Multi-bit magnetic memory using Fe_8 high spin molecules

Oren Shafir

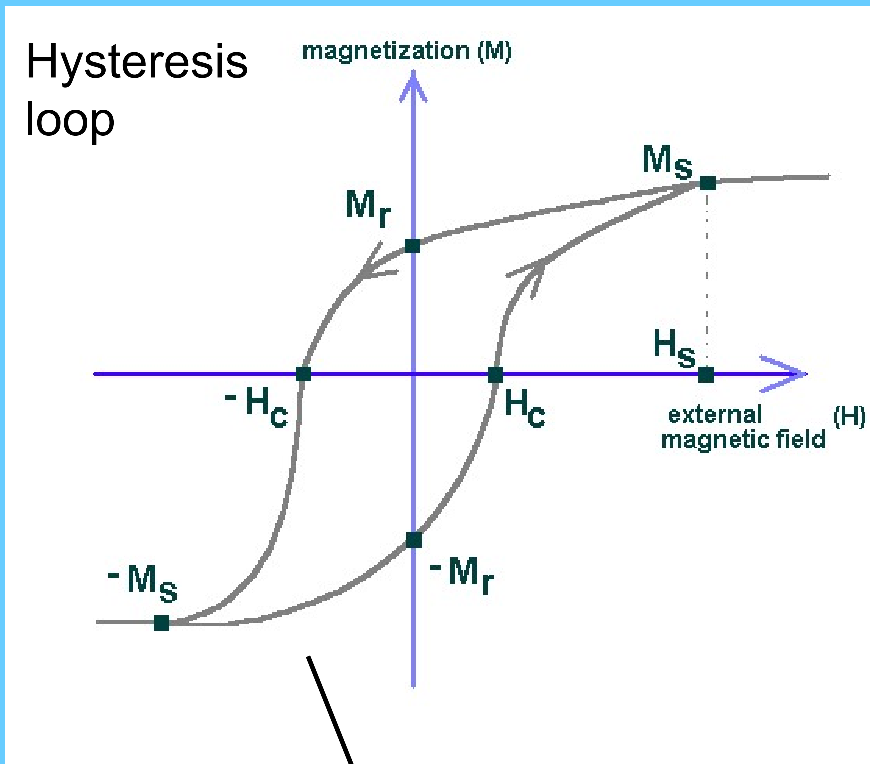
Magnetism Group, Physics Department

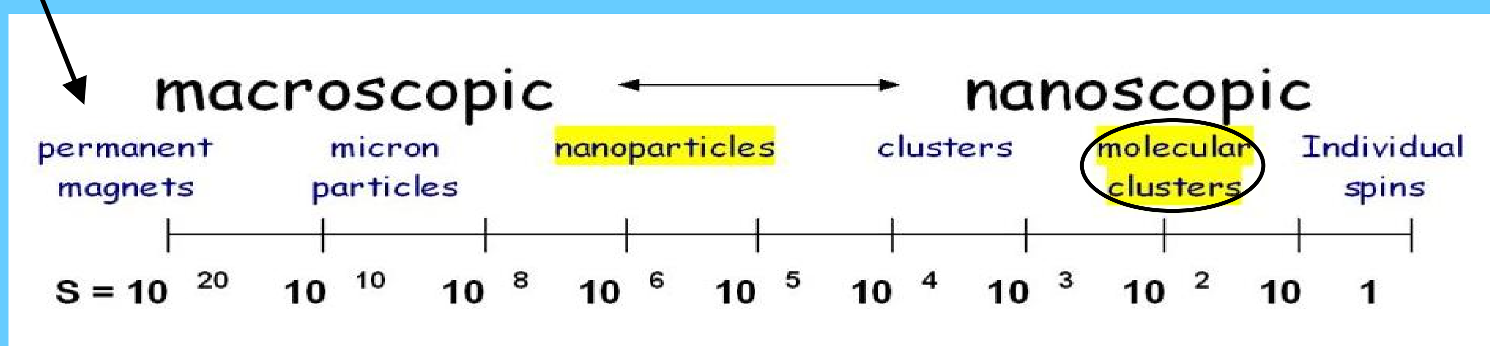
TECHNION
Israel Institute of Technology

Outline

- Preface: memory unit
- Fe8 as a high spin molecule
- Quantum tunneling In Fe8
- Experiments:
  - Faraday force magnetometer
  - μSR
- Discussion
- Summary

The “memory” of a memory unit

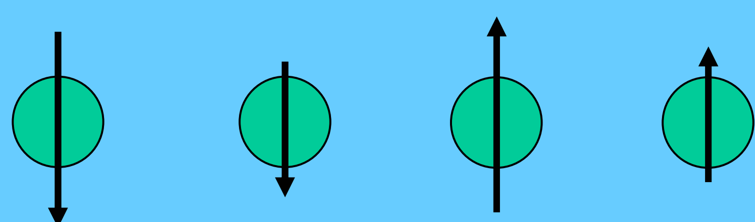




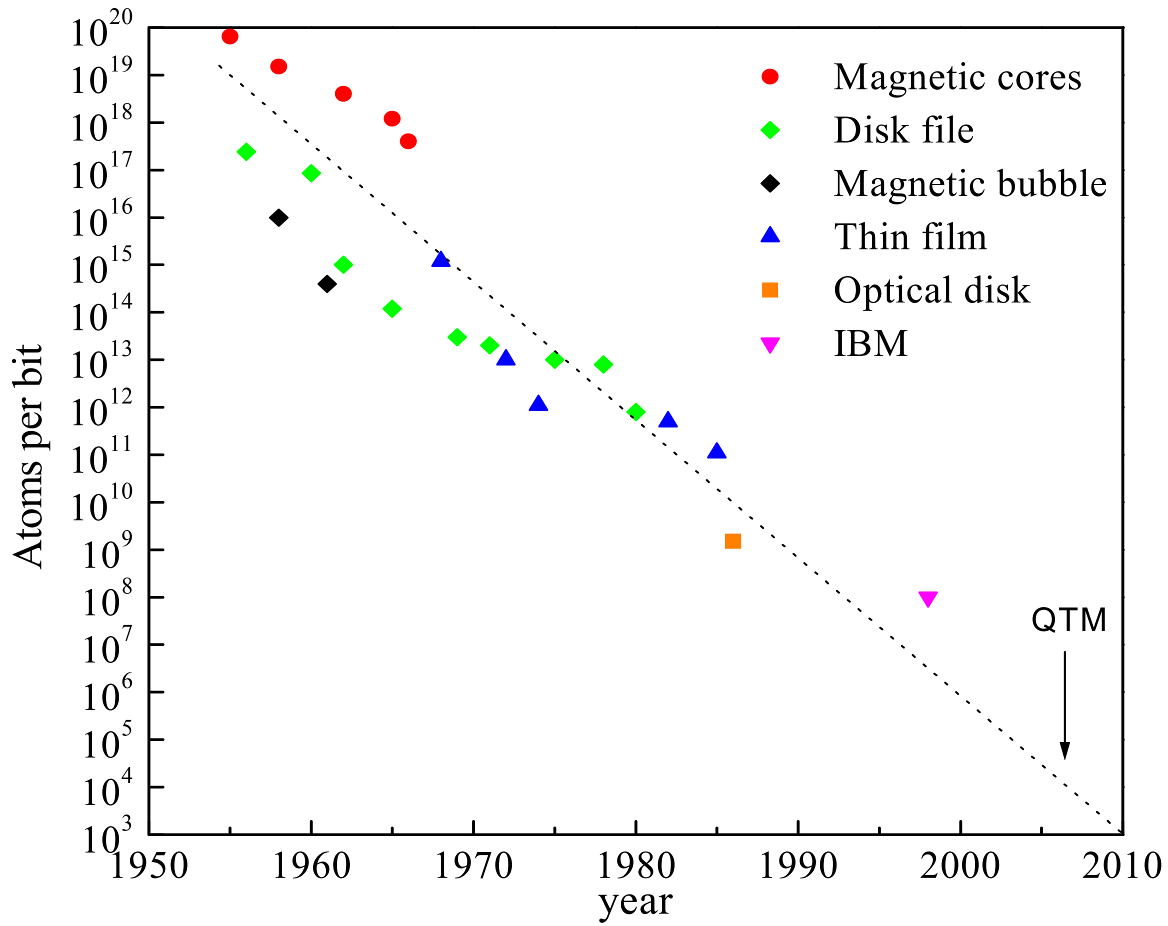
What do we mean by multi-bit memory?

- **Single-bit Memory** using the same measurement one can distinguish between two different preparation processes.

- **Multi-bit Memory** using the same measurement one can distinguish between more than two preparation processes.



Memory Unit Evolution



J. Harris and D. Awschalom, Physics World Jan.-1999

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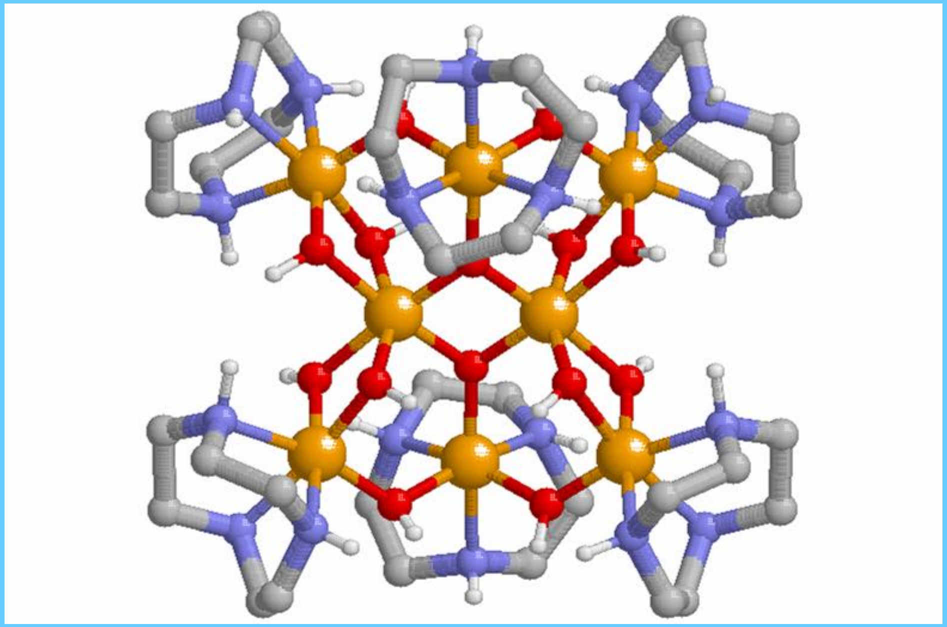
Molecules as magnetic memory

There are some properties that molecules must have if one wants to use them as magnetic memory:

- Existence of an hysteresis loop (energy barrier between two magnetization states) = **the molecule can "remember".**
- Large interaction between the spins in the molecule (**J**) = **the molecule acts as a single unit**.
- Weak magnetic coupling between the molecules = **every molecule behaves independently**.

Fe8 Molecule

$[Fe_8O_2(OH)_{12}(C_6H_{15}N_3)_6]Br_7(H_2O)Br8H_2O$



Iron

Oxygen

Nitrogen

Carbon

Hydrogen

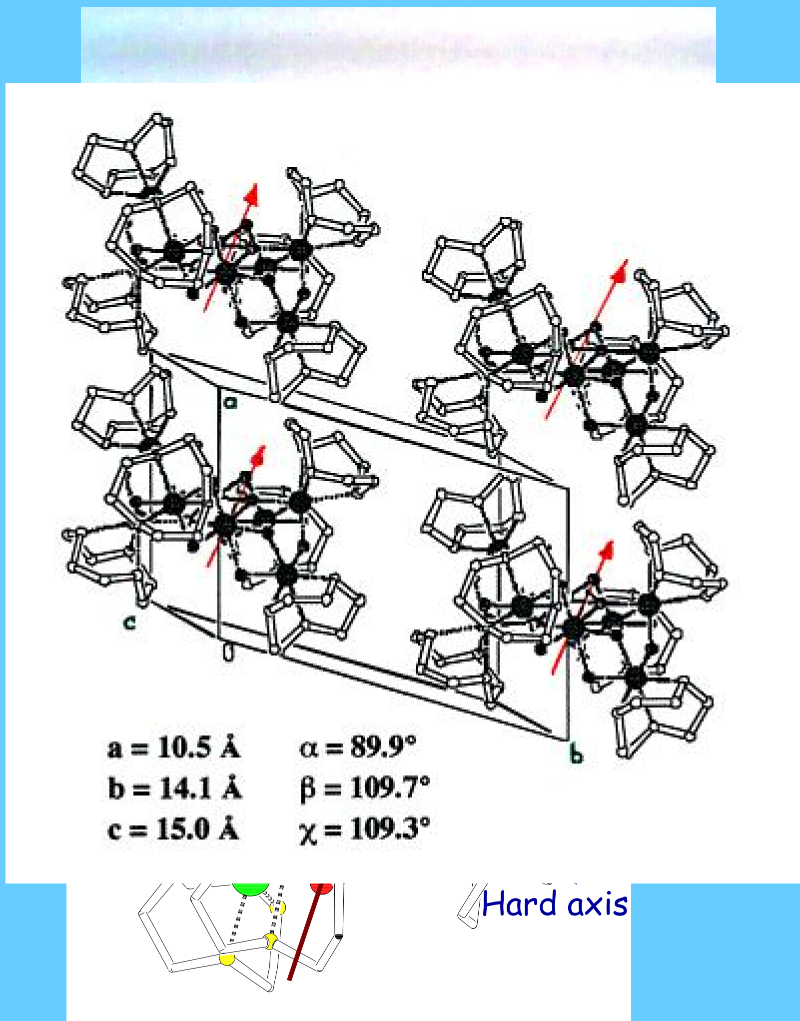
K. Wieghardt, K. Pohl, I. Jibril and G. Huttner, Angew. Chem. Int. Ed. Engl. 23 (1984), 77.

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

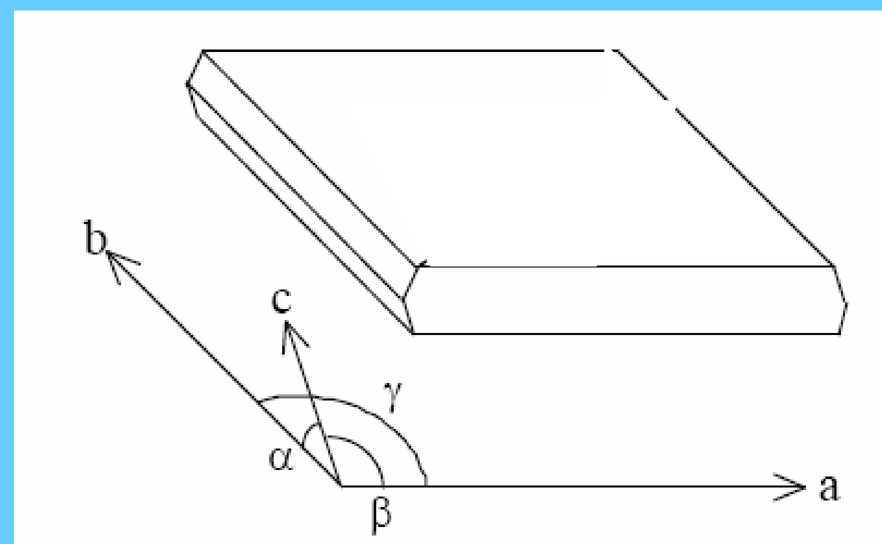
- The magnetic interactions between the molecules are negligibly small.

