Composition-Induced Magnetic Transition in GdMn$_{1-x}$Ti$_x$Si Intermetallic Compounds for $x = 0$–1

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Abstract: Magnetic intermetallic compounds based on rare earth elements and 3d transition metals are widely investigated due to the functionality of their physical properties and their variety of possible applications. In this work, we investigated the features of the electronic structure and magnetic properties of ternary intermetallic compounds based on gadolinium GdMn$_{1-x}$Ti$_x$Si, in the framework of the DFT + U method. Analysis of the densities of electronic states and magnetic moments of ions in Ti-doped GdMnSi showed a significant change in the magnetic properties depending on the contents of Mn and Ti. Together with the magnetic moment, an increase in the density of electronic states at the Fermi energy was found in almost all GdMn$_{1-x}$Ti$_x$Si compositions, which may indicate a significant change in the transport properties of intermetallic compounds. Together with the expected Curie temperatures above 300 K, the revealed changes in the magnetic characteristics and electronic structure make the GdMn$_{1-x}$Ti$_x$Si intermetallic system promising for use in microelectronic applications.

Keywords: phase transition; magnetic transition; electronic structure; physical properties; DFT + U; intermetallics

1. Introduction

Recently, researchers have paid much attention to magnetic cooling based on the magnetocaloric effect of solid-state working substances [1]. RTX ternary compounds (R = rare earth elements, T = 3d/4d/5d transition metals, and X = p elements) are a huge family of intermetallic compounds [2,3]. Most of these compounds crystallize into hexagonal, orthorhombic, and tetragonal crystal structures [2,4]. Due to the various crystal structures, unusual magnetic and electrical properties have been found in these compounds, such as complex magnetic orderings, valence fluctuations, unusual types of superconductivity, heavy fermion behavior, metamagnetism, spin glass, memory effect, magnetoresistance, magnetocaloric effect, etc. [5–8]. Although these compounds have been known for a long time, they have recently attracted greater interest, since they exhibit enormous magnitudes of the magnetocaloric effect and magnetoresistance [7,9,10]. The magnetic ordering temperatures in RTX range from very low temperatures to temperatures well above room temperature, for example, reaching 510 K in TbMnGe [11].

This allows the RTX series to cover a very large temperature range for a variety of functional applications [6]. RMnSi compounds, where R is a rare earth element, are intermetallic compounds with two magnetic sublattices R and Mn, in which the magnetic atoms are located in layers separated by silicon layers in the order R–Si–Mn–Si–R. The manganese sublattice is characterized by a significant localized magnetic moment of Mn ions [12]. Magnetic ordering in RMnSi compounds is formed due to different types of exchange interactions: R–R, R–Mn, and Mn–Mn. A change in interactions with decreasing temperature can lead to magnetic phase transition ferromagnetism—antiferromagnetism [13].
Several magnetic transitions were found in the GdMnSi compound at temperatures of 50, 275, and 310–325 K [13,14]. The lowest temperature corresponds to the antiparallel ordering of the magnetic moments of gadolinium ions relative to the moments of manganese ions; higher temperatures characterize the ferri- and ferromagnetic orderings of the moments of Mn ions [14]. At sufficiently high temperatures, large values of the magnetocaloric effect were found in GdMnSi [13]; it should be noted that in other ternary intermetallic compounds of the GdTX series, the magnetocaloric effect was also found [15]. The low-temperature saturation magnetization in GdMnSi, according to experimental data [16], is $5 \mu_B$, and in strong magnetic fields it increases to $8.8 \mu_B$ [17]. The Curie temperature $T_C = 294$ K was experimentally determined in GdTiSi [18]. The high Curie temperatures of the intermetallic compounds GdTISi and GdMnSi suggest that alloys of the intermediate composition GdMn$_{1-x}$Ti$_x$Si should have high ordering temperatures too. In the literature, there is only one article [19] with data on the crystal structure of synthesized samples in a wide range of Mn concentrations. Results of experimental measurements of the magnetic or spectral properties of these compositions have not been published in the literature, except for data for several samples with $x = 0–0.3$, which showed an increase in the Curie temperature to 387 K (in GdMn$_{0.7}$Ti$_{0.3}$Si) with increasing Ti content [20]. In [19], in almost all intermediate compositions of GdMn$_{1-x}$Ti$_x$Si compounds, in addition to the tetragonal phase of the CeFeSi-type, another secondary phase was found.

