Relaxation Dynamics in Molecular Magnets: From Ground-state Tunneling to Thermal Regime.

I. Tupitsyn and P. Stamp

Manifestations of Quantum mechanics on the large scale.

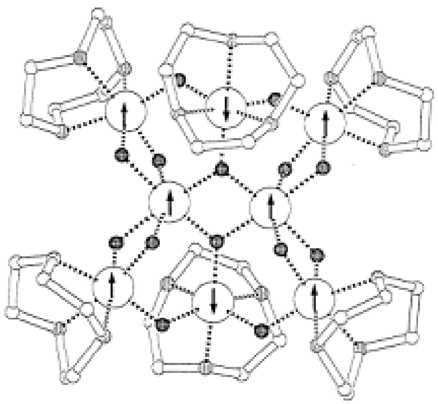
1) Superfluidity in liquid Helium
2) Superconductivity
3) Fractional Quantum Hall
4) Bose condensation
5) Quantum tunneling of the phase in a Josephson junction
6) Magnetism…

Early 70-s: Rare-earth intermetallics (Dy_3Al_2, $SmCo_{3.5}Cu_{1.5}$)
- fast magnetic relaxation in the Kelvin range.
Quantum tunneling of the magnetization?

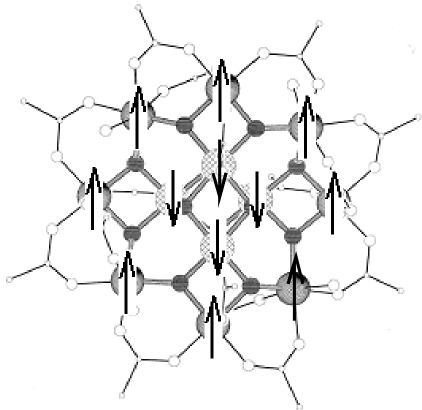
Early 90-s: Molecular crystals of interacting spins.

Examples:

Fe-8 octanuclear iron (3+) complex. Eight S=5/2 iron ions. Antiferromagnetic coupling. S=10 ground state (T < 10 K).



Mn-12 acetate. Four S=3/2 Mn(4+) ions and eight S=2 Mn(3+) ions. Antiferromagnetic coupling. S=10 ground state (T < 40 K).



First experimental evidences for the Quantum Tunneling of Magnetisation in molecular crystals.

Mn-12 (U_o~60 K)

(1) C. Paulsen, J. Park, B. Barbara, R. Sessoli, A. Caneschi **(1995)**;

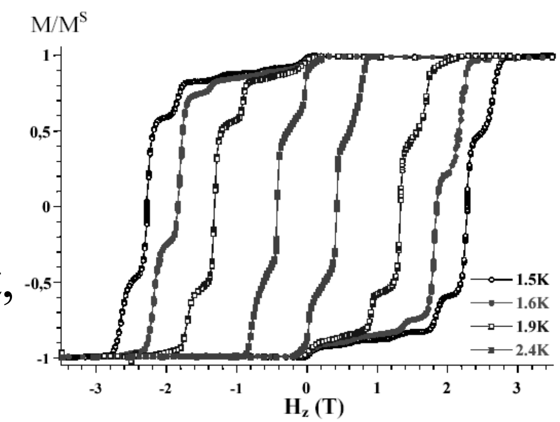
(2) B.Barbara, W. Wernsdorfer, L. Sampaio, J. Park, C. Paulsen, M. Novak, R. Ferre, D. Mailly, R. Sessoli, A. Caneschi, K. Hasselbach, A. Benoit, L. Thomas **(1995)**;

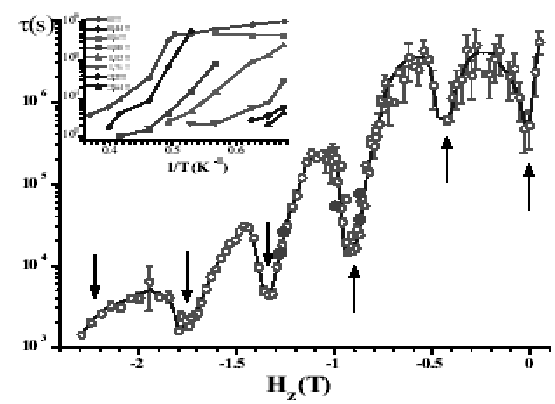
(3) M. Novak, R.Sessoli **(1995)**;

(4) L. Thomas, F. Lionti, R. Ballou, D. Gateschi, B. Barbara (1996);

(5) J. Friedman, M. Sarachik, J. Tejeda, R. Ziolo (1996).

(6) I. Chiorescu, R. Giraud, A. Canneschi, L. Jansen, B. Barbara **(2000)** - **Square-root law**





First experimental evidences for the Quantum Tunneling of Magnetisation in molecular crystals.

Fe-8 (U_o~25 K)

(1) (**powder**) C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, D. Gatteschi **(1997)**;
(2) (**crystal**) T. Ohm, C. Sangregorio, C. Paulsen **(1998)**;

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SQUARE-ROOT RELAXATION at $T<T_Q$~0.4K

$$M(t)=M(0)[1-(t/\tau_{short})]^{1/2}$$

(predicted by N. Prokofev and P. Stamp in 1998)

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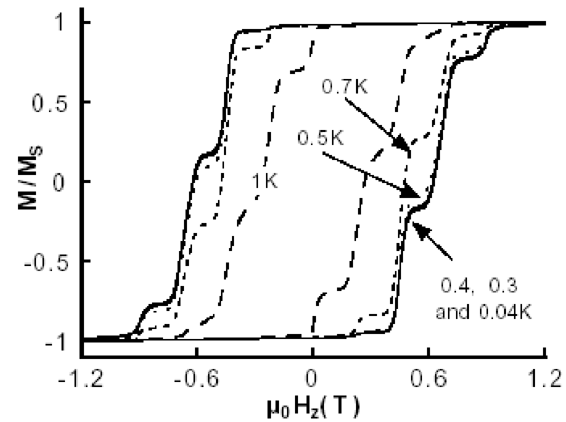
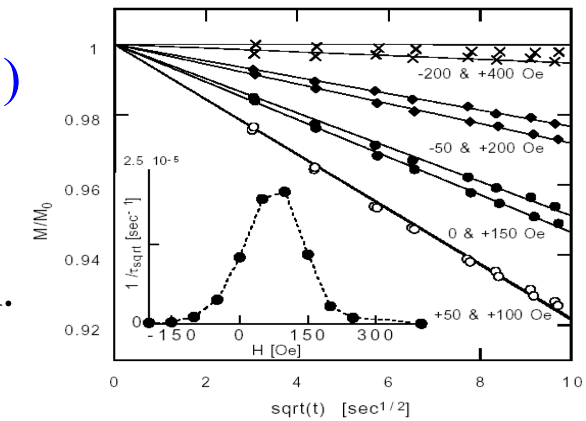
Hole digging experiments

(3) W. Wernsdorfer, T. Ohm, C. Sangregorio, R. Sessoli, D. Mailly, C. Paulsen **(1999)**;





The most spectacular evidence

Fe-8

oscillation of the tunneling splitting at T~40 mK

(4) W. Wernsdorfer, R. Sessoli (1999).

