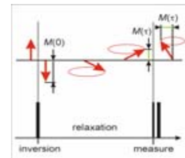
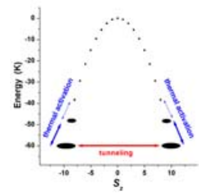
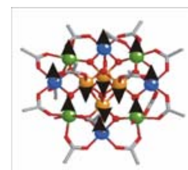
Nuclear spin dynamics

in the quantum regime

of Mn_{12}-*ac* molecular magnets



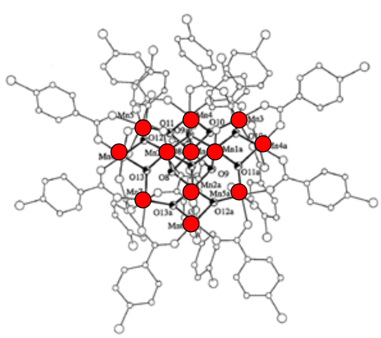




Andrea MORELLO

Kamerlingh Onnes Laboratory, Leiden University, The Netherlands

Molecular magnets



Stoichiometric molecular materials, containing a core of magnetic ions surrounded by organic ligands, forming an insulating crystalline structure.

- Strong (~100 K) intracluster superexchange interactions
- High total spin (typ. 10, max. 51/2)
- Uniaxial magnetic anisotropy (up to 65 K)
- intercluster dipolar interaction ~ 0.2 K

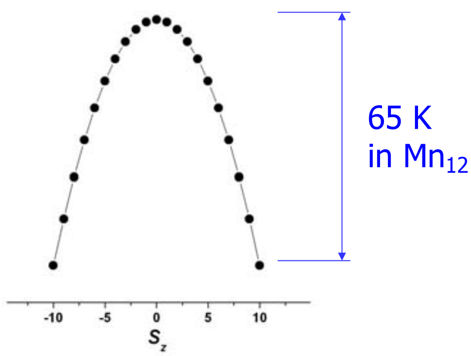
D. Gatteschi *et al.*, Science **265**, 1054 (1994)

Effective spin Hamiltonian

$H = -DS_z^2$

↓

Uniaxial magnetic anisotropy

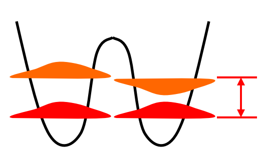


Effective spin Hamiltonian

$H = -DS_z^2 + C(S_+^4 + S_-^4)$

↓

Non-diagonal terms

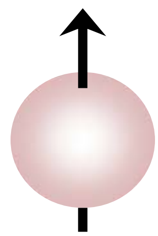


$|\psi_A\rangle \propto |\uparrow\rangle - |\downarrow\rangle$

$|\psi_S\rangle \propto |\uparrow\rangle + |\downarrow\rangle$

Single quantum spin

$H = -DS_z^2 + C(S_+^4 + S_-^4)$



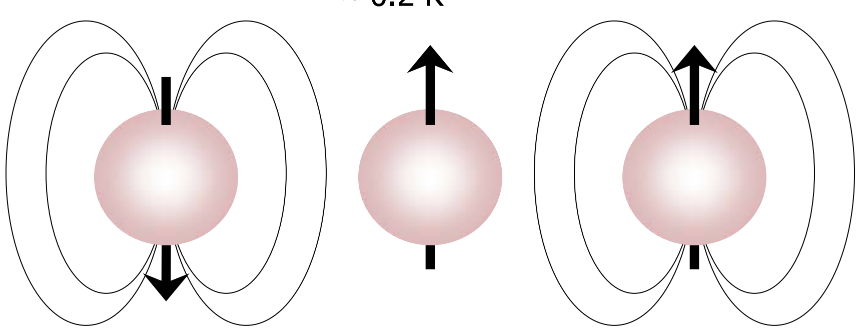
Beyond the isolated spin…

$H = -DS_z^2 + C(S_+^4 + S_-^4) + \boldsymbol{\Sigma}\ \boldsymbol{dip.}$

↓

dipole-dipole couplings

~ 0.2 K

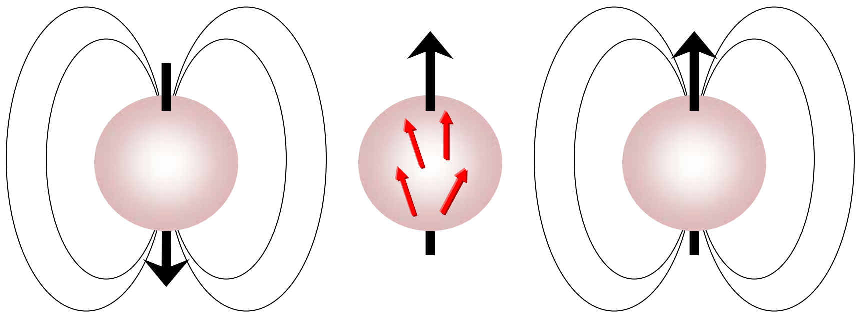


Beyond the isolated spin…

$$H = -DS_z^2 + C(S_+^4 + S_-^4) + \Sigma\, dip. + \Sigma\, \mathbf{hyp.}$$

↓

hyperfine coupling with nuclear spins
~ 0.1 K

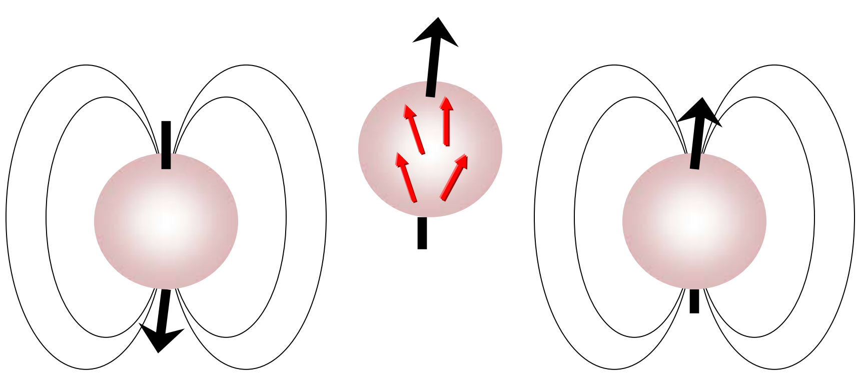


Beyond the isolated spin…

$$H = -DS_z^2 + C(S_+^4 + S_-^4) + \Sigma\, dip. + \Sigma\, hyp. + \mathbf{phonons}$$

↓

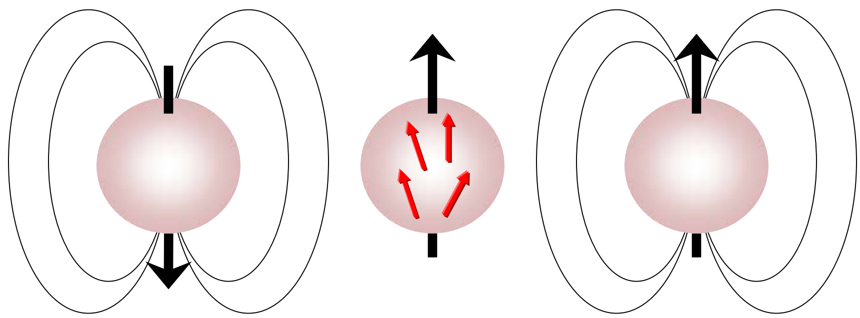
spin-lattice coupling



Beyond the isolated spin…

$$H = -DS_z^2 + C(S_+^4 + S_-^4) + \Sigma\, dip. + \Sigma\, hyp. + phonons - g\mu_B \boldsymbol{S}\cdot\boldsymbol{B}$$

↓ external magnetic field



Quantum spin + environment

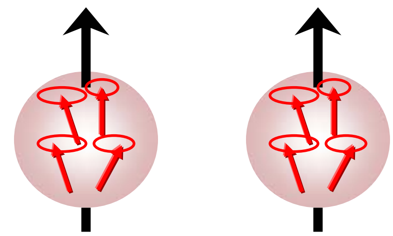
$$H = \boxed{-DS_z^2 + C(S_+^4 + S_-^4)} + \boxed{\Sigma\, dip. + \Sigma\, hyp + phonons} - \boxed{g\mu_B \boldsymbol{S}\cdot\boldsymbol{B}}$$

$-DS_z^2 + C(S_+^4 + S_-^4)$	$\Sigma\, dip. + \Sigma\, hyp + phonons$	$g\mu_B \boldsymbol{S}\cdot\boldsymbol{B}$
Quantum spin	Environment	Tunable Parameter
nanometer-sized	can be quite accurately calculated!	$B_{//} \rightarrow$ classical $B_{\perp} \rightarrow$ quantum

