CHEM40111/CHEM40121

Molecular magnetism

1 Fundamentals

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Course Overview

1 Fundamentals • Motivation • Origins of magnetism • Bulk magnetism	**5 Single-molecule magnets I** • Single-molecule magnets • Electrostatic model
2 Quantum mechanics of magnetism • Zeeman effect • Statistical mechanics • Magnetisation • Magnetic susceptibility	**6 Single-molecule magnets II** • Measuring magnetic relaxation • Relaxation mechanisms • Latest research
3 Magnetic coupling • Exchange Hamiltonian • Experimental measurements • Vector coupling	**7 Magnetic resonance imaging** • Paramagnetic NMR • Magnetic resonance imaging • Latest research
4 Magnetic anisotropy • Zero-field splitting • Impact on properties • Lanthanides • Spin-orbit coupling	**8 Quantum information processing** • Quantum information • DiVincenzo criteria • Latest research • ***Question time***

Intended learning outcomes

1. Explain the origin of magnetism arising from electrons in atoms and molecules using formal quantum-mechanical terms

2. Compare and contrast the electronic structure of metal ions in molecules and their magnetic properties, for metals across the periodic table

3. Select and apply appropriate models and methods to calculate molecular magnetic properties such as magnetisation, magnetic susceptibility and paramagnetic NMR shift

4. Deconstruct topical examples of molecular magnetism including single-molecule magnetism, molecular quantum information processing and MRI contrast agents

Who needs magnets anyway?

A thirst for data

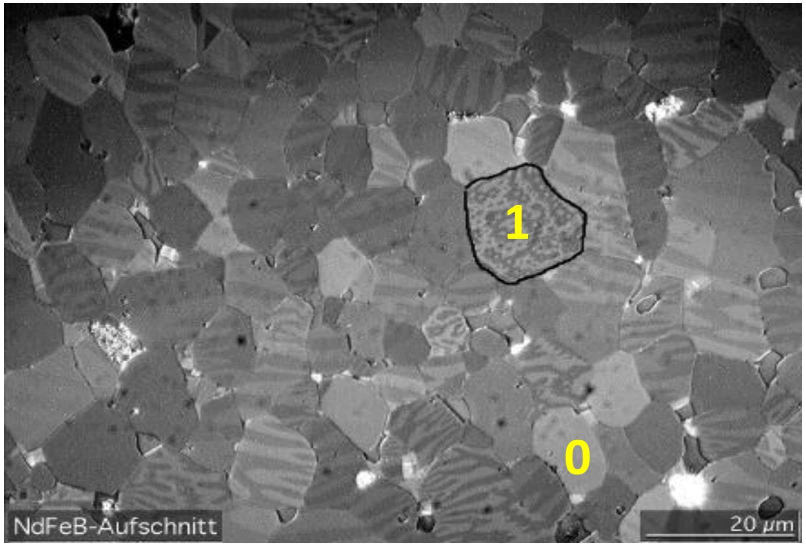
- Estimates of total data stored worldwide will grow to 44 trillion GB by 2020 [1]
  - That's 1270 full HD movies per person on Earth!

- We need a more compact method of storing all of this data
  - (It costs a lot to cool enormous data centres in the desert!)

[1] www.emc.com/leadership/digital-universe/2014iview/executive-summary.htm

Traditional tech

- Magnetic hard disk drives (HDDs) are the cheapest to store lots of data
  - Current data density ~ 190 GB in^{-2}

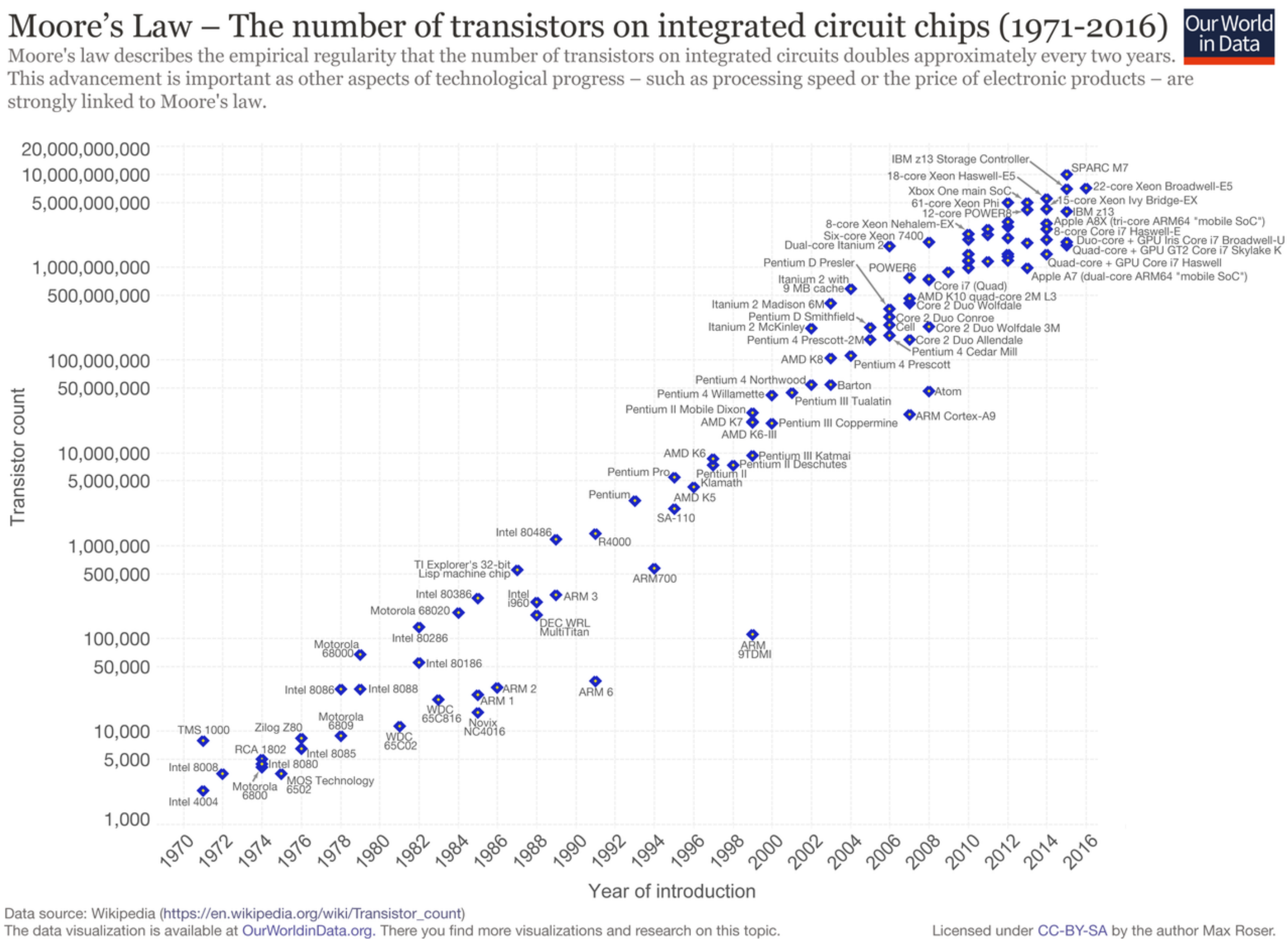


- Can't shrink magnetic domains infinitely
  - Atoms need to talk to each other!

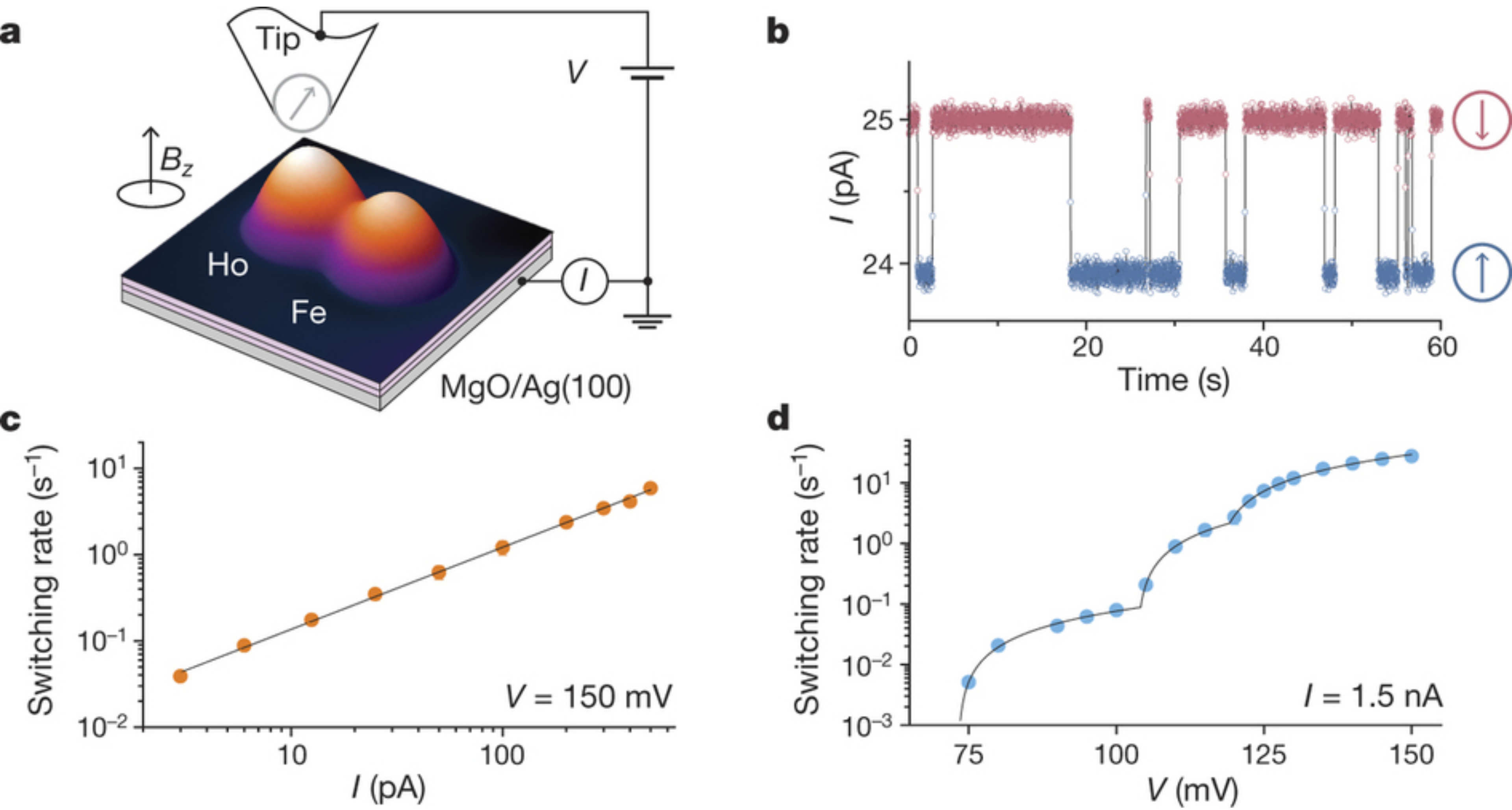
[1] www.emc.com/leadership/digital-universe/2014iview/executive-summary.htm

