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Magnetocaloric effect in ferromagnetic and ferrimagnetic systems under first and second order phase transition

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ABSTRACT

In this work we present a model to describe the magnetocaloric effect (MCE) in ferrimagnetic arrangements. Our model takes into account the magnetoelastic interactions in the two coupled magnetic sublattices, which can lead to the onset of the first order magnetic phase transition and the giant-MCE. Several profiles of the MCE, such as: the inverse- and giant-MCE were systematically studied. Application of the model to the ferromagnetic compounds $GdAl_2$, $Gd_5(Ge_{1.72}Si_{2.28})$, $Gd_5(Ge_2Si_2)$, and to the ferrimagnetic compound $Y_3Fe_5O_{12}$ was performed, showing a good agreement with the experimental data.

1. Introduction

The magnetocaloric effect (MCE) occurs when a temperature change in a magnetic material is observed upon applied magnetic field changes. The two thermodynamic quantities that characterize the magnetocaloric potential are ΔS_T (the isothermal magnetic entropy change) and ΔT_{ad} (the adiabatic temperature change) which are calculated or measured under applied magnetic field changes. The MCE was discovered in 1881 by Warburg [1] and its use principle in the magnetic refrigeration technology was suggested by Debye in 1926 and Giauque in 1927. More recent interest was due to the discovery of the first giant-MCE around room temperature in $Gd_5Si_2Ge_2$ in 1997 by Pecharsky and Gschneidner [2]. The state of the art in the MCE can be found in several recent review works [3–5].

The majority investigations reported on the magnetocaloric materials are experimentally performed by determining the curves of the magnetocaloric potential ΔS_T and ΔT_{ad} which present several different profiles associated with complex microscopic interactions among the magnetic ions. For examples the giant-MCE can be associated with a strong magnetoelastic interaction as is the case of $Gd_5Si_2Ge_2$ and the inverse-MCE (where a magnetic material cools down when the magnetic field is applied adiabatically) can be associated with magnetic anisotropies [6,7]. In this work, we present a magnetic model described by a Hamiltonian which takes into account two coupled magnetic sublattices, the Zeeman and the magnetoelastic interactions. Using this model the MCE was investigated in a ferrimagnetic system under the influence of the magnetoelastic interaction. The inverse-MCE and the giant-MCE was simulated and discussed systematically in terms of the model parameters. Applications of the model in the simple magnetocaloric material $GdAl_2$, giant-magnetocaloric materials $Gd_5(Ge_{1.72}Si_{2.28})$, $Gd_5(Ge_2Si_2)$, and in the ferrimagnetic material $Y_3Fe_5O_{12}$ were performed and compared with the experimental data.

2. Theory

In our model the magnetic system is formed by two sublattices (a and b) with ions exhibiting total angular momentum J^a and J^b, respectively, in the presence of an external magnetic field and in thermodynamic equilibrium. The Hamiltonian for this system is given by:

$$H = -\sum_{i,j,\alpha}\lambda_{\alpha\beta}^{(i,j)}J_i^{\alpha}J_j^{\beta} - \sum_{i,j}\lambda_{ab}^{(i,j)}J_i^{a}J_j^{b} - \sum_{i,j,\alpha}\zeta_{\alpha}^{(i,j)}(J_i^{\alpha}J_j^{\alpha})^2 - \mu_B\mu_0 h\sum_{i,\alpha}g_{\alpha}J_i^{\alpha}, \quad (1)$$

where α=a, b. The first two terms represent the exchange interaction where $\lambda_{ab}^{(i,j)}$, $\lambda_{aa}^{(i,j)}$ and $\lambda_{bb}^{(i,j)}$ are the inter and

