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Simulating the giant magnetocaloric effect-from mean-field theory to microscopic models

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Magnetocaloric materials are recognized as one of the major classes of magnetic materials for energy applications, and can be either employed as refrigerants in heat-pumping devices, or in thermomagnetic generators for energy conversion/harvesting. For both applications, having a material that presents a first-order magnetic phase transition is advantageous, as this typically leads to enhanced values of magnetization change in temperature (relevant to energy conversion) and of the magnetocaloric effect (relevant to heat-pumping). We present a brief overview of selected models applied to the simulation of applied magnetic field and temperature-dependent magnetization and magnetic entropy change of first-order magnetic phase transition systems, covering mean-field models such as the Landau theory of phase transitions and the Bean-Rodbell model, up to more recent developments using a Ising-like microscopic model with magnetovolume coupling effects. We highlight the fundamental and practical limitations of employing these models and compare predicted thermodynamic properties.

KEYWORDS

magnetic materials, magnetic refrigeration, energy harvesting, first-order phase transitions, magnetovolume coupling

1 Introduction

Magnetic materials have had, for several decades, wide-spread use in energy applications, including power generation, conditioning, conversion and transportation (Gutfleisch et al., 2011). Since the discovery of the giant magnetocaloric effect (GMCE) in the late 1990s (Pecharsky and Gschneidner, 1997), the use of magnetic materials for room-temperature refrigeration has been gathering the attention from both the scientific and industrial communities (Pecharsky and Gschneidner, 2008). The GMCE is typically observed only for first-order magnetic phase transition (FOMPT) materials, where a strong magnetovolume coupling is present. As the designation implies, the GMCE is considerably larger than the MCE of second-order magnetic phase transition (SOMPT) systems. While technologically challenging, the development and use of FOMPT materials for use in refrigeration devices is now commonplace, as seen from the number of current prototypes using these materials as refrigerants (Kitanovski et al., 2015). More recently, the use of magnetocaloric materials for energy generation from near room temperature thermal energy harvesting has also gathered attention (Waske et al., 2019). In this case, the sharp dependence of magnetization (M) on temperature (T) near the Curie temperature T_C of a FOMPT material enhances the energy-harvesting potential of a device, in a tunable operating temperature window. In short, for both refrigeration and thermal energy harvesting, the use of a first-order magnetic phase transition (FOMPT) material presents considerable advantages. The search for new and optimized

magnetocaloric materials for these applications is an on-going effort from the community. In this context, the use of magnetism models to both interpret experimental data and predict the magnetic and magnetocaloric performance of materials are valuable tools. Naturally, correctly describing the thermodynamics of a FOMPT is required to ensure the physical soundness of calculations. Nevertheless, when choosing a model to use, practical questions come into play, and in the end, the choice of a particular model becomes the result of the balance between the complexity of the model, the information being sought, and the computational cost.

In this work, we consider three distinct models which have been employed to describe quantitatively describe FOMPT materials, from mean-field models such as the Landau theory of phase transitions, the Bean-Rodbell model, and a microscopic Ising-like model with magnetovolume interactions. We employ these models to simulate both SOMPT and FOMPT systems with similar thermodynamic properties, such as a $T_C \sim 300$ K for the SOMPT, same spin values and saturation magnetization, and a similar value of critical field for the FOMPT system. Both magnetic field (H) and T dependent M and magnetic entropy change (ΔS_M) are simulated for the three considered models. The aim is to compare the obtained results both qualitatively and quantitatively, highlighting the fundamental and practical limitations of employing these models to describe real materials.

2 The Landau theory of phase transitions

The Landau theory of phase transitions has been previously employed to describe the GMCE of FOMPT systems, from describing the magnetoelastic coupling influence on the magnetocaloric effect in ferromagnetic materials (Amaral and Amaral, 2004), and the effect of magnetic irreversibility on estimating the magnetocaloric effect from magnetization measurements (Amaral and Amaral, 2009). The model starts from an expansion of the (Gibbs) Free Energy G on even powers of M, together with an Zeeman-like external field interaction term.