Traditional tech

- Solid state drives (SSDs) are lighter, more robust and faster
  - Current data density ~ 250 GB in^{-2}



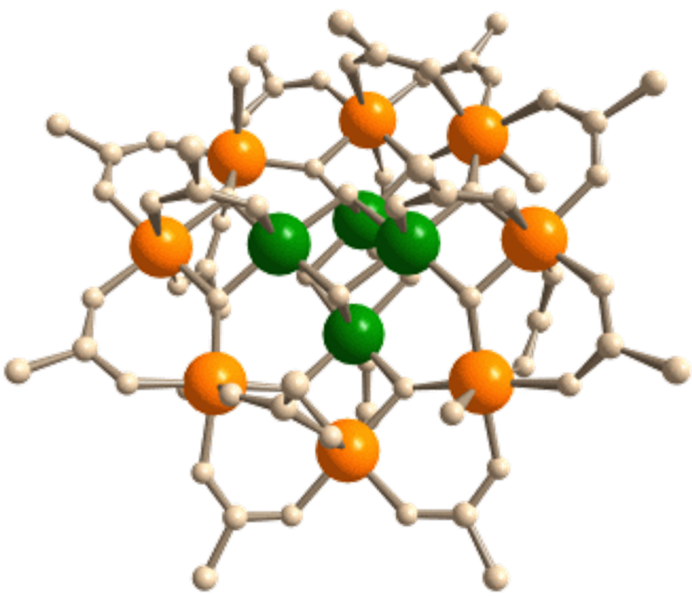
Atomic magnets



[1] F. Natterer *et al.*, *Nature*, 2017, **543**, 226.

Molecular magnets

- What about molecules? Can control properties with chemistry!
  - If we could store information in a molecule, what would the density be?



‘Mn_{12}’

~ 2 nanometres square

= 4 nm^2 bit^{-1}

= 6.2×10^{-15} in^2 bit^{-1}

~ 20,120 GB in^{-2}

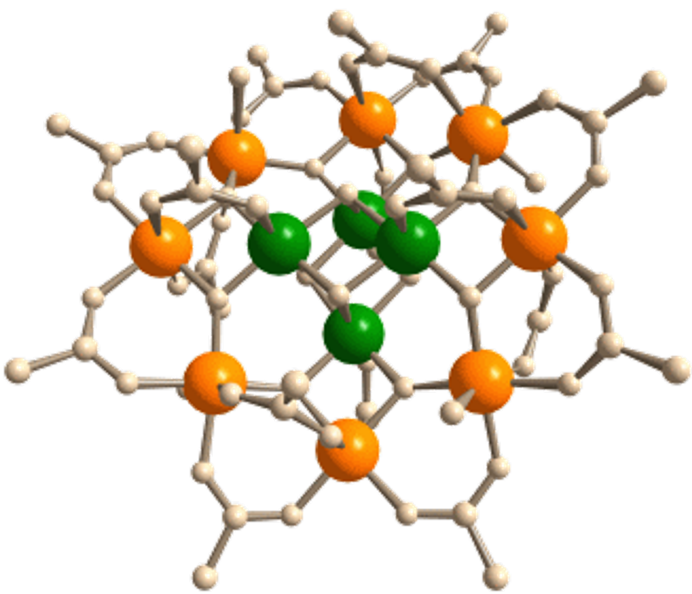
- *100 times better than current tech! (~ 200 GB in^{-2})*

- *Data centres 100 times smaller?*

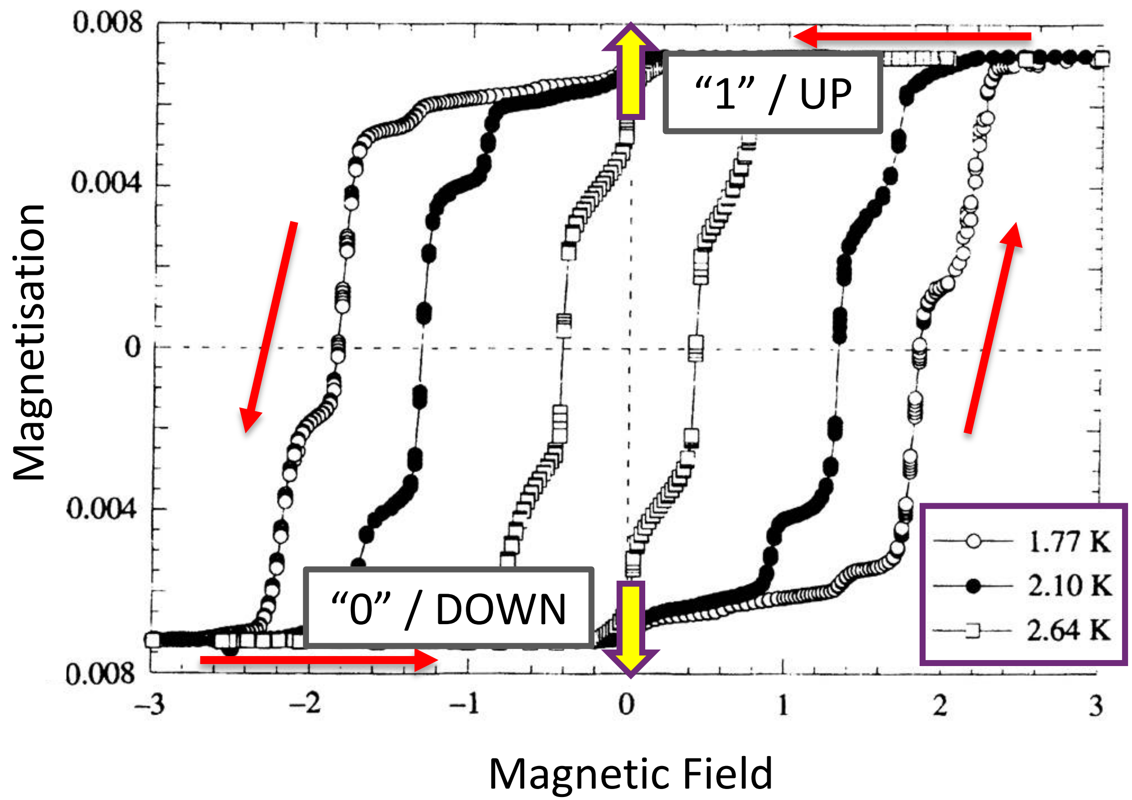
[1] R. Sessoli *et al.*, *Nature*, 1993, **365**, 141.

