The magnetocaloric effect in R_5Si_4 (R = Gd, Tb): a Monte Carlo calculation

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Abstract
In this work we calculate the magnetocaloric effect in the compounds Gd_5Si_4
and Tb_5Si_4. We use a model Hamiltonian of interacting spins, and treat
the spin–spin interaction in the Monte Carlo simulation. The theoretically
calculated isothermal entropy change and the adiabatic temperature change
upon variation of the magnetic field are in good agreement with the available
experimental data.

The magnetocaloric effect [1–4] is characterized by an isothermal entropy change upon
variation of the magnetic field, $\Delta S(T) = S(T, h^{\text{ext}} \neq 0) - S(T, h^{\text{ext}} = 0)$, and by a
temperature change $\Delta T_{\text{ad}}(T) = T_2 - T_1$ determined under the adiabatic condition $S(T_2, h^{\text{ext}} \neq 0) = S(T_1, h^{\text{ext}} = 0)$. The magnetocaloric effect has been experimentally investigated in both
rare earth compounds [5–14] and in transition metal compounds [15–20]. The rare earth metals
and their alloys are the most studied materials because of their large magnetic moments and
because of their magnetic ordering temperatures, which lie in the temperature interval from
0 to 350 K. The magnetocaloric effect in the series $Gd_5(Si_xGe_{1-x})_4$ and $Tb_5(Si_xGe_{1-x})_4$
has been intensively studied [5–14]. It has been shown that for $x > 0.5$ the compounds
$Gd_5(Si_xGe_{1-x})_4$ have an orthorhombic phase and undergo a second-order magnetic phase
transition. In this range of concentration the maximum value of the isothermal entropy
change upon variation of the magnetic field from 0 to 5 T is about 10 J kg^{-1} K^{-1}. The
compounds $Gd_5(Si_xGe_{1-x})_4$, for $x < 0.5$, exhibit a crystallographic transformation from
the orthorhombic to the monoclinic phase around the magnetic ordering temperature, and
undergo a first-order magnetic phase transition. As a result they exhibit large isothermal
entropy changes. The discovery of the giant magnetocaloric effect [5–7] in the compound
$Gd_5(Si_2Ge_2)$ at room temperature has made it a potential candidate for use as a magnetic
refrigerant in room temperature magnetic refrigerators. The magnetocaloric properties of the
series $Tb_5(Si_xGe_{1-x})_4$ are very similar [12–14] to those observed for $Gd_5(Si_xGe_{1-x})_4$. For
instance, for $x = 1$ the compound Tb_5Si_4 also crystallizes in the orthorhombic phase and

exhibits a second-order magnetic phase transition around 223 K. The isothermal entropy change around the magnetic ordering temperature for Tb_5Si_4 upon variation of the magnetic field from 0 to 5 T is about 10 J kg^{-1} K^{-1}.

From the theoretical point of view, the magnetocaloric effect in rare earth based compounds undergoing a second-order magnetic phase transition is usually described using the Heisenberg model Hamiltonian in which the spin–spin interaction is treated in the molecular field approximation [21–33]. In cases of rare earth compounds undergoing a first-order magnetic phase transition it is necessary to include an extra term in the Heisenberg model Hamiltonian, to account for the magnetoelastic coupling [29].

It is well known that around the magnetic ordering temperature the magnetic part of the specific heat calculated within molecular field theory is in disagreement with experimental data. This is an artefact of the mean field theory which does not consider short-range interactions. Nevertheless, the magnetocaloric quantities for rare earth based compounds obtained within molecular field theory are usually in good agreement with experimental data. This is because in when calculating the magnetocaloric quantities through the integral of the heat capacity there are some compensations so that the final results are very reasonable. Therefore, in order to understand the real physical mechanisms behind the magnetocaloric effect in rare earth based compounds it is very important to go beyond mean field theory to incorporate short-range interactions.

