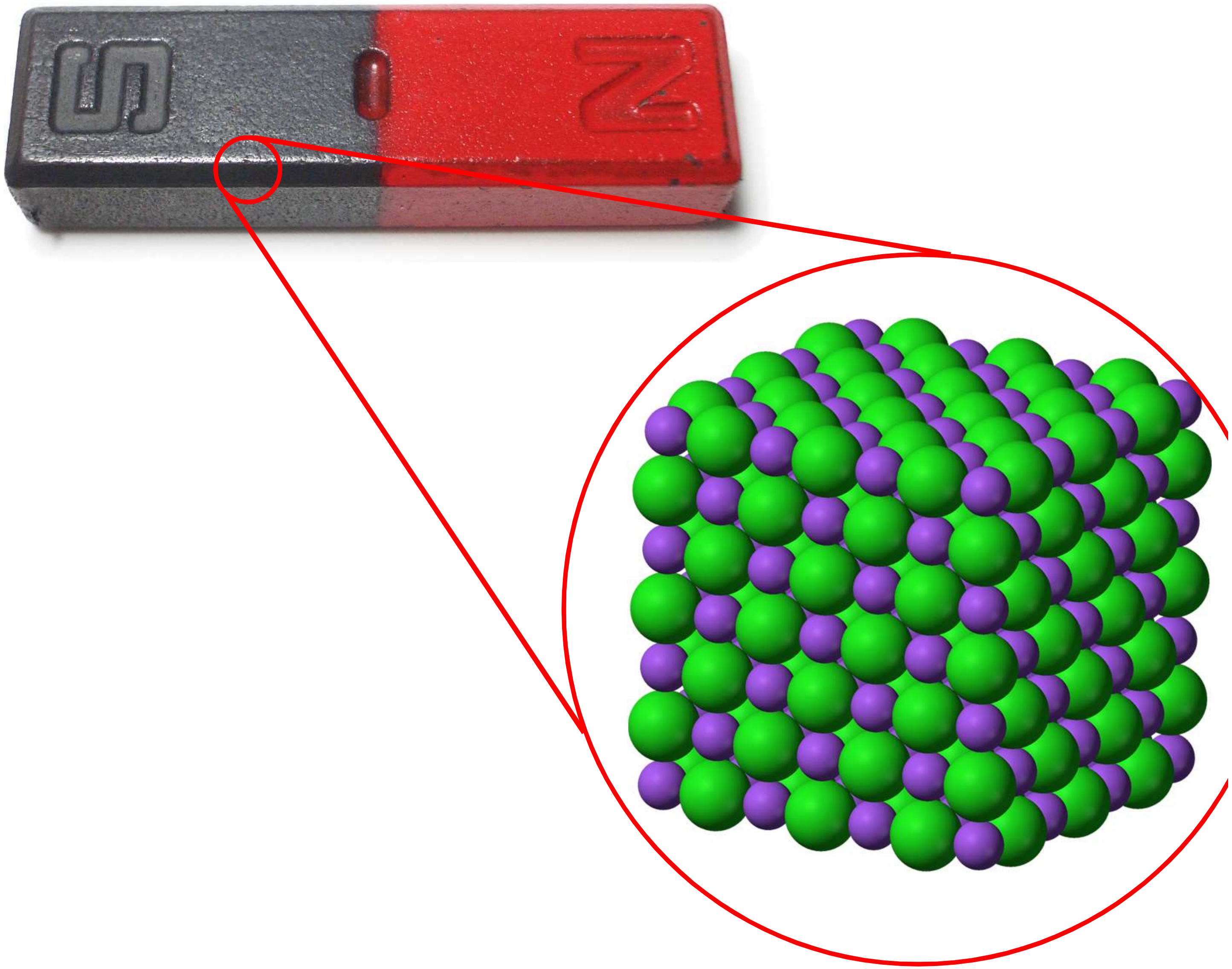
The versality of low dimensional molecular magnets on examples of magnetocaloric effect and magnetic relaxations.

Piotr Konieczny

Department of Molecular Magnetism

NZ37

Kraków 8.04.2021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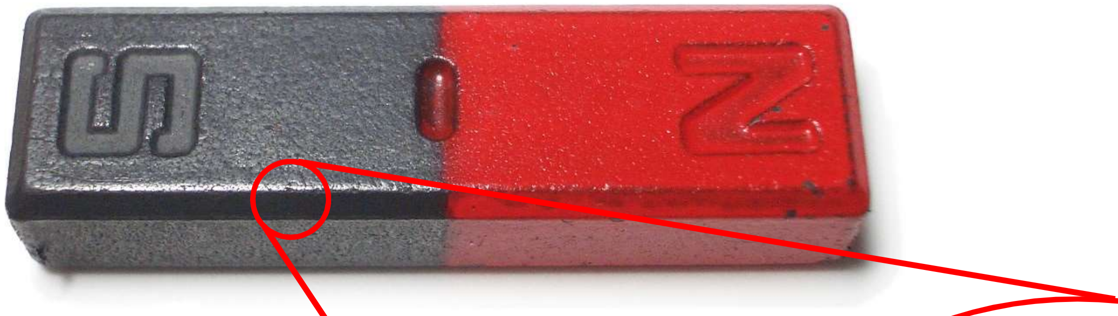
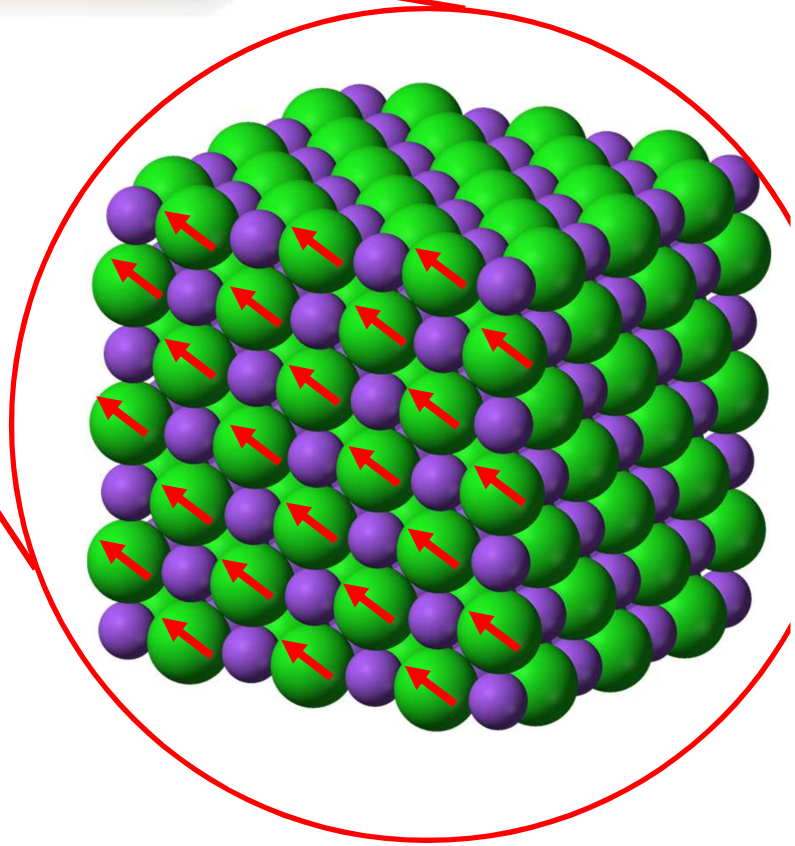




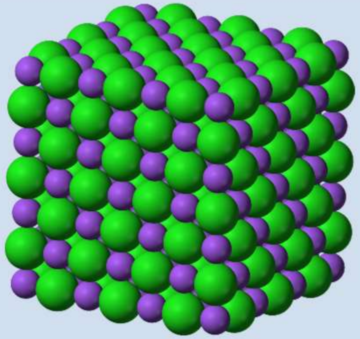
mostly:
3d metals: Fe, Co, Ni, …
4f rare earth: Dy, Tb, …

alloys

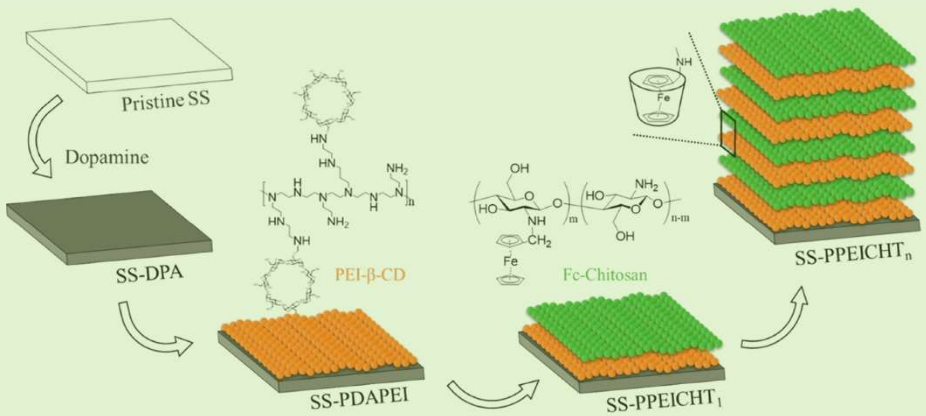
ceramics

vertical confinement

3D

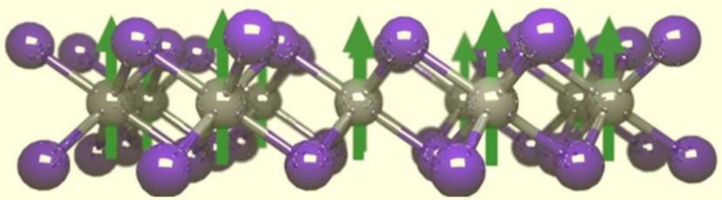


"semi" 2D



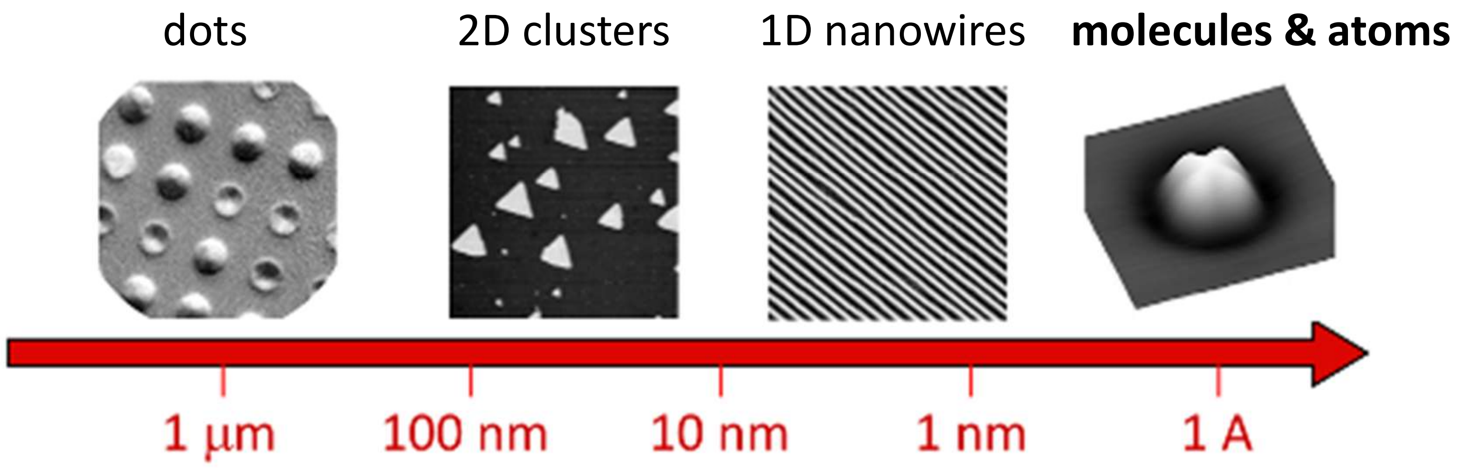
Ind. Eng. Chem. Res. 2016, 55, 41,

"pure" 2D

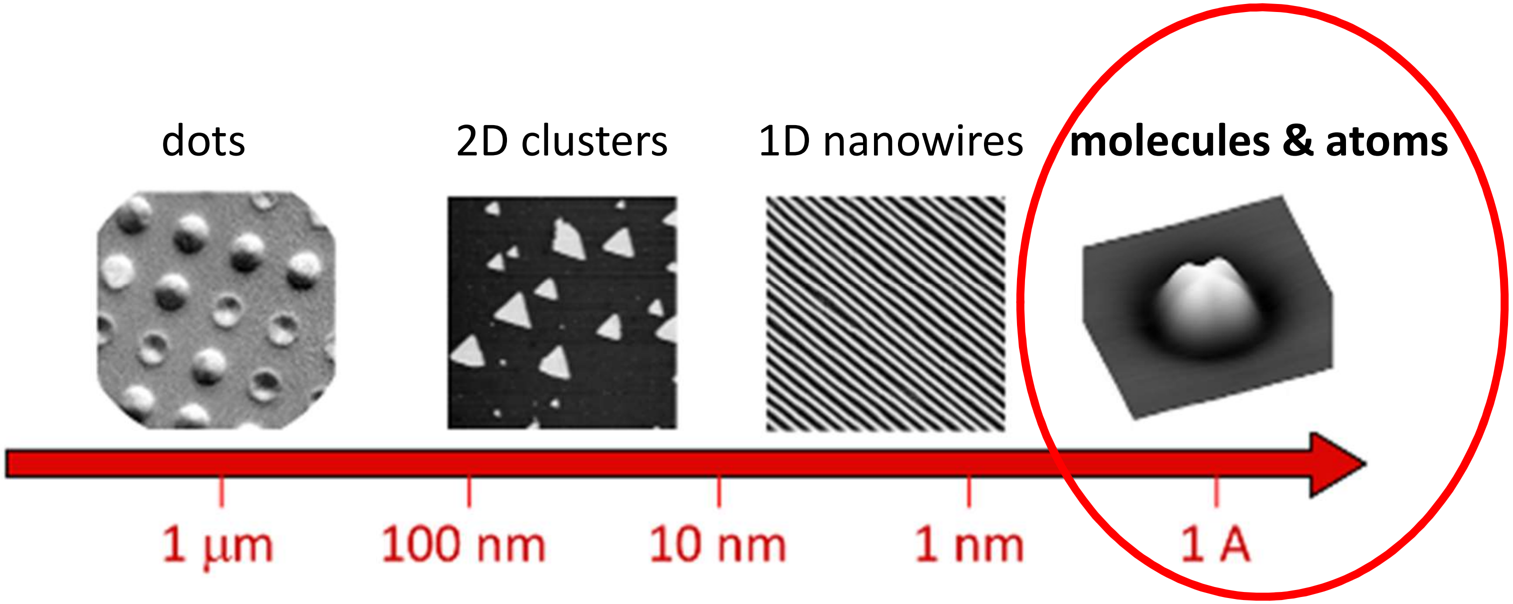


www.washington.edu
Nature 546, 270–273 (2017)

