Quantum Tunneling of the Magnetization in High Spin Molecules

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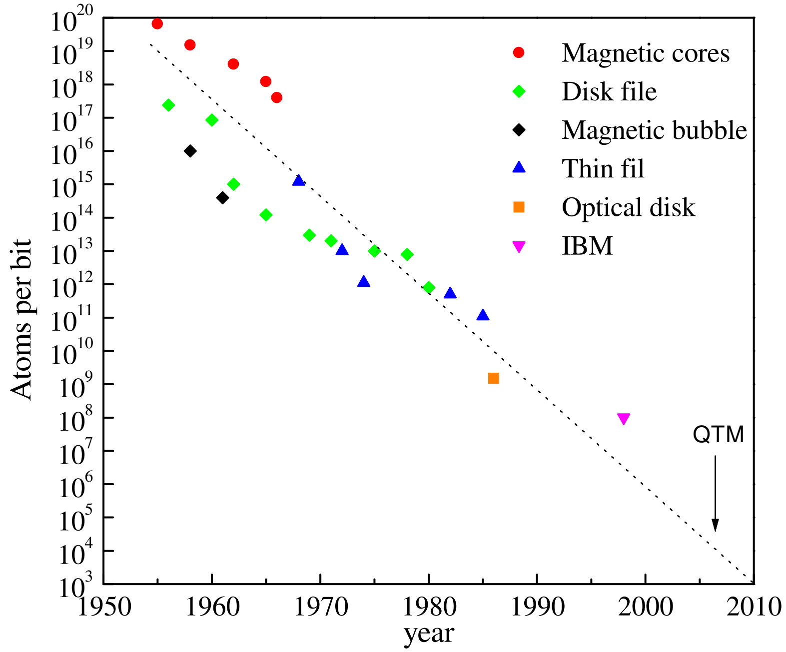
Introduction

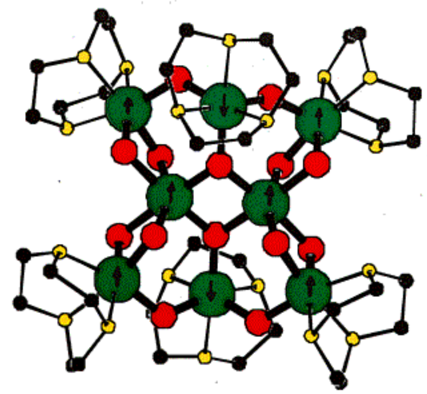
- **H**igh **S**pin **M**olecules (HSM) consist of coupled magnetic ions.
- At low temperatures HSM behave like giant spins.
- They crystallize in a lattice where they are magnetically separated.
- HSM can become the smallest magnetic writing unit.

Harris, *Physics World* (1999)

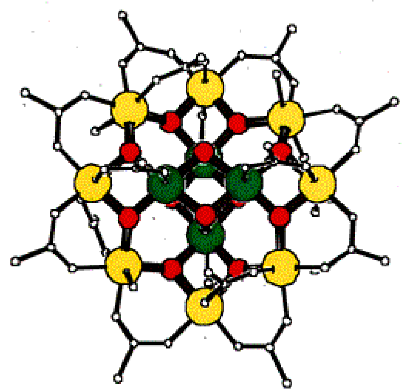


Most Studied HSM

- Fe_8 with ground spin state $S = 10$.
- 6 Fe ($S = 5/2$) ions coupled anti-ferromagneticly to 2 Fe ions.
- Mn_{12} with ground spin state $S = 10$.
- 4 Mn^{4+} ($S = 3/2$) ions coupled anti-ferromagneticly to 8 Mn^{3+} ($S = 2$) ions.



Fe_8

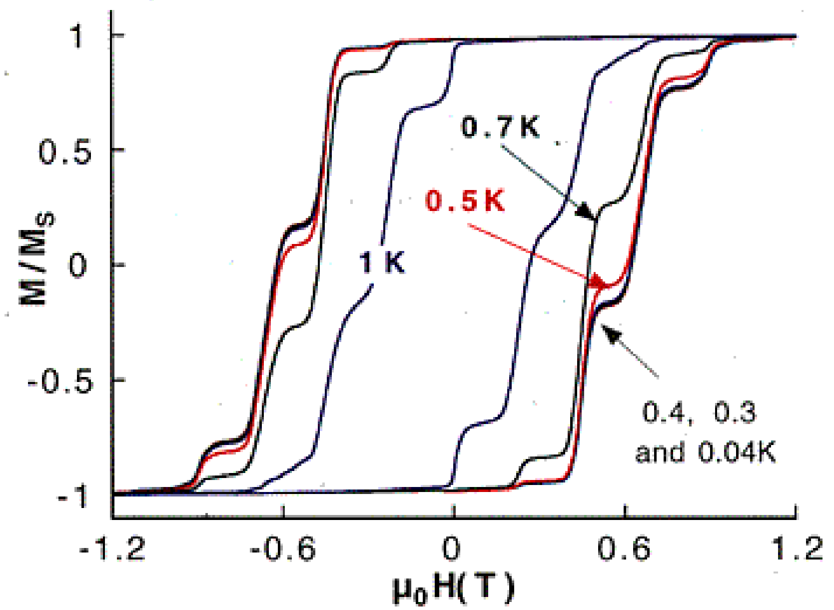


Mn_{12}

Quantum Tunneling of the Magnetization (QTM)

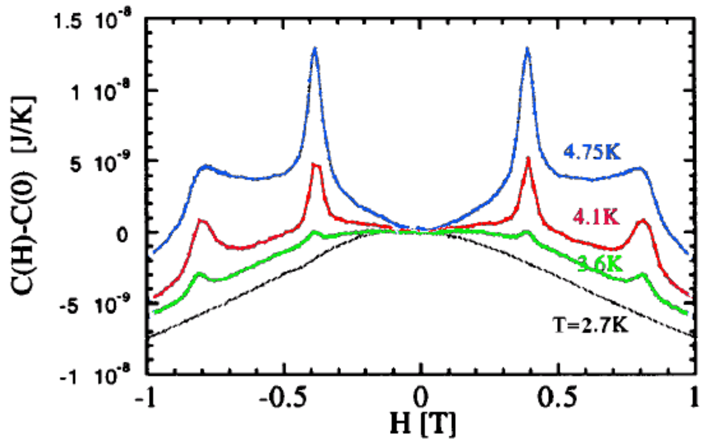
- QTM was first observed in Mn_{12} and then in Fe_8, through steps at regular intervals of magnetic field in the hysteresis loop.
- QTM provides a signature quantum mechanical behavior in macroscopic systems.