In this work we calculate the magnetocaloric effect in the compounds R_5Si_4 (R = Gd, Tb) using a model of localized interacting spins in which the spin–spin interaction is treated within the classical Monte Carlo simulation [34, 35]. We start with the following energy:

$$E = -\sum_{ij} \lambda_{ij} \vec{J}_i \cdot \vec{J}_j + \sum_i \zeta_i (\vec{r}_i \cdot \vec{J}_i)^2 - \sum_i g\mu_B \vec{J}_i \cdot h^{ext} \tag{1}$$

where $\langle ij \rangle$ run over the first next neighbours. In the above energy the first term is the contribution from the spin–spin interaction, where λ_{ij} is the exchange interaction parameter and J_i is the total angular momentum of the rare earth ions. The second term is the single ion anisotropy, where the vector $\vec{r}_i$ is the direction of the anisotropy and ζ_i is an anisotropic coefficient. The third term is the Zeeman interaction of the total angular momentum with an external magnetic field (h^{ext}). We consider the z components of the total angular momentum (J^z) as quantum quantities, which can assume discrete values in the interval $[-J, J]$. For a given J^z, the transverse components J^x and J^y were randomly chosen under the condition $(J^x)^2 + (J^y)^2 = J^2 - (J^z)^2$. Within this approach we restrict the number of available states so that the upper limit of the magnetic entropy $S_{mag} = \Re \ln(2J + 1)$, where $\Re$ is the gas constant, is reproduced.

To calculate the mean energy for a Monte Carlo cycle we use the following algorithm. We randomly generate an initial configuration of total angular momentum and calculate the energy of this initial configuration (E_I) according to equation (1). Then, we select a given site 'i', change the components of the total angular momentum and calculate the energy for this new configuration (E_F) according to equation (1). If $E_F < E_I$ the new configuration with energy E_F is accepted. If $E_F > E_I$, we generate a random number r such that $0 < r < 1$ and calculate the probability factor $p = e^{-\beta(E_F - E_I)}$, where $\beta = 1/k_B T$, k_B being the Boltzmann constant. If $r < p$ the new configuration of total angular momentum with energy E_F is accepted, otherwise the old configuration with energy E_I is preserved. We move to the next site, change the value of the components of the total angular momentum, calculate the new energy (E_F) and make the comparison between E_I and E_F to choose between the old and the new configuration. This process is repeated until all the lattice sites have been swept. To obtain reasonable values of the physical quantities, it is necessary to run thousands of Monte Carlo cycles. For a given

temperature, the mean value of the energy $\langle E \rangle$ is calculated by:

$$\langle E \rangle = \frac{1}{(N_C - N_0)} \sum_{i > N_0}^{N_C} E_i \tag{2}$$

where N_C represents the total number of Monte Carlo cycles and N_0 is the number of Monte Carlo cycles used for thermalization. The mean square energy $\langle E^2 \rangle$ is obtained by a relation similar to equation (2). At a given temperature, the average magnetization per rare earth ion is calculated by $M/\text{ion} = g \mu_B \langle J \rangle$, where the mean value of the total angular momentum per lattice site is calculated from:

$$\langle J \rangle = \frac{1}{(N_C - N_0)} \sum_{i > N_0}^{N_C} \left(\frac{1}{N_S} \sum_{k=1}^{N_S} J_k \right) \tag{3}$$

where 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 total heat capacity is made up of the contribution from the conduction electrons (C_{el}), from the crystalline lattice (C_{lat}) and from the magnetic ions.

The magnetic part of the heat capacity is calculated from

$$C_{mag}(T, h^{ext}) = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2}. \tag{4}$$

The contribution from the conduction electrons is taken as $C_{el} = \gamma T$, where γ is the Sommerfeld coefficient. The lattice heat capacity is given, in the Debye approximation, by [36]:

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

where N_i is the number of ions per formula unit and Θ_D is the Debye temperature. The total entropy is the sum of the contributions from the crystalline lattice (S_{lat}), from the magnetic (S_{mag}) ions and from the electron gas (S_{el}). The contribution from the magnetic ions to the total entropy is given by:

$$S_{mag}(T, h^{ext}) = \int_0^T \frac{C_{mag}(T, h^{ext})}{T} \, dT \tag{6}$$

where C_{mag} is the magnetic heat capacity calculated in equation (4). The contribution from the electron gas to the total entropy is taken as $S_{el} = \gamma T$. The lattice contribution to the total entropy, in the Debye approximation, is given by [31, 32]:

$$S_{lat}(T) = N_i \left[-3 \Re \ln \left(1 - e^{-\frac{\Theta_D}{T}} \right) + 12 \Re \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} \, dx \right]. \tag{7}$$

