Magnetic couplings and magnetocaloric effect in the GdTX (T=Sc, Ti, Co, Fe; X=Si, Ge) compounds

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Abstract
We compute the magnetocaloric effect (MCE) in the GdTX (T = Sc, Ti, Co, Fe; X = Si, Ge) compounds as a function of the temperature and the external magnetic field. To this end we use a density functional theory approach to calculate the exchange–coupling interactions between Gd3+ ions on each compound. We consider a simplified magnetic Hamiltonian and analyze the dependence of the exchange couplings on the transition metal T, the p-block element X, and the crystal structure (CeFeSi-type or CeScSi-type). The most significant effects are observed for the replacements Ti → Sc or Fe → Co which have an associated change in the parity of the electron number in the three dimensional level. These replacements lead to an antiferromagnetic contribution to the magnetic couplings that reduces the Curie temperature and can even lead to an antiferromagnetic ground state. We solve the magnetic models through mean field and Monte Carlo calculations and find large variations among compounds in the magnetic transition temperature and in the magnetocaloric effect, in agreement with the available experimental data. The magnetocaloric effect shows a universal behavior as a function of temperature and magnetic field in the ferromagnetic compounds after a scaling of the relevant energy scales by the Curie temperature $T_C$.

Keywords: magnetocaloric effect, RTX compounds, DFT, Monte Carlo

(Some figures may appear in colour only in the online journal)

1. Introduction
Gadolinium based compounds, in particular those in the GdTX family [1], have been the subject of numerous theoretical [2–5] and experimental [6–11] studies because of their potential use in refrigeration at room temperature using the magnetocaloric effect. The strong magnetocaloric properties of Gd systems are due to the large spins in the 4f Gd3+ ions and the exchange couplings between them that lead to magnetic phase transitions. A giant magnetocaloric effect is observed in Gd(Si2Ge2) at room temperature, associated with the presence of a first order ferromagnetic (I) ⇔ ferromagnetic (II) transition at $T \simeq 276$ K [12]. Pure gadolinium, which is also a strong magnetocaloric material at room temperature, presents a second order Curie transition at $T_C = 294$ K to a ferromagnetic ground state.

The magnetocaloric effect (MCE) is generally quantified by the entropy change $\Delta S_{\text{MCE}} = S(H) - S(0)$, when an external magnetic field $H$ is applied. To obtain a large MCE a high sensitivity of the material to magnetic field changes is required. This is the case, e.g., for temperatures close to a paramagnetic–ferromagnetic transition temperature where the MCE acquires its maximum values. For magnetic cooling applications it is important to maximize the MCE at the operation temperatures. A route to attain this goal is to control the magnetic transition temperature through the magnetic couplings.
which are determined by the conduction band structure and its occupancy.

The ternary RTX compounds (where R is a rare earth, T is a transition metal and X is a p-block element such as Si, Ge, Sb) present several examples of large MCE compounds. GdFeSi is a ferromagnet below $T_C = 118$K where the MCE attains its maximum value $\Delta S_M = -22.3$ J kg$^{-1}$K$^{-1}$.$^{3}$GdScSi and GdScGe are also ferromagnets with $T_C = 318$ K and $\Delta S_M = -2.5$ J kg$^{-1}$K$^{-1}$ and $T_C = 320$ K and $\Delta S_M = -3.3$ J kg$^{-1}$K$^{-1}$ for $\Delta H = 2$Tesla, respectively. GdCoSi is however an antiferromagnet with $T_N = 220$ K and a low MCE.$^{13–16}$

Among the variety of RTX crystal structures, we will focus on the tetragonal CeFeSi-type (space group $I4_1/mmm$) and CeScSi-type (space group $I4/mmm$) $R–X–T–X–R$ structures (see figure 1) and analyze the role of T and X in the magnetic properties for the $R =$ Gd case. As we show below, the results of this analysis will prove helpful interpreting the experimental results for other rare earths.