Wernsdorfer, QMAG (1999)

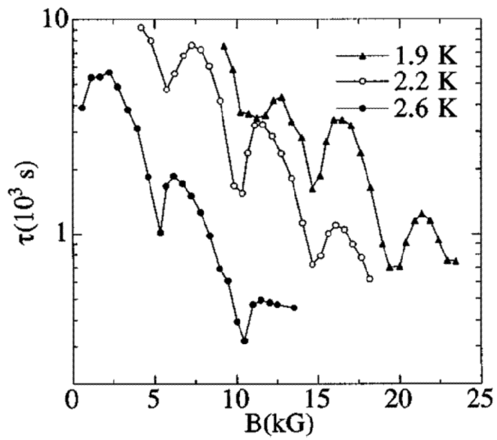


More QTM Experiments

Fominaya, *PRL* **79**, 1126 (1997)



Tejada, *Europhys. Lett.* **35**, 301 (1996)



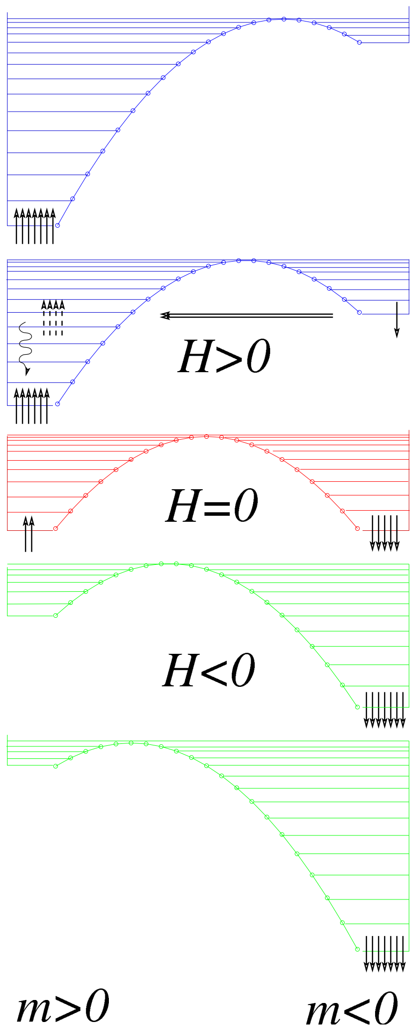
- The heat capacity of Mn_{12} single crystal shows peaks at regular intervals of magnetic field.
- The relaxation rate of the magnetization decreases drastically at regular intervals of magnetic field.

A Simple Model for QTM

- At low T the Hamiltonian for a single molecule is

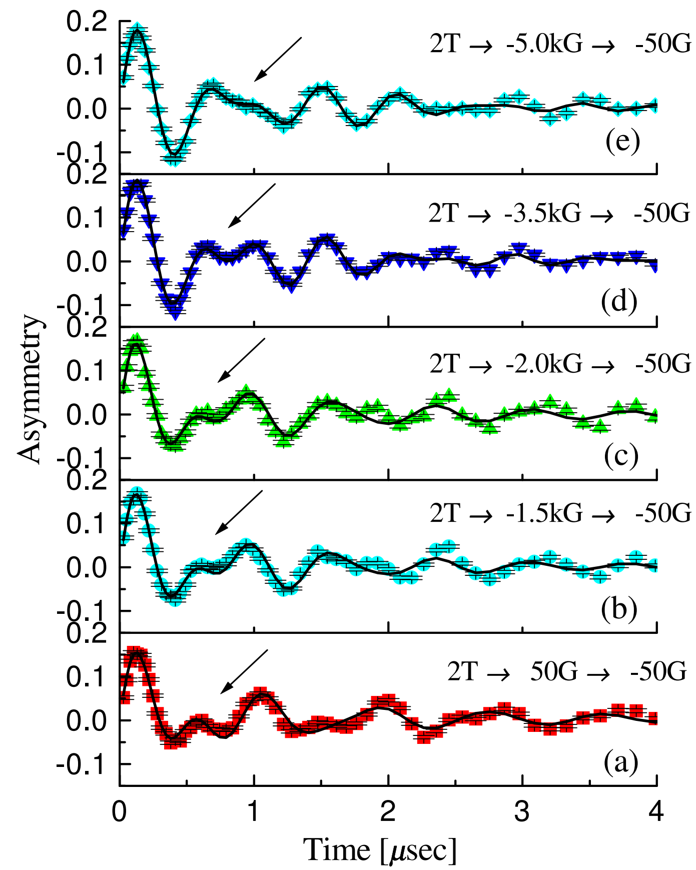
$$\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z$$

- Transition is due to quantum tunneling only.
- Tunneling occurs when two states on both sides have the same energy.
- Matching of energy levels is achieved when $H_z = \frac{nD}{g\mu_B}$



μSR in Fe_8

- All measurements were performed at 40 mK.
- We apply $H = 2$ T for 30 minutes.
- We sweep the field $H \to H_i \to -50$ Gauss.
- All measurements are performed at $H = -50$ Gauss.
- The asymmetry is different only if different matching fields $H_{\mathrm{match}} = 0, 2.1, 4.2, \cdots$ kG are crossed.



Problem

- The Hamiltonian of HSM is

$$\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z$$

- $\mathcal{H}$ commutes with S_z

$$[\mathcal{H}, S_z] = 0$$

therefore S_z should be conserved.

What induces tunneling ??

Theory of QTM

- In order to have tunneling additional terms $\mathcal{H}_\perp$ should be added to the spin Hamiltonian.
- Possibilities are:
  1. High order spin terms and crystal field.
  2. Transverse field.
  3. Spin-phonon interaction.
  4. Dynamic nuclear spins and dipolar interaction.
- We are interested in the dependence of tunneling on the spin value S.

Proposed Mechanisms

- Crystal Field: $\mathcal{H}_\perp = -\frac{g\mu_B}{2}\sum_{n=1}^{N} h_n \left(S_+^n + S_-^n\right)$

$$\boxed{\tau^{-1} = \frac{DS\hbar}{\pi}\left(\frac{g\mu_B h_N (S\hbar)^{N-2}}{2D}\right)^{2S/N}}$$

van Hemmen, *Europhys. Lett.* **1**, 481 (1986).

- Transverse Field: $\mathcal{H}_\perp = -g\mu_B H_x S_x$

$$\boxed{\tau^{-1} = \frac{2D}{\pi[(2m-1)!]^2\hbar}\frac{(S+m)!}{(S-m)!}\left(\frac{g\mu_B H_x}{2D}\right)^{2m}}$$

Chudnovsky, *PRL* **79**, 4469 (1997).

- Spin-Phonon: $\mathcal{H}_\perp \propto (S_k S_l + S_l S_k)$

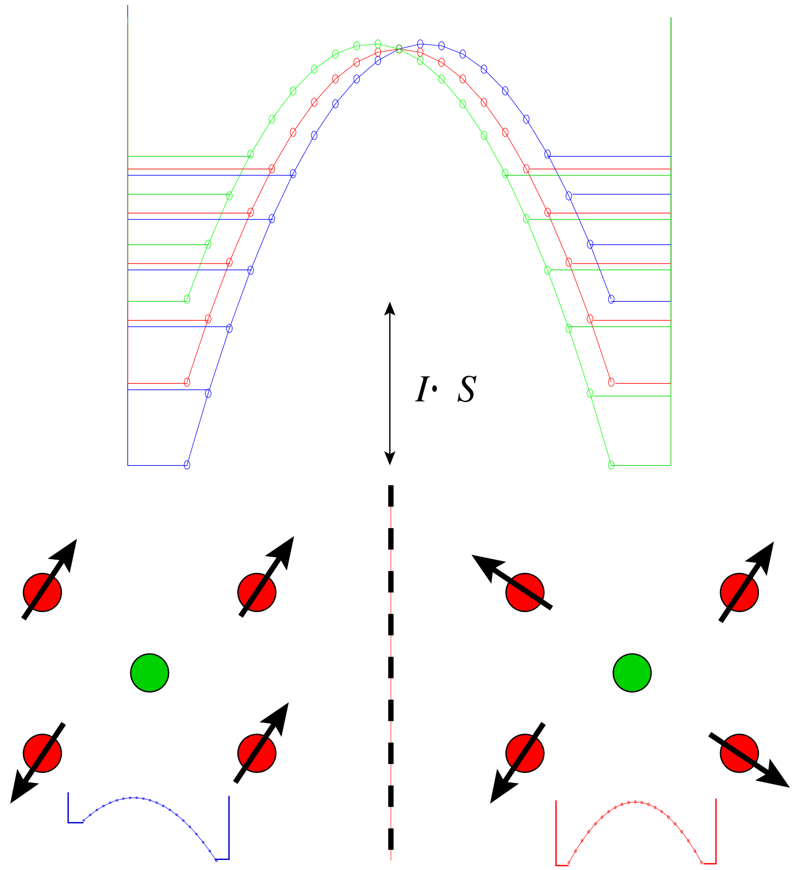
$$\boxed{\tau^{-1} = \frac{12}{\pi^2\hbar^4 c^5 \rho}| < S|\mathcal{H}_\perp| - S > |^2 (H_z S)^3}$$

Hartmann Boutron, *PRL* **75**, 537 (1995).

