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Molecular Magnetism

Chilling with Magnetic Molecules**

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The exploitation of magnetic materials is ubiquitous in our everyday life, with the most recent applications ranging from medicine to tribology. One peculiar feature of magnetic materials is the temperature change following a variation of the applied magnetic field in adiabatic conditions, and the first observation of this effect in metallic iron dates back to 1881. The first investigations of this phenomenon, known as the magnetocaloric effect (MCE) in paramagnetic salts to achieve low temperatures are part of the Nobel lecture of William F. Giauquem, who was awarded with the Nobel Prize in Chemistry in 1949.

MCE, which results in a temperature drop during an adiabatic demagnetization, is a valid alternative to gas decompression for cooling.[1] It can be exploited in cyclic magnetization and demagnetization processes by switching on and off the thermal link with the bath (Carnot cycle). The lack of mechanical moving parts makes this approach energetically more efficient and easier to use compared to standard cryogenerators or ^{3}He–^{4}He dilution fridges. Its use is particularly appealing for very demanding conditions, such as aerospace applications.

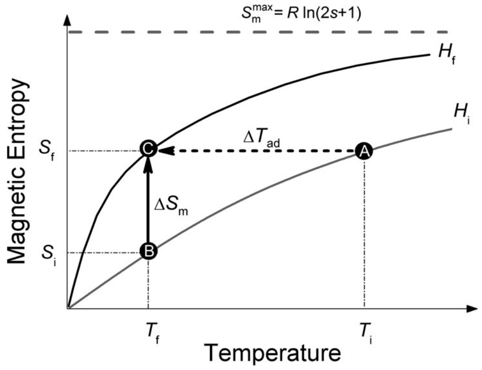

Figure 1. The thermodynamics of the demagnetization process. By changing the magnetic field from the initial value H_i to the final value $H_f < H_i$ a gain in magnetic entropy ΔS_m occurs during the isothermal process B→C, while a temperature drop ΔT_{ad} is observed during the adiabatic process A→C. The maximum magnetic entropy for a system with a spin s, $R\ln(2s+1)$, is indicated by the gray broken line.

MCE is indeed based on very basic principles of thermodynamics, that is, the entropy change ΔS_m of a magnetic system once it is exposed to a magnetic field that, in general, polarizes the magnetic moments, thus reducing the degrees of freedom of the system. When the field is brought back to zero, the magnetic contributions to the entropy increase (Figure 1). If the process of demagnetization occurs without any heat flow from the environment to the magnetic system, that is, in adiabatic conditions, a drop in temperature of the magnetic system ΔT_{ad} occurs. These two parameters, ΔS_m and ΔT_{ad}, characterize the magnetocaloric properties of a material. To understand which are the key parameters to adjust during the design of an optimized MCE material, it is useful to recall some basic thermodynamic relations:[1]

$$\Delta S_m(T,\Delta H) = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H \tag{1}$$

$$\Delta T_{ad}(T,\Delta H) = \int_{H_1}^{H_2} \left(\frac{T}{C}\right)_H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H \tag{2}$$

where H is the applied magnetic field and M and C are the field- and temperature-dependent magnetization and specific heat, respectively.

The first requirement for a large magnetocaloric efficiency is therefore a strong temperature dependence of the magnetization. This is observed close to the ordering temperature for a ferromagnet, while for a paramagnet it can only be achieved at low temperature. Thus ferromagnetic materials that are mainly based on lanthanide alloys or, more recently, on manganites, are investigated for cooling around room temperature, while paramagnetic demagnetization is used for cryogenic temperatures. Nuclear spins, which are polarized by a magnetic field only at lower temperatures, are employed to attain submillikelvin temperatures.

Research on high-temperature magnetocaloric materials to replace standard refrigeration has to face problems related mainly to thermal hysteresis of magnetically ordered materials. On the other hand, the use of paramagnetic materials as low-temperature refrigerants unfortunately requires relatively large fields to provide a relevant cooling power.

Molecular magnetism seems to be able to provide an alternative route for low-temperature MCE materials. The

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last two decades have been characterized by an intense investigation on magnetic molecules that are characterized at low temperature by a very slow relaxation of the magnetization and by the appearance of a magnetic hysteresis of molecular origin.[2] These materials, generally known by the evocative name of single-molecule magnets, are in general polynuclear coordination compounds characterized by a large spin multiplicity of the ground state, which is induced by moderate intramolecular magnetic interactions, a strong magnetic anisotropy, and vanishingly small intermolecular magnetic interactions.