$$G(T,M) = G_0 + \frac{1}{2}A(T)M^2 + \frac{1}{4}B(T)M^4 + \frac{1}{6}C(T)M^6 - M.H, \quad (1)$$

where A, B, and C are the temperature-dependent Landau coefficients. Typically A is assumed to be linear in temperature, establishing the Curie temperature T_C of the system: $A(T) = A'(T - T_C)$. This linear relation is valid in the susceptibility regime, obeying the Curie law:

$$\frac{H}{M} = \frac{C_{Curie}}{T - T_C}, \quad (2)$$

where C_{Curie} is the Curie constant of the system. For low M values, the A' parameter is then equal to the inverse Curie constant. Minimizing the free energy expression of Eq 1, an equation of state is derived:

$$\frac{H}{M} = A(T) + B(T)M^2 + C(T)M^4, \quad (3)$$

with a structure that allows fitting the well-known isothermal Arrott plot (H/M *versus* M^2) construction to determine the Landau coefficients' dependence on temperature from magnetization data. This approach was employed for both FOMPT (Amaral and Amaral, 2004) and SOMPT (Amaral et al., 2005) systems.

Here, we consider a trial system with $A' = 1.5 \times 10^2$, and constant B and C coefficients, $\pm 5 \times 10^{-1}$ and 1×10^{-4} respectively in cgs units, with $T_C = 300$ K. The A' value was chosen to correspond to the inverse Curie constant of a molecular mean-field system with spin $S = 1/2$, and a saturation magnetization of 100 emu/g. The chosen B value leads, when negative, to a critical field of ~ 25 kOe which is within values achievable in commercially available magnetometers with superconducting coils as applied field source.

The $M(H,T)$ and $\Delta S_M(H,T)$ data of **Figure 1**, using a positive B coefficient, show how a system with thermomagnetic behavior comparable to real SOMPT systems is obtained, with M around 40 emu/g at 50 kOe near T_C, and a maximum value of ΔS_M around 12 J/(K.kg) for a field change from 0 to 50 kOe.

When considering a negative B coefficient value, the system now shows a FOMPT, where discontinuities are present in both the magnetization and magnetic entropy change dependence in T and H, as shown in **Figure 2**.

As expected, the maximum ΔS_M increases considerably, up to values ~ 40 J/(K.kg). The FOMPT nature is clearly visible in the discontinuities in both $M(H,T)$ and $\Delta S_M(H,T)$ data. One of the main limitations of the Landau theory of phase transitions, in this context, is visible when the system reaches higher values of M. Due to the equation of state originating from a power expansion in M, the validity of this expansion fails for high M values, and the magnetization does not saturate even at very low T. This is an important fact that is often overlooked when fitting or extrapolating Arrott plots of experimental data in the high-magnetization regime. There is also no deep physical insight from the values of the B and C Landau parameters. One can observe a negative B value and justify its occurrence with effects such as magnetovolume coupling and electron condensation, depending on the particular physics of the system under study, but a quantitative analysis is typically not the objective of employing this model. As we will see in the next section, the use of the Bean-Rodbell model, overcomes some of these limitations.

3 The Bean-Rodbell model

The Bean-Rodbell model is an extention to the Weiss molecular field model, and was first reported in a study on the magnetic properties of MnAs, a system well-known to have strong magneto-volume coupling (Bean and Rodbell, 1962). The model imposes a linear relation between T_C and volume, as shown in Eq. 4.

$$T_C = T_0\left(1 + \beta\left(\frac{v - v_0}{v_0}\right)\right), \quad (4)$$

where β is positive and constant, v is volume, v_0 the equilibrium volume with no magnetic interactions, and T_0 the Curie temperature of the rigid system with $v = v_0$.

For a sufficiently large linear dependence of T_C on volume (large β value), the magnetic transition becomes first-order. The crossover point is established *via* the η parameter, which is defined for a system with compressibility K:

$$\eta = 40Nk_BKT_0\beta^2\frac{(S(S+1))^2}{(2S+1)^4 - 1}, \quad (5)$$

where S is the spin quantum number, N the spin density and k_B the Boltzmann constant. The transition is second-order for $0 < \eta \leq 1$, while for $\eta > 1$ the transition is first-order.