Ideal system to study environmental effects on a quantum spin at the nanometer scale

Nuclear spins in molecular magnets

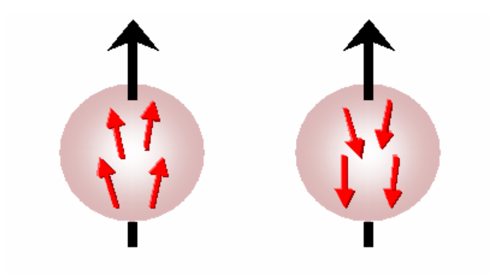
- … are an important source of decoherence



N.V. Prokof'ev and P.C.E. Stamp, Rep. Prog. Phys. **63**, 669 (2000)

Nuclear spins in molecular magnets

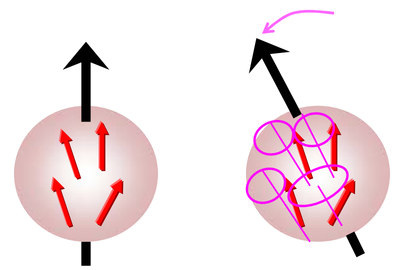
- … are an important source of decoherence
- … provide the fluctuating bias that allows quantum tunneling



N.V. Prokof'ev and P.C.E. Stamp, Rep. Prog. Phys. **63**, 669 (2000)

Nuclear spins in molecular magnets

- … are an important source of decoherence
- … provide the fluctuating bias that allows quantum tunneling
- … are sensitive to the (quantum?) fluctuations of the cluster's spin

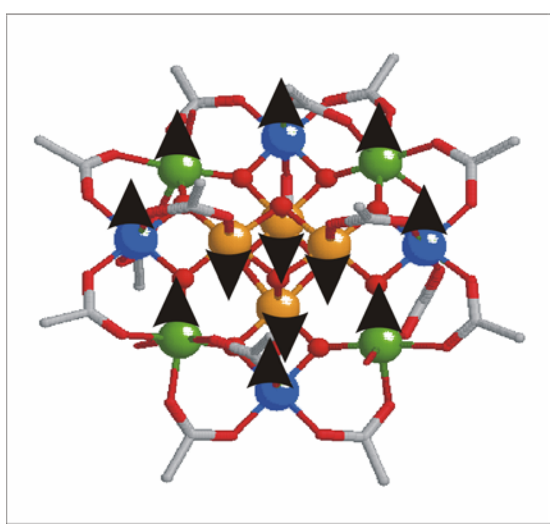


Nuclear spins can both influence and probe the dynamics of the cluster's spin

N.V. Prokof'ev and P.C.E. Stamp, Rep. Prog. Phys. **63**, 669 (2000)
A. Morello *et al.*, cond/mat-0211209 (2002)

Magnetic structure of Mn_{12}-*ac*

- 8 Mn^{3+} + 4 Mn^{4+} ions
- total spin $S = 10$
- 3 groups of inequivalent Mn sites
- the hyperfine field becomes a (strong) static field when the cluster's spin is frozen



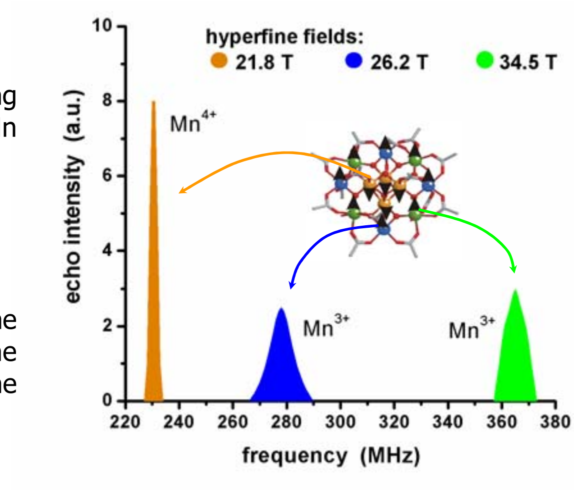
^{55}Mn NMR spectra in zero applied field

$I_{nuclear} = 5/2$

3 NMR lines corresponding to the 3 inequivalent Mn sites

central frequencies:
231, 277, 365 MHz

hyperfine field at the nuclear site parallel to the anisotropy axis for the electron spin

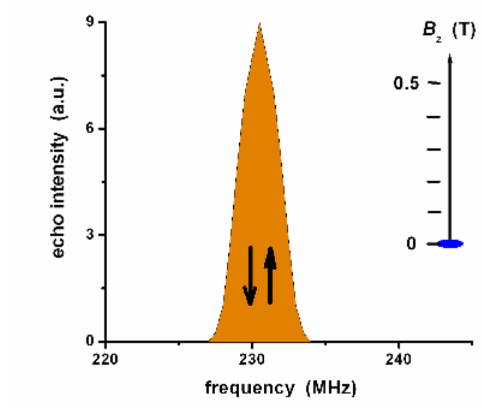


Y. Furukawa *et al.*, PRB **64**, 104401 (2001)
T. Kubo *et al.*, PRB **65**, 224425 (2002)

Effect of a magnetic field B_z // z

In a zero-field cooled sample:

one branch shifts up, the other down, depending on whether B_z sums or subtracts to the local hyperfine field

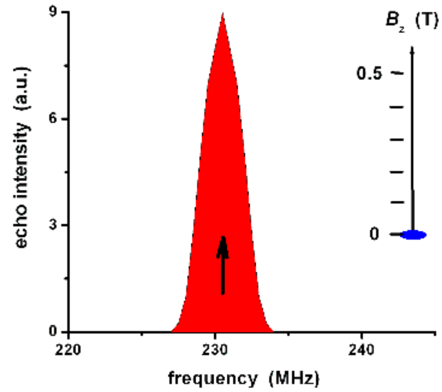


Y. Furukawa *et al.*, PRB **64**, 104401 (2001)
T. Kubo *et al.*, PRB **65**, 224425 (2002)

The case a fully magnetized sample

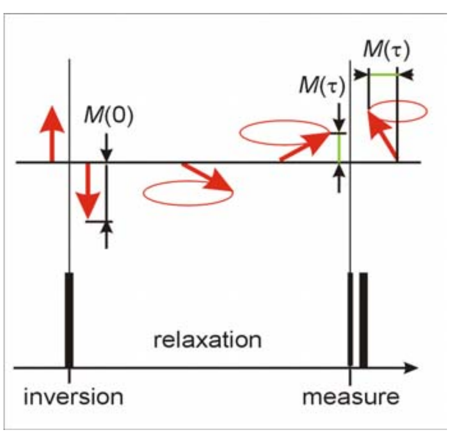
Now there is only one branch shifting up, since all the electronic spins are polarized

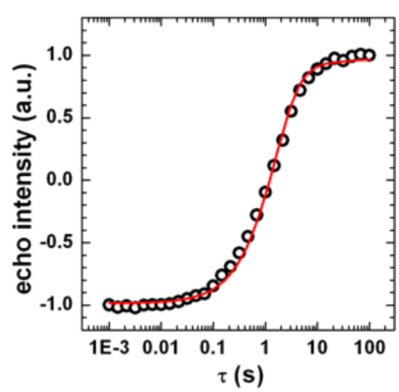
The population of the branches can be used to check the magnetization state!



Y. Furukawa *et al.*, PRB **64**, 104401 (2001)
T. Kubo *et al.*, PRB **65**, 224425 (2002)

Nuclear relaxation: inversion recovery





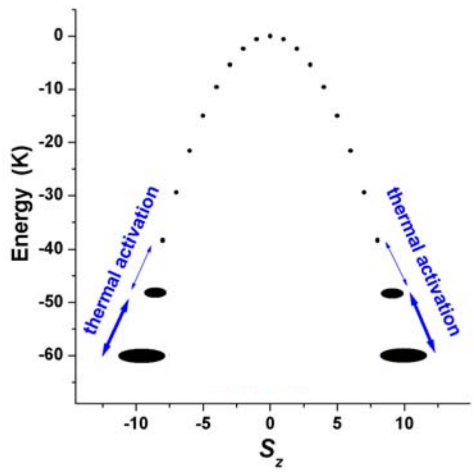
$$M(t) = A\,[\,1 - B\,(100/63 \exp(-30\,\boldsymbol{W}t) + 16/45 \exp(-12\,\boldsymbol{W}t) + 2/35 \exp(-2\,\boldsymbol{W}t)]$$

$\boldsymbol{W}$ = nuclear spin-lattice relaxation rate

A. Suter *et al.*, J. Phys.: Cond. Matter **10**, 5977 (1998)

Electron spin fluctuations

Thermal activation:
$\tau^{-1}_{s\text{-}ph} \sim 10^7 \exp(-\Delta E / k_B T)$
⇓
exponential T dependence



