$T_1$ and $T_2$ relaxation in NMR of spin-ice compounds

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Overview

Aim: explain NMR measurements in Dy$_2$Ti$_2$O$_4$ spin ice [Kitagawa and Takigawa]. at low temperature ($T < 0.5$K) so dynamics should be dominated by diffusing magnetic monopoles.

1. spin ice: monopoles and dynamics
2. what NMR measures: T1 (longitudinal) and T2 (dephasing) focus on T2 (more novel)
3. Experimental results: relaxation stretched-exponential in time
4. Theory: random local envt. gives stretched exponential
5. Expt. contradicts spin ice model! (slightly stuffed spin ice?)
1. Dipolar spin ice: set-up

Low-\(T\) ensemble is 2-in/2-out in every tetrahedron.

Elementary excitations: “monopole” defects in tetrahedra 3-in/1-out or 3-out/1-in.

(Added) field due to monopole has Coulomb form \(|\mathbf{B}| = Q/4\pi|\mathbf{R}|.\)

Unbound monopole density

\[ n \sim e^{-\Delta/2T}, \]

where \(\Delta/2 \approx 3\text{K}.\) (\(n < 10^{-2}\) at 0.5 K)

No more screening below \(\sim 0.5\) K.
Dynamics

Single flip base rate $\tau_0 = 10^{-8}$ to $10^{-3}$ s (?).
Valid if no cost, or downhill; otherwise $\times \exp(-\Delta E/T)$.
$\tau_0$ is believed to be temperature independent.

The only no-cost spin flip entails **monopole hop** to an
adjacent tetrahedron (any one of the 3 majority spins):

![Figure: Kitagawa and Takigawa](Random walking monopoles!)

**Additional field due to a dipole at** $R$: $\omega_d/R^3$.
*(I am glossing over some angular dependencies.)*

**Change** in field when monopole hops: **same**.
2. What NMR measures

Sala, Castelnovo, Moessner, et al [”field trip through spin ice”] addressed the instantaneous (static) local field: variation due to nearby monopoles splits NMR line. This talk: dynamic effects due to distant monopoles.

(Remark: thanks to this splitting, needn’t worry about diffusion of spin among different nuclei)

(Remark: muon spin resonance is similar – if muons don’t diffuse.)
**T**<sub>1</sub> and **T**<sub>2</sub> relaxation (reminder)

**T**<sub>1</sub> (longitudinal relaxation)

Start with nuclear spin quantized along the local field axis.

Relaxation function \( g_1(t) = \) correlation of that direction, decorrelated due to fluctuating *transverse* fields?

Dominated by **high frequencies**: sudden jumps in local field due to spin flips/ monopole hops.
$T_2$ (dephasing) is measured with **spin-echo** technique.

Relaxation function $g_2(2t)$ is transverse correlation between time 0 and time $2t$, with spin flipped by $\pi$-pulse at time $t$.

Then $g_2(2t) = \langle \cos \Phi \rangle$, where $\Phi = \text{accumulated phase difference for precession around quantization axis}$:

$$
\Phi \equiv \int_0^t \omega(t') \, dt' - \int_t^{2t} \omega(t') \, dt'
$$

($\omega(t) \equiv \text{change in precession rate due to fluctuating field}$.)

Fixed (or slow) $\Delta \omega(t)$ cancels. Fast fluctuations cancel too.

$\Rightarrow$ Dominated by fluctuations at frequencies $\sim 1/t$. 
3. Exp’tl results (Kitagawa & Takigawa)

sample data – stretched exponential forms

Both relaxations are stretched exponentials. Time scales $T_1 \sim 1 \text{ s (left)}$ and $T_2 \sim 10^{-4} \text{ s (right)}$. Data from Kitagawa & Takigawa at $T=0.5 \text{ K}$. My own guesses of parameters in $\exp[-(T/T_{1,2})^{\beta_{1,2}}]$. 
Measured temperature dependence of parameters

As $T \to 0$, we see $T_{1,2} \to \text{const}$ ($T_1 = 10^3 \text{s}$, $T_2 = 10^{-4} \text{s}$).
Also, $\beta_{1,2} \to \sim 1/2$.

Not predicted by theory (of monopole diffusion in spin ice).

(Data and fits from Kitagawa & Takigawa.)
Stretched exponentials

... due to inhomogeneous sum over different local environments: namely probe spins with different relaxation times.

Result: get \( \exp(-t^\beta) \) where \( \beta \) is smaller than the pure exponent for any single probe spin.

\( (\text{Known 50 yrs, for case of fixed paramagnetic impurities}). \)

There are no such impurities in the basic spin ice model; but we expect inhomogeneity due to distant monopoles, which hardly move during the experimental time \( t \).