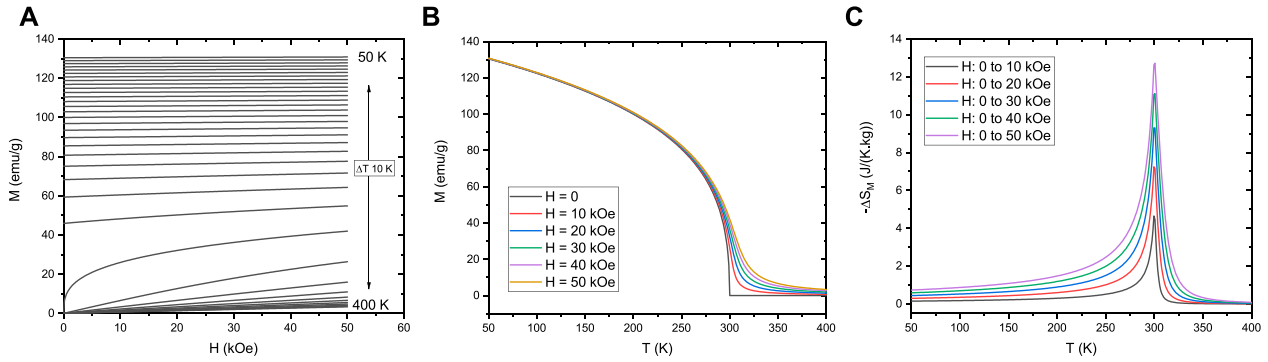

FIGURE 1
(A) Isothermal magnetization *M versus* applied magnetic field *H*, of a SOMPT system simulated by the Landau theory of phase transitions. Simulation parameters where chosen to correspond to a magnetic material with spin 1/2 and a saturation magnetization value of 100 emu/g. **(B)** Isofield *M versus* temperature *T* behavior, for *H* between 0 and 50 kOe. **(C)** Magnetic entropy change ΔS_M dependence on *H* change and *T*.

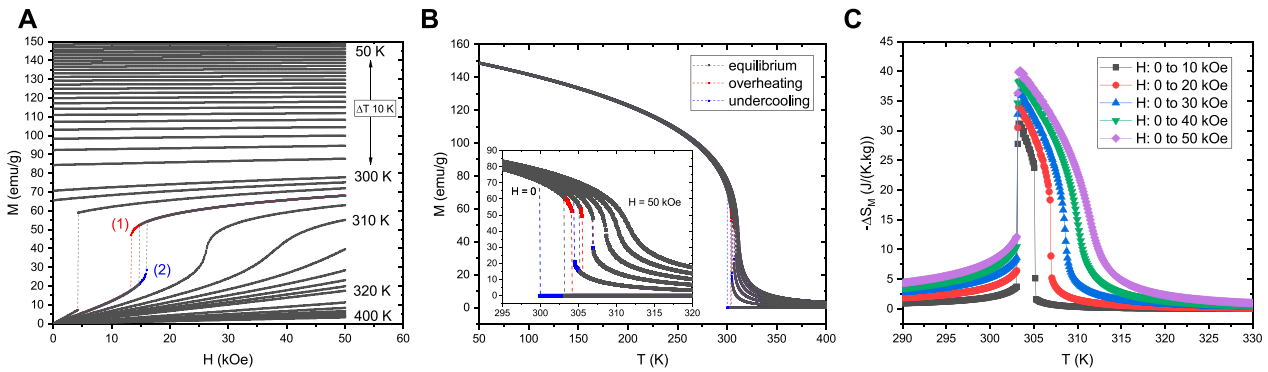

FIGURE 2
(A) Isothermal magnetization *M versus* applied magnetic field *H*, of a FOMPT system simulated by the Landau theory of phase transitions. Simulation parameters where chosen to correspond to a magnetic material with spin 1/2 and a saturation magnetization value of 100 emu/g, with a critical field value ~ 25 kOe. **(B)** Isofield *M versus* temperature *T* behavior, for *H* between 0 and 50 kOe. **(C)** Magnetic entropy change ΔS_M dependence on *H* change and *T*.

For a comparable system with the previous simulations using the Landau theory of phase transitions, we consider the following parameters for our Bean-Rodbell model calculations: $S = 1/2$, $T_0 = 300$ K, and a N value of 1.077×10^{22} spins/g, which corresponds to a saturation magnetization of 100 emu/g. For simulating a SOMPT, a null η value is used, with data for magnetization and magnetic entropy change shown in **Figure 3**.