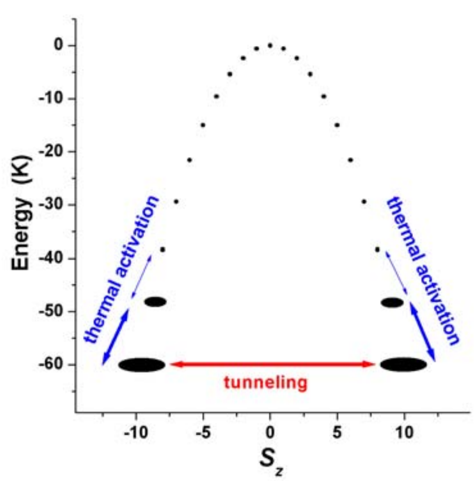
M.N. Leuenberger and D. Loss, PRB **61**, 1286 (2000)

Electron spin fluctuations

Thermal activation:
$\tau^{-1}_{s\text{-}ph} \sim 10^7 \exp(-\Delta E / k_B T)$
⇓
exponential T dependence

Tunneling:
$\tau^{-1}_{T} \approx (\Delta^2/\Gamma_2) \exp(-|\xi|/\xi_0)$
⇓
T independent
∝ (tunneling splitting)^2
depends on spin diffusion (Γ_2)

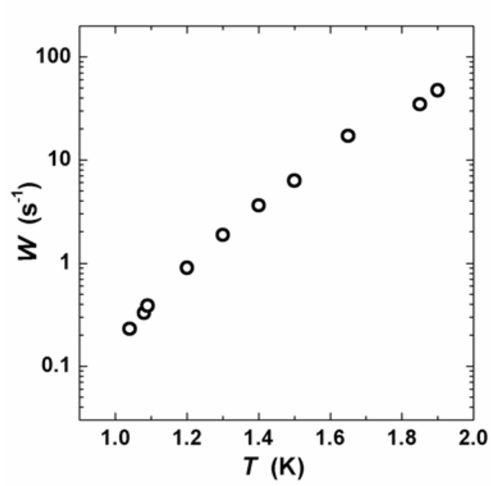
depends on external field
and magnetization state
$\xi = E_D + 2g\mu_B B_z$



M.N. Leuenberger and D. Loss, PRB **61**, 1286 (2000)
N.V. Prokof'ev and P.C.E. Stamp, J. Low. Temp. Phys. **104,** 143 (1996)

Thermally activated regime

$$W = \frac{\gamma_N^2}{4}\int \langle h_\pm(t)h_\pm(0)\rangle \exp(i\omega_N t)dt$$



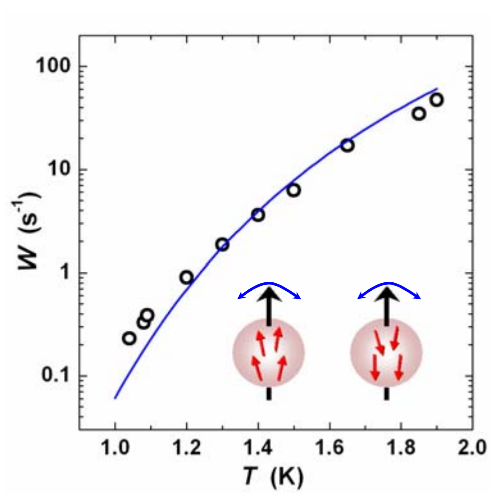
A. Morello *et al.*, cond/mat-0211209 (2002)

Thermally activated regime

$$W = \frac{\gamma_N^2}{4}\int \langle h_\pm(t)h_\pm(0)\rangle \exp(i\omega_N t)dt$$

$$\approx \frac{\gamma_N^2}{4}\langle h_\pm^2\rangle \frac{\tau_{s-ph}}{1+\omega_N^2\tau_{s-ph}^2}$$

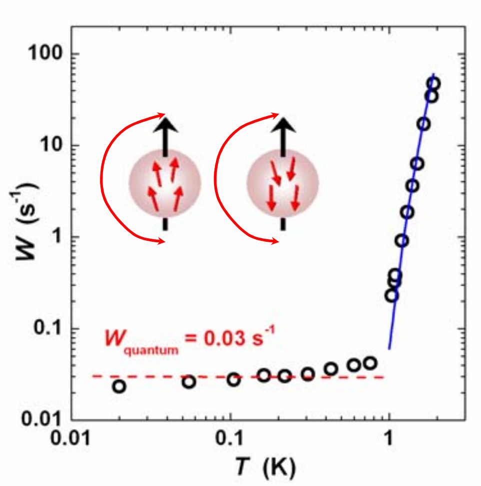
Above 1 K, the nuclear relaxation is driven by the thermal fluctuations (spin-phonon) of the *S* = 10 electronic spin



A. Morello *et al.*, cond/mat-0211209 (2002)
see also Y. Furukawa *et al.*, PRB **64**, 104401 (2001)

Quantum regime

The nuclear relaxation rate becomes temperature independent below $T \approx 0.8$ K
⇓
Tunneling fluctuations



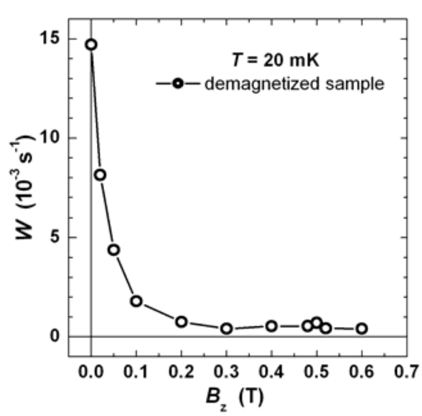
The same T - independent behavior is found in the magnetization loops!

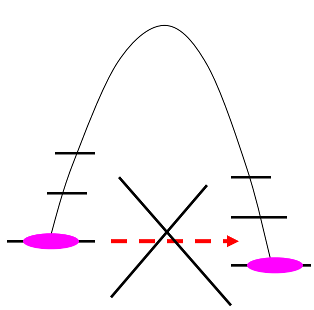
A. Morello *et al.*, cond/mat-0211209 (2002)
see also M. Ueda *et al.*, PRB **66**, 073309 (2002)

L. Bokacheva *et al.*, PRL **85**, 4803 (2000); I. Chiorescu *et al.*, PRL **85**, 4807 (2000)

External field B_z // z

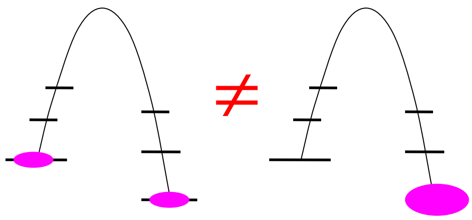
By applying an external field B_z, the resonance condition for tunneling is destroyed
⇓
nuclear relaxation slows down by a factor 30!



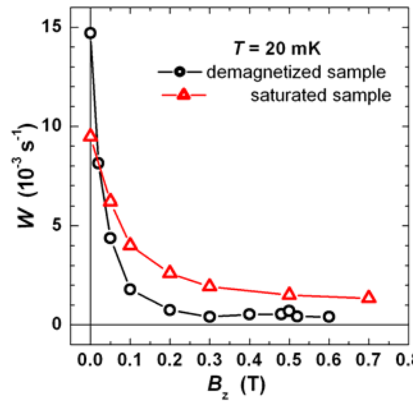


External field B_z // z

Both the zero-field value and the "linewidth" depend on the cluster's magnetization state.



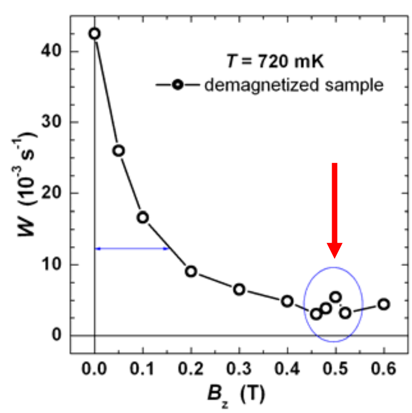
All this does not require any <u>macroscopic</u> change in the magnetization.

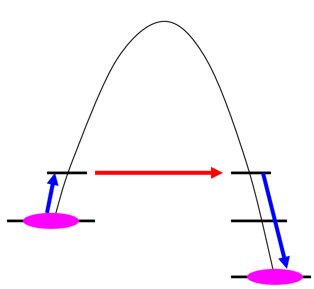


Higher temperature

At the edge of the quantum regime ($T \approx 0.7$ K):

A peak appears at $B_z \approx 0.5$ T (thermally assisted tunneling at the first level-crossing?)

