MOLECULAR NANOMAGNETS

alias

SINGLE MOLECULE MAGNETS

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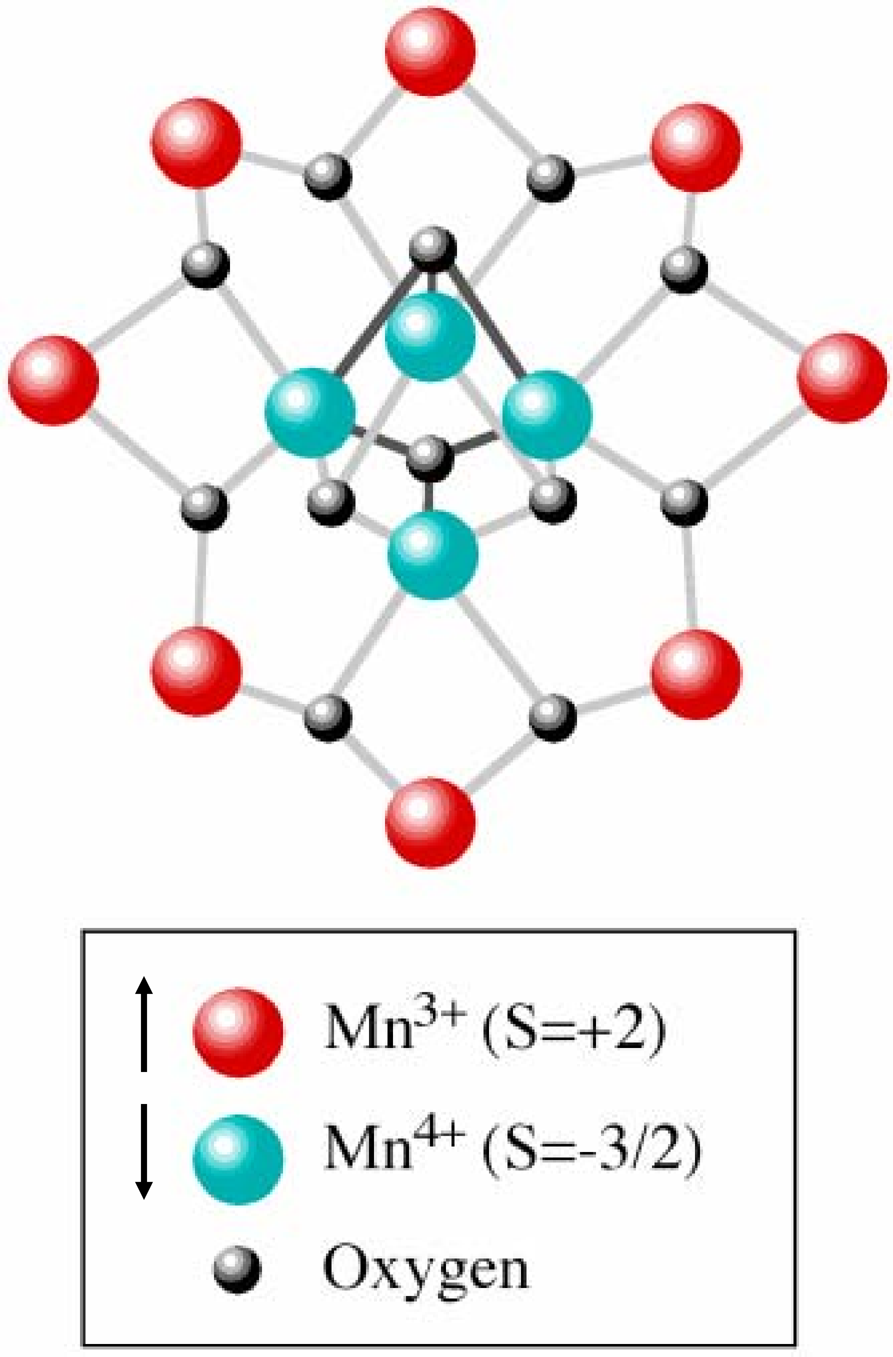
Mn_{12} Acetate Complex

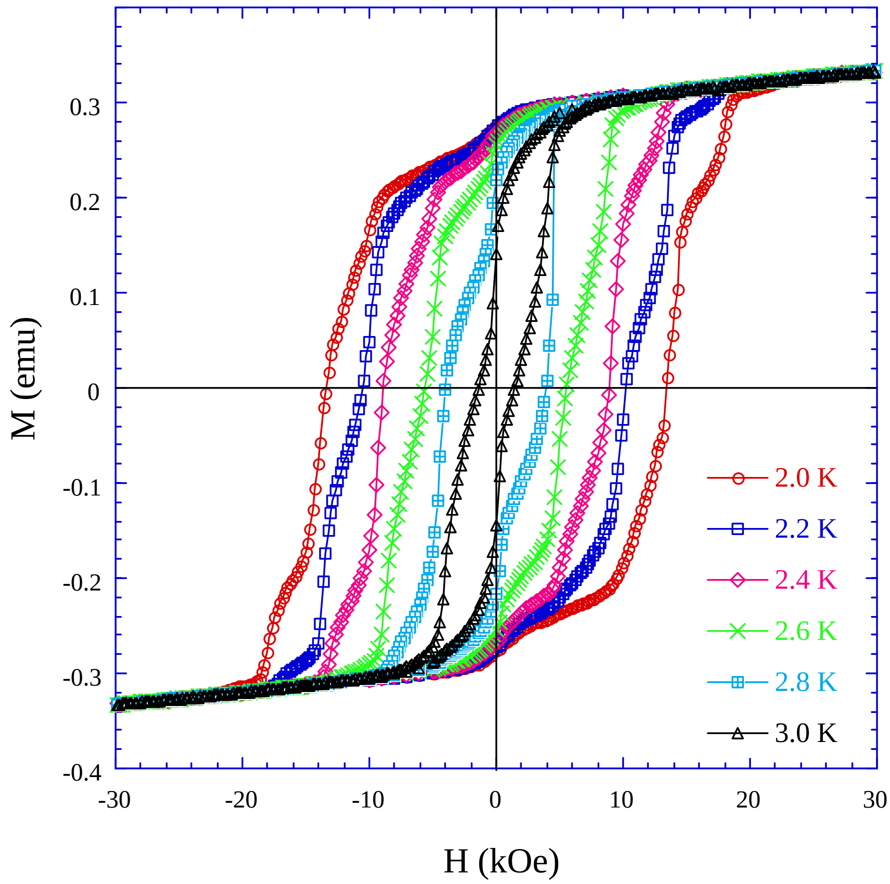
A tetragonal crystal containing a large (Avogadro's) number of weakly interacting magnetically identical spin-10 molecules.