For simulating a FOMPT, an η value of 1.35 is used, which increases the T_C to around 304 K, and leads to a critical field around 2.5 kOe, together with an increase in magnetic entropy change, as shown in **Figure 4**.

The Bean-Rodbell model simulation results are quite similar to those obtained by the Landau theory of phase transitions, for both the SOMPT and FOMPT. This could only be achieved by establishing comparable systems with the same Curie constant, and adjusting the values of the Landau B and the Bean-Rodbell η parameters to lead to similar values of the critical field. Note, however, how for the Bean-Rodbell data, the $M(H,T)$ data clearly saturates. The use of the model in the high-M region was useful in the simulation of mixed-phase FOMPT materials, and the validity of the use of the Maxwell relation in estimating ΔS_M in strongly first-order systems (Amaral and Amaral, 2009; Amaral and Amaral, 2010). It is also worth highlighting that, as opposed to the Landau theory of phase transitions, the fact that physically meaningful parameters such as spin and compressibility are defined in the model, a quantitative analysis of experimental data using the Bean-Rodbell model is possible, for both FOMPT and SOMPT systems (Amaral et al., 2007). Simulations using this model are computationally inexpensive, and it is possible to consider smooth distributions of T_C values, with hundreds of points, to describe disordered SOMPT (Amaral et al., 2008; Bahl et al., 2012) and FOMPT (Amaral and Amaral, 2014; Nielsen et al., 2017) systems.

While widely employed in the study of both SOMPT and FOMPT materials, the Bean-Rodbell model is not the right model for predicting a given material's magnetic and magnetocaloric performance. For this, an *ab initio* approach is required, which can start from using Density Functional Theory (DFT) to estimate relevant magnetic and physical properties of a given system. DFT calculations are typically performed at 0 K, so it is required to feed this parameters to a given model for estimating thermodynamic properties. A relatively straightforward approach is to estimate the Heisenberg exchange parameter J of a given material using DFT, and then use the calculated value in an Ising or Heisenberg model.

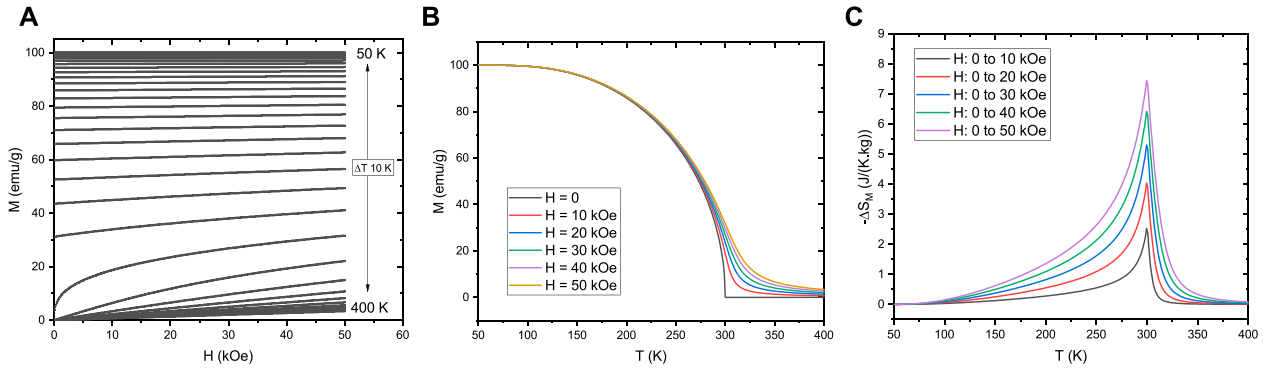

FIGURE 3
(A) Isothermal magnetization *M versus* applied magnetic field *H*, of a SOMPT system (η = 0) simulated by the Bean-Rodbell model, with spin 1/2 and a saturation magnetization value of 100 emu/g. **(B)** Isofield *M versus* temperature *T* behavior, for *H* between 0 and 50 kOe. **(C)** Magnetic entropy change ΔS_M dependence on *H* change and *T*.