Single crystal of Fe8

- Single array of nanomagnets

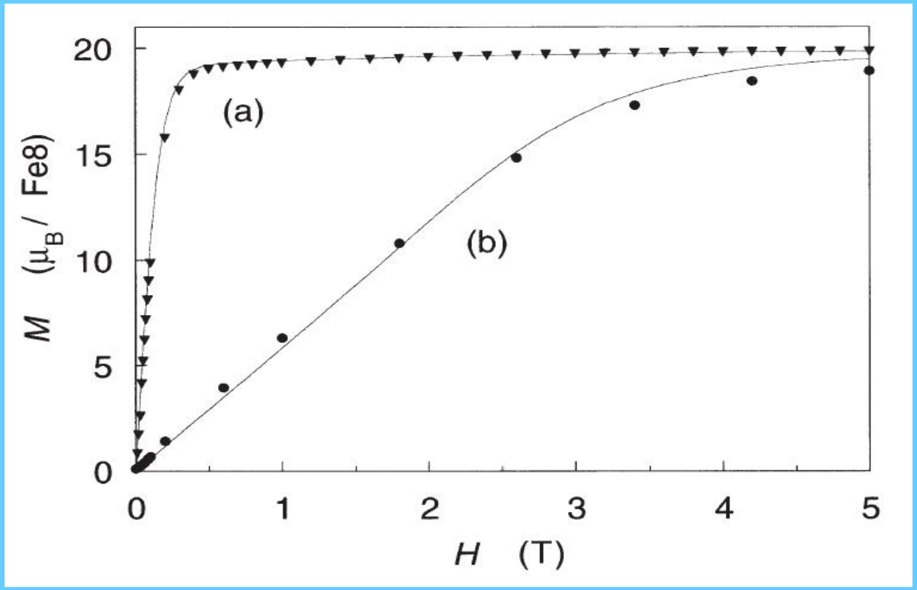


The magnetization is preferentially oriented parallel to an axis called the "easy axis“.

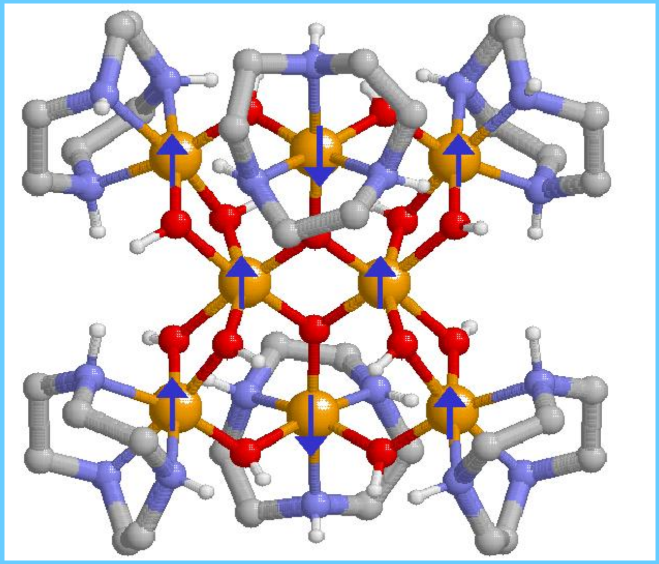


a = 10.5 Å	α = 89.9°
b = 14.1 Å	β = 109.7°
c = 15.0 Å	χ = 109.3°

The molecular spin in low temperatures



S=10



(a) is parallel to the easy axis.

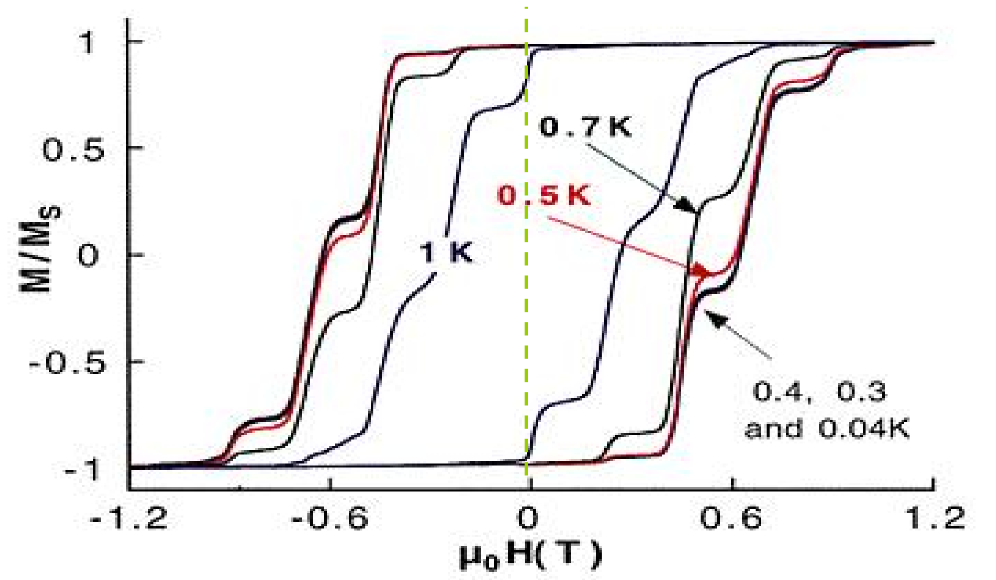
(b) is perpendicular to the easy axis.

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

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

This was confirmed by a polarized neutron-diffraction experiment.

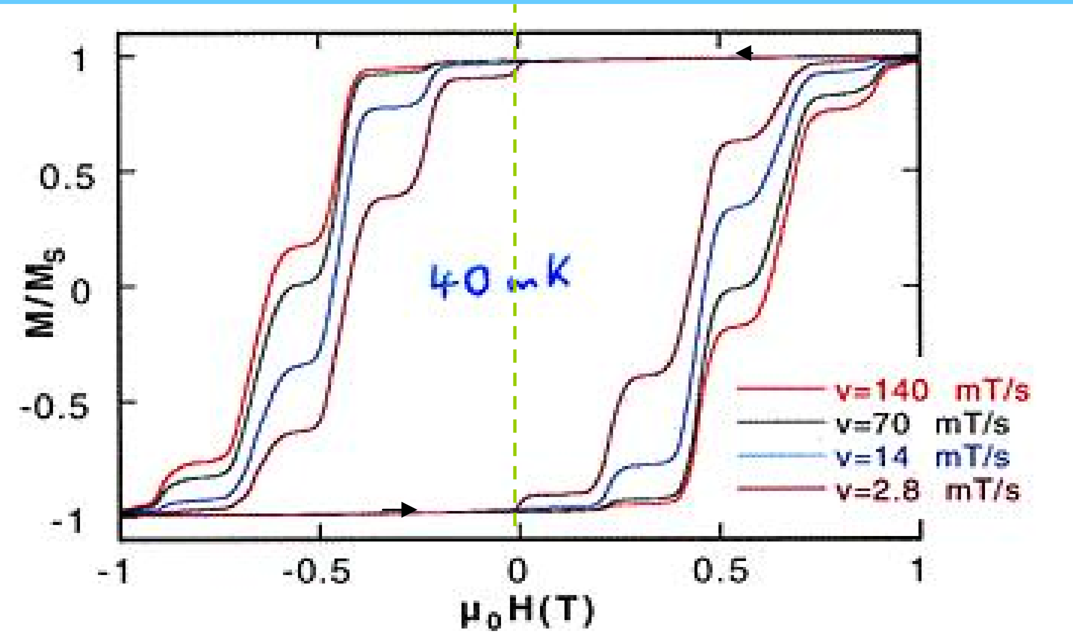
Hysteresis loop of Fe8 – Temperature dependence



A. Caneschi et al. JMMM 200, 182 (1999)

- There is a temperature dependence above 0.4K.
- Equally separated steps can be seen at $H_m \approx n \times 0.22T$
- The lower the temperature, the wider the hysteresis loop

Hysteresis loop of Fe8 – sweeping rate dependence



A. Caneschi et al. JMMM 200, 182 (1999)

- Equally separated steps can be seen at $H_m \approx n \times 0.22T$
- Fast sweeping rate → wider hysteresis loop

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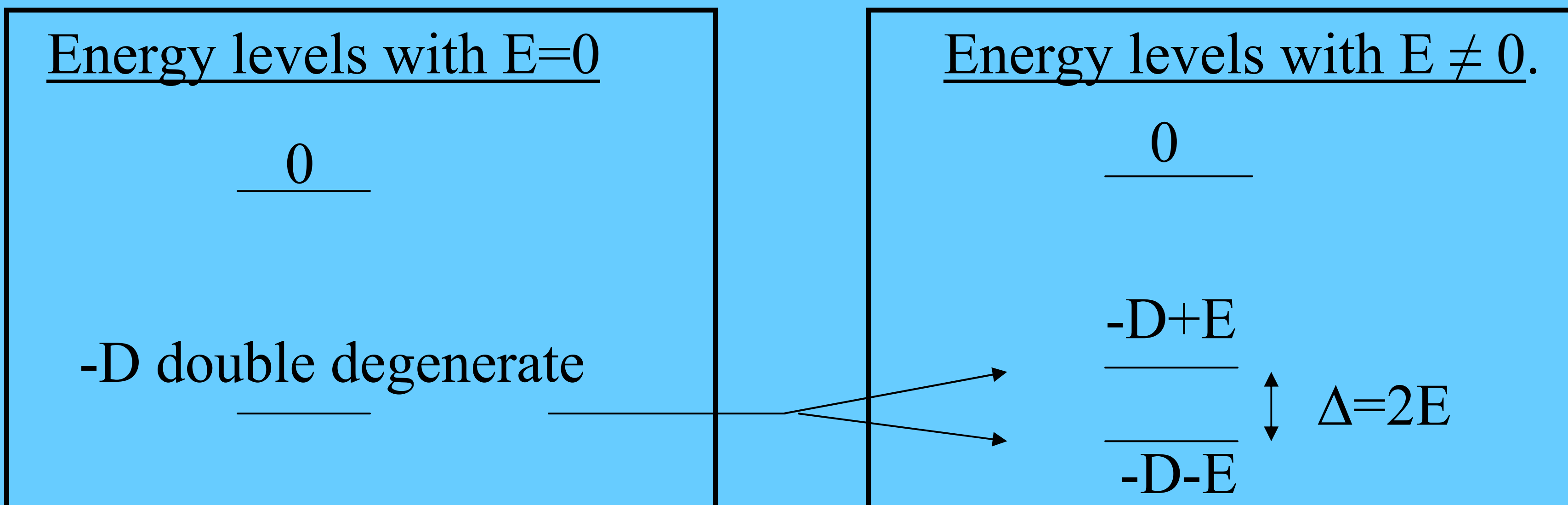
The concept of tunnel splitting: S = 1

$$\mathcal{H} = -DS_z^2 + E(S_x^2 - S_y^2) = \begin{pmatrix} -D & 0 & E \\ 0 & 0 & 0 \\ E & 0 & -D \end{pmatrix} \quad |up\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad |middle\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad |down\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$



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

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

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 are:

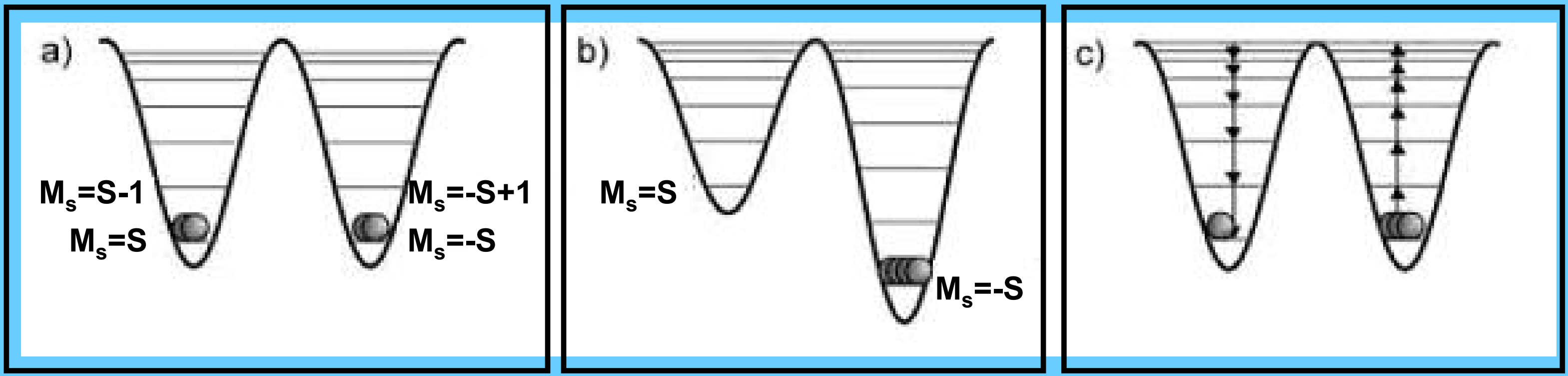
$$Energy(m) = -Dm^2 - g\mu_B H_z m$$

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

The tunnel splitting between the two degenerated ground states:

$$\Delta_{-S,S} = \frac{8D}{\left[(S-1)!\right]^2}(2S)!\left(\frac{E}{8D}\right)^S$$

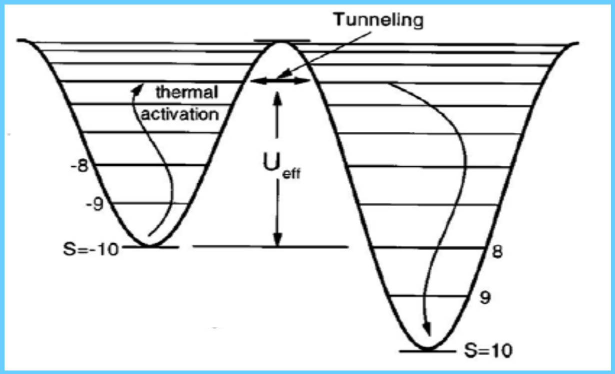
Experimental realization



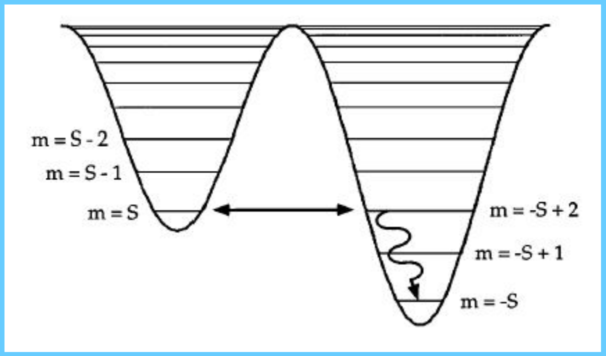
a) In zero field the two wells are equally populated.

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

c) After removing the field the system returns to equilibrium (thermally).



