



## Research articles

## Rotational magnetocaloric effect of anisotropic giant-spin molecular magnets

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## ABSTRACT

The magnetocaloric effect, that consists of adiabatic temperature changes in a varying external magnetic field, appears not only when the amplitude is changed, but in cases of anisotropic magnetic materials also when the direction is varied. In this article we investigate the magnetocaloric effect theoretically for the archetypical single molecule magnets  $\text{Fe}_8$  and  $\text{Mn}_{12}$  that are rotated with respect to a magnetic field. We complement our calculations for equilibrium situations with investigations of the influence of non-equilibrium thermodynamic cycles.

## 1. Introduction

Magnetocalorics is an important thermodynamic concept with many applications for instance in room-temperature or sub-kelvin cooling [1–7]. It rests to a large extent on the magnetocaloric effect (MCE) [8] which states that in adiabatic processes, i.e. processes with constant entropy, the temperature changes upon the variation of the external magnetic field. Nowadays research efforts focus e.g. on new materials [9–11] or theoretical optimization of (molecular) magnetic materials [12–15].

While the typical magnetocaloric process employs variations of the magnitude of the external field, some ideas focus on the effect of a rotation of the field or equivalently of the sample [16–20]. A practical reason for this approach is given by the fact that mechanical rotations of the sample can be performed much more quickly than field sweeps. However, the rotational magnetocaloric effect (rMCE) requires anisotropic magnetic materials [20–22]. In this article we therefore discuss how single-molecule magnets (SMM) perform as cooling agents in the kelvin temperature region. These materials are usually known for two other effects: slow relaxation and quantum tunneling of the magnetization [23–26]. Although their magnetocaloric properties have been investigated previously [18,19,27,28], they are often not considered for magnetic cooling in the ordinary sense, since their density of low-lying energy levels is small, which does not promise a larger MCE. Nevertheless, their large anisotropy makes them prospective candidates for the rMCE [18].

In this article we investigate two aspects of the rMCE. We first discuss the isentropes and isothermal entropy changes that can be

achieved in SMMs such as  $\text{Fe}_8$  and  $\text{Mn}_{12}$ . In a second part we set up a simple relaxation dynamics in order to estimate how time-dependent Carnot-like processes would perform for these molecular coolers.

The article is organized as follows. In Section 2 we introduce the model. Section 3 deals with the equilibrium rotational magnetocaloric effect whereas Section 4 discusses dynamical aspects. Our results are summarized in Section 5.

## 2. Model and numerical procedures

## 2.1. Model Hamiltonians

The low-temperature properties of single-molecule magnets with a large spectral gap between the ground state multiplet and higher-lying states can be rationalized using the giant spin approximation [29]. To this end the zero-field split ground state multiplet is generated by an effective one-spin Hamiltonian. For  $\text{Fe}_8$  the following giant spin Hamiltonian was developed [26]

$$\begin{aligned} H_{\text{Fe}_8} = & D_{\text{Fe}_8} \tilde{S}_z^2 + E_{\text{Fe}_8} (\tilde{S}_x^2 - \tilde{S}_y^2) + g_{\text{Fe}_8} \mu_B \vec{B}(t) \cdot \vec{\tilde{S}} \\ & + B_{4,\text{Fe}_8}^0 Q_4^0 + B_{4,\text{Fe}_8}^2 Q_4^2 + B_{4,\text{Fe}_8}^4 Q_4^4, \end{aligned} \quad (1)$$

with specific values of  $S = 10$ ,  $D_{\text{Fe}_8} = -0.295$  K,  $E_{\text{Fe}_8} = 0.05605$  K,  $|E_{\text{Fe}_8}/D_{\text{Fe}_8}| = 0.19$ ,  $B_{4,\text{Fe}_8}^0 = 2.3 \cdot 10^{-6}$  K,  $B_{4,\text{Fe}_8}^2 = -7.2 \cdot 10^{-6}$  K,  $B_{4,\text{Fe}_8}^4 = -1.2 \cdot 10^{-5}$  K, and  $g_{\text{Fe}_8} = 2.0$  [30].

In the case of  $\text{Mn}_{12}$ , Hamiltonian (2) proved to be appropriate

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$$\begin{aligned} \vec{H}_{\text{Mn}_{12}} = & D_{\text{Mn}_{12}} \vec{S}_z^2 + g_{\text{Mn}_{12}} \mu_B \vec{B}(t) \cdot \vec{S} \\ & + B_{4,\text{Mn}_{12}}^0 \mathcal{Q}_4^0 + B_{4,\text{Mn}_{12}}^4 \mathcal{Q}_4^4, \end{aligned} \quad (2)$$

with specific values of  $S = 10$ ,  $D_{\text{Mn}_{12}} = -0.65$  K,  $B_{4,\text{Mn}_{12}}^0 = -3.0 \cdot 10^{-5}$  K,  $B_{4,\text{Mn}_{12}}^4 = \pm 4.6 \cdot 10^{-5}$  K, and  $g_{\text{Mn}_{12}} = 2.0$  [31]. Higher order spin operators are expressed by means of Stevens operators

