The Abdus Salam
International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

International Atomic Energy Agency

SMR.1664 - 5

Conference on Single Molecule Magnets and Hybrid Magnetic Nanostructures

27 June - 1 July 2005

Inelastic Neutron Scattering of Single Molecule Magnets and Antiferromagnetic Wheels

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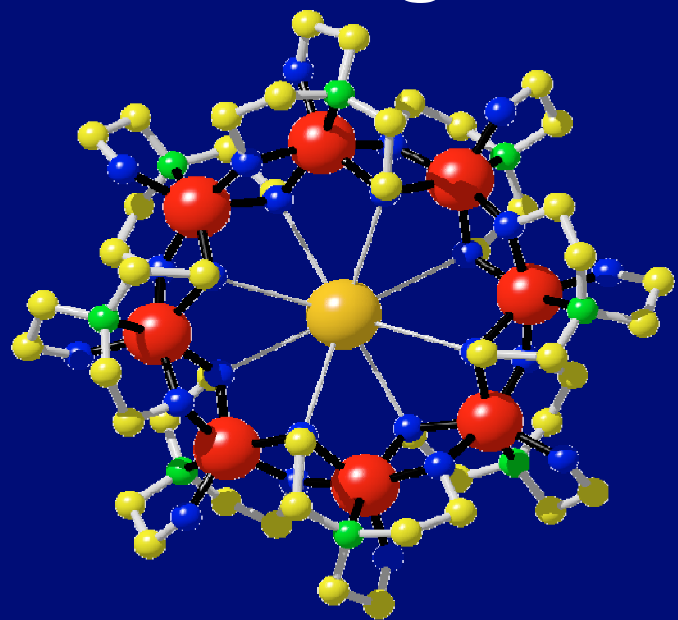
Inelastic Neutron Scattering of Single Molecule Magnets and Antiferromagnetic Wheels



Hans U. Güdel and Oliver Waldmann

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Trieste, June 27 - July 1, 2005

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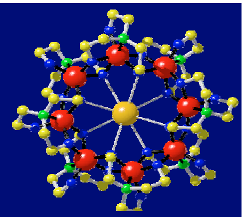
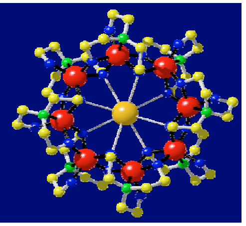
Inelastic Neutron Scattering of Single Molecule Magnets and Antiferromagnetic Wheels



- Inelastic neutron scattering
- Exchange interactions
- Anisotropy and zero-field splittings
- Relaxation dynamics
- Tunneling of the Neel vector in antiferromagnetic wheels
- Conclusions

Acknowledgments



- Hanspeter Andres
- Roland Bircher
- Grégory Chaboussant
- Chris Dobe
- Graham Carver
- Stefan Ochsenbein
- Andreas Sieber
- Oliver Waldmann

- Andreas Honecker
- Bruce Normand
- George Christou and his group
- Eugenio Coronado and his group
- Richard Winpenny and his group

- Albert Furrer INS

- Swiss National Science Foundation
- European Union

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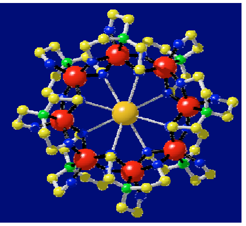
Optical Spectroscopy Versus Neutron Spectroscopy



Optical Spectroscopy

- Absorption
- Emission
- Electronic Raman Scattering
- EPR

No momentum transfer

$\Delta S = 0$

$\Delta M_S = 0$ $\Delta M_S = \pm 1$

Neutron Spectroscopy

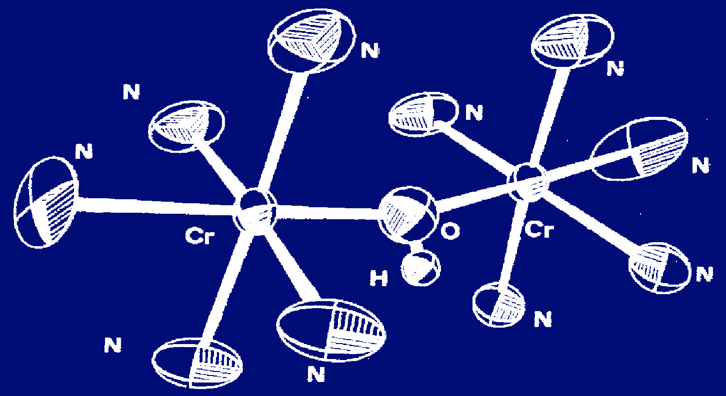
- Inelastic Neutron Scattering

Momentum transfer

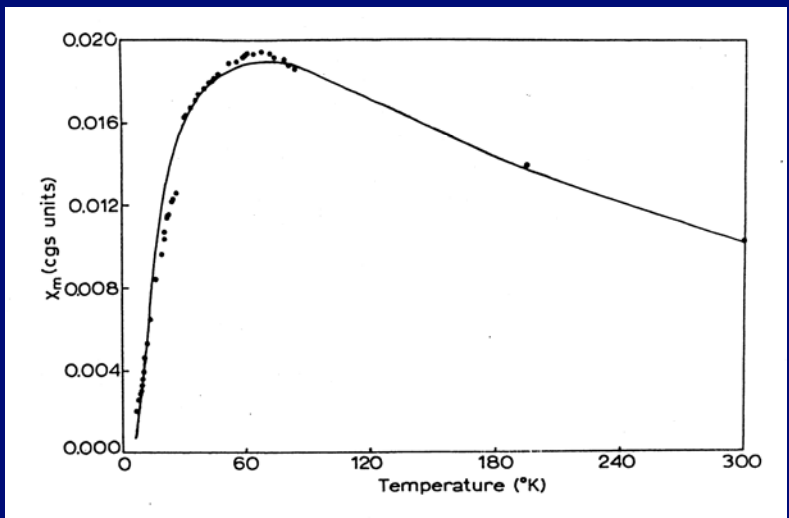
$\Delta S = 0$ $\Delta S = \pm 1$

$\Delta M_S = 0$ $\Delta M_S = \pm 1$

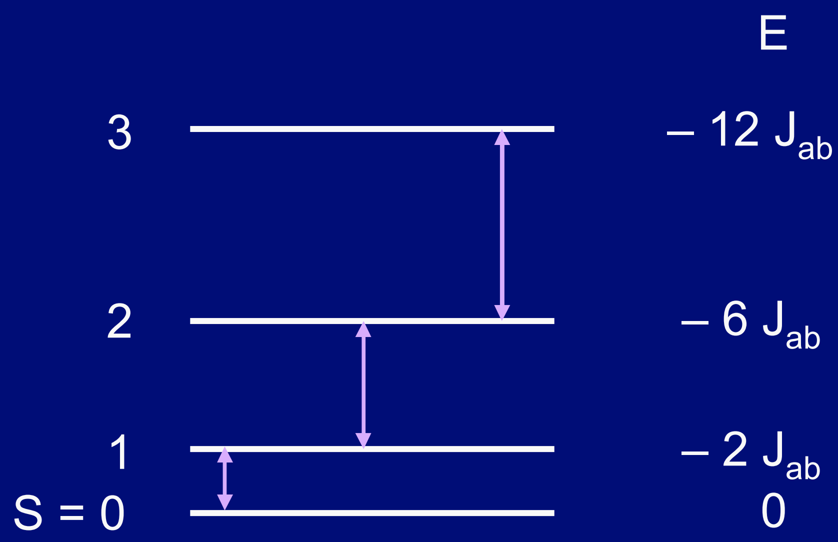
Acid Rhodo Complex
Bis-μ-hydroxo-pentamine chromium(III)



$$H_{ex} = -2 J_{ab}\, \mathbf{S}_\mathbf{a} \cdot \mathbf{S}_\mathbf{b}$$



W.E. Hatfield et al. 1973



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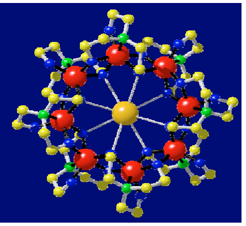
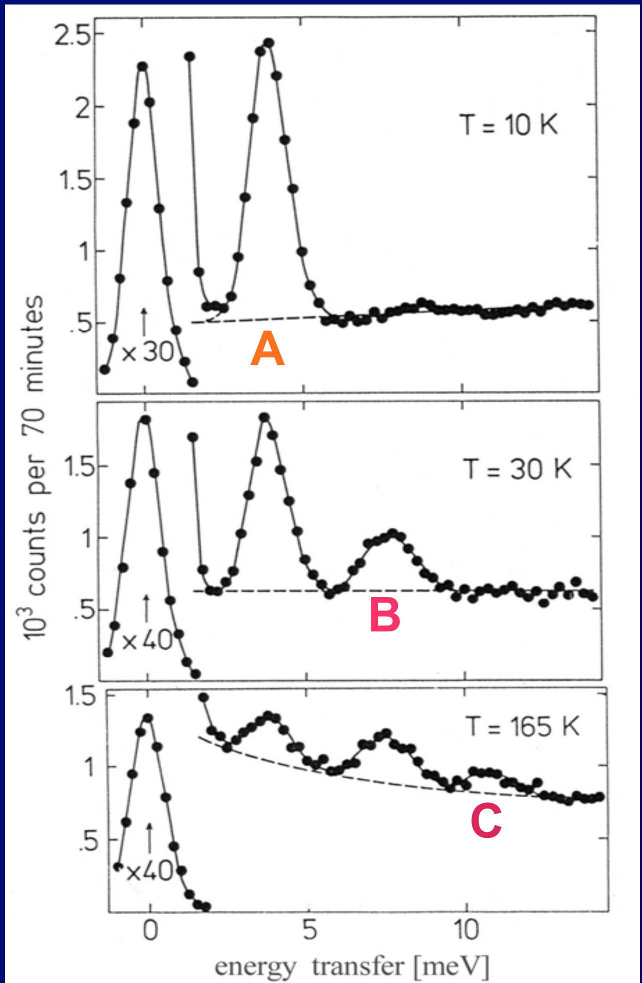
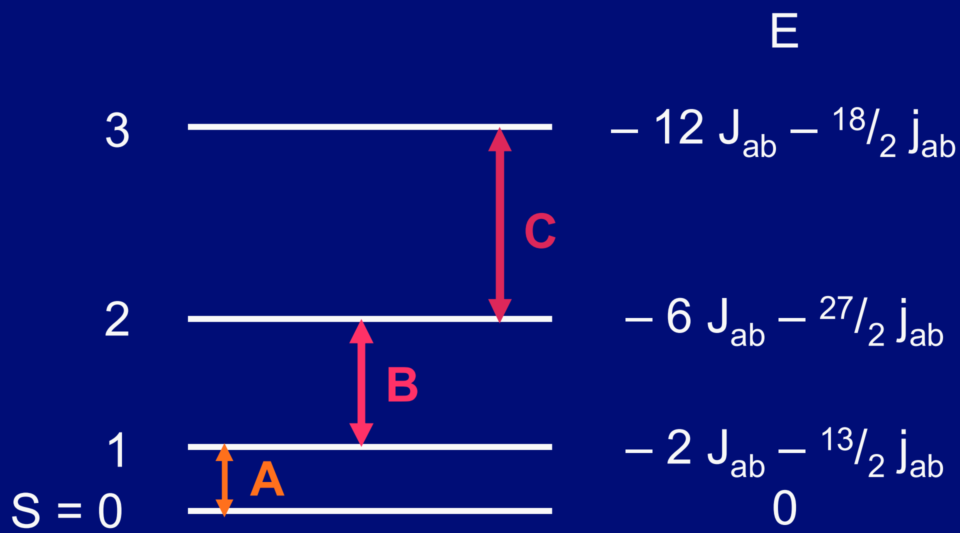
$[(ND_3)_5Cr(OD)Cr(ND_3)_5]Cl_5 \cdot D_2O$
Inelastic Neutron Scattering



