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Theoretical investigation on the magnetocaloric effect in the intermetallic Gd_4Sb_3

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ABSTRACT

In this work, we use the Monte Carlo method to calculate the magnetocaloric effect in Gd_4Sb_3 compound, which has second order ferro-paramagnetic phase transition near room temperature. The theoretically calculated isothermal entropy change and the adiabatic temperature change upon magnetic field variations are in good agreement with the available experimental data.

1. Introduction

The magnetocaloric effect (MCE), originally discovered by Warburg [1], is the capacity of some magnetic materials to heat up or cool down upon external magnetic field change. The MCE, which has great importance in the technology of magnetic refrigeration [2–4], is characterized by the isothermal entropy change (ΔS) and by the adiabatic temperature change (ΔT_{ad}) upon magnetic field variation. Besides the technological interest, the MCE provides fundamental information about the nature of magnetic ordering and the magnetic phase transition [5].

The magnetocaloric effect in the series of compounds $Gd_4(Bi_xSb_{1-x})_3$, whose crystalline structure belongs to the space group $I4\bar{3}d$, with the Gd atoms located at 16(c) [6], has been investigated by Niu et al. [7,8] considering the bismuth concentrations $x = 0, 0.25, 0.5, 0.75$and1.0. Experimental data show that these compounds exhibit a moderate MCE around 266 K. This important fact makes these compounds promise candidates to be used as magnetic refrigerant in magnetic refrigerators around room temperature [9]. Despite the large number of papers found in the literature, there is not yet a theoretical description of the magnetocaloric effect in this series of compounds. This fact together with the sizeable values of the magnetocaloric potentials ΔS and ΔT_{ad} around room temperature, are good motivations to theoretically study the magnetocaloric effect in the series of compounds $Gd_4(Bi_xSb_{1-x})_3$.

In the present paper, we theoretically study the magnetocaloric effect in the compound Gd_4Sb_3 by using a magnetic Hamiltonian that includes the exchange interaction between magnetic moments and the Zeeman effect.

In order to treat the two body interaction present in the model Hamiltonian, we used the Monte Carlo Simulation [10–13] and the mean field approximation. On the one hand, the mean field theory is the usual approximation to treat the two body interactions because of its simplicity. On the other hand, the theoretical investigation of the magnetocaloric effect in the compound Gd_4Sb_3, through the Monte Carlo simulation is very interesting because its magnetic and crystallographic structure [8] permits a construction of a proper boundary condition for magnetic lattice modeling.

Our calculations show that both approaches are able to explain the experimental data of the magnetocaloric effect. However, the mean field theory does not explain the magnetic part of the specific heat around the magnetic ordering temperature (T_C). At T_C, the magnetic specific heat calculated within the mean field approximation goes abruptly to zero in disagreement with experimental data. This inconsistency between the mean field theory and experiment occurs because it does not take into account short range interactions. This fact points out that the physical mechanisms involved in the MCE in Gd_4Sb_3 is better described in the Monte Carlo simulation.

2. Theory

We start with the following Hamiltonian:

$$\hat{H} = -2\sum_{l,m} J_{lm}\hat{\mathbf{S}}_l \cdot \hat{\mathbf{S}}_m - g\mu_B \sum_l \hat{\mathbf{S}}_l \cdot \mathbf{B}, \quad (1)$$

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where $J_{l,m}$ is the exchange interaction parameter, $\hat{\mathbf{S}}_l$ and $\hat{\mathbf{S}}_m$ are spin operators for the magnetic ions at l and m-sites, g is the Landé-factor, μ_B the Bohr magneton and $\mathbf{B}$ the external magnetic field.

