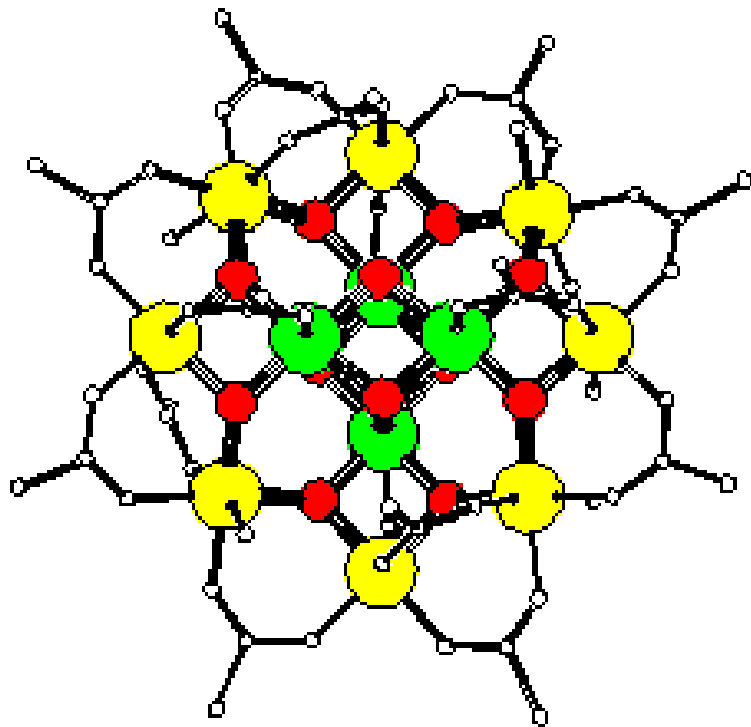


# Collective spin dynamics in the “Coherence Window” for Quantum Nanomagnets

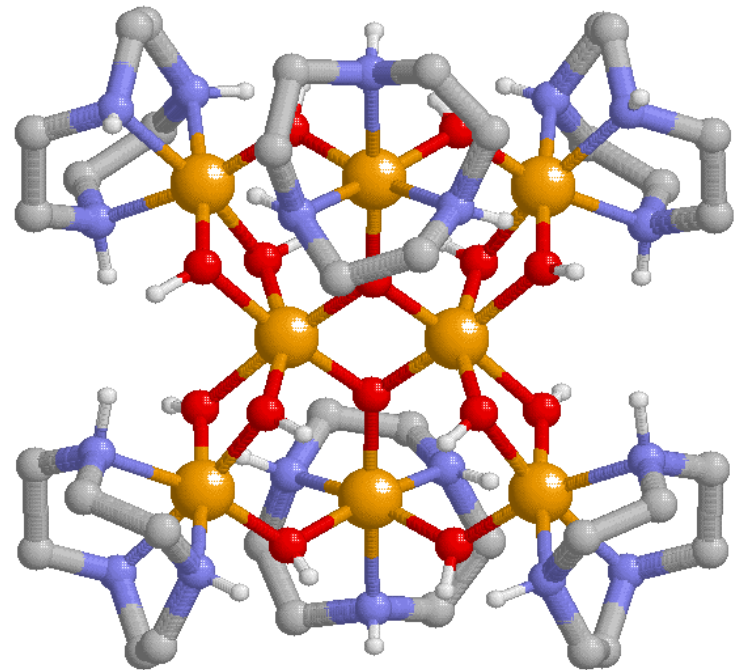
I.S. Tupitsyn (PITP, UBC)

## Two examples: (Single-molecule magnets)

$\text{Mn}_{12}$  ( $S=10$ )  
 $T < 40$  K



$\text{Fe}_8$  ( $S=10$ )  
 $T < 10$  K



## Hamiltonian of magnetic anisotropy

$$H_S^{(Fe)} = -DS_z^2 + ES_x^2 + K_4^\perp (S_+^4 + S_-^4) - g_e \mu_B \vec{H} \vec{S}$$

$$H_S^{(Mn)} = -DS_z^2 - K_4^\parallel S_z^4 + K_4^\perp (S_+^4 + S_-^4) - g_e \mu_B \vec{H} \vec{S}$$

(2S+1 states)

**Low-T limit** – only two lowest states are occupied  
 If  $\Delta_o \ll E_g$  ( $E_g$  is the spin-gap to the next levels)



each molecule can be modeled  
 as a **TLS**:

