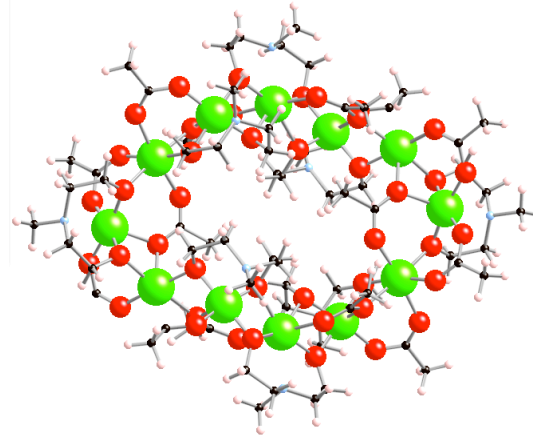


# Dzyaloshinskii-Moriya exchange interaction in single-molecule magnets



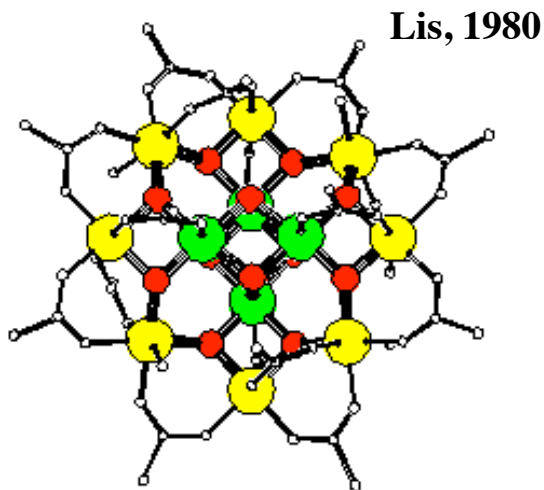
**Wolfgang Wernsdorfer, Benjamin Canals, Arnaud Ralko**  
**Institut Néel, CNRS, Grenoble**  
**T.C. Stamatatos, G. Christou**  
**Dept. of Chemistry, Uni. of Florida,**  
**Gainesville**

*Influence of the Dzyaloshinskii-Moriya exchange interaction on  
quantum phase interference of spins*  
**PRL 101, 237204 (2008)**



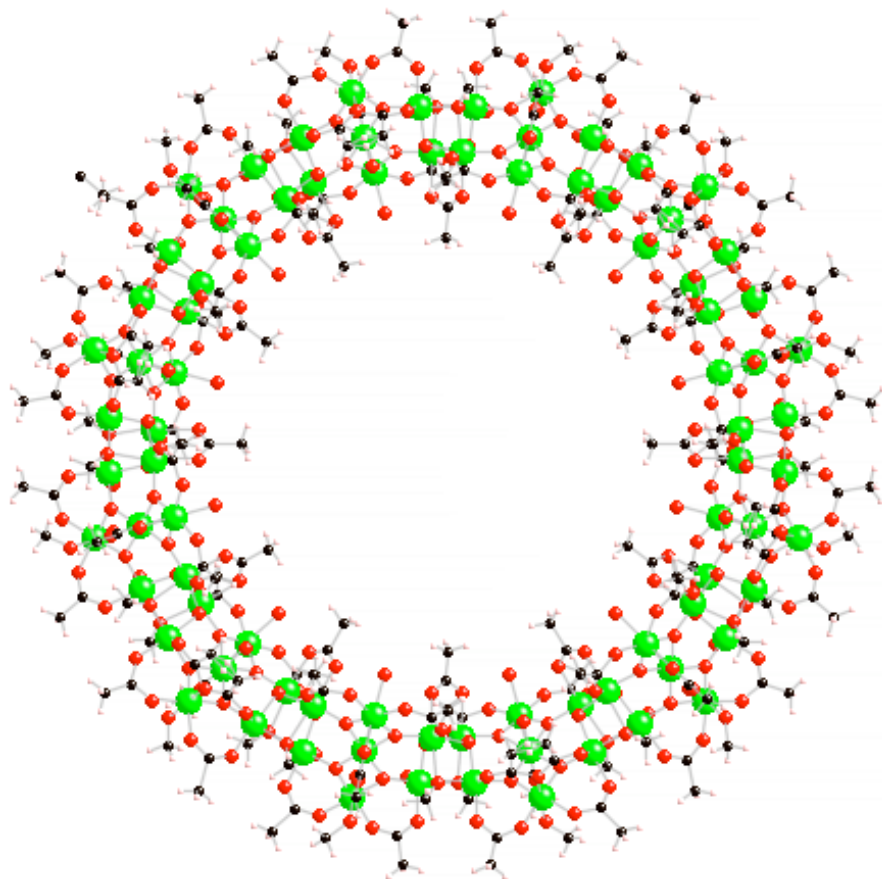
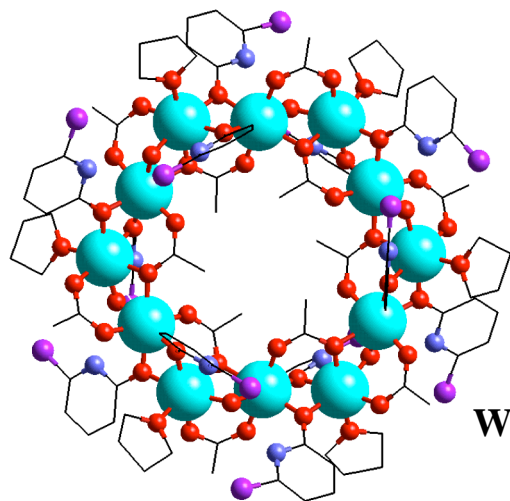
# Single-molecule magnets (SMM)

