Introduction to Magnetism Part II

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Introduction to Magnetism

1) Introduction and definitions

2) The Diamagnetism

3) The Paramagnetism

4) Magnetic phase transitions and magnetic orders

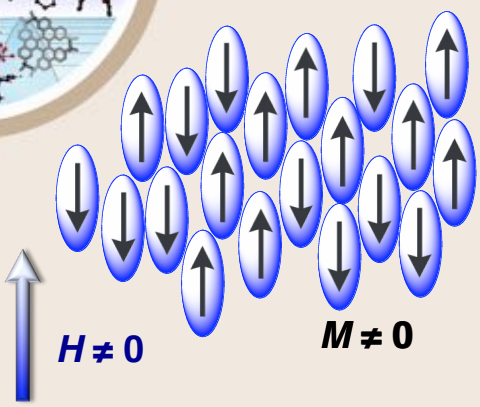
5) Molecular magnetism

6) Superparamagnetism and Single-Molecule Magnets

7) Single-Chain Magnets

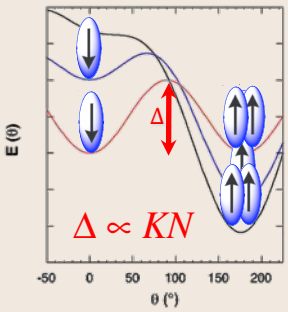
6) Superparamagnetism and SMMs

Single domain magnetic nanoparticles (with uniaxial anisotropy): classical case of uniform rotation

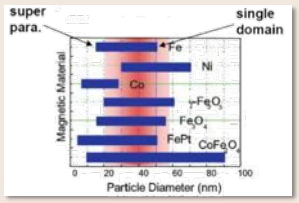


$H \neq 0$

$M \neq 0$



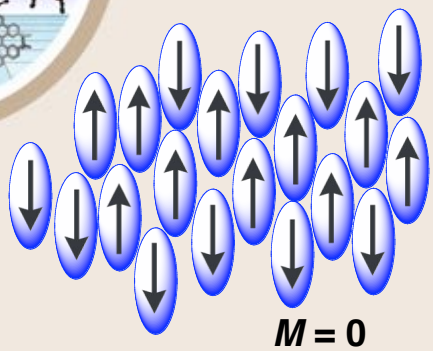
$\Delta \propto KN$



$T = 25^{o}C$

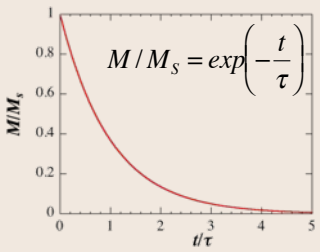
6) Superparamagnetism and SMMs

Single domain magnetic nanoparticles (with uniaxial anisotropy): classical case of uniform rotation



$M = 0$

Magnetization Relaxation
(monodispersed nanoparticles)

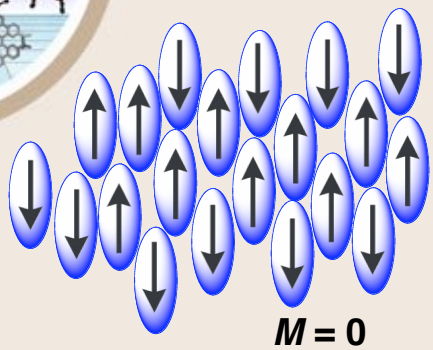


$M / M_S = exp\left(-\frac{t}{\tau}\right)$

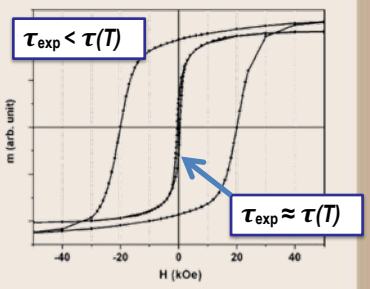
→ **Temperature effect:** $\tau(T) = \tau_0 exp\left(\frac{KN}{k_B T}\right)$ **activated relaxation**

6) Superparamagnetism and SMMs

Single domain magnetic nanoparticles (with uniaxial anisotropy): classical case of uniform rotation



$M = 0$

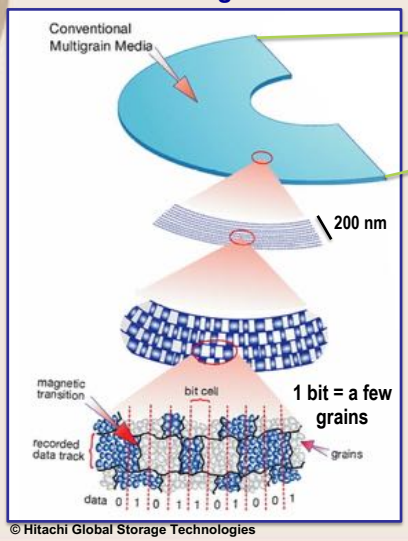


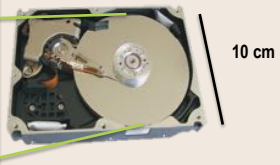
➡ Temperature effect: $\tau(T) = \tau_0 exp\left(\frac{KN}{k_B T}\right)$ activated relaxation

➡ bistability, hysteresis when $\tau_{exp} < \tau(T)$

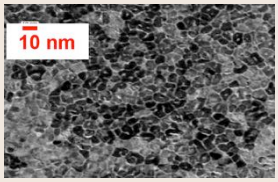
6) Superparamagnetism and SMMs

Information storage... Hard Disk Drives (HDD)...





Particle/grain sizes:
Ø = 5-8 nm

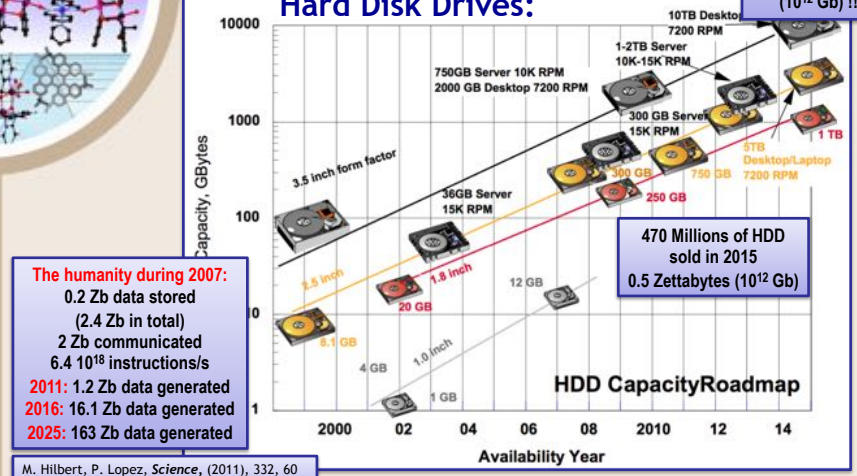


IBM Hard Drive
(35 Gb/in^2; CoPtCrB)
10 years of storage

6) Superparamagnetism and SMMs

≈ 500 millions of HDD sold every year since 2009
1 Zettabytes / year (10^{12} Gb) !!!

Hard Disk Drives:



470 Millions of HDD sold in 2015
0.5 Zettabytes (10^{12} Gb)

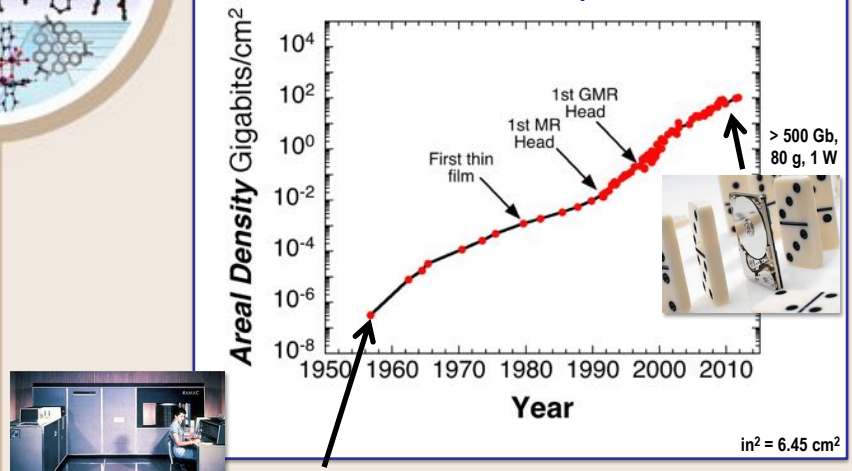
The humanity during 2007:
0.2 Zb data stored
(2.4 Zb in total)
2 Zb communicated
6.4 10^{18} instructions/s
2011: 1.2 Zb data generated
2016: 16.1 Zb data generated
2025: 163 Zb data generated

M. Hilbert, P. Lopez, *Science*, (2011), 332, 60
J. Mervis, *Science*, (2012), 336, 22

Sources: • E. Grochowski, T. Coughlin – IBM (2011)
• Gartner research

6) Superparamagnetism and SMMs

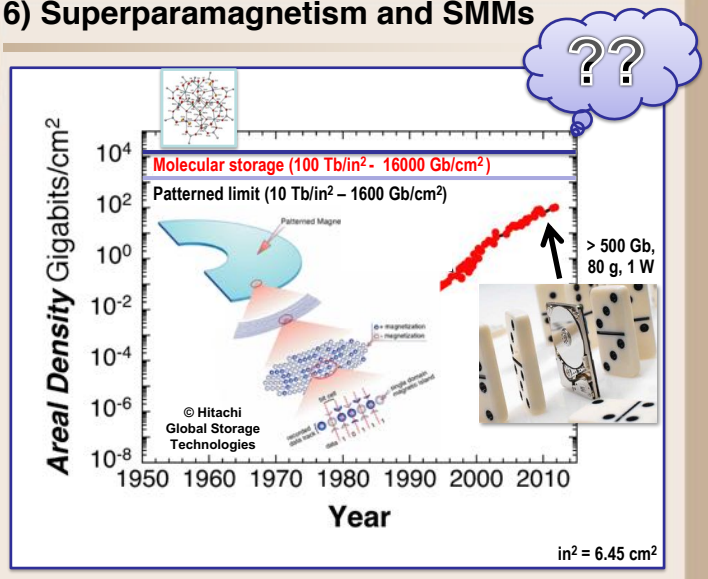
Hard Disk Drives:



1956: IBM RAMAC (1st HDD)
4.4 Mb, > 1 ton, >1 kW

Source: E. Grochowski – IBM (2011)

6) Superparamagnetism and SMMs



Source: E. Grochowski – IBM (2011)

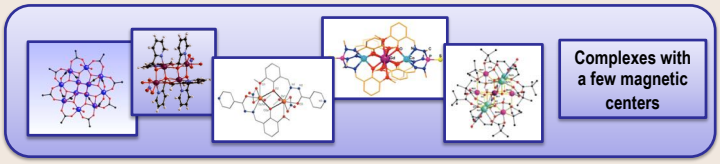
6) Superparamagnetism and SMMs

The main motivation in this field of research:

SMMs might be used as **elementary units** in **high density** memory devices

SMMs: monodispersed nano-objects

Ø < 2±0 nm



- Superparamagnetic properties (similar to nanoparticles)

