Exploration of selected room temperature magneto caloric materials using COMSOL multiphysics

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Abstract. Estimation of magneto-caloric effect is crucial to determine a material’s suitability for the desired operating conditions. The magneto-caloric effect can be measured in two ways—the magnetic entropy change and the adiabatic temperature change. These parameters are the prerequisites in evaluating a magnetic refrigeration system. In this work, an application is developed and tested for 3 materials (one Gadolinium and two Lanthanum alloys) using COMSOL multiphysics to estimate the final temperature of a Magneto-Caloric Material (MCM). The duration of the magneto-caloric effect is compared amongst 4 different cases of magnetic field change. Among the selected materials Gadolinium shows the highest adiabatic temperature difference of 12K at a field change from 0 to 5 tesla.

Keywords: Magneto Caloric Material, Magnetic Entropy, Magnetic Refrigeration

1. Introduction

In the search of sustainable refrigeration systems magnetic refrigeration plays an important role [1, 2]. Magnetic refrigeration is the application of a reversible effect known as the Magneto-Caloric Effect (MCE) which occurs only in certain types of materials known as the Magneto-Caloric Materials (MCMs). MCMs are generally environment friendly [3]. The MCE is the drop or rise in temperature of an MCM when it is either moved away from an external magnetic field (H) or moved into an external magnetic field, respectively. This drop and rise varies from one material to another. In order to select a suitable material for the desired operation it is necessary to evaluate the MCE. There are two parameters with which the MCE is measured—adiabatic temperature change (ΔTₐₐ) and isothermal magnetic entropy change (ΔSₘ). Figure 1 shows the difference between the two parameters. When the process is carried out such that the MCM is allowed to exchange energy with the environment, the change produced is an isothermal magnetic entropy change. If the process is carried out by isolating the MCM, it leads to an adiabatic temperature change.

There are two ways of measuring MCE—direct and indirect measurements [3]. Direct measurement involves measuring the temperature change of the sample MCM in isolation during magnetisation or demagnetisation. Indirect measurement involves the analysis of graphs such as the magnetisation (M) versus the external applied field (H), known as isothermal magnetisation (M-H) curves. In addition to conventional cooling environments this concept finds its application in electric vehicles HVAC as well [4new]
2. Literature survey

Expressions for entropy change based on thermodynamics concepts is the initial point of any numerical study. In the field of magnetic refrigeration, the entropy change is called the isothermal magnetic entropy change (ΔS_M). What one needs to evaluate the MCE of a material is the peak value of the MCE, which occurs at the Curie temperature (T_c) of the material [5]. The entropy (ΔS_M) is considered to be a function of two independent variables-temperature (T) and externally applied magnetic field (H) [6]. The total change in entropy is given by equation (1) where S is entropy, T is temperature and H is magnetic field [7].

\[ dS = \left( \frac{\partial S}{\partial T} \right)_H dT + \left( \frac{\partial S}{\partial H} \right)_T dH \]  

McMichael et al., presented a simplified formula for the evaluation of ΔS_M of iron-substituted gadolinium garnets [7], using M-H curves, which is shown in equation (2) where M is magnetisation, T is temperature and H is applied magnetic field. This formula is means that the magnetic entropy change is approximately equal to the area between the two magnetic isotherms divided by corresponding temperature difference between them.

\[ \Delta S_M \approx \frac{1}{\Delta T} \left[ \int_0^H M(T + \Delta T, H') dH' - \int_0^H M(T, H') dH' \right] \]

Arai et al., calculated the magneto-calaric properties of Gd based alloys employing the S=7/2 Ising model and the Monte Carlo method [8]. Hirayama et al., used specific heat-temperature (C_H-T) curves of spherical GdN materials to calculate ΔS_M and ΔT_ad [9]. Basso (2013) explains in great detail, the thermodynamics of the MCE [10]. Balli et al., analyzed the giant MCE in Mn_{1-x}(Ti_{0.5}V_{0.5})_xAs materials [11]. Zouari and Chehaidar have theoretically calculated the MCE in La_{2/3}Ca_{1/3}MnO_3 [12]. Kamran et al., developed a numerical model to optimize the performance of a multi-MCM magnetic refrigerator [13]. Specific heat data is also used to calculate the MCE in materials as utilized by Bjork et al., [14]. Bennati et al., used Magnetic Optical Imaging technique to analyse the source of hysteresis [15]. Basso provides the data for La(Fe_{1-x}Co_ySi_x)_13, for the variation of specific heat with temperature at different magnetic field strengths, and also explains in detail, all the aspects involved in the MCE [10]. Moore et al., showed that the sample geometry can be varied to significantly reduce the hysteresis in La(Fe_{1-x}Co_ySi_x)_13 [16]. Mehboob (2012) has presented a detail report of his experimental results on soft
magnetic materials [17]. Gozdur et al., have studied the effects of laminating an MCM [18]. Xia et al., studied the effects of MCE on its electrical properties along with its change in entropy [19]. The studies are not restricted to magneto caloric effects only. Giant barocaloric effects has also been studied [20].