The data available in the literature show the relevance and timeliness of studying the GdMn$_{1-x}$Ti$_x$Si system. The representatives of this series may have a number of interesting properties that make them promising for functional applications. Theoretical studies of the electronic structure and magnetic properties of GdMn$_{1-x}$Ti$_x$Si have not been performed previously.

2. Materials and Methods

In this work, we investigated GdMn$_{1-x}$Ti$_x$Si compounds with a tetragonal crystal structure of the CeFeSi-type (space group P4/nmm, SG 129) with 2 formula units per unit cell. Gadolinium ions occupy 2c positions (0.25, 0.25, $Z_{Gd}$), manganese and titanium ions occupy 2a positions (0.75, 0.25, 0), and silicon ions occupy 2c positions (0.25, 0.25, $Z_{Si}$). The coordinates for gadolinium are $Z_{Gd} = 0.6044$, and the coordinates for silicon are $Z_{Si} = 0.3922$ [19]. In Figure 1, the crystal structure of GdMnSi is plotted using the VESTA package [21]. To model the doped compositions, we used a supercell with 24 atoms. We checked possible configurations of Mn and Ti in the 3d sublattice and took into account only those with the lowest total energy in the doped cases. Gadolinium atoms are marked with large pink spheres, manganese atoms are dark purple, and silicon atoms are blue. Both compounds with a tetragonal structure are natural multilayer magnetic systems in which atoms of the rare earth element Gd, Mn or Ti atoms, and Si atoms are located in layers in the direction of the c-axis in the sequence Gd–Si–Mn$_2$ or Ti$_2$–Si–Gd.

The lattice parameters for pure and doped compounds according to the data of [19] are shown in Figure 2 for the CeFeSi-type phase only. One should note that in [19], for some samples (with $x = 0.4–0.6; 0.9$), the secondary phase $Ti_2Ga_4$-type (Gd$_3$Ti$_2$MnSi$_3$) admixture to the basic CeFeSi-type tetragonal phase was identified. In [20], which reports only $x = 0–0.3$ concentrations of this series, only the CeFeSi-type tetragonal phase was reported. In our theoretical investigation, we solely concentrate on the CeFeSi-type tetragonal phase, as it can provide a clear picture of the magnetic transition in the GdMn$_{1-x}$Ti$_x$Si family. Further synthesis of this family is required. It can be seen that for high titanium (low manganese) concentrations above 0.3, the lattice parameters $a$ and $c$ increase significantly; for titanium concentrations below 0.3, an increase in the $c$ parameter is observed. Thus, the volume of the cell increases. Apart from in [19,20], there are no experimental data on the structural and magnetic properties of this system, which is associated with the multiphase nature of the samples obtained [22].
In this work, the electronic structure and magnetic properties of intermetallic compounds were calculated within the DFT + U method [23] in the Quantum ESPRESSO software package [24], using the exchange correlation functional in the approximation of the generalized gradient correction (GGA) of the PBE version [25]. To take into account the strong electron correlations of 4f electrons of Gd, the U correction was included for the parameters of the direct Coulomb U = 6.7 eV and exchange J = 0.7 eV interactions. These values are generally accepted for Gd ions [8,23,26]. Thus, the rotationally invariant scheme of DFT + U was used [27]. Wave functions were expanded into plane waves, and interactions between ions and valence electrons were taken into account within the framework of the method of augmented plane waves. The calculations used the PAW potentials GGA-PBE-paw (Gd) [28] and pbe-spn-kjpaw (Ti, Mn, Si) from the pseudopotential library of Quantum ESPRESSO. The Gd potential is of the same type and approximation but with the 4f states explicitly included as valent, not semi-core, which is important for intermetallic compounds with magnetic moments of Gd ions.