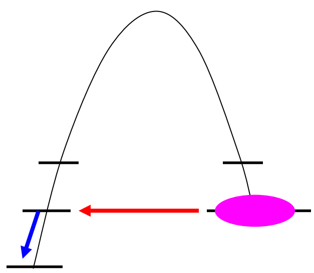


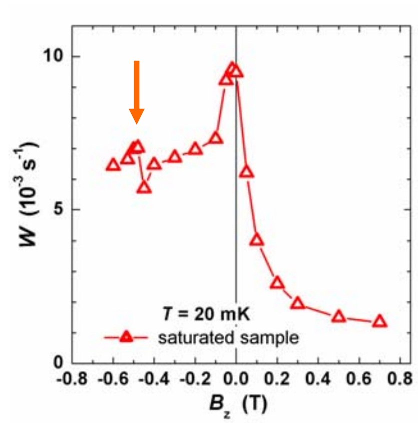


"Negative" fields

$W(B_z)$ is strongly asymmetric

A peak appears at $B_z \approx -0.5$ T (first level crossing?)



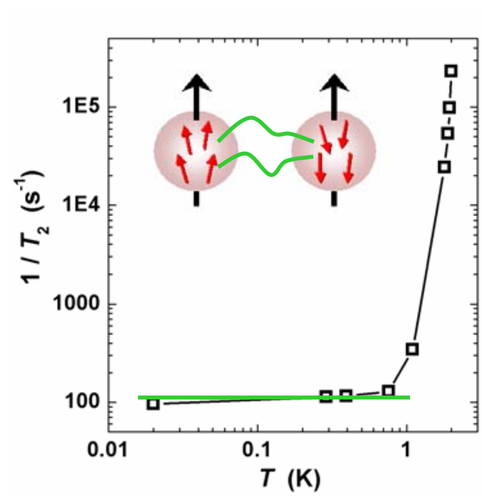


Nuclear spin diffusion

The transverse spin-spin relaxation rate at low T is determined by the dipolar interactions between nuclei

T_2 = 10 ms $\Rightarrow$ agrees with the calculated **intercluster** nuclear spin diffusion!

$T_1/T_2 \sim 10^3$ = the spin diffusion is **fast**



A. Morello *et al.*, cond/mat-0211209 (2002)

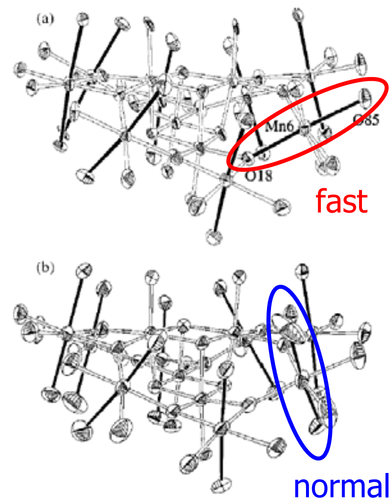
Fast-relaxing molecules

Every real sample contains minority species with one or two flipped Jahn-Teller axes

⇓

• Smaller anisotropy barrier (15 K or 35 K instead of 65 K)

Faster tunneling rate



Local anisotropy axis tilted ~ 10^{o} from the crystalline c - axis

⇓

An applied field breaks down the possible spin diffusion between nuclei in fast and slow molecules!

W. Wernsdorfer *et al.*, Europhys. Lett. **47**, 254 (1999)
Z. Sun *et al.*, Chem. Comm., 1973 (1999)

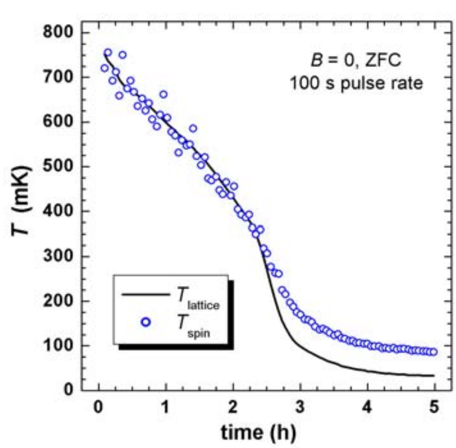
Nuclear spin temperature

Defined as the inverse of the spin echo intensity, renormalized at high T, recorded while cooling down the system

$$M = \frac{N \gamma^2 \hbar^2 I(I+1)}{3\, k_B\, T} H_{hyp}$$

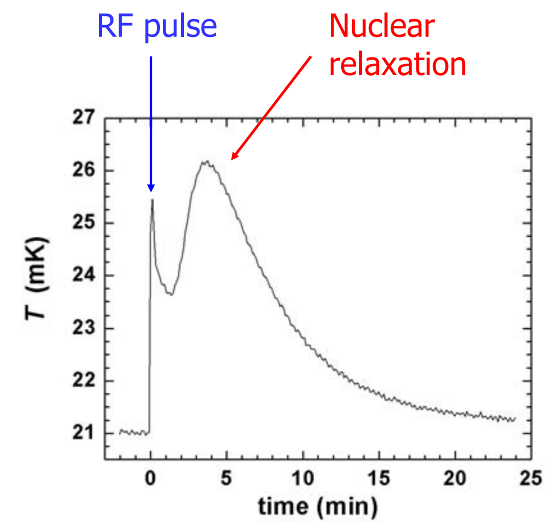
$$T_{spin}(t) \equiv T(t=0)\, M(t=0)\, /\, M(t)$$

Nuclear spins are "aware" of the lattice temperature!!



Heating effects

Conversely, we can observe the "heat wave" produced on the thermal bath by the nuclear relaxation!!



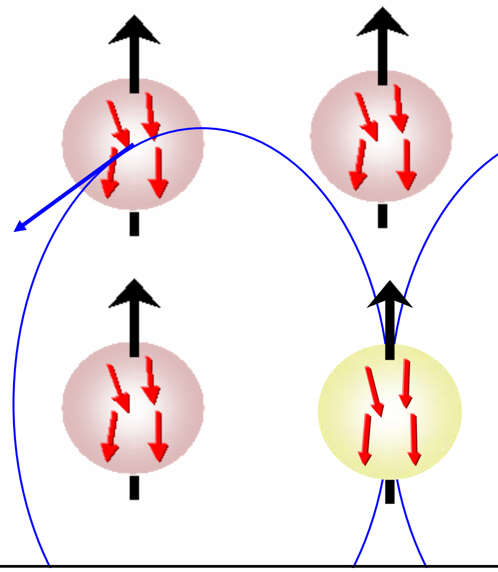
Experimental facts: summary

- the nuclear spin-lattice relaxation in the quantum regime is **surprisingly fast** (10 – 100 s)
- the field dependence of W shows most of the expected features of **tunneling resonance**
- the nuclear spins are in very good contact with the **thermal bath**
- the nuclear **spin diffusion is fast** compared to the timescale of spin-lattice relaxation

Relaxation by dipolar fluctuating fields

Assuming nuclear relaxation produced by dipolar fields fluctuating *locally* at the nuclei because of tunneling in neighboring clusters:

$$W \approx \frac{\gamma_N^2}{4}\left\langle h_{dip}^2 \right\rangle \frac{\tau_T}{1+\omega_N^2\tau_T^2}$$



Relaxation by dipolar fluctuating fields

Assuming nuclear relaxation produced by dipolar fields fluctuating *locally* at the nuclei because of tunneling in neighboring clusters:

$$W \approx \frac{\gamma_N^2}{4}\left\langle h_{dip}^2 \right\rangle \frac{\tau_T}{1+\omega_N^2\tau_T^2}$$

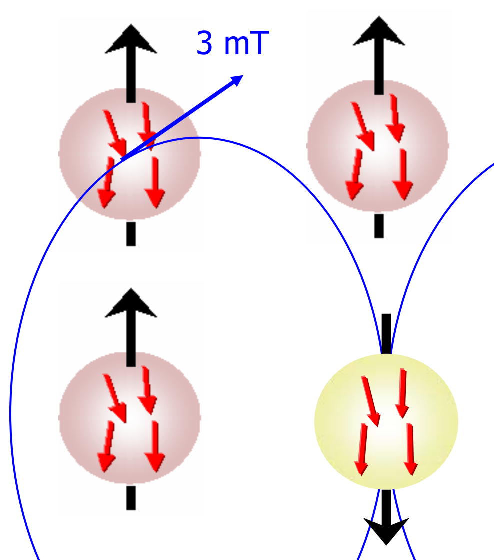
$W \approx 0.03\ s^{-1}$

$h_{dip} < 3$ mT

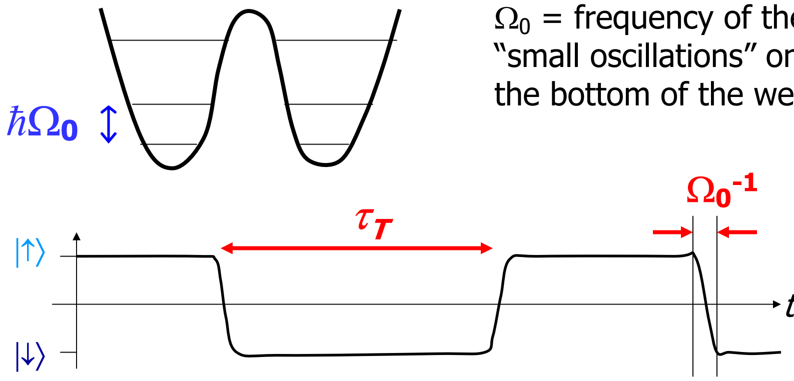
$\Downarrow$

$\boldsymbol{\tau_T^{-1} \sim 10^5\ s^{-1}}$

Unrealistic!