- Quantum properties: well defined quantum states

M. N. Leuenberger, D. Loss, ***Nature***, (2001), *410*, 789

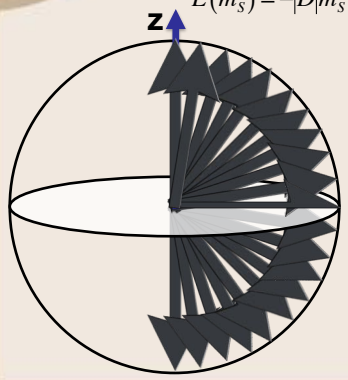
6) Superparamagnetism and SMMs

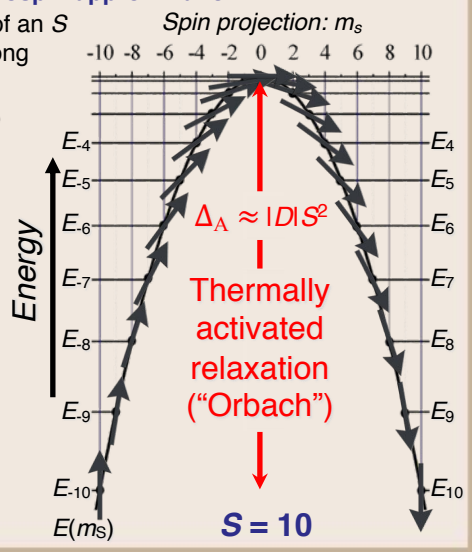
A SMM in the macrospin approximation:

The simplest case of an *S* high spin with a strong uni-axial anisotropy

$\mathbf{H} = D\hat{S}_z^2$ with $D < 0$

$E(m_S) = -|D|m_S^2$



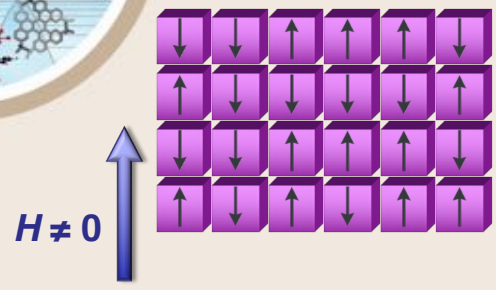


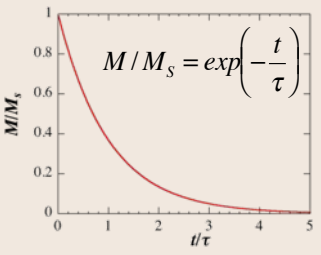
6) Superparamagnetism and SMMs

A crystal of isolated SMMs (*S*, *D*):

***T* ≠ 0** ***M* ≠ 0**

Magnetization Relaxation





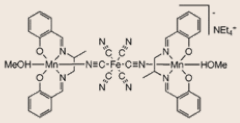
- **Temperature effect:** $\tau(T) = \tau_0 exp\left(\frac{\Delta_A}{k_B T}\right) = \tau_0 exp\left(\frac{|D|S^2}{k_B T}\right)$ **« Orbach »**
- **bistability, hysteresis when $\tau_{exp} < \tau(T)$ *(blocking temperature, T_B)***
- **Enhancement of T_B if *S* or *D* increase**

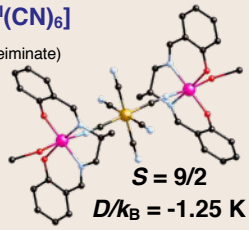
6) Superparamagnetism and SMMs

Determination of the relaxation time: an example…

$(NEt_4)[Mn^{III}_2(salmen)_2(MeOH)_2Fe^{III}(CN)_6]$

salmen^{2-}: *rac*-*N*,*N*'-(1-methylethylene)bis(salicylideneiminate)

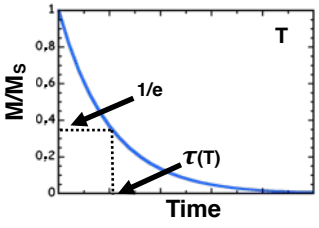


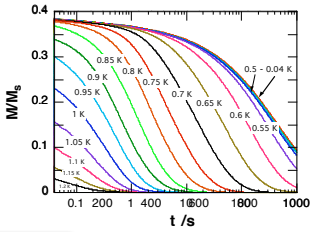


$S = 9/2$

$D/k_B = -1.25$ K

Direct measurements in time (dc)



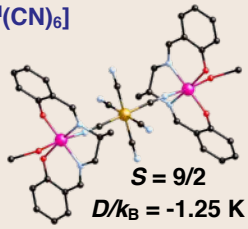


M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon and R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 3090

6) Superparamagnetism and SMMs

Determination of the relaxation time: an example…

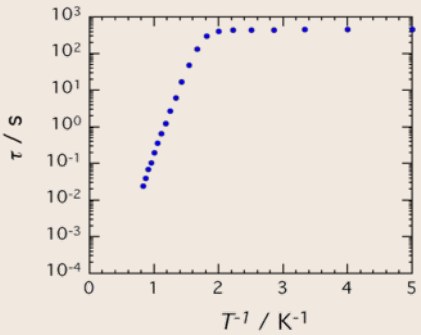
$(NEt_4)[Mn^{III}_2(salmen)_2(MeOH)_2Fe^{III}(CN)_6]$



$S = 9/2$

$D/k_B = -1.25$ K

Relaxation time (τ) deduced from the direct measurements in time



6) Superparamagnetism and SMMs

Determination of the relaxation time: an example…

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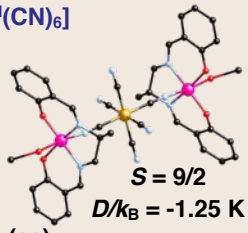
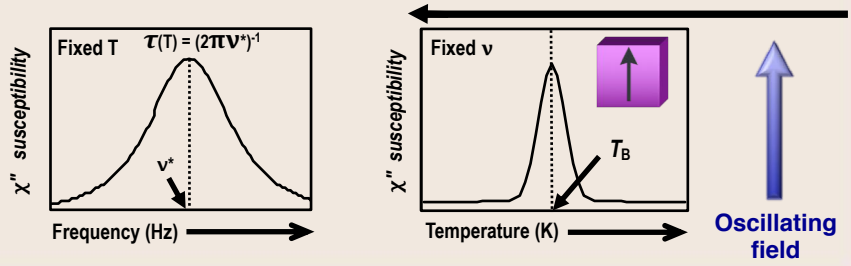


$S = 9/2$

$D/k_B = -1.25$ K

R. Boca, *Theoretical Foundations of Molecular Magnetism*, Elsevier Ed., p.107.

Measurements in frequency (ac)



6) Superparamagnetism and SMMs

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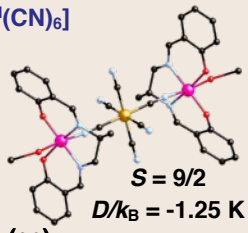

$S = 9/2$

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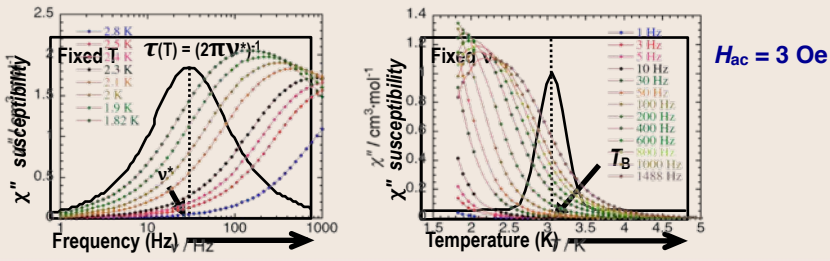
Measurements in frequency (ac)



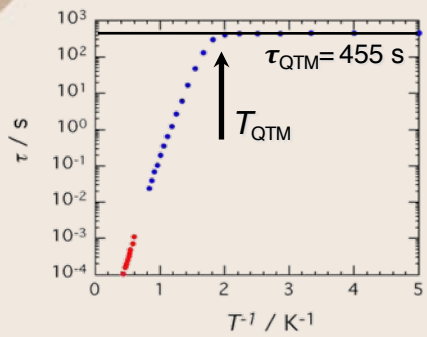
$H_{ac} = 3$ Oe

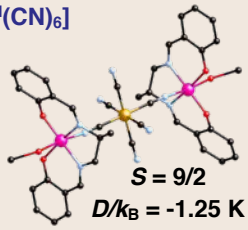
6) Superparamagnetism and SMMs

Determination of the relaxation time: an example…

$(NEt_4)[Mn^{III}_2(salmen)_2(MeOH)_2Fe^{III}(CN)_6]$

Relaxation time (τ) deduced from the dc and ac measurements





S = 9/2

D/k_B = -1.25 K

➡ $\tau = \tau_{QTM}$ because $\tau_{Orbach} > \tau_{QTM}$ below T_{QTM}

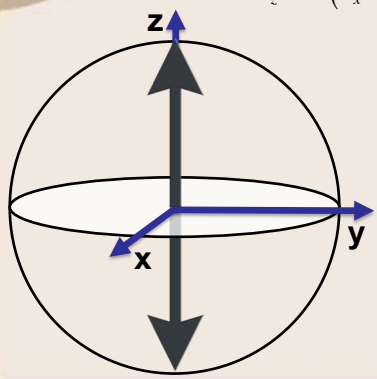
➡ A second mode of relaxation: Quantum Tunneling

6) Superparamagnetism and SMMs

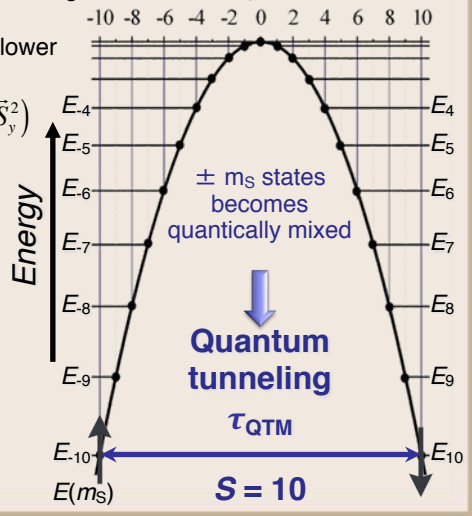
A second mode of relaxation: case for $k_BT << |E_{10}-E_9|$

To have quantum tunneling, the symmetry of the anisotropy must be lower than uni-axial:

$$\mathbf{H} = D\vec{S}_z^2 + E\left(\vec{S}_x^2 - \vec{S}_y^2\right)$$



Spin projection: m_s



6) Superparamagnetism and SMMs

Determination of the relaxation time: an example…

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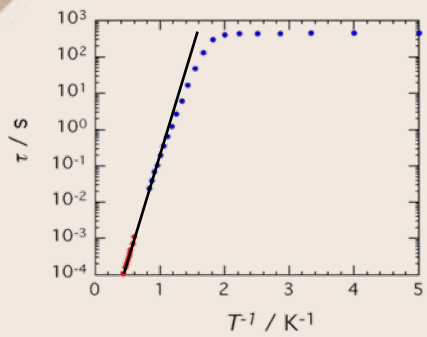
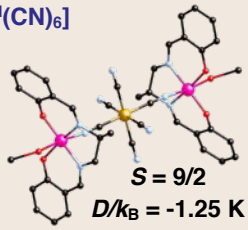
Relaxation time (τ) deduced from the dc and ac measurements





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6) Superparamagnetism and SMMs