$$Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$$

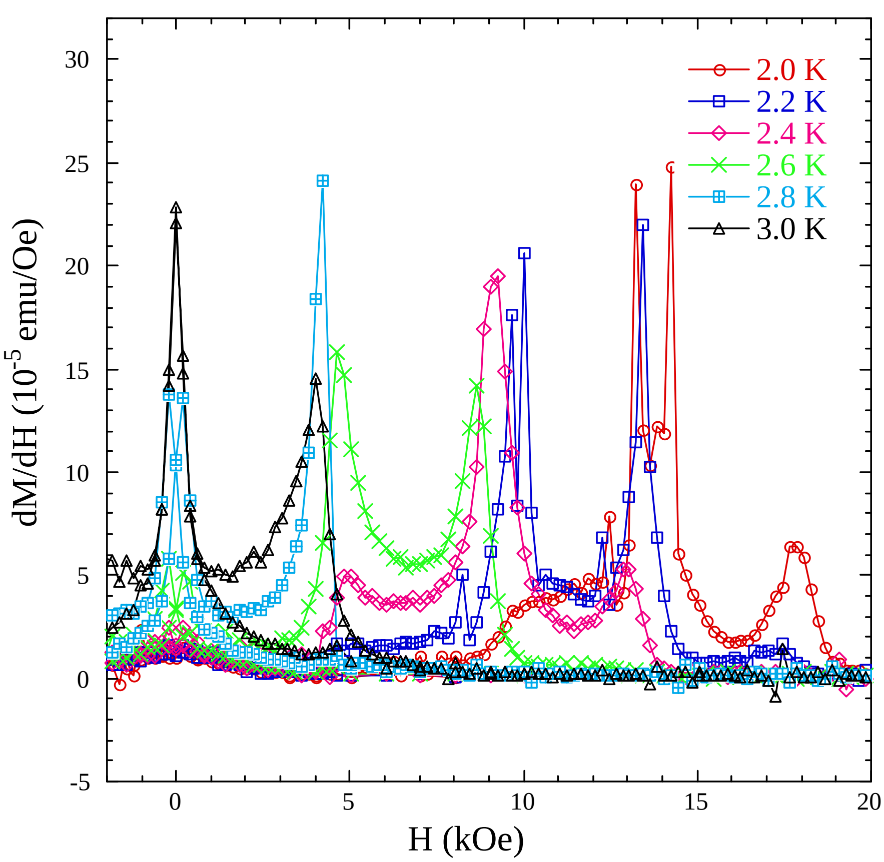
Uniaxial crystal, large anisotropy ≈ 60 K



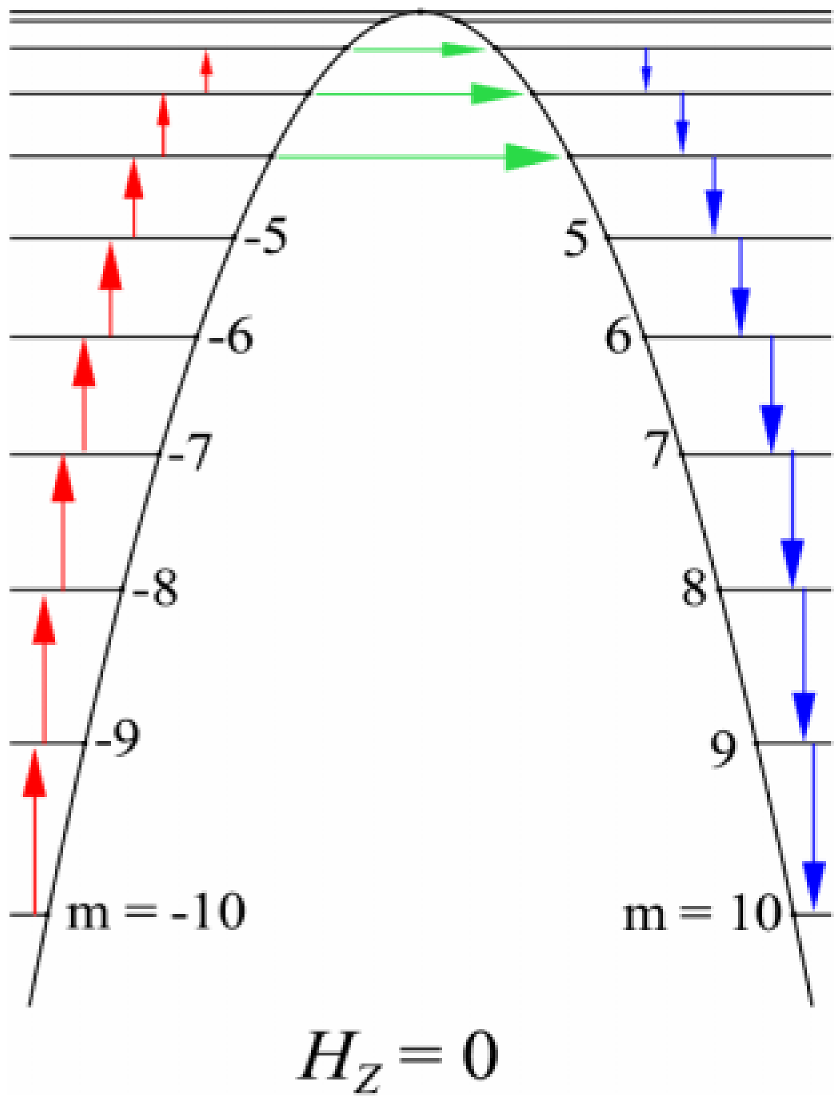
$$8 \times 2 \uparrow + 4 \times (3/2) \downarrow = 10 \uparrow$$