In order to calculate the energy given in Eq. (1), via the Monte Carlo simulation, we use a Potts-like model [10–12], where the z components of the spins were considered as quantum quantities, which can assume discrete values in the interval $-S \leq S^z \leq S$. Within this consideration, the maximum value of the magnetic entropy is $S_{mag} = R\ln(2S+1)$, where R is the gas constant [10–12]. For a given temperature and magnetic field, the average energy $\langle\hat{H}\rangle$ is calculated by:

$$\langle\hat{H}\rangle = \frac{1}{(N_C - N_0)}\sum_{i=N_0+1}^{N_C} E_i, \tag{2}$$

where E_i is the energy of the last spin configuration of a given Monte Carlo step. N_C represents the total number of Monte Carlo steps and N_0 is the number of Monte Carlo steps used for thermalization. A similar relation holds for the average square energy $\langle H^2\rangle$. At a given temperature, the average magnetization per Gd-ion was calculated by $M/\text{ion} = g\mu_B\langle\hat{S}\rangle$, where the average value of the spin angular momentum, for each lattice site is given by:

$$\langle\hat{S}\rangle = \frac{1}{(N_C - N_0)}\sum_{i=N_0+1}^{N_C}\left(\frac{1}{N_S}\sum_{k=1}^{N_S}\hat{S}_k\right)_i \tag{3}$$

The label "i" represents the Monte Carlo cycle, the label "k" represents the lattice sites and N_S represents the number of lattice sites. The magnetic heat capacity C_{mag} per magnetic ions, is given by:

$$C_{mag}(T,B) = \frac{\langle\hat{H}^2\rangle - \langle\hat{H}\rangle^2}{\kappa_B T^2}. \tag{4}$$

The contribution from the conduction electrons is $C_{el} = \gamma T$, where γ is the Sommerfeld coefficient; C_{lat} is the contribution from the crystalline lattice, which is in the Debye approximation given by:

$$C_{lat}(T) = 9RN_i\left[4\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3}{(e^x-1)}dx - \frac{\theta_D}{T}\frac{1}{(e^{\theta_D/T}-1)}\right], \tag{5}$$

where N_i is the number of ions per formula unit and θ_D is the Debye temperature. The total heat capacity is given by $C(T,B) = C_{mag}(T,B) + C_{lat}(T) + C_{el}(T)$. The total entropy of the compound $S(T,B) = S_{mag}(T,B) + S_{lat}(T) + S_{el}(T)$ is obtained in terms of total heat capacity (C) by:

$$S(T,B) = \int_0^T \frac{C(T',B)}{T'}dT'. \tag{6}$$

In the mean field approximation, the magnetization is also calculated by $M/\text{ion} = g\mu_B\langle\hat{S}\rangle$, where now the average $\langle\hat{S}\rangle$ is calculated in terms of the Brillouin function. In the absence of the crystalline electrical field, the magnetic entropy can be written as [5]

$$S_{mag}(T,B) = N_m R\left[\ln Z - xB_S(x)\right], \tag{7}$$

where $Z = [\sinh((2S+1)/(2S)x)][\sinh(x/2S)]^{-1}$ is the partition function; B_S is the Brillouin function, and $x = [g\mu_B B + J_{MFA}\langle\hat{S}\rangle]/(\kappa_B T)$ where J_{MFA} is the exchange interaction parameter. In the mean field approximation, $S_{lat}(T)$ and $S_{el}(T)$ are also obtained respectively in terms of $C_{lat}(T)$ and $C_{el}(T)$ by the second law of thermodynamics.

In the Monte Carlo simulations and mean field approximation, the quantities ΔS and ΔT_{ad} upon magnetic field variation are calculated respectively from $\Delta S = S(T, B\neq 0) - S(T, B = 0)$ and $\Delta T_{ad} = T_2 - T_1$ under the adiabatic condition $S(T_2, B\neq 0) = S(T_1, B = 0)$.

