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Review Articles

Calculation model on magnetocaloric effect (MCE) and relative cooling power (RCP) in composite materials at room temperature

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ABSTRACT

In this paper, a calculation model is proposed to measure magnetocaloric effect (MCE) and relative cooling power (RCP) in composites based on magnetic materials underscoring a giant MCE at room temperature. The two composite materials targeted are Gd-$Gd_5Si_2Ge_2$ and MnAs-$Mn_{1+\delta}As_{0.9}Sb_{0.1}$ due to their high magnetic entropy change ΔS_M over 270–300 K and 280–320 K.

Our selected composites could give a larger RCP value among existing magnetocaloric materials for magnetic refrigeration in the temperature range of 280–300 K which is desirable for ideal Ericsson-cycle magnetic refrigeration. The excellent magnetocaloric properties of these two magnetic composites make them attractive for active magnetic refrigeration at room temperature.

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1. Introduction

Magnetic refrigeration is a clean technology that uses a magnetic field to change the magnetic entropy of a material (the magnetocaloric effect, MCE), thus allowing the material to serve as a refrigerant. This technology provides a higher cooling efficiency (about 20–30%) than conventional gas compression techniques [1].

Many efforts have been spent both theoretically and experimentally in order to formulate new concepts of Active Magnetic Refrigeration (AMR) which permit magnetic refrigeration at room temperature (see as example Ref. [2]). The aim being to substitute the conventional refrigeration releasing greenhouse gases by a new technology preserving the environment and saving the energy consumption.

Producing a magnetocaloric material with a large magnetic entropy change ΔS_M over a wide temperature range, i.e., a large refrigerant capacity, is of capital interest for magnetic refrigeration applications. For ideal Ericsson cycle based magnetic refrigeration, a magnetocaloric material should possess a constant magnetic entropy change ΔS_M in the refrigeration temperature range [3]. Our ultimate objective is to work out a model providing magnetocaloric effect (MCE) and relative cooling power (RCP) calculations in magnetic composites materials. Indeed, several theoretical approaches and simulations have been used to predict and describe the MCE in ideal materials (see as examples Refs. [4]; [5]) while experimentally, since the discovery of giant MCE in $Gd_5Si_2Ge_2$ in 1997 [6], a vast variety of materials has been synthesized

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and the MCE field surged up. This progress covered pure magnetic elements and their solid solution alloys such as 4f elements (Gd, Nd, …), binary and intermetallic compounds such as R-M$_2$ materials (R = Dy, Ho, Er; M = Co, Al…), Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ and related materials that exhibit giant MCE, families of Mn-based compounds, La (Fe$_{13-x}$M$_x$)-based compounds and manganites (La$_{1-x}$M$_x$) MnO$_3$ where M = Na, Ag with quite important MCE (for a review see Ref. [7]).

For illustration, we choose the two composites Gd-Gd$_5$Si$_2$Ge$_2$ and MnAs- Mn$_{1+\delta}$As$_{0.9}$Sb$_{0.1}$ because of their high ΔS_M over 270–300 K and 280–320 K.

The paper is organized as follows: in Section 2, we introduce the model by giving the spin Hamiltonian and partition function. Then in Section 3, we calculate relevant thermodynamic parameters influencing the MCE. Section 4 is devoted to numerical results and discussions. Finally, we give conclusion and outlook.

2. Model

We first consider the Heisenberg Hamiltonian of a ferromagnetic αsingle-system given by

$$H_\alpha = -J_\alpha \sum_{\langle i,j\rangle} \vec{S}_{i,\alpha}.\vec{S}_{j,\alpha} - g\mu_B\mu_0 H_0 \cdot \sum_i S^z_{i,\alpha} \tag{1}$$

where Jα is the exchange interaction constant between nearest-neighbors (Jα > 0), $\vec{S}_{i,\alpha}$ (respectively $\vec{S}_{j,\alpha}$) are the spin operators acting on the site i (respectively j) and H$_0$ is the applied magnetic field parallel to the z-axis of spin. Here, g is the Landé factor, μ$_B$ is the Bohr magneton and μ$_0$ is magnetic permeability.