Tunneling traversal time

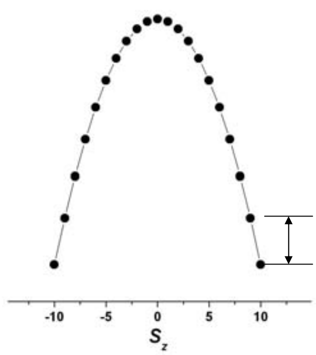


Ω_0 = frequency of the "small oscillations" on the bottom of the well

Ω_0^{-1} is the "tunneling traversal time"

N.V. Prokof'ev and P.C.E. Stamp, cond-mat/9511011 (1995)

Coflipping probability



in Mn_{12}-ac:

$\Omega_0^{-1} \sim 10^{-12}$ s

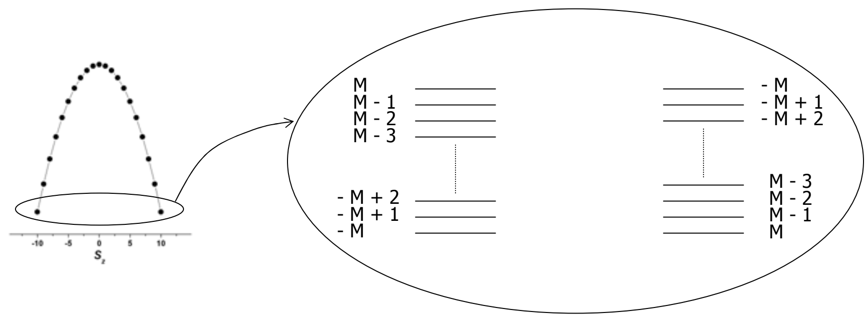
$\Uparrow$

$\hbar\Omega_0 \sim E_9 - E_{10} \approx 3 - 14$ K

The probability for the nuclear spins to "coflip" with the tunneling electron spin is ~ $(\omega_N / \Omega_0)^2 \sim 10^{-6}$

The nuclear spins "inside" a tunneling molecule do not coflip with it

Orthogonality blocking

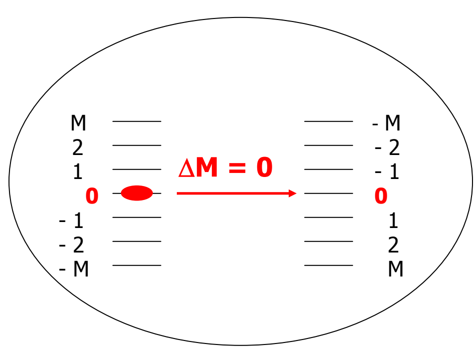


$H_{//} = \pm$ 21.8 T; $H_{\perp} \sim$ 5 mT $\Rightarrow$ $\kappa << 1$

The hyperfine-split manifolds on either sides of the barrier are simply mirrored with respect to the nuclear polarization.

N.V. Prokof’ev and P.C.E. Stamp, cond-mat/9511011 (1995)

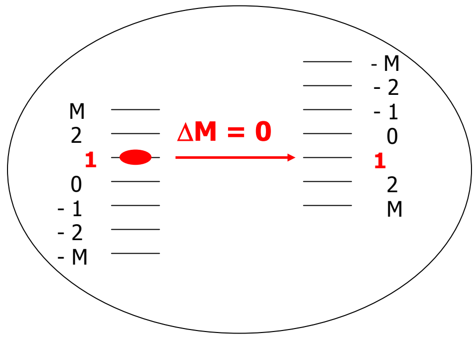
Unbiased case



The most probable tunneling transition (without coflipping nuclei) is between states with zero nuclear polarization.

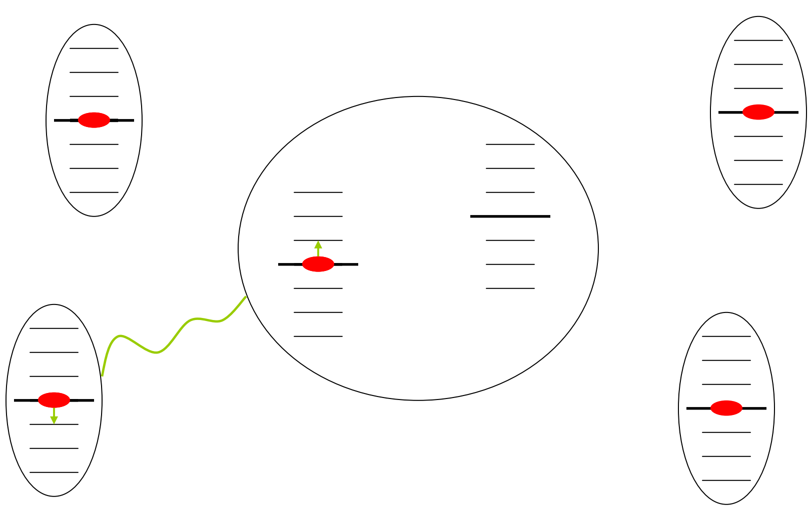
Biased case

e.g. by dipolar coupling with "slow" neighboring clusters

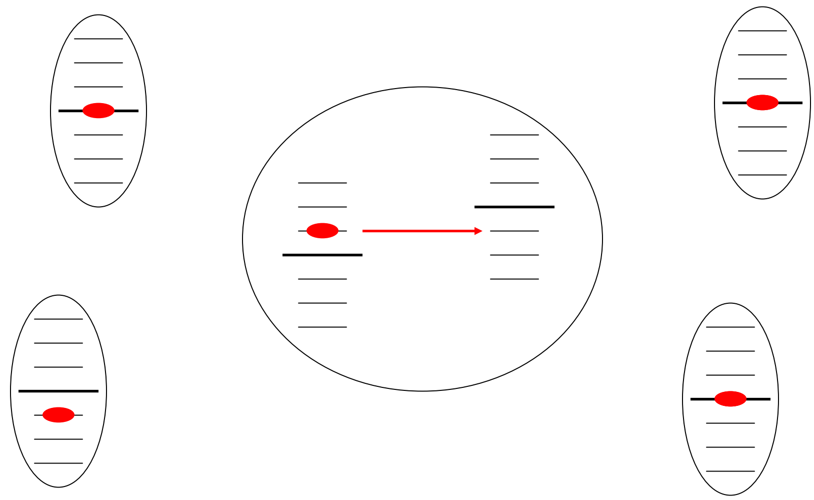


Now the ΔM = 0 transition requires an initial polarization (e.g. M = 1 here)