## Giant spins



**Mn<sub>12</sub> S = 10**

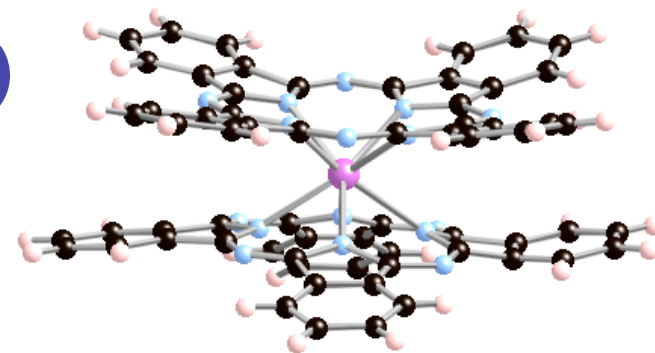
**Ni<sub>12</sub> S = 12**



**Mn<sub>84</sub>  
S ≈ 6**

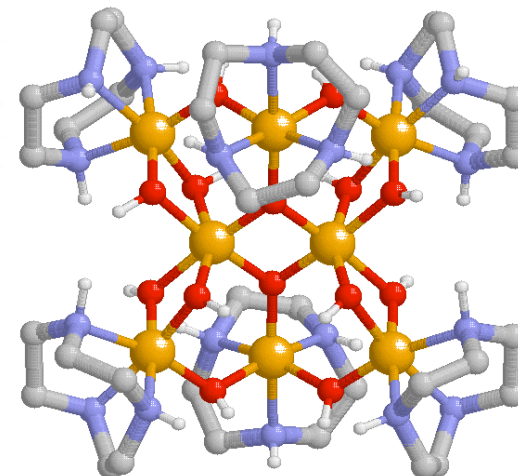
Christou, 2004

Wiegart, 1984

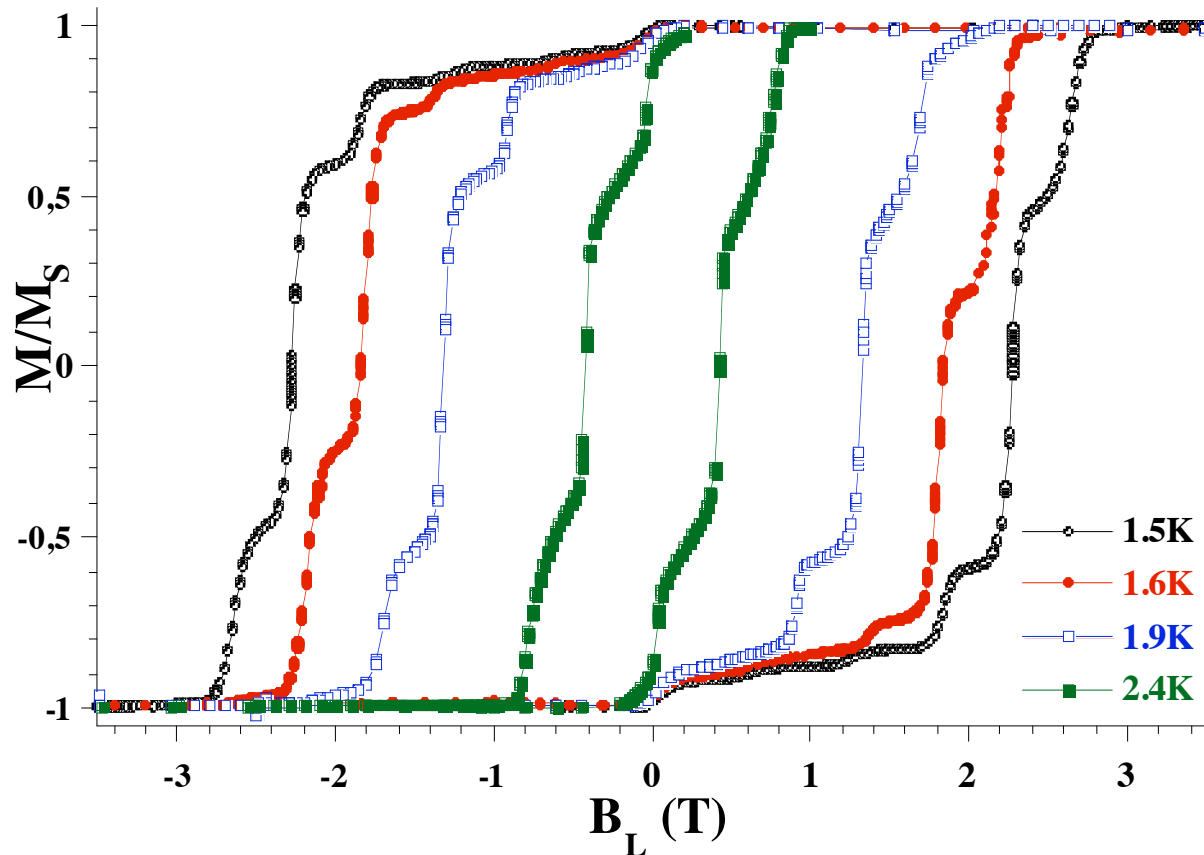


**Tb J = 6**

**Fe<sub>8</sub> S = 10**



# Beginning: $\text{Mn}_{12}\text{-ac}$



L. Thomas, B. Barbara,  
*et al.*, Nature (1996)

T. Lis, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 36, 2042 (1980)

R. Sessoli, D. Gatteschi, M. Novak, J.-L. Tholence, A.-L. Barra, *et al.* (1989-93)

**J. Villain**, F. Hartman Boutron, A. Rettori (1994)

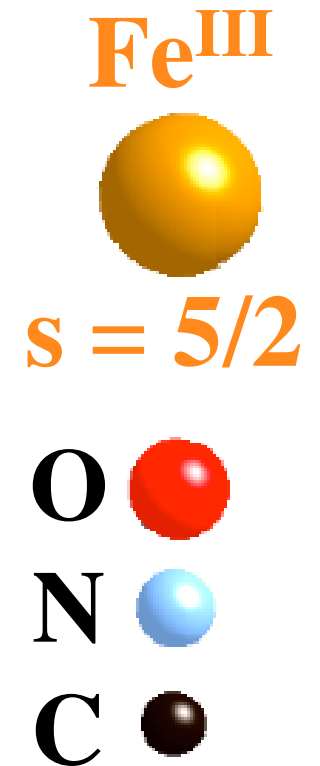
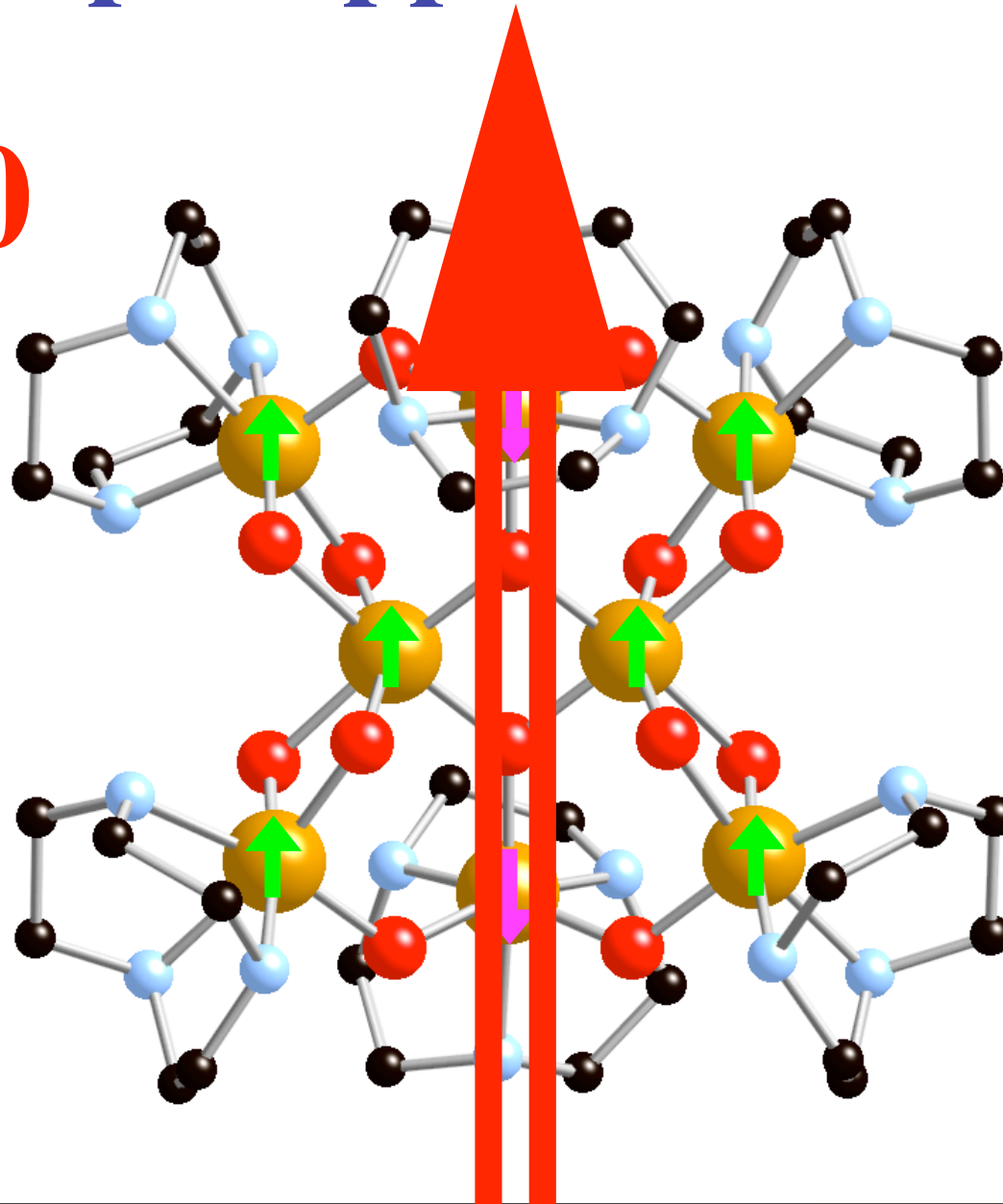
M. Novak, J.-L. Tholence, C. Paulsen, B. Barbara, *et al.* (1994)

J. Friedman, M. Sarachik, *et al.*, PRL (1996)

L. Thomas, B. Barbara *et al.*, Nature (1996)

# Giant spin approximation ( $\text{Fe}_8$ )

$$S = 10$$



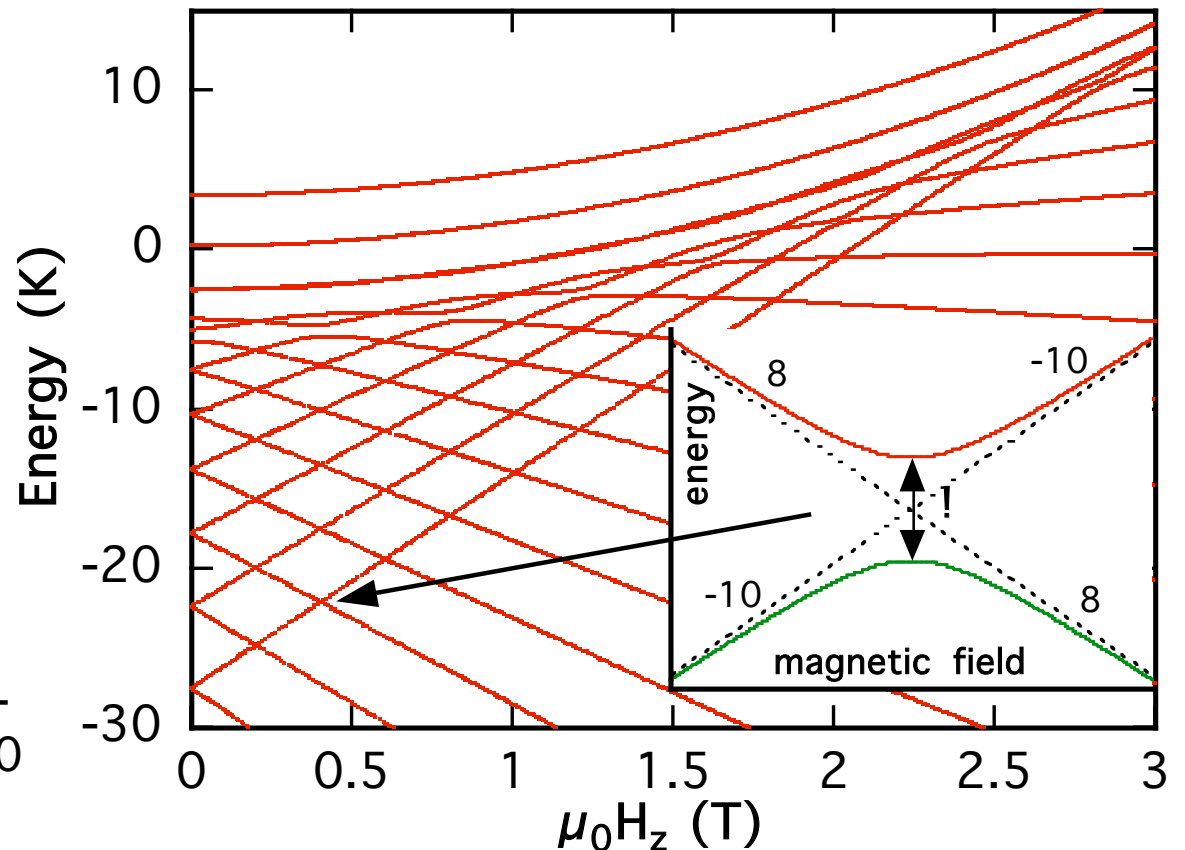
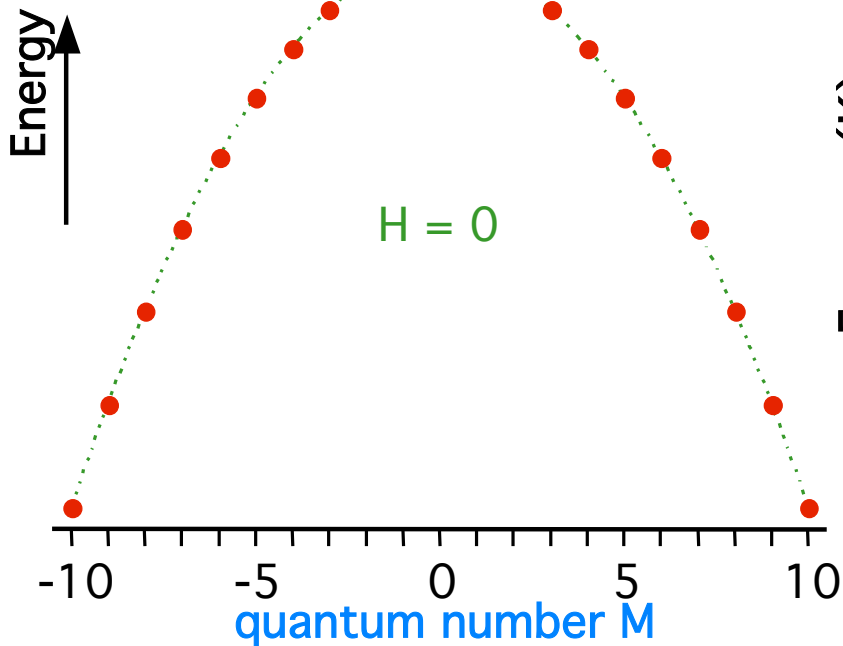
# Giant spin model

**Spin Hamiltonian:**  $H = -D S_z^2 + E (S_x^2 - S_y^2) + g\mu_B \vec{S} \vec{H}$

(2S + 1) energy states:  $M = -S, -S+1, \dots, S$

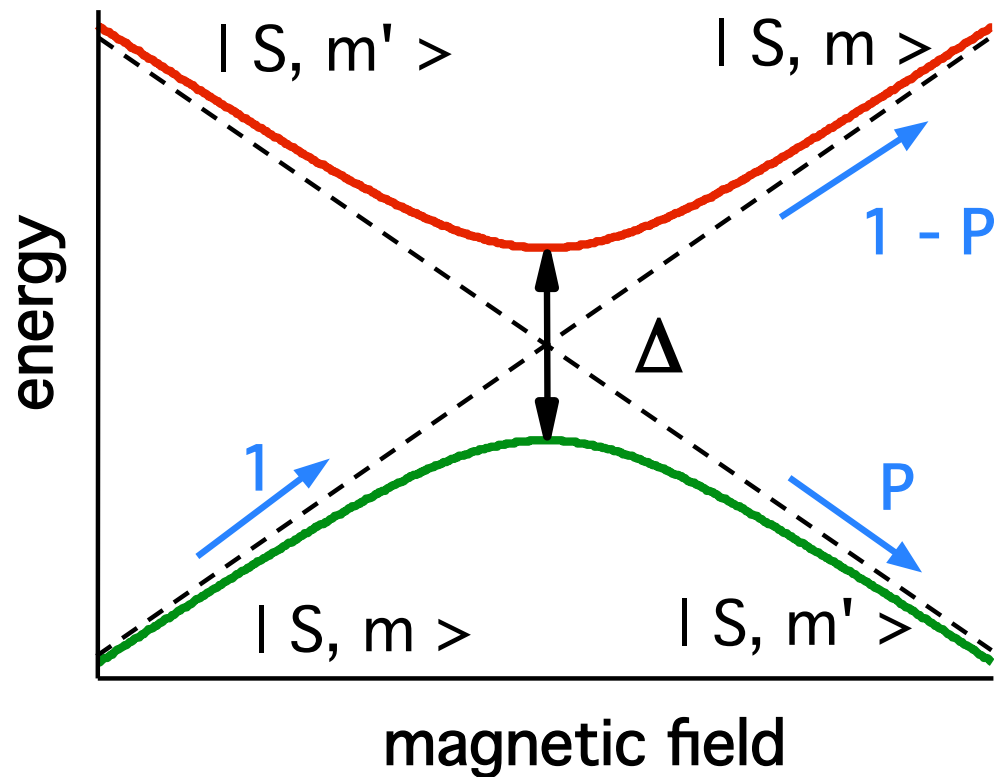
magnetic anisotropy energy

Zeeman energy



# Tunneling probability at an avoided level crossing

## Landau-Zener model (1932)



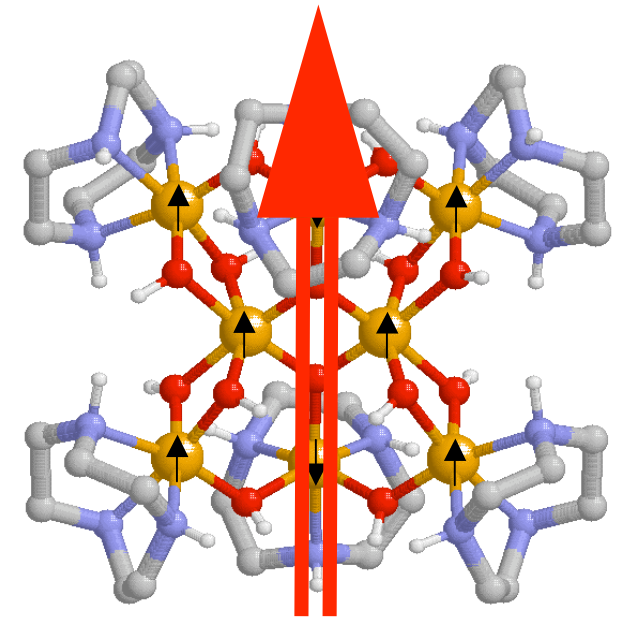
$$P = 1 - \exp\left[-c \frac{\Delta^2}{dH/dt}\right]$$

$$c = \frac{\pi}{2\hbar g\mu_B |m - m'| \mu_0}$$

L. Landau, *Phys. Z. Sowjetunion* **2**, 46 (1932); C. Zener, *Proc. R. Soc. London, Ser. A* **137**, 696, (1932);  
 E.C.G. Stückelberg, *Helv. Phys. Acta* **5**, 369 (1932); S. Miyashita, *J. Phys. Soc. Jpn.* **64**, 3207 (1995); ...