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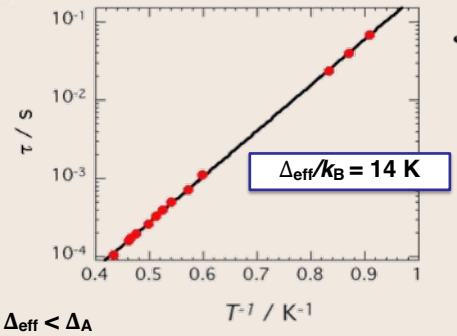
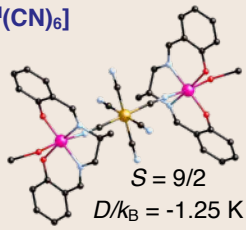




$S = 9/2$

$D/k_B = -1.25$ K

thus:

$|D|S^2/k_B = 25$ K

$\Delta_{eff} < \Delta_A$

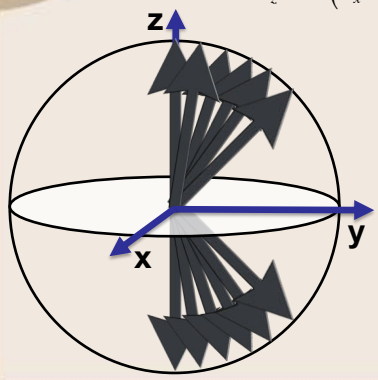
A intermediate mode of relaxation that is called "Thermally assisted quantum tunneling of the magnetization"

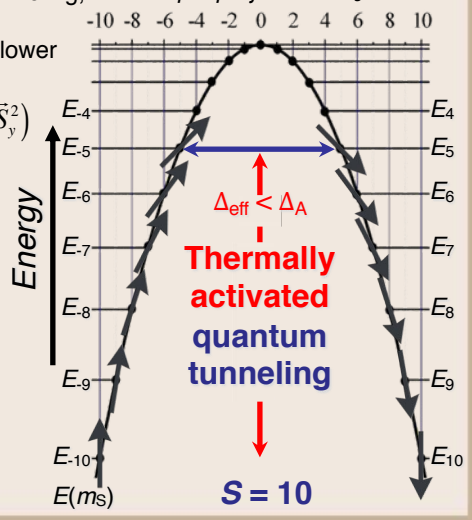
6) Superparamagnetism and SMMs

An intermediate mode of relaxation: $T > T_{QTM}$

To have quantum tunneling, the symmetry of the anisotropy must be lower than uni-axial:

$$\mathbf{H} = D\vec{S}_z^2 + E\left(\vec{S}_x^2 - \vec{S}_y^2\right)$$





6) Superparamagnetism and SMMs

Determination of the relaxation time: an example…

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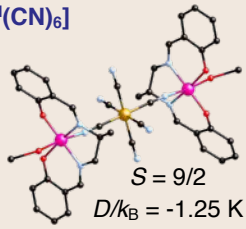

$S = 9/2$
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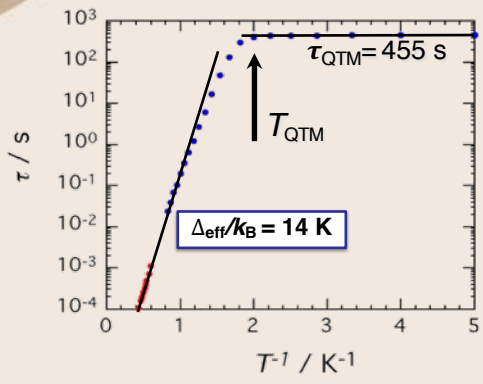
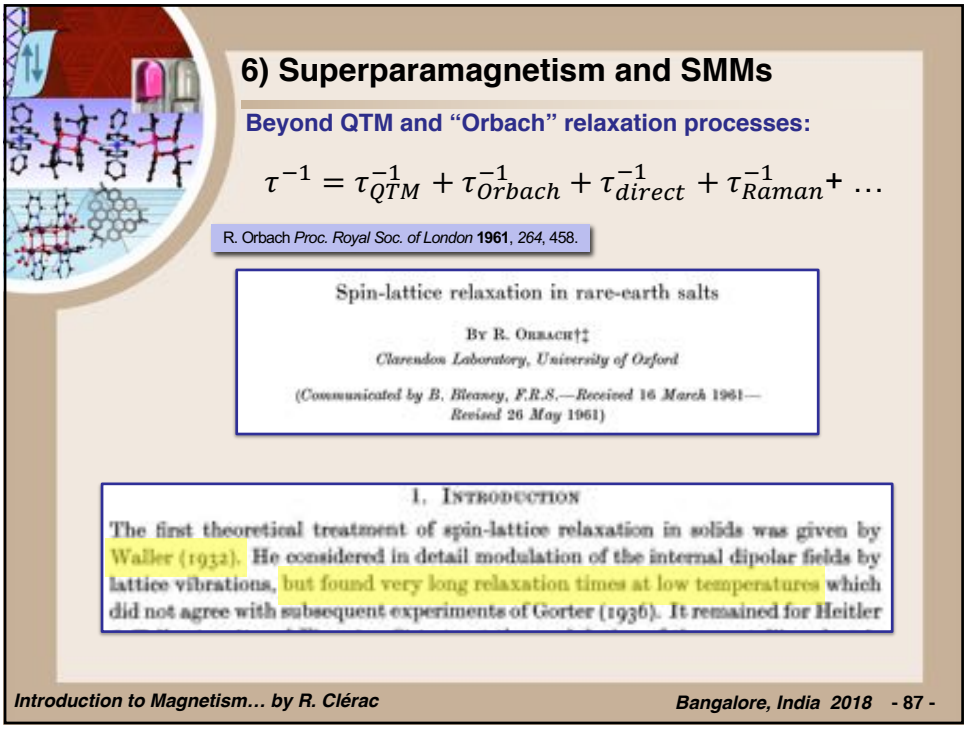


M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon and R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 3090



6) Superparamagnetism and SMMs

Beyond QTM and "Orbach" relaxation processes:

$$\tau^{-1} = \tau_{QTM}^{-1} + \tau_{Orbach}^{-1} + \tau_{direct}^{-1} + \tau_{Raman}^{-1} + \dots$$

R. Orbach *Proc. Royal Soc. of London* **1961**, *264*, 458.

Spin-lattice relaxation in rare-earth salts

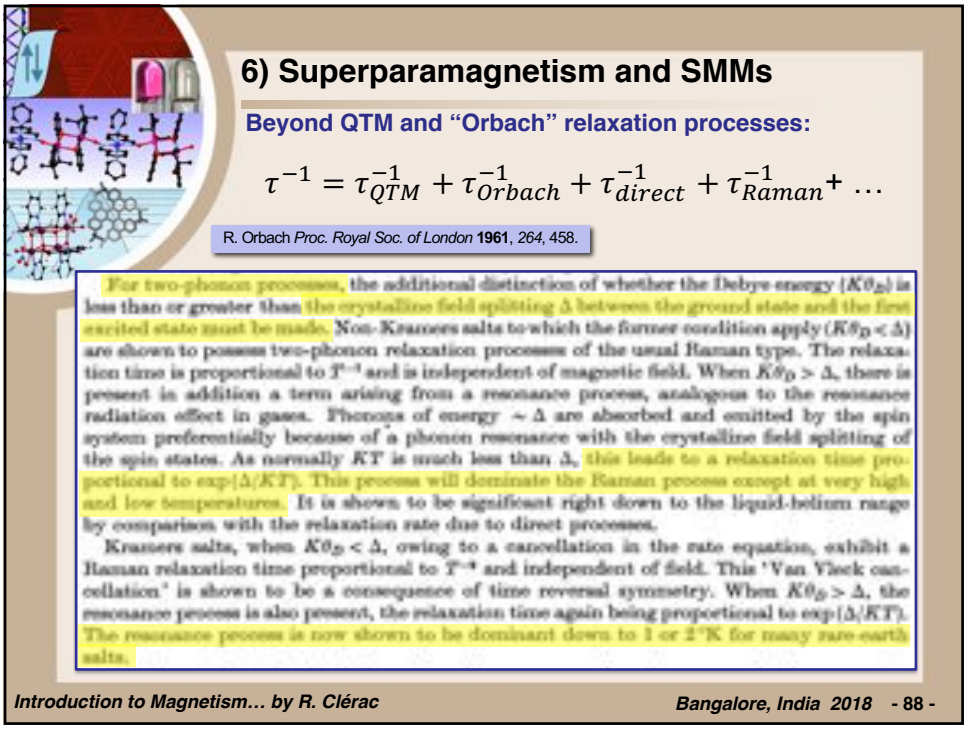
By R. Orbach†‡

Clarendon Laboratory, University of Oxford

(*Communicated by B. Bleaney, F.R.S.—Received* 16 *March* 1961—*Revised* 26 *May* 1961)

1. Introduction

The first theoretical treatment of spin-lattice relaxation in solids was given by Waller (1932). He considered in detail modulation of the internal dipolar fields by lattice vibrations, but found very long relaxation times at low temperatures which did not agree with subsequent experiments of Gorter (1936). It remained for Heitler



6) Superparamagnetism and SMMs

Beyond QTM and "Orbach" relaxation processes:

$$\tau^{-1} = \tau_{QTM}^{-1} + \tau_{Orbach}^{-1} + \tau_{direct}^{-1} + \tau_{Raman}^{-1} + \dots$$

R. Orbach *Proc. Royal Soc. of London* **1961**, *264*, 458.

For two-phonon processes, the additional distinction of whether the Debye energy ($K\theta_D$) is less than or greater than the crystalline field splitting Δ between the ground state and the first excited state must be made. Non-Kramers salts to which the former condition apply ($K\theta_D < \Delta$) are shown to possess two-phonon relaxation processes of the usual Raman type. The relaxation time is proportional to T^{-7} and is independent of magnetic field. When $K\theta_D > \Delta$, there is present in addition a term arising from a resonance process, analogous to the resonance radiation effect in gases. Phonons of energy $\sim \Delta$ are absorbed and emitted by the spin system preferentially because of a phonon resonance with the crystalline field splitting of the spin states. As normally KT is much less than Δ, this leads to a relaxation time proportional to $\exp(\Delta/KT)$. This process will dominate the Raman process except at very high and low temperatures. It is shown to be significant right down to the liquid-helium range by comparison with the relaxation rate due to direct processes.

Kramers salts, when $K\theta_D < \Delta$, owing to a cancellation in the rate equation, exhibit a Raman relaxation time proportional to T^{-9} and independent of field. This 'Van Vleck cancellation' is shown to be a consequence of time reversal symmetry. When $K\theta_D > \Delta$, the resonance process is also present, the relaxation time again being proportional to $\exp(\Delta/KT)$. The resonance process is now shown to be dominant down to 1 or 2 °K for many rare-earth salts.

6) Superparamagnetism and SMMs

Beyond QTM and "Orbach" relaxation processes:

$$\tau^{-1} = \tau_{QTM}^{-1} + \tau_{Orbach}^{-1} + \tau_{direct}^{-1} + \tau_{Raman}^{-1} + \dots$$

A clarification in 1966!!