Diorit Würenlingen
3-ax, λ = 2.34 Å



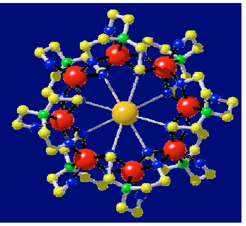


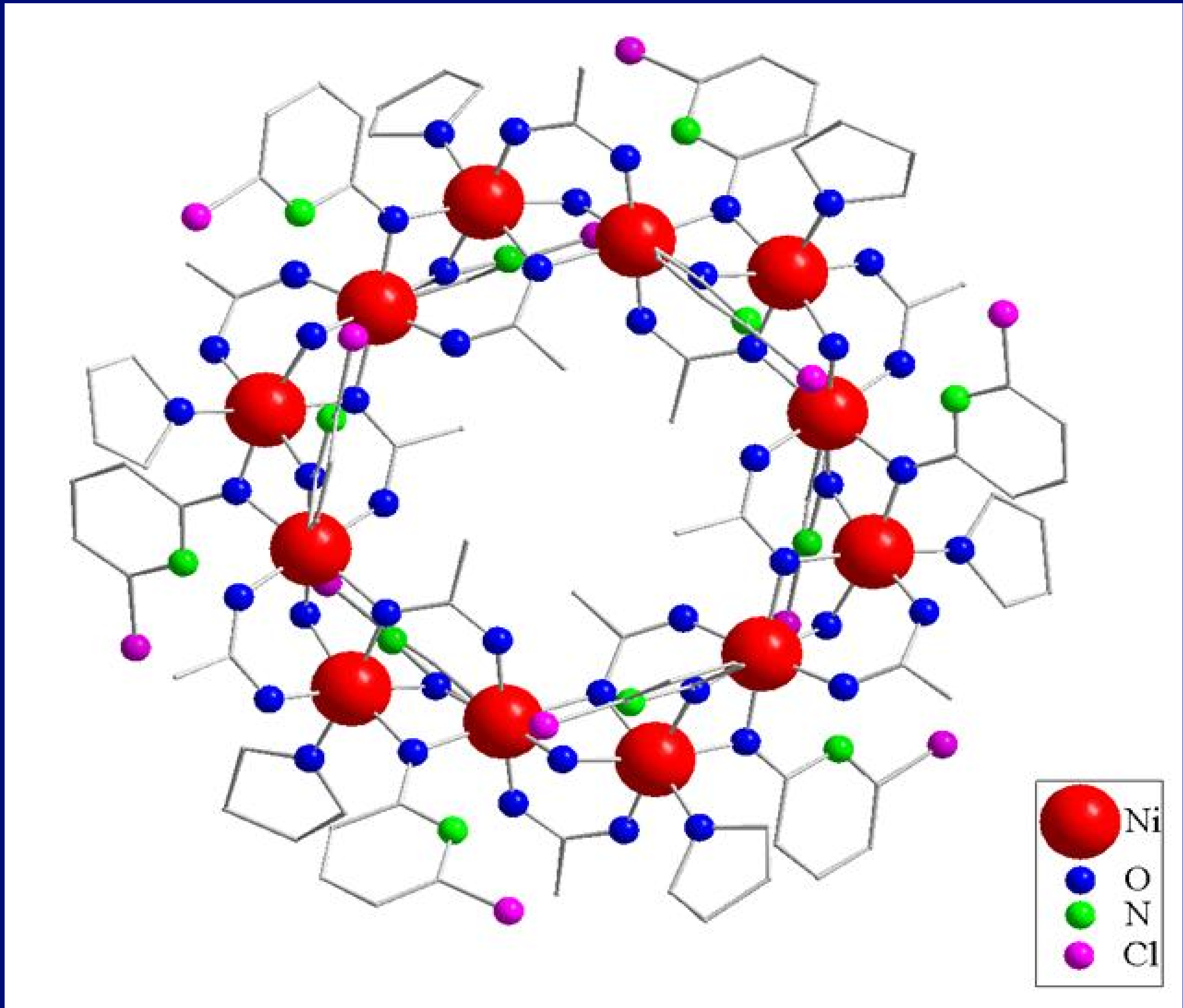
$$H_{ex} = -2 J_{ab} \mathbf{S_a} \cdot \mathbf{S_b} + j_{ab} (\mathbf{S_a} \cdot \mathbf{S_b})^2$$

$$-2 J_{ab} = 3.84 \pm 0.12 \text{ meV}$$
$$+ j_{ab} = 0.021 \pm 0.023 \text{ meV}$$