3. COMSOL application
The application developed using COMSOL multiphysics allows users to define the material, specify the amount of external magnetic field change and the temperature at which MCE is occurring. The calculation of the final temperature was done at the curie temperature (Tc) of that material. However, the simulation should also work at temperatures other than Tc.

3.1. Working of the application
The application is based on a COMSOL multiphysics model which consists of certain parameters, a variable and an interpolating function that act as input when running in the application format. The aim was to provide the user flexibility to choose any type of material to analyse the MCE, at given temperature.

The user can define any type of material by specifying the thermal conductivity (k), density (rho, ro) and the specific heat data location (notepad file). The specific heat data (interpolation function) accounts for its variation with respect to the temperature and magnetic field (H).

The external magnetic field, H (variable function) is entered as a polynomial equation of time which when traced gives an approximately smooth curve which reaches the maximum value of the applied magnetic field in less than 1 second. The initial temperature (‘Initial Temp’, Ti) is the temperature at which the MCE must be estimated. Isothermal magnetic entropy value (‘Magnetic Entropy’, Smag) also serves as one of the input values. The heat source is the object itself, acting as a volumetric source of heat and is calculated as a product of entropy, density and initial temperature. The size of the material can be defined using the ‘Square side length’ option. The transient nature of the temperature can be observed (using ‘Instant of Time’) with the help of this application. The graphic user interface (GUI) of the application is presented in the figure 2.

![GUI of the developed application.](image)

3.2. Materials chosen and their properties
As the required set of properties, which serve as inputs for this application, is not common in the literature available, the number of materials that were tested were limited to 3. However, to someone having access to the relevant data this application can serve as a useful tool to provide an idea regarding the performance of the material. The materials chosen are gadolinium (Gd), La(Fe$_{1-x}$Co$_x$Si$_x$)$_{13}$ and
LaFe$_{x}$Mn$_{y}$Si$_{z}$-H$_{1.65}$. The data for Gd [21, 22, 23], La(Fe$_{1-x}$Co$_{y}$Si$_{x}$)$_{13}$ [10 and 24] and LaFe$_{x}$Mn$_{y}$Si$_{z}$-H$_{1.65}$ [25, 26] were available in the literature referred.

4. Results and discussion

4.1. Estimation of $\Delta S_M$

The isothermal magnetic entropy change ($\Delta S_M$) can also be calculated separately, using MATLAB. To calculate the isothermal magnetic entropy change, the isothermal magnetisation curves were used to extract data points. These data points were used to generate a polynomial equation using MATLAB. The concept that the isothermal magnetic entropy change was equal to the area between two isothermal magnetisation curves divided by the temperature difference between them was used to calculate the $\Delta S_M$ [7]. It is recommended to possess the original data points which are used for the generation of the isothermal magnetic curves as this preserves the accuracy of the calculated value in MATLAB. The following table lists the values of $\Delta S_M$ calculated using MATLAB.

| Material         | Temperature, K | $\Delta S_M$, J/KgK | |Error|, % |
|------------------|----------------|----------------------|----------------|------------------|
| Gd               | 267.6          | 2.4 [27]             | 2.484          | [This work]      | 3.5              |
|                  | 277.8          | 3.2 [27]             | 3.38           | [This work]      | 5.625            |
| Fe$_{40}$Ni$_{38}$Mo$_{4}$B$_{18}$ | 600 | 1.1 [28]             | 1.1708         | [This work]      | 0.068            |
| Gd$_{60}$Al$_{20}$Co$_{20}$     | 109            | 10.1 [29]            | 9.921          | [This work]      | 1.77             |
| Mn$_{5}$Ge$_{2.5}$Si$_{3.5}$     | ~296           | 7.8 [30]             | 7.7402         | [This work]      | 0.766            |

4.2. Application of magnetic field

The final temperature of the MCMs have been calculated using the application for 4 different cases of magnetic field change ($\Delta H$). For each of the cases an equation is generated, based on the values of the magnetic field strength chosen (by the user) at particular times, and utilised in the application. The four cases are listed as follows.

i. L1: The magnetic field changes smoothly over time as shown in figure 2. The maximum value is attained at 0.8s.

ii. L2: The magnetic field instantaneously ramps to the maximum value of the magnetic field at 0$^{th}$ second. Due to this, specific heat becomes a function of temperature only.

iii. L3: The magnetic field varies with a fixed slope until the maximum values and then remains constant. The maximum value is attained at 0.5s.

iv. L4: The magnetic field achieves it maximum value with a fixed slope. The maximum value is attained at 1s.