2. Magnetic ground state and coupling constants

We performed density functional theory (DFT) total-energy calculations of the GdTX ($T = \text{Sc, Ti, Co, Fe}; X = \text{Si, Ge}$) compounds which indicate a ground state with magnetic moments localized at the Gd$^{3+}$ ions and allowed us to estimate the strength of the Gd–Gd magnetic interactions. We solved the resulting magnetic model to obtain the magnetic contribution to the specific heat, the magnetocaloric effect, and the Néel or Curie transition temperature.

2.1. Technical details of the DFT calculations

The total-energy calculations were performed using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof for the exchange and correlation functional as implemented in the WIEN2k code.$^{17,18}$ A local Coulomb repulsion was included in the Gd 4f shell and treated using GGA+$U$ which is a reasonable approximation for these highly localized states. Due to the localized character of the 4f electrons, the fully localized limit was used for the double counting correction$^{19}$. We described using the DFT+$U$ approximation the local Coulomb and exchange interactions with a single effective local repulsion $U_{eff} = U - J_{H} = 6$ eV, which has been successfully used in bulk Gd and other Gd compounds.$^{20–25}$ The APW + local orbitals method of the WIEN2k code was used for the basis functions$^{17}$. We used 1200 $k$-points in the Bloch zone for the full optimization of the crystal structures, and 200 $k$-points for the $2 \times 2 \times 2$ supercell total-energy calculations of the different magnetic configurations. The magnetic moments are localized on the Gd 4f orbitals and no significant magnetic moment is obtained in the transition metal.$^5$

2.2. Magnetic structure of the ground state and coupling constants

We explored different static configurations for the magnetic moments which are presented in figure 2 for the CeFeSi-type structures. The magnetic configurations used for the CeScSi-type structures are completely analogous, with the

$^5$The spin polarization on the transition metal of each compound was estimated from spin dependent DFT calculations projecting on the transition metal atomic orbitals. We found values between 0 and 0.8$\mu_B$ depending on the magnetic configuration of the Gd$^{3+}$ 4f magnetic moments and the transition metal. We expect the magnetocaloric properties of these compounds to be dominated by the much larger local magnetic moment in the Gd$^{3+}$ ions ($\sim 8\mu_B$).
same relative orientation of the magnetic moments inside each Gd layer and between the layers. The lowest energy configuration is identified as the magnetic ground state, which in all the analyzed cases corresponds to the type of order experimentally observed [26–32]: a ferromagnet for GdFeSi, GdTIGe

In these metallic compounds, the dominant Gd–Gd magnetic interactions are due to a Ruderman–Kittel–Kasuya–Yosida (RKKY) coupling between the Gd’s magnetic moments through exchange interactions with the conduction electrons, which decay in three-dimensional (3d) systems as an inverse third power of the inter Gd distance [33–35]. DFT calculations of the RKKY couplings in GdFeSi in reference [4] suggests an even faster decay with increasing inter Gd distance. As it is customary we considered a finite set of exchange interactions. The eight magnetic configurations considered allow us to calculate up to seven exchange couplings. We found that an accurate description of the system is obtained using a simplified model for the magnetic interaction between Gd$^{3+}$ magnetic moments, with three coupling constants (see figure 3) [27, 36]: an exchange coupling $K_0$ between nearest neighbour Gd atoms on each Gd layer (which is a square lattice), a coupling $K_1$ between nearest neighbours in different layers of the bilayer, and a nearest neighbour coupling between Gd in different bilayers. For the latter coupling there are two possibilities depending on the lattice type: $K_1$ associated with 4 neighbours in the CeFeSi-type structure, and $K_1$ associated with a single neighbour in the CeScSi-type structure (see figure 3). We found that including up to three additional magnetic couplings in the model only lead to minor quantitative differences in the calculated properties. The magnetic energy per Gd$^{3+}$ ion is presented in table 2 for the magnetic configurations of figure 2.