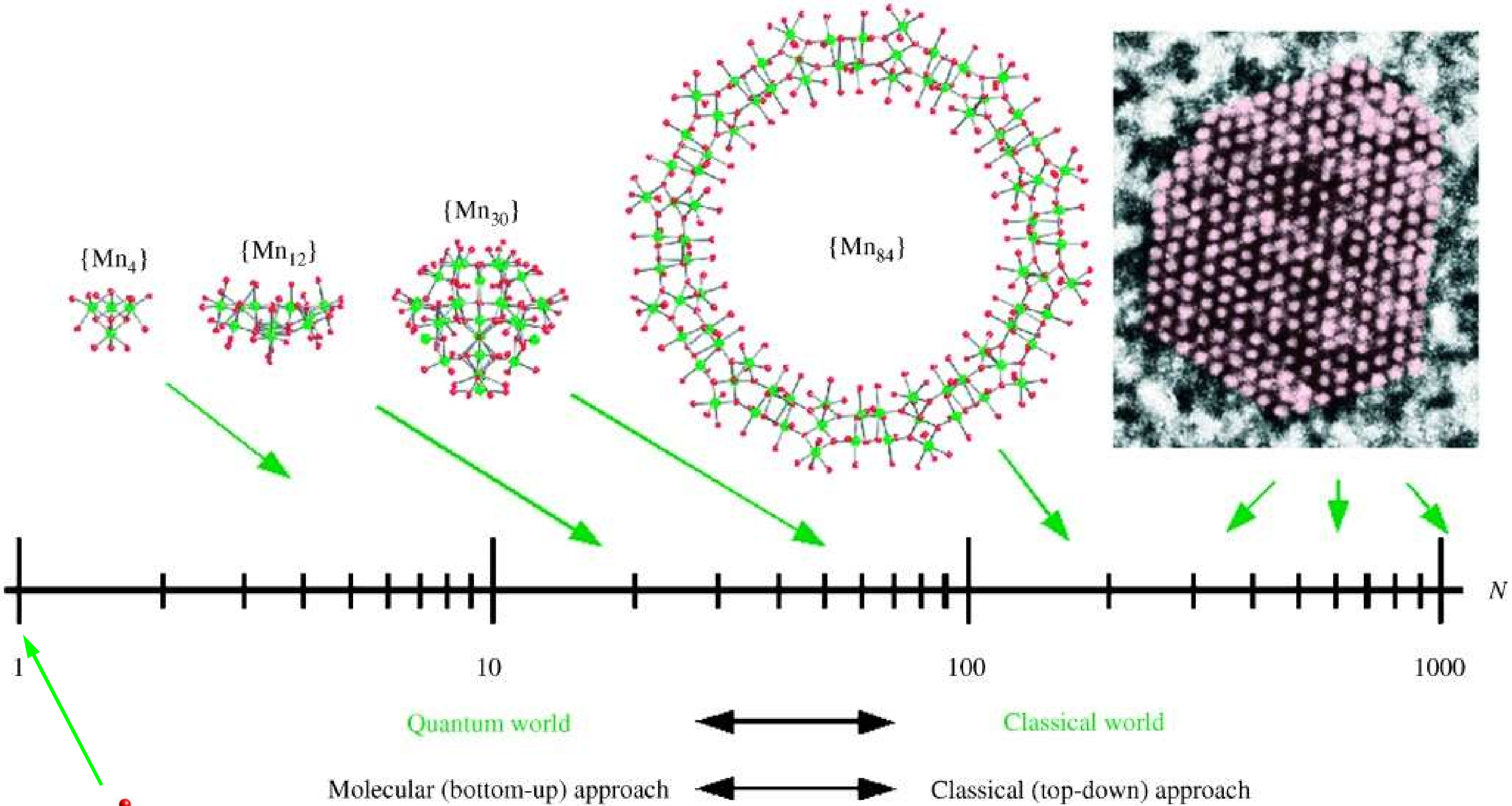
lateral confinement

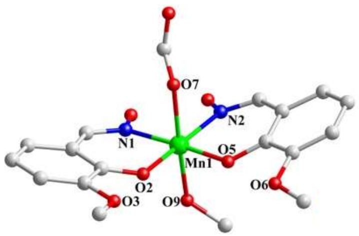


lateral confinement



variety of size

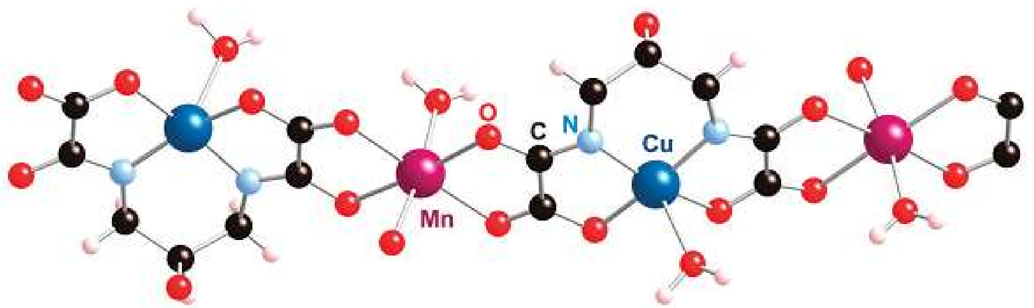




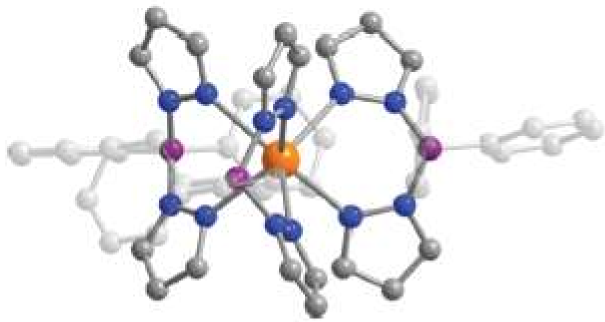
Angew. Chem. Int. Ed., 43 (16) 2117-2121 (2004)

Inorg. Chem. Com. 77, 27-30 (2017)

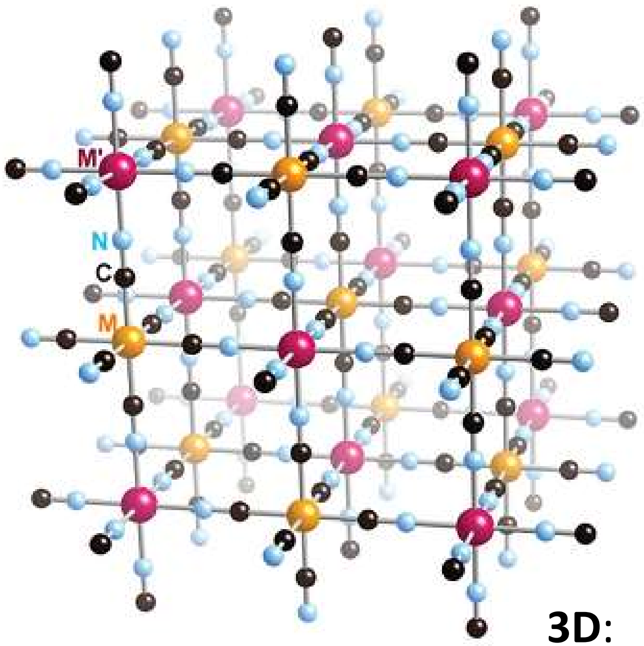
variety of dimensionality



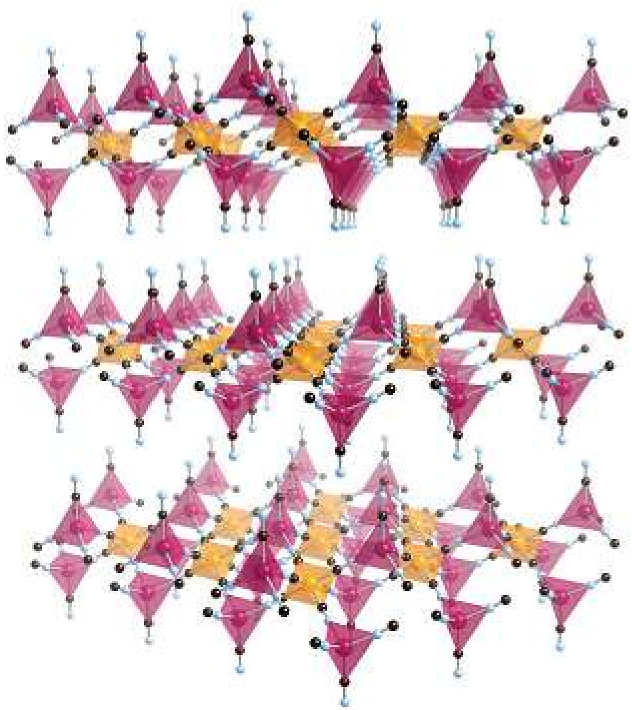
1D:
$Mn^{II}Cu^{II}(pbaOH) \cdot 3H_2O$



0D:
$U(Ph_2BPz_2)_3$



3D:
Prussian blue analogues

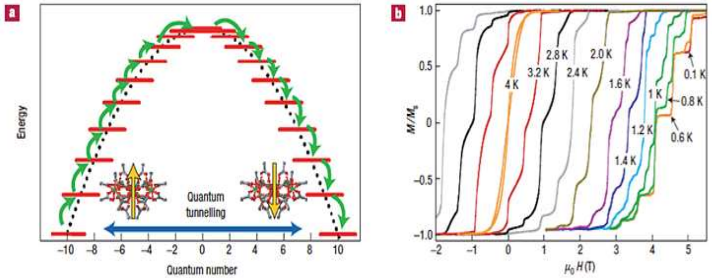


2D:
$[Net_4]_2Mn^{II}_3(CN)_8$

J. AM. CHEM. SOC. 2009, *131*, 12558–12559
Chem. Soc. Rev., 2011, **40**, 3266–3296

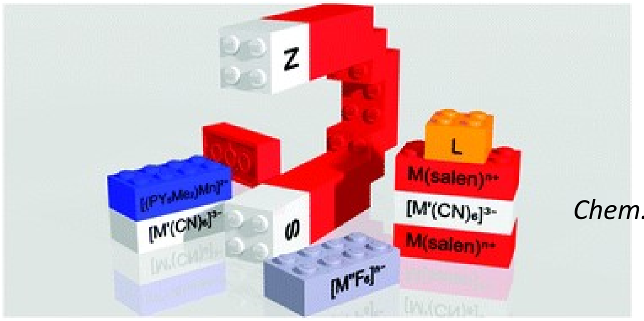
Molecular Magnets

Magnetic relaxations



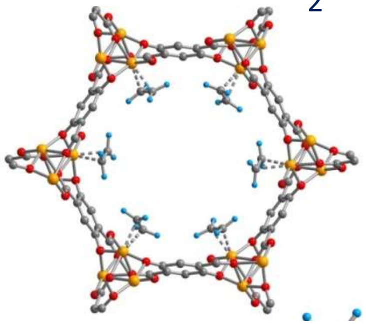
Nature Materials 7, 179-186 (2008)

Building-block approaches

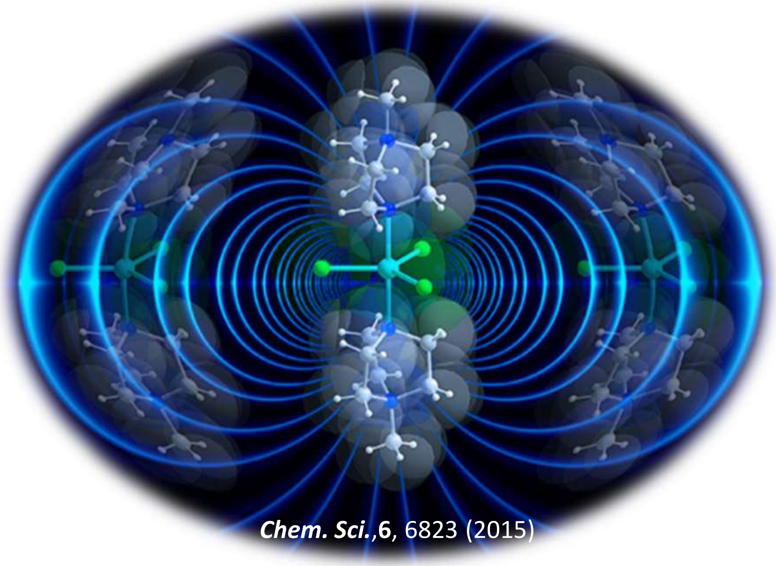


Chem. Commun. 50, 4396-4415 (2014)

Selective solid adsorbents CO_2

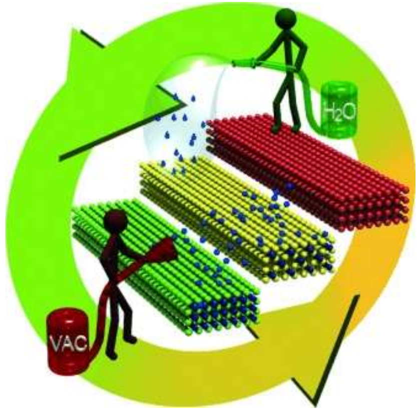


Science 2012, *335*, 1606-1610



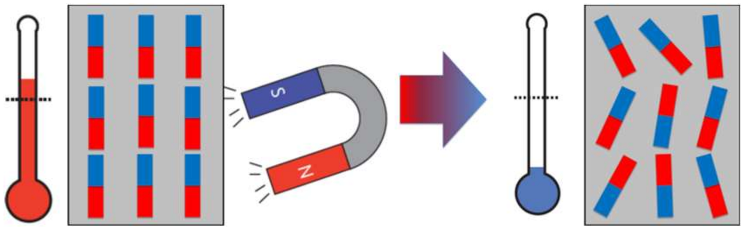
Chem. Sci.,**6**, 6823 (2015)

Magnetic sponge

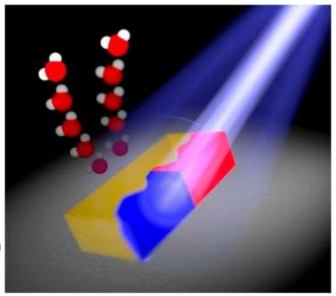


Angewandte Chemie 50,17 (2011)

Magnetocaloric effect

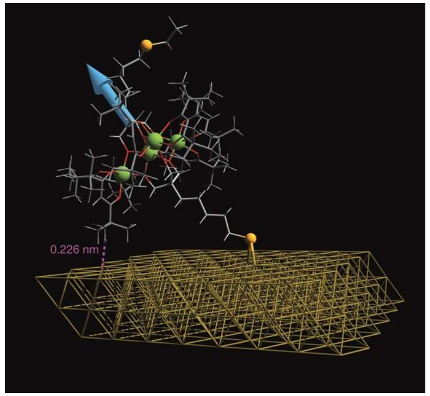


Photomagnetism



J. Am. Chem. Soc. 140, 46, 15876-15882 (2018)

Nanoscale

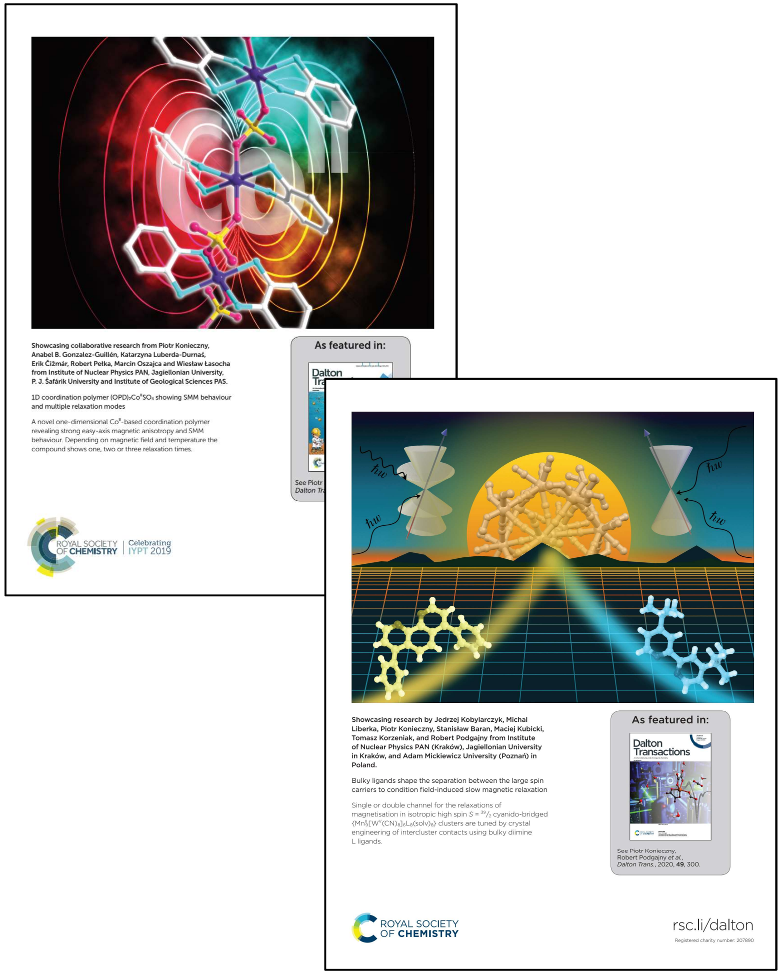


Nature 468, 417–421 (2010)

The Henryk Niewodniczański Scientific Award
Magnetism of low dimensional molecular magnets

Conventional and rotating magnetocaloric effect

1. **P. Konieczny***, S. Chorazy, et al., Inorg. Chem., 56 (2017) 7089-7098;
2. **P. Konieczny***, Ł. Michalski, et al.,Inorg. Chem., 56 (2017) 2777-2783;
3. **P. Konieczny***, R. Pełka, et al., Inorg. Chem., 56 (2017) 11971-980;
4. M. Fitta*, R. Pełka, **P. Konieczny**, M. Bałanda, Crystals, 9 (2019) 9;



Magnetic relaxations

5. **P. Konieczny***, R. Pełka, et al., Acta Phys. Pol. A, 131 (2017) 884-886;
6. **P. Konieczny***, A.B. Gonzalez-Guillén, et al., Dalton T., 48 (2019) 7560-7570;
7. Ł. Laskowski, I. Kityk, **P. Konieczny**, O. Pastukh, M. Schabikowski, M. Laskowska*, Nanomaterials, 9 (2019) 764;
8. J. Kobylarczyk, M. Liberka, **P. Konieczny***, et al., Dalton T., 49 (2020) 300-311;
9. **P. Konieczny***, R. Pełka, et al., J. Phys. Chem. C, 124 (2020) 7930-7937 ;
10. M. Laskowska, O. Pastukh*, **P. Konieczny**, et al., *Materials* (2020), *13*, 2624.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NEWS RELEASE 3-JUN-2020