To apply the Monte Carlo method to calculate the magnetocaloric effect in Gd_5Si_4 and Tb_5Si_4 we use a three-dimensional cluster of $6 \times 6 \times 6$ orthorhombic cells with eight R atoms per cell (R = Gd or Tb). The Landé factor and the total angular momentum were taken as $g = 2$; $J = 7/2$ for Gd and $g = 1.5$; $J = 6$ for Tb. The set of exchange interaction parameters λ_{ij} was chosen to correctly reproduce the experimental data of the magnetic ordering temperature, around 336 K (223 K) for Gd_5Si_4 (Tb_5Si_4). Here we take $\lambda_{ij} = 0.294$ meV for the compound Tb_5Si_4 and $\lambda_{ij} = 1.205$ meV for the compound Gd_5Si_4. The anisotropic coefficients for Gd and Tb ions were respectively taken as $\zeta = 0$ and $\zeta = 0.0294$ meV. In order to establish the magnitude of the z components of the total angular momentum of the rare earth ions at each lattice site we proceed as follows: we draw a random number r such that $0 < r < 1$
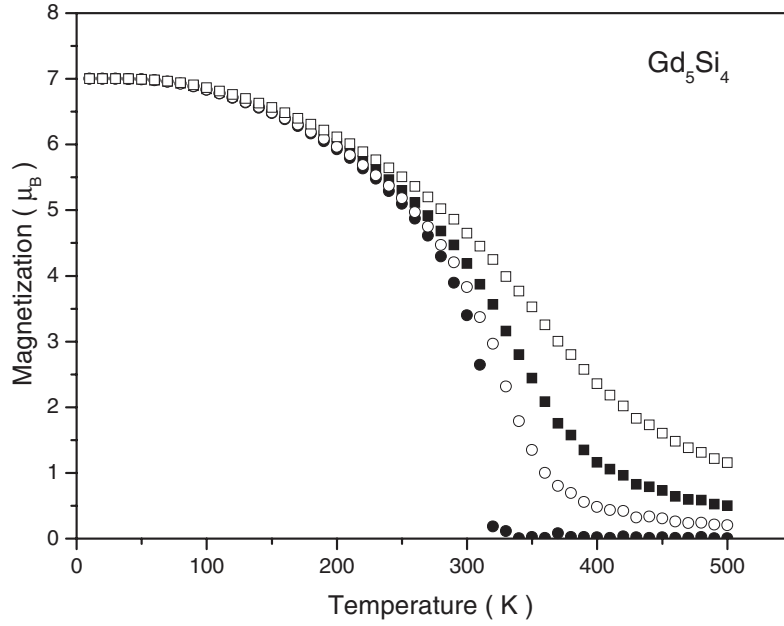
Figure 1. Temperature dependence of the magnetization of Gd$_5$Si$_4$ per Gd ion. Solid circles, open circles, solid squares and open squares represent the Monte Carlo calculations for $h^{\text{ext}} = 0$, $h^{\text{ext}} = 2$ T, $h^{\text{ext}} = 5$ T and $h^{\text{ext}} = 12$ T.

and fix the value of J^z according to the following scheme. If the random number (r) lies in the interval $[0, 1/(2J + 1)]$ we take $J^z = -J$. If the random number (r) lies in the interval $[1/(2J + 1), 2/(2J + 1)]$ we take $J^z = -J + 1$, and so on. In the general case if the random number lies in the interval $[(n - 1)/(2J + 1), n/(2J + 1)]$ we take $J^z = -J + (n - 1)$, where n is a integer number between 1 and $2J + 1$. The transverse components J^x and J^y were randomly established under the condition $(J^x)^2 + (J^y)^2 = J^2 - (J^z)^2$. We perform Monte Carlo calculations, using 4000 Monte Carlo cycles to obtain thermalization of the system. After thermalization we perform 3000 more Monte Carlo cycles to compute the average values of the physical quantities. Once the mean values $\langle E \rangle$, $\langle E^2 \rangle$ and $\langle J \rangle$ are obtained, we calculate the magnetization, the magnetic part of the heat capacity and the magnetic entropy. The lattice heat capacity for Gd$_5$Si$_4$ and Tb$_5$Si$_4$ was calculated from equation (5) using $\Theta_D = 350$ K and the electronic heat capacity was calculated from $C_{\text{el}} = \gamma T$ where $\gamma = 5.4$ mJ mol^{-1} K^{-2}. The parameters γ and Θ_D are in the usual range of values found in the literature [21].