Hans U. Güdel, Albert Furrer 1977

$[Ni_{12}(OAc)_{12}(chp)_{12}(H_2O)_6(THF)_6]$ · 9THF





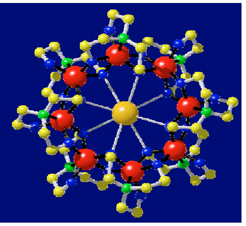
chp = 6-chloro-pyridone

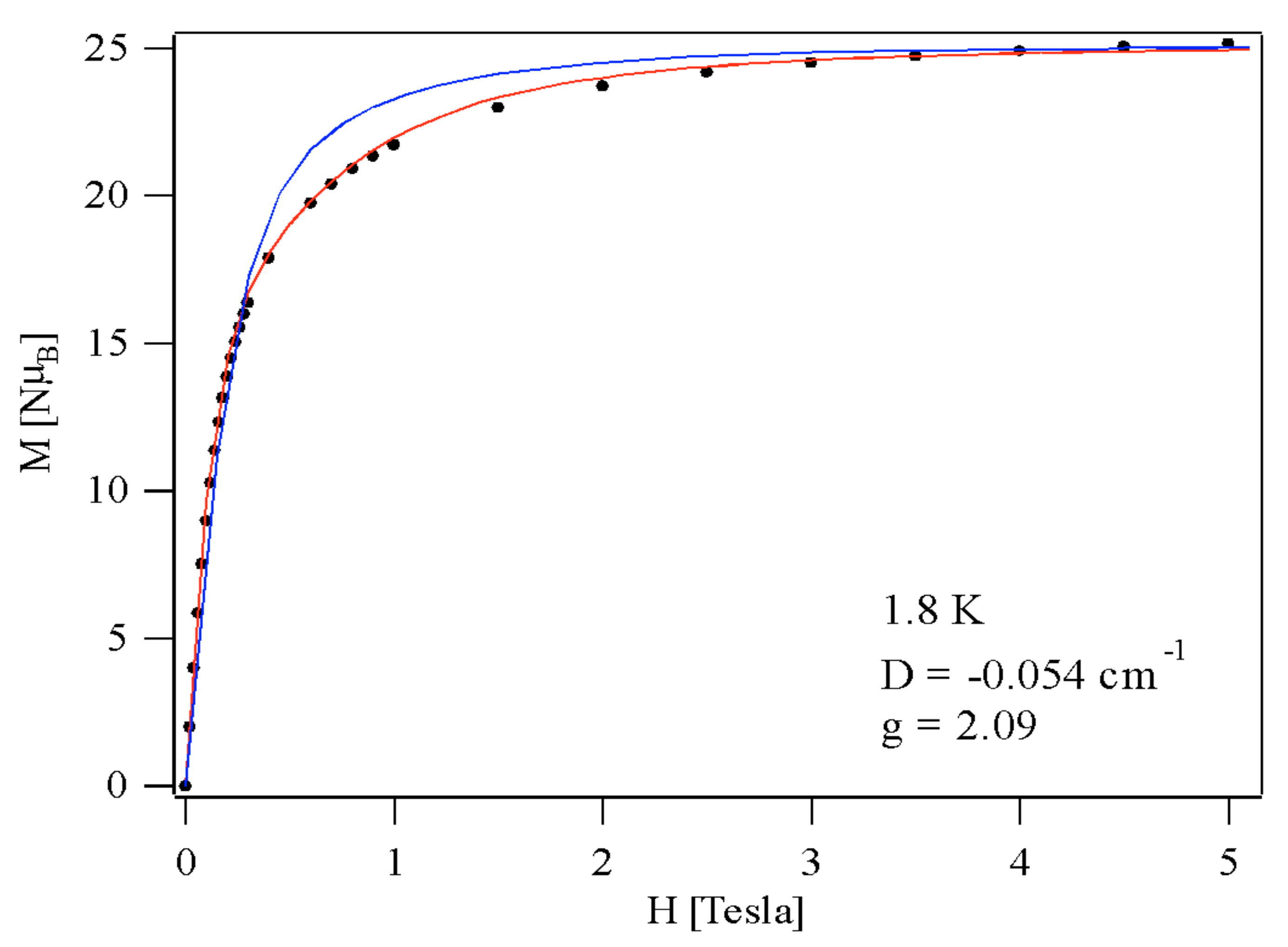
OAc = acetate

THF = tetrahydrofurane

Grégory Chaboussant, Hanspeter Andres, Mark Murrie, Richard Winpenny

$[Ni_{12}(OAc)_{12}(chp)_{12}(H_2O)_6(THF)_6]$ · 9THF

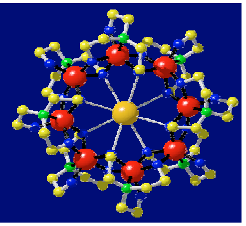




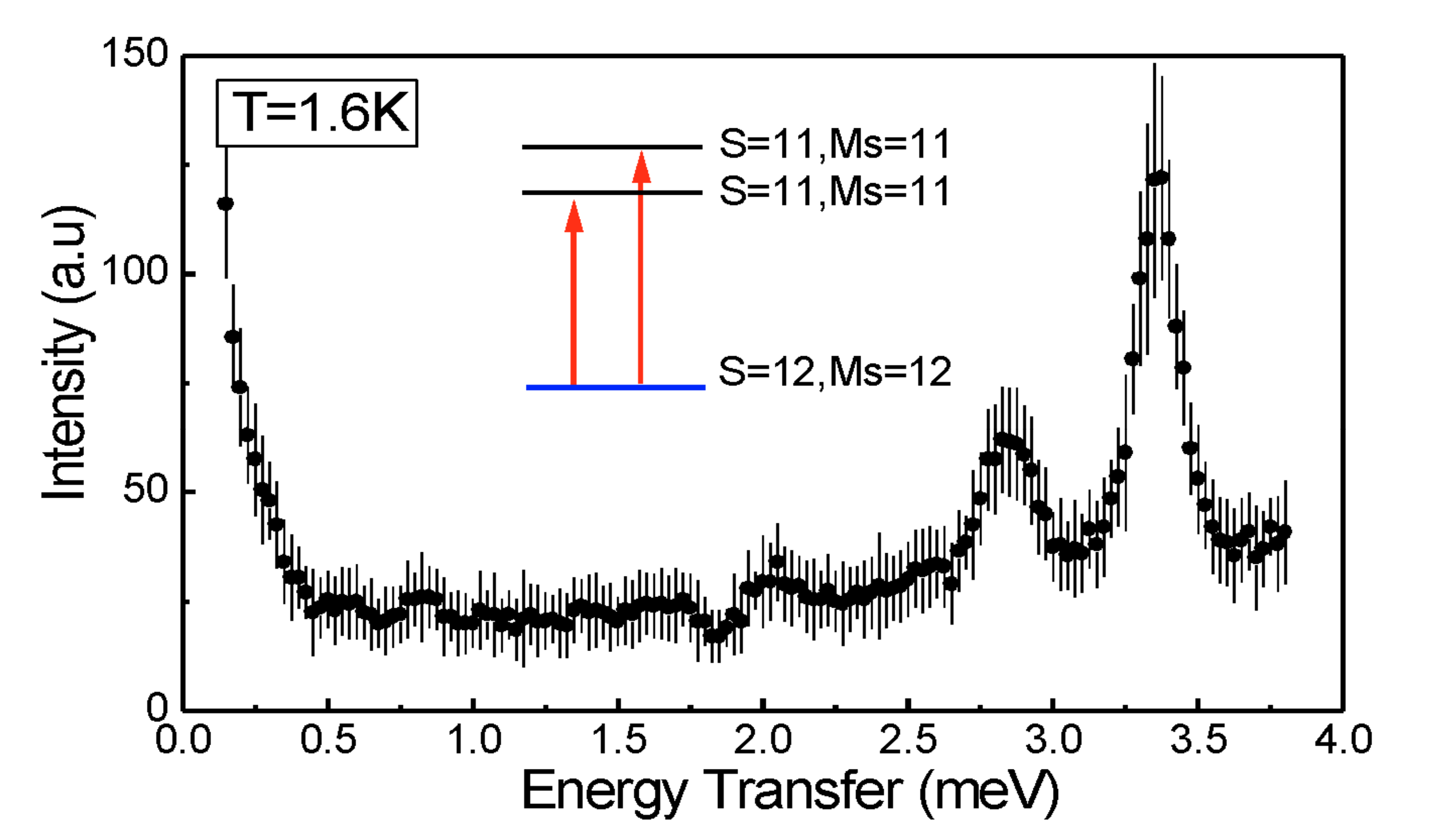
Ground State:
S = 12

Hanspeter Andres, Mark Murrie, Richard Winpenny

$[Ni_{12}(OAc)_{12}(chp)_{12}(H_2O)_6(THF)_6] \cdot 9THF$



Triple-axis TASP (PSI), Q_h = 0.85 Ang^{-1}



Hanspeter Andres, Grégory Chaboussant, Mark Murrie, Richard Winpenny

$[Ni_{12}(OAc)_{12}(chp)_{12}(H_2O)_6(THF)_6] \cdot 9THF$

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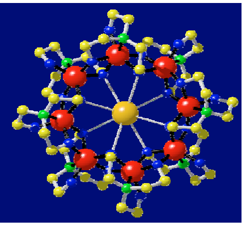
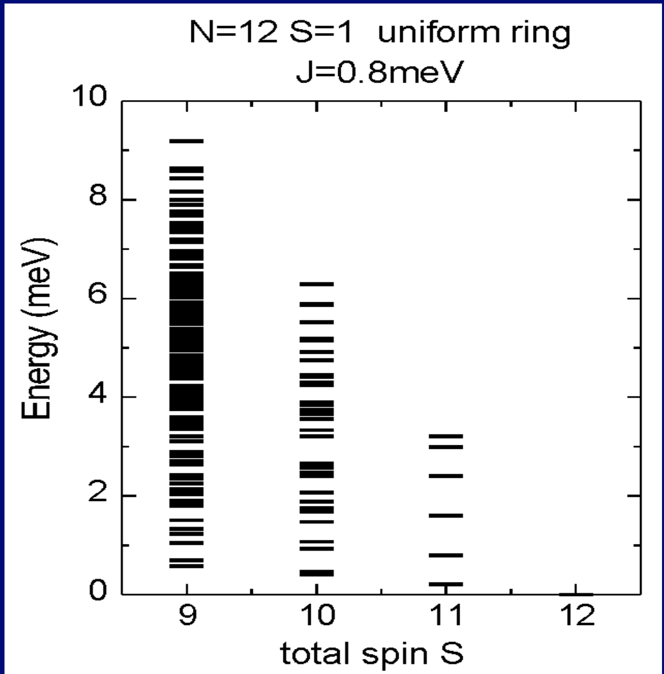
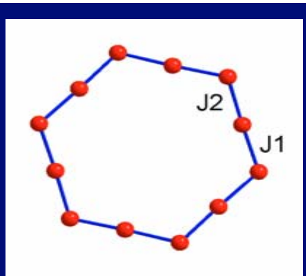
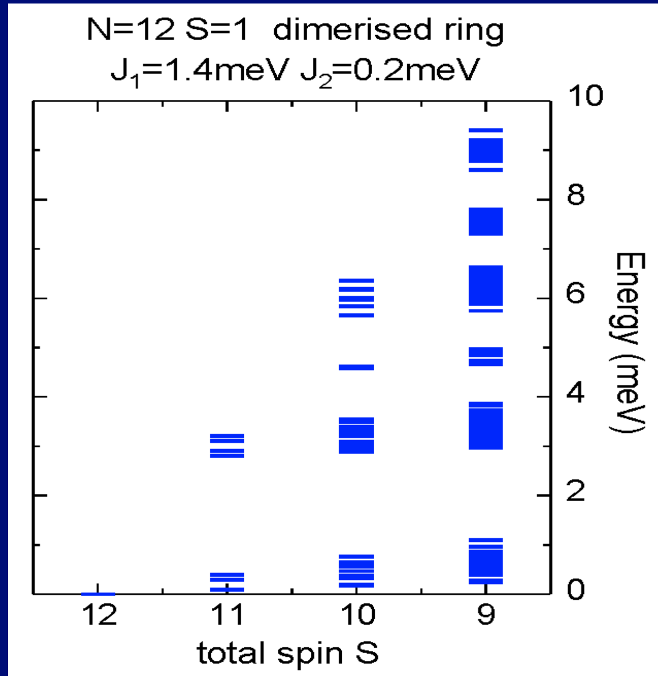
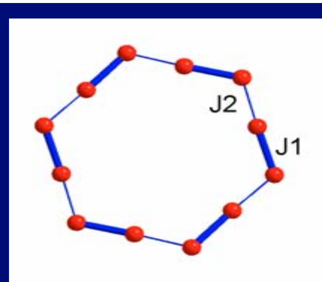






J1 = J2 = J



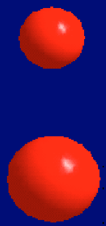


J1 >> J2

Effect of dimerisation

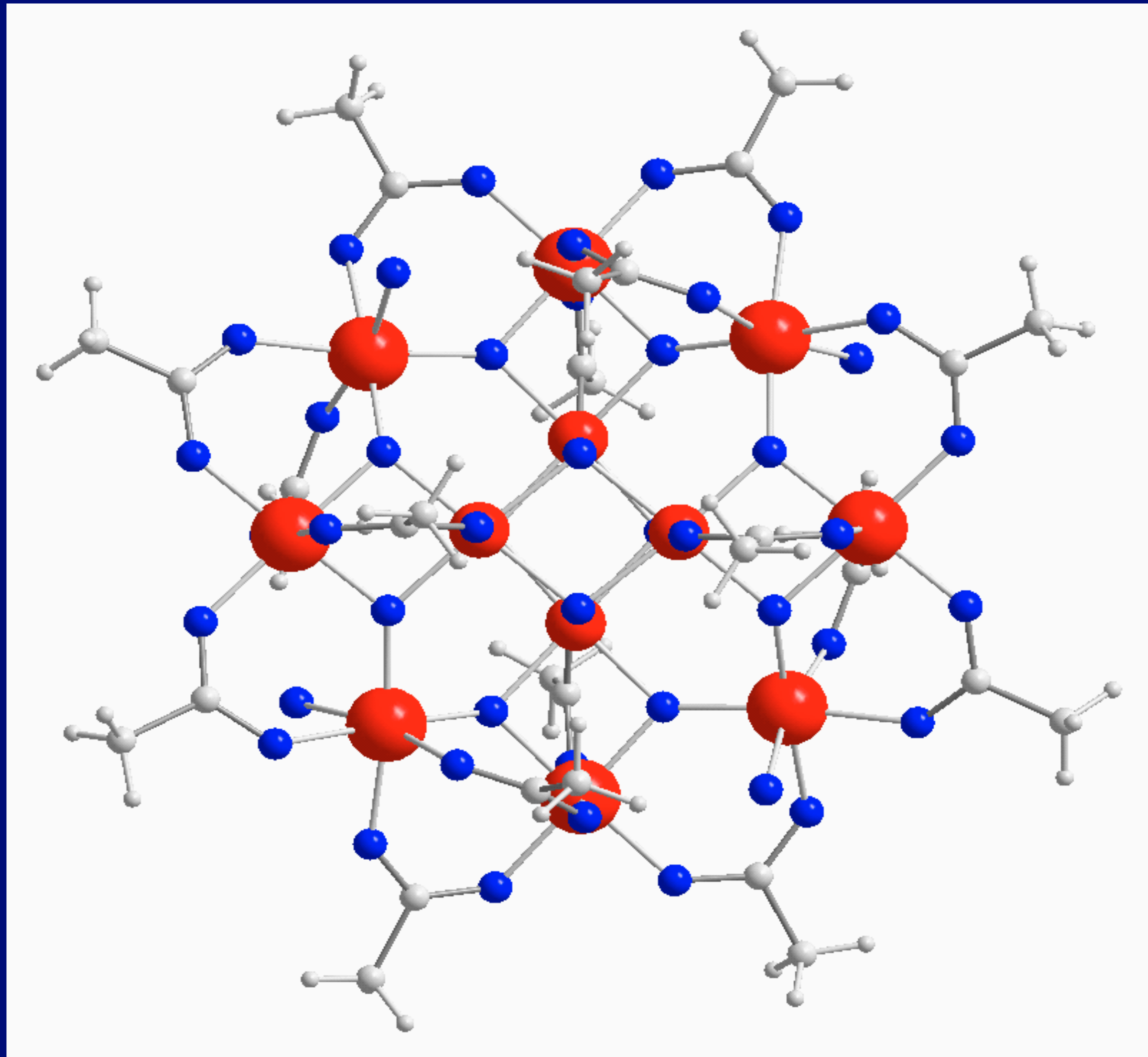
$Mn_{12}O_{12}(OAc)_{16}(H_2O)_4$

OAc = acetate



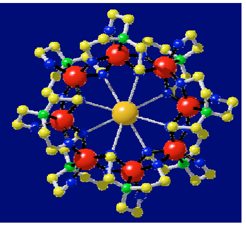
Mn^{4+}

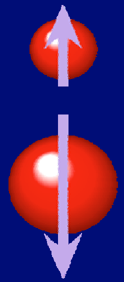
Mn^{3+}



T. Lis; Acta Crystallogr., B36 (1980) 2042

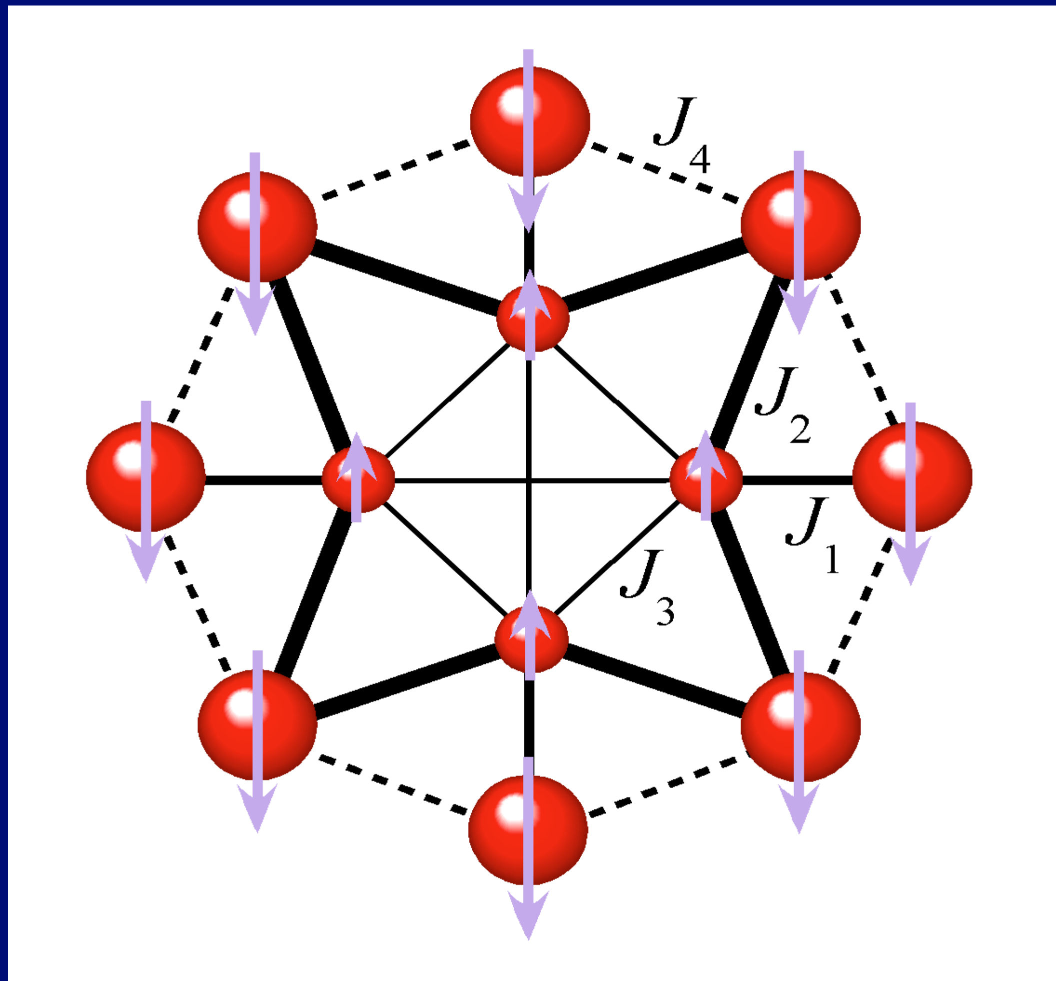
Exchange Interactions in Mn_{12} - Acetate





Mn^{4+}: $S = {}^{3}/_{2}$

Mn^{3+}: $S = 2$



Ground state:

$8 \times 2 - 4 \times {}^{3}/_{2} \;\Rightarrow\; S = 10$

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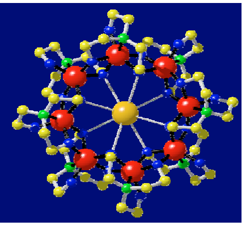
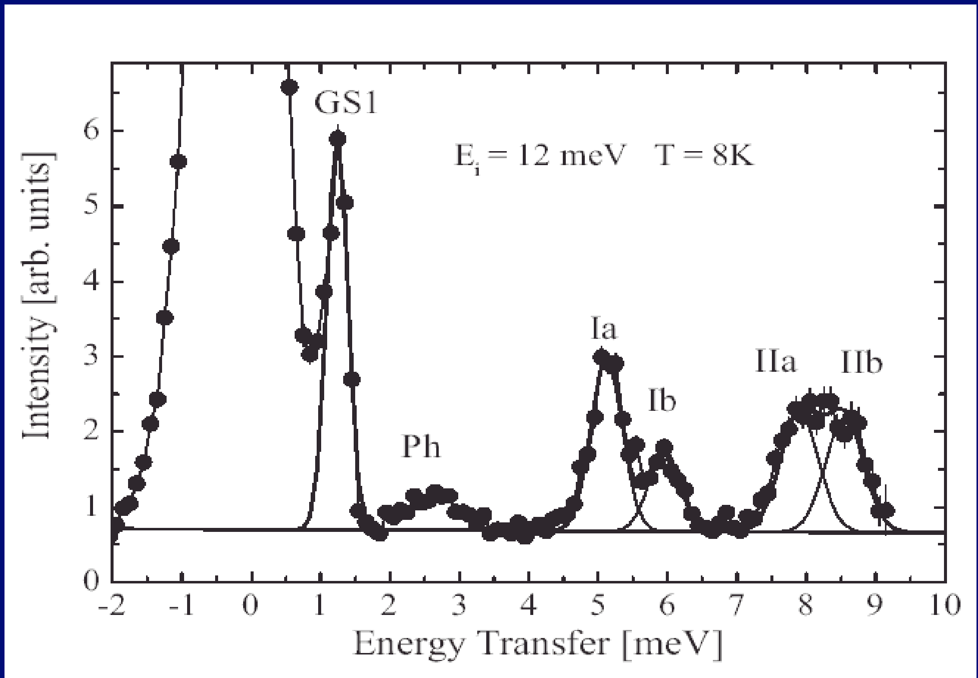
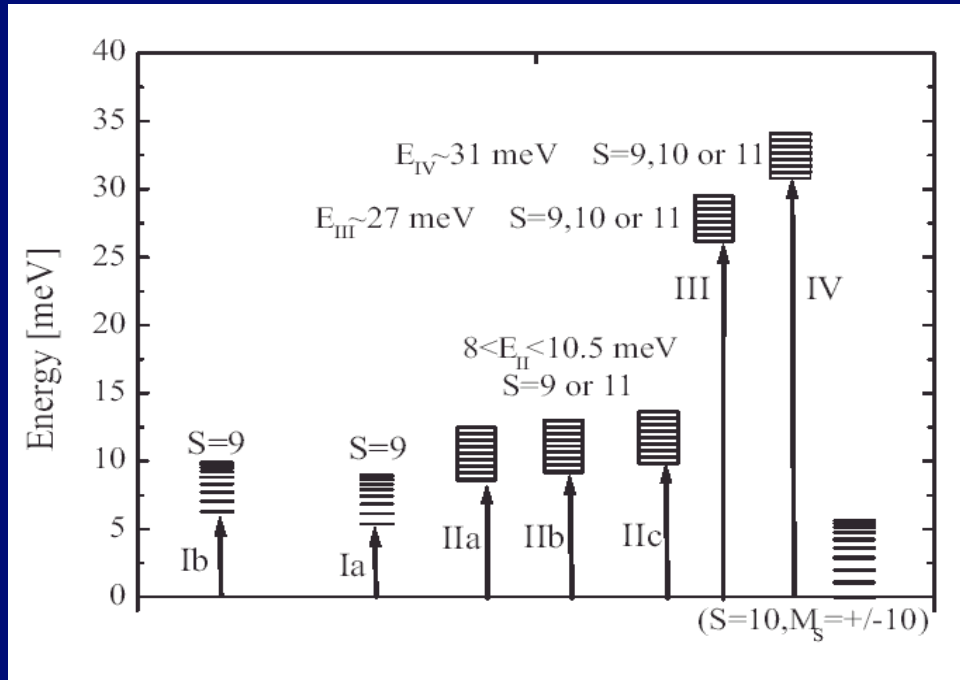
Exchange Interactions in Mn_{12} - Acetate

