



# Reprint of “Coordination compounds and the magnetocaloric effect” ☆,☆☆

Joseph W. Sharples<sup>\*,1</sup>, David Collison<sup>1</sup>

School of Chemistry, The University of Manchester, Oxford Road, Manchester, Lancashire M13 9PL, United Kingdom

## ARTICLE INFO

### Article history:

Available online 5 August 2013

### Keywords:

Magnetocaloric effect  
Magnetic refrigeration  
Gadolinium  
Coordination chemistry

## ABSTRACT

This review article examines the impact of zero-dimensional compounds in the field of magnetic refrigeration, 20 years after the modern age of molecular magnetism began. The remarkable advances in this area are brought out here by an examination of 3d, 3d–4f and 4f molecular compounds and more recent polymeric materials; we then assess which of these shows most promise for this application.

© 2013 The Authors. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

When the first single-molecule magnet (SMM) was discovered in 1993 [1] it ushered in a change in the old discipline of magneto-chemistry and the beginning of a new one, molecular magnetism. A “side-product”, distinct from the anisotropic high spin clusters, were magnetocaloric molecules, based on electronically isotropic metal clusters, using metals with high spin values, such as gadolinium(III), manganese(II) and iron(III). We should really say that this field was rediscovered by inorganic chemists. Since Giauque used  $[\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}]$  to achieve low temperatures in the early 1930s [2a], much research, particularly with alloys and metallic materials has followed, the major successes of which are refrigeration proto-types of gadolinium metal at room temperature [2b–d] and the gadolinium gallium garnet (GGG) [2e] for low temperature work. Molecular magnetism has greatly benefited from an unprecedented collaboration between physicists and chemists in recent years and we have a much improved understanding of what is required to improve the performance of magnetic refrigerants. This understanding suggests improvements can be made, regarding

the effect of factors such as anisotropy, spin and molecular interactions [2f,g]. Therefore, this review article will survey the literature since the beginning of this new age, by examining 3d, 3d–4f and 4f magnetic refrigerants, noting their suitability in various areas of their structure, synthesis, composition and their magnetic properties. Its organisation is as follows: we will begin with a brief look at the first 3d SMMs investigated for their magnetocaloric effect (MCE), followed by the more suitable isotropic iron(III) and manganese(II) clusters and isolated examples of other transition metal compounds. Then we will introduce 3d–4f compounds, examining the influence of lanthanide ions, including an extensive series of phosphonate grids and cages. Next will be homo-metallic gadolinium compounds segueing into polymeric species, which appear to offer significant advantages over zero-dimensional molecules. First of all, though, we will examine the origin of the magnetocaloric effect and its quantification from a chemist's point of view.

## 2. Refrigeration and the beginnings of magnetic cooling

Currently, cooling things down is most commonly achieved by the vapour-compression cycle for everyday applications such as refrigerators or air-conditioning units [3a]. For more specialist applications, such as low temperature magnetism or work in extreme environments such as outer space [3b,c], the use of dilution refrigeration can achieve temperatures down to around 2 mK, using the isotopes  $^4\text{He}$  and  $^3\text{He}$ . Paramagnetic materials can replace and outperform these methods through a physical process called the magnetocaloric effect and specifically through an adiabatic demagnetisation mechanism. An understanding of the physics of this process allows chemists to design and to synthesise compounds which may be useful in this context [3d]. Then, using the two parameters  $-\Delta S_M$  and  $\Delta T_{AD}$ , the magnetic entropy change and adiabatic temperature change respectively, the performance of these materials can be quantified.

DOI of original article: <http://dx.doi.org/10.1016/j.poly.2013.02.034>.

☆ The publisher would like to inform the readership that this article is a reprint of a previously published article. An error occurred on the publisher's side which resulted in the publication of this article in a wrong issue. As a consequence, the publisher would like to make this reprint available for the reader's convenience and for the continuity of the special issue. For citation purposes, please use the original publication details: J.W. Sharples, D. Collison/Polyhedron 54 (2013) 91–103. The publisher sincerely apologizes to the readership and in particular to the author of the respective article and deeply regrets the inconvenience caused.