Aharonov-Bohm oscillations

$\Delta_{S,-S}(H_\perp)=2\Delta_0\cos|\pi S-H_\perp/T_\perp|$

(E.N. Bogachek and I.V. Krive (1992) and A. Garg (1993))

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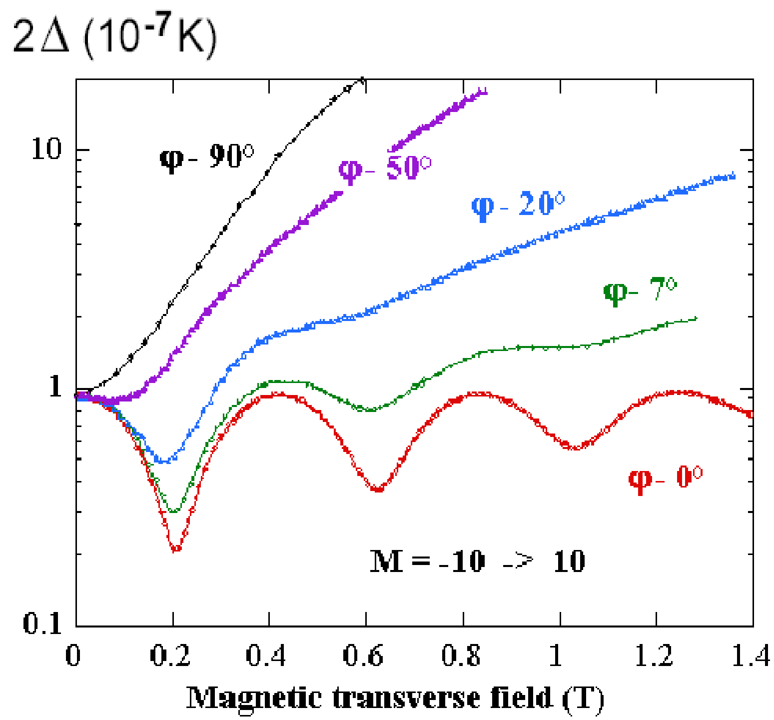
The Quantum Tunneling Phenomenon



Theoretical Efforts: a) Thermal Assisted Regime ($T>>T_Q$)

$$H=H_{MA}+H_{sp\_ph}$$

$$H_{sp\text{-}ph}=\sum_q(\hbar/2N_uM_u\omega_q)^{1/2}[iqV_q(\mathbf{S})C_q^+ - iqV_q^+(\mathbf{S})C_q]$$

$$V_q(\mathbf{S})\sim D(S_xS_z+S_zS_x) \text{ and } V_q(\mathbf{S})\sim D(S_+^2+S_-^2)$$

Mn-12

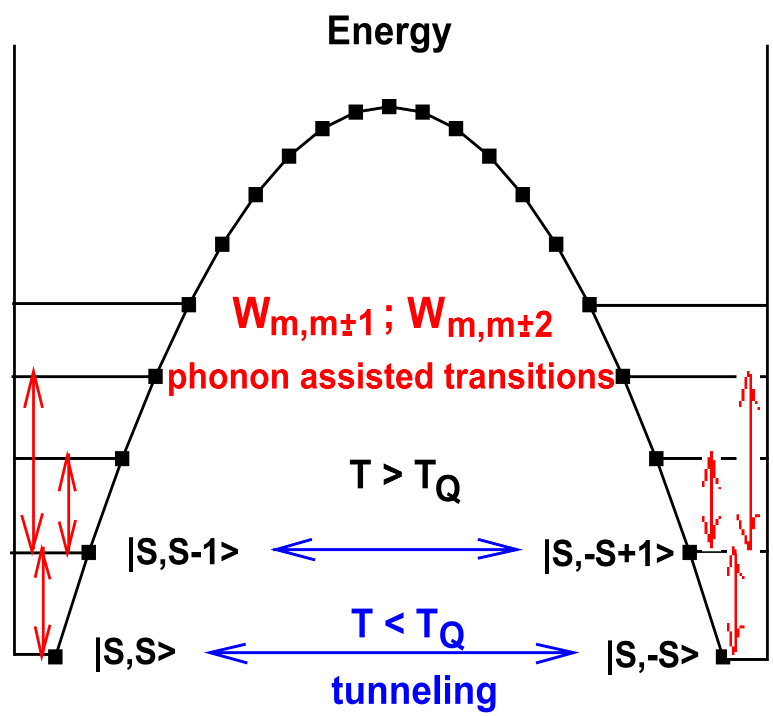
$H_{MA}=-DS_z^2 - K_{\|}S_z^4 + K_{\perp}(S_+^4 + S_-^4) - g\mu_B\mathbf{HS}$

Examples: F. Luis, J. Bartolome, J. Fernandez (1998); A. Fort, A. Rettori, J. Villain, D. Gatteschi, R. Sessoli (1998); M.Leuenberger, D. Loss (1999):

Fe-8

$H_{MA}= -DS_z^2 + ES_x^2 + K_{\perp}(S_+^4 + S_-^4) - g\mu_B\mathbf{HS}$

Examples: M.Leuenberger, D. Loss (2000):



Isolated molecule, No nuclear spin bath ⇒

Exponential relaxation

Theoretical Efforts: b) Quantum Regime ($T<T_Q$)

N. Prokofev and P. Stamp (1998)

$$H=1/2\sum_{ij}V_{i,j}^{(d)}\,\tau_z^{(i)}\tau_z^{(j)} + \sum_i \Delta_S\, \tau_x^{(i)} + \sum_{ik}V^{(N)}(\tau_z^{(i)},I_k)+H^{NN}$$

$V_{ij}^{(d)}=E_D(1\text{-}3\cos^2\theta)V_0/r^3$; $V^{(N)}$ -coupling to k-th nuclear spin; H^{NN}- inter-nuclear interaction. Coupling to the NB causes the spread in energy of the central spin state. The distribution of the NS biases is the Gaussian one with the half-width E_0.