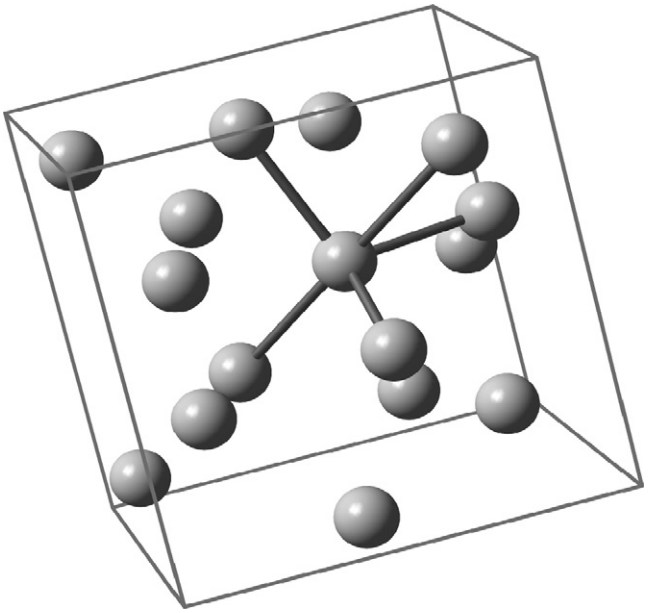

Fig. 1. Cubic structures in $I4\bar{3}d$ space group symmetry with 16 Gd atoms. The Sb atoms were not represented. The connections among a selected Gd atom and their nearest neighbors and next-nearest neighbors were shown.

3. Numerical results

In order to calculate the average energy and consequently the magnetocaloric potentials ΔS and ΔT_{ad} in Gd_4Sb_3 by Monte Carlo simulations, we use a tridimensional cluster of $5\times5\times5$ cubic unit cells. Each unit cell has 16 atoms of Gd arranged in such a way to compose a cubic structure in $I4\bar{3}d$ space group symmetry [6,8]. This cubic structure is presented in Fig. 1, where only the Gd atoms are shown. Each Gd atom has three nearest neighbors (NN) and two next-nearest neighbors (NNN); the Fig. 1 shows the connections between a selected Gd atom and their NN and NNN. The selected atom and its two next-nearest neighbors are positioned on a same straight line, along the diagonal of the cube. The crystal lattice structure formed by 125 unit cells has periodic connectivity, showing no edge effect. In this calculation, only the interactions between the nearest and next-nearest neighbors were considered. The exchange interaction parameters for nearest and next-nearest neighbors interactions in Gd_4Sb_3, used in the Monte Carlo simulation were taken as $J_{lm} = 1.34$ meV and $J_{lm} = 0.788$ meV, respectively. In the mean field model the effective exchange parameter used was $J_{MFA} = 19.5$ meV. The Landé factor was taken as $g = 2$ and the spin momentum of Gd as $S = 7/2$.

For a given temperature, we perform Monte Carlo simulation using 50,000 Monte Carlo steps, where 25,000 were used for thermalization of the system and 25,000 were used to compute the average values of the physical quantities. The average values of the energy and spin were calculated from Eqs. (2) and (3). The magnetic part of the heat capacity was calculated using Eq. (4) and the magnetic entropy was obtained from Eq. (6). The electronic heat capacity was calculated using $\gamma = 5.4\,\text{mJ/mol K}^2$ and the lattice heat capacity and entropy were calculated using $\theta_D = 200$ K. These parameters are in the usual range of values used in literature [5].

In Fig. 2, we plot the total heat capacity, per Gd ion, in the absence of applied magnetic field. The solid triangles represent the Monte Carlo results, the solid line represents the mean field results and the open triangles, the experimental data [7,8]. The inset represents the theoretical results and experimental data (open symbols) for the total heat capacity in the presence of applied magnetic field

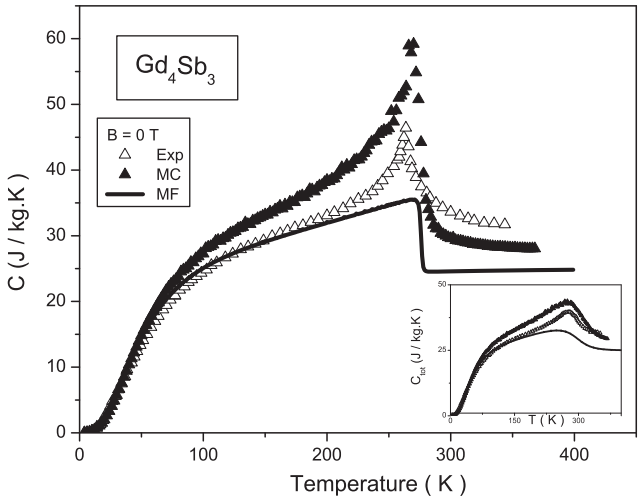

Fig. 2. Total heat capacity for $B = 0$. The solid triangles (solid lines) represent the Monte Carlo simulations (mean field calculations). Open triangles, the experimental data [7,8]. The inset represents the theoretical results and experimental data (open symbols) for B=5 T.