Molecular magnets

- <u>Definition</u>:
  - – Molecules that show magnetic memory effects

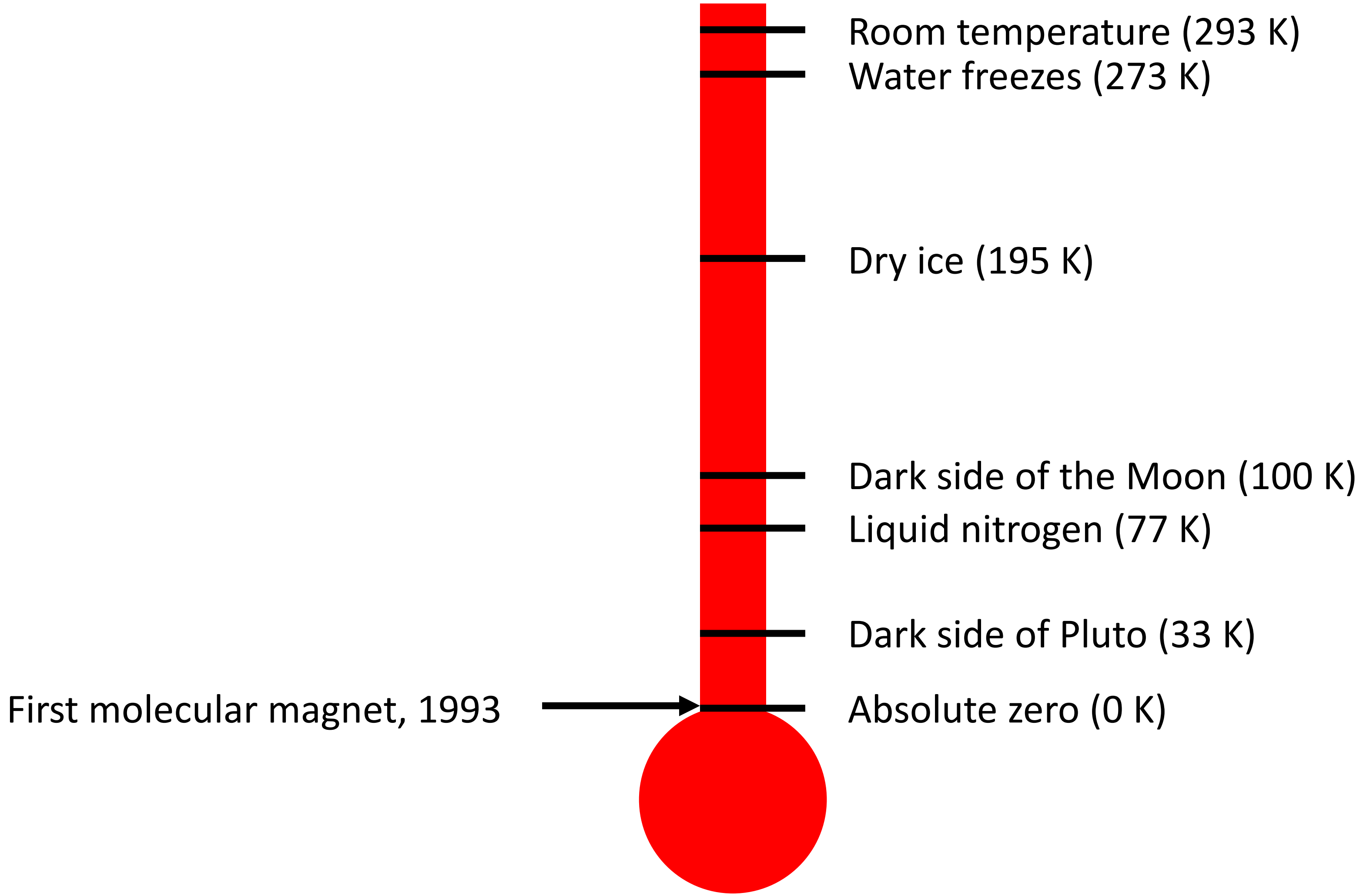


‘Mn_{12}’



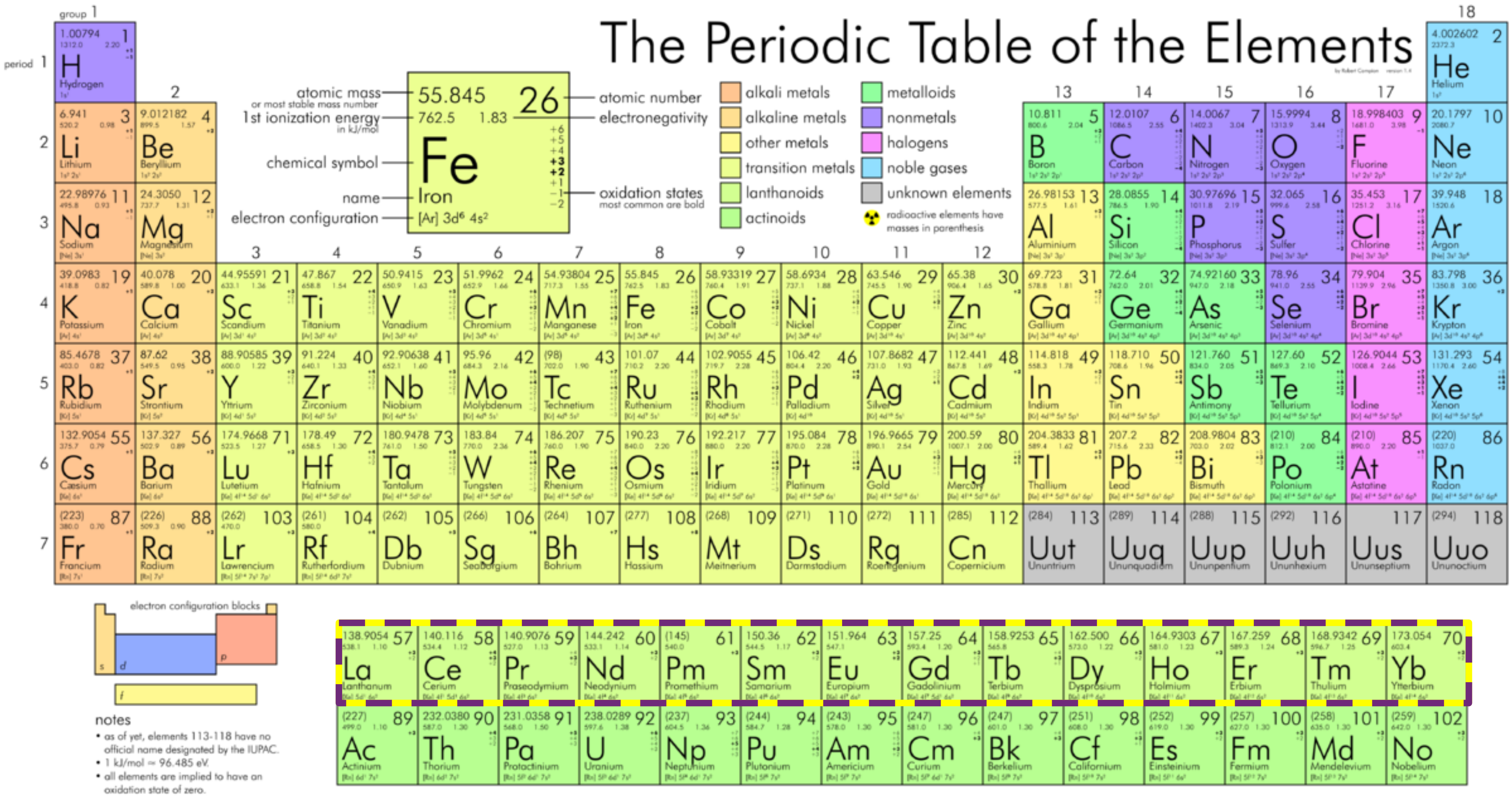
[1] R. Sessoli *et al.*, *Nature*, 1993, **365**, 141; [2] L. Thomas *et al.*, *Nature*, 1996, **383**, 145; [3] J. R. Friedman *et al.*, *Phys. Rev. Lett.*, 1996, **76**, 3830.

How cold is cold?



[1] R. Sessoli *et al.*, *Nature*, 1993, **365**, 141.

Lanthanides

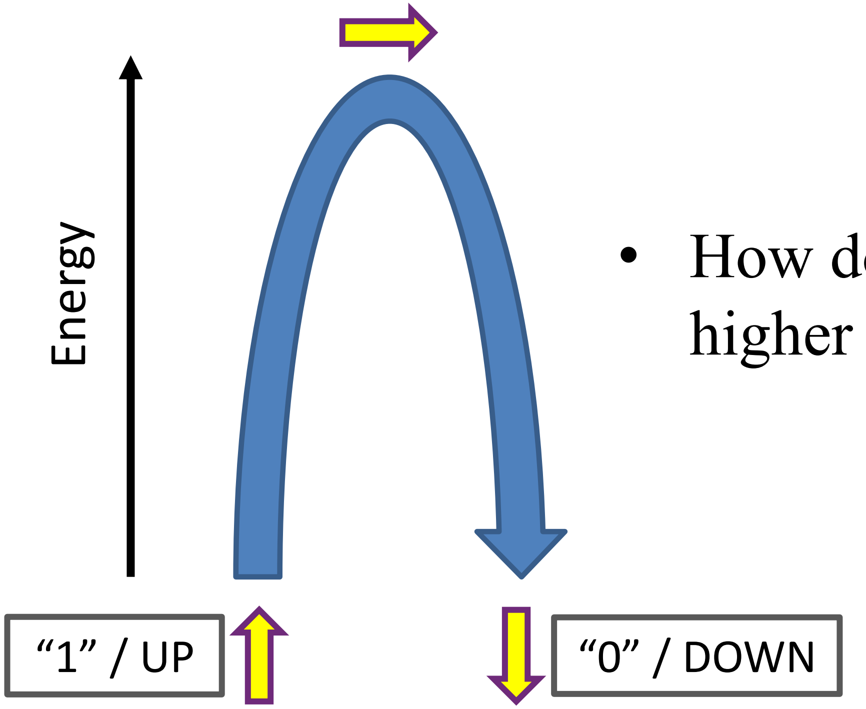


- Lanthanides are at the bottom of the Periodic Table
  - That means lots of electrons and lots of magnetism!