In figures 1 and 2, we respectively plot the temperature dependence of the magnetization of the compounds Gd$_5$Si$_4$ and Tb$_5$Si$_4$ calculated for $h^{\text{ext}} = 0$ T (solid circles), $h^{\text{ext}} = 2$ T (open circles), $h^{\text{ext}} = 5$ T (solid squares) and $h^{\text{ext}} = 12$ T (open squares). In figures 3 and 4 we respectively plot the total heat capacity ($C = C_{\text{mag}} + C_{\text{el}} + C_{\text{lat}}$) of the compounds Gd$_5Si_4$ and Tb$_5$Si$_4$ for $h^{\text{ext}} = 0$ T (solid lines), $h^{\text{ext}} = 2$ T (dashed lines) and $h^{\text{ext}} = 5$ T (dotted lines). From figure 4 we can observe a good agreement between our Monte Carlo calculations and the available experimental data [12] of the total heat capacity for the compound Tb$_5$Si$_4$. In figure 5, we plot the magnetic entropy for the compounds Gd$_5$Si$_4$ and Tb$_5$Si$_4$ obtained within the Monte Carlo calculations for $h^{\text{ext}} = 0$ T (solid circles), $h^{\text{ext}} = 2T$ (open circles), $h^{\text{ext}} = 5$ T (solid squares) and $h^{\text{ext}} = 12$ T (open triangles). From this figure we can observe that the calculated saturation values of the magnetic entropy, $S_{\text{mag}} = 17$ J mol^{-1} K^{-1} for Gd$_5$Si$_4$ and $S_{\text{mag}} = 21$ J mol^{-1} K^{-1} for Tb$_5$Si$_4$, are consistent with the maximum expected value of the
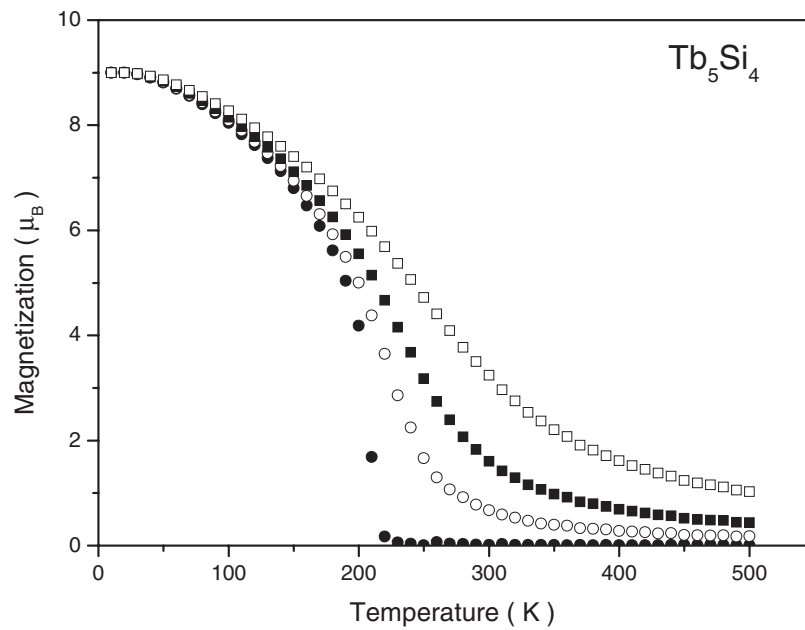
Figure 2. Temperature dependence of the magnetization of Tb_5Si_4 per Tb ion. Solid circles, open circles, solid squares and open squares represent the Monte Carlo calculations for $h^{ext} = 0$, $h^{ext} = 2$ T, $h^{ext} = 5$ T and $h^{ext} = 12$ T.
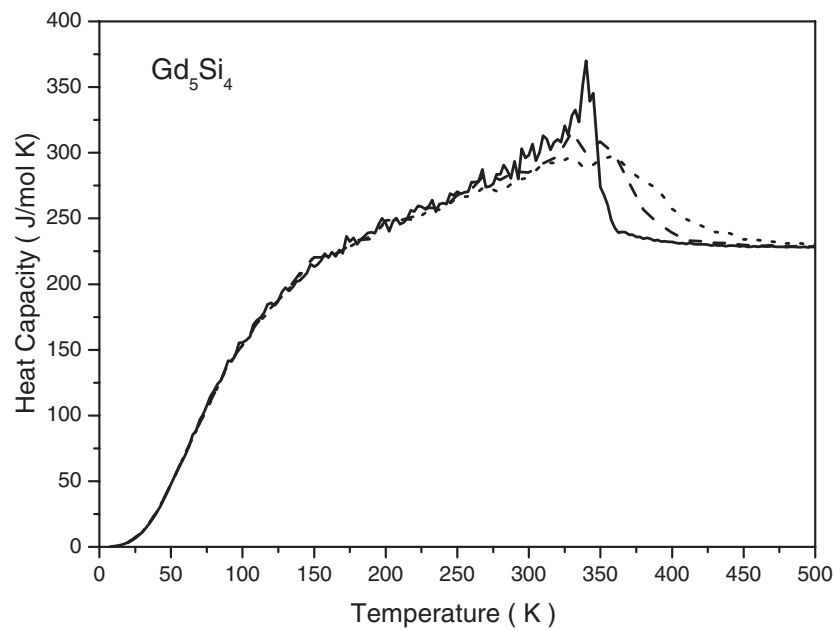