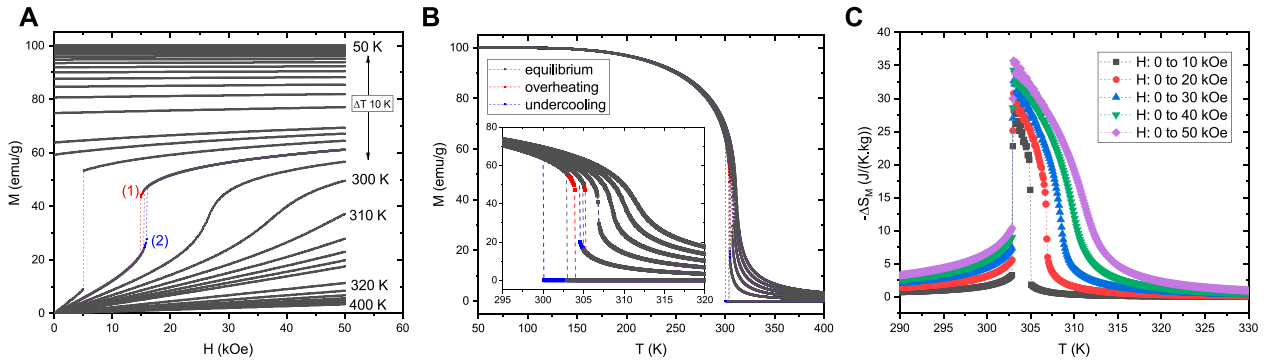

FIGURE 4
(A) Isothermal magnetization *M versus* applied magnetic field *H*, of a FOMPT system (η = 1.35) simulated by the Bean-Rodbell model, with spin 1/2 and a saturation magnetization value of 100 emu/g. **(B)** Isofield *M versus* temperature *T* behavior, for *H* between 0 and 50 kOe. **(C)** Magnetic entropy change ΔS_M dependence on *H* change and *T*.

Naturally, for describing a magneto-volume driven FOMPT, the model needs to include this coupling. In the next section, we will consider an Ising-like microscopic model with magnetovolume interactions.

4 Microscopic model with magnetovolume interactions

A FOMPT system can be described in simple microscopic models, such as the Ising and Heisenberg models, by including an explicit dependence of the magnetic exchange parameter *J*, together with a volume energy potential (Amaral et al., 2016):

$$\mathcal{H} = -\frac{1}{2}\sum_{i,j}\left[J(v)\,S_i \cdot S_j\right] + \frac{1}{2}Kv^2 - MH, \tag{6}$$

where *J* is the magnetic exchange parameter between S_i and S_j nearest-neighbour spins, *v* volume and *K* compressibility.

All the parameters required to simulate a given (real) magnetic system using this approach can be readily obtained by existing DFT packages. Estimating *J* for multi-component alloys is particularly relevant in the study of magnetocaloric materials, so the use of the Liechtenstein method (Liechtenstein et al., 1987) in systems where fractional site occupancy is accurately described by the Coherent Potential Application (Yonezawa and Morigaki, 1973) is a practical approach. These capabilities are available in the SPR-KKR (Ebert, 2005) and openmx (Ozaki et al., 2013) DFT packages. The estimate of the full $M(H,T)$ and $\Delta S_M(H,T)$ dependencies can be challenging using the standard Monte Carlo Metropolis method (Metropolis et al., 1953), as each (H,T) pair will require an independent calculation, and for the case of FOMPT the stabilization of the two order parameters, *M* and *v* is difficult and time-consuming. Another approach is to obtain the thermodynamic properties of the system with previously calculated Joint Density of States (JDOS) estimates. The JDOS of a given model (discrete or continuous) and of a given lattice (e. g. 2D, 3D) can be calculated by Monte Carlo methods such as the Wang-Landau method (Wang and Landau, 2001; Zhou et al., 2006), Random Path Sampling (Amaral et al., 2014) and the recently reported Flat Scan Sampling method (Inácio et al., 2022). As the JDOS is *T*, *H* and *v* independent, the full calculation of $M(H,T)$ and $\Delta S_M(H,T)$ dependencies for both SOMPT and FOMPT systems is robust and quickly achievable using a regular personal computer.

