

Computer simulation of the Giant Magnetocaloric Effect from spin models

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The derivation of the magnetocaloric effect is presented from a thermodynamical point of view, along with a description of the physical phenomena. The giant magnetocaloric effect is discussed as well as application of the magnetocaloric effect in magnetic cooling devices. A brief review of models to simulate the giant magnetocaloric effect are presented along with a semi-ab initio microscopical approach from simulations of the Ising model with magnetovolume interactions. We compare the magnetocaloric effect that arises from first order magnetic phase transitions with the one from second order magnetic phase transitions.

All the code used for this report can be found at the following GitHub repository: <https://github.com/jgci2000/MCE-ising>. The code for the Ising simulations can be found at <https://github.com/jgci2000/monte-carlo-ising>.

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Understanding magnetism and magnetic materials has always been an important field of study in condensed matter physics, due to their strange and exotic behaviours. One of those effects is the magnetocaloric effect (MCE). The MCE was discovered by Weiss and Piccard in 1917 [1] by observing a sizable and reversible temperature change in nickel near its Curie temperature. This phenomena has lead to the interest in the research of room temperature magnetic refrigeration with the first example being from Brown in 1976 [2]. Later in 1997, Pecharsky et al. [3] discovered the giant magnetocaloric effect (GMCE), in which a larger MCE can be measured leading to a better refrigeration cycle. This alternative to vapour-liquid refrigeration has proven to be more ecological and cost effective. The problem at hand is finding materials which exhibit a large quantity of MCE at room temperature.

The typical way for discovering new materials is creating a sample in the laboratory and running tests on the given sample. This process is time-consuming and expensive. Numerical simulation of such materials is a cost effective and relatively faster approach for finding new materials and structures, in general (as well as with a large MCE component). There are many approaches ranging from mean-field theory like to microscopic ones. One interesting case is that of ab-initio Density Functional Theory (DFT) calculations. From them we can design new materials that reproduce this kind of behaviour from simple magnetic models like the Ising model [4]. From this we can obtain better quantitative estimations of the MCE for real magnetic materials. This is the preferred approach on this work.

MAGNETOCALORIC EFFECT

The MCE was discovered by Weiss and Piccard in 1917 [1].¹ It manifests itself as the adiabatic change of the tem-

perature of a magnetic material under the action of an external magnetic field. More widely, it can be described also by the variation of the entropy of its magnetic subsystem under the effect of the magnetic field.

Consider a system of spin particles which has a phase transition from ferromagnetic to paramagnetic, or vice-versa, at some critical temperature. The total entropy of the system can be considered as the sum of the magnetic ordering entropy and the thermal entropy. Due to the thermal entropy, the magnetic moments of the spin particles will be naturally out of order, thus having a higher magnetic ordering entropy. With the application of a magnetic field, these magnetic moments will tend to align with the field thus lowering its magnetic ordering entropy. If this magnetic field is applied under adiabatic conditions (i.e. constant entropy), the thermal entropy should increase in order to preserve the total entropy of the system constant. Increasing the thermal entropy implies an increase in the temperature of the system. The opposite process, removal of an applied magnetic field, will cause cooling, under adiabatic conditions. This described change of temperature is the MCE.

The total entropy of a magnetic system is comprised of the magnetic entropy S_M , the lattice entropy S_l , from the phonon vibrations, and the electronic entropy S_e from conduction. Then we can write,

$$S(H, T) = S_M(H, T) + S_l(H, T) + S_e(H, T).$$

Note that it is only possible to separate the lattice entropy and electron entropy if we ignore phonon-electron interactions, for which some rare earth metal its possible [7]. Up to a first order approximation, we can neglect the field dependence of the lattice entropy and electronic entropy. Then the total differential of the entropy is

$$\begin{aligned} dS(H, T) &= dS_M(H, T) + dS_l(T) + dS_e(T) \\ &= \frac{C_M}{T}dT + \left(\frac{\partial S_M}{\partial H}\right)_T dH + \frac{C_l}{T}dT + \frac{C_e}{T}dT, \end{aligned}$$

where $C = \frac{\delta Q}{T} = T \left(\frac{\partial S}{\partial T}\right)_H$ is the heat capacity at constant field H for the different subsystems. Then, at constant temperature, the MCE is given by the quantity $\left(\frac{\partial S_M}{\partial H}\right)_T$. Using