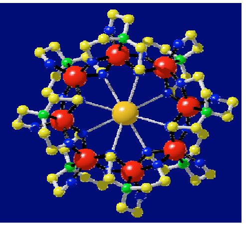


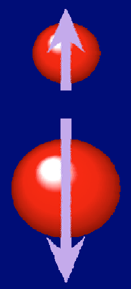




Deuterated Mn_{12}-acetate
Instrument MARI at ISIS
E_i = 12 meV

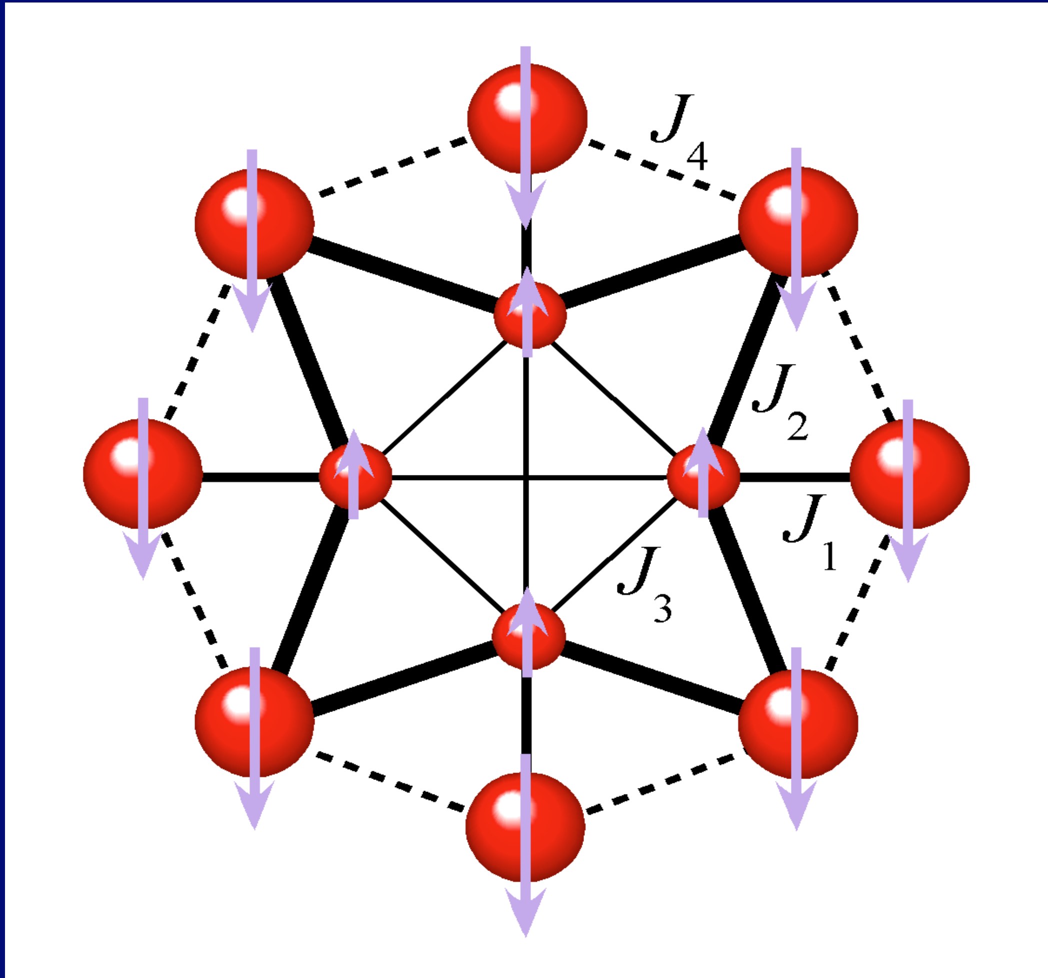
Exchange Interactions in Mn_{12} - Acetate





Mn^{4+}: $S = {}^3/_2$

Mn^{3+}: $S = 2$



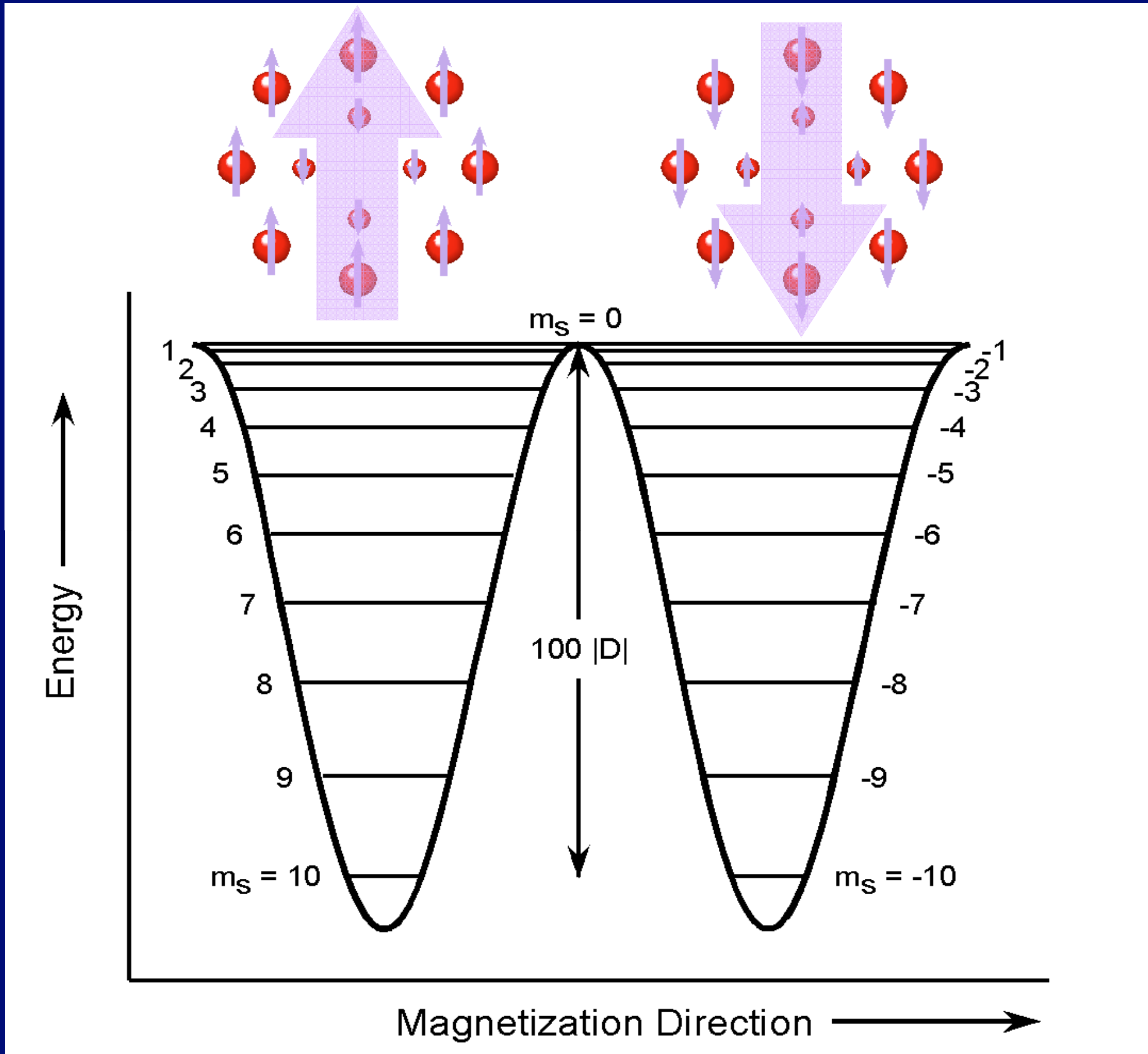
S = 10 ground state only in small part of parameter space

$J_1 \sim J_2 \sim 5.5$ meV

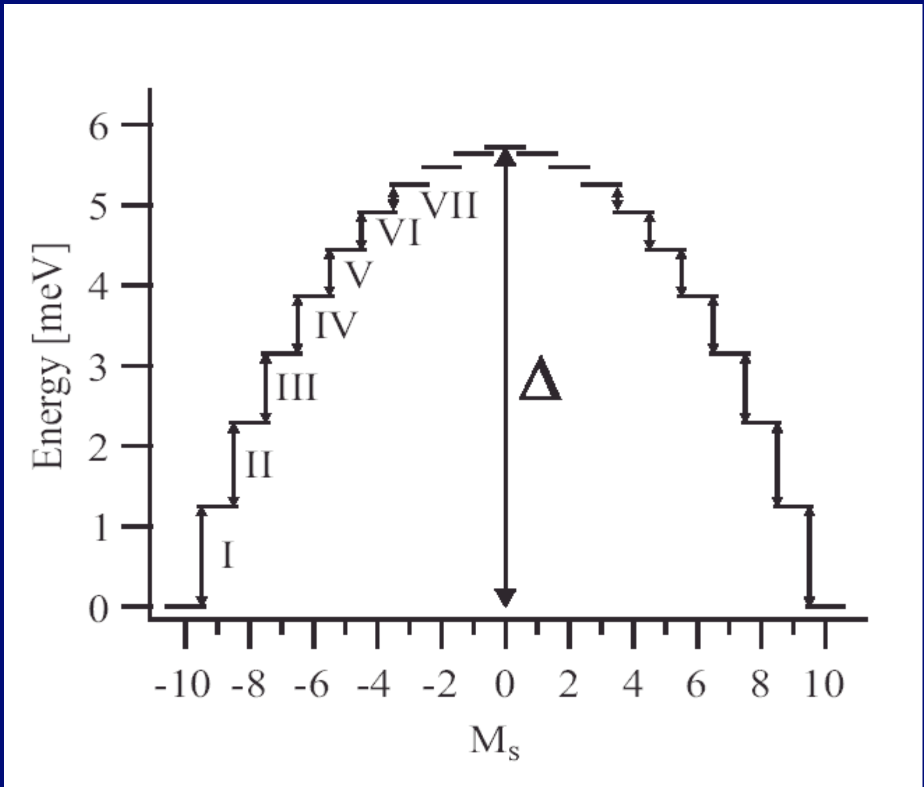
$J_3 \sim J_4 \sim 0.6$ meV

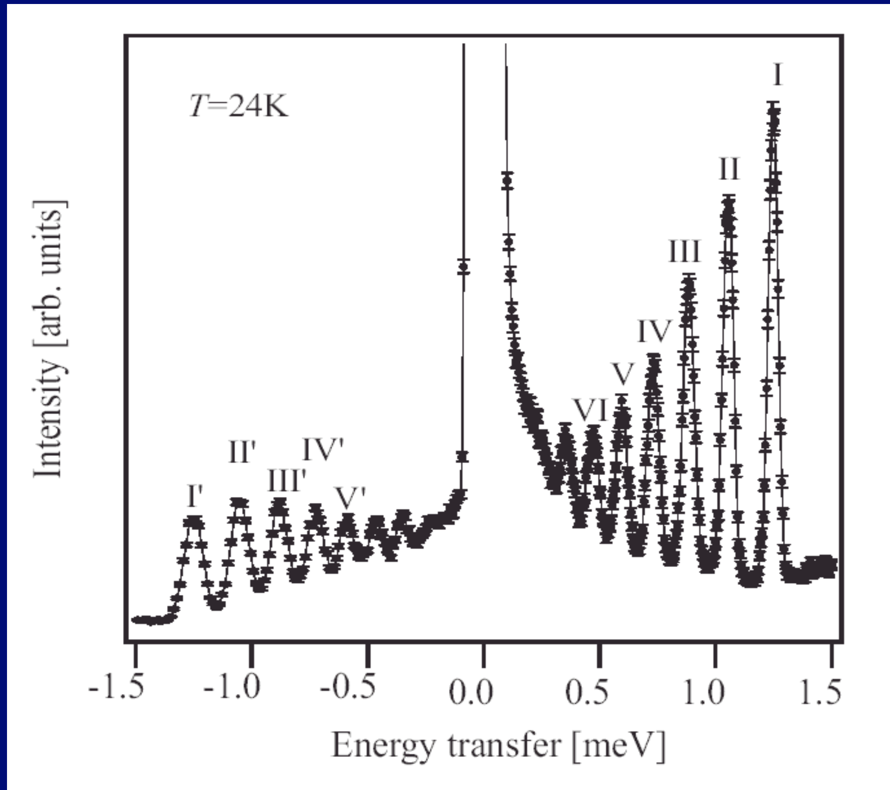
Grégory Chaboussant, Bruce Normand, Andreas Honecker