Figure 1. Crystal structure of the GdMnSi intermetallic compound, plotted with VESTA [21].

Figure 2. Changes in the parameters of the crystal structure a (a) and c (b) in GdMn_{1-x}Ti_{x}Si depending on x (the Ti concentration), according to the data of [19] for the CeFeSi-type phase.
3. Results

3.1. Magnetic Ordering and Moments

In our DFT + U calculations, the ferromagnetic (FM) ordering of the magnetic moments of manganese ions relative to each other was simulated. In the calculations, titanium and silicon ions remain nonmagnetic (up to 0.06 $\mu_B$). For Gd ions, the values of spin polarization obtained as a result of self-consistent calculations correspond to a magnetic moment of 7.21 $\mu_B$ per Gd ion (see Table 1) in good agreement with the experimental value of 7.47 $\mu_B$ in GdTiSi [18]. The total energy in the calculation for GdTiSi with ferromagnetic ordering of the magnetic moments of gadolinium ions was $-2119.4517$ Ry, and for GdMnSi $-2033.9852$ Ry. Additionally, simulations were performed with antiferromagnetic ordering of the magnetic moments of Gd. The total energy of GdMnSi in the calculation with the antiferromagnetic ordering of the magnetic moments of gadolinium ions was $-2119.4420$ Ry, which is higher than in the FM calculation by 0.0139 Ry (189 meV). The total energy of GdTiSi calculated with the antiferromagnetic ordering of the magnetic moments of gadolinium ions was $-2119.4420$ Ry, which is 0.0097 Ry (131 meV) higher than in the FM calculation. Thus, for the compounds GdMnSi and GdTiSi, the lowest total energy value was obtained for ordering of the FM type, in agreement with the experimental data [18,20].

Table 1. The values of the total and partial spin densities of electronic states at the Fermi energy in GdMn$_{1-x}$Ti$_x$Si for $x = 0–1$.

| Compound     | Total Magnetic Moment, $\mu_B$ | Gd Magnetic Moment, $\mu_B$ | Mn Magnetic Moment, $\mu_B$ | Ti Magnetic Moment, $\mu_B$ | Si Magnetic Moment, $\mu_B$ |
|--------------|-------------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|
| GdMnSi       | 4.86                          | 7.21                        | -2.41                       | -                          | 0.06                       |
| GdMn$_{0.8}$Ti$_{0.2}$Si | 4.66                          | 7.16                        | -3.28                       | 0.59                       | 0.01                       |
| GdMn$_{0.6}$Ti$_{0.4}$Si | 5.51                          | 7.19                        | -3.24                       | 0.63                       | 0.01                       |
| GdMn$_{0.5}$Ti$_{0.5}$Si | 6.09                          | 7.21                        | -3.03                       | 0.80                       | -0.01                      |
| GdMn$_{0.4}$Ti$_{0.6}$Si | 6.34                          | 7.21                        | -3.13                       | 0.67                       | -0.02                      |
| GdMn$_{0.2}$Ti$_{0.8}$Si | 7.09                          | 7.21                        | -3.17                       | 0.68                       | -0.03                      |
| GdTiSi       | 7.19                          | 7.21                        | -                          | 0.01                       | -0.03                      |

3.2. Electronic Structure

The calculated densities of electronic states and band structure of the intermetallic compound GdMnSi are shown in Figures 3 and 4, respectively. The data are given per formula unit for two opposite directions of majority and minority spin in the case of FM ordering. The Fermi energy ($E_F$) is located at zero energy. Intense peaks in DOS of this compound (Figure 3) are formed by several localized bands of different intensities. In the energy range from $-5$ to $6$ eV, there is a broad band of the density of electronic states formed due to the 3d states of manganese and 3p states of silicon. In the valence band from $-7.5$ to $-7$ eV for the majority spin and in the conduction band from $4$ to $5$ eV for the minority spin, there are narrow peaks of the 4f states of Gd. These peaks can be found in the band structure of GdMnSi in Figure 4 as tight packages of bands in the energy ranges discussed above. At the Fermi energy, there are a number of bands crossing $E_F$ from a number of electronic states of all ions in GdMnSi.

