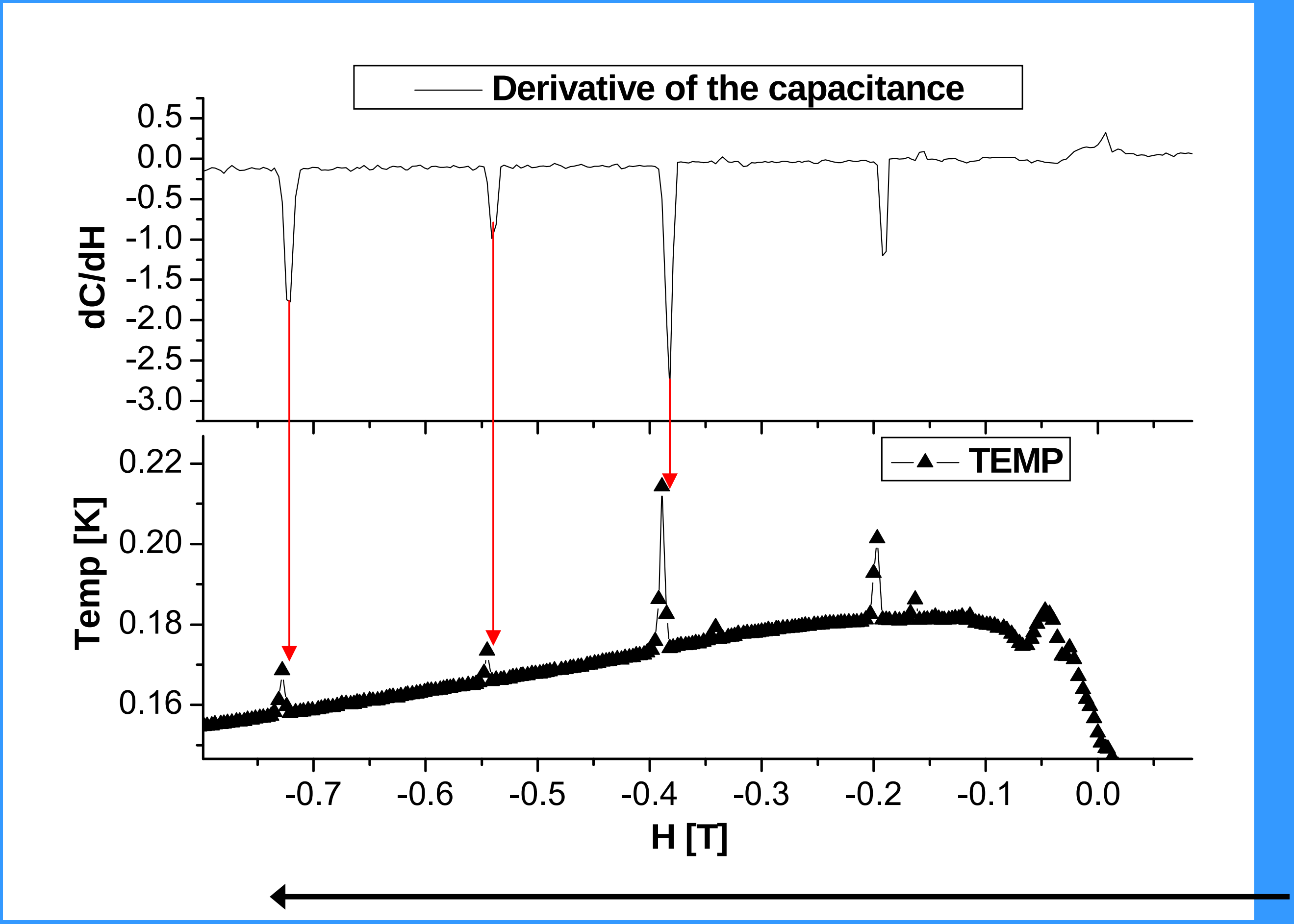
But…

Jumps and Temperature



sweep rate 0.1T/min

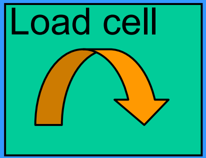
Jumps and Temperature



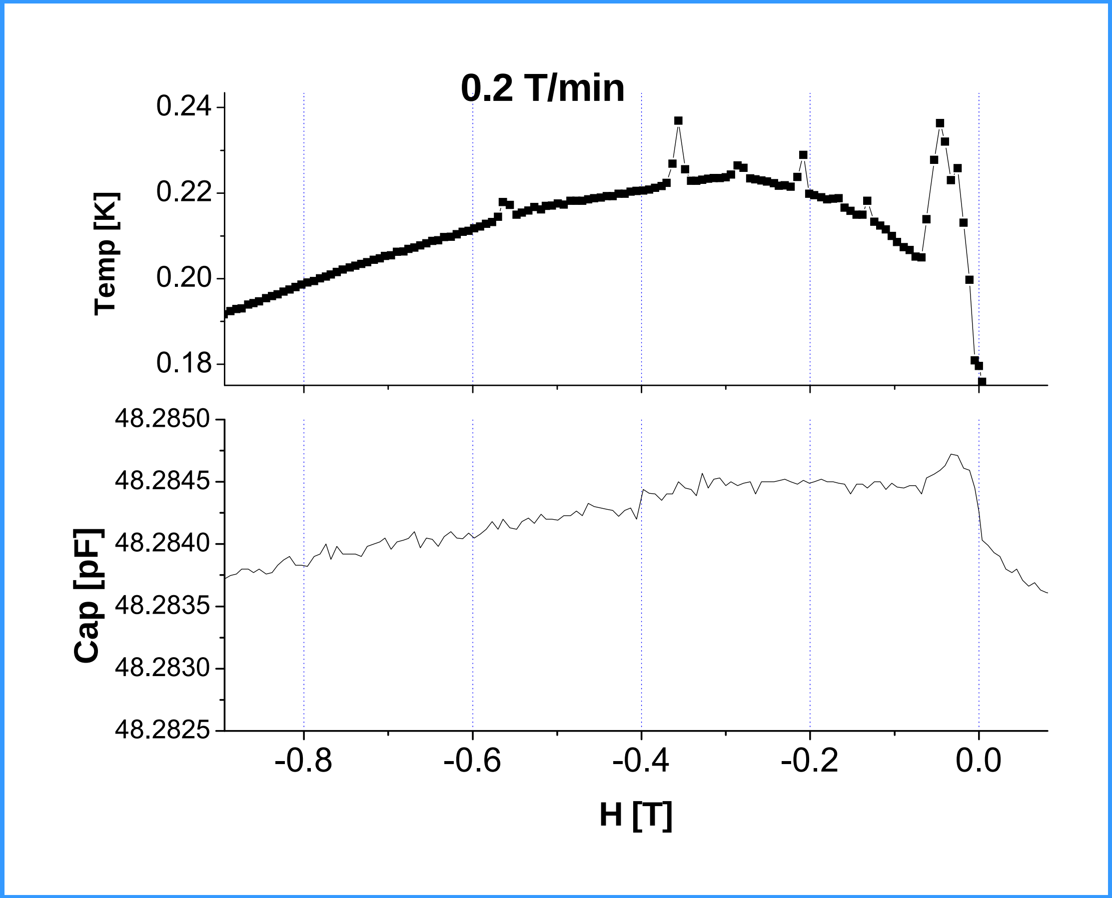
From positive to negative magnetic field

(sweep rate 0.1T/min)