$$\mathcal{Q}_4^0 = 35 \vec{S}_z^4 - [30S(S+1) - 25] \vec{S}_z^2 + 3S^2(S+1)^2 - 6S(S+1) \quad (3)$$

$$\begin{aligned} \mathcal{Q}_4^2 = & \frac{1}{4} [7 \vec{S}_z^2 - S(S+1) - 5] (\vec{S}^+)^2 + (\vec{S}^-)^2 \\ & + \frac{1}{4} ((\vec{S}^+)^2 + (\vec{S}^-)^2) [7 \vec{S}_z^2 - S(S+1) - 5] \end{aligned} \quad (4)$$

$$\mathcal{Q}_4^4 = \frac{1}{2} ((\vec{S}^+)^4 + (\vec{S}^-)^4). \quad (5)$$

It turns out that for the magnetocaloric investigations of this article only the terms given in the respective first lines of Eqs. (1) and (2) are relevant. The other terms, which determine the tunnel splitting, have a stark effect on the magnetization tunneling, but not on the thermal properties for the temperature and field ranges as well as orientations studied here. We therefore use only the first lines of (1) and (2) in the following calculations.

Since we are going to investigate the influence on the MCE of the relative orientation of the magnetic field with respect to the easy axis of the SMM, we define the coordinate system as shown in Fig. 1. The magnetic easy axis is parallel to the  $z$ -axis, whereas the field vector lies in the  $xz$ -plane with an inclination of  $\vartheta$  with the positive  $x$ -axis.

## 2.2. Equilibrium thermodynamics

Here and throughout the article we tacitly assume that the applied magnetic fields and the investigated temperatures do not violate the ranges of applicability of the giant spin models (1) and (2). In order to provide guidance about these scales we mention that the first  $S = 9$  multiplet of  $\text{Mn}_{12}$  is theoretically proposed at about 30 K [32] and experimentally found at about 10 K [33], which restricts temperatures to only very few kelvin and also fields to very few tesla to be meaningfully applied within the giant-spin model. A similar statement holds for  $\text{Fe}_8$ , where the giant spin model is applicable up to excitation energies of 20 K [29]. An example where the giant-spin model does not work is provided in Ref. [34].

Equilibrium thermodynamic observables can be obtained from the Gibbs potential  $G(T, \vec{B})$

$$G(T, \vec{B}) = -k_B T \log[Z(T, \vec{B})], \quad (6)$$

where  $Z(T, \vec{B})$  denotes the partition function. Entropy as well as magnetization are first derivatives of  $G(T, \vec{B})$ , i.e.

$$\mathcal{S}(T, \vec{B}) = -\frac{\partial}{\partial T} G(T, \vec{B}), \quad (7)$$

$$\vec{\mathcal{M}}(T, \vec{B}) = -\frac{\partial}{\partial \vec{B}} G(T, \vec{B}). \quad (8)$$

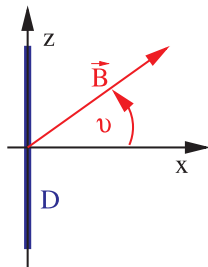


Fig. 1. Coordinate system used in the simulations.

## 2.3. Non-equilibrium thermodynamics

The infinitesimal work  $\delta W$  is defined by the variation of the magnetization

$$\delta W = \vec{B} \cdot d\vec{\mathcal{M}}. \quad (9)$$

Since this term is complicated to evaluate we use the following relation:

$$\oint d(\vec{\mathcal{M}} \cdot \vec{B}) = 0 = \oint \vec{B} \cdot d\vec{\mathcal{M}} + \oint \vec{\mathcal{M}} \cdot d\vec{B} \quad (10)$$

$$\Rightarrow \Delta W = -\oint \vec{\mathcal{M}} \cdot d\vec{B}. \quad (11)$$

The magnetization  $\vec{\mathcal{M}}$  can be obtained from the time-dependent density matrix. For the time evolution of the density matrix we employ [35]

$$\frac{d}{dt} \rho(t) = -i[H, \rho(t)] + c \cdot \lambda (\rho^{(\text{eq})}(T, \vec{B}) - \rho(t)), \quad (12)$$

with

$$\rho^{(\text{eq})}(T, \vec{B}) = \frac{1}{Z(T, \vec{B})} \sum_n |n\rangle e^{-\beta E_n} \langle n|, \quad (13)$$

where  $\beta = (k_B T)^{-1}$ .  $E_n$  and  $|n\rangle$  denote the eigenvalues and the corresponding eigenvectors of the Hamiltonian. The factor  $c$  depends on the nature of the current stroke in the process. For an isothermal process  $c = 1$ , for an adiabatic (or isolated) process  $c = 0$ . The factor  $\lambda$  denotes the coupling strength of the system to one of the heat reservoirs and can in principle be different for each heat bath.