LE JOURNAL DE PHYSIQUE — TOME 27, NOVEMBRE-DÉCEMBRE 1966, PAGE 782

MISE AU POINT

LA RELAXATION DES SPINS ÉLECTRONIQUES AVEC LE RÉSEAU
(Théorie élémentaire et méthodes de mesure du temps T_1)

Par JACQUES PESCIA,
Laboratoire de Physique du Solide Faculté des Sciences de Toulouse (1),

Résumé. — Dans une première partie, on définit le phénomène de relaxation, puis on précise les notions de température de spins et de réseau. On décrit ensuite les principaux processus de relaxation et l'on explicite le calcul des Temps T_1.
Dans une seconde partie, après avoir indiqué les ordres de grandeur des Temps de relaxation à mesurer, et l'origine des procédés de mesure, on passe en revue les techniques actuelles. Pour chaque méthode de mesure, on rappelle le principe sur lequel est fondée cette mesure, puis on décrit l'appareillage utilisé pour sa réalisation et l'on discute les performances obtenues.

Abstract. — In the first part, the relaxation phenomenon is described and the question of the existence of spin temperature is discussed. Calculation of spin-lattice relaxation time is explained for the different processes.
In the second part, we list the various measurement techniques. For each method, the basic principle is brought out, and a description of the apparatus is presented.

6) Superparamagnetism and SMMs

Beyond QTM and "Orbach" relaxation processes:

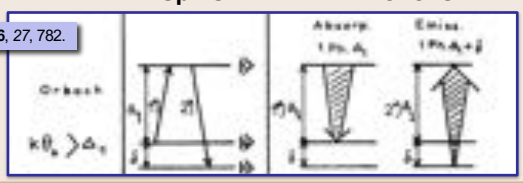
$$\tau^{-1} = \tau_{QTM}^{-1} + \tau_{Orbach}^{-1} + \tau_{direct}^{-1} + \tau_{Raman}^{-1} + \dots$$

Always a competition between these relaxation processes
Don't forget that only one relaxation time is measured !!!

Relaxation rate (τ^{-1})	Relaxation time (τ)
$\tau_{QTM}^{-1} = \dfrac{B_1}{1 + B_2 H^2}$	Temperature independent Increases in H^2
$\tau_{Orbach}^{-1} = \tau_0^{-1} exp\left(-\dfrac{\Delta_A}{k_B T}\right)$	Thermally activated dc-field independent (low fields)

J. Pescia *J. Phys.* **1966**, *27*, 782.

Spins Phonons



6) Superparamagnetism and SMMs

Beyond QTM and "Orbach" relaxation processes:

$$\tau^{-1} = \tau_{QTM}^{-1} + \tau_{Orbach}^{-1} + \tau_{direct}^{-1} + \tau_{Raman}^{-1} + \dots$$

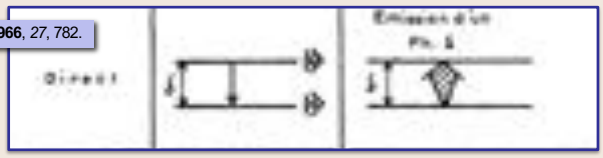
Relaxation rate (τ^{-1}) **Relaxation time (τ)**

$$\tau_{Direct}^{-1} = AH^m T$$

Linear in temperature
Decreases in H^m (m = 2 non-Kramers or m = 4 for Kramers)

Spins **Phonons**

J. Pescia *J. Phys.* **1966**, *27*, 782.



6) Superparamagnetism and SMMs

Beyond QTM and "Orbach" relaxation processes:

$$\tau^{-1} = \tau_{QTM}^{-1} + \tau_{Orbach}^{-1} + \tau_{direct}^{-1} + \tau_{Raman}^{-1} + \dots$$

Relaxation rate (τ^{-1}) **Relaxation time (τ)**

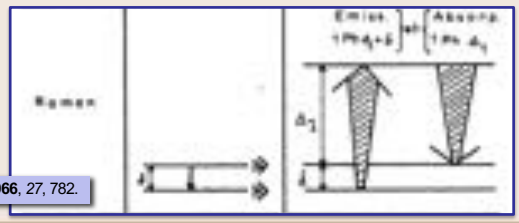
$$\tau_{Raman}^{-1} = C\frac{1 + C_1 H^2}{1 + C_2 H^2} T^n$$

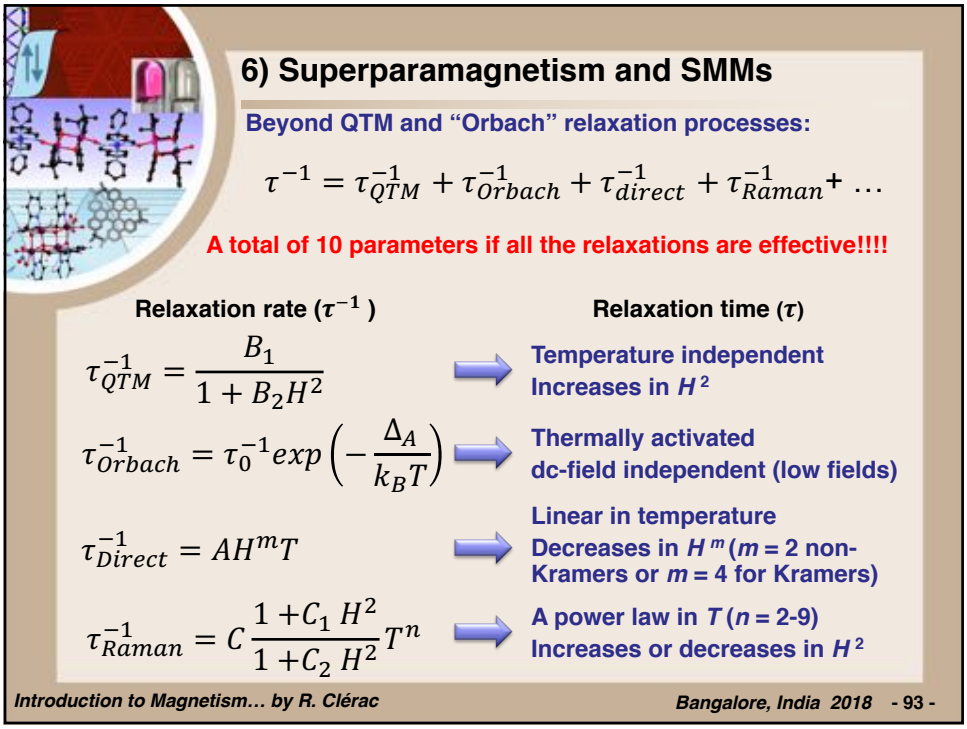
A power law in T (n = 2-9)
Increases or decreases in H^2

J. H. van Vleck, *Phys. Rev.* **1940**, *57*, 426.

Spins **Phonons**

J. Pescia *J. Phys.* **1966**, *27*, 782.





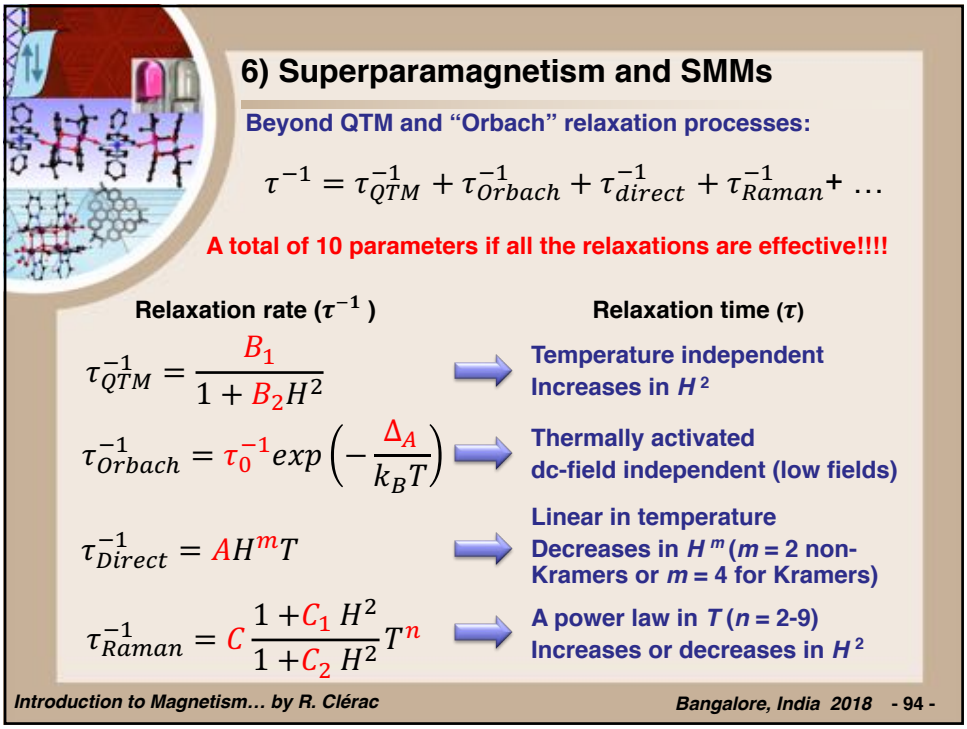
6) Superparamagnetism and SMMs

Beyond QTM and "Orbach" relaxation processes:

$$\tau^{-1} = \tau_{QTM}^{-1} + \tau_{Orbach}^{-1} + \tau_{direct}^{-1} + \tau_{Raman}^{-1} + \dots$$

A total of 10 parameters if all the relaxations are effective!!!!

Relaxation rate (τ^{-1})		Relaxation time (τ)
$\tau_{QTM}^{-1} = \frac{B_1}{1 + B_2 H^2}$	⇒	Temperature independent Increases in H^2
$\tau_{Orbach}^{-1} = \tau_0^{-1} exp\left(-\frac{\Delta_A}{k_B T}\right)$	⇒	Thermally activated dc-field independent (low fields)
$\tau_{Direct}^{-1} = A H^m T$	⇒	Linear in temperature Decreases in H^m (m = 2 non-Kramers or m = 4 for Kramers)
$\tau_{Raman}^{-1} = C \frac{1 + C_1 H^2}{1 + C_2 H^2} T^n$	⇒	A power law in T (n = 2-9) Increases or decreases in H^2



6) Superparamagnetism and SMMs

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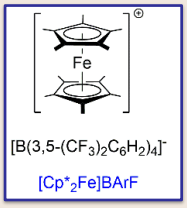
6) Superparamagnetism and SMMs

My (not THE) method to fit the relaxation time :

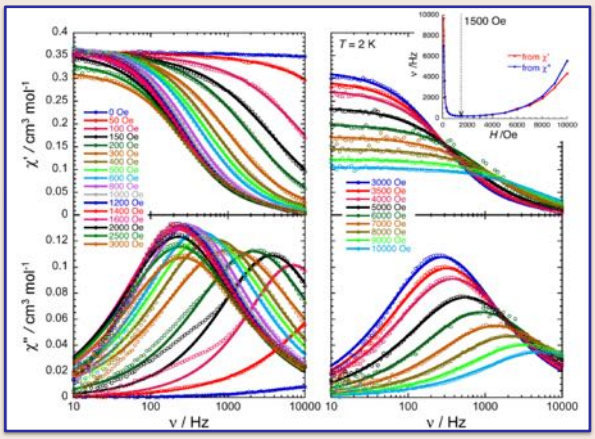
Jeremy Smith (Indiana University, USA) **2018**, *Submitted*

A ferrocenium complex
A spin ½ system



$[B(3,5\text{-}(CF_3)_2C_6H_2)_4]^-$

$[Cp^*_2Fe]BArF$



The slow relaxation of the magnetization is not observed in zero dc field but it is revealed under applied magnetic field.