☆☆ This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

\* Corresponding author. Tel.: +44 (0) 161 306 9260; fax: +44 (0) 161 275 4598.

E-mail address: [joseph.sharples@manchester.ac.uk](mailto:joseph.sharples@manchester.ac.uk) (J.W. Sharples).

<sup>1</sup> See also <http://www.molmag.manchester.ac.uk>.

If we apply a magnetic field to a paramagnet, it will increase in temperature, hence the term magnetocaloric, under adiabatic conditions (constant entropy). This occurs through a redistribution of entropy in the system [3e], the total entropy being given by

$$S_{\text{total}} = S_M + S_{\text{lattice}} + S_{\text{electronic}} \quad (1)$$

As the spin angular momenta,  $S$ , of each paramagnetic component, previously randomly arranged, align in the field, the magnetic entropy will decrease, as the spins become ordered (Fig. 1). As entropy is constant  $S_{\text{lattice}}$  increases to compensate; this can be imagined as the ions in the lattice moving around more and becoming more disordered, hence the material is hotter. An alternative view is that, upon applying a field, phonons are exchanged between the magnetic spin system and the lattice and the latter is raised to a higher vibrational state. Taking the hot paramagnet as a magnetically ordered system we can see how a refrigerator can be obtained thus: if a fluid at ambient temperature is passed over this material then we can obtain an ordered system at the same temperature as its surroundings, whilst remaining in a magnetic field. Switching this field off, an adiabatic demagnetisation, then cools the material below its starting temperature by  $\Delta T_{\text{AD}}$  as  $S_{\text{lattice}}$  is converted back to  $S_M$ . Alternatively phonons are passed back from the lattice to the magnetic system and a lower vibrational state is obtained. Either way, we end with a paramagnet cooler than its surroundings: a refrigerator.

All paramagnets exhibit this effect, but in order to classify a material as “good” or “bad” many chemists simply take the magnitude of  $-\Delta S_M$  as a guide. In fact the  $\Delta T_{\text{AD}}$  is a more direct measure of the performance. A majority of papers only report the  $-\Delta S_M$  measurements as this can be derived using the familiar Maxwell equations [3e] from magnetisation data, and so is more readily available than heat capacity analysis, which can give both parameters. A third parameter, the product of density and  $-\Delta S_M$  ( $-\rho - \Delta S_M$ ), with units of  $\text{mJ cm}^{-3} \text{K}^{-1}$ , can also be straightforwardly obtained and accounts for the composition of the material in bulk.

Out of necessity this review looks primarily at  $-\Delta S_M$  changes, unless a fuller characterisation is available, where  $\Delta T_{\text{AD}}$  will be described.

The magnetic entropy change is given by,

$$S_M = nR \ln(2S + 1) \quad (2)$$

where  $R$  is the gas-constant,  $\ln$  the natural logarithm and  $S$  the ground spin state of the components and  $n$  is the number of spins of the given  $S$  [3d]. As a large enough field will saturate the spins and give a zero magnetic entropy state, this is equivalent to the largest possible magnetic entropy change  $-\Delta S_M$ . In a homo-metallic coordination compound this is simply the number of metals with the given spin, whereas the calculation is a sum for hetero-metallic systems with different spins. Note that antiferromagnetic coupling can give ground state spins less than the possible maximum. For non-zero dimensional paramagnets  $n$  is the number of

spins in the repeat unit. The magnetic entropy of the system is related to the magnetic degrees of freedom or spin multiplicity ( $2S + 1$  term), such that increasing the maximum entropy change depends on increasing  $S$ , and, as the units of  $-\Delta S_M$  are  $\text{J kg}^{-1} \text{K}^{-1}$ , minimising the diamagnetic mass of the compound, this not contributing to magnetic entropy. Furthermore, anisotropy and consequent zero field splitting (ZFS) should be minimised as this decreases the maximum magnetic entropy change by ordering and splitting the ground spin state in zero field, reducing the entropy of this otherwise degenerate arrangement. Anisotropy barriers arising from ZFS, such as in SMMs, will hinder any repetition of magnetisation and demagnetisation below the blocking temperature,  $T_B$ , as the magnetisation is not easily saturated over several cycles.