The calculated densities of electronic states and band structure of GdTiSi are shown in Figures 5 and 6. Similar sharp peaks can be traced near $-7$ and $5$ eV in Figure 6, stemming from the spin-polarized Gd-4f electronic states. The densities of states in the GdMnSi and GdTiSi compounds are different for two opposite spin directions, since the resulting state is ferromagnetic both in the Gd lattice and in the sublattice of 3d metals. The density of states of manganese has a high intensity below $E_F$ for minority spin, and an intense broad peak for majority spin (1.25 eV) located above $E_F$. The X-ray photoemission spectrum shows filled electronic states corresponding to the total density of states in the calculations. The main features of the experimental spectrum of GdTiSi, namely, a peak at about 2 eV and a shoulder at about 0.7 eV, are present in the total density of states of GdTiSi in Figure 5 [18].
formed due to the 3d states of manganese and 3p states of silicon. In the valence band from –7.5 to –7 eV for the majority spin and in the conduction band from 4 to 5 eV for the minority spin, there are narrow peaks of the 4f states of Gd. These peaks can be found in the band structure of GdMnSi in Figure 4 as tight packages of bands in the energy ranges discussed above. At the Fermi energy, there are a number of bands crossing $E_F$ from a number of electronic states of all ions in GdMnSi.

**Figure 3.** The density of states of GdMnSi per formula unit. (a) Total and partial Gd-4f densities of states; (b) partial density of states for Mn-3d; (c) partial density of states for Si-3p. The Fermi level is a dashed vertical line.

**Figure 4.** Band structure of GdMnSi. (a) Majority spin projection; (b) minority spin projection. The Fermi level is a solid horizontal line.
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Figure 5. The density of states of GdTiSi per formula unit. (a) Total and partial Gd-4f densities of states; (b) partial density of states for Ti-3d; (c) partial density of states for Si-3p. The Fermi level is a dashed vertical line.

Next, we consider GdMn$_{1-x}$Ti$_x$Si compounds with partial substitution of titanium ions for manganese ions. As can be seen from Figure 5, for the compositions of GdTiSi, the 4f states of gadolinium have the highest intensity in the valence band, as well as in the conduction band (similar to GdMnSi, Figure 3). From Figures 3 and 5, one can see that the

Figure 6. Band structure of GdTiSi. (a) Majority spin projection; (b) minority spin projection. The Fermi level is a solid horizontal line.

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states of gadolinium practically do not change upon substitution of titanium for manganese; therefore, below we consider in detail the changes occurring in the 3d sublattice of Mn and Ti. In Figure 7, the densities of states of GdMn$_{1-x}$Ti$_x$Si compounds for $x = 0.2$ (a), 0.4 (b), 0.5 (c), 0.6 (d), and 0.8 (e) are shown with two opposite directions of majority (up) and minority (down) spin projections. A significant contribution to the density is made by a broad band formed by the 3d states of manganese and titanium, which lies near $E_F$ in the energy range from $-5$ to $8$ eV.

![Figure 7](image)

**Figure 7.** The partial densities of the 3d states of Mn and Ti per formula unit in the following compounds: (a) GdMn$_{0.8}$Ti$_{0.2}$Si; (b) GdMn$_{0.6}$Ti$_{0.4}$Si; (c) GdMn$_{0.5}$Ti$_{0.5}$Si; (d) GdMn$_{0.4}$Ti$_{0.6}$Si; (e) GdMn$_{0.2}$Ti$_{0.8}$Si. The Fermi level is a dashed vertical line.