Thermally assisted QT

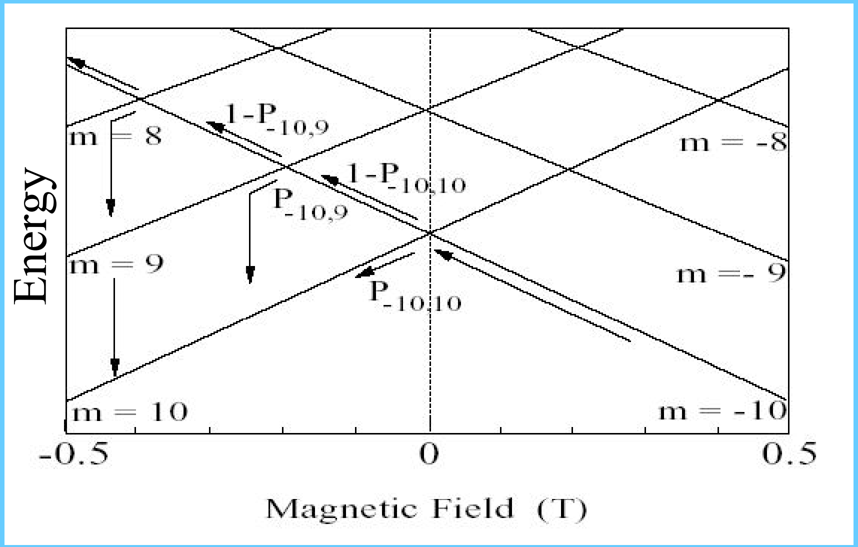


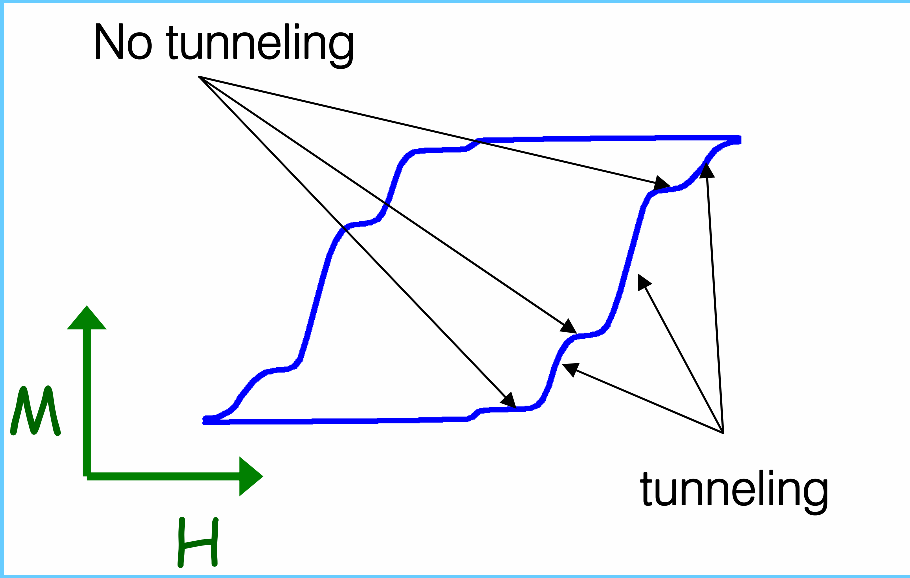
pure QT

The model and the hysteresis loop

$$\mathcal{H} = -DS_z^2 + E(S_x^2 - S_y^2) - g\mu_B \mathbf{S}\cdot\mathbf{H}$$

$$H_m(n) = \frac{nD}{g\mu_B} \approx n \times 0.22T.$$





Landau Zener model

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

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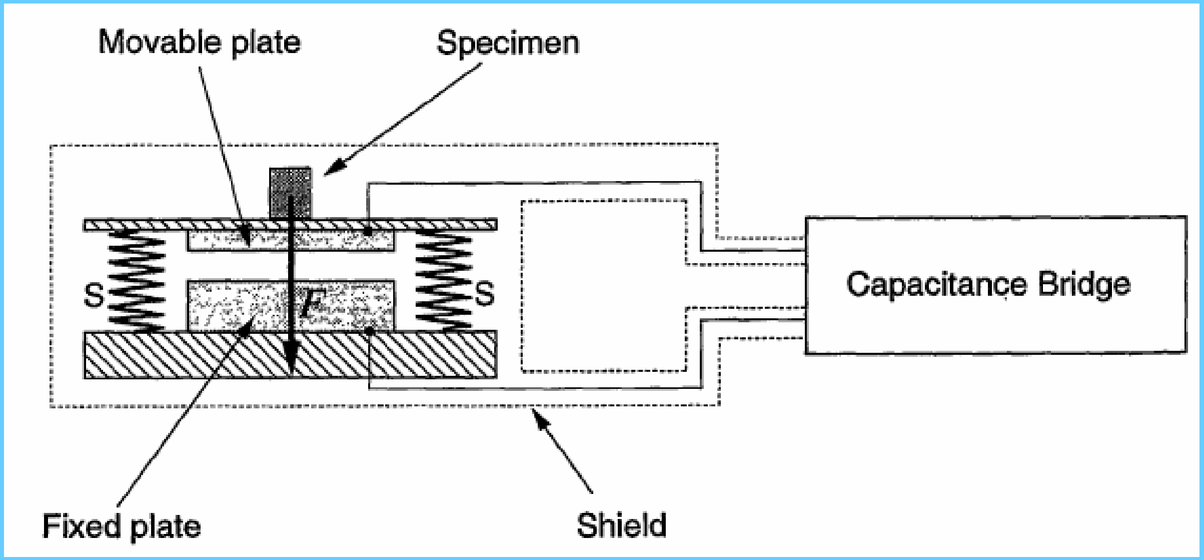
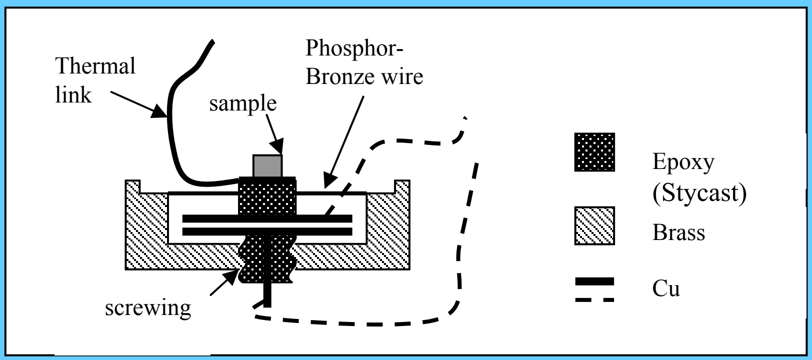
Faraday force magnetometer – Principle of measurement



- Measuring the varying capacitance.
- spatially varying magnetic field → magnetic force $\mathbf{F} = (\mathbf{M} \cdot \nabla)\mathbf{B}$
- The restoring force of the springs balances F .

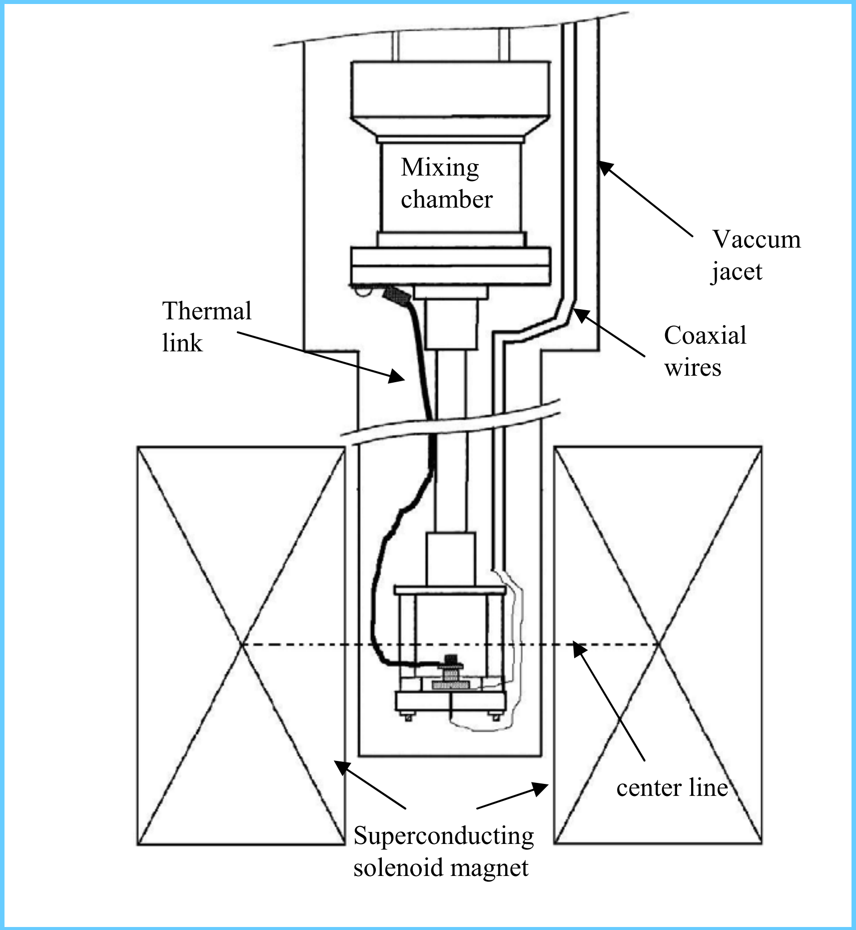
Faraday force magnetometer – The load cell



The movable plate is suspended by four wires of phosphor bronze.

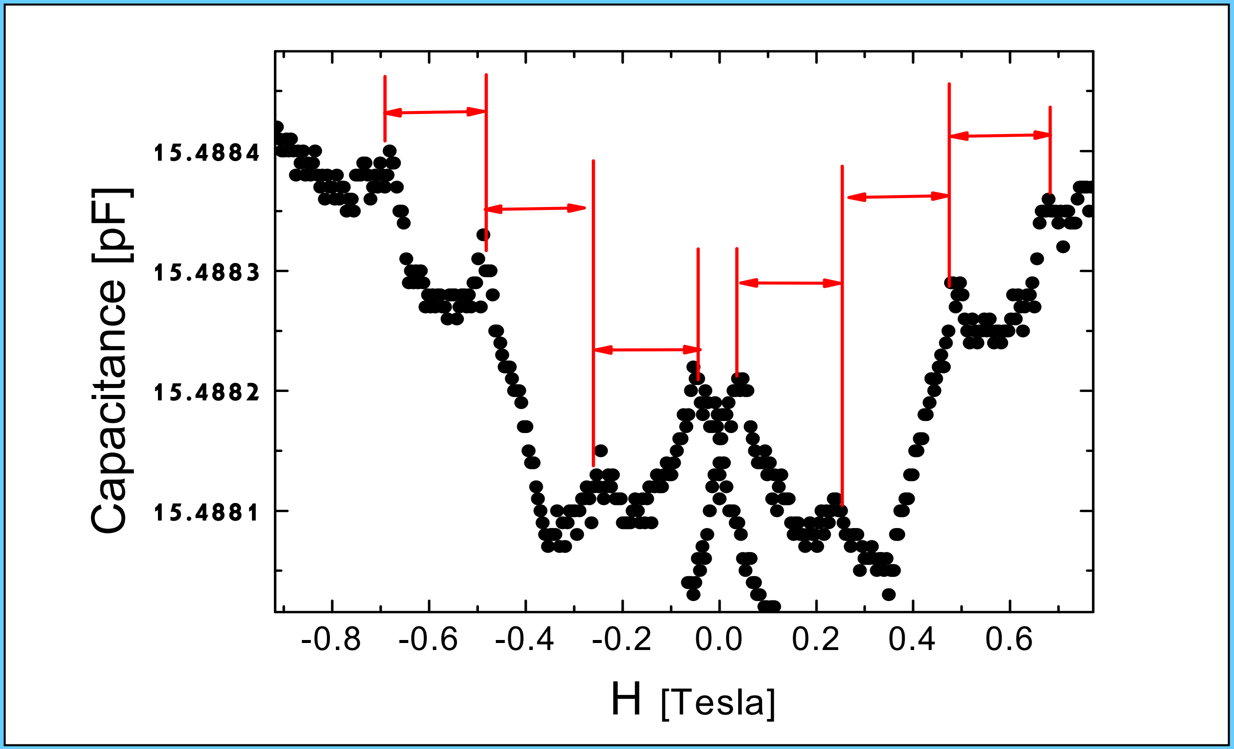
$$C_0^{-1} - C^{-1} = a \cdot M_z \frac{dB_z}{dz}$$

a – Calibration constant



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

Results - jumps in matching fields



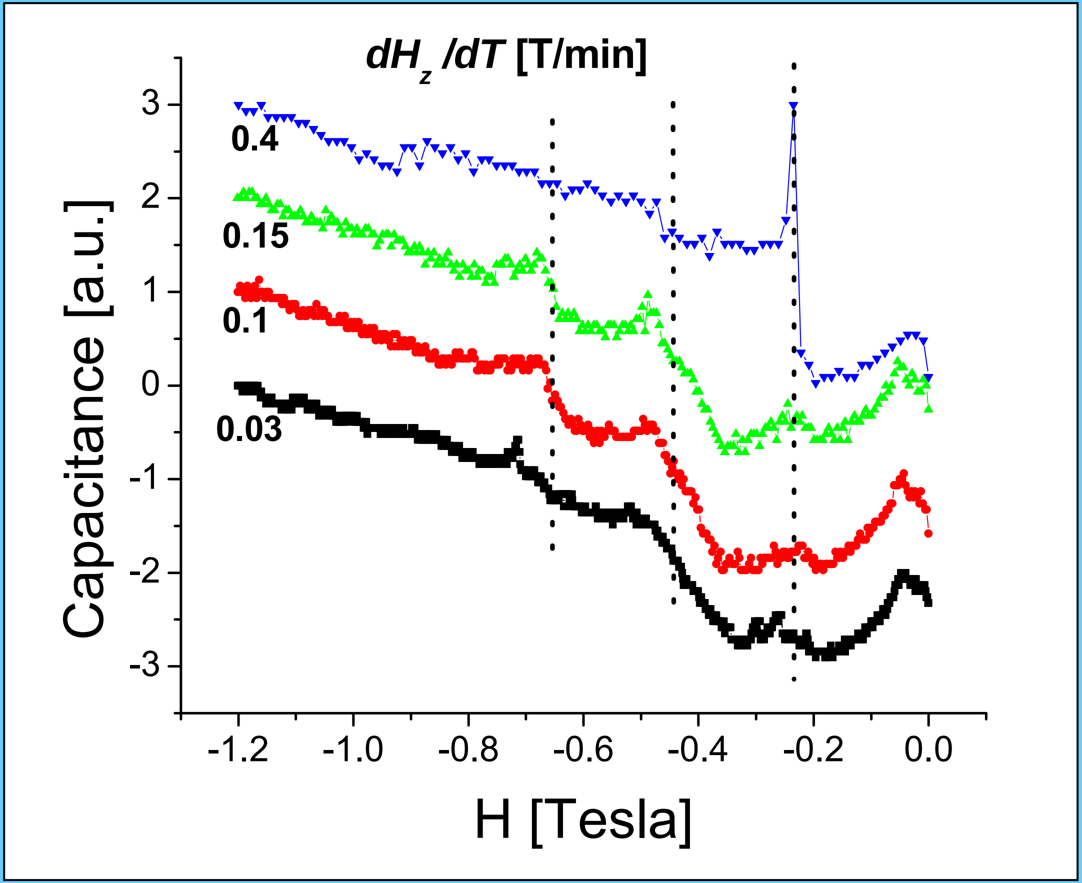
The capacitance verses the magnetic field

(*dH/dt* =0.15 T/min ,*T* =40*mK*)

The distance between steps is nearly constant

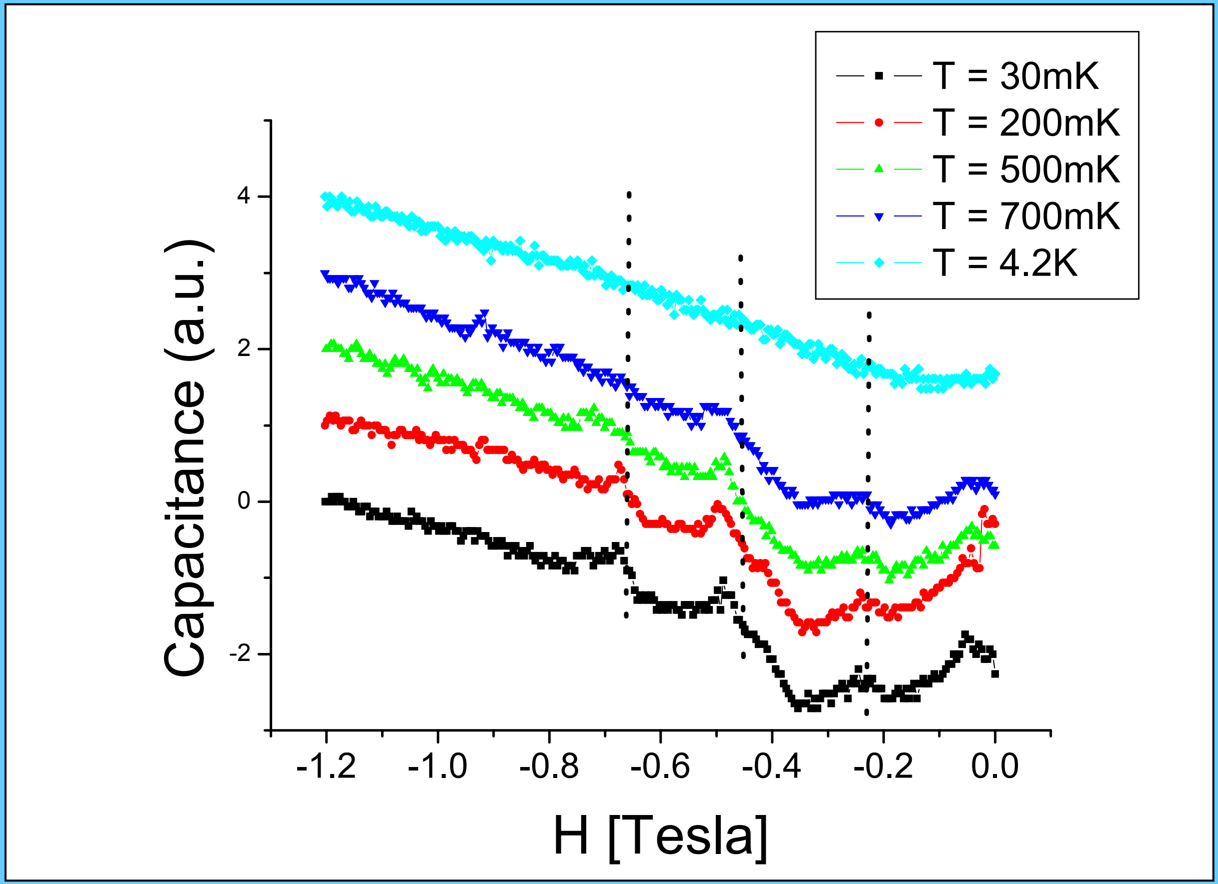
(the arrows are of equal length)

Sweep rate dependence



Capacitance in arbitrary units for various dH_z/dt (at T=40mK). The vertical dotted lines are at the approximate matching fields $H_m \approx n \times 0.21$T.