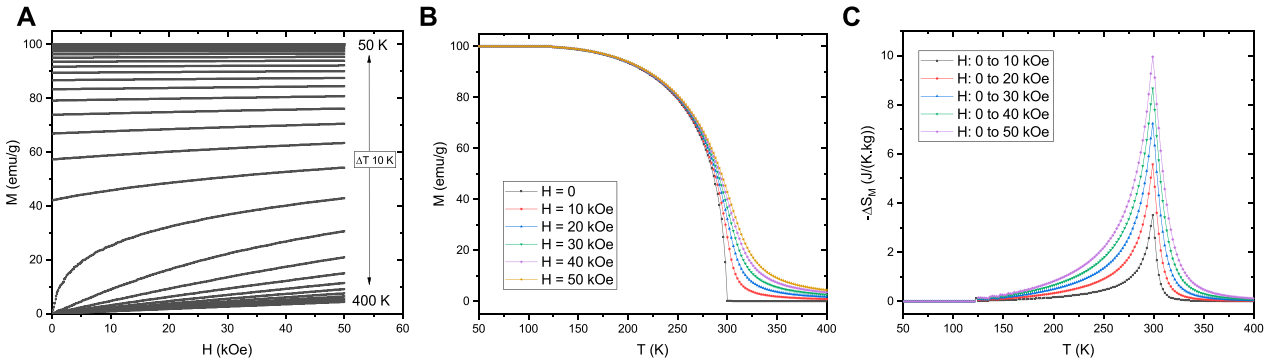

FIGURE 5
(A) Isothermal magnetization *M versus* applied magnetic field *H*, of a SOMPT system ($J^{'}$ = 0) from a Ising spin 1/2 3D lattice with 512 spins, considering a saturation magnetization of 100 emu/g and a magnetic moment value of 1 μ_B per spin. **(B)** Isofield *M versus* temperature *T* behavior, for *H* between 0 and 50 kOe. **(C)** Magnetic entropy change ΔS_M dependence on *H* change and *T*.

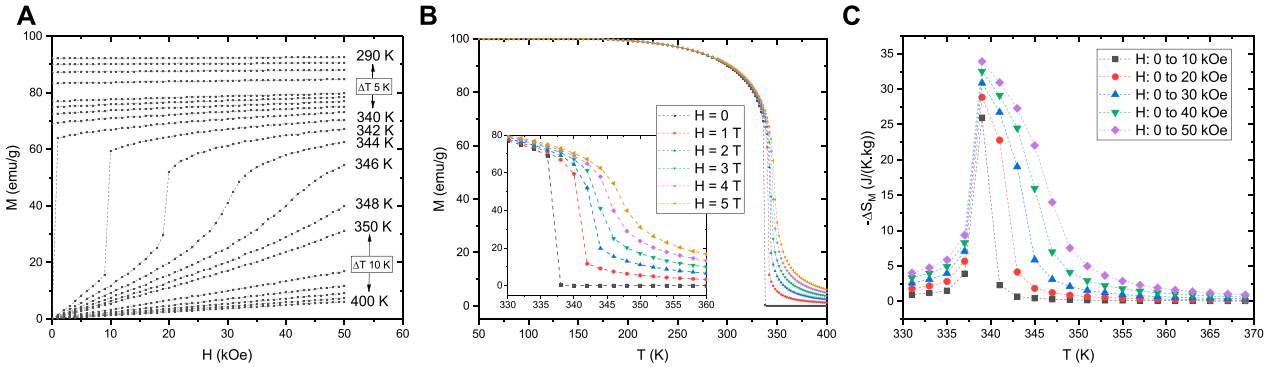

FIGURE 6
(A) Isothermal magnetization *M versus* applied magnetic field *H*, of a FOMPT system ($J^{'}$ = 2.8) from a compressible Ising spin 1/2 3D lattice with 512 spins, considering a saturation magnetization of 100 emu/g and a magnetic moment value of 1 μ_B per spin. **(B)** Isofield *M versus* temperature *T* behavior, for *H* between 0 and 50 kOe. **(C)** Magnetic entropy change ΔS_M dependence on *H* change and *T*.

For describing a comparable system to the previous mean-field simulations, we consider the Ising model of 512 spin 1/2 particles in a 3D lattice. In the case of the rigid system with a SOMPT, the J value is chosen to lead to a T_C of 300 K. The field interaction is calculated with a magnetic moment value of 1 μ_B per spin. Imposing a 100 emu/g saturation magnetization, a similar behavior compared to the previous mean-field models is obtained for magnetization and magnetic entropy change, as seen in Figure 5.