How to make a molecular magnet

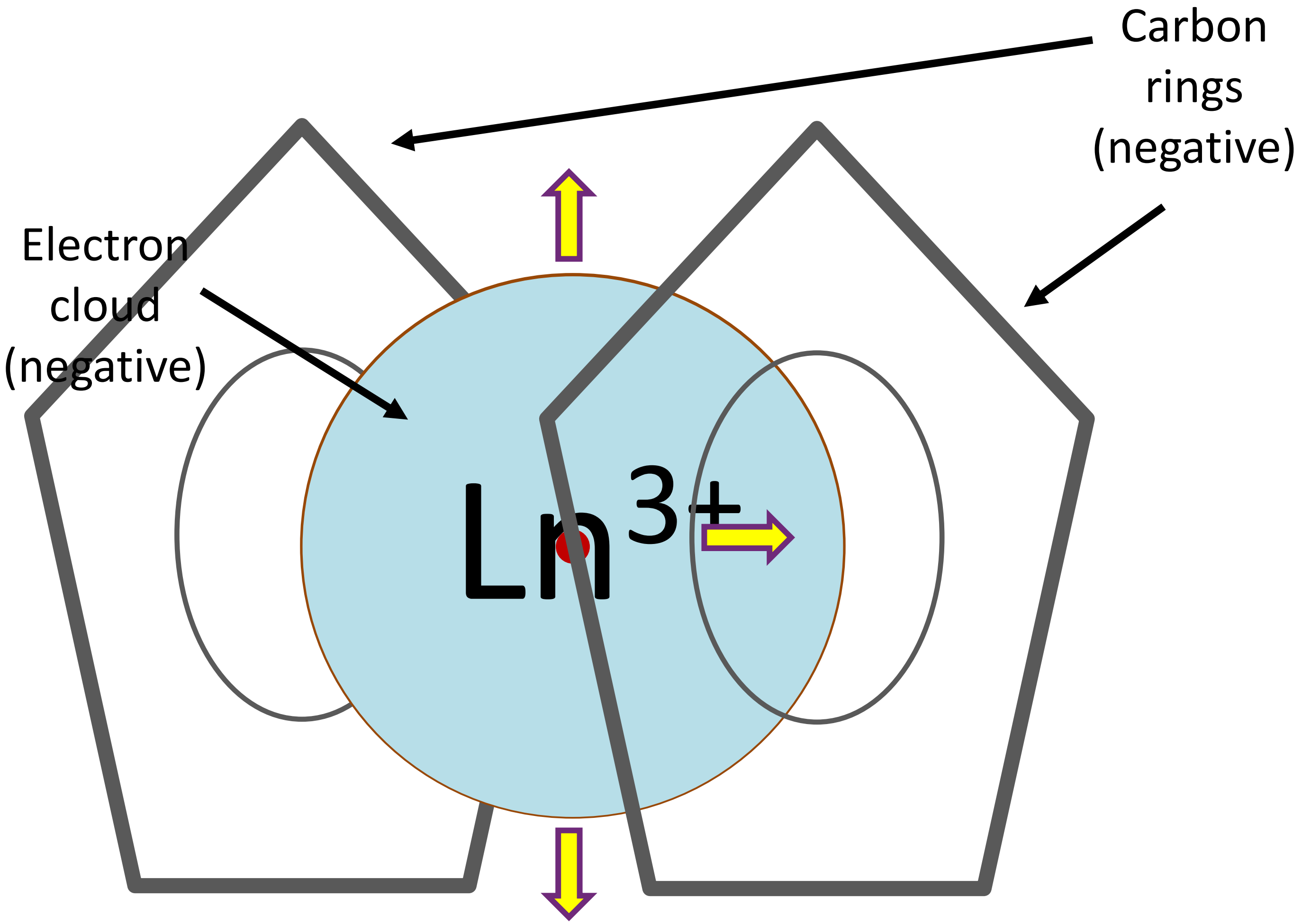
- But what shape molecule should we make?

- Want an ***energy cost*** to flip the magnetism from UP to DOWN
  - So it doesn't flip it until we want it to!
  - The higher the energy cost, the higher temperatures we can store memory!



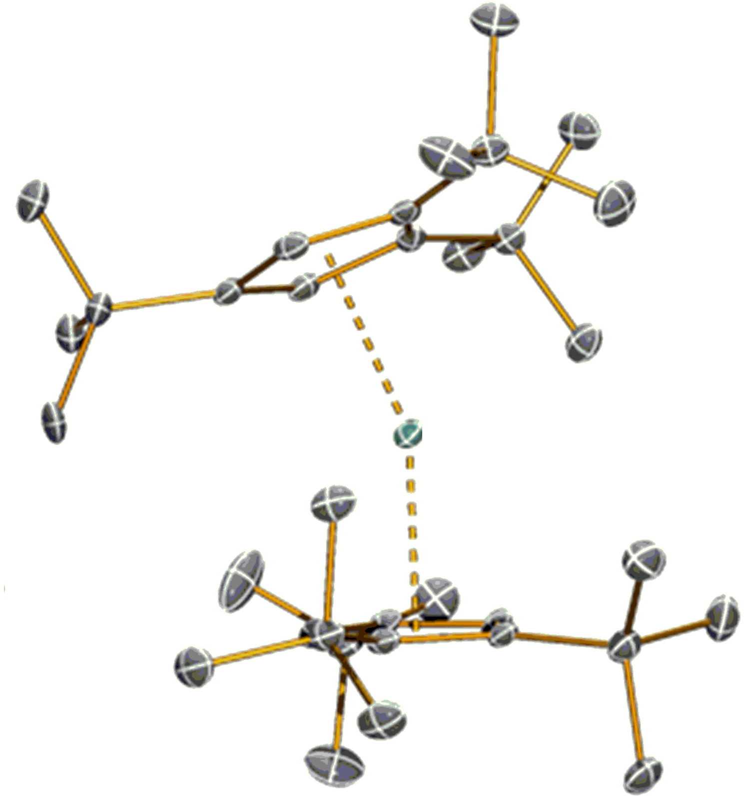
- How do we make SIDEWAYS higher in energy than UP or DOWN?

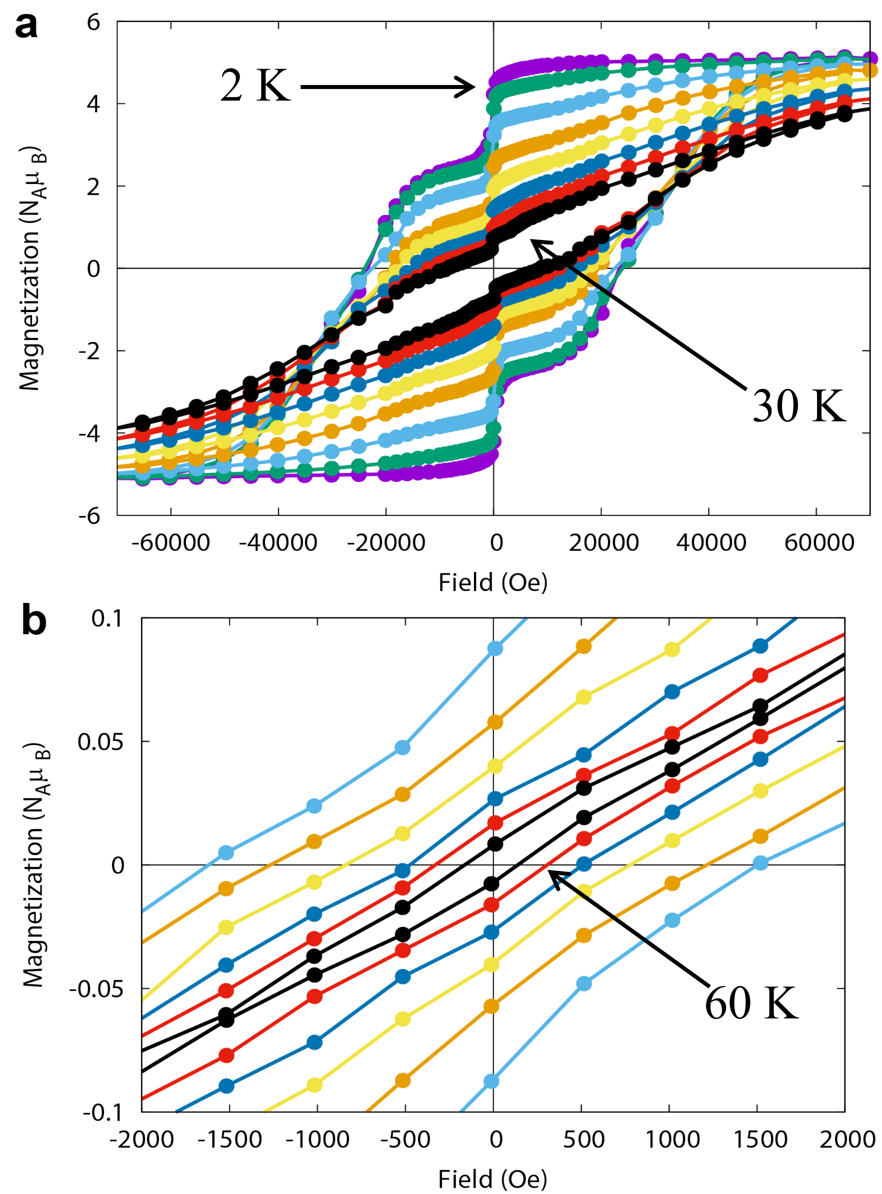
How to make a molecular magnet



- "Opposites attract" – this is Coulombs law of electrostatics! Also says that ***"Like charges repel"***

Does it work?