The energy differences between magnetic configurations calculated from first principles can be combined with table 2 to obtain the coupling parameters through a least squares analysis. The obtained couplings for the different compounds are presented in table 3. For all the studied compounds, the intra-bilayer couplings $K_0$ and $K_2$ are positive which indicates that in all cases the Gd magnetic moments in a given bilayer order

Table 1. Relative energy $\Delta E$ (in K) with respect to the ground state for the magnetic configurations of figure 2 for a DFT cell with 16 Gd$^{3+}$ ions. The AF3 configuration is unstable for GdCoSi. The underlined compounds correspond to the CeFeSi-type structure, and the rest to the CeScSi-type structure.

| Compound       | FM | GdCoSi | GdTISi | GdTIGe | GdTiGe | GdScGe | GdScSi |
|----------------|----|--------|--------|--------|--------|--------|--------|
| GdFeSi         | 0  | 198    | 305    | 424    |        |        |        |
| AF1            | 43 | 891    | 1608   | 1459   | 1967   | 1551   | 1537   |
| AF2            | 220| 0      | 0      | 0      | 1013   | 377    | 370    |
| AF3            |    | 711    | 1339   | 1442   | 1941   | 1220   | 1217   |
| AF4            | 466| 788    | 1609   | 1552   | 2197   | 1564   | 1546   |
| AF5            | 244| 661    | 1183   | 1281   | 2001   | 1223   | 1200   |
| AF6            | 243| 660    | 1183   | 558    | 1942   | 1220   | 1217   |
| AF7            | 302| 704    | 1572   | 1476   | 2071   | 1462   | 1431   |

Table 2. Magnetic energy as a function of the magnetic-exchange couplings for the different magnetic configurations considered in the CeFeSi-type and the CeScSi-type structures. $J = 7/2$ is the angular momentum of the Gd$^{3+}$ ion 4f electrons.

| Compound       | FM $E_{AF}^m/J^2$ | CeFeSi-type | CeScSi-type |
|----------------|------------------|-------------|-------------|
| GdFeSi         | $-4(K_0 + K_1 + K_2)$ | $-4K_0 - \tilde{K}_1 - 4K_2$ | $-4K_0 - \tilde{K}_1 - 4K_2$ |
| GdTiGe         | $-4(K_0 + K_1 - K_2)$ | $-4K_0 - \tilde{K}_1 + 4K_2$ | $-4K_0 - \tilde{K}_1 + 4K_2$ |
| GdCoSi         | $-4(K_0 - K_1 + K_2)$ | $-4K_0 + \tilde{K}_1 - 4K_2$ | $-4K_0 + \tilde{K}_1 - 4K_2$ |
| GdScSi         | $0$ | $\tilde{K}_1$ | $\tilde{K}_1$ |
| GdScSi         | $0$ | $\tilde{K}_1$ | $\tilde{K}_1$ |
| GdTiGe         | $4K_0$ | $4K_0 + \tilde{K}_1$ | $4K_0 + \tilde{K}_1$ |

Table 3. Calculated exchange couplings (in K) and the calculated Néel temperatures. Boldface indicates interplane couplings. Shaded cells correspond to Curie temperatures. The experimental Néel temperatures $T_N^\text{exp}$ are presented as a reference. The superscripts indicate the references from which the experimental values were extracted: a = [16], b = [29], c = [27], d = [30], e = [31], f = [32].

| Compound       | FM $K_0$ | FM $K_1$ | FM $K_2$ | $T_N^\text{MF}$ | $T_N^\text{MC}$ | $T_N^\text{QMC}$ | $T_N^\text{exp}$ |
|----------------|---------|---------|---------|-----------------|-----------------|-----------------|-----------------|
| GdFeSi         | 1.6     | -2.4    | -3.2    | 163             | 115.7           | 154             | 118$^a$         |
| GdTISi         | 4.5     | -10.3   | -4.1    | 386             | 284.5           | 363             | 175$^b$         |
| GdTIGe         | 4.4     | -10.4   | -3.8    | 745             | 554.5           | 710             | 400$^c$         |
| GdTiGe         | 8       | 17.0    | 9       | 646             | 477             | 620             | 412$^d$         |
| GdScGe         | 10.6    | 766     | 756     | 1145            | 637             | 840             | 376$^e$         |
| GdScSi         | 10.4    | 756     | 756     | 1145            | 637             | 840             | 376$^e$         |
| GdScSi         | 26.5    | 8.4     | 9.2     | 18.7            | 23.7            | 320$^f$         | 318$^f$         |