Jumps and Temperature

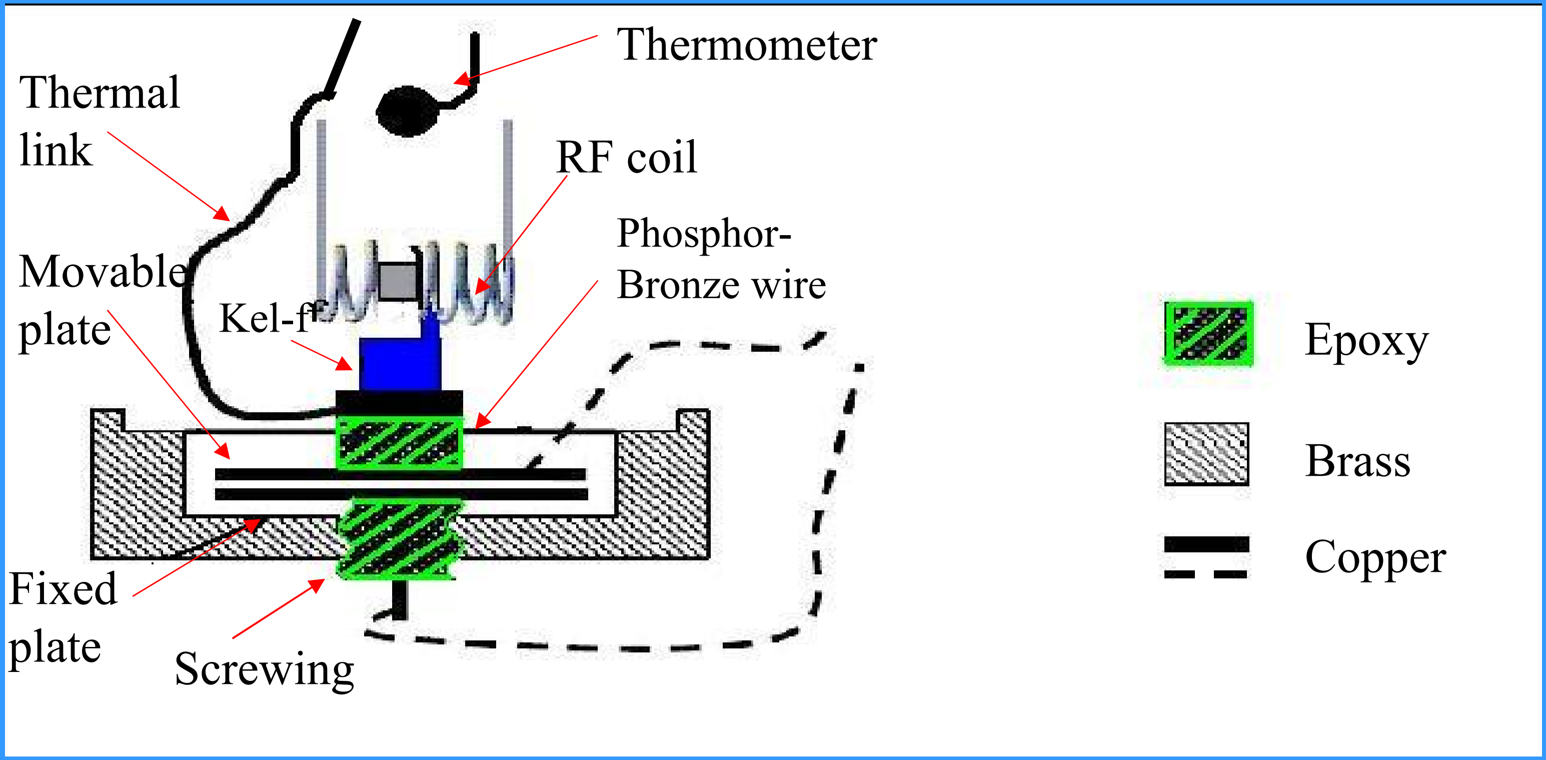


- Same measurement with “fixed” capacitance (no moving parts)



sweep rate 0.2T/min

New setup for the Faraday force magnetometer

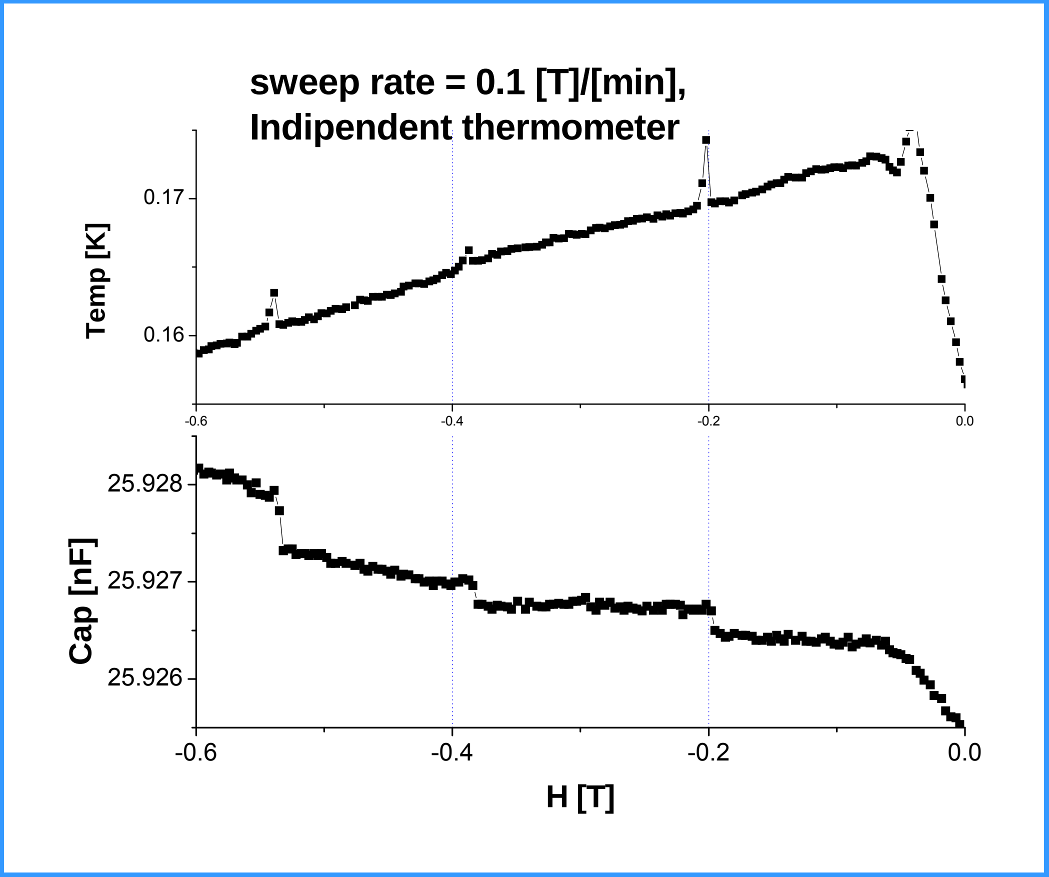


- The thermometer and the sample are connected to the DR separately.

Jumps and Temperature

Load cell

Same measurement without close thermal link between the sample and the thermometer.



Super-radiance

Superradiance from Crystals of Molecular Nanomagnets

E. M. Chudnovsky[1] and D. A. Garanin[2]

[1]*Department of Physics and Astronomy, Lehman College, City University of New York, 250 Bedford Park Boulevard West, Bronx, New York 10468-1589*

[2]*Institut für Physik, Johannes-Gutenberg-Universität, D-55099 Mainz, Germany*

(Received 18 April 2002; published 20 September 2002)

We show that crystals of molecular nanomagnets can exhibit giant magnetic relaxation due to the Dicke superradiance of electromagnetic waves. Rigorous theory is presented that combines superradiance with the Landau-Zener effect.

DOI: 10.1103/PhysRevLett.89.157201

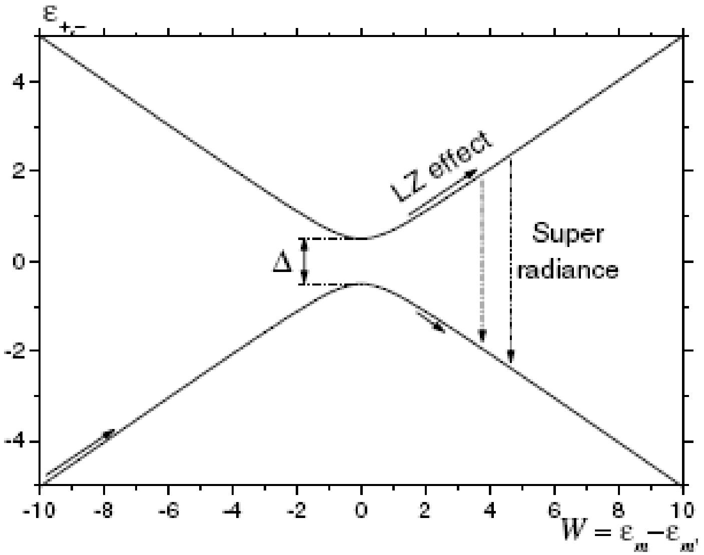


FIG. 1. A pair of tunneling-split levels vs energy bias W. Coherent light is emitted after crossing the resonance via superradiance.

Jumps and Temperature

- A jump in the Capacitance is always followed by a jump in the temperature.
- The temperature jumps are not caused by the mechanical movement of the load cell
- We believe that the cause of the heat burst is super-radiance (which has been seen in similar molecular magnet).

End

The exchange pathways connecting iron(III) in Fe8

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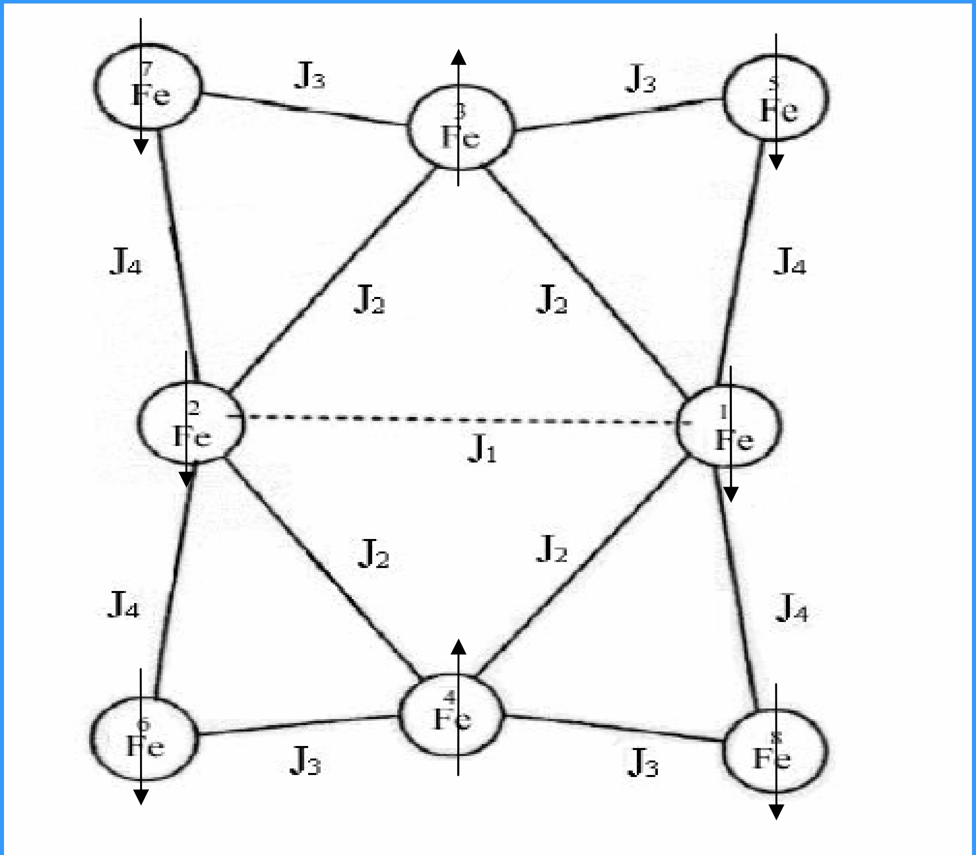