When 20% of manganese ions were replaced by titanium ions (compound GdMn$_{0.8}$Ti$_{0.2}$Si, see Figure 7a), titanium states with two peaks of low intensity below $E_F$ appeared, repeating the corresponding states of manganese, in the energy ranges from $-2$ to $-1.5$ eV and from $-1$ to $-0.5$ eV. Above $E_F$, broad bands of titanium states appeared for both spin directions. In this case, the intensity of all manganese states decreased; an intense peak with the minority spin in the range from 0 to 1 eV disappeared; and the peak with the majority spin, lying in the range from 0.5 to 1.5 eV, in GdMnSi (Figure 3) shifted higher in energy by approximately 0.5 eV, with its intensity decreasing by more than 30%, while the broad peak with the minority spin below $E_F$ shifted lower in energy.

When 40% of manganese ions were replaced by titanium ions (GdMn$_{0.6}$Ti$_{0.4}$Si, Figure 7b), the following changes occurred. Compared with GdMn$_{0.8}$Ti$_{0.2}$Si, an increase in all titanium states by a factor of 2 was observed. No new peaks appeared. The intensities
of all states of manganese decreased in proportion to the decrease in the concentration of manganese.

When 50% of manganese ions were replaced by titanium ions (GdMn$_{0.5}$Ti$_{0.5}$Si, Figure 7c), new peaks of titanium states appeared: a redistribution of the electron density took place, resulting in the formation of two maxima at the ends of the valence and conduction bands. For the minority spin above $E_F$, the peaks of the titanium states split, as a result of which two implicit maxima appeared at 1 eV, the peak at 2 eV increased significantly, and one more peak of titanium states appeared, which was higher in energy. The intensity of the manganese states increased in comparison with the compound GdMn$_{0.6}$Ti$_{0.4}$Si. Also, two separate maxima merged into one peak at 1.5 eV with the majority spin orientation.

When 60% of manganese ions were replaced by titanium ions (GdMn$_{0.4}$Ti$_{0.6}$Si, Figure 7d), a redistribution of the electron density occurred in the conduction band. The titanium states, separated into several distinct peaks, in the GdMn$_{0.5}$Ti$_{0.5}$Si compound formed a density with one intense peak in the range from 1.5 to 2.1 eV and one broad band in the range from 0 to 1.5 eV. The states of titanium above $E_F$ began to prevail over the states of manganese. All manganese states decreased: intense peaks with the minority spin in the range from –4 to –1.5 eV decreased by almost two times. The intense peak of the manganese states in the range from 1 to 2 eV split into two less intense peaks. At –1.8 eV for the minority spin, an intense peak was formed, which corresponds to a similar peak with the majority spin.

When 80% of the manganese ions were replaced by titanium ions (GdMn$_{0.2}$Ti$_{0.8}$Si, Figure 7e), a small peak was observed at the −1.1 eV level for the minority spin. The states of manganese decreased, on average, by two times. Compared with the pure compound GdTiiSi (Figure 5), the states of titanium in GdMn$_{0.2}$Ti$_{0.8}$Si are not symmetric, there are no intense peaks at $E_F$, and there are peaks lying lower in energy from –0.9 to –0.2 eV. In the GdMn$_{0.2}$Ti$_{0.8}$Si compound, the intensity of the minority spin peak lying from –2.1 to –1.2 eV is 50% less than in the GdTiiSi compound. In GdTiiSi, the titanium states for opposite spins are similar (see Figure 5b). In the GdMn$_{0.2}$Ti$_{0.8}$Si compound (see Figure 7e), the minority spin states of titanium below $E_F$ begin to be partially replaced by the manganese states.