Single Molecule Magnetism in Mn_{12} - Acetate



Anisotropy Interactions in Mn_{12} - Acetate

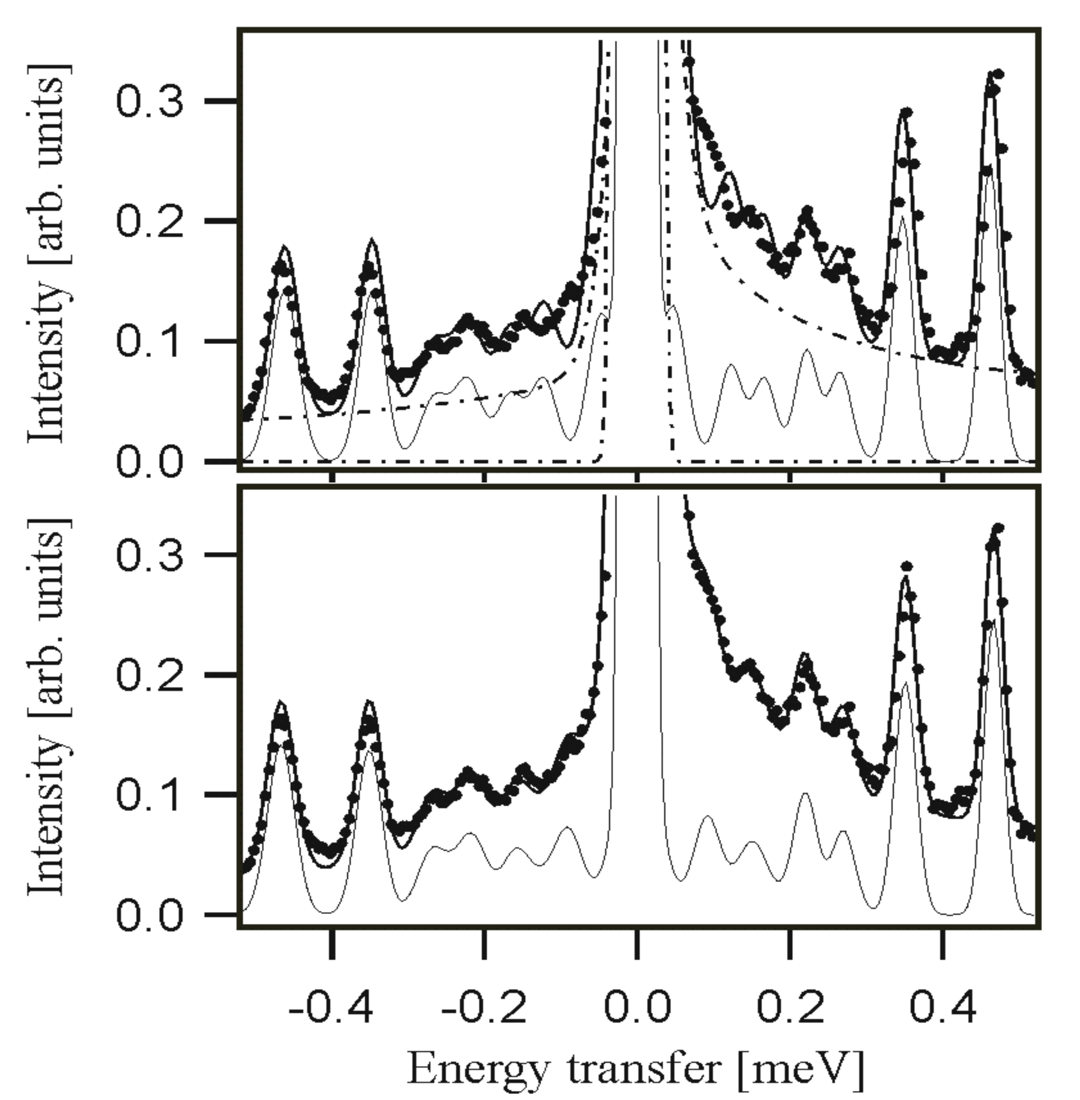




Energy barrier
INS transitions

Deuterated Mn_{12}-acetate
Instrument IN5 at ILL
λ_i = 5.9 Å

Anisotropy Interactions in Mn_{12} - Acetate

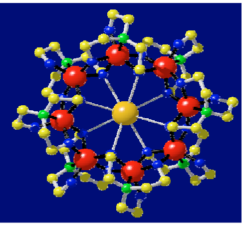


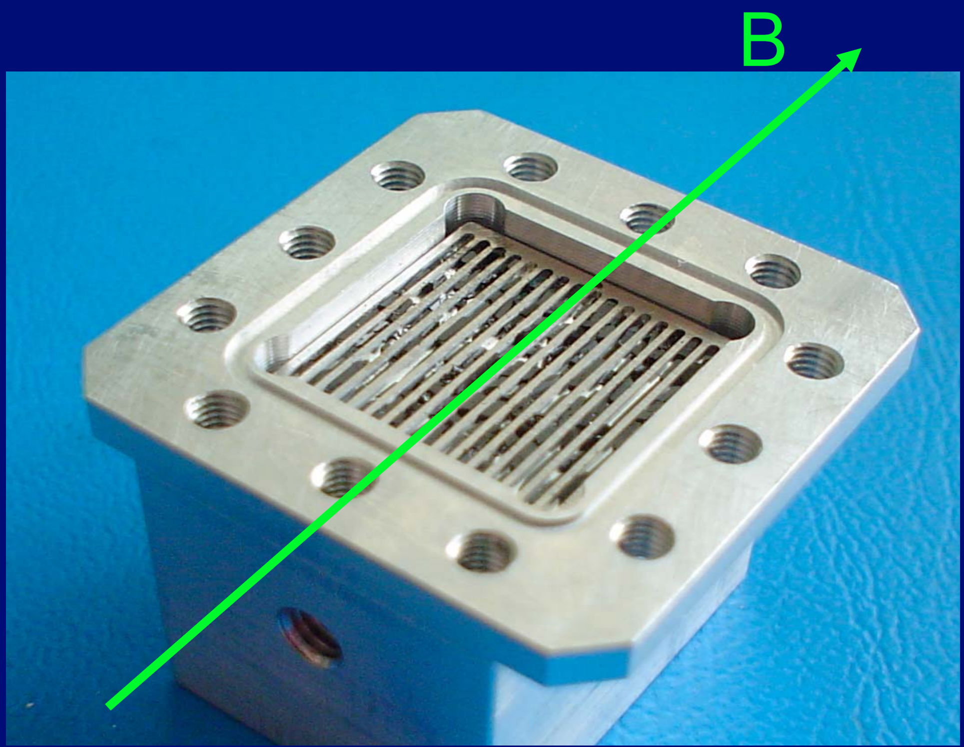
Axial model

Rhombic model

Deuterated Mn_{12}-acetate
Instrument IN5 at ILL
λ_i = 8 Å, T = 24 K

Inelastic Neutron Scattering on Mn_{12}-Acetate Crystals





≈ 500 crystals

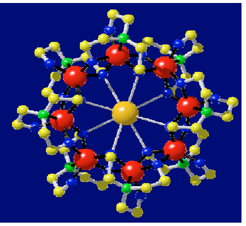
array of crystals + magnetic field

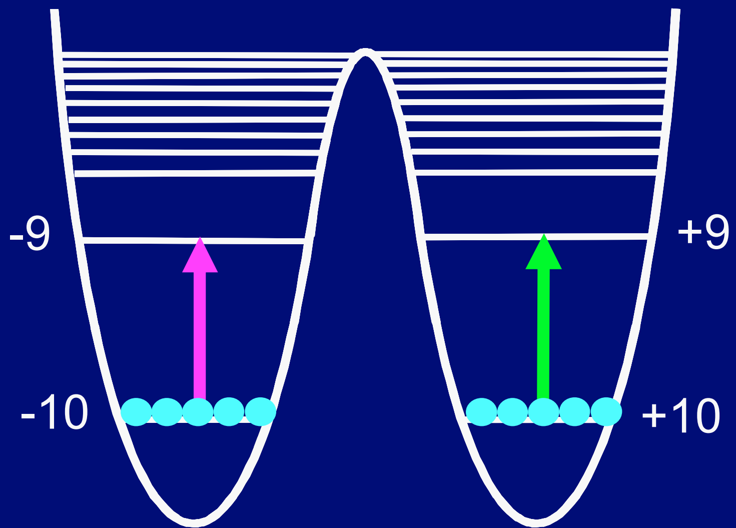
⇓

detection of slow magnetic relaxation by INS

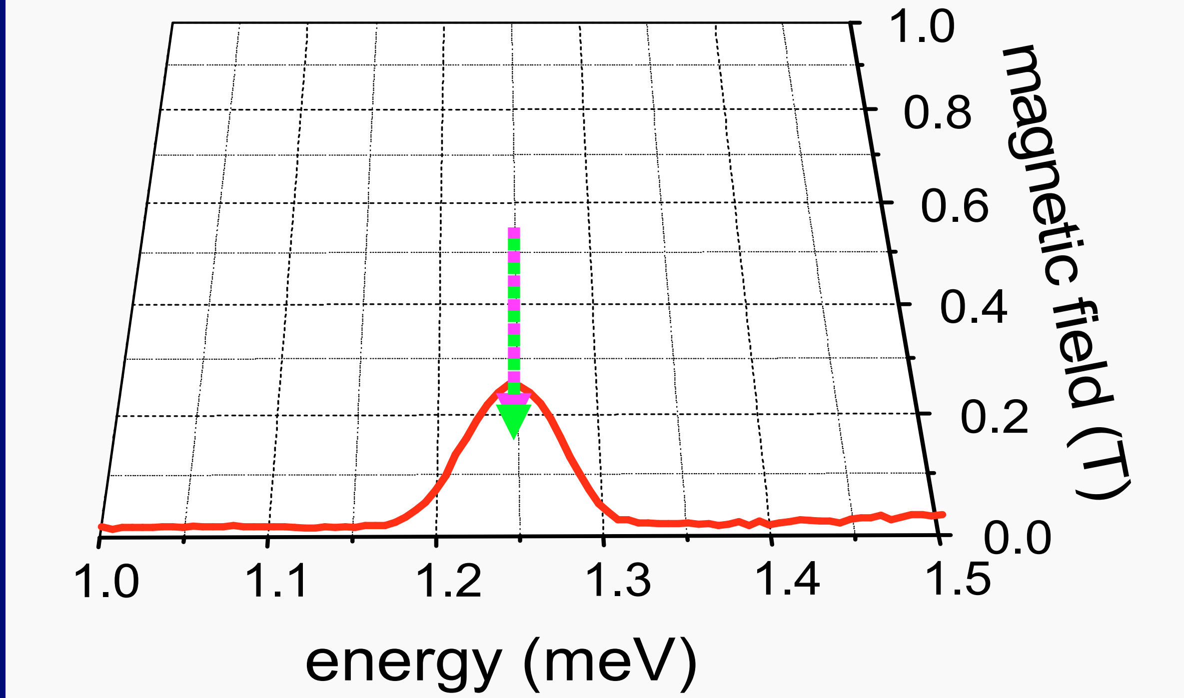
Chris Dobe, Graham Carver, Oliver Waldmann