J_1= -147K

J_2= -173K

J_3= -22K

J_4= -50K

C. Delfs, et al. Inorg. Chem. **32**, 3099 (1993).

Blocking Temperature

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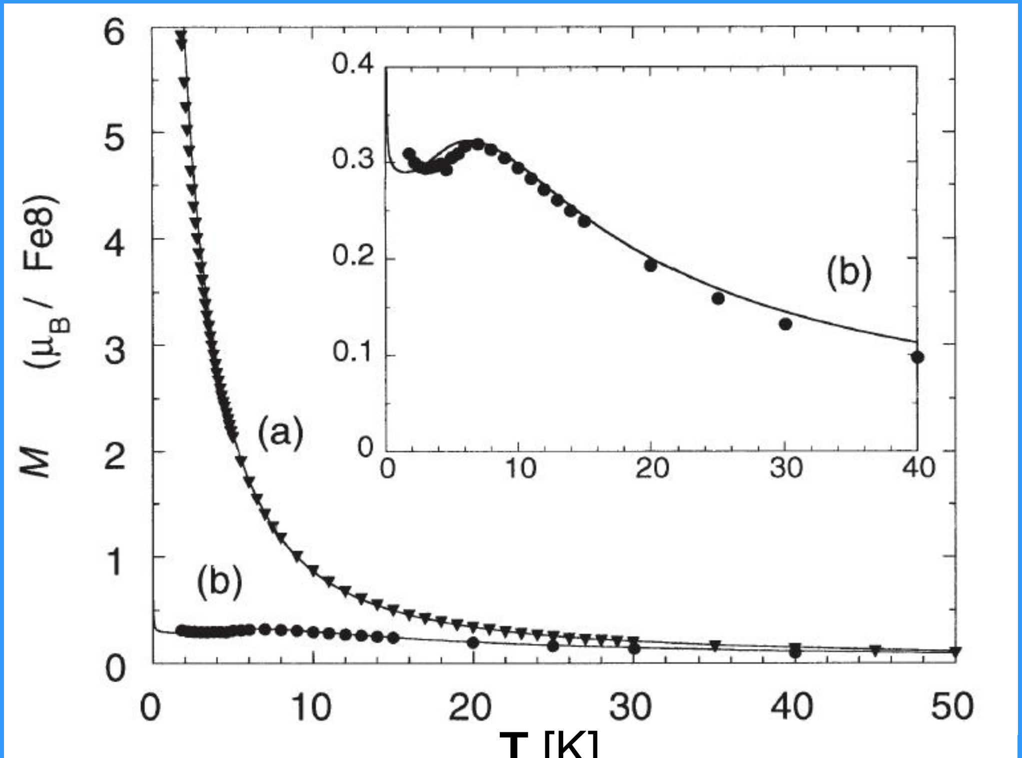
At temperatures lower than the magnetic coupling J between ions inside the molecule, the spins of the ions are locked, and the molecules behave like non -interacting spins.



(a) parallel to the easy axis

(b) perpendicular to the easy axis.

M. Ueda & S. Maegawa, J. Phys. Soc. Jpn. 70 (2001)

Zero field splitting

back

- The large S ground state has 2S+1 spin microstates, which correspond to the M_S states in the absence of **transverse anisotropy**.
- These can be split up in zero field by spin-orbit coupling or magnetodipolar interactions if S>½. This is called **zero-field splitting**.
- **Magnetodipolar interactions** are usually small (10^{-1} cm^{-1})
- Spin-orbit coupling can **mix orbital angular momentum** of the electronically excited state **into the ground state**.

Zero field splitting

back

- The **zero-field splitting** can be described by a term in the **spin Hamiltonian**:

$$\hat{\mathbf{H}}_{ZFS} = \hat{\mathbf{S}} \cdot \mathbf{D} \cdot \hat{\mathbf{S}}$$

- Here **D** is a 3 x 3 matrix:

$$\mathbf{D} = \begin{pmatrix} D_{xx} & 0 & 0 \\ 0 & D_{yy} & 0 \\ 0 & 0 & D_{zz} \end{pmatrix}$$

- We can rewrite the spin Hamiltonian term as:

$$\hat{\mathbf{H}}_{ZFS} = D[\hat{\mathbf{S}}_z^2 - S(S+1)/3] + E(\hat{\mathbf{S}}_x^2 - \hat{\mathbf{S}}_y^2)$$

- where:

$$D = 3D_{zz}/2$$
$$E = |D_{xx} - D_{yy}|/2$$

- The *D* term **changes the energies** of the M_S states.
- The *E* terms **mixes the M_S states** (with ΔM_S=2), i.e. the pure M_S states are no longer the energy eigenstates of the system.

Hamiltonian of Fe8

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$$H = -\gamma |S_z|^l - \frac{1}{2}\sum_{n=1}^{N} \alpha_n (S_+^n + S_-^n)$$

The effective spin Hamiltonian (without the Zeeman term):

$$\mathscr{H} = \mathbf{D}\, S_z^2 + E\,(S_x^2 - S_y^2) + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4$$

D	$\lvert E/D \rvert$	B_4^0	B_4^2	B_4^4	Lit.
−0.205	0.19	1.6×10^{-6}	-5.0×10^{-6}	-8×10^{-6}	[158]
−0.203	0.160	0.7×10^{-6}	8.06×10^{-8}	5.96×10^{-6}	[160]
−0.205	0.150	1.4×10^{-6}	8.06×10^{-8}	5.96×10^{-6}	[162]

$$O_4^2 = \{[7S_z^2 - S(S+1) - 5](S_+^2 + S_-^2) + (S_+^2 + S_-^2)[7S_z^4 - S(S+1) - 5]\}/4$$

$$O_4^4 = (S_+^4 + S_-^4)/2$$

$$O_4^3 = [S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3)S_z]/4$$

D. Gatteschi and R. Sessoli, Angew. Chem. Int. Ed. 42, No. 3 (2003), p. 268

Experimental realization

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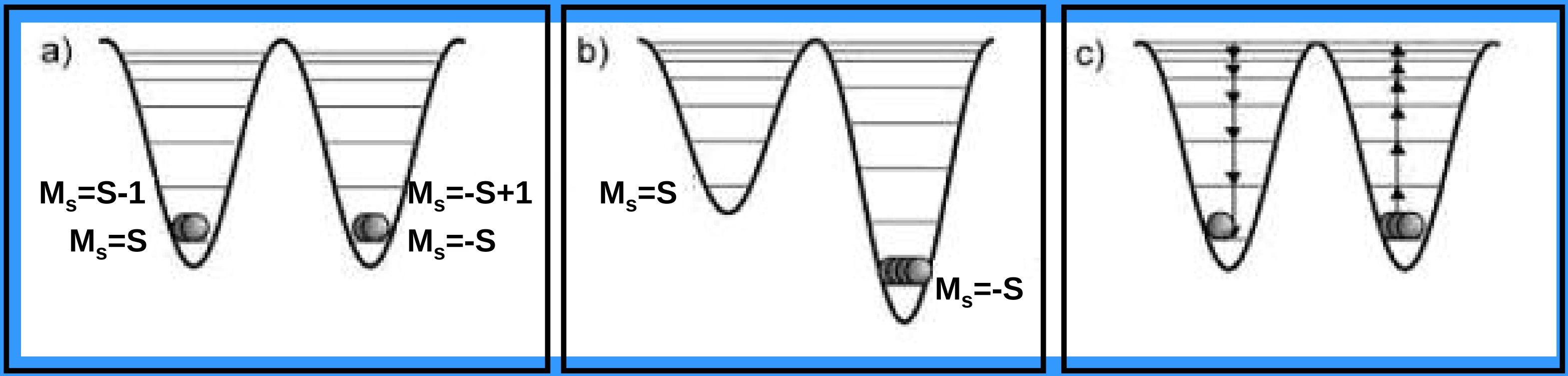
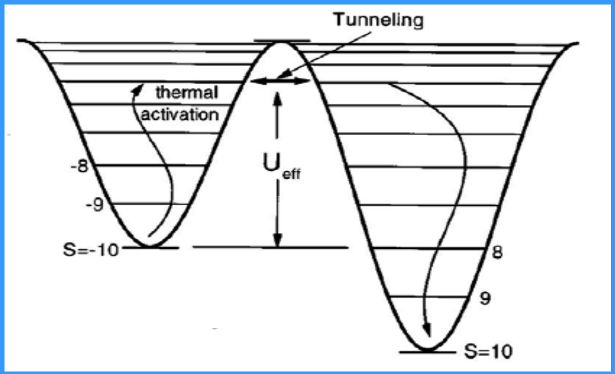


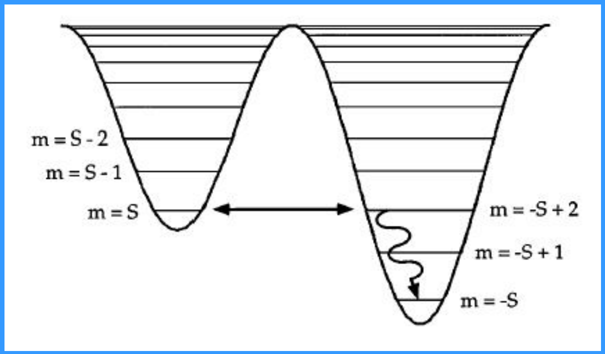
a) In zero field the two wells are equally populated.

b) An applied magnetic field selectively populates the right well.

c) After removing the field the system can returns to equilibrium (thermally) if T is high enough.