It was shown that at $T<T_Q$ each molecule relaxes incoherently at a rate:

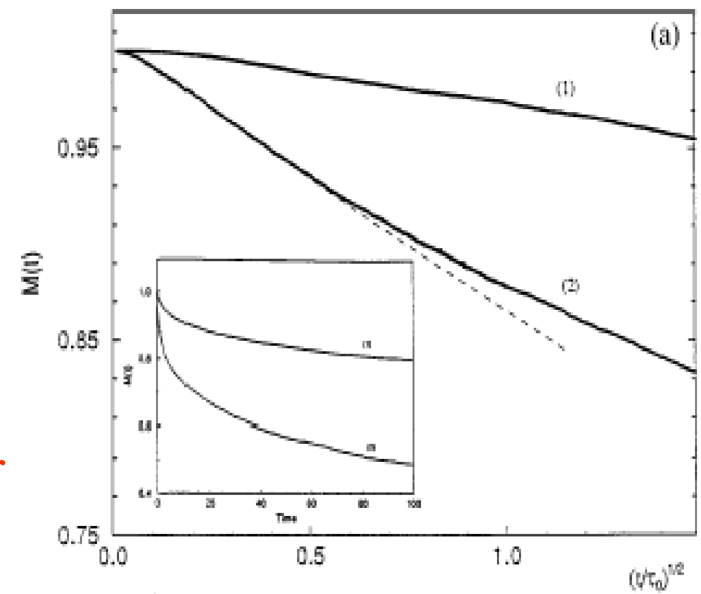
$$\tau_N^{-1}(\xi) = \tau_0^{-1}\exp(-|\xi|/\xi_0);\;\; \tau_0^{-1} = 2\Delta_{-S,S}^{\;\;2}/\pi^{1/2}\hbar\Gamma_{nd}$$

$$M(t)=\int d\xi \int(d\mathbf{r'}/V_0)\,[P_+(\xi,\mathbf{r'},t)- P_-(\xi,\mathbf{r'},t)]$$

$$M(t) \approx 1 - \mathrm{sqrt}(t/\tau_Q);\quad (\xi_0/E_D<t/\tau_o<\xi_0/E_D);$$

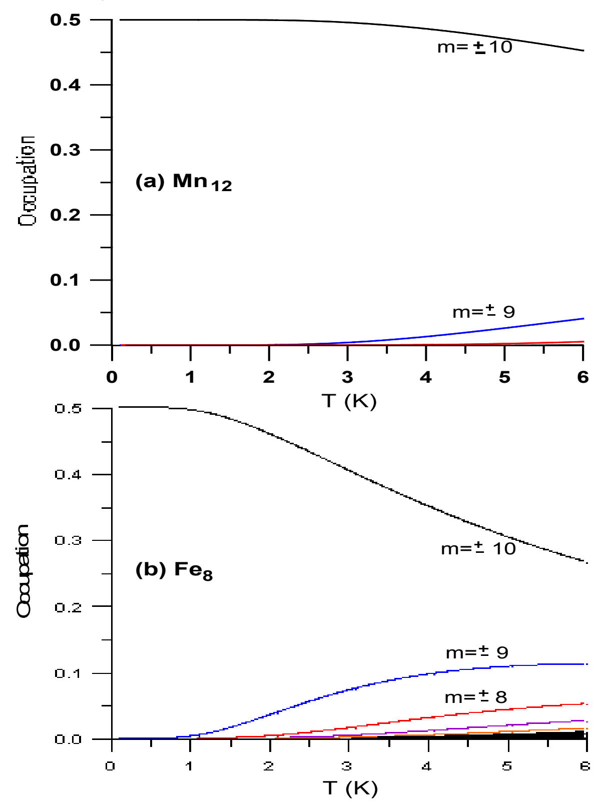
$$\tau_Q\sim(\Delta_S^{\;2}/E_D)\xi_o N(\varepsilon_o);\;\; \varepsilon_o=g\mu_B S H_Z$$

ξ_0- gives the change in the coupling energy when S flips; Γ_{nd} characterizes the rapidness of the NS diffusion in energy space (Theory of the Spin Bath 2000). If $\{\xi_0;\, \Gamma_{nd};\, E_0\} << E_D \Rightarrow$ hole in the dipolar fields distribution creates.



$T<T_Q$: only |+S>and |-S> are populated; $n_{ph}=(\exp(\hbar\omega/k_BT)-1)^{-1} \rightarrow 0$; relaxation is T-independent. Inter-spin interactions and nuclear spin bath are important. $\Rightarrow$ Short-time square-root relaxation.

$T>>T_Q$: all excited states are populated; $n_{ph}=(\exp(\hbar\omega/k_BT)-1)^{-1}$ =finite; Spin - phonon interaction is important. Molecules relax independently $\Rightarrow$ Exponential relaxation. At some T_{Th} ($T_{Th}>T_Q$) relaxation enters exponential regime. $\Rightarrow$



$T_Q<T<T_{Th}$: Crossover Regime

1) $n_{ph} \neq 0$; $W_{n,m} \sim |\langle n|V_{sp\text{-}ph}|m\rangle|^2 \neq 0$;

2) Tunneling can occur at $|m| \leq S$

Important interactions:

1) Inter-spin interactions;

2) With nuclear-spin bath;

3) Spin-phonon interactions

Crossover Regime

Approximations:

1) At $T<T_{Th}$ most of molecules are in states $S_z=\pm S$

$\Downarrow$

with exponential accuracy:

(a) $M(t)$ obeys the same equation as at $T<T_Q$:

$$M(t) = \int d\xi \sum_\alpha \alpha N_\alpha(\xi,t); \quad \alpha=S_z/S=\pm 1$$

($N_\alpha(\xi,t)=\int (d^3r/V_0)\, P^{(1)}_\alpha(\xi,\mathbf{r},t)$ – distribution of the dipolar fields)

(b) $P^{(1)}_\alpha(\xi,\mathbf{r},t)$ obeys the same kinetic equation as at $T<T_Q$:

$$dP_\alpha(\xi,\mathbf{r},t)/dt = \Gamma_C(\xi)\,[P_\alpha^{(1)}(\xi,\mathbf{r}) - P_{-\alpha}^{(1)}(\xi,\mathbf{r})] - \int (d^3\mathbf{r}'/V_0)\, d\xi'\, \Gamma_C(\xi') \times[P_{\alpha\alpha'}^{(2)}(\xi,\xi',\mathbf{r},\mathbf{r}') - P_{\alpha\alpha'}^{(2)}(\xi-\alpha\alpha' V^{(D)}(\mathbf{r}-\mathbf{r}'),\xi',\mathbf{r},\mathbf{r}')],$$

where $\Gamma_C(\xi)$ is the effective single-molecule relaxation rate, accumulating effects of both the nuclear spin bath and the phonon bath.