Dynamic Nuclear Spins and Dipolar Interaction

- Dipolar fields bring the spin states of the molecules out of resonance.
- Rapidly fluctuating hyperfine fields bring molecules initially to resonance.
- Tunneling changes the dipolar fields and brings more molecules to resonance.
- The tunneling rate in this case is

$$\boxed{\tau^{-1} \propto \frac{\Delta_0^2 T_2 |E_S - E_{-S}|}{E_D}}$$



Prokofév, *PRL* **80**,5794 (1998).

Strategy

- The Hamiltonian of anisotropic HSM is

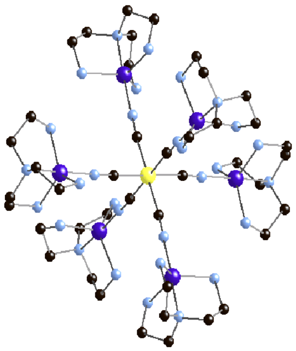
$$\mathcal{H} = -DS_z^2 - g\mu_B H_z S_z + \mathcal{H}_\perp$$

- For isotropic HSM $D \longrightarrow 0$

$$\mathcal{H} = -g\mu_B H_z S_z + \mathcal{H}_\perp$$

We can probe $\mathcal{H}_\perp$ directly!

Isotropic High Spin Molecules

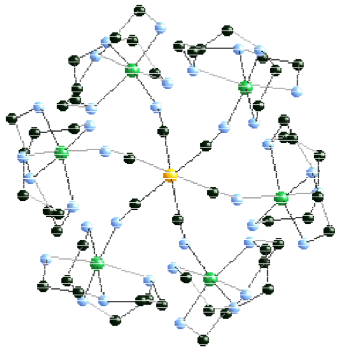


$\mathrm{CrCu_6}$

$S = 9/2$

$J_{\mathrm{Cr-Cu}} = 77\mathrm{K}$

$S_{\mathrm{Cu}} = 1/2$

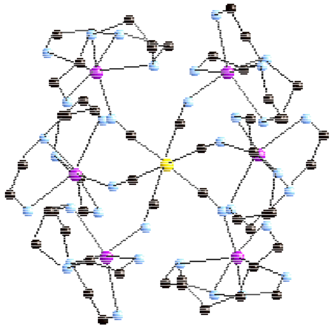


$\mathrm{CrNi_6}$

$S = 15/2$

$J_{\mathrm{Cr-Ni}} = 24\mathrm{K}$

$S_{\mathrm{Ni}} = 1$



$\mathrm{CrMn_6}$

$S = 27/2$

$J_{\mathrm{Cr-Mn}} = -11\mathrm{K}$

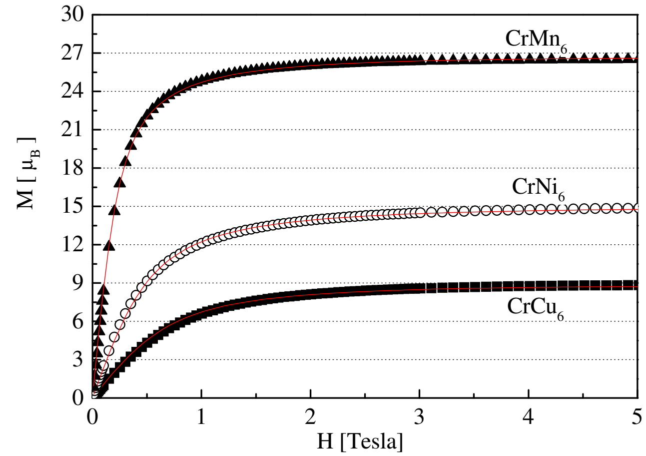
$S_{\mathrm{Mn}} = 5/2$

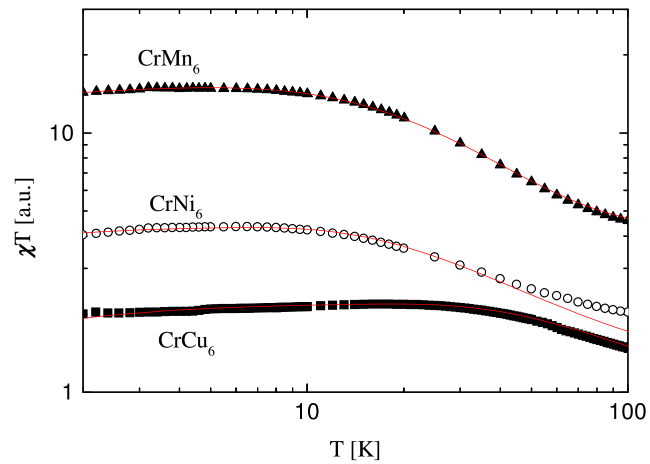
$S_{\mathrm{Cr}} = 3/2$

Magnetic Properties

- At high H and $T = 2$ K the magnetization per molecule saturates giving the value of S.
- M vs. H follows the Brillouin function of the corresponding S.
- At low H and low T the susceptibility saturates and shows no anisotropy.
- The susceptibility follows that expected from the Hamiltonian

$$\mathcal{H} = -J \sum_{i=1}^{6} \vec{S}_0 \cdot \vec{S}_i - g\mu_B \vec{H} \cdot \sum_{i=0}^{6} \vec{S}_i$$