$$H_{TLS} = -\Delta_o \hat{T}^x - \xi \hat{T}^z$$

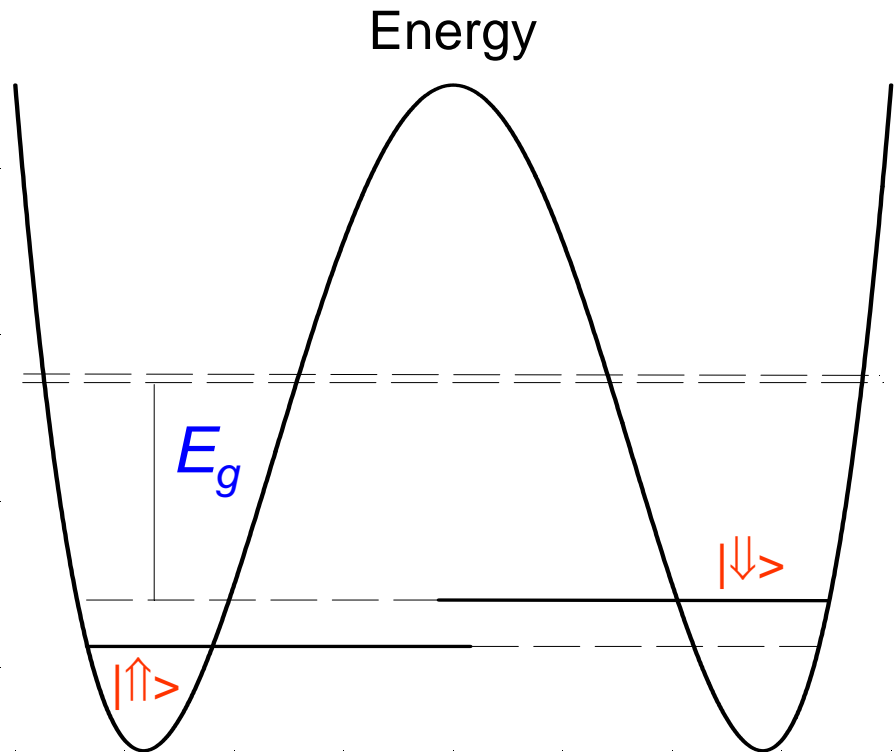
$\Delta$  - tunneling matrix element;  $\xi$  - bias.

$$E_{\downarrow, \uparrow} = 2\varepsilon; \quad \varepsilon = (\Delta_o^2 + \xi^2)^{1/2}$$

$$|\uparrow\uparrow\rangle = u|\uparrow\rangle + v|\downarrow\rangle$$

$$|\downarrow\downarrow\rangle = -v|\uparrow\rangle + u|\downarrow\rangle$$

$$(u, v) = [(\varepsilon \pm \xi)/2 \quad \varepsilon]^{1/2}$$



# “Coherence Window” for nuclear spin bath and phonons

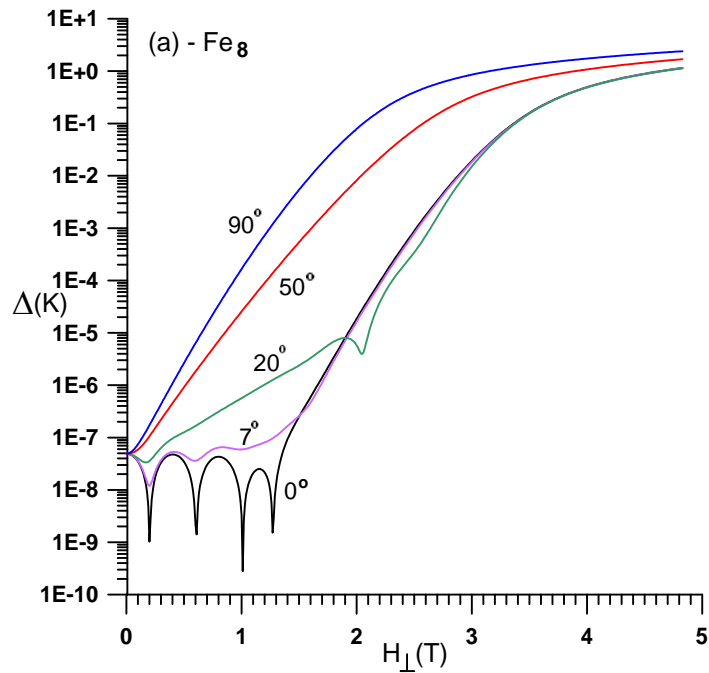
$\Delta_o$  changes with transverse magnetic field  $H_{\perp}$

Coherence window opens up at  $H_{\perp}^c$ , where the total nuclear spin bath and

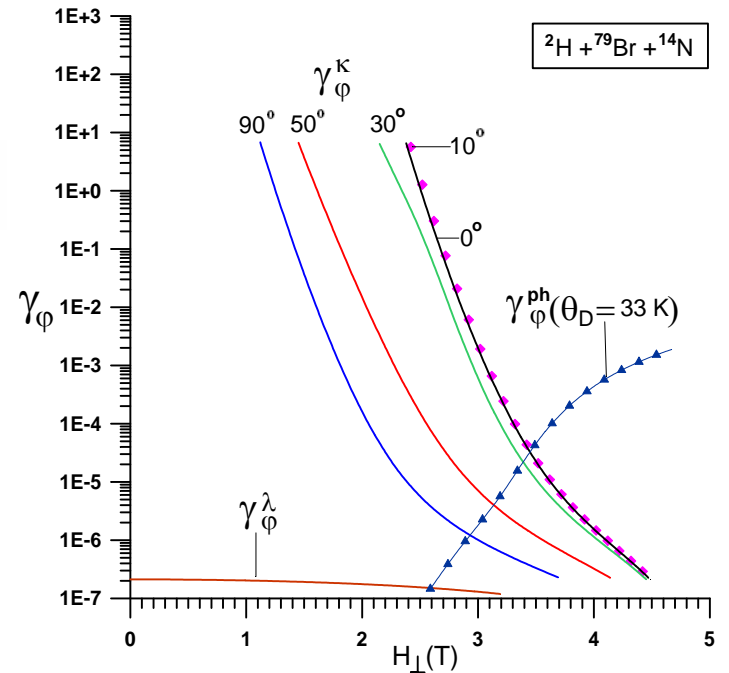
phonon decoherence rate  $\gamma_{\phi} = \hbar/(\Delta_o\tau_{\phi})$  reaches its minimum