Crossover Regime

Approximations:

2) Nuclear bath and phonon bath do not interact with each other *directly*. Thus:

$$\Gamma_C(\xi) = \Sigma_{m=1}^{S} \Gamma^m(\xi)\, B^m(T)$$

$$\boxed{\Gamma^m(\xi) = \Gamma^m{}_N(\xi) + \Gamma^m{}_P(\xi),}$$

where

$$B^m(T) = [\exp(E_{S,m}{}^{(0)}/k_B T) + \exp(E_{-S,-m}{}^{(0)}/k_B T)]/2,$$

$$E_{S,m}{}^{(0)} = E_S{}^{(0)} - E_m{}^{(0)}$$

$H_{MA} = H_0 + V_S$; $H_0 = -\, D\, S_Z{}^2 - g\mu_B \mathbf{SH}$; $H_0|m\rangle = E_S{}^{(0)}|m\rangle$

V_S = anisotropy terms

Nuclear effective rate $\Gamma^{m}_{N}(\xi)$

Parameters.

Static: E_0 characterizes the spread in energy of the state |S,S>

$E_0^{(m)}$ characterizes the spread in energy of the state |S,m>

(due to interactions with the nuclear spin bath)

$$E_0^{(m)} \approx [m^2 E_0^2 / S^2 - \Delta^2_m]^{1/2} \quad \text{if } \Delta_m < |m|\, E_0/S$$

$$E_0^{(m)} = 0 \quad \text{if } \Delta_m \geq |m|\, E_0/S$$

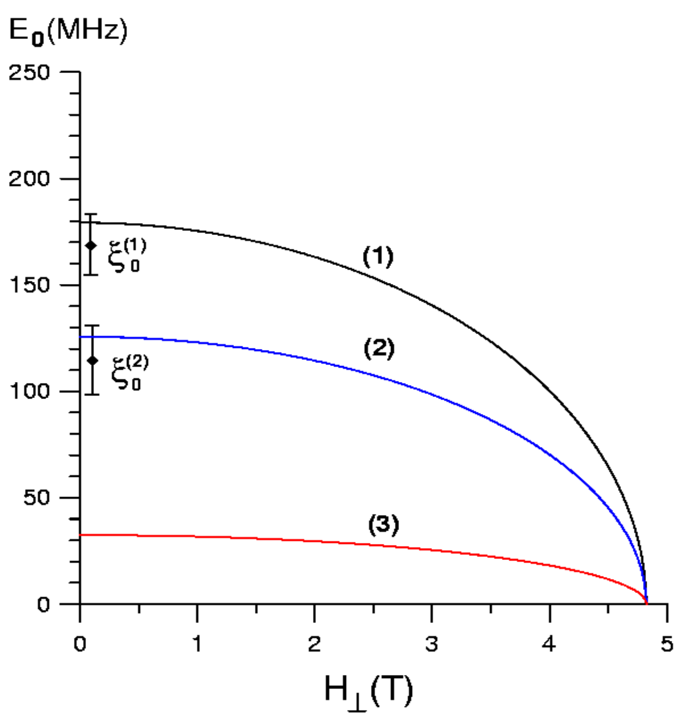
Dynamic: Analogously to $E_0^{(m)}$ we introduce $\Gamma_{nd}^{(m)}$ and $\xi_0^{(m)}$.

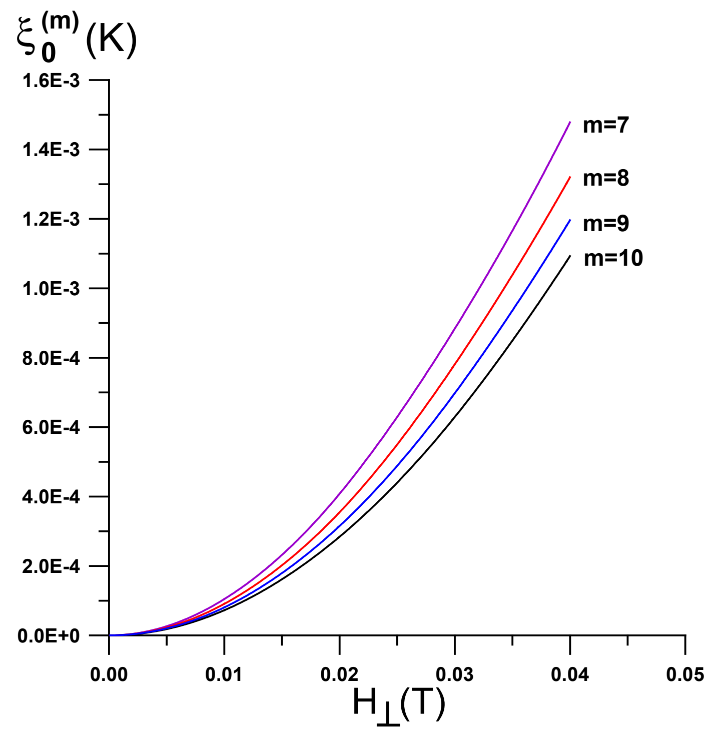
$$E_N^{(m)} = \max\{\xi_0^{(m)}, \Gamma_{nd}^{(m)}\}$$

giving the energy range, “covered” by the nuclear spin bath when S changes its state from |m> |-m>. If $H_\perp \neq 0$, $E_N^{(m)}$ can be of the order of $E_0^{(m)}$.

$$\Gamma^m{}_N(\xi) \sim [\, 2\,\Delta_m{}^2 / \pi^{1/2} \hbar E_N{}^{(m)}] \exp(-|\xi_m| / E_N{}^{(m)}) \bullet T_m$$

$$T_m = \exp(-\,\Delta_m{}^2 / 2 (E_N{}^{(m)})^2\,);\ \xi_m = g \mu_B m (\xi + H_z)$$





Phonon effective rate $\Gamma^{m}{}_{P}(\xi)$

$d\rho/dt = -1/\hbar[H,\rho(t)]$; $H = H_{MA} + H_{PH} + H_{SP\text{-}PH}$

(a) $\Delta_m \ll \max\{\hbar W_{n,m}, E_0^{(m)}\}$ - S_Z representation

$\Gamma^{(a)}{}_m \approx \Delta_m{}^2 W_m / (\xi_m{}^2 + \hbar^2 W_m{}^2)$;