M (emu)
H (kOe)
2.0 K
2.2 K
2.4 K
2.6 K
2.8 K
3.0 K



dM/dH (10^{-5} emu/Oe)
H (kOe)
2.0 K
2.2 K
2.4 K
2.6 K
2.8 K
3.0 K

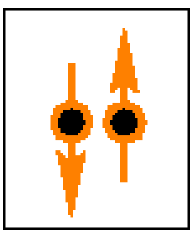

-5
-6
-7
-8
-9
m = -10
5
6
7
8
9
m = 10
$H_Z = 0$

Basic Physics of Mn_{12}

- **Magnetic Molecule** *Lis* 1980

$([Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O)$

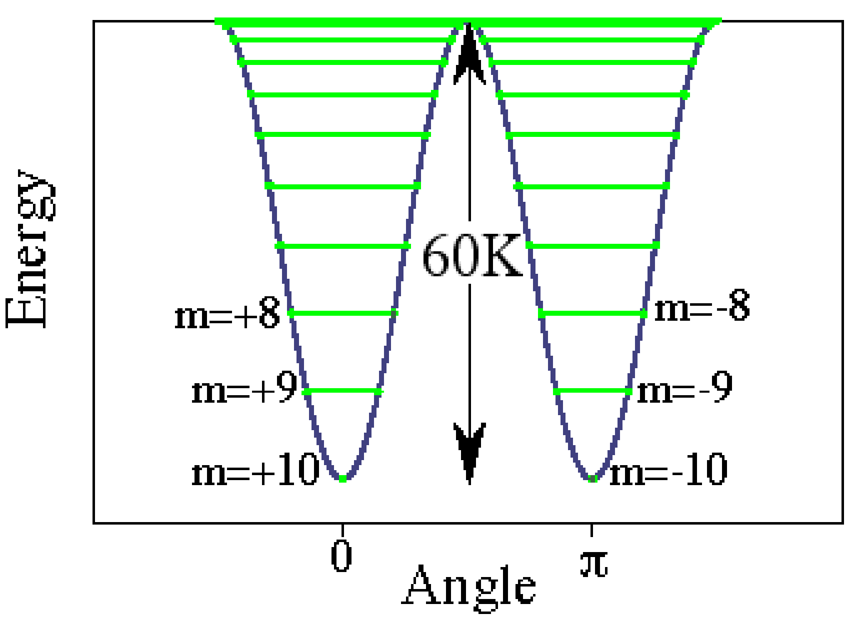
- **Magnetic Bistability**



$S = 10$
Ground State

Florence Group
Canesshi, Gatteschi, Sessoli, Barra, Brunnel, Guillot
1991

- **Superparamagnet with High Anisotropy**



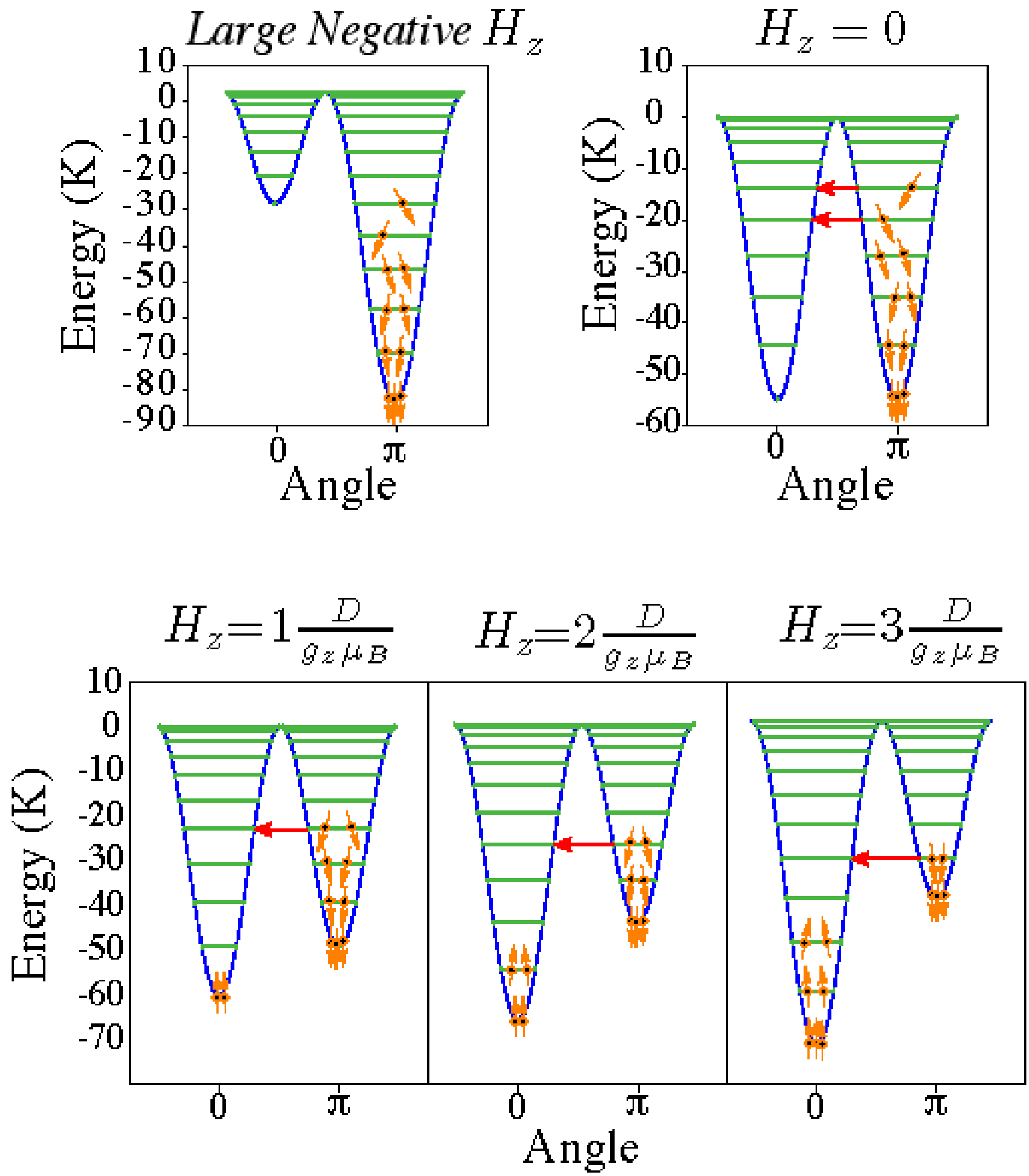
Florence Group
Sessoli, Gatteschi, Canesshi, Novak
1993