¹ In many sources it says that the MCE was first discovered by Warbug in 1881 [5]. This however is untrue as shown by [6]. This article is a very compelling and recommended read for those interested in the history of physics and magnetism.

the Maxwell-Relation $\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$, the MCE can be written as

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

which corresponds to a change in magnetic entropy

$$\Delta S_M(H, T) = \int_{H_0}^{H_1} \left(\frac{\partial M}{\partial T}\right)_H dH, \quad (1)$$

by changing the magnetic field $\Delta H = H_1 - H_0$. The minus sign is to ensure that the quantity is positive for the application of a magnetic field, i.e. $H_1 > H_0$. The adiabatic change in temperature is also given as

$$\Delta T(H, T) = - \int_{H_0}^{H_1} \frac{T}{C_M} \left(\frac{\partial M}{\partial T}\right)_H dH.$$

On another note, the change in magnetic entropy can also be measured by considering heat capacity data, as

$$\Delta S_M = \int_0^T \frac{C_M(H_1, T) - C_M(H_0, T)}{T} dT.$$

These two ways of computing the difference in magnetic entropy should coincide, but both may have different numerical imprecisions when doing the actual computation on a computer [8].

Since the MCE equations depend on $\partial M / \partial T$, at constant H , choosing a material where this quantity is maximized is important. The magnitude of this quantity defines the temperature range that can be obtained by the material. Thus, this effect can be seen especially in magnetic materials that undergo a phase transition from a ferromagnetic state to a paramagnetic state or vice-versa. As this quantity is maximal near the phase transition in a ferromagnetic material, it is important to choose a material which has the Curie temperature near room temperature. Gadolinium (Gd) based alloys are a prime example of materials that behave like that. It undergoes a second order phase transition from a ferromagnetic to a paramagnetic state at a Curie temperature around 300K. And from this data the MCE might be computed, Figure 1. The adiabatic temperature rise from pure Gd is of about 12K when the applied field changes from 0T to 5T.

Giant Magnetocaloric Effect

In the seminal work by Pecharsky et al. [3] the magnetocaloric properties of $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$, for $1 \leq x < 0.5$ are explored. They have shown that, for the case when $x = 2$, there is not only a second order phase transition from paramagnetic to ferromagnetic, but also a first order phase transition between two ferromagnetic states with different structures. The transition paramagnetic to ferromagnetic (I) occurs at $T_C(I) = 299\text{K}$ and the transition ferromagnetic (I) to ferromagnetic (II) at $T_C(II) = 276\text{K}$. This first order transition leads to an increase of about 2 times in the MCE, Figure 1, when compared to the MCE from pure Gd. This increase in the MCE from a first order magnetic-structural phase transition is called the giant magnetocaloric effect.

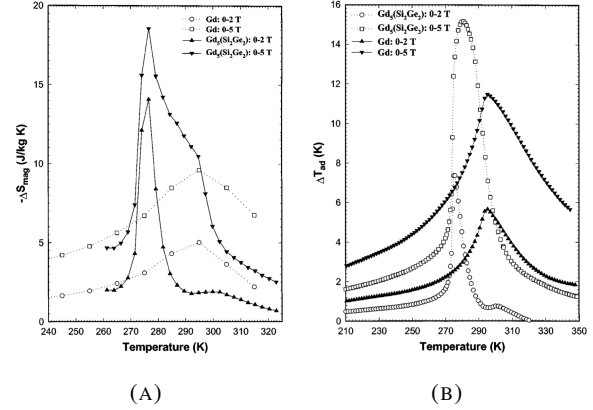


FIGURE 1: (A) Magnetic entropy change and (B) the adiabatic change in temperature of $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ and pure Gb between 240 and 325K for a magnetic field change 0 to 2 and 0 to 5T. Taken from [3].

Another thing to note is the breadth of the peaks for both the magnetic entropy change and the adiabatic temperature change. The pure Gd has a much larger spread of temperatures for which we can observe the MCE. This is due to the fact that in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$, there exists a first order phase transition so the total entropy as a function of temperature is discontinuous, thus allowing for a sudden change in the magnetic entropy. Also the higher value of MCE is observed since the change of the magnetization, for a first order transition, with the temperature is discontinuous and by Equation (1), this should result in a larger MCE.

The discovery of the GMCE has revolutionized the field of the MCE [9]. From this discovery onwards, the number of scientific publications with the word "magnetocaloric" in the title, abstract and keywords, has increased exponentially.