# Application of Landau-Zener tunneling

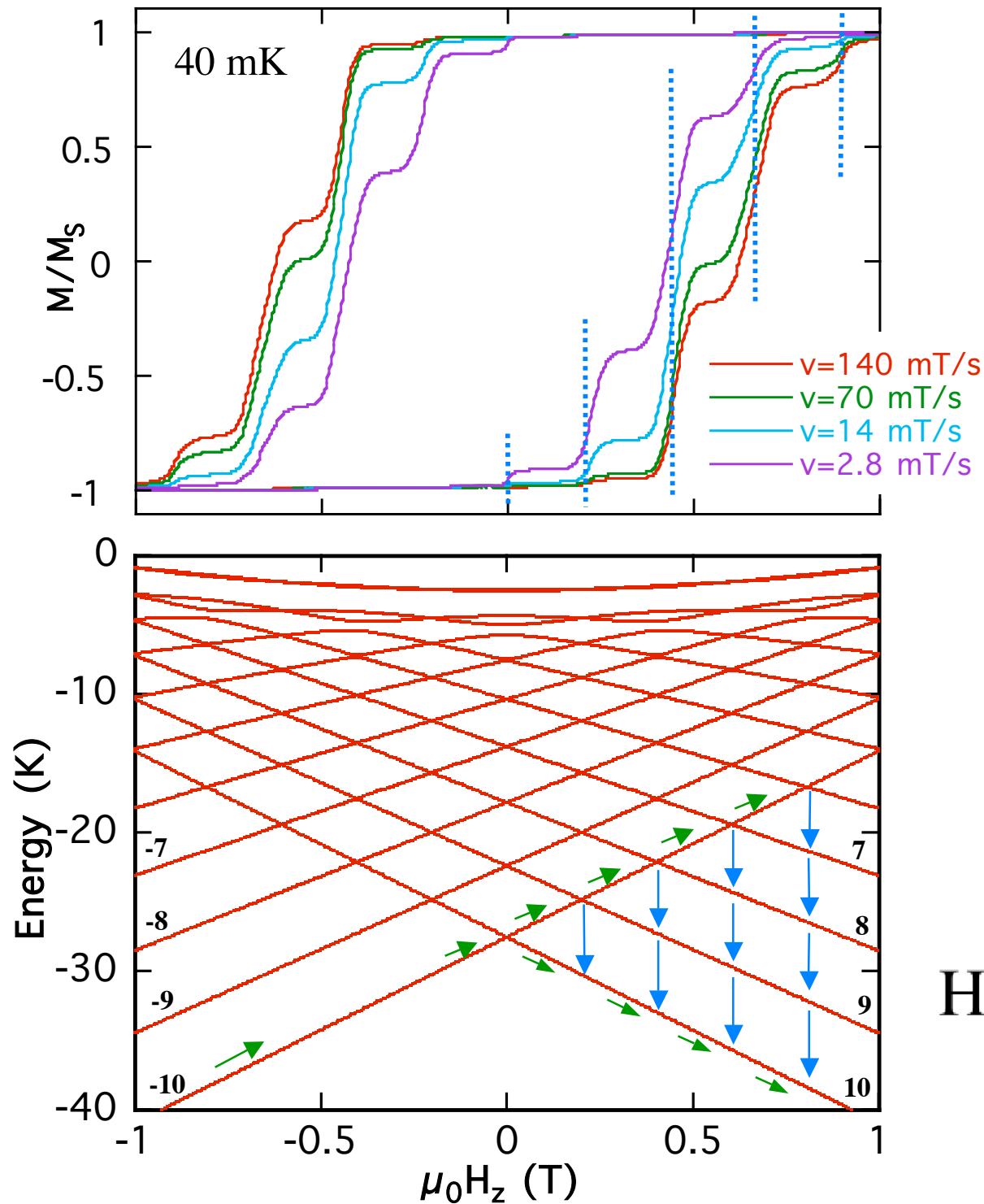
**Fe<sub>8</sub> S = 10**



$$\hat{H} = -D S_z^2 + E (S_x^2 - S_y^2) + g\mu_B \vec{S} \vec{H}$$

with  $S = 10$ ,  $D = 0.27$  K,  $E = 0.046$  K

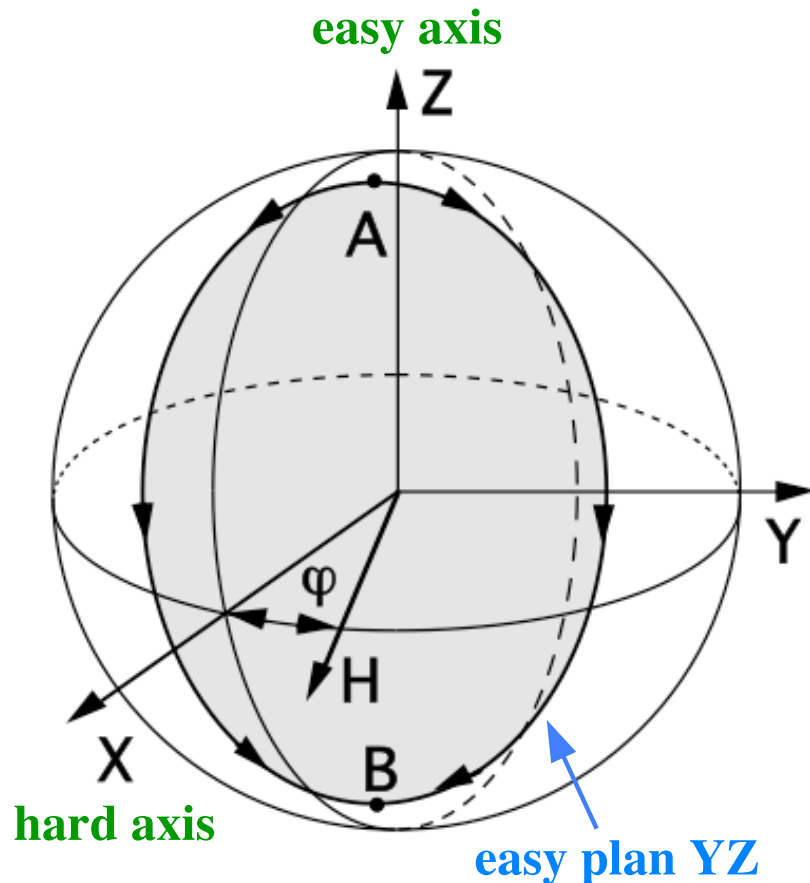
A.-L. Barra et al. EPL (1996)



# Giant spin Hamiltonian of Fe<sub>8</sub>

$$H = -D S_z^2 + E (S_x^2 - S_y^2) + g\mu_B \vec{S} \vec{H}$$

$$S_x H_x + S_y H_y + S_z H_z$$

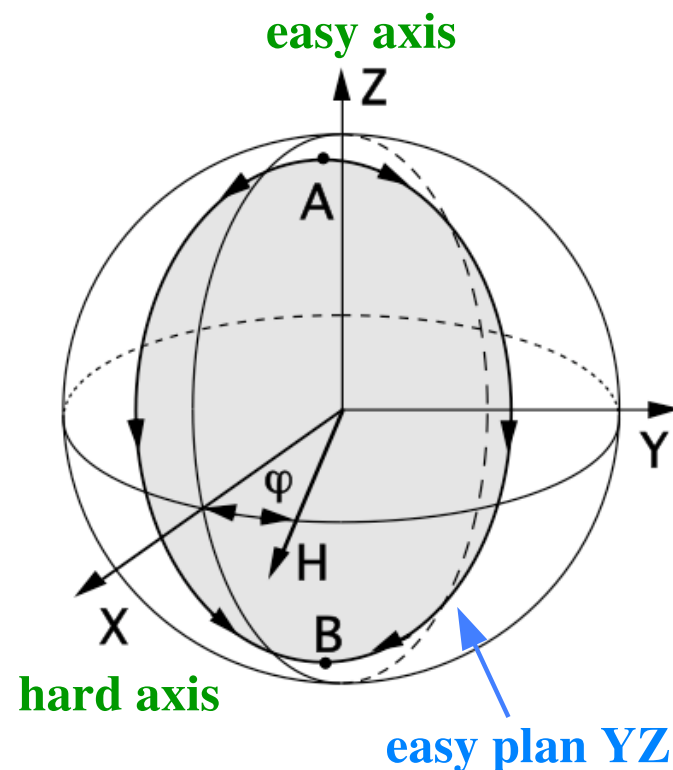
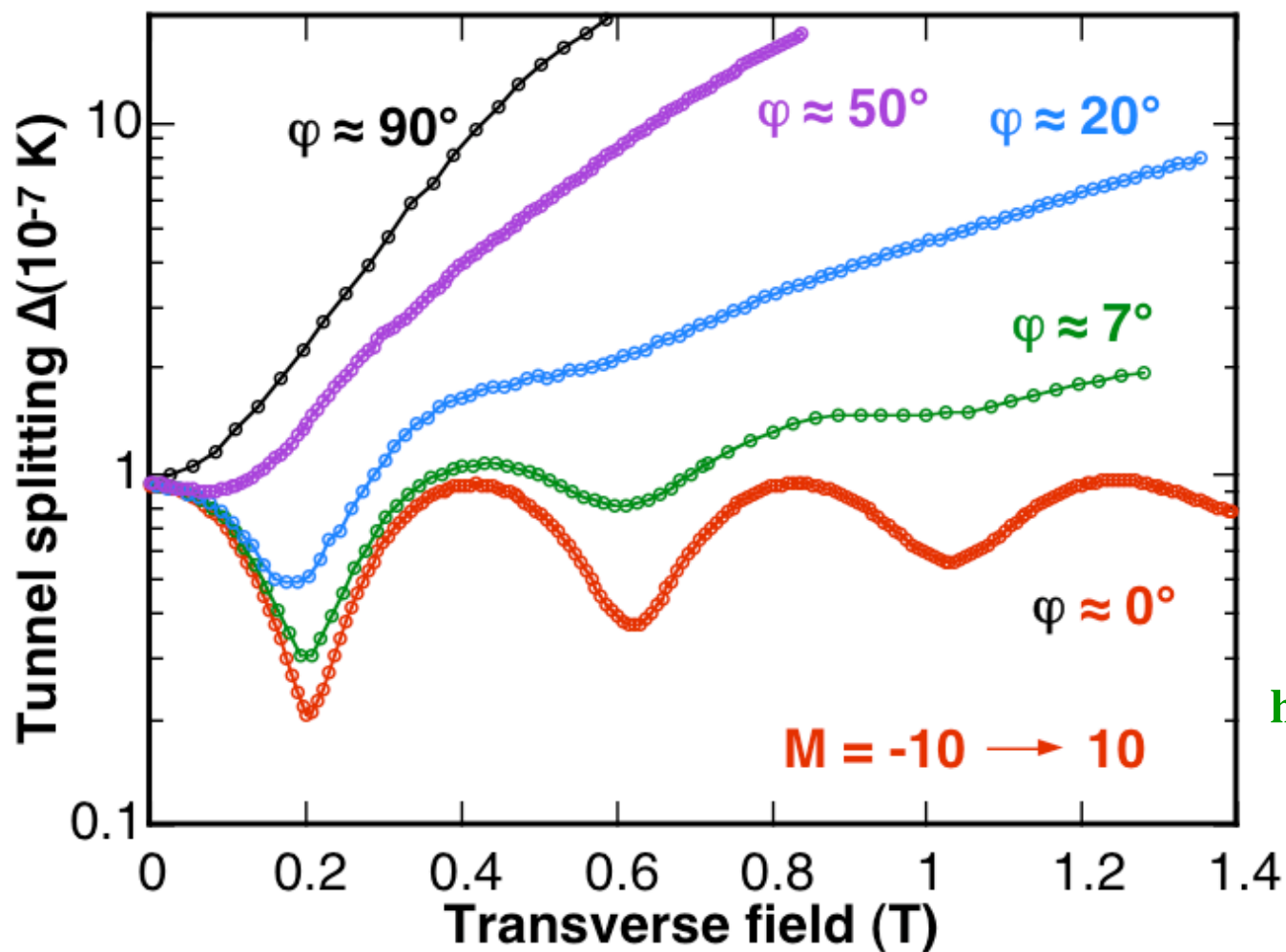


## Path integrals (Feynman)

destructive interference occurs whenever  
the shaded area is  $k\pi/S$ , for odd  $k$ .