Dr Conrad Goodwin
Dr David Mills

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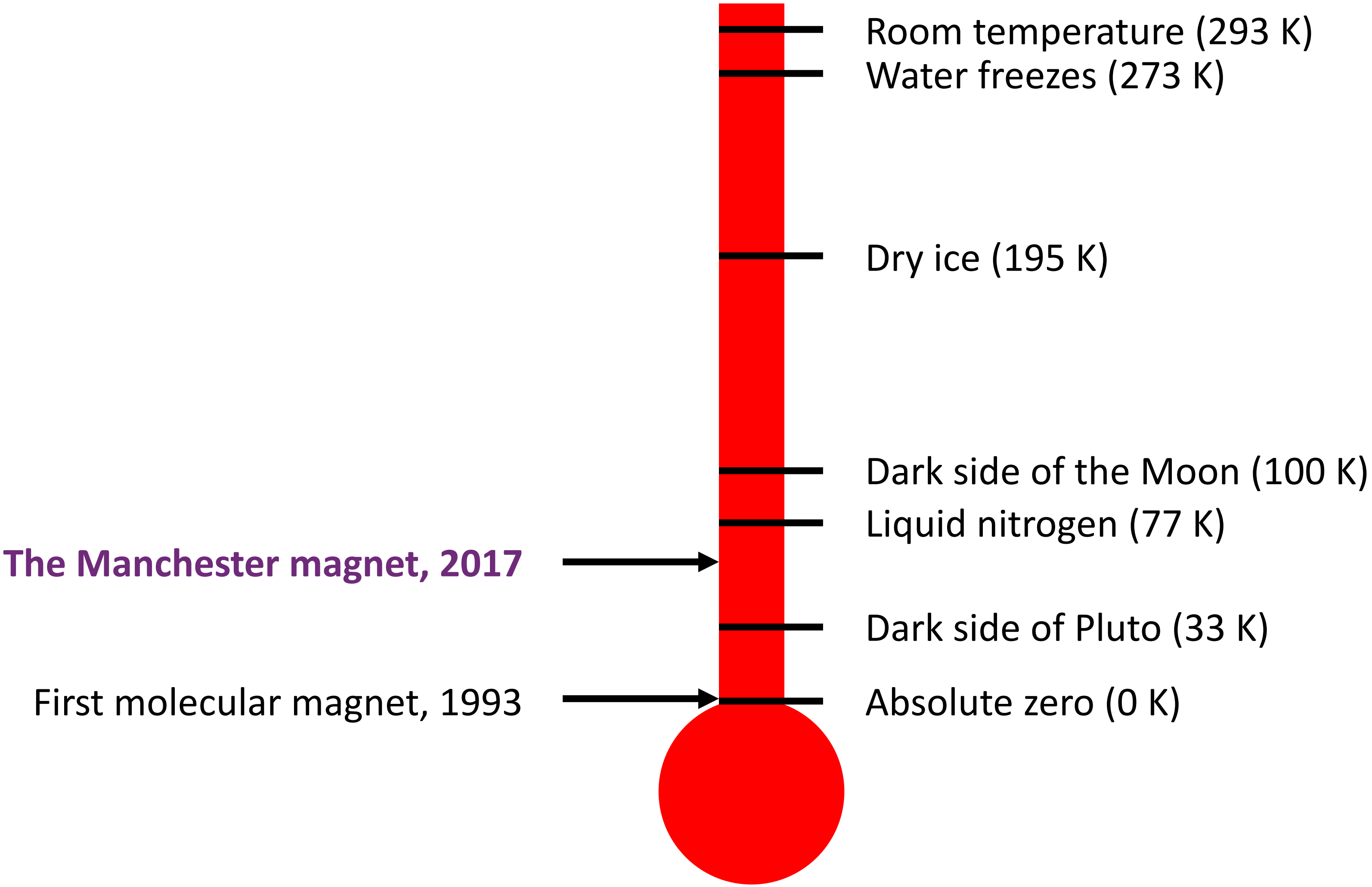
[1] C. A. P. Goodwin *et al.*, *Nature*, 2017, **548**, 349.

How cold is cold?

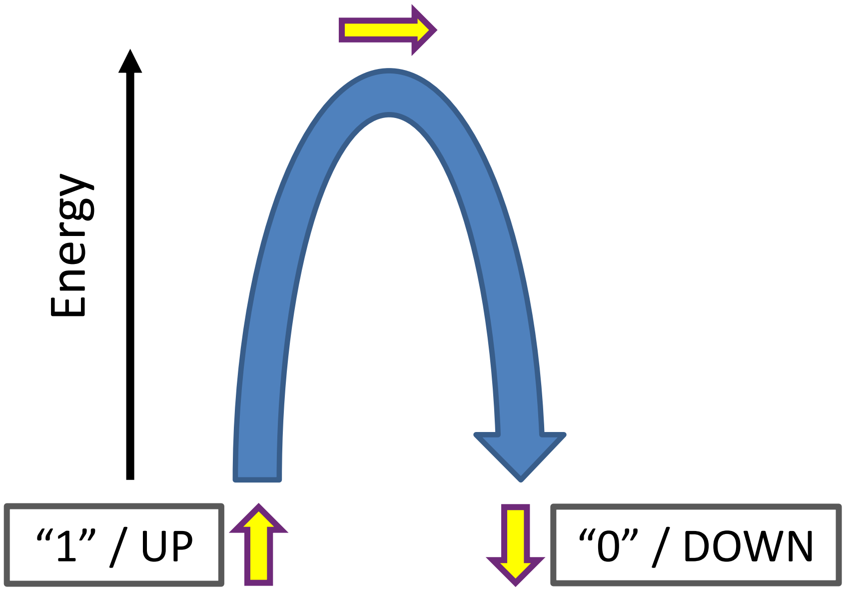


[1] R. Sessoli *et al.*, *Nature*, 1993, **365**, 141; [2] C. A. P. Goodwin *et al.*, *Nature*, 2017, **548**, 349.

Jumping the barrier

- We say ***"it needs energy"***…

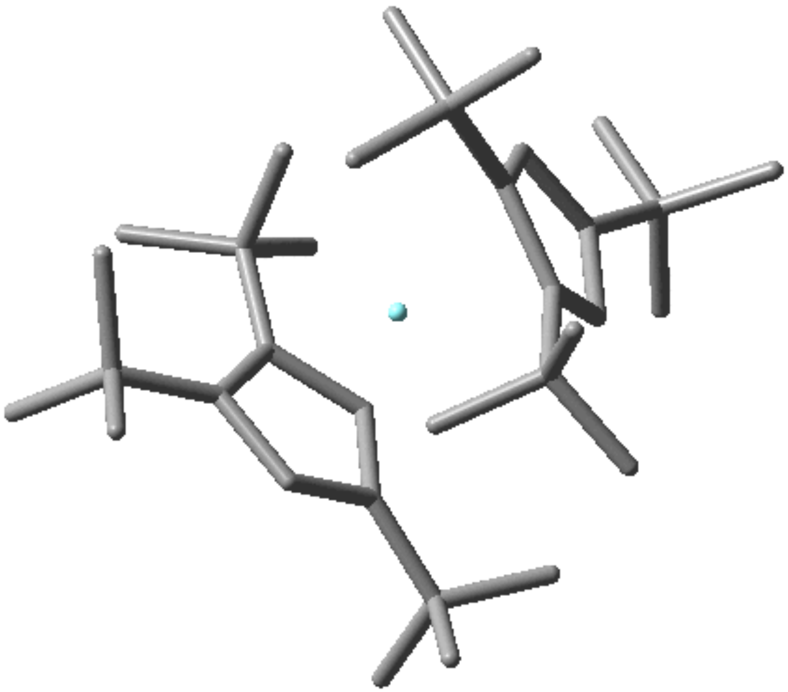
  …but what does that mean?



- The hotter something is, the more ***energy*** it has!

- Energy = Movement
  - Molecule move by vibrating

Jumping the barrier



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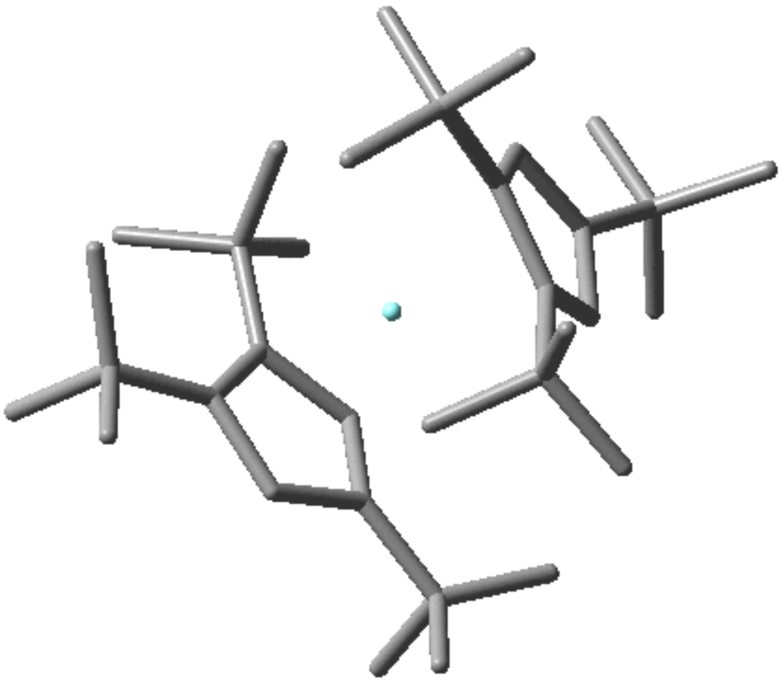