In order to solve Eq. (1), we make an approximation by defining an effective molecular field at the

$$i^{th}\ \text{site}: B_W = \frac{1}{g\mu_B}\sum_{j\in nn}\langle S_j\rangle J_{ij} \tag{2}$$

Therefore, the exchange interaction is replaced by the effective molecular field B$_W$ produced by the neighboring spins. We are now able to treat this problem as if the system were a simple paramagnet placed in a magnetic field B + B$_W$. The effective Hamiltonian can now be written as:

$$H_\alpha = -g\mu_B \sum_i S_{i,\alpha}(B_0 + B_W) \tag{3}$$

The assumption supporting this approach is that all magnetic ions experience the same molecular field. However, this may be rather questionable, particularly at temperatures close to a magnetic phase transition. For a ferromagnet, the molecular field will act so to align neighboring magnetic moments. This is because the dominant exchange interactions are positive. Since the molecular field measures the effect of the system ordering, we can assume that B$_W$ = λ M where:

$$\lambda = \frac{zJ}{(g\mu_B)^2 n} \tag{4}$$

Thus, λ characterizes the strength of the molecular field as a function of the magnetization (for a ferromagnet, λ > 0). Here z and n denote respectively the coordination number and the volume spin concentration. Both are related to the crystallographic structure of the material.

In this context, our Hamiltonian may be equally rewritten as:

$$H_\alpha = \sum_i H_{\alpha,i} \tag{5}$$

where $H_{\alpha_i} = -g\mu_B S_{i\alpha}(B_0 + B_W)$ whose the eigenvalues are given by $E_i = -g\mu_B m_i(B_0 + B_W)$ where −S ≤ m$_i$ ≤ S.

Since all individual Hamiltonians H$_{i,}$ α commute between them, the partition function becomes:

$$Z_\alpha = \prod_i Z_{i,\alpha} \tag{6}$$

where

$$Z_{i,\alpha} = \sum_{\{m_i\}} e^{\beta g\mu_B m_i(B_0+B_W)} = \sum_{m_i=-S}^{m_i=+S} e^{ym_i} \tag{7}$$

$y = \beta g\mu_B(B_0 + B_W) = \beta g\mu_B(B_0 + \lambda M)$; β = 1/k$_BT, k_B$ being the Boltzmann constant.

By performing the Zα calculation, we deduce the Helmholtz free energy for n spins per unit volume using the expression Fα = −n k$_B$ ln(Zα). Thus, the magnetization, the magnetic entropy per unit volume and the magnetic specific heat are expressed respectively by:

$$M(B,T) = M_S B_S(y) \tag{8}$$

$$S_M = nk_B\left[\ln\frac{sh(1+\frac{1}{2S})y}{sh\frac{y}{2S}} - yB_S(y)\right] \tag{9}$$

$$C_M = -nk_By^2\left[\frac{\left(1+\frac{1}{2S}\right)^2}{sh\left(\left(\frac{2S+1}{2S}\right)y\right)^2} - \frac{\left(\frac{1}{2S}\right)^2}{sh\left(\left(\frac{1}{2S}\right)y\right)^2}\right] \tag{10}$$

where B$_s$(y) is the Brillouin function and M$_{\text{<ce:inf>s}}$ $< /ce : inf >= ng\mu_B S$ is the saturation magnetization. Note that in absence of both exchange (paramagnetic system) and external magnetic field, one finds that the entropy of the assembly of magnetic moments has its maximum at M = 0, and its value is S$_M$(0) = nk$_B$ ln (2S + 1), corresponding to the upper limit for the entropy associated with the atomic magnetic moments with 2S + 1 discrete levels.

However, in our system where exchange is taken into account, the Eqs. (8)–(10) contain implicitly the magnetization M making hard the analytical resolution of the problem.

Thus, in order to overcome this difficulty and perform a numerical resolution, we have developed a computational program simulating the evolution of these variables with both magnetic field and temperature for a given set of microscopic parameters such as exchange interaction or spin size.

3. Thermodynamic study

For the characterization of the magnetocaloric response of a material, three main parameters can be studied: the isothermal magnetic entropy change, ΔS_M; the adiabatic temperature change, ΔT_{ad}; and the relative cooling power, *RCP* [8]. In order to calculate these parameters, we start form the Gibbs free energy G which is expressed in terms of internal energy U, extensive variables (entropy S and magnetization M) and intensive variables (temperature T and magnetic induction B$_0$) as follows:

$$G(T,P,B) = U + PV - TS - \vec{M}\cdot\vec{B} \tag{11}$$

Thus:

$$dG = \left(\frac{\partial G}{\partial T}\right)dT + \left(\frac{\partial G}{\partial B}\right)dB = -MdB - S_M dT \tag{12}$$

Where:

$$\frac{\partial}{\partial B}\left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial B}\right) \tag{13}$$

By using Maxwell-Weiss relation [3], we get:

$$\left(\frac{\partial M}{\partial T}\right) = \left(\frac{\partial S_M}{\partial B}\right) \tag{14}$$