A. Garg, *Europhys. Lett.* **22**, 205 (1993)

# Quantum phase interference in single-molecule magnets (**Berry phase**)

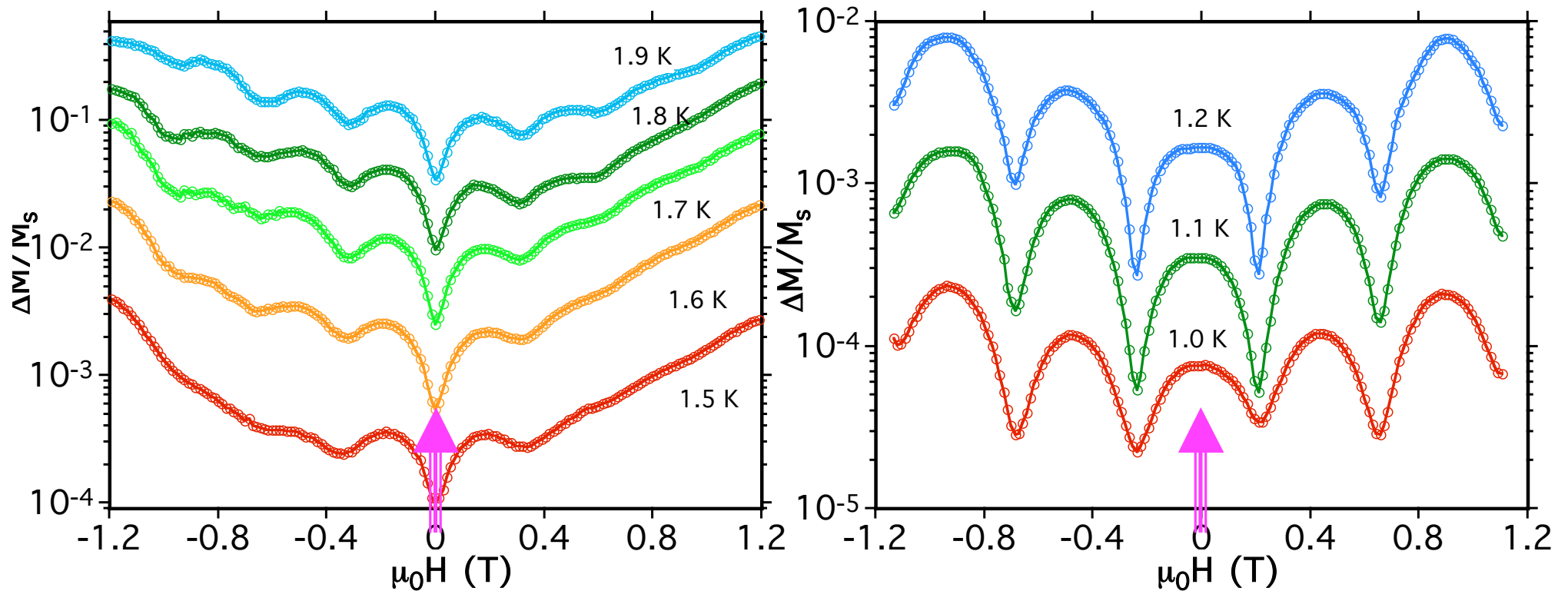


W. Wernsdorfer and R. Sessoli, *Science* 284, 133 (1999)

# Quantum phase interference and spin parity in $\text{Mn}_{12}$

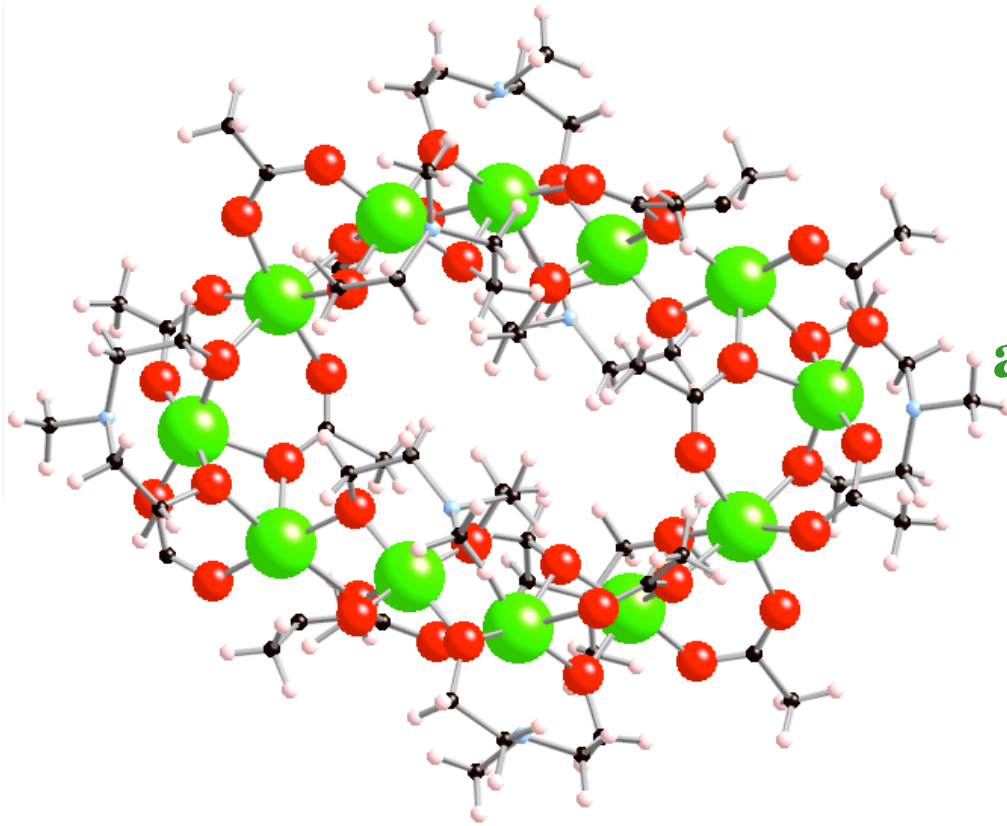
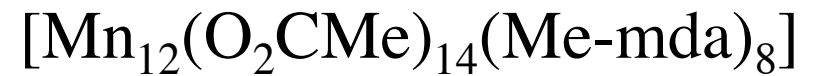
$[\text{Mn}_{12}]^{-e}$   
 $S = 19/2$

$[\text{Mn}_{12}]^{-2e}$   
 $S = 10$



W. Wernsdorfer, N. E. Chakov, G. Christou,  
PRL 95, 037203 (2005)

# " $Mn_{12}$ -mda wheel"



alternating  $Mn^{2+}$  and  $Mn^{3+}$  ions

triclinic space group  $P\bar{1}$

$$S = 7$$

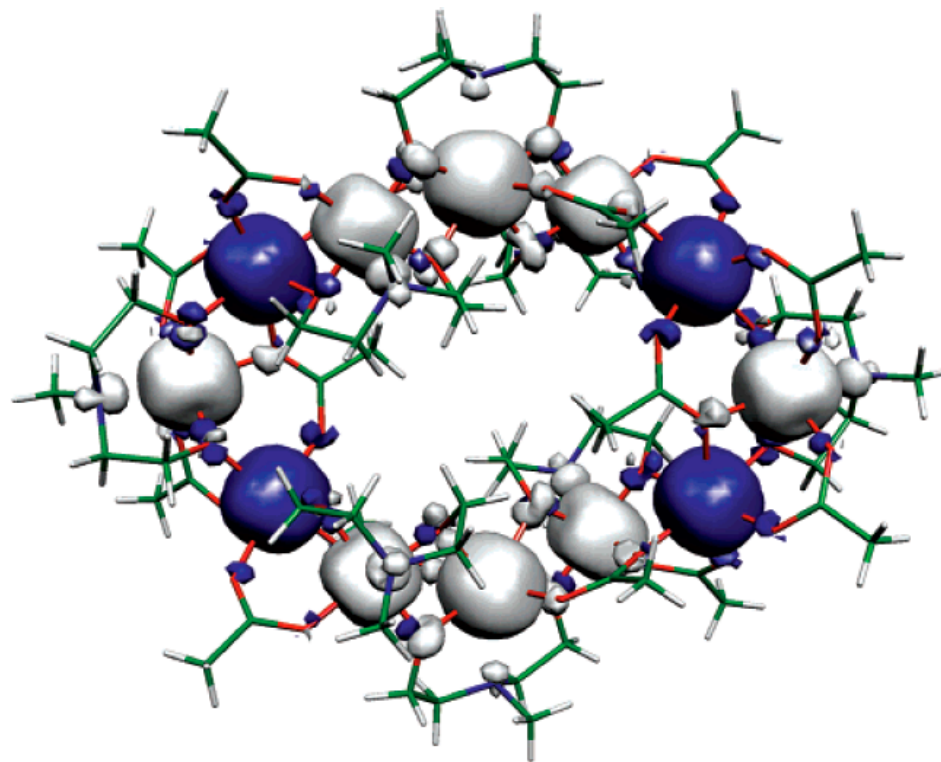
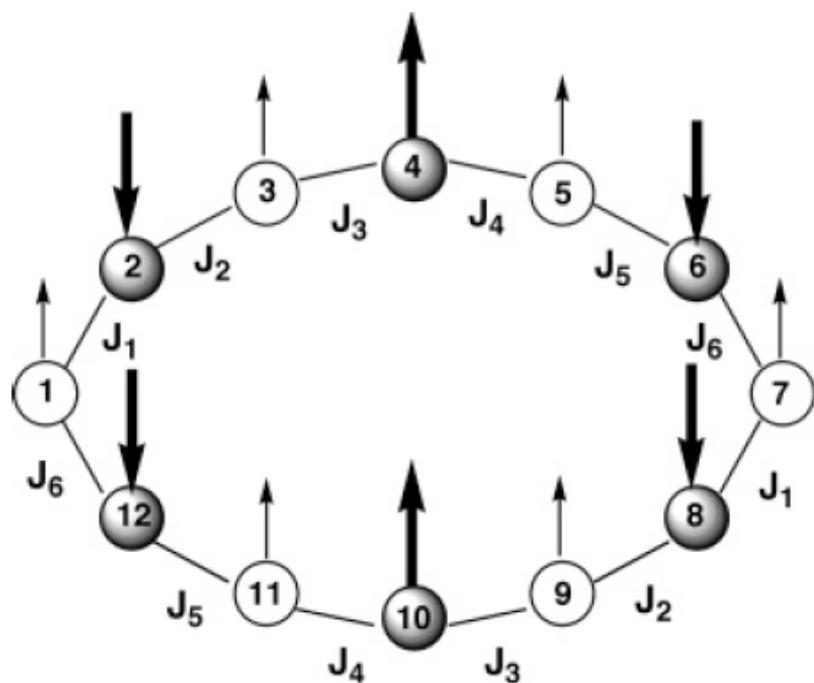
possibility of DM interactions

D. Foguet-Albiol et al., *Angew. Chem., Int. Ed. Engl.* 44, 897 (2005)

# Theoretical Study of the Magnetic Properties of an $Mn_{12}$ Single-Molecule Magnet with a Loop Structure: The Role of the Next-Nearest Neighbor Interactions<sup>†</sup>

*J. Chem. Theory Comput.* **2007**, *3*, 782–788

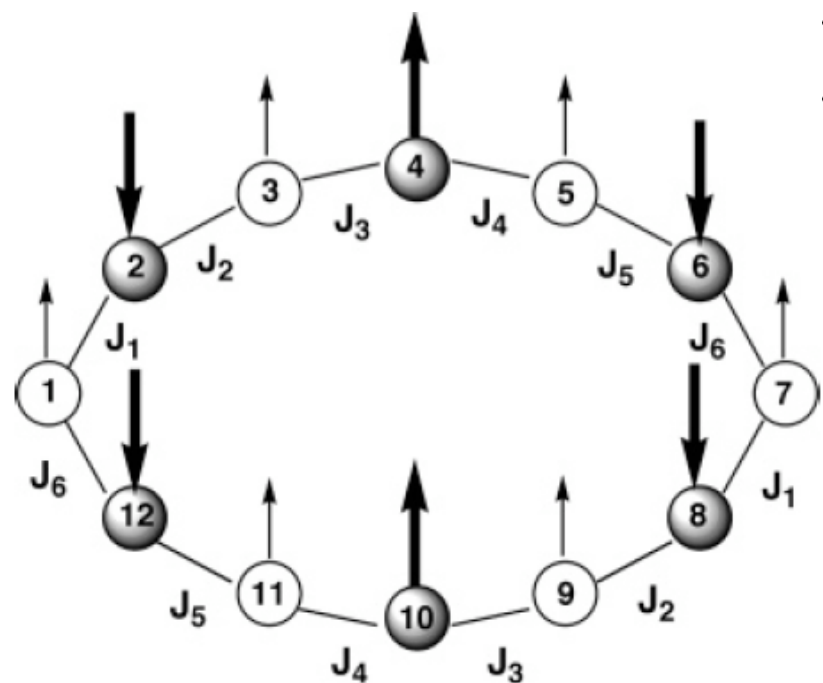
Joan Cano,<sup>§</sup> Ruben Costa,<sup>‡</sup> Santiago Alvarez,<sup>‡</sup> and Eliseo Ruiz<sup>\*,‡</sup>



# Theoretical Study of the Magnetic Properties of an Mn<sub>12</sub> Single-Molecule Magnet with a Loop Structure: The Role of the Next-Nearest Neighbor Interactions<sup>†</sup>