6) Superparamagnetism and SMMs

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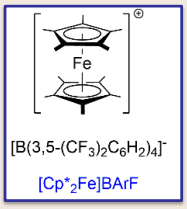

$[B(3,5\text{-}(CF_3)_2C_6H_2)_4]^-$

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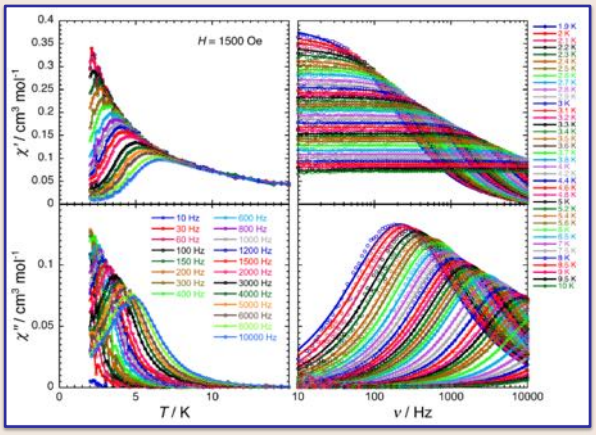

The slow relaxation of the magnetization is temperature dependent

6) Superparamagnetism and SMMs

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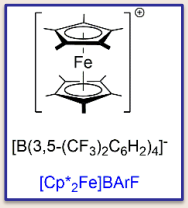
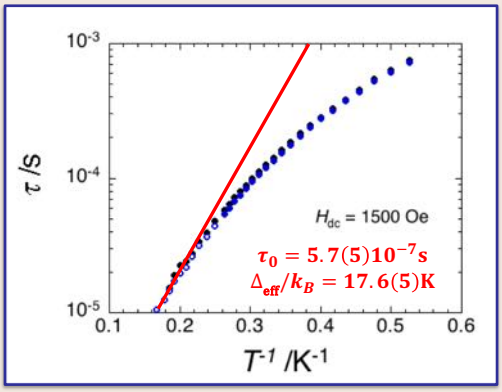
A spin ½ system





- **Spin ½ SMM !! Question: "Orbach" and QTM mechanisms?**
- **To answer: both field and temperature dependences of the experimental relaxation time are absolutely necessary !!**

6) Superparamagnetism and SMMs

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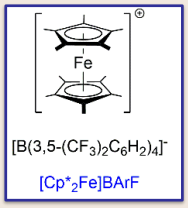
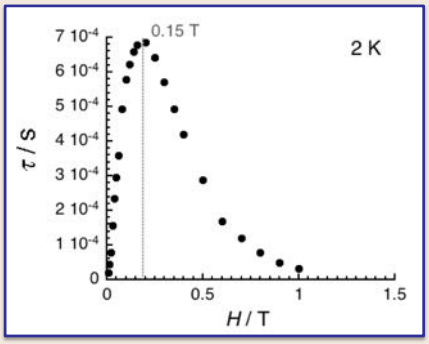
A spin ½ system





6) Superparamagnetism and SMMs

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6) Superparamagnetism and SMMs

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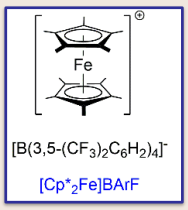

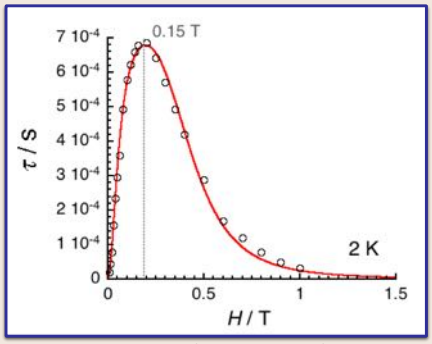

$$\tau^{-1} = \tau_{direct}^{-1} + \tau_{Raman}^{-1}$$

$$\tau^{-1} = A H^4 T + C \frac{1 + C_1 H^2}{1 + C_2 H^2} T^n$$

with A = 2.0 10^4 $K^{-1}T^{-4}s^{-1}$, C_1 = 280 T^{-2}, C_2 = 8.1 10^5 T^{-2} and 2^nC = 3.8 10^6 s^{-1}

6) Superparamagnetism and SMMs

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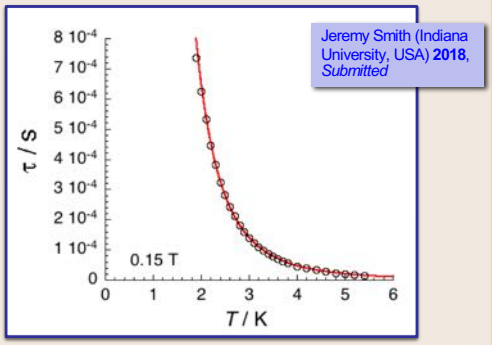
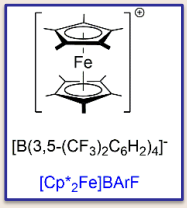


Jeremy Smith (Indiana University, USA) **2018**, *Submitted*

A ferrocenium complex

A spin ½ system



$$\tau^{-1} = AH^4T + C\frac{1+C_1H^2}{1+C_2H^2}T^n$$

With only n = 3.8 (optical and acoustic phonons? n = 9 for Kramer systems)
Fixing A = 2.0 10^4 $K^{-1}T^{-4}s^{-1}$, C_1 = 280 T^{-2}, C_2 = 8.1 10^5 T^{-2} and 2^nC = 3.8 10^6 s^{-1}

K. N. Shriyasta, *Phys. Stat. Sol. (b)* **1983**, *117*, 437; A. Singh, K. N. Shriyasta, *Phys. Stat. Sol. (b)* **1979**, *95*, 273.

6) Superparamagnetism and SMMs

Beyond QTM and Orbach relaxation processes:

$$\tau^{-1} = \tau_{Orbach}^{-1} + \tau_{QTM}^{-1} + \tau_{direct}^{-1} + \tau_{Raman}^{-1}$$

Take home messages:

- **All the paramagnetic molecules exhibit slow dynamics of the magnetization!! Known at least since 1932!**
- **In that sense all the paramagnetic molecules are potentially SMMs!!!**

So what is a SMMs?

- **RC: A paramagnetic molecule for which your experiment is able to observe the slow dynamics of the magnetization (*M* vs *time*, ac susceptibility, EPR, NMR, Mossbauer, …)**

6) Superparamagnetism and SMMs

The ingredients in order to obtain a SMM:

- **just need a paramagnetic molecule!**
- **the right experimental setup!!**

To promote the "Orbach" process:

- **high spin/ magnetic moment**
- **magnetic anisotropy**

Transition metals organized by ligands:

- 3d: Mn(III), Fe(III), Ni(II), Co(II), V(II)
- Lanthanides: Tb(III), Dy(III), Ho(III)
- Mixed metals 3d/3d or 4f/4f or 3d/4f
- Mixed spins: 3d/radicals

Synthesis methods:

- serendipitous! Most of the time…
- by design (only a few…)

There are thousands of SMM examples in the literature

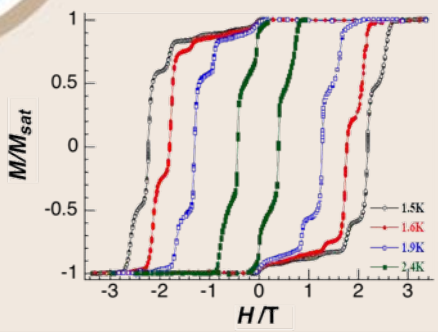
6) Superparamagnetism and SMMs

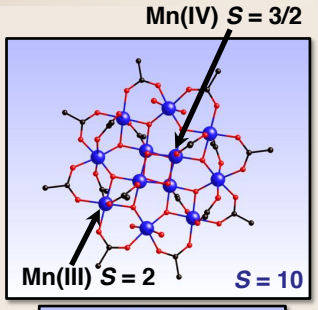
The most famous example!

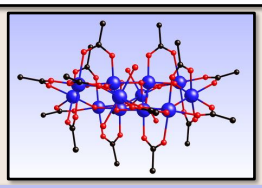
$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$

D/k_B = -0.66 K

$\Delta_{eff}/k_B \approx$ 61 K







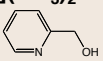
(a) Boyd, P. D. W.; Li, Q.; Vincent, J. B.; Folting, K.; Chang, H.-R.; Streib, W. E.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 8537; (b) Caneschi, A.; Gatteschi, D.; Sessoli, R. *J. Am. Chem. Soc.* **1991**, *113*, 5873; (c) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804; (d) Gatteschi, D. ; Caneschi, A.; Pardi, L.; Sessoli, R. *Science* **1994**, *265*, 1054; Thomas, L.; Lionti, F., Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145.

6) Superparamagnetism and SMMs

Another Mn-based SMMs:

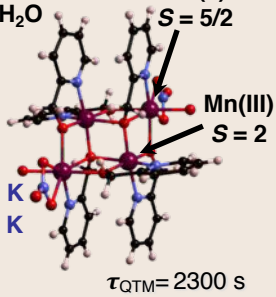
$[Mn_4(hmp)_6(H_2O)_2(NO_3)_2](NO_3)_2 \cdot 2.5H_2O$

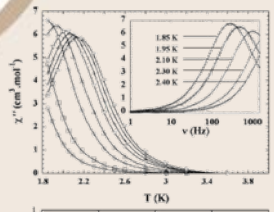
Hhmp: 2-hydroxymethylpyridine

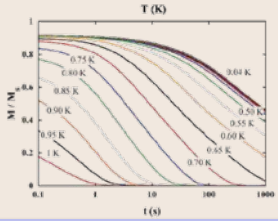


Mn(II) $S = 5/2$

Mn(III) $S = 2$





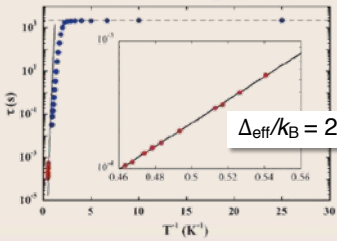


$S = 9$

$D/k_B = -0.35$ K

$\Delta_A/k_B = 28.4$ K

$\tau_{QTM} = 2300$ s

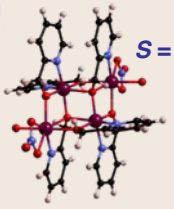


$\Delta_{eff}/k_B = 20.9$ K

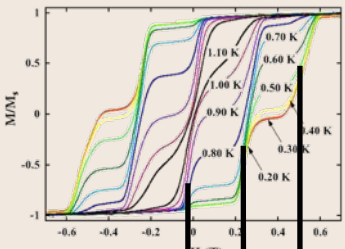
L. Lecren, W. Wernsdorfer, Y.-G. Li, O. Roubeau, H. Miyasaka, R. Clérac *J. Am. Chem. Soc.* **2005**, *127*, 11311