Anisotropy of spin-lattice relaxations in molecular magnets

THE HENRYK NIEWODNICZANSKI INSTITUTE OF NUCLEAR PHYSICS POLISH ACADEMY OF SCIENCES

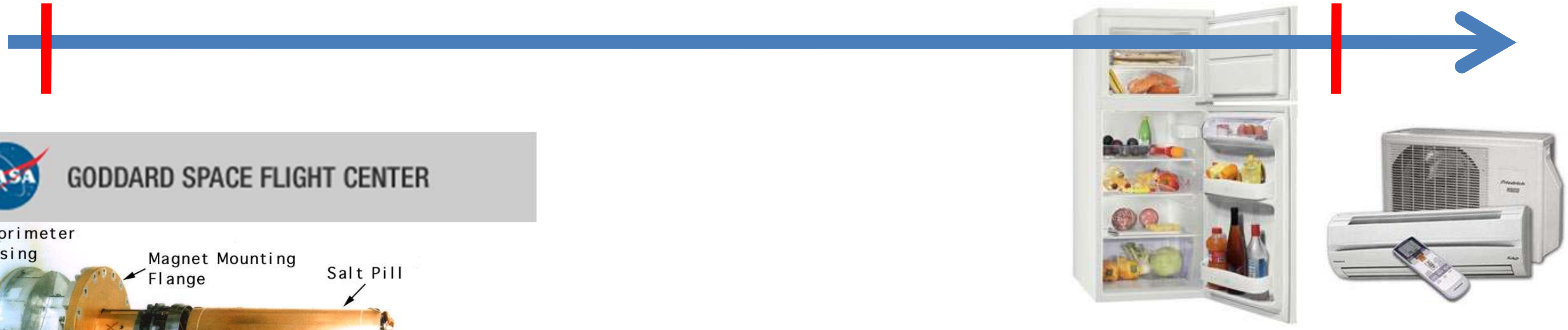
Other aspects of low dimensional magnetism

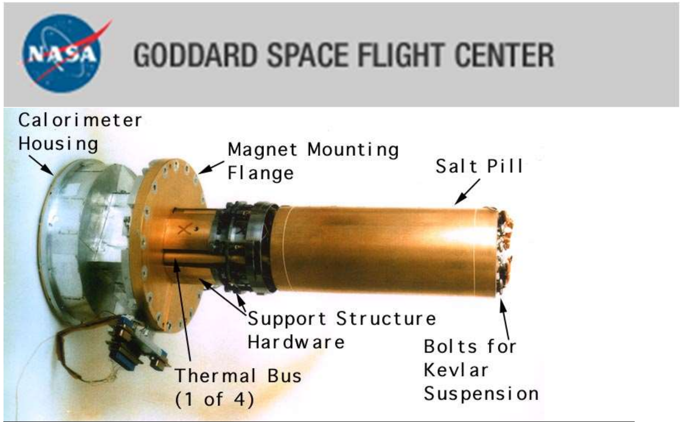
11. F. Setifi*, **P. Konieczny***, et al., J. Mol. Struct., 1149 (2017) 149-154;
12. **P. Konieczny***, R. Pełka*, et al.,Dalton T., 47 (2018) 11438-1144;
13. K. Luberda-Durnaś, **P. Konieczny**, et al., New J. Chem., 42 (2018) 18225-35
14. F. Setifi*, Z. Setifi, **P. Konieczny**, et al., Polyhedron, 157 (2019) 558-566;

Magnetocaloric Effect

heating or cooling of magnetic material as a consequence of changing magnetic field

Why magnetocaloric effect is important?



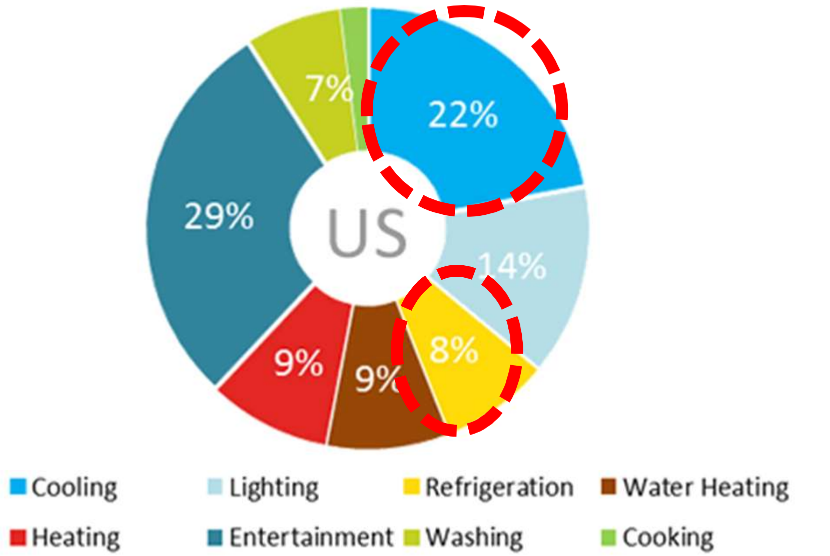


X-Ray Spectrometer (working temp. 65 mK)

Lowest temp.: < 40 mK

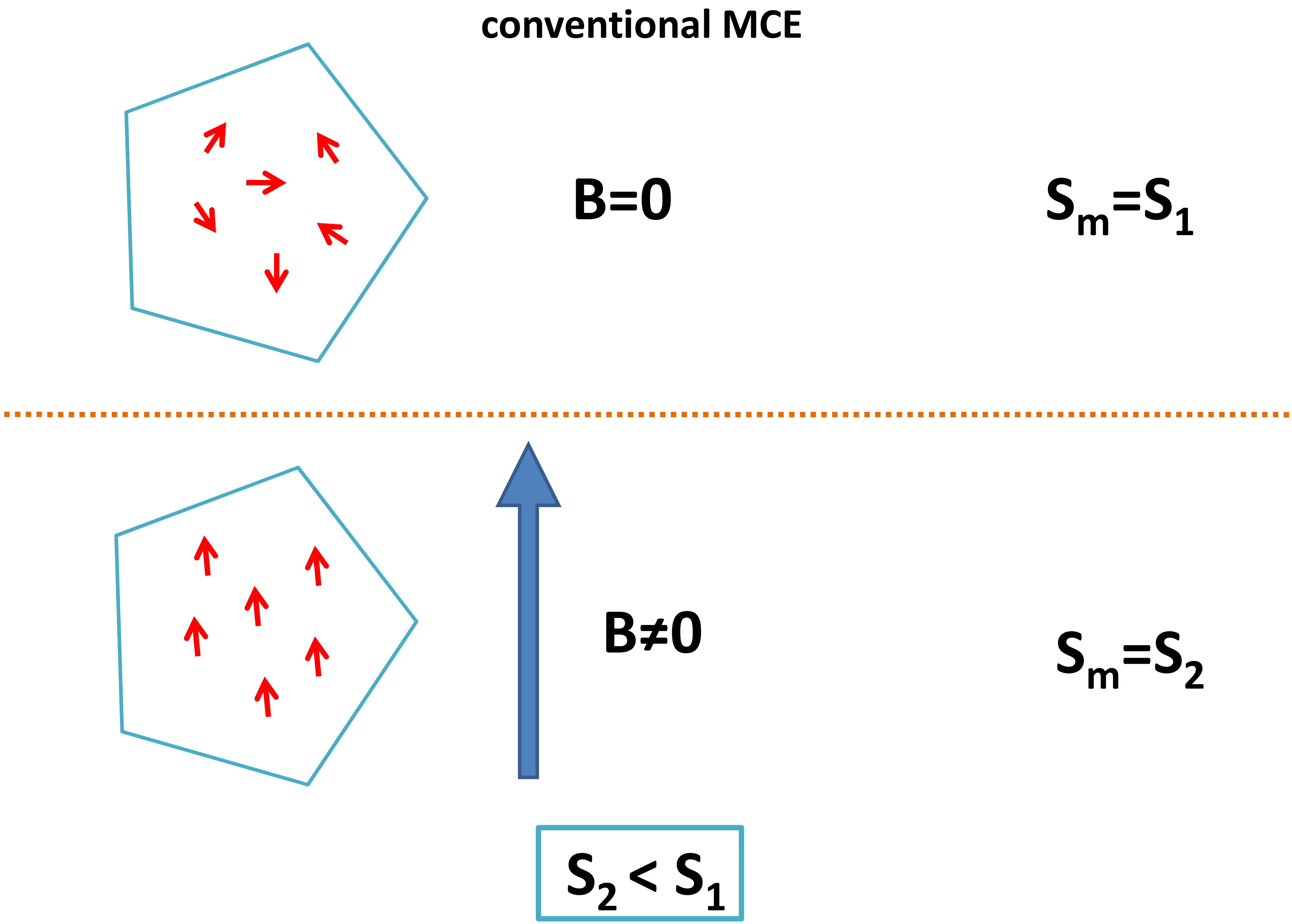
Stability at 100 mK: >48h

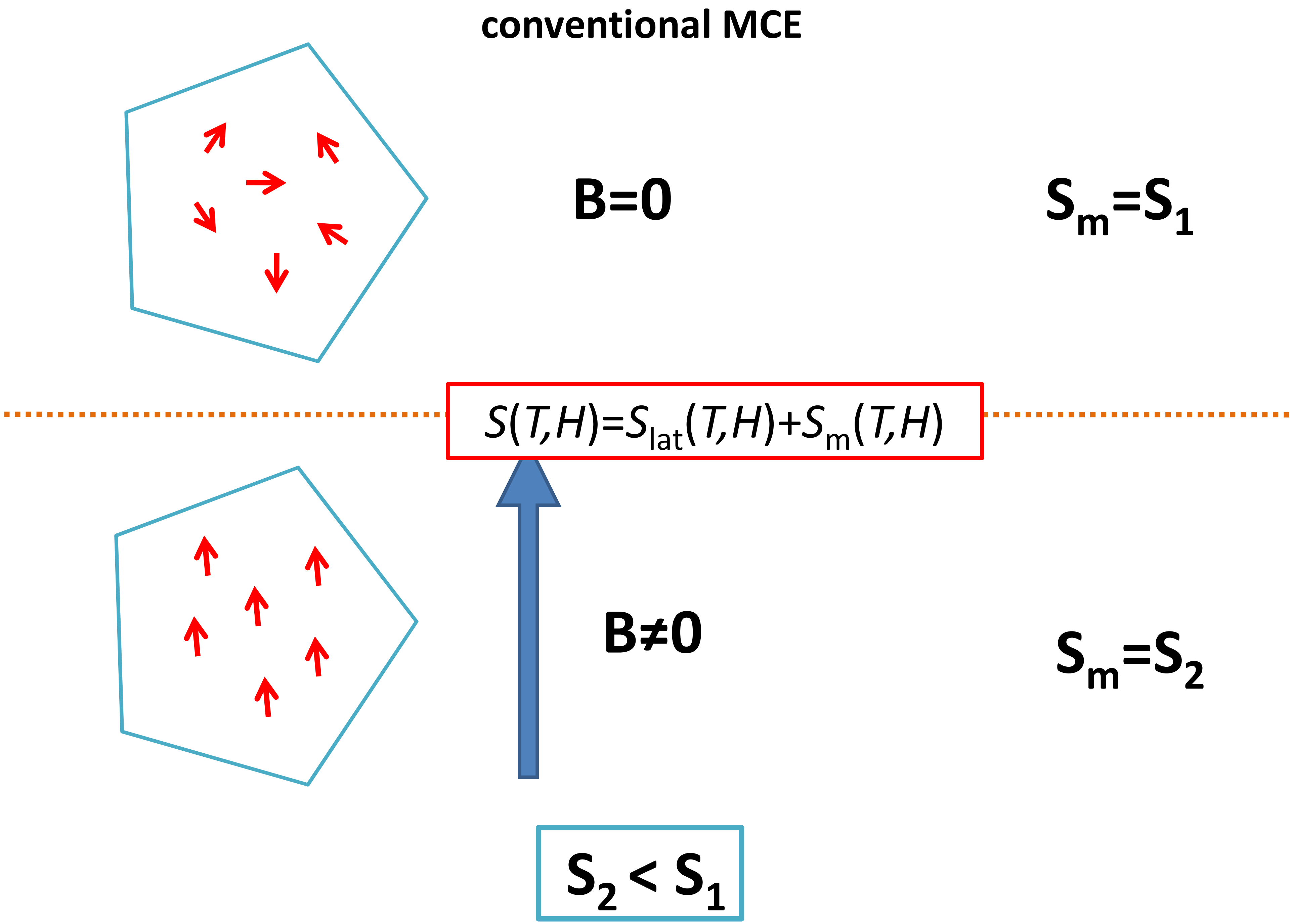
US Residential Power Usage (%)



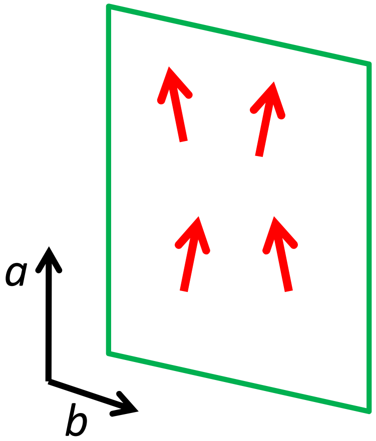
Source: EIA and DEFRA

Shrink That Footprint


conventional MCE
B=0
$S_m=S_1$
B≠0
$S_m=S_2$
$S_2 < S_1$


conventional MCE
B=0
$S_m=S_1$
$S(T,H)=S_{lat}(T,H)+S_m(T,H)$
B≠0
$S_m=S_2$
$S_2 < S_1$

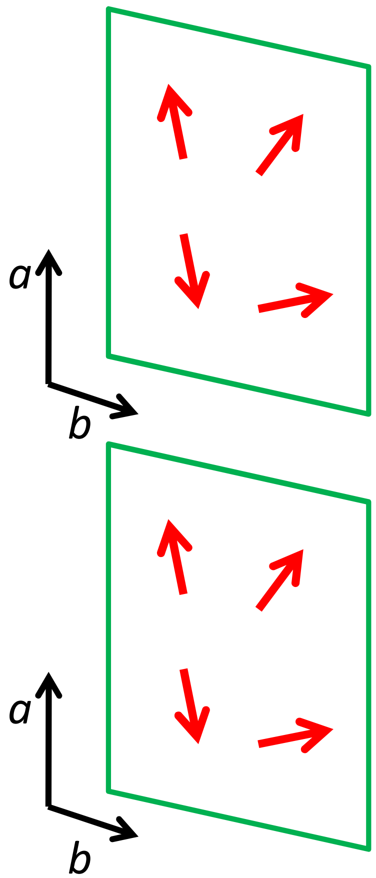
Rotating Magnetocaloric Effect (RMCE)