The first investigation of MCE in magnetic molecules indeed focused on the most investigated SMMs, namely Mn_{12} and Fe_8.[3] What could be considered side-products of the research on SMM can however be revealed as promising magnetic refrigerants. In fact, the simultaneous optimization of the spin value and of the magnetic anisotropy is not an easy task, and the recent literature is studded with reports of extremely high spin values for the ground state, the record being a Mn_{19} molecular cluster having a spin as large as 83/2 but no significant magnetic anisotropy.[4] A molecule with a large spin multiplicity, in the absence of magnetic anisotropy that splits the levels in zero field, is characterized by a large molar magnetic entropy that can be exploited in MCE. The cooling power is however associated to ΔS_m, an extensive property, and what is relevant for applications is the specific value for unit of mass of the refrigerant. The gain induced by using magnetic molecules, where the density of magnetic centers is significantly lower than in paramagnetic salts, could appear negligible. However, Equations (1) and (2) tell us that the response to the field and to the temperature are the relevant parameters, and these scale as the susceptibility, which, according to the Curie law, is quadratic with the spin value.

Exploiting this route, a high MCE was reported in 2005 in a Fe_{14} molecular cluster characterized by a ground state with spin $s=25$ and a vanishingly small magnetic anisotropy (Table 1).[5] The record is continuously broken as more and more magnetic molecules are synthesized and tested for MCE. Two connected research groups have recently reported very large values of ΔS_m (Table 1). In the first case, Zheng et al. used the bridging flexibility of phosphonate ligands to isolate 3d–4f molecular clusters.[6] The molecule accommodates six $s=1$ Ni^{2+} ions and six tripositive rare earth ions in a rugby-ball-shaped cage. The magnetism suggests weak interactions of lanthanide ions (Gd^{3+} and Dy^{3+}) between themselves and with the Ni^{2+} ions. On the contrary, the Ni^{2+} ions, arranged on triangles on the extremes of the rugby-ball-shaped molecules, exhibits moderate ferromagnetic interactions. Interestingly, the low symmetry of the molecule, which is rather common for the multiple bridging modes of phosphonates, also induces a weak antiferromagnetic interaction in the Ni_3 unit. The results of competing magnetic interactions is spin frustration, which increases the density of states that are close to the ground state, thus increasing the entropy gain when the material is demagnetized. The role of frustration in MCE has been theoretically investigated and found to be a precious tool to engineer molecular material for magnetocaloric applications.[7]

Table 1: Estimated specific entropy change $-\Delta S_m$ upon application of a magnetic field $\mu_0 H$ and temperature T for some magnetically isotropic molecular clusters.[a]

	$-\Delta S_m$ [J K^{-1} kg^{-1}]	$\mu_0 H$ [T]	T_{max} [K]	Ref.
Fe_{14}	17.6	7	6	[5]
Mn_{10}	13.0	7	2.2	[11]
Mn_{14}	25	7	3.8	[12]
Gd_7	23	7	3	[13]
Cu_5Gd_4	31	9	3	[14]
Ni_6Gd_6	26.5	7	3	[6]
Gd_2	41.6	7	1.8	[8]
$Gd_3Ga_5O_{12}$	27	5	5	[15]

[a] The clusters are named according to their metal nuclearity, and values are compared to the value reported for gadolinium gallium garnet, last row, the standard for low temperature MCE commercial applications.

Evangelisti et al. then immediately reported a new record value of 41.6 J K^{-1} kg^{-1} for $-\Delta S_m$. The magnetic molecule is a simple Gd^{3+} dimer that exhibits weak ferromagnetic intramolecular interactions.[8] Such a large effect, estimated from magnetization and specific heat measurements, and for the first time confirmed by direct MCE measurements, results from the use of simple acetates as ligands, thus increasing the percentage of magnetic constituents. It would be interesting to investigate the analogue material where most Gd^{3+} is replaced with Y^{3+}. Most dimeric units will thus contain only one paramagnetic center, thus allowing the role of the weak intramolecular magnetic interaction to be clarified. The material is however also appealing for other reasons. First of all, a significant MCE is also observed in relatively weak magnetic fields. Another feature is the large drop in temperature upon adiabatic magnetization, which is as large as 3 K for a change in the magnetic field of one Tesla.