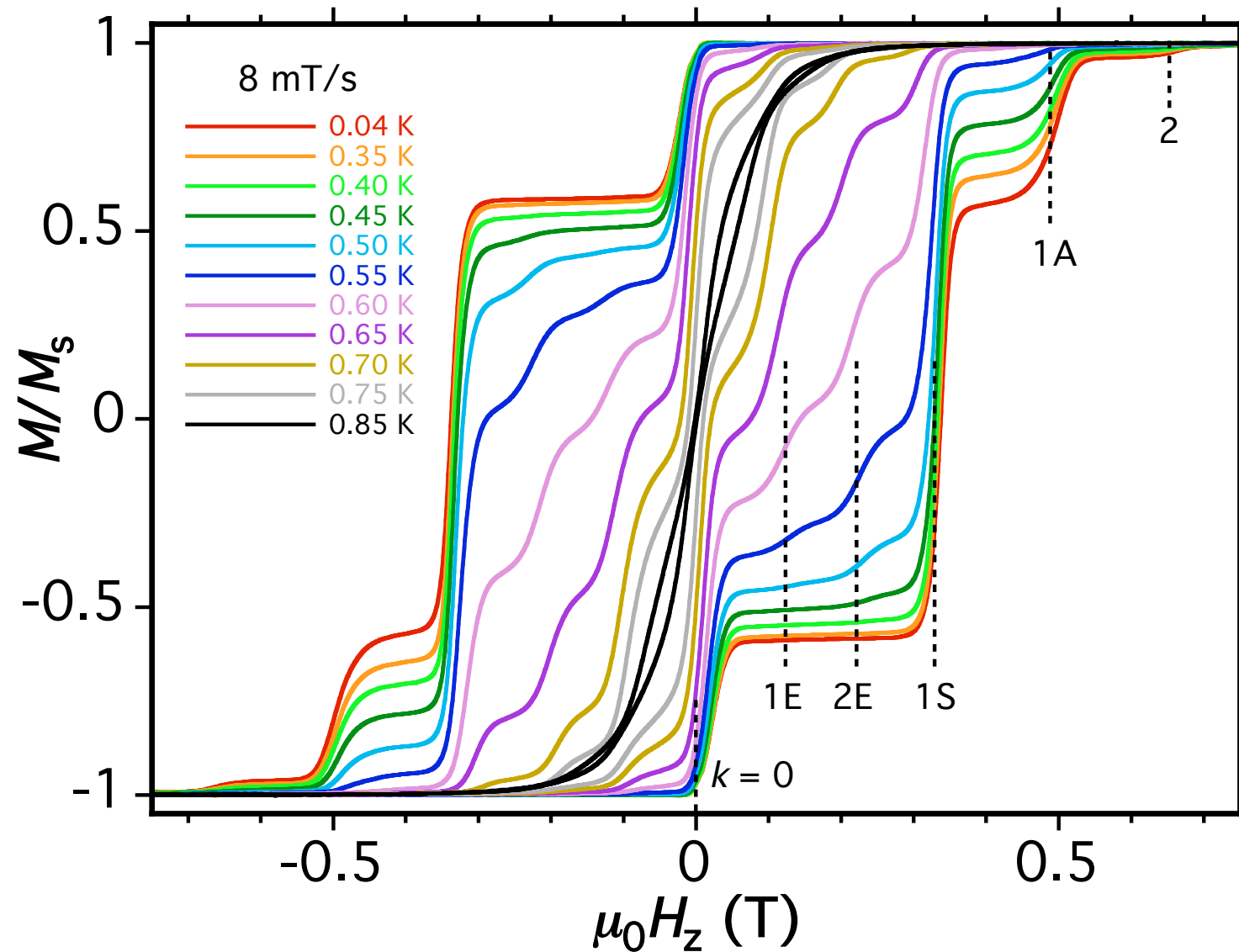
*J. Chem. Theory Comput.* **2007**, *3*, 782–788

Joan Cano,<sup>§</sup> Ruben Costa,<sup>‡</sup> Santiago Alvarez,<sup>‡</sup> and Eliseo Ruiz<sup>\*,‡</sup>



	(Siesta code)	(Gaussian code)	dinuclear models
	PBE	(cm <sup>-1</sup> ) B3LYP <sup>c</sup>	B3LYP-m <sup>d</sup>
J <sub>1</sub>	-11.4(-6.0)	-4.1(-5.6)	-2.8
J <sub>2</sub>	-18.3(-14.9)	-8.0 (-2.5)	-9.2
J <sub>3</sub>	+6.5 (+10.9)	+4.6 (+6.3)	+7.0
J <sub>4</sub>	+6.6 (+9.2)	+4.6 (+5.4)	+8.0
J <sub>5</sub>	-8.4 (-5.4)	-2.8 (-5.9)	-5.0
J <sub>6</sub>	-0.9 (+1.2)	-7.0 (-3.5)	+0.04

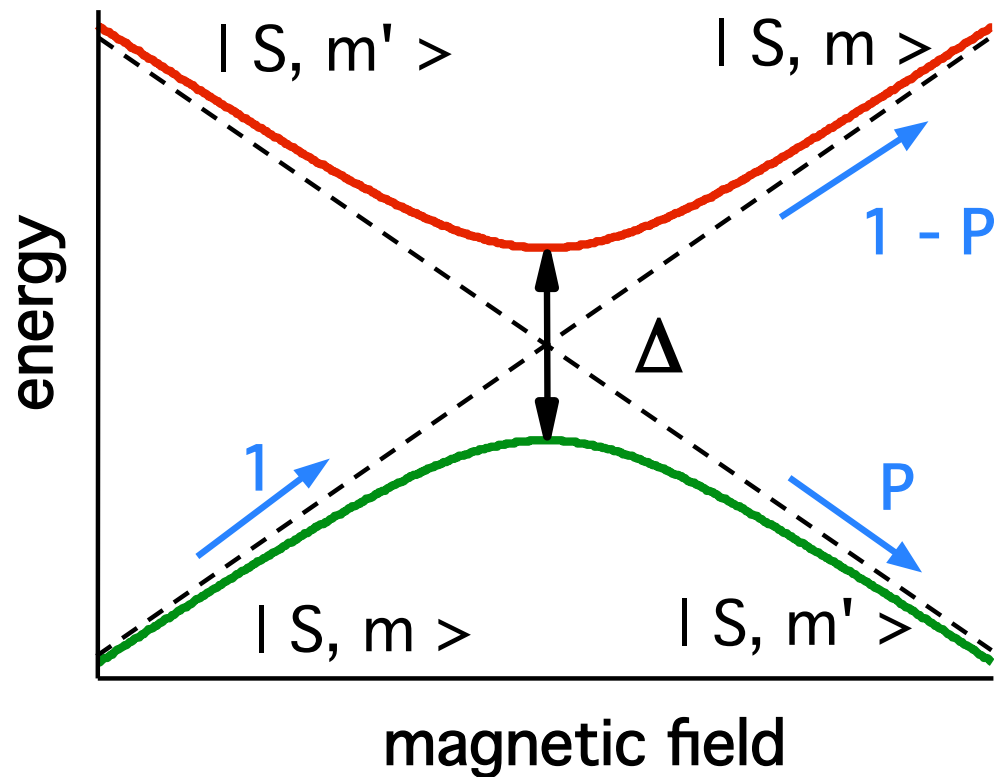
# Hysteresis loops of Mn<sub>12</sub> wheels



W. Wernsdorfer, T. C. Stamatatos, G. Christou, PRL **101**, 237204 (2008)

# Tunneling probability at an avoided level crossing

## Landau-Zener model (1932)



$$P = 1 - \exp\left[-c \frac{\Delta^2}{dH/dt}\right]$$

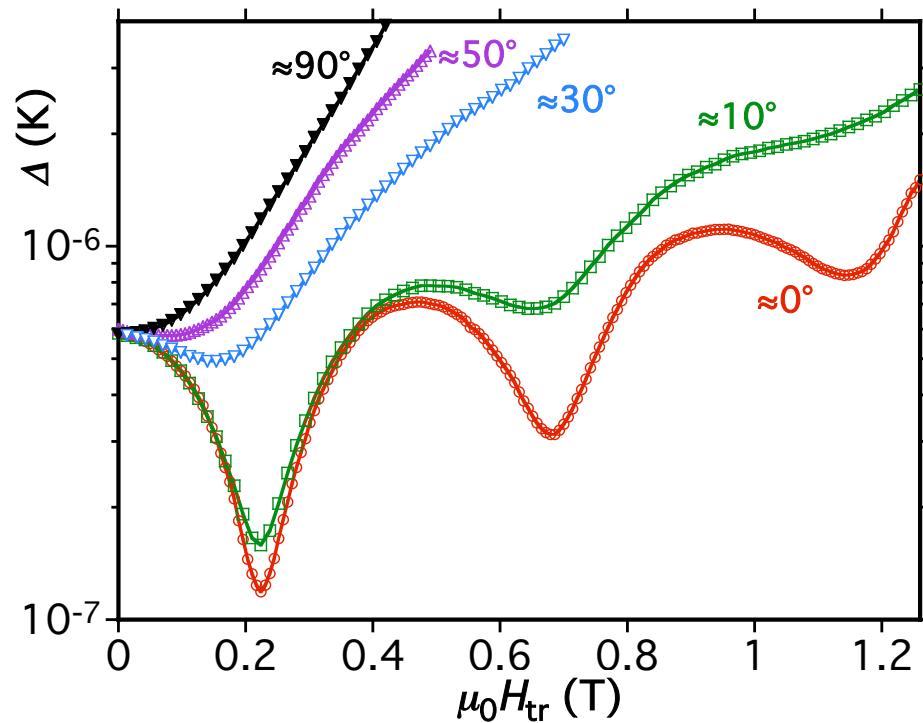
$$c = \frac{\pi}{2\hbar g\mu_B |m - m'| \mu_0}$$

L. Landau, *Phys. Z. Sowjetunion* **2**, 46 (1932); C. Zener, *Proc. R. Soc. London, Ser. A* **137**, 696, (1932);  
 E.C.G. Stückelberg, *Helv. Phys. Acta* **5**, 369 (1932); S. Miyashita, *J. Phys. Soc. Jpn.* **64**, 3207 (1995); ...

# Transverse field dependence of the tunnel splitting

## $H = 0$ transition ( $k = 0$ )

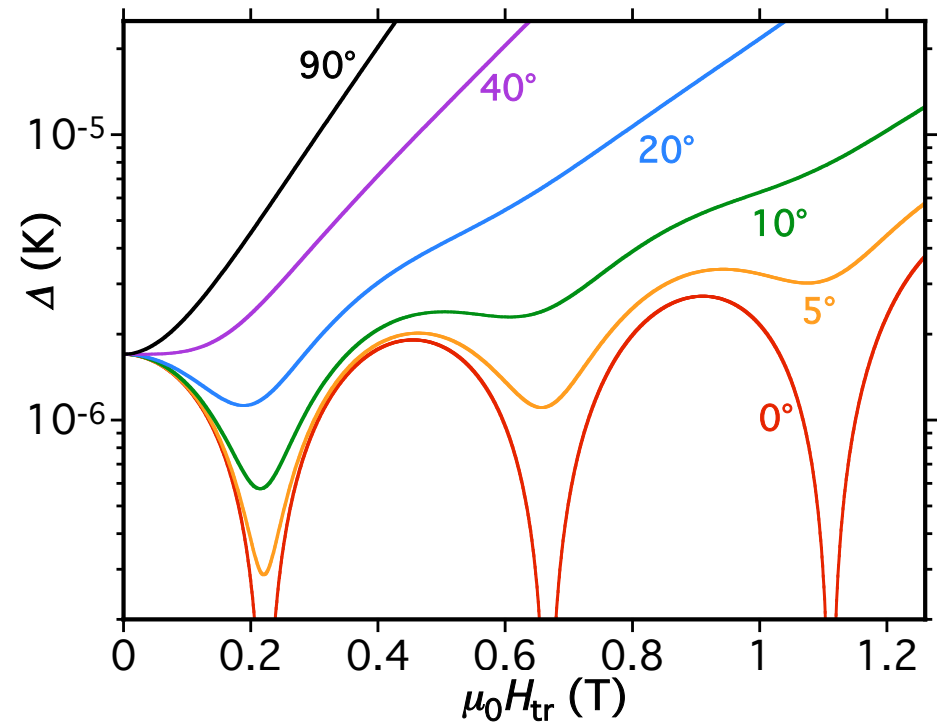
experiment



PRL **101**, 237204 (2008)