Thermally assisted QT



pure QT

The concept of tunnel splitting: S=1/2

$$\mathcal{H} = DS_z^2 + g\mu_B\left(h_x S_x - h_z S_z\right) = \begin{pmatrix} -D/4 - g\mu_B h_z & g\mu_B h_x/2 \\ g\mu_B h_x/2 & D/4 + g\mu_B h_z \end{pmatrix}$$

The eigenvectors and eigenvalues of $\mathcal{H}_0$ are:

$$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \rightarrow E_s = -D/4 + g\mu_B\sqrt{h_x^2 + h_z^2},$$

$$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \rightarrow E_{as} = -D/4 - g\mu_B\sqrt{h_x^2 + h_z^2}$$

$\Delta_0 = g\mu_B h_x$ known as tunnel splitting

$$\left|\left\langle \begin{pmatrix} 1 & 0 \end{pmatrix} e^{\frac{-i\mathcal{H}t}{\hbar}} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right\rangle\right|^2 = \frac{h_x^2}{h_x^2 + h_z^2}\left[\frac{1}{2} - \frac{1}{2}\cos\left(\frac{g\mu_B\sqrt{h_x^2 + h_z^2}\cdot t}{\hbar}\right)\right]$$

The spin will tunnel at a rate given by: $\Delta/\hbar = g\mu_B\sqrt{h_x^2 + h_z^2}\,/\hbar$

The concept of tunnel splitting: S=1/2

$$\mathcal{H} = DS_z^2 + g\mu_B\left(h_x S_x - h_z S_z\right) = \begin{pmatrix} D - g\mu_B h_z & g\mu_B h_x \\ g\mu_B h_x & D + g\mu_B h_z \end{pmatrix}$$

The eigenvectors and eigenvalues of $\mathcal{H}_0$ are:

$$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} \rightarrow E_s = -D/4 + g\mu_B\sqrt{h_x^2 + h_z^2},$$

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$\Delta_0 = g\mu_B h_x$ known as tunnel splitting

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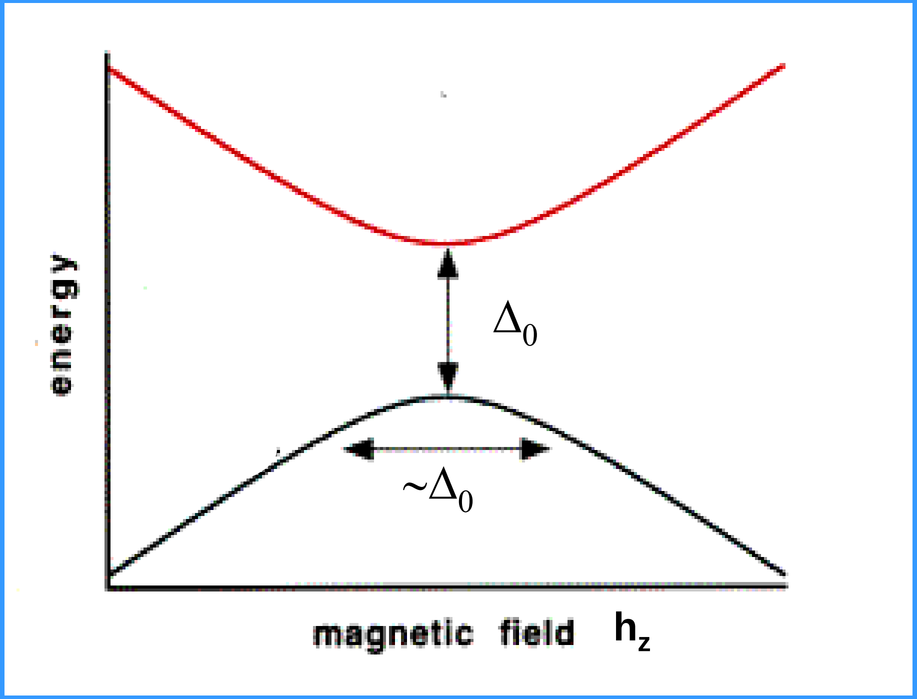
The spin will tunnel at a rate given by: $\Delta/\hbar = g\mu_B\sqrt{h_x^2 + h_z^2}/\hbar$

Zener time



$$\Delta_0 / \tau_{tunnel} > g\mu_B \frac{dh_z}{dt}$$

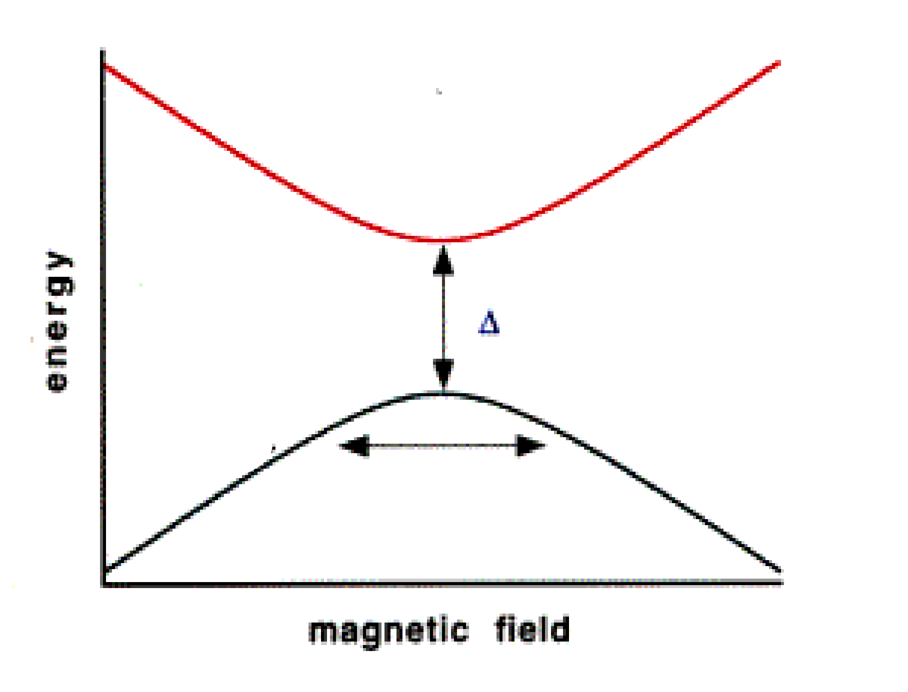
$$\tau_{tunnel} = \frac{\pi}{2\Delta_0}$$

$$\Delta_0 / \left(\pi\hbar / 2\Delta_0 \right) > g\mu_B \frac{dh_z}{dt}$$

$$\Delta_0^2 / \hbar g\mu_B \frac{dh_z}{dt} > 1$$

$$P_{m,m'} = 1\text{-}\exp\left[-\frac{\pi\Delta_{m,m'}^2}{2\hbar g\mu_B |m-m'| dH/dt} \right]$$

Zener Time – Mullen et al



$$\hbar\alpha / \Delta^2 >> 1$$ Adiabatic limit:

$$\rightarrow \tau_z \approx \sqrt{\hbar / \alpha}$$

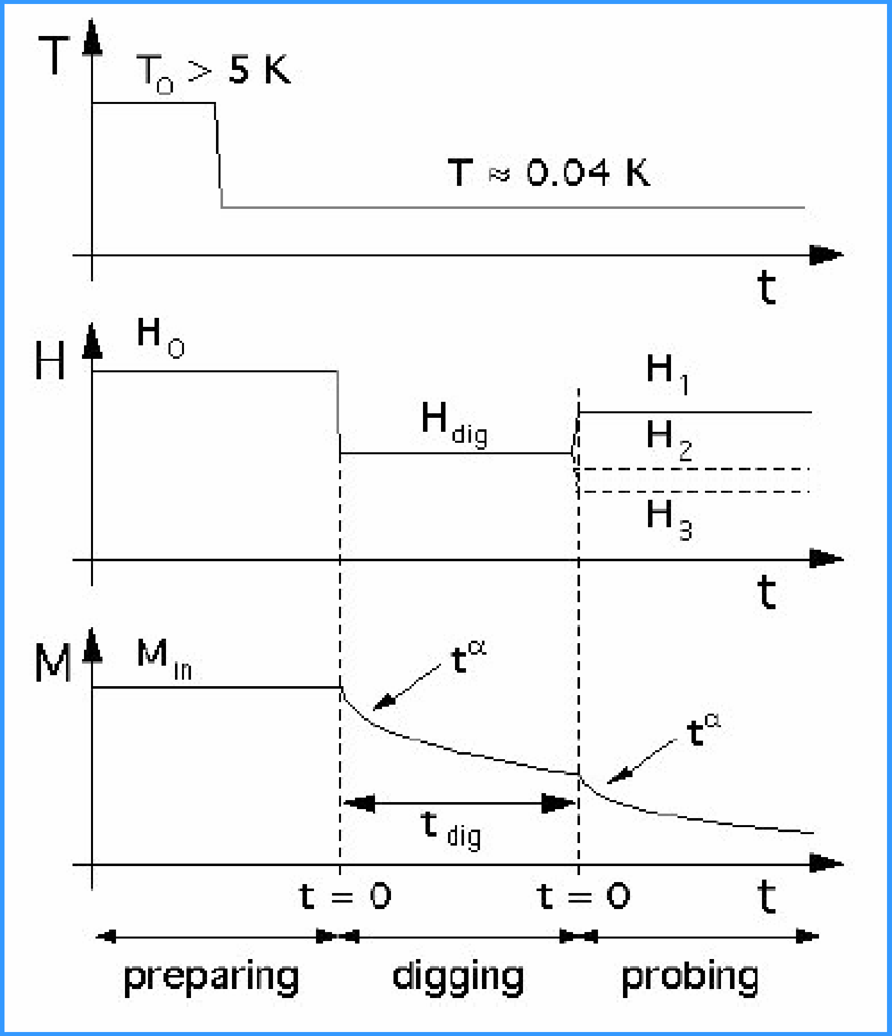
$$\hbar\alpha / \Delta^2 << 1$$ sudden limit:

$$\rightarrow \tau_z \approx \Delta / \alpha$$

$$\alpha = \lim_{\Delta \rightarrow 0} dE/dt = g\mu_B \, dh_z/dt$$

Hole digging

Wernsdorfer et al., Phys. Rev Letters, 84 (2000), 2965



Starting from M_{init}

applying a small field H_{dig} for a time t_{dig}

A field H is applied to measure the short time square root relaxation rate $\Gamma_{sqrt}(H, H_{dig}, t_{dig})$

$$M(H_z,t) = M_{\rm in} + (M_{\rm eq}(H_z) - M_{\rm in})\sqrt{\Gamma_{\rm sqrt}(H_z)t}$$

$$\Gamma_{\rm sqrt}(H_z) = c\frac{\xi_0}{E_D}\frac{\Delta^2_{\pm S}}{4\hbar}P(H_z)$$

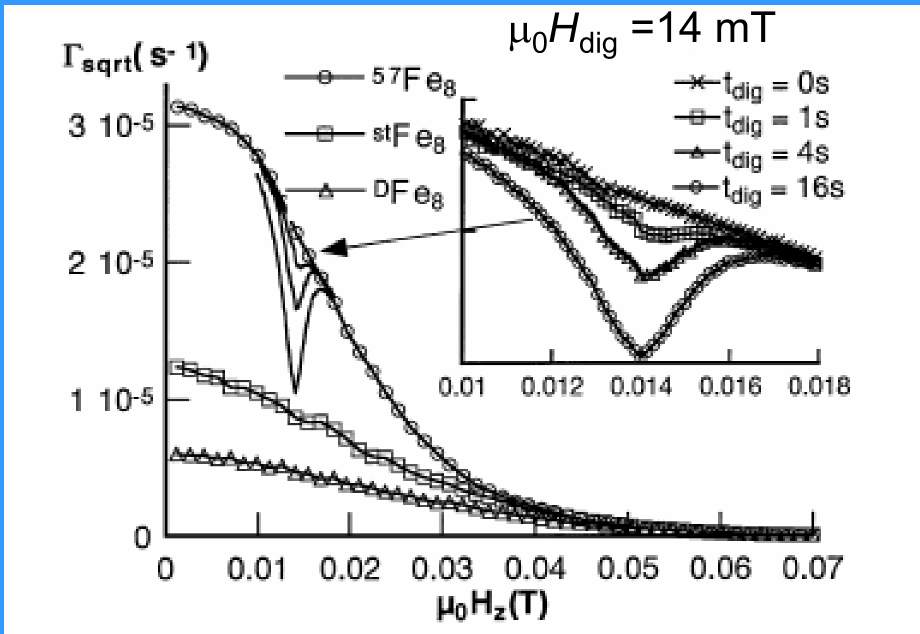
$P(H_z)$ – the normalized distribution of molecules which are in resonance at H_z

back

Hole digging

Wernsdorfer et al., Phys. Rev Letters, 84 (2000), 2965

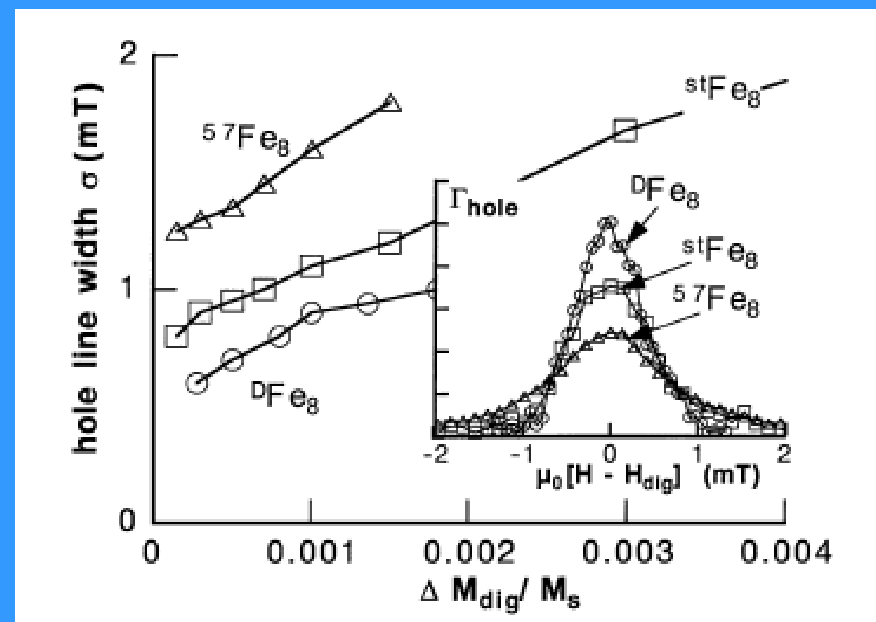
back



As a result ⟶ a very sharp "hole" is dug into the rather broad distribution of Γ_{sqrt}

$$\Gamma_{hole} = \Gamma_{sqrt}(H, H_{dig}, t_{dig}=0) - \Gamma_{sqrt}(H, H_{dig}, t_{dig})$$

The hole line width σ is close to the hyperfine level broadening



The nuclear effect on the QT - hyperfine interactions

Prokof’ev and Stamp

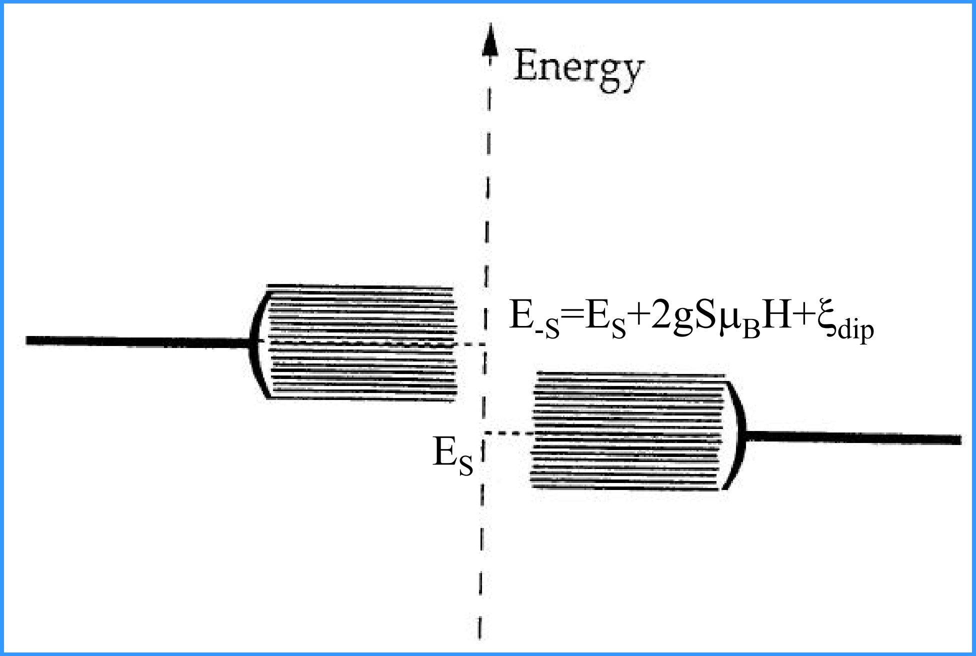
(Phys. Rev. Lett. 1998, 80, 5794)

The dynamic nuclear field change the energy levels.

Consequently, tunneling will start before and will end after matching conditions.

The effective tunnel rate at the matching field:

$$\Delta_{eff} \propto \Delta^2 \square T_2$$

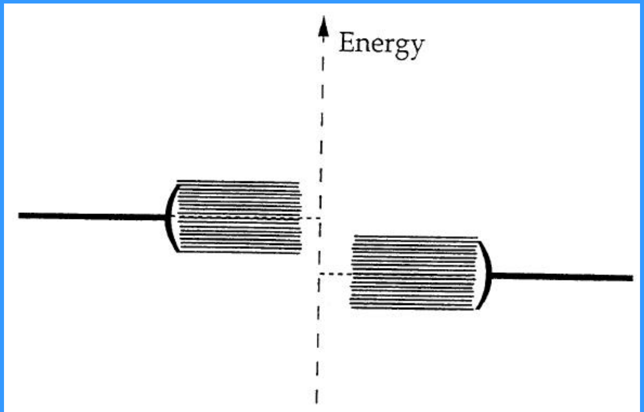


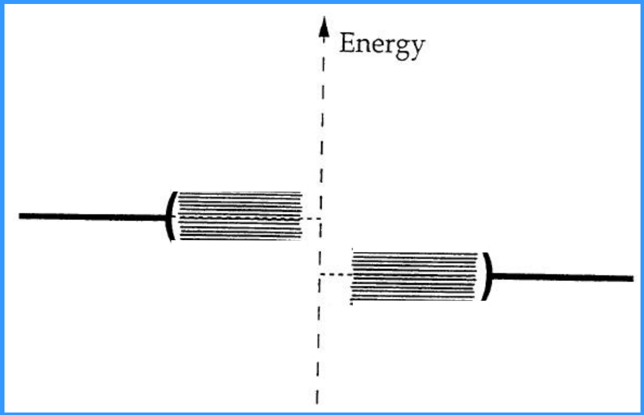
Research Goals

In this research we try to observe the effect of the nuclear spins on the QTM in Fe8 by examining the influence of RF (radio frequency) on its hysteresis loop.