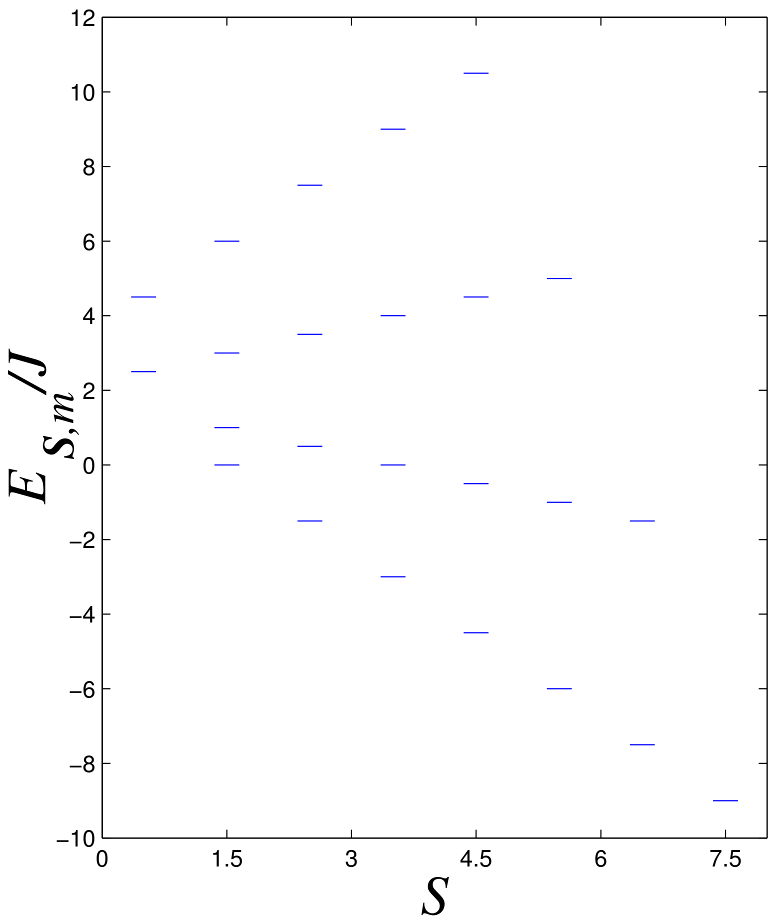




Calculation of the Susceptibility

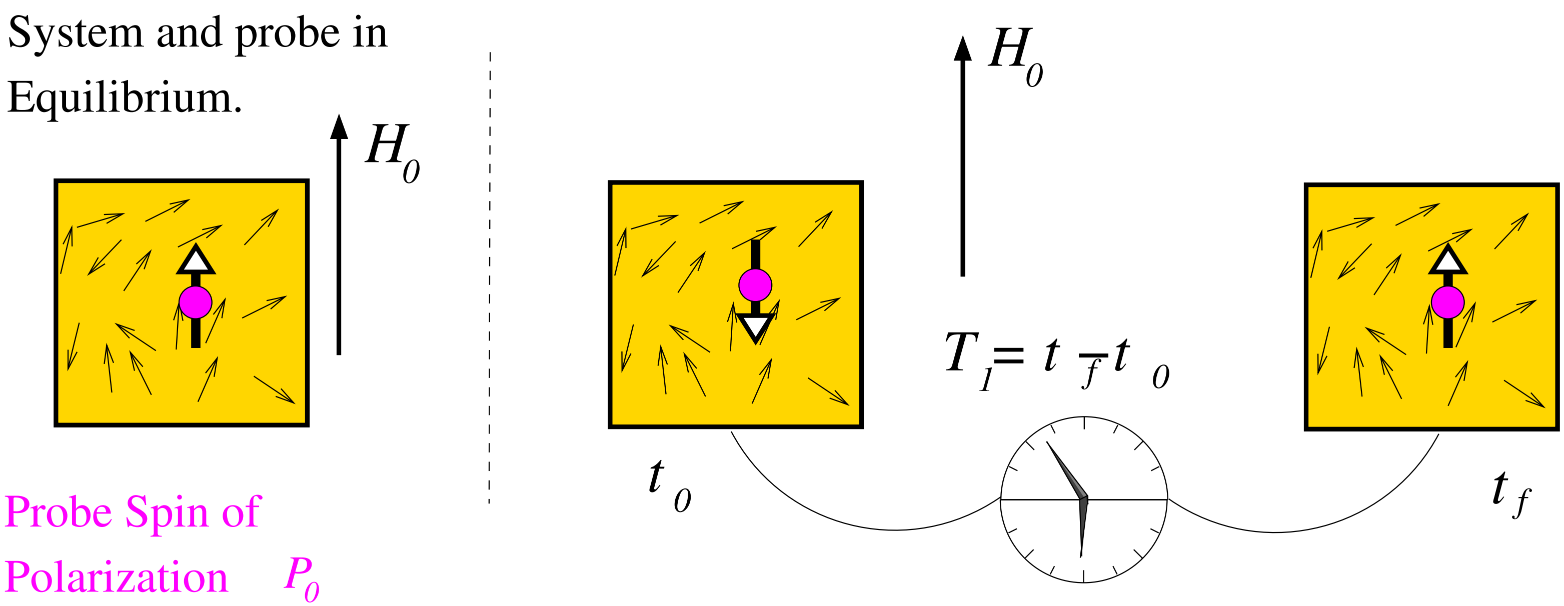
- We diagonalize the Hamiltonian $\mathcal{H}$
- We find the eigenstates $|S, m>$ and eigenvalues $E_{S,m}$.
- The susceptibility is

$$\chi = \sum_{|S,m>} \frac{m e^{-\frac{E_{S,m}}{T}}}{\mathcal{Z} H}$$



Spin Lattice Relaxation Time

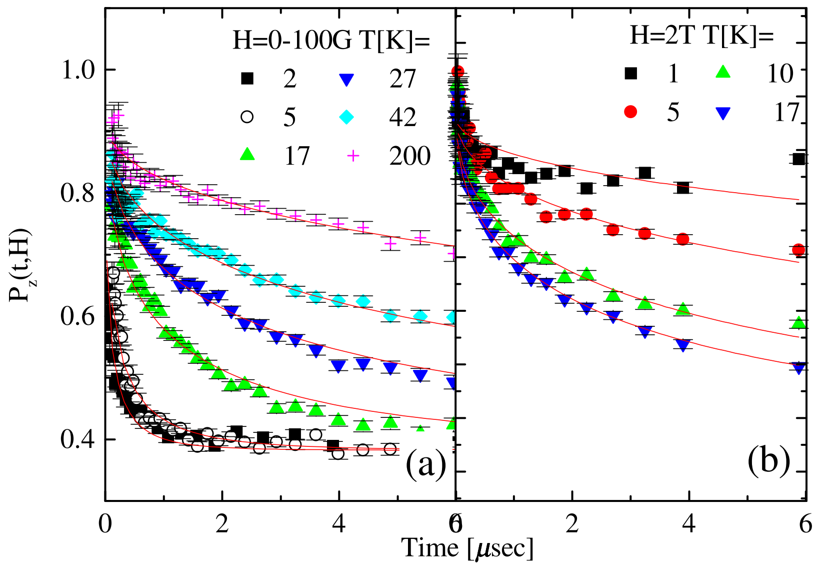
- It is the time that takes a probing spin to reach equilibrium



