A Comparative Study of the Electronic and Magnetic Properties of Gd₅Ge₄ and Gd₅Si₄ Compounds

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(Received May 20, 2014; revised manuscript received September 5, 2014)

Abstract We present a comparative study of electronic structure and magnetic properties of Gd₅Si₄ and Gd₅Ge₄ compounds using first principles full potential linearized augmented plane wave (FP-LAPW) method based on density functional theory (DFT) using the WIEN2k code. The local-spin density approximation with correlation energy (LSDA+U) method has been used as the exchange-correlation potential. The optimized lattice constants are in good agreement with the experimental data. The total and partial density of states (DOS) of Gd₅Si₄ and Gd₅Ge₄ show the difference in Si 3p-Gd 5d and Ge 4p-Gd 5d hybridization, which have an effective role in indirect exchange interaction. In addition, the magnetic moments of Gd, Si, and Ge atoms and the compounds are calculated to clarify the differences in the magnetic properties of these compounds.

PACS numbers: 71.15.Mb, 71.15.Mb
Key words: magnetocaloric compound, density functional theory, electronic and magnetic properties, exchange interaction

1 Introduction

The isothermal energy change or the adiabatic temperature change in response to the application and removal of an external magnetic field in a magnetic system is called magnetocaloric effect (MCE).[1] Magnetic refrigeration (MR) based on MCE is a promising alternative for vapor-cycle refrigeration. MR technology has many advantages such as high cooling efficiency (30–60% in a Carnot cycle), the development possibility of portable and the minimization of global-warming gases.[2]

Since the discovery of the giant magnetocaloric effect (GMCE) in intermetallic Gd₅Si₄Ge₂ compound near room temperature (Tᵣ ~ 276 K) by Pecharesky and Gschneidner (1997),[3] the Gd₅(SiₓGe₁₋ₓ)₄ alloys have received tremendous attention. The observed GMCE in Gd₅(SiₓGe₁₋ₓ)₄ (x = 0.24–0.5) alloys is due to a magnetostuctural transition from a paramagnetic monoclinic phase to a ferromagnetic orthorhombic phase upon cooling.[4] In Ge-rich Gd₅(SiₓGe₁₋ₓ)₄ compounds (0 ≤ x ≤ 0.4) a similar effect, the magnetostuctural transition from orthorhombic (Gd₅Ge₄-type)-antiferromagnetic to orthorhombic (Gd₅Si₄-type)-ferromagnetic, has been found.[5]

Both the end members in series of the Gd₅(SiₓGe₁₋ₓ)₄ MCE materials, Gd₅Si₄ and Gd₅Ge₄, at room temperature crystallize in Sm₃Ge₄-type orthorhombic structure (Pnma). [1] The crystal structure of these alloys is composed from infinite equivalent layers in the ac crystal plane that are stacked along the b-axis. Atomic layers making a slab can be considered as sequence Ge, Sm, Ge-Sm, Sm, Ge stacked along the crystal b-axis. In Gd₅Si₄ the covalent-like bonds between pairs of Si atoms connect the slabs with each other along the b-axis, known as O(I) allotrope, whereas in Gd₅Ge₄ such bonds between Ge atoms are absent, known as O(II) allotrope, at room temperature.[1]

Gd₅Si₄ used for the cooling of microelectronic chips[6] and introduced as a Candidate for hyperthermia treatment of cancer[7] is ferromagnet with Tₘ = 336 K, whilst Gd₅Ge₄ applied for the production of liquid He₂[8] orders ferromagnetically at Tₘ = 20 K and antiferromagnetically at Tₘ = 115 K.[8] It was proven that the indirect exchange interaction i.e. Ruderman–Kittel–Kasuya–Yosida (RKKY) mediated by spin polarized conduction electron plays an important role in determining the magnetic properties of these compounds,[9] and p-d hybridization is a significant ingredient in mediating indirect exchange interactions.[10]