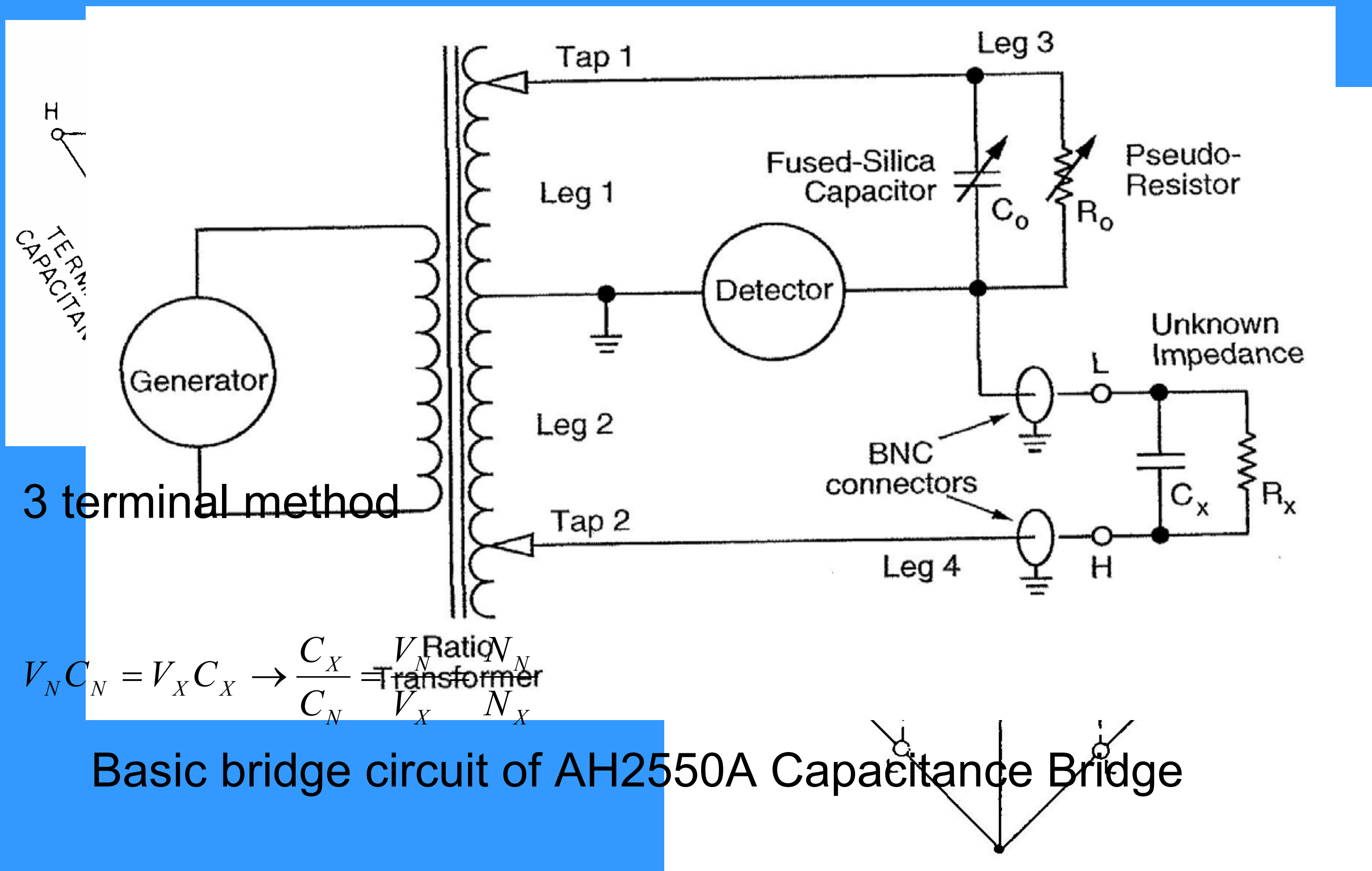
By giving a comb of RF pulses we “warm” the nuclei of the H atoms (more then 100 atoms in every molecule) and look at the effect on the magnetization curve.

$$\frac{\Delta_{eff}\left(T\rightarrow\infty\right)}{\Delta_{eff}\left(T\rightarrow 0\right)}\propto\frac{\Delta^{2}T_{2}\left(T\rightarrow\infty\right)}{\Delta^{2}T_{2}\left(T\rightarrow 0\right)}\geq 2$$





Capacitance bridge



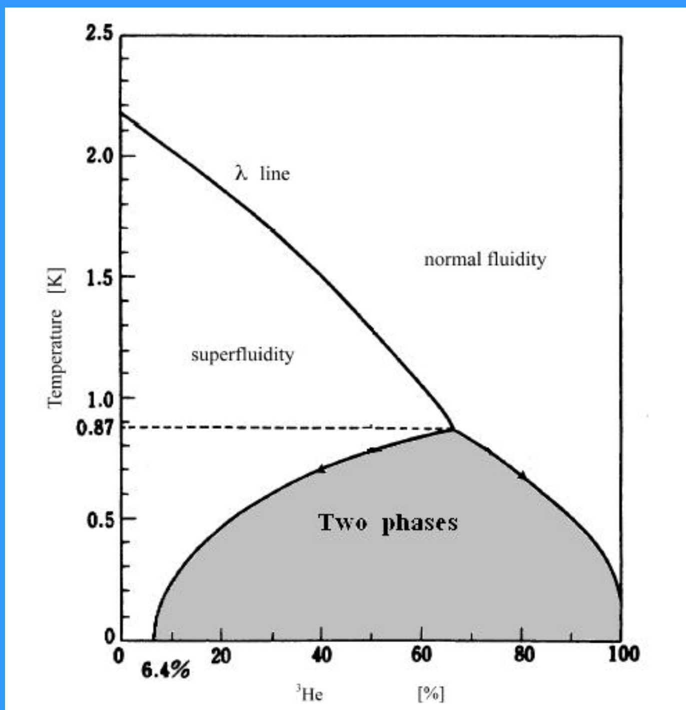
3 terminal method

$$V_N C_N = V_X C_X \rightarrow \frac{C_X}{C_N} = \frac{V_N}{V_X} = \frac{N_N}{N_X}$$

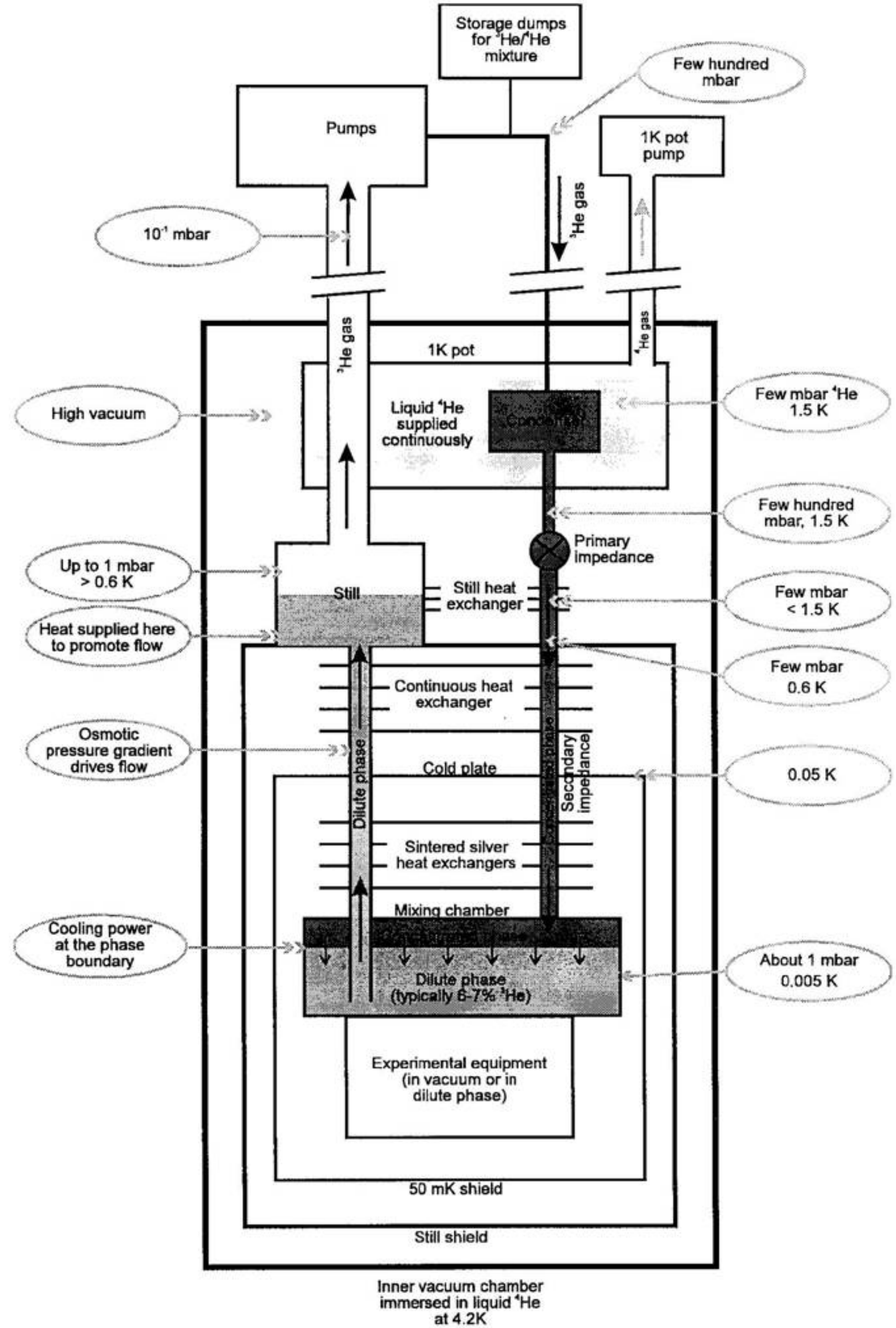
Basic bridge circuit of AH2550A Capacitance Bridge

A capacitance bridge with transformer ratio arms.