$$\frac{1}{\tau_{\phi}^{nu}} = \frac{E_o^2}{2\Delta_o\hbar}; \quad \frac{1}{\tau_{\phi}^{ph}} = \frac{S^2\Omega_o^2\Delta_o^3}{\Theta_D^4\hbar} \coth(\Delta_o/k_B T)$$

( $E_o$  - half-width of the nuclear bias distribution;  $\Theta_D$  - Debye energy;  $\Omega_o \approx E_g$ )



$$Q_{\phi} \sim 1/\gamma_{\phi}$$

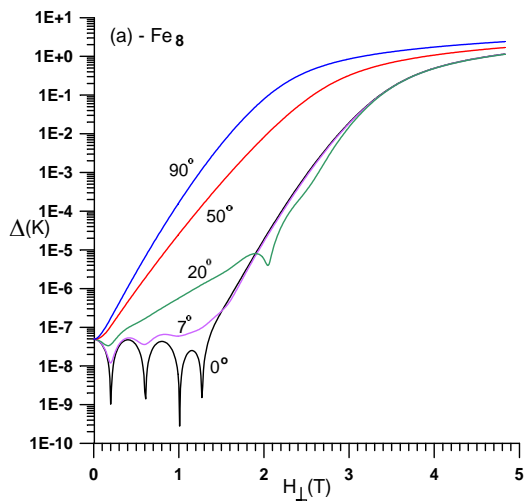


(P.C.E. Stamp, I.S. Tupitsyn, PRB 69, 014401, (2004))

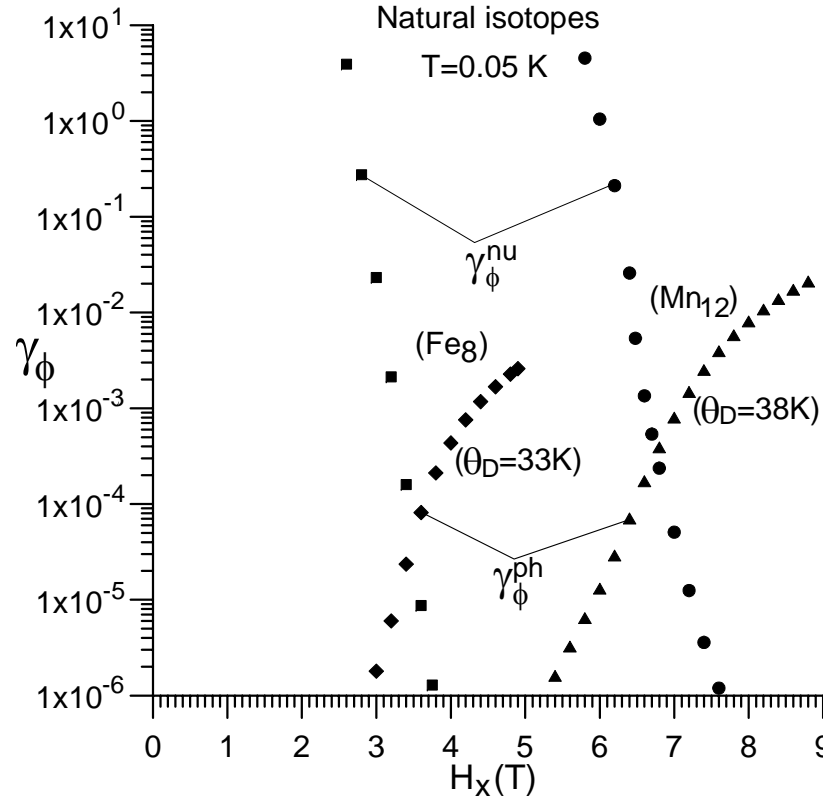
What kind of spin dynamics can then be expected in this Coherence Window at  $t < \tau_{np}$  in a crystal of SMM coupled to nuclear spin bath, to phonons and to each other via dipole-dipole interactions?

$$\tau_{np} = \min\{\tau_{\phi}^{nu}, \tau_{\phi}^{ph}\}$$

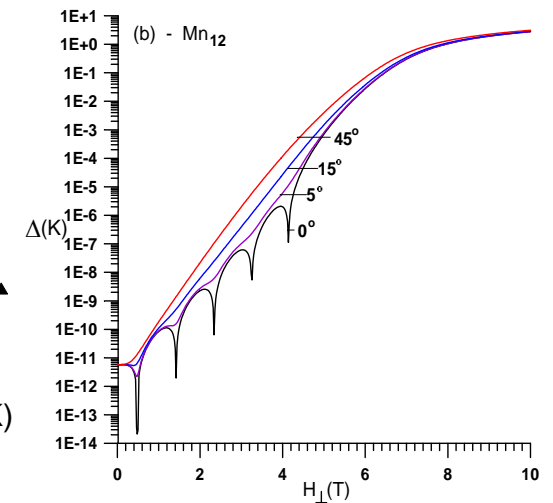
$T$ -equilibrated sample;  $H_{\perp} \parallel \mathbf{x}$  (no coherence optimization)