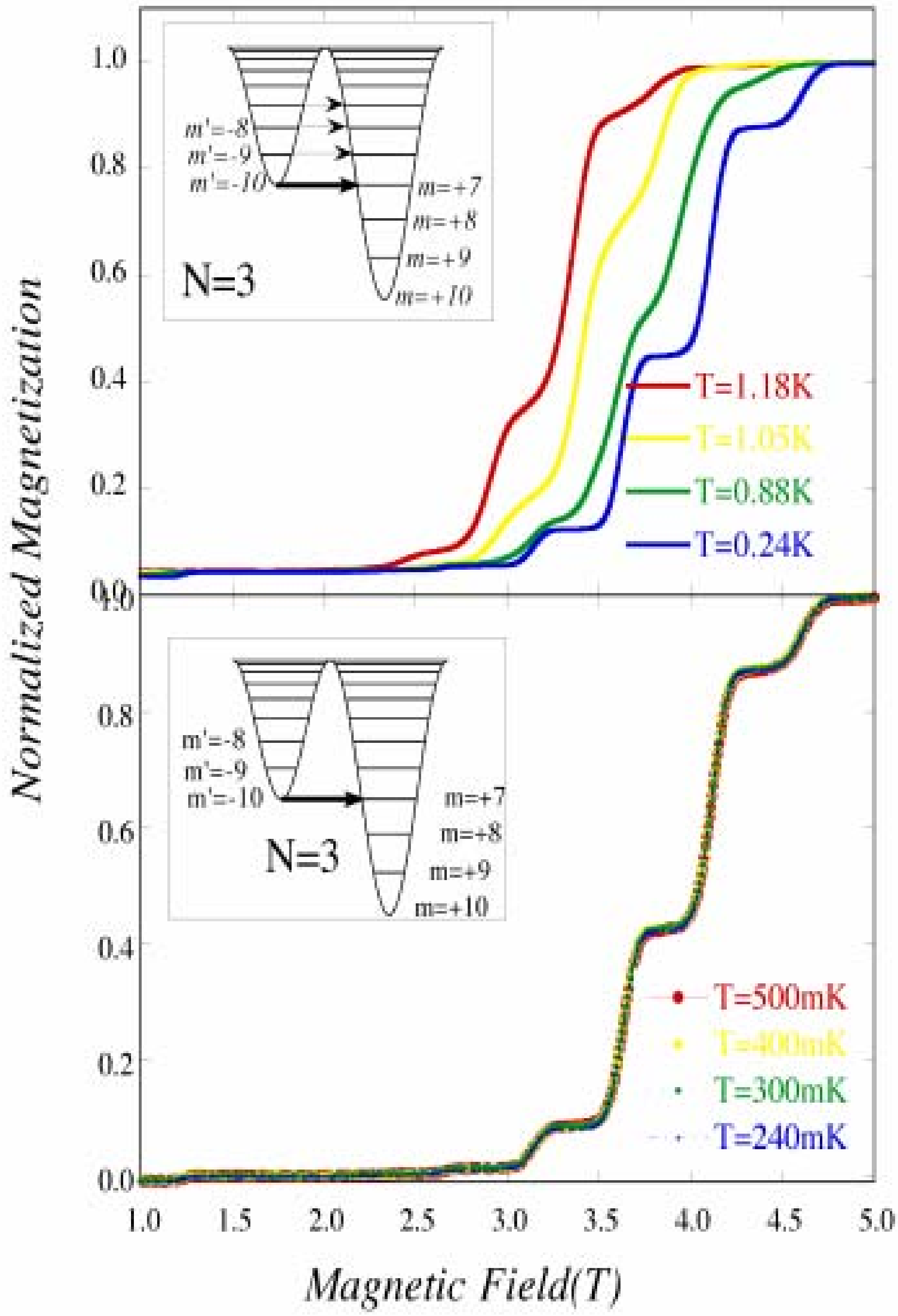
$$\hat{\mathcal{H}} = -D\hat{S}_z^2$$

$$\cos(\theta) = m/S$$

$$E_m = -Dm^2$$

Populated Energy Levels in a Swept Longitudinal Magnetic Field



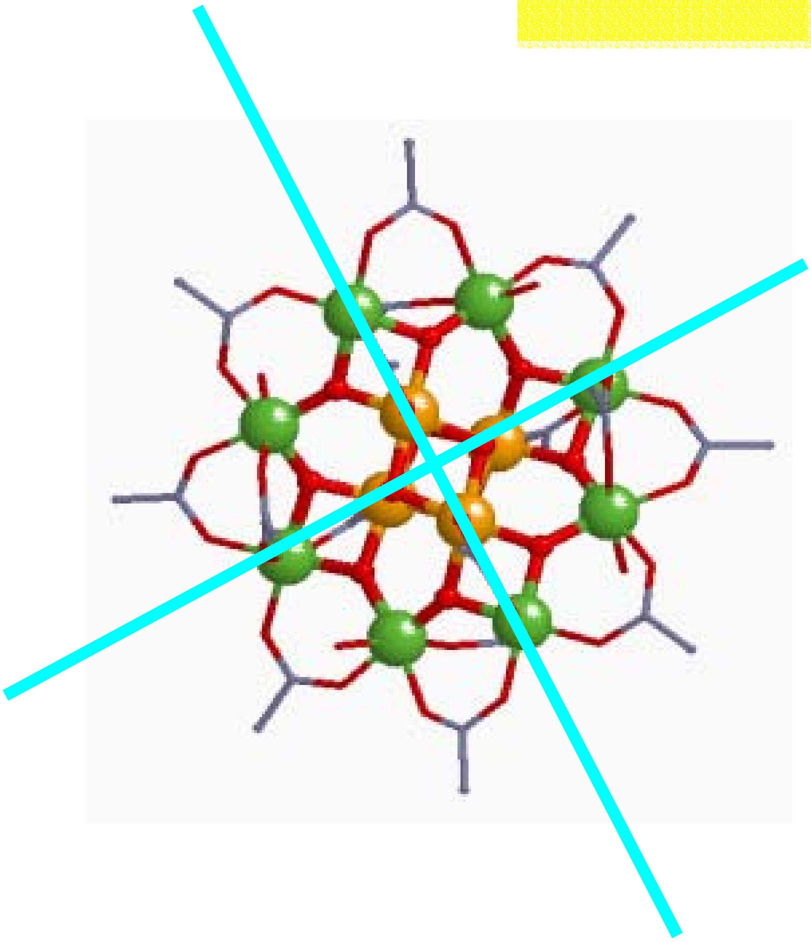


K. M. Mertes, Yoko Suzuki, M. P. Sarachik, et al.
PRL 87, 227205 (2001)

Are the steps observed in
the magnetic relaxation
of quantum mechanical origin?

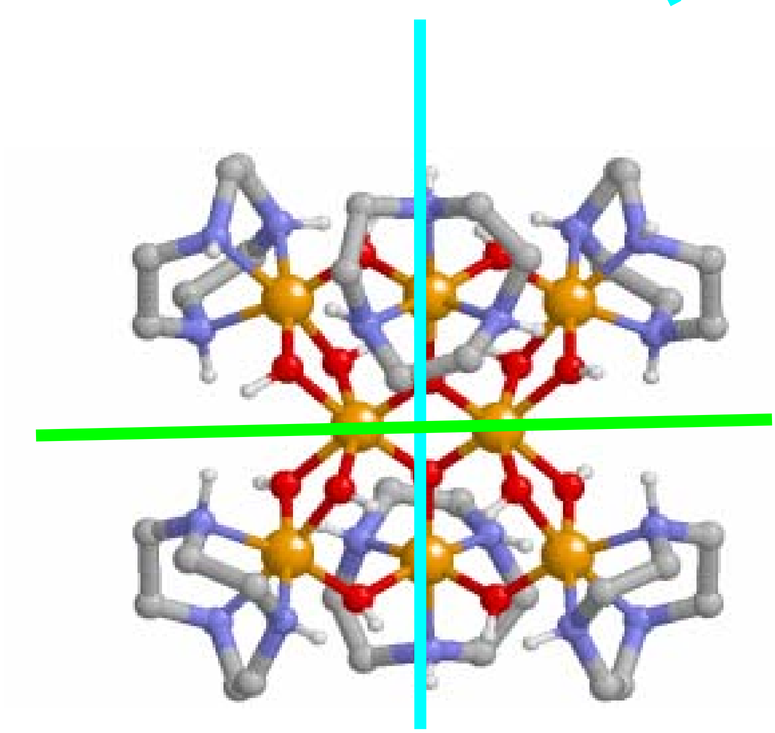
Are they due to spin tunneling?