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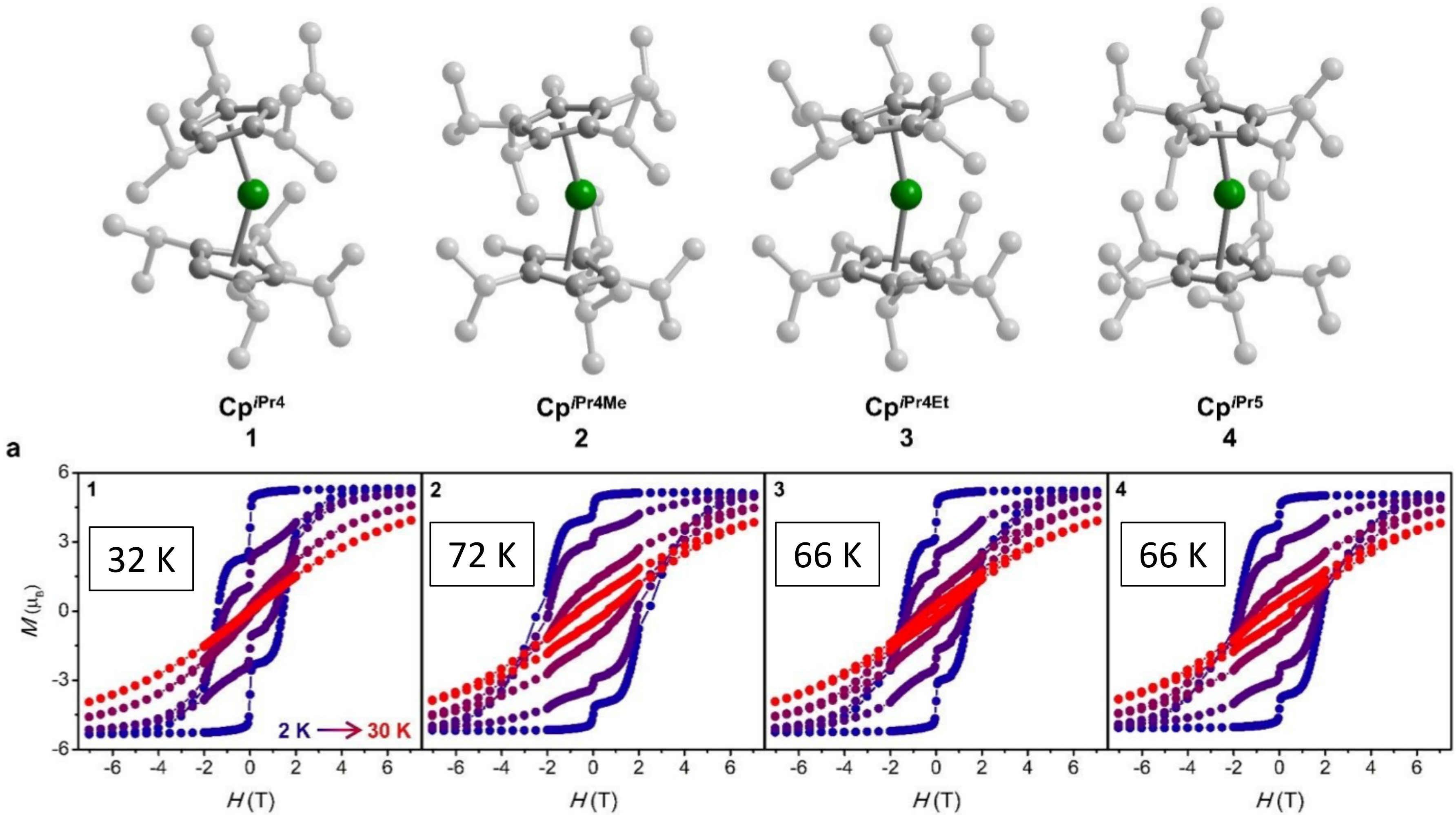
[1] C. A. P. Goodwin *et al.*, *Nature*, 2017, **548**, 349.

Good vibrations

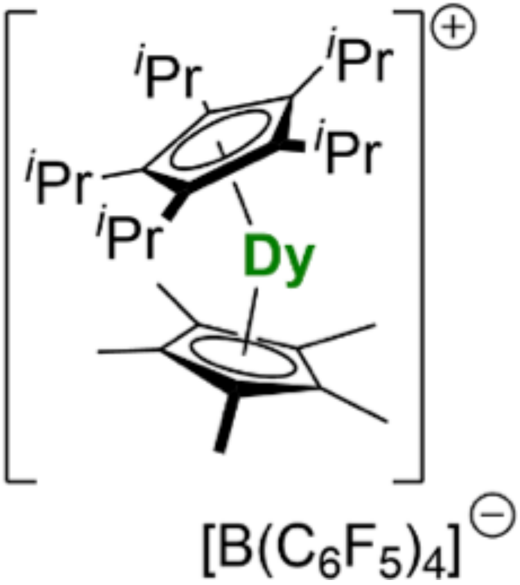
- New molecules:

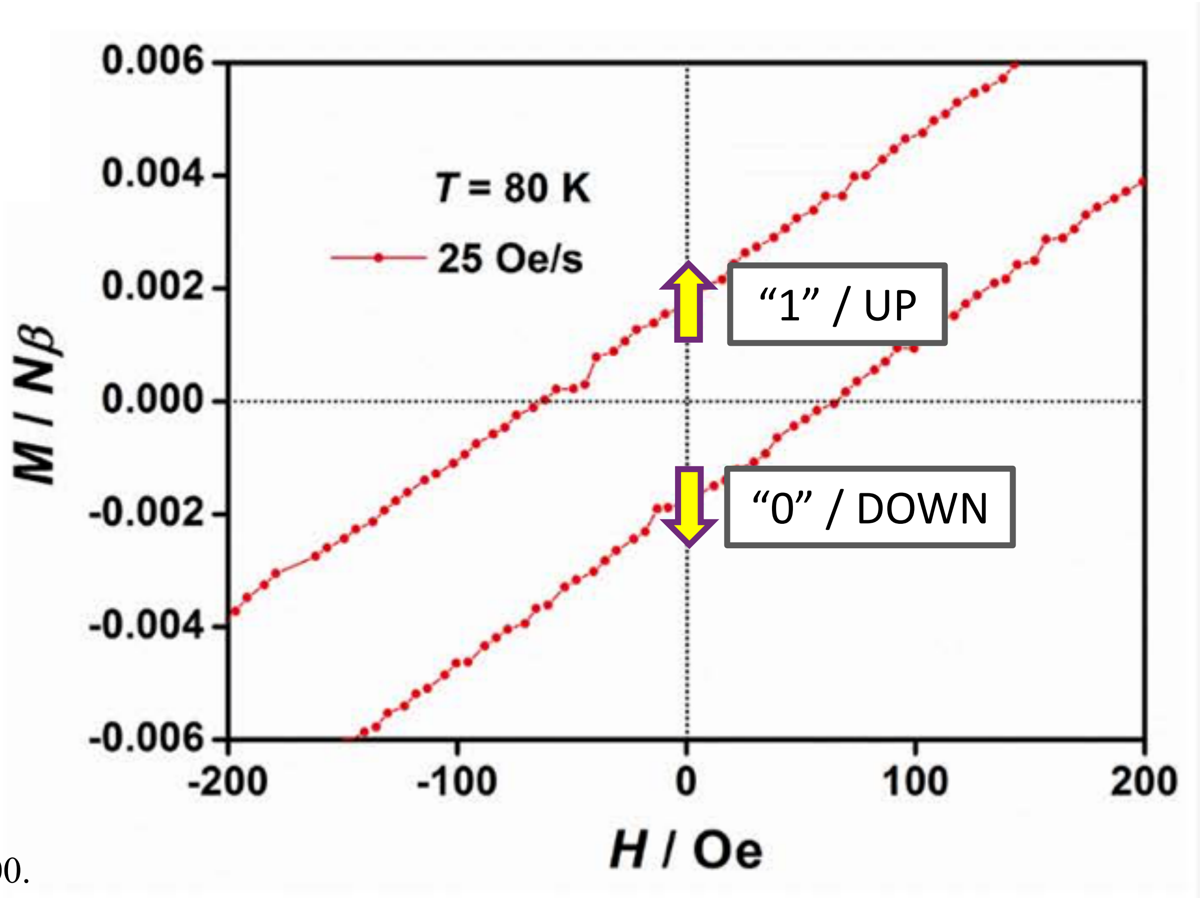


[1] K. R. McClain *et al.*, *Chem. Sci.*, 2018, 9, 8492.