The mean magnetization can easily be calculated from the density matrix:

$$\vec{\mathcal{M}}(t) = -g \mu_B \text{Tr}\{\vec{S} \rho(t)\}. \quad (14)$$

For the contribution to the mean work  $\Delta W$  done on or by the system during one stroke in the time interval  $[t_0, t_1]$  one finds with (11)

$$\Delta W(t_1, t_0) = -\int_{t_0}^{t_1} \vec{\mathcal{M}}(t) \cdot \dot{\vec{B}}(t) dt. \quad (15)$$

Eq. (11) is only valid for a full cycle. The contribution  $\Delta W(t_1, t_0)$  thus may contain contributions that are not work in a strict thermodynamic sense, but e.g. heat. Nevertheless, when added up to a full cycle those non-work contributions exactly cancel. Therefore, we discuss only quantities of full cycles or averages over many cycles in the remainder of the article.

The absorbed or emitted amount of heat  $\Delta Q(t_1, t_0)$  can be obtained from the change of the mean energy  $\langle H \rangle$  of the system via the rules of thermodynamics:

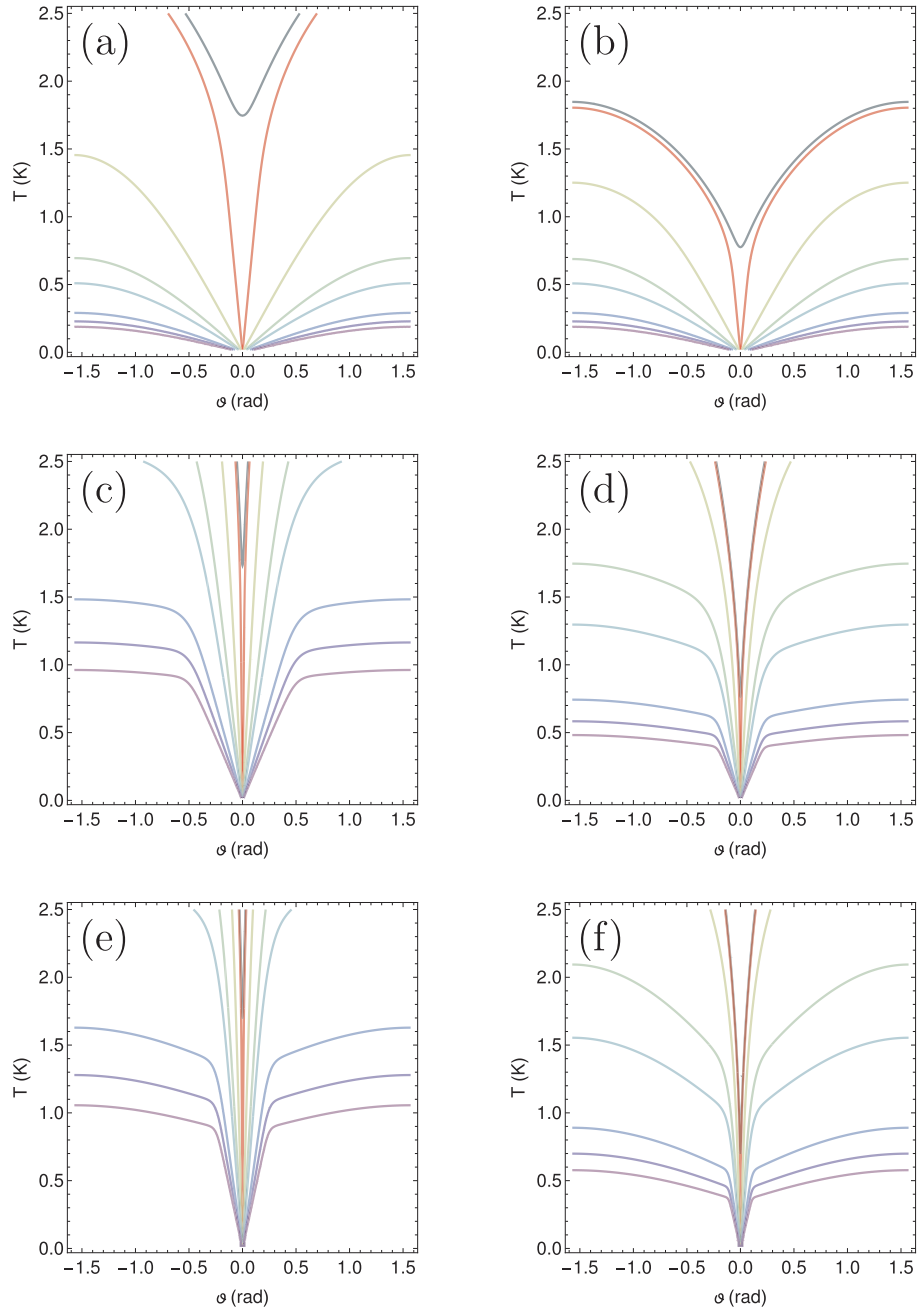
$$\langle H \rangle(t) = \text{Tr}\{H(t) \rho(t)\}, \quad (16)$$

$$\Delta \langle H \rangle = \langle H \rangle(t_1) - \langle H \rangle(t_0) = \Delta Q + \Delta W. \quad (17)$$

Again, due to the use of (15),  $\Delta Q$  is a heat in the strict sense only for a full cycle.