Figure 3. Total heat capacity of the compound Gd_5Si_4. Solid, dashed and dotted lines represent the Monte Carlo calculations for $h^{ext} = 0$, $h^{ext} = 2$ T and $h^{ext} = 5$ T, respectively.

magnetic entropy $S_{mag} = \Re \ln(2J + 1)$. In addition, we observe that around the magnetic ordering temperature, the magnetic entropy curves increase smoothly. This kind of behaviour
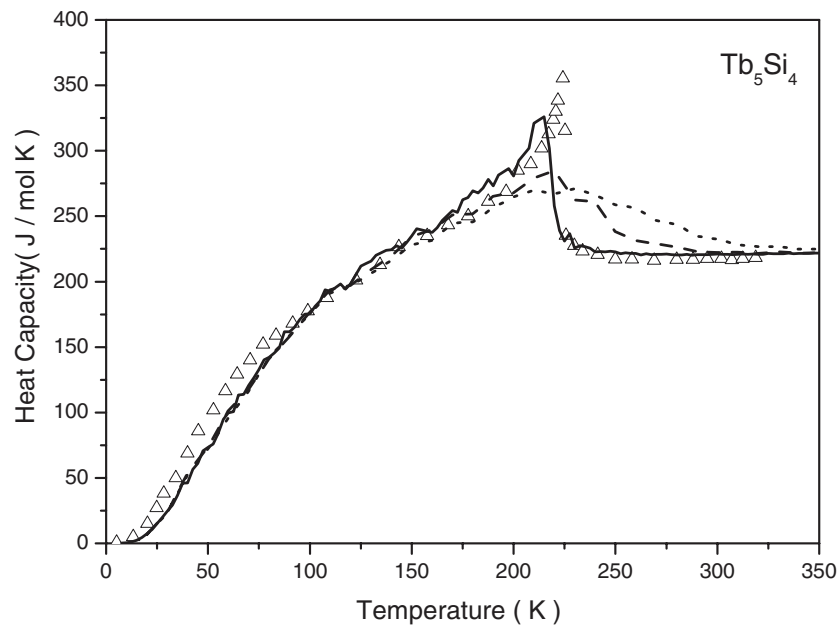
Figure 4. Total heat capacity of the compound Tb_5Si_4. Solid, dashed and dotted lines represent the Monte Carlo calculations for $h^{ext} = 0$, $h^{ext} = 2$ T and $h^{ext} = 5$ T, respectively. Open triangles are experimental data [12] for $h^{ext} = 0$.
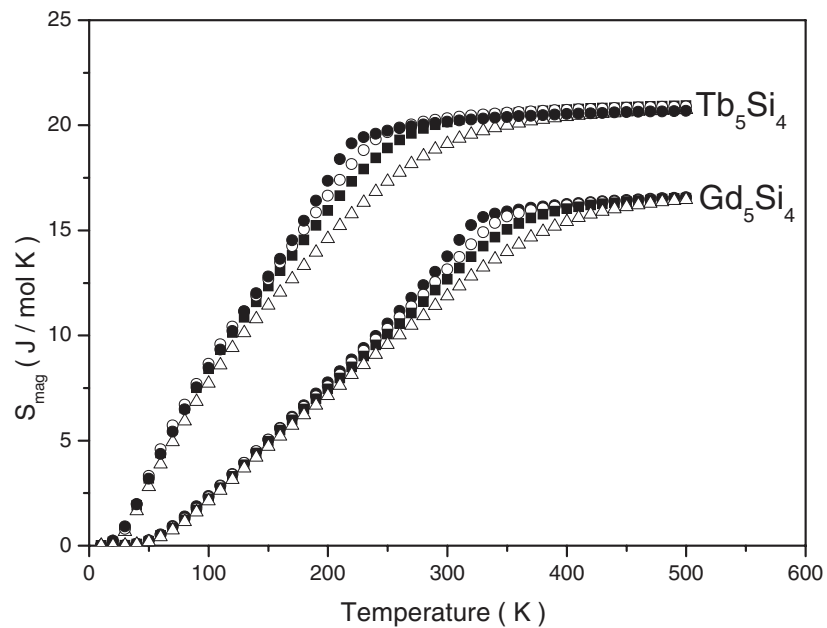