B=0

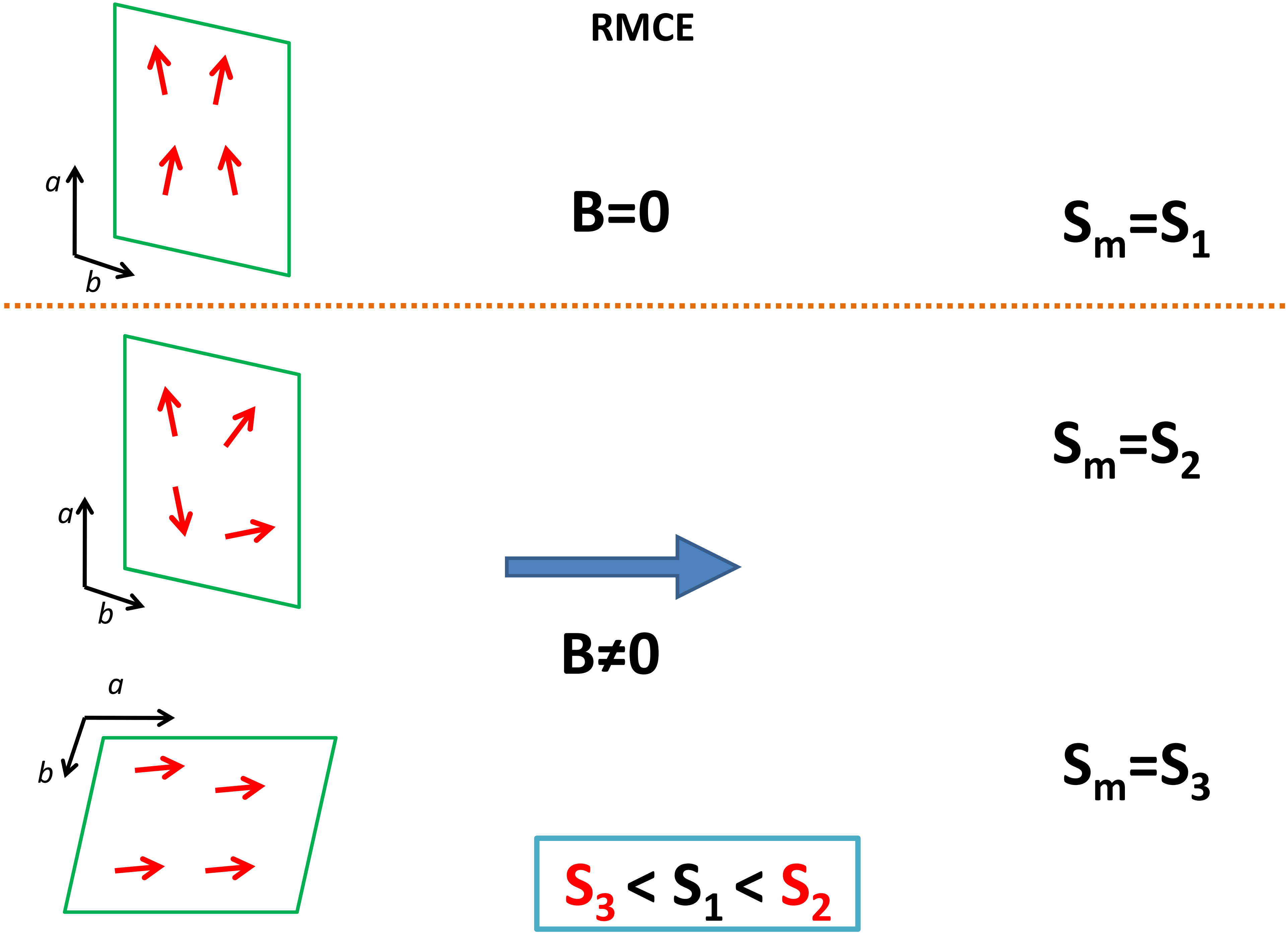
$S_m = S_1$

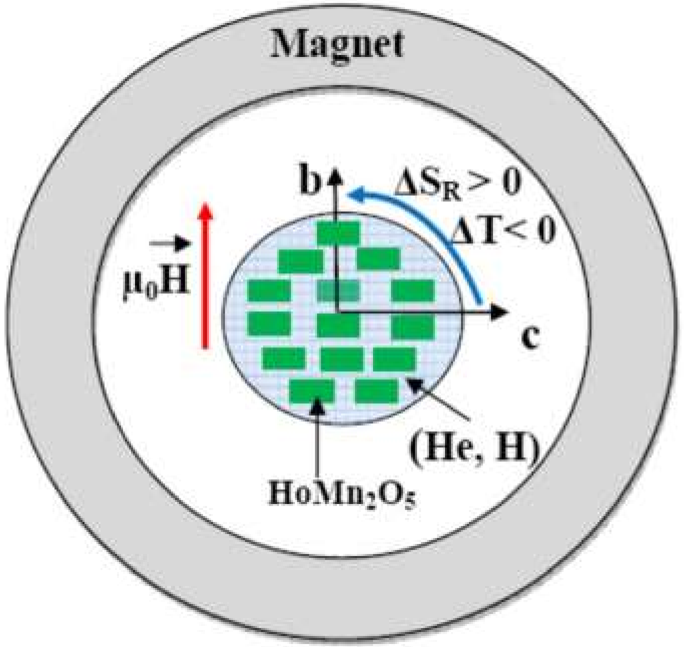
$S_m = S_2$



B≠0

$S_1 < S_2$


RMCE
a
b
B=0
$S_m = S_1$
a
b
$S_m = S_2$
B≠0
a
b
$S_m = S_3$
$S_3 < S_1 < S_2$



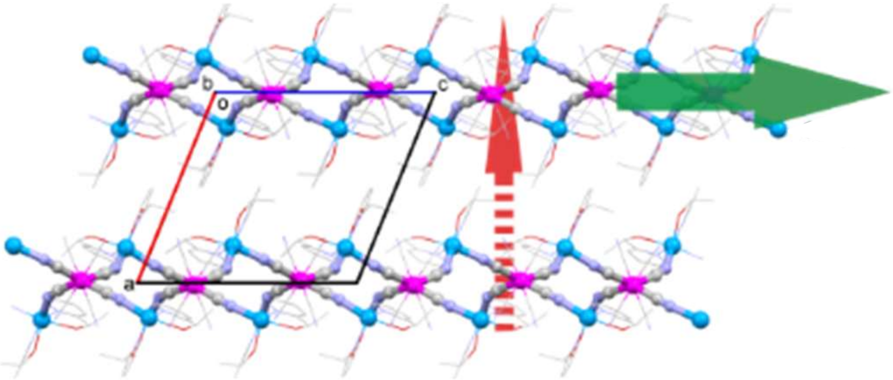
Scheme of rotating MCE cooling device for liquefaction of helium

Why RMCE is interesting?

- simple construction of refrigerator
- no change of magnetic field
- high efficient
- permanent magnets as field source

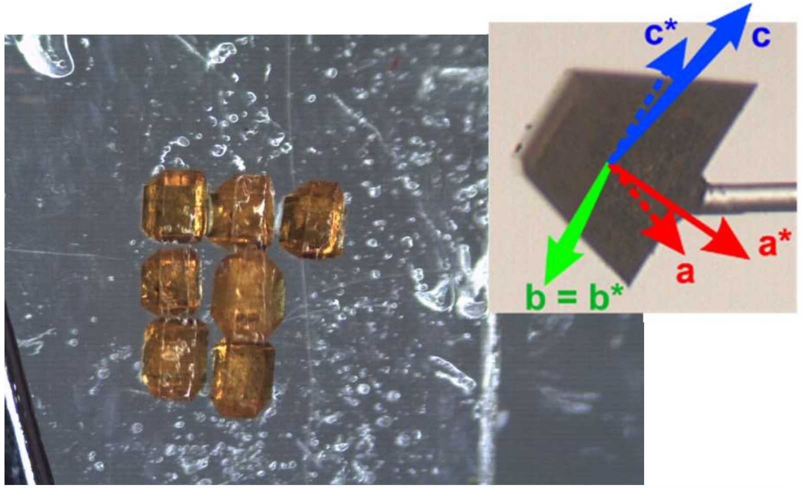
Appl. Phys. Lett. 104, ***2014****, 232402*

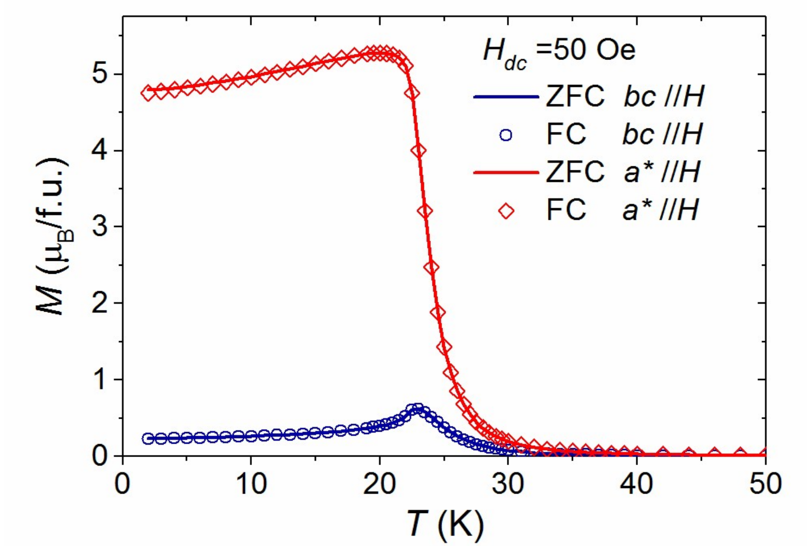
MCE and RMCE: **low anisotropy**

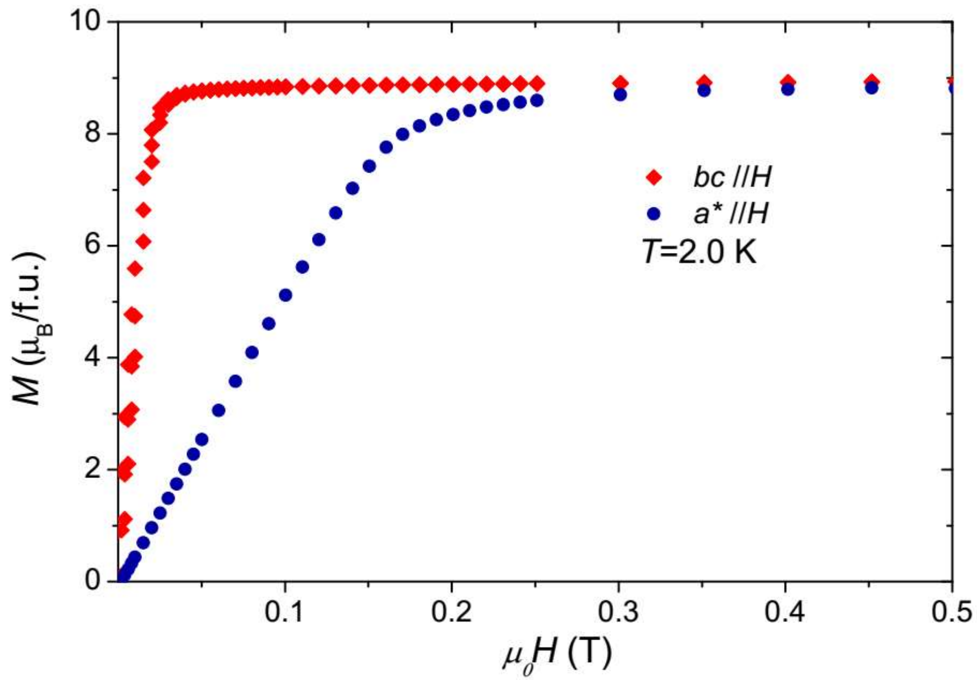


{[**Mn**^{II}(R-mpm)$_2$]$_2$[**Nb**^{IV}(CN)$_8$]}·4H_2O

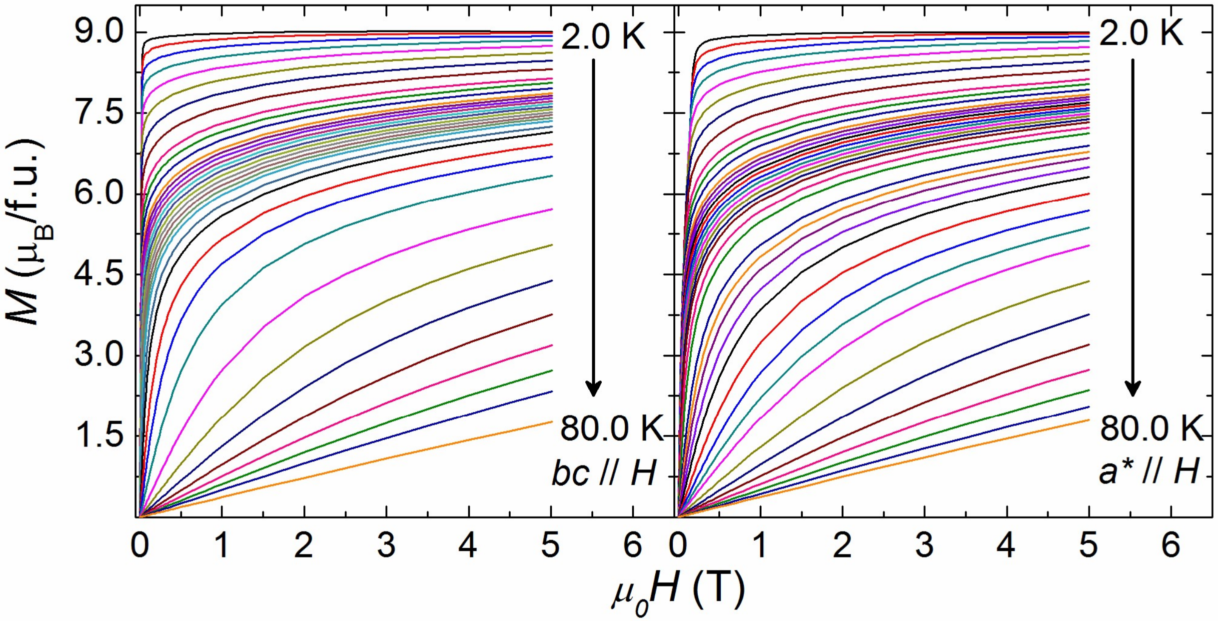
- magneticaly soft
- ferrimagnet, saturation: 8.99 μ_B/f.u. (Mn↑--↓Nb--↑Mn)
- weak easy plane (*bc*) type anisotropy
- *a** is the hard axis