## 3. Quasi-static MCE

Quasi-static (equilibrium) MCE investigates the thermodynamic functions (7) & (8) as given by (e.g.) the canonical ensemble. Of special interest are the isentropes, i.e. curves of constant entropy, whose slopes are the so-called cooling rates as well as the isothermal entropy changes – both figures of merit for MCE materials. Fig. 2 shows the isentropes of  $\text{Mn}_{12}$  (left column) and  $\text{Fe}_8$  (right column) for  $B = 0.1$  T,  $B = 1$  T, and  $B = 2$  T from top to bottom. Since both systems are modeled with rather similar Hamiltonians, the graphs for these two SMMs do look very similar. The behavior can be rationalized as follows. For a given and not too large magnitude of the external magnetic field the energy spectrum resembles a tilted parabola for  $\vartheta = \pi/2$  (l.h.s. of Fig. 3). In particular,



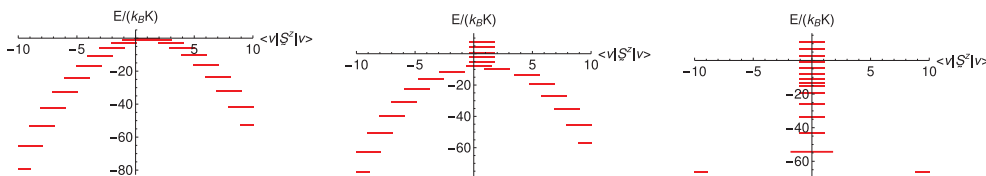
**Fig. 2.** Isentropes as a function of  $\vartheta$  of  $\text{Mn}_{12}$  (left column) and  $\text{Fe}_8$  (right column): (a)  $\text{Mn}_{12}$ ,  $B = 0.1$  T, (b)  $\text{Fe}_8$ ,  $B = 0.1$  T, (c)  $\text{Mn}_{12}$ ,  $B = 1$  T, (d)  $\text{Fe}_8$ ,  $B = 1$  T, (e)  $\text{Mn}_{12}$ ,  $B = 2$  T, (f)  $\text{Fe}_8$ ,  $B = 2$  T. Contours are drawn at entropy values  $\mathcal{S}/k_B$  of  $10^{-5}$ ,  $10^{-4}$ ,  $10^{-3}$ ,  $0.032$ ,  $0.1$ ,  $0.4$ ,  $0.68$ , and  $0.7$  (bottom to top curves in each panel).

the ground state is not degenerate. This situation changes towards  $\vartheta = 0$  (r.h.s. of Fig. 3), where the two ground state levels are virtually degenerate. This means that all isentropes with  $\mathcal{S}/k_B \leq \log 2$  head towards absolute zero at  $\vartheta = 0$ . In addition, the top panels of Fig. 2 display isentropes with  $\mathcal{S}/k_B = 0.7 > \log 2$  that only exhibit local minima at  $\vartheta = 0$ . All plots are symmetric about  $\vartheta = 0$ .

The cooling rate (slope of isentropes) assumes very large values

close to  $\vartheta = 0$ . This trend increases with increasing magnitude of the applied field. Therefore, large temperature variations should be achievable with only mild rotations in particular for stronger fields, which nevertheless is technically demanding.

The isothermal entropy change on the other hand is rather small since more than a twofold degeneracy of levels is not achievable in the physically permitted temperature and field ranges of the model. This



**Fig. 3.** Energy eigenvalues vs. magnetization along z-direction for  $\text{Mn}_{12}$  at  $B = 1$  T and  $\vartheta = \pi/2$  (left),  $\vartheta = \pi/4$  (middle), and  $\vartheta = 0$  (right).

leads to the characteristic curves displayed in Fig. 4. Shown is the negative entropy difference between final and initial orientation, i.e.

$$-\Delta\mathcal{S} = -(\mathcal{S}(T, B, \vartheta_f) - \mathcal{S}(T, B, \vartheta_i)). \quad (18)$$

The initial angle is always taken as  $\vartheta_i = 0$ . The colors of the three curves in each panel correspond to the three chosen final angles  $\vartheta_f$  displayed above the panels.

As one notices in all panels of Fig. 4 the isothermal entropy changes approach  $\Delta\mathcal{S}/k_B = \log 2 \approx 0.68$  at low temperatures. This is a result of the twofold degeneracy at  $\vartheta_i = 0$  and the vanishingly small entropy at all other angles  $\vartheta_f \neq 0$ . For elevated temperatures the entropy change rises a bit since then also higher lying levels are thermally populated. But due to the restricted number of levels, which are separated by gaps of the order of the anisotropy, this effect is small, albeit more pronounced for stronger external fields. The biggest entropy changes can be achieved by a rotation of  $\Delta\vartheta = \pi/2$  from the direction perpendicular to the easy axis into the direction of the easy axis.