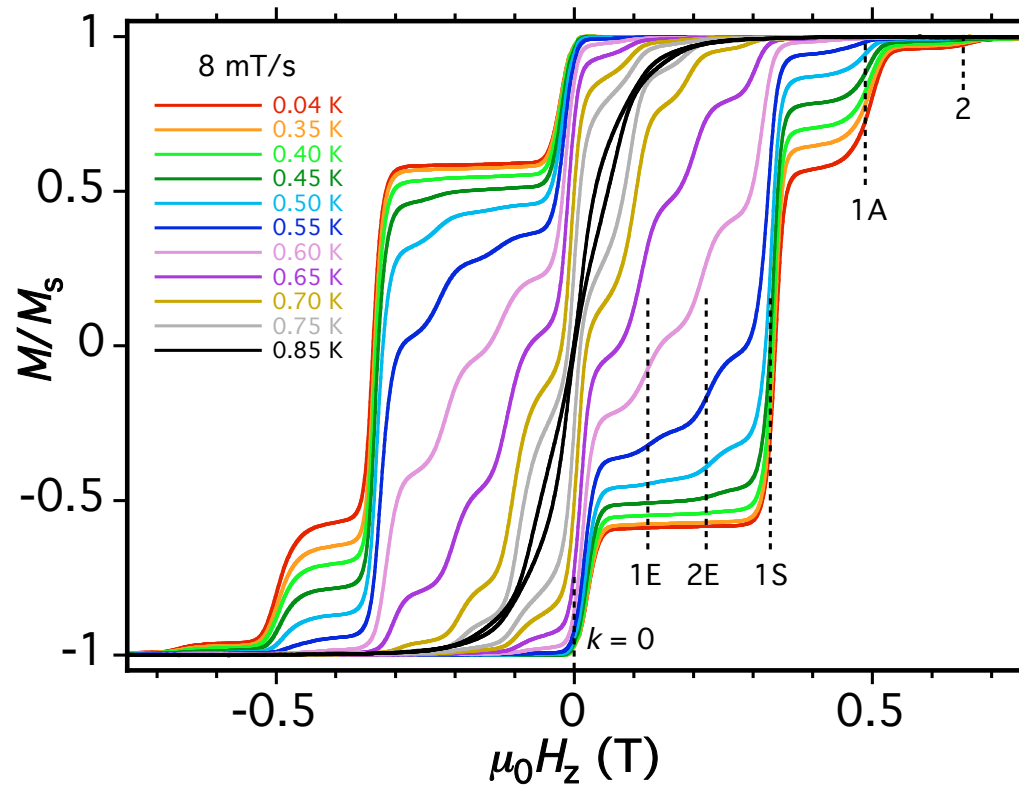
theory

$S=7$ ,  $D=-0.462\text{K}$ ,  $E=0.082\text{K}$

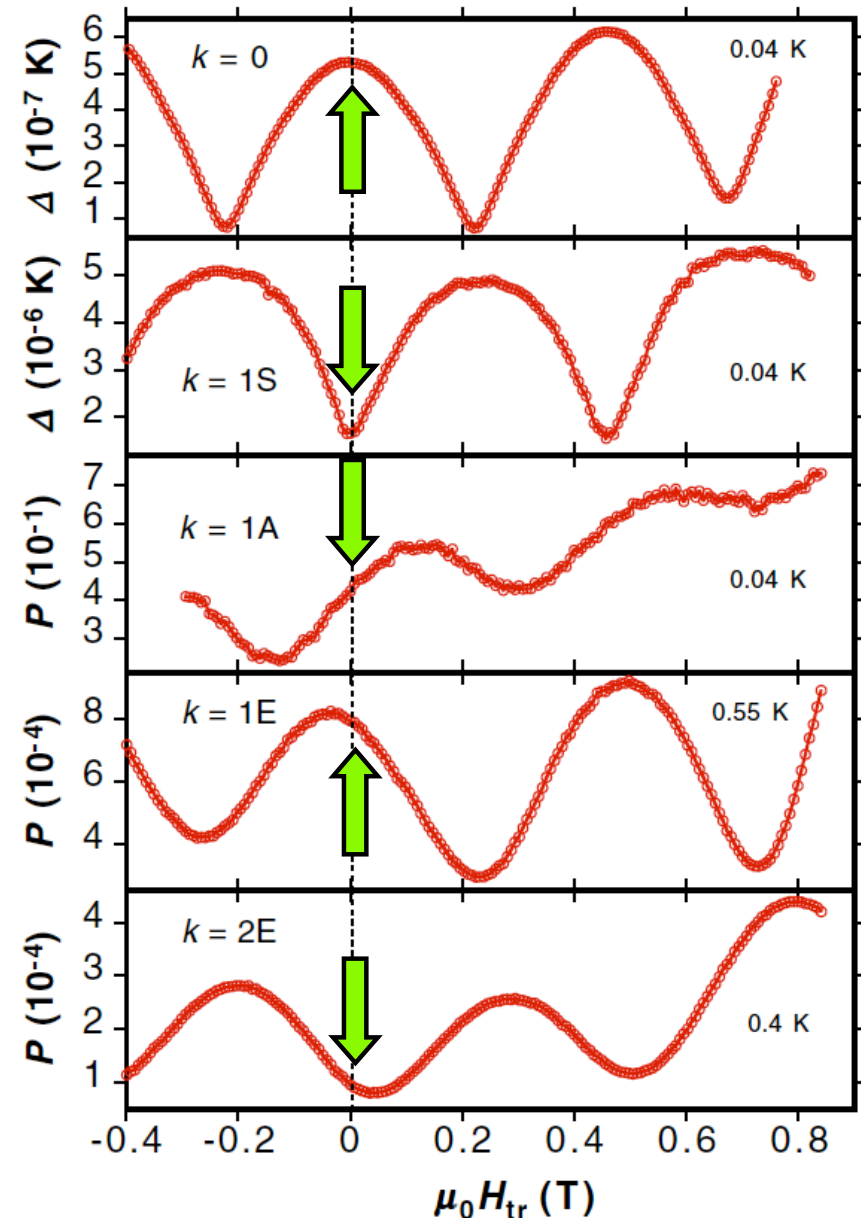


the giant spin model  $S=7$   
or the dimer model gives same plot

# Transverse field dependence of the tunnel splitting



PRL 101, 237204 (2008)



# Dimer model of two coupled $S = 7/2$

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{\text{ex}}$$

$$\mathcal{H}_i = -DS_{i,z}^2 + E(S_{i,x}^2 - S_{i,y}^2) - g\mu_B\mu_0\vec{S}_i \cdot \vec{H}$$

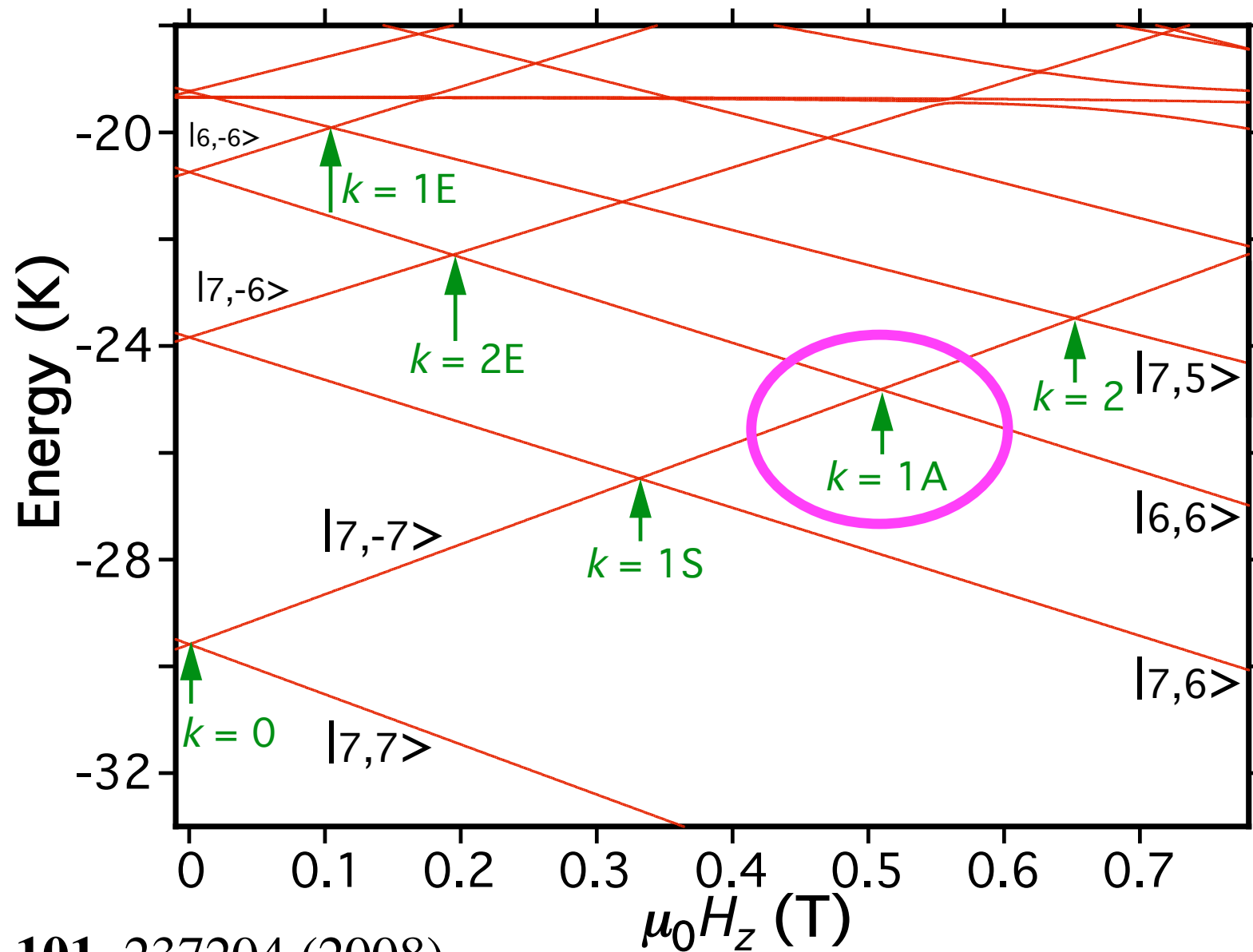
$$\mathcal{H}_{\text{ex}} = J\vec{S}_1 \cdot \vec{S}_2 + \vec{D}_{1,2} \cdot (\vec{S}_1 \times \vec{S}_2)$$

Dzyaloshinskii-Moriya vector



PRL **101**, 237204 (2008)

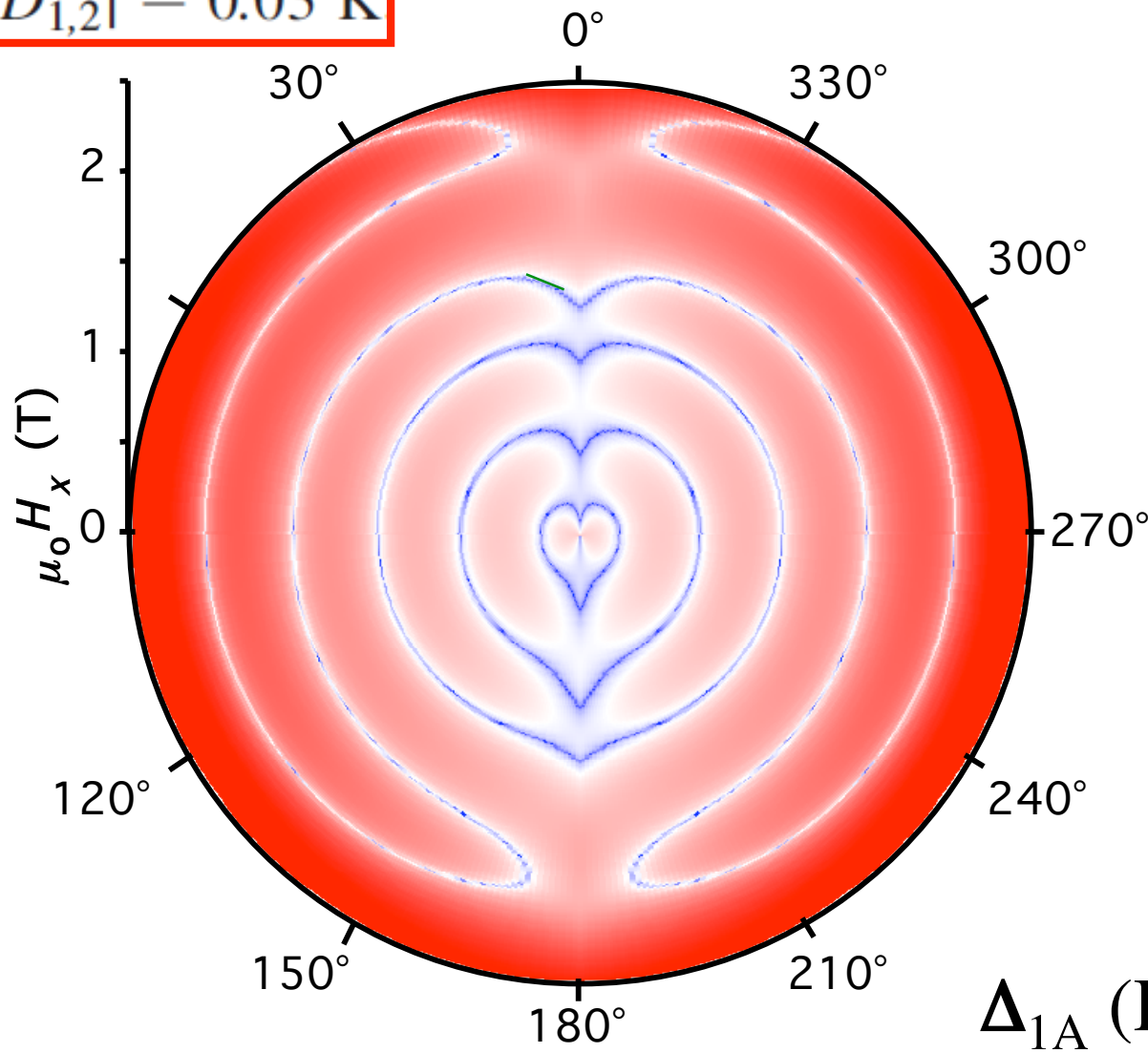
# Zeeman diagram of two coupled $S = 7/2$