Numerous experimental studies on the phase transition and magnetic properties of the Gd₅Si₄Geₓ-compounds have been reported but the theoretical investigation is very much limited. The calculation of electronic structure and magnetic properties were performed using tight binding linear muffin-tin orbital method in atomic sphere approximation (TB-LMTO-ASA) using the local-spin density approximation (LSDA) for Gd₅Si₄[9,11–13] and Gd₅Ge₄.[11,13–14] The LSDA+U approximation should be used for these compounds because the Gd 4f-orbitals are
rather localized; the 4f-electron correlations are expected to be strong. Mudryk et al.\cite{15} and Paudyal et al.\cite{16-17} have studied the magnetostructural phase transformation in Gd$_3$Si$_5$Ge$_{1.5}$ and Gd$_3$Ge$_4$ using the local-spin density approximations with correlation energy (LSDA+U) method implemented in the TB-LMTO scheme. To our knowledge, no reports on these compounds with full potential linearized augmented plane wave (FP-LAPW) method using LSDA+U approximation have been published yet.

In this work, we investigate the structural, electronic and magnetic properties of O(I) Gd$_3$Si$_4$ and O(II) Gd$_3$Ge$_4$ compounds in the ferromagnetic (FM) state by the computational package WIEN2k based on DFT calculations. The role of hybridization between 5d states of the Gd atoms and 3p (4p) states of the Si (Ge) atoms in RKKY exchange has been studied that is origin of difference in their RKKY interaction.

2 Crystal Structure and Computational Details

The two binary compounds Gd$_3$Si$_4$ and Gd$_3$Ge$_4$ crystallize in the orthorhombic Sn$_3$Ge$_4$-type structure with space group Pnma. There are 36 atoms (20 Gd and 16 Si/Ge atoms) in the unit cell.\cite{18} The building block of these compounds is the pseudo two-dimensional slabs, which are infinite in the ac plane but they have a thickness of about 7 Å along the b-axis.\cite{19}

The structural and electronic properties of these compounds are investigated using the computational package WIEN2k based on DFT calculations. Since Gd 4f-orbitals are rather localized, the 4f-electron correlations are expected to be strong. Consequently, the LSDA+U calculations have been chosen to include the on-site Coulomb interaction. Paudyal et al.\cite{16-17} employed $U = 6.7$ eV and $J = 0.7$ eV for the proper positioning of the occupied and unoccupied 4f bands of Gd atoms in Gd$_3$Ge$_4$ where $U$ and $J$ are the on-site coulomb energy and exchange parameter respectively. In this approximation, it is recommended that the effective Coulomb-exchange parameter $U_{\text{eff}} = U - J$ be used. Therefore we apply $U_{\text{eff}} = 6.0$ eV for both compounds.

Values of the used muffin-tin radii ($R_{\text{MT}}$) are 2.35 a.u. for Gd and 2.00 a.u. for Ge (or Si). The maximum value for partial waves inside the atomic sphere ($l_{\text{max}}$) is set to 10. For plane wave cut off, $K_{\text{max}} = 9.0/R_{\text{MT}}$ is used to expand the wave functions in the interstitial region and for the charge density Fourier series is truncated at $Q_{\text{max}} = 14$. The energy that separates the valence state from the core state has been chosen to be $-6.0$ Ry. The number of K points in the irreducible Brillouin zone (IBZ) for self-consistent cycles is taken as 126 for Gd$_3$Si$_4$ and 108 for Gd$_3$Ge$_4$ compound (the larger the unit cell volume, the fewer the number of K points) and the energy and charge convergence criteria are set to $10^{-5}$ Ry and $10^{-4}$ electrons, simultaneously. The energy convergence criterion is set to $10^{-5}$ Ry and simultaneously the criterion for charge convergence to $10^{-4}$ electrons. The effect of spin orbit coupling is neglected.