#### 4. Time-dependent Carnot-like processes

A discussion of the magnetocaloric properties as in section 3 or many publications of the field rests on the assumption of thermal equilibrium, i.e. on idealized quasi-static processes. However, a realistic cooling experiment or a Carnot process as one example of possible thermodynamic cycles is executed on short time scales of e.g. minutes [6] or shorter. Whether the system stays close to equilibrium depends on its typical relaxation times. In addition, especially for small quantum systems, it is not granted that the isolated parts of the processes, where no thermal contact is established, are indeed adiabatic. They may as well be unitary which is not the same. We do not want to get into this very complicated discussion and therefore assume that the isolated steps of our processes are described by a unitary time evolution. This assumption appears further justified since we investigate only fast processes in the following. Investigations of slower processes and processes other than Carnot-like are postponed to future investigations.<sup>1</sup>

The Carnot-like process consists of two isothermal (strokes II and IV) and two isolated processes (strokes I and III). The time evolution of the medium, in our case a single Mn<sub>12</sub> SMM (Fe<sub>8</sub> behaves practically identical and is thus not investigated), is modeled via the time evolution of its density matrix according to (12). Although the cycle time  $\tau_c$  is in reality only limited by the relaxation during the isothermal strokes, we choose for the sake of simplicity for all four strokes the same time duration. We choose  $T_h = 0.65$  K as the temperature of the hot reservoir and  $T_c = 0.5$  K as the temperature of the cold reservoir, respectively. The temperature span cannot be chosen much bigger for a cycle with realistic  $\vartheta$  variations, see Fig. 2, which hints already at a restricted usability of the rMCE for giant-spin molecular magnets.

For the coupling constant  $\lambda$  we choose  $\lambda_h = \lambda_c = 10^{-1}$  ps<sup>-1</sup>. Smaller values of  $\lambda$  simply lead to a shift to lower operating frequencies  $f = \tau_c^{-1}$  and a rescaling of the observed power. Since we investigate the Carnot-like process in the realization as a refrigerator important quantities of interest are the cooling power  $P$  and the efficiency  $\epsilon$ :

$$P = \frac{Q_c}{\tau_c}, \quad (19)$$

$$\epsilon = \frac{Q_c}{W}, \quad (20)$$

<sup>1</sup> We like to mention that we use the term *Carnot-like process* for our time-dependent version of the Carnot process, since the sub-processes (isothermal, adiabatic/unitary) are adapted accordingly. The major reason, that we investigate fast processes, is given by the intrinsic time scale of the molecular magnet which is ps. We thus adapt the relaxation due to the interaction with the environment accordingly in order to avoid inaccessibly long numerical simulation times. Our findings are qualitatively not altered.

where  $Q_c$  is the amount of heat taken from the cold reservoir and  $W$  is the amount of work absorbed by the system during one complete cycle.

The time dependent angle  $\vartheta(t)$  and the behavior of the coupling constant  $c\lambda$  is exemplarily shown in Fig. 5 for a cycle time of  $\tau_c = 20$  ns. Fig. 5 also shows the process in the corresponding  $T$ - $\vartheta$ -diagram. As will be used later, one finds that a minimal possible amplitude  $B_0 > 0$  exists that can satisfy  $\mathcal{S}_{\min}$  and  $\mathcal{S}_{\max}$  at the given temperatures of the heat reservoirs.

During the beginning of stroke I the system is in thermal equilibrium with the cold heat reservoir at temperature  $T_c$ . The system is then decoupled from the heat reservoir and the angle  $\vartheta$  is changed with constant angular velocity from  $\vartheta_0$  to  $\vartheta_1$  (compare stroke I in Fig. 5). Since the system evolves isolated during this stroke there is no heat exchanged with the reservoirs. The work can therefore be calculated via (17).

During stroke II the coupling to the hot heat reservoir is switched on while the angle  $\vartheta$  is further increased to  $\vartheta_2$  with a constant velocity that is different to that of the previous step. The system relaxes during this stroke towards thermal equilibrium with the hot heat reservoir, but depending on the time of contact with the bath, equilibrium is not necessarily reached. Since this stroke is isothermal the work must be calculated via (15). The amount of heat  $Q_h$  exchanged with the hot heat reservoir can then be calculated via (17).

For stroke III the system is again decoupled from the heat reservoir and the angle  $\vartheta$  is decreased with another constant velocity from  $\vartheta_2$  to  $\vartheta_3$  (compare stroke III in Fig. 5). Because this stroke is again isolated and there is again no heat exchange with any of the heat reservoirs the work can be calculated directly from (17).

During the last stroke IV the system is coupled to the cold heat reservoir at temperature  $T_c$  while the angle  $\vartheta$  is decreased with another constant velocity until the initial angle  $\vartheta_0$  is reached and the cycle is complete (compare stroke IV in Fig. 5). The system evolves towards thermal equilibrium with the cold heat reservoir as much as possible during contact time. Since this stroke is again isothermal the work must be calculated via (15). The amount of heat  $Q_c$  exchanged with the cold heat reservoir can then be calculated from (17).

