Estimation of magnetocaloric properties by using Monte Carlo method for AMRR cycle

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Abstract. In order to achieve a wide refrigerating temperature range in magnetic refrigeration, it is effective to layer multiple materials with different Curie temperatures. It is crucial to have a detailed understanding of physical properties of materials to optimize the material selection and the layered structure. In the present study, we discuss methods for estimating a change in physical properties, particularly the Curie temperature when some of the Gd atoms are substituted for non-magnetic elements for material design, based on Gd as a ferromagnetic material which is a typical magnetocaloric material. For this purpose, whilst making calculations using the $S=7/2$ Ising model and the Monte Carlo method, we made a specific heat measurement and a magnetization measurement of Gd-R alloy (R = Y, Zr) to compare experimental values and calculated ones. The results showed that the magnetic entropy change, specific heat, and Curie temperature can be estimated with good accuracy using the Monte Carlo method.

1. Introduction

Magnetic refrigeration which applies magnetocaloric effects of magnetic substances attracts attention as a useful refrigeration technology intended for a wide range of temperatures from very low temperatures used in outer space to room temperatures. CrK(SO$_4$)$_2$·12H$_2$O (CPA), GdLiF$_4$ (GLF), etc. are used as materials for the Adiabatic Demagnetization Refrigeration (ADR) in the region of very low temperatures materials [1], whereas Dy$_{3-x}$Gd$_x$Al$_5$O$_{12}$ (DGAG) and the like are used as materials for the Carnot Magnetic Refrigeration (CMR) in the region of liquid hydrogen temperatures [2]. Magnetic refrigeration in the room-temperature region has recently attracted attention from the viewpoint of protecting the global environment. In 1976 Brown et al. showed a potential for the magnetic refrigeration in the room-temperature region [3], and thereafter a variety of studies have been conducted since the presentation of Barclay et al. on the Active Magnetic Regenerative Refrigerator...
(AMRR) cycle [4]. It is currently found to be effective to layer multiple materials having different Curie temperatures in order to achieve wide range of refrigeration temperature in magnetic refrigeration [5]. Selection of suitable materials and optimization of layered structure are essential to obtain good refrigerating performances. However, it is difficult to produce every kind of materials experimentally to measure their properties for selecting proper materials and designing layered structure.

On the other hand, the Monte Carlo method is known to be effective as a method for evaluating physical properties of magnetic materials in calculations [6, 7, 8]. Here we will discuss a method for estimating Curie temperatures, specific heat and magnetic entropy changes of Gd alloys where the crystal structure is hexagonal, using the Monte Carlo method for the material design.

2. Calculation model

2.1 Theoretical model

The Monte Carlo method and the $S=7/2$ Ising model that is called Potts-like model in [6] were used to calculate the physical properties of magnetocaloric materials based on Gd in this study as with [6]. Hamiltonian of a system in the Ising model is shown as follows:

$$
\mathcal{H} = - \sum_{\langle i,j \rangle} \lambda_{ij} J_i \cdot J_j - g \mu_B H \sum_i J_i. \tag{1}
$$

Here, $\langle i,j \rangle$ shows a group of the closest lattice points, $\lambda_{ij}$ is the exchange interaction between these lattice points, and $H$ is the external magnetic field. In the $S=7/2$ Ising model, $J_i$ is the total angular momentum with a possible value of $J = \{-7/2, -5/2, ..., 7/2\}$. $g$ is the Lande factor, and $\mu_B$ is the Bohr magneeton.

In addition, the specific heat of a solid substance can generally be expressed as follows:

$$
C = C_L + C_E + C_M + C_N, \tag{2}
$$

where $C_L$ is the lattice specific heat, $C_E$ is the electronic specific heat, $C_M$ is the magnetic specific heat, and $C_N$ is the nuclear specific heat. The value of the nuclear specific heat is very low therefore can generally be ignored except for the very-low-temperature region.

The following Debye's formula for specific heat was used to make estimations:

$$
C_L = 9Nk_B \left( \frac{T}{\Theta} \right)^3 \int_0^{\Theta} \frac{x^4 e^-x}{(e^x-1)^2} dx, \tag{3}
$$

where $\Theta$ is the Debye temperature, $T$ is the temperature. $N$ is the number of lattice points, $k_B$ is Boltzmann constant, and $x$ is defined (4):

$$
x \equiv \frac{\hbar \omega}{k_B T}, \tag{4}
$$

where $\hbar \omega$ is the energy of the phonon of frequency $\omega$. The upper limit of integration is written as $\Theta/T$.