Dilution refrigerator – schematic view

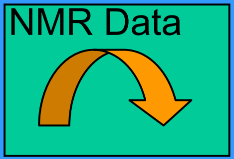


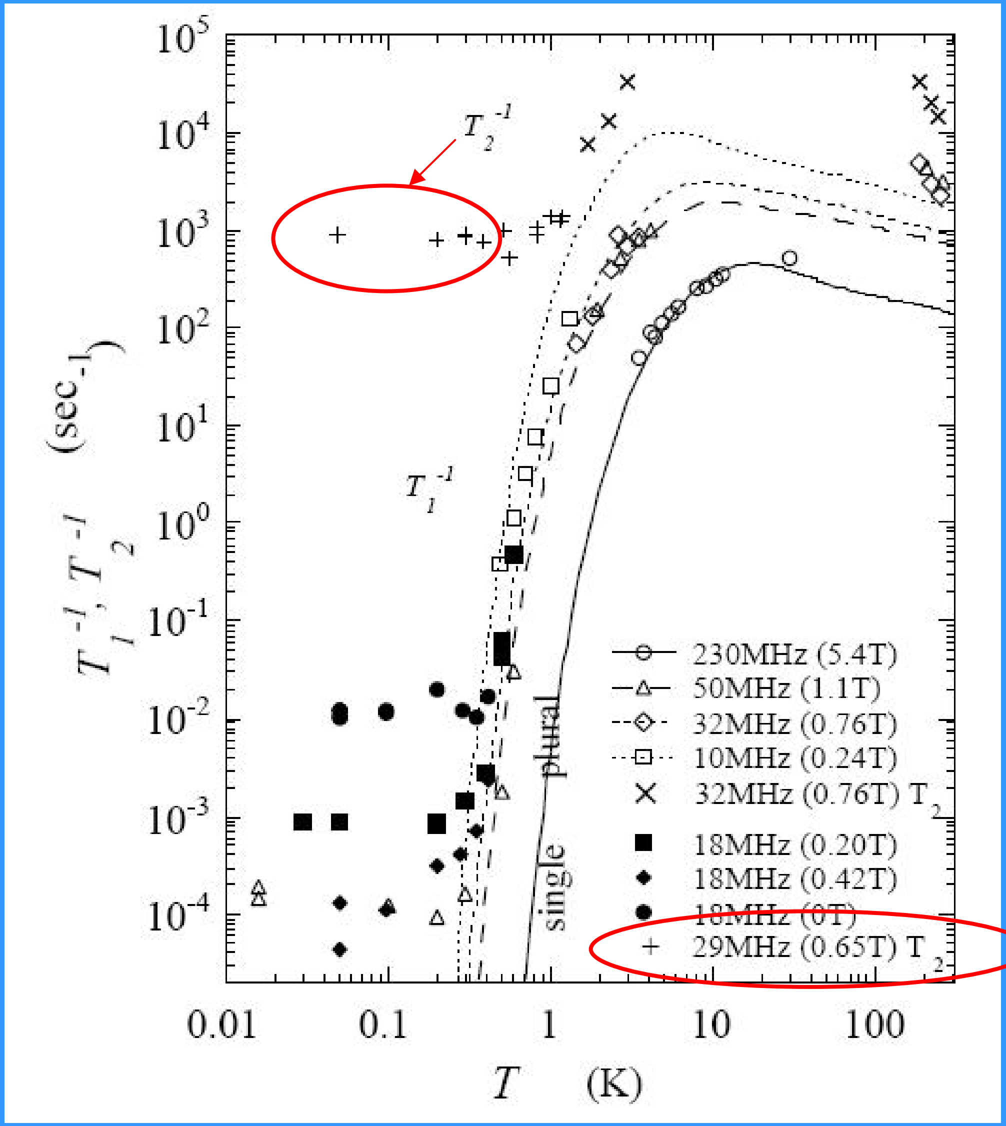
rmance.