The magnetic entropy change,  $-\Delta S_M$ , is maximised at the ordering-temperature of the material, i.e. the paramagnetic to (anti)ferromagnetic transition point,  $(T_N)T_C$ , greatly influencing the range in which a given material is useful. Indeed, below these ordering-temperatures  $-\Delta S_M$  decreases quickly [3e]. In principle the same metal ion can be used in a range of materials, each tuned by their ordering-temperatures for a particular temperature regime by a ligand set which governs its interactions with neighbouring ions. For example, to replace the dilution refrigeration method a material with almost non-interacting spins is required to maintain a high  $-\Delta S_M$  at low temperatures (mining the moon for the required, expensive and rare  $^3\text{He}$  is currently only a science-fiction alternative source, so there is a valid need for a replacement). One challenge here is to keep metals well separated in the crystal lattice, perhaps using sterically bulky ligands, whilst maintaining a low molecular weight for useful performance (*vide infra*) [3c]. Room temperature applications currently centre on various alloys and metals, such as gadolinium, which has a  $T_C$  of 293 K. The main focus of this article lies between these extremes, and is the small but rapidly increasing collection of metal coordination compounds, often termed clusters, which have been shown to outperform rivals in the low-temperature 0.5–20 K range.

The first significant  $-\Delta S_M$  for a cluster of the 21st century was found in  $[\text{Fe}^{\text{III}}_{14}(\text{bta})_6\text{O}_6(\text{OMe})_{18}\text{Cl}_6]$  where Hbta is benzotriazole [4a] (*vide infra*). High-spin clusters such as this can give larger  $-\Delta S_M$  values than for single ion species and this requires either ferromagnetic interactions between metals or non-complete cancellation of spins where antiferromagnetic coupling is present to give a high spin ground state; weakly coupled systems which can easily be saturated under applied field can also provide a further increase to  $-\Delta S_M$  due to the extra low lying magnetic states that are generated. These are populated under zero-field, providing extra degrees of freedom, but depopulated under applied field, giving a larger  $-\Delta S_M$ . Finally, clusters can also provide a benefit based on the geometrical arrangement of their spins in a spin frustrated system [5], a system where “all spin requirements cannot be satisfied simultaneously”, e.g. in an antiferromagnetically coupled, half-integer spin, equilateral triangle arrangement of metals. This generates easily accessible states in zero-field which contribute to a larger  $-\Delta S_M$  under applied field in a similar fashion to weak coupling. It is only with molecular materials that we can tune these properties of spin, anisotropy, geometry, and intra- and inter-molecular interactions, offering significant potential advantages over other materials in this field such as glasses and alloys.

### 3. Transition metal compounds

#### 3.1. From chaos, order

$\{[\text{Fe}^{\text{III}}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]\text{Br}_7 \cdot \text{H}_2\text{O}\}\text{Br} \cdot 8\text{H}_2\text{O}$  (1), where tacn is 1,4,7-triazacyclononane,  $[\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4\text{O}_{12}]$ .

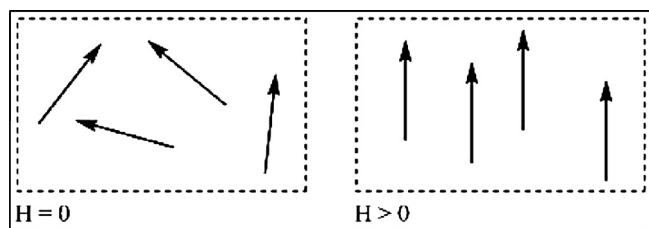


Fig. 1. Spins on individual metals, represented by arrows, are randomly aligned in zero field, left, and become ordered in the magnetic field, right, decreasing the magnetic entropy.

Download English Version:

<https://daneshyari.com/en/article/7766446>

Download Persian Version:

<https://daneshyari.com/article/7766446>

[Daneshyari.com](https://daneshyari.com)