$H_x^c(Fe_8) \approx 3.4 T$



(sample averaged rates)



$H_x^c(Mn_{12}) \approx 6.7 T$

## Model Hamiltonian

$$H = \sum_i (-\Delta_i \hat{\tau}_i^x - \xi_i^{en} \hat{\tau}_i^z) + \frac{1}{2} \sum_{ij} \hat{V}_{dd}(\vec{r}_{ij})$$

$$\hat{V}_{dd}(\vec{r}_{ij}) = \frac{E_D}{|\vec{r}_{ij}|^3} \left( \hat{\tau}_i^z \hat{\tau}_j^z - 3 \frac{(\hat{\tau}_i^x \vec{r}_{ij})(\hat{\tau}_j^x \vec{r}_{ij})}{|\vec{r}_{ij}|^2} \right) = \sum_{\{\alpha, \beta\}=\{x, z\}} V_{dd}^{\alpha\beta}(\vec{r}_{ij}) \hat{\tau}_i^\alpha \hat{\tau}_j^\beta$$

$\xi_i^{en}$  - external and nuclear longitudinal fields contribution

$\xi_i^d = -g_e \mu_B S_i^z H_i^z (dip)$  - dipolar contribution

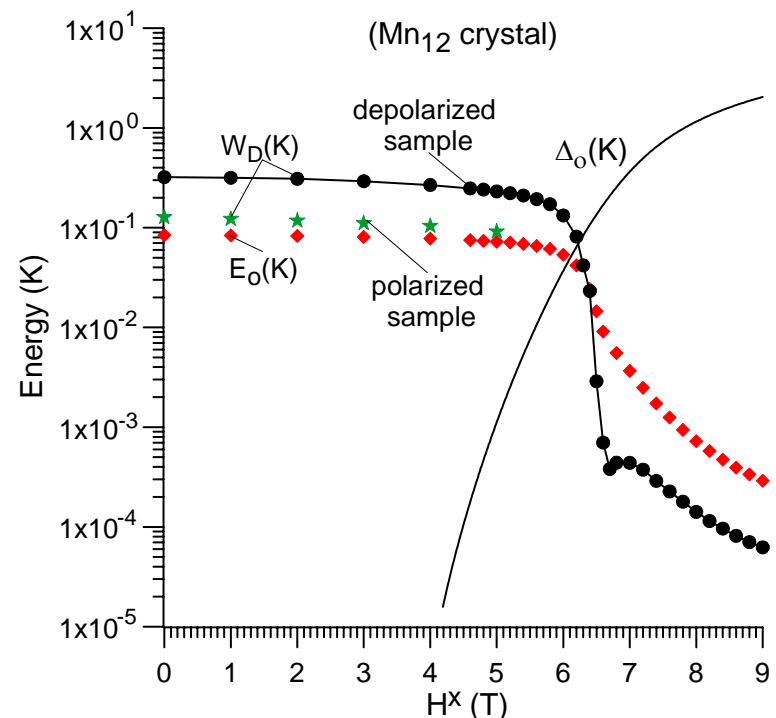
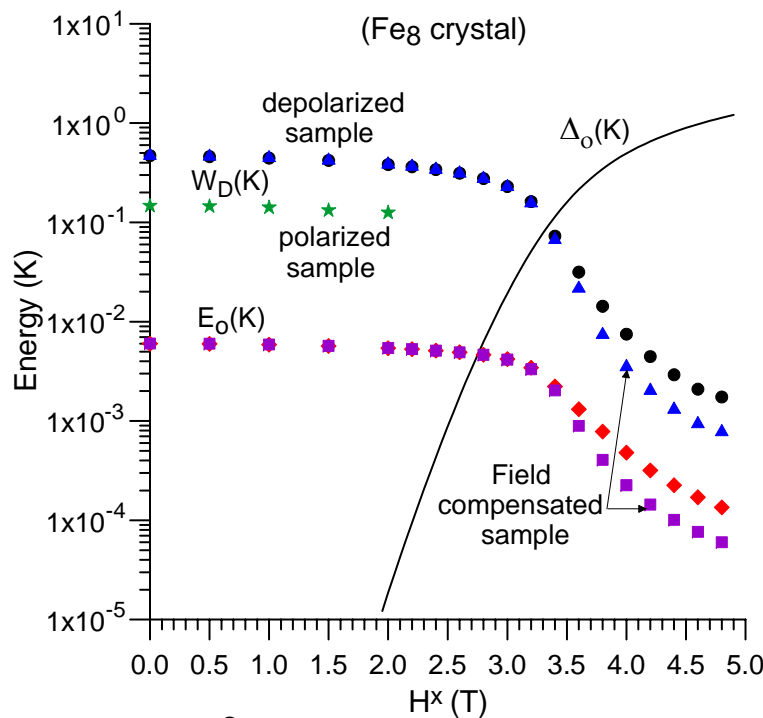
$$\hat{H}_i^z(dip) = \sum_{j \neq i} \frac{F_D}{|\vec{r}_{ij}|^3} \left( 3 \frac{(\hat{\tau}_j^z z_{ij} + \hat{\tau}_j^x x_{ij}) z_{ij}}{|\vec{r}_{ij}|^2} - \hat{\tau}_j^z \right)$$