Temperature dependence



Capacitance in a.u. for different temperatures (dH_z/dt=0.15 [T/min]). The vertical dotted lines are at the approximate matching fields $H_m \approx n \times 0.21$T

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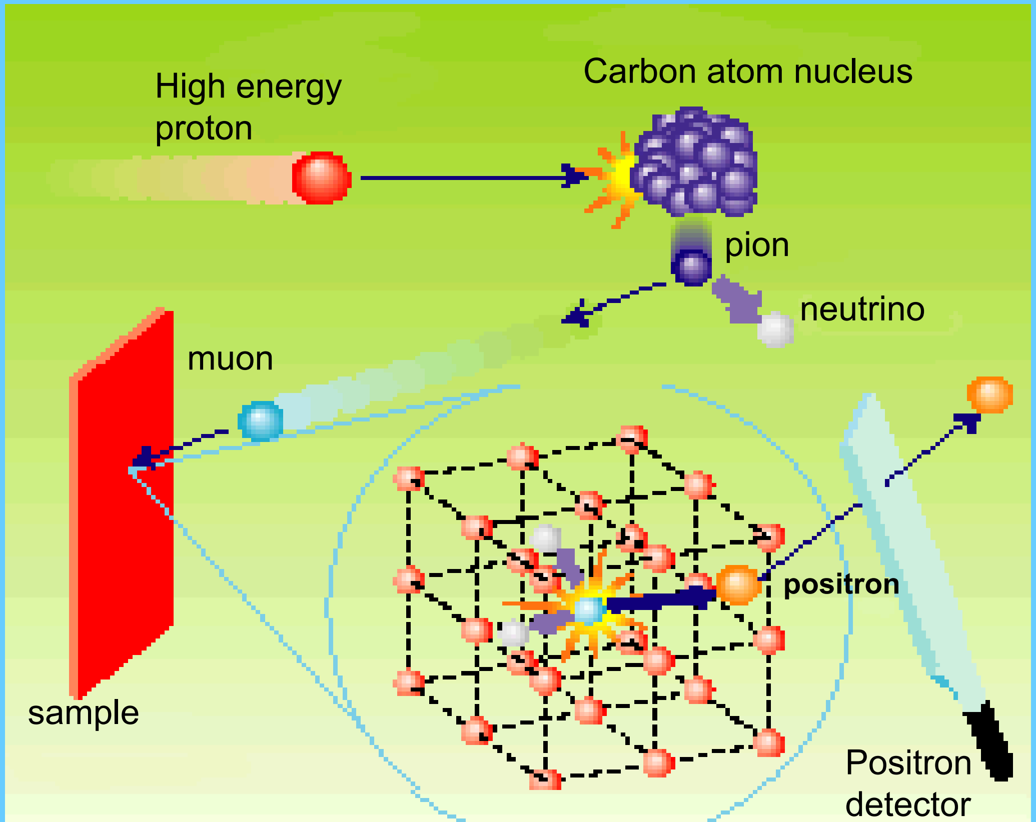
Why measure Fe8 with μSR?

We want to measure the magnetization of a few (or one) molecules

We need a **local probe**

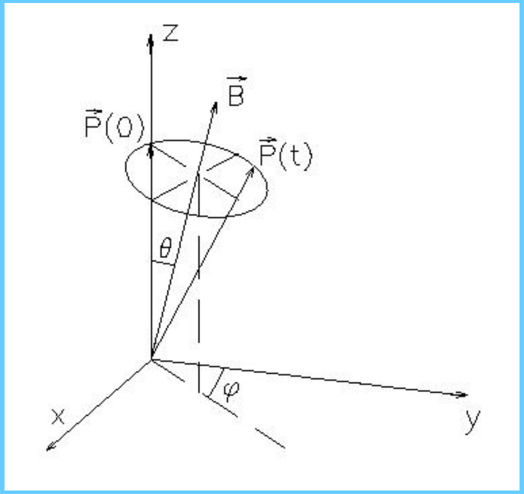
Moreover, there is an ongoing effort to make Fe8 films →
μSR is applicable to films (while most techniques are not).

μSR – Muon Spin Relaxation/Rotation



From the ISIS website

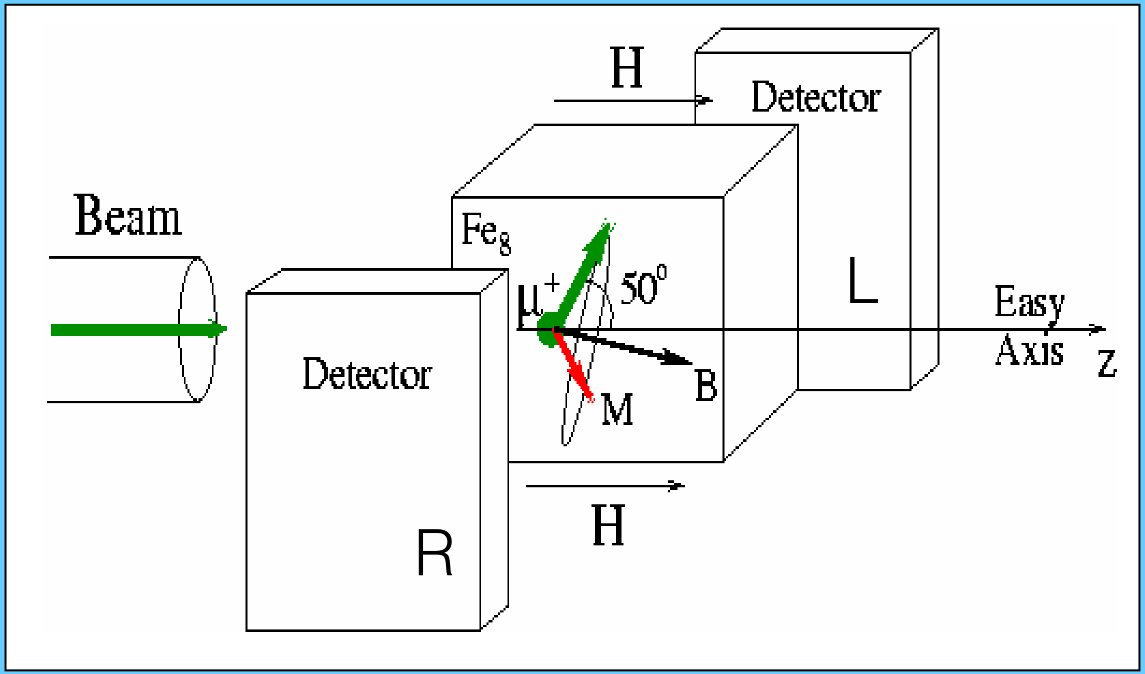
(ISIS - pulsed neutron and muon source located at the UK)



The muon provides information on the magnetic environment in its vicinity.

$$\omega_\mu = \gamma_\mu \cdot \vec{B}$$

μSR experiment setup



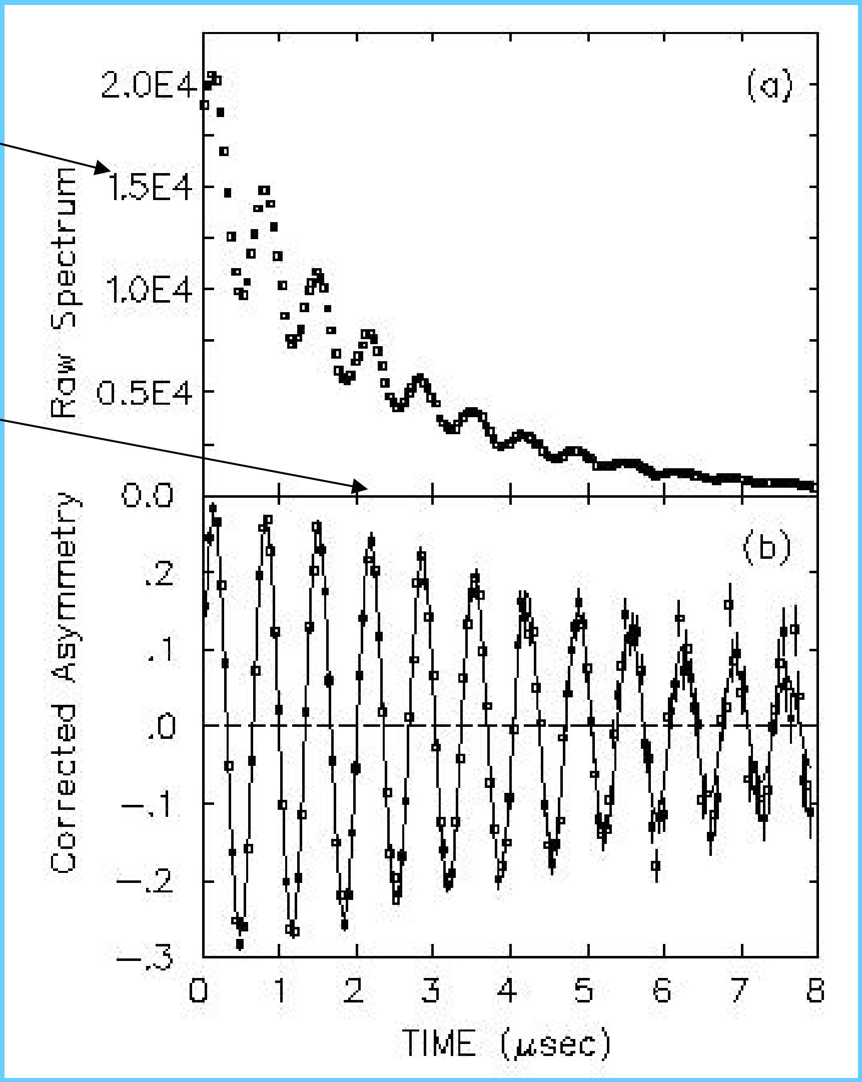
- The beam direction || easy axis of Fe8 || applied field.
- Temperature : ~100mK (minimize activation effects).
- The initial polarization of the muons is 50° relative to z.

Asymmetry

μSR

Detected positrons

time difference between the muon arrival at the sample and its decay



Corrected asymmetry:

$$A(t) = \frac{R(t) - L(t)}{R(t) + L(t)} \propto P_{\perp}(t)$$

The process - three step field cycle:

process

1. A strong negative field of -2T that is parallel to the z axis, polarizes the Fe8 molecules

2. The field is swept to an intermediate positive value H_i, at a rate of 4 mT/s

→ **<u>different process</u>**

3. The field is swept back to +50G at the same rate

→ **<u>same measurement</u>**

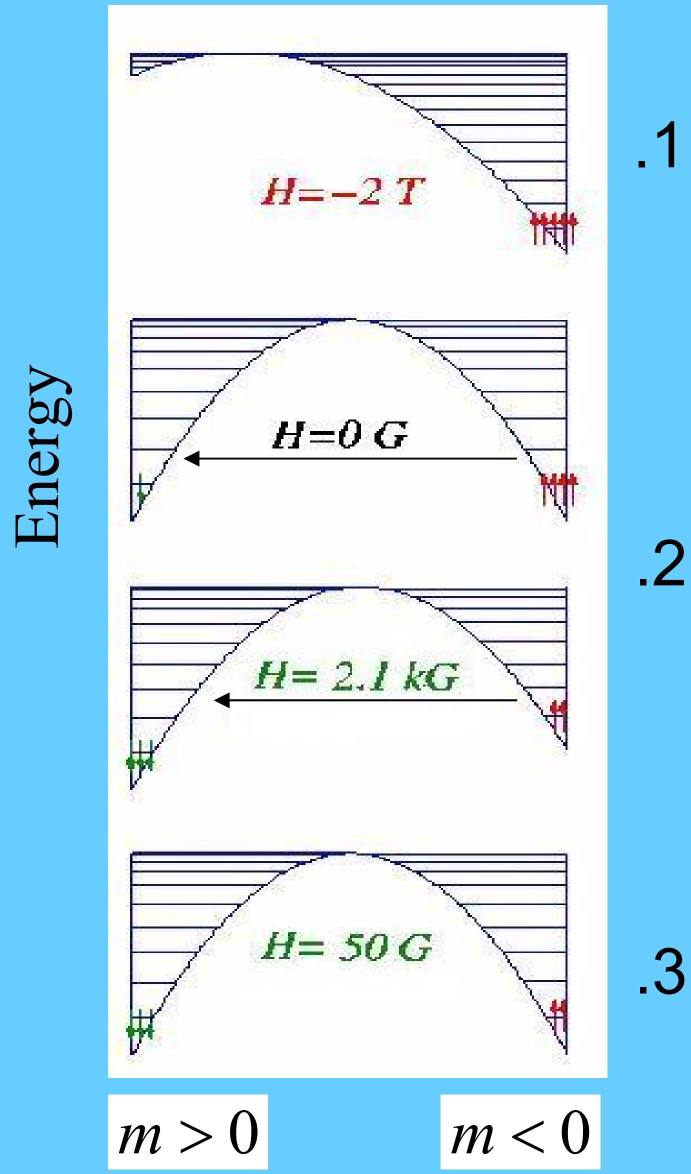
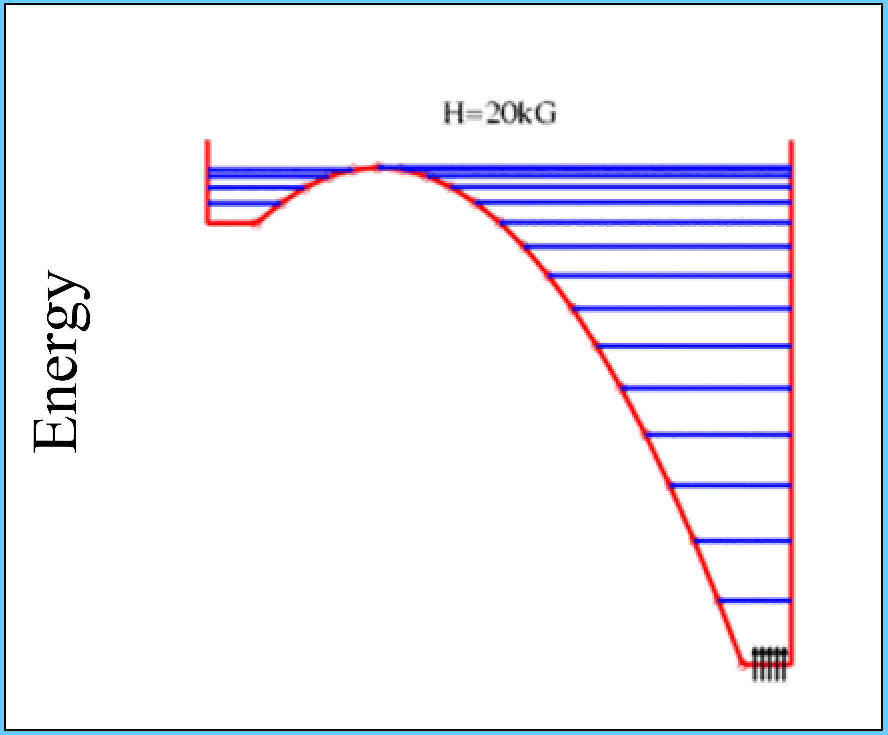
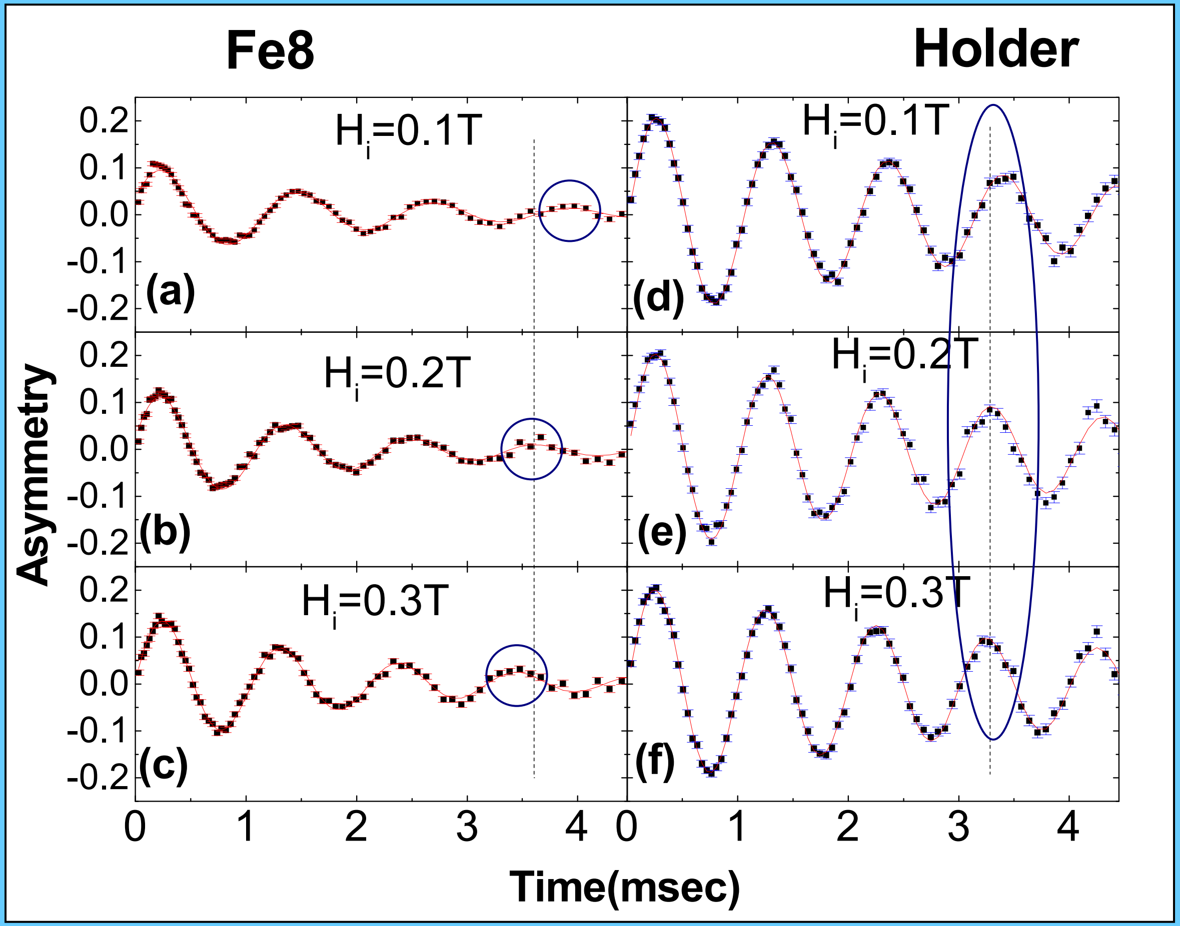


Illustration of the double well potential in the field cycle



$m > 0$ $m < 0$

Experiment results



- There is a difference in amplitude.

- The solid lines are the fit to the function:

$$A(t) = A\sin(\omega_\mu t)e^{-\lambda t}.$$

$$\left(\vec{\omega}_\mu = \gamma_\mu \cdot \vec{B}\right)$$

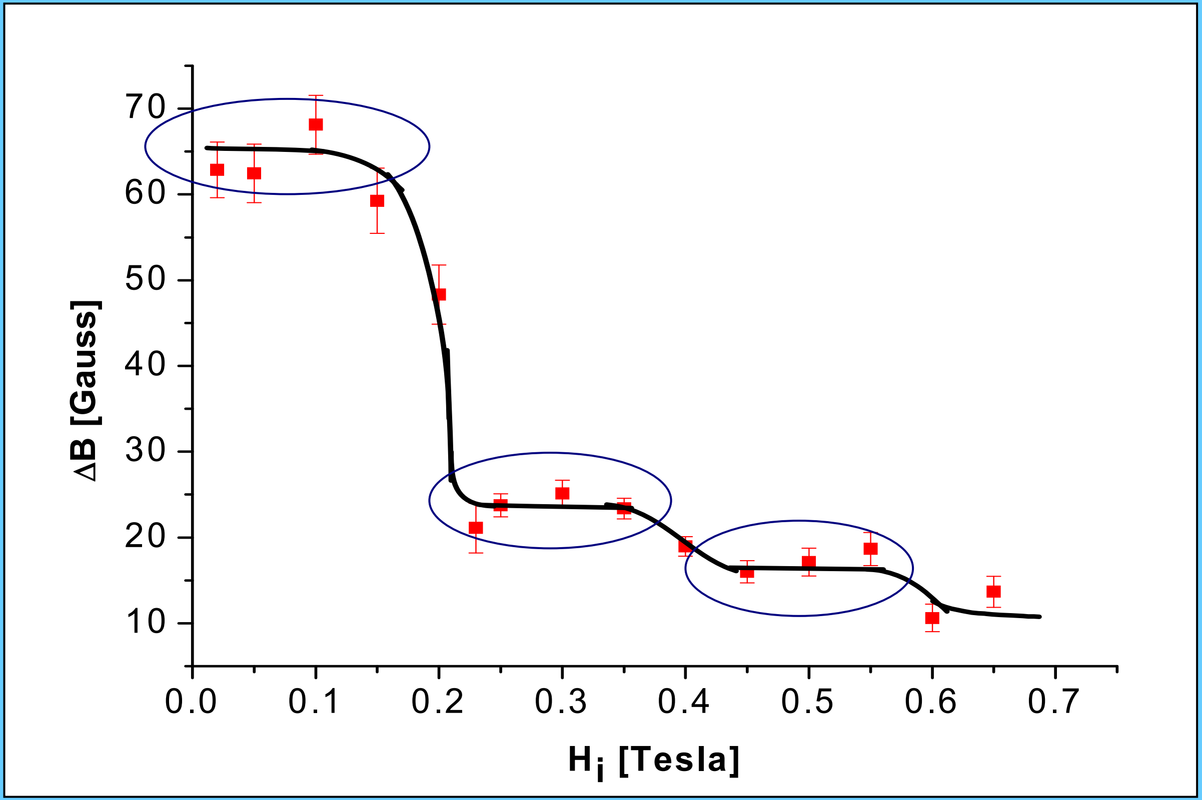
- Reproducibility

Asymmetry

Hematite

Analysis of the results

$$\Delta B = B_{Fe_8} - B_{Holder} = \frac{\omega_{Fe_8}(H_i) - \omega_{Holder}(H_i)}{\gamma_\mu}$$



- The process:

-2T→ H_i → 50G

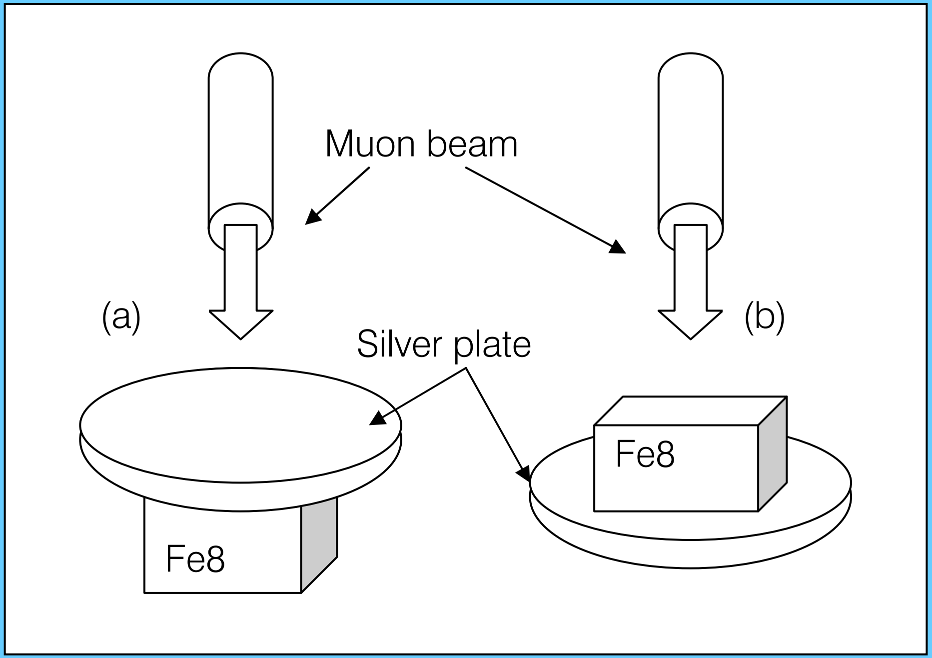
- Matching fields:

$$H_n = n \times 2.1kG.$$

$$n = 0,1,2...$$

(The solid line is a guide to the eye)

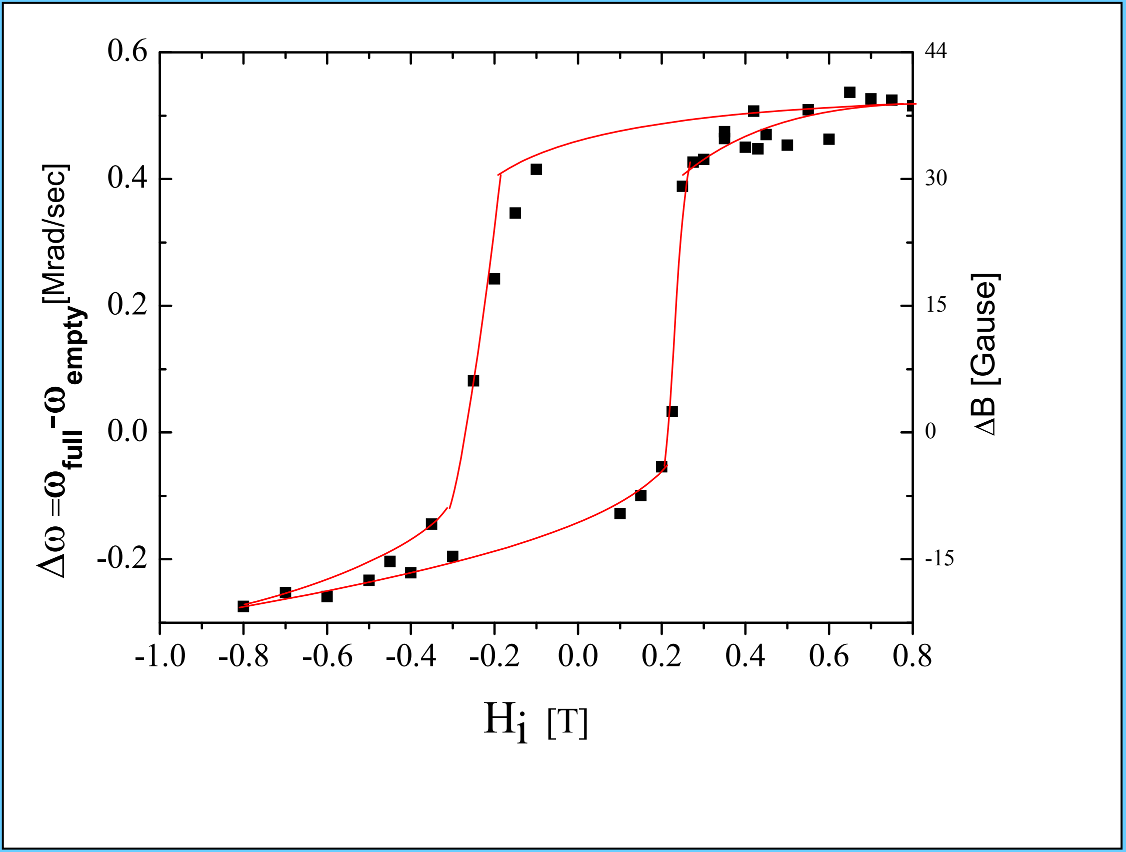
Two different setups



Several Fe8 single crystals were glued on a small silver plate.

In a different experiment the muons stopped in the silver plate

Analysis of the results – muons hit the silver plate



The resolution is worse, but a full hysteresis loop can be seen.