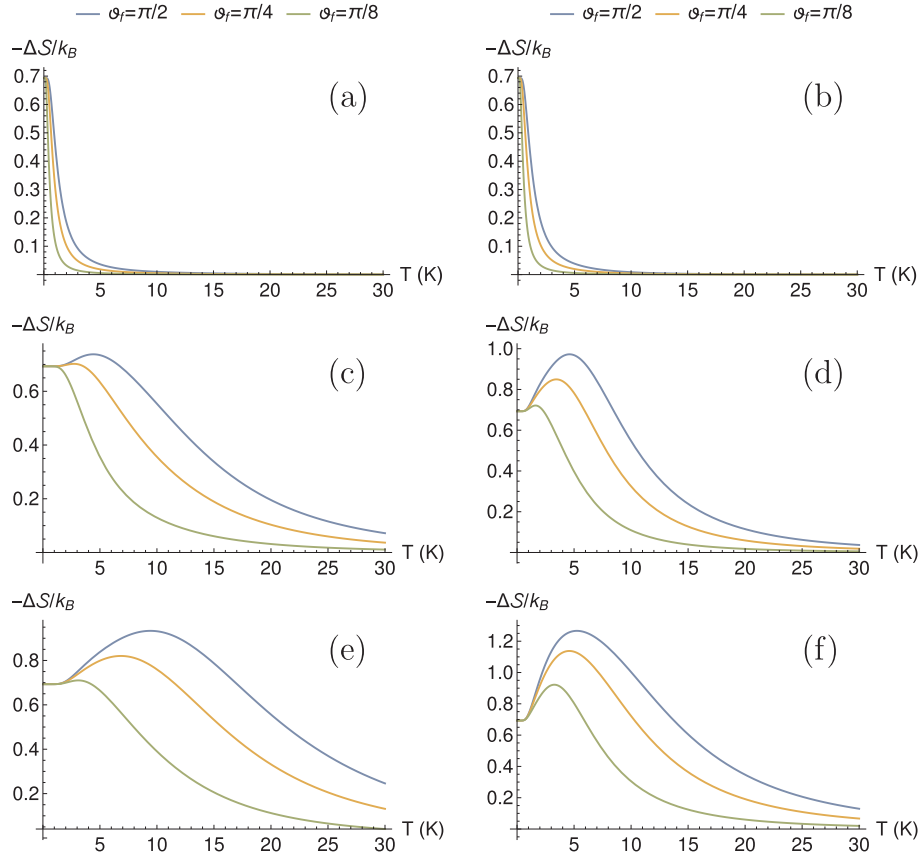
The observables presented in the following parts are evaluated after the system has been driven through a sufficient number of cycles in order to reach a steady state.

##### 4.1. Dependence of power and operating frequencies on the amplitude of $\vec{B}(t)$

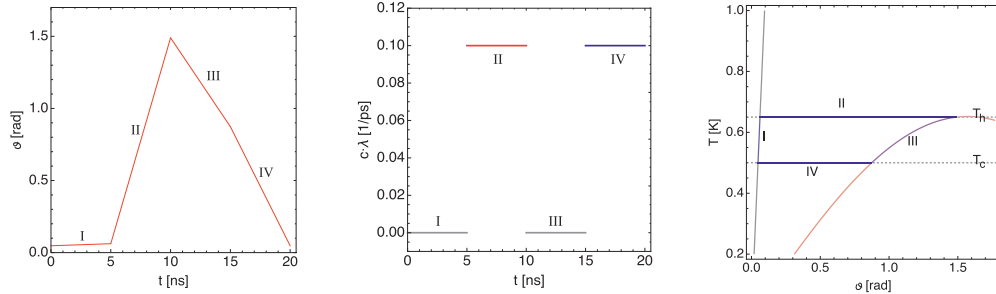
At first we investigate the influence of the amplitude  $B_0$  of the magnetic field  $\vec{B}(t)$  on the maximum cooling power  $P$ , the optimal operating frequency  $f_{\text{opt}}$ , the efficiency  $\epsilon_{\text{opt}}$  as well as on the maximum operating frequency  $f_{\text{max}}$ . Here the optimal operating frequency  $f_{\text{opt}}$  denotes the operating frequency and  $\epsilon_{\text{opt}}$  the efficiency at maximum cooling power. The maximum operating frequency  $f_{\text{max}}$  is the maximal frequency for which the Carnot-like cycle works as a refrigerator delivering heat from the cold heat reservoir to the hot one by consuming work. The results of our simulations are shown in Fig. 6. The angles  $\vartheta_0$  to  $\vartheta_3$  are chosen such that the process always operates between the two isentropes  $\mathcal{S}_{\max}/k_B = 0.68$  and  $\mathcal{S}_{\min}/k_B = 0.032$  and therefore with a fixed  $\Delta\mathcal{S}/k_B = 0.648$ .

The minimal possible amplitude  $B_0$  that can satisfy  $\mathcal{S}_{\min}$  and  $\mathcal{S}_{\max}$  at the given temperatures of the heat reservoirs is  $B_0 = 0.128$  T. As one can deduce from Fig. 6,  $P$ ,  $f_{\text{opt}}$  and  $f_{\text{max}}$  are maximal for this amplitude. Only the efficiency at maximum power  $\epsilon_{\text{opt}}$  is minimal. When one increases the amplitude  $B_0$ ,  $P$  decreases by 7.66% until the amplitude  $B_0$  reaches a threshold value of about 0.5 T. The optimal operating frequency  $f_{\text{opt}}$  decreases in the same time by 12.45% and  $f_{\text{max}}$  decreases by even 21.17%. The efficiency on the other hand increases by 17.15%. For larger values of  $B_0$  all observed quantities become independent of  $B_0$ .