The curves for each of the cases described above are shown in figures 3-6.
4.3. Estimation of duration of magneto caloric effect (MCE)

The application was run for 3 different materials and a total of 5 different conditions. The results are tabulated in Table 2. The duration of MCE i.e., the time taken by the application to attain the reported adiabatic temperature is tabulated according to the 4 cases of magnetic field change in the table 2.

| Material             | $\Delta H$, T | $T_i$, K | $\Delta T_{ad}$ (Reported), K | $\Delta T_{ad}$ (COMSOL), K | Duration of MCE, s |
|----------------------|---------------|---------|-------------------------------|----------------------------|-------------------|
| Gd                   | 2.0           | 267.60  | ~2.3                          | 2.4                        | 0.840 0.815 0.83 0.845 |
| La(Fe$_{0.844}$Co$_{0.079}$Si$_{0.077}$)$_{13}$ | 2.0           | 277.80  | ~3.2                          | 3.2                        | 0.905 0.865 0.885 0.910 |
| LaFe$_{11.2}$Mn$_{0.46}$Si$_{1.32}$-$H_{1.65}$ | 5.0           | 294.00  | 11.6                          | 12.0                       | 1.105 1.085 1.100 1.100 |
|                      | 1.5           | 293.00  | 2.6                           | 3.0                        | 0.980 0.965 0.980 0.980 |
|                      | 1.0           | 271.25  | 2.75                          | 2.75                       | 0.745 0.825 0.785 0.700 |

Where,
ΔH = Magnetic field change from 0 tesla
Ti = Initial temperature at which MCE occurs
ΔT_{ad} = Adiabatic Temperature change

The reported values of the adiabatic temperatures are achieved approximately in COMSOL multiphysics. The duration of MCE can be represented as L2<L3<L1<L4 with the exception of LaFe_{11.22}Mn_{0.46}Si_{1.32}H_{1.65}. The usual trend can be attributed to the time at which the magnetic field becomes maximum. The peculiar behavior of LaFe_{11.22}Mn_{0.46}Si_{1.32}H_{1.65} can be attributed to its specific heat curve (variation with respect to temperature and magnetic field) [25]. An in-depth 2D numerical model to simulate a laboratory-scale model was developed and explained in great detail by Peterson T F et al. [31]

### 4.4. Error Analysis

The most optimum method to apply the magnetic field is chosen as L1 in literature [32]. For the purpose of error analysis, we will consider the same. The duration of MCE is compared and tabulated in table 3. The formula to calculate the error is given by equation (3) [33].

\[
E = \left[\frac{(t_{L1} - t_{Ln})^2}{(t_{L1})^2}\right]^{\frac{1}{2}}
\]  

Where,

\(E\) = error
\(t_{Ln}\) = duration of MCE for case Ln (n = 1, 2, 3, 4)
\(t_{L1}\) = duration of MCE for case L1

| Material                  | ΔH, T | Ti, K | L1  | L2  | L3  | L4  |
|---------------------------|-------|-------|-----|-----|-----|-----|
| Gd                        | 2     | 267.6 | 0   | 0.029 | 0.011 | 0.005 |
|                           | 2     | 277.8 | 0   | 0.044 | 0.022 | 0.005 |
|                           | 5     | 294   | 0   | 0.0181 | 0.004 | 0.004 |
| La(Fe_{0.84}Co_{0.079}Si_{0.077})_{13} | 1.5  | 293   | 0   | 0.015 | 0     | 0   |
| LaFe_{11.22}Mn_{0.46}Si_{1.32}H_{1.65} | 1    | 271.25 | 0   | 0.107 | 0.053 | 0.060 |

**Table 3.** Error comparing different cases of applied magnetic field.

![Figure 7. Error in duration of MCE.](image-url)
The error analysis data is compared for the 3 materials at different temperatures and represented graphically in figure 7. It is clear from the figure that for a given material and temperature, the error is highest when L2 is considered. The least error is contained in L4, generally.

5. Conclusion
An application involving the specific heat as a function of temperature and magnetic field and magnetic field as a function of time was successfully developed and tested for 3 materials containing 5 different conditions. The duration of MCE was around 1s for the materials. The magnetic entropy change which serves as an input for the application can also be estimated using isothermal magnetisation curves, as presented here for 4 different materials. The application of magnetic field was applied in four different ways (for each material) and compared with each other. The user can define any material and apply a magnetic field change of his choice. The error analysis data helps in a way that it gives an idea of the duration of MCE, based on the nature of magnetic field change the user can utilize experimentally.

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