In 2006, Campos et al. [10] reported the discovery of a colossal MCE (CMCE) for MnAs when the manganese is replaced by iron, $\text{Mn}_{1-x}\text{Fe}_x\text{As}$. The reported increase in MCE is of "2.6 times the magnetic limit of MnAs". These findings were, however, shown to be not true. This is due to a mistake when using the Maxwell-Relation when computing ΔS_M . Amaral et al. [11] shows that the usage of such relations in coexistence magnetization phases (originated by first order transitions) results in a large peak in the magnetic entropy change. This defies the theory of thermodynamics, but is in accordance with some experimental results, such as the one reported by Campos et al.. Thus one can assume that the results are wrong. Also Balli et al. [12] repeated the experiments by Campos et al. and by the correct usage of the Maxwell-Relation. They report no CMCE for $\text{Mn}_{1-x}\text{Fe}_x\text{As}$ but find that it fits in to the GMCE category.

Magnetic Refrigeration

Before the discovery of the GMCE in 1997, there had not been many developments in the field of magnetic refrigeration. The most noteworthy work was by Brown in

1976 [2], as he proposed a magnetic heat pump working at almost room temperature. He used Gd plates (with a critical temperature of 294K) and drove the demagnetization/magnetization cycle with a 7T magnetic field, achieving an adiabatic temperature change of about 16K. This was revolutionary at the time. Such a device, however, was unfeasible as a general purpose cooling device, due to the strength of the magnetic field and that you would need a superconducting magnet to generate it. Thus such device is not commercially viable. Since then, many room temperature refrigerators have been designed using Gd-based alloys and mostly using a paramagnet as a source of magnetic field, as shown in Table 2 in [9].

Choosing a material where $\partial M/\partial T$ is high and has a Curie temperature near room temperature is critical when considering a material for a magnetic refrigerator. Another important aspect is the magnetic cooling capacity (q), which is the definition Gschneidner et al. [13] is

$$q = \int_{\text{FWHM}} \Delta S_M dT,$$

where FWHM integrating over the region between the full width at half maximum of the entropy. So choosing a material with a higher and narrower peak in magnetic entropy change will result in a larger cooling capacity.

The general efficiency of a magnetic cooling device is much larger than a gas compression cycle based device, so there is a need for the research and development for these novel materials with large MCE components. Furthermore, a magnetic cooling device does not use any gases, thus lowering its environmental impact in terms of global warming when compared to normal vapor refrigeration.

SIMULATING THE MCE

Throughout the years, there have been many different approaches on simulating the GMCE [14]. From mean-field theory models, to more in depth microscopic models. Choosing the model to use comes down to a balance between complexity and the accuracy of the results as well as computational cost. A more microscopic model, even quantum mechanical, will, in principle, have a more precise description of the system. This comes with an increase of computational cost. On the other hand, less complex model might only be able to describe the system on a qualitative level.

A simplistic approach to this is considering the Landau theory of phase transitions [15]. This gives a model for the Gibbs free energy $G(T, M)$ as a series expansion in even powers of M . A Zeeman-like term might be added to the expansion to represent the interaction with an external magnetic field. From this we can derive the quantities for the MCE. We can also fit this model to real materials through the so-called Arrott plots [16]. A more mean-field like approach is the Bean-Rodbell model [17]. This model is an extension of the Weiss molecular field and is good for simulating materials with a strong magneto-volume coupling. We impose a linear relationship between T_C and the

volume v ,

$$T_C = T_0 \left(1 + \beta \frac{v - v_0}{v_0} \right),$$

where β is just a constant and v_0 the equilibrium volume. For a large linear dependence of T_C on the volume, i.e. large β , the magnetic transition becomes first order. Then it is possible to simulate the GMCE. A more in-depth description and analysis of these models might be found at [14].

A more interesting approach to this problem is to consider an ab-initio approach [4]. For this we can start with a DFT calculation of the Heisenberg exchange parameter J for a given material and use the Ising or Heisenberg model to derive its properties under a magneto-volume induced first order phase transition. For this, let us consider the following Hamiltonian (proposed by [4]),

$$\mathcal{H} = - \sum_{\langle i,j \rangle} J(v) S_i S_j + \frac{1}{2} K v^2 - M H,$$

where the sum is conducted over neighboring sites i and j , v is the volume, K the comparability constant and $J(v)$ the magnetic exchange parameter with a dependence on the volume. Simulating a real magnetic system with this model is easily doable by existing DFT packages [14].