One needs to know the half-width  $W_D$  of the dipolar energies distribution in the *NPC-window*

Knowing the crystal and molecular structure and the Hamiltonian of magnetic anisotropy, both  $W_D$  and  $E_o$  can be calculated

All molecules are in states  $|\uparrow\rangle$  and  $|\downarrow\rangle$

Both states are obtained by solving the corresponding Hamiltonians of magnetic anisotropy in external magnetic field



Clusters of  $50^3$  Fe<sub>8</sub> or Mn<sub>12</sub> molecules (not a point dipole approximation!), arranged in a triclinic (Fe<sub>8</sub>) or tetragonal (Mn<sub>12</sub>) lattice arrays

In both systems in the NPC-window  $\Delta_o \gg \{W_D, E_o\}$

## Multimolecular processes in the limit $\Delta_o \gg \{W_D, E_o\}$

### Two interacting molecules

$$H = H^{TLS}_1 + H^{TLS}_2 + \sum_{\alpha\beta} V^{\alpha\beta} \tau^\alpha_1 \tau^\beta_2$$

Rewriting  $H$  in the basis  $\{ \uparrow\uparrow, \uparrow\downarrow, \downarrow\uparrow, \downarrow\downarrow \}$ , one finds that two “flip-flop” states  $|\uparrow\downarrow\rangle$  and  $|\downarrow\uparrow\rangle$  are separated from each other by the energy gap  $2|\varepsilon_1 - \varepsilon_2| \ll \Delta_o$  while two remaining states are separated from the  $|\uparrow\downarrow\rangle$  and  $|\downarrow\uparrow\rangle$  states by the energy gaps  $\sim 2\Delta_o$ .  $\Rightarrow$  **Two central flip-flop states** can be considered as a *new Effective TLS* with parameters:

$$\Delta_{ff} \sim |B|; \quad \xi_{ff} \approx |\varepsilon_1 - \varepsilon_2|; \quad B = -V^{zz} \frac{\Delta_1 \Delta_2}{\varepsilon_1 \varepsilon_2} + V^{xx} \frac{\xi_1 \xi_2}{\varepsilon_1 \varepsilon_2}$$
$$(\Delta_i/\xi_i \gg 1) \Rightarrow \Delta_{ff} \sim |V_{dd}^{zz}(R)| \frac{\Delta_1 \Delta_2}{\varepsilon_1 \varepsilon_2}; \quad \xi_{ff} \sim |\xi_1^2 - \xi_2^2|/2\Delta_o \ll \Delta_o$$

If  $\Delta_{ff} > \xi_{ff}$ , two molecules can form a **RESONANT PAIR** and if at  $t=0$  the pair is in state  $|\uparrow\downarrow\rangle$ , the probability to find this pair at time  $t$  in state  $|\downarrow\uparrow\rangle$  is

$$P_{(\downarrow\uparrow)(\uparrow\downarrow)} \sim \frac{\Delta_{ff}^2}{E_{ff}^2} \sin^2(E_{ff}t/\hbar); \quad E_{ff} \sim \sqrt{\xi_{ff}^2 + \Delta_{ff}^2}$$

Two *nearest-neighbor molecules* (fastest flip-flop transitions)

$$\Delta_{ff}^{nn} \sim \tilde{V}_{dd}(\Delta_1\Delta_2/\varepsilon_1\varepsilon_2) \text{ and } \xi_{ff}^{nn} = |\varepsilon_1 - \varepsilon_2|$$

$$(\tilde{V}_{dd} \sim E_D/(V_o^{(1)})^{1/3}; V_o^{(1)} - \text{volume per one molecule})$$

If  $\Delta_{ff}^{nn} > \xi_{ff}^{nn}$  two *nearest-neighbor molecules* are in resonance.

### Two interacting RESONANT PAIRS

At  $k_B T < \Delta_o (H_x)$  ( $H_x \sim H_x^c$ ) most of molecules are in states  $|\uparrow\rangle$  (ground state) and only  $N_{ex}(T) \sim N_o \exp(-2\Delta_o/k_B T)$  molecules are in states  $|\downarrow\rangle$  (excited state). Consider *two resonant pairs of nearest-neighbor molecules* separated by the average distance

$$R_{ex}(T) \sim (V_o^{(1)} N_o / N_{ex})^{1/3}$$

If  $\Delta_{ff}^{nn} > \xi_{ff}^{nn}$ , the same arguments as in the case of two molecules will lead to a conclusion about the existence of a “*second order*” *Effective TLS* with parameters:

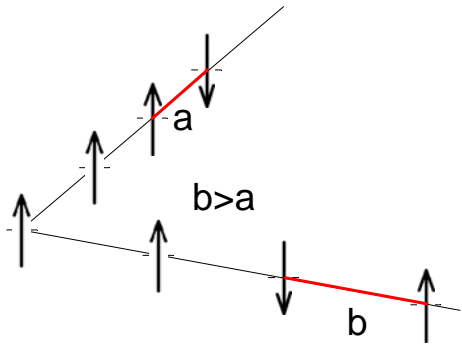
$$\Delta_{ff}^{(2)}(\vec{R}) \sim |V_{dd}^{zz}(\vec{R})| \frac{\Delta_{ff}^{nn} \Delta'_{ff}{}^{nn}}{E_{ff}^{nn} E'_{ff}{}^{nn}}; \xi_{ff}^{(2)} \sim |E_{ff}^{nn} - E'_{ff}{}^{nn}|$$

If  $\Delta_{ff}^{(2)}(R_{ex}) > \xi_{ff}^{(2)}$ , two *RESONANT PAIRS* are in resonance.