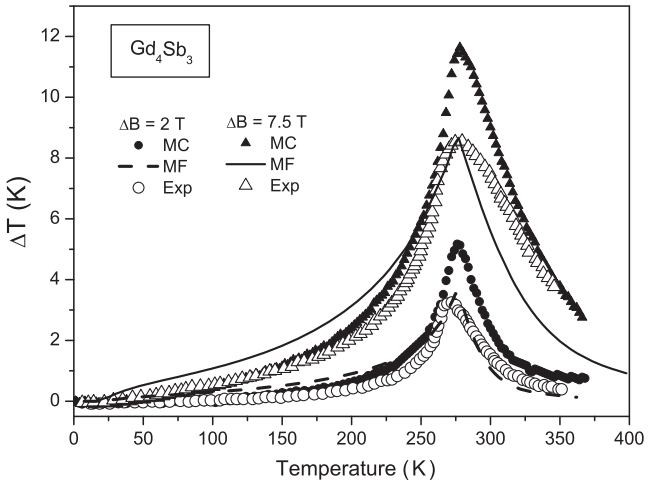

Fig. 4. ΔT_{ad} in Gd_4Sb_3 calculated using Monte Carlo simulation for ΔB=2 T (solid circles) and ΔB=7.5 T (solid triangles). The corresponding mean field calculations (experimental data) are shown by dotted (open circles) and solid lines (open triangles), respectively.

of 5 T. A good agreement between the results and the experimental data was obtained. At T_C, the magnetic specific heat calculated within the molecular field approximation goes abruptly to zero in disagreement with experimental data. This can be ascribed to the short range interactions which are not considered in the mean field approach [5]. Using the temperature dependence of the total entropy for the following variations of applied magnetic field: $\Delta B = 2$ T, $\Delta B = 5$ T, $\Delta B = 7.5$ T and $\Delta B = 10$ T, we calculate both the isothermal entropy change and the adiabatic temperature change. In Figs. 3 and 4, we plot the isothermal entropy change ($-\Delta S$) and the adiabatic temperature change (ΔT_{ad}) under magnetic field variations from zero to 2 T and from zero to 7.5 T, where solid circles and triangles represents the Monte Carlo results for $\Delta B = 2$ T and $\Delta B = 7.5$ T. The dotted and solid lines represents the mean field calculations for $\Delta B = 2$ T and $\Delta B = 7.5$ T, respectively. We also plot in these figures the experimental data [7,8]: open triangles represents $\Delta B = 2$ T and the open circles, $\Delta B = 7.5$ T. The maximum values of the MCE potentials, ΔS and ΔT_{ad}, occurs near the magnetic ordering temperature (T_C~266 K). Both theoretical results are in agreement with the experimental data. In Figs. 5 and 6, we

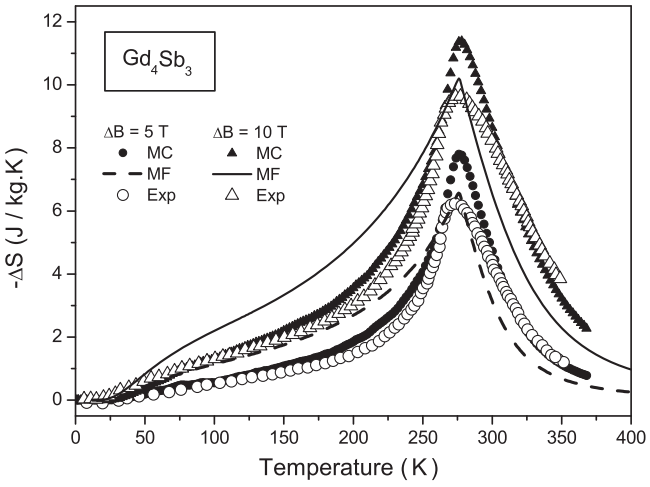

Fig. 5. ΔS in Gd_4Sb_3 calculated using Monte Carlo simulation for ΔB=5 T (solid circles) and ΔB=10 T (solid triangles). The corresponding mean field calculations (experimental data) are shown by dotted (open circles) and solid lines (open triangles), respectively.