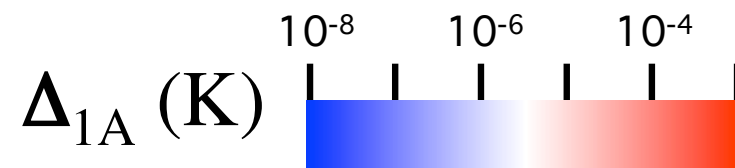
PRL **101**, 237204 (2008)

# Tunnel splitting for $k = 1\text{\AA}$ as a function of transverse field $H_x$ and the angle of the DM vector

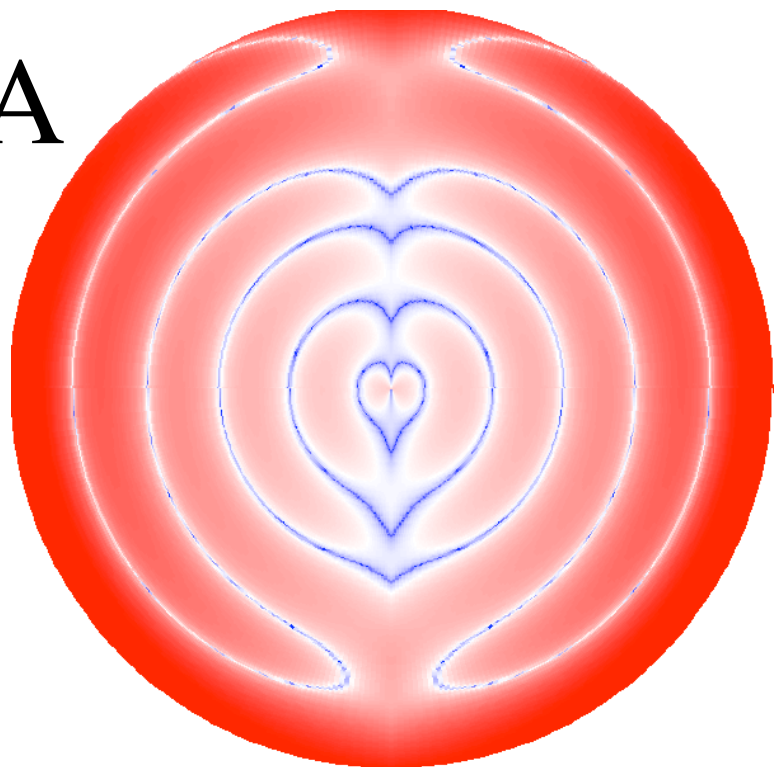
$$|\vec{D}_{1,2}| = 0.03 \text{ K}$$



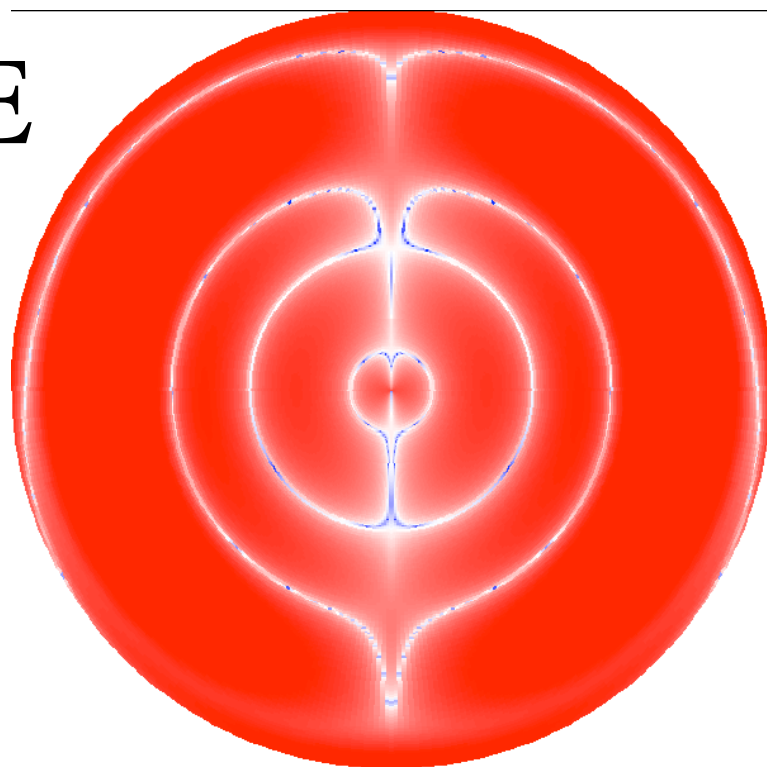
PRL **101**, 237204 (2008)



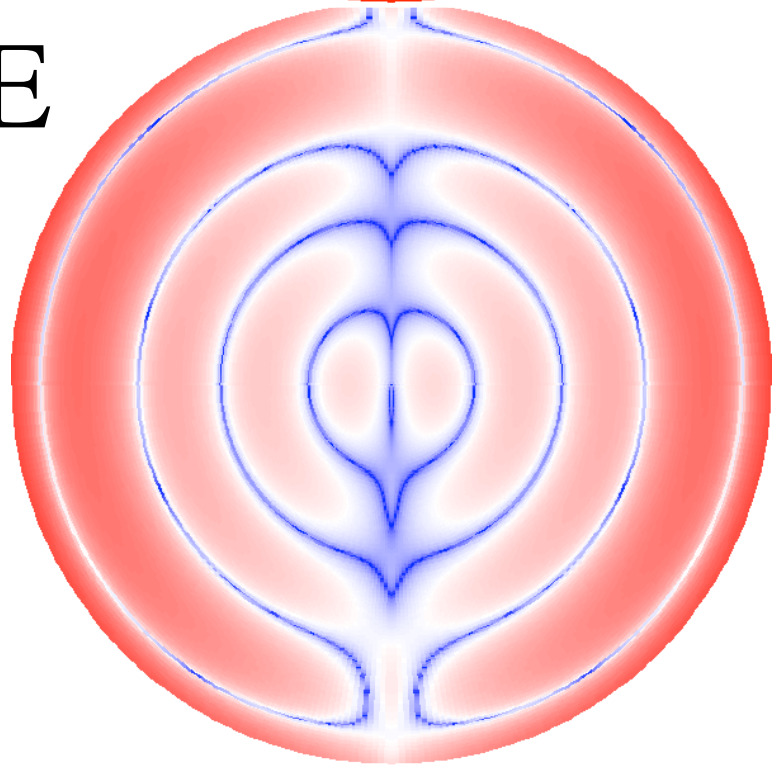
1A



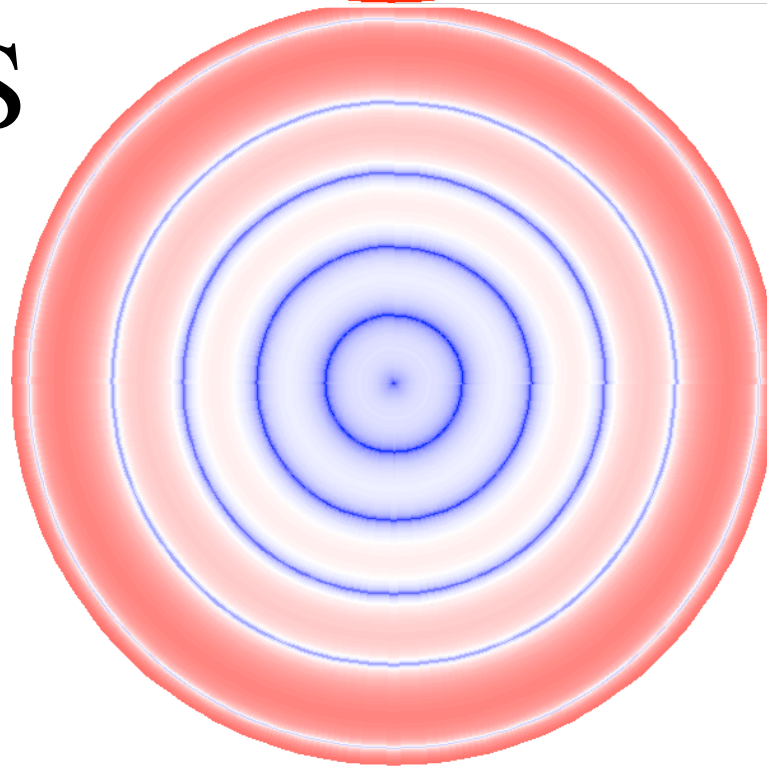
1E



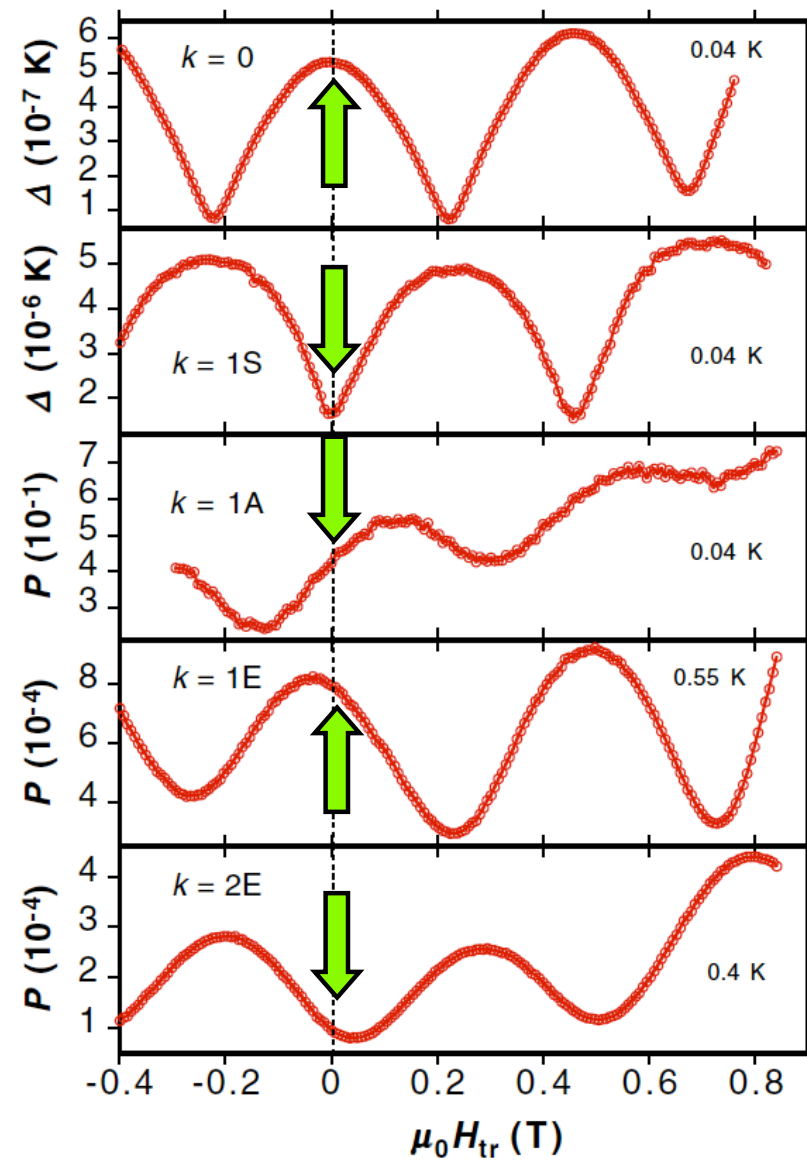
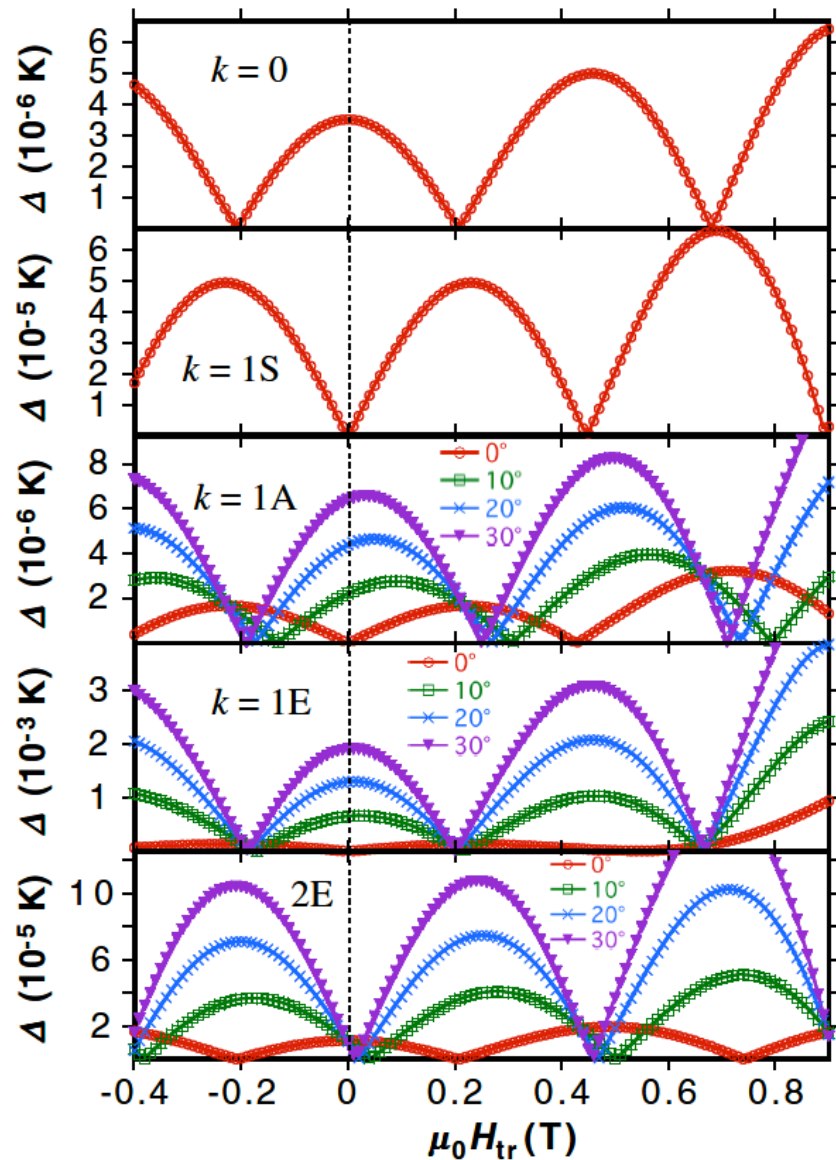
2E