(b) $\Delta_m \gg \max\{\hbar W_{n,m}, E_0^{(m)}\}$ - H_{MA} representation

$\Gamma^{(b)}{}_m \approx \Delta_m{}^2 W_m / (\Delta_m{}^2 + \hbar^2 W_m{}^2)$;

(c) $\Delta_m \lesssim \max\{\hbar W_{n,m}, E_0^{(m)}\}$ - S_Z representation (3 problems)

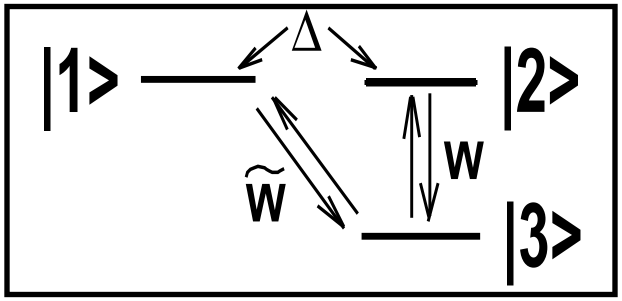
$\Gamma^{(c)}{}_m \approx \Delta_m{}^2 W_m / (\Delta_m{}^2 + \xi_m{}^2 + \hbar^2 W_m{}^2)$;

$W_m \approx 1/4 \sum_k (W_{m+k,m} + W_{-m-k,-m})$

$W_{m\pm2,m} = A S_{m\pm2} (E^{(0)}{}_{m\pm2,m})^3 n_{ph}(E^{(0)}{}_{m\pm2,m})$

$A \approx D^2/12\pi\rho_o c_s{}^5 \hbar^4$; $\rho_o = M/a^3$

$S_{m\pm2} = (S\pm m+2)(S\mp m-1)(S\pm m+1)(S\mp m)$



Magnetization relaxation. Analysis.

$$dM(t)/dt = -2 \int d\xi \, \Gamma_C(\xi)\,[N_+(\xi,t)-N_-(\xi,t)] = -\sum_m \Gamma^{(m)}{}_{int}(t)$$

Ellipsoidal sample

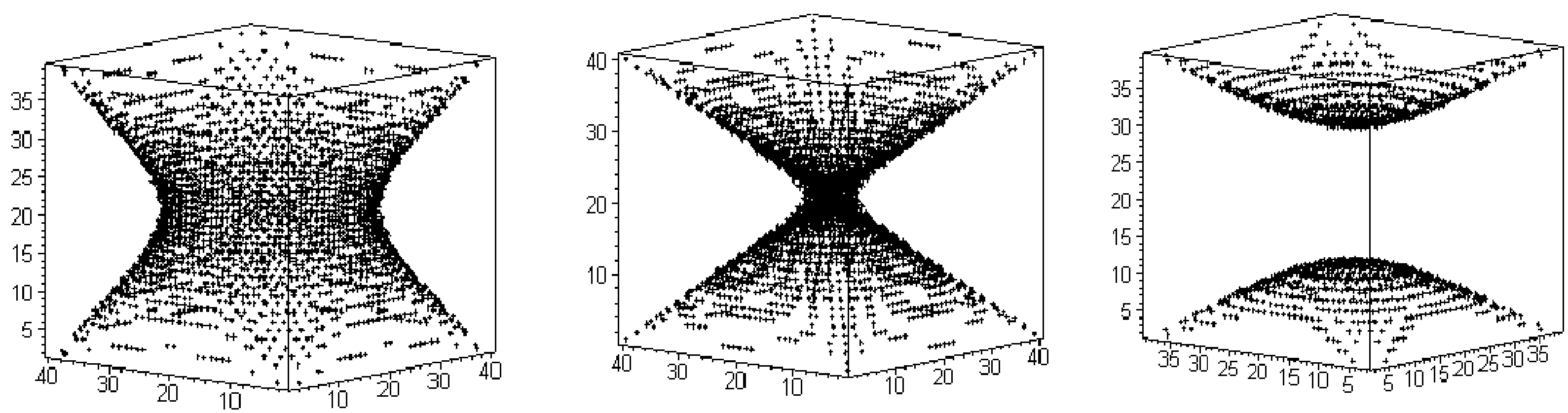
$$N_\alpha^{el}(\xi,t)=(1+\alpha M(t))(\Gamma_D/((\xi-H_D)^2+\Gamma_D^2)/2\pi;\ \{\Gamma_D, H_D\}\sim E_D$$

Sample of arbitrary shape

$\mathscr{F}^{(m)} \sim \mathscr{R}^{(m)}/W_D^{(m)}$, if $\mathscr{R}^{(m)}<W_D^{(m)}$ ($\mathscr{F}^{(m)}=1$, otherwise)

$$\mathscr{R}^{(m)}=\max(E_0^{(m)};\ \Delta_m;\ \hbar W_m);\ W_D^{(m)}\approx(|m|/S)W_D$$

(Polarized: $W_D \sim E_D$; Demagnetized: $W_D > E_D$)



$^{56}Fe_8$: $E_0 \sim$ 6 mK; $\Delta_7 \lesssim E_0^{(7)}$; $E_D \sim$ 0.1 K; $\Delta_6 \sim E_D^{(6)}$; $\Delta_5 > E_D^{(5)}$

Mn_{12} : $E_0 \sim$ 80 mK ; $\Delta_4 \lesssim E_0^{(4)}$; $E_D \sim$ 0.3 K; $\Delta_2 > E_D^{(2)}$

Initially polarized sample ($H_z < H_c^1$)

$N_\alpha^{el}(\xi,t)$: $\Gamma_D(t) \sim (1-M(t))$; $H_D(t) \sim (1-M(t))$; $M(t)=1-x(t)$

$x(t) \ll 1$

(1) At such T, that states with $\mathscr{R}^{(m0)} \ll W_D^{(m0)}$ dominate

$$\Gamma^{(m0)}_{int}(t) \sim M(t)/(1-M(t)) \Rightarrow M(t) \sim 1-\mathrm{sqrt}(t/\tau_{sr})$$

(<u>collective relaxation</u>)

(2) At such T, that states with $\mathscr{R}^{(m0)} \gg W_D^{(m0)}$ dominate

$$\Gamma^{(m)}_{int}(t) \sim M(t) \Rightarrow M(t) \sim 1-\exp(-t/\tau_{er})$$

(<u>independent relaxation</u>)

