
Magnetic properties of RTiGe compounds

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Abstract

Magnetic properties of RTiGe (R = Gd, Tb, Dy, Ho, Er, Tm, Y) compounds with CeFeSi-type structure have been studied by magnetization measurements in the temperature range 77–700 K in static magnetic fields up to 13 kOe. For TbTiGe, DyTiGe and HoTiGe the measurements have been carried on single-crystal samples. The coexistence of strong ferro- and antiferromagnetic interactions was found in RTiGe rare-earth compounds with low concentration of 3d electrons. The concentration dependencies of magnetic ordering temperatures, effective magnetic moments and paramagnetic Curie temperatures of these compounds have been determined. GdTiGe and TbTiGe orders at rather high temperatures, $T_N = 412$ and 288 K correspondingly, while ErTiGe and TmTiGe remain Curie–Weiss paramagnets down to 77 K. YTiGe is Pauli paramagnetic. The results are compared with those obtained on pure rare-earth elements and isotypic RTX compounds. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

RTX silicides and germanides with T = Mn, Fe, Co, Ru, Os [1–4] often crystallize in the tetragonal structure of CeFeSi type (space group, P4/nmm). According to Ref. [5], this structure may be considered as being built up of sheets perpendicular to the c direction, that is, one sheet per c transition period. Each sheet consists of five layers with sequence R–X–Ti–X–R. The sheets of CeFeSi structure correspond to the segments of ThCr$_2$Si$_2$ structure.

The magnetic properties of ternary rare-earth transition metal silicides and germanides have been widely described and discussed [1–6]. These investigations have indicated that the T component has no magnetic moment in most compounds, except for those with Mn. On the other hand, the rare-earth moments usually order at low temperatures [6].

The absence of the magnetic moment in 3d sublattice can be connected with the hybridization between Si p states and transition atom d states which leads to the filling of 3d band. From this
point of view it was of interest to search for magnetic ordered RTX compounds with T elements with low concentration of 3d electrons. The magnetic and crystalline properties of these compounds have not been studied up to now. It is known that among the 3d elements, the titanium atoms have only two 3d electrons (Ti: [Ar]3d24s2) while Mn, Fe, Co and Ni atoms possess a significantly more number of 3d electrons.

In the present work we report on the magnetic properties of the RTiGe (R = Gd–Tm, Y) compounds.

2. Experimental details

The RTiGe (R = Gd–Tm, Y) compounds were prepared in an electric arc furnace under an argon atmosphere using a non-consumable tungsten electrode and water-cooled copper tray. Germanium (purity, 99.99%), titanium (purity, 99.99%), and rare-earth metals (purity, 99.99%) were used as the starting components. Being obtained the ingots of RTiGe were remelted several times to insure homogeneity. The purity of the samples was checked by X-ray diffraction. The obtained diffractograms were identified and calculated using the CSD [7] and Reitan [8] programs. Analysis of the powder X-ray diffractograms show unambiguously that these compounds crystallize in the tetragonal CeFeSi-type structure (P4/nmm). Rare earth and germanium atoms occupy 2(c) site (1/4, 1/4, z) and the Ti atom occupies the special position 2(a) (1/2, 1/2, 0). The lattice parameters and the main interatomic distances of RTiGe compounds determined at room temperature are given in Table 1.

TbTiGe, DyTiGe and HoTiGe single crystals were extracted from the solidified ingots. The crystallographic orientations were determined by an X-ray back Laue diffraction method. The weight of the single crystals was about 2 mg.

The magnetic measurements were made in the static magnetic fields up to 13 kOe in the temperature range from 77 to 700 K. Single-crystal magnetization curves were obtained on the elongated spheroid shape samples, with field applied in (0 0 1) plane and along [0 0 1] axis, in the temperature range from 77 K to Néel temperature. The data were corrected for demagnetizing field.

3. Results

The main magnetic data for RTiGe compounds are listed in Table 1. GdTiGe orders at relatively high temperatures (TN ~ 412 K) and posses a small spontaneous magnetic moment (μs = 0.26 μB at TN = 77 K). Since the saturation is not reached both on polycrystal and powder samples in all the temperature range under fields up to 13 kOe, one may suggest a weak ferromagnetic ordering below TN, but the absence of single-crystal measurements does not allow us to predict its magnetic structure reliably.