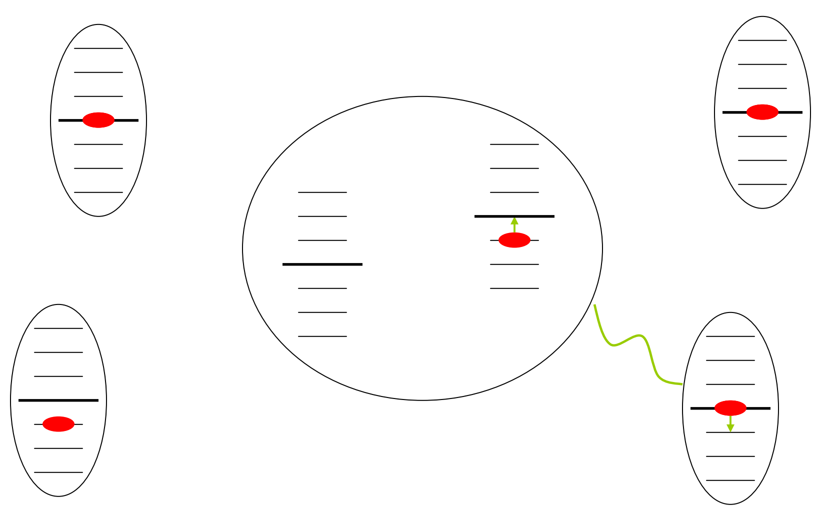
Nuclear flip-flops



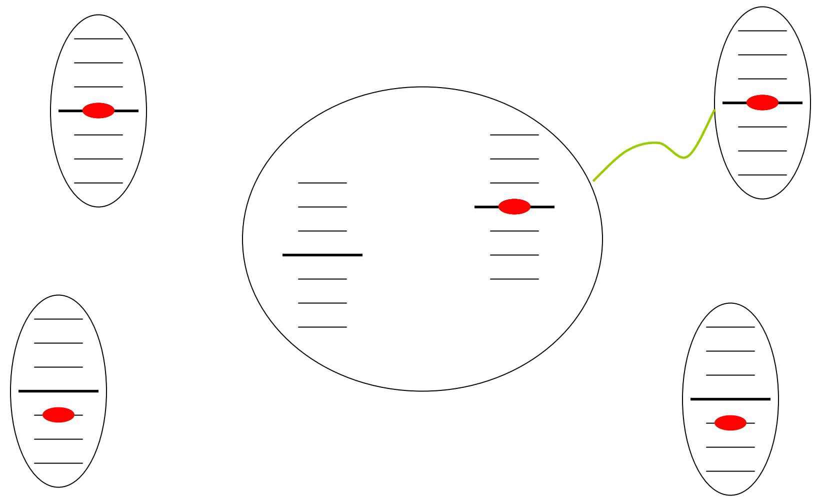
Nuclear flip-flops



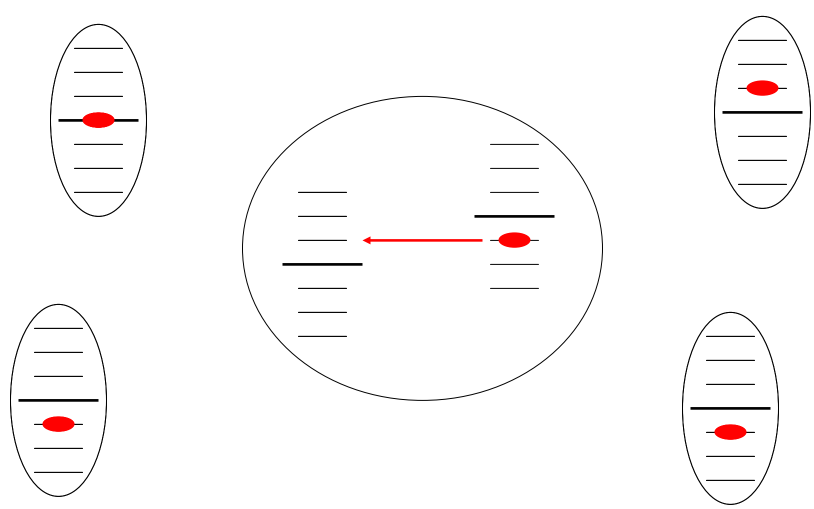
Nuclear flip-flops



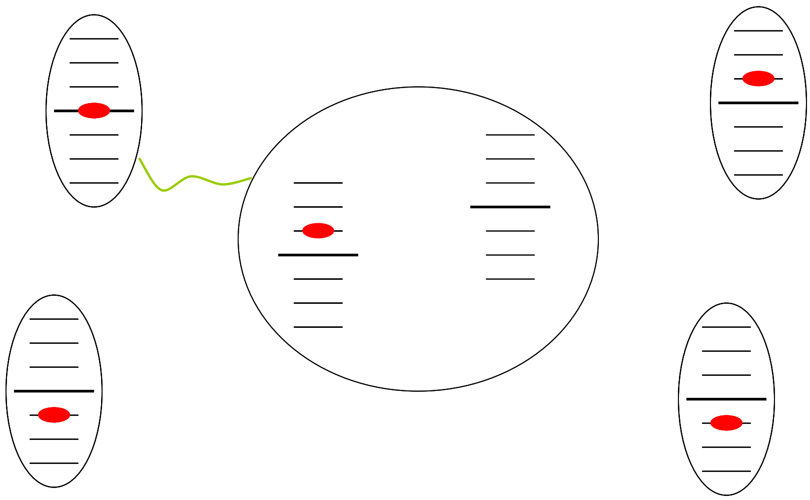
Nuclear flip-flops



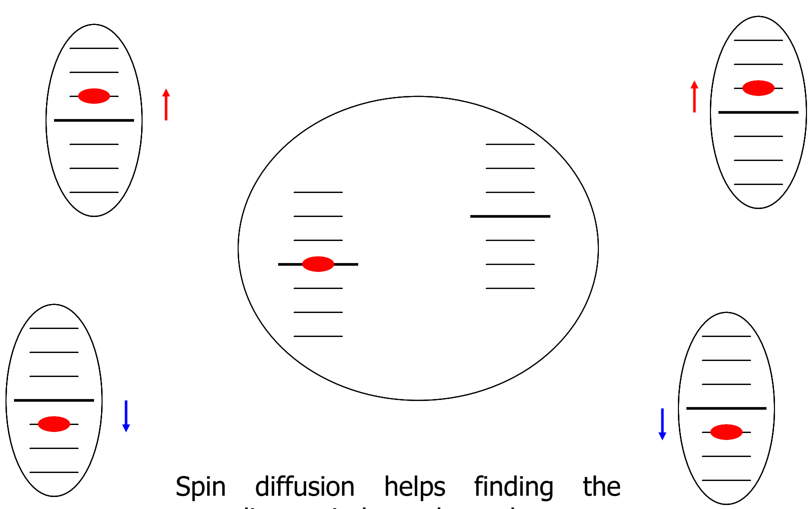
Nuclear flip-flops



Nuclear flip-flops

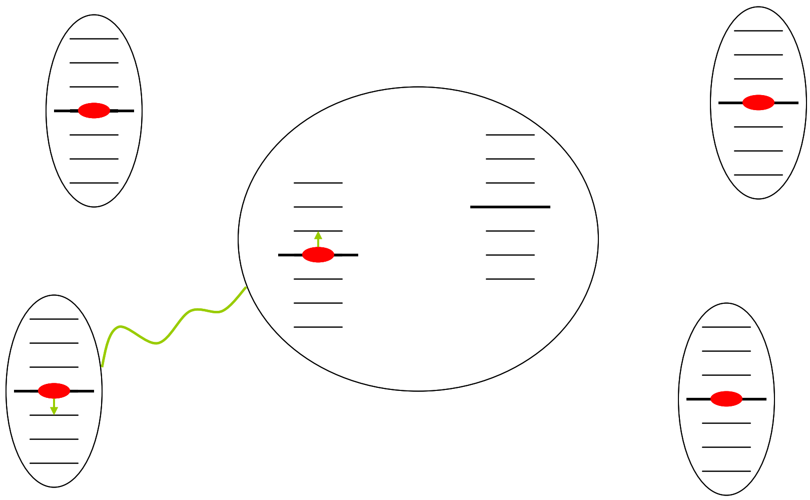


Nuclear flip-flops

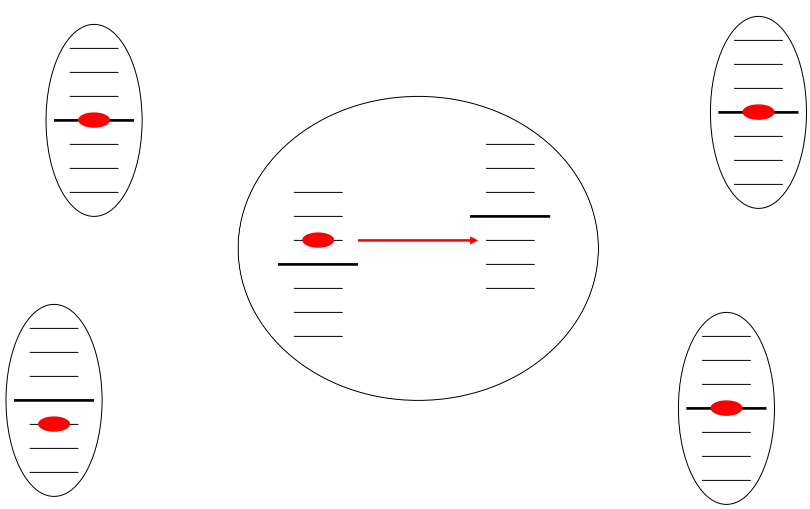


Spin diffusion helps finding the tunneling window, but does not change the total nuclear polarization