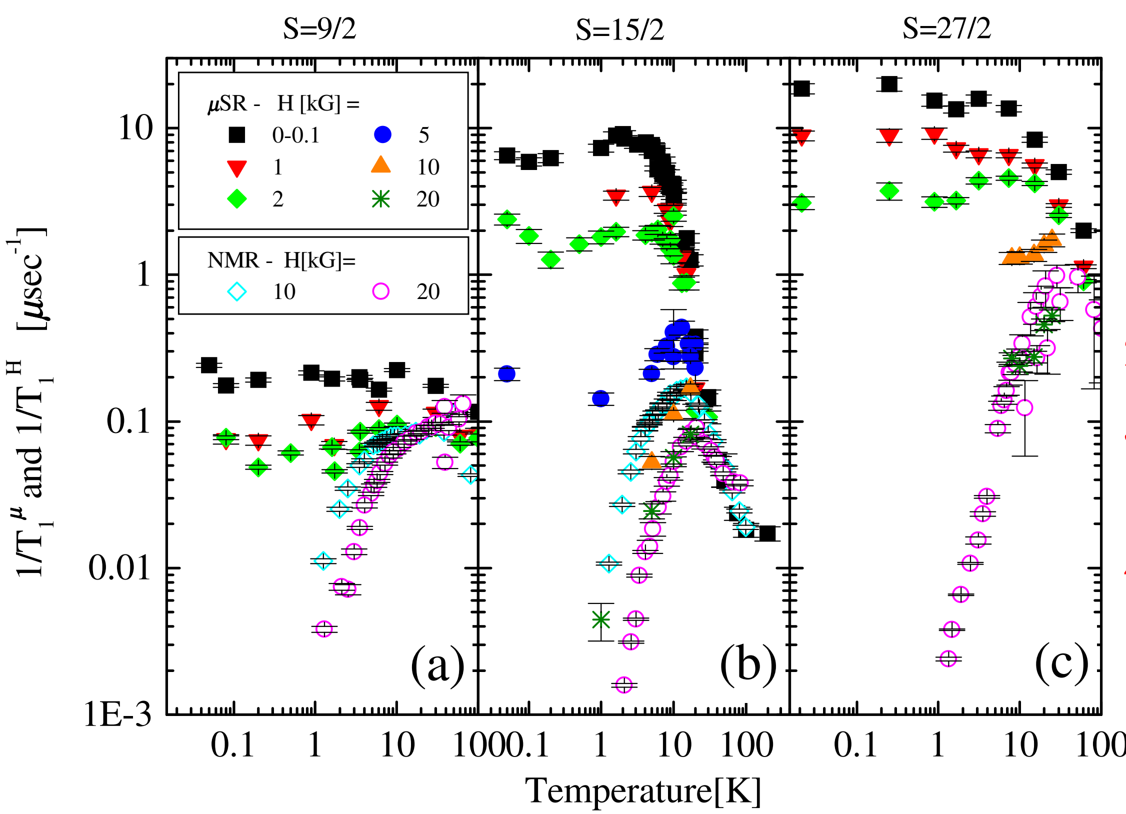
- In μSR $P_0 = 1$ and $P_f = 0$ while in NMR $P_0 = 0$ and $P_f = 1$.
- Only fluctuating fields $\vec{B}(t)$ contribute.
- Only transverse fluctuations $B_\perp$ contribute.

T Dependence of the μ^+ Polarization

- At $H = 0$ the muon polarization relaxation increases with decreasing temperature down to 5 K and then saturates.
- At $H = 2$ T and temperatures lower than ~ 17 K the relaxation decreases with decreasing T.



μSR and NMR Results



1. No T dependence at $H \to 0$, $T \to 0$.
2. Scale of T varies.
3. H dependence varies.
4. Different behavior in different H.

- The spin lattice relaxation rate measured by μSR and NMR at the same external field can be scaled.

The Spin Lattice Relaxation

- In spin lattice relaxation theory one assumes a fluctuating local field $\vec{B}(t)$ experienced by a local probe (muon or nucleus) of spin $\vec{I}$.

- The spin lattice relaxation time T_1 in this case follows

$$\frac{1}{T_1} = \frac{\gamma^2}{2} \int_{-\infty}^{\infty} dt \, \langle B_\perp(0) B_\perp(t) \rangle \exp(i\gamma H t).$$

- The correlation time τ and mean square of the transverse field distribution at the probe site in frequency units Δ^2 are defined by

$$\gamma^2 \langle \mathbf{B}_\perp(t) \mathbf{B}\perp(0) \rangle = \Delta^2 \exp\left(-t/\tau\right).$$

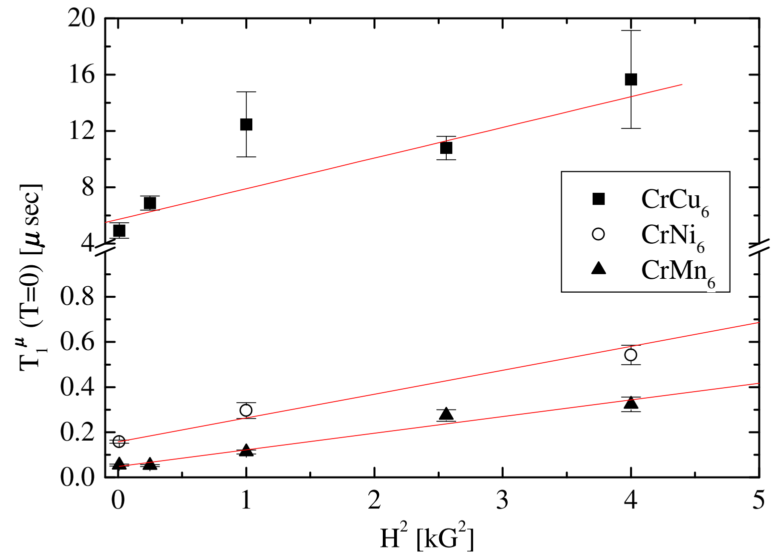
Field-Field Correlation Time

- The spin lattice relaxation rate is

$$\frac{1}{T_1} = \frac{\Delta\tau}{\omega^2\tau^2 + 1}$$

where in our system $\omega = g\mu_B H$.

$$T_1 = \frac{\omega^2\tau^2 + 1}{\Delta\tau}$$

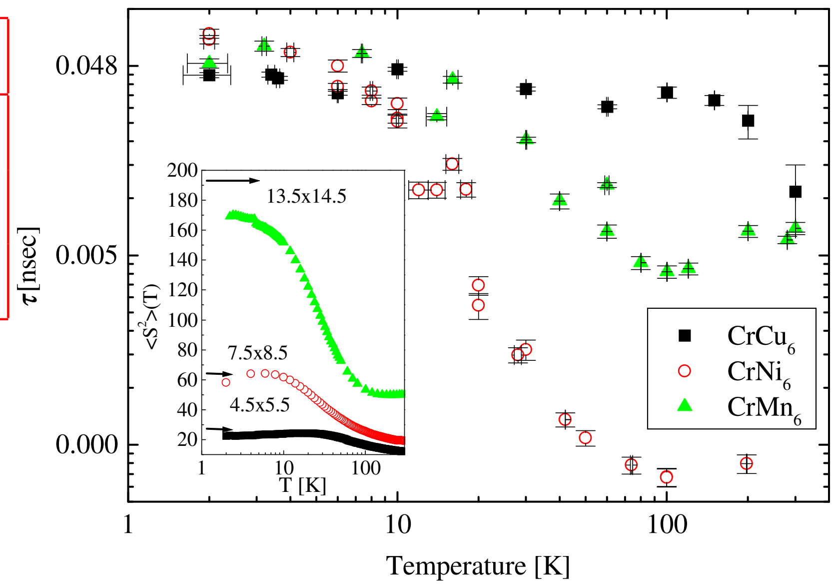


- The value of $T_1(T \to 0)$ depend linearly on H^2.

Field-Field Correlation Time

- From the linear fit of $T_1(T \to 0)$ vs. H^2 we have

	τ_{int} [nsec]	Δ [MHz]
$CrCu_6$	0.034(4)	4.9(9)
$CrNi_6$	0.053(4)	26(2)
$CrMn_6$	0.044(4)	38(2)



- The correlation time at all temperatures follows

$$\tau(T) = \frac{(g\mu_B)^2}{3k_B}\frac{S(S+1)}{T_1(T)T\chi(T)\Delta^2}.$$

- The correlation time depends weekly on S at $T \to 0$.