For the hot and cold temperatures  $T_c$  and  $T_h$ , respectively, chosen in



**Fig. 4.** Isothermal entropy changes of  $\text{Mn}_{12}$  (left column) and  $\text{Fe}_8$  (right column): (a)  $\text{Mn}_{12}$ ,  $B = 0.1$  T, (b)  $\text{Fe}_8$ ,  $B = 0.1$  T, (c)  $\text{Mn}_{12}$ ,  $B = 1$  T, (d)  $\text{Fe}_8$ ,  $B = 1$  T, (e)  $\text{Mn}_{12}$ ,  $B = 2$  T, (f)  $\text{Fe}_8$ ,  $B = 2$  T. The rotation is performed from the initial angle  $\vartheta_i = 0$  to the final angles  $\vartheta_f$  provided at the top. The curves are shown also for temperatures exceeding the applicability range of giant spin models.



**Fig. 5.** Exemplary time dependence of the angle  $\vartheta(t)$  (left hand side) and of the coupling constant  $c \cdot \lambda$  (middle). The coupling to the hot reservoir  $\lambda_h$  is shown in red, the coupling to the cold reservoir  $\lambda_c$  is shown in blue. The right hand side shows an equilibrium, i.e. fully relaxed Carnot process in the  $T$ - $\vartheta$ -diagram ( $B = 1$  T). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

our example, one also deduces from Fig. 2 that with increasing field strength  $B_0$  the maximum rotation angle decreases. Therefore, for large amplitudes  $B_0$  only very small rotations are necessary.

#### 4.2. Dependence of power and operating frequencies on $\Delta\mathcal{S}$

The quasi-static solution of the Carnot process yields a linear dependence between the heat extracted from the cold heat reservoir  $\Delta Q_c$  and the entropy difference  $\Delta\mathcal{S}$  between the two isentropes  $\mathcal{S}_{\min}$  and  $\mathcal{S}_{\max}$  of the process:

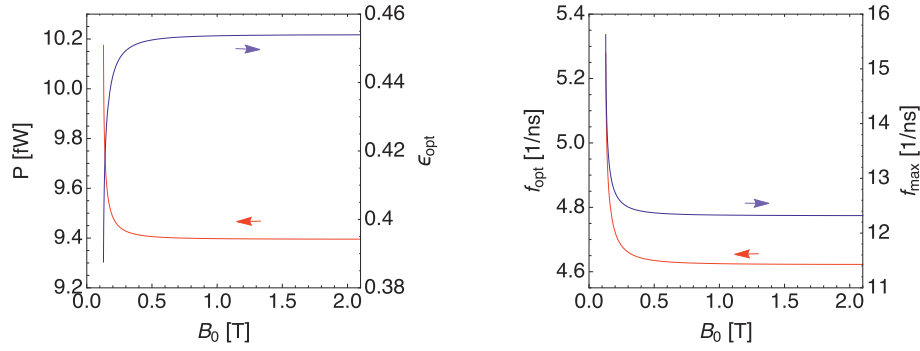
$$\Delta Q_c = T_c \cdot \Delta\mathcal{S}. \quad (21)$$

Thus a large value of  $\Delta\mathcal{S}$  is intended to maximize the cooling per cycle. To investigate if this still holds for the dynamic process we

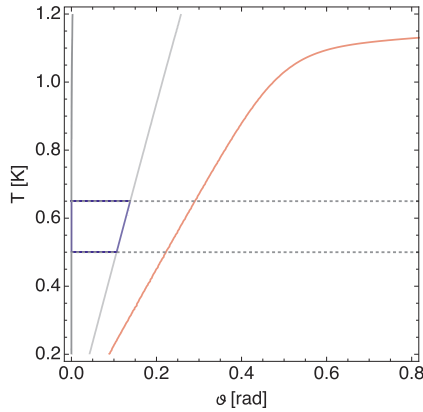
investigate again the maximum cooling power  $P$  and the corresponding efficiency at maximum cooling power  $\epsilon_{\text{opt}}$  as well as the operating frequencies  $f_{\text{opt}}$  and  $f_{\text{max}}$ . The amplitude  $B_0$  of the applied magnetic field is fixed at  $B_0 = 1$  T. We also fix the isentrope  $\mathcal{S}_{\max}$  to a value that is very close to the maximal possible value. We use  $\mathcal{S}_{\max} = 0.6931k_B$ . The other isentrope  $\mathcal{S}_{\min}$  is varied to achieve different  $\Delta\mathcal{S}$ . This is exemplarily shown in Fig. 7.