Good vibrations

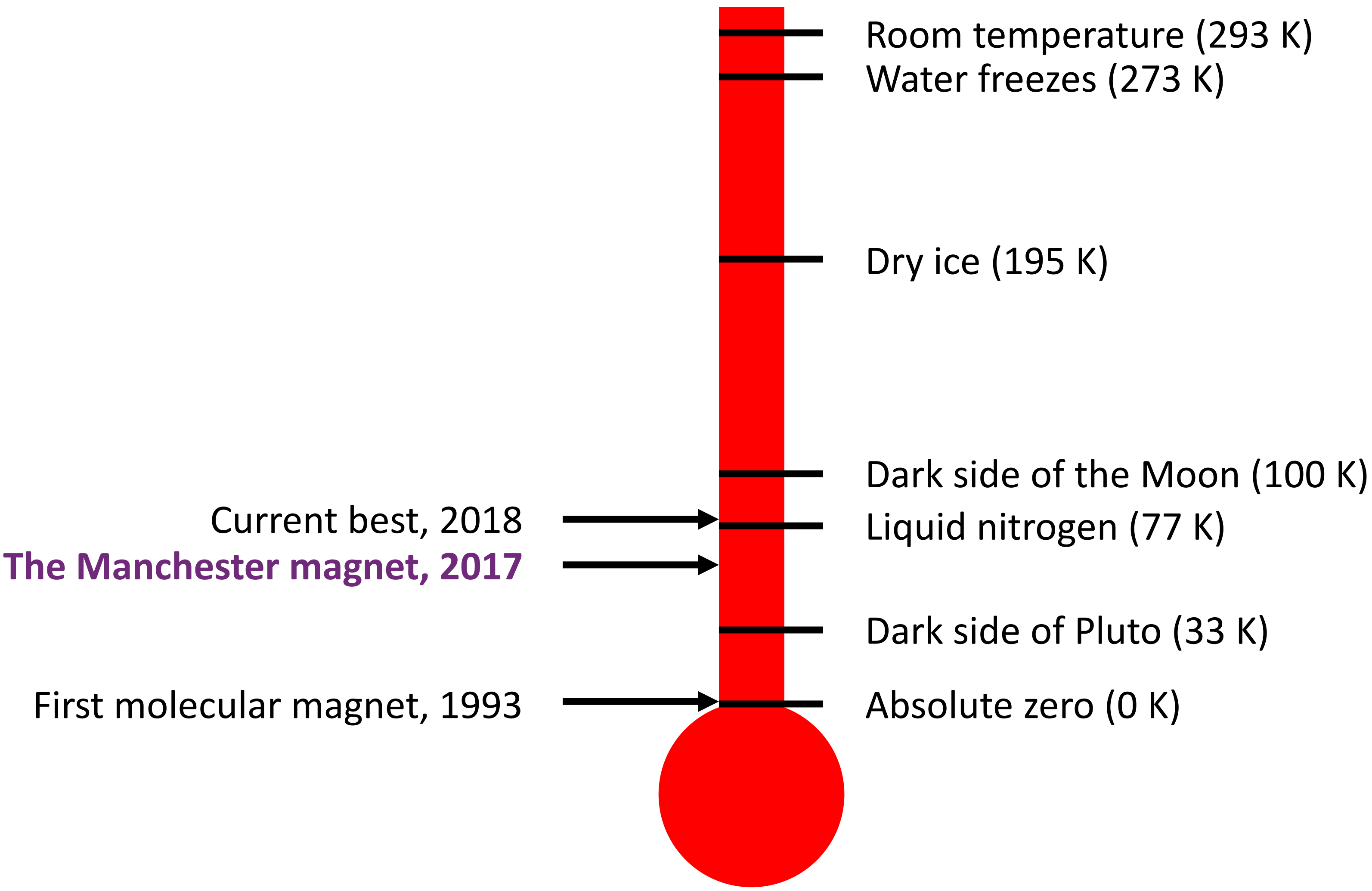
- New molecules:





[1] F.-S. Guo *et al.*, *Science*, 2018, **362**, 1400.

How cold is cold?



[1] R. Sessoli *et al.*, *Nature*, 1993, **365**, 141; [2] C. A. P. Goodwin *et al.*, *Nature*, 2017, **548**, 349; [3] F.-S. Guo *et al.*, *Science*, 2018, **362**, 1400.

Origins of magnetism

- Magnetism was known from ancient times due to naturally-magnetised magnetite Fe_3O_4:

- Experimentalists in the 19^{th} century such as Ørsted, Ampère and Gauss studied the relationship between electricity and magnetism

- The 1820's and 30's gave us the Biot–Savart law and Farady's magnetic induction

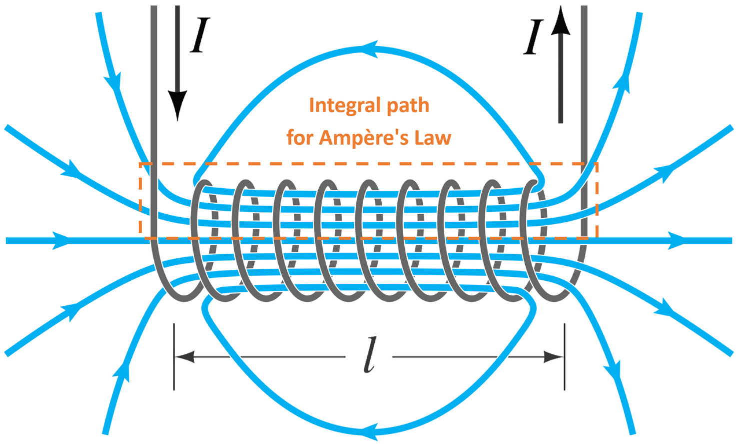
- Culminating in James Clerk Maxwell's theory of electromagnetism in the 1860's

Origins of magnetism

- <u>Biot-Savart Law:</u>
  - A magnetic field is generated by current flowing in a wire

- <u>Magnetic induction (Faraday):</u>
  - A change of magnetic flux through a loop generates a current

- These are the principles that allow:
  - Solenoids, Electromagnets
  - Electric motors, generators
  - Transformers



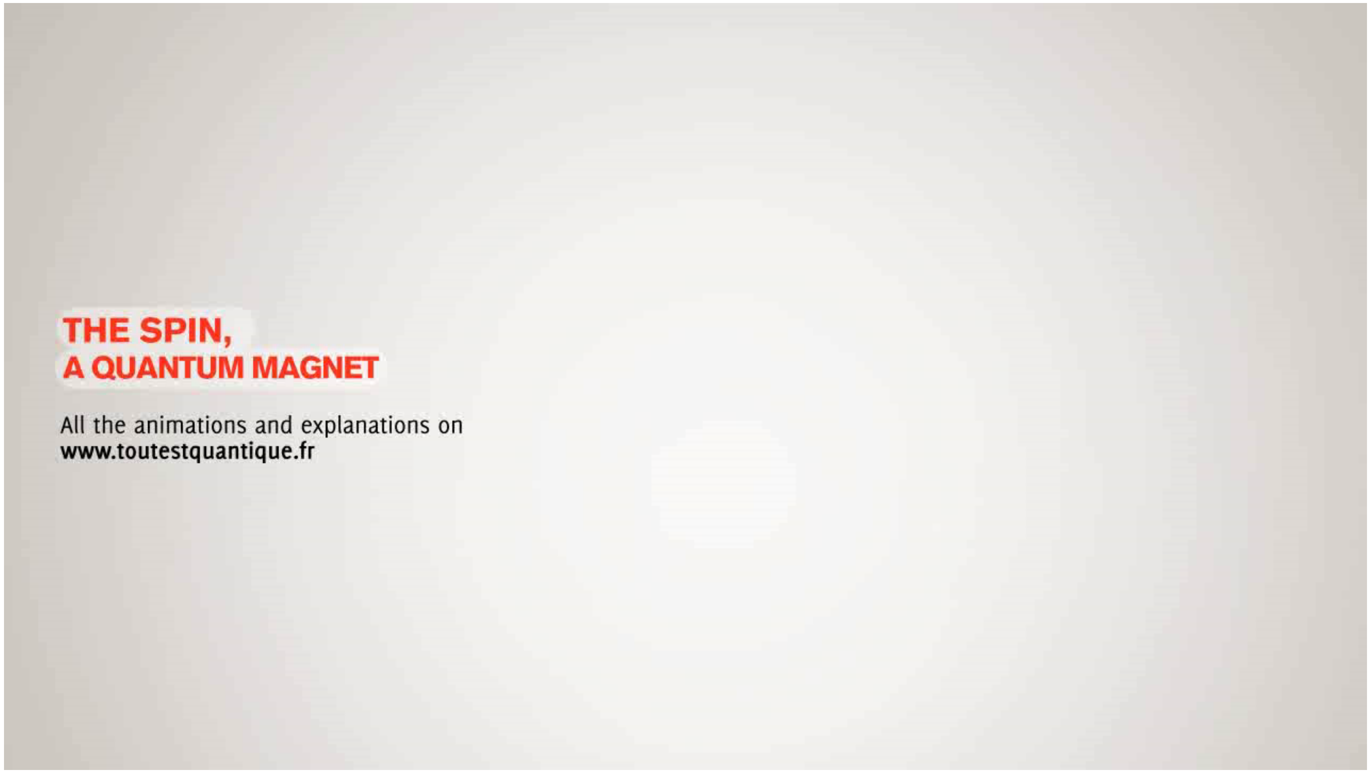
- Summary:
  - Moving charges generate magnetic fields, and magnetic fields can make charges move

Origins of magnetism

- Pauli and Dirac introduced non-relativistic and relativistic treatments of the electron spin

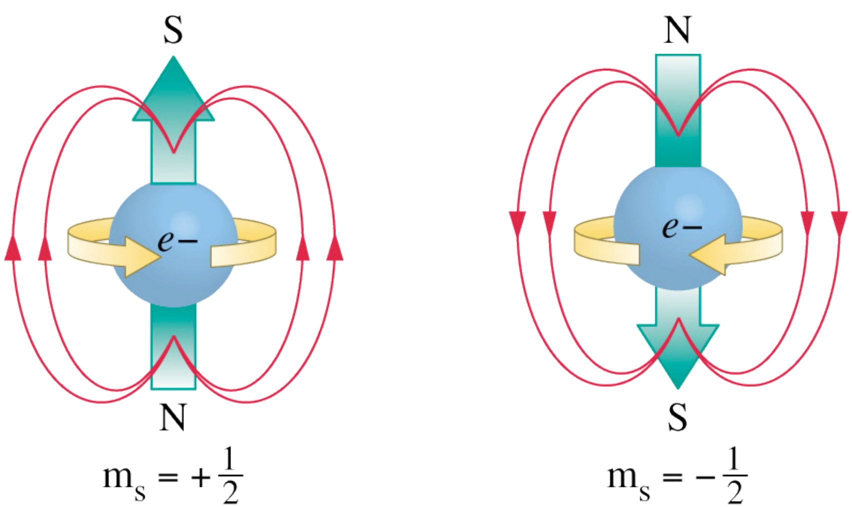
- Stern-Gerlach experiment showed that electron spin had a magnetic moment:

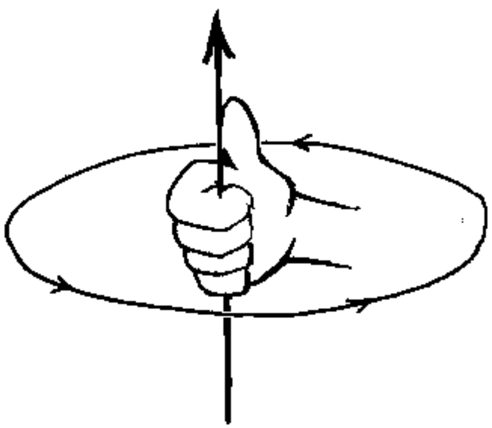
http://www.toutestquantique.fr



Spin and orbital moments

- Static magnetic moments arise from unpaired electrons
- Two sources of electron magnetism:
  - Spin angular momentum (quantum mechanical; no motion)
  - Orbital angular momentum (physical electron motion in 3D space)

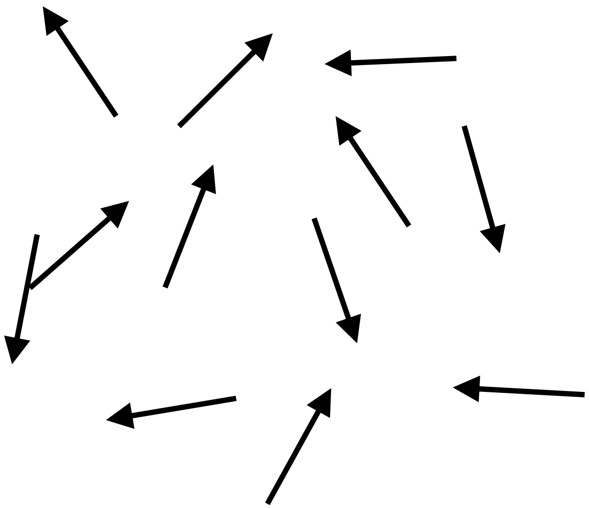




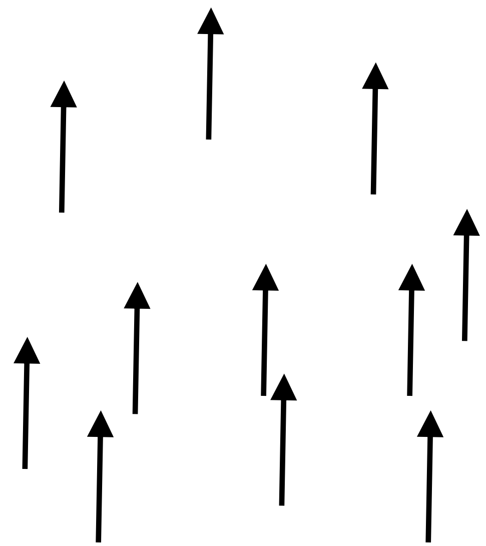
- The depiction of electrons spinning on axes is just a pictorial representation; electrons do not have physical dimensions

Paramagnetism

- <u>Paramagnets:</u>
  - Random orientation of magnetic moments in zero field

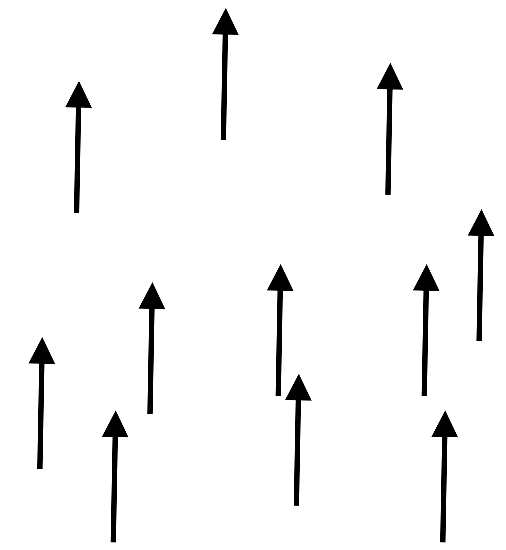


  - Application of a field causes the moments to align with field

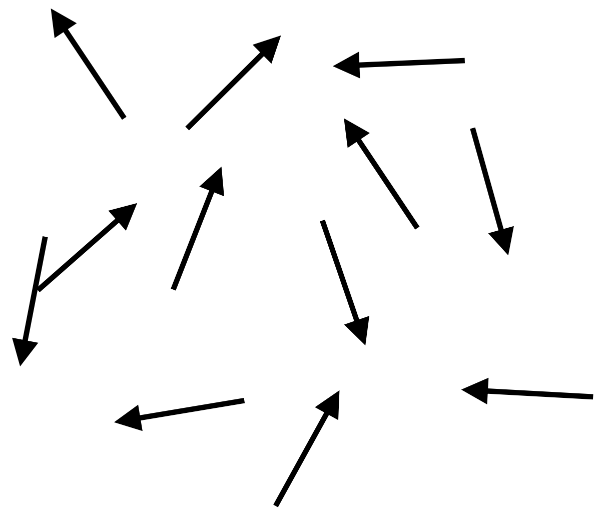


Ferromagnetism

- Ferromagnets:
  - Spontaneous alignment in zero field below Curie temperature (T_C)

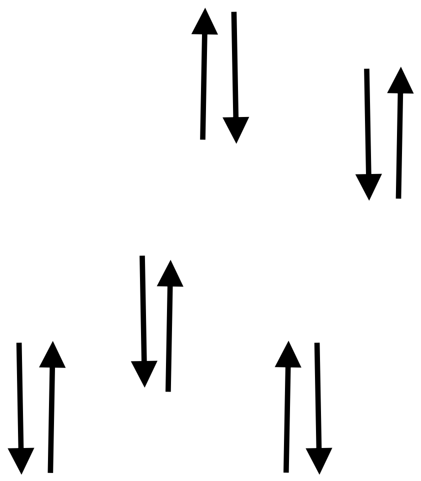


  - Raising the temperature above T_C disorders moments



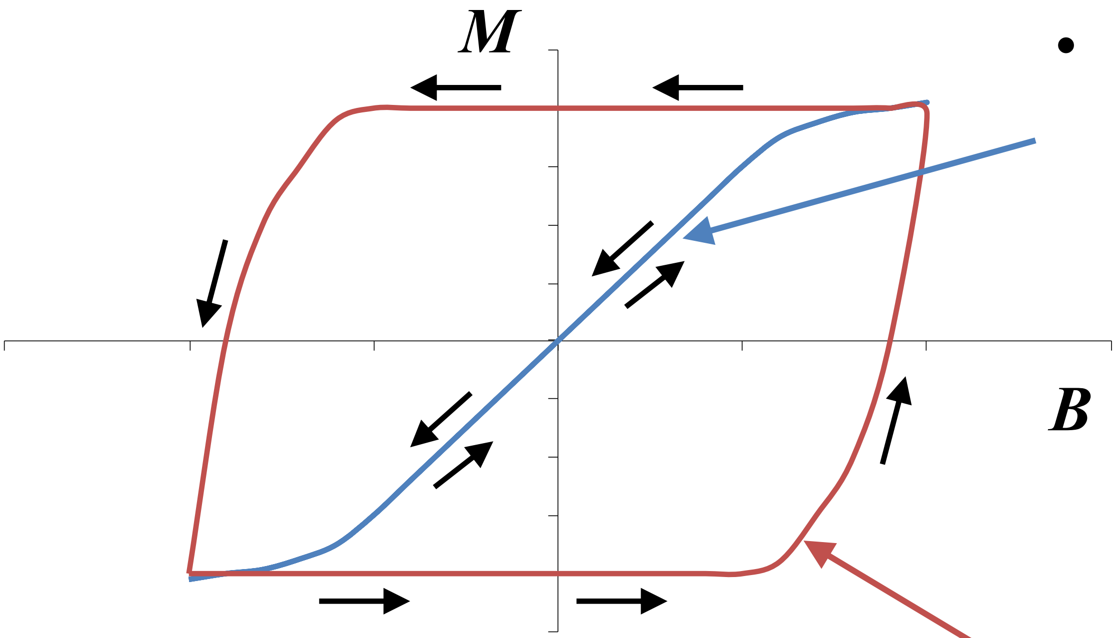
Diamagnetism

- <u>Diamagnets:</u>
  - Diamagnets are ***repelled*** by magnetic fields
  - Due to the electron pairs present in all materials
  - Even occurs in paramagnets and ferromagnets
  - ***MUCH*** weaker than paramagnetism or ferromagnetism



Paramagnetism vs Ferromagnetism

- Magnetisation (*M*) is the total magnetic moment of the sample



- <u>Paramagnet</u>:
  Magnetisation starts linear and saturates

- <u>Ferromagnet</u>:
  Magnetisation hysteresis

- <u>Diamagnetism</u>:
  Independent of field and very, very weak!