Calculation of T_1

- Assuming a coupling $A\vec{I}\cdot\vec{S}$ between the probe $\vec{I}$ and the molecular spin $\vec{S}$, the spin lattice relaxation rate is

$$\frac{1}{T_1} = \frac{A^2}{2}\int_{-\infty}^{\infty} \langle S_-(t)S_+(0)\rangle\, e^{i\omega t} dt$$

- For the spin states of $\mathcal{H}$ we obtain

$$\frac{1}{T_1} = \frac{A^2}{2\mathcal{Z}} \sum_{|S,m>} (S(S+1) - m(m+1)) \left(\frac{\tau_{S,m} e^{-\frac{E_{S,m}}{T}}}{1 + \omega'^2 \tau_{S,m}^2} \right)$$

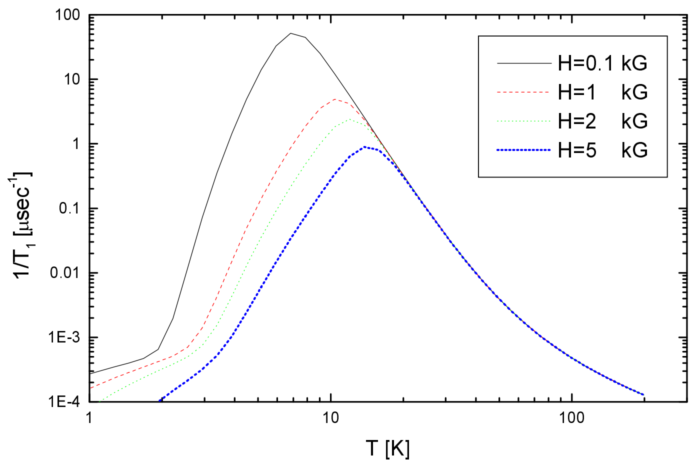
where $\tau_{S,m}$ is the lifetime of the level $|S,m>$ and $\omega' = (\gamma - g\mu_B/\hbar)H \simeq -g\mu_B H/\hbar$.

$1/T_1$ Due to Spin-Phonon Interaction

- Assuming that the finite lifetime of the levels is due to spin-phonon interaction

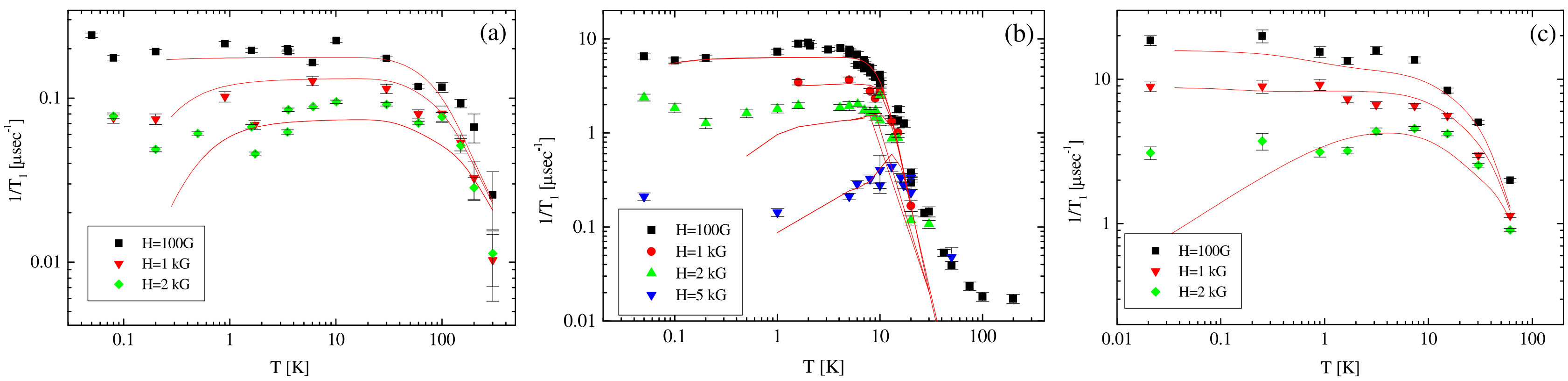
$$\tau_{sp}^{-1} = \frac{C(E_{\mathbf{S},m} - E_{\mathbf{S}',m'})^3}{\exp\left[(E_{\mathbf{S},m} - E_{\mathbf{S}',m'})/T\right] - 1}$$

- The behavior is similar to the experimental data at high T but differs at $T \to 0$.



Additional Constant Fluctuations

- To reproduce $1/T_1$ at low temperatures and low fields we assume $\frac{1}{\tau_{S,m}} = \frac{1}{\tau_{sp}} + \frac{1}{\tau_{int}}$ where τ_{int} is constant.



- With this we improve the agreement.

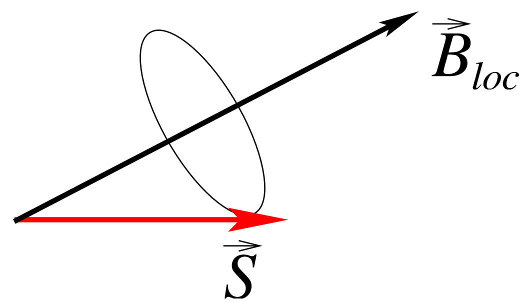
Discussion

- The correlation time τ_{int} depends weekly on S, ruling out crystal field and dipolar interactions.
- We have seen that spin-phonon interaction cannot account for the finite $1/T_1$ at low T.
- We are left with fluctuating hyperfine interaction $\vec{B}_{mol} = a\vec{i}(t) \cdot \vec{S}$.

Consider the Bloch equation

$$\frac{d\vec{S}}{dt} = g\mu_B \left[a\vec{i}(t) \times \vec{S} \right]$$

which is independent of S.



Conclusion

- The spin lattice relaxation in HSM is temperature independent at low temperatures.
- The spin-spin correlation time at low temperatures depends weekly on the molecular spin S.
- The molecular spin dynamics at high temperature is driven by spin phonon interaction, while dynamically fluctuating hyperfine fields induce the molecular spin dynamics at very low temperatures.

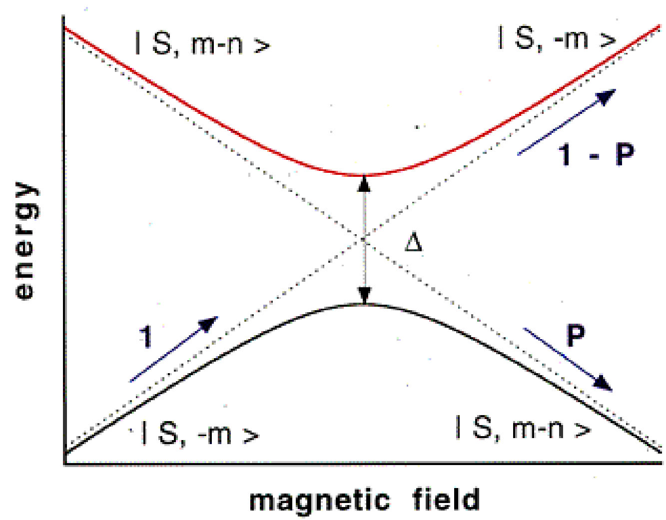
$$\boxed{\mathcal{H}_\perp \propto \vec{i} \cdot \vec{S}}$$

Landau-Zenner Tunneling

- Landau Zenner model is used for experiments with swept external magnetic field.
- The tunneling probability is