1S

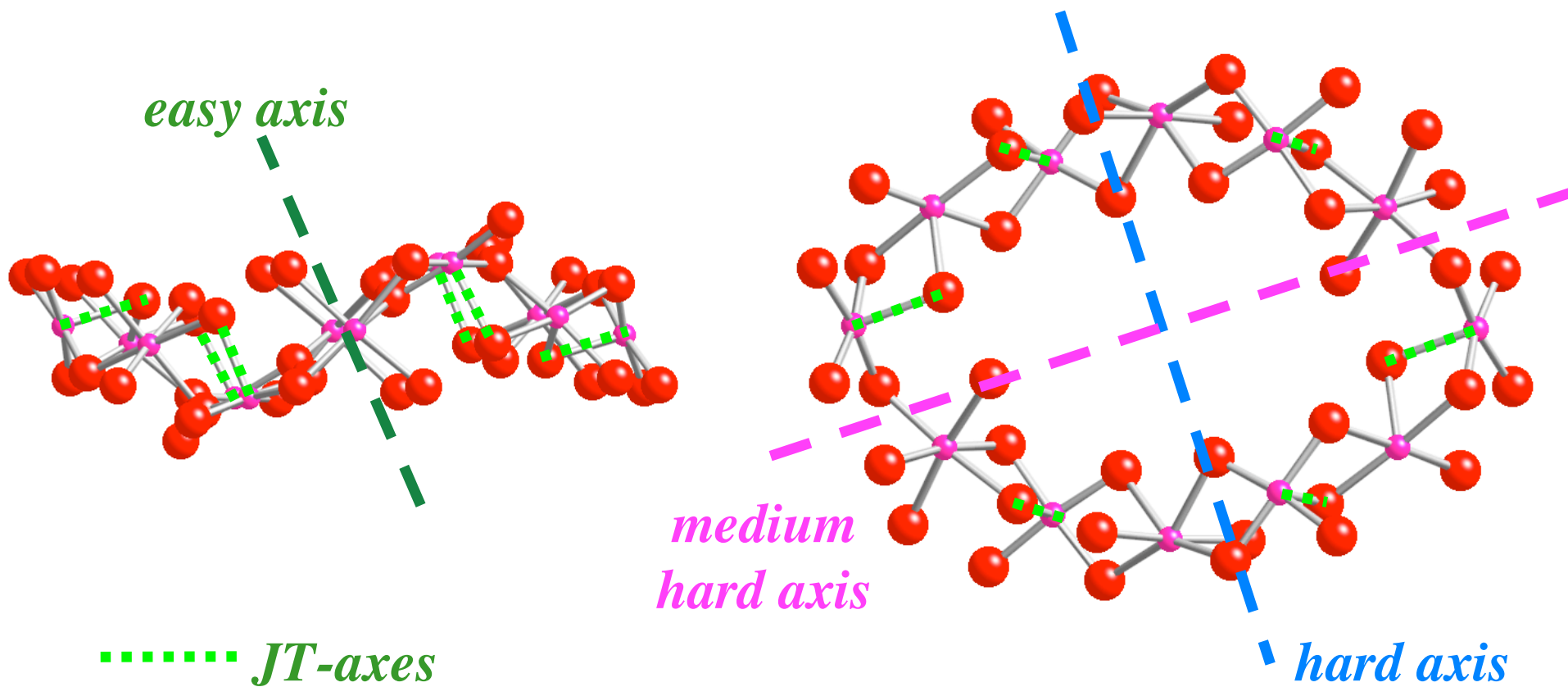
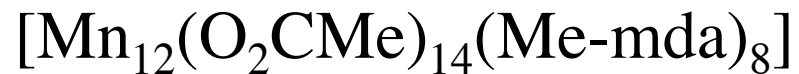


# Transverse field dependence of the tunnel splitting



PRL 101, 237204 (2008)

# " $Mn_{12}$ -mda wheel"

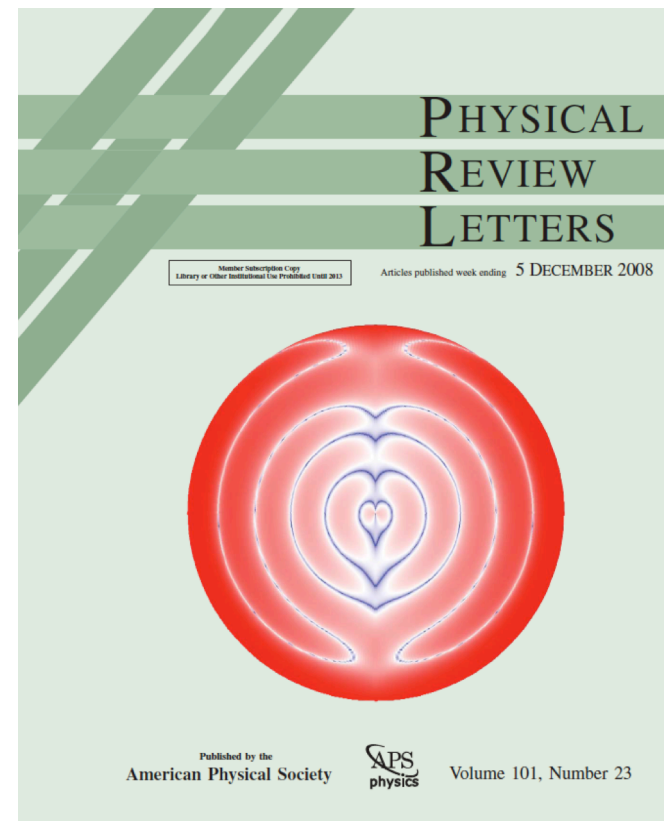
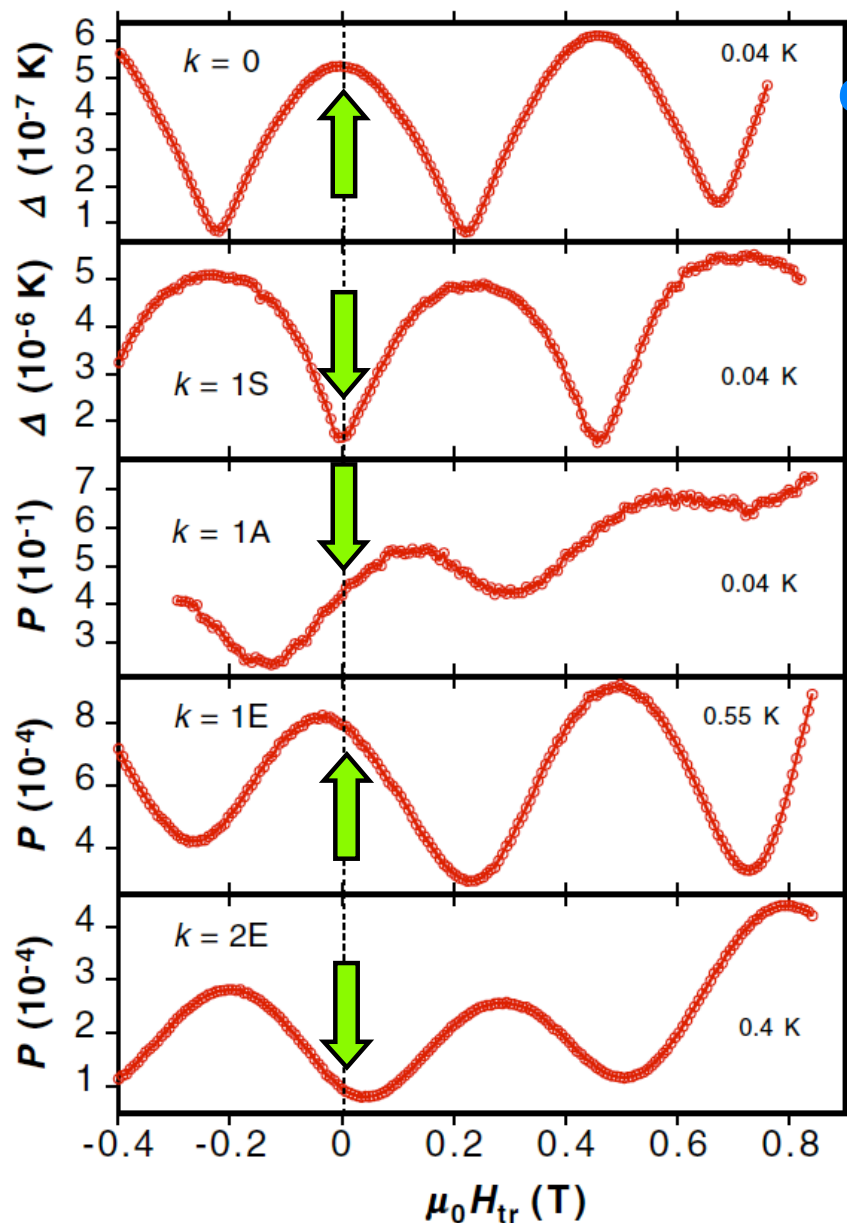


**side vue**

**top vue**

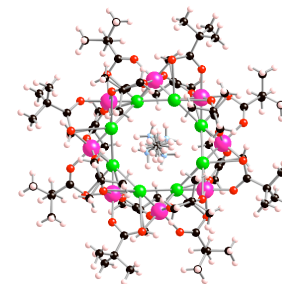
# Conclusion

Influence of the Dzyaloshinskii-Moriya exchange interaction on quantum phase interference of spins



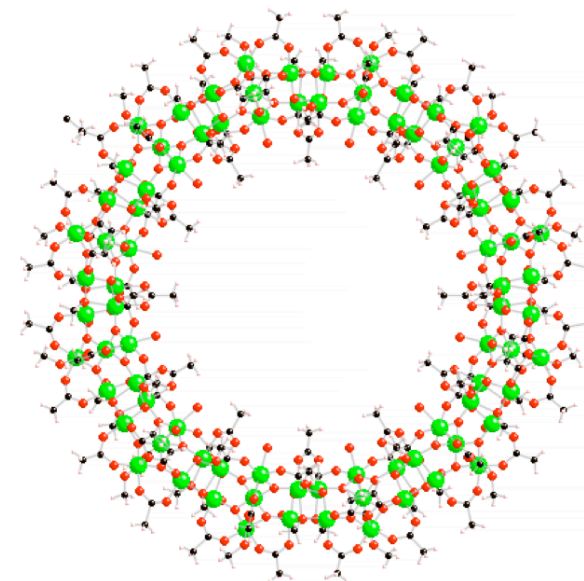
W. Wernsdorfer, T. C. Stamatatos,  
G. Christou, PRL **101**, 237204 (2008)

# Collaborations (Chemistry)



Winpenny, 2003

**Mn<sub>84</sub>**



Christou, 2004

Group of G. Christou, Dept. of Chemistry, Florida  
Group of E. Brechin, Univ. of Edinburgh, UK  
Group of R. Sessoli, D. Gatteschi, Univ. of Firenze, Italy  
Group of R. Clerac & C. Coulon, Univ. of Bordeaux  
Group of D. Hendrickson, Dept. of Chemistry, San Diego  
Group of A. Powell, Univ. Karlsruhe, Germany  
Group of T. Mallah, Univ. Paris Sud, Orsay  
Group of M. Yamashita, Tokyo Univ.  
Group of R. Winpenny, Univ. of Manchester, UK  
Group of A. Cornia, Univ. of Modena, Italy  
Group of A. Müller, Univ. de Bielefeld, Germany  
Group of V. Marvaud & M. Verdaguer  
Univ. P. et M. Curie, Paris  
Group of J.P. Costes, Univ. of Toulouse, France  
Group of K. Dunbar, Univ. of Texas, US  
Group of M. Julve, Univ. of Valence, Spain  
Group of P. Mialane, Univ. of Versailles, France  
Group of E. Coronado, Univ. of Valence, Spain  
Group of M. Ruben, FZ Karlsruhe, Germany

and many more ...



# Support



European  
Research  
Council