For all considered compounds, the values of the total densities of electronic states at $E_F$ are presented in Table 2. In GdMnSi, these values are lower, since Mn 3d states are highly polarized, as a result of which the minority states are almost completely filled, and $E_F$ passes through a pseudogap in the minority spin. On the contrary, in GdTiiSi the Ti 3d states are unpolarized and give a much higher density of states at $E_F$. An increase in the density of electronic states at $E_F$ for the majority spin of more than 50% is observed. Intermediate compositions are characterized by an increase in the density of electronic states at $E_F$ for the minority spin with an increase in the titanium concentration. The smallest value is found in GdMn$_{0.5}$Ti$_{0.5}$Si, which is associated with the same contribution from the Ti and Mn states to $E_F$. The high Curie temperatures of the intermetallic compounds GdTiiSi and GdMnSi and the high values of the electron density of states at $E_F$ for intermediate compositions suggest that alloys of the intermediate composition GdMn$_{1-x}$Ti$_x$Si will have similar properties.

Table 1 above shows the values of the total and partial magnetic moments of all ions in the Ti-doped GdMnSi compound. The magnetic moment of the gadolinium ion remains practically unchanged. The silicon magnetic moment remains close to zero (see the last column of Table 1). The total magnetic moment of 4.86 $\mu_B$ in GdMnSi is in excellent agreement with the data for a low-temperature saturation magnetization of 5 $\mu_B$ in GdMnSi [16]. With an increase in the titanium concentration, a decrease in the magnetic moment in the Mn and Ti sublattices is observed, since the magnetic Mn ions are replaced by nonmagnetic Ti ions. The total magnetic moment of GdTiiSi is increased by more than 60% compared with GdMnSi. Close values of the magnetic moments of manganese ions in the range of 3.3–3.8 $\mu_B$ were experimentally determined in the compounds GdMnGa and GdMnGe [12].
Table 2. The values of the total and partial spin densities of electronic states at the Fermi energy in GdMn$_{1-x}$Ti$_x$Si for $x = 0$–1.

| Compound          | DOS Value for Majority (Up) Spin, States/(eV f.u.) | DOS Value for Minority (Down) Spin, States/(eV f.u.) | Total DOS Value, States/(eV f.u.) |
|-------------------|---------------------------------------------------|-----------------------------------------------------|----------------------------------|
| GdMnSi            | 1.73                                              | 0.47                                                | 2.20                             |
| GdMn$_{0.8}$Ti$_{0.2}$Si | 1.45                                              | 0.91                                                | 2.36                             |
| GdMn$_{0.6}$Ti$_{0.4}$Si  | 1.43                                              | 0.59                                                | 2.03                             |
| GdMn$_{0.5}$Ti$_{0.5}$Si  | 1.36                                              | 0.35                                                | 1.71                             |
| GdMn$_{0.4}$Ti$_{0.6}$Si  | 1.22                                              | 1.01                                                | 2.22                             |
| GdMn$_{0.2}$Ti$_{0.8}$Si  | 1.11                                              | 1.38                                                | 2.48                             |
| GdTiSi            | 1.86                                              | 2.20                                                | 4.06                             |

Figure 8 clearly illustrates the substitution of Ti ions for Mn ions, which leads to an increase in the magnetic moment in the 3d Ti-Mn subsystem. This effect arises due to the opposite direction of the magnetic moments of Gd and Mn, which leads to a decrease in the total magnetic moment. The magnetic moment Gd practically does not change in all compositions. The arising moment in the 3d sublattice partially compensates for the large magnetic moment of Gd; as a result, the total magnetic moment in the system increases from 4.89 to 7.19 $\mu_B$.

Figure 8. Total and partial magnetic moments of ions in GdMn$_{1-x}$Ti$_x$Si depending on $x$ (concentration of Ti), $x = 0$–1.