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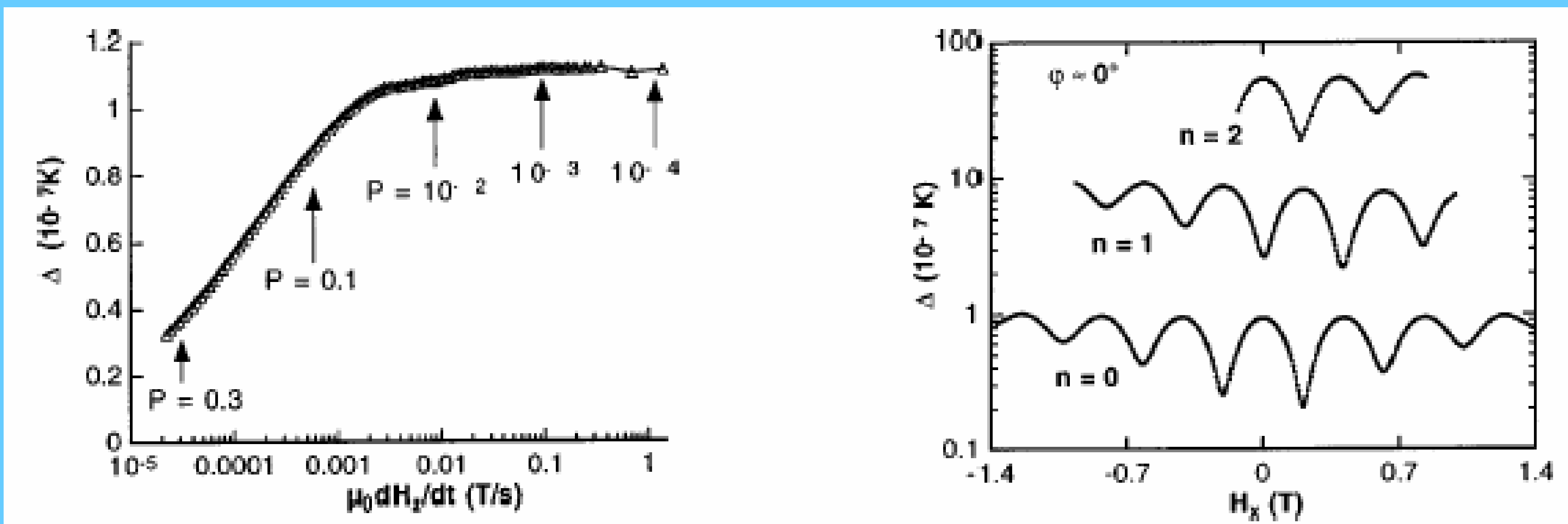
Comparison to the Landau-Zener model and to previous experiments

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



W. Wernsdorfer, R. Sessoli, Science 1999, 284, 133.

The probability to stay at m=-10

For example: 2kG < H_i < 4kG

H=0

$P_{-10,10}$ $1-p_{-10,10}$

Flip No Flip

H=2kG

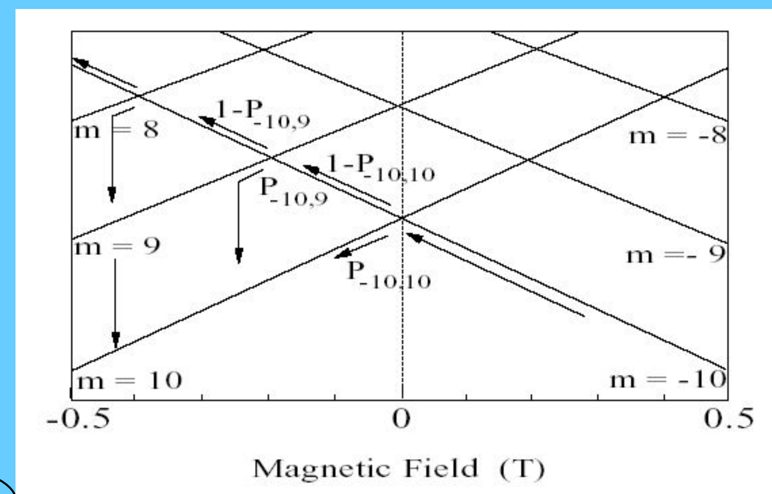
$P_{-10,9}$ $1-p_{-10,9}$

Flip No Flip

H=2kG

$P_{-10,9}$ $1-p_{-10,9}$

Flip No Flip



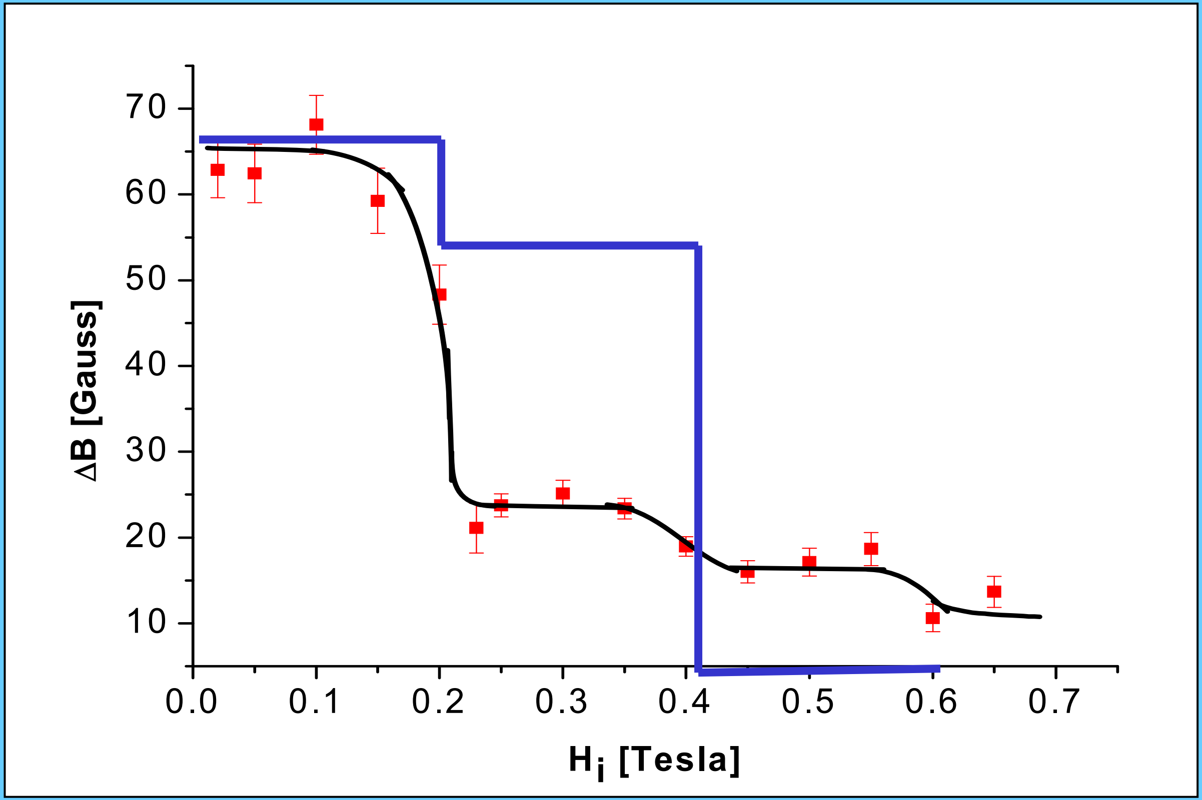
- The process:

$-2T \rightarrow H_i \rightarrow 50G$

The probability <u>not</u> to tunnel -

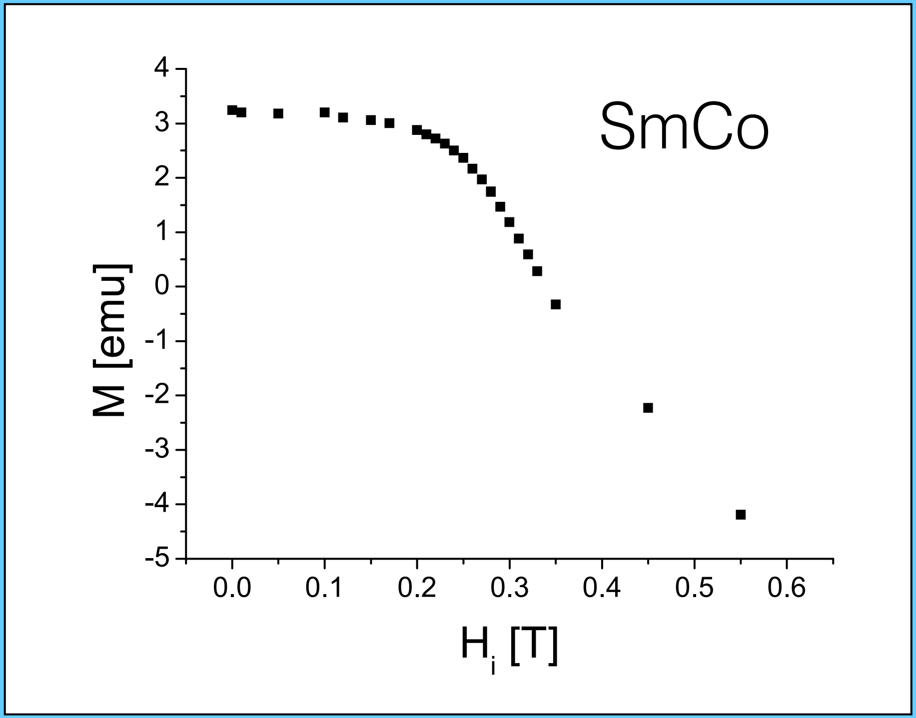
$(1-P_{-10,10}) \times (1-P_{-10,9})^2$

Comparison to the Landau-Zener model

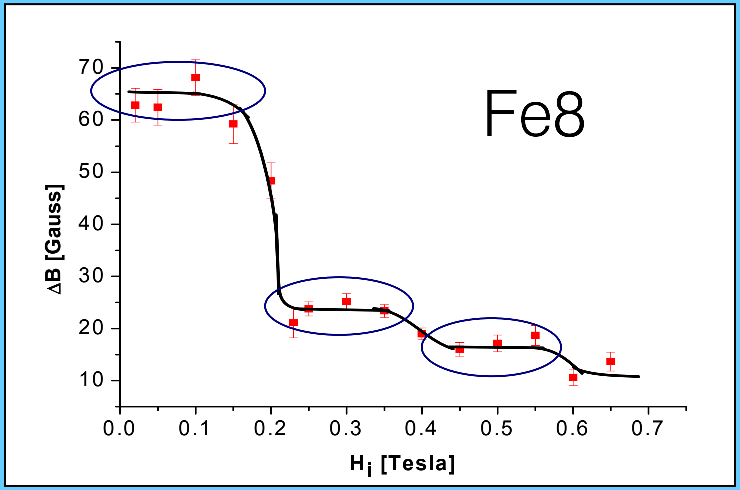


The agreement between theory and experiment is poor.

The same process for SmCo



$-2T \rightarrow H_i \rightarrow 50G$



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Summary

- The qualitative result from the Faraday force magnetometer demonstrates again the quantum nature of the Fe8 crystals.
- Using the mSR technique, which is also applicable to films, we observe quantum tunneling of the magnetization (QTM) in the Fe8 compound.
- We show that Fe8 can “remember” for at least 1/2 hour which intermediate field was visited. Using Fe8, we can distinguish between at least six processes by performing the same measurement.

This warrants Fe8 molecules the candidacy for a multi-bit magnetic memory.

Acknowledgments:

Dr. Y. Sheynin, Dr. M. Kapon, Prof. M. Kaftori - for sample preparation and characterization

Prof. E. Polturak and Prof. M. Resnikov - for helping with the DR

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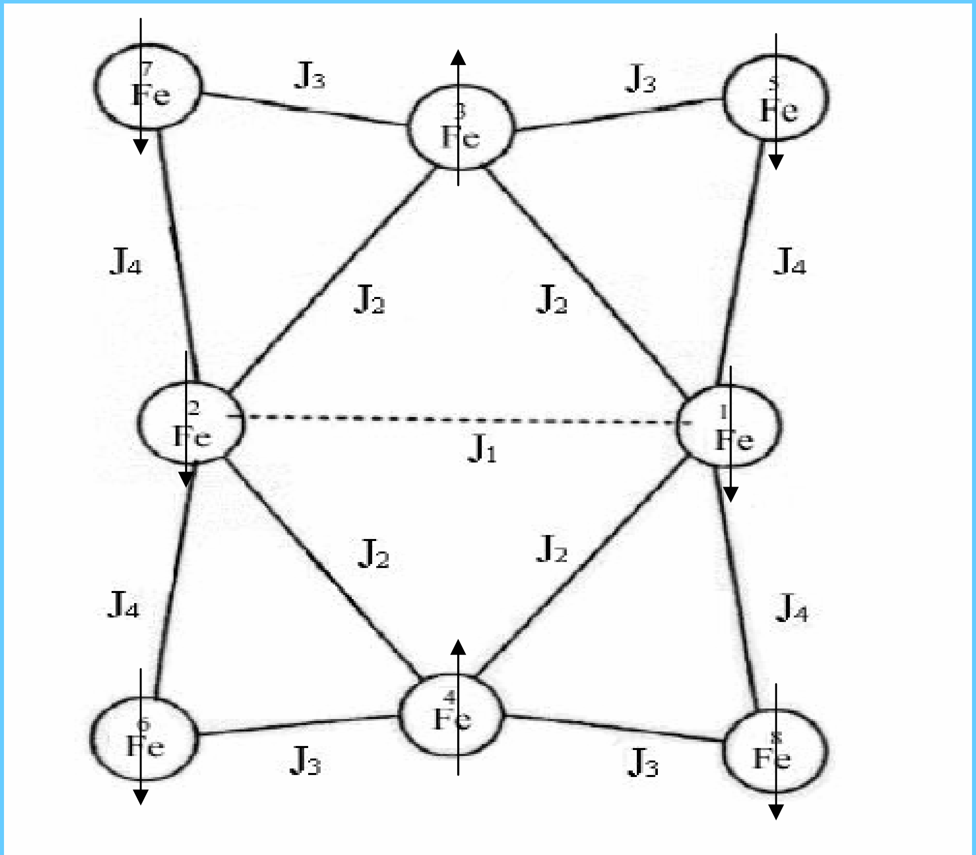
Special thank for Prof. Amit Keren.

End

The exchange path ways connecting iron(III) in Fe8

back



J_1= -147K

J_2= -173K

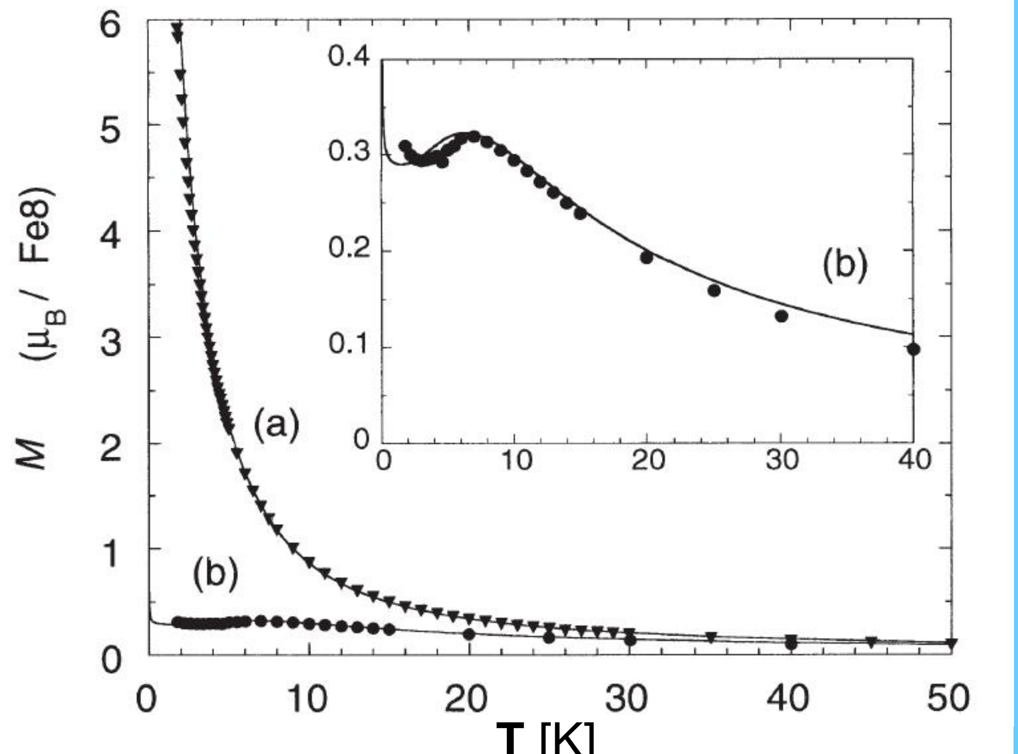
J_3= -22K

J_4= -50K

Blocking Temperature

back

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)

Hamiltonian of Fe8

back

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]

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

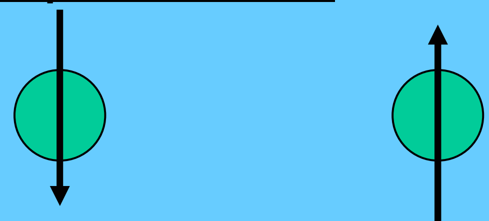
$$O_4^4 = (S_+^4 + S_-^4)/2$$

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

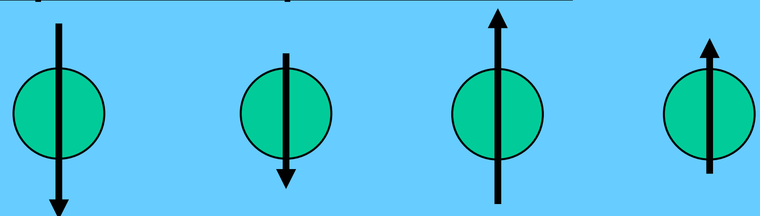
D. Gatteschi and R. Sessoli, Angew. Chem. Int. Ed. 42, No. 3 (2003), p. 268

What do we mean by multi-bit memory?