In order to estimate the full $M(H, T)$ and $\Delta S_M(H, T)$ quantities there might be some challenges if we use the standard Metropolis approach [18]. Here we have to perform a full and independent simulation for each pair of (H, T) . This becomes very time consuming, especially for the case where we introduce the volume dependence, since, instead of thermalizing just M , we have to thermalize v as well. On top of this, there are known tunneling effects between phases, which were reduced by the Swendsen-Wang [19] and Wolff [20] algorithms. In the last couple of decades, a new class of methods to simulate spin systems has emerged. Methods like the Wang-Landau sampling [21] and Flat Scan Sampling [22] estimate the joint density of states (JDOS) $g(E, M)$ of the system. The JDOS is a variable which counts the number of microstates available to the system with a particular pair (E, M) . With this, we can compute the partition function

$$Z(H, T, M, v) = \sum_E g(E, M) e^{-\beta \mathcal{H}(E, M, H, v)},$$

where $\beta = 1/(k_B T)$. With the partition function we can compute some thermodynamical potential ϕ as

$$\phi(H, T, M, v) = -k_B T \ln(Z(H, T, M, v)).$$

By the minimization principle we can compute the "true"² free energy of the system

$$G(H, T) = \min_{v, M} \phi(H, T, M, v).$$

² By "true" we mean the free energy in which the system will be at equilibrium, since it has to be minimized with respect with v and M .

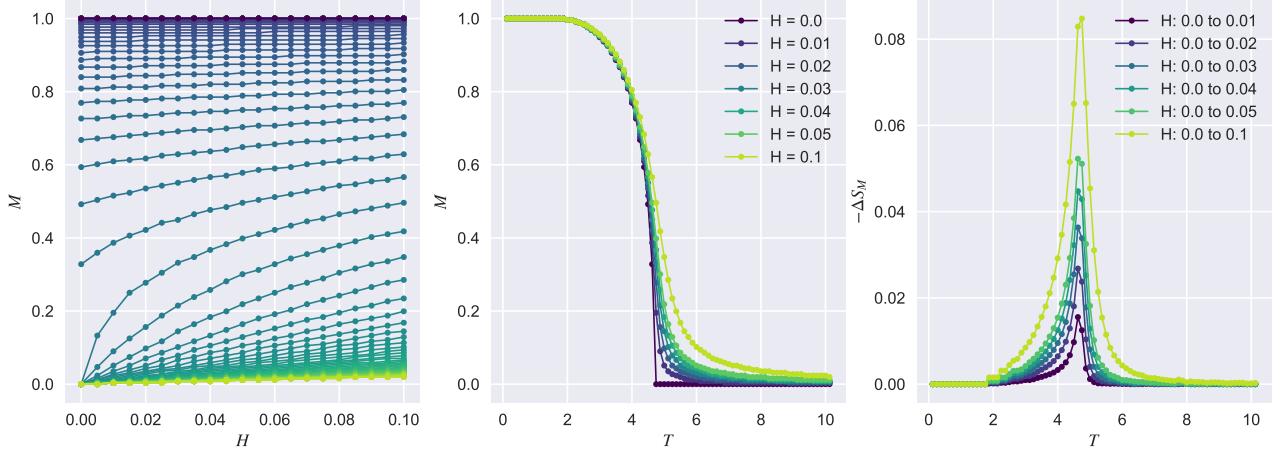


FIGURE 2: (A) Isothermal magnetization as a function of the applied magnetic field of a second order transition system ($J' = 0$) from an Ising spin 1/2 3D cubic lattice with 512 particles. (B) Isofield behaviour of the magnetization versus the temperature for different applied field values. (C) Magnetic entropy change as a function of temperature for different changes in the magnetic field.