4. Conclusions

In this paper, we report a study on GdMn$_{1-x}$Ti$_x$Si intermetallic compounds with a tetragonal crystal structure in a wide range of concentrations ($x$) from 0 to 1. For this, the theoretical DFT + U method was used, within which strong electronic correlations were taken into account for the 4f electronic states of gadolinium ions. The performed theoretical calculations for this system showed that with a change in the content of transition metals in the system, a significant change in the magnetic properties occurs; in particular, the total magnetic moment changes from 4.86 to 7.19 $\mu_B$. At the same time, the value of the magnetic
moment of Gd in GdMn$_{1-x}$Ti$_x$Si practically does not change. At the same time, in almost all GdMn$_{1-x}$Ti$_x$Si compositions, an increase in the total density of electronic states at the Fermi energy was found in comparison with the extreme compounds, which may indicate a significant change in the transport properties of intermetallic compounds. Together with the expected high Curie temperatures, the revealed changes in the magnetic characteristics and electronic structure make the GdMn$_{1-x}$Ti$_x$Si intermetallic system promising for use in practical applications, e.g., for ferromagnetic layers in multilayer structures for spin and microelectronics [29].

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**References**

1. Franco, V.; Blázquez, J.S.; Ipus, J.J.; Law, J.Y.; Moreno-Ramírez, L.M.; Conde, A. Magnetocaloric effect: From materials research to refrigeration devices. *Prog. Mater. Sci.* 2018, 93, 112–232. [CrossRef]

2. Gupta, S.; Suresh, K.G. Review on magnetic and related properties of RTX compounds. *J. Alloys Comp.* 2015, 618, 562–606. [CrossRef]

3. Zhang, H.; Shen, B.-G. Magnetocaloric effects in RTX intermetallic compounds (R = Gd–Tm, T = Fe–Cu and Pd, X = Al and Si). *Chin. Phys. B* 2015, 24, 127504. [CrossRef]

4. Gupta, S.; Suresh, K.G.; Nigam, A.K.; Lukoyanov, A.V. Magnetism in RRhGe (R = Tb, Dy, Er, Tm): An experimental and theoretical study. *J. Alloys Comp.* 2015, 640, 56–63. [CrossRef]

5. Kuchin, A.G.; Platonov, S.P.; Lukoyanov, A.V.; Volegov, A.S.; Gaviko, V.S.; Mukhachev, R.D.; Yakovleva, M.Y. Remarkable increase of Curie temperature in doped GdFeSi compound. *Intermetallics* 2021, 133, 107183. [CrossRef]

6. Gupta, S.; Suresh, K.G.; Nigam, A.K.; Kniazev, Y.V.; Kuz’min, Y.I.; Lukoyanov, A.V. The magnetic, electronic and optical properties of HoRhGe. *J. Phys. D Appl. Phys.* 2014, 47, 365002. [CrossRef]

7. Chen, J.; Shen, B.G.; Dong, Q.Y.; Hu, F.X.; Sun, J.R. Giant reversible magnetocaloric effect in metamagnetic HoCuSi compound. *Appl. Phys. Lett.* 2010, 96, 152501. [CrossRef]

8. Zhang, H.; Wu, Y.-Y.; Long, Y.; Wang, H.-S.; Zhang, K.-X.; Hu, F.-X.; Sun, J.-R.; Shen, B.-G. Large reversible magnetocaloric effect in antiferromagnetic HoNiSi compound. *J. Appl. Phys.* 2014, 116, 213902. [CrossRef]

9. Venturini, G.; Malaman, B.; Ressouche, E. Neutron diffraction study of the TbMnGe compound. *J. Alloys Comp.* 1996, 243, 98–105. [CrossRef]

10. Ivanova, T.I.; Nikitin, S.A.; Bogdanov, A.E.; Morozkin, A.V.; Suski, W.; Warchulskia, J.K. Effect of Ga substitution for Ge on magnetic and crystal properties of the GdMnGe$_{1-x}$Ga$_x$ intermetallics. *Intermetallics* 2005, 13, 857–861. [CrossRef]

11. Nikitin, S.A.; Ivanova, T.I.; Ovchenkova, Y.A.; Maslennikova, M.V.; Burkhanov, G.S.; Chistyakov, O.D. The influence of interatomic distances on magnetic ordering in RMnSi compounds (R = La, Y, Sm, and Gd). *Phys. Solid State* 2002, 44, 308–311. [CrossRef]