- **Single-bit Memory** using the same measurement one can distinguish between two different preparation processes.



- **Multi-bit Memory** using the same measurement one can distinguish between more than two preparation processes.



µSR process

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:

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

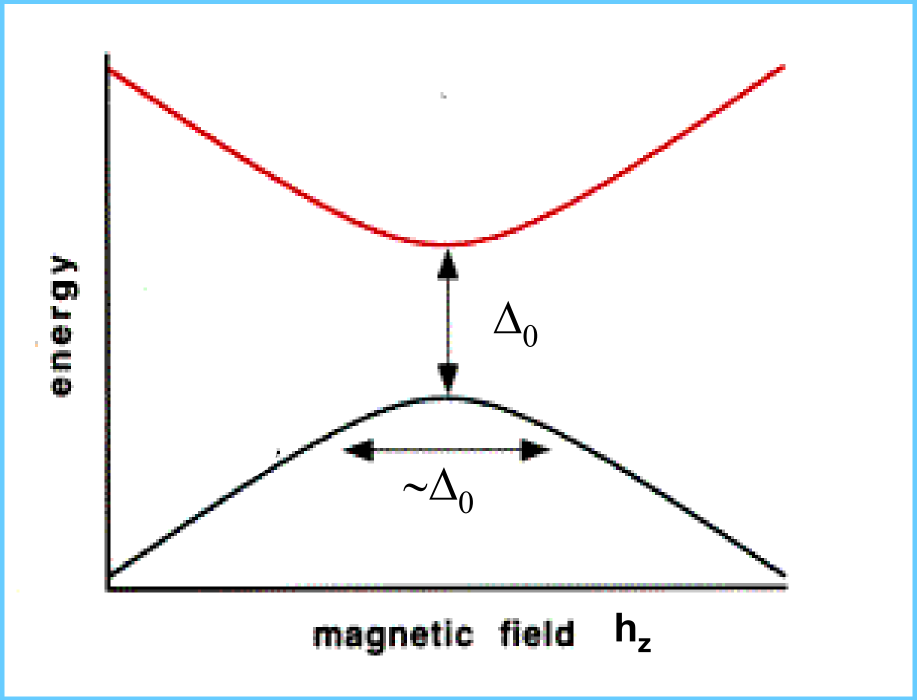
$$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \rightarrow E_{as} = -D/4 - g\mu_B\sqrt{h_x^2 + h_z^2}$$

$\Delta_0 = g\mu_B h_x$ 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: $\Delta/\hbar = g\mu_B\sqrt{h_x^2 + h_z^2}\Big/\hbar$

Zener time



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

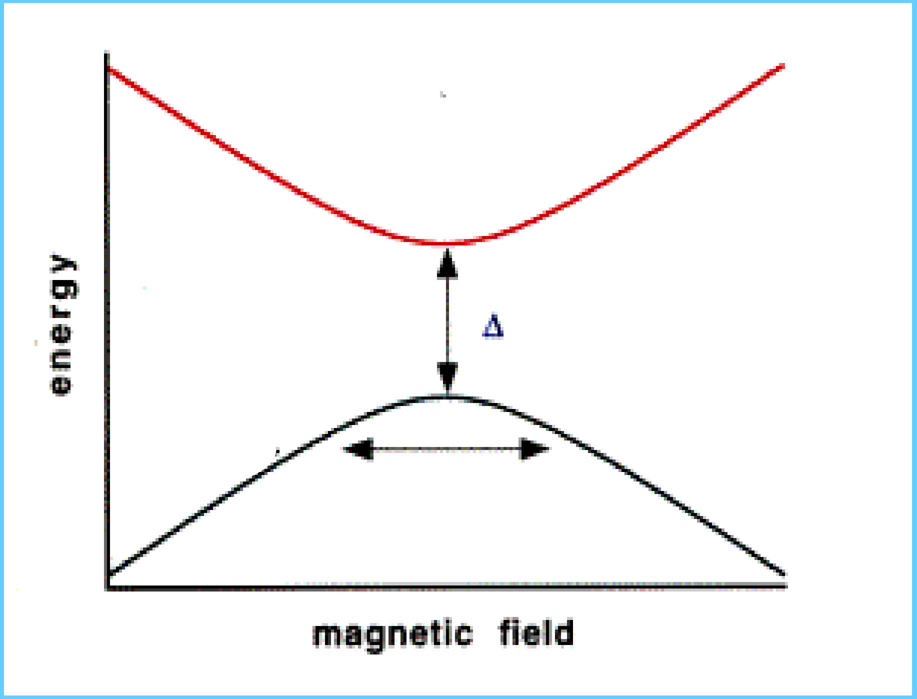
$$\tau_{tunnel} = \frac{\pi}{2\Delta_0}$$

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

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

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

Zener Time – Mullen et al



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

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

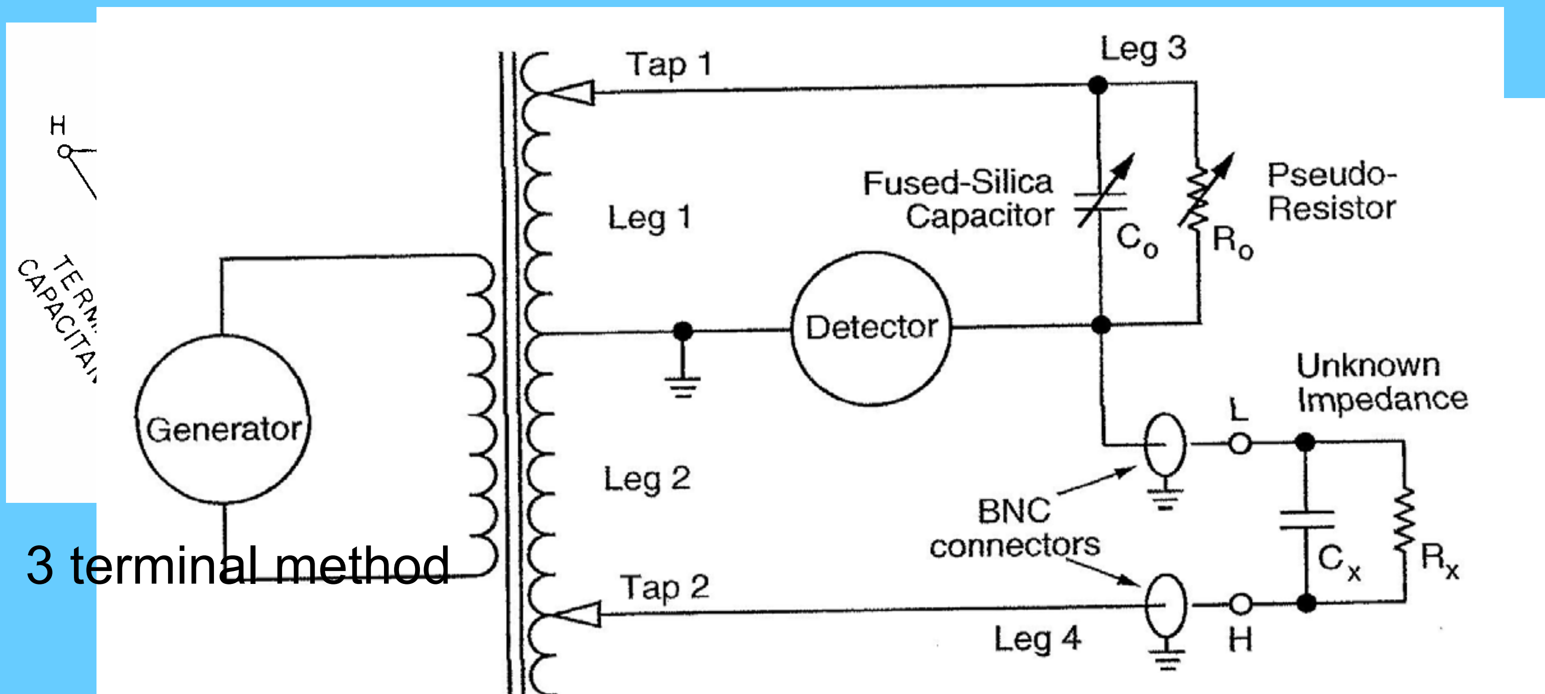
$$\hbar\alpha \big/ \Delta^2 << 1$$ sudden limit:

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

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

Capacitance bridge

magnetometer



3 terminal method

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

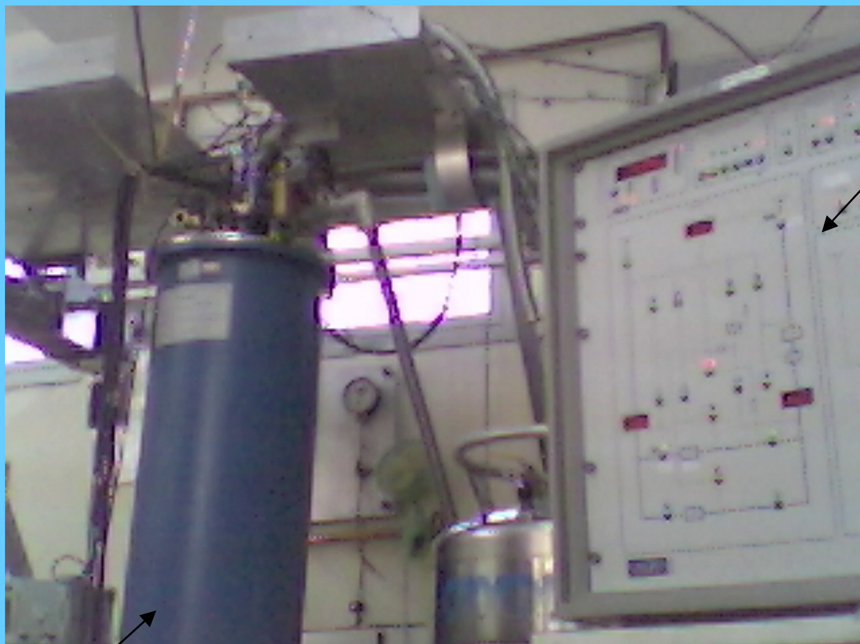
Ratio Transformer

Basic bridge circuit of AH2550A Capacitance Bridge

A capacitance bridge with transformer ratio arms.