Inorg. Chem. 2017, 56, 2777-2783

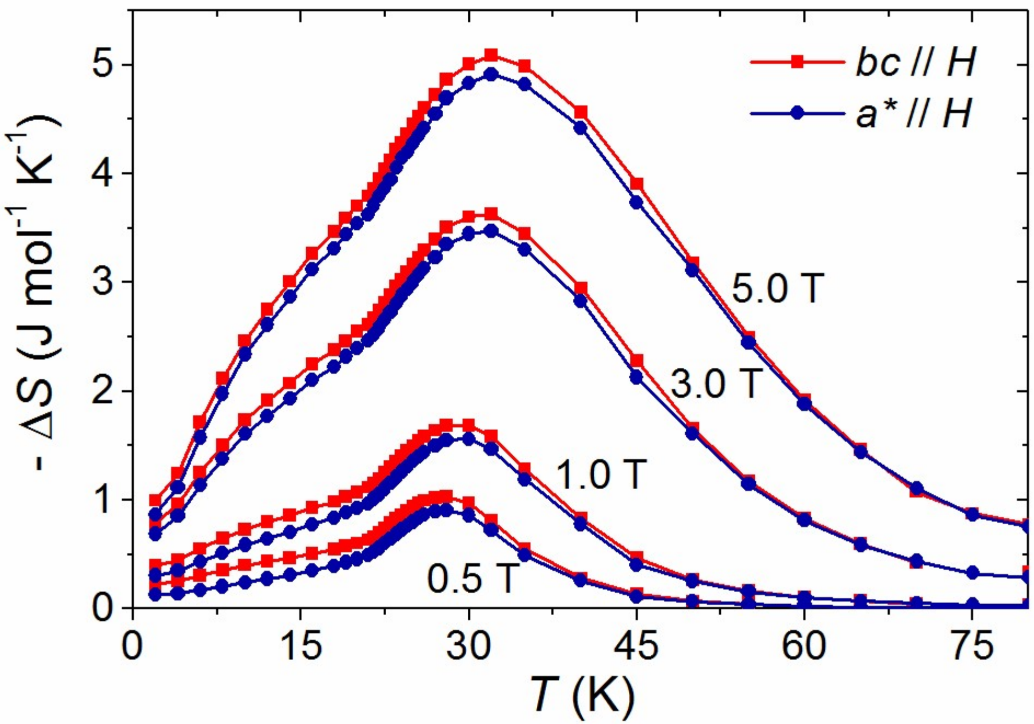


High field MCE

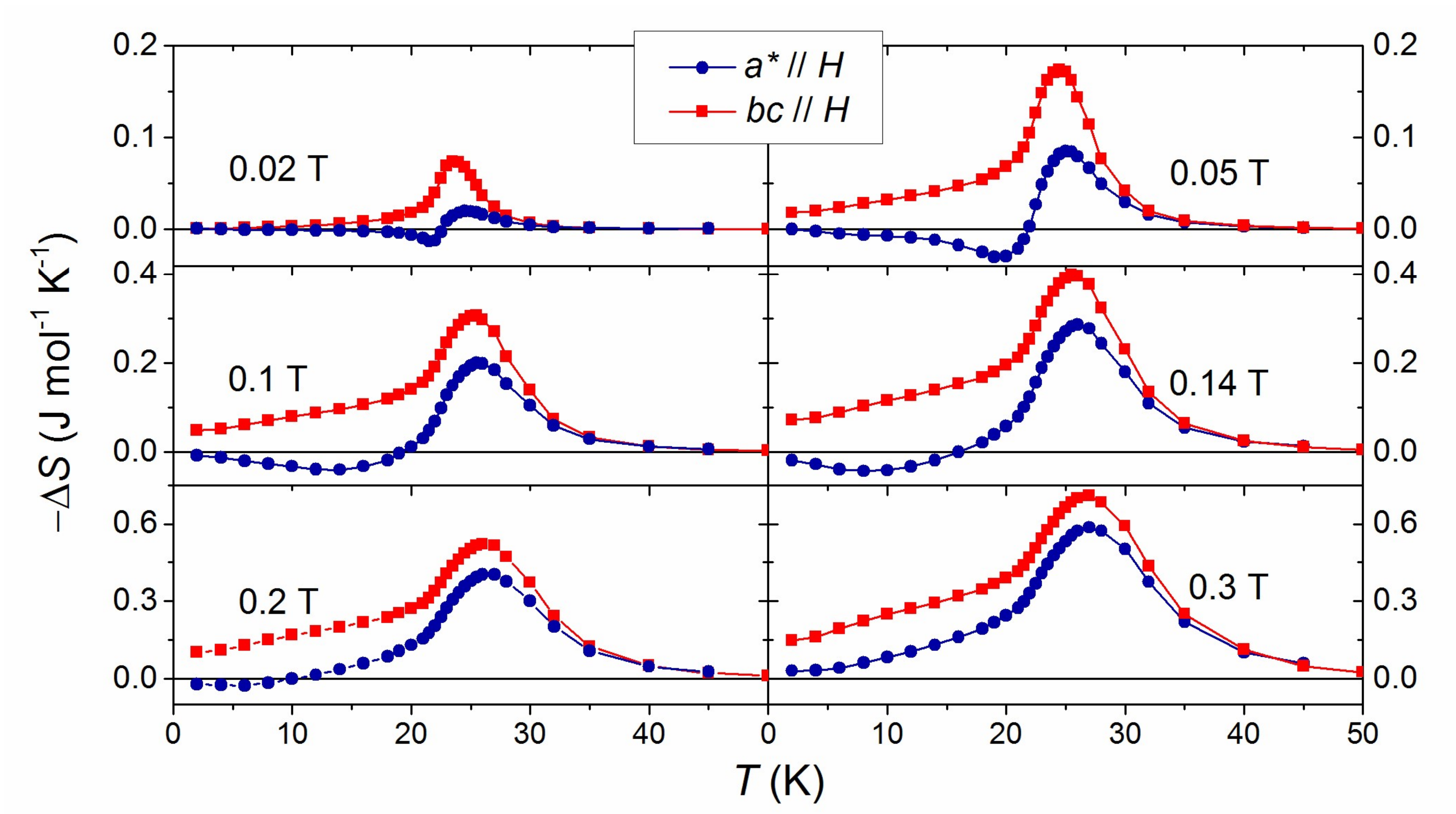
Indirect method

$$\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T$$

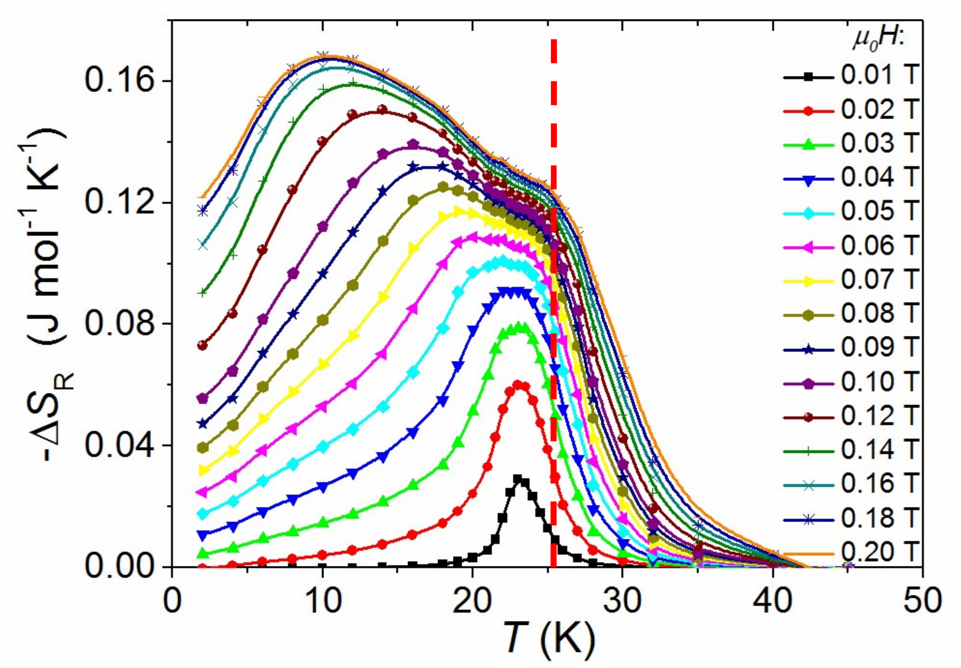
$$\Delta S = \int_0^{H\,\max} \left(\frac{\partial M}{\partial T}\right)_H dH$$



Low field MCE

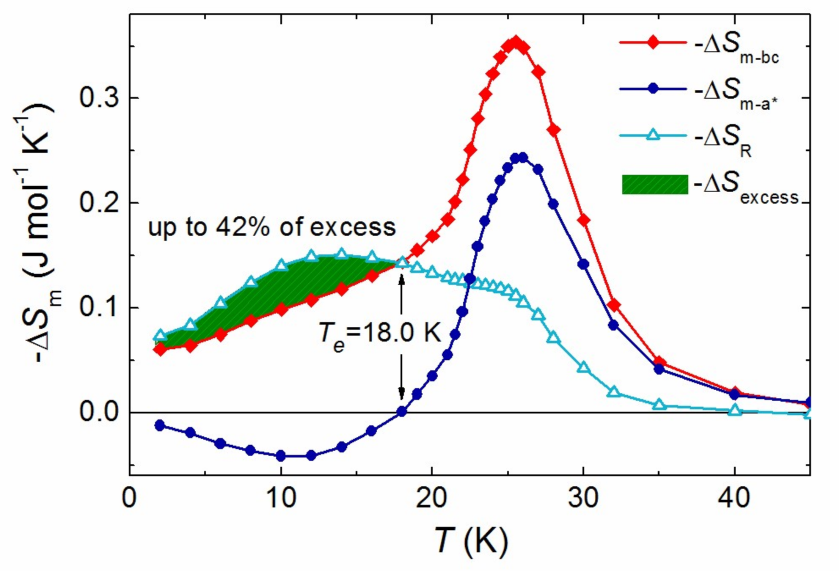


Inorg. Chem. 2017, 56, 2777-2783

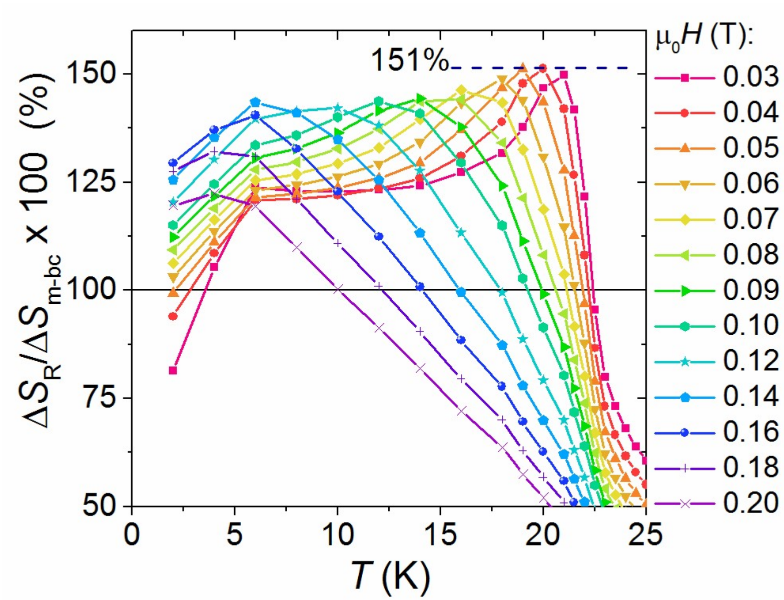


◄ Rotating MCE related to the rotation of crystal around *b* axis by 90º from *a**//*H* to *bc*//*H* **in constant field**

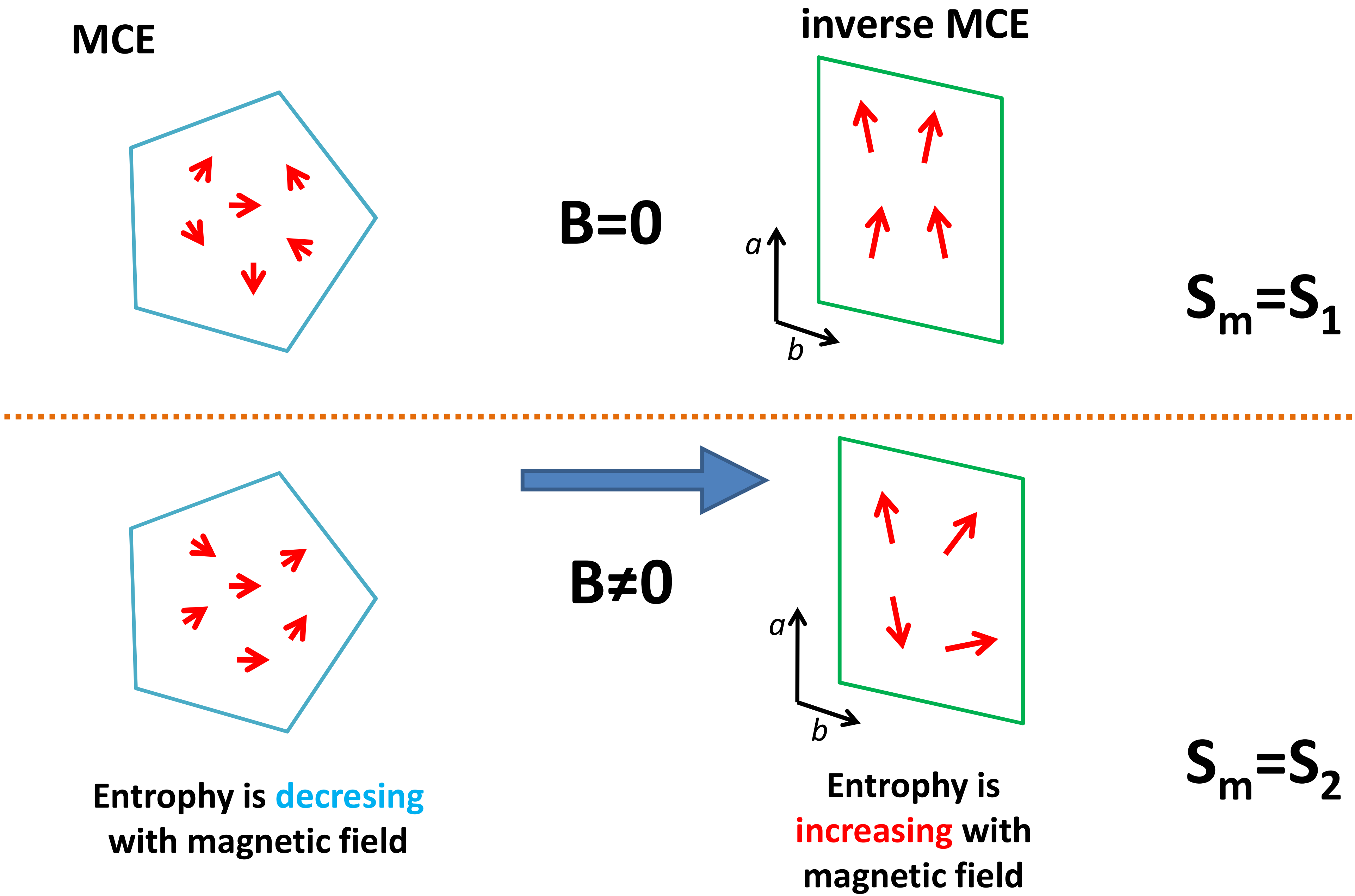
RMCE vs. MCE in 0.12 T



Excess of RMCE compared to MCE easy plane

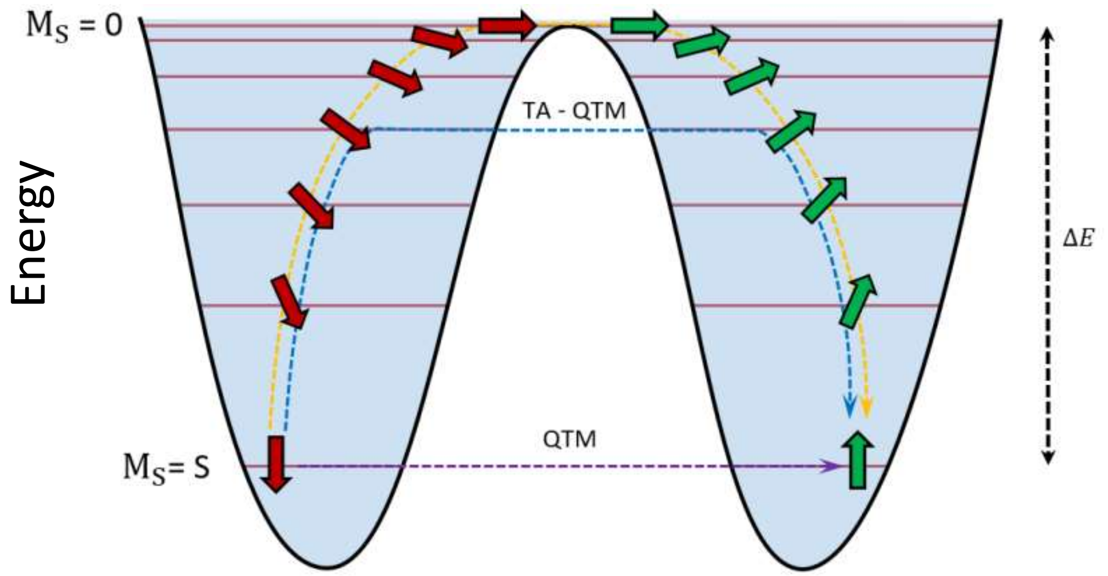


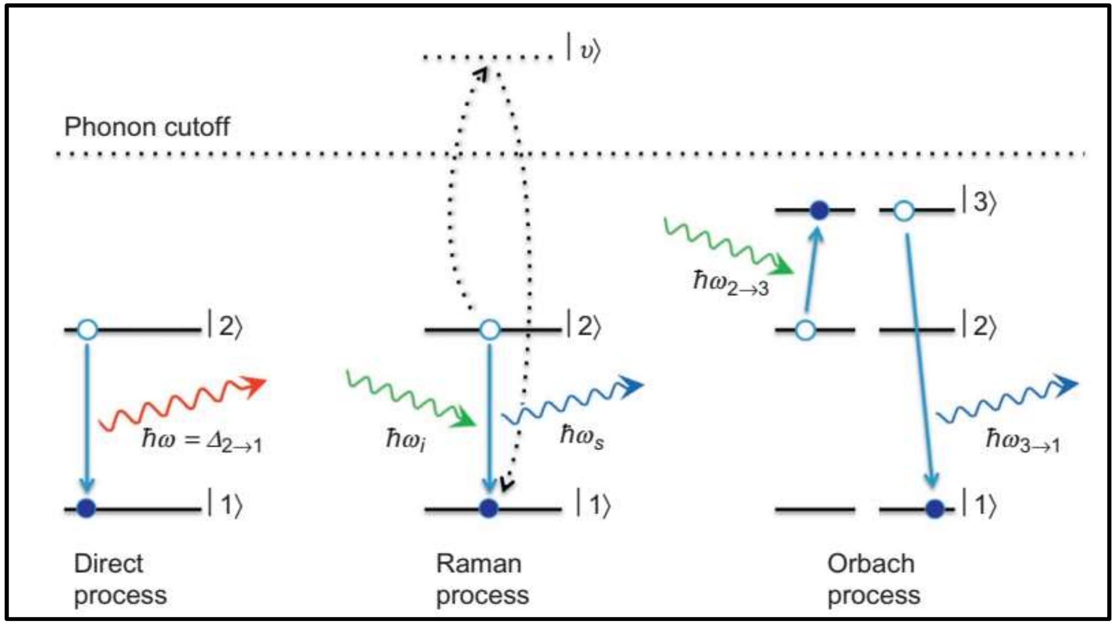
Inorg. Chem. 2017, 56, 2777-2783


MCE
inverse MCE
B=0
a
b
S_m=S_1
B≠0
a
b
S_m=S_2
Entropy is decresing with magnetic field
Entropy is increasing with magnetic field