Figure 5. Magnetic entropy of the compounds Gd_5Si_4 and Tb_5Si_4. Solid circles, open circles, solid squares and open triangles represent the Monte Carlo calculations for $h^{ext} = 0$, $h^{ext} = 2$ T, $h^{ext} = 5$ T and $h^{ext} = 12$ T.

in the magnetic entropy, which is usually observed in experimental data, is not observed in theoretical calculations within the mean field approach.
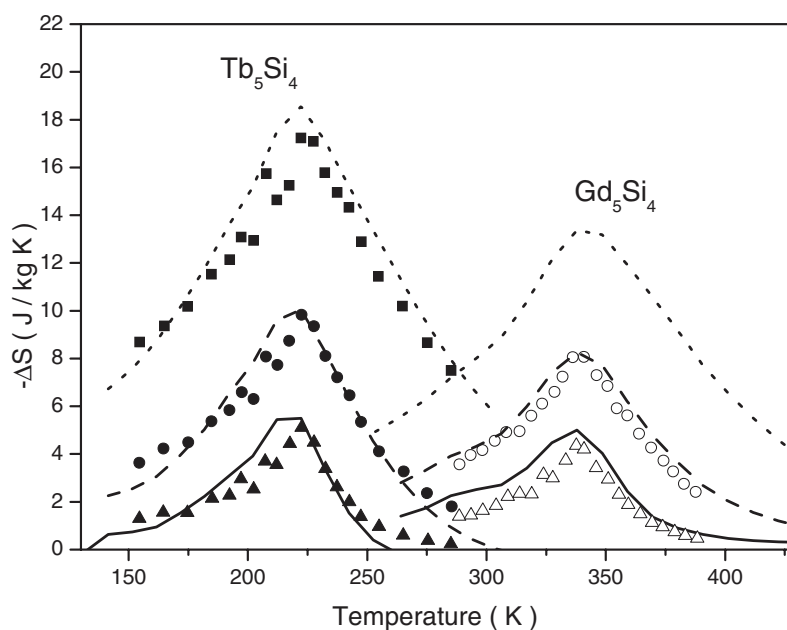
Figure 6. Isothermal entropy change in the compounds Gd_5Si_4 and Tb_5Si_4 for magnetic field variations from 0 to 2 T (solid lines), from 0 to 5 T (dashed lines) and from 0 to 12 T (dotted lines). Open triangles and open circles are experimental data [11, 12] for Gd_5Si_4 upon variation of the magnetic field from 0 to 2 T and from 0 to 5 T. The experimental data [13] for Tb_5Si_4 upon variation of the magnetic field from 0 to 2 T, from 0 to 5 T and from 0 to 12 T are respectively represented by solid triangles, solid circles and solid squares.