12. Schneidner, K.A.; Pecharsky, V.K. The influence of magnetic field on the thermal properties of solids. *Mater. Sci. Eng. A* 2000, 287, 301–310. [CrossRef]

13. Oboz, M.; Takik, E. Properties of the GdTX (T = Mn, Fe, Ni, Pd, X = Al, In) and GdFe$_x$Al$_6$ intermetallics. *J. Alloys Comp.* 2011, 509, 5441–5446. [CrossRef]

14. Nikitin, S.A.; Ivanova, T.I.; Tskhadadze, I.A.; Skokov, K.P.; Telegina, I.V. Magnetic anisotropy and magnetic properties of RTSi (R = Gd, Y; T = Mn, Fe) compounds. *J. Alloys Comp.* 1998, 280, 16–19. [CrossRef]

15. Ovchenkova, I.A.; Nikitin, S.A.; Ivanova, T.I.; Tskhadadze, G.A.; Skourski, Y.V.; Suski, W.; Nizhankovskii, V.I. Magnetic ordering and magnetic transitions in GdMn$_{1-x}$Ti$_x$Si intermetallics. *J. Alloys Comp.* 2008, 451, 450–453. [CrossRef]
18. Skorek, G.; Deniszczyk, J.; Szade, J.; Tyszka, B. Electronic structure and magnetism of ferromagnetic GdTiSi and GdTiGe. J. Phys. Condens. Matter. 2001, 13, 6397. [CrossRef]

19. Morozkin, A.V. Quaternary Gd$_3$Ti$_2$MnSi$_3$ compound in the GdMn$_{1-x}$Ti$_x$Si ($x=0\ldots1$) section of Gd-Mn-Ti-Si system at 1073 K. J. Alloys Compd. 1999, 292, 162–165. [CrossRef]

20. Nikitin, S.A.; Tskhadadze, I.A.; Morozkin, A.V.; Serepegin, Y.D. The influence of Ti on the itinerant magnetism of RTX compounds. J. Magn. Magn. Mater. 1999, 196–197, 632–633. [CrossRef]

21. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphological data. J. Appl. Crystallogr. 2011, 44, 1272–1276. [CrossRef]

22. Zhan, Y.; Ma, J.; Sun, Z.; Hua, Z.; Du, Y. The isothermal section of the Gd–Ti–Si ternary system at 773 K. J. Alloys Compd. 2009, 475, 268–272. [CrossRef]

23. Anisimov, V.I.; Aryasetiawan, F.; Lichtenstein, A.I. First-principles calculations of the electronic structure and spectra of strongly correlated systems: The LDA+U method. J. Phys. Condens. Matter 1997, 9, 767–808. [CrossRef]

24. Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Buongiorno Nardelli, M.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Cococcioni, M.; et al. Advanced capabilities for materials modelling with Quantum ESPRESSO. J. Phys. Condens. Matter 2017, 29, 465901. [CrossRef]

25. Perdew, J.P.; Burke, J.P.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868. [CrossRef]

26. Baglasov, E.D.; Lukoyanov, A.V. Electronic structure of intermetallic antiferromagnet GdNiGe. Symmetry 2019, 11, 737. [CrossRef]

27. Liechtenstein, A.I.; Anisimov, V.I.; Zaanen, J. Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators. Phys. Rev. B 1994, 52, R5467. [CrossRef] [PubMed]

28. Topsakal, M.; Wentzcovitch, R.M. Accurate projected augmented wave (PAW) datasets for rare-earth elements (RE = La–Lu). Comput. Mater. Sci. 2014, 95, 263–270. [CrossRef]

29. Vedmedenko, E.Y.; Kawakami, R.K.; Sheka, D.D.; Gambardella, P.; Kirilyuk, A.; Hirohata, A.; Binek, C.; Chubykalo-Fesenko, O.; Sanvito, S.; Kirby, B.J.; et al. The 2020 magnetism roadmap. J. Phys. D Appl. Phys. 2020, 53, 453001. [CrossRef]