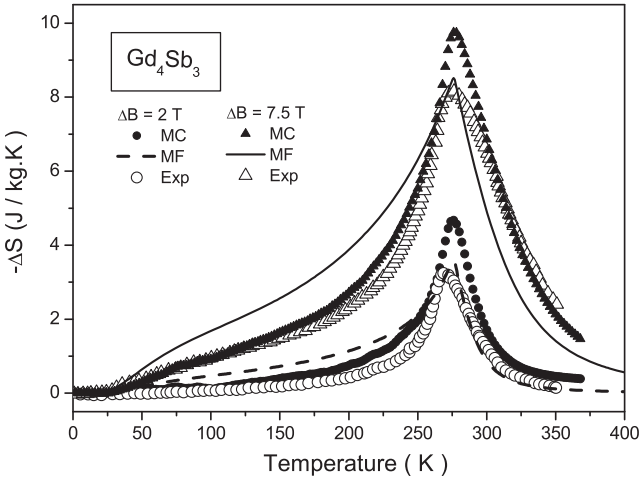

Fig. 3. ΔS in Gd_4Sb_3 calculated using Monte Carlo simulation for ΔB=2 T (solid circles) and ΔB=7.5 T (solid triangles). The corresponding mean field calculations (experimental data) are shown by dotted (open circles) and solid lines (open triangles), respectively.

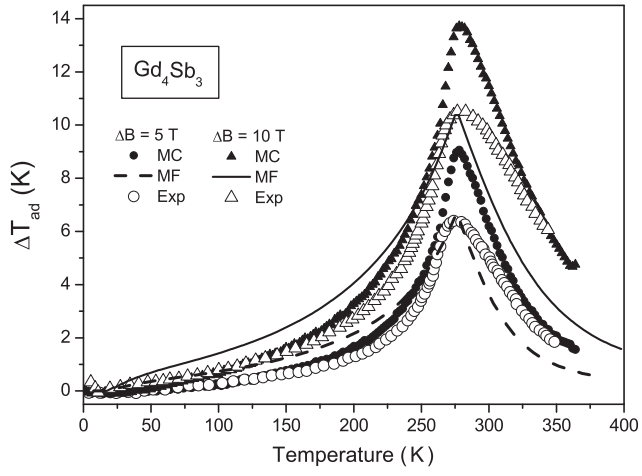

Fig. 6. ΔT_{ad} in Gd_4Sb_3 calculated using Monte Carlo simulation for $\Delta B = 5$ T (solid circles) and $\Delta B = 10$ T (solid triangles). The corresponding mean field calculations (experimental data) are shown by dotted (open circles) and solid lines (open triangles) respectively.

plot the isothermal entropy change and the adiabatic temperature change under magnetic field variations from zero to 5 T and from zero to 10 T. Again, we observed a good agreement between the theoretical results and the experimental data. The calculations confirm that the mean field approximation yields reasonable results for the magnetocaloric potentials ΔS and ΔT_{ad} but it fails in explaining the experimental data of specific heat around magnetic ordering temperature. In contrast, the Monte Carlo calculation describes well both the ΔS and ΔT_{ad} quantities, as well as the specific heat capacity.

4. Conclusions

In conclusion, in this work we discuss the magnetocaloric effect in Gd_4Sb_3, by using a Hamiltonian of interacting spins, where the spin–spin interaction was treated both in the Monte Carlo simulation and in the mean field approximation. The results with Monte Carlo simulations and mean field approach are in agreement with the available experimental data. Since the Monte Carlo calculations is much more time consuming than the mean field theory, the mean field theory can be used as a first attempt to obtain the trend of the magnetocaloric quantities. However, for a more realistic description of the physical mechanism involved in the magnetocaloric effect of Gd_4Sb_3 we should use the Monte Carlo calculations. This work is the starting point for the description of the magnetocaloric effect in the series $Gd_4(Bi_xSb_{1-x})_3$, where an antiferromagnetic phase appears as we increase the concentration of Bi.

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