Considering now a compressible system, with a linear dependence of J on volume, $J(v) = J_0 + J'(v - v0)/v0$ and a K value of 50, a J' value of 2.8 (in units of J_0) leads to a FOMPT with a critical field of ~ 25 kOe, comparable to the previous simulations of the Landau Theory of phase transitions and the Bean-Rodbell model, as shown in Figure 6.

While qualitatively the behavior of the Ising model simulations for both SOMPT and FOMPT systems are similar to the results of the mean-field models, a quantitative comparison highlights some differences. While for the mean-field models the change of T_C between the SOMPT and FOMPT is relatively small at around 3 K (~ 1% of T_C), for the case of the microscopic model, this value is substantially higher at ~ 40 K (~ 13% of T_C). In terms of the observed maximum values of $-\Delta S_M$ for an applied field of 50 kOe, for both SOMPT and FOMPT systems the obtained results are similar for all the considered models. These increase from ~ 10 J/(K.kg) of the SOMPT systems, to values ~ 35 J/(K.kg) for the FOMPT systems. These results highlight how these fundamentally different models can lead to quantitatively similar behaviors for both the $M(H,T)$ and $\Delta S_M(T,H)$ dependencies, with results comparable to real SOMPT and FOMPT materials.

5 Overview

In this work, we have explored three distinct magnetic models that can simulate the relevant thermodynamic properties of both SOMPT and FOMPT systems for application in magnetic refrigeration and thermal energy harvesting. One of the main objectives was to consider equivalent SOMPT and FOMPT magnetic systems with T_C values around room temperature, and to compare the simulated results, particularly $M(H,T)$ and $\Delta S_M(H,T)$, which are the main thermodynamic properties for these applications.

Landau theory allows to easily interpret experimental magnetization data by fitting the isothermal Arrott plots. The observation of negative values of the B coefficient (negative slopes

in the Arrott plots) is a sign of a FOMPT. With a full description of the temperature dependence of the A, B and C coefficients, it is straightforward to smooth, interpolate and, away for saturation, to extrapolate the (H, T) dependence of magnetization and magnetic entropy change data. Still, while it is possible to qualitatively interpret the values of the model parameters, they do not have a straightforward or quantitative physical interpretation. Nevertheless, the obtained $M(H, T)$ and $\Delta S_M(H, T)$ data are physically and quantitatively sound.

The Bean-Rodbell model, as an extension of the Weiss molecular mean-field model, while also a phenomenological model, has physical meaning to all its parameters. This allows to interpret experimental data of both SOMPT and FOMPT systems and estimate fundamental system properties such as spin value and quantify magnetovolume coupling. The validity of the simulations near M saturation, in contrast to the Landau theory, allows for accurate description of GMCE systems in a wider temperature range, including disordered and mixed phase systems. While the Bean-Rodbell simulation parameters have physical meaning, it is impossible to directly obtain input values of T_O and β from *ab initio* calculations at 0 K. To allow the prediction of the properties of a given material from DFT calculations at 0K, then a different approach is required.

A microscopic model approach, while typically more expensive in terms of computational cost, allows for more intricate and detailed simulation of model systems. As the main simulation parameter J, together with its dependence on system volume $J(v)$, are obtainable *via* DFT calculations, an *in silico* approach to predict the thermo-magnetic properties of new and optimized magnetic materials is possible. The use of prior JDOS of models such as the Ising and Heisenberg models, lowers computational cost for simulation of materials for arbitrary values of J and $J(v)$, and allows the description of the full $M(H, T)$ and $\Delta S_M(H, T)$ dependencies.

Our simulation results for the three models, for both SOMPT and FOMPT systems are both qualitatively and quantitatively in agreement. The $M(H, T)$ and $\Delta S_M(H, T)$ behaviors are similar, particularly the increase of the maximum ΔS_M value due to the change of a SOMPT to a FOMPT. The most notable differencebetween our obtained results is the larger change of T_C of the FOMPT system compared to the SOMPT, in the case of the compressible Ising model simulations. We highlight that all three models are physically sound, and the choice of which one to use will depend if the purpose is to interpret experimental data, or the *in silico* prediction of the performance of new and optimized magnetic refrigerants and ferromagnets for thermal energy harvesting.

Author contributions

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

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