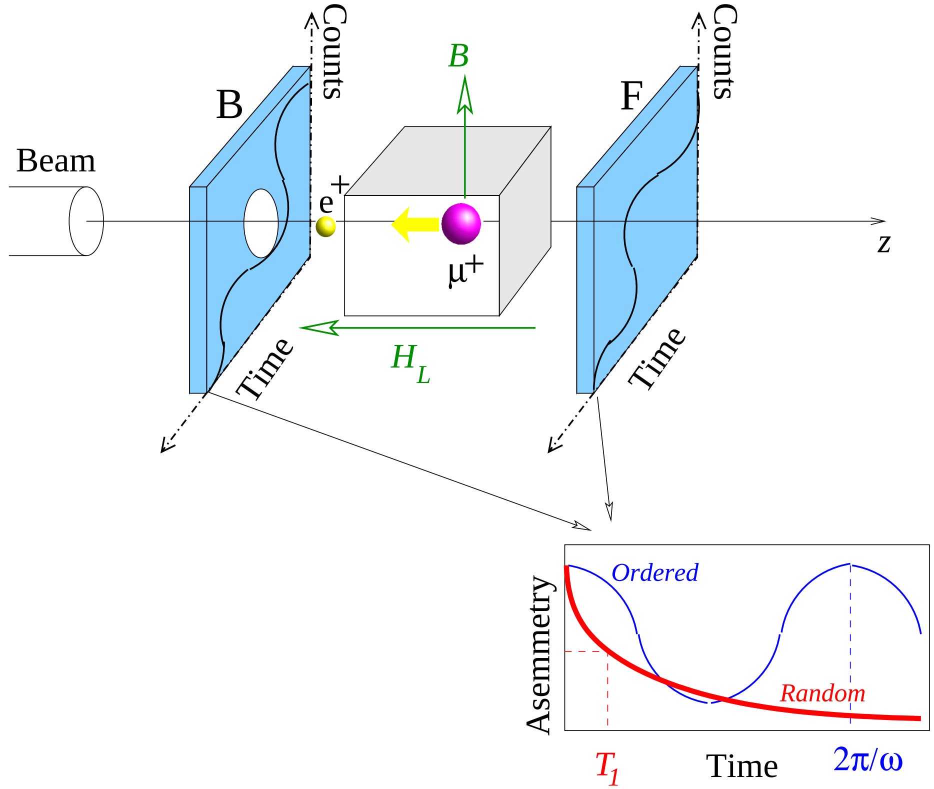
$$P = 1 - \exp\left[-\frac{\pi\Delta}{4\hbar g\mu_B S(dH/dT)}\right]$$

where Δ is the gap at the level crossing (tunnel splitting).



The μSR Technique

- The muons are 100% polarized.
- The positrons are emitted parallel to the muons polarization.
- Histograms of positron counts vs. time are collected in the F/B counters.



- The Asymmetry $= \frac{F-B}{F+B}$ is proportional to the polarization.
- Zero field, Longitudinal or transverse field can be applied.

Back

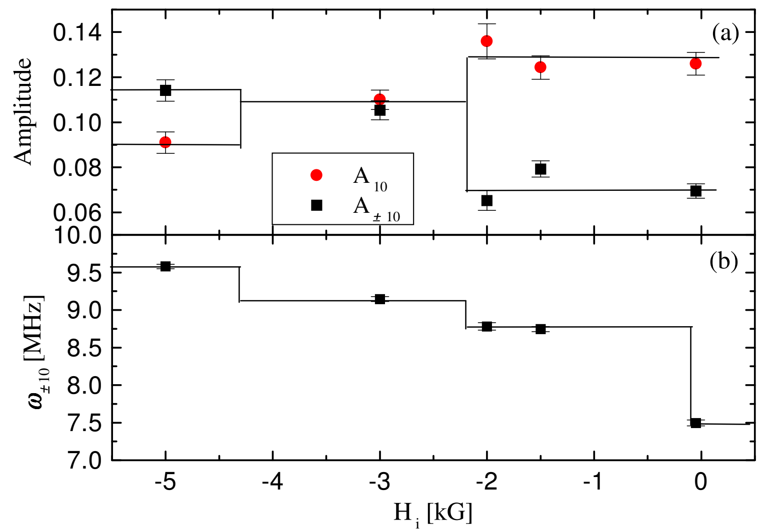
μSR in Fe_8

- We fit the asymmetry to

$$A(t) = A_{10}\sin(\omega_{10}t)e^{-\lambda_{10}t} + A_{\pm 10}\sin(\omega_{\pm 10}t)e^{-\lambda_{\pm 10}t}$$

- A_{10}, ω_{10} and λ_{10} represents the fraction of μ^+ near $m = +10$ state.

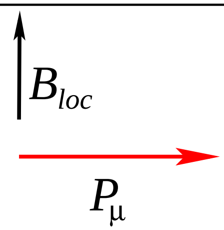
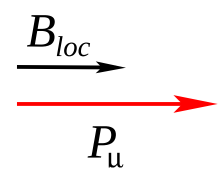
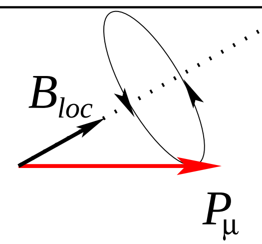
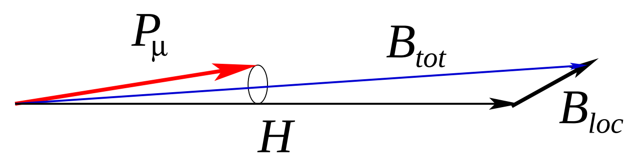
- $A_{\pm 10}$, $\omega_{\pm 10}$ and $\lambda_{\pm 10}$ represent the fraction of μ^+ near $m = \pm 10$ state.



- Steps in the value of $\omega_{\pm 10}$, A_{10} and $A_{\pm 10}$ coincide with the matching field values.

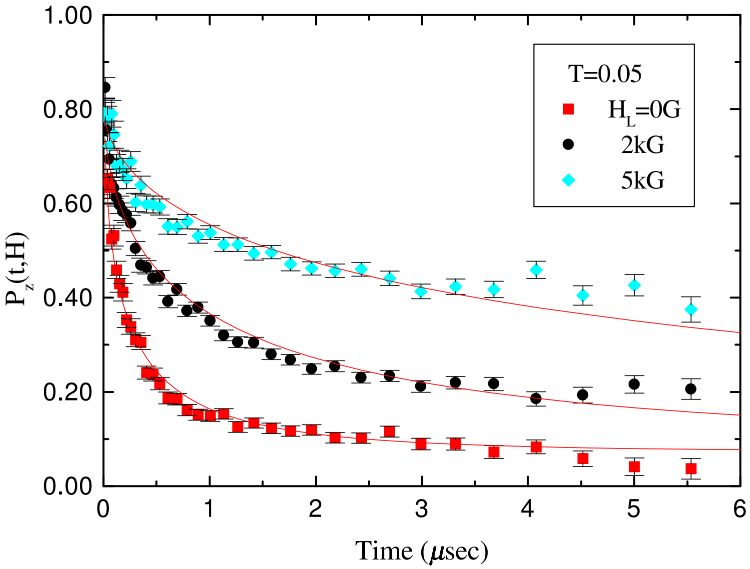
Back

Muon Spin Relaxation in a Static Field

Time scale of relaxation	Recovery in zero field	Decoupling in high longitudinal field
$t^{-1} \simeq \gamma\sqrt{< B_{loc}^2 >}$	  $\lim_{t\to\infty} P_z(t) = \frac{1}{3}$	  $\lim_{H\to\infty} P_z(t) = 1$

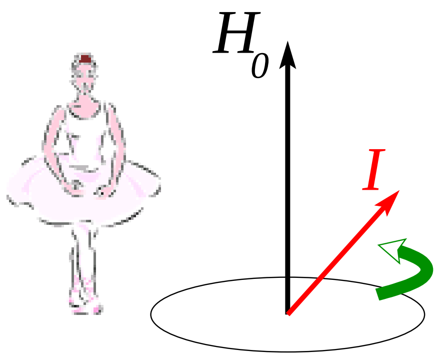
H Dependence of the μ^+ Polarization

- The μSR results in $CrNi_6$ at $T = 50$ mK show that
  1. There is no recovery, unlike the static local field case.
  2. The relaxation time scale is 1 μsec, and therefore $\sqrt{B_{loc}^2}$ should be ~ 10 G.
  3. Decoupling should occur at $H \sim 100$ G, but even at 5 kG there is no decoupling.