Resonance conditions (generic lattice)

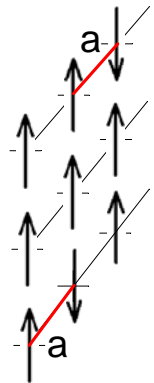
- a) Nearest - neighbor molecules in two pairs are located along different axes (with different lattice constants):



$$\tilde{\xi}_{ff}^{(2)} \sim \Delta_{ff}^{nn} \gg \Delta_{ff}^{(2)}$$

resonance might be impossible

- b) Nearest-neighbor molecules in two pairs are located along the same axis:



$$\tilde{\xi}_{ff}^{(2)} \sim \tilde{V}_{dd} (W_D / \Delta_o)^2 \ll \tilde{V}_{dd}$$

resonance is, in principle, possible

In a generic lattice with the same lattice constants resonance is also, in principle, possible

## Resonance conditions (generic lattice)

From the requirement:

$$\Delta_{ff}^{(2)}(\vec{R}) > \xi_{ff}^{(2)}$$

one can estimate the average “resonant distance” between two pairs:

$$R_{res}^{(2)}(H^\perp) \sim [V_o^{(1)}\tilde{V}_{dd}/\tilde{\xi}_{ff}^{(2)}(H^\perp)]^{1/3}$$

If  $R > R_{ph}$

$$R_{ph}(T, H^\perp) \sim [V_o^{(1)}\tilde{V}_{dd}\tau_\phi^{ph}(T, H^\perp)/\hbar]^{1/3}$$

phonon-assisted transitions in each molecule are faster – out of resonance

## Resonance is possible only if

$$R < R_m = \min\{R_{res}^{(2)}, R_{ph}\}$$

This happens at temperatures  $T > T_M$ :

$$T_M = \max\{T_{res}^{(2)}, T_{ph}\}$$

$$k_B T_{res}^{(2)}(H^\perp) \sim 2\Delta_o / \ln[\tilde{V}_{dd}/\tilde{\xi}_{ff}^{(2)}],$$

$$k_B T_{ph}(H^\perp) \sim 2\Delta_o / \ln[\Theta_D^4 \tilde{V}_{dd} / S^2 \Omega_o^2 \Delta_o^3]$$

## Correlated (coherent) clusters

If at  $T > T_M$  the average distance between excited molecules is  $R_{ex}(T) < R_M$ , all nearest - neighbor resonant pairs are able to come into resonance with each-other. If at these conditions  $t_c < \tau_{np}$

$$t_c \sim \hbar / |V_{dd}^{zz}(R_{ex})| \sim (\hbar / \tilde{V}_{dd})(R_{ex}^3 / V_o^{(1)}),$$

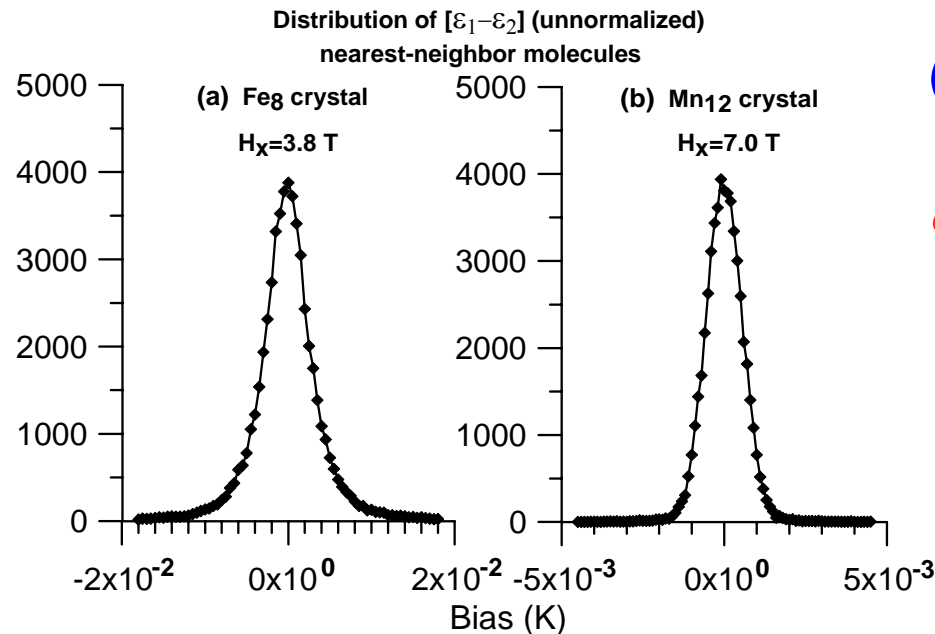
the whole hierarchy of correlated (coherent) flip-flop clusters can, in principle, appear and  $t_c$  is the cluster correlation time. **IF RESONANT PAIRS EXIST!**