S=10



Mn12

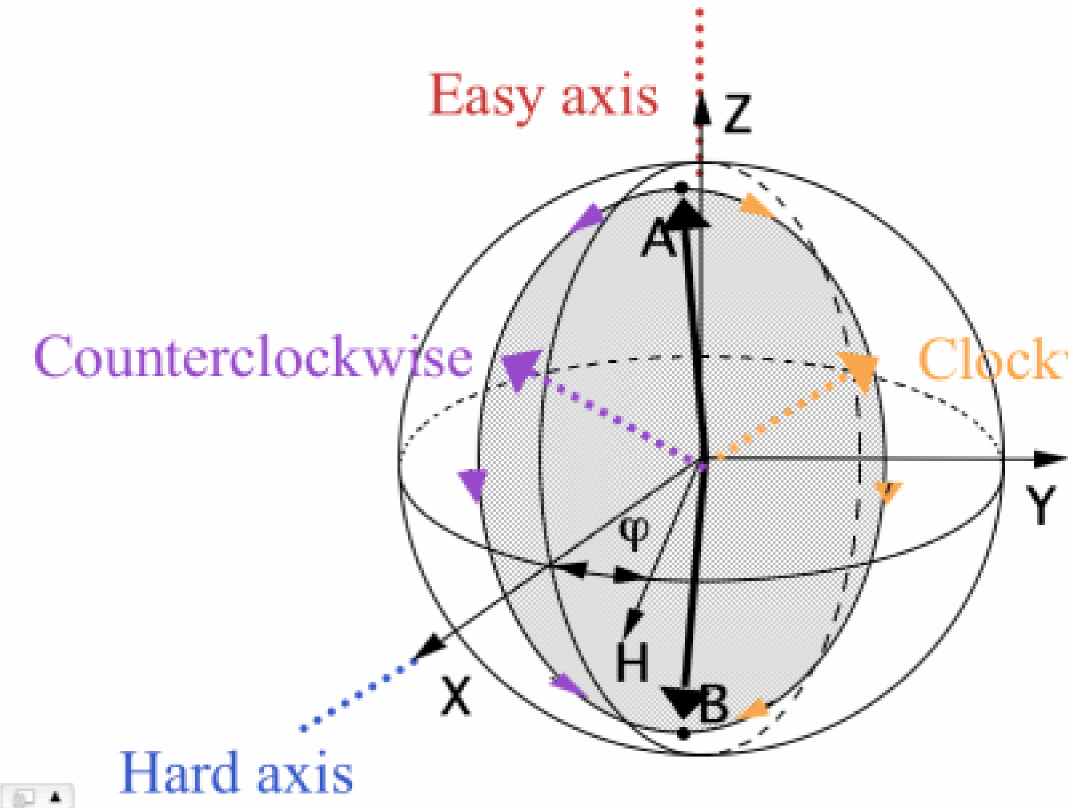
Four fold axis



Fe8

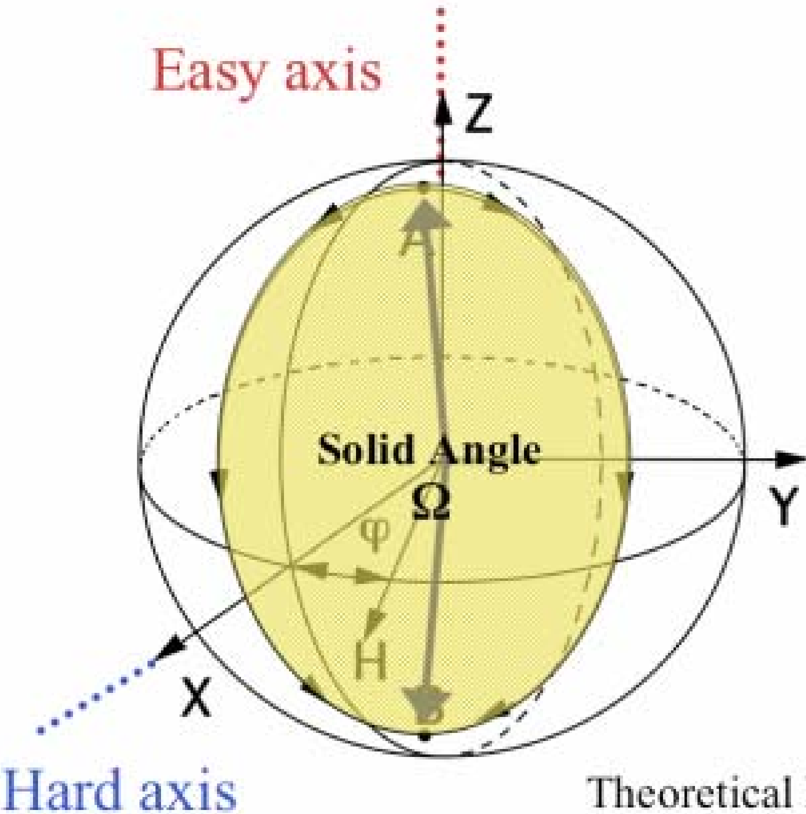
Two fold axis

Two Paths for Magnetization Reversal



Fe_8

Destructive Topological Interference



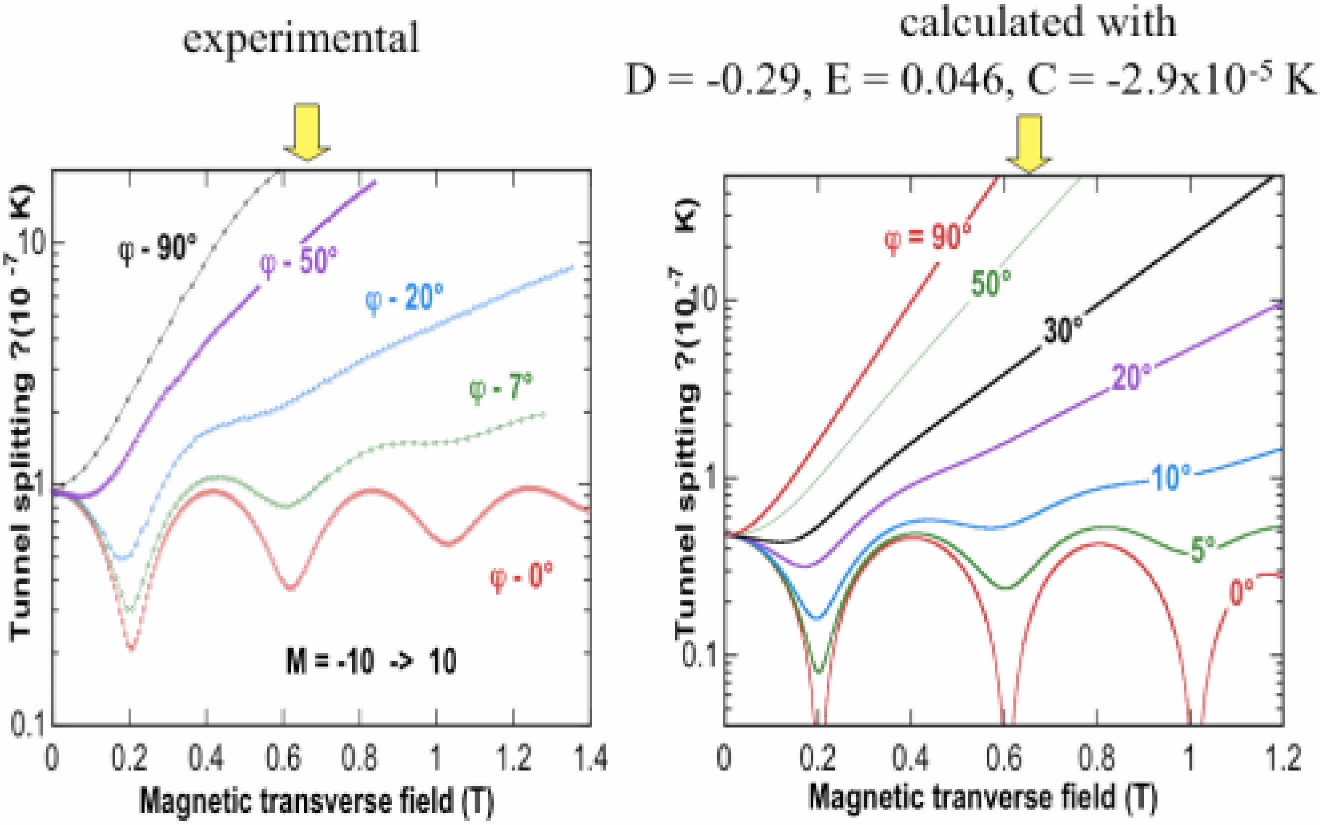
Equivalence between paths is maintained when **H** is applied along the Hard Axis.