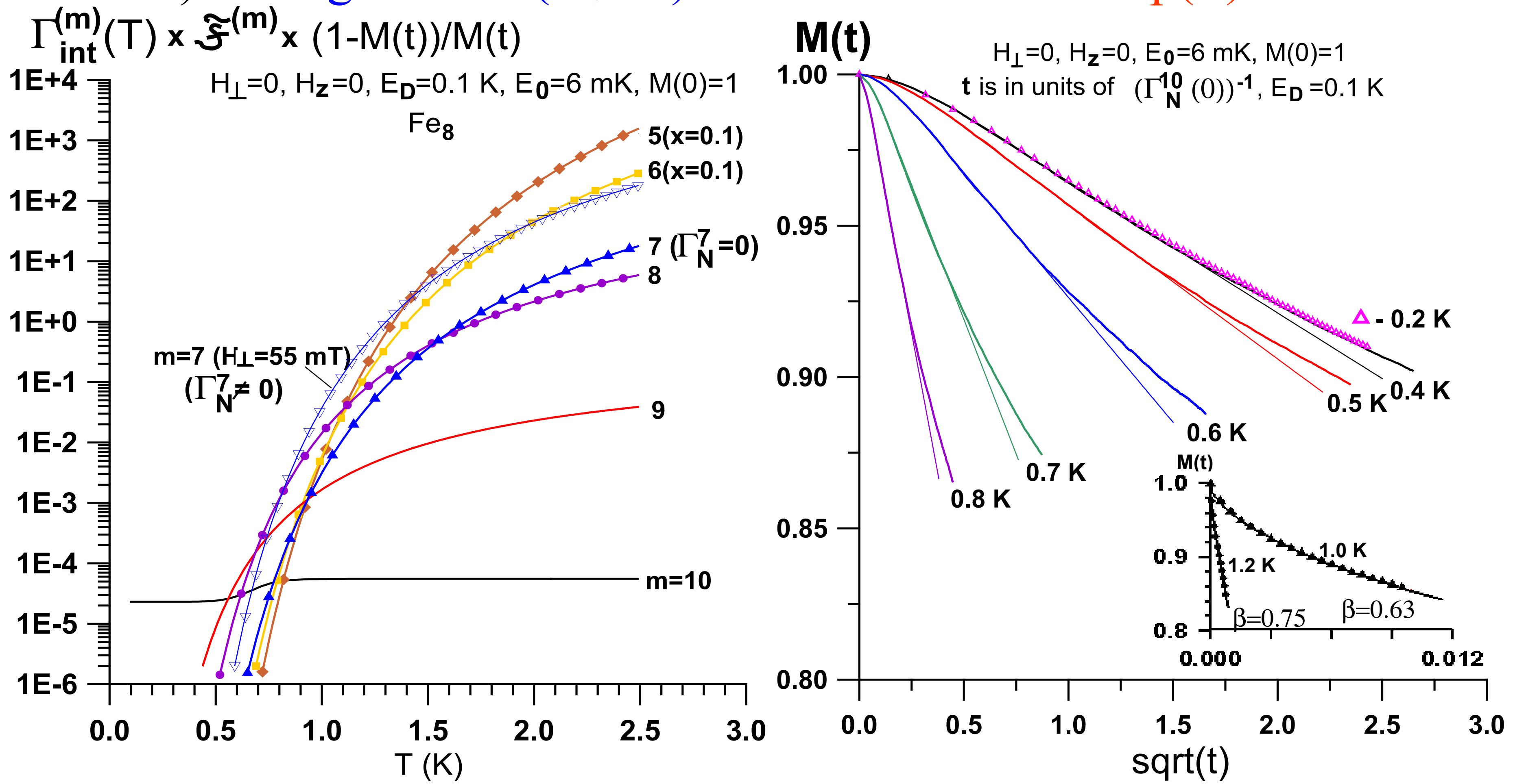
Fe-8: 1) at T ≲ 0.8 K (x≲0.1) only m=10-8 contribute ⇒ sqrt(t)

2) if $\Gamma^7_N \neq 0$ (fast NS diffusion or $H_\perp \neq 0$):

(a) effect of the NSB can be seen up to ~1.5 K

(b) short-time square-root law can be observable up to ~ 1 K

3) at longer times (x≳0.5) m=5 dominates ⇒ exp(-t)