Zeeman Splitting in Mn_{12}-Acetate Crystals



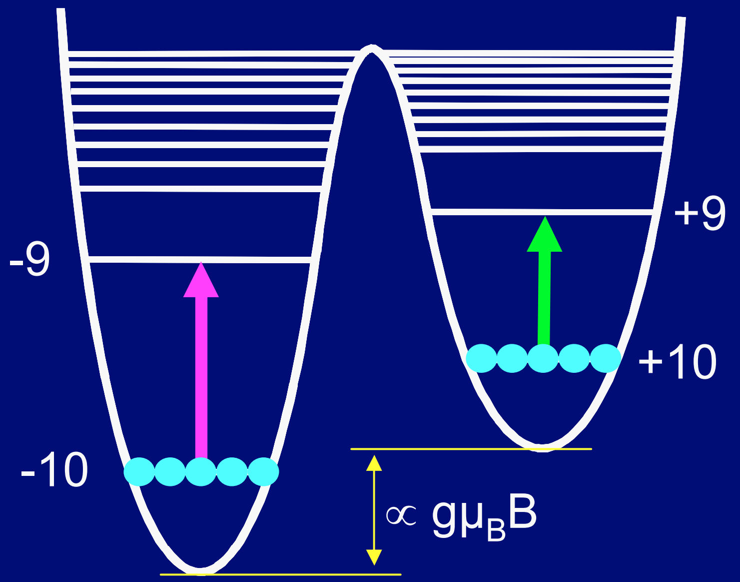


low temperature
zero magnetic field

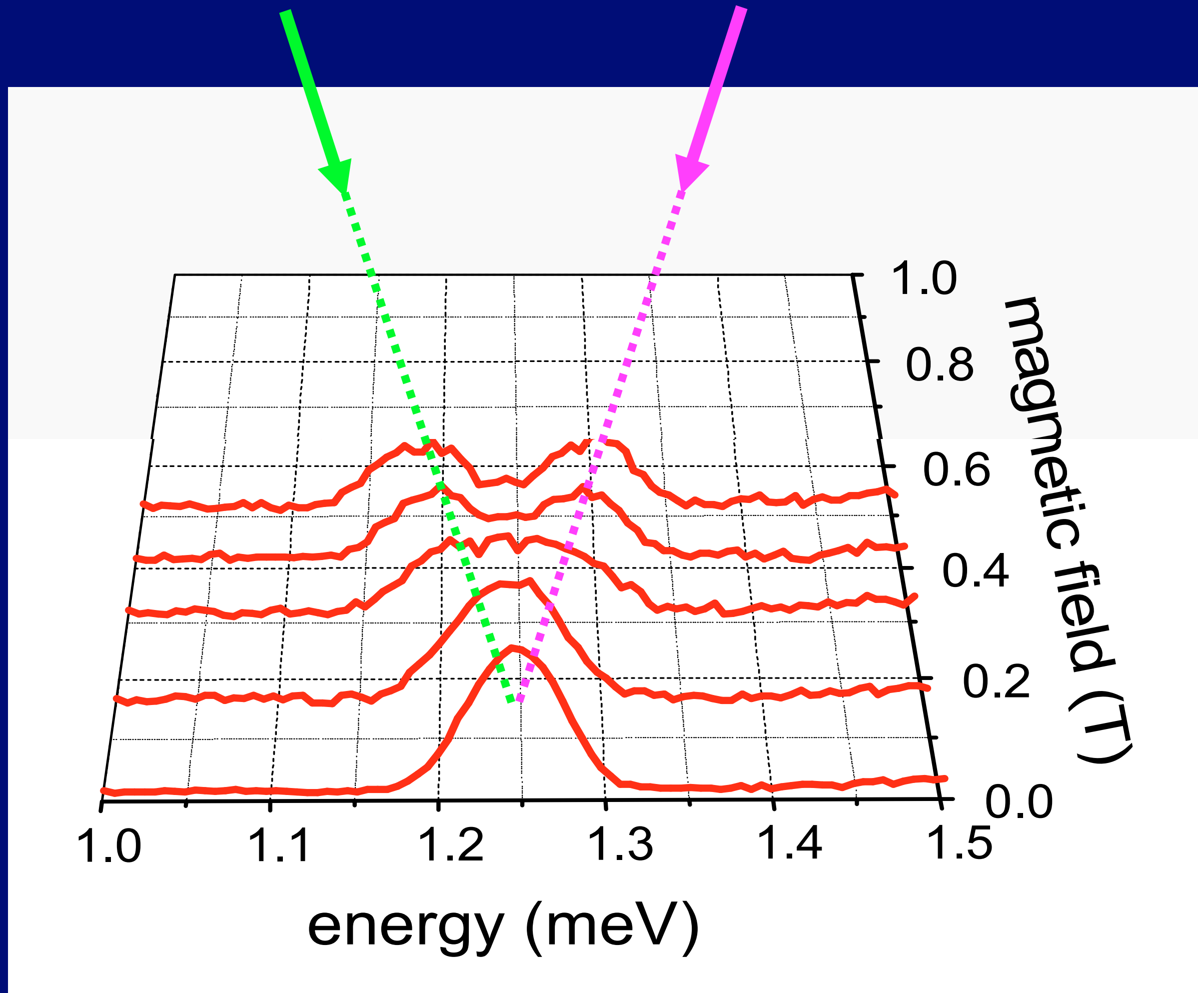


Instrument IN5 at ILL, λ_i = 5.9 Å, T = 1.5 K

Zeeman Splitting in Mn_{12}-Acetate Crystals



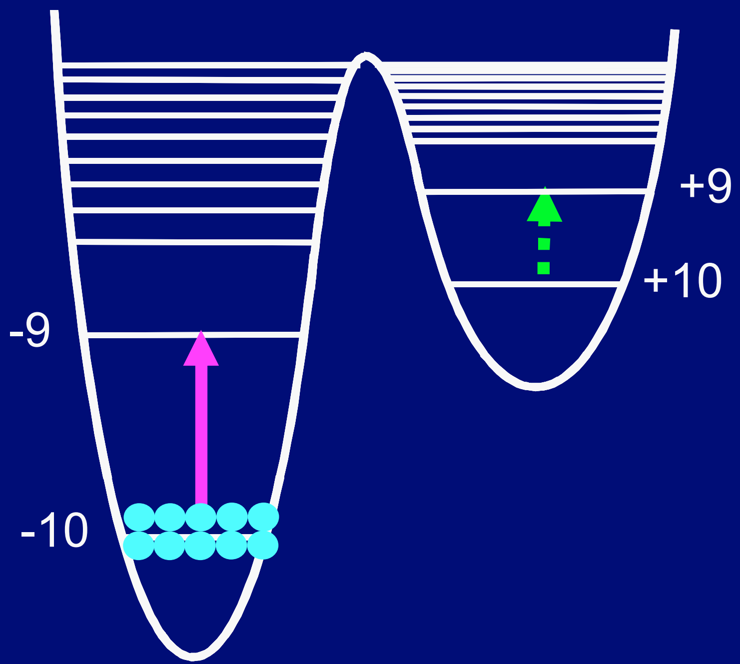
magnetic field
B > 0



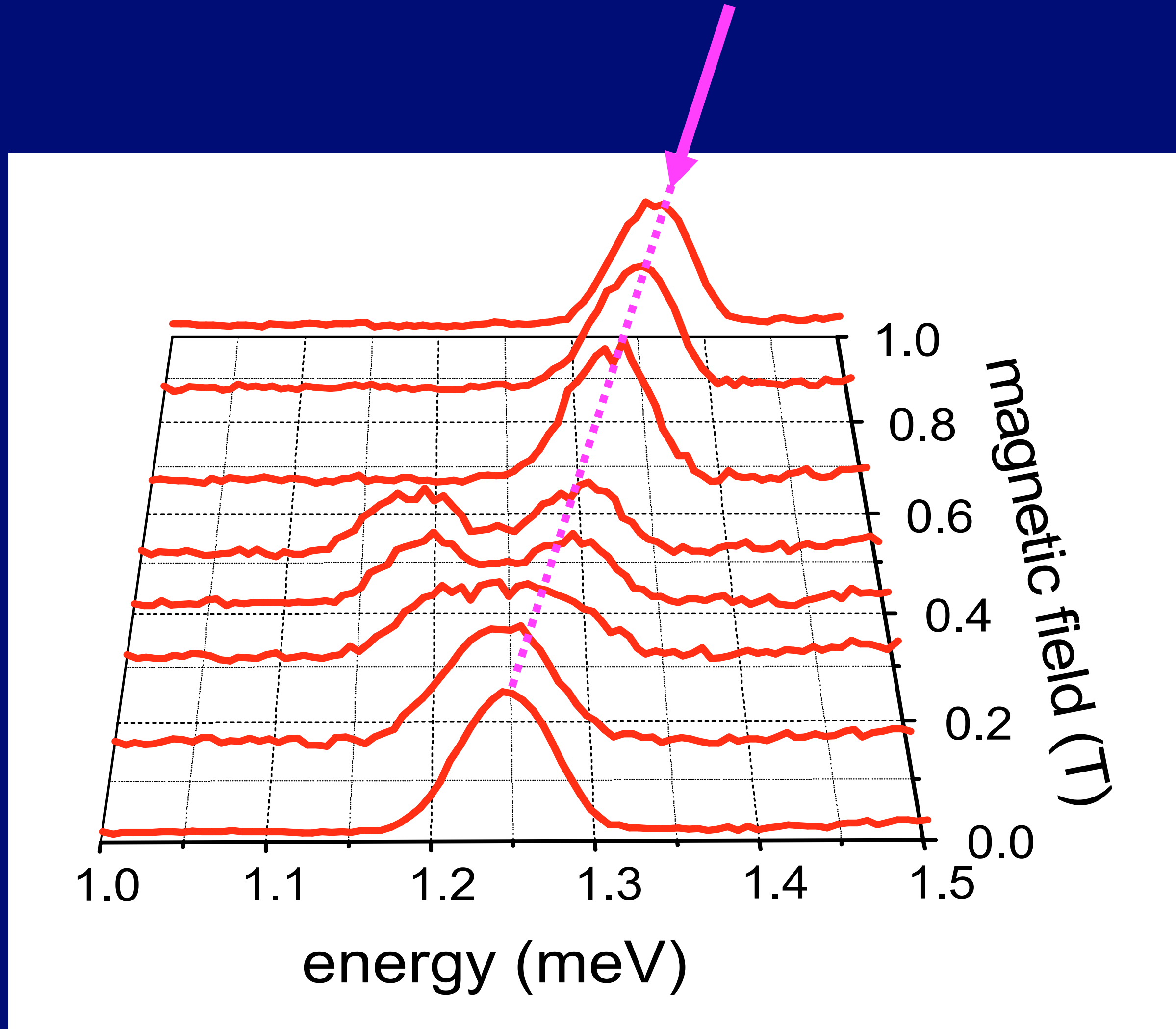
Instrument IN5 at ILL, λ_i = 5.9 Å, T = 1.5 K

Graham Carver, Oliver Waldmann

Zeeman Splitting in Mn_{12}-Acetate Crystals



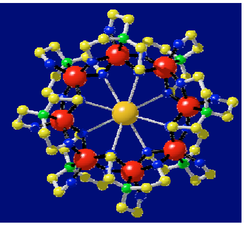
B too large
⇓
magnetization relaxed

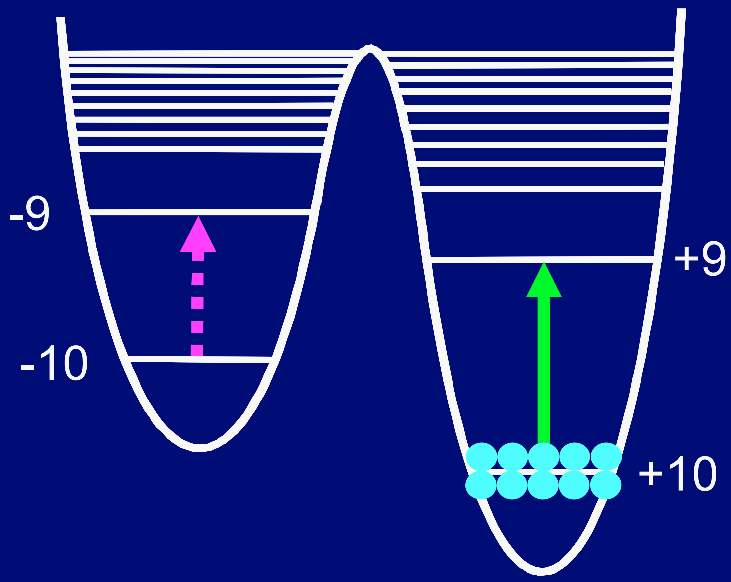


Instrument IN5 at ILL, λ_i = 5.9 Å, T = 1.5 K

Graham Carver, Oliver Waldmann

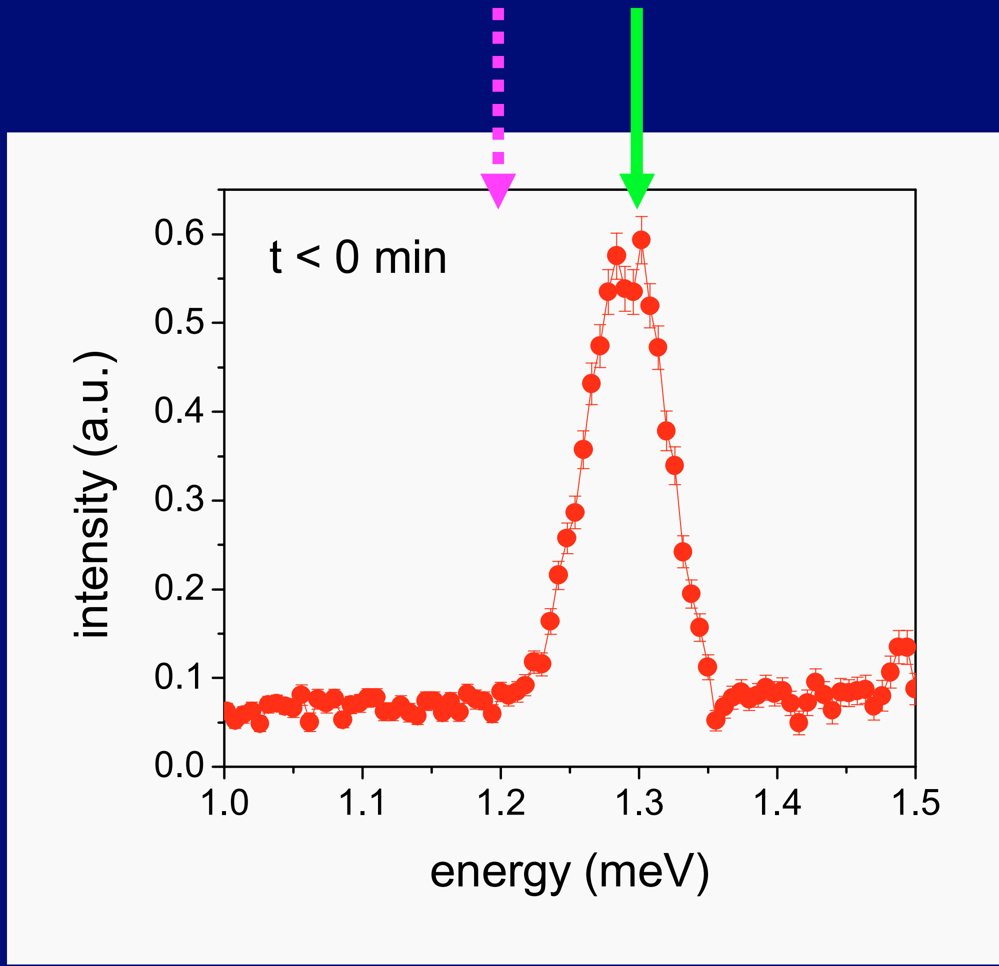
Magnetic Relaxation by Time-Resolved Inelastic Neutron Scattering





time t < 0:

B = -0.4 T



Instrument IN5 at ILL

λ_i = 5.9 Å, T = 2.65 K

Graham Carver, Oliver Waldmann

Magnetic Relaxation by Time-Resolved Inelastic Neutron Scattering

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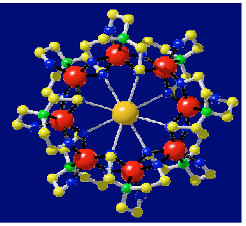
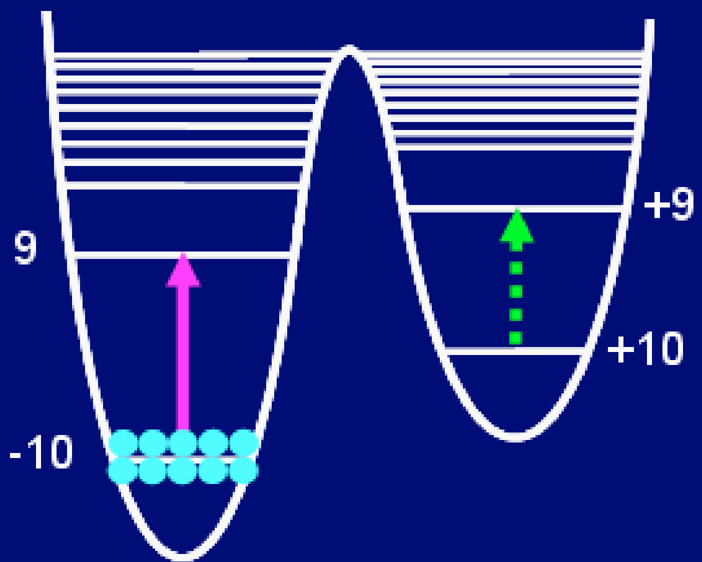
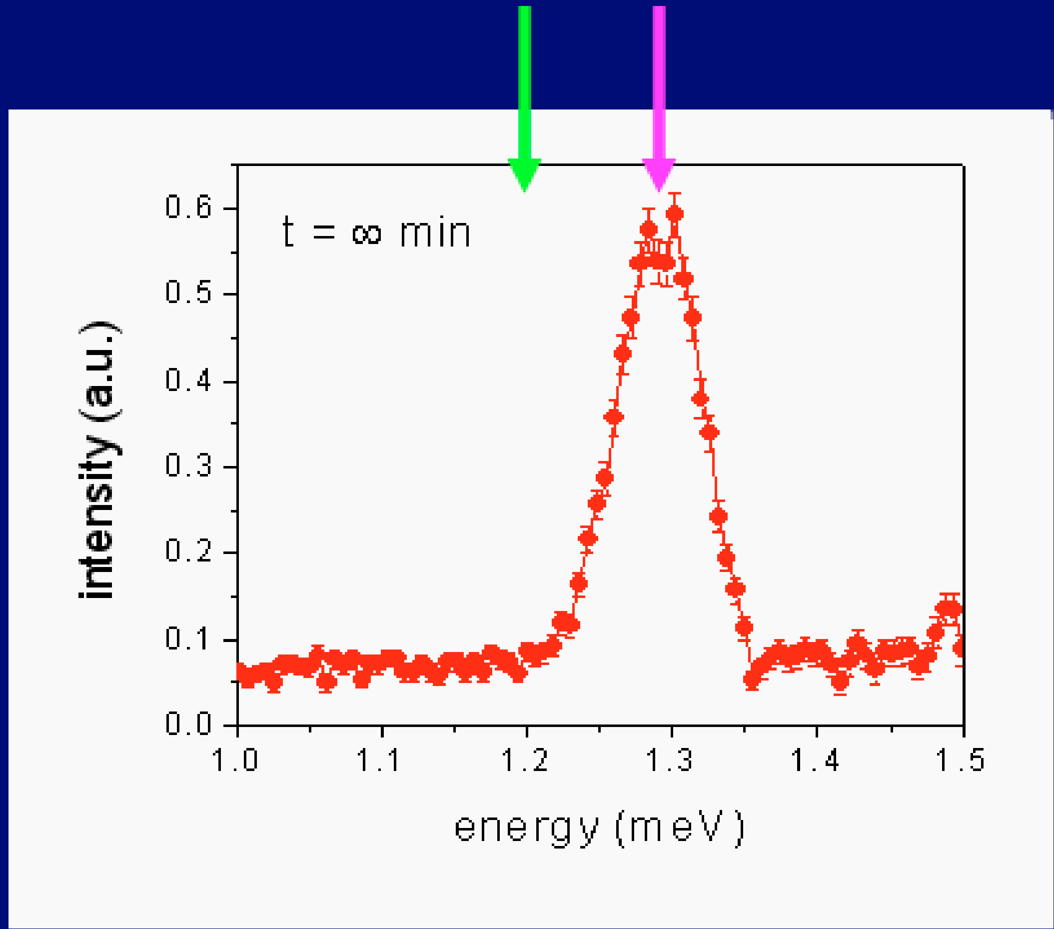




time t > 0:

B = +0.4 T

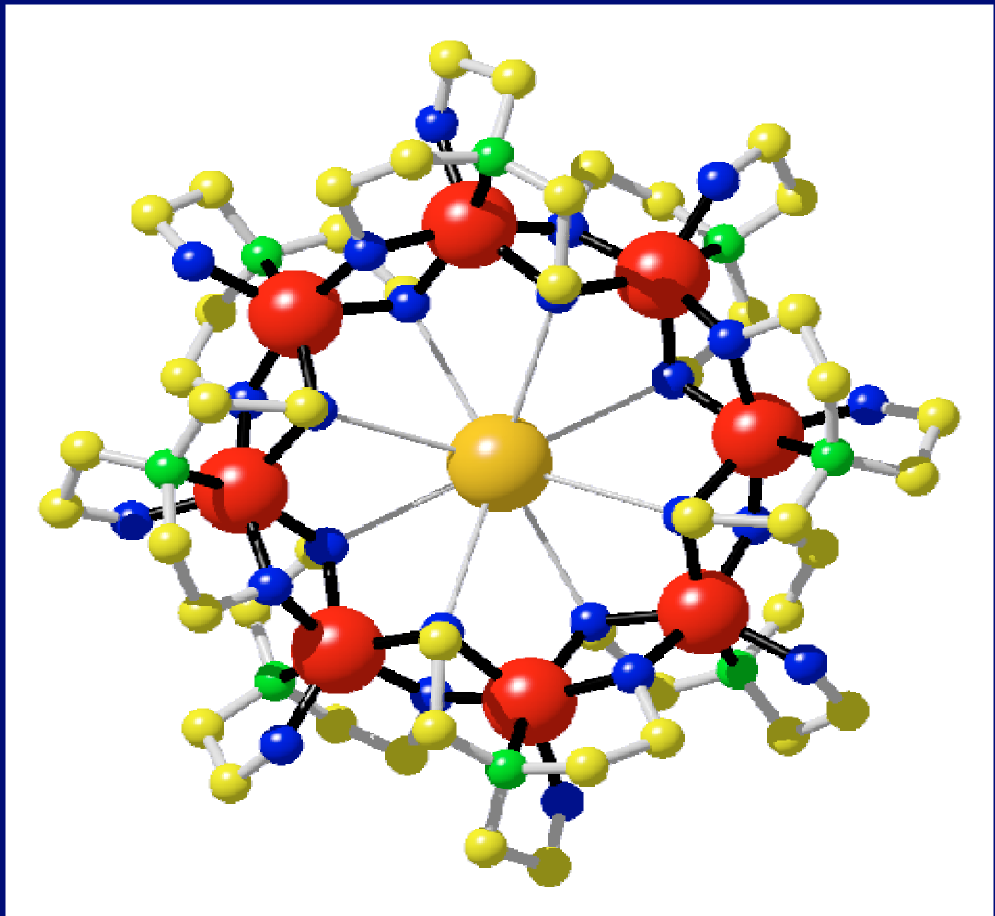


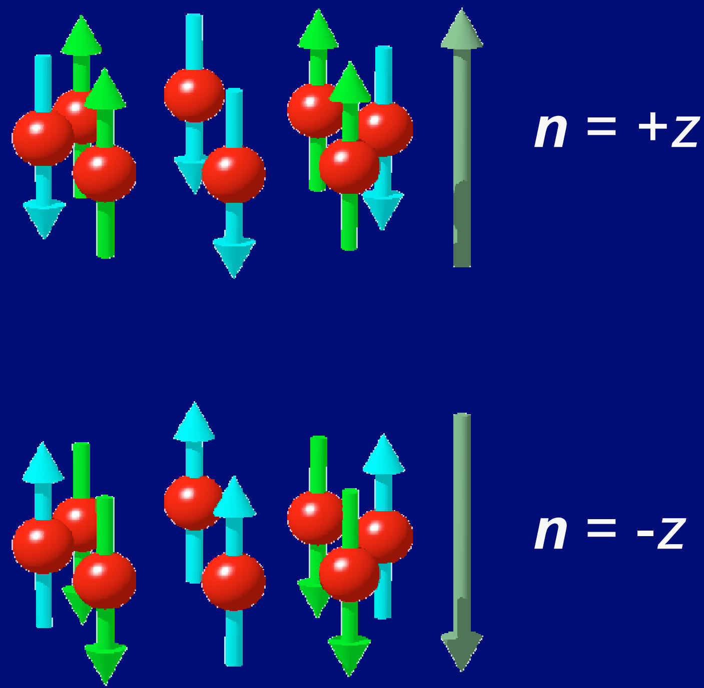
Instrument IN5 at ILL

λi = 5.9 Å, T = 2.65 K

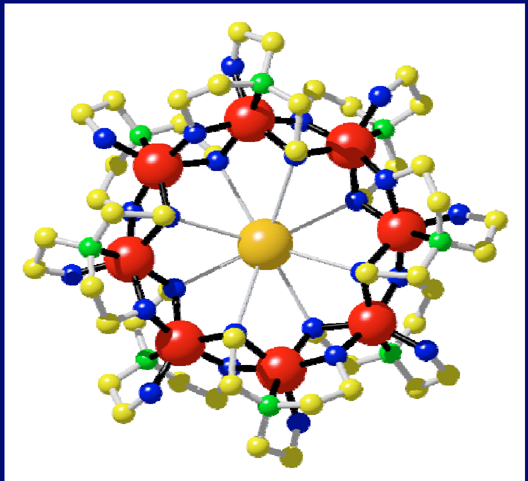
Graham Carver, Oliver Waldmann

Coherent Quantum Tunneling of the Néel Vector

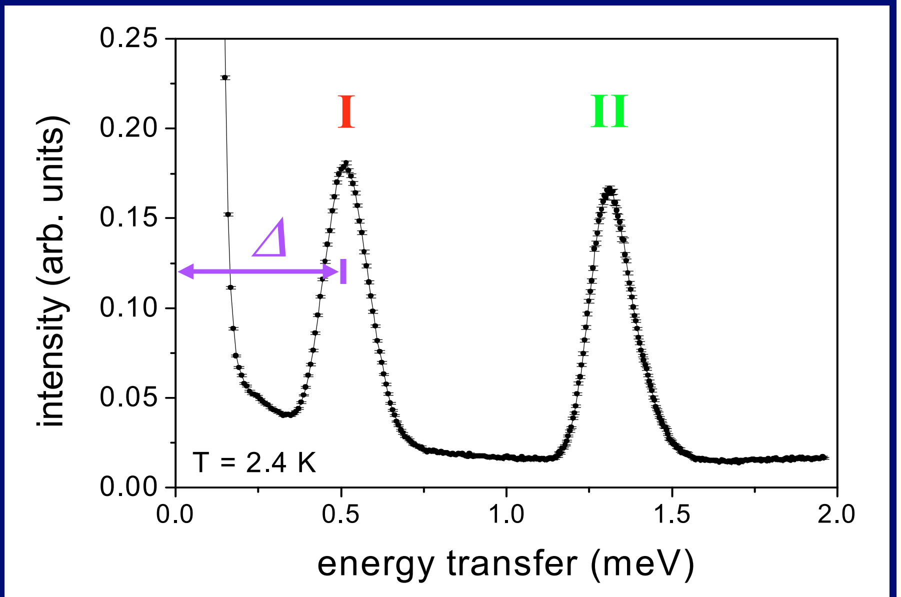


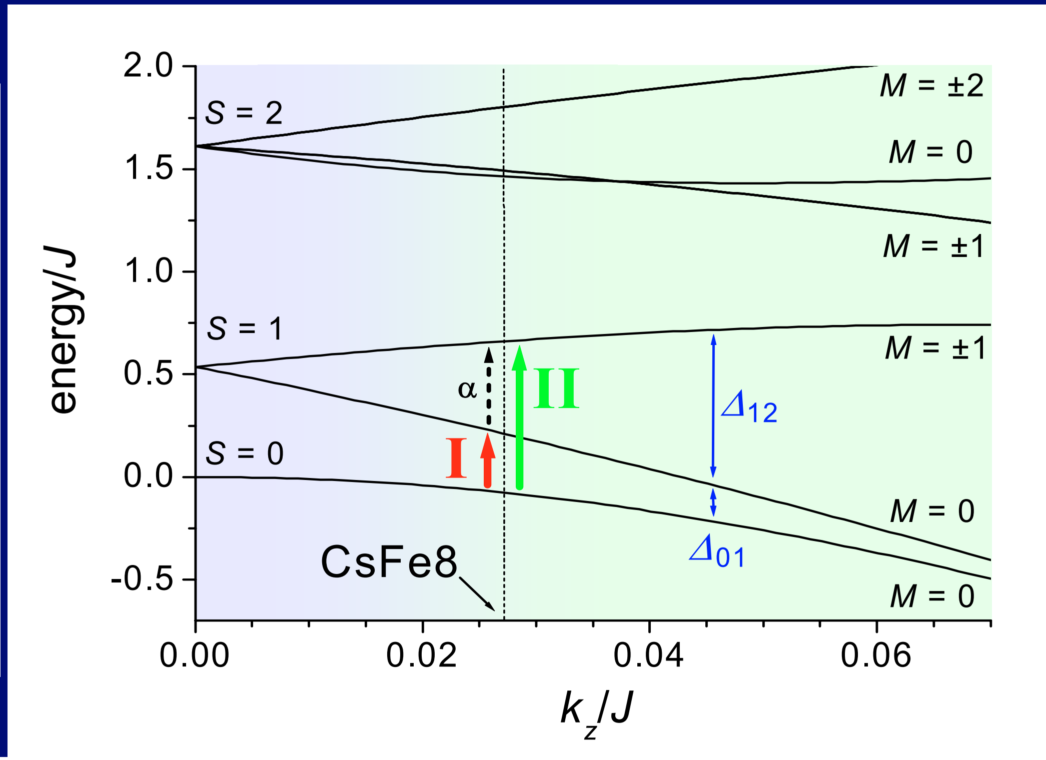


Coherent Quantum Tunneling of the Néel Vector

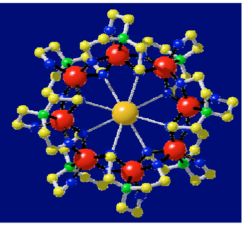


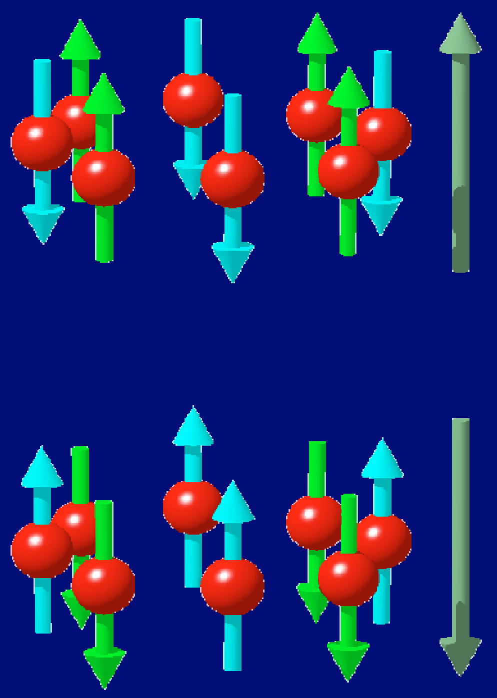
$$\hat{H} = J\left(\sum_{i=1}^{N-1} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} + \hat{\mathbf{S}}_N \cdot \hat{\mathbf{S}}_1\right) - k_z \sum_{i=1}^{N} \hat{S}_{i,z}^2$$





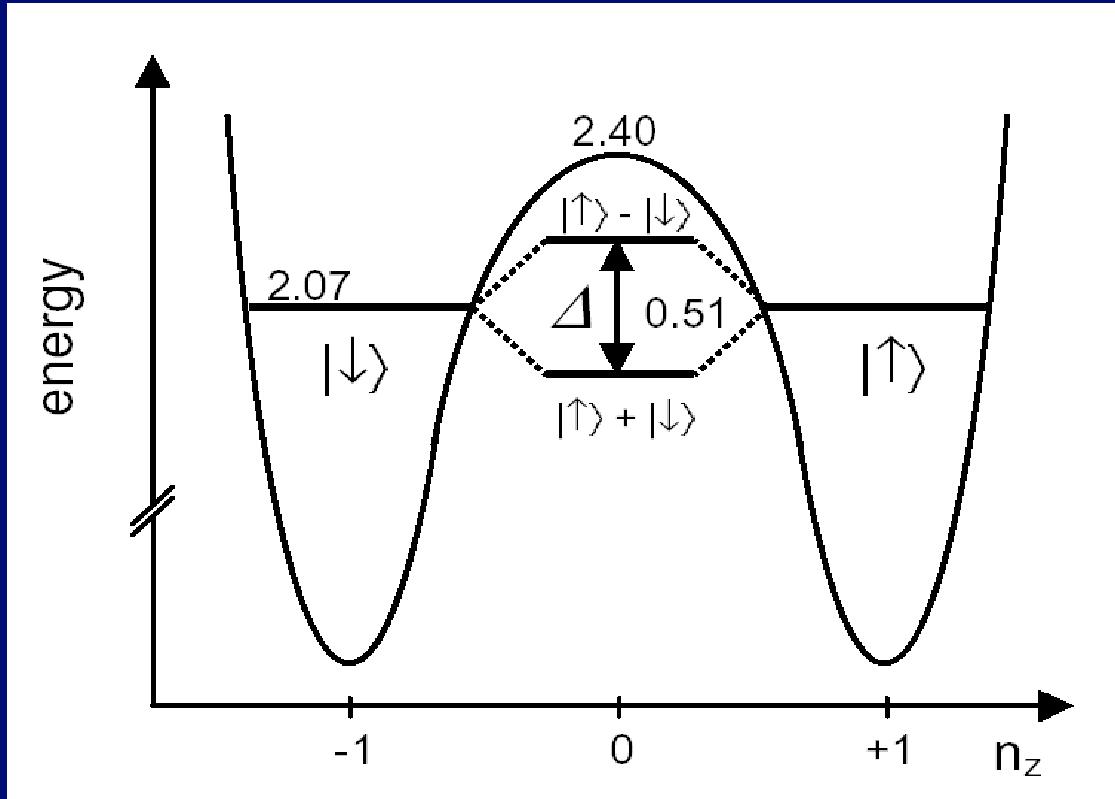
Coherent Quantum Tunneling of the Néel Vector





n = +z

n = -z

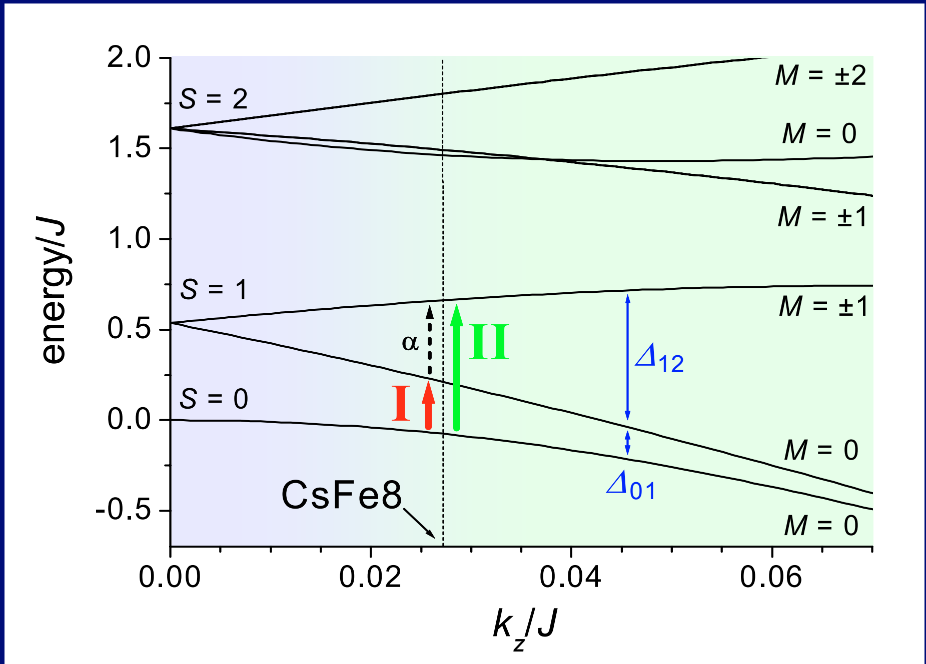


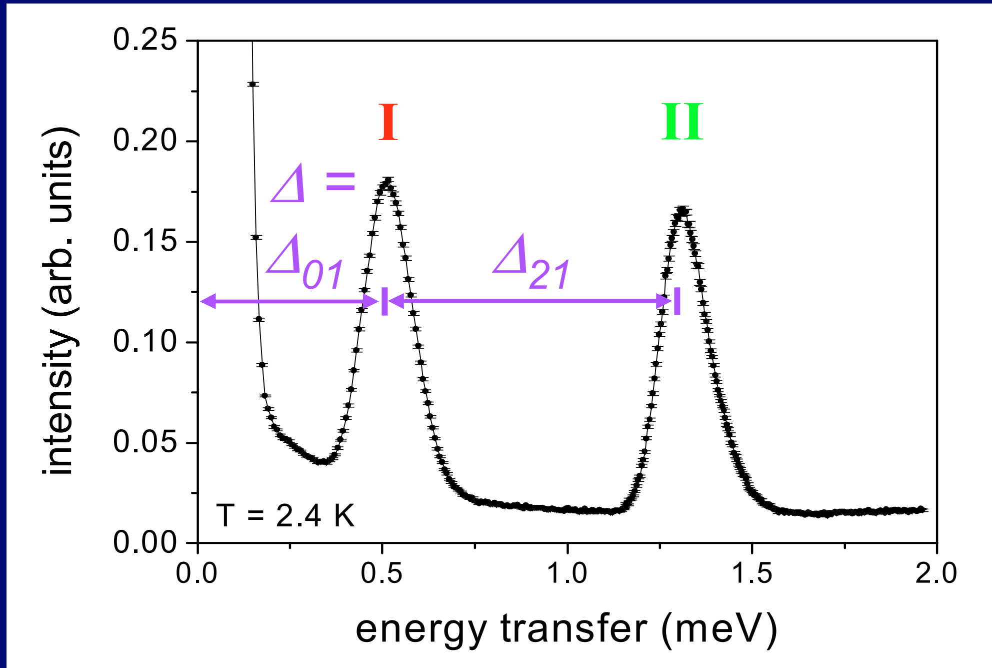
QM eigenstates:

$$\frac{1}{\sqrt{2}}\left(|\uparrow\rangle - |\downarrow\rangle \right)$$

$$\frac{1}{\sqrt{2}}\left(|\uparrow\rangle + |\downarrow\rangle \right)$$

Coherent Quantum Tunneling of the Néel Vector





Tunnel regime: $\Delta_{21} > \Delta_{01}$

Coherence:

- Experimental width < 120 µeV
- Decoherence time $\tau_\phi > 11$ ps
- Number of coherent oscillations $\tau_\phi \cdot \Delta / \hbar > 8.5$

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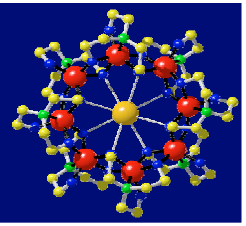
Conclusions



- Exchange and anisotropy splittings: Direct determination by inelastic neutron scattering with no external magnetic field
- INS : Access to cluster energy levels and wavefunctions
- Real-time spectroscopic relaxation measurements
- Application to ferro, ferri and antiferromagnetic clusters