Topological (Berry's) phase depends on solid angle Ω enscribed by the two paths.

Complete destructive interference occurs for certain discrete values of Ω.

Theoretical Prediction: A. Garg., 1993.

Measured Tunnel Splitting



W. Wernsdorfer and R. Sessoli, Science, 1999.

Why is this INTERESTING?

FUNDAMENTAL: Manifestations of quantum mechanical effects on a meso or macroscopic scale.

Borderline between quantum and classical regimes.

APPLIED:

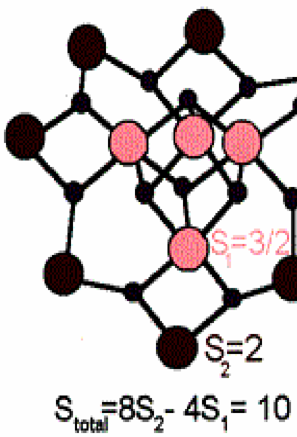
A. High density storage of information.

Smaller magnetic units
More thermal degradation
Lower operating temperatures

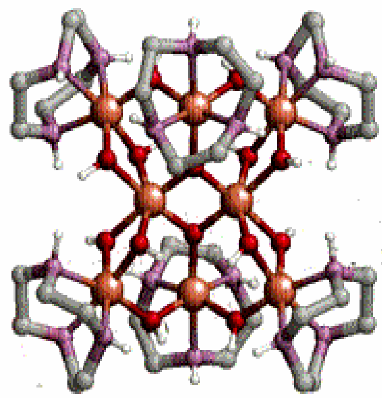
QUANTUM MECHANICAL TUNNELING SETS THE FUNDAMENTAL LIMIT ON THE SIZE OF SUB UNITS AND RELIABILITY OF MAGNETIC STORAGE.

B. Possible qubit for quantum computation.

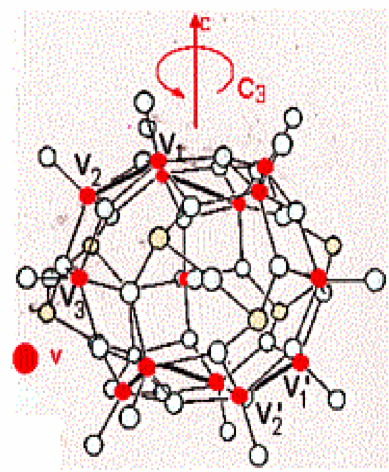
▶ $S = 10$: Mn_{12}, Fe_8. $S = 1/2$: V_{15}.



Mn_{12}



Fe_8



V_{15}

Magnetic clusters:

Mn, Mn_2, Mn_3, Mn_4, $[Mn_4]_2$, Mn_5, Mn_6, Mn_7, Mn_8, Mn_9, Mn_{10}, Mn_{11}, Mn_{12}, Mn_{13}, Mn_{16}, Mn_{18}, Mn_{21}, Mn_{24}, Mn_{26}, Mn_{30}

Fe_2, Fe_3, Fe_4, Fe_5, Fe_6, Fe_7, Fe_8, Fe_{10}, Fe_{11}, Fe_{13}, $Fe_{17/19}$, Fe_{19}

Ni_4, Ni_5, Ni_6, Ni_8, Ni_{12}, Ni_{21}, Ni_{24}

Co_4, Co_6, Co_{10}

Co_2Gd_2, Co_2Dy_2, Cr_{12}, $CrNi_6$, $CrNi_2$, $CrCo_3$, $Fe_{10}Na_2$, Fe_2Ni_3, Mn_2Dy_2, Mn_2Nd_2, V_{15}, Ho, ...

S = 0, 1/2, 1, 3/2, 2, 5/2, 4, 9/2, 5, ... 33/2

Hamiltonian

$$\mathcal{H} = - DS_z^{\;2} - g\mu_B H_z S_z - BS_z^{\;4} \;+ \mathcal{H}_{tunnel}$$

What drives the tunneling?

$$\mathcal{H}_{tunnel} = g\mu_B H_{tr} S_{tr} + C(S_+^{\;4} + S_-^{\;4}) + \ldots$$

$H_{tr} = H_{tr\,(dipole)} + H_{tr\,(nuclear)}$

$H_{tr\,(dipole)} \approx$ 300 Oe - too small

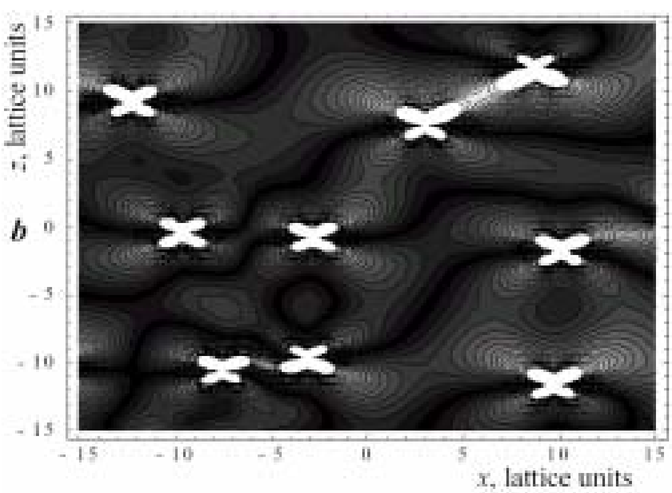
$H_{tr\,(nuclear)} \approx$ 300 to 500 Oe - too small

$C(S_+^{\;4} + S_-^{\;4})$, lowest order anisotropy term allowed by tetragonal symmetry, allows only every fourth step -

ALL STEPS ARE OBSERVED

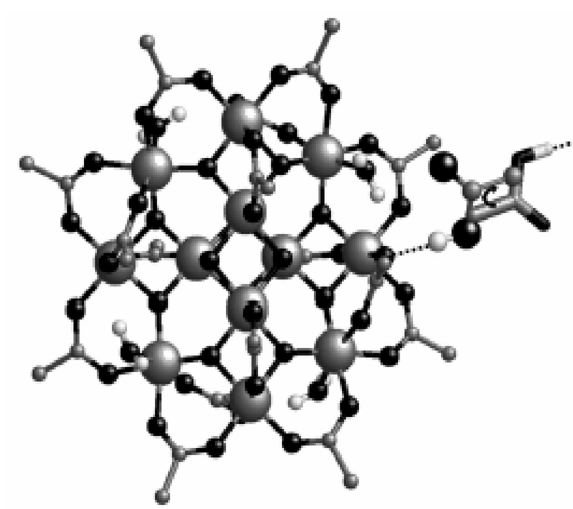
Origin of Spin Tunneling in Mn-12 Acetate

$$H = -D S_z^2 - F S_z^4 - g\mu_B B_z S_z - g\mu_B (B_x S_x + B_y S_y) + E(S_x^2 - S_y^2) + \ldots$$