## Can nearest-neighbor molecules create resonant pairs?

(Fe<sub>8</sub>)  $H_x = 3.8$  T

$$\begin{aligned} \xi_{ff}^{nn} &\approx 1.5 \times 10^{-3} \text{ K} \\ \delta\varepsilon &\approx 4.7 \times 10^{-3} \text{ K} \\ \tilde{V}_{dd} &\approx 0.12 \text{ K} \\ (\Delta_o &= 0.35 \text{ K}) \end{aligned}$$

YES

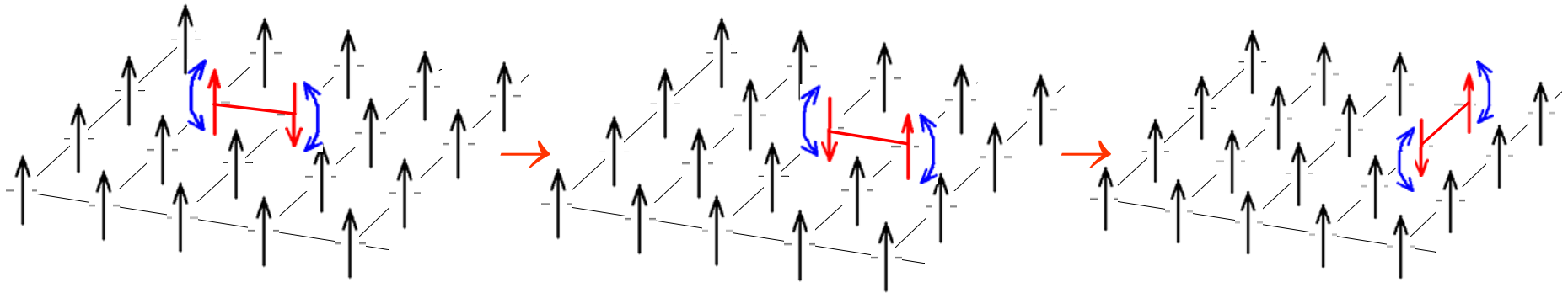


(Mn<sub>12</sub>)  $H_x = 7.0$  T

$$\begin{aligned} \xi_{ff}^{nn} &\approx 2.3 \times 10^{-4} \text{ K} \\ \delta\varepsilon &\approx 6.4 \times 10^{-4} \text{ K} \\ \tilde{V}_{dd} &\approx 0.07 \text{ K} \\ (\Delta_o &= 0.36 \text{ K}) \end{aligned}$$

YES

## “Propagation” of the flip-flop transition



For excited molecule the probability to create a resonance with all of its nearest-neighbor ground state molecules is the same (at least along of one axis)  $\Rightarrow$  The flip-flop transition is potentially mobile  $\Rightarrow$  “flipon” (a kind of magnon)

If  $\tilde{\Delta}_{ff}^{nn} > \tilde{\xi}_{ff}^{nn}$ , instead of interactions between immobile pairs of resonant molecules, one has a set of  $N_{ex}(T)$  “mobile flip - flop transitions”, flipons, diffusively propagating through the crystal (the “centers of mass” motion).



Decorrelation (dephasing)

## Decorrelation

(a) Flipons motion

(b) Spectral diffusion

(a) Flipons motion (motional dephasing)

Suppose that at  $t=0$  there is a correlated cluster of flipons, separated by the distance  $R_{ex}(T)$  ( $T_M < T < \Delta_o/k_B$ ). If at  $t > 0$  flipons will start to move along different axes, in a generic lattice all correlations can be suppressed already at  $t \gtrsim \hbar/\Delta_{ff}^{nn}$ . If we consider only a quasi – 1d motion of flipons (along the same axis), we estimate the *longest motional dephasing time*  $\tau_d^m$ . If  $\tau_d^m > t_c$ , correlated cluster with the average distance  $R_{ex}(T)$  can appear. If  $\tau_d^m < t_c$ , creation of correlated cluster with  $R_{ex}(T)$  is virtually impossible.

We approximate the flipon motion by the discrete 1d “Random Walks” model

$$R_{ex} + \delta R(t) \Rightarrow \delta \Delta^{(2)}(t) = \langle (\Delta_{ff}^{(2)})^2 - \langle \Delta_{ff}^{(2)} \rangle^2 \rangle^{1/2}$$

$$\tau_d^m = t_f N_d^m; \quad \sum_{N=0}^{N_d^m} t_f \delta \Delta^{(2)}(N) \sim \hbar; \quad t_f = \hbar/\Delta_{ff}^{nn}; \quad N = t/t_f$$

$$\text{(for large values of } N - \int_0^{\tau_d^m} dt \delta \Delta^{(2)}(t) \sim \hbar)$$

$$\langle \Delta_{ff}^{(2)} \rangle \sim \sum_{\tilde{r}_1, \tilde{r}_2 = -N}^N |V_{dd}^{zz}(R_{ex} + (\tilde{r}_1 - \tilde{r}_2)\tilde{a})| P_N(\tilde{r}_1) P_N(\tilde{r}_2)$$

with the condition:  $(R_{ex} + (\tilde{r}_1 - \tilde{r}_2)\tilde{a})/R_{ex} \geq \eta(T)$  -  $\eta(T)$  is the minimal possible (dimensionless) distance between two flipons