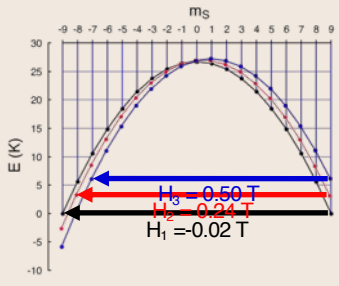
6) Superparamagnetism and SMMs

$[Mn_4(hmp)_6(H_2O)_2(NO_3)_2](NO_3)_2 \cdot 2.5H_2O$



$S = 9$

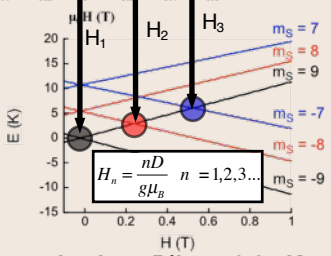




$H_3 = 0.50$ T

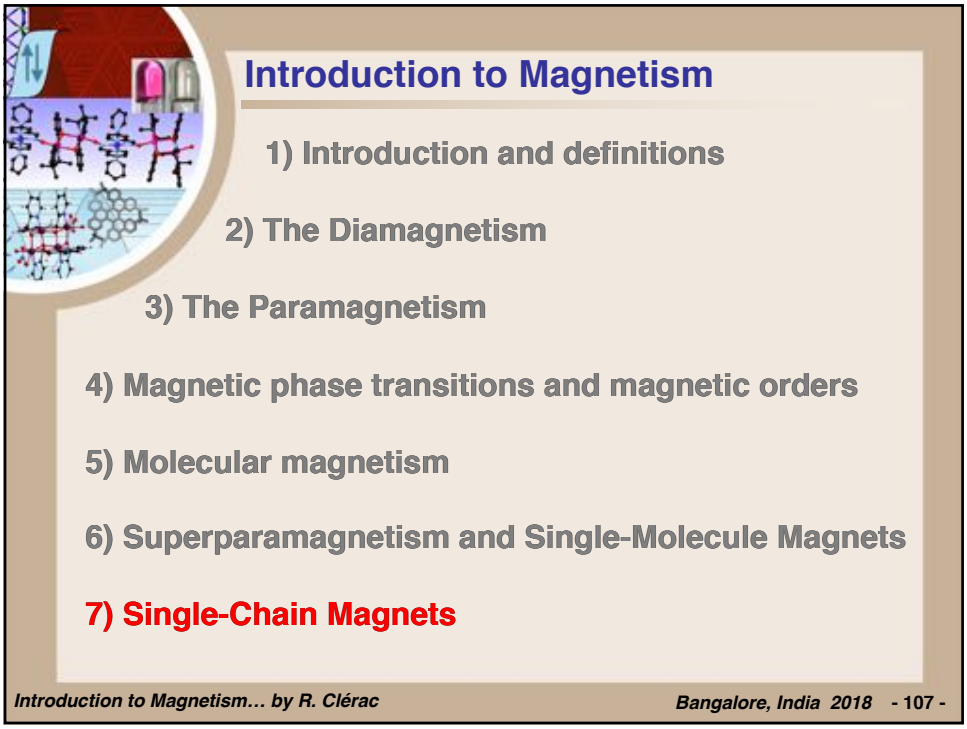
$H_2 = 0.24$ T

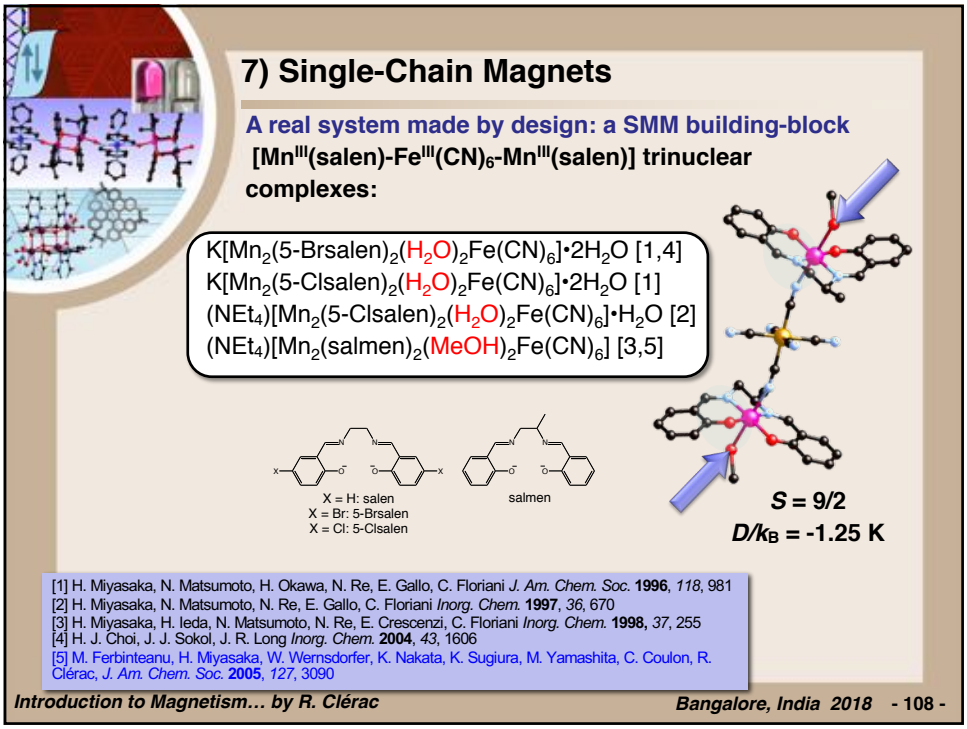
$H_1 = -0.02$ T



$H_n = \frac{nD}{g\mu_B} \quad n = 1,2,3...$

Resonnant quantum tunneling of the magnetization: $D/k_B = -0.35$ K


Introduction to Magnetism
1) Introduction and definitions
2) The Diamagnetism
3) The Paramagnetism
4) Magnetic phase transitions and magnetic orders
5) Molecular magnetism
6) Superparamagnetism and Single-Molecule Magnets
7) Single-Chain Magnets
Introduction to Magnetism... by R. Clérac
Bangalore, India 2018 - 107 -

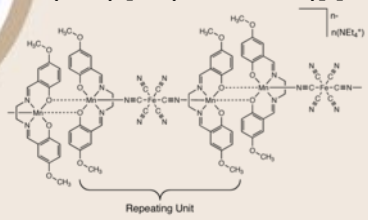

7) Single-Chain Magnets
A real system made by design: a SMM building-block
[Mn(III)(salen)-Fe(III)(CN)6-Mn(III)(salen)] trinuclear complexes:
K[Mn2(5-Brsalen)2(H2O)2Fe(CN)6]•2H2O [1,4]
K[Mn2(5-Clsalen)2(H2O)2Fe(CN)6]•2H2O [1]
(NEt4)[Mn2(5-Clsalen)2(H2O)2Fe(CN)6]•H2O [2]
(NEt4)[Mn2(salmen)2(MeOH)2Fe(CN)6] [3,5]
X = H: salen
X = Br: 5-Brsalen
X = Cl: 5-Clsalen
salmen
S = 9/2
D/kB = -1.25 K
[1] H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani J. Am. Chem. Soc. 1996, 118, 981
[2] H. Miyasaka, N. Matsumoto, N. Re, E. Gallo, C. Floriani Inorg. Chem. 1997, 36, 670
[3] H. Miyasaka, H. Ieda, N. Matsumoto, N. Re, E. Crescenzi, C. Floriani Inorg. Chem. 1998, 37, 255
[4] H. J. Choi, J. J. Sokol, J. R. Long Inorg. Chem. 2004, 43, 1606
[5] M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac, J. Am. Chem. Soc. 2005, 127, 3090
Introduction to Magnetism... by R. Clérac
Bangalore, India 2018 - 108 -

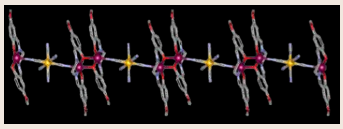
7) Single-Chain Magnets

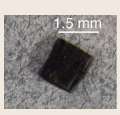
M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac, *J. Am. Chem. Soc.* **2005**, *127*, 3090

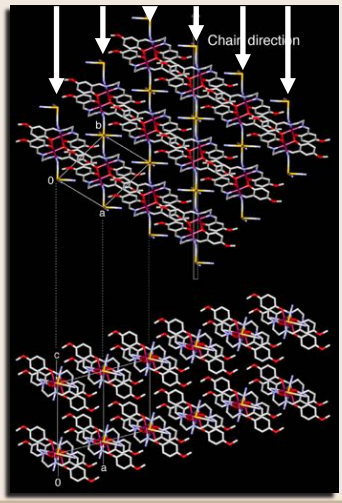
The structural arrangement:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$







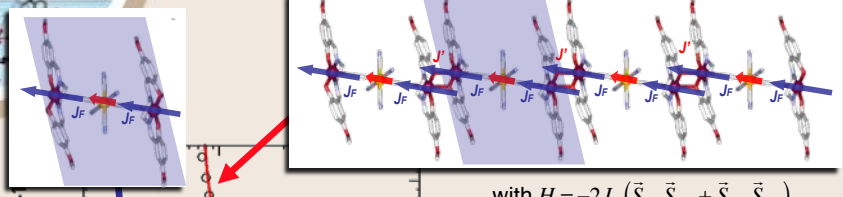


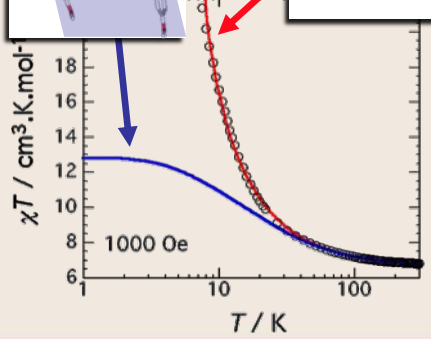
Isolated chains from a magnetic point of view

7) Single-Chain Magnets

The high temperature magnetic susceptibility:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$





with $H = -2J_F\left(\vec{S}_{Fe1}\vec{S}_{Mn} + \vec{S}_{Fe2}\vec{S}_{Mn}\right)$

An Heisenberg trimer model with inter-trimer J' interactions treated in a mean field approximation

J_F/k_B = +6.5(1) K

J'/k_B = +0.08(1) K

g = 2.03(2)

7) Single-Chain Magnets

A physicist view:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

J_F/k_B = +6.5(1) K

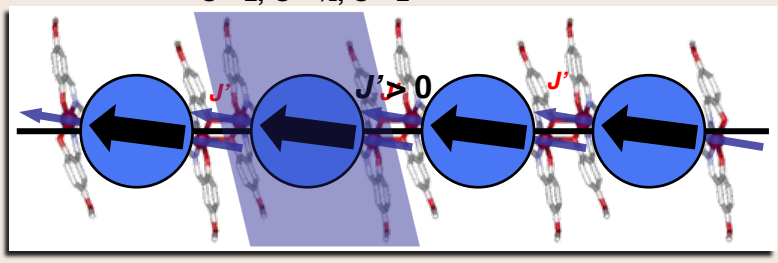
J'/k_B = +0.07(1) K

$J_{Mn\text{-}Mn}/k_B$ = +0.40(6) K

« S_T = 9/2 »

S = 2, S = ½, S = 2

because $|J_F| >> J_{Mn\text{-}Mn}$ and for $|J_F| >> k_B T$

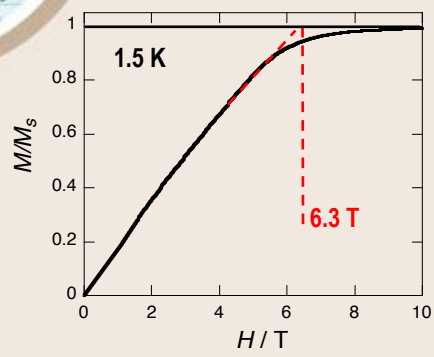


Chain of ferromagnetically coupled anisotropic S = 9/2 spins

7) Single-Chain Magnets

Single crystal measurements: *H* in the hard plane

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

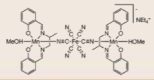


$$H = -2J'\sum_{-\infty}^{+\infty}\vec{S}_{T,i}\vec{S}_{T,i+1} + D\sum_{-\infty}^{+\infty}\vec{S}_{T,iz}^{2}$$