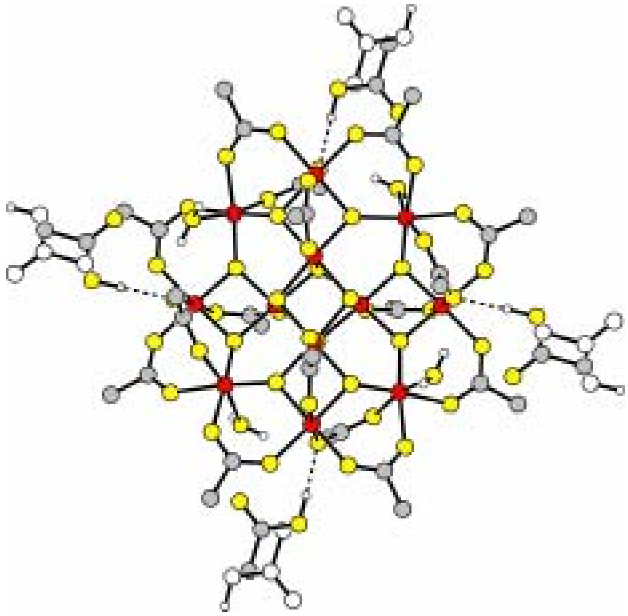
E. M. Chudnovsky and D. A. Garanin, PRL 87, 187203 (2001); PRB 65, 094423 (2002)

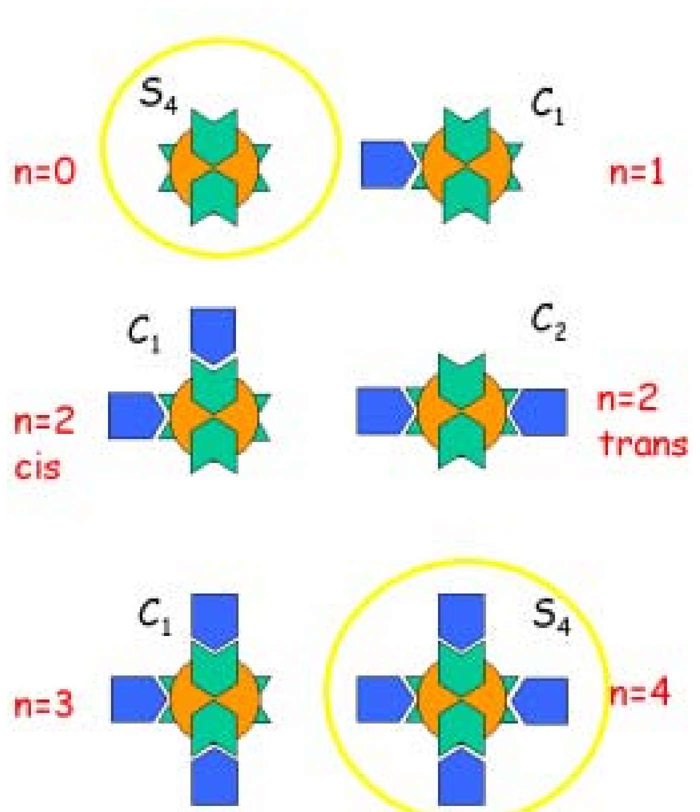
Dislocations in the Mn-12 Crystal Lattice