Figure 3. Magnetic couplings considered in the simplified model. The lines connect pairs of Gd atoms that are magnetically coupled (to avoid overloading the plot, not all couplings are drawn, but can be inferred from symmetry considerations) through the exchange coupling parameters $K_0$, $K_1$ (only for the CeFeSi-type structure), $\tilde{K}_1$ (only for the CeScSi-type structure), and $K_2$, as indicated in the figure.
The interbilayer couplings can be positive as in GdFeSi, GdTiGe (I4/mmm), GdScGe, and GdScSi leading to a ferromagnetic ground state or negative as in GdCoSi, GdTiSi, and GdTiGe (P4/mmm) which results in an A-type antiferromagnet. The replacement Si → Ge does not lead to a significant change in the exchange couplings of GdTiSi and GdScSi which is consistent with the very weak change in the transition temperatures observed in these compounds upon Si → Ge replacement. The replacements Fe → Co in GdFeSi and Ti → Sc in GdTiGe produce, however, a change in the sign of the interbilayer coupling $K_1$ and a strong reduction of $\tilde{K}_1$, respectively. These replacements have in common a change in the electron number provided by the transition metal atom, which changes the conduction band occupancy and the RKKY couplings. A double exchange coupling between the Gd magnetic moments through the 3d level of the transition metal atom, which changes the conduction band occupancy and the RKKY couplings. A double exchange coupling between the Gd magnetic moments through the 3d level of the transition metal naturally gives a change in the sign of the resulting coupling when the 3d level occupancy changes by one electron (see reference [37]), which may explain the observed behavior of the interbilayer couplings when the transition metal is replaced.

The compound GdTiGe is stable in both the CeFeSi-type (P4/mmm) and CeScSi-type (I4/mmm) structures, but its magnetic behavior depends strongly on the type of structure. GdTiGe (P4/mmm) is an A-type antiferromagnet while GdTiGe (I4/mmm) is a ferromagnet. Although the interlayer couplings are expected to change because of the different topology, the intrabilayer couplings also change and are roughly twice as large in the CeScSi-type structure.

3. Magnetocaloric properties

We performed a mean-field (MF) analysis and classical (CMC) and quantum Monte Carlo (QMC) calculations using the obtained magnetic couplings (see table 3) for each compound. We used the ALPS library (see references [38, 39]) for the numerical calculations with system sizes of up to $8 \times 8 \times 8$ magnetic moments. In figure 4 we present $\Delta S_m = S(0.1T) - S(H)$ calculated numerically using quantum Monte Carlo, as a function of the temperature for ferromagnetic and two antiferromagnetic compounds. The ferromagnetic compounds show a peak in $\Delta S_m$ for temperatures near the Curie temperature, whose height increases monotonically with increasing magnetic field. The maximum $\Delta S_m$ increases with decreasing $T_C$ while the width of the peak follows an opposite trend. The antiferromagnetic compounds show a much lower overall intensity of the MCE and a change in the sign of $\Delta S_m$ near the Néel transition.

In the mean-field approximation the scaling $H \rightarrow g \mu_B H/(k_B T_C)$ (where $g = 2$ is the g-factor) and $T \rightarrow T/T_C$ results in a universal curve for $\Delta S_m$ for the ferromagnetic compounds [40–43]. In the AFM compounds the maximum value of $\Delta S_m$ depends strongly on the value of the antiferromagnetic bilayer coupling ($K_1$ or $\tilde{K}_1$ depending on the crystal structure), since the Zeeman energy needs to be large enough to overcome it in order to be able to generate a sizable magnetization and the associated entropy change.