The following equation was used for the electronic specific heat:

$$
C_E = \gamma T, \tag{5}
$$

where $\gamma$ is the Sommerfield constant. The magnetic specific heat can be expressed as follows:
where $E$ is internal energy calculated by the Hamiltonian defined by Eq.(1), $<E^2>$ is the thermal average of the square of the energy, and $<E>$ is the thermal average of the energy. In addition, the entropy of the magnetic system is obtained through dividing the magnetic specific heat by the temperature and integrating it:

$$S_M = \int_0^T \frac{C_M}{T} \, dT.$$  

Furthermore, the magnetic entropy change is obtained by subtracting the entropy in magnetic field 0 from the magnetic entropy in magnetic field $H$.

$$\Delta S_M = S_M(T, H) - S_M(T, 0).$$

The calculation of the thermal average of the energy, specific heat, and magnetic entropy in the $S=7/2$ Ising model as described above cannot be made analytically. Thus we use the Monte Carlo method for making such calculations. It is a method for making statistical averages of energy and others by generating states randomly using random numbers. The method of generating a completely random state and making a statistical average is referred to as the random sampling; however, this method has poor calculation efficiency as there are many states occurring in parts that do not contribute to the average values. Therefore, we employed the method of weight importance sampling, which generates states according to the Boltzmann distribution for making statistical averages.

The Metropolis method was used for the generation of the state following the Boltzmann distribution. The renewal method for the total angular momentum $J_i$ with the Metropolis method is shown below [9].

1) $J_i$ is selected and varied at random.
2) The energy difference $\Delta E$ is calculated before and after a change in $J_i$.
3) A random number $r$ is generated, which has a value between 0 and 1.
4) If $\Delta E < 0$ or $r \leq \exp(-\Delta E/k_B T)$, then $J_i$ is adopted, else $J_i$ is reset.

The performance of these operations for the number of all lattice points is called 1 Monte Carlo Step (MCS). In the Monte Carlo method, the point where a constant MCS is reached is regarded as the thermal equilibrium, and statistical averages are made for subsequent trials.

### 2.2 Calculation condition

In this study, we examine through calculations the properties of Gd as the ferromagnetic material, which is a typical magnetocaloric material, including the specific heat, Curie temperature, and entropy change, and the impact on these properties when some of the Gd atoms are substituted for non-magnetic elements. In order to express the substitution for non-magnetic elements, we assume that crystal structures are hexagonal crystals same as Gd and some of the sites the lattice points are fixed at $J_i = 0$ at random. A value converted from the Curie temperature of Gd is used for $\lambda_{ij}$. Table 1 shows the calculation conditions used in this study.
Table 1. Calculation condition.

| Parameter                        | Value         |
|----------------------------------|---------------|
| Debye temperature \( \Theta \)   | 154 K [6]     |
| Sommerfeld constant \( \gamma \)| \( 8.97 \times 10^{-24} \) J K\(^{-2} \) |
| Exchange interaction parameter \( \lambda_{ij} \) | \( 7.438 \times 10^{-23} \) J |
| Bohr magneton \( \mu_B \)        | \( 9.274 \times 10^{-24} \) J T\(^{-1} \) |
| Lande factor \( g \)             | 2             |
| Boltzmann constant \( k_B \)     | \( 1.381 \times 10^{-23} \) J K\(^{-1} \) |
| External field \( H \)           | 0, 1, 5 T     |
| Number of lattice points \( N \) | \( 10^3 \)   |
| Crystal structure                | Hexagonal close packed |
| MCS (thermal equilibrium)        | 4000 MCS      |
| MCS (total)                      | 8000 MCS      |
| Number of iteration              | 30            |
| Boundary condition               | Periodic boundary condition |

3. Experimental
In order to verify the integrity of the calculation results, experiments were also performed. Gadolinium is a ferromagnetic element with Curie temperature \( T_C \) of 294 K (~21°C), and forms solid solution with nonmagnetic elements of Y or Zr. We prepared Gd-based binary alloys partially substituted by nonmagnetic element of Y and Zr. Polycrystalline samples of Gd\(_{100-x}\)Zr\(_x\) \((x = 1.5, 3)\) and Gd\(_{100-x}\)Y\(_x\) \((x = 2, 4, 6, 8, 10)\) were prepared by Arc melting method and subjected to homogenising anneal. All samples were confirmed to be single phase with hexagonal crystalline structure by X-ray diffraction (XRD). Magnetic properties were measured using the superconducting quantum interference device magnetometers (SQUID, Quantum Design), and magnetic entropy changes \( \Delta S_M \) were estimated based on Maxwell-relations using the magnetization curves.

\[
\Delta S_M = \int_0^H \frac{\partial M}{\partial T} dH,
\]

where \( M \) is magnetization. Specific heat measurement was performed using physical property measurement system (PPMS, Quantum Design).