3 Results and Discussion

3.1 Structural Properties

In order to study the structural properties of FM O(I) Gd$_3$Si$_4$ and FM O(II) Gd$_3$Ge$_4$, the experimental lattice parameters are used.\cite{18} Then, by calculating the total energy of primitive unit cell at different volumes for ferromagnetic (FM) alignment and fitting the data with Murnaghan equation of state\cite{20} the equilibrium lattice parameters and bulk modulus are obtained. The variation in the total energy as a function of volume is shown in Fig. 1. The Gd$_3$Ge$_4$ compound is found to be more stable than Gd$_3$Si$_4$ compound. In the next step, the $c/a$ ratio at equilibrium volume ($V_{\text{eq}}$) for these compounds is optimized (Fig. 2). The $(c/a)_{\text{eq}}$ value is obtained 1.035 and 1.011 for Gd$_3$Si$_4$ and Gd$_3$Ge$_4$, respectively. Table 1 summarizes the lattice constants and bulk modulus for Gd$_3$Si$_4$ and Gd$_3$Ge$_4$ as obtained from our structural optimization calculations. As expected, the equilibrium volume of Gd$_3$Ge$_4$ is higher than that of Gd$_3$Si$_4$ because of the larger atomic radius of Ge than Si. Moreover, the lattice parameter

![Fig. 1](image_url) The total energy versus primitive cell volume for Gd$_3$Si$_4$ and Gd$_3$Ge$_4$ with LSDA+U approximation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$V_0$ (Å$^3$)</th>
<th>$B_0$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd$_3$Si$_4$</td>
<td>7.375</td>
<td>14.533</td>
<td>7.637</td>
<td>818.6</td>
<td>86.167</td>
</tr>
<tr>
<td>Gd$_3$Ge$_4$</td>
<td>7.486</td>
<td>14.750</td>
<td>7.751</td>
<td>855.9</td>
<td>-</td>
</tr>
<tr>
<td>Gd$_3$Si$_4$</td>
<td>7.557</td>
<td>14.562</td>
<td>7.644</td>
<td>840.8</td>
<td>82.633</td>
</tr>
<tr>
<td>Gd$_3$Ge$_4$</td>
<td>7.697</td>
<td>14.831</td>
<td>7.785</td>
<td>888.7</td>
<td>-</td>
</tr>
</tbody>
</table>

“a” of Gd$_3$Ge$_4$ is significantly larger than that of Gd$_3$Si$_4$, whereas the lattice parameter “b” and “c” of Gd$_3$Ge$_4$ are a little larger than those of Gd$_3$Si$_4$. The bulk modulus B decreases from Gd$_3$Si$_4$ to Gd$_3$Ge$_4$—a larger lattice constant leads to a smaller bulk modulus (cell volume
\[ V_0, \text{as } B \sim V_0^{-1}[21]. \] We have an estimation of the lattice constants which are 1.5 and 1.8% less than the experimental values\[^{18}\] for Gd$_5$Si$_4$ and Gd$_5$Ge$_4$, respectively. The optimized lattice constants and the experimental atomic parameters are then used as the starting point to investigate the electronic properties. The optimized values of lattice constants for these compounds are not presented in other theoretical works.

### 3.2 Electronic and Magnetic Properties

In order to examine the difference in the electronic and magnetic properties, the partial electronic density of states (DOS) for Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ within LSDA+$U$ method was calculated. Figure 3 compares the average DOS of all Gd atoms, the average DOS of all Ge atoms and DOS for the Si atoms in both compounds. For Gd$_5$Si$_4$, the average DOS of all Gd and Si atoms in both spin directions displays pseudo-gaps, located at $-0.8$ eV (majority spin) and $-0.3$ eV (minority spin) with an exchange splitting of 0.2 eV. For Gd$_5$Ge$_4$, in the same energy range the average DOS of all Gd and Ge (the both spins) consists of sharp dips. In this range, the majority-spin and minority-spin peaks of Gd-5$d$ states are shifted about 0.15 eV by exchange interaction. These results are coincident with TB-LMTO calculations obtained by Skorek et al.\[^{11}\]

In Gd$_5$Si$_4$ (Gd$_5$Ge$_4$) in an energy range $-4$ eV up to the Fermi level the Si-3$p$ (Ge-4$p$) states with a small mixture of the Gd-5$d$ states are dominated. The dominant contribution at Fermi level for both compounds is related to Gd-5$d$ states.

**Fig. 2** The total energy versus c/a ratio for Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ with LSDA+$U$ approximation.

**Fig. 3** The average DOS of all Gd atoms (left) and the average DOS of all Ge and Si atoms (right) in the Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ compounds. The up and down arrow represent the spin up and spin down DOS respectively.