Figs. 1 and 2 show the field and temperature dependencies of magnetization of TbTiGe single-crystals measured in magnetic field applied in basal plane (σ∥) and along tetragonal axis (σ⊥). The compound is high-anisotropic, the easy direction of

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>zR</th>
<th>zGe</th>
<th>dO R-R (nm)</th>
<th>d1 R-R (nm)</th>
<th>d2 R-R (nm)</th>
<th>dR Ge (nm)</th>
<th>dR Tl (nm)</th>
<th>dTl Ge (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdTiGe</td>
<td>0.4064</td>
<td>0.7712</td>
<td>0.647</td>
<td>0.235</td>
<td>0.3662</td>
<td>0.4064</td>
<td>0.6154</td>
<td>0.3015</td>
<td>0.3396</td>
<td>0.2721</td>
</tr>
<tr>
<td>TbTiGe</td>
<td>0.4059</td>
<td>0.7667</td>
<td>0.659</td>
<td>0.276</td>
<td>0.3764</td>
<td>0.4059</td>
<td>0.5968</td>
<td>0.2913</td>
<td>0.3311</td>
<td>0.2934</td>
</tr>
<tr>
<td>DyTiGe</td>
<td>0.4037</td>
<td>0.7616</td>
<td>0.656</td>
<td>0.238</td>
<td>0.3714</td>
<td>0.4037</td>
<td>0.5967</td>
<td>0.2929</td>
<td>0.3307</td>
<td>0.2818</td>
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<tr>
<td>HoTiGe</td>
<td>0.4029</td>
<td>0.7585</td>
<td>0.662</td>
<td>0.281</td>
<td>0.3766</td>
<td>0.4029</td>
<td>0.5860</td>
<td>0.2881</td>
<td>0.3258</td>
<td>0.2934</td>
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<tr>
<td>ErTiGe</td>
<td>0.4018</td>
<td>0.7548</td>
<td>0.655</td>
<td>0.265</td>
<td>0.3682</td>
<td>0.4018</td>
<td>0.5930</td>
<td>0.2904</td>
<td>0.3288</td>
<td>0.2837</td>
</tr>
<tr>
<td>TmTiGe</td>
<td>0.3997</td>
<td>0.7495</td>
<td>0.656</td>
<td>0.267</td>
<td>0.3664</td>
<td>0.3997</td>
<td>0.5885</td>
<td>0.2886</td>
<td>0.3264</td>
<td>0.2826</td>
</tr>
<tr>
<td>YTiGe</td>
<td>0.4038</td>
<td>0.7619</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
magnetization is the c-axis. No spontaneous magnetic moment was detected at 77 K both on TbTiGe single crystal and polycrystal samples indicating antiferromagnetic ordering of this compound. At temperatures higher than 235 K deviation from the straight-line behavior occurs.

Magnetization curves of HoTiGe single crystals are presented in the inset of Fig. 3. Non-linear character of $\sigma_\perp(H)$ magnetization curves may be connected with the low magnetic temperature of this compound ($T_N = 115$ K).

The character of magnetization curves of DyTiGe single crystal is similar to those observed for TbTiGe and HoTiGe, but the values of magnetization reached at the magnetic fields up to 13 kOe are much smaller (0.62 $\mu_B$ for $\sigma_\perp(H)$ curves and 0.32 $\mu_B$ for $\sigma_\parallel(H)$).

The increase in the atomic number of the rare-earth element leads to a decrease in magnetic ordering temperatures of these compounds (see Table 2). The temperature dependence of the inverse susceptibility above $T_N$ obeys Curie–Weiss-type behavior with the positive paramagnetic Curie temperature $\theta_\mu$ for all investigated RTiGe compounds, except YTiGe, which is Pauli paramagnetic. The observed effective paramagnetic moments $\mu_{\text{eff}}$ are in good agreement with the theoretical values expected for the R$^{3+}$ ions.

4. Discussion

The dependencies of the magnetic ordering temperatures $T_N$ and paramagnetic Curie temperatures $\theta_\rho$ on the de Gennes function for RTiGe,
Fig. 3. Temperature dependencies of the magnetization along c-axis (1) and in basal plane (2) in applied magnetic field 10 kOe for HoTiGe single crystal. The inset shows magnetization curves for HoTiGe single crystal at 77 K.