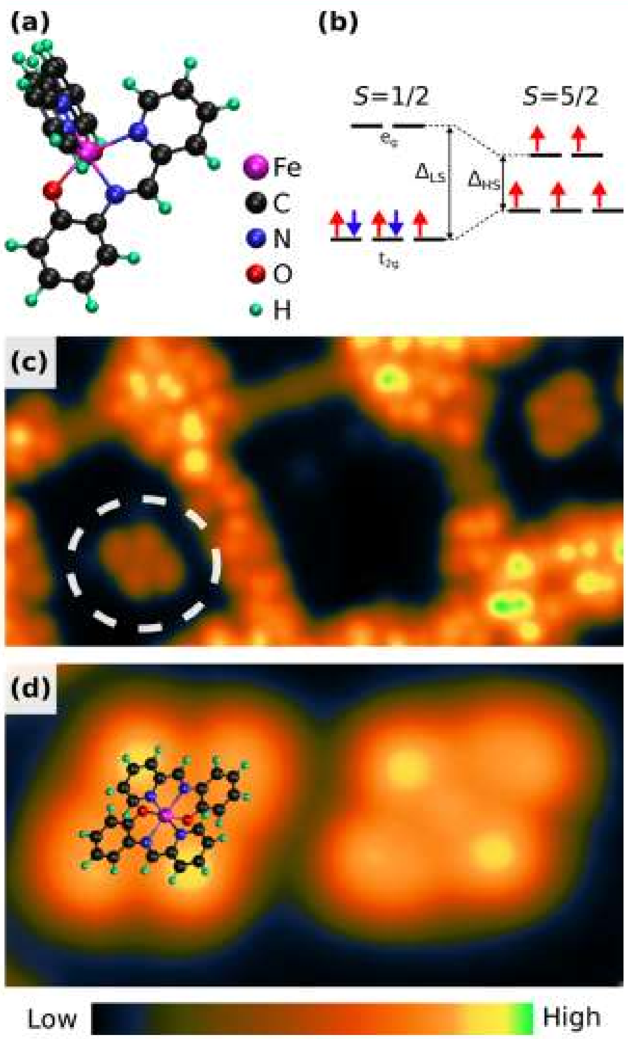
Magnetic relaxations

Spin-lattice relaxation





Examples

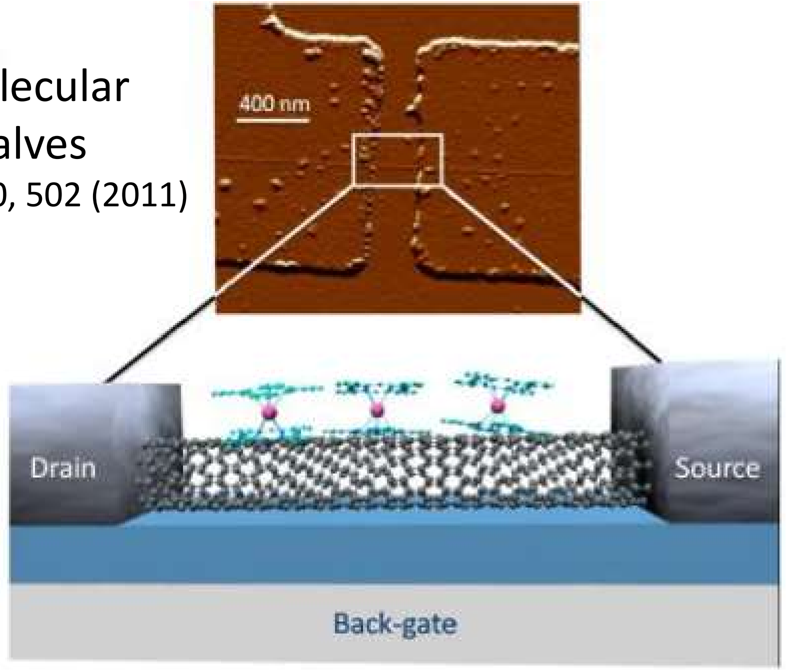


Memory units

Nano. Lett. 17, 6613 (2017)

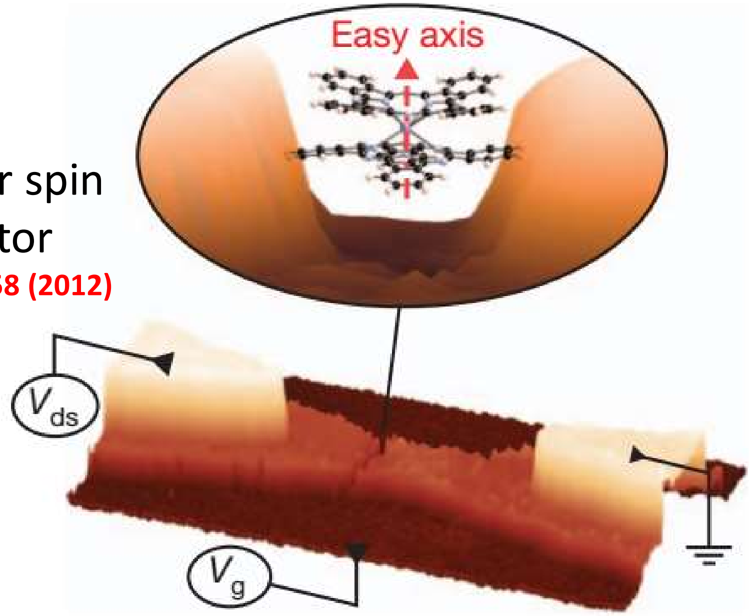
Supramolecular spin valves

Nature Mat. 10, 502 (2011)



Molecular spin transistor

Nature 488, 358 (2012)