For more details, the DOS of 5$d$ orbital of Gd atoms in Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ structures is also presented. Figure 4 shows that 5$d$ DOS of symmetrically inequivalent Gd atoms in Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ are different at the Fermi level. On
average, the spin up $5d$ DOS of all Gd atoms at the Fermi level in Gd$_5$Si$_4$ is higher than that in Gd$_5$Ge$_4$. As seen, the spin down $5d$ DOS of Gd atoms for Gd$_5$Si$_4$ in the energy range $-0.2$ to $-0.4$ eV below the Fermi level is zero; hence all the electrons in this energy range occupy spin up states. But the spin down $5d$ DOS of Gd atoms for Gd$_5$Ge$_4$ in the same energy range are nonzero showing that some electrons occupy the spin down states. As a result, it is expected that the magnetic moments of Gd-$5d$ states be much lower in Gd$_5$Ge$_4$ than in Gd$_5$Si$_4$ compound.

The magnetic moments of the Gd-$4f$ electrons are close to $7 \mu_B$, and magnetic moments of $6s$ and $6p$ electrons are negligible compared to $5d$ and $4f$ electrons. The main differences in the magnetic moments are in the $5d$ electrons of the different Gd atoms in these compounds. The exchange splitting in the minority and majority spin bands due to the local splitting gives rise to the $5d$ magnetic moments of Gd atoms. The $5d$ band splitting at the Fermi level for Gd$_5$Si$_4$ is higher than that for Gd$_5$Ge$_4$, resulting in a higher magnetic moments.

It should be noted that the hybridization between the $3p$ ($4p$) states of the Si (Ge) atoms and Gd-$5d$ states (as will be described further) leads to a small spin polarization on Si (Ge) atoms and these atoms gain a small induced magnetic moment. The small induced magnetic moment at Si (Ge)-sites is in the opposite direction to magnetic moment of the Gd-site. Table 2 summarizes the magnetic moments of Gd, Si, Ge atoms and compounds. The other theoretical and experimental data are also presented for comparison. The results show the total magnetization of
about 37.8 and 36.3 $\mu_B$/f.u. for Gd$_5$Si$_4$ and Gd$_5$Ge$_4$, respectively.

Table 2  Total ($\mu_B$/f.u.) and partial magnetic moment ($\mu_B$/atom) for Gd$_5$Si$_4$ and Gd$_5$Ge$_4$.

<table>
<thead>
<tr>
<th>Components</th>
<th>This work</th>
<th>Other work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WIEN2k</td>
<td>Theoretical</td>
</tr>
<tr>
<td>Gd$_5$Si$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd1 4(c)</td>
<td>7.22</td>
<td>7.33$^{[11]}$</td>
</tr>
<tr>
<td>Gd2 8(d)</td>
<td>7.14</td>
<td>7.25</td>
</tr>
<tr>
<td>Gd3 8(d)</td>
<td>7.15</td>
<td>7.24</td>
</tr>
<tr>
<td>Si1 4(c)</td>
<td>−0.027</td>
<td>−0.01</td>
</tr>
<tr>
<td>Si2 4(c)</td>
<td>−0.016</td>
<td>0.02</td>
</tr>
<tr>
<td>Si3 8(d)</td>
<td>−0.030</td>
<td>−0.01</td>
</tr>
<tr>
<td>Total</td>
<td>37.8</td>
<td>36.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Components</th>
<th>Gd$_5$Ge$_4$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd1 4(c)</td>
<td>7.13</td>
<td>7.18$^{[11]}$</td>
<td>7.36$^{[16]}$</td>
<td></td>
</tr>
<tr>
<td>Gd2 8(d)</td>
<td>7.06</td>
<td>7.13</td>
<td>7.24</td>
<td></td>
</tr>
<tr>
<td>Gd3 8(d)</td>
<td>7.06</td>
<td>7.19</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ge1 4(c)</td>
<td>−0.030</td>
<td>−0.01</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ge2 4(c)</td>
<td>−0.021</td>
<td>0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ge3 8(d)</td>
<td>−0.048</td>
<td>−0.04</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>36.3</td>
<td>35.6</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Our results show better agreement with the available experimental data compared to other theoretical data.$^{[11]}$ For example, our calculations are more successful in the description of antiparallel moments of Si and Ge atoms.