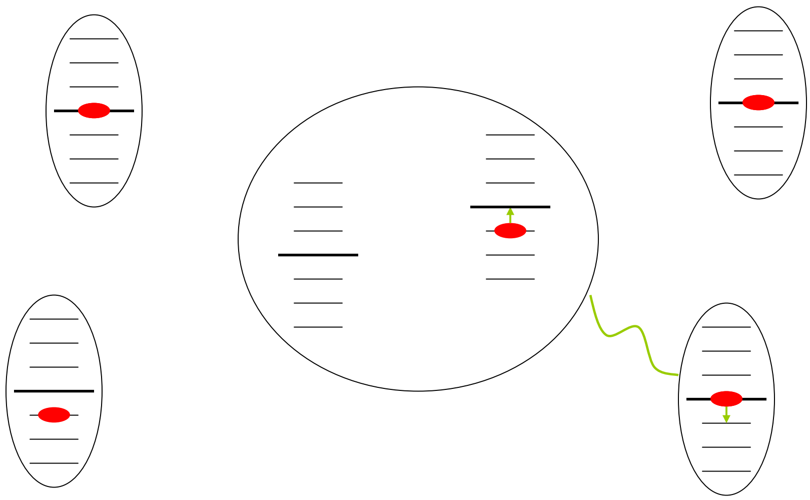
Spin-phonon interaction



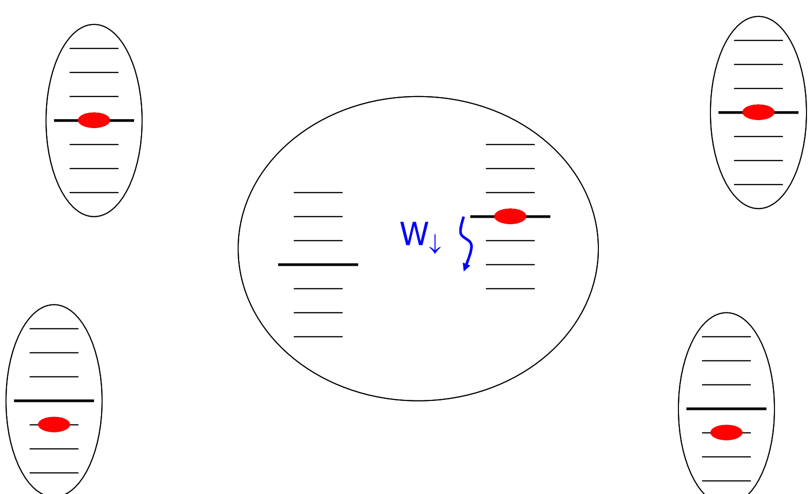
Spin-phonon interaction



Spin-phonon interaction

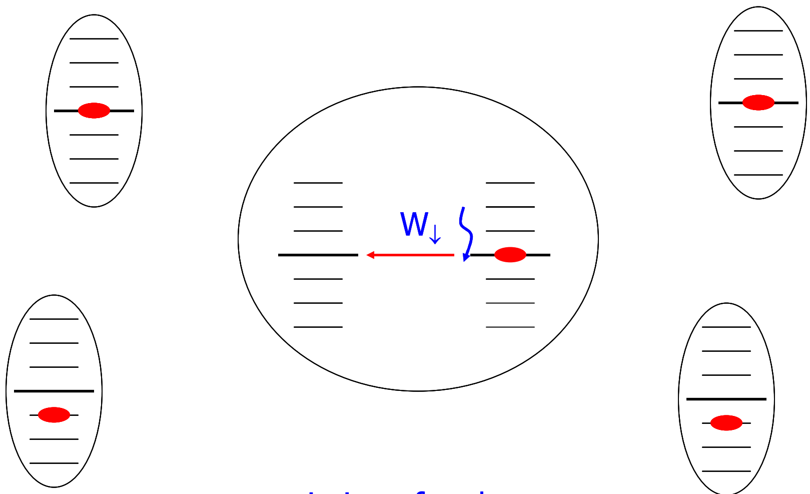


Spin-phonon interaction



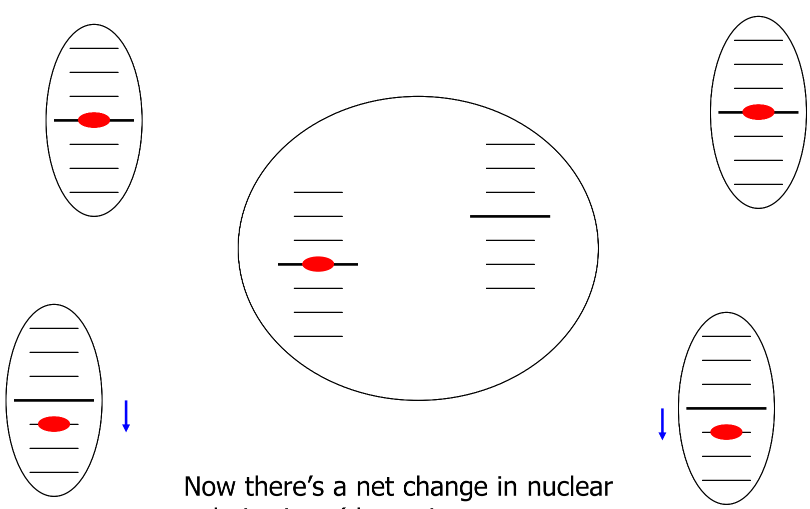
emission of a phonon

Spin-phonon interaction



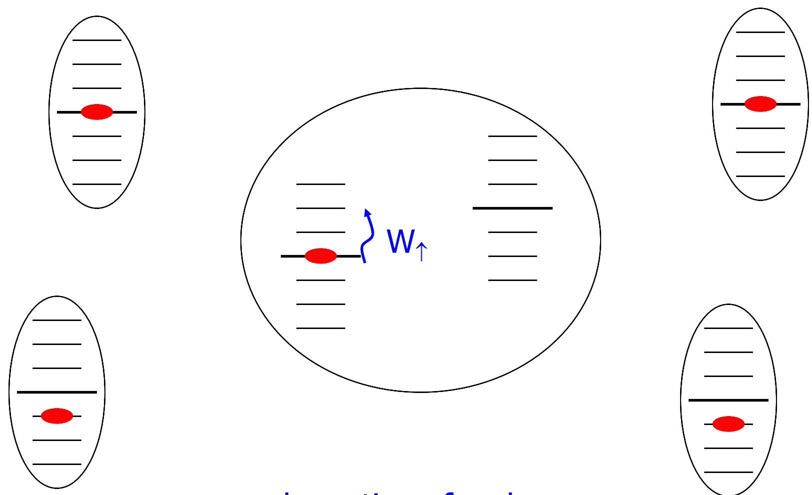
emission of a phonon

Spin-phonon interaction



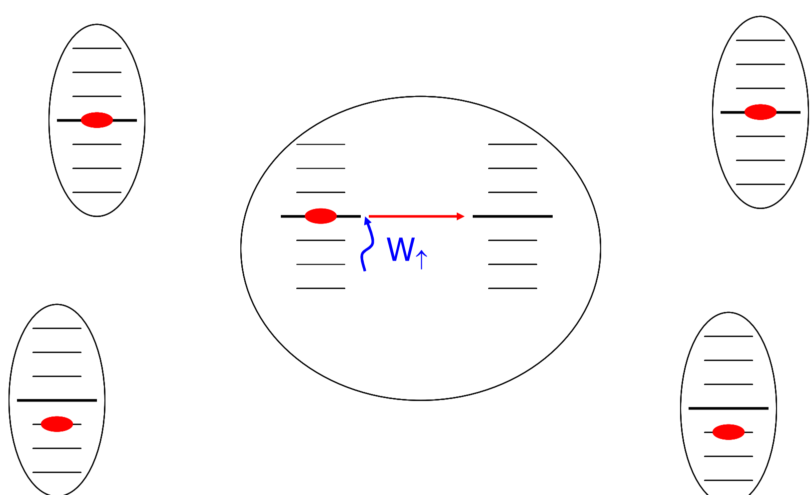
Now there's a net change in nuclear polarization (the spin temperature has been lowered!)