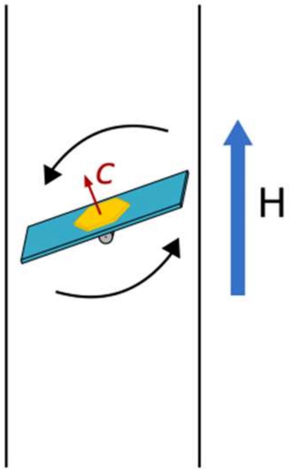


Anisotropy of magnetic relaxations

Experimental setup

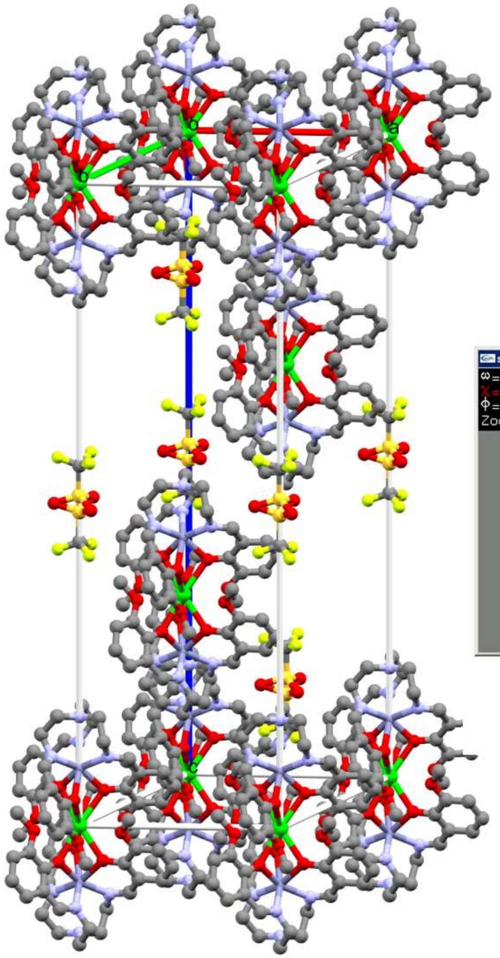
Room Temp.
Ambient pressure

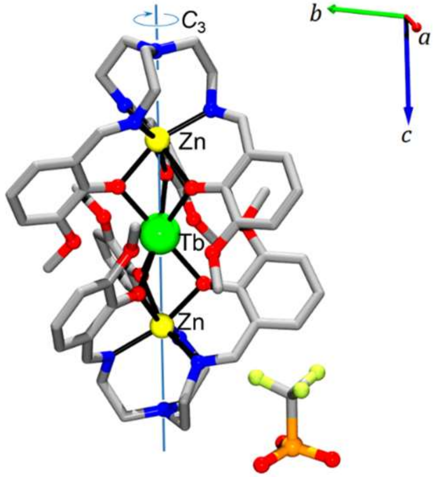
T=2.0 K
Low vacuum

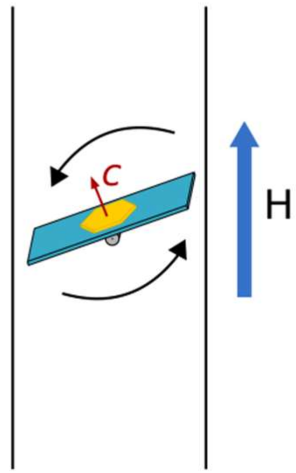


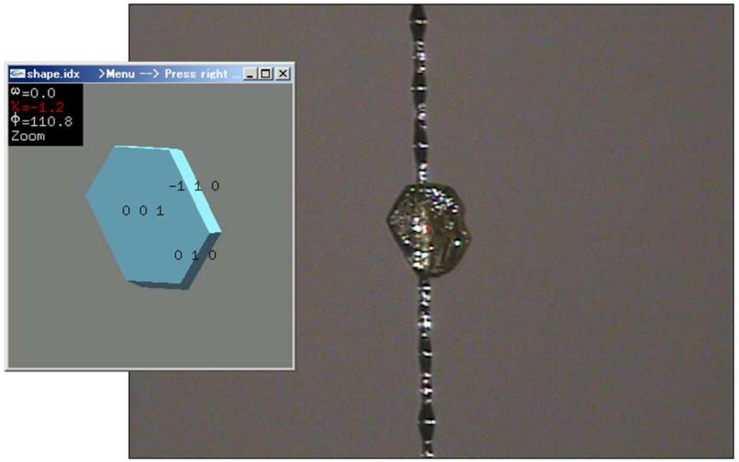
Anisotropy of magnetic relaxations

Sample



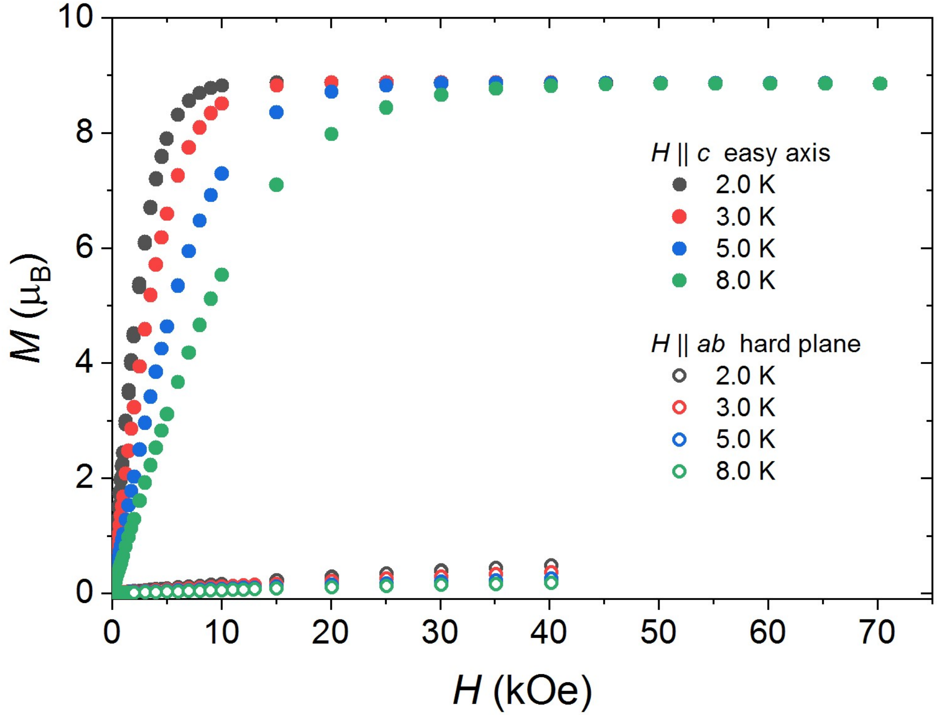


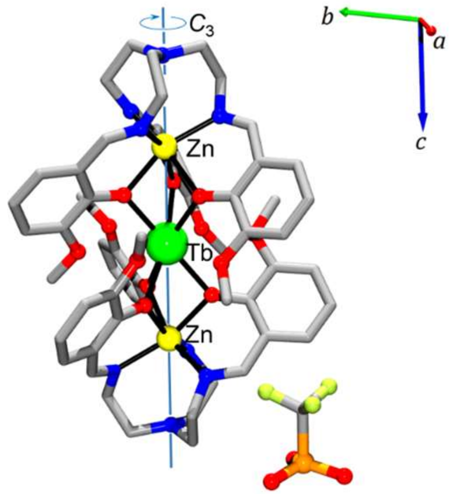


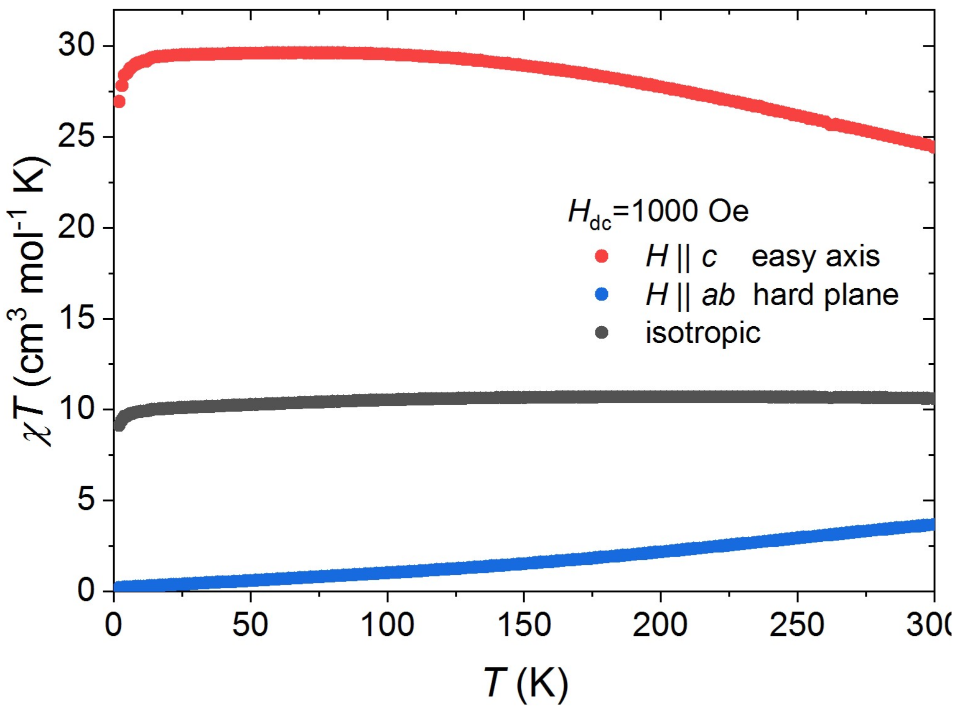


Anisotropy of magnetic relaxations

Dc magnetic properties - measurements

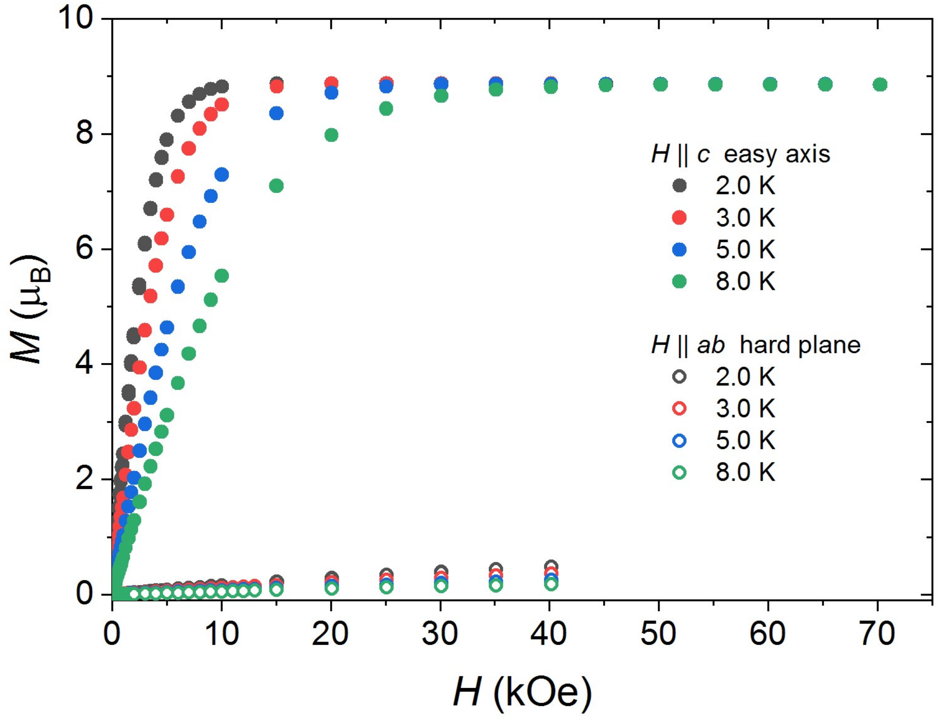


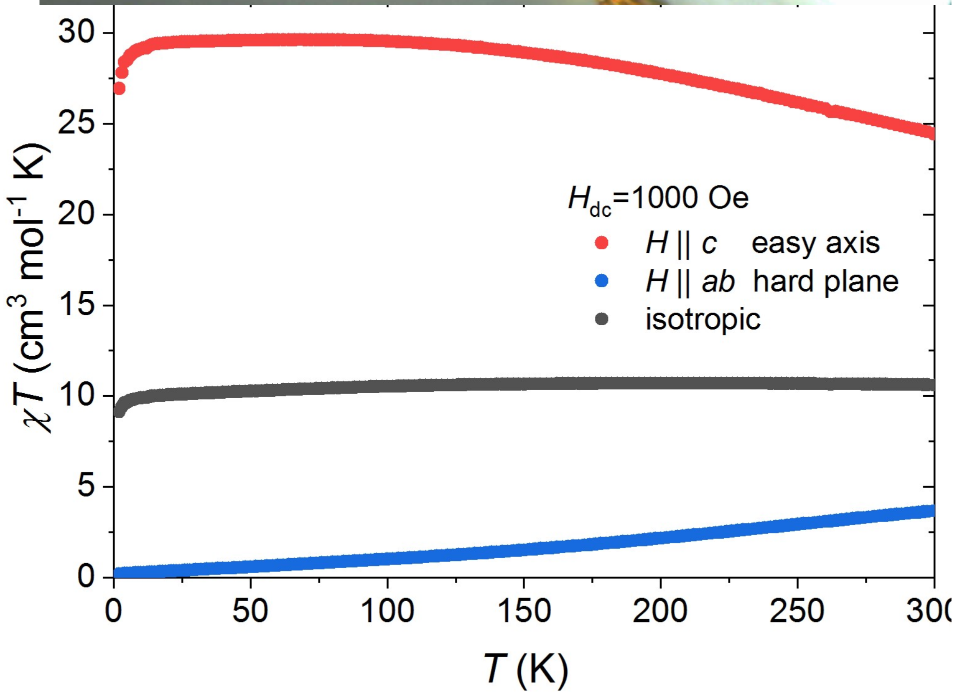




Anisotropy of magnetic relaxations

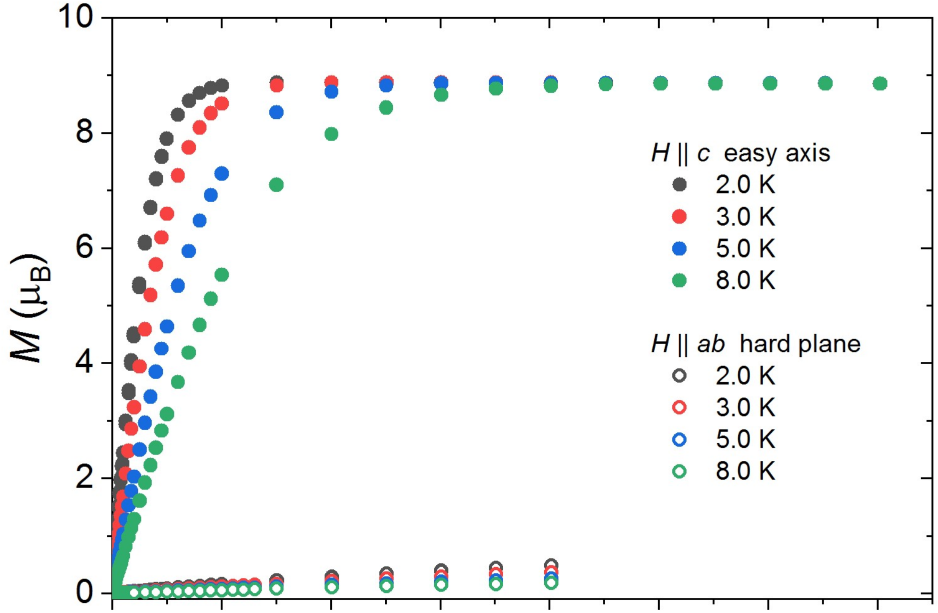
Dc magnetic properties - measurements

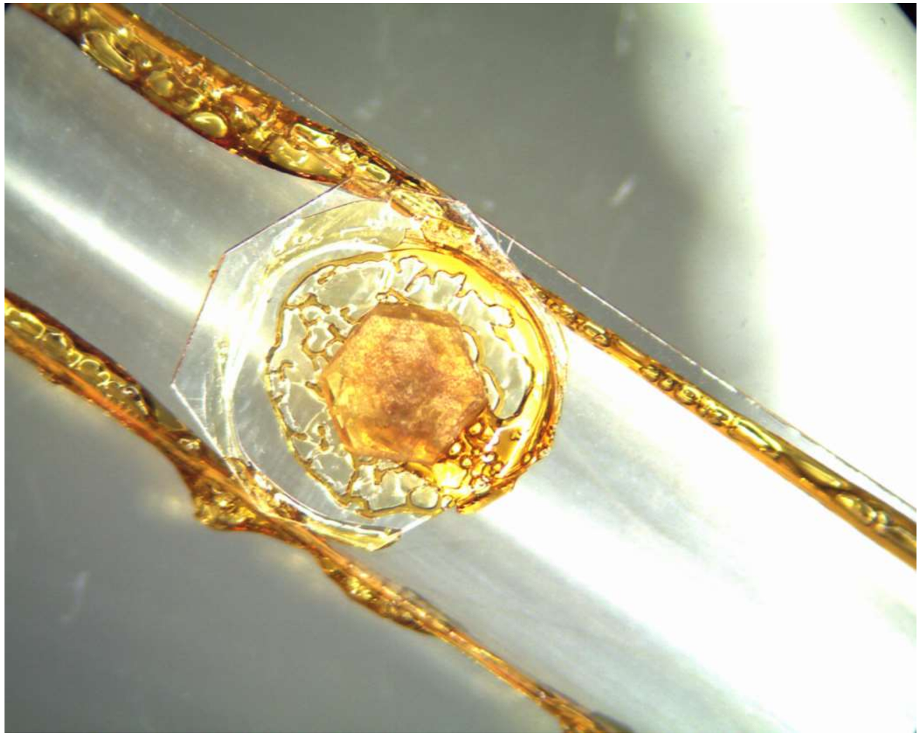


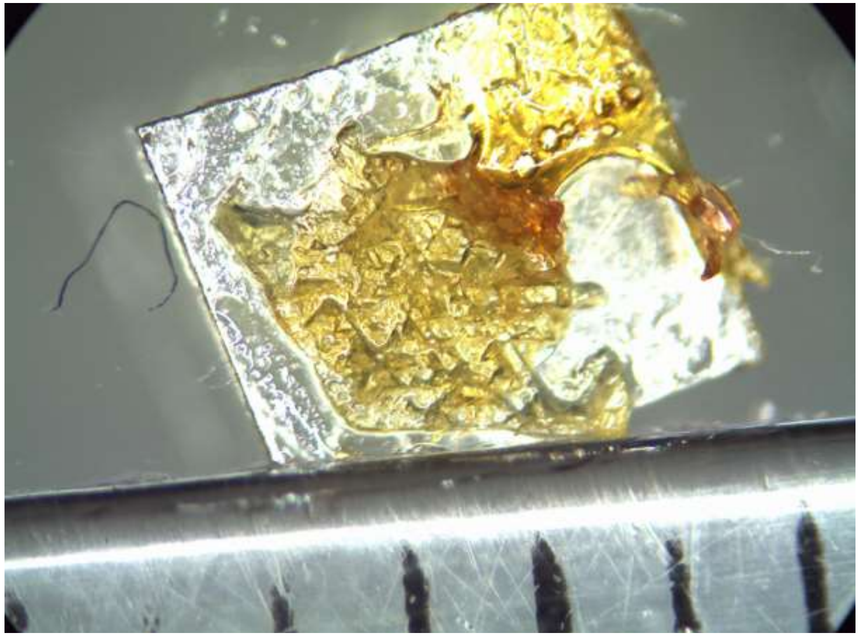


Anisotropy of magnetic relaxations

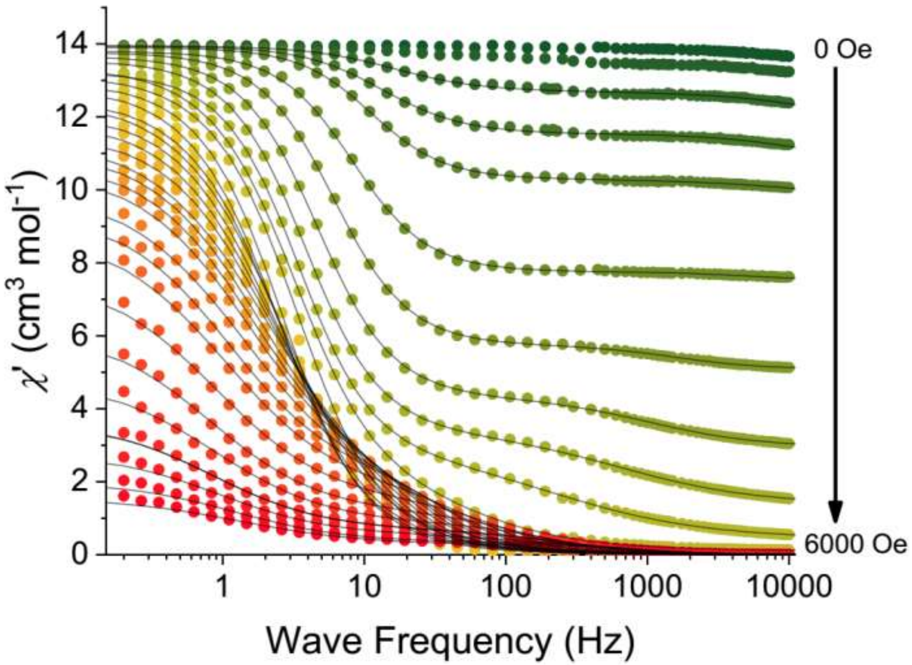
Dc magnetic properties - measurements

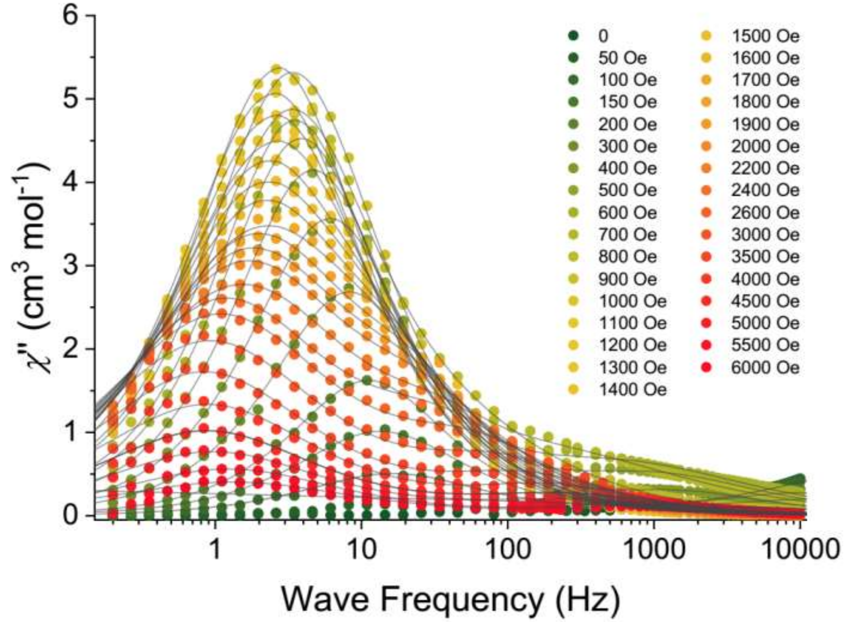




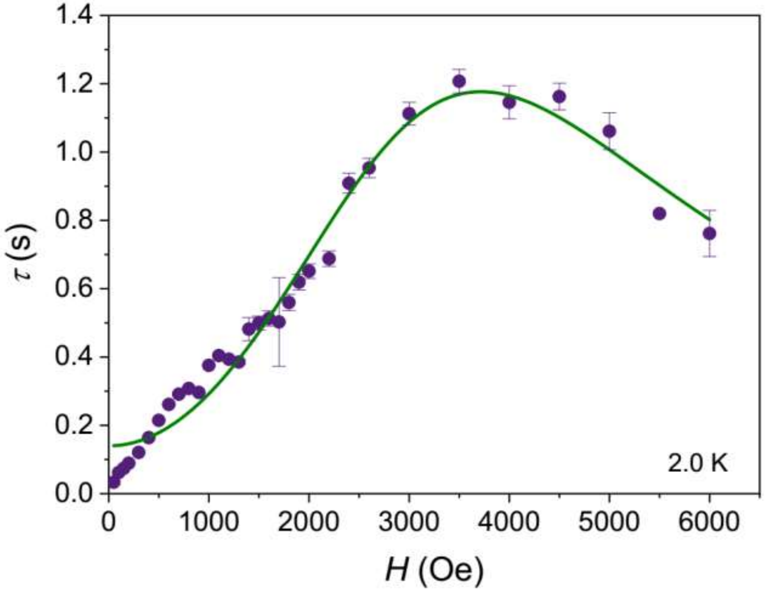


Anisotropy of magnetic relaxations

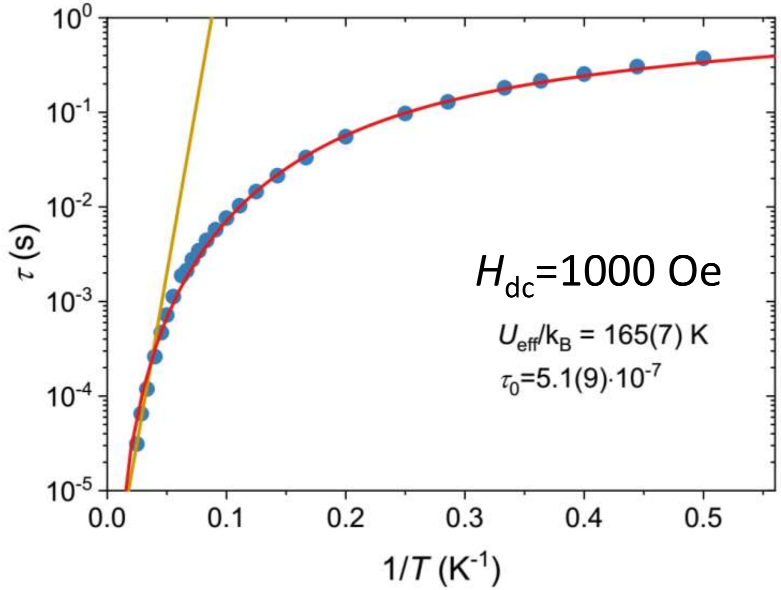




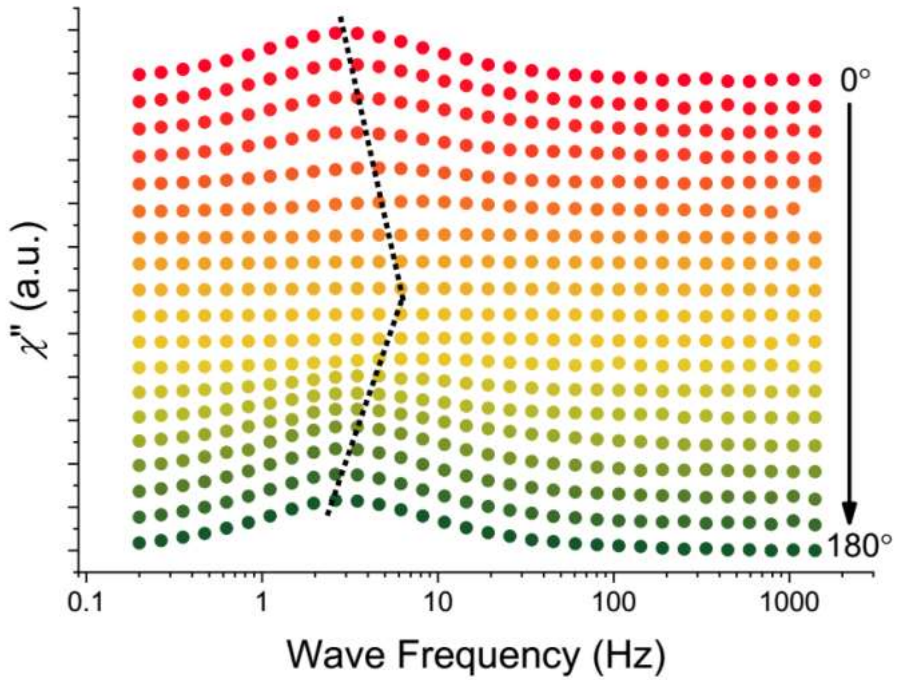
Dc field dependence

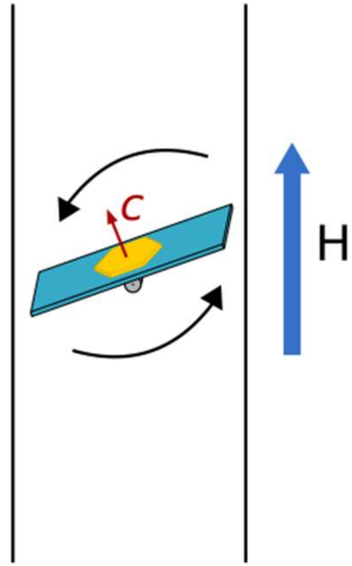