The scaling behavior is approximately followed in the CMC and the QMC calculations (see figure 5).

The maximum value of the entropy difference for a given external field is lower in CMC and QMC than in MF. This is due to the nature of the mean field solution in the paramagnetic state. At temperatures larger than the transition temperature $T_C$ there are no correlations between spins in the MF approximation which leads to a maximal entropy and a lack of energy fluctuations. For $H \neq 0$ the energy fluctuations and the entropy are dominated by the level splitting induced by the external magnetic field which is accurately described in the MF approximation. For $T > T_C$ and $H = 0$ the MF approximation overestimates the entropy but for $H \neq 0$ it results in a value similar to the one obtained using QMC. As a consequence, the MF approximation overestimates the entropy change when a magnetic field is applied.

The experimental entropy changes for GdFeSi, GdScGe and GdScSi are also shown in the insets of figure 5. At low (rescaled by $k_B T_C$) fields the experimental results (see reference [1] and references therein) are in very good agreement with the theory. The large field result, available for GdFeSi, is larger than what is expected from the theory, which could be due to additional magnetic degrees of freedom not

\[^6\] We expect the magnetic couplings to be dominated by the hybridization of the Gd 5d orbitals with the conduction band rather than by the Gd 4f hybridization. A simple estimation using effective atomic orbitals indicates that the latter is at least two orders of magnitude smaller than the former.
Figure 5. Magnetocaloric effect for different ferromagnetic compounds with both the temperature and the external magnetic field scaled by the corresponding $T_C$. The external magnetic field is $H = 2T$ for GdFeSi and $H = 2T(T_C/T_GdFeSi)^{0.125}$ for the other compounds. The insets show the entropy change as a function of the rescaled field at $T_C$. The open symbols correspond to experimental results with the magnetic field scaled by the experimental transition temperature (see reference [1] and references therein).

4. Conclusions

We studied the magnetocaloric properties of Gd based RTX compounds having the CeScSi-type or CeFeSi-type crystal structures. Based on density functional theory calculations we obtained the ground state magnetic configuration and the exchange couplings of a simplified magnetic Hamiltonian. The lowest energy magnetic configurations obtained were in agreement with the available experimental data and the calculated transition temperatures consistent with the reported values. We found a weak dependence of the magnetic properties upon Si $\leftrightarrow$ Ge replacement but a strong dependence of the interbilayer exchange coupling with the replacements Fe $\rightarrow$ Co and Ti $\rightarrow$ Sc that can even lead to a change of its sign and of the magnetic ground state configuration. The replacement of Si by the isoelectronic Ge produces only small changes in the magnetic couplings.

A wide range of RTX compounds that share the CeFeSi-type crystal structure present the same qualitative change in the transition temperatures upon T replacement and X replacement (see table 4).

| R  | Ce  | Nd | Sm | Gd | Tb | Dy | Ho | Er  | Tm |
|----|-----|----|----|----|----|----|----|-----|----|
| RTiSi | —  | —  | —  | 400 | 286 | 170 | 95 | 50  | 20 |
| RTiGe | —  | 150 | 260 | 412 | 270 | 170 | 115 | 41  | 15 |
| RFeSi | —  | 25  | 40  | 118 | 125 | 110 | 29 | 22  | —  |
| RCoSi | 8.8 | 7   | 15  | 175 | 140 | —  | —  | —   | —  |
| RCoGe | 5   | 8   | —   | —   | —   | —   | —   | —   | —  |

We also studied the magnetocaloric properties of the R = Gd compounds and found a universal behavior of the magnetocaloric effect as a function of the temperature for the ferromagnetic compounds when the external magnetic field and the temperature are scaled by the transition temperature of each compound. This result, which is exact in the MF theory, and approximate in CMC and QMC sets a limit to the maximum MCE that can be expected in these compounds for a given $T_C$ and external magnetic field.

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