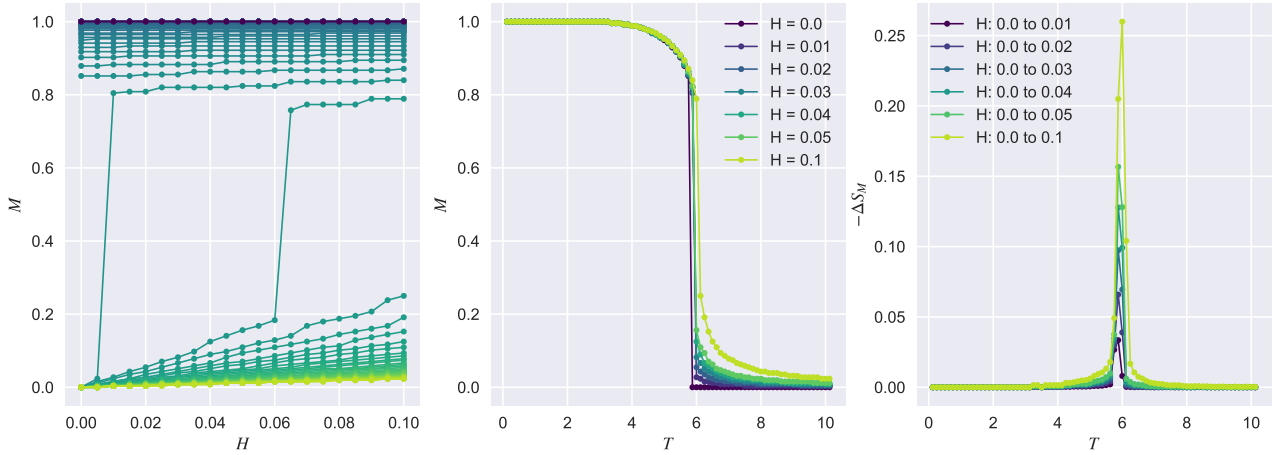


FIGURE 3: (A) Isothermal magnetization as a function of the applied magnetic field of a first order transition system ($J' = 3.5$) from an Ising spin 1/2 3D cubic lattice with 512 particles. (B) Isofield behaviour of the magnetization versus the temperature for different applied field values. (C) Magnetic entropy change as a function of temperature for different changes in the magnetic field.

With this we can compute all of the thermodynamic information by using the property that $dG = -SdT - MdH$ is an exact differential [15].

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

$$C = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_H \quad \chi = -\left(\frac{\partial^2 G}{\partial H^2}\right)_T$$

Moreover, from the minimization, we can pick out the values of magnetization and volume which minimize the free energy. These values have a different finite size scaling than the values encountered by the derivatives. For the infinite system, i.e. $N \rightarrow \infty$, they should behave the same. For finite systems, the values attained from the minimization process will have a qualitative and quantitative behaviour, Chapter 5 of [23].

Let us now consider a compressible system with a linear dependence on the volume, thus

$$J(v) = J_0 + J' \left(\frac{v - v_0}{v_0} \right),$$

where J_0 is the exchange parameter for when $v = v_0$ and J' is a positive constant. In the paramagnetic state, the system will prefer to be near its minimal volume, thus $v \approx v_0$. In the ferromagnetic state, however, it becomes more energetically favourable for the system to occupy more volume $v > v_0$, as the magnetic contribution to the energy is larger, thus a larger value of J is favourable.

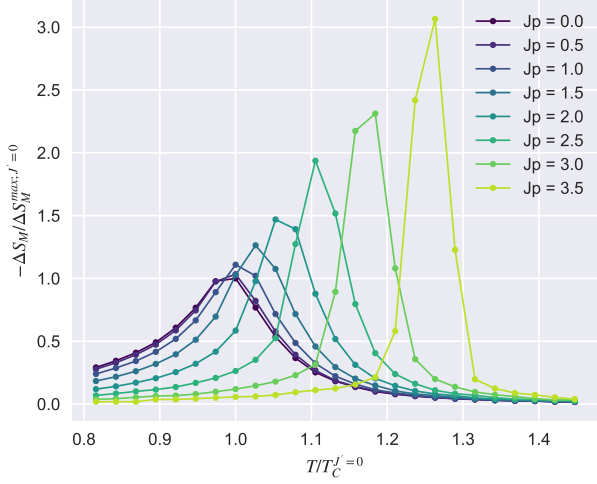


FIGURE 4: Magnetic entropy change as a function of temperature for an Ising system on a 3D cubic lattice with 512 spin 1/2 particles, for different values of the volume exchange constant J' . The change in magnetic field considered is from $H = 0$ to $H = 0.1$.

SIMULATION RESULTS

All the quantities used in this section will be in dimensionless units. Units could be added, but we want to evaluate the qualitative results of the magnetovolumic model.