A difference from paramagnetic impurities:
having flipped, impurity spin can only flip back again: net change in nuclear precession frequency \( \Delta \omega \) is bounded.
But monopole’s further motion adds on to its past motion – successive flips with the same sign are possible.
4. Theory of $T_2$ relaxation function

First, consider relaxation $g_R(t)$ due to a single flipping spin/monopole at distance $|R|$. Jump in precession frequency $\Delta \omega \propto$ jump in field $\propto 1/|R|^3$  
$\Rightarrow$ write $\Delta \omega = \omega_d/|R|^3$, where $\omega_d$ is a known constant.

Also, probability of a flip is $t/\tau_0$. Given a flip occurs, phase $\Phi \sim (\Delta \omega)t$, and $\langle \cos \Phi \rangle \sim \exp(-\langle \Phi^2 \rangle)$. Hence

$$g_R(t) \sim \exp \left[ - \left( \frac{\omega_d}{|R|^3} t \right)^2 \frac{t}{\tau_0} \right].$$

**Stretched exponential**

Now consider many independent flipping objects with density $n$. For each possible site $R$, use conditional probability:

$$g_2(t) = \prod_R \left( [1 - n] + n g_R(t) \right) = \prod_R \left( (1 - n[1 - g_R(t)]) \right) = e^{-nF_2(t)} ,$$
where

\[ F_2(t) \equiv \sum_R [1 - g_R(t)]. \]  

(\ast)

Recall

\[ g_R(t) \sim \exp \left[ - \left( \frac{\omega_d}{|R|^3} t \right)^2 \frac{t}{\tau_0} \right] \sim \exp[-(R_*/|R|)^6]. \]

So the r.h.s. of (\ast) is \( \sim 1 \) when \( R < R_* \) or \( \sim 0 \) when \( R > R_* \).

\( F_2(t) \) is the no. of sites inside \( R_* \) thus

\[ F_2(t) \sim R_*^3 \sim (\omega_D t)(t/\tau_0)^{1/2}. \]

**Result:** stretched exponential

\[ g_2(t) \sim \exp[-(t/T_2)^{3/2}] \]
5. Experiment contradicts theory! (2 ways)

Problem 1: Temperature dependence of $T_2$:

Theory says $g_2(t) = \exp[-nF(t)]$ where $F(t) \propto t^{\beta_2}$.
The only temperature dependence is in monopole density $n$.
That is,

$$g_2(t) = \exp[-n \text{Const} t^{\beta_2}] = \exp[-(t/T_2)^{\beta_2}]$$

Hence

$$T_2 \propto n^{-1/\beta_2} \propto e^{-\Delta/2\beta_2 T}.$$  

must have activated $T$ dependence. (Maybe $\tau_0$ has an activated $T$ dependence? no, that goes the wrong way.)

**Experiment**: $T_2$ becomes temperature independent.
Problem 2: exponent $\beta_2$:

In $g_2(t) = \exp[-(t/T_2)^{\beta_2}]$, theory says $\beta_2 = 3/2$ in the monopole diffusion regime.

Experiment says $\beta_2 \approx 1/2$ at low $T$.
This means $g_R(t)$ [relaxation due to a single flipping object near the probe spin] is not of form $\exp(-\text{Const} \, t^3)$ but just $\exp(-\text{Const} \, t)$.
That implies (a) the flipping object only flips back and forth, like a paramagnetic impurity not a monopole.
(b) flipping rate is short compared to measurement time, i.e.

$$\tau_0 \ll T_2 \sim 10^{-4}\text{s}.$$
Extracting parameters

One can derive (flipping impurity scenario)

\[ g_1(t) \sim \exp \left[ -n \text{ Const} \left( \left( \omega_d^2/\omega_0 \right) (t/\tau_0) \right)^{1/2} \right] \sim \exp[-(t/T_1)^{1/2}] \]

\[ g_2(t) \sim \exp[-n \text{ Const} \left( \omega_d^2 \tau_0 t \right)^{1/2}] \sim \exp[-(t/T_2)^{1/2}] \]

Here NMR resonant frequency \( \omega_0 \approx (2\pi)20\text{MHz} \), and effect of flipping moments is \( \omega_d \approx \omega_0/30 \).

If both relaxations are due to the same fluctuations,

\( \omega_0 \tau_0 \sim (T_1/T_2)^{1/2} = (10^3\text{s}/10^{-4}\text{s})^{1/2} \sim 3 \times 10^3 \Rightarrow \tau_0 \sim 10^{-5} - 10^{-4} \text{s} \).

Can also eliminate to get \( n \sim 5 \) (!!). (But this is missing the factors of order “unity”.)
Conclusion: what could it be?

Back-to-back monopole pair?
Slowly relaxing after quench... (Castelnovo et al 2010).
Flips back and forth, yes! But activated $\tau_0(T)$: no.

Dilution by nonmagnetic sites? similar behavior: no!

Nuclear spins fluctuations? Maybe: need to check this.

My best guess?
Extra magnetic (Dy) spins on the nonmagnetic (Ti) as in “stuffed spin ice” (Cava/Schiffer groups).
This site has exceptionally low coupling to the pyrochlore- lattice spins, so extra spins could be flipping freely.