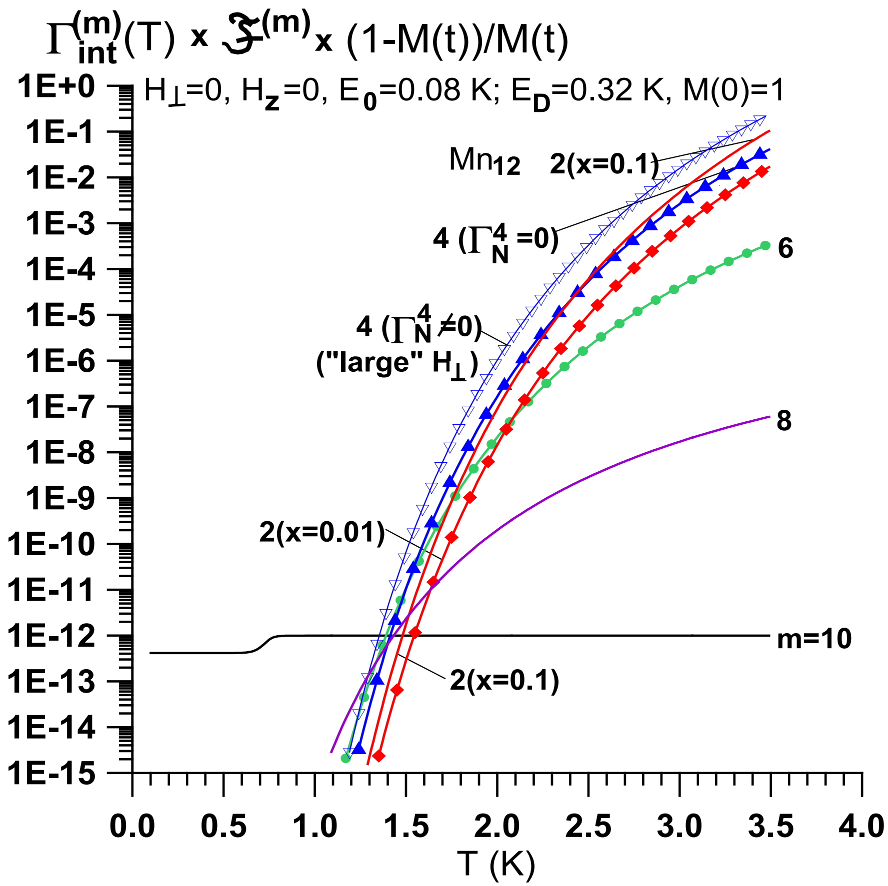


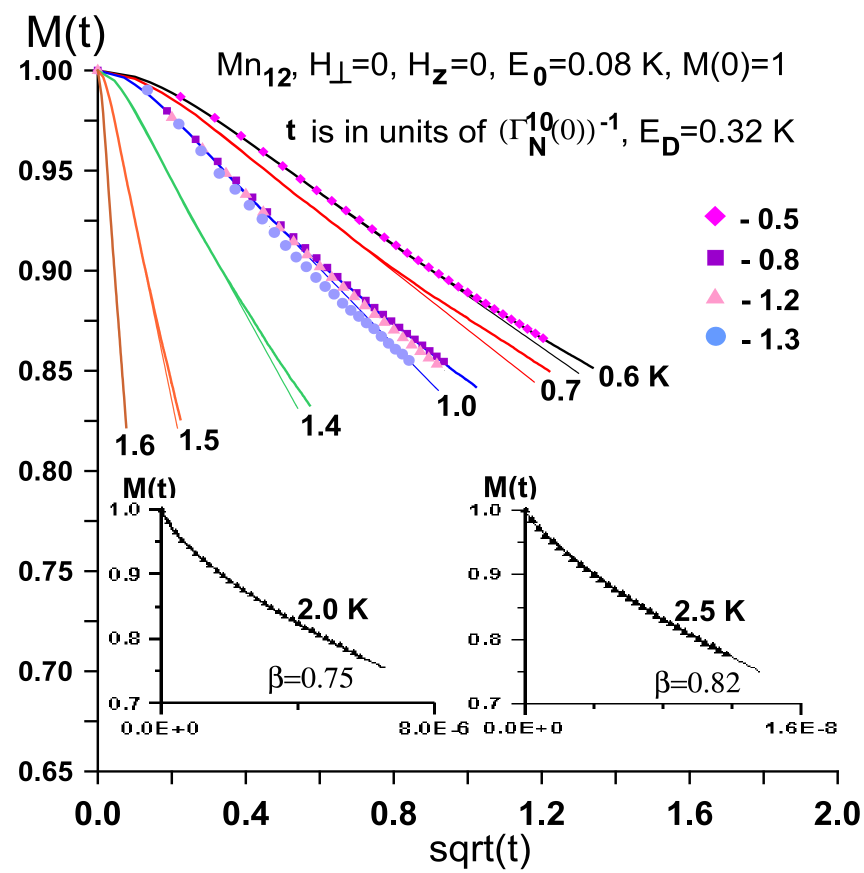
Mn12: 1) at $T<2$ K $m<2$ dominate ($x \lesssim 0.1$) $\Rightarrow$ sqrt(t) (at $x \gtrsim 0.5$-exp(-t))

2) at $T>1.4$ K $m=6$, 4 win rapidly $\Rightarrow$ observed abrupt transition from Ground-State Tunneling to Phonon Assisted regime

3) at $T \gtrsim 2.5$ K $m=2$ contributes significantly $\Rightarrow$ relaxation enters near-exponential regime

4) if $\Gamma^4{}_N \neq 0$ ($H_\perp \gtrsim 0.1$ T), exp(-t) can be seen only at $T>4$ K





Demagnetized sample (M(0)→0)

Dipolar field fluctuates rapidly ⇒ mean-field solution

(demagnetization field changes much slower than at M(0)=1)

Assume each molecule relax independently according to

$$\exp[-t\,\Gamma_{de}(\xi)]$$

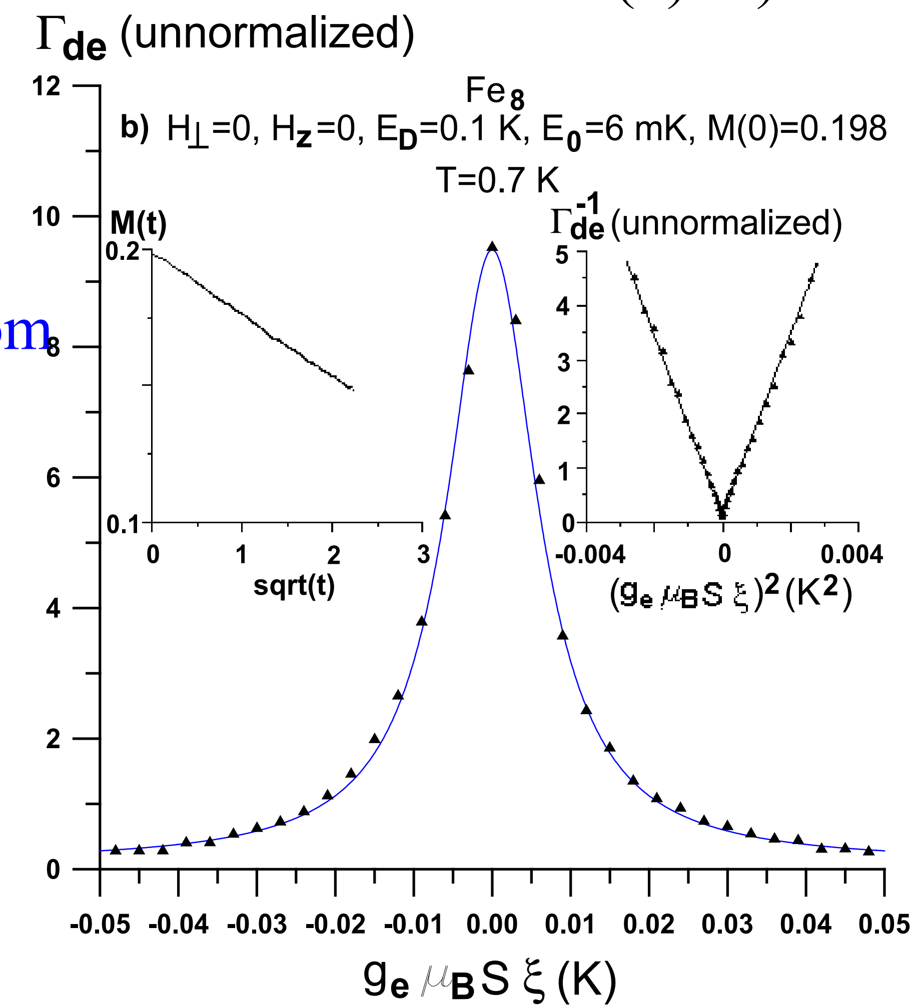
$\Gamma_{de}(\xi)^{-1}$ = time to bring molecule from ξ to resonance by dipolar fields fluctuations