Estimation of D

$$2DS_T^2 \approx g\mu_B S_T H_a$$

D/k_B = -0.94 K

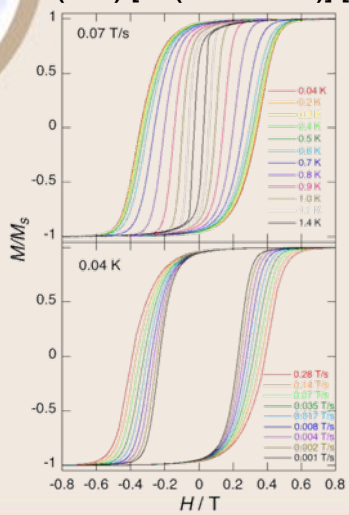


$D/k_B \approx$ -1.25 K

7) Single-Chain Magnets

Single crystal measurements: *H* along the easy axis

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$



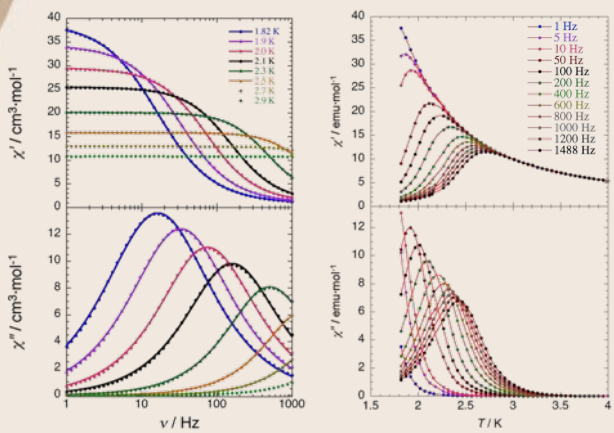
M vs *H*
hysteresis loops

Magnet behavior, i.e. slow relaxation of the magnetization compatible with SCM behavior

7) Single-Chain Magnets

Relaxation time measurements (ac susceptibility):

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

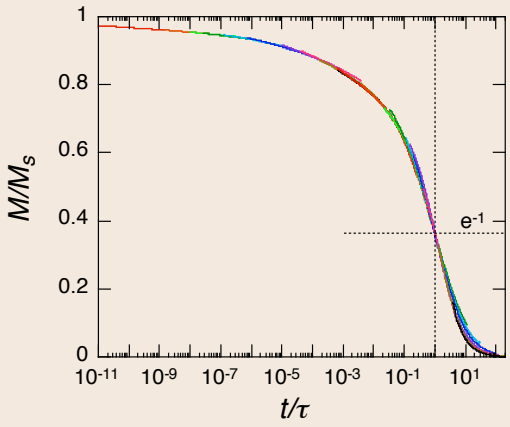


A single relaxation mode compatible with SCM behavior

7) Single-Chain Magnets

Relaxation time measurements (*M* vs time):

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

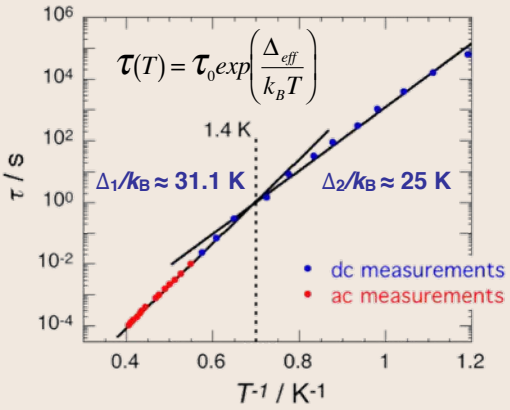


Determination of the relaxation time down to 0.8 K

7) Single-Chain Magnets

Relaxation time:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

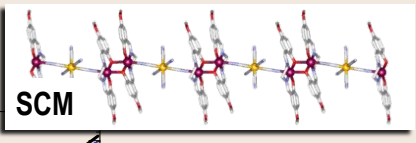


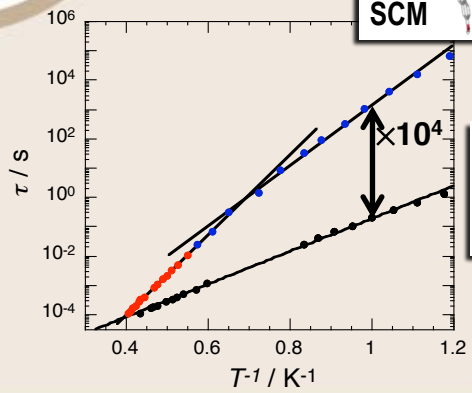
Crossover between two activated relaxation regimes

7) Single-Chain Magnets

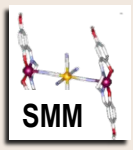
Relaxation time SMM vs SCM:

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$



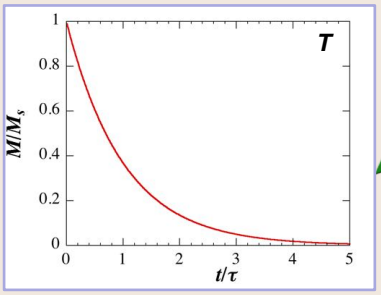


(NEt_4)
$[Mn(salmen)(MeOH)]_2[Fe(CN)_6]$



In a given temperature range the correlations enhance the relaxation time

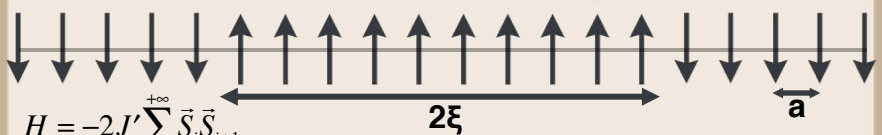
7) Single-Chain Magnets



(a) Glauber, R. J. *J. Math. Phys.* **1963**, *4*, 294; (b) *Struct. Bond.* **2015**, 164, 143; *Struct. Bond.* **2006**, 122, 163

$$M / M_S = exp\left(-\frac{t}{\tau}\right)$$

H ≠ 0



$$H = -2J'\sum_{-\infty}^{+\infty}\vec{S}_i\vec{S}_{i+1}$$

$$\tau(T) = \tau_i(T)\left(\frac{\xi}{a}\right)^2 = \tau_i(T)\,exp\left(\frac{2\Delta_\xi}{k_BT}\right) \text{ with } \Delta_\xi = 4J'S^2$$

7) Single-Chain Magnets

The relaxation time in a Single-Chain Magnet: Chain of ferromagnetically coupled Ising spins (Glauber)

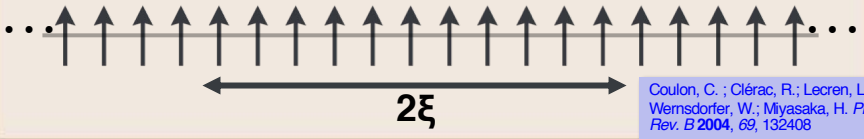
$$\tau(T) = \tau_i(T) exp\left(\frac{2\Delta_\xi}{k_B T}\right) \text{ with } \Delta_\xi = 4J'S^2$$

(a) Glauber, R. J. *J. Math. Phys.* **1963**, *4*, 294; (b) *Struct. Bond.* **2015**, 164, 143; *Struct. Bond.* **2006**, 122, 163

1) For a chain of anisotropic spins ($D < 0$ and $|D/J| > 4/3$: Ising limit) :

$$H = -2J' \sum_{-\infty}^{+\infty} \vec{S}_{T,i} \vec{S}_{T,i+1} + D \sum_{-\infty}^{+\infty} \vec{S}_{T,iz}^2$$

$$\tau_i(T) = \tau_0 exp\left(\frac{\Delta_A}{k_B T}\right) \text{ with } \Delta_A = |D| S_T^2 \Rightarrow \tau(T) = \tau_0 exp\left(\frac{2\Delta_\xi + \Delta_A}{k_B T}\right)$$



2ξ

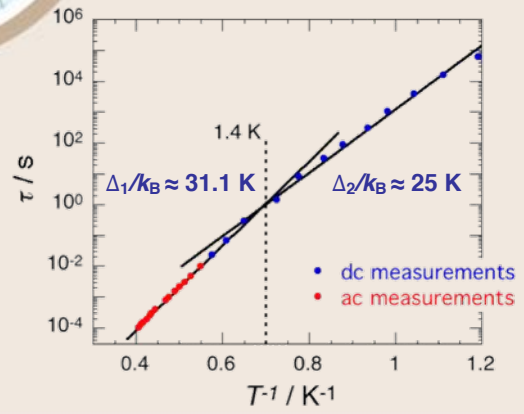
Coulon, C. ; Clérac, R.; Lecren, L.; Wernsdorfer, W.; Miyasaka, H. *Phys. Rev. B* **2004**, *69*, 132408

7) Single-Chain Magnets

Relaxation time: the Glauber's regime

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

with $S_T = 9/2$
$J'/k_B \approx 0.08$ K
$D/k_B = -0.94$ K



$$\tau(T) = \tau_0 exp\left(\frac{2\Delta_\xi + \Delta_A}{k_B T}\right)$$

with

$$2\Delta_\xi + \Delta_A = 8J'S_T^2 + |D|S_T^2$$

$\Delta_1/k_B = (8J' + |D|)S_T^2/k_B = 32$ K

7) Single-Chain Magnets

The relaxation time in a Single-Chain Magnet:

2) For a chain of anisotropic spins with a length *L*
(*D* < 0 and |*D*/*J*| > 4/3 Ising limit):

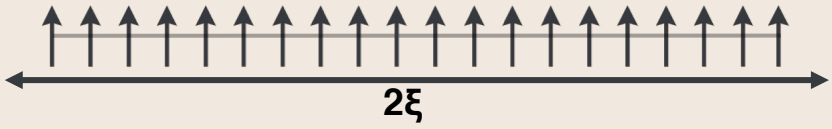
(a) Coulon, C. ; Miyasaka, H. ; Clérac, R. *Struct. Bond.* **2006**, *122*, 163
(b) Coulon, C. ; Clérac, R.; Lecren, L.; Wernsdorfer, W.; Miyasaka, H. *Phys. Rev. B* **2004**, *69*, 132408

$$H = -2J' \sum_{-\infty}^{+\infty} \vec{S}_{T,i} \vec{S}_{T,i+1} + D \sum_{-\infty}^{+\infty} \vec{S}_{T,iz}^2$$

for $2\xi < L$ ⇒ $\tau(T) = \tau_0 exp\left(\frac{2\Delta_\xi + \Delta_A}{k_B T}\right)$

for $2\xi > L$ ⇒ $\tau(T) = \tau_0 exp\left(\frac{\Delta_\xi + \Delta_A}{k_B T}\right)$

Luscombe, J. H. et al., *Phys. Rev. E* **1996**, *53*, 5852
Leal da Silva, J. K. et al., *Phys. Rev. E* **1995**, *52*, 4527