Spin-phonon interaction



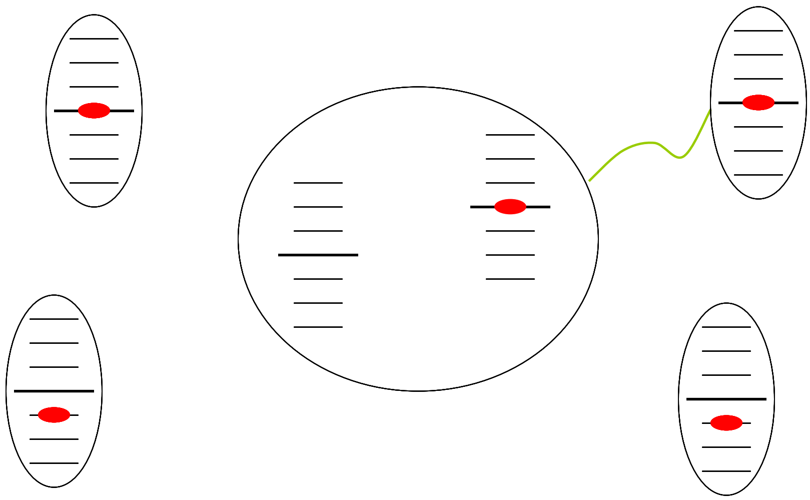
absorption of a phonon

Spin-phonon interaction

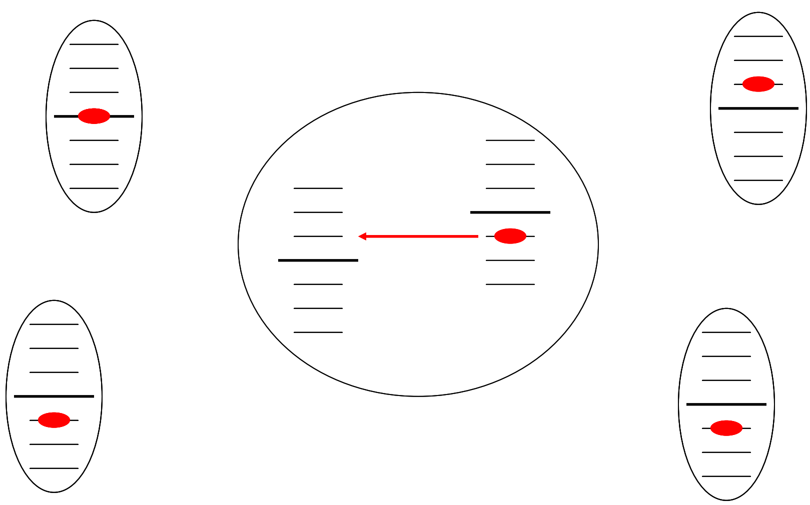


absorption of a phonon

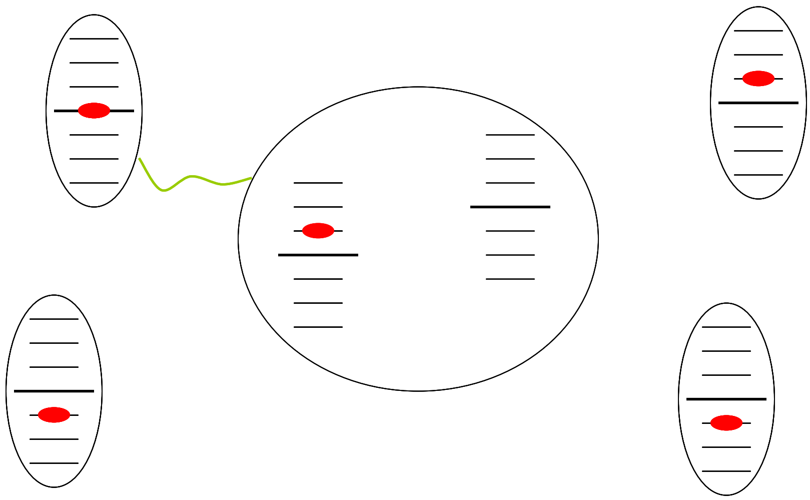
Spin-phonon interaction



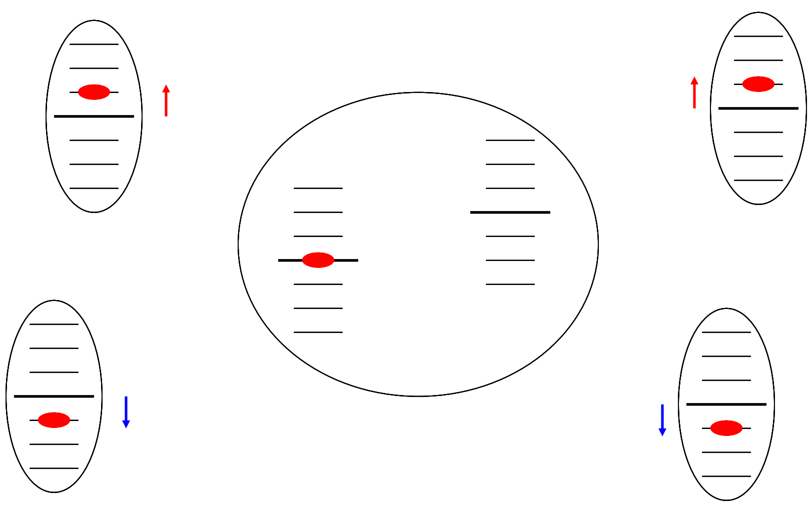
Spin-phonon interaction



Spin-phonon interaction

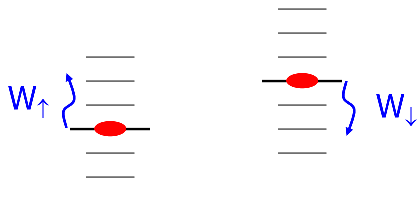


Spin-phonon interaction



Detailed balance

In this picture, it's easy to apply the condition of detailed balance to obtain the equilibrium nuclear polarization



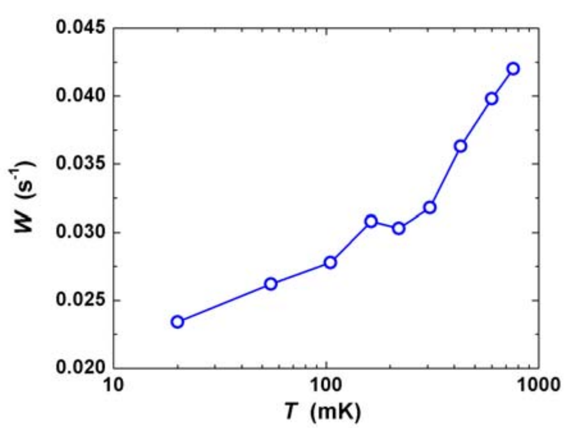
$$\frac{W_\downarrow}{W_\uparrow} = e^{\Delta E / k_B T}$$

$\Delta E = \hbar\omega_N \, \Delta M$
"irreversible" change in nuclear polarization

Does the bias energy (dipolar coupling) play any special role?

Low-T nuclear relaxation

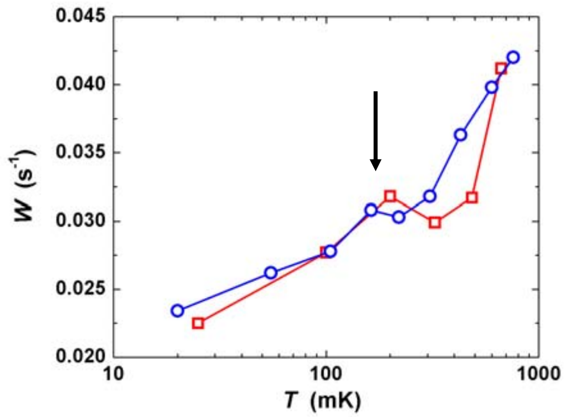
In the quantum regime, $W(T)$ tends to slightly increase with temperature (a factor 2 between 20 and 800 mK)



Low-*T* nuclear relaxation

In the quantum regime, *W* (*T*) tends to slightly increase with temperature (a factor 2 between 20 and 800 mK)

and shows a reproducible peak at T ≈ 180 mK, i.e. just the typical range of dipolar couplings!!



Relaxation rate

In the "fast molecules + spin diffusion" picture:

$$W \approx c\ \tau_T^{-1}$$

c = fraction of fast-relaxing molecules

e.g., $W \approx 0.03\ s^{-1}$ can be obtained with 1% molecules tunneling at $\tau_T^{-1} \approx 3\ s^{-1}$

Is this a realistic picture of the tunneling-driven nuclear spin-lattice relaxation?

Conclusions

The nuclear spin-lattice relaxation in Mn_{12}-ac at millikelvin temperatures is dominated by tunneling fluctuations, and is surprisingly fast

The nuclear spin system is in good thermal contact with the phonon bath

We believe that any realistic description of the nuclear spin dynamics should account for spin diffusion + tunneling in fast molecules + spin-phonon coupling

Open questions

How can we justify such a strong spin-phonon coupling as the experimental results require?

What are the consequences of the observed fast nuclear relaxation on the tunneling probability?

Is there any special interplay between intercluster dipolar coupling and lattice temperature?

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