A. Cornia et al., PRL 89, 257201 (2002)

Acetic Acid Disorder in the Mn-12 cluster

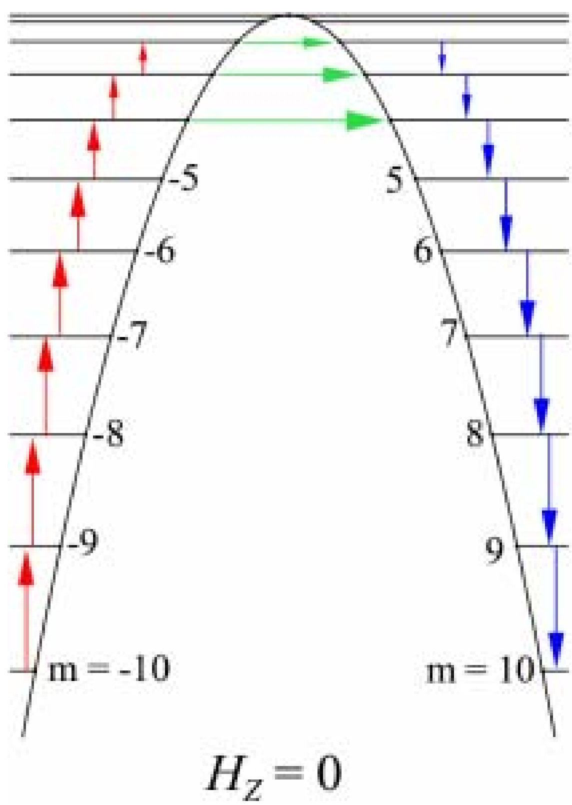


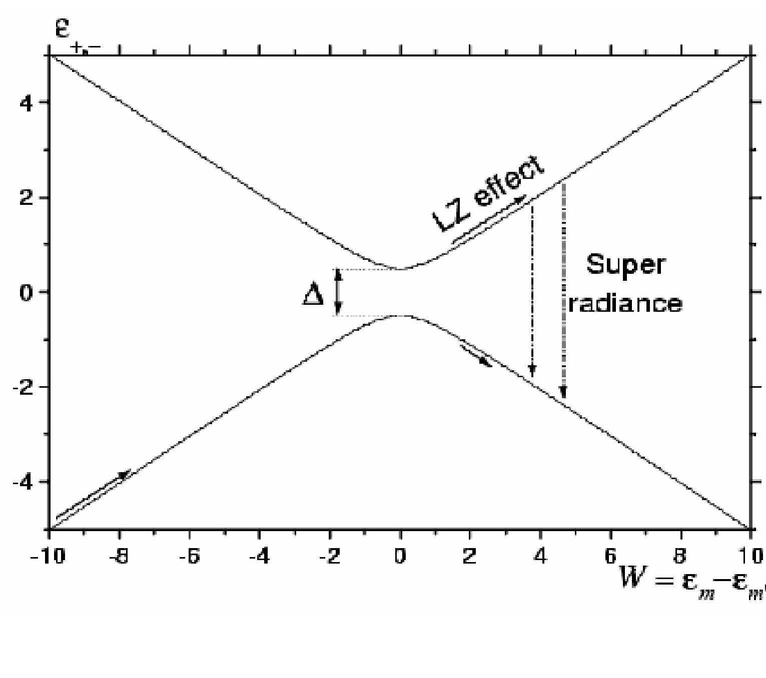


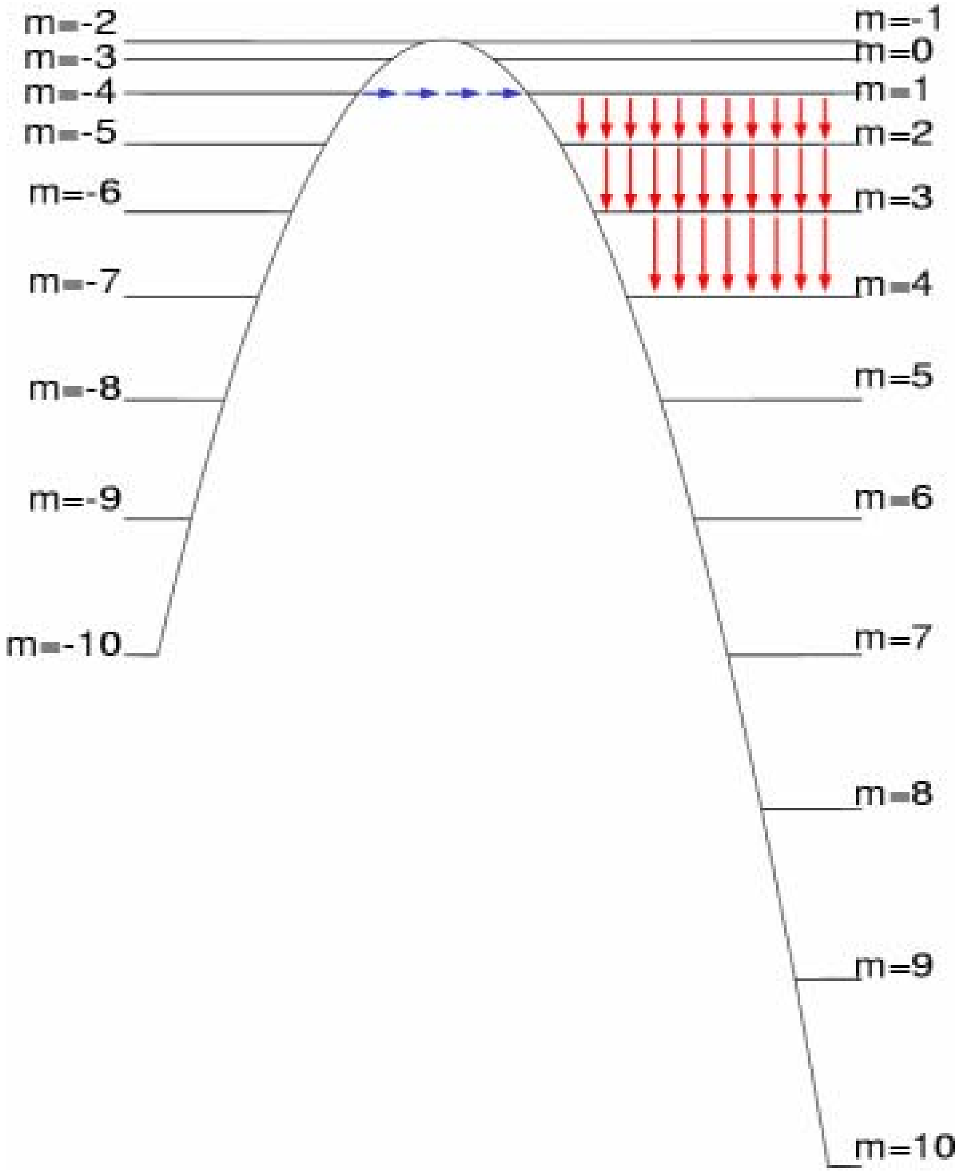
Six different chemical isomers

SUPERRADIANCE

(Chudnovsky & Garanin, PRL-2002)

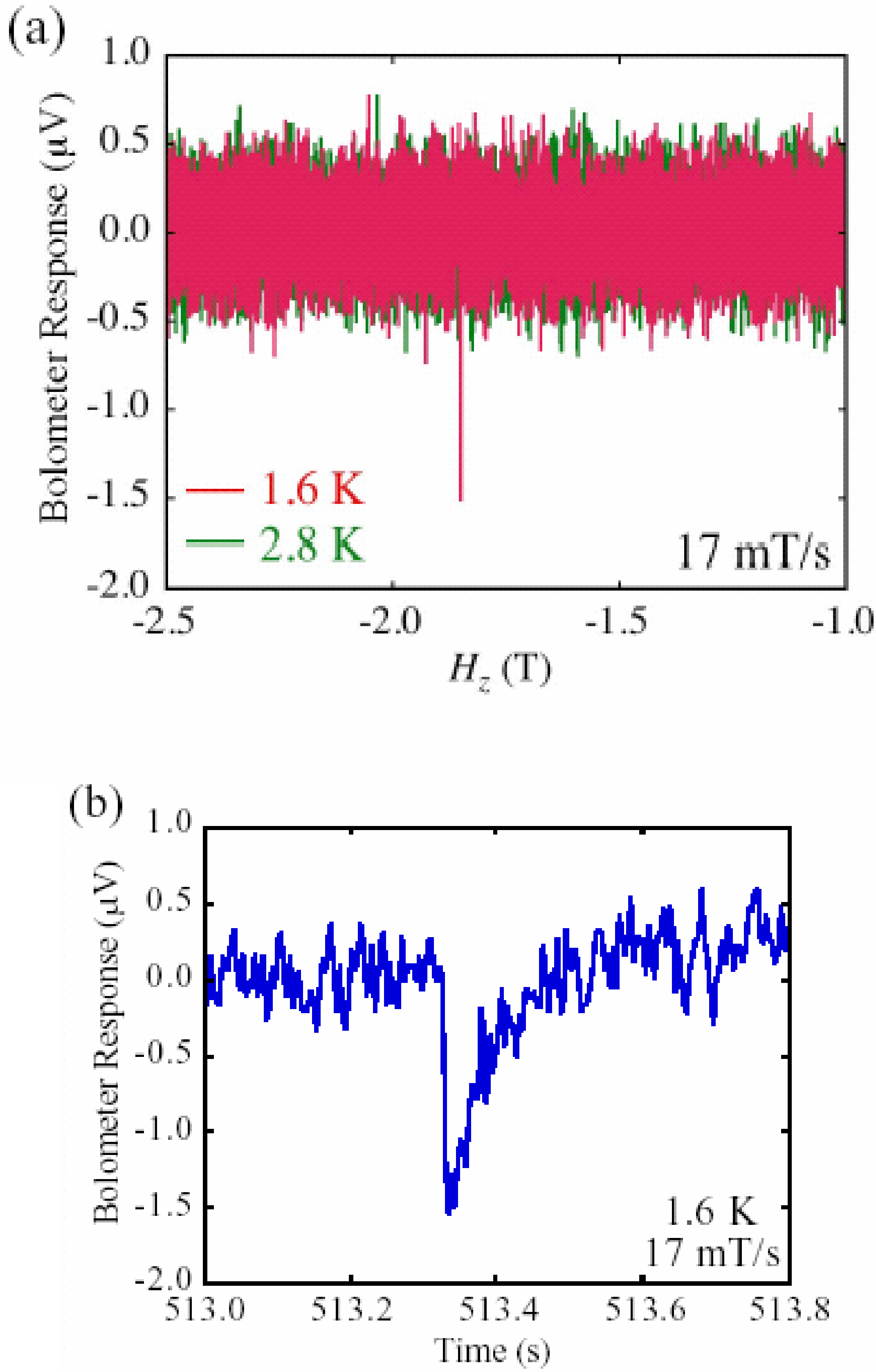






m = 1 to m = 2 transition: f = 0.08 THz

m = 9 to m = 10 transition: f = 0.35 THz


(a)
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
Bolometer Response (μV)
1.6 K
2.8 K
17 mT/s
-2.5
-2.0
-1.5
-1.0
H_z (T)
(b)
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
Bolometer Response (μV)
1.6 K
17 mT/s
513.0
513.2
513.4
513.6
513.8
Time (s)