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intra-sublattices exchange parameters between pairs of magnetic ions. The third term is the magnetoelastic interaction described by momentum operators [8], where $\zeta_a^{(i,\ j)}$, $\zeta_b^{(i,\ j)}$ are the a and b sublattices magnetoelastic parameters. The last term accounts for the Zeeman interaction, J^a, J^b, g_a and g_b represent the total angular momentum operators and the Landé factors of the a-ions and b-ions, $\mu_0 h$ is the external magnetic field and μ_B is the Bohr magneton. Under the mean field approximation the two coupled magnetic state equations can be obtained from Eq. (1) [9] and are given by:

$$M_a = N_a \mu_B g_a J_a B_J[\mu_B g_a J_a h_a / k_B T], \tag{2}$$

$$M_b = N_b \mu_B g_b J_b B_J[\mu_B g_b J_b h_b / k_B T]. \tag{3}$$

where the mean fields are:

$$h_a = \mu_0 h + \gamma_{aa} M_a + \gamma_{ab} M_b + d_a M_a^3, \tag{4}$$

$$h_b = \mu_0 h + \gamma_{bb} M_b + \gamma_{ab} M_a + d_b M_b^3. \tag{5}$$

where $B_J[x]$ is the Brillouin function, N_a and N_b are the numbers of magnetic ions per unit formula in the a- and b-sites respectively. The quantities γ_{aa}, γ_{bb} and γ_{ab} are the effective exchange parameters and d_a and d_b are the effective magnetoelastic parameters. The cubic magnetization dependence of the mean field due to the magnetoelastic interaction was thermodynamically described in the Bean and Rodbell model [10]. A particular case of the above model, for a single magnetic lattice with $J_a = J_b = J$; $g_a = g_b = g$ and $\gamma_{aa} = \gamma_{bb} = \gamma_{ab} = \gamma$ was previously discussed by some of us [11], which leads to the magnetoelastic parameter $d_{a,\ b} = C_{a,\ b}\eta$ where:

$$C_{a,\ b} = \frac{3}{5}\frac{(J+1)[(2J+1)^4 - 1]}{g^2 J^3 \mu_B^2 [2(J+1)]^4}\left(\frac{N_a + N_b}{N_{a,\ b}}\right)^3 \gamma, \tag{6}$$

and

$$\eta = \frac{5}{2}\frac{[4J(J+1)]^2 k_B K T_0 \beta^2 N}{[(2J+1)^4 - 1]}. \tag{7}$$

where k_B is the Bolzmann's constant, K the compressibility, T_0 the magnetic ordering temperature in the absence of the deformation and β measures the slope of the critical temperature curve on the cell deformation [11]. From the Landau theory of phase transitions, the condition $\eta > 1$ leads the magnetic system to undergo a first order phase transition.

The magnetic entropy can be obtained from the free energy and is given by:

$$S(T,\ h) = R \sum_{\alpha = a,\ b} N_\alpha [\ln Z_\alpha - x_\alpha B_{J_\alpha}(x_\alpha)], \tag{8}$$

where R is the gas constant and Z_α the partition function of the α-sublattice.

$$Z_\alpha = \frac{\sinh\left[\left(\frac{2J_\alpha + 1}{2J_\alpha}\right)\frac{\mu_B g_\alpha J_\alpha h_\alpha}{k_B T}\right]}{\sinh\left[\left(\frac{1}{2J_\alpha}\right)\frac{\mu_B g_\alpha J_\alpha h_\alpha}{k_B T}\right]}. \tag{9}$$

In our model the total entropy is the sum of the magnetic entropy, relation (8), and the lattice entropy, S_{latt}, in the Debye assumption. From the total entropy the magnetocaloric quantities can be directly obtained:

$$\Delta S_T(T) = S(T,\ \mu_0 h = 0) - S(T,\ \mu_0 h > 0), \tag{10}$$

$$\Delta T_{ad}(T) = T(S_T,\ \mu_0 h = 0) - T(S_T,\ \mu_0 h > 0). \tag{11}$$

3. Model application

In order to apply the model discussed above we considered five set of model parameters as displayed in Table 1. The first set, indicated in Table 1 as parametric, leads the magnetic system to order below $T_N = 194$ K in a ferrimagnetic arrangement. In this case both magnetic sublattices present ions with the same Landé factor and total angular momentum, namely $g_a = g_b = 2$ and $J_a = J_b = 7/2$. The nature of the ferrimagnetic arrangement arises since we consider different values for the numbers of the magnetic ions in a-sublattice (up oriented) and b-sublattice (down oriented) magnetic moments [9]. The inset in Fig. 1 shows the sublattices magnetizations M_a and M_b vs. temperature without magnetoelastic interaction $d_a = d_b = 0$. Since we adopted $\gamma_{aa} > \gamma_{bb}$, the magnetization in the a-sublattice decreases slowly than the magnetization in the b-sublattice. Therefore, an increasing in the net magnetization vs. temperature in the temperature range between $T = 0$ and $T_K \sim 90$ K is observed as shown in Fig. 1 for $d_a = d_b = 0$. In order to simplify the systematic study of the influence of the magnetoelastic interaction on this theoretical magnetic system we considered $d_b = 0$. When the magnetoelastic interaction increases from $d_a = 0$ to $d_a = 6 \times 10^3$ T^4/mev^3 as shown in Fig. 1, two important behaviors are observed: (1) for $d_a > 3 \times 10^3$ the order temperature increases and the magnetization is discontinuously destroyed, under a first order phase transition processes; (2) the temperature T_K increases with increasing d_a parameter. Fig. 2 shows the temperature dependence of the ΔS_T for magnetic field change from 0 to 5 T calculated using the same model parameters considered in Fig. 1. The discontinuity observed in ΔS_T at the ferri-paramagnetic phase transition temperature for d_a>3 $\times 10^3$ highlight the nature of the first order magnetic phase transition due to the magnetoelastic interaction. The inset in Fig. 2 displays the details of the inverse ΔS_T, below 150 K. The region of the inverse-MCE occurs below T_K which increases almost linearly with the d_a parameter. The zero values of the ΔS_T occurs at T_K, as expected from the Maxwell relation which relates the ΔS_T with the temperature derivative of the magnetization, i.e., at $T_K = T_K(d_a)$ maximum values of M vs. T occur as shown in Fig. 1.

Fig. 3 shows the temperature dependence of ΔS_T under magnetic field change from 0 to 5 T for $GdAl_2$, $Gd_5(Ge_{1.72}Si_{2.28})$ and $Gd_5(Ge_2Si_2)$. The symbols represent the experimental data [2,12,13] and the solid curves represent the theoretical calculation using the model parameters given in Table 1. The $GdAl_2$ is a conventional ferromagnetic material, with a second order phase transition at $T_C = 166$ K which leads to the adjustment of an

Table 1
Model parameters for $GdAl_2$, $Gd_4(Ge_{1.72}Si_{2.28})$, $Gd_4(Ge_2Si_2)$ and $Y_3Fe_5O_{12}$ compounds. For $Y_3Fe_5O_{12}$, N_a and N_b are the number of magnetic ions in a-sites and b-sites per unit formula.

Compounds	γ_{aa} (T^2/meV)	γ_{bb} (T^2/meV)	γ_{ab} (T^2/meV)	N_a	N_b	T_C (K)	T_N (K)	$d_a(10^3)$ (T^4/meV^3)	η
Parametric	300	0	−200	2/3	1/3	–	194	0–6	–
$GdAl_2$	205	205	205	1/2	1/2	166	–	0	0
$Gd_5(Ge_{1.72}Si_{2.28})$	220	220	220	1/2	1/2	244	–	19.10	3.7
$Gd_5(Ge_2Si_2)$	332.7	332.7	332.7	1/2	1/2	275	–	8.97	1.15
$Y_3Fe_5O_{12}$	101.50	63.51	−430.88	2	3	–	566	0	0