magnetometer

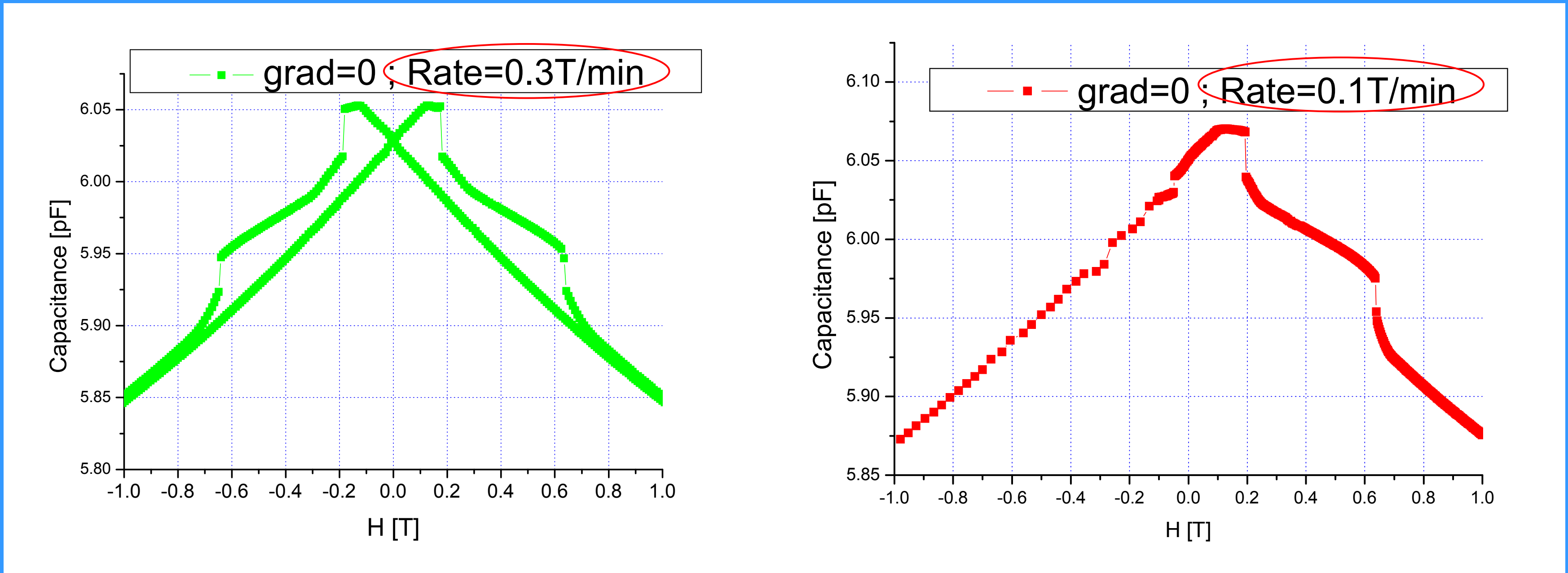
NMR data of Fe8 - Ueda et. al





M. Ueda, PhD thesis, Kyoto University, 2001
M. Ueda, S. Maegawa, S. Kitagawa, Phys. Rev. B. 66 (2001) 073309

Results - jumps in matching fields - 2004

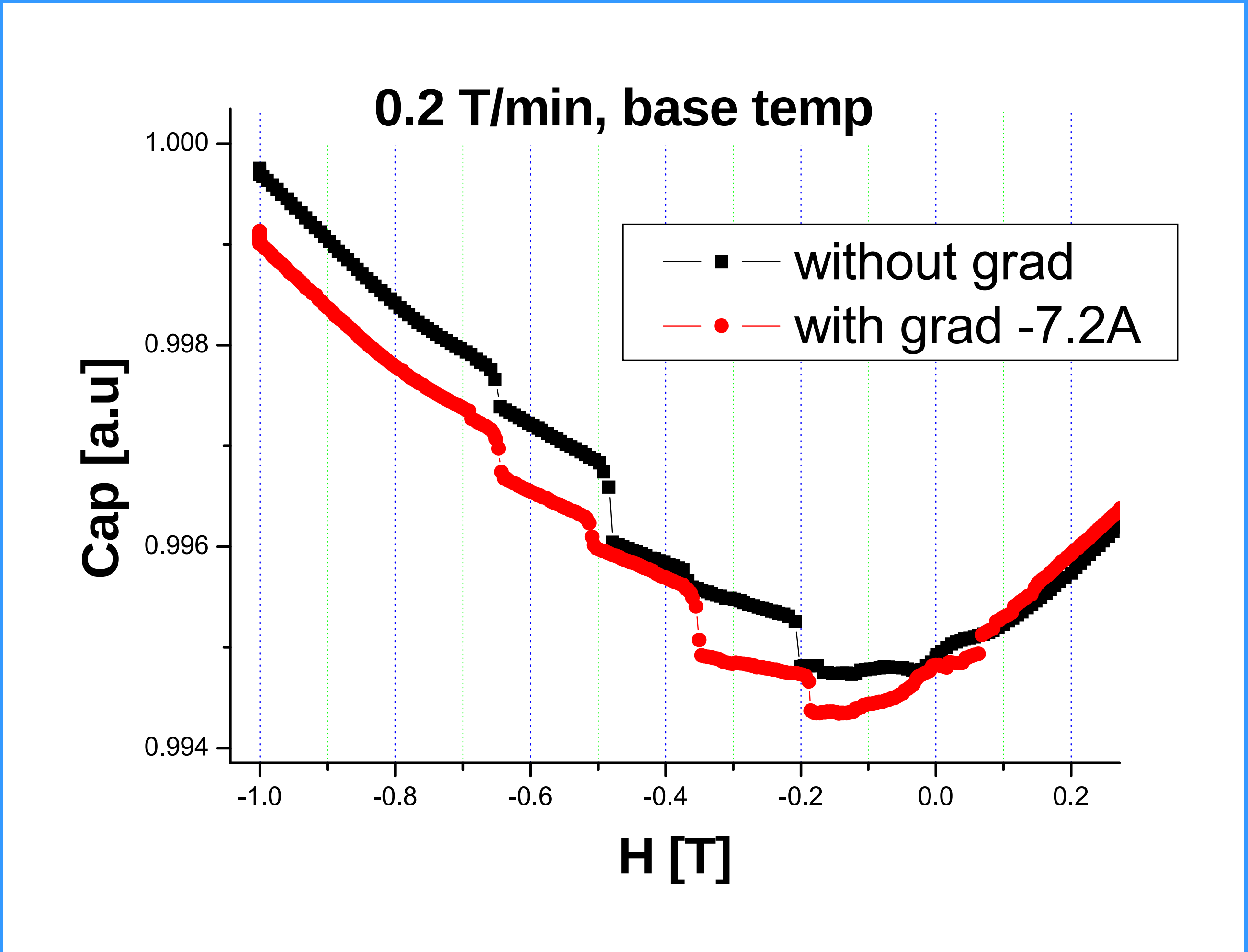


The capacitance verses the magnetic field

(*dH/dt* = 5, 1.6 *mT/sec, T* =100*mK*)

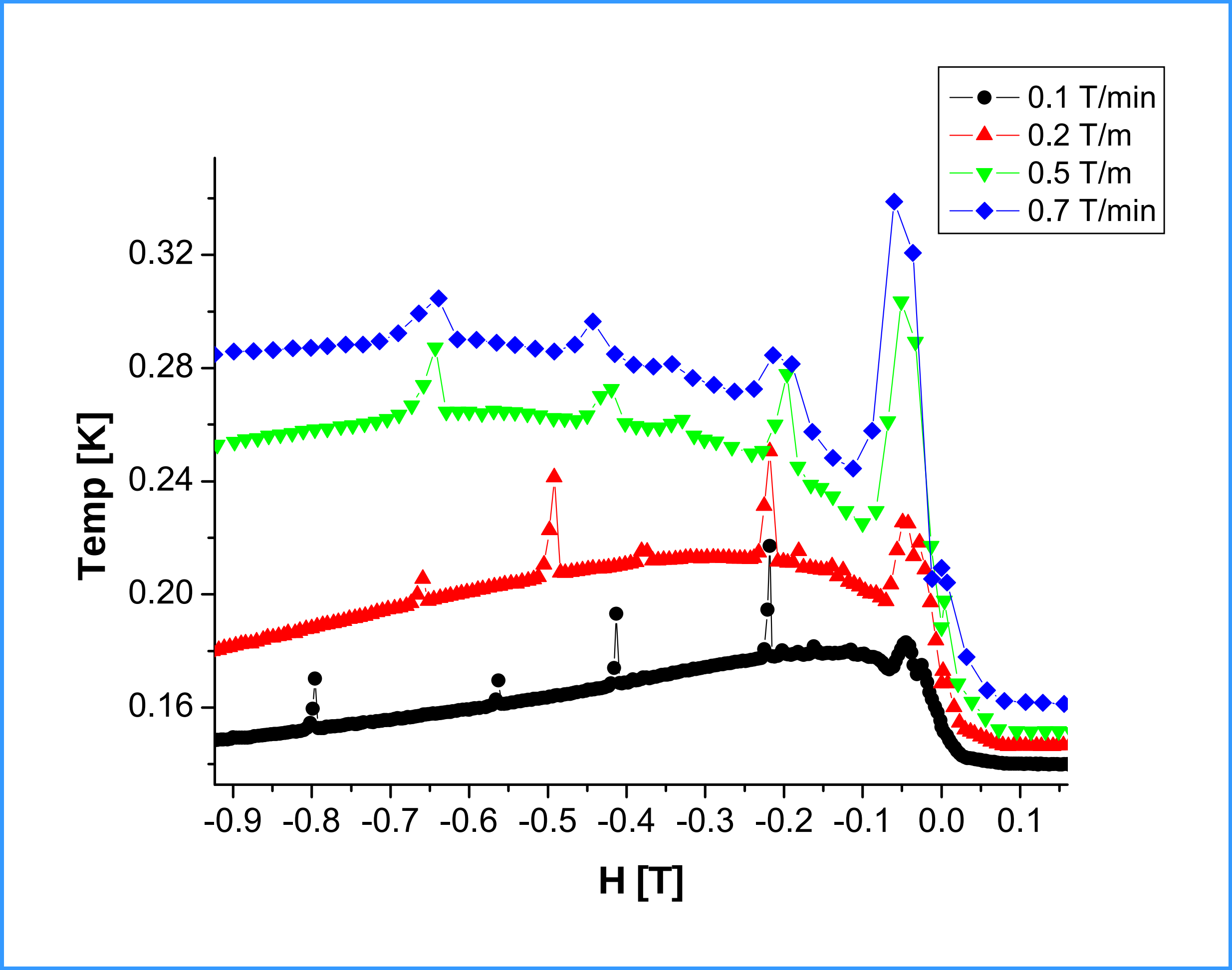
Sampling Rate: 1/1.7 *Hz*

With and without gradient coils



- The Gradient Coils give 100 Gauss/Cm (1 T/m)
- Because the sample is off-center, the gradient is a function of *H*.

Temperature and sweep rate



- The sample rate is similar to all runs

As said above, the orbital moment is quenched by the crystal field. This means that diagonal elements of the orbital moment vanish in all eigenstates of the Hamiltonian. However, the off-diagonal elements of the spin-orbit interaction $(\mathbf{L} \cdot \mathbf{S})$, which can be treated by perturbation theory, lift the 21-fold degeneracy of the $s = 10$ ground state resulting from exchange interactions in zero external field (Fig. 3). At the lowest perturbative order, which is 2, the anisotropy gives rise to a spin Hamiltonian of the form:

$$\mathcal{H}_a = -AS_z^2 \tag{2.1}$$

where z is the tetragonal axis. Magnetic measurements show that the z direction is an easy magnetization axis, which implies that A is positive. The numerical value of A in $Mn_{12}O_{12}$ will be discussed in the next section.

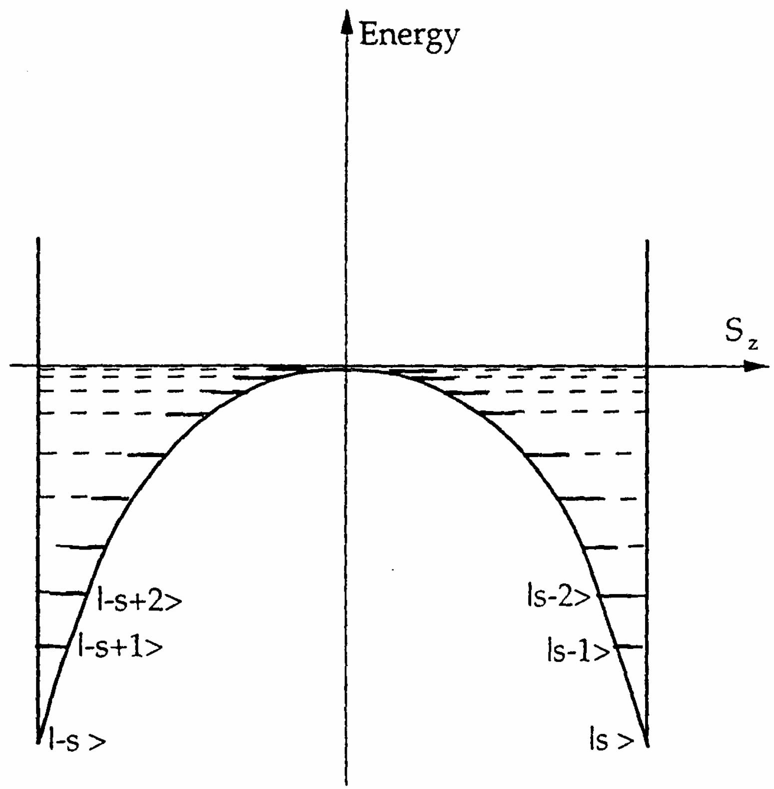


Fig. 3. Energy of the eigenvectors of the Hamiltonian (2.1), or of the Hamiltonian (7.2) for $H = 0$.

Phonons

Conservation of Angular Momentum in the Problem of Tunneling of the Magnetic Moment

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(Received 5 January 1994)

Tunneling of the magnetic moment has some unique features not encountered in other tunneling problems. The conservation of energy and angular momentum prohibits transitions between degenerate magnetic states in a free single-domain magnetic particle. For such transitions to occur, the particle must be firmly coupled with a large solid matrix that absorbs the change in the angular momentum. We show that the contribution of this effect to the tunneling rate is determined by the ratio of the magnetic anisotropy energy to the shear modulus of the matrix. An experiment is suggested that can test this prediction.