Temperature dependence

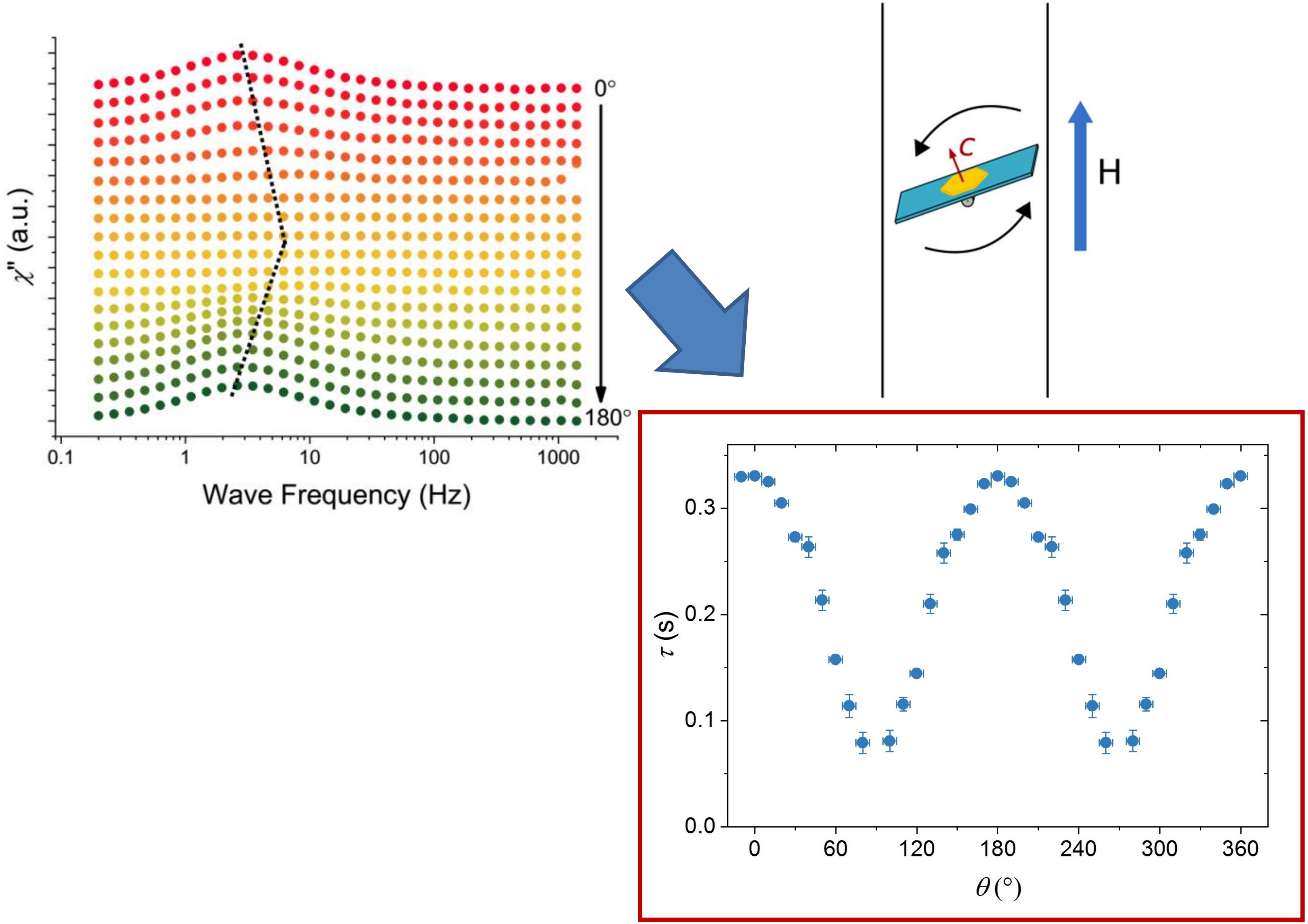


Anisotropy of magnetic relaxations

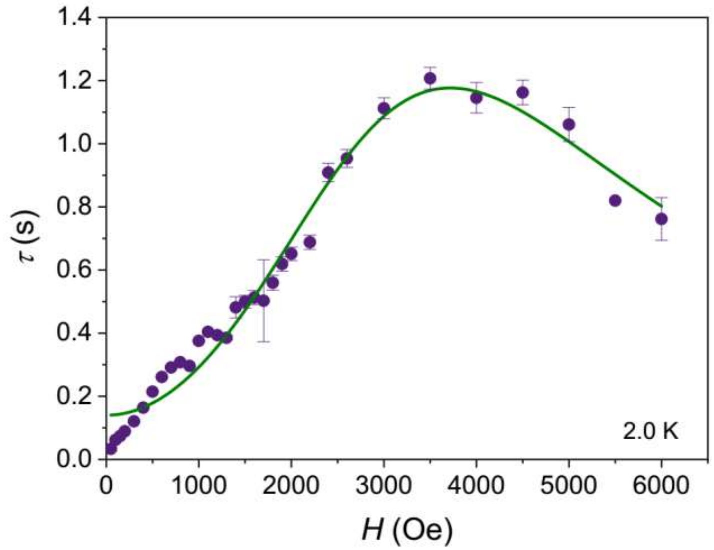


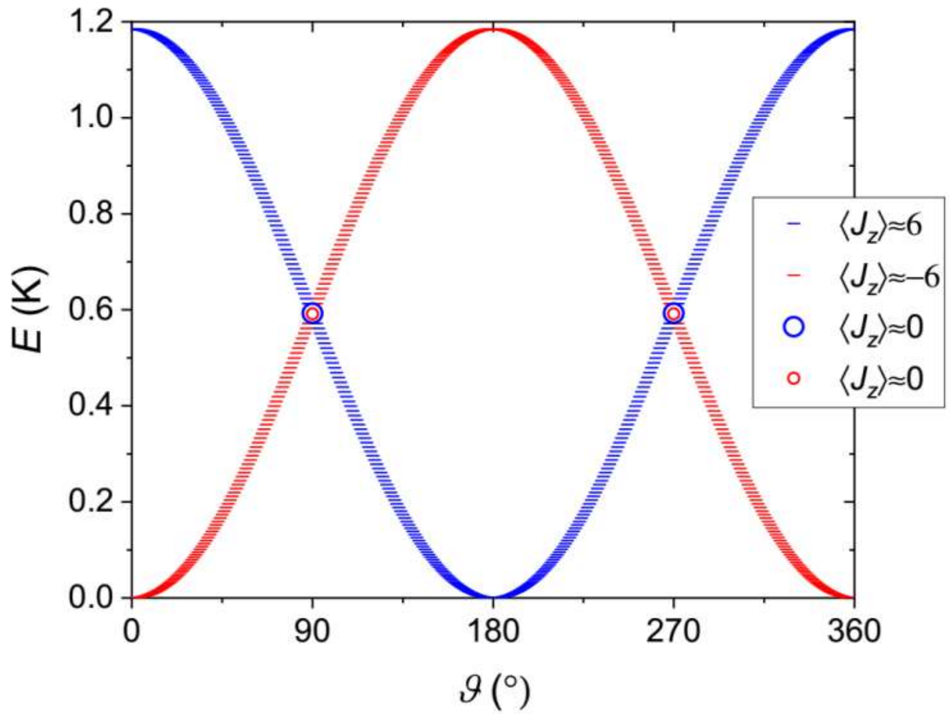


Anisotropy of magnetic relaxations



Anisotropy of magnetic relaxations



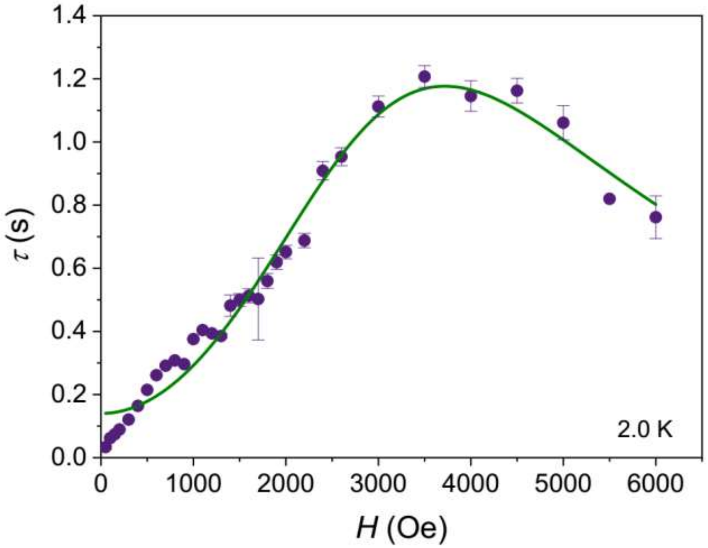


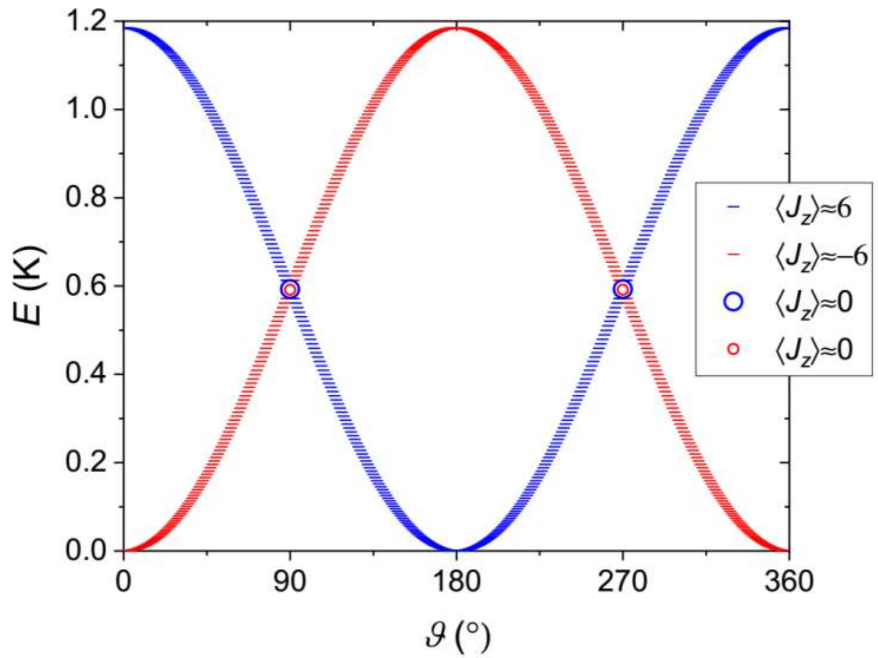
$$\tau^{-1} = \frac{A_1}{1 + A_2 H^2} + B_H H^2 T$$

$$\tau_{\mathrm{QTM}}^{-1} = \frac{4\omega^2 \eta}{1 + \eta^2 \left(E_6 - E_{-6}\right)^2 \hbar^{-2}}$$

$$\tau_{\mathrm{QTM}} = \frac{1 + \eta^2 \Delta E^2 \hbar^{-2}}{4\omega^2 \eta} = \frac{1 + Q_2 \left(H_0 \cos\vartheta\right)^2}{Q_1}$$

Anisotropy of magnetic relaxations





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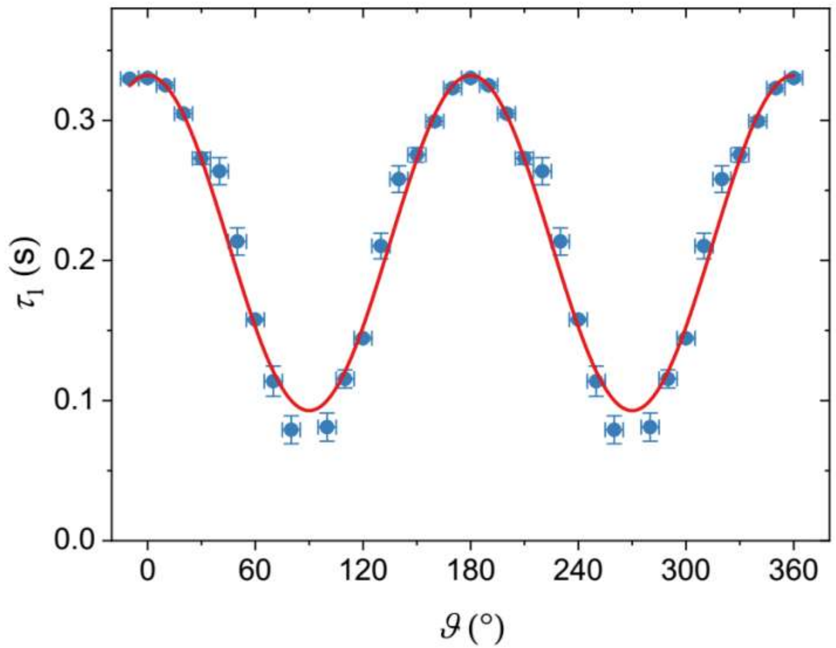
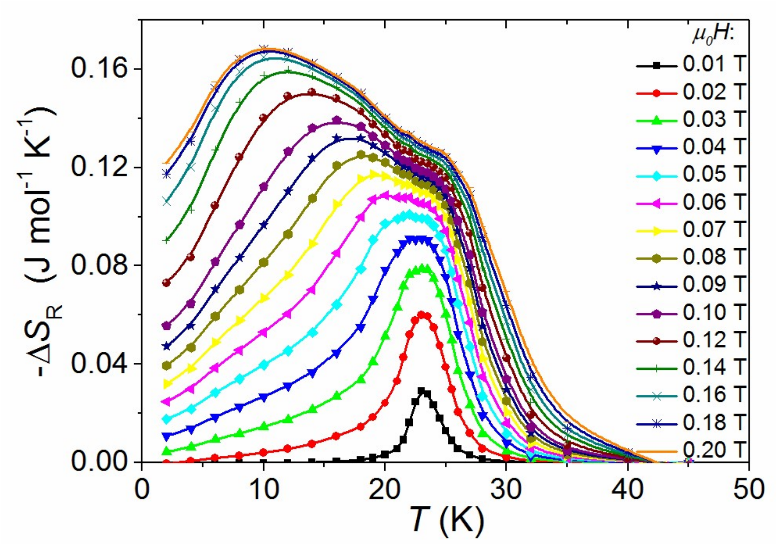
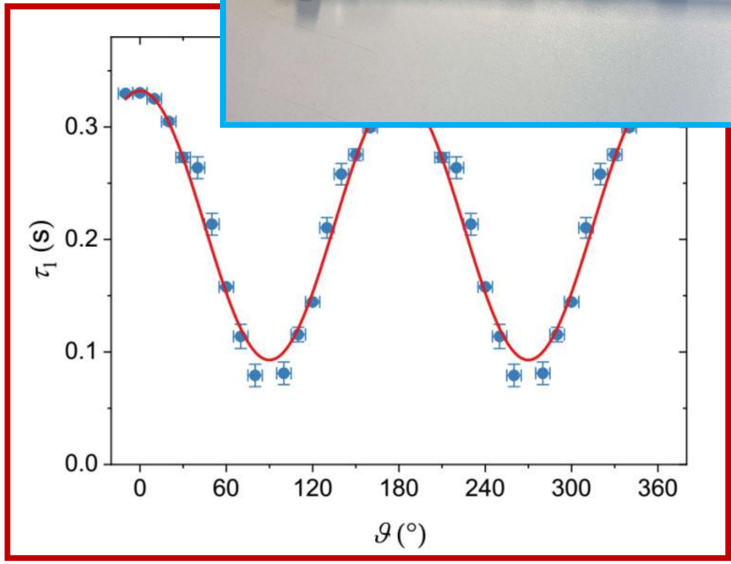


Conclusions

- RMCE between easy plane and hard axis
- Inverse MCE can enhance RMCE
- Crucial role of magnetic anisotropy

- Design and construction of a setup for angle-resolved ac susceptibility measurements
- Angle evolution of the relaxation time for an SMM
- Evidence of the anisotropy of magnetic relaxations





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