To further investigation of magnetic properties of Gd$_5$Si$_4$ and Gd$_5$Ge$_4$, we focus on $p$-$d$ hybridization as an effective agent in RKKY exchange interaction which is responsible for the magnetic ordering in Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ family. The RKKY interaction depends on distribution of conduction electrons.$^{[8]}$ The Gd-5$d$ states, which are strongly polarized, mediate the exchange interaction between the 4$f$ magnetic moments. The extent of $p$-$d$ hybridization (Si 3$p$-Gd 5$d$ and Ge 4$p$-Gd 5$d$ hybridization) is critical component in mediating indirect exchange interactions between localized Gd-4$f$ spins.$^{[10]}$

It should be noted that the change in the magnetism from the FM O(II) Gd$_5$Ge$_4$ to FM O(I) Gd$_5$Si$_4$ is related to the dramatic change in the interlayer bond length (i.e. Ge-Ge and Si-Si). Since Gd1 atoms of one slab are connected to Gd1 atoms of the neighboring slabs through long Ge3-Ge3 pairs in Gd$_5$Ge$_4$ or through short Si3-Si3 pairs in Gd$_5$Si$_4$, the difference in the overlap between Gd1-5$d$ and Si3-3$p$(Ge3-4$p$) states should be responsible for the difference in the exchange interaction. Figure 5 shows that the spin down 4$p$ DOS of Ge3 at and below the Fermi level is larger than the spin down 5$d$ DOS of Gd1, indicating 30% Gd1-5$d$ and 70% Ge3-4$p$ hybridization. Due to the weak Ge3-Ge3 bonding, the spin down 4$p$ states of Ge in FM O(II) Gd$_5$Ge$_4$ have been pushed toward the Fermi level, thus Ge3 atoms reduce magnetic moment on the Gd atoms surrounding Ge3 sites. In addition, the spin down 5$d$ DOS of Gd1 and the spin down 4$p$ DOS of Ge1 and Ge2 are almost identical at the Fermi level, illustrating 50% Ge1/Ge2 4$p$ and 50% Gd1-5$d$ hybridization in the same band. These results are in very good agreement with other theoretical calculations.$^{[16]}$ In contrast to Gd$_5$Ge$_4$, the spin down 5$d$ DOS of Gd1 and the spin down 3$p$ DOS of all Si atoms in Gd$_5$Si$_4$ are almost identical at the Fermi level, indicating nearly same hybridization between 5$d$ DOS of Gd1 and interslab/intraslab Si atoms as shown in Fig. 6. Therefore, the $p$-$d$ hybridization and exchange interaction in Gd$_5$Si$_4$ is stronger.

Fig. 6  (Left) The 5$d$ DOS of Gd1 and 3$p$ DOS of Si3. (Right) The 5$d$ DOS of Gd1 and 3$p$ DOS of Si1 and Si2 in FM O(I) Gd$_5$Si$_4$. 
4 Conclusion

Comparison between the electronic and magnetic properties of Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ has been obtained with FP-LAPW method within the density functional theory. The optimized lattice constants indicate the lattice parameter “a” of Gd$_5$Ge$_4$ is significantly larger than that of Gd$_5$Si$_4$. The structural results are in good agreement with the experimental values. For Gd$_5$Si$_4$ two pseudo-gaps located below Fermi level with an exchange splitting of about 0.2 eV. For Gd$_5$Ge$_4$, in the same energy range the average DOS of all Gd and Ge (the both spins) consists of sharp dips, and the majority-spin and minority-spin peaks of Gd-5d states are as well as shifted about 0.15 eV by exchange interaction. The 5d exchange splitting of Gd atoms in Gd$_5$Si$_4$ is larger than in Gd$_5$Ge$_4$, resulting in higher 5d magnetic moments of Gd atoms in Gd$_5$Si$_4$ as compared to Gd$_5$Ge$_4$. The difference in the indirect exchange interaction between these two compounds arises from the difference in the Si 3p-Gd 5d and Ge 4p-Gd 5d hybridization.

Acknowledgments

The authors would like to thank Mr. Zarei and Mr. Sarhaddi (University of Birjand) for valuable and useful discussions during the course of this work.

References