Dilution refrigerator

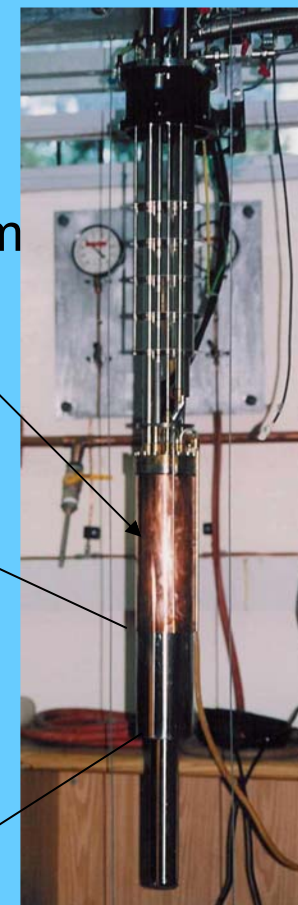
magnetometer

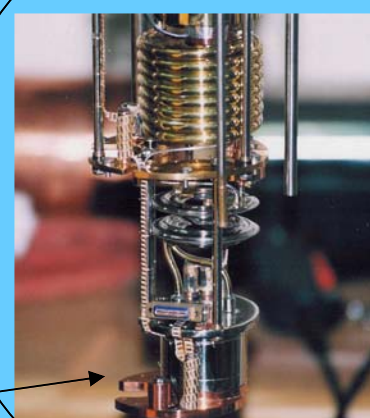


Control unit

outer Vacuum chamber

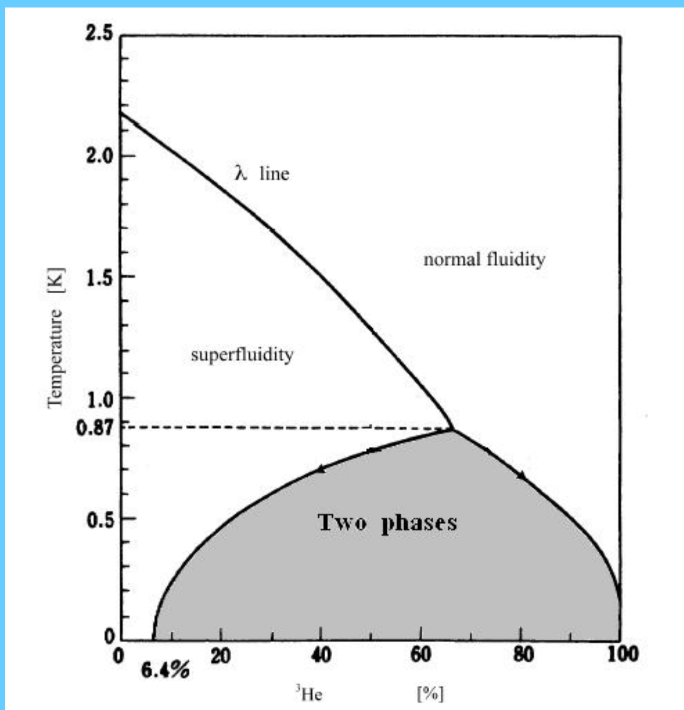
Inner Vacuum chamber





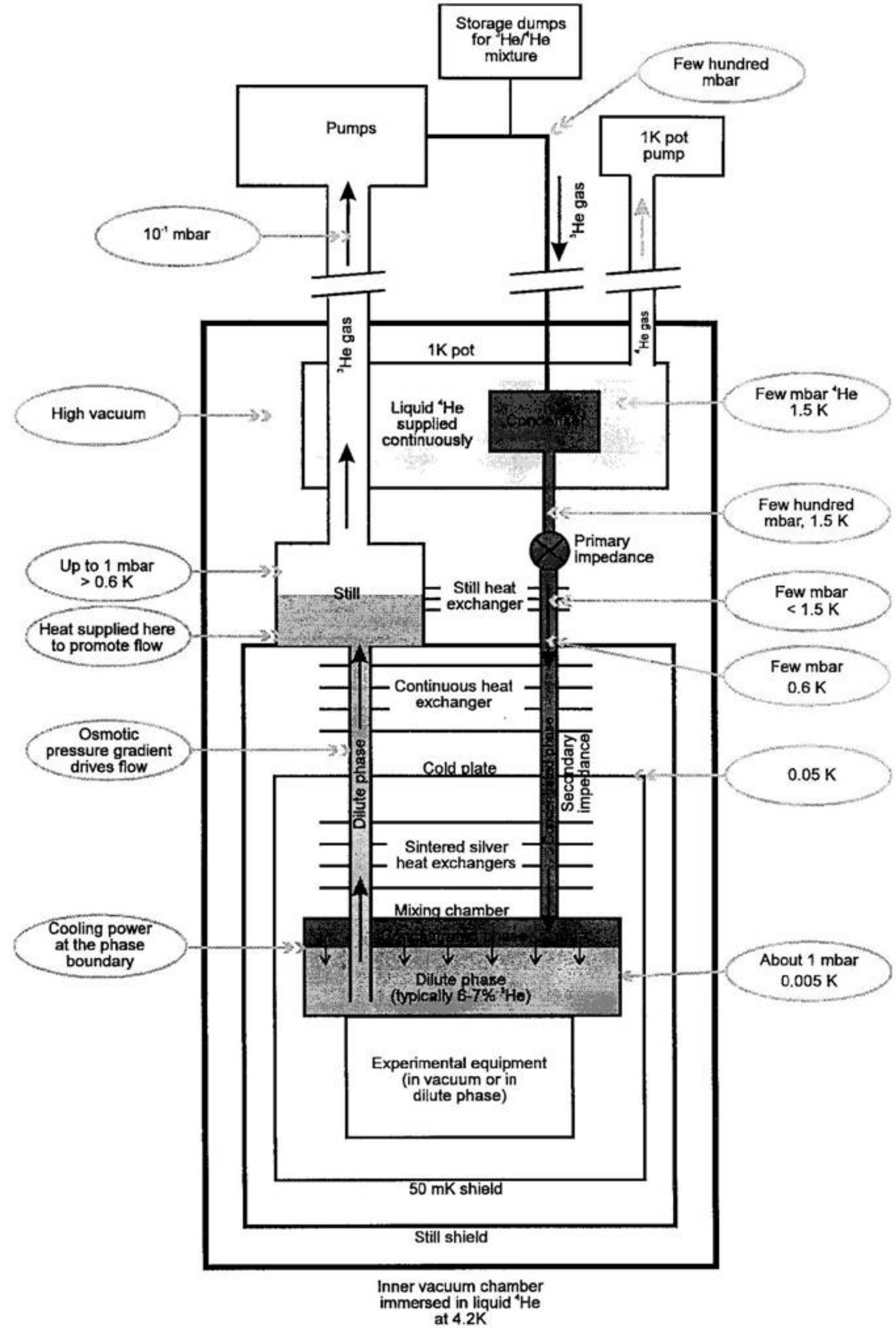
Mixing chamber

Dilution refrigerator – schematic view

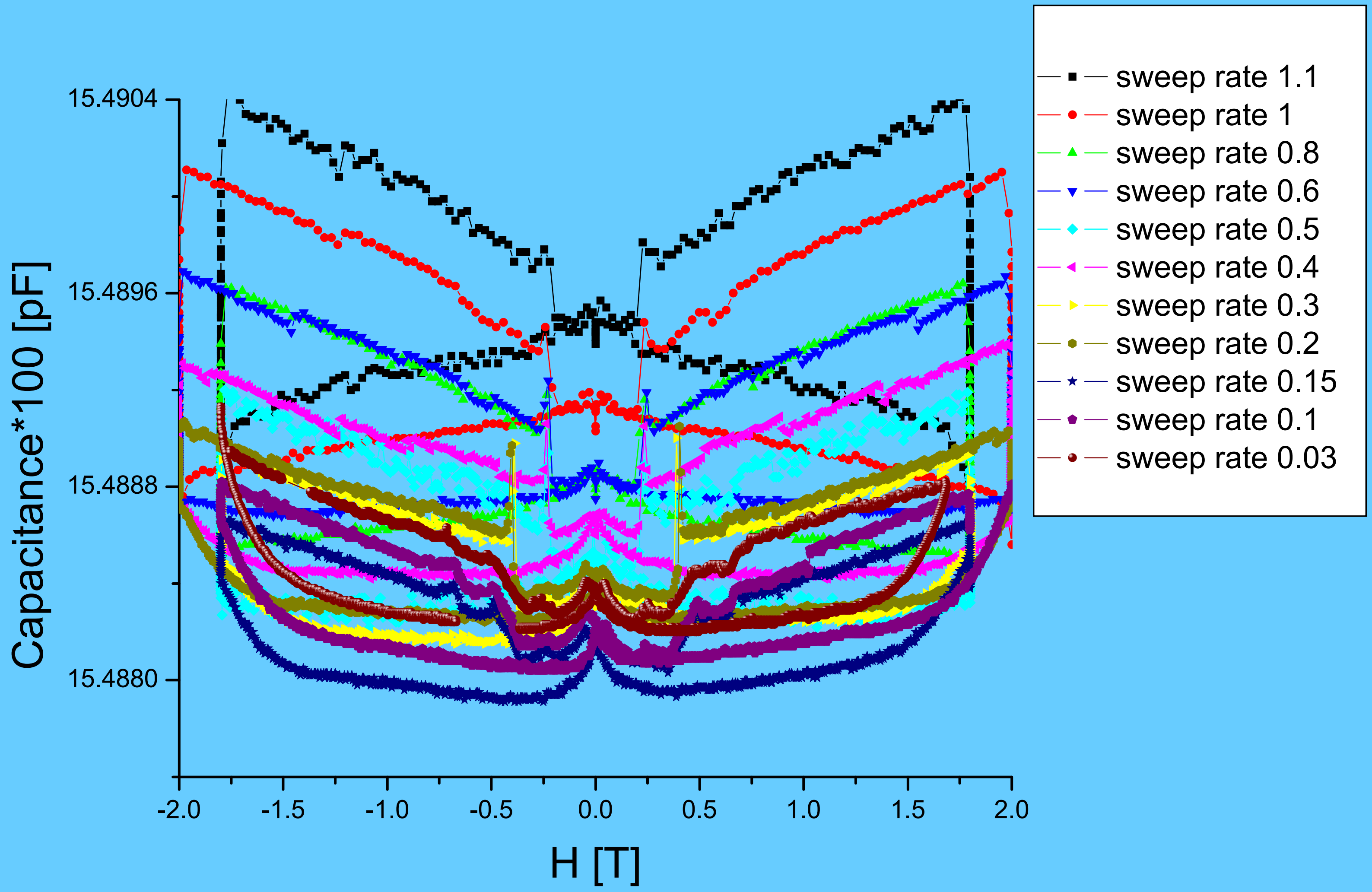


magnetometer

rmance.

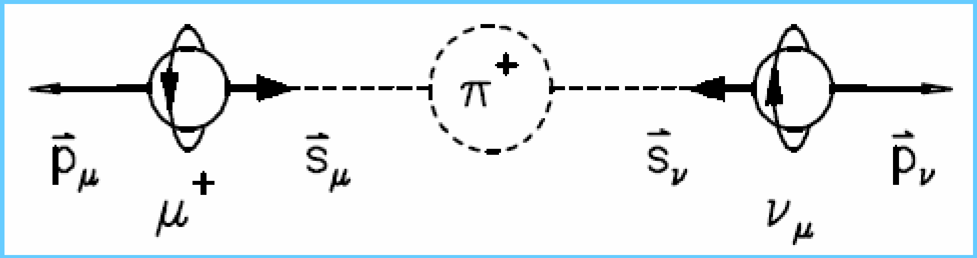


Changes due to eddy currents



Pion decay

$$\pi^{+} \rightarrow \mu^{+} + \nu_{\mu}$$



- Only left-handed neutrinos exist

- Pions have zero spin

- Pions at rest ($p_p = 0$) → Muons have a spin which is anti-parallel to their momentum

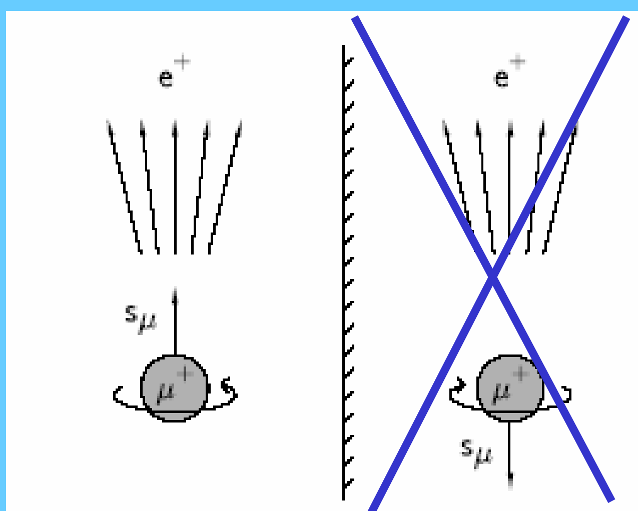
μSR

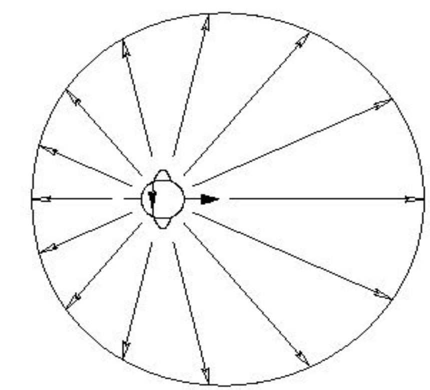
Muon decay

μSR

- The muon decays according to: $\mu^+ \rightarrow e^+ + \nu_e + \overline{\nu_\mu}$

- The positron is usually energetic enough to travel a substantial distance before annihilating.

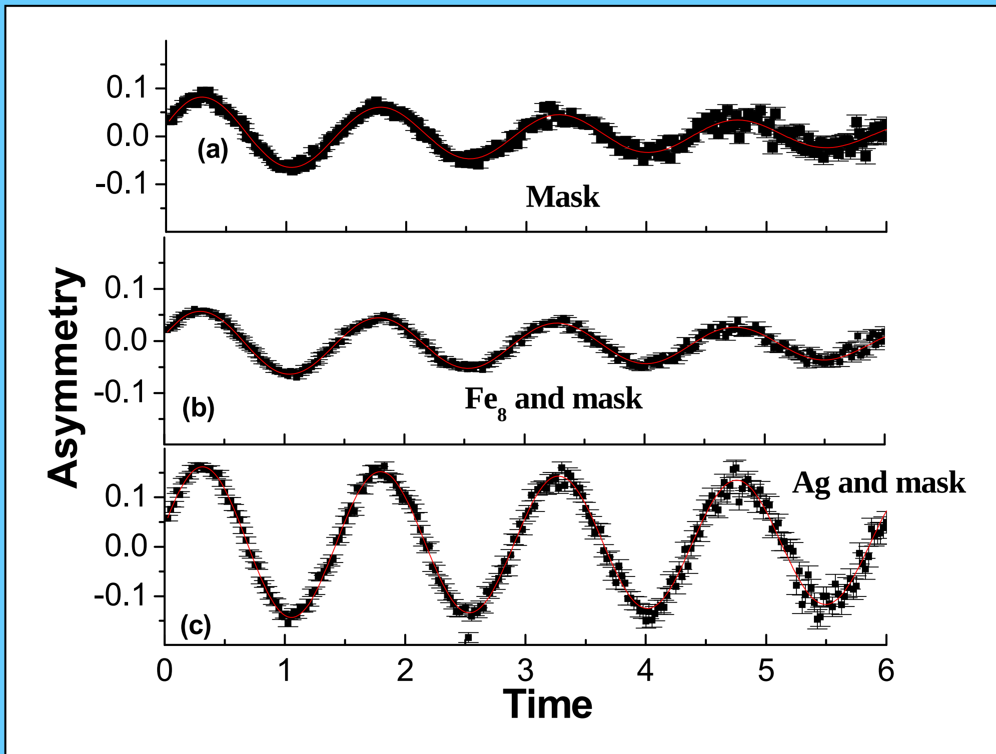


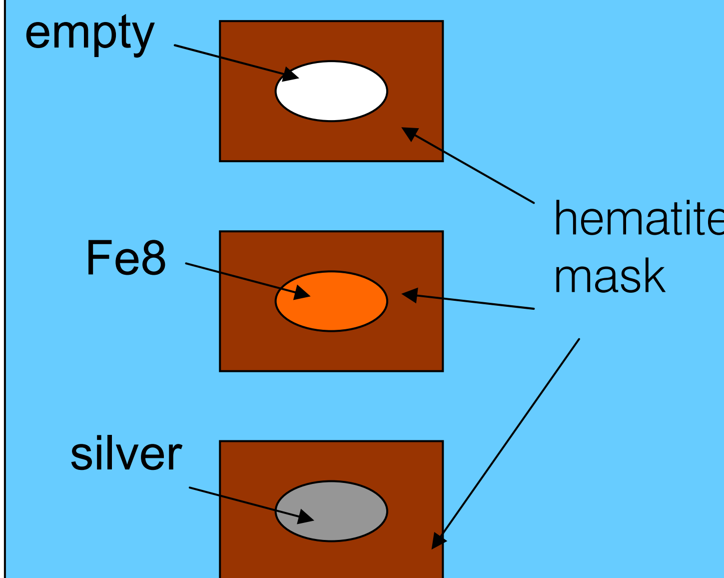


Angular distribution of positrons from muon decay, integrated over energy.

The violation of parity

Fe8 as hematite





The asymmetry of a hematite and glue mask (a) is very similar to mask and Fe8 (b), but different from mask and silver (c). Therefore, muons in Fe8 do not contribute to the asymmetry.

Comparison to the Landau-Zener model

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

$$\hbar = 7.6328 \times 10^{-12} \, [K]/[s]$$

$$\mu_B = 0.67170099 [K]/[T]$$

$$dH / dt = 0.245 [T]/[\mathrm{min}] = 4.083 \times 10^{-3} \, [T]/[s]$$

For $\Delta_{-10,10} = 10^{-7}$ K $\rightarrow$ $P_{-10,10} = 0.02$

For $\Delta_{-10,9} = 3 \times 10^{-7}$ K $\rightarrow$ $P_{-10,9} = 0.16$

For $\Delta_{-10,8} = 20 \times 10^{-7}$ K $\rightarrow$ $P_{-10,8} = 0.99$

Comparison to the Landau-Zener model

Starting point - $N_{-10} : N_{10} = 1:0$

H_i (intermediate field)	**The probability <u>not</u> to tunnel**	**$N_{-10} : N_{10}$**
$H_i < \sim 0.22T$	$1 - P_{-10,10}$	0.9776 : 0.0224
$\sim 0.22T < H_i < \sim 0.44T$	$(1-P_{-10,10}) \times (1-P_{-10,9})^2$	0.68 : 0.38
$\sim 0.44T < H_i < \sim 0.66T$	$(1-P_{-10,10}) \times (1-P_{-10,9})^2 \times (1-P_{-10,8})^2$	0 : 1

N_{-10} - the number of the molecules with spin up

N_{10} - the number of the molecules with spin down

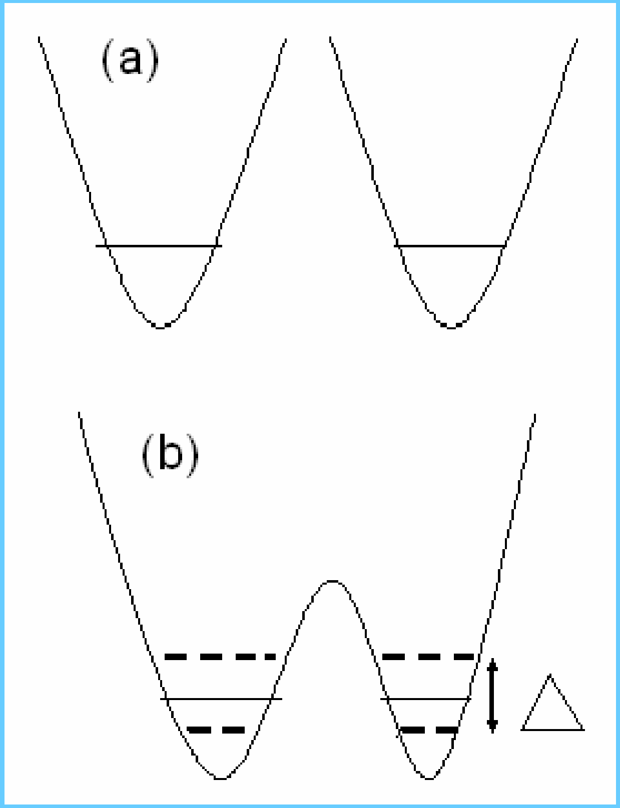
illustration

The simplest model – double well potential

Tunneling in a double well system:

a) Non-coupling states.

b) Coupling states giving rise to tunnel splitting, Δ.



The prediction

“The molecular approach to nanoscale magnetism”

A. Caneschi, D. Gatteschi, C. Sangregorio, R. Sessoli, L. Sorace, A. Cornia, M.A. Novak, C. Paulsen, W. Wernsdorfer
Journal of Magnetism and Magnetic Materials Vo. 200 (**1999**) p. 182-201

(referred to the result in Mn12)
“ These results…also make Mn12ac more appealing for technological applications as it represents a **multi- rather than a bi-stable single molecule memory unit**. **"**

Summary

- The experimental work:
  - Synthesizing Fe8 crystals
  - Assembling a dilution refrigerator
  - Fraday force magnetometer experiments (Design a load sensing variable capacitor; operating DR, SC magnet, capacitance bridge)
  - μSR experiments

end