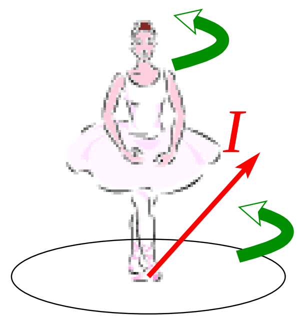


We conclude that even at 50 mK the $CrNi_6$ spins are dynamically fluctuating.

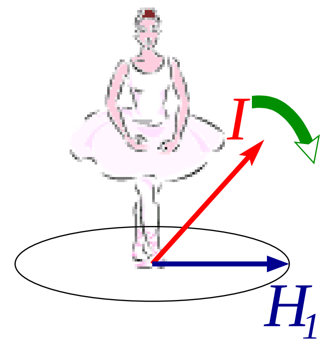
Principle of NMR



Ballerina watching spin rotating.



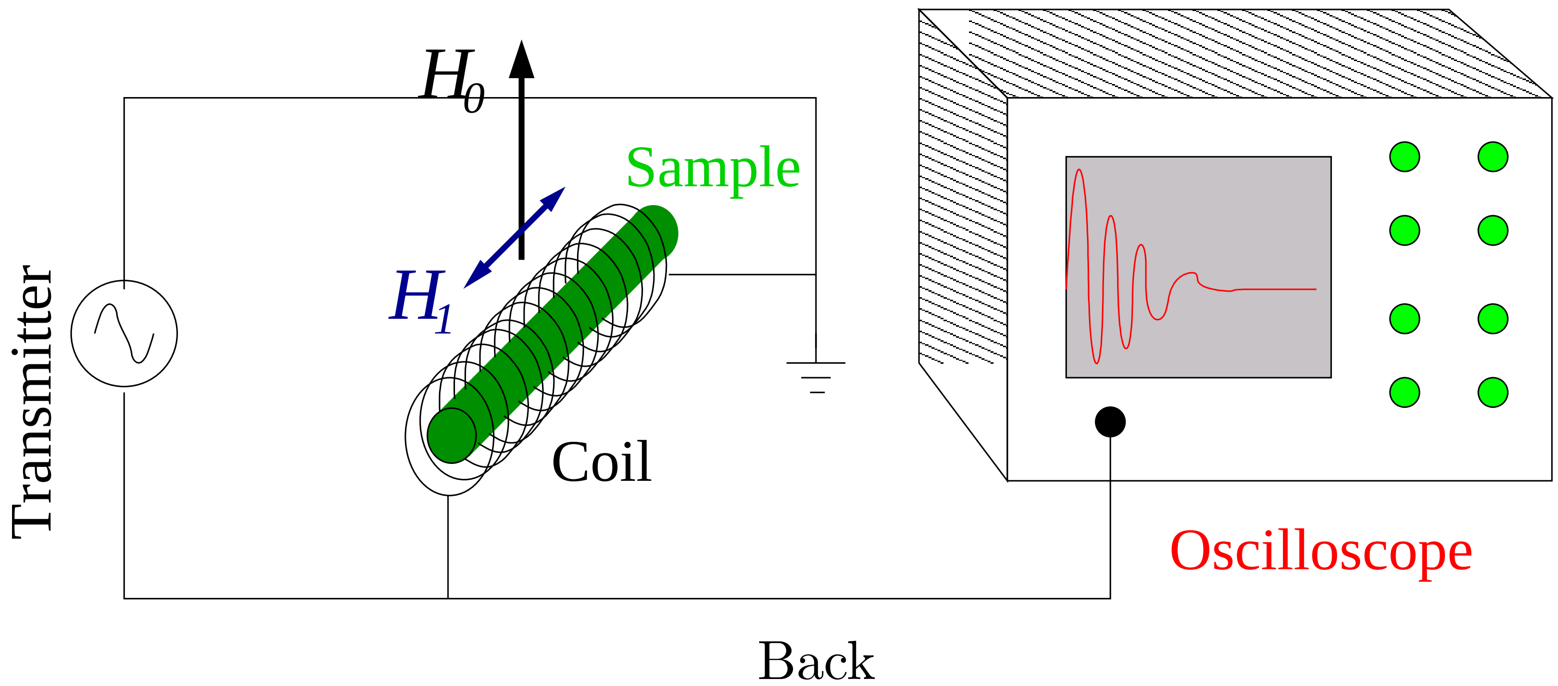
Ballerina and spin are rotating. From her point of view the spin is fixed so there is no field.



A rotating field H_1 is applied. Ballerina sees a fixed field so the spin is rotating around it.

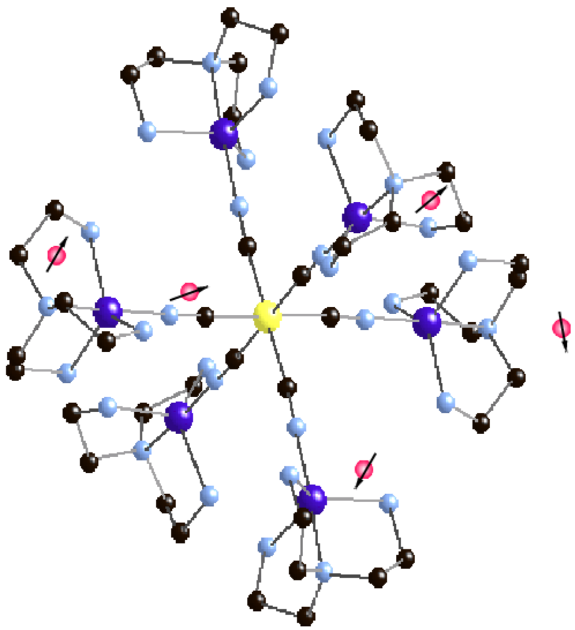
Back

Principles of NMR



The Polarization in Isotropic HSM

- In these HSM the muon could occupy many different sites in the sample as a result one must average over Δ.



- The polarization of a local probe, in the fast fluctuation $\tau\Delta \ll 1$, is given by

$$P(H,t) = (P_0 - P_\infty)\, e^{[-t/T_1]^\beta} + P_\infty$$

The Spin Dependence of the Tunneling Rate

Interaction	*Spin dependence of the tunneling rate* $\tau^{-}1$
High order spin terms	S^2 or higher
Spin-phonon	S^3
Static transverse field	higher than S^2
Dynamic hyperfine and dipolar	$1/S$