MC

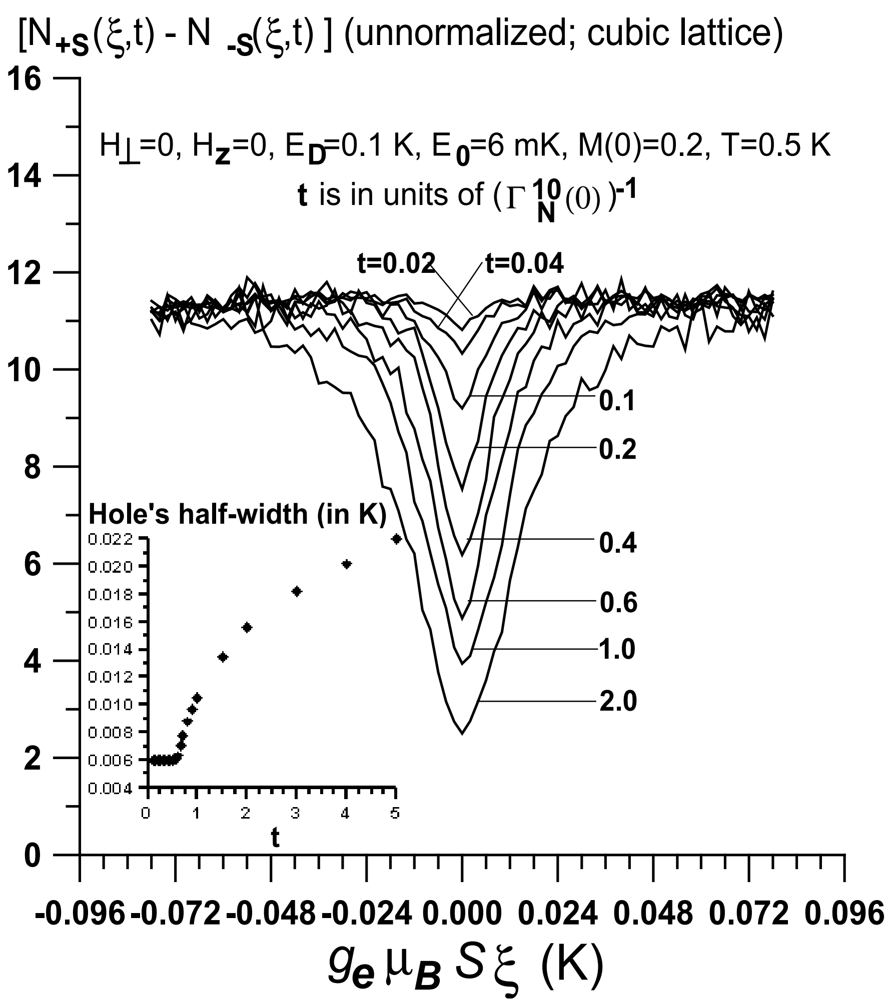
⇓

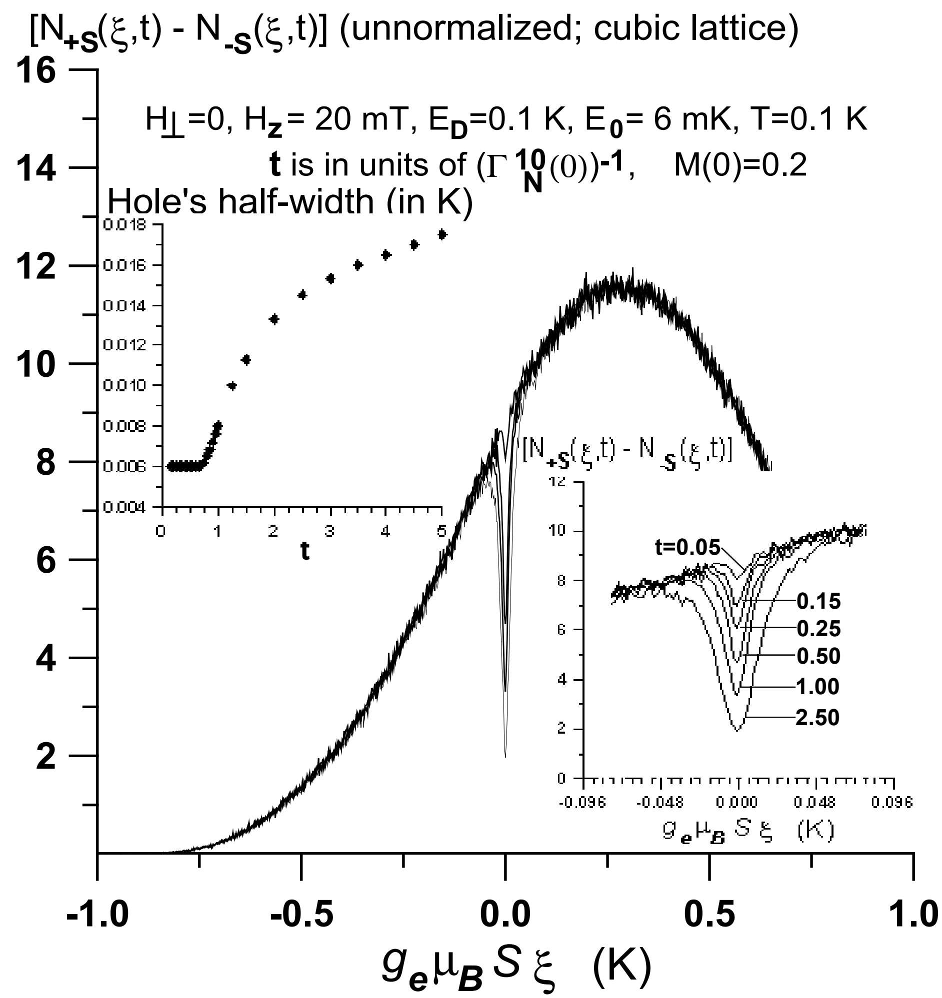
$$\Gamma_{de}(\xi) = \mathscr{R}^{(m)}/(\xi^2+(\mathscr{R}^{(m)})^2)$$

$$(\xi_m/E_0^{(m)} = g\mu_B S\,\xi/E_0)$$



$M(t)=\int d\xi\, \sum_\alpha \alpha N_\alpha(\xi,t)[M_{eq}+(M(0)-M_{eq})\exp(-t\,\Gamma_{de}(\xi))]$ at $t\,\Gamma_C(0) > 1$ ($\xi > E_0$ contributes), making integral dimensionless, we find $M(t) \sim \mathrm{sqrt}(t)$





Polarized sample (M(0)=1)

8-spin s=5/2, triclinic lattice

$N_{+S}(\xi,t)-N_{-S}(\xi,t)$ (unnormalized)