The results of our simulations are shown in Fig. 8. As one can see from the left hand side of Fig. 8 the maximum cooling power  $P$  grows almost linearly with  $\Delta\mathcal{S}$  (red curve). But there is a significant loss of  $P$  when  $\Delta\mathcal{S}$  gets larger than  $\Delta\mathcal{S}_{\text{opt}} = 0.668k_B$  (that is 96.44% of the maximum value of  $\Delta\mathcal{S}$ ). This loss is about almost 25% when the cycle is operated at maximum  $\Delta\mathcal{S}$  instead of  $\Delta\mathcal{S}_{\text{opt}}$ . In contrast to the quasi-static case the largest  $\Delta\mathcal{S}$  does not yield the maximum performance.



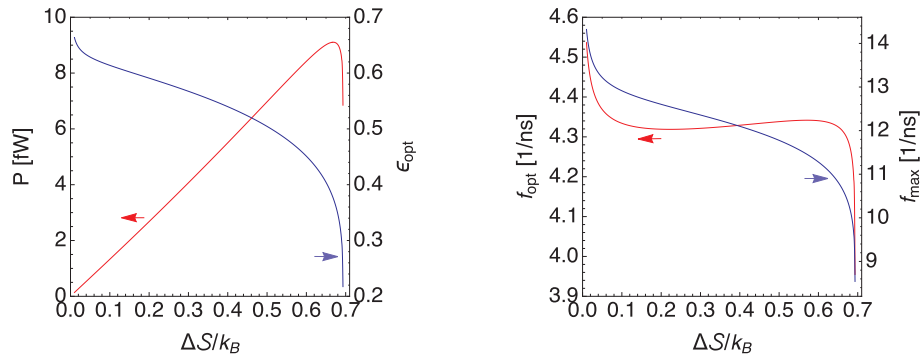


**Fig. 6.** Dependence of the maximum cooling power  $P$  and corresponding efficiency  $\epsilon_{\text{opt}}$  (left hand side) and the optimal and maximal operating frequency  $f$  (right hand side) on the amplitude of the magnetic field  $B_0$ . The curves belonging to the left axis are shown in red, the curves belonging to the right axis are shown in blue. Different scales are used. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 7.** Exemplary depiction of the Carnot-like cycle in the  $T$ - $\theta$ -diagram. The isentropes  $\mathcal{S}_{\text{max}}$  (black line) is fixed at  $\mathcal{S}/k_B = 0.6931$  while the isentropes  $\mathcal{S}_{\text{min}}$  (gray line) is varied between black line and red curve to achieve different  $\Delta\mathcal{S}$ . The temperatures of the two heat reservoirs are marked by dotted gray lines. A Carnot cycle is depicted in blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The efficiency  $\epsilon_{\text{opt}}$  at maximum power decreases monotonically with growing  $\Delta\mathcal{S}$  (blue curve in Fig. 8 l.h.s.), and the slope is larger for small as well as large values of  $\Delta\mathcal{S}$ . The same is true for the maximum operating frequency  $f_{\text{max}}$  (compare blue curve in Fig. 8 r.h.s.). The optimal operating frequency  $f_{\text{opt}}$ , red curve in Fig. 8 r.h.s., behaves differently, since it has a local minimum at  $\Delta\mathcal{S} = 0.222k_B$  (32.1% of the maximum  $\Delta\mathcal{S}$ ) and a local maximum at  $\Delta\mathcal{S} = 0.570k_B$  (82.36% of the maximum  $\Delta\mathcal{S}$ ).



**Fig. 8.** Dependence of the maximum cooling power  $P$  and corresponding efficiency  $\epsilon$  (left hand side) and the optimal and maximal operating frequency  $f$  (right hand side) on the value of  $\Delta\mathcal{S}$ . The curves belonging to the left axis are shown in red, the curves belonging to the right axis are shown in blue. Different scales are used. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 5. Summary and outlook

In this article we report investigations of the rotational magnetocaloric effect using single molecule magnets. We can conclude that the effect is present and may be used in cases where quick field changes, that are possible using mechanical rotations, are necessary. The isothermal entropy change, on the other hand, is limited since degeneracies larger than two do not arise and thus the entropy does not grow much above  $\mathcal{S}/k_B \approx \log 2$ . In addition, the shape of the isentropes in Fig. 2 suggests that only rather small temperatures and thus small temperature differences can be addressed with the rMCE in single-molecule magnets if one considers realistic changes of the angle  $\theta$ .

A description of the Carnot-like process as a time-dependent non-equilibrium process – using a simplified dynamics – reveals that for SMMs a threshold field amplitude exists above which the characteristic figures do not change any more. In addition and in contrast to the quasi-static case the largest  $\Delta\mathcal{S}$  does not yield the maximum performance. Instead the maximum cooling power is achieved with an optimal value for  $\Delta\mathcal{S}$  of only about 96 % of the maximum possible value.

In future investigations slow processes – which are numerically much more demanding – shall be studied. There we expect an additional impact of the intricate dynamics at avoided level crossings that should influence the magnetocaloric properties depending whether the avoided crossing is passed quickly or slowly. In addition, the interaction with the heat bath should include the relevant phonon degrees of freedom in order to take the phonon bottleneck into account [36–38,34,35]. This calls for a relaxation mechanism that is more realistic than outlined in (12).

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