4. Results and discussion
4.1 Results with Gd
Firstly, we show the results of calculations for Gd with the Monte Carlo method for comparison with experimental values in order to verify the accuracy of calculations with such a method.

Figure 1 shows the results of calculations together with the experimental values of magnetic specific heat for Gd with the lattice size considered in the calculations as a parameter. The experimental values here are obtained by subtracting the calculated values of lattice specific heat and electronic specific heat from the measured specific heat. It is found that if the lattice size is more than \( 8^3 \), the calculated value generally agrees with the experimental value. Figures 2 and 3 show the comparison between the calculated value and the experimental value for the specific heat and the change in magnetic entropy change in Gd. The calculated values in the Monte Carlo method are found to be in close agreement with the experimental values in the whole region.
4.2 Results with Gd-R alloy

Next, we describe calculated results for a system where a non-magnetic site ($J_i = 0$) is located randomly at some of the sites of the Gd lattice points.

Figure 4 represents the comparison between the calculated values and the experimental values for the specific heat in the 0 magnetic field in Gd$_{97}$Zr$_3$. It is found that Fig.4 can show their properties as a whole, although peaks of specific heat appear at somewhat higher temperatures and also values of specific heat are slightly lower in the calculated values than in the experimental values. Thus we derived the magnetic entropy change from the calculated results for the specific heat using Eq. (7) and Eq. (8). Meanwhile, we estimated the magnetic entropy change, using the results of magnetization measurements and Eq. (9) led by the Maxwell’s relations to compare both results. Figure 5 compares the experimental values and the calculated values for the magnetic entropy change. There are gaps in
peak locations as with the specific heat, however they are generally consistent with the experimental values.

![Graph showing specific heat vs temperature.](image1)

**Figure 4.** Comparison of calculation specific heat in zero external field and the experimental one in Gd$_{97}$Zr$_3$.

![Graph showing magnetic entropy change vs temperature.](image2)

**Figure 5.** Comparison of calculation magnetic entropy change and experimental one in Gd$_{97}$Zr$_3$.

Figure 6 shows the dependency of the Curie temperature of Gd$_{100-x}$Zr$_x$ and Gd$_{100-x}$Y$_x$ on the non-magnetic element concentration $x$. The solid lines and the dotted line represent the experimental results and the calculated results, respectively. In both of the experimental and calculated results, the Curie temperature shows a linear decrease with the increase of the non-magnetic atom concentration $x$. In addition, it was found from the experimental results that the Zr substitution shows a bigger drop in the Curie temperature than Y with an increase in $x$, whereas the calculated results were between both of them and roughly consistent with the experimental results. The difference in the dependency on the $x$ concentration between the Curie temperatures of Gd$_{100-x}$Y$_x$ and Gd$_{100-x}$Zr$_x$ may be related to the difference in concentration $x$ dependency of lattice constants and the difference in the change in the number of conductive electrons between them. The future examinations through more detailed calculations in consideration of these elements would be desired even when making calculations with the Monte Carlo method.
5. Conclusion
In this study we examined the estimation of physical properties of magnetic refrigeration materials using the Monte Carlo method. A typical ferromagnetic Gd was selected as the magnetocaloric material and partially substituted for non-magnetic elements for material design of layer multiple materials with different Curie temperatures for AMRR. As a result, we obtained the following conclusions:

1) It could be confirmed that the magnetic refrigerant properties of Gd could be calculated with high accuracy with the $S=7/2$ Ising model of the hexagonal crystal system and the Monte Carlo method.

2) The magnetic refrigeration characteristics of Gd-R alloy (R = Y, Zr) could generally be reproduced by the calculation in which some of the sites on the lattice points were replaced randomly with non-magnetic sites.

3) In order to estimate the Curie temperature with high accuracy, it is essential to clarify its physical mechanisms to be reflected in the calculation.

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