In order to have good simulations of the GMCE, first we need a precise simulation of the JDOS, since this will dictate a large part of the physics around the model. For this, we FSS method was preferred as it is more accurate and efficient than the WL method [22]. A large enough 3D system is also in order, thus the chosen system as a 3D Ising cubic lattice with 512 spin 1/2 and spin 1 particles, as we want to evaluate the dependence of the MCE on total spin.

The results for the MCE for a rigid system ($J' = 0$) and a compressible system with magnetovolumic interaction ($J' = 3.5$) can be seen on Figures 2 and 3, respectively. By looking at the isothermal and isofield magnetization plots, it is easy to verify that the rigid system undergoes a second order phase transition, as the magnetization is continuous. For the compressible system, the magnetization is discontinuous thus we observe a first order phase transition. To note that in the compressible system we see no trace of magnetic hysteresis since we can only simulate equilibrium states. On a mean-field approach we would be able to see such effects [14].

The magnetic entropy change ΔS_M on the rigid system has a wider but lower peak while the opposite is observed in the compressible system. This coincides with the experimental results gathered in Figure 1a.

In Figures 4 and 5 we can see the dependence of the magnetic entropy change on the volumic exchange parameter J' for the spin 1/2 and spin 1 cases, respectively. For both cases we see that the relative height of the maximal change in magnetic entropy increases as the exchange parameter increases. This is expected since the magnetovo-

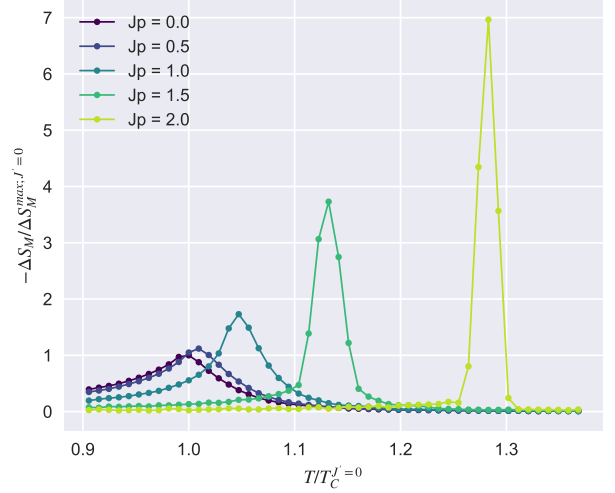


FIGURE 5: Magnetic entropy change as a function of temperature for an Ising system on a 3D cubic lattice with 512 spin 1 particles, for different values of the volume exchange constant J' . The change in magnetic field considered is from $H = 0$ to $H = 0.1$.

lomic coupling becomes stronger as we increase J' . Thus the first order transition is more pronounced as well, i.e. the discontinuity in the magnetization is more sudden.

By increasing the total spin of the particles from 1/2 to 1, we can see that the magnitude of the observed MCE is much greater. For the same value of J' , the MCE in the spin 1 case is approximately two-fold the MCE in the spin 1/2 case. This is due to the fact that the saturation magnetization for the spin 1 system is larger than for the spin 1/2, then the MCE (which is measured by $\partial M/\partial T$) has a larger magnitude. The total angular momentum of the lattice atoms might be another aspect to consider when searching for new magnetocaloric materials.

CONCLUSION

Here we have successfully reproduced the GMCE behaviour with a computational model. For further investigation, it is possible to compute the Heisenberg exchange parameter through DFT calculations for some material structure and compare the simulation results with real experimental data to access the accuracy of the magnetovolumic model.

In terms of computational costs, the JDOS simulations took the longest to compute. The computational time for JDOS simulations depends strongly on system size, lattice type and the spin number. Without magnetovolumic coupling, the simulation takes only a few minutes to run and with magnetovolumic coupling, it can take a little more than one hour on a personal computer.

Here we have shown that with this simple approach, considering a spin system with a lattice potential and volume-dependent exchange coupling, we can simulate the qualitative behaviour of the MCE and GMCE. The differences between the two phenomena are shown correctly, by

the increase of the change in magnetic entropy from a second order to a first order phase transition. Furthermore, by

computing the exchange parameters with DFT, we could have compared quantitative part of the model with experimental results.