### Generalized discrete “Random Walks” model

$$P_N(K_r, K_l) = \frac{N! p^{K_r} q^{K_l} s^{N-K_r-K_l}}{K_r! K_l! (N - K_r - K_l)!}$$

$p$  - probability to make one jump right;  $q$  - one jump left;  $s=1-p-q$  - stay at the same site ( $p+q+s=1$ )

$P_N(K_r, K_l)$  - (polynom distribution) the probability to find the corresponding “walk” with  $K_r$  jumps to the right and  $K_l$  jumps to the left from total  $N$  jumps

$$\tilde{r} = K_r - K_l$$

$$\langle \tilde{r} \rangle = N(p - q); \quad \langle (\Delta \tilde{r})^2 \rangle = 4Npq + Ns(1 - s)$$

$$\langle r^2(t) \rangle = 2D_f t; \quad D_f = \rho \tilde{a}^2 \Delta_{ff}^{nn} / 2\hbar; \quad \rho = 4pq + s(1 - s)$$

$$\tilde{a} \equiv (V_o^{(1)})^{1/3}$$

The solution of the equation for  $\tau_d^m$  can be found in the dimensionless form

$$D_f \tau_d^m / R_{ex}^2 = \tilde{\lambda}(\eta, \rho)$$

If  $\tau_d^m < t_c$ , creation of correlated cluster with average distance  $R_{ex}(T)$  is impossible. When  $\tau_d^m \sim t_c$ , cluster can appear. Thus, one can solve the equation:

$$D_f t_c(R_c) / R_c^2 = \tilde{\lambda}(\eta_c, \rho)$$

( $\eta_c = \eta(R_c)$ ) and find the average distance  $R_c$  and the temperature  $T_c$

$$k_B T_c \sim 2\Delta_o(H^\perp) / \ln[(R_c/\tilde{a})^3 - 1]$$

at which  $\tau_d^m \sim t_c$ . For  $p=q=s=1/3$  one finds:

$$R_c \sim 3\tilde{a}; \quad k_B T_c \sim 0.6\Delta_o(H^\perp)$$

*At this temperature correlated cluster with average distances between flipons  $R_c(T_c)$  can appear (if the scenario with  $p=q=s=1/3$  works)*

$$\tau_d^m \sim \rho^{-1/3} \text{ (if } s \rightarrow 1, \rho \rightarrow 0)$$

If flipons are essentially localized - correlated cluster can appear even at

$$T_M < T < T_c$$

and its life-time will be limited only by  $\tau_{np}$ .

### (b) Spectral diffusion

If  $\Delta_{ff}^{nn} \gg \xi_{ff}^{nn}$  and flipons can move, the effect of spectral diffusion is much weaker than the motional dephasing effect – the spectral diffusion time  $\tau_d^s$  is  $\sim (\tilde{\Delta}_{ff}^{nn} / \tilde{\xi}_{ff}^{nn})^3$  longer than  $\tau_d^m$ .

If  $\Delta_{ff}^{nn} < \xi_{ff}^{nn}$  and there are no *flipons*, immobile “lengthy” pairs of flip-flop molecules with  $\Delta_{ff}(R_{ex}) \sim \Delta_{ff}^{(2)}(R_{ex})$  can create correlated cluster. In this case the cluster spectral diffusion dephasing time is  $\tau_d^s \sim t_c$ , but  $\xi_{ff}^{(2)}$  is also  $\sim \Delta_{ff}(R_{ex})$  and correlations will be destroyed after the first flip - flop transition. This scenario is similar to that, known in dielectric glasses: A.L. Burin and Yu. Kagan, Sov. Phys. JETP 80, 761 (1995).



During the cluster **life-time**

$$\tau_d^{ms}(T) = \min\{\tau_d^m(T), \tau_d^s(T)\}$$

all molecules, belonging to cluster, can make  $\sim \Delta_{ff}^{nn} t_c / \hbar$  **coherent flip-flop oscillations**

$$P_{(\downarrow\uparrow)(\uparrow\downarrow)} \sim \frac{\Delta_{ff}^2}{E_{ff}^2} \sin^2(E_{ff} t / \hbar)$$

During the total nuclear spin/phonon coherence period  $\tau_{np}$  cluster can “reappear”  $\lesssim \tau_{np} / t_c$  times.

$p=q=s=1/3$ : At  $T \approx 0.25$  K and at  $H_x = 3.8$  T in  $\text{Fe}_8$  ( $\Delta_o = 0.35$  K) each molecule can make  $\sim 30$  flip-flop oscillations and cluster can reappear  $\sim 50$  times. In  $\text{Mn}_{12}$  at  $T \approx 0.25$  K and at  $H_x = 7.0$  T ( $\Delta_o = 0.36$  K) one can expect  $\sim 10$  flip-flop oscillations and  $\sim 50$  of cluster reappearance times. These numbers were obtained without the coherence optimization. If flipons are localized, number of flip-flop oscillations is limited only by  $Q_\phi \Delta_{ff}^{nn} / \Delta_o$ .