From the heat capacity curves, we calculate the total entropy for $h^{ext} = 0$, $h^{ext} = 2$ T, $h^{ext} = 5$ T and $h^{ext} = 12$ T. Using the temperature dependence of the total entropy, not shown in this paper, we calculated both the isothermal entropy change and the adiabatic temperature change for some magnetic field variations. In figure 6 we plot the calculated isothermal entropy change for the compounds Gd_5Si_4 and Tb_5Si_4 upon variation of the magnetic field from 0 to 2 T (solid line); from 0 to 5 T (dashed line) and from 0 to 12 T (dotted line). From this figure we can observe that for the compound Gd_5Si_4 the calculated isothermal entropy changes upon variation of the magnetic field from 0 to 2 T and from 0 to 5 T are in very good agreement with the available experimental data [11, 12]. From figure 6 we can observe that our calculated isothermal entropy changes for the compound Tb_5Si_4 are also in good agreement with experimental data [13]. In figure 7 we plot the calculated adiabatic temperature changes for the compounds Gd_5Si_4 and Tb_5Si_4 upon variations of the magnetic field from 0 to 2 T (solid line), from 0 to 5 T (dashed line) and from 0 to 12 T (dotted line). From this figure we can observe that the adiabatic temperature change upon variation of the magnetic field from 0 to 5 T for the compound Gd_5Si_4 is in good agreement with the available experimental data [11] (open triangles). Further experimental data are necessary to confirm our theoretical predictions for the other magnetic field variations and for the compound Tb_5Si_4.

In conclusion, in this work we have calculated the magnetocaloric effect in the compounds Gd_5Si_4 and Tb_5Si_4 using a model of interacting spins, where the spin–spin interaction is treated in the Monte Carlo simulation. The calculated curves for the isothermal entropy change and the adiabatic temperature change upon variation of the magnetic field are in good agreement with the available experimental data. Our present Monte Carlo calculations not only provide good
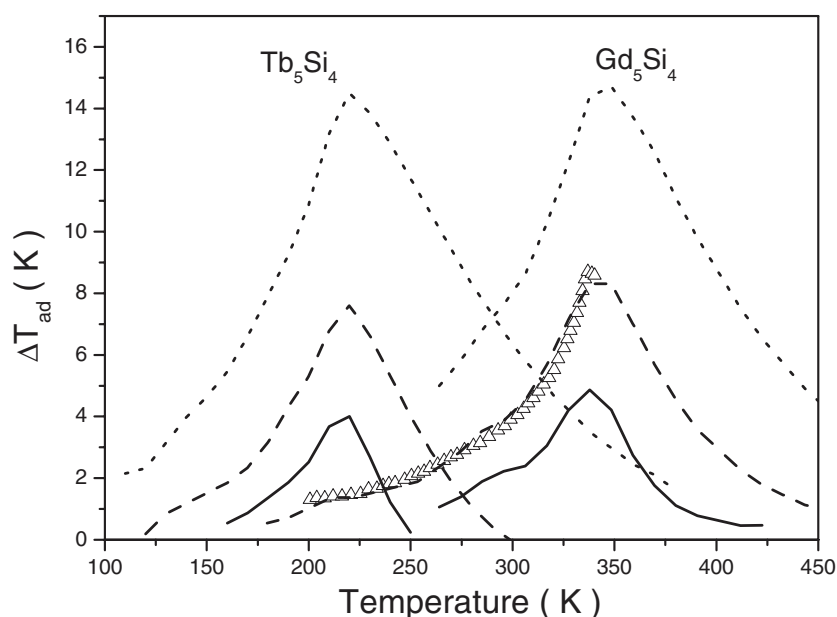
Figure 7. Adiabatic temperature change in the compounds Gd_5Si_4 and Tb_5Si_4 for variation of the magnetic field from 0 to 2 T (solid lines), from 0 to 5 T (dashed lines) and from 0 to 12 T (dotted lines). Open triangles are experimental data [11] for Gd_5Si_4 upon variation of the magnetic field from 0 to 5 T.

values for the magnetocaloric quantities ΔS and ΔT_{ad} over the whole range of temperature but also provide better values of the heat capacity around the magnetic ordering temperature, as compared with the values obtained within the mean field approximation. Therefore, the present paper based on the Monte Carlo simulation makes an important step forward in the theoretical description of magnetocaloric quantities in rare earth based compounds.

Acknowledgments

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