A large ΔT_{ad} is in fact required to have an efficient cooling, but this is inversely proportional to the specific heat. In complex magnetic molecules, the non-magnetic part of the specific heat (vibronic and electronic) quickly overwhelms the magnetic part upon increasing the temperature, thus limiting the use of molecular magnetic to refrigeration around liquid helium temperatures.

The significant increase in MCE efficiency of molecular materials increases their potentialities for applications but another difficulty must be overcome. To act as refrigerant, the MCE material must be placed in contact with the system to be cooled and heat must flow from the system to the refrigerant during the demagnetization, while during the application of the magnetic field the refrigerant must be in contact with a thermal bath to disperse the heat released. In all these phases, good thermal conductivity is an important prerequisite, but in general molecular materials are not good thermal conductors. As the MCE of magnetic molecules is not a cooperative phenomenon, Evangelisti et al. envision their exploitation at the single-molecule level for very special uses.[9] By depositing thin films or grafting the magnetic molecules directly to a surface, the problem of low thermal conductivity can be overcome. Magnetic molecules on surfaces have recently become the focus of an intense investigation,[10] and molecular chilling at the nanoscale appears to be a fascinating new scenario.

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[1] V. K. Pecharsky, K. A. Gschneidner, *J. Magn. Magn. Mater.* **1999**, *200*, 44 – 56.
[2] D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, UK, **2006**.
[3] F. Torres, J. M. Hernandez, X. Bohigas, J. Tejada, *Appl. Phys. Lett.* **2000**, *77*, 3248 – 3250.
[4] A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clerac, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Angew. Chem.* **2006**, *118*, 5048 – 5051; *Angew. Chem. Int. Ed.* **2006**, *45*, 4926 – 4929.
[5] M. Evangelisti, A. Candini, A. Ghirri, M. Affronte, E. K. Brechin, E. J. L. Mcinnes, *Appl. Phys. Lett.* **2005**, *87*, 072504.
[6] Y. Z. Zheng, M. Evangelisti, R. E. P. Winpenny, *Angew. Chem.* **2011**, *123*, 3776 – 3779; *Angew. Chem. Int. Ed.* **2011**, *50*, 3692 – 3695.
[7] J. Schnack, R. Schmid, J. Richter, *Phys. Rev. B* **2007**, *76*, 054413.
[8] M. Evangelisti, O. Roubeau, E. Palacios, A. Camón, T. N. Hooper, E. K. Brechin, J. J. Alonso, *Angew. Chem.* **2011**, *123*, 6736 – 6739; *Angew. Chem. Int. Ed.* **2011**, *50*, 6606 – 6609.
[9] M. Evangelisti, E. K. Brechin, *Dalton Trans.* **2010**, *39*, 4672 – 4676.
[10] A. Cornia, M. Mannini, P. Sainctavit, R. Sessoli, *Chem. Soc. Rev.* **2011**, *40*, 3076 – 3091.
[11] M. Manoli, R. D. L. Johnstone, S. Parsons, M. Murrie, M. Affronte, M. Evangelisti, E. K. Brechin, *Angew. Chem.* **2007**, *119*, 4540 – 4544; *Angew. Chem. Int. Ed.* **2007**, *46*, 4456 – 4460.
[12] M. Manoli, A. Collins, S. Parsons, A. Candini, M. Evangelisti, E. K. Brechin, *J. Am. Chem. Soc.* **2008**, *130*, 11129 – 11139.
[13] J. W. Sharples, Y. Z. Zheng, F. Tuna, E. J. L. McInnes, D. Collison, *Chem. Commun.* **2011**, *47*, 7650 – 7652.
[14] S. K. Langley, N. F. Chilton, B. Moubaraki, T. Hooper, E. K. Brechin, M. Evangelisti, K. S. Murray, *Chem. Sci.* **2011**, *2*, 1166 – 1169.
[15] R. D. McMichael, J. J. Ritter, R. D. Shull, *J. Appl. Phys.* **1993**, *73*, 6946 – 6948.