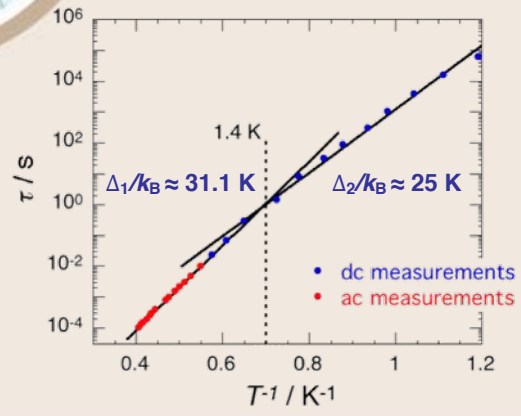


7) Single-Chain Magnets

Relaxation time: the finite-size chain regime

$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

with $S_T = 9/2$
$J'/k_B \approx 0.08$ K
$D/k_B = -0.94$ K



$$\tau(T) = \tau_0 exp\left(\frac{\Delta_\xi + \Delta_A}{k_B T}\right)$$

with

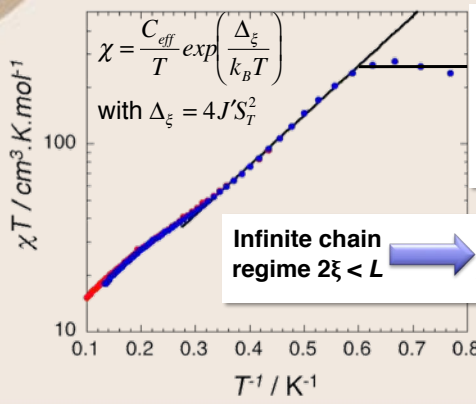
$$\Delta_\xi + \Delta_A = 4J'S_T^2 + |D|S_T^2$$

$\Delta_2/k_B = (4J' + |D|)S_T^2/k_B$
= 25.5 K

7) Single-Chain Magnets

Another evidence of the finite-size chain regime:
$(NEt_4)_2[Mn(5\text{-}MeOsalen)]_2[Fe(CN)_6]$

Ising Chain Model $H = -2J' S_T^2 \sum_{-\infty}^{+\infty} \vec{\sigma}_i \vec{\sigma}_{i+1}$



Finite chain regime $2\xi > L$ $\chi = n\frac{C_{eff}}{T}$
$n \approx 44$
$L \approx 60$ nm

Infinite chain regime $2\xi < L$ → $S_T = 9/2$, $J'/k_B = +0.08(1)$ K

7) Single-Chain Magnets

The ingredients in order to obtain a SCM:
- **chain architecture**
- **high-spin chain units with uniaxial anisotropy**
- **large intra-chain magnetic interaction**
- **as small as possible inter-chain interactions**

Transition metals organized by ligands:
- 3d: Mn(III), Fe(III), Ni(II), Co(II), V(II)
- Lanthanides: Tb(III), Dy(III), Ho(III)
- Mixed metals 3d/3d or 4f/4f or 3d/4f
- Mixed spins: 3d/radical and 4f/radical

Polynuclear complexes organized by linkers:
- SMMs
- anisotropic complexes

Synthesis methods:
- serendipitous!
- by design

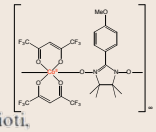
→ **There are a few SCM examples in the literature since 2001**

7) Single-Chain Magnets

The "first" chain exhibiting slow relaxation:

$Co^{II}(hfac)_2(NITPhOMe)$

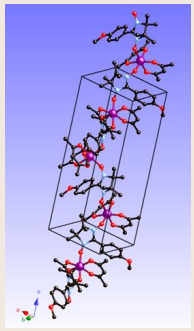
hfac: hexafluoroacetylacetonate
NITPhOMe: 4'-methoxy-phenyl-4,4,5,5-tetramethyl imidazoline-1-oxyl-3-oxide

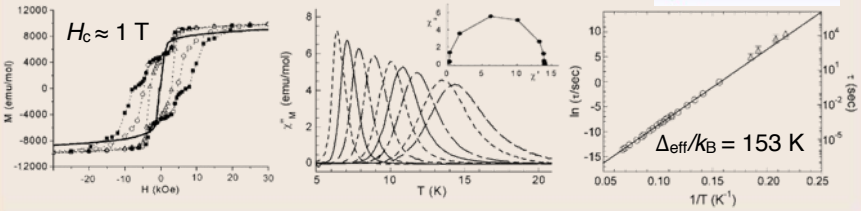


Cobalt(II)-Nitronyl Nitroxide Chains as Molecular Magnetic Nanowires**

Andrea Caneschi, Dante Gatteschi,* Nikolia Lalioti, Claudio Sangregorio, Roberta Sessoli, Giovanni Venturi, Alessandro Vindigni, Angelo Rettori, Maria G. Pini, and Miguel A. Novak

Angew. Chem. Int. Ed. **2001,** *40*, 1760





7) Single-Chain Magnets

The first chain named "Single-Chain Magnet":

$[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$

$saltmen^{2-}$: N,N'–(1,1,2,2-tetramethylethylene) bis(salicylideneiminate)
pao^-: pyridine-2-aldoximate; py: pyridine

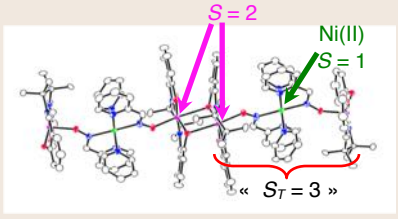
Evidence for Single-Chain Magnet Behavior in a Mn^{III}–Ni^{II} Chain Designed with High Spin Magnetic Units: A Route to High Temperature Metastable Magnets

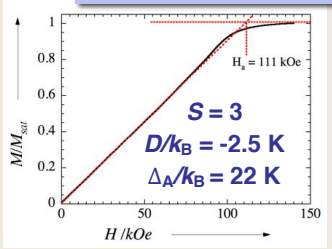
Rodolphe Clérac,*,† Hitoshi Miyasaka,*,‡,§ Masahiro Yamashita,‡ and Claude Coulon†

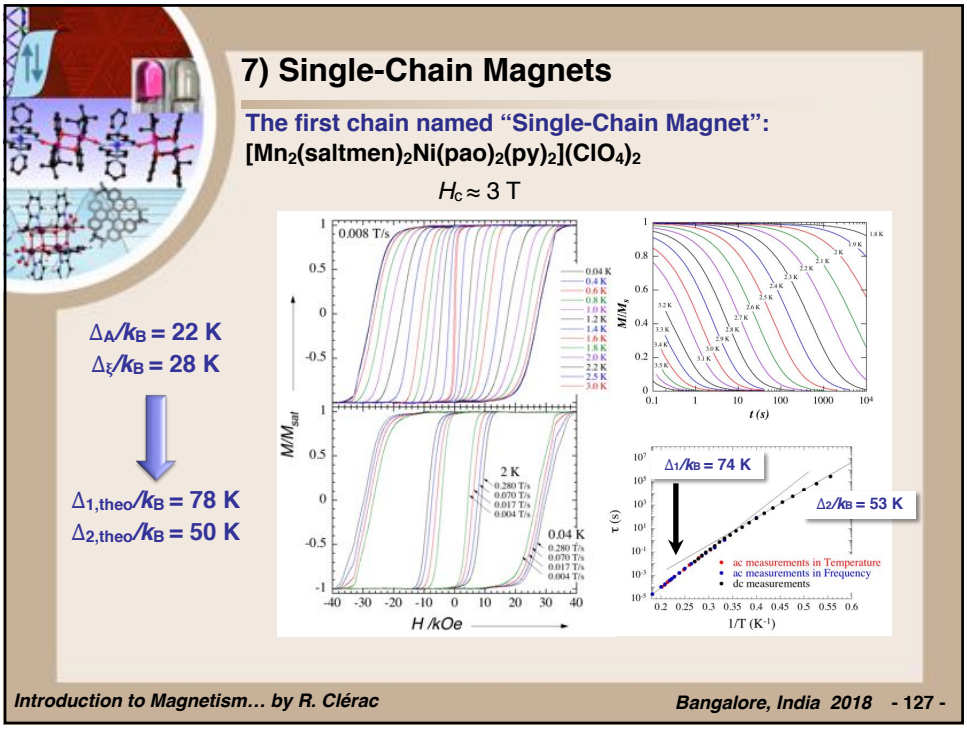
Contribution from the Centre de Recherche Paul Pascal, CNRS UPR 8641, avenue du Dr. A. Schweitzer, 33600 Pessac, France, and "Structural Ordering and Physical Properties", PRESTO, Japan Science and Technology Corporation (JST) and Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Minami-Ohsawa 1-1, Hachioji, Tokyo 192-0397, Japan

Received February 28, 2002

J. Am. Chem. Soc. **2002**, *124*, 43, 12837







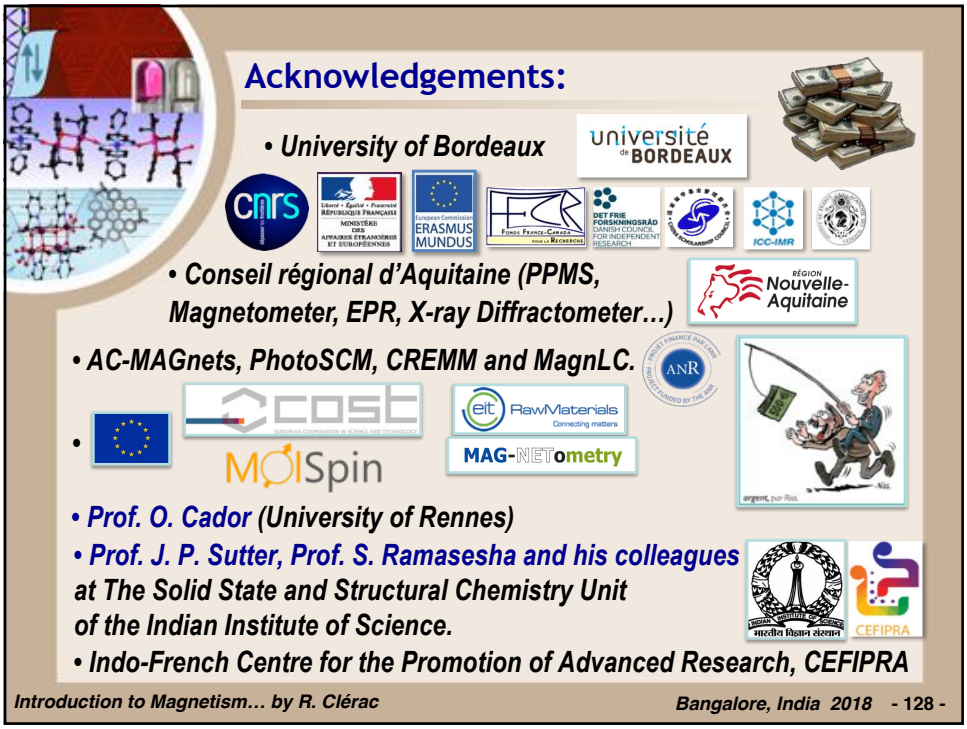
7) Single-Chain Magnets

The first chain named "Single-Chain Magnet":
$[Mn_2(saltmen)_2Ni(pao)_2(py)_2](ClO_4)_2$

$H_c \approx 3$ T

$\Delta_A/k_B = 22$ K
$\Delta_\xi/k_B = 28$ K

$\Delta_{1,theo}/k_B = 78$ K
$\Delta_{2,theo}/k_B = 50$ K



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The end…
Thank you for
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