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- [1] Weiss, Pierre, Le phénomène magnéto-calorique, J. Phys. Radium **2**, 161 (1921).
 - [2] G. V. Brown, Magnetic heat pumping near room temperature, Journal of Applied Physics **47**, 3673 (1976), <https://doi.org/10.1063/1.323176>.
 - [3] V. K. Pecharsky and K. A. Gschneidner, Jr., Giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$, Phys. Rev. Lett. **78**, 4494 (1997).
 - [4] J. Amaral, N. Fortunato, C. Amorim, and J. Gonçalves, Giant magnetocaloric effect of compressible Ising and Heisenberg lattices, (2016).
 - [5] E. Warburg, Magnetische untersuchungen, Annalen der Physik **249**, 141 (1881).
 - [6] A. Smith, Who discovered the magnetocaloric effect?, The European Physical Journal H **38**, 507 (2013).
 - [7] A. Tishin and Y. Spichkin, *The Magnetocaloric Effect and its Applications*, Condensed Matter Physics (CRC Press, 2016).
 - [8] V. K. Pecharsky and K. A. Gschneidner, Magnetocaloric effect from indirect measurements: Magnetization and heat capacity, Journal of Applied Physics **86**, 565 (1999), <https://doi.org/10.1063/1.370767>.
 - [9] K. Gschneidner and V. Pecharsky, Thirty years of near room temperature magnetic cooling: Where we are today and future prospects, International Journal of Refrigeration **31**, 945 (2008).
 - [10] A. de Campos, D. L. Rocco, A. M. G. Carvalho, L. Caron, A. A. Coelho, S. Gama, L. M. da Silva, F. C. G. Gandra, A. O. dos Santos, L. P. Cardoso, P. J. von Ranke, and N. A. de Oliveira, Ambient pressure colossal magnetocaloric effect tuned by composition in $\text{Mn}_{1-x}\text{Fe}_x\text{As}$, Nature Materials **5**, 802 (2006).
 - [11] J. S. Amaral and V. S. Amaral, The effect of magnetic irreversibility on estimating the magnetocaloric effect from magnetization measurements, Applied Physics Letters **94**, 042506 (2009), <https://doi.org/10.1063/1.3075851>.
 - [12] M. Balli, D. Fruchart, D. Gignoux, and R. Zach, The “colossal” magnetocaloric effect in $\text{Mn}_{1-x}\text{Fe}_x\text{As}$: What are we really measuring?, Applied Physics Letters **95**, 072509 (2009), <https://doi.org/10.1063/1.3194144>.
 - [13] K. Gschneidner Jr., V. Pecharsky, A. Pecharsky, and C. Zimm, Recent developments in magnetic refrigeration, in *Rare Earths '98*, Materials Science Forum, Vol. 315 (Trans Tech Publications Ltd, 1999) pp. 69–76.
 - [14] J. S. Amaral and V. S. Amaral, Simulating the giant magnetocaloric effect - from mean-field theory to microscopic models (2022), submitted for publication.
 - [15] R. H. Swendsen, *An Introduction to Statistical Mechanics and Thermodynamics*, Oxford Graduate Texts (Oxford University Press, Oxford, 2019).
 - [16] J. Amaral, N. Silva, and V. Amaral, Estimating spontaneous magnetization from a mean field analysis of the magnetic entropy change, Journal of Magnetism and Magnetic Materials **322**, 1569 (2010), proceedings of the Joint European Magnetic Symposia.
 - [17] C. P. Bean and D. S. Rodbell, Magnetic disorder as a first-order phase transformation, Phys. Rev. **126**, 104 (1962).
 - [18] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, Equation of state calculations by fast computing machines, J. Chem. Phys. **21**, 1087 (1953).
 - [19] R. H. Swendsen and J.-S. Wang, Nonuniversal critical dynamics in monte carlo simulations, Phys. Rev. Lett. **58**, 86 (1987).
 - [20] U. Wolff, Collective monte carlo updating for spin systems, Phys. Rev. Lett. **62**, 361 (1989).
 - [21] F. Wang and D. P. Landau, Efficient, multiple-range random walk algorithm to calculate the density of states, Phys. Rev. Lett. **86**, 2050 (2001).
 - [22] J. C. Inácio, A. L. Ferreira, and J. S. Amaral, Accurate estimate of the joint density of states via flat scan sampling 10.48550/ARXIV.2203.02718 (2022).
 - [23] J. C. Inácio, *Exploring the Ising model via Flat Scan Sampling*, bachelor thesis, found at this link, Universidade de Aveiro (2021).