Table 2
Magnetic ordering temperatures $T_N$, paramagnetic Curie temperatures $\theta_p$, effective magnetic moments and the mean-field coupling constants $\gamma_{12}$ and $\gamma_{11}$ of RTiGe compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_N$ (K)</th>
<th>$\theta_p$ (K)</th>
<th>$\mu_{eff}$ ($\mu_B$)</th>
<th>$\gamma_{11}$ (mole/emu)</th>
<th>$\gamma_{12}$ (mole/emu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdTiGe</td>
<td>412</td>
<td>317</td>
<td>8.3</td>
<td>85</td>
<td>-11</td>
</tr>
<tr>
<td>TbTiGe</td>
<td>288</td>
<td>248</td>
<td>9.4</td>
<td>49</td>
<td>-4.7</td>
</tr>
<tr>
<td>DyTiGe</td>
<td>175</td>
<td>120</td>
<td>10.7</td>
<td>21</td>
<td>-3.8</td>
</tr>
<tr>
<td>HoTiGe</td>
<td>115</td>
<td>101</td>
<td>10.1</td>
<td>17</td>
<td>-1.1</td>
</tr>
<tr>
<td>ErTiGe</td>
<td>33</td>
<td>9.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>YTiGe</td>
<td>PM Pauli</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

RFeSi [9] compounds and pure rare-earth metals [10] are presented at Fig. 4. The obtained $\theta_p((g_J - 1)J(J + 1))$ curve for RTiGe compounds practically coincide with the corresponding dependence for rare-earth metals. The value of the indirect exchange constant $A_{ex}$ was estimated from the equation

$$\theta_p = \frac{2}{3}(g_J - 1)^2J(J + 1) \frac{A_{ex}}{k_B}.$$ 

It was found that $A_{ex}$ is equal to 31 K which is near to the value obtained for pure rare-earth metals (31.5 K) [10]. The scatter of the experimental data in RTiGe series for $\theta_p$ can be explained by the errors in determination of $\theta_p$ on polycrystal samples.

The magnetic ordering temperatures $T_N$ of RTiGe series is essentially higher than those observed both on pure rare-earth metals and isotypical RTX compounds. Among the known CeFeSi-type structure compounds, the most high values of magnetic ordering temperatures (see Table 3) are characterized by the rare-earth silicides and germanides with Mn [3,11]. This fact is usually associated with the occurrence of essential $(1.5-3 \mu_B)$ magnetic moment on Mn in these series. While in RTX compounds with other 3d metals...
Table 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{C,N}$ (K)</th>
<th>References</th>
<th>Compound</th>
<th>$T_{C,N}$ (K)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdTiGe</td>
<td>412</td>
<td>This work</td>
<td>TbTiGe</td>
<td>288</td>
<td>This work</td>
</tr>
<tr>
<td>GdMnSi</td>
<td>316</td>
<td>[14]</td>
<td>TbMnSi</td>
<td>260</td>
<td>[16]</td>
</tr>
<tr>
<td>GdFeSi</td>
<td>125</td>
<td>[12]</td>
<td>TbFeSi</td>
<td>125</td>
<td>[9]</td>
</tr>
</tbody>
</table>

$^*$The compound with TiNiSi-type structure.
The comparison of the main interatomic distances of RTiGe compounds (Table 1) with other known RTX [4,12,14] series showed that the most essential changes of spacings have occurred in R–R and R–T distances in BaAl\textsubscript{4} slab while the corresponding changes of in-plane distances and R–R distances in W slab are much smaller. Thus, one can suppose the abrupt changes in magnetic interactions due to the modification of the band structure.

5. Conclusions

The obtained results indicate the occurrence of strong exchange interactions between R ions in RTiGe compounds. The strength of these interactions is the same for rare-earth metals and corresponding RTiGe germanides in spite of much low concentration of rare-earth elements in the latter case. This fact can be associated with the existence of indirect RKKY exchange via s–d conduction electrons in W slabs ($J_0$ and $J_2$ exchange integrals). The value of the negative exchange integral $J_1$ depends on $d_{\text{R,R}}$ interatomic distances and the hybridization of Ti 3d electrons with Ge 4p electrons and the structure of 3d band.

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References